NITROGEN DOPING EFFECT ON TIN-SELENIUM THIN FILMS FOR PHASE CHANGE MEMORY APPLICATIONS

CHARLES MUTHUI KAMAU [B.Ed. (Sc.)]
I56/CE/11177/2007

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

**Kamau Charles Muthui**

Department of Physics  
Kenyatta University  
P.O. BOX 43844 - 00100  
NAIROBI-KENYA

This thesis has been submitted for examination with our approval as University Supervisors.

**Dr. Njoroge W. K.**

Department of Physics  
Kenyatta University  
P.O. BOX 43844 - 00100  
NAIROBI-KENYA

**Dr. Patrick M. Karimi**

Department of Physics  
Kenyatta University  
P.O. BOX 43844 - 00100  
NAIROBI-KENYA
DEDICATION

This thesis is dedicated to my parents and my family.
ACKNOWLEDGEMENT

I would like to express my most sincere gratitude for the individuals that follow. My special thanks go to my supervisors Dr. W. K. Njoroge and Dr. P. M. Karimi for their tireless scholarly guidance and encouragement during the research work. Their vast knowledge in thin films and electronics research was a great contribution to the success of this work. I thank them for their willingness to see this thesis through to the end.

I am grateful to the entire staff of Physics department, led by Dr. C. Migwi and his successor Dr. W. Njoroge for being supportive throughout the research period. I also acknowledge the Physics laboratory technical staff led by Chief technician Mr. Njuguna for their technical support while carrying out my laboratory work. Thanks are due to Mr. Maina the chief technician, chemistry laboratory for his assistance in alloy preparation and in fabricating a special furnace tube.

I am also indebted to many others at the Mines and Geological department and UON Chiromo Physics laboratories for their assistance in structural and optical measurements. My due regards to my colleagues Karanja, Muga, Kirwa, Fanuel, Ogaro, Agumba, Kagiri, Munguti, Tuwei, Masinde ,Wekunda and Ketui just to mention a few. I sincerely thank you all for your support and advice during this research period. To my family, thanks for your moral support and love throughout my studies. I would like to take a moment to thank my wife, Mary, for her love and support through this entire process. Finally thanks to the almighty God without whom this work would not have been successful.
TABLE OF CONTENTS

DECLARATION...........................................................................................................ii
DEDICATION..............................................................................................................iii
ACKNOWLEDGEMENT.................................................................................................iv
TABLE OF CONTENTS.................................................................................................v
LIST OF TABLES..........................................................................................................ix
LIST OF FIGURES.......................................................................................................x
LIST OF ABBREVIATIONS, SYMBOLS AND ACRONYMS...........................................xiii
ABSTRACT................................................................................................................xiv

CHAPTER ONE
INTRODUCTION

1.1 Background........................................................................................................... 1
1.2 Problem statement and justification.................................................................3
1.3 Objectives of the study.......................................................................................4
  1.3.1 Main objective...............................................................................................4
  1.3.2 Specific objectives........................................................................................4
1.4 Rationale.............................................................................................................5

CHAPTER TWO
LITERATURE REVIEW

2.1 Introduction.........................................................................................................7
2.2 Properties of phase change materials............................................................9
2.3 GST phase change materials.............................................................................10
CHAPTER THREE
THEORETICAL CONSIDERATIONS

3.1 Introduction.................................................................23

3.2 Thin films........................................................................23

3.3 Evaporation........................................................................23

3.4 Conduction in semiconductors...........................................25

3.5 Sheet resistivity of thin films.............................................27

3.6 XRD structural analysis...................................................29

3.7 PCRAM device characterization.........................................32

3.7.1 Resistance-current (R-I) curves....................................33

3.7.2 I-V curves......................................................................33

3.8 Optical models, parameters and characterization..................34

3.8.1 Optical properties of thin film......................................34

3.8.2 Optical spectra simulation.............................................36

3.8.3 Optical models..........................................................36

3.9 PCRAM cell......................................................................38

CHAPTER FOUR
EXPERIMENTAL PROCEDURES

4.1 Introduction......................................................................41

4.2 Preparation of Sn_xSe_y alloys..........................................41
4.3 Preparation of nitrogen doped SnₓSeᵧ thin films...........................................41
4.4 Electrical characterization of the films...............................................................44
4.5 Optical data measurements and analysis.......................................................44
4.6 XRD measurement.........................................................................................45
4.7 PCRAM cell design, fabrication and characterization.........................................46
  4.7.1 PCRAM cell design......................................................................................46
  4.7.2 PCRAM cell fabrication...............................................................................48
  4.7.3 PCRAM cell characterization.......................................................................48

CHAPTER FIVE
RESULTS AND DISCUSSION

5.1 Optical characterization of N- SnₓSeᵧ................................................................50
  5.1.1 Optical reflectance and transmittance.........................................................50
  5.1.2 Simulated and experimental graphs of SnₓSeᵧ optical spectra.........................53
  5.1.3 Optical band gap of SnₓSeᵧ thin films.........................................................55
5.2 Effect of nitrogen doping on dielectric function..............................................57
  5.2.1 Optical transmittance...................................................................................57
  5.2.2 Simulated and experimental graphs of N-SnSe optical spectra.......................58
  5.2.3 Optical band gaps of nitrogen-doped SnSe films.........................................60
5.3 Effect of nitrogen doping on dielectric function..............................................62
5.4 Refractive index and absorption edge..............................................................70
5.5 Electrical characterization of N- SnSe...............................................................73
5.6 Structural properties.......................................................................................78
5.7 Electrical measurement of SnSe PCRAM device...........................................82

CHAPTER SIX
CONCLUSIONS AND RECOMMENDATIONS
6.1 Conclusions................................................................................................................. 84
6.2 Recommendations................................................................................................. 85
7.0 REFERENCES............................................................................................................ 86
8.0 APPENDICES.............................................................................................................. 92
    Appendix I: Photographs of Edward auto 306 sputtering system................. 92
    Appendix II: Photograph of Keithley Source Meter 2400 model ............... 93
    Appendix III: Set-up used to collect R-T data for the films ...................... 94
    Appendix IV: PANalytical X’Pert Pro XRD machine.............................. 95
    Appendix V: UV-3700 UV-VIS-NIR Spectrophotometer....................... 96
LIST OF TABLES

Table 5.1: Comparison of optical band gaps of as-deposited and annealed nitrogen doped - SnSe thin films...............................................................61

Table 5.2: Crystallization temperatures of N-SnSe thin films.................................75
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Schematic of thermal evaporation system</td>
<td>24</td>
</tr>
<tr>
<td>3.2</td>
<td>Schematic of 4-point probe configuration</td>
<td>28</td>
</tr>
<tr>
<td>3.3</td>
<td>X-ray diffraction pattern of SnSe-SnSe$_2$ composite</td>
<td>30</td>
</tr>
<tr>
<td>3.4</td>
<td>Schematic view of a vertical PCRAM cell</td>
<td>38</td>
</tr>
<tr>
<td>3.5</td>
<td>Schematic diagram showing top view and cross-section of lateral PCRAM cell</td>
<td>39</td>
</tr>
<tr>
<td>4.1</td>
<td>Schematic of probe head used in sheet resistivity measurement</td>
<td>43</td>
</tr>
<tr>
<td>4.2</td>
<td>Schematic cross-sectional view of the fabricated N: SnSe PCRAM cell</td>
<td>47</td>
</tr>
<tr>
<td>4.3</td>
<td>Schematic diagram showing typical I-V traces for a phase-change device</td>
<td>49</td>
</tr>
<tr>
<td>5.1</td>
<td>Graph of transmittance spectra of Sn$_x$Se$_y$ thin films for different mass ratios</td>
<td>50</td>
</tr>
<tr>
<td>5.2</td>
<td>Graph of reflectance spectra of Sn$_x$Se$_y$ thin films varied by mass ratios</td>
<td>52</td>
</tr>
<tr>
<td>5.3</td>
<td>Simulated and experimental transmittance curves for Sn$_x$Se$_y$ thin films</td>
<td>53</td>
</tr>
<tr>
<td>5.4</td>
<td>Dependence of optical bandgap on ratio of Sn: Se in as-deposited and annealed thin films</td>
<td>56</td>
</tr>
<tr>
<td>5.5</td>
<td>Transmittance curves of N-doped SnSe thin films</td>
<td>58</td>
</tr>
<tr>
<td>5.6</td>
<td>Simulated and experimental transmittance curves for N-SnSe thin films</td>
<td>59</td>
</tr>
<tr>
<td>5.7</td>
<td>Dependence of optical band gaps of the SnSe films on</td>
<td></td>
</tr>
</tbody>
</table>
nitrogen-doping .....................................................................................61

Figure 5.8 Dependence of $\varepsilon_1$ on N-doping level for amorphous SnSe thin films........................................................................................................63

Figure 5.9 Dependence of $\varepsilon_1$ on N-doping level for crystalline SnSe thin films ...............................................................................................64

Figure 5.10 Dependence of $\varepsilon_2$ on nitrogen doping level for amorphous N-SnSe thin films............................................................................65

Figure 5.11 Dependence of $\varepsilon_2$ on nitrogen doping level for crystalline SnSe thin films.....................................................................................66

Figure 5.12 Dielectric functions of amorphous and crystalline phases for 3 sccm N-SnSe thin film ........................................................................67

Figure 5.13 Dielectric contrast in 3 sccm N-SnSe thin films..........................68

Figure 5.14 Reflectance curves for amorphous and crystalline 3sccm N-SnSe film ............................................................................................69

Figure 5.15 Dependence of refractive index on nitrogen doping level in amorphous SnSe.....................................................................................71

Figure 5.16 Dependence of refractive index on nitrogen doping level in crystalline SnSe thin films ........................................................................72

Figure 5.17 Dependence of sheet resistivity on temperature for SnSe thin film....................................................................................................73

Figure 5.18 Resistivity as a function of temperature for 130-nm-thick, as-deposited nitrogen-doped SnSe thin films ..................................................74

Figure 5.19 Dependence of crystalline resistivity of SnSe on nitrogen doping...77

Figure 5.20 XRD scan of a blank glass substrate ........................................78
Figure 5.21: XRD scan for SnSe (a) amorphous and (b) crystalline thin films doped with 0, 1, 2, 3 and 4 sccm nitrogen.................................................. 80

Figure 5.22 XRD scan for SnSe with 4sccm Nitrogen ................................................. 81

Figure 5.23 I-V characteristics of N-SnSe PCRAM device tested in DC static mode................................................................. 83
# LIST OF ABBREVIATIONS, SYMBOLS AND ACRONYMS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>C/N</td>
<td>Carrier-to-Noise ratio</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary Metal Oxide Semiconductor</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>EEPROM</td>
<td>Electrically Erasable Programmable Read-Only-Memory</td>
</tr>
<tr>
<td>EM</td>
<td>Electro-Magnetic</td>
</tr>
<tr>
<td>FeRAM</td>
<td>Ferroelectric Random Access Memory</td>
</tr>
<tr>
<td>GIST</td>
<td>Ge–In–Sb–Te alloy</td>
</tr>
<tr>
<td>GST</td>
<td>Germanium-Antimony -Tellurium alloy</td>
</tr>
<tr>
<td>I-V</td>
<td>Current – Voltage</td>
</tr>
<tr>
<td>MEG</td>
<td>Multi-Exciton Generation</td>
</tr>
<tr>
<td>MRAM</td>
<td>Magnetoresistive Random Access Memory</td>
</tr>
<tr>
<td>NVM</td>
<td>Non-Volatile Memory</td>
</tr>
<tr>
<td>PCM</td>
<td>Phase Change Material</td>
</tr>
<tr>
<td>PCRAM</td>
<td>Phase Change Random Access Memory</td>
</tr>
<tr>
<td>PMC</td>
<td>Programmable Metallization Cell</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>Sn-Se</td>
<td>Tin-Selenium alloy</td>
</tr>
<tr>
<td>ST</td>
<td>Antimony-Tellurium alloy</td>
</tr>
<tr>
<td>$T_c$</td>
<td>Crystallization temperature</td>
</tr>
<tr>
<td>VLSI</td>
<td>Very Large Scale Integration</td>
</tr>
</tbody>
</table>
ABSTRACT
Phase change materials have been widely used in optical and electronic storage due to rapid and reversible phase transition between amorphous and crystalline states with remarkable resistivity and optical contrasts. More recently these materials have been identified as suitable candidates for phase change random access memory (PCRAM) applications due to their potential for high scalability, low power and fast speed operation. Despite these superior properties and enormous potential, high reset currents necessitating high power consumption have been attributed to existing PCMs. Nitrogen doping has been proposed as a solution to these problems according to Caravati, et al., (2011). In this work, Nitrogen doped Sn$_x$Se$_y$ phase change materials have been synthesized and characterized for optical, electrical and structural properties. The films were deposited by evaporation technique using Edwards Auto 306 Magnetron sputtering and evaporation system. Transmittance and reflectance data in the range 300-1700 nm were measured and calculated using Shimadzu 3700 DUV spectrophotometer for all the thin film samples. The optical measurements were simulated and analyzed using Scout software. Band gap values in the range 0.97 eV - 3.63 ± 0.005 eV were determined for SnSe thin films after doping with 0-5 sccm Nitrogen. Nitrogen doping was shown to increase the band gap in amorphous films with large increase seen between 0 sccm N$_2$ and 1 sccm N$_2$. X-ray diffraction (XRD) using XpertPro Panalytic XRD machine revealed the as-deposited films to be amorphous. The annealed films were found to be polycrystalline in nature with the number and height of peaks in the XRD scan increasing with increase in N$_2$ doping. Sheet resistivity that was determined using Keithley source meter and a four-point probe set-up, was in the range 1150-1250±1 Ω-cm and 9.3- 0.3±0.05 Ω-cm for the amorphous and crystalline states respectively. Lowest sheet resistivity was observed at 3sccm N$_2$ in amorphous SnSe films while crystalline resistivity gradually decreased as N$_2$ doping was increased. The large change in resistivity of order $10^5$ confirmed the phase change nature of the films. Nitrogen doping lowered the crystallization temperature from 107.8 ± 0.05°C at 0 sccm N$_2$ to a minimum of 72.8±0.05 °C at 3sccm N$_2$. From the I-V characteristics of the fabricated PCRAM cell, a threshold switching voltage, $V_{th}$ of 4.47 V at a current 1.04 mA was obtained.
CHAPTER ONE

