



# Electrochemical Deposition and Characterization of Thermoelectric Thin Films of $(Bi_xSb_{1-x})_2Te_3$

Master of Science Thesis [The Master Program Materials and Nanotechnology]

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## THESIS FOR THE DEGREE OF MASTER OF SCIENCE

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Cover: Scanning Electron Microscopy image of electrodeposited bismuth antimony telluride thin film on gold.

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## Abstract

Bismuth telluride and its derivative compounds are the conventional thermoelectric materials which have relatively high "Figure of Merit" (zT) values at room temperature. Recently, theoretical and experimental work has proven that low dimensional thermoelectric materials can produce higher zT than the bulk materials. Thus, in this work, we studied the preparation and characterization of thermoelectric thin films of bismuth antimony telluride ternary compounds. Thin films were synthesized by means of electrochemical deposition.

In the first part of the project,  $(Bi_xSb_{1-x})_2Te_3$  thermoelectric thin films were electrochemically deposited at potentiostatic conditions on gold-coated silicon substrates, from an aqueous acidic solution. The surface morphology, elemental composition, crystal structure and thermoelectric properties of the deposited films were investigated using SEM, EDX, XRD and ZEM-3, respectively. Our results show that continuously deposited thin films have an optimal composition of  $Bi_{0.5}Sb_{1.5}Te_{3.0}$  and give a highest power factor (221  $\mu$ W K<sup>-2</sup> m<sup>-1</sup>) for continuously electrodeposited films. In addition, we also found that the surface morphology and the elemental composition of the films can be manipulated by varying the solution concentration and the deposition potentials.

In the second part of the project, we studied a methodology for fabrication of p-type and ntype thermoelectric thin films of  $Bi_xSb_yTe_z$  compounds from one solution by varying the deposition potentials. It has been successfully demonstrated that n-type thin films of  $Bi_2Te_3$ based ternary compounds can be deposited at less negative deposition potentials, while p-type thin films of  $Sb_2Te_3$ -based ternary compounds can be obtained at more negative deposition potentials from the same solution.

**Keywords:** thermoelectric, bismuth antimony telluride, thin films, electrodeposition, crystal structure.

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## 1. Introduction

Global warming due to the use of the fossil fuel and the cost of the energy are big issues to the today's world. Therefore, interest of the people in thermoelectric materials which can be used to convert waste heat to electricity is gradually increasing, to use the energy with high efficiency. Thermoelectric materials can be mainly used either for power generation from waste heat or refrigeration [1]. One of the major advantages of thermoelectric materials is that it can be used to convert any kind of heat energy such as waste heat, solar energy, radiation heat, etc directly into electricity. Other advantages include no-moving parts, low maintenance and high reliability.

Thermoelectrics have a history more than 150 years. Estonian physicist Thomas Seebeck, first discovered the thermoelectric effect in 1821, showed that from two dissimilar conductors which are connected to each other, can produce electricity when one junction was subjected to heat. Some years later, in 1834 French physicist Jean Peltier found the reverse phenomenon that two dissimilar conductors which are connected to each other, can produce a temperature gradient when it is subjected to an electric current. With the development of thermodynamics for all forms of energy conversions, in 1851, W. Thomson (Lord Kelvin) found a relationship between Seebeck and Peltier coefficients and introduces the Thomson effect which was observed experimentally [2].

Efficiency of the thermoelectric materials can be expressed by dimensionless "Figure of Merit (zT)". Even though the thermoelectric materials give a number of advantages, the main problem is that the efficiency of the present thermoelectric materials is somewhat lower than desired. In the recent decades, by the theoretical predictions, researchers found that to improve the efficiency of thermoelectric materials, nanoengineering is a promising approach [3]. For instance, nanostructured two-dimensional Sb<sub>2</sub>Te<sub>3</sub>/Bi<sub>2</sub>Te<sub>3</sub> super-lattices show higher zT values than the conventional bulk Sb<sub>2</sub>Te<sub>3</sub> or Bi<sub>2</sub>Te<sub>3</sub> [4].

In this project, we mainly focus on producing thin films of  $(Bi_xSb_{1-x})_2Te_3$  thermoelectric materials using the electrodeposition, and correlate the observed crystal structure, film composition and surface morphology with measured thermoelectric properties, such as Seebeck coefficient, electrical resistivity and calculated power factor.

## 2. Thermoelectricity

## 2.1 Thermoelectric Effects

There are three main thermoelectric effects named as Seebeck effect, Peltier effect and Thomson effect. Imagine two dissimilar conductors, labeled as a and b, are connected as shown in Figure 1 and maintaining the junctions A and B at different temperatures  $T_1$  and  $T_2$ , respectively. When the temperature  $T_1>T_2$ , the open circuit electromotive force developed between C and D can be expressed as equations (1a) and (1b), where  $\alpha$  is the differential Seebeck coefficient ( $\alpha_{ab}$ ) between a and b. Other than  $\alpha$ , S also can be used as a symbol for Seebeck coefficient and the units of the Seebeck coefficient is *V/K* or more often  $\mu V/K$  [5].

$$V = \alpha (T_1 - T_2) \tag{1a}$$

$$\alpha = \frac{V}{\Delta T} \tag{1b}$$



Figure 1: Schematic diagram of Basic thermocouple

If an external electromotive force is applied between C and D (Figure 1) a current *I* is introduced in the clockwise direction, the rate of heating at one junction between a and b is *q* and the rate of cooling at the other junction is -q. Ratio between *q* and *I* is define as the Peltier coefficient ( $\pi$ ) as shown in equation (2) and the unit of the Peltier coefficient is *W*/A or Volts.

$$\pi = \frac{q}{I} \tag{2}$$

The Thomson coefficient describes the rate of generation of reversible heat q, when there is a flow of current I in a portion of a single conductor, which was subjected to a temperature difference T. Equation (3) describes this relationship when there is a small temperature difference and  $\beta$  is the Thomson coefficient. The unit of the  $\beta$  is V/K [5].

$$q = \beta I \Delta T \tag{3}$$

The Kelvin relationship can be obtained using above three thermoelectric coefficients and shows in equation (4a) and (4b) [5].

$$\alpha_{ab} = \frac{\pi_{ab}}{T} \tag{4a}$$

$$\frac{d\alpha_{ab}}{dT} = \frac{\beta_a - \beta_b}{T}$$
(4b)

Moreover efficiency of the thermoelectric materials can be determined by the dimensionless Figure of Merit (zT) as shown in the equation (5). So the efficiency of thermoelectric materials depends on Seebeck coefficient ( $\alpha$ ), absolute temperature (*T*), electrical resistivity ( $\rho$ ) or electrical conductivity ( $\sigma$ ) and the thermal conductivity ( $\kappa$ ) [6]. When zT > 1, then the material can be considered as a good thermoelectric material.

$$zT = \frac{\alpha^2}{\rho\kappa}T = \frac{\alpha^2\sigma}{\kappa}T \tag{5}$$

### 2.2 Carrier Concentration and Effective Mass

There are two types of carriers in a conductor, which are electrons or holes. Electrons are providing n-type conduction and the holes are providing p-type conduction. To have a high Seebeck coefficient, there should be only one type of charge carriers dominating in the material. By increasing the temperature of one side of a conductor, charge carriers tend to move from the hot side to the cold side. If there is an equal amount of n-type and p-type conduction, charge carriers will cancel out each other and therefore the Seebeck voltage will not be generated. Equation (6) shows the relation between charge carrier concentration and Seebeck coefficient, which can be plotted in a way as shown in Figure 2(a).  $m^*$  is the effective mass of the carrier and n is the carrier concentration. It can be found that insulators having low carrier concentration (n) have high Seebeck value. Although when the carrier concentration is low, according to the equation (7), where  $\rho$  is the electrical resistivity,  $\sigma$  is the electrical conductivity and  $\mu$  is the carrier mobility, the electrical conductivity also becomes low [6]. In Figure 2(a), it can be easily found that heavily doped semiconductors which have a carrier concentration in the range of  $10^{19}$  cm<sup>-3</sup> give the highest Power Factor ( $\alpha^2 \sigma$ ) values [5]. From the equation (6), it clearly shows that a high effective mass  $(m^*)$  gives high values for the Seebeck coefficient. Since heavy carriers with high effective mass moves slowly, it reduces the mobility of the carriers. Therefore by equation (7), this will reduce the conductivity.

