Sb-Te Phase-change Materials under Nanoscale Confinement

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This dissertation titled

Sb-Te Phase-change Materials under Nanoscale Confinement

by

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Abstract

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Sb-Te Phase-change Memory Materials under Nanoscale Confinement

Director of Dissertation: Gang Chen

Size, speed and efficiency are the major challenges of next generation non-volatile memory (NVM), and phase-change memory (PCM) has captured a great attention due to its promising features. The key for PCM is rapid and reversible switching between amorphous and crystalline phases with optical or electrical excitation. The structural transition is associated with significant contrast in material properties which can be utilized in optical (CD, DVD, BD) and electronic (PCRAM) memory applications. Importantly, both the functionality and the success of PCM technology significantly depend on the core material and its properties. So investigating PC materials is crucial for the development of PCM technology to realized enhanced solutions. In regards to PC materials, Sb-Te binary plays a significant role as a basis to the well-known Ge-Sb-Te system.

Unlike the conventional deposition methods (sputtering, evaporation), electrochemical deposition method is used due to its multiple advantages, such as conformality, via filling capability, etc. First, the controllable synthesis of Sb-Te thin films was studied for a wide range of compositions using this novel deposition method. Secondly, the solid electrolytic nature of stoichiometric Sb₂Te₃ was studied with respect to precious metals. With the understanding of 2D thin film synthesis, Sb-Te 1D nanowires (18 – 220 nm) were synthesized using templated electrodeposition, where
nanoporous anodic aluminum oxide (AAO) was used as a template for the growth of nanowires. In order to gain the controllability over the deposition in high aspect ratio structures, growth mechanisms of both the thin films and nanowires were investigated. Systematic understanding gained thorough previous studies helped to formulate the ultimate goal of this dissertation.

In this dissertation, the main objective is to understand the size effect of PC materials on their phase transition properties. The reduction of effective memory cell size in conjunction with multilevel cells could be promising to achieve high data densities. However the size reduction may result in changes in material properties. If phase transition properties of the materials are also tunable with respect to the size, then more attractive solutions could be realized. So we have reported the size effect on crystallization temperature of prototypical Sb$_2$Te$_3$ nanowires synthesized in AAO templates. Moreover, we have found that the reduction of nanowire size can elevate the crystallization temperature, which is crucial for data retention in PCM technology.

Energy dispersive X-ray spectroscopy, X-ray diffraction, electron microscopy and electrical resistivity measurements were used to characterize the composition, structure, morphology, and phase transition properties of the materials. We believe that this dissertation will provide new insights into the size effect of PC materials in addition to the controllable synthesis of PC thin films and nanowires through the novel electrochemical method.
To my beloved parents, wife and children.
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Chapter 1: Introduction

1.1 Phase-change Memory Materials

Rapid switching between two stable phases, crystalline and amorphous (Figure 1-1), with significant changes in optical reflectivity and electrical resistivity is the key for phase-change materials [1]. With the greatest appreciation to a prolific scientist and inventor, Stanford R. Ovshinsky, the practicality of utilizing this rapid reversible switching and property-change as a memory material was demonstrated in 1960’s [2]. After that, optical reflectivity change and electrical resistivity change have been successfully harnessed in optical (CDs, DVDs, BRDs, etc.) and electrical (PCRAM) memory applications [1, 3]. Among all the phase-change memory materials (PCMMs), Ge-Sb-Te (GST) alloys have captured a great deal of attention due to their excellent switching performance [4].

![Figure 1-1](image)

*Figure 1-1. Schematic representation of structural transition from crystalline to amorphous.*

To further enhance the properties of phase-change materials, one could harness the effects of nanoscale confinement [1]. Studies of 0D (nanoparticles) [5-12], 1D (nanowires) [13-16], and 2D (thin films) [17-20] confinements of the ternary GST have been conducted by a few research groups, and changes in the phase transition (i.e.,
melting and crystallization) temperatures have been reported due to confinement. So low dimensional confinement has the potential to overcome the challenges in future memory devices such as achieving high data density, high data processing speed, and low power consumption [21]. Unlike the charge-based memory technologies such as DRAM and FLASH, which have practical limitation for further scaling down due to charge storage and sensing mechanisms, PCM has an excellent capability to scale down due to its special current and thermal mechanisms [22]. Moreover, following the technological trends with scaling down, the reduction of effective memory cell size in conjunction with multilevel cells could be promising to achieve high data densities, but the size reduction may result in changes in material properties [23]. If phase transition properties of the materials are also tunable with respect to the size, then more attractive solutions could be realized. Currently, phase-change thin films play a main role in data storage and non-volatile random access memory [2, 24-26]. Phase-change nanowires (PCNWs), on the other hand, are very promising to overcome the above mentioned challenges for next-generation non-volatile memory.

Various techniques such as the vapor-liquid-solid method [13-16, 27, 28], the colloidal method [29], and the electrochemical deposition method [30-32] have been reported for the synthesis of PCNWs. In order to utilize nanowires in devices with enhanced material properties, it is crucial to have precise control over their composition, structure, morphology, and 3D alignment [33]. The template-guided electrodeposition method appears to be the most economical and efficient method that meets these requirements.
1.2 Sb-Te as a Phase-change Memory Materials

Remarkable material properties of certain chalcogenides have enabled a range of new applications by providing a basis for thermoelectric, superconductor, phase-change, and topological insulator behavior [34]. Among them, binary Sb-Te has captured a considerable attention due to its applicability as solely and an alloy basis [35-37]. Especially, for PCM applications, Sb-based compositions, which are known as fast growth materials due to the observed rapid crystallization [38] and tellurides, due to provided prosperity in optical and electronic devices [34], are playing a main role [37]. Moreover, the binary of Sb-Te are prototypical PCM materials which could provide a notable insight to enhance our understanding for similar complex materials.

Interestingly, both the pure Sb and Te crystallize at room temperature, but as an alloy, Sb-Te is capable of stabilizing both the crystalline and amorphous phases at room temperature, which is crucial for the application as a PCM material. The amorphous phase stabilization is due to three-fold cross-linking of Sb and Te-Te chains [39]. As reported in Bichara, Raty [40], Te can be partially three-fold coordinated at molten state due to the electronic interaction between lone pair orbitals, even though its usually two-fold coordinated. So at molten state structural preferences are similar to its amorphous state, therefore adding three-fold Sb can satisfy the demand of Te to stabilize its amorphous phase. Schematic atomic representation of molten and crystalline state for pure Te is shown in Figure 1-2, and at room temperature weak van der Waals bonds between Te-Te chains will break and easily crystallize into hexagonal structure.
1.3 Phase-change Memory as Non-volatile Memory

Computational memory can be divided into two types, volatile and non-volatile, depending on the retention capability of its content with respect to the power supply. Volatile memory is incapable of retaining its content without the power supply, but nonvolatile memory is capable of retaining its content regardless of the power supply. Moreover, the typical retention times expected here are around 10yrs. For an overall view of mature and emerging memory technologies in each type, classification of memory technology summarized in Figure 1-3 [41, 42].
So PCM is a prototypical non-volatile memory technology which has a significant potential of enabling new applications and memory architectures in a wide range of systems [43]. Especially, the PCM is capable of filling the performance gap between both memory and storage type memories, so it is also known as a promising technology for storage class memory (SCM) [44]. Comparison of other existing memory and storage technologies with respect to PCM is essential to highlight its capabilities as an SCM, and a qualitative representation is shown in *Figure 1-4* as discussed in Burr, Breitwisch [44]. Static (S) RAM or cache memory is the fastest memory and to fulfill the operation demand (1ns) of CPU, in order to maintain its high performance, both the SRAM and CPU share the same chip (on-chip memory). Regardless of its performance, effective cell
size is very large so there is a significant trade-off between cost and performance. However, dynamical (D) RAM is an off-chip memory, relatively less in both the performance and cost with respect to SRAM. Generally, SRAM and DRAM are known as memory technologies due to their higher performance to satisfy CPU needs, similarly FLASH and secondary storage memory (hard disk drives) are known as storage technologies due to their lower performance and excellence in cost-effective data storage. Importantly, PCM is more likely a merger of both the memory and storage; it is a promising alternative for DRAM in future and already performing better than NAND FLASH [43] and hard disk drives. According to the International Technology Roadmap for Semiconductors [45], PCRAM is outstanding with respect to other prototypical and emerging SCM technologies, and the comparison is shown in Table 1. Green face represents the positive feasibility with respect to its scalability (F<10nm), multi-level cell, 3D integration, fabrication cost, and endurance (10^9), and red and yellow faces are the worst and intermediate of those, respectively. Overall, the PCM technology has an excellent capability to enhance its performance cost-effectively to satisfy the memory needs from storage to memory by playing a magnificent role in NVM.
Figure 1-4 Comparison of cost vs performance for different memory and storage technologies, F represents the smallest lithographic size, so lower the cell area, higher the data density, and lower the production cost [46].

For PCRAM, the most commonly used mushroom cell structure with cell programmable and readable pulses are shown in Figure 1-5. Typically the selection of each cell for programming and reading was done through an access device, diode, BJT, or FET. At low resistance, a PC material (e.g. polycrystalline GST) is in crystalline phase. Change the resistance to high, a RESET pulse (high voltage (V) and short duration (t) sufficient to melt and quench) was applied to imitate the quenching effect to amorphize the material. To switch back to the low resistance state, a SET pulse (intermediate V and longer t sufficient to reach just above the crystalline temperature) was applied to imitate the crystallization effect. To read the programmed state, SET or RESET, READ pulse
was applied (very low V and short t sufficient to measure the existing resistance) to sense the cell resistance without any modification.

Table 1 *Potentials of the current prototypical and emerging research memory candidates for SCM application*[45]

<table>
<thead>
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<th>Memory</th>
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<th>Emerging (Table ERD5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>FeRAM</td>
<td>STT-MRAM</td>
</tr>
<tr>
<td>Scalability</td>
<td>📉 📉 🍀</td>
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</tr>
</tbody>
</table>

Progress of the PCRAM from concept demonstration to manufacturing is summarized in *Figure 1-6*, as presented in Bez [47], and both the PCM cell and array/chip are shown with respect to the scaling down tech node. Beyond the scalability
of PCRAM, stackable cross point array of PCRAM was also demonstrated as a confirmation of 3D integration by stacking few layers vertically [48].

![Figure 1-5](image)

**Figure 1-5** Most common PCRAM cell (mushroom) after a) RESET (high resistive) and b) SET (low resistive) programming and c) the nature of programmable (SET/RESET) and READ pulses with respect to temperature and time [49, 50].

However, to continue the technological trends to achieve higher performance, higher data density, and cost-effective memory, PCM needs to further scale down. More importantly, core of the PCM technology is the PC material and it significantly determines the functionality of the entire PCM technology [23]. Therefore, the variation of PC material properties with respect to scaling is crucial to investigate in order to acquire the expected goals in PCM technology to fulfill the future memory demands.
1.4 Future Trends of Data Generation, “Big Data Universe”

Current world is generating 2.5 quintillion bytes of data daily from diverse data generating sources, such as, climate information sensors, social media, purchase transactions, digital pictures and videos, mobile phones, etc. Astonishingly, 90% of the digital data available in entire world has generated during the last 2 years [51]. This data production is expecting to be 44 times greater in 2020 with respect to what it was in 2009 [52]. Clearly, the past, present, and future of the global data growth is presented in the infographic (Figure 1-7) to visualize the effective trends of this humongous challenge. Additionally, this rapid growth of global data directly challenges the data storage technologies and especially, to retain the expected performance and efficiency for the future technological demands, significant responsibility of the challenge expected to be sufficed by storage class memory solutions like PCM technology.
1.5 Dissertation Outline

With an extreme interest of merging our interest with the future technological trends of PCM technology, this study is focused to investigate the scaling effects of PC materials. Investigation is based on Sb-Te binary, due to its significance in this technology, and different nanoscale confinements of these materials as thin films and nanowires were synthesized by electrodeposition, which is a cost-effective and promising method of filling high aspect ratio structures.

To clearly support the motivation of this work, sufficient background is provided in introduction to deliver the broad perspectives. In addition to the given information
about the theory and methods from the 2nd chapter, more elaboration is provided on design and development of four-probe resistivity measurement system including its LabVIEW data automation. Chapter 3 provides a more generalized idea about the experimental procedure, since the experimental specifications are well-explained in sub-projects based chapters starting from the next.

In order to fulfill the ultimate goal of the dissertation, a systematic approach was followed through project management. Moreover, this work was not limited to the resources available at Ohio University, and multiple faculties available at Argonne National Lab (CNM, EMC, and APS) were also utilized. Starting from Chapter 4 to 8 are the five accomplished projects which lead to the overall fulfilment. First, the controllable electrochemical synthesis of Sb-Te materials under 2D confinement and corresponding compositional, morphological, structural and phase transitional material characterization are presented in Chapter 4, with an intention of revealing the controllable trends for effective material synthesis. Especially, these Sb-Te materials are good solid electrolytes and can be used in charge-based RAM applications, so Chapter 5 is dedicated to investigate the solid electrolytic nature of stoichiometric Sb$_2$Te$_3$ with precious metals (Au/Pt) through an RBS study. Chapter 6 is a 1D confinement study of Sb-Te materials. These nanowires were synthesized by templated electrodeposition, and both the commercial and home-made templates were used to cover a wide range of diameters (18-220nm). When materials are electrodeposited in high aspect ratio structures, diffusion constraints of electrochemical species play a significant role. In order to achieve the controllability over the deposition, understanding and exploring the growth mechanism of
nanowires in these structures are crucial, so Chapter 7 not only presents details of understanding the growth mechanism of nanowires but also compares the details with the growth mechanism of thin films. Chapter 8 is the ultimate goal of this entire dissertation which explores the scaling effects of \( \text{Sb}_2\text{Te}_3 \). Moreover, this is focused on phase transition property tuning with respect to 1D confinement, especially the crystallization temperature was tuned and observed a considerable increment of that. On the way of enhancing our knowledge in finding high performance, high efficient and cost-effective memory devices under scaling down constraints, observed crystallization temperature increment in PC materials is critically beneficial to improve the data retention of these PCMs. Finally, the overall findings and future prospects of this work are concluded in Chapter 9.
Chapter 2: Methods and Theory

2.1 Material Synthesis

2.1.1 Electrodeposition

Electrodeposition is a method of material deposition through an electrochemical reaction, and the electrically conductive materials (metals, alloys, semiconductors, semimetals, conductive polymers, and conductive oxides) are the only applicable candidates. Surface coating and metallurgy are the conventional usage of this technique, but the applicability in fabrication of integrated circuits, magnetic recording devices, multilayer structures and micro-electro-mechanical-systems (MEMS) [53] are the reasons for recent upsurge.

Study of nanoscale confinement of materials was initiated through thin films. Physical vapor deposition (PVD) (thermal evaporation, sputtering, laser ablation), chemical vapor deposition (CVD) (plasma enhanced (PECVD), metal-organic (MOCVD), atomic layer (ALD)), electrodeposition (ED), and solution-phase deposition (SPD) (spin and dip coating, spraying, printing) are the main deposition techniques used for thin films. Due to the complexity of CVD process, there is a high possibility of introducing contaminants compared to PVD. In addition to that, relatively high temperatures and high toxicity and volatility of precursors have demanded the extensive control of engineering, but the conformality of the deposition profile is outstanding with respect to PVD [54]. Contamination of nonmetallic (N, O) elements in the deposition is the main drawback observed in ED and SPD, but the capability of filling vias is an advantage for all methods except PVD [54]. The unique capability of forming micro or
nano structures into irregular surfaces or high aspect ratio structures from ED is the vital attraction toward the device fabrication in current and future technology, but the requirement of conductive substrate for ED is the major difference among other methods.

*Figure 2-1* a) schematic of metal- solution interface for Grahame triple-layer model and b) schematic of resultant electronic and ionic currents at the metal electrode respect to the over potential ($\eta$).

In electrodeposition, cations in the electrolyte will be reduced into corresponding elements ($A^{n+} + ne^- \rightarrow A$) to form thin or thick depositions at the cathode under applied potential through two/three electrode cell. Electrolyte is an ionic solution which consists of precursors of the deposition and can be acidic or base. Normally, the three electrode cell with working (WE), counter (CE), and reference (RE) electrodes is the convenient configuration for controllable elemental reductions at the cathode [53]. Elemental reduction occurs at the WE and the selection of the conducting substrate for WE depends on the experimental preference. However, the RE can be selected from the set of standard...
REs, mainly depending on the selected voltage range, pH, and temperature. General selection of CE is an inert electrode which can be an electron source or a sink, and platinum is the common candidate, but sacrificial CE can also be used in special occasions when stabilization of the electrolyte concentration is needed. Electrodeposition can be performed under constant direct current (DC) potential (potentiostatic) or current (galvanostatic), or non-DC periodic or pulsed source [55].

Formation of the electrode-electrolyte interface occurs soon after electrodes immersed in the electrolyte. In order to explore the kinetics and mechanics of the electrodeposition, knowledge of the metal-solution (electrode-electrolyte) interface is important [53, 55, 56]. Considering the formation of ionic layers at the vicinity of electrode due to hydration and rearrangement of ions, Helmholtz, Gouy-Chapman, Stern, and Grahame have modeled the system analogous to capacitors [53]. However, the Grahame’s triple-layer model shows an improvement with respect to the experiments [53], and according to that, two distinct closest approach planes, inner and outer Helmholtz planes, are possible with respect to the hydration of ions (Figure 2-1a), and anions can become dehydrated and reach closer to the electrode than cations. Once the interface comes to the equilibrium, reversible cell voltage (E) can be found from the Nernst equation (equation 1) [53, 55, 56], where $E^0$, R, T, z and F are the standard electrode potential, gas constant, temperature, number of electrons involved in the reaction, and Faraday’s constant, respectively. Nernst equation is a thermodynamic derivation from free-energy change, and reaction reversible potential can be changed by relative concentration of the reactants and products, temperature, and pH.
\[ E = E^0 + \frac{RT}{zF} \ln \frac{[\text{Reactants}]}{[\text{Products}]} \]

Contribution for the current is from both electrons, which moves due to ongoing reduction or oxidation reactions, and ions. At the equilibrium, current passing through the metal-solution interface will be equal and opposite. Therefore, the net current through the electrode can be observed once interface deviates from the equilibrium, and this external current is due to the over potential contributed from four rate-control partial reactions, charge-transfer, diffusion, chemical reaction, and crystallization [53]. Transferring charge carriers across the interface can be directly influenced by electrode potential, therefore the rate of charge-transfer reaction is determined by electrode potential [53]. Mass transportation from the electrolyte bulk to the interface and vice versa is due to diffusion, migration and convection, but the diffusion is the main among those and the rate defined from concentration gradients, moreover migration allows ions to drift due to potential gradient and convection moves substances due to density gradients [55, 57]. Both the chemical reaction ongoing at the solution and surfaces and crystallization, incorporation or removal of atoms from crystal at the metal/metal-ion interface, are rate controlling reactions [53]. With the consideration of above details, if charge-transfer is the rate determining step, when system departs from the equilibrium, net current density \( i \) and charge transfer over potential \( \eta \) is given from Butler-Volmer equation (equation 2), where, \( I \) and \( \alpha \) are exchange current density and transfer coefficient, respectively. Figure 2-1b schematically shows the resulting of net current density to be cathodic or anodic for both electronic and ionic carriers depending on the over potential, \( \eta \).
If mass transportation is the rate determining step, net current density can be simplified by Nernst diffusion layer-model, which consider a diffusion layer sandwiched between electrode and electrolyte bulk with a thickness of $\delta$ [53, 55-57]. Due to the reactions taking place at the electrode, surface depletion of the substance will occur and the formed concentration gradient assumed to be linear within the diffusion layer. Therefore, the net current density ($i$) will be inversely proportional to the thickness of depletion layer ($\delta$) as given in Equation 3, where, $D_{A^2+}$, $c_{bulk}$ and $c_{x=0}$, are diffusion coefficient and concentrations at the boundaries of $\delta$ for reducing ion, respectively. Moreover, attaining the steady-state diffusion due to maximum concentration gradient ($c_{x=0}$) will direct to the limiting diffusion current density ($i_L$), where reduction species will be reduced soon after reaching the electrode. Therefore, the deposition current density versus applied potential initially grows exponentially due to the charge-transfer from the reductions but get limited from mass transport for increasing potentials.

$$i = i_0 \left[ \exp \left( \frac{(1 - \alpha)zF\eta}{RT} \right) - \exp \left( - \frac{\alpha zF \eta}{RT} \right) \right]$$

$$i = i_0 \left[ \exp \left( \frac{(1 - \alpha)zF\eta}{RT} \right) - \exp \left( - \frac{\alpha zF \eta}{RT} \right) \right]$$

In order to electrodeposit two or more species to form an alloy compound, the possibility of codeposition needed to be explored. As stated above, the reversible potentials for any elemental reduction can be calculated from Nernst equation. This provides information regarding the required potential to trigger the deposition, unfortunately in most cases required species do not reduce at a common potential. For instance $\text{Cu}^{+2}/\text{Cu}$ and $\text{Zn}^{+2}/\text{Zn}$ reduction happens at 0.34 [58] and -0.76 V (NHE) [59], respectively. Interestingly, this can be overcome by selection of a complex forming
species to alter the relative active concentrations in the electrolyte to force the deposition to trigger at a common potential [55]. Therefore, the addition of cyanide has formed complexes to deposit Cu-Zn alloys about -1.3 V (NHE). Under potential and induced deposition are also two different phenomena can take place to form alloys from species which do not have a common elemental reduction potential, and for instance, codeposition of CdTe [60] and SbTe [61] can be considered, respectively. Limited introduction which will be sufficient for the scope of this study was provided from the detailed references [53, 55, 56] from the electrodeposition of semiconductors.

