CRYSTALLIZATION KINETICS AND STRUCTURAL PROPERTIES OF Sn₃Se₇ THIN FILMS FOR PHASE CHANGE MEMORY (PCM) APPLICATIONS

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A thesis submitted in partial fulfillment of the requirements for the award of the Degree of Master of Science (Electronics and Instrumentation) in the School of Pure and Applied Sciences of Kenyatta University

June, 2013
DECLARATION

This thesis is my original work and has not been presented for the award of a degree or any other award in any other university

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DEDICATION

This thesis is dedicated to my parents
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ABBREVIATIONS AND ACRONYMS

a.m.u  Atomic Mass Units
CMOS  Complementary Metal Oxide Semiconductor
CVD   Chemical Vapor Deposition
DDTA  Derivative Differential Thermal Analysis
DSC   Differential Scanning Calorimetry
DTA   Differential Thermal Analysis
EBST  Electron Backscatter Diffraction
GST   Germanium-Antimony-Tellurium alloy
HTPS  High Tension Power Supply
JMA   Johnson-Mehl-Avrami
MBE   Molecular Beam Epitaxy
PCM   Phase Change Memory
SILK  Stress Induced Leakage Current
T_c   Crystallization Temperature
T_p   Peak Transition Temperature
T_m   Melting point
XRD   X-Ray Diffractometry
**SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>Rate constant</td>
</tr>
<tr>
<td>$K_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>n</td>
<td>Avrami exponent</td>
</tr>
<tr>
<td>$\text{Sn}_x\text{Se}_y$</td>
<td>Tin selenium alloy</td>
</tr>
<tr>
<td>$\Delta E$</td>
<td>The activation energy for crystallization</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>Specific sheet resistivity</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Heating rate</td>
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</table>
ABSTRACT

As the future size of phase change random access memory is scaled down, its reliability in data retention, archival life and power consumption is often disturbed by problems such as elemental segregation and compositional variation caused by repetitive phase transformation. These phenomena are closely related to the crystallization kinetics under various environments. The crystallization kinetics at low temperature and slow transition rates of \( \text{Sn}_x\text{Se}_y \) thin films have been investigated using sheet resistance measurements based on the van Pauw technique. The thin films were deposited on glass substrates at room temperature using thermal evaporation technique using Edwards auto 306 magnetron sputtering system. Results show that the crystallization temperature, specific sheet resistivity and the activation energy for Sn-Se alloys can be varied over a wide range by adjusting the composition of the binary alloy. The crystallization temperatures for \( \text{Sn}_{30}\text{Se}_{70} \), \( \text{Sn}_{40}\text{Se}_{60} \) and \( \text{Sn}_{50}\text{Se}_{50} \) were found to be: 195.4±0.4°C, 156.6±0.3°C and 129.8±0.5°C respectively. The electrical contrast obtained from the sheet resistance vs. temperature measurements between the amorphous phase and the crystalline phase was at least \( 10^5 \) for \( \text{Sn}_{30}\text{Se}_{70} \), and \( \text{Sn}_{40}\text{Se}_{60} \) and less than \( 10^2 \) for the stoichiometric \( \text{Sn}_{50}\text{Se}_{50} \). The value of activation energy obtained from Kissinger analysis was lowest for \( \text{Sn}_{50}\text{Se}_{50} \) at 0.43±0.05 eV and highest for \( \text{Sn}_{30}\text{Se}_{70} \) at 0.63±0.06 eV. The activation energy for the films of the stoichiometric alloy \( \text{Sn}_{40}\text{Se}_{60} \) was 0.62±0.07 eV. From the alloys studied, the most promising stoichiometric alloys of \( \text{Sn}_x\text{Se}_y \) seems to be \( \text{Sn}_{30}\text{Se}_{70} \) and \( \text{Sn}_{40}\text{Se}_{60} \) because of their high electrical contrast of five orders of magnitude, high crystallization temperature better than the reported values of GST, and high activation energy that will increase the stability of the amorphous mark. The data stability at high temperatures is dependent on the crystallization temperature of the cell. The high values obtained for crystallization temperature will therefore ensure data stability and retention at elevated temperatures.
CHAPTER ONE
INTRODUCTION

1.1 Background to the study

At present, demand for mass storage has been increasing owing to increased information. Therefore, memory devices require improved performance to meet the needs of information hungry society. For such reasons, the demand for non-volatile memory has increased rapidly (Yamada et al., 1991). Phase change memory (PCM) is a new non-volatile memory that uses reversible phase transition of chalcogenide resistor (Tominaga et al., 1997; Raoux et al., 2008). The idea to use an amorphous to crystalline phase transition for information storage was born way back in 1960s by S.R. Ovshinsky who suggested a memory switch based upon changes in the properties of amorphous and crystalline phases of multi-component chalcogenides (Ovshinsky, 1968).

The amorphous phase tends to have high electrical resistivity, while the crystalline phase exhibits a low resistivity. The electrical contrast of at least 3 to 5 orders of magnitude is required for any material to qualify for PCM application (Chung et al., 2008). Although PCM has advantages over flash memory such as: fast switching speed, low programmable energy, high endurance, good data retention, improved compatibility with CMOS and excellent scalability (Qiao et al., 2006), it still requires advanced materials exhibiting lower power consumption, rapid phase transition and cyclic reliability (Park et al., 2007).
In this technology the information storage relies on a current induced reversible phase transition. A current pulse focused onto the area corresponding to the bit size, is employed to heat the PCM material, which induces the change between the amorphous and crystalline phases (Pirovano et al., 2004). Since the two phases feature a different resistivity (Burr et al., 2010), the electrical readout is performed with a low power probing electrical pulse. In this case the idea is to electrically induce the phase change in a PCM cell and associate the stored information to the corresponding high and low resistance values. Since both states are stable at room temperature (Raoux, 2009), no energy is required to keep data stored. This results in an inherently non-volatile memory technology.

There are Set and Reset operations in PCM. A current pulse of low intensity and relatively long duration crystallizes the film (Set operation), while a pulse of higher intensity but shorter duration is used for amorphization (Reset operation). Readout is performed at a lower current that does not change the phase (Ovshinsky, 1968). This is shown schematically in figure 1.1. A critical property of phase change material is the threshold switching (Adler et al., 1980; Pirovano et al., 2004; Redaelli et al., 2004; Ielmini et al., 2007). Without this effect PCM would not be a feasible technology, because in the high resistance state, extremely high voltages would be required to deliver enough power to the cell to heat it above the crystallization temperature (Burr et al., 2010). However, when a voltage above a particular threshold
Figure 1.1: Schematic diagram showing Temperature vs. Time graphs for Reset and Set pulses during programming of a PCM cell.

(V_t) is applied to a phase change material in the amorphous phase, the resulting large electrical fields greatly increase the electrical conductivity (Pirovano et al., 2004). With the previously resistive material now suddenly conducting, a large current flow which can then heat the material. The threshold switching effect serves to make possible the use of an applied voltage of a few volts, despite the high initial resistance of the device in the Reset state (Pirovano et al., 2004; Ielmini et al., 2007; Burr et al., 2010)

The phase change material Ge$_2$Sb$_2$Te$_5$ (GST) has been the most studied and optimized PCM material (Yamada et al., 1987; Suh et al., 2006; Heireche and Belhadji, 2007). It was originally developed for optical data storage (Raoux et al., 2009), due to its fast
crystallization and high optical contrast. It has been demonstrated that there are several drawbacks about the material properties of GST that need to be addressed. While for optical data storage applications the operating temperature is close to room temperature, for PCM it is about 85°C and for automotive applications even 150°C is required (Raoux et al., 2009). Since the crystallization temperature of GST is around 140°C depending on the heating rate (Friedrich et al., 2000), data retention at elevated temperatures is limited. Many researches show that the high crystallization temperature leads to high data stability and the high crystalline resistance reduces the reset operation power (Lee et al., 2005). It has been reported that materials with high optical contrast such as GST also show a relatively large increase in mass density upon crystallization (Pedersen et al., 2001). Repeated cycling in PCM applications can lead to void formation caused by the large difference in mass density between the two phases causing subsequent cell failure (Raoux et al., 2009). Elemental segregation is another failure mechanism that is observed for PCM cells with GST phase change material (Raoux et al., 2009). Antimony-rich areas are formed on top of the bottom electrode (Raoux et al., 2008) which deteriorates data retention because antimony-rich alloys are known to have a reduced crystallization temperature and archival life stability (Lee et al., 2005).

1.2 Kinetics of crystallization

For a successful quest for superior phase change materials, different strategies have been exploited. Thermal analysis has been widely used to investigate the crystallization kinetics of glasses (Lai (2003); Pirovano et al., 2004; Mehta et al., 2004; Redaelli et al.,
since it is very quick and needs small quantities of glass samples to acquire kinetic parameters. The determination of crystallization kinetics and the underlying mechanisms is of crucial importance for the performance of the material since it provides useful information that can be used to improve the switching behavior, enable a higher rate of data transfer and leads to the development of new materials with superior properties (Njoroge et al., 2001).

Two thermal analysis methods are available: One is the isothermal method known as Johnson-Mehl-Avrami (JMA) and the other method is non-isothermal that includes the Kissinger method (Cheng, 2001; Njoroge et al., 2001; Wuttig et al., 2002; Wamwangi et al., 2002; Njoroge et al., 2004; Heireche and Belhadji, 2007). In isothermal method, the sample is brought near to crystallization temperature very quickly and then any physical quantity which changes drastically is measured as a function of time. In non-isothermal method otherwise here called Kissinger method, the sample is heated at a fixed heating rate and the physical parameter is recorded as a function of temperature.

The disadvantage in isothermal method is reaching the required temperature instantaneously and taking the readings at that point without allowing the system time to stabilize (Rao et al., 2008). This drawback is eliminated in the Kissinger method where the measurements can be made in a relatively rapid and precise manner. In this Kissinger method, the parameters discussed are the activation energy $\Delta E$, the index $n$ (known as the
Avrami exponent) and the pre-exponential factor \((A)\). This work involved the study of the crystallization kinetics of various \(\text{Sn}_x\text{Se}_y\) alloys employing the Kissinger analysis.

