ELECTRICAL AND OPTICAL PROPERTIES OF AMORPHOUS SEMICONDUCTOR FILMS

By
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To Malati, my wife, who has been forced into the role simply as an observer as this research work has enveloped her husband's existence. Her faith and understanding, however, have indeed been helpful in completing this dissertation.
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a = interatomic distance
b = width of the potential barrier
c = velocity of light
d = thickness
D = optical density
es = calibrating signal
E = energy in general
E_a = activation energy
E_c = energy separating the localized states and the non-localized states
E_e = electron energy
E_{g(0)} = mobility gap at 0°K
E_{g(T)} = mobility gap at room temperature
E_H = activation energy required for hopping
E_{opt} = optical band gap
E_p = photon energy
E_{ph} = photoconductivity gap
\Delta f = bandwidth
F_B = breakdown field
g = an integer
h = Planck constant
\hbar = \frac{\hbar}{2\pi}
I = electrical current
I_{eq} = equivalent saturated diode current
I_{o} = intensity of the incident light
I_{T} = intensity of the transmitted light
k = extinction coefficient
k_{B} = Boltzmann's constant
m = free carrier mass
m^{*} = effective mass
n = refractive index
n_{l} = refractive index of the non-absorbing substrate
n_{i} = carrier concentration
N(E) = density of states
N_{c} = effective density of states in the conduction band
N_{V} = effective density of states in the valence band
q = electronic charge
R = resistance
R_{n} = equivalent noise resistance
T = temperature
T_{o} = optical transmission
V = volt drop across the sample
V_{B} = breakdown voltage
V_{d} = potential of atom
V_{t} = trap depth
x = coordinate
\alpha = absorption coefficient
\beta = thermal coefficient of the energy gap
\[ \beta_F = \text{a constant defined by equation (4.15b)} \]
\[ \gamma = \text{random variable} \]
\[ \xi = \text{coordinate in distorted space} \]
\[ \theta_{af} = \text{defined by equation (II.5a)} \]
\[ \theta_{fs} = \text{defined by equation (II.5b)} \]
\[ \varepsilon = \text{relative dielectric constant} \]
\[ \varepsilon_0 = \text{dielectric constant of vacuum} \]
\[ \varepsilon_d = \text{a parameter characterizing the disorder} \]
\[ \varepsilon_\infty = \text{dielectric constant of the bound charges} \]
\[ \lambda = \text{wavelength} \]
\[ \mu = \text{mobility} \]
\[ \nu = \text{frequency} \]
\[ \nu_{el} = \text{electronic frequency defined by } \nu_{el} = E_e/h \]
\[ \sigma = \text{conductivity} \]
\[ \sigma_H = \text{hopping conductivity} \]
\[ \sigma_0 = \text{a slowly varying function of temperature} \]
\[ \omega = \text{frequency defined by } \omega = 2\pi c/\lambda \]
\[ \omega_p = \text{plasma frequency} \]
\[ \tau = \text{relaxation time} \]
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ELECTRICAL AND OPTICAL PROPERTIES OF AMORPHOUS SEMICONDUCTOR FILMS

by

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Major Department: Electrical Engineering

This dissertation presents the studies on amorphous $\text{As}_2\text{Se}_3$-$\text{Sb}_2\text{Se}_3$ films, of electrical conductivity as a function of temperature, applied field, of photoconduction, optical transmittance, and the data on the optical gap, optical constants and their dispersion. Conductivity measurements suggest transport via non-localized states just across the mobility gap. The results of optical absorption indicate that the transitions occur from localized to non-localized bands. The data further suggest a very small localization. High field transport is found to obey the Pool-Frenkel law. The spectral response of the dc conductivity corresponds to an intrinsic transition.

The random nature of the lattice in the amorphous state produces: a) a potential fluctuation which destroys the periodicity;
and b) a fluctuation in the magnitude of the potential at each lattice site thereby causing some of the energy states to become "localized."

Taking into account the influence of these two effects in the existing band theory of crystalline solids, a plausible band model for the amorphous structures is postulated. The experimental results are found to be consistent with this model.

Dispersion relations for the amorphous state are simplified for both high and low frequencies. Optical results are interpreted using these relations.

Structure-sensitive parameters such as the mobility, the dielectric constant, the activation energy, the relaxation time, and the breakdown strength are determined from the analysis of the experimental data.
CHAPTER I
INTRODUCTION

The band structure and transport properties of amorphous materials have attracted increasing interest in recent years. New electronic devices have been developed\(^1,2\) using semiconducting glasses. Many materials with amorphous structure show interesting electronic properties such as: a) high photosensitivity,\(^3,4\) and b) high thermoelectric power.\(^5\)

Broadly speaking, these semiconducting glasses or vitreous semiconductors can be divided into two groups based on their different chemical constituents:

1) Chalcogenide glasses

One or more of the elements sulphur, selenium, or tellurium is combined with, for example, one or more of the elements such as silicon, germanium, phosphorous, arsenic, bismuth, thallium, or lead. This list encompasses most of the potential glass-forming combinations. Studies of the chalcogenide glasses have been pioneered by Kolomiets and his co-workers in Leningrad.\(^6\) The glasses having a composition \(\text{Tl}_2\text{Se}_{2.5}\text{As}_2\text{Se}_{2.5}\text{Te}_{0.5}\) were investigated in their early work.

2) The transition-metal oxide glasses

These are glasses in which the major constituent is a
transition-metal oxide. Denton, Rawson, and Stanworth were the first to study these materials. They reported measurements of the dc conductivity of glasses with compositions containing $V_2O_5$ and one oxide such as $P_2O_5$, $GeO_2$, $BaO$, or $PbO$.

Prior to the work to be reported below, the author spent some time investigating the electrical and optical properties of mixtures of $V_2O_5$ and $P_2O_5$. It was found impossible to fabricate samples of this material in thin film form. Limited measurements made on bulk samples showed the mobility of the current carrier to be very low. The photosensitivity was also very low. The experimental results were not reproducible from sample to sample. Efforts were discontinued in favor of a study of chalcogenide glasses.

Chalcogenide glasses can be deposited in thin films by evaporation or sputtering. A wide range of compositions can be obtained reliably. These glasses, for example, $Sb_2Se_3$, $As_2Se_3$, $Sb_2S_3$, $As_2S_3$, Bi-Se, and selenium, have found applications as photoconductors in vidicon-type camera tubes and in infrared optics and Xerography. Since their properties are relatively unaffected by the presence and variation of impurities these materials are of practical interest for electronic applications.