From GST ternary Te is the most studied element in electrodeposition, and the possible redox couples for aqueous Te are available in Pourbaix diagrams (potential-pH) [62]. Hall and Koenig [63], Schwarz and co-workers [64], and Fink and Dokras [65] have attempted elemental Ge electrodeposition by aqueous alkaline baths, but due to hydrogen evolution on Ge surface, deposition was extremely limited. Elemental Sb electrodeposition is possible from several methods [66], and has also achieved from aqueous chloride baths [67]. To fulfill the material synthesis in this dissertation, multiple electrodeposition setups were used as listed below.

- Princeton Applied Research / EG&G Model 273A Potentiostat/Galvanostat – Ohio University
- BASi Epsilon Potentiostat/Galvanostat – CNM, Argonne National Lab

2.1.1.1 Working Electrode for Thin Films

For thin film (TF) electrodeposition Au or Pt coated glass slides were used as the working electrodes. 300-500 nm thick Au(Pt) has been sputtered on typically #0 and #1
glass slides as shown in Figure 2-2a using a DC magnetron sputtering system (Denton Vacuum 502A) under 8 mT for 2 min. Then small pieces of sputtered glass with preferred size were separated using a diamond scribe and RCA cleaned prior to use as WEs.

Figure 2-2 a) Images of Pt/Au WE for TF electrodeposition and images of b) before and after Au coating for AAO and c) front and back view after proper insulation for NW WEs, and images of contact pad preparation steps for NW WE to be used in 4PRM.
2.1.1.2 Working Electrode for Nanowires from Commercial Templates

For the growth of nanowires (NW) by electrodeposition, anodic alumina (AAO) templates with a range of pore diameters (18-220 nm) were used (Figure 2-4 and Appendix E:). These AAO templates were purchased by commercial suppliers (Whatman International and Synkera Technologies, see Table 2) and modified to satisfy the experimental needs. Figure 2-2b shows the apparent differences of the commercial AAO templates before and after Au coating. Due to the brittleness of AAO templates, a piece of Cu tape was attached to the Au coated side of the template to have an easier contact to complete the circuitry. Then the entire Au coated side and circumference of the AAO template were carefully electrically insulated to assure the nanowire growth to take place from the uncoated side through the channels once it dipped in the electrolyte. To extend the understanding of modification, completely modified WE electrode for NW growth is shown in Figure 2-2c.

Unlike the WEs prepared for the regular NW synthesis, a special procedure has to be followed when the synthesized NWs are subject to 4PRM measurements. Since in the 4PRM experiments, samples will undergo thermal ramping and therefore must be compatible with that process. Complexities arose from the removal of back insulating polymer coating, so acquiring clean pieces of in-matrix NWs was highly unlikely. Mechanical or chemical removal attempts have damaged or contaminated the samples of interest. Therefore, a modified Au contact pad was designed not only to establish good electrical contacts but also to minimize the polymer in-contact of the template. After the successful growth of NWs, AAO template edges with adhesive polymer can be easily
scribed out to acquire undamaged and uncontaminated in-matrix NW template, which is extremely important for thermal characterization using a method similar to the 4PRM. As shown in Figure 2-2d final 4PRM NW WE can be prepared following a few steps. To selectively sputter Au contacts on to a thick microscope glass slide, first scotch tape was used to completely cover the top side of the glass slide and then the selector was used to remove the scotch tape to select the exposing area of the glass surface. After Au sputtering, the remaining scotch tape can be detached to realize the Au contact pad to attach the AAO template. As highlighted earlier, each and every step has to be performed very carefully to fabricate a usable WE by ensuring that the NW growth will take place only through pore channels.

<table>
<thead>
<tr>
<th>Commercial Supplier</th>
<th>Pore Size (nm)</th>
<th>Pore Length (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whatman International</td>
<td>220 and 20-200</td>
<td>50</td>
</tr>
<tr>
<td>Synkera Technologies</td>
<td>18, 35, 55, 80, 100 and 150</td>
<td>40</td>
</tr>
</tbody>
</table>

2.1.1.3 Working Electrode for Nanowires from Home-made Templates

AAO membranes were prepared by the well-established two-step anodization procedure [68]. Aluminum (Al) foils (99.99% purity, ESPI Metals Inc.) were ultrasonically degreased for 20 min in regent EtOH. Then the Al foils were dipped in 1.5M NaOH for 4 min and subsequently 1.5M HNO₃ for 2 min and thoroughly rinsed out with deionized water. The remaining water was removed by an air blower. Proper thermal treatment was necessary for the purpose of grain size enhancement of the Al foils. This was achieved by annealing the Al foils at 420 °C for 4 hours. Then the foils
were electropolished with a mixture of HClO$_4$ and ethanol solution at 0.2 °C for 10 min under 10 mA/cm$^2$ current density to improve the surface quality. One side of the Al foil was covered by a polymer coating to avoid reaction during the growth of the AAO template. The first-step anodization was performed on the Al foils for a couple of hours at 3°C and 40V of D.C. voltage using 0.3M oxalic acid [69], and schematic anodization circuitry is shown in Figure 2-3a. Then the created AAO layer was completely removed by dipping in H$_3$PO$_4$ acid for 30 min at 60°C. The second-step anodization was performed on the leftover dimples from the first-step anodization at 3°C with 40V of D.C. voltage for 30 min to attain hexagonally arranged porous structure. Alumina barrier thinning procedure [70] was performed just after the second-step anodization by reducing the voltage from 40V to 4V at a constant rate of 1V per min. The purpose of the thinning process was to break the alumina barrier between the Al layer and the pore channels. After that, the samples were cathodized at -5V for 5 min in a 0.5 M KCl solution and subsequently cathodized at -5V for a few minutes in distilled water for final cleanup. SEM micrographs of some of the acquired templates are shown in Figure 2-4, and pore diameter can be decreased or increased by selecting different acidic electrolytes.
Figure 2-3 Schematic of AAO template fabrication circuit and b) different fabrication stages of sample.

Figure 2-4 SEM micrographs of a), b), and c) commercial and d), e), and f) home-made AAO templates. Insets are low magnifications of the same micrograph.
2.1.1.4 Automation of Potentiostat/Galvanostat

Due to the limitations experienced in data acquisition of Princeton Applied Research / EG&G Model 273A Potentiostat/Galvanostat a significant modification was performed by establishing a proper read-in communication through LabVIEW programming. Earlier instrument was limited to PowerCV (Cyclic Voltammetry Software) measurements; however with this new implementation chronoamperometry and chronopotentiometry became possible without purchasing the instrument software for PowerSTEP. Since this program is capable of reading the raw data of the instrument through GPIB interface, output of any function of commands given by the front panel can be acquired through an array. Therefore, depending on future experimental needs, this program could be carefully implemented to replace other instrumental software such as PowerCORR (Corrosion Measurement Software) and PowerSINE (Electrochemical Impedance Software). Currently, the instrumental front panel is not integrated into the LabVIEW program, so the specific conditions and initiation have to be given only from the instrumental front panel, and then the data acquisition can be initiated through LabVIEW. Additional information about LabVIEW program is provided in Appendix D: Especially, with respect to the focus of this dissertation, these chronoamperometry curves or current-time curves provide immense information about the thin films and nanowire growth, which is crucial not only to understand the controllable growth mechanism but also to distinguish any abnormalities during the growth.
2.1.2 Sputter Deposition

Sputter deposition is a physical vapor deposition method commonly used in industry for thin film deposition [71]. In a basic sputtering setup target will be placed at the cathode and positive ions generated from the glow discharge will be accelerated towards the cathode to sputter out the target atoms through momentum transfer. These ejected atoms then get deposited on the substrate material as a thin film deposition [72]. Typical ionization gas is Argon and there are three sputtering methods known as direct current (DC), magnetron and radio frequency (RF) sputtering. However, the magnetron sputtering is more efficient over conventional dc sputtering due to its high ionization efficiencies and low operating voltages [71]. Regardless of the efficiency of magnetron sputtering, non-conducting target can be only sputtered with RF sputtering [73]. To fulfill the material deposition in this dissertation multiple sputtering systems were used as listed in below.

- D 502A Denton Vacuum DC Magnetron - Ohio University
- Home-made RF Magnetron - Ohio University
- Pelco SC4 DC Magnetron- Ohio University
- Emitech K675X DC Magnetron-CNM, Argonne National Lab

2.2 Material Characterization

2.2.1 Energy Dispersive X-ray Spectroscopy (EDX)

Continuum and characteristic X-ray generation is obvious in electron beam microscopy due to electron beam- specimen interactions. These continuum (Bremsstrahlung) and characteristic X-rays are generated due to deceleration of beam
electrons through Columbic interaction and ejection of inner shell electrons from specimen atoms, respectively. Once these X-ray photons are generated from the specimen, they can be detected with respect to the charge (photon will create electron hole pair) intensity from a cooled solid state semiconducting detector (Si(Li), HPGe), and converted into a voltage pulse using charge-voltage converter [74]. Finally, the spectrum can be analyzed from a computer X-ray analyzer after voltage pulse amplification. Generally, the range of energy used in scanning and transmission electron microscopy is capable of exiting more important characteristic X-rays of L and M, and complete K, L, and M shells, respectively, and these exited peaks will lead for important quantitative microanalysis of the specimen composition [74]. Calibration of the system is important for the accuracy and can be done using known specimens. After EDX spectral acquisition, characteristic peak-match can be done using sophisticated software (WinXAS) to find the area of the maximum peak intensity, which is related to the composition. Then, composition can be evaluated after reduction of effects due to atomic number (Z) and X-ray absorption (A) and florescence (F) [74] using a software (CITZAF). Especially, when exploring a specimen which has overlapping X-ray peaks (Sb and Te L lines) pure elemental spectra is important to find peak positions for the overlapped spectrum. Systematic approach of resolving the SbTe characteristic peaks for accurate compositional analysis is shown in 0. Moreover, depending on the specimen whether it is bulk, thin film or nanowire, electron diffusion length get limited and high spatial resolution and low ZAF correction can be observed for thin films relative to bulk. More conveniently, sufficient X-ray excitement can be done with careful selection of the
voltage and the accurate voltage selection can be gained by simulating the electron–
 specimen interaction using available software (electron flight simulator, DTSA).
Moreover, instead of probing the entire area shown in the screen, more localized probing
can be performed using NORAN System SIX™ X-ray microanalysis software to enhance
the understanding of the specimen.

2.2.2 Electron Microscopy (EM)

Beyond the limits of human eyes and even further which optical microscopy
reaches its limitation due to the diffraction, there is an extremely interesting technique
called electron microscopy which can be used to visualize and characterize matter with
few molecule-scale to atomic-scale resolution. Practical use of the de Broglie’s concept
of wave particle duality promoted the effective ideas to utilize these energized electrons
to break the limits of resolution [35] and currently it has developed into two main
branches known as scanning and transmission electron microscopy. Complete details of
theory and methods of this well established technique can be found elsewhere [35, 36,
75] therefore, only relevant details are outlined here.

2.2.2.1 Scanning Electron Microscopy (SEM)

SEM provides various capabilities to observe and characterize the specimen by
detecting diverse signals emerging after electron beam-specimen interactions. In this
excellent technique, beam of electrons were accelerated towards a specimen, and
outcomes of electron beam-specimen interactions were detected as secondary electrons
(SE), backscatter electrons (BSE), and foreshadow electrons, cathodoluminescence, and
scanning transmission electrons and energy dispersive X-rays (EDX), wavelength
dispersive X-rays, electron backscatter diffraction signals to acquire information of
topography, composition, crystal orientation, electric and magnetic field and composition
and structure of the specimen, respectively. Therefore, SEM is playing a main role in a
wide range of fields such as material science, life sciences, electronics, geology, natural
resources, industry and research [36]. Moreover, relatively large to small specimens from
insulating to conducting or semiconducting can be studied with respect to diverse aspects
by utilizing this relatively user friendly and convenient instrument. To fulfill the material
caracterization in this dissertation multiple SEMs were used and listed below.

- JEOL JSM-5300 SEM - Ohio University
- JEOL JSM-7500F FES/TEM - CNM, Argonne National Lab
- Hitachi S2460N NSEM - Ohio University
- Hitachi S4500 FESEM - Ohio University

2.2.2.2 Transmission Electron Microscopy (TEM)

TEM pushes the resolution limit even further to atomistic resolution. The concept
remains the same as SEM, but electrons are energized into much higher energies (100-
400 keV) to shrink the electrons wavelength even further. In the field of nano-
caracterization TEM plays a significant role by imaging, measuring, modeling, and
manipulating matter to satisfy the scientific needs [75]. Especially, the sample
preparation should be handled very carefully since electrons have to transmit through the
sample, so sample thickness should be comparable to the mean free path of electrons.
Main modes of the usage are imaging and diffraction, but functionalizing the sample
grids have extended the usage for in situ characterization [76]. To fulfill the material characterization in this dissertation multiple TEMs were used and listed below.

- JEOL JEM-1010 TEM - Ohio University
- JEOL JEM-2100F - CNM, Argonne National Lab
- FEI CM30T AEM – EMC, Argonne National Lab

2.2.3 X-ray Diffraction (XRD)

Interaction between monochromatic X-ray photons with matter is greatly used to reveal the structural information of a sample by considering the satisfaction of Bragg’s law, \(2d \sin \theta = n\lambda\), where \(d\), \(\theta\), \(n\) and \(\lambda\) are diffraction plane spacing, incident angle, diffraction order, and X-ray wave length, respectively. When the sample atoms have long range periodicity (crystalline), X-ray photons will constructively scatter from atomic planes (Bragg’s planes) resulting high intensity peaks [77]. XRD pattern for the sample can be collected by sweeping through a range of scattering angle (\(\theta\)) to excite different \(d\) s, and structure can be determined by matching with known standards from international center for diffraction data (ICDD).
Table 3 Comparison of structural parameters for crystalline GeTe, Sb$_2$Te$_3$, and Ge$_2$Sb$_2$Te$_5$. Where, [78]$^+$, [79]$^+$, [80]$^\#$, [81]$^\%$, and [82]$^@$.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>GeTe</th>
<th>Sb$_2$Te$_3$</th>
<th>Ge$_2$Sb$_2$Te$_5$</th>
<th>Ge$_2$Sb$_2$Te$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure</td>
<td>Distorted RS</td>
<td>RH layered</td>
<td>Stable HEX</td>
<td>Meta-stable RS</td>
</tr>
<tr>
<td>Space group</td>
<td>R3m</td>
<td>R-3m</td>
<td>-</td>
<td>R-3m</td>
</tr>
<tr>
<td>Anion sites</td>
<td>Te atoms ABCABC [0001]</td>
<td>Te atoms ABCBCACAB [0001]</td>
<td>Te atoms ABCABC [0001]</td>
<td>Te atoms ABCBCA [0001]</td>
</tr>
<tr>
<td>Cation sites</td>
<td>Ge atoms</td>
<td>Sb atoms &amp; vacancies at inter blocks</td>
<td>Ge &amp; Sb atom, &amp; vacancies at inter blocks</td>
<td>Ge &amp; Sb atom, &amp; vacancies</td>
</tr>
<tr>
<td>Bonds/length (Å)</td>
<td>3 Te-Ge: 2.85 (2.80)$^+$, 3.26 (3.13)$^+$</td>
<td>Center: 6 Te-Sb: 3.03 (2.89)$^+$</td>
<td>Te-Ge: 2.87, 3.23</td>
<td>Te-Ge: 2.87, 3.24</td>
</tr>
<tr>
<td></td>
<td>3 Te-Ge: 3.26 (3.13)$^+$</td>
<td>Edge: 3 Te-Sb: 3.20 (2.87)$^+$</td>
<td>Te-Sb: 2.97, 3.30</td>
<td>(2.83, 3.15)$^+$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Te-Sb: 2.96, 3.30</td>
<td>(2.91, 3.20)$^+$</td>
</tr>
<tr>
<td>$a_0$ (Å)</td>
<td>4.23 (4.17)$^#$</td>
<td>4.34 (4.26)$^+$</td>
<td>4.27 (4.22)$^@$</td>
<td>4.27 (4.26)$^@$</td>
</tr>
<tr>
<td>$c_0$ (Å)</td>
<td>3.64 (3.54)$^#$</td>
<td>10.43 (10.15)$^%$</td>
<td>17.89 (17.24)$^@$</td>
<td>18.36 (17.40)$^@$</td>
</tr>
<tr>
<td>Angle (°)</td>
<td>RH:57.69 (58.36)$^#$</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Theoretical study by Da Silva and co-workers [83] has provided a solid foundation for crystalline structure of GeTe, Sb$_2$Te$_3$ and Ge$_2$Sb$_2$Te$_5$ by first–principle calculations with reasonable agreement to experiments, and the corresponding crystalline structures are shown in Figure 2-5 with respect to conventional hexagonal lattice.

Moreover, Table 3 shows the calculated and experimental (given in parenthesis, if available) structural parameters for the GeTe, Sb$_2$Te$_3$ and Ge$_2$Sb$_2$Te$_5$. The most common feature was two bond lengths caused by Peierls-type bond dimerization and influenced by
different covalent radii. Formation of super lattices is also interesting, but for GST with Ge/Sb ≥ 1, Ge and Sb intermixed planes are energy minimized structures than unmixed planes due to aspiration of having Te atom surrounded by three Ge and Sb atoms [83]. In addition to that, existence of vacancy layers between blocks, except GeTe, also increase the complexity of structures. Similarly, with the increase of Sb concentration for Sb-Te compounds, subunit of Sb with distorted RS will be added to the basis, Sb$_2$Te$_3$ distorted subunit [78]. To fulfill the material characterization in this dissertation, multiple XRD instrumentations were used and listed below.

- Rigaku MiniFlex II- Ohio University
- SAXSess Small Angle Scattering System – Ohio University

*Figure 2-5 Left to right: Crystal structures with respect to conventional hexagonal lattice (dotted lines) of GeTe distorted rock salt (RS), Sb$_2$Te$_3$ rhombohedral (RH) and rock salt, and Ge$_2$Sb$_2$Te$_5$ stable hexagonal (HEX) and meta stable rock salt. Stacking sequence of A (0, 0, z), B (2/3, 1/3, z) and C (1/3, 2/3, z) respect to (1 × 1 × n) unit cell [83].*
2.2.4 Extended X-ray Absorption Fine Structure (EXAFS)

Allowing X-rays to excite a photoelectron through core-level absorption provides an excellent probe to explore the disordered (amorphous) structures. Identical energy edges for atomic core-levels facilitate to excite photoelectrons selectively in order to sense the local environment of the atom through interference [84]. Except the pair distribution function, which can be used to extract structural information from the diffused diffraction pattern, diffraction techniques are limited to ordered structures. Especially, the common crystalline distortion observed for the elements interested in this study enhances the importance of above introduced X-ray absorption fine structure (XAFS) to reveal crystalline phase in addition to amorphous phase. Acquired XAFS spectrum shows the quantum mechanical interference of the outgoing photoelectron from the exited edge site, and can be divided into two: X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) [84].

Table 4 Comparison of structural parameters for amorphous GeTe, Sb₂Te₃, and Ge₂Sb₂Te₅. Where, [78] *, [85] †, and [86] ++

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Amorphous GeTe *</th>
<th>Amorphous Sb₂Te₃ †</th>
<th>Amorphous Ge₂Sb₂Te₅ ++</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bonds/length (Å)</td>
<td>Te-Ge: 2.60</td>
<td>Sb-Te: 2.86</td>
<td>Te-Ge: 2.60</td>
</tr>
<tr>
<td></td>
<td>Te-Sb: 2.83</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coordination number</td>
<td>Ge: 3.30</td>
<td>Sb: 2.8</td>
<td>Ge: 3.85</td>
</tr>
<tr>
<td></td>
<td>(Ge-Te &amp; Ge-Ge)</td>
<td>Te: 2.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Te: 2.20</td>
<td></td>
<td>Sb: 3.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Te: 1.99</td>
</tr>
</tbody>
</table>

XANES is from multiple scattering of photoelectron, and it probes the local structure beyond the first-nearest neighbor, bond angle for mutual atoms, and density of
unoccupied-conduction states. EXAFS is more localized than XANES, and average coordination number, bond lengths, bond length disorder parameter or mean square relative displacement (MSRD), and chemistry of neighboring atoms can be investigated with respect to a chosen element [78, 85, 86]. Table 4 shows the structural parameters for amorphous GeTe, Sb$_2$Te$_3$, and Ge$_2$Sb$_2$Te$_5$ [78, 85, 86].