$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m * T \left(\frac{\pi}{3n}\right)^{\frac{2}{3}}$$
(6)

$$\frac{1}{\rho} = \sigma = n e \mu \tag{7}$$



Figure 2: Variations of thermoelectric properties; (a) Seebeck coefficient ( $\alpha$ ), electrical conductivity ( $\sigma$ ), Electrical Power Factor ( $\alpha^2 \sigma$ ) and; (b) Thermal Conductivity ( $\lambda$ ); with the carrier concentration [5].

## 2.3 Thermal Conductivity

In addition, to have a high zT value, thermal conductivity ( $\kappa$  or  $\lambda$ ) should be low as well. As shown in the Figure 2(b) and equation (8), thermal conductivity has two contributions, one from the heat transport by the electron and holes (electronic thermal conductivity -  $\kappa_e$ ) and heat transport by phonons (lattice thermal conductivity -  $\kappa_l$ ). Electronic thermal conductivity can be expressed by the Wiedemann-Franz law, as shown in equation (9).

$$\kappa = \kappa_e + \kappa_\ell \tag{8}$$

$$\kappa_e = L\sigma T = ne\mu LT \tag{9}$$

Where, L is Lorenz factor, 2.4 x  $10^{-8} J^2 / K^2 C^2$  for free electrons.

Generally lattice thermal conductivity ( $\kappa_l$ ) can be calculated by equation (8). So the correct value of  $\kappa_e$  is needed. However Lorenz factor really depends on the carrier concentration, for the materials with low carrier concentration, Lorenz factor will reduce about 20% from its normal value. Moreover in high temperatures, bipolar thermal conductivity also arises due to that more electrons release from the lattice while creating holes [6, 7].

Equation (9) gives the relation between  $\kappa_e$  and  $\sigma$ . It clearly shows that if we reduce the  $\kappa_e$ ,  $\sigma$  will be reduced as well. So the most promising approach is to reduce the lattice thermal conductivity ( $\kappa_l$ ). Glass has really low lattice thermal conductivity, since thermal conductivity in glass looks like a random walk of energy through the lattice, other than the transport through the phonons [6]. Nevertheless the problem is that glasses have low electrical conductivity because of their poor "electron-crystal" properties. Thus the requirement for a good thermoelectric material is "phonon-glass electron-crystal (PGEC)" behavior, while means working like amorphous glass for transferring phonons and acting like a crystal for transferring electrons.

## 2.4 Thermoelectric Devices

Thermoelectric devices for power generation or refrigeration are usually composed of two types of thermoelectric materials. Those are p-type and n-type of conductors called thermocouple legs, arms or thermoelements. As shown in Figure 3, those thermoelements are connected electrically in series and thermally in parallel. In a thermoelectric generator as shown in the Figure 3(a) when top side of the thermoelectric materials is heated up from the heat source, charge carriers of both n and p type legs tend to move to the bottom side. Majority carriers of the n-leg are electrons. When electrons move to the bottom side, that generate a current to the top side. Majority carriers of the p-leg are holes and those have positive charge. When holes move to the bottom side they generate a current into the bottom side. In a cooling module, as shown in the Figure 3(b), supplied electric current forces charge carriers in p and n legs to move to the bottom side. These movements transfer the heat from the top side to the bottom side and cool the top surface of the cooling device. This one module can only produce a small amount of power or cooling effect. Thus, for the practical usage, a

real thermoelectric device is manufactured by connecting a large number of those modules as shown in Figure 4 [6].



Figure 3: Schematic diagram of (a) Thermoelectric Generator, (b) Cooling module

In here let's use material figure of merit as zT and device figure of merit as ZT. Efficiency of a thermoelectric device (ZT) is not only dependent of the maximum zT of the material, since all thermoelectric properties ( $\alpha$ ,  $\sigma$ ,  $\kappa$ ) depend on the temperature. As an example state-of-art Bi<sub>2</sub>Te<sub>3</sub> materials have maximum zT value 1.1, but the device ZT is only about 0.7 for both power generation and refrigeration [6]. For the cooling devices ZT can easily be found by the equation (10)

$$\Delta T_{\max} = \frac{ZT_c^2}{2} \tag{10}$$

As shown in equation (11) for the power generator, maximum efficiency ( $\eta$ ) is used to determine the ZT. So the maximum efficiency depends on the Carnot efficiency ( $\Delta T/T_h$ ) [6].

$$\eta = \frac{\Delta T}{T_h} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{T_c}{T_h}}$$
(11)



Figure 4: Thermoelectric device [6]

#### 2.5 Thermoelectric Materials

#### 2.5.1 Skutterudite

Skutterudite has a cubic unit cell with CoAs<sub>3</sub> type structures and the space group Im<sup>-3</sup>. The unit cell of this is composed of eight corner shared by XY<sub>6</sub> (X = Co, Rh, Ir; Y = P, As, Sb) type octahedra. Moreover CoAs<sub>3</sub> is a AB<sub>3</sub> type perovskite structure. Figures 5(a) and 5(b) show the Skutterudite structure with CoSb<sub>3</sub> (original Skutterudite). It clearly indicates that Skutterudite have large void spaces in the body centered position of the cubic unit cell. Generally CoSb<sub>3</sub> has good power factor, but high lattice thermal conductivity. To improve the thermoelectric properties of these materials, one can introduce another element to fill those voids. Mainly lanthanide, actinide, alkaline-earth, alkali, thallium and Group IV elements are used for this void-filling. By introducing these elements we can change the carrier concentration of the material, because of the elements can be an electron donor or an acceptor. These new atoms can "rattle" inside those voids and can effectively reduce the lattice thermal conductivity. In this way Skutterudites can be modified to "phonon-glass electron-crystal (PGEC) materials. Generally when the atom inside the void becomes smaller and heavier, the disorder is higher, so it creates a larger reduction in lattice thermal conductivity [9].



Figure 5: Skutterudite,  $CoSb_3$  model structures, with void cages indicated by blue spheres. (a) Unit cell of the Skutterudite,  $CoSb_3$ . With octahedra made by pnicogen atoms (Sb) and transition metal (Co) inside. (b) To get the Co atoms to the corner of the unit cell, the model was shifted by  $\frac{1}{4}$ ,  $\frac{1}{4}$ . Sb squares are the only chemical bonds in this structure [9].

#### 2.5.2 Clathrates

Clathrates have open frameworks with tetrahedrally coordinated Al, Ga, Si, Ge or Sn forming cages that hosts an electropositive guest atom. There are at least eight types of Clathrates, but Type-I and Type-II have been most studied. Type-I has formula  $X_2Y_6E_{46}$  and X and Y are the guest atoms which sitting on the two dissimilar polyhedral cages  $E_{20}$  and  $E_{24}$ , where E is referred to the number of atoms tetrahedrally coordinate to the framework. Figure 6 shows the Type-I Clathrates structure of Na<sub>8</sub>Si<sub>46</sub> as an example. Type-II consists of  $E_{20}$  and  $E_{28}$  cages. Clathrates have low thermal conductivity, because of the "rattling" atoms and the wide open framework that it has [9].



Figure 6:  $Na_8Si_{46}$  structure with Si atoms (blue) at framework and different cages filled with the Na atoms, the tetrakaidecahedral cage (blue) and the pentagonal dodecahedral cage (green) [9]

## 2.5.3 Bismuth Antimony Telluride (Bi<sub>1-X</sub>Sb<sub>X</sub>)<sub>2</sub> Te<sub>3</sub>

Bismuth telluride and its alloys have high figure of merit (zT) for room temperature applications. They have been commercially available thermoelectric materials since 1960 s'. Commercial bismuth antimony telluride bulk alloys have high zT about 1, but recently M.S. Dresselhaus et al [8] showed that nanocrystalline bulk bismuth antimony telluride can be produced with zT about 1.4 at 100 °C. Because of this high zT values for bulk materials of bismuth antimony telluride, this material has been studied for electrodeposition in this project.

 $Bi_2Te_3$ ,  $Sb_2Te_3$  and  $Bi_2Se_3$  have the same crystal structure showing a trigonal symmetry, which has a rhombohedral unit cell with five crystallographic distinct atom positions. Figure 7 shows the layered structure of the  $Bi_2Te_3$ . For  $Sb_2Te_3$ ,  $Bi_2Se_3$ ,  $(BiSb)_2Te_3$  or  $Bi_2(TeSe)_3$ , Sb replaces to the Bi in this lattice and Se replaces Te [2].



