PROPERTIES OF AN AMORPHOUS CHALCOGENIDE SEMICONDUCTOR $Ge_{10}As_{20}Te_{70}$

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ABSTRACT

PROPERTIES OF AN AMORPHOUS
CHALCOGENIDE SEMICONDUCTOR
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By

Kelly Paul Golden

An amorphous chalcogenide semiconductor, $Ge_{10}As_{20}Te_{70}$, was produced and examined for physical, thermal, electrical, and optical properties. Material synthesis techniques are described. Important thermal characteristics are reported including glass-transformation, crystallization, and melting temperatures. Electrical properties reported include dc conductivity and ac admittance versus temperature, Seebeck coefficient, and reversible conductivity switching. Behavior of the optical absorbtion coefficient for high and low energies in the absorption edge is reported. Improved four-point probe dc-conductivity measurement apparatus is described; apparatus under construction for drift-mobility measurement is also described.

Amorphous $Ge_{10}As_{20}Te_{70}$ was synthesized from elemental starting constituents in evacuated silica ampuls. Mixed lump and powder raw materials were fused at 800 °C with agitation for about 20 hours; the melt was cooled slowly to 400 °C and then quenched rapidly to 0 °C. The resulting glass was dark, shiny, and very fragile; it fractured conchoidally and showed no structure by optical-microscopic or x-ray diffraction inspection. Density of amorphous $Ge_{10}As_{20}Te_{70}$ was 5.8 g/cm^3; Mohs hardness was about 2.8. Amorphous material crystallized readily; the crystallized state appeared less dense but harder than the amorphous state. Microscopic examination of crystallized material revealed a complex

network of crystallites; crystalline tellurium was identified from x-ray diffraction patterns.

Many thermal properties were determined. Specific heat for amorphous material was 0.289 J/(g °C) at 80 °C; glass transformation occurred at 120 °C. An unusual endothermic reaction accompanying glass transformation was correlated with annealing stabilization. Softening occurred at about 175 °C; crystallization occurred above 190 °C with an exothermic heat of reaction of about 6.1 J/g. Crystallized material had a specific heat of 0.314 J/(g °C) at 80 °C and melted at 340 °C. Heated $Ge_{10}As_{20}Te_{70}$ solid and liquid reacted only very slowly with the atmosphere.

Low-field dc electrical conductivity appeared to be thermally activated; at room temperatures 5×10^{-5} mhos/cm conductivity and 0.3 eV activation energy were typical for bulk material annealed about 10 hours at 100 °C. The activation energy was sensitive to temperature and annealing time and ranged from 0.2 to 0.5 eV. Low-temperature ac conductance was proportional to the 0.85^{th} power of frequency. Seebeck coefficient was approximately +300 μV/°C. Threshold and memory switching were observed at a field intensity of 2.65 kV/cm. Room temperature photoconductivity was very small. Electrical conductivity of crystallized material was high and practically independent of temperature at about 70 mhos/cm.

The optical-absorption edge was poorly defined, but located at about $\lambda = 1.7$ μm. At low energies in the absorption edge the absorption coefficient was exponentially dependent on photon energy; a critical energy value of 0.075 eV was determined. At higher energies

in the absorption edge the absorption coefficient was proportional to the square of photon energy; an optical-energy gap of 0.79 eV was found and compared to the measured thermal-activation energy for conductivity of 0.41 eV for an identical sample. Index of refraction was determined interferometrically in the absorption edge and at transmitting wavelengths; above $\lambda = 4$ μm the value was about 3.9.

A table of properties for $Ge_{10}As_{20}Te_{70}$, comparisons with work by others, theoretical interpretations of results, and suggestions for additional research are all included. Brief literature reviews of experiment and theory for non-crystalline electrical conductors and for conductivity switching are also supplied. All sections are extensively referenced; a bibliography containing over 500 citations is provided.

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Dedicated to my wife

Patricia Elaine Golden

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CHAPTER 1

AN INTRODUCTION

1.1 Introduction

In the past twenty years there has been much activity in solid-state chemistry, physics, and electronics. Much of the activity has been study of properties and applications of crystalline materials. Theories of behavior for crystalline semiconductors have been highly developed. Study of non-crystalline materials has only recently begun, however, and much remains to be learned. Non-crystalline or amorphous materials are of interest theoretically as an extension of the study of more highly ordered crystalline materials. Also, unusual, unexpected, and largely unexplainable electrical characteristics have been noted for some non-crystalline solids.

Glasses are the most familiar of non-crystalline materials. A well known type of glass, transparent window glass, is fabricated primarily from silica and other metal oxides by fusing the components at high temperature and allowing the melt to cool rapidly enough to become rigid without crystallizing. Many different glass compositions have been produced in this way and by other methods.

A few glasses are significantly electrically conductive. Most amorphous electrical conductors, or semiconducting glasses as they are sometimes called, contain a number of the sixth group of elements in the periodic-classification table as a major constituent. Semiconducting glasses may be classified into two groups: transition-metal oxide glasses, and chalcogenide glasses. Transition-metal oxide semiconductors (vanadium oxides are good examples) exhibit only relatively poor electrical

conductivity under normal conditions. Never-the-less these materials have important and useful electrical characteristics.

Chalcogenide glasses contain a major fraction of one or more of the members of group VI excepting oxygen: sulfur, selenium, and tellurium, combined with other elements from roughly the same region of the periodic table. A tremendous number of combinations have been formed as glasses; only a few have been studied extensively. Chalcogenide glasses have relatively high electrical conductivity and frequently show memory switching effects. The past several years have seen investigation of chalcogenide glasses for infrared-optical[1] and electrical-switching[2] applications. Recently there has been much effort to understand electrical effects in these non-crystalline or relatively-disordered materials at a theoretical level. However, difficulty in producing chalcogenide glasses and the awkward task of describing them in familiar crystalline terms has interfered with progress in the theoretical studies.

1.2 Choice of Material and Goals

Amorphous $Ge_{10}As_{20}Te_{70}$, a known semiconducting glass, was selected for comprehensive study of its physical, electrical, and optical properties. The research attempted to show that this material could be produced in a relatively easy and repeatable fashion, and that its characteristics could be measured using mostly conventional techniques. Much effort was devoted to the design and execution of experimental techniques; few theoretical interpretations were made. Also, considerable effort was devoted to the task of keeping abreast of recent developments regarding experiment and theory for chalcogenide semiconductors. Evaluations of data and correlations with available theory and similar experimental information are distributed in the text according to subject.

A composition diagram for the ternary germanium-arsenic-tellurium system has been published,[1] and is shown in Figure 1.1. Binary phase diagrams and other chemical characteristics for materials from this system are also available.[3-6] Reported compounds, eutectics, and glasses are indicated on the diagram. The glass-formation region, outlined in Figure 1.1, has been determined theoretically[69] and experimentally.[1,67] A computer program, CONVPCNT, used to replot the diagram with weight-fraction scales,[7] is shown in Table 1.1. Many compositions can be synthesized by direct mixture of elements or by mixture of elements and compounds. Similarly, glasses devitrify by separation into several elements or compounds. The computer program was also used to calculate weight and atomic-number fractions for mixtures of two or more elements and/or compounds from the Ge-As-Te system. Several mixtures or possible separations for the composition $Ge_{10}As_{20}Te_{70}$ are shown in the composition diagram as dashed lines.

1.3 Literature Review for the Ge-As-Te System

Discovery of reversible conductivity-switching effects in semiconducting glasses has stimulated study of amorphous chalcogenides.* Some of the research reported for Ge-As-Te materials is listed in the references for this and other chapters. Miscellaneous physical properties, including thermal and structural characteristics, have been determined.[1,8-22] Studies of electrical properties, especially switching, have been reported.[19-50] Finally, optical properties of Ge-As-Te glasses have been published.[1,51-61] Most of this information was very useful, though relatively little was for the specific composition $Ge_{10}As_{20}Te_{70}$.

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* Brief reviews of theory for non-crystalline electrical conductors and of experiment and theory for conductivity switching can be found in Appendix A and Appendix D respectively.

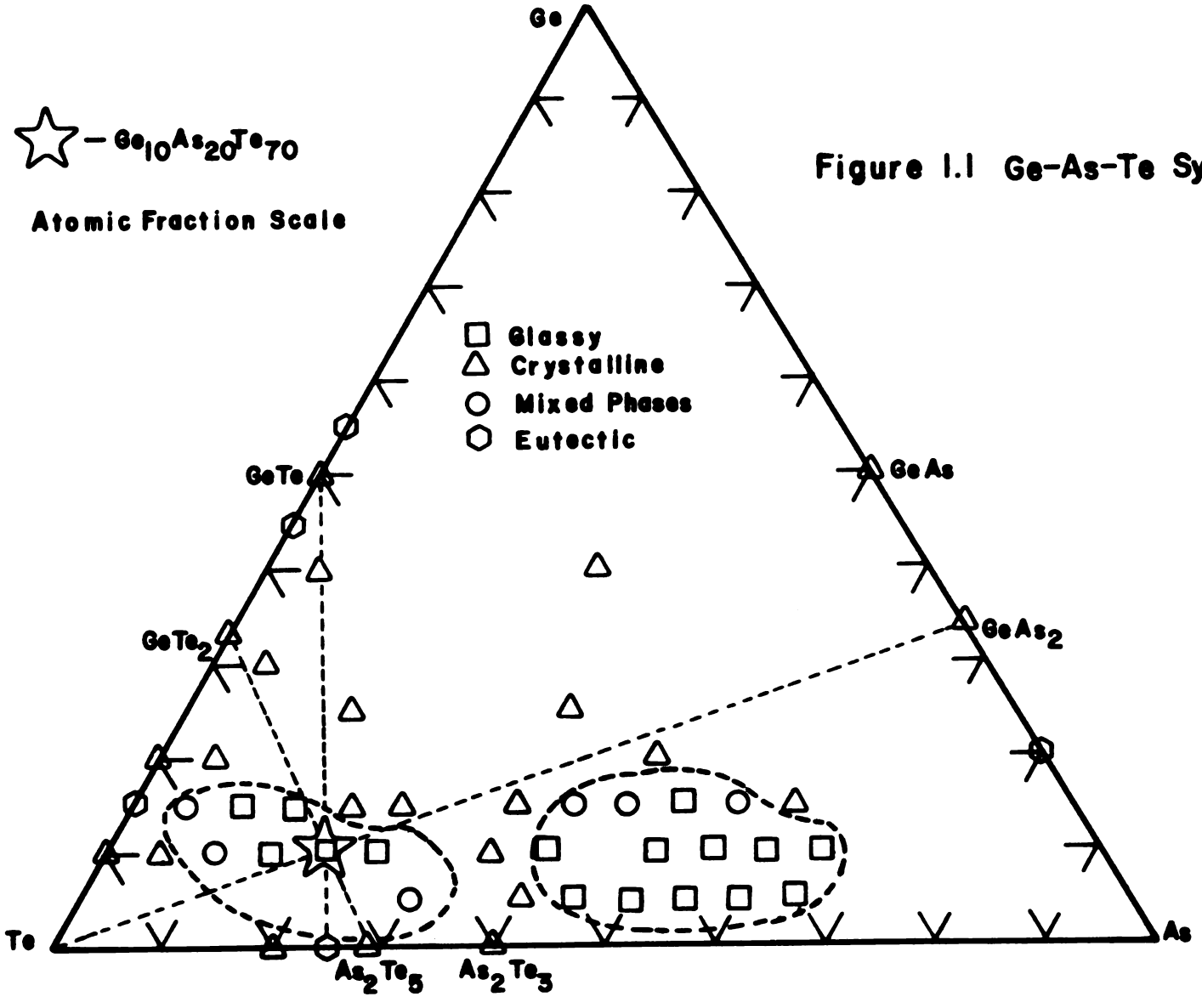

Figure 1.1 Ge-As-Te System

```
1 CØMMØN FRACT(5),M(5),C(20,10),N,NN
31 TE=127.6;AS=74.9216;GE=75.59;GETE=GE+TE;GETE2=GE+TE*2.
36 AS2TE3=AS*2.+TE*3.; AS2TE5=AS*2.+TE*5.
41 C(1,1)=TE;C(2,1)=AS;C(3,1)=GE;C(7,3)=2.
44 C(4,1)=GETE; C(5,1)=GETE2; C(6,1)=AS2TE3; C(7,1)=AS2TE5
48 C(1,2)=1.;C(2,3)=1.;C(3,4)=1.;C(4,2)=1.;C(4,4)=1.
49 C(5,2)=2.;C(5,4)=1.;C(6,2)=3.;C(6,3)=2.;C(7,2)=5.
52 PRINT," INPUT # CØNSTITUENTS"; INPUT,NN
55 PRINT," WHICH ",NN," CØNSTITUENTS"; INPUT,(M(K),K=1,NN)
57 PRINT," IN WHAT PERCENTAGES"; INPUT,(FRACT(K),K=1,NN)
60 PRINT," WHICH CØNVERSIØN TYPE?"; INPUT,NM; PRINT," "
63 GØ TØ(1,2,3),NM; 1 CALL MØLWT; GØ TØ 10
64 2 CALL WTMØL;GØ TØ 10;3 CALL WTAT;10 STØP;END
300 SUBRØUTINE MØLWT
301 CØMMØN FRACT(5),M(5),C(20,10),N,NN; DIMENSIØN W(5)
320 PRINT,"     MØLECULAR %                WEIGHT %"
321 PRINT," "; WT=0.
340 DØ 50 LL=1,NN;W(LL)=FRACT(LL)*C(M(LL),1);50 WT=WT+W(LL)
360 DØ 60 LL=1,NN; 60 W(LL)=100.*W(LL)/WT
370 PRINT 1000,(FRACT(K),K=1,5),(W(K),K=1,5)
375 1000 FØRMAT(" ",5(F6.2," "),"  ",5(F6.2," "))
380 RETURN; END
400 SUBRØUTINE WTMØL
401 CØMMØN FRACT(5),M(5),C(20,10),N,NN; DIMENSIØN W(5)
420 PRINT,"      WEIGHT %                MØLECULAR %"
421 PRINT," "; WT=0.
440 DØ 50 LL=1,NN;W(LL)=FRACT(LL)/C(M(LL),1);50 WT=WT+W(LL)
455 DØ 60 LL=1,NN; 60 W(LL)=100.*W(LL)/WT
465 PRINT 1000,(FRACT(K),K=1,5),(W(K),K=1,5)
470 1000 FØRMAT(" ",5(F6.2," "),"  ",5(F6.2," "))
480 RETURN; END
500 SUBRØUTINE WTAT
501 CØMMØN FRACT(5),M(5),C(20,10),N,NN;DIMENSIØN W(5),WW(5)
512 PRINT,"      WEIGHT %           TE%    AS%    GE%
513& (NØTE: ATØMIC%)"
516 PRINT," "; WT=0.
528 DØ 50 LL=1,NN;W(LL)=FRACT(LL)/C(M(LL),1);50 WT=WT+W(LL)
540 DØ 60 LL=1,NN; 60 W(LL)=100.*W(LL)/WT; DØ 70 LL=1,3
552 WW(LL)=W(1)*C(M(1),LL+1)/(C(M(1),2)+C(M(1),3)+C(M(1),4))
556 WW(LL)=WW(LL)+W(2)*C(M(2),LL+1)/
557&(C(M(2),2)+C(M(2),3)+C(M(2),4))
560 IF(NN.EQ.2) GØ TØ 70
564 70 WW(LL)=WW(LL)+W(3)*C(M(3),LL+1)/
565&(C(M(3),2)+C(M(3),3)+C(M(3),4))
572 PRINT 1000,(FRACT(K),K=1,5),(WW(K),K=1,5)
576 1000 FØRMAT(" ",5(F6.2," "),"  ",5(F6.2," "))
580 RETURN; END
```

Table 1.1 **Computer Program CONVPCNT**

1.4 Measurement Objectives

Complete and general characterization of amorphous $Ge_{10}As_{20}Te_{70}$ was desired. Useful determinations which could be conveniently accomplished using available equipment were done. Apparatus was designed and fabricated for the determination of several additional properties. In a few cases construction of equipment was not completed in time for measurements to be reported here.

Property measurements were begun with examination of gross physical characteristics such as density and hardness. Later, thermal analyses[62] were performed, including DTA, TGA, and TMA. Phenomena such as glass transformation, softening, crystallization, melting, quenching, and oxidation were observed by thermal-analysis techniques. X-ray diffraction and chemical-analysis techniques were used to determine composition and structure of glassy and crystallized material. Electrical conductivity and many other electrical properties were investigated. Finally, optical absorption and reflection measurements for bulk and thin-film samples were performed.

For simple crystalline semiconductors,[68] electrical current resulting from application of an electric field defines a material property,[63] conductivity:

$$\sigma \equiv J/E = \sum n_i q_i \mu_i$$

Contributions to conductivity due to charged current carriers, q_i, present with volume density, n_i, are proportional to the mobility, μ_i, of the i'th carrier type. Usually only hole and electron carriers are important, but other mechanisms for current flow have been identified for disordered materials. Understanding of electronic properties of materials requires determination of contributions and energetics for

each term and factor involved with conductivity. Much of the information can be obtained by independent measurements of conductivity and mobility versus temperature.

Measurement of conductivity versus temperature is fundamentally straightforward but was technically difficult for amorphous $Ge_{10}As_{20}Te_{70}$. Special four-point probe apparatus was designed and constructed for measurement of dc electrical conductivity versus temperature. Equipment fabricated by collegues was used for measurements of ac electrical admittance and switching characteristics. A simple method[65] was used for determination of the polarity and approximate magnitude of Seebeck coefficient.

Carrier-mobility measurements were complicated and difficult. The Hall effect,[63] often used for determination of carrier polarity and mobility for crystalline materials, was difficult to observe for amorphous $Ge_{10}As_{20}Te_{70}$. Hall mobility for amorphous chalcogenide semiconductors is usually very small and difficult to interpret. Direct determination of drift mobility[63] was considered most appropriate and apparatus was developed which used the electron-beam injection technique[64] for transit-time measurements.

Naturally, measurements performed gave results which suggested many additional studies of other characteristics. As time was an important factor, such further study was not practical. The broad collection of measurements made should, however, supply much of the information required for the establishment of simple hypotheses on the nature of electrical conduction and other processes for amorphous $Ge_{10}As_{20}Te_{70}$ and possibly other amorphous chalcogenide semiconductors.

CHAPTER 2

MATERIAL SYNTHESIS

2.1 Raw Materials

Acquisition of amorphous $Ge_{10}As_{20}Te_{70}$ and other amorphous semiconductors from commercial chemical suppliers and from other research organizations was not possible. Most suppliers either could not provide the requested compositions or would undertake their synthesis only upon receipt of an order for substantial quantities at high cost. Energy Conversion Devices, Troy, Michigan, an organization studying chalcogenide semiconductors would not supply the material for proprietary reasons. Information on synthesis technique was requested to aid the unfamiliar task of producing the amorphous materials. At the time of the requests, 1968, this information was highly proprietary, and only information found in open literature was available. Recently at least one organization* has offered chalcogenide glasses at reasonable cost, purities, and quantities.

A first step in the synthesis was selection and acquisition of pure starting materials. Several organizations** offered pure germanium, arsenic, and tellurium; most raw materials were purchased from Alfa Inorganics. Purity and usefulness of materials depended upon the form supplied. Fifty ohm-centimeter resistivity powdered and polycrystalline

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* Materials Research Corporation, New York, quoted $175 for 100 grams of 99.999% pure $Ge_{10}As_{20}Te_{70}$.

** Alfa Inorganics Division of Ventron Corp., Beverly, Massachusetts; K & K Laboratories Inc., Plainview, New York; Research Inorganic Chemical Corp., Sun Valley, California; Rocky Mountain Research Inc., Denver, Colorado; Apache Chemicals Inc., Rockford, Illinois; Materials Research Corporation, Orangeburg, New York; Atomergic Chemicals Co. Division of Gallard-Schlesinger, Carle Place, L.I., New York; American Smelting and Refining Company, South Plainfield, New Jersey; and several others.

germanium was satisfactory. Powder, shot and crystalline lumps of tellurium were available. The shot form was most frequently chosen as a compromise between handling ease and purity. Most powdered or crystalline arsenic was generally excessively oxidized. Accordingly, pure crystalline lumps packaged in inert gas were purchased and stored in a dessicator under dry nitrogen until used. Arsenic was exposed to the atmosphere for only a short period for weighing. Generally, lumps and shot were used in preference to powders to reduce dusting and to reduce losses due to adherence of powders to weighing tools and ampul walls. Also, lumps had less surface susceptible to oxidation or contamination.

Purity and correct stoichiometry of the final compositions was not of great concern; hence purity of starting materials was not too important. A primary consideration was that the synthesis procedure be repeatable and not difficult. This position was justified by the generally accepted thesis that impurities and slight compositional changes in amorphous semiconductors do not significantly affect their properties.[1,33,34] However, some workers do not agree that amorphous semiconductors are entirely impurity insensitive, and have been very careful in their preparation technique.[2,3,4,30]

2.2 Handling and Weighing

A serious consideration in the preparation of materials containing arsenic and tellurium was toxicity. These elements are generally considered highly toxic[5,8] and dangerous in all forms. Of particular concern was possible inhalation of powders and dust. All handling of elements and finished compositions was done initially in polyethylene glove bags (I^2R Instruments Inc., Cheltenham, Pennsylvania), and later in a glove box (Lab-Con-Co., Kansas City, Missouri). No attempt was made to purge

or otherwise control the atmosphere in these systems. This could easily have been done, however, had atmospheric contamination or oxidation been a problem.

A computer program, CONVPCNT,* was used to determine weight percentages of the elements in $Ge_{10}As_{20}Te_{70}$. The weight percentages were calculated as: tellurium-79.85%, arsenic-13.49%, and germanium-6.76%. Using these percentages, suitable large lumps of arsenic were chosen and weighed, and remaining ingredients were proportioned appropriately. Weighing was done inside the glove box to an accuracy of about 0.01 g using an analytical balance (Model DWL-5, Torsion Balance Company, Clifton, New Jersey). Initially, constituents were weighed into small dishes and transferred to the quartz ampuls. However, an excessive loss of raw materials occurred in transfer operations, and cumulative weighing of elements directly into the ampuls was finally used. Following this operation the ampuls were tapped lightly to shake down dust on the inside walls.

2.3 Evacuation, Sealing and Fusing

After raw materials were weighed into the quartz ampuls, loose-fitting quartz plugs were dropped in, and the ampuls were transferred carefully from the glove box to a simple vacuum system for evacuation and sealing.** After evacuation to about 10^{-3} torr and sealing, ampuls containing the raw materials were suspended in a rocking furnace for fusion. Many researchers prefer to backfill ampuls with a low pressure of inert gas. This procedure was not followed as an initial gas fill

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* The timesharing-computer program, CONVPCNT, was described in Section 1.2.

** Information about the ampuls, the vacuum system, and sealing procedures can be found in Appendix B.

would excessively increase pressure in the ampuls at high temperatures. For example, heating to temperatures near 1000 °C could multiply initial pressures by almost forty and possibly burst the ampuls. Near 1000 °C the vapor pressure of tellurium is about 760 torr, and the vapor pressure of sublimed arsenic is over 20 000 torr.[6,7,8] The ampuls were heated carefully in an armored furnace enclosed by a fume hood* to reduce hazards from an explosion.[31] No explosions occurred however, possibly because the volatile arsenic was dissolved or reacted almost as fast as it sublimed.

Many researchers[9,10] fuse elements into a homogenous composition by heating to a temperature high enough to melt all constituents. The highest melting point element used, germanium, melts at 937 °C , tellurium melts at 450 °C , and arsenic sublimes at 610 °C and 760 torr.[8] Materials were fused at several temperatures in the range from 500 °C to 1100 °C , and resulting mixtures usually appeared homogenous when sufficiently long reaction periods were provided. Tellurium melted at these temperatures and probably rapidly dissolved the arsenic; the melting point of the arsenic-tellurium alloy was less than 400 °C.[11] The arsenic-tellurium liquid then slowly dissolved the germanium, resulting in homogenous compositions produced at relatively low temperatures. Most $Ge_{10}As_{20}Te_{70}$ used was produced by fusing at 800 °C for twenty hours in a rocking tube furnace. A one-half hour warm-up period was provided to allow for solution of the arsenic, preventing build-up of an excessive arsenic vapor pressure.

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* A detailed description of the rocking furnace used is available in Appendix B.

2.4 Quench Technique

It is well known that glasses may frequently be created by rapid quenching of the liquid state.[12-15,30] This supercooling process results in a rigid liquid in which crystallization proceeds only very slowly. The nature of the glass formed depends strongly on the quench rate.[16] Many techniques for producing chalcogenide glasses use an air quench.[9,10] To obtain very fast cooling rates, a brine bath chilled to 0 °C was used. Saturated brine had a higher thermal conductivity and tended to boil less violently than plain water.[17,29] The quenching solution was enclosed in an armored vessel to reduce hazards from possible explosions. Ampuls were dropped directly from the furnace into the quenching bath. Cooling fused material to 400 °C , a temperature only slightly above the melting point of $Ge_{10}As_{20}Te_{70}$, prior to quenching resulted in faster quenching and lowered fragility of the glass produced. Boules of material were easily removed from ampuls, probably because differences of thermal expansion do not allow chalcogenide glasses to stick to fused silica. A small hole through the center of the cylindrical boules was noted; this probably was produced as the material cooled from the outside and shrunk away from the center.[29]

Amorphous materials produced by quenching of melts contained considerable strain, evidenced by extreme brittleness and difficulty in cutting and polishing.[3] Reduction of strains and modification of conductivity by annealing has been observed for these materials.[18,19] Strain and other characteristics of amorphous $Ge_{10}As_{20}Te_{70}$ could probably have been modified by changes in quenching and annealing processes. A series of experiments to test this hypothesis was not performed as the primary objective was development of a synthesis

technique for a single reproducible material. However, most samples were annealed for about ten hours at 100 °C , slightly below the glass transformation temperature. Annealing at higher temperatures often resulted in crystallization of samples. Even though annealed, the glass was quite fragile and often broke into many pieces at the slightest shock.

2.5 Sample Preparation

Amorphous $Ge_{10}As_{20}Te_{70}$ semiconductor material produced in the manner described was about one centimeter in diameter and about two centimeters long, or was in fragments thereof. Freshly fractured surfaces of randomly chosen lumps were used as samples on which properties were measured. Techniques for cleaning or modifying surfaces, such as chemical etching and sandblasting, did not significantly affect experiments. The only effective etchants found were aqueous solutions of ferric chloride, and concentrated nitric acid. Attempts to cut and polish samples almost always caused fractures, possibly due to the extreme brittleness and strained nature of the glasses.

Several thin, flat-sided bulk samples were obtained by grinding down larger lumps of the glassy material. Pieces of amorphous $Ge_{10}As_{20}Te_{70}$ were fastened to quarter-inch plate-glass substrates with CrystalBond 509 Adhesive, Aremco Products, Briarcliff Manor, New York, an acetone-soluble, low softening temperature mounting media. During mounting and grinding the temperature of the amorphous semiconductor was kept below 100 °C to avoid additional annealing or possible crystallization. Grinding was done under water, to prevent toxic dusting, on silicon-carbide sandpapers. Both sides of several lumps were flattened in this fashion. Samples thinner than about 250 μm broke during grinding or

mounting processes; polished surfaces were frequently severely pitted. However, unpolished wafers produced in this fashion were useful for many electrical and optical experiments.

Three additional techniques for producing flat-sided samples were attempted with little success. First, semiconducting glass melted and quenched in flat-sided silica ampuls was always broken during removal from the ampuls. Second, hot-pressing amorphous $Ge_{10}As_{20}Te_{70}$ above the softening temperature usually resulted in crystallization of the sample being shaped. Finally, melted material squeezed between chilled silica plates was usually partially crystallized, and was not useful for most purposes. This was probably due to an insufficient quenching rate. Polycrystalline films of $Ge_{10}As_{20}Te_{70}$ about 100 μm in thickness obtained in this manner were used for an optical absorption experiment.