2.2.5 *Four Point Probe Measurements (4PPM)*

In order to explore the electrical transport properties of bulk, thin films or nanowires four point probe measurement has proven to be a convenient method [87, 88]. Even though there are multiple methods available for resistivity measurements, selection should be according to the type of material, magnitude of the resistance, shape, and thickness of the material. For semiconducting thin or flat samples, four point collinear probe (4PCP) method can be considered. In this 4PCP method, four equally spaced probes brought into contact as shown in *Figure 2-6*, and a DC current (I) was passed through outer probes to measure the relative voltage drop (V) between inner probes. According to the derivation shown in Smits [88], sheet resistance ($\sigma$) can be found using equation 4, if I and V are known, where k is the correction factor based on the ratio of the probe to wafer diameter and on the ratio of wafer thickness to probe separation [89]. However, the measured resistance (V/I) is proportional to the sheet resistance and especially in our study the focus is to probe the relative resistance change with respect to the temperature, so the measured resistance is sufficient to satisfy our experimental demands.
\[ \sigma = \frac{\pi \ V}{\ln 2 \ I \ k} \]

*Figure 2-6* Schematic of 4-point collinear probes in contact with unknown flat resistive surface.

### 2.2.5.1 Design and Development

Cost-effective home-made 4-probe resistivity measurement (4PRM) setup was designed and developed due to the extreme interest in creating an industrial-standard setup by initiating from scratch. As shown in *Figure 2-7a* this 4PRM setup is capable of performing electrical transport and phase transitional measurements for both thin films and nanowires under multiple configurations, 4-wire, 2-wire, pseudo 4-wire, and I-V with temperature, pressure and ambient control. Moreover, through LabVIEW programming data acquisition and real time data graphing have been automated for convenience of the user.

Main chamber consists of 4-probe contacts, heating resistors, thermocouple and thermometer, and stage. 4-probe contacts are round tip pogo pins with length, travel
distance, and head size 33mm, 6.5mm, and 1.3mm respectively. These were specifically selected to minimize the sample damage when making connections and to facilitate an easier connection to the PCB. As shown in Figure 2-7b, 4 pogo pins were connected to a stack of PCB in collinear configuration with 3mm spacing. Stacked PCB not only reinforces the pogo-pin connections but also stabilizes the initial contacts of the sample throughout the measurement, and this is extremely important to enhance the signal to noise ratio. Heating requirement for the setup was satisfied by using two series resistors (Dale Rh-50-2Ω and 50w) stacking them vertically. Stacking configuration of resistors was used to minimize the temperature gradients observed in temperature profiles (not shown here) of the surface of top resistor. Effective heating from the bottom resistor promote more uniform temperature at the top surface where sample will be placed. It is always beneficial to use the minimum sample size possible to minimize the temperature gradients to impose the conditions for a thermal reservoir with respect to the sample. From the thermal profile studies of the surface, the best placement of the sample is at the center of the 15mm by 50mm top surface and perpendicular to its length. K-type thermocouple (TC) and Pt100 resistance temperature detector (RTD) were used to probe the surface (sample) temperature and resistor heating, respectively. Stage is a stainless steel platform which supports the above mentioned upper structure. More importantly, upper-stage structure sections were connected through ceramic interconnects to thermally isolate the upper structure (Figure 2-7c).

Schematic connection of the entire 4PRM setup is shown in Figure 2-8. After proper placement of the sample, PCB stack with 4 probes were vertically lowered and
connected to the sample (*Figure 2-7b*). Prior to performing measurements, the chamber was flushed a few times with N\textsubscript{2} to enhance the vacuum, and under current conditions, the vacuum could be lowered to 150 mT. In order to initiate the measurements both the LabVIEW program and the heating controller have to be started. Heating of the resistor is completely controlled by the TCU50 temperature control unit from Anton Paar relative to the RTD feedback. First, 4-wire and TC signals are fed into the Keithley 2000-20 Scan Card to properly channel them to the multi-meter. Then, the multi-meter communicates with LabVIEW program through the GPIB interface to display the acquired data. Relevant information about the LabVIEW program is provided in Appendix C: for reader’s convenience.

*Figure 2-7* Actual 4PRM setup a) in function b) under pseudo 4-wire configuration for NW measurements and c) close-up of inside chamber, highlighting the thermal isolation using ceramic connects.
Temperature calibration for the 4PRM setup is shown in Figure 2-9. Surface thermocouple has placed on the resistor surface at the vicinity of the sample with proper thermal contact, so that under the current setup standard sample temperature can be increased to 220 ºC. The discrepancy of the temperatures in control unit and the sample is due to the relative locations of the temperature probes. For safety concerns, RTD which communicates with the temperature controller unit is embedded in the resistor, so it always measures a higher temperature than the surface TC. To understand the worst possible temperature gradient in vertical direction, which sample could suffer with the current probing configurations, TC was placed above the sample on another silica piece with improper thermal contact, and the corresponding temperature variation is always lower than the surface temperature as expected.
Figure 2-8 Schematic connection diagram of 4PRM setup.
2.2.5.2 Thin films and Nanowire Configurations

For electrical transport and phase transition studies of thin films and nanowires, two different configurations can be used to establish sample-probe contacts. For thin films, it is more common with a 4-wire collinear configuration (Figure 2-10a), but for nanowires it is pseudo 4-wire configuration (Figure 2-10b). Especially for thin films the measured resistance is the resultant of top semiconducting (Sb-Te) and bottom conducting (Au) bilayer and the schematic parallel-resistor consideration is shown in Figure 2-7c. However, for the nanowires the measured resistance is simply the series-resistor consideration (Figure 2-7d). Under pseudo 4-wire configuration, this home-made 4PRM setup is currently capable of in-matrix nanowire characterization, but not limited to modification of different techniques depending on the requirements. As shown in Figure 2-12, in-matrix NW samples were carefully placed in between two Al contacts to
perform the measurements under pseudo 4-wire configuration. From overall experiments, this way of contacts provided the best signal to noise ratio for in-matrix NW characterization. Approximate size of the sample was 1mm × 1mm to minimize any related temperature gradients. Top and bottom contacts were made in a way to minimize the sample contact to avoid any short circuitry. Especially, the bottom contact was made out of Al sample pan used in differential calorimetry to assure the proper thermal contact to both heating surface and sample. Top contact also made out of electro polished Al, but has reinforced by a piece of copper to avoid bending due to the forces acting on it from the probes.

As-deposited Sb-Te exhibits a relatively high resistance (MΩ) due to its amorphous structure. Therefore, initially the measured resultant resistance is dominated by Au signal, but after phase transition of Sb-Te, the signal is overtaken by Sb-Te due to its low resistance when crystallized. To enhance the understanding of typical resistance vs temperature, the acquired curve is shown in Figure 2-11a for thin films. The most significant change of the resistance takes place at the peak point and the corresponding temperature can be considered as the phase transition temperature for Sb-Te. Resistance of conductors and semiconductors with respect to temperature is given according to the equation 2 & 3; however the modeled bilayer resistance is only capable to confirm the overall shape of the typical measured curve and that is due to actual limitation of determining the cross sections for the current paths through this bilayer. Unlike the thin films, nanowires show the typical semiconductor resistance change with respect to the temperature, and at the phase transition obvious change in its gradient can be seen as
shown in Figure 2-11b. To fulfill the material characterization in this dissertation multiple 4PRM setups were used and listed below.

- Home-made 4PRM setup- Ohio University
- 4-tip SEM Omicron UHV Nanoprobe - CNM, Argonne National Lab

*Figure 2-10 Schematics of a) 4-wire and b) pseudo 4-wire configurations for thin films and nanowires measurements and corresponding measured resultant resistance for c) thin films and d) nanowires. Contact pads and NW sample is shown for size comparison with a penny.*
2.2.6 Rutherford Backscattering Spectrometry (RBS)

RBS is an excellent non-destructive analytical method to study thin films or multi-layer thin films to extract the information about compositional depth profiles[90, 91]. In a typical setup, energized ions (alpha particles) were accelerated to collide or interact with target atoms of the sample. As a result of this interaction some alpha particles get backscattered elastically from the surface atoms and some penetrates into the depth by consuming its energy and then get backscattered. By acquiring theses backscattered alpha particles as a function of their energy, RBS can provide valuable
compositional information related to different sample depths [91]. Once the RBS spectra were acquired, corresponding analysis can be performed using RUMP [92] software package based on genplot. To fulfill the material characterization in this dissertation, RBS studies were conducted at the facility listed below.

- Ion beam analysis RBS system – Edawards Accelerator Lab, Ohio University

2.3 Material Theory

2.3.1 Switching Kinetics

Material property change due to the atomic arrangement is the key feature to use PCM in memory applications. So the basic understanding of the crystallization of amorphous material is crucial. Crystallization can be explained as a combination of two processes, crystal nucleation and crystal growth. If the crystal nucleation is initiated inside the substance, without any intervention of an alien substance, that is known as homogenous nucleation. However, if an alien substance plays a role such as an impurity or an interface, then that is known as heterogeneous nucleation [93].

Here only the sufficient details of classical nucleation theory [94-99] have been discussed according to the descriptive explanation given in Kalb [93]. Initially, the atoms are at liquid or amorphous phase and the thermal fluctuations trigger the tendency of crystal cluster formation. With the assumption of spherical shape of these clusters (Figure 2-13a), using Boltzmann statistics number of clusters at the equilibrium with radius $r$ is given from, where $\Delta G_{\text{cluster}}(r)$, $k_B T$, and $N_0$ the reversible work for crystal cluster formation, Boltzmann constant, absolute temperature, and the total number of atoms in the liquid of amorphous phase.
\[ N^{equ}(r) = N_0 e^{-\frac{\Delta G_{\text{cluster}}(r)}{k_B T}} \]

Figure 2-13b provides a quantitative glimpse of \( \Delta G_{\text{cluster}}(r) \) change with respect to the radius of crystalline cluster, when \( T \) is less than the melting temperature, \( T_m \). At critical radius of \( r, (r = r_c) \), \( \Delta G_{\text{cluster}}(r) \) reaches its maximum, so critical work for cluster formation \( \Delta G_{\text{cluster}}(r_c) = \Delta G_c \) can be written as,

\[ \Delta G_c = \frac{16\pi}{3} \left( \frac{\sigma^3}{\Delta G_{k,V}} \right)^2 \]

Where \( \Delta G_{k,V} \) and \( \sigma \) are Gibbs free energy change per unit volume between liquid or amorphous phase and crystalline phase and interfacial free energy per unit area, respectively. Moreover, when \( r < r_c \) cluster formation is energetically unfavorable, so the cluster-like formation undergo spontaneous decay. However when \( r > r_c \), cluster growth continues. With the contribution of previous work \([95, 96]\), the understanding of the cluster distribution was further enhanced and the formulation for steady state nucleation rate, \( I^{ss} \), can be written as,

\[ I^{ss} = s_c \times k \times N_0 \times \frac{1}{i_c} \left( \frac{\Delta G_c}{3\pi k_B T} \right)^{1/2} e^{-\frac{(\Delta G_c)}{k_B T}} \]

where, \( i_c, s_c, \) and \( k \) are number of atoms in the critical cluster, number of atoms in the surface of the critical cluster, and arrival rate of atoms from liquid or amorphous phase to critical crystalline cluster, respectively. Arrival rate of atoms, \( k \), can be considered under two limitations of crystallization kinetics, diffusion-limited and collision-limited, moreover still the medium is homogeneous and diffusion-limited so that refers to the local rearrangement to promote diffusive jumps through
liquid/amorphous-cluster interface other than a long-range diffusive field [97]. Diffusion-
limited crystallization is applicable to metallic alloys and ionic and covalent material as
well as phase-change material due to the necessity of rearrangements of neighbors and/or
coordination numbers [93]. Unlike the former, collision-limited crystallization promotes
atoms to move from liquid/amorphous to cluster through thermal vibrations, so this
scenario is common for pure metal or van der Waals bonded materials, but not for phase-
change materials [93]. Therefore, \( k \) for diffusion-limited and collision limited can be
written as,

\[
k = \frac{6D}{\lambda^2}
\]

\[
k = \frac{u_{\text{sound}}}{\lambda}
\]

respectively, where \( D, \lambda, \) and \( u_{\text{sound}} \) are diffusivity in liquid/amorphous phase, average
inter atomic distance, and sound velocity in liquid/amorphous phase, respectively. Using
Stokes-Einstein equation \( 3\pi\lambda\eta D = k_B T \), \( D \) can be replaced by \( \eta \), which is the liquid
shear viscosity and can be obtained experimentally. Then, for the diffusion-limited
crystallization, \( I_{ss} \) is

\[
I_{ss} = s_c \times \frac{2k_B T}{\eta \pi \lambda^3} \times N_0 \times \frac{1}{i_c} \left( \frac{\Delta G_c}{3\pi k_B T} \right)^{1/2} e^{-\left( \frac{\Delta G_c}{k_B T} \right)}
\]

As shown in Figure 2-13c, under heterogeneous nucleation [100, 101] due to the
existence of an alien phase, crystal cluster grows on the substrate as a spherical cap. \( \sigma, \)
l, \( s, c, \) and \( \theta \) denote the free interfacial energy, liquid, substrate, crystal, and wetting
angle respectively. Lower work for critical cluster formation and only in contact atoms
with alien substance can serve as nucleation sites are the main differences in
heterogeneous nucleation compared to homogeneous nucleation. If the in contact fraction of atoms, $\varepsilon$, (which is $\varepsilon \ll 1$), is known then using the same form of homogenous equation steady state nucleation rate for heterogeneous diffusion –limited nucleation can be given from,

$$I_{SS,het} = \varepsilon \times s_c \times \frac{2k_B T}{\eta \pi \lambda^3} \times N_0 \times \frac{1}{i_c} \left( \frac{\Delta G_c^{het}}{3\pi k_B T} \right)^{1/2} e^{-\left( \frac{\Delta G_c^{het}}{k_B T} \right)}$$

After nucleation the crystal growth can be continued in two means: interface-controlled growth and growth-controlled by long range diffusion. If no phase separation takes place, overall composition uniformity will retain, so liquid/amorphous-cluster interface become more crucial to promote diffusion-limited or collision-limited kinetics. However, atomic rearrangement frequency is independent of the interface position so that growth velocity is also time independent. Growth velocity, $u$, for diffusion-limited crystallization ($T \leq T_m$) observed in materials, such as, phase-change materials, given from

$$u = \gamma_s \times \frac{2k_B T}{\eta \pi \lambda^2} \left[ 1 - e^{-\left( \frac{\Delta G_{lc,atom}(T)}{k_B T} \right)} \right]$$

Where, $\gamma_s$ and $\Delta G_{lc,atom}$ are the fraction of sites where new atoms can incorporated and Gibbs free energy difference per atom between liquid/amorphous phase and crystal phase.
Overall, the phase-change materials are classified into two categories by mainly considering the dominated contribution of crystallization process, either nucleation or growth [102]. If the nucleation rate of a material is higher than the growth rate, that material is a nucleation–dominated material, similarly the other material is a growth-dominated material [3]. For further understanding corresponding differences are schematically shown in Figure 2-13d.
2.3.2 Phase Transition under Confinement

Excellence of the next generation PCM depends on the nature of phase transition between crystalline and amorphous phase. Therefore, the consideration of nanoscale confinement of PCM became the great interest to enhance its properties. Extensive discussions of effects of phase transition (freezing and melting) under confinement by Gelb et al [103], Christenson [104], and Alba-Siminesco et al [105] have provided insight to further enhance the PCM properties by confining the nanoscale confined PCMs over again. For instance, nanowires (1D nanoscale confinement of PCM) confined in AAO or silica matrix. Theoretical explanation for phase transition under confinement (capillary freezing/melting) can be explained thermodynamically [104]. Solid-liquid transition (melting) is the interest of the study since that can be considered as the mobility factor between crystalline and amorphous phase. With the consideration of both capillary-held solid-liquid equilibrium at a temperature below $T_m$, and cylindrical capillary pore with radius $r$, melting-point depression ($\Delta T$) can be derived using Clausius-Clapeyron and Kelvin equations (equation 12) [104]. Where, $\Delta H_f$, $V_l$, $V_s$, $\gamma_l$, and $\gamma_s$ are the enthalpy of latent heat of melting (fusion), molar volumes of liquid and solid, and surface energies of liquid and solid, respectively.

$$\Delta T = -\frac{T_m}{\Delta H_f} \frac{2}{r} [V_l \gamma_l - V_s \gamma_s]$$

This can be simplified into Gibbs-Thompson equation (equation 13) with the assumption of solid is wetted by its own melt ($\gamma_s-\gamma_l$ and $\gamma_{sl}$) and change in molar volume is neglected ($V_l=V_s=V_m$) at $T_m$. 

66
\[ \Delta T = \frac{2T_m V_m \gamma_{sl}}{r \Delta H_f} \]

Taking into account of the balance between bulk and surface free energy for solid and liquid, free energy difference is given from equation 14, where, \( A, \gamma_{li}, \gamma_{si}, V, \) and \( \Delta G_m \), are the total interfacial area, substrate-liquid and substrate-solid interfacial energy, total volume of confined material, and free energy of fusion, respectively.

\[ \Delta G = A[\gamma_{li} - \gamma_{si}] + V \Delta G_m \]

Therefore,

\[ \Delta T = \frac{A}{V} \frac{V_m T_m [\gamma_{si} - \gamma_{li}]}{\Delta H_f} \]

, and \( A/V \) is the geometrical factor of the confined solid, for instance, sphere and cylinder \( 3/r \) and \( 2/r \), respectively.
Chapter 3: Experiment

In order to provide an overall idea about the experimental procedure, more general details have been discussed here, but more specific information is clarified and elaborated under experimental section in each following chapters.

Electrolytes for the electrodeposition were prepared by dissolving precursors, SbCl$_3$, TeO$_2$ and GeO$_2$, in sodium citrate (NaCit), concentrated HNO$_3$, and concentrated H$_2$SO$_4$ solutions, respectively. Then the precursor solutions were mixed under agitation following the procedures described elsewhere [61, 106]. The final concentrations of each constituent were mixed according to the ratios tabulated below (Table 5 and Table 6). The pH value of the Sb-Te and Ge-Te final solutions were adjusted to 2.3 and 0.75, respectively by adding NaOH.

As shown in Figure 3-1 electrodeposition of Sb-Te thin films and nanowires, and Ge-Te thin films were carried out with traditional three-electrode cell using a potentiostat (Princeton Applied Research Model 273A). Au or Pt-coated glass slides and commercial (Whatman Anopore™ and Synkera™) and homemade AAO membranes were used as the working electrodes, and a platinum mesh and a saturated calomel electrode were used as the counter and reference electrodes, respectively. Au coated (~200nm thick) substrates for the thin films deposition were properly cleaned by rinsing thoroughly with de-ionized water and ethanol, and then thin films were deposited on substrate with effective area of 1 cm$^2$. Unless otherwise specified, throughout the thin film deposition, agitation (200rpm), current density (240 mC/cm$^2$), and electrolyte volume (80ml) were kept constant, and the resultant deposition was for 45s to achieve 70-125nm thickness of deposition. In order to
create a conductive path on the commercial AAO membrane, a thin layer of gold (~150nm thick) was sputtered on one side of the membrane and a piece of conducting copper tape was attached to the Au surface as an extension of the working electrode for an easy external circuit connection. To assure the nanowire growth inside the porous template, we completely covered the back Au surface with a polymer coating. For the homemade AAO, the unanodized Al foil was connected directly to the pore channels and thus can be used as a conductive path. A constant voltage of -600 mV was applied on the working electrode relative to the reference electrode, saturated calomel electrode (SCE), and the electrolyte was stirred by a magnetic stirrer at a constant speed of 200 rpm. The electrodeposition was conducted at room temperature and the aspect ratio of the nanowires was controlled by varying the deposition time.

![Figure 3-1](image)

**Figure 3-1** a) Laboratory thin film and nanowire electrodeposition setup and b) close-up of 3-electrode standard cell.

After thin films deposition, they were rinsed with de-ionized water and air dried for the characterization. Similarly, after the Sb-Te nanowires were formed inside the AAO template, the nanowire-template composite was dipped in a 1M NaOH solution for
few minutes to dissolve the AAO template. Then the exposed Sb-Te nanowires were ready for the characterization.

Table 5 *Relative precursor concentration and final pH of Sb-Te Electrolytes*

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>SbCl₃(mM)</th>
<th>TeO₂(mM)</th>
<th>NaCitrate(M)</th>
<th>HNO₃(M)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Pure Sb</td>
<td>15</td>
<td>0</td>
<td>0.21</td>
<td>1</td>
<td>2.3</td>
</tr>
<tr>
<td>2 Pure Te</td>
<td>0</td>
<td>15</td>
<td>0.21</td>
<td>1</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>5</td>
<td>0.21</td>
<td>1</td>
<td>2.3</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>12</td>
<td>0.21</td>
<td>1</td>
<td>2.3</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>9</td>
<td>0.21</td>
<td>1</td>
<td>2.3</td>
</tr>
<tr>
<td>6</td>
<td>7.5</td>
<td>7.5</td>
<td>0.21</td>
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<tr>
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<td>9</td>
<td>6</td>
<td>0.21</td>
<td>1</td>
<td>2.3</td>
</tr>
<tr>
<td>8</td>
<td>12</td>
<td>3</td>
<td>0.21</td>
<td>1</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Composition, morphology, atomic structure, and phase transition of thin films and nanowires were characterized by energy dispersive spectroscopy (EDS), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS), and 4-probe resistivity measurements (4PRM), respectively.