Figure 7: Layer structure of the  $Bi_2Te_3$  in hexagonal system, with atomic distance and major binding forces [2]

## 2.6 Application of Nanotechnology to Thermoelectric Materials

During the last decades lots of research has been focused on developing thermoelectric properties through nanoengineering. The theoretical predictions and experimental evidences have proven that nanotechnology can improve the properties of thermoelectric materials. Decreasing the characteristic length scale of the materials can affect the density of electronic states in the material as shown in Figure 8. According to equation (12) we can control the

Seebeck coefficient by controlling the density of electronic state of the materials. This kind of change of the Seebeck coefficient does not normally affect the electrical conductivity of the material. That is because; this change is not related to the number of carriers in the material like equation (6). Furthermore introducing many interfaces may lead to scattering of phonons more effectively than electrons, alternatively filtering out low energy electrons at interfacial potential barriers both of which will improve the figure of merit of the materials [10].



Figure 8: Density of Electronic states; (a) bulk 3D crystalline semiconductor, (b) 2D quantum well, (c) 1D nanowire or nanotube, and (d) 0D quantum dot [10]

$$\alpha = \frac{\pi^2 k_b^2 T}{3q} \left( \frac{d \ln N(E)}{dE} + \frac{d \ln \tau(E) \nu(E)^2}{dE} \right)_{E=E_T}$$
(12)

Where

N(E) = Density of electronic states

Theoretical predictions of thermoelectric figure of merit for low dimensional  $Bi_2Te_3$  like materials have been reported and are summarized in the Figure 9. It shows that 1D nanowire may produce higher zT than the 2D thin films [3].

There are a number of experimental evidences showing how nanotechnological applications improve the thermoelectric properties. Quantum-dot supperlattice (QDSL) structures made from PbTe/PbSe<sub>0.98</sub>Te<sub>0.02</sub> produced zT~ 1.6 and 3.5 at 300K and 570K, respectively. Another example is converting semimetal Bi nanowires to semiconductor Bi nanowires by reducing the radius of the wire. Through this way Sb-doped Bi nanowires were produced [10, 11].

Also, nanostructured two-dimensional  $Sb_2Te_3/Bi_2Te_3$  super-lattices showed higher zT values than the conventional  $Sb_2Te_3$  or  $Bi_2Te_3$  [4].



Figure 9: Calculated zT with the width of the quantum wire or quantum well for  $Bi_2Te_3$ -like materials for optimum level for transport in the highest mobility direction. Calculated zT for bulk using the corresponding 3D model is indicated by the dashed line [3]

## 3. Electrochemistry

## 3.1 Electrochemical Deposition

Electrodeposition is the technique that we used in this study to prepare thermoelectric thin films of  $(Bi_xSb_{1-x})_2Te_3$ . Thin films of bismuth antimony telluride are usually prepared by chemical vapor deposition (CVD) and physical vapor deposition (PVD) techniques which are relatively more expensive for large scale use [12-14]. Compared to those techniques, electrodeposition is a low cost and efficient method to produce thin films. The most interesting feature in electrodeposition is that, the composition and crystalline structure of the thermoelectric material can be controlled by adjusting the electrodeposition parameters [12, 15].

Electrochemical reaction is a chemical reaction which happens at the interface between an electron conductor (electrode) and an ionic conductor (electrolyte) of an electrochemical cell, because of the transfer of electrons in between the electrolyte and the electrode. This is basically a REDOX (Reduction-Oxidation) reaction. Oxidation reaction happens on the anode and the reduction reaction happens on the cathode.

In addition electrochemical deposition is the process that uses reduction reactions to deposit an element or a compound which is dissolved in the electrolyte as ions on top of an electrode. In this study we used three electrode system to deposit  $(Bi_xSb_{1-x})_2Te_3$  on gold electrodes. The three electrodes are named as working, counter and reference electrodes, respectively, as shown in the Figure 10. Working electrode is the one that we apply a desired potential to supply electrons to the electrolyte during reduction reaction or transfer electrons from the electrolyte during oxidation reaction. The reference electrode is a half cell which has a welldefined potential used to measure the potential of the working electrode. Therefore it should not pass any current through it. Counter electrode is used to maintain that current flow. Generally, the surface area of the counter electrode is larger than that of the working electrode in order to keep a uniform current flow through the working electrode.



Figure 10: Schematic diagram of the Three Electrode System

## 3.2 Cyclic Voltammetry

In Cyclic Voltammetry (CV), the potential of the working electrode is linearly swept between two potentials. The scan can be carried out for several times for one experiment. During this scan the current corresponding to the potential is recorded. The potential of the working electrode is measured against the reference electrode and the current of the working electrode is measured through the counter electrode. By this we can monitor the electrochemical reactions in the electrolyte.

During the forward scan in CV, when the scanning potential reaches the standard reduction potential for a reaction (or oxidation potential depending on the scanning direction), a so called Faraday current starts to increase in between electrolyte and the working electrode and reaches the maximum when it reaches the diffusion limit. When the reaction is limited by the diffusion, the reduction current starts to decrease and thus a peak appears during the potential scan. During the reverse scanning, the product that formed in the reduction process starts to oxidize. The peak that appeared during this has the reverse polarity when compared with the peak obtained by the forward scanning [16].

#### 3.3 Continuous Electrochemical Deposition

In electrochemistry, there are a number of deposition techniques available. In the present study, we used the continuous electrochemical deposition technique to prepare thermoelectric thin films of  $(Bi_xSb_{1-x})_2Te_3$ . First we run the CV curve for the electrolyte and used this to find out the favorable potential for the reduction. Then we used that potential as the depositing potential and constantly supplied that potential to the working electrode during a desired time interval. The deposition time was varied to control the thickness of the deposited films.

#### 3.4 Calculating Thickness

Faraday's law is given in equation (13) and was used to calculate the thickness of the deposited films. For the electrochemical deposition of  $(Bi_xSb_{1-x})_2Te_3$  from a solution of  $Bi^{3+}$ ,  $Sb^{3+}$  and  $HTeO_2^+$ , an 18 e<sup>-</sup> transfer is needed for each  $(Bi_xSb_{1-x})_2Te_3$  formed according to the reaction (3) in the section 5.1.2.2 in this report. Thus took the z as 18 and we then made an assumption that the current efficiency of the system is 100%.

$$m = \left(\frac{Q}{F}\right)\left(\frac{M}{z}\right) \tag{13}$$

Where

- m = mass of the substance that deposited at working electrode (g)
- Q = total electric charge passed through the working electrode (C)
- F = Faraday's constant (F=96,485 C/mol)
- M = Molar mass of the substance (g/mol)
- z = number of electrons transfer per unit of the compound

Then use the equation (14) to calculate the thickness of the film,

$$d = \frac{m}{V} = \frac{m}{A \times h} \tag{14}$$

Where

- d = Density of the film, assumed to be equal to density of compound
- m = mass of the film
- V = volume of the film
- A = area of the film
- h = thickness of the film

## 4. Experimental Methods

## 4.1 Electrodeposition Setup

The following conditions were used to prepare the electrolyte solution used. According to the Pourbaix diagrams, in pH=0 solutions, Bi and Te exist as completely dissolved  $Bi^{3+}$  and  $HTeO_2^+$ , respectively, and Sb exist as SbO<sup>+</sup> [17-19]. By adding tartaric acid SbO<sup>+</sup> forms  $[Sb_2(C_4H_4O_6)_2]^{2+}$  which is more soluble than SbO<sup>+</sup> [17]. The electrolyte was prepared with MilliQ water (18 MΩcm resistivity) collected from Barnstead E-pure filtration system. First Bi(NO\_3)\_3.5H\_2O (purity 99% analytical grade, Aldrich-Sigma) and TeO\_2 (purity 99% Aldrich-Sigma) were dissolved in 1M HNO\_3. While tartaric acid (purity 99% analytical grade, Aldrich-Sigma) was used to dissolve SbCl<sub>3</sub> (purity 99% analytical grade, Aldrich-Sigma) in MilliQ water. The two solutions were then mixed and the mixture was adjusted to pH=0. Nitrogen (N<sub>2</sub>) gas was bubbled for 10 minutes before each experiment in order to remove the dissolved oxygen in the electrolyte.

