D.C. PHOTOCONDUCTIVITY IN As_2Se_3 THIN FILMS

by

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ABSTRACT

D.C. PHOTOCONDUCTIVITY IN As_2Se_3 THIN FILMS

In this thesis, the D.C. photoconductivity in amorphous thin films of As_2Se_3 is investigated. The temperature dependence of dark, and photo currents are explored at the interval 240 - 360 K. Three regimes are observed in the photoconductivity at the given range of temperature. The results are criticized according to the theory and other data and found to be in accordance with them.

As₂Se₃ **İNCE FİLMLERDE D.C. FOTOİLETKENLİK**

Bu tezde As_2Se_3 ince filmlerde D.C. fotoiletkenlik incelenmiştir. Karanlık ve foto akımların 240 – 360 K aralığında sıcaklığa bağlı değişimleri araştırılmıştır. Fotoiletkenlikte verilen sıcaklık aralığında, üç ayrı rejim gözlenmiştir. Sonuçlar teoriyle ve diğer deney sonuçlarıyla karşılaştırılmış ve sonuçların onlarla uyumlu olduğu görülmüştür.

TABLE OF CONTENTS

AC	CKNC	OWLED	OGEMENTS	iii
AF	BSTR	ACT		iv
ÖZ	ZET			v
LI	ST O	F FIGU	JRES	vii
LI	ST O	F SYM	BOLS/ABBREVIATIONS	ix
1.	INTRODUCTION			
2.	THE	EORY		2
	2.1.	Order	and Disorder in Solids	3
	2.2.	Classif	fication of Amorphous Solids	4
	2.3. Electrical Properties of Semi-conductors			
		2.3.1.	Perfect Crystals	6
		2.3.2.	Nearly-Perfect Crystals	7
		2.3.3.	Amorphous Semi-conductors	8
			2.3.3.1. Photoconductivity in Amorphous Semi-conductors	11
	2.4.	As_2Se	$_3$ and its Properties \ldots \ldots \ldots \ldots \ldots \ldots	14
3.	EXF	PERIMI	ENTAL WORK AND RESULTS	18
	3.1.	Measu	rement Setup	18
	3.2.	Result	s of the Measurements	19
		3.2.1.	Dark Conductivity	20
		3.2.2.	Photoconductivity	21
4.	CON	CONCLUSION		
RE	EFER	ENCES	3	24

,

LIST OF FIGURES

Figure 2.1.	Resistivity as a function of temperature for several materials in	
	both crystalline and liquid states. The melting temperatures are indicated by an arrow	3
Figure 2.2.	Radial distribution function for amorphous Ge	4
Figure 2.3.	Schematic temperature dependence of mobility with both lattice and impurity scattering	9
Figure 2.4.	Various forms proposed for the density of states in amorphous semi- conductors. Localized states are shown shaded	10
Figure 2.5.	Temperature dependence of photocurrent in chalcogenides. The broken line is the dark current (schematic)	12
Figure 2.6.	Temperature dependence of recombination lifetime (ns) in amor- phous $AsTe_3$: A, 2×10^{18} photons $cm^{-2}s^{-1}$; B, 1.2×10^{19} photons $cm^{-2}s^{-1}$; C, 2.3×10^{19} photons $cm^{-2}s^{-1}$	14
Figure 2.7.	Temperature dependence of recombination lifetime in amorphous As_2Se_3 for 10^{15} (upper curve) and 2×10^{15} photons $cm^{-2}s^{-1}$	15
Figure 2.8.	Two possible structures for As_2Se_3 : (a) layers, (b) chains	16
Figure 2.9.	Temperature dependence of electrical conductivity in some amor- phous chalcogenide semiconductors, illustrating the relationship $\sigma = Ce^{-E/kT}$. Heavy lines are the experimental results and fine lines are the extrapolation to $1/T = 0$. (3); As_2Te_3 , (7); As_2Se_3 , (8); As_2S_3	17

Figure 3.1.	Measurement setup	19
Figure 3.2.	The voltage dependence of the dark-current at 313 K \ldots	20
Figure 3.3.	The temperature dependence of the dark current, at 10 V, in the temperature range $240 - 360$ K	21
Figure 3.4.	The temperature dependence of the photocurrent, together with the dark current, at 10 V, in the temperature range $240 - 360$ K .	22