The recent history of electronic device development shows the extreme importance of a thorough understanding of the physics of materials. A creative device designer is greatly aided by an intimate understanding of the atomic properties. He must have a clear picture of the physical processes which yield the conductivity $\sigma$, the dielectric constant $\varepsilon$, the mobility $\mu$, the density of states $N(E)$, etc. This is fundamental to the invention of possible new
devices. The effect of ambient conditions on these properties must be known. In spite of the fact that there has been some useful application of chalcogenide glasses, as mentioned above, the overall behaviour of these vitreous semiconductors is still poorly understood. For example, the concept of low field conduction is just being formulated. At this time there is no well-established physical model which explains the total behaviour of these materials.

The purpose of the work of this thesis is to provide that information for one important chalcogenide in thin film form. Both electrical and optical measurements have been used. The system $\text{As}_2\text{Se}_3-\text{Sb}_2\text{Se}_3$ was selected for this study mainly because results on bulk specimens of this composition showed a number of interesting properties. The results of the present work can be readily compared with the earlier work on bulk materials.

In summary, the purpose of this work is two-fold: a) to obtain data on device-oriented, structure-sensitive parameters such as the mobility, the dielectric constant, the activation energy, the breakdown strength, and the relaxation time; and b) to present a physical band model capable of explaining the experimental results.

In the following chapter the preparation of samples and the methods of experimental analysis are discussed. In Chapter III the results of experiments are presented. The analysis of the experimental results is given in Chapter IV. The results of this analysis and the proposed band model, described in Appendix I, are used to establish mechanisms of carrier transport. The findings are summarized in Chapter V, and suggestions for future work are presented.
CHAPTER II
EXPERIMENTAL PROCEDURE AND METHODS OF MEASUREMENTS

Experimental Technique

Sample Preparation

The compounds As$_2$Se$_3$ and Sb$_2$Se$_3$ used were of high purity (semiconductor grade 99.999+ percent, obtained from Semi-elements, Inc., Saxonburg, Pennsylvania). Each compound was weighed separately with precision and then they were mixed together (60 percent by weight As$_2$Se$_3$ and 40 percent by weight Sb$_2$Se$_3$ in this study) and ground to a fine powder in a mortar. The resulting material was then mixed thoroughly in a steel cylinder with a steel ball by vibrating in a Vig-O-Lug vibrator for three minutes so as to obtain a homogeneous mixture. Disks, 1 cm. in diameter and about 1 mm thick, were formed in a press at 7000 lbs/sq inch pressure at room temperature under vacuum, and were used for evaporation. A homogeneous mixture as made above was also used for evaporation in some runs. A complete evaporation system, including the substrate holder, shutter, crucible with heater is shown in Figure 2.1 by way of a picture. The vacuum system (Veeco Model #VS-EM776) employed a standard roughing pump, 6 inch diffusion pump, and a cold trap. The system was capable of reaching pressures below 10$^{-6}$ torr without a cold trap. All
FIGURE 2.1

PHOTOGRAPH OF EVAPORATION APPARATUS
films were deposited at an ambient pressure below about $5 \times 10^{-6}$ torr, as measured with the RG-75K Vecco ionization gauge. The evaporation was carried out in a bell jar system from a quartz crucible. The substrates were held at room temperature with a source-substrate distance of 15 cm in all the runs. The crucible was thoroughly cleaned in an ultrasonic bath, washed in hot trichloroethylene and dried with dry nitrogen ($N_2$) gas prior to each loading. Four types of substrates were used in this study. Corning electrically conductive coated 0211 pyrex, Corning 7059 glass (both obtained from Corning Glass Company, Corning, New York), NaCl crystals and silicon wafers with a grown SiO$_2$ (about 1 micron thick) insulating layer. After cleaning SiO$_2$ as described below, an aluminium or gold stripe, 25 mils wide and 100 mils long, was deposited by evaporation, using a commercially made molybdenum metal mask.

The preparation of the pyrex substrates (both coated and uncoated) proceeded as follows. The substrates were thoroughly washed with running deionized water. Then they were placed in an ultrasonic cleaner containing hot trichloroethylene (TCE) for 15 minutes, and finally, they were rinsed with TCE from a squeeze bottle to remove any loose particles left by the ultrasonic cleaner, and stored in methyl alcohol. The NaCl crystals were cleaned in running deionized water and rinsed immediately with alcohol and stored also in TCE. The SiO$_2$ was given a quick 10 seconds' dip etch and washed and dried with $N_2$. Immediately following this cleaning cycle, the substrates were transferred to the evaporation chamber. The system was pumped down
at least two to three hours prior to starting the evaporation run. Evaporation was found to be complete within the first minute. However, a time duration of 3 to 4 minutes was used for each evaporation cycle. The heater voltage was raised slowly with a variac until the evaporation just began. After 30 seconds, the shutter was opened for the deposition. Under these conditions 12 separate runs were made. After opening the system the samples were taken out. The samples intended for optical measurements were stored in a dessicator. The samples for electrical measurements were transferred immediately to another evaporation system for aluminium or gold deposition as top electrodes. A commercially fabricated molybdenum mask was used for the films on Si-SiO₂ substrates. The mask consisted of 8 strips, 25 mils wide, 100 mils long, and 100 mils apart. For other substrates aluminium or gold dots of varying diameter were evaporated using metal masks. Following this evaporation 3 mil diameter copper leads were attached with highly conductive electronic grade "DuPont 4922" silver paste.

**Thickness Determination**

Films deposited on Corning 7059 glass were used for thickness determination. Copper wire of 40 mil diameter was used to provide a step in the film geometry. One the top of this step aluminium was evaporated as a reflecting medium. The thickness of the film was measured using a Sloan Angstrommeter with a sodium light source.
The accuracy of the thickness measured was $\pm 100^\circ$A. For films more than 3 microns thick, the interferometric thickness was used.

