STUDY OF Sn$_x$Se$_y$ THIN FILMS FOR PHASE CHANGE MEMORY (PCM) APPLICATIONS

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DECLARATION

I declare that the work presented in this thesis is my original work and has not been presented for a degree in any other University or any other award.

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DEDICATION

This work is dedicated to my wife, Lucy, our son Morgan and our daughter Maureen.
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I would like to thank God who has led me all through with His unending grace. I would like to express my deepest gratitude and thanks to my two supervisors, Dr. Patrick M. Karimi and Dr. Walter K. Njoroge, for their excellent guidance, valuable comments and continuous support during the course of my study. Dr. C.M. Migwi, chairman physics department who gave me moral support and facilitated in ordering of chemicals in time. Dr. Daniel Wamwangi from centre of excellent in strong material, University of Witswatersrand, South Africa, for his contribution in fabrication and characterization of phase change memory.

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DEFINITION OF TERMS

*Amorphous*: state of a material where atoms lack proper order in their lattice.

*Bandgap energy*: This refers to the energy difference between the top of the valence band and the bottom of the conduction band which is found in insulators and semiconductors.

*Crystalline*: state of a material where atoms have a definite order in their lattice.

*Crystallization temperature*: This is the temperature at which phase transitions occurs.

*Evaporation*: This is a process of depositing thin films of material onto surfaces.

*Flash memory*: A type memory that stores information in an array of memory cells made from floating-gate transistors.

*KKR*: These are mathematical properties, connecting the real and imaginary parts of any Complex function which is analytic in the upper half plane.

*PCM*: This is a type of memory makes use of the reversible phase transition of the chalcogenide-based materials and data is stored as crystalline states.

*Reset*: This is a process to change phase from crystalline state to amorphous state.

*Set*: This is a process to change phase from amorphous to crystalline.

*Sheet resistance*: This is a measure of resistance of thin films that have a uniform thickness.

*Sputtering*: This is a process of ejecting material from a "target," that is source, which then deposited onto a "substrate e.g. glass slide in a vacuum chamber."
## ACRONYMS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>CD</td>
<td>Compact Disk</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DRAM</td>
<td>Dynamic Random Access Memory</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>DVD</td>
<td>Digital Versatile Disk</td>
</tr>
<tr>
<td>( E_g )</td>
<td>Bandgap Energy</td>
</tr>
<tr>
<td>FRAM</td>
<td>Ferroelectric Random Access Memory</td>
</tr>
<tr>
<td>GST</td>
<td>Germanium, Antimony and Tellurium (GeSbTe)</td>
</tr>
<tr>
<td>I-V</td>
<td>Current-Voltage Characteristics</td>
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<tr>
<td>KKR</td>
<td>Kramer Kronig Relations</td>
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<tr>
<td>MOSFET</td>
<td>Metal Oxide Semiconductor Field Effect Transistor</td>
</tr>
<tr>
<td>MRAM</td>
<td>Magnetoresistive Random Access Memory</td>
</tr>
<tr>
<td>PCM</td>
<td>Phase Change Random Access Memory</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
</tr>
<tr>
<td>SRAM</td>
<td>Static Random Access Memory</td>
</tr>
<tr>
<td>( T_g )</td>
<td>Glass Transition temperature</td>
</tr>
<tr>
<td>( T_x )</td>
<td>Crystallization temperature</td>
</tr>
<tr>
<td>UV-VIS-NIR</td>
<td>Ultra Violet- Visible light-Near Infra Red</td>
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Phase Change Random Access Memory (PCM) is one of the most optimized candidates for the next generation non-volatile memory due to its fast operation speed, high scalability, low power operation and fabrication costs. The transition from the amorphous to the crystalline phase is induced by heating the material above its crystallization temperature for a long enough time, and the switching back to the amorphous phase is realized by melting and quenching the material fast enough that it solidifies in the amorphous state. In this study the electrical and optical properties of various SnₙSeₙ alloys at room temperature and during annealing from 25-250 °C was investigated and subsequent electrical characterization of fabricated SnSe₄ PCM. An Edward Auto 306 RF/DC Magnetron evaporation chamber was used for thin film deposition. Transmission data in the range from 450 nm- 2500 nm was obtained using Shimadzu UV-VIS-NIR 3700/3700 DUV spectrophotometer. Optical bandgaps have been found to vary from 1.27-1.94 eV with decrease in tin concentration. I-V characteristics measurements were performed on the films using Keithley 2400 source meter interfaced with four point probe using computer to determine sheet resistivity. Sheet resistivity varied from 1150-1600 Ω cm. All the alloys have shown high sheet resistance at room temperature and low sheet resistance during annealing. This interprets that the samples were amorphous during deposition and changed to crystalline during annealing. The SnₙSeₙ alloys have different crystallization temperatures varying from 174-224 °C. Increase in tin concentration reduced the crystallization temperature. The PCM was fabricated based on SnSe₄ alloy since it had high crystalline temperature, low crystallization temperature and a wide band gap hence a better choice than other alloys of SnₙSeₙ. The PCM was found to have a threshold voltage of 3.71 V and its voltage and pulse width of amorphization and crystallization processes were 3.71 V, 90 ns and 1.3 V, 26 μs, respectively.
Chapter 1

INTRODUCTION

1.1 Background

Motivated by the potential applications of tin chalcogenides, investigations on these compounds are becoming particularly active in the field of materials science. Tin chalcogenides offers a range of optical band gaps suitable for various optical and optoelectronic applications. These compounds are also used as sensor and laser materials, thin films polarizers and thermoelectric cooling materials [Zainal et al., 2004].

As many newly developed digital electronic devices, such as digital cameras, camcorders, MP3 players and smart phones among others become popular, the demand for non-volatile semiconductor memory is increasing [Roberto et al., 2004]. However drawbacks such as long erasure time, scalability issues, limited cyclability and lower retention times are likely to make the existing flash memories (NAND type) lose their market-hold to other memories [Heone et al., 2005]. Recent research interest has established Phase change random access memory as a potential concept and candidate for non volatile memory applications.

The development of phase change random access memory (PCM) technology is being pursued very actively by several companies around the world. It is a very promising new non-volatile memory technology, in particular regarding its scaling properties. It holds the potential for a universal memory. This means that it could possibly replace several of the existing non-volatile memory technologies such as NOR and NAND flash and even
replace some currently volatile memory technologies such as DRAM with a non-volatile but equally high performance memory, opening up new memory and chip design concepts. Central to this technology are the phase change materials themselves [Kinam et al., 2007]. PCM technology is based on the remarkable difference between the resistivity of phase change materials in the amorphous and crystalline phase (three to five orders of magnitude is typical), and the repeatable and fast switching of the materials between these two phases. The transition from the amorphous to the crystalline phase is induced by heating the material above its crystallization temperature for a long enough time, and the switching back to the amorphous phase is realized by melting and quenching the material fast enough that it solidifies in the amorphous state. In optical recording, the difference in optical constants between the two phases is used to store information, and the application of phase change materials for re-writable CDs and DVDs is already a mature technology. Here, the switching and reading are performed by a laser pulse of variable power. If the PCM cell is in the amorphous state and a voltage is applied, only a very small current can flow because of the very high resistivity of the material in the amorphous phase. But if the voltage is raised above its so-called threshold voltage, the material suddenly becomes very conductive and a high current can flow, heating up the material to crystallize [Simone et al., 2008].

Phase change random access memory (PCM) is a new non-volatile memory that uses reversible phase transition of chalcogenide resistor. PCM has the following advantage compared to flash memory; it has fast switching speed, low programmable energy, high endurance, good data retention, improved compatibility with CMOS and excellent
scalability [Hwang et al., 2003]. There are Set and Reset operations in PCM. Reset operation is power-consuming process to change phase from crystalline state to amorphous state due to low resistance of the crystalline. Set operation is time consuming process to change phase form amorphous to crystalline due to nucleation and growth as shown in figure 1.1. Ge$_2$Sb$_2$Te$_5$ has been widely studied and optimized for PCM material [Lacaita et al., 2006]. However, it has some drawbacks such as, low crystallization temperature and low crystalline resistance. In order to solve these problems, a new material for the next generation PCM application needs higher crystalline temperature, higher crystalline resistance and faster phase change speed than Ge$_2$Sb$_2$Te$_5$. Researchers showed that the high crystallization temperature leads to high data stability and the high crystalline resistance reduces the reset operation power. Since PCM makes use of the reversible phase transition of the chalcogenide-based materials, the data is stored as crystalline states of the chalcogenide resistor [Lacaita et al., 2004].

![Temperature in programmed volume versus time](image)

**Fig. 1.1:** Temperature in programmed volume versus time (arbitrary units) during SET and RESET programming pulses for a PCM cell. $T_x$ and $T_a$ indicate crystallization temperature and melting point [Hudgens, 2008].
For a successful quest for fast phase change materials different strategies can be exploited. On the one hand understanding the kinetics of phase transformation and the role of stoichiometry could tailor the selection of fast, stable and non-volatile phase change materials. Accordingly there is need to distinguish the mechanism of recrystallization. While we take note that recrystallization is the crucial time limiting step in the storage process, the mechanisms of nucleation and growth should be clearly understood. A microscopic investigation of crystallization kinetics with a static tester and an atomic force microscope demonstrates that for different alloy compositions recrystallization proceeds either via growth from the crystalline rim or by nucleation and growth of critical nuclei. Furthermore the crystallization behavior at low temperature and long time scales gives information on the endurance and activation barrier against spontaneous recrystallization [Wuttig et al., 2002]. To determine the role of stoichiometry on these barriers could offer fast predictions of stable phase change alloys. In addition to the above role, theoretical calculation should be highlighted. Using Ab initio principles to determine the suitable metastable structures that don’t exhibit phase separation is also a step towards the efficient search for new superior phase change alloys [Wojciech, 2006]. In this work, a PCM cell with SnSe₄ as the active layer has been investigated for application as non volatile memories.

