2008

Preparation and Characterization of (GeSbTe)) Semiconductors for Phase-Change Optical Storage

Hessa Ali Humeid Al-Shamisi

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PREPARATION AND CHARACTERIZATION OF (GeSbTe) SEMICONDUCTORS FOR PHASE-CHANGE OPTICAL STORAGE

By
Hessa Ali Humeid Al-Shamisi

Supervised by
Dr. Hassan Ghamlouche
Physics Department
Faculty of Science, UAEU

Dr. Naser Qamhieh
Physics Department
Faculty of Science, UAEU

Dr. Saleh Thaker
Physics Department
Faculty of Science, UAEU

A Thesis Submitted to the Deanship of Graduate Studies in Partial Fulfillment of the Requirements for Degree of Master of Science in Materials Science and Engineering

2008
Acknowledgments

First, always and foremost, I thank almighty Allah for his blessing and for providing me the capability to successfully complete this work.

I would like to express my heartiest thanks and sincere gratitude to my supervisors, Dr. Hassan Ghamlouche, Dr. Naser Qamhieh and Dr. Saleh Thaker for their guidance, support, encouragement, patience, unlimited assistance, critical reviewing and providing me the required facilities during the work. I feel both honored and privileged to work with such a group.

Many thanks to Mr. Mohammed Elshaer (lab technician in the physics department) and Mr. Esam Attia (technician in the Central Lab Unit), for their help in preparing some experiments and analyzing the samples. Special thanks to Ms. Sadeeqa Ahmed, from the physics department, for her assistance and support.

Special appreciation is expressed to my colleagues and friends in UAE University, especially in the physics department.

No words can ever express my great gratitude and special thanks to my great family, especially my parents for their great support and my husband for his patience and great help throughout my study.
Abstract

In the last decade, the phase change optical recording based upon chalcogenide glasses has advanced remarkably at full-scale commercial applications in the form of rewritable compact disks (CD-RWs) and digital video disks (DVD-RWs). The principle of phase-change optical recording is based on a thermally induced reversible transformation between amorphous and crystalline phases. The search for recording materials possessing fast crystallization rate and long data retention has been pursued. Research results have revealed that Ge-Sb-Te compounds exhibit fast crystallization, which has been explained in terms of their single-phase structure.

In the present work, electrical properties of Ge-Sb-Te thin films using Impedance Spectroscopy, Current-Voltage, and Capacitance-Voltage techniques is presented. First, we studied the effect of the electrical contacts, deposited on top of Ge-Sb-Te films, on the measured electrical signal (Impedance Spectroscopy). To do this, three different configurations of the electrical contacts were prepared. The results show that the electrical contacts have no effect when the silver paste is placed on the gold electrodes away from the thin film under test. This guarantees no interaction between the silver paste and the film under test during the heating process. Also the results show that the order of depositing layers (material and the gold) is not important and what matters is the location of the silver paste on the gold electrodes.

Second, the Impedance Spectroscopy and Current-Voltage data shows similar resistance and relaxation frequency temperature dependence with activation energies 0.36 and 0.39 eV, respectively. Therefore the corresponding energy gap is estimated to be 0.72 eV and 0.78 eV. This result agrees with the optical gap (0.7 eV) reported in literature. This agreement confirms that Ge$_2$Sb$_2$Te$_3$ belongs to the chalcogenide family. In addition,
the I-V curves show that the amorphous-crystalline transition temperature ($T_c$) is around 135 °C.

Third, the Capacitance-Voltage measurements were performed on amorphous samples of In$_{0.3}$Ge$_2$Sb$_2$Te$_5$ and Ge$_2$Sb$_2$Te$_5$ thin films in order to study the effect of doping on the electrical properties of Ge$_2$Sb$_2$Te$_5$. The results show that inducing Indium to Ge$_2$Sb$_2$Te$_5$ decrease the capacitance of the sample as the bias voltage increases for the whole range of temperatures. However, the same behavior is observed for undoped sample (Ge$_2$Sb$_2$Te$_5$) only at temperatures close to the amorphous-crystalline transition temperature and at high applied bias voltages ($\geq 15$ volts). The behavior is attributed to the increase in electron concentration as the bias voltage and temperature increase. For In$_{0.3}$Ge$_2$Sb$_2$Te$_5$ sample, the indium can be considered as an additional source of free electrons. This would contribute to a further and significant decrease in the capacitance of In$_{0.3}$Ge$_2$Sb$_2$Te$_5$ sample, and eventually the capacitance becomes negative. The nonlinearity in the capacitance and conductivity could be related to the nucleation mechanism as the temperature becomes close to the amorphous-crystalline transition temperature. Finally in the conclusion I proposed some study to be conducted on Ge$_2$Sb$_2$Te$_5$ films.
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   "Novel preparation methods of electrical contacts in Ge-Sb-Te thin films", Applied

2. H. Ghamlouche, S. T. Mahmoud, N. Qamhieh, Sadiqa Ahmad and Hessa Al-

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CHAPTER I

INTRODUCTION

The ability to store information has been an important aspect of human development. Many events, knowledge and information in the world are preserved for future generation. Optical data storage, is one of the most successful new techniques for storing huge amounts of data [Erwin, 2006], [Libera, 1990] and [Ovshinsky, 1968]. Whereas the first optical storage products only allowed reading of the encoded information, nowadays both recordable and rewriteable storage media have been developed.

Phase-change media is a rewriteable optical storage media; recently it is used in many rewriteable products. This success is based on the discovery [Yamada, 1987] of alloys containing elements such as Ge, Sb and Te, and the forming of phase-change media to meet DVD specifications [Satoh, 2001]. Studying the characteristics of this material led to the development of three generations of optical storage products: compact disks (CD), digital versatile disks (DVD), and Blue-ray disks (BD) or high-definition digital versatile disks (HD DVD).

The formation of small amorphous marks in a crystalline matrix corresponds to writing of information, whereas the re-crystallization of the amorphous spots leads to the erasure of information. In recent years phase-change materials have also become of interest for developing non-volatile memories with a number of attractive features [Wuttig, 2005] and [Luo, 2004]. In applications as a non-volatile memory, the pronounced difference in electrical resistivity is used. The amorphous state has a high resistance. Applying a long voltage pulse locally heats the amorphous region and leads to re-crystallization. Applying a higher voltage pulse to the crystalline state with low resistance leads to local melting and the formation of an amorphous region on rapid quenching. The phase transitions from the amorphous to...
crystalline states, and vice versa, of Ge–Sb–Te and Se–Sb–Te films by applying electrical
pulses have been observed [Tanaka, 2002] and [Nakayama, 2003].

The first materials used were good glass formers such as Te-based eutectic alloys,
represented by Te₈₅Ge₁₅ doped with an element such as Sb, S and P [Ovshinsky, 1968].
Although these materials already showed electrical switching that could be used for electronic
storage, the time for crystallization was of the order of microsecond, partly because the first
alloys did not crystallize in a single-phase material. The first materials to show fast re-
crystallization and good optical contrast were Ge–Te [Chen, 1986] and Ge₁₁Te₆₀Sn₄Au₂₅
[Yamada, 1986] and [Ohno, 1989]. This give rise to the discovery of a new alloys, such as
Ge₁₁Sb₄Te₇, Ge₁₁Sb₁₁Te₁₄ and Ge₂Sb₂Te₅ [Yamada, 1987 and 1991]. Nowadays Ge₂Sb₂Te₅ and
related materials such as GeSbTe₅, GeSnSbTe, GeBiSbTe, GeBiTe and GeInSbTe [Kojima,
1998 and 2001], [Yusu, 2005] and [Kusada, 2006] have been tried, some of which are
frequently used in commercial products. The Ge–Sb–Te composition has been used in
commercial optical and electrical devices due to its fast crystallization. The most important
properties of Ge₂Sb₂Te₅ is the fast transformation between amorphous and crystalline phases.
Ge₂Sb₂Te₅ alloy exhibit best performance in data storage devices due to it's high thermal
stability at room temperature, high crystalline rate at high temperatures, and extremely good
reversibility between amorphous and crystalline phases [Zhiwei, 2006]. Recently, these
materials attracts the attention of the scientist to study and understand the crystallization
phenomena [Yamada, 1991], [Tomigava, 1999], [Weidenholf, 1999], [Friedrich, 2000],
[Gonzales, 2000], [Kolobove, 2004], [Wuttig, 2005], and [Wang, 2005]. The importance for
this research is to achieve a (i) high recording density, (ii) high data transfer rate and (iii) high
direct overwrite cyclability. The minimum recorder bit dimension can be significantly
decreased by using short wavelength lasers, which results in higher recording density [Liqiu,
1998]. Optimizations of the physical properties of the phase change material, particularly its
crystallization behavior is essential to increase the data transfer rate and overwrite cyclability [Martijn, 2003]. These studies have pointed out that the crystallization of the amorphous materials requires some incubation time to form the critical nuclei, which limits the speed of devices [Weidenholf, 2001].

