

Electrodeposition of Antimony Telluride Thin Films and Composition-Dependent Thermoelectric Characterization

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Abstract : Antimony telluride (Sb_xTe_y) thin films were synthesized by an electrodeposition method with a control of applied potential at room temperature. Characterization of electrical and thermoelectric properties such as conductivity, Seebeck coefficient, and power factor (P.F.) were conducted as a function of the chemical composition of the electrodeposited films. Morphology of thin films were dense and uniform and the composition was tailored from 25 to 60 at.% of the Sb content by altering the applied potential from -0.13 to -0.27 V (vs. SCE). The conductivity of the films were ranged from $2 \times 10^{-4} \sim 5 \times 10^{-1}$ S/cm indicating their amorphous behavior. The measured Seebeck coefficient of films were relatively high compared to that of bulk single crystal Sb_xTe_y due to their low carrier concentration. The variation of the Seebeck coefficient of the films was also related to the change of chemical composition, showing the power factor of $\sim 10 \mu\text{W/mK}^2$.

Keywords : Electrodeposition, Antimony Telluride (SbTe), Thin Film, Thermoelectric Properties

1. Introduction

Metal chalcogenides have many existing and potential applications in electronics, optics, magnetics, photovoltaics, sensors, and thermoelectrics. For example, pseudo-binary chalcogenides (e.g., GeTe, Sb_2Te_3) exhibit excellent phase-change properties desirable for phase change random access memory (PCRAM), which is being explored commercially. Also of significance, a new electronic phase called a topological insulator (TI) was recently discovered in various chalcogenide materials (e.g., Bi_2Se_3 , Bi_2Te_3 , and Sb_2Te_3). Importantly, some metal chalcogenides (e.g., Bi_2Te_3 , Sb_2Te_3) exhibit excellent thermoelectric figure-of-the-merit (ZT) for energy generation and cooling.¹⁻³⁾

Thermoelectrics, which convert directly between heat and electricity with no moving parts, leading to simple, silent, reliable operation, is an exciting alternative for conventional energy generators.

Metal chalcogenides attracted scientist's attention because of their promising TE properties evaluated by thermoelectric ZT which is defined as a dimensionless value ($=S^2\sigma T/\kappa$, where S is the Seebeck coefficient ($\mu\text{V/K}^{-1}$), σ is the electrical conductivity ($\Omega^{-1}\text{m}^{-1}$) and κ is the thermal conductivity ($\text{Wm}^{-1}\text{K}^{-1}$)). Highly doped semiconductors or semiconductors with a narrow band gap can exhibit the maximum zT. According to this theoretical study, various highly doped and narrow band gap bulk semiconductors have been investigated such as Bi_2Te_3 , PbTe, CoSb_3 and SiGe for n-type semiconductors and Sb_2Te_3 , PbTe, $\text{CeFe}_4\text{Sb}_{12}$ and SiGe for p-type semiconductors. These properties originate from their unique anisotropic lattice structure, which are strongly related to chemical composition, crystallinity and dimension of the materials. Moreover, the ability to tune electronic states from conductor to insulator by the varying cations is another reason for their fame.⁴⁻⁶⁾

Successful application of metal chalcogenides depends on synthesis techniques that can reproducibly fabricate controlled crystal structure,

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crystallinity and chemical composition in a cost effective manner. Electrochemical methods including electrodeposition, electroless deposition and galvanic displacement are high-yield, cost-effective and versatile processes for materials synthesis that operate near room temperature, have low energy requirements, and are capable of handling complex geometries at a variety of length scales. In addition, a wide range of materials including metals, alloys, compound semiconductors, and metal oxides with controlled properties and composition can be readily deposited. Furthermore, it is able to synthesize solid solutions and non-stoichiometric alloys that are difficult to make using other processes.⁷⁻¹⁰⁾

In this work, the electrodeposition was applied to provide Sb_xTe_y thin films with controlled chemical composition. The electrodeposition method was selected because of its ability to precisely tune the composition by simply adjusting applied potential as well as electrolyte concentration decoupling a change of crystallinity of the films. The composition effect on the characteristic of the synthesized films were investigated by measuring electrical and thermoelectric properties such as conductivity, Seebeck coefficient, and power factor (P.F.) at room temperature.

2. Experimental

Electrolyte was prepared by separately dissolving 2.4 mM TeO_2 in a concentrated HNO_3 solution and 3.6 mM Sb_2O_3 in 33 mM L-tartaric acid solution at 60°C. Once the oxides were completely dissolved, two solutions were mixed together and added 1 mM cetyl-trimethylammonium bromide (CTAB) with deionized water to reach final volume. The electrolyte was kept at 25°C and stirred at 300 rpm.

