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FOR REFERENCE ONLY
REFLECTIVITY STUDIES OF ANTIMONY THIN FILMS

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Supervisors: Dr. D. C. Emmony
Dr. R. P. Howson

Submitted for Ph.D. degree of
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Summary

Optical measurements on evaporated thin films of antimony in the infrared are shown to exhibit a distinct free carrier plasma edge in the region of 10.6 microns, and can be prepared in crystalline form at a relatively low temperature (265°C). These properties are some of those required in an investigation of thin film materials for modulators of radiation from a CO₂ laser at 10.6 microns where it is intended to sweep the plasma edge through the operating wavelength of the laser.

It is shown that it is possible to predict the optical properties of evaporated films of antimony in the infra red as a function of their thickness and changes in free carrier concentration. This is achieved by the interpretation of previous data on the optical properties of thin films of antimony with the use of detailed measurements of optical constants, in the near infra red, of polycrystalline material. The optical constants due to free carrier effects have been separated from those due to bound electrons and used in a computer program for film behaviour. A one carrier model was found adequate to account for free carrier dispersion with a relaxation time of $3.1 \times 10^{-14}$ sec found for a carrier density of $3.1 \times 10^{26}$ m$^{-3}$.

 Corrections are given to previously published curves for the reflectances of thin film semiconductors around the free carrier plasma edge.

It is shown from this analysis that significant modulation of the reflectance of antimony films will occur at 10.6 microns provided that sufficient excess carriers can be injected into the film, and that the magnitude of the effect can be increased if a material is used in which the maximum rate of reflectance rise of the plasma edge with wavelength, occurs at 10.6 microns.
An attempt to produce the required increase of free carrier concentration using electron bombardment from a high energy electron gun is described. The level of modulation is far below that expected from a simple calculation of the expected carrier concentration. It is shown that the poor response can be attributed to a reduced free carrier concentration due to enhanced recombination at surface discontinuities, since the free carriers generated in this way have an average mean free path which is far greater than the film thickness.

More success is achieved by the injection of majority carriers across a Schottky-type barrier layer which exists at an electrode-electrolyte interface or in a Schottky diode. Previous plasma edge reflection modulation data using gold in the visible region is verified and the mechanism of modulation is suggested. It is shown that this work can be extended into the infra-red and used to modulate the reflectance of antimony at 10.6 microns. The measured value of $\Delta R/R \sim 10^{-3}$ is in agreement with the value computed from the optical constants of antimony only.
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List of Principal Symbols

A  Slab thickness
B  Magnetic induction
b  Electron gun dimension
C  Capacitance
c  Velocity of light
D  Diffusion constant
D  Electrical displacement
D  Electron gun dimension
E  Electric field vector
e  Electronic charge
f  Frequency
f  Hall effect normalisation coefficient
f  Electron gun dimension
G  Coil form factor
G  Free carrier generation rate
E(x)  Free carrier generation rate per unit volume
I  Intensity
I  Current
Ia  Anode current
J  Radiation flux
J(x)  Normalised electron energy loss function
L  Diffusion length
M  Magnetic field vector
m*  Carrier effective mass
me  Electron mass
N  Free carrier concentration
n  Real part of refractive index
n*  Complex refractive index
(nI) Number of ampère turns
p Induced dipole moment
R Reflectance
R_H Hall coefficient
 ΔR Reflectance change
 ΔR\_R Modulation depth
r Fresnel reflection coefficient
r_0 Maximum penetration of electrons
s Surface recombination velocity
T Transmittance
t Fresnel transmission coefficient
t_1 Electron gun dimension
V_a Anode voltage
V_c Cut-off voltage
V_c^* Cut-off voltage when anode voltage is zero
v Diffusion velocity
w Angular frequency
w Width
w_a Resonance frequency
w_p Plasma frequency
z α\_2
z_0 Impedance of free space
α Absorption coefficient
α_p Polarisability
γ Damping constant
Δ Phase change on transmission
δ Phase change on reflection
δ Skin depth
\( \varepsilon_0 \)  Permittivity of free space
\( \varepsilon_r \)  Relative permittivity
\( \varepsilon_L \)  Lattice dielectric constant
\( \varepsilon \)  \( \frac{1}{2} \left( \frac{3}{D} \right) \)
\( \theta \)  Angle
\( \kappa \)  Imaginary part of dielectric constant
\( \lambda \)  Wavelength
\( \lambda_0 \)  Wavelength in free space
\( \lambda = \frac{\lambda}{(D \tau)^{1/2}} \)
\( \mu \)  Electrical mobility
\( \mu_0 \)  Permeability of free space
\( \mu_r \)  Relative permeability
\( \rho \)  Density
\( \sigma \)  Electrical conductivity
\( \phi \)  Angle
\( \psi \)  Phase angle
\( \chi \)  Volume susceptibility
CHAPTER I — INTRODUCTION

It is well known that at wavelengths beyond the fundamental absorption edge in materials, the dominant absorption mechanism for electro-magnetic radiation is by free carrier absorption. This work describes efforts to utilise this phenomenon to modulate infra-red radiation and in particular radiation of wavelength 10.6 microns which is emitted by a CO₂ laser.

For several years prior to the commencement of this project, research had been undertaken within the department into semiconducting thin films with properties approaching those of the bulk form. Part of this work had involved the observation of optical effects due to free electron plasmas, and particularly the plasma edge. This work raised the possibility of modulating the intensity of incident radiation by adjusting the free electron concentration within the film. Reflectance changes induced in this manner had been reported previously for bulk materials, but it was envisaged that thin film material may allow much larger effects to be observed, as optical interference under the right conditions would give enhancement of any material reflectance changes, and would also allow free carriers produced by an excitation process to be contained within a given volume having high refractive index discontinuities at the faces.

There is presently only one efficient method of modulating the output from a CO₂ laser. This utilises the electro-optic effect in crystals such as CdTe, ZnTe or more commonly GaAs. This method is not totally satisfactory since the crystals used must be carefully screened for mechanical strains or other non-uniformities which degrade their performance, and must be rigidly held in temperature compensated cells to achieve their maximum efficiency. Furthermore these are essentially small aperture devices which limit the maximum radiation power which can be modulated.
A modulator based on an easily prepared thin film of large area may well be much simpler to build and operate and could be used for much higher powers. It is also known that multipass methods improve the performance of any modulator system, and optical interference within the thin film may help in this respect.

Few publications have treated this work theoretically and only recently have attempts been made to relate the observed modulation characteristics to the fundamental electrical and optical properties of the modulator material. In this work a detailed analysis has been made of the properties which a material should have for use as a modulator at 10.6 microns. After a search of possible materials the semimetal antimony was chosen as having the properties most closely matching those required.

Two methods have been investigated for creating the required non-equilibrium carrier density in this material.

The first method chosen was to generate the required carriers directly within the material using a high energy electron beam. When a semiconductor or semimetal is bombarded with high energy electrons, a large fraction of the incident electrons goes into the production of excess hole-electron pairs. Electron beam carrier generation is convenient because the spatial distribution of carrier generation can be precisely controlled and samples of any shape may be used.

The general approach was to observe the reflectance of a thin film at 10.6 microns and to generate a large excess of free carriers by electron bombardment. Towards this end several subsidiary problems had to be solved, these included:
(i) An analysis of free carrier generation was made in order that the beam current and accelerating voltage necessary to generate the required free carrier concentration, could be determined.

(ii) The design and construction of an electron gun to fit these requirements.

(iii) The design and construction of a low power CO$_2$ laser to provide a source of 10.6 micron radiation.

For electrons generated by electron beam, the final carrier concentration is given by the product of generation rate and carrier lifetime. The second method used overcame this limitation by using majority carriers.

The technique employed the double layer structure present at an interface between a conductor and an electrolytic cell. This layer is typically $10^{-10}$ m thick and electrically acts as a capacitance of almost unlimited breakthrough strength. Consequently a potential difference of only a few volts is sufficient to produce a very high field, and large numbers of charges may be induced into a narrow region adjacent to the interface, remaining there until the applied potential is removed.

Carrier densities which can be achieved in this way are known to produce significant reflection changes in both metals and semiconductors. It is proposed to investigate whether this technique using pure or doped antimony thin film samples may be used to modulate 10.6 micron radiation. This work is described in chapter 8.

In chapter 2 is given a survey of the various phenomena which may be used to modulate the intensity of infra-red radiation including the electro-optic, magneto-optic and free carrier effects. A review of free carrier modulation is given up to the most recent information.
Chapter 3 deals with relevant theory of the optical properties of solids. The Drude-Zener theory is used to describe the contribution of free carrier effects to the optical constants of materials and the phenomenon of the plasma edge is explained. The reflectance of thin films having complex refractive indices is derived and particular attention is paid to the phase angles involved which appear ambiguously in the equations. Finally the reflectance of a hypothetical semiconducting thin film is computed as a function of wavelength, in order to show the effect of carrier mobility and film thickness on the plasma edge.

Chapter 4 describes the considerations behind the choice of material. A suitable material should be easily prepared in thin film form, which should exhibit a sharp plasma edge, preferably near the operating wavelength in order that significant reflection changes may be expected. It is shown that the material which best fits these requirements is antimony.

Chapter 5 describes the investigation of the optical properties of evaporated thin films of antimony in the infra-red as a function of their thickness and changes in free carrier concentration. This is achieved by the interpretation of previous data on the optical properties of antimony films, together with the use of detailed measurements of the optical constants of bulk polycrystalline material. A computer program is used to predict the modulation performance which may be expected.

Chapter 6 describes a theoretical investigation of the penetration of kilovolt electrons into solids in order to determine the electron beam current and acceleration voltage required to produce a specific free carrier density.

Chapter 7 describes the experimental equipment, and the attempts made to observe reflectance changes induced by electron pulses. The results are explained by reference to the previous chapter.
Chapter 8 describes the work using the electrolytic cell and Chapter 9 summarises the results of the investigation and indicates fruitful areas of further research.
CHAPTER 2

2.1 Possible methods of modulation of 10.6 μm radiation

Modulation methods for optical beams can be grouped into internal techniques dependent upon effects associated with the generator medium and external techniques, associated with devices outside the latter. This chapter is concerned with the latter for infra-red radiation particularly in the region of the output of the CO_2 laser at 10.6 μm.

2.1.1 Induced birefringence

One class of modulators is based on the electro-optic effect in which birefringence is induced in the media by the application of an electric field. Electro-optic materials may be divided into two classes. The first possess a quadratic (Kerr effect) effect: these include amorphous materials such as liquids. The second class comprises materials that exhibit a linear or Pockels effect – which include crystals having cubic or uniaxial symmetry.

The induced birefringence may have two useful effects. Thus if a light wave is polarised parallel with one of the axes an advance or retardation occurs and the wave is phase modulated. On the other hand if the wave is polarised \( \frac{1}{4} \lambda \) radians to the induced axes, the wave becomes elliptically polarised and if the medium is placed between two crossed polarisers, amplitude modulation occurs.

Modulation using the electro-optic effect may be performed at high frequency and hence broadband performance can be obtained. By making use of travelling wave structures, radiation of visible and near IR frequencies has been modulated at frequencies up to 1 GHz in KDP crystals \[1\]. The depth of modulation can be increased by adopting multipass methods as by making the modulator part of a Fabry-Perot resonator.
Mechanical strains and/or nonuniformities in the active medium tend to degrade electro-optic, as well as other forms of modulation, by producing variations in refractive index which scatter the beam and distort the wavefronts, and in birefringence which reduces the modulation depth.

Electro-optic modulation of 10.6 micron radiation has been based on GaAs since the more common electro-optic materials (KDP, ADP and LiTaO$_3$) are opaque in this region. The polariser and analyser can be Brewster stacks and a modulation depth of up to 30% can be obtained at MHz frequencies. It is expected that a long travelling wave modulator could be successfully operated.

An improvement on the performance of GaAs may be obtained by the use of crystals of ZnTe orCdTe which have increased electro-optic coefficients at 10.6 microns of 30% and 100% respectively.

A second class of modulators has been based upon the magneto-optic effect. When a magnetic field is applied to magneto-optic media, changes in refractive index occur that can result in different velocities of propagation for different directions or senses of polarisation of an incident EM wave. As with electro-optic materials, magneto-optic materials may be divided into two classes.

The Cotton-Mouton (Voigt) effect arises when a medium is made birefringent with an applied transverse magnetic field. For an incident e.m. wave, the refractive index has different values according as the electric vector is perpendicular or parallel with the magnetic-field direction. The change in refractive index is proportional to the square of the magnetic field and thus this phenomenon resembles the electro-optic Kerr effect.
The linear effect - magneto-optic rotation is known as Faraday rotation for transmission and Kerr rotation for reflection. Phenomenologically this effect arises as a measure of the dispersion due to cyclotron resonance absorption and is large for materials with high electrical mobilities. It is generally associated with regions of natural optical dispersion.

Of the magneto-optic phenomena available for optical modulation the Faraday effect is the strongest and therefore the most useful. A suitable medium situated in a magnetic field rotates the plane of polarisation of an incident wave through an angle proportional to the field. If in arrangements including a polariser and an analyser set orthogonally, an alternating field is applied then linear modulation may be obtained.

Magneto-optic effects also lend themselves to the construction of non-reciprocal devices. Thus if a magnetic medium is longitudinally polarised then absorption is large for the positive-rotating and small for the negative-rotating wave. The applied field is adjusted to give a rotation of $\frac{1}{4}\pi$ radians so that the wave reflected back from the output re-emerges with a polarisation orthogonal to that of the incident wave.

The high electrical mobility of InSb gives a large specific Faraday rotation and makes this material useful for a practical modulator [4] although the low fields encountered in waveguide structures would require the mobility to be increased by cooling. The practical lower wavelength limit would be about 300 microns.

Modulation over the wavelength range 1-5 microns has been achieved with the ferrimagnetic yttrium iron garnet which is transparent over this range [5].
Free carrier rotation in InSb has been used to rotate 10.6 micron radiation using a slab 0.5 mm thick which absorbs 10% of the incident radiation. A $\frac{1}{4} \pi$ radian rotation was obtained with a field of 5000 Gauss.

2.1.2 Acousto-optic methods

The acousto-optic effect has been used in two ways to modulate incident EM radiation. In the first the frequency of the incident light is altered by the Doppler effect due to reflection from travelling waves in the medium. In the other, radiation is diffracted by a standing acoustic wave in the medium.

The performance of acousto-optic modulators over a wide range of wavelengths has been reviewed by Sypek. Modulation of 10.6 μm wavelength radiation has been reported, in several materials, among these GaAs and GaP, which are transparent at this wavelength and which possess the good acoustic and optical properties required.

2.1.3 Electromechanical methods

Full depth modulation at low frequencies with specified waveforms e.g. square or sinusoidal can be readily achieved using electro mechanical methods, which can in principle work with EM radiation of any frequency. Optical beams may be modulated by techniques based on rotating vaned wheels, vibrating surfaces, diffraction and piezo electric control. Other modulators have been based upon moving mirrors, moving gratings or the mechanical stressing of a fused silica plate to produce optical activity.
2.1.4 Semiconductor field effect methods

Optical modulators based upon semiconductors can be grouped into field-effect and free carrier devices. The former gives negligible delay times. The optical absorption semiconduction is characterised by a sharp rise for frequencies above the band gap. If the medium is subjected to a large electric force, this absorption edge is shifted by the Franz-Keldysh effect to lower frequencies. A reasonably linear response is obtained if the modulating field is superimposed on a d.c. bias.

Absorption edge modulation has been demonstrated for frequencies up to 10 MHz. One device based on GaAs used a reverse biased p-n junction to obtain the necessary field. A modulation depth of 90% was observed at a wavelength of 1.56 microns (peak) using a modulating potential of only a few volts |9|.

2.2 Free carriers in solids

The process of formation of free carriers requires energy for overcoming the energy gaps between allowed bands or between local impurity levels and these bands. Under normal conditions this energy is supplied from the reservoir of thermal energy within the crystal, and an increase in temperature changes the electron energy distribution in the lattice and increases the number of free carriers (holes and electrons).

Free carriers (liberated by thermal ionisation) having densities corresponding to thermal equilibrium are known as equilibrium carriers.
Apart from thermal ionisation, carriers may be generated by a variety of other means e.g. ionisation by high energy photon (internal photo effect), by high energy particles (electron beams etc.), injection across rectifying contacts or by the application of strong electric fields (impact ionisation). In contrast to thermal ionisation, energy used to generate free carriers by these means is retained mainly by the carriers and the average thermal energy of the lattice remains practically undisturbed. Carriers formed in this way are therefore referred to as non equilibrium carriers.

Free carrier absorption can in the simplest way be described in terms of the classical dispersion theory. This theory (Drude-Zener) starts from an assumption that the motion of an electron is damped simple harmonic and leads to the expression for absorption ($\alpha$) of

$$\alpha = \frac{N e^2}{\sum \Sigma \sum m^* (\omega^2 + \nu^2)}$$  \hspace{1cm} (2.1)

where $N$ is the number of free carriers, $m^*$ the effective mass, $\omega$ the angular frequency and $\nu$ is the carrier-lattice collision frequency. The absorption thus depends on carrier density and frequency and rises rapidly with wavelength.

Spitzer and Fan [10] showed that the infra-red absorption of silicon and germanium could be explained using the Drude model for low or moderate carrier concentrations. For very high carrier concentrations (> $10^{25} \text{m}^{-3}$) there is some departure from the relation, but this may be explained in terms of a degenerate energy band scheme.

Free carrier infra-red absorption in germanium was shown by Briggs and Fletcher [11] and Newman [12] to be proportional to the concentration of free carriers independent of whether those carriers were introduced into the lattice by doping or injection (i.e. equilibrium or non equilibrium carriers).
The dependence of optical absorption (and reflection) upon the carrier effective mass was used by Spitzer and Fan [10] to estimate the effective mass of carriers in germanium at room temperature from reflection measurements alone. The value obtained of $m^* = 0.15 m_e$ compares well with the value $m^* = 0.145 m_e$ measured by cyclotron resonance. Moreover this procedure can be applied over very broad ranges of temperature and free carrier concentration, and was used by Kessler and Sutter [13] to study the non parabolicity of the conduction band in InSb by measuring the absorption of 16 samples with different carrier concentrations.

Free carriers cannot directly absorb photons because of the difficulty of preserving both energy and momentum. These conditions can be fulfilled through electron interaction with the crystal lattices. The absorption depends on the electron lattice collision frequency which also determines the conduction properties of the crystal. Inspection of equation (2.1) i.e. in the approximation of $\omega \tau >> 1$ shows that the simple Drude theory predicts an $\omega^{-2}$ dependence for the absorption coefficient $\alpha$ provided that the collision time $\tau$ is assumed to be frequency independent. Actually $\tau$ depends very critically on the type of scattering mechanism, and optical measurements have been used to identify scattering by optical phonons [VisVanathan (1960)], acoustic phonons [Fanet (1956)] and ionised impurities [Fan et al (1956)].

The dependence of absorption on carrier concentration allows the possibility of modulation by injection. Gibson (1953) [16] measured absorption modulation in germanium induced by varying the minority current in a diode. Newman (1953) [12] modulated 2.3 μm radiation by adjusting the current in a germanium diode, and the effect was used by Briggs and Fletcher (1953) [11] to measure the distribution of free carriers injected across a p-n junction.
The major problem is to inject sufficient carriers into the sample. Typically a sample of germanium may have $N = 10^{13}\text{mm}^{-3}$, $\mu = 0.3\text{m}^2/\text{v}\text{s}$, $\alpha = 0.4 \times 10^5\text{m}^{-1}$ and $\tau = 50\mu\text{sec}$. The diffusion length $\sqrt{\tau}$ corresponding to these parameters is 0.6 mm. The injected current must ensure that the concentration reaches say $6 \times 10^{13}\text{mm}^{-1}$ for a thickness equal to the diffusion length, and for the assumed lifetime of 50 $\mu\text{sec}$, this corresponds to an injection current of 20 Amp.$\text{mm}^{-2}$ which is very near if not greater than the heating limit of the sample.

2.3 *Generation of excess free carriers*

The concentration of non equilibrium free carriers in a material may be increased in several ways including ionisation by high energy photons, by high energy particles, by injection and by impact ionisation. In this section a review is given of optical modulation caused by excess free carriers which are generated by these means.

2.3.1 *Optically induced carrier modulation*

Free carriers may be generated in a material by the internal photo effect, and the number of holes and electrons is equal because the electrical neutrality of the crystal is preserved. The effect has been studied extensively by the use of photoconductivity, and a great deal of data has been obtained on such items as the lifetime of charge carriers, recombination mechanisms, impurity centres, on the nature of electrical contacts and the possible occurrence of space charge [18].

With the advent of the laser, much high photon fluxes became available and it was discovered [19] that certain materials exhibit a changed reflectance or absorbance for a period after intense illumination. In a typical arrangement a slab of material is inserted into the cavity, its loss inhibiting oscillation. During the build up of
population inversion weak laser action commences and eventually the material becomes saturated and substantially transparent. The highly inverted population combined with a low loss cavity then results in an intense output radiation pulse [20].

Several materials show photobleaching [21] under intense illumination. This process involves the removal of ground state molecules to other states having smaller absorption cross-sections at the exciting frequency. The population inversion so produced can in certain circumstances be made to amplify a weak electromagnetic wave with a different frequency which is propagated through the material simultaneously. Experiments with dye-absorbers show a weak pulse which may be amplified by up to 800 dB.

Enhanced reflectance by saturation is also known in germanium, silicon and gallium arsenide [22]. During intense irradiation a dense electron hole plasma is induced by thermal effects and the internal photoeffect and the reflectance is altered [23]. In one experiment [24] the reflectance of silicon at 10.6 μm was observed using a CO₂ laser as a probe. During irradiation the reflectance first decreased from 30% to 19% and then rose to 50% as the excitation was increased. The concentration of non equilibrium carriers at minimum reflectance corresponded to Δn = Δp = 2 x 10²⁵m⁻³.

Enhancement of the reflectance at 1.15 μm of a germanium crystal under irradiation with a Q-switched ruby laser has been observed [25] using a HeNe gas laser as the probe light. Instantaneous values for n and κ are given. Measurements have been extended to InSb and liquid selenium [26].

The reflectivity of metals also varies under conditions of intense illumination [27]. In this case the reflection coefficient falls since the incident radiation can have no effect on the concentration of conduction electrons but only reduces their mobility on account of heating effects.
2.3.2 Electrically induced free carrier modulation

The reflectance of semiconductors has been altered by injecting free carriers into the sample across a p-n junction [28], and since the depletion layer only is involved high frequencies have been achieved.

An improved performance can be obtained by using multiple internal reflections at a semiconductor interface [29].

The sub millimeter region is exceptionally well suited to free carrier modulation. This arises because the non equilibrium carrier concentration corresponding to 10 microns is $10^{25} \text{m}^{-3}$ while for 1000 microns (1 mm) is only $3 \times 10^{21} \text{m}^{-3}$ and proportionally fewer extra carriers are required to produce a useful reflectance change [30]. One successful device was based on a p-i-n structure placed in a waveguide while another used a magnetic field to divert a control current flowing through a strip towards a surface of large recombination rate [31].

The application of a very high field to a semiconductor (about 1 kV/mm) is known to increase the carrier mobility and from equation (2.1) reduce the absorption. The process involved is fundamentally the giving to carriers an energy greatly in excess of their equilibrium energy, i.e. making them "hot", which serves to reduce the relaxation time $\tau$. A successful modulator of 10.6 micron radiation working on this principle has been constructed. Kilovolt, microsecond electrical pulses were applied across a Ge crystal having a width of 2 mm, which produced hot carriers. Using a CO$_2$ laser a modulation depth of about 1% was observed [32].
Another form of carrier injection utilises the strong electric field in the dipole layer adjacent to a semiconductor-electrolyte interface. The Helmholtz or dipole layer is typically only $10^{-10}$ m thick and simulates a field electrode of nearly unlimited breakthrough strength and external potential differences of only a few volts cause drastic changes of the surface potential. The large electric field produced apparently affects the band structure of the semiconductor and alters the optical constants of the lattice at specific critical points. The resultant modulation spectrum can be very sharp and the technique has become widely used in the diagnostics of band structure [33].

If the electrode is metallic, i.e. a good conductor, the modulating field is screened out within atomic dimensions of the surface leaving a field free region over most of the penetration distance of the light. In copper for instance the field penetration depth of 0.5 Å should reveal little about the band structure to a depth of 100 Å which is typically probed by the light.

In spite of this argument reflectance modulation has been observed in Au, Ag and Cu by Feinleib (1966) [34] using the electrolytic technique. The modulation mechanism is unclear. One suggestion [35] depends on cooperation with changes in the optical constants of the electrolyte in the sense that the electrolyte acts as a sensitive probe for the discontinuities of the reflectance curve. Another argument has been proposed [36] which suggests that the observed modulation can be predicted from free carrier effects within the metal.

Free carrier effects are believed to account for electrolytic electroreflection measurements of some semiconductors in the infra-red. The accumulation or absence of free carriers in the surface region of a semiconductor can cause the dielectric response to differ slightly from that of the bulk. Modulation of the reflectance can result from
a field induced variation of this "antireflection coating" that the thin dielectric film represents. Axe and Hammer 1957 [37] observed peak modulations of several percent in the infra-red spectrum (10-15 \( \mu \text{m} \)) of germanium and gallium arsenide. The effect is particularly strong near Restrahlen or free carrier plasma frequencies.

A similar mechanism was proposed by Sosnowski [38] to account for the change of reflectance of germanium produced by injecting current carriers via diode action which was observed by Filinski [39].

A technique for the observation of these effects in the infra-red and other regions where the electrolyte is opaque to the probe light has been described by Hansen and Prosta [36]. Here the material is in the form of a semitransparent thin film on a transparent substrate which forms part of the wall of an electrolytic cell. The probe light is made to approach the film from the substrate side and undergoes partial reflection at the sample-electrolyte interface.

The modulation frequency is limited by the finite mobility in the ionic space charge layer. Measurements in many systems have shown no saturation of capacitance below 10 MHz [40].

2.3.3 \textit{Electron beam induced free carrier modulation}

When a semiconductor is bombarded with high energy electrons, a large fraction of the incident electrons goes into the production of excess hole-electron pairs. Electron beam carrier generation is convenient to use because the spatial distribution of generation can be precisely controlled and samples of any shape may be used.
Electron beams have been used extensively in the study of radiative recombination in highly excited semiconductors [42, 42]. Most interest has been centred on GaAs. It has been shown that the spectral shape and peak position of the radiative recombination in this material is free carrier concentration dependent [43] and the spectrum when excited by electron beam is similar to that from a GaAs diode [44].

With the advent of the semiconductor laser, electron beams have been used both for diagnostic purposes and for laser pumping [45, 47]. Both Klein [46] and Anderson [47] have stressed the importance of the spatial distribution of primary energy losses and the importance of the work of Spencer [48] and Ehenburg and King [49] in this respect.

Electron beams have been used to induce reflectance changes due to free carriers. Wittry and Kyser [50] used a converted electron probe microanalyser to produce a focussed 50 kV electron beam which modulated the reflectance and absorbance of a sample of germanium.

The modulated absorption at wavelengths longer than the bandgap was found to be primarily due to excess free carriers generated by the beam. It was expected that there should be a lack of linearity between response and current density because band-band Auger recombination reduces excess carrier lifetime [51] for carrier densities above $5 \times 10^{23} \text{m}^{-3}$. Such a non-linearity was not observed either due to lack of sensitivity or because of high surface recombination.

Pefley [52] has observed enhanced time dependent free carrier absorption in silicon induced by high energy electrons. In contrast to virtually all other investigations of this kind, it was ensured that free carriers were generated throughout the material; also free carrier lifetime was considerably longer than the excitation pulse. Pulses from a 10 MeV electron accelerator were employed to generate excess electrons in a
10 mm cube sample of 53 ohm-cm sample of n-type silicon. The absorption was monitored at 1.1 microns using a HeNe laser, and changes detected by a fast silicon photodiode were displayed on an oscilloscope. Estimates of free carrier concentration from absorption measurements agreed with the estimate from the total radiation dose of about $5 \times 10^{23} \text{m}^{-3}$. 
3. The Optical Properties of Absorbing Media

3.1 Introduction

The most easily observable optical properties of materials are the transmission coefficient $T$ and the reflection coefficient $R$, both of which are related to the refractive index $n$ and the absorption coefficient $\kappa$.

Consider first absorption. Light quanta are absorbed in a solid by two processes; (a) their energy can be used to raise an electron to a state in the band model by an energy equal to the photon energy $h\nu$, or (b) lattice vibrations may be excited. Observation of the latter process may give information about the bonding properties of the lattice, effective charges of the lattice atoms, and the characteristic frequencies of lattice vibrations.

In contrast the interaction of photons with the electrons is determined by the structure of the energy bands and consequently studies may give information or verification of the parameters of the band model. Light induced transitions may occur between different bands or within a single band. The first possibility leads to the appearance of an absorption edge at or near the minimum transition energy, and the shape of which depends upon the nature of the transition (i.e. direct or indirect), or alternatively leads to the appearance of absorption peaks if the transitions are confined to narrow energy regions. Measurements on such edges in the infra-red, visible or ultraviolet parts of the spectrum have enabled a quantitative band structure picture of many materials to be derived or verified.
Transitions within a single band (free carrier absorption) are determined by the nature, behaviour and number of charge carrier species. The effects of free carrier absorption can frequently be separated from absorption due to other phenomena, without the aid of any specific atomic model, and have led to very accurate measurements of carrier effective mass or carrier density together with other data on relaxation time and mobility.

All phenomena which determine absorption are also to be found in the reflection spectrum of materials, indeed, historically reflection phenomena in the far infra-red gave the first indications for the existence of lattice vibrations.

