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Electrodeposition of Bi_xTe_y thin films for thermoelectric application

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ABSTRACT

Electrochemically deposited bismuth telluride (Bi_xTe_y) thin films were grown from nitric acid baths on sputtered Au/Ni/Si substrates. The film compositions and morphology were strongly dependent on the deposition conditions. Surface morphologies varied from granular to needle-like structures depending on the Te content of the films. The power factor improved with the increase of Bi ions in electrolytes, and this may be due to the improvement of the crystal structure and no inclusion of excess Te phases. Annealing up to 200 °C in a reducing H_2 atmosphere did not improve the power factor due to the interdependence of the Seebeck coefficient and the electrical conductivity.

1. Introduction

In recent years, considerable interest has been generated in cleaner, more sustainable energy sources with the growing concerns over increasing energy costs and global warming associated with fossil fuel sources. Among the viable technologies, thermoelectric (TE) devices such as power generators and coolers have received increasing attention over the past few years owing to the capability of these devices of direct conversion between temperature differences and electrical voltages. The advantages of TE devices are their low-noise operations, low space requirements, ease of maintenance, and the fact that they are environmentally friendly. The performance of TE materials is evaluated by a dimensionless figure of merit, ZT, which is defined as $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature. Although there is no theoretical limit to the attainable ZT, in practice one parameter counteracts the other two, because of which ZT is typically bounded close to unity.

Bismuth telluride (Bi_2Te_3) is one of the most widely investigated TE materials and is possibly the only commercialized TE material suitable for near-room-temperature applications [1]. In addition, Bi_2Te_3 is a V_2–VI_3 binary chalcogenide compound semiconductor, which can be tailored for n- and p-type conductivities by adjusting the composition [2]. In addition to bulk Bi_2Te_3 materials, which are prepared by solidification process, Bi_2Te_3 thin films have attracted considerable interest because of their potential application in integrated TE devices, solid-state refrigeration technology, heat pump infrared sensors, and high efficiency photovoltaic solar cells [3–6]. In general, Bi_2Te_3 thin film materials can be obtained using chemical vapor deposition and physical vapor deposition [7–9]. However, these deposition methods have a high production cost and low deposition rate. In comparison, the electrodeposition process has the advantages of large area deposition, low production cost, low synthesis temperature, high throughput, and high growth rates [10,11].

In this report, Bi_xTe_y thin films were electrodeposited on an Au/Ni/Si substrate using an aqueous nitric acid electrolyte at room temperature with various electrolyte compositions. Prior to potentiostatic deposition, linear sweep voltammograms (LSV) were utilized to investigate the effect of the Bi ion concentration. Systematic studies were performed on electrodeposited Bi_xTe_y thin films to correlate their material and structural properties with their thermoelectrical and electrical properties.

2. Experimental details

Prior to potentiostatic electrodeposition, LSV were acquired with a standard three-electrode cell using a Au(80 nm)/Ni(30 nm)/Si substrate as the working electrode in solutions of 10 mM TeO_2 and 1.5 M HNO_3, wherein the $Bi(NO_3)_3$ concentration was varied from 2.5 to 10 mM. All experiments were conducted at room temperature with a fixed magnetic agitation rate of 300 rpm and a scan rate of 1 mV/s. Electrolytes were prepared by dissolving TeO_2 powders in concentrated nitric acid, followed by dissolution of $Bi(NO_3)_3$ powders in a separate container. Once the chemicals were completely dissolved, they were mixed together and were diluted with deionized water until the final volume was attained. The effects of the Bi ion concentration were investigated by varying the Bi ion concentration

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for a fixed applied potential of −0.1 V vs. Ag/AgCl. The agitation rate was the same as that during the acquisition of LSVs.

