Metal-modified Ge-Se glass films and their potential for nanodipole junctionless photovoltaics

Sakina Junaghadwala

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A Thesis

entitled

Metal-Modified Ge-Se Glass Films and Their Potential for Nanodipole Junctionless Photovoltaics

by

Sakina Junaghadwala

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the Master of Science Degree in Engineering

Dr. Daniel Georgiev, Committee Chair

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The University of Toledo

December 2011
An Abstract of

Metal Modified Ge-Se Glass Films and Their Potential for Nanodipole Junctionless Photovoltaics

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In this project, we studied Bi-Ge-Se and Zn-Ge-Se chalcogenide glass films as potential materials for novel, Junctionless nanodipole photovoltaic (PV) applications. The principle of operation of junctionless nanodipole PV devices is based on the use of nanocrystals, with uncompensated electric dipole moments, which are dispersed in a photoconductive host medium. The electric field of these nanodipoles serves to separate the photogenerated electron-hole pairs and thus generate photocurrent.

Bulk samples of these chalcogenide materials were prepared using a conventional melt quench technique, and thin films were then deposited by a thermal evaporation technique under high vacuum condition from the prepared bulk samples. The thin films were characterized by differential scanning calorimetry (DSC), scanning electron microscopy (SEM), X-Ray diffraction (XRD) and Raman spectroscopy.

Both types of glasses are based on the Ge-Se binary glass system. The as-deposited thin films prepared were amorphous, or glassy, in nature and had chemical compositions that were close to what is considered intermediate-phase Ge-Se glass with additions of small amounts of Bi or Zn. The glass transitions and the crystallization tendency of both the bulk materials and the thin films were studied by DSC. In an effort to induce the formation of a
crystalline, and preferably, a nano-crystalline phase, in the glass, glass samples were annealed at several different temperatures in the vicinity of their measured glass transition temperatures. The results from our XRD and Raman spectroscopy measurements indicated that upon annealing of Bi-Ge-Se films at 210°C, nanocrystals of Bi$_2$Se$_3$ are formed in the Bi-Ge-Se glass. At higher temperatures, c-GeSe and c-GeSe$_2$ formed as well and the glass material crystallizes too much for the purposes of nanodipole PV. The Bi$_2$Se$_3$ crystallites formed by disturbing the Ge-Se and Se chain structure are observed in the Raman spectra of the films. Thus we are confident we were able to obtain Bi$_2$Se$_3$ nanocrystals embedded in the Ge-Se glass matrix.

The results from our electrical measurements and specifically open-circuit voltage ($V_{oc}$) measurements upon illumination, of both as-deposited and annealed Bi-Ge-Se films can be interpreted in terms of the formation of nanodipole composite and this indirectly confirms the structural characterization results.

In the case of Zn-Ge-Se glasses, we have found that partial crystallization was difficult or impossible to induce, and no photovoltage could be measured.

The main result of these initial studies is that chalcogenide-glass-based systems, such as Bi-Ge-Se, provide a combination of material parameters and processing flexibility, which are attractive for the implementation of novel nanodipole PV devices. This work is expected to stimulate further research on the topic and lead to significant findings, and potentially, to the development of new technological solutions.

This thesis consists of two main parts. In the first part, Chapter 3, a detailed literature review is provided on the Bi-Ge-Se and Zn-Ge-Se glass systems, together with several other chalcogenide systems, which would also be of interest to such applications. In the second main part, Chapter 5, we present and discuss our experimental results. In
addition, the thesis has a short introductory chapter, and a chapter that briefly reviews the experimental techniques used. The last chapter gives the conclusions from our work.
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Chapter 1
Introduction

1.1 Structure of Chalcogenide Glasses

Chalcogenide glasses contain one or more chalcogenide elements i.e., sulfur, selenium or tellurium in combination with elements from the group IV\textsuperscript{th}, V\textsuperscript{th} or VII\textsuperscript{th} of the periodic table. The tendency of chalcogenide systems to form glasses, as well as the physical properties of the glasses, is determined by the character of the chemical bond formed between the atoms that make the glass and the composition of the elements. The tendency to form glass is possessed by chalcogenide compounds and alloys with predominantly covalent bonds. In a covalently constructed structural unit of chalcogenide glass, the maximum number of neighbors of an atom is equal to the number of valence bonds the atom can form. A continuous random network (CRN) is considered to be a good description of non-crystalline covalent solids.

Two models namely ‘Chain Crossing Model’ (CCM) and ‘Random Covalent Model’ (RCM) were proposed, that follow the 8-N rule bonding scheme. CCM has been adopted to understand the composition dependent property in a wide range of chalcogenide glasses. [1]

In CCM, heteropolar bonds are favored over the homopolar bonds. For a glass system which is $A_xB_{1-x}$ there is formation of A-B type bond. In an A rich compound, formation of A-B type followed by A-A bonds can be predicted. Similarly for a B rich compound the A-B bond is followed by B-B bond. [1]
The bond energies can be calculated using the following relation proposed by Pauling:

\[
D (A-B) = [D(A-A) \times D(B-B)]^{\frac{1}{2}} + 30(x_A - x_B)^2
\]

Where

- \(x_A\) – electronegativity of atom A
- \(D (A-A)\) – energy of the bond A-A

In CCM the group IV\textsuperscript{th}, V\textsuperscript{th} or VII\textsuperscript{th} of the periodic table which can be either threefold, fourfold or six-fold atoms act as a chain crossing point in the chalcogenide element chains. The bonds which have the highest bond energy are formed first followed by the lesser bond energy.

When any other element is included in the glassy network, the network is disturbed affecting the already existing covalent bonds and the material properties. It has been discussed in several studies that addition of Bi \(\geq 7\%\) to certain chalcogenide glasses changes the carrier type from p to n type. Thus Bi is very unique in this aspect compared to other group V elements P, As or Sb which do not alter the carrier type. It is assumed that the carrier type reversal is due to the formation of Bi\textsubscript{2}C\textsubscript{3} (C=Se, S). The coordination number of Bi is three [2]. Also it is assumed that beyond certain composition the Bi atoms consist of a positive charge.

Addition of Bi to a Bi\textsubscript{x}Ge\textsubscript{20}C\textsubscript{80-x} (C=Se, S) glass system affects the electrical and optical properties of the material. When the Bi content increases beyond \(~8-9\%)\, the DC electrical conductivity decreases drastically, the activation energy (\(\Delta E\)) decreases discontinuously, and the optical gap (\(E_g\)) drops exponentially and then almost remains unchanged beyond 9\% Bi. It is assumed that these changes tend to occur because Bi at 9\% gets positively charged i.e., Bi\textsuperscript{+3} are present. To compensate for these charges negatively
charged defects which are chalcogen-based \( C_1 \) are produced. The \( C^+ \) charges which are normally present due to the law of mass action are suppressed leaving behind the negative charge \( C^- \). These defects are present in concentration and are distributed during the melt quench of the glass formation. Due to these negative charges the Fermi level is unpinned and it shifts towards the conduction band edge [2], bringing about a carrier type reversal from \( p \) to \( n \) type.

### 1.2 The Intermediate Phase and the Related Glass Optimization Approach

By tuning the chemical composition of these multi-element glasses, technologically desired optical and electrical properties can be obtained. Recent progress in glass science has led to the concept of the intermediate phase [3], which is gaining more and more research interest. According to the intermediate phase ideas, network glasses that exhibit a level of self-organization (based on chemical bonding preferences and other), form three distinct phases depending on their connectivity, i.e. chemical composition. Glasses that have relatively low connectivity, namely well below and below an average coordinate number of 2.4 (which represents the so-called stiffness transition in completely random networks [4], [5] are termed floppy or under-coordinated glasses, comprising a floppy phase. An example of such glass would be a very chalcogen-rich composition such as a glass containing 90 % Se. These glasses generally exhibit excess built-in stress, as shown by thermal analysis and other methods, and can relatively easily undergo a transition to a phase separated material that is at least partially crystallized. Secondly, glasses having a coordination number that is well above 2.4, are over-coordinated or stress-rigid, and form a stress-rigid phase. Such glasses exhibit excess stress due to the excess number of chemical bond constrains leading to a fraction of
the bonds being significantly strained to form the glass network. Even though the excess bonding generally makes these materials more rigid, they can, upon introducing some energy (say by heating or applying pressure), undergo crystallization. An example of such glasses is Ge-Se glass, containing more than 30% of Ge. Thirdly, and most importantly, glasses with a somewhat intermediate connectivity, with average coordination number that is typically (but not necessarily) in the vicinity of 2.4 form a phase, or a compositional range that corresponds to optimally coordinated glasses, which are very difficult or impossible to crystallize, and have been shown to contain a minimum amount of stress. This represents the intermediate phase (IP), and besides resistance to crystallization, IP glasses are expected to have other properties that are also optimized within a given glass system, as recent published work has indicated [6], [7]. The IP ideas are of central importance to this project as the glass compositions we have chosen to work with, are close to the IP in Ge-Se glasses, which was expected to facilitate the dispersed nano-crystallization process as explained later in this thesis.

Chalcogenide glasses, with carefully tailored properties, can be used in various semiconductor devices. Traditionally most semiconductor devices utilize p-n junctions. These junctions are formed between a p-type and n-type material, either of the same material (homojunction) or different material (heterojunction). Conventional photovoltaic devices consist of a p-n junction, in which the depletion region develops a built-in electric field. When a photon with energy greater than that of the band gap passes through the solar cell, it gets absorbed and an electronic transition takes place forming an electron-hole pair. Before the electron-hole can recombine, they are separated by the built-in electric field, which then causes one quantum charge to flow through the circuit. Thus photocurrent is produced. To increase the efficiency of the solar cells different materials and fabrication techniques are
being investigated. Improving the efficiency and the cost of solar cells continues to be a major goal in this technology development.

1.3 Chalcogenide glasses for junctionless photovoltaic devices.

To overcome the complexities involved in the fabrication of p-n junctions, especially in otherwise very promising materials such as chalcogenides, recently the junctionless photovoltaic device has been proposed. In this device, nanoparticles, possessing an uncompensated electric dipole, are embedded in a polymer or glass host material, or even in a liquid [8]. The nanoparticles needed can be pyro- or piezo-electric particles, such as wurtzite CdS and CdTe or any others. In Figure 1-1 (a) CdS particles which possess the pyroelectric charge are responsible for the dipole properties where Cd is electrically more positive and S is more negative which is responsible for the polarization surface charge.

![Figure 1-1](image)

Figure 1-1. (a) CdS particles (of arbitrarily chosen cylinder shape) with pyroelectric charges responsible for dipole (p) properties (b) Aligned electric dipoles (solid arrows) and electric field lines (E: dashed arrows) caused by polarization [8]

These CdS particles strongly affect the operation of CdTe/CdS and CuIn(Ga)Se₂/CdS thin films. Properly stabilized nanoparticles which have a wurtzite structure origin have a permanent dipole. Besides wurtzite structures, zincblende ZnSe and CdS also exhibit large dipole moments which are linearly proportional to the sizes, this is an
intrinsic attribute of many non-metal particles with surface localized charge. When these dipoles interact the nanoparticles are aligned. [8]

Based on a similar approach the study of potential chalcogenide glass films for junctionless photovoltaic devices has been carried out. In junctionless nanodipole photovoltaic devices the electric field relies on the aligned nanodipoles, instead of junctions, for the separation of photogenerated carriers. In the implementation envisioned, the active material consists of nanoparticles that possess uncompensated electric dipole moment and are embedded in a photoconductive host. Such photovoltaic (PV) material structures would offer potential benefits in terms of simplicity of fabrication, environmental friendliness, and low cost.

The efficiency of a solar cell depends upon the bandgap of the material. For higher bandgap, the short circuit current is very low and for lower bandgap materials the open circuit voltage is low. The spectrum of sunlight covers a wide range from infrared to ultraviolet, which, for all practical purposes, is about 0.5 eV to 5 eV. When a photon is absorbed in a solar cell, an electron hole pair is generated, this is possible only if the photon has energy which is higher than that. So a material with higher bandgap will absorb less number of photons as compared to that of materials with lower band gap. Thus there is a tradeoff between the high open circuit voltage and low short circuit current for the variation in the band gap. For a solar cell to work with maximum efficiency it is preferred to have a bandgap close to about 1.5 eV. Many chalcogenide glass systems offer optical bandgap energy close to the optimum values needed in PV applications. The idea is to obtain films consisting of a dispersed nanocrystalline phase in a glassy host material that has suitable optical and electrical properties. This approach is based on observations that many nano-
crystals possess uncompensated electric dipole moments due to their imperfect crystallinity and the related chemical bond charge distribution.

The compositions of chalcogenide glass can then be tuned to obtain the desired optical and electrical properties. In this project, we present results from an initial study of the potential of chalcogenide glass films as materials for nanodipole junctionless PV devices. Various types of characterization work on bulk and thin-film Bi-Ge-Se glasses are presented and discussed. The potential of Zn-Ge-Se glasses in such applications is examined as well.
Chapter 2
Literature Review

2.1 The Ge-Se-Bi Glass System

The Ge-Se-Bi glass system is a p-type semiconductor for Bi approximately less than 7%. Beyond 7% Ge-Se-Bi glass system shows a carrier type reversal from p to n type [9]. Including a significant fraction of Bi (several percent or more) in Ge-Se results in the formation of clusters of Bi$_2$Se$_3$ and GeSe$_2$, thus the Ge-Se-Bi glass becomes microscopically phase-separated. The properties of most chalcogenide glasses are composition-dependent. Adding Bi to the Ge-Se system significantly affects the electrical and optical properties of the system. The anomalous behavior of Bi when included in larger quantity has made this material of interest to study. Several properties of the Ge-Se-Bi system have been studied and are reviewed below.

2.1.1 Glass Forming Region and Glass Molecular Structure

In the Ge-Se glass for about 20-30% Ge and 70-80% Se a large glass forming region is obtained. When Bi is included, the crystallization ability of the glass is increased. From Figure 2-1 it is seen that at 20% Ge the maximum amount of Bi that can be added is about 13%. Due to the high crystallization ability of these glasses, beyond 13% of Bi these glasses partially crystallize [9].
Addition of sulfur of selenium reduces the glass formation region. Glass forming region obtained by quenching in water and ice is much greater than that obtained from quenching in air or slow cooling [10].

In a Ge-Se glass, linear chains of Se and corner shared Ge-Se tetrahedron are present for Se rich glass. Addition of Ge at 33% reduces the Se linear chains or Se rings to form tetrahedron bridges of GeSe structure. [11]

![Figure 2-1](image)

Figure 2-1. The glass forming region in the Ge-Bi-Se system (solid line) and Ge-Bi-S system (dashed line). (1) Ge$_{25.5}$Bi$_{11.8}$S$_{62.7}$; (2) Ge$_{32}$Bi$_{16.1}$S$_{51.9}$; (3) Ge$_{18.6}$Bi$_{25.3}$S$_{56.1}$; (4) Ge$_{20.3}$Bi$_{6.9}$S$_{63.2}$; (5) Ge$_{29.2}$Bi$_{13.4}$S$_{57.4}$. [9]

The density of Bi-Ge-Se glassy alloys increases as the Bi content increase [12]. The crystallization ability of the Ge-Se-Bi glass is the highest when the bismuth content is maximum. Bi when included disturbs the Ge-Se glass network, at large Bi content the Ge-Se-Bi glass becomes unstable. When Bi $\geq$ 7% is included, on prolonged annealing the Ge-Se-Bi glass forms small inclusions of Se, Bi$_2$Se$_3$, GeSe [13], the bond energy of Ge-Se is the largest, followed by Bi$_2$Se$_3$ and Se chains. Thus the Se atoms first saturate the valences of Ge completely then saturate the Bi atoms. The Se atoms then form Se chains to satisfy the remaining valence requirements. Therefore Ge-Bi, Ge-Ge and Bi-Bi bonds are not formed.
since their bond energy is lower than that of the Se chains. These bonds give rise to surface dangling bonds during crystallization. These defects decrease the optical band gap [12] and reduce the activation energy. Besides, the formation of Bi₂Se₃ affects the electrical and thermal properties of the system, which have been discussed further.