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LIST OF SYMBOLS/ABBREVIATIONS

b	Probability per unit time per carrier density
E	Energy
E_a	Activation Energy
E_c	Conduction band energy level
E_F	Fermi energy
E_g	Energy gap
F	Electric field
G	Generation rate
Ι	Current
i_d	Dark current
i_p	Photocurrent
j_d	Dark current density
j_p	Photocurrent Density
k	Boltzmann's Constant
k	Wave vector
L	Mean free path
m	Mass
m^*	Effective mass
n	Carrier concentration
N_c	Effective density of states for electrons
N(E)	Density of states
Δn	Excess carrier density
p ·	Momentum
r	Position
R	Lattice vector
Т	Temperature
V	Potential

Phase

 θ

μ	Mobility
σ	Conductivity
au	Lifetime
ϕ	Wave function

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CFO Cohen, Fritzche, Ovshinsky

1. INTRODUCTION

Amorphous semiconductors form a large class of semiconductors, differing significantly from the crystalline variety, in their electrical and optical properties. The mathematical procedure to investigate them, is significantly more difficult than the one used for the crystalline semiconductors, due to the lack of symmetry and order. Still, amorphous materials can be produced cheaply and easily. This makes them attractive to be explored and used in industry. Photoconductivity is one of the important applications.

 As_2Se_3 is a chalcogenide semiconductor, which is investigated extensively. It is significantly photoconductive. In this thesis, the photoconductivity of As_2Se_3 thin films will be explored.

In the following sections, first the theoretical background of the amorphous semiconductors will be laid. The theory of the crystalline semiconductors will be briefly mentioned, then the amorphous theory will be developed, and the photoconductivity will be built upon the amorphous theory. Next the experimental setup and the procedures followed will be explained. At the conclusion, the compatibility of the results of the photoconductivity experiments in As_2Se_3 thin films, with the theory, and experiments performed by others will be explored.

2. THEORY

The term "non-crystalline" is self-explanatory, a non-crystalline (or amorphous) solid, liquid or glass, is "not-crystalline" on any significant scale. The principal structural order is governed by the approximate separation constant of nearest-neighbor atoms or molecules. The x-ray or neutron diffraction pattern of an amorphous material consists of one or more broad diffuse rings, when viewed on the plane normal to the incident beam. The pattern due to powdered crystalline material consists of a large number of sharp rings. This leads us to the result that the material doesn't have a unit of structure, repeating itself at periodic intervals, in three dimensions. For crystalline powder samples of smaller and smaller particle size, the pattern lines broaden continuously for small enough particle size, the pattern becomes similar to the amorphous one, which is in accordance with the above argument [1].

The major puzzle with amorphous solids is the non-periodicity. For the periodic case, Bloch's Theorem is in charge, which implies delocalized states, leading to the observed electrical properties of the solids. It seems that periodicity is of vital importance to the electrical conductivity of the given material. However, this suggestion can be tested easily. When the material undergoes the transition from the periodic to the non-periodic structure, namely, in the melting temperature, metals remain metals, insulator remain insulators, and semi-conductors remain semi-conductors (with the exception of materials which change their nearest neighbor environments upon melting). Typical results are shown in Figure 2.1. The importance of long-range periodicity is overemphasized. However, it is still of great importance, it enables us to solve the problem quantitatively. Without the perfect long-range order, one would have to solve the quantum mechanical problem of $\sim 10^{24}$ interacting electrons, moving in the fields of $\sim 10^{23}$ mutually interacting ion cores, arranged in an irregular pattern.

An important aspect in amorphous solids is, they exhibit a high degree of short range order. X-ray and electron diffraction results show that the nearest neighbor environments in amorphous Ge and Si are almost precisely the same as in the corresponding



Figure 2.1. Resistivity as a function of temperature for several materials in both crystalline and liquid states. The melting temperatures are indicated by an arrow [2] crystal. However, beyond about fifth-nearest neighbors the atoms are distributed nearly uniformly. In Figure 2.2, short range order and long range disorder for amorphous Ge can be seen [2].

