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The underpotential deposition of $Bi_2Te_{3-y}Se_y$ thin films by an electrochemical co-deposition method

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1. Introduction

Thermoelectric (TE) materials are special types of semiconductors that can directly convert heat to electricity [1]. Bismuth-based semiconductors are commonly used for thermoelectric devices such as thermoelectric generators [2] and coolers [3] and for optical storage systems [4]. Bi₂Te₃ and its derivative compounds are considered to be the best materials used in thermoelectric refrigeration at room temperature [5], in particular Bi₂Te_{2.7}Se_{0.3} and Bi_{0.5}Sb_{1.5}Te₃ for the n-type and p-type, respectively [6]. These are currently the most efficient thermoelectric materials at 25 °C in bulk form [7]. The performance of thermoelectric devices depends on the figure of merit (ZT) of the material. In comparison with bulk TE materials, thin film TE materials offer tremendous scope for ZT enhancement [8]. In the formation of high quality thermoelectric devices, a number of thin film formation methodologies are used, including: molecular beam epitaxy (MBE) [9], chemical vapor deposition (CVD) [10], flash evaporation [11], co-evaporation [12], and sputtering [13]. In general, these methods are performed in vacuum and are thermal methods, achieving compound formation by heating the reactants and substrate. However, electrochemical synthesis of thin films is an alternative to vacuum-based methods due

ABSTRACT

 $Bi_2Te_{3-y}Se_y$ thin films were grown on Au(111) substrates using an electrochemical co-deposition method at 25 °C. The appropriate co-deposition potentials based on the underpotential deposition (upd) potentials of Bi, Te and Se have been determined by the cyclic voltammetric studies. The films were grown from an electrolyte of 2.5 mM Bi(NO₃)₃, 2 mM TeO₂, and 0.3 mM SeO₂ in 0.1 M HNO₃ at a potential of -0.02 V vs. Ag|AgCl (3 M NaCl). X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) were employed to characterize the thin films. XRD and EDS results revealed that the films are single phase with approximate composition of $Bi_2Te_{2.7}Se_{0.3}$. SEM studies showed that the films are homogeneous and have micronsized granular crystallites.

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Electrochimica Acta

to their low cost and the ability to work at ambient temperature and pressure. In addition, the composition of the thermoelectric materials can be easily controlled through adjusting the concentration of electrodeposition solution.

Thin films can be formed via surface limited reactions by using Atomic layer epitaxy (ALE). Electrochemical surface limited reactions are generally referred to as underpotential deposition (upd) [14]. Electrochemical atomic layer epitaxy (ECALE), developed by Stickney and co-workers, is the result of combining upd with the principles of ALE to form a deposition cycle [15]. A layer of the compound is deposited by alternating the underpotential deposition of the metallic element with the underpotential deposition of the nonmetallic element in an ECALE cycle. However, this method is very time-consuming and produces a large amount of dilute wastewater due to the substrate being rinsed after each deposition. Automated deposition systems by ECALE were developed to overcome these problems [16]. Up to now, this method has been applied extensively to obtain thin films of CdTe [17], CdS [18], ZnSe [19], GaAs [20], PbSe [21], Bi₂S₃ [22], Bi₂Te₃ [8], ZnS/CdS [23] and Hg_(1-x)Cd_xTe [24]. Another particularly promising method is to deposit both species simultaneously from the same solution by the induced codeposition mechanisms. In this method, the reduction of the more noble component induced the reduction of the less noble component at a constant potential [25]. Recently, Demir and co-workers have developed a new electrodeposition method, which based on the co-deposition of Pb and S precursors at the upd of Pb and S [26].



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This method, a new electrochemical co-deposition method, is the combination of upd and co-deposition. II–VI compounds such as ZnS [27] and CdS [28] have been successfully formed by using the electrochemical co-deposition method.

Limited works have been reported on the electrochemical synthesis of $Bi_2Te_{3-y}Se_y$ thin films [29–31], nanowires [7] and nanotubes [32]. Furthermore, no work has been reported on the formation of $Bi_2Te_{3-y}Se_y$ thin film by both ECALE and electrochemical co-deposition method, where the co-deposition potential based on the upd of each element. In this paper, we first report the electrochemical co-deposition of thin films of n-type $Bi_2Te_{2.7}Se_{0.3}$ on Au(1 1 1) substrates. This composition is the one that is optimal for bulk thermoelectric applications of $Bi_2Te_{3-y}Se_y$ [33]. The appropriate co-deposition potential was determined by cyclic voltammetry. X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) were employed for characterization of the thin films.