Most of the experimental methods used to investigate the amorphous to crystalline transition have shown that resistance measurements are among the most sensitive [Friedrich, 2000]. However, results of DC measurements frequently depend on the nature of the electrical contacts. Morales-Sanchez et al. 2003 proposed AC impedance measurements to separate the contribution of contacts from the measured electrical response. The impedance measurements in amorphous Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} thin films, as a function of temperature, have shown that the contacts have a strong influence on their electrical properties. New configurations of electrical contacts have been used in order to minimize their effect on the total measured response of chalcogenide alloy Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} using AC impedance spectroscopy technique [Saleh, 2007].

The rapid and reversible amorphous-to-crystalline phase transformation is accompanied by increase in the optical reflectivity and the electrical conductivity. However, uncertainties about the optical band gap and electrical properties of this material have persisted. Hereafter, the optical properties of Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} phase change material had been investigated and it is shown that the optical absorption in all phases (amorphous and crystalline) follows the Tauc relation \( \alpha = B(h\omega - E_{g})^{2} \), where B is a constant and \( E_{g} \) is often taken as a definition of the optical gap, the so-called Tauc-gap, [Tauc, 1974], which corresponds to the optical transitions in most amorphous semiconductors, [Bong Lee, 2005]. The common feature of these glasses is the presence of localized states in the mobility gap. This is due to the absence of long range order as well as various inherent defects. In chalcogenide glasses, it is assumed that the localized states in the mobility gap are the charged defects D\textsuperscript{+} and D\textsuperscript{-} with negative effective correlation energy [see section 2.4]. This type of
defects usually pins the Fermi energy level in the middle of the forbidden energy gap and result in the absence of electron spin resonance signal [Street, 1978] and [Okamoto, 1984].

The investigation of electrical conductivity in chalcogenide glasses is a valuable tool for determining the position of the Fermi energy level in the energy gap of semiconductor materials.

The motivation of the present work is to investigate the electrical properties and the indium doping effects of Ge$_2$Sb$_2$Te$_5$ phase change materials using different techniques. The electrical measurements such as Current-Voltage (I-V) characteristics, DC conductivity, AC conductivity (Impedance Spectroscopy), and Capacitance-Voltage (C-V) analysis will be conducted. The data gathered from these measurements can give us a clear idea about the phase transition temperature, the nucleation process and the energy gap for these materials.

This thesis is organized as follows; after the introduction in chapter I, a basic theoretical overview of phase-change materials, specially, chalcogenide (Ge-Sb-Te) is presented in chapter II. In chapter III, the preparation of the bulk alloy and thin films of Ge$_2$Sb$_2$Te$_5$ using sputtering and thermal evaporation techniques in addition to impedance spectroscopy, I-V and C-V techniques are presented. The experimental results are discussed in chapter IV. The conclusion of the work is summarized at the end of the thesis.
CHAPTER II
THEORETICAL BACKGROUND

2.1 Introduction

In a rewritable disc, information is stored in the so-called phase-change layer. This is often a chalcogenide alloy, which can be reversibly converted from the crystalline to the amorphous state by a laser pulse. Applying short consecutive write pulses that cause melt quenching of the initially crystalline recording film controls writing of amorphous marks. Erasure of amorphous marks is achieved by heating the phase-change film to intermediate temperature levels above glass transition temperature ($T_g$) and below melting point ($T_m$) to induce re-crystallization. Characteristic temperature-time profiles that are associated with the write and erase processes are given in figure 1.

---

Fig. 1 Schematic of the temperature-time profiles associated with recording (left panel) and erasure (right panel) of amorphous marks in a crystalline layer [Erwin, 2006]
The phase-change materials used today are a result of a 30-years and still continuing period of empirical optimization of materials. A large number of phase-change materials have been proposed, but only a few materials meet the following requirements:

1- Writability: they have to enable writing of data.
2- Archiving: the stored information has to be stable.
3- Readability: easy to read.
4- Erasability: the information should be erasable.
5- Cyclability: the storage medium should allow numerous write/erase cycles.

These data storage requirements can be translated to media requirements (see Table 1).

**Table 1: Requirements for phase change media [Erwin, 2006]**

<table>
<thead>
<tr>
<th>Storage requirement</th>
<th>Material requirement</th>
<th>Material property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Writability</td>
<td>Glass former</td>
<td>Melting point/layer design, appropriate optical absorption</td>
</tr>
<tr>
<td>Archival storage</td>
<td>Stable amorphous phase</td>
<td>High activation energy, high crystallization temperature</td>
</tr>
<tr>
<td>Readability</td>
<td>Large signal to noise ratio</td>
<td>High optical contrast</td>
</tr>
<tr>
<td>Erasability</td>
<td>Fast re-crystallization</td>
<td>Simple crystalline phase, low viscosity</td>
</tr>
<tr>
<td>Cyclability</td>
<td>Stable layer stack</td>
<td>Low stresses, low melting temperature</td>
</tr>
</tbody>
</table>

2.2. Glass formation and the amorphous phase

In phase-change optical recording, information is stored by writing amorphous marks in a crystalline phase-change layer. This section will deal with the basics of the process of mark formation and the structure of the resulting amorphous phase. In figure 2 the volume of a liquid is considered that is cooled to below the melting temperature. At the melting point ($T_m$), crystallization may occur. As illustrated in figure 2, crystallization is accompanied by an abrupt change in volume at ($T_m$). It is, however, also possible that the liquid will become ‘undercooled’, getting more viscous with decreasing temperature, and
ultimately a solid phase will form. This solid is called a glass, and the temperature region in which the undercooled liquid acquires the properties of a solid is called the glass transition temperature ($T_g$). Glass formation is characterized by a gradual break in the slope of the volume vs. temperature diagram. For a given composition, the value of the glass transition temperature depends on the cooling rate. When cooled slowly (dashed line in figure 2), the glass transition temperature will shift to lower values, as the undercooled liquid has more time to adjust its properties to its metastable equilibrium values. However, cooling down slowly also increases the chance for crystallization.

![Diagram showing the volume as a function of temperature for a liquid, a glass, and a crystal.](image)

**Fig. 2** Volume as a function of temperature for a liquid, a glass and a crystal [Elliott, 1990]

The ability to form glasses is almost a universal property of condensed matter. In order to produce an amorphous material, crystallization should be bypassed. Crystallization
takes time and, therefore, the amorphous phase can be reached by cooling rapidly to below the glass transition temperature. In a phase-change optical disc, rapid cooling is made possible by the small volume that is amorphized and the special stacking of layers comprising the disc.

Amorphous solid, is a solid like any other if macroscopic properties like shape, shear stiffness etc. are considered. But, on an atomic scale there is a difference between crystalline and amorphous solids. The main difference between them is the length scale over which the atoms are related to one another by periodicity. A crystal material has an atomic structure that repeats periodically across its whole volume on the other hand, amorphous materials, like glass, have no long-range order at all. This is illustrated in figure 3. For example, all atoms in figure 3(b) satisfy their coordination number, each have three nearest neighbors at nearly the same distance. Nevertheless at short range there is variation in bond strength and fluctuation in bond angles. On the contrary, it has been discovered recently, that the well-known phase-change material GeSbTe shows a substantial difference in short-range order between the amorphous and the crystalline state. It still needs to be clarified if this is a generic feature of phase change materials.