1.3 Problem statement and justification

Alloy on the pseudo ternary tie line in Ge-Sb-Te phase diagram as well as the eutectic of Sb-Te and Ge-Sb binary alloys have been the extensively studied and optimized material systems for PCM technology due to their excellent properties (Heireche and Belhadji, 2007) such as:

- A reasonably high reflectivity contrast between the amorphous and crystalline states to ensure a successful READ process.
- High stability at room temperature to ensure longer archivability
- First or rapid reversible switching between the two storage states

Despite their widespread application, these materials have shown potential drawbacks which preclude their application in electronic storage as PCM devices (Heireche and Belhadji, 2007). These drawbacks include:

- Low crystallization temperature preventing their application (e.g data retention) at elevated temperatures
- Low SET (crystalline) resistance which increases the reset current of the PCM device.

A number of studies have been carried out in order to acquire advanced materials exhibiting lower power consumption, rapid phase transition, cyclic reliability and higher data retention ability. Research has shown that films from \(\text{Sn}_2\text{Se}_3\) posses a higher
crystalline resistance as compared to those from GST alloys. Despite the enormous potential technological importance of this material, very little information on its material properties has been reported. Therefore in this research, the crystallization kinetics of Sn\textsubscript{x}Se\textsubscript{y} alloys have been to establish the processes which are associated with the atomic rearrangements and their time scales during phase transition.

1.4 Objectives

1.4.1 Main objective

The general objective of this study is to investigate the crystallization kinetics and structural properties of Sn\textsubscript{x}Se\textsubscript{y} thin films for phase change memory applications.

1.4.2 Specific objectives

(i) To prepare Sn\textsubscript{x}Se\textsubscript{y} alloys at different atomic weight percentages based on the melt quenching method.

(ii) To deposit Sn\textsubscript{x}Se\textsubscript{y} thin films using evaporation technique.

(iii) To investigate electrical properties of as deposited and annealed Sn\textsubscript{x}Se\textsubscript{y} films.

(iv) To determine the activation energy for crystallization.
1.5 Rationale

Phase change memory (PCM) has several advantages including: Extremely large read dynamic range, reduced switching current and improved device size. As the future size of PCM is scaled down its reliability in data retention, archival life and power consumption is often disturbed by several problems such as elemental segregation and compositional variation caused by repetitive phase transformation. These phenomena are closely related to the crystallization kinetics under various environments. The determination of crystallization kinetics provides useful information that can be used to improve the switching behavior and also enable a higher rate of data transfer. Though GST has been studied and optimized for PCM applications, it faces drawbacks such as low crystallization temperature and low crystalline resistance. Thus in order to understand the processes which are associated with rearrangement of molecules and ions when forming a new phase a study on the crystallization kinetics of Sn\textsubscript{x}Se\textsubscript{y} alloys was required.
CHAPTER TWO
LITERATURE REVIEW

2.1 Introduction

A lot of research work has been done on phase change memory from structural to kinetics of crystallization. Most work has been based on stoichiometric GST. However, there exists renewed effort in exploring other potential candidates which have superior characteristics so as to overcome the weaknesses noted in the GST materials. Therefore, in this chapter, contributions of earlier researchers in the field of phase change memory and their various techniques of study are discussed. This chapter gives a clear description of the work already done in this field and identifies the existing knowledge gap which this work tries to address.

2.2 Motivation for PCM

In order for a PCM candidate to be considered a viable next generation memory option, it must demonstrate reliability in data retention, thermal crosstalk and endurance in bias polarity dependent effects (Burr et al., 2010). Sharma et al. (2005) prepared and characterized nanocrystalline Tin Selenium films prepared from its constituents (5N pure) by melt quenching technique and the thin films prepared using thermal evaporation technique at low partial pressure of Argon gas. A blue shift in the fundamental edge was observed due to reduction in the particle size.
Kolobov et al. (2005) investigated why phase change media were fast and stable in GST. Upon laser pulse induced amorphization, it was demonstrated that the order-disorder transition in Ge-Te and GST was due to a flip of Ge atoms from an octahedral position into a tetrahedral position without rupture of strong covalent bonds. This ensured fast disk performance and stability. Lee et al. (2005) investigated indium selenide thin films for phase change memory application using Resistance vs. temperature measurements and X-ray diffraction measurements. Only (0006) peak of gamma phase In$_2$Se$_3$ was observed in XRD pattern. Electron micro-probe analysis also confirmed no change in composition of indium selenide layers due to annealing up to 350°C. Chung et al. (2007) investigated the electrical and structural properties of various alloys of Tin-Selenide prepared by MBE. The results showed a high crystallization temperature and high activation energy.

2.3 Crystallization kinetics studies

Mehta et al. (2004) studied crystallization kinetics of some Se-Te-Ag chalcogenide glasses using DSC technique at different heating rates. Kissinger, Matusita and Bennett’s relations were used to evaluate the activation energy of crystallization ($\Delta E$). The results showed that the value of $\Delta E$ was less in ternary alloys as compared to binary alloys due to addition of Ag. Heireche and Belhadji (2007) studied non-isothermal crystallization of glasses based on GST alloys using DSC technique. Two glass transition temperatures followed by two crystallization peaks were observed. Matusita, Kissinger and Ozawa
models were used to calculate activation energy which was found to be higher in Tellurium than in GeTe.

Raoux et al. (2008) studied various phase change materials (Ge$_3$Sb$_5$Te$_5$, Ge$_{15}$Sb$_{85}$ and Ag-and In-doped Sb$_2$Te) prepared by magnetron sputtering and measured their crystallization times using static laser testers. The re-crystallization time of melt quenched amorphous material was found to be shorter than the crystallization time of as-deposited amorphous material. The crystallization time of as-deposited materials ranged from 150 ns for Ge$_3$Sb$_6$Te$_5$ to tens of μs for Ag and In-doped Sb$_2$Te, while the crystallization time for melt-quenched, amorphous materials varied between 20ns for Ge$_{15}$Sb$_{85}$ and about 1μs for Ge$_3$Sb$_6$Te$_5$. Rao et al. (2008) studied the kinetics of crystallization of the metallic glass 2826A (Ni$_{36}$Fe$_{32}$Cr$_{14}$P$_{12}$B$_6$) under non-isothermal experiments using Kissinger, Ozawa, Bosewell and Matusita & Sakka methods. The average value of activation energy for the glassy alloy prepared by single roller melt spinning technique for peak 1 was found to be 298kJ/mol. The frequency factor for second peak was higher than that for the first peak.

Singh et al. (2008) studied the effect of annealing on structures and effective thermal conductivity of Se$_{90}$In$_{10}$ using XRD and transient plane source (TPS) method, respectively. A considerable change was observed in both structures and effective thermal conductivity for annealing at 50°C for 2 hours due to structural relaxation and transformation. Park et al. (2008) studied the phase transition characteristics and device
performance of Si-doped GST thin films for phase change random access memory application using XRD, four point probe measurements and X-ray photoelectron spectroscopy (XPS). A difference of more than four orders of magnitude in sheet resistance between the amorphous and crystalline states was observed. Also, the activation energy for transformation decreased with increasing amount of Si in Si-doped GST.

Goo et al. (2011) proposed a new method of evaluating crystallization kinetics of Ge$_2$Sb$_2$Te$_5$ by In-situ resistance measurements. A linear relationship between the logarithmic time and reciprocal temperature in modified JMA equation was derived under the assumption that the proportion of resistance drop from the initial value is closely related to crystal fraction since crystal fraction assumes the existence of an amorphous matrix and hence the increase in the fraction would lead to a drop in resistance. Crystallization activation energy of 2.67 eV was obtained. A number of other groups have also investigated either alternate PCM materials or doped the GST as a way to increase data retention margins or reduce the power consumption of PCM devices.

Matsuzaki et al. (2005) showed that oxygen doping of GST films result in much higher activation energy due to smaller grain size which leads to improved data retention. Kim and Ahn (2005) showed that N-doped GST single cell PCM devices show retention lifetimes exceeding 10 years at 85°C. It was also concluded that the activation energy is lower for devices compared to blanket films because of process induced damage and
defects at the interface between the bottom electrode and the GST. These reported effects have to be minimized in order to maximize retention.

Morikawa et al. (2007) explored In-doped GeTe as a phase change material and showed that its retention properties are significantly better than GST, ranging from 10 years at 122°C to 156°C depending on the Indium fraction. From the review, it is evident that there exist other PCM candidates which crystallize with much higher speed and at much higher crystallization temperatures than the widely used GST (Njoroge et al., 2001; Raoux et al., 2008). Since future PCM technology calls for rapid switching, high density storage, low power consumption and improved retention, further extensive material and device research and development is needed to ensure improved stability and retention of the amorphous marks at high temperatures and also lower power consumption below current levels. It is on this basis that an investigation is sought on the crystallization kinetics and structural properties of SnₓSeᵧ films for PCM applications.
CHAPTER THREE
THEORETICAL CONSIDERATION

3.1 Introduction
Crystallization kinetics under various environments for confined PCM cells, determine the reliability of PCMs in terms of data retention, level of thermal crosstalk, cyclic endurance, bias polarity dependent effects, archival life and power consumption. In this chapter, theoretical overview of these phenomenological aspects of PCM technology, deposition techniques and in particular vacuum evaporation technique of film preparation and electrical measurements necessary for determination of crystallization kinetics are outlined. Theory of crystallization kinetics and structural characterization using XRD is also presented.

3.2 PCM data retention
In order for a non-volatile memory candidate to be considered a viable next generation memory option, it must demonstrate long term retention of stored data. The typical criterion is 10 years (or 100 000 hours) at 85°C, with fewer than 1 PPB (part per billion) retention failures at the array level over this entire lifetime, independent of the previous cycling history of the memory array (Burr et al., 2010). Since the crystalline SET state is a stable low resistance state, it is the stability of the quenched high resistance RESET phase which dominates retention issues. The amorphous phase suffers from two independent resistance altering processes namely: resistance drift and spontaneous
crystallization. The drift process is a steady increase in resistivity of the amorphous phase related to structural rearrangement of the amorphous chalcogenide and the dynamics of the intrinsic traps. Since this process increases the ON/OFF ratio, it does not cause any data loss for binary PCM devices.

