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Composition- and crystallinity-dependent thermoelectric properties of ternary $Bi_xSb_{2-x}Te_y$ films

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ABSTRACT

$Bi_xSb_{2-x}Te_y$ films with controlled compositions were synthesized by a simple and cost-effective electrodeposition technique followed by post-annealing, for thermoelectric applications. Tailoring the chemical composition of ternary $Bi_xSb_{2-x}Te_y$ materials is critical to adjust the carrier concentration and carrier type, which are crucial to determine their thermoelectric performance. Herein, the composition of electrodeposited $Bi_xSb_{2-x}Te_y$ film was simply tailored by controlling the [Sb]/[Bi] ratio in the electrolytes while maintaining their dense and uniform morphology. Crystallographic properties of the $Bi_xSb_{2-x}Te_y$ films, such as crystallinity and grain size changes, were confirmed by X-ray diffraction. Room-temperature measurements of electrical conductivity, Hall mobility, and carrier concentration revealed that the substitution of Bi with Sb decreased the carrier concentration, and increased the mobility. The Seebeck coefficient of the ternary $Bi_xSb_{2-x}Te_y$ films transitioned between p- and n-type characteristics with an increase in the Bi content. Moreover, the mobility-dependent electrical conductivity of the $Bi_{10}Sb_{30}Te_{60}$ film resulted in a high Seebeck coefficient owing to decreased carrier concentration of the film, leading to a power factor (PF) of ~490 $\mu W/m\,K^2$. This is more than 10 times higher than the PF values of binary nanocrystalline Sb_2Te_3 films.

1. Introduction

Advances in thermoelectric efficiency ($zT = \sigma S^2 T/\kappa$), where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature, has been restricted by the interdependency of these parameters. Therefore, properties of optimum thermoelectric materials have been determined by comparing σ, S, and κ [1]. According to various theoretical and experimental studies, chalcogenides with a narrow energy band gap ($E_g < 0.2$ eV) [2], specifically, antimony telluride (Sb_2Te_3) and bismuth telluride (Bi_2Te_3), and their derivatives such as bismuth antimony telluride ($Bi_{0.5}Sb_{1.5})_2Te_3$ and bismuth telluride selenide $Bi_2(Te_{0.8}Sb_{0.2})_3$, have successfully demonstrated the best thermoelectric performance at room temperature operations. By virtue of recently advanced nanotechnology and fabrication techniques, the enhanced zT values of 2.4 and 1.5 in Bi_2Te_3/Sb_2Te_3 superlattice and nanocrystalline Bi-Sb-Te bulk alloy, respectively, were recorded at room temperature [3].

Bismuth antimony telluride ($Bi_xSb_{2-x}Te_y$) is expected to be the best room temperature thermoelectric material owing to its reduced thermal conductivity, achieved by the substitution of Sb by Bi in the structure. Unique anisotropic electronic properties originating from weak van der Waals interactions between the Te atoms along the hexagonal c-axis of Bi-Sb-Te allow additional decrease in the thermal conductivity and directionality in thermoelectric performance [4,5]. Conventional synthetic techniques for the producing $Bi_xSb_{2-x}Te_y$ films, such as molecular beam epitaxy [6], metal organic chemical vapor deposition (MOCVD) [2,7], and solution synthesis techniques [8,9], which are normally considered directional crystallization techniques, show lack of control over the compositional and structural properties, owing to limited engineering factors in the systems. In comparison, electrodeposition provides diverse parameters to tailor the material properties of the films by controlling the applied potential, electrolyte concentration, temperature, agitation rate, surfactant type, *etc.* Owing to these advantages, various studies have investigated the electrochemical synthesis and characterization of the electrical and

Abbreviations: PF, power factor; FWHM, full width at half-maximum; SEM, scanning electron microscopy; EDS, energy dispersive X-ray spectroscopy; XRD, X-ray diffraction; MOCVD, metal organic chemical vapor deposition.

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thermoelectric properties of $Bi_xSb_{2-x}Te_y$ films. However, these findings were limited in terms of the deposition conditions used for achieving $Bi_xSb_{2-x}Te_y$ films of better compositions and morphologies to improve their thermoelectric performance [10–18].

In fact, the effect of unique microstructures was also proposed to understand the high zT of nanograined bulk Bi-Sb-Te, attributed to increased electrical conductivity and significantly decreased thermal conductivity [19]. According to Lan et al., besides precipitates, various low dimensional defects such as point defects or impurities, dislocations, and structural modulations were commonly observed in nanograined bulk alloys, which were responsible for large scattering of phonons and electrons [19]. Moreover, by adjusting adequate impurities such as Bi vacancy and Te antisite defects, the carrier type of the Bi-Sb-Te solid solution was transitioned between n- and p-type characteristics [9,19,20]. However, very few reports have systematically investigated compositional and structural modification to optimize the thermoelectric performance of the $Bi_xSb_{2-x}Te_y$ films, by adjusting the carrier type and concentration.

In this article, we report the control of the thermoelectric properties of the $Bi_xSb_{2-x}Te_y$ films by systematically adding Bi to the binary Sb_2Te_3 film. The $Bi_xSb_{2-x}Te_y$ films were synthesized by a potentiostat electrodeposition technique followed by post-annealing treatment. The composition of the $Bi_xSb_{2-x}Te_y$ films was tailored by adjusting the [Sb]/[Bi] ratio in the electrolytes. Measurement of electrical conductivity, mobility, carrier concentration, and Seebeck coefficient of the $Bi_xSb_{2-x}Te_y$ films revealed that the amount of Bi substituted in the films significantly altered the thermoelectric performances, and an optimum power factor (PF) was achieved for the $Bi_{10}Sb_{30}Te_{60}$ film.