2.6 Thin Film Production

The technique described for production of amorphous $Ge_{10}As_{20}Te_{70}$ has had a long and popular history.[21] Other quench methods such as splat quenching[22] have been used. Additional techniques for preparation of amorphous compositions include precipitation from solution and condensation from vapor. The latter method has been used with considerable success in the preparation of amorphous films.[23,28,29] Although it is possible to co-deposit two or more elements simultaneously from one or more sources onto a cold substrate,[24,25,35] an apparently more popular technique is evaporation or sputtering of pre-mixed and fused materials.[9]

Thin films of elemental semiconductors and other materials have been produced by sputtering.[26,28] Several organizations are using

this technique for the preparation of compound and alloy films.* Since sputtering apparatus was not available, a modified thermal-evaporation process[27] was used to produce thin films of $Ge_{10}As_{20}Te_{70}$. This method, used by others with success,[9,28] is a pseudo flash-evaporation technique from an alumina-coated resistance-heated baffled boat source.** Films produced in this fashion ranged in thickness from 0.01 μm to 5 μm. Films thicker than about 2 μm were prepared by cascading several flash-evaporated films on a single substrate. All films were deposited on thin soda-lime glass microscope cover slides. Of many instruments available for film-thickness measurement,[32] the most useful for measuring these chalcogenide films were found to be a Varian Interferometer and a Zeiss Light-Section microscope.

It is well known that segregation often occurs if alloys are thermally evaporated. The flash-evaporation technique employed reduced segregation since it allowed easy mixing of vapor species. Frequently, researchers have determined composition of films after deposition by electron-microprobe techniques.[19] Such determinations were not made for flash-evaporated films described here, but properties of films did not differ greatly from bulk source material. Considerable work remains to be done in the field of preparation of chalcogenide alloy films.

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* Energy Conversion Devices, Troy, Michigan, utilizes sputtering techniques in the production of Ovonic Switches.

** A complete description of the apparatus and process can be found in Appendix B.

CHAPTER 3

GENERAL PHYSICAL PROPERTIES

3.1 Introduction

Many properties for $Ge_{10}As_{20}Te_{70}$ are reported here. These properties are generally non-electrical and non-optical; included are appearance, density, hardness, thermal, and structural characteristics. Additional information reported by others is also discussed.

Thermal constants for Ge, As, and Te have been determined.[1] Ge melts at 937 °C with a heat of fusion, ΔH, of 0.468 kJ/g (8.1 kcal/mole). As sublimes to As_4 at 610.0 °C and 760 torr with ΔH = 1.73 kJ/g (31 kcal/mole). Te melts at 449.7 °C with ΔH = 0.138 kJ/g (4.2 kcal/mole); vaporization to Te_2 occurs at the melting point with ΔH = 0.433 kJ/g (13.2 kcal/mole) and vapor pressure 0.18 torr.

Mass spectrographic analysis[2] of vapors developed from heated $Ge_{10}As_{20}Te_{70}$ showed As_4 appearing above 262 °C with a heat of vaporization of 1.52 kJ/g (28 kcal/mole). Some arsenic was possibly only dissolved in the glass and appeared upon softening or crystallization. Te_2 appeared above 386 °C with a heat of vaporization of 1.12 kJ/g (34 kcal/mole). As_2Te_3, probably present in crystallized $Ge_{10}As_{20}Te_{70}$, was an excellent possible source for Te_2 vapors since the melting temperature of this compound is 362 °C. Except for arsenic, dissociation energies from $Ge_{10}As_{20}Te_{70}$ were generally greater than those from the covalently bonded elements.

Differences between ^{125}Te nuclear magnetic resonances in amorphous and crystallized $Ge_{15}As_4Te_{81}$ have been observed[3] and interpreted.[4] The resonance frequencies of ^{125}Te for tellurium dissolved in aqua regia

for crystalline tellurium, and for crystallized $Ge_{10}As_4Te_{81}$ were all the same. It was therefore concluded that a constituent of crystallized high electrical-conductivity $Ge_{15}As_4Te_{81}$ was crystalline tellurium. The resonance frequency for low electrical-conductivity amorphous material was lower than that for crystallized material. This was interpreted as a chemical shift arising from structural differences between the two states. Although the composition studied was not $Ge_{10}As_{20}Te_{70}$, it was assumed that similar characteristics would be observed for this material.

3.2 Microscopic Examination

Surfaces of amorphous and crystallized $Ge_{10}As_{20}Te_{70}$ were examined with a high quality optical microscope (Ortholux, Leitz-Wetzler Company, Germany). A lump of "silly putty" was used to attach pieces to a microscope slide for observation. Freshly-broken surfaces of amorphous material were dark, shiny, and "glassy" in appearance to the naked eye. Even at very high magnifications, microscope examination showed only stress-fracture lines and smooth surfaces. A freshly-broken piece of amorphous material was crystallized in a dry nitrogen atmosphere by increasing its temperature at a rate of 5 °C per minute until 240 °C was reached. The surface appearance after crystallization seemed metallic and dull as if sandblasted. Microscopic examination showed a complex network of interlocked fibers or crystallites, typically ten micrometers in length, criss-crossing and penetrating a previously smooth and unbroken surface. Photographs of typical untreated surfaces for amorphous and crystallized $Ge_{10}As_{20}Te_{70}$ are shown in Figure 3.1. It is believed that small crystallites of tellurium and other compounds were formed in the glassy matrix when the amorphous state was crystallized.

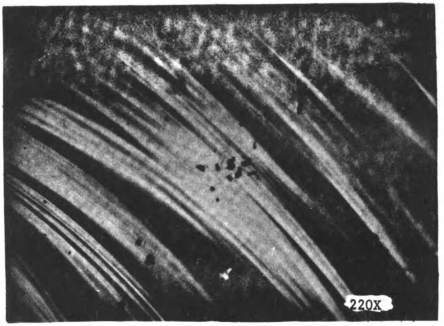

Figure 3.1a Amorphous $Ge_{10}As_{20}Te_{70}$, Magnified Surface

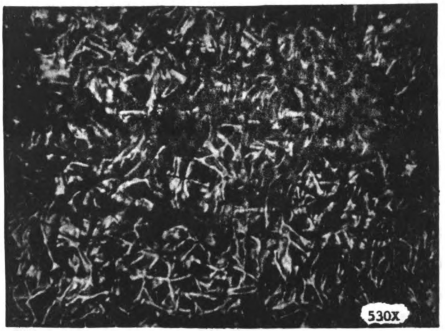

Figure 3.1b Crystalline $Ge_{10}As_{20}Te_{70}$, Magnified Surface

Additional careful examinations of physical appearance for crystalline and glassy $Ge_{10}As_{20}Te_{70}$ would probably yield considerable information. Depending upon quench and annealing treatments, several intermingling glassy and crystalline fractions might possibly be observed and identified. Scanning electron microscopy,[5,31] replica electron microscopy[6,12] and analytical electron-microprobe techniques have been used for detailed examinations of surfaces of chalcogenide glasses from the Ge-As-Te system.

3.3 Density and Hardness

A useful and easy to measure property of a material is density. Densities of the elemental constituents of the Ge-As-Te system have been tabulated:[8] germanium-5.32, arsenic-5.72, tellurium-6.24 g/cm^3 at 20 °C. A simple homogenous mixture with composition $Ge_{10}As_{20}Te_{70}$ should have an average density of 6.08 g/cm^3. However, an alloy could have significantly different density. Archimedes' method was used to measure the density of amorphous $Ge_{10}As_{20}Te_{70}$. An analytical scale (Gram-atic Balance B5, Mettler Instrument Co., Hightstown, New Jersey) was used to weigh samples in air and immersed in pure water at 15 °C. A large lump of material was suspended in the water by means of a fine wire hung from the balance.

The density of amorphous material was 5.68 g/cm^3. Compensation was made for suspension wire weight, and density, but not for surface tension effects on the wire or for the non-unity density of water. Density of amorphous $Ge_{10}As_{20}Te_{70}$ was measured by others[9,10] as about 5.6 g/cm^3 in a study which showed that the density of chalcogenide glasses was approximately proportional to their molecular weight. Crystallized material was not measured, but was suspected of being

somewhat porus.

Hardness could have been determined in several fashions, but scratch testing was simple and effective. In this method, the sample was scratched by harder and softer materials to locate hardness between that of two known materials. A usefully-accurate hardness scale was created of minerals with measured hardness, and careful technique. Amorphous $Ge_{10}As_{20}Te_{70}$ was found to be relatively soft: about 2.8 on the Mohs scale (about 100 on the Knoop scale), about the same hardness as pure gold. Chalcogenide glasses are generally relatively soft; hardness is approximately proportional to the softening temperature.[9,10] For comparison, ordinary soda-lime glass was about 5.8 on the Mohs scale. The hardness of $Ge_{10}As_{20}Te_{70}$ has been more carefully determined by others[9,11] to be 111 on the Knoop scale. The softness and fragility of these materials have severely limited their application to optics and other uses.

3.4 Thermal Analysis

Thermal-analysis techniques[13-16] were used to evaluate thermodynamic properties of $Ge_{10}As_{20}Te_{70}$. Following suggested procedures, characteristics such as heat capacity, critical temperatures such as melting points, and thermal reactions such as glass transformation, crystallization, and oxidation were observed. Thermal-analysis methods included thermo-gravimetric analysis, TGA, thermo-mechanical analysis, TMA, differential thermal analysis, DTA, and others. A thermal-analyzer system (Model 900, E. I. DuPont de Nemours & Co., Wilmington, Delaware) was used to obtain data reported here.

Thermo-gravimetric analysis examined changes of weight versus time and temperature. A typical gravimetric thermogram for amorphous $Ge_{10}As_{20}Te_{70}$ was virtually featureless and is therefore not shown.

Weight changes occurred only in pure oxygen or air atmospheres, began above the glass transformation temperature, and were positive and small. Surface oxidation only was believed to account for this, since weight changes were less than 0.5% for samples heated to 425 °C and held there for long times. TGA has also been used for studies of chemisorption in amorphous germanium.[17]

Thermo-mechanical analysis examined size changes and softening of samples versus temperature. Here, the penetration of a lightly-loaded probe into samples was monitored as a means for observation of softening[19] and melting. A typical penetration thermogram is shown in Figure 3.2. Indicated on the curve are softening, re-hardening upon crystallization, and melting. Contributions due to thermal expansion were negligible for these measurements. The thermal coefficient of expansion for chalcogenide glasses has been examined,[9,11,18,19] however, and was 18×10^{-6} m/(m × °C) for amorphous $Ge_{10}As_{20}Te_{70}$.[11]

For differential thermal analysis, the temperature of a sample was continuously compared with an inert reference material; differences in temperature due to thermal reactions of the sample were recorded as a function of the temperature of an enclosing furnace used to heat the sample and reference materials. Endothermic and exothermic heat effects associated with physical or chemical changes[20] in a sample (such as glass transformation, or crystallization) were monitored by this technique. A differential-scanning-calorimeter accessory for the thermal-analysis system was used to obtain the typical thermograms shown in Figure 3.3a for heating and Figure 3.3b for cooling.

Three prominent features[21,26] of these curves require comment. Glass transformation, at T_g, was characterized by an abrupt change in

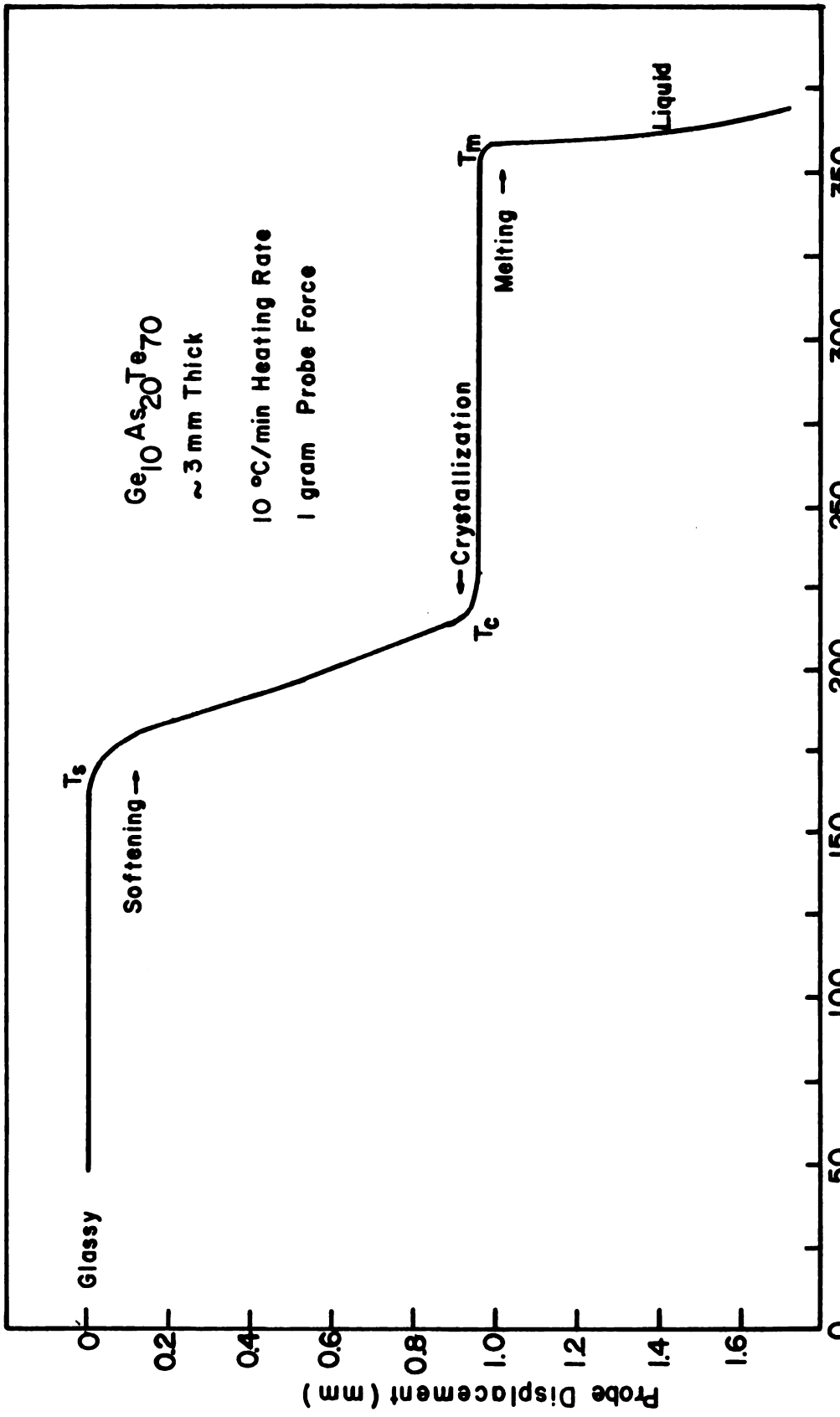

Figure 3.2 TMA Penetration Curve

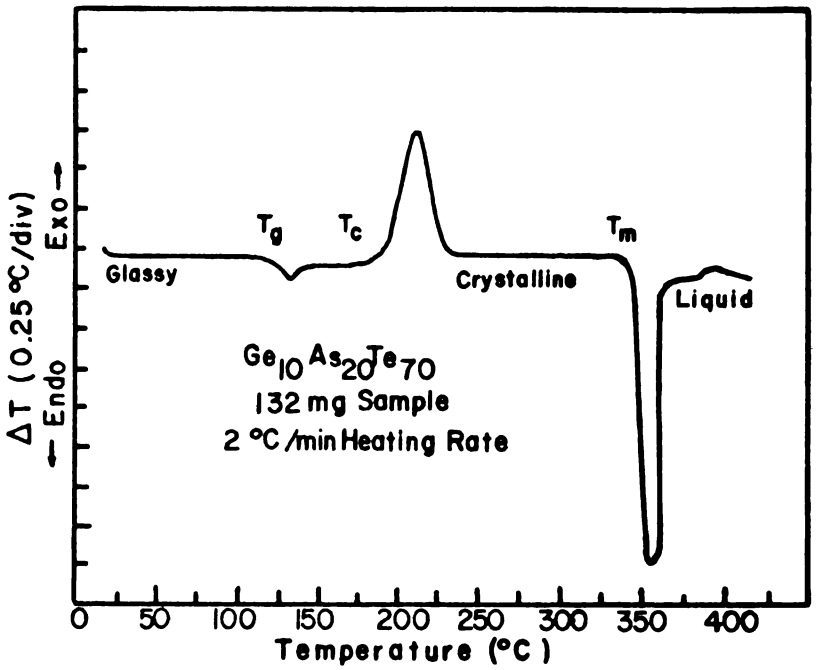

Figure 3.3a Typical DTA Curve

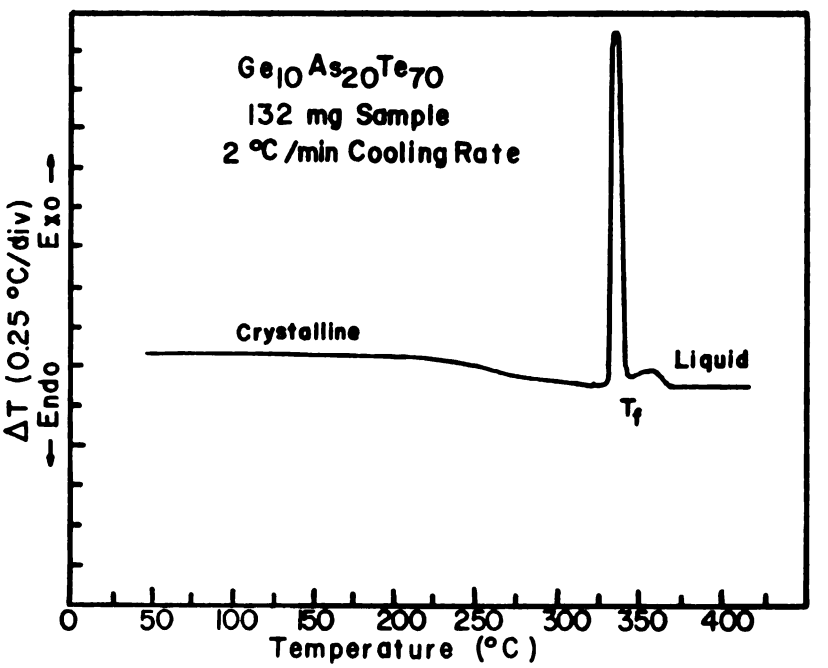

Figure 3.3b Typical DTA Curve

specific heat, or a baseline shift in the thermogram.[25] Crystallization began at T_c, and continued over a range of temperatures, liberating heat. Finally, melting of the crystalline phase, indicated by a strong endotherm, occurred at T_m.

Examples of thermograms obtained before and after annealing are shown in Figure 3.4. An unusual endotherm in the glass transformation region of the curve occurred only for annealed samples, and was interpreted as a stabilization process.[24] Anomalous thermograms such as in Figure 3.5 were obtained for a few glasses. The complex peak structure was characteristic of samples with several mixed phases,[12] and material showing this property was not used for further testing. Curves in the glass transformation region were similar to others for this material,[24] although the value determined for T_g was slightly lower than the reported value.[28] Sensitivity of the glass transition temperature to quench rate,[5,18] composition,[28] and annealing[24] are known, however. Carefully calibrated thermograms were also used to determine specific heat,[25] and heats of reaction.[26,27,32]

Much thermal investigation of chalcogenide glasses has been done in an attempt to explain threshold and memory electrical conductivity switching as a phase-change effect. Threshold-switching field intensities have been correlated with the glass-transformation temperatures.[28] Presence of multiple crystallization exotherms and other characteristics in thermograms are related to switching effects,[5,29,30] and attempts to control[18] phase transitions have led to exotic semiconducting and switching compositions.*

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* Energy Conversion Devices, Troy, Michigan, produces Ovonic Threshold switches containing films of approximate composition: Te-49%, As-33%, Ge-6%, Si-3%, Ga-9%.

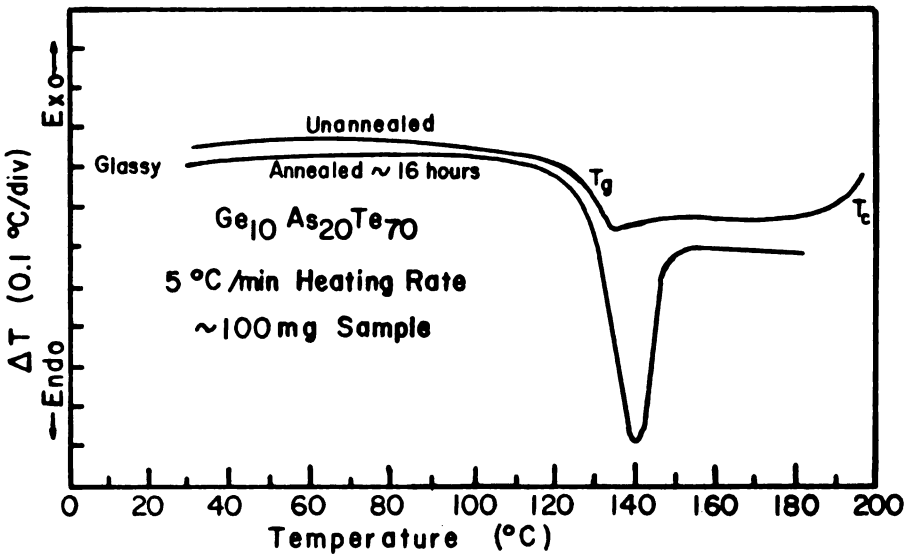

Figure 3.4 Glass Transformation DTA

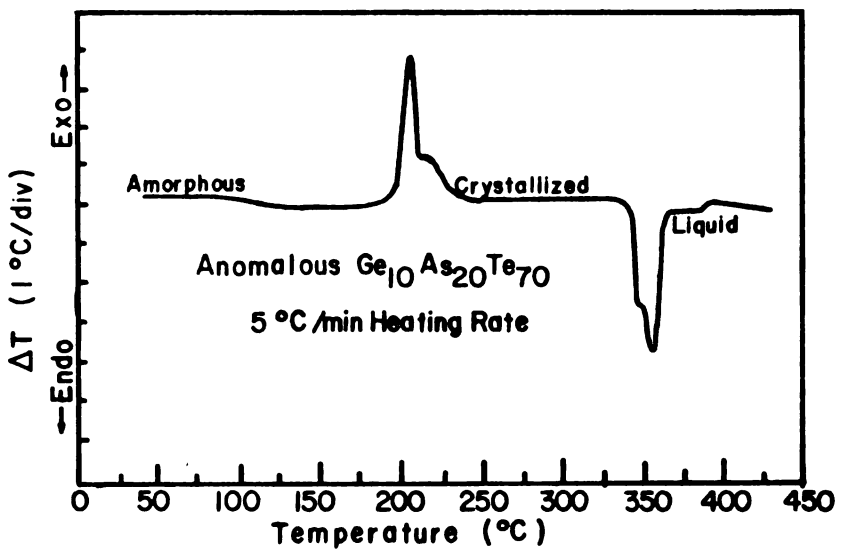

Figure 3.5 Anomalous $Ge_{10}As_{20}Te_{70}$ DTA

Properties of $Ge_{10}As_{20}Te_{70}$ determined by thermal analysis are listed in Table 3.1. In most cases, broken pieces of as-quenched (possibly annealed) bulk material were used as samples. Some information was taken directly from curves, but calorimetric information was calculated using data taken from the curves and additional calibration information. Considerable time and effort was required to collect this information; thermal analysis was generally a time consuming and complex activity.*

An especially-illustrative differential thermal-analysis experiment performed is illustrated in Figure 3.6 as three successive thermograms for the same sample. As shown by the first curve, a piece of un-annealed glassy $Ge_{10}As_{20}Te_{70}$ heated slowly exhibited glass-transformation, crystallization, and melting phenomena. The melted sample was then rapidly quenched (in the calorimeter) and reheated slowly in a similar fashion. A smaller and shifted crystallization exotherm was exhibited in the second thermogram, indicating that only a fraction of the sample had been returned to the amorphous state. After remelting the sample was allowed to cool slowly, and a third thermogram was run. The absence of a crystallization exotherm in the last thermogram demonstrated that the sample had been completely crystallized. Another experiment, not illustrated, involved rapid quenching from above the crystallization exotherm but below T_m; always produced was a curve similar to the third thermogram.

3.5 X-Ray Diffraction

A useful method for study of structure and composition of these materials was x-ray diffraction.[33-35] Experimentally, a sample was

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* Considerable instruction and contribution from Dr. L. Taylor and J. Tobias of the Owens-Illinois Inc., Okemos Research Laboratory, Okemos, Michigan is gratefully acknowledged.

Table 3.1

SUMMARY OF MEASURED THERMAL PROPERTIES

Characteristic	Temperature	Value	Conditions*
Heat Capacity	80 °C	0.289 J/(g °C)	glass annealed 16 hrs
Heat Capacity	80 °C	0.314 J/(g °C)	crystallized
Glass Transformation	120 °C	----------	unannealed glass
Stabilization	140 °C	2.87 J/g	glass annealed 16 hrs
Heat Capacity	160 °C	0.382 J/(g °C)	glass annealed 16 hrs
Heat Capacity	160 °C	0.288 J/(g °C)	crystallized
Crystallization	190 °C	6.11 J/g	heated @ 2 °C/min
Fusion	335 °C	----------	heated @ 2 °C/min

*Determined with 5 °C/min heating rate unless otherwise noted.

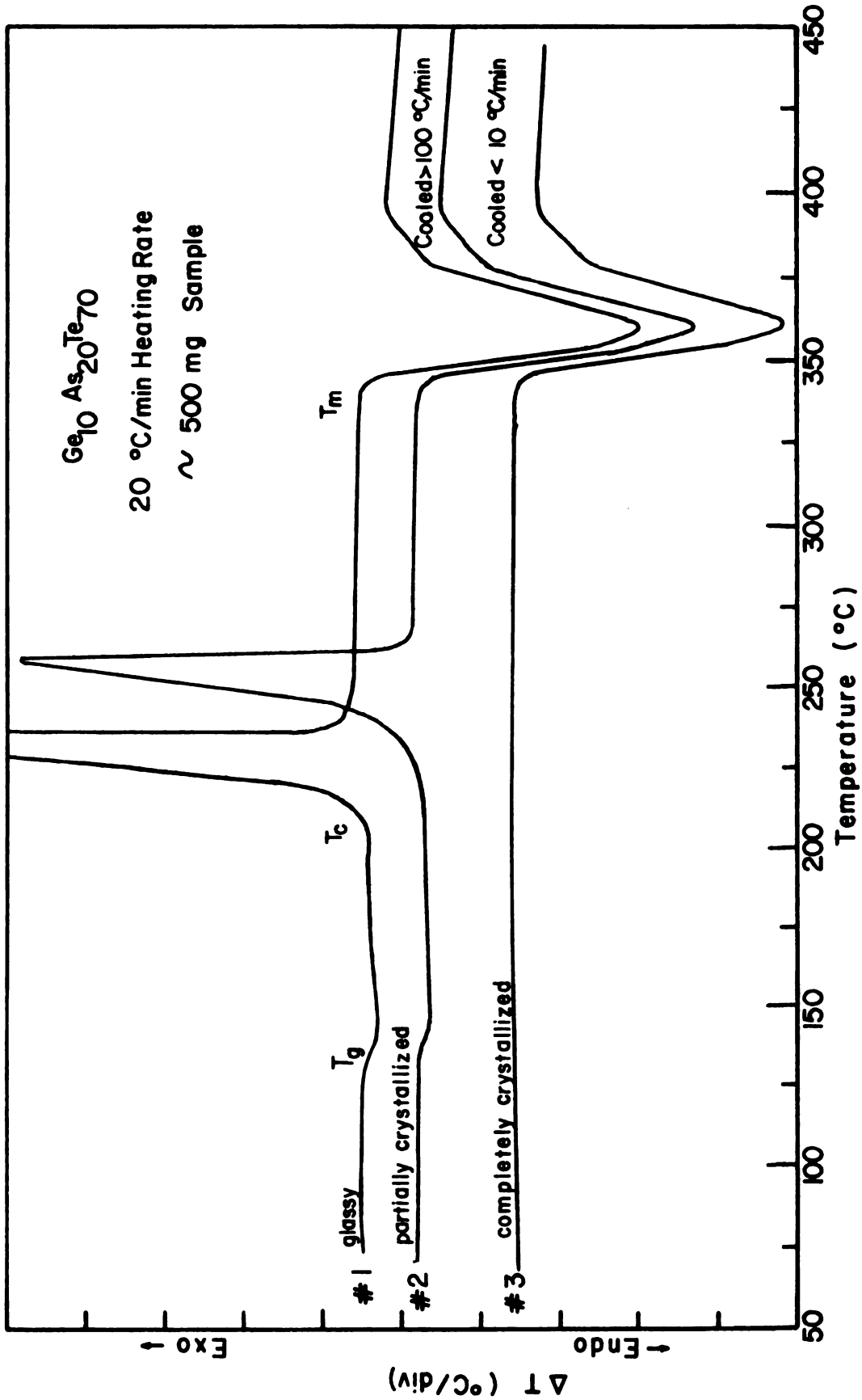

Figure 3.6 Quenching Process DTA

illuminated by a collimated source of monochromatic x-rays. Some of the radiation was scattered by electrons of the atoms without a change in wavelength. A diffracted beam was produced when certain geometrical conditions (the well known Bragg relation) were satisfied. These requirements were satisfied by regular arrangements of atoms in randomly oriented crystallites in crystallized $Ge_{10}As_{20}Te_{70}$. Diffraction patterns of crystals, or powdered crystalline materials, comprising both positions and intensities of diffraction effects, are fundamental properties of samples, and can be used for identification since they are almost as unique as fingerprints. If diffraction conditions are known, information on structure or the arrangement of atoms in the sample may also be determined.

