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Laser Damage Studies in the Ultra-Violet

by

Stephen Samuel Wiseall

A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of

Doctor of Philosophy of the
Loughborough University of Technology

November 1989

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I would like to thank all those who were involved in this project for their help and encouragement. In particular I would like to thank my supervisor David Emmony for his enthusiasm and many helpful discussions.

Thanks are also due to Martin Godfrey and Richard White who provided stimulating conversation and help with the photoacoustic work. Thanks are also due to the electron microscopy group in particular John Bates for the work on ripple patterns.

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Abstract

The work in this thesis is a study of excimer laser induced damage in optical materials. This includes characterization of the focused laser radiation, development of sensitive techniques for the early detection of laser damage and finally laser damage studies at 193 nm and 248 nm in crystalline materials, metal mirrors and dielectric coatings.

Characterization of the focused laser radiation involved pulse energy, temporal pulse profile and spatial profile measurements. This was assisted by development of a laser attenuator using a variable length liquid cell with a dynamic range of 25 dB. Non-linear absorption phenomena were observed in liquids at high intensities. Beam profiling methods were used to show the intensity distribution in the focal region of a lens was reproducible and approximated to a 2-D Gaussian function.

A video microscope system was developed using a helium neon laser probe beam to image scattering centres on an optical surface. A beamsplitter and photodetector were used to simultaneously produce a quantitative measure of the scattered light. Laser induced threshold damage was detected as micron sized damage pits. This system was used to show that particle ejection and reduced surface scattering can occur when a sample is irradiated just below its threshold level. Acoustic transducers were used to monitor laser damage and shown to be less sensitive at detecting threshold damage in thin films than the scattering system. The LIMA instrument was shown to have potential for the identification of thin film impurities.

Single shot damage thresholds at 193 nm of several crystalline fluoride materials were measured in the range 1 - 4 Jcm$^{-2}$. The damage threshold was higher for low refractive index materials and freshly cleaved surfaces of LiF and NaF. Colour centre formation in NaF was attributed to the formation of F centres and F$_2$ centres.

Thermal models of laser induced heating have been
developed to predict damage thresholds of metal mirrors. Good agreement was found between damage threshold measurements at 248 nm on high quality dielectric overcoated aluminium mirrors and the predicted melt thresholds. UV irradiation of SiO$_x$ overcoated aluminium mirrors was shown to greatly improve their UV reflectance below 300 nm. This was attributed to interstitial oxygen in the film converting SiO to SiO$_2$ without an apparent over-all change in the film stoichiometry. Laser irradiation of these mirrors at higher fluences resulted in formation of a quasi-random ripple pattern. Local parallel ripples were unambiguously associated with the presence of a fine scratch in the centre of the pattern. Mean ripple wavelength was shown to be proportional to local absorbed fluence and independent of shot number. The diffraction efficiency increase with shot number was associated with development of the ripple profile.

Detailed consideration of multi-layer dielectric coating performance at 248 nm led to the design of a 3 layer AR coating allowing a more flexible choice of materials than 2 layer designs. Absorption of HR coatings can be reduced by using a large high-low refractive index ratio to minimize layer number. Single shot damage thresholds at 248 nm of HR coatings varied in the range $0.3 - 7.9 \text{ Jcm}^{-2}$ and for AR coatings $0.8 - 1.65 \text{ Jcm}^{-2}$. Similar thresholds were predicted using a damage model based on laser heating of a spherical absorbing defect. A statistical model of laser damage was developed to predict laser damage probability as a function of defect density and laser spot size. A significant spot size dependence arises if on average there is less than one damage sensitive defect illuminated by the focused beam. Scattering centre densities of $20 - 35 \text{ mm}^{-2}$ greatly exceeded the density of the most damage sensitive defects which was $1 - 2 \text{ mm}^{-2}$. Spot size effects and threshold damage ambiguities can therefore be avoided with the use of a large beam area.
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I often say that when you can measure what you are speaking about and can express it in numbers, you know something about it, but when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind; it may be the beginning of knowledge, but you have scarcely in your thoughts advanced to the stage of science, whatever the matter may be.

William Thomson, Lord Kelvin
Chapter 1
Introduction

When high power pulsed laser radiation interacts with a solid material a wide range of effects can occur varying from a simple transient heating process to a dramatic explosive vaporization and plasma formation. Both of these effects involve the absorption of some of the laser energy and its subsequent observation in the form of heat, light, sound and kinetic energy of the ejected fragments. Although the absolute energy from a pulsed laser may be quite low their destructive nature arises because the pulsewidth is very short and the energy can be delivered in a small area. Typical laboratory devices have pulse energies in the range 0.001 - 1 J and pulsewidths in the range 0.1 - 100 ns, this corresponds to an energy flux or power of $10^4 - 10^{10}$ W. The energy output of the very largest systems is of the order 1 - 10 kJ corresponding to powers of $1 - 100 \times 10^{12}$ W.

Laser damage studies are concerned with characterizing and understanding this complex interaction process over the whole power range. A general feature of this dynamic process is that the interaction generally occurs on a time scale comparable with the laser pulse duration.

The potential destructive nature of high power lasers becomes very important when developing the optics associated with the laser cavity and other optical components in the system such as lenses, mirrors, windows, beamsplitters, etc. In the worst case the output power of the laser is limited by the destruction of the optical components in the laser cavity due to the extremely high power densities involved. One option is to increase the diameter of the optical components so that the power density they experience is reduced. This option is not usually acceptable because the diameter may be limited by other factors such as the laser pumping mechanism and secondly large diameter optics are extremely expensive and difficult to produce. This is a major incentive for
developing laser damage resistant optical components. A second important factor in complex laser systems involving many components is the need to minimize optical losses arising from absorption, scattering and surface reflections. As an example of the latter case if the transmission of a surface decreases from 99% to 98%, the over-all transmission involving 50 such surfaces decreases from 60.5% to 36.4%. This is equivalent to reducing the laser output energy by 40%. A further incentive is therefore to produce components with not only minimized absorption but also minimized optical losses.

The study of laser damage processes in ultra-violet optical materials needs the answers to at least five questions, these are

1. What is laser damage?
2. How is the laser damage threshold defined?
3. What causes laser damage?
4. How can laser damage thresholds be improved?
5. What are the general problems associated with laser damage at UV excimer laser wavelengths?

1) "What is laser damage?"

The answer to this question is not obvious and can depend on one's viewpoint. Laser damage to an optical component can be considered from two sides depending on whether the end-user application is considered. One approach is to define laser damage as a permanent degradation in the performance of the component for its intended application. From the users viewpoint it seems that this definition would be the most appropriate. The difficulty with this definition is that the degradation may be acceptable or unacceptable and secondly there is the difficulty of simulating the end-user environment for testing purposes.

As an example, if the reflectance of a high reflector in a laser cavity has decreased so as to prevent lasing action then clearly the component is unacceptable and may
be considered damaged. However, if the same component is used as a beam steering mirror external to the cavity then the over-all effect may be an acceptable reduced efficiency. The problem is compounded because the degradation in its performance may be initiated and or caused by the environment in which the component is used. A second effect may also be involved in which the degradation is an accumulative multi-shot effect enhanced by the environment in which it is used. These effects undoubtedly occur to some degree when the optical components are exposed to very hazardous environments such as that in the cavity of an excimer laser. This will involve contact with highly reactive gases such as fluorine and exposure to intense vacuum ultra-violet radiation and electron beam bombardment from the laser pumping process.

An alternative and more conservative definition of laser damage is any detectable degradation in the performance of the optical component. This definition neglects the end-user environment but has a built-in safety factor if the method used to detect the damage is sensitive. The onset of laser damage is usually at localised weak points called defects and takes the form of several damage pits distributed over the illuminated area. It is likely using this definition that all large laser systems will contain some damaged components. This is acceptable if they don't measurably degrade the over-all performance and the damage does not deteriorate with shot number or time. In this definition the observation of damage depends on the sensitivity of the technique used to look for it. This has important consequences for multi-shot testing since an accumulative change which is undetectable in one shot may become detectable after many shots. This definition was used in this work because it encouraged the development of sensitive methods for detecting damage and secondly for investigating multi-shot effects.
"How is the laser damage threshold defined?"

The first requirement in defining the laser damage threshold of an optical component is to characterize the laser beam in the interaction region. This includes measuring the absolute pulse energy incident on the test sample and also its distribution in space and time. The laser damage threshold in its most general form is defined as the incident laser intensity at which laser damage is observed. The incident intensity is preferred since the local value requires some assumptions on the distribution of the optical electric field in the component. The laser intensity is measured in Wcm⁻² although it is conventional to measure the damage threshold in terms of an energy density or fluence in Jcm⁻². An advantage in using the fluence is that the pulsed laser damage threshold of most optical materials is contained in the range 0.1 – 200 Jcm⁻². In general, the pulse energy and its spatial and temporal distribution should be measured for each shot. However, in some cases the pulsedshape of the laser and its spatial distribution in the interaction region do not change significantly from shot to shot. In this case it is sufficient to measure the pulse energy for each shot and calculate the peak incident fluence knowing that the energy density will scale linearly with the power density.

Since optical components tend to initially damage at defect sites laser damage threshold measurements have a probabilistic nature depending on whether the defect is illuminated above its own damage threshold. There appears to be no universally accepted definition of the single shot damage threshold representing the optical component as a whole. This also applies to the method for detecting threshold damage. Various laboratories have defined laser component damage thresholds in different ways. The two which are most popular are the fluence for which the damage probability is 50% and secondly the midway point between the maximum fluence which causes damage and the minimum fluence which does not. Two others are the onset threshold defined as the maximum fluence for which the
damage probability is zero and a fourth option defined as the minimum fluence for which the damage probability is unity. The advantage of using a large focused spot size for the experimental measurements is that all of these definitions approach the same value.

iii) "What causes laser damage?"

In general, laser damage is considered to be initiated at local sites called defects, however, the actual damage mechanism at these sites is poorly understood. It is the authors opinion that the most likely mechanisms include local linear and non-linear absorption and secondly electric field enhancement in the region of the defect.

iv) "How can laser damage thresholds be improved?"

The most generic way of improving the damage threshold must involve the removal of the defects using better and more controlled production methods or designing the optics, particularly thin film multi-layers so that defects have less effect. Recent developments in thin film coating methods hold promise for improvements arising from the manufacture stage. Some success at improving laser damage thresholds has arisen from modifying the electric field distribution in the multi-layer coating or adding protective barrier layers. Improvements have also been observed by pre-conditioning the component using multi-shot irradiation below its single shot damage threshold.

v) Laser damage at excimer laser wavelengths, (193 - 353 nm)

At excimer laser wavelengths scattering and absorption in many materials increases relative to that at visible and infra-red wavelengths. This tends to reduce the damage threshold of ultra-violet optics and limit the choice of useable materials, particularly thin films. This has important consequences for the most efficient rare gas halide excimer laser which operates at 248 nm.
Enhanced coupling efficiencies at short wavelengths and the potential to scale it to large sizes has meant the KrF laser has become an important candidate for inertial confinement studies at various laboratories throughout the world.
Chapter 2
Review of laser damage

2.1 Historical aspects

The first report of laser induced damage was by Maker et al who used a high power ~8 MW ruby laser to induce optical breakdown in air and various dielectric materials, (2.1). This followed shortly after the development of Q switching. Other early reports of laser induced damage to optical components are reviewed in the book by Ready, (2.2). Early laser damage investigations concentrated on breakdown studies using pulsed ruby lasers, (λ = 694 nm) and Nd glass lasers, (λ = 1060nm). This work was mainly of an observational nature and usually involved dielectric breakdown and plasma formation. As the subject became established it was quickly realized that reproducible studies of the breakdown phenomena and quantitative measurements of the breakdown electric field required accurate characterization of the laser beam in the interaction region. This problem was highlighted in an early review by Bloembergen, (2.3). In parallel with breakdown studies were extensive investigations of laser induced breakdown in gases. Detailed reviews of this work are contained in references 2.2, 2.4, and 2.5.

The need for more quantitative measurements was also driven by the development of large laser systems. This included damage threshold measurements on many of the associated optical components to determine safe operating levels and secondly investigations into how they could be improved. This resulted in the identification of intrinsic and extrinsic damage in bulk laser glasses. Intrinsic damage was considered to arise from the inherent optical electric breakdown strength of the pure material and represented an upper limit on the material damage threshold. Extrinsic damage was observed at reduced breakdown fields and attributed to local inhomogeneous regions generically called defects. The most well known and troublesome of which was the presence of small
platinum inclusions in the glass laser rods. Often, both types of damage were observed in the same sample. The probability of hitting a defect was reduced with use of tightly focused beams and subsequently eliminated by careful observations of the damage morphology. This created problems as noted in a review by Smith, (2.6) in measuring the spatial distribution of the energy in the interaction region due to a non-linear effect known as self-focusing. This effect produces an intensity dependent refractive index which tends to focus the beam and increase the peak field so enhancing the breakdown process. The quantitative measure of the intrinsic breakdown field can therefore be masked by self-focusing unless the effect can be corrected analytically or avoided.

The analogies with dc electrical breakdown meant that the intrinsic laser induced breakdown point was specified in units of electric field strength conventionally given in MVcm$^{-1}$. However, in later studies it became conventional to specify the damage threshold point as an energy density in Jcm$^{-2}$.

In the early 1970's interest in high power laser systems was extended with the development of the Transverse Excited Atmospheric, TEA CO$_2$ laser operating at 10.6 $\mu$m and the hydrogen-fluoride, HF or deuterium-fluoride, DF chemical laser operating at 2.8 $\mu$m or 3.8 $\mu$m respectively. This resulted in extensive efforts to develop damage resistant infra-red transmitting window materials, thin films and metal mirrors, particularly copper. A similar process has occurred in the 1980's with the development of large excimer laser systems. The problems of optical performance and laser damage at UV wavelengths are particularly difficult because of the increased intrinsic and extrinsic absorption and scattering and secondly significant contributions from non-linear effects which are enhanced as the photon energy increases relative to the material band-gap.

Since 1969 the most authoritative source of information on laser induced damage studies to optical
components has been the annual conference on "Laser Induced Damage in Optical Materials" held in Boulder, Colorado, USA. The conference proceedings are published through the National Bureau of Standards (Washington). An index of the proceedings during the period 1969 - 1978 is also available.

2.2 Review of laser induced damage processes

The discussion is conveniently divided into laser damage processes in metals, dielectrics and thin films. For an ideally uniform and homogeneous sample the surface damage threshold would be constant across the surface and the bulk damage threshold would be constant throughout the volume of the sample. In practice localized 'weak' points or defects determine the minimum intensity at which damage is observed. In the bulk of transparent materials these defects may include absorbing inclusions, bubbles, impurities, stoichiometry variations or even local refractive index variations. In surfaces and thin films, defects may also include residual polishing compounds and other absorbed/adsorbed contaminants and physical imperfections arising from the non-ideal microstructure such as scratches, grain boundaries, cracks and voids. It is therefore not surprising that in general the damage threshold follows the order, bulk thresholds > surface thresholds > thin film thresholds.

2.2.4 Laser induced damage in metals

The optical properties of metals are characterized by their large absorption coefficients, \( \alpha > 10^5 \text{ cm}^{-1} \). Pulsed laser damage processes in such materials are undoubtedly thermal in origin and arise from linear absorption if the pulsewidth is longer than the electron relaxation time, \( \ll 10^{-13} \) s, \( (2.7) \).

Most of the damage threshold measurements on metal mirrors have been done at the infra-red wavelengths of 2.8, 3.8 or 10.6 \( \mu \text{m} \). In this region the reflectance of polished or diamond turned metals such as copper, aluminium or molybdenum can be very high. Simple 1-D
thermal models have been used to predict the energy fluence required to heat the surface to some material dependent threshold temperature such as its melting point, (2.8). This model was extended by Sparks and Loh to allow for a temperature dependent absorption term, (2.9). These thermal models of optical absorption usually involve a square root dependence on the laser pulsewidth if diffusion processes are important. If the heating is considered adiabatic then no pulsewidth dependence arises. Comparison of the predicted functional dependence of the damage threshold with the polarization state and the angle of incidence of the laser light, the thermal properties of the metal and the initial temperature show excellent agreement with experimental results for high quality surfaces, (2.7,2.10,2.11). The models have been less successful at predicting the absolute values of the melt threshold with deviations typically of 25%, (2.7). These results were corrected for small spot size effects due to radial heat flow but no mention was made of significant effects which can arise from the shape of the laser pulse.

Three types of single shot surface damage morphology have been identified by Decker et al in metal mirrors, (2.11). These corresponded to surface slip, melting and pit formation. The surface slip was observed at the lowest fluence and occurred when the thermal gradient in the surface induced a surface stress beyond the yield point of the metal. This resulted in plastic flow and a localized surface undulation. The slip thresholds were the lowest thresholds for which damage was observed and were typically 70 - 80% of the melt thresholds. This plastic yield process has also occurred in multi-shot tests and resulted in the formation of areas of reduced specular reflectance on the mirror when irradiated at fluence levels above 50% of the single shot threshold, (2.11). As long as the material is heated beyond its plastic limit for each shot some yielding will occur. It appears to be an accumulative process and slowly grows until it is detectable. The pit formation thresholds were normally associated with non-uniform absorption due to
defects. In the work by Decker the pit formation thresholds also followed the temperature dependence expected of the metal which suggests the pits have a thermal origin. This could arise from adiabatic heating of a small local area of the metal which was insulated in a void or crack.

2.2b Laser induced damage in dielectric materials

2.2b1 Simple model of laser damage

The optical properties of dielectric materials are characterized by a region of low absorption, \( \alpha \approx 10^{-5} - 10^{-1} \text{ cm}^{-1} \) and a wide band gap. This region of optical transparency is bounded on the long wavelength infra-red side by high absorption due to interactions with lattice phonons and on the short wavelength ultra-violet side by direct electronic transitions. In any real material there is a residual absorption in the region of transparency which is attributed to defects and impurities.

Laser damage in dielectric materials has been widely studied with reviews given by Bloembergen, (2.3) and Smith, (2.6). Much of the work on bulk materials was concerned with intrinsic breakdown processes in very pure materials. An excellent more general review of the interaction of lasers with dielectric materials is given by M von Allen, (2.12). From a practical viewpoint the minimum damage threshold is determined by the defects since a user will be interested in utilizing the component over its whole aperture.

A simple but generalized model of laser damage in the transparency region can be considered in three stages

i The generation of free carriers by promotion of electrons into the conduction band

ii The free electrons in the conduction band increase the absorption and also generate heat via collisional interactions with the lattice.

iii Subsequent heating or plasma formation result in irreversible destructive damage.
The generation of free electrons in the conduction band can occur via several excitation processes which are discussed later. As the density of free electrons increases the material becomes more metal like and the absorption increases due to the increased electron density. The dynamic increase in the absorbed laser energy results in heating due to electron collisions with the lattice. This can ultimately lead to irreversible damage if the heating is sufficient.

2.2bii Non-linear effects

If the photon energy \( h\nu \) is less than the band gap energy \( E_g \) direct photon absorption and generation of free carriers is not possible. However, photon absorption and indirect carrier generation is possible due to the presence of intermediate energy levels within the band gap arising from the impurities and defects. An alternative thermal model based on laser heating of a spherical absorbing defect is considered in chapter 8.

At high powers the optical electric field associated with the laser can be sufficient to dynamically modify the optical properties of the material. The over-all effect is that the optical properties such as the dielectric constant of the material are no longer linearly related to the electric field. In this case the dielectric constant can be written in the more generalised form, \( \varepsilon = \varepsilon^{(0)} + \varepsilon^{(2)}E^2 + \ldots \) \( \varepsilon^{(0)} \) and \( \varepsilon^{(2)} \) are complex. The two non-linear phenomena which feature most strongly in laser damage studies are self-focusing and multi-photon absorption. The self-focusing effect arises from the real part of \( \varepsilon^{(2)} \) and can be expressed in a more convenient form as

\[ n = n^{(0)} + n^{(2)}I. \]
where $n^{(0)}$ is the normal refractive index, $I$ the laser intensity and $n^{(2)}$ is related to $\varepsilon^{(2)}$. The end result is an intensity dependent refractive index. If $n^{(2)} > 0$ then a propagating Gaussian beam will tend to focus in on itself increasing the axial intensity and enhancing any damage process. This non-linear effect of self-focusing has been reviewed in great detail by Akhmanov et al, (2.13). From the laser damage viewpoint self-focusing is troublesome in laser systems with long optical path lengths such as glass lasers. It can be avoided by operating well below the critical power level corresponding to the point at which self-focusing and diffraction are equal. In practice damage from self-focusing is observed as thin filamentary tracks arising from amplification of small amplitude variations across the beam.

The non-linear phenomena of multi-photon absorption features in many intrinsic bulk damage models and arises from the imaginary part of $\varepsilon^{(2)}$ in equation 2.1. The absorption of laser radiation with distance can be expressed as

$$\frac{\partial I}{\partial x} = -\alpha I - \beta I^2$$ \hspace{1cm} 2.3

where $\alpha$ is the absorption coefficient for linear absorption and $\beta$ is known as the two photon absorption coefficient. From the laser damage viewpoint two photon absorption can generate extra conduction band electrons, (or more correctly free carrier pairs). The arguments on two photon absorption apply equally well to the host dielectric material or any localized impurities. The possibility of laser damage initiated by two photon absorption in impurities or defects has not been considered as far as the author is aware.

As the laser wavelength is reduced the photon energy becomes a more significant fraction of the band gap and multi-photon absorption becomes more probable. Recent measurements on UV transmitting window materials at the excimer wavelength of 248 nm gave two photon absorption coefficients varying in the range
\[ \beta = 1.3 - 110 \times 10^{12} \text{ cm}^{-1}, \langle 2.14 \rangle. \] 
Large laser systems with power outputs around \(10^{11} \text{ W cm}^{-2}\) require thick output windows. In this case two photon absorption can easily reduce the overall transmission of the window to 50% even assuming no laser damage arises from the high absorption.

2.2bii Bulk damage models

There are two damage models which have become established in the literature for describing the formation of sufficient conduction band electrons to produce intrinsic optical breakdown in dielectric materials. These are

i Multi-photon ionization

ii Avalanche ionization

Both models are extensions of the simpler model described earlier. The difference between the two models is in how the dense conduction band electron plasma forms. In multi-photon ionization the model assumes that all the conduction band electrons are provided by multi-photon absorption processes described earlier. This damage process is expected to become significant at short wavelengths where the photon energy is greater than half the band gap. In either model catastrophic damage is considered to occur when the electron density reaches a critical value around \(10^{18} \text{ cm}^{-3}\). This figure is in good agreement with experimental measurements of the electron density made at the onset of surface breakdown in glass, \(\langle 2.15 \rangle\). At this density the plasma is considered highly absorbing and couples directly with the laser light resulting in truncation of the transmitted pulse and irreversible damage.

The basic process of avalanche ionization is one of electron impact ionization due to the acceleration of an electron by the electric field. The ionizing impact results in two electrons which are available for subsequent acceleration, this process continues resulting in an exponential increase in the electron density.
This model was originally proposed by Von Hippel, (2.16) and subsequently developed by Seitz, (2.17) to predict the dc electrical breakdown of alkali-halide crystals. In the avalanche model of laser damage an assumed initial electron density in the conduction band of about $10^8 \text{ cm}^{-3}$ grows rapidly by the avalanche process to the critical value around $10^{18} \text{ cm}^{-3}$, (2.3). The detection of breakdown is usually associated with the sharp truncation of the transmitted pulse. In this model the probability of damage is controlled by the probability of generating the initially required seed electrons. The statistical distribution of the time to breakdown, (from the beginning of the pulse to the truncation point) is associated with the variation in the time needed to generate the initial seed electrons, (2.18).

The earliest work linking avalanche ionization as a breakdown process operable at zero and infra-red optical frequencies was performed by Yablonovitch, (2.19) in 1971. He found a striking similarity between the trends of the breakdown field in alkali-halide crystals measured by Von Hippel, (2.16) at zero frequency and those measured by himself at the CO$_2$ wavelength of 10.6 µm. The basic wavelength dependence is given by, (2.6)

$$E_t = E_{dc} (1 + \omega^2 \tau^2)^{1/8}$$

2.4

where $E_{dc}$ is the dc breakdown field, $\omega$ is the angular frequency of the laser and $\tau$ is the electron-phonon collision rate. Equation 2.4 predicts little dependence of the breakdown field until the electron-phonon collision rate is comparable with the laser frequency. This general trend has been confirmed by Bass and Barrett, (2.20) with breakdown measurements at 1060 and 694 nm. The predicted increase in the damage threshold with laser wavelength has been measured in several wide band gap materials at 532 and 355 nm, (2.21). However, they also suggested that as the photon energy exceeds about half the band gap multiphoton absorption dominates over the avalanche process and the damage threshold decreases as the laser wavelength is...
reduced.

Several problems relating to the avalanche model have been highlighted in a review of avalanche breakdown theories given by Sparks, (2.22). This includes the reasonable question as to the origin of the initial $10^8$ cm$^{-3}$ seed electrons and absolute comparisons of theoretical and experimental breakdown fields. Sparks has introduced a modified breakdown process which can be considered as a hybrid of the avalanche and multi-photon models and is in good quantitative agreement with experimental results. In this model the seed electrons originate from multi-photon absorption across the band gap or from F centres. He also extended the avalanche process by introducing a three body photon-phonon-electron interaction known as a Holstein process. This three body process allows the electron to absorb an appreciable fraction of the photon energy whilst using the lattice phonon to conserve the wavevector. The rate of growth of the avalanche is therefore greater using the Holstein mechanism.

The combined model has also found favour elsewhere. Vaidyanathan et al, (2.23) has compared the breakdown fields for alkali-halides at wavelengths in the range 355 - 1060 nm and concluded that a combined multi-photon and avalanche model gives a better absolute agreement with experimental results than either of the models on an individual basis. They also note that comparisons are difficult in absolute terms because in most cases breakdown fields are governed by defects and impurities. The presence of defects has also been used in a model by Epifanov, (2.24) as the source of the $10^8$ cm$^{-3}$ seed electrons required to initiate the avalanche. In this case the probability of damage is determined by the probability of ionization of the defect in the interaction region.

2.2biv Laser induced damage on surfaces

In the early studies of laser damage on transparent components it was invariably observed that the exit
surface had a lower damage threshold than the entrance surface. This was explained by Crisp, (2.25) on the basis of interference between the incident and reflected waves at each surface. On the incident surface there is a 180 degree phase change due to the reflection at the more dense media whereas no phase change occurs at the exit surface due to reflection at the less dense media. This results in an intensity at the rear surface given by

\[ I_r = \frac{4n^2}{(n + 1)^2}I_f \]

where \( n \) is the refractive index and \( I_f \) the intensity at the front surface. Assuming \( n = 1.5 \) gives \( I_r/I_f = 1.44 \) and suggests the damage threshold of the exit surface should be 69% of the value at the entrance surface. This figure is in good agreement with experimental results, (2.26). A further test of this model was to measure the entrance and exit thresholds at the Brewsters angle where the reflectance for p polarised light is zero, (2.26). In this case no difference between the damage thresholds of the entrance and exit faces was measured. In more recent measurements at 248 nm, the average ratio of the entrance to the exit damage threshold on several on SiO\(_2\), CaF\(_2\) and MgF\(_2\) samples was around 1.2 - 1.3, (2.27). This figure is about 10 - 15% less than that given by equation 2.5. Similar observations were also made by Milam, (2.28) at 1060 nm on BK-7 glass surfaces.

A large body of experimental evidence is available which generally concludes that surface damage thresholds are less than the bulk values for the same material. Most of the early work on comparing bulk and surface thresholds was done on glass materials at 1060 nm, (2.29). Pulse truncation was used as the main evidence of intrinsic breakdown along with careful scrutiny of the damage morphology. In these cases the intrinsic surface breakdown field was at best equal to the bulk value. However, these comparisons excluded damage at the surface attributed to defects, involving little or no pulse truncation. The true surface thresholds were therefore
always less than the bulk values. In nominally low absorption materials the bulk thresholds are perhaps 2 - 10 times greater than the surface values.

Bloembergen, (2.30) has shown that the local electric field, $E_{\text{loc}}$ in the region of a defect in the form of a void can be expressed as

$$\frac{E_{\text{loc}}}{E_0} = \varepsilon \left[ \varepsilon + (1 - \varepsilon)L \right]$$

where $E_0$ is the incident field, $\varepsilon$ is the dielectric constant and $L$ a depolarization factor dependent on the shape of the void. The shape factor $L$ has a value of $1/3$ for a spherical void, $1/2$ for a cylindrical void and $-1$ for a V shaped void resembling a thin crack. The local electric field intensity is proportional to $nE^2$ where $n$ is the refractive index. Assuming a refractive index of 1.5, the electric field intensity is enhanced by a factor varying between 2.25 for spherical voids to 7.6 for cracks. The enhancement can become even more dramatic if the refractive index is high as occurs in the infra-red. The non-perfect roughened microstructure of the surface can result in an enhanced electric field which reduces the damage threshold. This effect also applies to voids in the bulk of the sample or within thin films where they are more numerous. The actual damage mechanism may be one of the intrinsic processes described earlier or simply localized linear absorption.

Recent studies by Pinnick et al, (2.31) on the laser induced breakdown of small liquid droplets in air have many similarities to electric field enhancement in the region of a defect. Their more rigorous calculations for the enhancement of the electric field both in and around a sphere show that at resonance conditions, enhancements of $10^6$ can occur. However, perhaps what is more important is that at a non-resonant condition enhancement factors of 100 can occur both in and near to the sphere. Their breakdown model of field enhanced multi-photon absorption was in excellent agreement with their measured wavelength dependence where the breakdown intensity increased.
approximately linearly with wavelength in the range 266 to 1060 nm. A further interesting feature was that the breakdown field for the droplets also increased as their refractive index decreased. This trend is in agreement with laser damage threshold measurements made using many different laser wavelengths, pulsewidths and materials.

They also comment that the multi-photon model without field enhancement failed to predict the observed wavelength dependence. This failure also applied to the avalanche ionization model both with and without field enhancement. It is the authors opinion that similar models should also apply to laser damage in solids since in practice damage thresholds are always limited by defects which can be considered as small, localized refractive index inhomogeneities.

2.3 Laser induced damage in thin films

The first order optical properties of reflectance and transmittance of a thin film multi-layer are calculated by representing the films as ideal, isotropic, homogeneous, non-absorbing slabs with differing refractive indices stacked one on top of another. The large number of defects within the multi-layer is attributed to the non-ideal microstructure and the presence of local absorbing impurities both within the bulk of the film and at the interfaces. This results in increased absorption and scattering over that arising from the same film material in bulk form. The abundance of defects usually means that thin film coated optics are the limiting components in any optical system and will have the lowest damage thresholds.

Many coating, deposition parameters influence the film microstructure which tends to make thin film properties more difficult to reproduce. A further problem with large optics is the difficulty in achieving the required optical performance over the whole area. This makes damage threshold trends and comparisons very difficult and has often resulted in damage threshold discrepancies in the literature.

Laser damage threshold measurements in thin films can
be divided into measurements on single layers and measurements on multi-layers. Single layer measurements are usually done to investigate laser damage mechanisms and secondly to help identify high damage threshold films for use in the more important multi-layer applications. The latter can be divided into high reflection coatings whose reflectance typically exceeds 99% and anti-reflection coatings whose reflectance may be less than 0.1%. Other widely used thin film multi-layer coatings include partial transmitters for beam splitters and thin film polarizers. Excellent introductions and reviews of laser damage in thin films are given by Lowdermilk and Milam, (2.32) and the experimental and theoretical papers of Walker et al, (2.33). At excimer laser wavelengths most of the damage threshold data in thin films has arisen from the Los Alamos and Lawrence Livermore national laboratories in the USA. This work is reviewed in detail in chapter 8.

The widest range of single shot damage threshold measurements on thin films is probably that of Walker et al, (2.33). Their work involved a detailed comparison between experimentally measured single shot damage thresholds at various laser wavelengths and pulsewidths and the damage mechanisms of avalanche ionization, multi-photon ionization and damage from absorbing inclusions. Their observations included:

i. The damage threshold decreased as the wavelength reduced from 1060 nm to 266 nm.

ii. The damage threshold scaled approximately as \((\text{pulsewidth})^{1/4}\).

iii. The damage threshold increased as the film thickness decreased.

iv. The threshold damage morphology consisted of several pits for films whose UV absorption edge was well away from the laser wavelength and uniform damage over the beam area when the film absorption was high.

v. The spatial density of the damage pits at the threshold level increased and their size decreased as the laser wavelength was reduced.
These features were found to be consistent with their model of a laser heated absorbing spherical defect. This required the sphere size to be comparable to the film thickness.

Few consistent factors have been identified for producing high damage threshold thin film coatings. Improvements can arise from the design stage, manufacture stage or some post manufacture treatment stage. It is the authors opinion that optimizing the coating process and the coating conditions for a particular film is probably where the greatest gains can be made.

2.4 Laser damage threshold scaling relationships

Laser damage threshold scaling relationships are useful since they can be measured experimentally and compared with predictions given by the various models of laser damage. They also have a further use as a design tool for new systems. The laser scaling variables include wavelength, pulsewidth, focused spot size and shot number. The optical component variables can include refractive index, absorption, scattering, band gap, surface roughness and many other thin film parameters such as thickness, stress, and deposition conditions, etc. A major difficulty is that the laser damage threshold is influenced by a large number of parameters and it is not always easy to isolate and vary just one parameter. The problem is compounded by the fact that different groups can measure widely varying thresholds for the same nominal component, (produced in the same coating run), with the same pulsewidth. In a recent round-robin test involving 1060 nm laser damage testing, the damage threshold was found to vary over a wide range, (2.34).

The functional form of the damage threshold scaling relationship with wavelength for dielectric materials is not obvious. For bulk breakdown in alkali-halides there appears little wavelength dependence down to about 694 nm. At wavelengths shorter than this the damage threshold generally decreases as the wavelength is reduced. This trend is expected as multi-photon absorption effects start.
to dominate over avalanche ionization. More success has been found in measuring the breakdown field dependence on the laser pulsewidth. Detailed measurements by Soileau et al, (2.35) indicate very little dependence of the breakdown field, $E_b$, on pulsewidth, $\tau$ in the range $\tau = 0.1 - 100$ ns. At shorter pulse widths the breakdown field follows $\tau^{-m}$ where $m = 0.3 - 0.5$. These trends are in good agreement with the avalanche model of Sparks, (2.22). The breakdown fluence in Jcm$^{-2}$ is proportional to $|E_b|^2 \tau$, giving a fluence dependence in the nanosecond region proportional to $\tau$ and an average dependence for short pulses of $\tau^{0.2}$.

The experimentally observed scaling factors for thin films are reviewed in chapter 8. Various scaling relationships based on ionization and plasma absorption have been developed by Bettis et al, (2.36,2.37) and tested on thin films and surfaces. When all of the parameters are combined together they give a predicted fluence dependence given by

$$F_b = A[p/(n^2 - 1)]^{2m}d^{-l} \sigma^{-2p} \quad 2.7$$

where $A$ is a material dependent proportionality constant, $p$ the material density, $n$ the refractive index, $m = 0.5$, $d$ the focused laser spot size, $\sigma$ the RMS surface roughness and $p = 0.5$. The general trend predicted by equation 2.7 with refractive index, spot size and pulsewidth has been widely observed. The pulsewidth dependence of the surface damage threshold has been studied in detail by Milam, (2.28) at 1060 nm on BK-7 and Rainer et al on fluoride crystals at 248 nm, (2.27). Both studies confirmed a square root dependence on the pulsewidth. However, this dependence does not necessarily imply a combined avalanche and plasma model since the thermal models in a metal and an absorbing defect can also give this dependence. The wavelength dependence is probably the critical identifying factor but is also the most difficult to measure accurately and consistently.
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Chapter 3
Pulsed laser diagnostics

3.1 Introduction

The basic experimental arrangement for the measurement of laser induced damage thresholds is illustrated in figure 3.1. A laser pulse is focused by a lens and the test sample is positioned in the focal region. The laser beam intensity \( I(x,y,t) \) and pulse energy incident onto the test sample are related by the integral equation

\[
E_{DP} = \int_t \int_y \int_x I(x,y,t) \, dx \, dy \, dt \quad 3.1
\]

In the most general situation the intensity function \( I \), measured in \( \text{Wcm}^{-2} \) may be different at each point in the focused beam. It follows from equation 3.1 that the incident beam power \( P(t) \) measured in watts is given by

\[
P(t) = \int_y \int_x I(x,y,t) \, dx \, dy \quad 3.2
\]

The fluence, \( F(x,y) \) or energy density incident onto the test sample is measured in \( \text{Jcm}^{-2} \) and is related to the pulse energy \( E_{DP} \) by

\[
E_{DP} = \int_y \int_x F(x,y) \, dx \, dy \quad 3.3
\]

Comparison between equations 3.1 and 3.3 shows that the fluence is calculated from the time integrated intensity given by

\[
F(x,y) = \int_t I(x,y,t) \, dt \quad 3.4
\]

To characterize high power focused glass laser systems,
FIGURE 3-1
TYPICAL FOCUSING GEOMETRY FOR A LASER INDUCED DAMAGE THRESHOLD MEASUREMENT
\((10^9 - 10^{11} \text{ Wcm}^{-2})\), it has been found necessary to record the on axis intensity, \(I(0,0,t)\) and the entire two dimensional distribution, \(F(x,y)\) for every laser shot, \((3.1)\). This is because the beam shape varies from shot to shot. Capturing and processing the two dimensional fluence distribution using a photographic process or vidicon camera can be very time consuming and labour intensive if required for every laser pulse. An alternative simpler approach is to assume the shape of the spatial distribution of the focused radiation does not vary from shot to shot. This was found to be the case with the KrF excimer and was adopted for laser damage testing procedures in this work. With a nominal constant laser pulse energy, a pinhole scan of the focal region reproduced the fluence function \(F(x,y)\). By measuring the total pulse energy, equation 3.3 was used to scale \(F(x,y)\) to calculate the peak fluence \(F_0\). It is convenient to further simplify this approach by assuming the spatial distribution \(F(x,y)\) is separable into the form

\[
F(x,y) = F(x)F(y)
\]

and to fit a Gaussian function to the experimental data in the \(x\) and \(y\) directions. The validity of doing this is considered in section 3.7. Fitting a Gaussian distribution to the spatial profile in the focal region had two main advantages:

1) Simplicity of calculating the peak fluence for laser damage test experiments
2) A mathematical representation of \(F(x,y)\) is convenient for the analysis of the laser damage threshold dependence on the focused spot size described in chapter 8.

The peak intensity was measured by recording the power \(P(t)\) incident onto the test sample using a fast detector. Integrating in time and scaling with equation 3.1 gave the peak power which was converted to power density by
dividing by the effective area. In practice an effective pulse duration was used to convert energy to peak power.

To fully characterize the laser intensity present in the focused interaction region, three parameters of the laser pulse were measured, these were:

1) The pulse energy, $E_{DP}$ incident onto the test sample
2) The effective spatial area of the beam, $A_0$
3) The effective temporal duration of the laser pulse, $\Delta$

The peak energy density or fluence, peak power and power density are then given by

$$F_0 = \frac{E_{DP}}{A_0} \quad (J/cm^2)$$

$$P_0 = \frac{E_{DP}}{\Delta} \quad (MW)$$

$$I_0 = \frac{E_{DP}}{A_0\Delta} \quad (MW/cm^2)$$

This chapter considers the various diagnostic techniques which are available for the control and measurement of laser pulse energy and power at the KrF wavelength of 248 nm. Section 3.2 reviews rare gas halide operating wavelengths and discusses some of the operational characteristics of the Lambda Physik EMG200 excimer laser used in this work. Sections 3.3 and 3.4 discuss the measurement of pulse energy and power at 248 nm. The performance of several detectors is compared in terms of their response speed and linearity. Section 3.5 compares the design and performance of several laser beam attenuators for use at 248 nm. Section 3.6 considers the calculation of the spatial distribution of the focused excimer laser radiation. Section 3.7 compares several experimental methods for the measurement of the transverse spatial profile of the focused excimer radiation.
3.2 Rare Gas Halide (RGH), laser characteristics

Optical fluorescent emission at ultra-violet wavelengths was first observed from Rare Gas Halide (RGH) excimer molecules in 1974. The development of the rare gas halide laser quickly followed. The first was the XeBr laser operating at 282 nm followed by KrF (248 nm), XeCl (308 nm), XeF (351 nm) and ArF (193 nm). The lasing wavelengths of the rare gas halide lasers are shown in figure 3.2 along with the wavelengths of the other excimers. The most efficient rare gas halide laser is the KrF laser with an operating efficiency typically exceeding 1% and a bandwidth (FWHM) of about 0.5 nm centred around 248.6 nm.

The lasing medium for rare gas halide lasers is a three component gas mixture at a pressure of a few atmospheres. The major component, greater than 90% is the buffer gas, usually chosen from helium, neon or argon. The remaining components are the rare gases argon or krypton and the halogen donor usually chosen from F₂, NF₃, Cl₂ or HCl. A population inversion is achieved by selective excitation reactions of the gas mixture in a plasma state. Excitation to the upper laser level primarily occurs through two types of reaction. The first is the so-called "harpooning" reaction involving an excited rare gas atom, R* and the halogen donor XY

\[ R^* + XY \rightarrow (RX)^* + Y \]  

where Y is the radical attached to the halogen. This process is very efficient if the halogen donor is F₂. The excited upper state is considered as an ionic combination R⁺X⁻. The second major formation process is three body ion-ion recombination

\[ R^+ + X^- + A \rightarrow (RX)^* + A \]  

where A is some third body which may be a buffer gas atom. Quenching reactions compete with radiative decay of the excited state (RX)*. In a typical laser gas mixture for
RARE GASES

126 146 172

RARE GAS HALIDES

ArF XeF XeCl XeBr XeCl IF
193 222 228 300 381 496

HALOGENS + INTERHALOGENS

F2 Cl2 ClF2 I2 BrF
157 259 254 352 354

MERCURY HALIDES

HgF HgBr HgCl
360 520 530

RARE GAS HALIDE TRIMERS

XeF XeCl
410 420 440 470

FIGURE 3.2

WAVELENGTHS OF EXCIMER LASERS
KrF the radiative and collisional quenching lifetimes are both of the same order in the range 5 - 10 ns, (3.3). It is clear from the reactions described in equations 3.9 and 3.10 that the pumping process requires the formation of excited and ionic rare gas atoms. This has been done by electron-beam pumping and avalanche electrical discharge pumping. Electron beam pumped devices have generally been developed at large national laboratories where they have been scaled to large sizes. An example is the SPRITE laser developed at the Rutherford and Appleton laboratories with a KrF output of 200 J in a 60 ns pulse. Electrical discharge pumped devices have seen rapid laboratory and commercial development mainly due to their amenable size. A fast electrical discharge circuit is required due to the short upper-state lifetime of KrF* and the pumping requirements in the UV. A uniform distribution of pre-ionization electrons is required in the inter-electrode region just prior to switching the main discharge in order to prevent streamer arc formation. The technology of pre-ionization developed for Transverse Excited Atmospheric, (TEA) CO₂ lasers has been used and extended to achieve uniform pre-ionization. Most developments of pre-ionization techniques have used UV pre-ionization from a series of spark discharges adjacent to and distributed along the main discharge length.

A commercial device, the Lambda Physik EMG200 excimer laser was used in this work. This is a single discharge pumped device operating at a gas pressure of about 2.5 bar. Most of the work was carried out at the KrF wavelength of 248 nm where the maximum specified output energy was 1 J at a maximum pulse repetition rate of 10 Hz. The 1.0 m laser cavity consisted of a plane/plane MgF₂ output coupler and a plane, nominal 100% reflectivity multi-layer dielectric rear reflector. The rear mirror was isolated from the discharge cell by a plane/plane MgF₂ window. The rectangular beam shape is approximately 26 x 9 mm at the laser output aperture. The divergence of the smaller dimension (vertical) is about 2 mrad. and horizontally about 4 mrad. These relatively high
divergence figures could be reduced at the expense of the pulse energy by spatial filtering. A typical gas mixture for KrF operation was 1:1.25:18.6 for fluorine, krypton and helium respectively. The fluorine was contained in a 5% F₂/95% Helium gas mixture. Special passivated gas regulators were used to handle the reactive fluorine gas. A careful gas handling procedure was devised to minimize the water content of the gas cell and to passivate the associated pipework before admitting the laser gas mixture. This was found to be important if the discharge region had been exposed to air for maintenance purposes. Most of the damage test experiments were done on a single shot basis or at low repetition rates. In this case one gas fill was sufficient for several days running. The initial deterioration in performance was a loss of output energy as the fluorine was consumed and could be restored by the addition of more fluorine. Further use resulted in discharge arc formation possibly from discharge reaction by-products. This should be avoided because of electrode damage and future loss of field uniformity. At high repetition rates the gas recycling fan contained within the discharge chamber was operated to replenish the discharge volume with fresh gas after each shot.

Recent developments in the technology of electrical discharge pumped excimer lasers have included the use of X-ray pre-ionization, magnetic switching to replace high voltage hydrogen Thyratrons and extended gas-fill lifetimes using cryogenic gas clean-up systems.

3.3 Laser beam sampling

Beam sampling is usually employed to enable on-line energy or power monitoring of the laser output whilst maintaining the detector in its linear operating range. The two main beam sampling techniques are beam scattering and amplitude splitting.

Beam scattering is usually done with a Lambertian surface and collecting a known fraction of the back scattered laser light. Attenuation factors down to 10⁻⁶ are easily achievable. The main disadvantage with
this technique is that the geometry does not conveniently fit into the experimental arrangement for laser damage testing. Other disadvantages include the approximation of the diffusing surface to a true Lambertian one and the likely laser induced surface damage as a result of the shallow skin depth over which the excimer laser radiation is absorbed.

The more convenient and simpler beam sampling technique is amplitude splitting using the Fresnel reflections from a flat homogeneous parallel sided slab of dielectric material. This is illustrated in figure 3.3, where only the two dominant Fresnel reflections, beams 2 and 3 are shown. The choice of beam splitter material is determined by the laser operating wavelength. At the KrF wavelength of 248 nm fused silica (Spectrosil B) has negligible absorption and has a refractive index, \( n_2 = 1.508 \). The absorption band edge for fused silica is around 200 nm, a more suitable beam splitter material for the ArF wavelength of 193 nm is therefore calcium fluoride (CaF\(_2\)) or magnesium fluoride (MgF\(_2\)). Considering figure 3.3 the most generalized energy balance equation for the incident laser light is given by

\[
R + T + SC + A = 1
\]

where \( R \) is the total specular reflectance (including multiple reflections), \( T \) - transmittance, \( SC \) - total scattering and \( A \) the total amount absorbed. In the case of fused silica at 248 nm the absorption, \( A \) is taken as zero. Initially a perfectly homogeneous parallel sided dielectric slab is considered with perfectly planar dielectric interfaces. In this case the total scattering \( SC \) is also zero and 3.11 simplifies to

\[
R + T = 1
\]

The KrF output from the EMG200 excimer laser was randomly polarized and therefore for the purposes of calculating the Fresnel transmittance and reflectance for
FIGURE 3.3

FRESNEL REFLECTIONS FROM A LASER BEAM SPLITTER
the beamsplitter shown in figure 3.3, the total laser energy can be considered divided equally into the two orthogonal polarization states, (the electric vector parallel to the plane of incidence, $P$ and the electric vector perpendicular to the plane of incidence, $S$). Using the notation shown in figure 3.3 the Fresnel intensity reflectance and transmittance values for the interface 1/2 are given by

$$ R_{P,12} = \frac{2}{\tan^2(\theta_i - \theta_t) + \tan^2(\theta_i + \theta_t)} $$

$$ T_{P,12} = \frac{n_2 \cos^2 \theta_t}{n_1 \cos \theta_i} \left[ \frac{2 \sin \theta_t \cos \theta_i}{\sin(\theta_i + \theta_t) \cos(\theta_i - \theta_t)} \right]^2 $$

$$ R_{S,12} = \frac{2 \sin(\theta_i - \theta_t)}{\sin^2(\theta_i + \theta_t)} $$

$$ T_{S,12} = \frac{n_2 \cos^2 \theta_t}{n_1 \cos \theta_i} \left[ \frac{2 \sin \theta_t \cos \theta_i}{\sin(\theta_i + \theta_t)} \right]^2 $$

where $P$ denotes the incident electric vector parallel to the plane of incidence and $S$ the incident electric vector perpendicular to the plane of incidence. Interference is ignored and multiply reflected beams are added on an intensity basis. Allowing for multiple reflections between the 1/2 and 2/1 interfaces and knowing $|R_{12}| = |R_{21}|$ and $|T_{12}| = |T_{21}|$ (for the beam splitter in air) the over-all intensity reflectance $R_{P/S}$ and transmittance $T_{P/S}$ for the $P$ or $S$ component is

$$ R_{P/S} = R_{P/S12} + \frac{(T_{P/S12})^2}{1 - (R_{P/S12})^2} $$
In the general case where a fraction of the incident laser energy, \( P \), is polarized parallel to the plane of incidence and the remaining fraction, \( S \), perpendicular to the plane of incidence, the over-all reflectance and transmittance is given by

\[
\frac{T_{P/S}}{S} = \frac{(T_{P/S12})^2}{1 - (R_{P/S12})^2} \tag{3.18}
\]

\[
R_{SLAB} = PR_P + SR_S \tag{3.19}
\]

\[
T_{SLAB} = PT_P + ST_S \tag{3.20}
\]

and

\[ P + S + 1 \tag{3.21} \]

The transmittance of a fused silica beam splitter (in air at 248 nm) as a function of incident angle calculated using equation 3.20 is shown in figure 3.4 for three polarization states. Random polarization is equivalent to the case \( P = S = 0.5 \). The deviation of the transmission from its zero angle of incidence value of 92.1% is not significant until the angle of incidence is greater than 35°.

Any real dielectric interface can be considered to have a finite, RMS surface roughness, \( \sigma \). This results in a scattering component, \( SC \) as described in equation 3.11. At an angle of incidence \( \theta_1 \) as shown in figure 3.3, the intensity of the diffusively scattered component, \( I_D \) relative to the specular component, \( I_S \), for each specular reflection is given by, (3.4, 3.5)

\[
\frac{I_D}{I_S} = \frac{1 - \exp[-(4\pi n_2 \cos \theta_1 / \lambda)^2]}{\exp[-(4\pi n \cos \theta_1 / \lambda)^2]} \tag{3.22}
\]

Using values of \( n_2 = 1.5085 \), \( \lambda = 248 \text{ nm} \), \( \theta = 0^\circ \) and a conservative figure of 5 nm for the RMS surface
FIGURE 3.4

Transmission of a fused silica beam splitter at 248 nm as a function of angle of incidence (three polarization states, P=1, S=1, P=S=.5)
roughness, (3.5) gives $I_D/I_S = 15.7\%$. This corresponds to an over-all percentage of scattered light relative to the input beam of 0.64\%. The same calculation but with the wavelength shifted to the visible region ($\lambda = 580$ nm) produces a scattered intensity about a factor of six down compared to the value at 248 nm.

At zero degrees incidence, equation 3.19 gives the over-all Fresnel reflectance for a perfect beam splitter of 7.9\%. The first two reflections shown in figure 3.3 are the dominant contributors to the over-all scattered intensity calculated using equation 3.22 and give a scattered percentage of 1.25\% relative to the input beam. The transmittance from equation 3.11 is therefore $[100 - (1.25 + 7.9)] = 90.85\%$. This figure compares with an average zero incidence angle value of 90.7 ±0.5\% measured on several Spectrosil B fused silica samples using a Perkin Elmer 323 spectrophotometer. The specular reflectance of the beam splitter was more difficult to measure accurately since it required an assumption for the reflectance of some mirror standards at 248 nm. An average value of 7.9 ±0.3\% was measured. Experimental data points are included on figure 3.4 for the transmission of a 3 mm thick sample of fused silica. The results suggest that the light output of the spectrophotometer was partially polarized towards the $S = 1$ direction.

Beam steering effects for both the reflected and transmitted rays are also illustrated in figure 3.3. The shift in the transmitted ray, $X$ and the separation between adjacent reflected rays, $Y$ are given by

$$X = d[\sin \theta_i - \cos \theta_i \tan \theta_t]$$

and

$$Y = \frac{d(n_1/n_2)\sin 2\theta_i}{\cos \theta_t}$$

where $d$ is the beam splitter thickness. The effect of the
back surface having a small wedge angle \( \alpha \) with respect to
the front surface is to increase the effective thickness
to \( d' \), where

\[
d' = d + f \tan \alpha \quad 3.25
\]

where \( \varphi \) is the beam splitter diameter and \( f \) a numerical
value which varies linearly between 0 and 1 depending on
the position of the incident ray with respect to the beam
splitter diameter. The second effect of the wedge angle \( \alpha \)
is to rotate the transmitted ray

\[
\theta_{TR} = \theta_1 - \sin^{-1} [n_2 \sin(\theta_t - \alpha)] \quad 3.26
\]

and rotate the reflected ray by

\[
\theta_{REF} = \theta_1 - \sin^{-1} [n_2 \sin(\theta_t - 2\alpha)] \quad 3.27
\]

Typically, a commercially purchased quality parallel
sided beam splitter has a wedge angle, \( \alpha \) less than 0.1°.
Using a beam splitter operating at its centre \( (f = 0.5) \), a
thickness \( d \) of 8 mm and a diameter \( \varphi = 50 \) mm gives an
effective thickness, \( d' = 8.04 \) mm from equation 3.25.
This differs by 0.5% from the nominal value. At ten
degrees incidence, \( \theta_{TR} = 0.15° \) and \( \theta_{REF} = 0.3° \) from
equations 3.26 and 3.27. The deviation of the transmitted
ray from the back surface is 0.48 mm. Similarly the Y
separation of the reflected beams is 1.84 mm.

Experimentally a helium neon laser was used to define
the optical axis, with a second identical beam splitter at
an angle of incidence \( -\theta_1 \) relative to the first to
compensate for the shift in the transmitted ray through
each beam splitter.

3.4 Pulsed laser energy and power measurements

3.4a Requirements

Two major requirements for laser damage testing are
measurements of the energy density and power density distribution incident onto the test sample and also their peak values. This requires measurement of the absolute laser pulse energy incident onto the sample for each laser pulse and also its temporal distribution. The basic experimental arrangement used for these measurements is shown in figure 3.5. Two beamsplitters, B/S1 and B/S2 were used to correct for the deviation in the optical axis as discussed in section 3.3. In this situation a separate energy and temporal pulse monitor are shown although they may be combined by integrating the temporal output. The energy incident onto the front surface of the test sample, (known as the damage plane) was calculated by measuring the Fresnel reflectance and transmittance of the two beamsplitters B/S1 and B/S2 as described in section 3.3.

The energy indicated by the energy monitor, \( E_{EM} \) is given by

\[
E_{EM} = (1 - K)R_1 E_{IN} \tag{3.28}
\]

where \( E_{IN} \) is the incident pulse energy onto the first beamsplitter, \( R_1 \) is the combined specular and diffuse reflection from beamsplitter B/S1 received by the detector aperture and \( K \) is a fractional loss factor which accounts for losses such as back reflections from the energy monitor. The laser pulse energy incident onto the damage plane, \( E_{DP} \), is given by

\[
E_{DP} = T_1 T_2 T_3 E_{IN} \tag{3.29}
\]

where \( T_1 \), \( T_2 \) and \( T_3 \) are the transmission factors for B/S1, B/S2 and the focusing lens respectively. Substituting equation 3.28 in equation 3.29 gives

\[
E_{DP} = T_1 T_2 T_3 \frac{E_{EM}}{(1 - K)R_1} \tag{3.30}
\]
FIGURE 3.5

EXPERIMENTAL ARRANGEMENT FOR LASER DAMAGE TESTING
The peak power incident onto the damage plane, $P_{DP}$, can be calculated from knowing, $E_{DP}$ and the equivalent pulse duration $\Delta$. The equivalent pulse duration of a waveform is the width of the equivalent pulse of the same area and height as the experimental one. The power, $P_{DP}$, incident onto the damage plane is then given by

$$P_{DP} = \frac{E_{DP}}{\Delta} \quad 3.31$$

The aim was to use the calorimeter to measure $E_{DP}$ and maintain the pulse measuring device in its linear range to measure $\Delta$. The general requirement was to be able to measure the peak energy density and power density incident onto the test sample with an accuracy of ±5%. This accuracy requirement for the peak energy density and power density were not easy to achieve at the KrF wavelength of 248 nm and some consideration is given to the most suitable detectors.

3.4b Detectors

Detectors can be broadly classified into two basic types, thermal detectors and photometric detectors. Thermal detectors respond to the temperature change as a result of energy absorption; examples include thermocouples, thermopiles, thermisters, bolometers and pyroelectric elements. Photometric detectors respond to the varying incident light intensity. Examples include the photoemissive detectors such as photomultipliers and vacuum photodiodes and solid state detectors such as PIN photodiodes and avalanche photodiodes. Thermal detectors are conveniently divided into calorimetric detectors and pyroelectric detectors.

3.4bi Calorimetric detectors

Calorimetric detectors for use with pulsed lasers consist of an absorbing element to absorb the incident laser radiation and a temperature sensor whose output is proportional to the resultant temperature rise and therefore absorbed energy. The absorbing element is
either a surface absorber or a volumetric absorber. Surface absorbers usually employ a spectrally non-selective absorbing black paint and rely on thermal conduction from the absorbing paint to the substrate (often metallic). Volumetric absorbers such as liquids have the inherent potential to handle higher incident power densities than surface absorbers. The temperature sensors are usually arranged around and in intimate contact with the absorbing element. For precision measurements the absorber needs a small temperature rise and a fast rise time to give a uniform temperature distribution throughout the absorbing element, \((3.6)\). The small temperature rise \((<473 \text{ K})\) is to minimize re-radiation losses which vary as \(T^4\) and keep the sensor in its linear operating range. The fast rise time, \((\text{typically less than } 1 \text{ s})\), is to minimize the loss of absorbed energy by conduction and also minimize the effects of spatial non-uniformity of response across the face of the absorber. The reference part of the sensor, e.g. the cold junction of a thermocouple, is usually mounted on a large heat sink so that it is in equilibrium with the ambient surrounding temperature. The \(e^{-1}\) cooling time is controlled by the loss of heat to the surroundings and is typically 20 - 50 times longer than the risetime, \((3.7, 3.8)\). The equilibrium time or reset time of the calorimeter is therefore about 5 - 6 times the \(1/e\) cooling time.

An energy balance equation can be written in terms of the energy measured by the calorimeter, \(E_{\text{EM}}\) and the energy loss, \(E_{\text{LOSS}}\). From figure 3.5

\[
R_1 E_{\text{IN}} = E_{\text{EM}} + E_{\text{LOSS}} \tag{3.32}
\]

The fractional loss factor used in equation 3.28 is defined as

\[
K = \frac{E_{\text{LOSS}}}{R_1 E_{\text{IN}}} \tag{3.33}
\]
The loss factor $K$ is a composite term representing many sources of energy loss and can be expressed as

$$K = \sum_{i} k_i \tag{3.34}$$

The major loss terms in equation 3.34 are window losses via reflection and absorber losses such as reflection, re-radiation and conduction. Table 3.1 lists several types of laser calorimeter, their typical energy measurement range and their typical reset times.

<table>
<thead>
<tr>
<th>CALORIMETER TYPE</th>
<th>ENERGY RANGE</th>
<th>RESET TIME</th>
</tr>
</thead>
<tbody>
<tr>
<td>METAL DISK</td>
<td>$10^{-2} - 10$</td>
<td>$10$</td>
</tr>
<tr>
<td>CONE</td>
<td>$2 \times 10^{-2} - 10^3$</td>
<td>$1 - 20$</td>
</tr>
<tr>
<td>THERMOPILE</td>
<td>$10^{-6} - 1$</td>
<td>$10^{-1} - 10$</td>
</tr>
<tr>
<td>LIQUID</td>
<td>$1 - 500$</td>
<td>$10 - 60$</td>
</tr>
</tbody>
</table>

Table 3.1
Pulsed laser calorimeter characteristics

The simplest device is the metal disk calorimeter, usually coated with an absorbing paint. Since the laser radiation is absorbed at a single surface the main limitation of the disk calorimeter is its power handling capability. The power handling capability of the cone calorimeter is superior to that of the metal disk because the absorption occurs over many reflections. This technique of using multiple reflections to absorb the laser energy has been used in other geometries such as cylinders and spheres. Thermopile calorimeters can be very sensitive and employ an array of thermocouples in series mounted on the backside of the absorbing surface. They can also offer a good uniformity of response over the absorbing surface aperture. Volumetric calorimeters have the highest power handling capability. The main disadvantage of the liquid calorimeter is the long reset time.
It is apparent from table 3.1 that an inherent disadvantage of all calorimeters for pulsed laser energy measurement is their single shot nature. Other disadvantages include the difficulty of absolute accurate calibration and their sensitivity to background thermal sources and air currents. Absolute pulsed laser energy measurements are usually achieved by using a detector whose calibration is traceable to national standards. In many laboratory situations a calibrated calorimeter is used as a secondary standard to calibrate detectors which may be more convenient to use such as pyroelectric or photometric detectors. The influence of background thermal sources can be minimized by operating a calorimeter in a differential mode using two identical absorbing elements viewing the same background scene. Air currents passing over the absorbing element can be minimized using a front cover window or recessing the absorbing element in a long tube.

A commercial device manufactured by Laser Instrumentation was used for absolute measurements of pulsed laser energy in this work. The shallow skin depth associated with surface absorption of excimer laser radiation meant that a volumetric absorbing element was more appropriate. The Laser Instrumentation model 17AN is a thermopile device using an "absorption in depth" glass disc as the absorbing element. Its calibration, traceable to National Physical Laboratory standards varies by ±3% over the sensing area. The main loss terms in equation 3.34 were minimized by operating without a cover window. Re-radiation from the glass disc was considered negligible at incident energy densities in the range 4 - 40 mJcm\(^{-2}\) with corresponding power densities of 0.16 - 1.6 MWcm\(^{-2}\) (25 ns pulse). The reflectance of the absorbing glass in the detector was measured at 248 nm as 4.9 ±0.2% giving \(K = 0.049 ±0.002\) in equation 3.28. To eliminate errors of calibration in using a secondary laboratory standard the Laser Instrumentation device was used to monitor the pulse energy in all single shot laser damage test experiments. The accuracy of measuring the pulse energy incident onto
the test specimen depends upon an error analysis of equation 3.30. The value of $T_1$, $T_2$, and $R_\text{i}$ are given in section 3.3 as 0.907 ± 0.005, 0.907 ± 0.005 and 0.079 ± 0.003 respectively. The transmittance of the planoconvex lens, $T_3$, at 248 nm was measured as 0.90 ± 0.005. The percentage error given for $E_{\text{EM}}$ is ±0.03. These combine to give an over-all percentage error in the measurement of pulse energy of ±4.9%. Equation 3.30 can be re-written as

$$E_{\text{DP}} = (9.85 \pm 0.48)E_{\text{EM}}$$  \hspace{1cm} 3.35

In the situation where only one beamsplitter was used, $T_2 = 1.00$ and equation 3.35 becomes

$$E_{\text{DP}} = (10.86 \pm 0.53)E_{\text{EM}}$$  \hspace{1cm} 3.36

These equations were used to calculate the pulse energy incident onto the test sample as shown in figure 3.5.

3.4b1i Pyroelectric detectors

The pyroelectric effect arises from the temperature dependence of the electric polarizability of certain ferroelectric materials below their Curie temperature. The domains of a ferroelectric material can be aligned along a single direction during its manufacture. Surfaces of the material normal to the polarization axis develop a surface charge as a result of a change in the polarization due to absorbed energy. Electrodes on these surfaces connected via an external circuit generate a current, $i(t)$, given by

$$i(t) = p(T)A\frac{dT}{dt}$$  \hspace{1cm} 3.37

where $p(T)$ is the pyroelectric coefficient, $A$ is the active area and $dT/dt$ the rate of change of temperature. Since the pyroelectric material responds to the rate of temperature change, its inherent response speed is much
higher than the calorimetric detectors discussed in section 3.4bi. Some pyroelectric materials are hydroscopic and should be operated with optical windows. The pyroelectric material is usually coated with a spectrally non-selective black paint to give a uniform response over a wide wavelength range (UV to IR). The absorbing element is therefore a surface and relies on conduction of the absorbed energy into the pyroelectric substrate. Adiabatic heating of the pyroelectric material during the laser pulse results in the output current, given by equation 3.37 being proportional to the laser intensity. This occurs when the laser pulse duration is much shorter than the thermal cooling time. This condition is generally satisfied for laser pulses in the nanosecond regime.

The electrical model of a pyroelectric detector can be represented as a current source in parallel with a capacitor, C and effective load resistor, R. The over-all detector response time is controlled by the time constant RC. Two modes of operation are therefore possible, a pulsed mode and a time integrating mode. Accurate resolution of the laser pulse requires that \( t_R < 2.2RC \), where \( t_R \) is the rise or fall time of the laser pulse. The output impedance of a pyroelectric material is typically \( >10^{12} \Omega \). A transconductance amplifier may be used to match the high output impedance of the pyroelectric material and still maintain an effective 50 Ω load resistance. This is then matched into a co-axial cable and a 50Ω terminated fast oscilloscope. In the time integrating mode the RC time is much longer than the pulse duration. This results in a much longer pulse whose maximum is proportional to the laser pulse energy, (3.9). The thermal cooling time limits the maximum pulse repetition frequency (PRF) of the detector.

Several commercial companies produce pyroelectric detectors. Those that operate in the pulsed mode can have risetimes as short as 1 ns (e.g. Molectron). The time integrating versions for measurement of pulse energy are more popular and calibrated versions are available (e.g.
Gen-Tec or Laser Precision). The reliability of their absolute calibration is questionable for use with excimer lasers. Measurements at 248 nm using a Gen-Tec ED500 were optimistic by a factor of two compared to the Laser Instrumentation thermopile discussed in section 3.4bi. This observation was also made elsewhere, (3.10). The RC time of the Gen-Tec ED500 was 4 ms with a reset time of 1 s. This limits the maximum useable PRF to 1/s. A typical damage threshold for surface absorbing pyroelectric detectors is 100 mJcm⁻² for a pulse duration of 25 ns, (3.11). Operation of the Gen-Tec ED500 in the incident energy density range of 4 - 40 mJcm⁻² (25 ns pulse, FWHM) resulted in a grey discolouration of the matt black absorbing surface. This may be caused by the shallow skin depth for absorption of the 248 nm laser radiation producing a surface damage threshold below the quoted figure of 100 mJ cm⁻². A very inexpensive source of small uncalibrated pyroelectric detectors are those produced by Eltech. The model 400 is a 2 mm diameter device mounted in a TO5 header and protected by a fused silica window. This detector was used extensively in the pinhole scanning experiments described in section 3.7.

3.4biii Photometric detectors

The general properties of all photometric detectors are listed below

1 Square law response to electric field
2 High response speed
3 Wide dynamic range
4 Strong wavelength dependent responsivity
5 High sensitivity
6 Generally poor surface uniformity over the sensor area
7 Generally poor reproducibility from detector to detector

A basic property of all photometric detectors is that they
respond to the incident light intensity, \( I \) given by

\[
I = \langle \mathbf{E} \times \mathbf{H} \rangle
\]

where \( \mathbf{E} \) and \( \mathbf{H} \) are the electric and magnetic field vectors of the optical field and the brackets indicate a time average. In terms of the optical electric field, photometric detectors can be considered as square law devices when the device output is proportional to the laser intensity. At 248 nm the period of the optical field is \( 0.827 \times 10^{-15} \) s. As far as the author is aware there are no detectors available with a response time of about \( 10^{-15} \) s.

The most important two factors for making accurate laser pulsed power measurements are the response speed of the detector relative to the laser pulse risetime and falltime and operation of the detector in its linear range. The response speed of a photometric detector can be described by the simple electrical model shown in figure 3.6. The detector is represented as an ideal current source in parallel with a capacitor \( C_1 \) and connected in parallel to an external load resistor \( R_{LD} \).

The capacitance, \( C_1 \) is given by

\[
C_1 = C_{DET} + C_S
\]

where \( C_{DET} \) represents the intrinsic device capacitance and \( C_S \) the stray capacitance arising from its mounting. In the linear range of operation a step input light source can be represented by a step input current source. The exponential voltage risetime defined from the 10% to the 90% points across the load resistor is given by

\[
t_r = 2.2R_{LD}C_1
\]

The load resistor \( R_{LD} \) cannot be made arbitrarily small to minimize the risetime. This is because the output voltage amplitude is proportional to \( R_{LD} \) and that the load
FIGURE 3.6
ELECTRICAL MODEL OF A PHOTOMETRIC DETECTOR

FIGURE 3.7
ELECTRICAL MODEL OF A SOLID STATE PHOTODETECTOR
impedance has to be matched into the characteristic impedance of a co-axial cable to prevent reflections. The other important factor in making laser power measurements is the linear dynamic range of the device. Two power density thresholds can be considered above which non-linear behaviour occurs. The first occurs above an incident power density \( P_p \) (measured in W cm\(^{-2} \)) above which the detector output current is no longer linearly dependent on the incident laser intensity. This limits the maximum peak power which can be measured unless the transfer curve is known. The second threshold occurs above a power density \( P_E \) when the total integrated detector current (total collected charge) is no longer linearly dependent on the incident pulse laser energy. Generally \( P_E > P_p \) and the linear dynamic range for pulse energy measurements is therefore greater than that for peak power measurements, (3.12). Operation above the threshold \( P_p \) was prevented with the use of attenuators (discussed in section 3.5) and using the device well below its specified peak saturation current.

The shallow skin depth for absorption of KrF excimer laser radiation at 248 nm implies a surface sensor to achieve high quantum efficiency. In some cases significant attenuation may be required due to the high detector sensitivity. This may introduce further problems in that the absorption characteristics of the attenuator may change with incident power density. The variation in surface uniformity was averaged out by illuminating the sensor area uniformly. In these investigations this was done by mounting an unpolished \( \text{MgF}_2 \) blank in front of the detector window to act as a transmissive diffuse source. The poor reproducibility from device to device was overcome by reference to the more consistent calibration of the Laser Instrumentation calorimeter described in section 3.4b1.

Photometric detectors can be conveniently divided into photoemissive devices and solid-state devices. Photoemissive devices such as the vacuum photodiode or the photomultiplier rely on the generation of photoelectrons...
from an illuminated photocathode. The spectral response of the photocathode is denoted by its "S" number. Generally, for UV response at 248 nm an S5 or an S20 photocathode is suitable with a fused silica window. The UV cut-off wavelength is mainly determined by the absorption characteristics of the transmitting window. In the case of the vacuum photodiode the photoelectrons are accelerated to an anode held at some positive potential with respect to the cathode. This results in a current which can flow through an external load. The photomultiplier can be considered as a multi-stage vacuum photodiode. The secondary electrodes of the photomultiplier are known as dynodes. Secondary electron emission from each dynode produces more electrons resulting in an avalanche process. Consequently, photomultipliers have high sensitivities even down to the single photon level. Generally, this extreme sensitivity is not required for laser power measurements. Saturation of the photomultiplier output current is the main problem at high incident power densities. The vacuum photodiode is a more suitable device for pulsed laser power measurements. It has a comparable response speed to the photomultiplier and can operate linearly at a higher pulsed output current. The main intrinsic factors which limit the response speed of the vacuum photodiode are:

1) The photoelectron transit time from cathode to anode
2) The spread in the photoelectron transit time due to the varying initial photoelectron velocities
3) The transit time of the current pulse across the photocathode
4) At high incident intensities space-charge effects may modify the electric field distribution between the cathode and anode increasing the transit time.

The bi-planar vacuum photodiode tries to meet these limitations by using a planar electrode geometry to achieve field uniformity at high electric fields, (operating voltage usually 1 - 4 KV). The threshold power
for non-linear operation can be maximized by illuminating the photocathode uniformly. Typically for a ±10% non-linearity between input laser power and output current (assuming uniform photocathode illumination) the maximum photocurrent is approximately half the space charge limited value, (3.13). The main disadvantages with the bi-planar vacuum photodiode is its high voltage operation and cost. Other inexpensive vacuum photodiodes are available with a UV response which operate at low voltage but with a reduced response speed and linearity. The alternative to the photoemissive detector is the solid-state device. These consist of a PN junction operating in the reverse-bias mode. Absorption of laser energy in the junction region results in the generation of electron-hole pairs. Those minority carriers generated within the depletion region or within a few diffusion lengths of it are swept through the depletion region due to the favourable electric field. A current can therefore flow through an external load resistor in response to the varying laser intensity. The absorption skin depth in silicon at 248 nm is less than 100 nm, (3.14). UV sensitivity can therefore be enhanced by utilizing a shallow PN junction depth. The electrical circuit model of a reverse biased solid-state photodetector is shown in figure 3.7. The dynamic resistance $R_D$ in parallel with the external load resistor is typically $>10^9$ Ω in the reverse bias mode. The series resistance $R_S$ is typically a few ohms and represents the resistance of the non-depleted region and the contact resistance of the diode. The junction capacitance, $C_j$, depends upon the extent of the depletion region and is given by, (3.15)

$$C_j/pF = \frac{12200A}{(\rho_n(V_0 + V_B))^{1/2}}$$

where $A$ is the active area in cm$^2$, $\rho_n$ is the substrate resistivity of the n type silicon in ohm-cm, $V_0$ the self-depletion bias = 0.33V and $V_B$ the reverse bias voltage. The junction capacitance, $C_j$, can be minimized by using a
small area sensor with a high resistivity substrate and operating at a maximum reverse bias voltage, $V_B$. The series resistance $R_S$ can also be minimized by operating at a maximum reverse bias voltage. This reduces the extent of the non-depletion junction region.

There are three basic types of solid-state photodiode detector suitable for pulsed laser power measurements when the laser pulsewidth is in the nanosecond region. These are:

i. A low capacitance planar device which operates with a high resistivity N type substrate.

ii. The PIN device which operates with an intrinsic semiconductor material between the P and N type regions of the junction. This increases the extent and resistivity of the depletion region reducing the junction capacitance and series resistance. They are designed for high field use with operating voltages up to 200 V.

iii. The avalanche device which is similar to the PIN device but is designed to operate at high bias voltage before full depletion. In this case, the acceleration of the minority carriers through the depletion region is sufficient to produce and avalanche multiplication of the carriers in a similar fashion to that achieved by the photomultiplier. The quantum efficiency of the avalanche device is high and can approach that of photomultipliers.

The main factors that govern the over-all risetime, $t_R$, of the solid-state photodiode are:

a. The charge collection time, $t_{CC}$ which represents the minority carrier transit time across the depletion region.

b. The electrical, $R_C$ component of risetime which is given by

$$t_{RC} = 2.2 (R_S + R_{LD}) (C_{LD} + C_S)$$

3.42
where \( C_s \) is the stray capacitance from cables and mounting and \( R_D >> R_S + R_{LD} \).

c. The third response time is the diffusion response time, \( t_D \). This represents the drift time of carriers through a zero or low field region. The overall risetime is approximated by

\[
    t_R \approx \left[ (t_{CC})^2 + (t_{RC})^2 + (t_D)^2 \right]^{1/2}
\]

and can be reduced by operating with a fully depleted PN junction at high fields. In this case the high field reduces the minority carrier transit time across the depletion region. A fully depleted PN junction minimizes the resistance \( R_S \) and junction capacitance, \( C_j \) thus reducing \( t_{RC} \) in equation 3.42. The diffusion response time in the UV can be minimized by operating with a shallow PN junction depth at a high reverse bias voltage. This reduces the drift distance for minority carriers in the near zero field region.

The detailed behaviour of the response of solid-state photodiodes to pulsed laser radiation has been considered by Edwards, (3.12). Linear operation below the threshold power density \( P_p \) for peak power and \( P_E \) for energy measurements is complicated by the presence of the diffusion current. This results in the photodiode risetime (10% to 90%) usually being less than the photodiode fall-time (90% to 10%). Conveniently, manufacturers usually quote a response risetime. Experimentally the diffusion current contribution is usually observed as a tail on the falling edge of the laser pulse. It can be reduced by operating at higher reverse bias voltages. The maximum current for linear peak power operation is typically in the range 5 - 50 mA for PIN diodes operating at bias voltages between 20 - 100 V, (3.12). The diffusion current tail can be present even at low input powers. At high incident power densities the problem can become more severe because the high density of generated electron-hole pairs modify the
electric field distribution in the depletion region, increasing the carrier transit time.

The performance of four detectors has been investigated, their basic operating parameters are listed in table 3.2. These data were taken from manufacturers catalogues. The ITL 1850 bi-planar vacuum photodiode is a commercial instrument with a 0.1 ns risetime and falltime and a wide linear dynamic range. Its performance at the

<table>
<thead>
<tr>
<th>TYPE</th>
<th>OPERATING VOLTAGE/V</th>
<th>WINDOW MATERIAL</th>
<th>WAVELENGTH RANGE</th>
<th>ACTIVE AREA/mm²</th>
<th>DEVICE CAPACITANCE CDET/pF</th>
<th>DEVICE RISTIME/ns</th>
<th>SATURATION CURRENT/mA</th>
<th>SATURATION CURRENT DENSITY/mAmm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITL 1850 VACUUM PHOTODIODE</td>
<td>1000-3000</td>
<td>FUSED SILICA</td>
<td>200-800</td>
<td>254</td>
<td>0.9</td>
<td>0.1</td>
<td>3000</td>
<td>11.8</td>
</tr>
<tr>
<td>PD1912 S5 VACUUM PHOTODIODE</td>
<td>9-30</td>
<td>U. V. GLASS</td>
<td>200-650</td>
<td>162</td>
<td>1.3</td>
<td>0.14</td>
<td>0.125</td>
<td>7.7 x 10⁻⁴</td>
</tr>
<tr>
<td>S1336 5BQ PLANAR PHOTODIODE</td>
<td>5 (TYP)</td>
<td>FUSED SILICA</td>
<td>190-1150</td>
<td>5.6</td>
<td>20.5</td>
<td>2.2</td>
<td>∼1.0</td>
<td>∼1.65</td>
</tr>
<tr>
<td>S1722-02 PIN CAPACITANCE</td>
<td>10-200</td>
<td>FUSED SILICA</td>
<td>200-1150</td>
<td>13.2</td>
<td>(V_B = 9V)</td>
<td>(AT 9V)</td>
<td>0.18</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Table 3.2
Comparison of four photodetectors for pulsed operation at 248 nm
KrF wavelength of 248 nm was compared to that of three laboratory built detectors. These three devices were coupled directly into a 50 Ω load resistor with no buffer amplifier. This was because high bandwidth buffer amplifiers were not readily available. They were housed in metallic boxes with internal battery operation. This helped isolate the detector circuitry from the electromagnetic discharge noise when the laser was fired. One laboratory built detector was based on an inexpensive low voltage vacuum photodiode, a Thorn-EMI, Gen-Com, PD1912-S5. The other two detectors were based on Hamamatsu solid-state devices. One was a planar, low capacitance device, a S1336-5BQ and the other a PIN S1722-02 device. The capacitance of the S1336-5BQ photodiode at a reverse voltage of 9V was calculated from the value given at 0V and using equation 3.41. The device risetime noted in table 3.2 was calculated using a 50 Ω load resistance. The saturation current density calculated from the saturation current and the device active area is very different for the two vacuum photodiodes. The two solid-state devices have saturation current densities within a factor of two of each other.

Analysis of pulsed detector outputs on oscilloscopes can be confusing when the detector risetime, $t_{DET}$, the oscilloscope risetime, $t_{SCOPE}$ and the actual pulse risetime, $t_{PULSE}$ are comparable. In this case, for independent risetimes, the over-all risetime, $t_r$, viewed on the oscilloscope can be approximated as

$$t_r = \left[ \left( t_{DET} \right)^2 + \left( t_{SCOPE} \right)^2 + \left( t_{PULSE} \right)^2 \right]^{\frac{1}{2}} \quad 3.44$$

Figure 3.8 shows two pulsed outputs resulting from 248 nm laser radiation incident on the ITL 1850 bi-planar vacuum photodiode. In case A, the detector was connected to a Tektronix 475A oscilloscope with a risetime of 1.4 ns. The other example is the detector output connected to a Tektronix 466 oscilloscope with a 3.5 ns risetime. Using the value of $t_{DET} = 0.1$ ns in table 3.2, the oscilloscope
risetimes and the experimentally measured risetimes, the pulse risetime from equation 3.44 is equal to 2.65 ns for case A and 2.6 ns for case B. The pulse width at the half intensity points, $\tau_{\text{FWHM}}$ is 25 ns in both cases. Varying the laser charging voltage, the pulse repetition rate up to 5 Hz and the gas recycling speed had little effect on the laser pulsewidth. The peak output current pulse of 10 mA into 50 $\Omega$ is well within the 3.0 amp maximum. The peak amplitude variation was less than 5% when operating the laser at a pulse repetition rate of 1/s.

Figure 3.9 shows two examples of the output from the PD1912 S5 detector connected to the Tektronix 466 storage oscilloscope. It is apparent that space-charge effects on the tail of the pulse play an important role even at low output levels. This is in agreement with the very low peak saturation current of 0.125 mA at a reverse bias voltage of 9V. The apparent variation in the pulsewidth, $\tau_{\text{FWHM}}$ with reverse bias voltage is shown in table 3.3 with the laser operating at 248 nm.

<table>
<thead>
<tr>
<th>PULSEWIDTH/ns</th>
<th>REVERSE BIAS/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau$</td>
<td>$V_B$</td>
</tr>
<tr>
<td>55</td>
<td>9</td>
</tr>
<tr>
<td>35</td>
<td>18</td>
</tr>
<tr>
<td>28-30</td>
<td>27</td>
</tr>
<tr>
<td>25-28</td>
<td>30</td>
</tr>
<tr>
<td>25-28</td>
<td>36</td>
</tr>
</tbody>
</table>

Table 3.3
Pulsewidth and reverse bias voltage
for the PD1912 S5 vacuum photodiode

The reduction of the pulsewidth with increasing reverse bias voltage indicates the saturation current increases with reverse bias voltage. Optimum operation was found to be below a peak output voltage of 20 mV (corresponding to a peak current of 0.4 mA) at a reverse bias voltage of 36 V. The detector risetime, $\tau_{\text{DET}}$ is 1.9 ns calculated from
FIGURE 3.8
ITL 1850 BIPLANAR VACUUM PHOTODIODE OUTPUT

A With Tektronix 475A Oscilloscope
\[ t_R = 33\text{ns}, \quad t_{\text{pulse}} = 265\text{ns} \]

B With Tektronix 466 Oscilloscope
\[ t_R = 4.8\text{ns}, \quad t_{\text{pulse}} = 2.6\text{ns} \]
Pulse width at half intensity
Points = 25 ns in both cases

FIGURE 3.9
PD 1912-S5 VACUUM PHOTODIODE OUTPUT

A Reverse Bias 36v, \( t_R = 5\text{ns} \)

B Reverse Bias 18v
equation 3.44. This corresponds to a capacitance of 17 pF. In this case the stray capacitance, $C_s$ of 15.7 pF dominates over the quoted cathode-anode capacitance of 1.3 pF. These figures have assumed a pulse risetime of 2.6 ns measured using the ITL 1850 bi-planar vacuum photodiode and an oscilloscope risetime of 3.5 ns.