Table 6 *Relative precursor concentration and final pH of Ge-Te Electrolytes*

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>GeO₂(mM)</th>
<th>TeO₂(mM)</th>
<th>NaHCO₃(M)</th>
<th>HNO₃(M)</th>
<th>H₂SO₄(M)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 Pure Ge</td>
<td>10</td>
<td>0</td>
<td>0.21</td>
<td>1</td>
<td>1</td>
<td>0.75</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>0.125</td>
<td>0.21</td>
<td>1</td>
<td>1</td>
<td>0.75</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>0.250</td>
<td>0.21</td>
<td>1</td>
<td>1</td>
<td>0.75</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
<td>0.125</td>
<td>0.21</td>
<td>1</td>
<td>1</td>
<td>0.75</td>
</tr>
</tbody>
</table>
Chapter 4: Controllable Synthesis and Characterization of Sb-Te Thin Films

4.1 Introduction

As emphasized in section 1.2, Sb-Te binary not only plays a significant role as a PCMM but also utilizes in multiple non-memory related applications, such as thermoelectric, solar cell, etc. Synthesis of binary Sb-Te thin films can be achieved from numerous techniques such as sputtering [107-110], thermal evaporation [111, 112], molecular beam epitaxy (MBE) [113], metal-organic chemical vapor deposition (MOCVD) [114], hydrothermal synthesis [115], solvothermal synthesis [116], and electrodeposition (ED) [61, 106, 117-125]. In general, the sputtering is the most common technique and RF magnetron [110], DC and RF magnetron [109] and ion beam sputtered [108] Sb$_2$Te$_3$ thin films have been experimented to reveal the influences of thermal treatments to achieve high quality Sb$_2$Te$_3$. Even though the sputtering is the widely used technique, ED is a more cost effective method which facilitates many degrees of freedom towards the control over film thickness and uniformity, crystal structure, and deposition rate [76, 126]. Moreover, the strengths and advantages of ED with respect to MBE and MOCVD are also significant [127]. In addition to that, a capability of growing nanowires using templated ED method, in order to fulfill the future demands of high-density memory devices, has also been explored [128].

It has been previously reported that, Sb-Te was electrodeposited using alkaline [119, 124], acidic [61, 106, 117, 118, 121-123] and molten [120, 125] electrolytes. Leimkühler et al. demonstrated an ED method to precipitate polycrystalline Sb$_2$Te$_3$ into indium tin oxide (ITO), ITO/TO, fluorine-doped TO, ITO/CdS/CdTe, and Mo substrates.
using an aqueous, acidic, and heated bath. Range of compositions from Sb$_2$Te$_3$ to Sb was deposited and the observed structural changes were successfully explained by gradual structural evolutions with respect to the lattice constants. Yang et al. developed an electrochemical atomic layer epitaxy method to deposit nanocrystalline Sb$_2$Te$_3$ on Pt substrates utilizing under potential deposition (UPD) and discussed the electrochemical aspects and structural characterization of the deposits. Moreover, the optimization of the synthesis conditions by understanding the growth mechanism of crystalline Sb$_2$Te$_3$ on Si(100) [117], the concentration relationship of Sb and Sb and Te of the deposit on glassy carbon and Sb(III) and (Sb(III)+Te (IV)) molten salt bath for crystalline Sb-Te alloys [120], the deposition mechanism for high quality polycrystalline Sb$_x$Te$_y$ on Au/Ni/Si substrate with analysis of structural and electrical properties [123], the determination of deposition mechanism of Sb$_x$Te$_{1-x}$ on Au coated quartz crystals from nitrate-tartrate bath by various electroanalytical techniques [122], and the effect of post-deposition treatment, hot uniaxial pressing, of Sb-Te thin films on Cu and degree of crystallinity [129] were studied more or less focusing to obtain enhanced crystalline structure. However, Huang et al. reported deposition of pure amorphous Sb$_x$Te$_y$ on TiN/Si substrates at room temperature, and Sb deposition was found to be induced by Te. Induced deposition was discussed in detail and phase transition temperature for Sb$_2$Te$_3$ was found to be 120°C. Among the ED studies of Sb-Te, a few studies [122, 123, 125] have used the noble metal [130] surface (Au) to grow Sb-Te thin films, and demonstrated the interest to grow amorphous Sb-Te thin films [61, 121]. Moreover, for the best of our knowledge, no previous studies have investigated a wide range of electrodeposited Sb-Te thin films to
understand the actual compositional, morphological, structural and phase transitional trends to achieve more controllability over material synthesis. In this study we have electrodeposited Sb-Te thin films to represent the full range of compositions and explored the relations with respect to morphology, structure and phase transition. This study will shed light on controlled synthesis of Sb-Te alloys which are crucial in future device applications.

4.2 Experimental Procedure

Electrodeposition of Sb-Te thin films was carried out potentiostatically (Princeton Applied Research Model 273A) at room temperature (25°C) utilizing a traditional three-electrode cell. Glass slides (thickness #1) covered by DC sputtered (PELCO) gold with thickness of 500-800nm were used as the working electrode (5mm x 15mm), and platinum mesh (15mm x 15mm) and saturated calomel electrode were used as the counter and reference electrodes, respectively. To enhance the adhesiveness of gold on to the substrate, layer of Ti (<50 nm) was sputtered on to glass slide prior to the Au sputtering.

Especially, to cover an effective and safe range of voltage with respect to elemental reduction, voltages were changed from -0.55V to -0.85V relative to the reference electrode, and agitation (200rpm) and electrolyte volume (80ml) were kept as constants. With the demand of those conditions resultant deposition for 45s could achieve 70-125nm thickness on 1cm² effective area of deposition. Working electrodes were thoroughly rinsed by deionized water before and after the deposition. Different compositions and thicknesses of the deposition were achieved by changing the relative precursor electrolytes and deposition time, respectively.
Composition, morphology, atomic structure, and phase transition of Sb-Te thin films were characterized by energy dispersive spectroscopy (EDS), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS), and 4-probe resistivity (4PR), respectively.

<table>
<thead>
<tr>
<th>Solution</th>
<th>SbCl₃ (mM)</th>
<th>TeO₂ (mM)</th>
<th>Sb/Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>0</td>
<td>Pure Sb</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>15</td>
<td>Pure Te</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>12</td>
<td>0.25</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>9</td>
<td>0.66</td>
</tr>
<tr>
<td>5</td>
<td>7.5</td>
<td>7.5</td>
<td>1.00</td>
</tr>
<tr>
<td>6</td>
<td>9</td>
<td>6</td>
<td>1.50</td>
</tr>
<tr>
<td>7</td>
<td>12</td>
<td>3</td>
<td>4.00</td>
</tr>
</tbody>
</table>

4.3 Result and Discussion

4.3.1 Elemental Polarization

Electrochemical kinetics of the elemental species with respect to varying voltage is crucial to achieving proper controllability over the respective elemental reductions. With the interest of identifying the elemental polarization range for pure Sb and Te (solutions 1 and 2), elemental polarization studies were performed by sweeping the potential from 0 V to -1 V (SCE) with a rate of 1 mV/s, without agitation at room temperature. Figure 4-1 shows the normalized current-voltage curves for both the Sb and Te reductions on Au and Pt surfaces. Expected reductions and respective reversible potentials (NHE) for active ions of the electrolyte at pH 2.3 are given in equation 16, 17,
18, and 19 [62], however the complexing effect of citrate in used electrolytes could be the reason for any deviated reversible potentials [61]. The onset of Sb reduction on Pt surface was less negative (-0.35 V) than that of on Au surface (-0.60 V), however the onset of Te reduction on Pt was more negative (-0.30) than that of on Au surface (-0.20 V). Current increase observed for more negative potentials was due to H₂ evolution from H₃O⁺, however around -0.82 V, Te⁻² reduction was more prominent in Te reduction on Au. Interestingly, both Sb and Te, alloy reduction on Au was possible in the range of -0.40 V to -0.60 V, where no elemental Sb can be reduced, and this is due to induced co-deposition [61]. Moreover, the reduction of Sb-Te alloys on Pt surface was also through co-deposition and observations were consistent with a previous study [106]. Generally, for Sb-Te alloy deposition more negative potentials than -0.85 V was avoided due to H₂ and H₂Te evolution. The most active voltage range of Sb reduction can be considered from -600mV to -700mV, however it is relatively narrower compared to the voltage range of Te reduction (-0.35 to -0.80 mV).

\[
\text{SbO}^+ + 2\text{H}^+ + 3\text{e}^- \rightleftharpoons \text{H}_2\text{O} + \text{Sb}
\]

\[\text{E}^0 (\text{NHE}) = 0.212 - 0.0394 \text{ pH} + 0.0197 \log(\text{SbO}^+)\]

\[
\text{HTeO}_2^+ + 3\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O} + \text{Te}
\]

\[\text{E}^0 (\text{NHE}) = 0.551 - 0.0443 \text{ pH} + 0.0148 \log(\text{HTeO}_2^+)\]
Figure 4-1 Elemental polarization curves for pure Sb and Te on two different substrates, both Au/SiO$_2$ on Silica and Pt/ SiO$_2$.

4.3.2 Sb-Te Electrodeposition

With the thorough understanding of pure Sb and Te elemental reductions, the study was extended to synthesizing Sb-Te alloys for a broad range of composition with morphological and structural control. As stated in the experimental procedure, five different electrolytes (Table 7) were used to electrodeposit Sb-Te alloys under voltage of -600mV for 45s with agitation of 200 rpm. Selection of both the -600mV and 45s was to promote a smoother deposition of alloy with a common lowest possible reduction voltage. Actually, the first 5s of the deposition was sufficient to entirely deposit the Sb-Te alloy on the dipped area of Au, and can be easily visualized the progression of the growth by tracking the color change from yellowish Au to grayish Sb-Te. However, 45s of deposition seems to be sufficient to grow a thin film with 100-150 nm thickness to avoid any additional complexities arising in material characterization due to insufficient
amount of material. Apparent surface quality of the as-deposited thin films for all five electrolytes can be seen from Figure 4-3 and the surface finish of deposition seems to be very smooth and gray in color. Reflection of the camera used in photography is also seen in the image.

Figure 4-2 As deposited thin films from five Sb-Te electrolytes with Sb/Te ratio, 1-0.25, 2-0.66, 3-1.00, 4-1.50 and 5-4.00.

4.3.2.1 Controllability of Composition

4.3.2.1.1 Relative Precursor Concentration

As emphasized in supportive sections (2.2.1, 0), EDX spectra for Sb-Te alloys have to be treated very carefully to find the accurate composition due to overlapping of Sb and Te characteristic L lines. Generally, at least four EDX spectra were acquired at 1k magnification to cover the entire sample for each thin film. Top, center and bottom of the sample and another random location, if compositional deviation is more than 2% then additional points will be considered to enhance the accuracy.

Figure 4-3a summarizes the compositional analysis performed for all five samples mentioned in prior section with ±2% uncertainty. Stoichiometric composition, Sb\textsubscript{40}Te\textsubscript{60}, for thin films was acquired by using Sb/Te=1.00 electrolyte. Sb richest alloy of Sb\textsubscript{74}Te\textsubscript{26} and Te richest alloy of Sb\textsubscript{13}Te\textsubscript{87} were deposited using electrolytes with Sb/Te
ratio of 4.00 and 0.25, respectively. Consistent to the observed high elemental reduction capability of Te with respect to Sb as explained in prior section, it confirms that electrolyte ratio of Sb/Te=40/60= 0.66 is insufficient to deposit stoichiometric Sb$_{40}$Te$_{60}$, and only could deposit Sb deficient but Te excessive Sb$_{30}$Te$_{70}$. Moreover, the higher the Sb/Te ratio of the electrolyte, the richer the Sb content in electrodeposited Sb-Te alloy and vice versa. Normalized EDX raw spectra shown in Figure 4-3b further confirms the accessible broad range of Sb-Te compositions for this interesting binary system and the systematic compositional change from Te-rich to Sb-rich alloys. Potassium and Titanium from microscope slide and adhesive layer were responsible for observed respective low and high energy substrate peaks. Interestingly, adjusting the relative precursor ratio of the electrolytes is the key for easy, precise and systematic control of the alloy composition.

Figure 4-3 a)Sb-Te compositional variation with respect to relative precursor concentration b) EDX raw spectra of Sb and Te L lines for (a)Sb$_{13}$Te$_{87}$, (b)Sb$_{50}$Te$_{70}$, (c)Sb$_{60}$Te$_{40}$, (d)Sb$_{48}$Te$_{52}$, and (e) Sb$_{76}$Te$_{24}$ thin films. Low and high energy substrate peaks were from K and Ti K lines, respectively.
4.3.2.1.2 Electrodeposition Potential

In order to understand the effects of deposition voltage and composition another set of thin films were electrodeposited by only changing the electrodeposition potential from -550mV to -850mV for all five electrolytes. Notably, there was an apparent change in the color of the deposition from gray to black for higher negative voltages. As shown in Figure 4-4, for the Te-richest electrolyte (Sb/Te=0.25) the color change initiated at less negative voltage (-750mV) but for the Sb-richest (Sb/Te=4.00) electrolyte thin films retained the gray color up to -800mV. Rest of the deposition made from other electrolytes supported the systematic change of color observed in the extremes.

![Figure 4-4 As deposited thin films from a) Sb/Te=0.25 and b) Sb/Te=1.00 electrolytes for a range of deposition voltages. Samples 1-7 are from -550mV to -850 mV with -50mV increments.](image)

According to the trends observed in Figure 4-5, there is a mild Sb-enrichment of thin film composition from -600mV to -750mV and the trend is relatively clear for the electrolytes with Sb/Te ≥ 1.00. Referring back to the elemental polarization (4.3.1), the voltage range for Sb reduction is the same as Sb-enrichment; therefore the active Sb reduction has contributed for the partial changes observed in composition. Moreover, Sb-Te can be still deposited for the under potential regime of Sb due to the induced
electrodeposition, while the Sb compositional change is relatively significant [61]. Interestingly, for the selected voltage range of the study, noteworthy changes in composition cannot be triggered by changing the voltage, but fine compositional changes could be achieved.

![Figure 4-5](image)

*Figure 4-5* Sb percent contribution in Sb-Te alloy system with respect to different deposition voltage for all five electrolytes.

4.3.2.1.3 Deposition Time

Thickness of the deposition depends on the deposition time, longer deposition time leads to thicker deposition regardless of the uniformity of the thickness. However, to examine whether there is a compositional dependency with the growth, electrodeposition was performed for three different time intervals (45s, 3min and 25min) for all the
electrolytes under -600mV and 200rpm. Importantly, up to 3 minutes of the deposition there is no significant variation in the composition for all the electrolytes, however for 25 min of deposition Sb percent composition has become relatively deficient to drive the Te enrichment of the deposition (Figure 4-6).

4.3.2.1.4 Replacing Sb with Ge

Te prefers to network with not only three-fold coordinated Sb type elements but also four-fold coordinated Ge type elements to form the corresponding alloy. However, under aqueous electrodeposition Ge incorporation with Te was complicated. Unlike the Sb-Te alloy system Ge-Te was limited to Te-rich compositions. The advantage of acquiring a broad range of compositions was confined to a narrow range with maximum of 33% of Ge (Figure 4-7), and that was also possible for an extreme precursor ratio (Ge/Te=80).

Figure 4-6 Sb percent compositional dependence with respect to different deposition time.
4.3.2.2 Controllability of Morphology

4.3.2.2.1 Relative Precursor Concentration and Electrodeposition Potentials

In order to provide a border insight of the controllability of surface morphology, SEM micrographs are summarized in Figure 4-8 as a morphological grid. Thin films for the micrographs were deposited by only changing the relative precursor concentration and the deposition voltage under constant deposition time (45s) and agitation (200rpm). Conveniently, the preferred morphology with expected composition could be acquired by carefully controlling over the relative precursor concentration of the electrolyte and the electrodeposition voltage. According to the systematic trends observed in Figure 4-8, an
increase in the electrodeposition voltage increases the surface roughness or surface area of the deposition without a significant change in composition. Especially, this could be very helpful in future applications to deposit preferred high surface areas of Sb-Te with cost effectiveness. Moreover, for the Te-rich electrolytes surface roughness initiated at lower electrodeposition voltages than Sb-rich electrolytes, and the systematic change of the surface roughness from Te-rich to Sb-rich further confirms the trend. Onset micrographs of low magnification are to indicate the large scale surface roughness of the films, in addition to that, another set of morphological grids are available in Appendix B: for each electrolyte with different magnifications. For the low electrodeposition voltages surfaces are more or less uniform and smooth, however, for the higher electrodeposition voltages deposition becoming more and more aggressive to enhance the surface roughness. In other words, for the lower ED voltages reduction species were driven or supplied from the bulk electrolyte to the reduction surface to just satisfy the existing demand, so the outcome is a more or less uniform surface. However, at higher ED voltages excessive supply of reduction species promotes the vertical growth of the deposition which eventually leads to the surface roughness.
Figure 4-8 SEM micrographs of surface morphology of thin films electrodeposited under different electrolyte and deposition voltages, and insets are low magnification micrographs of the same sample.
4.3.2.2 Deposition Time

With the knowledge of surface morphology variation with respect to the deposition voltage the next importance step is to study the time evolution of the surface morphology of more or less uniform surface acquired from low electrodeposition voltage. *Figure 4-9* summarizes the time evolution of the surface morphology for the entire set of electrolytes deposited under -600mV. At 45s of deposition surface roughness is insignificant and more or less uniform, however at 3min of deposition surface roughness has initiated and overgrowing protrusions can be seen. Unlike the protrusions observed in vertical growth of material with respect to increasing ED voltage, here protrusions have larger diameter confirming the non-aggressive growth. Overall, with the time evolution of the deposition more or less uniform surfaces will eventually change into rough surface with high surface area.

Interestingly, with the longer time of deposition (25min) non-uniform growth of material was evident as shown in *Figure 4-10*. Free standing dendrite growth at the edge of the substrate has relatively high rate of growth than regular surface of the substrate. The indication of the dendrite growth can be seen even at 3min of deposition, and for 25 min of deposition it has grown an average length of 80μm. However, this dendrite growth can be seen throughout the dipped edge of the conducting substrate and it is independent of the direction of electrolyte agitation or mass transportation. Overall preferentiality to have a high growth at the edge compared to regular surface could be due to more attraction of reduction species towards the edges. And that could be possible due to
localization of more electrons towards the edge of the conducting substrate so that the reduction species get higher opportunity to get reduced at the edge.

Figure 4-9 SEM micrographs of surface morphology of thin films electrodeposited under different electrolyte and deposition time.

Figure 4-10 SEM micrographs of dendrite formation at the edge of the sample due to non-uniform material growth and a) and c) are high magnifications to designate the overgrowth areas shown in b) respectively. Inset is another high magnification of a).
4.3.2.3 Controllability of Structure

4.3.2.3.1 Relative Precursor Concentration and Electrodeposition Potential

*Figure 4-11* shows the XRD spectra of Sb-Te thin films deposited under -600mV for 45s using Te-rich to Sb-rich electrolytes. In order to enhance the signal to noise ratio these spectra were acquired with 1 hour of X-ray exposure. Thin films deposited from Te-rich to Sb/Te=1.50 electrolytes have no Sb-Te crystalline peaks except the substrate peaks; therefore these as-deposited films were amorphous. However, some Sb atoms have phase separated for thin films deposited using Sb-rich electrolyte and can be seen in XRD spectra as a diffuse peak. Moreover, silica in the substrate has contributed to the amorphous-nature of the spectra, but it has not screened the contribution of the films in interest. Considering the entire range of compositions acquired in this study, all of the as-deposited Sb-Te were structurally amorphous except the low crystalline contribution from phase separated Sb for Sb-richest electrolyte.

*Figure 4-12* shows the XRD spectra Sb-Te thin films deposited using different ED voltages. It is clear that, for low ED deposition voltages up to -750mV as-deposited thin films of Te-richest electrolyte are amorphous. However, at high negative voltages for -800mV and -850mV crystalline peaks due to pure Te can be seen. Therefore, for the depositions performed at the high-end of the ED voltage more Te reduction takes place over Sb. The tendencies observed in Te-enrichment are consistent to the overall explanation provided as earlier (4.3.2.1and 4.3.2.2).
Figure 4-11 XRD spectra of Sb-Te thin films deposited for 45s using electrolytes with Sb/Te ratios. # represents the pure Sb peak and rest of the peaks is from substrate.

Figure 4-12 XRD spectra of Sb-Te thin films deposited for 60s using electrolyte with Sb/Te=0.25 ratio (Te-richest). * represents the pure Te peak and rest of the peaks are from substrate.
To acquire a better idea regarding the amorphous structure of the Sb-Te binary system EXAFS experiments were performed in 5-BM beamline at Advanced Photon Source (APS), Argonne National Lab. According to the prior mentioned (2.2.4) experimental details more or less uniform electrodeposited (under -600mV and 200rpm) thin films with wide range of compositions, Sb$_{13}$Te$_{87}$, Sb$_{30}$Te$_{70}$, Sb$_{40}$Te$_{60}$, Sb$_{48}$Te$_{52}$ and Sb$_{76}$Te$_{24}$, were exposed to synchrotron X-rays to acquire the corresponding EXAFS spectra ($\chi(r)$) of Sb edge, and the k$^3$ weighted, Fourier transformed and phase shift uncorrected spectra are shown in Figure 4-13. In addition to main peak, the smaller peaks near 1.0–2.0Å are mostly due to a termination effect caused by finite k range of Fourier transform and thus are neglected in the analysis. The $\chi(r)$ spectra were then fitted with ARTEMIS [131] using the appropriate scattering paths calculated from the Sb$_2$Te$_3$ model via FEFF [132]. The resulting structural parameters are presented in Table 8. Since the atomic numbers and radii of Sb and Te are close to each other, and they may not readily be distinguishable via EXAFS, the contribution from Sb neighbor atoms was replaced by Te atoms.