All electrochemical depositions were done at room temperature using conventional threeelectrode system and a potentiostat (Gamry Reference 600). As shown in the Figure 11, a PTFE reaction cell was used where the working electrode was placed horizontally at the bottom. Gold coated silicon wafer and Platinum mesh were used as working and counter electrodes, respectively. Ag/AgCl with 3M KCl electrolyte (Metrohm, 211.5 mV vs Standard Hydrogen Electrode at 20°C) was used as the reference electrode. (Bi<sub>x</sub>Sb<sub>1-x</sub>)<sub>2</sub>Te<sub>3</sub> thin films were prepared by the continuous electrodeposition method of which a constant voltage was applied. The gold working electrode was made as a gold-coated silicon wafer (antimonydoped n-Si(111) with a resistivity  $< 0.02 \ \Omega$  cm, Silicon Quest International, Inc.). This coating of gold on the silicon wafer was done by first cleaning the silicon wafer by ultra sonication in organic solvents. Then it was exposed to a mild oxygen plasma treatment (PE/RIH, 50 W) for 2 min to remove the organic contamination and surface particles. Next a 10 nm thick titanium layer was first coated on the cleaned silicon wafer to increase the adhesion of gold on the wafer. After that, 50 nm thick gold layer was coated on the wafer using physical vapor deposition (Evaporator, AVAC HVC600). Before this wafer was placed in the reaction cell, an In-Ga eutectic was coated on the unpolished backside of the silicon wafer as an ohmic contact.



Figure 11: Schematic of the Electro Chemical Deposition Setup. CE, RE and WE stand for Counter Electrode, Reference Electrode and Working Electrode, respectively.

## 4.2 Transferring Thin Films from Gold to Epoxy

Thermoelectric thin films were deposited on gold-coated Si substrates. But if one measures the thermoelectric properties of the as-deposited samples on top of gold, the highly conductive gold will influence the measurements. Thus before measurement of the thermoelectric properties, the thin films have to be separated from the gold and transferred to a non conducting support such as epoxy. Figure 12 shows the sample preparation procedure used and how the Thermocouples and Platinum electrodes of the ZEM-3 (instrument for measurement of electrical conductivity and Seebeck coefficient) were contacted with the film.

Each epoxy block was cut to 2mm x 3mm x 10mm in dimensions. Then silver paste was coated on the epoxy block as shown in Figure 12 to make a good electrical contact between the film and the platinum electrodes.



Figure 12: Schematic diagram of (a) and (b) transferring films from Au substrate to the epoxy support, (c) applying a silver coating and (d) setup used in the ZEM-3 to measure thermoelectric properties of films.

## 4.3 Characterization Techniques

#### 4.3.1 Scanning Electron Microscopy

Electrons have very short wavelengths, why the resolution of a scanning electron microscope can be about 0.1 nm. In an optical microscope lenses are used to focus the light whereas in electron microscopy magnetic fields are used to focus the electron beam. As shown in Figure 13, in scanning electron microscopy (SEM), the sample is scanned using a finely focused electron beam [20]. The primary reflected electron beam and the low energy secondary electrons which are emitted by the sample because of the initial electron beam are the detected. After that it maps the sample topography is mapped according to those detected beams. Samples for the conventional SEM should be conductive and electrically grounded. Otherwise charging can happen on the sample and it will reduce the intensity of backscattered electrons and the surface resolution. To get an image with high resolution of the sample, there should be more backscattered and secondary electrons near the surface. By this method we can clearly see the surface morphology, crystal size, surface defects, etc. [21]. During these studies, we used a Leo Ultra 55 FEG scanning electron microscope (SEM).



Figure 13: SEM setup, Electron/Specimen interactions. When electron beam strikes the sample, both phonon and electron signals are emitted [20]

#### 4.3.2 Energy Dispersive Analysis of X-Rays

Materials have a special ability to emit characteristic X-rays when subjected to an electron beam. In energy dispersive analysis of X-rays (EDX), those X-rays that emit from the sample are collected and separated them using a special detector (silicon–lithium detector). Then those signals are amplified and corrected for absorption and other effects. This will lead us to take a qualitative and quantitative analysis about the elements present in the sample [21].

#### 4.3.3 X-Ray Diffraction

In 1895, Wilhelm Röntgen first discovered the X-rays and he received the first Nobel Prize for Physics in 1901 for this discovery. In 1912, Max von Laue confirmed the wave nature of the X-rays and won the Nobel Prize for Physics in 1914 for his discovery. With this discovery, W.H. Bragg and W.L. Bragg (father and son) used the wave nature of X-rays to find the crystal structure of the NaCl and later the structures of KCl, ZnS, CaF<sub>2</sub>, CaCO<sub>3</sub> and diamond. Figure (14) shows the conditions that Bragg used to identify the X-ray reflection by the crystal. These reflected X-rays make an interference pattern. By this interference pattern and equation (15) which is the Bragg equation, the distance between two lattice planes ( $d_{hkl}$ ) can easily be obtained.



Figure 14: Bragg reflections of X-Ray from the crystal structure which have the lattice plane spacing  $d_{hkl}$  [21]

$$n\lambda = 2d_{hkl}Sin\theta_{hkl} \tag{15}$$

Where, n is an integral number of the wavelength,  $\lambda$  is the wavelength of the X-rays.  $d_{hkl}$  is the spacing between the crystal planes and  $\theta_{hkl}$  is the Bragg angle for which reflections of these planes occurred [21]. In this study, we used the X-ray diffractometer Siemens D5000 with a standard scintillation detector and with Cu K<sub>a</sub> radiation ( $\lambda = 1.542$ Å).

#### 4.3.4 Ulvac ZEM-3

Ulvac ZEM-3 is a commercially available instrument for measuring Seebeck coefficient and electrical resistivity of a material specimen. In this technique, a small temperature difference  $(\Delta T)$  is applied to the sample which is 10–30 °C and creates a Seebeck voltage  $(\Delta V)$ . According to the equation (1b), for small temperature differences  $\Delta V$  vs  $\Delta T$  plot shows a linear relationship. Thus by using the gradient of the graph, we can calculate the Seebeck coefficient ( $\alpha$ ). This method leads to removal of noise that can come with measuring of electromotive force. Because of the advanced setup of this instrument, we can measure the temperature and the voltage at the same point of the sample. For the measurements in this study, the base temperature was set at 25°C and the temperature difference ( $\Delta T$ ) between two ends of the film was varied as 10°C, 20°C and 30°C. Figure 15 shows the schematic diagram of the instrument [22].

To measure the electrical resistivity of the sample, the "four point probe method" was used. To do that, the instrument will pass a current (*I*) through the sample and measure the voltage difference (*V*) in between thermocouples A and B in Figure 15. Then Ohm's law (equation (16) is used to calculate the resistance (*R*). After that using equation (17), the resistivity ( $\rho$ ) of the sample is calculated by considering the length (*l*) between the probes and the cross-section area (*A*) of the specimen. At this time those thermocouples are working like connectors to the voltmeter. So it eliminates the effect of wiring resistance of the instrument to the results [22].

$$V = IR \tag{16}$$

$$R = \rho \frac{l}{A} \tag{17}$$



Figure 15: schematic diagram of the Ulvac ZEM-3 [22]

## 5. Results and Discussion

## 5.1 Project 1

Numerous of studies have been performed during the last few decades concerning bismuth telluride and antimony telluride [3]. Because those materials show useful thermoelectric properties in the temperature range 200-400 K [12]. As for the ternary compound bismuth antimony telluride the composition  $Bi_{0.5}Sb_{1.5}Te_3$  always gives the best thermoelectric properties both for bulk materials [23] or the thin films [17]. In these studies, we deposited  $(Bi_xSb_{1-x})_2Te_3$  thin films on gold substrates, using electrodeposition and then characterized the films by scanning electron microscopy (SEM) for surface morphology, energy dispersive X-ray spectroscopy (EDX) for the elemental composition and X-ray diffraction (XRD) for phase identification. The films were transferred to a non-conducting epoxy support where the electrical resistivity and Seebeck coefficient were measured using ZEM-3 at room temperature. To obtain reliable results, all the measurements were done on an insulating epoxy support and thus there were no effect from Au substrate to the measurements.

#### 5.1.1 Optimization of Film Composition

#### 5.1.1.1 Solution preparation

Concepts of the atomic behavior of Bi-Sb-Te have been taken in to account during the preparation of the solutions.  $Bi_2Te_3$  and  $Sb_2Te_3$  have trigonal systems which have rhombohedral unit cell with five atoms per molecule [2]. Therefore, for ternary compound  $(Bi_xSb_{1-x})_2Te_3$ , it can be suggested that either Sb atoms are incorporated into  $Bi_2Te_3$  lattice or Bi atoms are incorporated into  $Sb_2Te_3$  lattice. In the periodic table, Sb and Bi are in the same group while tellurium is in a different group. Therefore the substitution can happen on either bismuth or antimony atoms, not on tellurium atoms. The atomic radius of Bi=0.17 nm, Sb=0.159 nm and Te=0.16 nm [24].

