SOME ELECTRICAL PROPERTIES OF AMORPHOUS GERMANIUM,
INDIUM ANTIMONIDE AND GALLIUM
ANTIMONIDE FILMS

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CHAPTER I

INTRODUCTION

Electrical-conduction behavior of amorphous semiconductors has been a subject of great interest during the past twenty years. Some enthusiasm in this area of study is caused by the recent discovery of switching behavior¹ in some amorphous semiconductors. The main interest in this subject, however, is academic because amorphous semiconductors represent a class of materials which is completely different from ordinary solids.

Their electrical conductivities, as well as many other properties, are quite different from those properties in crystalline materials.

The electrical conductivities of all amorphous semiconductors (at least, those that are stable at room temperature) are intrinsic, i.e., conductivities decrease continuously as the temperature is lowered. The $\ln \sigma$ versus $1/T$ curves, however, are not linear except at the high temperature ends. The electrical conductivities are highly insensitive to impurities or doping.² Near room temperature, conduction of most amorphous semiconductors seems to result from electrons. At low temperatures, Hall effect measurements indicate that

conducting carriers are electrons,³ while thermopower measurements show that electrical conduction is due to holes.⁴

Optical absorption properties of amorphous semiconductors are also different from those of crystalline materials. For a crystalline material, a sharp edge is observed at a photon energy which is equal to the band gap. For an amorphous material, usually no sharp absorption edge is observed.

Any attempt to explain theoretically the electrical and optical behavior of an amorphous semiconductor is confronted with a tremendously large number of atoms put together randomly. The only regularity is the short range ordering up to the second nearest neighbors. As a result of this randomness, the most powerful tool in solid state physics--the Bloch Theorem--is inapplicable here. Some theories, however, have been made either with a phenomenological approach or by treating only a finite number (say, 12) of atoms arranged in certain ways. Some of these theories will be described later.

It is believed that the density of states in an amorphous semiconductor is determined mainly by the short-range ordering of atoms. Amorphous semiconductors of the same short-range ordering should, therefore, share some similar features in their electrical or many other properties.

Ge, Si, GaSb, InSb and GaAs form a class of amorphous semiconductors having tetrahedral short-range ordering. Three of these materials (Ge, InSb and GaSb) were chosen here for conductivity studies. Amorphous states of these materials were

prepared by sputtering onto cooled substrates. Conductivities of both the as-deposited and annealed states were studied. As a result, a model is proposed to explain the electrical conduction of these materials.

CHAPTER II

EXPERIMENTAL METHOD

A. Introduction

The experimental method developed here for measuring the electrical resistivity of as-deposited or annealed thin films is direct and straight-forward. The present method, however, allows one to measure the resistance of a thin film without exposing it to the atmosphere, and hence eliminates the possibility of contamination or formation of a non-conducting oxide layer at the junctions. In this work, three tetrahedrally coordinated semiconductors Ge, InSb, and GaSb were sputtered onto a glass substrate with two silver electrodes being previously evaporated on the substrate. All resistivity measurements were made in situ without opening the vacuum system of the sputtering apparatus. Temperature was controlled from room temperature to approximately -175°C with a liquid nitrogen-cooled substrate holder.

B. Theory of measurements

A Keithley model 616 electrometer was used to measure the resistance of the prepared thin films. This electrometer when used as an ohmmeter operates as a constant current source, and the readout is proportional to the voltage V developed across the terminals where $V = I \times R$. The constant current I

can be selected from 10^{-5} to 10^{-11} amperes by using different range settings on the electrometer.

Two factors may contribute considerable error to the resistance measurements. These are:

1. The voltage measurement across the input terminals of the electrometer could be due partly to the thermal EMF developed across the film.
2. If the semiconductor-metal junctions are non-ohmic the measured resistance is a function of voltage or current. In this case, the measured resistance changes as the constant current I is varied.

Three precautions were taken to prevent these errors.

1. Each resistance measurement was taken twice with the applied voltage in opposite directions. The average of these two values would exclude contribution from a thermal EMF.
2. To insure that the semiconductor-metal junctions are ohmic, the electrometer setting was frequently changed so that the current would change a few orders of magnitude. It turned out that, for the amorphous semiconductors and silver terminals used, the resistance R is a well-defined quantity.
3. To insure that the resistance measured was not from the junction, films of these materials were deposited on three electrodes, as shown in Figure 1. The resistance values R_1 and R_2 , as seen in the figure, were measured over a wide range of temperatures.

Fig. 1. Configuration of three silver electrodes and amorphous thin film used for resistivity measurements. R_1 and R_2 are resistance values between the electrodes as shown.¹ The ratio R_1/R_2 will be approximately two if the junction resistance is insignificant.

The ratio R_1/R_2 was found constant and $R_1/R_2 \approx 2$. This shows that the resistance at the junction is negligible.