**Film Structure**

A few structural studies were made. Two films examined by X-ray diffraction technique indicated that the films had an amorphous nature. One X-ray diffraction graph is shown in Figure 2.2. The composition of the compound used here (60 percent $\text{As}_2\text{Se}_3$ plus 40 percent $\text{Sb}_2\text{Se}_3$) is within the range of the glass formation as reported by N. S. Platakis, et al.\textsuperscript{12}

**Methods of Measurements**

**Optical Transmission**

The optical transmission in the infrared region from 2.5-16 microns was carried out at room temperature. A schematic diagram of the arrangement is shown in Figure 2.3. A Beckman Model #IR-10 spectrophotometer was used for the measurement. The light source was a nichrome wire and a permanently evacuated thermocouple was used as a detector. Samples on NaCl substrates were used for these measurements. The sample holder was attached over the entrance of the slit, so that the samples could easily be changed by removing the outer ring of the holder. The transmittance versus wavelength was recorded for 12 different samples. The response of evaporated $\text{Sb}_2\text{Se}_3$ films was also recorded for reasons discussed later.
Figure 2.2

X-Ray Diffraction Pattern
of Amorphous \( \text{As}_2\text{Se}_3 - \text{Sb}_2\text{Se}_3 \) Films
Beckman IR-10

Figure 2.3

Schematic Diagram of Arrangement for Infrared Transmission
**Optical Absorption**

The optical absorption measurements were carried out at room temperature and at liquid $N_2$ temperature from 0.7-2 microns using a Carry Model #14 double-beam, double-monochromator, ultra-violet, visible-near infrared recording spectrophotometer. For liquid $N_2$ temperature measurements, a specially constructed cryostat having a brass finger for sample mounting and with appropriate quartz windows for light transmission was placed in the sample holder compartment of the Carry 14. The whole system was purged thoroughly with dry nitrogen prior to starting the liquid $N_2$ measurement. Samples fabricated on Corning 7059 glass as well as on 0211 glass were used during these measurements. Absorbance curves were measured one after the other. In this manner, by taking the intensity ratio of two absorbance curves, one eliminates the effects of absorption at the interfaces. As the film composition might be different from each run-to-run because of the difference in substrate temperature and evaporation rate which are very difficult to control in such a multi-component system, it was decided, therefore, to determine the absorption constant for individual samples. Absorbance curves for 12 different samples were measured at room temperature and 6 different samples at liquid $N_2$ temperature under identical Carry 14 settings.

**Electrical Conductivity**

Figure 2.4 shows the electrode arrangement on the samples for
Conductivity and Photoconductivity Sample

High Field Conductivity Sample

Detail Showing The Types of Samples

Figure 2.4
the electrical measurements. Samples fabricated on Corning 0211 glass and on Si-SiO₂ substrates were consistently used for these measurements. The low-field conductivity was measured using an HP 413A micro-micro ammeter and a Harrison 6112A digital power supply. The ammeter was connected in series with the sample and the power supply, with the negative terminals connected to the common ground. The majority of measurements were made with one volt across the sample. A Statham Model #SD6 oven with an accuracy of ± 1°C was employed for temperature control. 30 to 40 minutes were allowed to stabilize the temperature before any readings were taken. High field data was taken essentially with the same instruments except that a higher-rated power supply was used.

**Photoconductivity**

Samples on Corning 0211 glass were employed for these measurements. An Aminco Grating monochromator, Model #4-8400, was used with a 650 watt tungsten movie projector lamp focused on the entrance of the monochromator. The sample was mounted inside the monochromator housing to avoid any background illumination. Light was focused on the back of the semitransparent substrate in order to eliminate any contact effect. The schematic of the set-up is shown in Figure 2.5. The photoconductivity was measured using a HP 413A micro-micro ammeter and a Harrison 6112A digital power supply. One volt bias was used for most of the data. The response was measured using a constant slit
Photoconductivity Measurements

Figure 2.5

(1) light source
(2) Aminco Grating Monochromator 4-840
(3) mounted sample
(4) D.C. biasing unit
width. The films showed considerable response covering the whole visible range. The relative spectral output of the projector, monochromator mirror, and lens combination was measured by an Optics Technology Model #615 power meter. The spectral response of the power meter was obtained from a curve supplied by the manufacturer.

Noise Spectrum

The system used to measure the noise spectrum is shown in Figure 2.6. The measurements were performed on samples having a sandwich cell configuration. The noise spectrum was obtained using a signal source as a voltage standard as follows:

The noise of the device under test was first measured. The standard signal was then applied by closing the switch, S. The variable attenuator and the gain of the system were adjusted so that the signal plus the noise gave the same reading as the noise with the calibration signal removed. The equivalent noise resistance, $R_n$, and the equivalent saturated diode current $I_{eq}$ were obtained from the following expressions, respectively.

$$ R_n = \frac{e_s^2}{4k_B T \Delta f \log_{10} \left( \frac{\text{total attenuation}}{10} \right)} $$  \hspace{1cm} (2.1)

$$ I_{eq} = \frac{e_s^2 R^2}{2q \Delta f \log_{10} \left( \frac{\text{total attenuation}}{10} \right)} $$  \hspace{1cm} (2.2)

Here $e_s$ is the standard calibrating signal, $k_B$ is the Boltzmann constant,
Figure 2.6

System to Measure Noise Spectrum
$T$ is the temperature in degrees Kelvin, $q$ is the electronic charge, $\Delta f$ is the effective bandwidth of the system, and $R$ is the resistance. The measurements were repeated for several values of bias current.
CHAPTER III
RESULTS OF THE EXPERIMENTS

Introduction

This chapter is concerned with a presentation of the results of the experiments described in Chapter II. Each of the studies will be described in turn.

Optical Measurements

Optical Transmission

Figures 3.1 and 3.2 show the infrared transmission spectra from 2.5-16 microns of thin layers of As$_2$Se$_3$-Sb$_2$Se$_3$ on NaCl substrates. A similar spectrum for a thin Sb$_2$Se$_3$ film, also on a NaCl substrate, is reproduced in Figure 3.3.

The refractive index $n$ versus wavelength $\lambda$ is shown plotted in Figure 3.4. The value of the refractive index was obtained from the interference maxima in the transmittance curves of Figures 3.1 and 3.2.

The analysis of the dispersion relations for the refractive index (see Appendix II) show that for relatively long wavelengths

$$n^2 = \varepsilon_\infty (1 - \frac{\omega^2}{\omega_p^2})$$

(3.1)

For short wavelengths
Typical Transmittance Spectra of Amorphous $\text{As}_2\text{Se}_3$-$\text{Sb}_2\text{Se}_3$ Films Deposited On NaCl At Room Temperature

Figure 3.1
Sample $P_2$

Transmittance Spectra of $As_2Se_3 - Sb_2Se_3$ film
Deposited on NaCl at Room Temperature

Figure 3.2
Sample $N_2$

Transmittance Spectra of $Sb_2Se_3$ Film

Deposited on NaCl At Room Temperature

Figure 3.3
\[ n^2 = \varepsilon_\infty (1 - \frac{\omega_p^2}{\omega^2}) \]  

(3.2)

Here \( \varepsilon_\infty \) is the optical dielectric constant arising from the combined effects of the bound charges, \( \tau \) is the relaxation time of free carriers, and \( \omega_p \) is the plasma frequency. Equation (3.1) is independent of wavelength while equation (3.2) shows that \( n^2 \) is linearly dependent on \( 1/\omega^2 \approx \lambda^2 \) for \( \omega \ll \omega_p \). Accordingly, the data of Figure 3.4 are shown again on Figure 3.5 as a plot of \( n^2 \) versus \( \lambda^2 \).