On the other hand, thermally activated crystallization of the amorphous material eventually leads to significant reduction in the resistance of the active layer, causing eventual retention failures for binary storage. Data retention measurements typically involve monitoring the resistance of the active layer that has been put in the RESET state. When the resistance of a cell drops below a threshold resistance (between the SET and RESET values), the cell is said to have suffered a retention failure. Similar to accelerated tests used on other non-volatile memory candidates, PCM retention measurements are done at higher temperatures to speed up this crystallization process and the subsequent resistance change. Using measurements done at a number of high temperatures (typically near 160°C) and a reasonable activation model, the retention properties of PCMs at 85°C can be predicted fairly well (Burr et al., 2010). The validity of the activation model and of the extrapolation from higher temperature measurements is strongly dependent on the nucleation and grain growth properties of the specific phase change material being used in the memory cell.
3.3 Thermal crosstalk in PCM

During the RESET operation, the peak temperature within a PCM device exceeds the melting point of the phase change material (Raoux et al., 2009). Since the extent of the amorphous plug quenched from the molten state must be larger than the critical dimensions of the limiting aperture, the material at the edge of this aperture is just over the melting point, and the peak temperature in the centre of the cell is well over the melting temperature (Yamada et al., 1991). It has been demonstrated with careful thermal simulations that at least out to the 65 nm node, the thermal crosstalk between cells should remain low enough that 10 year lifetime will not be significantly reduced by write disturbs from neighboring cells (Pirovano et al., 2003). The additive effects of retention and proximity both need to be considered to account for data integrity loss in high density PCM based cross-point memory arrays (Burr et al., 2010).

3.4 Cyclic endurance in PCM

Cyclic endurance is one of the strengths of PCM, especially in comparison to established Flash technologies, where stress induced leakage current (SILC) frequently limits device endurance to $10^4$-$10^5$ program erase cycles. The demonstration, as early as 2001, of $10^{12}$ SET–RESET cycles in PCM devices without any significant degradation of resistance contrast (Burr et al., 2010), was almost certainly a significant factor in the surge of interest in PCM technology that followed. Two different failure modes have been observed to occur after cycling, termed ‘‘stuck-RESET’’ and ‘‘stuck-SET’’ failure (Burr et al., 2010). In stuck-RESET failure, the device resistance suddenly and irretrievably
spikes, entering a “blown fuse” state that is much more resistive than the RESET state. These failures are typically attributed to void formation or delamination that catastrophically severs the electrical path through the device, typically at a material interface such as the heater to GST contact mushroom cell shown in figure 3.1.

Figure 3.1: A schematic diagram of a GST mushroom cell showing the location of the heater in relation to the programmable region of a PCM material (adapted from Raoux et al. 2009).

In contrast, in a stuck-SET failure, a gradual degradation of resistance contrast is typically observed. Typically, for a cell in this condition, larger amplitude RESET pulse proves sufficient to RESET the device and cycling can resume.
3.5 Polarity issues in PCM

A number of recent measurements of phase segregation in various types of phase change bridge devices, have forced a reinterpretation of the failure analysis results just described within the context of two previously unknown bias-polarity-dependent effects. It has been demonstrated that the amorphous plugs in their devices were shifted by the polarity of the applied bias, by as much as 100 nm (Burr et al., 2010). This effect was attributed to thermo-electric Thomson effect, in which the overlap of temperature gradients with electrical currents can lead to additional heat generation or absorption. Because the hot spot in the centre of a phase change device is surrounded by temperature gradients of opposite signs but the current flow is uni-directional, the Thomson effect acts to shift the centroid of the hot spot depending on the polarity of the applied voltage.

3.6 Deposition techniques

Many categories of deposition techniques exist: Physical vapour deposition (PVD), Chemical vapour deposition (CVD), Oxidation, Spin coating and plating. In PVD technique, films are formed by atoms that are directly transported from source to substrate through gas phase and they include sputtering and evaporation (Thermal evaporation and E-Beam evaporation) and Reactive PVD. On the other hand, in CVD technique, films are formed by chemical reaction on the surface of the substrate and they include Low-pressure CVD (LPCVD), Plasma-Enhanced CVD (PECVD), Atmosphere-Pressure CVD (APCVD) and Meta-Organic CVD (MOCVD). Evaporation and sputtering are the two main techniques employed in physical vapour deposition. In this
study, due to its advantages such as proper control on the film chemical composition, high deposition rate and low substrate heating during film deposition, vacuum evaporation technique has been adopted and is discussed in the next section.

3.6.1 Vacuum evaporation technique

Vacuum evaporation is also a widely used PVD technique. In this method, materials from a thermal vaporization source reach the substrate with little or no collision with gas molecules in the space between the source and substrate. The vacuum environment during evaporation provides the ability to reduce gaseous contamination in the deposition system to a low level. This technique is generally done using thermally heated sources such as tungsten wire coils or by high energy electron beam heating of the source material itself. Usually the sample is placed on evaporator boats which are heated until the elements vaporize and deposit on a substrate above the boat at a lower temperature. The vapour pressure and the chamber base pressure determine the amount of material that evaporates from the surface. Co-evaporation is a single stage growth technique which is complex requiring accurate control of all evaporation sources. Flash evaporation on the other hand, suffers from inherent problems such as poor reproducibility, inferior crystallinity and spitting of materials from evaporation sources. In this study, chalcogenide thin films were prepared by single source evaporation. Pre-determined masses of chalcogenide Sn$_x$Se$_y$, were placed directly on a single unheated evaporation
boat at room temperature and was followed by controlled increase in the boat temperature.

3.6.2 Arc Vapour Deposition Technique

Arc vapour deposition uses a high current, low voltage arc to vaporize a cathodic electrode (cathodic arc) or anodic electrode (anodic arc) and deposit the vaporized material on a substrate. The vaporized material is highly ionized and usually the substrate is biased so as to accelerate the ions towards the substrate surface.

3.6.3 Ion plating Technique

Ion plating utilizes concurrent or periodic bombardment of the depositing film by atomic-sized energetic particles, to modify and control properties of the depositing film. In ion plating the energy, flux and mass of the bombarding species along the ratio of bombarding particles to depositing particles are important processing variables.

3.6.4 Chemical vapour deposition technique

Thermal chemical vapour deposition is the deposition of atoms or molecules by the high temperature reduction or decomposition of a chemical vapour precursor species which contains the material to be deposited. Reduction is normally accomplished by hydrogen at an elevated temperature. Decomposition is accomplished by thermal activation. The deposited material may react with other gaseous species in the system to give compounds
CVD technique has numerous other names and adjectives associated with it such as Vapour Phase Epitaxy (VPE) when CVD is used to deposit single crystal films, Metalorganic CVD (MOCVD) when the precursor gas is a metalorganic species, Plasma enhanced CVD (PECVD) when plasma is used to induce or enhance decomposition or reaction, and low pressure CVD (LPCVD) when the pressure is less than ambient.

3.7 Theory of electrical measurements

3.7.1 Bulk resistivity in metals and semiconductors

In this section, we discuss the theory of electrical measurements in metals and semiconductors. There are differences between a metal and a semiconductor. However, a fundamental difference between a metal and a semi-conductor is that the former is monopolar (conducts current by means of charges of one sign only, electrons), whereas a semiconductor 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

$$J = (n\mu_n + p\mu_p)qE = \sigma E$$  (3.1)

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,

$$\sigma = (n \mu_n + p \mu_p) q \quad (3.2)$$

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

$$n = N_C e^{(\mu - E_G)/K_B T} \quad (3.3)$$

While the number of holes per unit volume is

$$p = N_v e^{-\mu/K_B T} \quad (3.4)$$

Where $N_C = \text{effective number of levels per unit volume in conduction band}$

$N_v = \text{effective} \quad \text{Number of levels per unit volume in the valence band}$

$E_G = \text{Band gap energy}$

$K_B = \text{Boltzmann constant}$ and

$\mu = \text{Mobility}$

Combining equations of $n$ and $p$ we obtain

$$np = N_c N_v e^{-E_G/K_B T} \quad (3.5)$$

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

For a pure semi-conductor,

$$n = p = (N_c N_v)^{1/2} e^{-E_G/2K_B T} \quad (3.6)$$

But

$$\sigma = (n \mu_n + p \mu_p) q \quad (3.7)$$
Thus for a pure semiconductor, $\sigma$ becomes

$$\sigma = pq(\mu_n + \mu_p)$$  \hspace{1cm} (3.8)

$$= (N_e N_v)^{1/2} q(\mu_n + \mu_p) e^{-E_g / 2k_B T}$$  \hspace{1cm} (3.9)

which can be written as,

$$\sigma = A_0 e^{-E_g / 2k_B T}$$  \hspace{1cm} (3.10)

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

Hence resistivity, $\rho$ can be expressed as

$$\rho = \frac{1}{\sigma} = \frac{1}{A_0} e^{E_g / 2k_B T} = B_0 e^{E_g / 2k_B T}$$  \hspace{1cm} (3.11)

where

$$B_0 = \frac{1}{A_0} = \frac{1}{((N_e N_v)^{1/2} q(\mu_n + \mu_p))}$$  \hspace{1cm} (3.12)

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

### 3.7.2 Sheet resistivity for thin films

Sheet resistivity or surface resistivity measurements have been done most widely following a procedure proposed by Van der Pauw model (Halperin 1996; Van der pauw 1958). The Van der Pauw technique, due to its convenience is used widely in semiconductor industry to determine the resistivity of uniform samples. In this technique,
one uses an arbitrary shaped thin-plate sample containing four very small ohmic contacts placed on the periphery, preferably in the corners of the plate. A schematic of a square Van der Pauw configuration is shown in figure 3.2.

