Optical scatter and damage testing of excimer laser components

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OPTICAL SCATTER AND DAMAGE TESTING OF EXCIMER LASER COMPONENTS

by

David Thomas Sheerin

A Doctoral Thesis

Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy at the Loughborough University of Technology.

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CHAPTER 1

INTRODUCTION

1.1 Introduction

A major problem facing the excimer laser industry at present is corrosion or contamination of optical components by one of the constituents of the lasing medium itself, namely fluorine. This results in significant loss of optical quality and hence efficiency.

It is well known that fluorine, in the presence of water vapour, etches fused silica and other glasses over a period of time. What is less well known is the effect that this phenomenon has on the optical quality of glass and any multilayer coatings that have been exposed to the fluorine, particularly at UV wavelengths. This is a worry especially at the Rutherford Appleton Laboratory (RAL).

The RAL is currently pursuing a feasibility programme into the possibility of producing Inertial Confinement Fusion (ICF) whereby small deuterium pellets are subjected to high intensity laser beams. The beams are produced from a large excimer laser facility using several multiplexed beams (SPRITE).

The SPRITE architecture encompasses angular multiplexing with Raman beam combining. A KrF laser chain is operated with angular multiplexing with X angularly separated beams each carrying a short train of Y pulses (see Fig. 1.1a overleaf). Extraction of KrF energy is thus by X x Y pulses in a long train. The KrF beams are demultiplexed to bring their pulses into coincidence as they pump a chain of Raman amplifiers which parallel the KrF laser chain. The Raman amplifiers are thin windowed gas cells with reflecting walls containing CH₄ at atmospheric pressure. A beam with a single pulse at the Stokes frequency interacts with X pump beams in the CH₄ gas and energy is transferred efficiently to the Stokes beam. Each pump beam carries a train of Y short pulses, and the total pump energy is extracted by a sequence of Y Stokes pulses each carried by a beam at a different angle to give an output of Y angularly multiplexed Stokes beams. The beam combining reduces the number of beams and allows the use of multiple parallel output amplifiers.
The facility provides technology and expertise that satisfies the needs of scientists from all over Europe who require high power densities at UV wavelengths for studying plasma physics and fusion projects. The laser beams themselves are separated in time and are recombined by placing mirrors at appropriate distances, (more of this in Chapter 3). Because, as mentioned before, fluorine chemically degrades silica, some of the light passing through will be scattered. This is of particular concern because if, at the first surface, beam energy from one component scatters into, say, the path of another, then the fine temporal coherence will be spoilt and so the final beam power is decreased. In order to offset these 'cross-talk' problems one must be aware of whether the scattering from the optical components is likely to be problematical.

The following extract is taken from the Rutherford Appleton report No. RAL-90-026:

"One of the most important points concerning angular multiplexing is the choice of interbeam angle. If this is too small then cross talk between beams can lead to prepulse on target. If the angle is too large then efficiency suffers.... Cross talk is caused by small angle scattering at the points where all beams overlap i.e. the amplifier optics and the laser medium itself. Causes of scattering are imperfections in multilayer coatings, etching by fluorine and dust in the laser gas. It would appear that minimum interbeam angles of around 5 mR° will need to be
employed giving rise to volumetric extraction efficiencies of around 75% for a typical large multiplexer."

Scatter from optical components is becoming an increasingly major problem in high energy laser optics, and more generally in the optical industry as a whole. It reduces signal power, limits resolution, produces optical noise and appears as an unexpected design problem in a number of optical systems.

The first serious attempts to measure optical scatter and use it to infer surface finish came about through the use of results from total integrated scatter (TIS) measurements\(^2,3\). Round robin experiments conducted during the 1970's between a variety of laboratories yielded results that were somewhat disappointing. Not only did TIS results differ by orders of magnitude from one institution to another but reproducibility was also a major problem during rounds, even using the same equipment at the same laboratory. Gradually, experience was gained in limiting contamination problems and appreciating those factors that contributed to noise from each inspecting instrument. In the mid 1970's measurement of scatter as a function of angle away from specular began to be used more often to obtain surface finish data\(^3-7\).

Presented in this thesis are results of experiments conducted at the Physics Department at Loughborough University in collaboration with the Rutherford Appleton Laboratory to investigate the optical properties of excimer laser components. The thesis itself covers two physical aspects of laser components that have a bearing on the final output power of the laser; scatter from the component and the damage threshold of the component. The former degrades the quality of the laser beam and the latter places a limit on the output power.

The first part of this thesis is given over to measuring the scattering properties of a host of different materials commonly found in laser systems, from ordinary substrates to multilayer, highly reflecting (HR) and anti reflecting (AR), coatings. Other experiments involve finding which of these materials are better in terms of exhibiting least scatter and how the scattering properties are changed when exposed to the corrosive atmosphere found in excimer lasers.

Chapter 2 is dedicated to presenting an introduction to scatter, how it arises, how it is quantified and to giving a summary of those instruments that are used to measure it. Also, whenever appropriate, a brief review is given so that the reader may put the current work into perspective with other results that have been published.
Chapter 3 is largely concerned with describing the experimental arrangement that was built at Loughborough to measure the near angle transmissive scatter of excimer laser components and how the presence of fluorine degrades the transmissive qualities of such components. Scatter data at other (shorter) wavelengths are also given so that the possibility of 'wavelength scaling', i.e. deriving how a sample will scatter at one wavelength from scatter data measured at another wavelength, may be examined.

Concern for increasing the damage threshold of materials has been widespread ever since the first laser was constructed. Over the years experience has taught that those materials which are the most pure and free of contaminants exhibit the highest damage threshold. The second half of this thesis is devoted to measuring the damage thresholds of such multilayer coatings so that a reliable coating design may be used to increase the output power of excimer lasers without suffering any degradation itself.

The damage testing of excimer laser components is given in Chapter 4 which begins with a review of damage testing at the excimer wavelength of 248 nm together with those models that are currently being used to explain why particular materials damage at a certain fluence. The damage testing facility is described together with an example of how such measurements are taken. The samples that were tested cover a wide range of materials from conventional multilayers to more esoteric designs that include using Teflon and PMMA as the coating materials.

Chapter 5 is a continuation of Chapter 4 in that the damage testing is continued but using a wide variety of pulselengths (from 450 fs to 25 ns). This was done because it was noticed that components fail at very low fluences at ultra-short pulselengths and it was found that a power law based on the length of the irradiating pulse was a good model for predicting when a particular coating will fail at any given pulselength.

Finally Chapter 6 provides a summary of all the results, what conclusions can be drawn from them and gives suggestions as to how future experiments may proceed to add to our understanding of precisely what materials are suitable for integration into high power excimer laser systems.
REFERENCES


CHAPTER 2

OPTICAL SCATTERING

2.1 Introduction

When an electromagnetic wave is incident upon a plane surface separating two media, it is reflected according to well known laws; the reflected field depends on the wavelength, the angle of incidence and the electrical properties (permittivity, permeability and conductivity) of the two adjoining media. These laws are in fact so well understood that the electrical properties of a material may often be determined by measuring its reflection coefficient alone.

What happens if the surface is not plane, however, but irregular, with periodic or random variations in height measured from a certain level? In actual fact no real surface is perfectly smooth. The extent to which surface roughness affects wave scattering is therefore of great interest. A large number of papers have been published over the years on the subject of scattering from rough surfaces and various models proposed to explain and predict measured data. None of these theories is general and rigorous at the same time although each model has its uses subject to certain limitations. Before these are gone into, however, it may be useful to review the properties of electromagnetic waves and the way they behave when incident upon a dielectric surface.

2.2 Mathematical Methods

Maxwell's equations provide an elegant summary of the laws of electromagnetism. They are most conveniently described by the vector notation:

i) Vectors are written in heavy type. A symbol such as \( \mathbf{E} \) stands for the vector and \( E \) for the magnitude.

ii) The product of two vectors such as \( \mathbf{E} \) and \( \mathbf{H} \) are written \( \mathbf{E} \cdot \mathbf{H} \) for the scalar product, whose value is \( EH \cos \theta \), and \( \mathbf{E} \times \mathbf{H} \) for the vector product, which is a vector of magnitude \( EH \sin \theta \) and whose direction is normal to the plane containing \( \mathbf{E} \) and \( \mathbf{H} \). A
rotation from \( \mathbf{E} \) to \( \mathbf{H} \) appears clockwise to an observer looking along the direction of the vector product.

iii) The symbols \( i, j \) and \( k \) are used for the unit vectors in the positive directions of the axes \( \mathbf{OX}, \mathbf{OY} \) and \( \mathbf{OZ} \) respectively. The standard vector operator, 'nabla', is written:

\[
\nabla = i \frac{\partial}{\partial x} + j \frac{\partial}{\partial y} + k \frac{\partial}{\partial z} \tag{2(1)}
\]

iv) The gradient of a scalar function (such as \( V \)) is written:

\[
\text{grad } V = \nabla V = i \frac{\partial V}{\partial x} + j \frac{\partial V}{\partial y} + k \frac{\partial V}{\partial z} \tag{2(2)}
\]

\( V \) is a scalar quantity whose value may change from point to point; \( \text{grad } V \) is a vector whose magnitude and direction may vary from point to point.

v) The magnitudes of the components of a vector \( \mathbf{E} \) along the axes are written \( E_x, E_y, E_z \) so that:

\[
\mathbf{E} = iE_x + jE_y + kE_z \tag{2(3)}
\]

vi) The divergence of a vector function \( \mathbf{E} \) is defined by:

\[
\text{div } \mathbf{E} = \nabla \cdot \mathbf{E} = \frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z} \tag{2(4)}
\]

A vector function whose divergence is zero everywhere is said to be solenoidal.

vii) The curl of a vector function is defined by:
\[
\text{curl } \mathbf{E} = \nabla \times \mathbf{E} = i \left( \frac{\partial E_z}{\partial y} + \frac{\partial E_y}{\partial z} \right) + j \left( \frac{\partial E_x}{\partial z} + \frac{\partial E_z}{\partial x} \right) + k \left( \frac{\partial E_y}{\partial x} + \frac{\partial E_x}{\partial y} \right)
\]

\[2(5)\]

ix) The symbol \( \nabla^2 \) when applied to a scalar \( (V) \) means:

\[
\nabla^2 V = \nabla \cdot \nabla V = \text{div} (\text{grad } V) = \frac{\partial^2 V}{\partial x^2} + \frac{\partial^2 V}{\partial y^2} + \frac{\partial^2 V}{\partial z^2}
\]

\[2(6)\]

The result is a scalar.

ix) The symbol \( \nabla^2 \) when applied to a vector \( (\mathbf{E}) \) means:

\[
\nabla^2 \mathbf{E} = i \nabla^2 . E_x + j \nabla^2 . E_y + k \nabla^2 . E_z
\]

\[2(7)\]

x) The divergence of the curl of any vector function is everywhere zero.

xi) The curl of the gradient of any scalar function is everywhere zero.

xii) The curl of the curl of a vector function \( (\mathbf{E}) \) is given by:

\[
\nabla \times (\nabla \times \mathbf{E}) = \text{curl} (\text{curl } \mathbf{E}) = \text{grad} (\text{div } \mathbf{E}) - \nabla^2 \mathbf{E}.
\]

\[2(8)\]

xiii) \( \text{div} (\mathbf{E} \times \mathbf{B}) = \nabla . (\mathbf{E} \times \mathbf{B}) = \mathbf{B} \cdot \text{curl } \mathbf{E} - \mathbf{E} \cdot \text{curl } \mathbf{B} \).

\[2(9)\]

2.3 Reflection and Refraction at a Dielectric Boundary

It is now necessary to understand the process of reflection and refraction in terms of Maxwell's equations when an electromagnetic wave is incident upon a dielectric boundary. However in order to describe these phenomena we must first consider the nature of the electromagnetic wave itself.
2.3.1 Definition of E and B

Historically the concept of electric field was derived from the observations of the mechanical forces exerted upon one another by two charged bodies. In a corresponding way, a concept of magnetic field was abstracted from the existence of forces upon magnets. In the light of modern day developments of electromagnetic theory it is recognised that there is no such thing as a free magnetic pole. The magnetic unit is a small closed loop forming a magnetic dipole. It is convenient to define two fields \( E \) and \( B \) by reference to an ideal situation in which the forces on a single electron, in vacuum, are assumed to be measured. This may be summarised by vector notation:

\[
- \mathbf{F} = e(\mathbf{E} + \mathbf{v} \times \mathbf{B})
\]

The force \( e\mathbf{E} \) which depends only on the position of the electron is called electrostatic; the force \( e(\mathbf{v} \times \mathbf{B}) \) which depends upon the position and velocity of the electron is called magnetic, (the force is negative because the charge on the electron is defined to be negative). The units are obtained by considering the fields due to a single electron. The electric field \( \mathbf{E} \) at a distance \( r \) from a charge \( e \) is:

\[
\mathbf{E} = \frac{1}{4\pi\varepsilon_0} \frac{e\mathbf{r}_0}{r^3}
\]

where \( \mathbf{r}_0 \) is the unit vector in the direction of \( r \).

To obtain a static magnetic field requires a continuous succession of electrons. These produce a current element \( \mathbf{J} = Ne\mathbf{v} \) where \( N \) is the number of electrons per unit path length and \( \mathbf{v} \) is the velocity relative to the observer. Dividing the observed field by \( N \), we find the magnetic field due to a single electron to be:

\[
\mathbf{B} = \frac{\mu_0}{4\pi} e(\mathbf{v} \times \mathbf{r}_0)
\]

The electric field is directed along \( r \), the magnetic field is perpendicular to \( r \) and \( \mathbf{v} \). \( \varepsilon_0 \) and \( \mu_0 \) are the permittivity and permeability of free space respectively. One of them can be chosen to give units of suitable size. The other is then fixed because the ratio of
the electric force to the magnetic force produced by an electron of known velocity can be measured. The result of this experiment requires

$$\frac{1}{\sqrt{\varepsilon_0 \mu_0}} = c$$

where $c$ is the velocity of propagation of all electromagnetic waves in vacuum (299,792 km/s).

### 2.3.2 Maxwell's Equations

The results of many experiments on electromagnetism were finally summarised by Maxwell in 1865. The field equations for dielectric media may be summed up in the following relations:

1. \[ \nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0} \quad (2.14) \]
2. \[ \nabla \cdot \mathbf{B} = 0 \quad (2.15) \]
3. \[ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (2.16) \]
4. \[ \nabla \times \mathbf{B} = \varepsilon_0 \mu_0 \frac{\partial \mathbf{E}}{\partial t} \quad (2.17) \]

The first equation is a consequence of differentiating Gauss' law\(^1\), $\rho$ representing the charge density. This will of course be zero for electromagnetic waves in a vacuum as there are no free charges. The second equation indicates that there are no sources of magnetic field corresponding to the electric charges which form the source of the electric field. The last two equations enunciate Faraday's law for the induction of an electric field (or current) by a varying magnetic flux and Ampere's law for the calculation of the magnetic field from a distribution of current.

In a dielectric medium, the relative permeability, (the ratio of the permeability of vacuum to that of the medium), $\mu_r$, and relative permittivity, (the ratio of the permittivity of vacuum to that of the medium), $\varepsilon_r$, must be left in the Maxwell's equations. The velocity of these waves is now \( \frac{1}{\sqrt{\varepsilon_0 \varepsilon_r \mu_0 \mu_r}} \). Since $\mu_r$ is very nearly 1,
the velocity of the waves is \( \frac{1}{\sqrt{\varepsilon_0 \mu_0}} \), and the refractive index \( n \) (the ratio of the velocity of the electromagnetic wave in vacuum to that in the medium) should be \( \varepsilon_r^{1/2} \). This is a relation that is found to be obeyed. Apparent violations are largely due to the measurement of the two quantities at different frequencies.

2.3.3 Electromagnetic Waves in Vacuum

We may now eliminate \( E \) and \( B \) in turn from these equations by applying the operator curl to eq. 2(16) to get:

\[
\text{grad (div } E) - \nabla^2 E = - \text{curl } \frac{\partial B}{\partial t}
\]

and, substituting for curl \( B \) from eq. 2(17):

\[
\nabla^2 E = \mu_0 \varepsilon_0 \frac{\partial^2 E}{\partial t^2}
\]

and similarly by applying the curl operator to eq. 2(17) and substituting for curl \( E \) from eq. 2(16) we get:

\[
\nabla^2 B = \mu_0 \varepsilon_0 \frac{\partial^2 B}{\partial t^2}
\]

These equations have the same form as the standard wave equation\(^1\). They indicate that variations of \( E \) and \( B \) travel with a velocity \( \frac{1}{\sqrt{\varepsilon_0 \mu_0}} \).

2.3.4 Boundary Conditions

The field equations of electromagnetism apply to the whole of one medium and, with a different set of constants, to a second medium. Mathematically we require a set of boundary conditions which specify how two solutions of the wave equation, each valid
on either side of the boundary, are to fit together at the boundary. So far we have only dealt with units of magnetic field, \( B \) and electric field \( E \). In addition it shall be necessary to introduce the auxiliary fields \( D \) and \( H \) which connect \( E \) and \( B \) to understand how electromagnetic waves interact with matter. If an electrostatic field is applied to a dielectric, it will become polarised. The polarisation will, if the material is isotropic, be parallel to the \( E \) field and will normally be proportional to the strength of it. A vector \( P \) can be defined within the material whose magnitude at each point is the dipole moment per unit volume there and its direction is that of the polarisation at the point. The magnitude of \( P \) at a point is obtained by averaging over a volume that is large on the atomic scale, so \( P \) is a macroscopic vector.

Now the polarisation charges will act as sources of the \( E \) field, along with other sources of charge which are present, and so should be included in the right-hand side of Maxwell's first equation, \( \nabla \cdot E = (\rho_f + \rho_{pol})/\mu_0 \) where \( \rho_{pol} \) denotes polarisation charge density and \( \rho_f \) is called the 'free charge' density; the latter comprises of all sources of charge other than \( \rho_{pol} \). \( \rho_{pol} \) may be obtained from \( P \) by letting lines of \( P \) start on negative polarisation charges and end on positive polarisation charges. By analogy with Gauss' flux law for \( E \) we can write a corresponding flux law for \( P \):

\[
\nabla \cdot P = -\rho_{pol}
\]

2(21)

The negative sign is needed because lines of \( P \) run in the opposite sense to lines of \( E \). This may now be substituted back into the equation for \( \nabla \cdot E \) to give:

\[
\nabla \cdot E = (\rho_f - \nabla \cdot P)/\mu_0
\]

2(22)

or \( \nabla \cdot (\mu_0 E + P) = \rho_f \)

2(23)

Note that as \( P \) is a macroscopic quantity, then so will be the vector \( E \) obtained from this equation. Finally, the auxiliary vector \( D = \mu_0 E + P \) may now be introduced and the first of Maxwell's macroscopic equations may be written:

\[
\nabla \cdot D = \rho_f
\]

2(24)

For the special case where the medium is isotropic and homogeneous, \( P \) is related to \( E \) by:

\[
P = \mu E
\]

2(25)
where \( \mu \) is the permittivity of the medium.

In a similar way, a magnetic field \( \mathbf{B} \) creates a magnetisation vector \( \mathbf{M} \) inside the medium and an analogous argument leads us to the equation:

\[
\nabla \times \mathbf{H} = j_r + \frac{\partial \mathbf{E}}{\partial t}
\]

2(26)

where \( j_r \) denotes currents arising from the motion of free charges. The auxiliary vector \( \mathbf{H} \) is defined by:

\[
\mathbf{H} = \frac{\mathbf{B}}{\mu_0} - \mathbf{M}
\]

2(27)

For the case of an isotropic homogeneous medium we obtain:

\[
\mathbf{M} = \chi_m \mathbf{H}
\]

2(28)

where \( \chi_m \) is a constant. Hence we can write:

\[
\mathbf{H} = \frac{\mathbf{B}}{\mu_0} - \chi_m \mathbf{H}
\]

2(29)

Therefore the constitutive relation for \( \mathbf{H} \) is:

\[
\mathbf{H} = \frac{\mathbf{B}}{\mu_0(1 + \chi_m)} = \frac{\mathbf{B}}{\mu}
\]

2(30)

where \( \mu \) is the permeability of the medium.

### 2.3.5 Propagation of Electromagnetic Waves at a Boundary

We must now consider the case when a plane wave meets a boundary between two media. If the wave falls onto a surface of a block of dielectric material, there is a partial reflection and a partial transmission of the incident energy. The incident plane wave may be written:

\[
\mathbf{E} = A \exp\{i(\omega t - \kappa r)\}
\]

2(31)
where $A$ is the amplitude, $\omega$ represents the angular frequency of the wave, $t$ the time and $\kappa r$ is the path difference between two wavefronts.

It has been shown$^{3-5}$ that the tangential components of $E$ and $H$ and the normal components of $E$ and $D$ are the same on both sides of the boundary. If the boundary between medium 1 and medium 2 is parallel to an OXY plane, we have:

$$
\begin{align*}
E_{1x} &= E_{2x} \\
H_{1x} &= H_{2x} \\
\varepsilon_1 E_{1z} &= \varepsilon_2 E_{2z} \\
\mu_1 H_{1z} &= \mu_2 H_{2z}
\end{align*}
$$

where $E_{1x}$ etc., refer to a point very near the boundary in medium 1 and $E_{2x}$ refers to a neighbouring point in medium 2. These conditions are not independent for, if the first two are satisfied, the relation between $H_{1z}$ and $H_{2z}$ follows from the fact that the Maxwell field equation 2(16):

$$
\frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} = \mu \frac{\partial H_z}{\partial t}
$$

must be satisfied in each medium. Similarly the relation between $E_{1z}$ and $E_{2z}$ is implied by the second pair of equations. Thus there are only four independent relations and we shall only use the first four as boundary conditions.

For the following discussion it is assumed that the effective value of $\varepsilon/\varepsilon_0$ for each medium is equal to $n^2$. Using this value we apply the boundary conditions. We shall choose a co-ordinate system so that the XY plane is the surface of separation and XZ is the plane of incidence. Let $\theta_1$ be the angle of incidence and the incident beam be plane polarised. The y components of the electric vectors in the incident, reflected and refracted beams may be given as shown in Fig. 2.3.5a overleaf$^2$:
Incident beam $E_{iy} = A_{iy} \exp i\{\omega t - \kappa(l_i x + m_i y + n_i z)\}$

Reflected beam $E'_{iy} = A'_{iy} \exp i\{\omega' t - \kappa'(l'_i x + m'_i y + n'_i z)\}$

Refracted beam $E_{2y} = A_{2y} \exp i\{\omega_2 t - \kappa_2(l_2 x + m_2 y + n_2 z)\}$

In these equations $A_{iy}$ is assumed to be real and positive. If the reflected or refracted beam has a phase difference of $\pi$ from the incident beam then $A'_{iy}$ or $A_{2y}$ will be real and negative respectively. A phase change of anything other than $\pi$ will be indicated by a complex value of the corresponding amplitude. Owing to the choice of axes:

$$l_i = \sin \theta_i, \quad m_i = 0 \quad \text{and} \quad n_i = -\cos \theta_i.$$  

Equation 2(32a) implies that:

$$E_{iy} + E'_{iy} = E_{2y}$$
when \( z = 0 \) for all values of \( x, y \) and \( t \). This in turn implies that the same coefficients of \( x, y \) and \( t \) must appear in all the exponentials of eqs. 2(34), 2(35) and 2(36). If we equate coefficients of \( t \) we have \( \omega_i = \omega'_i = \omega_2 \) so that the reflected and refracted beams have the same frequency as the incident beam, so from now on the suffix shall be omitted. As the reflected and incident beams are in the same medium, \( \kappa'_1 = \kappa_1 \). Finally equating coefficients of \( x \) and writing:

\[
I'_1 = \sin \theta'_1 \text{ and } l_2 = \sin \theta_2
\]

we obtain:

\[
\kappa_1 \sin \theta_1 = \kappa_2 \sin \theta_2 \text{ or } \sin \theta_1 = n_{12} \sin \theta_2.
\]

Hence electromagnetic waves obey all the experimental laws of reflection and refraction at a surface separating two isotropic media.

### 2.4 Magnitudes of Reflected and Transmitted Radiation

It is now necessary to calculate the fraction of incident energy which is reflected for different angles of incidence and planes of polarisation. We are interested in the components of the vectors resolved along some specified co-ordinate axis. The axis \( OY \) perpendicular to plane of incidence serves for all three beams and new axes \( W'_1, W'_1, \) and \( W'_2 \) in the plane of incidence and perpendicular to the plane of propagation. The positive directions of these new axes are shown in Fig. 2.4a:
They are such that an observer looking in the direction of propagation would need to make a clockwise rotation from the positive direction of \( W \) to the positive direction of \( Y \), i.e. \( W, Y \) and the direction of propagation, taken in that order, form a right-handed set of axes. The incident beam may be specified by giving:

\[
E_{1w} = A_{1w} \exp \{ \omega t - \kappa_1 (x \sin \theta_1 - z \cos \theta_1) \} \quad 2(41)
\]

\[
E_{1y} = A_{1y} \exp \{ \omega t - \kappa_1 (x \sin \theta_1 - z \cos \theta_1) \} \quad 2(42)
\]

The reflected and refracted waves are specified in a similar way. Since the direction of propagation of the reflected wave has a component in the positive direction of \( z \), \( n'_1 = + \cos \theta_1 \) (eqs. 2(35) and 2(37)). The problem is to deduce the amplitudes \( A'_{1w}, A'_{1y}, A_{2w} \) and \( A_{2y} \), when \( A_{1w} \) and \( A_{1y} \) are given. It can be shown that

\[
(\mu_1)^{1/2} H_{1w} = - (\varepsilon_1)^{1/2} E_{1w} \quad 2(43)
\]

\[
(\mu_1)^{1/2} H_{1y} = + (\varepsilon_1)^{1/2} E_{1y} \quad 2(44)
\]
and similar expressions for the other beams. The signs are the same in the corresponding expressions for $H'_{1w}, H_{2w}$ etc., because our three sets of local axes have all been made right-handed. We also have:

$$E_{ix} = - E_{1w} \cos \theta_1$$  \hspace{1cm} 2(45)

$$E'_{ix} = + E'_{1w} \cos \theta_1$$  \hspace{1cm} 2(46)

$$E_{2x} = - E_{2w} \cos \theta_1$$  \hspace{1cm} 2(47)

$$(\mu_1)^{1/2} H_{ix} = - (\mu_1)^{1/2} H_{1w} \cos \theta_1 = + (\varepsilon_1)^{1/2} E_{1y} \cos \theta_1$$  \hspace{1cm} 2(48)

$$(\mu_1)^{1/2} H'_{ix} = + (\mu_1)^{1/2} H'_{1w} \cos \theta_1 = - (\varepsilon_1)^{1/2} E'_{1y} \cos \theta_1$$  \hspace{1cm} 2(49)

$$(\mu_2)^{1/2} H_{ix} = - (\mu_2)^{1/2} H_{2w} \cos \theta_2 = + (\varepsilon_2)^{1/2} E_{2y} \cos \theta_2$$  \hspace{1cm} 2(50)

$$(\mu_1)^{1/2} H_{iy} = (\varepsilon_1)^{1/2} E_{1w}$$  \hspace{1cm} 2(51)

$$(\mu_1)^{1/2} H'_{iy} = (\varepsilon_1)^{1/2} E'_{1w}$$  \hspace{1cm} 2(52)

$$(\mu_1)^{1/2} H_{2y} = (\varepsilon_2)^{1/2} E_{2w}$$  \hspace{1cm} 2(53)

Each of these equations contains an exponential factor on either side. Since these factors are equal when $z = 0$, the boundary conditions become relations between the amplitudes. Applying the boundary condition of eq. 2(38):

$$A_{iy} + A'_{iy} = A_{2y}$$  \hspace{1cm} 2(54)

and applying the corresponding condition for $H_x$ and using eqs. 2(48), 2(49) and 2(50):

$$(\mu_2 \varepsilon_1)^{1/2} (A_{iy} - A'_{iy}) \cos \theta_1 = (\mu_1 \varepsilon_2)^{1/2} A_{2y} \cos \theta_2$$  \hspace{1cm} 2(55)

or

$$(A_{iy} - A'_{iy}) \cos \theta_1 = n_{12} A_{2y} \cos \theta_2$$  \hspace{1cm} 2(56)

since at optical frequencies, $\mu_1 = \mu_2 = \mu_0$. Similarly the condition for $E_x$ gives:
and the condition for $H_y$, using eqs. 2(51), 2(52) and 2(53) gives:

$$(\mu_z e_1)^{1/2} (A_{lw} + A'_{lw}) = (\mu_z e_2)^{1/2} A_{zw}$$  

2(58)

Once more, since $\mu_1 = \mu_2$ at optical frequencies, we have:

$$A_{lw} + A'_{lw} = n_{12} A_{zw}$$  

2(59)

Multiplying eq. 2(59) by $\cos \theta_2$, and eq. 2(57) by $n_{12}$, and subtracting, we obtain:

$$A'_{lw} = A_{lw} (n_{12} \cos \theta_1 - \cos \theta_2)/(n_{12} \cos \theta_1 + \cos \theta_2)$$  

2(60)

Using the sine refraction law (eq. 2(40)):

$$A'_{lw} = A_{lw} (\sin 2\theta_1 - \sin 2\theta_2)/(\sin 2\theta_1 + \sin 2\theta_2)$$  

2(61)

or

$$A'_{lw} = A_{lw} \tan (\theta_1 - \theta_2)/\tan (\theta_1 + \theta_2)$$  

2(62)

In a similar way, we obtain from eqs. 2(54) and 2(56):

$$A'_{ly} = - A_{ly} (n_{12} \cos \theta_2 - \cos \theta_1)/(n_{12} \cos \theta_2 + \cos \theta_1)$$  

2(63)

Using Snell's law:

$$A'_{ly} = - A_{ly} \sin (\theta_1 - \theta_2)/\sin (\theta_1 + \theta_2)$$  

2(64)

Substituting from eq. 2(60) into eq. 2(59) and simplifying:

$$A_{zw} = A_{lw} (2 \sin \theta_2 \cos \theta_1)/\{\sin (\theta_1 + \theta_2) \cos (\theta_1 - \theta_2)\}$$  

2(65)

Using eqs. 2(63) and 2(54):

$$A_{ly} = A_{ly} (2 \sin \theta_2 \cos \theta_1)/\sin (\theta_1 + \theta_2)$$  

2(66)
It can be seen that equations 2(60) to 2(66) are indeterminate for normal incidence. However eqs. 2(54) etc. can be solved directly to give:

\[ A'_{1w} = A_{1w} \frac{(n_{12} - 1)}{(n_{12} + 1)} \]  
\[ A'_{1y} = -A_{1y} \frac{(n_{12} - 1)}{(n_{12} + 1)} \]  
\[ A_{2w} = A_{1w} \frac{2}{(n_{12} + 1)} \]  
\[ A_{2y} = A_{1y} \frac{2}{(n_{12} + 1)} \]

These are known as Fresnel's reflection coefficients and give the amplitude reflectance at normal incidence.

2.5 Scattering from Rough Surfaces

We now know how electromagnetic waves interact with a plane dielectric boundary. We can give the reflectance and transmittance as a function of angle if the polarisation of the incident light and the refractive indices of each medium are known. If the boundary is not plane, however, but irregular with some height variation, then light will also be scattered into various directions. For a randomly rough surface, the scattered component will be continuously distributed in angle, whilst for a periodically rough surface it will be scattered into a number of discrete diffracted orders. For example, a sinusoidally rough surface will scatter according to the well known grating equation:

\[ \sin \theta_n = \sin \theta_i + n \frac{\lambda}{d} \]  

where \( \theta_n \) is the angle of diffraction, \( \theta_i \) is the angle of incidence, \( n = +1, +2, +3, \ldots \) is the order of diffraction, \( \lambda \) is the wavelength of light and \( d \) is the period of the grating. The positions of the diffracted orders are independent of the depth of the grating but the depth greatly affects the intensity of them.

Calculations of the amount and distribution of scattering have been made based on the scalar and vector approaches to electromagnetic boundary problems both of which can be used to predict the angular distribution of scattered light about the specular direction. The scalar theory, based on a scalar diffraction integral, has been developed.
by Davies⁶, Beckmann⁷ and Harvey⁸. The vector theory, based largely on perturbational or variational techniques or the Stratton-Chu-Silver diffraction integral⁹,¹⁰, has been developed by many authors¹¹-¹⁷. The perturbation technique was originated by Rayleigh¹⁸, extended by Rice²³, and used for the solution of both optical and radar problems.

Vector theory is more complete in that it includes the vector nature of the incident and scattered fields. With either theory, an assumption must be made about the form of the autocovariance function and other surface related parameters which are described in more detail in the succeeding sections.

2.5.1 Root-Mean-Square Roughness

Perhaps the most misunderstood surface statistical parameter is the root-mean-square (RMS) roughness, δ. It may be obtained as follows. Fig. 2.5.1a shows a cross section through a rough surface.