The resistance R_1 , as shown in Figure 1, can be related to the resistivity ρ according to

$$R_1 = \rho \frac{l}{w \times d} \quad (1)$$

where l = length of the thin film specimen

w = width of the film

d = thickness of the film

The thickness of the film was measured with a two-beam interference microscope with an accuracy of 100 Å.

C. Sample preparation and measurement system

All specimens studied were prepared by the RF sputtering technique onto Corning 7059 glass slides which were first cleaned in hot absolute alcohol. Two silver electrodes were then vacuum-evaporated on the glass slide. Two 5μ silver lead-wires were soldered onto the silver electrodes with an In-50a/0Sn alloy. This alloy adhered well with the glass slide and also provided good electrical contact with the electrodes. The glass slides with electrodes and attached silver wires along with an insulating mask were then fitted onto the specimen holder in the sputtering apparatus. The configuration of the assembly is shown in Figure 2.

The specimen holder was a hollow copper block cooled with liquid nitrogen or cold nitrogen gas transferred to its cavity through two stainless steel tubes. Sections of the two tubes were made of insulating ceramic material, such that the

Fig. 2. Configuration of assembly employed for in situ resistivity measurements. The glass substrate was cemented onto a copper plate for good thermal conduction. The stainless steel mask was insulated from the electrodes and amorphous films to make the in situ measurements possible. In the side view, the copper cover is not shown (true size).

Top View

Side View

specimen holder which formed part of the anode of the sputtering apparatus was electrically insulated from ground.

The temperature of the glass slide was measured with a type E chromel-constantan thermocouple. This thermocouple has a very linear EMF, from 20°C to -200°C, which covered the temperature range of the experiments.

Many working in the area of thin films have encountered the problem of not knowing the true temperature of the substrates. It is well known that in a vacuum it takes a long time for substrate materials such as glass and alkali halides to achieve a thermal equilibrium with their environment. To minimize such difficulties, the glass slide was first clamped onto the specimen holder in an attempt to get better thermal contact. The lowest temperature achieved was -120°C, which took two hours after the specimen holder itself was cooled to -190°C. A conductive epoxy (ACME no. 3021) was then used to cement the glass slide onto a copper plate, which was, in turn, clamped onto the specimen holder. As a result, the glass slide cooled instantaneously as the specimen holder was cooled down with cold nitrogen gas, and the lowest substrate temperature achieved was -175°C.

The sputtering apparatus used was an SEM-8620 RF J-Etch Module (Materials Research Corporation). The inert gas used was a commercial grade of pure argon, further purified with a Randex argon purifier. The vacuum chamber was first evacuated with a turbo molecular pump to below 4×10^{-7} torr before the specimen holder was cooled down and argon was introduced.

During sputtering, purified argon was continuously leaked into the chamber through a controlled leak valve, while the turbo molecular pump kept on pumping the chamber. By controlling both the gate valve of the pumping system and the opening of the leak valve, one could control the argon pressure in the chamber to within closed limits. All thin films in this investigation were prepared under the following conditions:

1. argon pressure: 2 microns
2. RF power: 200 watts
3. bias power applied to the substrate holder: 2%
4. Targets were always presputtered for 3 minutes before the shutter was opened and films were deposited onto the substrates.
5. Sputtering rate: ~ 1000 A/minute

All sputtering targets were discs 2" in diameter and consisted of

1. single crystal zone-refined Ge
2. polycrystalline electronic grade InSb (Cominco American Incorporated)
3. polycrystalline electronic grade GaSb (Cominco American Incorporated)

Once the films were prepared, their resistances were measured in situ. All films were prepared at ~ -150°C (during sputtering, the substrate temperature typically increased from -175°C to -150°C). They were first cooled down to -175°C and then allowed to warm up to room temperature. Because the specimen holder was maintained in vacuum, the time taken for

the films to warm up was considerable (approximately 4 hours). This turned out to be an advantage, because the thermocouple was made of wires of considerable mass (5 microns in diameter) relative to the specimen and had a longer response time to the temperature of the glass slide than did the amorphous thin film. At some temperature in the warming up process (see data graphs), the films were cooled down again to -175°C , and their resistance was measured as a function of temperature. After the films had been warmed up and kept at room temperature for more than 12 hours, the same procedure was repeated.

Thermocouple EMF's were converted to temperature with a Doric DS-350 digital thermalcouple indicator. Film resistances were measured with a Keithley Model 616 electrometer. Data were taken following the precautions mentioned in part B of this section.

CHAPTER III

COMPARISON OF EXPERIMENTS WITH THEORY

A. Mott's theory on electrical conductivity of non-crystalline semiconductors

A. 1. Summary of theoretical concepts

A theory on electrical properties of non-crystalline semiconductors has been developed by Mott.⁵ A summary of this theory is given as follows:

- (1) The density of states remains as a valid concept for non-crystalline as well as for crystalline materials.