The output from the S1336-5BQ and the S1722-02 at varying incident laser intensities is shown in figure 3.10 and figure 3.11. The tail on the pulse due to the diffusion current is clear even at low incident intensities. The detector risetime of the S1336-5BQ photodiode from figure 3.10a is 4.0 ns. This corresponds to a capacitance of 36 pF giving a stray capacitance, $C_s$ of 15.5 pF. A pulsewidth of 25 ns was measured below peak output voltages of 30 mV. The detector risetime for the S1722-02 photodiode is 2.9 ns. This corresponds to a capacitance of 26 pF giving a stray capacitance, $C_s$ of 11 pF. The stray capacitance for all three laboratory built devices was in the range 11 - 16 pF. An analytical approach to the calculation of the effective detector capacitance on the tail of the pulse is considered in appendix I. The load resistor was deliberately made unequal to the characteristic impedance of the co-axial cable. The step response from the resulting LCR network model gave an equivalent detector capacitance of the PD1912 S5 vacuum photodiode of 30 pF. This contrasts with the value of 17 pF calculated for the rising edge of the pulse. The detector fall-time of 3.3 ns compared to the risetime of 1.9 ns illustrates the effect of the space-charge reducing the response speed.
FIGURE 3-10
HAMAMATSU S1336 SBQ PHOTODIODE OUTPUT FROM KrF 248 nm LASER PULSE

FIGURE 3-11
HAMAMATSU S1722-02 PHOTODIODE OUTPUT FROM KrF 248 nm LASER PULSE
3.4c Calculation of peak power

The peak power incident onto the damage plane can be calculated by knowing the energy incident onto the damage plane, $E_{DP}$ as described in section 3.4bi and the equivalent pulse duration, $\Delta$. The equivalent pulse duration of a waveform is defined as the width of the equivalent pulse of the same area and height as the experimental one, (3.12). It relates the power to the energy. The power at the damage plane is given by

$$P_{DP} = \frac{E_{DP}}{\Delta} \tag{3.45}$$

The main assumption is that the pulse amplitude is linearly related to the pulse power. This requirement is most easily satisfied with the ITL 1850 bi-planar vacuum photodiode due to its very wide linear dynamic range. The experimental error in $P_{DP}$ is determined by the errors in $E_{DP}$ and $\Delta$. The error in $E_{DP}$ is about 5%, the error in $\Delta$ is given by the systematic error introduced by non-linearities and the experimental determination of the area under the pulse profile. An example is given in figure 3.12 of the output from the PD1912 S5 vacuum photodiode. The area under the profile was measured using an Apple IIe digitizing pad. The equivalent pulse is shown in figure 3.12 with a width of 22.8 ±0.9 ns. The approximate 5% error is the reproducibility of the measurement of the area under the pulse profile. The width of the actual pulse at the half intensity points is 25 ns. Similar results were produced with the ITL 1850 bi-planar vacuum photodiode. The equivalent pulse width $\Delta$ is plotted against the experimental pulse width, $\tau$, (FWHM) for the PD1912-S5 vacuum photodiode in figure 3.13. The least squares linear fit to the data points gave

$$\Delta = 0.7176 \tau + 6.012 \tag{3.46}$$

where $\Delta$ and $\tau$ are both measured in nanoseconds. The equivalent pulsewidth for a delta function input, $\tau \rightarrow 0$ is $\Delta = 6$ ns. This figure compares with 5.2 ns for the sum of
FIGURE 3.12
PD1912S5 DETECTOR OUTPUT FROM 248 nm LASER PULSE AND ITS EQUIVALENT PULSE

FIGURE 3.13
EQUIVALENT PULSE WIDTH $\Delta/\text{ns}$

EXPERIMENTAL PULSE WIDTH AT HALF INTENSITY POINTS, (FWHM), $\tau$

EQUIVALENT PULSE WIDTH VERSUS $\tau$ FOR PD1912S5 DETECTOR
the rise and fall times of this detector calculated in section 3.4biii. Experimentally, the pulsewidth \( \tau \) was measured and equation 3.46 used to calculate the equivalent pulsewidth, \( \Delta \). Generally in an experimental run the pulsewidth variation was less than 5\% and had a nominal value of 25 ns. This corresponds to an equivalent pulsewidth of 24 ns and an output power of 41.6 MW for a 1 J pulse. Damage tests were usually done by measuring the pulse energy at which damage occurred and using the locally measured value of \( \tau \) to calculate \( \Delta \). An exception to this was when the discharge gas had been in the laser cavity for some days. In this case the pulsewidth variation was greater than 5\% and usually required monitoring for each shot.

In order to check that the relative pulse profile remained constant throughout the output beam area a 1 mm diameter pinhole was attached to the ITL1850 vacuum photodiode and scanned in the horizontal and vertical directions through the approximate 3 x 1 cm raw beam output. A summary of the results is presented in figure 3.14. On the edge of the beam in both directions the pulse is distorted. In these regions the peak current is a factor of at least six down on that of the maximum in the central region. The distortion probably arises from the variation in the gain profile near to the limits of the discharge. To maintain a uniform pulse profile for damage testing an aperture was mounted in the central portion of the main laser output beam ahead of any other diagnostic equipment.
FIGURE 3.14

KrF LASER PULSE PROFILE AT VARIOUS LOCATIONS IN THE OUTPUT BEAM
3.5 Laser beam attenuators

3.5a Requirements

The main purpose of a laser beam attenuator for laser damage experiments is to vary the fluence incident onto the test sample. The peak fluence, \( F_0 \) incident onto the test sample as shown in figure 3.5 is given by

\[
F_0 = \frac{E_{DP}}{A_0}
\]

where \( E_{DP} \) is the pulse energy incident onto the test sample given by equation 3.30 and \( A_0 \) an effective focused beam area that gives the peak fluence \( F_0 \) measured in \( \text{Jcm}^{-2} \). The peak fluence incident onto the test sample can be changed by varying the effective beam area \( A_0 \) or the incident pulse energy, \( E_{DP} \). The former can be achieved by simply varying the distance between the focusing lens and the test sample. Initial damage experiments were done using this approach. The main problem with this method is the quantitative measurement of \( A_0 \) at several axial distances from the focusing lens. Several methods for the quantitative measurement of \( A_0 \) are considered in section 3.7.

The more convenient attenuation technique for laser damage testing is to vary the incident laser pulse energy, \( E_{DP} \). This may be done to a limited extent by varying the charging voltage on the power supply of the excimer laser. A more convenient and flexible approach is to use a variable attenuator usually mounted ahead of the focusing optics. Ideally the variable attenuator would have the following properties.

1) Infinite dynamic range
2) Attenuation in a simply resettable and controlled manner
3) Wide spectral range
4) No polarization dependence
5) Ability to handle high peak power and high average power
6) No beam distortion or steering.

Not all of these desired features are achievable at the same time. For damage testing experiments at 248 nm a dynamic range between 10 and 20 dB is sufficient. Vulnerability to laser-induced damage or non-linear effects at high peak powers are of particular concern. Avoidance of beam distortion effects must also be considered. This implies that multiply reflected beams should be strongly attenuated or displaced from the main transmitted beam.

3.5b Laser beam attenuation techniques

Three main effects have been considered to produce uniform laser beam attenuators, these are:

1) Reflection
2) Polarization
3) Absorption

Several laser beam reflection attenuator designs have been considered by Bennett and Byer, (3.16). Perhaps the simplest is to make use of the variation in transmittance of a fused silica beamsplitter with angle of incidence. The transmittance of a fused silica beamsplitter at 248 nm as a function of the angle of incidence is shown in figure 3.4. The main disadvantages of this approach include:

1) A limited dynamic range of 3 dB for an incidence angle variation from 40 - 80°.
2) The large incidence angle requires a large beamsplitter diameter making it of limited use for large excimer beam apertures.
3) A second beamsplitter is required which counter-rotates relative to the first to compensate for beam steering.
A much improved variation on this approach has been designed by Bennett and Byer and is commercially available, (3.17). It uses two pairs of counter-rotating fused silica wedges and has a dynamic range of 40 dB (for a polarized input) and an insertion loss of less than 1%. The fused silica wedges have broad-band response and high laser-induced damage thresholds. Its main disadvantage is the large incident angle required to achieve significant attenuation (>60°). This problem restricts its use for large aperture lasers. A third reflection attenuator design is considered in Appendix II. The design makes use of the difference in the Fresnel reflection coefficients for light polarized parallel (p component) and perpendicular (s component) to the plane of incidence. The design requires a polarized input beam and two or more fused silica beamsplitters mounted at some fixed large angle of incidence inside a tube which can rotate about its axis. To minimize insertion losses the incidence angle can be chosen as Brewsters angle (~57°). The beamsplitter pairs are used to compensate for beam steering. The plane of incidence can be varied by simply rotating the tube containing the optics about its axis. A tube rotation of 90° results in a polarized input beam changing from being parallel to the plane of incidence to perpendicular to it. For a pure linearly polarized input beam the design data for a two plate (fused silica) attenuator is given in table 3.4

<table>
<thead>
<tr>
<th>Angle of Incidence</th>
<th>Maximum Transmission</th>
<th>Minimum Transmission</th>
<th>Dynamic Range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>/dB</td>
</tr>
<tr>
<td>57</td>
<td>100</td>
<td>49</td>
<td>3</td>
</tr>
<tr>
<td>70</td>
<td>84</td>
<td>28</td>
<td>4.8</td>
</tr>
</tbody>
</table>

Table 3.4
Design data for a two plate laser attenuator at 248 nm
The dynamic range can be improved by using more plates. A ten plate design has a dynamic range of 10 dB. The dynamic range of this design is not as large as the wedge-plate design but has the advantage of a simpler adjustment mechanism. This design approach has been used by the Lawrence Livermore Laboratory for their laser damage testing experiments at the KrF wavelength of 248 nm, (3.18).

The operation of the two previous reflection attenuator designs requires a polarized input beam. Polarization can also be used as an attenuation technique itself via Malus' law. A slight variation on this is to use a rotatable half-wave plate placed between two crossed polarizers. Polarization methods at the KrF wavelength of 248 nm suitable for use in laser damage testing are limited. Plastic dichroic polarizer sheet absorbs below 400 nm. Calcite, air-spaced Glan-Laser polarizing beamsplitters also absorb below 400 nm and fluoresce below 300 nm. Wollaston or Rochon polarizing beamsplitters manufactured from MgF₂ or fused silica are possible alternatives which could operate at 248 nm and offer high damage thresholds. A major problem is that these devices are not readily available commercially and they would also need anti-reflection coatings on their parallel faces. This would make them very expensive. Probably the simplest laboratory technique to polarize the randomly polarized excimer laser output is the "stack of plates" polarizer considered in Appendix II. A ten plate polarizer design using fused silica has a transmission of 52% relative to the unpolarized input beam and a polarization ratio (p:s) of 21:1. A variation on the "stack of plates" approach is the thin film multi-layer dielectric polarizer. The design of multi-layer dielectric polarizers has been considered by Lissberger, (3.19). The polarization transmission ratio of multi-layer dielectric polarizers at the KrF wavelength of 248 nm has been observed to drift in the laboratory environment, (3.20). This has been attributed to their high angular sensitivity and the environmental stability.
of the dielectric layers to moisture absorption. An effective thin film polarizer for use at the XeCl excimer wavelength of 308 nm has been designed by Dobrowolski and Waldorf, (3.21). This device used a multi-layer (HFO₂/SiO₂) coating on a flat fused silica substrate mounted in a liquid cell.

Laser beam attenuators using absorption methods do not require a polarized input beam and therefore the insertion loss can potentially be much lower. Neutral density filters in the form of aluminium thin films deposited on fused silica substrates have been used at the Los Alamos laboratory for their laser damage test experiments at 248 nm, (3.22). The main problem is that the aluminium coatings have to operate near their own laser damage threshold. As an alternative, the transmittance of several thin plastic films at 248 nm was investigated. Commercially available transparent "cling-film" was identified as a candidate material. For measurement purposes the film was mounted in 35 mm slide holders. The transmittance of two different commercial types of cling-film as a function of the number of attenuating layers is shown in figure 3.15. The transmittance decreases as exp(-Nα) where N is the layer number and α the absorption coefficient for a single layer of film. The single shot laser damage threshold of the film was estimated as 0.5 J cm⁻². One problem with the film is clearly illustrated in figure 3.16 showing the decrease in the film transmittance as a function of the number of laser pulses incident onto the film. These measurements were done at an incident energy density of 0.17 J cm⁻² and a pulse repetition rate of one pulse/s. The change in slope for the film B in figure 3.16 after 150 shots coincided with the laser shot number at which physical damage was first noticed in the film. Examination of the films after these irradiation tests showed they had a yellow discolouration suggesting some photochemical change. A close examination of burn patterns of focused radiation from the KrF excimer using these films as attenuators indicated the absorption was
FIGURE 3-15

\( \ln (T) \) (CLING FILM TRANSMISSION AT 248 nm) VERSUS LAYER NUMBER FOR TWO DIFFERENT FILMS
TRANSMISSION OF A SINGLE LAYER OF CLINGFILM AT 248 nm

FIGURE 3.16
TRANSMISSION OF CLINGFILM AT KrF EXCIMER WAVELENGTH OF 248 nm (INCIDENT FLUENCE 0.17 J/cm²)
not homogeneous.

An alternative to thin film absorbers are volumetrically absorbing glass materials. Two volume absorbing glass materials manufactured by Schott, UG-5 and BG-24 were identified as candidate materials for use as neutral density filters at the KrF wavelength of 248 nm. Irradiation tests with the excimer laser were done to determine any transmittance changes. Initial tests were done on 0.5 mm and 1.0 mm thick samples of UG-5 and BG-24 for 1000 shots at an incident fluence of 0.3 Jcm\(^{-2}\). This level is the approximate output fluence of the Lambda Physik EMG200 excimer operating at 248 nm. The material BG-24 was observed to emit some visible fluorescence during the irradiation tests. The 0.5 mm thick samples showed no significant change of transmittance at 248 nm after the irradiation test. The transmittance of the 1.0 mm thick samples decreased by 10% as a result of the irradiation. The decrease in transmittance of a 2.4 mm thick sample of UG-5 subjected to 3000 shots at a fluence of 0.25 Jcm\(^{-2}\) is shown in figure 3.17. The transmission in the range 210 - 350 nm was measured on a Perkin Elmer, model 323 spectrophotometer. The transmission decreases from 51\% to 23\% at 248 nm as result of the irradiation tests. Subsequent tests showed that the maximum incident energy density to prevent transmission changes was below 0.1 Jcm\(^{-2}\). This limited the filter glass use as an attenuator to those test samples with low laser damage thresholds.

The design of an attenuator using absorbing solutions was considered as an alternative to solid neutral density filters because of the potential improved resistance to laser-induced damage at 248 nm. A convenient aqueous solution, stable to UV illumination and suitable for use as an absorber at 248 nm was a mixture of hydrated nickel sulphate, \((\text{NiSO}_4 \cdot 6\text{H}_2\text{O})\) and cobalt sulphate \((\text{CoSO}_4 \cdot 7\text{H}_2\text{O})\), (3.23). For convenience of use, the design aim was to operate with a fixed solution concentration and vary the attenuation by simply changing the liquid path length. The first cell design is illustrated in cross-
TRANSMISSION OF 2.4 mm THICK SAMPLE OF SCHOTT FILTER GLASS, UG-5/%

FIGURE 3.17
TRANSMISSION OF 2.4 mm THICK SAMPLE OF UG-5 FILTER GLASS VERSUS WAVELENGTH

BEFORE IRRADIATION

AFTER IRRADIATION
(3000 SHOTS, 0.25 J/cm^2)
\[ \lambda = 248 \text{ nm} \]
section in figure 3.18. It consisted of a perspex reservoir attached to an aluminium cylinder via a hollow brass collar. The aqueous solution of cobalt and nickel sulphate was simply sucked into or expelled out of the cell region by a hand driven piston. The fused silica windows on the front of the piston and aluminium housing had a clear aperture of 44 mm. The liquid cell length could be varied in the range 2.5-60 mm.

The analysis of the optical transmission of a glass cell containing an absorbing liquid is considered in chapter 5. The situation is simplified by ignoring multiple reflections due to the negligible reflectance of the fused silica window/liquid interface. Assuming the absorption by NiSO₄ and CoSO₄ are independent of each other and allowing for the intrinsic absorption of the distilled water, the cell transmittance is given by

\[ T = (1 - R)^2 \exp[-(\sigma_1 n_1 + \sigma_2 n_2 + \alpha)x] \]  \hspace{1cm} 3.48

where \( R \) is the reflectance of the air/fused silica window interface, \( x \) the liquid path length, \( \sigma_1 \) and \( \sigma_2 \) the absorption cross sections of NiSO₄ and CoSO₄, \( n_1 \) and \( n_2 \) the concentrations of NiSO₄ and CoSO₄ and \( \alpha \) the absorption coefficient for distilled water. Taking logarithms of equation 3.48 gives

\[ \ln T = -(\sigma_1 n_1 + \sigma_2 n_2 + \alpha)x + 2\ln(1 - R) \]  \hspace{1cm} 3.49

The experimental results of \( \ln(T) \) versus \( x \) for three different concentrations is shown in figure 3.19. The absorption coefficient of distilled water at 248 nm is 0.01 cm⁻¹, (3.23). The experimental values of \( \sigma_1 n_1 + \sigma_2 n_2 + \alpha \) are compared with the values calculated from data in references 3.23 and 3.24.
FIGURE 3-18

VARIABLE LENGTH LIQUID CELL ATTENUATOR DESIGN
FIGURE 3.19
LOGARITHM OF TRANSMISSION OF LIQUID CELL AT 248 nm VERSUS OPTICAL PATH LENGTH IN $\text{CoSO}_4$ AND $\text{NiSO}_4$ SOLUTION
GRAPH CONCENTRATION/gml$^{-1}$ \(\langle \sigma_1 n_1 + \sigma_2 n_2 + \alpha \rangle / cm^{-1}\)

LETTER \(n_1\) \(n_2\) \(\langle \text{NiSO}_4 \rangle\) \(\langle \text{CoSO}_4 \rangle\) EXP. REFERENCE

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.48</td>
<td>0.09</td>
<td>0.288</td>
</tr>
<tr>
<td>B</td>
<td>0.778</td>
<td>0.146</td>
<td>0.467</td>
</tr>
<tr>
<td>C</td>
<td>1.076</td>
<td>0.202</td>
<td>0.645</td>
</tr>
</tbody>
</table>

Table 3.5
Experimental results of the absorption coefficient of aqueous solutions of CoSO$_4$ and NiSO$_4$ at 248 nm compared with reference data.

The reference data was calculated from the absorption cross-sections of NiSO$_4$ and CoSO$_4$ at 248 nm quoted in references 3.23 and 3.24. A mean value was taken for comparison purposes, these are: \(\sigma_1\langle \text{NiSO}_4 \rangle = 0.201\) cm$^2$g$^{-1}$ and \(\sigma_2\langle \text{CoSO}_4 \rangle = 2.064\) cm$^2$g$^{-1}$. The good agreement between the results measured in this work and the reference data suggests scattering does not contribute significantly to the over-all extinction coefficient. This was tested by filtering the solution with a 0.1 \(\mu m\) filter. Within experimental error no significant difference was observed in the transmission measurements at 248 nm. A dynamic range of 25 dB was achieved with this device by varying the cell length from 2.5 mm to 60 mm. The minimum insertion loss with a liquid cell length of 2.5 mm was the range 15 - 20% depending upon the solution concentration. The absence of temporal pulse distortions in the transmitted beam was confirmed by scanning a pinhole through the transmitted beam and measuring the pulse profile at each location using the PD1912-S5 photodetector described in section 3.4. It was during early preliminary experiments with pure liquids that the non-linear effects described in chapter 5 were first observed.

If the nickel and cobalt sulphate solution was left in the cell for several days a large increase in the absorption at 248 nm was observed. This was traced to the rusting steel grub screws which held the fused silica windows in place. The leaching of iron into aqueous
filter solutions has often been found the cause of ageing effects, (3.25). The two main limitations of the first liquid cell attenuator were its limited clear aperture and small beam-steering effects due to the non-uniform hand driven motion of the piston. These effects were reduced with a second device made from stainless steel and having a clear aperture of 55 mm. The piston to change the liquid cell length was housed above the liquid reservoir and moved in and out by a fine screw thread. By this means a very controllable and uniform pressure was applied to change the liquid path length. A problem sometimes observed with both devices was the formation of small bubbles on the inner surface of the windows. This could be prevented by leaving the solution to stand whilst the bubbles floated to the surface and the solution temperature came into equilibrium with the surroundings.

3.6 Laser beam focusing

The multimode electric field distribution $E(x, y)$ from the EMG200 excimer laser can be represented as a linear sum of the well known Hermite-Gaussian distributions which have been used to describe single mode operation, (3.26)

$$E(x, y) = \sum_{i=1}^{\infty} A_i(t) H_m(\sqrt{2y/\rho_1}) H_n(\sqrt{2x/\rho_2}) \exp\left(-\frac{x^2}{\rho_1} + \frac{y^2}{\rho_2}\right)$$

$A_i(t)$ is a weighting parameter which may be a function of time during the laser pulse. The length of the EMG200 excimer laser cavity is about 1.0 m, corresponding to a round trip time of 6.6 ns. The excimer laser pulse duration of 25 ns therefore allows at most about 4 round trips in the laser cavity. The high gain excimer laser can be considered as almost super-radiant.

The Fresnel-Kirchoff diffraction integral has been used to calculate the three dimensional intensity distribution in the focal region of a perfect lens, (3.27). The analysis has been done with spherical waves and waves with a Gaussian, $\text{TEM}_{00}$ distribution and further
extended to include wavefront aberrations introduced by the lens, (3.27, 3.28). In the geometrical focal plane of an ideal lens the results reduce to those calculated by Fraunhofer diffraction. The Fraunhofer diffraction pattern in the geometrical focal plane of a lens can be considered as the two dimensional Fourier transform of the input distribution to the lens. Since the Fourier transform of each of the individual Hermite-Gaussian modes in equation 3.50 is its own Fourier transform, (3.26), the electric field distribution at the geometrical focal plane will also be represented by a linear sum of the modes of the form given in equation 3.50. Calculation of the intensity distribution represented by $|E(x,y)|^2$ from equation 3.50 therefore becomes extremely complicated.

The effect of adding various amounts of a TEM$_{01}$ mode to a TEM$_{00}$ mode is shown in figure 3.20. As higher order modes are added the profile widens and the peak intensity reduces. Thus, although the fluence distribution $F(x,y)$ at the lens focus may closely resemble a Gaussian distribution in the $x$ and $y$ directions this does not imply a true TEM$_{00}$ mode. Laser output from the excimer in the TEM$_{00}$ mode could be achieved by using a mode stop inside laser cavity at the expense of greatly reduced output energy. A more efficient way to generate a TEM$_{00}$ mode output in high gain systems is to use an oscillator-amplifier combination. This approach was not investigated in this work. It was sufficient for these laser induced damage studies that the fluence distribution function $F(x,y)$ in the test region be smooth and monotonic. The absence of beam 'hot-spots' in the test region also made identification of small scale laser induced damage less ambiguous. In circumstances where the laser gas mixture had been in the cavity for several days, arc formation across the main discharge sometimes created beam 'hot spots'.

Three 50 mm diameter fused silica, plano-convex lenses ($f = 100, 200, 300$ mm) were used as the focusing lenses for the laser damage experiments. They were used with their convex surfaces facing the incoming laser beam.
FIGURE 3.20
EFFECT OF ADDING VARIOUS AMOUNTS OF A TEM₀ mode TO A TEM₀₀ mode
to minimize spherical aberration. Laser damage threshold measurements were done at a fixed distance from the focusing lens in the focal region of each lens. A two dimensional Gaussian distribution was fitted to the beam profile measurements to calculate the peak fluence incident onto the test sample.

3.7 Focused KrF laser beam profiling

3.7a Laser burn pattern recording

Initial laser damage test experiments were done by varying the position of the test sample relative to the focusing lens and noting the lens-test sample distance at which laser induced damage was first observed. A different area of the test sample was irradiated after each laser pulse. The pulse energy incident onto the test sample and its effective beam area were used to calculate the damage threshold. The damage area resulting from irradiating a surface absorbing material with a single laser pulse was used as a qualitative measure of the effective beam area at a given distance from the lens to the front surface of the test sample. The ideal absorbing material has a single damage threshold, \( F_B \) and when irradiated above this level produces a clear, high contrast burn pattern whose dimensions are easily measured. The burn pattern was measured as a function of the lens-test sample distance (front face) for several absorbing materials at a nominal constant 0.4 J laser energy. The test materials were; polaroid land pack 667 film (exposed, unexposed and the grey reverse side) and Kodak laser burn paper. The burn pattern area at a fixed distance from the lens varied linearly with the pulse energy for all of the materials tested. The damage threshold of a KrF multi-layer dielectric reflector \((\text{Sc}_2\text{O}_3/\text{MgF}_2)\) manufactured by OCLI (Optical Coatings Laboratories Inc.) and previously damage tested at the Lawrence Livermore Laboratory was used as an absolute calibration of this approach. Its single shot KrF damage threshold was quoted as 6 - 8 Jcm\(^{-2}\). The single shot
The damage threshold calculated using the burn pattern area on
the grey, reverse side of the polaroid film was
7.9 ± 2.4 J cm⁻². The burn pattern on the grey polaroid
material as a function of the lens-sample distance is
shown in figure 3.21. Also included are some burn
patterns in the focal region. Laser induced damage after
a single pulse was first observed at 15.0 mm beyond the
focus of the f4 lens giving an effective area of
0.05 ± 0.015 cm². Plasma formation when the burn paper was
located in the focal region resulted in some difficulty in
measuring the burn pattern accurately. The expanding
plasma produced a weaker burn pattern concentric with the
main one as illustrated in figure 3.21. The main
experimental sources of error in the damage threshold
figure using this approach were:

1) A pulse energy accuracy of ±5%
2) Locating the lens-test sample distance at which
damage was first observed. This was partly
dependent on the damage detection method but was
typically accurate to ±1%.
3) The reproducibility of the burn pattern area,
d₁/d₂ which was about ±30%.

The availability of the variable length liquid
attenuator led to a more quantitative, absolute
measurement of the effective beam area at a fixed distance
from the lens using burn patterns. The fluence function
F(x,y) in the plane on the front surface of the test
sample can be represented as a two dimensional Gaussian
function given by

\[ F(x,y) = F₀ \exp \left( -\frac{2x²}{\rho₁^2} \right) \exp \left( -\frac{2y²}{\rho₂^2} \right) \]  

where \( F₀ \) is the peak fluence to be determined. The
function F(x,y) is assumed to be separable into two
orthogonal Gaussian functions with different \( \frac{1}{e²} \)
diameters \( \rho₁ \) and \( \rho₂ \) for the x and y directions.
KrF LASER BURN AREA AS FUNCTION OF LENS → SAMPLE DISTANCE
respectively. This approach tries to take account of the inherent rectangular nature of the output beam. The pulse energy incident onto the damage plane, $E_{DP}$, is given by substituting equation 3.51 into equation 3.3

\[ E_{DP} = F_{0} \cdot \pi \rho_{1} \rho_{2} / 2 \]  \hspace{1cm} 3.52

It follows from equations 3.6 and 3.52 that the effective beam area $A_{0}$ used to calculate the peak fluence $F_{0}$ is given by

\[ A_{0} = \pi \rho_{1} \rho_{2} / 2 \]  \hspace{1cm} 3.53

The laser burn materials were assumed to have a single burn threshold $F_{B}$. Substituting for $F_{B}$ in equation 3.51 and expanding gives

\[ \log_{10}(E_{DP}) = 0.2171 \left( \frac{d_{1}^{2}}{\rho_{1}^{2}} + \frac{d_{2}^{2}}{\rho_{2}^{2}} \right) + \log_{10}(A_{0}F_{B}) \]  \hspace{1cm} 3.54

Natural logarithms have been converted to base 10 and the substitutions

\[ d_{1} = 2x \] \hspace{1cm} 3.55a

\[ d_{2} = 2y \] \hspace{1cm} 3.55b

used. Equation 3.54 relates the pulse energy $E_{DP}$, with the burn pattern dimensions $d_{1}$ and $d_{2}$.

The burn pattern dimensions $d_{1}$ and $d_{2}$ at the focus of the f4 lens for differing values of $E_{DP}$ were measured using a travelling microscope. The results are plotted in figures 3.22 and 3.23 in the form of $\log_{10}E$ versus $d^{2}$ for two different burn paper materials. These were the reverse, grey side of the polaroid film and the black Kodak paper. The linear fit to the data suggests the initial assumption of using a 2-D Gaussian distribution for the fluence function $F(x,y)$ is valid. The least squares gradients and intercepts were used to calculate
FIGURE 3.22
KrF LASER PULSE ENERGY AS A FUNCTION OF BURN PATTERN DIMENSION, $d$.
FIGURE 3.23
KrF LASER PULSE ENERGY AS A FUNCTION OF
BURN PATTERN DIMENSION, $d_a$
the values of $\rho_1$, $\rho_2$ and the burn threshold $F_B$ for both materials. The results are summarized in table 3.6.

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>GREY</th>
<th>POLAROID</th>
<th>KODAK</th>
<th>PAPER</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_1$/mm</td>
<td>1.97</td>
<td>1.89</td>
<td>1.79</td>
<td>1.88  ± 0.1 (5%)</td>
</tr>
<tr>
<td>$\rho_2$/mm</td>
<td>0.60</td>
<td>0.69</td>
<td>0.665</td>
<td>0.65  ± 0.05 (7.7%)</td>
</tr>
<tr>
<td>$A_0$/10$^{-2}$cm$^2$</td>
<td>1.845</td>
<td>2.04</td>
<td>1.87</td>
<td>1.92  ± 0.08 (4.2%)</td>
</tr>
<tr>
<td>$F_B$/mJcm$^{-2}$</td>
<td>1475 ±127</td>
<td>357 ±28</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.6

KrF beam profile parameters at the focus of an f4 lens calculated using burn patterns.

The three sets of data given in table 3.6 suggest a reproducibility of about 5% for $\rho_1$, 8% for $\rho_2$ and about 9% for the area measurement, $A_0$. The contrast of the burn patterns in the Kodak paper was much higher than the polaroid material. The factor of four difference in the burn thresholds between the two materials is clearly illustrated in figures 3.22 and 3.23 with their different intercepts.

This burn pattern method of determining the effective beam area was simple to perform and did not involve the accidental destruction of any detectors! It was often used as a cross-calibration check on the more revealing methods of scanning apertures through the focused beam.

3.7b Photographic beam profiling at 248 nm with Dylux film

Photographic recording of the fluence distribution $F(x,y)$ in the focal region of a lens is a well established technique, (3.29). Kodak 1-Z film has been used for beam profile recording over the wavelength range 248 nm-1064 nm with a dynamic range greater than 500:1, (3.1). The main disadvantages of photographic recording of the laser beam
profiles for fluence measurements are:

1) The generation of the non-linear D-E calibration curve for each experiment.
2) The time consuming and inconvenient wet processing stage
3) The 2-D microdensitometer scans and numerical integration required to calculate the fluence distribution $F(x, y)$.

Self-calibrating methods have been developed which use a wedged beamsplitter downstream of the focusing lens to generate a low intensity replica of the focused beam, (3.1). Multiple reflections between a pair of tilted mirrors generate a series of beam replicas of known relative attenuation. These beams are recorded and used to generate the calibration curve. Ideally, further laser shots which require calibration should be recorded on the same film. Microdensitometer scans of the profiles can then be linearized and scaled to calculate the fluence distribution function $F(x, y)$.

Dylux 608 Registration Master film was identified as a candidate material for quantitative laser beam profiling with the KrF excimer, (3.30). The film develops a continuous tone blue dye image when exposed to radiation shorter than 400 nm. This overcomes the inconvenient wet processing stage. The film is sensitized to the mercury line at 254 nm and has an absorption peak at 625 nm. The Dylux film showed no sensitivity to the ArF excimer output at 193 nm. Dylux 503-1 image vaper is also available and was found to be useful for tracing beam paths. The stability of the image and the calibration of the film was measured and compared to results presented in reference 3.30.

A weak replica of the focused 248 nm radiation from a planoconvex f4, 200 mm focal length lens was generated using a 3° fused silica wedge downstream of the lens. Five Dylux film samples were exposed to a single laser pulse in the same axial location and with the same pulse
energy. The exposures were done in subdued lighting due to the film sensitivity to the fluorescent lights. The peak optical density of each of the samples was measured weekly over a ten week period. No reduction in the optical density of the blue image was measured in this period. This is in contrast to the results given in reference 3.30 where a 7% reduction was observed in the first few days. The optical density was measured by scanning the exposed film through a focused, chopped, helium neon beam and measuring the transmitted light with a photodetector. The blue image was found to bleach if the 1 mW helium neon beam was not attenuated by a factor of about 50. This irreversible bleaching was simulated by holding a soldering iron adjacent to the film. The previously observed 7% reduction in the image optical density may therefore be caused by temperature effects.

The optical density of the unexposed film was determined for 20 different samples. A cross calibration check of the optical density measurements was carried out using a Perkin Elmer model 323 Spectrophotometer. The average unexposed film optical density was 0.07 ±0.005. This is in contrast to the results measured in reference 3.30 where a background density of 0.03 was measured.

The fluence distribution function F(x,y) was recorded in the Dylux film at the lens focus and at intervals up to 120 mm beyond the lens focus. Seven Dylux film samples were exposed at the same pulse energy at a distance of 28 mm beyond the lens focus. Optical density beam profiles in orthogonal directions are shown for four samples in figure 3.24. The 'top-hat' profile of the beam and the stability of the profile from shot to shot are clear. The width of the beam at the half maximum points varied by ±3% for all of the samples. The peak optical density of the blue image (less the background value) was observed to saturate at 0.35 ±0.02. Independent measurements of the saturation optical density with an EMG100 KrF excimer produced a value of 0.3, (3.31). Both of these measurements are in contrast to those in reference 3.30 where the saturation optical density was about 0.6.
OPTICAL DENSITY OF EXPOSED DYLUX

FIGURE 3.24
ORTHOGONAL OPTICAL DENSITY BEAM PROFILES OF KrF EXCIMER LASER
Figure 3.25
Calibration of Dylux 608 film using KrF Excimer at 248nm.
The Dylux film was calibrated using the KrF laser by using an aperture to select a small area of the main output beam where the fluence was constant and measuring the pulse energy for each exposure. The calibration results and those presented in reference 3.30 are shown in figure 3.25. The calibration results measured in this work suggest a saturation optical density in the region of 0.3 and a linear dynamic range of 10 – 30 mJcm⁻². The advantage of the absence of a wet processing stage in using Dylux film is therefore off-set by its limited dynamic range. This made absolute measurement of peak fluences difficult.

3.7c Focused KrF laser beam profiling using scanning apertures

Experiments were done to compare the three techniques of knife edge scanning, slit scanning and pinhole scanning for beam profiling of focused KrF laser radiation. All three techniques involved scanning an aperture through the beam and monitoring the transmitted pulse energy. The knife edge and slit scanning methods spatially integrate the beam profile in the direction orthogonal to the scan direction. The measured beam profile using the pinhole can be considered as the convolution of the actual beam profile of interest and a "top hat" function whose diameter is the same as that of the pinhole. This assumes the detector mounted behind the pinhole has a constant responsivity over its area. Other beam profiling methods have been considered. These include the Ronchi ruling method, (3.32), the ribbon method, (3.33) and monitoring the transmitted pulse energy through several different sized pinholes located on the laser beam axis, (3.34).

The Ronchi ruling method is more suitable for continuous beams, the coarse transmission grating being susceptible to laser induced damage at 248 nm. Scanning a wire or ribbon through the focused beam and monitoring the transmitted energy is effectively the inverse of slit scanning but requires a more complicated numerical inversion. Monitoring the transmitted pulse energy
through several on-axis pinholes is a simple and convenient technique for measuring symmetrical Gaussian distributions. The exact re-location on-axis of several pinholes means that this technique is difficult for small, pulsed laser beams.

Beam profiles were measured at various axial planes between 200 and 275 mm from a fused silica, 300 mm focal length planoconvex lens. The f6 lens was used in preference to the f4 lens because of the easier alignment of the laser induced damage detection systems such as the video microscope described in chapter 4. The lens aberrations and the damage threshold error associated with relocating test specimens at a nominal fixed axial distance from the lens was also less for the longer focal length. Beam profiling using a weak replica of the focused beam generated from a wedge was avoided because of the alignment difficulty and therefore experimental error in measuring the beam profile in the same equivalent plane as the front surface of the test specimen. Direct scanning of the focused beam was achieved by attenuating the main output beam with the liquid attenuator and using a pyroelectric detector behind the aperture. The pyroelectric detector can tolerate a higher incident fluence before saturation or damage than a photodiode. A Gen Tec ED500 (area 25 cm²) was used for the knife edge and slit scanning experiments. An Eltech, model 400-E pyroelectric detector (area 0.03 cm²) was used for the pinhole scanning experiments because of its much better sensitivity (>800 compared to the Gen Tec model). The effect of the 5% variation in pulse energy from shot to shot was reduced by measuring the average pulse energy of 16 shots transmitted through the aperture for each measurement point.

3.7ci Knife edge scanning and slit scanning

The mathematical analysis of calculating the laser energy transmitted past a knife edge being scanned in the x direction through a focused beam is equivalent to that of scanning a slit of width Δx, when the slitwidth Δx
approaches infinity. The slit width in the \( y \) direction is assumed to be much greater than the beam dimension in this direction. In the case of a slit of width \( \Delta x \), the transmitted pulse energy for an incident fluence function \( F(x,y) \) is given by

\[
E_T = \int_{-\infty}^{\infty} \int_{x}^{x + \Delta x} F(x,y) \, dx \, dy \tag{3.56}
\]

Assuming the fluence function \( F(x,y) \) used previously in equation 3.51 as

\[
F(x,y) = F_0 \exp \left( -\frac{2x^2}{\rho_1^2} \right) \exp \left( -\frac{2y^2}{\rho_2^2} \right) \tag{3.57}
\]

Substituting equation 3.57 in 3.56 gives

\[
\frac{E_T}{E_0} = \frac{1}{2} \left( \text{erf}[a(x + \Delta x)] - \text{erf}[ax] \right) \tag{3.58}
\]

where \( \text{erf} \) is the error function defined as

\[
\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-t^2) \, dt \tag{3.59}
\]

and

\[
a = \sqrt{2}/\rho_1 \tag{3.60}
\]

\[
E_0 = \pi \rho_1 \rho_2 F_0 / 2 \tag{3.61}
\]

From equation 3.61, it is clear that \( E_0 \) is the total pulse energy incident onto the aperture and the ratio \( E_T/E_0 \) in equation 3.58 is the fraction of the total pulse energy transmitted through the slit. In the case of a knife
edge, the slit width $\Delta x \to \infty$ and $\operatorname{erf}[a(x + \Delta x)] \to 1$. Equation 3.58 then simplifies to give

$$\frac{E_T}{E_0} = \frac{1}{2} \left[ 1 - \operatorname{erf}(ax) \right]$$ 3.62

The main problem with accurate measurements using knife edge scanning is the inversion of equation 3.62 to calculate $\rho_1 = \sqrt{2}/a$. A number of approaches have been used including differentiation and curve fitting, (3.35). For small values of the product $ax$, the error function can be expanded to give

$$\operatorname{erf}(ax) = \frac{2}{\sqrt{\pi}} \left[ ax - \frac{(ax)^3}{3} + \frac{(ax)^5}{5} - \frac{(ax)^7}{7} + \ldots \right]$$ 3.63

The function $1/2[1 - \operatorname{erf}(ax)]$ can be approximated by using the first term of the expansion. This is valid for $|ax| < 0.5$. Equation 3.62 then simplifies to

$$\frac{E_T}{E_0} = 1 - 0.7979 \frac{x}{\rho_1}$$ 3.64

A razor blade was scanned through the unfocused KrF output beam. The results are plotted in figure 3.26 in the form $E_T/E_0$ versus the knife edge position. The $x$ axis has been adjusted so that $E_T/E_0 = 0.5$ at $x = 0$. The gradient of the linear section gives $\rho_1 = 2.41$ cm. The dotted line in figure 3.26 has been drawn where $ax = -0.5$, representing the expected limit of linearity for $E_T/E_0$ versus $x$.

A more convenient method for beam profiling is to use a narrow slit and directly measure the $1/e^2$ width from the measured profile. Beam profiles in the $x$ direction were measured using four different slit widths at an axial distance of 200 mm from the lens. The four profiles measured with slit widths of 0.46 mm, 0.19 mm, 0.09 mm and 0.04 mm are shown in figure 3.27. The ED500 pyroelectric detector signal amplitude is proportional to the...
FIGURE 3.26

KNIFE EDGE SCAN OF THE UNFOCUSED KrF EXCIMER OUTPUT
FIGURE 3.27
BEAM PROFILES OF EXCIMER LASER AT 248 nm PRODUCED WITH DIFFERENT SLIT WIDTHS

100
transmitted energy $E_T$. The $1/e^2$ radii measured from the peak amplitudes are given in table 3.7.

<table>
<thead>
<tr>
<th>SLIT WIDTH/mm</th>
<th>$1/e^2$ RADIUS, $\rho_1/$mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>2.71</td>
</tr>
<tr>
<td>0.09</td>
<td>2.71</td>
</tr>
<tr>
<td>0.190</td>
<td>2.75</td>
</tr>
<tr>
<td>0.460</td>
<td>2.83</td>
</tr>
</tbody>
</table>

Table 3.7
KrF focused beamwidth at an axial location
200 mm from the f6 lens

The overestimate of the experimental $1/e^2$ width of a Gaussian beam due to a finite slit size arises from the functional difference between equations 3.57 and 3.58. This has been considered in reference 3.36. The correction factor to the experimental $1/e^2$ widths for a given slit size can be calculated from the results presented in Appendix III. The calculations show that a correction of less than 1% is needed if the slit width is less than one tenth of the experimentally measured $1/e^2$ diameter. This situation is satisfied for all of the measurements shown in figure 3.27. The reproducibility of measuring the $1/e^2$ width was ±2%. The dip in the beam profile near to the maximum using the 0.46 mm slit was caused by slit damage and plasma formation.

3.7cii Pinhole scanning

Beam profiling using a pinhole offers the advantage compared to knife edge or slit methods of being able to map out the two dimensional fluence function $F(x,y)$. Beam profiles at a fixed distance of 236 mm from the f6 lens were measured to determine:
1) The reproducibility of measuring the beam profile for different liquid attenuator settings

2) The reproducibility of measuring the beam profile after setting up and aligning all of the optical diagnostic equipment

3) If the fluence function $F(x,y)$ was separable into the form

$$F(x,y) = F(x)F(y)$$

This was investigated by measuring six beam profiles in the $x$ direction spaced 0.2 mm apart and six profiles in the $y$ direction spaced 1.0 mm apart. The pulse energy transmitted through a 0.42 mm diameter pinhole was measured using an Eltech, model 400-E pyroelectric detector with a fused silica window. Initial experiments with the detector mounted 2.5 mm behind the pinhole resulted in pinhole and detector damage at an estimated incident fluence of $7.5 \pm 2.5 \text{ Jcm}^{-2}$. In subsequent experiments the incident fluence was reduced by a factor of $5 - 10$ and the detector was mounted at a distance between 10 - 70 mm behind the pinhole. The measured $1/e^2$ radius of the smaller beam dimension, $\rho_2$ for different attenuator settings are summarized in table 3.8.

<table>
<thead>
<tr>
<th>Relative Attenuation</th>
<th>Experimental value $\rho_2$/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.65</td>
</tr>
<tr>
<td>0.89</td>
<td>0.66</td>
</tr>
<tr>
<td>0.69</td>
<td>0.645</td>
</tr>
<tr>
<td>0.51</td>
<td>0.67</td>
</tr>
<tr>
<td>Mean</td>
<td>$0.656 \pm 0.01$</td>
</tr>
</tbody>
</table>

**Table 3.8**

KrF focused beam profile measurements 236 mm from the f6 lens with different attenuator settings

These measurements were done at a constant laser charging
voltage of 28 kV and PRF of 0.4 Hz. Approximately twenty pinhole positions were measured for each profile spaced at intervals of 0.05 mm. The best fit beam profile was interpreted by eye and the $1/e^2$ radius located where the amplitude fell to 0.1353 of the maximum. The measurements were reproducible to ±1.5%. These measurements were done with a pinhole radius of 0.21 mm giving a ratio $a/p_2 = 0.32$ and a correction factor of 0.945 from appendix III. This gives a Gaussian profile of 0.62 ±0.01 mm.

The optical system shown in figure 3.5 including the beamsplitters, liquid attenuator and the focusing lens were removed and re-aligned using a helium neon alignment beam. The smaller beam profile was again measured at a distance of 236 mm from the focusing lens. A factor of four dilution in the attenuator liquid was used for this second series of measurements and required longer liquid path lengths to achieve the same attenuation. The average $1/e^2$ radius was 0.60 ±0.02 mm giving a reproducibility of ±3%. The correction factor for $a/p_2 = 0.35$ is 0.934 due to the finite pinhole size. This gives a corrected Gaussian radius of 0.56 ±0.02 mm. The average from the two sets of data is 0.59 ±0.03 mm giving an error of about ±5%.

An area of difficulty for all of the profile measurements was in deciding the best way to determine the experimental value of $p_2$ from the raw data. Several approaches were considered, and included:

1) The best fit by eye and locating the profile width where the amplitude falls to $1/e^2$ of the maximum
2) The best fit by eye and measuring the area under the beam and fitting a Gaussian function with the same area and peak height
3) Linearizing the data and calculating the least squares gradient by taking logarithms and assuming the fluence function is described by equation 3.57

All three methods have been applied to the profile shown
in figure 3.28. The value of \( \rho_2 \) calculated using the three methods listed above are given in table 3.9.

<table>
<thead>
<tr>
<th>Experimental Method</th>
<th>Value of ( \rho_2/\text{mm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fit by eye</td>
<td>0.615</td>
</tr>
<tr>
<td>Area method</td>
<td>0.66</td>
</tr>
<tr>
<td>Linearized data</td>
<td>0.608</td>
</tr>
</tbody>
</table>

Table 3.9
Calculation of focused KrF \( 1/e^2 \) beam radius from experimental data in figure 3.28

The area under the profile was measured with a light pen attached to an Apple IIe computer. The area measurements were reproducible to ±1%. The difficulty in linearizing the data using logarithms is illustrated in figure 3.29. A plot of \( \ln(\text{pyroelectric detector signal}) \) versus \( (x - x_0)^2 \) is shown in figure 3.29 where \( x_0 \) was the vernier reading when the pinhole was located exactly at the maximum of the profile. Results are shown for three assumed values of \( x_0 = 5.578, 5.582 \) and 5.585 cm. The optimum choice of \( x_0 \) is not clear because of the experimental error in each of the points around the peak in figure 3.28. The three data sets in figure 3.29 suggest the best fit to a straight line occurs for \( x_0 = 5.578 \).

The simplest technique is the fit by eye and locating the radius where the amplitude falls to \( 1/e^2 \) of the maximum. This approach has been shown to be accurate, reproducible and in agreement with the other calculation methods if sufficient data points are taken. It is important to define the edges of the profile accurately using this method with many data points. Approximately 30 data points were taken over the measured profile.

At a distance of 236 mm from the f6 lens six beam profiles in the x and y directions were measured. In the y direction the profiles were measured 1.0 mm apart.
FIGURE 3.28
KrF BEAM PROFILE MEASURED WITH 420 μm PINHOLE NEAR THE FOCUS OF A 300 mm FOCAL LENGTH LENS
FIGURE 3·29

\[ \ln (\text{PYROELECTRIC DETECTOR OUTPUT}) \]
VERSUS \((x-x_0)^2\) FOR THE RESULTS SHOWN IN FIGURE 3·28
covering a range greater than the $1/e^2$ diameter. The results were similar to those described earlier, the average $1/e^2$ radius was $0.65 \pm 0.025$ mm. The profiles in the $x$ direction were spaced 0.2 mm apart, an example is shown in figure 3.30. The average $1/e^2$ beam radius was $2.5 \pm 0.1$ mm. All of these measurements were done with a 0.42 mm diameter pinhole. The consistency of the measured profiles show that the fluence function $F(x, y)$ can be separated into the form $F(x, y) = F(x)F(y)$. Beam profile experiments were also done at an axial distance of 273.5 mm from the lens using a 0.2 mm diameter pinhole. The experimental results at both axial planes and the corrected values for the finite pinhole size are summarized in table 3.10.

For damage measurements at an axial distance of 236 mm from the lens, a ±5.5% error in the effective beam area $A_0$ and a ±5% error in the pulse energy combine to give an error of ±7.5% in the peak fluence.

<table>
<thead>
<tr>
<th>AXIAL DISTANCE FROM LENS/mm</th>
<th>236</th>
<th>273.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_1/EXP$ (mm)</td>
<td>2.50 ± 0.1</td>
<td>1.70 ± 0.1</td>
</tr>
<tr>
<td>$\rho_1/CORR$ (mm)</td>
<td>2.49 ± 0.1</td>
<td>1.70 ± 0.1</td>
</tr>
<tr>
<td>$\rho_2/EXP$ (mm)</td>
<td>0.65 ± 0.025</td>
<td>0.27 ± 0.016</td>
</tr>
<tr>
<td>$\rho_2/CORR$ (mm)</td>
<td>0.62 ± 0.025</td>
<td>0.25 ± 0.015</td>
</tr>
<tr>
<td>$A_0/\text{mm}^2$</td>
<td>2.42 ± 0.13</td>
<td>0.667 ± 0.08</td>
</tr>
</tbody>
</table>

Table 3.10
Summary of focused KrF beam profile parameters at two axial distances from the f6 lens.
FIGURE 3:30
KR F BEAM PROFILE MEASURED WITH 420 µm PINHOLE NEAR THE FOCUS OF A 300 mm FOCAL LENGTH LENS
3.7d Beam profiling using automated systems

The disadvantage of the aperture scanning methods described in section 3.7c and the burn pattern methods described in section 3.7a is that the measurements represent beam profiles averaged over many laser shots. They are only useful as long as the beam profile from shot to shot remains stable and approximately constant. Photographic recording methods such as using Dylux film described in section 3.7b can record the two dimensional fluence distribution for a single shot. The disadvantage is the extensive time needed for calibration and inversion from optical density to energy density. The development of linear two dimensional detector arrays interfaced to computers for focused beam profiling offers many potential advantages. Powerful beam profiling systems based on Vidicon cameras have been used at the Lawrence Livermore laboratory for several years, (3.37). Their complete analysis time for a single shot is about 100 s. Absolute fluence measurements agreed with photographic methods to within ±10%. In recent years several automated beam profiling systems have become commercially available. These include two dimensional pyroelectric detector arrays (Spiricon), automatic pinhole scanning systems (Beamscan) and one dimensional silicon detector arrays (Delta Developments). Preliminary investigations were started to see if cameras based on CCD arrays could be used to measure the focused beam profile of a KrF laser. The problem being that CCD cameras show no significant sensitivity at 248 nm. The aim was to capture and digitize the focused image using a frame grabber and computer. The KrF laser radiation was focused into a cell containing a fluorescent dye solution (Rhodamine 6G). Analysis of the fluorescent emission captured on photographic film suggested fluorescence could be used as a wavelength converter from 248 nm and enable focused KrF beams to be recorded, (3.39). A small laboratory designed frame grabber system was built to demonstrate the profiling of any captured video image, (3.39). It had a variable position x and y cursor which could be moved.
anywhere over the captured video frame. It also gave an intensity profile along each cursor, superimposed on the video image. The translatable cursors were also found to be very useful for identifying surface damage in laser damage experiments. Although the frame grabber interface to the computer was not built a proof of principle was demonstrated. In recent work this two dimensional beam profiling technique has been developed very successfully at Loughborough University using commercial frame grabbers and digitizers, (3.40). The technique of using UV induced fluorescence as a wavelength converter has also been adopted in recently developed commercial systems.

3.7e Summary of beam profile measurements

Beam profiling was the most time consuming part of the diagnostic experiments needed for laser damage testing. Two different approaches have been investigated. The photographic Dylux film and the CCD camera recorded the two dimensional fluence distribution for a single shot. The burn pattern and aperture scanning methods gave an averaged profile over many shots. In the case of the focused KrF laser radiation from the EMG200, the output beam profile did not change significantly from shot to shot. In this case the averaged profile and the individual shot profile are considered approximately equal. Detailed pinhole scans of the two dimensional fluence function $F(x,y)$ have shown it to be separable into the form $F(x,y) = F(x)F(y)$. In the lens focal region the functions $F(x)$ and $F(y)$ are shown to be represented by Gaussian distributions with different $1/e^2$ beam radii. The use of CCD cameras and computers offers the promise of a fast and automatic technique of beam profiling for each laser shot. Any "hot spots" in the beam profile would also be quickly identified and ambiguous damage threshold measurements avoided.

3.8 Conclusions

The KrF laser diagnostic requirements for laser damage testing experiments have been examined in detail.
A volume absorbing thermal calorimeter was the most suitable method for measuring the absolute laser energy at low repetition rates. Several photodetectors were compared for measuring KrF laser pulse profiles. The commercial instrument, an ITL 1850 planar vacuum photodiode had the fastest risetime (<1 ns) and highest saturation current. Several candidate methods were investigated as laser beam attenuators at 248 nm. The large output beam area and the damage susceptibility of many absorbing solids led to the development of a variable length, liquid attenuator. The most consuming part of the diagnostic experiments was the measurement of the focused KrF laser beam profile at the same axial plane as the test sample. Several techniques were investigated. Pinhole scanning methods resulted in an area reproducibility measurement of about ±5%. The use of CCD cameras offers the promise of a very simple and quick beam profiling technique which may have many other applications.
3.9 References


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Chapter 4
Laser induced damage detection methods

4.1 Introduction

This chapter considers the development of sensitive diagnostic methods to detect laser induced threshold damage at excimer wavelengths. Most of the work was directed at detecting laser induced threshold damage at 248 nm in multi-layer dielectric films deposited on dielectric substrates. The films were configured as high reflection (HR) or anti-reflection (AR) coatings.

Laser induced damage to an optical component can be considered from two viewpoints depending on whether the end-user application is taken into account. One approach is to define laser induced damage to occur when the test component is permanently degraded for its intended application. The difficulty in damage testing optical components using this definition of laser damage is in simulating the end-user environment. As an example, a 50 mm diameter dielectric high reflector with a single 10 μm damage pit may prevent lasing if the component is mounted in a laser cavity. However, if the same component is used as an external cavity beam steering mirror then no reduction in its performance may be measurable. This assumes the 10 μm damage pit does not grow with subsequent laser pulses.

An alternative and more conservative definition of laser damage is any detectable degradation of the test component. This definition neglects the end-user application but has a built in safety factor if the damage detection method is sensitive. This definition was used in this work because it was helpful in developing sensitive damage detection methods. The sensitivity of the method used to detect laser induced damage therefore determines the laser damage threshold. Associated with each quoted damage threshold is the experimental error arising from the determination of the laser fluence and the damage detection process and a systematic error due to
the inherent calibration of the fluence measurement method and differing relative sensitivities between the damage detection methods.

Several potential damage detection methods are reviewed in section 4.2 including a comparison of their relative sensitivities. The most promising were matched to the requirements considered in section 4.3 for damage detection in thin films at excimer wavelengths. This resulted in an investigation into the performance and relative sensitivity of three damage detection methods.

- Optical microscopy, (section 4.3b)
- Imaging laser scattering, (section 4.3c)
- Photoacoustic detection, (section 4.3d)

Preliminary experiments were also done with a laser induced mass analyser instrument (LIMA) to investigate the chemical analysis of micron sized scattering centres in dielectric thin films, (section 4.3e).

4.2 Review of laser induced damage detection methods

In recent years, interest has increased in developing automated, in-situ, sensitive techniques able to detect laser induced threshold damage, (4.1). This has partly arisen from attempts to try to simplify and standardize damage test procedures so that they may be incorporated into commercial, high volume testing. In a recent round-robin experiment involving 1.06 µm laser damage testing of thin films at eight laboratories a wide range of damage thresholds were measured, (4.2). These damage threshold differences were even observed with similar laser pulse durations and beam spot sizes which suggests different damage identification methods may be partly to blame. This section contains a review of laser threshold damage detection methods including their advantages, disadvantages and a comparison between the different methods.
4.2a Breath-fogging test

One of the earliest methods used to detect laser threshold damage on surfaces was visual inspection after the breath-fogging test. With non-hydroscopic polished bare surfaces the breath-fogging test has been shown to be as sensitive as many other more sophisticated methods, (4.3). The sensitivity of the breath-fogging test to detect surface threshold damage is limited in inhomogeneous thin films where there are a large number of nucleation centres or where sub-surface damage occurs.

4.2b Optical and electron microscopy

Visual identification of laser induced threshold damage on surfaces has been improved with the use of optical microscopes. Often, long working distance (~ 150 mm), low power microscopes (x10 - 50) have been used for imaging damage sites on small test components. Final post-test analysis to identify threshold damage has usually been done by transferring the sample to the stage of a high quality microscope operating at magnifications of x200 - 400. Various techniques have been used to enhance the visual contrast of damage sites in transparent substrates and therefore ease the identification of threshold damage. These include the use of darkfield objectives, phase contrast objectives and the popular Nomarski interference objective. Comparison studies using these objectives to detect threshold damage in single layer films, multi-layer dielectric films (HRs and ARs) and on polished substrates has shown the Nomarski objective to be the most sensitive and simplest to use, (4.3). The technique of transferring the test sample to the stage of a high power microscope has two main disadvantages. The first is that threshold damage identification is after the damage test and is therefore time consuming. The second is the ambiguity which may result in identifying the difference between surface damage pits and scattering centres which were present in the coating prior to testing. This is important for coatings with a large number of scattering centres.
distributed over the focused damage beam area prior to testing. In recent years these disadvantages have been reduced with the use of video microscopy using pulsed, visible dye lasers, (4.4). A telescope and video camera combination collecting 15° off-axis scattered light from a dye laser pulse has been used to image the scattering centres in dielectric films. This approach has the advantage in producing a 'before and after' image of the test site making threshold damage identification simpler and less ambiguous. This technique was not able to identify which of the scattering centres imaged below the damage threshold level were most susceptible to damage. It was also noted in this work that the scattering centres imaged in dielectric films exhibited a substantial depolarization of the scattered light.

Two areas of optical microscopy which have not been pursued are the ultra-violet microscope, (4.5) and various forms of the laser scanning microscope, (4.6). The ultra-violet microscope has found applications in biology and uses a mercury or hydrogen light source filtered to give monochromatic illumination. The image is recorded in photographic film or with a UV image converter. The ultra-violet microscope may be useful as a non-destructive test method for identifying absorbing centres in excimer laser optics or as a quality control check. The scanning microscope can offer increased resolution compared to conventional microscopes and has been used for defect detection in semiconductor materials.

Electron microscopy has been used to study the microstructure of optical thin films and to image damage sites at very high magnifications. Electron microscopy is a post-test analysis method and can be divided into Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The former has a resolution of about 5 nm compared to the TEM with a resolution of about 0.3 nm. Both methods have the disadvantage of requiring the sample to be in a high vacuum and also the focused electron beam may damage the optical component. Dielectric test samples can suffer from charging problems.
resulting in loss of contrast in the image. This can be overcome in the SEM by overcoating the sample with an evaporated thin metallic film. The higher resolution of the TEM requires the difficult and time consuming process of producing a thin carbon surface replica overcoated with an evaporated metal coating.

The cross-sectional microstructure of multi-layer dielectric laser mirrors has been investigated in many materials using electron microscopy. Nodular growth defects observed within the multi-layer have been predicted from theoretical models and can originate from surface roughness, dust, microsplatter or molecular clusters formed in the vapour phase, (4.7). Nodular growth defects have been shown to act as preferred laser damage sites, (4.8). An example of nodular growth in a SiH/SiO₂ multilayer coating is shown in figure 4.1. The nodule appears to originate at the third SiH layer and not at the substrate. Generally the nodules are observed to be 1 - 2 μm in diameter, extend through several layers and originate at the substrate/film interface or within the multilayer, (4.8).

4.2c Light emission

The observation of a spark from a plasma was often used as an indicator of laser induced threshold damage. Experiments involving laser induced damage detection using a pulsed Nd.YAG laser have shown two forms of light emission, (4.3). The more easily identified is a spark originating from a plasma and often audibly detectable from the resulting shock wave. The second form of light emission is a diffuse light source which appears to glow. This may originate from a weak diffuse plasma, fluorescence or radiative emission from surface evaporated material. The sensitivity to detect short wavelength visible and UV emission from the plasma has improved with the use of photomultipliers and optical filters. The main disadvantage of the spark detection method is that threshold damage in the form of small pits often observed in dielectric coatings are not accompanied by any
FIGURE 4.1
NODULAR GROWTH IN SiH/SiO₂ DIELECTRIC
MULTILAYER, REPRODUCED FROM
REFERENCE 4.8
detectable light emission, (4.4). Spark formation is usually used as an indicator of laser induced damage above the threshold level.

4.2d Truncation of the transmitted laser pulse

Truncation of the transmitted laser pulse at wavelengths of 10.6 μm, 1.06 μm and 0.694 μm was first observed in laser induced gas breakdown studies, (4.9). The observed pulse truncation was attributed to the formation of a dense plasma absorbing the incident laser light. Subsequently, monitoring the transmitted laser pulse was used as a technique in laser damage studies to indicate damage formation resulting from the plasma. Pulse truncation has been observed in laser induced breakdown studies of surfaces, bulk materials and thin films at wavelengths of 10.6 μm, 1.06 μm and 0.694 μm, (4.10). An example is shown in figure 4.2 for the occurrence of internal damage in NaCl due to ruby laser irradiation.

A useful technique that uses pulse truncation has been developed by Milam et al., (4.11) to isolate the dominant laser induced damage mechanism in a given sample. The time to breakdown of 50 - 100 sites on a sample was measured using a 20 ns, constant intensity pulse switched out of a single mode ruby laser using a Pockels cell. The fractional number of undamaged test sites plotted against the time to breakdown is known as a survival curve. The functional form of the survival curve was used to identify the damage mechanism. Three examples of survival curves from experimental data are reproduced from reference 4.11 in figure 4.3. In figure 4.3a the abrupt transition at a given power density indicates linear absorption, figure 4.3b indicates damage due to localized absorbing centres and figure 4.3c damage due to avalanche ionization. The non-linear curve in figure 4.3c is representative of defect enhanced avalanche ionization.

Experimental investigations have been done with ruby and frequency doubled Nd:YAG (532 nm) lasers to determine if pulse truncation is a sensitive monitor of laser
FIGURE 4.2

PULSE TRUNCATION FOR A RUBY LASER PULSE TRANSMITTED THROUGH A NaCl SAMPLE

(REPRODUCED FROM REFERENCE 4.10)

A Reference pulse, no truncation

B Truncation and damage occurring at the peak field

C Truncation before peak field is reached
FIGURE 4.3

EXPERIMENTAL SURVIVAL CURVES REPRODUCED FROM REFERENCE 4.11

A  TiO₂ / SiO₂ Multi-layer dielectric film

B  Single layer Zr O₂ Film

C  Suprasil-1 fused silica
induced threshold damage in sapphire and dielectric thin films, (4.12, 4.13). The main experimental conclusion was that the observation of pulse truncation was not a sensitive indicator of threshold damage in single layer or multi-layer dielectric films. Threshold damage in thin films was usually in the form of a few 1 - 5 μm diameter pits. In some cases a plasma spark was detectable with no detectable dip in the transmitted pulse. At higher incident intensities damage in the form of several 10 - 20 μm diameter pits was observed. This involved the observation of a spark and pulse truncation. These observations can be explained by assuming laser induced threshold damage produces a low density vapour which is non absorbing at the laser wavelength. A typical focused beam diameter for laser damage studies is greater than 100 μm giving an area ratio relative to a 5 μm absorbing defect of 400:1. The over-all attenuation of the transmitted pulse would not be observable in this case. In the cases involving a spark and pulse truncation damage was more severe. This implies the formation of a denser plasma which could result in absorption of the laser pulse. At higher incident intensities well above the damage threshold level the plasma frequency and therefore absorption coefficient at the laser wavelength may be sufficient for pulse truncation to be readily observable. The observation of pulse truncation is therefore associated with the formation of a plasma which absorbs at the incident laser wavelength.

4.2e Optical laser probe beams

The use of laser probe beams in the study of laser induced damage can be conveniently divided into three methods depending upon how the probe beam interacts with the test sample, these are

1) Specular reflection
2) Laser induced scatter
3) Photothermal deflection
Each of these can be further sub-divided depending on whether the optical probe beam is a separate, CW or pulsed laser source or a delayed version of the damaging laser pulse at a lower intensity.

4.2 Specular reflection

Measurements of specular reflection have often been done in parallel with transmission measurements to investigate the dynamics of damage formation, (4.12). Early work investigating surface threshold damage in sapphire using a ruby laser has shown that the sharp truncation in the transmitted pulse associated with plasma formation is also accompanied by a sharp decrease in the specular reflectance, (4.12). A sensitive optical probe beam technique has been developed by Alyassini and Parks, (4.14), to detect threshold damage formation in multi-layer dielectric coatings deposited on Dove prism glass substrates. Their technique used a helium neon laser to internally probe the films at the film-air critical angle. This geometry made it very sensitive to structural variations at the film/air interface because of the large variation of reflectance with small incidence angle changes. The focused probe beam spot size of 8 μm at the test site was much smaller than the damaging pulse spot size of 70 μm. The detector output was synchronized with the arrival of the damage pulse at the test site. The minimum detectable transient change in the probe beam signal corresponded to the formation of a single, circular damage site with a diameter of 2 - 3 μm.

The transient decrease in the probe beam signal was attributed to film deformation during the damage pulse resulting in increased scatter and a reduced specular reflectance. The film deformation was attributed to melting, vaporization or cracking arising from thermal stresses. Surface Rayleigh waves were detectable by displacing the probe beam ~1 mm away from the test site and measuring the transient surface deformation as the waves passed.

Four types of threshold damage morphology observed in
the work of Alyassini and Parks are reproduced in figures 4.4a-d. In the case where the damage site appears with considerable debris, (figure 4.4a), the detected probe signal was large. In the case where the damage site was relatively free of debris and larger than the probe beam cross section, (figure 4.4b), the detected signal recovered to its original level 40 ns after the ruby laser pulse peak. When the damage site was debris free and smaller than the probe beam cross section, (figure 4.4c), a small signal was measured. Finally, in the case of MgF₂, threshold damage in the form of cracks resulted in a signal decrease some 25 ns after the end of the ruby laser pulse, presumably arising from thermal stressing.

The sensitivity of this technique to detect threshold damage was compared to that of spark formation, pulse truncation and visual observation of Laser Induced Scatter (LIS), (4.14). The sensitivity of the LIS method was improved by using a x40 telescope to view the damage site before and after irradiation. The probe method was found to be much more sensitive than either of the techniques of spark formation or pulse truncation, being able to detect damage at much lower levels. The comparison with LIS was closer although changes in the probe beam signal were observed in cases where changes in the LIS were not. It should be added that visual identification of low level LIS changes would be subjective and difficult to identify.

The dynamics of damage formation in MgF₂, ThF₄ and ZrO₂ thin films at 0.53 μm has been investigated using a time delayed version of the original damaging pulse to probe the specular reflectance, (4.13). Similar results to those observed in reference (4.14) were found, in particular, damage occurring after the main pulse due to thermal stressing.

Both of these methods of measuring the transient specular reflectance have been used to investigate the dynamics of melt formation in semiconductor laser annealing, (4.15). An abrupt change in the reflectance of silicon was attributed to the silicon melting.
FIGURE 4.4

S.E.M THRESHOLD DAMAGE PHOTOGRAPHS REPRODUCED FROM ALYASSINI AND PARKS, (4.14.)
4.2eii Laser induced scatter

Visual observation of increased scattering has frequently been used to detect laser induced damage to optical surfaces. A variety of illumination schemes have been used including incoherent sources, backscatter of the damage beam or using a separate helium neon probe beam. The earliest work tended to use the unaided eye and look for increased near axis (<15°) backward or forward scattering using a white light source or a helium neon laser, (4.3). The sensitivity of this technique was improved by using a x40 telescope to view the damage site before and after irradiation, (4.14). Dynamic measurements of reflection, transmission and near axis (<15°) backscatter from sapphire surfaces irradiated with ruby laser pulses near the threshold level have shown that pulse truncation and a reduction in the specular reflectance was accompanied by increased scattering, (4.12). Similarly, dynamic measurements on thin films described in section 4.2e1 using a helium neon laser probe beam have attributed threshold damage to small scale disruption of the coating causing increased scatter. This method, initially developed by Alyassini and Parks, (4.14) of probing the optical surface through the substrate at the film/air critical angle has been developed to produce a Total Internal Reflection Microscope, (TIRM), sensitive to threshold damage formation, (4.16). It was claimed that this viewing method reveals more surface features on very smooth surfaces than using a Nomarski objective. The generally favoured Nomarski objective is essentially an interferometer designed to view small scale microscattering induced by surface disruption such as threshold damage. In a comparison of several techniques to identify threshold damage (not including TIRM) the Nomarski objective was favoured for its ease of use and sensitivity, (4.3). Studies with video microscope systems have shown that imaging near axis visible laser backscatter from the incident damage pulse is a sensitive threshold damage indicator, (4.4). It was observed in these studies that damage was often initiated at

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pre-damage defect locations where the scatter level was above the background level. This work has recently been extended on a more quantitative basis using a helium neon laser probe beam, (4.17). Experiments have shown an approximate linear correlation between the probability of damage (at a laser wavelength of 2.7 μm) at a particular point on the test sample with the pre-damage scatter signal from the probe beam. The probe beam was adjusted to be coincident with, and have approximately the same spot size as the damage laser pulse at the test site. The small probe beam spot size of 70 μm was much smaller than the typically measured mean defect spacing of 220 - 330 μm. The probability of damage occurring at a particular fluence would therefore be higher in the cases of a high pre-damage scatter signal since this would correspond to illuminating one or more defects within the probe beam area.

4.2eiii Photothermal deflection

Monitoring photothermal effects using an optical probe beam has not extensively been used to detect threshold damage formation in laser damage studies. However, the sensitivity to measure low absorption levels and the potential high spatial resolution offer the possibility of a non-destructive test procedure.

The photothermal effect is caused by local heating of a sample after absorption of optical radiation. The excitation source is usually in the form of a chopped or pulsed laser beam. After optical absorption several de-excitation processes are possible, these include:

i) Thermal de-excitation
ii) Luminescence
iii) Photochemistry
iv) Photoelectricity
v) Energy transfer

The possible non-thermal de-excitation channels, (ii - v), may contribute to a delayed heat generation. The local
heating of the sample which may be in a solid, liquid or gaseous state results in the generation of a local, spatially and temporally non-uniform refractive index profile proportional to the local density. The density in turn is related to temperature profile. A propagating thermoelastic wave (sound wave) is also produced which results in a separate propagating refractive index profile. It is customary to describe these two photothermal absorption effects as thermal waves and acoustic waves if the excitation beam is amplitude modulated in a periodic fashion. In the case of a single laser pulse the lifetime of the local thermal refractive index profile is controlled by the thermal diffusivity of the surrounding medium. The direct detection of the photoacoustic pulse propagating at the local sound speed is considered in section 4.2f.

Three optical techniques have been used to detect the localized heating, these are:

i) self-defocusing
ii) probe beam refraction
iii) surface deformation

Self-focusing or thermal blooming arises from the thermal refractive index gradient generated by the pump beam affecting its own propagation. The derivative of the refractive index with temperature is usually negative and so the heated region acts like a negative lens defocusing the propagating beam.

The propagation of a separate, weak probe beam in the vicinity of the pump beam is also influenced by any local refractive index gradients. The probe beam refraction, (PBR), approach offers greater flexibility and increased sensitivity in measuring local absorption compared to the self-defocusing method. The disadvantage is increased complexity and a more difficult optical alignment. The two basic PBR arrangements are illustrated in figures 4.5 and 4.6. In the parallel PBR case used for transmission measurements the probe beam is collinear with the
FIGURE 4.5
COLLINEAR PROBE BEAM REFRACTION

FIGURE 4.6
ORTHOGONAL PROBE BEAM REFRACTION
OR "MIRAGE" PROBING

FIGURE 4.7
PROBE BEAM DEFORMATION FOR A THERMALLY
DISTORTED SURFACE
excitation beam. The position sensitive detector monitors the deflection of the probe beam. If the excitation is periodic then sensitive phase locking techniques may be used to monitor the detector output. The deflection of the probe beam is linearly related to the absorbed energy and is a maximum when the probe beam axis passes through the maximum refractive index gradient. A continuous wave pump beam with a Gaussian intensity profile has a maximum refractive index gradient at half the $1/e^2$ radius.

Although the collinear PBR configuration with a displaced probe beam offers the largest deflection this arrangement may not always be possible, such as with opaque samples, (4.18). A non-parallel configuration is also needed for spatially resolved probing. The configuration shown in figure 4.6 is known as orthogonal PBR or more simply as "mirage" probing. The probe beam is deflected by the refractive index gradient in the gas layer adjacent to the sample's surface. The spatial resolution of this technique is of the order of the thermal diffusion length in the surrounding gas.

Photothermal heating of a surface also causes distortions to the surface due to thermal expansion which can be monitored by a probe beam reflected off the surface as illustrated in figure 4.7. If the distance to the detector is large the deflection of the probe beam is dominated by the local surface gradient which is proportional to the surface displacement, (4.18). In reference 4.18 it is shown that the maximum surface displacement is linearly related to the local absorption coefficient. As in the case of collinear PBR it is usual to displace the incident probe beam axis to the point where the surface slope is a maximum. Rosencwaig et al., (4.19) have developed a sophisticated numerical model to describe the probe beam at normal incidence which takes account of thermal lens effects in the gas above the surface. Their theory and experimental results confirmed that the dominant probe beam deflection for normal incidence arises from surface deformation due to thermal expansion. An experimental comparison of the oblique
incidence and normal incidence methods showed a sensitivity increase by a factor of 230 times favouring the normal incidence method, (4.20).

Numerous applications of these photothermal techniques are described in a review given by Tam, (4.18). The collinear, displaced PBR method has been used to measure the absorption coefficients of gases, liquids and solids as low as 10^{-7} \text{cm}^{-1}. Other applications include trace gas detection below the parts per billion level, thermal diffusivity measurements of a hot gas, gas flow velocity, temperature and composition measurements and time resolved measurements to detect energy transfer and photochemical reactions.

The mirage PBR technique and the surface deformation probe beam technique have been used in CO\textsubscript{2} laser damage studies for threshold damage detection, (4.21). The probe beam deflection as a function of the incident CO\textsubscript{2} laser beam energy density is shown in figure 4.8 for the mirage effect. Above a threshold level a non-linear increase in the probe beam signal level was observed.

A surface deformation probe beam technique has been developed by Rosencwaig to achieve high spatial resolution aimed at microscopy imaging applications in semiconductors, (4.19). This approach has been extended and applied to the microscopic imaging of excimer laser coatings, (4.20). A two dimensional absorption map was measured of a Ta\textsubscript{2}O\textsubscript{5}/SiO\textsubscript{2} HR excimer laser mirror designed for 0° incidence at the XeF wavelength of 351 nm. It should be noted that the absorption map represents contours of absorbed energy which depends on the absorption length and absorption coefficient. Calibration of the interaction length to determine absorption coefficients is difficult. The absorption map was compared to a x100 dark field photomicrograph both before and after threshold damage testing with a XeF laser. Their results show that some, but not all of the micron sized, threshold damage sites observed in the dark field photomicrograph after testing corresponded with the local regions of high absorption before testing. It was also
DEFLECTION V

1000

100

10

THRESHOLD = 11 ± 0.2 Jcm⁻²

FIGURE 4.8 (reproduced from ref: 4.21)

SIGNAL DEFORMATION USING THE MIRAGE PROBE BEAM METHOD AS A FUNCTION OF THE INCIDENT CO₂ LASER ENERGY DENSITY FOR A H.R COATING ON A GERMANIUM SUBSTRATE
observed that occasionally, easily identified scattering centres visible before damage testing were not identified with the absorption maps. Several experimental factors may contribute to the apparently missed damage sites including the limited sensitivity and the scanning step size of 0.8 μm. Perhaps a more likely explanation is that other damage processes apart from linear absorption may be involved including two photon absorption and electric field enhanced defect damage. The limiting factor to the acceptance of this method as a quality control tool, especially for large optics is likely to be the enormous data acquisition time, seven hours for a 100 x 100 pixel array. The data acquisition time may be drastically reduced by generating a large area, transient, photothermal absorption image and capturing it on a thermal imaging camera. Subsequent digital image processing of many frames may then achieve a comparable sensitivity to the point by point approach.

4.2f Photoacoustic detection

The photoacoustic, (PA), effect arises from the absorption of optical radiation and the resulting generation of acoustic waves. PA generation at low illumination levels is usually attributed to the photothermal effect. Other mechanisms are however possible, those particularly relevant to laser induced damage detection include melting, shock wave formation, gas evolution, boiling, vaporization, ablation and plasma formation. Photoacoustic generation can be classified as either direct or indirect. In direct PA generation the acoustic wave is generated and detected in the sample where the excitation beam is absorbed. In indirect PA generation the acoustic wave is generated and detected in a coupling medium, usually a liquid or gas adjacent to the sample. In this latter case, periodic absorption of the optical radiation in the sample produces a thermal wave in the coupling medium which is detected as an acoustic wave. An extensive recent review of PA generation, detection and its applications has been given by Tam, (4.18). In
general, indirect PA generation requiring acoustic
detection in a coupling fluid in contact with the sample
does not provide as high a sensitivity as direct PA
generation, (4.18). As far as detection of laser induced
threshold damage is concerned, interest is therefore aimed
at direct, pulsed PA generation and detection in solids.

Laser induced generation of acoustic waves in metals
has been widely studied and an extensive review has been
given by Scruby et al., (4.22). Most of this work
involved surface absorption of Q-switched Nd.YAG lasers
(λ = 1.06 μm) and measuring the characteristics of the
resulting bulk, longitudinal and shear waves and surface
Rayleigh waves. This was done by detecting the surface
displacement of the back of the sample as the acoustic
wave arrived.

Three types of sensor have been developed to detect
the high frequency (0.1 - 10 MHz) photoacoustic pulses.
These are the piezoelectric transducer, (4.22), the
capacitance transducer, (4.23) and optical transducers,
(4.18). Several piezoelectric materials are commercially
available, the most widely used for these applications is
lead zirconate titanate, usually abbreviated to PZT.
Transducers produced using PZT as a sensing material are
commercially available but are also relatively easy to
manufacture. Several groups have investigated optimum
geometries, materials and construction, (4.21).
Increasing the detector area increases the sensitivity but
decreases the the detector risetime. The high frequency
performance of piezoelectric transducers to bulk wave
propagation has been shown to be limited by transit time
broadening effects, (4.24). For a source of spherical
acoustic waves on the axis of a circular PZT disc of
radius a at a depth z, the time delay δt between waves
reaching the centre and circumference of the disc is given
by

\[ δt = \frac{1}{C} \left( \frac{(z^2 + a^2)^{1/2} - z}{2a} \right) \]

where C is the sound speed. Experimental data with

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differing PZT disc diameters have shown equation 4.1 to be a good estimate of the piezoelectric detector risetime for bulkwave propagation, \(4.24\). The bandwidth limit, \(f\) in MHz due to transit time broadening is given by

\[ f = \frac{0.35}{\delta t} \quad 4.2 \]

where \(\delta t\) is in microseconds. Using typical parameters of \(a = 3.0\) mm, \(z = 10\) mm, \(C = 6000\ \text{ms}^{-1}\) gives an upper frequency limit of 4.8 MHz. The high frequency performance of piezoelectric transducers for surface wave detection is the requirement that the detector diameter \(2a\) be less than half the acoustic wavelength, \(4.21\). Piezoelectric transducers are capable of sensing extremely small, normal surface displacements. In calibration tests of a commercial device, the arrival of a 20 pm longitudinal step in the surface displacement was sensed with a resonant sensitivity of 10 mV/pm, \(4.25\). The high frequency resonances of these transducers are usually attributable to a thickness or radial resonance of the PZT ceramic disc. To achieve a flat frequency response requires operation well below the first resonance, usually below 1 MHz. A flat frequency response is therefore achieved at the expense of a reduced sensitivity. Experimentally the transducer housing is usually coupled to the sample back face with silicone grease or a similar material to match acoustic impedances. Associated with each PZT transducer is a trans-impedance amplifier to allow convenient signal capture on an oscilloscope.

A wide bandwidth (dc – 16 MHz) capacitance transducer sensitive only to normal displacements of the surface has also been used to investigate laser induced ultrasound in metals and to calibrate piezoelectric transducers, \(4.24\). The minimum detectable displacement in the presence of noise was of the order of one pm, \(4.26\). Experimental measurements of the capacitance transducer risetime of \(\approx 60\) ns is in agreement with the value calculated from equation 4.1 using an electrode diameter of 3 mm and a sample thickness, \(z = 10\) mm.
The advantages of a wide bandwidth and the absence of resonances meant unambiguous interpretation of transducer output waveforms was possible. This feature has been used to measure absolute surface displacements and to calibrate lower frequency performance piezoelectric transducers. The operational disadvantage is the need for a metallic, polished surface on the sample and the requirement to hold a separate capacitor electrode a few microns away from the surface of the sample.

Two optical techniques have been used to detect surface displacements due to the arrival of acoustic waves. The first is the probe beam technique of surface deformation described in section 4.2eiii. In this case the probe beam is displaced several thermal diffusion lengths away from the pump beam to avoid deflections due to thermal expansion, (4.18).