The Sb_xTe_x thin films were potentiostatically electrodeposited on an Au (80 nm)/Ni (20 nm)/Si substrate. A Pt coated titanium and a saturated calomel electrode (SCE) were used as the counter and the reference electrode, respectively. Linear sweep voltammetry (LSV) was conducted using the prepared electrolyte to explore the available

range for applied potential to deposit the Sb_xTe_y thin films. Based on this analysis, the applied potential was varied from -0.13 to -0.27 V (vs. SCE) in the solution stirred at 300 rpm. The deposition time was 10 min at room temperature. The electrodeposits were detached from conducting substrates using Torr Seal epoxy (Varian Vacuum Products, Lexington, Massachusetts).

Morphology and composition of the Sb_xTe_y thin films were investigated by scanning electron microscopy (SEM) (Jeol, JSM-5800) and energy dispersive X-ray spectroscopy (EDS). The electrical properties such as conductivity, Hall mobility, and carrier concentration were investigated by a custom-made Hall measurement unit in the van der Pauw configuration with four-point probes. The Seebeck coefficient was determined by a custom-made Seebeck measurement system by plotting measured Seebeck voltages as a function of temperature gradient across the sample ($S = \Delta V/\Delta T$).

3. Results and Discussion

The LSV analysis was performed to investigate the electrochemical reaction regarding the formation of binary Sb_xTe_y , with a control of the chemical composition. The appropriate deposition potentials to modulate the content of Sb in the films can be informed by interpreting the LSV curves. The CTAB surfactant, which helps to improve the morphology and density of the specimen, was utilized in the electrodeposition of Sb_xTe_y films. The effect of the CTAB on the reduction reaction was compared by investigating the LSV curve change in solutions with and without CTAB shown in Fig. 1. In general, the reduction of tellurium-based chalcogenides is required to overpotential deposition (OPD) of tellurium followed by underpotential (UPD) deposition of cations on the tellurium. In absence of the CTAB, the first reduction peak appeared at -0.07 (vs. SCE) is expected to show the OPD deposition of tellurium. In case of the solution containing the CTAB, however, the OPD of tellurium shifted more negatively. After -0.15 V (vs. SCE), the slope of the curve changed that

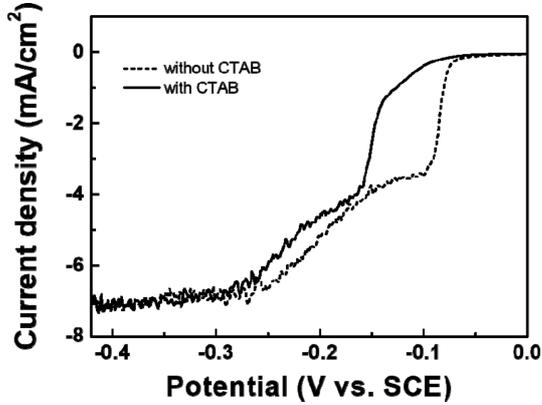
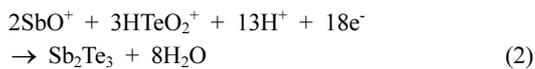
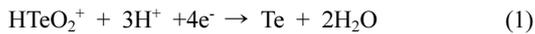


Fig. 1. Linear sweep voltammetry (LSV) analysis of electrodeposition of Sb_xTe_y films with (solid line) and without (dot line) cetyl-trimethylammonium bromide (CTAB) surfactant.

represents the UPD reaction. During this period, the reduction of antimony on tellurium is expected to form stoichiometric compound. Once the applied potential became more negative the OPD of antimony would be emerged where the antimony content increased. Difference in the curves from the two electrolytes was noticed at the shift of reduction potential ranges. The OPD of tellurium and UPD of antimony were shifted more negatively by using the CTAB surfactant that is because the adsorption of the surfactant on the films disturbing the formation of Sb_2Te_3 . Similar observations were reported in various acidic chalcogenide baths.¹⁰⁻¹²⁾ Accordingly, the surfactant ions tend to form a loose complex with the Sb^{2+} due to electrostatic attraction so that the deposition rate of Sb would be slow rather than that of tellurium. The overall electrochemical reaction of Te, Sb_2Te_3 is described, respectively, as follows:



Based on the LSV analysis, the Sb_xTe_y thin films were potentiostatically electrodeposited with controlled compositions. The composition was