The main factors determining the density of states for a given material are the first coordination number and the interatomic distance. Thus, if the former is unchanged, no major change in the density of states is likely, except when due to change in specific volume.

- (2) In semiconductors that do not have s-like conduction and valence bands, localized states occur at the band extremities (see Figure 3).

Energies values E_C and E_V in the conduction band and valence band, respectively, separate these localized states from non-localized (extended) states, and there is a drop by a factor of ~ 1000 in the mobility as the energy crosses these values. E_C and E_V are, therefore, called the mobility shoulders,

Fig. 3. Suggested models for density of states $N(E)$ and mobility $\mu(E)$ as functions of energy for different amorphous semiconductors. Localized states are shown shaded. States with energies below E_v are assumed to be filled.

- (a) Density of states based on the original Mott theory (1968).
- (b) E_c and E_v are mobility edges, and E_g defines a mobility gap.
- (c) Density of states in some glasses as suggested by Cohen, Fritzsche and Ovshinsky.⁷
- (d) Model suggested by Davis and Mott.⁶
(Ref. 9, p. 199)

and the energy difference ($E_C - E_V$) defines a mobility gap E_g , as shown in Figure 3.

Localization can occur for a given energy E for the following reasons:

- (a) There is a random potential at each atom (Anderson localization).
- (b) There is a fluctuation in the density or mean atomic distance.
- (c) There is an absence of long-range order.
- (3) The Fermi level lies near the middle of the band gap.

Davis and Mott⁶ have assumed that a fairly narrow (≤ 0.01 eV) band of localized states of sufficiently high density exists near the center of the energy gap to effectively pin down the Fermi energy E_F within a wide temperature range (see Figure 3d). Cohen, Fritzsche and Ovshinsky⁷ have alternatively suggested that, in certain glasses, the density of states is as shown in Figure 3c.

A. 2. Temperature dependence of d.c. conductivity

With the above model on density of states and mobilities of an amorphous semiconductor in mind, three mechanisms of electrical conduction can be distinguished.

- (a) Conduction due to carriers excited beyond the mobility shoulders into non-localized or extended states.

If the main current is carried by electrons, we expect, using notations of Figure 3,

$$\sigma = \sigma_0 \exp \{ - (E_C - E_F) / kT \} \quad (2)$$

Mott⁸ has argued that for coordination number $z = 6$, the pre-exponential term σ_0 is given by

$$\sigma_0 = 0.06 e^2 / \hbar a_E \quad (3)$$

where a_E is the separation between localized states. For $a_E = 4\text{\AA}$, $\sigma_0 = 350 (\text{ohm})^{-1}\text{cm}^{-1}$. A plot of $\ln \sigma$ versus $1/T$ will give a straight line if $(E_C - E_F)$ is a linear function of T over the temperature range measured. If we let

$$(E_C - E_F) = E(0) - \gamma T, \quad (4)$$

where γ is constant with dimension $\text{ev}^\circ\text{K}^{-1}$, the slope of such a plot will be E_0/k , and the intercept on the conductivity axis will be $\sigma_0 \exp(\gamma/k)$. For a γ of value $10^{-4} \text{ ev}^\circ\text{K}^{-1}$, $\exp(\gamma/k) = 3.2$.

(b) Conduction due to carriers excited into the localized states and the band edges, i.e., at E_A or E_B of Figure 3.

Again, if the main current is carried by electrons and conduction is by hopping, then

$$\sigma = \sigma_1 \exp \{ - (E_A - E_F + \Delta W_1) / kT \} \quad (5)$$

where W_1 is the activation energy for hopping and E_A is the energy at the band edge. σ_1 is expected to be a factor of $10^2 - 10^4$ less than σ_0 , due partly to an effective density of states lowered by a factor $\sim (E_C - E_A) / kT$, but mainly to a lower mobility μ . Only if μ_1 does not fall off too rapidly between E_C and E_A will the current be carried at E_A and a straight line be obtained on a plot of $\ln \sigma$ versus $1/T$ for this mode of conduction.

(c) Conduction due to carriers hopping (tunneling) between localized states near the Fermi energy.