INTRODUCTION

1.1 Background

The convergence of consumer, computer and communication electronic systems has led to a growing demand for non-volatile memory in devices. Phase-change Random Access Memory (PCRAM) is a type of non-volatile memory that employs reversible phase change in materials to store information. The materials utilized must be capable of changing their phase between amorphous and crystalline states at high speeds and within a convenient range of temperatures. Although touted as promising next generation storage media, there are still many challenges to be overcome in making PCRAM feasible commercially.

Flash memory devices have been around in one form or another since the early 1980s. Flash memory is the market leader today and is widely used in applications such as memory cards, USB flash drives, MP3 players, and solid-state drives for popular consumer products. Some electronics industry experts are predicting that flash memory will no longer be the dominant storage medium for these applications by 2015 according to Pronin (2011). Each burst of voltage across a flash cell during a write cycle causes degradation. The damage due to programming grows worse as the size of the cells decreases because the voltage necessary to program the device does not scale with the lithography. Currently, flash memory is dogged by number of practical problems such as scaling difficulties with shrinking chip lithography and finite number of erase-write cycles (Heone and Dae-Hwan, 2005). According to Gleixner et al. (2009), PCRAM cycling endurance is of the order of $10^8$ writes which
is significantly higher than the \( \sim 10^5 \) specified for floating gate technologies. The PCRAM cells perform better in data retention and are more robust in data disturbs.

Many promising new technologies (such as FeRAM, MRAM, PMC, PCRAM, and others) are under investigation and development as possible more scalable replacements for flash memory. PCRAM, compared to flash memory, has fast switching speed, low programmable energy, high endurance, good data retention, improved compatibility with CMOS technologies and has excellent scalability (Qiao et al., 2006). Apart from solving scaling issues that other conventional memories might face in the near future, PCRAM is capable of creating new functions and applications of its own with its fast write programming speed and direct overwrite capability (Daewon and Kinam, 2007). PCRAM is substantially faster and highly reliable, offering up to 100 million write cycles, compared to just about 5,000 writes per sector possible with flash memory.

On the material side, Ge\(_2\)Sb\(_2\)Te\(_5\) has been widely studied and optimized for PCRAM application. 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 PCRAM application must have a higher crystallization temperature and higher crystalline resistance with faster phase change speed than Ge\(_2\)Sb\(_2\)Te\(_5\). The operating temperature of a memory device depends on its application and scope. Embedded memory applications that operate at 85°C are common according to Wong et al. (2010). Research has shown that high crystallization temperature leads to high data stability while high crystalline resistance reduces the reset operation power according to Heone and Dae-Hwan (2005). A study by Kyung-Min et al. (2008)
compared crystalline resistivities of Ge$_2$Sb$_2$Te$_5$ (=1Ωcm) and Ge$_3$Sb$_7$Te$_5$ (=3Ωcm) with that of both SnSe$_2$ and Sn$_2$Se$_3$. Both SnSe$_2$ and Sn$_2$Se$_3$ alloys had larger resistivity values in the crystalline state of 26Ωcm and 23Ωcm respectively and could be used to minimize RESET current of PCRAM devices.

To enhance performance of PCRAM, doping has been applied to phase change materials. Among the various doping elements, nitrogen has been most widely used. Nitrogen doping in GST has been shown to increase the resistivity of the amorphous phase and can therefore reduce the power consumption of PCRAM (Park Il Mok et al., 2011). However, nitrogen doping has also been reported to retard the crystallization process which is critical for data-writing speed. Sn-Se system has been studied in the form of both single crystals and thin films (Yu et al., 2006). In this work, the effect of nitrogen doping on optical, electrical and structural properties of SnSe thin films is investigated.

1.2 Problem statement and justification

Phase change materials provide a nonvolatile storage mechanism that is amenable to process scaling. At present technology nodes, PCRAM writes require energy-intensive current injection resulting thermal stress in storage element that degrades current-injection contacts limiting endurance to hundreds of millions of writes. Phase change materials have been used successfully in optical storage but their high resistance contrast is yet to be fully developed for non-volatile memory applications (Raoux, 2009). Future prospects in the application of this technology in the design of scalable memory cells require that the problem of high reset current be circumvented.
The programming current is typically larger than 1mA and there is need to reduce it to µA regime for CMOS integration. The use of Nitrogen is a possible approach towards increasing the SET resistance and thus decreasing the reset current without compromising on the stability and the switching speed of phase change materials. A method of developing semiconductors that is simple and cheap is needed in developing countries to use available resources like tin, nitrogen and selenium to fabricate semiconductor devices such as phase-change random memory (PCRAM) and DRAM.

1.3 Objectives of the study

The study investigates the effect of nitrogen doping on the electrical, optical and structural properties of Sn-Se thin films

1.3.1 Main objective

The main objective this study was to investigate the effect of nitrogen doping on electrical, optical and structural properties of Sn-Se thin films.

1.3.2 Specific objectives

The specific objectives of the study were:

i. To prepare different Sn-Se thin films of different ratios.

ii. To deposit thin films of Sn-Se doped with different % of nitrogen by thermal evaporation.

iii. To perform optical characterization on the films.

iv. To carry out electrical characterization on the as-deposited and annealed thin film samples.
v. To perform structural characterization of the thin films.

vi. To fabricate a PCRAM based on optimized nitrogen doped Sn-Se alloy and characterize its switching behavior.

1.4 Rationale

Information technology in the recent past has been driven by the advancement in data storage technology and the incessant demand for more information. Presently the information being processed is stored in Dynamic Random Access Memory (DRAM). The RAM has a fast access and read times (20-80ns); however its volatility precludes its use as a universal non-volatile memory. While today’s high performance computing requires non-volatility of memory, researchers are trying to find the new technologies and materials to build a non-volatile RAM with the following properties;

- Fast access times to ensure large volumes of data are transferred within ns time scale.
- Highly scalable to increase data storage density without any thermal crosstalk.
- Low power consumption to enable easy integration to existing CMOS technology to drive the storage memory.
- Low cost processing and roll out.

The novel memory must adapt easily to existing lithographic steps or through additional incorporation of few processing steps (Pronin, 2010). Flash memory is the market leader today but has two big disadvantages of low endurance and inordinately long write times. It faces a potential threat from promising new technologies such as PCRAM, FeRAM, MRAM and other technologies which are under investigation and development.
The unique combination of properties of phase change materials and their success in optical storage applications has seen a revival in research and development activities (Raoux, 2009). In the quest for new semiconducting thin film materials for solar-energy conversion and PCRAM applications, the binary IV–VI compounds are being increasingly studied. Suitable physical properties, high abundance and low environmental impact of their constituent elements are additional advantages for large-scale applications according to Guille’n et al. (2010).
CHAPTER TWO
LITERATURE REVIEW

2.1 Introduction

Chalcogenide based phase change memory is being investigated as the next generation non-volatile memory (NVM) technology. The memory material exhibits a change in resistance during phase transition. This feature can be exploited to create a fast, highly scalable, reliable and radiation resistant memory according to Iellmini et al. (2005). The use of chalcogenides based alloys as potential memory cells having high endurance and retention capability with the possibility of multi-state operation was first described in 1968 by Stanford Ovshinsky in his pioneering work on electrical switching in disordered structures (Ovshinsky, 1968). However, material quality and power consumption issues in the earlier prototypes prevented commercialization of the technology. In recent years, there has been an explosion in research associated with phase change memory. This is due to the fact that the dominance of floating gate technology, which is the current NVM market leader, is expected to hit a roadblock beyond the 45 nm technology node due to scalability and reliability concerns (Lacaita, 2006).

Chalcogenides are materials composed of S, Se, Te or Sb. Application of heat induces a change in their internal structure resulting in the creation of the disordered state representing the amorphous phase (also known as RESET state). When the material is heated to its melting temperature and quenched quickly, the chemical bonds have no time to rearrange themselves resulting in the creation of a disordered mass which represents the amorphous phase (RESET state). This state denotes the memory bit 0.
Crystallization (SET state) is attained by heating the material beyond its glass transition temperature for a sufficiently long time. This state represents the memory bit 1. Typical switching times are 100 and 50 ns for the crystalline and amorphous transition respectively according to Lacaita (2006). Chalcogenides are very attractive as phase change memory materials since they can form a wide range of glasses and have a correspondingly wide variety of glass transition temperatures according to Campbell and Anderson (2007).

Although PCRAM has not reached commercialization stage for consumer electronic devices, nearly all prototypes devices make use of a chalcogenide alloy of germanium, antimony and tellurium (Gastec) called GST. The major challenge is the inherent difficulties of bringing a new technology into high enough production quickly enough to meet the manufacturing challenges of replacing an existing high-volume memory product. During the last decade there has been a number of new memory technologies such as phase change (PCRAM), conductive bridge (CBRAM), ionic oxide memory, polymer memory and molecular memory proposed to challenge conventional Flash NVM. Kim et al. (2010) presented results of a highly scaled PCRAM cell with sufficiently high cycling endurance and fast programming speed and small cell size to potentially challenge DRAM in future applications. This PCRAM cell showed potential to overcome the technology limitation of DRAM cell below 20nm technology node. Various researches have conducted various materials for PCRAM application among them Ge$_2$Sb$_2$Te$_5$, Si-Sb-Se and Sn-Se. In this study Nitrogen doped Sn-Se phase change material is investigated as a novel candidate for solid-state memory technology.
2.2 Properties of phase change materials

Phase change materials possess a unique set of properties. In particular, their optical and electrical properties are of great relevance to technological applications (Raoux, 2009). Some property requirements are similar for optical storage and PCRAM applications. The existence of stable crystalline and amorphous phases at optimal operating temperature is the most important parameter. Operation of the PCRAM device is hinged on the repeated cycling between the two phases. The crystallization time and crystallization temperature of a PCM strongly influence data rate, data retention and archival lifetime. Shorter re-crystallization times allow faster data rates in PCRAM devices (Geoffrey et al., 2010). Materials that can crystallize faster are preferred in memory cells because fast crystallization process generates very little atomic motion and hence reduces chances of phase segregation (Raoux et al., 2008).

In recent years, much attention has been paid to the III-VI group chalcogenide materials due to their wide applicability in solid state devices. The phase transformation of chalcogenide glasses has played an important role in their applicability. Among the IV-VI semiconductor compounds, tin sulphide (SnS), tin selenide (SnSe), germanium sulphide (GeS) and germanium selenide (GeSe) have the layered orthorhombic structure with eight atoms per unit cell forming biplaner layers normal to the largest c axis. In unit cell of SnS and SnSe, atoms in a single layer are joined to three nearest neighbors by covalent bonds which form zigzag chains along the b axis while there is only Van der Waals bonding between the layers. This typical crystalline structure results in strong anisotropic optical properties at low energies and more isotropic optical properties at higher energies, which gives them interesting properties at an intermediate between two dimensional and three-dimensional
semiconductors. These materials may find applications in the field of optoelectronics, holographic recording systems, electronic switching and infrared production and detection. The transparency of glasses is limited by the electronic and phonon absorption. The glasses made from heavy chalcogens such as Se or Te offer a huge advantage for developing materials that are transparent in the infrared (Bruno et al., 2009).