Fig. 3 Schematic representations of a crystalline and an amorphous structure [Elliott, 1990]
2.3 Phase-change materials

Suitable phase-change materials for optical recording have the ability to form glasses at time scales and temperatures that are appropriate for given conditions such as data transfer rate and available laser power. This requires that the glass formation takes typically less than 100 ns within an adequately cooled recording stack, and that the melting point is below 1000 °C, typically around 600 °C. Furthermore, the material should possess sufficient optical contrast between the amorphous and crystalline state. Some materials that fulfill these demands and that are currently applied in rewritable CDs and DVDs, are indicated in figure 4. The main constituents of these materials are antimony, tellurium and germanium [Erwin, 2006].

![Composition triangle of Sb, Te and Ge](image)

*Fig. 4 Composition triangle of Sb, Te and Ge [Erwin, 2006]*
Phase-change memory uses the unique behavior of chalcogenide glass, which can be "switched" between two states, crystalline and amorphous, with the application of heat. Nearly all memory devices make use of a chalcogenide alloy of germanium, antimony and tellurium (Ge-Sb-Te) called GST. It is heated to a high temperature at which point the chalcogenide becomes a liquid. Once cooled, it is frozen into an amorphous glass-like state which has a high electrical resistance. By heating the chalcogenide to a temperature above its crystallization point, but below its melting point, it will transform into a crystalline state with a much lower resistance. This phase transition process can be completed in as quickly as five nanoseconds, which makes chalcogenides suitable for memory devices.

2.3.1 Chalcogenides

Chalcogens are the group 6 elements in the periodic table, as shown in figure 5, they are sometimes known as the oxygen family. They consist of the elements oxygen (O), sulfur (S), selenium (Se), tellurium (Te), and the radioactive polonium (Po). The compounds of the heavier chalcogens (particularly the sulfides, selenides, and tellurides) are collectively known as chalcogenides. Unless grouped with a heavier chalcogen, oxides are not considered chalcogenides.

Chalcogenides have special electrical properties. They have no electron spin resonance and they cannot be doped since they have negative correlation energy defects. Chalcogenide alloys are glasses containing a chalcogenide element (sulphur, selenium or tellurium) as a substantial constituent [Mott, 1979].
Fig. 5 The periodic table of elements. The chalcogens appear in the sixth group of the table.

Germanium-Antimony-Tellurium (Ge-Sb-Te) GST, is a phase change material from the group of chalcogenide glasses, used in rewritable optical discs and phase-change memory applications. The new phase-change materials are likely p-type Ge-Sb-Te semiconductors. The melting point of this alloy is about 600 °C (900K). At 150 °C Ge-Sb-Te becomes pure fcc crystal, as shown in figure (6a), then it becomes pure hcp crystal at 400 °C as shown in figure (6b).

Ge$_2$Sb$_2$Te$_5$, whose trigonal crystal structure is depicted on the right-hand side in figure 6, consists of a sequence of hexagonal layers of Ge, Sb and Te. However, if short laser pulses are used to crystallize this material, a metastable structure is formed, which is characterized by six fold coordination of the atoms with the cubic arrangement characteristic for the rocksalt lattice.
This structural arrangement is shown on the left-hand side in figure 6. The Te atoms ‘occupy each site of their fcc sub-lattice in the NaCl structure. Alternating Ge, Sb, and vacancies occupy the sites of the other sub-lattice. Recent studies find compelling evidence for a pronounced local distortion away from the six fold coordinated sites, which considerably lowers the energy of the solid, [Erwin, 2006].

Fig. 6 Two crystalline phases of Ge₂Sb₂Te₅. On the right hand side the pure fcc crystal, and in left hand side the pure hcp crystal [Erwin, 2006].

As mentioned before, selenium (Se) and tellurium (Te) are considered semiconductors. In the amorphous phase lack of periodicity or long range order makes the wave vector $\vec{k}$ no more a good quantum number to describe the electrical properties. The only valid concept in amorphous phase is the density of state.
2.4 Density of states in amorphous semiconductors

Several models were proposed for the density of states of amorphous semiconductors. All used the same concept of localized states in the band tails which is different than the sharp bands in a crystal. The difference between these models of the amorphous semiconductor lies in the estimate of the extent of this tailing. An early model, namely Cohen Fritzsche-Ovshinsky (CFO), supposed that the amorphous structure would lead to overlapping band tails of localized states as shown in figure (7a). Those states derived from the conduction band (CB) would be neutral when empty and those from the valence band (VB) would be neutral when full. Such overlapping states would pin the Fermi-level energy \( E_F \) near the middle of the gap, a feature required by the electrical properties of these materials. The other principal feature of this model is the existence of the “mobility edges” at energies \( E_C \) and \( E_V \), in the CB and VB tails respectively. The mobility edges were introduced earlier by Mott, which is why the model is sometimes called the Mott CFO model. The difference between the two energies is called the mobility gap. Nevertheless, one of the major objections against the CFO model is the high transparency of amorphous chalcogenides below a well defined absorption edge [Mott, 1979].

An alternative suggestion to the CFO model for states in the gap is shown in figure (7b) [Mott, 1975]. This model assumes that the tails of localized states should be rather narrow, and they extend a few tenths of an electron-volt into the forbidden gap. The model also proposed the existence of a band of states near the middle of the gap, arising from defect centers, e.g. dangling bonds. These states may act both as deep donors \( (D^-) \) and acceptors \( (D^+) \) (charge defects). Single and double occupancy conditions lead to two bands separated by an appropriate correlation energy or Hubbard \( U \).
Adopting the above model for gap states in tetrahedral amorphous semiconductors such as Ge or Si clearly explains many of their electrical properties. For example, the observed electron spin resonance (ESR) signal reveals the presence of unpaired spins ascribed to electrons in dangling bond states. Moreover, at low temperatures, conduction occurs by variable range hopping, indicating that transport properties are dominated by a high density of states at $E_F$ [Qamhieh, 1996].

For the chalcogenides, the situation is different. There is plenty of evidence that chalcogenide glasses contain high density of gap states with $E_F$ pinned near mid-gap. However, none of the mentioned phenomena in the previous paragraph is normally observed (unless one first illuminates the material at low temperatures) [Mott, 1979]. Therefore, a rather different model is required for gap states in chalcogenides which gives a good description of many electrical and optical properties of these glasses. The model proposed that localized gap states are charged defects with negative effective correlation energy between electrons. The origins of this energy were soon understood in terms of the Valence-Alternation-Pair (VAP) model [Kastner, 1976].
Fig. 7 Density of states in amorphous semiconductors

(a) CFO model

(b) With bands of donor (E) and acceptor (Es) arising from the same defect (Mott and Davis model) [Mott, 1979]
2.5 Conduction in amorphous semiconductors

Although chalcogenides are p-type (conduction by holes), standard usage is to discuss equivalent conduction properties in terms of electrons. Conductivity is a macroscopic quantity which represents an average property of carriers as they move from site to site. Calculation of the conductivity therefore involves the transfer rate, scattering and trapping processes, as well as the appropriate averaging over the distribution of states. Conductivity is the product of the carrier density and the carrier mobility,

$$\sigma = n_e \mu$$  \hspace{1cm} (1)

The contributions to $\sigma$ are summed over the density of states,

$$\sigma = \int N(E) e \mu(E) f(E) dE$$  \hspace{1cm} (2)

Where $f(E)$ is the Fermi-function. Figure 8 shows schematically the variation of $N(E)$, $\mu(E)$ and $f(E)$ with energy $E$ and their contribution to the conductivity for states near the band edge.

![Figure 8](image)

**Fig. 8** Illustration of the density of states near the band edge, together with the carrier mobility $\mu(E)$, the occupation probability $f(E)$ and the conductivity $\sigma(E)$.

When there is a very high defect density in the middle of the band gap, as in tetrahedrally coordinated semiconductors like Si and Ge, conduction takes place by hopping at the Fermi
energy. Hopping conduction can also take place in the band tails where the density of states again becomes large, but the carrier concentration is lower. The much lower defect density in amorphous chalcogenides prevents this mechanism from contributing significantly at moderate temperatures and instead conduction takes place by electrons or holes at the band edges where both the density of states and the mobility increase with energy [Qamhieh, 1996]. Since our study is at relatively high temperatures (above room temperatures), the mechanism of extended states conduction is reviewed in the following section.