In general the optics of metals and insulators are linked to the optical indices $n$ and $\kappa$ which are regarded as constants for a particular material, i.e. dielectrics are treated as elastic materials without regard to their regions of resonance and metals are treated only in their regions of reflectivity. However the indices $n$ and $\kappa$ may change enormously when the material is observed with radiation of a different wavelength. A good phenomenological explanation of the wavelength dependence of the optical constants of a dielectric, may be obtained from the simple classical treatment of Lorentz, which treats the solid as an assembly of oscillators set into forced vibration by the radiation, modified to include damping forces due to for example collisions of electrons with phonons and impurity atoms. Many optical properties of various materials can be explained on this basis and quantitative descriptions of resonance effects of electronic, molecular, lattice vibrations etc. may be made.
Using these ideas it becomes evident that the optical properties of metals are characterised by the behaviour of free electrons in which the absence of restraining forces is mirrored by the absence of resonances, and the predictions of Maxwell's Theory are valid up to the frequencies of the near infra-red. At higher frequencies the optical constants show marked changes due to the fact that collisions do not allow the electrons to freely follow the electric field of the incident radiation.

Dielectrics are characterised by lattice vibrations, the frequency of which depends strongly upon the atomic mass of the material; these materials generally have a large band gap so their intrinsic absorption edge lies deep in the ultraviolet. Ionic dielectrics are capable of well defined, strong dipole oscillations which generally extend over the infra-red (Restrahlen). In wavelength regions where any of these oscillations occur there are large variations in the indices $n$ and $\kappa$ and these are manifested in the absorption and reflection spectra.

In this chapter the general macroscopic phenomena of reflection, absorption and transmission together with the Brewster and Critical angles are described in terms of the optical constants $n$ and $\kappa$ using Maxwell's equations. The wavelength dependence of the optical constants is then described with particular attention paid to the effects of free electrons or carriers. This earlier work is used in section (3.8) to develop the equations for the reflectance of a thin film of a conducting material. The properties of such films differ from the better known dielectric thin films, because the refractive index is complex, and the phase angles involved are in general neither zero nor $\pi$, consequently these films exhibit reflectance and absorption which varies in a complicated manner with wavelength, film thickness and free electron density. Finally the reflectance of a hypothetical semiconducting thin film is computed.
3.2 The propagation of E.M. waves in materials

The propagation of electromagnetic waves is described by the four Maxwell's equations, which deal entirely with macroscopic phenomena. For the case of an infinite homogeneous medium of dielectric constant $\varepsilon_r$ and magnetic permeability $\mu_r$, having a conductivity $\sigma$, these equations become a set of simultaneous partial equations, which may be solved to give the wave equations for the electric field vector $E$ and the magnetic field vector $H$:

\[
\begin{align*}
\nabla^2 E &= \mu_r \varepsilon_0 \varepsilon E - \frac{3E}{3t^2} + \sigma \frac{\partial E}{\partial t} \\
\nabla^2 H &= \mu_r \varepsilon_0 \mu H - \frac{3H}{3t^2} + \sigma \frac{\partial H}{\partial t}
\end{align*}
\]

(3.1)

(3.2)

These two equations are each of the general form for a wave motion in three dimensions. These equations may have a general solution of the form — for the $E$ vector

\[
E = E_0 \left[ \exp \left( j \omega (t - \frac{n^* r}{c}) \right) \right]
\]

(3.3)

where $\omega$ is the angular frequency, $n^*$ the complex refractive index of the medium and $c$ is the velocity of light in free space. Equation (3.3) is the equation for an unattenuated travelling wave. Combining equations (3.1) and (3.3) gives

\[
\frac{\omega^2 n^*}{c^2} E_0 = E_0 \left( \omega^2 \varepsilon \varepsilon_0 \mu \mu_0 + j \omega \sigma \mu \mu_0 \right)
\]

(3.4)

Put

\[
n^* = n - j \kappa
\]

(3.5)

where $n$ is the real part of the refractive index and $\kappa$ is the imaginary part, then

\[
n^2 - \kappa^2 = \varepsilon_r \varepsilon_0 \mu \mu_0 \frac{c^2}{\omega}
\]

(3.6)

\[
2n \kappa = \frac{\sigma \mu \mu_0}{\omega} \frac{c^2}{\omega}
\]

(3.7)
To understand the real significance of $n$ and $\kappa$ equation (3.3) may be rewritten as

$$E = E_0 \left[ \exp \left( \frac{-\kappa \cdot x_0}{c} \right) \cdot \exp j (\omega t - \frac{n \omega x}{c}) \right]$$

(3.8)

showing that the value of $\kappa$ determines the rate at which the wave amplitude decays, while $n$ determines the wave velocity in the medium. Thus a complex refractive index implies that the wave is being absorbed as it proceeds because the finite conductivity of the medium gives rise to a power loss through Joule heating.

Empirically the intensity ($I$) of a wave passing through an absorbing medium is found to be attenuated according to the equation

$$I = I_0 \exp (-\alpha x)$$

(3.9)

where $I_0$ is the initial intensity at $x = 0$ and $\alpha$ is the absorption coefficient. From equation (3.8) $\alpha$ can be related to $\kappa$ by the equation

$$\alpha = \frac{n \omega c}{c} = \frac{4 \pi n \kappa}{\lambda}$$

(3.10)

where $\lambda$ is the wavelength of the radiation.

The intrinsic impedance of the medium ($Z_o$) may be defined as $\frac{E_y}{H_z}$ so that

$$Z_0 = \frac{\mu \nu_0 c}{n^*}$$

(3.11)

The impedance is therefore a complex quantity but is independent of $x$ or $t$. This means that the ratio of $\frac{E_y}{H_z}$ is everywhere the same, but there may be a phase lag between them.

The full solution of equations (3.6) and (3.7) to find $n$ and $\kappa$ is rather complicated, but it may be simplified by considering the cases of a dielectric, a metal and a semiconductor separately.
3.2.1 **Dielectric Materials**

Dielectric materials are very poor conductors, therefore the conductivity \( \sigma \) and the free charge density \( \rho \) may be considered zero. Under these conditions equation (3.1) becomes

\[
\nabla^2 \mathbf{E} = \frac{\varepsilon_0 \mu}{\varepsilon_\infty} \left( \frac{\partial^2 \mathbf{E}}{\partial t^2} \right)
\]

which is the equation of a wave with velocity \( n \) given by

\[
n = (\varepsilon_\infty \mu_0)^{-\frac{1}{2}}
\]

with the particular value for free space \((\mu = 1, \varepsilon = 1)\) of

\[
c = (\mu_0 \varepsilon_0)^{-\frac{1}{2}}
\]

The wave velocity is given according to equation (3.8) by

\[
n = \frac{c}{n}
\]

Therefore

\[
n = (\varepsilon_\infty)^{\frac{1}{2}}
\]

For non-magnetic materials \( \mu = 1 \), therefore for a dielectric

\[
\varepsilon_\infty = n^2
\]

Also from equation (3.7), because \( \sigma = 0 \)

\[
2m\kappa = 0
\]

Therefore for a dielectric

\[
\kappa = 0.
\]
### 3.2.2 Metals

A metal has a very large conductivity, and the term containing \( \sigma \) therefore dominates equation (3.1). In this case

\[
\begin{align*}
    n^2 - k^2 &= 0 \\
    n &= \kappa = \left( \frac{\sigma \mu \nu_0 e}{\omega} \right)^{\frac{1}{2}}
\end{align*}
\]

(3.19) \hspace{1cm} (3.20)

It is possible to introduce a quantity \( \delta \) such that

\[
    n = \kappa = \frac{c}{\omega \delta}
\]

(3.21)

then the field components are propagated in the metal as

\[
    \exp \left( -\frac{x}{\delta} \right) \exp \left( j \left( \omega t - \frac{x}{c} \right) \right)
\]

(3.22)

from which it can be seen that \( \delta \) has the dimensions of length. \( \delta \) is known as the "skin depth", and the amplitude of the wave falls to 1/e of its initial value in a distance \( \delta \), while the apparent wavelength in the metal is \( 2\pi \delta \). The equation for \( \delta \) is

\[
    \delta = \left( \frac{2}{\omega \sigma \nu} \right)^{\frac{1}{2}}
\]

(3.23)

### 3.2.3 Semiconductors

The case of semiconductors and poor metals is intermediate between cases (a) and (b); \( n \) and \( \kappa \) now take values appropriate to the interaction of electromagnetic radiation with the electronic structure of the material, and are affected by the behaviour of both bound and free electrons within the lattice.
3.3 Reflection of waves at a boundary

Assume two non-conducting dielectric media separated by a plane at \( z = 0 \). When an electro-magnetic wave falls on this boundary there will in general be a reflected and a transmitted wave as shown in figure (3.1). The relative amplitudes of these waves relative to that of the incident wave may be computed from the well known Fresnel formulae.

It is possible to satisfy all conditions for incident polarised light by taking two cases. These are for the electric vector normal and parallel to the plane of incidence. By adding the field components of the three waves in each case, and applying the boundary conditions, that the tangential components of electric and magnetic fields are continuous across the boundary.

The field components of the three waves may be written in general as

\[
\begin{align*}
\text{Incident wave} & \quad E_i = E_{oi} \exp j (\omega t - n_i \mathbf{k}_i \cdot \mathbf{r}) \\
\text{Reflected wave} & \quad E_r = E_{or} \exp j (\omega t - n_i \mathbf{k}_r \cdot \mathbf{r}) \\
\text{Transmitted wave} & \quad E_t = E_{ot} \exp j (\omega t - n_t \mathbf{k}_t \cdot \mathbf{r})
\end{align*}
\]

It can be shown that the amplitudes of the various waves are

\[
\begin{align*}
r_i &= \frac{n_1 \cos \theta_i - n_2 \cos \theta_t}{n_1 \cos \theta_i + n_2 \cos \theta_t} \\ t_i &= \frac{2 n_1 \cos \theta_i}{n_1 \cos \theta_i + n_2 \cos \theta_t} \\ r_{ll} &= \frac{n_1 \cos \theta_t - n_2 \cos \theta_i}{n_2 \cos \theta_i + n_1 \cos \theta_t} \\ t_{ll} &= \frac{2 n_1 \cos \theta_i}{n_2 \cos \theta_i + n_1 \cos \theta_t}
\end{align*}
\]
Figure (3.1) The incident wave OA, the reflected wave OB and the transmitted wave OC.
where $r_{11}$ and $t_{11}$ are the amplitude coefficients of the reflected and transmitted rays, the subscripts $\parallel$ and $\perp$ indicate the electric vector of the wave is perpendicular or parallel to the plane of incidence respectively. $\theta_r$ and $\theta_t$ are the angles of incidence and transmission, $n_1$ and $n_i$ are the refractive indices of the first and second media.

For normal incidence equations (3.27)-(3.30) reduce to

$$r = r_{11} = \frac{n_1 - n_2}{n_1 + n_2} \quad (3.31)$$

$$t = t_{11} = \frac{2n_1}{n_1 + n_2} \quad (3.32)$$

If $n_1 < n_2$ then $r$ is negative, which indicates a phase change of has taken place at reflection. The intensities of the reflected and transmitted waves are given by

$$R = rr^* = \frac{(n_1 - n_2)^2}{(n_1 + n_2)} \quad (3.33)$$

$$T = tt^* = \frac{4n_1^2}{(n_1 - n_2)^2} \quad \frac{n_2}{n_1} \quad (3.34)$$

The factor $n_2/n_1$ is necessary because of the change in wave velocity in the second medium. The amplitude reflection coefficients $r$ and $t$ give both the magnitude and phase change on reflection.

### 3.3.1 Reflection from the surface of a conducting medium

When an electromagnetic wave is incident on the plane surface of a conducting medium, the amplitudes of the reflected and transmitted waves can be calculated in a manner essentially similar to those used for dielectrics. The refractive index and intrinsic impedance of a conducting medium are complex numbers and the formulae deduced for dielectrics may be taken over as they stand by use of complex
values for \( n_2 \) and \( z_2 \). It is found that on reflection from an absorbing material where \( n \) is complex, the reflection coefficient may in general be written as

\[
    r = |r| \exp(j\psi) \tag{3.35}
\]

where \( \psi \) is the phase change on reflection. In the case of dielectrics \( \exp(j\psi) \) is either 1 or \(-1\), indicating phase changes of 0 or \( \pi \).

### 3.3.2 The Brewster Angle

The amplitude reflection coefficient for an incident wave with the electric vector parallel to the plane of a dielectric interface was given by equation (3.27) as

\[
    r_{11} = \frac{-n_2 \cos \theta_i + n_1 \cos \theta_t}{n_2 \cos \theta_i + n_1 \cos \theta_t}
\]

It is readily shown that the condition that there be no reflection \((r_{11} = 0)\) is that

\[
    \sin 2 \theta_i = \sin 2 \theta_t
\]

which is satisfied if \( \theta_i \) and \( \theta_t \) are complementary angles i.e.

\[
    \theta_i + \theta_t = \frac{\pi}{2}
\]

so that the reflected and refractive rays are normal to one another. Using Snell's law this is shown to occur when

\[
    \tan \theta_i = \frac{n_2}{n_1} \tag{3.36}
\]

This is the Brewster angle at which the phase change on reflection changes by \( \pi \).
3.3.3 Total Internal Reflection

When the refractive index \( n_2 \) of the second medium is less than \( n_1 \), the application of Snell's law

\[
\sin \theta_t = \frac{n_1}{n_2} \sin \theta_i
\]

to find the angle of refraction leads to values of \( \sin \theta_t \) greater than unity when \( \sin \theta_i \) is greater than \( n_2/n_1 \). Since there is no real angle for which the sine is greater than one, and it is concluded that there is no refracted ray and the energy is all reflected.

However a transmitted wave must exist to satisfy the boundary conditions

\[
E_t = E_{ot} \exp\left(j (\omega t - n_2 k_r)\right) \quad (3.26)
\]

\[
= E_{ot} \exp\left(j(\omega t - 2k_o (x \sin \theta_t + y \cos \theta_t)\right)
\]

![Figure (3.2) Total Internal Reflection](image)

Substitute the relation

\[
\cos \theta_t = (1 - \sin^2 \theta_t)^{\frac{1}{2}} = (1 - \left(\frac{n_2}{n_1} \sin \theta_t\right)^2)^{\frac{1}{2}} \quad (3.37)
\]

At total internal reflection \( \frac{n_1}{n_2} \sin \theta_t > 1 \)  

\[
\text{Therefore} \quad \cos \theta_t = j \left(\frac{n_1}{n_2} \sin^2 \theta_t - 1\right)^{\frac{1}{2}} \quad (3.39)
\]
The transmitted wave is, from equation (3.26)

\[ E_t = E_{ot} \exp \left\{ n_2 k_0 \sqrt{\frac{n_1^2}{n_2^2} \sin^2 \theta_{i-1}} \right\} \exp j \left\{ \omega t - n_2 k_0 \sin \theta_{i-1} \frac{n_1}{n_2} x \right\} \]  \hspace{1cm} (3.40)

This is the equation of a wave which travels unattenuated parallel to the interface with a wavelength

\[ \lambda x = \frac{\lambda_o}{n_1 \sin \theta_{i-1}} \]  \hspace{1cm} (3.41)

where \( \lambda_o \) is the wavelength in free space. The transmitted ray is highly attenuated in the direction perpendicular to the interface in such a way that its amplitude decreases by a factor \( e \) over a distance

\[ \delta_y = \frac{1}{k_0 \left( n_1^2 \sin \theta_{i-1} - n_e^2 \right)^{\frac{1}{2}}} \]  \hspace{1cm} (3.42)
3.4 The Optical Properties of Materials

It has been shown in the preceding treatment that virtually all macroscopic phenomena of light propagation, such as reflection, refraction and absorption are derivable from Maxwell's equations. The electromagnetic wave theory, as presented in the preceding sections, has dealt with the indices and parameters as fixed constants, and ignored their wavelength dependence. Thus dielectrics were treated as elastic media without regard to their regions of resonant absorption, and metals were treated only at wavelengths of high reflectance. In fact there exist very large changes in the characteristics of both dielectrics and metals for different wavelengths. The classical approach provides a sound framework on which to describe all pertinent phenomena. This approach is based on the assumption that the optical properties of materials are governed by the behaviour of electrons, within the material. It is assumed that optically, metals are dominated by free electrons, dielectrics by bound electrons, and semiconductors by both.

The computation of the response of the changes to incident radiation amounts to setting up a driving force \( e^\text{int} \) in the Newtonian equation of motion, which depending on the structural model may or may not contain a restoring force (to describe free or bound electrons), or a damping term (due to inelastic collisions). The direct solution of motion will be real if the damping term is absent, and complex if it is present.
3.5 **The Optical Properties of Dielectrics**

It has been shown that for dielectric materials, the refractive index \( n \) is given by

\[
n = \sqrt{\frac{\mathcal{E}_r}{\mu_r}}
\]

and since \( \mu_r \) is generally unity for non-magnetic materials

\[
\mathcal{E}_r = n^2.
\]

From the standpoint of electromagnetic theory a dielectric is regarded as a continuous medium which becomes polarised under the action of a polarising field. The ratio of polarisation to the electric field producing it is proportional to the electric susceptibility and is substantially independent of field strength. The volume susceptibility \( \chi \) is related to the dielectric constant \( \mathcal{E}_r \) by the formula

\[
\mathcal{E}_r = 1 + \chi \quad (3.43)
\]

Modern atomic theory regards any medium as an assembly of atoms or molecules. When a uniform electric field is applied, electrons and nuclei are subjected to forces of different sign and the atom or molecule thereby acquires an induced moment \( P_i \) where:

\[
P_i = \alpha_p E \quad (3.44)
\]

\( \alpha_p \) is a constant called the "polarisability", \( E \) is the local field and is not necessarily equal to the applied field \( E_0 \).

The general relation between the dielectric displacement \( D \), the external field \( E_0 \), the polarisation \( P \) and the dielectric constant \( \mathcal{E}_r \) is

\[
D = \mathcal{E}_0 E + P = \mathcal{E}_r \varepsilon_0 E_0. \quad (3.45)
\]
Here $P$ is the induced moment per unit volume and is related to the local field $E$ by the equation

$$P = n_o \alpha E$$  \hspace{1cm} (3.46)$$

where $n_o$ is the number of dipoles per unit volume.

Also from equation (3.45)

$$P = (\varepsilon - 1) \varepsilon_o E.$$  \hspace{1cm} (3.47)$$

In order to relate the macroscopic dielectric constant $\varepsilon_r$ to the molecular polarisability $\alpha$, the relation between $E$ and $E_o$ is required.

For gases in which the dipoles are well dispersed $E = E_o$. For solids Lorentz showed that the local field is that predicted for a spherical void within the solid i.e.

$$E = E_o + \frac{P}{3\varepsilon_o}$$  \hspace{1cm} (3.48)$$

or more generally

$$E = E_o + \frac{CP}{\varepsilon_o}$$  \hspace{1cm} (3.49)$$

Then

$$P = N \frac{E + \frac{CP}{\varepsilon_o}}{\varepsilon_r}$$  \hspace{1cm} (3.50)$$

$$\varepsilon_o (\varepsilon_r - 1)E = N \frac{E + (\varepsilon_r - 1)E}{\varepsilon_r}$$  \hspace{1cm} (3.51)$$

Therefore

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{C N \alpha_p}{\varepsilon_o}$$  \hspace{1cm} (3.52),$$

which is the Clausius-Mossotti formula.
3.5.1 Optical Dispersion in Dielectrics

In the optical region, variation of the refractive index with wavelength is known as dispersion. In general refractive index increases as wavelength decreases and this is known as "normal dispersion". The reverse case where refractive index increases with increasing wavelength occurs in the vicinity of an absorption line and is known as "anomalous dispersion". Both cases have a simple explanation in terms of classical theory, based on the assumption that an atom contains electrons oscillating at certain natural frequencies and that the application of an alternating electric field sets such electrons into forced vibration, when the frequency of the applied field matches the natural frequency then resonance effects are observed.

The differential equation governing the motion of an elastically bound particle of charge $e$ and mass $m$ in an alternating field $E_0 \exp(\omega t)$, may be written

$$\frac{d^2x}{dt^2} + \gamma \frac{dx}{dt} + \omega_a^2 x = eE_0 \exp(\omega t)$$  \hspace{1cm} (3.53)

where $\omega_a$ is the natural angular frequency of the particle. The second term on the left hand side is a damping term which results from the fact that the particle loses energy as a result of collisions. The solution for this forced damped vibration is

$$x(t) = \frac{e}{m} \cdot \frac{E_0 \exp(\omega t)}{\omega_a^2 - \omega^2 + j\gamma \omega}$$  \hspace{1cm} (3.54)

For low density gases where the local field is equal to the applied field then:

$$C_r = \frac{Ne^2}{mE_0} \cdot \frac{1}{\omega_a^2 - \omega^2 + j\gamma \omega}$$  \hspace{1cm} (3.55)
For solids, assuming the internal field to be given by a Lorentz type expression then

\[ \varepsilon_r^* = \varepsilon_e + \frac{N}{1/\varepsilon_e^* - N/3} \]  \hspace{1cm} (3.56)

where \( \varepsilon_c \) is the contribution to the dielectric constant due to lattice effects. Proceeding as before gives

\[ \varepsilon_r^* = \varepsilon_e + \frac{N e^2}{m_o} \cdot \frac{1}{\omega_o - \omega^2 + j \omega - N e/3m} \]  \hspace{1cm} (3.57)

Comparing this with (3.55) for a gas, it is seen that by defining a new frequency

\[ \omega_o^2 = \omega_a^2 - \frac{N e^2}{3m} \]  \hspace{1cm} (3.58)

the same behaviour is obtained as above, i.e. the absorption frequency is displaced. The dielectric constant \( \varepsilon_r \) is complex and may be written

\[ \varepsilon_r = \varepsilon_r^1 - j \varepsilon_r^{11} = (n^*)^2 = (n - jk)^2 \]  \hspace{1cm} (3.59)

Therefore

\[ n^2 - k^2 = \varepsilon_r^1 \]  \hspace{1cm} (3.60)

\[ 2nk = \varepsilon_r^{11} \]  \hspace{1cm} (3.61)

Then

\[ \varepsilon_r^1 = n^2 - k^2 = \varepsilon_e + \frac{N e^2}{m_o} \left[ \frac{1}{(\omega_o^2 - \omega^2) + j \omega^2} \right] \]  \hspace{1cm} (3.62)

\[ \varepsilon_r^{11} = 2nk = \frac{N e^2}{m_o} \left[ \frac{\omega \gamma}{(\omega_o^2 - \omega^2)^2 + (\gamma \omega)^2} \right] \]  \hspace{1cm} (3.63)

Also

\[ n^2 = \frac{1}{2} (\varepsilon_r^1 + \varepsilon_r^{11}) + \varepsilon_r^1 \]  \hspace{1cm} (3.64)

\[ k^2 = \frac{1}{2} (\varepsilon_r^1 + \varepsilon_r^{11}) - \varepsilon_r^1 \]  \hspace{1cm} (3.65)
In figure (3.3) \((\Sigma_r^1 - \Sigma_r^1)\) and \(\Sigma_r^{11}\) are represented as functions of the frequency \(\omega\). Note that \(\Sigma_r^{11}\) contains the damping factor \(\gamma\) which has the dimensions of frequency; if there were no damping then there would be no absorption. In the absorption region the dielectric constant \(\Sigma_r^1\) depends on frequency, and the region for which \(\Sigma_r^1\) decreases with increasing frequency is referred to as the region of anomalous dispersion.

The formulae show that in the neighbourhood of \(\omega = \omega_o\) there is an absorption maximum and that \(n\) increases rapidly on decreasing \(\omega\) through this region. With continuing decrease in \(\omega\), \(n\) passes through a maximum and falls away asymptotically as the frequency gets further from \(\omega_o\).

However this asymptotic value is still greater than the value on the short-wavelength side of the absorption band, and if there is more than one absorption band, \(n\) increases on passing through each towards longer wavelengths.

Figure (3.4) presents the behaviour of \(n\), \(\kappa\) and the reflectance \(R\) as a function of frequency in the region of a characteristic resonance. The reflectance of a material is defined by the equation
\[
R = \frac{(n^*-1)^2}{(n^*+1)^2} = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2} \quad (3.66)
\]

Note: the maximum value of \(R\) lies at a frequency higher than \(\omega_o\).

In general the interaction of an E.M. field and the absorbing atom may be represented quantum mechanically by a set of linear oscillators corresponding to the allowed transitions. These individual contributions can conveniently be expressed in terms of \(f\) the oscillator strength. In practice the summation of oscillator strengths is determined by the atomic or molecular configurations, according to the mechanism involved.
Figure (3.3) Behaviour of $\varepsilon_{r}^{1} - \varepsilon_{L}$ and $\varepsilon_{r}^{11}$ as a function of frequency in the vicinity of the resonance frequency $\omega_{0}$.

Figure (3.4) The theoretical behaviour of a classical oscillator.
Dispersion phenomena can be associated with any polarisations which are unable to establish themselves completely before the applied fields are reversed. When the polarisation consists of the displacement of electrons relative to their corresponding nuclei, the characteristic frequencies lie usually in the visible and U.V. regions. If the polarisation involves elastic vibration of nuclei relative to one another the dispersion falls in the I.R. region. Dispersion in the sub millimetre region is usually associated with changes in orientation of polar groups of atoms.
3.6 The optical properties of conducting materials

Good conductors are characterised by the fact that valence electrons of the constituent atoms are not bound to fixed atom sites but free to move through the lattice with little or no restriction. The absence of forces restraining the electron to certain centres is characterised by the absence of resonances, and a variation of refractive index with frequency which is gradual (up to the frequencies of the near infra-red and visible for most metals).

However at very high frequencies, it is necessary to account for the finite resistance of a metal, which is due to collisions of the electrons with phonons and impurity atoms, the effect of which amounts to a damping force in proportion to the frequency of such encounters, and the equation of motion of electrons when driven by a field $E \exp(j\omega t)$ becomes:

$$m \frac{d^2x}{dt^2} + m\gamma \frac{dx}{dt} = -e E_o \exp(j\omega t)$$  \hspace{1cm} (3.67)

This equation has a solution

$$x = \frac{-eE \exp(j\omega t)}{m(\omega^2 + \gamma j\omega)}$$  \hspace{1cm} (3.68)

Giving

$$n^2 - \kappa^2 = \varepsilon_1 - \frac{Ne^2}{mE_o} \cdot \frac{1}{\omega^2 + \gamma^2}$$  \hspace{1cm} (3.69)

$$2\kappa = \frac{Ne^2}{mE_o} \cdot \frac{\gamma}{\omega} \cdot \frac{1}{\omega^2 + \gamma^2}$$  \hspace{1cm} (3.70)

$\gamma$ can be interpreted as $\frac{1}{\tau}$ where $\tau$ is the relaxation time i.e. the mean time between electron-lattice collisions. Then

$$n^2 - \kappa^2 = \varepsilon_1 - \frac{Ne^2}{mE_o} \cdot \frac{1}{\omega^2 + \frac{\tau}{\omega^2}}$$  \hspace{1cm} (3.71)

$$2\kappa = \frac{Ne^2}{mE_o} \cdot \frac{1}{\tau\omega} \cdot \frac{1}{\omega^2 + \frac{\tau}{\omega^2}}$$  \hspace{1cm} (3.72)
When the periodic time of the applied electric field is much shorter than the relaxation time, damping will be very low and 

\[ n^2 - \kappa^2 = \varepsilon_1 - \frac{Ne^2}{m\varepsilon_0} \cdot \frac{1}{\omega^2} \]  
(3.73)

\[ 2\pi \kappa \approx 0 \]  
(3.74)

It is clear from equation (3.73) that if one ignores the damping term (and hence absorption) the refractive index will decrease rapidly with decreasing frequency and will in due course reach unity. A further slight reduction in frequency would bring the index down to zero. To the same degree of approximation the reflectivity is

\[ R = \frac{(n - 1)^2}{(n + 1)^2} \]

Hence when \( n = 1 \) \( R = 0 \) and when \( n = 0 \) \( R = 1 \). Therefore one would expect that at some wavelengths the reflectivity of a material should fall to zero, and at a somewhat longer wavelength should rise to 100% producing the so-called "plasma edge" in the reflection spectrum.

In practice of course the presence of damping due to finite mobility and collision times prevents the reflectivity from reaching either 0 or 100% and generally smears out the edge to some degree.

![Graph](image-url)  

**Fig. (3.5)** The plasma reflection edge in a conducting material.
In general there is not one but several scattering mechanisms within the lattice, each with a characteristic scattering or relaxation time. When the distribution of scattering times is taken into account, the equations for the real and imaginary parts of the dielectric become

\[ n^2 - k^2 = \sum_i \frac{N_i}{m_i^* e \varepsilon_0} \left\langle \frac{1}{\omega^2 + \tau^{-2}} \right\rangle \]  

\[ 2n\kappa = \frac{N_e^2}{m^* e \varepsilon_0} \left\langle \frac{\tau^{-1}}{\omega^2 + \tau^{-2}} \right\rangle \]  

where the brackets signify averages over the distribution. These averages have been evaluated for various approximations by Schuman and Philips. However for many conditions a single average relaxation is a fair approximation to electron behaviour, although precise agreement between \( \tau \) values determined from plasma edge measurements and Hall effect mobility would not be expected.

### 3.6.1 Anomalous Behaviour of Conductors

When a metal is operated at sufficiently high frequencies or low temperatures, the mean free path of electrons is no longer small in comparison to the wavelength and the penetration depth. The current density at any point is now determined, not only by the electric field there, but also by the motion of electrons that arrive from distances less than the mean free path with velocities acquired in regions of different field strengths. The electrons may in fact spend part of their time outside the field of penetration and hence are less effective as carriers.
In this situation the simple Drude theory must be modified \[54\]. However for good conductors at room temperature, the values obtained in the infra-red from the anomalous skin effect modification are essentially identical to those determined by the simple Drude theory provided that conduction electrons are specularly reflected from the surface of a metal. If they are diffusely reflected, the calculated optical reflectance is slightly lower than that obtained from the simple theory. Experimental evidence indicates that the electronic reflectance is usually diffuse \[55\] but specular reflection can occur if surface irregularities are of the wavelength of conduction electrons.
3.7 Optical behaviour of semiconductors

It has been shown that bound electrons dominate the behaviour of non-conducting dielectrics while free electron effects predominate in a metal. In semiconductors both contributions are important: the former gives rise to intense absorption to the short wavelength side of the main absorption edge, while at long wavelengths free carrier absorption becomes significant.

For compounds with a significant degree of ionic there is always an intense (Restrahlten) absorption band in the far infra-red.

Covellite semiconductors Si Ge do not exhibit this intense absorption. At shorter wavelengths weaker absorption bands may be observed due to the excitation of two or more phonons, the intensity of the bands reducing with the number of phonons involved.