The more extensively investigated technique is optical interferometry. A stabilized, Michelson interferometer with a bandwidth of 10 MHz has been used to measure absolute surface displacements and to calibrate piezoelectric transducers, (4.27). The main advantage of the optical technique over the capacitance method is its non contacting nature. The major disadvantage is the approximate order of magnitude decrease in sensitivity compared to the capacitance transducer, (4.23).

Laser generated ultrasound in metals has been studied in great detail by using a capacitance transducer to monitor absolute surface deformation due to the arrival of acoustic waves, (4.22). Generally the measurements were done on-axis on the back surface of the metallic samples. Surface absorption of some of the incident pulsed laser energy resulted in the propagation of spherical longitudinal and shear waves which were detected separately due to their differing propagation speeds. The peak to peak variation in the longitudinal and shear wave amplitude as a function of the incident laser energy (and energy density) is shown in figure 4.9 for a polished aluminium sample. These data are reproduced from reference (4.22). It is apparent that two approximately
Plasma formation at estimated energy density 0.34 J cm$^{-2}$ for 17 ns Nd:YAG laser pulse.

(Reproduced from Reference 4.22)
linear regions can be identified, these are the thermoelastic region at low incident laser energies and the strong plasma region above an estimated energy density of $0.57 \text{ Jcm}^{-2}$. It is interesting that a surface plasma was initially observed around $0.34 \text{ Jcm}^{-2}$ resulting in only a small slope change. Representative waveforms from the thermoelastic and plasma regions are shown in figures 4.10 and 4.11. A positive displacement is in the direction away from the acoustic source. The longitudinal arrival in the thermoelastic region is therefore a small elevation of the back surface followed by a larger step like depression. The shear arrival (PZT is sensitive in the shear mode) is about a factor of four larger at a given laser energy than the longitudinal step. The corresponding sensitivities are $\sim 1.2 \text{ pm mJ}^{-1}$ and $4.7 \text{ pm mJ}^{-1}$ for the longitudinal and shear waves respectively, (4.26).

Acoustic generation in the thermoelastic region arises from thermal expansion. The simplest model is to assume absorption of a fraction of the incident laser energy results in adiabatic heating of the metal surface to a depth equal to the thermal diffusion distance. In the case of a metal, the thermal diffusion distance is greater than the "skin" depth for absorption of the optical energy. The heated region is free to expand normal to the surface but is constrained by the surrounding material parallel to the surface. This results in a shear stress amplitude larger than the longitudinal stress amplitude. The shear stress amplitude was found to be enhanced by using an aperture over the irradiated area to increase the lateral thermal gradient, (4.28). Thermal models which take account of the thermal conductivity of the sample have been used to predict all of the aspects of the waveform observed in figure 4.10. In this case adiabatic heating is not perfect and a small elevation of the back surface occurs before the large step like depression arising from expansion of the front surface. The amplitude of either step has been found to be proportional to the absorbed laser energy. In the
FIGURE 4.10 (reproduced from ref: 4.22)

SURFACE DISPLACEMENT IN THE THERMOELASTIC REGION, NO PHYSICAL DAMAGE TO ALUMINIUM SAMPLE
LASER ENERGY~5 mJ (0.17 Jcm⁻²)
SURFACE DISPLACEMENT

<table>
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<th>TIME / μs</th>
<th>100</th>
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<th>1000</th>
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<td>9</td>
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</tbody>
</table>

ENERGY DENSITY = 8.5 J/cm²

ENERGY DENSITY = 2.5 J/cm²

ENERGY DENSITY = 5.1 J/cm²

FIGURE 4.11 (reproduced from ref: 4.22)

SURFACE DISPLACEMENT IN THE PLASMA REGION AT INCREASING INCIDENT ENERGY DENSITIES
thermoelastic region a linear dependence of the signal amplitude on the incident laser energy has been observed in metal and dielectric samples for longitudinal, shear and surface Rayleigh waves, \((4.21, 4.28)\).

Acoustic generation in the plasma region is dominated by an efficient momentum transfer process arising from vaporization and particle ablation. Three acoustic waveforms measured in the plasma region of figure 4.9 are shown in figure 4.11. Initially, the longitudinal arrival is first a pulse like elevation of the surface and then at higher incident energy densities a step like elevation that continues for several microseconds. The acoustic generation mechanism has been modelled as a normal force whose duration is adjusted to fit the data combined with a contribution from the thermoelastic process described earlier, \((4.23)\). The normal force duration varied from \(-0.3 \mu s\) just above the plasma threshold to \(-10 \mu s\) at high energy densities. These results suggest that even at low energy densities just above the plasma threshold \((\sim 0.3 \text{ Jcm}^{-2})\) the sample's surface is maintained above the vaporization temperature well after the end of the optical pulse. At higher incident energy densities re-radiation from the plasma continues to ablate material from the surface for several microseconds. In this region a Laser Supported Combustion (LSC) wave forms where optical radiation is absorbed by the plasma which re-radiates at short wavelengths \((\sim 150 \text{ nm})\) and subsequently ablates more surface material.

In the plasma region, the variation of the longitudinal pulse amplitude with incident energy density was initially found to be linear followed by saturation and reduction, \((4.23)\). A similar effect has also been observed at laser wavelengths of \(0.35 \mu m, 0.69 \mu m\) and \(10.6 \mu m\) and has been attributed to the formation at high energy densities of a Laser Supported Detonation (LSD) wave, \((4.29)\). The LSD wave is a thin, highly absorbing plasma layer which shields the surface and reduces the impulse coupling efficiency.

The validity of the two basic acoustic generation
mechanisms of thermal expansion at a free surface and ablation has been demonstrated by the excellent agreement between the calculated and experimentally measured angular longitudinal wave distributions, (4.22). The nature of the measured waveform has been found to be influenced by various surface modifications. Enhanced longitudinal wave amplitudes have been observed by using a thin liquid coating on the metal surface. In this case, vaporization of the liquid resulted in a plasma with waveforms similar to those in figure 4.11. Thin glass slides clamped to the metal surface have also been used to enhance the longitudinal generation efficiency in the thermoelastic region, (4.22). Thermal expansion normal to the metal surface is constrained by the glass slide resulting in an increased normal stress.

It is clear from figure 4.9, that above 0.6 Jcm\(^{-2}\) a large change in slope occurs as the acoustic generation mechanism moves from the predominantly thermoelastic region to a strong plasma region. The ability of this method to accurately detect laser induced threshold damage therefore depends on the width of the transition region. In this region no one effect necessarily dominates towards the over-all photoacoustic signal level, contributions may arise from:

1) Thermoelastic effects  
2) Dynamic changes in the absorption coefficient  
3) Shock wave formation  
4) Vaporization  
5) Direct ablation or ablation from the plasma

Much of the published work has been concerned with laser generation of acoustic waves for non-destructive testing and calibration applications, (4.22). The initial work on the use of piezoelectric transducers to detect laser induced damage formation in optical components was done by RoscenaWaig and Willis, (4.30). Their damage threshold measurements were done using a Nd:YAG laser, (1 J, 1 ns), with a HR multi-layer (Si\(_2\)O\(_2\)/TiO\(_2\)) mirror coating.
deposited on a fused silica substrate. Good agreement (~10%) was found between the threshold defined from the change in the acoustic signal and a simple visual identification method. The photoacoustic signal \( q \) was found to follow a simple power law as derived from a log-log plot given by

\[
q = E^n
\]

where \( E \) is the incident energy density. Below the damage threshold the value of \( n \) was found to be approximately one as expected in the thermoelastic regime. Above the damage threshold the measured value of \( n \) was given as \( n = 4 \pm 1 \) for a dielectric high reflector and \( n = 1.2 \) for a metallic high reflector. These differences can be attributed to the different damage mechanisms having different photoacoustic generation efficiencies. In the initially low absorption dielectric sample, threshold damage results in a greatly increased absorption of the laser energy. In the metallic sample damage attributed to melting results in no large increase in absorption and therefore photoacoustic signal. This explanation is in agreement with the data represented in figure 4.9 where a small slope change in the longitudinal wave is observed above the plasma threshold (>0.34 Jcm\(^{-2}\)) for an aluminium sample.

This work has been extended to the CO\(_2\) laser wavelength of 10.6 \( \mu \)m. The initial work was done to predict laser induced failure in NaCl and KBr laser output coupler windows, (4.31). More recently this was extended as part of a wider study of damage detection in infra-red materials, (4.21). In this latter work a general observation gave \( n<2 \) for metallic samples, (Al, Cu, Mo, Ni/Cu) and \( n>2 \) for dielectric samples, (Ge, HR on Ge, KCl, NaCl). The single shot thresholds determined at 10.6 \( \mu \)m were generally observed to be about 10 - 20% lower than those published in the literature, (4.21). The data for a multi-layer HR coating on a germanium substrate are reproduced in figure 4.12. In this case the damage
FIGURE 4.12 (reproduced from ref: 4.21)

PHOTOACOUSTIC SIGNAL AS A FUNCTION OF CO₂ LASER ENERGY FOR A H.R COATING ON Ge SUBSTRATE
threshold of 16.2 Jcm\(^{-2}\) is much higher than the threshold of 11 ±0.2 Jcm\(^{-2}\) measured using the photothermal technique on the same sample, (see figure 4.8).

4.2g Charged particle emission

Laser induced particle emission from targets in a vacuum (~10\(^{-6}\) - 10\(^{-8}\) torr) has been extensively investigated but not with respect to the laser induced damage threshold, (4.32). Thermionic electron emission in metals has been found to be the dominant emission process at low incident laser intensities, other processes include multi-photon absorption and at UV wavelengths the single photon photoelectric effect. Laser induced heating of surfaces can also result in thermionic positive ion emission, (4.32). Most of the work on metals has concentrated on electron and ion collection from blow-off material and plasmas at levels well above the damage threshold. This has led to the use of "time of flight" mass spectrometers to study the ions emitted in the laser-surface interaction. A general observation was that for a Q switched ruby laser around 20 MW cm\(^{-2}\), most of the emitted ionic species were due to atoms and molecules present on the target surface and little surface disruption was observed, (4.32). At higher irradiances the surface vaporizes and substrate atoms and ions will dominate in the blow-off material. At the highest intensities essentially complete ionization of the vaporized material results in the formation of a dense plasma.

Positive ion collection has been used to study multiple shot laser induced degradation of GaAs, (4.33) and silicon, (4.34). The work on GaAs involved N on 1 damage tests where N varied from 1 to 100 and showed the onset of ion emission to occur at a fluence of 0.2 Jcm\(^{-2}\). This was well below the extrapolated zero probability damage threshold measured using a x200 Nomarski objective. Accumulation effects were also observed in the work on GaAs where ion emission first decreased after the first few shots (2 - 10) and then rapidly increased and
saturated. This was attributed to the surface being cleaned of impurities followed by surface damage corresponding to a large increase in the ion current. The 1 on 1 and N on 1 results in GaAs suggest ion emission could be used as a precursor indicator of the formation of physical damage ultimately leading to a decrease in optical performance.

4.2h Surface analysis

The semiconductor industry has used surface analysis methods extensively to identify the presence of impurities and confirm dopant profiles in many materials. These techniques can identify surface atomic or molecular species with high spatial resolution and can generate a depth profile using an ion beam gun. Their restricted use in identifying the causes of laser induced defect damage is probably related to their availability and high running costs. The most widely known method is the electron microprobe attached to most Scanning and Transmission Electron Microscope (STEM) systems. Other surface analysis techniques include Auger Electron Spectroscopy, (AES), X-ray Photoelectron Spectroscopy (XPS or ESCA) and Secondary Ion Mass Spectroscopy (SIMS).

An Auger spectrometer elemental surface map around a threshold damage site in a ZnSe/ThF₄ multi-layer coating has been used to identify the vertical spatial location and-chemical composition of an absorbing particulate, (4.8). Oxygen as an impurity associated with water was also observed in the hydroscopic ThF₄ layers. SEM and XPS techniques have also been used to identify nodular growth in a SiH/SiO₂ multilayer coating. An example is shown in figure 4.1. The nodules ~1 - 2 μm in diameter extend through several coating layers and were shown to be a cause of threshold damage.

4.2i Summary and comparison of damage detection methods

A summary is given of the main features which can be attributed to the damage detection methods reviewed in section 4.2a - h.
Breath-fogging
Useful for damage detection in high quality thin films for large area damage. Not sensitive for threshold damage formation in thin films.
Not a convenient method.

Optical microscopy
Sensitive at high magnifications with phase contrast or Nomarski objectives.
Preferred option as a 'before and after' damage comparison without moving the test sample.
Video microscopes have been used to image laser backscatter and view scattering centres in thin films.

Electron microscopy
Very high magnification and resolution
Requires high vacuum.
Image contrast not always good with dielectric samples.
Main use is as a tool for post-test analysis of the surface microstructure.

Light emission
Light emission can be considered as a detector of ionization and plasma formation.
Threshold damage can occur, especially in thin film optics without light emission.

Pulse truncation
Pulse truncation is related to the formation of a plasma which absorbs at the incident laser wavelength.
The plasma absorption coefficient depends upon the plasma frequency and the incident laser wavelength.
Threshold damage in thin films can occur without the formation of a plasma.
Survival curves can be used to indicate the dominant damage mechanism.
Optical laser probe beams

Specular reflection
A sensitive detector of thin film disruption is the internal, critical angle probe beam technique. Transient measurements can indicate the type and extent of threshold damage (see figure 4.4). The critical angle probe beam method is more sensitive than the visual laser scatter method. The critical angle probe beam method requires specially shaped substrates (Dove prisms) and requires stable alignment.

Laser induced scatter
Detects physical disruption of the surface
Visual sensitivity can be increased by the use of a x40 telescope in a 'before and after' test comparison. Dynamic changes in the transmission and specular reflection have been attributed to increased scatter. Optical microscopy using a Nomarski objective can be considered as a scatter method. Laser scatter can be imaged by video microscope systems. Laser scatter systems are simpler to implement than the internal critical angle specular reflection method. The damage probability at a given test site on a sample appears to correlate with the pre-damage scatter level.

Photothermal deflection
Very sensitive to low levels of absorption. The highest sensitivity is obtained when the probe beam diameter is much smaller than the excitation beam. Two geometries have been considered, the mirage effect and probe beam deflection due to surface expansion. The probe beam deflection technique is most sensitive for normal incidence. Scanned, linear absorption maps have been produced on excimer laser coatings. The scanning time on a point by point basis is very time consuming.
Not all of the threshold damage sites correlate with local high absorption sites.

**Photoacoustic detection**
Requires silicone grease as an acoustic coupling medium on the back surface of the test sample. Piezoelectric transducers create confusing waveforms because of transducer resonances but achieve high sensitivities. Two waveform regimes have been identified, the thermoelastic and the strong plasma regimes. Piezoelectric transducers have been used at infra-red wavelengths to measure laser damage thresholds. Various mechanisms can generate bulk waves due to laser absorption. Threshold identification has been done by extrapolating linearized data.

**Charged particle emission**
Requires high vacuum operation. It offers the possibility of an NDT method to predict physical damage thresholds. Spectroscopic measurements may be used to identify impurity surface species. The technique has been demonstrated in GaAs and silicon, the behaviour for dielectrics and dielectric thin films is uncertain.

**Surface analysis**
Requires high vacuum. The availability and test time may be limited due to the high cost of the equipment. The various techniques can normally be considered as post test analysis methods. The techniques offer high spatial resolution and chemical identification is possible. Depth profiles of species can be measured.

Few comparisons of the various techniques that have
been used to detect laser induced threshold damage have been given in the literature. A consideration by Milam, (4.3) of the suitability of methods to detect threshold damage in single layer, AR and HR dielectric films concluded that Nomarski microscopy is the optimum choice with increased visual forward angle scatter a close second. It should be noted that in the review given by Milam, optical probe methods and particulate emission were not pursued and photoacoustic methods were considered unreliable because of the presence of a signal due to linear absorption. The internal critical angle optical probe beam method developed by Alyassini and Parks (4.14) was shown to be much more sensitive to threshold damage detection than spark detection and pulse truncation and slightly more sensitive than the visual scatter method using a x40 telescope. The CO₂ laser damage threshold of several infra-red materials has been measured using the photoacoustic, optical mirage and laser scatter detection methods described in sections 4.2e-f, (4.21). Table 4.1 reproduces some of these data. It appears that the laser

<table>
<thead>
<tr>
<th>Material</th>
<th>Photoacoustic</th>
<th>Mirage</th>
<th>Laser Scatter</th>
</tr>
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<td></td>
<td>Jcm⁻²</td>
<td>Jcm⁻²</td>
<td>Jcm⁻²</td>
</tr>
<tr>
<td>Stainless</td>
<td>4.1</td>
<td>4.2</td>
<td>4.8</td>
</tr>
<tr>
<td>Steel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>11.9</td>
<td>13.8</td>
<td>-</td>
</tr>
<tr>
<td>Ge</td>
<td>14.6</td>
<td>11.0</td>
<td>-</td>
</tr>
<tr>
<td>HR/Ge</td>
<td>16.2</td>
<td></td>
<td>11.9</td>
</tr>
<tr>
<td>Au/glass</td>
<td>21.2</td>
<td></td>
<td>16.7</td>
</tr>
</tbody>
</table>

Table 4.1
Laser damage thresholds at 10.6 µm measured using three damage detection methods.
(Data reproduced from reference 4.21)
scatter method offers the lowest threshold for thin films. This may arise because the photoacoustic method is sensitive to macroscopic dynamic changes in laser absorption arising for example from substrate melting and laser scattering being more sensitive to small scale microscopic physical disruption of thin films.

4.3 Laser induced threshold damage detection at excimer laser wavelengths

4.3a Criteria for damage detection

It is clear from the review given in section 4.2 that laser induced damage detection methods can be broadly classified into in-situ and post-test damage detection. The broad aim in this work was to develop sensitive, in-situ methods which minimized the amount of post-test analysis.

The morphology of laser induced threshold damage in dielectric thin films at excimer laser wavelengths has been observed to be in the form of several 1 - 10 \( \mu \text{m} \) diameter pits, (4.35). This observation was also made in this work for threshold damage measurements at 193 nm and 248 nm on multi-layer dielectric high reflectors and anti-reflection coatings deposited on fused silica substrates. The pits were usually observed in the central area of the focused beam often coinciding with some of the scattering centres observed visually. The focused beam area at the test sample's surface was typically 0.5 - 2.5 \( \text{mm}^2 \). The damage pits were initially identified by post test examination of the sample at magnifications of 200 - 400x. Dark field objectives and Nomarski objectives were used with no obvious difference in sensitivity to detect threshold damage. The disadvantage of removing the sample from the test station and examining it under the microscope was in identifying the difference between damage pits and scattering centres which were present in the coating prior to testing. This problem was particularly important for coatings with a large number of scattering centres distributed over the focused beam area.
prior to testing. This resulted in some ambiguity in the
detection of threshold damage and therefore in measuring
the damage threshold.

It has been observed in this work and elsewhere,
(4.4) that scattering centres observed in thin films are
often (but not always) the locations for threshold damage.
Experiments have been done which indicate a correlation
between the pre-damage scatter level and the damage
probability at a given location, (4.17). The damage
process is usually attributed to a spatially, highly
localized increase in the film absorption. The technique
of photothermal deflection microscopy described in section
4.2f has shown that increases in the local film absorption
often (but not always) correspond to the spatial location
of threshold damage sites.

Little work has been done to try and identify which
of the observable scattering centres in a coating are
susceptible to laser damage. Chemical identification of
absorbing impurities such as metal inclusions, source
material film splatter or non-stoichiometric regions would
indicate how to improve the over-all component damage
threshold.

The main criteria which were applied to help decide
avenues of investigation for laser induced damage
detection were:

1) Sensitivity to detect or observe the formation of
   1 - 10 µm diameter damage pits
2) To detect or observe the formation of damage pits over
   a beam area of 0.5 - 2.5 mm²
3) To detect or observe the formation of damage pits
   without moving the test sample, i.e. an in-situ test.
   This allowed a "before and after" comparison to
   unambiguously identify threshold damage
4) To chemically identify any absorbing species in the
   thin film coating which initiate damage and therefore
   indicate how improvements may be made.
5) To develop techniques that are simple and convenient
to implement and operate.

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These criteria and the review section describing the published literature indicate that breath-fogging, light emission, spark detection and pulse truncation are not sensitive detectors of threshold damage at excimer laser wavelengths in thin film coatings. Electron microscopy and surface analysis methods have been used as post-test analysis tools. An Energy Dispersive Analyser (EDA) attached to an SEM machine was used to identify the unknown coating materials for several test samples. In one case, a high damage threshold HR mirror was identified as a multi-layer coating of $\text{Sc}_2\text{O}_3$ and $\text{MgF}_2$. In another case the HR mirror materials were identified as cryolyte ($\text{Na}_3\text{AlF}_6$) and ThF$_4$. The technique of charged particle emission for threshold damage detection or even as an NDT method offers promise. A surface analysis LIMA instrument (Laser Induced Mass Analyser) was used to investigate chemical identification of scattering centres in dielectric coatings. The LIMA instrument makes use of a frequency quadrupled Nd:YAG laser (266 nm) to ionize surface material which is subsequently analysed by a "time of flight" mass spectrometer.

A preliminary investigation was done at 248 nm using the pulse truncation technique to try and generate survival curves and isolate the dominant laser induced damage mechanism as described in section 4.2d. No pulse truncation was observed from a multi-layer HR dielectric reflector or a fused silica window for incident energy densities capable of generating an intense surface plasma. This result is not unexpected since in a simple plasma the absorption coefficient is given by, (4.9)

$$a = \frac{\omega^2}{\omega_{pe}^2}$$

where $\omega_{ei}$ is the electron-ion collision frequency, $\omega_{pe}$ is the electron plasma frequency and $\omega$ is the incident frequency. The ratio of the absorption coefficients of the same plasma to incident laser wavelengths of 0.248 $\mu$m
and 10.6 μm is 1827. To achieve the same degree of absorption at 10.6 μm requires ω_p^2 and therefore the electron density at 0.248 μm to be a factor of 1827 higher. Most of the reported pulse truncation experiments have been observed at infra-red wavelengths where the technique is more sensitive since it requires a less dense plasma for pulse truncation to be observed.

Experimental investigations of laser induced threshold damage detection in dielectric coatings at excimer laser wavelengths were concentrated in three areas, these were:

1) Optical microscopy  
2) Laser probe beams  
3) Photoacoustic methods

The techniques involving laser probe beams were biased towards laser induced scattering. The photothermal and total internal reflection methods are more complex and generally require the probe beam to be smaller than the excitation beam for maximum sensitivity.

4.3b Threshold damage detection using optical microscopy

Initially threshold damage was identified by post-test examination using a high quality, Vickers Microplan optical microscope. Several samples were examined to investigate the most suitable objective, magnification and illumination arrangement. The darkfield objectives were found to be convenient to use. At over-all magnifications greater than 100 times some AR coatings showed a faint 'crazing' which followed scratch marks presumably located at the substrate/film interface. Examination of some unused samples showed localized areas of damage about 200 - 1000 microns in diameter. These areas may be evaporant splatter produced as the electron beam heats the source coating material. Threshold damage in the thin film samples was in the form of several pits usually between 1 - 10 microns in diameter.

The simplest visual in-situ technique for identifying
threshold damage is the naked eye. The eye's sensitivity to detect defect damage was a maximum when the optical contrast between the defect and the background is also a maximum. A dark field illumination arrangement was therefore used to view the test sample in the vicinity of the incident excimer beam. The sensitivity was improved with the use of a long working distance microscope, (150 mm) with a magnification of 40x. Test samples with optically transparent fused silica or BK7 glass substrates were back illuminated about 20 degrees off-axis using a helium neon laser or front illuminated with a collimated white light source. The microscope was positioned to avoid the directly transmitted or specular reflected illuminating beam and achieve a high contrast image. Initially the microscope was adjusted to view the front surface of the test sample and image a damage site created well above the damage threshold. In this way as the test sample was traversed to a new position the microscope remained correctly viewing the front surface of the sample where the excimer beam was incident. Remaining experiments were then done at lower fluences to measure the damage threshold. The most sensitive was to detect threshold damage using helium neon laser illumination and to look through the microscope whilst the laser shot was fired. This gave an immediate 'before and after' image to compare. This was relatively simple for single shot tests but produced eye strain for multi-shot tests. Further difficulties arose when the test sample had a high initial background scatter level making identification of threshold damage more ambiguous.

A natural extension of this work was the development of a video microscope system which enabled a true systematic 'before and after' image comparison. Higher magnifications (60 - 460x) and a much greater degree of flexibility and convenience were further advantages. As described in section 4.2.b, video microscopes have also been used to capture near axis, (10 - 15 degree) pulsed dye laser scatter from scattering centres arising from threshold damage. The dye laser in this case was also the
the damaging beam.

In this work a separate helium neon probe beam was used to illuminate the test site. Two video cameras were used in combination with a colour monitor and a Betamax video recorder to produce permanent records. Each video camera was adapted to mount an extension tube and microscope objective to increase the magnification. The large Saticon video camera (an Hitachi colour camera, model number GP-5AE/K) had a built-in microphone which allowed verbal details of the test to be included on the video tape. The small CCD video camera (an Hitachi mono camera, model number KP-120U) had an advantage with its small size but which was offset with an automatic gain control which tended to reduce the aperture if a few bright scattering centres were present on an otherwise dark background as occurs in darkfield illumination. This had the effect of reducing the image contrast compared to the colour video camera. Two positions for the video camera were tried as shown in figure 4.13. At position A about 45 degrees off-axis from the helium neon beam a magnification of 60x was used. At position B on the axis of the helium neon laser the over-all magnification was 250x. Dark field illumination at position B was achieved by using a lens close to the sample to collect the scattered light and a small circular beam stop in the centre of the lens to block off the directly transmitted beam. This illumination technique was devised for the quantitative scattering method described in more detail in section 4.3c. The collected scattered light was imaged onto the video microscope rather than focused into a detector. In later developments of this work a wedged beam splitter was used to allow simultaneous use of the video microscope and scatter signal detector as shown in figure 4.13 to compare sensitivities of the two methods. The imaged scattering centres with the video microscope at position B had a much greater intensity than the same scattering centres imaged from position A. This is because the angular distribution of scattered light from individual scattering centres of the order of
FIGURE 4.13

SCHEMATIC DIAGRAM OF THE VIDEO MICROSCOPE AND LASER PROBE BEAM GEOMETRY FOR LASER INDUCED THRESHOLD DAMAGE DETECTION
1 - 10 μm in diameter is predominantly in the forward direction. In most of the testing the long working distance microscope was at position A and the video microscope at position B.

The experimental procedure was to adjust the video microscope magnification so that an extensive damage mark approximately equal to the 1/e² beam shape just fitted onto the colour monitor. This was typically at a magnification of 100x. Threshold damage, as observed previously was in the form of several scattering centres each one being between 1 - 10 microns in diameter. This technique was found to be very sensitive and could readily detect the formation of micron sized damage pits. Threshold damage was usually identified by the large increase in the scatter intensity from a scattering centre visible prior to irradiation. However, this was not always the case, sometimes the damaged scattering centres were not visible prior to irradiation.

Interest in producing a semi-automated damage test procedure led to the design and building of a prototype video frame grabber and digitizer, (4.36). The aim was to digitize, transfer to an external computer and subtract two video frames (after irradiation - before irradiation) and reconstruct the video image to detect whether laser induced damage had occurred. The digitizer was built with the following features as design aims

1) Ability to frame grab and digitize a single video frame
2) Ability to have translatable x,y cursors on the display monitor and also to display on the monitor the analogue intensity modulation along the x and y cursors.
3) Ability to transfer the digitized video frame to an external computer for further processing via a GPIB interface

Memory chip limitations on the prototype meant that a translatable window approximately 100 mm square compared to a screen size of 270 mm x 170 mm was available for frame grabbing and digital storage. The translatable x,y
cursors with their analogue intensity modulation covered the full screen size and were found to be very useful in identifying whether the scattering intensity from localized scattering centres had changed as a result of irradiation. The video microscope operating at a magnification of 460X and the x, y cursors were used to measure scattering centre size and number density on several samples. The results were in good agreement with the time honoured method of looking down a microscope and are similar to scattering centre densities \((10 - 20 \text{ mm}^{-2})\) measured elsewhere on high quality dielectric coatings for use at 2.7 \(\mu\text{m}\), \((4.17)\). The scattering centres were all in the range 4 - 20 \(\mu\text{m}\) in diameter. The effect on the scattering centre density of cleaning the optical surface with ethanol and acetone was measured on an unused multi-layer 248 nm AR coating deposited on fused silica. The mean scattering centre density before cleaning was 35 \(\pm 14 \text{ mm}^{-2}\) and after cleaning 25 \(\pm 10 \text{ mm}^{-2}\). Time constraints meant that the computer interface was not well tested.

It has been reported that a substantial portion of the backscattered light from defects damaged at the threshold level is depolarized, \((4.4)\). This was investigated with a polarizing analyser and the video microscope in position B in figure 4.13. The damaged and undamaged areas of several AR and HR multi-layer dielectric coatings designed for use at 248 nm were investigated. Depolarization of the scattered helium neon probe beam was not observed for a wide range of damage types varying from small single scattering centres to severe damage.

An interesting phenomena was observed on three samples investigated in detail using the video microscope; these were a multi-layer AR coating at 248 nm (sample 12a) and two multi-layer HRs also at 248 nm (samples 22a and 23a). At or just below their single shot damage threshold a particulate cloud was ejected from the surface of the sample as a result of the incident laser pulse. At incident fluences well below the single shot damage...
threshold (less than 1/10) no particle emission was observed. Similarly at thresholds well above the single shot damage threshold no particulate cloud was observed. Some examples were observed where the observation of one or more scattering centres indicated threshold damage had occurred and a particulate cloud was also emitted. The incidences where a particulate cloud was ejected from the surface exactly coincided with the observation of a decrease in the over-all scattered signal as discussed in section 4.3c. The cloud does not appear to originate from one part of the surface. Multi-shot irradiation tests below the single shot damage threshold sometimes resulted in the disappearance of a scattering centre. The samples were cleaned initially by dragging an ethanol wetted lens tissue across the surface and then again with a acetone wetted lens tissue. These results suggest this cleaning process may not be sufficient to remove the very small particles attached to the surface which may be held in place by molecular forces. Alternatively, the particulate cloud could arise from UV photoablation of organic impurities held in the coating. Results of UV irradiation tests described in chapter 8 for one sample suggest the apparent improvement in the damage threshold is caused by a reduction in the defect density of damage sensitive defects. This would naturally arise if particulate ejection removed some of the defects which initiate threshold damage. This process of pre-conditioning thin film coatings by irradiating them at low fluences to improve the single shot damage threshold is well recognized although its origin appears not to have been investigated in any detail.

Photothermal deflection methods have been used to create absorption contour maps on 50 mm diameter HR excimer laser mirrors as described in section 4.2eiii. The main disadvantage of this high resolution, very sensitive non-destructive testing method is the enormous testing time for the 100 x 100 pixel array. Developing the method for larger area optics clearly requires a much faster process. It is suggested that one option is to use
a thermal imaging camera to view the localized 'hot spots' arising from transient absorption of the pulsed laser radiation. The video microscope described above using visible light could be replaced with a thermal imaging microscope and the appropriate infra-red optics. Thermal imaging cameras are available in the 2 - 5 μm range with extensive electronic processing facilities such as frame averaging and automatic production of false colour temperature maps. The main difficulty is that the laser pulse duration of 25 ns results in localized transient heating which may last above the ambient for only 10 - 100 microseconds depending on the materials involved. The options for capturing such a short lived thermal image appear to be:

1) Maintain the local 'hot spot' above ambient by using a high laser repetition rate and using frame averaging to enhance the image.
2) Use a high repetition rate laser to trigger a fast frame scan thermal camera.
3) Use a long image retention time thermal camera tube and a long laser pulse length.
4) Use an infra-red detector array triggered by a single laser pulse with a peak hold facility on each pixel.

The first option makes use of 10 - 100 KHz pulse repetition rates which are not routinely available from excimer lasers. These rates could be achieved by simulating the excimer pulse using a modulated, CW, frequency quadrupled, Nd:YAG laser to give a 266 nm output. The second option is limited by the maximum video frame scan rate; at present the maximum single line scan rate is 2.5 KHz from one commercial thermal camera manufacturer, (Agema). The third option has been implemented for imaging transient visible laser scatter from a 0.5 μs dye laser pulse using a long image retention Saticon tube video camera, (4.4). It is possible that a similar technique could be implemented using a thermal video camera and a long pulse length, frequency quadrupled
Nd:YAG laser. The final option is somewhat speculative and is equivalent to using a sensitive CCG array in the single shot mode.

4.3c Threshold damage detection by imaging laser scattering using a helium neon laser probe beam

Darkfield illumination was found to be a sensitive method of imaging scattering centres because of the high visual contrast between the scattering centre image and the adjacent dark background. The technique also satisfies most of the criteria discussed in section 4.3a. The aim of this work was to develop a sensitive method of detecting threshold damage which gave a quantitative measure of the scattering signal before and after irradiation.

The angular distribution of scattered light from \( N \) randomly distributed surface scattering centres can be approximated by \( N \) times the distribution from a single scattering centre, \( \langle 4.37 \rangle \). Threshold damage at excimer laser wavelengths typically involved the formation of between one and ten scattering sites within the illuminated beam area. It is therefore useful to consider the angular distribution from a single scattering centre. The angular distribution of scattered light from a single scattering centre can be simply calculated by assuming the scattering centre to be approximated by an opaque disc whose diameter is much greater than the wavelength of light. This is valid for scattering centres observed in threshold damage studies at 248 nm where the diameters involved are within the range 1 - 20 microns. In this case the angular intensity distribution \( I \), in the far field is given by, \( \langle 4.37 \rangle \).

\[
I = I_0 \left( \frac{2J_0(x\sin\theta)}{x\sin\theta} \right)^2
\]

Where \( I_0 \) is the normalized intensity in the centre of the diffraction pattern, \( J_0 \) is a Bessel function (1st kind) and \( \theta \) is the scattering angle. The particle size factor \( x \), is given by

-165-
where $a$ is the particle radius, $n$ the refractive index of the host material and $\lambda$ the laser wavelength. Examples of the angular distribution given by equation 4.5 are shown in figure 4.14 for the helium neon laser wavelength of 632.8 nm, a host refractive index of 1.5 and particle diameters of 10, 20 and 100 microns. It is clear from figure 4.14 that most of the scattered light is contained in a central lobe less than 5 degrees wide in the forward scatter direction. The scattering intensity for a 20 $\mu$m diameter particle is down to 1/1000 of its initial value for a scattering angle of 1.5 degrees. An attempt was made to measure the angular distribution of the scattered light from a single damage defect in AR and HR coatings using a helium neon laser and a PIN photodiode scanned over a scattering angle range of $\theta = \pm 0.6$ degrees. This proved unsuccessful and simply reproduced the helium neon laser beam profile. This was probably because of the limited sensitivity of the PIN photodiode of 0.4 a/w compared to a typical avalanche photodiode sensitivity of 50 a/w and a photomultiplier sensitivity of 5000 a/w. The photomultiplier is therefore a factor of 12500 more sensitive than the PIN photodiode. Phase locking methods would also enhance the sensitivity.

The darkfield imaging arrangement devised to collect the on-axis scattered light is shown in figure 4.15. It's implementation for threshold damage detection is shown in figure 4.13 with the axis of the helium neon laser 20 degrees off the axis of the excimer laser. The front surface of the test sample was imaged onto the detector by the collection lens, the centre of which had a small circular beam stop attached to prevent transmission of the undeviated beam. The vertically polarized 5 mW helium neon laser had a $1/e^2$ diameter of 1.2 mm and was beam expanded to 3.6 mm using a x3 telescope. This diameter then matched the larger dimension of the rectangular profile of the excimer beam (3.4 mm x 0.5 mm) at the front surface of the test sample. A variable beam attenuator.
scattering intensity, $I$

\[ \text{particle diameter 100\,\mu m} \]

\[ \text{particle diameter 20\,\mu m} \]

\[ \text{particle diameter 10\,\mu m} \]

\[ \text{scattering angle} \theta / ^\circ \]

FIGURE 4.14
ANGULAR DISTRIBUTION OF SCATTERED LIGHT AT 632.8\,nm
FOR DIFFERENT Sized OPAQUE DISCS REPRESENTING ABSORBING DEFECTS
FIGURE 4.15
SCHEMATIC DIAGRAM OF THE HELIUM NEON LASER PROBE BEAM ARRANGEMENT FOR QUANTITATIVE MEASUREMENTS OF THE SCATTERED LIGHT FROM THE FRONT SURFACE OF A TEST SAMPLE
was used to prevent saturation of the detector or video camera. The helium neon beam was chopped using a mechanical chopper to enable phase locked detection. In this situation the scattered signal levels were sufficiently large that the detector output was connected directly to a digital oscilloscope (Gould Biomation 8000). The oscilloscope was externally triggered by the chopper synchronization pulse. Extensive signal processing was available within the oscilloscope including averaging, subtraction and cursor measurements. A helium neon laser narrow band optical filter was mounted in front of the detector to prevent background light producing added noise, the polarizer and analyser allowed depolarization studies. The detector was an RCA C30808 PIN photodiode with a 2.5 mm diameter active area and a 741 operational amplifier with a voltage gain of 20. The collection lens was a 50 mm diameter f2 lens used to demagnify the 3.4 mm object length by a factor of 0.7 to fit it on the detector active area. The small size of the active area of the detector meant that it acted as its own field stop and rejected scattered light originating from the back surface of the sample when used in the off-axis configuration as shown in figure 4.13. The distance from the front face of the test sample to the collection lens was about 24 cm giving a maximum collection angle of ±6 degrees from the centre line.

The optimum beam stop size was chosen by measuring the detector output from a damaged area (a single scattering centre) and a non-damaged area with various beam stop sizes using a previously tested sample, (an AR coating, sample 21a). The detector output as a function of the blocking angle is shown in figure 4.16. The diameter of the beam stop needs to be greater than the $1/e^2$ diameter of the helium neon beam at the collection lens which was about 3.6 mm. This corresponds to a blocking angle of ±0.43 degrees. A suitable blocking angle was ±0.78 degrees which was equivalent to a stop diameter of 6.5 mm. This gave a total collection solid angle of 0.134 steradians. The helium neon probe beam
FIGURE 4.16
SCATTERING SIGNAL AS A FUNCTION OF BLOCKING ANGLE FROM A LASER THRESHOLD DAMAGED AREA, (SINGLE DEFECT) AND NON-DAMAGED AREA OF A THIN FILM MULTILAYER
intensity at the edge of the beam stop has fallen by a factor of 679 times and the ratio of the detector output from the damaged area to the non-damaged area is about a factor of 10. The convergence of the scatter signal from the damaged area towards the value from the non-damaged area at scattering angles beyond about 2.5 degrees suggests the angular distribution of the scattered light from single scattering centres is indeed limited to a narrow cone in the forward direction. Furthermore, comparison with figure 4.14 suggests that the equivalent scattering centre particle diameter is much less than 10 microns.

An automated laser damage test system for use in the infra-red has been developed independently at the Naval Weapons Centre based on scattering of a helium neon laser probe beam, (4.38). Their system shows some similarities to the work described here. They use a small mirror mounted on the collection lens to reflect the undeviated beam. Their system operates in reflection (presumably because metallic mirrors are involved), uses a lock-in amplifier for signal analysis and is configured with a small probe beam diameter of 70 μm. Sensitivities to scatter changes of $10^{-6}$ per steradian are claimed, (4.1). The sensitivity to detect scatter changes in the system shown in figure 4.13 is about $10^{-4}$ per steradian. The difference in sensitivity probably arises from the way in which the signals were processed. The use of a lock-in amplifier typically gives an improved signal to noise ratio of about 100x.

The comparison of before and after irradiation scattering signals was done by defining a scatter ratio, $R$ given by

$$R = \frac{\text{scatter signal after irradiation}}{\text{scatter signal before irradiation}}$$

If as a result of irradiation no change is observed then $R = 1$. The variation of the scatter signal amplitude before irradiation over the test samples surface gave an
indication of its cleanliness and defect density. Variations between samples with nominally the same coating gave an indication of the quality control.

Depolarization studies of the scattered light were done by calculating the ratio $R$ with the polarizing analyser crossed and uncrossed on a 248 nm multi-layer dielectric AR coating deposited on a fused silica substrate, (sample 21a). The measurements were done at several fluences resulting in varying degrees of damage from the formation of individual scattering centres to severe damage resulting in a 1 x 0.25 mm beam footprint on the sample. In all cases the ratio $R$ was 1 with the analyser crossed, the amplitude of the scattered signal being the same whether the test site was damaged or not. When the analyser was uncrossed the ratio $R$ varied from 4 to 8 depending upon the severity and type of damage. These results show that no depolarization of the scattered helium neon probe beam was observed and therefore depolarization cannot be used to identify threshold damage. This result was also confirmed using the video microscope.

Four samples have been studied in detail, a summary is given in table 4.2. All four samples, 3 HRs and one AR had fused silica substrates and were designed for 0 degrees incidence. Three of the coating designs were for use at the KrF wavelength of 248 nm and one as a HR at the ArF wavelength of 193nm. The experimentally measured AR coating reflectance of sample 12a is higher than the design value of about 0.5% per surface.

The mean background scatter signals measured over about 60 test sites on each sample prior to testing were: 220 ±190 mV for sample 12a, 210 ±100 mV for sample 22a, 1950 ±780 mV for sample 23a and 105 ±30 mV for sample 24a. The scatter signal distributions for three samples 12a, 22a and 24a are shown in figure 4.17. The distribution for sample 12a appears to be multi-peaked producing a larger standard deviation. The multi-peaked distribution probably arose from the localized regions of film crazing at the substrate/film interface observed in this sample.
TABLE 4.2

Details of test samples for scatter measurements

The scattering level from sample 23a was about a factor of ten higher than the other samples listed, a high density of scattering centres were also easily visible with the unaided eye.

The scatter ratio R is plotted as a function of the incident fluence in figures 4.18 and 4.19 for those samples listed in table 4.2. The results shown in figure 4.18 for samples 12a, 22a and 23a follow an approximate linear trend for \( R > 1.0 \) when plotted on a logarithmic scale. The \( 1/e^2 \) excimer beam area at the test sample's surface was 0.667 mm\(^2\) for these tests. The measured scattering centre densities for these samples prior to testing was 25 - 35 mm\(^{-2}\) corresponding to illuminating 16 - 24 scattering centres within the excimer beam. The range in the scatter ratio for each sample at a given fluence where \( R > 1.0 \) represents the variability of the coating over the surface rather than illuminating two scattering centres instead of one as may be the case for very small beam sizes. Wide pre-damage scatter signal distributions appear to result in a wide spread in the scatter ratio, (for \( R > 1.0 \)). This is evident by comparing figure 4.17 with figures 4.18 and 4.19. In the case of sample 12a an AR coating, the data suggests at least in one area that laser induced damage occurred around 4.8 J cm\(^{-2}\).
FIGURE 4.17
SCATTERING SIGNAL DISTRIBUTIONS MEASURED ON THREE MULTI-LAYER DIELECTRIC SAMPLES PRIOR TO LASER DAMAGE TESTING
FIGURE 4.18
SCATTER RATIO $R$ VERSUS INCIDENT FLUENCE FOR THREE
MULTILAYER DIELECTRIC SAMPLES (1 AR AND 2 HR'S)
TESTED AT 248 nm
SCATTER RATIO VERSUS INCIDENT FLUENCE FOR A MULTILAYER DIELECTRIC HR MIRROR AT 193 nm
The definition of the damage threshold can depend on how threshold damage is identified to have occurred. A convenient method using these scattering results is to extrapolate the linear portion back to the fluence at which the scatter ratio just equals 1.0. This method has the advantage of using all of the data and overcomes the ambiguity which may arise in identifying threshold type damage. The alternative is to define the criteria for laser threshold damage to have occurred and then use this criteria to measure the damage probability at various fluences. The most suitable definition of the occurrence of laser threshold damage was for the scatter ratio, R to be greater than one. The damage probability plotted against the incident fluence for sample 22a is shown in figure 4.20. The damage probability was calculated using about 10 test shots at each fluence. The steepness of the transition from zero damage probability to 100% damage probability is due to the large excimer beam area relative to the mean defect spacing.

The three laser damage thresholds defined as the extrapolated fluence for which R = 1, the fluence for which the damage probability is 0% and the fluence for which the damage probability is 100% are compared in table 4.3 for the four samples

<table>
<thead>
<tr>
<th>SAMPLE NO.</th>
<th>EXTRAP. FLUENCE FOR R = 1.0 Jcm⁻²</th>
<th>FLUENCE FOR 0% DAM. PR. Jcm⁻²</th>
<th>FLUENCE FOR 100% DAM. PR Jcm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>12a</td>
<td>1.6</td>
<td>0.65</td>
<td>3.0</td>
</tr>
<tr>
<td>22a</td>
<td>0.77</td>
<td>0.6</td>
<td>0.93</td>
</tr>
<tr>
<td>23a</td>
<td>3.65</td>
<td>1.64</td>
<td>4.67</td>
</tr>
<tr>
<td>24a</td>
<td>0.04</td>
<td>-</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Table 4.3
Damage threshold measurements using laser scattering
Damage  probability

FIGURE 4.20
DAMAGE PROBABILITY OF A HR MULTILAYER DIELECTRIC MIRROR TESTED AT 248 nm
The lowest threshold for all of these data is that for the 0% damage probability except for sample 24a where the threshold was too low to experimentally measure accurately. The 0% damage probability fluence is the most conservative measure of the damage threshold and most importantly is independent of the damage beam spot size. All of the results show that the fluence at $R = 1.0$ corresponds to a value somewhere between the fluences for the 0% and 100% damage probabilities. The 100% damage probability fluence for the three HRs is equivalent to a scatter ratio of 1.5 and for the single AR coating 3.0. The three HR mirrors were made at different times, from different materials, have widely differing thresholds and were designed for different excimer wavelengths, (193 nm and 248 nm). The consistency of the scatter ratio of 1.5 being equivalent to the 100% damage probability may be a useful aid to the future automation of damage threshold measurements for all HR mirrors at excimer wavelengths.

Perhaps the most interesting aspect of the results shown in figure 4.18 is the observation that for all three samples the scatter ratio $R$ can be less than one. Comparison of the scatter signal after irradiation with the simultaneous video microscope recordings has shown the decrease in the scatter signal after irradiation to be caused by the ejection of a particulate cloud moving away from the surface. The cloud of particles does not appear to originate from one point on the surface. The reduction in the number of scattering centres within the excimer beam area reduced the scattering signal making $R < 1.0$. The minimum scatter ratio varied between the different samples. For sample 22a the minimum scatter ratio was 0.27 whereas the minimum for sample 12a was about 0.45 and for sample 23a 0.91. The reduction in the scatter signal after irradiation was usually observed to occur just below the damage threshold. The incident fluence range for which the scatter ratio is less than one is very narrow for sample 22a. Below a fluence of 0.4 Jcm$^{-2}$ the scatter ratio is constant at 1.0, between 0.4 - 0.75 Jcm$^{-2}$ the scatter ratio is less than one and above 0.75 Jcm$^{-2}$ the
scatter ratio is greater than one. Examples were also observed with all three samples using the video microscope where particulate ejection and threshold damage occurred together but the scatter ratio was still below one.

The various permutations can be explained with a simple model. Consider a total of N identical scattering centres randomly distributed over the incident beam area on the surface of the sample with identical scattering cross-sections $\sigma_1$ and illuminated by a constant helium neon laser intensity $I$. This situation is approximately correct in the central area of the helium neon probe beam. The scatter signal $S_1$, before irradiation is given by

$$S_1 = k(N\sigma_1 I)$$  \hspace{1cm} (4.8)

where $k$ is the proportionality constant. After irradiation a fraction $\alpha$ of the initial $N$ illuminated scattering centres have been ejected from the surface. The number remaining is $N(1 - \alpha)$ and of these a fraction $\beta$ are damaged each of which have scattering cross-sections $\sigma_2$. The scatter signal $S_2$ after irradiation is therefore given by

$$S_2 = kN(1 - \alpha)I((1 - \beta)\sigma_1 + \beta\sigma_2)$$  \hspace{1cm} (4.9)

The scatter ratio $R$, is therefore given by the ratio $S_2/S_1$

$$R = (1 - \alpha)(\beta(\sigma_2/\sigma_1 - 1) + 1)$$  \hspace{1cm} (4.10)

If $\beta = 0$ then no threshold damage occurs and the scatter ratio $R$ is controlled by the fraction of scattering particles ejected from the surface. At low incident fluences, say 1/10 of the damage threshold no particles are ejected, $\alpha = 0$ and $R = 1.0$. As the fluence increases with $\beta$ remaining zero, more particles are ejected, $\alpha$ increases and therefore the scatter ratio gets smaller. This is the case for sample 22a from 0.4 - 0.75 Jcm$^{-2}$. At
some fluence, threshold damage occurs as well as particle ejection. The scatter ratio increases, the rate depending on $\beta$ and $\sigma_2$. At higher incident fluences where $\sigma_2 > \sigma_1$ the scatter ratio is greater than 1.0.

The shape of the graphs in figure 4.18 can be explained using this simple model. However, the model makes no attempt to explain the origin of the emitted particulate cloud or the ejection mechanism. Studies at the ArF excimer wavelength of 193 nm suggest ablation of organic materials with no melting can occur when the laser photon energy is sufficient to directly break bonds, this process of absorption and dissociation has been called ablative photodecomposition, (4.39). It is possible that the emitted particulate cloud consists of organics and other impurity particles which are ablated from the surface as a result of this dissociation process. It would also explain why the surrounding film area appears to suffer little or no disruption. Results described in chapter 8 suggest that apparent improvements in the damage threshold can arise by irradiating the surface at fluences just below the single shot damage threshold. This effect is shown to be caused by a reduction in the surface density of the most damage sensitive defects, (at least for one sample). The results discussed in this chapter suggest that this reduction in the defect density can arise by the ejection of a particulate cloud. The origin, composition and variability between samples relating to the particulate cloud needs further investigation.

The formation of threshold damage with a scatter ratio less than one can add ambiguity to the determination of the damage threshold using the extrapolation approach or the probability approach. This ambiguity could be removed by defining threshold damage to occur when any change in the scatter signal is measured. However, no experimental evidence suggested that the particulate emission resulted in subsequent threshold damage formation after multi-shot tests at the same fluence.

The results in figure 4.19 for sample 24a show a plateau region for the scatter signal between 0.2 and 0.65
Above about 0.65 Jcm\(^{-2}\) there appears to be a slope change which coincided with the observation of damage to the fused silica substrate. Within the plateau region the incident fluence was sufficient to remove the dielectric coating but insufficient to damage the fused silica substrate in a single shot. The rather low damage thresholds for the dielectric film and substrate are probably due to absorption arising from the proximity to the absorption edge of silicon dioxide and aluminium oxide at 193 nm.

Cumulative tests have also been done at 193 nm on sample 24a to monitor the scatter signal as a function of laser shot number for different incident fluences. Initial N on 1 tests at the same site showed a scatter ratio of 1 for 250 shots at a fluence of 0.03 Jcm\(^{-2}\). After 50 shots at 0.065 Jcm\(^{-2}\) the scatter ratio was observed to decrease by 5% coinciding with particle emission from the surface. The results for measurements at three different test sites are shown in figure 4.21. At 0.11 Jcm\(^{-2}\) the scatter ratio quickly saturates at 5 in four shots. At 0.14 Jcm\(^{-2}\) the scatter ratio rises rapidly to 13 in four shots, thereafter decreasing as the damage process ablates film material exposing but not damaging an area of the substrate larger than the probe beam area. At 0.22 Jcm\(^{-2}\) the scatter ratio shows a local maximum of 18 after four shots then decreases as the substrate is exposed and finally increases due to substrate damage. Above 20 shots at this highest fluence, a strong surface plasma was observed, the saturation after 40 shots could be due to the plasma or the severe substrate damage having an area larger than the probe beam.
FIGURE 4.21
SCATTER RATIO AS A FUNCTION OF SHOT NUMBER
FOR MULTISHOT TESTS ON A HR COATING AT 193nm

sample 24a
HRat193nm
Al₂O₃/SiO₂

scatter ratio/R

C = 0.22 J/cm²
B = 0.14 J/cm²
A = 0.11 J/cm²

ArF shot number

20 40 60 80 100
4.3d Threshold damage detection at 193 nm and 248 nm using PZT transducers

Photoacoustic detection methods and the use of PZT transducers to determine laser induced damage thresholds at infra-red wavelengths have been described in section 4.2f. In this work, the sensitivity of two different PZT transducers to detect threshold damage at the excimer wavelengths of 193 nm and 248 nm was investigated. The basic geometry for the measurements is shown in figure 4.22. The PZT transducer was bonded to the back surface of the test sample using a thin layer of silicone grease as the acoustic couplant between the metal and glass surface. The transducer was held in place with a constant force using a small clamp. Two PZT transducers were used, a small high frequency laboratory built resonant transducer and a commercial transducer manufactured by Dunegan and Endevco, model number D9201A-0091. The transducer output was connected to a Dunegan & Endevco acoustic emission pre-amplifier, model number 1801-450-B and subsequently displayed on a Gould Biomation digital oscilloscope. The electromagnetic noise from the laser discharge was found to be a convenient trigger source for the oscilloscope for these acoustic waveform measurements. The details of the construction of the laboratory built device have been given elsewhere, (4.21), its schematic construction is shown in figure 4.22. The disc shaped piezoelectric material, PZT-5A was 6 mm in diameter and 1 mm thick with a large brass backing plate. No details of the construction of the commercial transducer were available except that the PZT disc had a diameter of 16 mm.

Most of the measurements were done off-epicentre. The intrinsic frequency response of a piezoelectric transducer to bulk waves can be estimated by requiring phase coherence of the propagating bulk wave over the aperture area of the piezoelectric element. This is expressed geometrically in figure 4.23, where the test sample thickness is d and the piezoelectric element has a diameter 2a and is displaced by a height h from the axis.
FIGURE 4.22
EXPERIMENTAL ARRANGEMENT FOR THE DETECTION OF
LASER INDUCED DAMAGE USING PZT TRANSDUCERS
FIGURE 4.23
GEOMETRY FOR CALCULATING THE FREQUENCY RESPONSE OF PZT TRANSDUCERS FOR OFF-EPICENTRE MEASUREMENTS
of the excimer beam. Phase coherence requires that the difference in the wave propagation distances \( Z_1 - Z_2 \), from the source to the bottom and top of the piezoelectric disc is less than half the acoustic wavelength for a displacement \( h > 0 \).

This can be expressed as

\[
\lambda > 2 \left[ (h + 2a)^2 + d^2 \right]^{1/2} - \left[ (h^2 + d^2) \right]^{1/2}
\]

4.11

If the PZT disc is on the axis of the excimer beam \( (h = -a) \) equation 4.11 is invalid and the phase coherence requirement is modified slightly to give

\[
\lambda > 2 \left[ (a^2 + d^2) \right]^{1/2} - d
\]

4.12

The frequency response calculated using equations 4.11 and 4.12 assuming a sound speed of 5970 ms\(^{-1}\), (4.21) for bulk longitudinal waves in fused silica is shown in figure 4.24 for the two piezoelectric transducers used in this work, \( (a = 3.0 \text{ mm or } a = 8.0 \text{ mm}) \) and a test sample thickness of 10 mm. The frequency response is plotted against the angle subtended by the centre of the piezoelectric disc relative to the excimer beam axis, \( \theta = \tan^{-1}(h + a)/d \).

These calculations suggest that the laboratory built device with the smaller piezoelectric crystal diameter of 6 mm has a much higher frequency response on-axis, (about a factor 7) than the commercial device manufactured by Dunegon and Endevco. At large angles, well off epicentre the response curves approach their asymptotic values of 0.5 MHz for \( a = 3 \text{ mm} \) and 0.19 MHz for \( a = 8 \text{ mm} \). The asymptotic values arise when the displacement \( h \approx d \) and equation 4.11 simplifies to the phase coherence requirement for surface waves, i.e. \( \lambda > 4a \).

In practice the frequency response of PZT transducers is complicated by reflections and resonances. Often, resonances of the PZT material itself occur in the form of a thickness or radial resonance. The frequency response on epicentre of the two PZT transducers to bulk
FREQUENCY RESPONSE OF PIEZOELECTRIC DISCS AS A FUNCTION OF OFF-EPICENTRE ANGLE

PIEZOELECTRIC DISC

TEST SAMPLE

EXCIMER BEAM AXIS

PZT DISC DIA = 6mm

PZT DISC DIA = 16mm

FIGURE 4.24
longitudinal waves is shown in figure 4.25. These measurements were made using a narrow pulsed ultrasonic source on the opposite face of the test sample and using a discrete Fourier transform to calculate the power spectrum from the captured time series originating from the transducer. This work on transducer calibration at Loughborough is described in much more detail in reference 4.39. The most obvious feature is the highly resonant nature of both transducers and that the laboratory built device has a much higher frequency response. The frequency response of the laboratory built device shows some sensitivity out to 6 MHz whereas the commercial device is limited to frequencies below 1 MHz in agreement with figure 4.24. The commercial transducer is about a factor of 100x more sensitive in the frequency range 0.2 - 0.8 MHz.

The captured time domain waveforms and their resulting spectra from laser impacts at 193 nm on a multilayer HR dielectric mirror, (sample 24a) and a 248 nm impact on a polished aluminium sample are shown in figure 4.26. The 193 nm laser impact was measured using the Dunegan & Endevco transducer and the 248 nm impact measured using the laboratory built transducer. In both cases the transducer was mounted on the back surface of the test sample. A high incident fluence was used to generate a strong surface plasma and excite all of the resonant modes of vibration of the transducer. It is clear for the case of the 248 nm laser impact on aluminium, the laboratory built transducer contains identical peaks to those shown in the calibration spectrum, figure 4.25. The calibration spectrum for the Dunegan & Endevco transducer in figure 4.25 contains few frequencies above 1 MHz, the dominant peak being at 0.635 MHz. The power spectrum measured using the 193 nm laser impact also has a dominant peak in this region. The piezoelectric thickness resonant frequency is given by \( \frac{C}{2L} \) where \( C \) is the longitudinal sound speed in the piezoelectric material, \( C = 3484 \text{ ms}^{-1} \) for PZT-5A, \( (4.21) \) and \( L \) is the piezoelectric crystal thickness. The
FIGURE 4.25

POWER SPECTRA OF TWO PZT TRANSDUCERS FOR LONGITUDINAL BULK WAVES
248 nm LASER IMPACT ON POLISHED ALUMINIUM (LAB. BUILT TRANSDUCER)

193 nm LASER IMPACT ON DIELECTRIC HR MIRROR (DUNEGAN + ENDEVCO TRANSDUCER)

FIGURE 4.26

TRANSUDER WAVE FORMS AND THEIR POWER SPECTRA FOR EXCIMER LASER IMPACTS ON SURFACES
dominant peak at \(1.807\ \text{MHz}\) in figure 4.25 corresponds to a sound speed of \(3614\ \text{ms}^{-1}\) using a thickness \(L = 1\ \text{mm}\). This value is within 4% of the literature value quoted above. This sound speed and the dominant resonance at \(0.635\ \text{MHz}\) for the Dunegan & Endevco transducer gives an estimated thickness of \(2.85\ \text{mm}\).

The ambiguity of analysing transducer waveforms which contain many resonant frequencies was avoided by capturing the initial bulk waveform arrival. The amplitude and time history of the transducer forcing function were captured before the transducer had time to resonate. In solids, with the transducer mounted on the back surface of the sample this corresponded to the arrival of a longitudinal wave since the shear wave velocity is approximately half the longitudinal wave velocity. To check the method, experiments were done with the Dunegan & Endevco transducer to measure the propagation time, \(T\), from the acoustic source to the transducer for differing propagation distances, \(l\). This was done by varying the off epi-centre distance \(h\) shown in figure 4.23 at an excimer beam fluence of \(0.13\ \text{Jcm}^{-2}\). This level was just sufficient to guarantee laser induced damage with each shot at \(193\ \text{nm}\) on the HR dielectric mirror. The results are shown in figure 4.27, the total propagation time from the source to the transducer is given by

\[
T = \frac{1}{C} + \tau
\]

where \(C\) is the sound speed in the test sample and \(\tau\) is the propagation time through the transducer to the piezoelectric material. Analysis of the data in figure 4.27 gives a sound speed in fused silica of \(5900 \pm 300\ \text{ms}^{-1}\) compared to the literature value of \(5970\ \text{ms}^{-1}\), (4.21). The intercept gives a propagation time through the transducer outer casing of about \(0.23\ \mu\text{s}\) corresponding to a thickness of \(1.4\ \text{mm}\) for steel. A typical transducer waveform is also shown in figure 4.27 including the electromagnetic pick-up from the laser discharge which lasts about \(2.2\ \mu\text{s}\).
FIGURE 4.27

BULK WAVE PROPAGATION TIME AS A FUNCTION OF SOURCE—TRANSDUCER DISTANCE
Initial laser damage threshold testing was done off-epicentre using the laboratory built transducer. The peak-peak acoustic signal amplitude plotted as a function of the incident fluence at 248 nm is shown in figure 4.28 for a three layer dielectric AR coating deposited on a fused silica substrate, (sample 21a). These measurements were done at the same test site, increasing the fluence after each shot. It is tempting to conclude that the N on1 damage threshold is about 4.5 Jcm$^{-2}$ corresponding to the change in slope, however the video microscope system monitored threshold damage at 0.35 Jcm$^{-2}$ and a small plasma was observed at 3.0 Jcm$^{-2}$. The large slope change at 4.5 Jcm$^{-2}$ corresponded to the observation of an intense plasma and the formation of a large damage footprint following the beam area. It is clear that this laboratory built transducer was not suitable for the detection of laser induced threshold damage at 248 nm in dielectric coatings even though it has been used for threshold damage detection at CO$_2$ laser wavelengths (4.21). The captured waveform at 5.0 Jcm$^{-2}$ is also shown in figure 4.28 and is similar to that observed in the plasma regime for the 193 nm dielectric HR sample shown in figure 4.27. Above 4.5 Jcm$^{-2}$ in the strong plasma regime the acoustic signal increases linearly with fluence. A similar initial linear increase with subsequent saturation as a function of shot number was been observed in measurements on a polished aluminium sample irradiated at 248 nm as shown in figure 4.29. A linear increase in the acoustic signal from the aluminium sample was also observed as the incident fluence was increased in the strong plasma region. This initial linear increase and subsequent saturation in the strong plasma region has been observed at other laser wavelengths (4.28, 4.29) and is described in section 4.2f. However, it is in disagreement with the infra-red damage threshold measurements made by Roscenwaig at 1.06 µm, (4.30) and Mahmood at 10.6 µm, (4.21). They observed an acoustic signal amplitude, A, to have a power law dependence on the
PK-PK ACOUSTIC SIGNAL / mV

STRONG PLASMA REGION

PK-PK ACOUSTIC SIGNAL AT 5 J cm⁻²

THRESHOLD DAMAGE OBSERVED WITH VIDEO MICROSCOPE

SMALL PLASMA OBSERVED

FIGURE 4.28

N ON 1 ACOUSTIC SIGNAL AMPLITUDE AS A FUNCTION OF THE INCIDENT FLUENCE AT 248 nm FOR A 3 LAYER DIELECTRIC AR COATING
FIGURE 4.29
PK - PK ACOUSTIC SIGNAL VERSUS SHOT Nº
FOR ALUMINIUM SAMPLE IRRADIATED AT 248 nm
incident fluence, \( F \), above the damage threshold given by

\[
A = F^n
\]

4.14

An example is shown in figure 4.12 where \( n = 1.8 \).

Generally it was observed that \( n > 2 \) for dielectric samples at 10.6 \( \mu \)m. Their analysis involved log-linear plots to calculate \( n \).

As described in section 4.2f, in the strong plasma regime the normal force duration required to model the measured surface displacement is several microseconds, this implies the plasma continues to ablate surface material well after the end of the laser pulse. It is therefore reasonable to expect that the time duration for which the surface plasma ablates material is linearly related to the laser energy. The saturation in the acoustic signal has been attributed to the formation of a Laser Supported Detonation (LSD) wave which shields the surface, whereas at lower intensities a Laser Supported Combustion (LSC) wave couples the laser energy into the plasma. This explanation may be valid at infra-red wavelengths where pulse truncation is used as evidence of the formation of an LSC wave, however no such pulse truncation has been observed in this work even at the highest incident fluences where intense plasmas were formed. This is because a much higher electron plasma density is needed to generate a plasma which absorbs at excimer wavelengths compared to infra-red wavelengths.

The Dunegan & Endevco transducer was used off-epicentre to measure the peak-peak acoustic signal amplitude as a function of the incident fluence at 193 nm on a HR multi-layer dielectric mirror, (sample 24a). Measurements on the epicentre were avoided because the acoustic pulse arrival could be hidden in the laser discharge noise and a thermoelastic signal would be generated from excimer laser absorption in the silicone grease on the back surface. The results are shown in figure 4.30 with two identifiable slope changes at 0.12 Jcm\(^{-2}\) and about 0.6 Jcm\(^{-2}\). These fluences
FIGURE 4.30

PK-PK ACOUSTIC SIGNAL FROM TRANSUDER / mv

1 ON 1 ACOUSTIC SIGNAL AMPLITUDE AS A FUNCTION OF THE INCIDENT FLUENCE AT 193nm ON A H.R DIELECTRIC SAMPLE
corresponded to the observation with the video microscope of threshold damage in the thin film coating and damage to the fused silica substrate respectively. Below 0.12 \text{ Jcm}^{-2} the signal amplitude was less than 3 mV, too small to be measured accurately, this region was considered to be the thermoelastic region. Between 0.12 and 0.6 \text{ Jcm}^{-2} increasingly larger areas of the dielectric coating were ablated resulting in a linear increase in the acoustic signal amplitude. In this ablation region no plasma emission was observed except at the rogue point at 0.35 \text{ Jcm}^{-2}. As described in section 4.2f, plasma formation is an efficient generator of longitudinal waves which explains why the acoustic amplitude of the rogue point is so high. The shape of the waveform for the arrival of the bulk acoustic waves in the thermoelastic and plasma regions was very similar, closely resembling those shown in figures 4.27 and 4.28. The success of the Dunegan & Endevco transducer for damage detection compared to the laboratory built device was probably due to its higher sensitivity at frequencies below 0.8 MHz.

In general, several mechanisms may contribute to the acoustic generation efficiency as the incident fluence is increased. If these mechanisms are contiguous then several slope changes of the form shown in figure 4.30 may be expected to occur. In increasing order of longitudinal wave acoustic generation efficiency these mechanisms include; increases of absorption in the thermoelastic region (threshold damage), shock wave formation, vaporization, ablation and plasma formation. An example of some previous work at 10.6 \mu m, (reproduced in figure 4.12), re-plotted with linear scales is shown in figure 4.31. In this example it is clear a second threshold exists at about 45 \text{ Jcm}^{-2}. When this data is plotted on a log linear scale the second threshold masquerades as a non-linear increase of the form given by equation 4.14 with \( n = 1.8 \). If several of these mechanisms occur simultaneously then a super-linear increase of the form given by equation 4.14 may be expected. An example of this latter effect is also shown in figure 4.31 where the
ACOUSTIC SIGNAL AMPLITUDE PK-PK / mV
10.6 μm / 1.06 μm

(Data taken from references (4.21 and 4.30)

Figure 4.31
ACOUSTIC SIGNAL VERSUS FLUENCE FOR DATA TAKEN AT 10.6 μm AND 1.06 μm
data are reproduced from reference 4.30, and arises from damage testing at 1.06 μm on a multi-layer dielectric mirror.

4.3e Surface impurity measurements using a laser induced mass analyser instrument

Charged particle emission arising from pulsed laser irradiation of surfaces has been widely used to investigate thermionic emission at low laser intensities and the analysis of ionic fragments at higher laser intensities, (see section 4.2g). As the incident intensity is increased the initial ionic species tend to originate from atomic and molecular surface impurities with little surface disruption observed. These impurities may well explain the origin of the particulate cloud emitted from the surface just below the single shot damage threshold. At higher laser intensities the surface vaporizes and substrate atoms and ions dominate the blow-off material.

The Laser Induced Mass Analyser, (LIMA), instrument is a commercially available surface analysis device which makes use of a pulsed, frequency quadrupled Nd YAG laser operating at 266 nm to ionize a local region of a surface which is subsequently analysed by a time of flight mass spectrometer. The instrument uses a video camera to view the specimen which is under high vacuum and a helium neon laser alignment beam to indicate the target location for the Nd YAG laser. A high spatial resolution is possible with a beam diameter of 3 μm at the surface of the specimen. The aim of this work was to identify the chemical constituents of scattering centres visible on the surface of thin film dielectric coatings. Scattering centres are often the locations for laser induced threshold damage and their chemical identification may indicate their origin, how their presence can be avoided and therefore how higher damage thresholds may be achieved.

A 248 nm multi-layer dielectric mirror (Sc₂O₃ and MgF₂), manufactured by OCLI Inc was used for this
preliminary investigation. The coating was deposited on a fused silica substrate and had a single shot damage threshold at 248 nm of 7.9 Jcm$^{-2}$. Some scattering centres were visible on the video monitor and were further identified by observing the change in the scattered helium neon target beam as it was scanned across the specimen's surface. The scattering centres had diameters in the range 5 - 30 microns. Unfortunately the photodiode which monitored the 266 nm laser energy was not calibrated and so only relative energy measurements were taken. The spectrum shown in figure 4.32 was produced with a single laser pulse at a relative laser energy of 5.5. The large Hydrogen peak and the very small carbon peak suggests that water rather than hydrocarbons was the dominant impurity at this location. Apart from hydrogen, the spectrum contains ionized species of scandium, oxygen, magnesium and fluorine arising from the coating material. No silicon is present indicating the laser damage process has not penetrated the multi-layer coating through to the substrate. A more complicated spectrum is shown in figure 4.33 which was measured from a low scatter area at a relative energy of 3.1. In this case 19 shots were required before an ionization signal was observed, ionic sodium, calcium and potassium appears to be present as well as higher mass fragments. The observation of approximately equal amounts of Na and K is often attributed to human contamination, (4.41).

A total of 16 test areas were measured on the mirror and a general observation was that several shots were required in the threshold region before any ion current was observed. Subsequent further shots often resulted in a decrease in the total ion current before an increase was observed. The spectrum from the initial ionizing pulse contained ionic molecular fragments rather than ionized atoms. This can be explained by assuming surface impurities such as organics ionize at the lowest laser intensity and are removed with further irradiation at this level. At higher laser intensities the ionized molecular fragments are broken up into individual ions. There was
FIGURE 4.32
IONISED SURFACE FRAGMENTS FROM A Sc\textsubscript{2}O\textsubscript{3}/H\textsubscript{g}F\textsubscript{2} HR MIRROR
IRRADIATED AT 266nm FROM A L.I.M.A. INSTRUMENT
(single shot relative energy = 5.5)
FIGURE 4.33
IONISED SURFACE FRAGMENTS FROM A Sc$_4$O$_9$/MgF$_2$ HR MIRROR
IRRADIATED AT 266nm FROM A LIMA INSTRUMENT
(19 shots, low scatter area, relative energy = 3.1)
no obvious trend in the impurities from scattering centres in this limited sample of sixteen test sites. In two cases however, a 5 µm and a 30 µm scattering centre were identified to contain iron, chromium and manganese. This suggests they were small stainless steel particles! The origin of these metallic particles is uncertain but they must influence the damage threshold on a local basis.

Metallic impurities of Fe, Mo and Ti in an Al₂O₃/Na₃AlF₆ HR reflector at 248 nm have also been observed using the LIMA instrument, (4.41). These impurities were attributed to previous coating runs, (TiO₂) and a metallic boat used for heating the evaporant.

The observation of a cleaning process using multi-shot laser irradiation at the ion emission threshold in GaAs is described in section 4.2g. In similar work using an 8 ns Nd:YAG laser pulse, in-vacuo photon desorption was shown to remove H₂O and C impurities in about 15 shots at a level below the single shot damage threshold, (4.42). A similar substrate cleaning process using a glow discharge for 10 minutes was found to be essential for producing good 'through the substrate' aluminium reflectors at 193 nm and 248 nm, (4.43). This work at 266 nm using the LIMA instrument on a multi-layer dielectric sample shows similar effects. The observation of an ion current at the ionization threshold could be used as an indicator of threshold damage. The main problem with the LIMA instrument was that the incident laser fluence was not measured and so only relative laser energy thresholds could be used. Measurements of ion emission from GaAs suggest the ionization threshold is lower than the damage threshold measured using more traditional methods such as with the Nomarski microscope objective, (4.33). The detection of ion emission may be a useful pre-cursor NDT method for indicating laser induced damage resistance.

The LIMA instrument could be developed into an extensive damage testing facility if the instrument could be modified to accept any of several external pulsed laser excitation sources and perhaps a separate probe beam source. This would allow threshold damage identification
to be made using the video camera, laser scatter or other probe beam methods to monitor the optical performance and the LIMA instrument to chemically analyse damage susceptible film areas.

4.3f Comparison of damage threshold detection sensitivities

It is apparent from section 4.3 that the laser induced damage threshold can be measured using a probabilistic or extrapolation approach. In the first case, threshold damage is defined to occur when some condition is met such as the detection of a scatter ratio greater than one. The probability of threshold damage occurring at a given fluence can then be experimentally measured. An example is shown in figure 4.34 where the damage probability is plotted as a function of the laser fluence using three different conditions to define the occurrence of threshold damage. All three methods were applied to each shot. The test sample was a 248 nm multi-layer dielectric mirror (sample 22a, HfO₂/SiO₂) deposited on a fused silica substrate. The three conditions to define the occurrence of damage were:

i Observation of damage using the long range x40 microscope in a 'before and after' observation mode.

ii Observation of an increase in the laser scatter detected by the video camera and viewed on the monitor.

iii The measurement of a scatter ratio greater than one

The results shown in figure 4.34 suggest that the laser scatter system described in section 4.3c was the most sensitive method to detect threshold damage, this being closely followed by the video microscope and the x40 microscope. A summary giving the damage thresholds for the 0% and 100% damage probabilities for several samples measured using the video microscope and the laser scatter probe method are shown in table 4.4.
FIGURE 4.34
DAMAGE PROBABILITY VERSUS FLUENCE AT 248 nm
FOR VARIOUS THRESHOLD DAMAGE DETECTION METHODS
Summary of damage thresholds for 0% and 100% damage probabilities using the video microscope and the laser scatter system to detect damage.

A general conclusion is that the video microscope and laser scatter method have similar sensitivities to detect threshold damage. This is perhaps not surprising since both methods are using the same optical arrangement, (figure 4.13). The major difference being the way in which the scattered light is displayed, from the camera as an image or from the detector as a quantitative signal.

The alternative method of measuring damage thresholds is the extrapolation approach. An example is shown in figure 4.19 where the scatter ratio is plotted as a function of the fluence, extrapolation of the graph back to where the scatter ratio is equal to one gives the damage threshold. The advantage of this method is that all of the data above the damage threshold is used and ambiguous identification of threshold damage is not crucial. A similar extrapolation approach was also applied to the acoustic data in figure 4.30 for the same sample. The threshold of $0.12 \text{ Jcm}^{-2}$ compares to the extrapolated threshold using the scatter ratio method of $0.04 \text{ Jcm}^{-2}$. The detection of laser induced scattering therefore appears to be a more sensitive method than the photoacoustic method for threshold damage detection in HR multi-layer dielectric films.

The results described in section 4.3c using the scatter ratio extrapolated to $R = 1.0$ give fluences
equivalent to damage probabilities within the range 40 - 80%. The most conservative definition of threshold damage is the 0% damage probability level and has the advantage of being independent of the laser spot size. Interest in developing automated systems for damage testing is likely to lead to the development of the extrapolation method because it is much simpler to measure.

4.4 Conclusions and recommendations

A detailed review of the various methods that have been used for laser induced threshold damage detection has been given. The experimental requirements for threshold damage detection at excimer wavelengths led to the development of three in-situ techniques using optical microscopy, laser scatter from a helium neon probe beam and direct photoacoustic detection using PZT transducers. A preliminary investigation was also carried out using a Laser Induced Mass Analyser, (LIMA), surface analysis instrument to investigate the chemical composition of scattering centres in thin films.

An optical microscope system based on a video camera has been developed. The video microscope used a dark field illumination arrangement to maximize the contrast between scattering areas and non-scattering areas and was able to detect the formation of micron sized damage pits. The before and after irradiation video images were recorded on a video recorder as well as verbal information about the test. A prototype video frame grabber with x,y cursors and digitizer was developed to allow video frame subtraction and enhanced threshold damage detection. An interesting phenomena was observed on several samples when they were irradiated just below their single shot damage threshold. A particulate cloud was ejected from the sample's surface. This coincided with the observation of a decrease in the scatter ratio below one. Multi-shot irradiation below the single shot damage threshold has been shown to reduce the defect density of the most damage sensitive defects, (see chapter 8). This pre-conditioning
process is likely to originate from the ejection of the particles observed with the video microscope system.

Future developments of the video microscope system could involve the use of an infra-red thermal imaging camera to image absorbing 'hot-spots' rather than scattering centres. This NDT method would be an implementation of the sensitive photothermal methods described in section 4.2eiii but with a much higher data acquisition rate.

The on-axis darkfield illumination method was also used to produce a quantitative measure of the scattered light. The scatter ratio defined as the scattered signal amplitude after irradiation divided by the scattered signal amplitude before irradiation was found to be a useful parameter for indicating the formation of threshold damage. A simple model was developed to explain how the scatter ratio can vary both in a positive and negative direction about one in the region of the damage threshold. Extrapolation of the scatter ratio to one gives a convenient and easy to measure damage threshold although the fluence at which the damage probability is zero is more correct. The 100% damage probability fluence for three multi-layer dielectric mirrors was equivalent to a scatter ratio of 1.5. This figure may prove useful as a guideline to any future automation of threshold damage measurements at excimer wavelengths.

Future developments of this work could include the use of more sensitive photodetectors combined with phase locked detection methods. Other optical probe methods worthy of further investigation include transient air/film critical angle probing using transparent substrates and probe beam refraction methods. Both of these techniques are likely to involve more complicated optics and greater alignment problems.

Photoacoustic detection of threshold damage at 248 nm and 193 nm has been investigated using two PZT transducers. The calculated high frequency sensitivity of both transducers to off-epicentre bulk waves was in good over-all agreement with their measured spectra.
Irradiation in the plasma regime resulted in a high frequency thickness resonance of the PZT crystal. Analysis of these resonant waveforms was avoided by capturing the bulk wave arrival on an oscilloscope. The peak-peak amplitude of the arriving bulk wave was used as a measure of the photoacoustic signal amplitude. Measurements with the laboratory built transducer gave an extrapolated threshold much higher than that measured using the video microscope. This was attributed to its lower sensitivity compared to the Dunegan & Endevco transducer which was a factor of about 100 times more sensitive in the range 0.2 - 0.8 MHz. The results measured with the Dunegan & Endevco transducer on a multi-layer dielectric mirror at 193 nm, (sample 24a) suggest two thresholds occur at 0.12 Jcm\(^{-2}\) and 0.6 Jcm\(^{-2}\). In general several mechanisms may contribute to the acoustic generation efficiency as the incident fluence is increased. If these mechanisms are contiguous then several thresholds are observed otherwise a super-linear increase in the acoustic signal amplitude above the thermoelastic threshold results. This interpretation also usefully explains data previously measured at the \(\text{CO}_2\) laser wavelength of 10.6 \(\mu\)m and the Nd.YAG laser wavelength of 1.06 \(\mu\)m. A major disadvantage of the direct photoacoustic method is the intimate contact required between the PZT transducer and the test sample and the use of silicone grease as a couplant.

Preliminary measurements of impurities in thin films using the LIMA instrument showed great promise. The detection of an ionization current also potentially offers a pre-cursor or NDT method for measuring laser induced damage resistance. The LIMA instrument could be developed to accept any of several external laser excitation sources and become a comprehensive damage testing facility, however this option may be expensive.

The comparison between the laser scatter and video microscope methods has shown them to have similar sensitivities to detect threshold damage. This is not surprising since they were both based on the darkfield
illumination method to image scattering centres in thin films. The photoacoustic method even with the more sensitive transducer showed a reduced sensitivity to detect threshold damage in thin films compared to the video microscope and laser scatter methods. The most conservative definition of the damage threshold is the 0% damage probability fluence which is independent of the damage laser spot size. The extrapolated threshold gives a fluence equivalent to damage probabilities in the range 40 - 80%. However, the extrapolated fluence is simpler to measure and may become accepted if automated damage testing facilities become established.
4.5 References

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Chapter 5
Laser-liquid interactions at 248 nm

5.1 Introduction

In the course of investigating liquids for use as laser beam attenuators at 248 nm, interesting temporal pulse distortions were observed at high intensities.

The experimental investigations, (see section 5.2) involved measuring the transmission of a 20 mm cell containing various solutions as the incident laser intensity was varied.

Deviations from the Beer-Lambert law at high laser intensities, (~16 MWcm⁻²) have been observed in distilled water, methanol, ethanol and several aqueous solutions of the transition elements. The effect was first observed due to the accidental contamination of spectrograde methanol from a cork stopper. Analysis of the solution indicated the presence of various transition elements, the main impurity being iron.

In section 5.3 several mechanisms are discussed as candidate processes to describe the observed experimental results. These include: linear absorption, plasma formation, self-focusing, stimulated scattering and non linear absorption. The results can be interpreted in terms of excited state absorption when the cross section for absorption from the excited state is larger than the cross section for absorption from the ground state.

5.2 Results

5.2a Experimental arrangement

The experimental arrangement is shown in figure 5.1. Pulse energy measurements were made using a Laser Instrumentation calorimeter and a fused silica beam splitter at position A in figure 5.1. A second beamsplitter at position B reflected approximately 8% of the main beam energy onto an f2, 100 mm focal length planoconvex lens, L. The solution of interest was placed
FIGURE 5.1

EXPERIMENTAL ARRANGEMENT; LASER-LIQUID INTERACTIONS AT 248 nm

FIGURE 5.2

CELL CONFIGURATION
within a 20 mm long quartz cell and the incident energy
density controlled by varying the lens-cell distance.
Beyond the focus, F, a ground glass screen was used as a
diffusing element to reduce the energy density incident on
the Thorn-EMI PD 1912 S5 vacuum photodiode. Although the
glass diffusing screen was absorbing at 248 nm, a
sufficient reflection was produced. A 3 mm aperture
mounted in front of the detector was centred on the axis
of the system, monitoring the peak transmitted pulse. The
precise location of the PD 1912 S5 detector was not
critical due to the presence of the diffusing screen.
This was tested by traversing the detector in an arc about
the optical axis. The transmitted pulse was captured by a
Tektronix 466 storage oscilloscope triggered by discharge
noise from the excimer laser. A typical pulse energy
variation from shot to shot in a manual single shot mode
was 5%. This could be reduced by operating at a constant
pulse repetition frequency.