![Diagram of rough surface profile]

The profile is being measured along a line of length L. This line defines a mean surface level, so that equal 'areas' under the line lie above and below it. Such height variations are measured perpendicular to line L in the ±z directions. Mathematically, this mean level may be defined as:
Consider N discrete, equally spaced, points along line L. The RMS roughness \( \delta \) is defined as the square root of the mean value of the squares of the distances \( z_i \) of the points from the mean surface level. This may be expressed as:

\[
\delta = \sqrt{\frac{1}{N} \sum_{i=1}^{N} z_i^2}
\]

Hence, the mean surface level must be calculated in order to define the RMS surface roughness. If the surface is wavy (i.e. has long surface roughness spatial components) the value calculated for \( \delta \) will generally depend on what length \( L \) is used for the measurement. In addition, if the data points represent averages of height variations over small areas of the surface, the RMS value will depend on the size of the areas. For these reasons, there is no unique value for the RMS of a surface. It depends on:

- The length \( L \) of the surface profile (maximum surface spatial wavelength),
- The surface area being averaged over for each measurement (lateral resolution) and
- The distance between data points (sampling distance).

The same surface can have many different values for the RMS roughness depending on the instrument used. Going one step further, because the roughness spatial wavelengths present in a profile of length \( L \) are sometimes limited to values less than \( L/2 \) we never obtain 'true' surface roughness with information about surface spatial wavelengths from zero to infinity. The measurements are then said to be 'band limited'. If the RMS roughness is calculated from a measurement of scattered light, either total integrated scattering or angle resolved scattering, the value of the RMS is similarly band limited. It will depend on the wavelength of light used and the range of angles from which the scattered light is collected.
2.5.2 Autocovariance Function

The autocovariance function is a measure of the correlation properties of the surface roughness. It is the product of two 'copies' of the same surface profile as one is shifted relative to the other. The amount of lateral shift between the two profiles is known as the lag length. A high positive value of the autocovariance function indicates that the surface feature will repeat itself for that particular lag length. The function has units of length squared. The value for a lag length of 0, i.e. no lateral shift, is of fundamental importance because it is equal to the square of the RMS roughness of the profile. An analytical definition of an autocovariance function for a surface profile of a finite length composed of discrete data points is given below:

\[ G(l) = \frac{1}{N} \sum_{i=1}^{N-1} z_i \cdot z_{i+1} \]

where \( l \) is the lag length integer, i.e. the distance between pairs of points whose correlation is being calculated and \( z \) is the height above or below the RMS level. The numerical value of the lag length is \( \tau = l \cdot \tau_0 \), where \( \tau_0 \) is the lateral distance between adjacent data points \( z \) along the surface profile. \( N \) is the total number of data points acquired in a complete profile scan (typically up to 5000).

An example of how an autocovariance function is calculated is shown Figs. 2.5.2a and 2.5.2b.

![Fig. 2.5.2a](image-url)
Fig. 2.5.2b

Fig 2.5.2a shows a synthetic profile consisting of 64 data points separated by the sampling distance $\tau_o$. The total profile length $L$ is therefore $64 \tau_o$. To calculate the autocovariance function, there are two 'copies' of the same profile. One is shifted relative to the other by integral multiples $l$ of $\tau_o$; the products of the height values of pairs of points are then calculated and summed. For the first point $G(0)$ in the autocovariance function, however, the shift distance is zero, so that the value for each point in the profile is multiplied by itself. There are $N = 64$ data points, so there will be 64 terms in the summation. The resultant is then divided by 64 to give the value of $G(0)$. $G(0)$ is the square of the RMS roughness defined by equation 2(73). For a shift distance of $l = 1$, point 1 is multiplied by point 2, point 2 is multiplied by point 3, and so on. Finally point 63 will be multiplied by point 64. There is no point 65, so there are now only 63 terms in the summation. However, we are calculating a windowed or biased autocovariance function so the summation is again divided by 64. Fig. 2.5.2a shows the copy of the profile shifted by a distance $\tau = 14 \tau_o$ so that $l = 14$. When products of pairs of points shifted by $14 \tau_o$ are added together and divided by 64, the value of $G(t)$ shown by the arrow in Fig. 2.5.2b is obtained. Each point on the $G(\tau)$ curve corresponds to a separate summation. The longest lag length will be when point 1 is multiplied by point 64, or a lag length of $63 \tau_o$. Since this product is divided by 64, $G(\tau)$ will be a very small number, making the $G(\tau)$ versus $\tau$ curve converge to zero.
The fourier transform of the autocovariance function, the power spectral density, is important for calculating angle-resolved scattering. More complete discussions of autocovariance functions and power spectral density functions may be found in references 19 - 26.

2.5.3 Power-Spectral-Density Function

The power-spectral-density function is the frequency spectrum of the surface roughness measured in inverse length units. This function is of particular interest in the study of periodic surface profiles such as those produced by single-point diamond turning. Very-near-angle scattering (of the order of fractions of a degree or arc second from specular) is produced by long wavelength surface spatial frequencies. Well-polished glass surfaces without scratches have only low frequency components in their power-spectral-density functions. Scratched or film-covered surfaces with short spatial wavelength structure have higher-frequency components in their power-spectral-density functions.

The power-spectral-density function is actually the square of the magnitude of the fourier transform of the surface profile or the fourier transform of the autocovariance function. It is better to use the autocovariance function as considerable smoothing of random noise takes place by this operation.

2.5.4 Angle-Resolved Scattering

This section deals with the theory of angle-resolved scatter (ARS) from correlated microirregularities. This theory, in contrast to Total Integrated Scatter (TIS) measurements, takes into account the state of polarisation of the incident and scattered light. The RMS roughness, \( \delta \), is assumed to be much less than the wavelength, \( \lambda \).

Following Elson, the expression for ARS is\(^{27,12}:\)
where $P_0$ is the incident power, $dP/d\Omega$ is the scattered power per solid angle, $\theta_0$ is the angle of incidence, $\theta_s$ is the scattering angle, $\epsilon$ is the dielectric constant of the surface ($\epsilon = N^2$, where $N = n - ik$ is the complex refractive index), $g(k - k_o)$ is the surface power spectral density function, $k_o$ and $k$ are the incident and scattered wave vectors given by:

$$k_o = \frac{2\pi}{\lambda} \sin \theta_0, \quad k = \frac{2\pi}{\lambda} \sin \theta_s;$$
$$q_o = \frac{2\pi}{\lambda} \cos \theta_0, \quad q = \frac{2\pi}{\lambda} \cos \theta_s;$$

$$q' = \left[ \epsilon \left( \frac{2\pi}{\lambda} \right)^2 - k^2 \right]^{1/2}, \quad q'_o = \left[ \epsilon \left( \frac{2\pi}{\lambda} \right)^2 - k_o^2 \right]^{1/2}. \quad 2(78)$$

The general equations for $X_\theta$ and $X_\phi$ are:

$$X_\theta = \frac{(q'_o \cos \phi - k k_o \epsilon) \cos \phi'}{q'_o + q_o \epsilon} + \frac{(2\pi / \lambda) q' \sin \phi \sin \phi'}{q'_o + q_o}; \quad 2(79)$$

$$X_\phi = \frac{2\pi}{\lambda} \left[ \frac{q'_o \sin \phi \cos \phi'}{q'_o + q_o \epsilon} - \frac{(2\pi / \lambda) \cos \phi \sin \phi'}{q'_o + q_o} \right]. \quad 2(80)$$

Here $\phi$ is the azimuthal scattering angle and $\phi'$ is the angle of the incident electric field vector measured relative to the plane of incidence. A schematic diagram showing the notation for the ARS formula is given in Fig. 2.5.4a overleaf.
For scattering in the plane of incidence the general equations become:

$$
\chi_\theta = \frac{(q \phi' - k e) \cos \phi'}{q \phi' + q e}, \quad \chi_\phi = \frac{2\pi}{\lambda} \frac{q \sin \phi'}{q \phi' + q e}
$$

which give p-polarised incident and scattered light when $\phi' = 0$ and s-polarised incident and scattered light when $\phi' = \pi/2$. These equations predict no s-polarised scattered light for p-polarised incident light and vice versa.

The above expressions assume that the surface is covered with a single opaque film whose optical constants are known. If there are multilayers, the expressions become more complicated. To gain a better understanding of the meaning of the terms contained in equation 2(75) it is necessary to look at different parts of the expression. The equation itself may be divided into two parts, the first, the optical factor, depends upon the intrinsic properties of the sample such as dielectric constant, refractive index and the polarisation state of the input beam. The second part of this equation depends upon the surface microirregularities, the term $g(k - k_0)$ or the power spectral distribution function. This may be called the surface factor.

The above equations predict that, as far as the optical factor is concerned, the scattered power is inversely proportional to the fourth power of the wavelength and is a function of the cosine of the angle of incidence and the cosine squared of the scattering angle. For s-polarised incident and scattered light in the plane of incidence and a constant wavelength, the optical factor changes very slowly with angle of
scattering out to angles of about 50°, then shows the characteristic $\cos^2$ dependence\textsuperscript{29}. The expression is insensitive to the optical constants of the material\textsuperscript{29} but does depend on the state of polarisation of the incident beam. As the RMS roughness is assumed to be much less than the wavelength, it follows that the state of polarisation of the incident light should be preserved, and there should be no conversion of the state of polarisation in the scattered light or a change to unpolarised light. The only way for a change to occur is if multiple scattering were to take place and as it is assumed that the surface roughness is a lot less than the wavelength of the incident radiation, this is considered to be unlikely.

For illustrative purposes only one form of the vector scattering theory has been given. Other papers have been published giving different forms of vector scattering theories arrive at similar expressions for the ARS given in terms of an optical factor and surface factor\textsuperscript{11,14,43,47,48,80-82}.

### 2.6 Bulk Scattering

Finally, because the succeeding chapters are primarily interested in scatter in transmission, a few words must be said on the importance of scatter within the bulk of the sample under investigation.

The theory for bulk scattering is separated conveniently into three regions: a) the scattering particle or inhomogeneity is much smaller than the wavelength of light; b) the two are similar in magnitude and c) the inhomogeneity is a lot greater than the wavelength of light. It is convenient to define a size parameter, $X$, where for spherical particles:

$$X = 2\pi N a/\lambda = N a k$$

where $a$ is the geometrical radius of the particle, $\lambda$ the wavelength of light, $k = 2\pi/\lambda$ (the wave vector) and $N$ is the ratio of the refractive index of the particle to that of the surrounding medium. Polar plots of the scattering patterns generated by the different classes of sizes for non-absorbing particles are shown below in Fig. 2.6a. In the Rayleigh region, forward and backscatter are the same and decrease as $X^6$ or $a^6$. This very strong size dependence ensures that even if there are many small inhomogeneities, particulates or voids in an optical material, they probably will not affect its optical
performance for wavelengths large compared to the particle size. In the diagram d represents the diameter of the scattering particle.

![Diagram showing Rayleigh and Mie scattering](image)

**Fig. 2.6a**

In the Rayleigh region, the shape of the particle or inhomogeneity has little affect on its scattering behaviour. However as the particle size becomes comparable to the incident wavelength its geometrical shape becomes important. As the particle size increases relative to the wavelength, strong forward scattering develops. Thus, forward scattering, which is the important parameter affecting optical resolution, is rising much more rapidly than total scatter in this region. Nevertheless, it is not increasing as rapidly as it was in the Rayleigh region, as shown for spherical particles in Fig. 2.6b. The average growth is slightly greater than $X^4$ as compared to $X^6$ for $X << 1$. Fig. 2.6b gives the percentage of the incident radiation which is scattered in the forward direction by a single particle.

![Graph showing forward scattering](image)

**Fig. 2.6b**
In the Mie region, the forward scattering values are large enough so that only a very few such defects may be allowed. For example, the signal intensity for a 15th magnitude star is compared with scatter from a particle illuminated by a 0 magnitude star in Fig. 2.6b. Large diameter defects are not allowed in such applications. There is a fine structure (not shown) on the forward scattering curve in the Mie region caused by resonances between the diffracted and refracted light through a transparent particle, so even stronger restrictions may apply to some discrete particle sizes.

2.7 A Review of Scattering in Laser Components

The 1970's and 1980's generated considerable concern over scatter in optical systems. Although it was often recognised in advance that low scatter optics were required for a given application, the specifications were usually either non existent or inappropriate. The earliest, most available and cheapest scatter measurement was the total integrated scatter (TIS) measurement. Until the mid 1980's most of the specifications written to handle scatter concerns were either TIS (given without either angle or frequency limits) or RMS roughness found from some sort of profile data. Surface roughness was often specified to control scatter, even though it was recognised that it would be difficult, futile and sometimes impossible to attempt to relate the roughness parameter(s) to actual component scatter.

Surface characteristics by analysis of scattered light is too large a subject to be adequately covered in this review section alone. Thus, only a few of the many papers published in this field will be highlighted and the interested reader is encouraged to consult the references contained within these works. This does not in any way endorse these papers in preference to any other but is intended only to accentuate the broad range of measurements that examination of scattered light from a surface can yield.

Several experimental investigations of the relation between surface roughness of machined metal surfaces or ground glass surfaces and the specular or diffuse reflectance had been reported prior to 196134-39 although an adequate and experimentally verified theory relating these properties had yet to be given. Then Bennett and Porteus40 reported an expression relating the roughness of a plane surface to its specular reflectance at normal incidence. The expressions are valid when the RMS roughness is small compared to the wavelength of light. The expression was based on the statistical treatment of the reflection of electromagnetic radiation from a rough surface derived by Davies6. Although this theory was developed in connection
with the scattering of radar waves from rough water surfaces, it is equally valid in the optical regime. The theory was slightly modified to give the expression:

\[ R_s = R_o \ e^{- \frac{4 \pi \sigma}{\lambda^2}} \]  

where \( R_s \) is the specular reflectance of the rough surface and \( R_o \) that of a perfectly smooth surface of the same material. Other expressions were also derived to take into account diffuse reflectance. This work was substantiated by Depew and Weir\(^4\) a decade later who used these expressions to compare the reflectance measurements with Talyserf readings of the surfaces of several samples of aluminium, mild steel and tool steel. The results by the two techniques were found to be generally comparable in spite of the wide range of roughness values.

The following year Hensler presented results from experiments performed on fused polycrystalline aluminium oxide surfaces using reflected 633 nm light\(^4\). It was shown that the wavelength and angular dependencies of the specular intensity can be understood in terms of optical scattering theory in the Kirchoff approximation for a surface with a gaussian roughness distribution\(^7\). An empirical relationship was found to exist between the mean surface grain size as was determined by microscopic observation using the line intercept method and the RMS surface roughness. These results formed the basis of an optical technique for rapidly estimating the mean surface grain size on high alumina substrates used in the microelectronics industry.

Periodic roughness produced by diamond-turned optics was examined by Church and Zavada in 1975\(^4\)\(^3\). The reason for this was that these surfaces were expected to provide the most conspicuous signature of machined optical surfaces. Expressions were given for the interpretation of data from differential-scatter, TIS, reflectometry and ellipsometric measurements in the limit of a highly conducting surface. The authors also mention how each technique is limited by its scattering geometry.

Using the formalisms developed in the previous paper for smooth sinusoidal gratings Stover was able to generate the spectral density function (SDF) from optical scattering measurements\(^4\)\(^4\). Interferometric and scattering results were compared for a rough (350 Å) machined surface and it was found that various steps in the manufacturing process could be distinguished. For instance, if the feed rate/rotation of a machine is known, this part of the roughness can be picked out from the SDF, and improvements can be studied without worrying about changes in other roughness sources such as random surface vibration or periodic spindle movement.

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The prediction of the angular distribution of scattered light from optical surfaces as a function of wavelength, optical constants of the material and spectral density function was made by Elson and Bennett in a paper published in 1979\textsuperscript{29}. They used a vector scattering theory which was composed of two parts: 1) an optical factor which depended on the wavelength, optical constants of the scattering surface and the angles of incidence and scattering and 2) a surface factor which depended only on the statistical properties of the surface. It was found that the shapes of the curves of the calculated and measuring scattering curves were in reasonable agreement, but the magnitudes were not. They go on to say that the reason for this was not clear as the RMS roughness of the samples tested calculated from TIS measurements and measured directly using a profilometer were in excellent agreement.

Scatter from multilayer optical coatings was considered by Carniglia\textsuperscript{45} using a new model which assumed that the roughness of the top surface of a given layer was due to the roughness introduced by the previously deposited layers and due to the variations in thickness of the layer itself. This model was compared to two existing models: one which assumed that the surfaces of the layers are completely uncorrelated and another which assumed that all the surfaces are identical to that of the substrate. The models were all compared with each other to three different designs: a single low index layer, a laser reflector and a narrowband filter. It was found that in the case of the single layer, the different models lead to different levels of scattering, especially with respect to diffuse reflected scatter. For the laser reflector and band pass filter, the general features are similar for several of the models, namely the scattering is high if the field penetrates the multilayer and low if it does not. The case of identical roughness is distinctly different in this regard. The difference between the additive surface roughness model and the uncorrelated surface roughness model is that they predict different levels of scattering over the rejection bands relative to the peak scattering levels. The author went on to mention that these differences should be measurable by experiment.

Scatter due to contamination of the surfaces of mirrors was addressed in a paper by Williams and Lockie in the same year\textsuperscript{46}. Here, they measured the BRDF of four separate mirrors and were able to demonstrate how dust, hydrocarbon oil, acrylic and peelable coatings degrade a low scatter mirror surface over a period of time. (BRDF stands for Bi-directional Scatter Distribution Function and is a differential function dependent on the incident wavelength, direction, scatter direction and polarisation state of the incident and scattered light. In practice, it is simply the ratio of the average scattered radiance (W/cm\(^2\) steradian) to average surface irradiance (W/cm\(^2\)). Results
taken in transmission are referred to as BTDF measurements; this is explained in more detail in sections 3.1.1 and 3.1.2). It was found that dust degrades the BRDF readings by the largest factor at angles of incidence greater than 40° and that films degrade BRDF at angles of incidence less than 10°. Although these results were generalisations it was mentioned that by measuring the surface BRDF gave a quantitative value for surface scatter whatever the cause of contamination and it was suggested that BRDF measurement can be used to monitor contamination levels in clean rooms and vacuum chambers.

Further work on multilayer optics were performed by Elson et al in 1980 using 633 nm incident radiation\textsuperscript{28}. The workers used a 24-layer dielectric mirror and compared the angular scatter to a vector scattering theory proposed earlier by Elson\textsuperscript{47}. Three different multilayer stack models were used to incorporate possible effects of different degrees of correlation between interfaces in the stack. This was necessary as only roughness height measurements were taken from the top surface. Results of the scattering curves for angles of incidence of 0°-50° showed that the measured data matched the correlated and partially correlated theories quite well in the region 30° or more from specular. The agreement was less satisfactory in regions toward specular and two possible explanations were given for this: 1) Mie scattering from centres such as particulates, which could have contributed primarily to the near specular directions and 2) there was insufficient data to characterise accurately the autocorrelation and cross-correlation of the stack interfaces. It was also noted that the calculated curves largely showed an overall decrease in scattering when going from 60° to 70° incidence. However, the measured curve seemed to increase slightly and it was suggested that this was due to increased substrate scattering. This paper was among the first to establish a relationship between scattering and surface/interface roughness for multilayer components with a host of papers being published in this area since then, (see for instance references 48-50).

The first reported measurements primarily concerned with BTDF data on dielectrics were those of Dereniak et al\textsuperscript{31}. In this paper the authors stipulate the measurement technique that was employed determined the combined surface and bulk scattering properties of the transmissive optical component and not the inherent scattering properties of the optical material. Results are presented for three different wavelengths: 633 nm, 3.39 \(\mu\)m and 10.6 \(\mu\)m. From the samples studied (three CVD ZnSe samples of different thickness: 6 mm, 9 mm and 25 mm), it was shown that surface scatter mechanisms dominate over bulk scatter mechanisms at shorter wavelengths, however this dominance was less pronounced at the larger wavelengths.
It was the authors contention that the primary scattering at 633 nm was due to microirregularities of the surface, and at 10.6 μm it was due to particulates on the surface. A simple wavelength scaling law was also presented but was shown to be inadequate to explain the wavelength dependence of these BTDF measurements, as it was developed for single surface scattering.

These same wavelengths were also used for examination of a single sample by Wang and Wolfe - a well-polished fused silica substrate that had a 70 nm thick evaporated coat of aluminium on its surface. By analysing data taken at different angles of incidence and polarisation, it was found that only the one-dimensional vector theory adequately fitted the data. No explanation was given for this and the authors conclude that a great deal more study needs to be done especially at other wavelengths and at angles closer to specular if a clearer understanding is to be arrived at.

Work describing the performance of a particular scatterometer was presented by Stover et al in 1984. The paper describes how the Montana State University scatterometer was used to measure the power spectral density (PSD) on centre-cut precision-machined flats. It was shown that the calculated PSD's were independent of incident angle and source polarisation, as expected. However, this relationship broke down when the sample began to be too rough. What was also investigated was that the bandwidth of the scatterometer was compared to that of a TIS instrument. Comparisons of the bandwidth-limited values of the RMS roughness between TIS measurements and differential scattering calculations were not conclusive. This paper demonstrated the bandwidth nature of commonly used surface statistics and the need to specify high and low frequency limits when making roughness measurements in the spatial regime.

A further scatterometer was described by the same author in collaboration with others. Although the scatterometer design will not be described here, it will be outlined in a later section. Results presented include the transmissive scatter at 633 nm from a high scatter Pyrex window and a precision-machined copper mirror used in a CO₂ laser system. Although these results were only preliminary, this instrument formed the basis for many other results that were presented over the years.

More TIS results were presented by Mattsson on a host of different materials with RMS roughness ranging from 1 Å to 150 Å. The equipment was built to the proposed ASTM, (American Society for Testing and Materials), standard for surface characterisation but which also had the option to perform TIS measurements at an
angle of incidence of $45^\circ$ and near-angle scatter measurements down to $1.3^\circ$. The apparatus was sensitive to scatter levels down to $\sim 10^{-6}$ of the incident intensity which meant measurements could be made down to the sub-Å region. Several results were reported for multilayer coatings which included the demonstration of a single 1100 Å thick aluminium film with a roughness of only around 3 Å.

One of the few papers dealing specifically with low angle scatter was that published by Ricks$^{37}$ who presented scatter data for a diamond-turned copper mirror and a conventionally polished aluminium coated mirror. The measured angles were from about one degree down to nearly $10^{-4}$ of a degree. The measured data was compared to two theories: the scalar scattering theory and the vector scattering theory. It was found that there was fair agreement between the predicted and measured but the agreement was not as good as would be desired and also that the vector and scalar scattering theories gave the same results.

In order to establish that different laboratories were conforming to standard procedures for scatter measurement and that such measurements were reproducible from one laboratory to the next a series of round-robin experiments were conducted in 1988 of a set of four master samples$^{38}$. The BRDF of the samples, (consisting of an aluminium disk with Desothane Aliphatic untinted white Polyurethane enamel for a diffuse white surface, an aluminium disk coated with gunship black Polyurethane enamel for a diffuse black surface, a bare molybdenum mirror with a surface roughness of about 45 Å RMS and an aluminised SiO coated glass mirror with a surface roughness of about 7 Å RMS), differed from different laboratories by nearly an order of magnitude and the paper highlighted the need for a standard test procedure. The author also went on to make a list of all the many considerations which must go into this type of effort and these are briefly: definitions, instrumentation, measurement limitations, measurement procedures, data format, surface model extrapolations, reference standards and common errors.

Experimental results of the scattering from thin films prepared by Ion Assisted Deposition (IAD) and ion Plating (IP) were presented by Amra in 1989$^{59}$. The coating materials that came under scrutiny in this study were TiO$_2$ and SiO$_2$ prepared by IAD and Ta$_2$O$_5$ and SiO$_2$ obtained by IP. The data suggested that in most cases measurement of the substrate was sufficient to predict scattering from any coating with a high accuracy. However, at very low scattering levels, (less than $10^{-6}$ of the incident light), it was stated that the prediction was limited by the presence of local defects in the coating.
Calculations performed to relate the stylus profile of a one-dimensionally rough surface to the angular distribution of the light scattered by such a surface was presented by Marx and Vorburger in 1990. This was approached in two ways; in the direct problem, the angular distribution of the scattered light calculated from the profile was shown to agree with the measured one, in the inverse problem, the RMS roughness and autocorrelation function were found by a least-squares fit to the measured angular distribution. The surfaces used in this study were a set of nine hand lapped stainless steel flats. They were first ball milled, then filed, and finally hand lapped. It was found that for the smoother surfaces (RMS < 0.22 μm), the RMS roughness was mostly determined by the ratio between the power of the specular beam and the total power of the scattered light; the computed values were proportional to those calculated directly from the stylus profiles. The values of the parameters obtained by the least-squares fit were affected by a variety of errors and agreed only with those obtained from the stylus profile. The values of the RMS roughness for the rougher surfaces could not be reliably determined by the least-squares fit procedure applied to the angular distribution for the diffuse scattering.

Another paper which looked primarily at near angle scatter was presented by Gu and Dummer. The measurements involved the statistical analysis of speckle data to separate the light energy into reflected and scattered components. In the investigation, measurements were made of small angle scattering of a vacuum-deposited aluminium mirror at normal incidence at 10.6 μm and of an IR filter at normal incidence at 10.6 μm. By employing Ricean statistics of the amplitude distribution for coherent glint with an additive scattered component of speckles, the scattered portion was partitioned from the total reflected signal at both wavelengths. Although the results were preliminary they demonstrated that useful measurements could be taken by a method that had heretofore not been seen, i.e. by using a monostatic laser interferometric reflectometer which was used to separate coherent light from scatter.

A paper that dealt with wavelength scaling, (which is a subject that was investigated as part of the research programme at Loughborough), was presented by Vernold and Harvey in 1991. They looked at the scatter from bare polished hot isostatic-pressed (HIP) beryllium. It had already been reported that bare polished HIP beryllium and chemical vapour deposited (CVD) silicon carbide mirrors exhibited higher scatter than would be expected based on mirror surface roughness data. In this particular study, four different wavelengths, (0.325 μm, 0.441 μm, 0.5145 μm and 0.6328 μm), were used to study bare HIP beryllium which had grain sizes on the order of 10 μm to 15 μm. By plotting the PSD against frequency, excellent agreement was obtained in
that all the curves were almost all superimposed on one another. However, when the 
wavelengths 0.6328 μm, 3.37 μm and 10.6 μm were used the curves showed little 
agreement. These results proved that the anomalous scattering was wavelength 
dependent, with the magnitude of the effect increasing as the test wavelength was 
increased. Therefore, other non-topographic scattering effects were responsible, and 
UV or visible scatter measurements could not be used in conjunction with scattering 
models to predict how this type of sample would scatter in the IR. However, other 
published data have confirmed the validity of such an approach with other materials66- 
69. A further paper presented by the same initial author showed that this non­

topographic scatter could be eliminated by coating the substrates with a thin layer of 
aluminium70. Both HIP beryllium and CVD silicon carbide scattered topographically 
and exhibited wavelength scaling characteristics. The reason why the samples did not 
initially wavelength scale was that it was found that the samples had polarisation 
dependent reflectivity characteristics. By not allowing the incident light to make 
contact with the substrate material, the anomalous scattering problem was largely 
solved.

Scattering from thin films was returned to in a paper by Kassam et a171. A theoretical 
model was presented that described the scattering from the actual volume of thin films, 
particularly those that exhibited typical columnar structures. The model was based on 
a first-order perturbation theory that concerned the fluctuation of the dielectric 
permittivity in the thin film. The minima of intensity that occurred at certain angles of 
the measured angle-dependent scattering of thicker films as a result of interference 
effects were found to be in sufficient accordance with the theoretical predictions from 
tests done on PbF2 films. It was also shown from TIS experiments that the mean 
lateral extension of the columns evolved approximately with the square root of the film 
thickness.

A further paper dealing with characterising the surface of a material by analysis of its 
scattering properties was presented by Jacobson et al in 199272. Angle-Resolved 
scattering was not the only method employed, however. The ARS measurements were 
compared with measurements that were obtained on a TIS instrument, a WYKO 
TOPO-2D profiler and a Talystep mechanical contact profiler. By taking the respective 
bandwidth of each instrument into account it was found that reasonable agreement 
between each instrument was achieved for all the samples tested, (which included 
polished molybdenum, polished copper, polished silicon and electroless nickel).
2.7.1 Summary

The above quoted works are just a small sample of the vast amount of literature that is available on how useful scatter can be in investigating the topographical nature of components. Analysing scatter has proved to be a useful surface diagnostic technique that is both rapid and non contact. A sample requires no special preparation, (e.g. etching or overcoating with a conducting film), and therefore is not destroyed as it is in some techniques such as when scanning electron microscopy and transmission electron microscopy are used. Mechanical profilers can sometimes deform a surface if the surface is too soft or if the stylus loading is too large. It is limited to examination of the top surface of a sample and is relatively slow to set up for examining smooth surfaces. In addition the stylus response can be non linear.

2.8 Measurement of Scatter

Measurement of scattered light as a function of angle has proved to be an invaluable method of determining the optical quality of materials. The work in this thesis revolves around the construction and use of a scatterometer to measure near angle forward scatter (i.e. less than 2° from specular). Before a detailed description of the instrument is discussed, it is necessary to look at some of the scatterometers developed elsewhere and to highlight those design features that have been incorporated into the Loughborough instrument.

2.8.1 E.I. du Pont de Nemours Company Inc. High Resolution Instrument

The basic layout of the instrument\textsuperscript{73} is shown in Fig. 2.8.1a. A capillary mercury arc source A is operated from a transformer connected to a voltage regulator. Light from source A, after passing through condenser D and a monochromatic filter combination E, illuminates the narrow slit I. The light emerging from slit I is collected by lens K and brought to a focus on the arc on which travels the receiving slit N and the phototube Q. The phototube input is supplied by a high-voltage regulated power supply. The phototube output goes to a special high-impedance strip chart recorder.

Unwanted diffraction originating at the slit I is removed from the field by the lens K which forms an image of the slit I on the arc described by the receiving slit N.
The sample is located at M on the optic axis above the centre of the turntable T. Light scattered by the sample falls on the receiving elements N and Q which, by rotation of the turntable, traverse arcs centred at M. The turntable is driven by a synchronous motor S through a worm gear W. A cam V, fastened to the drive shaft, periodically closes a microswitch U activating an auxiliary pen on a strip chart recorder indicating degrees or tenths of degree as required.
2.8.2 Low Angle Scatter Instrument

The Low Angle Scatter Instrument (LASI), constructed at Montana State University (MSU) is capable of scatter measurements down to 0.01° from specular for high scatter samples and below 0.1° for most samples\textsuperscript{44}. Fig. 2.8.2a shows the LASI configuration. The entire arrangement is mounted on a low vibration steel table. A continuous wave (cw) laser is chopped at 30 Hz and directed through a spatial filter/output lens combination which focuses the beam about one metre from the lens. The detector is mounted on an xyz translation stage which is located near the focused beam and held in place by a magnetic mount. The z-axis is adjusted manually but the x- and y-axes are motor driven. The detector assembly consists of a removable aperture, a removable #4 neutral density filter, a bandpass filter at the laser wavelength, a silica diffuser (to defocus the light) and a 5.6 mm diameter UV extended silicon photodiode. The detector electronics include a JFET op-amp (integral with the photodiode), a 100x programmable gain amplifier controlled by the computer and a two-pole low-pass filter designed to convert the 30 Hz square-wave signal to a 30 Hz sine wave. This signal and one from the reference detector (located near the spatial filter) are sent to the system electronics package and combined in a lock-in amplifier to produce an output voltage proportional to the peak-to-valley light signal observed by the detector. This voltage is normalised by the RMS value of the reference signal to remove laser power variations. The log of this ratio (1V/decade) is sampled by a 12-bit A/D converter in the computer.

![Diagram of LASI configuration](image)

Fig. 2.8.2a
2.8.3 Complete Angle Scatter Instrument

The Complete Angle Scatter Instrument (CASI), built at Toomay, Mathis & Associates Inc., is capable of continuous BSDF measurements from near specular to nearly 90° from normal and uses two different probe beam wavelengths - 10.6 µm and 0.633 µm. It possesses the ability to control, display and analyze scatter measurements taken at a fixed detector angle while the sample is xy raster scanned through a circular or rectangular pattern. Fig. 2.8.3a shows a block diagram of the major system components.