This is the process analogous to the impurity-conduction in heavily doped semiconductors, and σ in this mode of conduction is given as

$$\sigma = \sigma_2 \exp (-\Delta W_2/kT) \quad (6)$$

where $\sigma_2 \lesssim \sigma_1$ and ΔW_2 is the hopping energy of the order of half the width of the narrow band of localized states near E_F as seen in Figure 3d. Mott and Davis⁹ have shown that a straight line in a plot of $\ln \sigma$ versus $1/T$ is expected only if hopping is between nearest neighbors. As the temperature is lowered, it may become favorable for the carriers to tunnel to more distant sites; thus ΔW_2 will fall, and ultimately, the conductivity will be expected to behave as

$$\ln \sigma = A - B T^{-1/4} \quad (7)$$

The total conductivity for all processes is obtained as an integral over all available energy states. Thus, for states above E_F ,

$$\sigma = e \int N(E) \mu(E) f(E) dE \quad (8)$$

where $N(E)$ is the density of states, $\mu(E)$ is the electron mobility as a function of energy and $f(E)$ is the Fermi-Dirac distribution function. Figure 4 shows the schematic variation of $N(E)$, $\mu(E)$ and $f(E)$ with E for energies above E_F , and the manner in which $\sigma(E)$ may vary with temperature. This is also shown on a plot of $\ln \sigma$ versus $1/T$ in Figure 5. If the density of defect states is high, then process (b) will not dominate in any temperature range and a direct transition from (a) to (c) will result.

Fig. 4. Illustration of the effect of temperature on the mode of conduction.

$$\sigma(E) = e N(E) \mu(E) f(E); T_1 > T_2 > T_3.$$

(Ref. 9, p. 202)

Fig. 5. Illustration of the temperature dependence of conductivity expected from the model of Figure 4. Regions (a), (b) and (c) correspond to temperature ranges represented by T_1 , T_2 and T_3 , respectively.

B. Stuke's observations on electrical conductivity

The optical and electrical properties of some amorphous semiconductors (Ge, InSb, Se, Te and As_2Se_3) have been reviewed by Stuke.¹⁰ The important observations made by Stuke have been summarized as follows:

- (1) Intrinsic conduction in amorphous semiconductors predominates at much lower temperatures, in spite of a larger activation energy than the one in crystalline state (for example, see Figure 6 for the intrinsic conducting behavior of InSb). By intrinsic conduction, one means that conductivity can be expressed as

$$\sigma = \sigma_0 \exp \left(- \frac{E_g}{2kT} \right) \quad (9)$$
- (2) A large concentration of impurity atoms has only a small influence on the conductivity.
- (3) By annealing, the slope of the intrinsic conduction is increased. Stuke¹¹ has observed that by annealing flashed-evaporated InSb films between 300°K and 400°K. The value of σ decreases and the value E_g increases from 0.5 to 0.65 ev.
- (4) Amorphous InSb films prepared under different conditions have different band gaps covering a range from 0.4 to 0.65 ev. It is worthwhile to observe that these values are approximately 2-3 times the band gap for crystalline InSb.
- (5) Even though the value of E_g varies over a wide range, σ_0 is quite constant. Stuke¹¹ observed that, for different amorphous and crystalline InSb films, $\sigma_0 \approx 2 \times 10^3 (\text{ohm})^{-1} \text{cm}^{-1}$. Stuke claimed that this result stressed the fact

Fig. 6. Temperature dependence of electrical conductivity for amorphous and polycrystalline InSb before annealing (curve 1) and after annealing (curve 2).¹⁰ The energy values indicated on the curves are E_g 's defined in Equation 9 or twice the activation energy E_0 given in Equation 10.

that the high-temperature branch of the conductivity curve is due to intrinsic conduction of amorphous InSb.

- (6) Another significant feature that Stuke has observed is that, for the amorphous semiconductors InSb, Te, Ge, As_2Se_3 and Se, all curves of $\ln \sigma$ versus $1/T$ show a σ_0 value of about 10^3 - 10^4 $(\text{ohm})^{-1}\text{cm}^{-1}$ (Figure 7). This is known as Stuke's Rule.

C. Some theoretical approaches

Over the past few years many serious quantitative calculations have been attempted to relate the electronic features of amorphous Ge and Si to the structure of these materials. The most fruitful approaches have been those which (1) use simplified Hamiltonians to study the effect of "topological disorder,"¹² (2) try to analyze the problem by a consideration of the real energy band structure of even more complicated polytypes of crystalline Si and Ge, or (3) investigate the electronic structure of finite clusters approximating the atomic configurations expected in the amorphous solids.

The first approach has been used with great success by Weaire and co-workers¹²⁻¹⁵ who used a model Hamiltonian that included only a matrix element V_1 between basis functions associated with different bonds of the same atom, and a matrix element V_2 between basis functions associated with the same bond between two different atoms. In the limit of small V_1/V_2 (the covalent solid limit), a gap exists between the s and p states of isolated Si or Ge atoms; this limit, of course, would

Fig. 7. Extrapolation of intrinsic conduction to $1/T = 0$ for the amorphous semiconductors InSb, Te, Ge, As_2Se_3 and Se.¹⁰

produce metallic solids. Weaire¹¹ has shown that the former gap persists for any ratio V_1/V_2 up to $1/2$, despite the introduction of topological disorder, i.e., a non-periodic arrangement of the tetrahedrally coordinated networks. The disorder represented by a spread in the values of V_1 and V_2 is neglected. Thus, amorphous Si and Ge can possess sharp energy gaps, despite their lack of long-range periodicity. However, variations in matrix elements may result in band tails.