The objective of the resistivity measurement is to determine the sheet resistance $R_S$. Van der Pauw demonstrated that they are actually two characteristic resistances $R_A$ and $R_B$, with

$$R_A = \frac{V_{43}}{I_{12}}$$

$$R_B = \frac{V_{14}}{I_{23}}$$

Figure 3.2: Schematic diagram of a Van der Pauw configuration used in the determination of the two characteristic resistances (Van der Pauw 1958).
associated with the corresponding terminals shown in figure 3.2. \( R_A \) and \( R_B \) are related to the sheet resistance \( R_s \) through the Van der Pauw equation

\[
\exp\left(-\pi \frac{R_A}{R_s}\right) + \exp\left(-\pi \frac{R_B}{R_s}\right) = 1 \tag{3.13}
\]

which can be solved numerically for \( R_s \). To obtain the two characteristic resistances, a dc current \( I_{12} \) is swept onto contact 1 and 2 and the voltage \( V_{43} \) is measured across contact 3 and 4 as shown in figure 2. Next, one applies the current \( I_{23} \) into contact 2 and out of contact 3 while measuring the voltage \( V_{14} \) across contact 1 and contact 4. \( R_A \) and \( R_B \) are calculated by means of equations 3.14 and 3.15 respectively.

\[
R_A = \frac{V_{43}}{I_{12}} \tag{3.14}
\]

and

\[
R_B = \frac{V_{14}}{I_{23}} \tag{3.15}
\]

In figure 3.2, \( I_{12} \) is the positive dc current I injected into contact 1 and taken out of contact 2. \( I_{23} \) is the positive dc current I injected into contact 2 and taken out of contact 3. Other quantities one can derive from figure 3 are \( I_{34}, I_{41}, I_{21}, I_{14}, I_{43}, \) and \( I_{32} \). \( V_{12} \) is dc voltage measured between contacts 1 and 2 (\( V_1-V_2 \)) without applied magnetic field (\( B=0 \)), \( V_{23} \) is dc voltage measured between contacts 2 and 3 (\( V_2-V_3 \)), \( V_{34} \) is dc voltage measured between contacts 3 and 4 (\( V_3-V_4 \)). Likewise, \( V_{41}, V_{21}, V_{14}, V_{43} \) and \( V_{32} \) can also be derived. These values have to be checked for reciprocity to ensure internal consistency, ohmic contact quality and sample uniformity.
Another consideration during sheet resistance measurements is the sample geometry. It is preferable to fabricate thin films of semiconductors and adopt a suitable geometry. In figure 3.3, various geometries are presented. The cloverleaf design will have the lowest error due to its smaller effective contact size, but it is more difficult to fabricate than that of a square or rectangle.

![Diagram showing different sample geometries for Van der Pauw resistivity measurements](image)

- **Cloverleaf**: Contact at the corners. Preferred.
- **Square or rectangle**: Contact at the edges or inside the perimeter. Acceptable.
- **Square or rectangle**: Not recommended.

Figure 3.3: A schematic diagram showing different Sample geometries for Van der Pauw resistivity measurements (Van der Pauw 1958).

Most sheet resistivity measurements are made on semiconductor thin films on small surface area substrates. Since the measurements are made on finite sized areas, correction factors have to be used based on the sample geometry. These correction factors depend
on sample thickness, edge effects, thickness effects, and the location of the probe on the sample (Sun et al., 1996). Other considerations to ensure accurate four point probe measurements are the spacing of the probes and temperature effects. For very thin films (thickness \( t \ll \) probe spacing \( s \)), current rings instead of spheres are realized. Therefore the area \( A \) can be expressed as;

\[
A = 2\pi xt
\]

where \( x = \) probe spacing of the thin film and \( t = \) film thickness. The resistance \( R \) is given by,

\[
R = \frac{\rho x}{A}
\]

(3.17)

\[
R = \int_{s}^{2s} \frac{\rho dx}{2\pi x}
\]

(3.18)

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

(3.19)

and

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

(3.20)

The specific resistivity \( \rho \) can be determined from the thin film thickness (\( t \)) and the sheet resistance (\( R \)) in the form;

\[
\rho = R t 10^{-1} \mu \Omega cm
\]

(3.21)
3.8 Theory of crystallization kinetics

3.8.1 Nucleation and crystal growth in chalcogenide glasses

The crystallization process is in general a nucleation and growth transformation (Lee et al., 2005; Raoux et al., 2009; Heireche and Belhadji, 2007). Depending on the material, one or the other of these processes dominates the progress of crystallization. Nucleation can occur in the interior of the amorphous material (homogeneous nucleation) or at the interface of the amorphous material (heterogeneous nucleation) with the substrate, at the interface with the capping layer (if present), or at the sample surface which in practical cases will be a thin oxide layer unless the sample is prepared and crystallized in situ (Raoux 2009). In addition, for PCMs, the crystallization is assumed to be diffusion limited (as opposed to collision limited) because atoms jump by diffusion over the amorphous–crystal boundary. The final steady-state nucleation rate $I^{ss}$ is given by

$$I^{ss} = S_c \cdot \frac{2K_BT}{\eta \pi a^2} \cdot N_0 \cdot \Gamma_z \cdot \exp\left(-\frac{\Delta G_c}{K_BT}\right),$$

(3.22)

where $S_c$ is the number of surface atoms in a critical cluster, $K_B$ is the Boltzmann constant, $N_0$ is the total number of atoms in the amorphous phase per unit volume, $\Delta G_c$ is the reversible work for cluster formation at the critical radius, $\eta$ is the liquid shear velocity, $a$ is the average inter-atomic distance, $T$ is temperature and $\Gamma_z$ is a pre-factor called Zeldovich factor (Raoux 2009). For PCMs the nucleation rate shows a maximum between the glass transition temperature and the melting temperature.

Once the stable nuclei have formed, crystallization proceeds by growth from the crystal front. For PCMs, this process is interface controlled and independent of time. The growth
velocity is proportional to diffusivity because growth occurs by diffusive jumps of atoms over the amorphous-crystal boundary. The growth velocity is strongly temperature dependent and also has a maximum at temperature between the glass transition and melting temperature (Kalb 2008).

PCMs can be categorized into nucleation and growth dominated materials. For nucleated dominated materials, many nuclei are formed in a unit volume; these nuclei grow relatively slowly. Critical nuclei formation also occurs continuously during the growth process so that crystals of different sizes are formed (Kalb et al., 2004). For growth dominated materials, very few critical nuclei are formed after an often relatively long incubation time, but then crystallization occurs by rapid growth. For these materials, the crystals have similar sizes (Kalb et al., 2004). To distinguish between nucleation dominated material and growth dominated materials, recrystallization times of melt-quenched amorphous spot in a crystalline matrix as a function of spot size, was measured by the group Raoux et al. (2008). It was determined that if the crystallization speed depends on the spot size, crystallization proceeds mainly from the crystalline amorphous border and the material is growth dominated. However, if the crystallization speed does not depend on the spot size, crystallization occurs mainly by the formation of new crystals and the material is nucleation dominated.

For many technical applications, the dominant nucleation process is not homogenous but heterogeneous nucleation. The surrounding of the PCM plays an important role and
nucleation often occurs at interfaces. The heterogeneous nucleation rate can be many orders of magnitude larger than the homogenous nucleation rate (Raoux 2009), and in most PCM devices, there is an interface present between the amorphous material and crystalline material, so critical nuclei formation is not necessary for crystallization (Kalb et al., 2004). Static laser tester experiments have found that melt-quenched, amorphous materials can have crystallization times that are orders of magnitude shorter than those for as-deposited, amorphous materials (Raoux et al., 2009). This is due to the above mentioned existence of an amorphous-crystalline interface for melt-quenched growth dominated materials in these experiments.

Archival lifetime is important for the vitality of a data storage technology. For phase change technologies, archival lifetime means the stability of the amorphous area against spontaneous re-crystallization for long times and often at elevated temperatures. This property is of phenomenal significance and is related to the crystallization temperature and the activation energy. Materials with higher crystallization temperatures often have a better thermal stability. In optical storage, the archival lifetime is measured as the change in reflectivity of an amorphous mark in a crystalline disc. In PCM it is determined by the change in resistivity of the Reset (amorphized) cell over time.

Several factors contribute to nucleation and growth kinetics: temperature (Kalb et al., 2005), composition (Coombs et al., 1995; Wuttig et al., 2002; Lankhorst et al., 2005), Material interfaces (Ohshima 1996), device geometry (Lankhorst et al., 2005; Wu et al.,
device size (Wang et al., 2008), material thickness (Raoux et al., 2008) and device history (Coombs et al., 1995; Raoux et al., 2008). Of these, the two most important factors governing switching speeds are temperature and local composition. In fact, it has been reported that most of the macroscopically observable nucleation effects associated with geometry, size, thickness, device history and material interfaces can be understood in terms of varying local composition on the delicate balance between surface and volume energies that drive crystallization (Burr et al., 2010).

3.8.2 Thermal analysis

Thermal analysis has been used in the study of crystallization kinetics of glasses. There exist two thermal analysis methods: One is the isothermal method known as Johnson-Mehl-Avrami (JMA) in which glass samples are quickly heated up and held at a temperature above glass transition temperature and the other method is the constant heating rate known as the Kissinger method (Cheng, 2001; Heireche and Belhadji, 2007). The disadvantage in isothermal method is reaching the required temperature instantaneously and taking the readings at that point (Rao et al., 2008). The parameters usually discussed are the activation energy, the index n (known as the Avrami exponent) and the pre-exponential frequency factor. The crystallization process as has been discussed is a nucleation and growth transformation. In principle, given sufficient time, this transformation continues until complete. Although the degree of transformation does not depend on temperature, the velocity of transformation is strongly temperature
dependent. The JMA transformation equation relates the fraction of material transformed with time at constant temperature. The arguments used in this derivation are largely independent of models used to describe the mechanism of transformation. If a homogeneous reaction is assumed, the probability of transformation in any small region in a given time interval will be the same for all such regions in the untransformed volume. Therefore, the volume transformed in an infinitesimal time interval will be proportional to the volume remaining untransformed at the beginning of the time interval. This in effect leads to a first order rate process. Taking the total volume as $V_o$ and the volume transformed in time $dt$ as $V$, then the transformation could be expressed as

$$\frac{dV}{dt} = k(V_o - V)$$

leading to

$$\frac{V}{V_o} = \alpha(t) = 1 - \exp(-kt),$$

where $k$ is known as the rate constant and $\alpha(t)$ is the fraction of material transformed after a time $t$. Equation (3.24) was derived assuming a homogeneous reaction at constant temperature. However, the situation is more complex for nucleation and growth reactions. Such considerations are incorporated into the JMA equation which is given by

$$\alpha(t) = 1 - \exp[-k(t - t_o)^n],$$

where $t_o$ is the incubation time and the exponent $n=n_n+n_g$ can be related to growth mechanisms. When $0<n_n<1$, the process is said to be nucleated dominated and when $4\leq n_g\leq 1.5$, the growth mechanisms dominates. $k$ is usually found to follow an Arrhenius-type equation of the form
\[ k = k_o \exp\left(-\frac{\Delta E}{K_B T}\right) \]  \hspace{1cm} (3.26)

where \( k_o \) is a pre-exponential frequency factor. Combining Equations (3.25) and (3.26), one gets

\[ \ln\{-\ln[1- \alpha(t)]\} = \ln k + n \ln(t-t_o), \]  \hspace{1cm} (3.27)

Therefore a plot of \( \ln\{-\ln[1- \alpha(t)]\} \) versus \( \ln(t-t_o) \) at constant temperature will give a straight line with slope \( n \) and intercept \( \ln k \). Eq. (3.26) could be arranged to read as

\[ \ln k = \ln k_o - \frac{\Delta E}{K_B T} \]  \hspace{1cm} (3.28)

Thus by obtaining a series of values for \( \ln k \) at different \( T \), we are able to find \( \Delta E \) and \( K_o \).