2.5.1 Extended state conduction

The conductivity of any semiconductor can be expressed in the form of Eq. 2. The integral contains contributions from electron transport above $E_F$ and hole transport below $E_F$. When conductivity takes place far from the Fermi level, Boltzmann statistics can be applied to describe the occupancy. The conductivity due to a single type of carrier excited beyond the mobility edge into the extended states is given by

$$\sigma = \int N(E) e \mu(E) \exp\left[-\frac{E-E_F}{KT}\right] dE \quad (3)$$

For the particular case in which the mobility increases abruptly at the mobility edge energy, $E_c$, according to Mott’s view, then Eq. 3 gives

$$\sigma = \sigma_{\text{min}} \exp\left[-\frac{E_c-E_F}{KT}\right] \quad (4)$$

$\sigma_{\text{min}}$ is referred to as minimum metallic conductivity and is given by

$$\sigma_{\text{min}} = N(E_c) e \mu_c KT \quad (5)$$

where $\mu_c$ is the free carrier mobility at $E_c$. Mott calculated a value for $\sigma_{\text{min}}$, given by the expression

$$\sigma_{\text{min}} = \text{const} \frac{e^2}{\hbar a} \quad (6)$$
where $a_i$ is the interatomic distance and the constant lies in the range 0.026 and 0.1; $\sigma_{\text{min}}$ is usually in the order of 200-300 $\Omega^{-1}\text{cm}^{-1}$.

The conductivity in amorphous semiconductors is usually activated, and is described by

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

(7)

where $\sigma_0$ is the conductivity prefactor and $E_a$ is the activation energy. Comparing Eq. 4 and 7, one might conclude that a measurement of $\sigma(T)$ immediately gives the location of the mobility edge $(E_c - E_F)$, and the prefactor gives the conductivity at the mobility edge. However, the measurements are unhelpful in this regard as there is a huge variation in the values of $\sigma_0$.

The most obvious mechanism by which the prefactor varies is when the activation energy is temperature dependent,

$$(E_c - E_F) = (E_c - E_F)_0 - \delta T$$

(8)

where the constant value $\delta$ represents the first order approximation to the temperature dependence, and $(E_c - E_F)_0$ is the value extrapolated to zero temperature. Substituting Eq. 8 into Eq. 7, the expression for the conductivity becomes

$$\sigma = \sigma_0 \exp(\delta / k) \exp\left[-\frac{(E_c - E_F)_0}{K T}\right]$$

(9)

Therefore, within the linear approximation, the conductivity activation energy $E_a$ measures the value of $(E_c - E_F)$ and the prefactor $\sigma_0$ contains the additional term involving the temperature dependence, $\exp(\delta/k)$. Davis and Mott have made an estimate of $\sigma_0 \exp(\delta/k)$. They found values clustering round $10^3$ $\Omega^{-1}\text{cm}^{-1}$ for most amorphous semiconductors. An estimate for $\delta$ can be obtained from the temperature dependence of the optical gap.
2.5.2 Hopping conductivity

We have seen that structural defects give rise to localized states in the gap of amorphous semiconductors. However, one of the definitions of localized states is that the average conduction associated with the states at energy E is zero. Thus, conduction involving localized states can take place by hopping of electrons from full states to neighboring empty states, with phonon assistance. Hopping conduction dominates when the Fermi occupation factor in Eq. 2 gives the states nearest to the Fermi energy a sufficiently strong weighted contribution to the total conductivity. There are two ranges of localized states where conduction by hopping can take place:

1) **Conduction in band tails:** When carriers are excited into localized states at the band edges, hopping conduction can occur at energies close to the conduction band edges $E_A$ and $E_B$, (figure 7).

2) **Conduction in states around $E_F$:** If the density of states at the Fermi level is finite, then there is contribution from carriers with energies near $E_F$ which can hop between localized states by a process analogous to impurity conduction that takes place in heavily doped crystalline semiconductors. Hopping is to sites with the smallest distances and is therefore sometimes called nearest-neighbor hopping.
Fig. 9 Schematic illustration of the temperature dependence of conductivity expected for an amorphous semiconductor.

This behavior has been observed in several amorphous semiconductors at low temperatures, where the activated nature of band conduction ensures that it is smaller than the contribution from variable-range hopping. Figure 9 shows schematically the three conduction mechanisms and the change in it on lowering the temperature. If the density of defect states at $E_F$ is high, then conduction in the band tails will not be dominant at any temperature range and a direct transition from extended state to hopping conduction at $E_F$ will result [Qamhieh, 1996]. In the present work, only the first part of figure 9 at high temperature is to be considered, where, extended state conduction takes place.

2.6 AC conductivity

AC conductivity is one of the studies done on solids in order to characterize the bulk resistance of the crystalline sample. Measurement of AC conductivity can be done by different techniques. The currently used technique is the complex impedance spectroscopy. This study also gives information on electrical properties of materials and their interface with electronically conducting electrodes. The complex impedance spectroscopy...
measurement of AC conductivity is based on studies made on the measurement of sample impedance/admittance over a range of temperatures and frequencies and analyzing them in complex impedance plane. This is particularly characterized by the measurement and analysis of impedance (Z), admittance (Y) and plotting of these functions in the complex plane which is known as Nyquist diagrams. Impedance is a more general concept than resistance because it takes phase differences into account. In AC measurements, the resistance, R, is replaced by the impedance, Z, which is the sum of resistance and reactance.

Impedance can be written as

\[ Z = Z' + Z'' , \] (10)

where \( Z' \) is the real part and \( Z'' \) the imaginary part of \( Z \). \( Z \) is a vector quantity and may be plotted in the plane with either rectangular or polar coordinates as shown in figure 10.

The two rectangular coordinate values are

\[ \text{Re}(Z) = Z' = |Z| \cos \varphi , \] (11)

\[ \text{Im}(Z) = Z'' = |Z| \sin \varphi , \] (12)

with phase angle \( \varphi = \tan^{-1}(Z'/Z'') \) and the magnitude of \( |Z| = \left[ (Z')^2 + (Z'')^2 \right]^{1/2} \).

Fig. 10 Impedance vector representation.
In polar form, $Z$ may be written as

$$Z(\omega) = |Z| \exp(j \omega),$$  \hspace{1cm} (13)

Where, $\omega$ is the angular frequency

$$\exp(j \omega) = \cos(\omega) + j \sin(\omega)$$  \hspace{1cm} (14)

In general, $Z$ is frequency dependant. Impedance spectroscopy consists of the measurement of $Z(\omega)$ over a wide frequency range. It is from the resulting structure of $Z(\omega)$ vs $\omega$ that one derives information about the electrical properties of the electrode material system [Padma, 2002]. Impedance plane plots for the sample which can be considered as a capacitance (C) in series with the resistance (R), or (C) in parallel with (R) are shown in figure 11.

---

**Fig. 11** Impedance plots for series and parallel combinations of $R$ and $C$. 
Figure 11 also shows, the impedance spectra (Imaginary part of the impedance $Z''$ versus real part $Z'$ of the impedance for a certain temperature), where the resistance is equal to the diameter of the semicircle in Nyquist plot. The semicircle starts at high frequency then ends to a low frequency for a certain temperature but the shift on this semicircle depends on the temperature as we will see in the next chapters. At the semicircle peak one can get the relaxation frequency at which $\omega RC = 1$.

Impedance spectroscopy technique was used to study the AC conductivity and the capacitance of the samples with a series combination of R and C which is explained in the next chapters.
CHAPTER III

SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

Thin films of Ge$_2$Sb$_2$Te$_5$ were prepared by two different techniques (Sputtering & Thermal evaporation techniques) at different places as shown in table 2. (The bulk alloys of glassy Ge$_2$Sb$_2$Te$_5$ were prepared by rapid melt quenching technique). These alloys have been used as a source in the thermal evaporation technique to deposit films at two places, UAE University and the University of Leuven (Belgium).