The laser beams are chopped, spatially filtered and collimated. The diameter of the collimated beam may be varied by changing the focal length of the first lens. In addition to blocking stray radiation, the spatial filter serves to convert small angular deviations of the beam to power deviations. The power in the collimated beam is sampled by the reference detector and may be reduced, under computer control, by a neutral density filter. Turning mirrors bring the beam onto an off axis parabolic mirror, which refocuses the beam at the second spatial filter. This spatial filter acts as a near point source for the final mirror. The extra turning mirror between the parabolic mirror and the spatial filter allows the input beam to the parabolic mirror to be adjusted parallel to the output beam of the spatial filter. These three components are mounted on a translation stage that moves parallel to the input and output beams so that the focused spot can be moved without repositioning any of the components. This allows easy focusing of the beam on the detector observation path so that curved samples can be accommodated. A spherical focusing mirror can be used but an off axis parabolic mirror will reduce aberrations. Scatter from this mirror plays an important role in determining the instrumental signature.

The angle of incidence is adjusted at the sample mount. Several degrees of freedom are available. In addition to the raster xy motions, the sample may be translated along and rotated around its normal. It can also be tilted forward (or back) so that the plane of incidence is no longer horizontal. A tilt plate may be inserted, and held like the sample, to allow additional alignment freedom. Sample sizes up to seven inches in diameter may be rastered through the beam.
The detector head is shown in Fig. 2.8.3b. It consists of a scatter aperture, a lens, a bandpass filter, a spatial filter and the detector head. The scatter aperture together with its distance from the sample defines the solid angle of the detector, $\theta_s$. The lens images the illuminated sample spot onto the spatial filter and thus restricts the detector field of view which helps to reduce the signature $\lambda_{57}$. Alignment of these two components is accomplished by mounting the detector head on a stage which tilts the head in both azimuth and elevation. The detector aperture is moved through angles under motor control and can also be moved vertically to centre the aperture on the input beam.

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**Fig. 2.8.3a**

**Fig. 2.8.3b**
The detectors used are Si in the visible and HgCdTe at 10.6 μm. All of the detectors are operated as photovoltaic current sources. The first gain stage is a transconductance amplifier with programmable gain. This is followed by a bandpass filter and a programmable gain lock-in amplifier. An integrating analog to digital converter feeds the scatter and reference signals to the computer where the ratio is taken and stored. BSDF can be measured over 14 orders of magnitude. The Si detector head is linear over nine to ten orders of magnitude and additional orders are achieved through the use of interchangeable apertures and absorption filtering of the beam power. The equivalent electronic noise floor is a BSDF of about $10^{-7}$ sr$^{-1}$ with a 1 cm diameter aperture and a 5 mW HeNe incident beam. Scatter from dust in normal air limits operation to about $10^{-6}$ sr$^{-1}$ under these conditions.

The computer controls the motorised stages, amplifier gains and the analog to digital converter. The instrument software is driven through menus with default settings. After selecting the manual operation mode, the computer displays the detector power while the operator either commands the stages to move or manually adjusts the sample or detector. After the set up procedure has been completed the instrument searches for the centre of the focused beam using an automatic centre function. Then the operator directs a measurement scan to begin.

2.8.4 Variable Angle Scatter Instrument

This scatterometer built at the Wright Patterson Air Force Base in the United States was primarily built to investigate scatter in the mirrors used in ring laser gyros. Minimising retroreflection, or retroscatter, is important to the correct operation of optical gyros. These devices are ring lasers with cavity modes propagating in the clockwise and anticlockwise directions simultaneously. If the laser is rotated during operation, the two modes are frequency shifted in opposite directions. One Doppler shifts up and the other down. Rotation is detected by combining the two beams outside the laser and watching for motion of the resulting fringe pattern. The resolution with which rotation can be monitored is controlled by the degree to which the frequencies of the two counter propagating beams are separated. Retroscatter from the gyro mirrors acts to mix the two beams in the laser cavity and thus limit resolution.

The scatterometer itself consists of a HeNe laser light source, beam steering optics, a mirror/substrate mount and positioning stepper motors all mounted on a rotating table. The measuring instrument is a photomultiplier tube detector modified to operate as a
sensitive radiometer. This equipment has been reported to have the sensitivity of ten parts per billion. Fig. 2.8.4a is a plan view of the measuring arrangement. The Y axis comes out of the figure perpendicular to the plane of the diagram at the R-X intersection. Fig. 2.8.4b shows a schematic of the laser and beam conditioning optics. The beam splitter sends part of the beam to a power monitor to track laser power fluctuations. Output of the power monitor is fed to a computer to normalise each data point so that laser fluctuations are not a source of error in the data. The beam is collimated and is incident normal to the sample under study. Finally Fig. 2.8.4c is a diagram of the detector optics. The aperture mirror is used for precise positioning of the part being measured while eliminating scattered light from other sources.
2.8.5 MSU Differential Scatterometer

The Montana State University (MSU) scatterometer\textsuperscript{78} was designed and built in 1982. It is capable of making plane of incidence scatter measurements from any place on a five inch diameter mirror. Most of the design considerations are similar to those found in the more sophisticated LLNL system described in the next section. A block diagram of the MSU system is shown in Fig. 2.8.5a:
The light source is a linearly polarised 5 mW HeNe laser with an attached spatial filter and collimating telescope. A photo-transistor measures scattered light in the telescope to provide a normalisation signal proportional to laser intensity. A PDP11 computer monitors this signal and uses it to normalise out data variations due to slow (∼5%) intensity variations in the laser beam. Vertical polarisation (s-polarisation) is the normal mode of operation. Variations can be achieved by rotating the laser. The beam comes to a focus in the detector observation path. This arrangement places the detector in what is called the far field and creates the fortunate circumstance that each spatial frequency component, making up the surface, scatters (or diffracts) light into just one location in the detector observation hemisphere. In other words, there is a one to one relationship between roughness component frequency and scatter position. Focusing the beam allows the detector to measure scatter very close to the specular direction (which may be considered the zero frequency component). The laser position has to be slightly adjustable in height and angle to assure that the laser beam and detector path are in the same plane and that the laser beam centre intersects the xyz axis origin. The system can be easily expanded to accommodate other wavelength laser sources.

The circular movement of the detector defines the xz plane. Rotation of the entire sample mount about the y axis determines the angle of incidence. The sample mount must orient the reflecting surface of the mirror perpendicular to the xz plane and locate the surface so that it contains the y axis. This assures that the plane of incidence and the detector motion path are identical. There are a total of seven degrees of freedom in
the sample mount. The sample alignment procedure is simple and can be performed by watching the reflected laser light. The two 360° rotation axes need an accuracy of about 0.1°. Accuracy of the linear slides and tilt axes is not critical.

A photomultiplier tube is used for the detector. An RCA #8852 was chosen as having a relatively high sensitivity at 633 nm and a large maximum anode current (1 mA). The photo-cathode observes the light scatter signal through frosted glass (to reduce photo-cathode saturation), a band pass filter at 633 nm (to reduce room light noise) and an adjustable aperture (to limit total signal and allow some choice of the effective spatial frequency bandwidth observed by the detector at any given detector position).

Detector motion is achieved by means of a rotary table, centred about the y-axis, and driven by a stepper motor under computer control. Detector position for a given data point is determined by counting the number of steps the detector has moved through. Data can be taken about every 0.1°. The detector moves through 90° in about 15 minutes at a distance of about 40 cm from the mirror. Individual steps amount to only 0.001° so the system may be used with a small aperture over short segments to obtain a detailed scatter distribution. The region very near the specular beam may be measured in this manner. Data compression is achieved by using a log-linear feedback loop between the PMT output signal and the PMT high voltage bias. This type of circuit is fairly standard procedure\textsuperscript{11,80}. In this case a low pass active filter (approximately 1000 Hz) and a gain stage with an adjustable DC offset control is used to remove the room light signal with the laser off. The laser beam is not chopped. The specular beam is measured through a neutral density filter. The scattered light signal can also be measured with the filter in place but there is an unacceptable loss of signal for scatter at high angles for most samples.

2.8.6 LLNL Differential Scatterometer

The overall function of this system\textsuperscript{79} is very similar to that of the MSU system, with two exceptions. Firstly, the detector is capable of computer controlled motion throughout the entire observation sphere and secondly, the sample mount will allow measurement of any point on the surface of mirrors up to 14 inches in diameter. The entire scatterometer is located on a shock mounted steel table and enclosed in a cabinet. Fig. 2.8.6a shows a schematic of the apparatus. Note the addition of the a axis for detector motion out of the plane of incidence.
The source is a linearly polarised 15 mW HeNe laser with a polarisation rotator. An intensity signal is provided for the computer and the same focusing arrangement is used as that on the MSU instrument.

The sample mount is positioned on a large (approximately 70 cm diameter) rotary bearing, $\theta_o$, to provide angle of incidence control. As before, xyz slide and tilt axes are provided. Circular mirrors are held in place with a 14 inch scroll chuck. Other shapes are clamped to the face plate.

A photomultiplier is again used for the detector with a similar set of filters. Data compression is achieved by a similar feedback circuit to the high voltage power supply. The only major difference in signal processing is the use of a chopped beam and appropriate electronics to obtain a better signal to noise ratio before inputting to the computer.

The $\theta$, detector motion is achieved by the use of a circular rotary bearing located just outside the sample mount bearing. A second bearing located in the plane of incidence provides the $\alpha$ motion. Both motions are driven by stepper motors under computer control. Two axis control of the detector position over an operator determined path requires considerably more control electronics than that needed for the MSU system.

Fig. 2.8.6a
2.8.7 Summary

The foregoing represents a comprehensive but by no means exhaustive review of typical scatterometer designs over the past four decades. From the first scatterometer apparatus designed primarily to look at low to high angle scatter (the Du Pont instrument) it was recognised that when looking at a range of light intensities that could vary by a factor of $10^8$ or more special consideration had to be given to the detector response, data compression and instrumental signature, i.e. that reading given by the instrument when no sample was present.

The Du Pont instrument uses a combination of slits in front of the detector and neutral density filters in front of the mercury light source which allows the beam intensity to be varied from unity to about $10^{-6}$ of its initial intensity. However, this is very cumbersome and takes a lot of time for one run to be completed and the detector response is also quite slow.

The LASI system represents a considerable improvement in that it relies on a computer for the control and operation of the scanning runs. Because all data is also fed to the computer it is a relatively simple matter to process the data to obtain statistics on the surface profile of the sample. Data is presented in easily assimilated graphical form instead of a chart recorder and by having the sample beam, this time a chopped laser, it is possible to obtain a lower figure for the instrumental signature than the du Pont instrument. The LASI system is also able to operate at lower angles, down to 0.01° for high scatter samples.

CASI represents the first commercially available scatterometer and the first to utilise two different probe beam wavelengths. A comprehensive software package enables many functions to be performed on the data, for instance, the surface statistics package allows the PSD (power spectral density) to be calculated and plotted over the spatial frequency for scatter from smooth reflective surfaces. RMS slope and surface roughness can be plotted over selected spatial frequency ranges and calculated total integrated scatter (CTIS) is available from reflective surfaces and diffuse reflectance or transmittance from diffuse materials. This, however, is not a cheap instrument; the basic instrument costing £70,000 rising to £100,000 for a complete system.

It may seem inappropriate that this review should also include some scatterometers that have been primarily designed for looking at scatter in reflection mode only. However their inclusion is justified in that the great majority of scatterometers built
today are done so with a view to looking at reflected scatter of fine finished surfaces, such as mirrors, and hardly any with transmissive scatter a priority. It is also the author's contention that two of the instruments quoted (the MSU and LLNL differential scatterometers) can be easily modified to give transmissive data. The point being that work today concentrates on reflected scatter for the inspection of surface quality. Work with the Variable Angle Scatterometer for instance shows considerable evidence to suggest that any cleaning operation performed on an optic leads to a significant increase in its scatter (a fact verified by the author).

Valuable though these results may be, it remains a fact that each instrument reviewed is passive in that it is only capable of looking at the scatter of an optic when removed from its normal operating environment. Relatively little has been done to investigate the progression of transmitted scatter when under normal operating conditions which is the raison d'être for the Loughborough instrument.
REFERENCES


CHAPTER 3

EXPERIMENTAL MEASUREMENT OF SCATTER

3.1 Introduction

Described in this Chapter is the design and construction of a scatterometer that is similar in many ways to the types of instruments looked at previously. The impetus for constructing the instrument is that most commercial systems, as well as being very expensive, can offer a variety of operating modes such as scatter measurements over a wide range of angles (from near specular to >80°), an ability to give total integrated scatter measurements, raster scan measurements and an option to operate in transmissive and reflective modes - all of which are not needed.

Clearly, when the main focus of attention lies in the very near angle scatter in transmissive optics, a versatile piece of equipment is not required and so it was decided that a relatively simple arrangement was to be constructed that would enable the user to quickly obtain data for very near specular (i.e. <1°) directions.

3.1.1 How Scatter Measurements are Quantified

Scatter from optical components can fill the entire sphere centred about the sample. This light distribution is a function of wavelength, power, incident angle and sample characteristics (orientation, transmittance, reflectance, absorptance, surface finish, refractive index, bulk homogeneity, contamination, etc.). Scatter measurements are commonly expressed in terms of the Bidirectional Scatter Distribution Function, BSDF, (see overleaf). Reflection, transmission and volume scatter measurements are similarly described by the BRDF, BTDF and BVDF, which are merely subsets of the more generic BSDF.
3.1.2 Bidirectional Scatter Distribution Function (BSDF)

The notation and derivation for the BSDF is credited to Nicodemus\(^1\). The defining geometry, for reflection in this case, is shown below in Fig. 3.1.2a where the subscripts \(i\) and \(s\) are used to denote incident and scattered quantities respectively.

![Diagram of BSDF](image)

Fig. 3.1.2a

Nicodemus started with the general case of light reflected from a surface and made several logical approximations to acquire a simple manageable form for BRDF. Since the object here is an understanding of the use of the expression and not its complete derivation, this section will be restricted to the relatively simple case of a nearly collimated beam of light reflecting from a sample. He also assumed that the beam has uniform cross section, the illuminated reflector area \(A\) is isotropic, and all scatter comes from the surface and none from the bulk.

The BRDF may then defined in radiometric terms as the surface radiance divided by the incident surface irradiance. The surface irradiance is the light flux (watts) incident on the surface per unit illuminated surface area (not beam cross sectional area). The scattered surface radiance is the light flux scattered through solid angle \(\Omega_s\) per unit
illuminated surface area per unit projected solid angle. The projected solid angle is the solid angle multiplied by \( \cos \theta_s \) (see Fig. 3.1.2a). Thus BRDF becomes:

\[
\text{BRDF} = \frac{\text{differential radiance}}{\text{differential irradiance}} = \frac{\text{d}P_s / \text{d}\Omega_s}{\text{P}_i \cos \theta_s} = \frac{\text{P}_s / \Omega_s}{\text{P}_i \cos \theta_s} \quad 3(1)
\]

This equation is appropriate for all angles of incidence and all angles of scatter. Another way to look at the \( \cos \theta_s \) term is as a correction factor to adjust the illuminated area \( A \) to its apparent size when viewed from the scatter direction. Notice that the BRDF has units of steradian\(^{-1}\) and can take on either very large or very small values depending on the relative sizes of \( P_s \) and \( \Omega_s \). For instance, \( (P_s/P_i) \rightarrow 1 \) if the entire specular reflection is measured, so \( (\text{BRDF}) \rightarrow (1/\Omega_s) \) which can be very large. Scatter measurements well removed from specular generally encounter small values of \( P_s \) and require larger apertures. The differential form is more correct and is only approximated when measurements are taken with a finite aperture diameter. The term bidirectional is used because it depends upon both the incident direction \((\theta_i, \phi_i)\) and the scatter direction \((\theta_s, \phi_s)\) and, as intended by Nicodemus, can be viewed as directional reflectance per unit solid angle (in steradians) of collected scatter.

The assumptions made in this derivation are not completely correct in actual measurement conditions. For example, an incident laser beam is likely to have a Gaussian intensity profile instead of one that is uniform. Isotropic surfaces do not really exist and even good reflectors exhibit some degree of bulk scatter. For the case of a transmitting sample, where two surfaces as well as the bulk contribute to the scatter signal, the idea of illuminated surface area is not clearly defined. This means, therefore, that the BRDF, as measured, is no longer the scattered radiance divided by the incident irradiance. However the quantity expressed in the above equation can still be measured. The BSDF is then defined as a useful measurement parameter and not as the ratioed radiance and irradiance.

\[
\text{BSDF} = \frac{\text{P}_s / \Omega_s}{\text{P}_i \cos \theta_s} \quad 3(2)
\]

When the cosine term is dropped from the equation, the result is called the cosine corrected BSDF. Now, the light scattered from a particular sample into any given solid angle, from a hypothetical source, may be found by multiplying the appropriate value of the cosine corrected BSDF by the incident power and solid angle.
3.2 Scatterometer Design (Visible)

Initially, many optical arrangements were examined, which included a parabolic front-coated mirror as the final focusing element, however, it was found that a double spatial filter combination exhibited the least amount of instrumental signature (i.e. that signal obtained when no sample was present). The most likely explanation for this was that the mirror had to be used off-axis and so aberrations played a significant role in contributing to the near-angle signature. Also it was fairly easy to clean the glass surfaces by using 'Opti Clean', a viscous polymer that dries soon after application to a surface and which may then be pulled off, thus taking almost all particulate contamination with it.

Fig. 3.2a illustrates the basic components of the system.

The first spatial filter removed any beam fluctuations from the 10 mW HeNe laser light source by converting beam wander variations to beam intensity variations which in turn were monitored by a photodiode using a beam splitter. The second spatial filter removed scatter due to the glass plate which acted as the beam splitter used to sample the beam. It also presented a near point source which is imaged by the final focusing element (a microscope objective). This had the added advantage that the final spot could be focused very accurately if any curved samples were to be studied. The distance from the final focusing element to the focused spot was approximately 180 cm. The distance of the sensing element from the sample under study was 1 metre so that a translation of 1 mm by the photodiode represented a change in angle of 1 mR assuming the photodiode remained close to specular.
3.2.1 Electronic Arrangement

The electronic arrangement of the system involved converting the scattered light into a signal that could be directly measured by the computer. This was achieved in separate stages: the sensing element, the acquisition of this signal from background noise by phase sensitive detection, the amplification of this signal, the conversion of this analogue signal to a digital one, sending this signal to the computer via an interface card and finally translating the photodiode so that another angle from specular was sampled.

3.2.1.1 Sensing Element

Analysis of the scattered light required the conversion of the optical signal into an electrical voltage or current. In this instance a silicon photodiode was used having an active area of 1 mm², specifically it was a BPX 65 with a responsivity of 0.55 A/W at 850 nm. As seen in Fig. 3.2.1.1a the photodiode is operated in photoconductive mode, with the load resistor, $R_R$, forming the negative feedback loop of the operational amplifier so that the bias voltage across the photodiode remains independent of photocurrent. The operational amplifier used was a LF355N which possesses the advantages of high input impedance (around $10^{12}$ Ω) and low input bias current (30 pA).

Incident light on the photodiode raises electrons from the valence band to the conduction band of the semiconductor giving rise to a current flow. This photo-current passes through the resistor $R_f$ producing a voltage $V_{id} = i_{pd} R_f$ at the input of the amplifier which is proportional to the incident irradiance. The amplifier then buffers the signal to the next part of the circuit which is the phase sensitive detector (PSD). This part of the data retrieval will be dealt with in more detail in Section 3.2.1.2 but briefly the PSD is an instrument that has the ability to extract a signal from noise. This signal is then passed to the A/D converter.
3.2.1.2 Phase Sensitive Detection (PSD) and Other Noise Considerations

When measuring scattered light as a function of component quality, the instrument's own scatter and beam profile limit the minimum angle from specular at which scattered light from the test object can be detected. The broader the focused specular beam, the more difficult it is to take measurements at low angles. It is therefore important to limit the instrumental 'signature' as much as possible when taking low angle scatter data.

The scattering of light from most optical surfaces is small, particularly if the sample is very clean, so in order to pick up signals a way must be found that can detect them where the signal/noise ratio may be less than unity. Such a method is phase sensitive detection (PSD).

A PSD behaves like a band pass filter with an extremely narrow bandwidth; much narrower than can be obtained with passive circuitry. A block diagram of a PSD is shown in Fig. 3.2.1.2a overleaf:
A square wave reference signal, provided by a chopper running at 2 kHz, is used to control an electronic switch. In the positive half of the reference cycle, the signal is switched to A whilst in the negative half it is switched to B and inverted. The outputs of A and B are then integrated together over a controllable time period. The signals at different parts of the circuit are shown schematically below in Fig. 3.2.1.2b:

\[
\int_0^T (A + B) \, dt \cdot \frac{1}{T}
\]

Fig. 3.2.1.2b

Any signals which have a frequency which is different to the reference will average to zero in the integration stage. The longer the time over which the integration occurs, the closer the frequencies which can be distinguished. With the PSD, as with all other
filters, the bandwidth is proportional to the reciprocal of the time constant for integration.

As well as the sources of noise discussed already, a major contribution to the degradation of the signal was found to be the ambient lighting conditions of the laboratory. This was minimised by a light tight box painted matt black on the inside to minimise stray reflections. All equipment placed in the box were also painted black. To prevent scatter from the photodiode itself, its glass cover was removed. Shielding cables and the instruments in aluminium foil reduced RF interference coming from the computer. However some noise was still present on the data line leading from the log ratiometer to the A/D converter and it was found that putting a choke filter in the line reduced it to manageable proportions (see Fig. 3.2.1.2c).

![Fig. 3.2.1.2c](image)

A concerted effort was also made to keep the number of optical elements to a minimum, not only from the point of view of reducing costs and trying to have as high an incident laser power on the sample as possible, but equally as important, to reduce the number of optical surfaces which could contribute to instrumental signature. Neutral density filters used for attenuation of the laser light were always placed before the spatial filter so that any scatter from these elements would be diffracted into higher orders and hence eliminated.

To prevent unwanted reflected signals entering the photodiode from other parts of the equipment it was decided to place an aperture over the photodiode. Aperture diameter size is of crucial importance when taking near specular scatter measurements. This becomes clearer upon examination of Fig. 3.2.1.2d. It is known as aperture convolution due to the (necessary) finite size of the receiver aperture. Here the measurements were made of the same focused spot using circular receiver apertures of
three different diameters. The peak values decrease by over 30 % as the aperture diameter is increased from 350 μm to 1000 μm. The widths at the half power points, however, do the opposite.

This phenomenon is explained if one reconsiders the BSDF equation:

\[
\text{BSDF} = \frac{P_s / \Omega_s}{P_\text{i} \cos \theta_s}
\]

The value \( P_s \) is treated as the average over \( \Omega_s \) and the calculated BSDF assigned to the position \( \theta_s \). If the aperture is larger than the focused spot and centred on it then \( P_s \) is nearly \( P_\text{i} \) and the BSDF approaches the constant \( 1/\Omega_s \). Essentially the same value will be measured for any position \( \theta_s \) that allows a particular aperture to capture most of the focused specular light.
In these measurements, the aperture - sample distance was \( R = 100 \text{ cm} \) which gives the following values:

<table>
<thead>
<tr>
<th>Detector Aperture</th>
<th>( 1/\Omega_s (R^2/\pi r^2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 microns</td>
<td>1,273,240</td>
</tr>
<tr>
<td>750 microns</td>
<td>2,263,540</td>
</tr>
<tr>
<td>350 microns</td>
<td>10,393,792</td>
</tr>
</tbody>
</table>

As the aperture diameter is decreased, the flat section of the curve gets shorter. At 350 \( \mu \text{m} \) the aperture is about the size of the focused spot. If one treats each plot as the convolution of the apertures with the BSDF then all three plots are correct although the trace obtained with a smaller aperture has more structure contained within it. The advantage of using a large aperture is that the signal to noise ratio is increased although in work involving near specular measurements it is often advantageous to have a small aperture because there are usually large intensity variations over the testing range.

Bearing all of the above in mind it was decided that an aperture of 750 \( \mu \text{m} \) would be used as an arbitrary diameter as the detector was still capable of picking plenty of signal from cleaned samples out to as far as 20 mR from specular and also because this was larger than the speckle pattern that always modulates a BSDF pattern when a laser is used as the light source. It has been estimated that the speckle diameter is about half the focused spot diameter\(^2\) and so this value was deemed appropriate.

It may also be observed that there seems to be a slight lateral shift of around 250 \( \mu \text{m} \) in the maximum value of the 350 \( \mu \text{m} \) aperture curve. This slight inaccuracy was probably caused by the photodiode/aperture assembly not being exactly perpendicular to the incident probe beam, thereby leading to a small error in position of the sampling photodiode.

Another factor which had to be taken into account was that when taking close to specular measurements the photodiode could 'see' up along the optical path to the final focusing element. It was found that this was the most significant contribution to the signature. This was largely solved by placing an aperture directly in front of the sample being tested. However this also had its drawbacks. If the aperture was too large then it would become ineffectual and if it was too small then the rim of the aperture would start to scatter of its own accord as it struck the specular beam. Fig. 3.2.1.2e shows the effect of different size stops on the output of the PSD.
As can be seen there is an optimum diameter aperture between 7 mm and 10 mm and it was decided that an aperture of 8 mm would be used for all scatter experiments.

![Fig. 3.2.1.2e](image)

**3.2.1.3 Sampling and Amplification**

Because the scattered signal could change by as many as four orders of magnitude when working close to specular and the fact that the A/D converter and the computer could only resolve 256 discrete data levels a form of data compression was found to be necessary that converted the scattered light into a log format normalised to the incident intensity. The device used was a Lin/Log Ratiometer model 5048 manufactured by EG&G Brookdeal. This had the added advantage that intensity variations of the light source were automatically accounted for at this stage as both the signals from the beam sampling detector and the scatter detector were analysed.
3.2.1.4 Computer Interfacing

The computer used for control, data processing and data presentation was an Amstrad PC1640. This is an IBM PC compatible, with 640k byte of RAM and a 20M byte Winchester hard-disc drive plus a single floppy disc drive. All software was written in 'Turbo Pascal'. This is a fast version of the standard high level language Pascal and was developed and marketed by Borland International.

All information exchanged between the computer, the A/D converter circuit and the stepper motor goes via the interface card, the circuit diagram of which is shown in Fig. 3.2.1.4a. This is a commercially available interface card manufactured by Eltime Ltd. that is designed for image processing using their video frame-store. Because of the availability of the card it was decided that all peripherals used were to be electronically compatible with it.

![Circuit Diagram](image)

**Fig. 3.2.1.4a**

The active pins on the output of the interface card consist of eight data lines (D0 - D7), three address lines (A0, A7 and A8), a clock pulse (Φ) and a read/write signal (R/W). The addresses sent down pins A0, A7 and A8 are used to control the 3-line to 8-line decoder (74LS138), which in turn sends out a pulse on receipt of the correct address that enables the 74LS374 to latch data to or from the equipment, (see Fig. 3.2.1.4b). An octal bus transceiver, 74LS245, is used to buffer all signals on the data lines to and from the interface card, whose data flow direction is set by the R/W signal. Because of this two-way transmission of data it was also possible to write data to the
circuit so that the computer could drive a stepper motor once data acquisition was completed.

![Circuit Diagram]

Fig. 3.2.1.4b

The signal obtained from the photodiode was first amplified, converted to an eight-bit code by an analogue-to-digital converter and then sent to the computer for subsequent analysis. The photodiode was then translated and the process repeated.

The electronic circuitry employed to perform these tasks can essentially be divided into five parts: sampling and amplification of the electronic signal, phase sensitive detection of the signal, A/D conversion, interfacing of the data to the computer and a repeat of the procedure at a different angle from specular.

### 3.2.1.5 A/D Conversion

The A/D converter, an 8-bit Ferranti ZN448E, has an internal reference voltage ($V_{\text{ref}}$) of 2.56 V and it was decided that this was a convenient level to work with. If the analogue signal ($V_{\text{in}}$) is greater than or equal to $V_{\text{ref}}$ then all the output bits are high.
and a maximum limiting resolvable voltage is reached. In order to keep the output from the phase sensitive detector linear it was necessary to limit the maximum output from it to be less than its saturation voltage of 10 volts. An arbitrary limit of around 500 mV was therefore set to be the maximum signal from the PSD. So before any data conversion took place the PSD signal had to be amplified by a factor of 5. This was achieved by another operational amplifier, a low noise BIFET 071, used in the non-inverting mode. The amplified voltage was then sent to the analogue input of the A/D converter to be changed into an 8 bit code (see Fig. 3.2.1.5a).

![Data Lines](image)

**Fig. 3.2.1.5a**

### 3.2.1.6 Motion Controller

The stepper motor used to drive the translation stage was a RS 332-947 4-phase stepper motor with a 7.5° step angle. This was driven by a SAA1027 stepper motor driver chip. As mentioned in the Section above, it was possible to control this chip by writing data, rather than reading it via the 74LS245. To drive the motor, the computer sends a number to the port whose address activates pin 11 on the 74LS138 chip, (it is irrelevant what number is sent as long as the port is accessed.) This in turn then enables the lower 74LS374 in Fig. 3.2.1.4b to latch data to the voltage translator 4104. The numbers sent to the relevant port address activate the appropriate data lines which, after conversion to 12 volts, drive the motor.
3.2.2 Calibration

The data to the computer consists of eight bits giving a total of 256 resolvable signal levels. Obviously this data has to be interpreted as light intensity values and so it is necessary to ascertain precisely what intensity of light is equivalent to one bit. It is also required that the signal from the PSD be linear.

Fig. 3.2.2a shows the output from the PSD as a function of incident light intensity. Neutral density filters placed before the spatial filter allowed the intensity to be changed by a known amount as the optical densities of the filters themselves were known from manufacturer's data and were also checked independently.

By using a United Detector Technology model 371 optical power meter it was also possible to calibrate the output from the PSD to absolute power measurements.

![Power Meter Reading (nW)](image)

Fig. 3.2.2a

All measurements were performed using the focused specular beam and so heavy attenuation of the incident light was required using many neutral density filters. The resultant signal, (in the mV range), was then multiplied by the reciprocal of the transmission of the neutral density filter combination and accounts for the large values of absissa. As can be seen the output from the PSD was generally linear with a
calibration value associated with it of approximately 241 mV/nW or 1 mV = 4.15 x 10⁻¹² W. This had an accuracy of around 10%.

3.3 Errors in BTDF Measurements

A useful way of presenting scatter data is scattered light power density normalised to the incident light power and plotted as a function of angle from specular. Nicodemus stated, (see section 3.1.1), that if this quantity is also normalised by the cosine of the angle between the surface normal and the direction of scatter then the resulting expression was the differential scattered radiance normalised by the incident irradiance. For analysing optics in transmission, this expression has become known as the Bidirectional Transmissive Distribution Function.

BTDF is defined by:

\[
\text{BTDF} \equiv \frac{P_s/\Omega_s}{P_i \cos \theta_i}
\]  \hspace{1cm} (3.4)

where \(P_s\) is the scattered power measured by the detector with an aperture that subtends a solid angle of \(\Omega\) at the sample. The \(\cos \theta_i\) term gives the projection of the solid angle \(\Omega\) onto the sample surface.

A simple analysis has been performed based upon a similar method used by Rifkin et al⁵ that has allowed an estimate of the magnitude of the errors to be obtained for the system under the assumption that the four defining variables are mutually independent. To first order, the RMS error in the measured BTDF is:

\[
\frac{\Delta \text{BTDF}}{\text{BTDF}} = \left[ \left( \frac{\Delta P_s}{P_s} \right)^2 + \left( \frac{\Delta P_i}{P_i} \right)^2 + \left( \frac{\Delta \Omega}{\Omega} \right)^2 + \left( \frac{\Delta \theta_i \cdot \sin \theta_i}{\cos \theta_i} \right)^2 \right]^{1/2}
\]  \hspace{1cm} (3.5)

The first term in this expression refers to errors associated with the measurement of scattered power. These may be assumed to come from three sources: a) aperture misalignment, b) system noise, \(\Delta V_s\), in the receiver electronics and c) detector nonlinearity. Hence the RMS error in \(P_s\) is given by:
\[
\frac{\Delta P_y}{P_y} = \left[ \frac{\Delta I}{I} \right]^2 \left[ \frac{\Delta P_x}{P_x} \right]^2 + \left[ \frac{\Delta V_y}{V_y} \right]^2 + \left[ NL \right]^2 \right]^{1/2} \tag{3.6}
\]

where the first term
\[
\frac{\Delta P_y}{P_y} = \left[ \frac{m}{\theta_y} \right] \cos^{-1} \left[ \frac{R \cdot \cos \theta_d}{\sqrt{\Delta y^2 + R^2}} - \theta_d \right] \tag{3.7}
\]

is the error in the scattered power which comes from vertical aperture misalignment. \( R \) represents the detector distance (1 metre) and \( \Delta y \) is the vertical aperture misalignment (~ 0.1 mm). The derivation of this equation relies on the assumption that scattered power may be represented as a linear function with slope \( m \) (= -1) when plotted on a log-log scale. Though not absolutely correct, many optical samples do in fact scatter light consistent with this assumption.