Absorption by free electrons dominates the optical behaviour of metals, but becomes significant in semiconductors only at long wavelengths, due to the reduced free carrier concentration. The contribution of free carriers to the optical indices are described by the Drude equations. Detailed theoretical analysis of the behaviour in the neighbourhood of the plasma reflection minimum has shown that
such measurements can yield very accurate values for carrier concentration or effective mass (assuming that one or other is known from other data) and estimates of relaxation time and conductivity. In materials of known carrier concentration plasma edge measurements provide a good method of determining the effective mass of carriers. It has been used by Spitzer and Fan (1957) to measure the electron mass in InSb for a wide range of carrier concentrations, by Walton and Mishra (1968) to study p-type GaAs.

Conduction in semiconductors is by holes and electrons, and the contributions of different carrier species to the optical constants must be summed to obtain the contribution of free carriers to the optical constants.

Therefore in a semiconductor the contributions of both bound and free electrons must be considered and the complete expression for the optical constants will be given as a series of terms describing all possible oscillators, for example

\[
2n = \sum_{j} \frac{N_{e}^2}{m^* m_j} \cdot \frac{\omega \gamma}{(\omega^2 - \omega_j^2)^2 + \omega^2 \gamma^2} + \sum_{i} \frac{N_{e}^2}{m^* m_i} \cdot \frac{(\omega \tau_i)^{-1}}{\omega^2 + \tau_i^{-1}}
\]
3.8 The Optical Behaviour of Thin Absorbing Films

Optical studies of absorbing materials have long been interpreted on the basis of the Drude theory of free carriers, modified with the advent of quantum mechanics by the effective mass approximation. Spitzer and Fan [9] have used infra-red studies of semiconductors to determine the carrier-independent part of the dielectric constant, as well as the effective mass of carriers. The determination of effective mass by the infra-red studies is in good agreement with the values found by other techniques for determining effective mass[57].

By allowing for the loss term arising from the finite mobility of materials, the accuracy of the determination of the plasma frequency and hence the free charge parameters can be improved[58].

Interpretation in this manner, with evaporated semiconducting thin films, becomes more difficult because the lower mobility of materials in thin film form may considerably increase free carrier damping, and optical interference may also occur within the film. To interpret infra-red reflection measurements made on thin films, it has therefore been found necessary to gain a thorough understanding of the theory of the reflectivity of thin absorbing films.

The reflective and transmissive properties of absorbing films may be calculated by extending the theory for dielectric films, by assuming a complex refractive index for the material.

In this section the reflectance of an absorbing film in air, on a non-absorbing substrate is derived. Particular attention is given to the determination of the phase shifts which occur on reflection at each interface, and on transmission through the film, since these can be the source of much confusion.
The results are used to correct previously published curves of Howson [59], for thin film semiconductors in the region of the plasma edge.

3.8.2 Reflection from an absorbing film

Electromagnetic radiation is incident upon a thin film of refractive index $N = n-jk$ which separates media of non complex refractive indices $n_1$ and $n_3$.

Assume that the Fresnel reflection coefficient at each interface takes the form

$$ r^* = r \exp(j\delta) \quad (3.77) $$

where $\delta$ is the phase change which occurs on reflection.

Then

$$ r_0 = \left| \frac{(n_o - n)^2 + k^2}{(n_o + n)^2 + k^2} \right|^\frac{1}{2} \quad (3.78) $$

Figure (3.7) Reflection from an absorbing film.
\[ \tan \delta_0 = \frac{2n_0 k}{(n_0 - n)(n_0 + n) - k^2} \] 
(3.79)

Similarly \( r_1 = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \) 
(3.80)

\[ \tan \delta_1 = \frac{2n_1 k}{(n-n_1)(n+n_1) - k^2} \] 
(3.81)

and for the ray returning to the upper surface from the interior \( r_o^* = - r_o^* \) 
(3.82)

With reference to figure 3.7, the reflection amplitudes are

\[ a_{ro}^* + att r_1^* e^{-\Delta^*} + att r_1^* r_0^* e^{-2\Delta^*} + \ldots \] 
(3.83)

Here \( \Delta^* \) is the phase change which occurs on traversing the film thickness, \( d \), twice. Physically \( \Delta^* \) is a lag and has been included as \( e^{-\Delta^*} \). \( \Delta^* \) is defined by

\[ \Delta^* = \frac{4\pi (n-jk)d}{\lambda} = \frac{4\pi nd}{\lambda} - \frac{4\pi jkd}{\lambda} = \Delta - j\beta \] 
(3.84)

The reflection amplitudes then become

\[ r_o^* + att r_1^* e^{-\Delta^*} \left[ 1 + r_o^* r_1^* e^{-\Delta^*} + r_0^* r_1^* e^{-2\Delta^*} + \ldots \right] \] 
(3.85)

\[ = r_o^* + \frac{tt r_1^* e^{-\Delta^*}}{1 - r_o^* r_1^*} \] 
(3.86)

Now \( tt^1 = 1 - r_0^* r_1^* \); \( r_1^* = r_1^* \) 
(3.87)

Therefore the reflection coefficient is

\[ \frac{r_o^* + r_1^* e^{-\Delta^*}}{1 + r_1^* r_0^* e^{-\Delta^*}} \] 
(3.88)

Put \( r_o^* = r_o e^{j\delta} \) 
(3.89)

\[ r_1^* = r_1 e^{j\delta} \]
The reflectance $R$ then becomes

$$R = \frac{r_0 e^{j(\delta_1 - \Delta)} e^{-\beta}}{1 + r_0 r_1 e^{j(\delta_1 + s - \delta)} e^{-\beta}}$$

(3.90)

and

$$R = \frac{r_0 e^{j(\delta_1 - \delta_0 - \Delta)} e^{-\beta}}{1 + r_0 r_1 e^{j(\delta_1 + s - \delta)} e^{-\beta}}$$

(3.91)

ie the reflectance of an absorbing film is given by

$$R = \frac{r_0 e^{j(\delta_1 - \delta_0 - \Delta)} e^{-\beta}}{1 + r_0 r_1 e^{j(\delta_1 + s - \delta)} e^{-\beta}}$$

(3.92)

where $\theta = \delta_1 - \delta_0 - \Delta$

and $\theta = \delta_1 + \delta_0 - \Delta$

### 3.8.2 The Phase Angles

Compared to the incident light, the phase change $\Delta$ in equation (3.91) is clearly a lag, since physically it is introduced by the finite time which the light takes to traverse the film twice.

However the phase changes $\delta_0$ and $\delta_1$ are ambiguous since equations (3.80) and (3.82) both have two solutions. In order that the correct values be assigned to $\delta_0$ and $\delta_1$ in equation (3.91), it is necessary to consider carefully the reflections at each face of the film.

For simplicity numerical solutions of equation (3.91) are restricted to values between $0$ and $\pi$.

To determine if $\delta_0$ lies between $0$ and $\pi$, it is convenient to make $\kappa$ small and investigate the effect of making $n < n_0$ and $n > n_0$. The reflection coefficient is defined in these circumstances as

$$r_1 \exp j\delta_0 = \frac{n_0 - n}{n + n}$$

(3.93)
Therefore if \( n < n_0 \) one would expect \( \delta = 0 \), i.e. zero phase change, and if \( n > n_0 \) one would expect \( \delta = \pi \). For absorbing materials it has been shown that

\[
\tan \delta = \frac{2\kappa}{(n_0 - n)(n_0 + n) - \kappa^2} \tag{3.94}
\]

![Diagram](image)

**Figure (3.9)**

The quadrants in which lie (a) the phase shift \( \delta \), (b) the phase shift \( \delta_2 \).

When \( \kappa \) is small and \( n < n_0 \), then \( \tan \delta \) is small and positive, it is expected to have a value near to zero, and \( \delta \) must therefore lie in quadrant A of figure (3.8a). If \( n > n_0 \) then \( \tan \delta \) is small and negative, it is expected to have a value near to \( \pi \) and it must therefore lie in quadrant B of figure (3.8b). It is clear from this argument that \( \delta \) lies between 0 and \( \pi \).

\[
\tan \delta = \frac{2n_1 \kappa}{(n_1 - n)(n_1 + n) - \kappa^2} \tag{3.95}
\]

and

\[
x_2 \exp j\delta_+ = \frac{n - n_1^2}{n_2 + n} \tag{3.96}
\]

Using the same argument as before, one would expect \( \delta = \pi \) if \( n_1 > n \), and \( \delta = 0 \) if \( n < n_1 \). However in this case when \( n < n_1 \) \( \tan \delta_+ \) lies in quadrant D, and when \( n > n_1 \) \( \tan \delta_+ \) lies in quadrant C of figure (3.8b).
In this case therefore \( \delta_1 \) lies between \( \pi \) and \( 2\pi \). Since all phase angles are required to lie between 0 and \( \pi \) it is necessary to add \( \pi \) to \( \delta_1 \) to satisfy this condition. Therefore put

\[
\delta_1 = \delta_0 \tag{3.97}
\]

\[
\delta_1 = \delta_1 + \pi \tag{3.98}
\]

in equation (3.92) to give the intensity of reflection. The reflectance of an absorbing film is therefore

\[
R = \frac{r_1^2 + 2r_1 r_2 e^{-\beta} \cos \theta + r_2^2 e^{-2\beta}}{1 + 2r_1 r_2 e^{-\beta} \cos \theta + r_1^2 r_2 e^{-2\beta}} \tag{3.99}
\]

where \( \beta = \frac{4\pi kd}{\lambda} \) (3.100)

where

\[
\phi = \delta_1 - \delta_0 - \Delta + \pi \tag{3.101}
\]

\[
\theta = \delta_1 + \delta_0 + \Delta + \pi \tag{3.102}
\]

\[
\Delta = \frac{4\pi nd}{\lambda} \tag{3.103}
\]

### 3.8.3 Computation

It has been shown that the basic equations for free carrier dispersion are given in terms of the real and imaginary parts of the dielectric constant as follows.

\[
n^2 - k^2 = \varepsilon_L - \frac{N e^2}{m^* m e \varepsilon_0} - \frac{1}{\omega^2 + \tau_e^{-2}}
\]

\[
2nk = \frac{N e^2}{m^* m e \varepsilon_0} \cdot \frac{1}{\omega} \cdot \frac{1}{\omega^2 + \tau_e^{-2}}
\]

where \( N \) is the density of free carriers, \( \varepsilon_L \) is the dielectric constant, \( \varepsilon_0 \) is the permeability of free space, \( \omega \) is the angular frequency, \( \tau \) the
scattering time and \( m^* \) the effective mass of free carriers.

The theoretical reflectance curves predicted by Howson \[59\] have been recomputed using the correct phase angles described by equations (3.101) and (3.102). \( \frac{N}{m^*} \) was given values of 6, 3, 1.5, 0.75, 0.375, 0.188, all \( \times 10^{26} \text{m}^{-3} \), and \( \tau \) given values 3.2, 1.6 and 0.8 \( \times 10^{-14} \text{sec} \).

The reflectance of films 0.25, 0.5 and 1.0 \( \mu \text{m} \) thick were computed over a frequency range 1-6 \( \times 10^{13} \text{Hz} \), corresponding to wavelengths 5-30 \( \mu \text{m} \). The film was assumed to have a non-absorbing substrate of refractive index 1.5. A lattice dielectric constant of 16 was assumed which corresponds to Germanium.

The refractive index \( n \), and the extinction coefficient \( \kappa \) which were also calculated as a function of these parameters, are shown in figs. (3.9) and (3.10). These curves are identical to those given by Howson.

Given in fig. (3.11) are curves of reflectance variation with these parameters and with thickness. These curves are essentially similar to those given by Howson, although the spurious reflectance peaks have disappeared.

These curves show that the simple reflectance dip followed by a steep rise, experienced by bulk high mobility semiconductors, is not applicable to thin films. The reflectance of an absorbing film is considerably dependent on three parameters, \( \frac{N}{m^*} \), \( \tau \) and film thickness.

Plasma frequency effects are readily observed only in films of high \( \tau \), i.e. high mobility, since the relaxation time is directly related to the mobility \( \mu \) by the equation

\[
\mu = \frac{e\tau \mu}{m^* m_e}.
\]
Figure (3.9) Computed values for the real refractive index made for values of N/m² of A, 6 x 10^26 m⁻³; B, 3 x 10^26 m⁻³; C, 1.5 x 10^26 m⁻³; D, 0.75 x 10^26 m⁻³; E, 0.375 x 10^26 m⁻³; F, 0.188 x 10^26 m⁻³; shown as function of frequency for values of τ of (a) 3.2 x 10⁻¹⁴ s (b) 1.6 x 10⁻¹⁴ s (c) 0.8 x 10⁻¹⁴ s
Figure (3.10) Computed values of the extinction coefficient for the range of $N/m$ and $\tau$, used in figure (3.9) and using equivalent identifying symbols.
Figure (3.11)(i)

Reflectance resulting from computed values for refractive index and extinction coefficient given in figures (2.9) (2.10) for film thicknesses.
(i) \( d = 0.25 \, \mu m \)  (ii) \( d = 0.5 \, \mu m \)  (iii) \( d = 1.0 \, \mu m \)
Figure 3.11 (ii) Film thickness 0.5 μm.
Figure 3.11 (iii)

Film thickness 1.0 μm
This will be discussed further in chapter (4) concerning the choice of film material to show plasma effects.

A rise in the value of $N_{\text{in}}$ for the material has the effect of shifting the reflectance minimum to higher frequencies i.e. to shorter wavelengths.

Interference maxima are readily observed in fig. (3.9), especially in the 1.0 $\mu$m curves.

3.9.4 Conclusions

The reflectance of a thin film of semiconducting material may be considerably modified from that of the bulk material due to the effects of optical interference, and the increased damping resulting from reduced carrier mobilities in thin films.

The reflectance of a thin absorbing film may be calculated, taking account of the phase changes introduced by the absorbing nature of the material. A series of theoretical curves has been computed which shows that the reflectance of a film of given $N_{\text{in}}$ varies in a complex manner with the free carrier mobility and also with the film thickness due to optical interference effects.
4. MATERIALS

4.1 Introduction

The choice of material in which the change of reflectance is to be induced is most important, since the material should have optical properties which change rapidly when the free carrier concentration is adjusted. In this chapter a comparison between various possible materials will be made.

It has been shown that the reflectance of a material in air is given by

\[ R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2} \]

For many semiconductors:

\[ n^2 - \kappa^2 = \varepsilon_L - \frac{N_e^2}{m_e m^* F_0} \cdot \frac{1}{\tau^{-2} + \omega^2} \]

\[ 2n\kappa = \frac{N_e^2}{m_e m^* F_0} \cdot \frac{1}{\tau \omega} \cdot \frac{1}{\tau^{-2} + \omega^2} \]

A plasma frequency may be defined by

\[ \omega_p^2 = \frac{N_e^2}{m_e m^* F_0} \]

The important criterion for determining the usefulness of a material in which the optical effects of free carriers is to be observed is the exhibition of a sharp plasma edge. This is illustrated by reference to figure (4.1) where it is seen that in the region of the plasma frequency, a small change in the number of free carriers produces a comparatively large change of reflectance provided that the plasma edge is steep.
Figure 4.2 Reflectivity of five n-InSb samples
(from left to right $3.5 \times 10^{23}$ to $4.0 \times 10^{24}$ carriers m$^{-3}$)

[After Spitzer and Fan (1957)]

Figure 4.1
The effect of $\eta$ on the shape of the plasma edge
(a) $\tau \sim 10^{-16}$ sec
(b) $\tau \sim 10^{-16}$ sec
Whereas the position of the plasma edge with respect to wavelength is determined by \( N \) - the number of free carriers, the shape of the reflectance curve in the plasma region is dominated by the magnitude of the relaxation time \( \tau_c \) and the desired sharp plasma edge is associated with a high value for \( \tau_c \).

Using a simple band model, the electrical mobility \( \mu \) may be related to the relaxation time by the equation

\[
\mu = \frac{e \tau_c}{M^0 M_e}
\]

A material having high electrical mobility is therefore expected to have a well defined plasma edge. Consequently the important properties which a useful sample should possess are a high electrical mobility and an appropriate free carrier concentration.

Infra-red reflectance changes have been induced in bulk semiconductors using high energy (0.5MeV) electrons by Pefley (52). It was intended to attempt to reproduce those results in bulk silicon using much lower (5KeV) electrons although it is expected that the effect would be small Section (4.3) describes the properties of silicon samples which were used.

It was hoped that much larger reflectance changes would be observed using thin film material because the free carriers generated could be contained within a small volume. This chapter describes the search for a suitable material.
The choice of thin film material is complicated by the fact that the properties of materials in thin film form are often very different from those of bulk material; i.e. a plasma edge observed in bulk material may be completely absent in thin film form.

The procedure followed was to choose several promising materials, attempt to prepare them in reproducible thin film form and examine the thin film material by various means to decide if it is suitable.

4.2 Possible Materials

It is envisaged that the reflectance of a material is to be adjusted by the addition of extra free carriers to the lattice and causing the plasma edge to sweep through the operating wavelength. Since the addition of carriers can only move the plasma edge to lower wavelengths, the material which is to be used should possess a plasma edge at a wavelength at, or greater than the operating wavelength of 10.6 microns. This effectively eliminates the possibility of using metals which have plasma effects in the visible or ultra-violet, and limits the choice to semimetals or semiconductors. In consequence the following materials have been considered for use in the modulation experiment.

1. The elemental semiconductors silicon and germanium are considered because they are easily available, and because their properties are well known and documented. Optical absorption in both silicon and germanium was investigated by Spitzer and Fan [10] in the spectral region 1-45 microns, who showed the existence of free carrier absorption which rises with wavelength together with several small absorption bands due to lattice effects. The reflection spectrum of various doped samples of silicon (fig. (1.1) ) was measured by Howarth and Gilbert [60] and used to determine the effective mass which agreed well with the value determined from cyclotron measurements.
2. The III-V compound semiconductors, which are formed from the elements of groups III and V in the periodic table, are characterised by very high carrier mobilities (for InSb $\mu = 8m^2v^{-1}sec^{-1}$). The small band gap and low effective mass cause free carrier dispersion to be important and the plasma edge is very steep in these materials. Fig. (4.2) shows the reflectance of various doped samples of indium antimonide.

3. The semimetals tellurium, bismuth and antimony all have low melting points and high vapour pressures and are conveniently prepared in thin film form. The semimetals have properties which lie in general between those of semiconductors and metals. Tellurium lies in group 6 of the periodic table and has properties similar to selenium. Pure tellurium has a very high refractive index of 4.8, a carrier concentration in the range $10^{20} - 10^{22}m^{-3}$ and free carrier optical absorption is low.

Bismuth and antimony lie in group 5 of the periodic table. Pure bismuth typically contains $10^{24}m^{-3}$ free carriers which are holes. Reflection studies have shown bismuth to have an absorption band in the 1-10 micron region, together with little free carrier absorption.

Antimony has similar chemical properties to bismuth and their electronic properties are thought to be due to an overlapping band structure. Antimony typically contains greater than $10^{26}m^{-3}$ carriers, and exhibits marked optical free carrier absorption effects. Reflectance measurements have shown a plasma edge in antimony in the 10-20 micron region. Howson [6.] showed that by alloying antimony with a few percent of tin, substantial increases in free carrier absorption may be achieved and the plasma edge moved to shorter wavelengths.
4.3 Bulk Silicon

Pefley [10] has modulated the reflectance of bulk silicon by bombardment with very high energy (500 keV) electrons. In view of these results it was decided to repeat the measurements with lower energy 5 keV electrons, using bulk samples of high quality single crystal silicon which were available.

Electrical measurements made on selected samples gave the electrical conductivity and Hall mobility to be 20 ohm\(^{-1}\)m\(^{-1}\) and 1.5 v.m\(^{-1}\) respectively. These results are consistent with a material containing \(7.8 \times 10^{23}\)m\(^{-3}\) free carriers.

The reflectance of a typical sample is given in fig. (543) which shows a distinct plasma edge at long wavelengths. The reflectance minimum occurs at 25 microns. Using equation 4.1 for the plasma frequency and a value for the effective mass of 0.26 m\(_e\), the free carrier concentration was calculated to be \(8 \times 10^{23}\)m\(^{-3}\) which is in excellent agreement with electrical measurements.

Fig. (4.3) shows the computed reflectance change as a function of excess free carrier concentration for these samples. This figure will be discussed more fully in section (7.7).

4.4 Problems concerning the Preparation of Thin Films

The electrical mobility of materials in thin film form is in general less than the mobility of the bulk material. It has been shown that the mobility of a film may be increased if the temperature of the substrate is raised during evaporation. This is related to a rise in the crystallite size within the film [62]. To obtain films with crystallites of sufficient size for the electrical properties to approach bulk values requires substrate temperature close to the melting point of the material.
This effect can be explained as the consequence of an increase in the surface mobility of absorbed molecules and at the same time, with a rise in temperature re-evaporation takes place, leaving fewer nucleation sites available for condensation, consequently the growth of large crystallites is favoured.

There is in general a critical temperature above which complete re-evaporation of all or one of the component elements may evaporate.

Further crystallite growth can be obtained by heat treatment after evaporation. To be effective the annealing must be made at a temperature close to the melting point followed by slow cooling. However in such a case it is necessary to prevent the film from re-evaporating. This can be done by applying a protective coating over the film (a dielectric or oxide coating have been found satisfactory in this respect) or to anneal the film in an atmosphere of inert gas, e.g. argon.

The limited mobilities exhibited by films prepared at the highest temperature have been related to the high fault density within the films, and the high compressive stress resulting from thermal mismatch between the film and the substrate.

Deposition parameters such as the rate of deposition, and the vacuum conditions do have an effect on the properties of the film but these do not present a real problem.

Thin films of some chemical compounds can be obtained by direct evaporation; however most compounds decompose at temperatures which are necessary for evaporation. This usually leads to fractional distillation. In such cases the individual components might exhibit vapour pressures which differ by several orders of magnitude (see fig. 4,4).
Computed $\Delta R$ for the silicon samples as a function of free carrier concentration.
Vapour pressure data for various elements.

(after Honig [107] 1962)
Evaporation of InSb, or GaAs leads therefore to thermal decomposition and a preferential evaporation of the component with the higher vapour pressure. The resulting film does not correspond to a stoichiometric composition, and the desired electrical and optical properties are not obtained. Stoichiometric films of compounds may only be prepared if special techniques and extreme care are employed.

4.5 Thin Film Materials

4.5.1 Compound Semiconductors

Techniques are available for the preparation of thin films of compound semiconductors, which overcome the difficulties mentioned in section 4.3 and which allow the production of stoichiometric films of crystalline structure [63]. Optical and electrical measurements on films of InSb and InAs [64] show considerable dependence of their properties on the deposition parameters, particularly substrate temperature. The films of greatest interest which were prepared at the highest temperatures, exhibited large mobilities, but invariably had very rough surfaces which precluded optical measurements but showed considerable variation in their electrical properties.

Compound semiconductors were not considered for reflectance because of these difficulties.

4.5.2 Elemental Semiconductors and Semimetals

Problems of thin film composition do not arise for elemental materials, and the following have been evaporated in order to assess them in thin film form. They are Silicon, Antimony, Tellurium and Bismuth. At this time no germanium was available for deposition. Since germanium and silicon have similar bulk and thin film properties, it was considered sufficient to investigate silicon only.
4.6 The Evaporation Apparatus

4.6.1 The Evaporation System

The apparatus used for the evaporation of silicon and the semimetals is illustrated in fig. (4,5). The vacuum system is enclosed by an 18" glass bell jar, sealed by neoprene, and pumped by a standard 4" diffusion pump. There was no cold trap but the system was capable of an ultimate pressure of better than 10⁻⁶ torr.

An electron gun from Varian Associates was used to evaporate the source material. The substrates were mounted in a stainless steel substrate holder and heated with a pair of 750 watt cylindrical quartz lamps mounted in a reflector and heating the substrates indirectly by conduction through a stainless steel plate (see fig. (4.6,4.7) the substrate housing). The substrate holder was able to take up to four slides at a time.

Substrate temperatures were measured by placing a chromel-alumel thermocouple on the upper surface of the substrate. This introduced a small but unknown error in determining the exact temperatures of the film which was deposited on the lower surface.

The thickness of films transparent to 0.9 μm radiation could be monitored during evaporation, by observing the light reflected from the back of the glass substrate film system, using a silicon photo voltaic detector directly coupled to a "Servoscribe" pen recorder. Although no monochrometer was used, the combination of spectral characteristics of the quartz iodine lamp, operated at a relatively low filament temperature, together with the spectral response of the detector gave a response which was strongly peaked at 0.9 microns. Interference peaks could be observed, a refractive
Figure 4.5

1. Standard 18" bell jar.
2. Reflector.
3. Quartz iodine lamps.
4. Rubber seal.
5. Stainless steel plate.
7. Shutter.
9. Evaporating material.

To Pump
Figure 4.6. Photograph of substrate housing

Figure 4.7. Photograph of the Evaporation Unit
index assigned to the film from previous measurements and the film thickness determined by the equation

$$\theta_{\text{optical}} = \frac{k\lambda}{2n}$$

Film thickness was measured after evaporation using a Rank-Taylor-Hobson "Tallystep".

4.6.2 The Electron Beam Source

The electron beam evaporating source which was manufactured by Varian Associates Limited was of the type where the electron beam is bent 270° before reaching the target, by a magnetic field perpendicular to the direction of the beam.

The self accelerated type of gun (see fig. 4.8) uses the potential $V$, both to focus the beam and to accelerate the electrons to full velocity. The target material is contained in the hearth which is made of copper and water cooled. During evaporation a frozen layer of evaporated material is deposited across the copper surface, which insures total purity of the evaporant and avoids the highly corrosive characteristics of many elements when they are heated near their vapour temperature.

The power supply gave 5 kV and was current limited at 500 mA. This gave a total of 2.5 Kilowatts output in the beam. The source is capable of evaporating almost any material including refractory metals, and when the problems involved in using an electron gun have been understood, the source becomes a highly efficient evaporating unit, which is easy to use and requires only nominal maintenance.
Figure 4.8
Beam orientation in the electron gun

Figure 4.9
The characteristics $B = f(I)$ of the 4" magnet for an air gap of 2.5 inches.
4.6.3 The Substrates

The substrates used in this work were Corning 7059 glass slides of 1 x 0.5 inch. This is a glass which has been specifically designed for use as a substrate for thin films. Slides are specified and have a typical smoothness of less than 60 Ångströms and a volume resistivity at 500°C of at least $10^8$ ohm-cm.

Substrates were ultrasonically agitated and washed in deionised water and detergent Decon for ten minutes, rinsed three times in deionised water and once in isopropyl alcohol, followed by a hot vapour wash of isopropyl alcohol in a soxhlet immediately before insertion into the vacuum chamber. When the vacuum chamber was pumped down to $10^{-5}$ torr, the substrates were out-gassed for fifteen minutes at a temperature 100°C higher than the final operating temperature. Finally the required substrate temperature was achieved and evaporation took place.

4.7 Measurements on Films

4.7.1 Hall Measurements

A simple specimen holder was constructed in perspex with thin lead wires soldered by indium contacts onto the film. A large 4 inch air cooled electromagnet (Newport Instruments) together with its constant current power supply unit was calibrated for measurement. The characteristic of this magnet is shown in fig. (4,9).

A magnetic induction of 6 Kg was used with the pole separation of 2.5 inches. To avoid warming the sample low voltages and currents should be applied to the sample. The static characteristics $V_H = f(b)$ are shown in fig. (4,10) and are a linear function for antimony films (T24) for a current in the range $I = 1-5$ MA. For routine Hall effect measurement a current of 2-3 mA was used.
Figure 4.10
The static sensitivity characteristics for antimony films.

Figure 4.11
The dependence of coefficient $f(\ell/\omega)$ on the ratio $\ell/\omega$.
The measurements of hall voltages were made using a high impedance electrometer with an output impedance of greater than $10^{14}$ ohms and an accuracy of ±1% on all scales.

It is known that the value of the measured Hall voltage depends on the shape of the semiconductor slab in the manner shown in fig(4.11)

The Hall voltage reaches its full value only when the ratio of the film length to film width ($\frac{L}{W}$) is greater than 3.

The effective ratio for a sample with soldered contacts varied from sample to sample but was approximately 2. Fig (4.11) was used to adjust the Hall voltage on every sample.

The film thickness after deposition was measured with a Rank-Taylor-Hobson "Talleystep". With vertical magnification 5, 10, 10, horizontal magnification 50, 200 and 2000, and an adjustable stylus force from 1-30 mgms with a standard conical 12.5 µm radius tip for step height measurement, both film thickness and a measure of surface roughness can be estimated.

From these measurements values for the Hall coefficient, the conductivity, the carrier density and the Hall mobility could be obtained from the following equations:

- Hall coefficient $R_H = \frac{V_{Hd}}{B \cdot I}$
- Conductivity $\sigma = \frac{I}{V} \times \frac{L}{W}$
- Carrier concentration $n = \frac{1}{R_H \cdot e}$
- Hall mobility $\mu_m = R_H \cdot \sigma$
where $V$ is the voltage across the sample, $i$ is the current passing through it; $V_m$ is the Hall voltage, $B$ is the magnetic induction, $e$ is the electronic charge and $l$, $w$ and $d$ are the length, width and thickness of the film respectively.

### 4.7.2 Electron Microscope Measurements

The microstructure and surfaces of films prepared over a wide range of deposition conditions were examined with the scanning electron microscope using gold-palladium shadowing of \textit{forma} replicas. From such electron micrographs the micro crystallite sizes could be obtained.

### 4.7.3 Optical Measurements

Reflection and microtransmission measurements on the films have been made over a wavelength range of 2.5 - 40 µm, using a Perkin Elmer 407 grating infra-red spectrophotometer. Reflection measurements were primarily to observe the position and shape of the reflection plasma edge. Measurements were also made on the interference fringes in antimony films, and the results compared to those calculated from the known optical constants of antimony using a computer program.