1.2 Problem statement and justification

In the past decade, several chalcogenide material compositions have been studied to fulfill the requirements for a suitable phase change material. Among these, Ge–Te based
binary and ternary systems were investigated extensively as candidates for optical data storage [Kim et al., 2007; Wuttig (2005); Yamada (1991); Kolobov et al., 2004]. GeTe and SnSe have the same average number of valence electrons per atom and similar band gaps [Landolt-Börnstein (1998), Luo et al. (2004)]. Despite the similarity in the type of coordination, the structure of GeTe and that of SnSe is different. GeTe has a rhombohedral structure while SnSe has an orthorhombic structure [Polatoglou, 1986]. SnSe has potential applications in memory switching devices [Hema et al., 2005]. With this consideration in mind, there is need to study optical and electrical properties of SnₓSeᵧ compounds, to establish whether they can produce phase change alloys, and fabricated a PCM memory device.

1.3 Objectives

1.3.1 Main objective

The general objective of this study was to synthesize, conduct vacuum evaporation and perform optical and electrical characterization of SnₓSeᵧ thin films compounds and subsequently fabricate a PCM cell.

1.3.2 Specific objectives

The specific objectives of the study were:

(i) To prepare and synthesize SnₓSeᵧ compounds at different molecular mass.

(ii) To deposit SnₓSeᵧ thin films using evaporation method.
(iii) To determine the sheet resistivity of the various thin films at room temperature and during annealing.

(iv) To perform optical spectroscopy of the various Sn$_x$Se$_y$ compositions to determine optical constants such as, band gap energy, $E_g$, and the refractive index, $n$.

(v) To fabricate and characterize a PCM cell based on Sn$_x$Se$_y$ alloy.

1.4 Rationale

As many newly developed digital electronic devices, such as digital cameras, camcorders, MP3 players and smart phones among others become popular, the demand for non-volatile semiconductor memory is increasing. Currently Flash memory (NAND type) with a number of practical problems like scaling difficulties as chip lithography shrinks is the only available non-volatile memory and, thus, its market is expanding rapidly [Lacaita, 2006]. Phase change random memory is a new non-volatile memory that uses reversible phase transition of chalcogenide resistor. It has several advantages i.e., it has extremely large read dynamics range, reduced switching current and improved device size.

1.5 Thesis organization

Chapter 2 presents an overview about the research already done on optical and electrical characterization of Sn$_x$Se$_y$ and fabrication and characterization of a PCM based on
various alloys. Chapter 3 gives an insight on theoretical considerations of processes involved in development of PCM, existing types of memories, their working and their pitfalls as compared to PCM. It also highlight models used to simulate Sn_xSe_y alloys. Chapter 4 discusses the design ideas and the fabrication of the PCM. It also gives the method employed in preparation and characterization of the Sn_xSe_y alloy. Chapter 5 presents the results and discusses the theory behind the occurrence. Chapter 6, summarizes the work and present further improvements of PCM.
Chapter 2
LITERATURE REVIEW

2.1 Introduction

In 1968, Ovshinsky discovered a new order-disorder memory phenomenon in chalcogenide film materials, later termed “Ovonic Memory” and subsequently found a laser optical memory effect [Ovshinsky (1968), Feinleib et al., (2007)]. However, material quality and power consumption issues prevented commercialization of the technology. More recently, interest and research have resumed as flash and DRAM memory technologies are expected to encounter scaling difficulties as chip lithography shrinks [Kinam et al., 2007].

The crystalline and amorphous states of chalcogenide glass have dramatically different electrical resistivity, and this forms the basis by which data are stored. The amorphous, high resistance state is used to represent a binary 1, and the crystalline, low resistance state represents a 0 as shown in figure 2.1.

![Fig. 2.1: Non-volatile memory phase change showing amorphous and crystalline state](Hosaka et al., 2004).
Although PCM has not yet reached the commercialization stage for consumer electronic devices, nearly all prototype devices make use of a chalcogenide alloy of germanium, antimony and tellurium (GeSbTe) called GST. It is heated to a high temperature (over 600°C), at which point the chalcogenide becomes a liquid. Once cooled, it is frozen into an amorphic glass-like state and its electrical resistance is high. By heating the chalcogenide to a temperature above its crystallization point, but below the melting point, it will transform into a crystalline state with a much lower resistance. It is the switching time that makes PCM, and other replacements for flash memory, most interesting. PCM's temperature sensitivity is perhaps its most notable drawback, one that may require changes in the production process of manufacturers incorporating the technology.

Structure of a PCM cell is shown in figure 2.2. It consists of a GST layer, with top and bottom contacts for electrical control. Phase-change in the GST layer is allowed by electrical pulses through the resistor structure, resulting in Joule heating of the active chalcogenide layer and fast phase transition. The phase-change occurs in a programmable volume close to the interface between GST and the bottom contact, which is engineered in order to provide a good thermal insulation from the cold metal layers [Ielmini et al., 2004]. A high-current pulse (reset pulse, current) can bring the GST in the programmable volume above the melting point; if the current pulse is suddenly switched off, the liquid-phase GST is quenched in an amorphous structure, as a long-range order atomic structure would instead require a relatively long time to be established as shown in figure 2.3. The amorphous GST is characterized by a large resistivity, as a result of extremely small carrier mobility and an intrinsic-type band structure [Pirovano et al., 2004]. To restore a
crystalline structure, a set pulse with relatively small current is applied, allowing for a fast annealing of the disordered structure.

![Schematic of three PCM cells](image)

**Fig. 2.2**: Schematic of three PCM cells, after reset (a), and set operation (b, c) amorphous and crystalline GST phases are shown as light and dark colours, respectively [Ielmini et al., 2004].

The resistivity of the poly-crystalline structure resulting from the electrical pulse is markedly lower than the one of the amorphous phase. Therefore, the amorphous and poly-crystalline phase states can be made to correspond to two distinct logic values, the reset and set states, respectively. The two states can be easily probed by a fast current or voltage readout [Wojciech, 2006].

### 2.2 Related work on PCM

Most studies of PCM have been based on the Ge$_2$Sb$_2$Te$_5$ compound, which is a mixture of GeTe and Sb$_2$Te$_3$ and was originally developed for use in recording media of optical data storage devices, such as CD-RW and DVD-RW. Like other chalcogenide phase-
change materials, Ge$_2$Sb$_2$Te$_5$ shows a reversible phase transition between the amorphous and crystalline phases [Friedrich et al., 2000].

The switching behavior of indium selenide based phase-change memory cell has been researched. It was performed through the static mode (dc test) switching for a 5 µm-sized In$_2$Se$_3$ PCM. The pulsed mode switching of the 5µm -sized In$_2$Se$_3$ PCM device showed that the reset (crystalline to amorphous) of the device was done with a 70 ns-3.1 V pulse and the set (amorphous to crystalline) of the device was done with 10 µs-1.2 V pulses [Jae-Min et al., 2005].

Phase-change nonvolatile memory cell elements composed of Sb$_2$Te$_3$ chalcogenide have been fabricated by using the focused ion beam method. The contact size between the Sb$_2$Te$_3$ phase change film and electrode film in the cell element was 2826 nm$^2$ (diameter: 60 nm). The thickness of the Sb$_2$Te$_3$ chalcogenide film was 40 nm. The threshold switching current of about 0.1 mA was obtained. A RESET pulse width as short as 5 ns and the SET pulse width as short as 22 ns for Sb$_2$Te$_3$ chalcogenide was obtained [Bo et al., 2005].

A high speed chalcogenide random access memory based on Si$_2$Sb$_2$Te$_5$, which had outstanding data retention and electrical performance, was fabricated by 0.18 mm complementary metal oxide semiconductor technology. SET and RESET times were 31 and 10 ns when the corresponding voltage pulses were 2V and 3.5 V, respectively.
Si$_2$Sb$_2$Te$_5$ material possessed better data retention and lower threshold current comparing to Ge$_2$Sb$_2$Te$_5$ [Ting et al., 2007].

Research on phase change memory switching devices using two stacked layers of chalcogenide material Ge-based layer (GeTe or Ge$_2$Se$_3$), and a tin-chalcogenide layer (SnTe or SnSe) has been done. The work focused on exploring alternative materials and device structures suitable for phase-change memory operation. The observed switching was dependent upon the polarity of potential applied to the electrode adjacent to the SnTe or SnSe layer. The presence of Sn-chalcogenide provided better adhesion of the memory layer to the electrode [Kristy et al., 2007].