2.1. Order and Disorder in Solids

Some statements about long/short range disorder are made, so, a few words about order and disorder in solids may be useful. In solids, one can distinguish between compositional, positional, magnetic (spin) and electronic order. A perfect crystal in its ground state has perfect order. An imperfection in compositional order is an impurity, an imperfection in positional order is a defect, an imperfection in the magnetic order (of systems with atoms having a non-vanishing magnetic moment) is a reversed



Figure 2.2. Radial distribution function for amorphous Ge [2]

spin, an imperfection in the electronic order is an excited atom. There are also dynamic imperfections, which can be associated with all types of order, except compositional order. Phonons (lattice vibrations) perform dynamic positional disorder, magnons (spin waves) bring magnetic disorder, plasmons (plasma oscillations) in metals, and excitons in insulators lead to dynamic electronic disorder. At high temperatures complete disorder can occur. Since electrons are extremely light compared to the massive ion cores, they quickly adjust to changes of the state of the ion cores (adiabatic approximation). Thus the electronic energy levels are extremely sensitive to variations of composition, ionic position, and spin orientation [2].

2.2. Classification of Amorphous Solids

Amorphous solids are classified as the crystalline solids, i.e. by the type of the chemical bonding, which is the primarily responsible for the cohesive energy of the material. In crystalline solids, the major classes are ionic, covalent, metallic, van der Waals, and hydrogen-bonded materials. This classification method can also be used for the amorphous solids.

The field of amorphous semi-conductors can be broken down into ionic and covalent materials. The covalent materials will be grouped into two classes. The first one is purely elemental including materials such as Si, Ge, S, Te, Se, etc. The other class includes binary materials such as As_2Se_3 and GeTe, and multi-component materials such as boride, arsenide, and chalcogenide glasses. Being primarily covalent, the chemical composition can vary, as an example, As_2Se_3 does not have to contain 40% As and 60% Se. Since the material is amorphous, the crystalline structure doesn't rule, defects, dangling bonds, etc. are not problems. This signifies that covalent amorphous semi-conductors always have compositional, as well as positional disorder.

Before starting a more rigorous approach to the amorphous semi-conductor theory, some aspects should be mentioned. First, one-electron approximation in the crystal counterpart of the theory is still valid (at least for the extended states). This approximation primarily depends on the interatomic spacing, which equally applies on the amorphous semi-conductors. Secondly, N(E), density of states (the number of oneelectron states per unit volume in an infinitesimal energy range between E and E+dE), and μ , mobility (electronic velocity per applied electric field) are two vital concepts. In a perfect crystal, all states are delocalized, and the mobility of a state is infinite. But in real systems scattering mechanisms due to disorders severely limits the mobility. In addition to this, all states may be localized, so, charge can be transported due to tunneling between overlapping localized states, in this case mobility sensitively depends on the density of states [2].

2.3. Electrical Properties of Semi-conductors

A short discussion about Energy-Band Theory of Crystals may be useful to understand the non-crystal counter-part.

2.3.1. Perfect Crystals

With the adiabatic approximation in charge, Schrödinger equation for the electronic problem can be stated as

$$\sum_{i} \left[\frac{\mathbf{p}_{i}^{2}}{2m} + V(\mathbf{r}_{i}) + \frac{1}{2} \sum_{j \neq i} \frac{e^{2}}{|\mathbf{r}_{i} - \mathbf{r}_{j}|} \right] \phi_{n}(\mathbf{r}_{i}) = E_{n} \phi_{n}(\mathbf{r}_{i})$$
(2.1)

where \mathbf{p}_i and \mathbf{r}_i are the momenta and positions of the i_{th} electron. $V(\mathbf{r}_i)$ contains both the attractive potential between an electron and all the ion cores, and the (constant) mutual repulsion of the ion cores. Equation 2.1 is solved for the electron energy levels, E_n . $V(\mathbf{r}_i)$ is also periodic;

$$V(\mathbf{r}_i + \mathbf{R}_i) = V(\mathbf{r}_i) \tag{2.2}$$

for any lattice vector \mathbf{R}_i . The single-particle approximation cancels the electronelectron interaction term, putting it into $V(\mathbf{r}_i)$ as a contribution.