5.2b Cell Transmission

The geometry of the cell is shown in figure 5.2.
Medium 1 is air considered to have a unity refractive
index at 248 nm. Medium 2 is fused silica with a
thickness of 1 mm and a refractive index of 1.508 at
248 nm, (5.1). Medium 3 is the liquid of interest with
internal transmittance $T_{liq}$. The overall cell
transmission is given by

$$T_{CEL} = T_{w}^{2}T_{liq} \quad 5.1$$

where $T_{w}$ is the window transmission between the air/fused
silica interface and fused silica/liquid interface.

Assuming no absorption in the fused silica but making
allowance for multiple reflections within the window, $T_{w}$
is given by

$$T_{w} = \frac{T_{12}T_{23}}{1 - R_{12}R_{23}} \quad 5.2$$
where $T_{12}$, $R_{12}$, $T_{23}$, $R_{23}$ are the standard Fresnel expressions for transmittance and reflectance between the dielectric interfaces 1/2 and 2/3. In the case of the cell containing no liquid (medium 3 = medium 1) the calculated transmission figure is 84.5%. This is termed the "dry cell" transmission.

The dry cell transmission was experimentally measured at three axial locations of the cell relative to the lens ($x = 34, 68$ and $92$ mm). At each position the mean height of 30 transmitted pulses was calculated and compared with the mean pulse height when no cell was present. This produced an experimental dry cell transmission of 85 ±2% in good agreement with the calculated figure.

5.2c Solvent Transmission

For calibration purposes the transmission of the cell containing distilled water, spectrograde methanol and spectrograde ethanol was measured as a function of the lens-cell distance. The results are shown in figure 5.3. The experimental transmission of the cell at each position $x$ was calculated from

$$T_{\text{CELL}} = \frac{\text{Peak height of the pulse transmitted through the cell containing solvent}}{\text{Mean peak pulse height with no cell present}}$$

A transmission error of about 5% arises from the single shot measurements at each location of the cell.

The Fresnel reflectance loss at the fused silica/liquid interface is given by

$$R_{23} = \frac{(n_3 - n_2)^2 + k_3^2}{(n_3 + n_2)^2 + k_3^2}$$

In the case of distilled water, the refractive index at 248 nm is given by $n_3 = 1.378$ and $k_3 = 1.79 \times 10^{-8}$, (5.2). The imaginary component was calculated from a literature value for the absorption coefficient of 0.0125 cm$^{-1}$, (5.2). Since $k_3 \ll 1$ the effect on the reflectance is
FIGURE 5.3
TRANSMISSION OF FUSED SILICA CELL AT 248 nm
CONTAINING DIFFERENT SOLVENTS
negligible in equation 5.4 and can be ignored. Similarly, for all liquids with a reasonably high transmission at 248 nm, the influence of $k_3$ on the reflectance term $R_{23}$ is negligible. The calculated cell transmission of 89.3% for distilled water is in good agreement with the experimental data shown in figure 5.3a. The only exception was in the region of $x = 80$ mm when the cell was located at the lens focus. Similar transmission curves are shown in figure 5.3b for spectrograde ethanol and spectrograde methanol. The transmission value reduces to about 80% for distilled water and 70% for methanol and ethanol in the region of $x = 80$ mm (cell in focal region). The transmitted pulse with no cell present and that with the cell containing ethanol at $x = 75$ mm is shown in figure 5.4. The transmission data points marked in figure 5.3 with thicker lines were calculated by measuring the area under the temporal intensity profiles using a digitizing tablet connected to an Apple IIe computer. They are in agreement with the peak pulse height measurement method. The energy focused beyond the lens $L$ in figure 5.1 was measured as $\sim 4$ mJ. The beam area at the focus of the lens (no cell present) was estimated to be $\sim 1$ mm$^2$. This corresponds to a peak energy density of 0.4 Jcm$^{-2}$ and a peak power density of 16.7 MWcm$^{-2}$ (assuming a pulse width of 24 ns). The passage of the excimer pulse through the liquid was observed from the side using a x20 microscope. No visible plasma formation was observed even at $x = 80$ mm. In the case of ethanol, bubbles were formed when the cell was centred on the lens focus.
**Figure 5.4**
24.8 nm TRANSMISSION OF CELL CONTAINING ETHANOL

**Figure 5.5**
24.8 nm TRANSMISSION OF CELL CONTAINING "CORK SOLUTION"
5.2d Solution transmission

In the course of the transmission experiments with solvents an interesting effect was observed with methanol when a cork stopper was used on the cell top to reduce evaporation. A much larger transmission reduction was observed when the cell was at the focus. Further trial experiments were able to show that the cause of the effect was leaching of material from the brown 'veined' areas of the cork into the methanol.

A concentrated solution of this mixture was prepared, the remaining cork particulates were filtered out. A particle size analysis of the filtered solution using a Malvern Instruments 2200 analyser, showed that any remaining particles had a diameter <1.2 μm. The transmitted pulse when the cell was centred at the focus of the lens is shown in figure 5.5. The relative concentration of the cork solution A was twice that of cork solution B. The distorted transmitted pulse was reproducible across the aperture of the laser light scattered from the diffusing screen. This was measured by moving the detector and pinhole off axis.

The transmission data plotted as a function of the lens-cell distance x is shown in figure 5.6 for three relative cork solution concentrations of 4:2:1. The error in each experimental point is about 5%. No visible plasma was observed with the x20 microscope as the excimer beam passed through the liquid.
LIQUID CELL TRANSMISSION VERSUS LENS-CELL DISTANCE FOR THREE CORK SOLUTIONS A, B, C, \( (\lambda = 2.48 \text{ nm}) \)
5.2e Analysis of cork solution

The transmission of the cork solution was compared to that of spectrograde methanol in the wavelength range 200 - 2600 nm using a Perkin Elmer 323 Spectrophotometer. No significant difference was observed except the pure methanol had a sharper UV absorption edge.

The absorption coefficient was found to vary linearly with relative concentration (as to be expected by the Beer-Lambert Law) at 340 and 380 nm. The cork solution transmission at 248 nm was found to be constant within experimental error over the temperature range 293 - 330 K.

X-ray fluorescence was used to give an indication of the elemental content of the cork compound. The heavier elements present were: potassium, iron, calcium, manganese, chlorine and iodine. This was confirmed using an electron microprobe machine.

5.2f Transmission of various aqueous solutions containing transition elements

The presence of the transition elements iron and manganese in the cork solution led to an investigation of the transmission at 248 nm of various aqueous solutions containing transition elements. Preliminary investigations using the excimer laser were made on:

1) *Fe₂(SO₄)₃, CoSO₄, NiSO₄, CuSO₄·5H₂O
2) *ZnCl₂, *MnCl₂, SnCl₂, NaCl, AlCl₃, TiCl₂, CrCl₃·6H₂O
3) Pb(NO₃)₂, Fe₃(NO₃)₃·9H₂O, AgNO₃
4) *Nd₂O₃, *TiO₂

The five compounds marked with an asterisk were chosen somewhat arbitrarily for a more detailed investigation. They were chosen on the basis of:

A) Did they emit visible fluorescence?
B) Was any pulse reduction observed?
C) Were the compounds suspensions in aqueous solution?
D) Was there an apparent change in the transmission as the focus was approached?
The transmission reduction for the aqueous solutions should be compared to those shown in figure 5.3 for the pure solvents. The cell transmission reduction for distilled water was approximately 5% and for ethanol and methanol approximately 10%.

\( \text{Fe}_2(\text{SO}_4)_3 \) exhibited the largest transmission reduction. Two concentrations were tried, 0.67 g/l and 1.33 g/l. The cell transmission is plotted against lens-cell distance in figure 5.7. The data plotted in heavier ink were calculated from the area under the temporal intensity profiles for comparison. Yellow fluorescence and the formation of several very small bubbles (\( \sim 10 \mu \text{m} \) diameter) at random positions around the focus were observed after the pulse had passed. \( \text{Nd}_2\text{O}_3 \) was insoluble in distilled water and formed a cloudy suspension. The transmission of the suspension at a constant \( x \) value was observed to increase with time over a \( \sim 100 \) s period. This was attributed to gravitational settling of the larger suspended \( \text{Nd}_2\text{O}_3 \) particles. Transmission measurements were made at three concentrations after allowing the suspension to settle out. A logarithmic plot of the transmission of the cell when positioned at the lens focus (\( x = 80 \) mm) versus concentration is shown in figure 5.8. The transmission results for the cork solution and \( \text{Fe}_2(\text{SO}_4)_3 \) with the cell positioned at the focus and well away from the focus are also included for comparison. The normalized concentration of one equates to \( 94 \times 10^{-4} \) g/l for the \( \text{Nd}_2\text{O}_3 \) and 0.67 g/l for \( \text{Fe}_2(\text{SO}_4)_3 \). The transmission data at high intensities compared to that at low intensities is approximated by a constant 5 - 10% reduction attributed to the pure solvent and a much larger decrease attributed to an increased absorption coefficient. This represents a deviation from the Beer-Lambert law because the absorption coefficient is dependent on the laser intensity.

\( \text{ZnCl}_2 \) appeared to form an aqueous suspension of very fine particles (concentration 8 g/l). No significant cell transmission reduction was observed when compared to that of distilled water. The aqueous solution of \( \text{MnCl}_2 \) also at
a concentration of 8 g/l produced a violet fluorescence when illuminated with the 248 nm laser radiation. An approximate 10% reduction in transmission was observed when the cell was positioned at the lens focus. This was marginally more than the 5% observed with distilled water. Using the viewing microscope occasional bubbles were observed randomly distributed around the focal region with an estimated diameter of about 10 μm. 

TiO₂ also formed a suspension of particles in distilled water and produced a violet fluorescence when illuminated at 248 nm. At random locations around the focus, very small bubbles were again observed on some shots after the passage of the excimer beam. The cell transmission data is shown in figure 5.7 for comparison with the solutions of Fe₂(SO₄)₃. The unusual feature is that symmetrically around the lens focus the transmission appears to increase. These data suggest a more complicated mechanism than that for the cork solution and Fe₂(SO₄)₃.
FIGURE 5.7
LIQUID CELL TRANSMISSION VERSUS LENS-CELL DISTANCE, (\( \lambda = 2.48 \text{ nm} \))
FIGURE 5.8
LOGARITHMIC PLOT OF CELL TRANSMISSION VERSUS CONCENTRATION, ($\lambda = 2.48\ \text{nm}$)
5.3 Discussion of results

There are several phenomena which could explain the pulse distortion effects observed in the solvents and various aqueous solutions. Although there is insufficient data to consider each mechanism in great detail, some conclusions can be made.

Fluorescence was not expected to have an influence on the results because the fluorescence would be emitted uniformly over 4π steradians. The small amount of fluorescence light emitted in the forward direction to pass through the 3 mm entrance aperture to the detector would be insignificant compared with the transmitted beam. The mechanisms considered are: plasma formation, volumetric heating, self-focusing, stimulated inelastic scattering processes and laser induced photochemistry.

5.3a Plasma formation

As described in Chapter 4, laser induced plasma formation is often accompanied by the sharp truncation of the transmitted pulse at or around the peak of the pulse. This has also been observed by Newnam, (5.4) who was developing high power ruby laser attenuators using aqueous solutions of the transition metal ions Cu^{2+}, Ni^{2+} and Cr^{3+}. Figure 5.9 reproduces his results showing truncation of the ruby laser pulse after passing through a 2.6 mm path length cell containing the solution of interest. His general observations were that pulse truncation was only observed at high incident fluences of ~100 Jcm⁻², (10 GWcm⁻²), the truncation was more severe as the transition element concentration was increased and that the pulse truncation was greater with methanol compared to distilled water as the solvent. The almost vertical trailing edge of the transmitted pulse is quite different to that observed in this work. Newnam attributed his results to plasma formation. In the experiments at 248 nm, however, no light emission was observed. It is felt that plasma formation was not the origin of the pulse distortion.
FIGURE 5.9

(RESULTS REPRODUCED FROM REFERENCE 5.4.)
TRANSMISSION OF Q SWITCHED RUBY LASER PULSES THROUGH A 2.6 mm PATH LENGTH CELL CONTAINING

A - 80 g/l Cu Cl₂\cdot2H₂O with Methanol solvent
B - 80 g/l Cu Cl₂\cdot2H₂O with distilled water solvent

INCIDENT PULSE SHOWN ON THE RIGHT HAND SIDE
5.3b Volumetric heating and self-focusing

In the low incident laser intensity range the liquid transmission was constant as expected by the Beer-Lambert law. This is illustrated in figure 5.3 for distilled water, spectrograde methanol and spectrograde ethanol. Further evidence for a linear model is shown in figure 5.8 where the logarithmic transmission value varies linearly with relative concentration. The dip in transmission occurs in the range \( x = 70 - 90 \) mm for all cases except \( \text{TiO}_2 \). This was the range over which the lens focus remained within the liquid.

The observation of bubble formation after the excimer pulse had passed through the liquid was evidence of absorption and heating of the liquid. When the cell containing ethanol was placed at the lens focus a symmetrical line of bubbles was observed about the focus. Those bubbles which formed exactly at the focus, floated to the surface first. Their origin could be due to volumetric heating of the focal region and out-gassing of absorbed air or at higher temperatures, cavitation. In other cases, including the cork solution, bubbles were sometimes observed to form at random locations along the focal region. This was considered to be caused by localized heating of particulates in the solution. A particle size analysis of the filtered cork solution implied that any absorbing particles were less than 1.2 \( \mu \)m in diameter.

Heating of the liquid resulting from absorption of the laser radiation when the cell was in the focal region could be another mechanism producing the observed pulse distortion. The transient temperature rise during the time scale of the pulse could change the refractive index of the liquid. The variation of refractive index of the liquid with temperature is expressed in equation 5.5

\[
dN/dT = dn/dT - idk/dT
\]

where \( N = n - ik \) is the complex refractive index and \( T \) temperature. Transient self-focusing can occur if the
The first term on the right hand side of equation 5.5 is positive. This has been considered by Akhmanov et al, (5.5) who gives

\[ \frac{dn}{dT} = \langle \frac{dn}{dT} \rangle_\rho + \langle \frac{dn}{d\rho} \rangle_T \frac{d\rho}{dT} \]  

5.6

where \( \rho \) is the density. The first term in equation 5.6 is related to the temperature dependence of the polarizability and is generally positive, (5.5). The second term in equation 5.6 is due to thermal expansion and is generally negative, (5.5). The transient behaviour of thermal self-focusing is therefore determined by the acoustic propagation time across the beam. In this case, using the sound velocities noted in table 5.1 and a minimum beam width of 500 \( \mu \)m gives acoustic propagation times of 334 ns, 437 ns and 453 ns for water, ethanol and methanol respectively. The laser pulsewidth is about 24 ns and therefore only the term \( \langle \frac{dn}{dT} \rangle_\rho \) in equation 5.6 can contribute on this timescale. The influence produced by the second term in equation 5.5 depends upon its sign. On a transient basis relative to the laser pulsewidth, if \( \frac{dk}{dT} > 0 \) this leads to an increased absorption during the latter part of the pulse.

The change in \( n \) and \( k \) in equation 5.5 is related to the overall temperature rise \( \Delta T \). This has been considered by Newman, (5.4), for a linear absorption process in a liquid cell. The analysis is simplified to an adiabatic process (no heat loss) if the laser beam diameter, \( d \), is much greater than the thermal diffusion distance, \( l \). The thermal diffusion distance, \( l \), is given by, (5.6)

\[ l = (4D\tau)^{1/4} \]  

5.7

where \( D \) is the thermal diffusivity and \( \tau \) the laser pulse duration. The thermal diffusivity is given by

\[ D = \frac{K}{\rho C} \]  

5.8

where \( K \) is the thermal conductivity, \( \rho \) the density and
<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>METHANOL</th>
<th>ETHANOL</th>
<th>DISTILLED WATER</th>
</tr>
</thead>
<tbody>
<tr>
<td>THERMAL CONDUCTIVITY ( \frac{W \cdot m}{K} \times 10^{-2} )</td>
<td>0.202</td>
<td>0.171</td>
<td>0.609</td>
</tr>
<tr>
<td>DENSITY ( g \cdot cm^{-3} )</td>
<td>0.786</td>
<td>0.785</td>
<td>0.997</td>
</tr>
<tr>
<td>SPECIFIC HEAT CAPACITY ( \frac{J}{g \cdot K} )</td>
<td>2.54</td>
<td>2.44</td>
<td>4.18</td>
</tr>
<tr>
<td>THERMAL DIFFUSIVITY ( \frac{cm^2}{s} \times 10^{-9} )</td>
<td>1.011</td>
<td>0.826</td>
<td>1.4611</td>
</tr>
<tr>
<td>THERMAL DIFFUSION DISTANCE, ( \mu m )</td>
<td>0.098</td>
<td>0.092</td>
<td>0.118</td>
</tr>
<tr>
<td>SPEED OF SOUND/( ms^{-1} )</td>
<td>1103</td>
<td>1144</td>
<td>1498</td>
</tr>
</tbody>
</table>

**TABLE 5.1**

**THERMAL DATA OF METHANOL, ETHANOL AND DISTILLED WATER. THERMAL DIFFUSION DISTANCE CALCULATED ASSUMING A LASER PULSE WIDTH OF 24 ns.**
C the specific heat capacity. Literature values, (5,7) for methanol, ethanol and distilled water are listed in table 5.1. The thermal diffusion distance for all three liquids assuming a laser pulsewidth of 24 ns is about 0.1 μm. The smaller beam dimension at the focus is of the order of 500 μm and therefore no heat loss is involved. Assuming a simple Beer-Lambert law attenuation of the energy density with distance Z into the liquid given by

\[ F = F_0 e^{-\alpha Z} \]  

5.9

where \( F_0 \) is the incident energy density and \( \alpha \) the absorption coefficient, the energy absorbed in the range \( Z + dZ \) is given by

\[ dE = -\langle dF/dZ \rangle \cdot dZ \cdot dA \]  

5.10

where \( dA \) is the cross-sectional area. Differentiating equation 5.9 and substituting in equation 5.10 gives

\[ dE = \alpha F dV = \rho C \cdot dV \cdot \Delta T \]  

5.11

where \( dV \) is the heated volume and \( \Delta T \) the temperature rise. Equation 5.11 assumes no heat is lost to the surroundings. The temperature rise, \( \Delta T(Z) \) is therefore given by

\[ \Delta T(Z) = \alpha F_0 e^{-\alpha Z / \rho C} \]  

5.12

Equation 5.12 has a maximum for \( Z = 0 \), giving

\[ \Delta T_{\text{MAX}} = \alpha F_0 / \rho C \]  

5.13

For the case of the cork solution well away from the focus the absorption coefficient is 0.013 cm\(^{-1}\) from the gradient of the line in figure 5.8. Taking \( F_0 = 0.4 \) Jcm\(^{-2}\) and \( \rho \) and \( C \) for methanol, equation 5.13 gives a maximum temperature rise \( \Delta T_{\text{MAX}} = 2.6 \times 10^{-3} \) K. Fitting a straight line to the cork solution data in figure 5.8 with the cell at the lens focus gives \( \alpha \approx 0.13 \) cm\(^{-1}\). This produces a
\( \Delta T_{\text{max}} \) only ten times higher than the value listed above. The transmission of the cork solution at 248 nm was measured between 293 and 330 K and remained constant to within experimental error. Therefore, even if the response time of the self-focusing effect arising from \( \frac{dn}{dT} \) or the increased absorption arising from \( \frac{dk}{dT} \) in equation 5.5 is fast enough, the overall temperature rise is not likely to be significant for a linear absorption process.

The peak on-axis energy density, \( F_0 = 0.4 \text{ Jcm}^{-2} \) used in equation 5.13 to calculate the maximum temperature rise was based on the estimated value at the focus in air. Self-focusing effects which would enhance the peak energy density can arise from an intensity dependent refractive index. The refractive index, \( n \), \( \langle \text{real part} \rangle \) is expressed as

\[
\begin{align*}
  n &= n^{(0)} + n^{(2)} I \\
\end{align*}
\]

where \( n^{(0)} \) is the low signal refractive index normally observed and \( n^{(2)} \) the higher order term. The result is that at high laser intensities for \( n^{(2)} > 0 \) a laser induced waveguide is formed with a maximum refractive index on the optical axis where the intensity is a maximum. This tends to focus the beam, increasing the peak energy density.

Self-focusing can be identified by comparing the temporal profile of the transmitted pulse through the liquid on the optical axis to that off the optical axis. This is usually done by scanning a pinhole and detector through the beam in the transverse direction. An enhancement of the pulse on the optical axis arises from the waveguide effect caused by the intensity dependent refractive index. A problem which can mask this process is caused by the increased on-axis energy density producing dielectric breakdown or coherent inelastic scattering processes such as stimulated Brillouin scattering.

In the case of the excimer laser, filamentary self-focusing would be expected to occur because of the multi-
mode beam. This is normally observed as a transient filamentary breakdown track in the liquid. No such breakdown was observed. Furthermore, by traversing a pinhole and detector through the laser beam transmitted through the cell, no enhancement of the temporal profile on the optical axis was observed. In fact, these measurements indicated a pulse distortion across the whole area of the transmitted beam implying an absorption process rather than self-focusing.

5.3c Stimulated scattering

Excimer laser pulse compression in liquids using Stimulated Brillouin Scattering, (SBS), and Stimulated Raman Scattering, (SRS), has been observed previously, (5.8). The experimental observations described earlier are discussed in terms of the requirements for SBS and SRS to occur.

SBS and SRS are inelastic processes in which the incident photon transfers energy to (Stokes scattering) or extracts energy from (Anti-Stokes scattering) the nonlinear medium. Simple representations of Brillouin scattering and Raman scattering are shown in figures 5.10 and 5.11. In the case of SBS the Stokes line results in the formation of an acoustic phonon (density fluctuation or sound wave) and a scattered photon of frequency less than the incident photon. Conservation of momentum requires the wavevector addition of the scattered photon, \( k_s \), the acoustic phonon \( k_a \) and the incident photon \( k_i \) as shown in figure 5.10. Expressed mathematically the momentum and energy conservation laws require

\[
\begin{align*}
    k_s + k_a &= k_i \\
    k_s + k_a &= k_i
\end{align*}
\]

where the \( |k_i| = k_i \) and similarly for \( k_a \) and \( k_s \). For the case where \( k_s \) and \( k_i \) are \( k_a \), then from figure 5.10
FIGURE 5.10
BRILLOUIN SCATTERING

\( \vec{k}_i \): INCIDENT PHOTON WAVEVECTOR
\( \vec{k}_s \): SCATTERED PHOTON WAVEVECTOR
\( \vec{q} \): PHONON WAVEVECTOR

FIGURE 5.11
RAMAN SCATTERING PROCESS

\( h \gamma \): ABSORPTION
\( h(\gamma - \epsilon_1) \): STOKES LINE
\( h(\gamma + \epsilon_1) \): ANTI-STOKES LINE
where $\theta$ is the scattering angle. Substituting equation 5.17 in equation 5.16 gives,

$$k_s = k_i (1 - 2\sin\theta/2)$$  \hspace{1cm} 5.18

The maximum Brillouin frequency shift occurs for $\theta = \pi$ and results in a backscattered photon. In stimulated Brillouin scattering the backscattered Stokes photon has the largest gain and dominates the process.

The stimulated process can be thought of as a feedback mechanism whereby the frequency down shifted Stokes wave interferes with the incident wave creating a moving interference pattern. The moving interference pattern generates more acoustic phonons via electrostriction, maintaining the feedback process.

The Raman scattering process has an analogy with Brillouin scattering except that optical phonons (rotational - vibrational excitations) are involved. Because the Raman process is involved with molecules it is easier to visualize as an excitation process shown in figure 5.11.

Both SBS and SRS are threshold processes and generally require high laser intensities to initiate them. The scattered light intensity is given by:

$$I_s(L) = I_i(0) \exp(gI_iL)$$  \hspace{1cm} 5.19

where $I_i(0)$ is the incident intensity, $g$ the gain factor (measured in cm/MW), $L$ the interaction length and $I$ the local laser intensity. Table 5.2 compares typical wavelength shifts, relaxation times and gains for stimulated Raman scattering and stimulated Brillouin scattering, (5.9).

Line narrowed excimer lasers (line width $\sim 0.002$ nm $\equiv 0.3$ cm$^{-1}$) have been used to investigate SBS and SRS in liquids, (5.8). SBS studies in SF$_6$ and N$_2$ have shown that above the threshold intensity the gain, $g$, in equation...
<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>STIMULATED RAMAN SCATTERING</th>
<th>STIMULATED BRILLOUIN SCATTERING</th>
</tr>
</thead>
<tbody>
<tr>
<td>WAVELENGTH SHIFT/nm</td>
<td>( \sim 6 )</td>
<td>( \sim 0.006 )</td>
</tr>
<tr>
<td>RELAXATION TIME/ns</td>
<td>( \sim 0.001 )</td>
<td>( \sim 1 )</td>
</tr>
<tr>
<td>GAIN /cm/MW</td>
<td>( \sim 5 \times 10^{-8} )</td>
<td>( \sim 10^{-5} )</td>
</tr>
</tbody>
</table>

**TABLE 52**

**COMPARISON OF STIMULATED RAMAN AND STIMULATED BRILLOUIN SCATTERING.**
5.19 is linearly related to the pump line width, \(5.10\). The line width of the KrF excimer laser used for the experimental studies considered in this chapter was about 0.5 nm. Consequently the gain parameter of \(10^{-2}\) quoted for SBS in table 5.2 would be expected to be reduced to about \(10^{-4}\). This is because the KrF laser line width is about 100x larger than the typical Brillouin wavelength shift. Substituting in equation 5.19 the following parameters

\[
\begin{align*}
\text{Gain, } g, \text{ SBS/SRS} & = 10^{-4}/5 \times 10^{-3} \text{ cm/MW} \\
\text{Interaction length, } L & = 2 \text{ cm} \\
\text{Peak power density} & = 16.7 \text{ MWcm}^{-2} \\
\langle F \rangle & = 0.4 \text{ Jcm}^{-2} \\
\langle \tau \rangle & = 24 \text{ ns}
\end{align*}
\]
gives an amplification factor of \(<1\%\) for SBS and 18\% for SRS. The observed experimental transmission changes were larger than 18\% and also no backscattered light pulses were detected. It therefore seems unlikely that SBS or SRS was the cause of the observed pulse distortions.

5.3d Non-linear absorption

Optical bleaching of dye solutions is a well established method for Q switching lasers. The Beer-Lambert law expressed in equation 5.9 is valid provided the number of absorbing species does not change significantly during the absorption process, in this case the duration of the laser pulse (~24 ns). At high photon fluxes the number of absorbing species can be reduced and bleaching of the sample can occur.

Following Hercher, \(5.11\), a simple physical model of electronic excited state absorption is illustrated in the energy level diagram in figure 5.12. Excited state absorption has been considered as a mechanism in optical bleaching to account for the saturation of the transmission at high intensities at values less than 100\%.

Absorption at the wavelength of interest occurs for both the 1 \(-3\) and 2 \(-4\) transitions. Following the analysis given by Hercher, \(5.11\), \(\sigma_{13}\) and \(\sigma_{24}\) are the
FIGURE 5.12
ENERGY LEVEL DIAGRAM FOR EXCITED STATE ABSORPTION PROCESS.

TABLE 5.3
EXCITED STATE ABSORPTION DATA.

<table>
<thead>
<tr>
<th>RELATIVE CONCENTRATION</th>
<th>T₀ / EXP²L ± 01</th>
<th>T MINIMUM / EXP²L ± 01</th>
<th>δ²⁴/δ¹³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.93</td>
<td>0.67</td>
<td>5.5±0.5</td>
</tr>
<tr>
<td>2</td>
<td>0.91</td>
<td>0.53</td>
<td>6.7±0.8</td>
</tr>
<tr>
<td>4</td>
<td>0.85</td>
<td>0.37</td>
<td>6.1±0.6</td>
</tr>
</tbody>
</table>

| IRON SULPHATE (AQ)     |                 |                         |         |
| 1.33g/l                | 0.43±0.03       | 0.14                    | 2.3±0.2 |
| 0.66g/l                | 0.53±0.02       | 0.28                    | 2.0±0.2 |

| DISTILLED WATER        | 0.92            | 0.82                    | 1.9     |
| METHANOL               | 0.90            | 0.78                    | 2.3     |
| ETHANOL                | 0.90            | 0.72                    | 3.1     |

AV = 6.1±0.6
absorption cross-sections for the 1 - 3 and 2 - 4 transitions and the lifetimes for the 3 - 2 and 4 - 2 transitions are negligible. For this model, only levels 1 and 2 are appreciably populated. The steady state transmission, $T$, of an optically thick medium with these properties is given by

$$\ln(T) - \ln(T_0) = (\gamma_0 - 1)\ln \left[ \frac{\langle \gamma_0 + I_0/I_s \rangle}{\langle \gamma_0 + T_0/I_s \rangle} \right]$$  \hspace{1cm} (5.20)

where

$$\gamma_0 = \sigma_{13}/\sigma_{24}$$ \hspace{1cm} (5.21)

$T_0$ is the small signal transmission, $I_0$ the incident intensity and $I_s$ the saturation intensity. From equation 5.20, if $I_0/I_s << 1$ then $T/T_0 \approx 1$ and the transmission approaches the low signal value, $T_0$. Similarly, if $I_0/I_s >> 1$ and $I_0/I_s \approx \gamma_0$ then the transmission, $T$, approaches the limiting value $T_0 \langle \sigma_{24}/\sigma_{13} \rangle$. Therefore, if the cross-section $\sigma_{24}$ is greater than $\sigma_{13}$ the large signal transmission, $T$, will be less than $T_0$. The derivation of equation 5.20 assumes a constant incident intensity, $I_0$. Hercher, (5.11) has shown that the response time of the process is given by

$$t_r = \frac{\tau_{21}}{1 + I_0/I_s}$$ \hspace{1cm} (5.22)

where $\tau_{21}$ is the lifetime of the 2-1 transition. In the case where $I_0$ is a function of time, equation 5.20 can be considered valid whenever the incident intensity does not vary appreciably within a time $t_r$ given by equation 5.22. The excimer laser pulse rise time was about 10 ns, thus equation 5.22 requires $t_r < 1$ ns. This requirement is satisfied if the lifetime of the excited state is of the order of a few nanoseconds and $I_0/I_s > 1$. The experimental observation of a lower transmission at high incident laser intensities is illustrated for the three cork solutions in figure 5.6 and for the two aqueous solutions of iron sulphate in figure 5.7. The results in figure 5.7 for
TiO$_2$ particles in distilled water are suggestive of a more complicated excitation mechanism. The initial bleaching and final transmission reduction as the intensity increases suggests two excited states are involved. The upper level absorption cross-section being larger than the intermediate value which is lower than the ground state value.

The experimental data was fitted to equation 5.20, calculated values of the ratio $\sigma_{24}/\sigma_{13}$ are given in table 5.3. This involved the experimental low signal transmission, $T_0'$ and assumed the experimental minimum transmission was the limiting value, $T_0' = \langle \sigma_{24}/\sigma_{13} \rangle$. The results are consistent for the different concentrations. They give an average ratio of $\sigma_{24}/\sigma_{13} = 6.1 \pm 0.6$ for the cork solutions and 2.2 $\pm 0.2$ for the two aqueous solutions of iron sulphate. The ratio $\sigma_{24}/\sigma_{13}$ is also given in table 5.3 for the three solvents, distilled water (1.9), methanol (2.3) and ethanol (3.1). These results suggest excited state absorption may also be occurring in the pure solvents.

Analysis of the cork solution has shown it to contain the elements iron, manganese, calcium, chlorine and iodine. The valency of the ions is unknown. The electronic energy levels of the free iron ions are extensive, (5.12). Furthermore, the methanol solvent may act as a ligand resulting in a transition metal-ion complex. The result of this would be to further complicate the electronic energy level spectrum. In the case of aqueous iron sulphate the ratio $\sigma_{24}/\sigma_{13} = 2.2$ and is not significantly different to the values observed in the pure solvents.

Multi-photon absorption can occur in figure 5.12 if the two stage excitation mechanism is via a virtual excited state. Multi-photon absorption has been previously observed with a KrF laser at 248 nm using distilled water, (5.13). The suggestion is that multiphoton absorption is occurring in the solvents; distilled water, methanol and ethanol.

The transmission $T$ as a function of $I_0/I_0^*$ is plotted
in figure 5.13. Experimental values for the cork solution of $T_0 = 0.85$ and $\sigma_{24}/\sigma_{13} = 6.1$ were used from table 5.3. Similar graphs would result for the other cork solution concentrations but with differing initial and asymptotic values. An iterative technique was used to solve equation 5.20 (for a given value of $T_0$, $\gamma_0$ and $I_0/I_s$) in order to plot figure 5.13. This was done by writing equation 5.20 in the form

$$T = T_0 \left[ \frac{\langle \gamma_0 + I_0/I_s \rangle}{\langle \gamma_0 + T I_0/I_s \rangle} \right]^{\gamma_0-1}$$  \hspace{1cm} 5.23

and using an initial estimated value for $T$ on the right-hand side of equation 5.23 to calculate the next approximation. The convergence is rapid using a suitable initial estimate for $T$ and requires only 2-3 iterations.

The transmission curve in figure 5.13 was used as a transfer characteristic to calculate the effect on a real incident laser pulse. The results are shown in figure 5.14. Three possibilities are considered where the peak of the incident pulse is assumed to have the limiting values:

- curve A; $I_0/I_s = 0.01$
- curve B; $I_0/I_s = 1.0$
- curve C; $I_0/I_s = 10.0$

Curve A corresponds to the low signal case where the transmission $T$ is constant at $T_0$, (0.85). Curves B and C show the considerable effect on the transmitted pulse peak amplitude.
FIGURE 5.13
TRANSMISSION AS A FUNCTION OF $I_0/I_s$ FOR EXCITED STATE ABSORPTION FROM EQUATION 5.20

$T_0 = 0.85$

$\frac{\sigma_{24}}{\sigma_{13}} = 6.1$
LASER PULSE TRANSMISSION THROUGH NON-LINEAR MEDIUM FOR DIFFERENT INCIDENT LASER INTENSITIES
5.4 Conclusions and recommendations

The most likely cause of the observed transmitted pulse distortions and consequent non-linear absorption characteristic is laser induced photochemical reactions in the form of excited state absorption.

Recommendations to further this work can be divided into two areas. The first is improved and more extensive measurements using the basic technique already developed. The second is to use other experimental techniques which allow a more detailed understanding of the process. The suggestions for improving the basic experimental method are:

1) Improve the experimental arrangement in figure 5.1 by using a collimating lens after the cell and a further lens to focus the transmitted light into the detector. This would require the use of linear attenuators in front of the photodetector.

2) Vary the incident laser intensity by varying the incident energy. This would allow the transmission measurements to be calibrated relative to the laser intensity.

3) Use differing length liquid cells and a large number of concentrations. This would allow the effect of the cell windows to be removed and produce a more extensive test of the deviations from the Beer-Lambert law.

The radiative transitions involved in the excitation process may be observed by using a line narrowed excimer laser as a pump source and monitoring the fluorescence with a spectrometer. Photothermal deflection methods have been used for the detection of non-radiative relaxation of excited states, (5.14). In this technique the thermal deflection of a probe beam is monitored as a function of time.
5.5 References


5.4 B E Newnam, Ph.D Thesis, No 73-09, 317, University Microfilm, Ann Arbor, Mich, USA.


Chapter 6
Laser damage studies of alkali and alkaline-earth fluorides at 193 nm

6.1 Introduction

The only laser window and thin film materials which have a high transmission down to VUV wavelengths are the alkali and alkaline-earth fluorides. They have widespread use as UV window materials, an example being the use of MgF$_2$ or CaF$_2$ as the output coupler in the Lambda Physik EMG-200 excimer laser used in this work. Radiation damage and colour centre formation arising from irradiation with X-rays, electrons or neutrons has been extensively investigated with these materials, (6.1). The main aim of this work was a preliminary study of laser induced damage at 193 nm. This included measurements of damage thresholds at 193 nm and investigations of laser induced damage morphology and colour centre formation.

Six different synthetic single crystal fluoride materials in polished and/or cleaved form were supplied by the manufacturers BDH Chemicals Ltd, (6.2). The six materials which were investigated are listed in table 6.1

<table>
<thead>
<tr>
<th>Material</th>
<th>Refractive Index at 193 nm</th>
<th>Solubility in 100g water/g</th>
<th>Impurities</th>
<th>Abs. Coefficient at 193 nm/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>1.445</td>
<td>0.27</td>
<td>None</td>
<td>0.26 (0.15)</td>
</tr>
<tr>
<td>NaF</td>
<td>1.385</td>
<td>4.22</td>
<td>Al, Cl</td>
<td>0.13</td>
</tr>
<tr>
<td>MgF$_2$</td>
<td>1.441</td>
<td>0.0076</td>
<td>K, Cl</td>
<td>0.02* (0.41)</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>1.499</td>
<td>0.0017</td>
<td>None</td>
<td>0.22 (0.23)</td>
</tr>
<tr>
<td>SrF$_2$</td>
<td>1.510</td>
<td>0.00012</td>
<td>Ca</td>
<td>0.05</td>
</tr>
<tr>
<td>BaF$_2$</td>
<td>1.552</td>
<td>0.17</td>
<td>I</td>
<td>0.20</td>
</tr>
</tbody>
</table>

* polished sample

Table 6.1
Properties of fluoride crystal materials

-253-
The real refractive indices of the pure crystalline materials at 193 nm were calculated using dispersion equations, (6.3, 6.4, 6.5). The absorption coefficients at 193 nm were calculated from the experimentally measured transmission using a Perkin Elmer 323 spectrophotometer, the real index given in table 6.1 and the sample thickness. Simplifying assumptions were made by neglecting the contribution towards the reflectance arising from the imaginary part of the refractive index and neglecting multiple reflections. The nominal UV absorption edge for these materials is quoted as well below 193 nm (6.3, 6.6). The approximate factor of ten variation in the absorption coefficient, \( (0.02 - 0.26 \text{ cm}^{-1}) \) probably occurred because all of the samples except MgF\(_2\) were cleaved but not polished and therefore scattering contributed to the over-all extinction measurement. The absorption coefficient for the polished MgF\(_2\) sample where scattering contributed little to the extinction was 0.02 \text{ cm}^{-1}. Also quoted in table 6.1 (in brackets) are some literature values for the absorption coefficients at 193 nm, (6.7). They are in reasonable agreement with the experimental values except for MgF\(_2\).

The water solubility data quoted in table 6.1 was taken from references 6.3 and 6.6 and is an important indicator of the environmental stability of the crystal. It is apparent from table 6.1 that NaF is much more soluble in water than the other materials. Its hydroscopic nature explains the origin of the slightly milky appearance some of the cleaved samples of NaF had before they were used. Data presented in reference 6.6 suggested LiF was also hydroscopic. The samples were also tested for the presence of elemental impurities using an electron microprobe, the results are summarized in table 6.1. The presence of Al in NaF was not attributable to the polishing material because the sample was freshly cleaved.
6.2 Measurement of relative laser damage thresholds at 193 nm

The basic experimental arrangement for damage testing is that shown in figure 3.5. A single thin fused silica beamsplitter, (4 mm thick) was used to minimize absorption since the UV absorption edge of fused silica is considered to be in the range 180 - 220 nm depending on the fused silica type, (6.6). The optical transmission and reflectance of the beamsplitter at 193 nm and 20° incidence was measured as 86.8 ±0.6% and 8.5 ±0.5% respectively. These figures give an absorption coefficient of 0.11 cm⁻¹ for the fused silica beamsplitter at 193 nm. The 193 nm transmission of the fused silica, f2, 100 mm focal length lens at normal incidence was measured as 90% giving a calibration factor in equation 3.36 of 9.57. The distance from the Laser Instrumentation pulse energy monitor to the beamsplitter, (~250 mm) was made equal to the distance from the beamsplitter to the test sample, the extinction path length for the 193 nm radiation in air was therefore the same. Data presented in reference 6.6 suggests the absorption coefficient of air at 193 nm is about 2 x 10⁻⁴ cm⁻¹. The attenuation at 193 nm over a one metre path length in air is therefore about 2%. A distinct ozone smell was apparent after multi-shot testing which presumably arose from photochemical decomposition of oxygen. Ozone concentrations greater than about 0.1 ppm are toxic, the threshold concentration for detection by smelling is about 0.01 ppm, (6.6). As a result of this hazard a large extraction fan was fitted above the apparatus to vent any ozone outside the laboratory.

The fluence incident on the test sample was adjusted by varying the distance between the lens and test sample and noting the single shot pulse energy and the lens-test sample distance at which damage was first observed. Following the method described in section 3.7b, the beam area was measured using the exposed side of polaroid film as a burn material and measuring the burn area as a function of distance from the lens. An example is shown...
in figure 3.21. The experimental error in the calculated fluence arises from the error in the laser energy measurement, ~10% and the reproducibility of the burn area measurement, ~30% giving a combined error of about 32%. The calculated fluence represented some average value and not the peak value since the true spatial beam profile was not measured using this method. Laser damage was identified using a long working distance, x10 microscope to view a change in scattering from a helium neon laser as a result of irradiation.

6.3 Damage thresholds of alkali and alkaline-earth fluorides at 193 nm

In these experiments two damage thresholds were defined. The first being the minimum fluence to guarantee damage in a single laser shot at five test sites out of five. The second definition was the maximum fluence not to cause damage after 600 laser shots. The latter test was done at a pulse repetition rate of 2 Hz. These two definitions were considered to be useful from the practical viewpoint. A damaging spot size greater than 1 mm$^2$ was employed to cover a large percentage of the test specimen area and local variations due to cracks, scratches and impurities.

In table 6.2 are shown the single shot and multi-shot damage thresholds for two alkali fluorides, (LiF and NaF) and four alkaline-earth fluorides, (MgF$_2$, CaF$_2$, SrF$_2$, BaF$_2$). Three polished samples were tested, LiF, MgF$_2$ and SrF$_2$, the rest were cleaved specimens. The LiF and CaF$_2$ were supplied in two grades of purity, IR grade and UV grade. The damage tests were performed at 0° incidence.

All of the samples including the polished and cleaved specimens had a similar threshold damage morphology in the form of several pits on the front surface. The morphology of threshold damage was similar to that observed at 248 nm in thin films and suggests that localized defects were the damage initiating centres. The cleaved samples had single shot damage thresholds within the range 1.0 - 2.6 Jcm$^{-2}$. The polished samples of LiF and SrF$_2$ had thresholds
somewhat lower than their equivalent cleaved counter-parts. The polished sample of LiF produced a strong luminescence in the green originating from small surface scratches. The lower threshold of the polished LiF sample is therefore attributable to some polishing compound remaining in the surface. The LiF polishing compound was a fine alumina with ethylene glycol as the lubricant, (6.2).

### Table 6.2
Laser induced damage thresholds at 193 nm

<table>
<thead>
<tr>
<th>Crystal Type</th>
<th>Single shot damage threshold/Jcm$^{-2}$</th>
<th>Multi-shot damage threshold/Jcm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>±32%</td>
<td>±32%</td>
</tr>
<tr>
<td></td>
<td>No 1</td>
<td>No 2</td>
</tr>
<tr>
<td>LiF</td>
<td>3.9*</td>
<td>2.2</td>
</tr>
<tr>
<td>UV grade</td>
<td>2.4</td>
<td>3.3</td>
</tr>
<tr>
<td>Polished</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>NaF</td>
<td>1.3</td>
<td>2.9*</td>
</tr>
<tr>
<td>Cleaved</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgF$_2$</td>
<td>Polished</td>
<td>2.6</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>IR grade</td>
<td>2.1</td>
</tr>
<tr>
<td>UV grade</td>
<td>2.5</td>
<td>2.6</td>
</tr>
<tr>
<td>SrF$_2$</td>
<td>Cleaved</td>
<td>1.6</td>
</tr>
<tr>
<td>Polished</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>BaF$_2$</td>
<td>Cleaved</td>
<td>1.2</td>
</tr>
</tbody>
</table>

* These samples were cleaved and tested within several minutes.

The cleaved surfaces were all several days old before they were tested. The three exceptions, LiF (IR grade, No 1) and NaF (No's 2 and 3) were cleaved and tested within...
several minutes and are marked in table 6.2 with an asterisk. The damage threshold of the freshly cleaved surface of LiF is a factor of 1.6 greater than the damage threshold of the older cleaved surface. The improvement for NaF is even higher with a factor of 2.3. It seems likely that the freshly cleaved surface of these two hydroscopic materials had insufficient time to absorb moisture from the surroundings and create a surface absorbing layer. The surface damage threshold was therefore correspondingly higher.

The ranked, mean single shot damage threshold of the alkaline-earth fluorides from table 6.2 are \( \langle \text{MgF}_2 - 2.6 \text{ Jcm}^{-2} \rangle, \langle \text{CaF}_2 - 2.3 \pm 0.3 \text{ Jcm}^{-2} \rangle, \langle \text{SrF}_2 - 1.7 \text{ Jcm}^{-2} \rangle \) and \( \langle \text{BaF}_2 - 1.1 \pm 0.15 \text{ Jcm}^{-2} \rangle \). The errors are quoted from the spread in the thresholds given in table 6.2 and do not include a reproducibility factor of about 30%. The mean single shot damage thresholds of the older cleaved surfaces of LiF and NaF were \( 2.5 \pm 0.6 \text{ Jcm}^{-2} \) and \( 1.3 \text{ Jcm}^{-2} \). The multi-shot damage threshold was 2 - 4 times lower than the single shot damage threshold. Only in the case of MgF\(_2\) were the two thresholds comparable. Damage was generally observed to occur within the first 10 - 30 shots of a multi-shot test. The factor of 2 - 4 difference between the single shot and multi-shot thresholds and the general observation of damage within the first 30 shots suggests the damage detection process had a limited sensitivity. Improvements in methods for detecting threshold damage are considered in chapter 4.

The single shot damage threshold data plotted as a function of the refractive index is shown in figure 6.1. The trend of high index materials having lower damage thresholds has been observed previously in surface damage studies at 1.06 \( \mu \text{m} \) using several different glasses, \( \langle 6.8 \rangle \), in thin films, \( \langle 6.9 \rangle \) and in alkali halide crystals, \( \langle 6.10 \rangle \). The data shown in figure 6.1 for NaF appears to be somewhat lower than the general trend. Bettis, \( \langle 6.9, 6.11 \rangle \) has developed a laser damage model relating the threshold electric field to the material
FIGURE 6.1
SINGLE SHOT DAMAGE THRESHOLDS AT 193 nm OF ALKALI AND AKALINE-EARTH FLUORIDES
refractive index and atomic number density. The relationship is given by

\[ E^\text{th} = K \frac{N}{(n^2 - 1)} \]

where \( E^\text{th} \) is the threshold electric field, \( K \) is the constant of proportionality, \( N \) the molecular number density and \( n \) the refractive index. The model assumes some critical electron displacement above which an avalanche can occur and has been successfully applied to the data given in references 6.8 - 6.11.

The validity of this model on these data at 193 nm is shown in figure 6.2. The square root of the single shot damage threshold is plotted against \( N/(n^2 - 1) \). Reasonable linearity is observed for the alkaline-earth fluoride data with NaF and LiF being lower than predicted. Interestingly, this was also the case in previous measurements, (6.9,6.11) and was partly attributed to the differing surface roughnesses. This analysis suggests that the avalanche model is appropriate for the alkaline-earth fluorides even though threshold damage was usually in the form of several small pits. The suggestion that an avalanche process is at least partly involved in threshold damage was enhanced because of observations that were made through the microscope as the sample was irradiated. Two forms of threshold damage were identified, the first being pit formation accompanied by an increase in the scattering of the probe beam. The second was initially identified as localized defect luminescence which eventually became physically identifiable as smooth 'molten' areas which produced little increase in the probe beam scatter intensity. In the case of LiF, the apparent defect luminescence was observed as small sparks. It is suggested that two forms of threshold damage occur. The first arising from defect absorption, the resulting physical damage being detected as an increase in the probe beam scatter intensity but with no light emission. The second, involving small micro-avalanches perhaps initiated by absorbing defects and observed as localized light
FIGURE 6.2

SQUARE ROOT OF DAMAGE THRESHOLD PLOTTED AGAINST $N/n^2 - 1$ SEE EQUATION 6.1
emission. The formation of several small plasmas as a result of avalanche ionization has also been considered elsewhere as an alternative to defect absorption to explain threshold damage morphology in thin films, (6.12).

6.4 Laser induced damage morphology in fluoride crystals at 193 nm

Several interesting features of the damage morphology are illustrated in figures 6.3 - 6.10. All of the photographs are at a magnification of x100, (10 μm = 1 mm). At the highest incident energy densities, typically about a factor of ten greater than the single shot damage threshold the surface damage morphology was similar for all of the samples. An example is shown in figure 6.3 for a single shot at 26 Jcm\(^{-2}\) and consists of a blackened central zone in the shape of the beam footprint, (0.8 x 0.2 mm). The threshold fluence for the formation of the blackened central area in MgF\(_2\) was about 8.2 Jcm\(^{-2}\). Surrounding the blackened zone is a much larger area consisting of surface damage along lattice cleave lines. An example of this type of damage is shown in more detail in figure 6.4 arising from a single shot at 4.2 Jcm\(^{-2}\) on SrF\(_2\). All of the alkaline-earth fluorides exhibited these triangular cleaved surface patterns. The formation of these surface cleaved patterns was more efficient in the fluence range of about 3 - 6 Jcm\(^{-2}\). Close inspection of figure 6.4 shows Newton's rings in the centre of each cleaved particle. The central black circle indicates the point of contact of the particle with the surface and the number of rings the wedge angle with the bottom surface. The cleaved surface damage morphology for the two alkali fluorides LiF and NaF was rectangular rather than triangular. An example is shown in figure 6.5 for a multi-shot test on LiF at 1.7 Jcm\(^{-2}\). The more cubic structure of the alkali fluorides presumably generates the rectangular cleave patterns whereas the more tetrahedral structure of the alkaline-earth fluorides generates the triangular patterns. The origin of the cleaving is probably thermal shock which the surface experiences from
FIGURE 6.3
193nm LASER INDUCED DAMAGE OF MgF₂ AFTER A SINGLE SHOT AT 26Jcm⁻²

FIGURE 6.4
193nm LASER INDUCED DAMAGE OF SrF₂ AFTER A SINGLE SHOT AT 4.2Jcm⁻²

FIGURE 6.5
193nm LASER INDUCED DAMAGE OF LiF₆ (20 SHOTS AT 1.7Jcm⁻²)
the expanding surface plasma. This explains why the cleaved area extends over a region much larger than the beam footprint. This phenomena has been observed in previous damage studies on several crystalline materials at 1.06 µm and 10.6 µm, (6.8, 6.13).

The ring structure shown in figure 6.6 was only observed in multi-shot testing of LiF. The damage generally consisted of a heavily damaged central area containing some thermal cracking surrounded by several rings, the number of rings increased with shot number. The thermal cracking suggests plasma formation. The rings could be caused by plasma burn marks or deposition of material. As the plasma grows, the same process occurs at a greater radius.

Threshold damage which involved an increase in the helium neon probe beam scatter intensity was similar for all of the specimens. An example arising from 600 shots at 0.8 Jcm⁻² in SrF₂ is shown in figure 6.7. A schematic diagram of the development of threshold damage in LiF and NaF as a function of shot number is shown in figure 6.8. The damage morphology after the first shot consisted of several pits, the next shot resulted in the formation of parallel cleave lines. Subsequent shots increased the number and length of the cleave lines. After several shots, cleave lines appeared which were perpendicular to the original ones. The initial localized absorption must therefore generate a sufficient thermal impulse to cleave the samples in the surface region.

An interesting bulk damage phenomenon is shown in figure 6.9, the accompanying schematic in figure 6.10 illustrates the geometry. This type of bulk damage was only observed in LiF and SrF₂. The 'tadpole' like bulk damage extended throughout the whole thickness of the crystal, some of the bulk damage is out of focus in figure 6.9. The smooth and transparent state of the 'tail' suggests it has reached a molten state and re-solidified. The opaque 'head' could be the origin of the small spark-like flashes observed in LiF and noted in section 6.3. These were attributed to an avalanche process resulting in
FIGURE 6.6
LiF, POLISHED, 25 SHOTS FLUENCE 1.6 J cm$^{-2}$
($\lambda = 193$ nm)

FIGURE 6.7
SrF$_2$, POLISHED, 600 SHOTS FLUENCE 0.8 J cm$^{-2}$
($\lambda = 193$ nm)

FIGURE 6.8 A-D
DEVELOPMENT OF THRESHOLD DAMAGE WITH SHOT NUMBER IN LiF AND NaF
LiF, POLISHED, 3 SHOTS FLUENCE 1.9 J cm$^{-2}$

---

FIGURE 6.9

Entrance surface

$100-500 \mu m$.

$20-100 \mu m$

$1-2 \mu m$

FIGURE 6.10

3-D SCHEMATIC OF GEOMETRY IN FIGURE 6.9

FIGURE 6.11

BULK BREAKDOWN PRODUCED BY A 10.6 \mu m, 
~80 ns PULSE IN AN NaCl CRYSTAL (FROM REF: 6.14)
the formation of micro-plasmas. An example of bulk damage measured at 10.6 μm in NaCl is shown in figure 6.11, (6.14). The damage in this case was also attributed to an avalanche ionization process. Comparison between figures 6.9 and 6.11 shows the damage features to be very similar even in physical dimensions. The major discrepancy is the orientation of the tail with respect to the incident radiation. Figure 6.9 is viewed looking from the direction of the incident laser pulse, the 'tail' is angled away from the incident direction as shown in figure 6.10. However, the damage tail in figure 6.11 appears to be aligned with the incident direction. A possible explanation for this difference is that some form of filamentary self-focusing is occurring which can result in beam breakup for multi-mode beams, (6.15).

6.5 Colour centre formation in fluoride crystals

Colour centre formation in the alkali halides has been investigated in great detail, (6.1,6.16). The most widely studied colour centre is a point defect known as the F centre. The F centre is formed by the absence of a halide ion at a lattice site, (i.e. a vacancy) having an effective positive charge which becomes electrically neutral by trapping an electron. The trapped electron has been modelled using the 'electron, particle in a box' model giving the F centre a series of particular excitation energy levels, (6.17). Interactions with lattice phonons results in the lowest electronic transition of the F centre being broadened into a smooth, nearly Gaussian absorption band a few tenths of an electronvolt wide at room temperature, (6.1). The position of the F centre absorption peak for alkali halides is temperature dependent, the correction is about 3% towards longer wavelengths from data measured at 4.2 K to room temperature, (6.16). Transitions from the excited F centre results in F centre luminescence at a wavelength longer than the absorption wavelength. Aggregate F centres consisting of two (F₂) or more adjacent F centres have also been observed and have their own characteristic
absorption and emission bands, (6.1). They may occur by the initial formation of halide vacancies on adjacent lattice sites, or by subsequent association of vacancies through thermal or optical migration. Heating or exposure to light absorbed in the F band substantially increases the number of $F_2$ and $F_3$ aggregate centres, (6.1). The F band and the $F_2$ band absorption peaks at 4.2 K for LiF, NaF and MgF$_2$ are shown in table 6.3, (6.1, 6.17). The F centre absorption bands in pure CaF$_2$, SrF$_2$ and BaF$_2$ appear to be only observable at low temperatures, (6.1).

<table>
<thead>
<tr>
<th>Material</th>
<th>Absorption Peak/\lambda\text{ nm}</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F band</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$F_2$ band</td>
<td></td>
</tr>
<tr>
<td>LiF</td>
<td>244</td>
<td>440</td>
</tr>
<tr>
<td>NaF</td>
<td>334</td>
<td>502</td>
</tr>
<tr>
<td>MgF$_2$</td>
<td>260</td>
<td>370</td>
</tr>
<tr>
<td>CaF$_2$</td>
<td>375$^*$</td>
<td>-</td>
</tr>
<tr>
<td>SrF$_2$</td>
<td>325$^*$</td>
<td>434$^*$</td>
</tr>
<tr>
<td>BaF$_2$</td>
<td>361$^*$</td>
<td>545$^*$</td>
</tr>
</tbody>
</table>

* Irradiated and measured at 84 K

Table 6.3
F centre and $F_2$ centre absorption peaks in fluoride crystals

Intense ionizing radiation such as X-rays are able to generate electrons by promotion across the band gap from the valence band to the conduction band. The band gap of the alkali halides is in the region of 10 eV, (6.1). For linear absorption, the ArF excimer wavelength of 6.42 eV, (193 nm) cannot therefore promote electrons directly across the bandgap. However, impurities and F centres already present in the crystal offer a source of electrons for excitation into the conduction band, the resulting migration producing more F centres. At high incident laser intensities two photon absorption can also
contribute an electron source by direct promotion across the band-gap. The initial number of halide vacancies depends on the history of the material which involves thermal treatment, mechanical strain or prior radiation damage, (6.1).

Residual colour centre formation in the visible was observed in NaF, (yellow) and IR grade CaF\(_2\), (blue) after multi-shot irradiation at 193 nm. It is clear from table 6.3 that the effects of residual F centres in LiF and MgF\(_2\) would not be visible to the naked eye. The luminescence from the IR grade CaF\(_2\) was observed to be red at low intensities of irradiation and blue at higher intensities, both being below the nominal single shot damage threshold. The post-irradiation transmission spectra in the range 180 - 700 nm for the NaF sample and the IR grade CaF\(_2\) sample are shown in figure 6.12. Two characteristic absorption peaks are apparent at 350 nm and 510 nm for the NaF sample. These two absorption peaks correspond well with the room temperature corrected values of 344 nm and 517 nm taken from table 6.3. The width of the F centre absorption peak in figure 6.12 is 0.44 eV compared with a literature value of 0.39 eV, (6.17). The residual yellow colour in NaF arises from the strong absorption at the blue end of the spectrum. The approximate F centre number density can be calculated from an equation reproduced from reference 6.16

\[
N_f = 10^{17} \frac{n a W}{(n^2 + 2)^2}
\]

where \(N_f\) is the F centre density, \(n\) the material refractive index, \(a\) (cm\(^{-1}\)) the absorption coefficient at the peak of the F centre band and \(W\) the full width of the F centre band measured in eV. Equation 6.2 arises by assuming each F centre is represented as a damped harmonic oscillator and the total F centre absorption calculated as an assembly of \(N_f\) harmonic oscillators. Substituting values for NaF in equation 6.2 gives an F centre density of \(1.3 \times 10^{15}\) F centres cm\(^{-3}\). Intrinsic laser damage models of avalanche ionization in bulk materials usually
FIGURE 6.12

TRANSMISSION OF 193 nm IRRADIATED SAMPLES OF NaF AND CaF₂ (IR GRADE)
require the generation of approximately $10^8$ electrons cm$^{-3}$ as seed electrons to initiate the avalanche, (6.14). Even in nominally transparent, pure NaF where the absorption coefficient, $\alpha \approx 10^{-4}$ cm$^{-1}$, equation 6.2 predicts an F centre density of $2 \times 10^{12}$ cm$^{-3}$ well in excess of that required to supply the initial seed density of electrons. The presence of impurities at concentrations of the order $10^{18}$ cm$^{-3}$ in CaF$_2$ have been shown to enhance the intrinsic damage threshold by an order magnitude at the excimer wavelength of 248 nm, (6.18). This effect was attributed to the impurities acting as efficient electron acceptors continually trapping the conduction band electrons thereby hindering the formation of an avalanche.

Radiation damage to CaF$_2$ is known to be very sensitive to the presence of impurities particularly yttrium which produces absorption bands at 225, 335, 400 and 580 nm at room temperature, (6.1). Pure CaF$_2$ at room temperature shows little sensitivity to F centre formation, (6.1). The two absorption peaks in the IR grade CaF$_2$ at 382 nm and 598 nm shown in figure 6.12 are therefore likely to have arisen from impurities. The residual blue colour centres in the crystal arises from the strong absorption in the yellow around 600 nm. The red and blue luminescence presumably arose from emission at wavelengths somewhat longer than the two absorption band peaks at 382 nm and 598 nm.

6.6 Conclusions

This preliminary study of laser induced damage at 193 nm in fluoride crystals was divided into three areas, measurement of damage thresholds, an investigation of damage morphology and colour centre formation.

The single shot damage thresholds at 193 nm for all of the fluoride crystals were in the range 1 - 4 Jcm$^{-2}$. The reproducibility in the measurement of the fluence of about 30% and the sensitivity of the visual scatter method to detect threshold damage are obvious areas where improvements could be made. The multi-shot thresholds were 2 - 4 times less than the single shot thresholds with
damage usually observed within the first 30 shots of a multi-shot test. The damage thresholds of the freshly cleaved surfaces of LiF and NaF were factors of 1.6 and 2.3 higher than the respective older cleaved surfaces. This suggests the hydroscopic nature of these materials has a strong influence on the surface damage resistance at 193 nm.

The single shot damage threshold appeared to scale approximately inversely with refractive index. This observation has been made at other laser wavelengths and with other materials, \(6.8, 6.9, 6.10\). A scaling law devised by Bettis, \(6.9, 6.11\) was shown to be approximately followed by the alkaline-earth fluorides.

At levels above the single shot damage threshold the most interesting feature of the damage morphology was the difference in surface cleaving patterns between the alkali fluorides and the alkaline-earth fluorides. The more cubic structure of the alkali fluorides generated rectangular cleave patterns whereas the alkaline-earth fluorides generated triangular patterns. Threshold damage experiments showed that these cleave patterns can arise from local absorption and do not require the formation of an intense surface plasma. The most intriguing bulk damage phenomena was observed in LiF and SrF\(_2\) and was attributed to filamentary self-focusing resulting in avalanche ionization. Further evidence of the involvement of an avalanche process was observed in LiF where small spark-like micro-plasmas were sometimes observed to form at the threshold level.

Colour centre formation was observed in NaF and CaF\(_2\) as a result of multi-shot irradiation well below the single shot damage threshold. The colour centres in NaF were attributed to the formation of F centres and to a lesser degree, F\(_2\) centres. The F centre density in irradiated NaF was calculated to be about \(10^{15} \text{ cm}^{-3}\), well in excess of that required to supply an initial electron seed density of \(10^8 \text{ cm}^{-3}\) to trigger an avalanche process. Pure CaF\(_2\) is known to be resistant to the formation of F centres but very sensitive to the presence of
impurities. The colour centres in the IR grade CaF$_2$ were therefore attributed to impurities since no colour centres were observed in the UV grade CaF$_2$.

A natural extension of these threshold damage studies at 193 nm would be a comprehensive study of the surface and bulk damage thresholds of the UV transmitting alkali and alkaline-earth fluorides at the excimer wavelengths of 193 nm, 248 nm, 308 nm and 351 nm. No significant pulsewidth correction on the thresholds would be needed to determine the wavelength scaling since the laser pulsewidths would all be similar. The trend in the damage threshold as a function of laser wavelength, material bandgap and refractive index would help identify the dominant damage mechanism in this part of the spectrum. Radiation damage studies involving F centre formation may also indicate whether this source of electrons is a significant generator of seed electrons for an avalanche mechanism.

6.2 R Sparrow, private communication, BDH chemicals Ltd, Poole, Dorset, UK, 1982.


6.9 The refractive index dependence of pulsed laser induced damage, J R Bettis, A H Guenther, NBS spec pub, No 414, 1974.


Chapter 7
Laser damage studies with aluminium mirrors at excimer laser wavelengths

7.1 Introduction
This chapter is concerned with the use of metallic reflectors at excimer laser wavelengths. The main interest is at the KrF laser wavelength of 248 nm where high damage threshold metallic mirrors may offer an alternative and inexpensive option over multi-layer dielectric mirrors.

The application of metallic mirrors for use at UV wavelengths is divided into two areas. These are optical performance, (section 7.2) and the laser damage resistance at 248 nm, (section 7.3). A third area, (sections 7.4 and 7.5) involves investigations into how silicon oxide overcoated aluminium mirrors can be converted for use in the UV region.

The optical performance includes a review of the optimum deposition conditions required to maximize the reflectance in the UV and a theoretical model to predict the effect of an absorbing dielectric overcoat layer deposited on the aluminium. A review is also given of suitable dielectric overcoating materials and compared with some practical results.

Three laser damage models have been developed, all of which assume threshold damage occurs when the surface of the aluminium reaches some threshold temperature. The three models represent the situations of a semi-infinite metal and a thin film metal mirror deposited on an insulating substrate with and without a dielectric overcoating. Damage thresholds were found to vary in the range 0.1 - 0.68 Jcm\(^{-2}\) and be in good agreement with calculated values of the melt threshold of aluminium.

Irradiation of SiO\(_x\) overcoated aluminium mirrors at UV wavelengths has resulted in the improvement of the UV reflectance at low fluences and the formation of a rippled surface at higher fluences. The former effect is
attributed to the reduction of the oxide absorption at UV wavelengths and is considered in section 7.4. The formation of ripple patterns in the laser heated oxide/aluminium at higher fluences is attributed to intrinsic stress relief of the oxide. This effect is considered in detail in section 7.5.

7.2 Thin film metal mirrors for use in the UV

7.2a Optimum deposition conditions for aluminium thin film metallic reflectors for use at UV wavelengths

7.2a1 Review of previous work

The reflectance of the commonest thin film metals at normal incidence are shown as a function of wavelength in figure 7.1. Below 300 nm the only metallic thin film reflector suitable for near normal incidence use is aluminium with rhodium coming a poor second. A high quality optically polished aluminium blank for use in the UV is difficult to manufacture. The soft aluminium tends to tear away from the surface during the polishing process and the large crystallites produce a surface with a characteristic 'orange peel' effect. Aluminium coatings in thin form are therefore used. The main parameters which influence the reflectance of thermally evaporated aluminium thin films are listed in table 7.1. The optimum deposition parameters to maximize the vacuum UV reflectance, \(<\lambda = 90 - 220 \text{ nm}\) of thermally evaporated aluminium thin films have been extensively studied, \(<7.1,7.2,7.3,7.4\>). The optimum deposition parameters required to maximize the UV reflectance at wavelengths beyond 220 nm are somewhat relaxed compared to those required at vacuum UV wavelengths. The parameters can be broadly grouped into three areas, evaporation conditions, aspects relating to the substrate and degrading effects due to oxide formation.
FIGURE 7.1

REFLECTANCE OF FRESHLY DEPOSITED FILMS OF ALUMINIUM, COPPER, GOLD, RHODIUM AND SILVER AS A FUNCTION OF WAVELENGTH FROM 0.2-10.0 µm. DATA REPRODUCED FROM REFERENCE 7.1.
<table>
<thead>
<tr>
<th>Deposition parameters</th>
<th>Optimum values to maximize UV reflectance of aluminium coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporation speed</td>
<td>&gt;30 nm/s</td>
</tr>
<tr>
<td>Deposition pressure</td>
<td>-5 mmHg</td>
</tr>
<tr>
<td>Film thickness</td>
<td>50 - 700 nm</td>
</tr>
<tr>
<td>Al metal purity</td>
<td>99.99%</td>
</tr>
<tr>
<td>Vapour incidence angle</td>
<td>near normal</td>
</tr>
<tr>
<td>Substrate cleaning</td>
<td>glow discharge on the substrate</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>&lt;420 K</td>
</tr>
<tr>
<td>Substrate roughness</td>
<td>optical polish</td>
</tr>
<tr>
<td>Oxide layer formation</td>
<td>λ&gt;220 nm</td>
</tr>
<tr>
<td>Ageing tests</td>
<td>λ&gt;220 nm</td>
</tr>
</tbody>
</table>

Table 7.1
Optimum deposition parameters for maximum UV reflectance of thermally evaporated aluminium thin film coatings at λ>220 nm
Experimental data reproduced from references 7.1, 7.2, 7.3

The basic requirements for thermal evaporation are that the residual gas pressure be sufficiently low so that the mean free path of the evaporated atoms is larger than the source-substrate distance and that the rate at which the substrate is peppered with residual gas atoms be much less
than the rate coming from the evaporating source. The source material is usually evaporated from an electrically heated metallic boat of tungsten or molybdenum or alternatively direct electron beam heating of the source material contained in a water cooled metallic boat. The UV reflectance of thermally evaporated aluminium thin film coatings appears to be very sensitive to the presence of impurities. The requirement for a high deposition rate and a low background pressure therefore helps to minimize the effect of residual gas atoms, particularly oxygen. These deposition conditions also appear to produce a more compact film structure making the film less susceptible to further oxidation when the vacuum chamber is vented to air, (7.2). The high deposition rate also reduces the time for atomic orientation of the aluminium on the substrate surface restricting the growth of crystallites and so maintaining a low scatter surface. At pressures of $10^{-8}$ mmHg a proportionately lower aluminium evaporation rate has been found to be acceptable, (7.4). This rather low pressure is not readily achievable with most coating systems. At pressures of $10^{-5}$ mmHg the high constant deposition rate should be achieved prior to opening a shutter over the substrate, in this way other components within the vacuum chamber are coated with aluminium which form a fresh oxide surface and so reduce the partial pressure of the oxygen.

The minimum aluminium film thickness is determined by the skin depth for the penetration of the incident radiation. Assuming the refractive index of the aluminium is given by

$$N = n - ik$$  

where $n$ is the real part of the index and $k$ the imaginary part, the intensity skin depth is given by

$$\frac{1}{\alpha} = \frac{\lambda}{4\pi k}$$

where $\alpha$ is the absorption coefficient. The experimental
values of \( n \) and \( k \) have been measured on high quality aluminium films in the UV and visible wavelength range, (7.5). The data is reproduced graphically in figure 7.2. Using this data, the complex refractive index of high quality aluminium thin films at 248 nm is \( N = 0.175 - 12.7 \) giving a penetration depth of 7.3 nm from equation 7.2 and a reflectance of 91.9% at normal incidence, (see appendix IV). The minimum film thickness of 50 nm therefore corresponds to an internal film transmittance, \( e^{-50/7.3} \) of 0.1%. Thinner film thicknesses may be useful for excimer laser use as a beamsplitter at 248 nm if the substrate is non-absorbing. Stable, high quality aluminium films have been made with thicknesses down to 10 nm corresponding to an internal transmittance at 248 nm of 25%, (7.5).

The maximum aluminium film thickness is limited by the formation of large film crystallites resulting in increased scatter. The limiting thickness at a high deposition rate is about 700 nm for wavelengths beyond 220 nm reducing to a limiting thickness of about 500 nm for vacuum UV wavelengths.

Experiments have shown that source material purities of 99.99% are needed to maximize the vacuum UV reflectance of aluminium thin films, (7.3). At 220 nm the reflectance has been observed to decrease from 92% to 87% in going from 99.99% purity to 99.5% purity under identical coating conditions, (7.3) The main impurities in the aluminium source material were found to be iron, copper and silicon. Other potential sources of impurity arise from the evaporation boat and the substrate. The evaporation boat may contribute impurities of tungsten or molybdenum for thermal evaporation or a more likely case being material remaining in the boat from other coating runs.

The effect of the vapour incidence angle for thermal evaporation has been studied at high deposition rates and low pressures, \( (30 \text{ nms}^{-1} \text{ and } 10^{-5} \text{ mmHg}) \) and at low deposition rates and high pressures, \( (1 \text{ nms}^{-1} \text{ and } 10^{-4} \text{ mmHg}) \), (7.3). In the former case at wavelengths beyond 220 nm the reflectance of the film remained above 90% out
FIGURE 72

VARIATION OF THE COMPLEX REFRACTIVE INDEX \((n-ik)\)
WITH WAVELENGTH FOR HIGH QUALITY ALUMINIUM THIN FILMS.
DATA TAKEN FROM REFERENCE 7.5.
to vapour incidence angles of 60 degrees for film thicknesses up to 60 nm and 30 degrees for a film thickness of 200 nm. The poorer evaporation conditions resulted in a reflectance for thin and thick films which was very sensitive to the vapour incidence angle decreasing by about half for an angle of 60 degrees. The angle sensitivity was higher at vacuum UV wavelengths and so a design aim should be to use vapour incidence angles less than 30 degrees.

The substrate preparation has been found to have an important influence on the laser damage threshold of the metallic film in the vacuum UV and also the pinhole density, (7.4, 7.6). Apart from the usual chemical cleaning procedures, exposure of the substrate to a glow discharge for 5 - 10 minutes prior to coating has been found to greatly improve the damage threshold of the aluminium film at the ArF excimer wavelength of 193 nm, (7.6). This is probably because the glow discharge precleans the substrate and provides an ion bombarded surface which improves the adherence of the aluminium to the glass. The end result being a better reflectance uniformity, a greater mechanical strength and a reduced pinhole density.

Many materials including aluminium have a better adherence if they are deposited on a heated substrate. However, with aluminium, an increased substrate temperature results in an increased crystallite size which is observed as a surface roughness. This effect is greater at vacuum UV wavelengths, with thick films deposited at low deposition rates, (7.3). As an example the reflectance at 248 nm was observed to decrease from 92% to 90% in going from a substrate temperature of 303 K to 423 K for a coating deposited at 30 nms⁻¹. The same two substrate temperatures resulted in a reflectance decrease from 74% to 63% when the deposition rate was 1 - 2 nms⁻¹.

The substrate roughness is an important factor in producing aluminium reflectors for use in the vacuum UV since the scattering is very sensitive to wavelength. The
surface roughness and resulting scattering from the aluminium film has a contribution transmitted from the substrate and an intrinsic contribution arising from the aluminium film roughness itself, (plus an intrinsic contribution from any dielectric overcoat layer). Vacuum UV aluminium mirrors therefore tend to be deposited on room temperature substrates to minimize the crystallite size and intrinsic scatter from the coating.

The substrate roughness has also been found to greatly influence the formation of surface plasmon waves in the metal film, (7.7, 7.8). This effect has been observed experimentally as a resonance-like decrease in the specular reflection and can be enhanced by undercoating the metal film with a thick dielectric layer which increases the roughness of the metal film. A further enhancement of the resonance effect and a shift to longer wavelengths has been observed by overcoating the metal film with a thin dielectric layer, (7.8). In this situation, the prevention of the formation of an absorbing oxide layer using a dielectric overcoat can be more than compensated by the enhanced surface plasmon wave. The roughened surface contour is considered as a superposition of many 2D Fourier frequency components some of which efficiently couple the incident light into the surface plasmon wave.

The observation of a significant decay in the specular reflectance of a freshly deposited aluminium thin film at wavelengths shorter than 200 nm whilst still in the vacuum chamber is attributed to the formation of a thin absorbing oxide layer, (7.3). The decay in the reflectance is strongest in the vacuum UV where the oxide is highly absorbing and appears to go through two decay stages, (7.9). An initial fast decay rate lasting about 75 s was followed by a slower decay lasting about 40 minutes. The decay rate can be reduced by using a lower residual pressure or increased by the admission of either oxygen or air into the vacuum chamber within the first few minutes of forming the coating. At this stage the oxide layer thickness is considered to be between 2 - 5 nm.
Dielectric overcoats are usually added to the freshly deposited aluminium to prevent the oxide formation and therefore to maintain a high vacuum UV reflectance. A system of shutters is usually used so that the dielectric coating can be deposited on the aluminium within seconds to minimize the oxide formation time. A third stage decay in the vacuum UV reflectance of bare aluminium films has been observed over a time scale of several months and can be enhanced by storage at high humidity and exposure to ultraviolet radiation, (7.3). Films deposited at lower rates and higher pressures are more susceptible to this latter stage, presumably the more open film structure encouraging a slow oxide layer growth. At all three stages the reflectance was not observed to significantly decay at wavelengths beyond 220 nm coinciding with the absorption edge of aluminium oxide. The main reason why aluminium films are overcoated at wavelengths longer than 220 nm is that the aluminium film is very soft and easily damaged making cleaning extremely difficult. Using suitable coating thicknesses and materials the reflectance can be enhanced above that from the pure metal, this aspect is considered in section 7.2b.

7.2a1i Theoretical considerations

Theoretical calculations on the reflectance of bare metal mirrors and overcoated metal mirrors are considered in detail in appendix IV. In general the amplitude reflection coefficient $r$ is given by

$$r = \rho \exp(i\delta)$$

where $\rho$ is the magnitude of the reflection coefficient and $\delta$ is the phase change of the reflected light. The intensity reflection coefficient $R$ is given by

$$R = rr^*$$

where the asterisk represents the complex conjugate.
Substituting equation 7.3 in equation 7.4 gives

\[ R = \rho^2 \]

Each of the equations, 7.3 - 7.5 can have the subscript \( s \) or \( p \) representing the component of the electric field perpendicular or parallel to the plane of incidence. The calculated reflectance of an aluminium coating at 248 nm whose refractive index is given by \( N = 0.175 - 12.7 \) as a function of the incident angle is shown in figure 7.3. The metal coating thickness is assumed to be sufficient so that multiple reflections within the metal film are greatly attenuated and hence can be ignored in the calculations. At or near normal incidence the reflectance is 91.9%. The \( s \) and \( p \) components are not very sensitive to incident angle changes. The average reflectance, \( \langle R_s + R_p \rangle / 2 \) representing unpolarized light is relatively constant out to incident angles of 70 degrees. The phase change \( \delta \) as a function of the angle of incidence is shown in figure 7.4. At normal incidence in air the phase change is 140 degrees. This compares with a perfect dielectric where the phase change for normal incidence in air is 180 degrees. The phase change on reflection from a metal (or any material with a complex refractive index) is dependent on the refractive index of the incident medium, the angle of incidence and the complex refractive index of the metal.

The calculated effect at normal incidence on the reflectance of an aluminium coating at 248 nm of a varying aluminium oxide layer thickness is shown in figure 7.5. The refractive index of the aluminium coating is taken as \( N = 0.175 - 12.7 \). The refractive index of stoichiometric aluminium oxide, \( \text{Al}_2\text{O}_3 \) at 248 nm is about 1.7, (7.10). It is uncertain if the naturally grown oxide layer is stoichiometric and so calculations are included for the refractive index range \( n = 1.5 - 2.0 \). The reduction in reflectance for a 4 nm thick oxide layer with a refractive index of 1.7 is about 1.2%. The calculated reflectance is not very sensitive to the chosen values of \( n \) and \( k \) for
Figure 7.3

Theoretical reflectance of Al coating in air
(Refractive index N = 0.175-12.7)
FIGURE 7.4
CALCULATED PHASE CHANGE $\delta$ ON REFLECTION FROM Al COATING IN AIR, $n=0.175-\iota 27$ FOR Al.
FIGURE 7.5

VARIATION OF REFLECTANCE AT NORMAL INCIDENCE WITH Al. OXIDE LAYER THICKNESS, (λ = 2.48 nm)
aluminium. Assuming an oxide layer thickness of 4 nm and an index of 1.7; at normal incidence a 20% variation in k \((2.7 \pm 0.54)\) results in a reflectance variation from 86.5% to 93.3%. Similarly a 20% variation in n \((0.175 \pm 0.035)\) results in a reflectance variation of 90.75 ±1.8%. The presence of the thin oxide layer has little influence on the angular performance and is excluded from figure 7.3 for clarity. The s and p components closely follow those for the bare metal surface. At small angles of incidence the main effect is a small shift downwards of 1.2%.

At vacuum UV wavelengths an alternative to preventing oxide formation is to use the aluminium coating as a back reflector where the light travels through the substrate and onto the aluminium. This option is considered in appendix IV where the multiply reflected beams are added on an intensity basis. The calculated angular dependence of the reflectance is shown in figure 7.3 at a wavelength of 248 nm using a fused silica substrate with refractive index 1.5085. The main effect is a reduction of the normal reflectance to 89.6%. Aluminium coatings have been used in this way as mirrors at 193 nm. In this case it was found essential to run an ac glow discharge to clean the substrate prior to deposition to achieve an acceptable damage threshold for in-cavity use at the ArF wavelength of 193 nm.

If the oxide layer, \((n = 1.7)\) grows to a thickness of about 24 nm it can act as an anti-reflection coating for the aluminium mirror at 248 nm. The reduction in reflectance is greater with high index overcoats as shown in figure 7.5. The optical thickness of the overcoat for minimum reflectance is not a quarter wave because the reflectance at the metal surface even at normal incidence is not 180 degrees.

7.2aiii Experimental results with bare aluminium mirrors

Experimental tests were performed to confirm some of the optimum deposition parameters for aluminium considered in section 7.2ai. Thermally evaporated aluminium films were deposited near normal incidence at a pressure of 2 x
$10^{-5}$ torr on cleaned glass microscope slides using a heated, helical tungsten wire as the electrode. Various lengths of 99.9% purity aluminium wire were evaporated at different rates. The film thickness, (measured with a tallystep machine) and reflectance at 248 nm were measured for each sample. A reflectance of over 90% at 248 nm was achieved when the deposition rate was about 100 nm/s with film thicknesses varying from 60 - 80 nm.

Two batch runs of aluminium coatings deposited on microscope slides were also produced using the sputter deposition process, (7.11). This technique involved pumping the vacuum chamber down to $10^{-5}$ torr and then back filling it with argon to a pressure of $2.5 \times 10^{-3}$ torr. An rf glow discharge in the argon was used to sputter the planar aluminium target resulting in deposition of aluminium neutrals and ions onto the near-by substrate. The deposition rates are generally much lower for sputtered coatings compared to thermal evaporation. In the case of aluminium the deposition rate was 1.5 nm/s. The initial batch had a thickness of about 30 nm and all of the samples had a reflectance of about 72% at 248 nm. A similar reflectance figure was measured at the helium neon laser wavelength of 632.8 nm. The refractive index of these coatings was measured using an ellipsometer at 632.8 nm which gave $N = (2.8 \pm 0.2) - i(4.7 \pm 0.2)$. This figure is very different to the literature value at 632.8 nm of $N = 1.37 - 17.61$, (7.5). The discrepancy was traced with an SEM/TEM microprobe to the presence of 0.5 - 1% iron impurity in the aluminium coating. The origin of the impurity was traced to the sputtering of some metal pipes adjacent to the planar aluminium target, (7.11). A second batch of aluminium mirrors had reflectances of over 90% at 248 nm when the iron impurity was absent.