Figure 2.2 A plot as a function of the Bi concentration at a heating rate of 5K/min [11]

2.1.2 Thermal Analysis Data

DSC for bulk Ge-Se-Bi

The glass transition temperature of the Ge-Se-Bi glass is composition dependent. It increases with the increase of the Bi content [11]. Figure 2-2, obtained from the data in Ref [11] shows the dependence of T_g on the Bi content. The dependence of T_g on Bi composition is due to the mobility of the chains. Whenever there is a restriction in the mobility of these chains there is an increase in the glass transition temperature. Since addition of Bi in Ge-Se gives rise to the Bi₂Se₃ structures there is an increase in the T_g. Formation of c-Bi₂Se₃ is evident from the DSC of the bulk shown in Figure 2-3. The figure shows the DSC of bulk GeₓSe₈₀₋ₓBiₓ, for 3% and beyond at around 320°C c-Bi₂Se₃ is formed. It is seen that as the content of
Bi increases, the crystallization peak at 320°C becomes sharper and simultaneously the glass transition temperature also is seen to have shifted to a higher temperature.

![DSC Total Heat Flow (THF) curves of representative Ge<sub>20</sub>Se<sub>80</sub>-<sub>x</sub>Bi<sub>x</sub> samples, showing the evolution of one glass transition temperature (<i>T</i><sub>g</sub>); curves (a), (b), (c), (d), (e) and (f) correspond to samples with x=1, 2, 3, 5, 9 and 13 respectively. c-Bi2Se<sub>3</sub> percolation at Tc<sub>1</sub> and two crystallization exotherms (Tc<sub>1</sub> and Tc<sub>2</sub>) can be seen at 3 at.% of Bi and above. [15]

**DSC for thin film Ge-Se-Bi**

DSC measurements were carried out for thin films. Thin film samples of 30 nm for Ge<sub>20</sub>Se<sub>80−x</sub>Bi<sub>x</sub> were prepared from glassy bulk material on ultrasonically cleaned glass substrate using electron beam evaporation (Edward E-3606 coating system operated at a base pressure of 6.7x10<sup>-4</sup> Pa). These films were prepared at room temperature. The substrate was coated with NaCl and carbon films. The as-deposited film and the thermally treated films were floated off the substrate by immersing the film in distilled water and then were transferred to Cu microscope grids. DSC measurements were carried out for different compositions, at
x=10, 7.5 and 5. Similar results were obtained for all three compositions. Figure 2-4 shows the DSC thermogram for powdered specimen of Ge-Se-Bi. The DSC obtained from the powdered specimen appears to be quite similar to the DSC of the bulk sample for x=13 in Figure 2-3. In the powdered specimen $T_g=195^\circ C$ and crystallization peaks were observed at 320$^\circ C$ and 370$^\circ C$. At 320$^\circ C$ a polycrystalline phase is observed and a dendritic phase is observed at 370$^\circ C$. For lower Bi content (x= 0 and 2.5) the $T_g$ is lower and there is no crystallization peak [14]. At approximately the same temperatures for x=13 in Figure 2-3 crystallization peaks are observed. The two crystallization peak observed close to 320$^\circ C$ and 370$^\circ C$ correspond to c-Bi$_2$Se$_3$ and c-GeSe$_2$. Since the DSC of the thin film is similar to the bulk with approximately the same composition as well, the peaks observed in the thin film can also be assumed to be due to c-Bi$_2$Se$_3$ and c-GeSe$_2$. Besides, it can also be implied that the thermal properties of the bulk and the thin film do not differ greatly.

![DSC thermogram for Ge$_{20}$Se$_{70}$Bi$_{10}$ powder specimen (heating rate is 10K/min)](image)

Figure 2-4 DSC thermogram for Ge$_{20}$Se$_{70}$Bi$_{10}$ powder specimen (heating rate is 10K/min) [14]
2.1.3 **Electrical Properties**

Conductivity and Carrier Type Reversal

As mentioned above, on addition of Bi in the system c-Bi$_2$Se$_3$ clusters are formed thus the system is “microscopically phase separated”. Clusters of Bi$_2$Se$_3$ are embedded in a GeSe$_2$ backbone. With increasing bismuth concentration, the Bi$_2$Se$_3$ phase percolates in the Ge–Se matrix, with a percolation threshold at $x=3$ [15].

The reversal from the p to n type is due to the c-Bi$_2$Se$_3$ clusters. Addition of Bi also produces positively charged Bi$_3^+$ and Bi$_4^+$. The defects arise due to the rearrangements at the prevalent chain ends which are the D$^+$ and D$^-$ charged dangling bonds [16]. These are point defects in which the normal coordination cannot be satisfied. In the case of Bi$_2$Se$_3$, it is 2 for Se and 3 for Bi, the neutral dangling bonds therefore consist of an unpaired electron. These dangling bonds can be filled by either zero, one or two electrons, thus the total charge is given as D$^+$, D$^0$ and D$^-$ respectively. These charges also cause local lattice distortions due to the change in the electron occupation, this reaction is exothermic ($2D^0 \rightarrow D^+ + D^-$. Thus all defects are either positive or negative. D$^0$ occurs only by excitation [17]. However the defects do not bring about a change in the conduction type. Bi is homogenously distributed forming Bi$_2$Se$_3$ throughout the glass. Since Bi$_2$Se$_3$ are n-type conductor, it is concluded that the transition from p to n type is due to the Bi$_2$Se$_3$ crystals. Increase in Bi brings about a continuous change in the electronic structure of the material which increases the electrical conductivity in sputtered Ge-Se-Bi film. The transition from p to n type is due to shift of the Fermi level. The increase in the conductivity depends on this shift of the Fermi level, but this shift is very small [18]. At about 9% of Bi the carrier type reversal takes place thus the photoconductivity and the conductivity increase by up to twelve orders [16].
DC conductivity

![Figure 2-5. Variation of dc electric conductivity with temperature for film samples of different thickness [19]](image)

The dc conductivity varies with the temperature as seen in Figure 2-5, the relation between the temperature and the conductivity is given by: [14]

\[
\sigma = \sigma_0 \exp \left( - \frac{\Delta E_\sigma}{K_B T} \right)
\]

$\Delta E_\sigma$ - Thermal Activation energy

$\sigma_0$ - Pre-exponential factor

$\sigma_{RT}$ - Room temperature conductivity

Addition of Bi reduces the activation energy of the system thus the conductivity increases. Compared to other elements such as As or Sn when included in the Ge-Se system, the decrease in the activation energy of Ge-Se-Bi is much greater than that of Ge-Se-Sn and Ge-Se-As. This is because the bond energy of Bi-Se is the weakest (205 kJ/mol). Thus the activation energy and the conductivity depend on the chemical bond energies in the systems. [19]
There is a decrease in activation energy for Bi ≥10%. This causes the unpinning of the Fermi level and moves it towards the conduction band which induces the n-type conduction. Bi produces localized states near the conduction band so the electrical transport is due to the hopping of electrons after they are excited in the localized states. When there is no Bi the Fermi level is below the middle of the gap at about 5% of Bi the $E_f$ is shifted towards the middle of the gap but the conduction remains p-type. When Bi is increased up to 10% the Fermi level shifts above the middle of the gap and the conductivity increases abruptly. The conductivity also changes from p to n type. [20]. This is also supported by Figure 2-6 which shows the resistivity measured at 25°C for Ge$_{20}$Bi$_x$Se$_{80-x}$, the resistivity decreases gradually on addition of up to 9% of Bi. Between 9 - 10% of Bi the resistivity drops abruptly by four orders of magnitude beyond 10% it remains almost constant [21].

Figure 2-6. Compositional dependence of resistivity at 25°C, $\rho_{25}$, for Ge$_{20}$Bi$_x$Se$_{80-x}$ glasses: prepared from Ge, Bi2Se3 and Se; ○: prepared from Ge, Bi and Se. [21]
Chalcogenide glasses exhibit the properties for threshold and memory switching. These electrical properties and phenomena are influenced by the structural changes and could be related to the induced thermal transitions. In the chalcogenide glassy systems, glasses exhibiting no exothermic crystallization reaction above the glass transition ($T_g$) appear to be of the threshold switching type and the glasses exhibiting an exothermic crystallization reaction above ($T_g$) show a memory type of switching. Threshold switches are made near the center of the glass-forming region where the glass are stable and show no tendency to crystallize when heated or cooled slowly. [22]

Under high electric field chalcogenide glasses exhibit threshold and memory switching. Memory switching glasses form long chains of Se or Te in the glasses in which atomic arrangement occur easily. These chains contain high electric field which results in large power dissipation. In memory switching glasses, when electric field is applied the glass crystallizes and remains in the low ON state even after the field is removed. [19]

In threshold switches there is cross-linking of chains which causes steric hindrance and structural rearrangement becomes difficult. Thus when electric field is applied the original high resistance OFF is recovered since these materials have a high thermal stability and a large barrier for crystallization. [19]

Samples of Ge$_{20}$Se$_{80-x}$Bi$_x$ glasses were polished to 0.15 mm thickness to measure the I-V characteristic and switching properties. For Bi between 1≤x≤4 there is no switching up to 1100 V. A negative resistance and switching behavior is observed only in glasses with 5≤x≤13. The I-V characteristic and switching behavior is shown in Figure 2-7. From the Figure 2-7 it is seen that initially these glasses demonstrate an ohmic behavior. At threshold voltage ($V_T$) the sample switches from high resistance OFF state to a low resistance ON state. The switching here is not very ideal as many fluctuations are seen compared to other
chalcogenide glasses. The Ge$_{20}$Se$_{80-x}$Bi$_x$ behave as threshold switched when 5≤x≤11, for these compositions when the current is lowered in the ON state the glasses revert back to the high resistance OFF state. These samples can be switched multiple times with a ± 5% switching voltage each time. The holding voltage $V_{th}$ at which the samples revert back is less than the threshold voltage [15]

![Figure 2-7. I-V Characteristic and switching behavior of Bi rich Ge$_{20}$Se$_{80-x}$Bi$_x$ (5<x<13) glasses samples polished to 0.15 mm thickness. [15](5<x<13)](image)

There are several factors that affect the threshold voltage. One of which is the thickness of the film. The $V_{th}$ value increases linearly with the thickness of the film as shown in the Figure 2-8 for different compositions, in the range considered i.e., from 100-750 nm. [23]

The threshold voltage also varies with the change in the temperature. There is a decrease of $V_{th}$ exponentially as the temperature increases. The temperature of the semiconductor is raised due to joule heating. Since the conduction type of the material is of
an activated type, the conductivity of a sample will increase when heated. This allows more
current to flow through the heated regions and allow more joule heating which results in
further joule heating. Ultimately the temperature rise will become sufficient to intimate
thermal breakdown. [23]

![Figure 2-8. Thickness dependence of the threshold voltage $V_{th}$.][23]

Steady state breakdown occurs when the amount of heat generated by joule heating
cannot be removed by thermal conduction. [19]

$$\Delta T_{breakdown} = \frac{T^2 K_B}{\Delta E_\sigma}$$

2.1.4 Optical Properties

If there is no Bi the optical band gap of the glass (see Figure 2-9) is about 2 eV for
the Ge$_{20}$Se$_{80-x}$Bi$_x$. Addition of Bi reduces the bandgap to 1.2 eV for n-type material [14] i.e., at
$x \approx 9\%$. The bandgap decreases by approximately 20-40% when about 2.5% Bi n included.
Further increase in the Bi content causes very small change in the bandgap. After $7.5\%$ the
bandgap remains unchanged. [21]
Absorption in the Ge$_{20}$Se$_{80-x}$Bi$_x$ thin films (0<$x<$10 at %) is due to indirect transitions. The optical gap $E_o$ was found to decrease with increasing Bi content as seen in Figure 2-9. This trend was analyzed by using the chemical bonds approach. Addition of Bi leads to the formation of Bi-Se at the cost of Se-Se bonds. The number of the Se-Bi bonds increases with the increasing Bi content [14].

![Graph showing the dependence of the optical gap on Bi content](image)

Figure 2-9 The dependence of the optical gap on Bi content (in at %) for Ge$_{20}$Se$_{80-x}$Bi$_x$ thin films [14]

Electronic transition in most amorphous semiconductor material gives rise to optical absorption edge which is described by an s-shaped curve. The high absorption is due to the band to band transitions which are followed by the exponential Urbach tail and then a weak absorption tail. As we have discussed earlier addition of Bi gives rise to defects, these defects are responsible for these weak absorption edge. The exponential region is due to the randomness in the amorphous material. For a 100 nm Ge$_{20}$Bi$_{x}$Se$_{80-x}$ thin film optical measurements were taken at room temperature. Thus there is a relation between the bond strength and energy gap of the system. Increase of Bi from 0-25% decreases the optical
bandgap from 2.62 to 1.24 eV. Increase of Bi content also increases the density of state in the valence band. Localized states also created in the band gap. [20]

Absorption Coefficient

The absorption co-efficient for different composition of the Ge<sub>20</sub>Se<sub>80-x</sub>Bi<sub>x</sub> glass is shown in Figure 2-10, it is seen that on the addition of 2.5% Bi the absorption co-efficient shifts to a much lower energies. Between 2.5-7.5% there is minimal change. After 7.5% the absorption edge remains unchanged. [21]

Refractive Index

The refractive index (n) can be calculated by:

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

k- Extinction co-efficient

R- Reflectance
At all the different compositions of the film the value of ‘n’ decreases as the photon energy increases. Figure 2-11 shows the refractive index for varying Bi composition in Ge$_{20}$Se$_{80-x}$Bi$_x$ glass. Close to around 6 eV the refractive index appears to increase again, but as the Bi content is increased it seems that the refractive index tends to remain unchanged at higher Bi content. [24]

2.1.5 **Deposition of Thin Films of Bi-Ge-Se Glasses**

Some methods for the deposition of Ge-Se-Bi thin films are given below:

1. The bulk materials used in the thin film deposition were prepared by the melt quenching technique. The Ge, Se, Bi mixture which is about 99.99% pure is taken in an ampoule sealed under $10^{-3}$ Torr at 1200°C for 16 hrs in an oscillatory furnace. This mixture is then quenched in ice cold water. The alloys so obtained were used for thermal evaporation of thin films using the high vacuum coating unit and the technique used for deposition was flash evaporation. The films were deposited on ultrasonically cleaned glass substrate.

Thin films of Ge$_{20}$Se$_{80-x}$Bi$_x$ (x = 0, 4, 6, 8, 10, 12) were bombarded using a 75 MeV Ni

![Figure 2-11 Variation of refractive index 'n' with the incident photon energy for different compositions of the Ge$_{20}$Se$_{80-x}$Bi$_x$ [24]](image)
ion beam at room temperature at the beam current was kept at 5 nA and the fluency was kept at $5 \times 10^{13}$ ions/cm$^2$ for $x = 0, 4, 8, 10, 12$ thin films while it was varied from $5 \times 10^{12}$ ions/cm$^2$ to $10^{14}$ ions/cm$^2$ for the Ge$_{20}$Se$_{74}$Bi$_6$ thin film. The effective beam size, using a defocusing technique, was kept at 1cm$\times$1cm. The transmittance and reflectivity patterns for optical measurements in the spectral range 360 - 840 nm were obtained for normal incidence on the film surface using a Hitachi double-monochromator spectrophotometer model 330. [24]

2. Thin films of the samples were prepared from bulk samples by a thermal evaporation technique under vacuum deposited on highly cleaned glass substrates. The substrates were fixed onto a rotatable holder to obtain homogeneous deposited films at a distance of 0.25 m above the evaporator. The thickness of film samples was measured during deposition using a thickness monitor (Edwards, FTM) and confirmed after deposition by Tolansky’s interferometric method. [19]

3. Thin films of amorphous chalcogenide alloys with compositions Ge$_{25}$Se$_{75-x}$Bi$_x$, where $x = 0-17.4$ were prepared by sputtering in an Ar atmosphere at a partial pressure of $5 \times 10^{-3}$ Torr. The base pressure was about $2 \times 10^{-6}$ Torr. Prior to deposition the Pyrex chamber was baked out with IR illumination for about 4-5 h. Three different targets were used: Ge$_{25}$Se$_{75}$, Ge$_{20}$Se$_{70}$Bi$_{10}$ and Ge$_{20}$Se$_{67}$Bi$_{13}$. The desired amounts of Bi were placed on the surface of the first target in order to obtain the concentrations $x = 0-10$ the films were deposited on water-cooled Corning 7059 glass substrates. Typical thicknesses were about 1 µm.