For a perfect crystal since $V(\mathbf{r}_i)$ is periodic, the eigenstates must be Bloch states, of the form

$$\phi_{n,k}(\mathbf{r}_i + \mathbf{R}_i) = e^{i\mathbf{k}\cdot\mathbf{R}_i}\phi_{n,k}(\mathbf{r}_i)$$
(2.3)

where the label \mathbf{k} is a vector characterizing the translational behavior of the eigenfunction, and n is a positive integer called band index. \mathbf{k} is real and restricted to a given set of values called the first Brillouin zone. A result of the reality of \mathbf{k} is

$$|\phi_{n,k}(\mathbf{r}_i + \mathbf{R}_i)|^2 = |\phi_{n,k}(\mathbf{r}_i)|^2$$
(2.4)

for any \mathbf{R}_i . So any electron is equally likely to be in any primitive cell of the crystal, i.e. all states are delocalized. A second result is the phase coherence of the single-particle eigenfunctions. If the phase of $\phi_{n,k}(\mathbf{r}_i)$ is taken to be $\theta_{n,k}(0)$ at $\mathbf{r}_i = 0$ then

$$\theta_{n,k}(\mathbf{R}_i) = \theta_{n,k}(\mathbf{0}) + \mathbf{k} \cdot \mathbf{R}_i \tag{2.5}$$

A qualitative understanding of the formation of bands can be obtained by considering tight-binding approximation, in which a crystal is built up from an array of N atoms with infinite nearest-neighbor separation. In this limit the energy eigenvalues are the atomic energy levels. All the electron energy levels are the same for each of the N atoms, thus, any s level is 2N-fold degenerate, any p level is 6N-fold degenerate, so on, so forth. As the lattice parameter is reduced, an electron in an atom begins to feel the presence of the nearest-neighboring atoms, these enormous degeneracies are lifted. Provided that the interactions between atoms are small, the levels will not move very much in energy, but the atomic levels will spread into a narrow energy band. The importance of this argument is that, it doesn't depend on periodicity. The concepts of allowed and forbidden single-electron energies are independent of crystallinity. However, the delocalization of electron states can be established for periodic systems.

In a perfect crystal conduction occurs by means of thermal excitation of electrons and holes across the band gap, E_g , and the conductivity is given by [2]

$$\sigma = \sigma_0 e^{-E_g/2kT} \tag{2.6}$$

2.3.2. Nearly-Perfect Crystals

The introduction of defects and impurities destroys the periodicity, therefore the applicability of Bloch's theorem. However, if these have small densities, Bloch states become approximate eigenstates, and scattering between states having different **k**'s is introduced. Now, parameters such as the lifetime, τ (the average time an electron remains in a Bloch state), the mean free path, L (the average distance traversed by an electron before scattering into another Bloch state) will be introduced. Scattering

brings finite mobility, which may be written as

$$\mu = \frac{e\tau}{m^*} \tag{2.7}$$

 m^* being the effective mass of the electrons. $L = v\tau$, where v is the average electron velocity, so mobility is proportional to mean free path.[2] The electron conductivity will take the form

$$\sigma = en\mu_n \tag{2.8}$$

and the corresponding concentration of electrons will be

$$n_0 = N_c e^{-(E_c - E_F)/kT} (2.9)$$

where N_c is the effective density of states for the electrons, E_c is the conduction band level, E_F is the Fermi energy, determined by the impurities. The case for hole conduction will be vice versa [3].

2.3.3. Amorphous Semi-conductors

Two important assumptions made in the previous two sections may not always be valid. The first one is the adiabatic approximation, namely, the electronic problem is independent of the motion of ion cores. The second one is, electronic correlations are negligible. If a material is insulating, even if the single particle approximation predicts metallic behavior, it is called a Mott insulator. So, even for perfect crystals, the solutions may not be delocalized Bloch states, electronic correlation may lead to localization. In a Mott insulator, a single free electron and a single free hole attract each other, form a bound state called exciton, and lose their roles in the conduction process.