Many techniques existed for creating x-rays, orienting samples, and detecting the diffracted x-rays. An early-model Phillips (Norelco) counter diffractometer was used to perform the measurements cited. A re-plotted diffraction patern for glassy $Ge_{10}As_{20}Te_{70}$ is shown in Figure 3.7. Lumps of annealed, as-quenched bulk material were used as samples. Scattered intensity is shown plotted against crystal-plane spacings, d, which could cause diffraction according to the Bragg formula. Absence of sharp peaks in the pattern indicated the sample contained few crystallites of significant size. Broad peaks in the pattern, typical for amorphous materials, could have been used to analyze the small degree of short-range order[44] typically present in these materials. A radial-distribution function,[2,9] specifing the density of atoms or electrons as a function of radial distance from any reference atom or electron, is the maximum structural information that could have been obtained from such diffuse diffraction effects.

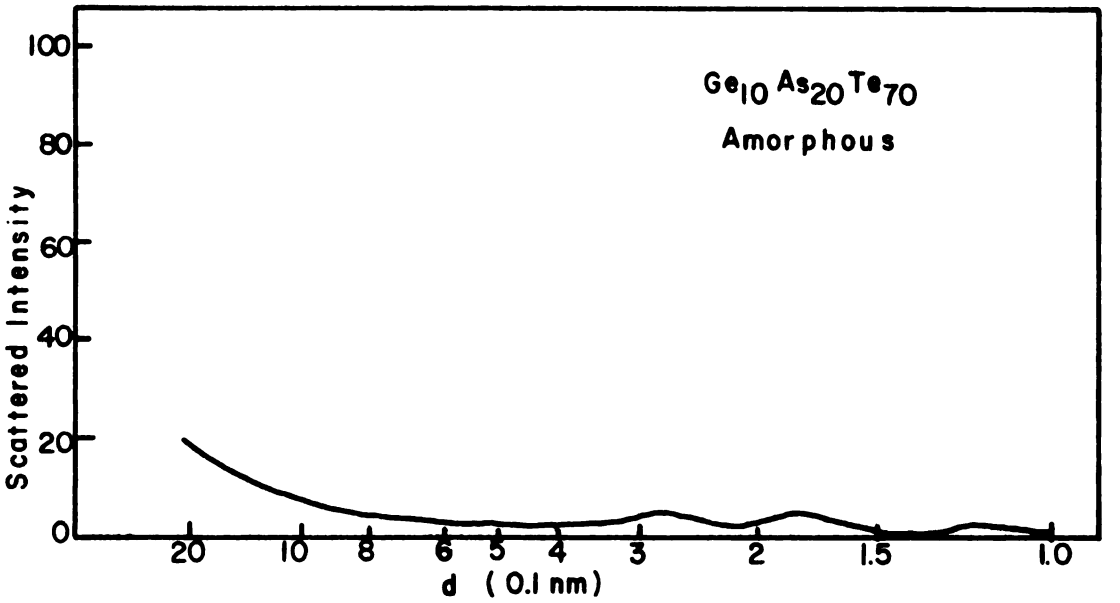

Figure 3.7 X-Ray Diffraction Pattern, Amorphous

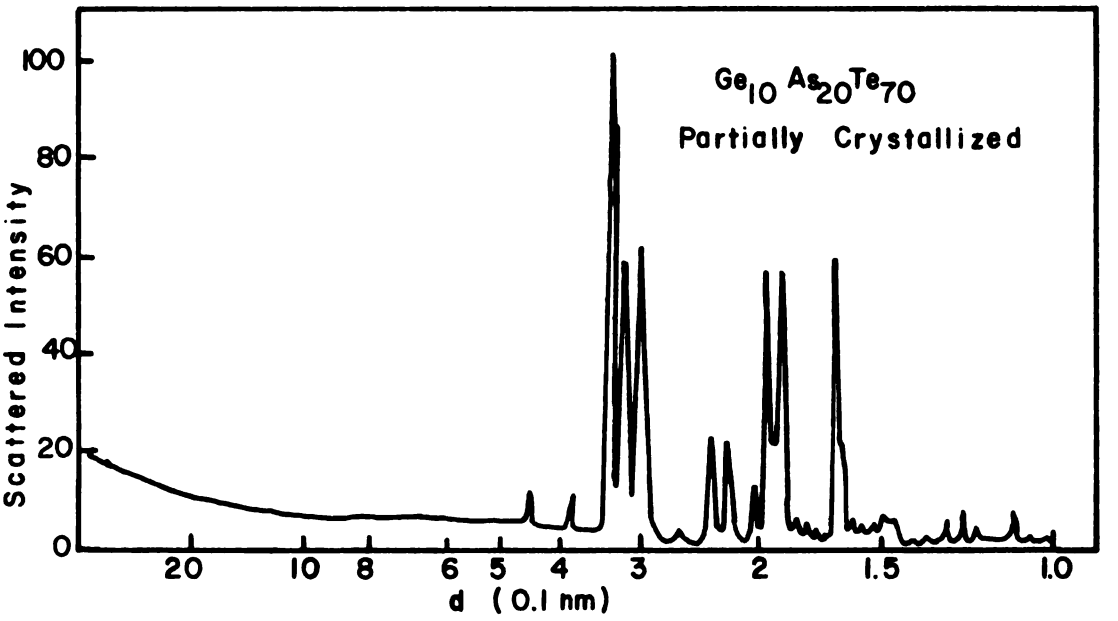

Figure 3.8 X-Ray Diffraction Pattern, Crystalline

This technique involving complex calculations, which has seen considerable recent application in the study of structure[39-41] of amorphous chalcogenides, was not used here.

Another pattern for crystallized $Ge_{10}As_{20}Te_{70}$, shown in Figure 3.8, contained many sharp peaks characteristic for crystalline materials. The ASTM x-ray powder-diffraction data file was used to positively identify tellurium as a major crystalline component in this pattern. Other crystalline species were certainly present in significant quantities, but as in many other cases[38] could not be identified, primarily due to the complexity of the pattern. Many workers[5,37,38] have used x-ray diffraction information simply to confirm the amorphous nature of their materials; this was the primary application here.

Similar techniques for investigating structure of amorphous materials[31,42,43] which offered advantages over x-ray techniques, were electron diffraction,[45] and neutron diffraction. Advantages of electron diffraction, beyond the utility of the higher-energy radiation source, were that electron-microscopic examination, microprobe analysis, and induced transformations could have been performed essentially simultaneously.[31]

3.6 Chemical Analysis

Ordinary wet-chemical quantitative-analysis techniques were capable of determining, with adequate accuracy, the composition of chalcogenide alloys. Wet-chemical analysis was performed* on a sample from an early batch of glassy $Ge_{10}As_{20}Te_{70}$. The results of this analysis were: germanium-7.83%, arsenic-14.41%, and tellurium-77.77% by weight.

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* Ledoux & Company, Teaneck, New Jersey, examined ten grams from batch #10, using pieces which had been exposed to the atmosphere.

The equivalent atomic-number formula was: $Ge_{11.44}As_{21.24}Te_{67.32}$, a slight but definite departure from the composition desired. Possibly the batch from which the sample was selected was not homogenous, or not carefully-enough compounded. Probably later batches were closer to the desired composition as techniques were improved. Oxygen was the only impurity component examined, and was 0.05% by weight including surface-absorbed gas. This significant fraction was possibly due to the use of oxidized raw materials, especially arsenic, early in the research program.

CHAPTER 4

ELECTRICAL PROPERTIES

4.1 Introduction

Amorphous chalcogenides are interesting for their unusual and potentially useful electrical properties. The science of electrical-property measurement has been organized and studied for crystalline materials.[1-7] Orderly collections of data have been published for a few materials,[8,9] but little definitive lieterature has appeared for amorphous chalcogenide semiconductors. Collection of electrical properties for the relatively new chalcogenide glasses was a goal for this research program. The collection process was routine for some characteristics but very complex for others.

An understanding of electrical conductivity required examination of factors contributing to the effect.[21] Factors experimentally investigated for $Ge_{10}As_{20}Te_{70}$ were electrical conductivity, Seebeck coefficient, conductivity switching, drift mobility, and photoconductivity. Dc and ac electrical conductivity versus temperature were measured. Seebeck coefficient was determined approximately. An injected-carrier transit-time drift-mobility measurement technique was adopted for future transport-properties experimentation. Photoconductivity at room temperature was briefly investigated. Few switching characteristics were examined in detail since this field was being thoroughly investigated by others.

Several additional properties have been determined and reported by others, primarily for chalcogenide glasses other than $Ge_{10}As_{20}Te_{70}$. Pressure effects and piezoresistance,[10-12] magnetic effects and

magnetoresistance,[13,14,95,120] and time-dependent effects[41] have been studied. Modification of characteristics by electron bombardment[15] and radiation exposure has been observed. Electronic tunneling has been investigated. Recombination and lifetimes of carriers have been reported for a few amorphous materials.[18,19]

4.2 Dc Electrical Conductivity

Many theories have been investigated for electrical conductivity of amorphous chalcogenide semiconductors; at ordinary temperatures a recent mobility-gap model may be accurate.* Examination of electrical conductivity was essential for confirmation of the theories considered for amorphous $Ge_{10}As_{20}Te_{70}$. Low-field dc electrical conductivity was measured at temperatures from -150 °C to +100 °C using four-point probe apparatus of improved design, specially constructed for this application.

Several standard methods[22,23] existed for measurement and interpretation[21] of dc electrical conductivity. Special techniques have been developed for certain applications,[24-26] including for use at very-low temperatures[27-30] and with very-high resistances.[30,31] Other unique conductivity measurement methods have been developed for unusual applications.[32-35] The four-point probe technique** was adopted here to measure conductivity for unprepared, randomly-shaped samples of amorphous $Ge_{10}As_{20}Te_{70}$ semiconductor material. This method was also adopted to minimize the effect of contacts on conductivity measurements. Unfortunately, four-point probe apparatus for low-conductivity measurements was not generally available, so special equipment was

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* A review of the theory for electrical conduction in non-crystalline conductors can be found in Appendix A.

** A description of apparatus and technique is in Appendix C.

designed and constructed.

The lowest temperature at which measurements were made was about 120 °K. Lower-temperature measurements were desired, but were not practical with existing apparatus. The highest temperature was less than 380 °K, avoiding possible change or destruction of samples due to annealing, crystallization, or deformation. Higher-temperature measurements, to the softening point, were possible, but were not performed. The conductivity of amorphous $Ge_{10}As_{20}Te_{70}$ ranged five orders in magnitude, increasing monotomically from about 10^{-8} mhos/cm at -150 °C to about 10^{-3} at +100 °C; typical conductivity at 27 °C, room temperature, was about 5×10^{-5} mhos/cm.

A plot of log conductivity versus reciprocal temperature, shown in Figure 4.1, resulted from tests of the low-field approximation. For semi-infinite samples, probe spacing, s, test current, I, and measured voltage between probes, V, conductivity was computed:

$$\alpha = \frac{I}{2\pi\, sV}$$

The approximate* electric-field intensity in the sample was:

$$E \approx \frac{V}{s}$$

and varied with temperature for the four-point probe method. The highest field anticipated occurred for a maximum-measurable probe voltage of about 15 V and a normal probe-point spacing of 0.0635 cm; and was about 200 V/cm. This was much lower than values usually associated with non-ohmic effects in amorphous chalcogenide semiconductors.[34,35] Since maximum electric fields occurred only for very-low sample temperatures difficulty with switching and other non-ohmic effects was not expected.[36]

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* This approximation was possibly low; the non-uniform electric field was probably higher at the surface near the probe points.

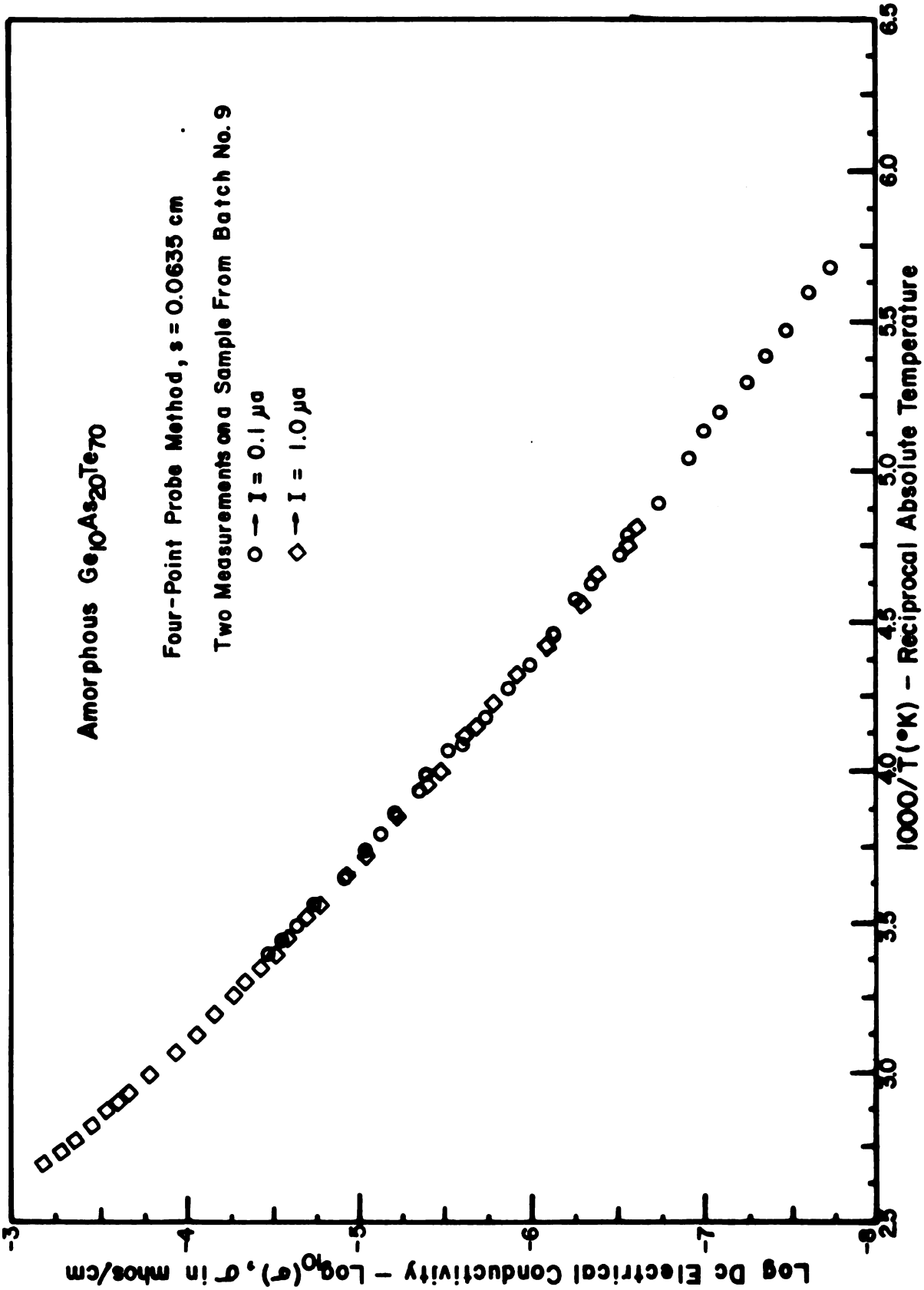

Figure 4.1 Test of Low-Field Approximation for Conductivity

Non-ohmic behavior, known for amorphous elemental semiconductors,[37-39] has been widely reported for amorphous chalcogenides.[40-49] However, electric-field dependency was not apparent for conductivity measurements reported here. The plot shown in Figure 4.1 was measured using a test current of 1.0 μa in addition to the most-frequently used value of 0.1 μa. As no differences were apparent, test fields used were assumed sufficiently low. Measurements of conductivity at elevated fields were not made.

Plots of log conductivity versus reciprocal temperature differed* somewhat from sample to sample. As seen in Figure 4.2, plots converged at higher temperatures and had slightly-different slopes at lower temperatures; greatest curvature was at high temperatures. Variations were attributed to differences in annealing and stabilization for the samples tested.

Observed variations might have been due to differences in geometry factors used for computation of conductivity from raw data.** This factor, unity for semi-infinite flat-sided samples, was essentially temperature independent and constant for a given sample; size and shape variations could cause only uniform vertical displacements of logarithmically-plotted conductivity. Absence of significant vertical displacements of data suggested sample size was satisfactorily semi-infinite. Finally, exact magnitude was not as important as the temperature dependence of conductivity.

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* In private conversation with the author, many investigators disclosed having experienced similar difficulties correlating data.

** A description of conductivity-computation techniques can be found in Appendix C.

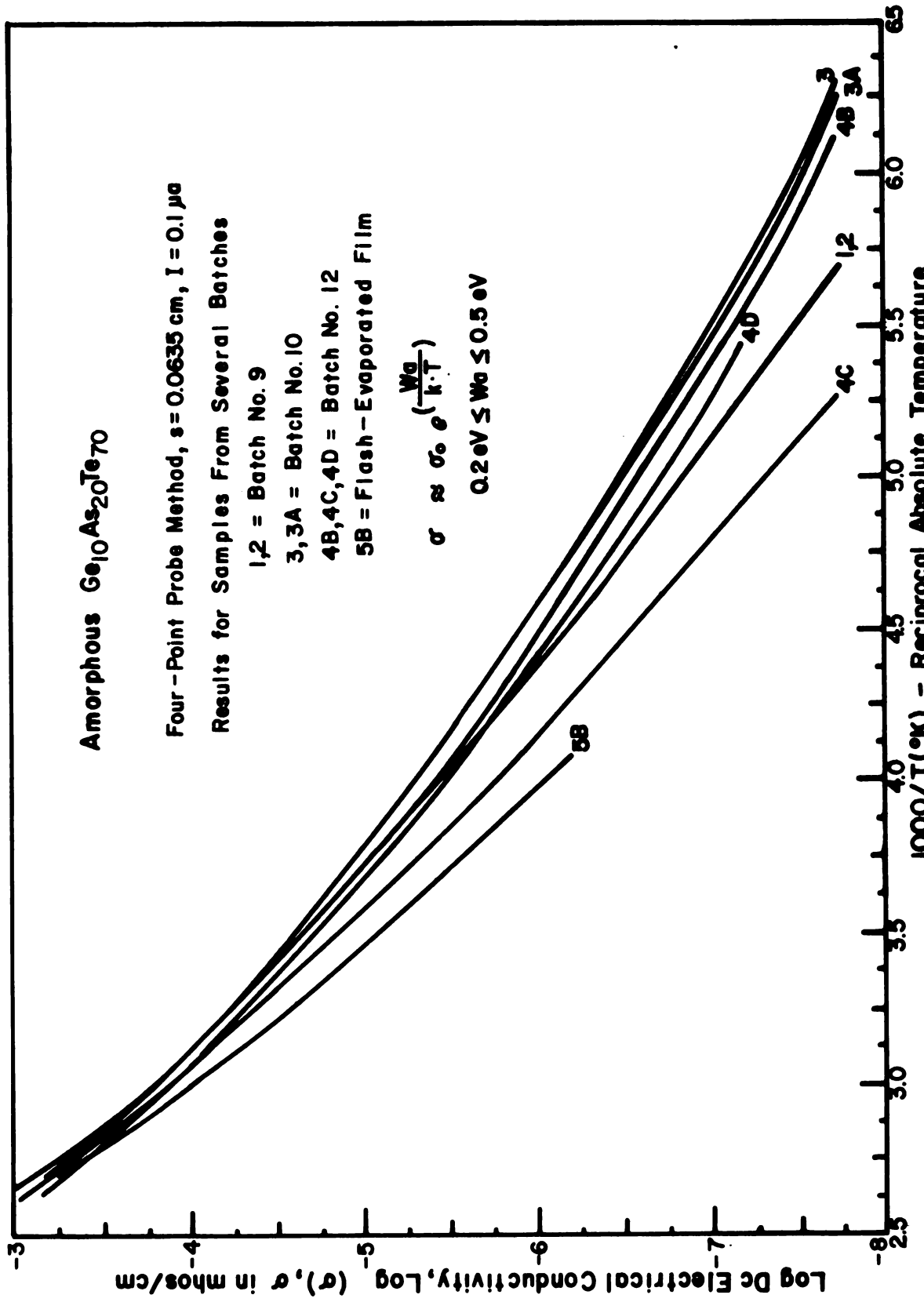

Figure 4.2 Electrical Conductivity versus Temperature

Several formula were empirically fitted to observed conductivity versus temperature behavior using computer programs. Conductivity appeared exponentially proportional to reciprocal absolute temperature over a fairly-wide temperature range, as indicated by the straight-line nature of the log-conductivity versus inverse-temperature curve. This characteristic, typical for amorphous chalcogenides,[37,38,42,48-55] corresponded to the relation:

$$\sigma = \sigma_0 e^{(-Wa/kT)}$$

Conductivity seemed to be thermally activated with an activation energy, Wa, of about 0.28 eV at 300 °K for bulk amorphous $Ge_{10}As_{20}Te_{70}$. Wa varied from sample to sample and with temperature. Values of 0.2 eV at low temperatures to 0.5 eV at high temperatures were observed. Electrical conductivity mechanisms for amorphous semiconductors were not well understood. It was suggested that carrier mobility in these materials was exponentially temperature dependent according to a mobility energy-gap model, accounting for observed temperature dependence of conductivity.

A computer program, DATAFIT, listed in Table 4.1, was used to fit the exponential relation to data in a least-squares sense.[56] Values for σ_0 and Wa were about 1.5 mhos/cm and 0.27 eV respectively.

Careful checks determined that observed variations in log-conductivity versus reciprocal-temperature data were not caused by measurement technique. For instance, remeasured samples showed almost identical results; measurements at several locations on the same sample caused only slight variations. Annealing due to thermal cycling during conductivity measurements appeared not to be signicant, possibly