2.3 GST phase change materials

Most studies of PCRAM have been based on the GST compounds originally developed for use in optical data storage devices, such as CD-RW and DVD-RW. Ge$_2$Sb$_2$Te$_5$ (GST) has been widely used as optical disk storage materials in rewritable versions of CD and DVD formats (Seung et al., 2009). Kin-Fu-Kao et al. (2008) developed a new phase-change material, Ga$_{20}$Te$_{30}$Sb$_{50}$ (G’TS) for nonvolatile phase change memory application. The G’TS material was designed based on GaSb-Sb$_2$Te$_3$ used to give a lower the melting point than that of conventional Ge$_2$Sb$_2$Te$_5$ (GST) phase-change alloy. The Sb-based G’TS showed growth-dominated crystallization leading to potentially enhanced crystallization speed for sub-photolithography process. Its sheet resistance in crystalline state was 650 $\mu$Ω-cm and 240 $\mu$Ω-cm for G’TS and GST films, respectively. The resistivity of amorphous GST was found to be more than one order of magnitude higher than that of amorphous G’TS film. The investigation of crystallization behavior of nitrogen doped Ge$_2$Sb$_2$Te$_5$-(N) phase change films by Seo et al. (1999) revealed that their crystallization process changes depending on the nitrogen content. The effective crystallinity of Ge$_2$Sb$_2$Te$_5$-(N) alloy films decreased with the increase in nitrogen content, mainly due to grain-size
refinement. Incongruent melting phenomenon suggested that multilevel control was feasible using the phase-change material Ga$_2$Te$_3$Sb$_5$ (Ga-TS) according to Kin-Fu-Kao et al. (2008). Electrical results showed that Ga-TS cells required 25% less RESET current compared to GST cells. Ga-TS also had a higher programming speed and ultra long data retention extrapolated to one million years.

Phase-change nonvolatile memory cell elements composed of Sb$_2$Te$_3$ chalcogenide have been fabricated and characterized by Liu et al. (2005) using the focused ion beam method. The contact area 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 were obtained. At least 1000 cycle times with a RESET/SET resistance ratio >30 times was achieved for Sb$_2$Te$_3$ chalcogenide PCRAM cell element.

Caravati et al. (2011) investigated the structural, electronic and vibrational properties of amorphous and cubic Ge$_2$Sb$_2$Te$_5$ doped with N at 4.2 atomic percent by means of large scale ab initio simulations. Their results suggested that nitrogen could be incorporated in atomic or molecular form in both the crystalline and amorphous phases of GST. They further suggested that N segregation at the grain boundaries during the crystallization of the amorphous phase resulted in size reduction of the crystalline grains and increased the crystallization temperature. You et al. (2009) investigated the influence of nitrogen doping on the performance of memory devices for low power consumption and multi-level storage. Doping nitrogen (N) into
chalcogenide phase-change materials was shown to result in higher resistivity and low-response to temperature changes. The former characteristic leads to high heating efficiency for phase change and could reduce the power consumption to about 1/10. The latter characteristic makes it easier to control phase change process in the memory device for multi-level storage by having a number of distinct resistance states.

For a PCRAM to be a feasible candidate for a next generation memory, the RESET operation power and duration of the SET operation need to be reduced. Ge$_2$Sb$_2$Te$_5$ (GST) has been widely studied and optimized as a PCRAM material because its amorphous and crystalline phase transition is reversible and rapid. However, GST has several disadvantages including a relatively long crystallization time and a low resistivity of the crystalline state (Liu et al., 2005). To address these problems, various investigations on new materials such as Sb$_2$Te$_3$, Se$_x$Sb$_{100-x}$ and In$_x$Sb$_{100-x}$ have been conducted (Raoux, 2009). Of these materials, Sb$_2$Te$_3$ appears the most promising as it has been extensively optimized (Seung et al., 2009). In contrast to nucleation-dominated GST, the crystallization mechanism of Sb$_2$Te$_3$ is growth-dominated and the SET operation time is shorter. In addition, the RESET operation power of Sb$_2$Te$_3$ is lower than that of GST due to its relatively lower melting temperature (Liu et al., 2005). However, Sb$_2$Te$_3$ has a very low crystallization temperature and data retention time is not guaranteed. This drawback can be resolved by using dopants such as Silver and Nitrogen. Steimer et al. (2006) investigated other classes of phase change materials without Ge in their amorphous phase that would provide an atomistic understanding of the speed and pronounced property contrast on crystallization.
Further insights in some amorphous structures leading to an atomistic understanding of the phase change process could be turned into design rules for future materials.

To understand the effect of nitrogen doping on Sb$_2$Te$_3$ film, the sheet resistance of N-doped Sb$_2$Te$_3$ thin films and the electrical switching phenomenon of PCRAM test cells using N-doped Sb$_2$Te$_3$ were investigated by Seung *et al.* (2009). They found that at all of the annealing temperatures, the N-doped Sb$_2$Te$_3$ sheet resistance increased due to crystallization of the material to a rhombohedral structure. They further showed that N-doping increased the crystallization temperature of Sb$_2$Te$_3$ thin films by suppressing grain growth and hence increased their thermal stability.

### 2.4 Mechanism of Threshold Switching in Chalcogenide Phase Change materials

Threshold switching is a transition process from high to low resistivity that results from a negative-differential resistance. Threshold switching is observed in amorphous semiconductors such as chalcogenide glasses. It plays dominant role in program/erase operations of phase-change memory. Fugazza *et al.* (2009) were able to show that Poole-Frenkel (PF) conduction account for the temperature and voltage dependence of the subthreshold current and for the dependence of the threshold voltage and current on temperature, mobility gap, and amorphous layer thickness. Kapov *et al.* (2007) developed the original Ovshinsky’s nucleation hypothesis into an analytical model of field-induced nucleation. The model based on the field induced nucleation showed dependence of the threshold voltage on phase change material parameters, such as the nucleation barrier, nucleation radius and characteristic time of phase transformation,
cell geometry, amorphous layer thickness, ambient temperature and switching delay time.

2.5 Tin and selenium alloys PCMs

Tin is a Block P, Group 14, Period 5 element with electronic configuration of 2, 8, 18, 18, 4. Tin atom has a radius of 140.5pm and a Van der Waals radius of 217pm. Selenium is a Block P, Group 16, Period 4 element with electronic configuration of 2, 8, 18 and 6. Selenium atom has a radius of 116pm and a Van der Waals radius of 190pm. Selenium is used in numerous glass compositions to increase their transparency in the infrared range and their stability against crystallization (Bruno et al., 2009). Selenium based binary chalcogenide glasses are thermally stable and can be shaped into sophisticated optical devices such as optical fibres, planar guides or lenses. Nevertheless, the transparency is limited at about 12 μm (depending on the thickness of the optical systems) due to the relatively small mass of the Se element. In the last few years, efforts have been undertaken to investigate the semiconducting behaviour of transition metal selenides. Among these materials, Tin monoselenide and Tin diselenide exhibit several interesting features, including their electronic and optical properties, which could be useful in solar cells manufacturing.

Tin monoselenide (SnSe) and tin diselenide (SnSe2) are narrow-gap semiconductors with band gap energy close to 1.0 and 0.9 eV, respectively and with high absorption coefficient that make them good absorber partners for thin-film photovoltaic devices. SnSe crystallizes in the orthorhombic crystal system with lattice parameters: a=11.50Å, b=4.15Å and c=4.44Å, which resembles a distorted NaCl rocksalt
structure. SnSe₂ crystals on the other hand have hexagonal CdI₂ structure type with lattice parameters: a=b=3.81 Å and c=6.14 Å (Guille’n et. al., 2010). Tin (II) selenide is an important binary IV–VI semiconductor compound with a wide range of potential applications in memory switching, infrared optoelectronics and as anode material for rechargeable lithium batteries.

SnSe has been explored as low cost, nontoxic, and environmentally friendly component for a variety of photovoltaic devices (Franzman, 2010). SnSe has low band gap and absorb in the infrared and near-infrared spectral region. It may also be possible that SnSe exhibit multiexciton generation (MEG) allowing it to generate more than one electron-hole pairs per absorbed photon which potentially increases the efficiency in solar cells. Bulk SnSe has both an indirect band gap at 0.90 eV and a direct band gap at 1.30 eV. As an earth-abundant, environmentally benign, and chemically stable material, SnSe is placed among the most promising candidates for solar cell application (Sheng et al., 2011). Due to quantum confinement effect SnSe nano-structured materials have tuneable band gaps which make them capable of absorbing a major portion of solar energy. The position of the valence and conduction band edges makes them interesting for solar energy storage via photo oxidation of water in a photoelectrochemical cell. They are also interesting for solar electricity generation, due to the favourable band gap energies. The materials especially nitrogen and tin are low cost, abundant and available substances.

Bhatt et al. (1992) analyzed photovoltaic properties of SnSe-SnSe₂ junctions. Based on the electric characteristics of the SnSe and SnSe₂ compounds, they suggested that these materials could be useful in photovoltaic devices manufacturing. Wang et al.
(2011) prepared SnSe$_2$ films using solution-processable chalcogenidometallate clusters which thermally decomposed into a crystalline SnSe$_2$. Laser testing of these films indicated very fast recrystallization times of 20 ns.

Nitrogen-incorporated SnO$_2$ thin film grown in gas mixture of N$_2$ - O$_2$ was studied by Pan (2006) and the binding energy was found to shift to the lower energy side after nitrogen was incorporated. The indirect optical band gap gradually decreased from 3.42 eV to 3.23 eV when the nitrogen flux ratio was increased from 0% to 40%. Bindu and Nair (2004) prepared the first tin selenium films by heating Sn-Se layers. By controlling the individual film thicknesses and conditions of heating, SnSe$_2$ or SnSe$_2$ + SnSe were formed. SnSe$_2$ and SnSe$_2$/SnSe composite materials are both n-type. SnSe is reported to be p-type with drift mobility for holes of approximately 0.7m$^2$V$^{-1}$s$^{-1}$ with an optical band gap of 1-1.27 eV and electrical conductivity of 0.01-0.2$\Omega^{-1}$cm$^{-1}$ (Bindu and Nair, 2004).

The switching behavior of Indium Selenide based phase-change memory cell has been researched by Heone and Dae-Hwan (2005). Amorphous In$_2$Se$_3$ resistor showed high resistance state at low voltage region and which drastically reduced below the threshold voltage. The pulsed mode switching of the 5µm-sized In$_2$Se$_3$ PCRAM device showed that the reset (crystalline to amorphous) of the device was done with a 70ns-3.1V pulse and the set (amorphous to crystalline) of the device was done with 10µs-1.2V pulses. A switching dynamic range ratio (R$_{high}$/R$_{low}$) of about 100 was achieved. Pathinettam et al. (2000) prepared and characterized a polycrystalline thin film of tin selenide by vacuum deposition at a substrate temperature of 423K. SnSe was found to be poor in crystalline nature and annealing the film at 573K for 2 hours
improved the crystallinity. Influence of substrate temperature on growth of tin selenide thin film prepared by flash evaporation has been studied by Hema et al. (2007). The electrical resistivity varied from 30 - 8.1 Ωcm in the thickness range (150 - 300nm). Sharma et al. (2005) prepared and characterized nanocrystalline SnSe (n-SnSe) thin film by thermal evaporation. A blue shift in the fundamental edge was observed due to reduction in the particle size. The band gap value increased to 2.18 ± 0.01 eV as compared to the bulk value of 1.68 ± 0.01 eV.

The use of tin alloys as an optical recording medium is reported by Takada et al. (1999). Good optical recording characteristics includes low melting point, low heat conductivity, appropriate light reflectance and bits have good shape. Tin is cheap and has low toxicity but its highly sensitive thin films are easily deteriorated by oxidation. Use of tin compounds or fine particles tin dispersed in a tin compound obviates these defects. Snₓ-Se₁₀₀₋ₓ alloy, with value of x between 40- 70, showed high sensitivity and high C/N ratio over a broad recording laser output range. Sn-Se system has been suggested for applications such as sensors and non-volatile memories (Sava et al., 2006). Sn-Se systems appear to lie at the boundary of phase-change properties and are poorly studied. Kyung-Min et al. (2008) found that SnSe, SnSe₂ and Sn₂Se₃ display different material characteristics when compared to GST alloys. Compared with Sn-Se alloys, GSTs shows a relatively lower optical contrast, lower crystalline resistivity and a lower recrystallization speed.