According to previous studies [18], for electrodeposition of stoichiometric  $Bi_2Te_3$ , the electrolyte should contain excess Bi ion. For the purpose of comparison, a series of solutions

with  $\{[Bi]+[Sb]\}=7.5 \times 10^{-3} M$ ,  $[Te]=10.0 \times 10^{-3} M$ ,  $[C_4H_4O_6]=0.67 M$  and  $[HNO_3]=1 M$  were prepared. Table 1 shows the electrolyte concentration of a series of solutions.

Solution	Bi(NO <sub>3</sub> ) <sub>3</sub>	SbCl <sub>3</sub>	HTeO <sub>2</sub> <sup>+</sup>
Solution	(x 10 <sup>-3</sup> M)	(x 10 <sup>-3</sup> M)	(x 10 <sup>-3</sup> M)
S1	6.0	1.5	10
S2	4.5	3.0	10
S3	3.0	4.5	10
S4	1.5	6.0	10

Table 1: Variation of concentration of electrolyte, of a series of solutions which have 0.67 M  $\rm C_4H_4O_6$  and 1 M  $\rm HNO_3$ 

#### 5.1.1.2 Cyclic Voltammetry studies

Figure 16 shows the Cyclic Voltammetry (CV) curves, of the four solutions. During the cathodic scan from open circuit potential (OCP), only one peak appeared for the solution S1 to S3. For the solution S4, three peaks can be observed. According to the CV curves of solutions S1 to S3, peak potentials at -90, -60 and -50 mV were used respectively, to continuously deposit films X1, X2 and X3 correspondingly. Films X4(A) and X4(B) were deposited at -40 mV and -250 mV, respectively, according to the two reduction peaks of the CV curve of solution S4.



Figure 16: Cyclic Voltammogram of 1M HNO<sub>3</sub> solutions containing; 6.0 mM  $Bi^{3+}$ , 1.5 mM  $[Sb_2(C_4H_4O_6)_2]^{2+}$  and 10.0 mM HTeO<sub>2</sub><sup>+</sup> (Blue); 4.5 mM  $Bi^{3+}$ , 3.0 mM  $[Sb_2(C_4H_4O_6)_2]^{2+}$  and 10.0 mM HTeO<sub>2</sub><sup>+</sup> (Maroon); 3.0 mM  $Bi^{3+}$ , 4.5 mM  $[Sb_2(C_4H_4O_6)_2]^{2+}$  and 10.0 mM HTeO<sub>2</sub><sup>+</sup> (Orange); on Au electrodes (electrode area is 0.24 cm<sup>2</sup>), sweep rate 10 mV/s

#### 5.1.1.3 Composition, phase identification and surface morphology studies

Table 2 shows the deposition potential and film composition of films X1 to X4(B). It shows that films X1 to X4(A) have high tellurium content and low antimony content. The composition of film X4(B) is comparable with the ideal composition  $Bi_{0.5}Sb_{1.5}Te_3$ . Figure 17 shows the antimony content of the deposited films with the antimony concentration of the solution. When comparing the films X4(A) and X4(B), it implies that composition of the film can drastically change by changing the deposition potential. Moreover, when comparing films X1 to X4(A) which were deposited at the main reduction peak potentials, both Bi and Sb content of the film decrease. Even though solution S4 has the highest Sb concentration in this series, film X4(A) shows the lowest Sb content. In contrast, solution S1 has the lowest Sb concentration of the series, but the film X1 has the highest Sb content. Thus, when the

deposition takes place at a more favorable reduction potential the Sb content of the deposited films seems to be dependent on the Bi concentration of the electrolyte. In other words, higher Bi concentration of the solution somehow facilitates the deposition of more Sb in the film. Figure 18 shows the XRD pattern of the film X4(B). In the XRD pattern, peaks observed at  $2\theta=38.18^{\circ}$  and  $44.39^{\circ}$  are due to the polycrystalline Au substrate. The most intense peak observed at  $2\theta=28.09^{\circ}$  along (0 1 5) direction matching with Bi<sub>0.5</sub>Sb<sub>1.5</sub>Te<sub>3.0</sub> (PDF: 04-002-0106) suggests that the most optimal solution ratio to prepare the films with the ideal composition as Bi<sub>0.5</sub>Sb<sub>1.5</sub>Te<sub>3</sub> of the ones tried is [Bi]=1.5 mM, [Sb]=6.0 mM and [Te]=10.0 mM, and more negative deposition potential is preferred.

Film	Deposition potential	Composition				
	vs. Ag/AgCl (mV)	Bi	Sb	Te		
X1	-90	1.61	0.26	3.13		
X2	-60	1.37	0.24	3.39		
X3	-50	1.11	0.14	3.75		
X4(A)	-40	0.71	0.06	4.23		
X4(B)	-250	0.43	1.2	3.37		

Table 2: Deposition potential and composition of the films X1, X2, X3, X4(A) and X4(B). Deposition time is 200 s for all the films.



Figure 17: Sb content of the film with Sb concentration of the solution. Value in parenthesis is the composition of the film X4(B) at high deposition potential (-250 mV)



Figure 18: XRD pattern of X4(B) (Red) and standard pattern Bi<sub>0.5</sub>Sb<sub>1.5</sub>Te<sub>3.0</sub> (PDF: 04-002-0106) (Blue)

Figure 19 shows the differences in surface morphology of the films X1 to X4(B). Film X1 shows a needle like structure with 300 nm large crystals. Film X2 has 600 nm large crystals with dendrite shape. Film X3 shows a ball like structure with 100 nm large crystals. Film X4(A) shows a smooth surface with 100 nm large crystals. Film X4(B) has 400 nm large flower-like crystals. This implies that the morphology of the film depends on the deposition potential, since deposition potential affects the diffusion of the atoms on the electrode surface as well as the film composition.



Figure 19: SEM images of the deposited films (a) X1, (b) X2, (c) X3, (d) X4(A) and (e) X4(B)

#### 5.1.2 Study of Thermoelectric Properties of the Films

#### 5.1.2.1 Solution preparation

From the above studies, the best found solution ratio to prepare the films with the ideal composition  $Bi_{0.5}Sb_{1.5}Te_3$  is [Bi]=1.5 mM, [Sb]=6.0 mM and [Te]=10.0 mM, [C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>]=0.67 M and [HNO<sub>3</sub>]=1 M. Then this solution was used to investigate the thermoelectric properties of the ( $Bi_xSb_{1-x}$ )<sub>2</sub>Te<sub>3</sub>.

#### 5.1.2.2 Cyclic Voltammetry studies

Figure 20 shows the Cyclic Voltammetry (CV) curve, for the solution, containing [Bi]=1.5 mM, [Sb]=6.0 mM, [Te]=10.0 mM, [C<sub>4</sub>H<sub>4</sub>O<sub>6</sub>]=0.67 M and [HNO<sub>3</sub>]=1 M on Au substrate. According to the Figure 20 cathodic peaks A, B, C and D are observed at the potentials of -10, -80, -130 and -230 mV respectively. In 1M HNO<sub>3</sub> solutions tellurium exists as  $HTeO_2^+$  form, written as Te<sup>IV</sup>, and it can strongly absorb onto the Au electrode [12]. Thus the peak A relates to the reduction of  $HTeO_2^+$  to Te<sup>0</sup> and is dominating. Peaks B, C and D correspond to a sequential reduction of Bi<sup>III</sup> and Sb<sup>III</sup> with Te<sup>0</sup> to form (Bi<sub>x</sub>Sb<sub>1-x</sub>)<sub>2</sub>Te<sub>3</sub> [12]. Also, the two major peaks C and D indicate a different mechanism for deposition of the (Bi<sub>x</sub>Sb<sub>1-x</sub>)<sub>2</sub>Te<sub>3</sub> [17]. Reduction reactions for peak C can be expressed as follows [17]

$$HTeO_2^+ + 3H^+ + 4e^- \rightarrow Te_{(s)} + 2H_2O$$
(1)

$$3Te_{(s)} + (2-x)Bi^{3+} + xSbO^{+} + 6e^{-} + 2xH^{+} \rightarrow Bi_{2-x}Sb_{x}Te_{3} + xH_{2}O$$
 (2)

While the overall reaction is

$$3HTeO_2^+ + (2-x)Bi^{3+} + xSbO^+ + (9+2x)H^+ + 18e^- \rightarrow Bi_{2-x}Sb_xTe_3 + (6+x)H_2O$$
 (3)

When the potential is more negative, antimony converts from its simple SbO<sup>+</sup> ion to  $[Sb_2(C_4H_4O_6)_2]^{2+}$  complex. So the peak is more related to reduction of  $[Sb_2(C_4H_4O_6)_2]^{2+}$  to Sb [17]. In the anodic scanning process there are four peaks with two major oxidation peaks. It means that the compounds which were formed during the cathodic scanning process were not in a single phase [15]. Peak E corresponds to the oxidation of a Bi rich phase of the film, while elemental Sb is also oxidizing in this region. Peaks F, G and H correspond to the oxidation of  $(Bi_xSb_{1-x})_2Te_3$  [17]. Therefore it is of interest to study the compounds that are

formed in the different cathodic potentials. Therefore, films C1, C2, C3 and C4 were deposited at potentials of -10, -80, -130 and -230 mV, respectively. The deposition time for the films C1, C2, C3 and C4 were fixed at 1000 s, 800 s, 670 s, and 620 s respectively, in order to achieve the same film thickness.



