One-step electrochemical preparation of the ternary \((\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3\) thin films on Au\((1\ 1\ 1)\): Composition-dependent growth and characterization studies

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ABSTRACT

This study reports on the synthesis of ternary semiconductor \((\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3\) thin films on Au\((1\ 1\ 1)\) using a practical electrochemical method, based on the simultaneous underpotential deposition (UPD) of Bi, Sb and Te from the same solution containing \(\text{Bi}^{3+}\), \(\text{SbO}^+\), and \(\text{HTeO}_2^+\) at a constant potential. The thin films are characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), energy dispersive spectroscopy (EDS) and reflection absorption-FTIR (RA-FTIR) to determine structural, morphological, compositional and optic properties. The ternary thin films of \((\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3\) with various compositions \((0.0 \leq x \leq 1.0)\) are highly crystalline and have a kinetically preferred orientation at \((0\ 1\ 5)\) for hexagonal crystal structure. AFM images show uniform morphology with hexagonal-shaped crystals deposited over the entire gold substrate. The structural and composition analyses reveal that the thin films are pure phase with corresponding atomic ratios. The optical studies show that the band gap of \((\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3\) thin films could be tuned from 0.17 eV to 0.29 eV as a function of composition.

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1. Introduction

V–VI group thermoelectric materials with numerous interesting features such as low maintenance, long life, no emissions of toxic gases and high reliability are widely used in thermoelectric, biomedical and optoelectronic applications\[1,2\]. The binary compounds, the growth rates of the two constituent materials \((\text{Bi}_2\text{Te}_3\) and \(\text{Sb}_2\text{Te}_3)\) must be equal and the conditions necessary for the growth of one constituent cannot impede the growth of the other. Furthermore, the structure and bonding of the two materials must be sufficiently similar to allow their facile mixing; otherwise, the formation of segregated structures such as two different binary compounds may occur \[9,10\]. Here, the growth rates, necessary conditions and lattice constants of the \(\text{Bi}_2\text{Te}_3\) and \(\text{Sb}_2\text{Te}_3\) are significantly similar. Various methods have been used to synthesize ternary \((\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3\) films, including physical vapor deposition \[11\], mechanical alloying \[12\] and potentiostatic electrodeposition \[3\]. In these studies, ternary compounds with only several values were prepared. No comprehensive study has yet been conducted on \((\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3\) compound in which \(x\) displays a broad variation.

Here, we report on the electrochemical synthesis of homogeneous ternary \((\text{Bi}_x\text{Sb}_{1-x})_2\text{Te}_3\) thin films in all proportions. Compared to other methods, electrodeposition of semiconductor materials is an alternative to vacuum-based methods due to their low cost and the ability to work at ambient temperature and pressure. Electrochemical Atomic Layer Epitaxy (ECALE) \[13\] techniques promise to overcome the problems associated with other electrodeposition methods, including the formation of highly polycrystalline deposits. In ECALE, a surface-limited reaction through underpotential deposition (UPD) is used to synthesize a compound by depositing each element from their separate solutions. ECALE is used to produce a wide variety of thin films \[14–16\]. \(\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3\) superlattice thin films have also been synthesized by ECALE \[17\].
Recently, we have modified this technique in a simple and convenient way for electrochemical deposition of compound semiconductor materials on the basis of a combination of co-deposition and the UPD [18]. We have shown that this method could be used to grow highly crystalline binary thin films of PbS [18], ZnS [6], CdS [7], PbTe [19] and Sb2Te3 [20]. In this study, we report on the synthesis of homogeneous ternary (Bi\(x\)Sb\(1-x\))2Te3 thin films with various compositions (0.0 ≤ \(x\) ≤ 1.0) using modified electrochemical technique. The thin films of (Bi\(x\)Sb\(1-x\))2Te3 have been characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), energy dispersive spectroscopy (EDS), and reflection absorption-FTIR (RA-FTIR) as a function of composition. The results indicate that our modified electrochemical method could also be used to deposit ternary semiconductor compounds.