Lee et al., (2006) studied the changes in the electrical conductivity occurring in a new composition of amorphous Ge$_1$Se$_1$Te$_2$ thin film for a high-performance nonvolatile phase-change memory. A phase-change random access memory device without an access transistor was successfully fabricated with the Ge$_1$Se$_1$Te$_2$ phase-change resistor, which has a much higher electrical resistivity than that of conventional Ge$_2$Sb$_2$Te$_5$, and its electric resistivity can be varied by the factor of $10^5$, related to the degree of crystallization. The static mode switching characteristics was tested for the 100 mm-sized Ge$_1$Se$_1$Te$_2$ PCM device. The results of pulsed mode switching of the 20 mm-sized Ge$_1$Se$_1$Te$_2$ PCM devices showed that the reset process of the device was accomplished with an 80 ns-8.6 V pulse and the set process of the device was accomplished with a 200 ns-4.3 V pulse.
2.3 Material requirements for PCM

A PCM can be fabricated with considerations of the following parameters.

a) *Crystallization speed*. This is the data rate limiting factor. Melt quenching can be inherently very fast if a strong enough current pulse can heat the material above the melting temperature [Simone *et al.*, 2008]. One also needs to bear in mind that crystallization times of an actual device can be influenced by factors such as surrounding materials, the thermal properties of the cell, and the size of the cell (in particular for growth-dominated materials).

b) *Melting temperature*. The melting temperature plays an important role in PCM devices because it determines the power required to RESET the cell. Most phase change materials have temperature in the range between 500 and 800°C [Simone *et al.*, 2008]. Melting temperature is typically determined by calorimetric measurements and is not only a function of the material composition but also a function of film thickness. This is extremely important when the scaling of PCRAM devices is considered.

c) *Resistances in both phases*. This determines the on/off ratio and also the required currents to SET (crystallize) and RESET (amorphize) the cell. The resistance, in both the amorphous ($R_{am}$) and the crystalline ($R_{c}$) phases, are essential parameters for device performance. The requirements are that the on/off ratio (more accurately it should be called off/on-ratio because it is $R_{am}/R_{c}$) is high enough for good read margin, and it is advantageous if both resistivities are relatively high, helping to reduce the RESET current by a larger voltage drop over the phase change material [Lankhorst (2002), Simone *et al.*, 2008].
d) **Crystallization temperature.** This determines the archival lifetime and maximum operation temperature. Crystallization temperature determines the threshold switching voltage due to crystal structure-induced carrier generation. The lower the crystallization temperature the lower the threshold memory switching voltage as well as lower activation energy [Simone *et al.*, 2008].

e) **Chemical stability.** If phase separation or materials aggregation occurs after repeated cycling, the cell performance will be influenced. Also, chemical reactions with the electrodes and the other surrounding material will influence cell performance. Chemical stability of the phase change material is essential as the material is repeatedly melted next to electrodes and a surrounding insulator. It has been found that repeated switching can lead to phase separation in PCRAM cells which, in turn, can lead to the failure of the cell [Simone *et al.*, 2008].

f) **Thermal conductivity.** Materials with low thermal conductivity lead to more efficient heating. Even though the thermal conductivity of the phase change material has a strong influence on the thermal properties of PCRAM cells, there is not much room in terms of optimization because most phase change materials have similar thermal conductivities [Simone *et al.*, 2008].

### 2.4 Related work on characterization of Sn$_x$Se$_y$

Motivated by the potential applications of tin chalcogenides, investigations on these compounds are becoming particularly active in the field of materials science. Tin
chalcogenides offer a range of optical band gaps suitable for various optical and optoelectronic applications [Zulkarnain et al., 2004]. Considerable attention has been given by various researchers in studying the properties of tin selenide. Due to its optical and electrical properties, SnSe has been utilized in memory switching devices. Among the methods used to prepare SnSe thin films are chemical bath deposition, vacuum evaporation, chemical vapour deposition and electrodeposition [Ana et al., 2005].

Preparation and characterization of a polycrystalline thin film of SnSe by vacuum deposition at a substrate temperature of 423 K has been done. The optical transmission measurement revealed that the SnSe thin films had a direct allowed band gap of 1.26 eV. Electrical conductivity study showed that the conductivity increases with increasing temperature [Pathinettam et al., 2000]. Tin selenide thin films using chemical method deposition has been carried out. The films were polycrystalline and covered the surface of the substrate completely. Photoelectrochemical test showed a p-type conduction mechanism. The band gap was found to be about 1.25 eV with direct transition [Zainal et al., 2004].

Hema et al. (2007) grown SnSe thin films by flash evaporation method at substrate temperatures, $T_s = 303 – 513$ K at an interval of 30 K. The optical absorption studies indicated a direct band gap of 1.26 eV with high absorption coefficient ($>10^4$ cm$^{-1}$) near the fundamental absorption edge. The films were found to have an electrical resistivity 8.1-30 $\Omega$ cm in the thickness range of 150 -300 nm.
Chapter 3

THEORETICAL CONSIDERATION

3.1 Introduction

The chapter describes the sputtering theory, thermal evaporation to produce binary alloys or compounds, theories on electrical resistivity and optical properties. Accordingly the theory of evaporation is explained from the thermodynamics stand point to determine the vapor pressure, the compositional stability of materials as well as the kinetic theory of gases to explain the atomistic process of evaporation. The theoretical background incorporates also the analytical techniques used in the characterization of thin film properties.

3.2 Sputtering

Deposition techniques for thin films mainly fall in two categories: Physical vapor deposition (PVD) and chemical vapor deposition (CVD). Evaporation and sputtering are the two main methods in physical vapor deposition. In this study, dc reactive magnetron sputtering method is used. Sputtering is a physical vapor deposition (PVD) technique whereby bombarding particles incident on a target collide with surface atoms thus dislodging them from the lattice through a transfer of energy as reported by Rodgers et al., 2004. The displaced lattice atoms as well as the bombarding particles (projectile) then undergo collisions with other lattice atoms, dislodging them and a chain reaction of collision ensues. Atoms with sufficient energy required to overcome the surface potential called the surface binding energy ($U_o$) will escape. There is a minimum projectile kinetic
energy needed to induce sputtering called threshold energy \( E_{th} \) and is given by Bohdansky et al., (2003).

\[
E_{th} = \frac{U_o}{\beta(1-\beta)} \quad \text{for} \quad \frac{M_1}{M_2} \leq 0.3
\]  

\[
E_{th} = 8U_o \left( \frac{M_1}{M_2} \right)^{\frac{1}{3}} \quad \text{for} \quad \frac{M_1}{M_2} > 0.3
\]

Where \( M_1 \) is Projectile mass, \( M_2 \) is Mean molecular mass per atom of a target and \( \beta \) is the maximum fractional energy transfer possible in a head-on collision given by:

\[
\beta = \frac{4M_1M_2}{(M_1 + M_2)^2}
\]

### 3.3 Evaporation

Thermal evaporation entails the transition of solids or liquids into the gaseous phase via joule heating at definite temperature in an evacuated ambient. Thermal evaporation occurs in three distinguishable steps which are outlined below.

(i). The transition of the condensed phase (solid or liquid) to the gaseous state.

(ii). The traversal of the vapor into space from the evaporated source to the substrate.

(iii). The condensation of the vapor on the substrate upon its arrival.

The theory of thermal evaporation is explained on the basis of thermodynamics and kinetics. The former approach provides a quantitative understanding of the evaporation rates, the compound stability and compositional changes during evaporation. The second
approach to understanding evaporation phenomena is based on the kinetic theory of gases to describe the atomistic processes of thermal evaporation. From the perspective of kinetic theory, the solid to gaseous transition is treated as an atomistic phenomenon which describes thermal evaporation in terms of the properties of individual particles. In the next section the kinetic gas theory will be discussed to interpret evaporation phenomena. The earliest systematic investigations to quantify evaporation rates in a vacuum are attributed to the scientific work of Hertz on mercury. Accordingly it was observed that the evaporation rate is proportional to the difference between the hydrostatic pressure, $P$ and the equilibrium pressure, $P^*$ on the surface. It therefore follows that there is a limit to the maximum evaporation rate attainable at a given temperature regardless of the thermal energy supplied to the evaporant. If there is no reaction of emitted molecules by the condensing surface, then the theoretical maximum rate is proportional to the impingement rate. Hence the number of molecules $dN_s$, evaporating from a surface area $A_e$ per unit time $dt$ is given by the expression;

$$
\frac{dN_s}{A_e \, dt} = \frac{P^* - P}{\sqrt{2 \pi m k T}}
$$

(3.4)

Where $m$ is the mass of molecule is, $k$ is Boltzmann constant and $T$ is the absolute temperature. The return flux is represented by the hydrostatic pressure of the evaporant. Equation 3.4 considers the molecules that are reacted back to the gaseous flux and incorporated in the evaporant. However a proportion of the reflected molecules also remains in the gaseous vapor and contribute to the evaporant pressure [Wamwangi, 2004].
3.3.1 Evaporation of Alloys

In the evaporation of compounds, the transition to the gaseous phase is often accompanied by a change in the composition of the condensate. This variation in composition arises due to the differences in the vapor pressure of the compound constituents. The vaporization of compounds can follow three viable routes namely; association or dissociation or both. Dissociation is characterized by changes in the stoichiometry of the compound particularly if one of the constituents is non volatile. However such effects on stoichiometry are seldomly observed in association. Dissociation therefore makes direct thermal evaporation of compounds quite difficult. However this is not encountered for compounds which enter the gaseous state either as complete molecules or also for compounds with comparable vapor pressures [Wamwangi, 2004]. To better understand the principles of evaporation we discuss the thermodynamic approach in the next section.

3.3.2 Kinetics of crystallization

Crystallization involves the phase transformation from a disordered state to an ordered one at a specific temperature. So the kinetics of crystallization entails mechanisms by which the crystallization speed at certain temperature values can be increased to obtain high growth rates which are a requisite for suitable rewritable phase change recording. In addition the resistance against crystallization should also be high at room temperature and slightly above to ensure that no spontaneous crystallization occurs. This point is also
related to the stability of a structure with respect to its other phases. This stability is
determined by the Gibbs free energy [Njoroge, 2002].

\[ G = U + pV - TS \]  

(3.5)

where \( U \) is the internal energy, \( p \) is pressure, \( V \) is the volume, \( T \) is the temperature and \( S \) is the entropy. The equilibrium state of a given phase is that for which the Gibbs free energy is a minimum. Moreover the free energy is a function of external variables such as temperature \( T \), which means it does not undergo any discontinuous change. Therefore at the temperature and pressure at which a structure undergoes a phase transition, the free energies of both phases will be equal. The transformation from \( \alpha \) to the \( \beta \) phase is determined by the difference in their Gibbs free energy. This is the driving force which determines the phase transition. Suppose we now consider a phase transition at a fixed pressure. For the stable phase, \( \alpha \) at lower temperature the internal energy will be lower while the second phase \( \beta \) will have higher entropy at high temperature. This is schematically illustrated in fig. 3.1 which shows the free energy as a function of configurational coordinates.