The reflectance of the thermally evaporated and impurity free sputtered coatings at 248 nm showed no decrease over a 50 day period and no change as a result of irradiating the surface at low levels with 248 nm excimer radiation. The avoidance of dust forming on the
microscope slides after they had been cleaned helped reduce the pinhole density in the aluminium coating. A general observation was that the coatings with the lowest pinhole density gave the highest reflectance at 248 nm.

7.2b Dielectric overcoating of aluminium mirrors for use at UV wavelengths

7.2b1 Theoretical performance of overcoated aluminium mirrors

Beyond 220 nm, single layer dielectric overcoats on aluminium mirrors are primarily used to protect the soft metal surface and boost the reflectance above that of the bare metal. A computer programme has been written based on the analysis described in appendix IV to calculate at any angle of incidence the reflectance of a thick metal film overcoated with an absorbing dielectric material with refractive index $n_1 - ik_1$. The calculated reflectance at the excimer wavelength of 248 nm at normal incidence as a function of the overcoat layer thickness for a high and low index material ($n_1 = 1.70$ and 1.38) is shown in figure 7.6. As used previously, the assumed index for aluminium is $0.175 - 12.7$. Plots are also given to show the effect of a complex index for the overcoating layer with the same real components and $k_1 = 0.01$. An absorbing overcoat layer results in the local average reflectance decaying with film thickness. If the overcoat layer has no absorption, ($k_1 = 0$), the variation of the reflectance at normal incidence with the coating layer thickness is periodic. In this case the local reflectance minima and maxima are independent of the film thickness. The stationary points, $\langle$reflectance minima and maxima$\rangle$ in the more general case, ($k_1 \neq 0$) are considered in appendix IV. The analysis reduces to the condition for which the total admittance of the film and substrate has a real value. At normal incidence this is given by

$$
\tan(2\Delta_1) = 2(n_1 k_2 - n_2 k_1)/A + 2k_1(k_1 k_2 + n_1 n_2)/(n_1 A \cos(2\Delta_1)) \quad 7.6
$$
FIGURE 7.6
VARIATION OF REFLECTANCE OF AN ALUMINIUM MIRROR WITH DIFFERING OVERCOAT INDICES AND THICKNESSES (NORMAL INCIDENCE, $\lambda=248\text{nm}$, $N_{AL}=0.175-2.71$).
where the subscripts 1 and 2 refer to the refractive indices of the overcoating and substrate respectively and $\Delta_1$ is the phase term at normal incidence given by

$$\Delta_1 = 2\pi n_1 d/\lambda \quad 7.7$$

and d the film thickness. The term $A$ in the denominator is given by

$$A = n_1^2 + k_1^2 - n_2^2 - k_2^2 \quad 7.8$$

If $k_1 = 0$ then equation 7.6 simplifies and can be solved analytically to give

$$\Delta_1 = 1/2. \arctan[2k_2n_1/(n_1^2 - n_2^2 - k_2^2)] + mn/2 \quad 7.9$$

where $m = 0, 1, 2, 3,...$ etc. Equation 7.9 is identical to that given by Macleod, (7.12). The arctan term in equation 7.9 is the phase change on reflection from a surface with complex index $n_2 - ik_2$, (the metal surface) from an incident medium with index $n_1$, (the overcoating). The denominator in equation 7.9 is usually negative for metals and so for $m = 0$ the arctan angle is greater than $\pi/2$ radians. The phase change on reflection from an aluminium surface in air, ($n_1 = 1.0$), as a function of the angle of incidence is shown in figure 7.4. The reflectance minima and maxima in figure 7.6 correspond to the case where multiple reflections from the metal surface are $\pi$ out of phase (as occurs initially) or in phase. The first turning point occurs at an optical thickness for the overcoating somewhat less than a quarter wave whereas that for a dielectric combination occurs at an optical thickness of exactly a quarter wave. The overcoating at this point can be thought of as having an effective optical thickness of a quarter wave when the phase change on reflection from the metal plus the phase change from the double transit though the film are combined. The overcoating thickness, d calculated from equations 7.7 and 7.9, (using $m = 0$ and 1) and the corresponding reflectance
minima and maxima for $n_1 = 1.0, 1.38, 1.70$, and $k_1 = 0$ are shown in Table 7.2.

<table>
<thead>
<tr>
<th>$n_1$</th>
<th>$R(\text{min})/%$</th>
<th>$d(\text{min})/\text{nm}$</th>
<th>$R(\text{max})/%$</th>
<th>$d(\text{max})/\text{nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>91.92</td>
<td>-</td>
<td>91.92</td>
<td>-</td>
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<td>81.99</td>
<td>23.455</td>
<td>93.37</td>
<td>59.93</td>
</tr>
</tbody>
</table>

Table 7.2

Theoretical reflectance minima and maxima at 248 nm and normal incidence for aluminium mirrors overcoated with a dielectric thin film

The reflectance maxima occur when the coating has an effective thickness of half a wave, or a multiple of this. The theoretical reflectance increase is only marginally greater than that for an uncoated surface, being about 0.8% for $n_1 = 1.38$ and 1.5% for $n_1 = 1.70$ at 248 nm. A high index overcoat layer can potentially achieve a higher reflectance but requires a better coating thickness control since the reflectance minima are lower and the periodicity shorter than for low index materials. These points are illustrated in Figure 7.6 where the reflectance near the maxima are greater than 90% for a thickness variation of ±25 nm around the peak for $n_1 = 1.38$ and ±18 nm for $n_1 = 1.70$. A low index overcoat is therefore more tolerable to coating thickness errors. The effect of having an absorbing overcoat layer with $k_1 = 0.01$ and the same values of $n_1$ are also shown in Figure 7.6. The average level of the reflectance now decreases with increasing coating thickness as expected. However, an effective coating thickness of a single half wave for a high index material with $k_1 = 0.01$ can still achieve a reflectance near to 90%.

The reflectance maxima can be increased above those shown in Table 7.2 by using quarter wave pairs of low index, $n_l$ and high index, $n_h$ materials deposited on the aluminium. The low refractive index material is deposited on the metal and must have an effective quarter wave
thickness so that the light reflected from the H-L interface is in phase with the light reflected from the L-metal interface. This approach is exactly what used to produce an all dielectric high reflector except that a high reflectance can be achieved with fewer layers. A useful approximation at normal incidence to calculate the reflectance, \( R_J \) for \( J \) quarter wave layer pairs (LH), has been developed from the analysis given by Macleod, (7.12). The reflectance in this case is approximately given by

\[
R_J = 1 - A / (n_h / n_l)^{2J}
\]  

7.10

where \( A \) is the absorption for an uncoated surface (\( J = 0 \)). The reflectance increases with the refractive index ratio \( n_h / n_l \) and the number of layer pairs. Assuming the high index material has \( n_h = 1.70 \) and the low index material \( n_l = 1.38 \) a single layer pair, \( J = 1 \) has a reflectance of 94.7% and a double layer pair has a reflectance of 96.5%.

7.2bii Dielectric overcoating materials for aluminium mirrors

Suitable dielectric overcoatings for aluminium mirrors at UV wavelengths are restricted to those materials in thin film form which have relatively low absorption. The criterion of \( k_1 < 0.01 \) can be used for this application from the theoretical calculations considered in section 7.2bi. This corresponds to an absorption coefficient at 248 nm of less than about 5000 cm\(^{-1}\). This criterion is perhaps a factor of ten higher than that required for multi-layer dielectric mirrors where the total coating thickness is much greater. A review of the most widely used low absorption dielectric materials for excimer laser mirrors is given in chapter 8. At vacuum UV wavelengths, (\( \lambda < 200 \) nm) LiF and MgF\(_2\) are the most popular overcoating materials for aluminium mirrors, (7.13). MgF\(_2\) is deposited in thin film form with a high tensile stress and LiF is considered hydroscopic. Both of these materials are soft, low index materials when
deposited onto room temperature substrates. Although MgF$_2$ has a smaller band-gap than LiF it has been shown to have a higher packing density when deposited onto a heated substrate, (7.14). This results in a reduced susceptibility to environmental changes arising from moisture absorption and also makes the coating harder therefore making cleaning easier. The refractive index of MgF$_2$ thin films is also dependent on the packing density because a low packing density can result in moisture absorption into the film voids.

The most popular overcoating for aluminium mirrors in the visible range is silicon oxide, SiO$_x$, the stoichiometry being sensitive to the deposition conditions, (7.12). Thermal evaporation of silicon oxide, SiO at low pressures and high deposition rates has been shown to result in a film with $x \approx 1$ and which is highly absorbing in the blue and UV regions, (7.10). Thermal evaporation of silicon oxide at low deposition rates and higher pressures has been shown to result in a more oxidized film with $x \approx 1.5$ but still showing absorption below 300 nm, (7.10). Low level ultra-violet irradiation of partially oxidized films on aluminium mirrors has been found to greatly increase the reflectance in the wavelength range 200 - 300 nm. This phenomenon is described in detail in section 7.4 and offers an inexpensive method of producing UV reflecting mirrors. Laser induced damage studies at 193 nm and 248 nm of these partially oxidized films has resulted in interesting ripple pattern formations which are described in section 7.5.

Silicon dioxide, SiO$_2$ and aluminium oxide Al$_2$O$_3$ have been produced in stoichiometric thin film form by reactive electron beam evaporation of the source material in the presence of oxygen, (7.10). These oxides form hard, high packing density films even at a substrate temperature of 303 K and have negligible absorption at 248 nm, (7.14). The absorption edge for SiO$_2$ is around 200 nm and for Al$_2$O$_3$ around 220 nm. It is the experience of the author that many manufacturers of aluminium mirrors for UV
use produce a MgF$_2$ overcoat layer deposited on a room temperature substrate. Beyond 220 nm an alternative choice from MgF$_2$ is Al$_2$O$_3$. It has a higher index and therefore higher reflectance, (see figure 7.6) and a higher packing density and hardness when deposited on a substrate at room temperature. The oxide also shows a high degree of adherence to the aluminium. The main disadvantage is that the higher index has a lower film thickness tolerance and therefore requires better control. A variation on this theme is the use of ThF$_4$ which has a relatively high refractive index at 248 nm, (n = 1.58), a good adherence to aluminium and a high packing density when deposited onto a substrate at room temperature, (7.15). A major disadvantage of using ThF$_4$ is that thorium is radioactive and great care is needed to ensure that no thorium containing dust is ingested when the vacuum chamber is cleaned. A high index fluoride which has not been used extensively for UV operation is LaF$_3$ with a refractive index of about 1.59 at 248 nm.

The reflectance at an incidence angle of ten degrees of several commercially produced aluminium mirrors with MgF$_2$ or ThF$_4$ overcoats was measured with the excimer laser operating at 248 nm. The reflectance was found to vary widely in the range 50 - 90%. A second series of aluminium mirrors overcoated with a whole range of materials and thicknesses were specified to the Clarendon laboratory, (7.6) and Culham laboratories, (7.4). These mirrors all had near normal incidence reflectances of over 90% at 248 nm and are considered in detail in section 7.3b. The low reflectance mirrors probably arose from either too low a deposition rate or too thick a coating for the aluminium. An interesting phenomenon is shown in figure 7.7 where the reflectance of two aluminium mirrors with fused silica substrates and ThF$_4$ overcoats are shown as a function of the incidence angle. Experimental measurements are shown for mirror A whose reflectance was measured through the overcoating and has a value of 89% at 10 degrees and mirror B with measurements made both through the substrate and the overcoating layer. The
FIGURE 7.7

REFLECTANCE AT 248nm VERSUS ANGLE OF INCIDENCE FOR TWO ThF₄ OVERCOATED ALUMINIUM MIRRORS.
reflectance of mirror B is clearly much lower than that of mirror A. Similar measurements were made though the overcoating layer for a second identical pair of mirrors produced on a BK-7 glass substrates made at the same time as mirrors A and B. The reflectance at a given angle was measured using the incident and reflected pulse energy averaged over 30 pulses. The aluminium coating thickness for mirror A was 200 nm and for mirror B 500 nm, (7.15). The corresponding ThF$_4$ overcoat thicknesses for mirrors A and B was equivalent to $\lambda/2$ and $3\lambda$ at normal incidence, (7.15). These thicknesses equate to $m = 1$ and $m = 11$ in equation 7.9.

A reasonable fit to the data for mirror B for the measurements made through the substrate was found for $n_2 = 0.65$ and $k_2 = 2.4$. A trial and error method was used to calculate these values from the analytical expressions given in appendix IV. The average value of the reflectance is plotted in figure 7.7 given by $R = (R_\theta + R_p)/2$ for unpolarized light. These $n_2$ and $k_2$ values for the aluminium coating were then used in equation 7.6 to calculate the ThF$_4$ overcoat thickness, $d$ assuming a real index $n_1 = 1.58$. Equation 7.6 cannot be solved analytically for $k_1$, a simple iteration process was therefore used with an initial estimate for $\Delta_1$ calculated by taking $k_1 = 0$. As the assumed value for $k_1$ decreases the solution of equation 7.6 for $d$ increases and rapidly approaches the asymptotic value for $k_1 = 0$ given by equation 7.9, (with $m = 0$). The difference in the optimum overcoating layer thickness between $k_1 = 0$ and $k_1 = 0.1$ using these parameters is 0.7%. The layer thickness for all practical purposes, $<k_1 = 0.001 - 0.01>$ is therefore given by equation 7.9, which can be solved analytically. In this case the calculated thickness for a $3\lambda$ overcoat layer using these parameters is 456.9 nm. This figure was then used to calculate the expected angular performance of the mirror with the light incident through the film using $k_1$ as a fitting parameter. The results shown in figure 7.7 indicate that $k_1 = 0.01$ gives a reasonable fit to the data. A similar exercise was
followed for mirror A, in this case the aluminium coating index was assumed to be given by \( n_2 = 0.175 \) and \( k_2 = 2.7 \) as used previously. The effective \( \lambda/2 \) thickness of the ThF\(_4\) overcoating is calculated as 65.3 nm for \( n_1 = 1.58 \). A reasonable fit to the data is again obtained for \( k_1 = 0.01 \). These calculations suggest the low reflectance for mirror B fundamentally arises from the change in the optical constants \( n_2 \) and \( k_2 \) which was probably caused by the much greater thickness of the metal film compared to mirror A. The reduction in the reflectance of mirror B to 23\% at an incidence angle of about 40 degrees is simply an interference phenomena where the effective film thickness acts as an anti-reflection coating.

7.3 Laser damage studies of aluminium mirrors at 248 nm

7.3a Laser induced melt thresholds of aluminium mirrors

Laser light is absorbed in metals by the interaction of photons with free electrons. The collision rate of excited electrons with lattice phonons in a metal at room temperature is greater than \( 10^{13} \) s\(^{-1}\). For laser pulsewidths in the nanosecond region many electron-phonon collisions can occur during the laser pulse and the absorbed energy can be considered instantaneously transferred into thermal energy. The resulting temperature rise due to absorption of laser radiation in a semi-infinite medium with boundary at \( z = 0 \) has been considered previously, (7.16,7.17,7.18,7.19). The heat flow equation for heating without phase change is given by

\[
\nabla^2 T(x,y,z,t) - \frac{1}{\rho c} \frac{\partial T(x,y,z,t)}{\partial t} = -\frac{A(x,y,z,t)}{K} \quad 7.11
\]

where \( T \) is the temperature as a function of position \( (x,y,z) \) and time \( t \), \( K \) the thermal conductivity and \( x (= K/\rho c) \) is the thermal diffusivity. The source term \( A \) is the heat production per unit volume per unit time. Equation 7.11 is valid for an isotropic medium whose thermal properties are independent of temperature. The heat loss to the surroundings by thermal re-radiation and
convection is considered negligible for most cases of practical interest involving nanosecond pulsed lasers, (7.18). The solution to equation 7.11 cannot be solved explicitly for all functions \( A(x,y,z,t) \) representing actual laser temporal and spatial profiles. A major simplification is to assume the spatial and temporal profiles to be separable in the mathematical sense. This assumption may not be valid for multi-mode lasers. A second simplification occurs if the transverse dimensions of the focused beam are large compared with the distance to which heat is conducted during the time of the laser pulse. In this case equation 7.11 simplifies to a \( z \) and \( t \) dependence since there is no significant temperature or source term dependence in the radial direction. Using these simplifying assumptions the source term becomes, (7.18).

\[
A(z,t) \approx (1-R)I(t)e^{-\alpha z} \tag{7.12}
\]

where \( R \) is the reflectance of the surface, \( I(t) \) is the incident intensity and \( \alpha \) the absorption coefficient. The simplest solution arises when the intensity is constant, given by \( I(t) = I_0 \) for \( t > 0 \). The intensity function is therefore represented as a step function at \( t = 0 \) to a constant value \( I_0 \). Using these simplifying assumptions the solution to equation 7.11 for a metallic like material where \( \alpha \approx 1 \), (typically \( \alpha \approx 10^5-10^6 \text{cm}^{-1} \) for metals), is given by, (7.18).

\[
T(z,t) = T_a + \left[ 2I_0(1-R)(xt)^{1/2}/K \right] \text{erfc}\left(\frac{z}{(4xt)^{1/2}}\right) \tag{7.13}
\]

where \( \text{erfc} \) is the integrated complementary error function and \( T_a \) the ambient temperature. The integrated complementary error function decreases in an exponential like way from its maximum value at \( z = 0 \). A convenient measure of the heat conduction distance for a time \( t \) is
the thermal diffusion length given by

\[ z = (4 \pi t)^{1/4} \]  \hspace{1cm} 7.14

At a distance \( z \) given by equation 7.14 the complementary error function decreases to about one tenth of its initial value and is representative of the distance to which heat is conducted and the temperature increased above the ambient. The requirement for a full 3-D analysis given by equation 7.11 therefore arises when the radial dimensions of the thermal source term are comparable to the thermal diffusion length given by equation 7.14. The temperature rise \( \Delta T(z, t) = T(z, t) - T_a \) is a maximum at the surface where \( z = 0 \), in this case equation 7.13 simplifies to

\[ \Delta T(0, t) = \left[ 2I_0(1 - R)/K \right](\pi t/\tau)^{1/4} \]  \hspace{1cm} 7.15

Equation 7.15 expresses the temperature rise for an incident constant intensity \( I_0 \) and can also be used to calculate the maximum temperature rise for a rectangular pulse by substituting \( t = t_p \) where \( t_p \) is the pulse duration. A non-rectangular pulse can be simply represented by its equivalent pulse duration \( \Delta \) as described in section 3.4c. A more sophisticated approach uses the Duhamel integral theorem which essentially divides the actual temporal profile into a series of narrow steps of differing height and uses equation 7.13 to calculate the temperature profile after each step. A pulse shape factor \( \beta \) is introduced which represents the deviation from equation 7.15 due to a non-rectangular pulse profile. The incident fluence, \( F_m \) for a given pulse duration \( t_p \) required to raise the surface temperature to its melting temperature is therefore given by

\[ F_m = \left( I_0 t_p \right)_m = \left\{ \left[ \beta (T_m - T_a) (\pi \rho \sigma C) \right]^{1/4} / 2 (1 - R) \right\} \left( t_p \right)^{1/2} \]  \hspace{1cm} 7.16

where \( \beta = 1 \) for a rectangular pulse of width \( t_p \) and peak
height $I_0$. In the case of a symmetrical Gaussian pulse with the same peak intensity and FWHM as the rectangular pulse $\beta \approx 0.666$, (7.20). A smoothed triangular pulse with the same peak intensity and FWHM gives $\beta \approx 1.9$. The latter figure was calculated from the results given in reference 7.18 for a triangular temporal pulse profile whose falltime is 4.8 times longer than the risetime. A triangular pulse with a long tail deposits its energy over a longer timescale and therefore the incident fluence required to raise the surface to some threshold temperature is higher. Equation 7.16 with $\beta = 1.0$ has been used previously with some success to predict laser damage thresholds at CO$_2$ laser wavelengths for copper, molybdenum and stainless-steel mirrors, (7.19). Equation 7.16 predicts a $t^{1/6}$ dependence of damage fluence with pulsewidth. The value of $\beta$ is dependent on the pulse shape and the spot size for nanosecond pulses. As the focused spot size decreases, radial diffusion may become significant requiring a full 3-D analysis which results in an increased value of $\beta$.

Table 7.3 gives some of the relevant thermal properties of aluminium, copper and fused silica at room temperature, (7.21). The thermal diffusion length is calculated assuming an equivalent rectangular pulse width, $\Delta$ of 24 ns.

The thermal diffusion length in aluminium or copper of around 3 $\mu$m is about a factor of ten higher than that for fused silica. This simple 1-D analysis is therefore valid until the focused laser spot size is in the micron region. If the laser spot size is much larger than this the temperature rise in the $x,y$ plane can be calculated from equation 7.15 using the local intensity $I_0(x,y)$ at that point. The temperature profile therefore follows the spatial profile of the beam in the $x,y$ plane. In general the thermal properties are temperature dependent. In the case of aluminium, over the temperature range 293 - 933 K the thermal conductivity decreases by about 10%, the density decreases by about 5% and the specific heat capacity increases by about 10%, (7.21,7.22). Similar
<table>
<thead>
<tr>
<th>Property</th>
<th>aluminium</th>
<th>copper</th>
<th>fused silica</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point $T_m / K$</td>
<td>933</td>
<td>1357</td>
<td>2073</td>
</tr>
<tr>
<td>Boiling point $T_b / K$</td>
<td>2740</td>
<td>2848</td>
<td>2683</td>
</tr>
<tr>
<td>Thermal conductivity, $K/Wcm^{-1}K^{-1}$</td>
<td>2.38</td>
<td>3.85</td>
<td>0.014</td>
</tr>
<tr>
<td>Density, $\rho/gcm^{-3}$</td>
<td>2.71</td>
<td>8.96</td>
<td>2.2</td>
</tr>
<tr>
<td>Specific heat capacity, $C/Jg^{-1}K^{-1}$</td>
<td>0.913</td>
<td>0.385</td>
<td>0.75</td>
</tr>
<tr>
<td>Thermal diffusivity, $x=K/\rho C/cm^2s^{-1}$</td>
<td>0.979</td>
<td>1.1160</td>
<td>0.008484</td>
</tr>
<tr>
<td>Diffusion length, $l=(4x\Delta)^{1/2}/\mu m$</td>
<td>3.065</td>
<td>3.27</td>
<td>0.285</td>
</tr>
<tr>
<td>Latent heat of fusion $Jg^{-1}$</td>
<td>397</td>
<td>205</td>
<td>237</td>
</tr>
<tr>
<td>Thermal expansivity $/10^{-6}K^{-1}$</td>
<td>23</td>
<td>17</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Table 7.3

Thermal properties of aluminium, copper and fused silica

(equivalent pulse duration = 24 ns)

Variations are also observed for copper. Melt threshold estimates are therefore calculated using the thermal properties at ambient temperature since the variation in $<\rho CK>^{1/6}$ is about 5%. The temperature dependence of the reflectance of metals such as silver, copper or aluminium at wavelengths beyond 1 $\mu m$ are in good agreement with the
free electron Drude model of a metal, (7.23). Assuming the results from the model are approximately valid at 248 nm the calculations suggest the reflectance of aluminium decreases linearly with temperature from 92% to 89.3% over the temperature range 293 to 933 K, (7.23). The experimental temporal profile shown in figure 3.8 suggests a close resemblance to a symmetrical Gaussian pulse but containing some high frequency oscillations near the peak. A correction factor of $\beta = 0.666$ is therefore appropriate in equation 7.16. Substituting the thermal properties of aluminium in equation 7.16 gives a melt threshold of $1.52 \text{ J cm}^{-2}$. This figure was calculated assuming an equivalent pulse duration of 24 ns and a high quality mirror with an average reflectance over the temperature range 293 - 933 K of 90.65%.

The variables in equation 7.16 can be conveniently grouped into thermal properties and the experimental variables of reflectance and pulsewidth. The options to substantially increase the melt threshold for a given pulsewidth are limited to operating the mirror at low temperatures, reducing the absorptance by increasing the reflectance or by modifying the thermal properties. In many situations operating the mirror at cryogenic temperatures is not practicable. The option to reduce the absorptance by increasing the over-all reflectance has been considered in section 7.2b1. Aluminium which has a low melting point is usually deposited in the form of a thin film to achieve a high reflectance in the ultraviolet. The option to modify the thermal properties of the thin aluminium film can be effectively achieved by depositing the aluminium coating on a semi-infinite metallic substrate. The thermal diffusion length in metals for a pulsewidth of 24 ns is much greater than the typical aluminium coating thickness of 0.1 µm as shown in table 7.3. A first order approximation is therefore to replace the thermal properties of aluminium in equation 7.16 with those of the substrate material. A "Figure Of Merit," FOM given by $(\rho CK)^{1/4}$ can be used to choose the best substrate material. The FOM normalized to that for
Substrate FOM Substrate FOM
(Normalized to Al) (Normalized to Al)

Pyrex 0.062 titanium 1.165
fused silica 0.063 copper 1.50
MgF₂ 0.131 platinum 1.89
Al₂O₃ 0.364 ruthenium 2.34
nickel 0.615 rhodium 2.77
chromium 0.69 niobium 3.30
molybdenum 0.75 tantalum 4.04
aluminium 1.00 silver 4.14
gold 1.03 zirconium 1.11

Table 7.4
Figure of merit, \( \langle \rho CK \rangle^{1/6} \) normalized to aluminium for several substrate materials.

Aluminium is given in table 7.4 for several candidate substrate materials. The density, thermal conductivity and specific heat capacity data used to calculate the FOM in table 7.4 were taken from references 7.20, 7.21, and 7.22. The exact analysis considered in section 7.3b for the uniform heating of a thin film on any substrate shows that the melt threshold over the FOM range 0 - 2.5 is approximately linear and given by

\[
F_m = (0.96 \langle \text{FOM} \rangle + 0.07) F_{al} \tag{7.17}
\]

where \( F_{al} \) is the melt threshold for aluminium given by equation 7.16 for a semi-infinite substrate. Equation 7.17 was calculated using an aluminium coating thickness of 100 nm. As the FOM decreases the second term in equation 7.17 becomes dominant and the heating of the film can be considered adiabatic. If the FOM>2.5 the melt threshold begins to saturate and is no longer a linear function of the FOM as given by equation 7.17. The FOM values are to be considered approximate because of the
temperature dependence of \( \rho, C \) and \( K \). The highest FOM relative to aluminium is that for silver with a value of 4.14. The use of silver as a substrate material for the aluminium coating offers the potential to increase the melt threshold by a factor of 3.74 from a calculated value of 1.52 J cm\(^{-2}\) to 5.68 J cm\(^{-2}\). A substrate manufactured from solid silver would be very expensive. An alternative is to use a thick coating of silver deposited on a suitable substrate so that it behaves as though it was semi-infinite in extent. This requirement is satisfied when the silver coating thickness is greater than the thermal diffusion length in silver. The thermal diffusivity of silver is 0.17 cm\(^2\) s\(^{-1}\) giving a thermal diffusion length of 128 \( \mu \)m for a 24 ns pulse. A high quality silver coating of this thickness may be possible to manufacture using electroplating methods and subsequent diamond turning of the coating to achieve a high polish. This technique has been used to manufacture high quality silver mirrors for use in the infra-red, (7.23). A further problem is the presence of pinholes in the aluminium coating which could lead to high local absorption in the substrate. A limiting pinhole density of about 1 cm\(^{-2}\) has been suggested for aluminium mirrors, (7.4). A possible option to overcome this is to use a metallic undercoat beneath the aluminium which has a high FOM and a relatively high reflectance at UV wavelengths. The most likely choice is rhodium which has a FOM of 2.77 and a normal incidence reflectance at 248 nm of about 61%.

The damage threshold of two aluminium mirrors deposited on copper and nickel substrates has been measured. The measurements were made near normal incidence at the KrF wavelength of 248 nm. The experimental and theoretical results for the mirrors are summarized in table 7.5.
Substrate Reflectance Calculated Melt Experimental Damage Threshold
/\% Threshold/Jcm^{-2} of aluminium coating /Jcm^{-2}
copper 69\pm 4 0.68\pm 0.09 0.6 \pm 0.06
nickel 84\pm 3 0.59\pm 0.12 0.6 \pm 0.2

Table 7.5
Comparison of the damage threshold and calculated melt threshold of aluminium mirror coatings deposited on metal substrates.

The melt thresholds were calculated using $\beta = 0.666$, the "Figure Of Merit" for copper and nickel given in table 7.4 and the experimentally measured reflectance at 248 nm. The aluminium coatings were thermally deposited at a rate of 1 nms$^{-1}$ to a thickness of 20 - 25 nm, (7.24). This low deposition rate probably explains why the reflectance figures are also rather low. Both of the mirrors were overcoated with an effective half wave layer of MgF$_2$. Two damage thresholds were observed for each mirror. The lower threshold was about 0.2 Jcm$^{-2}$ for both mirrors and corresponded to the fluence required to initiate damage to the dielectric overcoat layer without damaging the metal coating. Between 0.2 and 0.6 Jcm$^{-2}$ the overcoating layer was ablated over a large area leaving the metal coating intact. Around 0.6 Jcm$^{-2}$ the appearance of the substrate helped identify laser induced damage to the aluminium. The agreement of the theoretical and experimental measurements suggests that the melt threshold model is valid on metal substrates and that the damage threshold of aluminium mirrors could be increased by depositing the aluminium on a suitable semi-infinite metallic substrate. The best substrate material from the thermal viewpoint is silver with the highest FOM of 4.14. The presence of pinholes in the aluminium coating from a single deposition suggests the mirror be produced in two or more stages so that the probability of a pinhole remaining throughout the
coating is very small. An alternative is to use rhodium as an undercoat layer which has an FOM of 2.77 and a relatively high reflectance of about 60% at 248 nm. The potential increase in the damage threshold of the mirror can only be realized if the damage threshold of any dielectric overcoating layer is at least equal to the melt threshold of the metal in the absence of the overcoating. A simple option would be to operate without a dielectric overcoat layer.

7.3b Laser induced damage thresholds of aluminium mirrors deposited on insulating substrates

Aluminium mirror coatings are usually deposited on insulating substrates such as glass or fused silica and often have a half-wave dielectric overcoat layer to protect the soft aluminium and boost the reflectance at the design wavelength. In this case the absorption of laser radiation in the aluminium coating is not equivalent to the limiting case of a semi-infinite thermal model as described in section 7.3a. In the limit when the substrate and overcoating layer are perfect insulators laser induced heating of the aluminium coating can be considered adiabatic if the dielectric overcoating is non-absorbing. This represents the lower limit of the threshold fluence required to raise the absorbing coating to its melting temperature. The upper limit arises when the coating can be considered semi-infinite in extent so that conduction in the z direction is significant. If the thickness of the absorbing film is greater than the skin depth for the absorption of the laser radiation but much less than the thermal diffusion length, the absorbing coating can be considered thermally thin and therefore uniformly heated throughout its depth. This situation arises with aluminium films deposited on insulating substrates where the coating thickness is typically 100 - 500 nm, the skin depth at a laser wavelength of 248 nm is about 7.3 nm and the thermal diffusion distance is 3065 nm (from table 7.3). The thermal model to calculate the fluence required to raise the aluminium coating to its
melting temperature should therefore take account of heat loss to the substrate and heat loss to the overcoating layer, (if present).

It is difficult to limit highly absorbing surfaces to only melting with nanosecond pulsewidth lasers because of the very rapid temperature rise experienced by the surface, maximum rates may be of the order of $10^{10} \text{Ks}^{-1}$ (7.18). Several threshold fluences can therefore be defined ($F_a$-$F_d$) corresponding to the aluminium coating

a) at the melting point temperature,
b) in a fully molten state,
c) at the boiling point temperature,
d) fully evaporated.

Calculations of threshold fluences in section 7.3a were limited to the lowest threshold $F_a$ representing the aluminium coating at the melting point temperature. The threshold fluence $F_b$ includes the latent heat energy to melt the aluminium coating, $F_c$ includes the heat energy to raise the molten aluminium to its boiling point temperature and $F_d$ the latent heat of vaporization to evaporate the coating. In recent years great interest has been shown in all four of these processes due to the development of the laser read/write optical disk, (7.25). The Write Once Read Many, (WORM), optical disk used for archival storage makes use of a pulsed laser to create a small hole in an absorbing metallic coating deposited on an insulating substrate. The hole represents the logical bit which is read by monitoring the back reflectance of a low power read pulse from the same laser. Dynamic models of laser induced hole formation involving heating and melting have been developed, (7.25, 7.26, 7.27, 7.28), however, fewer models encompass all four stages a–d given above, (7.29, 7.30). Frequently 3-D models are used because the focused spot size is less than the thermal diffusion length. In this work the 1-D model developed by Stern, (7.28) has been adopted because the focused excimer laser spot size was several millimeters in diameter and
the aluminium coating can be considered uniformly heated throughout its thickness. This model is valid for any substrate and is not limited to insulating substrates.

The fluence \( F \) required to raise the surface of the aluminium coating of thickness \( h \) to its melting point is given by

\[
F = F_a \sum_{n=0}^{\infty} a^n (1 - b b^n \sum_{n=0}^{\infty} a_n (I((2n+1)d^*) d^*)^{-1})^{-1}
\]

where

\[
F_a = \rho C_h (T_m - T_a) / (1 - R)
\]

\[
a = (\Delta - 1) / (\Delta + 1)
\]

\[
b = 2 / (\Delta + 1)
\]

\[
\Lambda = (K_p C / K_s p_s C_s)^{1/4}
\]

\[
d^* = h / (4x\Delta)^{1/4}
\]

\[
x = (2n + 1)d^*
\]

and

\[
I(x) = (1 + 2x^2)erfc(x) - (2x^{-1/2}x) \exp(-x^2)
\]

The limiting fluence \( F_a \) given by equation 7.19 corresponds to adiabatic heating of the coating. The dimensionless variable \( \Lambda \) depends upon the square root of the ratio of the thermal properties \( K, \rho, C \) of the coating relative to those of the substrate. A combination of aluminium with a fused silica substrate gives \( \Lambda = 15.96 \), a copper substrate gives \( \Lambda = 0.665 \). Equation 7.18 was used to calculate the the corrected melt thresholds given by equation 7.17 for metallic substrates. The results given in table 7.4 indicate that sapphire would be the best choice of transparent substrate material.
dimensionless variable $d^*$ is the thickness of the coating relative to the thermal diffusion length in the coating material. In the limit a perfect insulating substrate corresponds to $\Lambda \rightarrow \infty$, $b \rightarrow 0$ and $F_a \rightarrow F_{ad}$. Equation 7.18 for $d^* \leq 1$ can be shown to reduce to equation 7.16 for a semi-infinite metallic substrate by expanding $I(x)$ as a power series in $x$. In the situation considered here $d^*$ is of the order of 0.03 and equation 7.18 can be shown to converge within a few terms for a metallic substrate and within 1% of the asymptotic value using 14 terms for a fused silica substrate. A computer programme was written to calculate equation 7.18 using 100 terms in the series expansion and a polynomial fit for the erfc function, (7.32). Single shot damage threshold measurements at 248 nm are compared with theoretical predictions for four aluminium coatings deposited on fused silica substrates in table 7.6.

<table>
<thead>
<tr>
<th>Coating thickness (nm)</th>
<th>Reflectance at 248 nm (%)</th>
<th>$F_{ad_2}$ (J/cm²)</th>
<th>$F_{a_2}$ (J/cm²)</th>
<th>Single shot Damage threshold (J/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>64</td>
<td>0.22</td>
<td>0.25</td>
<td>0.3</td>
</tr>
<tr>
<td>200</td>
<td>78</td>
<td>0.14</td>
<td>0.195</td>
<td>0.23</td>
</tr>
<tr>
<td>85</td>
<td>78</td>
<td>0.06</td>
<td>0.11</td>
<td>0.23</td>
</tr>
<tr>
<td>72</td>
<td>91</td>
<td>0.13</td>
<td>0.26</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Table 7.6
Comparison of the single shot damage threshold at 248 nm and the calculated melt threshold for aluminium mirror coatings deposited on fused silica substrates

The experimental values of the aluminium coating thickness and reflectance were used in equation 7.18 to calculate the adiabatic threshold $F_{ad}$ and that allowing for heat loss to the substrate $F_a$. Laser induced damage was identified using the video microscope system described in chapter 4 with back illumination using a white light source. This arrangement was sensitive to detecting hole
formation in the metallic coating arising from physical disruption, melting, evaporation or ablation. The experimental error in the fluence is about 10%. The heat loss to the fused silica substrate is significant especially for aluminium coating thicknesses less than 200 nm where the two calculated melt thresholds differ by about 50%. The experimental damage thresholds are somewhat higher than the calculated values because melting and evaporation have not been included in the calculation. This explains the large discrepancy between the experimental and theoretical results for the thinner coatings. A general observation was that laser induced damage to the aluminium coating was usually detected by the removal of the aluminium due to ablation or evaporation.

The damage threshold at 248 nm of several thermally evaporated aluminium coatings deposited on glass microscope slides are shown in figure 7.8 as a function of the ratio \( h/(1 - R) \). The coating thickness \( h \) was measured with a tallystep instrument. The theoretical predictions which allow for heat loss to the substrate are much larger than the experimental results, the latter being nearer to the theoretical results for adiabatic heating. This difference was attributed to the large pinhole density observed in these coatings. Two experimental results measured in different regions of the same mirror are shown at \( h/(1 - R) = 1444 \). The higher one at 0.4 Jcm\(^{-2}\) was measured in a region where the pinhole density was very low. The experimental data can be explained by assuming that the presence of a pinhole increases the localized surface absorptance or reduces the local thickness both of which would move the experimental results towards the lower curve in figure 7.8.

The adiabatic heating model which results in equation 7.19 has been extended to make allowance for heat loss to the substrate by considering an effective heated region in the substrate. The thickness of the heated region in the substrate, \( d_s' \), can be assumed to be some fraction of the
FIGURE 7.8

Laser induced damage thresholds at 248 nm for aluminium deposited on fused silica substrates as function of $h/(1-R)$. 

LASER WAVELENGTH = 248 nm
PULSE WIDTH = 24 ns

HEATING WITH SUBSTRATE LOSS INCLUDED

ADIABATIC HEATING
thermal diffusion length in the substrate and is given by

\[ d_s = \alpha_s l_s \quad 7.26 \]

where \( \alpha_s \) is a numerical fitting factor. A similar argument applies to the overcoat layer with effective thickness \( d_0 \), fitting factor \( \alpha_0 \) and thermal diffusion length \( l_0 \). The corrected adiabatic threshold is therefore given by

\[ F_s = F_{ad} \left( 1 + \frac{d_s \rho_s C_s}{\rho C} + \frac{d_0 \rho_0 C_0}{\rho C} \right) \quad 7.27 \]

In the absence of any overcoat layer equation 7.27 can be numerically equated to equation 7.18. This was achieved by using \( \alpha_s \) as a fitting parameter. The thermal properties of glass, fused silica and sapphire, (7.21, 7.22) were used to calculate the values of \( \alpha_s \) and \( d_s \) given in table 7.7.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Fitting parameter, ( \alpha_s )</th>
<th>Thermal diffusion length, ( l_s )/nm</th>
<th>( d_s = \alpha_s l_s )/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>borosilicate</td>
<td>0.298</td>
<td>254</td>
<td>75.7</td>
</tr>
<tr>
<td>glass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fused silica</td>
<td>0.395</td>
<td>285</td>
<td>112.6</td>
</tr>
<tr>
<td>sapphire</td>
<td>0.80</td>
<td>678</td>
<td>542.4</td>
</tr>
<tr>
<td>(Al_2O_3)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7.7

Thermal parameters for three insulating substrates for use in equation 7.27 for calculating the effective heated thickness in the substrate.
The effective heated thickness for sapphire is larger than that for glass or fused silica due to its higher thermal conductivity and density. The effective heated distance in a single layer dielectric overcoat depends upon its physical thickness relative to its thermal diffusion length. If the physical thickness of the dielectric overcoat layer is greater than its thermal diffusion length the value of $\alpha_0$ is estimated by using equation 7.27 with $\alpha_0 = 0$ and substituting the thermal properties of the overcoat for those of the substrate in equations 7.18 and 7.27. The fitting procedure is then repeated to make equation 7.27 numerically equal to equation 7.18. The simplest situation arises if the overcoat layer has the same thermal properties as the substrate giving $\alpha_s = \alpha_0$. In many situations the physical thickness of the overcoating is much less than its thermal diffusion length. In this case the overcoating is assumed to be uniformly heated and the effective heated thickness is equal to the physical thickness, $<d_0 = d>$. The adiabatic thermal model can also be simply extended to include; melting of the aluminium, heating to the vaporization temperature and evaporation. The fluence required to heat and fully melt the aluminium coating is given by

$$F_b = F_a + \frac{h\rho L}{(1 - R)} \quad 7.28$$

where $L$ is the heat of fusion. The fluence required to heat the aluminium coating to its vaporization temperature is given by

$$F_c = F_b + \frac{h\rho_1 C_1(T_b - T_m)\{1 + d_0 \rho_0 C_0/h\rho_1 C_1 + d_0 \rho_0 C_0/h\rho_1 C_1\}}{(1 - R)} \quad 7.29$$

where the subscript 1 refers to the thermal or optical properties of the aluminium in its liquid state. Finally, the fluence required to evaporate the coating is given by
where $V$ is the latent heat of vaporization. Equations 7.27 - 7.30 have been applied to several aluminium mirrors deposited on insulating substrates with no dielectric overcoats. The results are summarized in Table 7.8 for a

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Coating</th>
<th>Reflectance at 248 nm</th>
<th>$F_a \cdot 10^{-2}$</th>
<th>$F_b \cdot 10^{-2}$</th>
<th>$F_c \cdot 10^{-2}$</th>
<th>$F_d \cdot 10^{-2}$</th>
<th>$F \cdot 10^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>glass</td>
<td>(sputter coated)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>glass</td>
<td>30</td>
<td>72</td>
<td>0.05</td>
<td>0.06</td>
<td>0.16</td>
<td>0.32</td>
<td>0.18</td>
</tr>
<tr>
<td>glass</td>
<td>45</td>
<td>82</td>
<td>0.09</td>
<td>0.12</td>
<td>0.23</td>
<td>0.47</td>
<td>0.05</td>
</tr>
<tr>
<td>glass</td>
<td>65</td>
<td>88</td>
<td>0.17</td>
<td>0.225</td>
<td>0.35</td>
<td>0.71</td>
<td>0.07</td>
</tr>
<tr>
<td>glass</td>
<td>120</td>
<td>91</td>
<td>0.32</td>
<td>0.46</td>
<td>0.65</td>
<td>1.30</td>
<td>0.14</td>
</tr>
<tr>
<td>glass</td>
<td>160</td>
<td>49</td>
<td>0.07</td>
<td>0.10</td>
<td>0.33</td>
<td>1.21</td>
<td>0.05</td>
</tr>
<tr>
<td>Pyrex</td>
<td>72</td>
<td>91</td>
<td>0.23</td>
<td>0.32</td>
<td>0.46</td>
<td>0.85</td>
<td>0.45</td>
</tr>
<tr>
<td>Pyrex</td>
<td>242</td>
<td>91</td>
<td>0.53</td>
<td>0.82</td>
<td>1.13</td>
<td>2.46</td>
<td>1.20</td>
</tr>
<tr>
<td>Pyrex</td>
<td>100</td>
<td>91</td>
<td>0.28</td>
<td>0.40</td>
<td>0.57</td>
<td>1.17</td>
<td>0.55</td>
</tr>
<tr>
<td>(commercial)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fused silica</td>
<td>72</td>
<td>91</td>
<td>0.26</td>
<td>0.345</td>
<td>0.495</td>
<td>0.89</td>
<td>0.44</td>
</tr>
<tr>
<td>fused silica</td>
<td>85</td>
<td>78</td>
<td>0.115</td>
<td>0.16</td>
<td>0.32</td>
<td>0.79</td>
<td>0.23</td>
</tr>
<tr>
<td>fused silica</td>
<td>200</td>
<td>78</td>
<td>0.20</td>
<td>0.30</td>
<td>0.58</td>
<td>1.68</td>
<td>0.23</td>
</tr>
<tr>
<td>fused silica</td>
<td>500</td>
<td>64</td>
<td>0.25</td>
<td>0.40</td>
<td>0.99</td>
<td>3.74</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Table 7.8
Comparison of various calculated threshold fluences with the single shot damage threshold at 248 nm for several aluminium mirrors deposited on insulating substrates

* This threshold was measured on the low scatter area of the mirror, in other areas the threshold was 0.64 $\text{Jcm}^{-2}$. 

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sputter coated mirror deposited on a glass microscope slide, a series of thermally evaporated mirrors deposited on glass microscope slides and some commercially produced mirrors with fused silica and Pyrex substrates. Included in table 7.8 is the coating thickness, reflectance at 248 nm and the single shot damage threshold, F. The threshold fluences $F_a + F_d$ are given by equations 7.27 - 7.30. Average values of the thermal properties of aluminium and the substrate were used over the temperature range of interest. The thermal properties of aluminium in the liquid state are well tabulated, (7.21). The major unknown variable is the absorptance of the aluminium in the liquid state at 248 nm. Reflectance data at 488 nm suggests a decrease occurs from 94%, (at room temperature) to 57% in the liquid state, (7.31). This result was simply scaled to give a reflectance figure of 56% in the molten state at 248 nm. The most noticeable features from the calculated data is the relatively small contribution from the heat of fusion and the relatively large contribution from the heat of vaporization especially for thick films. The fluence required to heat the aluminium coating to its melting point at 933 K is comparable to that required to heat the coating from its melting point to its boiling point at 2740 K, this is due to the increased absorptance in the liquid state.

The fused silica and Pyrex substrate mirrors with a normal incidence reflectance of over 90% were produced by thermal evaporation at the Culham laboratories, (7.4). This also included the Pyrex substrate with the chromium undercoat beneath the aluminium. The criterion for damage to these mirrors was the initial removal of the aluminium coating. The damage threshold of these mirrors agrees well with the threshold $F_c$ for boiling. These results also show that there is no significant difference in the damage threshold between a Pyrex substrate which is absorbing at 248 nm and fused silica which is transparent. This is unlikely to be valid if the pinhole density is high. The argument for a chromium undercoat beneath the aluminium was that the chromium binds more tightly to the
glass and it also adheres very well to the aluminium, (7.4). A thin chromium undercoat of 10 – 20 nm thickness does not appear to significantly alter the damage threshold possibly because of the low figure of merit for chromium. A major improvement was observed for the thick aluminium coating where the coating removal threshold over the low scatter area of the mirror was 1.2 Jcm\(^{-2}\). The results shown in table 7.8 suggest the melt threshold for this mirror would be about 0.5 Jcm\(^{-2}\). The remainder of the mirror, where the scattering was more severe, had a threshold of about 0.64 Jcm\(^{-2}\). This was attributed to the growth of crystallites which is often observed for thick coatings.

Comparison of the damage threshold of the sputter deposited mirror with calculated values suggests threshold damage corresponds to partial evaporation of the coating. A similar comparison with the thermally evaporated mirrors shows that the single shot damage threshold is comparable to or less than the calculated threshold required to heat the coating to its melting point. This discrepancy is attributed to the presence of pinholes in the coating as discussed earlier. The remaining mirrors with fused silica substrates show that the single shot damage threshold corresponds to a partially or fully molten film.

The simple adiabatic model described above assumes the four processes of heating to the melting point, melting, heating to the boiling point and volume vaporization occur in series. A detailed dynamic model of laser induced material removal from thin absorbing films deposited on insulating substrates shows this is not strictly correct, (7.30). The dynamic model shows that there is a rapid increase in the surface evaporation and therefore vapour pressure as the film is heated above its melting point towards the boiling point. If the reactive vapour pressure on the surface overcomes the surface tension of the molten liquid then molten liquid can move away from the zone of irradiation. The removed material therefore appears in two phases – vapour and liquid. If the reactive vapour pressure exceeds the ambient pressure

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superheating of the molten material may also occur. The model also predicts that for focused spot sizes of several millimeters the dominant removal mechanism is surface evaporation whereas for micron sized beams a significant fraction is removed from the irradiation zone and re-deposited elsewhere in the liquid phase.

At higher intensities the vapour can be ionized resulting in the formation of a plasma. This can have a significant effect at infra-red laser wavelengths where the plasma can absorb the laser radiation and subsequently irradiate the surface with intense VUV wavelengths. At excimer laser wavelengths the generation of intense surface plasmas was not found to produce direct plasma absorption, (see section 4.3). However, surface damage from such a weak plasma was found to extend over an area greater than the beam profile. This involved material ablation and re-deposition of ablated material in a ring around the damage area as the expanding plasma hits the surface.

The damage morphology of the sputter coated aluminium mirror with a single shot damage threshold of 0.18 Jcm\(^{-2}\) is shown in figures 7.9 - 7.12 at various fluences. The focused laser spot size for these measurements was 3.8 x 1.3 mm. Figure 7.9 shown in transmission was taken after a single shot at a peak fluence of 0.24 Jcm\(^{-2}\), evaporation of the aluminium coating over an area of about 0.3 x 0.1 mm is apparent. This compares with a predicted volumetric evaporation threshold of 0.32 Jcm\(^{-2}\) as given in table 7.8. Surrounding the evaporated region but within the beam area are a large number of small holes in the coating with diameters varying from 2 - 25 µm. Figure 7.10 also in transmission and at the same magnification as figure 7.9 shows laser damage at a peak fluence of 1.2 Jcm\(^{-2}\). A sharply defined edge where the film has been removed is clearly visible, the width of the damage region extends over about 0.4 mm. Surrounding the central area there are a large number of circular holes formed in the film with clear evidence of hole coalescence. The holes are more clearly illustrated in figure 7.11 showing a local area of
FIGURE 7.9

PHOTOGRAPH IN TRANSMISSION OF 248nm SINGLE SHOT LASER DAMAGE MORPHOLOGY AT 0.24Jcm\(^{-2}\) ON AN ALUMINIUM COATING DEPOSITED ON A GLASS SUBSTRATE

FIGURE 7.10

248nm LASER DAMAGE MORPHOLOGY OF AN ALUMINIUM COATING AT A PEAK FLUENCE OF 1.2Jcm\(^{-2}\). NOTE HOLE FORMATION IN THE EDGE REGIONS
FIGURE 7.11
PHOTOGRAPH IN TRANSMISSION OF 248nm LASER INDUCED HOLE FORMATION IN AN ALUMINIUM COATING DEPOSITED ON A GLASS SUBSTRATE

FIGURE 7.12
PHOTOGRAPH OF THE SAME SITE AS FIGURE 7.11 BUT IN REFLECTION. NOTE SMALL CAPILLARIES ON THE HOLE EDGES.
figure 7.10 at higher magnification. The same view and magnification but imaged in reflection is shown in figure 7.12. Several mechanisms have been attributed to initiation of laser induced hole formation using micron sized beams incident on thin metallic films, (7.29, 7.30, 7.33). These include; mass transport due to melting and surface tension gradients, evaporation, reactive pressure gradients and blister formation. All of these factors can be influenced by the presence of surface inhomogeneities such as pinholes and film voids which are more populous for very thin coatings. The near perfect circular holes and the presence of coalescence suggests some type of melting/surface tension model. The most likely cause of hole formation for the results illustrated in figures 7.9 - 7.12 is therefore localized absorption producing local high temperature gradients and therefore localized melting. Since the temperature derivative of the surface tension of molten aluminium is negative, (7.31) a symmetrical outward radial force exists to transport the molten material. Close inspection of figure 7.12 shows the circumference of the holes to have many minute hair-like capillaries radiating from the hole edges. These features are not visible in the transmission photograph, figure 7.11 and may be caused by slight buckling of the film edge due to stress relief. Using the analysis given by Kivits et al, (7.33), the upper limit for the hole formation time $\delta t$ and radius of the frozen rim material at the edge of the hole, $r_{rim}$ are given by

$$\delta t = \frac{R}{(4\gamma/\rho h)^{\alpha}}$$  \hspace{1cm} (7.31)

$$r_{rim} = (Rh/2\pi)^{\alpha/2}$$  \hspace{1cm} (7.32)

where $\gamma = 0.910 \text{ Nm}^{-1}$ is the surface tension of the molten aluminium, (7.31), and $R$ is the radius of the hole. Substituting for a film thickness $h$ of 30 nm and a typical hole radius of 10 $\mu$m gives $\delta t = 43 \text{ ns}$ and $r_{rim} = 220 \text{ nm}$. The hole coalescence presumably arose as two or more separate holes grew and met to form an agglomerate. A
general observation over many samples was that the average hole size increased as the local fluence increased towards the beam centre. This is not unreasonable because at a higher fluence the molten aluminium would be at a higher temperature and therefore have more time to move radially before the hole expansion is halted as the aluminium cools and subsequently freezes. An interesting feature shown in figure 7.11 is the presence of holes superimposed on the large evaporated area. This could arise if the hole was formed very early in the pulse before local evaporation had initiated. The remaining material at the rim of the hole is still visible and presumably is present because the local fluence was insufficient to subsequently evaporate the extra film thickness at the rim. The calculated film thickness in this case at the rim of the hole, \(2r_{\text{rim}} + h\) is 740 nm. Since the laser pulsewidth is about 24 ns the hole formation time would have to be much shorter than the upper limit of 43 ns given by equation 7.31 or that the film locally remains in a molten state for times larger than the laser pulse duration.

7.3c Laser damage thresholds of dielectric overcoated aluminium mirrors at 248 nm

The damage threshold at 248 nm has been measured for aluminium mirrors with single layer dielectric overcoating materials of SiO\(_2\), Al\(_2\)O\(_3\), ThF\(_4\), MgF\(_2\), LiF and LaF\(_3\). The results are summarized in histogram form in figure 7.13. Within each dielectric group, each cross represents the single shot damage threshold of a single mirror. These measurements involved about 20 shots near to the damage threshold at separate locations on each mirror on a total of 26 mirrors. Each of the mirrors was specified to one of three vendors, Technical Optics, (7.15), the Clarendon laboratory, (7.6) and the Culham laboratories, (7.4). The optical thickness of the overcoat layer was specified as effectively \(\lambda/2\) at 248 nm for all of the mirrors except some of those from the Clarendon laboratory with multiple half-wave thicknesses. The single shot damage threshold ranged from 0.1 Jcm\(^{-2}\) to
FIGURE 7.13
SINGLE SHOT LASER DAMAGE THRESHOLDS AT 248 nm OF DIELECTRIC OVERCOATED ALUMINIUM MIRRORS
0.68 J cm\(^{-2}\) for the most damage resistant mirror. The experimental error on each point is about ±10%.

The damage threshold definition used for these measurements was that incident fluence which corresponded to a damage probability of 100%. The \(1/e^2\) spot size for these measurements was 2.08 x 0.88 mm. The onset of threshold damage was detected using the probe beam scatter method described in chapter 4. In a few circumstances the scattered signal was observed to decrease to 60 – 80% of its initial value after illumination with the excimer beam. This was attributed to ablation of surface contaminants such as dust particles because the signal reduction was coincident with the removal of scattering centres as viewed on the video microscope system. A similar phenomena was also observed with HR and AR multi-layer dielectric coatings and is described in chapter 4.

At high incident fluences the aluminium coating was ablated which resulted in a decrease in the over-all back-scattered signal. Threshold damage was generally observed as the formation of a few scattering centres with diameters in the range 10 – 30 \(\mu\)m in the dielectric overcoating. Coating damage was usually enhanced when pinholes and large scattering centres were deliberately illuminated by the excimer beam. Damage appeared to be initiated in the overcoating and it was sometimes possible to ablate the overcoating without apparently damaging the aluminium. No significant difference in sensitivity to detect threshold damage was measured between the video microscope method and the scatter ratio method.

The modified adiabatic thermal model developed in section 7.3b has been used to calculate the thresholds \(F_d\) given by equations 7.27 - 7.30 for the aluminium mirrors listed in figure 7.13. The basic input parameters for the model can be divided into thermal properties, optical properties and geometrical properties. The optical and geometrical properties such as reflectance and film thicknesses were often available as experimental data. The thermal properties of the substrate, the aluminium coating and dielectric overcoating were taken
from the literature, (7.21, 7.22). The predicted damage threshold given by equation 7.27 increases linearly with overcoating thickness and saturated at \( d_0 \) if reflectance variations are ignored. The calculated values of \( l_0, \alpha_0 \), and the effective heated depth, \( d_0 \), are given in Table 7.9 for the thin films which have been investigated.

<table>
<thead>
<tr>
<th>Thermal diffusion length in overcoating, ( l_0/\text{nm} )</th>
<th>Fitting parameter ( \alpha_0 )</th>
<th>Limiting heated depth ( d_0 = \alpha_0 l_0/\text{nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al}_2\text{O}_3 )</td>
<td>678</td>
<td>0.80</td>
</tr>
<tr>
<td>( \text{ThF}_4 )</td>
<td>726</td>
<td>0.40</td>
</tr>
<tr>
<td>( \text{LiF} )</td>
<td>479</td>
<td>0.43</td>
</tr>
<tr>
<td>( \text{MgF}_2 )</td>
<td>284</td>
<td>0.46</td>
</tr>
<tr>
<td>( \text{LaF}_3 )</td>
<td>290</td>
<td>0.42</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
<td>285</td>
<td>0.395</td>
</tr>
</tbody>
</table>

**Table 7.9**

Thermal parameters for dielectric overcoats for use in the modified adiabatic thermal model assuming a laser pulse length of 24 ns

(\# Specific heat capacity estimated as 1.0 Jg\(^{-1}\)K\(^{-1}\))

The experimental damage threshold was found to be closest to the threshold fluence required to raise the aluminium coating to its melting point, the theoretical values are marked as circles in figure 7.13. The agreement between the predicted value and the measured threshold is very good for \( \text{LaF}_3, \text{LiF} \), the higher threshold \( \text{MgF}_2 \) mirrors and \( \text{ThF}_4 \). This agreement is perhaps surprising because threshold damage appeared to be initiated locally in the overcoating layer. The melting points of the overcoatings are well in excess of that of the aluminium. Local heating of an overcoating layer to a temperature of the order of its melting point would therefore result in significant melting and evaporation of the aluminium. A local threshold temperature in the overcoating well below its melting point therefore appears to be sufficient to...
disrupt the overcoating. This threshold temperature is of the order of the melting point of aluminium, 933 K. Other possibilities arise for highly stressed films where tensile stress relief could result in film cracking and compressive stress relief film buckling. A large discrepancy is apparent for the $\text{Al}_2\text{O}_3$ results. The predicted high thresholds for these mirrors arises from the high thermal conductivity of the $\text{Al}_2\text{O}_3$.

The $\text{MgF}_2$ overcoated mirrors with damage thresholds below $0.3 \text{ Jcm}^{-2}$ and the mirrors with $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$ overcoats were produced by the Clarendon laboratory, (7.4). These mirrors were all produced on identical BK7 glass substrates with different multiple half-wave overcoat thicknesses and measured reflectances between 85 - 90% at 248 nm. The aluminium coatings were all thermally evaporated onto ambient temperature glass substrates. The dielectric overcoats were electron beam evaporated onto the aluminium. In the case of $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$, reactive evaporation was used by admitting oxygen into the vacuum chamber to maintain the coating stoichiometry. The aluminium coating thickness was about 100 nm for the $\text{MgF}_2$ and $\text{SiO}_2$ mirrors and about 30 nm for the $\text{Al}_2\text{O}_3$ mirrors. This resulted in a much higher pinhole density in the $\text{Al}_2\text{O}_3$ overcoated mirrors and may explain the large discrepancy between the predictions and experimental results. The overcoating thickness was calculated from equation 7.9 using the known optical thickness and an assumed refractive index at 248 nm for the overcoating and the aluminium coating, (see section 7.2b). The results are summarized in table 7.10 for $\lambda/2$, $5\lambda/2$, $13\lambda/2$ and the closest half-wave optical thickness to the effective heated depth, $d_0$.

Comparison of table 7.10 with table 7.9 shows that the $\lambda/2$ optical thicknesses at 248 nm are much less than the thermal diffusion lengths. In this case, laser absorption in the aluminium coating can therefore be assumed to uniformly heat the overcoat layer. The closest half-wave optical thickness to the effective heated depth, $d_0$ indicates the minimum thickness to achieve a maximum
Calculated overcoating thickness/nm

<table>
<thead>
<tr>
<th>Overcoating material</th>
<th>λ/2</th>
<th>5λ/2</th>
<th>13λ/2</th>
<th>Optimum thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgF₂ (n=1.38)</td>
<td>76.4</td>
<td>435.6</td>
<td>1154.6</td>
<td>λ</td>
</tr>
<tr>
<td>SiO₂ (n=1.51)</td>
<td>68.9</td>
<td>397.7</td>
<td>1055.3</td>
<td>λ</td>
</tr>
<tr>
<td>Al₂O₃ (n=1.70)</td>
<td>59.9</td>
<td>351.7</td>
<td>935.2</td>
<td>7λ/2</td>
</tr>
<tr>
<td>ThF₄ (n=1.58)</td>
<td>65.3</td>
<td>456.9/6λ/2</td>
<td>1000.7</td>
<td>4λ/2</td>
</tr>
<tr>
<td>LaF³ (n=1.59)</td>
<td>64.8</td>
<td>376.7</td>
<td>1000.6</td>
<td>λ</td>
</tr>
<tr>
<td>LiF (n=1.42)</td>
<td>73.9</td>
<td>423.3</td>
<td>1122.2</td>
<td>3λ/2</td>
</tr>
</tbody>
</table>

Table 7.10
Dielectric overcoating thickness calculations for aluminium mirrors at 248 nm

damage threshold as predicted by the modified adiabatic thermal model.

The MgF₂ mirror with the lowest threshold of 0.1 J/cm² had a λ/4 overcoat and therefore a lower reflectance whereas the thicker coatings, (3λ/2, 5λ/2, 13λ/2) all had thresholds around 0.2 J/cm². The damage morphology of some of these mirrors is shown in figures 7.14 - 7.15. Prior to testing, the 13λ/2 MgF₂ overcoating was observed to be covered in many fine cracks presumably due to its high tensile stress, (7.34). Hole formation in the aluminium is shown in figures 7.14 and 7.15 for the 13λ/2 and 5λ/2 MgF₂ overcoated mirrors. At thresholds in excess of 2 - 3 times the single shot damage threshold a large area of the overcoating was removed and debris left on the aluminium as shown in figure 7.14. At higher magnification, figure 7.15, hole formation is observed to form preferentially on 1 - 2 μm wide "crack-lines" present in the aluminium in the absence of the overcoating. These lines must act as localized centres of high absorption. The origin of these lines is uncertain, however the tensile stress cracks in the overcoating before irradiation suggest the effect could be transmitted to the
FIGURE 7.14
248nm LASER DAMAGE MORPHOLOGY OF A 13Å/2MgF₂ OVERCOATED ALUMINIUM MIRROR IRRADIATED AT 0.45Jcm⁻².

FIGURE 7.15
248nm LASER DAMAGE MORPHOLOGY OF A 5Å/2 MgF₂ OVERCOATED ALUMINIUM MIRROR IRRADIATED AT 0.57Jcm⁻².
aluminium coating.

The damage thresholds of the $\text{Al}_2\text{O}_3$ overcoated mirrors were all in the range $0.3 - 0.4 \, \text{Jcm}^{-2}$ and independent of thickness. The adherence of the $\text{Al}_2\text{O}_3$ to the aluminium was greater than that of $\text{SiO}_2$ and $\text{MgF}_2$ but threshold damage was limited by the presence of pinholes in the aluminium. The most damage resistant $\text{SiO}_2$ mirror with a threshold of $0.53 \, \text{Jcm}^{-2}$ compares with the predicted value of $0.4 \, \text{Jcm}^{-2}$ for a $13\lambda/2$ overcoat thickness. The fluence required to just evaporate the aluminium coating for the $13\lambda/2 \text{MgF}_2$ mirror and the $\lambda/4 \text{SiO}_2$ mirror was measured as $1.0 \, \text{Jcm}^{-2}$ and $0.6 \, \text{Jcm}^{-2}$ respectively. The corresponding boiling point fluences, $F_c$ are 1.06 and 0.43 $\text{Jcm}^{-2}$.

The $\text{ThF}_4$ overcoated aluminium mirrors were all produced at Technical Optics, (7.15). The coatings were electron beam deposited onto ambient temperature substrates. The coating details and the damage thresholds are given in table 7.11. The basic aim was to investigate the effect of increasing the aluminium coating thickness and overcoat thickness.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Damage threshold $\text{Jcm}^{-2}$</th>
<th>Calculated Overcoating thickness nm</th>
<th>Calculated aluminium thickness nm</th>
<th>Reflectivity</th>
<th>Laser damage threshold measurements made through the substrate.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BK-7</td>
<td>0.40</td>
<td>0.31</td>
<td>$\lambda/2$</td>
<td>65.3</td>
<td>200 87</td>
</tr>
<tr>
<td>fused</td>
<td>0.38</td>
<td>0.40</td>
<td>$\lambda/2$</td>
<td>65.3</td>
<td>200 89</td>
</tr>
<tr>
<td>silica</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>fused</td>
<td>0.3</td>
<td>0.26</td>
<td>$6\lambda/2$</td>
<td>456.9</td>
<td>500 64</td>
</tr>
<tr>
<td>silica</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BK-7</td>
<td>0.20</td>
<td>0.17</td>
<td>$6\lambda/2$</td>
<td>456.9</td>
<td>500 47</td>
</tr>
<tr>
<td>BK-7</td>
<td>0.15</td>
<td>0.07</td>
<td>$\lambda/4$</td>
<td>30.0</td>
<td>100 64</td>
</tr>
</tbody>
</table>

Table 7.11
Laser damage thresholds at 248 nm of
$\text{ThF}_4$ overcoated aluminium mirrors
* Laser damage threshold measurements made through the substrate.
The highest damage threshold mirrors of around $0.4 \text{ Jcm}^{-2}$ had $\lambda/2$ overcoats with 200 nm thick aluminium coatings and measured reflectances of 89% and 87% at normal incidence. Threshold damage corresponded to the ablation of the ThF$_4$. The threshold to just evaporate the aluminium for the $\lambda/2$ overcoating mirrors was $0.6 \text{ Jcm}^{-2}$ with no significant difference between the fused silica and glass substrates. The calculated values corresponding to the boiling point of the aluminium were $0.74 \text{ Jcm}^{-2}$ and $0.88 \text{ Jcm}^{-2}$ for the glass and fused silica substrates respectively. No significant improvement was observed in the damage threshold for measurements made through the fused silica substrate.

The modified adiabatic thermal model given by equation 7.27 predicts that the threshold scales linearly with the aluminium coating thickness and overcoating thickness. The poor reflectance figure of 47% for the mirror with the thick aluminium and ThF$_4$ coating has been attributed to the optical constants of the aluminium and absorption in the ThF$_4$ as discussed in section 7.2bii. In practice it appears a limiting aluminium coating thickness exists beyond which the specular reflectance reduces. This has been attributed to the growth of crystallites in the film as the thickness increases. The refractive index of the ThF$_4$ overcoating was calculated as $(1.58 - 10.01)$ giving an absorption coefficient of $5067 \text{ cm}^{-1}$ at 248 nm. The affect on the reflectance of increasing the thickness of an absorbing overcoat deposited on an aluminium mirror is shown in figure 7.6. A few % reduction in the normal incidence reflectance may be tolerable for a $\lambda/2$ overcoat, however, the absorption becomes much larger as the optical thickness increases. The results shown in figure 7.6 also suggest a 30 nm thick overcoat is approximately $\lambda/4$ and therefore produces a low reflectance. Threshold damage measurements with the thick overcoated mirrors were accompanied by a faint purple colour visible over the illuminated beam area, this suggests the coating had blistered and become detached from the substrate. Another unusual feature observed just above the threshold level.
with the thicker overcoats was the formation of 3 - 4 horizontal lines in the overcoat. These were attributed to buckling of the film due to stress relief. An example of laser ablation of the 6\(\lambda/2\) ThF\(_4\) overcoat at 0.3 Jcm\(^{-2}\) is shown in figure 7.16. The damage threshold for this mirror was 0.2 Jcm\(^{-2}\), extensive buckling of the remaining overcoat is evident.

The mirrors with the highest thresholds were produced at the Culham laboratories, (7.4). These were thermally evaporated coatings of aluminium, (100 nm thick) with \(\lambda/2\) dielectric overcoatings of MgF\(_2\), LiF or LaF\(_3\), the substrates were not heated. The reflectance for all of the mirrors at 248 nm was measured as greater than 91%, (7.4). The substrate materials were purchased from three different vendors with different polishing standards. The substrates with RMS roughnesses of ~ 1.5 nm were standard laser polished blanks. The 0.32 nm RMS figure was classed as a high quality laser polish, the 0.2 nm RMS figure probably represents the state of the art. The potential improvement of the adherence of the aluminium to the substrate was investigated with the use of a thin chromium undercoat layer between the substrate and the aluminium. The results are summarized in table 7.12 and suggest that the substrate material, the RMS roughness of the substrate and the presence of a chromium undercoat has no significant influence on the single shot damage threshold. The calculated melt threshold of the MgF\(_2\) overcoated mirror is 0.45 Jcm\(^{-2}\) with a glass substrate and 0.49 Jcm\(^{-2}\) with a fused silica substrate. The corresponding calculations for LaF\(_3\) and LiF were 0.56 Jcm\(^{-2}\) and 0.54 Jcm\(^{-2}\) respectively. These results are in good agreement in absolute terms with the experimental values and furthermore predict an increased threshold for the LaF\(_3\) due to its high density, 5.94 gcm\(^{-3}\) and LiF due to its relatively high specific heat capacity of 1.82 Jg\(^{-1}\)K\(^{-1}\) (7.22). The calculated boiling point temperature fluence \(F_c\) for all of the mirrors varies between 0.85 - 1.0 Jcm\(^{-2}\) which is also in good agreement with the experimental results in table 7.12.
FIGURE 7.16
SINGLE SHOT 248nm LASER INDUCED DAMAGE IN A
$6\lambda/2\text{ThF}_4$ OVERCOATED ALUMINIUM MIRROR IRRADIATED AT 0.3Jcm$^{-2}$. 
The main experimental conclusions from all three sets of damage threshold data is that there is an optimum aluminium coating thickness and overcoating thickness to achieve maximum reflectance and damage threshold. If the aluminium coating is too thin, (<30 nm) then threshold damage is limited by pinholes. If the aluminium coating is too thick then crystallite growth results in a reduction of the reflectance at 248 nm. The effect of varying the dielectric overcoating layer thickness was inconclusive since pinhole formation in the aluminium and

<table>
<thead>
<tr>
<th>Substrate</th>
<th>RMS roughness</th>
<th>λ/2</th>
<th>Damage threshold</th>
<th>Threshold to evap Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused silica</td>
<td>1.6 ±0.4</td>
<td>MgF₂</td>
<td>0.46 ±0.07</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>1.6 ±0.4</td>
<td></td>
<td>0.41 ±0.04</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>0.32 ±0.1</td>
<td></td>
<td>0.34 ±0.04</td>
<td>1.06</td>
</tr>
<tr>
<td>BK-7 glass</td>
<td>1.5 ±1.0</td>
<td></td>
<td>0.46 ±0.07</td>
<td>0.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substrate</th>
<th>RMS roughness</th>
<th>λ/2</th>
<th>Damage threshold</th>
<th>Threshold to evap Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused silica + Cr underco</td>
<td>0.3 ±0.1</td>
<td>MgF₂</td>
<td>0.46 ±0.07</td>
<td>1.13</td>
</tr>
<tr>
<td></td>
<td>0.2 ±0.1</td>
<td></td>
<td>0.41 ±0.04</td>
<td>1.36</td>
</tr>
<tr>
<td>BK-7 glass</td>
<td>1.5 ±0.4</td>
<td>LaF₃</td>
<td>0.55 ±0.05</td>
<td>&gt;1.13</td>
</tr>
<tr>
<td></td>
<td>1.5 ±0.5</td>
<td></td>
<td>0.68 ±0.07</td>
<td>-</td>
</tr>
<tr>
<td>BK-7 glass</td>
<td>1.5 ±0.5</td>
<td>LiF</td>
<td>0.55 ±0.05</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 7.12
Laser damage thresholds at 248 nm of MgF₂, LiF and LaF₃ overcoated aluminium mirrors with different RMS substrate roughnesses.

stress relief in the thicker overcoatings dictated the damage thresholds.

The modified adiabatic thermal model gives a good estimate of the damage threshold at 248 nm of high quality aluminium mirrors. On this basis, the optimum choice of
the half-wave dielectric overcoat thickness depends upon the thermal properties of the coating. The calculations suggest an optical thickness of $\lambda$ for $\text{SiO}_2$, $\text{MgF}_2$, $\text{LaF}_3$ and $7\lambda/2$ for $\text{Al}_2\text{O}_3$, $4\lambda/2$ for $\text{ThF}_4$ and $3\lambda/2$ for $\text{LiF}$. The optimum thermal choice of overcoating material is $\text{Al}_2\text{O}_3$. Similarly the optimum thermal choice of transparent dielectric substrate is sapphire, ($\text{Al}_2\text{O}_3$) and for metal substrates silver. The option to use no dielectric overcoat is attractive since damage is usually observed initially in the overcoating. The major disadvantage is that the very soft aluminium coating would be susceptible to physical damage and be very difficult to clean.

7.4 UV irradiation studies of $\text{SiO}_x$ overcoated aluminium mirrors

Thin films produced by the evaporation of silicon monoxide are frequently used for half-wave dielectric overcoatings on aluminium mirrors in the visible region. It is well known that the actual composition or stoichiometry of the oxide film, $\text{SiO}_x$, depends strongly on the deposition conditions, (7.10, 7.12). Evaporation at low pressures and high deposition rates results in a film with $x \approx 1$ which has high absorption in the blue and near UV regions. The formation of a true silicon monoxide film can be identified by its slight brown colour. Evaporation at lower rates and higher pressures results in a more oxidized film with $x \approx 1.5$. This is equivalent to 50% of the film being silicon monoxide and 50% being silicon dioxide. The oxidized film has a much greater transmission in the blue and near UV with the absorption band around 300 nm, (7.10). UV irradiation of such oxidized films deposited on aluminium mirrors has been found to greatly increase the mirror reflectance in the wavelength range 200 - 300 nm, (7.35, 7.36). However no reflectance change was observed in these studies when the overcoating was true silicon monoxide, $\text{SiO}$. In contrast, oxidation of $\text{SiO}$ to $\text{SiO}_2$ has been observed by irradiation at the ArF excimer wavelength of 193 nm, (7.37).

UV irradiation of $\text{SiO}_x$ overcoated dielectric mirrors
was therefore investigated because it offers a source of durable, inexpensive mirrors for use at excimer laser wavelengths. A further incentive was that controlled laser induced oxidation of SiO\textsubscript{x} to SiO\textsubscript{2} could have substantial benefits to the semiconductor industry, effectively replacing the high temperature thermal growth stage for the production of insulating SiO\textsubscript{2} on Si substrates, (7.37).

The reflectance over the wavelength range 210 - 700 nm has been measured for several silicon oxide overcoated aluminium mirrors with effective half-wave thicknesses of λ/2 at 500 nm. These mirrors were purchased from Melles Griot Ltd. The similarity of these data to that measured by Hass, (7.35, 7.36) suggested that the overcoatings were oxidized with x ≈ 1.5. UV irradiation experiments with these mirrors in air were done with the excimer laser operating at 248 nm, (at a low energy density) and also with a UV mercury discharge lamp. Ellipsometry at 632.8 nm and the surface analysis technique known as ESCA were used to investigate optical thickness changes and stoichiometry changes as a function of the UV irradiation time of the oxide.

The reflectance of several SiO\textsubscript{x} overcoated aluminium mirrors in the wavelength range 210 - 700 nm was measured for various cumulative laser shot numbers. A typical example is shown in figure 7.17 where a significant improvement in the reflectance is shown in the wavelength range 210 - 340 nm. No significant change in the reflectance was observed in the visible range. The mirrors were irradiated at the the KrF laser wavelength of 248 nm at a fluence of about 0.03 Jcm\textsuperscript{-2} and a pulse rate of 2Hz. The improvement in the reflectance is approximately linear up to about 250 shots and thereafter starts to saturate. At 248 nm the reflectance increases from 55% to 82% after 1870 shots. The reflectance peak around 240 nm shifts to slightly shorter wavelengths as the laser shot number and reflectance increases. The large increase in the reflectance must be caused by a reduction in the absorption coefficient of the SiO\textsubscript{x}.

-338-
FIGURE 7.17

REFLECTANCE OF AN SiOx OVERCOATED, (\lambda/2 \odot 500nm) ALUMINIUM MIRROR AS A FUNCTION OF THE LASER SHOT NUMBER AT 248nm, (0.03 J/cm², 2Hz).
whereas the peak shift around 240 nm is probably caused by a reduction in the optical thickness of the oxide coating. This effect could arise from a reduction in the physical thickness or a reduction in the real part of the refractive index.

These phenomena were further investigated by irradiating a series of SiO$_x$ overcoated mirrors in air with UV light from a quartz-envelope mercury discharge lamp at a distance of about 2 cm. The reflectance, refractive index and film thickness of each mirror was measured at 15 minute irradiation intervals over a total irradiation time of one hour. The improvement in the reflectance as a function of the UV irradiation time is shown in figure 7.18 at wavelengths of 210 nm, 248 nm and 350 nm. The size of the error bar indicates the variation between samples. The reflectance at 248 nm increased from 57\% to 81\% after 45 minutes irradiation and thereafter saturated. This saturation behaviour was also observed using the excimer laser as the irradiating source. The UV lamp source for these tests was a UV-141 EPROM eraser. Prior to using this UV source two other sources were tried, both had insufficient intensity to induce reflectance changes. The refractive index and film thickness of the SiO$_x$ overcoat layer of each mirror was calculated from ellipsometry measurements at 632.8 nm using the literature value for the refractive index of a 'good' aluminium thin film at this wavelength, (7.5). The variation of these measurements over the area of a given sample was a maximum of about 2 \%. Absolute values are only approximate since the actual refractive index of the aluminium coating for each mirror was unknown. The results for a typical mirror are summarized in figure 7.19. A marginal increase in the refractive index of about 1.5\% after 60 minutes irradiation was accompanied by an even smaller percentage decrease in the film thickness. Over an irradiation time of one hour there is a small, less than 1\% increase in the optical thickness. These data are in agreement with the reflectance measurements in the visible range where no significant change was
REFLECTANCE OF SiOx OVERCOATED ALUMINIUM MIRROR AS A FUNCTION OF UV IRRADIATION TIME.
FIGURE 7-19

REFRACTIVE INDEX AND FILM THICKNESS OF SiOx DIELECTRIC OVERCOAT AS A FUNCTION OF UV IRRADIATION TIME.
observed. The estimated half-wave film thickness of 145 nm calculated from equation 7.9 is in good agreement with the ellipsometry measurements. This estimate was calculated using the refractive index data for aluminium from figure 7.2, \( N = 0.67 - 16.0 \) and the refractive index of SiO\(_{1.5}\) as 1.58 at 500 nm, \( \lambda = 7.10 \).

In previous UV irradiation studies of SiO\(_x\) films, \( \lambda/2 \) @ 550 nm, five hours irradiation from a 435 W mercury discharge lamp resulted in a large reduction in the refractive index in the visible region, \( (1.57 - 1.48 \) @ 633 nm), towards that of SiO\(_2\), \( \langle 7.35,7.36 \rangle \). This indicated oxidation of the partially oxidized coating. However, the infra-red absorption spectra of these coatings indicated that conversion from SiO\(_{1.5}\) to SiO\(_2\) had not occurred. These previous studies also indicated that one hour of irradiation resulted in a reflectance figure within a few percent of that achieved in five hours and that 150 hours were needed to fully oxidize the coating to SiO\(_2\), \( \langle 7.10,7.35,7.36 \rangle \). Excimer laser irradiation at 193 nm of true SiO films has also been found to result in complete oxidation to SiO\(_2\), \( \langle 7.37 \rangle \). At a fluence of 0.11 Jcm\(^{-2}\) and a pulsewidth of 15 ns about 1000 pulses were sufficient for complete oxidation of a 100 nm thick oxide layer. Two conversion mechanisms were considered, the first being photochemical involving an excited state, SiO\(^+\) reacting with ground state SiO or oxygen resulting in the formation of SiO\(_2\). The second involved intense local heating to temperatures above 1500 K.

The surface analysis technique known as ESCA, (electron spectroscopy for chemical analysis) has been used to measure the stoichiometry of the SiO\(_x\) as a function of the UV irradiation time. The surface of each specimen was cleaned with propanol prior to testing. The ESCA instrument was calibrated using a fused silica polished blank. The oxygen/silicon ratio, \( x \), was measured on the samples surface and at depths sputtered into the oxide coating of 6, 25 and 50 nm. The results for three samples are summarized in table 7.13.
The stoichiometry of the oxide coating at the surface was about 2 indicating that the film surface was fully oxidized. This feature was observed even for sample 40-A which was not exposed to the UV source and may arise from surface oxidation or moisture adsorption. The surface spectra of all three samples also indicated the presence of C and Mg impurities. The former presumably from hydrocarbon adsorption, the origin of the Mg impurity is unknown. The surface impurity peak heights also appeared to be independent of the UV irradiation time. At a sputter depth of 6 nm into the oxide coating the unexposed sample is only partially oxidized with $x \approx 1.5$. All three mirrors were purchased from the same manufacturer with the same specification and very similar spectral reflectance measurements indicating that $x \approx 1.5$ is probably valid for all three samples prior to irradiation. An irradiation time of 150 minutes resulted in the complete oxidation of the top 50 nm of the oxide coating. The variation of the stoichiometry with irradiation time is shown in figure 7.20 at the surface and at a sputter depth of 6 nm into the oxide. These results assume the oxidation rate and the initial stoichiometry for the three mirrors were equal. A UV irradiation period of 45 minutes resulted in a corresponding stoichiometry of $\text{SiO}_x$. This rather small change explains why no significant refractive index change was observed in the visible range. In contrast,

<table>
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<th>Sample no</th>
<th>UV irradiation Time (mins)</th>
<th>oxygen/silicon ratio, (Sputter depths/nm)</th>
</tr>
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<tr>
<td></td>
<td></td>
<td>Surface</td>
</tr>
<tr>
<td>40-A</td>
<td>0</td>
<td>1.93 ± 0.02</td>
</tr>
<tr>
<td>38</td>
<td>90</td>
<td>1.98 ± 0.03</td>
</tr>
<tr>
<td>42</td>
<td>150</td>
<td>2.2 ± 0.03</td>
</tr>
</tbody>
</table>

Table 7.13
Stoichiometry of $\text{SiO}_x$ overcoated aluminium mirrors as a function of the UV irradiation time and sputter depth.
STOICHIOMETRY OF SiO$_x$ OVERCOATED ALUMINIUM MIRROR AS A FUNCTION OF UV IRRADIATION TIME. MEASUREMENTS TAKEN WITH ESCA.
the oxide absorption in the UV region was greatly reduced for the same irradiation period.