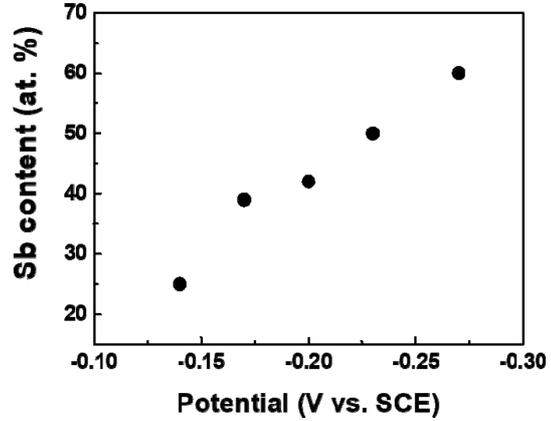


Fig. 2. Effect of applied potential on Sb content in Sb_xTe_y electrodeposits.

varied by the dominant reaction among OPD of Te, UPD of Sb and OPD of Sb depending on the applied potentials, which ranged from -0.13 V (vs. SCE) to -0.27 V (vs. SCE). As shown in Fig. 2, the Sb content increased as the applied potentials decreased which was expected in the LSV analysis. From this investigation, simple adjustment of applied potential in the electrodeposition method able to tailor the chemical composition in a wide range that would be strongly related to their electrical properties originated from unique anisotropic lattice structure and/or defects. Fig. 3 shows SEM images of electrodeposited Sb_xTe_y thin films with various compositions. The films showed dense and uniform morphology with the average thickness of $\sim 1 \mu m$. The surface morphology of the films became globular as the applied potential became more negative which might be due to faster growth rate.

The composition-dependent electrical and thermoelectric properties of Sb_xTe_y thin films were characterized in Fig. 4. The composition of the tailored Sb content ranged from 25-60 at.%. The range of the electrical conductivity was indicated from 10^{-4} to 10^1 S/cm which is much lower than that of bulk single crystal (Fig. 4a). From this observation, it is expected that crystallinity of electrodeposited Sb_xTe_y films were close to amorphous phase that is in accordance with

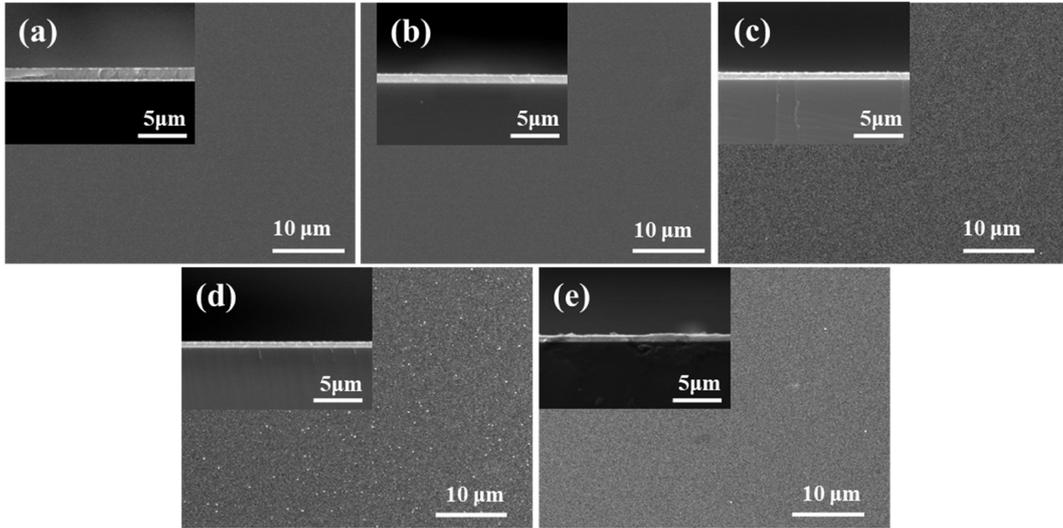


Fig. 3. SEM images of Sb_xTe_y thin films electrodeposited at -0.14 (a), -0.17 (b), -0.2 (c), -0.23 (d), and -0.27 (e) electrodeposits.