The second term in equation 3(6), \( \Delta V_y/V_y \), is the signal to noise ratio of the detector which consists mainly of thermal noise, (around \( 10^{-5} \) at 633 nm), while the third term, \( NL \), arises from system nonlinearities and as estimated from Fig. 3.2.2a was approximately 0.1.

The term \( \Delta P_x/P_x \) represents the measurement errors in \( P_x \),
\[
\frac{\Delta P_x}{P_x} = \left[ \frac{\Delta P}{P} \right]^2 + \left[ \frac{\Delta V_x}{V_x} \right]^2 + \left[ NL \right]^2 \right]^{1/2} \tag{3.8}
\]

The first term in the equation represents the loss of signal associated with the finite aperture of the receiver and may be reduced to less than 1 % if a sufficiently large aperture is used, whilst the last two terms have their usual meanings as described earlier.

The nonlinearity errors of the detector may be estimated by looking at the calibration graph (Fig. 3.3a) overleaf of the incident beam power on the sample, as measured by the United Detector Technology model 371 optical power meter, against the sampling
photodiode signal. This appears to be quite linear with an estimate of the error to be only 1 %.

![Graph showing photodiode reading vs power meter reading.](image)

**Fig. 3.3a**

Uncertainties in the solid angle, $\Omega$, contribute to the third term so that

$$\frac{\Delta \Omega}{\Omega} = \left[ \left( \frac{2 \Delta r}{r} \right)^2 + \left( \frac{2 \Delta R}{R} \right)^2 \right]^{1/2}$$  

3(9)

where

- $\Delta r$ = aperture tolerance (5 $\mu$m)
- $\Delta R$ = uncertainty in detector arm length (0.1 cm)
- $r$ = radius of aperture (375 $\mu$m)
- $R$ = length of detector arm (100 cm)
The last term is the error associated with the scatter angle, $\theta_s$. Toward grazing incidence this term grows quite large, but near specular is always very much less than 1 %.

An estimation of the mentioned error terms is given below:

<table>
<thead>
<tr>
<th>$\theta_s$</th>
<th>1 mR</th>
<th>10 mR</th>
<th>25 mR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{\Delta P_s}{P_s}$</td>
<td>$4.79 \times 10^{-3}$</td>
<td>$4.82 \times 10^{-5}$</td>
<td>$7.69 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\frac{\Delta V_s}{V_s}$</td>
<td>$10^{-5}$</td>
<td>$10^{-5}$</td>
<td>$10^{-5}$</td>
</tr>
<tr>
<td>NL</td>
<td>0.1, 0.01</td>
<td>0.1, 0.01</td>
<td>0.1, 0.01</td>
</tr>
<tr>
<td>$\frac{\Delta \Omega}{\Omega}$</td>
<td>0.027</td>
<td>0.027</td>
<td>0.027</td>
</tr>
<tr>
<td>$\frac{\Delta \theta_s \cdot \sin \theta_s}{\cos \theta_s}$</td>
<td>$10^{-4}$</td>
<td>$10^{-3}$</td>
<td>$2.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\frac{\Delta BTDF}{BTDF}$</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
</tbody>
</table>

As can be seen the final error for scatter readings throughout the range 1 mR to 25 mR are a constant 10 %, the most significant contribution to this are the nonlinearity errors of the sampling detector. All the following data thus have an associated error of 10 %.

### 3.3.1 Reproducibility

An analysis of the factors contributing to the BSDF parameter errors have been given above. To make sure that the measured readings are reproducible, a couple of runs were performed on a cleaned silica window. Ideally, the two sets of data should be identical, however, there were some slight variations (see Fig. 3.3.1a). The differences were, however, less than the experimental error associated with each datum and it was concluded that the instrument was capable of giving reliable, reproducible measurements.
3.4 Scatterometer Design (Ultraviolet)

For scatter experiments conducted at RAL using ultraviolet wavelengths, a slightly different arrangement was required, (see Fig. 3.4a). Because there was no way of producing high repetition pulses of 248 nm that would be required for phase sensitive detection, generation of ultraviolet radiation was provided by the process of frequency doubling (see section 3.4.1) the output from an Innova 90 argon ion laser, manufactured by Coherent Inc., operating at a wavelength of 514 nm. Two other wavelengths were thus made available to complement data taken at 633 nm at Loughborough, namely 514 nm and 257 nm. It was felt that the 257 nm radiation was close enough to the 248 nm that the samples would be used at in the SPRITE laser for useful measurements to be made.
Because of the limited availability of UV transmitting optics, a reflective focusing parabolic mirror had to be used. Also transportation of the computer hardware proved difficult so the photodiode was translated manually along a translation stage and the resulting signal read off an oscilloscope after having calibrated the photodiode.

The power incident on the sample was kept constant by internal monitoring by the frequency doubler and was measured to be $0.86 \pm 0.01 \text{ mW}$. Calibration of the photodiode yielded the figures: $1 \text{ mV} = 7.54 \times 10^{-12} \text{ W}$ at $514 \text{ nm}$ and $1 \text{ mV} = 2.25 \times 10^{-9} \text{ W}$ at $257 \text{ nm}$. Note that the photodiode becomes less sensitive as the wavelength decreases. These figures are subject to an error of 10%. From the point of view of reproducibility, these errors were similar to those encountered for the Loughborough instrument and were a lot less than 10%. Thus the data for this arrangement are also subject to an overall error of 10%.

### 3.4.1 Frequency Doubling

Frequency doubling or second harmonic generation (SHG) of radiation is a useful technique whereby high energy photons are produced from low energy photons.

As a light wave propagates through a medium its electromagnetic field exerts forces on the loosely bound (valence) electrons. Normally these forces are quite small and in a
linear isotropic medium the resulting electric polarisation is parallel with and directly proportional to the applied field. Consequently, one can write:

$$P = \varepsilon_0 \chi E$$ \hspace{1cm} (3(10))

where $\chi$ is a dimensionless constant known as the electric susceptibility. As the field becomes more intense however (such as those found in lasers) $P$ becomes saturated. Thus there is a gradual increase in the ever-present, but normally insignificant, nonlinearity as $E$ increases. Since the direction of $E$ and $P$ coincide in the simplest case of an isotropic medium, the polarisation may be expressed as a series expansion:

$$P = \varepsilon_0 (\chi E + \chi(2)E^2 + \chi(3)E^3 + \ldots)$$ \hspace{1cm} (3(11))

The usual linear susceptibility term, $\chi$, is much greater than the coefficients of the nonlinear term $\chi(2)$, $\chi(3)$ etc. and hence the latter terms contribute noticeably only at high amplitude fields.

If a light wave of the form $E = E_0 \sin \omega t$ is made incident on the medium, the resulting electric polarisation, $P = \varepsilon_0 \chi E_0 \sin \omega t + \varepsilon_0 \chi(2)E_0^2 \sin^2 \omega t + \varepsilon_0 \chi(3)E_0^3 \sin^3 \omega t + \ldots$, can be rewritten as $P = \varepsilon_0 \chi E_0 \sin \omega t + \frac{1}{2}(\varepsilon_0 \chi(2)) E_0^2 (1 - \cos 2\omega t) + \frac{1}{4}(\varepsilon_0 \chi(3)) E_0^3 (3 \sin \omega t - \sin 3 \omega t) + \ldots$. The $\cos 2\omega t$ term corresponds to a variation in electric polarisation at twice the fundamental frequency i.e. at twice that of the incident wave. The reradiated light which arises from the driven oscillators also has a component at this same frequency, $2\omega$. This is known as second harmonic generation.

Notice that, for a given material, if $P(E)$ is an odd function, i.e. if reversing the direction of the $E$ field simply reverses the direction of $P$, the even powers of $E$ must vanish. The requirements for SHG production by a crystal therefore is that it does not have a centre of symmetry or inversion centre and also that it be piezoelectric. Such a crystal is ammonium dihydrogen phosphate (ADP) which was used in this case to produce 257 nm light from 514 nm incident light.

3.5 Near Angle Transmissive Scatter from Samples Exposed to Fluorine

The following section is devoted to examining quantitative data for the scatter in transmitted light from both fused silica and a variety of commercially available highly reflecting (HR) multilayers and how the scatter is increased when such samples are
exposed to a fluorine environment such as that found in excimer lasers. The evolution of the scatter, due to etching, is looked into as well as the effect of changing the fluorine concentration.

3.5.1 Introduction

Whilst there exists in the literature many examples of looking at angle resolved scatter in reflective mode to establish surface quality criteria (see for example references 6-10 and references therein), relatively little work has been done in transmission, especially at low angles. A scatterometer was therefore designed and constructed to measure the near angle transmissive scatter from a variety of optical components, (see section 3.2). The initiative arose because little work had been done in this area and the fact that any scatter when using a multiplexed system, such as the SPRITE laser at RAL, can be critical to the final peak power achievable at the focus. Fig. 3.5.1a shows how this 'crosstalk' between the beams can detract from the optimum peak power. The top diagram shows an ideal multiplexer arrangement with no scatter from the windows whilst the bottom diagram shows the result of scattering from one surface of the amplifying medium giving rise to pre- and post-pulse effects on target.

![Diagram showing ideal and scattered multiplexer arrangement](image-url)
Optimisation of an optical system, therefore, relies heavily on knowing the optical efficiency of each element. Inherent in this analysis is being able to quantify the scattering characteristics of each element and how this could impair the final multiplexed pulse.

3.5.2 Fused Silica Exposed to Fluorine

Initial fluorine exposure measurements were performed on circular samples of fused silica substrates supplied by TecOptics in the Isle of Man. Each sample had a diameter of 50 mm and a thickness of 10 mm. In order to be able to make measurements in the excimer gas environment and to examine the change of scatter with time, the sample under test was mounted on the output window aperture of an Oxford Lasers excimer laser model KX2.

Surface preparation of each sample was limited to filling the laser three times with dry helium to dilute any atmospheric water vapour in the cavity to a pressure of 600 mbar absolute and pumped out again. The cavity was then left under vacuum for 12 hours to check the integrity of the seals. During this vacuum phase, the samples were heated in situ for 12 hours with a small IR lamp to try and minimise any adsorbed water left on the surface of the silica.

The silica substrates were subjected to differing concentrations of fluorine (which was in fact a 5% fluorine and 95% helium mix) when 50, 100 and 200 mbar were mixed with helium in the laser cavity giving a final fluorine partial pressure slightly higher than those found in excimer lasers. The volume of the laser cavity was 25 litres. Although it is well known that silica is etched in the presence of fluorine (by hydrofluoric acid), it was felt that these pressures would be used as further experiments were planned on multilayer optics and it was required that the correct fluorine concentration be found so that a discernible change in the optical property of a sample could be easily measured.

3.5.2.1 BTDF Scatter Results from Fluorine Etched Fused Silica

Fig. 3.5.2.1a shows the result of the first series of experiments carried out using a fused silica sample that was exposed to 200 mbar of the fluorine mix together with 600 mbar of helium. It shows scatter, in terms of BTDF, against angle from specular, in
mR. The line labelled '0 hrs' is simply the scatter due to the sample being present in the laser cavity prior to the fluorine mix being admitted. The window shows rapid degradation in surface quality with time as shown by the increase in scatter. This is especially noticeable at angles greater than 8 mR, where the scatter has gone up by a factor of nearly 100 in three quarters of an hour exposure. This result may be expected as the concentration of fluorine was fairly high. One interesting aspect to note is that it appears that the scatter after 1.75 hours seems less than that after 0.75 hours. This anomalous result could be explained by the fact that after 1.75 hours severe degradation had taken place and multiple scattering effects probably reduced the magnitude of the forward scatter signal. In order, therefore, to examine how the scatter evolves at other concentrations, experiments were conducted using less fluorine.
Fig. 3.5.2.1b shows the same procedure on an identical fused silica sample but this time only 100 mbar of the fluorine mix was admitted into the cavity. It differs from the previous graph in a number of ways. Firstly, the scatter does not reach as high a level as before, in general being a factor of 10 or less over the whole angular range. Secondly, the difference in scatter, although initially rapid, over a period of time is not as dramatic as before, changing on average by a factor of 3 over the 19.5 hour test period.
Fig 3.5.2.1c is indicative of the continuing trend that seems to be emerging. This again shows another fused silica sample but this time only exposed to 50 mbar of the fluorine mix. Little change is apparent. The scatter seems to be constant during the period of the experiment, differing only slightly from that scatter profile obtained when the sample was initially put into the laser.
Fig. 3.5.2.1d gives a clearer representation of the trend alluded to above. It shows the scatter exhibited by all three samples after three quarters of an hour exposure to the fluorine mix. As may be expected, the samples exposed to greater fluorine concentrations exhibit the greatest amount of scatter due to etching quicker.
The BTDF results shown in Figs. 3.5.2.1a-d were all obtained as the degradation proceeded. At a later stage, when the experiment was repeated by replacing the substrates in the laser, BTDF curves were obtained which did not match those originally obtained and furthermore, the scattered light in the detection plane was not very uniform as one might have expected from an isotropic scatterer. This indicated some additional structure on the surface of the fluorine etched windows.

A simple experiment to investigate this lack of angular symmetry of the scatter signal.
was therefore carried out. This involved time-exposure photography of the scattered laser radiation on a white screen placed in the same plane as the silicon photodiode (see Fig. 3.5.2.2a).

3.5.2.2 Photography of the Scatter Field

A greater understanding of the morphology of the roughness imparted to the surface by the fluorine mix may be achieved by looking at the resulting diffraction pattern obtained when laser light is passed through the sample. Whereas before, data in only one dimension was presented, a photograph of the diffraction pattern can yield data over the 360° around the specular direction. The photographs to be presented are of a screen placed at a distance of one metre from the diffracting surface. The central dark spot is a hole in the screen to let the unscattered zeroth order light through and is 4 mm in diameter. The angular dimensions of the photographs are therefore from 2 mR to around 30 mR from specular.

Fig. 3.5.2.2b shows the scattered/diffracted light obtained from the sample exposed to 200 mbar of fluorine mix. As expected, a lot of scatter is apparent together with 'streaks' that are apparently at right angles to each other.

Fig. 3.5.2.2c shows the same sample under identical conditions except that during the exposure, the sample was translated horizontally over a distance of 5 mm, (each exposure lasting 15 seconds). This procedure has the result that the scatter arising from random roughness variations on the sample has been smeared out over the photograph. However, the streaks have become more pronounced leading to the
conclusion that whilst the sample was being moved, the diffraction pattern arising from any periodic component has remained fairly constant.

The same procedure was repeated for the sample exposed to the 100 mbar mix. Fig. 3.5.2.2d shows the diffraction pattern when the sample was kept stationary during the exposure. Again, whilst both streaks and random scatter components are evident, Fig. 3.5.2.2e shows the result of moving the sample during the exposure and it may be seen that a smearing out of the random pattern has resulted whilst the streaks are greatly emphasised.
When the sample exposed to the 200 mbar fluorine mix was removed from the laser, the periodic etch marks were clearly visible to the naked eye (see Fig. 3.5.2.2f). It was therefore surmised that this highly regular grating appearance was due to hydrofluoric acid etching along preferential directions. These directions would be dictated by any micro scratches present on the surface before insertion into the laser. In order to verify this, electron microscope pictures were taken of a new silica sample.
3.5.2.3 Electron Microscope Photography of Fused Silica

Using a high power Transmission Electron Microscope (TEM), which looks at a carbon replica of the sample, photographs were taken of the surface of an unused silica substrate, again provided by TecOptics. Scratches were indeed seen at high magnification although the samples had to be tilted at an angle of 60° to increase the contrast and render them visible.

Fig. 3.5.2.3a shows a photograph taken at a magnification of 26,000 times, (the black blobs are residues of carbon adhering to the surface replica). Multiple periodic scratches are evident that seem to be all going in the same direction. Fig. 3.5.2.3b shows another part of the substrate at a magnification of 33,000 times. Here it can be seen that there are only two scratch marks but, once more, they are parallel. Finally, at a magnification of 66,000 times, Fig. 3.5.2.3c shows a single scratch highlighting the fact that many different densities of scratchmarks exist on the surface, although all appear to be the same size perhaps indicating a common source for the scratches.
3.5.3 BTDF Scatter Results from Fluorine Etched Fluoride Multilayers

After the experiments were concluded on the fused silica samples, work proceeded to investigate how the presence of fluorine affected the optical properties of fluoride multilayers that were already known to possess a high UV damage threshold. The reason lay in whether it was possible to actually have an optic in contact with the laser gas which would eliminate the need for windows and consequently reduce the number of surfaces that the UV laser light would have to travel through. This has the advantage of cutting down on reflection losses and possible sources for scattered light to originate.

The samples used for this particular study were multilayers composed of dysprosium fluoride/aluminium fluoride (DyF₃/AlF₃), dysprosium fluoride/cryolite (DyF₃/Na₃AlF₆), thorium fluoride/cryolite (ThF₄/Na₃AlF₆) and gadolinium fluoride/cryolite (GdF₃/Na₃AlF₆). All were designed to be high reflectors (HR's) at 248 nm and were deposited on fused silica. A table of some properties of these materials is given in Fig. 3.5.3a below. The preparation of each sample was limited to air blowing the surface before being put onto the laser cavity and the cavity being flushed three times with 400 mbar absolute of dry helium before the final filling of 600 mbar of helium and 100 mbar of the fluorine mix was admitted into the laser chamber. The final pressure of the fluorine mixture was decided upon when looking at previous runs performed on bare fused silica substrates as being both the most economical in terms of the amount of fluorine gas used and just enough to cause some degradation in the optical quality of the sample (if, indeed, any degradation was to take place).

Fig. 3.5.3b shows how the dysprosium fluoride/aluminium fluoride sample degraded rather badly when exposed to the fluorine mixture. The scatter has increased by nearly two orders of magnitude from its initial value and has clearly lost its usefulness as optic. Fig. 3.5.3c shows a photograph of the sample when light from a HeNe laser is passed through it. Evident damage sites are clearly apparent with the film scattering the laser light from over its whole area showing that all regions exposed to the fluorine suffered damage.
<table>
<thead>
<tr>
<th>Material</th>
<th>n (248 nm)</th>
<th>Melting Point (°C)</th>
<th>Heat Capacity (J/mol.K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DyF₃</td>
<td>1.56¹⁵</td>
<td>1154¹¹</td>
<td>71.5¹²</td>
</tr>
<tr>
<td>AlF₃</td>
<td>1.41¹⁵</td>
<td>1090¹¹</td>
<td></td>
</tr>
<tr>
<td>ThF₄</td>
<td>1.59¹³</td>
<td>1110¹¹</td>
<td>110.5¹²</td>
</tr>
<tr>
<td>Na₃AlF₆</td>
<td>1.35¹³</td>
<td>1012¹¹</td>
<td>215.89¹¹</td>
</tr>
<tr>
<td>GdF₃</td>
<td>1.61¹⁴</td>
<td>1231¹¹</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3.5.3a

Fig. 3.5.3b
The next sample to be tested was dysprosium fluoride/cryolite and Fig. 3.5.3d shows how this sample reacted to the presence of fluorine. As can be seen, little degradation is apparent, the scatter appearing not to alter significantly during the experimental period. When looked at afterwards, under room lighting, the coating appeared unchanged with no signs of damage, thereby proving superior in this aspect to the dysprosium fluoride/aluminium fluoride coating.

Fig. 3.5.3e shows how the scatter evolved on the thorium fluoride/cryolite combination. Although the sample itself is very scattery, being at least an order of magnitude greater than those samples tested previously, the scatter does not change leading one to the conclusion that this sample is also fluorine resistant.
Fig. 3.5.3d
Finally, Fig. 3.5.3f shows the evolution of scatter on the final sample, gadolinium fluoride/cryolite. In this case, as in the dysprosium fluoride/aluminium fluoride sample, the growth in the scatter is quite rapid, especially at angles close to specular which, from the point of view of multiplexing, is the critical area. The scatter has increased, roughly by one order of magnitude over the whole angular range, thus rendering it useless as a possibility for window replacement.
3.5.4 Conclusions

From the experiments conducted on the fused silica substrates, which were really just an exercise to determine the correct working fluorine concentration for later experiments, it became evident that an etch pattern was developing on the surface. The reason for this was not apparent at first but it was conjectured that microscratches left by impurities in the final polishing process acted as 'seeding sites' for preferential attack by hydrofluoric acid. This could explain why the lines appeared in a
periodic fashion giving rise to the observed diffraction image. This was confirmed some months later when electron microscope images of the surface of a new 'off the shelf' substrate did indeed show tiny scratches on its surface.

Further experiments were then conducted on fluoride multilayers that are currently being investigated for use as highly reflecting (HR) mirrors. Two out of the four samples studied damaged catastrophically - the multilayer completely losing its optical integrity and scattering large quantities of incident laser light. The fact that the two samples that did damage were DyF$_3$/AlF$_3$ and GdF$_3$/Na$_3$AlF$_6$ and the two that did not damage significantly were ThF$_4$/Na$_3$AlF$_6$ and DyF$_3$/Na$_3$AlF$_6$ suggests that the damage mechanism may be dependent on the quality of the film material rather than the chemical composition of the multilayer stack. Unfortunately, the number of samples were limited and so further work needs to be carried out to investigate how voids, inclusions, cracks, tares or any other optical contaminant affects the fluorine resistance of the HR. It may be, as in the case of the silica substrates, that the state of the surface texture is of paramount importance in resisting attack by fluorine.

3.6 Wavelength Scaling of Scatter Data

Fabrication of low scatter optical elements is becoming increasingly important to the success of critical high precision optical systems. Scattering from a surface is caused by various mechanisms, and therefore any theory of predicting scatter based on microroughness alone has many limitations$^{17-23}$. These limitations point to the obvious conclusion that in order to obtain information about the scattering characteristics, one must actually measure that surface's scatter and not merely its microroughness. Scatter measurements are therefore being used more and more as acceptance criteria for various optical components.

Researchers at RAL are very interested in the scattering properties of all components through which the SPRITE laser beams will pass (see section 3.4). The main area of concern lies in the scatter characteristics close to the specular beam so that cross-talk effects may be predicted. However, the Loughborough scatterometer uses a probe beam wavelength of 0.633 µm which is nearly 2.6 times the wavelength for which the optics will be used, namely 0.248 µm; scatter at the longer wavelength may give drastically different results from scatter at the shorter wavelengths. A way, therefore, must be found to predict scatter data at one wavelength from scatter measured at another.
If a surface may be described as smooth and clean, then a wavelength scaling law based on Fourier analysis may be applied\textsuperscript{21}. The term 'smooth' implies that the surface height variations are small when compared to the wavelength of light. This assumption is almost always true for optics. The adjective 'clean' implies that the sample scatter is dominated by diffraction from surface topography and not surface contamination. This wavelength scaling law allows one to predict scatter at various wavelengths and incident angles based solely on measuring scatter at one wavelength and incident angle. Using this technique information that was previously unmeasurable can be accurately predicted.

3.6.1 Theory

Several theories exist in the literature that are used to describe the scattering process. The one that is most commonly used is the Rayleigh vector perturbation theory which takes into account the full nature of the incident electromagnetic field and also includes higher order polarisation effects\textsuperscript{22-24}. However, if the surface microroughness is the only source of scattering then a simple scattering model making use of the scalar theory of diffraction implies scattering behaviour which is shift invariant with respect to the incident angle\textsuperscript{25}. This scalar model of scattering allows the derivation of a surface transfer function which relates the scattered light distribution to the surface's power spectral density function (PSD). If the PSD of a surface is known, then information about its scattering function at any wavelength and incident angle may be easily determined provided the surface exhibits linear shift invariant behaviour.

The micro-roughness of a surface can be modelled as overlapping periodic sinusoidal gratings\textsuperscript{22,26}. The grating frequencies on a surface can be found from the first order grating equation:

$$f = (\sin \theta_s - \sin \theta_i)/\lambda$$

Where $\lambda$ represents the wavelength of the testing light and $\theta_s$ and $\theta_i$ represent the scatter and incident angles respectively. Thus $f$ becomes the frequency of the grating causing the scatter. The grating frequency and direction determine the angle at which light will scatter, while the amplitude of the grating determines the magnitude of the scatter.
The following table presents the grating frequency components for the close to specular angles that were used and the wavelengths at which the scatter data were taken (incident angle, θ_i = 0):

<table>
<thead>
<tr>
<th>Scatter Angle, θ_s (mR)</th>
<th>0.633 μm</th>
<th>0.514 μm</th>
<th>0.257 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>6.319</td>
<td>7.782</td>
<td>15.564</td>
</tr>
<tr>
<td>5</td>
<td>7.899</td>
<td>9.728</td>
<td>19.455</td>
</tr>
<tr>
<td>6</td>
<td>9.479</td>
<td>11.673</td>
<td>23.346</td>
</tr>
<tr>
<td>7</td>
<td>11.058</td>
<td>13.619</td>
<td>27.237</td>
</tr>
<tr>
<td>8</td>
<td>12.638</td>
<td>15.564</td>
<td>31.128</td>
</tr>
<tr>
<td>9</td>
<td>14.218</td>
<td>17.509</td>
<td>35.019</td>
</tr>
<tr>
<td>10</td>
<td>15.798</td>
<td>19.455</td>
<td>38.910</td>
</tr>
<tr>
<td>11</td>
<td>17.377</td>
<td>21.400</td>
<td>42.801</td>
</tr>
<tr>
<td>12</td>
<td>18.957</td>
<td>23.346</td>
<td>46.691</td>
</tr>
<tr>
<td>13</td>
<td>20.537</td>
<td>25.291</td>
<td>50.582</td>
</tr>
<tr>
<td>14</td>
<td>22.116</td>
<td>27.236</td>
<td>54.473</td>
</tr>
<tr>
<td>15</td>
<td>23.696</td>
<td>29.182</td>
<td>58.364</td>
</tr>
</tbody>
</table>

When performing experiments based on reflective scatter and the surface is smooth, clean and reflective then the BRDF from a two dimensional surface can be converted into that surface's PSD by the following formula:

\[
(PSD)_{2D} = \frac{BRDF \lambda^4 10^8}{16 \pi^2 \cos \theta_i \cos \theta_s Q} \lambda^2 \mu m^2
\]

The symbol Q is the sample material polarisation factor and may be approximated as the surface reflectivity. The value of 10^8 has been added to give the PSD the units of Å^2μm^2. This choice of units is convenient because the RMS roughness is usually given in angstroms and the micrometers are convenient to describe lateral surface features that scatter visible light into angles observable by the detector.

The theory above has been developed for a single surface scattering. For scatter in transmission (i.e. BTDF measurements) there are two surfaces and the bulk scattering to consider. For the purposes of the following experiments it will be assumed that the bulk transmissive scatter is negligible compared to the scatter from both surfaces. This has been found to be true for ZnSe over the visible region. Scatter seen by eye also
originated from both surfaces rather than the bulk and so this assumption appears to be valid.

3.6.2 Results

The primary data set consists of results taken at 633 nm, 514 nm and 257 nm. The method by which the data were taken has already been outlined and will not be gone into here. Fig. 3.6.3a below shows the BTDF for a 1 cm thick silica substrate at the test wavelengths of 633 nm and 514 nm. For simplicity the instrumental signature has been subtracted from each corresponding data set.

![BTDF graph](image)

As can be seen there is significantly more scatter in the green part of the spectrum than there is in the red. To see if it was possible to wavelength scale these results, however, it was necessary to turn the corresponding BTDF into PSD data and to plot this against the appropriate grating spatial frequency. This is more complicated in transmission than in reflection because, as mentioned before, there are two surfaces to consider each with its corresponding reflectivity.
It was decided that to perform the conversion to calculate the PSD from BTDF data using eq. 3(14) that the value of \( Q \) would be the transmission of the sample rather than the reflectivity. This technique neither requires nor predicts an analytic expression for a wavelength scaling law, however if any scaling exists this would become apparent in the graphs as all the respective data lines for each wavelength would continue at the same gradient and should have some regions of overlap as the wavelengths used are not too dissimilar. Fig. 3.6.3b shows the PSD vs. spatial frequency for the silica sample.

![Graph of PSD vs. spatial frequency](image)

**Fig. 3.6.3b**

As can be seen there is some agreement between the two wavelengths with some divergence at higher spatial frequencies. Unfortunately at the time the UV scatterometer was used to make scatter measurements at 254 nm, this silica sample had been unobtainable and so it was impossible to say whether this trend continued into the UV.
Fig. 3.6.3c shows the PSD function at three different wavelengths for a DyF<sub>3</sub>/cryolite HR multilayer. As can be seen there is fair agreement in the visible but in the UV there does not appear to be any correlation. This could be explained by particulate contamination in the thin film materials or some other non-topographic scattering phenomena.

Fig. 3.6.3d shows the PSD function for a YbF<sub>3</sub>/cryolite HR multilayer. Agreement between the visible wavelengths is stronger in this case but again there is a more than proportionate UV scatter component.
Finally, Fig. 3.6.3e depicts the PSD function for a GdF$_3$/AlF$_3$ HR multilayer and shows an entirely different picture. Here, no wavelength scaling relationship is evident with scatter in the green even greater than that in the UV. Quite why this should be so is unclear at present and underlines that, in some cases, wavelength scaling is an inappropriate method for predicting scatter levels in different wavelength regimes if purely topographic models are to be used.
3.6.3 Conclusions

The technique of wavelength scaling to predict scatter at other wavelengths has now been around for a number of years and its applicability has been well documented. There are, however, no reported cases where scatter in transmission has been used in this way. The technique employed above is very similar to that used by other workers looking at reflected scatter.

For a majority of the samples looked at, namely fused silica, and HR multilayers of DyF₃/cryolite and YbF₃/AlF₃, there seemed to be fairly good agreement in the visible but none down to the UV. This trend became even more apparent when the GdF₃/AlF₃ multilayer was examined. In this case no agreement was found to exist at any two wavelengths and any wavelength scaling could be discounted for this sample. For all the samples, it was impossible to use visible scatter to predict how a given sample will scatter in the UV. Such anomalous scattering is therefore wavelength dependent and
the source of this increase in scatter is still under investigation in the scatter community\textsuperscript{30}. 
REFERENCES


CHAPTER 4

DAMAGE IN LASER COMPONENTS

The two major limiting factors affecting the optical performance of high power laser system mirrors are the optical losses and the damage threshold of the dielectric coatings. The former can be attributed to absorption, scattering, and poor design of the coating and the latter can be related to a variety of factors both intrinsic and extrinsic to the actual materials used in their fabrication.

This chapter is mainly concerned with describing the damage testing of highly reflecting (HR) and anti-reflecting (AR) dielectric coatings prepared for use at the KrF excimer laser wavelength of 248 nm; but first a short review of the previous work done to establish the damage threshold of UV coatings will be given as well as a description of those models put forward to describe and predict damage threshold criteria.

4.1 Introduction

When a beam of light is incident upon or passes through a transparent material, little or no effect may be seen. If, however, the incident light intensity is increased, the material may exhibit reversible effects such as strain, distortion, expansion and temperature rise. Increase the intensity of the light further still to such levels as those found in laser beams and the material may suffer irreversible effects such as cracking, pitting, melting, vaporisation or violent shattering. The occurrence of such irreversible effects indicates that laser induced damage has taken place.

Laser induced damage has a history as old as the laser itself\(^1,2\). In the early 1960's when the first Q-switched ruby lasers were constructed, it was possible to damage materials by merely exposing them to the radiation. These pulsed lasers produced radiation power that was an order of magnitude greater than any other light source available at the time.

Material failure due to intense laser radiation is now commonplace as a result of the increase in numbers of ever-more powerful lasers built to meet the requirements of
researchers studying plasma and inertial confinement fusion physics. Such materials form the weakest link in high power laser systems and so there is much work being done into the causes of laser induced damage, how to define and measure it and examining ways to prevent it occurring. Such an effort may be gauged by the contents in the Proceedings of the Boulder Damage Symposia held every year since 1969 and currently under the auspices of the SPIE (Society of Photo-Optical Instrumentation Engineers). A great deal of money and effort is being applied to develop new optical materials which are more damage resistant. This is a vitally important area since the ultimate advancement of high power laser systems is limited by the failure of the optical components that comprise them.

4.1.1 Definition of Laser Induced Damage

In order to discuss laser induced damage, a working definition must be agreed upon as to precisely what it means. Several definitions exist in the literature but for the purposes of this thesis the one given by Kerr will suffice:

"The detectable, irreversible, destructive alteration of a material substance by a sufficiently intense laser light source leading to a degradation of its optical properties"

It is important to note that in using this definition only those changes that are detectable are considered relevant. The case may be that changes in the structure of the material do indeed take place because of laser irradiation but are too small to be registered on the detecting apparatus. This, of course, is due to the sensitivity of the method used to monitor the onset of damage. Such considerations must be borne in mind when performing multiple shot experiments where it is found that the damage threshold of a particular material may be a lot lower than its single shot value. It seems that on a shot to shot basis changes are occurring that are not detectable. After enough shots, cumulative damage may be observed. Research has shown that this cumulative effect is well defined in materials such as polymers, the first effects being shown as early as 1966, and may be observed for intensities as low as two orders of magnitude below the single shot threshold.