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10 DØUBLE PRECISIØN A(5),AM(5,5),CØND(50),CØNDL(50),TK(50)
11 DØUBLE PRECISIØN TKI(50),XK,Q,PI,XLN2,CØNDLF,A1,A2,A3
12 DØUBLE PRECISIØN A4,A5,TO,E,AA
13 DIMENSIØN NS(50),PHI(50,5),Y(50),V(50),RW(250)
14 FILENAME IN,ØUT
15 CØNDLF(M)=A(1)*PHI(M,1)+A(2)*PHI(M,2)
20 PRINT," INFILE,ØUTFILE"; INPUT,IN,ØUT
30 XK=1.38053D-23; Q=1.60209D-19; PI=3.14159DØ
31 XLN2=0.693147DØ; XLØGE=0.434294DØ
40 LINE=Ø;LZERØ=Ø;ERR=Ø.; READ(IN,1) LL,S,XI,VØFF,THIK
51  1 FØRMAT(V)
60 10 READ(IN,1,END=15)  LL,TCMV,VV
70 LINE=LINE+1; NS(LINE)=Ø; V(LINE)=VØLT(VV,VØFF)
80 TK(LINE)=2.73D2+2.845D1*TCMV-6.074D-1*TCMV+TCMV
81 & -1.757D-1*TCMV*TCMV*TCMV-1.657D-2*TCMV*TCMV*TCMV*TCMV
82 & +6.961D-3*TCMV*TCMV*TCMV*TCMV*TCMV
85 TKI(LINE)=1.DØ/TK(LINE)
90 IF(10.*THIK.LT.S) GØ TØ 12
92 CØND(LINE)=.5DØ*XI/(PI*S*V(LINE)); GØ TØ 14
94 12 CØND(LINE)=XLN2*XI/(PI*THIK*V(LINE))
96 14 CØNDL(LINE)=DLØG(CØND(LINE))
100 PHI(LINE,1)=-Q*TKI(LINE)/XK; PHI(LINE,2)=1.DØ
110 Y(LINE)=CØNDL(LINE); GØ TØ 10
140 15 NS(1)=LINE; N=2
150 CALL DLSØMM(PHI,Y,A,RW,LINE,N,1,NS,AM,LINE,N)
160 A1=A(1); A2=DEXP(A(2))
200 PRINT," CØND = A * EXP( -E*Q/(K*T) )"
210 PRINT 5,A1; PRINT 6,A2
220  5 FØRMAT(" E = ",D25.16," ELECTRØN VØLTS")
221  6 FØRMAT(" A = ",D25.16," 1/(ØHM-CENTIMETERS)")
230 WRITE(ØUT,2)LZERØ,IN
231  2 FØRMAT(I1,6X,"1/T",6X,"ERRØR",6X,A8)
240 DØ 20 L=1,9;      ER=XLØGE*(CØNDLF(L)-CØNDL(L))
241 ER=ERR+ER*ER
250 20 WRITE(ØUT,3) L,TKI(L),ER
251  3 FØRMAT(I1," ",2(F10.6))
260 DØ 30 L=10,LINE; ER=XLØGE*(CØNDLF(L)-CØNDL(L))
261 ERR=ERR+ER*ER
270 30 WRITE(ØUT,4) L,TKI(L),ER
271  4 FØRMAT(I2,2(F10.6))
280 ERR=SQRT(ERR)/LINE
281 PRINT," AVE RMS FIT ERR IN LØG(CØND):",ERR
282 PRINT," LIST FILE: ",ØUT," FØR ERRØR VS. 1/T"
290 999 STØP; END
300 FUNCTIØN VØLT(VV,VØFF); VV=VV-VØFF
320 IF(VV.LT.0.0012)GØ TØ 100; IF(VV.LT.1.2)GØ TØ 110
340 VØLT=(VV+.03)/1.003; RETURN
350 100 VØLT=VV/1.01; RETURN
360 110 VØLT=VV/1.007; RETURN
370 END
```

Table 4.1 Computer Program DATAFIT

because temperatures used were not high enough or sufficiently sustained.

Differences among samples were therefore real. Boules of $Ge_{10}As_{20}Te_{70}$ produced by rapid quenching from the melt in silica ampuls appeared to have been quenched in a non-uniform manner; the outside of the boules were apparently more-rapidly cooled than the center.* Also, samples were annealed for various periods as long as about 16 hours. These treatments could have caused segregation of constituents, anisotropic or non-homogenous strains, or differences in stabilization.[57] Non-uniform characteristics from sample to sample were therefore probable, most-possibly caused by slight variations in annealing. Samples with exactly-known thermal histories were unavailable.

Recent measurement of electrical conductivity versus temperature[57] for amorphous $Ge_{10}As_{20}Te_{70}$ have indicated sensitivity of electrical properties to annealing. Curves plotted here were similar to those reported by others for short annealing periods. Effects of annealing at 99 °C for various periods are shown in Figure 4.3.[57] The slope at low temperatures decreased considerably with annealing periods greater than about ten hours. For no annealing the curve was remarkably straight and had a slope corresponding to an activation energy for conductivity of about 0.5 eV. All curves converged at higher temperatures, where annealing seemed to have little effect.

Exponential dependence of conductivity on temperature has been observed for other amorphous Ge-As-Te compositions[58,59] and for many additional amorphous chalcogenides; thermal activation of conductivity with an activation energy of about 0.5 eV was typical The

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* Information on preparation of amorphous $Ge_{10}As_{20}Te_{70}$ samples can be found in Chapter 2 and Appendix B.

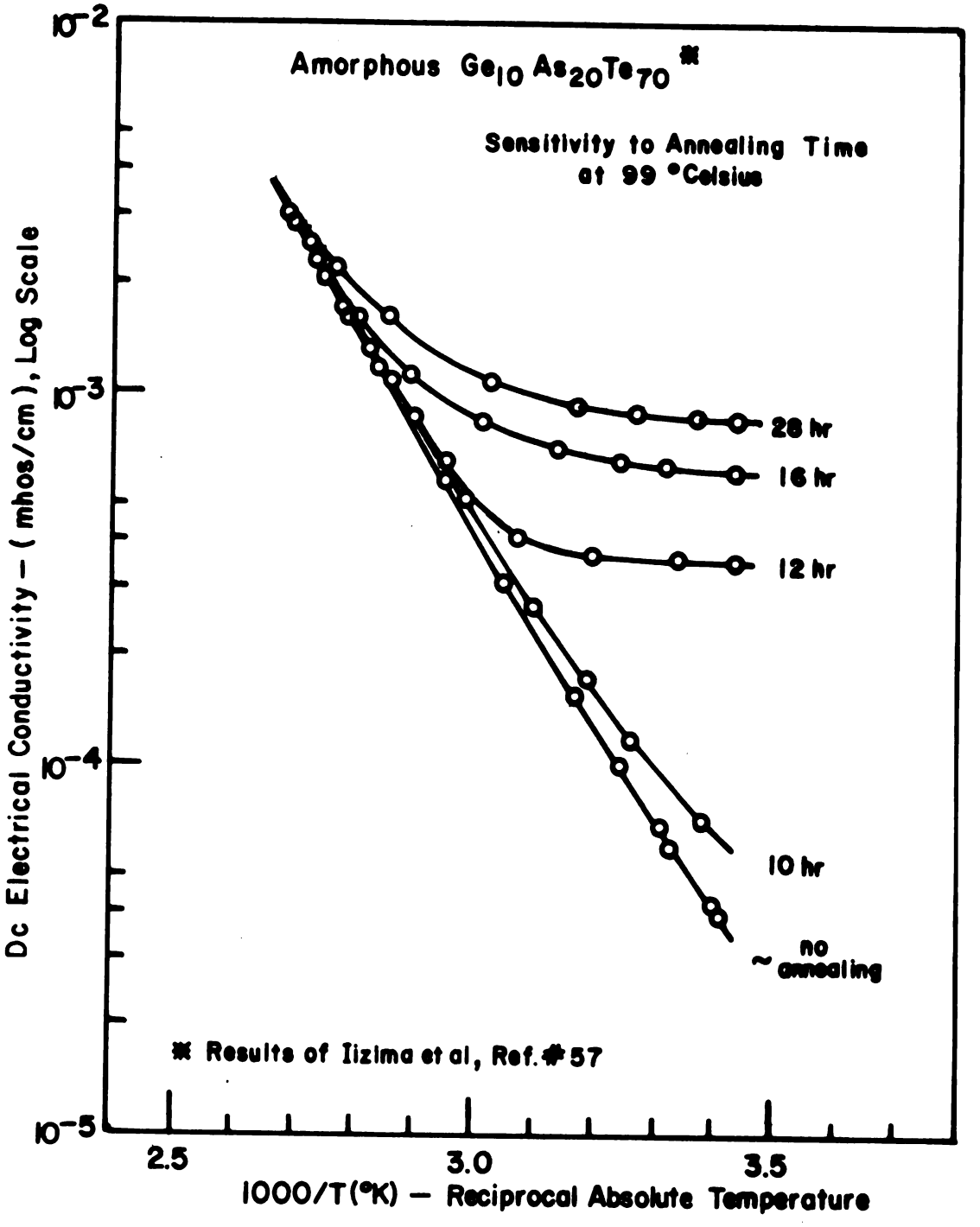

Figure 4.3 Conductivity versus Annealing Time at 99°C

activation energy for amorphous GeTe was 0.375 eV;[60-62] the value for As_2Te_3 was 0.46 eV.[40,63,64] Most investigators report thermal-activation processes for conductivity were dependent on electric-field intensity, purity, thermal history, and form (bulk or film) of the samples.

Attempts were made to explain curvature of log-conductivity versus reciprocal-temperature plots reported here. Modified versions of the computer program, DATAFIT, were used to fit data in a least-squares sense with theoretically-suggested relations.[73] Apparatus errors such as inaccurate temperature measurement and voltage-measurement nonlinearity were eliminated as sources for curvature. Power and polynomial functions of temperature used as pre-exponential factors were not useful for fitting data.[51,54] Also examined were fits to data involving temperature dependence of activation energy. Satisfactory fits were obtained but were not understandable physically and are not listed here. Electric-field dependence of activation energy was examined also, but suggested relations[42,45,47] did not fit data very well. Perhaps functions including terms or factors for several conduction processes[49] such as simultaneous drift and hopping could have been fitted to observed behavior; these were not investigated for lack of time and sufficient data.

Conductivity versus temperature measurements were made on amorphous $Ge_{10}As_{20}Te_{70}$ crystallized by slow heating to above the crystallization temperature.* The four-point probe technique was used with a test current of 0.1 ampere. Conductivity, substantially independent of

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* Thermal characteristics of $Ge_{10}As_{20}Te_{70}$ were reported in Section 3.4.

temperature over the range from -150 °C to +100 °C, was about 70 mhos/cm. Measured similarly, the conductivity of 99.999% pure single-crystal tellurium was 2.1 mhos/cm, slightly lower than for crystallized $Ge_{10}As_{20}Te_{70}$.* A small fraction of metallic arsenic (3×10^4 mhos/cm conductivity) could account for the higher conductivity of crystallized $Ge_{10}As_{20}Te_{70}$. Relatively few measurements were made on the crystallized state of $Ge_{10}As_{20}Te_{70}$.

4.3 Ac Electrical Admittance

Electrical admittance versus temperature and frequency were measured for amorphous $Ge_{10}As_{20}Te_{70}$. Ac measurements provided information on type and transport made for current carriers. Ac measurement techniques were also useful for eliminating certain contact problems.[111] Hopping, a mechanism for carrier transport characterized by conductivity which increases with frequency, was suggested as important for amorphous semiconductors at high frequencies and low temperatures. Information reported for As_2S_3,[114] As_2Se_3,[114,116] GeTe,[60,61] and for Ge[37] in amorphous form suggests hopping conduction may be important for many amorphous chalcogenides.

Information reported here** was obtained from a single piece of amorphous $Ge_{10}As_{20}Te_{70}$ ground to a thickness of about 0.04 cm; electrode area was not determined. Unusual and generally-unexplainable behavior was noted. As shown in Figure 4.4a, capacitance decreased with frequency increase at higher temperatures; conductance behavior was also complex. As shown in Figure 4.4b, at -180 °C

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* X-Ray diffraction patterns for crystallized $Ge_{10}As_{20}Te_{70}$ indicating the presence of crystalline tellurium were discussed in Section 3.5.

** H. Boem, Owens-Illinois Inc., Toledo, Ohio, performed the measurements.

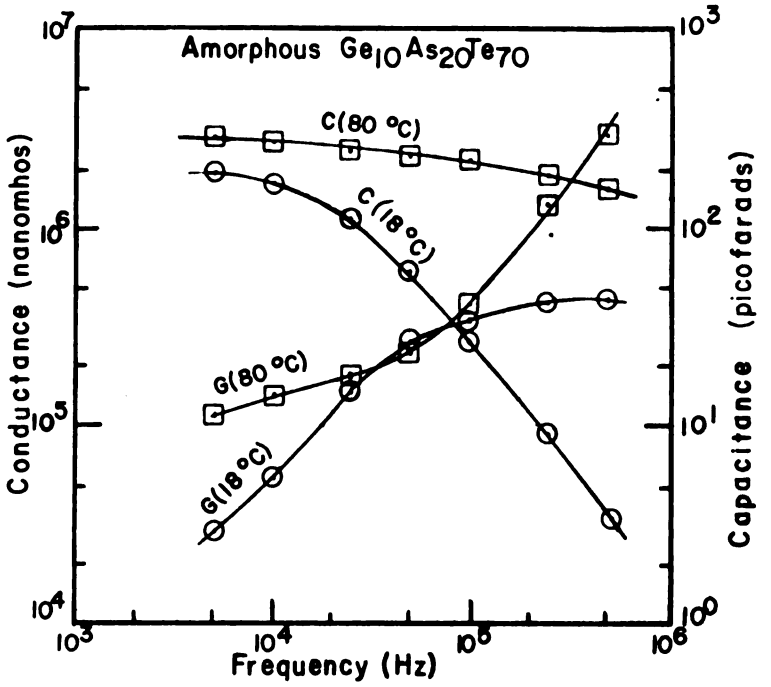

Figure 4.4a Admittance at Higher Temperatures

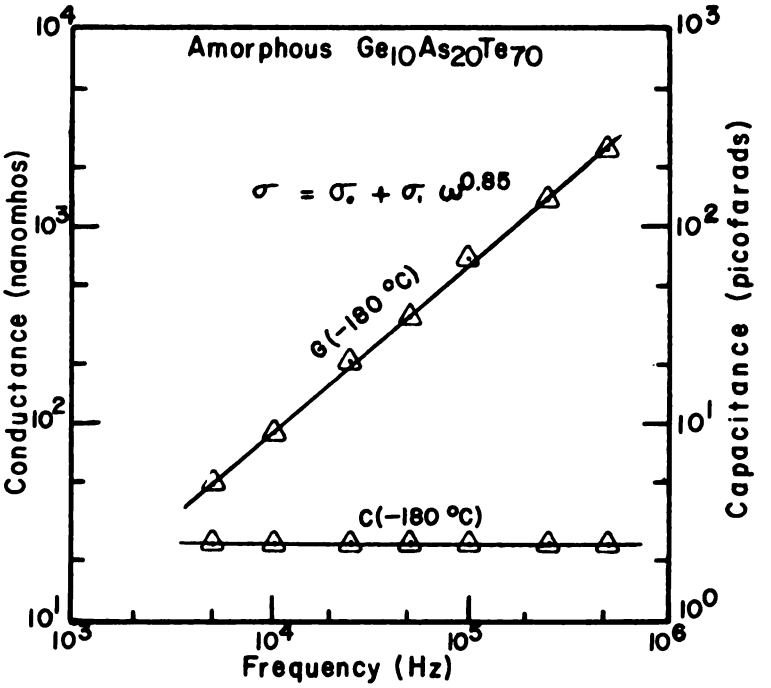

Figure 4.4b Admittance at −180 °Celsius

capacitance was independent of frequency and conductance was dependent on frequency in the following manner:

$$\sigma = \sigma_0 + \sigma_1 \omega^{0.85}$$

Similar behavior has been reported for amorphous $Si_{25}As_{25}Te_{50}$[113] where hopping was considered important. Negative capacitance for high dc-electric-field intensities has been reported for some amorphous chalcogenides.[117] Other anomalous ac characteristics have been reported for chalcogenide glasses.[118] Additional measurements of admittance may provide useful information for amorphous $Ge_{10}As_{20}Te_{70}$.

4.4 Thermoelectric Properties

Information was obtained for polarity and approximate magnitude of Seebeck Coefficient (thermoelectric power) of amorphous $Ge_{10}As_{20}Te_{70}$. Instruments to perform this measurement were offered commercially* but were not used. The hot-probe method,[65] frequently used for determination of carrier polarity, was used to make measurements. This technique is illustrated in Figure 4.5; the temperature difference between a heavy copper heat-sink and heated copper probe caused the generation of thermoelectric voltage between sample contacts. High sample resistance posed no problem as voltage was measured using a 10 GΩ input-resistance voltmeter (Hewlett-Packard Model 3450A Digital Multimeter). Calibration was established by measurement of materials with known Seebeck coefficient;[66] results indicated accuracy sufficient only for approximate quantative analysis.

Experimentation over a range of average sample temperatures showed the Seebeck coefficient was positive and large. Seebeck coefficient, Q,

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* For instance the Thermoelectric Probe, Electro-Impulse Inc., Red Bank, New Jersey.

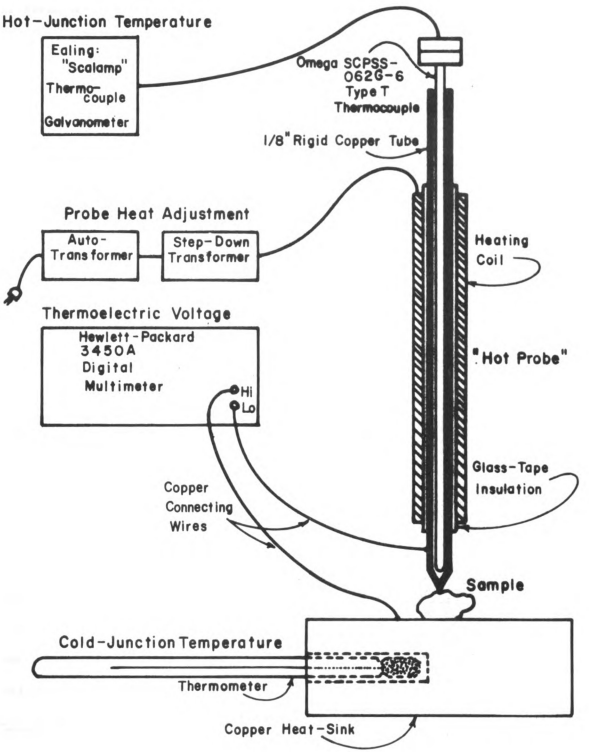

Figure 4.5 Hot-Probe Technique

at temperature T was computed:

$$Q = \frac{Vt}{\Delta T}$$

where ΔT is the temperature difference, T_0 is the average temperature and Vt is the thermoelectric voltage measured from the hot junction to the cold junction.[65] For T_0 = 50 °C and ΔT = 100 °C the Seebeck coefficient was about +300 μV/°C. Strangely,[50] the Seebeck coefficient appeared to increase slightly with temperature.

Although Seebeck coefficient is useful and easily-measured approximately,[5] little detailed information has been reported for chalcogenides,[67-69,89] except for materials commonly used for thermoelectric applications. Exact determination of thermoelectric coefficient versus temperature is difficult and not often performed. Similar information can sometimes be gathered by other methods. From the theory of semiconductors,[74] polarity of the dominant current carrier is indicated by the polarity of the Seebeck coefficient. Seebeck coefficient for glassy $Ge_{10}As_{20}Te_{70}$, and for practically-all amorphous semiconductors,[50,72] was positive. The dominant carrier was therefore positive as for p-type or hole conduction. The very-high Seebeck coefficient of crystalline and glassy chalcogenide semiconductors such as Bi_2Te_3 have led to their use in heat-pumping and power-conversion applications.[70,71,87]

4.5 Switching Characteristics

Considerable excitement has been created by discovery and application of reversible threshold and memory conductivity switching

in amorphous semiconductors.* Switching has been observed for amorphous elemental semiconductors,[75,76] for many compound-oxide and chalcogenide glasses, indeed for almost-all thin insulating layers.[77]

Simple tests of amorphous $Ge_{10}As_{20}Te_{70}$** indicated threshold and memory switching occurred at relatively-low voltages. Switching occurred in and across surfaces of bulk pieces, and through flash-evaporated thin films. Experiments with sharp-pointed electrodes placed about 625 microns (25 mils) apart on either side of a bulk sample showed switching at an electric-field intensity of about 2.65 kV/cm. Memory switching occurred with turn-on currents greater than about 1.0 ma. High, short current pulses returned switched-on devices to an off state. Evidence of filamentary conduction (appearance changes and erosion at electrodes) was apparent. Other organizations have observed switching in Ge-As-Te glasses at an electric field intensity of 2.6 kV/cm.[35] Studies of filament formation accompanying switching[78,79] suggest that memory is accomplished by segregation of crystalline tellurium, or other highly conductive material, from the glassy phase. This process was observed for crystallization of amorphous $Ge_{10}As_{20}Te_{70}$ by thermal-analysis, x-ray diffraction, and dc-electrical-conductivity measurements. Few switching measurements were performed as many others were already studying the effect for Ge-As-Te glasses.[36,58,80-86]

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* A brief review of the phenomena and theory of switching can be found in Appendix D.

** D. Mosher, Owens-Illinois, Inc., Toledo, Ohio. contributed some of the measurements of switching properties.

4.6 Drift Mobility

Mobility is an important and useful characteristic of semiconductors. Mobility versus temperature information is a key to understanding transport and scattering processes.[21] Unfortunately, mobility for high-resistance amorphous conductors is usually low and difficult to measure. Conventional Hall-mobility measurement[5,90] apparatus and technique adapted for the purpose[26,91,92] has provided anomalous results. Mobility for amorphous chalcogenides, derived from Hall-coefficient and dc-conductivity measurements, is very low (about 0.01 $cm^2/(Vs)$) and practically independent of temperature.[49,50,93-96] The sign of the Hall coefficient suggests n-type carriers, contrary to implications from thermoelectric experiments. It has been suggested[93] that amorphous conductors have p-type carriers; a significant (as high as 100 $cm^2/(Vs)$ possibly) temperature-activated form of drift mobility[97,51] is thought to account for the observed magnitude and temperature dependence of conductivity.[49-50] A mobility-gap model* has been proposed.[98-100,122]

Measurement of drift mobility in high-resistance amorphous semiconductors has been demonstrated using a transit-time technique.[104] This method uses short-duration light[105-107] or electron[101-103] pulses to generate a thin sheet, δ, containing N carriers of charge, q, at one surface of a sample of thickness, d. The technique is illustrated in Figure 4.6. The injected sheet of carriers was swept through the sample by the static electric field, E, established by the voltage source, Va. Transit-time, t_t, of the injected sheet of charge was measured by

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* A brief review of this and other theories for carrier mobility in amorphous chalcogenides can be found in Appendix A.

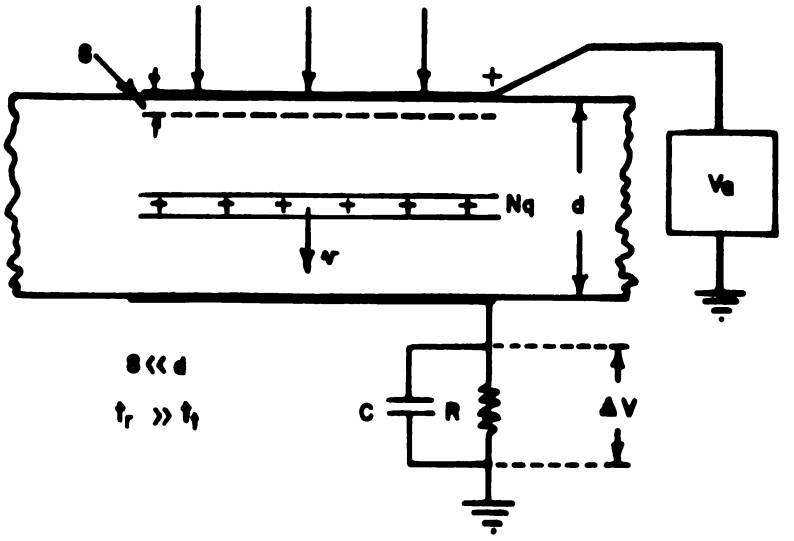

Figure 4.6 Drift-Mobility Measurement Method

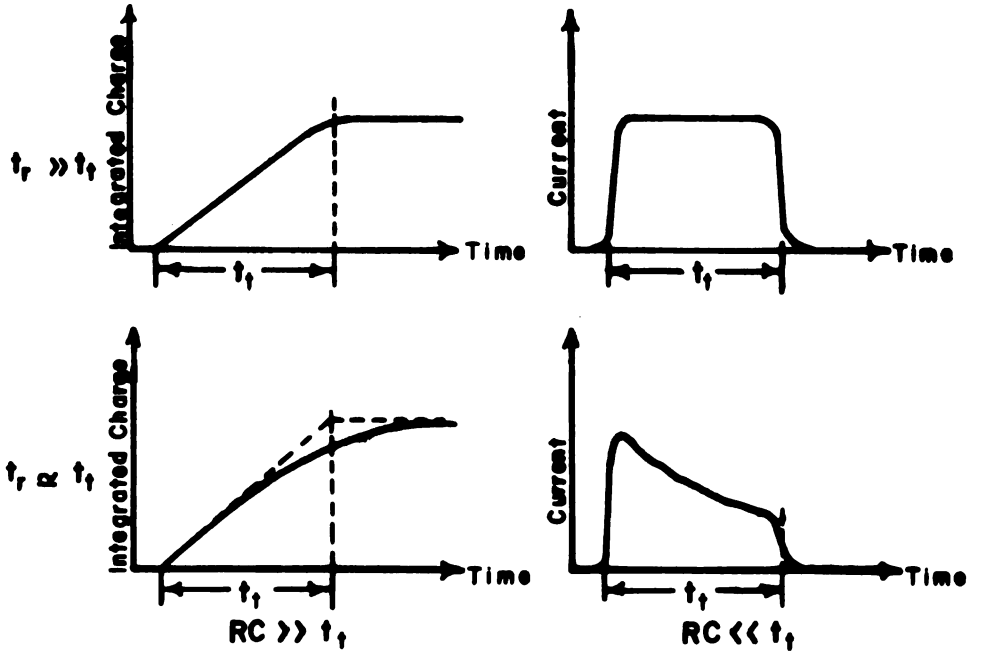

Figure 4.7 Typical Transit-Time Signals

observing currents induced in the sample circuit.[103,108] Depending on the time constant, RC, of the current-measurement network and relative carrier-recombination time, t_r, different signal shapes such as those in Figure 4.7 were observed. The mean carrier velocity through the sample can be determined:

$$v = \frac{d}{t_t}$$

Combining this with the definition of mobility allows the computation of effective drift mobility:

$$\mu = \frac{d}{t_t E}$$

Application of the drift-mobility measurement technique to amorphous $Ge_{10}As_{20}Te_{70}$ was considered. Electron-beam generation and injection of carriers was selected for its many advantages.[103] Sample pieces about 0.025 cm thick can be ground from larger pieces. Electrodes 1.0 mm in radius could complete a sandwich-like structure. A sample capacitance of about 5 pF* and dc resistance of about 20 kΩ would result. To avoid non-ohmic effects the test electric field must be maintained less than about the threshold-switching value of 2.6 kV/cm.[35] To minimize perturbing effects of the injected-charge field, N was chosen so that the test electric field, E, was much larger than for the injected carriers; mathematically[136] this is expressed:

$$E >> \frac{Nq}{2\varepsilon A}$$

where A was the area of the electrodes.[103] N must be less than 2×10^7 for:

$d = 0.025$ cm
$A = 0.01$ cm^2
$E = 10$ kV/cm
$\varepsilon = 50$
$q = 1.6\times10^{-19}$ C

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* Relative permitivity of amorphous $Ge_{10}As_{20}Te_{70}$, determined by ac-admittance tests, was possibly as high as 50.

An incident 0.1 μa pulse of 5 kV electrons 10 ns in length could generate about 6×10^5 carriers (assuming 0.5 eV activation energy). A 1% generation efficiency was assumed to account for various losses due to secondary emission and other processes.[103] The space-charge electric field produced by these carriers would be about 10 V/cm. Mobility values of about 100 $cm^2/(V\ s)$ are possible[96] and could produce a transit-time of 0.25 μs. A peak circuit current of 0.4 μa would result.[103,108]

An R value of 50 Ω provided a signal-pulse amplitude of 20 μV. Stray circuit and cabling capacitances added to the sample capacitance and raised C to about 50 pF for the application considered. The resulting RC time-constant of 2.5 ns was less than the transit time. The test electric field, E, was established with a 25 V power supply, resulting in a steady sample current of about 1.0 ma. Blocking electrodes could have been used.[103]

Alternatively if R = 20 kΩ, and added capacitance C = 0.005 μF were used, RC would have been 100 μs, much longer than the transit-time. The current pulse could have been integrated and a peak signal of about 20 μV would again have been produced. However, a voltage supply of 50 V would have been necessary to supply the additional steady state voltage drop across the test resistor, R.

Other values of N, R, C, and E could have been chosen, observing conditions that excessive fields be avoided, that small relative values of injected charge be used, and that the test signal be detectable. Different sample geometries might also have been chosen, within the constraints listed, provided construction of the necessary sandwich structure was practical.

Fabrication of apparatus to measure drift mobility was begun, and included modification of an available demountable CRT system. The CRT system included a high-vacuum pump (Veeco Model VS-400), and electron-beam gun assembly (RCA Model VC2126V4), and electronic circuits for accelerating, focusing, and deflecting the electron beam. A simple 60 pulse-per-second pulse generator was designed and constructed. The pulser controlled the electron gun to provide short jitter-free electron pulses, syncronized to the ac power-line frequency. Modification of the pulsing system may be necessary to provide shorter pulses.[109,110]

Use of a transformer in place of the RC circuit for measurement of the transit-time pulse did not provide sufficient sensitivity. An RC network, a wideband amplifier, and an oscilloscope were used for signal detection, amplification, and display. A wide-band amplifier containing two 50 Ω impedance-level X10-gain, and one 1 MΩ input-resistance X1-gain, 3 ns-risetime amplifier modules (Keithley Instrments Model 105) was acquired for use with both the R = 50 Ω and R = 20 kΩ cases. A dual-channel 50 Ω impedance-level wide-bandwidth higher-sensitivity amplifier system (Hewlett-Packard Model 8447) was considered for use with only the R = 50 Ω case. Signal waveforms were displayed with a sampling-oscilloscope system (Tektronix 1S1 plug-in with a Model 747 Oscilloscope), providing 1.0 cm of deflection for 20 μV signals. The risetime of the amplifier-oscilloscope system was less than about 10 ns. A block diagram of the system under construction is shown in Figure 4.8. A suitable temperature-controlled sample-holder and beam-calibration target[110] has not yet been developed. Adaptation of the apparatus for conductivity