Most of the early work on estimating the band structure of amorphous Si and Ge used the known crystalline diamond cubic results as a starting point.¹⁶⁻¹⁸ These approaches were generally not in agreement with the observed optical properties. Recently, a new approach was introduced by Joannopoulos and Cohen¹⁹ and by Ortenberger and co-workers,²⁰ who applied the Empirical Pseudo-potential Method (a method using the form factors obtained from a fit of the optical properties of the diamond cubic material) to the polytypes of crystalline Si and Ge. The polytypes investigated included a wurtzite structure, a body centered cubic structure with eight atoms per unit cell (Si III), and a simple tetragonal structure with 12 atoms per primitive cell (Ge III). The calculated band gaps for the Ge III structure of both Ge and Si are 1.5 eV and 1.6 eV, respectively. Noting that the density of Ge III is 10% greater than that of amorphous Ge, one expects the gap to decrease in direct correspondence with the density of these materials. If a primitive cell larger than the Ge III structure is considered, the structure will be closer to that of an amorphous network.

The cluster approach has been employed both by Keller²¹⁻²² and by McGill and Klima,²³ who applied the multiple scattering theory to clusters of various sizes and obtained a "pseudogap," or a region of low density of states between two regions of higher density of states, or bands. Also, this theory states that as the size of the cluster is increased, the density of states in the pseudogap region falls, consistent with the idea that a real gap does exist in the infinite cluster, i.e., the amorphous solid. The significance of this approach is that the local configuration, such as the tetrahedral configuration, is responsible for the formation of a pseudogap. The effects of varying the boundary conditions on the cluster have also been studied. It was shown by Keller²¹ that, either when the cluster is subjected to periodic boundary conditions or when the environment is represented by a dispersive medium outside the cluster, a true gap results.

D. Experimental results

All experimental data were plotted as $\ln \sigma$ versus $1/T$ in Figures 8-11. Four specimens were studied: amorphous Ge, GaSb and two amorphous InSb specimens. The first three specimens were prepared under the same sputtering conditions: the background pressure before introduction of purified argon to the vacuum chamber was 1×10^{-7} torr; the films were never annealed above room temperature. The last specimen was prepared at the background pressure of 8×10^{-7} torr; the film, once warmed up to room temperature, was further annealed at

Fig. 8. Measured conductivity of amorphous Ge film plotted as a function of $1/T$. T_s is the initial substrate temperature where the film was prepared. The arrows indicate the directions of temperature changes. Two arrows in opposite directions imply a reversible process; an arrow in only one direction indicates an irreversible process. Different segments of the curves are approximated by

$$A: \sigma = 3.84 \exp \left(- \frac{0.06784 \text{ ev}}{kT} \right) \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$B: \sigma = 3.03 \exp \left(- \frac{0.07987 \text{ ev}}{kT} \right) \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$C: \sigma = 2.222 \times 10^1 \exp \left(- \frac{0.1871 \text{ ev}}{kT} \right) \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$D: \sigma = 3.20 \exp \left(- \frac{0.1428 \text{ ev}}{kT} \right) \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$E: \sigma = 3.668 \times 10^{-1} \exp \left(- \frac{0.1058 \text{ ev}}{kT} \right) \text{ ohm}^{-1} \text{ cm}^{-1}$$

Fig. 9. Conductivity of amorphous GaSb film plotted as a function of $1/T$. Symbols on this figure are described in Figure 8. Different segments of the curve are approximated by

$$A: \sigma = 2.58 \exp \left(- \frac{0.0627 \text{ ev}}{kT} \right) \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$B: \sigma = 1.667 \times 10^4 \exp \left(- \frac{0.3015 \text{ ev}}{kT} \right) \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$C: \sigma = 1.783 \times 10^3 \exp \left(- \frac{0.2557 \text{ ev}}{kT} \right) \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$D: \sigma = 2.852 \times 10^1 \exp \left(- \frac{0.2000 \text{ ev}}{kT} \right) \text{ ohm}^{-1} \text{ cm}^{-1}$$

Fig. 10. Conductivity of amorphous InSb thin film plotted as a function of $1/T$. Symbols for this figure are given in Figure 8. Different segments of the curve are approximated by

$$A: \sigma = 8.78 \times 10^2 \exp \left(- \frac{0.0656 \text{ ev}}{kT} \right) \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$B: \sigma = 1.209 \times 10^4 \exp \left(- \frac{0.2185 \text{ ev}}{kT} \right) \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$C: \sigma = 2.458 \times 10^2 \exp \left(- \frac{0.1476 \text{ ev}}{kT} \right) \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$D: \sigma = 1.952 \exp \left(- \frac{0.0944 \text{ ev}}{kT} \right) \text{ ohm}^{-1} \text{ cm}^{-1}$$