Figure 20: Cyclic Voltammogram of 1M HNO<sub>3</sub> solution containing 1.5 mM  $\text{Bi}^{3+}$ , 6.0 mM  $[\text{Sb}_2(\text{C}_4\text{H}_4\text{O}_6)_2]^{2+}$  and 10.0 mM HTeO<sub>2</sub><sup>+</sup> on Au electrode (electrode area is 0.95 cm<sup>2</sup>), sweep rate 10 mV/s

#### 5.1.2.3. Surface morphology, composition and phase identification studies

Table 3 shows the deposition potential and the composition of each film, before and after annealing. Annealing was carried out at  $130^{\circ}$ C for 2 hours in Ar atmosphere. Compositional changes were observed after the annealing process for film C1 and C2 but not for films C3 and C4. As shown in Figure 20, films C1 and C2 were prepared at peaks A and B which are the minor reduction peaks compared to peaks C and D. It suggests that the two potentials (-10 and -80 mV) are not favorable for the deposition of stoichiometric (Bi<sub>x</sub>Sb<sub>1-x</sub>)<sub>2</sub>Te<sub>3</sub>. Therefore, Bi, Sb and Te atoms in the films were not bonded in a stoichiometric fashion, and it appears

that loosely bonded atoms made from the same element, can easily sublimate during the annealing process. This would result in the observed difference in composition before and after annealing.

Peaks C and D which are the major reduction peaks in the Figure 20 correspond to favorable potentials for depositing  $(Bi_xSb_{1-x})_2Te_3$ . Thus, in films C3 and C4, Bi, Sb and Te atoms are bonded in a stoichiometric way and no sublimation is observed during the annealing process. Furthermore, C3 and C4 are the films which have the composition near to the desired values  $Bi_{0.5}Sb_{1.5}Te_3$ . This indicates that the composition of the deposited films is depending on the deposition potential.

Thin film	Deposition	(	Composition	n
sample	potential vs. Ag/AgCl (mV)	Bi	Sb	Те
C1	- 10	0.68	0.00	4.32
C1_ann		0.78	0.00	4.22
C2	- 80	0.51	0.96	3.53
C2_ann		0.61	0.23	4.16
C3	- 130	0.40	1.34	3.26
C3_ann	150	0.38	1.39	3.23
C4	- 230	0.38	1.28	3.34
C4_ann		0.42	1.26	3.32

Table 3: Deposition potential and composition of the films C1, C2, C3 and C4, before and after annealing (annealed samples of C1, C2, C3 and C4 were named as C1\_ann, C2\_ann, C3\_ann and C4\_ann respectively)

Figure 21 shows the differences in surface morphology of the films C1 to C4. C1 has a really smooth surface with crystal size less than 100 nm. C2 has 200 nm large crystals with ball like shape. C3 has a really rough surface with 1  $\mu$ m large, dendrite shape crystals. C4 is also has really rough surface with 1  $\mu$ m large flower shape crystals. It indicates that morphology of the film depends on the deposition potential, since deposition potential affects the diffusion of the atoms on the electrode surface as well as the film composition. Apparently when a higher negative deposition potential is used it produces more rough surfaces.



Figure 21: SEM images of the deposited films (a) C1, (b) C2, (c) C3 and (d) C4.

XRD patterns of the four films before and after annealing, carried out on the Au substrate are shown in Figure 22. Annealing was done at 130°C for two hours in an Ar atmosphere to improve the properties. For the XRD patterns annealing was done, when samples were on the Au substrate and to measure properties annealing were done, when samples on the epoxy support. Because for some of the samples, we found migration of Au to the samples while annealing. The degrading temperature of epoxy is 250°C (according to the manufacturer) and is much higher than the annealing temperature. In all the XRD patterns the polycrystalline Au peaks due to the substrate are observed at  $2\theta$ =38.18° and 44.39°. C1 shows a crystalline structure. And it matches with the crystalline tellurium structure (PDF: 01-079-0736), with the most intense peak at  $2\theta$ =27.56° along (0 0 1) direction. Also this tellurium peak has a very high intensity. These observations confirm the EDX result which is giving high tellurium content in the film. Moreover C1 also matches the Bi<sub>3</sub>Te<sub>4</sub> pattern (PDF: 00-038-0458), giving intense peaks at  $2\theta$ =27.72° along (1 0 7) and 38.36° along (0 1 14) directions which are overlapping with Te peaks and the peak at  $2\theta$ =40.83° along (1 1 0) direction with a more

dominating form for Bi<sub>3</sub>Te<sub>4</sub>. This confirms that Bi in the film exists as Bi<sub>3</sub>Te<sub>4</sub>. Before annealing film C2 shows an amorphous structure. However when annealed on Au substrate it will combined with Au and matches the pattern of crystalline AuTe<sub>2</sub> (PDF: 04-004-4340), with the most intense peak at  $2\theta$ =29.54° along (-1 1 1) direction. Also it agrees with Bi<sub>0.7</sub>Sb<sub>1.3</sub>Te<sub>3.0</sub> (PDF: 04-002-6284), with most intense peak at  $2\theta$ =28.04° along (0 1 5) direction. C3 shows a crystalline structure without annealing and it matches with the pattern of Bi<sub>0.5</sub>Sb<sub>1.5</sub>Te<sub>3.0</sub> (PDF: 04-002-0106) with highest intense peak at  $2\theta$ =28.09° along (0 1 5) direction. This confirms the EDX results which gives the composition of the film as Bi<sub>0.40</sub>Sb<sub>1.34</sub>Te<sub>3.26</sub>. In C4 both before and after annealing the patterns look similar and match that of Bi<sub>0.5</sub>Sb<sub>1.5</sub>Te<sub>3.0</sub> (PDF: 04-002-0106) with the most intense peak at  $2\theta$ =28.09° along (0 1 5) direction. When compared this with the EDX data for C4 which is Bi<sub>0.42</sub>Sb<sub>1.26</sub>Te<sub>3.32</sub>, C4 is somewhat matching the desired composition Bi<sub>0.5</sub>Sb<sub>1.5</sub>Te<sub>3.0</sub>. Before annealing, C4 has broader peaks than C3. However after annealing, peaks belonging to C4 get sharp and indicates that annealing helps to increase the crystallinity of the film.



Figure 22: XRD patterns of film C1 to C4 before and after annealing

#### 5.1.2.4 Thermoelectric properties of the films

Table 4 shows the thermoelectric properties of the films C1 to C4 before and after annealing. For film C2, we cannot measure the thermoelectric properties before annealing. Moreover in the XRD patterns C2 is amorphous before annealing and after annealing it is a crystalline structure. This confirms that, the properties of C2 cannot be measured before annealing is because of its amorphous nature. (Following Figures 23, 24 and 25 drawn from the data in Table 4)

	H	Before Anneal	ling		After Anneali	ng
	Resistivity (μΩ m)	Seebeck coeff. (µV/K)	Power factor (µW/m K <sup>2</sup> )	Resistivity (μΩ m)	Seebeck coeff. (µV/K)	Power factor $(\mu W/m K^2)$
C1	279.0	81.0	23.0	392.0	39.8	4.0
C2	N/A	N/A	N/A	212.7	168.2	133.1
C3	432.0	102.0	24.0	113.3	158.3	221.0
C4	1960.0	159.0	12.0	847.0	170.0	34.0

Table 4: Thermoelectric properties of the film C1 to C4, before and after annealing

Figure 23 shows the variation of the resistivity of the films C1 to C4. When increasing the deposition potential the resistivity first decreases and that increases after -130 mV. Considering the CV curve in Figure 20, we suggest that most favorable potential for deposit Bi-Sb-Te is -130 mV. The composition of the film C3  $Bi_{0.38}Sb_{1.39}Te_{3.23}$  is consistent with the desired standard pattern of  $Bi_{0.5}Sb_{1.5}Te_{3.0}$  (PDF: 04-002-0106). Here we got the lowest resistivity value 113.3  $\mu\Omega$  m, for the same film as well.