The lattice vibrational quanta are called phonons. There always exist lowfrequency long-wavelength oscillations called acoustic phonons. If more than one type



Figure 2.3. Schematic temperature dependence of mobility with both lattice and impurity scattering [3]

of atom are included in the material, high-frequency long-wavelength oscillations occur, called optical phonons. These optical phonons couple with the electrons, invalidating the adiabatic approximation. This electron-phonon coupling can be thought as a quasiparticle called polaron. The polaron has lower energy than the corresponding electron, but larger effective mass, carrying the lattice distortion as it travels through the material. A localized polaron can contribute to conduction by hopping between equivalent sites. In this case the temperature dependence of mobility will be in the form

$$\mu = \mu_0 e^{-E_a/kT} \tag{2.10}$$

where E_a is the energy necessary for a polaron to hop. This dependence can be used to distinguish between hopping conduction and standard band conduction, which in low temperature region increases (due to impurity scattering) and high temperature region decreases (due to lattice scattering) with temperature. The schematic T dependence of μ for standard band conduction can be seen in Figure 2.3.

The corresponding concept in amorphous semi-conductors for conduction and valence bands in periodic semi-conductors is the mobility edge. The mobility edge separates the localized and delocalized states. In the mobility gap conduction is due to hopping. The delocalized states in the amorphous semi-conductors are not Bloch



Figure 2.4. Various forms proposed for the density of states in amorphous semi-conductors. Localized states are shown shaded [4]

states.

There have been several models proposed for the crucial concept density of states, N(E), in the field of amorphous semi-conductors. For the perfect crystal case, $E^{\frac{1}{2}}$ dependence is obtained, neglecting all the electronic correlations and ion cores, while the effect of ion cores are included via the effective mass, m^* . These two assumptions are not valid in our case. Some important models can be seen in Figure 2.4. The models in Figure 2.4 are the following: (a) Overlapping conduction and valence band tails due to Cohen *et al*, the CFO (Cohen, Fritzsche, Ovshinsky) model; (b) a real gap in the density of states appropriate for a continuous random network without defects; (c) the same as (b) with a partially compensated band of defect levels; (d) the same as (b) with overlapping bands of donor (E_Y) and acceptor (E_X) levels arising from same defect [4].

The effects of the (localized) states can be briefly stated as;

- pinning the Fermi energy
- deviations from the straight line plot of $\log\sigma$ versus $\frac{1}{T}$
- providing recombination centers for electrons and holes (for instance in photoconduction).

2.3.3.1. Photoconductivity in Amorphous Semi-conductors. When a photon is absorbed, an electron-hole pair is created. These electrons and holes can contribute to the conduction while they survive. The following analysis will be valid for situations in which G, the number per volume, per time of free electrons and holes produced by the radiation, will be equal to the number of photons absorbed. j_p is defined as the excess current density produced by the radiation. In this analysis, it is assumed that only one type of carrier contributes to the conduction process, which can be generalized to the case when both contribute. There are two cases of interest.

In the first case, electron and holes are trapped, they do not escape, and they recombine from these trap states, which are near the Fermi level. In this case j_p is proportional to G (monomolecular behavior). The carriers form a quasi-equilibrium states near the mobility edge, localized states at the band edge, and perhaps the defect states. If recombination takes place from the lowest of these states, and is not temperature activated, the T dependence of j_p is that of μ .

In the second case the recombination rate of the electrons is proportional to the number of holes. In this case the plot of j_p against 1/T is as in Figure 2.5, with j_p proportional to $G^{1/2}$ (bimolecular behavior) when $j_p > j_d$, j_d being the dark current, but proportional to G when $j_p < j_d$. Bimolecular behavior is normal in chalcogenides.

The analysis is as follows. The carriers form a quasi-equilibrium either in the conduction band itself or with shallow defect traps below it. If Δn is the excess density of these carriers due to the radiation, then the photocurrent density j_p is given by

$$j_p = e\mu F\Delta n \tag{2.11}$$

where F is the applied field. The lifetime of these carriers is denoted by τ , and Δn is



Figure 2.5. Temperature dependence of photocurrent in chalcogenides. The broken line is the dark current (schematic) [4]

given by

$$\Delta n = G\tau. \tag{2.12}$$

The quantity b is defined such that, bN is the probability per unit time that a majority carrier recombines when there are N minority carriers (trapped or otherwise) per unit volume. The lifetime of the carriers will be

$$\tau = \frac{1}{b(\Delta n + n_0)} \tag{2.13}$$

where n_0 is the concentration of trapped or free minority carriers in the dark, and n_0 is strongly dependent on T. The variation of photocurrent is similar for all chalcogenides, and is of the general form shown in Figure 2.5.