Fig. 11. Conductivity of another amorphous InSb thin film specimen plotted as a function of $1/T$. Symbols on this figure are explained in Figure 8. The only differences between the specimen applying to this figure and that of Figure 10 are that the former was annealed at 45°C for 30 minutes and was prepared in a background pressure of 8×10^{-7} torr. Different segments of this curve are approximated by

$$\text{A: } \sigma = 3.64 \times 10^2 \exp \left(- \frac{0.06763 \text{ ev}}{kT} \right) \text{ ohm}^{-1} \text{cm}^{-1}$$

$$\text{B: } \sigma = 1.21 \times 10^4 \exp \left(- \frac{0.2253 \text{ ev}}{kT} \right) \text{ ohm}^{-1} \text{cm}^{-1}$$

$$\text{C: } \sigma = 1.323 \times 10^3 \exp \left(- \frac{0.1730 \text{ ev}}{kT} \right) \text{ ohm}^{-1} \text{cm}^{-1}$$

45°C for 30 minutes before it was cooled down again. The data for this specimen are plotted in Figure 11.

The thicknesses of the films are 3100 Å for the Ge film, and 2200 Å for all the others.

Segments of the curves in Figures 8-11 were approximated by straight lines. The equations for these linear regions are given in the captions of these figures.

E. Discussion

From the curves shown in Figures 8-11, one can observe the following general features.

- (1) Segments of the curves can be represented by the formula

$$\sigma = C \exp \left(- \frac{E_o}{kT} \right) \quad (10)$$

The conductivity of an as-deposited film can be represented by one equation, while the conductivity of an annealed film can be broken into segments represented by equations of this form.

- (2) In the range of temperature investigated, conductivities of these specimens decreased continuously, and no extrinsic conducting behavior was observed.
- (3) The pre-exponential terms C's in Equation 10 for the high temperature portions of the various curves are given as:

Ge (Fig. 8) $C = 2.222 \times 10^1 \text{ (ohm)}^{-1} \text{cm}^{-1}$

GaSb (Fig. 9) $C = 1.667 \times 10^4 \text{ (ohm)}^{-1} \text{cm}^{-1}$

InSb (Fig. 10) $C = 1.209 \times 10^4 \text{ (ohm)}^{-1} \text{cm}^{-1}$

InSb (Fig. 11) $C = 1.213 \times 10^4 \text{ (ohm)}^{-1} \text{cm}^{-1}$

If C is replaced by σ_0 , Stuke's Rule would be observed by GaSb and InSb. Ge, however, showed a much lower value of C . This is because the value C here is extrapolated from a portion of the curve below 20°C, while the σ_0 value ($10^4 \text{ ohm}^{-1}\text{cm}^{-1}$) shown in Figure 6 was extrapolated from a portion between 20°C and 350°C.

- (4) For all four specimens, the conductivities at low temperatures before being annealed to room temperature were a few orders of magnitude higher than the corresponding values for annealed films in the same temperature range. The activation energies of all these curves were approximately 0.065 ev. The same activation energy was not observed in annealed specimens.
- (5) By comparing the two InSb specimens, prepared and annealed under different conditions, one sees only that the activation energy for the intrinsic conduction of the specimen annealed at a higher temperature is slightly higher than the activation energy for the other InSb specimen (E_0 in equation 10 to be 0.2253 and 0.2185 ev, respectively). Otherwise, there is no major qualitative difference between Figure 10 and Figure 11.

Some of the pure theoretical approaches outlined in Section C of this chapter represent interesting approaches, and they give some insight into the electronic structure of amorphous materials. They are, however, at the present stage, not yet very useful for numerical evaluation of conductivity or data analysis. On the other hand, Mott's theory, even though

phenomenological in nature, is well developed and applicable to numerical data. Attempts will, therefore, be made to interpret the data given in the last section in terms of Mott's theory.

In Figure 8, the conductivity of the annealed Ge specimen was measured from 20°C to -175°C. Over this range of temperature E_0 (see Equation 10) varies from 0.1871 to 0.1058 ev, and the pre-exponential term C ($\sim \sigma_0$) changes from 22.2 to 0.367 (ohm)⁻¹cm⁻¹. From Figure 7, one notices that the temperature range investigated here (20°C to -175°C) did not include the intrinsic conduction region (Stuke¹¹) or the region controlled by mechanism (a) in Mott's theory. An E_0 of 0.1058 ev could not be due to Mechanism (c) because it was assumed by Mott and Davis that the width of the band at E_F is less than 0.01 ev and the activation energy (E_0) for Mechanism (c) should be approximately one-half of the band width. Mott and Davis gave the values of E_0 and C for Mechanism (a) in Ref. 2 as $E_0 \sim 0.54$ ev and $C \sim 4 \times 10^3$ (ohm)⁻¹cm⁻¹. Therefore, according to Mott's theory (see Figure 3 for notations), one has