For the stoichiometric composition with 2% of experimental uncertainty, the average Sb-Te bond length is 2.84Å and in consistent with the reported previous studies for a- Sb$_2$Te$_3$ [86] and, the average Sb-Te bond lengths in a-Ge$_1$Sb$_2$Te$_4$ and a-Ge$_2$Sb$_2$Te$_5$ [133] that lie on the pseudo-binary line of Sb$_2$Te$_3$ and GeTe [4]. However, the average Sb-Te bond length is shorter than that of obtained from density functional (DF) calculations for a- Sb$_2$Te$_3$ [134] and a-Ge$_2$Sb$_2$Te$_5$ and a-Ge$_1$Sb$_2$Te$_4$ [135-139]. The Sb coordination numbers of 3.0(0.3) obtained from our EXAFS analysis are consistent to the
ones in amorphous Sb$_2$Te$_3$ or a- Ge$_1$Sb$_2$Te$_4$ and a- Ge$_2$Sb$_2$Te$_5$ as reported previously [85, 133]. Again, these numbers are slightly over estimated (~ 4.0) in DF calculations of a-Sb$_2$Te$_3$, a- Ge$_1$Sb$_2$Te$_4$ and, a- Ge$_2$Sb$_2$Te$_5$ [134-139].

Figure 4-13 Magnitude of $k^3$ weighted $\chi(r)$ spectra of Sb K-edge EXAFS data (uncorrected for phase shift). $k$ ranges chosen for the Fourier Transform is 3-10 Å$^{-1}$

Considering the non-stoichiometric samples, average Sb-Te bond lengths are slightly larger than the stoichiometric composition, Sb$_{40}$Te$_{60}$, in addition to observed larger coordination numbers. Generally, for an identical stoichiometric composition only Sb-Te bonds will be possible, but for non-stoichiometric compositions towards Sb-rich and Te-rich, there is a high tendency to have Sb-Sb and Te-Te bonds in addition to Sb-Te, respectively. Simply, increasing the coordination number for non-stoichiometric
compositions means there will be more than three atoms at the vicinity of Sb. Therefore, Sb bond length has to be increased to accompany more than three atoms at its vicinity. In addition to that, the bond lengths provide a gauge of structural stability, therefore stoichiometric composition has more stable amorphous phase.

### Table 8 Structural parameters from EXAFS Analysis

<table>
<thead>
<tr>
<th>Composition</th>
<th>Bond-length (Å)</th>
<th>Coordination</th>
<th>MSRĐ (10⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb₁₃Te₈₇</td>
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<td>2.86±0.01</td>
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<td>8.26±0.77</td>
</tr>
</tbody>
</table>

#### 4.3.3 Sb-Te Phase Transition

Amorphous to crystalline phase transition studies for the thin films were performed using the home-made four-probe resistance measurement setup and the additional experiment details are given in section (2.2.5). Figure 4-14 shows the thin film resistance (normalized) change with respect to temperature. The common trend of initiating and ending with a low value of resistance by moving through a peaking value is completely due to the conductor-semiconductor coupled resistance as explained in section 2.2.5. As explained in section 1.2 pure Te forms two fold covalent bonding between neighbors to form a coil like random walk structure, and these coils will interact with weak Vander Waals forces, which are inadequate to stabilize the amorphous phase.
So at the room temperature this structure will easily crystallize due to further weakening of cross linking of Vander Waals [39].

*Figure 4-14* Phase transition curves from 4PRM for Sb-Te thin films.

In this study, all the compositions, from 13% to 76% of Sb, exhibited a stable amorphous phase at room temperature through stronger cross linking initiated between Te-Te coils through Sb, and displayed the phase transition with respect to change of temperature. Phase transition temperature for the compositions ranged from 110 to 120°C and the lowest was corresponding to the stoichiometric composition which is consistent with the previous study performed for similar binaries GeSb and GeTe [140]. In addition to that, Huang, Kellock [61] has observed 120 °C as the phase transition temperature for Sb$_{49}$Te$_{51}$ composition electrodeposited on TiN under similar synthesis conditions.
After phase transition crystalline structure of Sb-Te thin films were examined by utilizing XRD. Monochromatic Cu Kα1 (λ=1.5406 Å) X-rays were swept over a range of 2θ from 5° to 90° with a rate of 0.5°/min. However, the Figure 4-15 shows the sectioned XRD spectra of all deposited compositions of thin films over a range of 2θ from 25° to 35°, for a better visualization of the main crystalline peaks. All the samples have accomplished 4PRM characterization followed by an isothermal annealing at 150°C for 100 min under 200mT vacuum. As-deposited thin films were confirmed to be amorphous from XRD, and the observed peaks (marked with *) were only from the substrate, Au/Ti sputtered glass. Nevertheless, the annealed thin films of all compositions were crystallized into stoichiometric Sb₂Te₃ (PDF-03-065-3678) rhombohedral with R-3m and Sb (PDF-01-071-3737) cubic with Pm-3m or AuTe₂ (PDF-03-065-2307 and PDF-01-079-1616) monoclinic with C2/m crystalline phases and space groups, respectively. Observed crystalline peaks of Te-rich, Sb₁₃Te₈₇ (Figure 4-15a) and Sb-rich, Sb₇₆Te₂₄ (Figure 4-15e) thin films were ascribed respect to Sb₂Te₃ (marked with *) with AuTe₂ (marked with ▼) and Sb₂Te₃ with Sb (marked with ♦) crystalline multi phases, respectively. Moreover, Sb₃₀Te₇₀ (Figure 4-15b) thin films also crystallized into Sb₂Te₃ and AuTe₂ (marked with △) multi phases, but relative to Sb₁₃Te₈₇ thin film, AuTe₂ phase has a relatively more shrunk unit cell volume. However, Sb₄₈Te₅₂ (Figure 4-15d) thin film was crystallized into Sb₂Te₃ and Sb multi-phase as Sb-rich thin film. More or less, Sb₄₀Te₆₀ thin film was crystallized into Sb₂Te₃ single phase with extremely low Sb phase due to observed 2% compositional uncertainty. Interestingly, intensity variation of the main crystalline peak, (015) of Sb₂Te₃ from Te-rich to Sb-rich provides an insight for the
tendency of phase separation through bond satisfaction. Te-rich, Sb$_{13}$Te$_{87}$ has formed the least amount of stoichiometric Sb$_2$Te$_3$ phase due to the limited Sb percentage, but the rest of the Te has mostly crystallized into stoichiometric AuTe$_2$ by blending with substrate Au. Similarly, the study of Sb$_{30}$Te$_{70}$ film further confirms the trend with relatively more Sb$_2$Te$_3$ phase compared to the previous composition. Even though Te prefers to network with Au under deficient environment of Sb, Sb prefers to network with itself instead of Au or O. Therefore, Sb-rich Sb$_{76}$Te$_{24}$ has formed Sb$_2$Te$_3$ by entirely networking with available Te, and the remaining Sb atoms have phase separated to pure Sb. Similarly, Sb$_{48}$Te$_{52}$ has relatively lower fraction of Sb phase compared to Sb$_{76}$Te$_{24}$.

Thermodynamical assessment of Sb-Te system by Ghosh [141] explains that system could equilibrate into Sb, Te, Sb$_2$Te$_3$ and intermediate phases of δ (at. % Sb from 82-63) and γ (at. % Sb from 68-55). Moreover, the at. % of Sb from 70 to 43 can form a layered structure with Sb$_2$ bilayer with Sb$_2$Te$_3$ five layer tetradymite slabs [142]. Therefore, the observed Sb and Sb$_2$Te$_3$ crystalline multiphase in Sb$_{76}$Te$_{24}$ and Sb$_{48}$Te$_{52}$ thin films could be due to the formation of these layered structures of Sb-Te. However, a similar studies [61] which crystallized thin films in range of at. % of Sb from 37-57, have crystallized into Sb$_2$Te$_3$ and haven’t observe any existence of multi phases. Yamada and Ohno [143, 144] demonstrated that (Te$_{80}$Ge$_5$Sn$_{15}$)$_{100-x}$Au$_x$ like Te-rich alloys with Au dopants could crystallized into AuTe$_2$ phase, and our study also confirms the same that Te-rich compositions (Sb$_{13}$Te$_{87}$ and Sb$_{30}$Te$_{70}$) aspired to crystallize into AuTe$_2$ even by stimulating diffusion of substrate Au atoms into the Sb-Te matrix. Actually, beyond the phase transition temperature the tendency of atomic rearrangement and phase separation
have created limitation to model the metal-semiconductor bi-layer resistance variation observed in 4PRM measurements for the Sb-Te system.

Figure 4.15 X-ray diffraction patterns of electrodeposited (a) Sb$_{13}$Te$_{87}$, (b) Sb$_{30}$Te$_{70}$, (c) Sb$_{40}$Te$_{60}$, (d) Sb$_{48}$Te$_{52}$, and (e) Sb$_{76}$Te$_{24}$ thin films, after 100 min isothermal annealing at 150$^\circ$C.

4.4 Conclusions

Binary Sb-Te thin films were successfully electrodeposited to cover a broad range of compositions using acidic aqueous electrolytes. Regarding the controllability over the deposition, relative precursor ratio of the electrolyte, deposition voltage and time plays a significant role. Acquiring different compositions and morphologies are possible by mainly tuning the relative precursor ratio and deposition voltage, respectively. All the
compositions were able stabilize the Sb-Te amorphous phase at room temperature and showed the phase transition to \( \text{Sb}_2\text{Te}_3 \) crystalline phase. In conclusion, this study provides a clear insight for comprehensive understanding the synthesis of Sb-Te alloys under compositional, morphological and structural control by disclosing the systematic trends in the active voltage range of Sb reduction. Moreover, we believe that this study will enhance the understating of Sb-Te (or similar) binary to be utilized in future device applications with more effectiveness.
Chapter 5: Understanding the Solid Electrolytic Nature of Electrodeposited Sb$_2$Te$_3$ by Au and Pt Diffusion: an RBS Study

5.1 Introduction

Chalcogenide glasses have been widely used in different device applications [37, 46, 107, 145, 146]. More importantly, they have played a major role in memory applications such as phase change memory (PCM) [49] and conductive-bridge random access memory (CBRAM) [147]. Among the chalcogenide glasses, Sb$_2$Te$_3$ is a well-known prototypical PCM material. Moreover, Sb- and Te-based glasses have been used as CBRAM switching material [147]. In both of these memory applications, the chalcogenide glass is sandwiched between two electrodes, and one electrode is an electrochemically inert element such as Au, Pt, and W. So understanding the solid electrolytic nature of Sb$_2$Te$_3$ with respect to the contacting layer (e.g. Au and Pt) is important. Moreover, the atomic diffusion in this simple binary could provide a new insight into understand the ionic diffusion observed in CBRAM during the electron-conducting filament formation.

In addition to that, for the future device applications there is a considerable demand for high aspect ratio structured devices such as nanowire-based PCRAM [148]. The most widely used method for synthesizing PCM and CBRAM material is sputtering [54, 147], but it is incapable of creating high aspect ratio structures to fulfill the future needs. Among all other synthesizing methods, electrodeposition has an excellent capability of via filling. So it is important to study electrodeposited materials to understand their solid electrolytic nature.
In this study, we have focused on exploring the solid electrolytic nature of stoichiometric \( \text{Sb}_2\text{Te}_3 \) thin films synthesized by an electrochemical method. Au and Pt atoms were diffused into the \( \text{Sb}_2\text{Te}_3 \) films with and without thermal annealing. Scanning electron microscopy, energy dispersive X-ray spectroscopy, Rutherford backscattering spectroscopy, X-ray diffraction were used to characterize the morphology, composition, compositional depth profiling, and atomic structure, respectively. We believe this study will enhance the understanding about the solid electrolytic nature of \( \text{Sb}_2\text{Te}_3 \) and provide some insights for their better usage in device applications.

5.2 Experiment

Amorphous \( \text{Sb}_2\text{Te}_3 \) thin films were electrodeposited potentiostatically (Princeton Applied Research Model 273A) using a standard three-electrode cell at room temperature under -600mV and 200rpm. The electrolyte for the electrodeposition was prepared according to the similar procedures described elsewhere [61, 106] by using \( \text{SbCl}_3 \) (Acros Organic 99.5%) and \( \text{TeO}_2 \) (Acros Organic 99+%) as precursors. To avoid any dissolvability issues \( \text{SbCl}_3 \) and \( \text{TeO}_2 \) were dissolved in sodium citrate (NaCit) and concentrated \( \text{HNO}_3 \), respectively. After electrolyte preparation, the relative species concentrations for the final volume (80ml) were \( \text{SbCl}_3 : \text{TeO}_2 : \text{NaCit} : \text{HNO}_3 = 7.5\text{mM} : 7.5\text{mM} : 0.21\text{M} : 1\text{M} \) and pH was adjusted to 2.3 by adding 1M NaOH.

Au and Pt were deposited onto #1 SiO\(_2\) glass slides with a thickness of 200-300nm by DC magnetron sputtering (Denton Vacuum 502-A) to use as working electrodes (WEs). Standard RCA cleaning procedure was performed for the WE prior to the electrodeposition. Saturated calomel electrode and Pt mesh were used as the reference
and counter electrodes, respectively. In order to obtain different thicknesses in the same sample, different dip levels were maintained with respect to the deposition time. First 45s of the electrodeposition, Au working electrode was dipped in the electrolyte to cover an approximate area of 15mm × 10mm, and then the dipping area was reduced to 10mm × 10mm and 5mm × 10mm by raising the working electrode, respectively to deposit material for total of 75s and 105s. Similar steps were performed to deposit different thicknesses on Pt at deposition times of 45s and 90s. After electrodeposition one third of the deposition was masked and sputtered with Au (Pt) (same as the back layer) to passivate the deposition and half of the passivated area was separated and annealed at 200 °C for 100 min. As shown in Figure 5-1 both samples have different regions to study with respect to non-passivation, passivation, thermal treatment and thickness of the deposited material.

The morphology and composition of depositions were studied using field emission scanning electron microscopy (FESEM) (Hitachi S4500) and energy dispersive X-rays spectroscopy (EDX) (Thermo Fisher Scientific NORAN System SIX X-ray Microanalysis in Hitachi S2460N), respectively. Cu Kα X-ray diffraction (XRD) under transmission mode (SAXSess, table top small angle X-ray scattering system) was used to study the structural changes of the deposition before and after thermal treatment. In order to probe the Au and Pt diffusion in Sb₂Te₃ by compositional depth profiling, Rutherford backscattering spectrometry (RBS) was used. RBS experiments were performed at Edwards Accelerator Laboratory; Ohio University using α particle with energies of 3.035
and 3.07 MeV and an angle of 168° with respect to the incident beam. RUMP analysis package was used to model the acquired RB spectra.

Figure 5-1 Schematics of electrodeposited Sb\textsubscript{2}Te\textsubscript{3} thin film on a) Au and b) Pt to demand different thicknesses and non-passivated, passivated and passivated-annealed regions for RBS study.

5.3 Result and Discussion

According to the studies described in Chapter 4: with the careful selection of deposition parameters Sb\textsubscript{2}Te\textsubscript{3} thin film can be electrodeposited with controllable morphology, composition and structure. As shown in Figure 5-2a and b, for 45s of deposition of Sb\textsubscript{2}Te\textsubscript{3} on Au and Pt, the films are more or less uniform and can be approximated to free of pinholes type defects, and a density as 6.5 g/cm\textsuperscript{3} was used in RUMP modelling. Moreover, the composition of the film was re-confirmed by modelling the EDX spectra using WinXAS to carefully rule out the K and Ti characteristic X-ray peaks overlap with SbTe peaks (Figure 5-2c) and ZAF correction.
was conducted using CitZAF. For both Au and Pt WEs as–deposited Sb$_2$Te$_3$ structure is amorphous and can be confirmed from the XRD spectra (not shown here).

Figure 5-2 SEM micrographs of electrodeposited Sb$_2$Te$_3$ thin films for 45s on a)Au b)Pt and c) EDX spectra of Sb$_2$Te$_3$ with contribution of substrate K(*) and Ti(+) peak in background.

In order to understand the Au and Pt diffusion into Sb$_2$Te$_3$, first, the RBS spectra of the same thickness of Sb$_2$Te$_3$, but different imposed conditions (passivated-annealed, passivated and non-passivated) were focused to explore the main trends. According to Figure 5-1, regions corresponding 45s of deposition which is 3, 6 and 9 for Au and 2, 5 and 8 for Pt are subjected to RBS study and acquired and modeled (red) spectra are shown in Figure 5-4. For the passivated regions, deposited layered structures can be seen for Au (Pt)/ Sb$_2$Te$_3$ / Au (Pt) from Figure 5-4b (e). However, the back Au peak is not resolved from Sb$_2$Te$_3$ and it appears as a shoulder towards the high energy side of that merged peak. But for the Pt, just one atomic number difference is sufficient to resolve the
RB spectra from Sb$_2$Te$_3$. Even though films were passivated after 2 hours of deposition, no oxygen incorporation was found in the film. To specifically probe the oxygen, alpha particles with oxygen resonance energy (3.035MeV) were used. Unlike Pt very mild diffusion of Au was found in the region of the interest as tabulated in Table 9.

![Figure 5-3 Confirmation of thickness variation for Au system](image)

However, Au has been observed from surface to very few angstroms in depth in exposed region, and we believe that could be due to improper masking during the Au sputtering. Nevertheless, the high Au incorporation in layer 3 relative to layer 2 implies Au has diffused into Sb$_2$Te$_3$ from the back Au layer, but no evidence was seen related to Pt diffusion. According to the model, outer most layer has high oxygen incorporation than next depth layer (exposed layer 1 Vs 2), therefore more likely the oxygen incorporation has initiated from the surface and diffused into the thin film, but this is more reasonable for Au system than Pt since there is no significant surface oxidation can be seen from RBS for Pt system.
The passivated-annealed region for Au consists of crystallized and phase separated material, furthermore, the complete vanishing of the layered-nature (Au/Sb$_2$Te$_3$/Au) observed in RB spectrum is due to thorough blending of materials, which confirms the capability of high mobility of these type atoms under thermal agitation. Unlike Au the mobility of Pt seems to be insignificant, and Pt was able to preserve its featured layered structure in RB spectra even after the thermal treatment (Figure 5-4d). Interestingly, the trends observed for 45s were the same for all other different deposition times. This effective blending of atoms or promising solid electrolytic nature is due to very large thermal vibrations in crystalline phases of Sb-Te system which randomize the atomic distribution similar to a liquid phase, as discussed in Yamada [39]. However, with respect to Pt, high capability of blending with Au is due to negative bonding enthalpy for AuTe$_2$ and AuSb$_2$ compounds [149].

Table 9 *Compositional variation of exposed, passivated, and passivated-annealed regions respect to modelled multiple layers. Layer 1 is the outermost (surface) and the increasing layer numbers are in depth towards the glass substrate (the final layer).*

<table>
<thead>
<tr>
<th>Region</th>
<th>Layer</th>
<th>Sb</th>
<th>Te</th>
<th>Au</th>
<th>O$_{Au}$</th>
<th>Pt</th>
<th>O$_{Pt}$</th>
<th>Ti</th>
<th>Zn</th>
<th>Si</th>
</tr>
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<tbody>
<tr>
<td>Exposed</td>
<td>1</td>
<td>0.4</td>
<td>0.6</td>
<td>0.15</td>
<td>0.15</td>
<td></td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>2</td>
<td>0.4</td>
<td>0.6</td>
<td>0.03</td>
<td>0.10</td>
<td></td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.4</td>
<td>0.6</td>
<td>0.60</td>
<td>0.00</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td></td>
<td>5</td>
<td></td>
<td></td>
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<td>2.00</td>
<td></td>
<td>0.50</td>
<td>0.50</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Sealed</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>2</td>
<td>0.4</td>
<td>0.6</td>
<td>0.01</td>
<td>0.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>3</td>
<td></td>
<td></td>
<td>1.00</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>4</td>
<td>2.00</td>
<td></td>
<td>2.00</td>
<td>0.50</td>
<td>0.50</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sealed-annealed</td>
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<td>0.4</td>
<td>0.6</td>
<td>0.40</td>
<td>1.00</td>
<td></td>
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<tr>
<td></td>
<td>2</td>
<td>0.4</td>
<td>0.6</td>
<td>0.80</td>
<td>0.30</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>3</td>
<td>0.4</td>
<td>0.6</td>
<td>1.80</td>
<td>1.00</td>
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<td></td>
<td>4</td>
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<td>0.50</td>
<td>0.50</td>
<td>1.00</td>
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</tr>
</tbody>
</table>
Figure 5-4 RBS spectra for the passivated-annealed, passivated and exposed regions, where Sb$_2$Te$_3$ thin film was electrodeposited for 45s for Au (a, b and c) and Pt (*d, e and f), respectively. S-surface, T-top and B-bottom. * overlapped with e
5.4 Conclusions

In conclusion, amorphous Sb$_2$Te$_3$ thin films with different thicknesses were successfully electrodeposited to study the diffusion of precious metals (Au and Pt) under different conditions. Regardless of the Sb$_2$Te$_3$ thicknesses Au diffusion seems to be significant compared to Pt. Even at room temperature Au diffusion was observed, however with respect to the thermal agitation very efficient blending of Au in Sb$_2$Te$_3$ was observed. Overall, Sb$_2$Te$_3$ can be used as a good solid electrolyte to promote diffusion of Au than Pt.
Chapter 6: Templated Electrodeposition of Sb-Te Nanowires: Synthesis and Characterization of High Aspect Ratio Nanowires

Partially adapted from “Sb-Te Phase-change Nanowires by Templated Electrodeposition”

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6.1 Introduction

Rapid switching between two stable phases, crystalline and amorphous, with significant changes in optical reflectivity and electrical resistivity is the key for phase-change memory [1]. Among all the phase-change memory materials (PCMMs), Ge-Sb-Te (GST) alloys have captured a great deal of attention due to their excellent switching performance [4]. To further enhance the properties of phase-change materials, one could harness the effect of nanoscale confinement [1]. Studies of 0D (nanoparticles) [5-12], 1D (nanowires) [13-16], and 2D (thin films) [17-20] confinement of the ternary GST have been conducted by a few research groups, and changes in the phase transition (i.e., melting and crystallization) temperatures due to confinement have been reported. The low dimensional confinement has the potential to overcome challenges for future memory devices such as to achieve high storage density and low power consumption [21]. Currently phase-change thin films play a main role in data storage and random access nonvolatile memory [2, 24-26]. Phase-change nanowires (PCNWs), on the other hand, are very promising to overcome the above mentioned challenges for next-generation non-volatile memory: e.g., Yu et al. [148] have proposed a nanowire-based PCRAM. Various techniques such as the vapor-liquid-solid method [13-16, 27, 28], the colloidal method [29], and the electrochemical deposition method [30-32] have been
reported for the synthesis of PCNWs. In order to utilize nanowires in devices with enhanced material properties, it is crucial to have precise control over their composition, structure, morphology, and 3D alignment [33]. The template-guided electrodeposition method appears to be the most economical and efficient method that meets these requirements.