2.1.6 Potential Applications

Ge$_{15}$Bi$_{37}$Se$_{48}$ film is suitable for recording medium with an optical contrast of 44% and it is found that the film is crystallized into multiple polycrystalline state on thermal
annealing. The Bi impurity induced structural modifications in the parent Ge-Se glass are reflected in the optical gap. [7]

2.2 The Ge-Se-Zn Glass System

Addition of Zn in the Ge-Se system does not affect the Ge-Se glass network extensively. For below 5% of Zn, the system is almost unaffected. At 5% Zn the Se atoms tend to bond with Zn, however there is no trace of Ge-Zn bonds. This may be because the bond energy of Zn-Se could be less than that of Ge-Zn [25]. Most of the chalcogenide glasses possess the properties of threshold and memory switching. The Ge-Se-Zn glasses show a memory switching behavior. Very little study has been carried out on the Ge-Se-Zn glass system. Some properties of the glass are discussed below.

2.2.1 Glass Forming Region and Glass Molecular Structure

![Figure 2-12 Region of glass formation in the Se-Ge-Zn system. [25]](image)

The glass forming region of the Ge-Se-Zn glass system (see Figure 2-12) is close to the Ge-Se side, this is because of the low solubility of Zn. Ge is between 0 - 43%. The Ge:Se ratio is about 9:1 with up to 5% of Zn. The low solubility of Zn and the narrow glass forming region are due to the high degree of delocalization of electrons. Zn forms metallic bonds in the system which reduces the glass forming capacity. [25]
When Zn is included in Ge-Se, Ge-Zn and Zn-Se bonds are formed having a bond length of 2.57±0.05 eV and 2.44±0.03 eV respectively. These bond lengths do not vary with composition [26]. In amorphous materials the structure is randomly oriented; there is a range of variation in the bond length between the atoms in the glass structure. So even if there is variation in the composition of the glass, the bond lengths will still be random. Thus the bond length is independent of composition.

![Figure 2-13. Raman spectra of Ge_{40}Se_{60} (labeled 'Undoped') and (Ge_{40}Se_{60})_{77}M_3 where M=In, Sb, Zn or Sn. [28]](image)

When Zn is included in Ge-Se, Ge-Zn and Zn-Se bonds are formed having a bond length of 2.57±0.05 eV and 2.44±0.03 eV respectively. These bond lengths do not vary with composition [26]. In amorphous materials the structure is randomly oriented; there is a range of variation in the bond length between the atoms in the glass structure. So even if there is variation in the composition of the glass, the bond lengths will still be random. Thus the bond length is independent of composition.

![Figure 2-14 Raman spectra of ZnSe for different thickness from 30-100 nm measured using a 442 nm laser line. [27]](image)

The Raman spectra of the Ge_{40}Se_{60} glass are shown in Figure 2-13. Addition on Zn between 1-3% does not cause much change in the Raman spectra. At 200 cm\(^{-1}\) corner
sharing tetrahedron features of Ge₄₅Se₆₀ are observed. Ge-Ge bonds in Ge₂Se₆ ethane like units are seen at 175 cm⁻¹ shows the Raman spectra for different thickness from 30-100 nm of ZnSe (see Fig. 2-14) [27], it seen that at about 250cm⁻¹ and 450cm⁻¹ there are strong peaks that correspond to ZnSe. However in Figure 2-13 there are no peaks observed at 250 cm⁻¹ or near 450 cm⁻¹, so it is assumed that the (Ge₄₅Se₆₀)ₓ Zn₁ do not form any ZnSe structures. The unaffected Ge-Se system when Zn up to 3% is included may be due to the difference in the bond energies. In this case the bond energy of Ge-Se and Se chains may be higher than that of Zn-Se and Ge-Zn. It is possible if the content of Zn is increased the Ge-Se glass may be affected but not to a very great extent. However it is not possible to include large amount of Zn since Ge-Se-Zn glass is formed for only up to 5% of Zn. Thus the addition of small amount of Zn to the (Ge₄₅Se₆₀)₁₀₀₋ₓ Znₓ (Z=1-3%) does not bring about a significant structural change in the bonding of the bulk samples [28].

2.2.2 Thermal Analysis Data

The glass transition, crystallization and melting temperature increase as the content of Ge increases in the system. [25].

<table>
<thead>
<tr>
<th>Composition, mol %</th>
<th>Tg, °C</th>
<th>Tc, °C</th>
<th>Tm, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se₉₉Ge₃Zn₂</td>
<td>49</td>
<td>160</td>
<td>269</td>
</tr>
<tr>
<td>Se₈₉Ge₁₀Zn₃</td>
<td>86</td>
<td>243</td>
<td>287</td>
</tr>
<tr>
<td>Se₇₈Ge₁₀Zn₃</td>
<td>92</td>
<td>360</td>
<td>435</td>
</tr>
<tr>
<td>Se₆₉Ge₃₃Zn₇</td>
<td>104</td>
<td>441</td>
<td>531</td>
</tr>
<tr>
<td>Se₅₉Ge₂₉Zn₂</td>
<td>115</td>
<td>445</td>
<td>571</td>
</tr>
</tbody>
</table>

When Zn is added in the Ge₄₅Se₆₀ glass the glass transition temperature is shifted to a lower temperature. Three crystallization peaks are observed one of which is very close to the glass transition temperature. The glass transition temperature for 1% and 3% Zn is about 340°C and 310°C respectively. Figure 2-15 shows the DSC for 1% and 3% Zn.
Thus on addition of Zn even though the Raman spectra seems to be unaffected as discussed in Section 3.2.1, the DSC data shows that increasing the content on Zn affects the Ge-Se bond network lowering the glass transition, crystallization and the melting temperature [28] Although these results were obtained for a-Ge<sub>40</sub>Se<sub>60</sub> glass system, we assume that the relation between the Zn content and the glass transition temperature is valid even for Ge<sub>20</sub>Se<sub>80</sub> glass system. Since, from the data in Table 2-1 Thermal properties of samples from the SeGeZn system. we see that when the composition of Zn is kept constant varying the Ge-Se composition the T<sub>g</sub>, T<sub>c</sub> and T<sub>m</sub> are increasing, but when the content of Zn is varied these temperature are reduced.

2.2.3 Electrical Properties

Conductivity

Zn alloyed a-Ge-Se materials show very low conductivity [29]. The electrical conductivity at 150 K was measured for the activation energy given in Table 2-2. The obtained electrical conductivity measurements were 3.02×10<sup>-24</sup>, 2.4×10<sup>-15</sup>, 4.75×10<sup>-16</sup> for E<sub>a</sub>
= 0.66 eV, 0.41 eV, 0.43 eV respectively. Thus at 150 K the conductivity of Ge-Se-Zn is very low, implying this material to be highly resistive [24].

Switching

Most of the chalcogenide glasses demonstrate a threshold or a switching behavior. In Ge-Se-Zn glasses, when the films are deposited by co-sputtering of Ge$_x$Se$_{1-x}$ and Zn, the creation of a conducting path in the presence of electric field is possible. The composition of the material is tuned such that it remains in the amorphous state. Under electric field chains present in the material crystallize to form the conducting path. Thus metal doped memory cell can be obtained which is in the amorphous state. [30]

2.2.4 Optical Properties

Addition of Zn in large quantity to the Ge-Se system does not change the optical gap significantly as seen in Table 2-2. Zn is generally tetrahedrally coordinated. However to observe a reduction in the bandgap it is necessary for Zn to adopt a metallic coordination which will produce dangling ends instead of a tetrahedral coordination. The drop in the bandgap value is due to the dangling ends [29]. This has been observed for up to 27% Zn. The activation energy ($E_a$) drops to about 0.8 eV from 1.32 eV when Zn is added. It is assumed that the Fermi level is shifted by about 0.5 eV [29]. The drop in the bandgap is observed for a increase in the Zn content from 0 to 19%, which is a significant increase in the Zn content. Close to around 5% of Zn, Zn-Se are expected to be formed. Zn-Se is a wide bandgap semiconductor with a bandgap of about 2.7 eV, thus altering the Zn content in the Ge-Se-Zn system tuning of the bandgap becomes possible [29]
Table 2-2 Optical gaps ($E_{04}$ and $E_{03}$) and conductivity activation energies ($E_a$) in ternary alloys of Ge-Se-Zn [29]

<table>
<thead>
<tr>
<th>Ge$_x$Se$_y$Zn$_z$</th>
<th>$E_{04}$ (eV)</th>
<th>$E_{03}$ (eV)</th>
<th>$E_a$ (eV)</th>
<th>$2E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x%</td>
<td>y%</td>
<td>z%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>51</td>
<td>0</td>
<td>1.28</td>
<td>0.95</td>
</tr>
<tr>
<td>54</td>
<td>27</td>
<td>19</td>
<td>1.23</td>
<td>0.99</td>
</tr>
<tr>
<td>53</td>
<td>24</td>
<td>23</td>
<td>1.21</td>
<td>1.02</td>
</tr>
<tr>
<td>50</td>
<td>23</td>
<td>27</td>
<td>1.27</td>
<td>1.18</td>
</tr>
</tbody>
</table>

The transmission spectrum for Ge$_{20}$Se$_{75}$Zn$_5$ is shown in Figure 2-16. From the figure we see that for 5% of Zn the Ge$_{20}$Se$_{75}$Zn$_5$ transmit light only after 400 nm. [29]

Figure 2-16. Transmission spectra for Ge$_{20}$Se$_{75}$Zn$_5$ thin films [29]

2.2.5 **Deposition of Ge-Se-Zn Glass Thin Film**

1. Thin films of 0.35 µm-1.25 µm were deposited on substrates at room temperature using Radio-Frequency (RF=13.6MHz) sputtering in argon atmosphere. Ge target were use with pellets of Se and Zn foil placed. Hydrogenated samples were obtained by introducing hydrogen along with argon. The RF power was 240 W. Using XRD the amorphous nature of the thin samples was confirmed. [29]

2. Films were deposited by thermal evaporation of bulk Ge$_{20}$Se$_{75}$Zn$_5$. This bulk samples were produced using melt quench technique. The thin films were deposited on a glass substrate which was at room temperature and a vacuum of about $2\times10^{-6}$ Torr using
Denton Vacuum DV 502 A. The rate of evaporation and the thickness was controlled by quartz crystal DTM 100 monitor. To produce a homogenously thick film mechanical rotation at 30 rpm was performed. [26]

2.2.6 Potential Applications

Thin films of Ge\textsubscript{x}Se\textsubscript{1-x} alloyed with Zn exhibit the property of a memory switching [30], and there are potential photonic applications, related, especially, to the IR spectral region.

2.3 The Ge-Se-Sb Glass System

The Ge-Se-Sb glasses have been of importance due to their interesting optical properties, which include low transmission losses and transparency to IR radiation from 3-18 µm. thus this glass is used for making IR optical fibers. Addition of Sb to the Ge-Se system also brings about a significant variation in the electrical properties of the films, the conductivity of the films increase with the Sb content while the switching voltage tends to decrease. [31] It is supposed that the structure of these glasses is complicated due to structural units containing mainly Ge-Se, Sb-Se and also Ge-Ge, Ge-Sb and Sb-Sb bonds [32]. The probability of the bonds to exist depends on their bond energies and on the composition of the elements. The electrical and optical properties are discussed in relation to varying temperature and chemical composition.

2.3.1 Glass Forming Region and Glass Molecular Structure

The glass forming region of Ge-Se-Sb is enclosed by 5-35% Ge, 5-40% Sb and the rest being Se [10]. In a Ge-Se system the large glass forming region is close to the selenium corner. To obtain a good glass i.e., to avoid crystallization during melt quench in air, the ideal
glass composition is close to 10-20% Ge and up to 20% Sb. When this mixture is cooled slowly a stable glass is obtained. [33]

In Figure 2-17 it is seen that the glass forming region is comprised of Sb ≥ 5% with Ge about 10%. For a material to be used as a practical optical material, it is expected that within this region the material should possess good thermal stability, $T_g \geq 150^\circ C$ and a thermal expansion co-efficient of $17 \times 10^{-6} \circ C^{-1}$. It was found that the material with the above composition would possess all these properties. Along the dashed edge there is partial crystallization of the glass. [34]

![Figure 2-17 Glass forming region of GeSeSb.](image)

As discussed earlier, the chalcogenide glasses follow the CCM model where the probability of the homopolar bond to exist is very low. At low Sb content (>10%) the Se atoms first combine with the Ge atoms then with Sb. The remaining Se then combine with themselves. For about 10% Ge, 42,5 Se atoms are required to saturate the Ge and Sb atoms. Thus Se forms a chain like structure which are interlinked with Ge and Sb atoms [1]. In RCM Ge-Ge bonds are present and since the bond energy results exclude the Ge-Ge bond energy, this bond is not formed thus this implies even the Sb-Ge and Sb-Sb bonds are not present since their energies are even lower [1].
Table 2-3. Bond energies at room temperature and 1000°C [1]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond energy (kJ mol⁻¹)</th>
<th>Relative probability at:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>27°C</td>
</tr>
<tr>
<td>Ge-Se</td>
<td>206.77</td>
<td>1</td>
</tr>
<tr>
<td>Sb-Se</td>
<td>183.89</td>
<td>1.0 × 10⁻⁴</td>
</tr>
<tr>
<td>Se-Se</td>
<td>184.10</td>
<td>1.1 × 10⁻⁴</td>
</tr>
<tr>
<td>Ge-Ge</td>
<td>157.32</td>
<td>2.4 × 10⁻⁹</td>
</tr>
<tr>
<td>Ge-Sb</td>
<td>141.17</td>
<td>3.7 × 10⁻¹²</td>
</tr>
<tr>
<td>Sb-Sb</td>
<td>126.36</td>
<td>9.9 × 10⁻¹⁴</td>
</tr>
</tbody>
</table>

At higher Ge content, i.e., glasses with 25% Ge consist of structural units of the type GeSe₂ and Sb₂Se₃ only (making up a total of Ge₂₅Sb₁₀Se₆₅) with neither excess of Ge or Se. Thus for the composition Ge₂₅Sb₁₀Se₆₅ a completely cross linked three dimensional network consisting of GeSe₂ and Sb₂Se₃ unit is attained and hence the resulting structure is the most rigid for this composition. [35]

GeSe and Sb₂Se₃ structures are scattered in Ge₂₀SbxSe₈₀₋ₓ. Addition of Sb increases the electrical conductivity and rigidity of the lattice and consequently the glass transition temperature (T_g). This is because when the Sb content is increased, weak Ge-Ge and Se-Se bond break to form strong Ge-Se and Sb-Se bonds. The Ge-Se and the Sb-Se structure give rise to valence and conduction bands tailing into the gap of the semiconductor. These

![Figure 2-18 Compositional dependence of Tg at different heating rates [36]](image-url)
dangling bonds originate from electropositive atoms which are Ge and Sb atoms. On annealing the conduction band and the related state gaps are reduced since in Ge$_{20}$Sb$_5$Se$_{75}$ specimens, some of the weak Ge-Ge or Se-Se bonds are replaced by stronger GeSe$_2$ bonds [22].

2.3.2 Thermal Analysis Data

Thermal data of the Ge-Se-Sb is highly composition dependent. At lower Ge content continuous chain network is formed, but at higher Ge content (>25%) structural units of Ge-Se$_2$ and Sb$_2$Se$_3$ are formed. These structural units increase the glass transition temperature. ($T_g$) of the system. The Figure 2-18 shows the relation between the composition and the $T_g$ for the Ge$_x$Sb$_{40-x}$Se$_{60}$ glass [36].