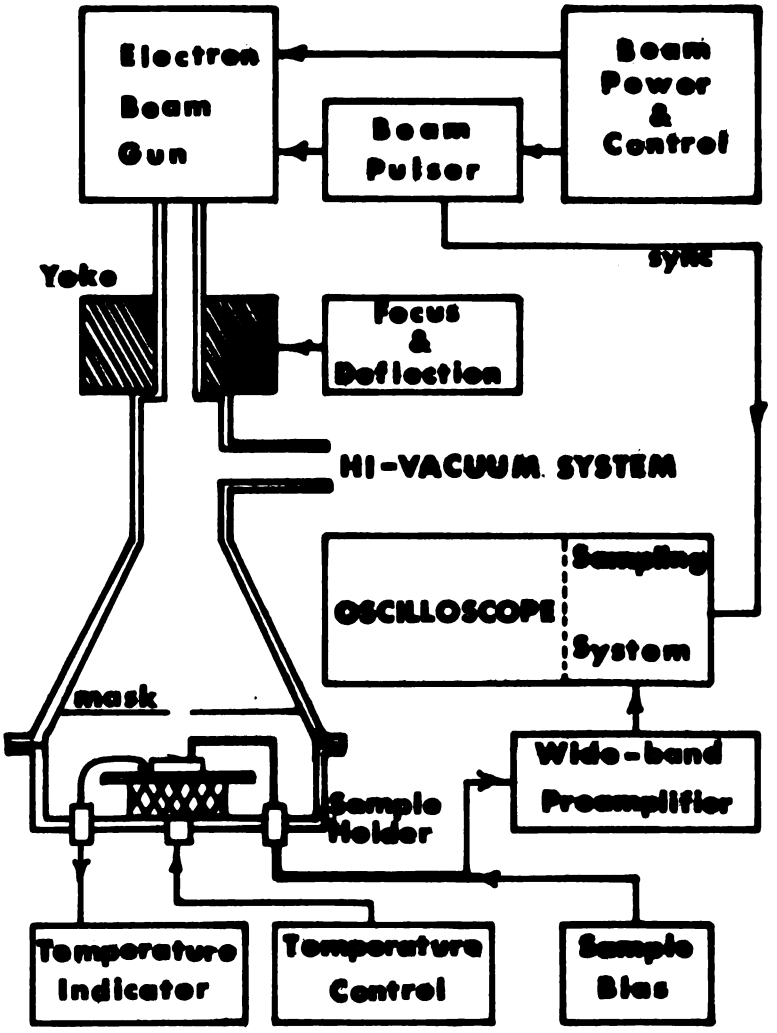

Figure 4.8

DRIFT MOBILITY MEASUREMENT SYSTEM

measurement[32,33] was contemplated.

Conditions for measurement of drift mobility in amorphous $Ge_{10}As_{20}Te_{70}$ were established and analyzed. The experiment appeared feasible, but results are not reported here as construction has not been completed.

4.7 Photoconductive Effects

Amorphous $Ge_{10}As_{20}Te_{70}$ was examined for photoconductive effects. Photoconductivity can be defined as the difference between electrical conductivities measured under illumination and in the dark.[7] Photoconductive generation of carriers provided a convenient technique for measurement of lifetime and mobility of current carriers[5,20] and therefore was important to the investigation of electrical properties. Photoconductive effects have been observed for amorphous Se,[105,107,124] GeTe,[125-128] As_2Se_3,[129] As_2Te_3,[130,131] and for many other chalcogenides.[123] Photoconductive effects have also been investigated for switching glasses from the Ge-Si-As-Te system.[132-134]

Semiconducting samples illuminated with photons with energy beyond the absorption edge absorb much of the incident radiation near the surfaces generating a number of current carriers.* A thin sheet of carriers produced in this fashion has been used for measurements of drift mobility in amorphous semiconductors using the transit-time technique.[107,135] The number of excess carriers generated and the volume of sample in which they are generated can be controlled by adjustment of wavelength and intensity of the incident radiation. Since photoconductivity results from the generation of excess carriers it is

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* In amorphous semiconductors carrier-generation processes are complex. Excess carrier generation may be thought of as an activation of mobility for an additional number of current carriers. See Appendix A.

sensitive to wavelength and intensity of illumination. Conductivity measured for amorphous $Ge_{10}As_{20}Te_{70}$ was not very sensitive to illumination at any wavelengths at room temperature. Very sensitive measurements were able to detect only slight photoconductive effects for moderate illumination with radiation at the absorption edge ($\lambda \approx 1.7$ μm). Measurements were not made at lower temperatures.*

Valuable information can be gained from the photoconductive relaxation curve obtained upon interruption of sample illumination. Exponential decay of photoconductivity with time can be related to lifetime of the excess carriers causing the photoconductive effects. Photoconductive-decay experiments have been performed for several amorphous chalcogenide semiconductors.[127,128,131-134] In general, the early part of the relaxation was very fast; the last part was very slow. The slow (hours at low temperature) decay was attributed to recombination of trapped carriers.[131,133,134]

Very-long post-illumination relaxation times have interfered with lifetime measurements. Estimates of lifetime for amorphous As_2Te_3 have been made as short as 50 ns.[131] Measurements of lifetime have not yet been made for amorphous $Ge_{10}As_{20}Te_{70}$. Equipment for measurement of photoconductivity versus temperature and wavelength is under construction. Equipment is also under construction for determination of lifetime of carriers generated by photoconductive[30] and electron-beam injection.

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* Low-temperature conductivity measurements cited in this work were determined with light-shielded apparatus.

CHAPTER 5

OPTICAL CHARACTERISTICS

5.1 Introduction

Reflectivity, absorption coefficient, and index of refraction were measured for glassy and crystallized $Ge_{10}As_{20}Te_{70}$. Initially, approximate reflectance and transmittance were determined. Later, careful measurements of absorption coefficient versus photon energy were also made. Only approximate reflection corrections could be made, and a region of the curve was undetermined due to difficulty obtaining suitable sample thicknesses. Results in accordance with theory were generally obtained.

Optical measurements, especially infrared absorption, have been very valuable for investigating semiconductor carrier energetics and other solid-state properties.[1-3,8] Calibrated optical measurements have been used to determine impurity content of crystalline[4] and vitreous materials.[5-7] Study of optical characteristics of chalcogenide glasses began with the discovery of infrared transmission in As_2S_3,[9,10] resulting in considerable effort to apply these materials to infrared optics.[11-14,52] Surveys of optical characteristics for amorphous chalcogenide semiconductors have appeared recently.[14-18,48,57]

Many theoretical and experimental discussions of optical properties for amorphous semiconductors have been published. Early interest in arsenic-trisulfide-like glasses has continued.[19-26] Amorphous germanium[18,27-31] and amorphous silicon[30-32] have been studied, inpart to compare properties for the amorphous state to well known properties for the crystalline state. Selenium, readily rendered into

an amorphous condition,* has been studied extensively.[18,33-36] Also, optical properties of amorphous GeTe have been investigated.[37,38]

Relations between optical absorption and electrical conductivity have been reported.[43] Electroabsorption[15,47,49] experiments have been performed, showing only a slight effect. Reflection measurements have also been made.[49-51] Index of reflection has been measured directly,[13,53] by using reflection data,[1,14,52] and by analyzing interference effects.[55] The index of refraction frequently has a strong temperature dependence;[53] this effect has been suggested for light deflection applications.

5.2 Reflectance and Transmittance

Data reported here was gathered using a spectrophotometer (Perkin-Elmer Model 450) with a 45°-reflectance accessory (Perkin-Elmer 350 Specular Reflectance Accessory). Pieces of amorphous $Ge_{10}As_{20}Te_{70}$ with smooth parallel sides were not available; attempts to cut and polish this fragile material were generally unsuccessful. All reflectance measurements were therefore made on flash-evaporated films (typically several μmeters in thickness), and interference effects were present. Orthogonal reflectance, which provides equal optical-path lengths for both reflectance and transmittance tests would have been preferred, but equipment was not available. The total averaged 45° reflectance for a thin film of material on glass microscope coverslides, is shown in Figure 5.1. Reflectance included contributions from both front and back surfaces. The values were larger than values normally reported for reflectance of chalcogenide glasses.

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* Vitreous selenium is possibly the best known amorphous semiconductor. It is used as a photoconductive element in the electrophotographic process, xerography.

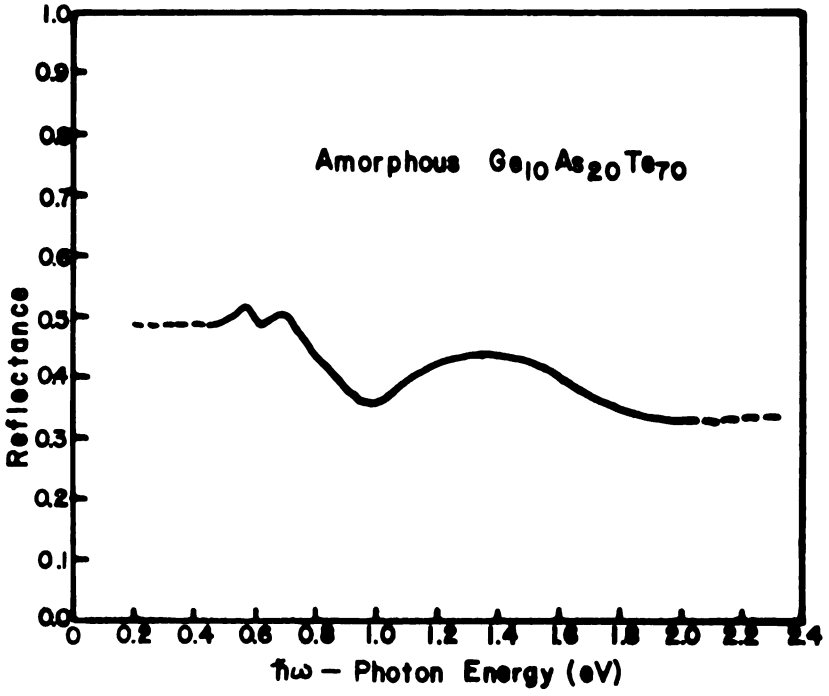

Figure 5.1 Average 45° Reflection

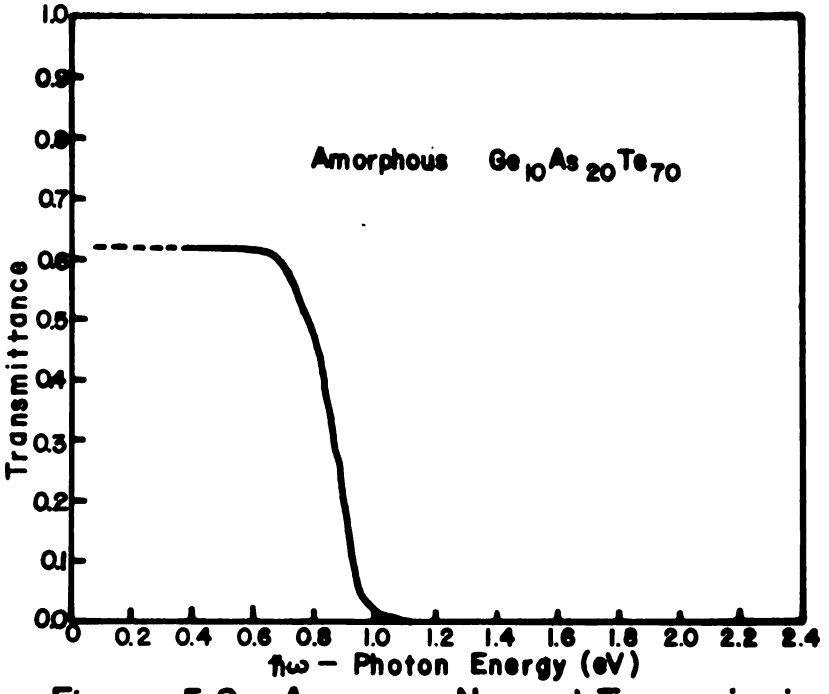

Figure 5.2 Average Normal Transmission

Averaged normal transmittance is shown in Figure 5.2. Film thickness in both cases was about 4.5 μm, and interference fringes in the transparent region ($\lambda > 1$ μm) were averaged. These results are qualitatively typical for all samples examined, but especially for reflectance were not quantitatively accurate.

5.3 Absorption Coefficient

It was desired to compare the energy gap for optical activation with the energy gap for thermal activation in $Ge_{10}As_{20}Te_{70}$. Careful measurements of optical absorption versus photon energy can provide useful information about the optical-energy gap. For crystalline semiconductors, in the region of the spectrum where $\hbar\omega \sim W_g$ (the optical-absorption edge), there is a rapid increase of optical absorption as a function of photon energy as electrons are excited across the energy gap, W_g. In amorphous materials the same process is much more complex;[18,39] the absorption edge is not usually well defined.[45] The absorption coefficient increases at-first exponentially with photon energy;[40,45,46] no part of the curve can be identified positively with an optical-energy gap. At higher energies, the absorption coefficient increases according to the relation:

$$\alpha \sim (\hbar\omega - Wg)^m$$

or in a more complex manner. Frequently, a small discrepancy exists between the energy gap determined optically and thermally.[42]

Near-infrared absorbance was measured for amorphous $Ge_{10}As_{20}Te_{70}$ film and bulk samples using the previously-cited spectrophotometer. Absorbance at longer wavelengths (2.5 μmeters to 16 μmeters) was measured using a simpler instrument (Perkin-Elmer Model 437B). The spectrophotometers provided data directly in absorbance units, A, which

were logarithmically related to transmittance,[59] T:

$$A = \mathrm{Log}_{10}(1/T)$$

The double-beam technique was used to compensate for atmospheric and substrate absorptions. Exact correction for reflectance,[1,58] scattering, and interference effects was not practical. Instead, approximate correction for reflection, by subtraction of equivalent absorbance, and averaging of interference fringes was done. Typical characteristics reported here resulted from many collections of data.

Flash-evaporated films (0.1 μmeters to 5 μmeters in thickness) were used for short-wavelength measurements. Ground-down larger pieces, and freshly-broken chips of bulk glassy $Ge_{10}As_{20}Te_{70}$ were used for measurements at longer wavelengths. Samples from 5 to about 100 μm in thickness were not obtainable, resulting in gaps in data gathered for absorption coefficient versus wavelength.[15] Absorbance as high as 6 was measured through the use of special neutral-density filters* in the reference-beam path. Careful adjustment of apparatus was necessary in order to maintain constant optical bandwidth to assure repeatability for data gathered in the absorption edge.

Absorption coefficient, α , defined by Lambert's law for known thickness, d:

$$T = e^{-\alpha d}$$

was computed[58] according to the relation:

$$\alpha = \mathrm{Log}_e(10) \times \frac{A}{d}$$

The natural log of absorption coefficient plotted versus photon energy, $\hbar\omega$, is shown in Figure 5.3. An exponential dependence of absorption was

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* Photo-etched thin-metal screens were used. These screens are available from Buckbee-Mears Co., St. Paul, Minnesota. They were individually calibrated for absorbance versus wavelength.

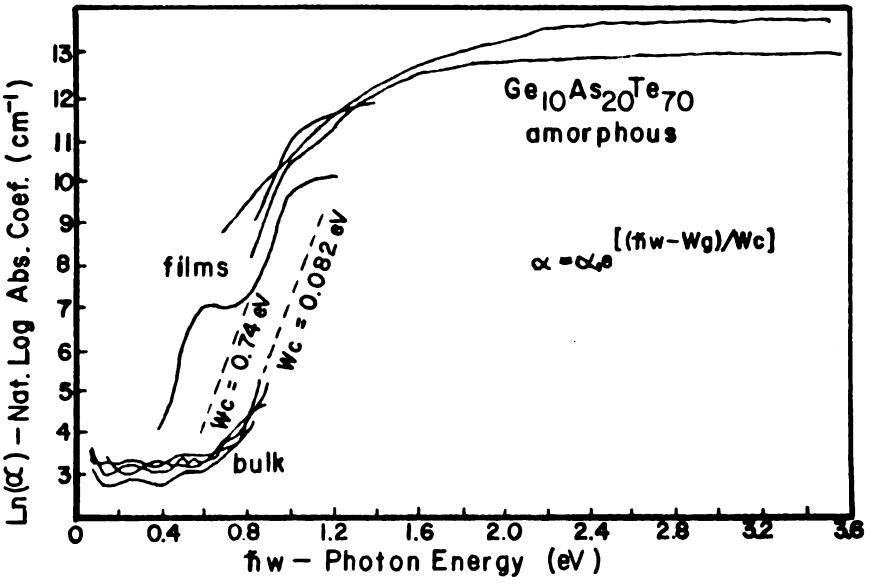

Figure 5.3 Optical Absorption, Exponential Behavior

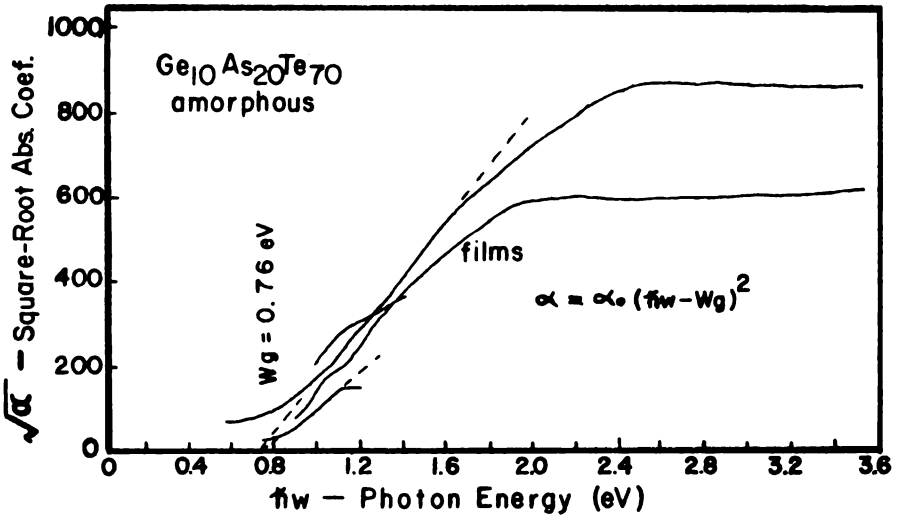

Figure 5.4 Optical Absorption
Square-Root Dependence

suggested by the straight-line nature of much of the curve. Exponential behavior of the band edge has been explained in terms of internal electric fields,[45] or transitions between localized energy states, but no explanation has been generally accepted. Over a range of photon energies α appeared to empirically fit the relation:[45]

$$\alpha = \alpha_0 e^{\{(\hbar\omega - Wg)/Wc\}}$$

Values for α_0 and W_g were not determined, but W_c was about 0.07 to 0.08 eV, similar in magnitude to values reported by others for many amorphous materials.[45]

Indirect optical transitions, involving absorption or emission of a phonon, gives the following dependence for absorption coefficient in crystals:

$$\alpha = \alpha_0(\hbar\omega - Wg^1)^2$$

The indirect optical-energy gap, Wg^1, normally is approximately the same as the thermal-energy gap derived from electrical conductivity measurements. Wg^1 is usually well defined only for crystalline semiconductors. The square-root of absorption coefficient versus photon energy is shown in Figure 5.4. An optical-energy gap Wg = 0.76 eV, was found for amorphous $Ge_{10}As_{20}Te_{70}$ by projecting the curve until it intercepted the $\alpha = 0$ axis.

Dependence of optical-absorption coefficient on photon energy according to the relation:

$$\alpha = \alpha_0(\hbar\omega - Wg)^m/(\hbar\omega)$$

has been reported by many workers.[39,41,44,45,56] A value for m of 2 was typical. The square-root of the product of photon energy and absorption coefficient, $\sqrt{\alpha\,\hbar\omega}$, was plotted versus photon energy, $\hbar\omega$,

to test the validity of this relation.

These curves, shown in Figure 5.5, were similar to those in the previous figure. Straight-line behavior over a wide energy range, with a change in slope at an intermediate energy, was apparent. An optical-energy gap of 0.79 eV was obtained by projection of the curve to the $\alpha = 0$ axis.

5.4 Absorption of Partially Crystallized Material

Several pieces of glassy $Ge_{10}As_{20}Te_{70}$ were melted and pressed into films 20 to 50 μm in thickness using anvils which were flat and cold. Electrical conductivity of the resulting films was high, indicating the film was partially crystallized and suggesting that the quenching rate was insufficient for complete glass formation. Differential thermal analysis of the films showed a small-area crystallization exotherm, indicating that the material was partially glassy. Optical absorption of completely-amorphous material compared to that for partially-crystallized material is shown in Figure 5.6. An absorption band in the wavelength range from 4 μm to 5.5 μm, and a shift in wavelength of the absorption edge from about 1.7 μm to 2.7 μm can be identified with crystallization.

5.5 Index of Refraction

The index of refraction, n, was determined for amorphous $Ge_{10}As_{20}Te_{70}$ in transmission regions. Three common techniques exist for the determination of index of refraction. Angle of deflection can be determined for wedge-shaped samples and related to index of refraction.[14] Reflectivity can be related to index of refraction since at transmitting wavelengths:[1]

$$T_{ave} = (1 - R)/(1 + R) = 2n/(1 + n^2)$$

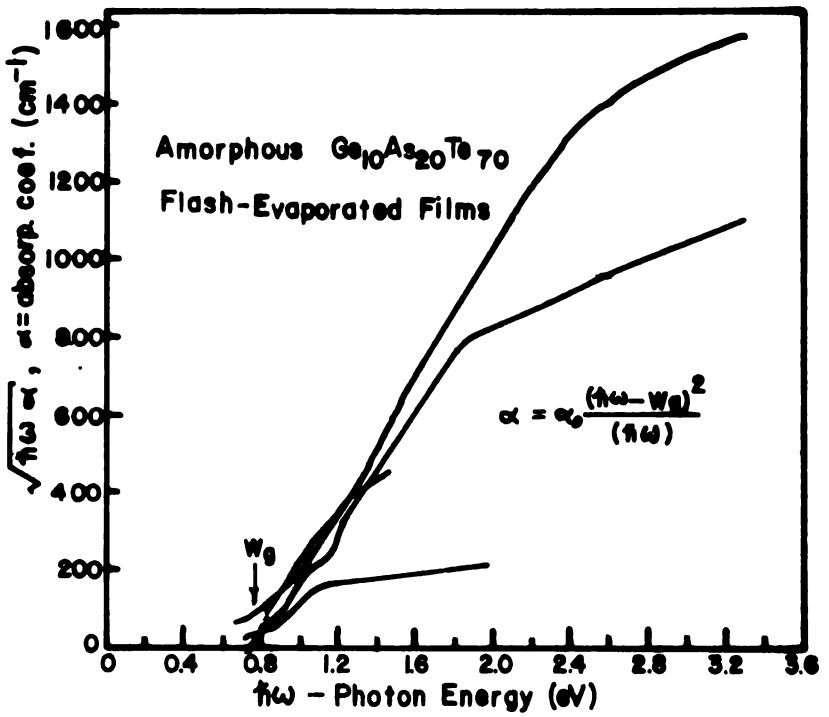

Figure 5.5 Optical Absorption Spectrum

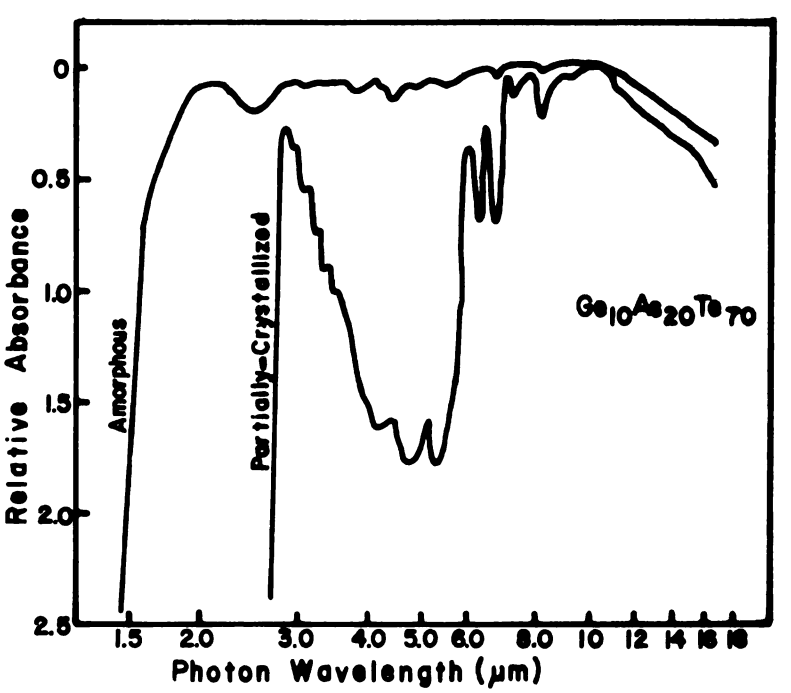

Figure 5.6 Absorbance: Amor. vs Cryst. Material

Finally, index of refraction can be determined[1,55] from spacings of interference fringes observed during measurement of absorption. This latter method was used for measurement of index of refraction for 4.5 μm-thick flash-evaporated films of $Ge_{10}As_{20}Te_{70}$.

Two minima (or maximum), selected from an absorbance interference pattern, found at λ_1 and λ_2 wavelengths, were related to index of refraction, n, and thickness, d, according to the formula:[1,55]

$$n = \frac{\Delta N}{2d} \frac{\lambda_1 \lambda_2}{\lambda_2 - \lambda_1}$$

where ΔN was the number of complete fringes between λ_1 and λ_2. If the exact order, N, of a fringe at λ_o is known, a simpler relation[1] is applicable:

$$n = \frac{N \lambda_0}{2d}$$

Fringe order was determined unambiguously for a 4.5 μmeter-thick film of amorphous $Ge_{10}As_{20}Te_{70}$, n was calculated, and results are shown in Figure 5.7. Above about 4 μm wavelengths, $n \sim 3.9$ was determined, agreeing approximately with values obtained by the reflectiviy technique. Others[13] have determined $n = 3.6$ in the transparent region of Ge-As-Te glasses.

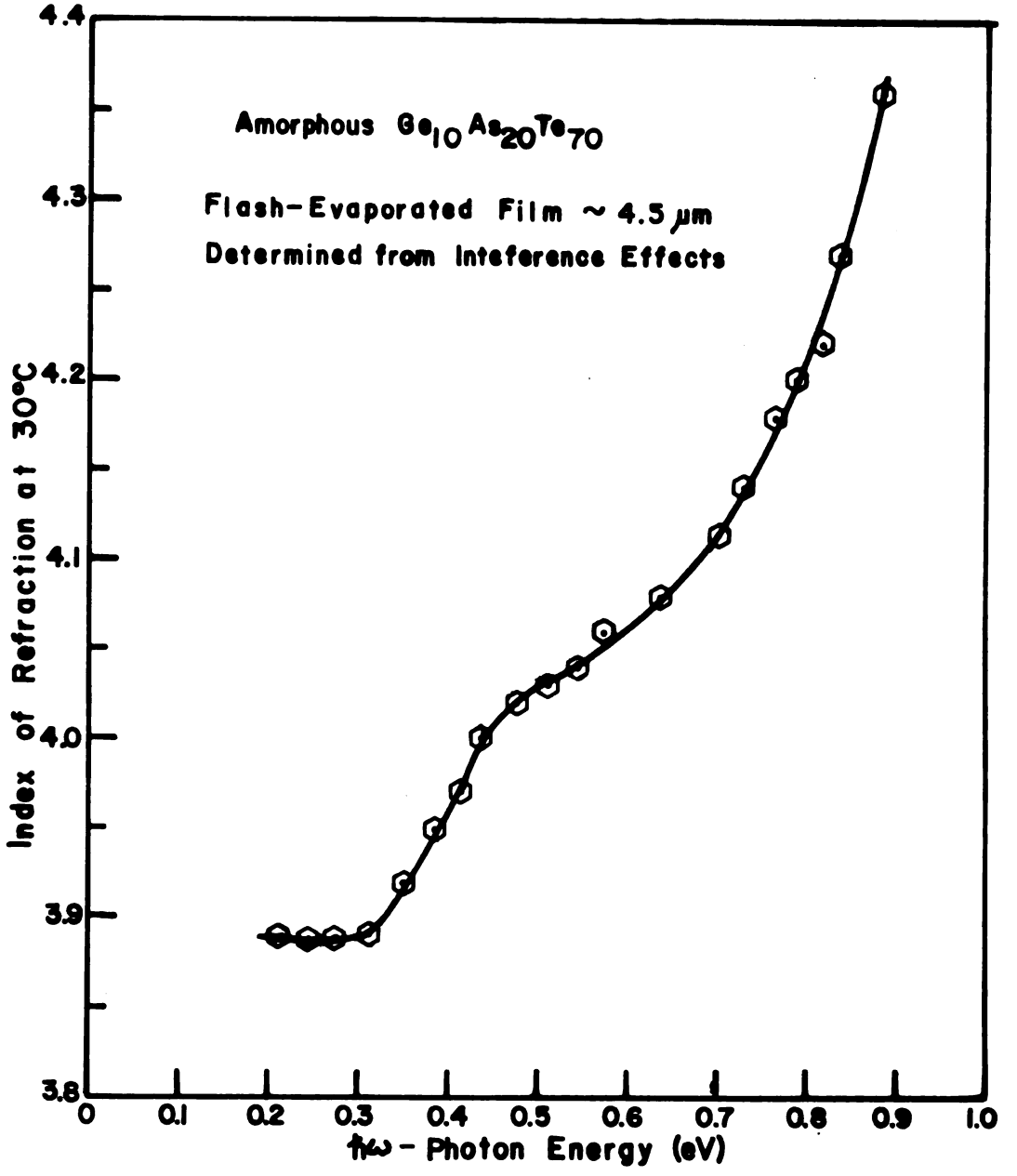

Figure 5.7 Index of Refraction vs $\hbar\omega$

CHAPTER 6

CONCLUSIONS

6.1 Summary of Results

Many plans formulated early in the research program were subsequently modified in carrying out experimental work to determine the physical, electrical, and optical properties of amorphous $Ge_{10}As_{20}Te_{70}$. Experimental and theoretical literature for this subject area was thoroughly reviewed. Many interesting semi-theoretical conclusions were made concerning this semiconducting chalcogenide glass based upon measurements reported here and published information.

Synthesis of amorphous $Ge_{10}As_{20}Te_{70}$ was generally difficult; techniques were relatively complex and potentially dangerous; precautions were necessary to avoid possible ingestion of powders and vapors from this very toxic substance. Preparation by fusion of constituent elements in an evacuated silica ampul proved satisfactory; adequate quenching was obtained by dropping the heated ampul into a 0 °c brine bath. Large batches, greater than about 50 g, prepared in 15 mm-bore ampuls did not quench uniformly; smaller batches were highly stressed and quite fragile. Measurements and evaluations were hampered by problems in preparing large, flat, or thin samples. Annealing did not significantly reduce brittleness of the glass. Comparison of measurements reported here with other results indicated that long-term annealing may be needed to completely stabilize amorphous $Ge_{10}As_{20}Te_{70}$; electrical conductivity at low temperatures was very sensitive to quench rate and annealing time. Useful films of amorphous $Ge_{10}As_{20}Te_{70}$ were prepared by flash evaporation of bulk material. Flash evaporation and RF sputtering appear very

attractive as a means for preparing thin samples for evaluation.

Thermal properties were measured using thermo-gravimetric, thermo-mechanical, and differential-thermal analysis techniques. Temperature dependence of dc electrical conductivity was measured over a wide temperature range using four-point probe apparatus of improved design, constructed for this application; results confirmed theories for thermal activation of conductivity. Measurements of frequency dependence of low-temperature ac admittance suggested that hopping carrier-transport modes may be important. Seebeck coefficient, determined approximately using the hot-probe method, was positive; this suggested the polarity of current carriers in amorphous $Ge_{10}As_{20}Te_{70}$ was positive. Brief examination of switching effects revealed threshold and memory switching occurred readily; the threshold electric-field intensity was measured. Techniques were suggested for a novel and feasible method for drift mobility measurement. Experiments showed that photoconductive effects were practically negligible at room temperature. Finally, dependence of the optical-absorption coefficient on photon energy in the absorption edge was examined in detail.

A comprehensive summary of properties as determined for amorphous and crystallized $Ge_{10}As_{20}Te_{70}$ is given in Table 6.1.

6.2 Suggested Additional Research

Suggestions for additional experimentation and analysis arose throughout the research program. Improvements of technique and extensions of experimental methods appeared as a direct consequence of the experimental work. Questions and suggestions arose during analysis and intra-comparison of experimentally derived properties. Theoretical and experimental work in the area of amorphous materials has been extensive

Table 6.1 Summary of Properties of $Ge_{10}As_{20}Te_{70}$

Property	Amorphous State	Crystallized State
Appearance	Fractured conchoidally, shiny and dark. No structure observable by optical microscopy or x-ray diffraction.	Dull and grayish. Crystallites ∿ 10 μm long visible. X-ray diffraction pattern indicated crystalline tellurium and other crystallites.