### 4.8 Silicon Thin Films

#### 4.8.1 Preparation

Films of silicon have been prepared by the evaporation of silicon in a vacuum of approximately $10^{-5}$ torr onto Corning 7059 glass substrates at temperatures between ambient and 600°C in a range of thicknesses from 0.1 to 2.0 µm. The method of preparation and the apparatus have been described in previous sections. Crystalline lumps of pure 5N
silicon (Koch Light Laboratories) were used as the starting material and were evaporated from the copper hearth of the electron gun. By adjusting the power a molten region could be formed on top of the lump. By experience it was found that if the power was increased in an attempt to evaporate at this stage then the molten area expanded, and exploded due to thermal shock when it touched the thermal hearth.

To overcome this problem, it was found necessary to adjust the accelerating voltage, move the molten area to the side of the lump and at a fairly low power, allow a small amount of silicon to flow into the hearth. This when solidified effectively formed a silicon crucible, which was in good thermal contact with the hearth, thus reducing thermal gradients and the possibility of further molten silicon coming into contact with the cold hearth.

It was then possible to raise the power, evaporate silicon, open the shutter and deposit the film on the substrate.

4.8.2 Properties of Silicon Films

The reflectance of a typical silicon film on glass is presented in fig. (4.12). The structure which is shown is associated with absorption bands of the glass substrate and not the film. No plasma edge may be observed.

The electrical resistivity of these films is presented in fig. (4.16) as a function of substrate temperature. The maximum substrate temperature which could be achieved in the vacuum system was approximately 700°C which is some 400°C below the melting point of Silicon. Consequently
Figure 4.12
The reflectance of an optical silicon film

Figure 4.13
The electrical resistivity of silicon films as a function of substrate temperature.
although the resistivity of the films exhibits the expected fall with increasing substrate temperature, the best films still have a resistivity of $10^4$ ohm.m. Assuming a free carrier concentration of say $10^{24}$ m$^{-3}$, this is equivalent to an electrical mobility of $6 \times 10^{-10}$ m$^2$V$^{-1}$s$^{-1}$, and a relaxation time of $6 \times 10^{-22}$ seconds, which is far too long for any plasma effects to be evident.

This is consistent with the fact that the Hall effect was not observed in any sample.

In view of the very small carrier relaxation times in these films, due to the low substrate temperatures which could be used, it is evident that these films are unsuitable for modulation experiments since the plasma edge is virtually non-existent.

4.9 Antimony Films

Thin films of antimony have been prepared by evaporating 99.999% antimony onto substrates of glass, sapphire and silicon at various substrate temperatures. All films had a bright specular metallic appearance.

Reflectance measurements made on early antimony films deposited on glass at room temperature, showed the presence of a slowly rising plasma edge with the minimum at approximately 11 microns. Previous experience with thin films suggested that the structural, electrical and optical properties of the films would show a considerable dependance upon the deposition parameters, particularly the substrate temperature. In order to investigate the plasma edge in antimony films, and to choose the optimum deposition conditions, antimony films have been prepared over a range of substrate temperatures from ambient to 300°C, and in a range of thicknesses from 0.1 to 2 microns. In all antimony films deposited conduction was by holes.
The preparation of these thin films was investigated because an analysis given in section (8.4) showed that the modulation effect might be greater for thin films in which the plasma edge was shifted to a lower wavelength so that 10.6 microns was the wavelength of maximum reflectance rise with wavelength.

Howson [61] has shown that the optical properties of antimony can be adjusted by adding small percentage of tin to the antimony lattice. This has the effect of raising the number of free carriers while allowing the bound structure to remain almost unaltered. The addition of 2-3% tin is sufficient to shift the plasma edge to the required wavelength.

The production of thin films of compounds or alloys is complicated since the evaporation rates and vapour pressures of the constituents are usually very different. Figure (4.4) shows that this is the case for antimony and tin, indeed at 1000°C the vapour pressure of antimony exceeds that of tin by over six orders of magnitude.

Two techniques were investigated to see if antimony-tin alloys could be successfully prepared with the desired properties.

In the first, antimony and tin were mixed and melted together in various proportions up to 90% tin, under an inert atmosphere of argon in a silica crucible and allowed to solidify into an ingot. The ingot was subsequently broken and pieces were evaporated onto glass or silicon substrates at a substrate temperature of 200°C. They were then annealed at this temperature for fifteen minutes. Figure (4.14) shows a typical reflectance spectrum of a film prepared in this manner. The plasma edge appears to be similar to that of pure antimony, and it is concluded that only antimony was evaporated from the ingot.
In the second technique the elements were weighed in appropriate proportions into separate crucibles. These samples were then successively totally evaporated onto the substrate at a substrate temperature of 200°C. In this way the quantity of tin actually in the film could be accurately assessed. The films were subsequently annealed for three hours at 280°C.

The reflectance spectra of films prepared in this way is shown in figure (4.14), and are greatly changed from that of antimony, but the plasma edge is poorly defined. It was found difficult to obtain reproducible results, and some of the films showed contamination by the crucible material (carbon).

The antimony-tin alloy films described here are not considered to be acceptable. The lack of success can be mainly attributed to the shortage of time available to do this work near the end of the project. Techniques are available for the evaporation of mixtures of elements with differing vapour pressures [64] and it is considered that better quality films could be prepared if more time was spent investigating the empirical problems involved.
Figure (4.14)

The reflectance of some antimony and antimony-tin alloys.

1. Pure antimony. 2. Antimony-tin alloys evaporated from the ingot.
3, 4. Alloy films prepared by evaporating constituents separately.
4.10 Tellurium and Bismuth Films

Films of Tellurium and Bismuth have been prepared by evaporating the appropriate element onto glass substrates at various temperatures. Tellurium films had a dark, matt appearance and those of bismuth appeared grainy.

The total electrical resistance of a typical bismuth film was found to be greater than $10^{11}$ ohms, and no Hall effect could be detected, which indicates that these films are probably amorphous. This is consistent with the electron micrograph of a bismuth film shown in fig. (4.15), which shows the bismuth to be present as a cluster of unconnected globules deposited on the substrate surface. It is apparent that the resistance measured is probably due to surface leakage currents.

A typical tellurium film was found to have a resistivity of the order of $10^{-2}$ ohm.m and a Hall mobility of $6 \times 10^{-2} m^2 v^{-1} s^{-1}$. These figures are consistent with a crystalline material containing free carriers. Fig. (6.15a) shows an electron micrograph of the surface of a tellurium film which had a Talystep measured thickness of 6 microns. This shows that the film is made up of long narrow crystals which point out of the surface of the film. The arrangement of the crystals is such as to reduce the reflection of incident light, and explains the matt appearance of the films.

Typical reflectance spectra for the films are shown in fig. (4.16). The spectrum of bismuth films features a minimum followed by a rise of reflectance in the 5-10 micron region, which appears similar to a plasma edge. However Howson [61] has shown that this structure is due to an absorption band, and reference to Harris and Piper [66] shows the plasma edge to lie in with the reflection minimum at 30 microns.
Figure 4.15
Electron micrographs of the surface of (a) Tellurium and (b) Bismuth films taken at a magnification of 10,000.
Figure 4.16

The measured reflectance of typical films
of (a) bismuth (b) tellurium.
The reflectance curve for tellurium shows several maxima and minima at low wavelengths. The position and number of these peaks was found to vary with film thickness, which indicates that they are caused by optical interference. No plasma edge is observed in the wavelength region covered but the crystalline nature of the films and the relatively high carrier mobility suggests that a plasma edge should be present in the spectrum. A calculation assuming the concentration of free carriers in tellurium equal to the measured value has been made which revealed that if a plasma edge were present it would occur in the 30-35 micron region.

Neither the bismuth nor tellurium films which were prepared are considered to be suitable for the reflectance modulation experiment.
4.11 The preparation of antireflection coatings

Many antimony films were deposited on silicon substrates, which are transparent to 10.6 micron radiation. Silicon has a large refractive index and in some circumstances the high reflectance of the rear substrate surface complicated the analysis of results. Antireflection coatings were therefore evaporated onto the rear of the substrates in order to minimise the reflectance at 10.6 microns.

Two possible materials for the coatings were considered. These were cerium oxide and zinc sulphide having quoted refractive indices of 2-2.3 and 2.3 respectively, dependent on the substrate temperature. Ceric oxide was tried first but it was found that the evaporation temperature required of greater than 1600°C was too high and evaporation of the carbon crucible used to contain it also occurred. The electron beam was also unstable and no further attempts were made.

Zinc sulphide evaporated at much lower and more convenient temperatures and it was found that the substrate did not have to be heated, ensuring greater protection for the antimony film on the other side. Difficulty was experienced with material jumping out of the crucible, and several types of covered and baffled crucibles were tried to overcome this problem. It was found eventually that an open crucible was easiest to use provided care was taken to keep the evaporation rate low.

The film thickness was monitored by using a dummy glass slide which was coated simultaneously. Light was reflected by this film from a lamp to a silicon photodetector, the output of which was displayed on a chart recorder. The spectral response of the detector combined with the spectral output of the lamp gave an overall response which was strongly peaked at 0.9 microns, and as the film thickness increased, maxima and minima of reflectance were displayed on the recorder.

Figure (5.14) shows the effect of a film on a silicon substrate, and upon the reflectance of an antimony film on the reverse side of a substrate.


4.12 Conclusions

A survey has been made of materials to determine which may be useful in reflectance modulation experiments. A useful material should be capable of being easily prepared in crystalline thin film form, which exhibits well defined plasma effects in the reflectance spectrum.

Antimony has been found to fit these requirements because it has a low melting point and high vapour pressure which allows the production of crystalline thin films. The electrical and optical properties of such films approaches those of bulk material, and in particular antimony films exhibit the sharp plasma edge which is desired for modulation work.

The properties of samples of bulk silicon have also been described.
5. **ANTIMONY**

5.1 *Introduction*

Optical measurements on evaporated thin films of antimony in the infra-red have shown that they exhibit a distinct free plasma in the region of 10.7 - 11.6 μm, and can be prepared in a crystalline form at relatively low temperatures (265°C). These properties are some of those required in an investigation of thin film materials for modulators of radiation from a CO₂ laser at 10.6 μm where it is intended to increase the free carrier density in some way and sweep the plasma edge through the operating wavelength of the laser.

In order to make meaningful measurements and to predict the thickness of film which would give the optimum effect it is necessary to know the optical constants of the film, both those due to free carrier effects and those due to bound carriers. These are obtained by comparing measurements made on antimony films, with the data of Harris and Corrigan [6,7] (H & C) on films prepared in a similar way, and, with more detailed measurements made by Howson [6] on polycrystalline bulk material.

It is possible to obtain a detailed set of optical constants due to bound and free carriers, so that the optical properties of thin films of antimony of various thicknesses can be predicted, and the effect of changing the free carrier density on the reflectance of a film in the region of the infra-red plasma edge examined.
5.2 The Bulk Properties of Antimony

Antimony is a semimetal which occupies group V of the periodic table. It has an atomic number of 51, atomic weight 121.75 and valence 0, -3, +3 or +5. Metallic Antimony is extremely brittle and of flakey crystalline texture and crystallises in a rhombohedral structure. It is a poor conductor of heat and electricity. It is available commercially with a purity of 99.999+\%.

Antimony has a boiling point of 1380°C and a comparatively high vapour pressure, which makes it a convenient material to prepare in thin film form by vacuum evaporation. Heating in an inert atmosphere near the melting point allows efficient annealing to take place and very crystalline films can result.

There is some discrepancy in the literature concerning the electrical properties of antimony. Howson [61] made Hall effect measurements to determine a Hall coefficient of $R_H = +2.2 \times 10^{-8}$ (m.k.s. units) and a conductivity $\sigma = 2.42 \times 10^6 \text{ mho m}^{-1}$. On a simple picture of all carriers confined to one band, these figures correspond to a carrier concentration of $2.8 \times 10^{26}\text{m}^{-3}$, a mobility of $3.1 \times 10^{-2}\text{m}^2\text{V}^{-1}\text{sec}^{-1}$, a relaxation time $\tau$ of $5 \times 10^{-14}\text{sec}$. The carrier concentration given by Howson is of the same order of magnitude as the value of $N = 5 \times 10^{26}\text{m}^{-3}$ quoted by Lenham et al [68] for measurements on single crystal samples of Antimony.

Papers by Nanney [69] and Harris and Corrigan [67] quote the data of Shoenburg [70] who found $N = 3.7 \times 10^{25}\text{m}^{-3}$. However the electronic specific heat which has been given by Wolcott [71] is $6.3 \times 10^{-4}\text{J. K}^{-1}\text{mole}^{-1}$. 
A calculation by Nanney [69] using the figure of \( N = 3.7 \times 10^{19} \text{m}^{-3} \) showed that carriers could under these conditions, be expected to contribute only about 10% of the experimental total. This discrepancy may be resolved if a value for \( N \) close to the Howson/Lenham values is taken.

The electronic properties of antimony are generally believed to arise from a slight overlap between an otherwise full valence band and the conduction band. Saunders and Oktü [72] have discussed the band structure of antimony in terms of the model shown schematically in figure (5.1). The bands overlap in such a way that optical interband transitions are prohibited by the need to conserve momentum of electrons, and only transitions which involve the greatest number of electrons are apparent in optical absorption. The fact that though zones overlap, direct optical transitions cannot take place, gives a satisfactory explanation of the optical and electrical properties of antimony.

Both Howson [61] and Saunders and Oktü [72] discuss low percentage antimony-tin alloys. Tin contains one valence electron less than antimony, and therefore adds holes to the lattice. The general effect is to assume that the band structure of antimony remains the same and that the tin addition merely lowers the Fermi level. It has been calculated that 1% addition of tin to the antimony lattice is sufficient to lower the Fermi level such that conduction is by holes only.

The optical properties of bulk polycrystalline antimony has been measured by Howson [61] and of single crystal antimony by Lenham et al [68] both using conventional polarimetry methods. The behaviour of the real and imaginary parts of the dielectric \( 2nk \) and \( n^2 - k^2 \) are presented in fig. (5.2), comparing the data of Howson with that of Lenham.
Figure 5.1

Schematic diagram of the electron ($e$) and hole ($V_1, V_2$) bands in antimony and antimony-tin alloys.

Figure (5.2)

(a) $n^e - n^e$ (b) $2\alpha/k$ vs wavelength in microns

Curve 1 Lenham et al. [53]
Curve 2 Howson [52]
In studies of the optical parameters of metals, the absolute values of the optical constants are often found to be sensitive to the surface treatment which the sample has been given, but the shapes of the dispersion curves in general and the energies of the absorption maxima and minima are preserved for sensible surface preparations. The similarity between the two sets of curves indicates therefore that polycrystalline antimony may be treated as isotropic for infra-red optical measurements, which is a reasonable assumption since the interaction between radiation and matter requires a comparatively short length of atomic order within the lattice compared to the length of interaction between free carriers and the lattice.

An absorption band is shown most clearly in the $2nk$ curves, this extends over the range 1-10 $\mu$m and peaks at approximately 3 $\mu$m. At longer wavelengths, the regular increase in $k$, associated with free carrier absorption is observed in the rise of $2nk$ and the fall in $n^2 - k^2$. 
5.3 Properties of Antimony Films

The preparation of annealed antimony films on substrates of glass, sapphire or silicon has been described in chapter (4) as have the methods used for the measurement of film thickness, electrical conductivity and Hall coefficient.

Previous experience of semiconducting thin films suggested that the structural and electrical properties of films would show a considerable dependence upon the deposition parameters, particularly substrate temperature. In order to investigate the effect in antimony, and to choose the optimum deposition conditions, antimony films have been prepared over a range of substrate temperatures from ambient to 300°C and in a range of thicknesses from 0.1 to 2 μm. In all antimony films deposited, conduction was by holes.

Fig. (5.3) presents the dependence of the electrical characteristics of antimony films on substrate temperature. Carrier mobility was found to increase with substrate temperature from values of \(4 \times 10^{-3} \text{m}^2\text{v}^{-1}\text{sec}^{-1}\) at ambient temperature to almost \(1 \times 10^{-3} \text{m}^2\text{v}^{-1}\text{sec}^{-1}\) at the highest substrate temperature. It was found that the mobility of low temperature substrate films could be raised to that of high temperature substrate films, by subsequent annealing. Harris and Corrigan found a similar dependence of the resistivity of films evaporated under similar conditions. They found that the resistance of antimony films on glass substrates, fell rapidly when the substrate temperature was raised from 115°C to 175°C and rose more slowly at higher temperatures.
The conductivity, Hall coefficient, mobility and carrier density as a function of substrate temperature for film thickness 0.3 - 0.6 μm
The conductivity, Hall coefficient, mobility and carrier density of antimony films as a function of film thickness for a substrate temperature of 265°C.

Figure 5.4

N - carrier concentration \( \times 10^{-26} \) (m\(^{-3}\))

RH - Hall coefficient \( \times 10^8 \) (m\(^3\)c\(^{-1}\))

\[ \mu \text{ mobility} \times 10^3 \text{ (m}^2\text{V}^{-1}\text{s}^{-1}) \]

\[ \sigma \text{ conductivity} \times 10^{-5} \text{ (}\Omega^{-1}\text{m}^{-1}) \]
Harris and Corrigan give data which shows a small change of both mobility and carrier concentration with thickness, Fig. (5.4) presenting the electrical parameters of antimony films vs film thickness shows that there is a variation of mobility with film thickness, but the carrier concentration remains constant.

Dependence of electron mobility on substrate temperature can be explained simply by a correlation between the substrate temperature and crystallite size within the film. Crystallite or grain boundaries in the film may act as scattering centres and consequently reduce carrier mobility to a value considerably less than that of a bulk crystal.

Films of the best quality are shown in figs. (5.3), (5.4) to have carrier concentrations of $3.7 \times 10^{26} \text{m}^{-3}$ and mobilities of $0.9 \times 10^{-2} \text{m}^2\text{v}^{-1}\text{sec}^{-1}$ which corresponds to a carrier relaxation time of $1.5 \times 10^{-14} \text{seconds}$.

Carrier concentration in thin film antimony is therefore less than that of bulk polycrystalline material which was measured by Howson [61] to be $2.8 \times 10^{26} \text{m}^{-3}$, while carrier mobility in bulk antimony ($3.1 \times 10^{-2} \text{m}^2\text{v}^{-1}\text{sec}^{-1}$) is higher than that of the thin film form.

To confirm the assumption that the average crystallite size increases rapidly with increasing substrate temperature, and to obtain an estimate of the microcrystallite sizes within antimony films, the surface of a range of films prepared at different substrate temperatures was examined by a Cambridge Instruments "Stereoscan" scanning electron microscope.

The electron micrographs presented in fig. (5.5) indicate that the growth of crystallites in films from $<0.1 \mu\text{m}$ at ambient substrate temperature, to $>2 \mu\text{m}$ at the highest substrate temperature. These pictures agree with measurements made by Harris and Corrigan on similar films, who
Figure 5.5
Stereoscan photographs of the surface of antimony films deposited at substrate temperatures
(a) 25°C  (b) 100°C  (c) 200°C  (d) 280°C
also found from electron diffraction measurements that the crystallites were predominantly orientated with their trigonal axes normal to the substrate.

Infra-red reflection measurements were made on the films to observe the plasma edge. It has already been pointed out (chapter 3) that the rate of rise of reflectance at the plasma edge increases rapidly when the carrier relaxation time $\tau_e$ becomes large. This occurs when the mobility and therefore the substrate temperature is high. Fig. (5.6) shows that the slope of the plasma edge is a function of substrate temperature. Films deposited on substrates at high temperature show a plasma reflection edge with a sharp rise in reflectivity similar to that exhibited by bulk antimony.

The Drude expressions which describe the behaviour of reflectance in the region of the plasma edge do not allow the computation of $\tau$ directly. Harris and Corrigan have however measured the optical constants $n$ and $k$ of similar films, over a series of wavelengths up to 120 $\mu$m. It will be shown in section 5.4 that it is possible to calculate $\tau$ from the published data, and a correlation between the optical relaxation time and the electrical mobility may be proven.

The reflectance spectra of fig. (5.6) also show some reflectance peaks at wavelengths less than 10 $\mu$m. Harris and Corrigan commented that these were probably due to interference effects. It will be shown in section (5.6) that this is indeed the case.
Figure 5.6

The reflectance of antimony thin films as a function of substrate temperature.
5.4 Free Carrier Data

The optical properties of a mechanically polished microcrystalline surface of bulk antimony have been measured by Howson [61] in the wavelength range from 2.5 to 12 μm with a bandwidth of 0.3 μm using the method of Beattie and Corrie [73] as applied by Beattie [74]; the elliptically polarised radiation created by reflection of plane polarised light from the surface, was analysed with a polariser and an empirical solution for the real and imaginary parts of the dielectric constant $n^2 - k^2$ and $2nk$ obtained.

In order to assess the influence of free carrier absorption on these values, Howson attempted to adjust the free carrier concentration without significantly altering the band structure. Alloys of antimony with tin and tellurium were tried for this purpose; tin has one valence electron less per atom than antimony and reduces the number of conduction electrons; tellurium with one more should reduce the supply. The results are presented in fig. (5.7). These show that the alloys with tin were much more successful for this purpose.

Alloying with greater proportions of bismuth, which is a material of similar valence and crystal structure and forms solid solution alloys, showed much smaller effects than encountered with tin and tellurium, showing a gradual change of properties from those of antimony to those less affected by free carrier effects exhibited by Bismuth. They are shown in fig. (5.8).

The shape of all the curves discussed is governed by two contributions

(i) That due to free carriers,

(ii) That due to bound carriers which is limited to a region 2-20 μm.
Figure 5.7
The optical constants of antimony-tin and antimony-tellurium alloys after Howson 5.2.
1. Polycrystalline antimony. 2. Antimony 1.22% tin
3. Antimony 2.82% tin. 4. Antimony - 1.97% Tellurium.
5. Antimony - 1.19% Tellurium.
Figure (5.8a).
The optical constants of antimony-bismuth alloys
Figure 8.8b

The optical constants of antimony bismuth alloys
i.e. \[ 2nk = (2nk)_{\text{bound}} + (2nk)_{\text{free}} \] (5.1)

\[ n^2 - k^2 = (n^2 - k^2)_{\text{bound}} + (n^2 - k^2)_{\text{free}} \] (5.2)

Assuming that conduction within antimony is by different groups of electrons or holes, then the contribution of free carriers to the optical constants is given classically by the Drude theory as:

\[
(2nk)_{\text{free}} = \sum_i \frac{N_i e^2}{m_i^* m_e} \cdot \frac{1}{\tau_i \omega} \cdot \frac{1}{\omega^2 + \tau_i^{-2}}
\] (5.3)

\[
(n^2 - k^2)_{\text{free}} = \varepsilon_L - \sum_i \frac{N_i e^2}{m_i^* m_e} \cdot \frac{1}{\omega^2 + \tau_i^{-2}}
\] (5.4)

where \( N_i \) = concentration of a carrier species

\( m_i^* \) = effective mass of that species

\( \tau_i \) = relaxation time of that species

\( m_e \) = electronic mass

\( \varepsilon_L \) = dielectric constant due to lattice effects

The data provided by Harris and Corrigan is useful because it extends up to 120 \( \mu \)m, and this allows the free carrier parameters to be calculated.

Assuming initially that a single carrier species dominates, the Drude equations may be rewritten:

\[ n^2 - k^2 = \frac{2nk}{\lambda} \cdot \frac{2\pi e \tau}{m^* m_e} \cdot \frac{1}{\omega^2 + \tau^{-2}} \] (5.5)

Figure (5.9) shows a plot of \( n^2 - k^2 \) vs \( 2nk/\lambda \) using the data given by Harris and Corrigan for an antimony film 0.1 \( \mu \)m thick. It is shown to be a straight line over the region 25 - 120 \( \mu \)m where the band carrier effects are negligible. This implies that equation (5.5) and the single carrier approximation are both acceptable.
Figure 5.9

$n^2 - \kappa^2$ vs $2\kappa/\lambda$ for antimony at various wavelengths
From the slope and intercept

\[ \tau_c = 3.1 \times 10^{-14} \text{ sec.} \]

\[ \varepsilon_L = 90 \]

Substituting these values into equation (5.5) for values at long wavelengths, where interband absorption makes a negligible contribution

\[ \frac{N}{m^*} = 5.9 \times 10^{26} \text{ m}^{-3} \text{ kg}^{-1} \]

If a value for \( m^* = 0.29 \) is assumed, then \( N = 2 \times 10^{26} \text{ m}^{-3} \).

The value obtained for the carrier independent part of the dielectric constant of 90 is in good agreement with the value of 80 ± 5 estimated by Nanney [69] for the "static" dielectric constant of a single crystal of antimony (which was nearly isotropic with regard to crystalline orientation) and with the value of 95 ± 5 estimated for thin antimony deposits by Harris and Corrigan [67].

The carrier concentration given above does not agree with the value of \( 3.6 \times 10^{25} \text{ m}^{-3} \) given by Shoenburg [70].

Taking the value of \( N \) given from Hall measurements of Harris and Corrigan as \( 3.1 \times 10^{26} \text{ m}^{-3} \) (this compares with \( 2.9 \times 10^{26} \text{ m}^{-3} \) for the present films) a value for \( m^* \) of 0.5 (+ 0.1) is obtained. Values of \( \tau \) obtained from Hall effect measurements on the films, which should not necessarily equal those obtained optically, go from \( 1.7 \times 10^{-14} \) at film thickness 0.5 μm and above to half that at 0.1 μm.

Using the values of \( \frac{N}{m^*} \) and \( \varepsilon_L \) found in this way \( n^2 - K^2 \) and \( 2nK \) can be calculated as a function of wavelength and compared to the measured results on bulk material. A comparison is shown in figure (10) for antimony and for an antimony-tin alloy in which case \( \frac{N}{m^*} \) has been adjusted to give most suitable agreement.
Fig. (5.10) presents the contribution of free carriers to the optical constants of antimony. It is clear that interband processes are important in the region 2-10 μm but at higher wavelengths the optical constants are increasingly dominated by free carrier effects.

These results show that the free carrier optical behaviour of antimony can be adequately described by a single carrier species (holes) with a concentration of $3.1 \times 10^{26} \text{m}^{-3}$ and a single relaxation time of $3.1 \times 10^{-14} \text{sec}$.

5.5 **Bound Carrier Data**

After the contribution due to free carriers has been extracted from the measured parameters $2nk$ and $n^2 - k^2$, the remaining contribution is due to interband transitions and will be denoted $(2nk)_{\text{band}}$ and $(n^2-k^2)_{\text{band}}$. The interband contribution has been extracted from the optical constants of antimony and antimony-tin alloys by accepting the value of $\tau$ as being constant and using $N/m^*$ as an adjustable parameter. Fig. (5.10) presents the resultant dispersion curves.

Analysis of the absorption band is not easy but is helped by using an absorption coefficient vs photon energy presentation shown in fig. (5.11).

The curves shown in fig. (5.7) indicate that there is some modification of interband processes as the percentage content of tin is increased. This is due to the fact that the addition of tin, which has one valence electron less than antimony, lowers the Fermi level in antimony such as to increase the number of holes and reduce the number of electrons.

The change of interband effects with increased majority hole concentration is not rapid, and it is proposed to assume that the contribution of interband effects to the optical constants of antimony will remain constant when further carriers are injected into or extracted from the lattice. This
Figure 5.10

Bound and free carrier contributions to the optical constants of antimony
assumption is justified for small changes in carrier concentration. Using this approximation it is then possible to predict the effect of a change in free carrier concentration upon the optical constants, and thereby the reflectance of antimony.
Figure 5.11

Absorption coefficient vs photon energy for antimony
5.6 Computation of Reflectance

Following the procedure given in chapter (3), a computer program has been developed to generate, from the known optical constants of antimony, the reflectance of an antimony film, on a non-absorbing substrate, as a function of wavelength. In order that the contribution of free carriers to the reflectivity may be computed, the optical constants of antimony are written as the sum:

\[ n^2 - k^2 = (n^2 - k^2)_{\text{free}} + (n^2 - k^2)_{\text{bound}} \]

\[ 2nk = (2nk)_{\text{free}} + (2nk)_{\text{bound}} \]

The latter terms have been presented in figure (5.8) as a function of wavelength and represent the contribution of bound carriers to the optical constants of antimony. The free carrier contributions are calculated from the Drude equations (5.3, 5.4) using the values \( N/m^* = 5.9 \times 10^{26}, \tau = 9.1 \times 10^{-14}\text{sec.}, \sigma_L = 90 \), which were determined in section (5.4).

In order to compare the computed reflectance curves with the reflectivities of real films, reflectances were computed for films of various thickness on non-absorbing substrates of refractive indices 1.5 and 3.5.

5.6.1 Films on Glass Substrates

The transmission and reflection of Corning 0759 substrate glass is shown in fig. (5.9). It can be seen that this material becomes highly absorbing at wavelengths above 3 \( \mu \text{m} \), and the refractive index therefore becomes a function of wavelength. The computation of the reflectance of a film on such a substrate becomes complicated and reflectance computations were therefore not attempted for films on glass.
Figure (5.13)

The transmittance and reflectance of

of substrates: (a) Corning 0579 glass (T)
(b) Corning 0579 glass (R), (c) sapphire (R),
(d) silicon (R).
5.6.2 Films on silicon

The reflectance-wavelength curve measured for a thin wafer of silicon used for a substrate is presented in figure (5.13) which shows that the reflectance is independent of wavelength. This curve exhibits a plasma edge with a minimum at 25–30 microns, and that the sample is essentially nonabsorbing up to this wavelength.

Figure (5.14) shows the reflectance of an antimony film on a silicon substrate, from both the antimony side and the silicon side. It should be noted that whereas the transmittance is the same regardless of the direction of the incident beam, the reflectance depends upon the refractive index of the adjacent medium.

Also shown is the effect of a wavelength antireflection coating on the silicon side of the substrate on the reflectance of the unit when viewed from the silicon side. The deposition of such films has been described in section 4.11.

5.6.3 Films on sapphire

In order to compare the reflectance measurements made by Harris and Corrigan of antimony films on sapphire, calculations were performed for antimony films of thickness 0.625 μm and 0.25 μm respectively on a substrate of refractive index 1.5. In this case there were some differences between the experimental conditions and the theoretical model. These are explained with reference to the
Figure (5.14)

The reflection spectrum of an antimony film on silicon
(a) viewed from the antimony side.
(b) viewed from the silicon side.
(c) viewed from the silicon side with an anti-reflection coating.
reflectance spectrum of sapphire shown in fig (5-13). The following points should be noted.