Ge$_x$Sb$_{40-x}$Se$_{60}$ are considered to be good glasses at x= 20, 25 and 27 since no crystallization peaks are observed after the glass transition. At x=15 and 10 a weak exothermal peak is observed which is due to the Sb$_2$Se$_3$ crystallization. Crystallization of GeSe$_2$ and GeSe is observed at x=32 and 35. Ge-Se-Sb do not crystallize isothermally because of their complex structure, this also makes it difficult to obtain the individual crystal phase separately. With about 20% Sb and Ge >20% a stable glassy structure can be obtained. On prolonged isothermal annealing the stable structures of GeSe$_4$ tetrahedron or Sb$_2$Se$_3$ pyramids can be alienated in the glassy network. [36]

Table 2-4. Temperature and activation energy of crystallization. [36]
The transition temperatures for 10°C/min heating rate are listed in Table 6 for the composition of \( \text{Ge}_{2.5} \text{Se}_{7.5-x} \text{Sb}_x \). [37]

Table 2-5. Glass transition temperature as a function of composition [37]

<table>
<thead>
<tr>
<th>composition</th>
<th>( T_g ) k</th>
<th>( T_0 ) k</th>
<th>( T_c ) k</th>
<th>( T_m ) k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb5</td>
<td>518.24</td>
<td>627.44</td>
<td>739.6</td>
<td>714.78</td>
</tr>
<tr>
<td>Sb10</td>
<td>533</td>
<td>808.85</td>
<td>839.56</td>
<td>634.08</td>
</tr>
<tr>
<td>Sb15</td>
<td>487.8</td>
<td>824.87</td>
<td>929.6</td>
<td>778.92</td>
</tr>
<tr>
<td>Sb18</td>
<td>536.1</td>
<td></td>
<td>611.07</td>
<td></td>
</tr>
<tr>
<td>Sb20</td>
<td>430.28</td>
<td>469.42</td>
<td>493.51</td>
<td>581</td>
</tr>
</tbody>
</table>

\( T_g \) - Glass transition temperature

\( T_o \) - Temperature corresponding to the maximum crystallization temperature

\( T_c \) - Crystallization Temperature

\( T_m \) - Melting Temperature

Figure 2-19. Temperature dependence of the dc electrical conductivity of the composition investigated in the chalcogenide glass system \( \text{Se}_{75} \text{Ge}_{25-x} \text{Sb}_x \) [38]

A single endothermic glass transition and an exothermic crystallization peak is observed, this
indicates the homogenous nature of these glasses. Sb rich glasses have low thermal stability but high crystallization ability. [37]

### 2.3.3 Electrical Properties

**Conductivity**

The dc electrical conductivity is independent of the temperature below the glass transition temperature ($T_g$); it increases with the Sb content. Sb forms three weak bonds, in addition to three strong bonds. The weaker bonds are directed towards the Se rings or chains; this weakens the Se-Se bond. The Sb-Se bonds formed are weaker than the Se-Se bonds, which results in higher conductivity. [38]

Bond energies of Ge-Se, Sb-Se, Se-Se, Ge-Ge, and Sb-Sb bonds are 56, 51, 49, 45, and 30 kcal/mol. Ge forms covalent bond with Se. Increasing Sb in $\text{Se}_{75}\text{Ge}_{25}\text{Sb}_x$, increases the density of the weaker bonds in the system, compared to the covalent bonds formed by Ge-Se atoms. The electrical properties of a system are dominated by the covalent bonds. The A single endothermic glass transition and an exothermic crystallization peak is observed, this indicates the homogenous nature of these glasses. Sb rich glasses have low thermal stability but high crystallization ability. illustrates the variation in conductivity with respect to temperature for different compositions of Sb. From the figure it is seen that for the conductivity increases with the Sb content [38]

The dc conductivity is the least in the $\text{Ge}_{25}\text{Sb}_{10}\text{Se}_{65}$ composition since the Ge-Se and Sb-Se bond are stronger than that in other Ge or Se rich compositions so the conductivity will result from breaking up the Ge-Se and Sb-Se bonds. [35]
When the sample is annealed to the crystallization temperature, it crystallizes completely and the conductivity rises drastically. When the Ge$_{20}$Sb$_{50}$Se$_{30}$ glass is annealed at 220°C the conductivity remains almost unchanged, that is because the crystallization temperature is much higher than the $T_{\text{ann}}$. Thus we assume that at very low temperature the conductivity remains unchanged. [22]

![Graph showing I-V characteristics](image)

Figure 2-20. The I-V of a representative Ge$_7$Se$_{61}$Sb$_{12}$ glass, revealing the threshold switching behavior with fluctuations in the I-V characteristics. The arrows show the forward and the return path of the characteristic. Inset is the magnified portion of the ohmic behavior. [31]

### Switching

GeSeSb glasses demonstrate threshold switching behavior. Figure 2-20 shows the I-V characteristic of Ge$_7$Se$_{61}$Sb$_{12}$ where the threshold voltage is about 674.45 V. A similar behavior was observed in glasses of composition Ge$_7$Se$_{63-x}$Sb$_x$ for 21 ≤ x ≤ 32. The variation in the switching voltage with varying Sb content is shown in Figure 2-21, from the figure we see that the threshold voltage decreases as the content of Sb is increased. Before the sample switches to low resistance ON state an ohmic behavior is observed up to the threshold
voltage \((V_T)\) which is the high resistance OFF state. On reducing the current the samples revert back to the high resistance OFF state. [31]

The fluctuations seen in the switching for the Ge\(_{7}\)Se\(_{93-x}\)Sb\(_{x}\) (particularly in samples with higher Se content) may be due to the burning of the sample around the electrode, generation of noise, visible light, material ablation and local melting of the material. At the electrode region due to the increase in current there is large diabatic joule heating suddenly rises the temperature at the electrode and causes the material to melt in the and splashing of the material in the active zone. [31]

![Figure 2-21. Composition dependence of switching voltages \(V_T\) of Ge\(_{7}\)Se\(_{93-x}\)Sb\(_{x}\) glass. [31]](image)

GeSeSb glasses demonstrate threshold switching behavior. Figure 2-20 shows the I-V characteristic of Ge\(_{7}\)Se\(_{61}\)Sb\(_{32}\) where the threshold voltage is about 674.45 V. A similar behavior was observed in glasses of composition Ge\(_{7}\)Se\(_{93-x}\)Sb\(_{x}\) for \(21 \leq x \leq 32\). The variation in the switching voltage with varying Sb content is shown in Figure 2-21, from the figure we see that the threshold voltage decreases as the content of Sb is increased. Before the sample switches to low resistance ON state an ohmic behavior is observed up to the threshold
voltage ($V_T$) which is the high resistance OFF state. On reducing the current the samples revert back to the high resistance OFF state. [31]

The fluctuations seen in the switching for the Ge$_{0.7}$Se$_{0.3-x}$Se$_x$ (particularly in samples with higher Se content) may be due to the burning of the sample around the electrode, generation of noise, visible light, material ablation and local melting of the material. At the electrode region due to the increase in current there is large diabatic joule heating suddenly rises the temperature at the electrode and causes the material to melt in the and splashing of the material in the active zone. [31]

2.3.4 Optical Properties

Bandgap

![Graph](image.png)

Figure 2-22. The variation of the optical energy gap with Sb content for the Ge$_x$Sb$_y$Se$_{1-x-y}$ system data for x=0.2 is given by $\bullet$, for x=0.33 by * and for x=0.15 by + [40]

The composition of the film does not change with the film thickness. However variation in the film thickness affects the optical properties of the film. Refractive index of a film decreases with the thickness of the film, the clusters formed introduce empty zones.
These zones reduce the average refractive index and the band gap increases the $E_c$ parameter. [39]

The optical energy gap depends on Sb content for samples of composition $\text{Ge}_x\text{Sb}_y\text{Se}_{1-x-y}$, where $x = 0.2$. It can be seen from Figure 2-22 that the energy gap decreases almost linearly with increasing antimony content. [40]

**Absorption Coefficient**

![Figure 2-23. Transmission spectra for different Films. [32]](image)

The typical range of transmission spectrum for $\text{Ge}_{28-x}\text{Se}_{72}\text{Sb}_x$ ($0\% \leq x \leq 28\%$) is in the range of 200-1100 nm for a 205-207 nm film. There are no sharp absorption edges observed in the materials in the glassy state. The absorption co-efficient depends on the Ge content. The absorption coefficient is low for higher content of Ge [41]. Figure 2-23 shows the transmission spectrum for various Ge content. [32]

### 2.3.5 Thin Film Depositon of Ge-Se-Sb glasses

1. The $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ films was deposited by RF-sputtering from 5cm diameter IG2 and IG5 VITRON commercial targets, using an Alcatel Dion 300 device equipped with a PFG
300 RF Huttinger, 13.56 MHz, 300 W generator. Before the deposition, the chamber was evacuated down to approximately $10^{-4}$ Pa to avoid ambient contamination. An operating argon pressure comprised between 1 and 10 Pa was used. A low RF power, 25 W, was imposed because of the dielectric character of the chalcogenide glasses. Microscope slides (7.6×2.6 cm$^2$) were used as substrates. The substrate holder was cooled down by water circulation. The adherence of the films on the substrates was checked by the classical adhesive tape test. [39]

2. Four compositions of the Ge$_{28-x}$Se$_{72}$Sb$_x$ for 0<x<24 chalcogenide glass system were prepared using melt quench technique. The appropriate amounts of high purity materials (99.9999 at. %) were taken in an evacuated silica ampoule. The ampoule was placed in an oscillation furnace. The temperature of the furnace was raised slowly up to 1000°C to reduce the vapor pressure. For up to 10 hrs the temperature was maintained while periodically rocking the mixture to obtain a homogenous material composition. The molten material was then quenched in ice water to obtain the glassy sample. The thin films were prepared by thermal evaporation technique using high vacuum plant (Edward 306 A). The films were deposited on a well-cleaned glass substrate. The glass substrates were cleaned by ultrasonic cleaner, in distilled water and alcohol environment. The substrate was then placed at a tangent to a suitable holder which would rotate horizontally. The distance between the substrate and boat is about 10cm. the temperature in the vacuum was pumped down to 1.3 MPa (105 Torr). The temperature of the material was raised in steps until all the material evaporated. [12]

2.3.6 Potential Applications

1. Fabrication of Optical fibers. [42]
2. \( \text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60} \) can be used as opto-chemical sensors due to their good chemical and thermal stability at \( T_g = 362^\circ \text{C} \) and \( 278^\circ \text{C} \). [39]

### 2.4 The Ge-Se-Te Glass System

Glasses consisting Te become easily vitreous when quenched at high speed, these glasses are used for optical memory devices. It is difficult to obtain a polycrystalline phase due to their unstable amorphous nature and their long conversion time to polycrystalline phase. To obtain the polycrystalline phase it is preferred to use materials that have a high crystallization speed. Ge-Sb-Te was used due to their high crystallization speed and good data storage capability. It was found that replacing Sb with Se improves the speed of the device, due to the small size of the Se atoms. Electrical properties relevant to switching and the material properties of the Ge-Se-Te glasses have been discussed. [43]

#### 2.4.1 Glass forming and glass molecular structure

The forming regions for the Ge-Se-Te glass are shown in Figure 2-24. The glass forming compositions change for different quenching techniques. To obtain a good bulk glass the composition for Ge should be between 5-50\% and Se >50\%, the rest being Te. From the figure we see that the glass forming region obtained by water quench is much larger than the other slow quenching techniques. [44]

Addition of tellurium introduces defects. These defects reduce the glass forming ability and the optical transmission of the glass. Te also increases the tendency of crystallization which causes phase separation. As compared to selenium and sulfide the higher refractive index and the transmission is shifted due to longer wavelength by about
20\mu m [45]. When more than 50% Ge is added the glass crystallizes completely. Below 50% Ge the glass is partly vitreous [46].

According to the Raman spectra of the film prepared in it is seen that when Te is added the Se-Se bonds at 260 cm$^{-1}$ diminish, forming Ge-Se bonds edge sharing tetrahedron

![Graph of the Ge-Se-Te system]

Figure 2-24. Glass formation in the Ge-Se-Te system, showing quenching techniques required to produce single-phase amorphous samples. Dots correspond to compositions successfully prepared as single-phase glasses. [44]

as seen at 216 cm$^{-1}$. No Ge-Te bonds are observed. Introduction of Te increases the overall coordination number and increases as the Te content increases [47]. There is a decrease in the $E_g$ which is an evidence of the formation of Se-Te bond. This is explained by the fact that the bonding energies of Se-Te, Ge-Se and Se-Se bonds 195, 230 and 225 kJ mol$^{-1}$ and the bond energy of Se-Te is the lowest which causes the decrease in the bandgap. [47]

The Raman spectra in Figure 2-25 have been acquired using Fourier transform Raman Spectrometer (Bruker model IFS/FRA 106). The Raman scattering was excited by a laser beam with $\lambda=1064$ nm. The resolution of the Raman spectrometer was 1 cm$^{-1}$, and 100 scans were recorded. The spin coated Ge-Se-Te films were mechanically peeled from the substrates and pressed into aluminum targets for the Raman spectra measurements. [47]
2.4.2 Thermal Analysis Data

DSC measurements were performed for 10-25 mg of Ge$_{50}$Se$_{50}$Te$_x$ (10≤x≤40) glasses prepared by conventional melt quench technique using Perkin Elmer DSC-2 under pure argon atmosphere. While heating at the rate of 15 K/min two types of crystallizations were observed depending on the composition of the glass. At x=20 and 40 single exothermic peaks were observed at approximately 225°C and 375°C respectively, while at x=10 two exothermic peaks were observed at about 450 and 475°C. The material tends to crystallize when Te content is increased; this reduces the T$_g$, T$_c$ and T$_c$-T$_g$ [44].

The glass transition temperature for different compositions are given below: [48]

Table 2-6 Glass transition temperature for different composition of Ge-Se-Te glass [48]

<table>
<thead>
<tr>
<th>Composition</th>
<th>T$_g$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge$<em>{10}$Se$</em>{50}$Te$_4$</td>
<td>368-385.4</td>
</tr>
<tr>
<td>Ge$<em>{30}$Se$</em>{50}$Te$_2$</td>
<td>536.3-557</td>
</tr>
<tr>
<td>Ge$<em>{40}$Se$</em>{30}$Te$_1$</td>
<td>322.5-332.2</td>
</tr>
</tbody>
</table>
2.4.3 Electrical Properties

Conductivity and Photoconductivity

The electrical conductivity of the film is sensitive to the Ge content; it increases with the increase in the Ge content. Conductivity of a-Se_{80-x}Te_{20}Ge_{x} was measured in dark and in the presence of light. It was observed that the glass is thermally activated in dark as well as in the presence of light.

Figure 2-26 and Figure 2-27 show the photoconductivity and the conductivity at different intensities of light. It is seen that the conductivity increases with the increase in the intensity. In the presence of light the Fermi level splits into quasi femi level and moves towards the conduction band. Thus in the presence of light the activation energy is smaller in compared to that in the dark [49].
Switching

GeSeTe glasses exhibit a switching property. The switching speed of a device depends upon the time needed for crystallization. For higher crystallization temperature, the time for crystallization is longer this means the speed of the device is delayed. From Figure 2-28 shows the crystallization temperature of Ge_{52}Se_{06}Te_{44}, Ge_{47}Se_{15}Te_{38}, and Ge_{49}Se_{35}Te_{16} are

![Figure 2-27. Conductivity at different light intensities in a- Se_{80-x}Te_{20}Ge_{x} [49]](image)

![Figure 2-28. The resistance changes with the change in the crystallization temperature for the Ge-Se-Te system. [50]](image)

![Figure 2-29. Current–voltage characteristics the edge contact type cell structures with Ge_{50}Te_{50}, Ge_{52}Se_{06}Te_{42}, Ge_{47}Se_{15}Te_{38}, and Ge_{49}Se_{35}Te_{16}. The threshold voltage increases as the increasing of Se content. [50]](image)
220, 246 and 255°C, respectively. The switching speed can be estimated from the slope of the change in resistance during crystallization [50].