2. Experimental

2.1. Chemicals

All the electrolyte solutions for electrochemical works were prepared from reagent grade chemicals and deionized water (resistivity > 18 MΩ cm). Prior to each electrochemical experiment, the working solution was deaerated with bubbling N2 for 15 min. (Bi\(x\)Sb\(1-x\))2Te3 electrodeposition was carried out in a solution containing 0.001 M TeO2 (Merck) and by varying the concentration (total 0.001 M) of Sb2O3 (Merck) and Bi(NO3)3 (Merck) with a pH value of 1.5 due to the solubility behaviors of Bi, Sb and Te species [21–24].

2.2. Electrochemistry

The measurements were carried out in a conventional three-electrode cell system (C3 Cell Stand, BAS) under an N2 atmosphere, at room temperature with a BAS 100B/W Electrochemical Workstation. The working electrode was a (1 1 1)-oriented crystal gold (Johnson Matthey, 99.999%) prepared with a pure gold wire in hydrogen–oxygen flame. A platinum wire was used as a counter electrode. All the potentials were referenced to a 3 M Ag/AgCl reference electrode. The deposition time was 30 min.

2.3. Characterization of materials

The absorbance spectra of (Bi\(x\)Sb\(1-x\))2Te3 thin films deposited on Au Plates were measured using a variable angle reflection rig in conjunction with a Perkin–Elmer Spectrum One FT-IR spectrometer in the spectral range of 1000–4000 cm\(^{-1}\) at room temperature. All measurements were achieved by an average of 100 scans and a resolution of 2 cm\(^{-1}\).

XRD experiments for thin films on Au(1 1 1) were performed on a Rigaku Advance Powder X-ray Diffractometer instrument using Cu Kα radiation (\(\lambda = 1.5405 \text{ Å}\)), operating at 30 kV and 30 mA over a 2θ range of 20–60°. The XRD phases present in the deposits were identified with the help of the Joint Committee on Powder Diffraction Standards–International Center for Diffraction Data (JCPDS–ICDD).

The elemental compositions (Bi/Sb/Te) of the (Bi\(x\)Sb\(1-x\))2Te3 deposits were determined by EDS with a JEOL-JSM-6060LV system coupled to the scanning electron microscope. The operating conditions for EDS analysis include an accelerating voltage of 15 kV, a beam current of 5 nA, a working distance of 15 mm, and a live time of 60 s for each run.

Morphologies of the films were inspected by non-contact mode NC-AFM (PicoSPM, Molecular Imaging Inc.). All images were taken in air. 225 μm length, 7 μm thickness and 38 μm width silicon nitride cantilevers with a spring constant of 48 N/m and a resonant frequency of 190 kHz for NC-AFM were used. AFM images were taken from different zones of the films to check their homogeneity.

3. Results and discussion

3.1. Electrochemical deposition

In order to determine a constant deposition potential for all precursors for simultaneous co-deposition of the ternary (Bi\(x\)Sb\(1-x\))2Te3 from the same solution, the cyclic voltammetric measurements of all precursors were recorded at the UPD region for each precursor in separate solutions in the same medium. Fig. 1a presents the cyclic voltammogram of 1.0 mM Bi\(^{3+}\) on the Au(1 1 1) substrate at the UPD region of Bi (pH 1.5). The cathodic peak A (around 240 mV) and anodic peak A’ (around 260 mV) indicate the surface-limited deposition and desorption of Bi, respectively. The bulk deposition of Bi occurs at the potential of ~25 mV (not shown in Fig. 1a). These results suggest the necessity of maintaining a constant deposition potential for all precursors in order to achieve simultaneous co-deposition of the same thin films.
Similar electrochemical behaviors of Bi\textsuperscript{3+} in acidic solution have previously been observed \cite{25}.

The cyclic voltammogram shown in Fig. 1b was obtained for antimony UPD on the Au(1 1 1) working electrode in a solution containing 1.0 mM Sb\textsuperscript{3+} (Sb\textsuperscript{5+}) ions in acidic aqueous solution (pH 1.5). This voltammogram contains two redox couples corresponding to the deposition and stripping of Sb atomic layers. The anodic stripping peaks, labeled B and C (around 80 mV and 5 mV, respectively), correspond to the deposition and stripping of Sb atomic layers. The anodic bulk deposition of Te does not occur until −200 mV.