We used scanning electron microscopy (SEM, JEOL, JSM-5800) operated at an accelerating voltage of 20 kV and energy dispersive spectroscopy (EDS, Bruker AXS, XFlash 4010) equipped in SEM was also used to investigate the surface morphologies and compositions of the electrodeposited Bi_xTe_y films. To confirm the crystal structure, X-ray diffraction (XRD) patterns were measured on a Bruker D8 Advanced X-ray diffractometer using Cu–Kα radiation at a voltage of 40 kV and a current of 40 mA. The scanning was conducted with a scanning rate of 2° min^{-1}, a step size of 0.02°, and a 2θ range from 10° to 80°. In-situ XRD experiments were conducted on the same diffractometer by changing the temperature from room temperature to 200 °C at a rate of 10 °C/min. The effect of the annealing temperature on the crystal structures was also investigated for cases of annealing at 60, 100, 160, and 200 °C for 30 min under 5% hydrogen in nitrogen environments. The thermoelectric and electrical properties of the deposited films were measured after the films were detached from the substrate by Torr Seal epoxy (Varian Vacuum Products, Lexington, Massachusetts). The electrical properties and Seebeck coefficient were evaluated by utilizing a custom-made Hall effect measurement unit in the van der Pauw configuration and the four-point probe method, and home-built Seebeck measurement equipment, respectively. The Seebeck coefficient was determined from plots of the measured Seebeck voltage as a function of the temperature difference (<2 °C) across the specimen ($S = \Delta V/\Delta T$).

3. Results and discussion

LSVs of electrodeposited Bi_xTe_y thin films on Au/Ni/Si substrates were measured to investigate the electrochemical reaction. As shown in Fig. 1(a), the first reduction peak for 2.5 mM $Bi(NO_3)_3$ in the electrolyte was observed at approximately 0.1 V vs. saturated calomel electrode (SCE), which corresponds to the reduction of $HTeO_2^+$ ions to the element Te(s), which was followed by the underpotential deposition of Bi^{3+} onto Te(s) at approximately −0.0 V vs. SCE. The Bi required for Bi_2Te_3 formation can only be deposited as a result of underpotential deposition due to the negative Gibbs free energy of Bi_2Te_3. Thus, deposition of Bi_2Te_3 is limited by the deposition of Te. The reduction reaction can be expressed as follows [12]:

$$3HTeO^{2+} + 2Bi^{3+} + 9H^+ + 18e^- = Bi_2Te_3 + 6H_2O. \qquad (1)$$

As shown in Fig. 1(a), upon addition of Bi^{3+}, there is a shift in the potential to more negative values. If this process was due to the reduction of Bi^{3+}, then we would expect a potential shift in the opposite direction, i.e., to more positive values [13]. However, because increasing the concentration of Bi^{3+} results in relatively less $HTeO_2^+$ being available for deposition, a shift to more negative potentials is reasonable. In addition, an increase in the current density is also observed. Fig. 1(b) shows the ratio of Te to Bi in Bi_xTe_y films as a function of the $Bi(NO_3)_3$ concentration in electrolytes obtained from a quantitative analysis using EDS. The Bi content in the electrodeposited films increased as the Bi^{3+} concentration in the electrolytes increased. This is attributed to the increased reduction of Bi^{3+} in electrodeposits. The deposited Bi content became saturated, which is expected because the current density of LVS also became saturated. Near-stoichiometric Bi_2Te_3 thin films were obtained from electrolytes containing 5 mM $Bi(NO_3)_3$.