The resistivity contrast between the crystalline and the amorphous phase of SnSe₂ amounts to 5-6 orders of magnitude and the activation energy for crystallization (1.93 eV) is found to be in same range as for typical GST alloys. In addition, there is a
pronounced density contrast between the crystalline and the amorphous phase, which is larger than the density change typically observed in GST alloys. In this respect Sn-Se alloy resembles but also deviates from generic phase-change materials making it an interesting material from which one can learn clues for phase-change properties. Further it has been shown that nitrogen doping of Sn-Se changes the properties of the system. In this study Sn-Se alloys doped with nitrogen were prepared and the corresponding thin films deposited by thermal evaporation. The effects of nitrogen on electrical, optical and structural properties were investigated for suitability in phase change memory applications.

2.6 Effect of nitrogen doping in phase change materials

Yeh et al. (2005) investigated the thermal, optical and recrystallization properties and the microstructure of nitrogen-doped Ge–In–Sb–Te (GIST) phase-change material when irradiated by blue laser. The experimental results showed that nitrogen doping at the condition of N₂/Ar sputtering gas flow ratio of 3% enhanced the recrystallization speed of GIST recording layer up to 1.5 times. However, the disk failed when too much nitrogen (N₂/Ar of 5.0%) was introduced. Too much nitrogen doping resulted in too many void-like defects on sample surface and changed the phase constitution of GIST layers causing poor data recordings. Nitrogen doping produces tiny precipitates uniformly distributed in the GIST recording layer. These tiny precipitates are thought to provide numerous preferential sites for heterogeneous amorphous–crystalline phase transition which promotes the recrystallization speed of GIST materials. According to Lee et al. (2010) nitrogen doping in Ge₂Sb₂Te₅ (GST) increases resistivity and lowers programming current.
Carbon and Nitrogen-doped GeTe are promising materials for use in phase change memories since the addition of C or N increases the stability of the amorphous phase. Sousa et al. (2011) in their work on nitrogen doped GeTe-based phase change materials found that addition of N in Ge\textsubscript{50}Te\textsubscript{50} increased both the crystallization temperature and activation energy. XRD and Raman spectra revealed reduced grain size and suppressed Ge segregation. From XPS results they concluded that amorphous GeN domains continued to exist even after the crystallization of GeTe had occurred. The programming characteristics i.e. the reset current and the set speed remained unchanged while the retention properties largely improved. According to Pan et al. (2006) nitrogen doping leads to a blue shift in the absorption edge due to refinement of nanostructures and could therefore be used to modify material properties. Do et al. (2011) investigated the crystallization behavior of nitrogen-doped Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} (NGST) thin films using static laser heating and transmission electron microscopy. Compared to as-deposited NGST, the melt-quenched NGST showed a significantly faster crystallization with a shorter incubation time. Their findings indicated that the grain size was smaller in the crystallized NGST with higher nitrogen content.

2.7 Nitrogen doping in Sn\textsubscript{x}Se\textsubscript{y} alloy systems.

Ana et al. (2005) used chemical route to synthesize SnSe and studied the influence of annealing temperatures on the crystalline structure of the SnSe by X-ray diffraction. The SnSe samples were analyzed before and after thermal treatment under nitrogen. The ‘as synthesized’ SnSe showed low crystallinity and in the XRD pattern was identified the orthorhombic SnSe—space group pattern was identified. The pattern obtained for material annealed at 300 °C showed the presence of orthorhombic
phase. The material annealed at 600 °C under nitrogen showed a much more complex XRD pattern. Bindu and Nair (2004) utilized vacuum-deposited thin film of Sn and Se to prepare SnSe and SnSe$_2$ thin films. This was achieved by heating Se–Sn stack at 200 °C in a nitrogen atmosphere for 1 h or by heating in air at 400 °C for about 5 min. Although the role of nitrogen was not explained, it is evident that the temperature at which SnSe and SnSe$_2$ formed was much lower in nitrogen than in air.

The metal–insulator transition in crystalline phase-change materials is due to strong disorder usually associated only with amorphous solids according to Siegrist et al. (2011). Controlling the degree of disorder in crystalline phase-change materials might enable multilevel resistance states in upcoming storage devices. One way of achieving this is by introducing dopants such as nitrogen.

### 2.8 Phase change random access memory

Phase-change materials possess a unique combination of properties that make them promising candidates for the memory material in phase-change RAM (PCRAM) devices (Raoux et al., 2008). Phase change memory changes a small region of a PCM from an amorphous state to a crystalline state and back again. In a typical PCRAM device, heating/melting affects only the material in a small area around the tip of the resistor. Erase/RESET pulses set high resistance or logical 0 by forming an area of an amorphous layer on the device. Erase/RESET pulses are higher, narrower, and steeper than Write/SET pulses. A SET pulse, which sets a logical 1, re-crystallizes the amorphous layer back to the crystalline state.
Phase change memories are expected to be used in devices such as disk caches in servers, hybrid non-volatile memory caches and flash file systems (Prince et al., 2011). They can replace NOR flash in code applications. They are potentially useful as memory in portable, industrial and smart metering systems. Several companies have shown integrated process technologies for phase change memory in technologies ranging from 90 nm to 45 nm. Since the PCM is a new technology there are several issues still being addressed. These include:

- Resistance thermal program disturb of neighboring cells in the RESET state.
- Stability at high temperatures.
- Electromigration and voids in the PCM element.
- Data loss due to resistance drifts in the amorphous phase.
- High write current.
- Oscillatory behavior due to noise in the amorphous state.

In an attempt to overcome these limitations, several novel strategies based on material combinations and memory cell architecture designs are being explored for PCMRA applications.

The rising demand for consumer electronics such as digital cameras, smart phones, iPads and MP3 players amongst others has kept the demand for non-volatile semiconductor memory rising. These devices can be scaled to sizes much smaller than flash memory and are based on a new technology that combines longer lifetimes, lower power and better memory density. Phase change memory has great scalability potential and can support multi-level storage per cell. Nanocrystalline thin films have been a subject of intensive studies due to the fact that their nanoparticles exhibit size-dependent electronic band gap energies, melting temperatures, solid-solid phase
transition temperatures and pressures. A lot of work has been done on group II-VI and group III-VI nanocrystalline materials and not much work has been reported in the group IV-VI nanomaterials. Among the group IV-VI compounds tin selenide (SnSe) has potential applications in memory switching devices (Sharma et al., 2005). This work reports on the effects of nitrogen doping in SnSe thin films. The effect of N doping on 130 nm SnSe thin films was investigated through optical, electrical and structural characterization.
CHAPTER THREE
THEORETICAL CONSIDERATIONS

3.1 Introduction

This chapter outlines the theories behind the experimental procedures used in this study. Theoretical backgrounds on thermal evaporation, thin film optical and electrical measurements and structural characterization are presented.

3.2 Thin films

Thin films are prepared by depositing a layer of a material ranging from a fraction of a nanometer to several micrometers in thickness on a substrate. The atomistic nature of materials is evident in thin films which exhibit properties different from bulk properties of the same materials. The thin film properties are often far much better than the bulk properties and are influenced by the deposition parameters. In practical applications, the thickness of a thin film is controlled to within a few tens of nanometers to give the desired properties.

3.3 Evaporation

Techniques for depositing thin films are classified into two broad categories; physical vapor deposition (PVD) and chemical vapor deposition (CVD). In this study, thermal evaporation which is a PVD method was used due to its relatively lower cost, less complexity and ease of use. Many versions of evaporation exist. Among them are co-evaporation, flash evaporation and single source evaporation. Usually the sample is
placed on evaporator boats which are heated above the melting points of the elements until they vaporize and deposit on a substrate above the boat at a lower temperature. 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.

**Figure 3.1**: Schematic diagram of thermal evaporation system.

Figure 3.1 shows a schematic diagram of a thermal evaporation system. In this system a resistance wire or boat usually made of high melting point (such as Mo, Ta or W) is used as the heat source to vaporize the material of interest to practical deposition
rates. This is done in a high vacuum, both to allow the vapour to reach the substrate without reacting with or scattering against other gas-phase atoms in the chamber, and reduce the incorporation of impurities from the residual gas in the vacuum chamber. Only materials with a much higher vapour pressure than the heating element can be deposited without contamination of the film. Because the chamber is at a greatly reduced pressure, there is a very long mean free path for the free atoms or molecules, and the heavy vapour is able to reach the moving substrates at the top of the chamber. Here it condenses back to the solid state, forming a thin, uniform film.

The evaporation rate is proportional to the difference between the equilibrium vapor pressure of the liquid material and the vacuum pressure above it according to Langmuir (1916). The mass evaporation rate per unit area in vacuum $\Gamma$ is given by Langmuir's equation:

$$\Gamma = 5.834 \times 10^{-2} (M / T)^{1/2} P (g / cm^2) / s$$

(3.1)

Where $M$ is the molecular weight of the evaporating species (in g), $T$ is the temperature of the liquid (in K), $P$ is the equilibrium vapor pressure (in torr) of the liquid metal at the temperature $T$. It is assumed that $P$ is so much greater than the vacuum pressure that the latter can be neglected (Langmuir, 1916).

3.4 Conduction in semiconductors

This section looks at the electrical resistivity in semiconductors. A semiconductor has 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

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

(3.2)

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,

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

(3.3)

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

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

(3.4)

While the number of holes per unit volume is

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

(3.5)

where $N_c$ = effective number of levels per unit volume in conduction band

$k_B$ = Boltzmann constant and

$\mu$ = Chemical potential

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

$$np = N_c N_v e^{-E_c/k_BT}$$

(3.6)

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

For a pure semi-conductor,

$$n = p = (N_c N_v)^{1/2} e^{-E_c/2k_BT}$$

(3.7)

But,

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

(3.8)
Thus for a pure semiconductor, $\sigma$ becomes

$$\sigma = pq(\mu_n + \mu_p)$$

$$= (N_c N_v)^{1/2} q(\mu_n + \mu_p) e^{-E_c/2k_bT}$$  \hspace{1cm} (3.10)

This can be written as,

$$\sigma = A_0 e^{-E_c/2k_bT}$$  \hspace{1cm} (3.11)

where,  \hspace{1cm} $A_0 = (N_c N_v)^{1/2} q(\mu_n + \mu_p)$

Hence resistivity, $\rho$ can be expressed as

$$\rho = \frac{1}{\sigma} = \frac{1}{A_0} e^{E_c/2k_bT} = B_0 e^{E_c/2k_bT}$$  \hspace{1cm} (3.12)

where  \hspace{1cm} $B_0 = \frac{1}{A_0} = \frac{1}{((N_c N_v)^{1/2} q(\mu_n + \mu_p))}$  \hspace{1cm} (3.13)

This expression suggests that the resistivity in semiconductors will decrease with increase in temperature.

### 3.5 Sheet Resistivity of Thin Films

Sheet resistivity of the fabricated thin films was measured following the Van der Pauw model using a 4-point probe setup shown in figure 3.2. The set-up consists of four equally spaced metal tips with finite radius. Each tip is supported by a spring on the other end to minimize sample damage during probing. The four metal tips are part of mechanical stage which travels up and down during measurements. High impedance current was sourced from Keithley 2400 source meter and supplied through the two outer probes. The corresponding voltage, measured across the inner two probes, was used to determine the resistivity.
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:

$$A = 2\pi x$$  \hspace{1cm} (3.14)

where $x$ is the distance between voltage measurement probes.

$$R = \frac{\rho x}{A}$$  \hspace{1cm} (3.15)

$$R = \int_{s}^{2s} \frac{\rho dx}{2\pi x}$$  \hspace{1cm} (3.16)

$$R = \frac{\rho}{2\pi t} \ln 2$$  \hspace{1cm} (3.17)

$$\rho_s = \frac{2\pi R}{\ln 2}$$  \hspace{1cm} (3.18)

Consequently, for

$$R = \frac{V}{2I},$$  \hspace{1cm} (3.19)

the resistance of the thin film sheet is given by:
\[ R_S = \frac{\pi}{\ln 2} F(Q) \frac{V_{dc} + V_{bc}}{2I} \left[ \frac{\Omega}{\text{Square}} \right] \]  

(3.20)

where F and Q are the symmetry and correction factors respectively. F is a function of Q and is valid for Q less than 10. It is expressed in the form

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

(3.21)

Where, \( \frac{(V_{dc} + V_{bc})}{2I} \) is the average resistance. The specific resistivity \( \rho \) can be determined from the thin film thickness and the sheet resistance is in the form;

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

(3.22)

### 3.6 XRD Structural analysis

After the discovery of X-ray by Roentgen in 1895, the physical nature of X-rays remained unexplored for several years, until 1912, when German physicist Max von Laue suggested that crystalline materials diffract X-rays, and in doing so reveal their structure. X-ray diffraction (XRD) is one of the most powerful non-destructive techniques for qualitative and quantitative analysis of crystalline compounds. Information that can be obtained includes:

- Types and nature of crystalline phase present.
- Structural make-up of phases.
- Degree of crystallinity.
- Amount of amorphous content.
- Microstrain, size and orientation of crystallites.