A similar reduction in the absorption of the silicon oxide at UV wavelengths with little change in stoichiometry has been observed by Hass, (7.35, 7.36). More recently, ArF excimer laser irradiation measurements described in reference 7.37 were done at a high fluence and in a spectral region where the absorption coefficient of true SiO is metallic like, \( \alpha = 0.7 \times 10^6 \, \text{cm}^{-1} \). The conversion process was attributed to photochemical effects and/or intense local heating. In other studies, UV irradiation of gold and glass surfaces has resulted in favourable surface cleaning effects which have been unambiguously attributed to the removal of adsorbed hydrocarbons, (7.38). This explanation is appealing since no film stoichiometry change is involved. However, the ESCA results for the mirrors described in table 7.13 indicated that the amount of carbon surface impurity was independent of the UV irradiation time.

The relatively small change in film stoichiometry but large change in the UV reflectance can be explained by assuming the presence of interstitial oxygen in the film. The oxygen could arise from the atmosphere or from moisture. UV irradiation for short periods could then induce the conversion of SiO to SiO\(_2\) via a photochemical reaction with the interstitial oxygen or increased diffusion arising from thermal heating. The overall oxygen/silicon ratio would then remain constant, the percentage of SiO\(_2\) in the film would increase and therefore the UV absorption decrease. This process is likely to vary with film depth since the stoichiometry prior to irradiation appears to be depth dependent, especially near the surface. The complete oxidation of the film could arise from additional atmospheric oxygen or moisture and the gradual diffusion of the interstitial oxygen held in the surface. The results in figure 7.20 show that the surface stoichiometry increases with irradiation time reaching a value greater than 2 after 150 minutes.
The origin of the mechanism could be further investigated by UV irradiating $\text{SiO}_x$ thin films in a vacuum or an inert atmosphere and monitoring their stoichiometry and film reflectance in the visible and UV in real time. This would be possible with some simple additions to an ESCA instrument.

7.5 Laser induced ripple pattern studies in dielectric overcoated aluminium mirrors

7.5a Review of previous work

In recent years the formation of ripple patterns on laser irradiated surfaces has been widely studied. These ripples or surface undulations have been observed in metals, (7.39-7.41), semiconductors (7.40-7.43), and dielectric materials, (7.44,7.45). Such ripple patterns have been produced with a diverse range of experimental parameters including laser pulsewidths varying from 80 ps to 200 µs, laser wavelengths varying from the UV to the IR and ripple wavelengths varying from sub-micron to tens of microns. The widespread interest arises from their academic appeal and their potential use in the solid state electronics industry. The formation process can be divided into identifying the origin of the laser intensity modulation pattern and secondly the physical mechanism by which the intensity variations are permanently imprinted into the irradiated surface. Six mechanisms have been identified to explain the origin of Laser Induced Ripple Patterns, (LIRP) and are described below.

a) Laser Induced Thermo-mechanical Ripples, (LITR) formed by buckling due to stress relief of thin films.

b) Laser Induced Inhomogeneous Melting Ripples, (LIIMR) formed as a result of inhomogeneous surface absorption leading to a quasi-random distribution of melt pools which resolidify to form a random distribution of surface undulations.
c) Laser Induced Surface Tension Ripples, \( \text{LISTR} \) arising from thermally induced surface tension gradients resulting in mass transport which is subsequently frozen in as the surface solidifies.

d) Laser Induced Capillary Waves, \( \text{LICW} \) formed by the generation and subsequent "freezing in" of capillary, \( \text{(surface tension)} \) waves on a fully molten surface.

e) Laser Induced Periodic Surface Structures, \( \text{LIPSS} \) formed as a result of interference between the incident light and a scattered wave or an induced surface electric field.

f) Laser Induced Surface Acoustic Waves, \( \text{LISAW} \) formed by the rapid absorption of laser radiation and propagation of surface acoustic waves which are subsequently frozen in as the surface region solidifies.

The basic imprinting mechanism is that the material melts, undergoes deformation and finally after irradiation solidifies. The mechanism of deformation depends on the laser fluence and the material involved, \( \text{(7.16)} \). A theoretical model considered by Emmony et al, \( \text{(7.46)} \) shows that solidification of a hemispherical melt pool in a semi-infinite material results in a ripple profile for the solid surface. This model which neglects any surface tension gradients arises from the assumption that the solid-liquid interface is hemispherical and that the solid and liquid phases occupy different volumes due to their different densities. This process can explain the ripple imprinting mechanism involving localized melting due to local high absorption as in LIIMR and laser intensity modulation as in LIPSS. The other four processes involve a fully molten surface and may be observed under the same conditions as LIIMR or LIPSS except at higher energy densities. The first, LITR arise from movement of the film layer as it floats on the liquid surface. The second, LISTR simply involves mass transport by surface tension gradients. The others, LICW and LISAW involve
wave propagation and record the displacement of the surface at the instant of solidification. In recent work at 1.06 µm, LIIMR, LIPSS and LICW have all been observed on the same Ge sample at increasing thresholds of 0.15, 0.3 and 0.5 Jcm$^{-2}$ respectively, (7.47).

7.5ai Laser induced thermo-mechanical ripples

Laser induced thermo-mechanical ripples are reviewed in some detail because of their close resemblance to the ripple patterns observed in the silicon oxide overcoated aluminium mirrors described in section 7.5c.

Buckling of thin films due to compressive stress relief is a well established phenomenon even in the absence of laser heating, (7.48). In general, film shear stress is considered to have three components, intrinsic, thermal and adsorption induced. Film stress measurements during deposition have shown the stress to depend on various factors such as evaporation rate, substrate temperature, film thickness, time after evaporation and exposure to the atmosphere, (7.34). The deposition of SiO$_2$ thin films on glass like substrates results in a compressive stress whereas the deposition of MgF$_2$ generally results in a tensile stress. If the shear stress at the film-substrate interface exceeds the adhesive forces then stress relief can occur. This can result in cracks for tensile stress relief, an example being the aluminium mirror described in section 7.3c with the 13λ/2 MgF$_2$ overcoat layer. An increase in compressive stress sufficient to form ripples or buckles with a periodicity of about 1 µm has been observed in SiO$_2$ films on the uptake of water vapour from breathing on the film, (7.48).

Film deposition at a high substrate temperature can result in thermal stress on cooling due to differential thermal contraction of the substrate and coating. Laser heating of thin films can therefore be considered a very direct method for producing significant thermal stress resulting in buckling due to laterally constrained thermal expansion. An example is shown in figure 7.16 for KrF.
laser heating of a $6\lambda/2$ ThF$_4$ coating on aluminium showing significant buckling predominantly perpendicular to the ablated film edge.

Laser annealing of semiconductors has been widely investigated and an extensive review is given by Poate et al, (7.49). Many of the semiconductor processing stages are done with a mask of $\text{SiO}_2$ thermally grown on the silicon substrate. This situation is therefore similar to that of an $\text{SiO}_x$ overcoating on aluminium. Laser annealing studies of such composite structures have been studied in detail, (7.50, 7.51). This involved the observation of LIRP in the oxide layers with the following characteristic features.

i) The threshold for ripple pattern formation is close to the energy density required to melt the silicon.

ii) The ripple pattern periodicity is independent of the angle of incidence, laser wavelength and polarization state.

iii) The average wavelength of the ripple increases with the oxide thickness. A wavelength variation from $2 - 9 \ \mu\text{m}$ was observed for an oxide thickness variation of $32 - 230 \ \text{nm}$, (7.51).

iv) The underlying silicon is rippled in step with the overlying oxide with the $\text{SiO}_2$/Si interface remaining continuous with no voids.

v) Rectangular windows in the oxide film have higher ripple amplitudes at window corners. Circular and rectangular windows have radially aligned ripples at the window edge.

vi) Ordered ripples tend to form in the region of interfaces such as at film edges and at oxide thickness changes. Over large oxide areas the ripples appear to be randomly orientated. An example reproduced from reference 7.49 is shown in figure 7.21.

vii) At the interface between a thick and thin oxide layer very ordered ripples parallel to the boundary are formed.
FIGURE 7.21
LASER INDUCED RIPPLES IN $\text{SiO}_2$ DEPOSITED ON A SILICON SUBSTRATE
(REPRODUCED FROM REFERENCE 7.49)

FIGURE 7.22
CONCENTRIC RIPPLES IN LASER IRRADIATED ALUMINIUM ATTRIBUTED TO CAPILLARY WAVES FROZEN INTO THE SURFACE
(REPRODUCED FROM REFERENCE 7.53)
Small isolated islands of oxide do not show ripples even when large areas nearby areas do. The width of these small islands was found to permanently increase in proportion to their width.

The generally accepted formation mechanism is that the laser energy is directly absorbed by the silicon resulting in a stressed oxide layer heated by conduction and floating on a pool of molten silicon. The stress can relax by localized buckling during the period in which the silicon is molten. The increase in ripple wavelength with oxide thickness can be understood in terms of the smaller angle to which a thicker, stiffer membrane will be bent for the same lateral stress. The stress was originally attributed to thermal expansion and plastic flow of the oxide, (7.50). However, a continuation of this work has attributed it to the relaxation of compressive stress in-built in the oxide and arising from the cool-down stage during its original thermal growth, (7.49). This description of compressive stress relaxation is appealing since it is also in agreement with ripple pattern formation on unheated surfaces described earlier.

Another option whilst the silicon is molten is that the buckling is converted to lateral strain over the whole oxide layer. The maximum deformation speed of the oxide is limited to the sound speed, \( v = 5000 \text{ ms}^{-1} \) in \( \text{SiO}_2 \). In a typical melt time of 200 ns this gives a propagation distance of 1 mm. Therefore oxide islands smaller than 2 mm would be expected to relax their stress by lateral strain resulting in the absence of ripples. This description is in reasonable agreement with the experimental observations. In regions where the oxide is constrained by surrounding oxide in all directions random ripples result. When one dimension of the oxide raft is smaller than the critical value, the buckling strain is relieved in that direction but not in the orthogonal direction. Transmission of the stress from a thick oxide layer to an adjacent thin oxide layer can result in significant local buckling of the thin oxide.
7.5aii Laser induced inhomogeneous ripples

On uncoated silicon, LIIR formation has been reported at thresholds fractionally above the melt threshold using a Nd:YAG laser with a pulsewidth of 200 μs, (7.52). The surface undulations had a characteristic feature size of about 1 - 5 μm and were erasable by irradiating the surface at a higher intensity. The alignment of the ripples was independent of the beam polarization. This phenomena has also been observed just above the melt threshold in Ge, (7.47) and was attributed to an instability arising from the change in absorptance on melting, (7.16). The end result for a perfectly homogeneous beam is the random formation of molten patches which re-solidify giving a feature size which is related to the melt depth. Local modulation of the beam intensity due to dust particles in the air or local high surface absorption due to defects, grain boundaries or scratches can result in local periodicities superimposed on the random pattern, (7.16).

7.5aiii Laser induced surface tension ripples

Laser welding and hole drilling applications in metals frequently results in a solidified surface with a single smooth concentric ripple around the heated area, (7.53). This is usually attributed to the thermally induced surface tension gradient in the molten metal. The surface tension of most molten metals decreases with temperature resulting in an outward radial force which moves the molten material away from the central area towards the periphery which is at a lower temperature. The over-all effect is to depress the liquid surface in the centre and produce a raised liquid surface at the edge of the molten area. As the height difference increases a pressure head induces a counter flow and an equilibrium is reached, (7.39). The distorted surface becomes permanent when the transported liquid freezes. Evidence of surface tension effects in laser heated aluminium thin films on glass substrates is shown in figures 7.11 and 7.12. In this case the aluminium is sufficiently thin that radial
mass transport has resulted in hole formation.

7.5aiv Laser induced capillary waves

At elevated fluences the formation of ripple patterns in laser irradiated germanium, (7.47), aluminium, (7.41, 7.54) and silicon, (7.55) has been attributed to transient laser induced capillary waves. The waves whose formation is independent of laser wavelength and polarization propagate on a fully molten surface and may be permanently recorded as the "surface displacement" at the instant of freezing. A permanent record is only produced when the forcing function generating the waves or the wave amplitude decay time is comparable with the duration for which the surface is molten. An example of concentric rings in aluminium at the periphery of the interaction region is shown in figure 7.22. This ring structure was only observed above the vaporization threshold. Similar results using the excimer wavelengths of 193 nm on silicon, (7.55) and 248 nm on aluminium, (7.41) have also been observed. In both cases the incident intensity was sufficient to generate a surface plasma. The formation of LICW on a molten surface has been more rigorously identified by using an optical probe beam to measure transient oscillatory diffraction from ripples propagating on the surface, (7.47, 7.53). The frequency of the waves was then compared to that predicted by the dispersion equation for capillary waves on a liquid surface.

7.5av Laser induced periodic surface structures

The observation of LIPSS is the most widely studied laser induced ripple phenomenon and is characterized by a very regular ripple pattern which can extend over large areas, a recent extensive review is given by Clark, (7.41). The ripple wavelength is of the same order as the laser wavelength and is dependent on the polarization of the incident laser light and the angle of incidence. A generally observed phenomenon is that the at low fluences the ripple contrast increases with shot number and reaches
a steady state after 10 - 30 shots. In early experimental studies on germanium at a laser wavelength of 10.6 μm an optical interference model was used to describe the observed angular dependence, \( \langle 7.42 \rangle \). The two coherent sources being the incoming beam and laser light scattered from a surface defect or scratch. This interference phenomenon imprinted into the surface has also been observed when the scattering centre is a dust particle in the air adjacent to the surface and results in a characteristic Airy pattern, \( \langle 7.16 \rangle \).

Many experimental studies have shown that the angular dependence of the ripple wavelength is given by \( \lambda/(1 \sin \theta) \) or \( \lambda/\cos \theta \), where \( \theta \) is the angle of incidence, \( \langle 7.16, 7.42, 7.54 \rangle \). The particular dependence being influenced by the polarization of the incident light, the laser fluence and the material involved. A more recent detailed theory has been developed by Sipe et al, \( \langle 7.56 \rangle \) and has some similarities to the simpler interference model described above. The imprinted fringe pattern can be considered to arise from interference between the incident laser light and an induced surface electric field arising from the microscopically rough surface. Theoretical results at the laser wavelengths of 1060 nm and 530 nm, \( \langle 7.40 \rangle \) and more recently at 248 nm, \( \langle 7.41 \rangle \) show that the predicted resonance peaks of the surface field are in excellent agreement with the measured ripple wavelengths.

An inter-pulse feedback process has been shown to have a strong influence on the development of the ripples, \( \langle 7.47 \rangle \). The Fourier component of the initially randomly rough microscopic surface corresponding to the resonance condition induces an intense surface electric field and therefore a high local intensity. Near the threshold intensity this results in random localized melting and can be considered equivalent to the laser induced inhomogeneous ripples described in section 7.5aii. During the second pulse the spatial Fourier component of the surface corresponding to the same resonance condition again preferentially induces localized heating and
melting. As the surface solidifies between pulses, ripples form at the spatial wavelength corresponding to the resonance condition. This feedback process continues until a steady state is reached usually after 10 - 30 pulses.

7.5a Laser induced surface acoustic waves

The observation of long wavelength ripples in silicon using an ArF laser has been attributed to the formation of acoustic standing waves in the molten surface, (7.55). Similar observations have also been made in GaAs using a ruby laser; (7.57). The instant of freezing is considered to form a permanent record of the surface displacement in a similar way to that for capillary waves. In the case of silicon the observed ripple wavelength was found to be in reasonable agreement with the calculated acoustic wavelength knowing the speed of sound in silicon and assuming the wave period was 14 ns, (equal to the laser pulsewidth). This equates to a frequency of 71 MHz, in good agreement with piezoelectric transducer measurements out to 90 MHz. In the case of GaAs the standing acoustic waves were attributed to a non-linear interaction between two simultaneously oscillating longitudinal modes in the laser. This model requires the propagation of an acoustic wave at the very high frequency of 572 MHz.

7.5b Laser induced capillary waves in shallow liquids

The propagation of waves on liquid surfaces, particularly water has been widely studied, (7.58). The dispersion relationship for such surface waves in a liquid of depth \( h \), density \( \rho \) and surface tension \( \gamma \) is given by

\[
\omega^2 = (gk + \gamma k^3/\rho) \tanh(kh)
\]

where \( \omega \) is the angular frequency and \( k \) the wavenumber. The main constraint on the derivation of equation 7.33 is that the peak surface displacement be much less than the wavelength. Water waves are usually classified as gravity waves or ripples depending on the dominant term in
equation 7.33. Surface tension is dominant if \( k \gg (\rho g / \gamma)^{1/4} \).

For molten aluminium just above its melting point \( \rho = 2400 \text{ Kgm}^{-3} \) and \( \gamma = 0.91 \text{ Nm}^{-1} \) giving a limiting wavelength of 0.039 m. Similar values apply to many other metals and semiconductors suggesting surface tension effects dominate for micron sized ripple features. Equation 7.33 therefore simplifies to

\[
\omega^2 = (\gamma k^3 / \rho) \tanh(kh) \tag{7.34}
\]

Following the water wave analogy, two limiting conditions can be applied to equation 7.34, the first when the liquid is considered shallow, \( kh \ll 1 \) and the second when the liquid is considered deep, \( kh \gg 1 \). In the case of a shallow liquid, \( \tanh(kh) \approx kh \) and 7.34 simplifies to

\[
\omega = (\gamma h / \rho)^{1/4} k^2 \tag{7.35}
\]

In the deep liquid case, \( kh \gg 1 \), \( \tanh(kh) \approx 1 \) and equation 7.34 becomes.

\[
\omega = (\gamma / \rho)^{1/2} k^{3/2} \tag{7.36}
\]

In the deep liquid case the dispersion equation is independent of the liquid depth. Equation 7.36 with the 3/2 index dependence has been used to confirm the existence of LICW in molten germanium using the transient thermal diffraction method, (7.47). These measurements involved a laser pulsewidth of 20 ns, a surface melt duration of 200 ns and ripple periodicities of 30 - 60 ns depending on the wavelength.

Viscous forces cause the amplitude of the waves to decay in time. The wave amplitude \( A \) (at time \( t \)) can be expressed as

\[
A = A_0 e^{-t / t_d} \tag{7.37}
\]

where \( A_0 \) is the initial amplitude and \( t_d \) is the time constant which is given by
Equation 7.38 indicates that the shorter wavelength ripples rapidly decay in time. They will only be frozen into the surface if their decay time is comparable to the duration for which the surface is molten or if the mechanism which seeds the waves continues throughout the period for which the surface is molten. The observation of LICW at fluences producing a surface plasma, (7.41, 7.54, 7.55) suggest the plasma itself could maintain the periphery region in a molten state for long periods and also act as the seeding source for capillary waves. The results described in section 4.2f indicate that the surface plasma continues to influence the surface for times much longer than the laser pulsewidth. These times which scale with the laser fluence range from about 0.3 - 10.0 μs.

A further constraint on the observation of LICW frozen into a transiently molten surface is that the ripple period be much greater than the time for the molten pool to freeze. The frozen surface profile then represents a 'snapshot' of the displaced liquid surface arising from the capillary wave. The time taken for a molten layer to freeze, Δt, can be estimated from the ratio of the melt depth h to the solid-liquid interface velocity, v. The velocity of the solid-liquid interface is determined by the rate of heat extraction from the interface into the bulk. Following the analysis considered by Poate, (7.49) the velocity of the solid-liquid interface for a semi-infinite material is given by

\[ v = \frac{K(\partial T/\partial z)_i}{\Delta H_m \rho} \]  

where \( K \) is the thermal conductivity around the interface region and \( \Delta H_m \) is the heat of fusion. Near to the threshold for melting the temperature gradient at the interface, \( (\partial T/\partial z)_i \) is estimated as

where \( \eta \) is the viscosity.
\[ \frac{\partial T}{\partial z} \bigg|_{z=0} \approx \frac{T_m}{(2\pi \tau)^{1/2}} \] 7.40

where \( T_m \) is the melting temperature, \( x \) the thermal diffusivity and \( \tau \) a characteristic time comparable to the duration for which the surface is molten. At the melting threshold this characteristic time is approximated by the laser pulse duration. Substituting equation 7.40 into 7.39 gives the time to freeze a molten pool of depth \( h \) as

\[ \Delta t \approx \frac{(2\pi \tau/K)^{1/2}(\rho \Delta H_m / T_m)}{h} \] 7.41

Substituting the thermal properties of aluminium from table 7.3 in equation 7.41 gives a freezing rate of \( 84.9t^{1/4} \) ns/nm. This gives a freezing time of \( 1.5 - 3.8 \) ns for a melt depth of \( 100 \) nm and melt durations of \( 30 - 200 \) ns. These calculations show that for shallow melt depths in aluminium, the freezing time is much shorter than the melt duration suggesting that LICW can easily be frozen into the surface. This has been readily observed on polished aluminium samples after irradiation at \( 2 - 3 \) J/cm\(^2\) at the excimer wavelength of \( 248 \) nm, (7.41). The thermal properties of silicon and germanium, (taken from reference 7.49) show the freezing times to be about \( 6 - 7 \) times greater than that of aluminium. This suggests that LICW frozen into the surface of these semiconductor materials would only be observed for shallow melt depths or for capillary waves with long wave periods.

It appears that little consideration has been given to the possibility of LICW in shallow liquids. In the extreme limit as \( kh \to 0 \) no wave propagation arises. In the more moderate regime of \( kh < 1 \), a weak dependence of ripple wavelength on melt depth is given by equation 7.35. The possibility of shallow liquid LICW exists for laser heating of thin aluminium coatings deposited on insulating substrates. The maximum molten layer thickness being limited to the coating thickness. Another possibility is the situation at high fluences where vaporization and plasma formation produce shallow melt depths.

Equation 7.34 has been solved by an iterative
procedure for the propagation of capillary waves in molten aluminium. For modelling purposes a major unknown was the ripple period or characteristic seeding time. The capillary ripple wavelength as a function of the melt depth $h$ is shown in figure 7.23 for four assumed values of the ripple period. These equate to the total excimer laser pulse duration, 30 ns, a typical melt duration $\sim 200$ ns and a typical surface plasma duration $\sim 1000$ ns. Ripple wavelengths varying from 0.6 - 13 $\mu$m are possible depending on the melt depth and wave period. The most noticeable feature is that the ripple wavelength is quite insensitive to the melt depth, $h$ for wave periods of tens of nanoseconds. Ripple wavelengths varying from 0.6 - 1.3 $\mu$m arise by assuming the capillary wave period is given by the total laser pulse duration of 30 ns. The decay time is dependent on the viscosity, $\eta = 0.001$ Nsm$^{-2}$ for aluminium, (7.41), density and capillary wavelength. Substitution in equation 7.38 gives a decay time which varies from 11 - 51 ns for ripple wavelengths of 0.6 - 1.3 $\mu$m.

The laser induced damage morphology of the dielectric overcoated aluminium mirrors described in section 7.3c revealed a single example of ripples in the aluminium coating as shown in figure 7.24a-b. The ablation of the $\lambda/4$ MgF$_2$ overcoat layer is clearly shown well away from the ripple region. The high frequency coherent ripples with a wavelength of about 0.8 $\mu$m are modulated by more random ripples with a feature size of 3 - 5 $\mu$m. The aluminium coating is intact in this region since the photographs were taken in reflection. A ripple wavelength of 0.8 $\mu$m corresponds to a melt depth of 30 nm from figure 7.23 and a decay time of 39 ns. This assumes the laser pulse width of 30 ns is equal to the wave period. The decay time of the capillary waves is therefore comparable to the laser pulse duration. The predicted melt depth is somewhat less than the aluminium coating thickness of 100 nm. Calculations to uniformly melt the aluminium suggest a threshold fluence at 248 nm of 0.22 Jcm$^{-2}$ whilst the measured ablation threshold to remove the overcoating
CAPPILLARY WAVE WAVELENGTH VERSUS DEPTH FOR MOLTEN ALUMINIUM.
SHORT WAVELENGTH RIPPLES OBSERVED IN A λ/4 MgF₂ OVERCOATED Al. MIRROR IRRADIATED AT A PEAK FLUENCE OF 1.06 J/cm² AT 248nm. RIPPLE WAVELENGTH ~ 0.8μm IN Al. COATING.

FIGURE 7.24a

FIGURE 7.24b
was about 0.1 Jcm\(^{-2}\). The ripples were observed in a localized concentric band between a severe damage region with a peak fluence of 1.06 Jcm\(^{-2}\) and the ablated film edge at 0.1 Jcm\(^{-2}\). At this peak fluence an intense surface plasma was produced. Since the ripples were observed in an area where the aluminium was intact the local fluence from the excimer beam is likely to have been low. Melting of the top 30 nm of the aluminium coating could arise from the intense short wavelength radiation produced by the expanding surface plasma. This may also explain why the ripples were observed in a concentric ring around the central damage area.

The time to freeze a thin molten aluminium layer deposited on an insulating substrate was estimated by using the thermal diffusivity \(x\) and thermal conductivity \(K\) of the insulating substrate in equation 7.41. This is valid if the thickness of the metal layer is much less than its thermal diffusion distance. An increased freezing time arises because the rate of extraction of the latent heat is reduced by the lower thermal conductivity of the substrate. Substituting the thermal properties of fused silica in equation 7.41 gives a freezing time rate of 1286\(^{16}\) ns/nm, this is a factor of over 15 times that calculated for a pure aluminium sample. This gives a freezing time of 6.7 ns assuming a melt depth of 30 nm. This estimated freezing time is about one quarter of the assumed wave period. The likely effect of this is to reduce the contrast of the frozen in ripples.

Although the experimental evidence is somewhat limited the calculations are consistent with the suggestion that the coherent ripples shown in figure 7.24a-b are capillary waves frozen into the surface. Their formation was observed at high fluences and appears to be associated with the presence of the surface plasma. The expanding plasma could heat the surface via its short wavelength radiation and further act as a seeding source for the capillary waves. The constraints of the wave decay time and the surface freezing time act as filters on the capillary wavelengths which are ultimately frozen into
7.5c Excimer laser induced ripple patterns in SiO$_x$ overcoated aluminium mirrors

The formation of laser induced ripple patterns in SiO$_x$ overcoated aluminium mirrors has been investigated at 193 nm and 248 nm. The discussion is conveniently divided into measurements at low fluences, mainly at 193 nm and those at higher fluences, mainly at 248 nm. The beneficial effect of irradiating a SiO$_x$ overcoated aluminium mirror at 0.03 Jcm$^{-2}$ is clearly shown in figure 7.17. In the course of these experiments some samples were irradiated at fluences around 0.1 - 0.2 Jcm$^{-2}$. This resulted in a laser beam 'footprint' on the sample's surface showing characteristic diffraction colours which varied with viewing angle when illuminated with white light.

7.5ci Measurements at low fluences

At 193 nm, two mirrors labelled and A and B were investigated at low fluences. The normal incidence single shot damage threshold for mirror A was 0.1 Jcm$^{-2}$ and for mirror B 0.18 Jcm$^{-2}$. A damage threshold of 0.25 Jcm$^{-2}$ was measured at 248 nm on a separate but similar mirror. The damage morphology was investigated using optical microscopy and STEM, (Scanning and Transmission Electron Microscopy). Photomicrographs are shown of the damaged surface of mirror A in figure 7.25a-b. These results were observed after 3 pulses at 45 degrees incidence at 0.3 Jcm$^{-2}$. The incident laser light was randomly polarized for all of these measurements. The surface, (with the oxide coating still intact) appears to consist of a quasi-random distribution of almost uniformly sized 'globules'. Superimposed on the random pattern are local linear and elliptical features which appear to be made up of coalesced globules. This suggests a melting mechanism was involved. The linear features were quite common over the whole damage area whilst the observation of elliptical patterns was rare.
FIGURE 7.25a-b
193nm DAMAGE OF SiO$_x$ OVERCOATED ALUMINIUM MIRROR
IRRADIATED AT 0.2 J/cm$^2$, (3 SHOTS, 45° INCIDENCE)

FIGURE 7.26a-b
248nm DAMAGE OF SiO$_x$ OVERCOATED ALUMINIUM MIRROR
IRRADIATED AT 0.25 J/cm$^2$, (3 SHOTS, NORMAL INCIDENCE)
Similar ripple like damage features were observed at 248 nm. Two examples are shown in figure 7.26 taken after 3 shots at normal incidence just above the damage threshold. The photomicrograph shown in figure 7.26a was taken with a Nomarski objective and that in figure 7.26b with an interference objective. The quasi-random distribution of the ripples appears to extend over longer distances than the more 'globular' pattern produced at 193 nm. The random ripples illustrated in figure 7.21 appear to be very similar to those produced at 248 nm. The main difference being that the SiO$_x$ overcoating is absorbing at UV wavelengths. Ripples of a similar type have not been observed on nominally low absorption overcoatings irradiated at 248 nm. This includes LiF, LaF$_3$, SiO$_2$, ThF$_4$, Al$_2$O$_3$ and MgF$_2$ with thicknesses varying from $\lambda/4$ to $13\lambda/2$. Some difference in the laser induced damage morphology between 193 nm and 248 nm is not unexpected since the initial sample reflectance at 193 nm was about 10% and at 248 nm about 55%. After 3 shots at 0.1 Jcm$^{-2}$ the normal incidence specular reflectance at 248 nm decreased to 15 - 25%. This reduction could arise from increased absorption and/or increased scatter.

The damage morphology was also investigated as a function of the laser shot number, (1 - 20 shots) and the angle of incidence, (0 - 25 degrees). These measurements were done with a small aperture located in the centre of the unfocused beam where the intensity was relatively constant. The development of the damage morphology was investigated using a STEM. The use of SEM resulted in poor contrast pictures because of the shallow ripple depth and charging of the insulating silicon oxide overcoat layer. The favoured option was TEM, this required the production of carbon surface replicas using a standard acetate/carbon coating method. The carbon replicas were mounted at 45 degrees and coated with a thin layer of thermally evaporated gold to enhance the contrast in the TEM. Most of the TEM micrographs were investigations of the 193 nm results.

A generally observed feature was that visual damage
was initiated within 3 - 4 shots or not at all. The optimum fluence region was just above the single shot damage threshold. At 193 nm, a fluence of 0.2 Jcm\(^{-2}\) on mirror B, (at normal incidence) produced no ripples when the surface was tilted beyond about 30 degrees and irradiated with up to 60 shots. In this case, the fluence incident on the tilted surface is given by \(F_0 \cos \theta_i\) and the absorbed fluence given by

\[
F_{\text{ab}} = F_0 (1 - R(\theta_i)) \cos \theta_i
\]

where \(R(\theta_i)\) is the reflectance at an incident angle \(\theta_i\) and \(F_0\) is the fluence equal to or just above the threshold value at normal incidence. The extinction coefficient of the oxide layer was used as a fitting parameter to make the calculated and experimental reflectances of the mirrors agree at normal incidence. This analysis gives a complex refractive index of the SiO\(_x\) at 193 nm of 1.73 - 10.2 and 1.70 - 10.05 at 248 nm. The data was then used to calculate the absorption term \(1 - R(\theta_i)\) in equation 7.42. This procedure is similar to the approach used in section 7.2bii. At 193 nm and over the incident angle range 0 - 30 degrees, the calculated absorption of the overcoated mirror increases from 0.90 to 0.95. At 248 nm and over the same incident angle range the calculated absorption increases from 0.45 to 0.48. Therefore over the angle range 0 - 30 degrees the angular dependence of the absorbed fluence is dominated by the \(\cos \theta_i\) term. Using \(F_0 = 0.2\) Jcm\(^{-2}\), the limiting incident angle is calculated as 25.8 degrees when the fluence incident on the tilted surface, \(F_0 \cos \theta_i\) reduces to the threshold value of 0.18 Jcm\(^{-2}\).

The data in table 7.14 was taken from figure 7.2 for aluminium and from reference 7.10 for the SiO\(_x\) film. The main assumption about the SiO\(_x\) film was that \(x = 1.5\). The film thickness of 145 nm is considered in section 7.4. The skin depth data given in table 7.14 compares with the thermal diffusion distance of 285 nm for SiO\(_2\), (see table 7.3). The oxide film and the aluminium film can therefore
be considered uniformly heated.

A Tallysurf instrument was used to measure the surface profile of different damage sites exposed to differing shot numbers. These measurements were done with a small probe tip, (2.5 x 0.1 \( \mu \)m). A comparison between the surface profile after 1 shot and 20 shots is shown in figure 7.27. These measurements were done after irradiation at normal incidence at 0.2 Jcm\(^{-2}\). A general trend was that the ripple height increased from about 50 - 80 nm after one shot to 180 - 200 nm after about 10 shots, the ripple height thereafter remaining constant. In parallel with this was the development of a sinusoidal profile at low shot numbers, (figure 7.27a) to one with a flattened trough at higher shot numbers, (figure 7.27b).

Some examples of TEM micrographs at differing shot numbers and angles of incidence are shown in figures 7.28 - 7.32. The 'globule' diameter was measured from many TEM micrographs and found to vary from about 0.9 - 1.7 \( \mu \)m with a relatively constant ripple wavelength of about 2.5 \( \mu \)m. Several extra features are also revealed in figures 7.28 - 7.32. The origin of the parallel ripples is unambiguously identified with a scratch in the centre of the pattern. The ripples parallel to the scratch are made up of individual globules which have coalesced with other adjacent globules to form a continuous ripple. The influence of the scratch is clearly shown in figure 7.28 where the parallel ripples only extend to where the scratch terminates and in figure 7.29 where the change in direction of the scratch is followed by the ripples. A high magnification view of the scratch in figure 7.29 is
FIGURE 7.27
SURFACE PROFILES OF SiO₂ OVERCOATED ALUMINIUM MIRRORS
IRRADIATED AT 193nm (NORMAL INCIDENCE, 0.2 J cm⁻²)

A) 1 SHOT
B) 20 SHOTS
FIGURE 7.28
193nm IRRADIATION OF SiO$_x$ OVERCOATED Al. MIRROR AT 0.2 Jcm$^{-2}$; (SINGLE SHOT, 25° INCIDENCE, Mg X 2000)
NOTE SCRATCH IN CENTRE OF PATTERN.

FIGURE 7.29
193nm IRRADIATION OF SiO$_x$ OVERCOATED Al. MIRROR AT 0.1 Jcm$^{-2}$; (20 SHOTS, 0° INCIDENCE, Mg X 2000)
NOTE CHANGE IN DIRECTION DUE TO SCRATCH.
shown in figure 7.30. Measurements from many TEM micrographs taken at high magnification have shown that most of the scratch widths were in the range 0.15 - 0.25 μm. Circular and curved ripples are shown in figure 7.31 and 7.32 respectively. No similar pit or absorption feature was observed in the centre of the circular patterns presumably due to the limited sensitivity of the replication process.

Although TEM micrographs were used to directly measure the local microscopic ripple wavelength a more suitable method was used to measure the local average macroscopic ripple wavelength. This was done by using the optical diffraction pattern generated by the rippled surface. Illumination of the damage area with a one mm diameter helium neon laser at normal incidence produced circular first and second order diffraction rings. The second order ring was at a reduced intensity compared to the first order ring. The diffraction angle was measured by directing the helium neon laser through a small aperture in a screen and observing the rings in reflection. The central radius of the first ring, r plotted as a function of the the distance between the mirror and the screen, L is shown in figure 7.33. The gradient of the line corresponds to a constant diffraction angle given by

\[ \tan \theta = \frac{r}{L} \]  

A least squares fit to the data shown in figure 7.33 gives a diffraction angle of 15.75 degrees. Similar measurements on the second order ring confirmed it to be at twice the diffraction angle of the first order ring. A constant diffraction angle shows that the 2-D surface profile must contain periodic components. The Tallysurf results shown in figure 7.27 indicate that the surface can be approximated as sinusoidal. Scattering from a 1-D sinusoidal surface results in a 1-D diffraction pattern with maxima given by the standard grating equation. In a simplistic way the 2-D surface can be considered as a
FIGURE 7.30
HIGH MAGNIFICATION VIEW OF FIGURE 7.29 (Mg X 10,000) SHOWING THE SCRATCH WITH A WIDTH OF 0.2μm

FIGURE 7.31
CIRCULAR RIPPLES IN SiOₓ OVERCOATED Al. MIRROR IRRADIATED AT 193nm. (0.1 Jcm⁻², 45° INCIDENCE, 3 SHOTS, Mg X 2000)
FIGURE 7.32
CURVED RIPPLES IN SiO$_x$ OVERCOATED AL. MIRROR IRRADIATED AT 193nm. (0.1 J/cm$^2$, 45° INCIDENCE, 10 SHOTS, Mg X 1500)
RADIUS OF FIRST DIFFRACTION RING

\[ r / \text{mm} \]

**FIGURE 7.33**

RADIUS OF DIFFRACTION RING VERSUS SCREEN DISTANCE FOR THE RIPPLED SURFACE SHOWN IN FIGURE 7.25.
circular array of 1-D sinusoids with random phase differences. The resulting diffraction pattern therefore consists of concentric rings whose intensity is amplitude modulated by the diffraction pattern from a single 'globule'. This simple model can also explain the observation of 1-D diffraction patterns superimposed on the circular rings as the damage site was translated across the helium neon beam. In this case, the 1-D diffraction pattern corresponded to the helium neon laser illuminating the parallel ripples shown in figure 7.29. The orientation of the parallel ripples in the plane of the surface determined the orientation of the 1-D diffraction pattern. The detailed mathematical theory of scattering from periodic 2-D sinusoidal surfaces and also randomly rough surfaces has been considered by Beckman, (7.59). In the case of sinusoidal surfaces the dominant diffraction direction in the plane of scattering is given by the grating equation

\[ \sin \theta = \sin \theta_i + m \lambda / \Lambda \] 7.44

where \( \theta \) is the diffraction angle, \( \lambda \) the laser wavelength, \( m \) the diffraction order and \( \Lambda \) the spatial wavelength of the ripple. The angular width of the diffraction ring \( \Delta \theta \) was used as an estimate of the corresponding variation in the spatial wavelength \( \Delta \lambda \) from equation 7.44. Differentiating equation 7.44 with respect to \( \theta \) gives

\[ \Delta \lambda = m \lambda \cos \theta (\sin \theta - \sin \theta_i)^{-2} \Delta \theta \] 7.45

Substituting \( \theta_i = 0 \) for normal incidence, \( \theta = 15.75 \) degrees \( \lambda = 0.6328 \) \( \mu m \) and \( m = 1 \), (first order diffraction) gives a ripple wavelength of 2.33 \( \pm 0.26 \) \( \mu m \). The approximate 10% variation in ripple wavelength was calculated using equation 7.45 with a measured angular width, \( \Delta \theta \) of \( \pm 1.84 \) degrees. The angular width arising
from the instrument function is given by,

\[ \Delta \theta' = \frac{2\lambda}{N\Delta \cos \theta} \]  

where \( N \) is the number of illuminated ripples, (7.60). The instrument broadening decreases as the illuminated grating distance, \( \Delta \) increases. Using \( \Delta = 1000 \mu m \), (the helium neon beam diameter) and \( \theta = 15.75 \) degrees gives \( \Delta \theta' = 0.07 \) degrees. The instrument broadening effect, \( \Delta \theta' \) is therefore negligible compared to the measured angular width \( \Delta \theta \).

The diffraction method was also used to measure the ripple wavelength as a function of shot number, angle of incidence and position on the damage site. The results in figure 7.34 show the ripple wavelength plotted as a function of sample position as the damage site was scanned through the helium neon beam. These results were obtained at 193 nm after irradiation at 0.2 Jcm\(^{-2}\) at normal incidence. At each measurement point the optical transmission of the sample was also measured. The results for one, three and ten shots show that the ripple wavelength is independent of shot number and varies by about 5% in a systematic way over the scan range of 2 mm. The main effect of the increasing shot number was the greatly increased diffraction efficiency presumably due to the increased ripple height and changed profile. The transmission measurements ranged from about 2 \( \times 10^{-6} \) to about 50 \( \times 10^{-2} \) and followed the profiles shown in figure 7.34. These results suggest the aluminium remains intact but its thickness is modulated, presumably due to melting and solidification. Measurements in the orthogonal scan direction showed similar results except the minimum ripple wavelength was about 2.35 \( \mu m \).

The ripple wavelength plotted as a function of the angle of incidence is shown in figure 7.35. The results were obtained by measuring similar profiles to those shown in figure 7.34 and taking the central peak ripple wavelength as a representative value. The data points at 0, 10, 15 and 25 degrees incidence are in good agreement.
RIPPLE WAVELENGTH VERSUS POSITION ON DAMAGE SITE FOR 193nm IRRADIATED SiOx OVERCOATED Al MIRRORS. (0.2 J/cm², NORMAL INCIDENCE).

FIGURE 7.34
FIGURE 7.35

RIPPLE WAVELENGTH VERSUS ANGLE OF INCIDENCE FOR SiO$_x$ OVERCOATED Al MIRRORS IRRADIATED AT 193nm.
with the fitted curve given by

\[ \lambda = \lambda_0 \cos \theta_i \]  

7.47

where \( \lambda_0 \) is the ripple wavelength at normal incidence. The author is unaware that this angular dependence has been observed previously. The angular sensitivity to ripple pattern formation described earlier, the association of a scratch with the formation of parallel ripples and the wavelength variation given by equation 7.47 suggest the ripples have a thermal origin, their wavelength being related to the local absorbed fluence.

7.5cii Measurements at high fluences

The most interesting features of the damage morphology arising from irradiating the mirrors at high fluences were observed on the edge of the damage site. An example is shown in figure 7.36 which includes two views of the same site, one taken in reflection and the other in transmission. These results were obtained at 248 nm with a single shot at normal incidence and at a peak fluence of 1.85 J cm\(^{-2}\). Three regions, A, B and C are conveniently defined for discussion purposes.

The SiO\(_x\) film edge between regions A and B is clearly visible in figure 7.36a. In region C the overcoating layer has been ablated leaving at least some areas of the aluminium coating intact and other areas with holes in the aluminium film. Similar holes have been described earlier, (section 7.3b) and attributed to random localized absorption inducing a surface tension gradient in the molten aluminium. A TEM photograph of the holes in the aluminium film in the transition region A - C is shown in figure 7.37. Clear evidence of hole coalescence is indicated. In regions A and B two sets of parallel ripples radiating away from the film edge are visible. Those in region A are elongated holes in the aluminium with a wavelength of about 2 - 3 \( \mu m \) as shown in the TEM photograph in figure 7.38. Close inspection of figure 7.36b shows that the elongated holes were formed by the
FIGURE 7.36a
SINGLE SHOT, 248nm LASER DAMAGE AT 0° INCIDENCE ON A SiO₂ OVERCOATED Al MIRROR IRRADIATED AT A PEAK FLUENCE OF 1.85 J/cm². (PHOTOGRAPH TAKEN IN REFLECTION)

FIGURE 7.36b
THE SAME DAMAGE SITE AS FIGURE 7.36a EXCEPT THE PHOTOGRAPH WAS TAKEN IN TRANSMISSION MODE
FIGURE 7.37
HOLE FORMATION IN THE Al FILM IN THE TRANSITION REGION A-C OF FIGURE 7.36a

FIGURE 7.38
ELONGATED HOLE FORMATION IN THE Al FILM IN THE REGION A OF FIGURE 7.36a
coalescence of several small holes all of about the same size. The radial growth of the holes does not extend beyond the SiO$_x$ film edge.

The photograph shown in figure 7.36a suggests the ripples in region B associated with the SiO$_x$ film edge were not simply extensions of the elongated holes in region A. This is shown in figure 7.36b where no ripples are visible beyond the film edge. Measurements of the local aluminium content of the ripples in region B with an electron microprobe indicated the aluminium thickness was modulated rather than having holes as in region A. A further observation was that the ripples were most apparent along the SiO$_x$ film edge in the corner region. A TEM photograph of the film edge region is shown in figure 7.39. In this area the elongated holes in the aluminium become much thinner and less apparent. However, faint tracks do appear to continue to the film edge and match with the ripple peaks in the SiO$_x$ film. These tracks could simply be remnants of the rippled oxide surface prior to evaporation or ablation of the overcoating. The ripples in the SiO$_x$ film are shown in figure 7.40 and have a close resemblance to those at 248 nm considered in section 7.5c1.
FIGURE 7.39
248nm LASER INDUCED RIPPLE PATTERN FORMATION NEAR THE ABLATED FILM EDGE OF THE SiO₂ OVERCOATED Al. MIRROR SHOWN IN FIGURE 7.36a

FIGURE 7.40
248nm LASER INDUCED RIPPLES IN THE SiO₂ OVERCOATED Al. MIRROR - REGION B OF FIGURE 7.36a
7.5ciii Discussion of results

Several of the ripple formation mechanisms reviewed in section 7.5a can be easily discounted. These include laser induced capillary waves and laser induced surface acoustic waves because of the random distribution of the ripples. The localized linear and circular features are made up of coalesced surface 'globules' and therefore must have the same fundamental formation mechanism but with some form of local symmetry. The wavelength of laser induced periodic surface structures, at normal incidence is given by $\lambda$ or $\lambda/n$. The ripple wavelength observed in this work was about $10\lambda$. Furthermore the angular and polarization dependence of the LIPSS differ strongly from the results described in section 7.5ci. The only similarity to LIPSS was the observed inter-pulse feedback process which increased the ripple height as a function of shot number and resulted in saturation after about 10 shots.

The formation of laser induced thermo-mechanical ripples, LITR has previously been observed in SiO$_2$ films deposited on silicon substrates. Many of the experimental observations previously observed, (see section 7.5ai) are similar to those described in section 7.5ci-ii. Comparison of figures 7.26 and 7.36a with figure 7.21 shows several similarities in the damage morphology. This includes the formation of random ripples, the formation of ripples perpendicular to oxide film edges and the preferential formation of perpendicular ripples at corners of rectangular windows in the oxide. In figure 7.36a the film edge arose from ablation of the overcoating suggesting the ripples formed after the evaporation process. Other similarities include the formation of ripples parallel to oxide thickness changes and the formation threshold being similar to that needed to melt the substrate material. These similarities suggest the ripples observed in the SiO$_x$ overcoated aluminium mirrors can also be classified as laser induced thermo-mechanical ripples. However some differences are apparent. These include; the absorption of the oxide at UV wavelengths,
the variation of the ripple wavelength with position on the damage site and the ripple wavelength dependence on the angle of incidence. These results suggest the ripple wavelength is linearly related to the absorbed fluence. Using this assumption, the ripple wavelength is therefore given by

\[ \lambda = kF_0(1 - R(\theta_1))\cos\theta_1 \]  

from equation 7.42, where \( k \) is the proportionality constant. Equation 7.48 approximates to equation 7.47 when the absorption term \( 1 - R(\theta_1) \) is constant. This occurs for the SiO\(_x\) overcoated aluminium mirrors at angles less than about 30 degrees. The ripple wavelength dependence on the laser wavelength and polarization is represented by the Fresnel reflectance, \( R(\theta_1) \). The polarization dependence is fairly weak at shallow angles of incidence. Using the ripple wavelength data shown in figure 7.35, \( \langle \Lambda_0 \rangle = 2.66 \mu\text{m}, F_0 = 0.18 \text{Jcm}^{-2}, R(0) = 0.10 \) @ 193 nm) the proportionality constant is given by \( k = 1.64 \times 10^{-3} \text{ cm}^3\text{J}^{-1} \). At 248 nm this corresponds to a minimum ripple wavelength of 1.85 \mu\text{m} at the threshold of 0.25 Jcm\(^{-2}\). A good test of the validity of equation 7.48 would be to measure the ripple wavelength at large angles of incidence where the variation of reflectance with angle is high and where there is a large difference between the S and P polarized directions.

Although equation 7.48 can be tested experimentally it gives no indication of the actual physical mechanism by which the ripples are formed. The basic formation mechanism is assumed to be that attributed to the previously observed LITR. This involves absorption of the laser radiation by the oxide and aluminum resulting in subsequent melting of the aluminium surface region. Stress relief of the oxide raft floating on the molten aluminium occurs via buckling of the film since it is constrained laterally by the non molten areas. Three forms of stress occur in thin films, these are intrinsic, thermal and adsorption induced. Therefore stress
relaxation via buckling of the oxide must have originated from one of these processes. It is unlikely that adsorption induced stress can occur over such short time scales and is neglected. Constrained lateral thermal expansion of the oxide can result in buckling. As the absorbed fluence increases so does the temperature and thermal expansion and therefore the ripple wavelength decreases. This is opposite to the effect postulated with equation 7.48. The alternative is intrinsic stress which is known to be compressive in SiO2. The mechanism to allow the absorbed fluence to increase the ripple wavelength via relaxation of the intrinsic stress is uncertain. It is noted in section 4.2f that clamping a thin glass slide over a laser heated metal surface results in an increased normal stress due to the restricted thermal expansion of the aluminium. This enhanced normal stress may also contribute to the buckling mechanism.

The ripples in the aluminium in figure 7.36a consist of elongated holes made up of a series of small coalesced holes of about the same size. Hole formation in the molten aluminium arises from a local radial surface tension gradient produced by a local thermal gradient. The local thermal gradient must be produced by a local absorption centre. Since the holes in the aluminium are aligned radially the spatial distribution of the absorption centres is also radial. The most likely explanation is that the heated oxide forms a rippled surface during the early part of the laser pulse, this increases the absorption along the ripple peaks leading to more extensive melting and hole formation in the aluminium. The spatial distribution of the holes is along the ripple direction and as they grow and coalesce they form a continuous elongated hole.

An estimate of the ripple deformation time can be made by assuming the maximum velocity is given by the speed of sound, (5000 ms⁻¹) and the distance moved is of the order of the spatial wavelength, (2.5 μm). This gives a deformation time of 0.5 ns suggesting the ripples could easily form in the overcoating layer within a single laser
pulse. This simple model of an undululating surface increasing the laser absorption is also able to explain the observed ripple profile change with shot number at low fluences. The deformation after the first shot results in a sinusoidal profile. The sinusoidal surface increases the laser absorption for the second shot so producing the inter-pulse feedback mechanism. The process continues until a steady state is reached when the absorbed energy no longer changes the ripple profile. The absorption process could arise from a surface electric field enhancement in the absorbing overcoat because the peak-peak ripple height is comparable to the laser wavelength. A similar process could also explain the preferential absorption of laser radiation along a scratch and the associated ripples parallel to the scratch. In this case the scratch width is comparable to the laser wavelength in the oxide overcoating and a resonant effect seems more likely. A similar electric field enhancement has been considered previously for scratches in pure dielectric materials, (7.44).

7.6 Conclusions
The performance of metallic reflectors at UV wavelengths has been investigated in three areas. These were optical performance, laser damage resistance at 248 nm and the effect of UV irradiation on silicon oxide overcoatings.

7.6a Optical performance
A review has been given of the optimum deposition conditions of thermally evaporated aluminium to achieve maximum reflectance at UV wavelengths. The effect of the evaporation rate and ageing were tested experimentally. Theoretical calculations have shown that the effect of a typical thermally grown aluminium oxide layer at wavelengths greater than 220 nm is to reduce the reflectance by about 1%. The major reason to use a dielectric overcoating in this region is to protect the soft aluminium coating and to boost the reflectance above
that of the uncoated aluminium. Theoretical calculations have shown that the maximum increase in reflectance is at most a few percent for a single layer and occurs when the overcoating is effectively $\lambda/2$ thick. In this case, the actual optical thickness of the overcoating layer is less than $\lambda/2$ since allowance must be made for the phase change on reflection from the aluminium. The reflectance can be greatly increased above that of the uncoated aluminium by using a multi-layer dielectric stack deposited on the aluminium.

Many dielectric overcoatings used in the visible suffer from absorption at UV wavelengths. A theoretical model was developed to predict the performance of thick film metal mirrors overcoated with absorbing dielectric material. This model suggested that the maximum tolerable absorption coefficient at 248 nm for a high index dielectric overcoating is about $5000 \text{ cm}^{-1}$ for an effective half wave layer. Beyond this figure the reflectance of the overcoated mirror is greatly reduced compared to the uncoated aluminium mirror. The theoretical model was used to fit experimental reflectance measurements of a ThF$_4$ overcoated aluminium mirror measured both through the substrate and through the overcoating. This analysis was able to show that the low mirror reflectance arose predominantly from the poor optical constants of the aluminium coating.

MgF$_2$ and LiF are the the most frequently used dielectric overcoatings in the far UV. At the excimer wavelength of 248 nm a better choice is Al$_2$O$_3$ since it deposits with a high packing density at room temperature, has a higher adherence to the aluminium and has a higher refractive index to increase the reflectance. The disadvantage of Al$_2$O$_3$ is that it requires reactive electron beam evaporation to achieve stoichiometric deposition and a closer control of the coating thickness.

7.6b Laser damage resistance at 248 nm

Three thermal models of laser absorption in metal surfaces have been developed to predict the laser damage
threshold of metal mirrors at 248 nm. All use the basic assumption that laser induced damage is observed when the surface reaches some threshold temperature.

A theoretical model has been developed to predict the laser fluence required to heat the surface of a semi-infinite metal to some threshold temperature. The resulting expression depends on the thermal properties of the metal, the absorption of the laser radiation and the laser pulsewidth. A shape factor was introduced to distinguish between rectangular, Gaussian and long-tailed triangular temporal pulse shapes. The model predicts that the fluence required to raise the surface of a semi-infinite polished aluminium sample to its melting point is 1.52 Jcm\(^{-2}\). This assumes a gaussian laser pulse with a FWHM of 24 ns and a mirror reflectance of about 90%. The options to substantially increase the melt threshold for a given pulsewidth are to operate the mirror at low temperatures, reduce the absorptance by increasing the reflectance or to modify the thermal properties.

Operation at cryogenic temperatures is not practicable in many cases. The reflectance can be increased by using multi-layer dielectric stacks deposited on the aluminium. However the damage threshold of the dielectric stacks may then be less than the melt threshold of the aluminium. The final option is to modify the thermal properties of the mirror. This can be done by depositing a thin aluminium coating on a polished metal substrate so that heat conduction is dominated by the thermal properties of the substrate. A figure of merit was devised for the substrate, FOM = \(\rho Ck\)^{1/4}, to enable the optimum choice from the thermal viewpoint. The damage thresholds of two aluminium mirrors deposited on copper and nickel substrates were in good agreement with the calculated melt thresholds using the FOM for copper and nickel. The highest FOM is that for silver with a value of 4.14 relative to the value of aluminium. Potential substantial improvements in the melt threshold may be possible with the optimum choice of metallic substrate.

Aluminium mirrors are usually produced in thin film
form and deposited on insulating substrates such as glass or fused silica. A laser damage model has been developed which takes account of heat loss into any substrate material. This model predicts that even with an insulating glass like substrate the melting point threshold of the aluminium is significantly above that for adiabatic heating when the coating thickness is less than 200 nm. This model was also used to show that the FOM of the substrate material is linearly related to the melt threshold of the aluminium for FOM values less than about 2.5.

The damage threshold of aluminium thin films deposited on glass microscope slides was found to be closer to the threshold value calculated from adiabatic heating of the aluminium. This was attributed to a high pinhole density in the coating. Comparison with higher quality mirrors showed better agreement. The highest measured single shot damage threshold was 1.2 Jcm⁻² measured from a low scatter area of an aluminium coating 242 nm thick. At fluences above the single shot damage threshold circular holes were observed to form in the aluminium and were attributed to radial surface tension gradients due to non-uniform heating.

A modified adiabatic heating model has been developed to predict the damage threshold of thin film aluminium mirrors deposited on insulating substrates with dielectric overcoatings. The modified adiabatic heating model makes allowance for heat loss from either side of the aluminium by assuming an equivalent heated layer in the substrate and overcoating. This equivalent heated layer is calculated as some fraction of the thermal diffusion length in the substrate or overcoating. Several thresholds were defined using this approach. These include; melting of the aluminium, heating to the vaporization point and evaporation.

Experimental single shot damage thresholds were measured in the range 0.1 - 0.68 Jcm⁻². This involved several different dielectric overcoating materials and thicknesses. In general the experimental damage threshold
was found to be in good agreement with the calculated melt threshold for the high quality aluminium mirrors with $\lambda/2$ dielectric overcoats. A $\text{LaF}_3$ dielectric overcoated aluminium mirror was found to have the highest threshold of 0.68 Jcm$^{-2}$. On some mirrors the pinhole density in the aluminium was the limiting factor. This was the case for mirrors with $\text{Al}_2\text{O}_3$ overcoatings where the predicted thresholds were greater than 1 Jcm$^{-2}$ due to the high FOM of sapphire.

The damage threshold was not influenced by the choice of insulating substrate material, (BK-7 or fused silica), the RMS roughness of the substrate or the presence of a chromium undercoat beneath the aluminium. A general observation was that there appeared to be an optimum thickness for the aluminium coating and the overcoat layer. If the aluminium coating was too thick the optical absorption increased which more than compensated for its greater thermal capacity. If the overcoating was too thick stress relaxation effects produced cracking of the film for tensile stress or rippling for compressive stress. Threshold damage was generally observed as the formation of several scattering centres in the dielectric overcoating. In some cases the overcoating was ablated without any apparent damage to the aluminium.

The investigation of laser induced ripple patterns in absorbing oxide materials led to a search for similar ripple patterns in the non-absorbing dielectric overcoated mirrors. No such ripple patterns were observed, however a single example of coherent waves with a ripple wavelength of 0.8 $\mu$m was observed in the aluminium. These ripples were attributed to the 'freezing in' of laser induced capillary waves propagating in the shallow molten surface of the aluminium. A theoretical analysis has shown that a wide range of capillary waves can propagate on the molten surface of aluminium and that they can propagate in shallow liquids. The propagation of capillary waves in molten aluminium with wave periods of tens of nanoseconds is shown to be insensitive to the melt depth and have wavelengths of 0.5 - 1.0 $\mu$m. Only the waves which are
propagating at the time of solidification and have a significant wave amplitude are observed frozen into the surface. A further constraint on the observation of capillary waves frozen into the surface is that the 'time to freeze' be much shorter than the wave period. Estimates of this latter effect show the 'time to freeze' is about 6 – 7 times longer in germanium or silicon than in aluminium. Similar estimates of the 'time to freeze' a thin aluminium coating deposited on a glass substrate gives a factor of 15 times that for aluminium and may explain the rarity of their observation.

7.6c UV irradiation of SiO$_x$ overcoated aluminium mirrors

A greatly improved UV reflectance of SiO$_x$ overcoated aluminium mirrors has been observed after KrF laser irradiation at low fluences, ~ 0.03 Jcm$^{-2}$. This is attributed to the reduction of the oxide absorption as a function of laser shot number. About 1870 shots were required to increase the reflectance at 248 from 55% to 82%. The improvement was greater at shorter UV wavelengths. Similar improvements were also observed by irradiating the sample with an intense continuous wave UV source for different times.

The surface analysis technique known as ESCA was used to show that the large increase in the reflectance was not caused by a large change in the oxygen/silicon ratio in the film. Long irradiation times do increase the oxygen/silicon ratio towards the value of two. Ellipsometry measurements at 632.8 nm suggested no significant change in the physical thickness was involved. The large improvement in the UV reflectance was attributed to the likely presence of interstitial oxygen held in the porous film structure and probably originating from atmospheric gas or moisture. UV irradiation for short times could induce photochemical reactions or increase thermal diffusion of the interstitial oxygen due to heating. The resultant effect is the conversion of SiO to SiO$_2$ with the over-all stoichiometry remaining approximately constant but the film absorption at UV
wavelengths reduced due to the higher percentage of SiO₂ in the film.

Irradiation of the SiO₂ overcoated mirrors at higher fluences, ~ 0.1 - 0.2 Jcm⁻² resulted in the formation of ripple patterns in the oxide layer. Optical microscopy and TEM have shown the damage morphology to consist of a quasi-random rippled surface. Local symmetrical features in the form of parallel and concentric ripples were also observed. The parallel ripples are associated with the presence of a scratch located in the centre of the pattern. Tallysurf measurements of the rippled surface profile have shown its development as a function of shot number. Initially it starts as a sinusoidal surface and develops into a profile with a flattened trough and an increased peak-trough height. Optically this is observed as a greatly increased diffraction efficiency but with no change in the ripple wavelength. It is suggested that this inter-pulse feedback process arises from the rippled surface enhancing the surface electric field resulting in increased energy absorption and heating. This mechanism can continue until the increased energy absorption no longer alters the ripple profile and results in a steady state.

Measurements of the diffraction pattern of the rippled surface have shown the ripple wavelength to depend on the illuminated position on the damage site and on the angle of incidence. These results are consistent with the conclusion that the ripple wavelength is proportional to the absorbed fluence. The physical formation mechanism of the ripples is considered to arise from stress relief of the oxide layer. The dependence of the ripple wavelength on the absorbed fluence suggests the stress relief of the oxide layer must be intrinsic rather than thermal in origin.
7.7 References


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Chapter 8
Laser damage studies of multi-layer dielectric coatings at 248 nm

8.1 Introduction

Two major limiting factors in the design of high power laser systems are the optical losses and the damage threshold of the dielectric coatings. The losses can be attributed to absorption, scattering, poor design and the stability of the coating. The damage threshold is influenced by a multitude of parameters including its intended application. This chapter is mainly concerned with High Reflecting, HR and Anti-Reflecting, AR dielectric coatings at the KrF excimer wavelength of 248 nm. It is broadly divided into effects which influence optical losses given in sections 8.2 - 8.3 and damage threshold measurements including some associated laser damage models in sections 8.4 - 8.6.

The optical losses of absorption and scattering are greatly influenced by the porous microstructure of the thin film. A review is given of the thin film acceptance criteria for use at UV wavelengths and the current trends in the development of the various thin film deposition techniques. The over-all loss factors are also influenced by the design of the multi-layer coating. A review of AR and HR multi-layer dielectric coating design is given with particular reference to the KrF wavelength of 248 nm. At UV wavelengths, there is a restricted choice of high and low index materials with low absorptions. Several AR coating designs are compared at 248 nm including two and three layer quarter wave and non-quarter wave combinations. Closed form expressions are also developed to allow estimates of volumetric and interface absorption and scattering from AR and HR coatings.

There is an enormous amount of literature on the design, manufacture and application of optical thin films. An excellent general introduction is the book by Heavens, (8.1). Two further books were found to be extremely
useful and are widely quoted. The first by Pulker, (8.2) contains a detailed review of different coating methods and the associated film microstructure. The second by Macleod, (8.3) contains an extensive chapter on film admittance, the same notation being used in this work relating to AR and HR coating designs.

The damage thresholds of a range of HR and AR dielectric coatings at 248 nm are included and discussed. This involves comparisons with polished blank surfaces, used and unused samples and the definition of a multi-shot threshold. The results are also compared to other published work.

Two laser damage models have been developed both concerned with absorbing defects. The first model represents damage arising to a laser heated dielectric sphere surrounded by a dielectric host material. Laser damage is assumed to occur when the sphere reaches some material dependent threshold temperature such as its melting point. The predicted damage threshold is calculated as a function of the particle size and absorption. Various damage threshold scaling relationships are predicted and compared with previously published data.

The second laser damage model is concerned with the spot size dependence of the laser damage threshold. The optical surface is assumed to contain a random 2-D distribution of absorbing defects. A significant spot size dependence is predicted if the average number of illuminated defects within the beam area is less than one. The definition of the damage threshold has a significant effect on its absolute value if spot size effects are important. This model has also been used to investigate the spatial distribution of defect centres on an optical surface and also pre-conditioning effects using multi-shot irradiation.
8.2 Thin film dielectric materials for use in the ultra-violet

8.2a Thin film acceptance criteria

The simplest way to identify potential thin film materials for use at excimer laser wavelengths is to firstly consider the optical properties of the same materials in bulk form. The most obvious optical requirement is for low absorption which in bulk materials can be considered for an absorption coefficient $\beta < 1 \text{ cm}^{-1}$. At 248 nm this identifies several alkali and alkaline-earth fluorides, ($\text{LiF, NaF, MgF}_2, \text{CaF}_2, \text{SrF}_2, \text{BaF}_2$), and several transition element oxide and fluoride materials, ($\text{SiO}_2, \text{Al}_2\text{O}_3, \text{HfO}_2, \text{Sc}_2\text{O}_3, \text{Y}_2\text{O}_3$ and $\text{LaF}_3$). In this transparent region the absorption coefficient is limited by the presence of impurities and absorbing defects. Unfortunately not all of these materials are easy to produce in thin film form and those that are typically have absorption coefficients in the UV region perhaps 100 to 1000 times their bulk values when vacuum deposited in a conventional manner. The criterion for a nominally low absorption film is therefore one for which $\beta < 1000 \text{ cm}^{-1}$. As well as acceptable optical properties and a high damage threshold the film(s) must also pass several tests of mechanical and chemical integrity and stability. These include adhesion to the substrate and/or adhesion to adjacent film layers, hardness and abrasion resistance for cleaning purposes and resistance to adsorption of impurities from the environment such as moisture or atmospheric oxygen. The films may also be in a crystalline, polycrystalline or amorphous state, the grain size influencing the amount of scattering. A useful general guide to the optical, mechanical, chemical and thermal properties of thin films is given in reference 8.4.

The preparation of the substrate surface is also important since this forms the first film interface. Grinding, polishing and cleaning of the substrate have been extensively investigated to optimize compatibility.
with thin film deposition. A review of these processes is contained in reference 8.2. Prolonged exposure of the substrate to the atmosphere prior to film deposition can result in contamination of the surface with moisture, hydrocarbons (from handling) and dust particles. Substrate cleaning usually involves two stages, the first being a combination of chemical and physical cleaning often involving solvents and the second, (for vacuum deposition), glow discharge cleaning just prior to film deposition in the coating plant.

Many of the film acceptance criteria are greatly influenced by the film microstructure which in general is somewhat more porous than the same material in bulk form. This results in a greatly increased surface area and a large number of voids in the film. The void fraction of the film is usually expressed in terms of the packing density defined as the ratio of the density of the film to the density of the same material in bulk form. Typically, packing densities for thin films are observed in the range 0.6 - 1.0 depending on the deposition process and deposition conditions. The large surface area and the presence of voids in the film can have important 'knock on' effects influencing many other film properties including:

1. Absorption and scattering
2. Refractive index
3. Geometrical and optical thickness and homogeneity
4. Hardness
5. Stress
6. Chemical stability
7. Thermal stability
8. Environmental stability

The porous microstructure of many thin films results in increased scattering within the bulk of the film and at interfaces between other films. The uptake of moisture into the voids of the film changes the void refractive index from 1.0 to approximately 1.38 at 248 nm. The
The macroscopic effect of this is to reduce the effect of volumetric scattering since the index difference between the voids and bulk is less and increase the effective refractive index and therefore optical thickness of the film. This latter effect is most strikingly observed as a shift in the reflectance maxima or minima for HR or AR coatings to longer wavelengths when air is first admitted into the vacuum chamber of a coating plant housing the sample.

Most materials in thin film form are in a state of stress either compressive or tensile. Two dominant types of stress have been identified, these are thermal and intrinsic. Thermal stress can arise from differential expansion of the substrate and adjacent film layer when the component is heated or cooled. Intrinsic film stress is usually attributed to the inherent microstructure of the film and can be influenced by the uptake of moisture. In catastrophic cases where the tensile or compressive stress is excessive cracking or delamination of the film can occur. The uptake of moisture and the diffusion of other impurities such as oxygen into the film can also result in undesirable chemical reactions and an increased sensitivity to operating temperature due to outgassing of moisture. Conversely, the process of baking the films at high temperatures after deposition has been used to increase the packing density and stabilize the film to environmental changes, (8.5). This baking process has been observed to increase the extinction coefficient of several oxide materials at 250 nm. This effect may be caused by increased scattering due to an increased crystallite size rather than increased absorption.

8.2b Optical thin film deposition methods

The optical and physical properties of nominally low absorption thin films are very sensitive to the film microstructure and its crystalline state. The wide range of deposition techniques and variables within a technique means that a coating may fail an acceptance criterion using one deposition method and be accepted using another.
This is particularly true for properties such as stress and stability but may also include the damage threshold. Ideally, a large number of samples are needed to identify trends. This is an expensive approach especially if optimization of different coating processes is involved in the comparison. It is therefore useful to briefly consider the various coating techniques which are currently in use and those which are still in the development phase. The film properties can then be considered relative to the coating process. An added complication for multi-layer large optics is the requirement for producing constant layer thicknesses over large areas at practical deposition rates. A detailed review of coating processes is given by Pulker, (8.2), Macleod, (8.6) and more recently by several authors in the SPIE conference proceedings, Thin Film Technologies III, (8.7).

The deposition of thin films generally occurs in a subtractive or additive way using chemical, physical or molecular processes. The subtractive process is limited to preferential removal of substrate constituents using chemical leaching or high energy particle bombardment. In this case the film layer is in intimate contact with the substrate. These subtractive layers generally result in a delicate, porous skeleton-like surface layer whose effective refractive index is lower than the bulk substrate value. This limits their application to AR coatings for reducing reflectance. In recent years interest in these coatings has been revived when it was discovered that the damage threshold of the AR coated surfaces at visible and near IR wavelengths was considerably higher than that from conventional, evaporated AR films, (8.8).

The additive methods of thin film formation have been much more widely studied. The additive processes can be broadly divided into molecular, chemical and physical processes. Each is reviewed separately with the main emphasis on physical vapour deposition.
8.2.1 Molecular thin film deposition

Technology 'spin-off' from the semi-conductor industry has been used to produce novel AR coatings at 10.6 μm on small diameter optics, (8.9). This involved the film growth method of Molecular Beam Epitaxy, MBE using two materials in up to 100 stratified layers, each about 10 nm thick. The damage thresholds were at least equal to that of the uncoated substrate and in some cases up to six times that of the uncoated substrate. The main disadvantages of this process apart from equipment cost and availability is the limited deposition rate and perhaps more importantly the limited substrate size for uniform films. These techniques are likely to be used more frequently as solid state lasers and integrated optics are developed.

8.2.1i Chemical thin film deposition

The chemical deposition method can be sub-divided into a wet process or a dry process. The wet process basically involves the deposition of films from solution using spinning or dipping techniques. These methods have been used to produce AR coatings at 248 nm with high damage thresholds compared to established vacuum coating methods, (8.10). The main problem being their very porous microstructure leaving them susceptible to mechanical damage and contamination. The other chemical deposition process, (dry process) is Chemical Vapour Deposition, CVD. This process basically involves film components in the vapour phase reacting chemically to form thin solid films as a solid-phase reaction product which condenses out on the substrate. The chemical reactions are usually considered to occur near to or on the substrate surface. The reactions can be enhanced or activated in several ways including the use of substrate heating, plasmas, UV or X-ray irradiation or particle bombardment using electrons or ions from plasmas or ion guns. The application of pure CVD processes for the production of optical components in laser systems appears to be limited. However, in recent years great interest has been shown in reactive and
activated Physical Vapour Deposition, PVD. This has somewhat blurred the differences between CVD and PVD.

8.2biii Physical vapour deposition

In PVD, coatings are produced on the solid surface in the vapour phase. This method is based on the purely physical effect of vapour condensation on the substrate in a vacuum and is the most widely used technique for the production of laser optics. Chemical reactions are also sometimes involved in so called reactive PVD processes. The chemical reactions can be enhanced using the same techniques as those for CVD, these include:

1) Thermal activation using substrate heating
2) Photon irradiation with a UV or X-ray source
3) Particle bombardment with energetic electrons, ions or neutrals from plasmas or ion guns.

There are two basic types of PVD process, evaporation and sputtering. Both techniques are used under varying degrees of vacuum. The evaporation process can be further sub-divided into conventional evaporation and four energy assisted processes called Activated Reactive Evaporation, ARE, Ion Assisted Deposition, IAD and Reactive Ion Plating, RIP and Ion Cluster Beam Deposition, ICBD. An important difference between the methods is the different energies of their volatilized film material atoms at the substrate. These range from about 0.1 - 0.2 eV in conventional evaporation, about 1 - 10 eV in ARE, ICBD and sputtering and perhaps 10 - 100 eV in the case of IAD and RIP. The mobility and diffusion of the film atoms condensed on the substrate has a significant effect on the film microstructure. Generally, increasing the energy of the vapour atoms at the substrate results in a denser film with a higher index and improved adhesion to the substrate. The differences between the processes become somewhat blurred when the activating methods are also included since they add energy to the growing film increasing the chemical activity and the surface mobility.
Conventional evaporation

The evaporation process is basically a physical one in which the evaporant material is vaporized and condenses on a solid substrate. The conventional evaporation process simply involves evaporation of the source with no added energy contribution to the growing film except perhaps substrate heating. Two evaporation sources have been developed, these are resistance heating using an electric current as the thermal source and electron beam heating. Evaporation by resistance heating uses a refractory metal or metal oxide container to hold the source material. Contamination of the film can sometimes occur from evaporant chemical reactions with the boat material or residual gases. The favoured evaporation method uses electron beam heating which minimizes contamination since only the central area of the evaporant is melted. The electron beam is usually deflected through large angles, (270 degrees) to minimize contamination of the evaporant from the electron filament. Coating uniformity is achieved with a combination of coating plant geometry, rotating substrates and for large optics, multiple sources. In the latter case, real time monitoring of the deposition process is done on a small witness sample located in a position representative of the large component.

Most conventionally evaporated thin films have a microstructure consisting of close-packed columns or columnar crystals. The voids between the columns are largely responsible for the observation of low film packing densities and the uptake of water vapour when air is first admitted into the vacuum chamber. The formation of the columnar structure is attributed to the limited mobility of the condensing atoms and molecules together with shadowing effects of uncoated portions of the substrate by atoms or molecules which have already condensed. Deposition with a high substrate temperature increases the packing density, hardness, adherence and stability of evaporated films. This is attributed to the change in film microstructure with substrate temperature.
and can be described by the so-called "Structure Zone Model", (8.2). In this model the microstructure of the film is allocated to one of three zones depending on the substrate temperature relative to the evaporant melting point, \( T_m \). The conditions are given in table 8.1.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Film microstructure</th>
<th>Substrate temperature, ( T_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 1</td>
<td>columns &amp; voids</td>
<td>( T_s &lt; 0.26T_m )</td>
</tr>
<tr>
<td>Zone 2</td>
<td>dense columns</td>
<td>( 0.26T_m &lt; T_s &lt; 0.45T_m )</td>
</tr>
<tr>
<td>Zone 3</td>
<td>polycrystalline</td>
<td>( T_s &gt; 0.45T_m )</td>
</tr>
</tbody>
</table>

Table 8.1
Structure zone model for evaporated coatings, (8.2)
(Temperature in Kelvin)

Evaporation onto a room temperature substrate therefore results in a zone 1 type microstructure consisting of columns and voids. Since the melting point of many refractory metal and metal-oxides is about 2300 K or above, most evaporated oxide films even at substrate temperatures of 500 K still remain in zone 1 with a columnar microstructure. To achieve a zone 2 microstructure with denser columns and less void space with a lower melting point material such as MgF\(_2\) (mp about 1539 K) requires a substrate temperature in excess of 400 K. Increasing the substrate temperature adds energy to the growing film which can also be achieved at lower substrate temperatures in other ways by irradiating the growing film with energetic particles. This method forms the basis of the enhanced evaporation techniques ARE, IAD and RIP.

The requirement for low UV absorption and the proximity of the UV absorption edge means that fully stoichiometric oxide and fluoride films are needed. Many inorganic materials evaporated under high vacuum undergo
some dissociation and condense out as non-stoichiometric films. An example of a low UV absorption fluoride material in which this occurs is cryolyte, Na₃AlF₆. Evaporation of this source material at temperatures varying in the range 1153 K - 1293 K resulted in a film material with varying amounts of NaF, Na₃AlF₆ and Na(AlF₄), (8.2). Similar measurements on MgF₂ films have shown the degree of dissociation to be much less. Conventional evaporation of MgF₂ using indirect resistance heating or an electron beam source required substrate temperatures of about 600 K to achieve a packing density of 0.98. The poor environmental stability of MgF₂ films deposited on room temperature substrates is usually attributed to moisture absorption into the voids.

The problem of dissociation is particularly apparent for high melting point oxide materials such as Al₂O₃. This can be partly corrected by flowing oxygen into the coating plant at low pressure whilst the evaporation and condensation process is continuing. This technique is known as Reactive Evaporation, RE and involves a chemical reaction of the evaporant and flowing gas usually at or near the substrate's surface. The evaporant is usually in the form of the metal or sub-oxide. The reaction to form the stoichiometric film can be enhanced using substrate heating.

In recent years the complementary techniques of Activated Reactive Evaporation, ARE, Ion Assisted Deposition, IAD, Reactive Ion Plating, RIP and Ion Cluster Beam Deposition, ICBD have been developed. All four methods involve irradiating the growing film with excited atoms/molecules or ions generated from an ion gun or from a plasma running in the vacuum chamber. The distinction between ARE and IAD appears to be based on the mean energy of the irradiating particles. The technique of ARE is considered a low energy process in which the mean ion energy impinging on the film is much less than 100 eV whereas the mean ion energy of the irradiating particles in IAD can be several hundred eV. From the ion energy viewpoint there appears to be little difference between
IAD and RIP, however the former is usually achieved with ion guns and the latter by using a plasma inside the vacuum chamber. The technique of RIP often involves the use of biased substrates to attract the ions for bombardment. Recent reviews of ARE have been given by Ebert, (8.11,8.12) and both IAD and RIP by Pulker, (8.2,8.13).

Activated Reactive Evaporation, ARE

The ARE method developed by Ebert has been used to produce many oxide coatings with absorption coefficients less than 10 cm\(^{-1}\) in the visible. These results also showed that the lowest absorption coatings arise from using negatively ionized oxygen with a mean energy around 10 - 20 eV. Irradiating the growing film with more energetic particles resulted in an improved adherence and packing density but an increased absorption due to preferential sputtering of oxygen in the growing film. The largest reduction of absorption comparing RE and ARE was observed for BeO in which a reduction from 1200 cm\(^{-1}\) to 10 cm\(^{-1}\) was observed. This material together with SiO\(_2\) was used to produce a 35 layer quarter wave mirror with a reflectance of 99% at 193 nm, (8.11).

Ion Assisted Deposition, IAD

The IAD method can be considered a variation of the ARE method in which an ion gun is used to irradiate the growing film usually with ion energies of several hundred eV. This can result in substrate heating during deposition to 500 - 600 K. Irradiation with the more energetic ions usually results in very hard, low stress, stable, high packing density films. However, the production of low UV absorption oxide films has been found to require irradiation with ion energies less than 100 eV, (8.6). This is in good agreement with the observations of Ebert, (8.11). The application of IAD has been mainly aimed at producing metal-oxide films since preferential sputtering of the oxygen in the film can be partly compensated by using oxygen ion beams. Investigations of
fluoride coatings for UV use appears to have been limited to MgF$_2$, (8.14) and LaF$_3$, (8.15). In the case of MgF$_2$, oxygen ions resulted in oxygen contamination of the film as well as tungsten from the ion gun filament. IAD of LaF$_3$ using 500 eV argon ions in preference to oxygen ions gave an absorption coefficient of less than 150 cm$^{-1}$ at 250 nm. These results and those found using ARE suggest the use of low energy argon or fluoride ions to produce hard, stable, low UV absorption fluoride coatings.

Reactive Ion Plating, RIP

Reactive ion plating is a plasma process in which evaporation is performed in the presence of an argon gas discharge and a reactive gas. In collisions and electron impact reactions coating material ions are formed and accelerated in the presence of the biased substrate so that film growth occurs under the influence of ion bombardment. A modified ion plating process has recently been developed for optical coatings known as Reactive Low-Voltage Ion Plating, RLVIP, (8.13). In this technique the ion energy incident onto the substrate is about 10 - 50 eV which minimizes optical absorption whilst still producing a hard, high packing density, stable film with bulk like properties. The excellent stability and compact nature of the microstructure has led to the suggestion by Pulker, (8.16) of extending the structure zone model to a fourth compact vitreous zone where the effective substrate temperature due to ion bombardment exceeds the melting point of the evaporant. The major advantage of this process over other methods is the high deposition rate and its potential for scaling to produce large diameter components. A disadvantage with the technique is that it requires the molten evaporant to be electrically conducting. This usually limits the evaporant materials to metals and sub-oxides.

Ion Cluster Beam Deposition, ICBD

Another recent development in coating technology which uses low energy ions is Ion Cluster Beam Deposition,
IeBD, (8.12). This technique uses a cluster of a few hundred to a few thousand molecules with a single elementary charge. In an electric field the cluster reaches the same energy as an atomic ion. On striking the substrate the cluster breaks up into individual molecules with the kinetic energy being shared to give a mean molecule energy of a few eV. The main advantage of this method is the possibility to deposit fluoride materials as well as oxides.

Gas discharge and ion beam sputtering deposition

Sputtering involves the removal of atoms or molecules from a target usually via the action of an inert gas glow discharge or the use of ion guns. The energetic target atoms then condense on the substrate to form the film. The sputtering process is reviewed in some detail by Pulker, (8.2). Reactive sputtering using oxygen as the reactive gas in the presence of argon as the main constituent has been used to produce hard, stable, high packing density oxide coatings. Sputter deposition has also been used to produce high index intermediate compounds such as Y₄Al₂O₉ and MgAl₂O₄ by using a mixed composition oxide target, (8.17). The use of a substrate bias can increase the energy of the film atoms incident on the substrate and also enhance the growth process by ion bombardment. It is only in recent years that the evaporation methods of ARE, IAD, and RLVIP have been applied to the production of laser coatings to produce film microstructures comparable to sputtered coatings. The main disadvantages of sputtering appears to be the relatively low deposition rate compared to some of the evaporation processes and the difficulty of achieving uniform deposition over large areas.

A recent review of reactively sputtered oxide films for UV use suggested all of the high index oxide coatings, (Al₂O₃, Y₂O₃, HfO₂, ZrO₂) had a zone 3, polycrystalline microstructure except SiO₂ which was amorphous, (8.17). A major loss factor at UV wavelengths was identified as scattering and was reduced by decreasing the crystallite
grain size. Minimum scattering was observed for amorphous low index films such as SiO₂. The main difficulty was in producing amorphous high index oxide coatings. Recommendations for future work included the use of substrate biasing and/or the use of mixed oxides. This work is in general agreement with that of Pulker, (8.15).