In regime I, the photocurrent is less than the dark current $(j_p < j_d)$. The thermally generated minority carriers will be bigger than the photogenerated carri-

ers $(n_0 > \Delta n)$. The lifetime will be approximately

$$\tau = \frac{1}{bn_0} \tag{2.14}$$

and according to 2.12, Δn will be

$$\Delta n = G/bn_0 \tag{2.15}$$

giving the monomolecular behavior (~ G). The temperature dependence is that of μ/bn_0 . n_0 will increase with increasing T, so Δn and therefore j_p will decrease with increasing T.

In regime II, the photocurrent is larger than the dark current $(j_p > j_d)$. The photogenerated carriers will be bigger than the thermally generated minority carriers $(n_0 < \Delta n)$, so recombination will be between photogenerated holes and electrons. The lifetime will be approximately

$$\tau = \frac{1}{b\Delta n} \tag{2.16}$$

and according to 2.12, Δn will be

$$\Delta n = \sqrt{G/b} \tag{2.17}$$

giving the bimolecular behavior (~ $G^{1/2}$). The temperature dependence is that of $\mu/b^{1/2}$.

The temperature dependence of τ is critical in the analysis. To have a brief idea, it is given in Figure 2.6 for $AsTe_3$, and alternatively in Figure 2.7 for As_2Se_3 . It can be seen from the graphs that, at high temperature region (regime I), τ decreases with increasing T, consistent with the photocurrent behavior. At low temperature region (regime II), τ is weakly dependent on T, leaving the T dependence of j_p to μ [4].



Figure 2.6. Temperature dependence of recombination lifetime (ns) in amorphous $AsTe_3$: A, 2 × 10¹⁸ photons $cm^{-2}s^{-1}$; B, 1.2 × 10¹⁹ photons $cm^{-2}s^{-1}$; C, 2.3 × 10¹⁹ photons $cm^{-2}s^{-1}$ [4]

2.4. As_2Se_3 and its Properties

 As_2Se_3 crystallizes in a monoclinic layer structure, in which each As atom is bonded to three Se atoms in a flat triangular pyramid arrangement, three Se atoms forming the base, and an As atom the apex. Each Se atom is part of two bases, fulfilling covalent bonding requirements, and extending the structure to a two-dimensional space. A projection of this layer onto a plane is shown in Figure 2.8 (a). The nearest neighbor As - Se distance is 2.36 Å. Since all the covalent bonding requirements are fulfilled within a single layer, the layers are hold together by weak Van der Waals forces. The smallest interatomic distance between layers is 3.66 Å, about one and a half of the As - Se bond length within the layers. The material is very easily cleaved parallel to the layer planes. In addition to the layer structure, a one-dimensional chain-like structure is possible for As_2Se_3 , by allowing two $AsSe_3$ pyramids to share a common edge, as shown in Figure 2.8 (b), rather than just a corner. No allotropic crystal form has been found based on such an arrangement, but, it is a possible candidate for a



Figure 2.7. Temperature dependence of recombination lifetime in amorphous As_2Se_3 for 10^{15} (upper curve) and 2×10^{15} photons $cm^{-2}s^{-1}$ [4]

component of the structure of amorphous As_2Se_3 .

There is strong evidence that, the short range order is essentially the same as in the crystal, the $AsSe_3$ pyramids being preserved with only small distortions. The longrange order is obtained not by cross-linking layers or formation of chain-like polymers, but primarily by small deformations within the layers. The nearest-neighbor As - Sedistance is 2.45 Å, slightly larger than in the crystal, but the nearest-neighbor interlayer distance remains 3.66 Å.

Probably because of the fact that inter-layer forces are primarily Van der Waals interactions, the glass transition temperature of As_2Se_3 is relatively low, 460 K [2].