Some of the methods used to quantify crystalline phases in mixtures include external standard methods, the reference-intensity-ratio (RIR) method, chemical methods and
the whole pattern fitting Rietveld method. The Rietveld method is the most accurate and reliable method used for quantification and characterization of inorganic and organic compounds (Taylor, 2001). It is also used for crystal structure refinement to determine size and strain of crystallites. When a sample irradiated with a parallel beam of monochromatic X-rays, the atomic lattice of the sample acts as a three dimensional diffraction grating which causes the X-ray beam to be diffracted at specific angles. The diffraction pattern, that includes positions (angles) and intensities of the diffracted beam, provides different information about the sample.

Figure 3.3: X-ray diffraction pattern of SnSe-SnSe₂ composite (Aguiar, 1999)
The figure 3.3 below shows an X-ray diffraction pattern of SnSe-SnSe$_2$ composite (Aguiar, 1999) obtained when its microstructures were analyzed using X-ray diffraction. The prominent Bragg reflection occurred in the (400) plane. According to Kumar et al. (2011) the deposition technique plays an important role in determining the preferred orientation. Angles are used to calculate the interplanar atomic spacings (d-spacings). Because every crystalline material will give a characteristic diffraction pattern and can act as a unique ‘fingerprint’, the position (d) and intensity (I) information are used to identify the type of material by comparing them with patterns for over 80,000 data entries in the International Powder Diffraction File (PDF) database, compiled by the International Center Diffraction Data (ICDD) formerly known as Joint Committee on Powder Diffraction Standards (JCPDS). The ICDD database is available from the Diffraction equipment manufacturers or directly from ICDD.

The position of diffracted peaks also provides information about how the atoms are arranged within the crystalline compound (unit cell size or lattice parameter). The intensity information is used to assess the type and nature of atoms. Determination of lattice parameter helps understand extent of solid solution in a sample. Width of the diffracted peaks is used to determine crystallite size and micro-strain in the sample according to Post and Bish (1989). The peak position and intensity from a phase can also be used to quantitatively estimate the amount of that phase in a multi-component mixture. Rietveld quantification formula is not used for amorphous or poorly crystalline materials because they do not contribute to diffraction peaks.
3.7 PCRAM device characterization.

The voltage and current values of the RESET and SET pulses used should be carefully selected to produce melting and re-crystallization in the phase change material. RESET pulses should raise the temperature to just above the melting point and then allow rapid cooling of the material to the amorphous phase. SET pulses should raise the temperature just above the re-crystallization temperature but below the melting point while allowing for a longer cooling time. The pulse width and fall time for a SET pulse should therefore be longer than for a RESET pulse. In functional testing, pulse widths of one microsecond or shorter are usually sufficient. A pulse of this duration will produce enough energy either to melt PCM material or to re-crystallize it. Pulse voltages need to be as high as 6V, and it is desirable for them to be higher, to reach melting temperatures. Current values range from 0.33mA.

Fall time for a RESET pulse is a critical parameter. The state of the PCM technology determines the required minimum for a fall time. Currently, it is a common requirement to have 30-50 nanoseconds. Newer materials are expected to push that requirement to shorter fall times. If the pulse fall time is longer than the required time, the material may not effectively quench into an amorphous phase. Critical parameters for PCM device characterization are recrystallization rate, data retention, drift and read disturb. Current re-crystallization rates are now as short as several tens of nanoseconds but they may soon drop to as little as a few nanoseconds. The SET phase is a lower energy state and phase change materials tend to re-crystallize spontaneously. The rate of crystallization is temperature dependent. Therefore, data retention can be defined as a maximum temperature at which data, the RESET state, will remain stable for a specified time period. Data retention is typically 10 years.
A measurement of how many times a memory cell can be successfully programmed to the 0 and 1 states is called cycling endurance. The newer multi-state memory cells with additional distinct states mentioned previously allow packing more memory into a single cell, which modifies cycling endurance test procedures. Drift is simply a measure of the drift of the cell’s resistance over time. Read Disturb is an evaluation of how the read procedure impacts on the stored state. The measurement pulse must be less than 0.5V. Higher voltages will lead to Read Disturb problems.

### 3.7.1 Resistance-current (R-I) curves

The RI curve is one of the most common parameters collected during PCM characterization. A pulse sequence is sent through a device under test, DUT. The first pulse, a RESET pulse, sets the resistance of the DUT to the high value. It is followed by a DC-read or MEASURE pulse that is usually 0.5V or lower in order to avoid affecting the state of the DUT. This is followed by a SET pulse and another MEASURE pulse. The entire sequence is repeated multiple times, with the amplitude of the SET pulse slowly increased to the value of the RESET pulse. SET resistance values range from one mega-ohm to several kilo-ohms, depending on the value of the SET current.

### 3.7.2 I-V curves.

To generate the I-V curves, the starting point is a DUT that was previously RESET to its highly resistive state. Then voltage applied to the DUT is swept from low to high values. The dynamic switch from a high- to low-resistive state in the presence of a load resistor produces a characteristic RI curve with a snapback, an area of negative
resistance. Snapback itself is not a feature of PCMs or of PCM testing, but rather a side effect of the R-load technique that has long been used to obtain both RI and I-V curves.

In the standard R-Load measurement technique a resistor is connected in series with the DUT, allowing current to be measured across the DUT by measuring the voltage across the load resistor. Active high impedance probes and an oscilloscope are used to record the voltage across the load resistor. Current across the DUT will be equal to the applied voltage \( V_{\text{APPLIED}} \) minus the voltage across the device \( V_{\text{DEV}} \), divided by the load resistance. The values of the load resistor usually range from one to three kilo-ohms. This technique involves a tradeoff: if the load resistance is too high, RC effects and the voltage division between the R-Load and the DUT limits this technique's performance; however, if the resistor value is too small, it impacts on the current resolution.

3.8 Optical models, parameters and characterization

When light is incident on a semiconductor, the optical phenomena of absorption, reflection, and transmission are observed. From measurement of these optical effects, it is possible to obtain much of the information on the optical parameters.

3.8.1 Optical properties of thin film

Optical measurement constitutes the most important means of determining the band structures of semiconductors. Photo induced transitions can occur between different bands, which lead to the determination of the energy band gap, or within a single band
such as free carrier absorption. Optical measurements can also be used to study lattice vibrations. Transmittance is usually used for films and reflectance for bulk samples. The transmission coefficient $T$ and the reflection coefficient $R$ are the two important quantities generally measured. For normal incidence they are given by:

$$T = \frac{(1 - R^2) \exp(-4\pi/\lambda)}{1 - R^2 \exp(-8\pi\alpha/\lambda)}$$  \hspace{1cm} (3.24)

$$R = \frac{(1 - n)^2 + k^2}{(1 + n)^2 + k^2}$$  \hspace{1cm} (3.25)

where, $\lambda$ is the wave length, $n$ the refractive index, $k$ the absorption constant, and $x$ the thickness of the sample. The absorption coefficient per unit length $\alpha$ is given by:

$$\alpha = \frac{4\pi k}{\lambda}$$  \hspace{1cm} (3.25)

By analyzing the $T - \lambda$ or $R - \lambda$ data at normal incidence, or by making observations of $R$ or $T$ for different angles of incidence, both $n$ and $k$ can be obtained and related to transition energy between bands. The absorption coefficient determines how far into a material light of a particular wavelength can penetrate before it is absorbed. The absorption coefficient depends on the material and also on the wavelength of light which is being absorbed.

Semiconductor materials have a sharp edge in their absorption coefficient, since light which has energy below the band gap does not have sufficient energy to excite an electron into the conduction band from the valence band. The absorption coefficient is not constant but depends strongly on wavelength. The probability of absorbing a photon depends on the likelihood of having a photon and an electron interact in such a way as to move from one energy band to another. It is only those electrons which are directly at the valence band edge that can interact with the photon to cause absorption.
As the photon energy increases, a larger number of electrons can interact with the photon and result in the photon being absorbed.

### 3.8.2 Optical spectra simulation

The use of computer simulation in analysing optical spectra is now a standard method in spectroscopic ellipsometry. Simulation software can be used to investigate the effect of varying different parameters without any experimental effort and costs according to Theiss (2002). Simple optical analysis procedures are most often based on some crude assumptions which can be avoided using a simulation approach. It is only through simulation that complicated spectral features of multilayer stacks can be understood. Simulation is also used to check the quality of spectroscopic measurements and can be a precursor to successful thin film products.

### 3.8.3 Optical models

Each material has a very characteristic frequency dependence of its optical constants. The key to good spectrum simulation results is the right choice of optical constant models. The most important step in spectrum simulation is the choice of the optical constants. If the materials in the system under investigation cannot be described with fixed literature data, flexible models have to be used. Three basic types of excitations are acceleration of free charge carriers by the electric field of the light wave, excitation of vibrational modes and optical interband transitions of the electronic system. Drude model or its extensions is usually used to describe the acceleration of free charge carriers by the electric field of the light wave. The classical Drude model of free charge carriers leads to a simple expression of the susceptibility with only two parameters, the plasma frequency and the damping constant (Theiss, 2002). If the
effective mass is known, these quantities can be directly related to the charge carrier density and their mobility, or the resistivity of the material.

The plasma frequency is proportional to the square root of the carrier density while the damping constant is proportional to the inverse of the mobility. Characteristic for the presence of many charge carriers (like in metals) is the large imaginary part of the refractive index. If it is larger than the real part, no wave propagation is possible in the material. This leads to a 'rejection' of incoming waves, i.e. to a high reflectance. Radiation penetrating a metal is absorbed very efficiently in a very thin film. In most cases for doped semiconductors or metals the Drude model works quite well.

Vibrational modes with resonance frequencies that depend on the masses of the atomic cores and the strength of the restoring forces are taken into account using oscillator models. Vibrational modes leave 'finger prints' or signature of a material in the infrared. These are used in numerous applications for material identification in the chemical industry. A rough description can be achieved by summing up harmonic oscillator terms with three parameters. These are the resonance frequency, the damping constant and the oscillator strength proportional to the concentration of microscopic oscillators.

Interband transition models are usually quite asymmetric and very strong. They are not easy to model because in most cases several transitions overlap each other. Often it is not even easy to see how many excitations one should use. In addition, theoretical quantum mechanical considerations result in expressions for the imaginary part of the dielectric function only. The corresponding real part must be constructed making use
of the Kramers-Kroning relation. Fortunately, the required Hilbert transform can be performed in two steps with Fast Fourier Transform algorithms which make the computations reasonably fast on modern computers. The OJL model is very successful for amorphous oxides and nitrides according to Theiss (2002).

### 3.9 PCRAM cell

Most of today's exploited cell designs are based on the vertical cell design proposed by S. Ovshinsky in the 1960s (Ovshinsky, 1968). In this type of cell design, the phase change material is sandwiched between a common ground top-electrode and a vertical bottom electrode as shown in figure 3.4.

![Figure 3.4: Schematic view of a vertical PCRAM cell. (Merget, 2007)](image-url)
This design is seen as most attractive in terms of area requirement. However, there is poor thermal management due to ambient heat loss in the switching zone and the current cross-section is geometrically defined by the bottom electrode. High reset current is therefore required and this severely limits its use in memory devices.

In lateral cell design shown in figure 3.5, two electrodes are aligned laterally on top of a phase change film. The current flows are in a lateral direction through the cell. A lithographically defined lateral constriction defines the area of highest current density and hence the switching zone of the lateral cell. In this type of design, the film thickness and one lithography size can be controlled to reduce power consumption. Considerable reduction in reset current is possible because of the greater ability to reduce contact area.

![Figure 3.5: Schematic diagram showing top view and cross-section of lateral PCRAM cell. (Merget, 2007)](image-url)
Currently the lateral cell design is only implemented with advanced lithographic techniques and has a lower density because of the planar structure. The design thought to be more suitable for fast growth materials according to Merget (2007). The current density is highest within the constriction which is the switching zone. Temperature distribution has shown that heat is well confined within the switching zone so that lower reset current is used.
CHAPTER FOUR

EXPERIMENTAL PROCEDURES

4.1 Introduction

This chapter presents a detailed description of materials and experimental procedures used in preparation and characterization of thin films. Fabrication and characterization of the PCRAM device based on N-SnSe is also discussed in this section.

4.2 Preparation of Sn$_x$Se$_y$ Alloys

The Sn$_x$Se$_y$ alloys were prepared from high purity (99.999 %) elemental tin and selenium granules at predetermined mass ratios. Tin and selenium granules were weighed and placed in a clean silica glass tube which was then sealed after purging with argon to expel and exclude air. The tube was then sealed and allowed to cool. The alloy was then heated to 800$^\circ$C using LPG burner and then allowed to cool. Reheating for 5 minutes was repeated three times while agitating the alloy to enhance mixing and ensure homogeneity. The samples were then ground in a porcelain mortar. For each Sn$_x$Se$_y$ alloy, four sets of ground samples were prepared and used in testing reproducibility. An Edwards 306 vacuum coater was used for the thin film deposition.