For the Kissinger method, a first-order rate process is given by

\[ \frac{\partial x}{\partial t} = k(1-x)T \]  \hspace{1cm} (3.29)

Without loss of generality, \( k \) is defined by eq. (3.26). For time independent temperature changes,

\[ \frac{dx}{dt} = \left[ \frac{\partial x}{\partial t}\right]_T. \]  \hspace{1cm} (3.30)

After combining eq. (3.29) and (3.30), the following expression is obtained:

\[ \frac{d}{dt} \left[ \frac{\partial x}{\partial t}\right] = \left[ \frac{\Delta E}{K_B T^2} \frac{dT}{dt} - k_o \exp\left(-\frac{\Delta E}{K_B T}\right) \right] \frac{\partial x}{\partial t}. \]  \hspace{1cm} (3.31)

The requirement that the left hand side of the eq. (3.31) should vanish for an exothermic or endothermic peak gives

\[ \ln \left[ \frac{\beta}{T_c^2} \right] = -\frac{\Delta E}{K_B \cdot T_c} + \text{const}, \]  \hspace{1cm} (3.32)
where $T_c$ corresponds to crystallization temperature and $\beta = \frac{dT}{dt}$ = rate of heating. If a plot of $\ln \left( \frac{\beta}{T_c^2} \right)$ versus $\frac{1}{T_c}$ gives a straight line, then its slope yields $\left( -\frac{\Delta E}{k_B} \right)$, from which $\Delta E$ is easily determined. (Cheng, 2001).

3.9 Theory of structural measurements by XRD

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of materials. A crystal lattice is a regular three-dimensional distribution (cubic, rhombic, etc.) of atoms in space. These are arranged so that they form a series of parallel planes separated from one another by the inter-planar distance $d$, which varies according to the nature of the material. For any crystal, planes exist in a number of different orientations each with its own specific $d$-spacing. When a monochromatic X-ray beam of wavelength ‘$\lambda$’ is projected onto a crystalline material at an angle $\theta$, diffraction peaks only appear when the distance travelled by the rays reflected from successive planes differs by $n\lambda$ according to the equation 3.33, where the number $n$ is a whole number.

$$2d\sin\theta = n\lambda \quad \text{3.33}$$

By varying the angle $\theta$, the Bragg's Law conditions are satisfied by different $d$-spacing in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the sample. Where a mixture of different phases is present, the resultant diffractogram is formed by addition of the individual patterns. The presence of prominent peaks is
characteristic of a crystalline phase while the absence of diffraction peaks is characteristic of the amorphous phase. Based on the principle of X-ray diffraction, a wealth of structural information about the film under investigation is obtained.
CHAPTER FOUR
MATERIALS AND METHODS

4.1 Introduction

This chapter presents a detailed description of the materials used in this study, which includes: their stoichiometric composition, nature and size of the substrate material. The chapter also describes the steps followed in preparation of the alloys, deposition of the films, measurement of film thickness and methods employed in electrical measurements.

4.2 Preparation of Sn\textsubscript{x}Se\textsubscript{y} alloys

To prepare Sn\textsubscript{x}Se\textsubscript{y} alloys, the constituent elements (5N pure) were weighed according to their atomic weight percentages. The electronic balance used for these measurements had an accuracy of 0.0001 g (SHIMADZU, Model: ATY224). Table 4.1 represents the procedure used to calculate the stoichiometric weight of the various constituents of Sn\textsubscript{x}Se\textsubscript{y} samples weighing 2.5 g. The measured mixture of constituent elements was placed in a clean silica tube (diameter = 0.8 cm, length = 14 cm) and then heated in argon ambient using Oxyacetylene burner to temperatures over 800°C for the elements to melt. Once the elements had melted, the tube was shaken to improve on homogeneity of the prepared alloys. The ampoule was then sealed by heating its walls and bending it carefully and sealing it up. Since selenium has a tendency to react with oxygen and is recognized as a high vapour pressure, care and precaution was taken to avoid any explosion during heating and sealing process. The heated melt was then cooled to obtain
the desired alloy. The alloy was then ground in a porcelain motor to obtain fine particles of the alloy which was stored in clean sealed polythene bags.

Table 4.1: The stoichiometric weights of constituent elements of samples of 2.5g each prepared in this work.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>Percentage (%)</th>
<th>Atomic weight (a. m. u)</th>
<th>Atomic weight x percentage</th>
<th>Actual weight taken (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn$<em>{30}$Se$</em>{70}$</td>
<td>Sn</td>
<td>30</td>
<td>118.71</td>
<td>3561.3</td>
<td>0.9796</td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>70</td>
<td>78.96</td>
<td>5527.2</td>
<td>1.5204</td>
</tr>
<tr>
<td>Sn$<em>{40}$Se$</em>{60}$</td>
<td>Sn</td>
<td>40</td>
<td>118.71</td>
<td>4748.4</td>
<td>1.2514</td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>60</td>
<td>78.96</td>
<td>4737.6</td>
<td>1.2486</td>
</tr>
<tr>
<td>Sn$<em>{50}$Se$</em>{50}$</td>
<td>Sn</td>
<td>50</td>
<td>118.71</td>
<td>5935.5</td>
<td>1.5014</td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>50</td>
<td>78.96</td>
<td>3948.0</td>
<td>0.9986</td>
</tr>
</tbody>
</table>

4.3 Preparation of Sn$_x$Se$_y$ thin films

4.3.1 Substrate used

Ordinary glass slides measuring 25.4 mm by 76.2 mm by 1 mm were used as substrates for preparing Sn$_x$Se$_y$ films. It is essential to clean the surface of the substrate on which thin film is to be deposited, because, these thin films readily adhere to a clean insulating surface. If the surface is contaminated with foreign substances like oil or grease, the adhesion of film will be degraded and there will be a tendency for the film to crack and peel. There are also chances of pin holes to be present in thin films. Thus, it is necessary to thoroughly clean substrates before loading them into a vacuum deposition system. In
this work, cleaning of the substrates was done using soap solution. The cleaning process involved scrubbing the substrate in the soap solution, then rinsing thoroughly with distilled water. This procedure was repeated five times for cleaning single substrate. The cleaned substrates were placed on the substrate holder directly above the boat so that the vapours of the material are deposited on them.

4.3.2 Deposition system

The Sn$_x$Se$_y$ thin films were produced in Edwards 306 sputtering/evaporation system employing the evaporation technique. The schematic diagram of a deposition system is as shown in figure 4.1. The deposition chamber is mounted over the diffusion/vacuum pump [Make: M/s Hind High Vacuum Ltd., Model: VS-65D] to maintain vacuum in the deposition chamber. The deposition chamber was cleaned with methanol prior to the deposition. The walls of the chamber were coated with aluminium foil to avoid coating them during evaporation. Before every deposition, the vacuum chamber is evacuated to a vacuum of (3-4) x10$^{-5}$ mbar using the diffusion pump backed by a roughing pump. The chamber has two copper electrodes. The boat used to evaporate the sample consisted of molybdenum (Mo), which has very high melting temperature ($T_m$= 2623°C. This molybdenum boat was connected between the two copper electrodes. The electrodes were connected to a high current, low voltage source to pass high current through the boat which was containing the ground samples of the alloy. By passing high current, the material in the boat turned into molten state and vapours were formed. These vapours were transported to the substrate by convectional currents and the films were deposited.
on the rotating substrates. After deposition, the slides containing the deposited film were kept in the deposition chamber in the dark for 2 hours so that the films attain thermodynamic equilibrium. The films were then removed from the chamber and stored in slide holder.
Figure 4.1: Schematic diagram showing various parts of a thin film deposition system
(adapted from Sharma 2007)
4.3.3 Film thickness

The film thickness was measured using the Alpha Step IQ profilometer with a resolution of 0.012Å, vertical range of (100Å-0.4mm). The profilometer was first switched on and left to warm for 10 minutes so that it can stabilize. The sample film was then placed below the stylus which was kept retracted while the sample was being moved. During measurement, the stylus was moved across the film surface while the sample and the sample stage were kept stationary. This enabled the surface to be scanned and the step height to be measured. The difference in the step height at regions containing the film and those without the film gave the film thickness.

4.4 Electrical characterization

The film sheet resistance was measured by four point probe with a square array following a procedure proposed by Van der Pauw. A schematic diagram showing the four point probe arrangement of the film is shown in figure 4.2. 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 application of the current across contacts AB and the measurements of the voltage across contacts DC were done using Keithley source meter. From these two values, the sheet resistance of the film was computed. Sheet resistance of the films was measured at various temperatures in order to determine the crystallization temperatures. This was done by heating the films in a conventional LINDBERG/BLUE Mini mite Tube Furnace under a steady argon flow. The films were placed in a quartz tube (internal diameter 3cm) and placed in the furnace. The quartz tube was fabricated in the laboratory
to ensure that its internal diameter can accommodate the size of the films under study and also to facilitate the flow of argon during annealing. The measured sheet resistance values were independent of the sample geometry and were easily converted into sheet resistivity using the equation

\[ \rho = R_s t \]  \hspace{2cm} (4.1)

Where \( \rho \) is the sheet resistivity, \( R_s \) is sheet resistance and \( t \) is film thickness. These measurements were performed at different heating rates and the corresponding crystallization temperatures (\( T_c \)) were determined from the minimum of the derivative of sheet resistance.