The cyclic voltammogram of Au(1 1 1) electrode immersed in a solution containing 1.0 mM Te\textsubscript{2}O\textsubscript{3} at pH 1.5 at the UPD region of Te is shown in Fig. 1c. The peaks, labeled D\textsuperscript{+} and E\textsuperscript{+} (around 580 mV and 510 mV, respectively), correspond to the desorption of Te atomic layer while the peaks, labeled D and E (around 350 mV and 90 mV, respectively), correspond to the surface-limited deposition of Te atomic layer. The electrochemical bulk deposition of Te does not occur until the potential reaches −50 mV in the acidic solution (pH 1.5). These observations agree with those obtained in acidic solution by us \cite{27} and others \cite{28,29}.

Fig. 1d shows the overlapped cyclic voltammograms of bismuth, antimony and telluride UPDs obtained under the same conditions. If the potential of the working electrode is kept constant at a potential between +80 mV and −30 mV (shown as co-deposition region in Fig. 1d), Bi, Sb and Te are supposed to deposit underpotentially at the electrode surface. These underpotentially deposited Bi, Sb and Te atoms react with each other to form the ternary (Bi\textsubscript{x}Sb\textsubscript{1−x})\textsubscript{2}Te\textsubscript{3} compound semiconductor at the electrode surface and (Bi\textsubscript{x}Sb\textsubscript{1−x})\textsubscript{2}Te\textsubscript{3} covers the electrode surface in a short time. Fig. 2 shows the bulk deposition potentials of Bi, Sb and Te on the (Bi\textsubscript{x}Sb\textsubscript{1−x})\textsubscript{2}Te\textsubscript{3}-covered Au electrode. As can be seen from the cyclic voltammograms in Fig. 2, the bulk deposition potentials of Bi, Sb and Te are never reached even on the (Bi\textsubscript{x}Sb\textsubscript{1−x})\textsubscript{2}Te\textsubscript{3}-covered Au electrode surface if the potential of electrode set to a potential which is in the range of co-deposition region. Since the potentials in the co-deposition region shown in Fig. 1d is limited for the UPD deposition of Bi, Sb and Te atomic layers but not for their bulk deposition. It should promote the atom-by-atom growth of (Bi\textsubscript{x}Sb\textsubscript{1−x})\textsubscript{2}Te\textsubscript{3} thin films with various compositions (0.0 ≤ x ≤ 1.0) by simply using different Bi:Sb mole fractions from the same solution.

Fig. 3 shows the absorption spectra of (Bi\textsubscript{x}Sb\textsubscript{1−x})\textsubscript{2}Te\textsubscript{3} films in the range of 4000–1000 cm\textsuperscript{-1} obtained by electrochemical deposition for 30 min at different mole fractions of Bi:Sb. The absorption edges measured for the deposits with x values in a sequence of 1.00, 0.75, 0.50, 0.25 and 0 are 1360 cm\textsuperscript{-1} (7340 nm), 1720 cm\textsuperscript{-1} (5800 nm), 1920 cm\textsuperscript{-1} (5210 nm), 2060 cm\textsuperscript{-1} (4850 nm) and 2310 cm\textsuperscript{-1} (4320 nm), respectively. The fundamental absorption edge at 4320 nm and 7340 nm corresponds to binary semiconductor Sb\textsubscript{2}Te\textsubscript{3} and Bi\textsubscript{2}Te\textsubscript{3} films at the two ends of the figure. In these spectra, we can clearly see that the absorption edge blue-shifts with increasing Sb ratio in the ternary thin films.