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

Thoroughly cleaned ordinary glass slides measuring 38 mm by 25 mm by 1 mm were used as substrates for preparing nitrogen doped Sn-Se thin films. The substrates were cleaned with a solution of H$_2$SO$_4$ and HNO$_3$ in distilled water, and then washed successively with acetone, alcohol and distilled water. The substrates were then
heated at 120 °C to remove any moisture or methanol present. The vacuum chamber of the vacuum coater was cleaned to remove any dust debris. The glass substrates were then mounted on the substrate holder and the alloy sample placed on the evaporation boat. The vacuum chamber was sealed and flushed with argon to remove any residual oxygen prior to deposition and pumped down to high vacuum of 3.0 x 10^{-5} mbar at room temperature. The alloy sample in the tungsten evaporation boat was then heated in N$_2$ /Ar atmosphere to evaporate onto the glass substrates. During deposition, Ar (99.999%) gas flow rate was fixed at 20 sccm and N$_2$ (99.999%) gas flow was varied from 0-5 sccm to vary the level of nitrogen doping in Sn$_x$Se$_y$ thin films. The nitrogen doping level was controlled by adjusting the gas flow meters to give required N$_2$/Ar mixture ratio.

### 4.4 Electrical Characterization of the films

Lindberg Mini-Mite TF55035A tube furnace was used to anneal the films during the electrical characterization at various temperatures. The heating rates or ramp rates were controlled by programming the furnace’s UT150 controller. The furnace tube was first purged with argon gas to create an inert atmosphere. Argon gas flow of 1sccm in the furnace tube was maintained during heating and cooling. The films were heated at a ramp rate of 50°C per minute from room temperature to the annealing temperature of 250 °C. The annealing dwell time was 30 minutes. The films were then cooled to 25 °C at a rate of 50°C per minute. Keithley 2400 Source meter in four-wire sensing mode was used together with a four point probe set-up. During the sheet resistivity measurements, probe spacing, s of 10mm was maintained for all the thin films. The films thickness, t was measured using a surface profilometer ranged
between 110-135nm. A fixed current, sourced from the Keithley 2400 source meter, was injected into the thin film through the two probes and the corresponding voltage is measured between the other two probes.

The electrical resistivity measurement of the thin films was done using the four point probe geometry adopting the Van der Pauw method. With a symmetrical square geometry adopted as shown in figure 4.1, the probe leads were connected to the source meter for voltage and current measurements.

**Figure 4.1**: Schematic of probe head used in sheet resistivity measurement (Agumba, 2010)
The values so obtained from source meter interfaced to a computer were used for plotting I-V curves from which sheet resistivity was computed.

4.5 Optical data measurements and analysis

Optical properties of the thin film samples were determined by use of the Shimadzu Solid Spec 3700 UV-VIS-NIR Spectrophotometer. The Spectrophotometer is designed for the highest sensitivity and has three detectors. A photomultiplier tube (PMT) detector is used for the ultraviolet and visible region. InGaAs and PbS detectors are used for the near-infrared region. The use of the InGaAs and PbS detectors makes the sensitivity in the near-infrared region extremely high. High sensitivity measurement in this range is not possible with conventional spectrophotometers. The SolidSpec’s InGaAs detector allows high sensitivity measurements in the switchover range. The SolidSpec-3700DUV uses materials with low absorption in deep UV for the light sources, detectors and integrating spheres. It has the capability to measure from 3300 nm down to the deep ultraviolet region at 165 nm with the direct detection unit or to 175 nm with an integrating sphere, by purging both the optical and the sample compartment with nitrogen gas. The large sample compartment (900W x 700D x 350H, mm) allows large samples to be measured with a non-destructive analysis method. The vertical optical path makes it possible to measure large samples while keeping them horizontal. The entire sample area of 12 inches or 300 x 300 mm samples is measurable by mounting the automatic X-Y stage option.
Automatic measurements can be performed in SolidSpec-3700DUV with the optional automatic X-Y stage by entering the intervals and the rotation angles for the sample. The powerful software package UV Probe for system control and data processing functions allows an easy operation and includes a wide variety of data processing functions such as peak/valley detection, area calculation and others. The transmittance and reflectance data was obtained at normal incidence in spectra range of 300nm-1700nm. The measured spectra were first exported to Scout 2.4 software for use in simulation modeling. The purpose of modeling was to extract the optical parameters after reproducing the measured spectra. The materials used (tin, selenium, air and nitrogen) were defined in the system and layer stacks set up. The spectra and model parameters to be varied ('fitted') were selected. This was done inorder to minimize the difference between simulated and measured spectra. The model was changed automatically until the measured data was reproduced with good quality to determine optical parameters and the band gap, $E_g$ through simulations.

4.6 XRD Measurement

Nitrogen doped Sn$_x$Se$_y$ thin films X-ray diffraction patterns were measured using the Bragg-Brentano method. PANalytical PW 3040/60 Xpert Pro XRD machine using high-power Cu K$_\alpha$ ($\lambda = 1.5406$ Å) XRD diffractometer was used. The X-ray power was 1200 W (30 mA x 40 kV). Its solid state detector was used for energy dispersive discrimination of the K$_\beta$ component of the diffracted X-rays and for enhancing the signal to noise ratio. Silicon standard sample was used as internal standard to calibrate the machine prior to taking the measurements.
The samples were first cut to required length of 25mm using a glass cutter and packed into standard sample holders, 2 mm in depth, to minimize the effect of preferred orientation. For optimum comparison, the samples were run under identical experimental conditions; scan step 0.05° 2θ, 0.7 s per step within the 2θ range 15–70°. This is the range where the most informative reflections from the structures occur. The ambient temperature in the XRD machine during scanning of the thin films was 22°C.

4.7 PCRAM cell design, fabrication and characterization

The details of the techniques used in design, fabrication and characterization of N-SnSe lateral PCRAM cell are discussed.

4.7.1 PCRAM cell design

The PCRAM design shown in figure 4.2 was adopted from the lateral design proposed by Merget et al. (2007). The PCRAM device was fabricated on a clean glass substrate on which successive layers of SiO₂ and N: SnSe thin films were deposited. The film was mechanically etched to introduce a constriction defining the active switching region with two aluminium electrodes placed left and right of this active region.
4.7.2 PCRAM cell fabrication

The N: SnSe PCRAM cell was fabricated on clean glass substrate. Using Edwards Auto 306 evaporation and sputtering system, 100nm layer of sub-stoichiometric SiO$_2$ was deposited by reactive DC sputtering of a silicon target in 20sccm of oxygen gas. The reactive sputtering was performed in the oxygen and argon ambient with the ratio 5:1 using a 200W RF power at pressure of $2.6 \times 10^{-2}$ mbar. A second 120nm thin film of N: SnSe was deposited by thermal evaporation. A thin strip of aluminium was used to mask off a 1mm wide switching zone on the N: SnSe layer. A 100nm thick aluminium film was then deposited on either sides of the masked strip to serve as cell electrodes. The chamber pressure during deposition of Al contacts was $4.0 \times 10^{-5}$ mbar. Using a scribe, PCRAM cells were mechanically etched and a further layer of SiO$_2$ deposited to passivate the switching zone. The switching zone area was approximately $1\text{mm}^2$. 

**Figure 4.2:** Schematic cross-sectional view of the fabricated N: SnSe PCRAM cell.
4.7.3 PCRAM cell characterization

The electrical characterization of the fabricated PCRAM cell was carried out using the standard R-Load measurement technique using a Keithley 2400 source meter, a 30V variable DC supply and digital multimeters. The N: SnSe PCRAM cell was connected in series with a 1KΩ resistor and directly accessed. This allowed current, I to be measured across the PCRAM cell by measuring the voltage across the load resistor. The difference between the supply voltage and the potential drop across the load resistor, V was calculated and used in plotting the I-V curve for the PCRAM cell. Due to the nature of the regulated power supply used it was not possible to precisely control the resolution the supply voltage. To minimize the effect of joule heating in the load resistor a dwell time of one minute was allowed each time the supply voltage was increased.

Figure 4.3 shows a schematic diagram of typical I-V traces for a PCRAM device (Baclay, 2009). During the SET operation, there is a point where the resistance of the phase-change material drops suddenly. According to Baclay (2009) this phenomenon takes place at the threshold voltage of the material and is referred to as the “snap-back” region of the device, due to the shape of the IV trace. The “snap-back” shown in the I-V curve is not typical of the PCRAM device but of the method used to measure the current and the voltage.
Figure 4.3: Schematic diagram showing typical I-V traces for a phase-change device (Baclay, 2009)
CHAPTER FIVE
RESULTS AND DISCUSSION

5.1 Optical characterization of Sn₅Seₓ.

5.1.1 Optical reflectance and transmittance

The normal incidence reflectance and transmittance data for undoped and doped films in the range 300-1700 nm was first normalized and exported to the Scout software. The measured substrate spectra agreed with simulated spectra for the different sample ratios. The measured optical transmittance spectra were plotted as a function of wavelength as shown in Figure 5.1.

![Graph of transmittance spectra of SnₓSeᵧ thin films for different mass ratios](image)

**Figure 5.1:** Graph of transmittance spectra of SnₓSeᵧ thin films for different mass ratios
Figures 5.1 shows the measured transmittance spectra of Sn\textsubscript{x}Se\textsubscript{y} thin films. It is observed that the transmission is generally higher in the IR range than in the visible range for the films. Further, it is observed that Sn\textsubscript{x}Se\textsubscript{y} films with higher Se content have higher transmittances but drops at higher value. Strong optical absorption in the UV is evident in the Sn\textsubscript{x}Se\textsubscript{y} films. However, films with higher Se content are observed to have lower absorption in the VIS and UV regions and have lower transmittances.

An oscillatory behavior is observed in both the transmittance and reflectance optical spectra in Sn\textsubscript{x} Se\textsubscript{y} films at wavelengths above 800nm are due to constructive and destructive interference of the light waves. The thin films reflectance is low and lies between 0-45 percent in the visible region. Low reflectivity shows that the thin films are good absorbers of light energy that generates more electron-hole pairs.
Figures 5.2 shows the measured reflectance spectra of Sn$_x$Se$_y$ thin films. It is observed that the reflectance is generally lower in the IR range than in the visible range for the films. Strong optical absorption in the UV is evident in the Sn$_x$Se$_y$ films. However, films with higher Se content are observed to have lower reflectance in the VIS and UV regions.
5.1.2 Simulated and experimental graphs of Sn$_x$Se$_y$ optical spectra

The SCOUT 2.4 program was used to analyze measured transmittance and reflectance spectra. The spectra of the relevant thin film samples recorded in the spectrophotometer were manually loaded and analyzed by SCOUT. The optical spectra given by the simulations of the experimental results fitted the measured data for all the films. The various optical parameters data were obtained from the simulations. The figures 5.6 (a-e) show the experimental and the simulated curves for thin films prepared using different ratios of Sn: Se.

![Graph showing simulated and experimental spectra for Sn:Se[1:0.2]](image)

**Figure 5.3 (a):** Simulated and experimental spectra for Sn: Se[1:0.2]
Figure 5.3 (b): Simulated and experimental spectra for Sn: Se [1:1]

Figure 5.3 (c): Simulated and experimental spectra for Sn: Se [1:1.4]
5.1.3 Optical band gap of Sn$_x$Se$_y$ thin films

The optical band gaps of the Sn-Se alloys were obtained using Scout 2.4 software. The experimental data was fitted to simulated data to generate the optical band gaps. O JL model, Drude, Lorentz oscillator and Harmonic oscillator (HO) models were used as the susceptibilities in the simulations. These models were used to treat the three basic excitations: Interband transitions, vibrational modes and the acceleration of free charge carriers (electrons, holes) to obtain flexible and realistic optical models.
Optical band gap energies in the range 0.96-2.11 eV were obtained. The values obtained compare with the band gap value range of 1.18-1.75 eV reported by Kumar et al. (2010), 1.27-1.94 eV by Karanja (2010) and optical band gap of 1–1.27 eV by Bindu and Nair (2004).

Figure 5.4: Dependence of optical bandgap on ratio of Sn: Se for as-deposited and annealed thin films.