(i) If the absorption constant of antimony is low at a particular wavelength, then the reflectivity of the film/substrate system may be modified by a change of refractive index of the substrate.

(ii) In the region 2-10 μm the reflectivity of sapphire is approximately constant at 0.05 corresponding to a refractive index of approximately 1.5.

(iii) Sapphire becomes absorbing above 10 μm, which corresponds to the beginning of a restrahlen absorption band. The result is to increase the apparent reflectivity of an antimony film on sapphire, more rapidly with wavelength than is predicted from the optical constants of antimony.

The results of the computation, using a refractive index of 1.5, are presented in fig (5-13) and show that the computer calculations are a good fit to the measured curves. The various reflection peaks at short wavelengths, which were attributed by Harris and Corrigan to optical interference, are in fact predicted by this procedure. The rise in wavelength at the plasma edge is less steep than that reported, because the reflectance of antimony films reported by Harris and Corrigan are modified above 10 μm by the rapid rise in the reflectance of the sapphire substrate.
Figure 5.15a

Computed and measured reflectance curves for a 0.25 μm thick antimony film.
Figure 5.15b
Computed and measured curves for antimony film 0.625 \( \mu m \) thick
The optical constants of antimony are the sum of contributions due to bound carriers and free carriers. If the excitation is small, then an increase in free carrier concentration will have a small effect upon the bound carriers, and the bound carrier contribution to the optical constants may be assumed to be constant.

Although this assumption is not strictly true at higher excitation levels, it is instructive to use this approximation in order to estimate the reflectance change which might be achieved with an increase in the free carrier concentration. Making this assumption, the reflectance curves for antimony films on a non-absorbing substrate of refractive index 1.5, have been recomputed for films having excess free carriers. Figure (5.17) shows the recomputed reflectance curves for films having free carrier concentration of double the natural concentration, with film thicknesses 0.625 μm, 0.25 μm, 0.15 μm, 0.08 μm.

It is clear that the resultant change in reflectance depends not only upon the change of carrier concentration but also upon film thickness. The interference peaks in films 0.625 and 0.25 μm thick appear at higher carrier concentrations, although they are attenuated due to higher absorption within the film. In general, higher film absorption tends to reduce the effect of film thickness on the reflectance spectrum.
Figure 5.16a

Effect of excess carriers on computed reflectance of antimony films of various thicknesses.

Curve 1 - normal carrier concentration $N = 1.7 \times 10^{26} \text{ m}^{-3}$

Curve 2 - $N = 3.4 \times 10^{26}$

(a) film thickness 0.525 μm
Figure 5.16b: Reflectance of Film Thickness 0.25 μm.
Reflectance

Figure 5.16d

Film thickness 0.08µm
5.8 \textit{Reflectance Modulation}

The change in reflectance of an antimony film makes possible the intensity modulation of infra-red radiation, reflected from the film. This may be done by adjusting the reflectance of the film due to a change in free carrier concentration. Fig (5.16) shows that the efficiency of modulation is a function not only of free carrier density, but is also a function of film thickness and the wavelength of radiation.

If intensity modulation is to be successful it is clearly necessary to establish the optimum wavelength and film thickness of which reflectance changes occur.

The available data and theory allow this to be done. First the modulation performance of thin films of pure antimony will be described, and then it will be shown that better results may be obtained by using doped or alloyed samples of antimony.

5.8.1 \textit{Pure antimony films}

For reflectance modulation the quantities $\Delta R$ and $\Delta R/R$ are of interest. These quantities have been computed for thin films made from pure antimony; the results are presented in fig (5.17). This shows the reflectance changes $\Delta R$ and $\Delta R/R$, induced when the free carrier concentration is arbitrarily doubled.

The maxima exhibited by both curves are due to optical interference, and it is evident that there are optimum thicknesses for maximum $\Delta R/R$ or $\Delta R$. 
The dependence of reflectance changes $\Delta R$ and $\frac{\Delta R}{R}$ on film thickness.
Further investigation has been done which showed that these optimum film thicknesses remain constant for different excitation levels.

Fig. (5.18) shows the variation of $\Delta R/R$ as a function of the number of non equilibrium excess carriers ($\Delta n$) assuming an antimony film of thickness 0.12 microns (corresponding to the maximum in fig. (5.17)). This allows the reflectance change of an antimony film to be computed for a specific increase of the free carrier concentration. Alternatively if a reflectance change $\Delta R/R$ is observed it is possible to work backwards and compute $\Delta n$.

5.8.2 Doped Antimony Films

Fig. (5.19) presents the computed reflectance (at 10.6 microns) of bulk antimony which contains excess free carriers. This shows that the addition of extra free carriers initially has a comparatively small effect upon the reflectance. The addition of greater numbers of free carriers ($n = 10^{26} - 10^{27} \text{m}^{-3}$) is characterised by a large change of reflectance. (This corresponds to a shift of the plasma edge in antimony to 10.6 microns.) At very high excess carrier densities the reflectance is again insensitive to $\Delta n$.

For work on reflectance modulation it is desirable that $\Delta R/R$ should be large. This occurs when the slope of the curve in fig. (5.19) is greatest, and is illustrated by reference to fig. (5.20). Here $dR/dn$ (computed for bulk antimony) is plotted as a function of the equilibrium carrier density ($n$) in bulk antimony. It is evident that $\Delta R/R$ may be increased by a factor of $\sim 7$ by using antimony with the appropriate equilibrium carrier density $n = 5.0 \times 10^{26} \text{m}^{-3}$ and it would appear advantageous to adjust the free carrier concentration in antimony to this optimum value, by doping or alloying with another element.
Figure 6.18
Variation of $\Delta R$ with excess carrier density for a film of optimum thickness
Figure 5.19

Reflectance of an antimony-like lattice as a function of free carrier density.

Figure 5.20

$\frac{\delta R}{\delta n}$ as a function of carrier density for an antimony-like lattice showing an optimum value at $5 \times 10^{26}$ m$^{-3}$. 
5.9 Conclusions

It has been shown possible to predict the optical properties of evaporated films of antimony in the infra-red as a function of their thickness, and changes of free carrier concentration. This was achieved by the interpretation of previous data on the optical properties of thin films of antimony with the use of detailed measurements of the optical constants in the near infra-red of poly-crystalline material.

The optical constants due to free carrier effects have been separated from those due to band electrons and used in a computer program for thin film behaviour. A one carrier model was found adequate to account for free carrier dispersion with a relaxation time of $3.1 \times 10^{-14}$ sec found for a carrier density of $3.1 \times 10^{26} \text{m}^{-3}$.

Finally the reflectance changes which may be induced by an adjustment of the free carrier concentration in evaporated films of antimony and antimony alloys have been predicted.
Chapter 6  The Production of Free Carriers by Electron Beam Bombardment

6.1 Introduction

When a semiconductor is bombarded by comparatively high energy electrons, a large fraction of the energy of the incident electrons goes into the production of excess electron-hole pairs. These excess carriers in general have a finite lifetime, and for a continuous beam of given current and voltage, the concentration of excess free carriers will rise until the rate of generation equals the rate of recombination.

In order to make meaningful measurements and to predict the optical properties of semiconductors and semimetals exposed to such radiation, it is necessary to have information concerning the density and distribution of induced carriers. Sections 2 and 3 are therefore concerned with the generation of carriers by kilovolt electrons as a function of depth, electron energy and target atomic number, and the solution of the diffusion equation to find the resultant spatial and temporal distribution of excess carriers respectively.

6.2 Energy Dissipation of Fast Electrons in Solids

The absorption and scattering of electrons by nuclei and by other electrons has been studied since the early days of radioactivity using naturally occurring $\beta$-particle emitters as sources. It was soon discovered that the slowing down of electrons in matter by interaction with atomic electrons inevitably introduces a large degree of straggling, due to the high probability of the loss of a large amount of energy in a single collision. This straggling is greatest for slow electrons in materials of a high atomic number, and it implies that the range of electrons is not sharply defined.
If a monoenergetic beam of electrons is passed through an absorber, the transmitted intensity as a function of absorber thickness is shown as in fig (6.1).

By extrapolation the sloping part of the curve to the axis or to the level of background, an extrapolated range \( R_0 \) may be defined and this procedure is sufficiently reproducible to permit such ranges to be used in establishing a range energy curve. To a good approximation, ranges expressed in mg cm\(^{-2}\) are independent of the material of absorber.

The theory of the penetration of electrons in matter has been placed on a solid basis by Lewis [77] and Spencer [48] who combined the results of energy-loss theory Bethe [78] with the theory of elastic scattering (Rutherford-Mott). As a final result Spencer [48] has produced a computer program to compute extensive tables of the spatial distribution of energy dissipation of electrons from several keV upwards, in a number of representative substances, e.g. carbon, aluminium, copper, tin, lead and polystyrene. Procedures are given such as that one may interpolate electron energy and/or atomic number of material.

Klein [79] noted that there is one difference between the experimental situation and that described by the theory. In the experiment the zero plane separates the medium and vacuum whereas in the theory the medium extends over all space. Thus in the experiment the energy dissipated in the medium is less the energy lost by backscattering.

The tabulations of Spencer have been verified by the work of Ehrenburg and King [49] who studied the glow produced in a number of luminescent materials by a narrow bundle of cathode rays with electron energies between 10-80 keV.
Figure 6.1
Range-energy curve for electrons after Katz and Penfold [6.1] 1952

Figure 6.2
The variation of $J(x)$ with depth $x$ for electron penetration into antimony and silicon at source energies of 10, 20, 50 KeV using Spencer's tables [6.3]
The close agreement between energy dissipation curves of Ehrenburg and King after allowing for backscatter and the theoretical tabulations computed by Spencer allowed Anderson [47] to use Spencer's tables to estimate the regions of maximum energy dissipation in electron beam exerted laser crystals.

It is proposed to use Spencer's tables to determine the energy dissipation curves of 4 keV electrons in antimony and silicon.

6.2.1 Description of the Tabulations

Basically Spencer has tabulated $J$, a non dimensional energy distribution vs. $x$, a non dimensional electron penetration distance over a range of energies $E_0$, for the materials carbon, aluminium, copper, tin, lead and polystyrene.

$J(x)$ is plotted for several source energies for absorption in aluminium in fig (6.2).

There are two types of interpolation of interest:

(i) Interpolation of source energy $E_0$ - the distribution shapes are known experimentally and expected theoretically to be rather independent of source energy, particularly for non relativistic energies. The curves in fig 6.2 show very little change with variation in source energy and it is therefore proposed to assume that the $E_0 = 25$ keV curve is true for all source energies.

(ii) Interpolation of atomic number $Z$ - this is more difficult but it can be done using standard interpolation formula. However the materials of interest, antimony and silicon, have atomic numbers 51 and 14 which differ by only one from the elements tin and aluminium and it is therefore proposed to assume that the curves given in fig 6.2 for tin and aluminium are valid
for antimony and silicon.

6.2.2 Calculation of Real Energy Distribution

The non dimensional quantities $x$ and $J(x)$ require to be changed to the real parameters $z$, the real depth of penetration and $\frac{\delta E}{\delta z}(z)$ the rate of energy loss per unit volume. This is achieved by using the equations

(1) \[ z = x \rho r_0 \]

where $\rho = \text{the material density}$

$r_0 = \text{maximum depth of penetration}$

$r_o$ is tabulated by Spencer for any combination of parameters.

(2) \[ F(z) = \rho \left( \frac{\delta E}{\delta r} \right)_{E_0} J(x) \times 1.6 \]

$\times 10^{-12} \text{Joules cm}^{-3}$

$= 3.33 \times 10^{-12} \left( \frac{\delta E}{\delta r} \right)_{E_0} J(x)$

where $F(z) = \text{energy dissipated cm}^{-3}$

$\left( \frac{\delta E}{\delta r} \right)_{E_0}$ is the average stopping power of the material which is also tabulated by Spencer.

Using these relations fig (6.3) shows $F(x)$.

The rate of energy lost per cc by one electron as a function of the depth of penetration in silicon and antimony.
Figure 6.3

$F(x)$ - the real rate of energy loss as a function of real penetration $x$ in (a) silicon (b) antimony
6.2.3 Calculation of the Rate of Production of Carrier Pairs

The stopping time for electrons amounts to a few picoseconds \[46\]. During the primary ionisation process electrons are lifted from the low states in the valence band to high states in the conduction band. In the secondary process the excess energy serves to produce further charge carriers and to excite the phonon states of the lattice. This amounts a time amounting to 1 p sec.

Each electron which is absorbed by the material in the manner described above must produce many free carrier pairs along its path.

For a current \( i \) - the number of electrons hitting the target per second is \( n = \frac{i}{e} \).

The number of electrons absorbed per \( \text{cm}^2 \) per second is \( n = \frac{i}{Ae} (1-r) \text{ sec}^{-1} \text{ cm}^{-2} \) where \( A \) is the area of the target and \( r \) is the fraction of electrons which are backscattered.

If the rate of loss of energy of one electron is \( F(x) \) and the energy required to form one free carrier pair is \( E \) electron volts, then the total carrier generation rate per cc is given by

\[
E_E(x) = \frac{i}{Ae} (1-r) \cdot \frac{F(x)}{E}
\]

The energy required to produce ionisation in silicon is \( E = 3.6 \text{ eV} \ [46] \).

Example for silicon  \( E = 3.6 \times 1.6 \times 10^{-19} \) Joules, \( i = 100 \text{ mA} \)

\( A = 0.1 \text{ cm}^2 \quad r = 0.2 \)

Then \( E_E(x) = 6.3 \times 10^{36}F(x). \)

Fig (6.3) shows the rate of production of carrier pairs in silicon and antimony assuming an electron beam energy of 5 kV and a current 100 mA.
No value is available for \( E \) for antimony, but a value of 3.6 \( \text{eV} \) has been assumed for comparison. From a knowledge of the overlapping band structure of antimony it is probable that this value is too high which implies that the number of carrier pairs produced in antimony will be greater than is shown in fig (6.3).

6.3 The Continuity Equations

When the densities of free electrons and holes are functions of space and time, the rate of each can be expressed through a continuity equation. The density of excess carriers will tend to change as a net result of

(i) Carrier generation processes

(ii) Carrier recombination processes

(iii) Carrier diffusion and drift.

Assume an electron current density \( I_n \) signifies a flow of \( (-I_n/z) \) electrons across a plane of area 1 cm\(^2\), normal to the direction of flow electrons.

\[
\begin{align*}
- \left( \frac{I_n}{q} \right) & \quad \xrightarrow{\text{eq} \ } \quad 0 \quad \xrightarrow{\text{eq} \ } \quad \left[ I_n + \left( \frac{\partial I_n}{\partial x} \right) \delta x \right] q^{-1}
\end{align*}
\]

The basic equation governing the behaviour of excess minority carriers, in which the concentration is a function of space and time is

\[
\frac{\partial n_n}{\partial t} = -\left( \frac{1}{e} \right) \nabla I_n - \frac{n_n(X)}{\tau_e} + gE
\]  

(6.1)

where \(- \frac{1}{e} \nabla I_n\) represents the number of electrons leaving unit volume per unit time due to the hole density \( n \), \(- n / \tau\) represents the number of electrons disappearing/sec due to recombination assuming an average lifetime of \( \tau_e \) for each electron.
\( g_e \) represents the number of electrons generated per unit volume per second by external means. A similar continuity may also be written for minority holes

\[
\frac{\partial n_e}{\partial t} = -\frac{1}{e} \nabla V - \frac{p(x)}{\tau_p} = g_e \tag{6.2}
\]

When the spatial variations of \( n(x) \) or \( p(x) \) have certain forms it is possible to solve equations (6.1) and (6.2) for some specific and rather simple variation of lifetime with concentration. In a much larger number of cases it is possible to examine the phenomenon of spatial dependence only on the basis of a very simplified model for which \( \tau_n \) does not depend on carrier lifetimes at all.

When this simplified model is adapted an attempt may subsequently be made to fuse the results of the enquiry (assuming constant \( \tau \)) with knowledge about the behaviour of the bulk lifetime (when there is no spatial dependence problem). Such attempts are generally unsatisfactory and a simplified model of a concentration independent lifetime will be assumed in the rest of this work.

The simple model assuming carrier lifetime independent of carrier concentration allows equations (6.1) and (6.2) to be solved no matter how \( g_e \) and \( I \) depend on position and time (Blakemore 1960-4).

The earliest experiments on the motion of excess minority carriers in a single crystal (Shockley [29]) indicated that electron hole recombination may occur on crystal surfaces. This surface recombination is associated with localised flow levels, and depends on the relationship of the Fermi level and the surface flow energy which in turn depends on whether a surface barrier exists or not.
These properties of the surface are sensitive both to the physical condition of the surface region and the chemical nature of its environment. With thin films the surface properties depend very strongly upon the evaporation conditions e.g. pressure evaporation rate, temperature of substrate etc.

When recombination occurs at the surface, there is a flow of electrons to the surface and a flow of conventional current $I_n$, away from the surface. Shockley defines a quantity $S$ - the surface recombination velocity which is defined by the equation for p-type material.

$$I_n = -en_p S$$

or for n-type

$$I_p = +en_p S$$

The numerical value of $S$ depends on the equilibrium carrier concentration, the height of the surface barrier and the density of the surface states. In germanium at room temperature values from 50 to $10^5$ have been observed, and in silicon $S$ has been made to vary by several orders of magnitude by change of atmosphere surrounding the sample (Benny and Marten). [81]

This recombination behaviour of any semiconductor surface is to a greater or lesser extent, dependent on the magnitude of $S$ means that even when excess carriers are created more or less uniformly through the volume of a sample, the outer regions become preferentially depleted, this process of diffusion to the surfaces persists so long as excess carriers recur.

The rigorous solution of equations is not possible in practice, however several terms may be neglected, e.g. the condition of charge neutrality is assumed. The following assumptions have been made in the analysis of the diffusion equation.
A wide parallel beam is usually incident on the surface of the material.

The material is homogeneous and free from barriers or traps.

Only one type of carrier is taken into consideration.

The steady state spatial distribution of carriers produced by photoinionisation or electron beam excitation has been discussed by several authors \[82-84\] all of whom included the effects of surface recombination. The time dependence of such generation has largely been ignored. Since a pulsed electron beam has been used to inject free carriers into a material it is clearly important to have an estimate of the likely carrier densities which might be produced.

Blakemore [83] solved the continuity equation for photo injected carriers in a thin film slab assuming a carrier generation rate independent of depth, Kyser and Wittry [44] assumed the distribution of carrier generation with depth for an electron beam excitation to be approximately Gaussian, in a semi-infinite solid and Gergley [86] solved the continuity equation for two cases where distributions of carrier generation in a semi infinite solid were (a) exponential (b) parabolic.

The solution of the continuity equation for a specific case where both carrier generation and recombination are functions of time and position is very difficult and the following cases will therefore be considered separately.

1. The time dependent case in which generation and recombination are position independent.

2. Steady state case where generation is independent of time and position but including the effects of surface recombination.

3. Steady state case where both generation and recombination are position dependent.
6.3.1 Transient Carrier Distribution in a Slab

Assume carriers are generated uniformly at a rate \( g_0 \) throughout a slab of dimension \( l \). No carriers are produced after a period of seconds, and the surface recombination velocity at each face is assumed to be zero.

The diffusion equation for the electrons in the film is:

\[
D \frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau} + gE = \frac{dn}{dt}
\]  

(6.4)

where \( gE = G \{H(t) - H(t-a)\} \)

(6.5)

\( H \) is the impulse function.

Equation (6.4) may be rewritten in Laplace Transform form

\[
\frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau} \left(\frac{1}{\tau} + \frac{1}{p}\right) + \frac{G}{\tau D} (1 - e^{-pa}) = 0
\]

(6.6)

This equation has the solution

\[
n = \frac{G(1-e^{-pa})}{p(\tau+\tau/\tau)} + A e^{-qx} + B e^{+qx}
\]

(6.7)

where \( q = \frac{p + \frac{1}{\tau}}{\tau} \)

(6.8)

Assume \( S_0 = S \xi = 0 \), the boundary condition becomes

\[
\left(\frac{3n}{\partial x}\right)_{x=0} = \left(\frac{2n}{\partial x}\right)_{x=\xi} = 0
\]

(6.9)

Therefore \( A = B = 0 \) and equation (6.6) becomes

\[
n = G(1-e^{-pa}) \left\{ \frac{1}{p} - \frac{1}{p+1/\tau} \right\}
\]

(6.10)

and therefore

\[
n e = G(1-e^{-t/\tau}) - G \left(1-e^{\frac{t-a}{\tau}} \right) H(t-a)
\]

(6.11)

i.e. for the period \( t > a \)

\[
n e = G(1-e^{-t/\tau})
\]

(6.12)
and for the period \( t \geq \alpha \)
\[
ne = Gr(1-e^{-t/\tau}) - Gr(1-e^{-t-a/\tau})
\] (6.13)
or rearranging
\[
ne = Gr(e^{a/\tau-1})e^{-t/\tau}
\] (6.14)

Equation (6.14) indicates that there is a limiting carrier concentration \( Gr \) and in order to generate high concentration a long lifetime \( \tau \) is essential. Figure (6.4) shows the growth of concentration with time for a typical sample and generation pulse. It is seen that when \( \alpha \gg \tau \)
\[ n \approx Gr, \] when \( \alpha \ll \tau \quad n \rightarrow 0 \) and when \( \alpha = \tau \) then \( n \) is approximately \[ \frac{1}{3} Gr. \]

6.3.2 **Steady state solution with surface recombination**

Recombination of excess carriers may occur in the bulk of a material or at the surfaces. The magnitude of the former effect is associated with the bulk lifetime \( \tau \) and that of the latter with the surface recombination velocity \( s \). The net effect of surface recombination is to preferentially deplete the regions near surfaces of carriers.

The distribution which results is illustrated by considering a sample in the form of a large sheet whose principle faces are \( x = 0 \) and \( x = 2A \), in which carriers are generated at a rate \( gE \) independent of position or time. The continuity equation for steady state is

\[
\frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau} + gE = 0
\] (6.15)

which has a solution of the form
\[
n = \tau n gE \left\{ 1 - G \exp \left\{ \frac{-x}{(D\tau)^{1/2}} \right\} - H \exp \left\{ \frac{-x}{(D\tau)^{1/2}} \right\} \right\}
\] (6.16)
Figure 6.4
The rise and decay of excess carrier density with time.

Figure 6.5
Excess carrier density in a sample of thickness 2\(\lambda\), having a diffusion length 0.5\(\lambda\).

(a) \(s_1 = 0, s_2 = \infty\)
(b) \(s_1 = V, s_2 = \infty\)
(c) \(s_1 = \infty, s_2 = \infty\)

Figure 6.6
Variation of total excess carrier density produced by ionising radiation as a function of photon energy.
\( G \) and \( H \) depend on the appropriate boundary conditions. The quantity \( (D/\tau)^{\frac{1}{2}} \) has the dimensions of length and is known as the diffusion length \( (L) \). Another quantity which is often used is the diffusion velocity \( (v) \) equal to \( (D/\tau)^{\frac{1}{2}} \).

The boundary conditions for surface recombination are

\[
\frac{\partial n}{\partial x} \bigg|_{x=0} = s_1 n_1 \tag{6.17}
\]
\[
\frac{\partial n}{\partial x} \bigg|_{x=2A} = s_2 n_2 \tag{6.18}
\]

In terms of these conditions and the parameters listed the solution of (6.15) is

\[
n_c = r n g \exp \left( \frac{x}{L} \right) - G \exp \left( -\frac{x}{L} \right) - H \exp \left( -\frac{x}{L} \right) \tag{6.19}
\]

with

\[
G = \frac{s_2 (v + s_1) \exp(2A/L) + s_1 (v - s_2)}{(v + s_1)(v + s_2) \exp(2A/L) - (v - s_1)(v - s_2)} \tag{6.20}
\]
\[
H = \frac{s_2 (v - s_1) \exp(2A/L) + s_1 (v + s_2) \exp(4A/L)}{(v + s_1)(v + s_2) \exp(4A/L) - (v - s_1)(v - s_2)} \tag{6.21}
\]

Simplifications occur in the expressions for both \( G \) and \( H \) when \( s \) becomes infinite at either surface (or both).

Figure (6.5) shows how \( n \) (expressed as units of \( r g \)) varies with \( x \) when the diffusion length is one quarter of the sample thickness \( 2A \).

For each of the curves it is assumed that \( s_2 = \infty \) on the rear surface; the curves then correspond to three values of front surface recombination velocity.
6.3.3 **Effect of the spatial distribution of generation**

Excess carriers may appear in semiconductors either because they have been injected electrically or because the material has been exposed to an ionising influence. In neither case is it possible to set up an initial distribution which is completely uniform throughout a volume.

Where the ionisation is caused by a radiation flux $J_0$, the excess generation rate is given by an equation of the form

$$g_E(x) = (1-R)J_0 \times \exp(\alpha x) \quad (6.22)$$

where $R$ is the reflectance and the absorption coefficient. For photons of progressively higher energy $\kappa$ becomes larger than $(2A)^{-1}$ and most incident photons create hole-pairs. It would seem from equation (6.22) that the number of excess pairs maintained per unit area of the sample by unit photon flux should reach an upper limiting value

$$\frac{\ln 2A}{J_0} \int_0^\infty g_E(x) \, dx \rightarrow \tau_n (1-R) \text{ as } \alpha \rightarrow \infty \quad (6.23)$$

for large photon energies. As de Vore [87] has pointed out this objective is frustrated when there is any surface recombination - for the high energy (readily absorbed) photons create hole-electron pairs in large numbers close to the front of the surface, and the surface has the opportunity to promote rapid recombination.

Figure (6.6) shows schematically how the integral of equation (6.23) might vary with photon energy when $s$ takes different values. This argument has been used by de Vore [87] to explain the photon energy dependence of photoconduction. By solving the diffusion equation for generation which was an exponential function of sample depth he obtained the following equation for the total number of carriers in steady state.
\[ N = nT \cdot \frac{1 - e^{-z}}{1 + \Sigma \coth(1/e \lambda)} \cdot \left\{ 1 + \Sigma \lambda \coth(\lambda z) - z \coth(\frac{z}{2}) \right\} (6.24) \]

where 
\[ z = \frac{a \lambda}{2} \]
\[ E = s \left( \frac{1}{D} \right) \]
\[ \lambda = \frac{k}{(D \tau)^{1/2}} \]

A similar reduction of the total number of carriers can be expected for electron beam excitation, especially where carriers are generated within a diffusion length or two of the sample surface.

### 6.3.4 Summary

The results of sections 6.3.1, 6.3.2 and 6.3.3 may be summarised as follows.

1. The limiting number of carriers which may be generated is determined by the product of generation rate and carrier lifetime. This limit may only be reached if the length of the generating pulse is several times longer than the lifetime.

2. The effects of surface recombination are important within a distance of 2-3 diffusion lengths of the surface. In this region the free carrier density may be reduced by several orders of magnitude if the surface recombination velocity is high.

3. The total number of free carriers may be further greatly reduced below the expected value if generation occurs near to the surface.
The distribution of the energy dissipation of fast electrons in antimony and silicon has been described with the help of a monograph by Spencer. The results indicate that if all incident electrons are to be stopped within a thin film of thickness 1 micron, then the accelerating voltage should be less than 7 kV.

The subsequent behaviour of generated carriers may be determined by the use of the continuity equation which allows for diffusion and recombination. Several cases have been considered and it was shown that for a given generation rate, the final free carrier concentration depends upon carrier lifetime, generation pulse length and the surface recombination velocity.
Chapter 7: ELECTRON BEAM EXPERIMENT

7.1 Introduction

In this chapter an account is given of the attempt to observe induced reflection changes at 10.6 microns, in samples of bulk silicon and thin film antimony, when subjected to bombardment by 5 kV electrons from an electron gun. Details of the design and construction of apparatus, particularly the electron gun, are given and the problems which were associated with electrical pick-up are described. Finally the results are discussed with the aid of photoconduction measurements made on the samples.

7.2 The Electron Gun

An electron gun was chosen as a means of producing a large number of electron whole pairs inside a crystal or thin film. The important design criteria were that the carriers be deposited in the sample in a short time (about 4 psec) and that the beam energy should be such that all electrons were stopped within the target, which may be less than 1 micron thick. Calculations* have shown that electrons which have been accelerated by 5-10 kilovolts have a range of 0.5-1 micron in the type of materials which might be used. A 5 kV, 100 mA power supply was available and it was therefore decided to design a gun with a maximum accelerating voltage of 5 kV.

The gun was also designed to have the following characteristics:

1. Good precision in the determination of the time at which the ionising action begins

*See Chapter 6
2. A focussed spot approximately 4 mm diameter in order that the whole cross section of the incident laser beam be reflected from an exciting surface.

3. Repetitive working.

4. Large current bursts to induce large numbers of excess carriers.

5. The gun should be demountable for convenience.

6. A beam deflection system to aid alignment of the electron and incident laser beams.

An electron gun has been realised which supplies electron bursts with the following principle characteristics:

1. Energy of electrons 1-5 kV.

2. Average current per burst 100 mA.

3. Duration of each burst about 4 μsec.

4. Focussed spot size down to 3 mm diameter.

5. Deflection range 25 mm in X or Y direction.

6. Fully demountable.

In this section a short account is given of important parameters which must be considered in the design of an electron gun, followed by a description of the gun which has been built.

While a light emitting body can be used immediately as a source of light rays, a simple electron emitter such as a thermionic cathode is not sufficient for the production of electron beams in practical apparatus. Electrons leaving the filament must first be accelerated and their kinetic energy increased many times, before they may enter a particular electron optical device.
Electrons from the cathode will eventually follow, approximately, the lines of force since within a small distance from the cathode, the kinetic energy of all electrons is still small in comparison with the potential drop along its length. On their way to the anode the electrons gain energy. Eventually their kinetic energy is much greater than the potential drop along a given field element and the electron may deviate considerably from the direction of the field. For this reason it is possible to accelerate the emission of a relatively large cathode surface through a small aperture of the anode into a relatively field free region of space.