2. Experimental

Cyclic voltammetry and controlled potential electrolysis experiments were performed with a PAR model 2273 potentiostat/galvanostat connected to a three electrode cell (K0269A Faraday Cage, PAR) at 25 °C. The Au(111) working electrode similar to a ball-shaped droplet was (111)-oriented single-crystal gold (Alfa-Johnson Matthey, 99.995%) prepared as previously described by Hamelin [34]. An Ag|AgCl (3 M NaCl) (Bioanalytical Systems, Inc., West Lafayette, IN) was used as reference electrode and a platinum wire was used as counter electrode. Solutions were prepared with deionized water (i.e., >18 M Ω). The electrolyte for the deposition of Bi₂Te_{2.7}Se_{0.3} thin films contains a mixture of 2.5 mM Bi(NO₃)₃, 2 mM TeO₂, 0.3 mM SeO₂, and 0.1 M HNO₃. The pH value of the solutions was 1.2 ± 0.1 . Prior to each experiment, the electrolyte solutions were purged with purified N₂ gas for 15 min. All experiments were performed at 25 °C. The deposition potential for $Bi_2Te_{3-\nu}Se_{\nu}$ was determined from cyclic voltammetry data of Bi, Te, and Se. The electrodeposition of $Bi_2Te_{3-\nu}Se_{\nu}$ thin films were performed at -0.02 V since this potential value is suitable with the upd of Bi, Te, and Se.

Characterization of the films was carried out with different techniques. The XRD patterns were recorded by an X-ray diffractometer (Rigaku, D-max 2200, Japan) using CuK α radiation (λ = 1.54050 Å). The morphologies of the films were examined by SEM, JEOL, JSM-6060LV. The chemical compositions of the films were determined by an energy-dispersive X-ray spectrometer (EDS) attached to the SEM.

3. Results and discussion

3.1. Cyclic voltammetry

The cyclic voltammograms for an Au(111) substrate in 3 mM and 0.3 mM SeO₂ solutions, recorded at the upd region, are shown in Fig. 1. Different responses were observed in each cyclic voltammogram. In the voltammetric behavior of 3 mM SeO₂ + 0.1 M HNO₃ solution, scanning the electrode potential between 1.05 and 0.25 V gave rise to peaks C1–C3, which are usually associated with Se upd [35,36]. On the reverse scan, the stripping peak at 0.91 V corresponds to stripping of Se upd. When the electrode was immersed into 0.3 mM SeO₂ + 0.1 M HNO₃ solution, all of the peak currents decreased. Most upd involves the formation of a single atomic layer, such as Bi [8] and Te [37]. However, Stickney has suggested that the total Se deposited in the upd process is two more monolayers [38]. It can be seen that charge involved in the upd peaks decrease in the voltammogram of 0.3 mM SeO₂, indicating that



Fig. 1. Cyclic voltammograms of Se from $Au(1 \ 1 \ 1)$ obtained from 3 mM and 0.3 mM SeO₂ solution in the upd region. The scanning rate is 100 mV/s.

the Se deposited may be depend on Se species concentration or kinetic of deposition process. In addition, peak C1 overlaps with peak C2 and cannot be distinguished. If potential of working electrode is scanned more negative potentials through -0.05 V, the Se bulk deposition does not occur. From Fig. 1, it can be noticed that decreasing Se ion concentration causes a shift of the deposition peaks C1 and C3 towards more negative potential, indicating that the deposition process is significantly more sluggish with the Se ion concentration decreasing, which should be attributed to kinetic complications due to the lowering of the Se ion concentration. Consequently, voltammetric investigations show that the charge involved in the upd peaks and the potential of deposition curves of the upd peaks strongly depend on the Se ion concentration below approximately 3 mM. Similar characteristics of the upd dependence on the Se ion concentration have been observed by Alanyalıoğlu et al. [36]. As can be seen in Fig. 2, if the potential is scanned towards more negative values in the voltammogram of 3 mM SeO₂, the Se bulk deposition occurs at about 0.11 V (peak C4) and its corresponding oxidative stripping peak is seen at 0.75 V. On the contrary, during the positive scan between -0.25 and 1.05 V, the oxidative stripping of the Se bulk at 0.75 V nearly disappears in the voltammogram of 0.3 mM SeO₂. The voltammetric behavior of Se bulk deposition is consistent with what has been reported by Qiao et al. [39].

Fig. 3 shows the cyclic voltammograms for Bi electrodeposition on the Au(111) substrate. When potential of the Au(111) electrode is scanned between +0.40 V and -0.02 V, reductive peak I, which corresponds to the Bi upd is seen (thin curve). If potential of Au(111) working electrode is scanned through more negative



Fig. 2. Cyclic voltammograms of Se from 3 mM and 0.3 mM SeO₂ in a 0.1 M HNO₃ solution on Au(111) electrode at a scan rate of 100 mV/s.

potentials than -0.02 V, a second reductive peak II appears at -0.07 V for deposition of Bi bulk (thick curve). Reversing the potential scan, the oxidation of the Bi bulk occurs giving an anodic current peak III. When the potential is scanned towards more positive values, an anodic peak IV, which corresponds to the oxidation of Bi upd, is observed at about 0.23 V. The voltammetric behavior of Bi on Au(111) is in good agreement what has been reported in the literature [40]. Accordingly to the cyclic voltammograms, if we keep the potential of the electrode constant at a potential that is in range from 0.19 to -0.02 V, which is more positive values than the onset of bulk Bi, an atomic layer of Bi will be deposited at the electrode.