Table 2: General information about the samples under investigation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Prepared at</th>
<th>Contact type</th>
<th>Composition</th>
<th>Deposition Technique</th>
<th>$T_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Aachen University</td>
<td>Fig. 15-a</td>
<td>Ge$_2$Sb$_2$Te$_5$</td>
<td>Sputtering</td>
<td>145 °C</td>
</tr>
<tr>
<td>2</td>
<td>Aachen University</td>
<td>Fig. 15-c</td>
<td>Ge$_2$Sb$_2$Te$_5$</td>
<td>Sputtering</td>
<td>145 °C</td>
</tr>
<tr>
<td>3</td>
<td>Leuven University</td>
<td>Fig. 15-c</td>
<td>Ge$_2$Sb$_2$Te$_5$</td>
<td>Thermal Evaporation</td>
<td>140 °C</td>
</tr>
<tr>
<td>4</td>
<td>UAE University</td>
<td>Fig. 15-b</td>
<td>Ge$_2$Sb$_2$Te$_5$</td>
<td>Thermal Evaporation</td>
<td>135 °C</td>
</tr>
<tr>
<td>5</td>
<td>UAE University</td>
<td>Fig. 15-b</td>
<td>Ge$_2$Sb$_2$Te$_5$</td>
<td>Thermal Evaporation</td>
<td>135 °C</td>
</tr>
<tr>
<td>6</td>
<td>UAE University</td>
<td>Fig. 15-b</td>
<td>In$_{0.3}$Ge$_2$Sb$_2$Te$_5$</td>
<td>Thermal Evaporation</td>
<td>150 °C</td>
</tr>
</tbody>
</table>

The amorphous structure and stoichiometry of the films were identified by X-ray diffraction and Energy Dispersive X-ray analysis EDX as shown in figures (12 & 13). X-ray spectroscopy is a technique which allows checking whether the material is amorphous or crystalline. Using this technique, the amorphicity of evaporated Ge$_2$Sb$_2$Te$_5$ film was
confirmed. Sample was characterized by the appearance of diffraction lines due to the formation of a crystalline state. To check the amorphicity of our sample X-ray diffraction spectroscopy were performed using Philips diffractometer with CuKα X-radiation source. Figure 12 shows the diffraction pattern in the range of 2θ = 0-80°. The absence of any sharp peaks indicates the amorphous nature of the quenched material. EDX is an analytical technique used for the elemental analysis, as shown in figure 13 three peaks appear for the three elements in the sample used Ge₂Sb₂Te₅ which are characteristic of an element's atomic structure.

Gold electrodes were evaporated for electrical contacts using three different configurations. Three different techniques were used to analyze the thin films. 1) The DC four probes technique has been used to measure the I-V curves and hence the resistance of the samples. From this technique one can determine the amorphous-crystalline transition temperature. 2) The impedance spectroscopy technique was used to study the AC conductivity and the capacitance of the samples. 3) The capacitance-voltage technique was used to study the capacitance of the film as a function of temperature and frequency.

![X-ray diffraction spectrum of Ge₂Sb₂Te₅ film as deposited](image)

**Fig. 12** X-ray diffraction spectrum of Ge₂Sb₂Te₅ film as deposited
3.1 Sample preparation

3.1.1 Preparation of bulk materials

Rapid quenching technique has been used to prepare the bulk alloys of the phase-change materials. This technique is historically the most established one and it is still the most widely used in the preparation of amorphous chalcogenide materials [Qamhieh, 1996]. The method consists of weighing and mixing the high purity constituents followed by melting in sealed evacuated quartz ampoules. The melt is continuously rotated to ensure homogenization. Subsequently, the melt will vitrify when cooled by quenching in either air or ice water. More rapid quenching has also been used in preparing amorphous chalcogenides, e.g. roller quenching for Sb3S3 and melt-spinning for Te-Se, Ge-Se and Te-Ge alloys.

The bulk alloys of glassy Ge2Sb2Te5 were prepared at UAE University from 99.995% pure Ge, Sb, and Te by rapid melt quenching technique, as shown in figure 14. The materials with proper constituents were sealed in an evacuated quartz tube (at 10⁻³ Pa) and heated at 1050 °C for 24 hours in a rotating cylindrical furnace to ensure homogenization.
Fig. 14 Schematic illustration of experimental arrangement used for producing amorphous Ge₂Sb₂Te₅ bulk samples.

3.1.2 Thermal Evaporation Technique (TE)

This technique is perhaps the simplest and possibly the most widely used method for producing amorphous solids in thin film forms. TE is normally performed in vacuum and involves resistive or electron-beam heating of a boat containing the material to be evaporated. The material is melted then evaporated and finally condensed onto a cold substrate. This method is suitable for relatively low melting-point compounds, such as chalcogenides.
3.1.3 Sputtering Technique

Sputtering is a physical vapor deposition process whereby atoms in a solid target material are ejected into the gas phase due to bombardment of the material by energetic ions.

The process can be thought of a large cluster of atoms, collide by energetic ion. The first collision pushes atoms deeper into the cluster, subsequent collisions between the atoms can result in some of the atoms near the surface being ejected away from the cluster. The number of atoms ejected from the surface per incident particle is called the sputter yield.

3.1.4 Deposition of electrodes

Gold electrodes were evaporated for electrical contacts in three different ways, as shown in figure 15. In the first method figure (15a), gold is evaporated on top of Ge-Sb-Te film. In the second method figure (15b), gold is evaporated first on the glass substrates and then Ge-Sb-Te film is deposited. In the third method the material is deposited on a part of the glass and then the gold is deposited on top of it such that part of the gold electrode surface touches only the substrate, as shown in figure (15c).
3.2 Measuring Technique

3.2.1 The impedance spectroscopy

Impedance is an important parameter used to characterize electronic circuits, devices, and the materials used to make devices. Impedance (Z) is generally defined as the total opposition a device or circuit offers to the flow of an alternating current (AC) at a given frequency, and is represented as a complex quantity which is graphically shown on a vector plane. An impedance vector consists of a real part (resistance, R) and an imaginary part (reactance, X) as shown in figure 10, [Kazunari, 2003].

Fig. 15 Schematic diagrams of the electrical contacts.
Impedance spectroscopy (IS) is a powerful method of characterizing many of the electrical properties of materials and their interfaces with electronically conducting electrodes. It may be used to investigate the dynamics of bound or mobile charge in the bulk or interfacial regions of any kind of solid or liquid material: ionic, semiconducting, mixed electronic-ionic and even insulators (dielectrics) [Ross, 1987].

Impedance spectroscopy measurements were performed in this work using 1260 Solartron impedance analyzer in the range of 1Hz–10MHz, with amplitude of 0.5 volt and zero bias. Silver paste has been used to make contact between the coaxial cable and the gold electrodes. The measurements were performed at different temperatures from 30-130 °C. The temperature was measured by a K-type thermocouple, and the samples were heated in Argon gas environment. Figure 16 shows the circuit connections for an impedance measurement. In this figure the current (I) is applied across the sample and the voltage (V) is then measured across it. The impedance is then given by: \( Z = \frac{V}{I} \)

Z60 and Zview have been used for data acquisition and analysis. These pieces of software were supplied by Solartron especially for the 1260 solartron impedance analyzers.
3.2.2 Current-Voltage technique

Four probes technique was used to measure the DC resistance of three samples which were prepared from the same batches of samples 2, 3 and 4. The samples were heated from room temperature up to 170 °C at a heating rate of 5 °C/min.

3.2.3 Capacitance-Voltage technique

Capacitance-Voltage measurements were performed on amorphous and crystalline samples using Keithley 590 CV meter at two operating frequencies, 100 kHz and 1 MHz. The circuit for the CV Analyzer is similar to the impedance measurement connection shown in figure 16.

The samples were heated inside a Faraday-cage and Argon gas environment. The measurements were performed for a sweep of voltages from -20 to +20 volts at different temperatures. K-type thermocouple has been used to measure the samples temperatures. This measurement is used to find the dependence of both capacitance and resistance on applied bias voltage, temperature and frequency.

For the I-V and C-V measurements, we have written our own programs for data acquisition using Labview. This later is a graphical programming tool used mostly in instrument automation.
CHAPTER IV
RESULTS AND DISCUSSIONS

4.1 DC Measurements

Four probes technique has been used to measure I-V characteristics of sample 4 using the sample configuration shown in figure (15b), in addition to two other gold electrodes.