When the Se content is over 40% the slope of the resistance is high, thus the crystallization occurs slowly. But when the content of Se is less than 40% the crystallization temperature increases as compared to other cases. When there is no Se in the GeTe system the threshold voltage is about 2.1 V. On increasing the Se content (see Figure 2-29) in the Ge\textsubscript{50}Te\textsubscript{50}, Ge\textsubscript{52}Se\textsubscript{48}Te\textsubscript{44} is 1.4 V and increasing the Se content from 15 to 35, Ge\textsubscript{47}Se\textsubscript{35}Te\textsubscript{38} and Ge\textsubscript{49}Se\textsubscript{15}Te\textsubscript{36} is 1.8 and 1.9 V, respectively. Thus the threshold voltage of PRAM can be reduced by reducing the Se content. Microstructure analysis suggests that the stable FCC single phase and the hexagonal Te influence on the threshold voltage as well as the crystallization temperature. [50]

![Figure 2-30. Static mode switching I-V characteristic of Ge\textsubscript{1}Se\textsubscript{1}Te\textsubscript{2}. [43]](image)

Se atoms can easily move around because of the small atomic radii and their bond angle can easily be deformed due to their high compressibility. Hence the Se based atoms do not regain their initial state easily as a result of which they always exhibit memory switching. A chalcogenide thin film of Ge\textsubscript{5}Se\textsubscript{1}Te\textsubscript{2} is prepared by thermal evaporation at the deposition rate of ~0.5 nm/s. The film thickness was 100 nm. A PRAM device is then
prepared by encapsulating thin film of Ge\textsubscript{1}Se\textsubscript{1}Te\textsubscript{2} between SiO\textsubscript{2} and Al electrode layer. It is then heated for a few tens of nanosecond which leads the material to a transition of phase change from the thermodynamic equilibrium condition.

The IV characteristic seen in Figure 2-30 were then measured with Hewlett Packard 4155 semiconductor parameter analyze. In the first sweep the amorphous Ge\textsubscript{1}Se\textsubscript{1}Te\textsubscript{2} shows very high resistance. When the threshold voltage is reached which is about 7.6 V the electrical resistance of the device is drastically reduced. This conducting path can either be the connected crystalline domains or the linked crystalline defects. Once the path is formed most of the current flows and generates heat as the current increases. Thus a phase change from amorphous to crystalline is completed as the current in increases and the resistance remains same even if the current is increased. This is called as the dynamic resistance. To increase the writing power and reduce the writing current the dynamic resistance has to be reduced this can be achieved by reducing the the interfacial area between the thin film and electrode. [43]

2.4.4 Optical Properties

![Figure 2-31. Variation of Optical gap (Eg) with coordination number \(<r>\) for the three sets of Ge-Se-Te glasses. [51]](image)
E<sub>g</sub> decreases initially as the average coordination number \(<r>\) is increased (i.e. when the Ge concentration is increased) and then exhibits a local maximum at \(<r> = 2.67\). The Figure 2-31 shows the variation in the optical bandgap with respect to the coordination number, which is given by the following relation: [51]

\[
< r \geq \frac{[(X)Z_{Ge} + (Y)Z_{Te} + (100 \times X - Y)Z_{Se}]}{100}
\]

**Refractive index**

![Image](image_url)

Figure 2-32 Variation of Refractive index with \(h\nu\) for Ge\(_{10}\)Ge\(_{80-x}\)Te\(_x\) (\(x=0, 30\)) thin films. [52]

The refractive index is reduced when Te is included in the Ge-Se glass system. For about 30% Te transmission spectrum of the Ge-Se-Te glass is shifted to a higher wavelength and the fringes are smaller this is shown in Figure 2-32. The relation between the transmission spectrum and the refractive index is given by:

\[
n = [M + (M^2 - s^2)^{1/2}]^{1/2}
\]

where \(M = \frac{2s}{\tau_m} - \frac{(s^2+1)}{2}\) for transparent region

and \(M = 2s \frac{\tau_m - \tau_m}{\tau_m \tau_m} + \frac{(s^2+1)}{2}\) for weak and medium absorption region.
$T_M$ and $T_m$ are the maximum and minimum transmission values respectively, and ‘s’ is the refractive index of the substrate. Thus from the equation we can see that on the addition of Te the fringes ($T_M - T_m$) become smaller, thus the refractive index of the material reduces. [52]

Absorption co-efficient

The optical bandgap tends to decrease when Te is included. For a wavelength of 1000nm the absorption coefficient was measured. The optical bandgap of Ge$_{10}$Se$_{90}$ is about 1.87 eV. On addition of Te up to 30% the bandgap is reduced to 1.27 eV, the absorption coefficient was found to be $0.34 \times 10^4$ and $0.27 \times 10^4$ for Ge$_{10}$Se$_{90}$ and Ge$_{10}$Se$_{60}$Te$_{30}$ respectively [52]. The Figure 2-33 shows the absorption coefficient at $x=0, 30$ for Ge$_{10}$Se$_{90}$, Te$_x$ glass. It observed that when Te is included, for lower photon energy also there is not much variation in the absorption coefficient.

![Figure 2-33 Variation of absorption coefficient ($\alpha$) with $h\nu$ for Ge$_{10}$Se$_{90-x}$Te$_x$ ($x = 0, 30$) thin films. [52]](image_url)
Addition of Te introduces defect states in the amorphous glass structure, which causes the decrease in the optical gap. This is because Te bonds with Ge, to form Ge-Te bonds, breaking the Ge-Se bonds. The average bond energy of all the bonds in the Ge\textsubscript{10}Se\textsubscript{60}Te\textsubscript{30} is lower than that of Ge\textsubscript{10}Se\textsubscript{90}. Since the optical gap is sensitive to the bond energy the decrease in the optical gap is observed.

### 2.4.5 Thin Film Deposition

Bulk chalcogenide samples of Ge\textsubscript{20}Se\textsubscript{80−x}Te\textsubscript{x} system, where \( x = 0, 2.5, 5, 7.5 \) and 10 at\%, were prepared from pure elements in evacuated quartz ampoules placed in a rocking furnace \((T=990^\circ C \text{ for } 24 \text{ h})\). Glass melts were quenched to room temperature. The glass was then dissolved in a mixture of amines. Thin films were coated by spinning for 20s at a spin speed of 2000 rpm in argon an atmosphere. The vacuum furnace stabilization of spin coated samples was carried out by heating at 70\(^\circ\)C for 10 h. Ge–Se–Te films (thickness of approximately 100 nm) were coated on glass, SiO\textsubscript{2} and Si substrates. The accelerating voltage of the primary electron beam was 20 kV. Films were coated onto Si substrates. [47]

### 2.4.6 Potential Applications

Ge\textsubscript{1}Se\textsubscript{1}Te\textsubscript{2} can be used as an alternative for phase change random access memory (PRAM) instead of the conventional Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} PRAM devices. These device exhibit switching properties i.e amorphous and crystalline phase when 50 ns, 7.3 V set pulse is applied and 30 ns, 7.4 V reset pulse is applied. [43]
2.5 The As-Se-Te Glass System

As-Se-Te glasses have good transparency between 3-11 µm. The required optical properties and a good chemical stability can be obtained easily by modifying the composition of the As-Se-Te glass system (see Figure 2-34). Some glass compositions are stable against devitrification whereas some compositions have the tendency to crystallize. These glasses are widely used for the preparation of optical fibers. [53]

2.5.1 Glass Forming Region and Glass Molecular Structure

The crystallization significantly depends on glass composition and heating rate. The glasses with 10, 15 and 20% Te show very low tendency to crystallization at different heating rate. The crystallization depends on the impurity content in glass.

High purity glasses have no crystallization or have only a single stage homogeneous crystallization and one- or two-dimensional crystal growth mechanism. [54]

In As$_{40}$Se$_{60-x}$Te$_x$ glass system when Se is replaced by Te, the three dimensional structural unit of AsSe$_{3/2}$ transforms in layer structure with As$_2$Te$_3$ chains made up of bi-
coordinated Se and Te atoms. The Van der Waals bonds between these chains decreases the \( T_g \) \[55\]

2.5.2 **Thermal Analysis Data**

Parameters of Te-As-Se glasses [55]

<table>
<thead>
<tr>
<th>Properties</th>
<th>( \text{As}<em>{30}\text{Se}</em>{30}\text{Te}_{30} )</th>
<th>( \text{As}<em>{30}\text{Se}</em>{30}\text{Te}_{25} )</th>
<th>( \text{As}<em>{30}\text{Se}</em>{30}\text{Te}_{20} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Glass transition temperature ( T_g/\text{°C} ), (heating rate of 5 K/min)</td>
<td>125 ± 2</td>
<td>140 ± 2</td>
<td>129 ± 2</td>
</tr>
<tr>
<td>2 Temperature of crystallization, (at heating rate of 3 K/min) onset ( T_g/\text{°C} )</td>
<td>-</td>
<td>-</td>
<td>230 ± 2</td>
</tr>
<tr>
<td>exothermal maximum ( T_g/\text{°C} )</td>
<td></td>
<td></td>
<td>271 ± 2</td>
</tr>
<tr>
<td>3 Temperature of solidus ( T_p/\text{°C} )</td>
<td>-</td>
<td>-</td>
<td>297 ± 2</td>
</tr>
<tr>
<td>liquidus ( T_l/\text{°C} )</td>
<td></td>
<td></td>
<td>313 ± 2</td>
</tr>
<tr>
<td>4 Position (( \mu \text{m} )) of the short-wave absorption edge, at the absorption coefficient of 1 cm(^{-1})</td>
<td>1.23 ± 0.01</td>
<td>1.36 ± 0.01</td>
<td>1.23 ± 0.01</td>
</tr>
<tr>
<td>0.1 cm(^{-1})</td>
<td>1.40 ± 0.01</td>
<td>1.58 ± 0.01</td>
<td>1.40 ± 0.01</td>
</tr>
<tr>
<td>5 Position (( \mu \text{m} )) of the long-wave absorption edge, at the absorption coefficient of 1 cm(^{-1})</td>
<td>17.90 ± 0.05</td>
<td>17.70 ± 0.05</td>
<td>18.00 ± 0.05</td>
</tr>
<tr>
<td>0.1 cm(^{-1})</td>
<td>12.82 ± 0.05</td>
<td>12.88 ± 0.05</td>
<td>14.80 ± 0.05</td>
</tr>
<tr>
<td>0.01 cm(^{-1})</td>
<td>10.84 ± 0.05</td>
<td>11.53 ± 0.05</td>
<td>11.64 ± 0.05</td>
</tr>
<tr>
<td>6 Band optical gap, eV</td>
<td>0.93</td>
<td>0.86</td>
<td>0.9</td>
</tr>
</tbody>
</table>

\( \Delta E \) is a function of the electronic energy levels of the chemically interacting atoms in the glass (and hence of the emerging band gap) while \( T_g \), reflects the rigidity of the lattice and is a complex function of the interaction energies and the masses of the constituent atoms. The substitution of Te by Se is isovalent. The decrease in \( \sigma \) at a constant temperature brought about by substitution of Te by Se also indicates that \( \Delta E \) is related to lone pair band conduction band energy gaps. \[56\]

2.5.3 **Electrical Properties**
DC conductivity variations with temperature for the four glass compositions studied are shown in Figure 2-36 which is As$_{40}$Se$_{10}$Te$_{50}$, As$_{40}$Se$_{20}$Te$_{40}$, As$_{40}$Se$_{30}$Te$_{30}$ and As$_{40}$Se$_{40}$Te$_{20}$. [56]

Figure 2-36. The Variation of DC conductivity with temperature plotted in as ln 6 against 1/T. The inset shows the data in the high temperature region where change in the slope corresponding to Tg is clearly seen. O, As$_{40}$Se$_{10}$Te$_{50}$; ∆ As$_{40}$Se$_{20}$Te$_{40}$; x As$_{40}$Se$_{30}$Te$_{30}$ and • As$_{40}$Se$_{40}$Te$_{20}$ [56]

DC conductivity variations with temperature for the four glass compositions studied are shown in Figure 2-36 which is As$_{40}$Se$_{10}$Te$_{50}$, As$_{40}$Se$_{20}$Te$_{40}$, As$_{40}$Se$_{30}$Te$_{30}$ and As$_{40}$Se$_{40}$Te$_{20}$. The results show that at any given temperature the conductivity increases as the content of
Se decreases. At higher temperature which is above 250 K the conductivity increases as the Se : Te ratio is decreased. $\Delta E$ and $T_g$ also decrease with decreasing Se: Te ratio. The linearity of the In $\sigma$ against $1/T$ above about 250 K indicates that the conductivity is thermally activated in this region where $\sigma$ varies as: [56]

$$\sigma = \sigma_0 \exp \left( - \frac{\Delta E}{kT} \right)$$

Where $\Delta E$ is the corresponding activation energy.

I-V characteristics of dark conductivity and photoconductivity of As$_{40}$Se$_{25}$Te$_{35}$ were measured using 610°C Keithley Electrometer in the samples having the “gap type” gold electrodes with distance approximately 1 mm between them. The inter-electrode space was irradiated by the He-Ne laser light with intensity 2.75 W/cm$^2$.

The I-V characteristics of the typical As$_{40}$Se$_{25}$Te$_{35}$ film in darkness and under laser light

![Graph](image)

Figure 2-37. Variation of optical band gap, $E_o$, with composition parameter, $x$. $\bullet$, AsxTe0.05Se0.95-x, with $x = 0.30, 0.35, 0.40, 0.45$ and 0.50. $o$, AsxTe0.10Se0.90-x, with $x = 0.30, 0.35, 0.40, 0.45$ and 0.50. $*$, Values obtained using UV-VIS-NIR spectrophotometer. Lines are drawn through the data symbols ($\bullet$ and $o$) as a guide for the eye. [58]
irradiation are shown in the Figure 2-35 or comparison, the similar volt-ampere characteristic of the As$_{35}$Se$_{45}$Te$_{10}$ films is also shown. From the Figure 2-35 it is seen that the I-V of these films is a linear characteristic. From these linear characteristics the values of conductivity were $6 \times 10^{-4} \, \Omega^{-1} \cdot \text{cm}^{-1}$ and photoconductivity $2 \times 10^{-4} \, \Omega^{-1} \cdot \text{cm}^{-1}$ for As$_{40}$Se$_{25}$Te$_{35}$ film and $5 \times 10^{-7} \, \Omega^{-1} \cdot \text{cm}^{-1}$ and $1 \times 10^{-6} \, \Omega^{-1} \cdot \text{cm}^{-1}$ for As$_{45}$Se$_{45}$Te$_{10}$ film were determined. [57]

2.5.4 Optical Properties

Optical Bandgap

![Graph showing optical bandgap variation](image)

Figure 2-38. Transmission spectrum of the As$_{40}$Se$_{25}$Te$_{35}$ with thickness 1um. [57]

The optical properties of the As-Se-Te glass vary with the glass composition. Figure 2-37 shows the variation of optical band gap with composition for As$_x$Te$_{0.05}$Se$_{0.95-x}$ and As$_x$Te$_{0.10}$Se$_{0.90-x}$ (with $x = 0.30, 0.35, 0.40, 0.45$ and $0.50$) systems. From the figure it is observed that the bandgap decreases as the As content is increased. However beyond 40%

![Graph showing absorption coefficient](image)

Figure 2-39. Absorption co-efficient spectrum from the non irradiated (1) and from Xe lamp irradiated(2) As$_{40}$Se$_{25}$Te$_{35}$ film [57]
As, the rate at which the bandgap reduces is much lower. The variation obtained using a UV-VIS-NIR spectrophotometer are also plotted in the same graph. [58]

AsSeTe films have a high refractive index. Introduction of 10% of tellurium in the As-Se film was shown to increase the value of refractive index up to ~ 3.2 at 850 nm. Transmission spectrum of the As$_{40}$Se$_{25}$Te$_{35}$ film of about 1 μm thickness is usually between 500 – 2500 nm as shown in Figure 2-38. It is seen that the film starts to transmit the light only after 900 nm, practically all visible light is absorbing in the film of this thickness. Figure 2-40 and demonstrate the spectra of refractive index and absorption coefficient obtained on the base of analysis of the transmission spectrum. At shorter wavelength the refractive index and the absorption coefficient have large values. The refractive index is between 2.7 and 3.6 and the absorption coefficient in the studied spectral range has values $1 \times 10^3 - 4 \times 10^3$ cm$^{-1}$. [57]

![Figure 2-40. Refractive index for non-irradiated (10 and from Xe lamp irradiated (2) As$_{40}$Se$_{25}$Te$_{35}$ film [57]](image)

2.5.5 Thin Film Deposition

1. Thin films of As-Se-Te were prepared using (AsSe)$_{100-x}$Te$_x$ as the initial glasses. The films were deposited by vaccum evaporation from a quartz crucible at a pressure of $(1-3) \times 10^{-6}$
Torr on a silicate glass substrate that was at room temperature. Between 0.4-3.5 µm thick films were deposited at the rate of 30-40 Ås\(^{-1}\). \[57\]

2.5.6 **Potential Applications**

1. AsSeTe chalcogenide glasses are materials that are photosensitive and have a large refractive index that is in the range of 2.5 to 3. These properties make these glasses particularly suitable for the fabrication of photonic crystals. \[59\]

2. High purity As-Se-Te glasses are used for core-clad multimode fiber using the double crucible technique. Up to 10m of fiber was obtained which was then cut into 1m for the measurements. The optical losses obtained from these fiber were about ±4% for 1000 dB/km and about ±8% for 100 dB/km. \[53\]
Chapter 3

Experimental Characterization Techniques

The characterization techniques and fabrication methods relevant to this project are reviewed in this chapter.