Figure 4.2: Schematic diagram showing the arrangement of the film in the quartz tube during thermal cycling
4.5 Characterization of crystallization kinetics

For each stoichiometric combination of Sn_xSe_y under investigation i.e. Sn_{30}Se_{70}, Sn_{40}Se_{60} and Sn_{50}Se_{50}, different temperature dependence of sheet resistance curves were obtained. The heating rates were varied between 1K/min and 10K/min. For each run, fresh specimen of the film was used. The crystallization temperature for each specific heating rate was obtained from the minimum of the first derivative of sheet resistance. The Kissinger plots according to equation (3.32), were used in determining the activation energies for each stoichiometric sample.
CHAPTER FIVE

RESULTS AND DISCUSSION

5.1 Introduction

The crystallization kinetics of Sn$_{30}$Se$_{70}$, Sn$_{40}$Se$_{60}$ and Sn$_{50}$Se$_{50}$ thin films were successfully determined using temperature dependent sheet resistance measurements. This chapter presents the results of measurements of film thickness, electrical measurements by four point probe for the as-deposited and as-annealed films and Kissinger plots for various phases of the films under investigation. Discussion on the results and a comparison with the reported values for GST are also presented.

5.2 Measurement of film thickness for as deposited films

The film thickness of the as deposited films was measured using the Alpha Step IQ profilometer with a resolution of 0.012Å and vertical range of (100Å-0.4mm). The thickness for Sn$_{30}$Se$_{70}$, Sn$_{40}$Se$_{60}$ and Sn$_{50}$Se$_{50}$ thin films was about 200 nm. The measuring instrument had an error bar ±0.1 nm.

5.3 Measurement of sheet resistance for as-deposited films

Table 5.1 shows the sheet resistance for as deposited films of Sn$_{30}$Se$_{70}$, Sn$_{40}$Se$_{60}$ and Sn$_{50}$Se$_{50}$ as measured by four point probe method. The values obtained are compared with those obtained for GST by Friedrich et al. (2000) and Park et al. (2008).
Table 5.1: Sheet Resistance of As-deposited films of $\text{Sn}_x\text{Se}_y$ in this work

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sheet Resistance (Ω/Sq.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As deposited ± 0.5 MΩ/Sq.</td>
</tr>
<tr>
<td>$\text{Sn}<em>{30}\text{Se}</em>{70}$</td>
<td>$1.75 \times 10^8$</td>
</tr>
<tr>
<td>$\text{Sn}<em>{40}\text{Se}</em>{60}$</td>
<td>$1.95 \times 10^8$</td>
</tr>
<tr>
<td>$\text{Sn}<em>{50}\text{Se}</em>{50}$</td>
<td>$4.6 \times 10^6$</td>
</tr>
</tbody>
</table>

The sheet resistance values for $\text{Sn}_{30}\text{Se}_{70}$ and $\text{Sn}_{40}\text{Se}_{60}$ were obtained as $1.75 \times 10^8$ and $1.95 \times 10^8$ respectively. These values are approximately twice the sheet resistance of the widely used GST which was found to be 90 MΩ by Friedrich et al. (2000) and 90.3 MΩ by Park et al. (2008). The sheet resistance of $\text{Sn}_{50}\text{Se}_{50}$ (4.6 MΩ) is however lower than that for GST. The higher sheet resistance in the amorphous state contributes to lower $R_{\text{SET}}$ current. Therefore, $\text{Sn}_{30}\text{Se}_{70}$ and $\text{Sn}_{40}\text{Se}_{60}$ are effective materials to reduce power consumption in the PCM device.

5.3.1 Variation of sheet resistance with temperature for $\text{Sn}_{30}\text{Se}_{70}$

The graph in figure 5.1 shows the sheet resistance versus temperature for 200 nm $\text{Sn}_{30}\text{Se}_{70}$ thin film heated at a rate of 5K/min within a temperature range of 25°C and 275°C. At room temperature, the sheet resistance of $\text{Sn}_{30}\text{Se}_{70}$ film was 175 MΩ and decreased to 1.43KΩ within a temperature range of 180°C and 210°C where a steep decline was observed.
Figure 5.1: Sheet resistance versus temperature for Sn$_{30}$Se$_{70}$ film heated at a rate of 5K/min.

The sharp drop in sheet resistance within a temperature range 180°C and 210°C is due to the fact that Sn$_{30}$Se$_{70}$ is a phase change material and therefore it is changing the phase from an amorphous film to a crystalline film. The continuous drop in sheet resistance for
Figure 5.2: The curve of derivative of sheet resistance versus temperature showing crystallization temperature at 195.4±0.4°C.

Temperatures before the onset of phase transition and after the transition demonstrates the semiconductor nature of the alloy. The exact temperature at which this transition from amorphous to crystalline material occurs was obtained by differentiating the variation of sheet resistance versus temperature and the derivative plotted against temperature. A Gaussian surface for single peak is used to generate the error bars. Figure 5.2 shows the
plotted curve. The lowest point of the curve gives the crystallization temperature, $T_c$ of the Sn$_{30}$Se$_{70}$ thin films. Crystallization temperature $T_c$ is defined as the temperature at which the maximum rate of crystal fraction change occurs. At this temperature, a phase change material changes phase from amorphous to crystalline. The crystallization temperature determined from the graph for Sn$_{30}$Se$_{70}$ films at a heating rate of 5K/min was 195.4±0.4°C. The value is much higher than 149°C reported for GST by both Friedrich et al. (2000) and Park et al. (2008). This high value is desirable for PCM applications because it ensures thermal stability of the cell at elevated temperatures. The difference in sheet resistance between amorphous state and the crystalline state was more than five orders of magnitude, which would contribute to adequate SNR (signal to noise ratio) to distinguish the recording of SET and RESET states without confusion.

5.3.2 Variation of sheet resistance with temperature for Sn$_{40}$Se$_{60}$

The graph in figure 5.3 shows the sheet resistance versus temperature for 200nm Sn$_{40}$Se$_{60}$ thin film heated at a rate of 5Kmin$^{-1}$ within a temperature range of 25°C and 245°C. At room temperature, the sheet resistance of Sn$_{40}$Se$_{60}$ was found to be 195 MΩ. This value decreased upon annealing and an abrupt decrease was observed around 150°C and 175°C. This abrupt decrease again is an indication that Sn$_{40}$Se$_{60}$ is a phase change material. The crystallization temperature was obtained as 156.6±0.3°C. This value is lower than that obtained for Sn$_{30}$Se$_{70}$ thin films. Although this value is lower than that for Sn$_{30}$Se$_{70}$, it is still higher than the reported value of 149°C for the GST (Friedrich et al. (2000) and Park
et al. (2008)). This is desirable because it increases data retention at high temperatures. The change in sheet resistance during phase transition is more than five orders of magnitude which imply that the material is also suitable for PCM application.

![Sheet resistance versus temperature](image)

**Figure 5.3**: Sheet resistance versus temperature for Sn$_{40}$Se$_{60}$ thin film heated at a rate of 5K/min
5.3.3 Variation of sheet resistance with temperature for Sn\textsubscript{50}Se\textsubscript{50}

The graph in figure 5.4 shows the variation of sheet resistance versus temperature when Sn\textsubscript{50}Se\textsubscript{50} thin film is annealed at a heating rate of 5K/min. The results for Sn\textsubscript{50}Se\textsubscript{50} show a

![Graph showing the variation of sheet resistance with temperature for Sn\textsubscript{50}Se\textsubscript{50} thin film.](image)

Figure 5.4: Variation of sheet resistance with temperature for Sn\textsubscript{50}Se\textsubscript{50} thin film heated at a rate of 5K/min.

Similar behaviour as those for Sn\textsubscript{30}Se\textsubscript{70} and Sn\textsubscript{40}Se\textsubscript{60} but the transition temperature is much lower than the other stoichiometric combinations. At room temperature, the sheet
resistance of Sn$_{50}$Se$_{50}$ was 4.6 MΩ and decreased to 226 KΩ within a temperature range of 110°C and 140°C where a steep decline was observed. The peak temperature showing the temperature at which the material undergoes phase transition from amorphous to crystalline state, was obtained as 129.8±0.5°C. This temperature is slightly lower than that for GST which is a well known phase change material. Although Sn$_{50}$Se$_{50}$ is not a suitable candidate to replace the GST as an alternative phase change material, this temperature is above the operating temperature for PCM (85°C) as reported by Raoux et al. (2009). This means that based on transition temperature, PCM cells from Sn$_{50}$Se$_{50}$ will be stable at room temperature but stability will be limited at the operating temperature of PCMs.

5.3.4 Comparison of crystallization temperatures of various Sn$_x$Se$_y$ films with GST

The summary results for the different crystallization temperatures for various stoichiometric combinations are tabulated in table 5.2. The crystallization temperatures for the Sn$_{30}$Se$_{70}$ and Sn$_{40}$Se$_{60}$: 195.4±0.4°C and 156.6±0.3°C are higher than 149°C for GST (Friedrich et al., 2000; Park et al., 2008) at a similar heating rate of 5K/min. Sn$_{50}$Se$_{50}$ has a lower $T_c$ of 129.8±0.5°C which is undesirable for PCM application. This means that based on transition temperature, Sn$_{30}$Se$_{70}$ and Sn$_{40}$Se$_{60}$ can increase the data retention in PCM devices.
Table 5.2: Crystallization temperatures of Sn\textsubscript{30}Se\textsubscript{70}, Sn\textsubscript{40}Se\textsubscript{60} and Sn\textsubscript{50}Se\textsubscript{50} films at heating rate of 5 K/min in comparison with value reported for GST.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Transition temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn\textsubscript{30}Se\textsubscript{70} (in this work)</td>
<td>195.4 ± 0.4</td>
</tr>
<tr>
<td>Sn\textsubscript{40}Se\textsubscript{60} (in this work)</td>
<td>156.6 ± 0.3</td>
</tr>
<tr>
<td>Sn\textsubscript{50}Se\textsubscript{50} (in this work)</td>
<td>129.8 ± 0.5</td>
</tr>
<tr>
<td>Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} (Friedrich \textit{et al.}, 2000; park \textit{et al.}, 2008)</td>
<td>149</td>
</tr>
</tbody>
</table>