7.2.1 Triode Emission Systems

In good emission systems, the whole emission from the cathode passes the aperture in the anode with no electrons being intercepted. As early as 1903 Wehnelt showed that it was essential to use an auxiliary electrode, placed between the anode and the cathode for focussing electron emission towards the anode. The auxiliary electrode may also serve the additional purpose of controlling the intensity of emission. In this case "intensity modulation" is effected by changing the potential of the auxiliary electrode. This electrode is called the grid or modulator.

The simplest emission systems are triodes containing a cathode, a grid electrode and an anode, but a more sophisticated system might contain many electrodes which may be of a complicated structure.

It is essential however that the focussing action be independent since this allows freedom to focus the beam without affecting other important gun parameters such as the cut-off characteristic.
Figure 7.1
Various triode emission systems showing the significance of dimensions D, b, t and f.

Figure 7.2
A three-electrode einzel electro-static lens showing the equipotentials.
Therefore it is convenient to divide the electron gun into two portions - the triode and the focusing lens which might be electrostatic or magnetic.

7.2.2 The triode

The triode emission system generally has a flat equipotential cathode which may be heated directly or indirectly. The grid-electrode is generally a flat diaphragm with a circular aperture which is mounted in a tubular sleeve for support and which serves the additional purpose of shielding the electron rays from external electro-static disturbances. The anode is also an aperture flat disc. The diameter of the apertures is generally small compared to the radius of the discs, therefore an electrostatic screening is automatically provided.

Many electrode arrangements have been used successfully in the triode and a few are shown in Fig (7.1).

The potential difference between the grid G and the cathode C has a dominant effect upon the gun characteristics, and a small change in the grid potential may cause a very great change in the emission current.

There are many possible electrode combinations, and in order to optimise the performance of the gun, the following points may be considered.

1. The anode current \( I_a \) of a space charge limited diode is related to the anode voltage by the equation (Parker (7.1))

\[
V_c = \frac{K_z D_1^3}{t_1 b_1 f_1}
\]

where \( K_z \) is a constant, \( D_1 \), \( t_1 \), \( b_1 \) and \( f_1 \) are defined in figure (7.1).
3. The triode cut-off is proportioned to the first anode voltage. It can be shown (Moss [89], Parker [88])

\[ V_c = K_z (V_a + V_{c^*}) \]  \hspace{1cm} (7.4)

where \( V_{c^*} \) is the voltage required to cut off the anode current when the anode potential \( V_a \) is zero, i.e., \( V_{c^*} \) is a small voltage required to overcome the finite velocity of electrodes leaving the cathode due to thermionic emission. \( V_{c^*} \) is small and may be neglected in the triode then.

\[ V_c = K_z V_a \]  \hspace{1cm} (7.5)

Therefore combining (7.3) and (7.5)

\[ V_c = K_4 \frac{P_2 V_a}{\xi_4} \]  \hspace{1cm} (7.6)

and

\[ I_a = K(V_c)^{3/2} \]  \hspace{1cm} (7.7)

Equation (7.7) is important because it has been found to be true (within 10%). When the cut-off voltage \( V_c \) is changed by alteration of the geometry of the triode i.e., wide changes in grid spacing or hole diameter. Therefore to a first approximation \( K \) is independent of anode voltage or triode geometry. Moss [89] found the best value of \( K \) to be three for a wide range of triodes.

\[ I_a = 3(V_c)^{3/2} \]  \hspace{1cm} (7.8)

where \( I_a \) is measured in microamps and \( V_c \) is measured in volts.

Equation (7.8) may be used to estimate the cut-off voltage in a triode which is capable of emitting a current of 100 mA

\[ I_a = 10^5 = 3 \ (V_c)^{3/2} \]

Therefore \( V_c = 1050 \) volts, i.e., any gun which will deliver 100 mA will require a negative voltage of approximately one kilovolt applied to the grid to produce cut-off. This simplifies triode design since the cut-off voltage is automatically decided when the triode current capability is chosen. The designer is free to choose \( V_a \) by varying the electrode geometry and equation (7.6)
may be used to indicate the relative importance of the electrode dimensions in determining the ratio $V_c/V_a$.

### 7.2.3 The electrostatic final lens

A well designed electrostatic focussing lens may be made compact, and should take a negligible current, so that it can be supplied from a high resistance chain across the main HT supply. It is therefore easy to vary the focussing anode voltage by tapping in at a suitable point on this chain. A good account of the properties and construction of electrostatic lenses is given by Klemper and Barnett [90]. A typical electrostatic final lens is shown in fig. (72).

This lens consists of three coaxial tubes with equal radii and equal separation of 0.1R. Klemper and Barnett [90] give the variation of focal length of the lens as a function of the length and the voltage of the intermediate tube.

It is sufficient to approximate the performance of this lens to the equivalent "thin" lens obeying the simple optical laws and situated at the centre of the middle tube.

The electrostatic may be of compact construction and it requires very little power to operate.

### 7.2.4 The magnetic final lens

In a magnetic field the electron is accelerated in a perpendicular direction to both the field vector and its own velocity. Any axially symmetrical magnetic field acts as a converging lens on an incident beam of electrons travelling along that axis. Such a field may be generated by ordinary electric coils (air coils) or iron shielded coils or by permanent magnets. Klemper and Barnett [90] have described
many magnetic lenses, but of particular interest is an iron shielded coil of 1500 turns of fine wire with an inner and outer radius of 25 and 58 mm respectively. The shape of the field contour lines of the axial component of flux density due to this coil are described in detail.

These contour lines are very similar to the equipotential lines of an electrostatic lens. The performance of this lens may also be approximated to the equivalent "thin lens" which has the focal length \( f \) given by

\[
f = \frac{G Ve}{(nI)^2}
\]  

(7.9)

where \( Ve \) is the energy of the incident electrons, \( nI \) is the number of ampere turns of the coil and \( G \) is the coil form factor which is approximately equivalent to 9. Equation (7.9) shows that a current of 0.25 amps produces a focal length of 20 cm.

The magnetic lens is often convenient since it may be situated outside of the vacuum tube. It is easy to construct, there are no high voltage engineering problems and the focal length may easily be varied.

7.2.5 The Completed Gun

A cross section diagram of the whole of the demountable gun is shown in fig. (7.3) which has been drawn approximately to scale. The assembly is mounted on a water cooled stainless steel plate and the electrodes are made of stainless steel.

The electrons are emitted directly from a heated tungsten coil and are accelerated towards the anode which has a potential of 5 kV. The emission current is suppressed by means of a negative potential of 1200 volts applied to the grid. The current is switched by applying a 4
Figure 7.3

The demountable electron gun
(a) Magnetic focusing coil (b) Glass vacuum system (c) O-ring seal
(d) Anode (e) Control electrode (f) Filament (g) Electrical lead-throughs
μsec positive pulse to this electrode of 1300 volts from a pulse generator that operates up to frequencies of 65 Hz. The electron pulse detection system may be triggered from the same trigger source in order to have exact synchronization between the electron beams arrival on the target and the signal response. To ensure high voltage stability the vacuum inside the chamber is maintained at better than 10⁻⁴ torr.

A major problem was electrical breakdown between the various electrodes when the gun became hot during operation. Therefore great effort was made to design the system so as to reduce surface electrical leakage paths. In this situation it was found that an adapted car sparking plug, which was O-ring sealed into the base plate, made an efficient, low cost, high voltage lead through and eliminated one major area of breakdown.

An electrostatic final lens was tried but this too was found to be particularly susceptible to electrical breakdown. It was replaced by a magnetic lens in the form of an air coil of 1500 turns of 30 mm radius operating at a current of up to one amp. This lens was capable of focussing the beam to a spot 3 mm diameter on a target 100 mm from the coil. By using a target covered in soot from a luminous gas flame it was quite easy to observe the spot.

Two orthogonal sets of coils (not shown in fig. (7.3)) of a few hundred turns of light gauge enamelled copper wire were also placed around the vacuum tube to deflect the beam. These coils required a current of only a few tenths of an amp to deflect the beam up to 25 mm in any direction at the target.
The electrical characteristics of the gun are shown in fig. (7.4).

The gun is currently operated with an accelerating voltage of 4 kV and a current to the target of \(\sim 150\) mA.

The gun is generally operated with the target (anode) at a high voltage and the cathode at earth potential.

Fig. (7.5) shows the electrical circuit of the gun. The beam current may be measured by the potential across the load resistor \(R_c\) of 1000 ohms.

Fig. (7.6) shows the gun in position on the vacuum system and the electrode structure.

7.3 Miscellaneous Apparatus

7.3.1 The CO₂ Laser

A low power carbon dioxide laser has been constructed to deliver up to 5 watts of radiation in a beam of 5 mm diameter. The laser is mounted on a trolley, containing the power supply and gas control which can be raised or lowered in order to align the laser beam with a target. A photograph of the complete assembly is presented in fig. (7.7).

The laser has a narrow bore (6 mm diameter) discharge tube of fused silica, with a gold coated stainless steel mirror at one end, and a flat water cooled germanium output mirror at the other.

A gas mixture of helium, nitrogen and carbon dioxide in the volume ratio 4:1:1 is used, and the gas pressure can be accurately adjusted to the operating pressure of 15-16 torr by the use of a needle valve.
Figure (7.4)
Electrical characteristics of the electron gun

Figure (7.5)
The electron gun circuit
Figure 7.6
Photographs of electron gun (2)
Figure (7.7)

Photograph of the laser and the laser power supply
The most efficient lasing action was found experimentally to occur when the discharge was operated with a potential difference of 9 kV and a current of 20 mA. The discharge was D.C. and was supplied from the built-in power supply. The circuit diagram for the power supply is presented in fig. (7.7). The power supply is based upon a low cost neon sign transformer, the output of which is voltage doubled to obtain the open circuit voltage of 15 kV.

7.3.2 The Electron Gun Pulse Unit

The pulse circuit for the electron gun is required to produce repetitive pulses of up to 1500 volts magnitude and of several microseconds duration. This may be satisfactorily achieved by rapidly discharging a delay line through its own characteristic impedance \([q_1]\) as shown in fig. (7.8).

A lumped delay line of characteristic impedance 1.5 kΩ is charged to high voltage via a 0.5 MΩ resistor, and subsequently discharged via a mercury-wetted relay into a 1.5 kΩ resistor. The pulse which then appears across this resistor has a voltage equal to half the voltage on the line and a duration equal to twice the delay length of the line.

The mercury-wetted relay acts as a very fast switch with a contact-make time of less than 10 n.sec, and although the relay was rated at only 750 volts, it was found to operate satisfactorily up to 3000 volts at 60 Hz provided that the current was limited. It was therefore found necessary to use a line with the high impedance of 1.5 kΩ.

Using this circuit pulses of variable voltage and length could be conveniently generated with a repetition rate of up to 60 Hz.
Figure (7.9)

Circuit used to simulate noisy pulse from the pyroelectric detector
The reflected CO$_2$ laser beam was monitored using a Mullard Infrared pyroelectric detector. This device is based on a small crystal, across which a potential difference appears when heated by incoming radiation. Electrically the crystal acts as a capacitance. The incoming radiation must therefore be chopped, and the response of the crystal is proportional to the chopping frequency. A following built-in amplifier having a $\frac{1}{F}$ frequency characteristic ensures a linear output from the device, up to a chopping frequency of 100 kHz. The maximum signal output is 1 volt. This detector is intrinsically very noisy and produces approximately 100 mV R.M.S. of noise. The detector was required to detect and measure modulation signals less than $10^{-3}$ times that of the incident radiation. This represents a detector output of less than 1 mV which is completely masked by the inherent noise of the detector.

The problem of recovering a small repetitive signal from a large noise background may be solved by the use of a Phase Sensitive Detector (P.S.D.), provided that a reference signal, of the same frequency as that to be detected, is available. The P.S.D. operates on the principle that the incoming signal is full wave rectified at the frequency of the reference signal, and all input signals except those having components at the reference signal are averaged to zero, the rest are full wave rectified and appear as a d.c. voltage proportional to the R.M.S. voltage of the buried signal. In this way the magnitude of repetitive signals which are buried in noise may be measured.

However the P.S.D. is not successful for a repetitive train of short pulses having a low duty cycle, which is the case in the present experiment, because the R.M.S. voltage of such a signal is extremely small.
The mercury wetted relay also presented a problem in that the repetition frequency was not stable causing the PSD to operate incorrectly. For these reasons the PSD could not be used in this experiment.

These problems may be overcome by the use of a Boxcar Detector which is a sampling correlation instrument. This instrument is designed to recover the waveform of repetitive signals buried in noise when a reference is available coherent with the signal repetition rate. It uses a gate which is opened to sample a small section of the waveform each cycle. This sampled information is then averaged in the manner of the PSD, with the result that the output due to noise averages towards zero. The output of the averager is therefore the mean value of that section of the waveform being sampled. The sample is progressively delayed with respect to the reference with each successive cycle and thus a profile of the complete waveform is built up, which may be plotted on an X-Y recorder.

The Boxcar was tested by simulating a typical signal which may be produced by the photo detector, in varying degrees of background noise. Fig. (7.9) indicates how this was done.

The noise derived from the pyroelectric detector in which the window was obscured, and a pulse from a signal generator were added together using an operational amplifier. The result was observed both on an oscilloscope and by the boxcar. Fig. (7.10a) shows the signal with no noise is accurately detected by the boxcar. Figs. (7.10b) and (7.10c) show that despite large noise backgrounds, the input pulse is still accurately plotted. This result allows confidence in the ability of the boxcar detector to measure the modulation signal on the laser beam.
Figure (21)
Boxcar input and output with different noise levels
Figure (σΩ)
7.4 Experimental

Fig. (7.11) shows the full layout of the electron beam modulation experiment.

The beam from the CO$_2$ laser was made to pass through a rocksalt window and be reflected by the sample inside the vacuum system, into the pyroelectric detector. The sample was then bombarded by the focussed electron beam and the signal from the pyroelectric detector together with a reference pulse from the electron gun were fed into the Boxcar unit, and the resultant output displayed on an X-Y recorder. For several later runs the experimental arrangement was adjusted so that the intensity of the beam transmitted by the sample could be monitored.

The samples used were antimony films deposited on glass or silicon substrates. Measurements were also made on thin (0.05 mm) single crystal slices of silicon and an attempt was made to correlate induced reflectance changes with minority carrier lifetime measurements made from photoconductivity measurements. Samples of single crystal germanium and lead-tin-telluride which were available were included for interest also.

The procedure for aligning both the CO$_2$ laser and electron beams on the sample were as follows.

(i) Using a beam splitter the beam from a small HeNe laser was aligned with that from the CO$_2$ laser.

(ii) The sample was replaced by a target which had been previously covered in lamp black since it had been found that the carbon on such a target glowed when bombarded by electrons from the gun, allowing the current distribution in the beam to be visualised. Using this target the beam was focussed by adjusting the magnetic lens current, and centred using the deflection coils.
Figure (7.11)  
Layout of the electron beam experiment

Figure (7.12)  
Circuit for photoconduction measurements
(iii) Using the HeNe laser beam the CO$_2$ laser was also centred on to the target.
(iv) The target was replaced by the sample.
(v) The reflected HeNe laser beam from the sample was directed into the pyroelectric detector 20 ft away.
(vi) The HeNe laser and beam splitter were removed. The CO$_2$ laser beam was mechanically chopped and observed by the detector. Final fine adjustments were made.

This last operation gave an output from the detector of typically 0.6 volts peak-peak. Assuming an antimony film has a reflectivity of 70% at 10.6 μm (as determined by infrared reflectance measurements described in Chapter 4), then a change of reflectance of 1% is equivalent to a change of detector output of 9 mVolts, or alternatively 900 mV's at the output of the Boxcar (which has a gain of x100). With no modulation signal input, there was a drift at the Boxcar output of approximately 100 mVolts, which limited the resolution of the experiment to a change of reflectivity $\frac{\Delta R}{R} > 0.1\%$.

7.4.1 The problem of electrical pickup

Initial attempts to observe reflectance modulation revealed the presence of severe electrical pickup, when the electron gun was operated. The pickup was traced to the switching pulse applied to the electron gun which was of 1500 volts magnitude and a few microseconds long. The interference was sufficient to completely mask any modulation signal and consequently a considerable effort was made to reduce it to an acceptable level. This included the following:
(i) All earth loops were traced and eliminated. All equipment and instruments were re-earthed at the electron gun only.

(ii) The pulse unit was redesigned so as to minimise radiation flux escape, by replacing the lumped delay line with 200 m of 75 ohm coaxial cable.

(iii) The pulse unit was removed as far from the experiment as possible (into another laboratory 60 ft away), and the switching pulse made to travel to the gun along high quality low loss coaxial cable which was double screened by an extra cover of heavy copper braid.

(iv) All other cables which carried the high intensity 1.5 kV pulse were double screened with copper braid.

(v) The electrical supply for the pyroelectric detector was altered from mains to batteries, and both the detector and batteries were fitted into an earthed cast box containing only a window for the detector.

(vi) The Boxcar unit and associated low noise amplifier and X-Y recorder were built into a metal cabinet to reduce the effect of stray capacitance between connecting leads, and a high frequency filter was incorporated into the mains supply.

(vii) Both the detector and Boxcar equipment were placed on the opposite side of the laboratory from the electron gun (a distance of approximately 20 ft).

Subsequent runs operating laser, electron gun and Boxcar equipment revealed that these measures had reduced electrical pickup by a factor of better than 1000 and that the resolution of the experiment was limited by Boxcar drift, even when the electron gun was in operation.
7.5 Attempts to observe Reflectance Modulation

After the problems of electrical pickup had been resolved further attempts were made to observe induced reflectance modulation. A total of 12 runs were completed using different samples. These included:

(a) Four antimony films deposited on Corning 7059 glass substrates and annealed at 250°C. Thickness range 0.08-2.0 μm.
(b) Four antimony films deposited on single crystal slices and annealed at 250°C. Thickness range 0.12-0.8 μm.
(c) One single crystal of Germanium.
(d) One single crystal of Lead-Tin-Telluride.
(e) Two single crystal slices of silicon.

Induced reflectance changes were not observed in any of these samples. A typical Boxcar output showed that the output was essentially unchanged whether or not there was a modulation signal into the detector. This implies that in all cases the induced change in reflectance of the sample was less than the limit of resolution of the experiment, i.e. $\frac{AR}{R} > 10^{-3}$. The relevant operating conditions of the electron gun during these attempts were as follows:

- Acceleration Voltage: 3 kV
- Pulse Current: 100 mA
- Pulse Duration: 4 μsec
- Area of Bombardment: 0.3 cm²

In some of the early runs, it was discovered that the films had been completely destroyed in the target area; this was found to be due to a d.c. component in the electron beam current, which was corrected. All subsequent samples showed no apparent damage when examined under a microscope.
7.6 Photoconduction Measurements

Photoconduction measurements have been made in order to estimate minority carrier lifetimes in the samples used. This was done using the circuit shown in fig. (7/2), together with a stroboscope which was capable of producing light pulses of variable length $3 \mu\text{sec} - 10 \text{ m.sec}$, at variable frequency $10 - 10 \text{ k Hz}$. The circuit load resistor $R$ was generally made equal to the overall unilluminated resistance of the sample, which was approximately 200 ohms for a silicon sample of dimension $2 \times 1 \times 0.05 \text{ cm}$, and about 5 ohms for a thin film of antimony. The circuit voltage was adjusted to give a current of $50 \text{ mA}$. A fast reverse biased silicon photo-diode was used to monitor the light pulse and the output from this together with the volt drop across the load resistor $R$ were displayed on an oscilloscope. Typical results are presented in fig. (7/3).

The photographs show the result of a 3 microsecond long light pulse on samples of silicon and antimony. It is seen that carriers with a lifetime of approximately $5 \mu\text{sec}$ were produced in the silicon sample in sufficient numbers to change the sample's conductivity appreciably.

No photoconduction effect was observed in any sample of antimony.

7.7 Discussion of Results

Reflection changes induced by electron beam bombardment in samples of silicon and antimony have been found to be below the experimental limit of detection, although calculations made in chapter 5 indicate that easily observable changes should occur, provided that sufficient free carriers are generated by each electron beam burst.
Photoconductance in samples of (a) silicon, (b) antimony film 0.5 μm thick. The top trace in each photograph is the light pulse output from the stroboscope monitored with a fast photodiode. Scales are 2 μsec and 0.005 volts per division.
Reference to figures (4.3) and (5.10) indicates that less than \(\sim 10^{24} \text{m}^{-3}\) excess free carriers were induced in the samples of silicon and antimony.

A simple estimate may be made of the excess carrier density generated in the silicon sample (bulk lifetime 5 \(\mu\)sec) using the relation \(n = \frac{qE}{\tau}\). For a 100 mA 4 KV beam on an area of 10 mm\(^2\) this gives \(n = 1.5 \times 10^{27} \text{m}^{-3}\).

This calculation cannot be done for antimony since data is not available for carrier lifetime in bulk antimony, but a similar figure is found if the lifetime is greater than 5 nanoseconds.

These estimates are based on the implicit assumption that excess carrier concentration is dependent on carrier generation rate and lifetime alone. However carriers are generated by the electron beam in close proximity to the samples' surfaces, and it will now be shown that the effects of the surfaces are important and may be used to explain the results.

When the carrier concentration distribution is non-homogeneous (caused for instance by surface recombination) computation of the reflectance according to eq. (3.99) becomes complicated since the value of \(N\) which should be used is uncertain. One approach which may allow the magnitude of \(\Delta R/R\) to be estimated is to assume the correct value of \(N\) to be equal to the average free carrier concentration over the depth of penetration of the incident probe radiation. For the samples of antimony and silicon used the penetration depth is greater than the sample thickness and the carrier concentration required in the computation will be assumed to be the average concentration taken throughout the sample thickness.

The photoconduction effect is also proportional to the average excess carrier concentration and the results of section (7.6) may therefore be used to aid the interpretation of reflectance measurements.

It is most convenient to discuss the results for silicon first and those for antimony later.
The relative change of the electrical conductance of a photoconductor upon illumination has been shown by Schockley \[80\] to be proportional to the relative change of carrier concentration for low injection levels. For constant current conditions then

\[
\frac{\Delta V}{V} = - \frac{\Delta n}{n}
\]

where \( r \) is the standing voltage across the sample and \( n \) is the equilibrium majority carrier concentration. The samples used had a typical conductivity of 20 ohm\(^{-1}\)m\(^{-1}\) corresponding to an impurity concentration of \( \sim 10^{21}\) m\(^{-3}\). The measured photoconductance signal was \( \frac{\Delta V}{V} = 2 \times 10^{-3} \). Therefore it may be assumed that the number of carriers injected by each pulse of light is \( 2 \times 10^{18}\) m\(^{-3}\).

A comparison of the intensity of light from the stroboscope and the intensity of the blue spectral line of a small 80 watt mercury lamp, allowed an estimate to be made of the number of photons emitted per pulse. By making allowance for the area and reflectance of the sample it is estimated that greater than \( 7 \times 10^{12} \) photons were absorbed by the sample during every light pulse.

The total volume of the sample was 0.1 cc. If it is assumed each photon ionises one carrier pair, then the number of carriers injected per pulse is \( 7 \times 10^{18} \) m\(^{-3}\), i.e. it would appear that 500x more carriers are injected into the sample than are observed by photoconductance.

Although this calculation is necessarily approximate, the photon density quoted is a conservative estimate, and is probably accurate within an order of magnitude. After allowance is made for error, the number of carriers which were observed by photoconductance is still significantly below the number expected.
The difference may be accounted for by a careful examination of the behaviour of carriers subsequent to their generation, using the conclusions of section 6.3.

The first observation to be made is that the length of the generation pulse is approximately equal to the bulk free carrier lifetime in silicon of 5 microseconds. According to section 6.3.1 the carrier density cannot rise above $\sim \frac{1}{3} g \varepsilon \tau$.

Secondly the effects of surface recombination must be allowed for. The silicon sample used had a thickness of 500 microns, a diffusion depth of $\sim 150$ microns, and the carriers are generated in a region within 1-2 microns of the surface. Clearly surface recombination effects will be important. An estimate of the final free carrier density which may be attained may be made using equation 6.24 given by de Vore \[ \text{(67)} \] for generation which falls exponentially with depth by assuming the value of the absorption coefficient ($\alpha$) of equation 6.24 to be equal to the reciprocal of the depth of generation by the electron beam, i.e. $\alpha^{-1} = 1$ micron. Then the free carrier density is

$$N = g \varepsilon \tau \left( \frac{1 - e^{-\Sigma}}{1 + \Sigma \coth(\frac{1}{2} \lambda)} \right) \left( 1 + \Sigma \frac{\lambda \coth(\frac{1}{2} \lambda) - z \coth(\frac{1}{2} z)}{z^2} \right)$$

(7.10)

where $z$, $\lambda$ and $\Sigma$ have the same values as before.

For the silicon sample the sample width ($L$) is much greater than the diffusion length $L$, i.e. $\lambda$ is very large, and 7.10 reduces to

$$n = g \varepsilon \tau \cdot \frac{V}{s + v} \cdot (1 - e^{-\alpha L}) \left( 1 + \frac{s}{V} \cdot \frac{L}{L + \alpha L} \right)$$

(7.11)

For the idealised case of zero surface recombination, having uniform excitation throughout its volume $s + 0$, $\alpha + \infty$ and 7.11 reduces to

$$n = g \varepsilon \tau$$

which is expected when surface recombination can be neglected.
For a sample with a finite surface recombination velocity, where carriers are generated near the surface, then

\[ n = \frac{g e T}{S+S} \cdot (1 - e^{-aT}) \]

For a moderate value of \( s \), the exponential term is very small and can be neglected.

The reduced value for \( n \) due to the effects of both surface recombination and generation pulse length is therefore

\[ \frac{n}{gE} = \frac{1}{3} \frac{S}{(v+s)} \]

The value of \( \frac{S}{V} \) has been found to vary up to \( 10^3 [\text{cm}] \) according to the nature and purity of the sample, the condition of the surface and the atmosphere. A value of \( \frac{S}{V} \) of only 10 is sufficient to account for the discrepancy between the expected free carrier density \( (gE) \) generated by stroboscope pulses and the value determined from the photoconduction response.

The situation with electron beam generated carriers is very similar to those generated by visible light pulses, since 4 kV electrons have a range of \( \sim 0.5 \) microns in silicon. Therefore carriers are produced in a similar region to those produced by visible light, and it is reasonable to assume that the effects of surface recombination will also be similar, i.e. values of \( \frac{S}{V} > 10 \) and \( N = 0.02 x \frac{gE}{m} \) may be assumed. The carrier concentration which is generated by electron beam may then be calculated as

\[ N = 2 \times 10^{-2} \times \tau \times \frac{1}{e} \times \frac{V}{V_o} \times \frac{1}{L \times A} \]  \hspace{1cm} (7.14)

For a 100 mA 4 kV beam \( N \) becomes \( 6 \times 10^{22} \text{m}^{-3} \). Reference to figure (4.3) shows that such an increase in carrier concentration should produce a reflectance change \( \frac{\Delta R}{R} = 5 \times 10^{-5} \) which is below the experimental limit of detection, i.e. the assumption of a modest surface recombination velocity may explain why no reflection changes were observed.
7.7.2 Antimony

Interpretation of antimony data is complicated by the fact that neither photoconduction nor electro-reflection effects were observed.

However an estimate may be made of the maximum number of free carriers which are induced in each case such that these effects cannot be observed.

Again use will be made of the results of section (6.3).

For a very thin sample \( l \ll L_p \), equation (6.24) reduces to

\[
N = g \tau \cdot \frac{\frac{L}{L_p}}{2s} \cdot \frac{v}{2s} \left\{ 1 - e^{-\alpha l} \right\}
\]  

(7.15)

For antimony samples

\[ l = 0.1 \, \mu m, \quad \alpha = (1.5 \times 10^{-2}) \, \mu m^{-1} \]

\[ \therefore \alpha l = 0.1/0.015 = 6. \]

\[ e^{-\alpha l} = 0.002 \]

\[ \therefore (1 - e^{-\alpha l}) \to 1 \]

(7.16)

\[
N = g \tau \cdot \frac{\frac{L}{L_p}}{2s} \cdot \frac{v}{2s} \left\{ 1 - e^{-\alpha l} \right\}
\]

(7.17)

for light of wavelength 0.5 \( \mu m \) \( \alpha = 0.015 \, \mu m^{-1} \) and \( (1 - e^{-\alpha l}) \to 1 \).

For electron beam excitation the electron beam energy was adjusted so that the sample was uniformly excited and the term \( (1 - e^{-\alpha l}) = 1 \).

i.e. in both cases

\[
N = g \cdot \frac{\frac{L}{2s}}{2s}
\]

(7.18)

This is a remarkable result. For very thin films the final free carrier concentration is determined solely by surface recombination effects, and the bulk lifetime of the material is of no consequence.
This is true for antimony if \( \xi << L_p = (Dr)^{1/2} \)

or \( \tau >> \frac{\xi^2}{D} \) \hspace{1cm} (7.19)

For antimony \( D = 1.5 \times 10^{-3} \text{m}^2 \text{.sec}^{-1} \)

\( \therefore \tau >> \frac{10^{-14}}{1.5 \times 10^{-3}} = 6 \times 10^{-12} \)

i.e. provided the bulk lifetime \( \tau >> 6 \text{ p.sec} \), then the assumption of \( \xi << L_p \) is correct, and equation (A) may be used to estimate carrier lifetimes.

No measurement of surface recombination velocity in antimony films appears to have been reported, but values of up to \( 10^5 \text{ m.sec}^{-1} \) have been observed.

Let a value of \( s = 10^3 \text{ m.sec}^{-1} \) be assumed in order to get an order of magnitude calculation of the induced free carrier concentrations.

For photoconductance assume a quantum efficiency of unity but a reflectance of 90%.

i.e. \( g = 10^{18} \text{ sec}^{-1} \) in volume \( 2 \times 10^{-11} \text{ m}^3 \)

\( \xi = 10^{-7} \text{ m} \)

\( s = 10^3 \text{ m.sec}^{-1} \)

\( \Delta N = \frac{2 \times 10^{12}}{2 \times 10^{-11}} \times \frac{10^{-7}}{2 \times 10^{-3}} = 5 \times 10^{12} \text{m}^{-3} \)

Again \( \frac{\Delta r}{r} = \frac{\Delta n}{n} \)

Therefore \( \Delta r = \frac{10^{18} \times 0.25}{3 \times 10^{25}} = 10^{-9} \text{ volts} \)

i.e. for very thin films such as those of antimony, the photoconductive signal is estimated at 1 n.volt.