**Optical Absorption**

Optical absorption studies were performed in the range from 0.7-1.5 microns. The direct measurement was of the optical density \( D \) of the material under test. \( D \) is defined by the expression

\[ D = \log_{10} \frac{I_T}{I_o} \]  

(3.3)

where \( I_o \) is the intensity of the incident light and \( I_T \) is the intensity of the transmitted light. \( I_o \) and \( I_T \) are also related by the expression

\[ I_T = I_o \exp(-\alpha d) \]  

(3.4)

where \( \alpha \) is the absorption coefficient and \( d \) is the thickness of the film under test. Equations (3.3) and (3.4) may be combined to yield

\[ \alpha = (2.3 D)/d \]  

(3.5)
Refractive Index \( n \) vs \( \lambda \)

Sample \( \#P_2 \)

Figure 3.4
\( \varepsilon = 12 \)

Graph of \( n^2 \sim \lambda^2 \)

Sample \# \( P_2 \)

Figure 3.5

\( \lambda_{\tau} = 3.08 \mu \)
Hence, the results of the measurements of optical absorption can be readily presented in terms of the absorption coefficient $\alpha$.

Figure 3.6 shows the results of the measurements of $\alpha$ as a function of the energy of the incident photons. The data show the behaviour at both 300°K and 77°K.

**Electrical Measurements**

**Conductivity Versus Temperature**

The electrical conductivity of thin films of $\text{As}_2\text{Se}_3-\text{Sb}_2\text{Se}_3$ was measured over a temperature range from 230°K to 370°K. The samples were fabricated as discussed in Chapter II. Most of the data were on films with a bulk conductivity of about $10^{-9}$ mhos per cm at room temperature. Films with conductivities of this magnitude were considered "good." The conductance of these films was proportional to the area and inversely proportional to the thickness as would be expected for a well-defined conduction mechanism. Anomalous effects occurred in films of lower apparent conductivity. Some of these films showed an erratic "switching" behaviour. The conductance then did not show a well-defined dependence on film geometry.

Figure 3.7 shows a typical curve of conductivity versus $1/T$. The slope of this curve can be used to determine a thermal activation energy for current carriers. The value obtained from measurements averaged over ten samples is $1.64 \pm 0.02$ ev.
Optical Absorption Data
Sample – e₃

Absorption Coefficient, $\alpha^2 (\text{cm}^2 \times 10^6)$

Energy – $h\nu \text{ (ev)}$

Figure 3.6
$\sigma_o = 2.2 \times 10^2 \text{ (ohm} \cdot \text{cm.)}^{-1}$

Semilog Plot of Conductivity vs Reciprocal Temperature

from slope

$E = 0.83 \text{ ev.}$

Figure 3.7
Field Dependence of the Conductivity

Measurements were made of the conductivity for relatively high applied electric fields ($5 \times 10^5$ volts/cm maximum). These measurements were repeated at several different temperatures.

Typical data are shown on Figure 3.8. Here the logarithm of the current is plotted as a function of the square root of the volt-drop across the sample. The slope of this curve can be used to determine a value for the dielectric constant of the material. The intersection of the three curves yields an estimate of the field intensity required for electrical breakdown.

Photoconductivity

The conductivity of the samples was also measured as a function of the energy of incident light. The spectral response for a typical sample is shown in Figure 3.9. Here the photocurrent is normalized to the per unit incident power as measured with the optical power meter. These data can be used to yield a value for the optical band gap of the material. The value obtained for the curve shown is $E_{\text{ph}} = 1.7$ ev. It is clear from Figure 3.9 that thin films of $\text{As}_2\text{Se}_3-\text{Sb}_2\text{Se}_3$ are sensitive photoconductors over the range of visible light.

Noise Spectra

Some preliminary measurements were made of the fluctuations
Sample E_{3c}
Semilog Plot of I vs V^{1/2}

Figure 3.8
Photoconductivity Response
Sample # P₄

Figure 3.9
in current in biased samples. Figure 3.10 shows the equivalent noise resistance versus frequency. The spectrum shows a $1/f$ dependence over the entire range. It is, therefore, not possible to determine a single well-defined time constant. Rather it appears that a wide distribution of time constants is involved in the conduction process.

Figure 3.11 shows the results of noise measurements on one of the anomalous low resistance films described above. The noise spectrum approaches the value of the thermal noise of the sample at high frequencies. The excess low frequency noise again varies as $1/f$. 
Figure 3.10

NOISE SPECTRUM

EQUIVALENT CURRENT $I_{eq}$(amps)

FREQUENCY (Hz)
Figure 3.11

NOISE SPECTRUM
CHAPTER IV

ANALYSIS OF THE RESULTS

Introduction

This chapter is concerned with a discussion of the experimental results presented in Chapter III. It will be shown that the results are in good agreement with the proposed energy band model. The experimental data are used to determine the mobility of carriers, relaxation time, the dielectric constant of the material, and the energy gap.

Analysis of Optical Results

Measurements of the optical characteristics of the $\text{As}_2\text{Se}_3 - \text{Sb}_2\text{Se}_3$ films were made in the infrared region from 0.7-16 microns. The measurements from 0.7-2 microns were made on the Carry Model #14 spectrophotometer which most readily measures optical density of the material. From 2.5-16 microns the measurements were made on a Beckman Model #IR-10 system which readily measures optical transmission.

The optical transmittance spectra show maxima and minima because of interference effects. The difference in wavelength of adjacent maxima was used to determine the refractive index of the material. The method is described in detail in Appendix II. The refractive
index (see Figure 3.4) is relatively constant for long wavelengths and then increases sharply for short wavelengths. According to Maxwell's equation $^{13}$

$$\epsilon = n^2$$ (4.1)

the relative dielectric constant. The value $(2.26)^2 = 5.11$ obtained at very long wavelengths is in good agreement with other measurements of the dielectric constant of typical chalcogenide glass. $^5$ All of the transmittance curves of the $\text{As}_2\text{Se}_3-\text{Sb}_2\text{Se}_3$ films showed a sharp dip corresponding to strong absorption at $\lambda = 12.5$ microns. This is equivalent to strong absorption when photon energy is about 0.1 ev. and is evidence of an energy level in the band gap of the material.

Figure 3.3 shows a curve without this dip in transmittance. This result was obtained with a film of pure $\text{Sb}_2\text{Se}_3$ rather than the 60-40 composite film.