It is also important that any changes in the material under test by the laser beam be permanent ones. In other words if the changes produced are only transitory then laser damage is not considered to have taken place. If, however, the material has not
returned to its initial state by the time another laser pulse arrives then there could be a cumulative effect which could lead to permanent changes i.e. damage. This is significant in work analysing the dependence of damage threshold on pulse repetition frequency, (PRF)\textsuperscript{12-15}. It has been observed that the damage threshold of a material can fall dramatically as the repetition rate is increased.

In recent years it has also been reported that the single shot damage threshold can be dramatically increased by irradiating the surface of a material with a number of sub-damage threshold fluence pulses. Such laser conditioning, as it has been called, has been verified by the author on fluoride thin films and more will be said on this subject later in this thesis.

4.1.2 A Review of Excimer Laser Induced Damage at 248 nm

The concept of bound-free excimer system as a laser medium was initially enunciated in 1960\textsuperscript{16}. The first successful laboratory demonstrations, however, were not accomplished until the mid 1970's.

The earliest reported results for the damage thresholds of dielectric multilayers at 248 nm were those of Foltyn and Newnam\textsuperscript{17,18}. The coatings, which were all supplied by commercial vendors and research organisations, were all quarter-wave dielectric stacks of various oxide and fluoride materials. Single shot damage thresholds were not investigated as all tests were performed with the laser, a Lumonics 861 Multigas Excimer System, running at 35 Hz. The pulselength was between 10 and 12 ns FWHM with a mean spot diameter (1/e\textsuperscript{2}) of 0.62 mm. The laser induced damage to the coatings was observed visually with the aid of a 25 to 100x microscope and bright white light illumination. Placing filters in the way of the beam allowed the fluence to be changed easily.

The testing procedure consisted of irradiating ten sites at each test fluence which were distributed over the entire surface of the sample. In these tests, the damage threshold was defined as the highest fluence at which 10 out of 10 sites survived 1000 shots without damage. Additionally an 'upper limit' was defined which is the highest fluence at which at least 1 of 10 sites survived 1000 shots without damage. These limits provide information of the uniformity of the coating's damage resistance and the potential performance of this design. The results are presented briefly overleaf.
<table>
<thead>
<tr>
<th>Materials</th>
<th>Threshold (J/cm²) 10/10</th>
<th>Upper Limit (J/cm²) 1/10</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbF₂/Na₃AlF₆</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>HfO₂/SiO₂</td>
<td>0.9ₐ</td>
<td>1.2ₐ</td>
</tr>
<tr>
<td>Al₂O₃/NaF</td>
<td>1.0ₗ</td>
<td>1.9ₗ</td>
</tr>
<tr>
<td>Sc₂O₃/MgF₂</td>
<td>1.4ₖ</td>
<td>2.5ₖ</td>
</tr>
<tr>
<td>ThF₄/Na₃AlF₆</td>
<td>2.9ₜ</td>
<td>3.7ₜ</td>
</tr>
</tbody>
</table>

a - Average value of 2 different samples,
b - Average value of 8 different samples,
c - Average value of 3 different samples two of which were 45° reflectors,
d - Average value of 2 different samples.

Additionally the authors observed that in some of the materials, (Al₂O₃/NaF, Sc₂O₃/MgF₂ and HfO₂/SiO₂), a 20 - 25 % improvement in damage resistance could be obtained if they were subjected to subthreshold pre-irradiation treatment.

Although by current standards these thresholds seem a trifle low, these materials were to become subject to intense study so that today dielectric stacks capable of withstanding fluences an order of magnitude greater than these reported are not uncommon. To underline this point the same authors the very next year reported that the average damage threshold for selected materials had been increased to the 3 - 4 J/cm² range.

In the same year it was reported that it was possible to increase the damage threshold of a variety of HR's and AR's by adding a halfwave undercoat or overcoat. In the case of the HR, where the laser energy is concentrated in the outer part of the coating, an overcoat is added to the top of a standard quarterwave stack, and for an AR, where the energy penetrates to the substrates, an undercoat, or barrier layer, is added. Previous experiments had demonstrated that 1064 nm high reflectors had benefitted from such treatment by as much as 50 %²¹,²². It was suggested that in the case of the HR, the overcoat adds mechanical strength to the coating, holding it together at laser energies where it would otherwise damage, and in the case of the AR, the undercoat was thought to improve the adhesion of the coating to the substrate, thereby strengthening the interface which was a weak point in this type of coating.

The damage testing itself was carried out at LLNL (Lawrence Livermore National Laboratory) using 20 ns pulses. The laser beam was focused to provide a uniform intense beam over a region 100 µm in diameter at the sample surface. Unlike the
damage testing looked at previously, each site was irradiated with a single laser pulse. Before and after irradiation, the sample was examined visually and using Normarski microscopy. Any permanent alteration of the surface was considered to be damage. The damage threshold was defined to be midway between the lowest fluence which produced damage and the highest fluence which did not produce damage.

The HR samples consisted of 19 quarterwave layers of scandium oxide and magnesium fluoride on BK-7 glass substrates. Two low index \((n \approx 1.5)\) materials were used for the halfwave overcoats: magnesium fluoride and silicon dioxide. 18 HR's were tested in all, six without an overcoat, six with a silica overcoat and six with the magnesium fluoride overcoat. The results are given below:

<table>
<thead>
<tr>
<th>Overcoat Material</th>
<th>Average Threshold ((\text{J/cm}^2))</th>
<th>Standard Deviation ((\text{J/cm}^2))</th>
<th>Maximum Threshold</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>2.7</td>
<td>0.4</td>
<td>3.2</td>
</tr>
<tr>
<td>(\text{SiO}_2)</td>
<td>5.7</td>
<td>0.6</td>
<td>6.5</td>
</tr>
<tr>
<td>(\text{MgF}_2)</td>
<td>6.9</td>
<td>1.1</td>
<td>8.5</td>
</tr>
</tbody>
</table>

As can be seen, the data indicates that the damage threshold is increased by the addition of a low index halfwave overcoat and nearly a factor 2.5 for the magnesium fluoride overcoat.

Two material combinations were used for the AR coatings: scanda/magnesium fluoride and scanda/silica. The materials used for the barrier layer were magnesium fluoride and silica. For these experiments, a total of 24 coatings were tested, four each of six designs. The results overleaf indicate that the magnesium fluoride barrier layers improve the thresholds of the AR's only slightly, yielding an average improvement of 14%. The silica barrier layer improves the average threshold by 40%. This is a significant improvement and is about the same magnitude as has been observed when using undercoats with 1064 nm coatings.
<table>
<thead>
<tr>
<th>AR Materials</th>
<th>Undercoat Material</th>
<th>Average Threshold (J/cm²)</th>
<th>Standard Deviation</th>
<th>Maximum Threshold (J/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc₂O₃/MgF₂</td>
<td>None</td>
<td>4.4</td>
<td>0.3</td>
<td>4.7</td>
</tr>
<tr>
<td>Sc₂O₃/MgF₂</td>
<td>MgF₂</td>
<td>4.8</td>
<td>0.6</td>
<td>5.3</td>
</tr>
<tr>
<td>Sc₂O₃/MgF₂</td>
<td>SiO₂</td>
<td>5.6</td>
<td>0.4</td>
<td>6.1</td>
</tr>
<tr>
<td>Sc₂O₃/SiO₂</td>
<td>None</td>
<td>4.0</td>
<td>0.5</td>
<td>4.6</td>
</tr>
<tr>
<td>Sc₂O₃/SiO₂</td>
<td>MgF₂</td>
<td>4.9</td>
<td>0.4</td>
<td>5.4</td>
</tr>
<tr>
<td>Sc₂O₃/SiO₂</td>
<td>SiO₂</td>
<td>6.1</td>
<td>0.6</td>
<td>6.7</td>
</tr>
</tbody>
</table>

It can be seen that overcoats can make a significant improvement in the damage thresholds of HR's at 248 nm, with magnesium fluoride being the most effective. Also, barrier layers are effective in raising the thresholds of 248 nm AR's with silica proving to be the best choice of undercoat.

These were not the only tests conducted at the LLNL during 1981. Rainer et al.²³ measured the laser induced damage thresholds for 248 nm wavelength light of over 100 optical coatings from commercial vendors and research institutions. All samples were irradiated once per damage site with temporally multi-lobed 20 ns pulses generated by a KrF laser. The beam cross section at the sample surface was typically 1.5 mm in diameter, but had an irregular shape. Damage was defined to be a permanent alteration of the sample surface that was detectable by examination of the site before and after irradiation. Comparison was done by naked eye and both visually and photographically by either bright or dark field Normarski microscopy at magnifications ranging from 55 to 1060. An average of seven sites were tested on each sample and the damage threshold was defined to be the median value of the highest fluence that caused no damage and the lowest fluence that produced damage.

The histogram overleaf shows measured laser damage thresholds of 77 highly reflecting multilayers. The samples from commercial vendors had already been used in LLNL laser systems so that some were many years old. The other samples represent various types of research grade samples which were either sputter deposited, e-beam deposited without overcoats or e-beam deposited with overcoats. The median damage thresholds and number of samples tested for each category is also summarised.
### Laser Damage Thresholds of 77 HR Coatings

<table>
<thead>
<tr>
<th>Type</th>
<th>HR</th>
<th>AR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial</td>
<td>1.8</td>
<td>3.3</td>
</tr>
<tr>
<td>Research (sputter deposited)</td>
<td>1.0</td>
<td>--</td>
</tr>
<tr>
<td>Research (e-beam deposited)</td>
<td>3.1</td>
<td>4.2</td>
</tr>
<tr>
<td>non overcoated HR, non undercoated AR</td>
<td>6.3</td>
<td>5.4</td>
</tr>
<tr>
<td>Research (e-beam deposited) overcoated HR, undercoated AR</td>
<td>6.3</td>
<td>5.4</td>
</tr>
</tbody>
</table>

#### Diagram

- **Overcoated e-beam Samples**
- **Nonovercoated e-beam Samples**
- **Sputtered Samples**
- **Commercial Samples**

#### Table

<table>
<thead>
<tr>
<th>Damage Threshold (J/cm²)</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>10</td>
</tr>
<tr>
<td>1.5</td>
<td>5</td>
</tr>
<tr>
<td>2.5</td>
<td>5</td>
</tr>
<tr>
<td>3.5</td>
<td>10</td>
</tr>
<tr>
<td>4.5</td>
<td>5</td>
</tr>
<tr>
<td>5.5</td>
<td>5</td>
</tr>
<tr>
<td>6.5</td>
<td>10</td>
</tr>
<tr>
<td>7.5</td>
<td>5</td>
</tr>
<tr>
<td>8.5</td>
<td>5</td>
</tr>
</tbody>
</table>
The histogram below shows the damage thresholds of 43 AR films, again supplied by commercial vendors and research institutions. These data are also summarised in the table on the previous page. It was found that the median thresholds of both commercial AR coatings and research AR coatings without undercoats were higher than median thresholds of corresponding HR films. However, the best sets of HR research samples tested were still superior to the best sets of AR research samples.

The damage thresholds of the samples in the above study have exhibited levels around the 6 J/cm² mark for both AR and HR films, with the highest thresholds of 8.5 to 9.4 J/cm² being observed. These results together with similar data presented by two of the authors in an invited paper the same year represented the highest thresholds for dielectric multilayers reported up until that time.

Rainer and Deaton presented a survey of single pulse laser damage thresholds the following year at a variety of wavelengths, including 248 nm (having a pulse length of 20 ns), of commercially available thin film coatings and bare polished substrates. In
most cases the samples were purchased for use in the various lasers at LLNL. The
table below gives the distribution of damage thresholds of vacuum deposited reflection
and antireflection coatings, together with data for bare polished fused silica:

<table>
<thead>
<tr>
<th>Surface Type</th>
<th>Number</th>
<th>Spread (J/cm²)</th>
<th>Median (J/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Reflector</td>
<td>19</td>
<td>0.3-8.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Partial Reflector</td>
<td>3</td>
<td>1.9-4.7</td>
<td>2.0</td>
</tr>
<tr>
<td>Dichroic Reflector</td>
<td>1</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>Antireflector</td>
<td>9</td>
<td>0.7-9.4</td>
<td>4.3</td>
</tr>
<tr>
<td>Polished Fused Silica</td>
<td>4</td>
<td>4.0-7.9</td>
<td>5.7</td>
</tr>
</tbody>
</table>

It was noted that the surface damage thresholds for fused silica were lower than for
some films and it was the authors' contention that the particularly high UV absorption
of the polishing compounds may have been the dominating factor for the low
thresholds in this case. This work confirmed the general trend of monotonically
decreasing laser damage thresholds with decreasing wavelengths for all categories of
reflective and antireflective coatings as well as bare surfaces as data for 266, 355, 532
and 1064 nm were also given but at a pulse length of 0.7 ns, (1.0 ns at 1064 nm). It
was also noticed that the antireflecting coatings had, in general, larger damage
thresholds than the highly reflecting coatings but it was mentioned that a majority of
the highly reflecting coatings were several years old and it was surmised that both
ageing of the older films and more refined technology used on the newer films could
have accounted for this phenomenon.

The Los Alamos UV damage test facility had meanwhile been improved to include a
remote video monitoring system\textsuperscript{26} providing capabilities for high throughput testing
and real time beam monitoring. A high resolution video system was attached to the
eyepiece of a long working-distance microscope which provided not only for operator
safety but allowed use of a video recorder for preserving visual images of damage
onset and growth during irradiation. The results of preliminary tests using this
equipment is summarised overleaf with a common pulselength of 10 ns at a repetition
frequency of 35 Hz.
<table>
<thead>
<tr>
<th>HR Coating</th>
<th>Threshold at 248 nm (J/cm²)</th>
<th>Threshold at 308 nm (J/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ThF₄/Na₂AlF₆</td>
<td>3.3</td>
<td>2.8</td>
</tr>
<tr>
<td>Al₂O₃/SiO₂</td>
<td>3.0</td>
<td>5.2</td>
</tr>
<tr>
<td>Sc₂O₃/SiO₂, MgF₂</td>
<td>2.9</td>
<td>5.4</td>
</tr>
<tr>
<td>Same as above, non-qw</td>
<td>4.2</td>
<td>6.8</td>
</tr>
</tbody>
</table>

The data for 308 nm is included because it highlights, like the previous work, that there is evidence to suggest a wavelength scaling law exists. Interestingly enough, the results for damage thresholds at 248 nm were slightly lower than their previously reported results¹⁹, and may presumably be put down to the increased sensitivity in determining the onset of damage.

In one study scandium oxide as a damage resistant, high index, laser coating was tested exhaustively²⁷. Both AR's and HR's containing scandium oxide were investigated; for AR coatings, the effects of undercoat layers and choice of low index material were examined, while in the HR studies, the effects of overcoat layers, substrate materials, deposition temperature and number of layers in the coating were examined.

The basic HR design consisted mainly of 19 quarterwave thick layers of Sc₂O₃/MgF₂, all of which were e-beam evaporated onto both polished fused silica and BK-7 glass substrates. Halfwave thick overcoats of either MgF₂ or SiO₂ were added to the top of the quarterwave stacks of some samples. Two material combinations were used in a 4-layer design for the AR coating: Sc₂O₃/MgF₂ and Sc₂O₃/SiO₂. All were deposited onto polished fused silica. The effect of undercoats on damage resistance was tested by the addition of a halfwave thick layer of either MgF₂ or SiO₂ between the AR stack and the substrate. The experimental procedure consisted of irradiating each site with a single pulse from a discharge pumped KrF laser with a pulse length of approximately 20 ns.

From the point of view of HR's, it was found that all films without overcoats had damage thresholds below 4 J/cm², while all with overcoats had thresholds above 4 J/cm². The median thresholds for non overcoated and overcoated films were 3.1 J/cm² and 6.3 J/cm² respectively. Among overcoated films the median threshold for coatings with MgF₂ overcoats was 20% greater than the median threshold SiO₂ overcoats. The other variables which were tested - deposition temperatures, number of layers and
substrate materials - affected damage thresholds by amounts less than the measurement uncertainty. Within experimental uncertainty, it was found that there were no changes in the thresholds.

The only variable which caused a significant increase in the damage threshold of the AR's was the presence or absence of undercoats. Averaged over all coatings made in 4 runs, improvements obtained by use of SiO$_2$ and MgF$_2$ undercoats were 38 % and 17 % respectively. Among coatings produced in a single run, the largest improvements obtained by use of these two undercoats were 56 % and 35 % respectively. There was no significant difference between damage thresholds of Sc$_2$O$_3$/MgF$_2$ and Sc$_2$O$_3$/SiO$_2$ films. The Sc$_2$O$_3$/SiO$_2$ film had a wider range of thresholds, and those with SiO$_2$ undercoats had the highest median threshold (6.1 J/cm$^2$) of all the film and undercoat combinations tested.

For both designs of film, reproducibility was found to be good with the average variation being 12 %, although it was noticed that larger variations occurred among those HR films deposited on fused silica which exhibited crazing due to differences in thermal expansion coefficient.

This study was then extended to cover a wide variety of halfwave-thick layers of 15 oxide and fluoride materials, and for HR coatings made from 13 combinations of these materials. Several physical properties of the single-layer films were also measured. Of the HR coatings tested, those made of Sc$_2$O$_3$/MgF$_2$ and of MgO/LiF had the highest median threshold which were, respectively, 5.6 J/cm$^2$ and 7.0 J/cm$^2$. The thresholds of single-layer films ranged from 1 J/cm$^2$ for ZrO$_2$ to more than 20 J/cm$^2$ for SiO$_2$ and ThF$_4$; no reason was given for this exceptional result. Thresholds were greatest in films of materials for which refractive index and absorption were small, and position of the UV edge, (which was defined as that wavelength at which the transmission of a coating with a 1.5 μm optical thickness was 50 %), was well below 248 nm. Thresholds of single-layers, it was reported, did not correlate with film stress.

Measurements of thresholds for halfwave thick single layer films did not identify the materials from which the reflectors with greatest threshold were fabricated. The survey was moderately successful in identifying material characteristics which affect thresholds of reflectors, and identified a promising material combination, MgO/LiF, which had not been previously studied.

In reflectors made of pairs of materials having a common high index material, and
various low index materials, the largest thresholds for the reflectors correlated with use of the low index material with the lowest refractive index. In reflectors with a common low index material, thresholds correlated with use of the high index material with the lowest absorption.

1982 was also the year in which it was first reported that a damage facility had been established at Loughborough\textsuperscript{29}. It was based around a Lambda Physik EMG 200 excimer laser, giving a nominal 1 Joule of 248 nm radiation in a 30 ns pulse (FWHM). Among the results presented were those for damage testing on a variety of unidentified multilayer dielectric reflectors. It was noted that there was no great difference in damage thresholds whether a silica or Pyrex substrate was used and that when an excimer mirror was exposed to a fluorine environment, the damage thresholds was found to be markedly reduced. Other effects noticed were that there was a reduction in the damage threshold of used mirrors compared to unused mirrors of the same kind. The used mirrors had a large number of milky blotches visible when illuminated in white light which the authors attributed to fluorine attack on the multilayers and/or substrates.

Foltyn and Jolin the following year presented results of an extensive survey of materials and vendors for multilayer dielectric reflectors at both 248 nm and 351 nm\textsuperscript{30}. The laser pulse lengths at 248 nm and 351 nm were 15 ns and 12 ns FWHM respectively, and the pulse repetition frequency was 35 Hz. Both sets of results were generated with a nominally 0.5 mm mean spot diameter. Briefly, damage threshold was defined as the zero-percent intercept of a damage probability curve, or alternately, as the highest fluence at which damage could not be produced.

During the course of testing hundreds of ultraviolet reflectors involving twelve different material combinations, multilayer stacks of Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} were seen to demonstrate a superior ability to withstand laser induced damage. In an attempt to explain the wide range of thresholds exhibited by different materials, two theoretical models were invoked. The first one was an avalanche breakdown process which was first put forward at the Boulder Damage Symposium in 1975\textsuperscript{31}, and the second was a model where strongly absorbing spherical inclusions are the absorbing defects\textsuperscript{32}. Unfortunately, it was alleged that neither the theory nor experiment was sufficiently mature to allow a conclusion about which model, if either, was correct.

Interestingly, in this paper, the authors presented the design of each coating which was:
where $S$ is the fused silica substrate, $H$ and $L$ are the quarterwave layers of the high and low index material and $n$ is the number of layer pairs deposited in order to achieve high reflectance. Although the emphasis had previously been on reflectors, the authors also showed results that were obtained on AR coatings using different designs. These results are shown below and illustrate that the damage thresholds for AR's can be as high as for reflectors composed of the same materials.

<table>
<thead>
<tr>
<th>Design*</th>
<th>Threshold (J/cm$^2$) 248 nm, 15 ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S\text{HL}$</td>
<td>3.4</td>
</tr>
<tr>
<td>$S\text{LLHL}$</td>
<td>6.0</td>
</tr>
<tr>
<td>$S\text{L'LHL}$</td>
<td>5.1</td>
</tr>
<tr>
<td>$S\text{L'LHL'}$</td>
<td>4.9</td>
</tr>
</tbody>
</table>

* $S$ = Substrate (Suprasil 2), $H = \text{Al}_2\text{O}_3$, $L = \text{SiO}_2$, $L' = \text{MgF}_2$.

A review of all damage threshold measurements performed at LLNL at wavelengths of 248 nm and 251 nm was published the following year$^{33}$ and adequately summarises all test runs done since 1980. A lot of the preceding may be found in this paper which represents a good synopsis of damage threshold as a function of many different parameters; coating material, HR's and AR's, single and multilayers, bulk damage, pulsewidth and film thickness. This review was later supplemented and updated by Rainer and Hildum$^{34}$.

In the same year it was announced that a new breed of coating based upon porous silica had been developed$^{35,36}$. The production of such coatings involved the preparation of a silica sol in ethanol from a high purity organic silicate starting material and application of this sol, by spin or dip, to substrates at room temperature followed by an air dry. No further processing was required and it was found that the coatings obtained had a high damage threshold as well as exhibiting excellent optical performance. For instance, initial damage testing experiments yielded thresholds between 4 and 5 J/cm$^2$ at 248 nm with a 15 ns pulse, rising to 8.5 - 10 J/cm$^2$ at 346 nm using a 0.6 ns pulse. Such coatings were to become the focus of much attention during the following years.

Colloidal coatings also came under study by researchers at the Rutherford Appleton
Laboratory (RAL) who investigated the damage thresholds of colloidal silica (COLSI) coatings at 1.06 μm and 248 nm\(^3\). For the purposes of brevity only those results for 248 nm will be given. The technique used for applying the coatings was by spinning. Continuous coatings by spinning and dipping have been the subject of considerable effort in the past\(^{38}\). The workers at RAL found that it was possible to deposit mixed glass composition and most oxide dielectrics from solution by this technique. Overcoatings had previously been shown to be a possible means of preventing COLSI coating contamination in vacuum systems. A fresh COLSI coating was placed in a vacuum chamber, using no special materials or precautions to minimise the presence of hydrocarbon vapours, and allowed to become contaminated over a 24 hour period. It was found that the transmission fell by 4 % - 7 % over a wavelength range 400 nm - 800 nm. The coating was then baked in air for 2 hours at a temperature of 110 °C and remeasured. It was found that the optical performance of the film was completely recovered.

The results below show that high damage thresholds are easily achieved using these materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Damage Threshold J/cm(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\lambda = 248) nm, (t = 10) ns</td>
</tr>
<tr>
<td>silica substrate (uncoated)</td>
<td>17</td>
</tr>
<tr>
<td>COLSI coating on silica using</td>
<td>2</td>
</tr>
<tr>
<td>undistilled material</td>
<td></td>
</tr>
<tr>
<td>COLSI coating on silica using</td>
<td>8</td>
</tr>
<tr>
<td>distilled material</td>
<td></td>
</tr>
<tr>
<td>Evaporated AR coating on silica</td>
<td>2</td>
</tr>
<tr>
<td>(various)</td>
<td></td>
</tr>
</tbody>
</table>

A fully automated damage test facility based at the Laser-Laboratorium Göttingen was reported for routine measurements on UV optical components\(^{39}\). This was set up as part of the EUREKA program 'High Power Excimer Lasers'. The experimental arrangement used for damage determination includes a dielectric filter with angle-dependent transmission. By rotating this attenuator with the help of a computer controlled stepper motor the output energy of the employed excimer laser (EMG 202 MSC ILC, Lambda Physik), and hence energy density on the target, could be varied over almost two orders of magnitude. The necessary fluence values for controlled damage were obtained by focusing the beam onto the sample with a spherical lens.
Three diagnostic beams were derived for characterisation of the test pulse, i.e. measurement of pulse energy with a pyroelectric detector, temporal waveform with a vacuum photodiode and the spatial profile for each irradiating laser pulse. The profiling system consisted of a special UV sensitive video camera and a PC-based digital image processing board (frame grabber). The details of this system are described elsewhere\textsuperscript{40}. Damage thresholds were defined as the average of the lowest damaging and highest non-damaging fluence. Single pulse damage thresholds have been measured for some unidentified HR coatings at 248 nm and 193 nm. It was found that damage is dominated by impurities in the dielectric coating. Evidence for this was provided for by examination of video microscope images taken before and after irradiation with 50 pulses of 1.5 J/cm\textsuperscript{2} at 248 nm which showed that damage originated at defect or impurity sites which were visible before testing.

In a few cases, however, it was observed that laser induced changes on the sample, as seen by video microscopy, did not necessarily correlate with functional failure of the component. Hence an alternative technique was applied for damage recognition. This was performed with the help of a beam splitter (see below). The UV radiation is reflected from the sample at normal incidence and measured with a pyroelectric detector. Above the damage threshold, the reflectivity drops drastically with increasing fluence, since increasing portions of the HR coating are ablated.

By proper evaluation of the pyroelectric signals with the help of a digital storage oscilloscope as well as averaging over many pulses, a sensitivity $< 0.2\%$ is achievable. This functional test can also be performed in a similar way for the transmitted signal in the case of substrates or AR coatings.

The next major damage testing results were presented by Itoh et al\textsuperscript{41} in Japan.
high index materials used were $\text{Al}_2\text{O}_3$, $\text{Sc}_2\text{O}_3$, $\text{ZrO}_2$, $\text{HfO}_2$ and $\text{Y}_2\text{O}_3$, and the low index materials were $\text{SiO}_2$ and $\text{MgF}_2$. The fluence from an excimer laser (20 ns FWHM) was able to be varied from 0.3 J/cm$^2$ to 8.0 J/cm$^2$ with a constant spot size of 550 μm. The threshold was determined as the mean value of the maximum fluence without damage and the minimum fluence with damage. The single pulse damage threshold was detected in a variety of ways. One method involved detecting the scattered light of a HeNe laser passing coaxially with the excimer laser beam. In the second method, the damage site was observed from the back side with a low magnification optical microscope. Finally, the sample surface was observed with a Normarsky optical microscope with a magnification of 1000. The damage sites were also observed with a scanning electron microscope (SEM). The results are summarised below.

In the case of the AR's it was found that damage occurs at the interface of the film and substrate as no damage was observed by the SEM and that the undercoat was not effective for increasing damage thresholds. The morphology of the damage sites resembled a bubble of size 1 μm with an 'orange peel' texture for all coating materials. As the fluence was increased, the diameter of the bubble did not grow but increased the number of damage sites within the irradiated region suggesting that the damage mechanism was non-absorbing in nature.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specifications</th>
<th>Damage Threshold (J/cm$^2$, 248 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}_2\text{O}_3/\text{SiO}_2$</td>
<td>OC:SiO$_2$</td>
<td>2.29</td>
</tr>
<tr>
<td>Sc$_2$O$_3$/SiO$_2$, MgF$_2$</td>
<td>OC:SiO$_2$, NQW-I</td>
<td>1.37</td>
</tr>
<tr>
<td>Sc$_2$O$_3$/SiO$_2$, MgF$_2$</td>
<td>OC:SiO$_2$, NQW-II</td>
<td>1.35</td>
</tr>
<tr>
<td>Sc$_2$O$_3$/SiO$_2$, MgF$_2$</td>
<td>OC:SiO$_2$</td>
<td>1.65</td>
</tr>
<tr>
<td>ZrO$_2$/SiO$_2$</td>
<td></td>
<td>&lt;0.6</td>
</tr>
<tr>
<td>HfO$_2$/SiO$_2$</td>
<td></td>
<td>0.8</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$/SiO$_2$</td>
<td>OC:SiO$_2$, NQW-I</td>
<td>1.66</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$/SiO$_2$</td>
<td>OC:SiO$_2$</td>
<td>1.56</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$/SiO$_2$</td>
<td>OC:MgF$_2$</td>
<td>6.50</td>
</tr>
<tr>
<td>HfO$_2$/SiO$_2$</td>
<td>OC:MgF$_2$</td>
<td>2.31</td>
</tr>
<tr>
<td>$\text{Y}_2\text{O}_3$/MgF$_2$</td>
<td>OC:MgF$_2$</td>
<td>2.35</td>
</tr>
</tbody>
</table>

Measurements on the HR's showed that the highest threshold was obtained when the high index material was $\text{Al}_2\text{O}_3$. This higher threshold was got in the sample with a half-wavelength overcoat of the low index material. In these HR coatings, damage started
from the surface and grew with increasing fluence.

Another point worth mentioning is the localisation of the damage. In the HR coatings, damage started in the centre of the beam even if the power distribution of the laser beam is uniform. The temperature was the highest in the centre of the beam, but the electric field and the distribution of the thermal stresses was uniform within the beam.

The effects of the film design was also considered. Non-quarter-wavelength film of high reflection coatings did not give higher damage thresholds. This showed that the electric field was not the main cause of damage. However, the sample with the overcoat had a higher threshold than the normal film. When the over-coat is of half-wavelength thickness, it has no effect optically and it was suggested that the overcoat acts to suppress the evaporation of the top layer of the stack. It was also shown that there was a strong correlation between damage threshold and absorption.

Damage threshold results of thin films deposited by different techniques were presented the next year by Starke et al. The damage testing was performed by the Laser-Laboratorium, Göttingen, with a KrF excimer laser with a gaussian spatial profile with a 1/e² crosssection of 0.65 mm and a pulselength of 25 ns (FWHM). The threshold values were determined by a 'one on one' procedure. Film damage was detected by on-line dark field microscopy. The samples tested were single HfO₂ and Al₂O₃ films of arbitrary thickness between 250 and 650 nm and highly reflecting quarter wave optical thickness (QWOT) stacks at 248 nm with SiO₂ as the low index material.

The different deposition processes used to produce the films were Reactive Ion Plating (RIP), Ion Beam Sputtering (IBS) and electron beam evaporation coating. The damage threshold results (J/cm²) for the HfO₂ coatings are presented below:

<table>
<thead>
<tr>
<th>Coating Process</th>
<th>Single Layers</th>
<th>QWOT: (HfO₂/SiO₂)₁₁/HfO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>RIP</td>
<td>0.5-0.75</td>
<td>0.5-0.95</td>
</tr>
<tr>
<td>e-beam</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>IBS</td>
<td>0.15-0.3</td>
<td>not tested</td>
</tr>
</tbody>
</table>

It was seen that the sputtered HfO₂ films had very low damage thresholds compared with e-beam coatings. The appearance of the damaged areas of the film showed that the damaging mechanism was intrinsic. The high absorption of the film caused the
temperature to exceed the melting point. This behaviour was supported by the observation that the damage threshold was correlated to the film absorption. The higher the absorption the lower the damage threshold as had already been shown by Itoh et al\textsuperscript{41}.

These films exhibited an extrinsic damage mechanism. Damage by the laser only occurred in the vicinity of included microscopic impurities. Values of damage threshold are between those of e-beam and IBS coatings. There was found to be no correlation between damage threshold and absorption or film thickness. IBS HfO\textsubscript{2}/SiO\textsubscript{2} alternating layer systems damaged at included defects also. Damage thresholds were in the same range as those of single HfO\textsubscript{2} layers. The values of conventional coatings were not reached.

The damage mechanism at 248 nm in Al\textsubscript{2}O\textsubscript{3} is of the defect induced type irrespective of the coating process. Again there was no correlation between damage threshold and layer thickness or film absorption, (see below):

<table>
<thead>
<tr>
<th>Coating Process</th>
<th>Single Layers</th>
<th>QWOT: (Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2})\textsuperscript{22}/Al\textsubscript{2}O\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>RIP</td>
<td>2.8-3.85</td>
<td>1.7-2.5</td>
</tr>
<tr>
<td>e-beam</td>
<td>2.3</td>
<td>4.12</td>
</tr>
<tr>
<td>IBS</td>
<td>1.8-2.4</td>
<td>1.8-3.5</td>
</tr>
</tbody>
</table>

The most resistant Al\textsubscript{2}O\textsubscript{3} single layers were produced by RIP where damage thresholds of up to 3.85 J/cm\textsuperscript{2} have been measured. Values of the e-beam and IBS films were nearly equal, about 2.3 J/cm\textsuperscript{2}.