![Free energy diagram](image)

**Figure 3.1**: The free energy diagram for two phases, \( \alpha \) and \( \beta \) of the same compound a function of the configurational coordinates.
The transformation from the $\alpha$ to the $\beta$ phase will be determined by the difference in the Gibb's free energy. However how fast this transformation takes place is determined by the kinetics via the activation energy for this transition. The magnitude of the activation energy determines the kinetics of transformation and it constitutes the nucleation and growth terms which will be discussed in the next section.

### 3.3.3 Nucleation

Nucleation can occur in two possible forms, namely homogeneous and heterogeneous nucleation. The distinction between these two mechanisms comes from the fact that in homogeneous nucleation the probability to form subcritical nuclei at any point is the same within the volume of the parent phase. Heterogeneous nucleation on the other hand is due the presence of foreign particles which decrease the surface energy needed to form new particles. Consequently new particles of smaller size than those required in homogeneous nucleation are stable and the rate of heterogeneous nucleation is made much faster. Nucleation starts with the formation of small atom clusters. At a certain fixed temperature, the clusters with sizes greater than the critical size, $r^*$ become stable nuclei. Otherwise they shrink and eventually vanish. The critical size of the nuclei is influenced by the competition between surface tension and free energy density difference between the amorphous and crystalline phases. This yields an energy barrier that should be overcome to obtain a critical nucleus. The change in Gibbs free energy change due to the formation of nuclei of radius $r$ is given by the contributions of the surface, the volume and elastic energy terms in the form:
\[ \Delta G = 4\pi r^2 \gamma + \frac{4}{3} \pi r^3 \Delta G_v + \Delta G_e \]  

(3.6)

where \( \Delta G_v \) is the Gibbs free energy per unit volume, and \( \gamma \) is the surface energy per unit area at the interface of the new and parent phases, \( \Delta G_e \) denotes the elastic term. The dependence of the free energy on the nuclei size is shown schematically in figure 3.2. Also included in this figure are volume and the surface components. The volume term predominates the surface term at higher radii, and this leads to negative free energy and hence stable nuclei. Equation 3.6 assumes a spherical nucleus with isotropic surface tension. The volume term is negative and it decreases as \( r^3 \) while the second term is positive and increases as \( r^2 \). Thus \( \Delta G \) passes through a maximum, which we denote by \( \Delta G^* \). The critical radius to obtain a stable nucleus is now given as:

\[ r^* = \frac{-2\gamma}{\Delta G_v} \]  

(3.7)

The critical Gibbs free energy is obtained by substituting for \( r^* \) in equation (3.7) to get:

\[ \Delta G^* = \frac{16\pi \gamma^3}{3(\Delta G_v)^3} \]  

(3.8)

A schematic diagram of the temperature dependence on nucleation and crystal growth rates is shown in fig. 3.2. The strong dependence of nucleation and crystal growth rates on temperature is illustrated in this figure. The nucleation rate increases with temperature
and then reduces to zero at the melting temperature \( T_m \) because of the decrease in the driving force to zero. The growth rate increases in a similar manner but at a higher temperature. The occurrence of the maxima of each process at different temperature regimes provides a way of distinguishing between fast-nucleation and fast growth materials. This was illustrated and it has been used to distinguish phase change alloys on the basis of their nucleation and growth behavior [Wamwangi, 2004]. Figure 3.2 illustrates the distinction between nucleation and growth dominated phase change alloys.

![Fig. 3.2: The free energy of formation of nuclei as a function of size. \( \Delta G \) increases when \( r < r^* \), hence the embryos are unstable and quickly break away since \( \Delta G \) is positive, the system will approach equilibrium when \( \Delta G \) decreases, and this happens when \( r > r^* \) since \( \frac{\partial \Delta G}{\partial r} \) is now negative [Njoroge, 2002].](image)

The crystallization rate reaches a maximum at some temperature for each mechanism. This shows that the peak temperature for nucleation and grain growth is much lower than that in direct grain growth. The implication is that the annealing temperature will always
affect the crystallization behavior of the active layer during the erasure process. To explain this point one sees from both figures that annealing at low temperature increases both nucleation and grain growth whereas high temperature annealing leads to direct grain growth.

![Diagram showing nucleation and growth rates](chart.png)

**Fig. 3.3:** Schematic representation of the temperature dependence of nucleation and growth rates. $\Delta T$ is the degree of undercooling which is defined as the difference between the instantaneous temperature $T$ and the melting temperature $T_m$ [Njoroge, 2002].

### 3.4 Electrical Resistivity

In this section, comparison between electrical resistivity in metals and semiconductors has been made. There are many differences between a metal and a semiconductor. However, a fundamental difference between a metal and a semi-conductor is that the
former is unipolar (conducts current by means of charges of one sign only, electrons), whereas a semi-conductor is bipolar (contains two charge carrying particles of opposite sign). One carrier has a negative charge (free electron) of mobility $\mu_n$ and the other has a positive charge (the hole), of mobility, $\mu_p$. These particles, when subjected to an electric field $E$, would move in opposite directions, but since the current of each is in the same direction, their current density $J$, is given by:

$$J = (n\mu_n + p\mu_p)qE = \sigma E$$

(3.9)

Where $n$ is the concentration of free electrons, $p$ is the concentration of holes, $\sigma$ is the conductivity, and $q$ is charge of the carrier.

Therefore,

$$\sigma = (n\mu_n + p\mu_p)q$$

(3.10)

It is found from Fermi-function and density of states calculations that the number of electrons per unit volume is expressed as;

$$n = N_c e^{(\mu-E_c)/k_BT}$$

(3.11)

While the number of holes per unit volume is given by;

$$p = N_v e^{-\mu_p/k_BT}$$

(3.12)
Where $N_c$ is the number of levels per unit volume in conduction band is, $N_v$ is the number of levels per unit volume in the valence band, $E_g$ is the band gap energy, $K_B$ is the Boltzmann constant and $\mu$ is the mobility. Combining equations in $n$ and $p$ we obtain;

$$np = N_cN_v e^{-\frac{E_g}{2k_BT}}$$  \hspace{1cm} (3.13)

The result is a function of temperature only and is independent of impurity concentration.

For a pure semiconductor,

$$n = p$$  \hspace{1cm} (3.14)

Therefore equation 3.13 becomes,

$$n=p=(N_cN_v)^{\frac{1}{2}} e^{-\frac{E_g}{2k_BT}}$$  \hspace{1cm} (3.15)

But $\sigma = (n\mu_n + p\mu_p)q$  \hspace{1cm} (3.16)

Thus for a pure semiconductor, $\sigma$ is given by:

$$\sigma = pq(\mu_n + \mu_p)$$  \hspace{1cm} (3.17)

Therefore inserting equation 3.15 into 3.16, yields
\[ \sigma = (N_e N_v)^{1/2} q(\mu_n + \mu_p) e^{-E_g / 2k_B T} \]  

(3.18)

which can be written as;

\[ \sigma = A_0 e^{-E_g / 2k_B T} \]  

(3.19)

Where \( A_0 = (N_e N_v)^{1/2} q(\mu_n + \mu_p) \)

Hence resistivity, \( \rho \) can be expressed as;

\[ \rho = \frac{1}{\sigma} = \frac{1}{A_0} e^{E_g / k_B T} = B_0 e^{E_g / k_B T} \]  

(3.20)

Where,

\[ B_0 = \frac{1}{A_0} = \frac{1}{((N_e N_v)^{1/2} q(\mu_n + \mu_p))} \]  

(3.21)

The final expression suggests that the resistivity will decrease with increase in temperature for a semi-conductor.

### 3.5 Sheet Resistivity of Thin Films

Sheet resistivity of thin films can be determined using Van der Pauw model. For very thin films (thickness \( t << \) probe spacing\((s)\)), current rings instead of spheres are realized. Therefore the area \( A \), can be expressed as;
\[ A = 2\pi xt \]  
\[ R = \rho x / A \]  
\[ R = \int_{s}^{2s} \frac{\rho dx}{2\pi x} \]

Where \( s \) is the probe spacing as shown in figure 3.4;

**Fig. 3.4:** A schematic illustration of probe tips on film sample.

\[ R = \frac{\rho}{2\pi} \ln 2 \]  
\[ \rho_s = \frac{2\pi R}{\ln 2} \]

Consequently, for \[ R = \frac{V}{2I} \],
The resistance of the thin film sheet is given by: -

\[ R_s = \frac{\pi}{\ln 2} F(Q) \frac{V_{DC} + V_{BC}}{2I} \left[ \frac{\Omega}{\text{Square}} \right] \]  \hspace{1cm} (3.28)

Where F and Q are the symmetry and correction factors, respectively.

For \( V_{BC} \leq V_{DC} \), \( Q = \frac{V_{DC}}{V_{BC}} \) and vice versa. F is a function of Q and is valid for Q less than 10. It is expressed in the form;

\[ F = 1 - 0.34657 \left( \frac{Q-1}{Q+1} \right)^2 - 0.09236 \left( \frac{Q-1}{Q+1} \right)^4 \ldots \]  \hspace{1cm} (3.29)

Where \( \frac{V_{DC} + V_{BC}}{2I} \) is the average resistance. Average resistance is obtained from the slope of the average resistance curves using linear regression with the regression section selected manually. The specific resistivity \( \rho \) can be determined from the thin film thickness and the sheet resistance in the form;

\[ \rho = R_s t 10^{-4} \mu \Omega \text{cm} \]  \hspace{1cm} (3.30)

Where \( t \) is the film thickness and \( R_s \) is the sheet resistance of the samples.
3.6 Optical Properties

In this section, a brief theory on the optical constants of materials is given. First, a discussion of the physical meaning of the optical constants, and later a discussion of the dominant optical absorption processes encountered in materials and some models used to describe the kinds of absorption [Sodky, 2003].