8.2c Summary of optical properties of thin films at 248 nm

This section includes a literature survey of the refractive indices of low absorption thin film at 248 nm. Some coatings fail acceptance criteria on grounds of marginally high absorption at 248 nm, stress or stability. These factors may not be so relevant if the films are deposited using the various ion assisted techniques described in section 8.2.b. Table 8.2 includes the refractive index, extinction coefficient and absorption edge data at 248 nm for a range of oxide and fluoride materials.

These data are reproduced from references 8.17 - 8.23 and can be classified into high index oxides and low index fluorides. Few measurements of the extinction coefficient are available at 248 nm, the results given in table 8.2 were taken mainly from reference 8.23 and include the effect of scattering. The actual absorption coefficient is therefore less than that calculated using k in table 8.2. The location of the absorption edge is therefore a better indicator of the relative absorption between the films. The general trend is that the fluorides show lower absorption than the oxides. The only two high index fluorides, CeF₃ and PbF₂ have absorption coefficients around 1000 cm⁻¹ at 250 nm, (8.20). Improvements in coating methods may allow the deposition of these coatings with an absorption edge <250 nm. The highest index oxide material shown in table 8.2 is ZrO₂ which may be useable if the absorption edge could be maintained around 225 nm. The remaining oxide materials have all been used in multi-layer mirrors designed for use at 248 nm, (8.23). The choice of a high index coating at the ArF excimer wavelength of 193 nm becomes more restrictive since the
### Table 8.2

<table>
<thead>
<tr>
<th>Film</th>
<th>Refractive index at 248 nm</th>
<th>Abs edge/nm</th>
<th>coating method</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.17 - 2.47, 0.006</td>
<td>225 - 260</td>
<td>RS, RE</td>
</tr>
<tr>
<td>HfO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.15 - 2.36, 0.002</td>
<td>215 - 220</td>
<td>RS, RE</td>
</tr>
<tr>
<td>Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.0 - 2.155, 0.002</td>
<td>210 - 220</td>
<td>RS, RE</td>
</tr>
<tr>
<td>Sc&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.11, 0.002</td>
<td>205</td>
<td>RE</td>
</tr>
<tr>
<td>ThO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.90 - 2.00, 0.005</td>
<td>200 - 250</td>
<td>RE</td>
</tr>
<tr>
<td>Y&lt;sub&gt;4&lt;/sub&gt;Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;9&lt;/sub&gt;</td>
<td>1.97</td>
<td>220</td>
<td>RS</td>
</tr>
<tr>
<td>MgAl&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.90</td>
<td>220</td>
<td>RS</td>
</tr>
<tr>
<td>MgO</td>
<td>1.83 - 1.89, 0.002</td>
<td>200</td>
<td>RS, RE</td>
</tr>
<tr>
<td>BeO</td>
<td>1.82, 0.001</td>
<td>&lt;190</td>
<td>ARE</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.66 - 1.73, 0.0004</td>
<td>&lt;200</td>
<td>RS, RE</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.42 - 1.52, &lt;0.001</td>
<td>&lt;200</td>
<td>RS, RE</td>
</tr>
<tr>
<td>PbF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.05, 0.002</td>
<td>~250</td>
<td>RH</td>
</tr>
<tr>
<td>CaF&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.80, 0.002</td>
<td>~250</td>
<td>RH</td>
</tr>
<tr>
<td>LaF&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.59 - 1.61, 0.001</td>
<td>&lt;200</td>
<td>EB</td>
</tr>
<tr>
<td>ThF&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.58 - 1.59, &lt;0.001</td>
<td>&lt;&lt;200</td>
<td>RH, EB</td>
</tr>
<tr>
<td>YF&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.54, &lt;0.001</td>
<td>&lt;200</td>
<td>EB</td>
</tr>
<tr>
<td>CaF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.48</td>
<td>&lt;200</td>
<td>EB</td>
</tr>
<tr>
<td>Na&lt;sub&gt;3&lt;/sub&gt;AlF&lt;sub&gt;6&lt;/sub&gt;</td>
<td>1.35 - 1.40, 0.007</td>
<td>&lt;200</td>
<td>EB</td>
</tr>
<tr>
<td>MgF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.38 - 1.43, &lt;0.001</td>
<td>&lt;200</td>
<td>EB</td>
</tr>
<tr>
<td>LiF</td>
<td>1.37, 0.001</td>
<td>&lt;&lt;200</td>
<td>EB</td>
</tr>
<tr>
<td>NaF</td>
<td>1.35, 0.009</td>
<td>-</td>
<td>EB</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>coating method</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS, RE</td>
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<tr>
<td>RS, RE</td>
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<td>RS, RE</td>
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<tr>
<td>RE</td>
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<tr>
<td>RE</td>
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<tr>
<td>RS, RE</td>
</tr>
<tr>
<td>RS, RE</td>
</tr>
<tr>
<td>ARE</td>
</tr>
<tr>
<td>RS, RE</td>
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<tr>
<td>RS, RE</td>
</tr>
<tr>
<td>RH</td>
</tr>
<tr>
<td>RH</td>
</tr>
<tr>
<td>EB</td>
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<td>EB</td>
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<tr>
<td>EB</td>
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<tr>
<td>EB</td>
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</tbody>
</table>

Absorption edge of many of the oxides is around 200 nm.

8.2d Damage thresholds of single layer dielectric coatings in the UV region

The damage thresholds of single layer films in the excimer wavelength region have been reported in some detail in references 8.21 - 8.23. The damage thresholds were measured at the KrF wavelength of 248 nm or the
quadrupled NdYAG wavelength of 266 nm. Most of the films were deposited using electron beam evaporation. The experimental conditions and the definition of the damage threshold are important factors when comparing different data sets. The 248 nm results in reference 8.23 were measured with a 1 - 3 mm 1/e² spot size and a 20 ns pulsewidth. The 266 nm results in references 8.21 and 8.22 were measured with 1/e² spot sizes around 0.15 mm and pulsewidths of 5, 15 and 22 ns. The damage threshold definition for all three data sets was the midway point between the minimum fluence which caused damage and the maximum which did not.

The most extensive set of results involving 15 films have been measured by Milam et al at 248 nm, (8.23). Their results are reproduced in figure 8.1 and are more likely to be independent of the spot size and threshold definition due to the larger illuminated area. The damage threshold covers the range 0.2 - 25 Jcm⁻² corresponding to ZrO₂ and ThF₄. The ordering and the actual threshold values of the films in the three data sets vary considerably making direct comparisons difficult. This is partly due to the definition of the damage threshold which is dependent on the defect density and spot size.

Various scaling relationships have been investigated with this data, the most noticeable is a decrease in the damage threshold as the absorption edge of the film is approached. A second trend which may also be due to the approach of the absorption edge is the observation of a decrease in the damage threshold as the refractive index, (real part) increases. This latter phenomenon has also been observed at visible and infra-red wavelengths and forms the basis of using non-quarter wave dielectric films in AR and HR coatings to move the electric field peak into the low index film where the threshold is higher, (8.24).

These damage threshold trends for single layer films are useful for identifying which materials are unsuitable for multilayer coatings but not necessarily the most suitable. The use of the most damage resistant films does not necessarily produce the most damage resistant AR or HR
Figure 8.1

Laser damage thresholds of $\lambda/2$ thick films measured at 248 nm with 20ns pulses. Data reproduced from reference 8.23
coatings. If stress build-up is not a problem it seems likely that this is because the coating conditions in a given plant have not been optimized for each film. In many cases, it is not possible to do extensive investigations for all coatings. In practice, promising coatings are identified and the deposition conditions subsequently optimized. This appears to be the case for materials like Sc₂O₃. It seems likely that as many of the recently developed coating techniques are applied to high power laser optics new or alternate film materials will be identified and the optimization procedure repeated.

8.3 Design of anti-reflecting and high reflecting multi-layer dielectric coatings at 248 nm

8.3a General concepts

The problems of optical absorption and scattering in thin films become severe in the UV region where the choice of low absorption materials is limited compared to that in the visible and scattering is greatly increased for the same surface roughness. Conservation of energy requires that

\[ R + T + A + S = 1 \]

where \( R \) is the specular reflectance, \( T \) the transmission, \( A \) the absorptance and \( S \) the total scattered fraction. Absorption and scattering can be sub-divided into a volumetric effect and an interface effect, \((8.25)\). Volumetric absorption is characterized by the absorption coefficient for each film and is generally much higher than that of the same material in bulk form.

At interfaces, absorption and scattering can be further sub-divided into effects at the air-film interface, effects at the film-film interfaces and effects at the film-substrate interface. The effect on the damage probability of small absorbing defects distributed at the interfaces in a multi-layer stack is considered in section
The absorption at a given interface will depend on the absorption cross section of the defects, the number of illuminated defects and the local electric field intensity. The macroscopic effect of the defects at low incident intensities is to increase the interface absorption and scattering. At high incident laser intensities the absorbing defects may result in significant local heating and destruction of the coating. This laser damage mechanism is considered in section 8.5.

An added complication at high intensities is the possibility of non-linear absorption by the absorbing defect. In some cases the absorbing defects may be several microns in diameter and extend throughout the multi-layer, an example being the growth nodule shown in figure 4.1.

The increased volumetric scattering and absorption over that in bulk form are influenced by the film microstructure and the electric field distribution within the multi-layer stack. The problems of absorption and scattering in the UV suggest that the design aim should be to minimize the number of film layers and modify the electric field distribution so that the maxima are not at the interfaces but in the more damage resistant layer.

The simplest optical model of a multi-layer coating is to initially assume there is no scattering, \( S = 0 \) and the interface absorption is negligible. This is equivalent to representing each film in the stack as an ideal homogeneous isotropic slab. Using this model, the reflectance, transmittance and absorptance of an assembly of thin films can be calculated using the concept of optical admittance considered by Macleod, \( 8.3 \). The multi-layer is effectively replaced by a single surface which has an input optical admittance \( Y \) given by

\[
Y = \frac{C}{B}
\]

The parameters \( B \) and \( C \) arise from the characteristic matrix for the whole assembly. If the multi-layer coating is considered to consist of \( q \) layers, the characteristic
The matrix of the assembly is simply the product of the individual characteristic matrices for each layer taken in the correct order. This gives

\[
\begin{bmatrix}
B
\end{bmatrix} = \prod_{r=1}^{q} \begin{bmatrix}
\cos \Delta_r & i \sin \Delta_r / \eta_r \\
\eta_r \sin \Delta_r & \eta_r \cos \Delta_r
\end{bmatrix} \begin{bmatrix}
1 \\
\eta_m
\end{bmatrix}
\] 8.3

The order of multiplication is important; the first layer with \( r = 1 \) corresponds to the film adjacent to the incident medium and the final \( q \)th layer is adjacent to the substrate. The notation and geometry for a single layer is shown in appendix IV. The admittance of the \( r \)th layer is given by \( \eta_r \) and the phase thickness \( \Delta_r = 2\pi n_r d_r \cos \theta_r / \lambda \). \( \eta_m \) is the substrate admittance. Equation 8.3 can be used to calculate the reflectance, \( R \), the transmittance, \( T \) and absorptance \( A = (1 - R - T) \) of a multi-layer thin film assembly. The analysis is given by Macleod, (8.3) resulting in

\[
R = \left| \frac{\eta_0 B - C}{\eta_0 B + C} \right|^2
\] 8.4

\[
T_o = 4\eta_m \text{Re}(\eta_0) / \left| \eta_0 B + C \right|^2
\] 8.5

\[
A = 4\eta_0 \text{Re}(BC^* - \eta_m) / \left| \eta_0 B + C \right|^2
\] 8.6

In terms of the total admittance the reflectance is often written as \( R = \left| \eta_0 - Y / (\eta_0 + Y) \right|^2 \) where \( \eta_0 \) is the admittance of the incident medium which is assumed to be real. The transmittance of a thin film assembly is independent of direction even if absorbing layers are present. This is not generally true for reflectance except when there is no absorption in any of the layers. The laborious nature of calculating the characteristic matrix of the thin film assembly for a large number of layers has been greatly reduced by the wide availability of computers.
The characteristic matrix of a single thin film takes on a simple form if the optical thickness, \( N_1d_1\cos\theta \) is an integral multiple of quarter or half waves given by

\[ N_1d_1\cos\theta = n(\lambda/4) \quad (n = 0, 1, 2, 3, \ldots) \quad 8.7 \]

This gives a phase thickness of

\[ \Delta_1 = n(\pi/2) \quad 8.8 \]

For \( n \) even, \( (n = 0, 2, 4, 6 \text{ etc.}) \), \( \cos\Delta_1 = \pm 1, \sin\Delta_1 = 0 \) and the optical thickness of the layer is an integral number of half wavelengths. In this case the characteristic matrix for a single film becomes

\[
\begin{bmatrix}
1 & 0 \\
0 & 1
\end{bmatrix}
\]

This is the unity matrix and can have no effect on the reflectance or transmittance of the assembly at the wavelength for which the optical thickness of the coating is an even number of half wavelengths. This results in half wave layers often being called absentee layers.

For \( n \) odd, \( (n = 1, 3, 5 \text{ etc.}) \), \( \sin\Delta_1 = \pm 1, \cos\Delta_1 = 0 \) and the optical thickness of the layer is an odd number of quarter wavelengths. The characteristic matrix in this case becomes

\[
\begin{bmatrix}
0 & 1/\eta_1 \\
\eta_1 & 0
\end{bmatrix}
\]

If a substrate or combination of thin films has an admittance \( Y \), then the addition of an odd number of quarter waves of admittance \( \eta \) alters the admittance of the combination to \( \eta^2/Y \). This effect makes the optical properties of multi-layer quarter wave films relatively
easy to calculate. Usually only two or three different materials are involved in designs and a convenient shorthand notation used to denote quarter wave thicknesses is H, M or L where H refers to the highest of the three indices, M the intermediate value and L the lowest.

The presence of scattering from a surface can be considered in terms of the decrease in the specular reflectance and transmittance given by equations 8.4 and 8.5. Experiments have shown that scattering in multi-layer thin films is predominantly from interface roughness, (8.25). Interface scattering arises from a roughness contribution from the substrate and/or previous layer and an intrinsic roughness contribution from the thin film. The scattering intensity from each interface depends on the local surface roughness and the local electric field intensity. Several theoretical models of scattering in multi-layer films have been developed depending on the degree of correlation of the interface roughness with the previous layer, (8.25). The simplest is the correlated model where the film surface roughness exactly reproduces the surface roughness of the substrate. In this case, multi-layer scattering is equivalent to that from a single surface of equal reflectance, (8.25). At normal incidence the decrease in the specular reflectance, AR and transmittance, AT is then given by

\[ \Delta R = R \left( \frac{4 \pi \sigma}{\lambda} \right)^2 \]
\[ \Delta T = T \left( 2 \pi \sigma / \lambda \right) (n_m - 1)^2 \]

for \( \sigma \ll \lambda \), where \( \sigma \) is the RMS height of the surface irregularities around the mean and \( n_m \) is the substrate refractive index. For an optical window with good AR coatings (<0.1% per surface), the light scattered per window is approximately \( 2 \Delta T \). At a wavelength of 248 nm and using a fused silica substrate, \( n_m = 1.5085 \) a scattered fraction of 0.1% per surface results from an RMS roughness figure of 2.5 nm. The same roughness figure of 2.5 nm for a HR dielectric mirror results in a scatter
level of 1.6% at a wavelength of 248 nm. The RMS figure must be reduced to 1 nm to achieve a tolerable 0.25% scatter level.

A simple computer programme was written to calculate the reflectance and transmittance of multi-layer thin films at 248 nm. The two main simplifying assumptions were that dispersion is negligible over the wavelength range of interest and that the coatings were non-absorbing. The first simplification is valid since interest is centred at a single laser wavelength. The second assumption makes the analysis much simpler but does not indicate the absorption within the multi-layer. The absorption for AR coatings was calculated from approximate closed form expressions derived in appendix V. The absorption of HR coatings with quarter wave thicknesses was calculated from approximate closed form expressions given by Bennet, (8.25).

8.3b Anti-reflection coating designs at 248 nm

The reflectance of a multi-layer coating is zero when the admittance of the assembly is equal to the admittance of the incident medium. This occurs when \( (\eta_0 B - C) = 0 \) from equation 8.4. The simplest form of anti-reflection coating is a single layer. Substituting \( q = 1 \) in equation 8.3 and using \( (\eta_0 B - C) = 0 \) for zero reflectance gives

\[
\eta_0 [\cos \Delta_1 + i \eta_m \sin \Delta_1 / \eta_1] = i \eta_1 \sin \Delta_1 + \eta_m \cos \Delta_1
\]

Making the simplifying assumption that \( \eta_0, \eta_1 \) and \( \eta_m \) are real corresponding to the case of no absorption and equating real and imaginary parts of equation 8.11 gives

\[
(\eta_0 - \eta_m) \cos \Delta_1 = 0 \quad 8.12
\]

and

\[
(\eta_0 \eta_m / \eta_1 - \eta_1) \sin \Delta_1 = 0 \quad 8.13
\]
Since \( \eta_o \neq \eta_m \) the condition for zero reflectance requires \( \cos \Delta_1 = 0 \) and \( \eta_1 = (\eta_o \eta_m)^{1/2} \). These conditions are met for a coating whose optical thickness is an odd multiple of quarter waves and whose refractive index at normal incidence in air is given by \( \eta_1 = (\eta_m)^{1/2} \). The simplest case is that for a single quarter wave layer. The refractive index of fused silica at 248 nm is 1.5085 giving a required coating index at normal incidence of 1.2282. Vapour deposited thin films with such low refractive indices are not available. The lowest index thin film materials for use at 248 nm are NaF or Cryolite, \( \text{(Na}_3 \text{AlF}_6 \) both of which form hydroscopic soft coatings with indices around 1.35. A single quarter wave thickness of either of these materials deposited on a fused silica substrate has an admittance at normal incidence of \( \eta_1^2/\eta_2 = 1.207 \). This gives a normal incidence reflectance of 0.88% compared to an uncoated surface of 4.1%. This figure could be reduced to 0.12% by using a sapphire substrate since the refractive index of sapphire is about 1.7 at 248 nm. At angles of incidence other than normal, the phase thickness of the layer is reduced and the admittance of the coating depends on the polarization state of the incident light. For a given layer thickness the wavelength corresponding to the minimum becomes shorter.

In recent years interest has been shown in graded-index AR surfaces. This is because of their high surface damage threshold compared to conventionally produced vacuum deposited AR coatings, (8.25). Two chemical techniques have been developed to produce graded index AR coatings for laser applications, these are the Neutral Solution Process and the Sol-Gel process, (8.26). In the former, carefully controlled chemical etching and leaching of a glass surface is used to produce a porous and skeleton like surface layer which has a low effective refractive index. At 1060 nm this technique has produced surfaces with a specular reflectance of around 0.1 - 0.2% and a surface scatter figure of about 0.05%, (8.26). Substituting this scatter figure into equation 8.10 and
assuming $T \approx 1$ with an effective substrate index of 1.23 gives an RMS roughness of 16.5 nm. The calculated scatter figure at 248 nm is some eighteen times higher than that at 1060 nm at 0.9% per surface. The Sol-gel process offers the possibility of graded index coatings on a wide range of substrates. This technique involves the formation of a transparent gel film on the surface of the substrate by dipping or spinning. The film is subsequently heated and dried again resulting in a porous microstructure which has a low effective index.

The condition for zero reflectance from a single layer, Equation 8.11 can be simply extended to two layers by substituting $q = 2$ in Equation 8.3 and requiring $\langle \eta_o B - C \rangle = 0$. Equating real and imaginary parts gives

\[
\tan^2 \Delta_1 = \frac{\langle \eta_m - \eta_o \rangle \langle \eta_2^2 - \eta_o \eta_m \rangle \eta_1^2}{\langle x \eta_o \eta_m - \eta_1^2 \rangle} \quad 8.14
\]

\[
\tan^2 \Delta_2 = \frac{\langle \eta_m - \eta_o \rangle \langle \eta_0 \eta_m - \eta_1^2 \rangle \eta_2^2}{\langle x \eta_2^2 - \eta_o \eta_m \rangle} \quad 8.15
\]

where

\[
x = \eta_1^2 \eta_m - \eta_o \eta_2^2 \quad 8.16
\]

Equations 8.14 and 8.15 have been derived assuming the film and substrate admittances are real. In general $\langle \eta_m - \eta_o \rangle > 0$ so that real solutions to equations 8.14 and 8.15 exist for the remaining terms either all positive or any two negative and the third positive. The problem is simplified by assuming normal incidence in air because the refractive indices replace the admittances and $\eta_o = 1.0$. In this case, the all positive term solution requires $\eta_1^{\langle \eta_m \rangle^{1/4}}$. This choice is not a realistic option for low index substrate materials where $\eta_m \approx 1.5$. The only possible option for low index substrates is given by the constraint $\eta_2^{\langle \eta_m \rangle^{1/4}}$. This constraint requires that the high index film must be adjacent to the substrate and sets a minimum high index once the substrate and low index film are chosen.
The most well known solution occurs when both films have a quarter wave optical thickness. This is the limiting solution when \( n_2 = n_1 (n_m)^{\frac{1}{2}} \) and can be simply derived by equating the admittance of a two layer quarter wave coating, \( Y = \frac{n_1^2 \eta_m}{\eta_2} \), to \( \eta_0 \). The above relationship can be used to help identify suitable high index materials given the restricted choice of low index low absorption thin films at 248 nm. For zero reflectance the refractive index of the high index film should be greater than or equal to the calculated minimum value of \( n_2 \). The refractive index and absorption coefficient at 248 nm of suitable thin films are considered in section 8.2. Some results for a given low index material with a fused silica substrate are shown in Table 8.3.

Alternative high index oxide thin films for use at 248 nm may include \( \text{MgO} \) (\( n = 1.83 \)), \( \text{Sc}_2\text{O}_3 \) (\( n = 2.11 \)), \( \text{HfO}_2 \) (\( n = 2.25 \)), \( \text{Y}_2\text{O}_3 \) (\( n = 2.11 \)), \( \text{ThO}_2 \) (\( n = 1.90 \)) and \( \text{ZrO}_2 \) (\( n = 2.25 \)). These refractive indices and those quoted in Table 8.3 are reproduced from reference 8.23 and represent films with high packing densities.

<table>
<thead>
<tr>
<th>Low index material</th>
<th>Refractive index at 248 nm</th>
<th>Calculated ( n_2 = n_1 (n_m)^{\frac{1}{2}} )</th>
<th>Nearest high index material</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Na}_3\text{AlF}_6 )</td>
<td>1.35</td>
<td>1.66</td>
<td>LaF(_3), ( n = 1.59 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ThF(_4), ( n = 1.59 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Al(_2)O(_3), ( n = 1.70 )</td>
</tr>
<tr>
<td>( \text{MgF}_2 )</td>
<td>1.38</td>
<td>1.695</td>
<td>Al(_2)O(_3), ( n = 1.70 )</td>
</tr>
<tr>
<td>( \text{SiO}_2 )</td>
<td>1.44</td>
<td>1.77</td>
<td>Al(_2)O(_3), ( n = 1.70 )</td>
</tr>
</tbody>
</table>

Table 8.3
Possible thin film materials for use at 248 nm in a LH(Sub) AR coating design

The results in Table 8.3 show that even using a minimum index of 1.35 requires a high index material with \( n_2 \geq 1.66 \) for zero reflectance. The calculated reflectance variation with wavelength for the three combinations listed in Table 8.3 are shown in figure 8.2. The all
fluoride and all oxide combinations have similar profiles with a reflectance minima around 0.18%. This may be acceptable since both combinations offer stability advantages and furthermore the scattering level is likely to be of this order for any of the coating designs. The all oxide combination would be suitable for laboratory use since the hard coatings would be resistant to water absorption and make cleaning simpler. The all fluoride combination may be useful for in-cavity use where resistance to chemical attack by fluorine gas is important. The only thin film pair in table 8.3 which meets the zero reflectance constraint is the MgF$_2$-Al$_2$O$_3$ combination. This coating design is known as a V coat because of its characteristic profile and has a reflectance below 0.1% over the range 238 - 260 nm. This design is relatively insensitive to individual coating thickness changes. A variation of 10% produces an increased reflectance of 0.2% at 248 nm. The coating performance is more sensitive to index variations. A 3% variation in the low index produces a 0.15% increase in reflectance whereas a 3% variation in the high index produces a 0.05% increase.

The absorption of AR coatings influences both the damage threshold and the light throughput. The over-all absorption can be estimated by summing the absorption at each interface and using the absorption coefficients of each film to calculate the volumetric absorption. The contribution to absorption from defects at an interface can be estimated by considering an average defect with radius $a$, absorption efficiency $Q_d$ and defect density $\lambda$. In this case the absorption at a single interface, $A_{int}$, is given by

$$A_{int} = \lambda Q_d \pi a^2$$  

This assumes that the dimensions of the illuminating beam are greater than the average spacing between the defects. Even in the most severe case of $Q_d = 1$ corresponding to a highly absorbing defect the over-all absorption only

-428-
REFLECTANCE / %

FIGURE 8.2

SPECTRAL PERFORMANCE OF SEVERAL AR COATING DESIGNS AT 248 nm
becomes significant when $\lambda a^2 > 0.01$. This corresponds to the total absorption cross-sectional area of all of the illuminated defects being greater than 1% of the illuminated area. Assuming the defects at each interface are distributed in a random independent fashion, the overall absorption for $N$ interfaces is given by $\sqrt{N A_{\text{int}}}$. Defect densities of about 25 mm$^{-2}$ with a mean radius of about 5 $\mu$m have been measured on a three layer AR coating designed for use at 248 nm, (see section 8.6). This corresponds to an absorption of 0.2% per interface and an overall absorption of 0.4% for $N = 4$. This figure is comparable to the expected contribution of volumetric absorption in the UV region where the absorption coefficient of many thin films is around 500 cm$^{-1}$.

Approximate closed form expressions have been calculated in appendix V for the volumetric absorption of a three layer AR coating. The absorption is estimated from the average power dissipated in each film knowing the electric field intensity at each interface. The electric field intensity at each interface relative to the incident value is calculated from recursive expressions given by Levi, (8.27). The expressions for absorption reduce to those given by Bennett, (8.25) in the simplified case of quarter wave layers. In the UV region, the extinction of nominally low absorption coatings is of the order of $k \approx 10^{-4} - 10^{-3}$. This corresponds to an absorption coefficient $\beta$ in the range 50 - 500 cm$^{-1}$. The calculated absorption at 248 nm of a two layer quarter wave AR coating for different assumed values of the extinction coefficient are shown in table 8.4. The high index $n_2 = 1.70$ and the low index $n_1 = 1.38$. A comparison is also given with an exact calculation of the absorption from equation 8.6, (8.28).

The approximate values are in good agreement with the exact calculations and indicate an absorption figure of less than 0.1% requires film absorption coefficients of less than 125 cm$^{-1}$ corresponding to an extinction coefficient of $0.25 \times 10^{-3}$. This figure is difficult to achieve since many of the coating materials used at 248 nm
have extinction coefficients around $10^{-3}$ corresponding to an absorption coefficient of 500 cm$^{-1}$. The absorption for $n_1 = 1.38$ in percentage terms can be written as $A(\%) = 0.257 + 0.31n_m/n_2^2$. Although the absorption is minimized by using a high index for $n_2$, the absolute value only changes from 0.43% for $n_2 = 1.70$ to 0.35% for $n_2 = 2.2$.

<table>
<thead>
<tr>
<th>Extinction/Absorption coefficient from Appendix V</th>
<th>Approx Absorption</th>
<th>Exact calculation of Absorption from equation 8.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k/\beta (\text{cm}^{-1})$</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>$10^{-5}/5$</td>
<td>0.004</td>
<td>-</td>
</tr>
<tr>
<td>$10^{-4}/50$</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>$10^{-3}/500$</td>
<td>0.43</td>
<td>0.42</td>
</tr>
<tr>
<td>$10^{-2}/5000$</td>
<td>4.30</td>
<td>4.40</td>
</tr>
</tbody>
</table>

Table 8.4
Calculation of the volumetric absorption at 248nm of a two layer quarter wave AR coating deposited on a fused silica substrate, \( (LH(Sub), n_2 = 1.70, n_1 = 1.38, n_m = 1.5085) \)

An alternative two layer design using non quarter wave thicknesses is possible if the constraint $n_2 > n_1 (n_m)^{1/4}$ is satisfied. The coating thicknesses are calculated from equations 8.14 and 8.15 by substituting for $n_1$, $n_2$ and $n_m$. In the case of MgF$_2$ and Al$_2$O$_3$ the design changes from the quarter wave layer design LH(Sub) to (0.955L)(0.87H)(Sub). This design has a similar profile to that shown for the quarter wave solution given in figure 8.2. The potential advantage of this design is the reduced thickness of the films resulting in a lower volumetric absorption compared to the all quarter wave designs. However, the expressions given in appendix V suggest the reduction in absorption is marginal decreasing from 0.43% to 0.39%.

Dielectric coatings consisting of three or more layers have generally been developed for broadband use. The most well known is the three layer design containing a
high index half wave absentee layer between the outer two quarter wave layers. A review of the various multi-layer quarter wave and non-quarter wave options is given by Macleod, (8.3). The design of three layer AR coatings at a single wavelength has been considered by Baer, (8.29) and more recently by Nagendra and Thutupalli, (8.30).

An alternative, three layer single wavelength V coat design which appears not to have been previously considered involves the use of equivalent layers. The basic idea is to use a symmetrical combination of three layers, ABA which has an equivalent admittance \( \eta_e \) and phase thickness equal to that for a single quarter wave. The condition for zero reflectance is achieved by equating the equivalent admittance to that required for zero reflectance from a single layer coating. The normal incidence condition for zero reflectance from a single layer quarter wave coating is that its index be given by \( n_1 = (n_m)^{1/4} \). This gives \( n_1 = 1.2282 \) for a fused silica substrate at 248 nm. Following Macleod, (8.3) the equivalent phase thickness is a quarter wave when

\[
\cos(2\Delta_a) = (\eta_b^2 + \eta_a^2)(\eta_e^2 - \eta_a^2)/(\eta_b^2 - \eta_a^2)(\eta_e^2 + \eta_a^2)
\]

8.18

and

\[
\tan(\Delta_b) = 2\eta_a\eta_b/[(\eta_a^2 + \eta_b^2)\tan(2\Delta_a)]
\]

8.19

where \( \Delta_a \) and \( \Delta_b \) are the phase thicknesses of the layers A and B and \( \eta_a \) and \( \eta_b \) are the respective admittances. The problem is simplified by considering normal incidence in which case the admittances are replaced by the refractive indices. In the case of \( \eta_e < \eta_a \) and the index of the middle layer being greater than that of the outer layers, \( \eta_b > \eta_a \), the constraint for a real solution to equation 8.18 gives \( \eta_b > \eta_a^2/\eta_e \). Substituting \( \eta_e = 1.2282 \) gives the constraint on the minimum value of the high index, \( \eta_b > 0.8142\eta_a^2 \). Three designs for use at 248 nm are shown in table 8.5 involving an all fluoride coating, design 1, a mixed fluoride and oxide coating, design 2, and an all
oxide coating, design 3.

<table>
<thead>
<tr>
<th>Design 1</th>
<th>Design 2</th>
<th>Design 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>index of layer A</td>
<td>(1.35(Na_3AlF_6))</td>
<td>(1.38(MgF_2))</td>
</tr>
<tr>
<td>optical thickness A</td>
<td>0.697L</td>
<td>0.691L</td>
</tr>
<tr>
<td>index of layer B</td>
<td>(1.59(ThF_4/LaF_3))</td>
<td>(1.70(Al_2O_3))</td>
</tr>
<tr>
<td>optical thickness B</td>
<td>.609H</td>
<td>1.625H</td>
</tr>
</tbody>
</table>

Table 8.5
Design details of symmetrical, (ABA), three layer AR coatings at 248 nm

The coating thicknesses are specified relative to a quarter wave thickness for the low index material, L and the high index material H. The spectral performance of the 'design 2' three layer AR is shown in figure 8.2. Its bandwidth is fractionally narrower than the two layer quarter wave V coat design also shown in figure 8.2. Both coating designs use the same refractive indices of 1.38 and 1.70, the minimum value of the high index for design 2 is 1.55. The spectral performance of designs 1 and 3 closely follow that for design 2. The advantage of the three layer design over the two layer design is its greater degree of flexibility in choice of coating materials whilst still maintaining a high optical performance. This is illustrated in figure 8.2 where the two layer all oxide and all fluoride quarter wave combinations have a much higher reflectance minimum than the three layer designs using the same materials.

Also included in figure 8.2 is a three layer proprietary design for use at 248 nm produced by Technical Optics, (8.31). This AR coating design has a reduced optical performance compared to the quarter wave two layer designs and also the symmetrical three layer designs. Its implementation resulted in a transmittance minimum at
270 nm presumably due to moisture uptake of the low index material, this resulted in a reflectance at 248 nm of around 1%.

The absorption of the symmetric three layer designs given in table 8.5 were calculated using the expressions given in appendix V assuming an extinction coefficient of $10^{-3}$ for each layer. The calculated absorption in each layer and the total absorption are summarized in table 8.6. Calculations are also included for the proprietary three layer design produced by Technical Optics, (8.31).

<table>
<thead>
<tr>
<th>Design</th>
<th>A % out</th>
<th>A % mid</th>
<th>A % inn</th>
<th>A % tot</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design 1</td>
<td>0.18</td>
<td>0.36</td>
<td>0.16</td>
<td>0.70</td>
</tr>
<tr>
<td>(k=10^{-3})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Design 2</td>
<td>0.18</td>
<td>0.355</td>
<td>0.155</td>
<td>0.69</td>
</tr>
<tr>
<td>(k=10^{-3})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Design 3</td>
<td>0.21</td>
<td>0.23</td>
<td>0.20</td>
<td>0.64</td>
</tr>
<tr>
<td>(k=10^{-3})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tech Opt</td>
<td>0.08</td>
<td>0.385</td>
<td>0.22</td>
<td>0.685</td>
</tr>
<tr>
<td>(k=10^{-3})</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8.6

Calculated volumetric absorption of three symmetric AR coating designs at 248 nm, (designs 1 - 3 in table 8.5) and a three layer proprietary design produced by Technical Optics, (8.31). The absorption was calculated assuming an extinction coefficient of $10^{-3}$ for each layer.

The over-all absorption of all four designs is similar although the distribution of the absorption varies somewhat between the layers following the layer thicknesses. The calculated absorption for design 2 is about 60% greater than that for the two layer design using the same indices and $k = 10^{-3}$ for each layer. This is
simply due to the increased over-all layer thickness. The measured scattering plus absorption of the Technical Optics coating was about 0.1 - 0.2%, \((1 - R - T)\) suggesting the extinction coefficient of the films was nearer to \(10^{-4}\).

8.3c High-reflection coating designs at 248 nm

The simplest high reflectance multi-layer dielectric coating is the quarter wave stack. This consists of alternate quarter wave layers of high index and low index materials stacked one on top of another. The high reflectance is achieved because the beams reflected from all of the interfaces in the assembly are of equal phase when they reach the front surface where they combine constructively.

The design of HR mirrors with a modified electric field distribution has been considered by Gill et al, (8.24) and shown to improve the damage threshold by about 40% in the visible and near infra-red regions. The basis of the technique relies on the observation that the damage threshold of low refractive index materials in bulk or thin film form is usually higher than that for high index materials. The surface damage threshold of crystalline fluoride materials at 193 nm, (see chapter 6) and that of \(\lambda/2\) films at 248 nm, (8.23) also appears to generally follow this trend. The coating design uses non-quarter wave thicknesses for the outer few layers to shift the electric field maxima at the H-L interfaces to within the low index coating. A further advantage of this design is that the electric field maxima are not at the film interfaces where defect absorption may be significant. Only the thicknesses of the outer 2-4 layers are modified since the electric field intensity decays by the ratio \((n_i/n_h)^2\) for each H-L layer pair, (8.24). These effects have also been investigated with HR mirrors at 248 nm by Newnam et al, (8.32) who observed an average onset threshold improvement of about 50%.

For the purposes of calculating the optical performance it is simpler to consider the HR multi-layer
stack to be made up of quarter wave layers only. The reflectance in the ideal case of no scattering can be calculated from equation 8.3 giving the characteristic equation of the thin film assembly. The expressions for reflectance and transmittance, (equations 8.4 and 8.5) considerably simplify by assuming normal incidence and negligible absorption. Assuming the number of layers \( q = 2p + 1 \) and the high index is outermost on both sides then the design can be abbreviated to \((HL)^{2p}H\) with an admittance given by

\[
Y = \left(\frac{n_h}{n_l}\right)^2 \frac{n_h}{n_m} \tag{8.20}
\]

where \( n_h \) and \( n_l \) are the refractive indices for the high and low index layers respectively. The reflectance in air from equation 8.4 is given by

\[
R = \left(\frac{1 - Y}{1 + Y}\right)^2 \tag{8.21}
\]

The greater the number of layers for a given ratio \( \left(\frac{n_h}{n_l}\right) \) the greater the reflectance. Maximum reflectance for a given odd number of layers is obtained with the high index layer outermost. If the admittance \( Y \gg 1 \) the reflectance simplifies to

\[
R \approx 1 - \frac{4}{Y} \tag{8.22}
\]

and

\[
T = 1 - R \approx \frac{4}{Y} \tag{8.23}
\]

These expressions show that when the reflectance is high the addition of a HL layer pair reduces the transmission by a factor \( \left(\frac{n_l}{n_h}\right)^2 \) and that for a given number of layers the reflectance increases as the ratio \( \left(\frac{n_h}{n_l}\right) \) increases. An estimate of the number of layer pairs, \( p \) required to achieve a particular reflectance value can be calculated from equation 8.22 by substituting for the admittance \( Y \)
given by equation 8.20. Assuming the required reflectance is greater than or equal to some factor $\zeta$ the minimum number of layer pairs is given by

$$p = 0.5 \log\left(\frac{4n_m/n_h^2(1-\zeta)}{\log(n_h/n_l)}\right)$$

For a high reflector as part of a laser cavity a minimum reflectance of $\zeta = 0.99$ is desirable. The minimum number of layer pairs $p$ and the overall number of layers $q = 2p + 1$ are shown for four mirror designs in table 8.7.

<table>
<thead>
<tr>
<th>$n_h$</th>
<th>$n_l$</th>
<th>$n_h/n_l$</th>
<th>No of layer pairs, $p$</th>
<th>Total No of layers, $q$</th>
<th>Absorption %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.20</td>
<td>1.44</td>
<td>1.527</td>
<td>6</td>
<td>13</td>
<td>0.44</td>
</tr>
<tr>
<td>1.70</td>
<td>1.38</td>
<td>1.232</td>
<td>13</td>
<td>27</td>
<td>1.25</td>
</tr>
<tr>
<td>1.70</td>
<td>1.44</td>
<td>1.180</td>
<td>17</td>
<td>35</td>
<td>1.51</td>
</tr>
<tr>
<td>1.59</td>
<td>1.35</td>
<td>1.178</td>
<td>17</td>
<td>35</td>
<td>1.75</td>
</tr>
</tbody>
</table>

Table 8.7

High reflectance mirror designs for use at 248 nm, $(HL)^2P(H(Sub))$. Substrate assumed to be fused silica, $n_m = 1.5085$ with film absorption coefficients, $\beta = 500$ cm$^{-1}$.

These combinations of high and low index thin films can be produced using HfO$_2$ ($n_h = 2.20$), Al$_2$O$_3$ ($n_h = 1.70$), ThF$_4$ or LaF$_3$ ($n_h = 1.59$), SiO$_2$ ($n_l = 1.44$), MgF$_2$ ($n_l = 1.38$) and Na$_3$AlF$_6$ ($n_l = 1.35$). The number of layer pairs $p$ in table 8.7 has been corrected upwards to the nearest integer to give the number of layers $q = 2p + 1$ to achieve a minimum reflectance of 99%. The designs with a ratio of $n_h/n_l$ less than about 1.2 require in excess of thirty layers to achieve a reflectance greater than 99%. In this case, if the deposition rate is low, accurate control and monitoring of the deposition process is required to
maintain the coating thickness and index uniformity. A large number of layers is also likely to result in higher interface absorption and scattering and an increased volumetric absorption. At 248 nm an estimate of the scattering from a HR mirror, (section 8.3a) gives a figure of 0.25% for an effective RMS roughness of 1 nm. An estimate of the interface absorption for a twenty layer coating gives an upper limit of 0.9%. The volume absorption of a multi-layer quarter wave HR coating can be calculated using an expression given by Bennett, (8.25).

\[ A = \lambda (\beta_l + \beta_h)/2(n_h^2 - n_l^2)[1 - (n_l/n_h)^{2p + 1}] \quad 8.25 \]

where \( \beta_{l/h} \) is the absorption coefficient of the low or high index film. Equation 8.25 represents an approximation to that given by equation 8.6 by calculating the average electric field intensity in each layer from the values at the interfaces. The absorption values for the HR mirror designs shown in table 8.7 were calculated assuming the absorption coefficient for the low and high index films were equal at 500 cm\(^{-1}\). This corresponds to an extinction coefficient of \( k \approx 1 \times 10^{-3} \) at 248 nm. For a given absorption coefficient it is preferable to use a high ratio of \( n_h/n_l \) to minimize the interface and volumetric absorption. An absorption figure at 248 nm of less than about 0.2% arises by using low index films with \( k \approx 1 \times 10^{-4} \). This figure is comparable to that expected for scattering from a high quality multi-layer.

The reflectance of two HfO\(_2\)/SiO\(_2\) quarter wave dielectric stacks with \( p = 9 \), (19 layers) and \( p = 4 \), (9 layers) are shown in figures 8.3a and 8.3b. Both mirrors were produced in the configuration (HL)\(^2\)Ph(Sub) on a fused silica substrate. The reflectance was calculated from the measured transmittance using a Perkin Elmer 323 spectrophotometer. At the design wavelength of 248 nm the 19 layer coating had a measured transmittance of 0.25% corresponding to a reflectance of 99.75% if absorption and scattering are ignored. The corresponding reflectance value for the 9 layer mirror was 91.5%. These reflectance

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REFLECTANCE MEASUREMENTS OF A 19 LAYER HfO₂/SiO₂ HR MULTILAYER

REFLECTANCE MEASUREMENTS OF A 9 LAYER HfO₂/SiO₂ HR MULTILAYER
figures and the corresponding layer numbers can be used to solve equation 8.21 simultaneously for the refractive index of the HfO$_2$, $n_h$ and the SiO$_2$, $n_l$. This approach is justified since the two mirrors were produced during the same coating run. After some manipulation equation 8.21 can be re-written as

$$Y_1 = \frac{1 + R_1^{1/2}}{1 - R_1^{1/2}} \quad 8.26$$

where the subscript $i = 1$ or 2 corresponds to the two mirrors with differing numbers of layer pairs. The negative sign arising from taking the square root is used to ensure that $Y_1 > 1$. Substitution of equation 8.20 in equation 8.26 for the two cases of $p = p_1$ and $p = p_2$ results in

$$n_h = \left(\frac{Y_{1m}}{R_{1m}}\right)^{1/2\left(2+e-1\right)} \quad 8.27$$

$$n_l = \left(\frac{Y_{1m}}{R_{1m}}\right)^{1/2p_1} \quad 8.28$$

where $e = p_2/p_1$. Substituting values of $R_1 = 0.9975$ and $R_2 = 0.915$ in equation 8.26 gives $Y_1 = 1598.0$ and $Y_2 = 45.0$. Substituting these values in equations 8.27 and 8.28 and using $p_1 = 9$ and $p_2 = 4$ gives $n_h = 1.976$ for the HfO$_2$ and $n_l = 1.383$ for the SiO$_2$. These coatings were produced with a substrate temperature of 250°C giving a packing density in excess of 0.9, (8.33). The refractive index values are somewhat lower than the literature values quoted in section 8.2. The theoretical profiles are in reasonable agreement with the experimental results shown in figures 8.3a and 8.3b at wavelengths longer than 240 nm. They were generated by using the high and low index values calculated from equations 8.27 and 8.28. The model ignores dispersion effects and assumes the absorption is zero. At wavelengths shorter than 240 nm dispersion and absorption are significant as the absorption edge of HfO$_2$ is approached.

The reflectance and transmittance of the 19 layer
coating were also measured with the excimer laser resulting in $T = 0.25\%$ and $R = 99\%$. Simply assuming the remainder is divided equally between absorption and scattering gives $A = 0.375\%$ and $S = 0.375\%$. Ignoring interface absorption and assuming $\beta_d = \beta_h$ for simplicity gives an equivalent film absorption coefficient of 300 cm$^{-1}$ and an RMS roughness figure of 1.2 nm.

As shown in figure 8.3a the behaviour of the high reflectance zone is limited in extent. On either side of the plateau the reflectance falls abruptly to a low oscillatory value. The addition of extra layers does not significantly effect the width of the high reflectance zone but does increase the reflectance within it and the number of oscillations. The width of the high reflectance zone expressed in terms of the wavelength can be shown to be given by, (8.3)

$$\Delta \lambda = \lambda_o \left[ (1 - \Delta g)^{-1} - (1 + \Delta g)^{-1} \right]$$  \hspace{1cm} 8.29

where

$$\Delta g = 2/\pi \sin^{-1}\left( \langle n_h - n_i \rangle / \langle n_h + n_i \rangle \right)$$  \hspace{1cm} 8.30

The width of the high reflectance zone is dependent on the design wavelength $\lambda_o$ and the refractive index ratio $n_h/n_i$. If $\Delta g \ll 1$ then equation 8.29 simplifies to $\Delta \lambda = 2\Delta g\lambda_o$ with the width symmetrical about the design wavelength $\lambda_o$. For the high reflectance mirror shown in figure 8.3a the calculated width of 56.3 nm is somewhat wider than the experimental value of about 36 nm. The width of the high reflectance zone for the designs considered in table 8.7 vary from 26 nm for the lowest $n_h/n_i$ value to 67 nm for the highest $n_h/n_i$ value.

8.4 Laser damage thresholds of HR and AR coatings at 248 nm

Damage threshold measurements have been made on 18 HR dielectric coatings and three AR coatings. The results are summarized in tables 8.8 and 8.9. All of the
substrates were fused silica except the HR mirror with a threshold of 0.75 Jcm\(^{-2}\) which was Pyrex. The damage thresholds were all measured at 248 nm except a single HR mirror which was tested at 193 nm and had a low threshold of 0.1 Jcm\(^{-2}\). The single shot damage threshold for most of the samples was defined as that incident peak fluence for which the damage probability was one. This definition was used for the large spot size measurements, (>5mm\(^2\)). In the cases where a small spot size was used, (<1mm\(^2\)) the onset threshold was more appropriate. This is the maximum fluence for which the damage probability is zero. The onset threshold is more time consuming to measure because the probability of damage needs to be evaluated at several fluences. The two definitions rapidly approach each other if the number of damage sensitive defects illuminated by the focused beam is greater than one.

The single shot threshold was measured by irradiating the sample at about 10 different test sites over a wide fluence range. This single shot testing procedure is sometimes known as a 1 on 1 test. The test sites were distributed over the whole sample area to try and identify weak regions. The sample was then irradiated at a further 10 sites with smaller fluence increments to more accurately locate the threshold value. Finally the sample was irradiated at a further 5 sites to determine the fluence for which the damage probability was one. The measurement procedure for the onset threshold is considered in section 8.6. The damage threshold of the HR coatings was measured at a tilt of a few degrees to prevent reflections back into the laser cavity.

Multi-shot or N on 1 tests have also been investigated. In this case the observation of threshold damage was delayed for a certain shot number at the same test site. Two types of multi-shot test were identified. In the first, threshold damage was usually observed within the first 2 - 5 shots but which sometimes extended to 20 - 30 shots. This effect is associated with the sensitivity of the method used to detect threshold damage. In the second much rarer case, threshold damage was

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delayed for several hundred shots. The cause of this process is uncertain but is presumably related to some accumulative process such as photochemical changes. Both of these effects led to a multi-shot threshold defined as the maximum fluence for which the damage probability is zero after 600 shots at 2 Hz. This somewhat pragmatic definition makes some allowance for both multi-shot effects and also offers a conservative threshold value for use in design. The 600 shot onset thresholds are marked with an asterisk in table 8.8 and 8.9. The results indicate that this threshold is 2 - 5 times less than the single shot threshold.

The effect on the single shot damage threshold of pre-conditioning the sample with multi-shot irradiation at lower levels was initially investigated on a single HR coating and a single AR coating. Irradiation of the BaO/SiO₂ HR coating with 1000 shots at 0.25 Jcm⁻² improved the damage threshold from 1.3 to 2.0 Jcm⁻². Improvements of about 20% in the onset threshold in some HR coatings at 248 nm have been observed previously, (8.34). Irradiation of the Design Optics AR coating with 600 shots at 1.0 Jcm⁻² improved the single shot damage threshold from 1.65 to 4.7 Jcm⁻². This method for improving the single shot damage threshold was investigated in greater detail for the three layer AR coating produced by Technical Optics. In contrast, the measurements on this sample, (see section 8.6) suggested UV laser irradiation at low levels reduces the defect density of the most damage sensitive defects but does not significantly change the onset threshold. Both of these effects can be explained by assuming multi-shot irradiation initially removes the most damage sensitive defects such as the most absorbing ones and subsequently at higher shot numbers or fluences removes the less absorbing defects.
<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Coating materials</th>
<th>Single shot threshold Jcm$^{-2}$</th>
<th>Multi-shot threshold Jcm$^{-2}$</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical Optics</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$_3$AlF$_6$/ThF$_4$</td>
<td>2.6</td>
<td>1.3 (20 shots)</td>
<td>41 layers</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>0.5*</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>0.5 (10 shots)</td>
<td></td>
<td>Pyrex sub, used mirror</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td></td>
<td></td>
<td>Blotches in film, R = 85%</td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td></td>
<td></td>
<td>As above</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td></td>
<td></td>
<td>As above</td>
</tr>
<tr>
<td>HfO$_2$/SiO$_2$</td>
<td>0.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$/SiO$_2$</td>
<td>0.1</td>
<td></td>
<td></td>
<td>$\lambda = 193$ nm</td>
</tr>
<tr>
<td>Fused silica blank</td>
<td>12.3</td>
<td>4.3*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Dynasil 4000)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clarendon Laboratory</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HfO$_2$/SiO$_2$</td>
<td>1.0</td>
<td>0.5 (3 - 5 shots)</td>
<td>19 layer R = 99%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>0.75*</td>
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<td>9 layer R = 91%</td>
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<tr>
<td></td>
<td>0.65</td>
<td></td>
<td></td>
<td>7 layer R = 80%</td>
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<tr>
<td>Ebert, Univ of Hanover</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>BeO/SiO$_2$</td>
<td>1.3</td>
<td>0.25*</td>
<td></td>
<td>35 layers dep using ARE</td>
</tr>
<tr>
<td>CVI</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.1 (30 shots)</td>
<td></td>
<td>used mirror</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td></td>
<td></td>
<td>R = 50%</td>
</tr>
<tr>
<td>OCLI</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sc$_2$O$_3$/MgF$_2$</td>
<td>7.9</td>
<td>4.3*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 8.8
Damage thresholds of HR dielectric mirrors at 248 nm
Manufactured Coating materials Single shot Multi-shot Comment

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Coating materials</th>
<th>Single shot</th>
<th>Multi-shot</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical Optics</td>
<td>SiO$_2$MgF$_2$, SiO$_2$MgO(Sub)</td>
<td>0.65</td>
<td>-</td>
<td>Measured refl of coating .9%</td>
</tr>
<tr>
<td></td>
<td>MgF$_2$, SiO$_2$MgF$_2$(Sub)</td>
<td>0.8</td>
<td>-</td>
<td>As above</td>
</tr>
<tr>
<td>Design Optics</td>
<td>?</td>
<td>1.65</td>
<td>1.0$^3$</td>
<td>Measured refl of coating .35%</td>
</tr>
</tbody>
</table>

Table 8.9
Damage thresholds of AR dielectric coatings on fused silica substrates at 248 nm

The single shot damage threshold at 248 nm of the HR mirrors covers the range 0.3 - 7.9 Jcm$^{-2}$ and can be broadly divided into three regions. These are a low region below 1 Jcm$^{-2}$, an intermediate region between 1 - 3 Jcm$^{-2}$ and an upper region which includes the threshold of 7.9 Jcm$^{-2}$. This latter figure is about 2/3 that of the front surface damage threshold of the polished fused silica. The damage threshold of 12.3 Jcm$^{-2}$ for the fused silica compares with values of 8 - 12 Jcm$^{-2}$ measured by Rainer et al for several samples of the same material (8.35). Their measurements of the single shot front surface damage threshold of CaF$_2$ and MgF$_2$ were about twice that of the fused silica in the range 15 - 25 Jcm$^{-2}$. In these materials the bulk and surface thresholds were about equal.

The damage morphology was usually in the form of several obvious damage pits randomly distributed around the beam centre. However, the damage morphology of the HfO$_2$/SiO$_2$ coatings was in the form of many very fine scattering centres in the shape of the beam. This type of
damage morphology has been observed previously in HfO\textsubscript{2} films damaged at 266 nm and indicated the coating was operating near to its absorption edge since identical features were observed to occur as the known absorption edge of other films was approached, (8.21).

The results in table 8.8 can be compared with an extensive set of measurements made by Milam et al, (8.23) and reproduced in figure 8.4. Their investigations of the Sc\textsubscript{2}O\textsubscript{3}/MgF\textsubscript{2} mirrors have shown that the damage threshold can be more than doubled by simply adding an outer half wave overcoat of SiO\textsubscript{2} or MgF\textsubscript{2}. The Sc\textsubscript{2}O\textsubscript{3}/MgF\textsubscript{2} mirror in table 8.8 was also produced by OCLI and had been previously tested at the Lawrence Livermore laboratory where a threshold of 6 - 8 Jcm\textsuperscript{-2} was measured. This figure is within 13% of the value measured here and represents a good cross-calibration check. The effect on the damage threshold at 248 nm of moving the peak standing wave electric field intensity into the more damage resistant low index layers has been reviewed by Newnam et al, (8.32). His results suggest improvements in the onset threshold of about 50% are possible relative to an all quarter wave mirror. Similar investigations by Milam et al, (8.23) at 355 nm suggested improvements of about 60% were possible by modifying the outer two layer pair thicknesses. The simplest option seems to be the use of a half wave overcoat barrier layer to improve the damage threshold.

Several witness samples of all fluoride mirrors were produced by Technical Optics. Their main application was for in-cavity use on the large KrF laser facility at the Rutherford and Appleton laboratory, (8.36). This required 300 mm diameter optics although the witness samples were much smaller with diameters of 25 or 50 mm. It is interesting to compare the damage thresholds of the rather 'blotchy' used samples in the range 0.3 to 0.75 Jcm\textsuperscript{-2} with the unused 'good' samples with thresholds in the range 1.65 - 2.6 Jcm\textsuperscript{-2}. This illustrates the problems of simulating the end-user environment in a laser damage test. In this case the chemical attack of the fluorine
Laser damage threshold measurements on dielectric HR mirrors at 248nm. Results reproduced from reference 8.23.
gas and its compounds and the radiation from the laser discharge have reduced the damage threshold by an average factor of four.

The thin film materials Na$_3$AlF$_6$ and ThF$_4$ tend to produce soft coatings when deposited at room temperature. A further requirement at the Rutherford and Appleton laboratory was for a large number of beam steering mirrors to be located in the normal laboratory environment. This preferentially required hard and stable all oxide HR coatings. This resulted in the manufacture of HfO$_2$/SiO$_2$ combinations which had rather low thresholds around 0.5 - 1 Jcm$^{-2}$. The three HfO$_2$/SiO$_2$ coatings produced by the Clarendon Laboratory, (8.33) were all produced in the same coating run and show the threshold increases with the number of layer pairs and reflectance. The results in figure 8.4 show that thresholds around 4 Jcm$^{-2}$ are achievable with these materials. The BeO/SiO$_2$ coating was produced by the Activated Reactive Evaporation method developed by Ebert, (8.11). This coating method using these materials has been used to produce HR mirrors at 193 nm. The damage threshold of this sample was probably limited by the large number of scattering centres apparent in the coating. This contrasted with the OCLI mirror where the visually observed scattering was very low.

The single shot damage threshold at 248 nm of the AR coatings covers the range 0.8 - 1.65 Jcm$^{-2}$. These thresholds are the onset values and differ significantly from the spot size dependent values such as those corresponding to a damage probability of 50%. The somewhat lower thresholds of the AR coatings produced by Technical Optics are partly attributed to the relatively high coating reflectance at 248 nm of 0.9%. This figure shows a reduction to below 0.3% at 270 nm which may be caused by optical thickness changes due to moisture absorption. These few examples compare with thresholds in the range 4 - 6 Jcm$^{-2}$ measured by Milam et al, (8.23,8.37). Their measured thresholds were found to improve by 25 - 50% with the use of half wave undercoats of SiO$_2$ or MgF$_2$ deposited on the substrate prior to
deposition of the AR coating. The pre-conditioned single shot damage threshold of 4.7 Jcm\(^{-2}\) for the Design Optics coating compares with the values published by Milam. The damage morphology with this sample was usually in the form of a single damage pit. The visual scattering from this sample was also very low as it was for the HR coating from OCLI and suggests a correlation of the damage threshold with pre-damage scattering.

8.5 A laser damage model based on absorbing defects

8.5a Development of the model
The model most often used in the study of impurity-dominated laser damage assumes a spherical absorbing particle embedded in an infinite non-absorbing host material. The exact solution for the interaction of a plane electromagnetic wave with a sphere has been given by Mie, (8.38). The solution gives the field distributions both inside and outside the sphere. In the case of an absorbing sphere a fraction of the distributed electromagnetic energy inside the sphere is converted to heat. The heat conduction equations can then be used to determine the temperature distribution both inside and outside the sphere. This assumes the laser pulse duration \(\tau\) is much longer than the energy conversion time. Damage is assumed to occur when the laser heated particle reaches some critical material dependent temperature, \(T_c\). Above this temperature catastrophic damage arises from material fracture, vaporization, shock wave formation or plasma formation. In early work on glass laser systems the impurity was attributed to platinum inclusions in the glass host. The solutions to the heat flow equations both in the particle and in the surrounding glass have been given by Hopper and Uhlmann, (8.39) for the case of a perfectly conducting particle in intimate thermal contact with the glass host. The critical temperature was considered that for which the induced stress exceeded the strength of the glass. A simplified thermal analysis for metal and absorbing dielectric particles has also been
given by Sparks, (8.40).

The threshold damage morphology at 248 nm of the HR and AR coatings described in section 8.4 was usually in the form of several micron sized damage pits distributed randomly around the central beam area. This suggests that the damage process is initiated at local 'weak points' generically called defects. Similar observations at UV wavelengths have also been made elsewhere, (8.21, 8.23). Measurements of absorption contour maps of HR mirrors for use at the XeF wavelength of 351 nm have suggested that some of the threshold damage sites are caused by localized regions of high linear absorption, (8.41). Apart from localized absorption, alternative damage mechanisms could include non-linear absorption at the defect site or electric-field enhancement by the defect.

The simplest model is therefore to represent the defect as a spherical, linearly absorbing impurity embedded in an infinite non-absorbing dielectric medium. The localized increase in absorption could arise from non-stoichiometric film regions, evaporant splatter or local impurities such as dust particles. Laser damage is assumed to occur when the particle with radius 'a' reaches some material dependent threshold temperature which for convenience is taken as its melting point. The problem reduces to that of solving the heat conduction equation in spherical coordinates both in the particle, 0<r<a and in the surrounding medium, r>a. A thermal source term inside the particle generates heat at a rate A (J s⁻¹ cm⁻³) due to the absorption of the laser radiation. The two equations are given by

\[ \nabla^2 T_i - \frac{1}{x_i} \frac{\partial T_i}{\partial t} = - \frac{A(r, \theta, \varphi, t)}{K_i} \quad 0<r<a \quad 8.31 \]

\[ \nabla^2 T_h - \frac{1}{x_h} \frac{\partial T_h}{\partial t} = 0 \quad r>a \quad 8.32 \]

where \( x \) and \( K \) are the thermal diffusivity and thermal conductivity and the subscripts \( i \) and \( h \) refer to the impurity and host material. Equations 8.31 and 8.32 have been written assuming the thermal properties \( x \) and \( K \) are
independent of temperature, (8.42). The source term in its most general form is expressed with an \( (r, \theta, \phi) \) dependence. To simplify the problem the sphere is assumed to be uniformly volumetrically heated by an incident rectangular laser pulse with width \( \tau \) and constant intensity \( I_o \), (Wcm\(^{-2}\)). In this case the thermal source term inside the sphere has no \( (r, \theta, \phi) \) dependence and can be written as

\[
A = \begin{cases} 
3\sigma I_o/4\pi a^3 & 0<t<\tau \\
0 & t>\tau 
\end{cases} \quad 8.33
\]

where \( \sigma \) is the absorption cross section, (in cm\(^2\)) given by the expressions calculated by Mie, (8.38). Using the notation of Van de Hulst, (8.43) the absorption cross section is given in terms of the absorption efficiency \( Q \) and the geometrical cross section of the sphere.

\[
\sigma = Q\pi a^2 \quad 8.35
\]

The absorption efficiency is expressed in terms of the relative refractive index of the sphere \( m \) and a non-dimensional size parameter \( x \) given by

\[
m = (n - ik)/n \quad 8.36
\]

\[
x = 2\pi a n /\lambda_o \quad 8.37
\]

where \( n_i \) is the real index, \( k_i \) the extinction coefficient of the sphere and \( \lambda_o \) the laser wavelength in a vacuum. In general the Mie expressions are complicated. Considerable simplification results if \( m << 1 \) and \( x >> 1 \) giving

\[
Q = 1 + 2\exp(-\omega)/\omega + 2[(\exp(-\omega) - 1)/\omega^2] \quad 8.38
\]

where \( \omega = 4\pi k_i/n_h \). This result has been reproduced from reference 8.43.
The sphere is assumed to be in intimate thermal contact with the host material implying no thermal resistance at the interface. The boundary conditions at the interface then become

$$T_i = T_h \quad \text{at } r=a$$  \hspace{1cm} 8.39

$$K_i \frac{dT_i}{dt} = K_h \frac{dT_i}{dt} \quad \text{at } r=a$$  \hspace{1cm} 8.40

The solution to equations 8.31 and 8.32 using the boundary conditions in equations 8.33 - 8.34 and 8.39 - 8.40 has been given by Goldenberg and Trantor, (8.44). Their solution can be used to calculate the incident fluence at time $t$ required to raise a thin spherical shell of the sphere to the critical temperature $T_c$ given by:

$$F \cdot I_{ot}/T_r \cdot 4\pi a T_i \left[ A + B - C \int_0^\infty \exp(-y^2/(a+\beta))\sin(\eta y/a)\,d\eta \right]$$  \hspace{1cm} 8.41

where $A = K_i / (3K_h)$, $B = (1 - r^2/a^2)/6$, $C=2ab/\pi$, $\gamma = a^2 / k_i$

$b = (K_h/K_i) (x_i/x_h)^{1/2}$, $c = 1 - (K_h/K_i)$, $\alpha = \sin \gamma$ and

$\beta = \gamma \cos \gamma$. Equation 8.41 is valid for $0 < t < \tau$ and $F$ has a maximum value at the end of the laser pulse. The fluence has also been corrected for the optical transmittance of the air-host interface, $T_r$. This neglects any thin film interface effects which may enhance the local intensity above or below the incident value. Equation 8.41 was initially used by Lange et al, (8.45) at $r = a$ to calculate the damage threshold dependence on the thermal properties of the host material.

8.5b Approximations in the model

Before evaluating the solution given by equation 8.41 it is useful to consider the physical situation that it is representing and some of the approximations involved. The model is representative of an absorbing defect embedded in an infinite dielectric host material. This requires that the dimensions of the host material be much larger than...
the sphere diameter and the thermal diffusion distance in the host. This is illustrated in figure 8.5 for the case of a single layer film. At UV wavelengths the film thickness is typically some tens of nm and the thermal diffusion distance about 300 nm, \( \langle \text{SiO}_2 \rangle \) and \( \tau = 24 \text{ ns} \). If the sphere diameter or thermal diffusion distance in the host is comparable to the film thickness then the initial assumption of an infinite dielectric host is strictly invalid. A better approximation may be a cylinder whose heat loss is in the radial direction only. In the case of a multi-layer film the approximation of an infinite host may be valid for a small defect. However in this case the thermal properties of the composite host material are represented by some average value.

An added complication at UV wavelengths is the bulk absorption and therefore heating of the dielectric host surrounding the sphere. The results in section 8.2 suggest the absorption coefficient of thin films at 248 nm is typically in the range 50 to 500 cm\(^{-1}\). This implies the absorption coefficient of the sphere must be greater than the bulk absorption coefficient of the film. In the cases where the absorption coefficient is spatially uniform over the film area threshold damage would be in the form of a beam 'footprint' following the fluence distribution in the beam. This beam footprint at the threshold level has been observed in several oxide films tested at 266 nm, whereas the fluorides produced a defect like damage morphology, (8.21). In general, the absorption coefficient of fluoride materials in the UV is less than that of oxides. These tests also included TiO\(_2\) and ZrO\(_2\) films whose damage morphology changed from defects to a beam footprint in the region of the absorption edge. The formation of threshold damage in the form of defects can therefore be used to indicate the absorption edge is well away from the laser wavelength.

A significant simplification of equation 8.31 arises by assuming uniform volumetric heating of the sphere. A simple argument for large spheres, \( \langle x \rangle \gg 1 \) suggests the intensity skin depth should be much larger than the
FIGURE 8.5
AN ABSORBING DEFECT MODEL FOR LASER DAMAGE
sphere diameter. The intensity skin depth is the inverse of the absorption coefficient, and varies from 20 - 200 \( \mu m \) for absorption coefficients in the range 500 - 50 cm\(^{-1}\). The maximum sphere diameters are perhaps one tenth of these values. The absorption coefficient or skin depth for the sphere therefore limits the maximum particle size for which the assumption of uniform volumetric heating is valid.

In general, the thermal source distribution function can only be calculated by numerically evaluating the Mie solutions for the electric field distribution inside the sphere, (8.46). The electric field distribution inside the sphere for a size parameter \( x \) around one has been calculated for visible and infra-red laser radiation incident on spherical water droplets, (8.46). The calculations suggest considerable inhomogeneities with local electric field intensity enhancements of a factor of at least \( 10^2 \). Experiments on the laser breakdown of large transparent droplets have shown that the electric field enhancement can lead to non-linear processes such as stimulated Raman scattering and multi-photon absorption, (8.47). This latter process ultimately leads to breakdown and plasma formation. This more rigorous analysis also shows the electric field distribution inside the sphere is only uniform for the case of \( x \ll 1 \). This constraint on particle size is much more severe than that considered above. At 248 nm and with a host index of \( n_h = 1.5 \) this condition requires a sphere radius \( a \ll 26 \) nm. This restriction on the maximum particle size can perhaps be relaxed somewhat when considering the distribution of thermal energy inside the sphere. In this case, the diameter of the sphere should be less than the thermal diffusion distance in the sphere. Since the defects are considered weakly absorbing, their thermal properties are likely to be similar to the host material. This gives a maximum particle diameter \( 2a \ll 300 \) nm assuming an SiO\(_2\) host with \( \tau = 24 \) ns.

The restrictions \( m \ll 1 \) and \( x \gg 1 \) limits the optical properties and size of the sphere for which equation 8.38
can be used to make a good estimate of the absorption cross section. The first inequality requires both \( \frac{n_i}{n_h} - 1 \ll 1 \) and \( k_i/n_h \ll 1 \) and suggests the real refractive index of the impurity must be similar to that of the host material and that the sphere should be weakly absorbing. The second inequality, \( \lambda \gg 1 \) limits the minimum particle size for a laser wavelength of 248 nm to \( a > 26 \) nm for a typical host index of 1.5.

The final approximation is represented by equations 8.39 and 8.40 implying zero thermal resistance. This requires intimate thermal contact between the sphere and the surrounding film comparable to that observed in a soldered joint. If the defect is located in a film void this would produce a high thermal resistance suggesting almost adiabatic heating of the defect.

8.5c Application of the model

A computer programme was written based on equation 8.41 to calculate the incident fluence at 248 nm required to raise the absorbing sphere to its melting point. The model was applied to the case of a spherical impurity of \( \text{SiO}_x \), where \( x = 1.5 \), surrounded by an \( \text{SiO}_2 \) host material. This combination was chosen because it meets the refractive index criteria considered in section 8.5b and is likely to occur in practice. The optical and thermal properties are summarized in table 8.10.

The refractive index of the host material is given the bulk value at 248 nm. In thin film form the refractive index of the host material depends on the packing density of the film. The refractive index, (real part) of \( \text{SiO}_x \) is somewhat higher than that of \( \text{SiO}_2 \) and is assumed to have a value of about 1.6. The extinction index is difficult to estimate but is assumed to span the range which is likely to occur for nominally low absorption thin films at 248 nm. The thermal properties of the \( \text{SiO}_{1.5} \) impurity are assumed equal to the \( \text{SiO}_2 \) host material. For clarity the subscripts \( i \) and \( h \) for the thermal properties are dropped. Over the temperature range 298 - 1973 K the thermal diffusivity is relatively
<table>
<thead>
<tr>
<th></th>
<th>Host material</th>
<th>Impurity material</th>
</tr>
</thead>
<tbody>
<tr>
<td>refractive index</td>
<td>1.5085</td>
<td>1.6 - i(0.001-0.01)</td>
</tr>
<tr>
<td>at 248 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>(W cm⁻¹ K⁻¹)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal diffusivity</td>
<td>0.0085</td>
<td>0.0085</td>
</tr>
<tr>
<td>(cm² s⁻¹)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>melting point</td>
<td>1973</td>
<td>1973</td>
</tr>
<tr>
<td>(K)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

laser wavelength = 248 nm, laser pulsewidth = 24 ns

Table 8.10
Optical and thermal properties of the impurity and host material for use in the absorbing spherical defect damage model

class. However, the thermal conductivity increases from 0.014 - 0.02 W cm⁻¹ K⁻¹ in the range 298 - 1023 K and thereafter remains constant, (8.48). The value at the higher temperature is therefore more appropriate.

The absorption efficiency is plotted in figure 8.6 as a function of the sphere diameter for four assumed values of the extinction coefficient covering the range \( k_i = 0.001 - 0.05 \). The absorption efficiency is only dependent on the particle radius \( a \), the extinction coefficient of the sphere \( k_i \) and the wavelength \( \lambda \) in the combination \( a k_i / \lambda \). For a given value of \( \lambda \) and \( k_i \) the absorption efficiency is initially almost linear with particle size and subsequently saturates as it asymptotically approaches one. An important feature is that \( Q < 1 \) for small low absorption spheres, \( (k_i < 0.001) \). In contrast the absorption efficiency rapidly approaches
one for highly absorbing spheres, \(k_i > 0.05\) with diameters greater than one micron.

The fluence required to raise a thin spherical shell of a sphere to its melting point is plotted as a function of \(r/a\) in figure 8.7. The fluence distribution was calculated for sphere radii of 0.1 \(\mu\)m and 0.5 \(\mu\)m and has been normalized to that at the centre, \(r = 0\). The profile arises from the temperature distribution in the sphere which for a given fluence is a maximum at the centre of the sphere. Similar profiles result for other sphere radii and show that the fluence required to heat the centre of the sphere to a given temperature is approximately half that needed to heat the edge of the sphere to the same temperature. This arises from the increased heat loss into the host material at the edge of sphere relative to that at the centre of the sphere. A further damage criterion is therefore defined as that fluence required to raise the centre of the sphere to its melting point. This is in contrast to Lange et al who used the fluence required to heat the edge of the sphere to its melting point, (8.45).

Some care is needed in numerically evaluating equation 8.41 for small values of \(r/a\) and \(r/a = 0\). The fluence in equation 8.41 is controlled by the difference between two relatively large numbers \(A + B\) and the integration term. The integrand at \(y = 0\) decreases as \(r/a\) decreases and also shows a small amplitude oscillation about zero for large values of \(y\), (in this case \(y > 5\)). Therefore even if the percentage error in the numerical integration is small, the error in the fluence can be large. This effect becomes amplified as \(r/a\) decreases and the oscillating component contributes a larger percentage area of the total. The accuracy of the integration was compared to an exact analytical solution given in reference 8.42 for the case considered here of \(r = 0\) and the thermal properties of the spherical impurity and host.
ABSORPTION EFFICIENCY AT 248 nm

**FIGURE 8.6**

ABSORPTION EFFICIENCY AT 248 nm VERSUS SPHERE DIAMETER FOR DIFFERENT IMAGINARY VALUES OF THE SPHERE INDEX $R_i$
Figure 8.7

Normalized fluence required to raise a thin shell of a sphere at radius $r$ to its melting point.

Normalized fluence

sphere radius = 0.5μm

sphere radius = 0.1μm

$r/a$
equal. The solution is given by

\[ F = 8K\frac{c\tau}{3T_r}Qa\left[1 + [\langle 1/2Z^2 \rangle - 1]\text{erf}(Z) - \left\{ \frac{1}{\langle n^2 Z \rangle} \exp(-Z^2) \right\} \right] \]

where \( Z = a/(2\langle x\tau \rangle)^{1/6} \) and \( \text{erf} \) is the error function. The dimensionless variable \( Z \) is the ratio of the particle radius to the thermal diffusion distance during the laser pulse. Equation 8.41 at \( r = 0 \) is in good agreement with equation 8.42 when the upper limit on \( y \) is extended sufficiently. The fluence as a function of the sphere diameter is shown in figure 8.8 for three assumed values of the sphere extinction coefficient, 0.001, 0.005 and 0.01. Since in practice a distribution of defect sizes is likely to occur, laser damage will be initiated at the sphere radius for which the fluence is a minimum given by \( \delta F/\delta a = 0 \). These minima occur for sphere radii around 500 - 600 nm corresponding to \( Z\approx 2 \) and have values of 8.33, 1.82 and 1.00 J/cm\(^{-2}\) for the three values of \( k_i \). This compares with experimental damage thresholds from section 8.4 typically in the range 2 - 4 J/cm\(^{-2}\) and suggests the extinction coefficient of the defects was in the range 3 - 5 x 10\(^{-3}\). This corresponds to absorption coefficients in the range 1500 - 2500 cm\(^{-1}\).

The fluence scaling relationships with particle size, wavelength, pulsewidth and thermal properties can be estimated by simplifying equation 8.42 to apply to large and small particles. This can be expressed as \( a\langle 4\pi\tau \rangle^{1/6} \) for large particles and \( a\langle 4\pi\tau \rangle^{1/6} \) for small particles. This equates to the sphere radius being greater or less than the thermal diffusion distance during the laser pulse which in SiO\(_2\) is about 300 nm. At the larger particle sizes the assumption of uniform volumetric heating is not satisfied, however the predicted scaling relationships may still be valid.

The simplest case is that for large particles, \( \langle Z\rangle \geq 1 \) in which the exponential term in equation 8.42 approaches zero and the \( \text{erf} \) term approaches one. In this case

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FLUENCE INCIDENT ON HOST MATERIAL / J cm⁻²

ENERGY DENSITY AT 248 nm TO HEAT THE CENTRE OF A VOLUMETRICALLY HEATED SPHERE LOCATED IN A SiO₂ HOST MATERIAL AS A FUNCTION OF PARTICLE DIAMETER

\[ \chi h = \chi_l = 0.0085 \text{ cm}^2 \text{s}^{-1} \]
\[ K_h = K_l = 0.02 \text{ W cm}^{-2} \text{K}^{-1} \]

LASER PULSEWIDTH = 24 ns
LASER WAVELENGTH = 248 nm

\[ k_i = 0.001 \]
\[ k_i = 0.005 \]
\[ k_i = 0.01 \]
equation 8.42 reduces to

\[ F(Z>1) = 4\rho CT_c a/3QT_r \]  

and is independent of laser pulsewidth. The product of the density and specific heat capacity is used to replace the ratio \( K/x \). This expression is also valid at intermediate values of \( Z=2 \) where the \( \delta F/\delta a = 0 \). Equation 8.43 is the same as that derived by assuming adiabatic heating of the sphere and predicts the fluence scales with the ratio \( a/Q \). The results shown in figure 8.6 indicate the absorption efficiency scales approximately linearly with particle radius, \( \langle a/Q \rangle \) for lightly absorbing spheres but saturates at one for more highly absorbing spheres. The scaling relationship therefore depends on the sphere absorption.

For lightly absorbing spheres the damage threshold of the sphere scales linearly with \( \rho CT_c a/k_i \) and is independent of the sphere radius. This occurs for \( k_i = 0.001 \) in figure 8.8. This linear dependence on wavelength is valid in spectral regions where the extinction coefficient has little wavelength dependence. In the UV region the extinction coefficient generally increases as the wavelength decreases suggesting a scaling relationship of the form \( k_i \propto 1/\lambda^n \). In this case the damage threshold of the sphere would scale with wavelength as \( \lambda^{n+1} \). For more highly absorbing spheres \( Q=1 \) and the damage threshold of the sphere scales as \( \rho CT_c a \) and is proportional to the sphere radius but independent of wavelength and absorption coefficient. In this situation the fluence is still relatively insensitive to the particle radius as indicated in figure 8.8.

For the case of small particles, \( Z<1 \) the exponential term in equation 8.42 approaches 1 and the erf term reduces to zero giving

\[ F(Z<1) = 8KT_c \tau/3QaT_r \]  

For lightly absorbing spheres the damage threshold of the
Small particles
Z<1

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<table>
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<tbody>
<tr>
<td>Q+1</td>
<td>Q = ak₁/λ</td>
</tr>
</tbody>
</table>

Large particles
Z>1

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</thead>
<tbody>
<tr>
<td>Q+1</td>
<td>Q = ak₁/λ</td>
</tr>
</tbody>
</table>

F = KTₖ/aₖ
\[\text{or } F = Tₖ(PCK_k)\]

Table 8.11
Summary of predicted damage threshold scaling relationships using the laser heated sphere model

<table>
<thead>
<tr>
<th>Scaling parameters</th>
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</thead>
<tbody>
<tr>
<td>Reference</td>
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<tr>
<td>t⁻¹</td>
</tr>
<tr>
<td>8.21</td>
</tr>
<tr>
<td>8.23</td>
</tr>
<tr>
<td>8.22</td>
</tr>
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</table>

Table 8.12
Summary of the experimental damage threshold scaling relationships with pulsewidth, wavelength, thermal properties of the film and film thickness

sphere scales with KTₖ τₖ/a₂k₁ and therefore has a high sensitivity to particle radius as shown in figure 8.8. This is also the particle size region for which the criteria for uniform volumetric heating is valid. For highly absorbing small particles, Q+1 and the damage threshold scales with KTₖ τₖ/a. In both cases the sphere damage threshold scales with the pulsewidth whereas for adiabatic heating it is independent of pulsewidth. This
scaling relationship for highly absorbing small spheres is different to that calculated by Lange et al, (8.45) where a definite minimum fluence was found which scaled with \( T_c \left( \rho \cdot c \cdot K \cdot \tau \right)^{\lambda} \) in the region \( Z < 1 \). This difference arises because they considered the temperature rise at the surface of the sphere where the thermal properties of the host material control the heat loss. This surface heating has analogies with the 1-D heating models considered in chapter 7 where a similar square root scaling relationship was found to occur.

The scaling predictions are summarized in table 8.11 and can be compared with experimental results on thin films summarized in table 8.12. These results were taken from data in references 8.21, 8.22 and 8.23.

The most comprehensive testing of the wavelength and film thickness dependence is given in reference 8.21. This involved testing of 9 single layer films, (3 fluorides and 6 oxides) at 266, 353, 532 and 1064 nm at \( \tau = 5 \) and 15 ns and 5 film thicknesses from \( \lambda/8 - \lambda \).

These results suggest the damage threshold scales approximately linearly with wavelength. This is in contrast to the data from reference 8.22 where results at 266 nm and 355 nm gave an approximate quartic relationship. Both of these results can be accounted for by assuming a lightly absorbing defect in which \( Q \propto ak/\lambda \). The quartic relationship arises if the absorption coefficient has a \( 1/\lambda^3 \) dependence. The pulselength dependence to account for all of the measurements is given by the spread in the index parameter \( m \). In reference 8.21 the average for each film was very close to \( m = 0.5 \); however the modal value was about 0.35. In two examples, \( \text{ZrO}_2 \) and \( \text{MgO} \) the damage threshold scaled linearly with pulselength for all thicknesses and wavelengths. The pulselength dependence from reference 8.23 was determined with 351 and 355 nm dielectric AR and HR coatings at pulselengths of 0.6, 1, 5 and 9 ns. The average value both for AR and HR coatings was about \( m = 0.3 \). The predicted pulselength scaling relationships vary in the range \( m = 0 - 1 \) depending on the particle size.
and absorption coefficient. An added complication is that the experimental scaling relationship is expected to be sensitive to the shape of the laser profile as well as its width at half maximum intensity. This is considered in chapter 7 where 1-D laser heating of highly absorbing surfaces is compared for rectangular, Gaussian and long-tailed triangular shaped pulses.

The damage threshold dependence on the thermal properties of the host material were investigated in reference 8.45 where a linear dependence on $(\rho CK)^{1/2}$ was found for the experimental data in reference 8.23. Neither this trend nor a linear dependence on $KT_C$ or $\rho CT_C$ was found in the other data sets. The main difficulty in comparing these scaling predictions is in using reliable values of thermal properties since they all have a temperature dependence and the values in thin film form may be different from the bulk values.

The damage threshold dependence on the film thickness was investigated in reference 8.21. Their results indicate that for film thicknesses less than about $\lambda$ the damage threshold increases as the film thickness decreases. By assuming the sphere size is comparable to the film thickness the sphere damage threshold scales as $1/\alpha$ or $1/\alpha^2$ depending the the absorption cross section. Over a range of film thicknesses the functional form is very similar to that shown in figure 8.8 where the damage threshold is fairly insensitive to sphere diameter, (or film thickness) at larger sizes.