Figure 17 shows the current versus voltage (I-V) curves for Ge$_2$Sb$_2$Te$_5$ film at different temperatures (70-150°C). The I-V curves are straight lines at the measured temperature and voltage ranges. This indicates that the material has an ohmic resistance, which can be calculated from the slope of the I-V curve at each temperature [Qamhieh, 2007].

The resistance of sample 4 is plotted as function of temperature as shown in figure 18. A sharp drop in the resistance is evident at $T \approx 135^\circ$C ($10^3/T = 2.45$ K$^{-1}$). This temperature is the amorphous-crystalline phase transition temperature ($T_c$) of the material, [Wang, 2005]. Below this temperature the $ln R$ versus $1/T$ curve is a straight line in the measured temperature range. The resistance $R$ can, therefore, be expressed by the well known Arrhenius relation [Mott, 1979],

$$\sigma \propto e^{-E_v/kT} \quad \text{or} \quad R \propto e^{E_v/4kT}$$

(15)

where $\sigma$ is the conductivity, $E_v$ is the activation energy for dark conductivity and $k_B$ is the Boltzmann constant. From figure 18, the value of $E_v$ is estimated to be 0.36 eV.
Fig. 17 I-V curves for Ge$_2$Sb$_2$Te$_5$ (Sample 4) films at different temperatures a) in the amorphous phase and b) around and after the transition to the crystalline phase.
Fig. 18 Resistance of Ge$_2$Sb$_2$Te$_5$ film (Sample 4) as a function of temperature. The dashed line is the linear fit of the resistance in the amorphous state.

The amorphous-crystalline transition temperatures ($T_c$) of Ge$_2$Sb$_2$Te$_5$ films have been roughly determined using resistance measurements as listed in table 2. Sample 2, 3 and 4 were heated from room temperature up to 170 °C at a heating rate of 5 °C/min. Figure 19 shows the sample resistance as function of temperature for three samples prepared from the same batch of samples 2, 3 and 4. The sharp drop in the resistance appears at temperatures of 145 °C (sample 2), 140 °C (sample 3) and 135 °C (sample 4). The temperature at which the sample resistance drops by several orders of magnitude is the amorphous-crystalline transition temperature [Wang, 2005].
Fig. 19 Resistance measurements as a function of temperature for samples prepared at Aachen, Leuven and UAE. The amorphous-crystalline transition temperatures $T_C$ are 145 °C, 140°C and 135°C, respectively.

4.2 Impedance spectroscopy measurements

The impedance spectrum at different temperatures ($T=80-120^\circ$C) for sample 4 are shown in figure 20 each point in the impedance spectrum represent the imaginary part of the impedance $Z''$ versus its real part $Z'$ at a certain frequency and temperature. It can be observed that at the same temperature, the distribution of the data points fit with one semicircle from low to high frequency, the so called Nyquist plot. A parallel resistor and capacitor (RC) equivalent circuit accurately fit the frequency data [Barsoukov, 2005]. Hence the electrical properties of Ge$_2$Sb$_2$Te$_5$ film can be associated with a simple RC equivalent circuit. $R$ is determined from the radius of the semicircle and $C$ is determined by
using the frequency at the peak of each semicircle (relaxation frequency, $f_o$), where $2 \pi f_o RC = 1$ should be satisfied (see figure 11). As expected, the diameter of the semicircle keeps decreasing with increasing the temperature. Moreover, the semicircle peak shifts toward higher frequency as the temperature increases. These two behaviors are due to the thermal activation process that occurs in semiconductor materials. The relaxation frequency obtained is plotted against temperature, as shown in figure 21. It is obvious from the figure that the Log of the frequency is increase as the temperature increase according to the Arrhenius relation. This shows similar phenomena of the conductivity dependence on the temperature.

$$f_o \propto e^{-E_v/k_BT}$$  \hspace{1cm} (16)

The activation energy, $E_v$, calculated from the slope of the straight line fit is found to be 0.39 eV. This value is relatively close to the one obtained by I-V measurements.

The temperature behavior of the DC and AC measurements indicate that the conduction in these glasses, Ge$_2$Sb$_2$Te$_5$, is through an activated process having single activation energy in the investigated temperature range, where both resistance and relaxation frequency have the same temperature dependence. The calculated activation energy values from figures 18 and 21 are close to each other, 0.36 and 0.39 eV, respectively. To first approximation, the value of the activation energy determines the position of the Fermi energy level with respect to the conducting mobility edge. If Ge$_2$Sb$_2$Te$_5$ film has chalcogenide characters, this means that the Fermi energy level is pinned in the middle of the energy gap, $E_g$ [Mott, 1979]. Therefore the energy gap can be estimated to be $E_g = 2E_v$. The corresponding energy gap obtained from I-V measurements and AC impedance spectroscopy are 0.72 and 0.78 eV, respectively. This value for the energy gap is in good agreement with the optical gap $E_o = 0.7$ eV measured by [Bong Lee, 2005]. This can be reserved as an evidence for the chalcogenide nature defects in
amorphous Ge$_2$Sb$_2$Te$_5$ films, which is characterized by the negative effective correlation energy charge centers D$^+$ and D$^-$. 

![Impedance spectra for a Ge$_2$Sb$_2$Te$_5$ (Sample 4) film at different temperatures.](image)

**Fig. 20** Impedance spectra for a Ge$_2$Sb$_2$Te$_5$ (Sample 4) film at different temperatures.

![Frequency at the peak of the semicircle as a function of $10^3/T$ ($K^{-1}$).](image)

**Fig. 21** Frequency at the peak of the semicircle as a function of $10^3/T$ ($K^{-1}$). The slope of the dashed line determines the activation energy.
Figures 22, 23, 24 and 25 show the imaginary part of the impedance as function of frequency at different temperatures below $T_c$ for samples 1, 2, 3 and 4 respectively. Figure 22 shows the presence of two peaks. The peak at low frequency is attributed to the electrical contacts, whereas the peak at high frequency is attributed to the contribution of the material under test [Morales, 2003]. The appearance of the contacts effect in figure 22 is due to the fact that these measurements have been made using the contact type shown in figure 15a. Figures 23, 24 and 25 show only one peak at high frequencies that is related to the material contribution, whereas the contribution of the contacts disappears at low frequencies. The disappearance of the contacts effect in figures 23, 24 and 25 is due to the fact that these measurements have been done using the contact type shown in figures 15c, 15c and 15b, respectively. Figure 26 shows a typical example of the impedance spectra of samples 1 and 4. It can be seen that the spectrum of sample 1 consists of two well defined semicircles, whereas the spectrum of sample 4 consists of only one semicircle. As has been shown above, the low frequency semicircle describes the electrical properties of contacts and the one at high frequency describes the electrical properties of the material. It is evident from the above results that the place where the silver paste is put on the sample plays a crucial role in electrical measurements. In the configuration of figure 15a, the silver paste is placed on the gold that is deposited over the tested material. During the heating process the silver paste might penetrate the gold and interact with the material. Such interaction could be the reason for having similar behavior for the peaks due to the contacts and the one due to the material, as shown in figure 22. The decrease in both peaks amplitudes is due to the decrease in the resistance of the material as the sample heats up. Moreover, both peaks shift toward higher frequency as the temperature increases. This is due to the activation phenomena of the carriers in the semiconductor materials [Barsoukov, 2005].
It is worth to note that there are no preferences in the order of deposition between the gold and the materials since the effect of the contacts disappears in the configurations shown in figures (15b) and (15c). Beside that, the silver paste should be placed on the gold film only to avoid any direct contact between the silver paste and the material. This will guarantee that there is no interaction between the silver paste and the material during the heating process.

\[ T = 80^\circ C \]
\[ T = 90^\circ C \]
\[ T = 100^\circ C \]
\[ T = 110^\circ C \]
\[ T = 120^\circ C \]
\[ T = 130^\circ C \]

Fig.22 Imaginary impedance as a function of frequency for sample I at different temperatures in the amorphous state.
Fig. 23 Imaginary impedance as a function of frequency for sample 2 at different temperatures in the amorphous state.

Fig. 24 Imaginary impedance as a function of frequency for sample 3 at different temperatures in the amorphous state.
Fig. 25 Imaginary impedance as a function of frequency for sample 4 at different temperatures in the amorphous state.