Physical	Density was 5.8 g/cm^3. Hardness ∿ 2.8 Mohs. Fragile, highly stressed. Difficult to cut or polish.	Density less than amorphous state, somewhat porous. Harder and tougher than amorphous state.
Thermal	Glass-transformation temperature = 120 °C. Endothermic reaction for 16 hours annealing at 100 °C was 2.97 J/g; peaked at 140 °C. Specific heat = 0.289 J/(g °C) @ 80 °C = 0.382 J/(g °C) @ 160 °C. Crystallization above 190 °C, ΔH ∿ 6.11 J/g. Thermal-expansion coef = 18 μm/(m °C). Softening temperature ∿ 175 °C.	Melting temperature = 340 °C. Atmospheric oxidation less than 0.5% for long heating times at 425 °C. Specific heat = 0.314 J/(g °C) @ 80 °C = 0.288 J/(g °C) @ 160 °C. As_4 liberated above 262 °C, ΔH = 1.52 kJ/g. Te_2 liberated above 386 °C, ΔH = 1.12 kJ/g.
Electrical	Low-field dc electrical conductivity appeared to be thermally activated: $\sigma = \sigma_0 e^{(-Wa/kT)}$ $\sigma \sim 5\times10^{-5}$ mhos/cm; Wa ≈ 0.2 - 0.5 eV, was sensitive to temperature and annealing time. Ac conductance at -180 °C fitted: $\sigma = \sigma_0 + \sigma_1\omega^{0.85}$ Seebeck coefficient ∿ +300 μV/°C. Threshold and memory switching possible. Switching electric field = 2.65 kV/cm. Photoconductivity very small at 20 °C.	High dc electrical conductivity ∿ 70 mhos/cm, practically independent of temperature. Conductivity higher than can be accounted for by crystalline tellurium alone.

Table 6.1 (cont'd)

Property	Amorphous state	Crystallized state
Optical	Absorption edge $\lambda \sim 1.7$ μm, poorly defined. At low energies in absorption edge: $\alpha = \alpha_0 e^{\{(\hbar\omega - Wg)/Wc\}}$ where: $Wc \approx 0.075$ eV @ 30 °C $Wg = 0.79$ eV @ 30 °C. At higher energies in the absorption edge a better formula was: $\alpha = \alpha_0(\hbar\omega - Wg)^2/(\hbar\omega)$ Wg was slightly less than twice the thermal-activation energy for conductivity, Wa. Wa was about 0.41 eV @ 30 °C for optical-test film samples. Index of refraction ~ 3.9 for $\lambda > 4$ μm.	Well defined absorption edge at $\lambda = 2.8$ μm. Strong absorption band 4 μm < λ < 5.5 μm.

and brisk; significant advancements have been reported recently. Published results have only served to generate additional questions and suggest subjects and opportunities for additional research.

The following list summarizes suggested steps for improving experimental techniques and obtaining additional information about electrical-current-carrier type and transport mode:

1. Improve methods for material synthesis. Determine sensitivity of properties to annealing and other preparational techniques. Examine procedures for cutting and polishing samples.

2. Adapt four-point probe conductivity measurement apparatus for a wider range of temperatures. Obtain a better low-current source and dc-voltage preamplifier.

3. Fabricate apparatus for ac-admittance measurement over wide temperature and frequency ranges.

4. Fabricate apparatus for measurement of photoconductivity versus wavelength for a wide range of temperatures. Measure time response of photoconductivity to determine lifetime of carriers.

5. Measure electric-field intensity dependence of dc conductance, ac admittance, and photoconductivity.

6. Measure Seebeck coefficient versus temperature.

7. Determine drift mobility as a function of temperature and electric-field intensity by transit-time measurements using photoconductive and electron-beam injection.

8. Determine normal reflectance as a function of wavelength for bulk and film samples.

9. Make additional measurements of absorption in the absorption edge.

10. Measure energies of thermal reactions using DTA techniques. Investigate effects of annealing time and quenching rate.

11. Determine property sensitivity to impurities and composition.

12. Investigate switching effects and determine composition and structure of crystallized material.

These were the most important suggestions which arose; certainly many more would occur with continued work.

APPENDIX

APPENDIX A

NON-CRYSTALLINE ELECTRICAL CONDUCTORS

Part 1 -- Historical Introduction

Identification and description of non-crystalline materials has become important in recent times. Several reviews of characteristics of the amorphous state have been published.[1-4] Considerable study of non-crystalline materials has provided information necessary for classification and description of amorphous semiconductors.[5,6] Information about preparation and physical chemistry of amorphous semiconductors has become available.[7-11] Much progress in the study of semiconducting glasses has been reported at conferences.[12-17]

Early research into characteristics and applications of non-crystalline electrical conductors began in the Soviet Union with the work of academician A. F. Ioffe.[18-19] Much of the early theoretical work was summarized by Gubanov.[20] In the western world early work on disordered electrical conductors began as an extension of crystalline-semiconductor research; understanding of electrical properties of perfectly-crystallized solids prompted study of less-perfect materials. Many excellent general reviews of electrical properties of crystalline solid-state materials are available.[21-25] Several short surveys of work on amorphous semiconductors have been published.[6,26,27] Professor N. F. Mott has contributed greatly to the understanding of electrical conduction in disordered materials.[28-35]

Non-crystalline conductors can be separated into about five categories: electrolytes, organics, liquid metals, oxide glasses, and chalcogenide glasses. Electrical conduction in electrolytes has been

studied extensively as a branch of chemistry.[36] Much of the work on organic semiconductors has also been done by chemists.[37] N. F. Mott initiated study of liquid metals in 1960, and considerable work has since been done.[38,39] Transition-metal oxides, studied initially as an extension of ordinary silicate-glass technology, are an important category of disordered solid-state electrical conductors.[40,41] Perhaps the potentially most-important category is chalcogenide glass, a family of materials containing sulfur, selenium, or tellurium as a major constituent. Chalcogenides, investigated for some time for useful thermoelectric properties, became especially important with the recent development of conductivity switching effects* by S. R. Ovshinsky.

Part 2 -- Theory of Electrical Conductivity

Work on theory of electrical conduction in disordered materials began primarily in the Soviet Union.[20] Presence of short-range order in amorphous materials was suggested from atomic radial-distribution functions derived from x-ray diffraction data.[43] Long-range order was absent, confirmed by the absence of sharp peaks in the x-ray diffraction pattern. The familiar quantum-mechanical treatment for electrons in crystalline semiconductors was extended to disordered materials, by assuming a perturbed periodic arrangement of atoms in which long-range order was completely disrupted. It was determined that an energy-band model was applicable[44-55,59] even for situations in which there was no long-range order. However, it was determined that the mean-free path for electrons was very short, comparable to interatomic spacings, for only slight variations in nearest-neighbor distance.

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* A short review of phenomena and theory of switching can be found in Appendix D.

Studies of localized electrons have indicated that the electrons can interact significantly.[56-62] N. F. Mott has suggested that the electronic-wave functions may be considered localized only for energies below some particular value, and that transition to free-electron behavior is similar to phase or other thermodynamic changes.[63-68] The Mott nonmetal-metal transition has been studied extensively in an attempt to understand switching pehnomena.[69-72]

Considerable study has been made of carrier dynamics in disordered materials. N. F. Mott has noted characteristics similar to compensated impurity-level conduction for crystalline semiconductors.[34,35] A form of carrier motion by thermally-activated hopping from one localized state to another has been described for polarons in transition-metal oxide glasses,[88,89] and seems applicable to some amorphous chalcogenides.[90,99] Space-charge conduction at high fields has been observed for insulators[91-95] and may be important for amorphous semiconductors. Double-injection processes have been studied to explain switching initiation.[96-98] Chemical bonding and electrical conductivity have been related for amorphous conductors.[100-102] An internal electric-field theory has been used to account for optical absorption in some amorphous chalcogenides.[103]

K. W. Boer has studied disordered conductors and contributed greatly to understanding of conduction mechanisms.[73-77] Cohen, Fritzsche, and Ovshinsky have suggested a simple band model (CFO Model) for electrical conduction in amorphous semiconductors.[78] Together with theoretical contributions by N. F. Mott, these hypotheses have provided tentatively-satisfying explanations for properties of some disordered electrical conductors. The model assumes ambipolar

conductivity for a high density of carriers in self-compensated material.[75] An energy-band model for mobility is used, resulting in a mobility gap rather than a gap in the density of states to account for temperature activated conductivity. Exponential dependence of mobility, a frequently noted property for disordered electrical conductors,[79,80] results. P-type conduction occurs due to a higher effective energy-level density in the "valence" band.[75] Much progress understanding electrical conductivity for amorphous semiconductors has resulted from application of the CFO model.[38,81-86]

APPENDIX B

MATERIAL PREPARATION TECHNIQUES

Part 1 -- Silica Ampul Method

A popular technique for preparing toxic or reactive alloys is fusion in evacuated ampuls. This process was employed for the preparation of amorphous $Ge_{10}As_{20}Te_{70}$ from elemental starting constituents. Lumps, shot, and powders of germanium, arsenic, and tellurium were carefully weighed into quartz-glass ampuls. The selection and application of ampuls is described in this section.

Initially, inexpensive, non-transparent "satin-surface" silica tubing, 12 mm-inside diameter and 0.4 mm-wall thickness, was obtained.* However, this silica form was difficult to handle for most glassblowing operations, and was suspected of contaminating the semiconductor. The more expensive and transparent variety of silica tubing was used successfully. Pieces 30 cm long were sealed at one end and constrictions were formed near the center.

Considerable skill is required to work softened silica; considerable trial-and-error learning and practice was required. Quartz-glass fusing and forming operations were performed using an oxygen-hydrogen hand torch** with and without a holder. High-density welder's goggles were used for safety and eye protection.

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* All silica materials discussed here were obtained from Thermal American Fused Quartz Co., Montville, New Jersey.

** The glassblowing equipment was mostly obtained from National Welding division of Veriflo Corp., Richmond, California.

Subsequently, silica ampuls were procured already closed at one end* but without constrictions. Forming constrictions and sealing off the ampul under vacuum was difficult so a different sealing technique was adopted. A small dimple, formed in the wall of the ampuls before filling, supported a short close-fitting silica plug* dropped into the ampul just before evacuation. After evacuation, ampuls were sealed by fusing the walls to the plug. Seals formed in this manner never cracked or leaked.

Evacuation of the ampuls was done using a small vacuum system specially fabricated for the purpose. A mechanical vacuum pump (Welch DuoSeal Model 1400B) was connected with flexible copper tubing to an all-glass manifold including valves and traps. One trap was chilled by liquid nitrogen to capture toxic vapors created during the sealing operation. Another was filled with glass wool to capture dust particles drawn from the ampul during evacuation. The input connection to the vacuum system was a ground-glass tapered joint. A mating joint was coupled to silica ampuls by a short length of rubber hose. The rubber hose allowed easy inexpensive connections, and the ordinary-glass tapered joint allowed rotation of the ampul during sealing. Ampul pressure, measured by a Pirani gauge attached to the system, was reduced to below 10^{-3} torr with the aid of the cold trap.

After evacuation and sealing, ampuls were disconnected from the vacuum system and a hole was drilled above the seal for a wire used to hang the ampuls in the rocking tube furnace. Also, excess tubing length was removed. After fusion, quench, and annealing ampul contents, the

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* Vitreosil tubing, 16 mm-bore, normal-wall and transparent, closed-one-end, and matching 15 mm-O.D. silica rod stock was obtained in one-foot lengths from the previously-mentioned manufacturer.

ampul was carefully opened in a disposable glove bag. Usually ampuls were fractured by a sharp blow; resulting in broken samples. Some ampuls were opened carefully using an ordinary glass-cutting saw, but attempts to slice amorphous material while still in ampuls were not successful. Pieces of glassy material, exhibiting conchoidal fracture, are shown in Figure B-1.

Part 2 -- Rocking Tube Furnace

A small 2000-watt tube furnace, of unknown manufacture, was available for the research program. This furnace, about 3.5 cm bore and 0.5 meter long, was layer wound with nichrome wire and amply insulated for high-temperature operation. A steel outside casing completed construction. The furnace was suspended from a bracket and enclosed by a fume hood as illustrated in Figure B-2.

The furnace was rocked at approximately one cycle per second about the pivot by a small variable-speed motor and eccentric drive. The maximum displacement of the bottom of the furnace was only about 5 cm. The ampul, suspended from outside and above the furnace by a 0.5 mm-diameter nickel or stainless-steel wire, tapped the inside walls of the furnace lightly each stroke. This was considered advantageous, and abrasion of the ampuls caused no difficulties. Rocking was stopped upon completion of heat treatments, the thermocouple was removed, and an armored quench-bath was arranged directly below the bottom of the furnace. Quenching was accomplished simply and quickly by cutting the suspension wire, allowing the ampul to drop directly into the quench-bath.

Furnace temperature was monitored by a cromel-alumel thermocouple inserted into the bore through the bottom opening. This thermocouple

Figure B-1 Pieces of Amorphous $Ge_{10}As_{20}Te_{70}$

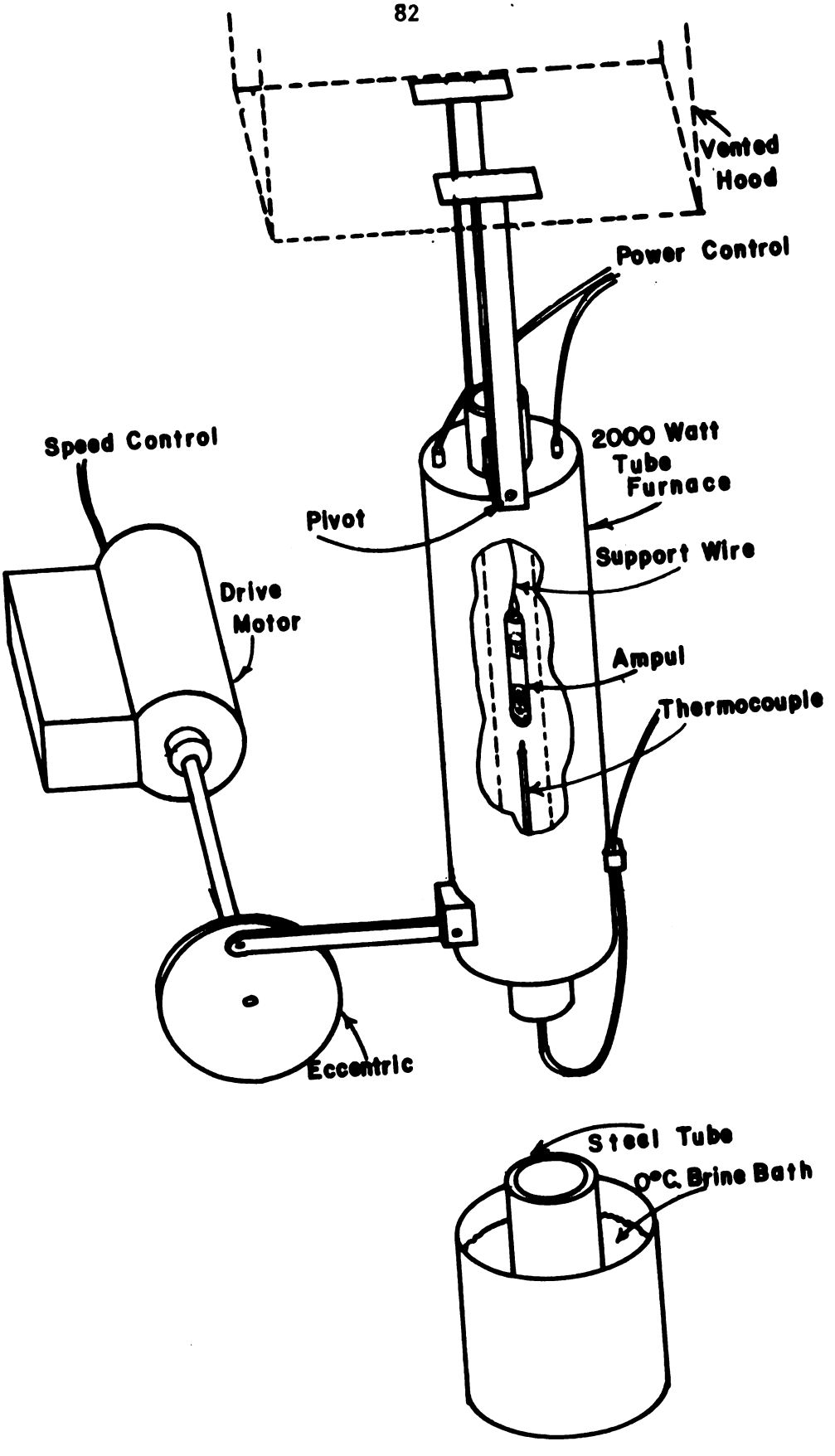

Figure B-2 Rocking Tube Furnace

was also used for temperature control by use of an on-off type temperature controller (Honeywell-Versatronic Model-R7161B, 0-1200 °C. type-K). A silicon-controlled rectifier-type power control was used to adjust heating rate by proportioning available power. Manual programming was used. The furnace arrangement and operation was versatile and easy to use; it proved satisfactory in every respect.

Part 3 -- Flash Evaporation of Films

Many techniques exist for preparation of thin films. Thermal evaporation from resistance-heated filaments or boat sources is a well established practice. Not so-well known are flash and quasi-flash-evaporation techniques. In the ordinary flash-evaporation method lumps of material to be vaporized are dropped piece-by-piece onto a preheated crucible and vaporize practically upon contact. However, some materials vaporize too violently or segregate greatly, and cannot be flash evaporated from an ordinary open crucible.

An arrangement is available which provides an indirect path for travel of vapors and which allows easy mixing of vapors prior to emission. This arrangement, generally called a baffled source,* is illustrated in Figure B-3. Evaporation of materials which react with metals from which sources are constructed (molybdenum, tantalum), requires a thin coating of aluminum-oxide powder to be sintered onto the interior of the source. Very-rapid resistance heating of sources can sometimes be obtained. Occasionally, sufficiently-rapid evaporation rates can be obtained simply by switching on a very-high power source. This form of quasi-flash-evaporation was utilized to deposit thin films of $Ge_{10}As_{20}Te_{70}$.

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* "Baffled-Box" type evaporation sources (alumina-coated interiors if specified) are available from R. D. Mathis Co., Long Beach, Calif.

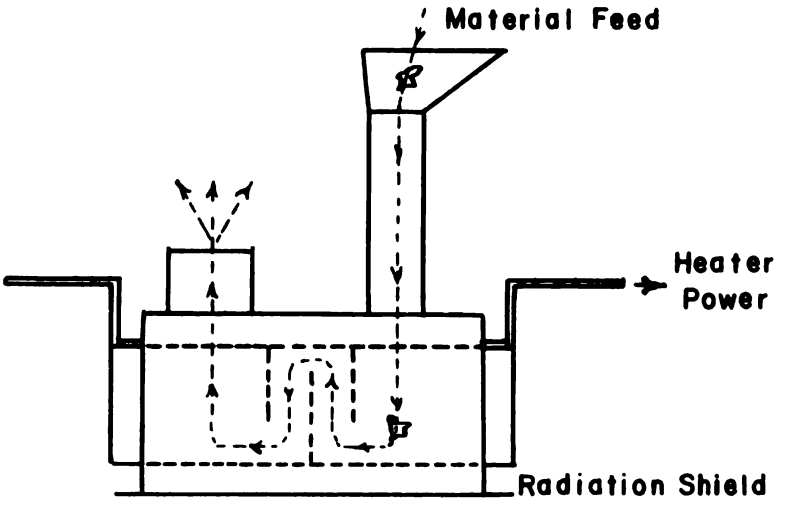

Figure B-3a Flash Evaporation, Baffled Boat

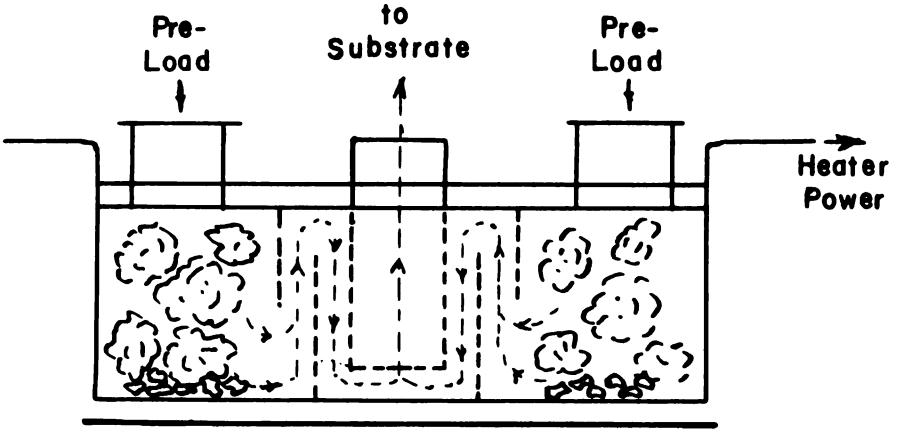

Figure B-3b Quasi-Flash Evaporation, Baffled Boat

An alumina-coated "baffled-box" source was obtained (R. D. Mathis Types SM10 & SM11) and installed in a conventional vacuum coater (Norton Co. (N.R.C.) Model 3176) replacing an ordinary resistance-heated filament source. A holder for thin-glass* substrates was also installed. Very-thin film-glass substrates were used for minimum interference with optical-absorption measurements. The substrates were dc-glow-discharge cleaned prior to evaporation coating. The substrates were not heated during evaporation, but were allowed to come to equilibrium with room temperatures prior to evaporation. Evaporation operations occurred rapidly enough so that radiant heating from the source was not a problem.

A few grains of glassy $Ge_{10}As_{20}Te_{70}$ material were loaded into the boat source. A correct mixture of powdered elements might have been used instead, but this possibility was not investigated. The substrate holder was arranged about 30 cm from the source; shielding was used where necessary to simplify later toxic clean-up operations. The chamber was evacuated to less than 10^{-6} torr and heating current (greater than 400 amperes initially) was switched on abruptly. Vaporization of the entire load of material appeared to occur in less than twenty seconds.

Film thickness was controlled by substrate-to-source distance and by initial-load size. Films thinner than 0.1 μm were frequently pinholed; suitable films as thick as 1.0 μm were obtained in a single flash-evaporation step. Successive identical evaporations reduced difficulties with pinholes, and allowed buildup of films several μm in

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* 48 mm × 50 mm Number-1 Exax cover glass/#19160, Kimble division of Owens-Illinois Inc., was used for this purpose.

thickness. No layer-interface problems were noticed, even though films were exposed to the atmosphere between evaporation steps. Adhesion to substrates was very good.

Segregation difficulties, frequently observed when evaporating alloys, were not apparent. Evaporated films were not annealed. Structural differences from bulk material were possible and probable. Electrical and optical properties of quasi-flash-evaporated films differed only in an accountable manner from properties of bulk material quenched from a melt. However, careful analysis of data for differences was not performed, and exact composition of films was never determined.