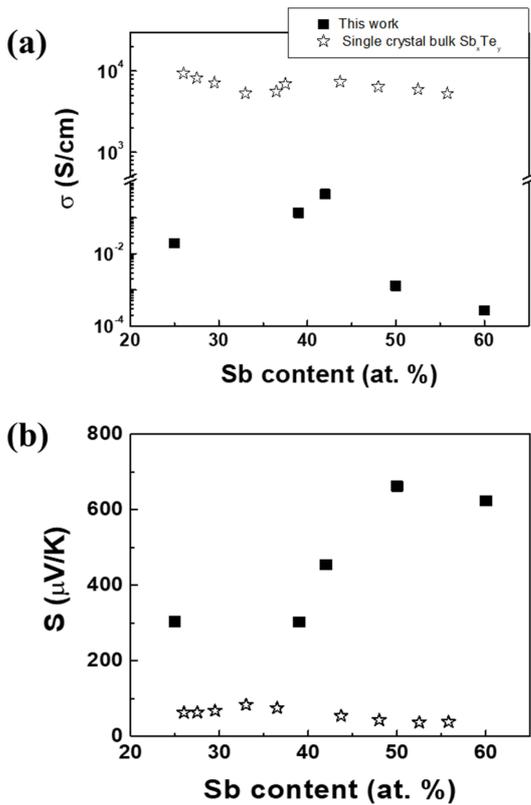


Fig. 4. Effect of the chemical composition on the electrical conductivity (a) and Seebeck coefficient (b) of the Sb_xTe_y films.

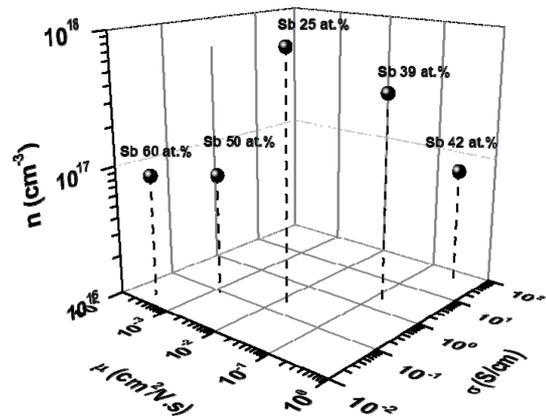


Fig. 5. Effect of the chemical composition on the conductivity, mobility, and carrier concentration of the Sb_xTe_y films.

previous reports.^{7,10-11)} The variation of electrical conductivity is explained by anti-site defects dominant property of the Sb_xTe_y films that is caused by the existence of Sb atoms on the Te lattice sites.¹³⁾ As the composition deviated from near stoichiometry the electrical conductivity decreased. The Seebeck coefficient, however, was much higher than that of the bulk Sb_xTe_y which demonstrates the interdependency between Seebeck

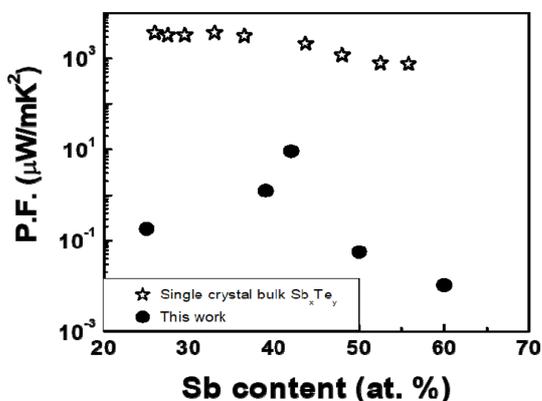


Fig. 6. Effect of the chemical composition on the power factor of the Sb_xTe_y films.

coefficient and electrical conductivity. Based on the measurements, the Seebeck coefficient of composition-varied Sb_xTe_y electrodeposits increased as the Sb content increased (Fig. 4b). The effect of the composition on the transport properties were indicated in Fig. 5. The increased mobility values of the near-stoichiometric films affected their relatively high electrical conductivity. The calculated power factor ($P.F. = \sigma S^2$) values were indicated that near-stoichiometric Sb_xTe_y films show the best performance at room temperature (Fig. 6). Although the thermoelectric performance was not reached to the bulk property, further improvement of crystallinity and crystal structure of the amorphous films would be expected to increase their thermoelectric performance.

4. Conclusions

In this work, the Sb_xTe_y thin films were synthesized by an electrodeposition method with a control of applied potential at room temperature. Dependence of electrical and thermoelectric properties such as conductivity, Seebeck coefficient, and power factor (P.F.) were investigated as a function of the chemical composition of the electrodeposited films. From this observation, the films showed amorphous behavior such as such low conductivity and relatively high Seebeck coefficient. In addition,

due to the effect of the anti-site defects the Seebeck coefficient of the films was dependent on the change of chemical composition, showing the power factor of $\sim 10 \mu W/mK^2$ in the near-stoichiometric films.

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