3.6.1 Optical constants

The optical constants are parameters which characterize how a material will respond to excitation by an electromagnetic field at a given frequency. For isotropic materials, two real parameter (or one complex parameter) are sufficient for this purpose. Consider a point inside the material of interest at which some externally applied electric field $\tilde{E}$ exists. The polarization field $\tilde{P}$ is defined as the additional electric induced at that point by the external field, and is (in the absence of non-linear effect) proportional to the external field:

$$\tilde{P} = \tilde{\chi}_e \varepsilon_0 \tilde{E}$$

(3.31)

Where $\chi_e$ is the electric susceptibility of the material, and $\varepsilon_0$ is the free space dielectric constant. The displacement field $\tilde{D}$ can be shown from Maxwell’s equations to equal the external electric field plus the polarization field, yielding;
\[ \bar{D} = (1 + \bar{\varepsilon}) \varepsilon_0 \bar{E} \]  

(3.32)

The complex dielectric function of the material is defined as the constant of proportionality between the displacement and electric field:

\[ \varepsilon \equiv (1 + \bar{\varepsilon}) \varepsilon_0 \]

\[ = \bar{\varepsilon} \varepsilon_0 \]  

(3.33)

Where \( \bar{\varepsilon} \) is the complex dielectric constant of the material (\( \bar{\varepsilon} = \varepsilon_1 + i \varepsilon_2 \)) and \( \varepsilon_r \) is the complex relative dielectric constant for the material. Thus,

\[ \bar{D} = \bar{\varepsilon} \bar{E} \]  

(3.34)

Thus, it has been shown that the dielectric function represents the degree to which the material may be polarized by an electric field. It has a complex quantity, and the imaginary part of the dielectric function has the useful property of being proportional to the amount of power absorbed per unit time and unit volume at a point in the material from the applied field. This is a natural quantity for the calculation from physical absorption models. The real and imaginary parts of the relative dielectric function are very commonly tabulated in the literature as optical constants of materials [Sodky, 2003].
A second representation of the optical properties of a material also based on the effect that the material has an electromagnetic wave propagating through the material. The propagating electromagnetic wave is given by;

\[
\vec{E}(\vec{r},t) = \vec{E}_0 \exp \left( \frac{i 2 \vec{n} \vec{q} \cdot \vec{r}}{\lambda} \right) \exp(-i\omega t)
\]  

(3.35)

Where \( \vec{q} \) is the unit vector along the direction of wave propagation, \( \vec{n} \) is the complex index of refraction \( n + ik \), \( \lambda \) is the wavelength of the light in the vacuum, \( \omega \) is the angular frequency of the wave, \( \vec{E}_0 \) is a complex vector constant specifying the amplitude and polarization state of the wave. The complex index of refraction \( \vec{n} = n + ik \) governs the change in amplitude and phase of the wave as it propagates. The quantity \( n \) is the real index of refraction, \( k \) is the index of absorption, which also known as the extinction coefficient. The complex index of refraction and the complex dielectric function of a material are related by;

\[
\tilde{\varepsilon} = \vec{n}^2
\]  

(3.36)

The length of propagation of the wave in the material after which the phase of propagating wave will change by \( 2\pi \) is determined by the real part of the index of refraction \( n \), and equals the wavelength of the propagating wave (in free space) divided by the real part of the material index of refraction. The amplitude of the propagating wave will decay to \( 1/e \) of its original amplitude after propagating a distance equal to the
wavelength divided by \(2\pi\) times the imaginary part of the complex index of refraction (the extinction coefficient).

Thus the optical constants \(n\) and \(k\) represent the optical properties of a material in terms of how an electromagnetic wave will propagate in the material. Alternatively, the real and imaginary parts of the dielectric function contain the same information in terms of how the material responds to an electric field. Both types of optical constants are commonly encountered in the literature, and the choice of optical constant type is generally determined by the application.

### 3.6.2 Kramer-Kronig relation (KKR)

The real and imaginary parts of the complex index of refraction are not independent quantities, nor are the real and imaginary parts of complex dielectric function. The Kramer-Kronig relation, derived from the requirement that the material cannot respond to an applied electric field prior to the application, connects the real and imaginary parts of the complex index of refraction and complex dielectric function as follows:

\[
n(E) - 1 = \frac{2}{\pi} \int_0^\infty \frac{E' k(E')}{E'^2 - E^2} dE' \tag{3.37}
\]
\[ \varepsilon_1(E) - 1 = \frac{2}{\pi} \int_0^\infty \frac{E' \varepsilon_2(E')}{E'^2 - E^2} dE' \]  

(3.38)

In other words, if the spectrum of the absorptive part of the optical constants is known, the real part may be evaluated from equations (3.37) or (3.38). The optical properties of all materials are determined completely by the types, strength and the model of the optical absorption processes which occur in the material given in the section below.

### 3.6.3 The OJL Interband Transition Model

The OJL model for interband transition gives expressions for the density of states (DOS) for the optical transition from the valence band to the conduction band. Parabolic bands are assumed with tail states exponentially decaying into the band.

![Density of states N(E)](image)

**Fig. 3.5:** Parabolic bands with tails exponentially decaying into the band gap, according to the OJL model [Sodky, 2003].
The original parameters of the OJL density of states model are the energies $E_V$ and $E_C$, the ‘damping constants’ of the valence and conduction band $\gamma_V$ and $\gamma_C$, respectively, as well as the masses of the valence and conduction band $m_V$ and $m_C$ as shown in figure 3.5. These expressions,

$$ E_{M,V} = E_V - \frac{1}{2} \gamma_V $$  \hspace{1cm} (3.39)  

and

$$ E_{M,C} = E_C + \frac{1}{2} \gamma_C $$  \hspace{1cm} (3.40)  

denote the mobility edges of the valence and conduction band, respectively. The mobility gap, $E_o$, in the OJL model is therefore given by;

$$ E_C + \frac{1}{2} \gamma_C - \left( E_V - \frac{1}{2} \gamma_V \right) = E_o $$  \hspace{1cm} (3.41)  

By applying boundary conditions to the solutions of Maxwell’s equation, one is able to solve the problem of determining the light transmitted and reflected at a boundary separating two optically different media. In a defect free crystalline semiconductor, the absorption spectrum terminates abruptly at the energy gap. In contrast, in an amorphous semiconductor, a tail in the absorption spectrum encroaches into the gap region. This tail in the absorption spectrum makes the absorption edge of an amorphous semiconductor difficult to define experimentally. Although, it is recognized that the distribution of states
exhibits a square-rood functional dependence in the tail region, the exact form of the tail is still the subject of considerable controversy. Therefore O'Leary, Johnson and Lim (OJL) established a clear relationship between the form of the optical absorption spectrum and the form of the distribution of electronic states.

In amorphous semiconductor, momentum is a poor quantum number. As result, only energy conservation needs to be satisfied for a successful optical transition. This being the case, it can be shown that the optical absorption coefficient is given by:

$$\alpha(\hbar \omega) = D^2 (\hbar \omega) J(\hbar \omega), \quad (3.42)$$

Where $J(\hbar \omega)$ denotes the joint density of states (JDOS) function and $D^2 (\hbar \omega)$ being the optical transition matrix element. The JDOS can be expressed as,

$$J(\hbar \omega) = \int_{-\infty}^{\infty} N_c(E)N_v(E - \hbar \omega) dE \quad (3.43)$$

The function $D^2 (\hbar \omega)$ can be considered as;

$$D^2 (\hbar \omega) \approx 1/(\hbar \omega) \quad (3.44)$$
3.6.4 Interband absorption

Interband absorption is the most important type of optical absorption. It occurs when an electron in bound state in the materials absorbs a single photon from the light beam and jumps to a higher energy level in the materials. Semiconductor and dielectric materials exhibit an energy gap in their band structure, with the Fermi level of the material lying somewhere within the bandgap. Thus interband absorption will not occur for these materials until the photon energy exceeds the energy difference between the highest occupied electron energy level and the lowest unoccupied energy level [Mark, 2001].

3.6.5 Energy Band gap

Energy band gap generally refers to the energy difference between the top of the valence band and the bottom of the conduction band. Energy band gap may either be direct or indirect. In semiconductor physics, a direct band gap means that the minimum energy of the conduction band lies directly above the maximum energy of the valence band in momentum space. Electrons at the conduction-band minimum can combine directly with holes at the valence band maximum, while conserving momentum. The energy of the recombination across the band gap will be emitted in the form of a photon of light as shown in figure 3.6.
Indirect bandgap is a bandgap in which the minimum energy in the conduction band is shifted by a k-vector relative to the valence band. The k-vector difference represents a difference in momentum as shown in figure 3.6. Semiconductors that have an indirect bandgap are inefficient at emitting light. This is because any electrons present in the conduction band quickly settle into the energy minimum of that band. Electrons in this minimum require some source of momentum allowing them to overcome the offset and fall into the valence band. Photons have very little momentum compared to this energy offset. The momentum of a photon being absorbed is negligible and direct transitions are essentially 'vertical' in k-space.

**Fig. 3.6:** Schematic representation of direct and indirect transitions of silicon. For the direct transition the minimum of the valence and conduction bands is at the Γ point of the wave vector. Transitions take place via the same k vector. For indirect transition, a phonon is required to conserve momentum. The minimum of the conduction and the maximum of the valence bands do not have the same wave vector [Wamwangi, 2004].
3.7 Memory Technologies

Non volatile memories work differently. In the next section, we have highlighted working mechanisms as well as their limitations.

3.7.1 Flash memory

This is a non-volatile computer memory that can be electrically erased and reprogrammed. Flash memory works by modulating charge (electrons) stored within the gate of a MOS transistor [Ielmini et al., 2005]. The gate is constructed with a special "stack" designed to trap charges (either on a floating gate or in insulator "traps"). The presence of charge within the gate shifts the transistor's threshold voltage, $V_{th}$, higher or lower, corresponding to a 1 to 0, for instance. Changing the bit's state requires removing the accumulated charge, which demands a relatively large voltage to "suck" the electrons off the floating gate as shown on figure 3.7. This burst of voltage is provided by a charge pump which takes some time to build up power.