In the case of RIP, damage thresholds of Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2} multilayer coatings were lower than those of single layer Al\textsubscript{2}O\textsubscript{3} layers. Damage thresholds of ionplated SiO\textsubscript{2} layers were about 4.58 J/cm\textsuperscript{2} so it was surmised that this was not the cause of the degraded values of the multilayers. The effect of interface absorption was assumed to play a significant part in this. The highest damage thresholds were reached with conventional e-beam evaporation. IBS coatings were slightly more resistant but the values of e-beam coatings were not reached. Irrespective to the coating process the damage mechanism of Al\textsubscript{2}O\textsubscript{3}/SiO\textsubscript{2}-multilayer coatings was of the defect induced type.

In conclusion it was noted that RIP and IBS were successful techniques to produce optical thin films with high packing densities. Films of HfO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} with
higher refractive indices than e-beam films were able to be deposited. In particular SiO$_2$ films showed no observable water content, which is present in films deposited by conventional coating technologies. IBS films showed high absorption losses and low damage thresholds which was attributed to film contamination in the coating chamber. With RIP single layers of SiO$_2$ and Al$_2$O$_3$ were deposited which had low absorption losses and higher damage thresholds than e-beam evaporated films. In RIP HfO$_2$ films no improvement in these properties was seen. Damage thresholds of high reflecting QWOT stacks were found to be considerably lower than those of e-beam stacks. In the case of HfO$_2$/SiO$_2$ coatings, this was found to be consistent with the inferior properties of HfO$_2$ single layers. The low values of the RIP and IBS Al$_2$O$_3$/SiO$_2$ coatings were not explained.

A database of all work carried out at the LLNL was presented in the next year. This paper summarised work done over an eight year period plus selected results spanning over a fourteen year period at LLNL using thirteen different laser systems. The primary emphasis has been with the fundamental 1064 nm radiation by Nd:Yag. However, the results presented cover a wide range of wavelengths, pulse durations, (from < 1 ns to 84 ns), repetition rates and irradiation modes, from single shot to a variety of multiple-shot laser-conditioning techniques. Although not much data is presented for 248 nm radiation, it does provide a concise summary of the extensive database that exists at LLNL from 1064 nm to 248 nm.

The subject of the dependence of deposition parameters on damage threshold was again addressed by Kolbe et al. Conventional evaporation as well as IAD and IBS processes were used to develop low-loss dielectric mirrors and AR coatings for the wavelength range 130 to 250 nm. Firstly, single layers of SiO$_2$, Al$_2$O$_3$, HfO$_2$, AlF$_3$, MgF$_2$, LaF$_3$, NdF$_3$ and GdF$_3$ were deposited by conventional evaporation upon which the refractive indices, extinction coefficients and packing densities were measured. With optimised parameters, HR and AR coatings were deposited and integrated scatter measurements were performed on them. Damage testing at 193 nm and at 248 nm was performed but only the 248 nm data shall be presented here.

It was found that among the single fluoride layers, (which were all approximately 300 nm thick), a significant reduction in scatter was achieved by those films deposited by IAD or IBS. Although the data presented was only qualitative, it demonstrated that the microstructure of the layers deposited by IAD or IBS was advantageous for optical applications. Their extinction losses in the UV/VUV range, however, were significantly higher than those of layers deposited conventionally using advantageous
Among the multilayer stacks, like the single layer films, it was established that the integrated scatter values of nearly all mirrors deposited by IAD or IBS are smaller than those of the corresponding mirrors deposited conventionally. The damage thresholds of the mirrors are shown below:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conv.</th>
<th>IAD</th>
<th>IBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃/SiO₂</td>
<td>1.8-2.0</td>
<td>1.8-2.0</td>
<td></td>
</tr>
<tr>
<td>HfO₂/SiO₂</td>
<td>1.7-1.8</td>
<td>1.8-2.0</td>
<td></td>
</tr>
<tr>
<td>LaF₃/AlF₃</td>
<td>1.7-1.9</td>
<td>0.2-1.0</td>
<td>1.4-1.6</td>
</tr>
<tr>
<td>LaF₃/MgF₂</td>
<td>9.0-13.0</td>
<td>0.2</td>
<td>2.4-2.5</td>
</tr>
<tr>
<td>NdF₃/MgF₂</td>
<td>8.4-11.8</td>
<td>0.2-0.3</td>
<td>-</td>
</tr>
<tr>
<td>GdF₃/MgF₂</td>
<td>9.8-12.0</td>
<td>0.9</td>
<td>-</td>
</tr>
</tbody>
</table>

At both 193 nm and 248 nm similar tendencies were observed: the thresholds of mirrors containing oxide layers were rather small. The same was true for the fluoride mirrors deposited by IAD or IBS if compared to the corresponding conventional mirrors. In contrast to other published data, a clear superiority of the conventionally deposited fluoride mirrors over the oxide mirrors was seen.

The latest damage testing on dielectric multilayers at 248 nm were those performed by Izawa et al. HR coatings were prepared by evaporation. All coating materials except for AlF₃ were evaporated by using an electron beam. Only AlF₃ was evaporated by a thermally heated boat. This was because this material is known to easily splash when it is evaporated using an electron beam. The HR coatings were of quarter wave design for a normal incidence beam and each had a halfwave overcoating of low index material the same one of which was used in the main stack. The number of layers was about 50 for the Al₂O₃/SiO₂ HR coating, and about 30 for the other coatings. The substrate material was polished fused silica whose RMS roughness was 5 Å when measured with an atomic force microscope and 1 Å with a Zygo profilometer.

4.1.2.1 Summary

The above review represents almost all of the published work on damage threshold measurements performed at 248 nm on excimer laser components. Over thirty years of research has culminated in laser components being able to withstand over an order of
magnitude increase in power density since the early days of excimer laser research in the early 1960's. It has been found that in order to achieve high damage thresholds, not only must the constituent materials have to be of the utmost purity but their method of deposition must also be carefully considered to avoid contamination of the thin film. Work has also been performed on increasing the damage thresholds of thin films after they have been made by either additional overlayers or by illuminating the sample with low intensity laser irradiation. Such laser conditioning is still the subject of much research and results will be presented in this thesis which verify this latter technique as a possible means of increasing the efficiency of at least some thin film combinations. Finally, the choice of materials for laser mirrors and windows is probably the single most important factor in determining threshold limits for any particular multilayer combination. In this thesis much emphasis will be put on rare earth fluoride multilayers which have only recently been the subject of damage research and show some signs of being in some ways superior to conventional multilayer designs.

4.2 Damage Mechanisms

The damage of an optical thin film by short pulse laser irradiation can be considered to be due to a combination of three physical processes: the absorption of radiant energy, the heating of the impurities and adjacent film and the thermo-mechanical response of the film/substrate system. These processes do not occur independently and may operate to some extent after the laser pulse. The complete process of absorption depends strongly not only on the optical properties of the material but also on its temperature and state. However, because it is the purpose of many damage test studies to determine the physical processes that occur whose onset precede material damage, investigation of isolated mechanisms can be of great assistance in determining the role of material and design variables in laser-material interactions.

The three models most frequently used in describing damage mechanisms in thin films are the electron avalanche model, the multiphoton ionisation model and enhanced absorption by impurities embedded in the thin film as well as a combination of two or more of them. Because of uncertainties in many of the parameters that each theory employs, none can be relied upon to make accurate predictions of damage thresholds. For example, the multiphoton absorption and electron avalanche models depend strongly on the band structure of the material; whereas the impurity model requires knowledge of the size, shape, type and distribution of the inclusions.
The three basic models will be outlined below although it must be emphasised that each theory is ongoing with modifications and improvements being made on a continual basis. The interested reader is therefore referred to the Proceedings of the Boulder Damage Symposia which is held annually for the most up to date numerical studies.

4.2.1 Electron Avalanche Model

In the electron avalanche model of dielectric breakdown, a small number of 'seed' electrons drift upward in energy in the conduction band through interaction with the laser electric field, suffering retardation losses due to scattering from phonons. Each electron undergoes a random walk of progressively increasing kinetic energy until it reaches a threshold energy \( E_t \). The electron then drops to the bottom of the conduction band after creating an exciton. Rapid photoionisation of the exciton injects a second electron into the conduction band. If the electric field is high enough, sufficient numbers of electrons are created (~ \( 10^{18} \text{ cm}^{-3} \)) to damage the sample through joule heating.

The rate at which the electron gains energy from the electric field is given by the following relation\(^46\):

\[
\left( \frac{dE}{dt} \right)_G = \frac{e^2 \tau_k E^2}{m^* (1 + \omega^2 \tau_k^2)}
\]  \(4(1)\)

where \( \omega \) is the frequency of the electric field, \( \tau_k \) is the relaxation time of the electron, \( m^* \) is the effective electron mass, \( e \) is the electronic charge and \( E \) is the laser electric field.

The rate of energy loss due to phonon scattering is given by:

\[
\left( \frac{dE}{dt} \right)_L = \frac{\hbar \omega_p}{\tau_i}
\]  \(4(2)\)

where \( \omega_p \) is the average phonon frequency and \( \tau_i \) is the relaxation time for large and small angle scattering. Damage may be assumed to occur when the rate of energy gain is greater than the rate of loss i.e.:
Most theories of electron-avalanche breakdown assume an initial electron density of $\sim 10^{10} \text{ cm}^{-3}$ before laser illumination. Additionally, the (temperature)$^2$ dependence of the lattice constant and phonon frequencies are generally ignored. This results in an overestimation for damage thresholds, for instance, the calculated breakdown for sodium chloride is $9.0 \text{ MV/cm}$ at $10.6 \mu\text{m}$ which is over four times the observed value of $2.1 \text{ MV/cm}$.

The value of $\tau_k$ plays a very important part in the energy gained from the electric field. The energy gain will be small when the electron momentum is rapidly altered by large angle scattering from phonons, i.e. with small $\omega \tau_k$ the phonon collisions inhibit the acceleration of the electron by changing its momentum to the opposite direction imparted by the electric field. Equally as much, in the other limit of $\omega \tau_k \approx 1$, i.e. slow momentum change, the energy gained by the electron will again be small. Here the electron is accelerated and then decelerated by the oscillating field. This process will happen many times before the electron will undergo a momentum changing collision. The energy gained in one half of the cycle is lost during the next. The momentum energy gain, a function of the momentum relaxation time $\tau_k$ occurs at $\omega \tau_k = 1$. At this point on average the electron momentum is reversed every time the electric field is reversed.

Sparks has demonstrated that the experimental data contradicts the assumption of initial electrons since the calculated conductivity for an electron density of $10^8 - 10^{10}$ cm$^{-3}$ will lie in the semiconductor range rather than the dielectric range. Also, dielectric conductivities lie in the range $10^{-14} - 10^{-22} (\Omega\text{cm})^{-1}$ and if the value of $10^{-14} (\Omega\text{cm})^{-1}$ is taken as a lower limit and substituted in the conductivity equation, or rather $10^{-12} (\Omega\text{m})^{-1}$, and taking $2 \times 10^{-15} \text{ s}^{-1}$ as the value for $\tau_e$, and $m^*$ shall be approximated to the electron rest mass (9.1 x $10^{-31} \text{ kg}$), we obtain an electron density of:

$$N_e = \frac{m^* \sigma}{e^2 \tau_e} = 2 \times 10^{10} \text{ m}^{-3} \text{ or } 2 \times 10^4 \text{ cm}^{-3}$$

The probability of finding an electron in the focal volume will be proportional to $N_e V$, where $V$ is the interaction volume. For good focusing, $V$ is about $10^{-10} \text{ cm}^3$. We therefore have $N_e V \sim 2 \times 10^{-6}$. This negligibly small probability of finding an electron in the interaction volume indicates that there is not a sufficient electron density to
initiate damage. To overcome these difficulties, Sparks et al.\textsuperscript{49} introduced a number of modifications to the electron avalanche theory:

- electrons are not restricted to only interacting with phonons in the first Brillouin zone as they were in previous theories;
- both optical and acoustic phonons are assumed to interact with electrons;
- the electron phonon scattering rate depends on the electron energy;
- the starting electrons are not present initially and must be generated by the laser pulse;
- the lattice constant and the phonon frequencies are temperature dependent.

The observed values of breakdown were in very close agreement with the theoretical thresholds calculated using these new modifications. Figure 4.2.1a shows the results of theoretical\textsuperscript{46} and experimental\textsuperscript{50} breakdown thresholds found for a variety of materials tested at 1.06 $\mu$m. The calculated thresholds for wavelengths less than 1 $\mu$m were, however, less successful in agreeing with experiment. Multiphoton absorption was therefore invoked as a damage mechanism for these wavelengths and will be outlined in a later section.

Electron avalanche theory has now been established as a damage mechanism and it will now be gone into in more detail.
There are three stages in the breakdown process:

4.2.1.1 Liberation of Initial Electrons

Several sources exist from which the initial electrons could come. One of these could be shallow traps which result in chemical imperfections, colour centres etc.; for example the F-centre which is comprised of an electron localised at a cation vacancy is located within 1-3 eV of the conduction band of the host lattice. In NaCl, the F-centre lies about 2.4 eV below the conduction band. Hence two photons from Nd lasers (2.33 eV) can generate an electron in NaCl by two photon absorption. However, at 10.6 μm (0.112 eV), the 2.4 eV transition would require over 21 photons. It is likely therefore that other mechanisms are responsible for generating the initial electrons at this wavelength. In general, the supply of initial electrons has various origins and the exact quantities of electrons made available will depend upon several factors: the damage threshold, pulse duration, laser photon energy and the energy gap of the impurity.

Finally, as further evidence that the initial electrons causing the avalanche have to be generated, Yasojima et al\(^\text{31}\), measured the laser induced breakdown in KCl, KI and LiF. A DC bias was applied to the sample in order to collect the charge induced by the laser pulse. The results showed that the collected charge increased as \(I^n\) (where \(I\) is the laser intensity and \(n\) is a constant) at power levels below the breakdown threshold. In the pre-breakdown region, however, the collected charge increased exponentially with increasing laser intensity leading to final breakdown. From these data the mechanism of damage was concluded to progress as follows: free electrons from shallow donor levels such as colour centres are accelerated by the laser electric field and cause electron-avalanche, which is analogous to the case of DC breakdown.

4.2.1.2 Electron Multiplication and Plasma Production

The second stage in the breakdown process is the multiplication of the initial electrons by the incident photons. Energy is supplied to the generated electrons which, at the same time, undergo inelastic collisions with the lattice at a rate of \(t_k^{-1}\) thus producing more electrons and so the avalanche proceeds. The exponential growth of the electron density may be described by the following relation\(^47\):

\[
N(t) = N_0 e^{\frac{E_0}{kT}}
\]

4(5)
where \( N_0 \) is the initial number of electrons per unit volume, \( E(t) \) is the laser pulse electric field, \( t_p \) is the pulse duration and \( \eta \) is the probability per unit time for an electron to undergo an ionising collision, this is equivalent to the probability for an electron to reach the ionisation energy. Breakdown occurs when \( N \) exceeds \( 10^{18} \, \text{cm}^{-3} \). At this density the energy deposition rate by absorption of laser light is significant and consequently a plasma is formed.

Experimental evidence has shown that the plasma build-up time is very short. For example Anthes et al.\(^{52}\) used a streak camera with a resolution of 6 ps to monitor plasma build-up in the breakdown of silica by 25 ps 532 nm laser pulses. They measured a build-up time of less than 10 ps (and this time may have even been limited by the resolution of the camera).

### 4.2.1.3 Heat Transfer from the Plasma to the Lattice

The final stage of the breakdown process follows the production of the plasma. The plasma absorbs energy from the laser pulse and the rate of absorption \( W(t) \) at a time \( t \) is given by\(^{46}\):

\[
W(t) = \frac{e^2 \tau_k}{m^*} \frac{|E(t)|^2 N(t)}{1 + \omega^2 \tau_k^2}
\]

The temperature of the lattice can then be calculated by simply integrating the above equation to give:

\[
T(r, z, t) = \frac{1}{C} \int_{-\infty}^{t} W(r, z, t) \, dt
\]

where \( C \) is the heat capacity of the dielectric. The major heating of the lattice will begin at this stage, the plasma channelling energy from the laser to the lattice. It is evident that the thermal properties of the sample are important at this stage. Associated effects such as thermally induced stress and crack production may be important in other materials also such as thin film coatings.

The electron avalanche theory, whilst providing a framework within which to operate, suffers from several limitations. Its frequency dependence is unsure, needing other mechanisms capable of generating the initial seed electrons and, as Sparks\(^{46}\) has
pointed out, the probability of finding an electron in the focal volume experiencing large angle phonon collisions in phase with the optical field is negligible. Since then other mechanisms have been investigated for providing and sustaining an avalanche. These include mechanisms such as photon-electron-phonon processes and intra-band transitions.

4.2.2 Multiphoton Absorption

The incentive to understand multiphoton processes, (a good review of which is given by Mahr\textsuperscript{53}), increased with the arrival of UV and VUV lasers. Early on in the days of the first UV lasers it was thought that NaCl would be an ideal window material. However, it was found that working at the KrF wavelength of 248 nm (5.0 eV) that 50% losses were occurring due to two photon absorption. This could quickly lead to damage as the free electrons generated were numerous. As a result of this the interplay between electron avalanche and multiphoton ionisation has been considered and a number of discussions can be found in the literature\textsuperscript{54-56}.

The absorption of light by a material can be expressed as an exponential attenuation:

$$I(x) = I_0 e^{-\alpha x}$$ \hspace{1cm} 4(8)

Here the attenuation is the result of multiple individual absorptions of single photons by the material's system. This is referred to as linear absorption as the differential attenuation rate is proportional to the first power of the light intensity i.e.:

$$\frac{dI(x)}{dx} = -\alpha I_0$$ \hspace{1cm} 4(9)

To be more general, however, the other attenuation terms should also be included into the equation, especially when the light intensity reaches $10^8$ to $10^9$ Wcm$^{-2}$ regime. These levels are easily achieved by lasers. The differential attenuation of the above relation then becomes:

$$\frac{dI(x)}{dx} = -\alpha I - \beta I^2 - \gamma I^3$$ \hspace{1cm} 4(10)

where $\beta$ is the two photon absorption coefficient and $\gamma$ is the three photon absorption coefficient. The nth term will be proportional to $I^n$. 

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The occurrence of multiphoton processes is not only related to the light intensities but also to the energy conservation relations. In materials with a band gap greater than the energy of a single photon but less than the energy of two photons it is possible for transitions to occur by the simultaneous absorption of two photons from a sufficiently intense laser beam.

Although the expression for the two photon absorption transition rate can be written down from second order perturbation theory it has proven difficult for workers to proceed further from the basic equation. A different approach was then developed by Keldysh\textsuperscript{57} by directly modifying the wave functions to account for the strong electric field. From his expressions values have been predicted for the breakdown thresholds of a number of crystals\textsuperscript{58}. It has been calculated\textsuperscript{58} that the electric field strengths needed for breakdown caused solely by multiphoton processes of an order higher than four are much larger than measured experimental values, and this mechanism can be thought of playing only a minor role.

For cases where the dielectric band gap is around four times the photon energy, the damage field strengths predicted by the Keldysh formula are smaller than those obtained by the avalanche theories and in closer agreement with experiment. By assuming the two theories to be independent mechanisms, models combining the effects of both have been developed\textsuperscript{59} and closer agreement with experiment has been achieved.

4.2.3 Embedded Impurity Model

The model that is usually used in the study of impurity dominated damage starts with a spherical particle embedded in a non absorbing host\textsuperscript{60-64}. The damage threshold is defined as that moment when the surface of the impurity reaches some critical temperature. In practice, it may be the case that the threshold is not sensitive to the absolute temperature since the rate of change of temperature with respect to time is very large. Whatever temperature is chosen, though, must be material dependent (e.g. its melting point).

The temperature, $T$, as a function of position, $r$, from the centre of the impurity at time $t$ is given by\textsuperscript{65}:
\[
\frac{1}{D_i} \frac{\partial T_i}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T_i}{\partial r} \right) + \frac{A}{K_i}, \quad 0 \leq r < a
\]

\[
\frac{1}{D_h} \frac{\partial T_h}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial T_h}{\partial r} \right), \quad r > a
\]

\[T_i(r) = T_h(r) = 0, \quad t = 0\]

where \(D\) is the thermal diffusivity, \(K\) is the thermal conductivity, \(a\) is the radius of the impurity and the subscripts \(i\) and \(h\) refer to the inclusion and host respectively. \(A\) is a source term which relates the rate at which heat is deposited in the host by the inclusion and can be rewritten in terms of the incident laser intensity, \(I\), and the absorption cross section, \(Q\), as:

\[A = \frac{3QI}{4\pi a^3}, \quad 0 < t < t_i\]

\[A = 0 \quad t > t_i\]

where \(t_i\) is the laser pulse duration.

It is unknown at present what the thermal contact is like between the inclusion and host so ideal boundary conditions are assumed:

\[T_i = T_h\]

\[K_i \frac{dT_i}{dr} = K_h \frac{dT_h}{dr} \quad \text{at} \quad r = a\]

The exact solution to the differential equations at the top of this page have been solved with the above boundary conditions to give the result\(^{65}\):
\[ T = \frac{3Ql}{4\pi K_h a} \left\{ \frac{1}{3} K_n b + \frac{1}{6} \left( 1 - \frac{r^2}{a^2} \right) \right\} \]

\[ - \frac{2ab}{\pi} \int_0^{\pi/2} \frac{\sin y \cos y \sin \left( \frac{r}{a} \right) \, dy}{c \left( \cos^2 y + b^2 \sin^2 y \right)} \]

4(15)

where \( b = \frac{K_n}{K_h} \sqrt{\frac{D_h}{D_k}} \), \( c = 1 - \frac{K_n}{K_h} \), and \( \gamma = \frac{a^2}{D_h} \)

This solution is based upon the assumption that the absorption cross section along with the thermal constants are independent of temperature.

Because an optical thin film is typically of the order of an optical wavelength or less in thickness, the radius of any inclusion will in most cases be half a wavelength or less. For these sized particles, the absorption cross section is derivable from Mie scattering theory\textsuperscript{66,67} which depends on the complex refractive index and the radius of the inclusion together with the dimensionless size parameter \( q = 2\pi a/\lambda_h \) where \( \lambda_h = \lambda_n/n_h \) is the wavelength of the radiation in the host. Here, \( \lambda_n \) is the wavelength of the radiation in free space and \( n_h \) is the real part of the refractive index of the host.

Using equation 4(15) for \( T \) and the well known expression for Mie scattering\textsuperscript{66,67}, the incident laser intensity \( I \) that must be applied for a time \( t \) in order to raise a point at \( r \) to a temperature \( T \) can be determined.

The above model has been used by several authors\textsuperscript{63,64,68,69} with varying amounts of modifications and has lent itself to considerable refinement over the years. For instance Koldunov et al\textsuperscript{70} presented a model of laser induced damage which related the damage to thermal explosion of the inclusion and for this they introduced modified parameters for the inclusion absorption coefficient. No longer was it assumed to be independent of temperature but very strongly related to temperature as soon as an 'activation energy' had been reached. Also, Fuka et al\textsuperscript{71} modified the theory to allow variations in the thermal conductivities and the imaginary part of the refractive index of a thin film. Comparison to experimental results showed good agreement although the authors stressed that the model probably still needed further adaption.
4.2.4 Surface Damage

It is a well documented observation that the bulk damage threshold of a transparent material is substantially greater than that at its surface. It has been found that surfaces of such bulk materials, even those that are scrupulously cleaned or that have been obtained by cleavage in vacuum, have a lower damage threshold than the bulk. For laser glass and sapphire, the best obtainable surface damage thresholds have been ~ 5 times less than that of the bulk\textsuperscript{72-74}. If the surface is contaminated with additional dirt, the damage threshold may be even lower. Another major contribution to low surface damage threshold is the presence of surface imperfections resulting from the polishing process in the form of grooves, cracks or pores\textsuperscript{75}. If it is to be assumed that the dimensions of such imperfections are small compared to the wavelength, since the surfaces are assumed to have been prepared to optical quality, then the electric field configuration in the neighbourhood of these physical imperfections can be calculated by the methods of electrostatics\textsuperscript{76}. Figure 4.2.4a shows a linearly polarised wave normally incident on a dielectric with dielectric constant \( \varepsilon = n^2 \) (where \( n \) is the refractive index of the material). The case for a spherical pore, a cylindrical groove and a crack in the shape of an oblate spheroid will be considered and the strength of the enhanced electric field will be given at points A, B and C respectively. Typical dimensions are \( c = 0.1 \mu m \), \( a = 1 \mu m \) and \( r = 0.1 \mu m \),

![Diagram](image)

**Fig. 4.2.4a**

The field inside the cavity, \( E_0 \), is given in terms of the field inside the uniform dielectric as follows:
where \( L \) is the appropriate depolarisation factor which depends on the shape of the imperfection. Note that the field at points A, B and C in the dielectric is equal to the field in the pore.

a) Sphere

For the case of the sphere, \( L = 1/3 \) and

\[
E_{\text{enh}} = \frac{3\epsilon}{2\epsilon+1} E_0
\]

b) Cylinder

For the cylinder, with its axis perpendicular to the paper, \( L = 1/2 \) and

\[
E_{\text{enh}} = \frac{2\epsilon}{\epsilon+1} E_0
\]

c) Crack

In this case, \( L = 1 - \frac{\pi}{2} \frac{c}{a} \) or \( L = 1 \) for \( \frac{c}{a} \ll \frac{1}{\epsilon} < 1 \)

where \( c \) is the width of the crack and \( a \) is its length. In this limit, the field at point C is

\[
E_{\text{enh}} = \epsilon E_0
\]

The greatest enhancement, especially for a high index material is thus caused by a crack. As it is the interaction between the electric field and the surface via absorption and subsequent avalanche, such defect sites are highly susceptible to early damage.

As mentioned earlier, the damage threshold at the surface could be increased and made equal to the bulk damage threshold by extremely fine polishing and one would not need to eliminate cracks and scratches with dimensions less than 0.01 \( \mu \text{m} \). However, even with this small dimension there would still be enhancement in the electric field,
but the region of enhancement is so limited that the avalanche could not develop. If the
diffusion time of the carriers out of the edge region is shorter than the duration of the
laser pulse then the damage threshold will be increased, compensating for the decrease
in damage threshold due to field enhancement.

The implications for coated surfaces is serious. From microscopic examination it is
known that most coatings faithfully replicate the surface contour of the substrate so
the coatings will experience an enhanced electric field also. Experiments performed on
three AR-coated germanium samples deposited in the same run showed that the
sample with visible polishing scratches failed at 70% of the damage threshold of the
other two which did not have visible scratches.

4.3 Damage Test Facility

The damage test facility at Loughborough was first conceived in 1981 and has been
used since then to give UV damage thresholds on a variety of samples from highly
reflecting multilayer thin films to bulk crystalline materials. It is centred around a
Lambda Physik EMG 200 excimer laser giving a nominal 1 J of energy at 248 nm at a
maximum repetition rate of 1 Hz. The pulse duration is between 25 and 30 ns between
the half power points. The energy fluctuation from pulse to pulse is around 5%.
However, over a period of time, the output energy can decrease and so it is of primary
importance to monitor the energy output from the laser on a pulse to pulse basis.
Though other wavelengths have been used, it is now primarily a source for 248 nm
radiation, using krypton and fluorine as the lasing constituents and helium as a buffer
gas.

The facility has changed substantially since the early days where the image processing
side of the characterisation of the excimer laser beam relied upon an Apple II
microcomputer but nowadays processing is much faster as an IBM compatible
computer is now used, speeding things up considerably. The energy density in the
target plane was initially varied by moving the sample to, or away from, the focus thus
changing the spot size and allowing possible spurious effects of air breakdown at the
focus. This arrangement was improved over the years by having the sample placed
stationary in the target plane and having a variable length dye cell attenuator placed in
the beam path and a variety of calibrated UV neutral density filters. The energy of the
beam can then be attenuated in a very controlled manner. A computer and a frame
store is now in use that profiles the beam after a damage run is finished thus making
the old method of profiling the beam by burn paper patterns obsolete. Damage
detection is performed by a schlieren imaging, or scattering, technique that is both
sensitive and easy to set up.

4.3.1 Optical Arrangement

The optical arrangement of the damaging side of the apparatus is shown in schematic
form in Fig. 4.3.1a. Radiation from the laser passes through an aperture consisting of
four glass microscope slides that act to limit and shape the beam. It then passes
through the dye cell attenuator. This consists of a piston and cylinder arrangement with
fused silica windows which is filled with a UV absorbing dye (rhodamine 6G)
dissolved in distilled water. As the piston is pulled out, the dye solution is drawn into
the cell from a reservoir, and the path length of the laser light through the dye
increases, decreasing the beam energy.

The energy of each laser pulse is monitored by splitting off 8% of the laser output at a
fused silica plate. This known fraction is then incident upon a calibrated Gentek energy
meter. By looking at the peak of the output voltage on an oscilloscope, it is possible to
infer the energy of the pulse that is hitting the target, if allowance is made for any
neutral density filters that are placed before the target.

The laser pulses are focused onto the sample by a 20 cm focal length fused silica lens.
This produces a focal spot of approximately 1.5 mm by 0.75 mm - the beam being
essentially gaussian in one direction and top-hat in the other, (see Fig. 4.3.1b). This
allows high enough fluences to be obtained to damage most materials.
4.3.2 Damage Detection Arrangement

A schlieren imaging system is used to monitor any damage caused by the incident laser beam by having the light from a small power HeNe laser shone through the site where irradiation takes place, Fig. 4.3.2a. The amount of illumination may be varied using a rotating polaroid filter as the output from the HeNe laser is linearly polarised. Two simple crown glass lenses then image the site onto a CCD camera with a magnification
magnification such that the area of the excimer pulse on the sample will nearly fill the whole of the TV screen monitor. The first lens has a focal length of approximately 20 cm and the second a focal length of around 5 cm. The insertion of a knife edge at the focus of the first lens allows acquisition of schlieren images. The knife edge is positioned so that it just cuts off the undeviated laser beam. This first lens is of comparatively low f/number (large aperture) so that it receives a lot of scattered light as soon as the optic under test damages. This is a highly sensitive technique for damage detection as practically any modification to the surface of the sample by the excimer laser pulse will produce scattered light. The onset of damage therefore becomes immediately apparent as an increase in the light level of the schlieren image appearing on the monitor.

By adjusting the energy of the beam via the dye cell attenuator and insertion of neutral density filters and reading off the energy contained in the beam via the Gentek, one is able to roughly estimate that energy at which the sample begins to damage.
4.3.3 Operation

In order to take meaningful data it is essential that the testing methodology is identical for each sample. This means that the same operating procedure is used for each sample so that they may be compared to each other under identical irradiation conditions. The actual damage threshold is quite hard to define, depending as it does on several factors - spatial and temporal properties of the laser and the area of irradiation. Damage threshold is therefore not a well defined number as one particular site may not damage after many shots whereas another site may damage after only one shot at the same fluence.

It is normal practice for damage data to be presented in terms of probability of damage at a given fluence, five different sites being irradiated at any one fluence. If the sample does not damage after the first shot for all five sites then the fluence is increased by either reducing the length of the dye cell attenuator and/or removing a neutral density filter, keeping a record of the Gentek reading at all times. This process is repeated until all sites damage first time after one shot. This is known as the 100 % probability damage threshold and allows a graph to be drawn of the probability of damage against fluence once the profile of the laser beam at the focus has been measured. If more than one sample is to be tested, it must be placed in the same plane as the previous one. For this purpose, two optical posts act as a reference plane and allow the user, by manipulating a micrometer, to place the sample at the same distance from these two posts as the previous sample.

4.3.4 Beam Profiling

Once the damage testing has been completed and a record is made of the energy at which the sample(s) damaged, it is necessary to gain a knowledge of how this energy is distributed in the laser beam at the target plane. There exists more than one method of measuring the transverse beam intensity, different methods being suited to different varieties of laser.

The simplest and least quantitative method involves burn paper which relies on placing photographic or some other heat sensitive paper in the beam and obtaining information from the pattern formed by the laser pulse. The drawbacks to this method are that the damage threshold of the paper is often unknown and the dynamic range of the paper is severely limited, moreover, the process is very non-linear. It does, however, give
some qualitative data as to the spatial profile of the beam and provides a quick test of the approximate intensity distribution, although calibrating this pattern to actual fluence values is not possible.