### 8.6 A laser damage probability model based on the spatial distribution of defects

#### 8.6a Development of the model

The dependence of the laser damage threshold on the focused laser spot size has been widely reported in the literature, (8.49, 8.50). Generally for small spot sizes, the damage threshold increases as the beam size decreases. This phenomena has been observed in thin films as well as in bulk materials and their surfaces. At UV wavelengths
in nominally low absorption films threshold damage is usually initiated at localized 'weak' sites called defects. The simplest impurity damage model considers a single isolated defect and is discussed in section 8.5. Damage was considered to occur via linear absorption when the incident fluence reached a value sufficient to heat the particle to a critical temperature. In this case damage at an individual defect has a definite threshold value. The damage probability dependence on the spot size for a single isolated defect has two states depending on whether the defect is illuminated above or below its threshold value.

Threshold damage of the thin film samples considered in section 8.4 was generally in the form of between one to five scattering centres randomly distributed around the central area of the focused beam. Therefore the logical extension of the single defect model is to consider an optical surface with a random two-dimensional distribution of defects. A damage threshold dependence on the spot size arises when the mean defect spacing is comparable to the spot size dimensions. The is the main reason why the threshold damage measurements described in section 8.4 were done with a relatively large spot size. The theory follows that initially given by Foltyn, (8.49) with some modifications for multi-layer coatings since his results appear to predict a damage probability greater than one as the incident fluence relative to the damage threshold of the defect is increased. The fluence distribution in the focal region of the excimer laser can be represented by a two-dimensional Gaussian intensity function given by

$$ F = F_0 \exp(-2x^2/\rho_1^2)\exp(-2y^2/\rho_2^2) $$  \hspace{1cm} 8.45

where $\rho_1$ and $\rho_2$ are the characteristic 1/e^2 radii of the distribution in the x and y directions and $F_0$ is the peak on-axis energy density. The validity of equation 8.45 in the focal region of the excimer laser is considered in chapter 3. The surface is assumed to be populated with a single type of defect with a damage threshold $F_t$ and an
average spatial 2-D defect density $\lambda$. In reality the defects are likely to have a distribution of thresholds due to their differing sizes and absorption coefficients. A more complicated damage model which uses a distribution of defect thresholds has been developed by Porteus and Seitel, (8.51). For simplicity, the Foltyn model with a single defect threshold is used.

The defects are assumed to have a Poisson spatial distribution, the probability of there being one or more defects within an area $A$ of the surface is equal to $1 - (\text{probability of there being no defects within the area } A)$. This is simply given by

$$P = 1 - \exp(-\lambda A)$$  \hspace{1cm} 8.46

The probability of damage occurring is therefore given by equation 8.46 if within the area $A$ the fluence, $F_F$. Equation 8.45 can be re-arranged to give the area $A = \pi x_t y_t$ within which $F_F$.

$$A = (\pi \rho_1 \rho_2/2) \ln(F_o/F_t)$$  \hspace{1cm} 8.47

Substituting equation 8.47 into 8.46 gives the damage probability

$$P = 1 - (F_t/F_o)^N$$  \hspace{1cm} 8.48

where

$$N = \lambda \pi \rho_1 \rho_2/2$$  \hspace{1cm} 8.49

The damage probability must be within the range $0<P<1$ implying equation 8.48 is only valid for $0<F_t/F_o$. The index term $N$ is given by the product of the defect density $\lambda$ and the beam area $\pi \rho_1 \rho_2/2$ and represents the number of illuminated defects within the beam area. The damage probability is plotted as a function of $F_o/F_t$ in figure 8.9 for $N$ ranging from 0.1 to 5. The number of defects within the beam area $\pi \rho_1 \rho_2/2$ has a significant effect on
Damage probability is plotted as a function of \( \frac{F_0}{F_1} \) for different values of the index parameter, \( N \).

\[ \text{damage probability} = 1 - \left( \frac{F_1}{F_0} \right)^N \]
the damage probability. The initial slope is proportional to the number of illuminated defects, $N$. For small spot sizes or low defect densities, $(N<1)$ the damage probability is fairly insensitive to changes in the ratio $F_o/F_t$. However, when the number of defects in the beam area is greater than five the transition of the damage probability from 0→1 is rapid. The only damage probability which is independent of the defect density and spot size is the maximum peak fluence for which the damage probability is zero. This is called the onset threshold and occurs when $F_o/F_t = 1$.

In the case of a multi-layer coating the damage probability can be modified to take some account of the local electric field intensity experienced by the defect. This is controlled by the distribution of the electric field in the multi-layer coating assuming the presence of the defect only induces a small perturbation on the field. Two types of defect can be considered depending on their size relative to the film thickness. In the case of large defects, comparable to the film thickness, their absorption is assumed to be proportional to the electric field intensity averaged over the defect diameter. This corresponds to defect diameters of about 40 nm for quarter wave films at 248 nm to about 1000 - 2000 nm for multi-layer HR reflectors at 248 nm. This approach is similar to that used to calculate the volumetric absorption of multilayer coatings described in appendix V. However, for large defects the discussions in section 8.5 suggest the local electric field distribution could be significantly altered from that in the absence of the defect.

The simpler case is that of small defects in which the local electric field is a small perturbation from that in the absence of the defect. In this case, the most damage sensitive defects are likely to be those at thin film interfaces where contamination is likely and the electric field often has a local maxima. Using the notation for thin films given in appendix V, the fluence at the $j^{th}$ interface, $F_j$, relative to the incident fluence
\( F \) is given by

\[
F_j = \alpha_j F_0
\]  

8.50

where \( \alpha_j = |E_j/E_i|^2 \) is the square of the electric field at the \( j^{th} \) interface relative to the incident field. The damage probability at the \( j^{th} \) interface is therefore given by

\[
P_j = 1 - \left( \frac{F_t}{\langle \alpha_j F_0 \rangle} \right)^N
\]  

8.51

In analogy with a single surface the probability of damage at the \( j^{th} \) interface must be zero if \( F_t > \alpha_j F_0 \). The total probability of damage at one or more interfaces is equal to 1 - (probability of no damage at any of the interfaces). This is given by

\[
P = 1 - \prod_j (1 - P_j)
\]  

8.52

where the \( (1 - P_j) \) is the probability of no damage at the \( j^{th} \) interface. Equation 8.52 assumes the probability of damage at any given interface is independent of that at any other interface and that the defect density is equal at all interfaces. This can be written in an alternative form by substituting for \( P_j \) giving

\[
P = 1 - \left( \frac{F_t}{F_0} \right)^N \prod_{j=1}^{q} \langle \alpha_j \rangle^{-N}
\]  

8.53

where \( q \) is the number of contributing interfaces in the coating. Equation 8.53 is only valid for \( \alpha_j \neq 0 \) which arises when the electric field at the interface goes to zero. For the case of a multi-layer quarter wave HR mirror with a design configuration \( \langle HL \rangle^2 PH(Sub) \), the local electric field intensity is a maximum at each H-L interface and is zero at each L-H interface. The distribution of the electric field in a HR reflector is
considered in reference 8.25 and gives the ratio $\alpha_j$ as

$$\alpha_j = \langle 1/n_h^2 \rangle \langle n_l/n_h \rangle^j - 2 \quad \text{for } j = 2, 4, 6 \text{ etc} \quad 8.54$$

$$\alpha_j = 0 \quad \text{for } j = 1, 3, 5 \text{ etc}$$

where $n_h$ and $n_l$ are the high and low refractive indices of the films in the multi-layer. The electric field intensity decreases by $\langle n_l/n_h \rangle^2$ at each H-L interface relative to that at the first interface. Therefore the defects which contribute to the damage probability are those at the H-L interfaces where $j = 2, 4, 6 \text{ etc}$. The effect on the damage probability of the first four contributing interfaces of a HR reflector are shown in figure 8.10. This calculation was done assuming $n_l = 1.5$ and $n_h = 1.7$ and $N = 1.5$. This corresponds to an illuminated beam area containing an average of one defect. The $j^{th}$ interface can only make a contribution to the damage probability when $F_o/F_t$ exceeds $1/\alpha_j$. The intercept is therefore given by $1/\alpha_2$ corresponding to the first H-L interface. The onset threshold which is independent of the spot size and defect density is therefore given by $F_o = F_t n_h^2$. This suggests that the damage resistance for a given value of $F_t$ at the onset is maximized by using a high index outer layer.

The contribution to the damage probability of several layers is to extend the region over which it is approximately linear with $F_o/F_t$. As the number of illuminated defects increases the damage probability rapidly approaches one. This is also illustrated in figure 8.10 where the damage probability for the first H-L interface with $N = 1$ can be compared with that for $N = 17$. This rapid and approximate linear transition has been observed experimentally in a HR mirror as shown in figure 4.20. The decay of the electric field distribution in the multi-layer becomes more rapid as the refractive index ratio $n_h/n_l$ increases. This implies damage will tend to be located in the outer layers and for a given value of $F_o/F_t$ and $N$ the damage probability is less.

-472-
FIGURE 8.10

DAMAGE PROBABILITY PLOTTED AGAINST THE NORMALIZED INCIDENT ENERGY DENSITY FOR A MULTILAYER HR MIRROR

$q = 1$, $q = 2$, $q = 3$, $q = 6$

$n_1 = 1.5$, $n_h = 1.7$, $N = 17$

$n_L = 15$, $n_h = 1.7$, $N = 10$
8.6b Application of the model

The damage probability model was investigated in some detail with a multi-layer dielectric AR coating deposited on a 50 mm diameter fused silica substrate. This also included an investigation into the apparent improvements in the damage threshold resulting from irradiating the sample at sub-threshold levels. This so-called pre-conditioning effect was initially observed on a HR and AR sample described in section 8.4 and resulted in a significant increase in the single shot damage threshold. The AR coating used in this study was a three layer proprietary design manufactured by Technical Optics, its design details are given in appendix V.

8.6bi Defect density measurements

Prior to damage testing it was decided to investigate if the spatial distribution of the defects approximated to a Poisson distribution and secondly if it was influenced by UV irradiation from a discharge lamp and subsequently irradiation at low fluence levels from the excimer laser. One half of the sample was irradiated with a Thorn-EMI 250 Watt mercury arc lamp at a distance of 10 cm for durations of 1, 5 and 30 hours. The reflectance, (at 248 nm) transmittance, (from 210 - 350 nm) and defect density were measured after each irradiation period both on the irradiated and non-irradiated parts of the sample. Prior to each set of measurements the sample was cleaned by pulling a methanol and then acetone wetted lens tissue across the sample's surface. Defect density measurements were made using a microscope with bright-field illumination and counting the defects within a 0.36 mm² sample area. About 100 sample areas were needed to get a representative average density. The defects were observed as small dark particles and had diameters typically in the range 1 - 5 μm. This method of identification for the defects is sensitive to the particles reflectance and is therefore not able to distinguish between high scattering or high absorption. The results both on the irradiated and non-irradiated parts of the sample are summarized in
Table 8.13

The effect of UV irradiation on the reflectance, transmittance and defect density of a three layer AR coating.

The results in table 8.13 show that to within experimental error the continuous short wavelength radiation from the discharge lamp had no effect on the optical properties of the coating at 248 nm nor the defect density. Furthermore, the stability of the wavelength dependence of the transmittance and the location of the reflectance minima of 0.3% at 270 nm suggests no index or physical thickness changes were involved. The defect density is given in mm\(^{-2}\) since typical beam dimensions were usually 0.5 - 2 mm. However, it is conventional to give the fluence in Jcm\(^{-2}\). The error in the defect density of about 50% was taken as \(\pm\) one standard deviation around the mean. An alternative way of expressing the mean defect density is the mean defect spacing, \((\lambda)^{-1/2}\) and suggests the defects are a few hundred microns apart.

A typical result for the distribution of the defect density is shown in figure 8.11 together with a Poisson fit to the data. The Poisson curve was plotted using the mean number of defects in a sample area, \(\mu = 11.75\) and
Figure 8.11
DEFECT DENSITY DISTRIBUTION FOR A THREE LAYER AR COATING PRODUCED BY TECHNICAL OPTICS

NUMBER OF SAMPLE AREAS

AVERAGE DEFECT DENSITY
\[ \lambda = 32 \pm 12 \text{mm}^{-2} \]
is a reasonable fit to the experimental data. For a perfect Poisson distribution the standard deviation is \( \sqrt{\mu} \), giving 3.43 which compares with an experimental value of 4.37. This example was taken from measurements on the irradiated half of the sample after 30 hours irradiation. The defect density of three other AR coatings was also measured using this approach and varied between 20 - 35 mm\(^{-2}\). The procedure for measuring defect densities became more convenient with the development of the video microscope described in chapter 4.

The variability of the local defect density across the diameter of the sample is shown in figure 8.12. These results were measured by calculating the defect density in each sample area which in this case was 0.09 mm\(^2\). The local defect density varies considerably over the diameter of the sample with maxima in excess of 100 mm\(^{-2}\). The defects tended to appear in highly localized clusters or groups resulting in large variations in the defect density. The assumption of a constant average defect density over the samples surface is approximately true if these localized regions of high defect density are excluded. This was attempted by measuring damage thresholds in the nominally low scatter areas. The defects could also be classified into two size ranges where about 90% were less than 5 \( \mu \)m in diameter, (mostly in the range 1 - 3 \( \mu \)m), the remaining 10% were observed to be 5 - 10 \( \mu \)m in diameter. The large variation in the local defect density is similar to the results given in chapter 4, where a large variation in the the pre-damage scatter signal was observed over the sample area.

Since no apparent changes were observed for low power UV irradiation of the sample, high power laser irradiation at 248 nm was tried. This involved 1000 pulses at increasing fluences of 0.003, 0.014, 0.026, 0.22, 0.34, 1.89 and 3.9 Jcm\(^{-2}\). After each 1000 shots at a given fluence the reflectance, transmittance and defect density was measured as before. Within the experimental errors no changes were observed until irradiation at 1.9 Jcm\(^{-2}\). At this level threshold damage was observed in localized
Figure 8.12

Local defect density versus sample area position across the diameter of a three layer AR coating deposited on fused silica.
areas. The results for the corresponding defect densities are given in Table 8.14

<table>
<thead>
<tr>
<th>Size Range (μm)</th>
<th>Non-Irradiated</th>
<th>Irradiated Half with 6000 Shots</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 5</td>
<td>35.4 ±15.3</td>
<td>30.9 ±15.2</td>
</tr>
<tr>
<td>5 - 10</td>
<td>1.7 ±2</td>
<td>4.7 ±4.8</td>
</tr>
</tbody>
</table>

Table 8.14
Defect density measurements on the irradiated and non-irradiated areas of a 3-layer AR coating for two defect size ranges

These results suggest that about 10% of the defects in the size range 1 - 5 μm are most susceptible to laser damage. This presumably arises from the variation in the absorption cross section and thermal properties.

8.6bii Laser damage probability measurements

The laser damage probability on the irradiated and non-irradiated parts of the three-layer AR coating was measured at various fluences in the range 0.8 - 5.0 J/cm². The single shot damage probability was determined by damage testing using 10 - 20 sample areas and noting the fraction of the sites which damaged at each fluence. The damage probability is plotted as a function of the peak test fluence in Figure 8.13. Error bars are given for the fluence measurement but not the damage probability. The error in the damage probability arises from the restricted number of shots at each fluence and the sensitivity of the video microscope to detect threshold damage. Since the number of shots varied between 10 - 20 at each fluence an error in the observation of ±1 shot corresponds to an error in the damage probability of 5 - 10%. The solid
Figure 8.13
Damage probability at 248 nm versus energy density for the non-irradiated and irradiated areas of a three layer AR coating.
lines represent the best fit to the data as determined by equation 8.52. This was calculated by writing the damage probability at the jth interface as

\[ P_j = 1 - \exp(-\lambda A_j) \]

and the total damage probability

\[ P = 1 - \prod \exp(-\lambda A_j) \]

The data was linearized by taking logarithms giving

\[ \ln(1 - P) = -\lambda \Sigma A_j \]

where \( A_j \) is the area at the jth interface where \( F_{t,aj} F_0 \).

A plot of \( \ln(1 - P) \) versus \( \Sigma A_j \) gave the defect density \( \lambda \) from the gradient. Experimental values of the beam size, \( \rho_1 = 1.7 \text{ mm} \) and \( \rho_2 = 0.25 \text{ mm} \) and calculated values of \( \alpha_j \) from appendix V were used in the fitting procedure. The onset thresholds were estimated from a simple visual best line fit through the data points. The results are summarized in table 8.15 both for the non-irradiated and irradiated areas of the sample.

UV irradiation of the sample has not significantly changed the onset threshold but has reduced the defect density of the most damage sensitive defects. This is in contrast to the two pre-conditioned samples discussed in section 8.4 where large improvements in the onset threshold were observed. The reduction in the defect density of the most damage sensitive defects on the

<table>
<thead>
<tr>
<th>Non-irradiated half</th>
<th>Irradiated half</th>
</tr>
</thead>
<tbody>
<tr>
<td>Onset threshold/Jcm(^{-2})</td>
<td>0.8</td>
</tr>
<tr>
<td>Fitted defect density/m(^2)</td>
<td>1.7 ± 0.9</td>
</tr>
</tbody>
</table>

Table 8.15
Onset threshold and defect density for the results shown in figure 8.13

pre-conditioned part of the sample may be associated with some form of annealing process or ablation of the particulate material from the surface. In the former case
the defects are still present but the absorption of some of them has reduced and in the latter the defects are absent from the coating. The ablation process is consistent with the observations discussed in section 4.3.c where a decrease in the surface scattering coincided with the observation of particulate ejection from the surface when irradiated just below the threshold level.

Defect densities of 1 - 2 mm$^{-2}$ are comparable to values of 3.2 mm$^{-2}$ measured by Foltyn on a HR mirror, (8.49). It is interesting to compare the experimentally fitted defect densities of 1 - 2 mm$^{-2}$ with the counting measurements made before damage testing which were about 25 - 35 mm$^{-2}$. These results suggest that less than 10% of the defects which were counted using the microscope prior to damage testing were involved in the initial formation of laser damage. The fitted defect densities are also in reasonable agreement with the measured change in the defect density of the larger defects near the threshold level.

There appears to be no universally accepted definition of the single shot laser damage threshold. Various laboratories have defined the laser induced damage threshold in different ways. One definition is the fluence at which the damage probability is 50%. A second definition is the mid-way point between the minimum fluence which causes damage, $F_{\text{min}}$, and the maximum fluence which does not, $F_{\text{max}}$. The damage threshold definition used in section 8.4 is the incident fluence corresponding to a damage probability one. These various threshold definitions including the onset fluence where the damage probability is zero are compared in table 8.16.

These results show significant variations in the damage threshold depending on its definition. Similar large apparent variations in the damage threshold were also measured for several HR and AR samples using the scatter ratio method to detect threshold damage, (see section 4.3c). All of these definitions would tend towards the same value for large spot sizes when the number of illuminated defects in the beam is greater than
Experimental damage thresholds at 248 nm of a three layer AR coating defined in various ways

One. The defect density of the most damage sensitive defects is around 1 – 2 mm\(^{-2}\) suggesting focused spot sizes greater than a few mm\(^2\) should be used to avoid this ambiguity. The alternative is to use a small spot size and measure the onset threshold by curve fitting.

Multi-shot effects are illustrated in figure 8.14 where the number of laser shots required to eject particles from the surface is plotted as a function of the peak fluence. Particle ejection was observed with the video microscope and required an increasing shot number as the fluence was reduced. This observation of particle ejection is similar to the single shot results for several other AR and HR coatings described in section 4.3c. The particles are assumed to be organic material or dust which are ejected when the the absorbed energy reaches some threshold value, \(\varepsilon_t\). If this threshold value is high then local damage is likely to occur. An accumulative process appears to be involved for particle ejection and may be explained by an increase in the absorption cross section of the impurities with shot number. If the impurities are organic it is reasonable to assume photochemical reactions are involved. A simple model assumes the absorption efficiency increments a constant amount, \(\Delta Q\) for each shot.
Figure 8.14
Shot number at 248nm required to observe surface particle ejection as a function of fluence for a three layer AR coating.
The condition for particle ejection is then given by

$$\epsilon_t = \pi a^2 (Q_o + (N - 1) \Delta Q) F_o$$  \hspace{1cm} 8.56

where $a$ is the defect radius, $Q_o$ is the initial particle absorption cross section and $N$ the shot number. For a given value of $\epsilon_t$ equation 8.56 predicts an inverse relationship with shot number $N$ and fluence $F_o$. The rate of change of $N$ with $F_o$ in figure 8.14 is greater for the irradiated area of the sample than the non-irradiated area. This requires that the increment in the absorption cross-section per shot on the irradiated area be less than that from the non-irradiated area. This is consistent with the association of pre-conditioning with the ablation of particulates from the surface.

8.7 Conclusions

The performance of multi-layer dielectric HR and AR coatings at 248 nm has been investigated in terms of their optical losses and their laser damage thresholds. The optical losses include effects arising from coating design, film stability, absorption and scattering. The damage threshold at 248 nm and two associated models of laser damage have been investigated for a range of HR and AR coatings.

The acceptability of low UV absorption bulk materials deposited in thin film form is greatly influenced by the film microstructure. A detailed review of the various current and developing coating techniques has been given. There appears to be a trend towards energy assisted deposition techniques using plasmas or ion beams to irradiate the surface as the film grows. The optimum ion energy to produce hard, stable, stoichiometric coatings with minimum optical absorption is in the range 10 - 100eV. However, with the exception of sputtering, the damage threshold of coated optics produced using these newer techniques has not apparently been reported. This may be related to commercial considerations.

A review of the damage thresholds of single layer
thin films at 248 nm has been given. The use of the most damage resistant single layer films does not necessarily produce the most damage resistant multi-layer films. It is the authors opinion that often the difference between apparently high and low damage threshold multi-layer coatings is the optimization of the coating conditions for a given combination of materials. This procedure is expensive and time-consuming to follow for many different combinations. In practice a few promising candidates are tried and subsequently optimized. This procedure appears to have been followed in identifying $\text{Sc}_2\text{O}_3/\text{MgF}_2$ as high damage threshold material combinations for HR mirrors at 248 nm.

The design of AR and HR dielectric coatings at 248 nm has been considered in some detail. Closed form expressions were developed to estimate the interface and volumetric absorption and scattering from AR and HR dielectric coatings. Scattering can be a serious problem at short wavelengths. At 248 nm the estimated surface scattering from a good AR coating is 0.1% for an RMS roughness figure of 2.5 nm. The same roughness figure applied to a HR coating gives a scatter level of 1.6%. In the case of a HR coating the RMS roughness figure must be reduced to 1 nm before an acceptable 0.25% scatter level results.

The limited choice of high index and low index thin film materials at 248 nm led to a comparison of the design of various two and three layer quarter wave and non-quarter wave AR coatings. No significant advantage can be gained from using two layer non-quarter designs at 248 nm from the absorption viewpoint. A symmetric three layer design based on equivalent layers was considered. To the authors knowledge, this design approach has not previously been reported. However, this again may be limited by commercial constraints. The advantage of the three layer symmetric design is that it allows a much more flexible choice of coating materials but still achieves a spectral performance comparable to the two layer quarter wave $V$ coat design. Its disadvantage is the potential increased
absorption from the greater coating thickness which is offset by a wider choice of low absorption films.

Calculations were done on the number of layers required to achieve a given reflectance in a HR multi-layer stack. The results indicate that typically between 13 - 35 layers are needed to achieve a reflectance of 99% depending on the high-low refractive index ratio of the films. This process was reversed to calculate the average values of the high and low refractive indices of the layers using two HR mirrors deposited at the same time but with differing layer numbers. There are significant advantages in using a large high-low refractive index ratio since this reduces the number of layers required for a given reflectance and also reduces the over-all absorption assuming the same extinction index.

The damage thresholds at 248 nm of the dielectric HR coatings were in the range 0.3 - 7.9 Jcm\(^{-2}\) and the AR coatings 0.8 - 1.65 Jcm\(^{-2}\). The damage threshold of HR coatings which had been previously tested in the cavity of a KrF laser were on average four times less than the same unused samples. A multi-shot threshold was defined as the maximum fluence for which no damage was observed after 600 shots. The multi-shot threshold was typically 2 - 5 times less than the single shot threshold. Threshold damage was usually observed within 2 - 5 shots of a multi-shot test. Pre-conditioning using multi-shot irradiation improved the damage threshold of a single HR coating from 1.3 to 2.0 Jcm\(^{-2}\) and for a single AR coating from 1.65 to 4.7 Jcm\(^{-2}\). The highest damage threshold AR coating and HR coating both had very low surface scattering.

A thermal model of laser damage has been developed to represent defect damage in dielectric materials. The model represents the defect as a spherical, linearly absorbing impurity embedded in an infinite non-absorbing dielectric host. Laser damage is considered to occur when the laser heated sphere reaches some material dependent threshold temperature such as its melting point.

The model has been applied to an absorbing SiO\(_{1.5}\) spherical particle embedded in an infinite SiO\(_2\) host.
material. For a given absorbed laser energy the temperature rise of the sphere is a maximum at its centre. The energy density required to raise the centre of the sphere to its melting point was calculated as a function of sphere diameter and extinction coefficient. The minimum value defined as the damage threshold occurred for sphere radii around 500 - 600 nm and varied in the range 1 - 8 Jcm$^{-2}$. This is also the approximate range over which the damage threshold of HR reflectors was measured. These results suggest that the absorption coefficient of most of the defects must be in the range 1500 - 2500 cm$^{-1}$ corresponding to thresholds of 2 - 4 Jcm$^{-2}$. The model predicts various scaling relationships with laser wavelength, pulsewidth, particle size and thermal properties. The functional form of the scaling relationships depend on the particle size relative to the thermal diffusion length and the absorption of the particle. These scaling relationships are compared with previously published data and show reasonable agreement in some cases.

A laser damage model has been developed based on the 2-D distribution of defects on an optical surface. The model gives the laser damage probability in terms of the spatial defect density, the illuminated beam area and the damage threshold of the defect. The model has been extended to include contributions from small defects distributed at thin film interfaces where the electric field is non-zero. The contribution of this effect requires additional information on the coating design. Significant laser damage threshold spot size effects are predicted if the average number of illuminated defects within the beam area is less than one. The damage probability model has been investigated in some detail with a three layer non-quarter wave AR coating deposited on a fused silica substrate. One half of the sample was used to investigate pre-conditioning effects of UV irradiation from a mercury discharge lamp and subsequently 248 nm laser irradiation. The defect density and optical properties were independent of UV irradiation time. The
Defects were shown to approximately follow a Poisson distribution with an average defect density of $20 - 35 \text{ mm}^{-2}$. This range also covered that measured on several other samples. Sometimes the defects were observed to form in clusters where the local defect density exceeded $100 \text{ mm}^{-2}$. The defects appeared to be in two size ranges with about 90% in the range $1 - 5 \mu m$ and the remainder in the range $5 - 10 \mu m$.

The damage probability was measured as a function of the incident fluence and the theoretical results fitted to the data using the onset threshold and the defect density as variables. The effect of pre-conditioning had no significant effect on the onset threshold but did reduce the defect density of the most damage sensitive defects from $1.7 \text{ mm}^{-2}$ to $1.0 \text{ mm}^{-2}$. It seems likely that this reduction is due to ablation of particulate material from the pre-conditioned half of the sample when it was irradiated with the excimer laser. This is also in agreement with the multi-shot tests. The experimentally fitted defect densities of $1 - 2 \text{ mm}^{-2}$ suggest that the most damage sensitive defects represent less than 10% of the visually observed defects counted prior to damage testing.

The damage probability results were also used to show significant variations in the damage threshold depending on its definition. The only threshold definition which is independent of the laser spot size and defect density is the onset threshold. However, if a large spot size is used for damage testing the various definitions of the laser damage threshold tend towards each other. The use of a large spot size is also quicker since only about $10 - 20$ sites need to be tested.
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- 493 -


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Chapter 9
Conclusions and Recommendations

The work in this thesis divides naturally into four categories, these are

i Characterization of the focused 248 nm laser radiation in the interaction region of the sample

ii Development of in-situ sensitive methods for the detection of laser induced threshold damage

iii Laser liquids interactions at 248 nm

iv Laser damage studies of

(a) crystalline fluoride materials at 193 nm
(b) aluminium mirrors at 248 nm
(c) multi-layer dielectric reflectors at 248 nm.

These four sections are semi-autonomous and so conclusions and recommendations are given for each section.

9.1 Beam characterization at 248 nm

Characterization of the focused KrF laser radiation at the axial plane of incidence on the test sample involved pulse energy, temporal pulse profile and spatial profile measurements. A volume absorbing thermal calorimeter was found to be most suitable for absolute pulse energy measurements at low repetition rates. The performance of three laboratory built pulse detectors was compared to that of a commercial high voltage vacuum photodiode. The laboratory built devices suffered from a limited linear dynamic range and an increased pulse falltime due to space charge effects in the low voltage vacuum photodiode and diffusion current effects in the two solid state detectors. Various beam attenuation techniques were examined to vary the fluence incident onto
the test sample. The large output beam area and the damage susceptibility of many absorbing solids at 248 nm led to the successful development of a variable length liquid cell attenuator. An attenuation range of 25 dB was routinely available.

The most time consuming part of the diagnostic experiments was the measurement of the focused KrF beam profile at the same axial plane as the test sample. This involved investigations using burn patterns, a photographic method using Dylux film and several aperture scanning methods using edges, slits and pinholes. These techniques were able to show that the fluence distribution function in the focal region of a lens was reproducible and could be represented as the product of two Gaussian functions in the x and y directions. The Dylux film involving no wet processing stage offered the potential to measure the 2-D beam profile for each shot. However, measurements of the peak fluence were difficult because of the limited linear dynamic range of the film. Preliminary investigations were made using a CCD camera for single shot beam profiling using the fluorescence from a rhodamine dye solution and a laboratory built frame grabber with x and y cursors. This technique offers the promise of a very simple and quick beam profiling method which may have many other applications.

9.2 Laser induced damage detection methods

Probably the most important work in this thesis involved the diagnostic methods for the detection of laser induced threshold damage. Three techniques were investigated in detail, these were optical microscopy, laser scattering from a helium neon probe beam and photoacoustic detection using PZT transducers. A preliminary investigation was also carried out using a Laser Induced Mass Analyser, (LIMA), surface analysis instrument to investigate the chemical composition of scattering centres in thin films.

A video microscope system was developed based on dark-field illumination to maximize the optical contrast
between scattering and non-scattering areas. This system was able to detect threshold damage in the form of micron sized damage pits. The on-axis dark-field illumination was obtained with a helium neon probe beam with its specular reflection blocked off. The use of a video recorder allowed a simple visual before and after irradiation comparison. The use of the x-y cursors on the prototype frame grabber allowed a simple analogue comparison of defect sizes. An interesting feature was the observation of a particulate cloud of particles ejected from the surface of some samples when irradiated just below the threshold level. This also coincided with the reduction in the quantitative scattering signal and appears to be the origin of many pre-conditioning effects observed by irradiating the sample below the threshold level. The origin of these particles is uncertain but could be due to photo-ablation of organic material in the coatings.

The use of a beamsplitter and photodetector enabled a measure of the scattered radiation in parallel with the video image. The effect of excimer laser irradiation was measured using a scatter ratio, $R$ defined as the scatter signal after irradiation divided by the scatter signal before irradiation. Several samples with $R<1$ were observed when irradiated just below the threshold level. Extrapolation of the damage data back to $R = 1$ was found to be a useful and sensitive method of measuring the damage threshold and offers the potential for automation. A further advantage was that it does not rely solely on subtle identification of micron sized defects.

Future developments of the video microscope could include the ability to do frame subtraction to allow a more systematic before and after irradiation comparison. The sensitivity of the scatter system could be improved with the use of a more sensitive detector and the signal to noise ratio improved using a phase locked amplifier. A more speculative development could include the use of a thermal imaging camera as an NDT or laser damage method for imaging absorbing defect hot spots rather than
scattering centres. A comparison between the scattering image and the thermal image would also give some clues as to the damage mechanism. Other optical probe beam techniques worthy of further investigation include the transient air/film critical angle technique and probe beam refraction methods. There general disadvantages include increased complexity and greater alignment problems.

Photoacoustic measurements using PZT transducers were less sensitive at detecting threshold damage in multi-layer thin films at 193 nm or 248 nm than using the laser scattering method. The transducers also have the disadvantage of being directly attached to the component with a couplant grease. In general two signal regimes were identified, the thermoelastic signal and the much larger signal associated with plasma formation. In both regimes the signal amplitude was found to vary linearly with fluence which is in contrast to previous measurements at 10.6 μm and 1.06 μm. This is explained by assuming several factors contribute to the acoustic signal amplitude which may appear in a contiguous fashion to produce several thresholds or simultaneously to produce a non-linear response.

Preliminary measurements of impurities in thin films using the LIMA instrument showed great promise. The detection of an ionization current also offers a potential NDT method for measuring laser induced damage resistance. The LIMA instrument could be developed into an extensive laser damage measurement facility if it could be adopted to accept several laser excitation sources, and a modified target beam for measuring scattering signals. This facility would allow the chemical identification of the defects which initiate damage and also allow a more detailed investigation into pre-conditioning effects.

9.3 Laser-liquid interactions at 248 nm

In the course of investigating the use of liquids as laser beam attenuators at 248 nm some interesting temporal pulse distortions were observed in the transmitted pulse at high incident intensities. This corresponded to
deviations from the linear Beer-Lambert law when the liquid cell was located in the region of the lens focus where the power density was estimated as 17 MWcm$^{-2}$. Small reductions in the transmission were observed for distilled water and spectrograde methanol and ethanol. A much more significant reduction in the transmission was observed with methanol solution accidently contaminated with leached compounds from a cork stopper. The leached compounds were shown to contain iron and manganese. This led to an investigation of the optical transmission at 248 nm of several aqueous transition element solutions.

The reduction in the absorption at high intensity was described by a two stage non-linear absorption process which is effectively the reverse of optical bleaching. The reduction of the transmission at high intensities requires the absorption cross-section for the upper state to be higher than that of the lower state. The results suggest the absorption cross-section for the upper state was a factor of six times that for the lower state for the cork contaminated methanol whereas factors of 2 - 3 were involved for the pure solvents. The excitation model has similarities to multi-photon absorption if the excited state is virtual. This suggests two or three photon absorption in the pure liquids. These preliminary experiments would benefit from being repeated in a more systematic manner to look specifically for non-linear effects.

9.4a Laser damage studies of fluoride crystals at 193 nm

Preliminary investigations were made of laser damage in several fluoride crystalline materials at 193 nm. This involved measurements of the damage threshold at 193 nm, investigations of the damage morphology above the threshold level and colour centre formation. As far as the author is aware these damage thresholds were the first reported measurements at 193 nm.

The single shot damage threshold of the front surface for all six fluoride materials varied in the range 1 - 4 Jcm$^{-2}$. The damage threshold of freshly cleaved
surfaces of LiF and NaF were factors of 1.6 and 2.3 higher than the damage thresholds of the older cleaved surfaces. This suggests the hydroscopic nature of these materials has a significant effect on the damage threshold at 193 nm. The damage threshold was generally higher for the low index materials and found to approximately follow a previously determined scaling relationship. The damage morphology at the threshold level was in form of several pits. At higher intensities a rectangular surface cleaving pattern was observed for the the alkali fluorides and a triangular one for the alkaline-earth fluorides. Unusual bulk damage phenomena were observed in LiF and SrF$_2$ which was attributed to filamentary self-focusing. Colour centre formation was observed in infra-red grade CaF$_2$ and NaF when irradiated below the single shot damage threshold. The colour centres in CaF$_2$ were attributed to impurities and those in NaF to F centres and F$_2$ centres. The F centre density was estimated to be about $10^{15}$ cm$^{-3}$, well in excess of that needed to supply the seed electrons for an avalanche breakdown process.

A natural extension of these measurements would be a systematic study of damage thresholds at the excimer wavelengths of 193, 248, 308 and 353 nm. The trend in the damage threshold as a function of wavelength, band gap and refractive index may help identify the dominant laser damage process in this region.

9.4b Laser damage studies of aluminium mirrors at 248 nm

The performance of aluminium mirrors at 248 nm was investigated in three areas. These were optical performance, laser damage resistance at 248 nm and the effect of UV irradiation on silicon oxide overcoated aluminium mirrors.

The optical performance of aluminium mirrors was investigated on a theoretical basis at 248 nm. The results and measurements suggest that a half wave dielectric overcoat at 248 nm only marginally improves the reflectance but does give the delicate aluminium coating some protection. The standard aluminium overcoat material
at UV wavelengths is MgF₂, a better choice at 248 nm is Al₂O₃ since the packing density and adherence of the film is much higher than that of MgF₂ when deposited on a room temperature substrate. The disadvantage is that it requires reactive electron beam evaporation for its deposition. A theoretical model was developed to show that the maximum tolerable absorption coefficient to maintain a high reflectance at 248 nm for a half wave overcoat is about 5000 cm⁻¹. This model was also used to fit theoretical angular reflectance data to experimental results to determine the absorption coefficient of the overcoat layer. Aluminium mirrors with a reflectance of the order of 99% can be achieved by depositing 3 or 4 quarter wave, layer-pairs on top of an optimally deposited aluminium mirror. The author is unaware that the damage threshold of such mirrors has been tested at 248 nm.

Three thermal models involving absorption of laser radiation in metal mirrors were developed. All assume the damage threshold corresponds to absorption and heating to some critical temperature such as the melting point. The three models represent the situations of heating of a semi-infinite metal surface, heating of a metal film deposited on a substrate, (insulator or conductor) and a modified adiabatic model which accounts for heat loss into the dielectric overcoat layer and the insulating substrate. The experimental damage thresholds of several high-quality dielectric overcoated aluminium mirrors was measured in the range 0.1 - 0.68 Jcm⁻² at 248 nm. In general they showed good agreement with the predicted threshold corresponding to the melting point of the aluminium. The damage threshold of these mirrors was not influenced by the choice of insulating substrate material, RMS roughness of the substrate or the presence of a thin chromium undercoat between the substrate and the aluminium.

The good agreement with the thermal model has encouraged the use of the semi-infinite model to predict the melt threshold of an aluminium sample with a high quality mirror surface. At 248 nm and assuming a
pulsewidth of 24 ns the melt threshold is calculated as $1.5 \text{ Jcm}^{-2}$. The use of a thin aluminium film and a thermally thick more highly conducting undercoat can improve this value due to the increased conduction. A figure of merit was devised to show that the use of a thick undercoat layer of silver can improve the predicted melt threshold to $5.7 \text{ Jcm}^{-2}$.

Large improvements in the UV reflectance of $\text{SiO}_x$ overcoated aluminium mirrors were observed by irradiating the mirrors with a continuous UV lamp source or multi-shot irradiation at 248 nm at low fluences. ESCA and Ellipsometry were used to show that the large initial improvement in the reflectance was not caused by a significant increase in the oxygen/silicon ratio in the film. However, long irradiation times did convert the $\text{SiO}_{1.5}$ to $\text{SiO}_2$. The initial large improvement in the UV reflectance was attributed to interstitial oxygen held in the film structure perhaps as water vapour which was excited and released to convert the highly absorbing regions of SiO in the film to $\text{SiO}_2$ without any over-all change in the stoichiometry.

Laser irradiation of the $\text{SiO}_x$ overcoated aluminium mirrors around $0.1 - 0.2 \text{ Jcm}^{-2}$ resulted in the formation of ripple patterns in the oxide layers. Optical microscopy and TEM have shown the damage morphology to consist of a quasi-random rippled surface with an average ripple wavelength of 2.5 $\mu\text{m}$. Local symmetrical features in the form of parallel and concentric ripples were also observed. The parallel ripples were associated with the presence of a scratch located in the centre of the pattern. Tallsurf measurements have shown the ripples developing from an initial sinusoidal profile into one with a flattened trough and an increased peak height. Optically this was observed as an increased diffraction efficiency but with no average wavelength change. Measurements of the associated diffraction pattern have shown the average ripple wavelength to depend on the illuminated position on the damage site and the angle of incidence. These results are consistent with the idea...
that the average ripple wavelength is proportional to the absorbed fluence. The author is unaware that this form of ripple wavelength dependence has been observed previously.

A good test of this model would be to measure the ripple wavelength at large angles of incidence where the reflectance variation with angle is high and the reflectance difference between s and p polarized light significant. The actual ripple formation mechanism also needs more investigation such as transient measurements of the ripple formation process.

9.4c Laser damage studies of multi-layer dielectric coatings at 248 nm

The performance of multi-layer dielectric HR and AR coatings at 248 nm was investigated in terms of their optical losses and their laser damage thresholds.

The design of multi-layer dielectric AR and HR coatings was considered in some detail. This resulted in the design of a three layer symmetrical AR coating at 248 nm with spectral performance comparable to a two layer quarter-wave V coat design but with a much more flexible choice of film materials. This latter point is important in the UV region where the choice of low absorption materials is more restricted. Estimates of the absorption of a HR coating show the importance of using as large a ratio of the high refractive index to the low refractive index as possible. This reduces the required number of layers to achieve a given reflectance and reduces the over-all absorption assuming the same extinction index.

The damage threshold of the HR coatings were in the range 0.3 - 7.9 Jcm^{-2} and the AR coatings in the range 0.8 - 1.6 Jcm^{-2}. The damage threshold of 7.9 Jcm^{-2} was measured on a Sc_{2}O_{3}/MgF_{2} multi-layer which had previously been tested at the Lawrence Livermore laboratory to have a damage threshold of 6 - 8 Jcm^{2} at 248 nm. A multi-shot threshold was also defined and was typically 2 - 5 times less than the single shot values. In general, multi-shot damage was usually observed within the first 30 shots.
Pre-conditioning tests on a single HR sample improved the single shot damage threshold from $1.3 \text{ to } 2.0 \text{ Jcm}^{-2}$ and for an AR sample $1.65 \text{ Jcm}^{-2}$ to $4.7 \text{ Jcm}^{-2}$. However, detailed studies of the pre-conditioning effect on another AR sample simply reduced the defect density of the most damage sensitive defects whilst the onset threshold was unchanged.

A thermal model of defect damage was developed based on a single absorbing spherical defect located in an infinite dielectric host. The sphere damage threshold was defined as the incident fluence required to raise the centre of the sphere to its melting point. The model was applied to a $\text{SiO}_{1.5}$ sphere embedded in a $\text{SiO}_2$ host and irradiated at the laser wavelength of 248 nm. The minimum sphere damage thresholds occurred for sphere radii of 500 - 600 nm and were in the experimentally observed range of $1 - 8 \text{ Jcm}^{-2}$. These results suggest that the absorption coefficients of the most damage sensitive defects in thin films at 248 nm are in the range 1500 - 2500 cm$^{-1}$ corresponding to mid-range damage thresholds of $2 - 4 \text{ Jcm}^{-2}$.

This model predicts various laser damage threshold scaling relationships depending on the particle size relative to the thermal diffusion distance and secondly the particle absorption efficiency. The comparisons with published data were considered inconclusive because of the variability in the experimental results.

The validity of the model could be greatly improved by removing the requirement for uniform volumetric heating of the sphere. This could be done by numerically integrating the exact Mie solutions for the electric field intensity distribution inside and near to the sphere. The various models of laser damage would then have a common origin - electric field enhancement at defects, with the subsequent damage mechanism at a given defect dependent on the degree of enhancement.

A statistical model of laser damage was developed based on a 2-D distribution of defects on an optical
surface. The laser damage threshold dependence on the spot size and defect density is significant if the spot size is comparable to the mean defect spacing. The distribution of the defects on an AR coating was shown to follow an approximate Poisson distribution with an average defect density in the range $32 \pm 12 \text{ mm}^{-2}$. The laser damage probability of this sample was measured as a function of the incident fluence with the theoretical model adjusted to fit the data. This involved the onset threshold at which the damage probability is zero and the defect density, (for a known spot size). This fitting procedure required defect densities in the range $1 - 2 \text{ mm}^{-2}$ suggesting less than 10% of the counted defects were involved in the initial stages of damage. Significant variations in the damage threshold arise depending on how it is defined. The onset threshold is the only value which is independent of the laser spot size. At such low defect densities a spot size of at least a few mm$^2$ is preferred to avoid ambiguities arising from different definitions of the damage threshold.
Appendix I Transient electrical circuit model of a photodetector

The importance of impedance matching the equivalent load resistance of a photometric detector into a co-axial cable and oscilloscope was noted in section 3.4.biii. The general electrical network can be represented by three impedances as shown in figure 1. The impedance $Z_1$ is represented as an ideal current source in parallel with a load resistor $R_{LD}$ and capacitor $C_1$ given by

$$C_1 = C_{DET} + C_S$$

where $C_{DET}$ is the intrinsic device capacitance and $C_S$ the stray capacitance arising from mounting the detector. The impedance $Z_1$ represented by the parallel combination of $R_{LD}$ and $C_1$ is given by

$$\frac{1}{|Z_1|} = \left[ \frac{1}{R_{LD}^2} - (\omega C_1)^2 \right]^{1/2}$$

where $\omega$ is the frequency. Equation 2 simplifies to

$$Z_1 = R_{LD}$$

if $\omega << 1/R_{LD} C_1$. A step input current pulse has a voltage risetime, $(10 - 90\%)$ across the resistor given by

$$t_r = 2.2 R_{LD} C_1$$

The impedance $Z_2$ is that represented by a co-axial cable and $Z_3$ that represented by the oscilloscope. The impedance "looking in" through terminals CC in figure 1 is equal to $Z_1$ if the characteristic impedance of the co-axial cable is matched to $Z_1$ and the co-axial cable is terminated with its own characteristic impedance. In this way the input capacitance of the oscilloscope and the capacitance of the co-axial cable do not influence the response time of the photodetector. Furthermore, there are no impedance mis-matches between the detector and co-axial cable and the co-axial cable and oscilloscope. This
FIGURE 1
GENERAL NETWORK MODEL OF PHOTOMETRIC DETECTOR CO-AXIAL CABLE AND OSCILLOSCOPE

FIGURE 2
NETWORK MODEL OF AN UNMATCHED PHOTODETECTOR CO-AXIAL CABLE AND OSCILLOSCOPE

FIGURE 3
SIMPLIFIED MODEL OF FIGURE 2
IF \( R_{SC} \gg R_{LP} \)
AND \( C_a = C_o + C_{sc} \)
prevents the formation of reflections.

The more general case of a non-matched system is illustrated in figure 2. In this case the load resistor is not equal to the characteristic impedance of the co-axial cable. The co-axial cable is modelled as a simple inductor and capacitor combination. The inductance, \( L_0 \) and capacitance \( C_0 \) vary with cable length. Typical values for a UR67 cable of characteristic impedance \( Z_0 = 50 \, \Omega \) are \( L_0 = 250 \, \text{nh/m} \) and \( C_0 = 100 \, \text{pF/m} \). The co-axial cable is not terminated and \( Z_3 \) is represented by a parallel combination of the oscilloscope input capacitance, \( C_{SC} \) and input resistance \( R_{SC} \). The Tektronix 466 oscilloscope has an input capacitance of \( C_{SC} = 20 \, \text{pF} \) and \( R_{SC} = 1 \, \text{M\Omega} \). For analysis purposes the circuit can be simplified to that shown in figure 3. The input oscilloscope resistance \( R_{SC} \) can be neglected if \( R_{SC} \gg R_{LD} \), the co-axial cable capacitance \( C_0 \) and input oscilloscope capacitance \( C_{SC} \) can be combined to give

\[
C_2 = C_0 + C_{SC}
\]

The trailing edge of the laser pulse is represented as a negative step input of height \(-I_0\) from the current source. It follows from Kirchoff's law and the three current loops shown in figure 3 that

\[
i_1 + i_2 + i_3 = i(t)
\]

\[
i_2 R_{LD} - \frac{1}{C_1} \int_0^t i_1 \, dt = 0
\]

\[
\frac{L_0}{\text{dt}^2} + \frac{1}{C_2} \int_0^t i_3 \, dt - i_2 R_{W} = 0
\]

The voltage across the load resistor \( R_{LD} \) is given by

\[
V = \frac{R}{2 \, \text{LD}}
\]
The Laplace transforms of equations (6) - (9) are given by

\[ I_1 + I_2 + I_3 = I \]  \hspace{1cm} \text{(10)}

\[ I_2 R_{LD} - \frac{I_1}{sC_1} = 0 \]  \hspace{1cm} \text{(11)}

\[ L_0 s I_3 + \frac{I_3}{sC_2} - I_2 R_{LD} = 0 \]  \hspace{1cm} \text{(12)}

\[ V = I_2 R_{LD} \]  \hspace{1cm} \text{(13)}

where the Laplace transform operator \( L \) is given by

\[ L[i_k(t)] = I_k(s) \quad (k = 1 - 3) \]  \hspace{1cm} \text{(14)}

and \( s \) is the transform parameter to be solved. The Laplace transform of the negative input current step is given by

\[ I = \frac{-I_0}{s} \]  \hspace{1cm} \text{(15)}

Equation 15 together with equations 10 - 13 can be used to show that the Laplace transform of the output voltage across the load resistor, \( V \) is given by

\[ V = \frac{-I_0 R_{LD} (1 + s^2 C_2 L_0)}{a s (s^3 + a s^2 + b s + c)} \]  \hspace{1cm} \text{(16)}

where

\[ \alpha = R C_1 C_2 L_0 \]

\[ a = 1/R_{LD} C_1 \]

\[ b = \frac{C_1 + C_2}{C_1 C_2 L_0} \]

\[ c = 1/R_{LD} C_1 C_2 L_0 \]  \hspace{1cm} \text{(17)}
The cubic polynomial in equation 16 can be written as

\[ s^3 + as^2 + bs + c = (s - s_1)(s^2 + ds + e) \]  

where \( s_1 \) is a real root of the polynomial. The quadratic term can be re-written by "completing the square"

\[ s^2 + ds + e = (s + d/2)^2 + (e - d^2/4) \]

Substituting equations 18 and 19 into equation 16 gives

\[ V = \frac{-i_0 R_{LD}(1 + s^2 C_2 L_0)}{\alpha(s - s_1)(s + d/2)^2 + (e - d^2/4)} \]

The two terms in the numerator in equation 20 can be separated and have "relatively" standard inverse Laplace transforms. The output voltage \( V \) across the load resistor is therefore given by

\[ V = \frac{i_0 R_{LD}}{\alpha} \left[ A_3 \cdot e^{ft} \sin(gt + \phi_1) + A_2 - A_1 \cdot e^{s_1 \cdot t} \right] - \frac{i_0 R_{LD} C_2 L_0}{\alpha} \left[ A_4 \cdot e^{s_1 \cdot t} + A_5 \cdot e^{ft} \sin(gt + \phi_2) \right] \]

where

\[ \begin{align*}
A_1 &= \frac{1}{s_1((f + s_1)^2 + g^2)}
A_2 &= \frac{1}{s_1(f^2 + g^2)}
A_3 &= \frac{1}{(f^2 + g^2)((f + s_1)^2 + g^2)}
A_4 &= \frac{1}{s_1((f + s_1)^2 + g^2)}
A_5 &= \frac{1}{(f^2 + g^2)/(s_1 + f)^2 + g^2)}
\phi_1 &= \tan^{-1}\left(\frac{g}{f}\right) + \tan^{-1}\left(\frac{g}{f + s_1}\right)
\phi_2 &= \tan^{-1}\left(\frac{g}{f + s_1}\right) - \tan^{-1}\left(\frac{g}{f}\right)
\end{align*} \]

and

\[ \begin{align*}
f &= d/2
\phi &= e - d^2/4
\end{align*} \]

A computer programme was written in BASIC to calculate equation 21 as a function of time. The theoretical results shown in figures 4 and 5 should be compared with the experimental results given in figures 6 and 7 for the
NORMALIZED VOLTAGE RESPONSE ACROSS LOAD RESISTOR TO A NEGATIVE STEP INPUT INTO AN UNMATCHED PHOTODIODE CIRCUIT, (SEE FIGURE 3)
FIGURE 5
NORMALIZED VOLTAGE RESPONSE ACROSS LOAD RESISTOR TO A NEGATIVE STEP INPUT INTO AN UNMATCHED PHOTODIODE CIRCUIT
FIGURE 6
PD1912-S5 DETECTOR OUTPUT
1.0 m CO-AXIAL CABLE $Z_o = 50\Omega$
$T_{fall} = 352$ ns

FIGURE 7
PD1912-S5 DETECTOR OUTPUT
A - 0.375 m CO-AXIAL CABLE $Z_o = 50\Omega$
$T_{fall} = 176$ ns
B - 3.75 m CO-AXIAL CABLE $Z_o = 50\Omega$
$T_{fall} = 907$ ns
C - 6.15 m CO-AXIAL CABLE $Z_o = 100\Omega$
$T_{fall} = 914$ ns
PD1912 S5 vacuum photodiode. The load resistor \( R_{LD} = 1 \, \Omega \), the capacitance \( C_2 \) and inductance \( L_0 \) depend on the coaxial cable length. In figure 4 a falltime between 320 and 360 ns is predicted for a capacitance \( C_1 \) varying between 25 and 40 \( \text{pF} \). This compares with the experimental fall time of 352 ns shown in figure 6 using a 1 m coaxial cable of characteristic impedance \( Z_0 = 50 \, \Omega \) \((L_0 = 250 \, \text{nm}^{-1}, C_0 = 100 \, \text{pFm}^{-1})\). The expected response using three different coaxial cable lengths assuming \( C_1 = 30 \, \text{pF} \) is shown in figure 5. Curves A and B are for cables with a characteristic impedance \( Z_0 = 50 \, \Omega \) and curve C for cable of characteristic impedance \( Z_0 = 100 \, \Omega \) \((L_0 = 500 \, \text{nm}^{-1}, C_0 = 50 \, \text{pFm}^{-1})\). A comparison of the experimental and theoretical results are shown in table 1.

<table>
<thead>
<tr>
<th>EXPERIMENTAL</th>
<th>THEORETICAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{\text{FALL}} ) /ns</td>
<td>( T_{\text{FALL}} ) /ns</td>
</tr>
<tr>
<td>( T_{\text{PERIOD/ns}} )</td>
<td>( T_{\text{PERIOD/ns}} )</td>
</tr>
<tr>
<td>( 176 )</td>
<td>( 188 )</td>
</tr>
<tr>
<td>( 907 )</td>
<td>( 925 )</td>
</tr>
<tr>
<td>( 914 )</td>
<td>( 875 )</td>
</tr>
<tr>
<td>( 40.0 )</td>
<td>( 40 )</td>
</tr>
<tr>
<td>( 60.0 )</td>
<td>( 60 )</td>
</tr>
</tbody>
</table>

Table 1
Comparison between experimental and theoretical falltime and oscillation period, data taken from figures 5 and 7.

Some ambiguity exists in the estimate of the falltime in figure 7B and 7C due to the oscillating component. The period of the oscillations in figure 5 are in good agreement with experimental measurements although the damping seems to be less in figure 7C compared to the predicted results. The theoretical 90% - 10% falltimes are also in good agreement with the experimental values.
Appendix II Laser attenuator design based on the "stack of plates" polarizer

The transmission of polarized light through a single fused silica beamsplitter is considered in section 3.3. The transmission is expressed in terms of the Fresnel equations for p and s components of the incident light. A BASIC programme which runs on an Apple IIe computer was written to calculate the transmittance of an n plate "stack of plates" polarizer by repeated application of the Fresnel equations used to describe the transmission through a single plate, (equations 3.13-3.21 in section 3.3). The transmittance of the p and s components, $T_p$ and $T_s$, and the polarization ratio $T_p/T_s$ as a function of incidence angle are shown for a 10 plate design in figure 1. Randomly polarized light was assumed at the input and fused silica as the plate material with a refractive index of 1.5085 at 248 nm. The ten plates are shown as two groups of five to compensate for beam steering. At the Brewsters angle of about 57° the polarization ratio $T_p/T_s$ is 21. This represents the transmitted beam being polarized with 95.5% in the p state and 4.5% in the s state. The over-all transmission is 52% relative to the input beam. The polarization ratio, $T_p/T_s$ increases at larger angles of incidence but is compensated by the reduced over-all transmission. At an incidence angle of 70° the polarization ratio is 195. This represents the output being polarized with 99.5% in the p state and 0.5% in the s state. The over-all transmission in this case is reduced to 24%.

A simple reflection type laser beam attenuator uses two or more beamsplitters mounted inside a tube at Brewsters angle. The plane of incidence onto the beamsplitters can be simply changed by rotating the tube about its axis. In this case p polarized incident light with a maximum transmission is converted to s polarized incident light with a minimum transmission by a tube rotation of 90°. The calculated performance of a multi-plate, variable attenuator is shown in figure 2. The maximum or minimum transmission of the attenuator as a
FIGURE 1
10 PLATE STACK OF PLATES POLARIZER DESIGN AT 248nm
TRANSMISSION OF 
ATTENUATOR

VARIABLE 
ATTENUATOR
PLATES AT
\( \Theta = 57^\circ \)
FUSED SILICA \( n = 1.5085 \)

10 PLATE 
POLARIZER

FIGURE 2
TRANSMISSION OF MULTI-PLATE ATTENUATOR
(\( \lambda = 248 \text{ nm} \))
function of plate number was calculated assuming the
degree of polarization achieved with the 10 plate, "stack
of plates" polarizer at the incidence angle of 57°, (95.5%
p state, 4.5% s state). A ten plate attenuator achieves a
dynamic range of about 10 dB, (maximum transmission 95%,
minimum transmission 9%). The combined transmittance of
the ten plate polarizer and ten plate variable attenuator
is 49%-4.7%. The high insertion loss of 51% is due to the
need to polarize the input beam to the attenuator.

An alternative to the stack of plates polarizer would
be to use an internal laser-cavity fused silica window
mounted at Brewster's angle. The laser output would then
be polarized, overcoming the high insertion loss arising
from the "stack of plates" polarizer. This approach was
not investigated with the Lambda Physik EMG 200 excimer
because of its compact design.
Appendix III The effect of scanning a finite sized pinhole through a Gaussian laser beam profile

Measurements of focused KrF laser beam profiles using scanning pinholes are considered in section 3.7cii. For small focused beams the need to maintain detector linearity and a sufficient signal to noise ratio means that pinhole diameters may have to be a significant fraction of the $1/e^2$ beam radius. In this case, the laser intensity over the pinhole area for a given pinhole position relative to the beam is not constant. The effect on the measurement of a Gaussian beam profile is that the experimentally measured $1/e^2$ radius is larger than the actual Gaussian beam radius. A correction can be applied to the experimental data if the fluence function $F(x,y)$ is known.

A non-symmetrical Gaussian function $F(x,y)$ is assumed to represent the fluence distribution.

$$F(x,y) = F_0 \exp(-2x^2/\rho_1^2) \exp(-2y^2/\rho_2^2)$$  \hspace{1cm} (1)

The arbitrary pinhole position relative to the Gaussian beam is illustrated in figure 1. The pinhole with radius $a$ is centred at $x_a, y_a$. The equation of the circle defining the edge of the pinhole is given by

$$(x - x_a)^2 + (y - y_a)^2 = a^2$$  \hspace{1cm} (2)

The pulse energy transmitted through an elemental area $\delta x \delta y$ within the pinhole is given by

$$\delta E_T = F(x, y) \delta y \delta x$$  \hspace{1cm} (3)

The total pulse energy transmitted through the pinhole is given by

$$E_T = \int_{x}^{y} \int_{y} F(x, y) dy dx$$  \hspace{1cm} (4)

where the integral extends over the area defined by the edges of the pinhole, given by equation 2. For the
CO-ORDINATE SYSTEM FOR THE PINHOLE LOCATION RELATIVE TO THE FLUENCE DISTRIBUTION $F(x,y)$
pinhole centred at \((x_a, y_a)\) the limits of the \(x\) integration are given by

\[
x_{\text{MAX}} = x_a + a \quad \text{MIN}
\]

and the limits of the \(y\) integration are given by

\[
y_{\text{MAX}} = y_a + \left[ a^2 - (x - x_a)^2 \right]^{\frac{1}{2}} \quad \text{MIN}
\]

Expanding on equation 4 gives

\[
E_T = F_0 \int_{x_{\text{MIN}}}^{x_{\text{MAX}}} \exp\left(\frac{-2x^2}{\rho_1^2}\right) \int_{y_{\text{MIN}}}^{y_{\text{MAX}}} \exp\left(\frac{-2y^2}{\rho_2^2}\right) dy \, dx
\]

The \(y\) integration in square brackets in equation 7 is not separable because the \(y\) limits depend upon \(x\) as given in equation 6.

A computer programme was written in BASIC to calculate the ratio \(E_T/F_0\) in equation 7 as a function of the position of the pinhole. The main input parameters were

1) Gaussian radii, \(\rho_1\) and \(\rho_2\)
2) Pinhole radius, \(a\)
3) Pinhole location, \(y_a\)
4) Start value, final value and step size for \(x_a\)
5) The number of grid points contained within the pinhole.

For calculation purposes the pinhole was divided into a rectangular array of \(4\alpha\beta\) points where \(\alpha\) and \(\beta\) are input parameters. For the range of pinhole and Gaussian radii considered a grid of 100 points was sufficient.

Typical Gaussian radii were chosen with \(\rho_1 = 2.5\) mm \(\rho_2 = 0.5\) mm (and vice versa) and a symmetric profile with
\( \rho_1 = \rho_2 = 0.5 \text{ mm} \). The correction factor for an experimentally measured profile with a 1/e\(^2\) radius \( \rho_{\text{exp}} \) and a pinhole radius, \( \rho \), can be calculated from the results shown in figure 2. The correction factor for a slit (reproduced from reference 3.37) has also been included. The x axis in figure 2 for the case of a slit represents the ratio, slit width/\( \text{exp}'1 \) 1/e\(^2\) diameter). For the case of a 0.42 mm diameter pinhole with measured 1/e\(^2\) radii of 2.5 mm and 0.65 mm, the correction factors are 0.995 and 0.945 respectively. The 5.5% correction factor for the smaller 1/e\(^2\) radius is about the same as the experimental reproducibility in the original measurements. The correction factors on the same experimental radii of \( \rho_1 = 2.5 \) mm and \( \rho_2 = 0.65 \) mm but measured with a 0.42 mm slit width are 0.994 and 0.928. These calculations suggest that pinhole diameters or slit widths of (1/5 - 1/10) of the 1/e\(^2\) experimentally measured diameter have no significant correction if the reproducibility of the measurements is 2 - 5%. 

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CORRECTED BEAM PROFILE WIDTH
DEPENDENCE ON PINHOLE RADIUS

FIGURE 2

NORMALIZED CORRECTED BEAM PROFILE WIDTH
( $\rho_{\text{TRUE}} / \rho_{\text{EXP'LY}}$ )

BEAM CONTOUR
SCAN DIRECTION
SLIT CORRECTION

SYMMETRICAL GAUSSIAN
$\rho_{\text{pin}} = 0.5 \text{ mm}$

$1/e^2$ RADIUS OF UNCORRECTED BEAM

RADIUS PINHOLE, $a$

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Appendix IV Reflectance calculations for absorbing thin films

The basic geometry used to represent a single thin dielectric film deposited on a substrate is shown in figure 1. The orientation of the electric and magnetic vectors for the p and s components follows that given by Macleod, (7.12). Following the analysis given by Macleod, (7.12), the characteristic equation for such a thin film is given by

\[
\begin{bmatrix}
E_a \\
H_a
\end{bmatrix} = 
\begin{bmatrix}
\cos \Delta_1 & i \sin \Delta_1 / \eta_1 \\
\eta_1 \sin \Delta_1 & \cos \Delta_1
\end{bmatrix}
\begin{bmatrix}
E_b \\
H_b
\end{bmatrix}
\]

The matrix notation gives the total tangential electric and magnetic fields, \( E_a \) and \( H_a \) at the input interface in terms of the total tangential electric and magnetic fields, \( E_b \) and \( H_b \) transmitted to the final interface. The characteristic matrix of the thin film is defined in terms of the phase thickness of the coating, \( \Delta_1 \) and the modified oblique optical admittance of the film \( \eta_1 \). The phase thickness of the thin film is given by

\[
\Delta_1 = (2\pi / \lambda) d_1 N_1 \cos \theta_1
\]

where \( \lambda \) is the optical wavelength of interest, \( d_1 \) is the physical thickness of the coating and \( N_1 = (n_1 - ik_1) \) is the complex refractive index of the thin film. The angle of incidence \( \theta_1 \) is given by

\[
n_0 \sin \theta_0 = N_1 \sin \theta_1 = N_2 \sin \theta_2
\]

The refractive index of the incident medium is assumed to be real. Equation 3 is an expression of Snell's law where the refractive index \( N_1 \) and therefore \( \sin \theta_1 \) can be complex and similarly for the substrate with complex index \( N_2 \) and refracted angle \( \theta_2 \). Using the notation given by Macleod, (7.12) a modified optical admittance \( \eta \) is defined for each medium in terms of \( E \) and \( H \).

\[
\eta = H / E
\]
BOUNDARY a

PHYSICAL THICKNESS, $d_i$

BOUNDARY b

INCIDENT MEDIUM
INDEX $n_0 = n_0$

THIN FILM
INDEX $n_i = n_i - ik_i$

SUBSTRATE
INDEX $n_2 = n_2 - ik_2$

FIGURE 1
THIN FILM GEOMETRY FOR REFLECTANCE CALCULATIONS
Using the subscripts \( p \) and \( s \) to represent incident light polarized parallel to the plane of incidence or perpendicular to the plane of incidence respectively the modified optical admittance for oblique incidence is given by

\[
\eta_s = \eta N \cos \theta \\
\eta_p = \eta N / \cos \theta
\]

where \( \eta \) is the admittance of free space, \((2.6544 \times 10^{-3})\) Siemans. Comparison of equations 5 and 6 shows that \( \eta_p = (\eta N)^2 / \eta_s \). The admittance of the incident medium \( \eta_0 \), the thin film \( \eta_1 \) and the substrate \( \eta_2 \) can be calculated by using the appropriate refractive index and incident angle in each medium. By analogy with equation 4 an input optical admittance of the total system, \( Y \) can be defined as

\[
Y = H_a / E_a \tag{7}
\]

Substituting equation 7 in equation 1 gives

\[
\begin{bmatrix}
B \\
C
\end{bmatrix} = \begin{bmatrix}
\cos \Delta_1 & i \sin \Delta_1 / \eta_1 \\
\eta_1 i \sin \Delta_1 & \cos \Delta_1
\end{bmatrix} \begin{bmatrix}
1 \\
\eta_2
\end{bmatrix} \tag{8}
\]

The over-all complex admittance can be expressed as

\[
Y = C / B = (\alpha + i \beta) / (\gamma + i \varepsilon) \tag{9}
\]

where \( \alpha = \eta_2 \cos \Delta_1 \), \( \beta = \eta_1 \sin \Delta_1 \), \( \gamma = \cos \Delta_1 \) and \( \varepsilon = (\eta_2 / \eta_1) \sin \Delta_1 \) from equation 8. The problem of calculating the over-all reflectance reduces to that for an incident medium with admittance \( \eta_0 \) and a second medium with admittance \( Y \). The amplitude reflection coefficient \( r \)
is therefore given by

\[ r = \frac{\eta_0 - Y}{\eta_0 + Y} \]  \tag{10}

Equation 10 is identical to that used at a single semi-infinite dielectric interface except that the admittance \( Y \) replaces the admittance of the second medium. Substituting equation 9 in equation 10 gives

\[ r = \frac{Z_1 + iZ_2}{Z_3 + iZ_4} \]  \tag{11}

where \( Z_1 = (\eta_0 \gamma - \alpha), \ Z_2 = (\eta_0 \varepsilon - \beta), \ Z_3 = (\eta_0 \gamma + \alpha) \) and \( Z_4 = (\eta_0 \varepsilon + \beta) \). An alternative and perhaps more useful form of equation 11 can be written as

\[ r = \rho e^{i\delta} \]  \tag{12}

where \( \rho \) is simply the magnitude of the reflection coefficient and \( \delta \) is the overall phase change on reflection. Comparison of equations 11 and 12 gives

\[ \rho = \left(\frac{Z_1^2 + Z_2^2}{Z_3^2 + Z_4^2}\right)^{1/2} \]  \tag{13}

and

\[ \delta = \arctan \left(\frac{Z_2Z_3 - Z_1Z_4}{Z_1Z_3 + Z_2Z_4}\right) \]  \tag{14}

The intensity reflection coefficient or reflectance is given by

\[ R = rr^* = \rho^2 \]  \tag{15}

where the asterisk denotes the complex conjugate. A computer programme was written to calculate the reflectance and phase change using equations 13 - 15. The \( Z \) parameters were calculated in terms of the admittance of the incident medium, the thin film, the substrate and the phase change \( \Delta \) of the light transmitted through the thin film. The basic input parameters are the real index of
the incident medium, (usually air), the refractive index of the thin film layer, the refractive index of the substrate and the angle of incidence. Complications arise if the thin film or the substrate material has a complex refractive index. In the former case the phase change $\Delta_1$ given by equation 2 is complex and can be expressed as

$$\Delta_1 = \langle 2\pi d_1 / \lambda \rangle \left( \eta_1^2 - k_1^2 - n_0^2 \sin^2 \theta_0 \right) - i 2 n_1 k_1 \frac{\eta_1}{\eta_2}$$  \hspace{1cm} (16)

Similar expressions result when calculating the $s$ component admittance of the thin film $\eta_1$ and the substrate $\eta_2$. The $p$ component was calculated from the relationship between $\eta_s$ and $\eta_p$. The analysis was carried out using the phasor form for complex numbers since this makes the roots of a complex number and the product or quotient of two complex numbers simpler to calculate. Some care was needed using this approach to make sure that the principal value of phase angle was calculated. This required attention to the signs of the real and imaginary components in the Argand diagram to make sure the correct quadrant was used for the phase angle.

The effect of varying the thickness of an aluminium thin film on the normal incidence reflectance at 248 nm is shown in figure 2. The aluminium film is assumed to have an index $N_1 = (0.175 - i 2.7)$ deposited on a fused silica substrate with an index $N_2 = 1.5085$. Above a thickness of 50 nm the aluminium behaves optically as though it is semi-infinite in extent. In this case the effect of multiple reflections within the aluminium film are negligible. This arises because of the very shallow skin depth for the penetration of the optical radiation into the metal surface. In this case, the total admittance $Y$ approaches the value $\eta_1$ and equation 10 becomes equivalent to the standard Fresnel equation for reflection from a single interface. This approach was used to calculate the reflectance variation of aluminium with incident angle in figure 7.3 and the corresponding phase change shown in figure 7.4.

Aluminium thin film reflectors have also been used
FIGURE 2

CALCULATED REFLECTANCE OF AN ALUMINIUM COATING AT NORMAL INCIDENCE AS A FUNCTION OF COATING THICKNESS.
with the excimer laser light incident through the transmitting substrate. The reflectance can be estimated by adding intensities from the multiple reflections within the substrate. The over-all reflectance is given by the sum of an infinite geometric series and reduces to

\[ R = \frac{R_{12} + (T_{12})^2 R_{23}}{1 - R_{23} R_{12}} \]  

where \( R \) and \( T \) refer to the standard Fresnel reflectance and transmittance expressions and the subscripts 12 and 23 refer to the air/substrate and substrate/metal interfaces respectively. The comparison between equations 15 and 17 as a function of the angle of incidence is shown in figure 7.3. Equation 17 was also used to calculate the angular dependence of the reflectance using \( n_2 \) and \( k_2 \) as fitting parameters to experimental data. This is illustrated in figure 7.7.

The computer model has also been used to predict the performance of dielectric overcoated aluminium mirrors. In particular this was done for dielectric overcoatings which show some degree of absorption at 248 nm. The optical properties of aluminium were used to calculate the admittance of the substrate, \( n_2 \) and the optical properties of the thin film to calculate \( n_1 \). In general, the total admittance of the thin film and substrate combination is complex and can be written in phasor form as

\[ Y = ae^{i\sigma} \]  

where \( a \) is the magnitude and \( \sigma \) the phase angle.

Substituting equation 18 in equation 10 and calculating the reflectance via equation 15 gives

\[ R = \frac{(n_0^2 + a^2 - 2n_0a\cos\sigma)}{(n_0^2 + a^2 + 2n_0a\cos\sigma)} \]  

It is clear from equation 19 that the stationary-points, (maxima and minima) are given by \( \left(\frac{\partial R}{\partial \sigma}\right) = 0 \). This occurs for \( \cos\sigma = \frac{m}{a} \) and \( m = 0, 1, 2, 3 \text{ etc.} \). The stationary points therefore arise when the admittance of the
film-substrate combination is real. The minima occur for
m = 0, 2, 4,... and the maxima for m = 1, 3, 5,... As
the dielectric over-coating thickness is increased from
zero the reflectance curve initially decreases to the
first minima, this effect is illustrated in figure 7.5.
If the extinction coefficient of the of the overcoating is
zero, the reflectance variation with coating thickness is
periodic as shown in figure 7.6. The effect of low
absorption is to damp the oscillations.

The general condition for stationary points can be
calculated from equation 9 and knowing that the admittance
Y must be real. In the case of an absorbing overcoat
deposited on a thick metal coating the variables α, β, γ
and ε are also complex. After extensive manipulation by
separating equation 9 into its real and imaginary parts
and eliminating Y the condition at normal incidence for
the reflectance maxima or minima becomes

$$\tan(2\Delta_1) = \frac{2(n_1k_2 - n_2k_1)}{A + 2k_1(k_1k_2 + n_1n_2)/(n_1\cos(2\Delta_1))}$$  \hspace{1cm} 20

where

$$A = n_1^2 + k_1^2 - n_2^2 - k_2^2$$  \hspace{1cm} 21

Equation 20 gives the phase thickness $\Delta_1$ for maximum or
minimum reflectance and can be used to calculate the
physical coating thickness via equation 2. The validity
of equation 20 can be extended to non-normal incidence if
the values of $n_1$, $k_1$, $n_2$ and $k_2$ are replaced with the real and imaginary components of the film and substrate
admittance given by equation 5 or 6. If the extinction
coefficient of the overcoating layer is zero then equation
20 simplifies to

$$2\Delta_1 = \arctan[2k_2n_1/(n_1^2 - n_2^2 - k_2^2)] + m\pi$$  \hspace{1cm} 22

which has been calculated previously, (7.12). A simple
computer programme was written to solve equation 20 using
an iterative procedure. An initial estimate of $A_1$ was made using $k_1 = 0$, typically about five iterations were needed before the solution stabilized. The solution was investigated in detail for $n_1 = 1.58$, $n_2 = 0.65$ and $k_2 = 2.4$. This situation corresponded to a low reflectance aluminium mirror overcoated with ThF$_4$, (mirror B in figure 7.7). The solution to equation 20 as a function of $k_1$ is shown in figure 3. The solution is expressed as a percentage of the physical thickness of the overcoating for $k_1 = 0$. As the extinction coefficient of the overcoating layer increases the optimum coating thickness reduces compared to that for $k_1 = 0$. For $k_1 < 0.1$ the optimum coating thickness deviates by less than 0.7% from the value for $k_1 = 0$. In many cases, where the overcoating layer has low absorption, the optimum coating thickness can therefore be calculated using equation 22.
PARAMETERS
\[ \lambda = 248\text{nm} \]
\[ n_r = 1.58 \]
\[ n_i = 0.65 \]
\[ R_s = 2.4 \]

FIGURE 3
SOLUTION TO EQUATION 20 IN TERMS OF COATING THICKNESS RELATIVE TO THAT FOR \( R_s = 0 \).
Appendix V Calculation of the electric field at the interfaces of a three layer AR coating

The electric field enhancement at the interfaces of a multi-layer thin film coating can be calculated using recursive equations giving the electric field at the \( j^{th} \) interface in terms of the electric field at the \((j + 1)^{th}\) interface. This notation requires the \( j^{th} \) film to be located between the \( j^{th} \) and \((j + 1)^{th}\) interfaces.

Interest is limited to the three layer AR coating shown in figure 1 where \( j \) extends from one to five. The positive and negative subscripts on the electric field amplitude \( E \) represent the total positive and total negative going wave amplitudes at each interface. The coatings are assumed to be non-absorbing so that the phase change in each layer is real. It is convenient to use the recursive equations developed by Levi, (8.27) given by

\[
E_j^+ = 0.5 \left( (1 + c_j)E_{j+1}^+ \exp(-i\phi_j) + (1 - c_j)E_{j+1}^- \exp(i\phi_j) \right)
\]

\[
E_j^- = 0.5 \left( (1 - c_j)E_{j+1}^+ \exp(-i\phi_j) + (1 + c_j)E_{j+1}^- \exp(i\phi_j) \right)
\]

where

\[
c_j = \frac{n_j}{n_{j-1}}
\]

and the phase thickness \( \phi_j \) is given by

\[
\phi_j = 2\pi n_j d_j / \lambda
\]

The total electric field at the \( j^{th} \) interface is given by

\[
E_j = E_j^+ + E_j^-
\]

It is convenient to define an electric field ratio, \( \alpha \) in terms of the square of the electric field at the \( j^{th} \) interface relative to the incident field at the first interface. This is given by

\[
\alpha_j = |E_j/E_1|^2
\]
Figure 1

Electric field configuration in a three layer dielectric coating, superscript + denotes positive going wave and - a negative going wave.
If \( E_j \leq E_1^- \) then \( \alpha_j < 1 \) and the peak field at the \( j^{th} \) interface is reduced compared to the incident field.

For the example shown in figure 1 the \( j = 5 \) interface is located in the substrate so that \( E_5^- = 0 \) giving \( E_5^- = E_5^+ \). This limits the reflectance calculation to that from the multi-layer and excludes the contribution from the back surface of the substrate. In the case of a perfect AR coating the overall reflectance is equated to zero giving \( E_1^- = 0 \). In this case the intensity incident on the air-film interface, \( (j = 1) \) must be equal to the intensity incident on the substrate-substrate interface, \( (j = 5) \). This gives

\[
|E_1^+|^2 n_o = |E_5^+|^2 n_m
\]

If the incident medium is air, \( (n_o = 1.0) \) the electric field ratio at the substrate-substrate interface is therefore given by

\[
\alpha = \frac{1/n}{5/m}
\]

Substituting \( j = 4 \), (film-substrate interface) in equations 1 and 2 gives

\[
E_4^+ = 0.5(1 + n_m/n_3)E_5^+ \exp(-i\phi_4)
\]

\[
E_4^- = 0.5(1 - n_m/n_3)E_5^+ \exp(-i\phi_4)
\]

Adding equations 9 and 10 gives

\[
E_4 = E_5^+ \exp(-i\phi_4)
\]

Substituting for \( E_5^+ \) from equation 7 gives

\[
\alpha_4 = |E_4/E_1^+|^2 = 1/n_m
\]

Equations 8 and 12 show that the electric field amplitude is constant in the substrate and equal to that at the interface between the inner film and the substrate.
typical value of \( n_m = 1.5 \) gives \( \alpha_4 = 0.667 \). The electric field at the film-substrate interface is therefore 0.816 times that of the incident field. This assumes a perfect AR coating and neglects any coherent effects arising from reflection from the back surface of the substrate.

Substituting \( j = 3 \) in equations 1 and 2 and adding gives

\[
E_3 = E_4^+ \exp(-i\phi_3) + E_4^- \exp(i\phi_3)
\]

Substituting for \( E_4^+ \) and \( E_4^- \) from equations 9 and 10 and using equation 7 gives

\[
\alpha_3 = \frac{|E_3/E_1|^2}{A^2/n_m + B^2n_m/n_3^2} = \cos^2(\phi_3/n_m) + n_m\sin^2(\phi_3/n_3^2)
\]

A similar approach was used to calculate \( \alpha_2 = |E_2/E_1|^2 \).

Using \( j = 2 \) in equations 1 and 2 and adding gives

\[
E_2 = E_3^+ \exp(-i\phi_2) + E_3^- \exp(i\phi_2)
\]

Substituting for \( E_3^+ \) and \( E_3^- \) gives \( E_2 \) in terms of \( E_4^+ \) and \( E_4^- \). Equations 9, 10 and 7 were then used to express \( E_2 \) in terms of \( E_1^+ \). After some manipulation this gives

\[
\alpha_2 = |E_2/E_1|^2 = A^2/n_m + B^2n_m/n_3^2
\]

where

\[
A = \cos\phi_2\cos\phi_3 - n_3\sin\phi_2\sin(\phi_3/n_2)
\]

\[
B = \cos\phi_2\sin\phi_3 + n_3\sin\phi_2\cos(\phi_3/n_2)
\]

In the case of a perfect AR coating, \( E_1^- = 0 \) and therefore \( \alpha_1 = 1 \). Equations 12, 14 and 16 reduce to those given by Bennett, (8.25) when applied to quarter wave thicknesses. However, these expressions are valid for any three layer AR coating and have been applied to the two and three layer non-quarter wave AR coatings considered in section 8.3. In particular they have been used in equation 8.52.
to fit the theoretical damage probability profile to the experimental results measured for a three layer non-quarter wave AR coating produced by Technical Optics, (8.31). The details of the design are given in table 1 below.

<table>
<thead>
<tr>
<th>Layer index</th>
<th>thickness/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>substrate</td>
<td>1.506</td>
</tr>
<tr>
<td>1</td>
<td>1.32</td>
</tr>
<tr>
<td>2</td>
<td>1.506</td>
</tr>
<tr>
<td>3</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Table 1
Three layer non-quarter wave AR coating design for use at 248 nm (Design produced by Technical Optics)

These expressions can also be used to estimate the volumetric absorption in each layer if the absorption is low. The power absorbed in a medium with index $n$ is proportional $nE^2$ where $E$ is the local electric field strength. For nominally low absorbing films, the volume absorption per unit incident power in the film between the $j^{th}$ and the $(j+1)^{th}$ interface is given by, (8.25)

$$A_j = \beta_j d_j \langle n_j E^2 \rangle_{av}/E_1^2$$  \hspace{1cm} \text{19}$$

where $\beta_j$ is the absorption coefficient, $\langle \beta_j = 4\pi k_j/\lambda \rangle$ and $\langle n_j E^2 \rangle_{av}$ is the average intensity in the film. Equation 19 was used to estimate the absorption by calculating $\langle |E_{j+1}|^2 + |E_j|^2 \rangle/2$ for each film. Equations 12, 14 and 16 were used to give the absorption in the outer, middle and inner layers as

$$A_1 = 0.5\beta_1 d_1 n_1 (1 + \alpha_2)$$  \hspace{1cm} \text{20}$$

$$A_2 = 0.5\beta_2 d_2 n_2 (\alpha_2 + \alpha_3)$$  \hspace{1cm} \text{21}$$

$$A = 0.5\beta d_n (\alpha + \alpha)$$  \hspace{1cm} \text{22}$$
These expressions were used in section 8.3 to estimate the over-all absorption at 248 nm of two layer quarter wave coatings compared with exact calculations. They were also used to estimate the absorption of two layer and three layer non-quarter wave AR coating designs at 248 nm.