One limitation of flash memory is that although it can be read or programmed a byte or a word at a time in a random access fashion, it must be erased a "block" at a time. Another limitation is that flash memory has a finite number of erase-write cycles [Kian Chiew, 2006].
3.7.2 Dynamic Random Access Memory (DRAM)

Dynamic random access memory (DRAM) is a type of random access memory that stores each bit of data in a separate capacitor within an integrated circuit. Since real capacitors leak charge, the information eventually fades unless the capacitor charge is refreshed periodically. Because of this refresh requirement, it is a dynamic memory as opposed to SRAM and other static memory [Rabaey et al., 2003]. The advantage of DRAM is its structural simplicity: only one transistor and a capacitor are required per bit, compared to six transistors in SRAM. This allows DRAM to reach very high density. Like SRAM, it is in the class of volatile memory devices, since it loses its data when the power supply is removed. Unlike SRAM however, data in DRAM may still be recovered for a short time after power-off [Scheik et al., 2000].
3.7.3 Magnetoresistive Random Access Memory (MRAM)

Magnetoresistive Random Access Memory (MRAM) is a non-volatile computer memory, which has been under development since the 1990s. Increase in density of existing memory technologies notably Flash RAM and DRAM kept MRAM in a niche role in the market, but its proponents believe that the advantages are so overwhelming that MRAM will eventually become dominant for all types of memory, becoming a true "universal memory". In MRAM data is continued stored by magnetic storage elements. The elements are formed from two ferromagnetic plates, each of which can hold a magnetic field, separated by a thin insulating layer. A memory device is built from a grid of such "cells". This approach requires a fairly substantial current to generate the field, however, which makes it less interesting for low-power uses, one of MRAM's primary disadvantages. Additionally, as the device is scaled down in size, there comes a time when the induced field overlaps adjacent cells over a small area, leading to potential false writes [Roberto, 2007].

3.7.4 Ferroelectric RAM (FeRAM or FRAM)

Ferroelectric RAM (FeRAM or FRAM) is a random access memory similar in construction to DRAM but uses a ferroelectric layer instead of a dielectric layer to achieve non-volatility. FeRAM advantages over Flash include: lower power usage, faster write speed and a much greater maximum number (exceeding $10^{16}$ for 3.3 V devices) of
write-erase cycles [Kian Chiew, 2006]. FeRAM disadvantages are: much lower storage densities than Flash devices, storage capacity limitations and higher cost. In a FeRAM cell capacitor the dielectric structure includes ferroelectric material, typically lead zirconate titanate (PZT) [Kinam, 2007]. A ferroelectric material has a nonlinear relationship between the applied electric field and the apparent stored charge. Specifically, the ferroelectric characteristic has the form of a hysteresis loop, which is very similar in shape to the hysteresis loop of ferromagnetic materials. When an external electric field is applied across a dielectric, the dipoles tend to align themselves with the field direction, produced by small shifts in the positions of atoms and shifts in the distributions of electronic charge in the crystal structure. After the charge is removed, the dipoles retain their polarization state.

3.7.5 Static Random Access Memory (SRAM)

Static random access memory (SRAM) is a type of semiconductor memory where the word *static* indicates that, unlike dynamic RAM (DRAM), it does not need to be periodically refreshed, as SRAM uses bistable latching circuitry to store each bit. SRAM exhibits data remanence, but is still volatile in the conventional sense that data is eventually lost when the memory is not powered Each bit in an SRAM is stored on four transistors that form two cross-coupled inverters. This storage cell has two stable states which are used to denote 0 and 1. Two additional *access* transistors serve to control the access to a storage cell during read and write operations. A typical SRAM uses six MOSFETs to store each memory bit [Rabaey et al, 2003].
Chapter Four

EXPERIMENTAL PROCEDURES

4.1 Introduction

This chapter presents a summary of the evaporation technique and preparation of thin films. Measurement of sheet resistivity of thin films as per the Van der Pauw model, optical measurements and the experimental procedure that was adopted is also explained. Fabrication and characterization of PCM is also described in this section.

4.2 Preparation of SnₓSeᵧ Thin Films

Ingots of SnₓSeᵧ have been prepared using constituent elements of (99.999% pure) tin and selenium (obtained from M/S Aldrich, USA) weighed in different molecular compositional ratio. In each case a sample of SnₓSeᵧ was prepared and the samples were weighed using high precision digital balance. A silica tubes, 1cm diameter and 15cm long were prepared for holding samples together. Then the samples were subjected to temperature above 1200°C in furnace until compound melted the silica tube was thoroughly shaken to ensure heating uniformity then the samples were allowed to cool down. This process was repeated two or three times in order to ensure homogeneity before the samples are ground in a porcelain motor. The chalcogenide thin films were prepared by single source evaporation as shown in figure 4.1. The powdered samples were placed one at a time in a molybdenum evaporator boat in Edward 306 sputtering system. Here, the powdered SnₓSeᵧ alloy of predetermined masses were placed directly
on a single unheated evaporation boat at room temperature followed by controlled increase in the boat temperature up to 900°C under high vacuum conditions. The pressure inside the vacuum chamber was pumped down to $2 \times 10^{-6}$ millibars before starting the evaporation process. Cleaning of the slides was done before deposition of thin films was performed. The substrate holder was rotating during deposition to get thin films with uniform thickness. A mechanical shutter was used to avoid any contamination on the substrates which were at ambient temperature. The deposition rate (1 nm/sec.) of the prepared films were controlled by a quartz crystal monitor, hence the thickness. The exact thicknesses of the films were measured, after breaking the vacuum, using surface profilometer. For each sample four sets were prepared to be used in testing for reproducibility.

![Schematic diagram of evaporation unit used to deposit SnₓSeᵧ alloys.](image)

**Fig. 4.1:** Schematic diagram of evaporation unit used to deposit SnₓSeᵧ alloys.
4.3 Electrical Measurement using Four Point Probe

The electrical resistivity measurements of the thin films were be done using the four point probe arrangement as per the Van der Pauw set up. The effectiveness of this method in determining sheet resistance depends on the sample conditions, namely:

(i). The sample should be homogeneous in thickness, but in principle it can also have any arbitrary shape.

(ii). The sample should also be flat and compact with no isolated holes. Porous samples lead to high sheet resistance due to poor electrical contacts.

With a symmetrical square geometry adopted, the probe leads were connected to the sourcemeter for voltage and current measurements and display as shown below.

![Schematic diagram of four point probe set up for resistivity measurement.](image)

**Fig.4.2:** Schematic diagram of four point probe set up for resistivity measurement.

A current $I_{AB}$ was applied through contacts A and B and the potential drop $V_{DC}$ across the contacts D and C measured. The values obtained were sent to the computer for
plotting I-V curve to be used for sheet resistance computation. Sheet resistance of the samples was measured at room temperature and during annealing from 25-250 °C in order to determine the transition temperatures of each sample. This was done by placing samples in an evacuated quartz tube of an electric furnace under a steady argon flow. The furnace was programmed to heat at the rate of 10 K/min.

The measured sheet resistance, $R_s$, was independent of the sample geometry and can be converted into resistivity $\rho$ by the equation 4.1 given below.

$$\rho = R_s \times d$$

(4.1)

Where $d$ is the sample thickness.

4.4 Optical Measurements

Optical properties of the thin film samples were determined by use of the transmission data in the range from 450 nm- 2500 nm and obtained using Shimadzu UV-VIS-NIR 3700/3700 DUV spectrophotometer as shown on figure 4.2. To obtain values the optical constants; the band gap, the refractive index, and the extinction coefficient. Scout software developed by Theiss was used to fit experimental to the simulated data. To generate the simulated data, we have used OJL model together with harmonic oscillator susceptibility.
4.5 Fabrication of SnSe$_4$ Phase Change Memory

This research also aimed at fabricating a PCM cell. SnSe$_4$ alloy has been used for PCM fabrication due to its highest crystalline resistivity, highest resistance contrast in the order of 10 and lowest crystallization temperature as compared to other Sn$_x$Se$_y$ alloys. High crystalline resistivity ensures a low reset current for low power consumption in PCM devices. According to $P = I^2R$, higher resistivity gives better heating efficiency. High resistance, in both the amorphous ($R_{am}$) and the crystalline ($R_x$) phases, are essential parameters for device performance. The requirements are that the on/off ratio (more accurately it should be called off/on-ratio because it is ($R_{am}/R_x$) is high enough for good read margin, and it is advantageous if both resistivities are relatively high, helping to reduce the RESET current by a larger voltage drop over the phase change material. Low
crystallization temperature is necessary to determine the archival lifetime and maximum operation temperature, crystallization temperature is one of the essential material parameters that determines the data retention in PCM. SnSe$_4$ possesses a relatively large electronic band-gap required in order to reduce threshold current [Ting et al., 2007].

The PCM device was fabricated on a substrate silicon single crystal wafer with (100) orientation. A 100-nm-thick SiO$_2$ layer which acts as a thermal insulator were deposited by reactive DC sputtering on the silicon wafer to reduce electron tunneling. The sputter system was pumped down to pressure of 2x10$^{-6}$ millibar. The silicon target was sputtered with 20 sccm of oxygen gas. The gas flow was controlled by mass flow meters, interfaced to a computer. A 100-nm-thick Aluminum electrode was deposited by RF sputtering on one side of the PCM device while the other side was masked off as shown below. A SiO$_2$ layer was again deposited however a section of bottom electrode was masked off to create space for contact between Chalcogenide resistor and the Aluminum electrode. The ground SnSe$_4$ was placed on the molybdenum boat and evaporated and deposited on the space earlier masked off with an area of 25 mm$^2$. Finally, Aluminum was deposited as the top electrode.