Other techniques rely upon scanning small portions of the laser beam by a photodiode or some other optical transducer, eventually obtaining the spatial profile over many shots if a pulsed system is used. This is dependent upon the laser having a reproducible profile to give an accurate measurement. At Loughborough it has been estimated that the EMG 200 excimer laser has a shot-to-shot reproducibility of 5%. If a pinhole is to be used as the front aperture of the photodetector, care must be taken to attenuate the beam so that the multiple shot damage threshold is not reached as the pinhole will be subject to a great many shots. Because the analysis is done where the beam is focused, the beam is widely converging and diverging in space and caution must therefore be used that the damage threshold of the surface of the photodetector is also not exceeded. The disadvantages of this method are that it provides information in only one line, the path followed by the detector, and although easy to use, it is very cumbersome.

Photographic techniques provide a means of obtaining the spatial profile of the whole beam in two dimensions in only one shot but the resulting patterns are hard to interpret. Scanning techniques offer means of obtaining accurate data but only after many shots and are tedious to obtain. This method though, along with knife edge inversion techniques, still remain popular today.

The beam profiling technique used at Loughborough combines aspects of both of the above methods, imaging the fluorescence, caused by firing the laser onto a glass plate in the same plane as the samples, onto a CCD which is essentially a multi-aperture detector comprising of an array of pixels. This 2-D profile pattern is then fed into a framestore where it is possible to use image processing routines to obtain the peak fluence in the beam

4.3.4.1 Hardware Specifications

The profiling system was developed at Loughborough in conjunction with workers at the Central Laser Facility at the Rutherford Appleton Laboratory. It consists of a camera connected to a computer controlled framestore, a trigger unit used for synchronisation, a glass slide used for converting the UV radiation to visible light and a
monitor so that the user can see precisely what the camera sees, or the result of any image processing algorithms. Fig. 4.3.4.1a gives a block diagram of these components and how they are connected.

![Block Diagram](image)

**Fig. 4.3.4.1a**

### 4.3.4.1.1 UV to Visible Light Converter

Because the CCD within the camera only responds to light within the wavelength range 400 to 1100 nm, a way must be found to linearly convert radiation at 248 nm to visible. It was discovered\(^8^3\) that a borosilicate microscope cover slide provides a convenient and cheap fluorescer in the visible when illuminated with UV radiation. It also has a reasonably high damage threshold (1-2 J/cm\(^2\)) and is easily replaced if it does become damaged. The glass slide itself has a thickness of around 150 \(\mu\)m and a UV penetration depth of around 1 \(\mu\)m\(^8^4\) and because it is transparent to its own fluorescence, it may be easily imaged in transmission, providing a good two dimensional representation of the beam. The linear range of the fluorescence was found to be between 10 \(\mu\)J/cm\(^2\) and 10 mJ/cm\(^2\).

### 4.3.4.1.2 CCD Camera

The camera used for both the schlieren damage detecting arrangement and the subsequent beam profiling arrangement was an EEV model P46311. The picture generated by the camera was comprised of two fields consisting of 312.5 lines each.
Both fields combine to make a video picture of 625 horizontal lines called a frame. Each field is comprised of alternate lines from the frame so that the first field contains information in lines 1, 3, 5 etc., and the second field 2, 4, 6 etc. To build up an image on the TV screen, both fields are interleaved, the first taking 20 ms to display on the screen and the second a further 20 ms. The entire frame therefore takes 40 ms to show. The frame synchronisation pulses (syncs) come in two forms, one to tell the monitor that a new picture is being transmitted and so to start scanning from the top left hand corner of the screen as it is the first field, and the other to tell the monitor that the second field of the frame is being transmitted and therefore to start scanning from the middle of the second line down on the monitor. The difference in these two frame syncs is merely one of duration.

Along with picture information, the video signal also has line sync pulses to tell the monitor to begin scanning a new line and field sync pulses so that the monitor knows to begin scanning a new field and therefore must start scanning from the top of the screen once more.

4.3.4.1.3 Video Framestore

The beam profiling system in use here is based around an Image III Framestore, produced by Eltime Ltd., connected to a TV monitor. This is a computer controlled digital picture store which is capable of storing one picture at a resolution of 512 x 512 pixels, two pictures at a resolution of 512 x 256 pixels or four pictures at a resolution of 256 x 256 pixels. This latter resolution was used for beam profiling. Each pixel has an associated 6-bit grey level allowing 64 intensity levels ranging from 0 (black) to 63 (white). Once the framestore has been initialised by the host computer, it is ready to accept video signals coming from the camera. The framestore was modified so that not only could it snatch a real-time full field by computer software but could also be triggered by an external pulse. The snatch is synchronised to, and starts from, the first field sync that it receives from the camera after the trigger pulse is sent. The entire video field is then captured, digitised and sent to the relevant store.

The picture can be then visualised as a 256 x 256 array with a simple cartesian coordinate system with (0, 0) as the top left and (256, 256) as the bottom right. This allows software routines to be written that can either read or write any pixel level, (0-63), to any location. It is therefore possible to perform such processes as image subtraction, addition, inversions or enhancements within or throughout any of the
4.3.4.1.4 Computer

The computer used for the control of the framestore and the running of subsequent image analysis routines was an Amstrad 1512 IBM compatible PC. It possessed a 40 Mbyte hard disc and a 512 kbyte floppy disc drive so that captured frames could be stored onto disc and any analysis done at a later stage. Most of the control programs were written in Turbo Pascal although some were written in assembler language to shorten the image processing times.

4.3.5 Synchronisation

The excimer laser pulse lasts for around 30-40 ns in total, the induced fluorescence that it causes on the glass slide, however, lasts for around 100 μs, and the frame for one picture from the camera integrates over a 40 ms time period. It becomes clear, therefore, that careful synchronisation of the component parts is necessary if the induced fluorescence in the glass slide is to be captured by the framestore.

A control trigger box was built to take care of the system timing requirements. Its function, when an external fire button was pressed, was to wait until it detected a field sync pulse from the camera. It then sent out two pulses, one to trigger the laser to fire and the other to trigger the framestore to capture a frame from the camera. Fig. 4.3.5a gives the timing sequence of all triggering pulses and shows how the relevant signals are timed from the field syncs from the camera so that the correct frame is captured. Note that the framestore triggers on a negatively going pulse.
4.3.6 Image Analysis Routines

Once a picture of the profile of the laser beam had been captured, it was necessary to analyse this image to ascertain what the peak fluence in the beam was and whether there were any hot spots present.

Software was written that allowed a line profile to be taken through the image, either horizontally or vertically, to find what the peak pixel value was and how many pixels were between the $1/e^2$ points, taking care to make sure that the pixel value was in the linear regime. At this point a careful note was made of the reading of the Gentek. This gave an idea of what energy was incident on the glass slide after any neutral density filters had been allowed for.

After this had been completed, a further routine was performed on the stored image that added all the grey levels of the pixels together. A note was taken of this value and another frame was snatched but with the laser not incident on the glass slide and the summation routine repeated. This value was subtracted from the first to give the net amount of grey levels over the whole field produced solely by the laser.
The final stage of the analysis was to record the actual beam dimensions in terms of millimetres. A further routine is used along with a calibrating image such as an illuminated square of known dimensions (e.g. 2 mm x 2 mm) placed in the same plane as the glass slide. A picture was then captured of this image and cursors drawn around the sides of this square. The program then gives the number of pixels between each cursor position so that the user is able to establish how many pixels in each direction, horizontally or vertically, correspond to one millimetre. These two numbers are not the same because the framestore and monitor combine to give an aspect ratio of approximately 3/2.

4.3.7 Fluence Calculations

The last part of the procedure is to use the gathered data and convert it to a peak fluence in the beam. Obviously, the largest grey level in any particular pixel represents that part of the beam which is most intense and is where the samples under test damage first and so this grey level must be converted into a fluence in J/cm².

The total number of grey levels, \( G_i \), is given by:

\[
G_i = \left( \sum_{i=0}^{63} g_i n_i \right)_{TOTAL} - \left( \sum_{i=0}^{63} g_i n_i \right)_{BACKGROUND}
\]

where the first term represents the sum of grey levels in the image with the laser beam profile and the second term represents the sum of grey levels in the image when the laser beam is blocked off. \( n_i \) is the number of pixels that have a grey level \( g_i \).

The energy per grey level is then given by:

\[
e_g = \frac{E}{G_i}
\]

where \( E \) is the total energy in the beam at the target plane. This is calculated from the reading from the Gentek and also allowing for any neutral density filters placed to attenuate the beam. The energy falling on a pixel of grey level \( g_i \) is:

\[
e_p = \frac{E g_i}{G_i}
\]

The area of a single pixel is \( 1/n_x n_y \) in mm², where \( n_x \) is the number of pixels
corresponding to 1 mm horizontally in the target plane and \( n_y \) is the number of pixels corresponding to 1 mm vertically in the target plane. The fluence, therefore, at any pixel \( f_p \) is:

\[
 f_p = E g_i n_x n_y / G_t \tag{4(23)}
\]

The real fluence is then found by finding the peak grey level in the profiled image and substituting it in for \( g_i \) in the above equation, giving a value \( f_{\text{peak}} \).

### 4.3.7.1 Example

To give a clearer understanding as to how the above procedures lead to a plot of probability of damage against fluence an example of a typical damage testing run on a sample will now be given together with the results of the calculations performed on the data so that final fluence levels may be ascertained.

The table overleaf shows how many times the sample, (in this case a hafnia/silica HR multilayer), damaged for different readings on the Gentek on five individual sites. Each result is the number of shots needed to damage the sample with the Gentek reading constant. If the sample survived for more than 10 shots at all sites then it was assumed that the probability of damage at that fluence was zero. Also shown is what value of neutral density filter (if any) were used to attenuate the beam.

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Gentek Reading (mV)</th>
<th># shots to damage</th>
<th>Neutral Density Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>&gt;10 x 5</td>
<td>3.5</td>
</tr>
<tr>
<td>2</td>
<td>16</td>
<td>&gt;10 x 5</td>
<td>3.5</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>&gt;10, 1, &gt;10, 1, 1</td>
<td>none</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>1 x 5</td>
<td>none</td>
</tr>
</tbody>
</table>

After the above data had been recorded it was necessary to convert the Gentek reading to peak fluence readings at the target plane.

First, a frame was grabbed which showed the fluorescence exhibited by a glass slide placed in the target plane when the excimer laser beam was fired (see Fig. 4.3.4.1a). The grey levels of all the pixels were then summed giving a total of 233254 grey levels.
A maximum pixel level of 50 was also found for this image. Another frame was then grabbed but with the laser aperture closed so that a 'noise' level was recorded. The pixel levels of this frame were also summed to give the value 151855. The value of $G_t$ for this profiling session was therefore 81399.

The total energy of the laser beam that gave rise to this grey level total at the target was given by the reading of the Gentek (6.8 mV) multiplied by 92/8 (as it was assumed that the beam splitter only allowed 4 % of the incident radiation to reflect off each surface and hence 92 % through to hit the target) multiplied by a calibration factor (0.481 mJ/mV). Finally this figure had to be divided by the attenuation factor of the neutral density filter (160). Were a neutral density filter not used then in all likelihood the glass slide would damage. The total energy of the laser beam giving rise to the fluorescence was thus 0.235 mJ.

An energy of 0.235 mJ therefore gave rise to a total number of grey levels of 81399 so that the energy per grey level was $2.89 \times 10^{-6}$ mJ/grey level. At this stage no spatial dimensions were known so it became necessary to measure an image of known size. The image that was measured was a 2 mm x 2 mm square placed at the target plane. Using the control software to manipulate the image it was found that 2 mm in the vertical direction corresponded to 145 pixels and 2 mm in the horizontal direction corresponded to 82 pixels. In the horizontal direction 1 mm therefore corresponded to 41 pixels and in the vertical direction to 73 pixels (measured to the nearest pixel). Previous measurements on the profile of the laser beam yielded the result that the horizontal profile (i.e. that distance between the 1/e^2 points) was 78 pixels in length and the vertical profile was 45 pixels in height, thus the image dimensions were 1.90 mm x 0.62 mm. The area of the image was therefore 1.18 mm².

Substituting all of the above data into eq. 4(23) to find what fluence level corresponded to the peak pixel value gives:

$$f_p = \frac{0.235 \text{ mJ} \times 50 \times 41 \text{ mm}^{-1} \times 73 \text{ mm}^{-1}}{81399}$$

or

$$0.432 \text{ mJ/mm}^2$$

This figure is calculated for the Gentek reading of 6.8 mV and when using a neutral density filter of 160. Therefore if one is using the Gentek reading to establish what the fluence value is with respect to 1 mV and with no filter in place then the normalised figure must be multiplied by a factor of 160/6.8. Therefore the final fluence at the
target plane for any value of Gentek reading is 10.16 mJ/mm²/mV, or 1.02 J/cm²/mV. Using the above figure one can immediately see that the fluence values for runs 1-4 are 2.91 J/cm², 4.66 J/cm², 6.12 J/cm² and 7.14 J/cm² respectively. Hence a graph may now be plotted showing probability of damage against fluence for the above four runs:

4.4 Damage Test Results

The following section describes results taken at Loughborough over a period of three years on a variety of multilayer components, samples using 'unconventional' materials such as Teflon and bulk materials. For this reason this section will be divided into two sub-sections, one comprising of damage test data related to conventional multilayer components and the other consisting of damage test data to materials not at present commonly used for coating materials, such as Teflon and PMMA.

4.4.1 Conventional Multilayers

The first results to be presented complement scatter data presented in section 3.5.3 in that they show the damage thresholds of the multilayer components tested for fluorine resistance before they were subjected to the BTDF experiments.
Fig. 4.4.1a below shows the damage probability against fluence for the dysprosium fluoride/aluminium fluoride sample.

Fig. 4.4.1a

This shows a very high damage threshold, surviving single shot energies approaching 10 J/cm². The output on the monitor used for viewing the schlieren image of the damage site was very dark indicating that the coating was clean and free from defects. Also if one examines the BTDF graphs in section 3.5.3 it may be seen that this sample also had the lowest initial BTDF scatter distribution of the four multilayer samples exposed to fluorine which again emphasises the good homogeneous quality of this particular coating.

Fig. 4.4.1b overleaf shows the damage probability against fluence for the dysprosium fluoride/cryolite multilayer. The damage threshold for this coating was particularly poor, the threshold being almost an order of magnitude lower than for the dysprosium fluoride/aluminium fluoride coating looked at previously. Although this sample too had a fairly low initial BTDF curve, it was noticed that there were a lot of areas where the schlieren image did appear quite bright indicating that the film was far from uniform. However, this sample had a higher tolerance to fluorine than the previous sample.
Fig. 4.4.1c overleaf shows the result of damage testing the thorium fluoride/cryolite sample. This sample had a moderate damage threshold approaching those typically shown by excimer laser components. The schlieren image appeared quite clear despite having the largest initial BTDF reading suggesting perhaps that the scatter site used was not typical of the film as a whole.
Fig. 4.4.1c

Fig. 4.4.1d
Finally Fig. 4.4.1d shows how the gadolinium fluoride/cryolite sample was able to withstand quite high energy densities before damaging. Like the dysprosium fluoride/aluminium fluoride sample, it was able to survive shots of up to $10 \text{ J/cm}^2$. This is somewhat surprising as it had a very high initial BTDF reading although the schlieren image indicated that the sample was fairly clean.

Among other rare-earth multilayer coatings that were damage tested over this period of time were ytterbium fluoride/cryolite and a further dysprosium fluoride/cryolite sample. Although this latter sample had previously been damage tested, (see Fig. 4.4.1b), on this particular occasion the sample appeared clear with no crazing lines evident under schlieren illumination. Fig. 4.4.1e shows the ytterbium fluoride/cryolite data. This graph was typical of two similar samples which exhibited disappointingly low damage thresholds even though they appeared to be the cleanest samples tested, with very dark schlieren images of the surface.

Fig. 4.4.1f shows how the new dysprosium fluoride/cryolite damage threshold has considerably improved over the previous sample. It was noted at the time that the dysprosium fluoride used in the coating was of a purer quality than that used previously, highlighting the need for contaminant-free raw materials.
Fig. 4.4.1f

Fig. 4.4.1g
Most excimer HR's and AR's these days are composed using hafnia/silica as the multilayer constituents and to put the above results into context with what can be obtained with 'ordinary' samples a representative hafnia/silica sample was damage tested so that comparisons could be made as to whether these new rare-earth multilayers offered a significant improvement over conventional designs. Fig. 4.4.1g on the previous page shows the results of damage testing an 'off the shelf' hafnia/silica sample. As can be seen the sample appears to withstand moderate energy densities but falls far short of the thresholds for some of the rare-earth multilayers tested.

4.4.2 New Coating Materials

Dielectrics are not the only constituents that can be used for coating materials. As part of the continuing search for high threshold designs for laser optics it was decided that other substances would be used for HR's and AR's. The first of the results in this section shows the probability of damage for a spin coated colloidal Teflon window. It was noted at the time that the coating had 'streaks' radiating from the centre where the liquid precursor was initially deposited. As may be seen from Fig. 4.4.2a the damage threshold is quite low probably due to the fact that the colloidal coating, by its very nature, was highly anisotropic although there have been reports of this type of coating exhibiting large damage thresholds85,86.

Another coating type that was investigated was a random phase plate (RPP)87 consisting of PMMA as the coating material. A random phase plate consists of a random array of transmitting areas which induce a phase shift of either 0 or π. The production process at RAL may be divided into three separate stages:

i) Computer generation of a suitable matrix pattern and printed onto an acetate sheet,

ii) The production of a master mask by duplicating the acetate onto a chrome coated quartz plate using optical lithography,

iii) The production of RPP's by transferring the mask pattern onto a UV sensitive coating which has been spun onto a suitable substrate. The thickness of the coating can be controlled to produce a π phase shift at the wavelength being used.

Fig. 4.4.2b shows the probability of damage for the PMMA random phase plate. As can be seen, the RPP has only a moderate damage threshold matching almost exactly the colloidal coating characteristics.
Fig. 4.4.2a

Fig. 4.4.2b
4.5 Laser Annealing

The following section describes experiments conducted to try and improve the damage thresholds of thin films by subjecting them to many low fluence non-damaging laser shots. The idea of laser processing thin films by such a method is not new, what is novel, however, is the fact that such a treatment has been seen to considerably enhance the damage thresholds of the new rare-earth fluorides that have been verified by workers at Loughborough to be an improvement on current multilayer designs from the point of view of maximising damage threshold.

4.5.1 Experimental Procedure

The experimental procedure used for the investigation of the conditioning effect was similar to that used by Izawa et al. Here, the laser conditioning was conducted by ramping the incident fluence on a particular sample site using the same pulses as those for damage testing. In our case we first irradiated the site with 10 sub-threshold, low fluence, shots at a repetition frequency of 1 Hz. The energy of the laser pulse was then increased slightly and the process repeated. This procedure was continued until the sample eventually damaged.

4.5.2 Results

Fig. 4.5.2a below shows the results of laser conditioning our first sample, gadolinium fluoride/cryolite. Each vertical arrow indicates an irradiation of 10 shots at that particular fluence. Also shown on this and the succeeding graphs are the normal 1 shot damage threshold probability results indicated by a dashed line. As can be seen, this sample is able to withstand very high fluence levels before progressively damaging at around 12 J/cm². This high threshold is to be expected as the 1-on-1 damage test result, (Fig. 4.4.1d), indicated the single shot damage threshold to be over 10 J/cm². What is more interesting is that at 12 J/cm² the sample initially had a probability of damage after one shot of approximately 70% indicating that even though the initial damage threshold was high, it is possible to improve this by the pre-irradiation treatment.

Fig. 4.5.2b shows the result of the conditioning treatment for the thorium fluoride/cryolite sample. Of all the samples tested, this particular one showed the most
dramatic improvement in damage threshold. After conditioning, the damage threshold may be seen to be around 9 J/cm$^2$, this may be compared to its nominal 1 shot damage threshold (and Fig. 4.4.1c) of around 4 J/cm$^2$. The damage threshold has thus been improved by over 100%!

Fig. 4.5.2a
Fig. 4.5.2b

Fig. 4.5.2c shows the result of the ramping irradiation treatment for the dysprosium fluoride/aluminium fluoride sample. This does not show any appreciable improvement over the 1-on-1 damage tests, (Fig. 4.4.1a), showing that perhaps this coating has been optimised as far as its damage threshold is concerned and that there were few defects in the coating for the conditioning to remove. Further corroboration for this assumption lies in the fact that of all the coatings tested, this particular one had the darkest schlieren image indicating few scatter sites (i.e. defects).
Finally, Fig. 4.5.2d shows the result of the treatment on the dysprosium fluoride/cryolite sample. Like the previous sample not much improvement can be seen if one compares it with its corresponding 1-on-1 damage probability graph (dashed line and Fig. 4.4.1f).
4.6 Conclusions

There can be little doubt that the new rare-earth fluoride multilayers offer a significant improvement over conventional multilayer materials. This Chapter has been mainly devoted to quantifying this improvement together with pushing the established damage thresholds even higher by the process of laser annealing.

Attention has been focused on four new multilayer coating designs namely gadolinium fluoride/cryolite, thorium fluoride/cryolite, dysprosium fluoride/aluminium fluoride and dysprosium fluoride/cryolite. Tests were also performed on a conventional hafnia silica coating together with other novel materials such as Teflon.

The gadolinium fluoride/cryolite sample performed very well having a damage threshold over 10 $\text{J/cm}^2$ which could also be improved by the ramping irradiation procedure to above 12 $\text{J/cm}^2$.

The next coating to be tested, thorium fluoride/cryolite, has a disappointingly low damage threshold of only around 5 $\text{J/cm}^2$ but exhibited the greatest improvement when
subjected to low energy pulses. The annealing treatment enhanced the damage threshold by over 100 % to around 9 J/cm², thus proving beyond doubt that this method may be used to improve damage thresholds where high laser power densities may be encountered.

The dysprosium fluoride/aluminium fluoride sample was a consistent high performer in terms of damage threshold although not much improvement was seen during the ramping fluence experiments possibly indicating that this coating was as good as it was going to get and that no amount of conditioning was going to make any improvement.

The final sample that was tested for both the 1-on-1 and annealing experiments was the dysprosium fluoride/cryolite sample. It too had quite a large damage threshold of around 9 J/cm² and like the previous sample not much improvement was seen when subjected to the laser conditioning.

Another coating design was also looked at during the 1-on-1 experiments, namely ytterbium fluoride/cryolite where it was found to have a very low damage threshold (around 2 J/cm²) and it was therefore not subsequently tested further.

Of the other materials tested was a Teflon colloidal coating and a PMMA random phase plate. These two samples did not have a high damage threshold, both of them damaging at around 2 J/cm².

In conclusion, therefore, it may be said that the new rare-earth fluorides have tremendous potential from taking over from conventional hafnia/silica multilayer designs. These coatings have also benefited from the application of a ramping fluence pre-irradiation treatment whereby the damage threshold in certain coatings have increased substantially.
REFERENCES


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CHAPTER 5

PULSELENGTH DEPENDENCE OF LASER DAMAGE

5.1 Introduction

As development of high-power excimer lasers continues, it has become increasingly apparent that ever-higher laser damage threshold optics are required. The majority of damage threshold measurements to date have been ascertained from commercial excimer lasers which have pulselengths of a few tens of nanoseconds where measured thresholds are of the order of a few joules per cm². However, pulses used in contemporary laser and plasma physics research are usually a few tens of picoseconds or less and it is found that the damage thresholds of the associated optics are also considerably reduced.

Published work on the damage thresholds of multilayer optics at other wavelengths suggest that it may be possible to use a scaling law of the form

\[ \text{laser damage threshold} \propto (\text{pulselength})^x \]

in the microsecond to nanosecond regime, where values between 0.25 and 0.5 are found for the exponent, x. It is the case, however, that designers of high power, short-pulse ultraviolet laser systems are faced with the problem that there is a lack of published data on short pulselength damage thresholds and simply extrapolating long pulselength damage data to picosecond pulselengths using the above scaling law may be unreliable, as it assumes that the damage mechanisms operating at 1 picosecond are the same as those at 10 nanoseconds. It is therefore of considerable interest to determine what the value of x is in the above relation.

This chapter is devoted to presenting the results of the laser damage thresholds of a variety of dielectric multilayers at pulselengths between 25 ns and 450 fs carried out at Loughborough University, the Rutherford Appleton Laboratory and at the Max-Planck Institut für Biophysikalische (MPB) in Göttingen, Germany. These are among the first reported measurements to cover such a wide temporal range with the same test samples.
A short review is given first, however, detailing the previous work that has been done regarding the influence of pulse duration on laser damage thresholds.

5.2 A Review of the Dependence of Pulse Duration on the Laser Induced Damage Thresholds of Optical Materials

Early work on the modelling of possible mechanisms of the pulsewidth dependence of damage thresholds threw little light onto exactly what mechanisms were primarily responsible. The first experiments on the pulsewidth dependence of laser damage were conducted at the ruby wavelength of 694 nm. The first reports detailing the dependence of damage threshold on pulse duration were those of Avizonis et al. who observed that ruby rods damaged at much lower power densities at 10 ns than they did at 100 ns. Seven different pulse durations were used between these two extremes. The damage was observable to the naked eye, consisting of numerous fracture planes and bubbles internal to the ruby. Fig. 5.2a summarises these results.

![Graph showing the dependence of damage threshold on pulse length](image)

Zverev et al. presented similar results at the same wavelength with pulse durations from 15 ns to 60 ns by varying the resonator length from 60 cm to 490 cm. Damage at 15 ns occurred at around 300 J/cm² and at 60 ns at about 900 J/cm². The samples were
composed of ruby and leucosapphire crystals. The difference between this work and the previous paper was that the rods were tested by focusing laser light into the volume of the sample instead of being part of the laser itself. This could account for the large discrepancy in damage threshold between these two workers.

Newnam et al\(^4\) also presented results showing that the damage threshold decreased with decreasing pulse duration. However, these experiments were performed on only one sample - a single layer ZrO\(_2\) film on BSC-2 glass using pulsewidths of 9 ns and 35 ns. It was found that the damage threshold fell by approximately 25% using the shorter pulse as opposed to the longer one. A more comprehensive study was performed by Bliss et al\(^5,6\) who conducted experiments on a variety of dielectric multilayer thin films. Again, a ruby laser was used for the damage tests with 20 ps pulses. To complement this mode-locked system, a standard Q-switched ruby laser system was also constructed having a pulsewidth of 23 ns FWHM. Like the previous laser this one also operated in a single longitudinal TEM\(_{00}\) mode. Eight mirrors were damage tested at both pulselengths and the results are presented below:

<table>
<thead>
<tr>
<th>Mirror</th>
<th>no. of layers</th>
<th>Threshold at 20 ps(^a) (J/cm(^2))</th>
<th>Threshold at 23 ns(^b) (J/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)/SiO(_2)</td>
<td>9</td>
<td>1.6</td>
<td>43</td>
</tr>
<tr>
<td>TiO(_2)/SiO(_2)</td>
<td>7</td>
<td>2.2</td>
<td>30</td>
</tr>
<tr>
<td>TiO(_2)/SiO(_2)</td>
<td>9</td>
<td>1.8</td>
<td>30</td>
</tr>
<tr>
<td>TiO(_2)/SiO(_2)</td>
<td>18</td>
<td>1.6</td>
<td>33</td>
</tr>
<tr>
<td>ZrO(_2)/SiO(_2)</td>
<td>13</td>
<td>1.9</td>
<td>23</td>
</tr>
<tr>
<td>ZrO(_2)/SiO(_2)</td>
<td>13</td>
<td>1.8</td>
<td>58</td>
</tr>
<tr>
<td>ZrO(_2)/SiO(_2)</td>
<td>25</td>
<td>2.9</td>
<td>47</td>
</tr>
<tr>
<td>ZnS/ThF</td>
<td>21</td>
<td>0.6</td>
<td>16</td>
</tr>
</tbody>
</table>

\(^a\)For the mode-locked pulse the beam diameter at half the on-axis energy density was 197 \mu m.

\(^b\)For the Q-switched pulse the beam diameter at half the on-axis energy density was 130 \mu m.

The first reported results of damage measurements for different pulse durations at infra-red wavelengths were those presented by Wang et al\(^7\). They used a UV preionised CO\(_2\) TEA laser, operating at 10.6 \mu m, giving a typical pulse energy of around 200 mJ at a pressure of 550 Torr. By control of the transverse discharge, variation of the gas mixture and total pressure, and operation of the low pressure
discharge for longitudinal mode control, four types of pulses could be selected. The basic pulse consists of a typical TEA laser gain-switched partially mode-locked pulse with an equivalent pulse length of 0.6 μs. A pulse consisting of a 1 μs single longitudinal mode pulse followed by a tail (equivalent pulse length 1.9 μs), a 4 μs equivalent pulse length gain-switched pulse, and a 6 μs single longitudinal mode pulse were available by modifications to the laser parameters and operation of the low pressure CO₂ discharge section.

The results below show damage thresholds for a single thorium fluoride - zinc selenide dielectric enhanced reflector on a silver overcoated molybdenum substrate surface using this system:

<table>
<thead>
<tr>
<th></th>
<th>Damage Threshold</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.6 μs Mode-Locked</td>
</tr>
<tr>
<td>Multiple Shot Threshold</td>
<td>50-290 J/cm²</td>
</tr>
<tr>
<td></td>
<td>80-480 MW/cm²</td>
</tr>
<tr>
<td>Single Shot Threshold</td>
<td>15-75 J/cm²</td>
</tr>
<tr>
<td></td>
<td>25-125 MW/cm²</td>
</tr>
</tbody>
</table>

As can be seen, although there is a wide range of values over which damage occurs, the ranges for this sample overlap substantially for the different pulse lengths employed, indicating essentially a constant energy density damage threshold. From this data, therefore, it was hard to establish any power law dependence and it was surmised that the dominant damage mechanism was the presence of metallic, highly absorbing, inclusions as put forward by Milam et al. However, it was suggested by others that the damage could be attributable to pin holes and defects in the dielectric coating rather than metal rich defects as regions of high metal concentration were not seen in the vicinity of damage sites.

A model for the pulse duration dependence was proposed by Bettis et al in 1976. It was based on the absorption of the laser pulse by the resulting electronic plasma and the subsequent heating of the plasma which would heat, craze and otherwise photodegrade the surface of the surrounding dielectric. The model predicted inverse relations between the threshold field and both the square root of the beam diameter.
and the fourth root of the pulse duration. It followed therefore that \( \sqrt[4]{td_{th} E_{th}} = A \) constant. Results from several authors were presented, at both 1.06 \( \mu \)m and 10.6 \( \mu \)m, primarily using NaCl and KCl and all seemed to agree with the model with any variations put down to material imperfections. However, further work on NaCl and KCl windows suggested that a \( t^{1/3} \) power law was a better approximation for 10.6 \( \mu \)m which was based on data collected for 1.7 ns to 65 ns pulses\(^{10}\).

In 1978 results by Milam\(^{11}\) were presented for linearly polarised 1064 nm radiation for pulses with durations 0.17 ns, 1.0 ns, 1.6 ns and 3.2 ns. Entrance-surface and exit-surface thresholds on four BK-7 glass windows with different RMS surface roughness were measured. It was noted that the damage thresholds were approximately proportional to the square root of the pulse duration, but were insensitive to variations in surface roughness when the surface roughness was below 25 Å. It was also found that by carefully cleaning the samples increased the damage thresholds at 3.2 ns by removing surface particulates.

A much more gradual pulsewidth dependence was put forward for the ultraviolet by Newnam et al\(^{12}\). Tests performed on a single QW layer of ZrO\(_2\) at 355 nm using 27 ns and 20 ps pulses suggested that a \( t^{1/6} \) law was apparent. As can be seen this is a much more moderate relationship than has heretofore been seen.

A wide range of thin film dielectric multilayer mirrors, both oxides and fluorides, were tested under differing pulselengths, (5 ns and 15 ns), wavelengths (1.06 \( \mu \)m, 0.53 \( \mu \)m, 0.35 \( \mu \)m, and 0.26 \( \mu \)m), and film thickness by Walker et al\(^{13,14}\). These papers represented the first work to present comprehensive self-consistent data on well characterised samples using a wide range of parameters which could be varied in such a way that the relative effect of each on damage threshold could be assessed. It was found that there was no laser pulselength dependence in the TiO\(_2\) films at 1.06 \( \mu \)m, (a fact that had been reported previously by Lowdermilk et al\(^{15}\) who performed experiments using 0.17 ns, 1.0 ns, 1.6 ns and 3.5 ns; they also found that a square root scaling law was exhibited by bare, polished substrates), but, at 0.53 \( \mu \)m the damage threshold is higher for 15 ns than for 5 ns pulses. No explanation was given for this dependence on wavelength for the presence of a pulselength relationship. The MgO films behaved the same at 0.53 \( \mu \)m, 0.35 \( \mu \)m and 0.26 \( \mu \)m in that they did show a pulselength dependence at these wavelengths but not at 1.06 \( \mu \)m. Interestingly enough, the fluoride films showed a much stronger dependence of damage on pulsewidth at 0.26 \( \mu \)m than the oxides. In fact Al\(_2\)O\(_3\), SiO\(_2\) and ZrO\(_2\) film data indicated a weaker
pulsewidth dependence at 0.26 μm. The only oxide films which exhibited a marked time dependence at 0.26 μm were MgO and HfO₂.