In this study, we report synthesis of Sb-Te PCNWs by the electrochemical method using commercial and home-made anodic aluminum oxide (AAO) membrane as the nano-porous template. The composition, diameter, and aspect ratio of the nanowires were varied by selecting the proper templates and controlling the growth conditions. The morphology, composition, structure and phase-transition of the nanowires were characterized by scanning and transmission electron microscopy, energy dispersive X-ray spectroscopy, X-ray and electron diffraction, and 4-probe resistivity measurements. The relationship between the structure and processing conditions of the nanowires were established. Moreover, the nanowires show quite different growth behavior from that of thin films under identical synthesis conditions, which implies more complex growth mechanism of the nanowires.

6.2 Experiment

AAO membranes were prepared by the well-established two-step anodization procedure [68]. Aluminum (Al) foils (99.99% purity, ESPI Metals Inc.) were ultrasonically degreased for 20 min in regent EtOH. Then the Al foils were dipped in 1.5M NaOH for 4 min and subsequently 1.5M HNO₃ for 2 min and thoroughly rinsed out with deionized water. The remaining water was removed by an air blower. Proper
thermal treatment was necessary for the purpose of grain size enhancement of the Al foils. This was achieved by annealing the Al foils at 420 °C for 4 hours. Then the foils were electropolished with a mixture of HClO$_4$ and ethanol solution at 0.2 °C for 10 min under 10 mA/cm$^2$ current density to improve the surface quality. One side of the Al foil was covered by a polymer coating to avoid reaction during the growth of the AAO template. The first-step anodization was performed on the Al foils for a couple of hours at 3°C and 40V of D.C. voltage [69]. Then the created AAO layer was completely removed by dipping it in H$_3$PO$_4$ acid for 30 min at 60°C. The second-step anodization was performed on the leftover dimples from the first-step anodization at 3°C with 40V of D.C. voltage for 30 min to attain hexagonally arranged porous structure. Alumina barrier thinning procedure [70] was performed just after the second-step anodization by reducing the voltage from 40V to 4V at a constant rate of 1V/min. The purpose of the thinning process was to break the alumina barrier between the Al layer and the pore channels. After that, the samples were cathodized at -5V for 5 min in a 0.5 M KCl solution and subsequently cathodized at -5V for a few minutes in distilled water for final cleanup.

The electrolyte for electrodeposition was prepared by dissolving precursors SbCl$_3$ and TeO$_2$ in a sodium citrate (NaCit) solution and a concentrated HNO$_3$ solution, respectively. Then the precursor solutions were mixed under agitation following the procedures described elsewhere [61]. Unless otherwise stated, the final concentrations of each constituent were SbCl$_3$: TeO$_2$: NaCit: HNO$_3$ =7.5mM: 7.5mM: 0.21M: 1M. The pH value of the final solution was adjusted to 2.3 by adding NaOH. Electrodeposition of Sb-Te nanowires and thin films was carried out with a traditional three-electrode cell using a
potentiostat (Princeton Applied Research Model 273A). Commercial (Whatman Anopore™ and Synkera™) and homemade AAO membranes as well as gold-coated glass slides were used as the working electrodes, and a platinum mesh and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. To create a conductive path on the commercial AAO membrane, a thin layer of gold (~50nm thick) was sputtered on one side of the membrane. Then a piece of conducting copper tape was attached to the gold surface as an extension of the working electrode for an easy external circuit connection. To help nanowires grow inside the porous template, we covered completely the gold surface that was not in contact with the membrane with a polymer coating. For the homemade AAO, the unanodized Al foil was connected directly to the pore channels and thus can be used as a conductive path. A constant voltage of -600 mV (SCE) was applied on the working electrode, which was immersed in the electrolyte that was stirred by a magnetic starrier at a constant speed of 200 rpm. The electrodeposition was conducted at room temperature and the aspect ratio and length nanowires were controlled by varying the template and deposition time.

After the Sb-Te nanowires were formed inside the AAO template, the nanowire-template composite was dipped in a 1M NaOH solution for a few minutes to dissolve the AAO template. Then the exposed Sb-Te nanowires were ready for characterization.

6.3 Result and Discussion

6.3.1 Electron Microscopy

In templated electrodeposition, the aspect ratios of the NWs are outlined by two factors, pore diameter of the template and the deposition time, in order to control the
diameter and length of NWs, respectively. Commercial templates were selected to cover a broad range of pore diameters (220±10, 150±12, 100±10, 80±8, 55±6, 35±3, 20±2, and 18±3nm) with 40-50 μm template lengths, however the homemade templates were fabricated under more controllability with preferred pore diameters (100-30 nm) and lengths (0.5-10 μm) with less uncertainty (±2) compared to the commercial. In addition to that, the homemade AAO template has the unanodized Al foil that is directly in contact with the alumina pore channels unlike the commercial AAO template. Therefore, there is no need to coat the template with a metal layer such as gold. After successful electrodeposition of Sb-Te NWs using AAO templates, templates were partially dissolved to expose the NWs for electron microscopy studies.

*Figure 6-1* shows SEM micrographs of Sb-Te nanowire bundles grown from both the gold-coated commercial and home-made AAO membranes, and only four different sizes were shown with respect to their diameters (220nm, 100nm, 60nm, and 18nm) in order to represent the entire range of study. Insets are included to provide additional information about the cross-sections and growth densities of each representation, and magnifications of the micrographs are inconsistent. The nanowires were continuous, uniform, and equivalent to the dimensions of the used templates, therefore the spatial constraints for the growing NW inside its channel were properly controlled by the template. NW growth has initiated from the conducting edge of the channel and progressed along the channel by proper filling from bottom to top. In addition to the main electrolyte (Sb/Te=1) mentioned here, NW growth along the channels was consistent with that of the other electrolytes (pure Sb, pure Te and Sb/Te from 0.25 to
4.00). Unlike Figure 6-1c, tips of high aspect ratio NWs (Figure 6-1a, b, and d) could easily bundle together after removal of the matrix support, and similar observations have been seen in a previous study [30]. This bundling up of nanowires was caused by capillary forces during drying, which could be minimized by supercritical drying for better alignment of the nanowires [30]. The contrast between the top and bottom of the nanowires are due to incomplete etching of the AAO template at the bottom.

*Figure 6-1* SEM micrographs of Sb-Te nanowire bundles after dissolution of AAM template; a) 220nm b) 100nm and d) 18nm using commercial templates and c) 60nm using home-made template. Insets are low magnifications of the same to provide an idea about the cross-section and growth density (c) has different magnification).
In order to highlight the via filling capability of electrodeposition method, Figure 6-2 summarizes two examples. AAO templates can be fabricated as split channels, which were more clearly shown in Figure 6-2a where template channel can branch-off into sub channels by splitting 220 nm channels into several 20 nm sub-channels. Interestingly, the material has completely filled the sub braches first and then continued to the main channel. Similarly, if channels get cracked and enlarged, the filling will completely utilize the entire available space by properly promoting the dense filling according to Figure 6-2b. So these observations further confirm that electrodeposition is a promising method for future device applications due to its excellent via filling capability.

*Figure 6-2* SEM micrographs to highlight the growth potentials of electrodeposition a) split- and b) crack-channel.

Amorphous Sb-Te alloys crystalize around 110°C (Chapter 4:) therefore, in TEM characterization when NWs are subjected to high energy electron beams a significant
increase in sample temperature could be possible, so a special attention is crucial to avoid any crystallization of the amorphous nanowires. However, Figure 6-3a shows insets corresponding to electron diffraction patterns of 220 nm NW before and after e-beam damage or induction. According to that, amorphous to polycrystalline transition could be facilitated by TEM e-beam. But, with careful controlling of the e-beam intensity actual structural information can be acquired without crystallizing the sample as shown in Figure 6-3b for 80 nm NW. In consistent to the observations of electron diffraction, X-ray diffraction patterns of the nanowires were also further confirmed the amorphous structure of as-deposited Sb-Te NWs.

![Figure 6-3 TEM micrographs and electron diffraction pattern for Sb-Te NWs a) 200 nm and b) 80 nm.](image)

### 6.3.2 Energy Dispersive X-ray

The composition of nanowires was analyzed by energy dispersive X-ray (EDX) spectroscopy, and the X-ray microanalysis software, NORAN System Six, was also used in addition to WinXAS modelling of EDX spectra. In order to inspect the compositional uniformity along the length of NWs both the cross sectioned in-matrix and liberated NWs were used. Generally, the home-made templates used in this study were relatively short...
(< 5μm) compared to the length of commercial templates (40-50μm) and no significant compositional variation was observed along the NWs beyond 2% uncertainty of its composition. In contrast for the longer channels, compositional uniformity changes towards the end of the length and Te enrichment can be observed, and for more clarity compositional variation for three different sizes of NWs are shown in Figure 6-4. Figure 6-4b and a show the line scan for the first 20μm of 40μm total length of 100nm NWs and exact orientation of the line scan, respectively. Moreover, for additional confirmation of the composition, different points were also selected as shown in Figure 6-4c. Overall, for 100nm NWs, composition uniformity of Sb$_{40}$Te$_{60}$ was maintained along the channel for considerable length, but for the last 8-5μm length, Te enrichment became prominent with a Te extremely rich composition. Similarly, Figure 6-4d shows the compositional variation along the full length of 18 nm NWs, and beyond 35 μm a clear trend of Sb suppression can be seen. However, the Sb suppression or more specifically, the deviation from the expected stoichiometric composition is more prominent in the 220 nm NWs and observed at relatively shorter lengths beyond 20 μm. As shown in Figure 6-4e, EDX spectra confirm a significant Sb% decrease in the 220nm NWs along its length. Surprisingly, both the TFs and NWs were electrodeposited under same conditions, and the composition of NWs has initiated with the same composition, but the composition changed along the length. Unlike the NWs, TFs were grown on Au coated glass slides, so K and Ti background peaks can be seen in addition to Sb and Te peaks. Also the contribution of the second peak of K is embedded in the first Sb-L peak, so the increase
of Sb-L peak for TFs is not real and both TFs and NWs (initial) have the same composition, Sb$_{40}$Te$_{60}$.

**Figure 6-4** Composition analysis for 100 nm NWs a) SEM image indicating the line scan along the length of NW bundles and b) corresponding Sb (red) and Te(green) variation, c) multiple selections for points scans, d) Sb% change along the length of the channel for 18nm NWs and e) normalized raw spectra for TFs and 220 nm NWs deposited under same conditions, * and + are substrate peaks for K and Ti from glass slide and only present in TFs as a background signal for NWs composition changes along the channel from stoichiometric to Te-rich.

Comparison of material overgrowth under similar deposition conditions is shown in **Figure 6-5** for NWs and TFs. For 25 min of TFs deposition, surface to edge uneven
growth can be seen, and lateral dendrite growth (Figure 6-5b) along the edges dominates in the deposition. However for NWs, the overgrowth is uniform as shown in Figure 6-5a. For the given 100 nm NW template filling time is approximately 120 min, but the deposition has continued for 315 min. Moreover, the overall trend of Te-enrichment in the composition is the same for both TFs and NWs, and Te growth seems to be more preferential over Sb when diffusion constraints are less significant.

It is known that diffusion of SbO$^+$ and HTeO$_2^+$ ions onto the electrode surface is the initial step of the growth of Sb-Te alloy [30]. The rate of deposition for both ions depends strongly on the applied voltage and the diffusion of these species from bulk electrolyte to reduction surface through the channel. As the length of the channel increases, the ionic mobility or ionic concentration gradient could change drastically demanding constraints for the species diffusion. In the electrolyte, SbO$^+$ forms citrate complexes [61], however the effective sizes of these complexes are unclear for both SbO$^+$ and HTeO$_2^+$, so the species selectiveness through the pores are also unknown. Unlike
SbO⁺, HTeO₂⁺ reduction is possible at low negative voltages, in addition to that, SbO⁺ get induced to reduce as an alloy with Te [61]. Even though there are some similarities between TFs and NWs deposition, NWs growth seems to be more complex. Especially, when NWs were grown on very long channels, proper understanding of the growth process is crucial to establish the compositional uniformity along the channel.

6.3.3 X-ray Diffraction

In-matrix Sb-Te NWs were subjected to structural characterization using a tabletop X-ray small angle scattering system equipped with Cu Kα radiation. 2D X-ray intensity patterns were acquired from 0° to 40° of angle. According to the acquired spectra, as-deposited Sb-Te NWs confirmed to be amorphous. Moreover the NWs grown using the other electrolytes (Sb/Te=0.25-4.00) were also free of any crystalline peaks related to Sb-Te binary. However, depending on the Te-enrichment towards the channel end, Pure Te crystalline peaks can be seen. For instance, XRD spectrum of the as-deposited overgrown sample shown in Figure 6-5a exhibited peaks only related to pure Te, and Sb-Te has retained its amorphous phase. However, after thinning the overgrowth layer by mechanical polishing, intensities of the observed pure Te peaks were systematically reduced. Moreover, the Te diffraction peaks vanished after continuing the polishing beyond complete removal of overgrowth layer, and that provides a confirmation of the localization of Te-enrichment towards the channel-end.

As-deposit amorphous Sb₂Te₃ NWs can be subjected to phase transition studies using a home-made 4PRM setup. In this method, In-matrix 1 mm² sized NW sample was connected under pseudo 4-wire configuration and the resistance of NWs was measured
with respect to the temperature increase. Amorphous phase of these types of materials display a high resistance, but once crystallized resistance drop significantly with a contrast of a few orders of magnitude. As shown in Figure 6-6a for successfully grown Sb$_2$Te$_3$ 100 nm NWs, clear phase transition from amorphous phase to crystalline phase can be seen with a significant change of resistance. Also, the temperature corresponding to the onset of resistance change can be considered as the crystallization temperature, i.e. 111 °C. In contrast, pure Te is crystalline, and it exhibits the regular behavior as a semiconductor with respect to the temperature, so as shown in Figure 6-6b no resistance contrast or phase transition can be seen, but the resistance increases drastically beyond 120 °C. Similar behavior has been seen for the other sizes of pure Te NWs, and more importantly, this behavior also can be seen for Te-enriched Sb-Te samples.

Figure 6-6 Resistance vs temperature 4PRM measurement curves for in-matrix NWs a) Sb$_2$Te$_3$ 100nm and b) pure Te 35nm
This exotic behavior of resistance shoot up is purely related to the electron transport constraints demanded by 1D nanostructure under thermal agitation. Most probably Te could recrystallize at this temperature and generate more grain boundaries in this nano-confined structure to destroy the electron conduction path by grain boundary scattering. Moreover, the tiny band gap could vanish due to the temperature increase to display the metallic behavior with respect to the temperature, which may also contribute to the increase of resistance with temperature.

After phase transition, the crystalline structure of NWs was studied using XRD. As stated earlier, sub sets of XRD spectra are shown in Figure 6-7 for the NWs deposited under identical conditions. For the convenience of identification or comparison, electrodeposited pure Te 80 nm NW (Figure 6-7b) and DC-magnetron sputtered Sb$_2$Te$_3$ TF (Figure 6-7f) XRD spectra are included with the other NW spectra. In consistent to sputtered films, electrodeposited TFs also crystallized (Figure 6-7e) into Sb$_2$Te$_3$ single phase. In contrast, 18, 100, and 220 nm NWs crystallized into two phases, pure Sb$_2$Te$_3$ and Te phase as shown in Figure 6-7a, c, and d, respectively. These XRD spectra of NWs further confirm the Te-enrichment towards the channel-end which is discussed under compositional analysis. Prominently, nanowire crystallization has dominated by Sb$_2$Te$_3$ phase which assures the compositional uniformity of the filling along the channel for a considerable length. The ratio between Sb$_2$Te$_3$/Te phases could also reflect the effective filling fraction of the channel length with preferred Sb$_2$Te$_3$. Reasons for the substrate peaks and amorphous bulging are due to back coated Au and selection of the sample size, respectively.
Figure 6-7 Normalized XRD spectra for a) 18 nm, c) 100 nm, and d) 220 nm NWs, and e) TF electrodeposited under same conditions using Sb/Te=1 electrolyte, b) 80 nm NW pure Te electrodeposited, and f) DC magnetron sputtered from Sb$_2$Te$_3$ target.

6.4 Conclusions

We have successfully grown Sb-Te nanowires using a templated electrochemical method. The nanowires with different compositions, diameters, and aspect ratios were
synthesized by selecting the proper templates and varying the electrodeposition conditions. Growth of the nanowires depends on the length of template channels, electrolytes, and deposition conditions. The nanowires have a more complex growth mechanism than thin films. Our study demonstrates that the templated electrodeposition method is a versatile and economical approach to grow PCNWs with well controlled structure and 3D morphology.
7.1 Introduction

Sb-Te is a useful alloy which can be found in several applications such as phase-change [37], thermoelectric[145], solar cell [107], and topological insulator [150] devices. Currently thin films are commonly used in device application[45, 150], but in future the 1D confined high aspect ratio structures (nanowires) will play a significant role. So there is a huge interest in confining material in high aspect ratio structures for various device applications, but synthesizing material in those structures with proper controllability is still challenging.

Synthesis of binary Sb-Te thin films can be achieved from numerous techniques such as sputtering [107-110], thermal evaporation [111, 112], molecular beam epitaxy (MBE) [113], metal-organic chemical vapor deposition (MOCVD) [114], hydrothermal synthesis [115], solvothermal synthesis [116], and electrodeposition (ED) [61, 106, 117-125]. However, among those synthesis techniques electrochemical method has an excellent void-filling capability which could suffice the future expectations. Unlike the thin films, very few groups have electrochemically synthesized Sb-Te nanowires [30, 32, 128], and to the best of our knowledge, no group has explored the growth mechanism to acquire the controllability over the material synthesis. Especially, in alloy deposition, composition could change along the length of the deposition. Difficulty of synthesizing the preferred composition is disastrous in device applications since material properties are a sensitive function of the composition.
It has been found that the growth mechanism of amorphous nanowires is different from that of thin films and even more significantly different from that of metallic nanowires. Therefore, in this study we have carefully investigated the growth mechanism of Sb-Te thin films and nanowires in order to understand the governing parameters of the growing process. The growth mechanism has been investigated for both TFs and NWs by emphasizing the governing parameters to identify the trends. Finally, controlling the composition along the NW length has been demonstrated for the NW growth. It is hoped that our study will shed light on the growth mechanism of amorphous nanowires prepared by electrodeposition and benefit their device applications.

The growth mechanism has been studied using chronoamperometry curves acquired under potentiostat electrodeposition. In addition to that, energy dispersive X-ray spectroscopy, X-ray diffraction and electron microscopy have been used to characterize the composition, structure and morphology of the materials.

7.2 Experiment

The electrolyte for electrodeposition was prepared by dissolving precursors SbCl$_3$ and TeO$_2$ in a sodium citrate (NaCit) solution and a concentrated HNO$_3$ solution, respectively. Then the precursor solutions were mixed under agitation following the procedures described elsewhere [61]. Unless otherwise stated, the final concentrations of each constituent were mixed according to Table 10 in order to acquire seven electrolytes. The pH values of the final solutions were adjusted to 2.3 by adding NaOH. Electrodeposition of Sb-Te nanowires and thin films was carried out with a traditional three-electrode cell using a potentiostat (Princeton Applied Research Model 273A).
Commercial (Whatman Anopore<sup>TM</sup> and Synkera<sup>TM</sup>) AAO membranes and gold-coated glass slides were used as the working electrodes, and a platinum mesh and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. To create a conductive path on the commercial AAO membrane, a thin layer of gold (~50nm thick) was sputtered on one side of the membrane. Then a piece of conducting copper tape was attached to the gold surface as an extension of the working electrode for an easy external circuit connection. To help nanowires grow inside the porous template, we covered completely the gold surface that was not in contact with the membrane with a polymer coating. A constant voltage (SCE) was applied on the working electrode, which was immersed in the electrolyte that was stirred by a magnetic stirrer at a constant speed of 200 rpm. The electrodeposition was conducted at room temperature and corresponding chronoamperometric curves were acquired to understand the growth mechanism.