The same data used in Figure 3.4 are used again in Figure 3.5. This time they are presented as $n^2$ versus $\lambda^2$. As is discussed in Appendix II the intercept of the short wavelength and long wavelength asymptotes of this curve define a wavelength related to the reciprocal mean free life time of the carriers. The intercept occurs at $\lambda^2 = 10.0$ or $\lambda = 3.16$ microns. This corresponds to

$$\tau = 1.64 \times 10^{-15} \text{ sec}$$ (4.2)

The extrapolation to $\lambda^2 = 0$ yields the dielectric constant of the bound charges

$$\varepsilon_{\infty} = 12$$ (4.3)
The value of $\tau$ can be used to determine the mobility of carriers since $\mu = (q/m^*)\tau$. If one assumes $m^* = m$, the result is

$$\mu = 2.86 \text{ cm}^2/\text{volt-sec} \quad (4.4)$$

This low value is consistent with the results of electrical measurements as will be seen later.

The results of the optical absorption measurements are displayed as $\alpha^2$ versus photon energy $E_p$ in Figure 3.6. As described earlier $\alpha$ is the absorption coefficient. The curves show a change in slope with increasing energy. The increase is sharper at liquid nitrogen temperature than at room temperature. Both curves show little evidence of a significant tail. This is in agreement with the results reported by Platakis, et al.,$^{12}$ for this material in bulk form, and by Donovan, et al.,$^{14}$ and by Tauc$^{15}$ for amorphous germanium films. The intercept at $\alpha^2 = 0$ is defined as the minimum optical band gap. Accordingly, this yields

$$E_{\text{opt}} = 1.442 \text{ ev.} \quad (4.5)$$

at 300$^\circ$K, and

$$E_{\text{opt}} = 1.568 \text{ ev.} \quad (4.6)$$

at 77$^\circ$K. Assuming that the absorption edge depends linearly on temperature in this range (such a linearity has been assumed by Edmonds$^{16}$ for $\text{As}_2\text{Se}_3$) the thermal coefficient of the energy gap is given by

$$\beta = -5.3 \times 10^{-4} \text{ ev/}^\circ\text{K} \quad (4.7)$$

which agrees to the value reported by Kolomiets and Mamontova$^{17}$ for $\text{4As}_2\text{Se}_3-\text{As}_2\text{Te}_3$ glass.
The observed $\alpha^2$ ($E-h\nu$) dependence can be explained as follows. In crystalline semiconductors such a dependence is found\textsuperscript{18} if: a) the density of states in the valence band is parabolic; b) the conduction band is flat; and c) the probability of transition is independent of energy. Observed data (see Figure 3.6) of As\textsubscript{2}Se\textsubscript{3}-Sb\textsubscript{2}Se\textsubscript{3} films satisfy these conditions if transitions between occupied localized states in the valence band edge and the empty non-localized levels in the conduction band are considered. This is in good agreement with the proposed band diagram (see Figure 1.5).

**Analysis of Electrical Measurements**

**Low Field Conduction**

In a pure single crystal semiconductor the conduction can only occur by excitation of carriers across the energy gap $E_t$. Thus, the carrier concentration $n_i$ varies as

$$n_i = (N_c N_v)^\frac{1}{2} \exp\left(-\frac{E_t}{2k_B T}\right)$$

(4.8)

where $N_c$ and $N_v$ are, respectively, the densities of available states in the conduction and valence bands, $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature in degrees Kelvin. The conductivity $\sigma$ is given by

$$\sigma = n_i \mu q$$

(4.9)

Here $\mu$ is the carrier mobility and $q$ is the electronic charge. The mobility is a slightly decreasing function of temperature and hence

$$\sigma = \sigma_0 \exp\left(-\frac{E_t}{2k_B T}\right)$$

(4.10)
According to the proposed energy band model (discussed in Appendix I) electrical conduction in an amorphous semiconductor, can take place by: a) intrinsic excitation of non-localized states; and b) a hopping process between the localized states. The dc conductivity in the first case will vary as

$$\sigma = \sigma_0 \exp \left(-\frac{E_a}{k_B T}\right)$$

(4.11)

where \(\sigma_0\) is a slowly varying function of temperature, and \(E_a\) is the activation energy related to the width of the energy gap, \(k_B\) is the Boltzmann constant, and \(T\) is the temperature in degrees Kelvin. [Note the similarity between equations (4.10) and (4.11).] In the second process the conductivity caused by hopping would show a temperature dependence which could be expressed as

$$\sigma_H \sim \exp \left(-\frac{E_H}{k_B T}\right)$$

(4.12)

Here \(E_H\) is the activation energy required for the hopping process.

Experimental results\(^{19, 20, 21}\) indicate: a) that \(E_H\) is generally very small (<0.2 ev.); and b) that \(E_H\) is, itself, temperature dependent. The experimental result of this work, which were made on the highest quality (lowest conductivity) samples which could be fabricated, showed little evidence of the hopping mechanism. The thermal value of the energy gap is well defined. No impurity effects could be observed.\(^{10, 22}\) The data of Figure 3.7 are typical of the results of the conductivity measurements over a wide range of temperatures. The thermal value of the energy gap, averaged over 10 high quality samples was \(E_g(T) = 1.50\) ev. (see Appendix III), which is slightly larger than the optical gap of 1.442 ev.
It is important to attempt to explain the conduction mechanism. It has been proposed\(^2^3\), \(^2^4\) that the carrier transport can be viewed as a diffusion process rather than an intrinsic transport as is observed in pure crystal semiconductors. The transport occurs through non-localized states near \(E_c\), the edge of the mobility gap, for which the mean free path is of the order of the interatomic separation, \(a\). For such a transport mechanism the upper limit to the mobility is expressed as\(^2^4\)

\[
\mu \leq \frac{q a^2 \nu_{el}}{6 k_B T} \tag{4.13}
\]

where \(a\) is the interatomic distance, and \(\nu_{el}\) is the electronic frequency defined by \(\nu_{el} = \frac{E_e}{\hbar}\), \(E_e\) is the energy of the electron, and \(\hbar\) is the Planck constant. For typical values of \(\nu_{el} = 10^{15}\) per sec, \(a = 3.0\) Å the value of the upper limit to this mobility is then given by

\[
\mu \approx 5 \text{ cm}^2/\text{volt-sec} \tag{4.14}
\]

The deduced magnitude of the mobility from the optical data and the results of the conductivity measurements as discussed above, on \(\text{As}_2\text{Se}_3\)-\(\text{Sb}_2\text{Se}_3\) films are, hence, in good agreement with the diffusion model. Recent drift mobility measurements in amorphous silicon in conjunction with conductivity measurements\(^2^5\) also concur with this conclusion.