$$E_C = 0.54 \text{ ev}$$

$$E_A = 0.106 \text{ ev}$$

$$E_F = 0.000 \text{ ev}$$

$$\sigma_0 = 4 \times 10^3 \text{ ohm}^{-1}\text{cm}^{-1}$$

$$\sigma_1 \sim 0.367 \text{ ohm}^{-1}\text{cm}^{-1}$$

A similar analysis was made of the data given in Figure 9, and one obtains the following values for the annealed GaSb specimen:

$$E_C = 0.302 \text{ ev}$$

$$E_A = 0.200 \text{ ev}$$

$$E_F = 0.000 \text{ ev}$$

$$E_g = 2 (E_C - E_F) = 0.604 \text{ ev}$$

$$\sigma_O = 1.67 \times 10^4 \text{ ohm}^{-1} \text{cm}^{-1}$$

$$\sigma_1 = 2.85 \times 10^1 \text{ ohm}^{-1} \text{cm}^{-1}$$

Again, Mechanism (c) was not observed in the temperature range investigated.

By analyzing the data in Figures 10 and 11, one obtains the following information on annealed InSb specimens:

$$E_C = 0.225 \text{ ev}$$

$$E_A = 0.0944 \text{ ev}$$

$$E_F = 0.000 \text{ ev}$$

$$E_g = 0.45 \text{ ev}$$

$$\sigma_O = 1.21 \times 10^4 \text{ ohm}^{-1} \text{cm}^{-1}$$

$$\sigma_1 = 1.95 \text{ ohm}^{-1} \text{cm}^{-1}$$

Mechanism (c) was not observed.

Similar to the annealed specimens, the as-deposited films (before being annealed to room temperature) showed electric conducting behavior governed by Equation 10. The E_O value for all four specimens are small compared with $(E_A - E_F)$ or $(E_C - E_F)$; they vary from 0.063 to 0.08 ev. The values of C were comparable with σ_1 for these materials, but were smaller than σ_O . Whether this was a result of shifts in E_F due to a

different distribution of localized states, or a result of widening of the band-tail ($E_C - E_A$) is uncertain.

One further comment has to be made about the value of σ_0 . Mott has predicted the conductivity at the mobility edge E_C to be approximately $350 \text{ ohm}^{-1} \text{ cm}^{-1}$. Stuke, on the other hand, has observed that a few amorphous semiconductors have σ_0 values between $10^3 \text{ ohm}^{-1} \text{ cm}^{-1}$ and $10^4 \text{ ohm}^{-1} \text{ cm}^{-1}$. The results presented here agree quite well with Stuke's Rule. Mott's calculated result of σ_0 is approximately one order of magnitude lower than the σ_0 value given by Stuke's Rule. This discrepancy, however, will not prove or disprove Mott's theory.

Finally, it is worthwhile to mention that, even though Mott's theory has qualitatively explained the experimental results given here as well as data given elsewhere, the fits are never unique. For example, the well known equation

$$\ln \sigma = A - B T^{-1/4} \quad (7)$$

where A and B are constants, agrees perfectly with Walley and Jonscher's²⁴ result on amorphous Ge over a wide range of temperatures (20°C to -195°C), but not with Chopra and Bahl's²⁵ result on the same material. Even if Equation 7 agrees with experimental results over a wide range of temperatures, it still does not mean that conduction at a temperature as high as 20°C is controlled by an electron-hopping mechanism.

It is reasonable for Mott to assume that the density of states is mainly determined by the first coordination number, and that there is no major change in density of states in going from crystalline to amorphous semiconductors. Nevertheless, it

is not obvious that most parts of the conduction and valence bands remain extended or unlocalized, since the Bloch theorem becomes invalid in amorphous materials. Also, the concept of a mobility shoulder which cuts off localized states from the extended states seems only an interesting assumption. The results of drift mobility measurements⁶ are not conclusive.

The data presented here can be explained in an alternative way based on the concept of localized valence electrons. A full account of this model will be given in the next section.

F. A proposed model

The basic assumptions involved in this model are

- (1) All conducting electrons are in free or extended states within a band of sharp edges.
- (2) All valence electrons are localized. Owing to the lack of long-range periodicity and nonuniform interatomic distances, a sharp band edge does not exist.

The electrons in the conduction band are free because the conduction band is built of many empty localized states of approximately the same energy. The wave-functions of these localized states overlap with one another in real space. An electron excited to the conduction band can, therefore, move from one localized state to another, and appears to be free.

On the other hand, valence electrons are not free because all neighboring states of the same energy are filled

with electrons. According to Pauli's Exclusion Principle, they are unable to move freely.

The effect of non-uniform interatomic spacing on the density of states is shown in Figure 12. A plot of density of states is shown in Figure 13. Note that in Figure 13, not all states in the valence band are filled. The extra states in the valence band are results of structural disorder.