5.3.5 Comparison of sheet resistance for as deposited and annealed films

Table 5.3 shows a comparison of sheet resistance for as deposited and annealed films. The obtained values have also been compared with those for GST as reported by Friedrich \textit{et al.} (2000) and Park \textit{et al.} (2008). In the as deposited state, the sheet resistance for Sn\textsubscript{30}Se\textsubscript{70}, Sn\textsubscript{40}Se\textsubscript{60} and Sn\textsubscript{50}Se\textsubscript{50} is 1.75 x 10\textsuperscript{8}Ω/Sq., 1.95 x 10\textsuperscript{8}Ω/Sq. and 4.6 x 10\textsuperscript{6}Ω/Sq. respectively while in the annealed state, the sheet resistance is 1.43x10\textsuperscript{3}Ω/Sq., 1.56 x 10\textsuperscript{3}Ω/Sq and 2.26x 10\textsuperscript{5}Ω/Sq. respectively. These values were
used to compute the specific resistivity values for the respective combinations using the
known values of film

Table 5.3: Sheet resistance for as deposited and annealed films of Sn$_{30}$Se$_{70}$, Sn$_{40}$Se$_{60}$ and
Sn$_{50}$Se$_{50}$ in comparison with the values reported for GST.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sheet Resistance (Ω/Sq.)</th>
<th>Sheet Resistance (Ω/Sq.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As deposited</td>
<td>As annealed</td>
</tr>
<tr>
<td>Sn$<em>{30}$Se$</em>{70}$ (in this work)</td>
<td>(1.75 ± 0.005) x 10$^8$</td>
<td>(1.43 ± 0.005) x 10$^5$</td>
</tr>
<tr>
<td>Sn$<em>{40}$Se$</em>{60}$ (in this work)</td>
<td>(1.95 ± 0.005) x 10$^8$</td>
<td>(1.56 ± 0.005) x 10$^5$</td>
</tr>
<tr>
<td>Sn$<em>{50}$Se$</em>{50}$ (in this work)</td>
<td>(4.6 ± 0.05) x 10$^6$</td>
<td>(2.26 ± 0.005) x 10$^5$</td>
</tr>
<tr>
<td>Ge$_2$Sb$_2$Te$_5$ (Friedrich et al., 2000)</td>
<td>9.0 x 10$^7$</td>
<td>4.4 x 10$^5$</td>
</tr>
<tr>
<td>Park et al. (2008)</td>
<td>9.03 x 10$^7$</td>
<td>4.4 x 10$^5$</td>
</tr>
</tbody>
</table>

thickness. The films of Sn$_{30}$Se$_{70}$ and Sn$_{40}$Se$_{60}$ show an electrical contrast of more than
five orders of magnitude. Since an electrical contrast of at least three orders of magnitude
is required for a substance to be used as a phase change material (Chung et al., 2008), the
two combinations qualify for PCM application based on the electrical contrast and the
Transition temperature. The electrical contrast for Sn$_{50}$Se$_{50}$ is less than two orders of
magnitude which is below the mandatory threshold. Although the material has a
favorable sheet resistance in the crystalline phase, it does not show sufficient contrast to separate the signal from noise during phase transformation. It is evident that the films of Sn$_{30}$Se$_{70}$ and Sn$_{40}$Se$_{60}$ have a higher sheet resistance than GST in the amorphous state and the GST has a higher sheet resistance in the crystalline state. These findings are in close comparison with the findings of Chung et al. (2008) who reported high electrical contrast of 5 orders for SnSe$_2$ and Sn$_2$Se$_3$ thin films and a low contrast of less than two orders for SnSe thin films.

Table 5.4: shows sheet resistivity for the two states of the films of Sn$_{30}$Se$_{70}$, Sn$_{40}$Se$_{60}$ and Sn$_{50}$Se$_{50}$ in comparison with the value reported for GST.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sheet Resistivity as deposited (Ω cm)</th>
<th>Sheet Resistivity As annealed (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn$<em>{30}$Se$</em>{70}$</td>
<td>(2.888 ± 0.010) x 10$^3$</td>
<td>(1.788 ± 0.010) x 10$^{-2}$</td>
</tr>
<tr>
<td>Sn$<em>{40}$Se$</em>{60}$</td>
<td>(3.764 ± 0.010) x 10$^3$</td>
<td>(1.981 ± 0.010) x 10$^{-2}$</td>
</tr>
<tr>
<td>Sn$<em>{50}$Se$</em>{50}$</td>
<td>(9.810 ± 0.100) x 10$^{-1}$</td>
<td>(3.277 ± 0.010) x 10$^{-6}$</td>
</tr>
<tr>
<td>Ge$_2$Sb$_2$Te$_5$</td>
<td>1.350 x 10$^3$</td>
<td>4.950 x 10$^{-2}$</td>
</tr>
</tbody>
</table>

(Friedrich et al., 2000; Park et al., 2008)
The sheet resistivity of Sn\textsubscript{30}Se\textsubscript{70}, Sn\textsubscript{40}Se\textsubscript{60} and Sn\textsubscript{50}Se\textsubscript{50} for as-deposited and annealed films have also been compared with the GST as shown in table 5.4. The film specific sheet resistivity is expressed by equation 3.21.

5.4 Determination of activation energy for crystallization

The films of Sn\textsubscript{30}Se\textsubscript{70}, Sn\textsubscript{40}Se\textsubscript{60} and Sn\textsubscript{50}Se\textsubscript{50} were annealed at heating rates: 1, 2.5, 5, 7.5 and 10K/min within a temperature range of 25\textdegree{}C to 300\textdegree{}C. Each stoichiometric alloy was annealed independently and fresh samples were used in each run. The results of various runs are presented as well as the calculated values of crystallization parameters.

5.4.1 The activation energy for crystallization for Sn\textsubscript{30}Se\textsubscript{70}

Figure 5.5 shows the variation of sheet resistance for Sn\textsubscript{30}Se\textsubscript{70} films upon annealing at different heating rates. The graphs show a shift in crystallization temperature towards higher temperatures as the heating rate is increased.
Figure 5.5: Variation of Sheet resistance versus temperature for Sn$_{30}$Se$_{70}$ thin films annealed at different heating rates.

For the respective heating rates, the crystallization temperatures were obtained from the minimum of the derivatives of the sheet resistance. The graphs in figure 5.6 show various shifts in the crystallization temperatures as the heating rates are varied. For all the heating
rates, the value of crystallization temperatures for Sn₃₀Se₇₀ were much higher than room

Figure 5.6: Variation of the derivative of sheet resistance versus temperature for Sn₃₀Se₇₀ thin films annealed at different heating rates.

temperature. This is an important advantage for this Sn₃₀Se₇₀ alloy because it is essential to prevent self transition of recording materials between the two phases: amorphous and
crystalline. Hence one can expect the PCM made from this alloy to remain stable in its amorphous or crystalline states at room temperature.

The measured values of crystallization temperature ($T_c$) for the glassy alloys of Sn$_{30}$Se$_{70}$ at different heating rates and other crystallization parameters necessary for calculating activation energy using Kissinger equation are summarized in table 5.5.

Table 5.5: Crystallization parameters of Sn$_{30}$Se$_{70}$ used to acquire Kissinger plot for calculation of activation energy.

<table>
<thead>
<tr>
<th>Heating rate $\beta$ (±0.05 K/min)</th>
<th>$T_c$ ($^o$C)</th>
<th>$T_c$ (K)</th>
<th>$1000T_c^{-1}$ (K$^{-1}$)</th>
<th>$\ln(\beta T_c^{-2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>159.3±0.4</td>
<td>432.3±0.4</td>
<td>2.3132±0.0021</td>
<td>-12.1382±0.0518</td>
</tr>
<tr>
<td>2.5</td>
<td>179.3±0.3</td>
<td>452.3±0.3</td>
<td>2.2109±0.0015</td>
<td>-11.3124±0.0214</td>
</tr>
<tr>
<td>5.0</td>
<td>195.4±0.4</td>
<td>468.4±0.4</td>
<td>2.1349±0.0018</td>
<td>-10.6892±0.0117</td>
</tr>
<tr>
<td>7.5</td>
<td>203.4±0.5</td>
<td>476.4±0.5</td>
<td>2.0991±0.0022</td>
<td>-10.3176±0.0087</td>
</tr>
<tr>
<td>10.0</td>
<td>221.6±0.5</td>
<td>494.6±0.5</td>
<td>2.0218±0.0020</td>
<td>-10.1049±0.0070</td>
</tr>
</tbody>
</table>

The Kissinger plot for Sn$_{30}$Se$_{70}$ alloys is shown in figure 5.7. The obtained values of the slope were used to calculate the activation energy according to the equation 3.32, which is

\[
\ln(\beta T_c^{-2}) = -\frac{\Delta E}{k_B} \left( \frac{1}{T_c} \right) + \text{constant}
\]

The activation energy was found to be 0.63±0.06 eV.
5.4.2 The activation energy for crystallization for Sn$_{40}$Se$_{60}$

The graph in figure 5.8 shows the variation of sheet resistance versus temperature for Sn$_{40}$Se$_{60}$ thin films annealed at different heating rates. The results show a positive shift in the steep decline of sheet resistance as the heating rate is increased. For the heating rates of 1, 2.5, 5, 7.5 and 10K/min the crystallization temperatures obtained from the minimum
Figure 5.8: Graph of Sheet resistance versus temperature for Sn$_{40}$Se$_{60}$ thin films annealed at different heating rates showing positive shifts in steep decline in sheet resistance with increase in heating rates

of the derivatives of the sheet resistance are 126.7±0.2°C, 135.9±0.2°C, 156.6±0.3°C, 166.1±0.4°C and 175.0±0.3°C respectively. For all the heating rates, the values of crystallization temperature for Sn$_{40}$Se$_{60}$ were much higher than room temperature. The measured values of crystallization temperature ($T_c$) for the glassy alloys of Sn$_{40}$Se$_{60}$ at
different heating rates and other crystallization parameters necessary for calculating activation energy using Kissinger equation are tabulated in table 5.6.

Table 5.6: Crystallization parameters of Sn$_{40}$Se$_{60}$ used to acquire Kissinger plot for calculation of activation energy.