High Field Conduction

It is a well-established experimental fact\(^2^6\), \(^2^7\), \(^2^8\) that at
fields in excess of some $10^4$ volts/cm many dielectric films as well as amorphous semiconductor films $^{20, 29, 30}$ exhibit current voltage characteristics of the form

$$I \sim \exp \beta_F V^{\frac{1}{2}} \quad (4.15a)$$

with

$$\beta_F = \frac{q}{k_B T} \left( \frac{q \pi \epsilon \epsilon_0 d}{e} \right)^{\frac{1}{2}} \quad (4.15b)$$

Here $I$ is the current in amperes, $V$ is the volt drop across the sample, $\epsilon$ is the relative dielectric constant, $\epsilon_0$ is the dielectric constant of vacuum, and $d$ is the thickness of the film. This is evidence of either Schottky or Pool-Frenkel (PF) $^{31}$ effect.

It is clear that the curves of Figure 3.8 obey the equation (4.15a). The slope of the straight lines increases with decreasing temperature. This change is consistent with the PF theory. According to this theory the slope is determined from the equation (4.15b). For a typical temperature of $296.5^\circ K$, the value of this slope from the plot is 0.96. Using this value in equation (4.15b) the dielectric constant is given by

$$\epsilon = 6.65 \quad (4.16)$$

which is a reasonable value compared to 5.11 obtained from the optical data.

The lines extrapolated in the high field region meet at $V = V_B = 256$ volts. This then yields the field strength for the electric breakdown and is given by

$$F_B = 1.96 \times 10^6 \text{ volts/cm} \quad (4.17)$$
The curves also indicate that the slopes of $\ln I$ versus $1/T$ have a tendency of increasing from negative towards zero. Hence, the correct form of the equation (4.15a) should be

$$I \sim \exp\left[-\frac{3V}{q\epsilon\epsilon_0 d} \left(\frac{qV}{\pi\epsilon_0 \epsilon d}\right)^{1/2}\frac{1}{k_B T}\right]$$

\hspace{1cm} (4.18)

This is evidence of field-enhanced thermal emission from a localized level or trap level at $V_t$. The depth of the trap level is determined from the equation (4.18), using $V = V_B$, and is given by

$$V_t = 0.446 \text{ ev.}$$

\hspace{1cm} (4.19)

The trap depth may correspond to a maximum in the statistical distribution of localized levels. These levels may be due to structural defects, short range order fluctuations. Results of Kolomiets, et al., for $Tl_2 SeAs_2 Te_3$ and $As_2 Se_3$ glasses also show evidence of trap levels.

The physical model, in agreement with the observed high field transport behaviour, for $As_2 Se_3$-$Sb_2 Se_3$ films is schematically displayed by Figure 4.1.

**Photoconductivity**

The spectral response of the photoconductivity is displayed in Figure 3.9. There is no wavelength at which the response vanishes completely. In such a case the band gap is defined as the energy at which the response has fallen to half value. This yields
Figure 4.1

HIGH FIELD EMISSION MODEL
\[ E_{ph} = 1.70 \ (\pm \ 0.02) \ \text{ev.} \quad (4.17) \]

as the photoconductivity gap.

This implies an intrinsic gap for the following reasons: a) the absorption due to localized states would not give rise to photoconductivity; and b) the recombination time for transitions from the tail of the valence band to the non-localized states in the conduction band might be considerably less than that for the intrinsic process.

The difference between the photoconductivity gap, \( E_{ph} \), and the optical gap, \( E_{opt} = 1.442 \ \text{ev.} \), can be explained as follows. The photoconductivity results from the carriers, which are excited from the non-localized states in the valence band to the non-localized states in the conduction band, whereas the optical gap is due to the transitions of the carriers from the localized states in the valence band edge to the non-localized states in the conduction band.

**Noise Spectra**

Figure 3.10 shows the equivalent noise resistance versus frequency. The measurements were made on samples of \( \text{As}_2\text{Se}_3-\text{Sb}_2\text{Se}_3 \) films of well-defined conductivity. The spectrum shows a \( 1/f \) dependence over the entire range. It is, therefore, not possible to define a single well-defined time constant. Rather, it appears that a wide distribution of time constants is involved in the conduction process.
Figure 3.11 shows the results of noise measurements on one of the anomalous low resistance films described in Chapter III. The noise approaches the value of the thermal noise of the sample at high frequencies. The excess low frequency noise again shows a $1/f$ dependence.
CHAPTER V

CONCLUSION

Summary

The important optical and electrical parameters of amorphous As$_2$Se$_3$-Sb$_2$Se$_3$ films obtained during this investigation are compiled in Table 5.1. Some significant contributions of this work are:

a) development of a band model, based on previous work on amorphous solids;

b) the successful analysis of the experimental data on evaporated films of As$_2$Se$_3$-Sb$_2$Se$_3$ using the proposed model; and

c) the determination of structure-sensitive, device-oriented parameters.

The transport mechanism and the optical absorption were studied in terms of this model and found to be quite consistent. The transitions from the localized states in the valence band edge to the empty non-localized states in the conduction band were found to explain satisfactorily the observed $\alpha^2$-E behaviour. The minimum optical gap, $E_{opt} = 1.442$ ev. was obtained. The observed dc conductivity was found to be consistent with a diffusion process. This behaviour was found to be predominant due to the non-localized states across the mobility gap. A thermal activation energy (mobility gap) $E_g(T) = 1.50$ ev., was found. The high field conductivity was found to obey field enhanced thermal emission (PF-law) from a deep
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistivity (ohm-cm) at 300°K</td>
<td>$\pm 10^9$</td>
</tr>
<tr>
<td>Mobility (cm$^2$ V$^{-1}$ sec$^{-1}$) at 300°K</td>
<td>$&lt; 5$</td>
</tr>
<tr>
<td>Optical band gap (ev) at 300°K</td>
<td>1.442</td>
</tr>
<tr>
<td>Optical band gap (ev) at 77°K</td>
<td>1.568</td>
</tr>
<tr>
<td>Temperature coefficient of optical band gap</td>
<td>$-5.3 \times 10^{-4}$</td>
</tr>
<tr>
<td>Electrical band gap (ev) at 300°K</td>
<td>1.50</td>
</tr>
<tr>
<td>Breakdown strength (volts/cm)</td>
<td>$\approx 2 \times 10^6$</td>
</tr>
<tr>
<td>Photoconductivity gap (ev) at 300°K</td>
<td>1.7 ($\pm 0.02$)</td>
</tr>
<tr>
<td>Refractive index (at 5 microns and 300°K)</td>
<td>2.26</td>
</tr>
<tr>
<td>Dielectric constant (static)</td>
<td>5.11</td>
</tr>
<tr>
<td>Relaxation time (sec)</td>
<td>$1.63 \times 10^{-15}$</td>
</tr>
</tbody>
</table>
The dielectric constant estimated from this PF-mechanism agreed reasonably well with that determined from the optical data. The photoconductivity was observed to be intrinsic, yielding the band gap, $E_{ph} = 1.7 \pm 0.02$ ev. at $\lambda_2$.