After the Sb-Te nanowires were formed inside the AAO template, the nanowire-template composite was dipped in a 1M NaOH solution for a few minutes to dissolve the AAO template. Then the exposed Sb-Te nanowires were ready for the characterization.

<table>
<thead>
<tr>
<th>Solution</th>
<th>SbCl&lt;sub&gt;3&lt;/sub&gt; (mM)</th>
<th>TeO&lt;sub&gt;2&lt;/sub&gt; (mM)</th>
<th>Sb/Te</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>0</td>
<td>Pure Sb</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>15</td>
<td>Pure Te</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>12</td>
<td>0.25</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>9</td>
<td>0.66</td>
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<td>5</td>
<td>7.5</td>
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<td>12</td>
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7.3 Result and Discussion

In this study, the focus is on the growth mechanism of electrodeposited Sb-Te materials under different nanoscale confinements. Unlike the other deposition methods, electrochemical deposition is a charge guided process. More clearly, ionic species in an electrolyte can be reduced onto a conducting electrode (working) through a triggering potential. With the interest of understanding the Sb-Te alloy deposition, first the study was focused to understand the electrochemical kinetics with respect to varying voltage for elemental species. The current versus voltage curves or polarization curves provide a great deal of information about the reduction specie; such as, oxidation, reduction potential and its range, reaction intensity, etc. *Figure 7-1* shows the elemental polarization curves for both pure Sb and Te reduced on Au/ SiO$_2$ using pure elemental electrolytes (Solution 1 and 2) by sweeping voltage from 0 to -1 V with a rate of 1 mV/s under 0 rpm agitation. Especially at pH of 2.3, ionic forms of SbCl$_3$ and TeO$_2$ precursors were claimed to be SbO$^+$ and HTeO$_2^+$ [62]. Moreover, the corresponding elemental reductions and the reversible potentials for the ionic species are according to Eq. 20 and 22 and Eq. 21 and 23, respectively. Importantly, Te deposition is initiating at a lower potential (-350 mV) than Sb (-550 mV). Moreover, Te and Sb reductions range from -350 mV to -800 mV and from -550 mV to -800 mV, respectively. Overall, as an elemental species, Te is more preferential in reduction than Sb. However, due to the citrate complexing effect even at lower reduction voltages, where only Te can be reduced, Sb can also get reduced through induced electrodeposition [61]. As highlighted in *Figure 7-1*, the golden window plays a crucial role in alloy deposition to enrich the Sb% of the
Sb-Te alloy, because from -600 mV to -700 mV Sb reduction current increases with respect to that of Te. The safest voltage range for alloy deposition was claimed to be from -550 mV to -800 mV (Chapter 4:). This selection is not only to avoid any unnecessary Te-enrichments at low voltages but also to avoid hydrogen evolution and other over reductions at high voltages. Moreover according to our previous study (Chapter 4:), the most productive way of controlling the composition was by selecting the proper electrolyte (Sb/Te), instead of the reduction voltage. However, when diffusion constraints for reduction species are significant, deposition potential could also play a major role to acquire the controllability.

Figure 7-1 Elemental polarization curves for pure Sb and Te on Au/SiO₂ substrate.

\[
\begin{align*}
SbO^+ + 2H^+ + 3e^- & \rightarrow H_2O + Sb
\end{align*}
\]
\[ E^0 \text{ (NHE)} = 0.212 - 0.0394 \text{ pH} + 0.0197 \log(SbO^+) \]  
\[ \text{HTeO}_2^+ + 3\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O} + \text{Te} \]  
\[ E^0 \text{ (NHE)} = 0.551 - 0.0443 \text{ pH} + 0.0148 \log(\text{HTeO}_2^+) \]

According to Jin et al. [30] templated electrodeposition process has been explained in few main steps: 1) both HTeO\(_2^+\) and SbO\(^+\) have to diffuse through the channel and get adsorbed by the surface due to the electric field, 2) adsorbed ionic species are reduced into corresponding elements according to Eq. 20 and 22, 3) reduced elements react to form alloy and 4) formed alloy nucleates and grows along the channel [151]. However, step 4) is more related to the crystalline material growth, but at step 3), after reduction atomic migration should be somewhat random to achieve amorphous material through solid-state reactions. Step 1) is the rate determining step, because in order to continue the following steps 2), 3), and 4), ionic species must diffuse from bulk to the reduction surface through the channel, which demands additional diffusion constraints. Moreover, step 1) to 3) could affect the final composition of Sb-Te alloy.

In consistent to the above discussion, as a pure elemental deposition or Sb-Te alloy deposition, Te reduction is more prominent than Sb electrokinetically. Therefore in the Sb-Te alloy deposition, Te reduction rate could influence various parameters such as reduction current, composition, etc. Figure 7-2 shows chronoamperometric curves for pure Te electrodeposition in two different templates (35 nm and 80 nm) under identical deposition conditions. Electrodeposition was performed under constant voltage (~-600 mV) and agitation (200rpm) using the same electrolyte. Both the pore size and density of the template are related to the effective surface available for the species reduction.
According to the top views of templates (Figure 7-2c and d), pore densities are different in addition to pore sizes. However, the reduction surface areas are seem to be more or less equal, otherwise initial stage of chronoamperometric curves cannot overlap. Even though the template lengths were the same (40 μm), there is a significant difference in the template filling time. Actually the template filling time is directly related to the species diffusion, from bulk to the reduction surface, through the pore structure as emphasized earlier as the rate determining step. Therefore, HTeO$_2^+$ diffusion is more preferred in 80 nm channels than in 35 nm channels, and pore size is effectively modifying the HTeO$_2^+$ diffusion. Especially, the area of the template confirmed to be independent of the template filling time, since time needed to fill full or a quarter area of a template is approximately the same. When the deposition continues to grow along the channel length, the travel distance for a species to reach the reduction surface also decreases, and that could be the reason for minor gradient change observed in current rate during the in-channel growth time, $t_{\text{fill}}$.

Once these reduction species reach the reduction surface by progressing through the diffusion constraints, the next main step is the growth. In order to enhance the understanding of the material growth, actual morphological changes were tracked along the evolution of growth for both thin films and nanowires as shown in Figure 7-3. Except for the working electrodes, the rest of the deposition conditions were identical. For the first 45 s of TF deposition, surface is more or less uniform, but after 2 minutes some overgrowing protrusions can be seen. So the surface roughness has increased and reached an extreme at 25 minutes of deposition. For the thin films, diffusion constraints are not
significant as nanowires, and more interestingly, surface roughness has increased considerably during the time of deposition. On the other hand, larger surface roughness enhances the surface area, so the relative number of species reduced can be increased, and thus the current increases.

Figure 7-2 Chronoamperometric curves for pure Te electrodeposition under identical condition (solution 2, 80ml, -600 mV, 200 rpm at room temperature) except the template pore size 35 nm and 80 nm, b) and c) SEM top view micrographs of 80 nm and 35 nm templates, respectively.

In contrast, the nanowire growth (Figure 7-3) initiates from the bottom of the channel and continues to the top with proper stability. During the filling, no significant surface roughness or reduction surface enlargement was observed. Therefore, the reduction current is mainly controlled by the species diffusion instead of increase in the reduction surface area, as seen in TFs.
Unlike the material growth inside the channel, outside growth of the template (overgrowth) is significantly less affected by the diffusion constraints. So the growth is somewhat similar to TFs and surface roughness gets increased considerably. Importantly, surface roughness of TF overgrowth is significantly higher than that of NWs as shown in Figure 7-4.
Figure 7-4 SEM micrographs of the overgrowth of a) thin films and b) nanowires deposited under identical conditions (solution 5, 80ml, -600 mV, 200 rpm at room temperature)

Typical electrodeposition chronoamperometric curves for both the TFs and NWs are shown in Figure 7-5. With the understanding of main influential parameters for the deposition current, species diffusion and reduction surface area enhancement, variations of the chronoamperometric curves can be explained.

Figure 7-5 Chronoamperometric curves for Sb-Te a) thin film and b) 100 nm nanowire deposition under identical condition (solution 5, 80ml, -600 mV, 200 rpm at room temperature). Sectioned regions denote the stages of the material growth. Chronoamperometric curve in inset of b) is for Pd elemental growth [152].
Each chronoamperometric curve has divided into multiple stages with respect to the evolution of growth. For 30 min of TFs deposition and 300 min of NWs deposition, they have completed the entire growth by processing through nucleation, uniform growth, overgrowth, and extreme overgrowth, and nucleation, in-channel growth, channel merge, and overgrowth, respectively. During the nucleation, ionic species diffuse closer to the surface, get adsorbed to the reduction surface, get reduced into corresponding elements, and form an alloy by undergoing atomic migration and solid state reaction. Initial reduction of species happens on the Au surface, but afterwards material growth continues with reductions happening on the formed alloy. Overall, for the nucleation stage there is no difference in the growth mechanism between TFs and NWs. Especially for the amorphous depositions, atomic migration should not be promoted; otherwise atoms could migrate into the energy minima position instead of the local minima to undergo the solid state reaction to become crystalline. There is a relatively limited time (<60 s) window for acquiring uniform growth in TF deposition, and during that time the growth current will be reasonably constant assuring the uniformity of the reduction surface area. However, at the overgrowth regime emergence of protrusions can be seen, these protrusions contribute for a significant change in the reduction surface area and contribute to the steepest current rate in the entire growth. Once all the protrusions covered the area of initially smooth surface, entire growth will further continue to extreme overgrowth stage. At this stage protrusions were significantly starting to grow, so the increase in the reduction surface area is slowed. Therefore the steepness of the current rate is slightly decreased. Changing
of the reduction surface area due to the dip level fluctuation related to agitation is the reason for observed fluctuation in the chronoamperometric curve.

In-channel growth of NW is limited by diffusion constraints. Unlike the TFs, the reduction surface area can be approximated to be a constant. In an ideal situation where diffusion doesn’t play a role, current should be a constant, since the reduction area is also a constant. However, in reality the smaller the pore sizes, the slower the species diffusion. Therefore, the current rate becomes steeper for larger pore sizes. In this stage of growth, gradient of the chronoamperometric curve slightly increases, and that is due to shortening of the channel length as the material grows, so species can reach the reduction surface relatively soon. Importantly, if the pore size is large, HTeO$_2^+$ diffusion become effective, so this could easily couple with the former, and Te-enrichment could happen towards the end of the channel. Moreover Te-enrichment for in-channel growth can be easily seen from chronoamperometric curves, and apparent increase in its gradient can be observed due to more and more Te reduction. At the next stage of growth, significant increase in reduction surface can be seen due to channel merging. Therefore, the species reduction was boosted by contributing to the steepest current rate during the entire growth. Finally the NWs undergo the overgrowth stage, but no significant change in the reduction surface compared to the TFs, so growth current was saturated. Interestingly, as shown in the inset of Figure 7-5b, Pd nanowire growth along the channel is completely different from the Sb-Te NW growth. In this case, initially nanotubes were formed and then core of the nanotubes were filled to form the solid NWs.
Effective sizes of working electrodes used TF and NW were $1.5 \times 0.5 \text{ cm}^2$ and $1.0 \times 1.0 \text{ cm}^2$, respectively, but the reduction surface area of the NW is not the same as the size of the working electrode due to its porous AAO matrix. However, the initiating current values of chronoamperometric curves provide an idea about the actual used reduction surface area for the electrodeposition. Importantly, the change of current during the process provides an insight about how diffusion constraints and increases in reduction surface area contribute to the overall growth, and the change of current for TFs is one order of magnitude higher than that of NWs.

Due to the mismatch of electrochemical reactivity, preferentiality of the reduction is higher for $\text{HTeO}_2^+$ than $\text{SbO}^+$. Furthermore, this could be even worse when the deposition is under diffusion constraints, since the pore size could easily modify the $\text{HTeO}_2^+$ diffusion. As a result, a deviation from the compositional uniformity can be observed along the length of the nanowires. When the pore size gets smaller, effective diffusion of $\text{HTeO}_2^+$ decreases and vice versa and therefore the Te-enrichment for larger pore sizes initiated at a shorter length than the smaller pore sizes. In other words, when $\text{HTeO}_2^+$ is experiencing diffusion limitations, electrodepositing NWs is more likely in maintaining the composition consistent to the real precursor ratio, which is the exact composition acquired in TFs investigation, as mentioned in previous study (Chapter 4:).

In consistent to the findings, when NWs were electrodeposited under identical conditions, i.e. same electrolyte (solution 5), deposition voltage (-600 mV), template length (40 μm), agitation (200 rpm), and temperature (25 °C), using two different templates, Te-enrichment was observed for 220 nm at shorter length (25 μm), but that was not observed
for 55 nm until 35 μm, as shown in Figure 7-6b. Figure 7-6a shows the composition variation along the channel length for the 200 nm NW deposition performed under constant voltage (-600), but different HTeO$_2^+$ concentration. According to extensive study performed on Sb-Te thin film deposition (Chapter 4:), Sb-Te can be deposited with preferred composition by mainly adjusting the precursor concentration ratio. So this NW deposition was initiated with solution 6 and systematically TeO$_2$ partial ratio was increased to trigger the Te reductions to observe an extreme effect. Interestingly, for the first 5μm length composition was uniform and consistent to the expected composition, Sb$_{48}$Te$_{52}$. This is an extremely important finding for the future device applications, because materials can be deposited with preferred composition even in extremely high aspect ratio structure by accessing through a diffusion limited long channel. Moreover, if compositional uniformity along the length of the wire is needed to be reestablished by overcoming the Te-enrichment, then two main parameters can be used, precursor concentration ratio to modify HTeO$_2^+$ concentration in the electrolyte and deposition voltage to trigger Sb reduction (golden window) over Te in the deposition. The former is the main factor, but latter is also more prominent under diffusion-limited (NW) deposition than TF deposition (Chapter 4:). For instance, just by changing the voltage, the composition could be changed from Sb$_{40}$Te$_{60}$ to Sb$_{50}$Te$_{50}$. Furthermore, the inset of Figure 7-6a shows an example of 200nm NW growth under compositional control, and the same electrolyte (solution 6) was used, but the voltage was increased systematically in order to reestablish same composition, Sb$_{48}$Te$_{52}$ during deposition.
7.4 Conclusions

In summary, we have successfully investigated the growth mechanism of both the TFs and NWs synthesized using electrodeposition. During the electrodeposition, the growth current can be influenced by two main factors; reduction surface and species diffusion. In TFs growth, current is more driven by enlargement of the reduction surface, but in NWs, in-channel growth is more driven by species diffusion constraints. Moreover, alloy deposition of electrochemically dissimilar species is complicated, and establishing the composition uniformity over the deposition is challenging. However, with the overall explanation which we have provided regarding to the growth mechanism of TFs and NWs, by subdividing the entire growth process into a few stages, it will provide an insight about the trends and how those could get influenced by main factors. Overall, we believe that this study will enhance the understanding of the growth mechanism of Sb-Te
or similar materials in order to achieve better controllability in synthesizing under nanoscale confinements.
Chapter 8: Size-dependent Crystallization of Sb$_2$Te$_3$ Nanowires: Exploring the Scalability of Phase-change Materials and Tunability of Phase Transition Properties.

8.1 Introduction

Phase-change memory (PCM) is a potential candidate for next-generation non-volatile memory [45]. Unlike the other memory technologies, PCM is a storage-class memory technology which could significantly revolutionize across the memory hierarchy by substituting both the memory-type and storage-type technologies with cost-effective and energy-efficient solutions [44]. Capability of switching between two stable structural phases, amorphous and crystalline, rapidly and repeatedly with significant contrast in material properties are the key for PCM [23, 44, 49]. Switching of the PC material can be done optically or electrically, and the corresponding reflectance-change and resistance-change are used in optical (CD, DVD, BD) and electronic memory (PCRAM) technologies, respectively [23].

Success of PCM technology mainly depends on PC materials [21, 23], and the capability of optimizing their properties with respect to the future technological trends is crucial. Especially, the scaling down of tech node should be promising for PCM technology to succeed in future. Once materials are scaled down into thin films (2D), nanowires (1D), and nanoparticles (0D) their relevant material properties usually change from their bulk [21]. Moreover, the size could also tune or further change the properties of PC materials and few groups have investigated the size-effects of phase transition properties, e.g. crystallization and melting temperatures, in thin films [17-20, 153] and nano-pits [154], nanowires [14, 16, 155-157], and nanoparticles [158]. Overall, these
size-effect studies of PC materials were limited to investigating the changes of melting
temperatures; and only the nano-pit and nanoparticle studies have focused on the changes
of crystallization temperature. So we believe that providing an insight regarding the size
dependent crystallization for PC nanowires is a necessity.

In regards of PC materials, crystallization temperature is an important parameter
related to the data retention, which typically requires 10 years of archival time [44] at a
temperature substantially higher than the operating temperatures, depending on different
applications [1]. Stabilizing its amorphous phase with high resistance is mandatory for
this technology; otherwise the basic requirement to function as memory material with two
distinguishable resistive states is not satisfied. So an increase in crystallization
temperature stabilizes the amorphous phase further to enhance the data retention.

Antimony telluride, Sb$_2$Te$_3$, is a prototypical PC material which plays an
outstanding role as it contributes to the well-known pseudo-binary line of GeTe-Sb$_2$Te$_3$
used in PCM technology [39]. Compared to GeTe, Sb$_2$Te$_3$ has lower crystallization
temperature, but the crystallization temperature can be elevated systematically to stabilize
the amorphous phase by adding Ge [39]. However, instead of combining with other
elements, if Sb$_2$Te$_3$ can enhance its stability of the amorphous phase, more interesting
PCM applications could be possible due to the simplicity of this material. Therefore,
exploring the size-effects of Sb$_2$Te$_3$ not only broadens our horizons regarding the material
but also offers novel pathways to tune material properties which could ultimately enhance
its applicability.
Electrodeposition is a promising material synthesis method in creating high aspect ratio structures, which can be useful for the PCM technology [54]. However, existing PCM studies have commonly used vapor-liquid-solid (VLS) method [14, 16, 155-157] for synthesizing high aspect ratio structures, such as PC NWs, and these as-synthesized NWs are crystalline. Up to date, there have been no studies on the size-dependent phase transition behavior of electrodeposited PCM materials. So here we have synthesized high aspect ratio amorphous Sb$_2$Te$_3$ NWs using templated (anodic alumina membranes) electrodeposition to study the size effect on the crystallization temperature.

8.2 Experiment

Amorphous Sb$_2$Te$_3$ NWs were synthesized by templated electrodeposition for a wide range of diameters (18-220 nm) by extending our knowledge from a previous study [128]. In this effort, the electrodeposition was performed with standard three electrode cell using Princeton Applied Research Model 273A Potentiostat/Galvanostat under constant potential (-600 mV) at room temperature (25 ºC). Pt mesh (15 mm x 25 mm) and saturated calomel electrode were used as the counter and reference electrodes, respectively, and the commercial (Synkera Technologies, Inc– Pores-18±3, 35±3, 55±6, 80±8, 100±10 nm, length – 40 μm, and area– 1 cm$^2$ and Whatman Anopore™ – Pores– 220±10 nm, length – 50 μm, and area– 1.33 cm$^2$) anodic alumina membranes (AAM) were used as working electrodes after sputtering a thick layer (~500 nm) of Au on one side of AAM using a DC magnetron sputtering system (Denton Vacuum DV502A). During the electrodeposition, corresponding ionic species move along these high aspect ratio channels of AAM and initiate the reduction from the Au surface to grow as a
nanowire. With the ongoing species reductions, material growth follows the spatial constraints demanded by the template, AAM, so that the material growth along the channels will become the NWs with similar dimensions as the pores. In order to assure the growth along the channels, the rest of the conducting areas such as the Au sputtered on the back and edges of the AAM of the working electrode has to be properly insulated, but complexities arising against the removal of the back insulating polymer coating after the electrodeposition, and acquiring clean pieces of in-matrix NWs was very difficult because mechanical or chemical removal attempts can easily damage or contaminate the sample of interest. Therefore, a modified Au contact pad was designed not only to establish good electrical contacts but also to minimize the polymer in-contact of the template (2.1.1.2).

Electrolyte for the electrodepositing was prepared by dissolving precursors, SbCl$_3$ in sodium citrate (NaCit) and TeO$_2$ in concentrated HNO$_3$ solutions separately, as described elsewhere [61, 106]. Even though, SbCl$_3$ dissolves rapidly in NaCit under agitation at room temperature, TeO$_2$ dissolves slowly in concentrated HNO$_3$ under agitation, so temperature was elevated to 60 °C. Then, these properly dissolved precursor solutions were mixed together to achieve final concentrations of constituents, SbCl$_3$: TeO$_2$: NaCit: HNO$_3$ =7.5mM: 7.5mM: 0.21M: 1M, in 80ml of volume. In order to promote the preferred elemental reductions by having ionic forms of SbO$^+$ and HTeO$_2^+$ [106], the pH of the final solution was adjusted to 2.3 by adding NaOH.