For direct band gap semiconductors, the widely used method of plotting (ahv)\textsuperscript{2} versus the energy (hv) is adopted to determine the band gap of the semiconductor thin films \cite{30}. The E\textsubscript{g} can thus be estimated from a plot of (ahv)\textsuperscript{2} versus the photon energy (hv). As shown in Fig. 4, the estimated band gaps for (Bi\textsubscript{x}Sb\textsubscript{1−x})\textsubscript{2}Te\textsubscript{3} deposits with various compositions were found to be E\textsubscript{g} = 0.17 eV, 0.21 eV, 0.24 eV, 0.26 eV, and 0.29 eV. The band gaps for (Bi\textsubscript{x}Sb\textsubscript{1−x})\textsubscript{2}Te\textsubscript{3} deposits with mole fractions x of 1.0 and 0 were found to be 0.17 eV and 0.29 eV, which resemble the values for the band gap energies of the bulk Bi\textsubscript{2}Te\textsubscript{3} \cite{31} and Sb\textsubscript{2}Te\textsubscript{3} \cite{4}, respectively. The band gap E\textsubscript{g} is thus observed to increase from 0.17 eV to 0.29 eV as the concentration of Sb increases in the (Bi\textsubscript{x}Sb\textsubscript{1−x})\textsubscript{2}Te\textsubscript{3} deposits. Recent advances in ternary semiconductor nanocrystals or thin films have shown that their band gaps and then their optical emissions can be tuned by changing their constituent stoichiometries. According to the Vegard’s Law \cite{32}, the band gap of bulk ternary alloys varies linearly with composition by the equation of

$$E_{\text{g\_\text{ally}}} = xE_{\text{A}} + (1 - x)E_{\text{B}},$$

where x is the mole fraction, E\textsubscript{A}, E\textsubscript{B}, and E\textsubscript{ally} are the band gap energy (or other properties) of pure A, pure B, and the alloy A\textsubscript{x}B\textsubscript{1−x}, respectively. The band gap dependency of BiSbTe\textsubscript{3} thin films as a function of the composition is shown in Fig. 5. These results clearly demonstrate that the band gap of BiSbTe\textsubscript{3} thin films electrodeposited at −10 mV for 30 min is directly related to the film composition.
3.3. Morphological, structural and compositional characterization of (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ thin films

Fig. 6 shows the AFM images of the films with different compositions of the ternary (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ electrodeposited on Au(1 1 1) substrate at $-10$ mV for 30 min. The line scans across a grain is indicated by an arrow in the lower panel of figures. Fig. 6a–e represent the surface morphologies of (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ thin films with $x$: 0.0, 0.25, 0.5, 0.75 and 1.0, respectively. The AFM images of all the films show uniform surface morphology over the entire Au(1 1 1) substrate surface. Most of the grains are almost hexagonal in shape, while some of them are spherical in shape. The average crystalite sizes of (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ films observed for 0.0 and 1.0 of the $x$ values were about 100 nm and 200 nm in diameter, with standard deviations of 13.7 nm and 21.9 nm, respectively.

Fig. 7 shows the XRD patterns of the (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ films prepared at different compositions on Au(1 1 1) substrate. XRD patterns correspond to rhombohedral phase of (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$, with hexagonal crystal structure indicating that the (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ thin
films are in single crystalline nature of as-grown material. For $x = 0.0$, the preferential orientation was along (0 1 5) plane at 28.2° (2θ scale) as matched with the standard JCPDS-ICDD data card 15-0874 of Sb$_2$Te$_3$ (Fig. 6a). Fig. 7b–d shows that the (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ thin films are composed of mixed crystallites of both Sb$_2$Te$_3$ and Bi$_2$Te$_3$. Namely, the single crystalline structure of (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ films is considered to be a mixture of Sb$_2$Te$_3$ and Bi$_2$Te$_3$ crystallite films. The crystallographic phases of compounds are in good agreement with the hexagonal crystal structure. The peaks in the XRD patterns of (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ thin films ($0.0 \leq x \leq 1.0$) were located in between those of hexagonal Sb$_2$Te$_3$ and Bi$_2$Te$_3$. For $x = 1.0$, the XRD diffractogram consists of a strong diffraction peak at 27.7° (2θ scale) arising from (0 1 5) reflections from Bi$_2$Te$_3$ (Fig. 7e). This indicates that the crystallites in the ternary films of Bi$_2$Te$_3$ have a preferred growth in (0 1 5) direction. The weaker diffraction at 38.2° corresponds to (1 1 1) reflection of Au, which belongs to a single crystalline substrate in this study. The standard cards pertaining to Bi$_2$Te$_3$ and Au are JCPDS-ICDD 15-0863 and 04-0784, respectively. No phase-separated Bi or Sb was observed in these samples. These results indicate that highly crystalline deposits of ternary compound semiconductor (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ can be grown by this method at a kinetically preferred orientation on Au(1 1 1) as a result of the controlled growth processes associated with low deposition rate [18].