**Suggestions for Future Work**

An experimental study of transport behaviour and its relation to process parameters such as substrate temperature, evaporation rate, and the composition of the films would be relevant. It would be of immediate interest to investigate the nature of the trap distribution in the band gap to understand fully the photoconductivity process. This could be investigated by measuring:

a) temperature dependence study of photoconductivity at various light intensities;

b) thermally stimulated current; and

c) photoconductivity decay experiment.

The independent measurement of the mobility and its temperature dependence would help substantiate the proposed band model and the transport behaviour.

The technique of sputtering should be capable of producing high quality amorphous films because temperatures close to room temperature are maintained throughout the system. A systematic study of electrical and optical properties of films produced by this process would be in order.
APPENDIX I

BAND STRUCTURE OF AMORPHOUS SOLIDS

The usual derivation of an energy band model assumes an ideal periodic crystalline structure. However, this assumption of long range order is not required for the existence of an energy band structure. X-ray diffraction studies of many non-crystalline materials (materials in which only short range order can exist) show patterns characteristic of well-defined order.

The electrical conductivity of metals shows very little change when the material changes from a single crystal solid state to the (amorphous) liquid state. The disappearance of long range order can, therefore, have only a very small effect on the density of quantum states.

The temperature dependence of the electrical conductivity of many well-known amorphous materials shows a negative temperature coefficient similar to that of single crystal semiconductors. This gives strong evidence for an energy gap.

Application of the quantum theory to these materials should, therefore, begin with the assumption that: a) the energy band model applies; and b) that perfect short range order exists. Then with appropriate incorporation of the effects introduced because of the long range disorder a one-dimensional band model can be derived. This can be accomplished as follows.
Consider the change in the periodic potential $V(x)$ when the single crystal solid is disordered (see Figure I.1). Because of fluctuations in the distance between neighbouring atoms, this periodic potential $V(x)$ shows fluctuations of two types: 1) the locations of the maxima and minima of the periodic potential shift in a random fashion; and 2) the magnitude of the maxima and minima of the periodic potential fluctuate randomly. Fluctuations in the spacing would disturb the periodicity of $V(x)$. However, by transforming the $x$-coordinate of the periodic potential $V(x)$ to a distorted coordinate $\xi$ such that

$$\frac{d\xi}{dx} = \frac{1}{1+\epsilon_d \gamma}$$

Where $\epsilon_d << 1$ is a constant parameter that characterizes the degree of disorder, and $\gamma$ describes the statistical nature of the value of the distance between each pair of adjacent atoms so that $\bar{\gamma} = 0$ and $\gamma^\prime = 1$. One obtains a periodic function $V(\xi)$ and, consequently, the Schrödinger equation for a system with a periodic potential $V(\xi)$ plus some perturbing terms is obtained for the disordered lattice.

The detailed analysis shows that the essential features of the crystalline lattice band structure are retained except for a smearing or "tailing" of the band edges. Thus, the effective band gap becomes narrower in the disordered material. Numerical solutions obtained for a disordered chain using irregularly spaced $\Delta$-type potential barriers as shown in Figure I.2 also reveal this general characteristic.

Next consider the effect of fluctuations in the magnitude of the maxima and minima of the periodic potential $V(x)$. These magnitudes
Figure I.1(a)

A regular (crystalline) one-dimensional array of atoms with spacing $a$.

Figure I.1(a)

Potentials of atoms in figure I.1(a)
Figure I.1(c)

A disordered (glassy) one-dimensional array of atoms

Figure I.1(d)

Potentials of atoms in figure I.1(c)
Figure 1.2(a)

A disordered one-dimensional array of atoms

Figure 1.2(b)

Corresponding $S$-barrier model (Reference 40)
fluctuate randomly because of the following interrelated causes: a) a random potential at each atom; b) fluctuations in the density or in interatomic distance; and c) fluctuations in the boundaries defining the regions of short range order. Many of the potential wells will have the depth and width necessary to act as traps. As a result, some band (or allowed) states which are represented by (Bolch) wave functions become localized in the disordered state. The suggestion that, in an amorphous material, there might be traps or localized states for an electron with energies lying in a continuous range below the conduction band was first made by Fröhlich. 41

In doped and compensated semiconductors the energy states of an electron in the impurity band are normally assumed localized. The theories of impurity band conduction developed by Miller and Abrahams, 42 Mott and Twose, 43 Pollak 44, 45 and others are based on this assumption. Localization means that the wave function has a probability amplitude decreasing exponentially with distance from the center of localization. An electron in the localized state is effectively trapped by the disordered lattice and it can move from one localized state to another only by "hopping." This hopping process of conduction occurs in an energy gap in a disordered lattice in which the mobility is negligible so that the dc conductivity is zero at low temperature. This energy gap has been described as "mobility gap" 46 (or limits of the localization regions) in contrast with the conventional crystalline semiconductor band gap in which the density-of-states is zero. The density-of-states, thus, has a tail toward the extremities
of each band in which the states are localized as shown by the shaded area in Figure I.3. 47, 48

From the above discussion it can be concluded that in spite of the absence of a periodicity in the disordered materials, the essential features of the band structure are retained. However, at the extremities the band edges become smeared and because of the random fluctuations in potential wells some of the states enter into the forbidden gap and become localized. This, therefore, reduces the effective band gap. The non-localized states retreat deeper into the energy bands.