Figure 23: Electrical resistivity of the different  $(Bi_xSb_{1-x})_2Te_3$  films.

Figure 24 shows the Seebeck Coefficient varying with increasing the negative deposition potential. For film C1 the Seebeck value is very low, and for film C2 to C4 the Seebeck value is comparable. C4 has the highest Seebeck value of 170  $\mu$ V/K. Moreover the positive Seebeck values indicate that all the films are p-type semiconductors.

![](_page_43_Figure_3.jpeg)

Figure 24 Seebeck Coefficient of the different (Bi<sub>x</sub>Sb<sub>1-x</sub>)<sub>2</sub>Te<sub>3</sub> films

Figure 25 shows the variation of power factor with increasing the negative deposition potential. From film C1 to C3 the power factor increases while for C4 it decreases. Film C3 shows the highest power factor value of 221  $\mu$ W/m K<sup>2</sup>.

![](_page_44_Figure_1.jpeg)

Figure 25: Power Factor of the different  $(Bi_xSb_{1-x})_2Te_3$  films

#### 5.2 Project 2

Many researchers in the world currently study thermoelectric materials for energy recovery and refrigeration applications. Electrodeposition is an economical way to produce thermoelectric materials in mass scale. To make an energy recovery or refrigeration device using thermoelectric materials, we need both n-type and p-type semiconductor thermoelectric materials. Normally people use one electrolyte to produce the n-type materials and another electrolyte for the p-type material. In this project we studied possibility of making p-type and n-type thermoelectric materials by electrodeposition using the same electrolyte. This will give several advantages to the production of thermoelectric materials. We can, e.g. use this method to prepare microelectronic coolers by electrodeposition, without changing the electrolyte [25]. By this way it helps to reduce the number of steps in the production process. Another advantage is that we can use the same solution for production of multilayers of thermoelectric materials by electrodeposition without changing the electrolyte [4].

#### 5.2.1 Cyclic Voltammetry Studies

Table 5 shows the concentrations of the solutions that were used for this study. Figure 26 shows the cyclic voltammetry (CV) curves, of the four solutions. During the cathodic scan from open circuit potential (OCP), two major reduction peaks and one minor reduction peak appeared for solutions A, B and C, and three major reduction peaks appeared for solution D. The appearance of different peaks during the cathodic scann process indicates different mechanisms for the deposition of  $(Bi_xSb_{1-x})_2Te_3$  [17, 15]. For solution A (blue), peaks A1, A2 and A3 appeared at -47 mA, -90 mA and -230 mA respectively, for solution B (red), peaks B1, B2 and B3 appeared at -47 mA, -100 mA and -230 mA respectively, for solution C (green), peaks C1, C2 and C3 appeared at -35 mA, -110 mA and -230 mA respectively, and for solution D (light blue), peaks D1, D2 and D3 appeared at -10 mA, -130 mA and -230 mA, respectively. In 1M HNO<sub>3</sub> solutions tellurium exists as HTeO<sub>2</sub><sup>+</sup> with tellurium in oxidation state IV, and it can strongly adsorb onto the Au electrode [12]. Thus, the peaks which appeared at area P were likely the reduction of HTeO<sub>2</sub><sup>+</sup> to Te<sup>0</sup>. Peaks which appeared at areas Q and R corresponded to a sequential reduction of Bi<sup>III</sup> and Sb<sup>III</sup> with Te<sup>0</sup> to form (Bi<sub>x</sub>Sb<sub>1-x</sub>)<sub>2</sub>Te<sub>3</sub> [12]. Reduction reactions for peaks appearing at area R can be expressed as [17]

$$HTeO_2^+ + 3H^+ + 4e^- \rightarrow Te_{(s)} + 2H_2O$$
(1)

 $3Te_{(s)} + (2-x)Bi^{3+} + xSbO^{+} + 6e^{-} + 2xH^{+} \rightarrow Bi_{2-x}Sb_{x}Te_{3} + xH_{2}O$  (2)

While the overall reaction is

 $3HTeO_2^+ + (2-x)Bi^{3+} + xSbO^+ + (9+2x)H^+ + 18e^- \rightarrow Bi_{2-x}Sb_xTe_3 + (6+x)H_2O$  (3)

When the potential is more negative antimony converts from its simple SbO<sup>+</sup> ion to  $[Sb_2(C_4H_4O_6)_2]^{2+}$  complex. So the peak is more related to reduction of  $[Sb_2(C_4H_4O_6)_2]^{2+}$  to Sb [17].

Table 5: variation of concentrations of electrolyte, in the series of solutions used which also contain 0.67 M  $C_4H_4O_6$  and 1 M  $HNO_3$ 

Colution	Bi(NO <sub>3</sub> ) <sub>3</sub>	SbCl <sub>3</sub>	$HTeO_2^+$
Solution	$(x \ 10^{-3} M)$	(x 10 <sup>-3</sup> M)	(x 10 <sup>-3</sup> M)
А	6.0	6.0	10
В	4.5	6.0	10
С	3.0	6.0	10
D	1.5	6.0	10

Moreover in Figure 26, there are two major oxidation peaks (areas S and T) that appeared in the anodic scan process for all four solutions and a minor oxidation peak. This indicates that the compound which deposited during the cathodic scan process is not in a single phase for all four solutions [15]. Peaks that appeared at area S correspond to the oxidation of a Bi rich phase of the film, while elemental Sb also oxidizes in this region. Peaks that appeared at area T correspond to the oxidation of  $(Bi_xSb_{1-x})_2Te_3$  [17].

Two cathodic peak potentials observed in areas P and R were used for thin film deposition from each solution and the thermoelectric properties of the prepared films were measured. Table 6 shows, the film samples prepared from different solutions at different deposition potentials and the corresponding compositions of the films after annealing. Annealing was carried out at 130 °C for 2 hours in Ar atmosphere.

![](_page_47_Figure_0.jpeg)

Figure 26: (a) Cyclic Voltammogram of Solution A (blue), B (red), C (green) and D (light blue) on Au electrodes (electrode area is 0.96 cm<sup>2</sup>), sweep rate 10 mV/s. (b) the area marked by a black box in Figure 26(a) is enlarged in the Figure 26(b). Orange box P, in Figure 26(a) marks the area of the 1<sup>st</sup> reduction peaks that appeared for all four solutions. Orange boxes Q and R mark the areas of the 2<sup>nd</sup> and 3<sup>rd</sup> reduction peaks that appeared for all four solutions, respectively. Orange boxes S and T mark the areas of the 1<sup>st</sup> and 2<sup>nd</sup> oxidation peaks that appeared for all four solutions, respectively. From both figures, reduction peaks in area P are A1, B1, C1 and D1; reduction peaks in area Q are A2, B2, C2 and D2; reduction peaks in area R are A3, B3, C3 and D3

Table 6: Elemental compositions of the films electrodeposited from different solutions which have different concentrations as described in Table 5, at different deposition potentials. Films deposited at peak potentials in area P (less negative potentials), named with P after the solution name (AP, BP, CP and DP). Films deposited at peak potentials in area R (more negative potentials), named with R after the solution name (AR, BR, CR and DR)

Solution	Concer	ntration (x	10 <sup>-3</sup> M)	Film	Constant potential	Composition		
	Bi	Sb	Те	(mV)		Bi	Sb	Те
А	6.0	6.0	10.0	AP	-47	1.61	0.26	3.13
11		0.0		AR	-230	0.43	1.2	3.37
В	4 5	6.0	10.0	BP	-47	1.38	0.13	3.48
D				BR	-230	0.94	1.11	2.95
C	3.0	6.0	10.0	СР	-35	1.07	0.04	3.90
C	5.0			CR	-230	0.70	1.16	3.15
D	15	6.0	10.0	DP	-10	0.78	0.00	4.22
	1.5			DR	-230	0.42	1.26	3.32

#### 5.2.2 Study of Thermoelectric Properties of the Films

Table 7 shows the thermoelectric properties of all the eight films categorized in two groups as, films deposited at less negative potential and at more negative potentials, respectively. It clearly indicates that films deposited at less negative potentials give negative Seebeck values, except film DP, indicating n-type semiconductors. In contrast, films deposited at more negative potentials show positive Seebeck values, indicating p-type semiconductors. This suggests that p-type and n-type thermoelectric films can be electrodeposited from one electrolyte which contains  $Bi^{3+}$ ,  $Sb^{3+}$  and  $Te^{4+}$ , by merely changing the deposition potentials. Nevertheless, there might be a limitation that when the  $Bi^{3+}$  concentration in the solution is as low as 1.5 mM, only a p-type film containing a large amount of Te was obtained. It is found that the films deposited at less negative potentials always contain a limited amount of Sb since the redox potential of Sb deposition is high due to the high redox potential that Sb has with the complex agent used. It is noticeable that the Sb deposition is likely dependent on the amount of Bi presented in the solution. Comparing the film AP to DP, a lower Bi concentration leads to less Sb deposited in the films. With a lower amount of Sb, the ternary films thus are mainly composed of  $Bi_{2-x}Te_{3+x}$  crystals where some of the Bi atoms are

replaced by Sb atoms. These BiTe based ternary compounds are therefore n-type semiconducting. In contrast, the films deposited at more negative potentials contain more Sb than Bi. The crystal structure of the films is based on  $Sb_{2-x}Te_{3+x}$  where some of the positions of Sb atoms are substituted by Bi atoms, which shows p-type semiconductivity.