3.1 Differential Scanning Calorimetry (DSC)

The Differential Scanning Calorimeter (DSC) is used for different types of thermal analysis; these analyses include obtaining the melting, crystallization, and glass transition temperature, polymorphism, specific heat, kinetic studies and other reactions. DSC is a twin instrument, comprising a sample and a reference calorimeter within a common thermal enclosure, the two calorimeters are assumed to be identical. The output of the DSC is the difference between the heat flows measured by each of the calorimeters. The advantages of using of twin calorimeters including cancellation of heat leakage and temperature disturbances common to both calorimeters.

The conventional DSC and the Modulated DSC (MDSC) are widely used for the thermal analysis. In a conventional DSC the heating rate of the sample and the reference is linear. In MDSC a sinusoidal modulation is superimposed on the conventional linear heating ramp to impose a heating profile in which the average sample temperature continuously increases with time but not in a linear fashion. The net effect of imposing this more complex heating profile on the sample is the same as if two experiments were run simultaneously on
the material – one experiment at the traditional linear (average) heating rate and one at a sinusoidal heating rate.

The PerkinElmer Diamond DSC has been used for thermal analysis of our samples. This is a conventional DSC instrument. The instrument has a very high sensitivity for the detection of weak transitions or small polymorphic forms. Platinum resistance thermometer (PRT) are used to measure the sample temperature, this provides better accuracy than thermocouples. The independent dual furnaces are constructed of platinum-iridium alloy with independent platinum resistance heaters and temperature sensors.

Specifications of the PerkinElmer Diamond DSC are as follows:

- Temperature range: -170 °C to 730 °C
- Calorimetry accuracy / precision: < +/- 1% / < +/- 0.1%
- Scanning rates heating/cooling: 0.01 °C to 500 °C/min
- Available cooling options are Intracooler 1P: -10 °C to 730 °C and Cryofill: -170 °C to 300 °C

*Principles of DSC*

![Figure 3-1. Differential scanning calorimeter](image)
The DSC consists of two separate furnaces for the sample and the reference sides. This is shown in Figure 3-1. The system can be divided into two control loops, the average temperature loop and the differential temperature loop. The average temperature loop ensures that the sample and reference sides are heating at the programmed rate. The differential temperature loop maintains identical temperatures between the reference and sample pans regardless of the different amount of heat needed to enter the sample side. This process ensures that the sample is always kept at the same temperature of the reference regardless of any changes that occur within the sample requiring more or less heat flow. When an endothermic process occurs such as softening or melting, more heat is added to the sample side relative to the reference to make up for a difference in temperature. With an exothermic process less heat is added to the sample relative to the reference side.

3.2 Scanning Electron Microscopy (SEM) with EDS

The Scanning Electron Microscope (SEM) is a microscope that uses electrons instead of light to form an image. The advantage of using the SEM instead of a light microscope is its large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification.

The Hitachi S-4800 High Resolution Scanning Electron Microscope has been used to obtain the surface images of our thin films. This is a cold field emission high resolution scanning electron microscope with many advanced features. These features include:

- A resolution of 2.0 nm at 1kV for low voltage applications.
• An objective lens design with "Super ExB Filter" technology. The Super ExB Filter collects and separates the various components of pure SE, compositional SE and BSE electron signals.

• A specimen stage for large sample applications with 110mm x 110mm stage movement and computer controlled 5 axes motorization with graphical interface software.

The SEM may also be equipped with Energy Dispersive Spectrum (EDS) this enables the SEM to perform compositional analysis as well. The EDS reveals the materials and any contaminations relative concentration.

*Principles of SEM*

The Figure 3-2  Electrons are generated in the electron gun. The most commonly
used gun is a tungsten-hairpin gun in which a tungsten filament serves as the source of electrons. By applying a current through the filament the tungsten wire heats up and emission of electrons is achieved. Generated electrons will be focused in front of an anode. To move the electrons down the column, a voltage difference between the tungsten filament and the anode will be applied. This voltage differences is called the accelerating voltage and can be varied between 0.2 and 40 kV determining the energy and wavelength of the electrons within the beam. The beam of electrons will be condensed and focused as a fine spot on the specimen by 2 to 3 electromagnetic lenses located in the microscope column. Two main functions of the first two lenses, condenser lens 1 and condenser lens 2, are to control the beam current (number of electrons striking the specimen) and the final size of the area illuminated on the specimen (spot size). The final lens is be used primarily to focus the beam of electrons on the surface of the specimen. The deflection coils are used to move the electron spot forth and back in a raster pattern across the specimen. The stigmator coils are used to correct for irregularities in the beam. If not corrected the electron spot focused on the specimen may be elliptical instead of round, a major reason for loss in resolution in the SEM. Upon interaction of the electron beam with the sample, various signals (secondary electrons, back scattered electrons and x-rays) are produced and can be detected. The secondary electron detector will detect low energy electrons produced near the surface of the specimen providing a predominantly topographical image. The back scattered electron detector will detect high energy electrons that have been scattered backward and providing information about the presence of differences in atomic number of a sample.

Principles of EDS

In EDS analysis, an electron strikes the sample knocking off some electron from the atom in the specimen. When these electrons are knocked off they leave behind a vacant
space. These empty spaces in the inner shell are occupied by the electrons from the higher-energy level (outer-shell). In order to do this the electrons from the high-energy level have to release some energy, this energy emitted is in the form of x-rays. The amount of energy released depends upon from which shell the electron jumps and to which inner shell. The amount of x-ray emitted is unique for every element. Thus an energy spectrum is obtained corresponds to a single element. The larger the peak in the spectrum, the larger the concentration of that particular element in the region.

3.3 X-Ray Diffraction

X-ray diffraction (XRD) is a non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure materials. X-ray diffractometers consist of three basic units which are X-ray tube, a sample holder, and an X-ray detector. Various applications such as in-plane and normal geometry phase identification, quantitative analysis, lattice parameter refinement, crystallite size determination and depth-controlled phase identification can be performed. Typically the Bragg-Brentano geometry (Figure 3-3) is used to perform XRD, GIXRD and SAXS can be used for thin films and powdered samples.

The Bragg-Brentano geometry is widely used among diffractometers. In the diffractometer the relationship between $\theta$ (the angle between the direction of the incident beam and the specimen surface) and $2\theta$ (the angle between the directions of incident beam and the diffracted beam) is maintained throughout the analysis. The angle $2\theta$ of maximum intensity is called the Bragg angle. $r_s$ and $r_d$ are fixed and equal and define the diffractometer-or measuring circle in which the specimen is always at the centre. The geometry is called $\theta - 2\theta$ geometry if the tube is fixed and the rotation of the specimen and receiving slit are
coupled in a ratio $\theta$ : $2\theta$. It is called $\theta$ - $\theta$ geometry if the specimen is fixed and both the tube and receiving slit rotate at an equal angle $\theta$. During rotation of the components the radius of the focusing circles changes.

Relation for the scattering angles is given by the Braggs equation:

$$2d \sin \theta_n = n\theta$$

![Figure 3-3. Bragg-Brentano geometry](image)

GIXRD

X-ray diffraction measurements of "thin" (1-1000 nm) films using conventional $\theta/2\theta$ scanning methods generally produces a week signal from the film and an intense signal from the substrate. One of the ways to avoid intense signal from the substrate and get stronger signal from the film itself is to perform a $2\theta$ scan with a fixed grazing angle of incidence, popularly known as GIXRD. The fixed angle is generally chosen to be slightly above the critical angle for total reflection of the film material. [60]

The Rigaku Ultima III high resolution X-ray diffraction (XRD) instrument is used. Various applications such as in-plane and normal geometry phase identification, quantitative analysis, lattice parameter refinement, crystallite size determination and depth-controlled phase identification can be performed. In addition to standard Bragg Brentano geometries,
the system is capable of grazing incidence diffraction (GIXRD), transmissive and reflective small-angle X-ray scattering (SAXS).

Instrument Specifications:

Generator: Cu target with a rated tube voltage of 20-60 kV operated at 40 kV and 44 mA

Detector: Scintillation Counter detector

Goniometer: In plane arm with a radius of 285 mm; scanning modes of theta S, theta d and theta S/theta d coupled can be used with a minimum step size of 0.0001 degrees

Optics: There is automatic alignment of tube height, goniometer, optics and detector. The Divergence, Scattering and Receiving slits are fixed or auto variable. Soller slits - incident beam and diffracted beam 0.5 and 5 degrees

*Principles of XRD*

X-ray diffractometers consist of as mentioned earlier consist of a X-ray tube, a sample holder, and an X-ray detector. X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being $K_\alpha$ and $K_\beta$. $K_\alpha$ consists, in part, of $K_{\alpha_1}$ and $K_{\alpha_2}$. $K_{\alpha_1}$ has a slightly shorter wavelength and twice the intensity as $K_{\alpha_2}$. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. $K_{\alpha_1}$ and $K_{\alpha_2}$ are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuK$_\alpha$ radiation = 1.5418 Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the
intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to the computer.

3.4 Raman Spectroscopy

Raman Spectrometer can be used for chemical identification, characterization of molecular structures, effects of bonding, stress on a sample and determination of crystallographic orientation of a sample. The intensity of spectral features in is directly proportional to the concentration of the particular species. In this technique the sample is illuminated with monochromatic light and using a spectrometer to examine light scattered by the sample. At the molecular level photons can interact with matter by absorption or scattering processes. Scattering may occur either elastically, or inelastically. The elastic process is termed Rayleigh scattering, while the inelastic process is termed as Raman scattering. The electric field component of the scattering photon perturbs the electron cloud of the molecule. Raman scattering occurs when the system exchanges energy with the photon and the system subsequently decays to vibrational energy levels above or below that of the initial state. The frequency shift corresponding to the energy difference between the incident and scattered photon is termed the Raman shift. Depending on whether the system has lost or gained vibrational energy, the Raman shift occurs either as an up- or down-shift of the scattered photon frequency relative to that of the incident photon. The down-shifted and up-shifted components are called the Stokes and anti-Stokes lines respectively. A plot of detected number of photons versus Raman shift from the incident laser energy gives a Raman spectrum. Crystals compose of molecules with specific vibrational energy levels,
instead the crystal lattice undergoes vibration. These macroscopic vibrational modes are called phonons.

There are two types of vibrational spectroscopy, which are the dispersive Raman spectroscopy and Fourier Transform (FT) Raman spectroscopy.

---

**Figure 3-4.** The working of a FT-spectrometer

The FT-Raman spectroscopy in Figure 3-4 uses an interferometer to produce an interferogram, which encodes the unique frequencies of the Raman scattering into a single signal. The signal is measured very quickly, making signal averaging fast and accurate. The interferometer employs a beam splitter optimized for near-infrared (NIR) radiation, which divides the incoming Raman scatter into two optical beams, one transmitted and one reflected. The reflected beam travels to and reflects off of a flat fixed mirror. The transmitted beam travels to and reflects of a flat moving mirror, which has a constant frequency and fixed motion. The two beams recombine at the beam splitter. Depending on
their path difference, the two beams constructively and destructively interfere with each other. Constant frequency and fixed motion of the moving mirror modulates the interference pattern. The resulting interferogram has the unique property that every data point (a function of the moving mirror position) has information about every frequency of the Raman scatter collected from the sample.

In Dispersive Raman spectrometers Figure 3-5, lasers are used as a photon source due to their highly monochromatic nature, and high beam fluxes. This is necessary as the Raman effect is weak, typically the Stokes lines are $\sim 10^5$ times weaker than the Rayleigh scattered component. In the visible spectral range, Raman spectrometers use notch filters to cut out the signal from a very narrow range centered on the frequency corresponding to the laser radiation. Most Raman spectrometers for material characterization use a microscope to focus the laser beam to a small spot ($<1$-$100 \mu$m diameter). Light from the sample passes back through the microscope optics into the spectrometer. Raman shifted radiation is

![Schematic diagram of a micro-Raman spectrometer.](image)
detected with a charge-coupled device (CCD) detector and a computer is used for data acquisition and curve fitting. These factors have helped Raman spectroscopy to become a very sensitive and accurate technique.

The Jobin Yvon Horiba Confocal Raman Spectrometer has been used to obtain the vibrational spectroscopy of our samples. This is a dispersive Raman spectrometer. The Raman spectrometer includes the following specifications:

- He-Ne laser with line excitation at 632 nm and 785 nm diode laser
- Diffraction grating of 1800 g/mm and 600 g/mm
- Confocal pinhole adjustable from 0 to 1500 & micron
- Olympus BX41 microscope with objectives 10x, 50x and 100x
- CCD detector and optical imaging that enables to focus on individual particles as small as 10 microns in diameter.

### 3.5 Electrical Measurements

The following types of electrical measurements are of interest to this project:

- Photovoltaics (PV) characterization
- I-V characteristics
- Resistivity /Four probe measurement
- Hot probe measurement
3.5.1 Photovoltaic (PV) characterization

As-deposited and annealed thin films of both compositions with thickness of 1.2µm, deposited on conducting glass substrates (CTO), were used to measure open circuit voltage, \( V_{OC} \), under incandescent-bulb illumination close to 1.0 AM. The thin films turned out to have a significant concentration of pinhole defects, which made such electrical measurements very difficult due to shorting. The films were exposed to light through the bottom transparent contact, whereas a top (i.e. back) contact of somewhat resistive conductive polymer was used, in order to circumvent the effects of current leakage through shunting entities that become detrimental for a simple metal contact. This is the reason why other types of back contacts (such as silver or carbon conducting paste, vacuum-deposited Cu or Al, and other) did not work well. The conducting polymer does not cover the film surface completely and therefore does not shunt the chalcogenide film.

Open circuit voltage (\( V_{OC} \)) measurements were done on the thin films deposited on the transparent conducting substrate. The Figure 3-6 above shows the set-up used to

Figure 3-6. Set-up for performing PV measurement. Inset to the right is a top view of the sample.
perform the PV measurements of the films. The top view enlarged version of the sample is also shown in the figure. As it seen there are many pin-holes in the sample. Avoiding these pinholes while performing the measurements is difficult. If a contact created, overlaps these pinholes the contacts are shorted giving almost zero open circuit voltage. The light source used to illuminate the sample is a 50W incandescent light bulb. The light source illuminates the thin film; and the corresponding open circuit voltage \( V_{oc} \) is measured using a digital multimeter.

3.5.2 \textbf{I-V characteristics}

The I-V characteristics of the thin films were obtained using a Keithley 2410 sourcemeter. The sourcemeter was interfaced with the computer using the GPIB configuration which is the default set for this sourcemeter. A program written in LabView 8.0 was used to control the device. Range of current to be sourced to the thin film is defined in the program and the number of points. The step size was calculated accordingly. The readings obtained were saved as a text file. A similar set–up as shown for photovoltaic measurement was used for the I-V measurement as well. The probes were connected to the the Keithley sourcemeter instead of the multimeter. To obtain the readings current was sourced and the corresponding voltage was measured.

![Figure 3-7. A collinear four point probe](image-url)
3.5.3 **Four Probe Measurements**

The four probe measurement is mainly used to obtain the sheet resistance (see Figure 3-7). The sheet resistance is given as:

\[ R_s = \frac{\rho}{t} = 2 \pi \frac{s}{l} F \frac{\Delta V}{I} = 4.532 \frac{\Delta V}{I} \]

Where, \( \rho \) = resistivity

\( t \) = film thickness

\( s \) = probe spacing

\( \Delta V \) = voltage difference between 2 and 3

\( F \) = correction factor

![Four point probe operation circuit](image)

Figure 3-8. Four point probe operation circuit

The resistivity of the film can be obtained from the sheet resistance. Thus the conductivity is obtained.

\[ \sigma = \frac{1}{\rho} \]

There are several resistances that are considered. The probe resistance can be determined by shorting the two probes and measuring the resistance. The contact resistance \( R_c \) is due to the interface between the tip of the probe and the surface of the film and when
the current flows it spreads out in the film, there is spreading resistance $R_{sp}$. These are shown in Figure 3-8. The sheet resistance is given by $R_s$.