Working electrodes were thoroughly rinsed by deionized water before and after the deposition and followed by an air drying process. Duration of the electrodeposition
was limited to the fulfillment of the AAM length to exclude any overgrowth. Depending on the characterization techniques NW-AAM composite was dipped in 1M NaOH to dissolve the matrix, AAM, and dipped back in deionized water to get rid of residues, if synthesized NWs need to be exposed.

Composition, morphology, atomic structure, and phase transition of Sb$_2$Te$_3$ NWs were characterized by energy dispersive X-ray spectroscopy (EDS), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and 4-probe resistivity (4PRM), respectively.

8.3 Result and Discussion

The physical morphologies of the as-deposited NWs are more or less uniform in their diameters and consistent to the dimensions of the templates, AAM, used for the electrodeposition, as shown in Figure 8-1. Surface roughness seen in NWs for Figure 8-1b is due to the residues of AAM etching. Moreover, template channels were confirmed to be uniform not only from the cross sections of the templates (not shown) but also from the uniformness of diameters of the grown NWs, even though some surface roughness can be seen on the top surfaces of templates. The surface roughness is due to the final finish of their fabrication and independent of the dimensional uniformity along the channel. Therefore, theses NWs are reasonably enclosing a broad range of diameters from 18nm to 220 nm for exploring the size-effect of Sb$_2$Te$_3$. 
Figure 8-1 SEM micrographs of synthesized Sb$_2$Te$_3$ NWs with different diameters a) 18±3, b) 35±3, c) 55±6, d) 80±8, e) 100±10, and f) 220±10 nm and the insets show the corresponding template used for the deposition.
In order to confirm the composition of NWs, EDS spectra (Figure 8-2a) were acquired along the cross-section of the template to cover the entire length using NORAN Six X-ray Microanalysis system, and the corresponding SEM micrograph for 55nm in-matrix NWs is shown in the inset of Figure 8-2b. Similarly, liberated or free standing NWs were also considered for the compositional uniformity analysis and multiple points and areas (Figure 8-2c) were selected to acquire spectra. Then, the acquired spectra were modelled using WinXAS [159] to accurately resolve the overlapping characteristics L-peaks of Sb and Te and the atomic number, absorption, and fluorescence correction were performed using CitZAF to calculate the composition. For all of the NWs Sb$_{40\pm3}$Te$_{60\pm3}$ compositional uniformity was confirmed along the length as shown in Figure 8-2b.
As-deposited Sb$_2$Te$_3$ NWs were subject to XRD for an exposure of 1hr in order to acquire 2D scattering patterns which can be converted into intensities versus θ, covering 0-40°, using a table top small-angle scattering system (SAXSess Anton Paar) equipped with Cu Kα monochromatic X-ray radiation. As shown in Figure 8-3, for the entire range of NWs only Au peaks was seen, which were corresponding to the sputtered conducting coating at the back of AAM. Usage of in-matrix NWs over free-standing NWs is beneficial not only for XRD measurements but also for phase transition measurements because 1) less probability of NW surface contamination due to the matrix encapsulation and no chemical or mechanical procedures to be followed for matrix removal and 2) a cost-effective and convenient measuring capability under pseudo 4-wire configuration avoiding any additional complicated steps, such as depositing lithographic contacts.

The phase transition, amorphous to crystalline, of these NWs were studied using a home-made 4PRM setup, which is capable of measuring the resistance of in-matrix NWs under pseudo 4-wire configuration while heating with a rate of 26 °C/min. This 4PRM system is LabVIEW automated and I-V signals were acquired through Keithley 2000-20 multi-meter (refer 2.2.5 for more details). In order to minimize the temperature gradients while heating, the sample size has minimized to an approximate area of 1mm$^2$, so that the uniform heating can be estimated along the entire thickness of AAM. Moreover, the heating chamber was triple flushed using N$_2$ gas prior to thermal ramping and measurements were acquired under 200 μT vacuum pressure. As seen in Figure 8-4a change of the resistance of these in-matrix NWs with respect to the temperature is having the typical behavior of a semiconductor, decreasing resistance with respect to the
increasing temperature. Importantly, there is a significant change in resistance ($\sim 10^3 \Omega$) related to the structural phase transition from amorphous to crystalline, and the temperature at the corresponding onset point can be considered as the crystallization temperature, $T_{crys}$ [160]. After the phase transition crystalline structure was confirmed by XRD and found to be in rhombohedral phase (R-3m) of Sb$_2$Te$_3$ (PDF-03-065-3678) (Figure 8-3) which is consistent to the previous study of Sb$_2$Te$_3$ thin films (4.3.3). Moreover, the low resistance related to the cooling down curve confirms the retention of the phase transition from stable amorphous phase to its crystalline phase.

![Figure 8-3 a) XRD patterns of as-deposited, crystallized, and annealed for 55 nm in-matrix NWs. The size of as-deposited sample is relatively larger (2 × 10 mm) compared to the others (2 × 2 mm) b) cross section of in-matrix NWs to observe the NW-AAO interface](image)

For the entire range of NWs, clear phase transition from amorphous to crystalline was observed, and the $T_{crys}$ variation with respect to the diameter of the NW is shown in
Interestingly, for the NWs with diameter of 220nm, the largest in diameter representing the bulk, showed crystallization at 110 °C with ±6 °C uncertainty which is consistent to the previous studies of Sb$_2$Te$_3$ thin films ($T_{crys}$=115 ±5 °C) with 100-150 nm thickness. Corresponding $T_{crys}$ for both 100nm (111 ±5 °C) and 80 nm (112 ±5 °C) NWs did not show a significant change with respect to 220 nm within the uncertainty. However, the trend of increasing $T_{crys}$ initiated starting from 55 nm (115 ±5 °C) NWs and further confirmed the trend from 35nm (125 ±5 °C) NWs. Moreover, the smallest, 18nm NWs showed the highest $T_{crys}$ with 156 ±5 °C, which is 36 °C increase of $T_{crys}$ with respect to the bulk. In order to provide an insight about the feasible range of $T_{crys}$ tuning with respect to the careful selection of the diameters of NWs, Figure 8-4a represents the resistance versus temperature curves for the largest, onset and smallest diameters of NWs.

Figure 8-4 a) Resistance vs. temperature curves from 4PRM for NWs with different diameter 220, 55, and 18nm and insets shows pseudo 4-wire connection configuration for in-matrix NWs and b) Crystallization temperature vs. NW diameter to visualize the scaling effect.
To the best of our knowledge, there have been no previous studies on the size dependent phase transition behavior of electrodeposited PC materials, but there are several other studies of thin films [17-20, 153], nanowires [14, 16, 155-157], nanoparticles [158], and nano-pits [154] which have used different methods of synthesis, such as sputtering, VLS, and colloidal synthesis. Especially for the NW studies crystalline NWs (GeTe, Ge$_2$Sb$_2$Te$_5$, In$_2$Se$_3$, and Sb$_2$Te$_3$) were synthesized using VLS method and the phase transition behavior, either melting [14, 16, 155, 156] or crystallization [157], was investigated by directly exposing a single NW to an energetic electron beam using a TEM or incorporating a single NW into a PCM device, which is capable of performing SET/RESET functions similar to a PCM cell by accessing the NW through proper contacts, respectively. For GeTe [156] and In$_2$Se$_3$ [155] NWs (40-80 nm), a significant reduction in melting temperatures was observed compared to their bulk from 725 to 390 °C and 890 to 680 °C, respectively, and the melting temperature reduction was further confirmed for Ge$_2$Sb$_2$Te$_5$ NWs [16]. Supporting the same idea, Lee et al [14] demonstrated a significant RESET current reduction (from 4.0 mA for 200 nm to 0.42 mA for 28 nm) for GeTe NWs. Beside the above mentioned NW studies regarding the melting temperatures, Yu et al [157] have investigated the scaling effect of glass transition temperature ($T_g$) and threshold voltage ($V_{th}$) of switching, and they found that there is no clear correlation with $T_g$, but $V_{th}$ can be reduced under constant field only down to 10nm of amorphous domain length, and thereafter $V_{th}$ get saturated, which is a promising fact regarding the further scalability of PC materials. In addition to the overall
promising findings of the existing NW studies, our study provides new information about the capability of data retention of PC material by uplifting $T_{\text{crys}}$.

Even though there are no NW studies for a direct comparison, our findings agree with the overall trends observed in thin films, nanoparticles, and nano-pits. In a study performed by Raoux et al [153], a set of PC materials, Ge$_2$Sb$_2$Te$_5$, N-doped Ge$_2$Sb$_2$Te$_5$, Ge$_{15}$Sb$_{85}$, Sb$_2$Te, and Ag- and In- doped Sb$_2$Te, were investigated to explore the scaling effect by decreasing the thickness of the thin films in order to observe any changes in $T_{\text{crys}}$. Crystallization of the thin films was tracked by time-resolved XRD with respect to the temperature increase, and interestingly, scaling effects were seen with an increase in $T_{\text{crys}}$ for all of the PC materials when thicknesses were reduced to less than 10 nm. Moreover, amorphous to crystalline transition was observed up to 1.3-2.0 nm thicknesses of these PC materials and the relevant $T_{\text{crys}}$ were further increased. Importantly, the scaling effects for thin films were not seen until 10nm thicknesses, but for the NWs, effects were prominent and started at a diameter smaller than 55 nm, which is promising for the future PCM technology.

GeTe-Sb$_2$Te$_3$ pseudo-binary compositions play a significant role in PCM technology [39] and according to Yamada et al [143] systematic increase of $T_{\text{crys}}$ for thin films can be seen along the pseudo-binary line by adding GeTe into Sb$_2$Te$_3$. Notably, just by 1D scaling down and proper selection of the size of Sb$_2$Te$_3$, comparable $T_{\text{crys}}$ can be achieved similar to Ge$_{15}$Sb$_{85}$.

Furthermore, GeTe [158] nanoparticles coving a range of diameters from 5.0-1.8nm displayed a similar behavior of increasing $T_{\text{crys}}$ (240 °C compared to bulk) with
respect to the reduction of its diameter. In addition to that, In$_2$Se$_3$ [154] with different thicknesses (45-2nm) were deposited into nano-pits of a substrate and the change of both the $T_{\text{crys}}$ and $T_m$ were observed using TEM. As noticed in previous cases $T_{\text{crys}}$ increased by 160°C and $T_m$ decreased by 190°C with respect to the nominal film thickness change from 45nm to 2nm. However, to emphasize the importance of the environment of PC material, whether it is encapsulated, exposed, or patterned, 20-55nm size of GeSb [19] nanostructures were deposited with 80-100nm spacing, and relatively small decrease of $T_{\text{crys}}$ was observed with respect to the size reduction.

There is not much information about the nature of crystallization for Sb$_2$Te$_3$ NWs, but the growth-dominated crystallization has been demonstrated for thin films [161]. Regarding the crystal nucleation, the role of AAO-NW interface was not investigated due to the limitations of current experiments. So at this point it is unclear whether crystal nucleation is either homogenous or heterogeneous. In order to confirm the wettability of NW-AAO interface, cross-sectional SEM micrographs (Figure 8-3b) were examined and a partial contrast was observed in between NW and AAO interface, which can be claimed as an extremely small spacing. Moreover, the compositional uniformity along the channel length was confirmed with 3% of uncertainty and the significance of that is unclear for homogenous nucleation. However, the interfacial effects cannot be ignored in NWs due to its high surface to volume ratio; therefore we believe that heterogeneous nucleation could be playing a significant role compared to homogenous nucleation.

Decreasing the melting temperature of NWs with respect to the depression of its diameter is due to the decrease of its surface energy [162]. As claimed in melting
temperature depression, surface energetics plays a crucial role in upsurge of crystallization temperatures as we observed in our study. Explanation is similar to the discussion given in Caldwell, et al [158] for nanoparticles. According to that, the surface energy of amorphous phase is lower than crystalline phase so with the reduction of size amorphous phase stability increases by further lowering its surface energy. Similarly for the NWs with reduction of its diameter, surface energy of its amorphous phase decreases. In other words, the amorphous phase becomes energetically preferred than the crystalline phase so that the amorphous to crystalline activation barrier for the transition increases. As explained above, increasing of crystallization temperature with respect to scaling of PC material is encouraging for the future of this technology, but the increasing $T_{\text{crys}}$ gets limited by decreasing $T_m$, which can give a hint about the ultimate limitation of scaling for PC material.

8.4 Conclusions

In conclusion, the crystallization temperature of prototypical Sb$_2$Te$_3$ NWs can be tuned with respect to its diameter. This profound size-effect of increasing the crystallization temperature with decreased diameter is promising for the future of PCM technology regarding data retention [21]. Our results confirms that crystallization temperature can be increased with a significant amount (at least 36 ºC) compared to its bulk.

Especially, the synthesis method of electrodeposition is a cost-effective approach which could be applied efficiently in PCM device fabrication to create high-aspect ratio nanostructures [54], and we have successfully synthesized high aspect ratio PC NWs,
which demonstrated phase transition with expected resistance contrast (at least two orders of magnitude) to be utilized in PCM device applications. Moreover, the demonstrated phase transition of in-matrix PC NWs could provide confidence to develop high density NW memories in future as a novel approach. Furthermore, in order to enhance the accuracy and sensitivity of the resistance levels in multi-level cells, the observed size-effect could be utilized to tune the phase transitions along the length of the NW systematically, e.g. by modifying the diameters as two segments along the length, first segment with a larger diameter and the second segment with a relatively smaller diameter, then with the thermal ramping, the first segment will undergo crystallization before the second, if crystallization could be localized to the first segment. Likewise with a systematic phase transition of segments better resolutions could be achieved between multi resistance levels once overall resistance is measured.
Chapter 9: Future Prospects

Even though this dissertation is focused on Sb-Te materials, the gained knowledge from the synthesis to characterization can be readily applicable to extend our understanding for the same or similar systems. To modify the material properties further, the studies can be extended mainly to investigate the doping-effects and interfacial-effects. Especially to combine both the memory and logic capabilities for these materials (magnetic PC materials) magnetic dopants could be added and can be investigated under different nanoscale confinements. In addition to that, interfacial-effects also could be explored to trigger the diverse properties of material. When studying the materials under nanoscale confinements, the interfacial-effects cannot be ignored. With proper investigation smart interfaces could be found to promote the material properties. Overall, these effects could be coupled to improve the material properties for better usage. In addition to those, the device-like approaches also possible to further broaden our horizons, as discussed below.

Instead of a 2 bit memory cell multiple bits can be stored in a multi-level cell. This approach is an attempt to enhance the data density in PCM technology by defining multiple resistance levels in a single cell. If resistance levels are not resolved properly, the accuracy of the defined bit level is problematic. In order to enhance the resolution of the cell resistance, the knowledge gained from the size-dependent crystallization can be applied. As shown in Figure 9-1a, the PC material can be confined into serially connected segments with different diameters. In consistent to our study, the crystallization temperature for each segment is different and increases with respect to the
reduction of diameter. If the segment crystallization can be localized then (crystallization localizer), the segment resistance also can be selectively lowered. Which means each segment can act as a variable resistor to switch between high and low resistances. Ultimately when the resultant resistance is measured after selectively switching the segments, more resolved resistances can be measured.

There is a huge interest in finding the novel cell structures for PCM technology in order to replace the common cell structure. Main motivation is to reduce the cell size, and the nanowire-based cell structure is a promising solution. So the nanowire-based PC material array (Figure 9-1b) could be synthesized and investigated by extending our prior knowledge of templated electrodeposition. In this case, the usage of AAO template is not only capable of aligning the NWs, but also capable of localizing the electrical and thermal cross talks between NWs.

Solid electrolytic nature and the species diffusion are interesting to study due to key applications. In CBRAM, species were biased to diffuse through solids to create a conducting-filament. The filament formation in solids is not well understood, therefore to enhance our understanding ionic or atomic diffusion can be studied using a similar setup as shown in Figure 9-1c. The solid electrolyte can be electrodeposited into AAO and the diffusive species can be sputtered into one side of AAO. Then the species diffusion can be thermally or electrically triggered through the channels selectively. Unlike the natural diffusion, this is more directed and confined to diffuse in 1D, which is preferred in most applications. Moreover, the species diffusion through the channels can be easily probed by compositional depth profiling (RBS).
Figure 9-1 Schematic of a) material confinement (crystallization localizer) b) nanowire-based PC material array in AAO template with diode as an access device c) material confined array in AAO template to study 1D ionic and atomic diffusion.
References


52. CSC. BIG DATA UNIVERSE BEGINNING TO EXPLODE. 2015; Available from: http://www.csc.com/insights/flxwd/78931big_data_universe_beginning_to_explode


152. Cherevko, S., et al., *Electrodeposition mechanism of palladium nanotube and nanowire arrays*. (1533-4880 (Print)).


Appendix A: Compositional Analysis for Overlapping EDX Sb-Te Peaks

Figure A-1 Summary of steps used in EDX analysis.

Figure A-2 Modelled EDAX spectrum using Pseudo Voigt for peaks and Polynomial for background.
area under profile functions:

total: 559.45578
Pseudo Voigt: 26.605259
Pseudo Voigt: 54.322242
Pseudo Voigt: 90.917663  
Area of Sb (L) highest intensity peak
Pseudo Voigt: 125.43380 
Area of Te (L) highest intensity peak
Pseudo Voigt: 48.690369
Pseudo Voigt: 75.227533
Pseudo Voigt: 48.377538
Pseudo Voigt: 8.864401
Pseudo Voigt: 0
Pseudo Voigt: 24.966853
Pseudo Voigt: 39.151466
Pseudo Voigt: 0
Polynomial: 16.898659

Figure A-3 Portions of the results of modelled spectra using WinXAS and corrected ZAF using CITZAF.

<table>
<thead>
<tr>
<th>Element</th>
<th>Area</th>
<th>K-Ratio</th>
<th>Atomic Proportion</th>
<th>Composition</th>
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</thead>
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<tr>
<td>Ge</td>
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<td>0.000</td>
<td>0.000</td>
<td>0</td>
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<tr>
<td>Sb</td>
<td>90.918</td>
<td>0.420</td>
<td>18.147</td>
<td>43</td>
</tr>
<tr>
<td>Te</td>
<td>125.434</td>
<td>0.580</td>
<td>24.000</td>
<td>57</td>
</tr>
<tr>
<td>Total</td>
<td>216.351</td>
<td>1.000</td>
<td>42.147</td>
<td>100.000</td>
</tr>
</tbody>
</table>

Figure A-4 Portion of the EXCEL template used in calculating K-Ratios and final Composition.
Appendix B: Grids of Surface Micrographs for Sb-Te Thin Films

Figure B-1 Surface micrographs of electrodeposited thin films using electrolyte Sb/Te=0.25 under different deposition voltages with multiple magnifications
Figure B-2 Surface micrographs of electrodeposited thin films using electrolyte Sb/Te=0.66 under different deposition voltages with multiple magnifications
<table>
<thead>
<tr>
<th>Electrodeposition Voltage (mV)</th>
<th>500nm</th>
<th>1µm</th>
<th>5µm</th>
<th>50µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>850</td>
<td></td>
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<tr>
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<td>550</td>
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</tbody>
</table>

Figure B-3 Surface micrographs of electrodeposited thin films using electrolyte Sb/Te=1.00 under different deposition voltages with multiple magnifications
Figure B-4 Surface micrographs of electrodeposited thin films using electrolyte Sb/Te= 1.50 under different deposition voltages with multiple magnifications
Figure B-5 Surface micrographs of electrodeposited thin films using electrolyte Sb/Te=4.00 under different deposition voltages.
Appendix C: Automation of 4PRM Setup using LabVIEW

Figure C-1 Front panel of the LabVIEW program
Figure C-2 Block diagram of the LabVIEW program.
Appendix D: Automation of Potentiostat/galvanostat using LabVIEW

Figure D-1 Front panel of the LabVIEW program
Figure D-2 Block diagram of the LabVIEW program.
Appendix E: SEM Micrographs of Commercial AAO Templates

Figure E-1 SEM micrographs of commercial templates under high and low magnification
Appendix F: Artistic SEM Micrographs Captured during Research

Figure F-1 Artistic SEM micrographs acquired during sample characterization
Appendix H: Publications, Conference Presentations, and Seminar

Publications


Conference Presentations
5. “Size Dependent Phase Transition behavior of Phase-change Sb$_2$T e$_3$ Nanowires” GOMD 2015

6. “Solid Electrolytic Nature of Sb-Te Phase-change Thin films” APS-Ohio Spring 2013

7. “Sb-Te Phase-change Nanowires by Templated Electrodeposition” MRS Spring 2012


Seminar
Appendix I: Awards and Recognition

1. 1st Place Poster Award ($500): ACerS Glass & Optical Materials Division (GOMD-DGG), Miami, FL 2015

2. 1st Place Poster Award ($200): Student Research & Creative Activity Expo, Ohio University 2014

3. 1st Place Poster Award ($200): Student Research & Creative Activity Expo, Ohio University 2013

4. CMSS Studentship Awards ($5500): Condensed Matter & Surface Science, Ohio University 2011/12

5. 1st Place Poster Award ($500): ACerS Glass & Optical Materials Division (GOMD), Savannah, GA 2011