Relevant to the discussion and consistent with the observed electrical and optical properties of amorphous As$_2$Se$_3$-Sb$_2$Se$_3$ films, the energy band diagram can be proposed as shown schematically in Figure I.4, with appropriate density-of-states diagram drawn also schematically in Figure I.5. The electrical and optical data on these films are analyzed, using this band model, in Chapter IV.
Figure I.3

Density-of-states in a disordered lattice
Figure I.4
Proposed Energy-Band Diagram of Amorphous: As$_2$Se$_3$-Sb$_2$Se$_3$ Films

--- --- --- gap width
(for strictly periodic system)

\[
\text{localized states}
\]
\[
\text{non-localized states}
\]
Figure I.5 PROPOSED DENSITY of STATES for AMORPHOUS $\text{As}_2\text{Se}_3\text{Sb}_2\text{Se}_3$ SYSTEM

$E_{\text{ph}}$ Photoconductivity Gap
$E_{\text{opt}}$ Absorption Edge
$E_g(T)$ Mobility Gap

Non-Localized Region

/// Localized Region
APPENDIX II

DISPERSION RELATION

The classical theory of absorption and dispersion of a free electron gas leads to the following expressions for the optical constants:

\[
n^2 - k^2 = \varepsilon_\infty \left[ 1 - \frac{2 \omega_p^2}{1 + \omega^2 \tau^2} \right]
\]  

(II.1a)

and

\[
2nk = \frac{2}{\nu_p} \varepsilon_\infty \left[ \frac{\tau}{\omega (1 + \omega^2 \tau^2)} \right]
\]  

(II.1b)

\(n\) is the refractive index, \(k\) is the extinction coefficient, \(\varepsilon_\infty\) is the optical dielectric constant arising from the combined effects of the bound charges, \(\tau\) is the relaxation time, \(\omega_p\) is the plasma frequency, and \(\omega\) is the frequency defined by \(\omega = \frac{2\pi c}{\lambda}\), with \(c\) the velocity of light, and \(\lambda\) the free space wavelength. These equations may be simplified for the limiting cases of high and low frequencies. In the first case \((\omega^2 \tau \gg 1)and n^2 > k^2 which is true in the range where these equations are applicable, the equation (II.1a) reduces to

\[
n^2 = \varepsilon_\infty \left[ 1 - \frac{2}{\omega_p^2} \right]
\]  

(II.2a)

whereas for low frequencies \((\omega^2 \tau \ll 1) equation (II.1a) reduces to

\[
n^2 = \varepsilon_\infty \left[ 1 - \frac{2 \omega_p^2 \tau^2}{\omega^2} \right]
\]  

(II.2b)

so that \(n^2\) does not depend any more on \(\lambda\). \(\tau\) is related to the free carrier mobility \(\mu\) by.
REFRACTIVE INDEX 'n' AND ITS DETERMINATION

When a ray of light is incident on a thin parallel sheet of transparent material, multiple reflections take place inside the sheet and at selected wavelengths constructive and destructive interference will occur in the reflected transmitted beams. If a spectral measurement of the transmission $T_0$ is carried out, a series of fringes will be obtained. The values of the wavelengths at which $T_0$ shows maxima and minima can be used advantageously to determine the refractive index $n$. The condition for the occurrence of extremum values for $T_0$ are

$$4n \lambda = g \lambda \left[ 1 - \frac{(\theta_{af} + \theta_{fs})}{\pi g} \right]$$

(II.4)

where $g$ is an integer. The parameters $\theta_{af}$ and $\theta_{fs}$ are phase angles due to reflections at the air-film (af) and film-substrate (fs) interfaces and are given by

$$\tan \theta_{af} = \frac{2k}{(n_a^2 - n_1^2 + k^2)}$$  \hspace{1cm} (II.5a)

and

$$\tan \theta_{fs} = \frac{2n_1k}{(n^2 - n_1^2 + k^2)}$$  \hspace{1cm} (II.5b)

where $n_1$ is the refractive index of the non-absorbing substrate.

In the films under investigation for $n = 2.26$, $k = 10^{-3}$ and $n_1 = 1.5$, which are typical numbers, the values of $\theta_{af}$ and $\theta_{fs}$ are negligibly small ($< 10^{-3}$). Thus, the simplified form of equation (II.4)

$$4n \lambda = g \lambda$$

(II.6)
may safely be used to determine \( n \), provided \( g \) is known. There is the difficulty that in general the order of the fringe (i.e., the value of \( g \)) is not known. The usual method of overcoming this difficulty is to measure the wavelengths of two adjacent transmission maxima, for example, and apply the equations giving

\[
4\pi d = g\lambda_1 \quad \text{(II.7a)}
\]

\[
4\pi d = (g+1)\lambda_2 \quad \text{(II.7b)}
\]

solving these two equations gives the value of \( g \)

\[
g = \frac{\lambda_2}{(\lambda_1 - \lambda_2)} \quad \text{(II.7c)}
\]

and, hence, gives \( n \) at various wavelengths using equation (II.6).
APPENDIX III

MOBILITY GAP

In crystalline semiconductors the energy gap determined from a plot of log $\sigma$ versus $1/T$ is generally not in good agreement with that deduced from optical absorption or photoconductivity experiments. The reason for the discrepancy is that the energy gap itself is temperature dependent. This is also found in amorphous materials. The true activation energy can then be determined as follows:

Assume that all terms but the linear term in a Taylor series expansion of $E_g(T)$ are negligible. To a first approximation $E_g(T)$ can, therefore, be written as

$$E_g(T) = E_g(0) + \beta T$$  \hspace{1cm} (III.1)

Thus, the energy gap corresponding to the slope of a log $\sigma$ versus $1/T$ plot is the energy gap at $T = 0^\circ K$. Therefore, from Figure 3.7 this energy gap is

$$E_g(0) = 1.64 \pm 0.02 \text{ ev.}$$  \hspace{1cm} (III.2)

With $\beta = -5.3 \times 10^{-4} \text{ ev./}^\circ\text{K}$, from the optical data, the true energy gap, called the "mobility gap," at room temperature is given by

$$E_g(T) = 1.50 \text{ ev.}$$  \hspace{1cm} (III.3)

This value is used in comparing with that obtained from the optical absorption measurements in the band diagram (see Figure 1.5).
BIBLIOGRAPHY


Pundlik K. Chaudhari was born April 15, 1930, in Nanded, India. In June, 1949, he was graduated from Pratap High School in Amalner, India. He received, in June, 1953, the degree of Bachelor of Science from the University of Poona, India, and in June, 1957, the Degree of Bachelor of Electrical Engineering from the Gujarat University, also in India. From June, 1957, to August, 1960, he served as a lecturer in Electrical Engineering, Engineering College, Poona, India. In June, 1962, he received the Degree of Master of Science in Electrical Engineering from the University of Toledo. From June, 1962, to August, 1963, he served as an Assistant Electrical Engineer at Owens-Illinois Technical Center, Toledo, Ohio. From September, 1963, to March, 1966, he was employed as a graduate assistant in the Department of Electrical Engineering, Syracuse University and did some graduate work. From June, 1966, to August, 1968, he was a Senior Associate Engineer at IBM Corporation. In September, 1968, he entered the Graduate School of the University of Florida and was employed as a graduate assistant in the Department of Electrical Engineering. He has held that position until the present time while he pursued his work toward the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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