2. Experimental section

2.1. Synthesis of $Bi_xSb_{2-x}Te_y$ films

$Bi_xSb_{2-x}Te_y$ films were potentiostatically electrodeposited by controlling the concentration of the electrolytes at a fixed applied potential of −0.1 V (*vs.* saturated calomel electrode). According to our previous work on the electrodeposition of binary Sb_xTe_{1-x} films, the morphology of the films are expected to be highly dependent on the applied potentials [21,22]. In order to electrodeposit $Bi_xSb_{2-x}Te_y$ films with a uniform and dense morphology, we maintained the same parameters such as the applied potential, deposition temperature, and agitation, used in our previous work. The chemical composition of the ternary $Bi_xSb_{2-x}Te_y$ films was tailored by controlling the $Bi(NO_3)_3{\cdot}5H_2O$ concentration, which was chosen as the Bi^{3+} source in the electrolytes. The electrolyte was prepared by separately dissolving 2.4 mM TeO_2 in a 1 M HNO_3 solution, 3.6 mM Sb_2O_3 in 33 mM L-tartaric acid solution at 60 °C, and 400–1000 μM $Bi(NO_3)_35H_2O$ in deionized water. The dissolved solutions were then mixed and diluted to a final volume of 1 L with deionized water. The concentration of $Bi(NO_3)3{\cdot}5H_2O$ in the electrolyte was varied between 400, 600, 800, and 1000 μM, to achieve ternary $Bi_xSb_{2-x}Te_y$ with tailored compositions. The working electrode was an e-beam evaporated Au (80 nm)/Ni (20 nm) film on a Si substrate. A Pt-coated titanium electrode and saturated calomel electrode were used as the counter and reference electrodes, respectively. A potential of −0.1 V *vs.* saturated calomel electrode was applied and the electrolyte was maintained at 25 °C, and magnetically stirred at 300 rpm.

2.2. Sample preparation

For electrical and thermoelectric characterization, the thin films were transferred from the Au/Ni/Si substrate to a non-conductive Torr Seal epoxy substrate (Varian Vacuum Products, Lexington, Massachusetts). The entire film was successfully transferred without cracking. The final dimensions of the samples used for characterization were cm^2.

2.3. Characterization

Morphology and composition of the synthesized $Bi_xSb_{2-x}Te_y$ films were analyzed by scanning electron microscopy (SEM) (Jeol, JSM-5800) and energy dispersive X-ray spectroscopy (EDS). The effect of the composition on the crystallographic property of the $Bi_xSb_{2-x}Te_y$ films were investigated as a function of the Bi content, by X-ray diffraction (XRD) (Bruker D8 ADVANCE). In addition, a post-annealing process was performed to further enhance the structural properties; the films were annealed at 200 °C for 30 min under nitrogen atmosphere with 5% hydrogen. The annealing process involved sequentially varying the annealing temperatures from 30 to 200 °C for 30 min under the nitrogen atmosphere with 5% hydrogen, to investigate the effects of improvements in crystallinity on the electrical and thermoelectric properties. The electrical conductivity, Hall mobility, and carrier concentration of the films were measured on a custom-built Hall measurement unit in the van der Pauw configuration using four-point probes. The Seebeck coefficient was determined using a custom-made Seebeck measurement system by plotting the measured Seebeck voltages (ΔV) as a function of temperature difference ($\Delta T < 2$ °C) across the sample ($S = \Delta V/\Delta T$).

3. Results and discussion

3.1. Material properties of $Bi_xSb_{2-x}Te_y$ films

Owing to the high thermoelectric performance of Bi_2Te_3-based alloys near room temperature, the electrodeposition of Bi_2Te_3 based films has been widely performed with the aim to enhance their electrical and thermoelectric properties. For this, the influence of various electrodeposition parameters such as the applied potential, the [Sb]/[Bi] ratio, and the type of acid added to the electrolytes were studied in correlation with the morphology, composition, and crystallinity, which are critical factors determining the thermoelectric performance of the films [15,17,23]. Dependence of the Seebeck coefficient on the composition of the films was clearly manifested; however, independent control over a uniform morphology using a direct electrodeposition technique remains a

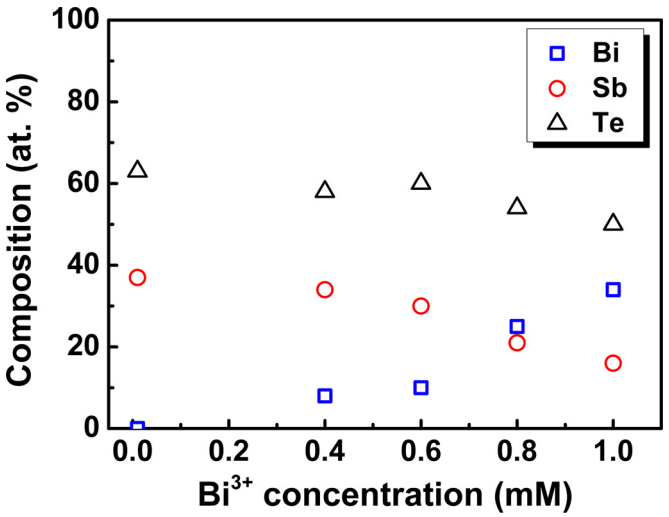

Fig. 1. Effect of Bi^{3+} concentration on the composition of $Bi_xSb_{2-x}Te_y$ films.

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