3.5.4 **Hot Point Probe Measurement**

![Figure 3-9 Hot probe measurement basics](image)

Hot point probe measurement is a technique commonly used to determine whether the semiconductor is p-type or n-type. Carriers diffuse more rapidly near the hot probe. This leads to a particle current away from the hot probe and an electrical current away (p type) or towards (n-type) the hot probe.

3.6 **Thin Film Preparation**

Several techniques thin film preparation techniques have been discussed in the previous chapter. Some of which are the thermal evaporation, RF sputtering, chemical bath deposition and flash evaporation technique. The thermal evaporation technique has been used in this project for the preparation of Ge-Se-Bi and Ge-Se-Zn thin films.

3.7 **The synthesis of our Bi$_4$Ge$_{20}$Se$_{76}$ bulk glass**

Proper amounts of high-purity Ge, Se and Bi, or Ge, Se, and Zn, precursors, were sealed in pre-cleaned, evacuated quartz ampoules and then heated in a temperature-controlled furnace, upon following a specially designed temperature profile, to react the
precursors. The bulk Bi$_4$Ge$_{35}$Se$_{76}$ and Zn$_5$Ge$_{20}$Se$_{75}$ glasses were then obtained by the conventional melt quench technique (see Chapter 3). The bulk samples were then used to prepare thin film by thermal evaporation technique.
Chapter 4
Results and Discussion

4.1 DSC results on bulk and thin-film Ge-Se-Bi material

We performed DSC on several samples of the Ge-Se-Bi bulk glass, as well as thin film material. From the DSC results we identified the glass transition and determined the crystallization temperature of the glass. Using the information on the crystallization temperature obtained from these DSC experiments, we then decided on what annealing temperature to use in order to try to induce partial crystallization in the films. Any small amount of crystalline phase in the material may show as a weak small melting peak in the DSC data. Three samples of different weights were prepared. Figure 4-1 shows DSC data on three different bulk samples as indicted in the caption and explained below, the first panel showing the prevailing typical case.

4.1.1 DSC of Ge-Se-Bi bulk sample

Bulk and thin film samples of Ge-Se-Bi were studies using DSC. These samples were sealed in aluminum pans. The DSC run was performed between 80-400°C at the rate of 20°C/min

- A glass transition is observed close to 225°C in all the three samples during the first run. This glass transition temperature is very close to the transition temperature of Ge_{21}Se_{79}. Since the Ge-Se-Bi glasses are composed of a large portion of Ge-Se in the system, the glass transition being close to the Ge-Se system is reasonable.
Beyond 320°C the Ge-Se-Bi glass begins to crystallize, up to about 400°C the glass seems...
to crystallize completely. At about 320°C c-Bi2Se3 is formed. As discussed in section 2.1.1 c-Bi2Se3 and GeSe2 are formed at 320°C and 370°C respectively. Thus up to 400°C the glass has completely crystallized.

- At about 260°C a small peak is observed in the 3rd DSC. It may be due to melting of some structures which are already present in the bulk glass during the formation of the glass. This temperature is very close to the melting temperature of Se-chains.

- During the second run of the bulk samples, again a glass transition is observed at the same temperature which is at around 225°C. However the glass transition observed during the second run is very weak. We assume that during the first run the glass may have not crystallized completely and a very small fraction of the glass which has not crystallized shows the weak glass transition.

4.1.2 DSC of Ge-Se-Bi Thin Film

To study the DSC of Ge-Se-Bi thin films samples were prepared by peeling off from the glass substrate. The flakes obtained from were sealed in an aluminum pan. The DSC was performed from 120-400°C at the rate of 10°C/min (see Figure 4-2).

- The DSC obtained from the thin film also shows a glass transition at about 225°C like the bulk samples. But the glass transition here is very weak compared to that seen in the bulk glass. During the second run in the bulk sample we have seen that for smaller fraction of the glass remaining, the glass transition gets weaker. The thin film sample in the pan is much less compared to the bulk sample. Thus the glass transition of the thin film is much weaker compared to that of the bulk glass which is seen during the first run.
The thin film begin to crystallize at a much lower temperature i.e., at about 260°C. Compared to the bulk glass the thin film crystallizes slowly up to 350°C. This is because the pan consist of very small flakes of Ge-Se-Bi which are not in very good thermal contact within the pan, thus the heat distribution is not even. The particles which are close to the surface of the pan tend to crystallize first then the sample further from the surface towards the center of the pan crystallize. Thus, for a wide range of temperature the crystallization is observed.

Figure 4-2. DSC of Ge-Se-Bi thin film (0.45um); Sample weight :3.93mg; Total weight: 28.15mg; Run 1: 120-400°C at 10°C/min

The glass transition in the bulk and the thin film occurs at the same temperature. However the crystallization and the crystalline behavior differ due to the different nature of this thin film sample. Generally, the thin film material represents a much less relaxed and
“defective” state (due to voids, higher concentration of wrong and dangling bonds etc.) of the original glass material. Therefore, on one hand the thin film material would contain a higher concentration of crystallization sites (defects within the material and at the substrate interface), but the growth of the crystals (i.e. from any crystalline nuclei or nanocrystals) may be inhibited by the same defective material morphology. In addition, the film flakes are in a rather poor thermal contact with each other and with the Al pan, which therefore significantly impedes the proper DSC experiment and may have affected the results somewhat. However, we are confident that the main result related to identifying presence and the location of the glass transition is little affected, and we believe this result is of substantial importance to understanding the nature of the thin films of such materials.

4.1.3 DSC of Bulk sample of Ge-Se-Zn

The Figure 4-3 shows the DSC for the Ge-Se-Zn bulk sample. The bulk material was sealed in an aluminum pan and a DSC run was performed from 50°C-350°C increasing the temperature slowly at the rate of 20°C/min. our observations from the DSC obtained are as follows:

- A weak glass transition is observed close to 250°C, this temperature is very close to that of Ge-Se glass transition temperature.
- Up to 350°C we do not observe any crystallization in the sample. It is quite reasonable to accept this since ZnSe have a very high crystallization temperature which is close to about 450°C.
• The absence of any endothermic peak in the DSC also confirms the absence of any crystal structures in the bulk material.

![DSC data on Zn-Ge-Se bulk material](image)

Figure 4-3. DSC of Ge-Se-Zn bulk samples

4.2 Scanning Electron Microscopy (SEM)

To study the nature of the films surface, we acquired the top view SEM images of the films. These images were obtained for a voltage of 20 kV and for different scale of 5 μm, 3 μm and 1 μm. SEM for 0.45 μm and 1.2 μm of Bi-Ge-Se and 1.3 μm Zn-Ge-Se films which were as deposited and annealed were taken. The purpose was to observe any physical changes in the film surface after they were annealed and if there was any damage caused to the film. From the SEM we are notice the difference in the film surface for different thickness. These results have been compared and discussed below:
4.2.1 Ge-Se-Bi 0.45µm film: as-deposited and annealed at 210°C

Figure 4-4 Top view SEM images of 0.45 µm Ge-Se-Bi as-deposited and annealed thin films. the images are taken using 20kV energy for different magnification of the film at a working distance of 14-15 mm (a) image of as-deposited film for a scale of 5 µm (b) image of as-deposited film for a scale of 3 µm (c) image of as-deposited film for a scale of 1 µm (d) image of annealed film for a scale of 5 µm (e) image of annealed film for a scale of 3 µm (f) image of annealed for a scale of 1 µm.
Figure 4-4 shows the top view SEM image of the Ge-Se-Bi 0.45 µm thin films annealed and untreated. These films were deposited by thermal evaporation on a glass substrate. The films were annealed at 210°C in a N₂ atmosphere for 5mins.

- Figures a, b & c are the SEM images for different areas of the untreated films. The surface of these films has a coarse grain like morphology. The typical grain size seen in the 0.45µm films is ~300nm.

- Due to the uneven surface of the films and the defects, it may get difficult to create a good contact with the surface of the films while performing any sort of electrical measurements.

- The film thickness also varies throughout the film, since many electrical properties of the material are thickness dependent. The electrical measurements may also vary throughout the film.

- On annealing the samples, the surface looks somewhat even compared to that of the untreated films. Figures d, e and f are the SEM images for the films annealed at about 210°C. However it appears that there are small craters formed in the film after annealing.

- Due to the craters it is possible the substrate (TCO) of the film is exposed, which may get shorted giving almost zero voltage reading while performing the electrical measurements.
4.2.2 Ge-Se-Bi 1.2µm film: as-deposited and annealed at 210°C

Figure 4-5 Top view SEM images of 1.2 µm Ge-Se-Bi as-deposited and annealed thin films. The images have been acquired using voltage of 20 kV for different magnification of the film at a working distance of 14.9 mm (a) image of as-deposited film for a scale of 5 µm (b) image of as-deposited film for a scale of 3 µm (c) image of as-deposited film for a scale of 1 µm (d) image of annealed film for a scale of 5 µm (e) image of annealed film for a scale of 3 µm (f) image of annealed for a scale of 1 µm.
In Figure 4-5 we see the SEM image of the Ge-Se-Bi 1.2µm as-deposited and annealed thin film. The films are deposited BK-7 glass and annealed up to 210°C in N₂ atmosphere for about 5 mins.

- Both the films i.e the untreated and the annealed films have a granular surface. However compared to the 0.45 µm untreated films these films have a comparatively even surface.

- After the films are annealed at 210°C we see bright white spots all throughout the film. This may be Bi. The Bi is content may be higher towards the surface of the film. These white spots are missing from the thinner films, so we assume that Bi is spread homogenously within the film.

- Due the higher content near the surface of the film obtained there may be some variation in the electrical measurements obtained from these films.

- The typical grain size seen in the 1.5µm films is ~150nm. As seen in the images a and d the surface of these films have some defects which make it difficult to obtain the electrical measurements.
4.2.3 Ge-Se-Zn 1.2µm film: as-deposited and annealed at 300°C

Figure 4-6 Top view SEM images of 1.5 µm Ge-Se-Zn as-deposited and annealed thin films. The images have been acquired using voltage of 20 kV for different magnification of the film at a working distance of 14.9 mm (a) image of as-deposited film for a scale of 5 µm (b) image of as-deposited film for a scale of 3 µm (c) image of as-deposited film for a scale of 1 µm (d) image of annealed film for a scale of 5 µm (e) image of annealed film for a scale of 3 µm (f) image of annealed film for a scale of 1 µm.
Figure 4-7 shows the top view SEM images of the Ge-Se-Zn films. These images are for untreated and annealed films of 1.5 µm thickness. These films are also deposited on BK-7 glass by thermal evaporation. The annealing of the films was performed in N\textsubscript{2} atmosphere for approximately 5 minutes.

- The a,b and c of Figure 4-8 are the SEM of the as-deposited films. Over a larger area (5 µm and 3 µm) very bright white spots are observed. It is speculated that these bright spots may be Zn which is not fully networked in the Ge-Se glass matrix. These spots are spread throughout the film. But in smaller region of about 1µm the spots are missing.

- Compared to the Bi-Ge-Se films these films seem to have a much level surface. Also the grain size in the Zn-Ge-Se films is much smaller ~100nm.

- The annealed films which are the d, e and f images also look very similar to that of the untreated film. However the bright spots in the annealed films are smaller than those seen in the untreated films. Also the number of the spots seen in the same area size is much more than that of the untreated films. Also, these films have some defects.

4.3 Energy Dispersive Spectroscopy (EDS)

We obtain the EDS data to verify the composition of the thin films. From different areas of the film we acquired the EDS, to determine the homogenous nature of the film. By obtaining the EDS for films of different thickness we can also determine if there is any variation in the composition of the film with the varying thickness. The EDS data for different thickness of Bi-Ge-Se films and Zn-Ge-Se annealed and untreated films have been tabulated below:
4.3.1 **EDS data for Ge-Se-Bi 1.2µm, as-deposited and annealed thin films**

Table 4-1 EDS data for Bi-Ge-Se 1.2µm untreated and annealed thin films

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated 1</td>
</tr>
<tr>
<td>Ge</td>
<td>22.29</td>
</tr>
<tr>
<td>Se</td>
<td>68.94</td>
</tr>
<tr>
<td>Bi</td>
<td>8.76</td>
</tr>
</tbody>
</table>

The table above gives the EDS data for the 1.2µm Ge-Se-Bi untreated and annealed films. We see that the Bi content in these films is high. As we have observed from the SEM image of these films, it appears that Bi is very close to the surface of the film. Thus while obtaining the EDS data, most of the signal may have been picked from the Bi, due to which the data obtained may show a higher Bi content.

4.3.2 **EDS data for Ge-Se-Bi 0.45µm, as-deposited and annealed thin films**

Table 4-2 EDS data for 0.45µm Bi-Ge-Se annealed and untreated thin films

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated 1</td>
</tr>
<tr>
<td>Ge</td>
<td>23.48</td>
</tr>
<tr>
<td>Se</td>
<td>76.51</td>
</tr>
<tr>
<td>Bi</td>
<td>-</td>
</tr>
</tbody>
</table>

In Table 4-2, we have the EDS data for the 0.45 µm Bi-Ge-Se films which are untreated and annealed to 210°C. These films consist of about 4% Bi. From the SEM image of this film we see some white dots in the Figure 4-5(c) and (f) we speculate these to be Bi, but unlike the 1.2 µm films, the amount of Bi was too small to be detected by the EDS method. We assume that in the 0.45 µm film the Bi content is distributed throughout the
film, but since the ratio of Bi in compared to Ge and Se is very low the EDS data signal from Bi is very weak.

4.3.3 **EDS data of Ge-Se-Zn as-deposited and annealed films.**

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated 1</td>
</tr>
<tr>
<td>Ge</td>
<td>23.48</td>
</tr>
<tr>
<td>Se</td>
<td>76.51</td>
</tr>
<tr>
<td>Zn</td>
<td>-</td>
</tr>
</tbody>
</table>

The table above gives the EDS data of the Zn-Ge-Se thin films. The absence of Zn in the EDS data is due to its very small fraction of Zn as compared to Ge and Se. The Zn content in the film is around 2.3% which is assumed to have spread homogenously throughout the film. It is possible the signal may have been collected from a region which has no Zn or the signal from the Ge and Se may have suppressed the weak signal from Zn. However presence of Zn is confirmed from the Raman spectra of the film.
4.4 X-Ray Diffraction

4.4.1 XRD for Ge-Se-Bi Thin Film

The XRD of the sample was obtained in order to examine the crystallinity of the original and the annealed thin films and determine the nature of any crystalline phase observed. The peak width seen in the XRD is, most generally, inversely proportional to the crystallite size. Thus the size of the crystallites formed can be determined, in principle. The relation between the peak width and crystal size is given by:

\[ L = \frac{K\lambda}{B(2\theta)\cos\theta} \]

Using the above relation the size of the nano-crystal formed in the film when annealed at different temperature have been calculated in Table 4-4.

![Figure 4-7 XRD of Ge-Se-Bi thin film](image-url)
Table 4-4 Size of the nano-crystals formed in the Bi-Ge-Se thin films annealed at different temperatures, obtained using the 29deg peak from the XRD pattern in Figure 4 8

<table>
<thead>
<tr>
<th>Crystallite size (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
</tr>
<tr>
<td>Film at 250°C</td>
</tr>
<tr>
<td>Film at 300°C</td>
</tr>
</tbody>
</table>

An XRD patterned obtained from Ge-Se-Bi 0.45µm thin films is shown in Figure 4-7. The data correspond to as-deposited thin films, as well as films, annealed at 210°C, 250°C and 300°C. These data were collected in a GIXRD configuration of the experiment, in which the beam was almost parallel beam to the film surface, thus maximizing the signal. A relatively slow scan in the range 10-70 deg was performed at a speed of 2deg/min. The following represents a summary and a brief discussion of our observations.