**Fig. 4.4:** Schematic cross-sectional view of the PCM test device [Lee et al., 2006].
4.6 Electrical Measurement of Phase Change Memory

4.6.1 DC Test of a PCM

The operation behaviours of the fabricated devices were characterized by electrical measurement system, in which the voltage pulses for SET and RESET operations were provided by a programmable pulse generator Agilent 81104A. The transition from the low conductive amorphous state to the high conductive crystalline state is caused by the wide electric pulse. This transition and the wide electric pulse are called a set operation and a set pulse, respectively. On the other hand, the transition from the high conductive crystalline state to the low conductive amorphous state is caused by the narrow electric pulse. This transition and the narrow electric pulse are called a reset operation and a reset pulse, respectively. Current-Voltage (I-V) characteristics were measured with Keithley 2400 digital sourcemeter. Current was applied to the PCM device and the voltage was measured.

4.6.2 Pulsed mode Test

Pulse mode test was done using Agilent 81104 pulse generator. Initially the chalcogenide was in amorphous state. The pulse width (time) was varied and the corresponding voltage and current recorded.
5.1 Electrical Characterization of Sn\textsubscript{x}Se\textsubscript{y}

Temperature dependent sheet resistance measurements were performed between 25-230°C on 150 nm thin films of SnSe, Sn\textsubscript{4}Se\textsubscript{7}, Sn\textsubscript{2}Se\textsubscript{5} and SnSe\textsubscript{4} and their results are plotted in fig. 5.1, 5.2, 5.3 and 5.4 respectively. The SnSe alloy had a sheet resistance corresponding to 92 MΩ/□ and its corresponding room electrical resistivity was 1400 Ωcm. Upon annealing the sheet resistance decreased gradually up to 200 KΩ/□ at 224°C where a gradual phase transition was observed. This data is close to 215°C reported by Kyungmin et al., 2008. After this transition the sheet resistance decreases by 4 orders of magnitude.

The Sn\textsubscript{4}Se\textsubscript{7} alloy had a sheet resistance of 71.8 MΩ/□ and its corresponding electrical resistivity was 1000 Ωcm. Upon annealing the sheet resistance decreased suddenly to 132 KΩ/□ at 220°C where crystallization temperature was observed. After this transition the sheet resistance decreased by 5 orders of magnitude. The Sn\textsubscript{2}Se\textsubscript{5} alloy has a sheet resistance corresponding to 77.4 MΩ/□. Upon annealing the sheet resistance decreases suddenly to 95 KΩ/□ at 184°C where crystallization temperature is observed. After this transition the sheet resistance decreases by 8 orders of magnitude. The SnSe\textsubscript{4} alloy had a sheet resistance corresponding to 98 MΩ/□. Upon annealing the sheet resistance decreases suddenly to 0.95 MΩ at 174°C where a phase transition is observed. After this
transition the sheet resistance decreased by 10 orders of magnitude. This alloy had a room electrical resistivity of 1600 Ω cm. However, crystallization temperature of alloys depends on mode of preparation [Kyungmin et al., 2008]. Such a large change in magnitude of sheet resistance could be attributed to a phase transition. In all the samples, when cooled their sheet resistance remained fairly constant.

It is evident from fig.5.5, that at room temperature, all the alloys were amorphous and after annealing, they all became crystalline. Transition temperature shift to the higher temperatures with increase in tin concentration. This is because different material compositions have different heat of formation.

**Table 5.1: Comparing composition of tin in the alloy and transition temperature.**

<table>
<thead>
<tr>
<th>Sn&lt;sub&gt;x&lt;/sub&gt;Se&lt;sub&gt;y&lt;/sub&gt; alloy</th>
<th>% Sn</th>
<th>Order of contrast</th>
<th>Crystallization Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnSe&lt;sub&gt;4&lt;/sub&gt;</td>
<td>20</td>
<td>10</td>
<td>174</td>
</tr>
<tr>
<td>Sn&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;5&lt;/sub&gt;</td>
<td>28</td>
<td>8</td>
<td>184</td>
</tr>
<tr>
<td>Sn&lt;sub&gt;4&lt;/sub&gt;Se&lt;sub&gt;7&lt;/sub&gt;</td>
<td>36</td>
<td>5</td>
<td>220</td>
</tr>
<tr>
<td>SnSe</td>
<td>50</td>
<td>4</td>
<td>224</td>
</tr>
</tbody>
</table>

From the table 5.1, it’s clear that crystallization temperature of Sn<sub>x</sub>Se<sub>y</sub> alloy is dependant on material composition. Crystallization temperature is one of the essential material parameters that determines the data retention in PCM. It’s a strong function of the material and can vary over a large temperature range depending on the material compositions. Crystallization temperature also depends on the material the phase change
layer is sandwiched between and for thin films thickness below 10 nm it depends quite strongly on the film thickness [Heone et al., 2005].

![Graph](image)

**Fig. 5.1:** Temperature dependent sheet resistance measurement for 150 nm SnSe measured at a heating rate of 10 K/min.

![Graph](image)

**Fig. 5.2:** Temperature dependent sheet resistance measurement for 150 nm Sn₄Se₇ measured at a heating rate of 10 K/min.
Fig. 5.3: Temperature dependent sheet resistance measurement for 150 nm Sn$_2$Se$_5$ measured at a heating rate of 10 K/min.

Fig. 5.4: Temperature dependent sheet resistance measurement for 150 nm SnSe$_4$ measured at a heating rate of 10 K/min.
Fig. 5.5: Sheet resistivity against temperature (a), (b), (c), (d) of SnSe₄, Sn₂Se₅, Sn₄Se₇ and SnSe respectively.
5.2 OPTICAL CHARACTERIZATION

To obtain optical constants, scout software was used to fit experimental to the simulated data and the results presented in figure 5.6, 5.7, 5.8 and 5.9. To generate the simulated data, we have used OJL model together with harmonic oscillator susceptibility [Theiss, 2000]. It can be seen that refractive index decreases as concentration of tin is increased as shown on fig. 5.10. This is true based on semi-empirical relation between the refractive index and band gap in a relation called Moss rule [Moss, 1950].

\[ E_g n^4 = \text{Constant} \]  \hspace{1cm} (5.3)

According to this rule a lowering of \( n \) tends to increase \( E_g \). A question remains what causes the microscopic origin of the change in band gap. Investigation by Futsuhara et al., (1998), provided the answer that the optical band gap is related to the difference ionicity. Ionicity in a single bond increases with the difference in values of electronegativity between two elements forming the single bond [Sodky et al., 2003]. Figure 5.11 shows the spectral transmittance for 150 nm Sn<sub>x</sub>Se<sub>y</sub> thin films prepared at different stoichiometric ratio as a function of wavelength. Transmission seems to vary with increase in wavelength as well as material composition. When composition of tin increased, the transmittance decreased considerably since tin is basically reflective.
Fig.5.6: Transmittance against wavelength for simulated and experimental data for SnSe.

Fig.5.7: Transmittance against wavelength for simulated and experimental data for Sn₄Se₇.
Fig. 5.8: Transmittance against wavelength for simulated and experimental data for Sn$_2$Se$_5$.

Fig. 5.9: Transmittance against wavelength for simulated and experimental data for SnSe$_4$. 
**Fig. 5.10:** Variation of refractive index as a function of wavelength for Sn₄Se₇ thin films with 150 nm thickness.

**Fig. 5.11:** Transmittance versus wavelength for 150 nm SnₓSeᵧ thin films alloys.
Using equation (5.4), suggested by Bardeen et al., (1956) optical band gap and type of transition is determined by:

\[(\alpha hv)^\frac{2}{n} = A(hv - E_g \pm E^p)\]  

(5.4)

Where A is edge width parameter, \(E^p\) is phonon energy, \(v\) is the frequency, \(h\) the Planck’s constant, while \(n\) carries the value of either 1 or 4. \(E^p = 0\) for direct transition as there are no phonons involved. The graphs below in figure 5.12, 5.13, 5.14 and 5.15 shows the plot of \((\alpha hv)^{2/n}\) as a function of \(hv\) for the film which \(n=1\). The bandgap, \(E_g\), has been obtained from a straight line plot of \((\alpha hv)^{2/n}\) as a function of \(hv\). Extrapolation of the line to the base line, where the value of \((\alpha hv)^{2/n}\) is zero, will give \(E_g\). If a straight line graph is obtained for \(n = 1\), it indicates a direct electron transition between the states of the semiconductor, whereas the transition is indirect if a straight line graph is obtained for \(n = 4\). A linear trend is apparent where \(n\) in the relationship (5.4) equals 1. The straight-line behavior in the figure 5.12, 5.13, 5.14 and 5.15 testifies a direct transition of the band structure.

A plot of \((\alpha hv)^2\) as a function of \(hv\) is shown in figure 5.12 and it is linear in the strong absorption near the fundamental absorption edge. Since the value of \(\alpha\) is in the order of \(10^6\) m\(^{-1}\) and the absorption coefficient is measured at room temperature, the presence of exciton bands is not likely to be possible. Therefore, the absorption is from a band to band transition and it is only due to an allowed direct transition from the top of the valence band to the bottom of the conduction band at the center of the Brillouin zone.
The band gap energy value obtained for the direct transition was 1.27 eV for the SnSe thin film. This energy band gap is comparable with those reported by various researchers for SnSe using different preparation techniques as shown in table 5.2.

The direct band gaps were 1.77 eV, 1.83 eV and 1.94 eV for figure 5.13, 5.14 and 5.15 respectively. From figure 5.13, 5.14, 5.15 the plots of $(\alpha h\nu)^2$ versus $h\nu$ indicates that there is some tailing in the band gap below the absorption edge. This indicates that there is a high concentration of impurity states in the polycrystalline thin films which can cause a perturbation of the band structure with the result that the parabolic distribution of the states will be disturbed by a prolonged tail into the energy gap [Hady et al., 1999].