Fig. 26 Impedance spectra for samples 1 and 4 at $T = 80^\circ$C.
4.3 Capacitance-Voltage measurements of Ge$_2$Sb$_2$Te$_5$ and In$_{0.3}$Ge$_2$Sb$_2$Te$_5$

Influence of indium doping on the crystallization kinetics of Ge$_2$Sb$_2$Te$_5$ has been investigated by [Wang, 2005]. The results indicate that indium might play an important role in modifying the crystallization kinetics of Te-based phase change materials. Therefore, we investigate below the influence of indium doping using Capacitance-Voltage measurements.

Amorphous thin films of Ge$_2$Sb$_2$Te$_5$ (S5) and In$_{0.3}$Ge$_2$Sb$_2$Te$_5$ (S6) are prepared by thermal evaporation technique. Both films have a thickness and a separation between the gold electrodes of about 0.8 $\mu$m and 1 mm, respectively. Pre-deposited gold electrodes on glass substrates are used for the electrical contacts as shown in figure (15b).

The capacitance variation of Ge$_2$Sb$_2$Te$_5$ (S5) and In$_{0.3}$Ge$_2$Sb$_2$Te$_5$ (S6) with applied bias voltage ranged from -20V to +20V, as shown in figures 27 and 28 at different temperatures for 100 kHz and 1 MHz. The two figures (27 and 28) show a bell shape curve where the capacitance attains a maximum value, and it is more pronounced at 100 kHz-frequency and at temperatures close to amorphous-crystalline transition temperature ($T_C$). However, a negative capacitance is observed for sample S6 at 100 kHz-frequency and 125°C temperature, as shown in figure (28a).
Fig. 27(a) Capacitance variation of sample S5 as a function of applied bias voltage (-20V to +20V) for temperatures: 45, 65, 85, 105 and 115 °C. The frequency is 100 kHz.

Fig. 27(b) Capacitance variation of sample S5 as a function of applied bias voltage (-20V to +20V) for temperatures: 45, 65, 85, 105 and 115 °C. The frequency is 1 MHz.
Fig. 28(a) Capacitance variation of sample S6 as a function of applied bias voltage (-20V to +20V) for temperatures: 65, 85, 105, 115 and 125 °C. The frequency is 100 kHz.

Fig. 28(b) Capacitance variation of sample S6 as a function of applied bias voltage (-20V to +20V) for temperatures: 65, 85, 105, 115 and 125 °C. The frequency is 1 MHz.
Figures 29 and 30 show, respectively, the capacitance variation of samples S5 and S6 as a function of temperature for different applied bias voltages (0-20 volts) at 100 kHz (figures (29a) and (30a)) and 1 MHz (figures (29b) and (30b)). In figure (29a) the capacitance increases with temperature for bias voltages less than 15 volts and it shows a maximum at ~105 °C for voltages greater than 15 volts. In figure (30a) the capacitance decreases for all bias voltages and becomes negative at temperatures greater than 115°C. At high frequency (1MHz) figures (29b) and (30b) show that the capacitance increases with temperature for all bias voltages, and no negative capacitance was observed at high frequency (1MH).

![Fig. 29(a)](image)

**Fig. 29(a)** Capacitance variation of sample S5 as a function of temperature for different applied bias voltages, ranging from 0-20 volts. The frequency is 100 kHz. Solid lines are to guide the eye.
Fig. 29(b) Capacitance variation of sample S5 as a function of temperature for different applied bias voltages, ranging from 0-20 volts. The frequency is 1 MHz. Solid lines are to guide the eye.

Fig. 30(a) Capacitance variation of sample S6 as a function of temperature for different applied bias voltages, ranging from 0-20 volts. The frequency is 100 kHz. Solid lines are to guide the eye.
Fig. 30(b) Capacitance variation of sample S6 as a function of temperature for different applied bias voltages, ranging from 0-20 volts. The frequency is 1 MHz. Solid lines are to guide the eye.

To compare the capacitance variation with temperature, variation of the normalized capacitance \( \frac{C}{C_{45^\circ}} \) of S5 and S6 for 0 and 20 volts bias are shown in figures (31a) and (31b), respectively. These figures summarize the three effects: temperature, applied bias voltage and frequency. A decrease toward negative values of the capacitance for S6 at 100 kHz and 0 bias voltages is observed in figure (31a). A more pronounced decrease in the capacitance of S6 at 100 kHz is observed at higher bias (20 volts), as shown in figure (31b). The capacitance of S5 starts decreasing at high temperature at 20-volts bias, as shown in figure (31b).
Fig. 31(a) Normalized capacitance of samples S5 and S6 as a function of temperature for applied bias voltage of 0 volts. The data is shown for both 100 kHz and 1 MHz. Solid lines are to guide the eye. Error bars are systematic and estimated to be about 5%.

Fig. 31(b) Normalized capacitance of samples S5 and S6 as a function of temperature for applied bias voltage of 20 volts. The data is shown for both 100 kHz and 1 MHz. Solid lines are to guide the eye. Error bars are systematic and estimated to be about 5%.
The capacitance variation and negative capacitance effect in homogenous semiconductor (barrier free) has been studied by [Penin, 1996]. In the case of application of an alternating voltage across a certain semiconducting material, the equivalent capacitance measured by a CV meter is given by [Majeed Khan, 2005].

\[ C_e = \left( \frac{A \sigma_{dc}}{d} \right) \left[ \frac{\tau_m - \frac{\tau}{1 + \omega^2 \tau^2}}{\frac{\varepsilon}{4\pi \sigma_{dc}}} \right], \quad (16) \]

where, \( A \) is the area of the plate capacitor and \( d \) is the dielectric thickness. \( (\tau_m = \frac{\varepsilon}{4\pi \sigma_{dc}}) \)

is the Maxwellian dielectric relaxation time, \( \varepsilon \) is the dielectric constant and \( \tau \) is the dielectric relaxation time. After substituting \( \tau_m \), Eq. (16) can be written as:

\[ C_e = \left( \frac{A \varepsilon}{4\pi d} \right) \left[ 1 - \frac{4\pi \tau \sigma_{dc}}{\varepsilon (1 + \omega^2 \tau^2)} \right], \quad (17) \]

At low temperatures \((T \ll T_c)\), the conductivity of Ge-Sb-Te film is low, hence the second term of Eq. (17) can be ignored and the capacitance is given by:

\[ C_e = \frac{A \varepsilon}{4\pi d}, \quad (18) \]

As the temperature increases and gets close to \( T_c \), crystallization occurs by the mechanism of nucleation and growth. In such a mechanism, small crystalline nuclei form initially, which subsequently grow [Erwin, 2006]. In this mechanism, the area of the nuclei increases and the separation between the islands decreases and hence the equivalent capacitance of Eq. 18 increases.

The conductivity of a semiconductor can be increased either by doping or increasing the temperature. Doping with indium can be considered as a source of free electrons that increase the conductivity of the sample. The nonlinear behavior of the sample’s capacitance with the applied bias voltage might be related to the nucleation mechanism. Due to nucleation, two phases will be formed in the sample, amorphous film
and crystalline islands. The interface (junction) between the two phases might behave as a potential barrier and the charge carriers are accumulated at the junction. At low bias voltage, the electric field is not sufficient for the charge carriers to overcome the barrier. Therefore, the conductivity of the film is not affected. As the applied bias voltage increases, the charge carriers gain enough energy from the applied electric field and overcome the barriers and hence the conductivity increases. Therefore, at high temperature, close to $T_c$, and at high bias voltage the second term of Eq. (17) becomes more dominant over the first term and hence the capacitance decreases, as shown in figure (30a). Since the conductivity of indium doped film (S6) is much greater than the undoped one (S5), the second term of Eq. (17) increases. This leads to a direct decrease of the capacitance for all applied bias voltages, as shown in figure (30a). Eventually, the capacitance becomes negative when $\frac{4\pi \tau \sigma_{DC}}{\epsilon (1 + \omega^2 \tau^2)}$ is greater than one. The phenomena of negative capacitance has been observed in other semiconducting materials such as Cd$_3$As$_6$ [Gould, 1999], CdTe [Ismail, 1996] and CdSe [Oduor, 1997].