The d.c. conductivity, σ , of most of the chalcogenide glasses including As_2Se_3 near room temperature obeys the relation

$$\sigma = \sigma_0 e^{-E_a/kT} \tag{2.18}$$

where E_a defined as the activation energy. Generally, $\ln \sigma$ is a fairly linear function



Figure 2.8. Two possible structures for As_2Se_3 : (a) layers, (b) chains. [2]

of 1/T (Figure 2.9), and variable-range hopping conductivity behaving even approximately as $Ae^{-B/T^{1/4}}$ is not generally observed. Measurements of thermopower show these glasses to be p-type.

In the observations upon photoconductivity, the three regimes described in the last section are observed. Chalcogenides, especially As_2Se_3 is a good example of the model described in the previous section.



Figure 2.9. Temperature dependence of electrical conductivity in some amorphous chalcogenide semiconductors, illustrating the relationship $\sigma = Ce^{-E/kT}$. Heavy lines are the experimental results and fine lines are the extrapolation to 1/T = 0. (3);

 As_2Te_3 , (7); As_2Se_3 , (8); As_2S_3 [4]

3. EXPERIMENTAL WORK AND RESULTS

The experiments are performed on thin films of As_2Se_3 , including two types of measurements, which are I-T (current vs. temperature) and I-V (current vs. voltage).

The films are prepared by thermal evaporation technique using Edwards Coating System, E306A. Bulk As_2Se_3 is placed in a tungsten boat, or basket, and is evaporated on glass substrates at a pressure about $7 \times 10^{-6}mbar$. Then aluminium is evaporated similarly, coating the As_2Se_3 film, constituting the electrodes (contacts).

3.1. Measurement Setup

The setup used for the measurements, is composed of a programmable picoammeter/voltage source (Keithley, Model 487), a temperature controller (Lakeshore, Model 300), a computer communicating with the first two components, and an aluminum sample holder, specifically designed for this experiment (figure 3.1).

For an I-V measurement, the voltage source is adjusted either by hand, or through the computer. The time needed for stabilizing the current may change, so taking the data by hand is generally more advantageous. The computer makes the instrument apply successive voltages at constant time intervals. The current value is read by the computer or manually entered to it. The computer program takes an average value of the currents at the last 10% of the time interval suppressing the effects of fluctuations. The temperature is kept constant by the temperature controller.

The I-T measurements are similarly performed with the same setup. In this case the computer communicates with both the voltage source/ammeter and the temperature controller. The sample is kept at constant voltage, and the temperature is gradually raised. For temperatures lower than room temperature, liquid nitrogen is used to cool the system. The sample holder is placed in a container above the liquid nitrogen. Then the temperature is raised by the resistance in the sample holder under



Figure 3.1. Measurement setup

the sample governed by the temperature controller.

But for photoconductivity measurements taking the data by hand is more advantageous. If the temperature value is taken, when the temperature is gradually increasing, there exists a temperature difference between the temperature sensor (Lakeshore, Model PT100) and the sample. But in order to calculate the photocurrent (light current minus dark current) these two current values must be taken at very close temperatures. A temperature difference in the order of 2-3K causes a considerable error due to the exponential dependence of the current with respect to the temperature. So, the data were taken in 10K (sometimes 5K) steps waiting for the temperature to stabilize.

The thicknesses of the thin films are measured with an interferometer (Varian, 980-4006). The thickness measurements give approximate values, because, the thickness is not homogeneous through the whole film.

3.2. Results of the Measurements

The thickness of the thin film sample is approximately 4419 Å. This is a reasonable value. If the thickness is too small, the great resistance of the film will make the measurements very difficult to perform. Currents will be very small, leakage resistances



Figure 3.2. The voltage dependence of the dark-current at 313 K

will be more effective. If the thickness is too big, one would observe the bulk properties of the material.

3.2.1. Dark Conductivity

The current-voltage measurements show that the sample (and the contacts) are Ohmic. Figure 3.2 shows the I-V characteristic of the sample.

The current-temperature measurement show that the dark conductivity obeys the Equation 2.18. Figure 3.3 shows the I-T characteristic of the sample.

The activation energy E_a is calculated as 0.713 eV for the sample, whose I-T is shown in Figure 3.3, in the temperature range 240 - 360 K.