The experimental limit of detection was only 1 millivolt and therefore no signal should be observed.
For electron beam injection

\[ g = 6 \times 10^{29} \text{m}^{-3} \text{sec}^{-1} \]

\[ = 10^{-7} \text{m} \]

\[ s = 10^{3} \text{m} \text{sec}^{-1} \]

Then

\[ \Delta N = 3 \times 10^{19} \text{n}^{-3} \]

By reference to fig. (5.18), a change of free carrier concentration of this magnitude corresponds to a reflectance change of only \( \frac{\Delta R}{R} = 6 \times 10^{-8} \)

which again is far below the limit of detection with the equipment available.

7.8 Discussion

Free carrier reflectance or absorption modulation has been observed previously in silicon and germanium for different excitation conditions than those reported here.

McCoy and Wittry [50] observed modulated absorption (\( \frac{\Delta I}{I} \approx 10^{-3} \)) in 0.5 mm thick samples of germanium using electron beam excitation. The beam was operated with an accelerating potential of 50 kV and a current density of 120 mA onto the sample. The estimated beam penetration was 15-20 microns. If the carriers so produced are assumed to be spread over the diffusion depth (\( \approx 100 \) microns) then their conditions correspond to a generation rate of about 10 times that in the present investigation for silicon. Since the carriers were also generated a little further from the surface (but still well within a diffusion length of it) it is to be expected that the observed effect should be about 10 times the value found in the present arrangement.
Pefley [52] observed reflection modulation also \((\frac{\Delta R}{R} > 10^{-3})\) using 5 MeV electrons fired into a 10 mm cube of silicon, and estimated the excess carrier concentration to be \(7 \times 10^{23} \text{m}^{-3}\) from the radiation dosage alone. In this case the carriers were generated more or less evenly throughout a large sample and surface effects may be safely ignored.

Bobrova et al [25] used a ruby laser to generate free carriers in silicon. Although the penetration depth was estimated at only 15 microns, the incident power was so great (> 1 MW) that free carrier concentrations of up to \(10^{26} \text{m}^{-3}\) were achieved.

The observed reflectance modulation was correspondingly large \(\frac{\Delta R}{R} \approx 0.3\).

This work also investigated the effect of surface preparation, and it was shown that the free carrier concentration achieved could be reduced by a factor of 5 by merely polishing the surface, which had the effect of producing surface strain, or discontinuities and increasing 2.

These reports do not disagree with the present results but rather they indicate the need to use higher power ionisation sources to raise the free carrier generation rate, and the advantage to be gained if the effects of surface recombination can be minimised.

7.9 Conclusions

An interpretation of the optical properties of silicon and antimony has indicated that reflection changes in the far infra-red at 10.6 microns may be induced in these materials by adjusting the free carrier concentration. It was calculated that the use of antimony in thin film form would enhance this effect because of optical interference. Initial calculations showed that sufficient free carriers may be generated within these materials by direct ionisation using a 4 kV, 100 mA electron gun.
Using a specially designed electron gun together with a small CO$_2$ laser and other equipment built in the laboratory, an attempt has been made to measure this effect.

Reflection changes were not observed. From a knowledge of the detection equipment it is concluded that $\frac{\Delta R}{R} < 6 \times 10^{-8}$ for antimony films and $< 5 \times 10^{-5}$ for silicon samples. These values are several orders of magnitude below the values which had been estimated when the effects of surface recombination were neglected.

The discrepancy between the expected and experimental figures may be explained by noting that the carriers are generated near to material surfaces and allowing for the effects of surface recombination. In silicon a modest value for the surface recombination velocity has been shown to be sufficient to account for the difference. In antimony the behaviour of excess carriers is even more dominated by surface effects because of the close proximity of two surfaces. In thin films such as those of antimony where the film thickness is much less than the diffusion length, carriers may collide with the surfaces very many times within the time which they would take to recombine in bulk material. In this situation the final excess carrier concentration is independent of the bulk lifetime, being determined only by the diffusion length and recombination velocity, and is very much smaller than would be expected from the bulk properties.

Three conclusions arise from this work:

(a) The use of thin film material does not increase the reflectance changes as envisaged since the advantage of optical interference is far outweighed by the much reduced excess carrier concentration which may be generated.
(b) In order to minimise the effects of surface recombination, bulk samples should be used which are excited throughout their volume. If an electron beam is to be used this requires that very high > 100 keV accelerating voltages must be used, such as was successfully employed by Pefley [52].

(c) Due to these difficulties, it is not envisaged that a practical infra red modulation system may be built using electron beams to inject minority carriers into a thin film.
8. ELECTRIC FIELD MODULATION

8.1 Introduction

Chapter (7) has described the effort to modulate the reflectivity of antimony films and silicon slabs by the injection of minority carriers using an electron gun. This was not successful due to the short lifetimes and finite surface recombination effects exhibited by these samples. However the calculations given in Chapter (5) to predict the reflectance changes which might be expected due to a small adjustment of free carrier concentration are encouraging. It was therefore decided to attempt to adjust the concentration of majority carriers which are not subjected to the restrictions of carrier lifetime.

One method of achieving this is to make the sample one plate of a parallel plate dielectric capacitor. A typical configuration could be envisaged as fig. (8.1).

The sample, which might be an antimony film, would be separated from another conducting electrode by a dielectric medium of thickness $d$. The dielectric should be transparent to the radiation which is to be modulated. A voltage $V$ applied to the plates of such a capacitor should induce a charge $(C \cdot V)$ to move from one plate to another where $C$ is given by

$$ C = \frac{E \cdot \varepsilon_0}{d} \quad (8.1) $$

For example the capacitance of an air gap 1 mm wide having an area of cross section 1 cm² is $36 \times 10^{-14}$ Farad. A potential of 1 kV applied to the plates of such a capacitor would transfer a charge of $36 \times 10^{-11}$ Coulombs or $24 \times 10^8$ electrons from one electrode to the other. Unfortunately such a charge is insufficient to induce an observable reflectance change in the spectral region of interest.
Figure 8.1
An arrangement to use a parallel plate capacitor configuration to alter the majority carrier distribution.

Figure 8.2
(a) Helmholtz (b) Gouy-Chapman and (c) Stern models for the double layer
A much larger effect may be obtained by making use of the electrical
dipole layer between an electrolyte and the surface of an electrode
which is immersed in it. This layer has the properties of a large
capacitance $q_2$, and a simple model of it is given in fig. (8.2a).

The first quantitative discussion of this double layer was given in 1819
by Helmholtz, who suggested the picture shown in fig. (8.2a), a layer of
ions at the solid surface and a rigidly held layer of oppositely charged
ions in solution. The electrical potential corresponding to such a charge
distribution is shown. Such double layers are supposed to exist not only
at plane surfaces in a liquid but also at the junction of a metal and
semiconductor providing no diffusion of the phases has taken place
(Schottky diode).

This structure for the charge distribution is clearly analogous to a
parallel plate condenser with the distance between the plates replaced
by the thickness of the double layer.

In order to estimate the capacitance of the Helmholtz double layer at
a metal/electrolyte interface, it is assumed that the structure consists
of a layer of positive ions immediately adjacent to a negatively charged
surface. Many common ions have an effective radius of $2 \times 10^{-10}$ m and
accordingly this figure may be taken as the minimum thickness of the
double layer. The value of the dielectric constant of the layer presumably
lies between unity (the value for vacuum) and the bulk dielectric constant
of the electrolyte (about 80 for water). If for simplicity the value of
$\varepsilon$ in equation (8.1) was taken as 8 then

$$C = 36 \ \mu\text{F. cm}^{-2}$$

Measurements of double layer capacities do indeed give values of this
order of magnitude.
The application of a potential difference of only one volt across such an interface may transfer a charge of \( 36 \, \mu\text{C} \), which is equivalent to \( 2 \times 10^{14} \) electrons \( \text{cm}^{-2} \) from one medium to the other.

It will be shown later that this charge is confined to a region near the interface, the width of which depends on free carrier concentration and the applied potential. If the electrons were confined to a region 0.1 \( \mu\text{m} \) wide, then an excess charge density of \( 2 \times 10^{25} \, \text{m}^{-3} \) may be attained. Further since it is majority carriers which are involved, this charge distribution will be maintained for so long as the potential difference across the interface is maintained. A change of free electron (or carrier) concentration of this magnitude is sufficient to produce marked changes in the optical properties of most materials of interest, particularly semiconductors in the infra red, but also metals near their plasma frequencies.

So far only the effects of free electrons or carriers on the optical properties of the media have been considered. However, because the width of the double layer is so small, a potential difference of only a few volts is sufficient to create electric fields so great that the bound electrons and the atomic structure of the material are affected. It is apparently possible to modulate the band structure particularly near critical points in the lattice, which may result in the modulation of certain frequencies of incident light corresponding to the energy levels associated with the critical points. This is known as the Franz-Keldish effect.
8.2 The nature of the double layer

The double layer may be conveniently treated in two parts relating to the electrolyte and electrode side of the interface.

8.2.1 The electrolyte side of the double layer

Metal-solution interfaces lend themselves particularly to the study of the double layer and of the metals mercury is pre-eminent. Being a liquid mercury is readily cleaned and its surface is free from mechanical strains.

After the early work of Helmholtz more accurate measurements showed that the capacity of the double layer was a slowly varying function of the nature of the electrolyte, and the potential difference applied across the interface. It was found necessary to modify the Helmholtz model to account for these phenomena.

Govy and Chapman saw that the changes in solution at the Helmholtz layer would attract unlike changes causing a more extensive disturbance of the bulk change distribution near the phase boundary than Helmholtz had predicted. Both Govy and Chapman independently proposed a diffuse layer on the solution side in which a majority of ions, of opposite charge to the electrode, extended into solution. The Govy-Chapman model is shown in Fig (8.2b).
However the calculated capacitance of this structure was much greater than observed. This shortcoming of the wholly diffuse double layer is not inherent in the model proposed by Stern (1924) who recognised that ionic absorption at the surface could play an important role. Briefly in the Stern model, the electrical double layer may consist of a layer of electrons within the electrode, a layer of specifically absorbed ions at the surface, and a diffuse layer consisting of an ionic atmosphere in which ions of opposite charge to those on the electrode are in excess of their normal concentration, whereas those of the other charge are in defect (see fig. (6.2c)).

The total charge density of the Stern layer is equal to the sum of the charge densities of the Helmholtz and Gavy-Chapman layers and the capacity of the Stern layer is derived by treating it as a condenser in series using the expression

\[
\frac{1}{C_S} = \frac{1}{C_H} + \frac{1}{C_D}
\]  

(8.2)

where the subscripts refer to S - Stern layer, H - Helmholtz layer, D - diffuse layer.

Graham [92] who has more recently reviewed the theory of the double layer, showed that in spite of the relatively large variation of \(C_D\) with the concentration of solution, the double layer capacity is dominated by the contribution from the Helmholtz layer.

For example if the observed double layer capacity is 25 μF/cm², the calculated capacity of the diffuse layer was shown to be 250 μF/cm², which is not very different from the total value. Further, if due to concentration changes the value of \(C_D\) has fallen to 125 μF/cm², and the total capacitance of the double layer remains constant, the capacitance of the Helmholtz layer rises to a new value of 31 μF/cm². Therefore a wide variation in the capacity of the diffuse layer is compatible with relatively small variations of the observed capacity of a double layer with a Stern structure.
The Stern structure has been further modified to account for solvated and non-solvated ions in solution, but with this modification it is possible to account for the observed shape of the capacity-applied potential curves for mercury-electrolyte interfaces at various ionic concentrations.

8.3.2 The electrode side of the double layer

The dependence of the induced potential on depth in the electrode is dependent on the nature and conductivity of that electrode. In high conductivity metals - gold, silver, copper, etc. the potential field due to the interface may extend into the bulk by only a fraction of one Angström. However the field may extend to a depth of several thousand Angströms in low impurity semiconductors.

The importance of this in electroreflectance has been emphasised by Seraphin [109]. In a semiconductor the space charge may extend into the bulk by the same order of magnitude as the incident radiation field extends. The light therefore experiences a region in which the dielectric response differs significantly from that of the bulk, and reflectance modulation may result from the field induced variation of this "anti reflection coating" which this region represents.

Axe and Hammer [97] have proposed such a mechanism to account for reflectance peaks of 1-2% in the regions near the plasma frequencies of Germanium and Gallium Arsenide.
8.3 Electrolytic Electroreflectance

The strong electric field in the dipole layer adjacent to a semiconductor electrolyte interface was first used in the electro-optical work by Williams [93] in 1960. Shaklee [94] later modified Williams' work and developed a reflectance modulation technique whereby the optical properties of solids were periodically perturbed by the application of a strong electric field. The resulting change in reflectance of the solid was observed using phase sensitive detection techniques.

Electro effects have since been observed in many semiconductors [95] and have provided useful information concerning band structures. Although there is difficulty in the interpretation of the data obtained [96] it is hoped that the technique may become a powerful diagnostic tool.

Most of the work has centred on the use of the Franz-Keldisch effect to observe critical points in the band structure of solids.

The usual experimental set up is shown in fig. (8.3) and a typical electroreflectance curve is presented in fig. (8.4) which illustrates the line structure obtained. For most of the spectral range the reflectance is quite insensitive to the presence of an applied field. These wide regions of passivity are separated by narrow regions of photon energies where the reflectance change is almost resonant in nature.

A response so localised deserves an explanation in terms of the electronic structure of the material. However, experiment and theory are only beginning to exploit it.

It became clear from early work that reflectance modulation was to be expected at wavelengths where the slope of the reflectance-wavelength curve showed sharp discontinuities. In this context Axe Hammer [97]
Figure 8.3
A typical arrangement for electroreflectance measurements.

Figure 8.4
An electroreflectance spectrum showing the discreet nature of electroreflectance.
predicted "resonances" in the modulation spectrum near lattice restrahlen and free carrier plasma frequencies in semiconductors, which they observed in Germanium and Gallium Arsenide. They did this by extending electroreflectance studies deep into the infra-red by the use of extremely thin layers of electrolyte in order to reduce optical absorption.

The modulation spectrum Br Sb doped Germanium ($n = 7 \times 10^{24}\text{m}^{-3}$) is presented in fig. (6.5), and shows the general observation that the greatest modulation depth $\Delta R/R$ occurs at the wavelength where the slope of the $R(\lambda)$ curve is the greatest, and falls to zero in regions where the reflectance is independent of wavelength. Typically $\Delta R/R = 1-2\%$ at maximum.

A development which allows modulation in the infra-red but does not require very thin layers of electrolyte was described by Hansen et al. [98] who have devised a method of attenuated total reflection. In this technique, which is shown diagrammatically in fig. (6.6), the electrode takes the form of semi absorbing or transparent thin film on a transparent substrate, and the light beam approaches the interface from the more dense medium, at angles near critical.

The electrical situation at the surface of a semi-conductor is particularly favourable for the performance of electroreflectance measurements. A space charge is normally induced in the surface region which extends, with respect to the order of magnitude, as far as the light penetrates into the reflecting surface. The reflected therefore sees a material under the strong electric field of a potential barrier.

In 1966 Feinleib [99] reported the observation of electroreflection phenomena in metals - gold and silver, which came as a surprise because calculations showed that the modulation field was expected to penetrate less than one Angstrom into the metal. Nevertheless electric field modulation of the
Figure (8.5)
Electroreflectance spectrum of doped Germanium
(after Axe and Hammer [97])
(R and ΔR have arbitrary units)

Figure (8.6)
Diagramatic representation of the Hansen internal reflection technique.
The origin of electroreflectance in metals is in dispute. One suggested explanation [99, 101] proposes that it is caused by modulation of the refractive index of the solution which is in contact with the gold, but it has been shown that this cannot be the case because this effect would not produce the observed electroreflectance spectrum [102]. Another theory assumes modulation of the optical properties of a thin surface layer of gold. However it has been shown that the electric field penetrates less than 1 Å into the gold and should not greatly affect the properties to a depth of 100 Å which is the typical depth of penetration of the probe radiation.

In chapter 5 an analysis was made of the optical properties of antimony in order to predict the modulation performance which can be expected from free carrier effects, and the modulation spectrum \( \frac{\Delta R}{R}(\lambda) \) was predicted. The use of this approach to calculate \( \frac{\Delta R}{R}(\lambda) \) for gold from its optical constants alone may both help to resolve this argument and also verify the general approach and conclusions of chapter 5 for antimony.

Although the electric field may penetrate only about one atomic layer, since the mean free path of electrons in gold at room temperature is much longer (400 Å [103]) than the field penetration depth, electrons from the bulk material may be reflected from the surface and have their own properties perturbed when the electron concentration changes. In this case an order of magnitude expression for the electroreflectance spectrum can be obtained by assuming that carriers are evenly distributed to a depth equal to the field penetration depth, and further that this is also equal to the radiation penetration depth. (For gold at 0.5 microns this is approximately true since \( \kappa = 1.84 \)).
The analysis of the optical constants of gold is relatively straightforward since it has been shown [104] that intra-band and interband effects can be quantitatively separated without the use of a specific theoretical model. In this connection it is possible to write $\Sigma(w)$ in the form

$$\Sigma(w) = \Sigma_{\text{free}}(w) + \Sigma_{\text{bound}}(w)$$

which separates the intraband contribution, characteristic of free electrons from the interband contribution.

In the infra-red, the latter is effectively zero and the optical constants of gold in this wavelength range have been shown to be in excellent agreement with the predictions of the Drude theory [103], when the parameters $\tau = 2.46 \times 10^{-14}\text{sec}$, $N = 5.9 \times 10^{28}\text{m}^{-3}$ and $F_L = 11$ are used.

In general the optical constants of gold may be computed as a function of excess free electron concentration, using the known data for gold together with these Drude parameters. Figure (8.7) shows the variation of $n$ and $k$ with free electron concentration at a wavelength of 0.55 microns. Each pair of constants $n$ and $k$ corresponds to a reflectance $R$.

Using this data, the electroreflectance modulation spectrum $\frac{\Delta R}{R}(\lambda)$ has been computed for a series of excess free electron concentrations in gold. The results are shown in figure (8.8).

For electroreflectance measurements described by Hansen [98], the capacitance of the interface was $40 \ \mu\text{F.cm}^{-2}$ and a modulation signal of 0.7 volts peak-peak was applied. Therefore in every cycle $33 \ \mu\text{C.cm}^{-2}$ electrons were injected or extracted from the film. It is assumed for the purposes of this calculation that these excess carriers are evenly distributed over the penetration depth of light of $400 \ \AA$ (which is almost equal to the diffusion length of electrons in gold). Therefore the net excess electron concentration produced by the modulation signal is $\sim 10^{25}\text{m}^{-3}$. 
free electron concentration (m$^3$)

Figure (8.7)
n and $k$ for gold computed as a function of free electron concentration

Figure (8.8)
computed electroreflectance spectrum of gold showing the results of Feinleib and the reflectance $R$. 
The experimental curve determined by Feinleib [ ] is included in figure (8.8). It will be observed that the shapes of all the curves are similar and all peak at 5000 Å. The experimental curve is most closely fitted by the computed curve for \( N = 6 \times 10^{25} \text{m}^{-3} \). This can be explained by making allowance for the non-uniform distribution of electrons near the surface or by assuming that the excess electrons are distributed over a depth smaller than 400 Å.

It has been shown that the optical properties of gold do indeed change with applied field, and the main features of electroreflectance observed by Hansen may be explained by a shift of the plasma edge in gold due to a change of electron concentration. This calculation was based on the assumption that the excess free electrons were evenly distributed over a depth equal to the diffusion length of electrons in gold. Such an assumption is justified since although the modulation field may penetrate only one atomic layer, electrons within a diffusion length or so of the surface will be continually reflected from the surface, and their properties will be perturbed by the field.

By using only the published optical constants for gold, a modulation spectrum \( \frac{\Delta R}{R} (\lambda) \) was calculated, which was remarkably consistent in its main features with that observed previously.

While a concise proof of the assumption of free electron distribution cannot be given, the results of this calculation do show that modulation of the optical properties of gold may account for the experimental observations. Further, the analysis indicates that the general approach given in chapter 5 to compute reflectance modulation due to free carriers using the optical constants of the material alone is consistent with known and observed modulation phenomena.
Using the results of chapter 5, figure (8.11) shows the modulation spectrum $\frac{\Delta R}{R}(\lambda)$ which is expected for pure antimony, when the equilibrium carrier density is increased by the amounts $\Delta n = 1 - 5 \times 10^{24} \text{m}^{-3}$. These curves demonstrate the previously discussed fact that when the modulation effect due to free carriers is small, then the modulation spectrum is centred near the wavelength of steepest reflectance rise in the plasma edge. It is also noticed that the quantity $\frac{\Delta R}{R}$ is larger for a given $\Delta n$ than was predicted for gold (fig. (8.8)). This is because gold contains many more carriers than antimony and for a given $\Delta n$ the relative change of carrier concentration is correspondingly smaller.

Typically the Helmholtz capacitance in the electrolytic cell is $10 \, \mu\text{F} \cdot \text{cm}^{-2}$ and the modulating voltage is $\sim 3$ volts. If the excess charge is assumed to be distributed evenly throughout a film of thickness 0.5 microns, then at every cycle about $2 \times 10^{24} \text{m}^{-3}$ carriers are injected or extracted from the film.

It is apparent that if the modulation in pure antimony is observed at 10.6 microns, then a modulation $\frac{\Delta R}{R}$ of the order of $10^{-3}$ should be expected. Conversely if the modulation is observed at 13 microns then a $\frac{\Delta R}{R}$ of $\sim 10^{-2}$ is expected. It is clearly desirable to observe the modulation at 15 microns, but this could not be done with the apparatus available.

Another way in which the modulation effect at 10.6 microns might be increased is to use a material having a plasma edge in which the steepest reflectance rise occurs at 10.6 microns. The optical properties of antimony-tin alloys have been described in chapter 4. The addition of 2-3% of tin into the antimony lattice does not affect the band structure greatly, but has been shown to shift the plasma edge to near the desired wavelength. Using the optical data of antimony - 2.83% tin
given by Howson [61], the expected modulation spectrum \( \frac{\Delta R}{R} (\lambda) \) has been computed for injected carrier concentrations of \( 1 - 5 \times 10^{24} \text{ m}^{-3} \).

The result figure (8.9b) shows that for \( \Delta n = 10^{24} \text{ m}^{-3} \), \( \frac{\Delta R}{R} \) is almost an order of magnitude greater than would be obtained for pure antimony at 10.6 microns, and approximately the same as would be observed at 13 microns. Figure (8.10) shows the variation \( \frac{\Delta R}{R} \) as a function of \( \Delta n \) for the three cases.

It is therefore proposed to use the electrolytic cell with both pure antimony and antimony-tin alloy films in order to see if an increased modulation effect can be observed.
Figure (8.9)

The computed modulation spectrum $\frac{\Delta R}{R}$ ($\lambda$) for different injected carrier densities

(a) pure antimony  (b) antimony - 2.83% tin
Figure 8.10
The computed modulation $\frac{\Delta R}{R}$ as a function of injected carrier density

- curve 1  pure antimony at 10.6 microns
- curve 2  pure antimony at 13 microns
- curve 3  antimony - 2.83% tin at 10.6 microns
8.5 The electroreflectance of gold

It was decided to build an electrolytic cell and attempt to reproduce the previously observed reflectance modulation of gold in the visible part of the spectrum near the plasma frequency in order to gain experience of the construction and use of a suitable cell, and the phase sensitive detection system prior to an attempt to use the same equipment to modulate the radiation from a CO$_2$ laser at 10.6 microns.

8.5.1 The electrolytic cell

A diagram and photograph of the cell are presented in figures (8.11) and (8.12). The cell is made of perspex and all electrodes are held in position by neoprene 0-ring seals. The electrolyte was a 0.1 molar solution of sodium sulphate in triple distilled deionised water. The modulating electrode was a thin gold film of approximately 500 mm$^2$ area, which had been evaporated onto glass at a substrate temperature of 200°C.

Electrical contact was made to the gold film by an indium soldered joint, which was not in contact with the electrolyte.

The second electrode was formed from a piece of gold-platinum gauze of very high specific surface (with a total area of probably more than 100 cm$^2$). Gold-platinum electrodes are generally used in electrochemical work of this kind. The high surface area is required because a double layer structure also exists at the surface of this electrode, and the capacitance of this layer should be made large in comparison to that of the electrode to be studied.

A third electrode has also been included in the cell. This is a calomel reference electrode, and is included because there is no practical means of measuring a single electrode potential without reference to some other
Figure 8.11

The electrolytic cell

Figure 8.12

Photograph of the cell
electrode potential. This circumstance arises from the fact that an electrolytic cell must contain two electrodes, at least, before an external circuit can be completed. It is possible to measure changes in single electrode potentials if it is ensured that the other electrode which completes the circuit containing the measuring instrument maintains a constant potential during observation. The calomel reference electrode does this and in addition, potentials measured by using a calomel electrode may be related to potentials on the "fundamental" hydrogen potential scale of electrochemistry.

The calomel electrode may be used only in conjunction with a high impedance electrometer to measure potentials, and must not be allowed to take a current of more than $10^{-9}$ amps.

The total capacitance $C_T$ of the cell may be written

$$\frac{1}{C_T} = \frac{1}{C_S} + \frac{1}{C_G}$$

where $C_S$ and $C_G$ are the capacitances due to double layers at the thin film and gauze electrodes. $C_G$ is much greater than $C_S$ because of the large specific area of the gauze and its effect on the total capacitance may therefore be neglected.

The differential capacity of the cell $C_T$ was measured using a Marconi Bridge. This unit has facilities which enable the oscillator frequency to be externally controlled, and a bias control to allow a standing voltage to be applied across the electrodes while measuring the capacitance. Fig. (8.13a) shows that the measured capacitance is almost independent of frequency up to 50 k Hz.
Cell capacitance as a function of (a) frequency and (b) bias potential for gold and antimony films.
Unlike normal capacitors the capacitance of the double layer varies with the d.c. potential, and the dependence is shown in fig. (8.13b) together with the variation of current with applied potential. Fig. (8.14) illustrates the circuit which was used to make the current-voltage measurements. The rapid rise of current at high voltages (positive or negative) corresponds to the onset of irreversible Faraday effects such as the liberation of gas at an electrode.

8.5.2 Experimental Arrangements

It has been shown that the modulation of light by a gold interface is a function of wavelength and peaks strongly at 5000 Å. Since no monochromator was immediately available, it was decided to attempt to observe reflectance modulation at just one wavelength - that of the mercury green line at 5461 Å which is fairly near to the maximum modulation wavelength. Also since the same electrolytic cell was to be used later for work in the infra-red, where the high optical absorption of the electrolyte necessitated the use of the Hansen and Prostak technique of total internal reflection [98], the gold electrode was fabricated in the form of a semitransparent film 200-400 Å thick, deposited on a glass substrate. The film thickness was estimated from optical absorption. The experimental arrangement is illustrated in figure (8.15).

The photodetector used was a reverse biased high speed photodiode. Reference to the characteristics of this device (figure (8.16) ) indicates the importance of operating the device in a reverse bias mode. Operation of the photodiode in an unbiased or forward bias mode gives a response which is approximately proportional to log (light intensity). Only when a reverse bias is applied does the response become linear. In operation the photodiode was used with a 1 kΩ load resistor, and it had a measured response time, using a stroboscope of better than 1 microsecond.
Figure (8.14) The use of the reference electrode

Figure (8.15) Experimental arrangement for modulation

Figure (8.16) Characteristics of the photodiode
The light from a point source high pressure mercury lamp which was transmitted by an interference filter centred on the mercury green 5461 Å line, was reflected from the sample in the electrolytic cell and focussed on the photodetector. The output from this was fed into a conventional Brookdeal series 400 phase sensitive detection system, which included a high gain low noise amplifier and a coherent filter. The reference was provided from the signal generator which drove the electrolytic cell. After trials were made using this equipment, it was found necessary to replace the mercury arc lamp by a tungsten halogen lamp in order to reduce noise and increase stability.

The operation of the P.S.D., which has been discussed more fully in chapter (7) is to extract all signals in phase with a reference signal (in this case from the signal generator) amplify and rectify them and give a d.c. output proportional to the in-phase input signal.

By this means the modulation signal was extracted from the background noise, and a d.c. output, proportional to the change in reflectance $\Delta R$ obtained. The output of the P.S.D. was most easily related to the peak-peak photodetector signal by reference to a previously measured calibration curve. Finally it was possible to compute the required parameter $\Delta R / R$.

8.5.3 Results and Discussion

Electroreflectance modulation was observed in each of the four gold films used. These films had thicknesses of approximately 200, 220, 300 and 380 Å (as estimated from optical absorption). Presented in figure (8.17a) is the variation of the modulation depth $\Delta R / R$ at 5461 Å as a function of the modulation frequency at 0.8 volts peak to peak.
Figure (8.17) $\frac{\Delta R}{R}$ as a function of frequency and signal voltage $\frac{R}{R}$ for gold films of thicknesses 0.2, 0.22, 0.3, and 0.38 microns.
Figure (8.18)

(a) refers to a metal-semiconductor junction not yet in equilibrium. (b) Equilibrium has become established by the formation of a Schottky layer.
The large error bars indicate the magnitude of background noise even after phase sensitive detection. Curve A shows the frequency cut-off which was observed in the first run. This was investigated and found to be due to the photodetector being incorrectly biased. When this was corrected, frequency independence of $\frac{AR}{R}$ was observed in all samples as shown. Figure (8.17b) shows the typical variation of $\frac{AR}{R}$ with the peak-peak voltage of the applied modulation field, at a modulation frequency of 420 Hz.

The independence of $\frac{AR}{R}$ from frequency has been previously observed only up to a maximum frequency of 1.2 kHz [98]. The measurements presented here show that $\frac{AR}{R}$ is virtually independent of frequency in the frequency range 15 Hz - 50 kHz. This result corresponds to figure (8.13) which shows that the capacitance of the double layer is also independent of frequency in this range, and it indicates that the relaxation processes involved must be more rapid than 50 kHz. In fact it has been proposed by Graham [100] that the frequency response of the double layer is restricted only by the finite mobilities of charge carriers near the interface, and the double layer capacitance has been measured up to a frequency of 10 MHz with no apparent relaxation.