Based on the above assumptions, one can estimate the conductivity of an amorphous semiconductor qualitatively.

$$\sigma = e n \mu (E_C) \quad (11)$$

where e = electron charge

$\mu(E_C)$ = mobility at the conduction band

n = number of electrons in the conduction band.

The n is determined by the density of states at the valence band; but n is not determined by the density of states at the conduction band because we assume that the conduction band has sharp edges. Also, the number of electrons excited to the conduction band is not determined by Fermi-Dirac statistics, because the electrons in the valence band are localized and, therefore, do not form a free electron gas which is the necessary condition for Fermi-Dirac statistics to apply. The number of free electrons n can, however, be determined by Boltzmann statistics as

$$n = \sum_i n_i \exp \left[- \frac{(E_C - E_i)}{kT} \right]$$

where n_i is the density of states at the localized level i , and

Fig. 12. Schematic diagram showing the effect of non-uniform interatomic distance on the energy of bonding electrons. As the interatomic separation varies from site to site, the localized electrons will have different energies, and a band with a diffuse edge results.

Fig. 13. Schematic density of states of an amorphous semiconductor based on the model of localized valence electrons and free (non-localized) conduction electrons. The valence band has a diffused edge results from nonuniform interatomic distances. (See Figure 12)

E_i is the corresponding energy for the localization. Equation 11 yields

$$\sigma = e \mu (E_C) \sum_{i=1}^N n_i \exp \left[- \frac{(E_C - E_i)}{kT} \right] \quad (12)$$

For example, if one lets

$$\begin{aligned} (E_C - E_1) &= 0.22 \text{ ev} & n_1 &= 10^4 \\ (E_C - E_2) &= 0.15 \text{ ev} & n_2 &= 10^2 \\ (E_C - E_3) &= 0.09 \text{ ev} & n_3 &= 1 \\ & & n_i &= 0 \text{ for } i > 3 \end{aligned}$$

By substituting the above numerical values in Equation 12, one can reproduce the $\ln \sigma$ versus $1/T$ curve for annealed InSb.

Some consequences of this model are worth mentioning.

- (1) By using Boltzmann statistics instead of Fermi-Dirac statistics, the activation energy in the high temperature region (intrinsic condition) is $(E_C - E_V)$, instead of one-half of this value. This will probably explain why the activation energy for an amorphous semiconductor at a high temperature is always two to three times the activation energy of the corresponding crystalline semiconductor.
- (2) Since all valence electrons are localized, electrons will have a much higher mobility than holes.
- (3) Since there are some unfilled states in the valence band, no extrinsic conducting behavior should be observed in highly doped or impure specimens.
- (4) The conducting behavior of as-deposited films at a low temperature may be explained by some structural defects, resulting in electron-occupying states slightly below

the conduction band and, therefore, resulting in a small activation energy.

In addition to the results reported here, electrical conducting behavior of other amorphous semiconductors also fits into the framework of this model. For instance, Anseau²⁶ conducted a similar experiment on $\text{Te}_x\text{Tl}_{1-x}$. His experimental results are shown in Figure 14. One notices that the $\ln \sigma$ versus $1/T$ curves are very similar to those reported here:

- (1) The as-deposited state and annealed state are well distinguished in both Figures 14a and 14b.
- (2) The curves for the annealed states can be approximated by a sum of exponential terms as shown in Equation 12.

Fig. 14. Conductivity versus reciprocal temperature for amorphous $\text{Te}_{66}\text{Tl}_{34}$ (14a) and $\text{Te}_{45}\text{Tl}_{55}$ (14b) alloy films deposited at liquid nitrogen temperature (77°K). The energy values indicated on the figures are activation energies. Three branches are shown for the curve of each alloy film: branch (1) is the as-deposited state, branch (2) is the intermediate state and branch (3) is the annealed state.
(Ref. 26)

CHAPTER IV

SUMMARY

Three tetrahedrally coordinated amorphous semiconductors Ge, InSb and GaSb were prepared by sputtering of these materials onto cooled substrates. The as-deposited films represent metastable states which are not stable at room temperature. These metastable states are semiconductors of comparatively high conductivity and low activation energies. The conductivity of an annealed film is intrinsic in nature down to -175°C (98°K); impurities have little or no effect on the intrinsic character. The electrical conductivity of an annealed film can be described as

$$\sigma = \sum_i C_i \exp \left(- \frac{E_i}{kT} \right)$$

A model has been proposed to explain the present data as well as other data. Basic assumptions of this theory are:

- (1) Valence electrons in an amorphous semiconductor are localized.
- (2) Electrical conduction results from electrons excited to free or extended states. These extended states form a conduction band with sharp edges.

Mott's theory, which involves different assumptions, was also evaluated with the present data.

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