At high frequency (1MHz), the second term of Eq. (17) decreases and the first term is dominant for the whole range of temperature and applied voltage. Therefore, at high frequency the capacitance increases as shown in figures (29b) and (30b).
CONCLUSION

Investigation of the electrical properties of Ge-Sb-Te thin films using Impedance Spectroscopy, Current-Voltage and Capacitance-Voltage techniques has been presented.

First, the electrical contacts effects on the electrically measured signal have been studied using Impedance Spectroscopy technique. Three different configurations of the electrical contacts are studied. The results show that the effect of the electrical contacts disappears when the silver paste is placed only on the gold electrodes away from the thin film under test. This is related to the fact that the silver paste will not interact with the material during the heating process. The results show that the order of depositing layers (material and the gold electrodes) is not important, whereas the position of the silver paste on the gold electrode is the more significant.

Second, the electrical properties of Ge$_2$Sb$_2$Te$_5$ thin films using Impedance Spectroscopy and Current-Voltage measurements have been presented. The data shows similar resistance and relaxation frequency temperature dependence with activation energies of 0.36 and 0.39 eV, respectively. Therefore the corresponding energy gap is estimated to be 0.72 eV and 0.78 eV (This value is in good agreement with the values reported in literature [Bong Lee, 2005]). This agreement between electrical and optical measurements confirms that Ge$_2$Sb$_2$Te$_5$ belongs to the chalcogenide family. The measured amorphous-crystalline transition temperature ($T_c$) is found to be 135 °C.

Third, Capacitance-Voltage measurements have been performed on amorphous samples of In$_{0.3}$Ge$_2$Sb$_2$Te$_5$ and Ge$_2$Sb$_2$Te$_5$ thin films in order to study the indium doping effect on the electrical properties of Ge$_2$Sb$_2$Te$_5$. The bias voltage, temperature and frequency effects have been investigated. The results show that the capacitance of In$_{0.3}$Ge$_2$Sb$_2$Te$_5$ sample decreases as the bias voltage increases for the whole range of temperatures. However, the same behavior is observed for Ge$_2$Sb$_2$Te$_5$ sample at
temperatures close to the amorphous-crystalline transition temperature and at high applied bias voltages (≥ 15 volts) only. The dependence of the sample’s capacitance on bias voltage and temperature is attributed to the increase in the free electron concentration as the bias voltage and temperature increase. For \( \text{In}_{0.3}\text{Ge}_{2}\text{Sb}_{2}\text{Te}_{5} \) sample, the indium can be considered as an additional source of free electrons. This would contribute to further decrease in the capacitance of \( \text{In}_{0.3}\text{Ge}_{2}\text{Sb}_{2}\text{Te}_{5} \) sample. The negative capacitance effect might be attributed to a significant increase of the film’s conductivity due to temperature and applied bias voltage. The nonlinearity in the capacitance and conductivity could be related to the nucleation mechanism as the temperature gets close to the amorphous-crystalline transition temperature.

Chalcogenide glasses are versatile semiconductor and dielectric functional materials. They possess a number of well known peculiar properties like photo-induced change of optical parameters and electrical switching. Research options still abound to identify alloys with very low switching voltages, and to demonstrate a sufficient number of read-write and erase cycle. Seeking new materials with very low voltage switching and investigating the optical and electrical properties of these materials are attracting much attention. Moreover, investigations of photo-physical processes in amorphous chalcogenide layers were extended towards the nanostructure. The nano-layered films were in the focus of development of a new photosensitive, optical recording media. These topics provide future research opportunities.
References


فولت. ويعزى سبب ذلك إلى زيادة تركيز الإلكترونات الحرة عند رفع الجهد الكهربائي ودرجات الحرارة. أما بالنسبة لعينة In0.3Ge2Sb2Te5 فقد أشارت الدراسات السابقة للاستقرار والحرارة. وهذا الشيء يساهم في تعزيز إلى أن تصل إلى قيم مماثلة. إن العلاقة اللاحقة بين السعة الكهربائية لعينة In0.3Ge2Sb2Te5خفض قيمة السعة الكهربائية لعينة الكهربائية وقابلية التوصيل يرجع إلى عملية التلور الحادة كلياً اقتربنا من درجة حرارة الانتقال من الحالة اللاحورية إلى النوروية.
تحضير و دراسة خصائص مواد شبه موصلة (GeSbTe) لغرض التخزين البصري من خلال تغيير الحالة البلورية.

الخلاصة

لوفي السنوات العشر الأخيرة تقدماً تجارياً كبيراً في مجال التسجيل البصري القائم على استخدام مواد زجاج الكالكوجينات على شكل أقراص مضغوطة (CD) لاستخدام أقراص فيديو رقمية (DVD). إن التغير المتباين بين الحالة الغير بلورية والبلورية بواسطة التأثير الحراري هو الأساس في عملية التسجيل البصري. لذلك، سعي حديثاً للبحث عن مواد تسجيل تعتمد على تغير بلوري سريع ومدى طويل للحفاظ على المعلومات، ولقد أظهرت نتائج البحث أن مركب Ge-Sb-Te يشبه هذه المادة.

Ge-Sb-Te يعرض العمل الحالي دراسة الخواص الكهربائية للغشاء الرقيق المكون من مادة Ge2Sb2Te5ة باستخدام المعاودة المطبخية، طريقة التيار وفرق الجهد الكهربائي (I-V) وطريقة السعة وفرق الجهد الكهربائي (C-V).

أولاً

تمت دراسة تأثير الوصلات الكهربائية المربعة على سطح الغشاء الرقيق Ge-Sb-Te على الإشارة الكهربائية المقدسة من خلال تصميم ثلاث توزيعات مختلفة للوصلات الكهربائية. أظهرت النتائج بأنه لا تأثير للوصلات الكهربائية إذا وضع المعجون الفضي على الطبقة الكهربانية الذهبية بدون أن يلمس الغشاء الرقيق.

هذا التصميم يضمن عدم تفاعل المعجون الفضي مع مادة الغشاء الرقيق خلال عملية التسجيل. بالإضافة إلى ذلك، أوضحت النتائج عدم امتصاص في ترسيب الطبقات (مادة الغشاء الرقيق والأقطاب الذهبية) والمهم هو بعد المعجون الفضي على الأقطاب الذهبية للعينة المقدسة.

ثانياً

أوضحت نتائج طيف الإشارة والتغير مع فرق الجهد الكهربائي (I-V) بأن هناك تشابه في علاقة المقامة والتزدد (Relaxation frequency) بالنسبة للحرارة من خلال قيم الطاقة المنتشرة والتي تساوي 0.39 وا. 0.36 إلكترون و وظيف تعزز النتيجة 0.72 إلكترون و. هذا يؤكد أن مادة تتسمى لحالة الكالكوجين. بالإضافة إلى ذلك، نجحت دراسة التبادل مع فرق الجهد بناء على درجة الحرارة التي تتم عنها انتقال المادة من الحالة اللافتورية إلى البلورية تساوي °C 135.

ثالثاً

أجريت دراسة لفقر الجهد مع السعة الكهربائية (C-V) لعينات من الغشاء الرقيق الغير متبلورة من مادة In0.3Ge2Sb2Te5 و Ge2Sb2Te5 وذلك لمعرفة تأثير إضافة الإنديوم على الخواص الكهربائية لـ In0.3Ge2Sb2Te5 و Ge2Sb2Te5. أوضح النتائج بأن السعة الكهربائية لعينة In0.3Ge2Sb2Te5 و Ge2Sb2Te5 لجميع درجات الحرارة المقدسة. وهذا السلوك يظهر في العينات الأخرى متسقة لعمر الإنديوم فقط عند درجات الحرارة العالية من درجة حرارة التحول من الحالة اللافتورية إلى البلورية وعند فرق جهد أكبر من 15
جامعة الإمارات العربية المتحدة
عمادة الدراسات العليا
برنامج الماجستير

تحضير ودراسة خصائص مواد شبه موصله (GeSbTe) لغرض التفزيز البصري
من خلال تغيير الحالة البلورية.

رسالة مقدمة من الطالبة:
حصة علي حميد الشامسي

إلى جامعة الإمارات العربية المتحدة
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2008