SEM images in Fig. 2(a) clearly show that the morphology of electrodeposited Bi_xTe_y thin films depends on the Bi^{3+} concentration in the electrolytes and the stoichiometry of the films. The Bi_xTe_y films deposited at 2.5 and 5 mM $Bi(NO_3)_3$, which had Te-rich and near-stoichiometric films, respectively, appeared to have granular structures. As the Bi^{3+} concentration increases, the granular structure changes to a dense arrangement of needle-like crystals. The size of the needle-like structures in Bi-rich Bi_xTe_y films deposited from electrolytes containing 7.5 mM $Bi(NO_3)_3$ were smaller than those of 10 mM $Bi(NO_3)_3$. This significant morphology change in Bi_xTe_y films with electrolyte composition may be related to the different nucleation mechanisms of Bi and Te in non-stoichiometric Bi_xTe_y thin films. Fig. 2(b) shows the XRD patterns versus the electrolyte concentration of $Bi(NO_3)_3$. The standard cards for Bi_2Te_3, Te, and Au are JCPDS No. 82-0358, No. 86-2269, and No. 04-0784, respectively. The main diffraction peak from almost stoichiometric Bi_xTe_y films can be indexed as a rhombohedral structure with the space group $R\overline{3}m$ (015), which indicates that the crystallites have a preferred growth along this direction. The Bi_xTe_y films deposited using the electrolytes containing 2.5 mM $Bi(NO_3)_3$ show a Te peak. The Te-rich deposited thin films consisted of both a Bi_2Te_3 and a Te phase. The Te phase significantly influenced the thermoelectric and electrical properties of the Te-rich Bi_xTe_y thin films, which will be explained later. We observed additional (101) and (110) peaks from thin films with $Bi(NO_3)_3$ concentrations of more than 5 mM. In addition, broadening of the peak was observed, which may be attributed to the distorted structure that results from the incorporation of more Bi in the lattice.

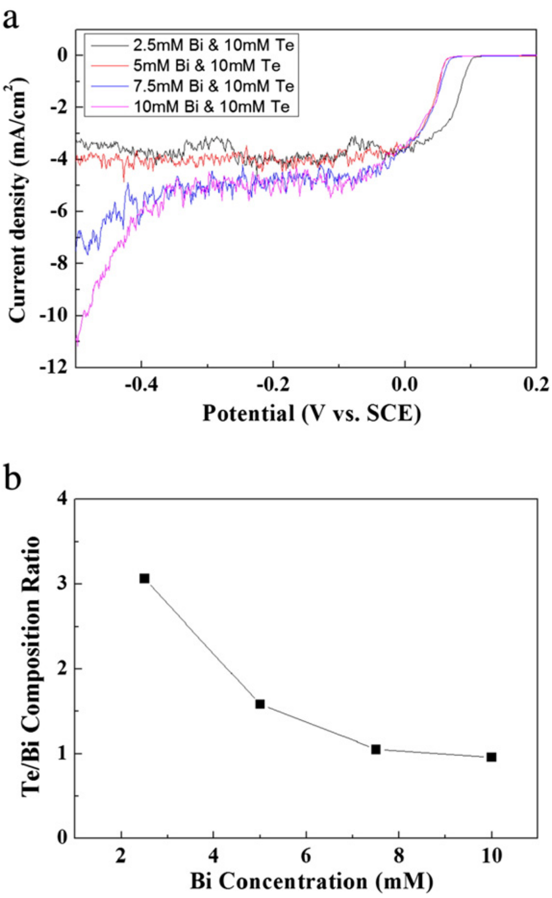

Fig. 1. (a) LSV of Bi_xT_y deposited on Au/Ni/Si substrates using solutions consisting of 2.5–10 mM $Bi(NO_3)_3$, 10 mM TeO_2, and 1.5 M HNO_3. The scan rate was fixed at 1 mV/s. (b) The ratio of Te to Bi content in Bi_xTe_y films as a function of different concentrations of $Bi(NO_3)_3$ in the solutions.

Fig. 3 shows the relationship between the Seebeck coefficient and the electrical properties of Bi_xTe_y films as a function of the $Bi(NO_3)_3$ concentration. As the Bi concentration in the electrolytes increases, the electron concentration increases from 4.9×10^{19} to $2.4 \times 10^{21}/cm^3$, which may be attributed to the formation of an increased number of defects such as Bi interstitials and/or Te vacancies (not shown here). The Bi_xTe_y films deposited using the electrolyte containing 2.5 mM $Bi(NO_3)_3$ exhibit p-type conductivity. It is known that a Bi vacancy