	Constant	(	Compositi	on	<b>D</b>	~	Power
Film	potential (mV)	Bi	Sb	Те	$(\mu\Omega m)$	Seebeck coeff. (µV/K)	factor (µW/mK <sup>2</sup> )
AP	-47	1.61	0.26	3.13	52.2	-90.6	157.0
BP	-47	1.38	0.13	3.48	119.0	-57.6	27.9
СР	-35	1.07	0.04	3.90	41.5	-63.9	98.0
DP	-10	0.78	0.00	4.22	392.0	39.8	4.0
AR	-230	0.43	1.2	3.37	993.0	60.3	3.7
BR	-230	0.94	1.11	2.95	835.0	75.1	6.8
CR	-230	0.70	1.16	3.15	1150.0	110.0	10.5
DR	-230	0.42	1.26	3.32	847.0	170.0	34.0

Table 7: Thermoelectric properties and elemental compositions of the films which were electrodeposited from different solutions given in Table 5. Here the films are grouped into two categories as; films were deposited at less negative potential and at more negative potentials.

# 5.2.3 Further Studies of Thermoelectric Properties of the Films with Different Deposition Potentials

According to the properties of the films, peak potentials located in area P in Figure 26 can produce n-type semiconductors and peak potentials located in area R in Figure 26 can produce p-type semiconductors. So it is of interest to study the peak potentials appearing in area Q in Figure 26. Table 8 gives an extended version of Table 7, with the composition and the thermoelectric properties of the films which were deposited using the peak potentials at area Q in Figure 26 added as well. Figure 27 indicates the variation of resistivity, Seebeck coefficient and power factor of different films from the same solution, which were electrodeposited at less, intermediate and more negative potentials after annealing.

Table 8: Extended version of Table 7, thermoelectric properties and elemental compositions of the films which were electrodeposited from different solutions described in Table 5 (here the films are grouped into three categories as; films deposited at less, intermediate and more negative potentials). AQ, BQ, CQ and DQ are the films deposited at intermediate negative potentials, from peak potentials at area Q in Figure 26.

Solution	Cor (2	ncentra x 10 <sup>-3</sup> N	tion (I)	Film	Constant potential	C	ompositi	on	Resistivity	Seebeck coeff.	Power factor										
	Bi	Sb	Te		(mV)	Bi	Sb	Te	(μω 111)	$(\mu V/K)$	$(\mu W/mK^2)$										
				AP	-47	1.61	0.26	3.13	52.2	-90.6	157.0										
А	6.0	6.0	10.0	AQ	-110	1.51	0.41	3.08	115.0	-94.2	77.0										
				AR	-230	0.43	1.20	3.37	993.0	60.3	3.7										
				BP	-47	1.38	0.13	3.48	119.0	-57.6	27.9										
В	4.5	6.0	6.0 10.0	BQ	-100	1.14	0.76	3.10	240.0	-75.5	23.7										
				BR	-230	0.94	1.11	2.95	835.0	75.1	6.8										
				СР	-35	1.07	0.04	3.90	41.5	-63.9	98.0										
С	3.0	6.0	10.0	CQ	-110	0.82	0.95	3.23	210.0	88.7	37.6										
														CR	-230	0.70	1.16	3.15	1150.0	110.0	10.5
				DP	-10	0.78	0.00	4.22	392.0	39.8	4.0										
D	1.5	6.0	10.0	DQ	-130	0.38	1.39	3.23	113.3	158.3	221.0										
				DR	-230	0.42	1.26	3.32	847.0	170.0	34.0										

From Table 8 and Figure 27, it can be seen that with increasing depositing potential, the film resistivity gradually increases (compare the three films of each solution). This may be due to that with increasing deposition potential more Sb is deposited, while the deposition of Bi is reduced. Moreover intermediate negative potential deposition of solution C shows a positive Seebeck value, even though it has a negative Seebeck value when deposited at less negative potentials. From Figure 27(b), during the intermediate negative potential depositions from this solution series a clear trend in the Seebeck coefficient can be found. That is, when increasing the Sb content of the solution comparing to the Bi content, it leads to formation of films with decreasing negative Seebeck value and increasing positive Seebeck values. This results confirms that, Sb tends to dope the n-type  $Bi_2Te_3$  to the p-type  $(Bi_{1-X}Sb_X)_2Te_3$ . As our objective is to produce both p-type and n-type thermoelectric materials from the same electrolyte, Solution C seems to be optimal and n-type  $(Bi_{1-X}Sb_X)_2Te_3$  thin films can be produced at less negative potentials and p-type materials  $(Bi_{1-X}Sb_X)_2Te_3$  thin films can be produced at intermediate or more negative potentials.

![](_page_51_Figure_0.jpeg)

Figure 27: Variation of thermoelectric properties of films electrodeposited from different solutions described in Table 5 with the different deposition potentials described in Table 7. (a) Resistivity ( $\mu$ Ohm m), (b) Seebeck coefficient ( $\mu$ V/K) and (c) Power factor ( $\mu$ W/m K<sup>2</sup>). In all three figures; P, Q and R are less, intermediate and more negative potentials respectively. Solution A (in Blue), Solution B (Maroon), Solution C (in light green) and Solution D (in Purple)

## 6. Conclusions

In this study we have worked with electrodeposition of  $(Bi_xSb_{1-x})_2Te_3$  thin films from solutions containing 1M HNO<sub>3</sub> and 0.67 M C<sub>4</sub>H<sub>4</sub>O<sub>6</sub> and different concentrations of bismuth, tellurium and antimony ions. By investigations of various concentration ratios for the electrolytes, it was found that when the deposition takes place at the main reduction peak potential a more favorable reduction for the compound is achieved and a higher Bi concentration in the solution facilitates the deposition of more Sb in the film.

From project 1, we found that the optimal concentration ratio to deposit  $Bi_{0.5}Sb_{1.5}Te_{3.0}$  with high thermoelectric properties is [Bi]=1.5 mM, [Sb]=6.0 mM and [Te]=10.0 mM. The lowest resistivity of 113.3  $\mu\Omega$ .m and highest power factor of 221  $\mu$ WK<sup>-2</sup>m<sup>-1</sup> were obtained from the continuously electrodeposited films.

From project 2, we succeeded to produce p-type and n-type thermoelectric thin films by electrodeposition from the same concentrated electrolyte, even though it has lower thermoelectric properties than the p-type or n-type thin film thermoelectric materials made by electrodeposition by conventional way (using two separate and different electrolytes for p-type and n-type thin film materials and make them separately).

## 7. Future Works

Transferring thin films from gold to epoxy is a hard process. It can introduce some cracks and also may introduce some defects to the arrangement of atoms in the lattice, which will introduce some additional electrical resistance. So it would be good to find a better way to transfer the films or use another kind of substrate like polyaniline instead of gold, which conduct electricity at room temperature but become non-conducting at all after it heating it at a high temperature.

For project 1 it is of great interest to use pulse electrodeposition technique to deposit the films and measure the properties. This technique works like deposition time ( $t_{on}$  at potential  $E_{on}$ ) and resting time ( $t_{off}$  at potential  $E_{off} = 0$  mV), and then repeating this cycle again and again. During  $t_{on}$  rapid co-deposition of the material will take place. During  $t_{off}$  deposition process still continuing and this low potential limits the growth rate. It beneficially fills up the pores of the already deposited film. Since it is suggested that by introducing a relatively long pulse-off surface ion depletion will be minimized, which consequently improves the roughness and compactness of the deposited films.

For project 2 it is also good to use the pulse electrodeposition technique. Moreover more variation in the concentration of the bismuth antimony telluride solution could be tried. Also it would be interesting to try this method with other solutions used for electrodeposition of thermoelectric thin films.

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