APPENDIX C

DC CONDUCTIVITY MEASUREMENT

Part 1 -- General Considerations

The four-point probe method was used to measure electrical conductivity of amorphous $Ge_{10}As_{20}Te_{70}$ semiconductor. This technique overcame difficulties associated with high-resistance and rectifying contacts, frequently observed at metal-semiconductor connections. It also permitted measurement of conductivity for samples having a variety of sizes and shapes. These and other advantages proved useful for measuring conductivity in lump and film samples of $Ge_{10}As_{20}Te_{70}$.

It was first anticipated that conductivity of amorphous $Ge_{10}As_{20}Te_{70}$ would be comparable to or slightly less than that observed for familiar crystalline semiconductors. Measurement, however, indicated conductivity was as low as 10^{-6} mhos/cm. This led to refinement of a conventional four-point probe system to provide low leakages, high sensitivity, and good isolation between current supplies and voltmeters. The system developed is described here.

The basic technique for four-point probe conductivity measurement[1,2] is illustrated in Figure C-1. Four pointed probes were placed on a relatively-flat surface of material to be measured. A fixed current passed through the outer electrodes developed voltage drops in the material near the probes. Voltage drops at the current-supply contacts were absorbed by the current-supply system. The voltage drop between the two inside probes was determined without causing any current to flow in these electrodes through the use of a high-resistance voltmeter floating with respect to the current supply. Since no current flowed

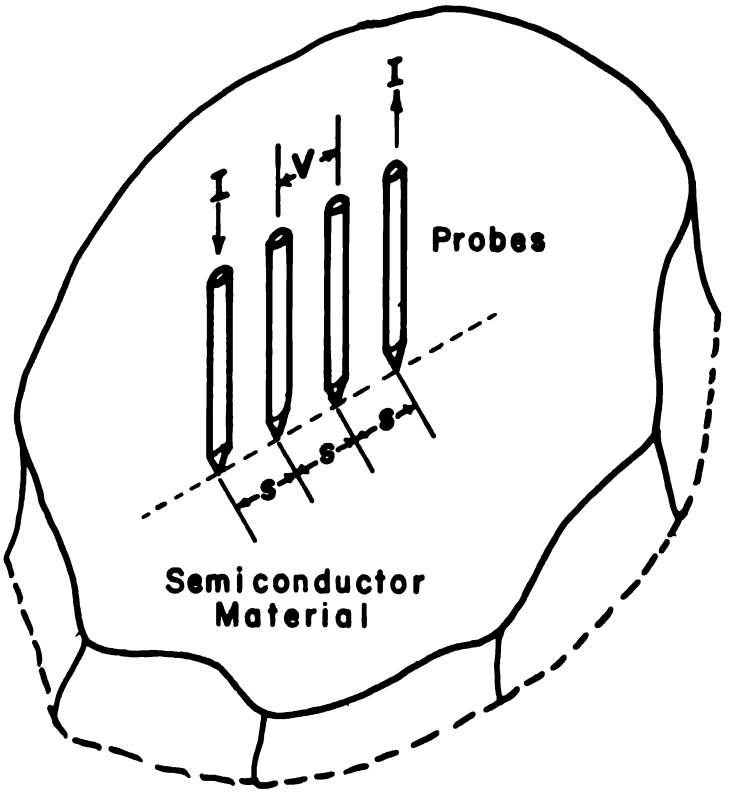

Figure C-1a Four-Point Probe

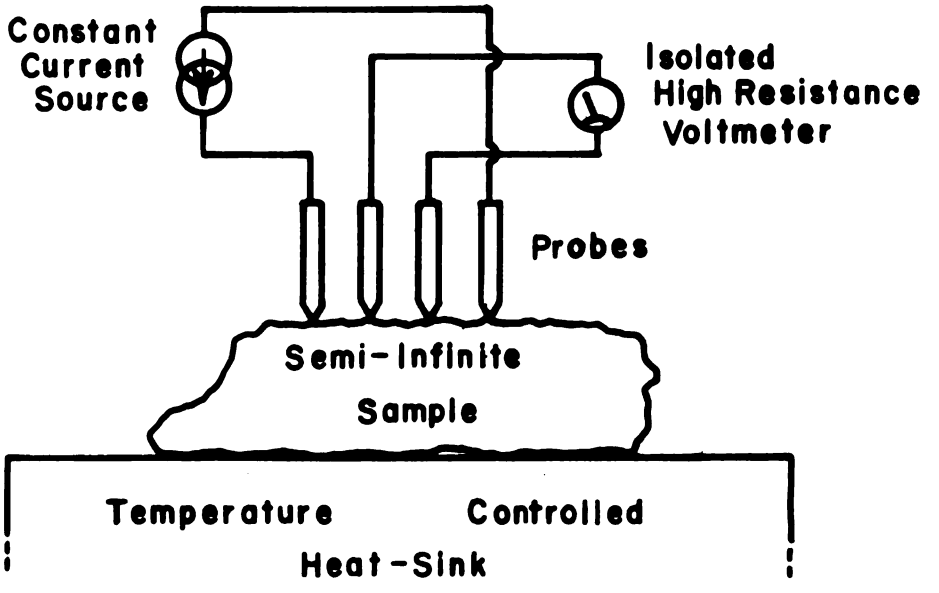

Figure C-1b Four-Point Conductivity Measurement

in the voltmeter circuit, voltage drops at these contacts were eliminated. Several arrangements of probes or contacts have been used.[4,5] Four in-line and equally-spaced probes were used. For an arbitrarily-shaped sample conductivity may be computed:

$$\sigma = \frac{I}{2\pi \times s \times V} \times \Phi$$

where Φ is a geometry-dependent correction factor. For flat-sided semi-infinite samples frequently approximated by large lumps, this factor is unity. Φ has been determined for many other cases and geometries such as samples with boundries near the measurement and very-thin samples.[1,2,5-8] Many applications and variations of the four-point probe conductivity-measurement technique have been developed and studied.[9-12,50]

Part 2 -- Four-Point Probe Head

Purchase of a suitable four-point probe conductivity-measurement system was attempted, but apparatus was not generally available. Several systems have been offered recently, however, such as the Sylvania Model RM-1 Surface-Resistivity Meter. Electronic systems for existing probe-head assemblies have also become available.*

Probe-head assemblies were available from several sources.** An Abacus Model A4P-25 probe head was fastened to a discontinued resistivity-test stand (Model JP, Baird Associates Inc., Cambridge, Massachusetts) used to hold and position the probe head. The chosen probe head consisted of four adjustable-coil spring-loaded tempered-steel

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* Hewlett-Packard Model 4329A Resistance Meter and digital ohmmeters such as the Hewlett-Packard Model 3450A Multi-Function Meter.

** A. & M. Fell, LTD, London, England; Dumas Instrument Company, Costa Mesa, California; and Abacus Instruments division of Alessi Industries, El Segundo, California.

probe pins equally spaced 0.0635 cm ± 1% by a cast-epoxy guide block. Maximum-available probe pressure, about 180 grams, was used. The manufacturer's technique and others[13] were used to maintain sharpness of the points.

Part 3 -- Description of Electronic Subsystems

Several factors were considered in the choice of an appropriate constant-current supply for the system. Measurement over a wide conductivity range was desired and since conductivity was fairly low, it was necessary to use a well-isolated current source having good regulation and high-voltage capability. Initially, the design of an isolated constant-current source was attempted, following the example[14,15] of a Model LCD-078 Constant-Current Converter, Argonaut Associates, Beaverton, Oregon. Good isolation was maintained first through the use of battery packs, and later by special isolation transformers.[16] Unfortunately however, a system with sufficiently-high isolation, regulation, and voltage could not be developed. Schematic diagrams of two trial systems are given in Figure C-2.

Eventually, a suitable constant-current source (Hewlett-Packard CCB-6181B Constant-Current DC Power Source) with an isolated and guarded output of 0 - 2.5/25/250 milliamperes at a maximum of 100 volts, was obtained. This instrument had quite satisfactory isolation and represented about the state-of-the-art for such systems.[17,18,19] Also recently offered are other supplies.* A Keithley Model 225 Constant-Current Supply, capable of supplying highly-regulated currents

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* Luchter Instruments, Walnut Creek, California; Electronic Measurements, Neptune, New Jersey; and Keithley Instrument Co., Cleveland, Ohio. The Hewlett-Packard CCB-6186B with higher-resolution and higher-voltage capability has recently become available.

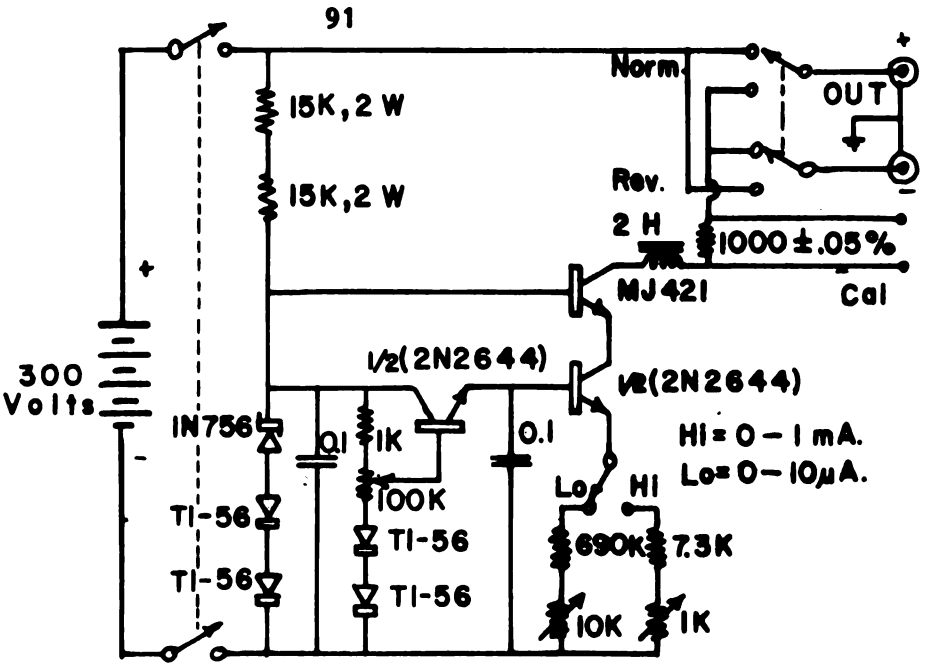
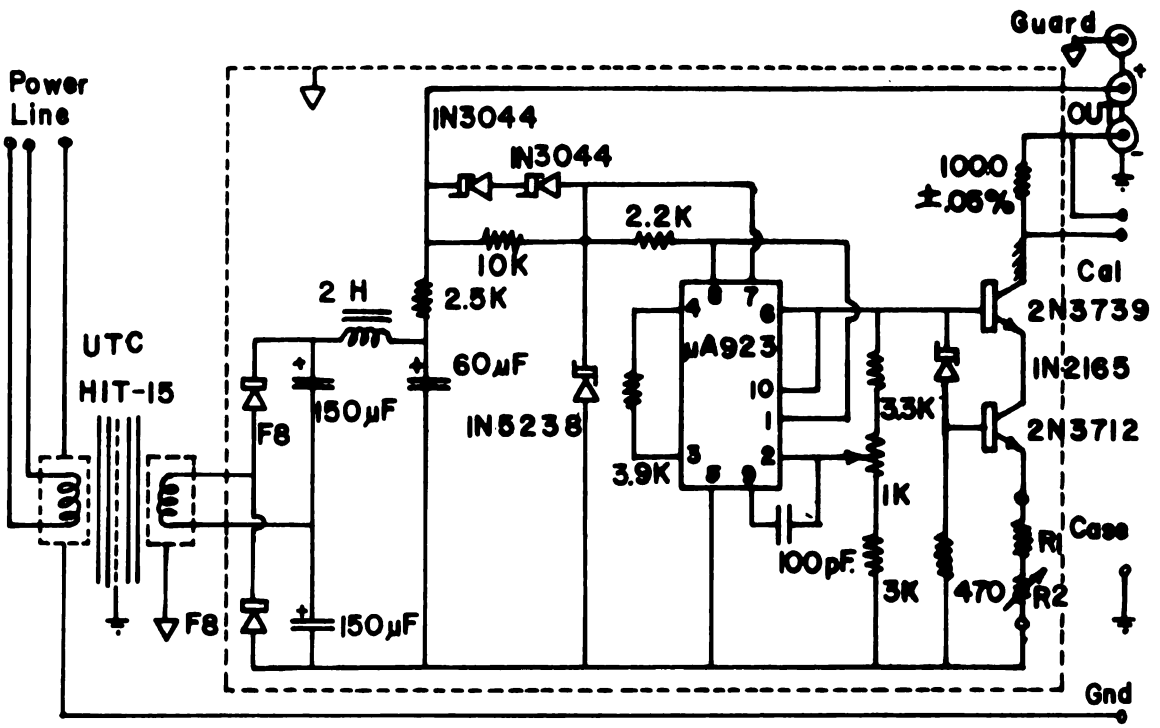


Figure C-2a Trial Constant-Current Supply



$R1 + R2 = 5 \text{ Volts} / I_{out}$

Figure C-2b Trial Constant-Current Supply

as low as one nanoampere, would have been used had it been available when needed.

For many measurements it was necessary to use a test current of 0.1 microampere. This was not attainable from the Model CCB-6181B Supply. A simple but effective method for obtaining this constant current is illustrated in Figure C-3. The dc constant-voltage supply used is a highly-stable and well-isolated model. It was necessary to adjust this system manually to achieve constant-current operation when very-low conductivities were measured. As will be described, most of the conductivity-test system operated almost automatically; manual adjustment proved practical for maintaining constant current. Power-dissipation limitations prohibited use of this system to provide higher currents. Fortunately, operation at a current above one microampere was achieved satisfactorily by using the Model CCB-6181B Supply.

Considerable time and effort was taken for development of a suitable voltage-measuring system with input resistance about 10 GΩ (to prevent loading). A system of the form shown in Figure C-4 was developed, to measure and record conductivity over a wide range with accuracy and minimum operational manipulation. It was impractical to sufficiently isolate a voltmeter from the current source by separately floating these subsystems. Instead, the center of a differential amplifier was referenced to one-half the voltage developed across the current supply, (as supplied by a divider as in Figure C-3).

Design of the preamplifier involved many considerations.[20-25] The preamplifier developed, shown in Figure C-5, was a differential dc type with high differential and common-mode input resistances. High common-mode rejection permitted moderate imbalances of electrode

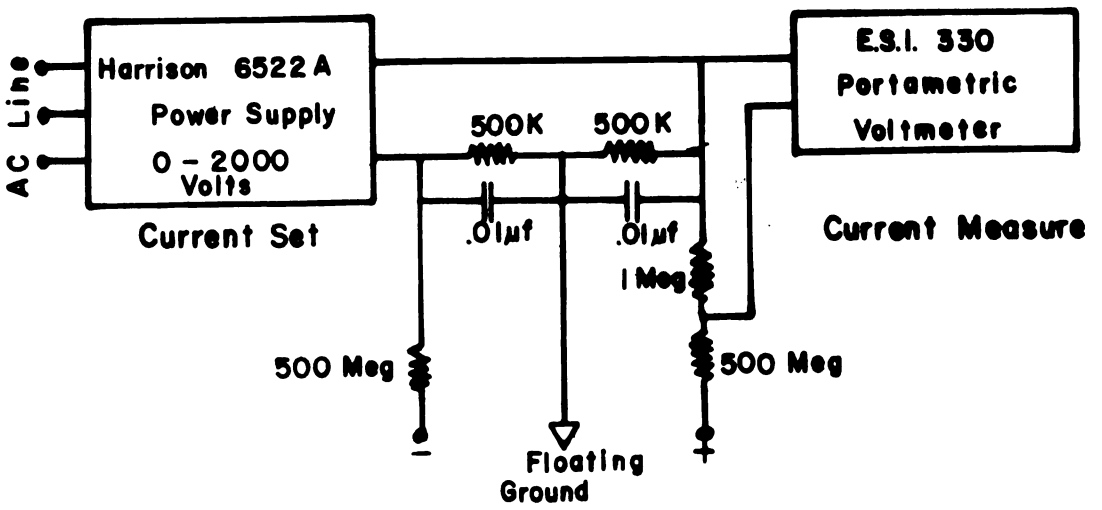


Figure C-3
A Special 0.1μA Constant-Current Supply

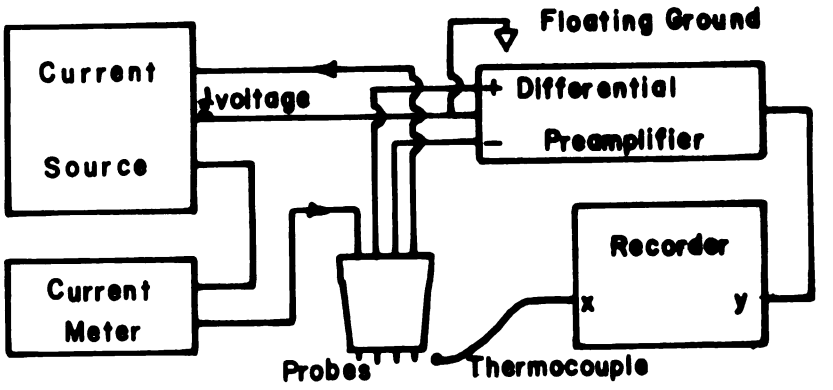


Figure C-4
DC Conductivity-Measurement System Diagram

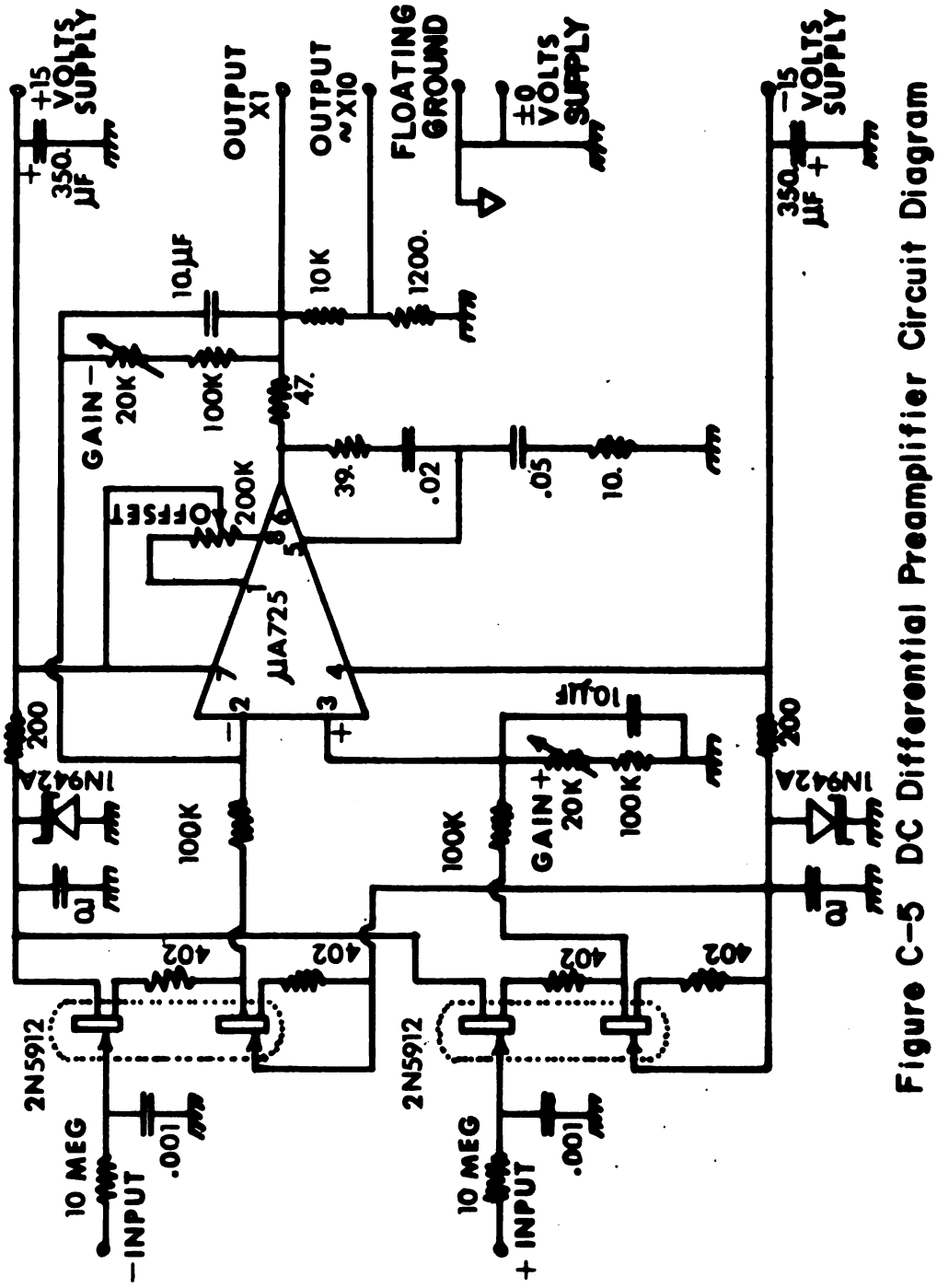


Figure C-5 DC Differential Preamplifier Circuit Diagram

voltages due possibly to inequal contact resistances. Usually, the voltage midway along the drop across the current supply was approximately the same as that found at the sample surface near the center of the probe array.

Several features of the differential preamplifier require explanation. The device used to achieve differential to single-ended conversion was a Fairchild-Semiconductor μA725 amplifier-microcircuit with high stability. Adjustable feedback[26-28] was used to set gain to 1 ± 0.1% with common-mode rejection greater than -80 decibels. Choice of unity-gain resulted from several trial measurements to determine the size of voltages to be monitored. Risetime of the amplifier was set to about one second to reject noise and 60 Hz signals. High input resistance was obtained by addition of temperature-compensated field-effect-transistor voltage followers at the inputs of the feedback amplifier. Protection against high transients was provided by RC networks in the input leads.

Care was taken in the design of the differential preamplifier to assure maximum thermal stability. The microcircuit was a premium type and input FET's were matched pairs. The dc power supply for this amplifier was a balanced and stabilized commercially-available system. Special, highly-stable or precision components were used where appropriate. The output voltage offset could be nulled and was quite stable. A useful range from less than 1 mV to greater than 10 V, the maximum output of the microcircuit amplifier, was available.

A commercially-available preamplifier could not be selected as during early stages of design of the conductivity-measurement system characteristics required for the amplifier were not firmly established.

Properties characteristic to differential amplifiers[29-32] such as gain, linearity, common-mode rejection, input resistance, dc stability, etc. were measured for the developed amplifier and found satisfactory. Any of several commercially-available data-acquisition systems would have been suitable; possibly the conductivity-measurement system could have been improved through application of one of them.

Data was recorded with a Bryans Model 22000 X-Y Auto Plotter. Voltage measurements were recorded on the Y-axis over five or more orders of magnitude by range-switching sensitivity of the plotter. Accuracy and linearity of the voltage-measurement system were established using a Hewlett-Packard 3450A digital multimeter for calibration. Also, a panel digital voltmeter (Model 4304, API Instruments, Chesterland, Ohio), was used to continously monitor the output of the preamplifier.

Temperature of the sample was measured[33,34] using a specially calibrated copper-constantan thermocouple.[35,36] A reference thermocouple was maintained at 0 °C by means of a water-ice bath. The difference between sample and reference-thermocouple voltages was recorded directly on the X-axis at the X-Y plotter. Also, a galvanometer (Scalamp Model, Ealing Corp., Cambridge, Mass.) was available to continuously monitor temperatures. The sample thermocouple was placed adjacent to the sample during conductivity measurements, and prior to use was calibrated[36-38] against several standard-melting-point references.* A temperature versus thermocouple-voltage curve plotted by this process is shown in Figure C-6. A General-Electric Mark-I timesharing computer program, POLFIT***,[39] was used to generate

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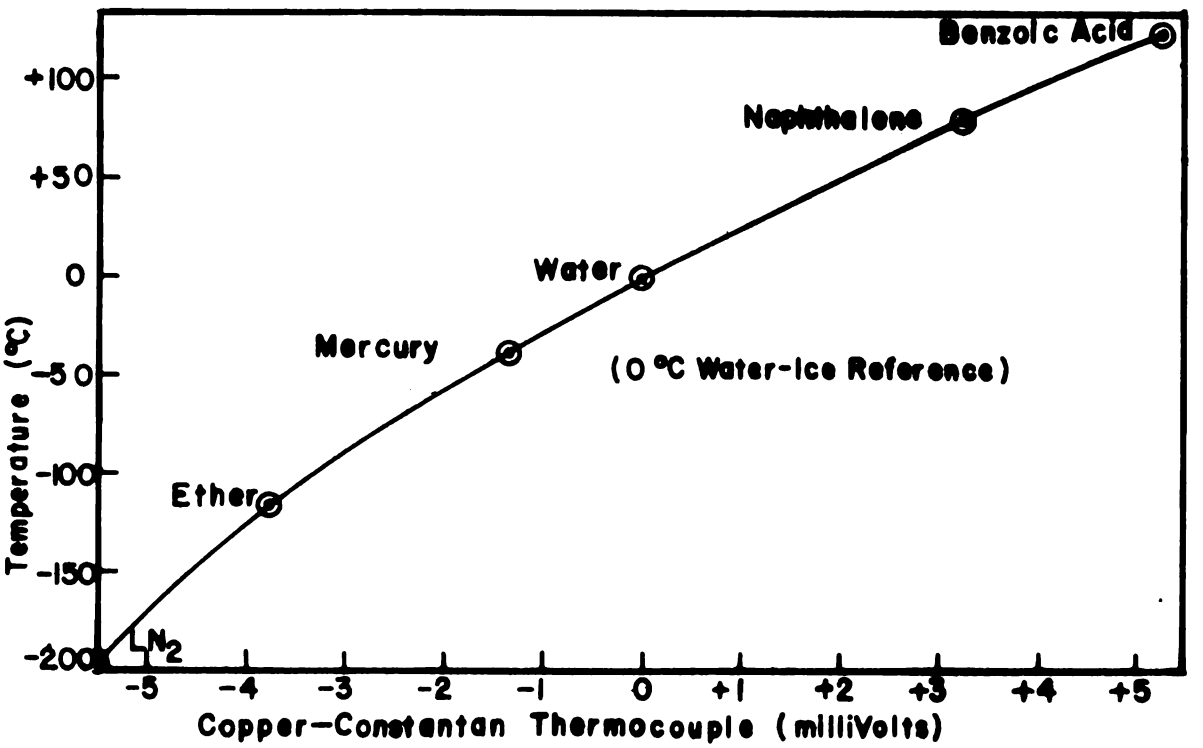
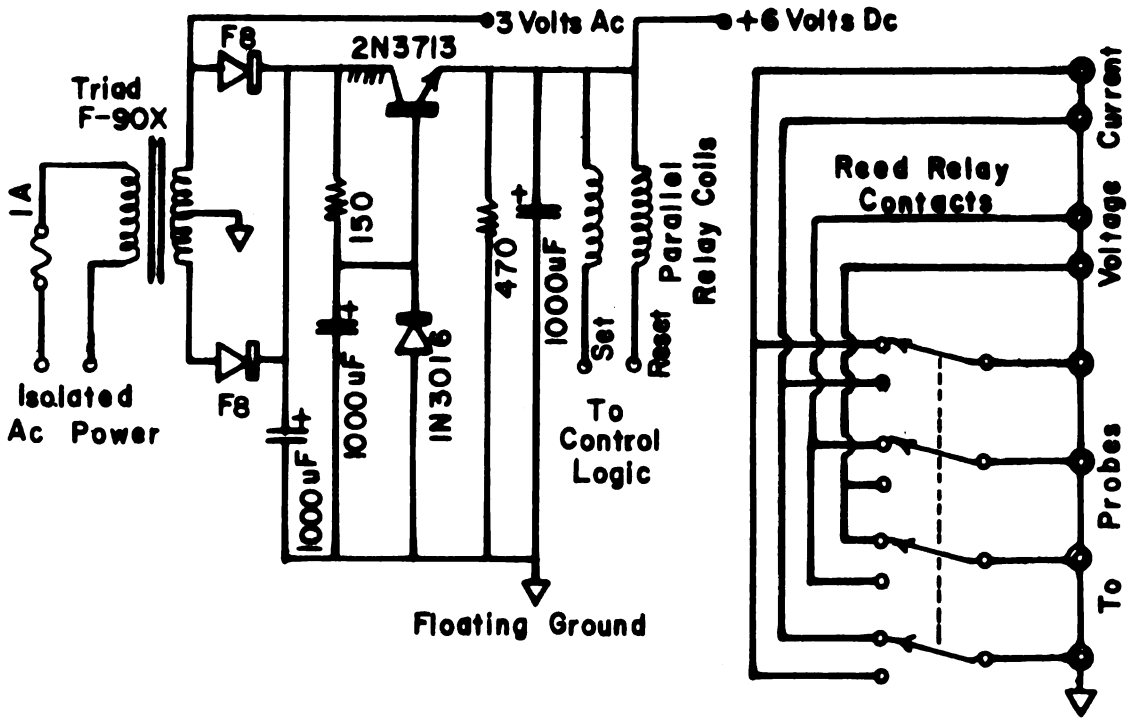
* ThermMetric Standards, T-420 etc.; Fisher Chemical Company.



Thermocouple Calibration
Figure C-6



Probe-Reversing System
Figure C-7

a polynomial equation fitting the data in a least-squares sense:

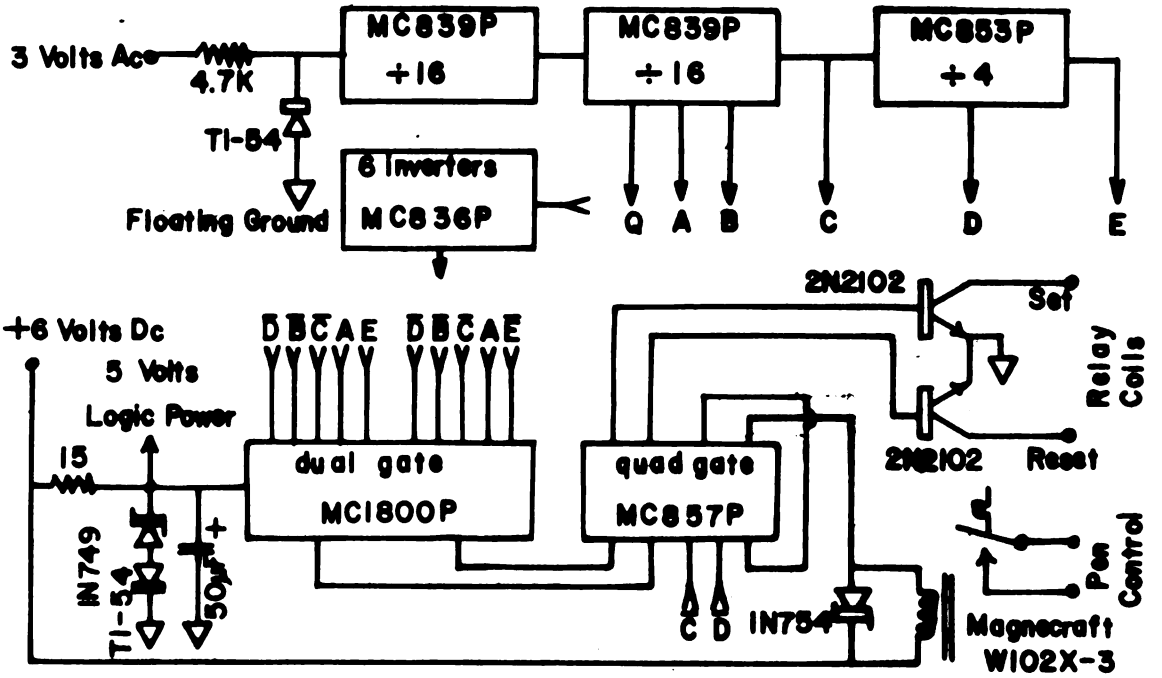
$$T[°K] = 273. + 28.4 \times Vt - 0.607 \times Vt^2 - 0.176 \times Vt^3 - 0.0166 \times Vt^4 + 0.00696 \times Vt^5$$

where Vt was the thermocouple millivoltage. This equation was used instead of the curve to determine temperature from recorded data.

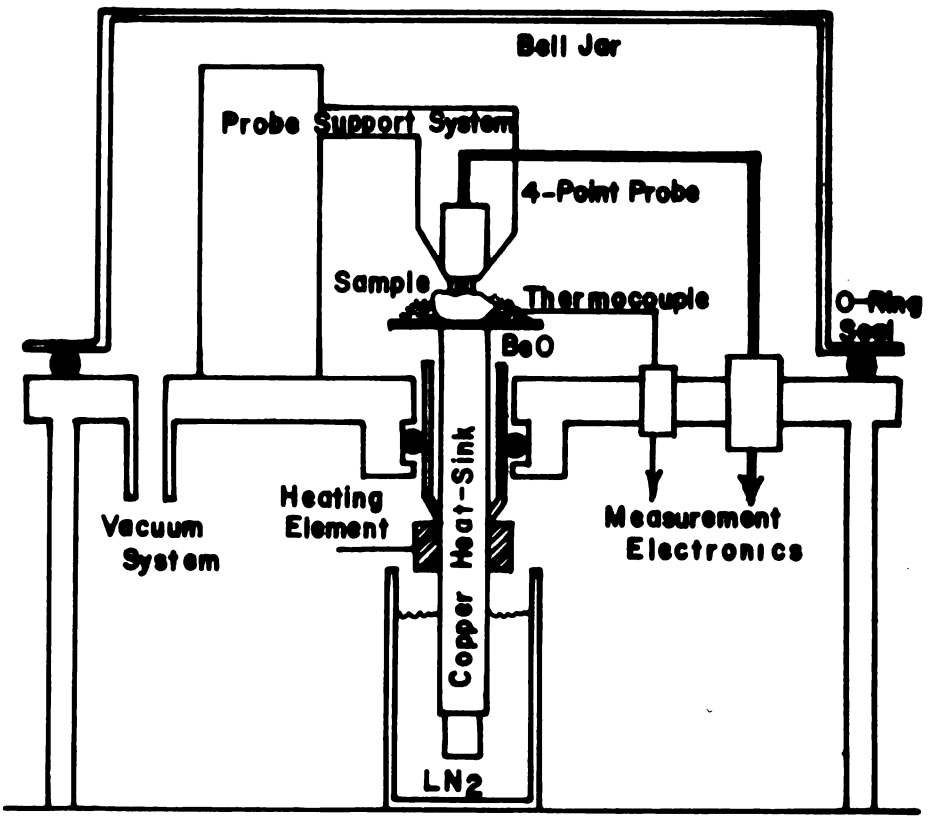
Several additions were made to the simple conductivity measurement system described previously. A system for periodically reversing the direction of test-current flow[3,9,10,40] (and voltage measurement) was added to average sources of error such as unbalanced thermoelectric voltages generated at probe contacts. Four Magnecraft 103LMPCX9 Magnetic Latching-Reed Relays[41-43] were modified by removal of cases and terminal strips to reduce leakage currents, and used as periodic-reversing switches. Circuit diagrams of the switching system and associated power supply are shown in Figure C-7.

A function sequence controller was added to complete the electronic system. The controller provided automatic periodic operation of the reversing switch described earlier, and automatic lifting of the X-Y plotter pen during switching operations. A schematic diagram of the control system is shown in Figure C-8. Logical operations performed here require no comment except to note that the pen was lifted about one-second prior to switching and was returned to operation three-seconds following switching (to prevent recording of switching transients). A complete period of operation required approximately seventeen seconds.

The common reference for the differential preamplifier (and other subsystems) was returned to a mid-voltage point at the current source. This necessitated isolated power supplies for the subsystems.



Function Sequence Controller
Figure C-8



Sample Holder & Temperature Control System
Figure C-9

An ultra-shielded power-line isolation transformer[16,24,44,45] (United Transformer Company Model HIT-15, 150-Watt) was used to supply the preamplifier power supply (Model 2Q15-100PC, Elasco Inc., Bloomfield, Connecticut), the six-volt relay-power supply, the digital panel meter, and the X-Y plotter. The secondary-winding box-shield was connected to the floating-ground system. Better operation was noted when the floating-ground system was allowed to remain isolated from earth ground. This probably reduced small unbalanced leakage currents to earth ground existing in the isolated current source and all shielding systems.

Part 4 -- Sample-Temperature Control

A simple technique was chosen to control temperature of samples. Early experiments indicated need to cover samples with dry gas to prevent condensation of atmospheric water vapor during low-temperature measurements. Accordingly, the four-point probe head and samples were enclosed by a bell jar which could be evacuated and refilled with dry nitrogen. Sample temperature was managed by remote control. Many systems have been developed for temperature control.[46,47,48] Three systems were considered for this application: thermoelectric modules, heat-sink conduction, and cold-gas-flow cooling of an electrically-heated sample-holding stage.

The thermoelectric technique[49] was tried with limited success. Materials-Electronic-Products Corporation Model-CP7-17-10 and Cambridge-Thermionic Corporation Model-801-3958-01 ceramic-insulated thermoelectric modules were used both separately and in cascade. A water-cooled heat-sink was used to establish the temperature of the bottom surface of the modules at about 10 °C. By changing the direction and magnitude of current flowing through the modules, the upper surface

could be maintained in the range from -50 °C. to +120 °C. with good stability. Unfortunately, early experiments indicated a need for substantially-lower sample temperatures. Attempts to lower temperatures further by the thermoelectric technique failed primarily due to a decrease in heat-pumping efficiency of the modules at low temperatures. It was noted that a minimum pressure in the bell jar of about 100 torr was required to ensure good thermal conductivity at the sample, module, and heat-sink interfaces.

As seen in Figure C-9, the heat-sink-conduction technique was finally adopted. A copper rod was used as a stage to establish sample temperature; an electrically-heated element was attached. The bottom end of the rod could be immersed in liquid nitrogen. The high thermal-conductivity copper rod was insulated from the bell-jar baseplate by means of a stainless-steel sleeve brazed to the rod, and by means of an O-ring vacuum coupling. Samples were electrically insulated from the top of the rod by means of Thermalloy Company Type-B-1000-63 beryllium-oxide mounting plates. Wakefield-Engineering thermal compound was used to affix the plates to the rod in a removable fashion. Lumps of thermal compound were used to hold samples in place upon the mounting plates. Samples could be cooled to slightly lower than -150 °C. in this manner. Thermal losses due to rod-mounting technique, and assorted interfacial thermal drops seemed to prohibit lower-temperature operation.

Another system was considered for control of temperature of a barrel-like sample stage by means of electrical-heating and flow of evaporating liquid nitrogen. Such a system could easily be directed by a simple on-off controller to establish the value and rate of change

of temperature to any reasonable value. The heat-sink conduction technique operated quite satisfactorily, so effort required to implement the gas-flow-and-heater method was not expended.

Electrical connection to the probe head was made through the bell-jar baseplate by means of Amphonel UG-254A/U and UG-909/U type BNC bulkhead connectors and RG-59/U coaxial cable. Use of double-shielded and guarded coaxial interconnecting cables was considered; fortunately need for such measures was not indicated from tests of the system.

Part 5 -- System Operation and Data Analysis

The previously described system for four-point probe conductivity measurements was operated as follows. A large (compared to the probe spacing of 25 mils) piece of semiconducting material was fixed to a mounting plate and placed atop the copper rod. Temperature was lowered by evaporation of liquid nitrogen at the lower end of the copper heat-sink rod. Suitable graph paper was put on the X-Y plotter. With sensitivities set properly, the heat-sink was allowed to warm while constant current was maintained through the sample (sometimes manually). Accelerated warm-up and maintenance of elevated temperatures was accomplished with the electrical heater. A single run begun in this fashion required several hours for completion.

Data was gathered in the form shown in Figure C-10. Several features should be noted. The voltage drop, and hence electrical conductivity, appeared exponentially dependent on temperature. Data was gathered over about five orders of magnitude of voltage by range-switching Y-axis plotter sensitivity. At higher temperatures, and higher conductivities, the voltage drop was small and subject to interference by thermoelectric effects and noise. These effects were

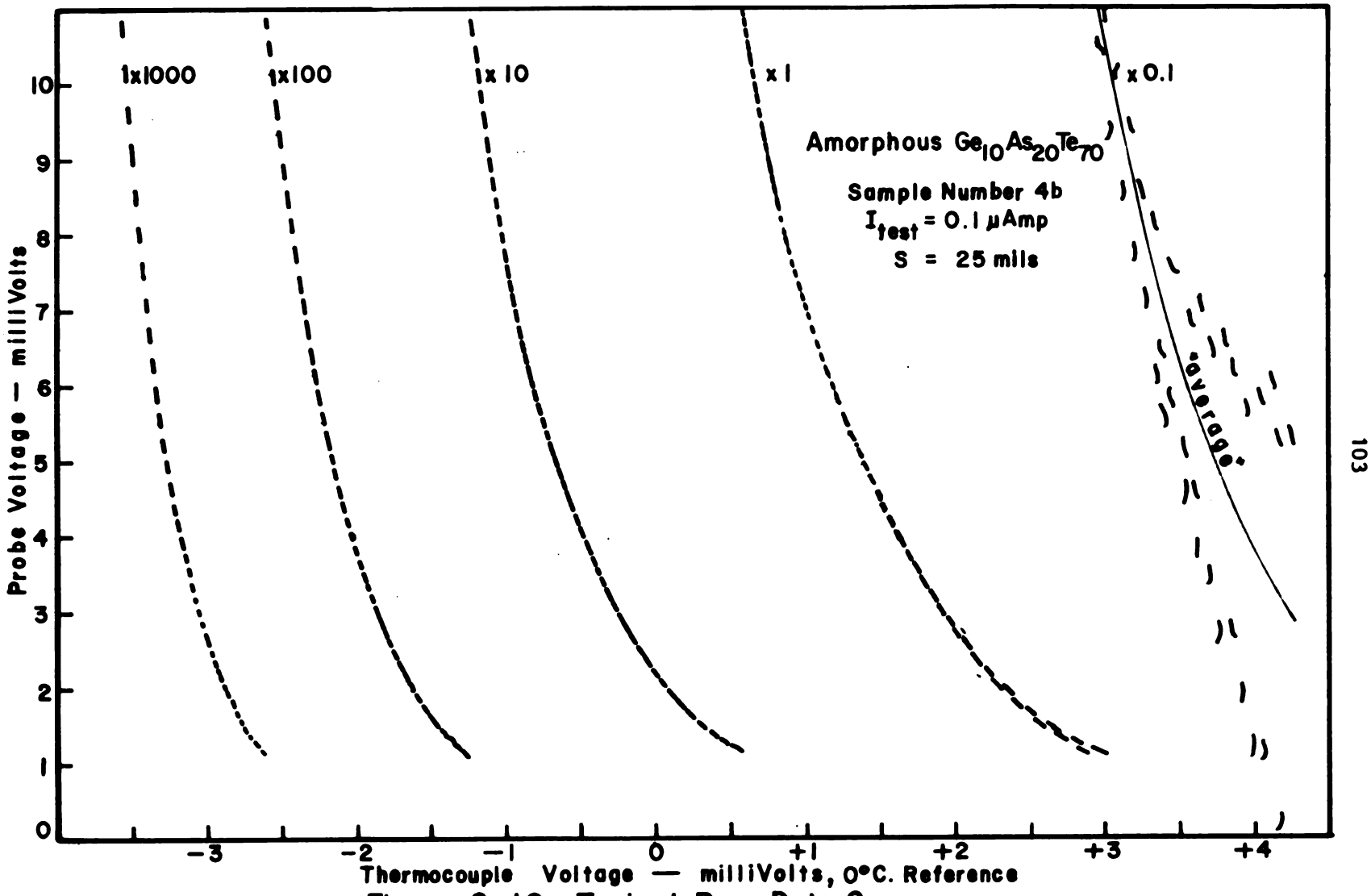


Figure C-10 Typical Raw-Data Curve

observed by automatic periodic reversal of sample-current direction as described earlier.

Data interpretation required many difficult calculations so a computer program was developed to convert information tabulated from the curves to a more useful table of conductivity versus temperature. This Fortran computer program, illustrated in Table C-1 , can be run on the General-Electric Mark II computer timesharing system, and produces output of the form shown in Table C-2 . Data was tabulated from curves by hand, but possibility exists for automatic digital-data acquisition in a form which can be fed directly to a computer. Logarithm of conductivity, inverse Kelvin temperature, and activation energy corresponding to exponential temperature dependence were also determined and tabulated.