Figure 5.4 shows the variation in optical band gap energy with different ratios of Sn: Se thin film samples. It is observed that for the as-deposited samples the optical band gap increased as the concentration of tin in the alloy reduced to a maximum band gap of 2.11 eV at Sn1Se1.4. Further increase in Sn concentration gives lower band gap. In the annealed films, lowest band gaps are achieved at around Sn: Se 1:1 ratio. The increase in Eg to a peak at Sn: Se 1: 0.4 is due to the defects introduced Se in tin lattice. The changes in optical band gaps can be attributed to formation of new
structural units with lower optical threshold energy and whose presence contributed to lowering of the mean value of band gap in the crystalline Sn$_x$Se$_y$ alloys. Change in the local environment around the Sn nuclei as the concentration of Se was increased is attributed to the changes in the band structure. One of the changes is the band gap narrowing due to the formation of density-of-states tails resulting from inhomogeneous impurity distributions. Increase in the interband transition energy at higher Sn-Se ratio is probably due to the filling of the conduction band by electrons. Band gap narrowing on annealing is attributed to decrease in the number of crystal defects and the transition to more ordered crystalline state. The lower band gaps achieved at around Sn: Se 1:1 is due to the composition of the alloys being near-stoichiometric forming a composite mixture of SnSe and SnSe$_2$. Lowering of E$_g$ at higher Se concentrations is attributed to material losses on annealing due to the high vapour pressure of Se causing bubbles nucleation and porosities (Aguiar et al., 1999).

5.2 Optical characterization of N- SnSe

5.2.1 Optical transmittance

Figure 5.5 shows the transmittance spectra of as-deposited SnSe doped with 0, 1, 2, 3, 4 and 5 sccm N. The optical transmittance spectra show strong absorption in the UV relatively high transmittance in the IR range for all the films. However the films doped with 1 and 5 sccm N have higher transmittances. No clear trend due to effect of nitrogen doping is seen and the variations in the transmittance spectra are attributed to variations in the film thickness or possibly due to formation of new phases due to nitrogen addition.
Figure 5.5: Transmittance curves of N-doped SnSe thin films

Broad peaks are observed in some of the curves. The shifts of the transmittance spectra representing shifts of the absorption bands show no clear trend. The transmittance spectra exhibit a behavior typical of amorphous thin films where a broad absorption is evident compared to sharp absorption that usually characterizes crystalline materials.

5.2.2 Simulated and experimental graphs of N-SnSe optical spectra.

The experimental and simulated transmittance data for N-SnSe were plotted against wavelength for the different nitrogen gas flow rates as shown in figures 5.6(a), 5.6 (b) and 5.6(c).
(a) 0 sccm N\text{SnSe}

(b) 1sccm N-SnSe
Figure 5.6 (a-c): Simulated and experimental transmittance curves for N-SnSe thin films

The simulated curves fitted perfectly into the experimental curves. The simulated transmittance spectra were used to generate the various optical constants.

5.2.3 Optical band gaps of nitrogen-doped SnSe films

The optical band gaps for both amorphous and annealed N-SnSe films obtained through simulations are shown in table 5.1 and plotted as a function of nitrogen flow in figure 5.7. The nitrogen gas flow in the deposition chamber was varied in the range 0-5 sccm while argon gas flow rate was maintained at 20 sccm. From table 5.1, the
as-deposited films are observed to have higher optical band gaps than the annealed N-SnSe films.

**Table 5.1:** Comparison of optical band gaps of as-deposited and annealed nitrogen doped - SnSe thin films.

<table>
<thead>
<tr>
<th>NITROGEN FLOW (sccm)</th>
<th>AS-DEPOSITED, $E_g \pm 0.005$ (eV)</th>
<th>ANNEALED, $E_g \pm 0.005$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.97</td>
<td>0.94</td>
</tr>
<tr>
<td>1</td>
<td>3.57</td>
<td>1.84</td>
</tr>
<tr>
<td>2</td>
<td>3.53</td>
<td>1.77</td>
</tr>
<tr>
<td>3</td>
<td>3.22</td>
<td>1.65</td>
</tr>
<tr>
<td>4</td>
<td>3.34</td>
<td>2.05</td>
</tr>
<tr>
<td>5</td>
<td>3.63</td>
<td>2.00</td>
</tr>
</tbody>
</table>

**Figure 5.7:** Dependence of optical band gaps of the SnSe films on nitrogen-doping.
A large change in the optical band gap was observed when the nitrogen flow rate was increased from 0-1sccm. The band gap change was from 0.97eV to 3.57eV. Further increase in the nitrogen flow rate showed slight changes in the band gap and the lowest band gap was observed at 3sccm N. The inhomogeneous impurity distribution of nitrogen is thought to be responsible for wide band gap in the as-deposited films. Nitrogen incorporation may also cause fluctuations in potential which may destroy the translational symmetry of the crystal.

5.3 Effect of nitrogen doping on dielectric function

The dielectric function of a material describes the electrical and optical properties in response to excitations by electromagnetic waves. It describes the electric polarizability, susceptibility and absorption properties of the material and is given as the complex dielectric function comprising of the real, \( \varepsilon_1 \) and the imaginary components, \( \varepsilon_2 \). The dispersion in the real and imaginary constants depicts the excitation behavior of all materials (semiconductors, insulators and metals). The real and the imaginary parts of the dielectric constant are related to the refractive index, \( n \) and the absorption, \( k \) of materials according to the expressions:

\[
\varepsilon_1 \pm i\varepsilon_2 = (n \pm ik)^2
\]

where \( \varepsilon_1 \) is the volume polarization and \( \varepsilon_2 \) is the volume absorption vibrational energy. The quantity \( \varepsilon_1 \) represents how much a material becomes polarised when an electric field is applied due to creation of electric dipoles. When the applied field is oscillating such as in case of alight wave, the sign of \( \varepsilon_1 \) can either be positive or negative depending on whether the induced dipoles are oscillating in or out of phase with the applied field. When the induced dipoles oscillations become large enough, it
is possible for the material to start absorbing energy from the applied field. When absorption occurs, the quantity $\varepsilon_2$ becomes important. When a material is transparent $\varepsilon_2$ is zero and becomes non-zero when absorption begins. Thus $\varepsilon_2$ represents absorption in a material. Written together $\varepsilon_1$ and $\varepsilon_2$ form the complex dielectric constant and are related by the Kramers-Kronig relationship.

Figure 5.8: Dependence of $\varepsilon_1$ on nitrogen doping level for amorphous SnSe thin films

Figure 5.8 shows the dependence of the real part of the dielectric function on nitrogen doping in as-deposited SnSe thin films. For the amorphous thin films, the values of $\varepsilon_1$ increased with increase in the level of nitrogen doping in the visible spectrum and near IR. The dielectric constant $\varepsilon_1$ does not vary significantly with wavelength in 5 sccm N-SnSe films. Higher N doping levels are observed to give higher values of $\varepsilon_1$ indicating a higher degree of polarization in the thin films.
Dependence of $\varepsilon_1$ on nitrogen doping level for crystalline SnSe thin films is shown in figure 5.9. The crystalline thin films gave the highest values of $\varepsilon_1$ at a nitrogen doping level of 3sccm. The values of $\varepsilon_1$ show a pattern markedly different from that of the amorphous films. This difference in dielectric constant is due to change in structure affecting the ability of the material to polarise.

![Graph showing dependence of $\varepsilon_1$ on nitrogen doping level for crystalline SnSe thin films.](image)

**Figure 5.9:** Dependence of $\varepsilon_1$ on nitrogen doping level for crystalline SnSe thin films

The spectral dependence of $\varepsilon_2$ on N doping in both amorphous and crystalline N- SnSe thin films is shown in Fig. 5.10 and Fig. 5.11 respectively. It is observed that the onset of optical absorption for the amorphous films has the longest wavelength at 2-3 sccm nitrogen doping level which also corresponds to the highest values of $\varepsilon_2$ in the crystalline films. The main $\varepsilon_2$ peaks of crystalline SnSe thin film are much stronger
and shifted to higher frequencies compared to amorphous SnSe thin films. By Kramers-Kronig analysis, this translates into smaller values of $\varepsilon_1$ for the as-deposited films.

![Graph showing the dependence of $\varepsilon_2$ on nitrogen doping level for amorphous SnSe thin films.](image)

**Figure 5.10:** Dependence of $\varepsilon_2$ on nitrogen doping level for amorphous SnSe thin films.

Usually the dielectric constant increases slowly with frequency or decreases with wavelength (normal dispersion). However, in the neighbourhood of an atomic transition the material exhibits anomalous dispersion, in which the dielectric constant decreases sharply with frequency accompanied by absorption of light. Peaks observed in figure 5.10 indicate the onset of interband absorption. At critical points in the BZ,
transitions accumulate to produce a peak in the absorption spectrum. It is important to note that absorption peaks fall in the UV to VIS range in Fig 5.10 and Fig 5.11.

**Figure 5.11:** Dependence of $\varepsilon_2$ on nitrogen doping level for crystalline SnSe thin films

Figure 5.12 shows a comparison of dielectric functions of amorphous and crystalline phases for 3 sccm N-SnSe thin films. In all N-SnSe thin films, it is observed that the dielectric constant, $\varepsilon$ is significantly higher in the crystalline than in the amorphous phase. This agrees with the results by Anbarasu and Wuttig (2011) who found that the optical dielectric constant was much larger in the crystalline state than in the amorphous state for all phase change materials they studied.
According to Wuttig (2009) this difference in the dielectric function of the amorphous and crystalline phases can be attributed to resonant bonding. Resonance bonding is the cause of the large optical dielectric constant observed in all crystalline IV–VI compounds. Resonance bonding results in larger optical dielectric constants than in pair bonded materials because it gives smaller average band gaps (bonding–antibonding splitting) and larger optical matrix elements than in electron pair bonding.
It is observed in figure 5.13 that the dielectric contrast is higher in the IR than in the VIS. The analysis of reflectance spectra show that the dielectric functions of the amorphous and crystalline state differ significantly as observed in Fig. 5.12. This difference in the dielectric function of the two different states is due to resonant bonding. The crystal structures of phase change materials are all based on distorted cubic structures and all possess resonant bonding according to Raoux (2009). Resonance bonding is therefore the cause of their higher optical dielectric constants. The existence of resonant bonding requires a longer-range order than the conventional electron pair bond of the 8–N rule. An electron pair only requires the ordering of the nearest neighbours forming the pair bond. Resonant bonding, on the contrary, requires the second and higher neighbours to be aligned.
In the amorphous state, this higher level of ordering is not possible, and so the structure reverts to a simple 8–N rule structure, which requires a lower level of ordering. This emphasizes that the bonding between the phases differs not only in coordination numbers but also in their medium range order. It is only the change in local order that can explain the strong optical contrast in crystalline and amorphous phases.

![Reflectance curves for amorphous and crystalline 3sccm N-SnSe film](image)

**Figure 5.14:** Reflectance curves for amorphous and crystalline 3sccm N-SnSe film

Figure 5.14 shows the differences in the reflectance spectra in for amorphous and crystalline 3sccm N-SnSe thin films. The oscillations in the amorphous thin films are seen to persist for shorter wavelengths (higher energies) which are clear evidence for a larger band gap in the amorphous state. The reflectance in the crystalline state is
lower than in the amorphous state and does not reach the value of 1. This indicates that the film absorbs some of the photons even below the band gap. This absorption can be attributed to the presence of free carriers which also affect the oscillation amplitude. It is also observed that the reflectance minima are significantly closer spaced for the crystalline sample. This effect is not due to the decrease in film thickness upon crystallization, which would lead to a corresponding increase in the spacing of the reflectance minima, if the refractive index does not change. The pronounced decrease of the distance between the reflectance minima can only be explained by a strong increase in the refractive index. According to Wuttig (2009) this phenomenon is common for all phase change materials.

5.4 Refractive index and absorption edge

The absorption edge or band edge is defined as the transition between the strong short-wavelength and the weak long-wavelength absorption in the spectrum of a solid, generally a semiconductor. The spectral position of this edge is determined by the energy separation between the valence and conduction bands of the material. In the case of transparent solids, the absorption edge can be measured using transmittance techniques. Figure 5.15 shows the dependence of refractive index on the N-doping in amorphous N-SnSe thin films.

The refractive index of amorphous SnSe thin films is observed to show strong dependence on the N doping. In the doping range 0-2 sccm N, the refractive index is observed to decrease with increase in N-doping. Further increase in N-doping gradually increases the refractive index as seen at 3, 4, and 5 sccm N. High values of
refractive index at 5 sccm N are observed to correspond to high transmittances in the transmittance spectra shown in figure 5.5.

**Figure 5.15:** Dependence of refractive index on nitrogen doping level in amorphous N-SnSe thin films.

Figure 5.16 shows the dependence of the refractive index on the doping level in crystalline N-SnSe thin films. Materials with larger band gaps will have smaller real part of dielectric constants and therefore, smaller real part of refractive indices. Compared with the amorphous films, the crystalline N-SnSe thin films are observed to have higher refractive index. The higher refractive index in the crystalline state is due to the changes in internal structure on annealing the films. The N doped crystalline films show highest refractive index at 3 sccm N. Higher and lower values of nitrogen doping are observed to give lower values of refractive index.
Figure 5.16: Dependence of refractive index on nitrogen doping level in crystalline SnSe thin films.