- The as-deposited film is amorphous/glassy in nature, since no sharp peaks are observed. However it is assumed that there could be some crystallization which is not very strong, due to the broad peak at about 29.5 deg and 40 deg. The size of the crystals formed can be determined by the peaks’ width.

- In the XRD of the sample annealed at 250°C the peaks at 29.5 and 40 deg become sharper, two more tiny features at 42 and 44 deg are observed which are assumed to be cBi₂Se₉. Thus the films annealed at two fifty tend to have crystallized partially forming nanosized crystals. From the DSC data also we have seen that the thin films begin to crystallize closely near 250°C.
When the film is annealed at 300°C, the peaks that were observed in films annealed at 250°C are very strong. Here most of the Bi is assumed to have crystallized along with some crystallization of GeSe₂ which is assumed due to the small peak at 18 deg. Thus the film annealed at 300°C is almost crystallized completely.

The strongest peak which is at 29.5 deg matches very closely with (015) reflection of a hexagonal Bi₂Se₃. The c-Se can also be speculated at 29.5 deg. However since the bond energy of Bi₂Se₃ is larger than that of Se we assume that the peak at 29.5 deg is due to the presence of c-Bi₂Se₃.

Since the films consist of only about 4% of Bi and assuming that most of the Bi have crystallized forming c-Bi₂Se₃, the rest of the material would most likely be amorphous with small crystals of GeSe₂ and Se.

4.4.2 XRD for Ge-Se-Zn Thin Film

Figure 4- shows the XRD data, obtained from Ge-Se-Zn thin films. These are for the as-deposited and thin films annealed close to 300°C, and again, the observations and their brief discussion is given in a bullet form below.

- The XRD of both the, deposited and the annealed film is very similar.
• No sharp crystallization peaks were observed in the annealed films. Thus it can be assumed that at 300°C no crystal structures are formed in the Ge-Se-Zn films.

• At about the 17 deg, there is a small peak that appears to be a little sharper compared to the as-deposited film. This can be assumed to be due to the presence of weak GeSe$_2$ structures. At about 300°C the GeSe$_2$ begins to crystallize. So when the film is annealed close to 300°C the GeSe$_2$ begin would have just started to crystallize, thus imperfect GeSe$_2$ crystals might be present.

• The broad peak between 20-30 deg is signal collected from the substrate.
4.5 Raman Spectroscopy

4.5.1 Raman spectroscopy of Ge-Se-Bi Thin Film

Raman spectra of bulk, as-deposited and annealed films at 240°C and 290°C were obtained and the results are shown in Figure 4-9 below. Our observations are given in bullet form.

- From the Raman data obtained, the bulk spectra shows a lineshapes related to Ge-Se glass, with GeSe$_4$ tetrahedron mode which is around 190 and 210 cm$^{-1}$ and Se$_n$ mode at 260 cm$^{-1}$.
- The minute peaks observed at about 175 cm$^{-1}$ can be attributed to a Bi$_2$Se$_3$ phase.

Figure 4-9 Raman spectroscopy of Ge-Se-Bi bulk glass, as-deposited film and thin films samples annealed at 240°C and 290°C.
• At 115 cm\(^{-1}\) and 135 cm\(^{-1}\), the two low wave number peaks are artifacts which appear due to Raman system excitation filtration. These peaks are seen in all the spectra.

• The Raman spectra of the bulk sample are quite different from the thin films. However the spectra of the thin film annealed at 240\(^\circ\)C does not differ much from the as deposited film. At 300\(^\circ\)C the film appears to be more crystalline.

Presence of imperfect BiSe nanocrystalline phase can be speculated even though GeSe is higher in concentration in the film annealed at 240\(^\circ\)C and the as-deposited film.

In the films annealed at 290\(^\circ\)C the peaks at 175 cm\(^{-1}\) and 130 cm\(^{-1}\) tend to have become stronger. Thus the imperfect BiSe could have become perfect crystals or peak at 175 cm\(^{-1}\) could also be due to the presence of GeSe structures.

4.5.2 Raman Spectroscopy of Ge-Se-Zn Thin Film

The Figure 4-10 shows the Raman spectra of Ge-Se-Zn annealed and untreated thin films. The Raman of the annealed and the thin film are very similar. It is quite reasonable to accept this, since even the SEM images and the XRD of these films have not varied much.

• The double peak which is around 202 cm\(^{-1}\) and 219 cm\(^{-1}\) correspond to Ge-Se. In the absence of Zn both the peaks are well defined and sharp. However here we see that the peak at 219 cm\(^{-1}\) has almost diminished.

• The peak at 202 cm\(^{-1}\) is due to the symmetric bond stretching of GeSe\(_4\) clusters, and 219 is assigned to rings of five to eight Ge which are interconnected with Se.

• Since the intensity of the peak at 219 cm\(^{-1}\) is weaker than that at 202 cm\(^{-1}\), we assume that the introduction of Zn in the Ge-Se system has affected Ge-Se interconnect, forming ZnSe structures. At around 251 cm\(^{-1}\), the peak which is not very sharp is related to the presence of ZnSe and Se-Se structures.
• Close to 500 cm\(^{-1}\) there is a weak peak which correspond only ZnSe. The peaks at 251 and 500 cm\(^{-1}\) correspond very closely to the Raman of ZnSe in 5. This is why we assume the peak at 251 cm\(^{-1}\) is partly due to ZnSe.

Thus we assume that in the Ge-Se-Zn glass, the Ge-Se network is disturbed by the presence of Zn but there are no perfect crystals of ZnSe formed. The structures on ZnSe that are formed are very weak. The formation of these weak structures of ZnSe may be due to the low Zn content in the films.

Figure 4-10 Raman spectroscopy of Ge-Se-Zn annealed and untreated thin film
4.6 Electrical Measurements

The electrical measurements were performed for the Bi-Ge-Se and Zn-Ge-Se thin films deposited on the TCO. We tried to measure the open circuit voltage, conductivity, I-V curve and determining the carrier type of the material. Our films had a significant number of defects - mainly scratches, holes and pinholes, therefore all electrical measurements performed on these films were challenging. We speculate the variations observed are due to the improper contacts created between the film surface and the TCO. A loose contact may result in a very high voltage drop whereas a very firm contact may penetrate through the film causing a short circuit. The results obtained from our electrical measurements are discussed below:

4.6.1 I-V Characteristic of Ge-Se-Bi Thin Film

Figure 4-11 Switching behavior of a 0.45 µm Ge-Se-Bi thin film
• I-V curve of the a-Ge-Se-Bi thin films shows the characteristic of a memory switch. Up to the threshold voltage it demonstrates an ohmic behavior i.e., it remains in the high resistance OFF state. After which the voltage switches back to the low resistance ON state.

• The threshold voltage \( V_T \) varies linearly with the thickness of the film.

![Switching behavior of a 1.2 µm Ge-Se-Bi thin film](image)

**Figure 4-9** Switching behavior of a 1.2 µm Ge-Se-Bi thin film

• For the 0.45 µm thin film the switching voltage during the first run is about 1.3 V as seen in Figure 4-11. Whereas for the 1.2 µm thin film the switching occurs at about 4.5 V (Figure 4-9).

• During the second and third runs there is no switching observed, the slope of the I-V remains unchanged keeping the material in the low resistance ON state. Since there is no switching observed in the material after the first run, these can be said to behave as memory switches as discussed in the electrical properties of Ge-Se-Bi in Section 2.1.3.
However a good switching is not observed everytime. The switching may vary depending on the contact created between the film and electrode. In the case of a loose contact, the switching may include a lot of noise.

In the Figure 4-10, at about 1.7 V there appears to be a switching. But while the voltage reverts back, at about 0.6 V the voltage rises again to approximately 1.2 V before it switches completely to the low resistance state. This may be due to localized melting at the contact. The temperature at the contact of the film is raised due to joule heating. This heating may melt the film. We believe after melting there may be crystallization immediately again which causes the fluctuation is switching.

In a case when creating the contact if the electrode penetrates through the film, then the contact is shorted to the conducting oxide raising the voltage abruptly to the compliance voltage.

The switching may fail to occur if the conducting path is not formed at the typical switching voltage. In this case if the current passed is increased, the switching may occur.
at a higher voltage for the same film thickness. The conducting path in these films is formed by crystallization between the contact and the TCO.

4.6.2 I-V Characteristic of Zn-Ge-Se Thin Film

Figure 4-11 Switching behavior of a 1.2µm Ge-Se-Zn thin film

The Figure 4-11 shows the switching behavior of the Zn-Ge-Se thin film. We tried to measure this behavior from several points on the film, but we observed the switching behavior only for some points. These films switched at approximately 2.05 V.

4.6.3 Photovoltaic (PV) characterization

Open circuit voltage was measured for the as-deposited and the annealed films of Ge-Se-Bi and Ge-Se-Zn of 0.45 µm and 1.2 µm thin films.

Ge-Se-Bi Thin Films

The $V_{oc}$ measurement results showed the following:

- The *as-deposited* Ge-Se-Bi of both 1.2 µm- and 0.45 µm-thick films exhibited substantial $V_{oc}$ values: up to 100 mV.

- 1.2µm-thick Ge-Se-Bi films, annealed in dry N$_2$ atmosphere for 5 min at temperatures in the range 200 – 240°C showed $V_{oc}$ values that were comparable or slightly higher than the
V_{oc} values measured before the annealing. However, the polarity of the V_{oc} voltage was opposite to the polarity of their V_{oc} before the annealing. This observation was reproduced with several annealed samples, but not with all of them.

- The reversal of the polarity upon annealing was not observed in any of the 0.45 µm-thick films.

The open circuit voltage for the 0.45 µm and 1.2 µm films as-deposited and annealed at 210°C and 270°C has been measured, we obtained the following results:

<table>
<thead>
<tr>
<th>Film Thickness</th>
<th>As-deposited</th>
<th>Annealed at 210°C</th>
<th>Annealed at 240°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45 µm</td>
<td>30-100mV</td>
<td>5-50mV</td>
<td>0.2-0.4mV</td>
</tr>
<tr>
<td>1.2 µm</td>
<td>100mV</td>
<td>&gt;100mV (rev. pol)!!!</td>
<td></td>
</tr>
</tbody>
</table>

- When the films are annealed, nanocrystals of Bi_{2}Se_{3} are expected to be formed in a Ge-Se glass matrix. These crystals are spread homogenously throughout the film. The size of the crystals formed increases as the temperature is increased.
- The Bi_{2}Se_{3} crystals have a rhomboderal structure and are thermoelectric material, thus there is an uncompensated electric dipole. These nanodipoles are randomly distributed throughout the film. We assume these crystals are in the direction of the growth of the film contributing to the built electric field, this field will add up to any potential at the TCO/ chalcogenide interface and the will also add to the field responsible for the photo generated carriers.

Ge-Se-Zn Thin Films

The Ge-Se-Zn films did not show any significant voltage.
4.6.4 **Conductivity: Four probe measurements**

**Ge-Se-Bi Thin Films**

The conductivity measurements were carried out for the as-deposited and the annealed film of 0.45 µm thickness. At several points on the film the conductivity was measured. The following readings were obtained:

Table 4-5 Conductivity measurements of 0.45 µm Ge-Se-Bi films at different points on as-deposited and annealed films

<table>
<thead>
<tr>
<th>GeSeBi</th>
<th>As-deposited σ (S/cm)</th>
<th>Annealed at 240°C σ (S/cm)</th>
<th>Annealed at 270°C σ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.47x10⁻³</td>
<td>0.6869</td>
<td>63.13x10⁻³</td>
</tr>
<tr>
<td>2</td>
<td>38.83x10⁻³</td>
<td>0.7198</td>
<td>81.74x10⁻³</td>
</tr>
<tr>
<td>3</td>
<td>33.48x10⁻³</td>
<td>0.8143</td>
<td>75.36x10⁻³</td>
</tr>
<tr>
<td>4</td>
<td>32.26x10⁻³</td>
<td>0.7579</td>
<td>64.59x10⁻³</td>
</tr>
<tr>
<td>5</td>
<td>31.14x10⁻³</td>
<td>0.6775</td>
<td>59.54x10⁻³</td>
</tr>
</tbody>
</table>

- The as-deposited film and the film annealed at 240°C and 270°C showed a reading throughout the film with a variation of about ±20% at different points.
- The average conductivity of the as deposited film and the film annealed at 240°C and 270°C is about 32.844x10⁻³ S/cm, 0.7313 S/cm and 68.872x10⁻³ S/cm respectively.
- We see that the conductivity of the film annealed at 270°C tends to decrease as compared to that of the film annealed at 240°C.

**Ge-Se-Zn Thin Films**

We also tried to measure the conductivity for the Ge-Se-Zn films. However these films were highly resistive. The resistivity for both the films i.e., the as-deposited and the
annealed films were about 1000 M\(\Omega\). Thus obtaining any conductivity measurements for these films was almost impossible.

4.6.5 **Hot point probe measurement**

We performed the hot point probe measurement to investigate the conductivity type of the Bi-Ge-Se and the Zn-Ge-Se films. The following results were obtained:

Table 4-6 carrier type of the Ge-Se-Bi and Ge-Se-Zn untreated and annealed films

<table>
<thead>
<tr>
<th></th>
<th>Bi-Ge-Se</th>
<th>Zn-Ge-Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>p-type</td>
<td>n-type</td>
</tr>
<tr>
<td>240(^\circ)C</td>
<td>p-type</td>
<td>-</td>
</tr>
<tr>
<td>Close to 300(^\circ)C</td>
<td>n-type</td>
<td>n-type</td>
</tr>
</tbody>
</table>
Chapter 5
Conclusions

5.1 Bi-Ge-Se glasses and films

- Thin films of Ge-Se-Bi (0.45 µm and 1.2 µm) and Ge-Se-Zn (1.3 µm) were prepared by a thermal evaporation technique.

- From our DSC results we see that the thermal parameters of the thin films do not vary much from that of the bulk samples. The glass transition temperature for both the samples is at about 220°C, and the crystallization temperature for the thin film is slightly lower than that of the bulk sample. The thin films do not show a glass transition during a second run of DSC.

- When a thin film sample is annealed at a temperature which is below the crystallization temperature, but at or above the glass transition temperature, nano-crystals of Bi$_2$Se$_3$ appear to form. We speculate that they are homogenously spread throughout the film.

- At a temperature which is higher or equal to the crystallization temperature the films tend to crystallize completely forming structure of Ge-Se$_2$, Ge-Se and Bi$_2$Se$_3$.

- For the 0.45 µm and 1.2 µm film an open circuit voltage ($V_{OC}$) of up to 100 mV can be measured upon illumination. Our interpretation of these intriguing results is the following. This voltage measured may solely be due to the Schottky barrier between the surface and TCO. When these films are annealed, the nanodipole align in the direction of the electric filed. Upon illumination the aligned dipoles produce a voltage of an
opposite polarity. In the 1.2 µm film this voltage is very high giving a net voltage of a large negative potential upon illumination. However in the 0.45 µm films the voltage produced by the films is not large enough to result in a negative net voltage thus the open circuit voltage measured in these films is low, ~4.5-10 mV

- The as-deposited films exhibit a memory switching behavior. For the 0.45µm film the switching is observed between 1.2-1.5 V. For the 1.2 µm films at ~4.5 V we can observe the memory switching. The annealed films do not show any switching behavior.

5.2 Zn-Ge-Se glasses and films

- Thin films of Zn-Ge-Se were deposited on TCO and BK-7 glass of 1.3 µm thickness. These films were also prepared by a thermal evaporation technique.
- The Zn content, which is about 3% in these films, does not seem to affect the Ge-Se glass properties significantly. From the XRD data we see that the Zn-Ge-Se annealed film is no different from the untreated film. Thus annealing the film up to 300°C does not cause the formation ZnSe related crystalline structures. To crystallize the glass, we may have to anneal the films to a higher temperature but the Zn-Ge-Se films cannot be annealed to a higher temperature since this will crystallize the Ge-Se glass.
- The Zn-Ge-Se glass is not very responsive to illumination, and no open circuit voltage can be measured for the untreated or annealed films. The films are highly resistive.
- These films show a memory switching behavior with a switching voltage of ~2.05 V.
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