Figure 3.3. The temperature dependence of the dark current, at 10 V, in the temperature range 240 - 360 K

3.2.2. Photoconductivity

The temperature dependence of the photocurrent together with the dark-current is shown in Figure 3.4. Regime II can be easily identified. i_p is higher than i_d and increases with increasing temperature. For regime I, the decreasing of i_p with increasing temperature is not very clear, especially at the higher end of the temperature. It was not possible to go to higher temperatures, and observe the behavior more precisely, because, the resolution of the ammeter becomes insufficient, when the temperature is high enough to create a large magnitude difference between i_d and i_p . Also thermal fluctuations in i_d become comparable with i_p .



Figure 3.4. The temperature dependence of the photocurrent, together with the dark current, at 10 V, in the temperature range 240 - 360 K

4. CONCLUSION

First, the thin films do behave linearly in the -50V - 50V interval. The highest electric field applied is approximately 2.5×10^5 V/m (50 V/0.2 mm). This field is not enough to create high field effects.

The activation energy for the dark conductivity of the sample is found to be 0.713 eV, in the temperature range 240 - 360 K. This value is reasonable (different values in the range 0.60 to 1 eV have been reported [2]). The thickness of the sample is approximately 4419 Å; a reasonable value.

The photoconductivity of the sample generally shows the basic characteristics described in the theory. There is no certain boundary separating regime II and regime III. At the lower limit of the temperature of the measurement, both the dark and photo currents were unmeasurable by the picoammeter used in the experiment (figure 3.4). Probably, a higher precision ammeter would solve the problem.

In the measurement shown in Figure 3.4, the decreasing behavior of the current with increasing temperature, at the higher temperature limit is obscure. This results from the fact that, the setup did not allow me going to higher temperatures. The magnitude difference between the dark and photo current increases so much that $(i_d$ is so bigger than i_p that) the magnitude of fluctuations in the dark current reaches the magnitude of the photocurrent. In this case the photocurrent cannot be measured. These fluctuations occur, because at high temperatures, it becomes harder for the temperature controller to keep the temperature at a constant value, so the fluctuations in the temperature causes the current to fluctuate as well.

In summary, the results of the photoconductivity measurements in As_2Se_3 thin films produced in the laboratory are in accordance with the theoretical and experimental results obtained by other workers.

REFERENCES

- 1. Kittel, C., Introduction to Solid State Physics, John Wiley & Sons, New York, 1986.
- 2. Adler, D., Amorphous Semiconductors, CRC Press, Ohio, 1971.
- Streetman, B. G., Solid State Electronic Devices, Prentice-Hall International, New Jersey, 1995.
- Mott, N. F. and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, Clarendon Press, 1979.
- Kurtuluş Ö., Transport Properties in Amorphous Chalcogenide Glasses, Ms. Thesis, Boğaziçi University, 2001.
- Rose, A., Concepts in Photoconductivity and Allied Problems, Interscience Publishers, New York, 1963.
- 7. Elliot, S. R., Physics of Amorphous Materials, Longman, 1984.
- 8. Zallen R., Physics of Amorphous Solids, Wiley, 1983.
- 9. Weiser K., Journal of Non-crystalline Solids, 8-10, 922, 1972.
- 10. Ovshinsky, S. R., Physical Review Letters, 21, 1450, 1968.
- 11. Henisch, H. K., Scientific American, November, 1969.
- 12. Adler, D., Electronics, September 28, 1970
- 13. Adler D., Reviews of Modern Physics, 40, 714, 1968.
- 14. Moss and S. C., J. F. Graczyk, Physical Review Letters, 23, 1167, 1969.

- 15. Seitz, F., J. Phys. Chem., 57, 737, 1953.
- 16. Adler, D., Solid State Phys., 21, 1, 1968.
- 17. Reitz, J. R., Solid State Phys., 1, 1, 1955.
- 18. Weinrich, G., Solids, John Wiley & Sons, New York, 1965.
- Cohen M. H., H. Fritzsche and S. R. Ovshinsky, *Physical Review Letters*, 22, 1065, 1969.
- 20. Owen A. E., Contemp. Phys., 11, 257, 1970.
- 21. Zallen R., M. L. Slade and A. T. Ward., Phys. Rev., B3, 4257, 1971.