Fig. 8 shows the close-up view of the (0 1 5) reflections for various Bi:Sb proportions. The diffraction peaks for the (0 1 5) are located at 28.2°, 28.1°, 27.9°, 27.8° and 27.7°. As $x$ decreases, the diffraction peaks of samples gradually shift toward a higher value of 2θ, indicating the formation of ternary system of V–VI compounds in between Bi$_2$Te$_3$ and Sb$_2$Te$_3$ compounds. The lattice parameters ($a$) of the ternary semiconductor films for preferentially oriented (0 1 5) reflection were estimated from the XRD spectra by applying Vegard’s Law [32]. Table 1 summarizes the calculated lattice parameters and shift of (0 1 5) diffraction peak of (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ thin films.

The elemental compositions (Bi/Sb/Te) of electrodeposited (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ films have been determined by the EDS technique. A representative EDS spectrum for (Bi$_{0.5}$Sb$_{0.5}$)$_2$Te$_3$ consists of Bi, Sb and Te peaks indicating that the film is pure phase with an approximate stoichiometry of 1:1:3 (Fig. 9). In addition to this
Table 2
The elemental compositions (Bi/Sb/Te).

<table>
<thead>
<tr>
<th>Formula</th>
<th>The molar percentage in solution</th>
<th>The atomic percentage in film by EDS</th>
<th>(Bi + Sb)/Te</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Bi</td>
<td>Sb</td>
<td>Te</td>
</tr>
<tr>
<td>Bi₂Te₃</td>
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<td>0.0</td>
<td>50.0</td>
</tr>
<tr>
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<td>12.5</td>
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</tr>
<tr>
<td>(Bi₀.₅Sb₀.₅)₂Te₃</td>
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<td>25.0</td>
<td>50.0</td>
</tr>
<tr>
<td>(Bi₀.₂₅Sb₀.₇₅)₂Te₃</td>
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<tr>
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<td>0.0</td>
<td>50.0</td>
<td>50.0</td>
</tr>
</tbody>
</table>

spectrum, all the EDS data are also given in Table 2. As shown in Table 2, atomic percentage of the Bi:Sb in films is in close agreement with the volumetric ratio of the elemental precursors taken in the solution during electrodeposition. We found that the quantitative atomic ratio of (Bi + Sb) and Te are approximately 40% versus 60% for (BiₓSb₁₋ₓ)₂Te₃ films, a ratio which is close to 2:3 stoichiometries.

4. Conclusions

In summary, we have shown that the ternary semiconductor (BiₓSb₁₋ₓ)₂Te₃ thin films could be deposited underpotentially by an electrochemical co-deposition method at room temperature from the same solution containing Bi³⁺, SbO⁺ and HTeO₂⁺ on Au(1 1 1) substrate at a constant potential. The electrodeposited (BiₓSb₁₋ₓ)₂Te₃ films with various compositions (0.0 ≤ x ≤ 1.0) were homogeneous and in highly crystalline structure, which was grown at a kinetically preferred orientation at (0 1 5) on Au(1 1 1). The dependence of the band gap on the alloy composition is found to be linear and the band gap could be tuned from 0.17 eV to 0.29 eV by changing the concentration ratio of (Bi + Sb) solutions during electrochemical deposition. The present results indicate that ternary compound semiconductor thin films could be successfully prepared by this UPD-based electrochemical co-deposition technique.

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