<table>
<thead>
<tr>
<th>Heating rate $\beta$ (±0.05 K/min)</th>
<th>T$_c$ ($^\circ$C)</th>
<th>T$_c$ (K)</th>
<th>1000T$^{-1}$ (K$^{-1}$)</th>
<th>ln($\beta T_c^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>126.7±0.2</td>
<td>399.7±0.2</td>
<td>2.5019±0.0013</td>
<td>-11.9814±0.0510</td>
</tr>
<tr>
<td>2.5</td>
<td>135.9±0.2</td>
<td>408.9±0.2</td>
<td>2.4456±0.0012</td>
<td>-11.1107±0.0249</td>
</tr>
<tr>
<td>5.0</td>
<td>156.6±0.3</td>
<td>429.6±0.3</td>
<td>2.3277±0.0016</td>
<td>-10.5162±0.0114</td>
</tr>
<tr>
<td>7.5</td>
<td>166.1±0.4</td>
<td>439.1±0.4</td>
<td>2.2774±0.0021</td>
<td>-10.1546±0.0085</td>
</tr>
<tr>
<td>10.0</td>
<td>175.0±0.3</td>
<td>448.0±0.3</td>
<td>2.2321±0.0015</td>
<td>-09.9070±0.0063</td>
</tr>
</tbody>
</table>

The Kissinger plot for Sn$_{40}$Se$_{60}$ alloy is shown in figure 5.9. The obtained value of the slope was used to calculate the activation energy according to the Kissinger equation 3.32. The activation energy ($\Delta E$) was found to be 0.62±0.07 eV.
This value compares well with what was obtained by the group Chung et al. (2008) on a similar combination where they reported an activation energy of 0.57±0.09 eV. The obtained value is higher than that reported for GST (0.39 eV) (Friedrich et al., 2000; Park et al., 2008). This is a desirable property since the activation energy affects resistance to
thermally activated re-crystallization. Therefore, the high obtained values of activation energy would contribute to increased stability against recrystallization.

5.4.3 The activation energy for crystallization for Sn$_{50}$Se$_{50}$

Figure 5.10 shows the variation of sheet resistance versus temperature of Sn$_{50}$Se$_{50}$ thin films annealed at different heating rates. The results show a positive shift in crystallization temperature as the heating rate is increased as was the case for the other stoichiometries.
Figure 5.10: Graph of Sheet resistance versus temperature for Sn$_{50}$Se$_{50}$ thin films annealed at different heating rates. A positive shift in the steep decline of sheet resistance with increase in heating rate is observed.

For all the heating rates, the values of crystallization temperatures were higher than room temperature and just slightly higher than the operating temperature for PCM which is
85°C (Raoux et al., 2009). This means, based on the crystallization temperature, PCM cell from this material will be stable at the operating temperature. The obtained values of crystallization temperature (T_c) at different heating rates and other crystallization parameters are tabulated in table 5.7.

Table 5.7: Crystallization parameters of Sn_{50}Se_{50} used to acquire Kissinger plots for calculation of activation energy.

<table>
<thead>
<tr>
<th>Heating rate $\beta$ (±0.05 K/min)</th>
<th>$T_c$ (°C)</th>
<th>$T_c$ (K)</th>
<th>1000T^{-1} (K^{-1})</th>
<th>ln($\beta T^{-2}_c$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>97.4±0.4</td>
<td>370.4±0.4</td>
<td>2.6997±0.0029</td>
<td>-11.8292±0.0522</td>
</tr>
<tr>
<td>2.5</td>
<td>114.5±0.7</td>
<td>387.5±0.7</td>
<td>2.5806±0.0047</td>
<td>-11.0031±0.0236</td>
</tr>
<tr>
<td>5.0</td>
<td>128.6±0.4</td>
<td>401.6±0.4</td>
<td>2.4900±0.0025</td>
<td>-10.3815±0.0120</td>
</tr>
<tr>
<td>7.5</td>
<td>147.7±0.3</td>
<td>420.7±0.3</td>
<td>2.3770±0.0017</td>
<td>-10.0689±0.0081</td>
</tr>
<tr>
<td>10.0</td>
<td>161.5±0.5</td>
<td>434.5±0.5</td>
<td>2.3015±0.0026</td>
<td>-09.8458±0.0073</td>
</tr>
</tbody>
</table>

The Kissinger plot for Sn_{50}Se_{50} alloy is shown in figure 5.11. The obtained value of the slope was used to calculate the activation energy according to the Kissinger equation (3.32). The activation energy was found to be $\Delta E = 0.43 \pm 0.05$ eV. This value is comparable with that for GST (0.39eV) as reported by Friedrich et al. (2000) and Park et al. (2008).
Figure 5.11: The Kissinger plot for calculation of activation energy for films of Sn$_{50}$Se$_{50}$

For all samples, a positive shift in the position of the steep decline in sheet resistance with increasing heating rate was clearly observed. Also, the values of crystallization temperature of the alloys at all heating rates: 1, 2.5, 5, 7.5 and 10K/min was much higher than the room temperature and PCM operating temperature which is 85°C (Raoux et al., 2009). This is an important advantage for these alloys because it is essential to prevent self transition of recording materials between the two phases. Hence one can expect the
PCM made from this alloy to remain stable in its amorphous and crystalline states at the operating temperature.

The values of activation energies obtained for various stoichiometric samples: Sn$_{30}$Se$_{70}$ (0.63 eV), Sn$_{40}$Se$_{60}$ (0.62 eV) and Sn$_{50}$Se$_{50}$ (0.43 eV) were higher than that for the GST (0.39 eV) as reported by Friedrich et al. (2000). Since the crystalline SET state is a stable low resistance state, it is the stability of the quenched high resistance RESET phase which dominates retention issues (Burr et al., 2010). The amorphous phase suffers from two independent resistance altering processes: resistance drift and spontaneous crystallization (Burr et al., 2010). Although resistance drift does not cause any data loss, thermally activated crystallization leads to significant reduction in the resistance of the active layer, causing eventual retention failures for the binary storage. Njoroge et al. (2001) reported that the resistance to re-crystallization is proportional to the activation energy. Therefore, the high obtained values of activation energy for these alloys (Sn$_{30}$Se$_{70}$, Sn$_{40}$Se$_{60}$ and Sn$_{50}$Se$_{50}$) imply that PCM cells made from these samples will have higher stability against recrystallization.
CHAPTER SIX

CONCLUSION AND RECOMMENDATION

6.1 Conclusion

The crystallization kinetics of various stoichiometric combinations of the Sn-Se system have been successfully investigated using sheet resistance versus temperature measurements. The alloys were prepared by melt-quenching technique in Argon ambient and thin films were deposited on glass substrates using thermal evaporation method. The results show that the crystallization temperature, specific resistivity and the activation energy for Sn-Se alloys can be varied over a wide range by adjusting the composition of the binary alloy. The crystallization temperatures for Sn$_{30}$Se$_{70}$, Sn$_{40}$Se$_{60}$ and Sn$_{50}$Se$_{50}$ were found to be: 195.4± 0.4°C, 156.6± 0.3°C and 129.8± 0.5°C respectively. These values seem to become more favorable with addition of selenium in the Sn-Se system. In the as-deposited state, the sheet resistance for Sn$_{30}$Se$_{70}$, Sn$_{40}$Se$_{60}$ and Sn$_{50}$Se$_{50}$ was found to be 1.75 x 10$^8$ Ω/Sq., 1.95 x 10$^8$ Ω/Sq. and 4.60 x10$^6$ Ω/Sq. respectively while in the annealed state, the sheet resistance obtained was 1.43x10$^3$ Ω/Sq., 1.56x 10$^3$ Ω/Sq. and 2.26 x 10$^5$ Ω/sq. respectively. The electrical contrast obtained from the sheet resistance versus temperature measurements was at least 10$^5$ for Sn$_{30}$Se$_{70}$, and Sn$_{40}$Se$_{60}$ and less than 10$^2$ for the stoichiometric Sn$_{50}$Se$_{50}$. The value of sheet resistance for the two alloys Sn$_{30}$Se$_{70}$ and Sn$_{40}$Se$_{60}$ is twice the value obtained for GST (9.0x10$^7$ Ω) implying the materials are good for PCM application. The value of activation energy obtained from Kissinger analysis was lowest in the film for Sn$_{50}$Se$_{50}$ at 0.43 eV and highest in the film
for Sn_{30}Se_{70} (0.63 eV). The activation energy for the films of the Sn_{40}Se_{60} alloy was obtained to be 0.62 eV. It is interesting to note that when the selenium concentration in Sn-Se system was increased, the activation energy was found to increase, hence the material become more favorable for PCM application with respect to this property and this also shows that Selenium based alloys are better glass formers compared to Tellurium based alloys.

From the alloys studied, the most promising alloys for PCM applications were found to be Sn_{30}Se_{70} and Sn_{40}Se_{60}. This is because of their high sheet resistance in the amorphous state, high electrical contrast of five orders of magnitude, and high crystallization temperature. The range of values obtained for $\rho$, $T_c$ and $\Delta E$ are in good agreement with work by Chung et al. (2008) except for the low crystallization temperature obtained for Sn_{50}Se_{50} films. It is expected that the crystallization kinetics results of various Sn$_x$Se$_y$ thin films obtained in this research, will provide potentially critical insight in the search for better PCM materials that exhibit superior properties better than the current levels.

6.2 Recommendation for future work

This research mainly investigated the crystallization kinetics of thin films using temperature dependent sheet resistance measurements and Kissinger analysis. However, further research is recommended by use of methods such as Scanning electron microscopy (SEM) and X-ray Diffractometry (XRD) in order to correlate the change in electronic properties to change in structure. There is also need to study the density
changes as a function of temperature since the film density change upon crystallization leads to considerable stresses which can limit the lifetime of storage media (Njoroge et al., 2001). Also recommended is compositional verification in the ingot and thin films by advanced methods such as X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry and Energy dispersive X-ray (EDX). There is need for AFM measurements to establish the nucleation rates, incubation times as well as the recrystallization times. These proposed methods will help in improving the efficiency of the melt quenching method as a reliable alloy preparation technique and consequently enable further material research and development towards development of superior PCM devices. It is recommended to the University that a team be organized at the physics department level, to fabricate PCM cells using alloys of Sn$_{30}$Se$_{70}$ and Sn$_{40}$Se$_{60}$ for testing and possible commercialization.
REFERENCES


Heireche L. and Belhadji M. (2007). Non-isothermal Crystallization in Ge$_{15.5-x}$Te$_{84.5}$Sb$_x$ (0.5<x<1.5). *Journal of Ovonic Research* 3: 15-20


APPENDICES

Appendix I: Photograph of Edwards Auto Magnetron Sputtering System used in this work
Appendix II: Photograph of Keithley 2400 Source meter with LINDBERG BLUE furnace used in this work
Appendix III: Photograph of KLA Alpha Step IQ profilometer