The nitrogen doped SnSe thin films show large increase in refractive index on crystallizing. Introduction of nitrogen in the Sn-Se alloy may lead to formation free carriers and presence of more covalent bonds may saturate the defects in the amorphous material increasing the mobility gap leading to a strong increase in refractive index on crystallization.
5.5 Electrical characterization of N-SnSe

Lindberg Mini-Mite TF55035A tube furnace was used to heat the as-deposited thin films during the I-V characterization. The heating rates or ramp rates were controlled by programming the furnace’s UT150 controller. Ramp rate during heating and cooling was $5^\circ\text{C}$ per minute. The furnace tube was first purged with argon gas and a gas flow of 1sccm Ar was maintained during heating and cooling. The data collected was used to plot the sheet resistivity-temperature curves for the different N-SnSe thin films.

![Figure 5.17: Dependence of sheet resistivity on temperature for SnSe for 130-nm-thick thin film.](image)

The temperature dependence of sheet resistivity is shown in figure 5.17. Large and gradual decrease in sheet resistivity is observed during heating. The phase transition spans over $30^\circ\text{C}$ and is due changes that involves atomic diffusion to the crystalline
phase. During cooling, sheet resistivity slightly increases with decrease in temperature. The change in resistivity by about four (4) orders of magnitude confirms the phase change nature of the films. The increase in the electrical conductivity is due to the increase of grain size reducing scattering by the grain boundaries.

Figure 5.18 shows the temperature dependence of resistivity on nitrogen doping of the films during heating. The N-doped and undoped SnSe films both show a single phase transitions.

![Resistivity as a function of temperature for 130-nm-thick, as-deposited nitrogen-doped SnSe thin films.](image)

**Figure 5.18:** Resistivity as a function of temperature for 130-nm-thick, as-deposited nitrogen-doped SnSe thin films.
Similar structural changes which are accompanied by a major drop of resistance have been reported in Ge$_2$Sb$_2$Te$_5$ films by Friedrich et al. (2000). These films were shown to undergo a structural change from an amorphous to rock salt structure at around 140°C and finally to a hexagonal structure around 310°C. It was further noted that the transition temperatures range for the various N-SnSe thin films varied with the nitrogen doping level. It is observed that nitrogen doping changes the crystallization behavior of SnSe and leads to a more gradual phase transition which occurs at lower temperature compared with the undoped material (0 sccm N SnSe). The temperature window (~ 20°C) upon which these phase transition takes place is comparable to that of Ge$_2$Sb$_2$Te$_5$ (T=20 °C) as reported by Kyung-Min et al. (2008). The Gaussian minima of the first derivative of the R-T curves during heating were used to determine the crystallization temperatures of the films.

**Table 5.2:** Crystallization temperatures of N-SnSe thin films

<table>
<thead>
<tr>
<th>N (sccm)</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>T$_c$ (°C) ± 0.05</td>
<td>107.8</td>
<td>95.0</td>
<td>86.7</td>
<td>72.8</td>
<td>95.3</td>
<td>102.3</td>
</tr>
</tbody>
</table>

Table 5.2 shows the crystallization temperatures of N-SnSe thin films. The temperature at which phase transition occurred showed a strong dependence on the N-doping level. Results showed a decrease in crystallization temperature to minima of 72.8 °C in 3 sccm N thin film as shown in Table 5.2. Further increase in N-doping raised the crystallization temperatures. This was probably due to incorporation of
nitrogen in bonded form or as trapped atoms in the alloy leading to a decrease in resistivity.

The observed crystallization temperatures are given in table 5.2. The normal working temperature for memories is 0°C to 85°C for the consumer products, -40°C to 105°C for industrial uses and -40°C to 150°C automotive applications. A phase change material needs to retain data at the operation temperature of the memory. The crystallization temperature of a suitable material must be substantially higher than the operating temperature. While low crystallization temperatures may be desirable to reduce power consumption during resistive heating, it compromises data retention. Results suggest that N-doping can be used to vary the crystallization temperature of N-SnSe and that 3 sccm N SnSe thin films with a $T_c = 72.8 \, ^\circ C$ are not suitable for use in memory applications.

Figure 5.19 shows the dependence of crystalline resistivity of SnSe on nitrogen doping. The undoped SnSe alloy had room temperature resistivity values in the crystalline state of about $9.3 \pm 0.05 \, \Omega cm$ which gradually decreased as the nitrogen doping was increased as seen in figure 5.19. The decrease in electrical resistivity with increase in Nitrogen flow is due to grain boundary scattering.
The resistivity values are lower but comparable to those obtained by Bindu and Nair (2004) of 100-5 $\Omega$cm and 30 - 8.1 $\Omega$cm obtained by Hema et al. (2007) in the film thickness range (150 - 300nm). These values are higher than the crystalline resistivities of Ge$_2$Sb$_2$Te$_5$ (=1 $\Omega$cm) and Ge$_4$Sb$_7$Te$_5$ (=3 $\Omega$cm) reported by Kyung-Min et al. (2008). This suggests that the SnSe alloy could be used to minimize RESET current in PCRAM devices. According to Torbjörn et al. (2002) N doping should improve holes mobility and hence could be used to vary crystalline resistivity and crystallization temperature.
5.6 Structural properties.

XRD measurements were carried out using Panalytical PW3040/60 XPert Pro XRD machine using Cu Kα (λ = 1.5406 Å) radiation. XRD scans for as-deposited and annealed films were carried out with rayons power set at 40KV at 30mA (1200W). An XRD scan of blank glass slide was ran after calibrating the XRD machine using the silicon standard sample. The broad peak appearing at low angle in figure 5.20 is due to the amorphous glass substrate itself.

![XRD scan of a blank glass substrate.](image)

**Figure 5.20**: XRD scan of a blank glass substrate.
Figure 5.21 shows the XRD scans for both amorphous and annealed nitrogen doped thin films. The prominent Bragg reflection was occurring at or around 30° corresponding to (400) and (111) diffraction planes. The presence of sharp and well-defined diffraction peaks in XRD confirmed the polycrystalline nature of the annealed films. The XRD patterns show that the as-deposited films are amorphous in nature. The XRD scans for the as-deposited thin films show a low degree of crystallinity. In the crystalline N-SnSe films, the number of diffraction peaks is observed to increase as the amount of N-doping is increased. The more complex XRD pattern obtained at 4% N-doping suggests formation of multiphases.
Figure 5.21: XRD scan for SnSe (a) amorphous and (b) crystalline thin films doped with 0, 1, 2, 3 and 4 sccm nitrogen.
Figure 5.22: XRD scan for SnSe doped with 4sccm Nitrogen.

Figure 5.22 shows the XRD scan for SnSe thin film doped with 4sccm Nitrogen. The XRD patterns of the annealed film showed an increase in the number and sharpness of peaks as the rate of nitrogen flow was increased. The very strong and sharp (400) peak indicates a highly preferred orientation of the crystallites. The X-ray diffraction analysis showed that solid crystalline phases have the same crystal characteristics of the individual SnSe and SnSe$_2$ structures. The peak positions and intensity are similar to those of SnSe-SnSe$_2$ composites as seen in Figure 3.3 adopted from Aguiar et al. (1999). A similar pattern was obtained by Nariya et al. (2009) for SnSe crystals prepared in a horizontal furnace. An increase of the number of crystallites on annealing seen in the scans is attributed to nitrogen doping. It is possible that nitrogen interstitials may form nucleation sites which would result in better crystallization. According to Raoux et al. (2009) addition of nitrogen can control the amount of
nanoscale order in the amorphous matrix and drastically alter the consequent nucleation behavior of the phase change material. The XRD results are in good agreement with published values recorded in the International Centre for Diffraction Data (ICDD) standard.

5.7 Electrical measurement of SnSe PCRAM device.

The current – voltage (I-V) characteristics of the fabricated PCRAM cell were obtained using Keithley 2400 source meter, a digital multimeter and a 30V DC power supply. The PCRAM cell had a threshold switching voltage, \(V_{th}\) of 4.47 V at a current of 1.04 mA. The I-V curves shown in figure 5.23 were used to approximate values of the RESET, SET and READ voltage pulses. RESET pulses should raise the temperature to just above the melting point and then allow rapid cooling of the material to the amorphous phase. The fall time of the RESET pulse is a critical parameter that determines if melt crystallization will occur. SET pulses should raise the temperature just above the re-crystallization temperature but below the melting point. The material should be allowed to cool slowly for it to crystallize. READ pulses should have a value lower than the threshold voltage and should not disturb the state of the cell. The pulse width and Fall time for a SET pulse should be longer than for a RESET pulse.

Pulse duration is determined by the energy required to either to melt PCM material or to re-crystallize it. SET and RESET pulse voltages need to be higher than the threshold voltage of 4.47V for this PCRAM cell. Fall time for a RESET pulse is a critical parameter. The state of the PCM technology determines the required minimum for a fall time. It is a common requirement to have 30-50 nanoseconds fall
time according to Pronin (2010). Newer materials are expected push this to shorter fall times.

![Figure 5.23: I-V characteristics of N-SnSe PCRAM device tested in direct access DC static mode.](image)

The material may not effectively quench into an amorphous phase if the pulse fall time is longer than the required time. From the I-V curves in figure 5.23 the approximate values of the RESET, SET and READ voltage pulses are; 0.3-2.5mA READ current, 6V SET voltage and 9V RESET voltage.
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The effect of nitrogen doping in tin–selenium thin films for phase change memory applications has been investigated. Thin films of N-SnSe were deposited at room temperature on glass substrates using reactive thermal evaporation. Threshold switching was observed in the films with resistivity dropping by 5 orders of magnitude. Increasing nitrogen concentration led to a more complex XRD pattern due to formation of multiphases of SnSe, SnSe$_2$ and Sn$_2$Se$_3$. The optical band gap increased from 0.97 eV at 0 sccm N to 3.57 eV at 1 sccm N. Nitrogen flow rates greater than 1 sccm showed slight changes in the band gap. The N-SnSe films generally had high transmittances (over 70%) that increased with increase in nitrogen doping. In the doping range of 0-5 sccm N, the resistivity decreased from 1280 – 1150 $\Omega$cm and 9.3 - 0.3 $\Omega$cm for amorphous and crystalline N-SnSe films respectively. The crystallization temperature, T$_c$ decreased with increase in nitrogen doping from 107.8 $^\circ$C at 0 sccm N to a minimum of 72.8 $^\circ$C at 3 sccm N before increasing to 102.3 $^\circ$C at 5 sccm N. Fabrication of N-SnSe PCRAM cell was done successfully. The PCRAM cell had threshold switching voltage, $V_{th}$ of 4.47 V at a current 1.04 mA.

The optical, electrical and structural properties of N-SnSe thin films show strong dependence on the nitrogen doping level. The N-SnSe thin films had band gap energy of 0.97-3.63 eV that makes them good absorbers of photons of different energies in the VIS. The peak efficiency for solar energy conversion occurs for a bandgap in the range 0.9 to 1.6 eV and so N-SnSe thin films are of interest. Possible applications of
N-SnSe include photovoltaic solar cells, solar energy storage, and transparent windows in IR detectors and in multi-bit phase change memory applications.

6.2 Recommendations

To gain further insights into the influence of N dopants on the crystalline and amorphous SnSe alloys, a more systematic study considering both phases is strongly recommended. Heavy ion elastic recoil detection analysis (HI-ERDA) by X-ray photoelectron spectroscopy (XPS) to determine the composition of the thin films after N doping is suggested. Further research is recommended by use of Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) which have high resolution for analysis due to the small de Broglie wavelength of the electrons that allows examination of very fine details of the thin films. The Wavelength dispersive X-ray spectroscopy (WDXRF) chemical analysis or EDX (Energy-dispersive X-ray spectroscopy) analysis is necessary to determine the quantity and identify the form in which N occurs in the alloys. Further it would also be essential to determine the recrystallization and amorphisation behavior of the doped alloys.
REFERENCES


Kim S., Cho S and Cho E., (2010). High performance PRAM cell scalable to sub-20nm technology with below 4F$^2$ cell size, extendable to DRAM applications. In the proceedings of the 2010 *Symposium on VLSI Technology (VLSIT)*. doi 10.1109/VLSIT.2010.5556228.


APPENDICES

Appendix I: Photograph of Edwards Auto 306 vacuum coater.
Appendix II: Photograph of Keithley Source Meter 2400 model.
Appendix III: Set-up used to collect R-T data for the films
Appendix IV: PANalytical X’Pert Pro XRD machine
Appendix V: UV-3700 UV-VIS-NIR Spectrophotometer