```
10 DIMENSION COND(50),CONDL(50),CONDLD(50),TK(50),TKI(50)
11 DIMENSION A(50),V(50)
12 FILENAME IN,OUT
20 PRINT," INFILE,OUTFILE,TO"; INPUT,IN,OUT,TO
30 XK=1.38044E-23;Q=1.60206E-19;PI=3.14159;XLN2=.693147
40 LINE=0; LZERO=0; IERR=0; TKIO=1./TO; NORDER=9
50 READ(IN,1) LL,S,XI,VOFF,THIK; 1 FORMAT(V)
60 10 READ(IN,1,END=15) LL,TCMV,VV
70 LINE=LINE+1; V(LINE)=VOLT(VV,VOFF)
80 TK(LINE)=273. + 28.45*TCMV - .6074*TCMV*TCMV
81 & - .1757*TCMV*TCMV*TCMV - .01657*TCMV*TCMV*TCMV*TCMV
82 & + .006961*TCMV*TCMV*TCMV*TCMV*TCMV
90 IF(10.*THIK.LT.S) GO TO 12
92 COND(LINE)=.5*XI/(PI*S*V(LINE)); GO TO 10
100 12 COND(LINE)=XLN2*XI/(PI*THIK*V(LINE)); GO TO 10
110 15 PRINT," NUMBER OF DATA POINTS: ",LINE; PRINT," "
120 DO 20 I=1,LINE; LN=LINE+1-I; TKI(I)=1./TK(LN)
150 20 CONDL(I)=ALOG(COND(LN))
170 LINEL=LINE-1; DO 30 J=2,LINEL
180 30 CONDLD(J)=-((CONDL(J)-CONDL(J-1))/(TKI(J)-TKI(J-1))
181     & + (CONDL(J+1)-CONDL(J))/(TKI(J+1)-TKI(J))
182 & + (CONDL(J+1)-CONDL(J-1))/(TKI(J+1)-TKI(J-1))
183     &)*XK/(Q*3.)
185 CONDLD(1)=CONDLD(2); CONDLD(LINE)=CONDLD(LINE-1)
190 DO 60 J=1,LINE
200 60 A(J)=EXP( CONDL(J)+CONDLD(J)*TKI(J)*Q/XK )
220 ETO=-FDRVUL(TKIO,TKI,CONDL,LINE,NORDER)*XK/Q
230 AA=TNT1(TKIO,LINE,TKI,A,NORDER,IERR)
240 PRINT," COND=A*EXP( -E*Q/(K*T) ) @ ",TO," KELVIN"
241 PRINT," E = ",ETO," ELECTRON-VOLTS"
242 PRINT," A = ",AA ," 1/(OHM-CENTIMETERS)"
250 WRITE(OUT,4) LZERO,IN
251  4 FORMAT(I1,7X,"COND",6X,"T",3X,"LOG(COND)"
252     &,4X,"1/T",6X,"E",6X,A8)
260 DO 40 K=1,9; KK=LINE+1-K; CL=0.4342945*CONDL(KK)
280 40 WRITE(OUT,2) K,COND(K),TK(K),CL,TKI(KK),CONDLD(KK)
290  2 FORMAT(I1," ",E12.3,F7.1,F8.2,F10.6,F7.3)
300 DO 50 K=10,LINE; KK=LINE+1-K; CL=0.4342945*CONDL(KK)
320 50 WRITE(OUT,3) K,COND(K),TK(K),CL,TKI(KK),CONDLD(KK)
330  3 FORMAT(I2,E12.3,F7.1,F8.2,F10.6,F7.3)
340 PRINT," LIST FILE: ",OUT,"FOR MORE DATA OUTPUT"
350 PRINT," "; 999 STOP; END
400 FUNCTION VOLT(VV,VOFF); VV=VV-VOFF
410 IF(VV.LT.0.0012)GO TO 100; IF(VV.LT.1.2)GO TO 110
420 VOLT=(VV+.03)/1.003; RETURN
430 100 VOLT=VV/1.01; RETURN
440 110 VOLT=VV/1.007; RETURN
450 END
```

Table C-1 Computer Program DATA

0	CØND	T	LØG(CØND)	1/T	E	IN4B
1	0.180E-07	160.4	-7.74	0.006235	0.137	
2	0.214E-07	163.9	-7.67	0.006101	0.137	
3	0.243E-07	165.7	-7.61	0.006037	0.156	
4	0.269E-07	167.4	-7.57	0.005975	0.169	
5	0.309E-07	169.1	-7.51	0.005914	0.204	
6	0.410E-07	172.5	-7.39	0.005799	0.207	
7	0.531E-07	175.8	-7.27	0.005689	0.200	
8	0.755E-07	180.7	-7.12	0.005535	0.193	
9	0.103E-06	185.5	-6.99	0.005391	0.208	
10	0.164E-06	191.8	-6.78	0.005214	0.215	
11	0.199E-06	194.9	-6.70	0.005131	0.244	
12	0.229E-06	196.4	-6.64	0.005091	0.242	
13	0.274E-06	199.5	-6.56	0.005013	0.193	
14	0.324E-06	202.5	-6.49	0.004937	0.211	
15	0.394E-06	205.6	-6.40	0.004864	0.218	
16	0.505E-06	210.1	-6.30	0.004760	0.220	
17	0.664E-06	214.6	-6.18	0.004660	0.236	
18	0.934E-06	220.5	-6.03	0.004534	0.238	
19	0.120E-05	225.0	-5.92	0.004445	0.249	
20	0.168E-05	230.9	-5.77	0.004331	0.226	
21	0.190E-05	233.8	-5.72	0.004277	0.227	
22	0.223E-05	236.8	-5.65	0.004224	0.259	
23	0.260E-05	239.7	-5.59	0.004172	0.260	
24	0.304E-05	242.6	-5.52	0.004121	0.259	
25	0.376E-05	247.0	-5.42	0.004048	0.242	
26	0.484E-05	252.8	-5.31	0.003955	0.232	
27	0.614E-05	258.6	-5.21	0.003866	0.243	
28	0.838E-05	265.9	-5.08	0.003761	0.271	
29	0.109E-04	271.6	-4.96	0.003682	0.288	
30	0.132E-04	275.8	-4.88	0.003625	0.278	
31	0.157E-04	280.1	-4.81	0.003571	0.266	
32	0.194E-04	285.7	-4.71	0.003501	0.296	
33	0.221E-04	288.4	-4.66	0.003467	0.319	
34	0.263E-04	292.6	-4.58	0.003418	0.295	
35	0.323E-04	298.0	-4.49	0.003356	0.272	
36	0.420E-04	305.9	-4.38	0.003269	0.282	
37	0.560E-04	313.7	-4.25	0.003188	0.315	
38	0.740E-04	321.2	-4.13	0.003114	0.349	
39	0.109E-03	330.7	-3.96	0.003023	0.403	
40	0.157E-03	338.7	-3.80	0.002952	0.368	
41	0.190E-03	345.3	-3.72	0.002896	0.376	
42	0.220E-03	348.5	-3.66	0.002870	0.460	
43	0.251E-03	351.6	-3.60	0.002844	0.461	
44	0.301E-03	355.7	-3.52	0.002811	0.490	
45	0.378E-03	360.8	-3.42	0.002772	0.495	
46	0.469E-03	365.8	-3.33	0.002734	0.508	
47	0.666E-03	373.7	-3.18	0.002676	0.508	

Table C-2 Output from DATA Program

APPENDIX D

REVERSIBLE CONDUCTIVITY SWITCHING

Part 1 -- Historical Introduction

Knowledge of conductivity-switching effects has existed for more than ten years. Early published reports[1-3] of switching at point contacts to amorphous chalcogenides were available in 1962. Much of the early work was done on glasses developed primarily for encapsulation of crystalline-semiconductor devices, diodes and transistors.[4] Recognition of the utility of switching effects led to preliminary investigations.[5,6] Apparently, instability of early switching devices prevented immediate development of the phenomena; continued development and study was not done until recently by these early investigators.[7,8]

An independent investigator, S. R. Ovshinsky* discovered useful switching phenomena in many materials, and in the early 1960's began manufacture of relatively-stable devices utilizing the effect.[9-11] Publication of subsequent research into reversible switching for disordered materials[12] generated considerable excitement in research, industrial, and business fields.[13-21] Many excellent surveys of work on these devices (referred to by the manufacturer as Ovonic switches) have been published.[22-26]

Part 2 -- The Switching Phenomena

Reversible conductivity switching has been observed extensively since early reports.[27-32] The process occurs when a piece, or film, of material exhibiting the effect is placed between two electrodes and

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* Energy Conversion Devices, Inc., Troy, Michigan, founded by S. R. Ovshinsky, has pioneered research on amorphous-semiconductor devices.

a suitably-high voltage is applied. Below some threshold electric-field intensity, typically about 10^4 volts/cm, most materials exhibit low conductivity, less than about 10^{-5} mhos/cm. However, as the applied electric field exceeds the threshold value, the glassy material "switches" to a highly-conductive condition, remaining in this state until the electric field is reduced nearly to zero. Threshold switching can often be repeated indefinitely without degradation of switching material or electrodes.

Switching occurs as a highly-conductive filament-like channel is grown from the positive electrode towards the negative electrode.[31] A short delay, about one microsecond, occurs before switching if the electric field is applied abruptly. After the short delay, switching takes place very rapidly, in less than 0.25 nanoseconds. Apparently the device remains in a low-conductance condition until a highly-conductive filamentary channel is completely formed between electrodes.

Certain glasses remain highly conductive after switching, even if the applied electric field is removed, provided the device current was allowed to reach a high-enough value previously. This memory switching process seems to be associated with a modification or change of state for material forming the filament.[32] For some glasses, the low-conductance condition can be regained by passing a brief, high-current pulse through the device. Memory switching also appears to be indefinitely repeatable for some materials.

While stable, repeatable switching at relatively-low applied fields occurs primarily in amorphous chalcogenide glasses, switching has been demonstrated for many materials.[20,33] Threshold switching and memory switching have been reported for amorphous elemental

semiconductors,[34-39] for transition-metal oxide semiconducting glasses,[40-44] for many metal-oxide films,[11] and for some polymers.[45,46] Practically any thin insulating film can be switched[11,20] a few times.

The only commercially-available switching device employing threshold and memory-switching effects, the Ovonic threshold switch (Energy Conversion Devices, Inc.), is fabricated in thin-film form. Voltage is applied to electrodes on either side of a thin (about one μmeter in thickness) film of amorphous chalcogenide glass, basically a Ge-Si-As-Te composition. A highly-stable, radiation-resistant device results if the area of contact at the electrodes is restricted somewhat to assure that the filament always is formed at the same location. Relatively-low switching voltages, about ten volts typically, are required. The threshold switching voltage is sensitive to temperature,[47,48] about 1% per degree Celsius. Characteristics of similar devices and materials showing switching properties are generally available in literature cited in this chapter.[49-68]

Part 3 -- Theory of Switching

Theory for reversible conductivity switching in amorphous semiconductors is not yet clear. Complete hypotheses for the mechanism of initiation and maintenance of threshold switching have not been reported, though excellent progress in the understanding of conduction processes for disordered materials is being made.* Theory satisfactorily accounting for electric-field history and temperature dependence

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* A discussion of the theories related to electronic conduction in disordered materials, particularly amorphous chalcogenides, can be found in Appendix A as a literature review.

of switching delay has also not been developed. Electrothermal explanations for switching has proved satisfactory for some disordered materials, but this explanation seems not to account for particularly-abrupt switching observed for some other materials. Whatever the cause for initial formation of filamentary-conducting channels between electrodes, plausible explanations for memory behavior have been developed which assume phase transformations in the filament due to dissipated power.

Some amorphous materials, notably boron, vanadium oxide, and several chalcogenides, show negative differential conductance[67] on application of suitably-high electric fields. This effect, possibly due to self heating, can lead to constriction of current into a relatively-small filament[68,69] between electrodes. Filament formation, observed for many materials,[70-73] is prominent in amorphous-semiconductor switching devices. Phase transformation or alteration of material properties within the filament is suggested. Perhaps negative differential admittance can account for apparent negative capacitance observed for amorphous chalcogenide glasses at high fields short of switching intensities.[74]

Memory switching has been thoroughly examined. Determination of composition of conducting filaments has been done using differential thermal analysis,[95,96,100,103] electron-microprobe analysis,[32] and x-ray diffraction analysis.[97] Study of bulk amorphous semiconductors has generally indicated a tendency towards crystallization at temperatures substantially below the melting point. Tellurium crystallites have been identified in crystallized material,[97,99] as reported in Chapter 3 for $Ge_{10}As_{20}Te_{70}$. It is suspected that

filaments are melted and requenched to the glassy state upon application of a short high-current "turn-off" pulse.

Theoretical investigations[75] have showed that electrothermal effects are a probable cause for switching in materials showing a tendency towards differential negative conductance. Examination of such hypotheses has led to reasonably satisfactory explanations[76,77] for time delays[78] and switching,[79,80] in a few cases. Switching voltage has been strongly correlated with thermal properties such as glass-transformation temperature.[101,102] Many excellent discussions of energy-controlled thermal-switching processes have been published.[81-84,104]

Other suggested processes for initiation of switching in disordered materials include anomalous field emission,[85] zener-like tunneling,[86] double injection,[87] and Mott transformation.[88] Sophisticated quantum-theoretically-based suggestions such as a new mobility-gap model for electronic conduction in amorphous semiconductors[89] may lead to satisfactory explanations for initiation of switching.[90,91] Excellent reviews of theory for switching have recently been presented;[92,93] many of these generally discount electrothermal initiation.[90,94]

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