The tails in the optical spectra of the films could be due to the broadening of the impurity levels due to their spatial overlap into a band. At high concentrations, the impurity band merges with the nearest intrinsic band. Due to this, the Fermi level will lie inside the parabolic portion of the appropriate band. Thus, less activation energy will be needed for the electrons to move from the Fermi level into the conduction band. The tails could also be due to ionized donors which could exert an attractive force on the conduction electrons and a repulsive force on the valence band. On a microscopic level, the nonhomogeneous distribution of the impurities to a smearing of the band edges [Zulkarnain et al., 2004].
Table 5.2: SnSe band gap energy reported by various researchers [Pathinettam et al., 2000].

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Method of deposition</th>
<th>Band gap energy (eV)</th>
<th>Nature of transition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Vacuum</td>
<td>1.26</td>
<td>direct</td>
<td>PATHINETTAM</td>
</tr>
<tr>
<td>2.</td>
<td>Vacuum</td>
<td>1.21</td>
<td>direct</td>
<td>DANG TRAN QUAN</td>
</tr>
<tr>
<td>3.</td>
<td>Reactive evaporation</td>
<td>1.21</td>
<td>direct</td>
<td>JOHN et al</td>
</tr>
<tr>
<td>4.</td>
<td>Laser ablation</td>
<td>0.94</td>
<td>direct</td>
<td>TEGHIL et al</td>
</tr>
<tr>
<td>5.</td>
<td>Vacuum</td>
<td>0.935</td>
<td>indirect</td>
<td>BHATT et al</td>
</tr>
<tr>
<td>6.</td>
<td>Electrodeposition</td>
<td>1.30</td>
<td>indirect</td>
<td>ENGELKEN et al</td>
</tr>
</tbody>
</table>

Table 5.3: Comparative data on SnₙSeₙ alloys.

<table>
<thead>
<tr>
<th>SnₙSeₙ alloy</th>
<th>% of Sn</th>
<th>Energy gap</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnSe</td>
<td>50</td>
<td>1.27</td>
</tr>
<tr>
<td>Sn₄Se₇</td>
<td>36</td>
<td>1.77</td>
</tr>
<tr>
<td>Sn₂Se₅</td>
<td>28</td>
<td>1.83</td>
</tr>
<tr>
<td>SnSe₄</td>
<td>20</td>
<td>1.94</td>
</tr>
</tbody>
</table>

From table 5.3, the increase in concentration of tin lowered the optical band gap; this is due to new structural units formed with lower optical threshold energy. The presence of such units, contributed to the lowering of the mean value of the bandgap in the alloys [Iovu et al., 1999].
Fig. 5.12: A graph of $(\alpha h \nu)^2$ against photon energy of as-deposited 150 nm SnSe thin film.

Fig. 5.13: A graph of $(\alpha h \nu)^2$ against photon energy of as-deposited 150 nm Sn$_4$Se$_7$ thin film.
Fig. 5.14: A graph of \((a/hv)^2\) against photon energy of as-deposited 150 nm \(\text{Sn}_2\text{Se}_5\) thin film.

Fig. 5.15: A graph of \((a/hv)^2\) against photon energy of as-deposited 150 nm \(\text{SnSe}_4\) thin film.
5.3 Electrical Measurement of Phase Change Memory

5.3.1 DC Test (Voltage Switching)

The operation behaviors of the fabricated devices were characterized by electrical measurement system, in which the voltage pulses for SET and RESET operations were provided by a programmable pulse generator (Agilent 81104A). However, the I–V test was conducted in steady-state using Keithley 2400 sourcemeter.

Voltage sweeping switching behavior of PCM is shown in figure 5.16. The initial state of phase change material is amorphous, since SnSe$_4$ is deposited at room temperature and no further heating was followed, the resistivity at low voltage region is high. The device initially showed high resistance 8.5 $M\Omega$ below a certain threshold voltage. However, when the applied voltage exceeds the threshold value (3.71 V), the current increases abruptly due to generation of a large number of carriers at high fields followed by Joule-heating-induced amorphous to crystalline phase transition, called the threshold switching phenomena. Once the voltage reached threshold voltage ($V_{th}$), a negative differential resistivity occurs, which makes SnSe$_4$ switching from highly resistive state to a conductive state. Threshold switching allows the phase transition to occur at modest voltages. When exceeding critical electrical field strength, carriers fill the trap states in the amorphous phase. This results in the formation of highly conductive filaments in the amorphous state and consequently leads to the desired phase transition [Hangbing et al.,]
The increasing current flowing through the device may heat up the device and leads to the transformation from amorphous state to crystalline state [Lee et al., 2005].

The threshold memory-switching voltage is generally a function of the energy barrier for reaching the conducting crystalline state, crystallization temperature and the electronic properties such as bandgap and the density of trap states. In addition, crystallization temperature is also a crucial thermodynamic factor for determination of the threshold switching voltage due to crystal structure induced carrier generation. The lower crystallization temperature is expected to decrease the threshold memory-switching voltage as well as the lower activation energy for crystallization, since the electronic conducting state can be easily reached. Threshold values are useful to determine the safe data reading conditions, such as, operation voltages without destroying the written logic states. Second sweep only shows ohmic behavior since crystallization is done by first sweep [Lee et al., 2005].
Fig. 5.16: Static mode I–V characteristics of SnSe₄ PCM device.

5.3.2 Pulsed Mode Test

The pulsed-mode switching behavior of PCM cell is shown in figure 5.17 and figure 5.18 for RESET and SET operations respectively. After sweeping the device in static mode, as-deposited amorphous phase-change resistor was crystallized and its electric resistance was set to low state. Then, 90 nm short pulses were applied. For low voltage ($V < 3.0 \text{ V}$) pulses, phase-change resistor was not heated up to its melting temperature and no transition was observed. However, for sufficiently high voltage ($V > 3.7 \text{ V}$) pulses, phase-change resistor was heated above its melting temperature. Since the pulse width is only 90 ns, phase-change resistor was just melted and quenched. Thus, amorphization was occurred, and the electrical resistance was set to high. This operation is called RESET.
and is shown in figure 5.17. Once transition is occurred, 90 ns short pulse cannot supply sufficient energy for crystallization, since the electric resistance of amorphous resistor is too high (energy is proportional to voltage $^2 \times$ time / resistance).

For crystallization of phase-change resistor to occur, 26 $\mu$s long pulse was applied. For low voltage ($V < 1.0$ V) pulses, amorphized region of phase change resistor was not crystallized since there was no drastic change in resistance i.e. no transition occurred. When a high voltage ($V > 1.3$ V) pulses was used, crystallization occurred on amorphized region and electrical resistance was returned to low state this process is called SET operation and is shown in figure 5.18. This is because crystallization process is governed by nucleation and growth step and sufficiently long pulse causes the phase-change resistor to crystallize at low voltage [Lee et al., 2005].

![Fig. 5.17](image-url)

**Fig. 5.17:** Resistance versus Reset voltage for a pulsed-mode switching behavior of SnSe$_4$ phase change memory test device.
Fig. 5.18: Resistance versus Set voltage for a pulsed-mode switching behavior of \( \text{SnSe}_4 \) phase change memory test device.
Chapter 6

CONCLUSION AND OUTLOOK

6.1 Conclusion

The optical characterization revealed that optical band gap and refractive index of all alloys were dependent on concentration of constituent elements. Optical band gap was found to increase as tin concentration lowered. The band gap energy varied from 1.27-1.94 eV, and direct transition was observed.

Electrical resistivities of the samples were done at room temperature varied from 1150-1600 $\Omega$ cm, these values reduced considerably during annealing. SnSe$_4$ was found to have the highest electrical resistivity of 1600 $\Omega$ cm at room temperature. All the samples were found to have the crystallization temperature that increased with increase in tin concentration. Crystallization temperature varied from 174-224 °C. The SnSe$_4$ alloy was found to have relatively wider bandgap, low crystallization temperature and higher sheet resistance as compared to other alloys and hence it was used in PCM fabrication.

The Phase change memory (PCM) was found to have switching behaviour at a 3.71 V threshold voltage. Programming time was determined with RESET and SET operations by measuring resistance as a function of pulse width. In the RESET performance, the programming time of 90 ns as pulse width were used with 3.71 V. In the SET process, pulse voltage was fixed at 1.3 V and the device changed from high resistance state to low resistance state when pulse width exceeded 26 $\mu$s.
6.2 Research for further work

Sn$_x$Se$_y$ phase change alloys investigated in this work showed different values of crystallization temperatures. Activation energy of SnSe$_4$ alloy should be determined by applying Kissinger analysis method. Activation energy affects reactivity and chemical affinity of the alloy. Hence by determining activation energy, one can establish whether alloy is chemically stable at room temperature. Chemical stability of the phase change material is essential as the material is repeatedly melted next to electrodes and a surrounding insulator. It has been found that repeated switching can lead to phase separation or materials aggregation in PCM cells which, in turn, can lead to the failure of the cell.

The melting and glass transition temperature of SnSe$_4$ should be accurately determined. There are a number of ways for determining the glass transition temperature, $T_g$. One of these methods which is also quite popular and extensively used is the so called differential scanning calorimetry or simply DSC. In the absence of a DSC device temperature dependent sheet resistance measurements can also be used to observe phase transitions. Such measurements provide a simple and fast way for estimating the $T_g$ as the lower limit of the transition temperature. This assertion is valid especially when we assume by first approximation that the $T_x$ is very close to the $T_g$ values for most phase change alloys. $T_g$ is usually very close to the crystallization temperature $T_x$. It has additionally been shown that the mechanism of recrystallization, i.e., the distinction
between nucleation or growth dominated phase change alloys, is frequently related to the 
value of $T_g/T_m$. This ratio is typically around 0.5 for suitable phase change alloys 
[Kyungmin et al., 2008].

X-ray diffraction measurement should be conducted on the samples to determine the 
structural change during deposition and after annealing.

Hall measurements should be done on the Sn$_x$Se$_y$ alloys to determine whether its p-type 
or n- type as this could open other areas of applications such as solar cell applications, 
light emissions diode fabrications and sensors etc.
REFERENCES