Swain et al. produced results the following year which showed the effect of laser cleaning on the damage thresholds of AR surfaces at different pulselengths (1 ns, 3 ns, 6 ns, 9 ns and 20 ns) using 1064 nm radiation. It was observed that the damage thresholds were increased by a factor of two by pulsed laser irradiation at fluence levels just below the 1-on-1 damage threshold. Damage thresholds of these AR surfaces increased with the square root of the laser pulselength for all pulselengths tested and that the improvement in threshold due to laser cleaning occurs over this entire range of pulse durations also. The increase in damage threshold due to laser cleaning was explained by the removal of absorbing impurities from the surface by subthreshold pulses. It was noted that scanning electron microscope photographs of the surface indicated that particles were visible in areas that were not subjected to non-on-1 irradiation but absent from irradiated areas.

Rainer et al. the following year presented more results in the ultraviolet. They used 351 nm and 355 nm pulses with durations of 0.6 ns, 1 ns, 5 ns and 9 ns to measure thresholds for a variety of AR and HR coatings. Although they also measured damage thresholds as a function of laser wavelength and film thickness, only those results pertaining to pulselength scaling will be given here. A summary of the data is given below:

<table>
<thead>
<tr>
<th>Number</th>
<th>Coating</th>
<th>Materials</th>
<th>Layers</th>
<th>OC/UCa</th>
<th>xᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HR</td>
<td>Sc₂O₃/MgF₂/SiO₂</td>
<td>21c</td>
<td>λ/2 MgF₂</td>
<td>0.37</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>ZrO₂/SiO₂</td>
<td>15</td>
<td>λ/2 SiO₂</td>
<td>0.51</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>ZrO₂/SiO₂</td>
<td>&quot;</td>
<td>None</td>
<td>0.10</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>Ta₂O₅/SiO₂</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.17</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>HfO₂/SiO₂</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.46</td>
</tr>
<tr>
<td>6</td>
<td>AR</td>
<td>HfO₂/SiO₂</td>
<td>4c</td>
<td>λ/2 SiO₂</td>
<td>0.35</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>ZrO₂/SiO₂</td>
<td>&quot;c</td>
<td>&quot;</td>
<td>0.30</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>MgF₂/SiO₂</td>
<td>5c</td>
<td>&quot;</td>
<td>0.22</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>Sc₂O₃/SiO₂</td>
<td>4c</td>
<td>λ SiO₂</td>
<td>0.19</td>
</tr>
</tbody>
</table>

ᵃOC = overcoat on HR's; UC = undercoat on AR's.
ᵇTemporal scaling coefficient: threshold ∝ tᵇ.
ᶜNon quarterwave-thick layers.
For the five high reflectors $x$ ranged from 0.10 to 0.51, averaging 0.32. The four AR coatings had $x$ values from 0.19 to 0.35 with an average of 0.27. Values of $x$ in other 355 nm damage experiments span the range $-0.05 \leq x \leq 0.74$, although most are between 0.3 and 0.4\textsuperscript{11,14}. These earlier tests were primarily for single-layer coatings, but the results are in general agreement for these multilayer coatings. However, the range of observed scaling factors were so large that this data provided little insight into the mechanism responsible for damage.

At the same time a report was presented of round robin damage experiments performed at eight separate laboratories on commercially available AR and HR coatings at 1.06 $\mu$m\textsuperscript{18,19}. Of the wealth of data that was produced a few tentative conclusions were drawn of which the one pertinent to pulselength scaling was that $x$ lay in the range 0.72-0.77 for two HR and the multilayer AR's, and with $x = 0.59$ for a V-type AR coating, instead of the expected 0.5. These values were obtained from a double log fit of the average damage threshold energy density $E_0$ vs. $t$ with sufficiently high correlation coefficients of 0.62 to 0.88. A presentation of the regression analysis for this data is presented in reference 21. The fact that there was less spread for shorter pulses meant that damage was more deterministic than probabilistic, as was the case for longer pulses. Similar results obtained from irradiating sol-gel AR coatings confirmed the $t^{0.5}$ dependence at this wavelength\textsuperscript{20}.

At ultraviolet wavelengths, Rainer et al\textsuperscript{22} produced results of experiments performed at 248 nm using 20 ns pulses and added these results to those presented by Deaton et al\textsuperscript{23} at 266 nm with puls elengths of 100 ps and 700 ps using fluoride crystals as the samples. It was observed that straight line fits to these few data points indicated that the front surface thresholds scaled as the square root of the pulselength. This relationship was confirmed at the XeCl excimer wavelength of 308 nm when Taylor et al\textsuperscript{24} used pulses ranging from 7.5 ns to 300 ns to irradiate silica substrates and commercially available fused silica fibres. It was found that the maximum energy that could be transmitted through the fibres increased approximately with the square root of the laser pulse duration.

In a series of experiments incorporating 351 nm puls elengths of 9 ns, 26 ns, 54 ns and 625 ns, it was found by Foltyn et al\textsuperscript{25} that laser damage thresholds increased as $t^{0.36}$ and that the exponent ranged, for different samples, from 0.23 to 0.48. Samples included $\text{Al}_2\text{O}_3/\text{SiO}_2$ in both AR and HR multilayers, HR's of $\text{ScO}_2/\text{SiO}_2$ and $\text{HfO}_2/\text{SiO}_2$ and an Al-on-pyrex mirror. These results were then compared to other workers' results and a useful summary was drawn up which is shown overleaf:
<table>
<thead>
<tr>
<th>Reference</th>
<th>Wavelength (µm)</th>
<th>Pulselength Range (ns)</th>
<th>Scaling Exponent*</th>
<th>Range</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>1.05</td>
<td>0.004-0.008</td>
<td>0.0-0.5</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.69</td>
<td>0.020-23</td>
<td>0.4-0.5</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.36</td>
<td>0.020-27</td>
<td>0.2</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>0.53</td>
<td>0.03-0.15</td>
<td>0.1-0.9</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>0.27</td>
<td>0.1-0.7</td>
<td>0.0-0.7</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1.06</td>
<td>0.17-0.32</td>
<td>0.3-0.5</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1.06</td>
<td>0.17-3.5</td>
<td>0.0-0.5</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>0.36</td>
<td>0.6-9</td>
<td>0.1-0.5</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1.06</td>
<td>1-9</td>
<td>0.3-0.6</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10.6</td>
<td>1.7-65</td>
<td>0.2-0.3</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0.27</td>
<td>5-15</td>
<td>0.0-1.0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0.36</td>
<td>5-15</td>
<td>0.0-0.8</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0.53</td>
<td>5-15</td>
<td>0.0-0.8</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>1.06</td>
<td>5-15</td>
<td>0.0-0.7</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>0.35</td>
<td>9-625</td>
<td>0.2-0.5</td>
<td>0.4</td>
<td></td>
</tr>
</tbody>
</table>

*The value of x in the relationship: threshold fluence \( \propto (\text{pulselength})^x \)

The above is a compilation of published scaling results of test data covering wavelengths from 248 nm to 10.6 µm and more than five decades in pulselength. The results seem remarkably consistent. While scaling exponents for individual tests vary widely, the average scaling rate has a nearly constant value from 4 ps to 625 ns. Thresholds improve as \( t^{0.3-0.4} \) for picosecond pulses, and continue to do so for pulselengths up to a microsecond. It is apparent from this data that a cube root scaling, as opposed to a square root scaling, is a more accurate rule of thumb for the exponent on average although individual samples could scale quite differently.

The first results using different pulselengths at 248 nm were those of Mann et al. They used a pulse extension unit to stretch the excimer laser pulse which relied upon utilising a multiple reflection optical delay line in combination with a set of partial reflectors. This device allowed stretching of an excimer laser from its initial value (25 ns) up to 200 ns in steps of 25 ns.

Damage was monitored on-line by help of video microscopy, which allowed examination of the damage site to be tested on a monitor during the laser irradiation. The samples investigated were 4 substrate materials, 4 single layers, 4 multilayer...
coatings, and, as a reference, an aluminium mirror. Plotting the damage threshold against pulselength on a log-log format and fitting the data to straight lines allowed the exponent x to be determined for each sample. The results are shown below:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Exponent x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suprasil</td>
<td>0.48</td>
</tr>
<tr>
<td>BaF₂</td>
<td>0.56</td>
</tr>
<tr>
<td>CaF₂</td>
<td>0.59</td>
</tr>
<tr>
<td>SrF₂</td>
<td>0.79</td>
</tr>
<tr>
<td>SL Al₂O₃</td>
<td>0.35; 0.47</td>
</tr>
<tr>
<td>SL HfO₂</td>
<td>0.45; 0.57</td>
</tr>
<tr>
<td>SL LaF₃</td>
<td>0.86</td>
</tr>
<tr>
<td>SL SiO₂</td>
<td>0.89</td>
</tr>
<tr>
<td>HR Al₂O₃/SiO₂</td>
<td>0.51; 0.45</td>
</tr>
<tr>
<td>HR LaF₃/MgF₂</td>
<td>0.15</td>
</tr>
<tr>
<td>HR Sc₂O₃/SiO₂</td>
<td>0.83</td>
</tr>
<tr>
<td>HR HfO₂/SiO₂</td>
<td>0.58; 0.73</td>
</tr>
<tr>
<td>HR Al</td>
<td>0.50</td>
</tr>
</tbody>
</table>

HR: High Reflecting Component  
SL: Single Layer

If the thermal model proposed by Guenther et al ¹⁹ is correct then a $t^{1/2}$ power law dependence of the damage threshold should be seen and the results of the bare substrates Suprasil, BaF₂ and CaF₂ strongly support this theory. However, the exponents calculated for the single layers and multilayer thin films show some partial deviations from this law indicating the additional influence of other damage mechanisms for coated substrates.

5.2.1 Summary

Ever since the first laser was operated it had been known that samples damaged at lower energy densities for shorter pulselengths with all other variables being equal. The above review is a concise collection of almost all the work performed in determining the dependence of damage threshold on pulselength and in evaluating the validity of various models to explain this effect. No model, however, remains suitable for all samples with the damage threshold varying from $t^{0.05}$ to nearly $t^{1.00}$. Work carried out
at Loughborough University, RAL and at The Max Planck Institute has investigated the pulselength scaling phenomenon for fluoride and conventional multilayers at 248 nm. Studies showed that the pulselength relationship varied as $t^{0.25-1.00}$ with the fluoride multilayers having a marked improvement over conventional designs.

5.3 Experimental Determination of Pulselength Scaling for Oxide and Fluoride Multilayers at 248 nm

Following on from the results in section 4.4.1 which showed that selected fluoride multilayers were capable of withstanding relatively high fluence levels of pulsed 248 nm radiation from a commercial excimer laser system, it was decided that other irradiation regimes would be investigated. The impetus for these series of experiments was provided by the fact that the SPRITE KrF multiplexed laser system at the Rutherford Appleton Laboratory (RAL) operates at a substantially shorter pulse duration than the damage test facility at Loughborough which workers at RAL were relying on for damage test data of multilayer components.

To establish a pulsewidth scaling law it is desirable to use as many different pulsewidths as possible, preferably over several orders of magnitude, on the same samples at the same wavelength and ideally using the same detection method to establish threshold criteria. The rest of this Chapter is devoted to presenting the results of experiments conducted at Loughborough, RAL and the Max Planck Institut für Biophysikalische (MPB) in Göttingen, Germany.

5.3.1 Samples

The reported success of Izawa et al\textsuperscript{28} in the use of rare-earth fluoride/cryolite multilayers to obtain increased damage threshold for nanosecond 248 nm pulses encouraged us to begin a programme of coating development using these materials. The results presented in reference \textsuperscript{28} suggest that the best high-index materials are gadolinium fluoride and lanthanum fluoride and indeed previous work at Loughborough had established that these materials did have a markedly improved damage threshold at this wavelength\textsuperscript{21}. Because of difficulties experienced with deposition of good films of lanthanum fluoride, efforts were concentrated on gadolinium fluoride and dysprosium fluoride, in combination with cryolite and
aluminium fluoride as the low-index materials. Material combinations for which damage test data are provided are as follows:

A, B: Gadolinium fluoride/Cryolite  
C: Dysprosium fluoride/Aluminium fluoride  
D: Gadolinium fluoride/Aluminium fluoride  
E: Dysprosium fluoride/Cryolite  
F, G: Hafnium oxide/Silica

The hafnium oxide/silica combination is now used by most commercial manufacturers of dielectric mirrors as standard HR's in the UV, and samples were obtained from two different suppliers for comparison with the fluoride multilayers. All these multilayers were deposited by electron-beam evaporation, and all were normal incidence HR's at wavelengths between 248 nm and 260 nm.

5.3.2 Irradiation Conditions

Damage measurements were made on the above samples at three different laboratories, with inevitable variations in experimental conditions from one to another. The measurements at 25 ns were made at Loughborough, those at 10 ps, 1 ps and 450 fs at RAL and those at 600 fs at MPB.

As far as practicable, the following procedure was used for all measurements. The sample was exposed to the damaging laser beam at or near the focus of a lens, and viewed by dark-field schlieren imaging to detect the onset of damage, as outlined in Section 4.3 in Chapter 4. The dark field image of the sample surface is very sensitive to the increase in scatter from sites where damage has occurred, and indeed the criterion for damage used for these experiments was the first observation of a permanent (and usually increasing) level of scatter from a previously non-scattering (i.e. undamaged) site. The measurements at 20 ns, 10 ps, 1 ps and 600 fs were made using this technique, while for the 450 fs measurements a lamp filament was imaged onto the sample, and the surface viewed by eye against a dark background. Undamaged sites were exposed to pulses from the laser at repetition rates between 1 and 4 Hz until either damage occurred at the site or more than 100 shots had been delivered without evidence of damage. This procedure was repeated for a range of laser fluences around the damage threshold. At each pulse length, the number of shots required to cause damage was recorded, at each fluence level, for up to 5 different
sites on the sample. These data allowed both the 100 % damage fluence (i.e. that fluence which will invariably damage the sample in a single shot) and the maximum fluence at which the sample will survive undamaged for a large number of shots to be determined. The latter number is probably more important to the laser designer.

5.3.3 Laser Sources

At Loughborough the laser source was a Lambda Physik EMG 200 excimer laser giving pulses of 25 ns FWHM. The samples were placed at the focus of a lens of 20 cm focal length, and the energy in the pulses was varied by adjusting the thickness of a dye cell containing a solution of Rhodamine 6G. The maximum number of pulses on any one site, however, was limited to 10. More details about this optical arrangement may be seen in Chapter 4.

At RAL, the front end of the SPRITE laser29 was used to provide pulses of up to 3 mJ at 249 nm. The focusing lens had a focal length of 75 cm and was moved relative to the sample to vary the size of the irradiated region and hence the fluence. Pulse energies were found by using the known pulse repetition rate combined with measurements of the average power in the beam immediately before the sample. While damage measurement were being made, a split-off fraction of the beam was monitored to ensure that the average power remained constant.

At MPB the laser source was a hybrid dye-excimer system of the type developed by Szatmári and others30. Samples were placed at the focus of a 3 m focal length lens and attenuators were used to vary the pulse energy, which was monitored on a shot-to-shot basis.

5.3.4 Fluence Determination

In all cases the energy or power monitoring yielded the average fluences incident on the sample; however, the relevant quantity in assessing damage thresholds is the peak fluence, not the average. Diffraction effects and non-uniformities in the beams produced significant intensity variations at or near the focus, with peak intensities several times greater than the average. To account for these effects, beam profiles were recorded at the sample plane using CCD cameras with video or frame storage; at RAL this was done for each position of the lens. The integrated grey level over the
spot area in the stored image was assumed to be proportional to the average fluence, and the value of the highest grey level then yielded the peak fluence. The peak fluences were found to range from 1.6 to 2.8 times the average. This technique was used for all except the 450 fs data, for which beam profiles were not obtained. The 450 fs data were corrected using the peak-to-average ratios measured for corresponding spot diameters with 10 ps pulses; the focusing lens and the beam diameter were the same, and the B-integral for the 450 fs pulses was estimated to be 2.5, so self-focusing effects would not cause much degradation of the beam profile.

Uncertainties in the damage fluences are associated mainly with fluctuations in laser energy, which were typically ±15% for the picosecond and subpicosecond pulses, and ±10% for the 25 ns pulses. Each peak-to-average ratio was made from several recorded spot profiles, and the values found to be consistent to ±5%. Uncertainties in the damage fluence at 450 fs are estimated at ±30%, because the peak fluence values were less reliable and also because the sample viewing technique used was probably less sensitive to the onset of damage. Uncertainties in pulselengths are relatively small: the lasers at Loughborough and MPB are well-characterised, and their pulselengths are accurate to within ±10% of the quoted values. The pulselengths used at RAL were measured in independent experiments just before or after the damage tests and their accuracy is also around ±10%.

5.3.5 Experimental Results

The results obtained for the multilayers above are given below in Tables 1 and 2. The entries in the tables are the laser fluences in J/cm² which either damaged the sample in a single shot (Table 1) or caused no damage after many shots (Table 2).

<table>
<thead>
<tr>
<th>Sample</th>
<th>450 fs</th>
<th>600 fs</th>
<th>1 ps</th>
<th>10 ps</th>
<th>25 ns</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.0</td>
<td>0.70</td>
<td>0.95</td>
<td>3.5</td>
<td>13.5</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>1.03</td>
<td>0.95</td>
<td>2.5</td>
<td>10.5</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>11.0</td>
</tr>
<tr>
<td>D</td>
<td>-</td>
<td>1.18</td>
<td>0.95</td>
<td>2.2</td>
<td>10.5</td>
</tr>
<tr>
<td>E</td>
<td>-</td>
<td>0.92</td>
<td>0.95</td>
<td>2.5</td>
<td>10.5</td>
</tr>
<tr>
<td>F</td>
<td>0.3</td>
<td>0.29</td>
<td>0.56</td>
<td>1.3</td>
<td>6.0</td>
</tr>
<tr>
<td>G</td>
<td>-</td>
<td>-</td>
<td>0.56</td>
<td>1.1</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Table 1
### Table 2

In Figs. 5.3.5a and 5.3.5b the data from Table 2 are plotted, i.e. the 'survival fluences' of the various multilayers as a function of laser pulselength.
Laser Fluence (J/cm²)

Pulselength (ns)

Fig. 5.3.5a
It is clear that all the fluoride samples have greater resistance to damage than the hafnia/silica comparison samples, and that this difference, a factor of between 2.5 and 3, is maintained over the range of pulselengths investigated. There is little to choose between the different material combinations in the fluoride coatings tested, and in fact the two gadolinium fluoride/cryolite combinations A and B are respectively the best...
and the worst of the fluoride samples. The difference between them lies in the type of pumping used in the coating plant: the coater used for sample A was cryopumped, while for sample B a conventional oil diffusion-pumped coater was used. The lower damage threshold of sample B may be due to contamination associated with the oil.

The scaling of damage behaviour with pulselength can also be seen from these two graphs. The change between pulselengths of 25 ns and 10 ps corresponds to an exponent of $x \approx 0.25$, while for shorter pulses an exponent of 0.5 fits the data fairly well. Other workers have obtained exponents in the range 0.25 to 0.4 in the nanosecond pulse regime, which are consistent with these results. For some of the fluoride samples the exponent appears to increase again at shorter pulselengths, becoming closer to 1 between 1 ps and 600 fs.

For completeness graphs summarising the data in Table 1 are presented in Figs. 5.3.5c and 5.3.5d below. These graphs give the smallest fluences for which the samples damaged after only 1 shot and as such represent an 'upper limit' on the optical strengths of such materials using today's technology. Interestingly, almost all of these materials have threshold curves that match the trend alluded to in the previous graphs; namely that for subnanosecond pulses, a different scaling exponent seems to be applicable than for pulses operating in the nanosecond regime.
Fig. 5.3.5c
5.3.6 Discussion

The above graphs show several interesting features. For instance, it may be seen that there is a tendency for the damage thresholds to decrease more quickly as one moves into the sub-picosecond regime. Also, as one looks at all the graphs together there seems to be a non-linear power law relationship for different pulselengths, i.e. it seems that the data points lie on a curve rather than a straight line. The reason for this is unclear at present but may be due to two different intrinsic damage mechanisms dominating in different time regimes.

It is unlikely that thermal mechanisms play a role in such short pulse durations as it is easy to show that for a 1-dimensional dielectric with a typically low thermal
conductivity of around 0.5 Wm⁻¹K⁻¹ that the timescale for heat to diffuse from a typical spot of radius 10 μm is in the microsecond regime.

5.3.6.1 Role of Peak Electric Field in the Damage Tests

The possible intrinsic damage mechanisms by which a dielectric suffers laser induced damage has already been covered. These models will now be used to discuss why the graph data points are situated as they are.

In electron avalanche, two conditions must be satisfied to initiate damage. Firstly, the intensity must be high enough so that conduction electrons gain energy from the laser radiation faster than they lose it to the surrounding medium and, secondly, the laser energy density must be high enough to create a critical number of conduction electrons within the duration of the pulse (~ 10¹⁸ cm⁻³). Therefore for very short duration pulses the limiting quantity is energy density while for longer pulses it is intensity.

For the shorter pulses, then, electrons gain energy from the field much faster than they can dissipate it to the surrounding medium after the pulse has ceased, and, because heat effects may be neglected, it can be assumed that the electron avalanche model is an intensity dependent mechanism at all the pulse durations under scrutiny. (The solid straight line segments of the curves in Fig. 5.3.6.1a overleaf are drawn through the data points given in Fig. 5.3.5d with the appropriate pulse duration dependence to give constant energy density (horizontal straight line) and constant intensity (line at 45° gradient) thresholds.) It can be seen that the femtosecond and picosecond data seem to corroborate this model but that there seems to be some divergence when looking at the nanosecond data.
At the high intensity levels which can be reached with lasers, conduction electrons may also be created by the simultaneous absorption of several photons. As the probability for n-photon absorption increases as n decreases, anything which affects the number of photons required to get electrons into the conduction band will influence the probability of the multiphoton process. The photon energy is therefore an important parameter. Additionally, raising electrons to excited states by optical pumping or altering the energy band structure by adding impurities could affect the importance of the multiphoton absorption by, for instance, adding new metastable states.

The probability of n-photon ionisation depends upon the electric field strength by a factor $E^{2n}$, so $N$ (the conduction electron number density) is proportional to $E^{2n}\Delta t$ where $\Delta t$ is the pulselength. The transfer of energy from a field $E$ with wavelength $\lambda$ to electrons of effective mass $m^*$ coupled to longitudinal optical phonons may be characterised by an optical absorption coefficient:

$$\alpha = \frac{16\pi^2 Ne^2 \gamma}{\lambda m^* E_0^2}$$

5(1)
where $\gamma$ is the rate at which the field does work on the electron. If $\alpha$ is averaged over the pulse duration $\Delta t$, the dependence of damage threshold on pulse duration is given by\textsuperscript{33}:

$$\text{damage threshold} \propto \Delta t^{(n-1)/(n+1)}$$ \hspace{2cm} 5(2)

For a two-photon therefore, a line of gradient 1/3 would be applicable in describing the pulselength relationship, and indeed this seems to be the case when looking at Fig. 5.3.6.1a where a dotted line of the appropriate gradient is drawn between 1 ps and 25 ns.

In summary, there are several ways in which the conduction electrons could be involved in the damage process. Evidence of their importance is found for example, in the observation that the introduction of impurities which could serve as electron traps changes the damage threshold.

\textbf{5.3.7 Conclusions}

In conclusion, damage measurements have been made at 248 nm on a variety of fluoride-based multilayer high reflectors over a wide range of pulselengths; the work is also published in reference 34. It has been found that they have a significantly higher damage resistance than conventional oxide-based multilayers, the scaling of damage threshold with pulselength is very similar, and consistent with scaling laws obtained for longer pulselengths and other UV wavelengths. It is also the case, however, that the data obtained seems to suggest that different values for the scaling constant, $x$, may exist according to what pulselength regime is being investigated. By applying the two mechanisms most used to explain laser induced damage, (electron avalanche absorption and multiphoton absorption), it may be tentatively suggested that these two mechanisms are operating but tend to dominate in different time regimes. More data in the femtosecond and nano/microsecond regions are needed to verify this.
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CHAPTER 6

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The work covered in this thesis covers two important aspects that both directly relate to the optical performance of excimer laser components, namely their scattering properties and their damage thresholds.

The first part details the construction of a scatterometer and its subsequent use in determining the optical quality of a host of components commonly found in excimer laser systems. These include highly reflecting multilayer components and substrates. This was done with a view to replacing laser windows with the HR multilayers directly in contact with the lasing chamber. If successful, this would improve the efficiency of the laser by reducing the number of surfaces through which the laser light must traverse, thus minimising scatter, transmission and reflection losses that are inherent in any transmissive optical arrangement. The samples were placed on the output window aperture of a small commercially available excimer laser. Primary experiments concentrated on establishing how resistant certain excimer laser components were to different concentrations of fluorine which is one of the typical lasing constituents found in excimer laser systems. The first samples to be tested were uncoated fused silica substrates, really done as an exercise to establish the correct fluorine concentration for any chemical degradation to become apparent. It was initially found that after a period of time the component under study suffered degradation due to chemical attack. This manifested itself by an increase in the level of scattered light from a HeNe laser used as a probe beam. Several interesting results were found. First of all, it was noticed that the scatter from the silica substrate did not scatter homogeneously. In fact there was a pronounced asymmetry to the resulting scatter/diffraction pattern. This seemed indicative of periodic structures present on the surface which had come into contact with the fluorine. Upon closer examination it was discovered that the surface of the silica had periodic scratches and the idea was put forward that the origin of these scratches were microscopic grooves left behind after the final polishing process which acted as seeding sites for preferential chemical attack by the fluorine. This proposition was verified when electron microscope pictures of a virgin substrate surface did indeed show tiny periodic scratches. Furthermore by using different concentrations of fluorine it was found that the density of scratches was
dependent on the concentration of fluorine to which the sample was exposed. Further experiments were then conducted on selected fluoride multilayers (samples were restricted to those that TecOptics were prepared to manufacture). Of the four different highly reflecting samples examined, two damaged catastrophically by completely losing their optical integrity and scattering large quantities of incident laser light, and two did not damage significantly. The two designs that did damage were composed of DyF₃/AlF₃ and GdF₃/Na₃AlF₆ and the two that remained unchanged were ThF₄/Na₃AlF₆ and DyF₃/Na₃AlF₆. This suggests that the damage mechanism, rather than being dependent on the chemical composition of the multilayer stack, may rely upon the quality of the thin film material. Unfortunately, the number of samples that were available were limited to these samples and so further work could proceed to investigate how voids, inclusions, scratches or other optical contamination affects the fluorine resistance of highly reflecting multilayers. It could well be, as in the case of the silica substrates, that the state of the surface texture is the governing factor in resisting fluorine attack.

The samples tested so far were all designed to operate at a wavelength of 248 nm, which is a lot less than the probe beam wavelength of 633 nm which was used for the scatter measurements made at Loughborough. There exists, however, a technique known as wavelength scaling which allows one to predict scatter at one wavelength from the scatter characteristics at another provided that the scatter arises purely from microtopographic features on the surface and that the roughness is a lot less than the wavelengths employed. Although the experiments presented in this thesis were the first to use this technique in transmission, the methodology is very similar to that reported elsewhere and several interesting results were found. Firstly, of the two different visible wavelengths used, (633 nm and 514 nm), there appeared to be some evidence for wavelength scaling to exist for several of the samples under study, namely fused silica and HR multilayers of DyF₃/Na₃AlF₆ and YbF₃/AlF₅. However, when scatter at 257 nm was measured it was found that there was little, if any, agreement with scatter data taken at the visible wavelengths. This was highlighted when a GdF₃/AlF₃ sample was tested. In this case there appeared no agreement with any two wavelengths. A possible source for such scatter could be particulates in one or all of the layers used in the coating or perhaps scattering from micro inclusions within the bulk of the substrate. Whatever the cause it remains clear that for the moment it is not possible to wavelength scale down to the UV from visible wavelengths for transmissive samples due to some wavelength dependent scatter mechanism.
Another important property that multilayer components must possess, apart from exhibiting little scatter, is to have as high a damage threshold as possible so that high throughput powers may be achieved. Most 'off-the-shelf' excimer laser multilayer HR's are composed of alternating layers of hafnia and silica. During the course of this project other material combinations were damage tested to see if the nominal damage threshold of 4-5 J/cm², which is typical for hafnia/silica multilayers, could be improved upon. It was found that several rare-earth fluoride multilayers did indeed have substantially higher damage thresholds and, what is more, that these thresholds could be further increased by subjecting them to a number of low-fluence, sub-threshold laser pulses. The first multilayer design that was tested was composed of layers of DyF₃ and AlF₃. This sample had a high damage threshold approaching 10 J/cm² for a single shot and also had a low scatter profile when measured in the scatterometer. Multilayers composed of DyF₃/Na₃AlF₆ and ThF₄/Na₃AlF₆ fared less well, each having thresholds around 4-5 J/cm². However, a cleaner specimen of the DyF₃/Na₃AlF₆ sample proved to have a higher damage threshold of 9 J/cm² when tested later, showing how important it is to have clean, homogeneous materials when depositing the multilayers. Another rare-earth sample that was damage tested was YbF₃/Na₃AlF₆ but this proved to have a disappointingly low damage threshold of only 2 J/cm². Rare-earth fluorides were not the only type of samples that were damage tested. A coating made from PMMA was also tested but proved to have a very low damage threshold of less than 2 J/cm² as did a Teflon coated colloidal window. It would seem, therefore, that multilayer rare-earth fluorides offer the best alternative to conventional multilayers at the moment.

As was mentioned before, it was found that by a process of laser annealing, whereby the sample under test was subjected to a number of low fluence shots and gradually increasing the fluence, it was found that the damage threshold could be increased, sometimes by a surprising margin. The GdF₃/Na₃AlF₆ sample damage threshold was raised from 10 J/cm² to 12 J/cm², but the DyF₃/AlF₃ and DyF₃/Na₃AlF₆ samples were largely left unchanged. The greatest improvement shown was that of the ThF₄/Na₃AlF₆ whose damage threshold increased from 4 J/cm² to around 9 J/cm², thus proving beyond doubt that this method may be used to improve damage thresholds of even low damage threshold components.

It may be seen that these new rare-earth fluorides offer significant improvements over conventional multilayer designs, both from the point of view of having low scatter and also of having a substantially higher damage threshold with the potential for increasing it still further by laser conditioning of the surface.
Because these multilayer components were to be fitted in the SPRITE laser at The Rutherford Appleton Laboratory which operates with a much shorter pulselength, the final part of the thesis is devoted to examining the dependence of pulse duration on the damage threshold; it was hoped that by looking at the damage threshold at one pulselength that the damage threshold at another may be inferred. It has been known for some time that the damage threshold is dependent on the how long the irradiation lasts and a power law of the form \( \text{DAMAGE THRESHOLD} \propto t^\alpha \) is often quoted with values of \( \alpha \) ranging from 0.25 - 1.00; \( t \) being the pulselength. Five pulselengths were used to establish the value of the exponent: 450 fs, 600 fs, 1 ps, 10 ps and 25 ns. All of the above fluoride multilayers were included in the survey together with a typical hafnia/silica multilayer. It was clear that at all pulse durations the fluoride samples had greater resistance to damage than the hafnia/silica sample with the GdF\(_3\)/Na\(_3\)AlF\(_6\) sample having a slightly higher damage resistance at all pulselengths. This may reflect the fact that this sample had been coated in a chamber that had been cryopumped, whereas all the other samples were deposited in conventional oil-diffusion-pumped coaters. Residual contamination associated with the oil may be responsible for the lower damage thresholds for the other samples. It was found that the change between 25 ns and 10 ps corresponded to an exponent of \( \alpha = 0.25 \), whereas for shorter pulselengths an exponent of 0.5 fits the data fairly well. For some of the fluoride samples this exponent appeared to increase once more at shorter pulselengths, becoming closer to unity between 1 ps and 600 fs. This may be indicative of a change in the mechanism of damage, perhaps arising from multiphoton absorption or electron avalanche operating at different time regimes. Further study will be necessary to confirm this and it will also be useful if even shorter pulselengths could be used to see whether this trend continues.

This thesis has hopefully gone some way into establishing rare-earth fluorides as possible contenders for ousting more traditional materials used in excimer laser components. They have been shown to have exceptionally high damage thresholds which can be enhanced by prior treatment. There also exists the possibility of replacing the laser windows themselves with these dielectric HR multilayers although much more work is needed to find the correct multilayer combination and how to lay them down with no contaminants or surface imperfections that could act as potential starting points for chemical attack by fluorine (or, more accurately, hydrofluoric acid).