The rise of modulation depth $\frac{AR}{R}$ with applied voltage has been reported previously [98] and these measurements provide confirmation. The magnitude of $\frac{AR}{R}$ should be linear with charge.

The magnitude of $\frac{AR}{R}$ is $8 \times 10^{-4}$ for a modulation voltage of 0.8 volts peak-peak. Hansen and Pollack [98] report a value $\frac{AR}{R} = 70 \times 10^{-4}$ using a 50 nm gold film for the same wavelength of light. However they used multiple reflections (5 in all) to increase the magnitude of the effect. When reduced to one reflection this figure becomes $\frac{AR}{R} = 14 \times 10^{-4}$ which is similar to that reported here. Both sets of results are below the value of $\frac{AR}{R} = 20 \times 10^{-4}$ for bulk gold at this wavelength reported by Feinleib.
8.6 Reflectance Modulation Using a Schottky Diode

The strong electric field in the dipole layer adjacent to a metal-electrolyte interface has been used to adjust the distribution of majority carriers in the metal to produce reflectance modulation. Another device which may be used to achieve the same results is a Schottky diode.

The Schottky diode is based upon the Schottky barrier, which is a physical barrier at a metal-semiconductor interface. To explain the nature of the physical barrier layer consider an ideal contact between a metal of work function $\phi_m$ and an n-type semiconductor. Before equilibrium has been established the energy band scheme may be represented by fig (8.18). The effective work function of the semiconductor is given by the energy between its Fermi level and the vacuum level; let this difference be $\phi_s$. Thus if $\phi_s < \phi_m$ electrons will flow from the semiconductor into the metal. Consequently the metal acquires a negative surface charge and the semiconductor charges up positively. Now, because the density of donors is relatively small, the donors will become ionised over a region which extends into the semiconductor, i.e. a space charge rather than a surface charge is created.

Reflectance modulation using a Schottky diode depends on the formation of a Schottky barrier when a thin semitransparent metal film is deposited on the front or reflecting face of a semiconductor. Light reflected from the interface may then be modulated in intensity in the same manner as occurs with the electrolytic interface.
Schottky diodes are comparatively easy to fabricate and could be applied to a wide range of materials and wavelengths. Despite the intensive investigation of metal-semiconducting junctions as rectifying contacts and optical detectors [104] the Schottky barrier has only recently been used for electroreflectance measurements [105], where it was shown that for a silver on Gallium Arsenide Schottky diode, the magnitude of electroreflectance was similar to that obtainable with an electrolytic cell, but the energy resolution was an order of magnitude greater. In this case the modulation spectrum due to the semiconductor was investigated, but the possibility arises of observing reflectance modulation due to the metal itself corresponding to the plasma edge.

An experimental Schottky diode of gold on silicon was fortunately available on loan from Manchester University, and the possibility of observing reflection modulation corresponding to the plasma edge of gold was investigated at 5461 Å. The diode was used in place of the electrolytic cell with the apparatus described previously in section (8.5.2).

Reflectance modulation was observed although it was rather lower than was observed with the electrolytic cell. Figures (8.19a) and (8.19b) show the magnitude of the observed effect as a function of the pk-pk voltage and frequency of the modulating signal. It was noticed that the level of the ambient light affected the results and the figures presented were measured in darkness.

This work was done at the very end of the time available, and further work was unfortunately not possible, but it is understood that the reflectance modulation spectrum \( \frac{AR}{R} (\lambda) \) has since been measured using the same Schottky diode. The spectrum obtained is similar to that expected for gold near the plasma edge. These results if verified are the first observations of electroreflectance in metals using a Schottky diode.
Figure (8.19) $\Delta R$ as a function of frequency and signal voltage for the Schottky diode.
8.7 Electroreflectance in antimony

Reflectance modulation near the plasma reflection edge of gold has been observed by making use of the electrical double layer at the interface between an electrolyte and a gold electrode. This was done by using an electrolytic cell of the type described by Hansen [98]. The measured reflectance changes were in substantial agreement with values reported previously.

It is proposed to use the same electrolytic cell to modulate the reflectance of an antimony or antimony alloy thin film at 10.6 microns and to assess the possibility of using this technique to modulate the output of a CO₂ laser.
The samples used were either pure antimony or antimony-tin alloys on substrates of single crystal silicon slices 0.5 mm thick and 50 mm diameter which were kindly supplied by Plessey Limited.

Antimony films were deposited at a substrate temperature of 280°C in the manner described in section (4.9). The preparation of antimony-tin alloy films was more complicated, because the evaporation of any binary compound is difficult since the constituents usually have different evaporation rates and vapour pressures. Figure (4.4) confirms that this is the case for antimony and tin. The methods which were tried to make alloyed films of the required constitution have been described in section (4.9.1). Some of the films prepared did exhibit reflection spectra corresponding to those which might be expected from antimony-tin alloy films; i.e. the plasma edge was shifted to shorter wavelengths. These films were subsequently used in the cell.
8.7.3 Experimental arrangements

The electrolytic cell was the same as that described in section 8.5. The electrolyte was again 0.1 M Na$_2$SO$_4$ solution, but the gold on glass thin film electrode was replaced by an antimony film on a substrate which is transparent to 10.6 micron radiation.

The capacitance was measured as a function of the applied bias potential using the circuit shown in fig. (8.14). The capacitance was found to be independent of the modulation frequency up to the highest value measured of 50 KHz, and of potential to about 2 volts.

The experimental layout is shown schematically in figure (15). The radiation from a CO$_2$ laser is reflected from the sample face, in the electrolytic cell, towards a Mullard pyroelectric detector, which has a linear response up to 100 KHz. A mechanical light chopper is included to aid alignment of the optical system. During alignment the chopped output from the detector was displayed on an oscilloscope and the laser power adjusted so that the detector was not saturated.

The electrolytic cell was driven as before from a conventional signal generator which also served as a reference for the phase sensitive detection system (P.S.D). This system included the Brookdeal 411 phase sensitive detection unit, the 450 low noise amplifier and the coherent filter unit.
The observation of reflectance modulation in antimony and antimony-tin alloy thin films was made difficult by several factors.

(i) The inherent noise of both the radiation source (CO₂ laser discharge) and the detector (pyroelectric) was several orders of magnitude greater than the d.c. filament lamp and photodiode which were used previously for the gold measurements.

(ii) The parameter which is measured by the arrangement used is not the ratio \( \frac{AR}{R} \), but the change in intensity of the reflected radiation, which was later converted to \( \frac{AR}{R} \) numerically. Although the P.S.D. was operated with a long time constant of 3 seconds, variations of the incident radiation from the laser appeared at the output of the P.S.D. causing drift and a reduction of detection sensitivity.

(iii) An unexpected problem was the tendency of both antimony and antimony alloy films to dissolve into the electrolyte. Investigations showed that the rate of disappearance of the films into solution was not greatly affected by the concentration of electrolyte and attempts to reduce the rate by adjusting the d.c. bias across the cell were unsuccessful. The application of an alternating potential was found to accelerate the process and in a modulation experiment a film might completely dissolve in from 5 to 20 minutes. Furthermore the films which were most promising from a modulation point of view were the thinnest and disappeared most rapidly. This phenomenon severely restricted attempts to produce reproducible results.
Attempts to observe reflectance modulation at 10.6 microns using the electrolytic cell were made with six antimony films having thicknesses from 0.1 to 1.2 microns, and five alloy films of thicknesses from 0.1 to 0.6 microns. All of the films were destroyed by dissolving into solution within 5-10 minutes when the modulation signal was applied.

The resolution of measurement was limited to $\frac{\Delta R}{R} > 5 \times 10^{-4}$ by drift and noise in the output of the P.S.D. Reflectance modulation above this level was observed in only two samples, which were the thickest films (0.1 and 0.15 microns) of alloyed antimony. In each case, if the incident radiation was cut off from the cell or detector, or the modulating signal was removed from the cell the output of the P.S.D. fell to zero.

The rapid disappearance of the films prevented a detailed investigation of reflectance modulation. In one film the voltage dependence of modulation was examined. The result is presented in fig. (8.20a) which shows that the modulation rises with increased signal voltage. Modulation was measured as a function of frequency with the other sample (0.15 μm), and it was found that $\frac{\Delta R}{R}$ is essentially frequency independent (figure (8.20b)). At the highest frequencies used the fluctuations of the P.S.D. output were reduced as indicated by the smaller error bars.

Reflection modulation was not observed in the other samples used; i.e. for these $\frac{\Delta R}{R} < 5 \times 10^{-4}$.
Figure (8.20) $\Delta R$ as a function of frequency and signal voltage for antimony films of thicknesses $0.1$ and $0.15$ microns.
8.8 Conclusions

An electrolytic technique has been successfully used to observe reflectance modulation due to free carriers.

Using an electrolytic cell, the previously observed free carrier reflection modulation at the plasma edge of gold in the visible was observed. The limit of detection was better than $\frac{\Delta R}{R} < 10^{-4}$, and at a wavelength of 0.564 microns a modulation depth of $\frac{\Delta R}{R} = 5 \times 10^{-3}$ was observed which was in agreement with published values.

A calculation of the expected modulation depth $\frac{\Delta R}{R}$ was made using only the known optical constants of antimony in the manner which was outlined in Chapter 5. The computed value for $\frac{\Delta R}{R}$ is in agreement with the measured value within the uncertainty involved. The agreement between this calculation and experiment suggest that modulation does occur due to free carriers within the metal.

It was observed that the electrolyte-electrode interface had the properties of a Schottky carrier and that a Schottky diode which also possesses such a barrier should exhibit similar reflectance modulation effects. A Schottky diode of gold on silicon was investigated, and reflectance modulation was observed.

The electrolytic cell was used to investigate reflection modulation of antimony films at 10.6 microns. Due to noise in the laser and detector the limit of sensitivity was only $\frac{\Delta R}{R} > 10^{-3}$. Reflectance modulation was observed with $\frac{\Delta R}{R} \sim 1 \times 10^{-3}$; the magnitude was found to rise with modulating potential but to be independent of modulating frequency.

It was calculated that the number of carriers injected or extracted in every cycle was $3 \times 10^{24} \text{ m}^{-3}$ and assuming that the excess carriers are uniformly distributed through the depth of the film, it was estimated that this corresponded to $\frac{\Delta R}{R} = 2 \times 10^{-3}$ which is at least of the right
order of magnitude, more close agreement can be achieved by assuming more complicated distributions.

The magnitude of reflectance modulation should be increased by a factor of 7-8 at this level of carrier injection by using films of antimony - 2.83% tin, but attempts to prepare suitable films to verify this were unsuccessful.
Chapter 9

Conclusions and proposals for further work

It has been shown that the optical properties of evaporated films of antimony in the infra-red may be predicted as a function of their thickness and changes of free carrier concentration. The optical constants due to free carrier effects have been separated from those due to bound electrons and used in a computer program for thin film behaviour. A one carrier model was found adequate to account for free carrier dispersion with a relaxation time of $3.1 \times 10^{-14}$ sec found for a carrier density of $3.1 \times 10^{26}$ m$^{-3}$.

This analysis showed that the reflectance of antimony films at 10.6 microns could be changed sufficiently to modulate the output of a CO$_2$ laser at this wavelength, by suitably adjusting the free carrier concentration within the material. In order to investigate this possibility, attempts were made to adjust the free carrier concentration in two different ways.

In the first method carriers were injected directly by impact ionisation from high energy electron beam bombardment using a specially constructed electron gun which was designed so that the maximum fraction possible of beam power was transferred to the film. Reflectance modulation was not observed above the limit of detection of the apparatus which was limited by noise and electrical pickup. A subsequent analysis showed that the mean free path of carriers in the film was far greater than the film thickness and it was probable that the excess free carrier concentration was greatly reduced below the expected value to due enhanced surface recombination, which resulted in a correspondingly low reflectance change.
The second method overcame this limitation by using majority carriers which were injected into the film across a Schottky-type barrier layer which exists between an electrolyte and an electrode immersed in it, using a specially constructed electrolytic cell. Using this technique a reflectance modulation $\frac{AR}{R}$ of about $10^{-3}$ was observed with antimony films at 10.6 microns, and an analysis suggested that an improvement on this could be achieved by using films prepared from an antimony-tin alloy, in which the plasma edge was shifted a little to shorter wavelengths. It is therefore envisaged that a modulation depth at 10.6 microns, of 5% could be achieved with the electrolytic cell set up for normal incidence.

Although a reflectance charge of 5% does not appear to be very useful for modulation purposes it is anticipated that larger changes of radiation intensity can be achieved by various means.

For instance by using the film with polarised light at the pseudo-Brewster angle, a relatively small change of refractive index could produce a much larger change of reflectance. It was shown by Hansen and Pollack that $\frac{AR}{R}$ for gold film using the electrolytic cell could be increased by up to $x10$ over normal incidence by measuring at $72^\circ$.

Alternatively the film of antimony could possibly be used as one mirror in a CO$_2$ laser cavity where it is envisaged that the reflectance is adjusted so as to change the gain of the cavity from less than to greater than unity resulting in an amplification effect.

By the use of these or some other means it may well be possible to modulate the output of a CO$_2$ laser by up to 50%. This is a worthwhile aim and towards this end the following proposals for future work are made.
1. Future work should be concentrated on majority carrier devices (electrolytic cell and Schottky diode) since problems of carrier lifetime can be ignored.

2. More information is required about the wavelength dependence of reflection modulation in order to associate the measured effects to the known optical properties of the materials used. Therefore a monochrometer-detector system should be built or purchased for use in the infra-red region 1-20 microns.

3. Using this apparatus detailed investigations of other electrolyte-metal or electrolyte semiconductor interfaces may be undertaken. Dr Hansen, lecturer in Chemistry at Loughborough University, who has been studying such interfaces for several years, has expressed a favourable reaction to this idea, and it has been proposed to form a joint interdisciplinary team for research into this area.

4. The modulation of the reflectance of antimony films in the infra red should be investigated further.

5. Further effort should be made to prepare antimony-tin alloy films which are reproducible and have the desired optical properties.

6. The possibility of preparing antimony on silicon Schottky diodes should be investigated. If the preliminary result found with the gold on silicon diode is correct, then modulation should be possible with the former. Such a device may be more attractive than the electrolytic cell, since the application of a voltage across the layer should not be complicated by Faraday currents and chemical reactions which may occur in the cell.
7. Techniques to amplify the effect of the induced changes of optical properties of the film should be investigated. For example, by using polarised light at the Brewster angle, it is known that the modulation depth $\frac{\Delta R}{R}$ can be increased by up to an order of magnitude. Another proposal is to use the thin film as one mirror in a laser cavity and use it to adjust the gain of the laser. Alternatively it may be possible to arrange an optical system whereby a relatively small change could switch the system from a condition of total internal reflection to one of partial transmission. The last effect would be particularly attractive since it would achieve 100% modulation.

It is believed that the proposals put forward here together with the basic experience gained in this project may possibly lead to the development of a simple cheap and effective method of modulating infra red radiation.
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Chapter 5 of this thesis forms the basis of a paper which has been submitted to the Journal of Applied Physics for publication.

A preprint of this paper is presented in the appendix.
OPTICAL PROPERTIES OF THIN FILMS OF ANTIMONY

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Abstract

It is shown that it is possible to predict the optical properties of evaporated films of antimony in the infra-red as a function of their thickness and changes in free carrier concentration. This is achieved by the interpretation of previous data on the optical properties of thin films of antimony with the use of detailed measurements of optical constants, in the near infra-red, of polycrystalline material.

The optical constants due to free carrier effects have been separated from those due to bound electrons and used in a computer program for thin film behaviour. A one carrier model was found adequate to account for free carrier dispersion with a relaxation time of $3.1 \times 10^{-14}$ sec found for a carrier density of $3.1 \times 10^{28} \text{m}^{-3}$. 
OPTICAL PROPERTIES OF THIN FILMS OF ANTIMONY

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1. Introduction

Optical measurements on evaporated thin films of antimony in the infra-red have shown that they exhibit a distinct free carrier plasma edge in the region of 10.7 - 11.6 μm and can be prepared in a crystalline form at relatively low temperatures (265°C). These properties are some of those required in an investigation of thin film materials for modulators of radiation from a CO₂ laser at 10.6 μm where it is intended to sweep the plasma edge through the operating wavelength of the laser.

In order to make meaningful measurements and to predict the thickness of film which would give the optimum effect it is necessary to know the optical constants of the film, both those due to free carrier effects and those due to bound carriers. These are obtained by comparing the data of Harris and Corrigan (1964) (H & C) with films prepared in a similar way and with more detailed measurements made on polycrystalline bulk material. It is possible to obtain a detailed set of optical constants due to bound and free carriers, so that the optical properties of thin films of antimony of various thicknesses can be predicted and the effect of changing the free carrier density observed.
2. Preparation and Properties of Antimony Films

In order to justify the use of the results of measurements made on thin films in comparison with those reported here on bulk material it was thought necessary to reproduce those measurements of optical and electrical properties that could be made. An investigation of the change of properties with thickness would indicate how close these were to approaching those of bulk materials.

After Harris and Corrigan (1964, 1965) antimony films have been prepared by evaporating 99.99% pure antimony in a vacuum of better than 10^{-6} torr using an electron beam evaporating system. Substrates of either glass or sapphire were mounted 250 mm above the crucible and heated during evaporation to 140°C. These films were subsequently annealed "in situ" at 250°C.

Film thickness was measured using a Rank Taylor Hobson Talystep which was accurate to ± 5%, and reflectance measurements were made using a Perkin-Elmer spectrophotometer type 457 over a wavelength range 2.5 - 40 μm. A typical curve for film of 0.25 μm thickness is shown in figure 1 together with a comparison with bulk material and a film evaporated onto a substrate at room temperature. Hall and electrical conductivity measurements made on these films are shown in figure 2 as a function of film thickness and substrate temperature. They indicate a move towards lower mobilities at thicknesses below 0.5 μm but the carrier density remains constant.
The reflection curves are similar to those presented by H & C and are characterised by interference fringes at short wavelengths followed by a steep rise in reflectivity due to the free carrier absorption edge in the region of 10.7 - 11 μm. The sharpness of this rise in reflectivity indicates that the film is crystalline and this view is supported by an electron micrograph of the surface of film, showing that the film is made up of crystallites 2-3 μm diameter.

3. Free Carrier Data

The optical properties of a mechanically polished microcrystalline surface of bulk antimony were measured in the wavelength range from 2.5 to 12 μm with a bandwidth of 0.3 μm using the method of Beattie and Connin (1955) as applied by Beattie (1955); the elliptically polarised radiation created by the reflection of a plane polarised beam from the surface was analysed with a polariser and an empirical solution for the real and imaginary parts of the dielectric constant 2nK and n² - K² obtained, n is the refractive index and K the extinction coefficient.

In order to assess the influence of free carrier absorption on these values attempts were made to adjust the free carrier concentration without significantly altering the band structure. Alloys of antimony with tin and tellurium were tried for this purpose; tin has one valence electron less per atom than antimony and reduces the number of conduction electrons, tellurium with one more should increase the supply. The results are presented in figure 3, these show that the alloys with tin
were much more successful for this purpose. (This might be expected when Hall effect measurements had indicated that conduction in antimony was by holes.) The reflectance versus wavelength is shown for Sb in figure 1.

Alloying with greater proportions of bismuth, which is a material of similar valence and crystal structure and forms solid solution alloys, showed much smaller effects than encountered with tin and tellurium, showing a gradual change of properties from those of antimony to those exhibited by bismuth (which are less affected by free carrier effects). They are shown in figure 4.

The shape of all these curves is governed by two contributions:

1. that due to free carriers
2. that due to bound carriers which is limited to a region 2-20 μm, i.e.,

\[ 2nK = 2nK_{\text{bound}} + 2nK_{\text{free}} \]

\[ n^2 - K^2 = (n^2 - K^2)_{\text{bound}} + (n^2 - K^2)_{\text{free}} \]

Assuming that conduction within antimony is by different groups of electrons or holes, then the contribution of free carriers to the optical constants is given classically by the Drude theory as:

\[ (2nK)_{\text{free}} = \sum \frac{N_n e^2}{m^* m_e c_0} \cdot \frac{1}{\omega m} \cdot \frac{1}{\omega^2 + \tau^2} \]

\[ (n^2 - K^2)_{\text{free}} = \varepsilon_L - \sum \frac{N_n e^2}{m^* m_e c_0} \cdot \frac{1}{\omega^2 + \tau^2} \]

where

- \( N \) = Concentration of electrons or holes
- \( m^* \) = Relative effective mass
- \( m_e \) = Mass of an electron
- \( \tau \) = Relaxation time
- \( \varepsilon_L \) = Dielectric constant due to lattice effects
The data presented by H & C is useful because it extends up to 120 μm, and this allows the free carrier parameters to be calculated.

Assuming initially that a single carrier species dominates, the Drude equations may be rewritten

\[
\frac{n^2 - \kappa^2 - \epsilon_L}{\epsilon_L} = \frac{2nK}{\lambda} = \frac{\hbar^2}{m^* e^2} \cdot \frac{1}{\omega^2 + \tau^{-2}}
\] (3)

Figure 5 shows a plot of \(n^2 - \kappa^2\) vs \(\frac{2nK}{\lambda}\) using the data given by H & C for an antimony film 0.1 μm thick. It is a straight line over the region 25-120 μm where the bound carrier effects are negligible. This implies that equation (3) and the single carrier approximation are both acceptable.

From the slope and intercept

\[
\tau = 3.1 (\pm 0.1) \times 10^{-14}\text{sec}
\]

\[\epsilon_L = 90 (\pm 10)\]

and substituting values into (3)

\[
\frac{N}{m^*} = 5.9 \times 10^{26}
\]

The value of \(\epsilon_L = 90\) is close to the published values of 80 (± 5) (Nanney, 1962) and 95 (Harris & Corrigan, 1964).

Taking the value of \(N\) given from Hall measurements by H & C as 3.1 x \(10^{26}\) m\(^{-3}\) (this compares with 3.5 x \(10^{26}\) m\(^{-3}\) for thin films and 2.9 x \(10^{26}\) m\(^{-3}\) for bulk material found in this paper) a value for \(m^*\) of 0.5 (± 0.1) is obtained. Values of \(\tau\) obtained from Hall effect measurements on the films, which should not necessarily equal those obtained optically, go from 1.7 x \(10^{-14}\) at film thickness of 0.5 μm and above to half that at 0.1 μm.
Using the values of \( \frac{N}{m} \) and \( \tau \) found in this way \( n^2 - K^2 \) and 2nk can be calculated as a function of wavelength and compared to the measured results on bulk material. A comparison is shown in Figure 3 both for antimony and for an antimony tin alloy in which case \( \frac{N}{m} \) has been adjusted to give the most suitable agreement. It would appear that the curves match those that would be expected for free carrier absorption in these materials and if this free electron contribution is subtracted from the values of 2nk and \( n^2 - K^2 \) that were measured then a conventional plot of absorption coefficient \( \alpha \), versus photon energy energy can be obtained (figure 6) predicting an optical energy gap of 0.11 electrons volt.

4. Calculation of the properties of thin films

After Howson (1970) the energy reflectance of a thin absorbing film on a substrate of refractive index 1.5 is given by

\[
R = \frac{r_1^2 + 2r_1r_2 e^{-\beta \cos \theta} + r_2^2 e^{-2\beta}}{1 + 2r_1r_2 e^{-\beta \cos \theta} + r_1^2 r_2^2 e^{-2\beta}}
\]  

(4)

where

\[
r_1 = \frac{(n - 1)^2 + K^2}{(n + 1)^2 + K^2}
\]  

(5)

\[
r_2 = \frac{(n - 1.5)^2 + K^2}{(n + 1.5)^2 + K^2}
\]  

(6)

\[
\beta = \frac{2\pi kd}{c}
\]  

(7)

\( r_1, r_2 \) are the Fresnel amplitude coefficients of the two surfaces and \( \beta \) is the absorption constant of the film, which has a complex refractive index of \( n-jK \). \( \theta \) and \( \phi \) are computed phase changes on transmission and reflection and are obtained from the appropriate Fresnel coefficients. We have that
\[ \tan \delta_1 = \frac{2K}{(1-n)(1+n) - K} \]  (8)

\[ \tan \delta_2 = \frac{3K}{(1.5-n)(1.5+n) - K} \]  (9)

and the phase change on traversing the film is given by

\[ \Delta = \frac{4\pi n v_d}{c} \]  (10)

Physically \( \Delta \) is unambiguously a phase retardation, and if numerical solutions for \( \delta_2 \) and \( \delta_1 \) are restricted to angles between 0 and 180°, the equations for \( \phi \) and \( \theta \) are:

\[ \phi = \delta_2 - \delta_1 - \Delta + \pi \]  (11)

\[ \theta = \delta_2 + \delta_1 - \Delta + \pi \]  (12)

The original paper (Howson 1970) gives the opposite sign for \( \Delta \). Reflectance curves using equations (11) and (12) were computed using the data for \( N_{\text{film}} \) and \( \tau \) given by Howson. Comparison of these curves with those originally given show them to be similar, except that the anomalous spikes in figures 3.1a and 3.2a of that paper have disappeared.

Following this procedure, a computer program has been developed to generate from the optical constants of antimony the reflectance of antimony films as a function of wavelength.

In order to compare the reflectance measurements made by Harris and Corrigan with the computer generated curves, calculations were performed for antimony films of thickness 0.625 \( \mu \)m and 0.25 \( \mu \)m respectively. The results shown in figure 8 show that the computer calculations are a good fit to the measured curves, and that the various reflection maxima at short wavelengths, which
have been attributed to optical interference are in fact predicted by this procedure.

5. The effect of excess free carriers

The optical constants of antimony are the sum of contributions due to bound and free carriers. If a carrier density change is small, then there will be a very small effect on the bound carriers, and the bound contribution to the optical constants may be assumed constant. Although this assumption is not strictly true at higher levels, it is instructive to use this approximation in order to estimate the reflectance change which might be achieved with an increase in free carrier concentration. Making this assumption, the reflectance curves for antimony films have been recomputed for films having excess free carriers which compare with Sb films alloyed with tin. Figure 9 shows the computed reflectance curves for films having a free carrier concentration of $1.2 \times 10^{27} \text{m}^{-3}$ with film thickness 0.25 and 0.625 μm. It is clear that the effect of changing the free carrier concentration is also dependent upon the thickness of the film. A plot, figure 10, of the absolute and relative change in reflectance as a function of thickness reveals an optimum film thickness of 0.12 μm, which yields the greatest change in reflectivity @ 10.6 μm for a small change in free carrier concentration.

The change in reflectivity may possibly be used as a measure of the change of free carrier density. Taking the optimum thickness of 0.12 μm figure 11 indicates that changes in free carrier density of the order of $10^{20} \text{m}^{-3}$ will give a $10^{-5}$ change in the reflectance of the film.
6. **Conclusion**

The interpretation of previous measurements together with new ones made on thin film and bulk antimony have led to the ability to predict the optical properties of thin films of that material in the wavelength region from 2-12 μm as a function of both thickness and free carrier density. The influence of the changing of free electron concentration was demonstrated by alloying antimony with small amounts of tin.

Bulk antimony has free carriers which can be represented for their optical effects as being holes with a relaxation time of $3.1 \times 10^{-14}$ secs and a density of $3.1 \times 10^{26} \text{m}^{-3}$. Interband effects show an absorption edge at 0.11 electron volts.

With this knowledge the influence of changing the free carrier density by injection of some kind on the reflection properties at a wavelength of 10.6 μm, that of the CO$_2$ laser, has been assessed.

Changes in the free carrier concentration have been made by the excitation of hole-electron pairs by a 4 K e.v. electron beam, by making the film an electrode in an electrolytic cell and for comparison by alloying antimony with tin. No change in reflectance was observed for direct excitation indicating that the carrier lifetime was less than 10 ns. but a change of reflectance of $1 \times 2\%$ at 10.6 μm wavelength was given by excess carriers being held in the film by the electric field of an electrolytic cell capacitance. By comparison with measurements and predictions made with gold films in the visible region of
the spectrum a much larger effect is predicted for films with their plasma edge shifted nearer to 10.6 μm; this should be achieved by alloying antimony with 3% of tin.
1. Reflectance as a function of wavelength shown for films of antimony evaporated on to substrates at, A, room temperature and, C, 200°C compared with that calculated for polished polycrystalline bulk material (C).

2. The conductivity, Hall coefficient, mobility and carrier density shown as (a) a function of substrate temperature for film thicknesses between 0.3 and 0.6 μm, and (b) a function of film thickness for a substrate temperature of 265°C. \( n_{th} \) is in all cases negative, indicating that the carrier concentration is of holes.

3. The real and imaginary parts of the dielectric constant, \( n^2 - k^2 \) and \( 2nk \) respectively, shown as a function of wavelength for polished polycrystalline bulk samples of A antimony, B antimony 1.22% tin, C antimony 2.83% tin, D antimony 1.19% tellurium and E antimony 1.97% tellurium. F and G show respectively the estimated free electron contribution to the dielectric constant for antimony and antimony 2.63% tin. H shows those values obtained by H & C for antimony.

4. The optical constants of alloys of antimony with bismuth; A is Sb, B is Bi - 72.7% Sb, C is Bi 57.61% Sb, D is Bi 29.44% Sb and E is Bi alone.

5. \( n^2 - k^2 \) versus 2nλ/λ for the data of H & C for a film 0.1 μm thick.

6. The optical constants of the bound electrons contribution for antimony.
7. Absorption coefficient, $a$, shown as a function of photon energy for the bound (inter-band) electron absorption in antimony.

8. Computed reflectance versus wavelength curves compared to results reported by H & C (dotted line) for films (a) 0.25 $\mu$m and (b) 0.625 $\mu$m thick.

9. Computed reflectance curves, A for antimony films and B for films with the electron density increased to $1.2 \times 10^{27} \text{m}^{-3}$ shown for (a) a film thickness of 0.625 $\mu$m and (b) for 0.25 $\mu$m.

10. Absolute ($\Delta R$) and relative ($\frac{\Delta R}{R}$) reflectance changes in thin films for the increase in density indicated in figure 9 shown as a function of thickness.

11. The computed reflectance change shown as a function of excess carrier density for the optimum film thickness of 0.12 $\mu$m.
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E follows APO closely.