The cyclic voltammetric behavior of an Au(111) electrode in 2 mM TeO_2 and 0.1 M HNO_3 electrolyte is shown in Fig. 4a. In the range of the electrode potential between 0.90 and -0.02 V, the voltammogram is characterized by two cathodic features, labeled C1 and C2 as well as two anodic peaks, labeled A2 and A1. The reduction peaks are associated with the Te upd. The stripping peaks A2 and A1 correspond to dissolution of Te upd. If potential of working electrode is scanned more negative potentials through -0.02 V, the Te bulk deposition does not occur. When the potential is scanned towards more negative values in the voltammogram, the Te bulk deposition peak occurs at about -0.09 V, labeled C3, and its corresponding oxidative stripping peak, labeled A3, is at 0.47 V. These cyclic voltammograms are similar to that reported previously by authors [37,41,42].

Fig. 4b shows the cyclic voltammograms of the Au(111) electrode in a solution of 2.5 mM Bi(NO₃)₃ + 2 mM TeO₂ + 0.1 M HNO₃. These cyclic voltammograms are different from cyclic voltammo-



Fig. 3. Cyclic voltammograms of 2.5 mM $Bi(NO_3)_3$ in a $0.1\,M$ HNO_3 solution on Au(111) electrode. The scanning rate is 100 mV/s.

grams of 2 mM TeO₂. Sweeping negatively from an initial potential of 0.90 V, three reductive peaks (labeled 1-3) are observed. The subsequent anodic stripping peaks were observed at 0.23, 0.44, 0.51 and 0.62 V, labeled as 4, 5, 6 and 7, respectively. Electrochemical "window-opening" experiments, in which the switching potentials were varied, indicate that peaks 3/5 are conjugated. In comparison with Fig. 4a, peak 1 arises at about 0.28 V, shifts 70 mV to a more negative potential in comparison with its counterpart peak, labeled C1. Shifting of first Te upd peak in the presence Bi(III) ions is consistent with the results in a Cd–Te system that has been reported by Gomez et al. [43]. When the potential is scanned towards more negative values, a relatively broad cathodic peak, labeled 2, is observed 0.13 V and shifted to a more positive potentials compared with second Te upd peak, labeled C2, in Fig. 4a. By comparing Fig. 4b with Fig. 3, peak 2 occurs at more negative potentials than Bi upd peak, labeled I. These observations indicate that the peak 2 is considered to be result of both Bi upd peak and second Te upd peak. As the potential swept to lower values, a third reductive peak, labeled 3, appears around -0.09 V for both Bi bulk and Te bulk. On the reverse scan, an anodic peak, which corresponds to the oxidation of Bi bulk, is not observed at about 0.03 V, in comparison with Fig. 3. The scan proceeded resulted in an oxidative peak (labeled 4), which appears at the same potential as in Fig. 3 and corresponds to the oxidation of Bi upd. The second anodic peak, labeled 5, occurs at about 0.44 V, is shifted by about 30 mV to a more negative potential compared with peak A3 in Fig. 4a. Since the peak, labeled 3, is the co-deposition of Bi₂Te₃ bulk, the second anodic peak, labeled 5, may be assigned to the oxidation of Bi₂Te₃ bulk. These findings are in agreement



Fig. 4. Cyclic voltammograms of the Au(111) electrode recorded at 100 mV/s in solution containing (a) 2 mM TeO_2 and 0.1 M HNO₃, and (b) $2.5 \text{ mM Bi}(NO_3)_3$, 2 mM TeO_2 and 0.1 M HNO₃.

with the results in a Bi–Te system as reported by previously workers [1,44,45]. The last two anodic peaks, labeled 6 and 7, appear at the same potentials in comparison with their counterpart peaks, labeled A2 and A1, in Fig. 4a. If we keep the potential of the electrode constant at -20 mV, which correspond both Bi upd and Te upd, Bi and Te will be deposited simultaneously at the electrode at this potential.

Cyclic voltammetry analysis of the Au(111) electrode in the deposition solution was carried out to determine the appropriate electrodeposition potential based on the upd for $Bi_2Te_{3-y}Se_y$ deposition. Fig. 5 displays the six voltammetric cycles of the Au(111) electrode in a solution of 2.5 mM $Bi(NO_3)_3 + 2$ mM $TeO_2 + 0.3$ mM $SeO_2 + 0.1$ M HNO₃, each successive lower potential. Sweeping negatively from an initial potential of 1.0 V, three reductive features, i–iii, are observed. When the potential sweep is reversed at -0.15 V and scanned positively, six stripping features, iv–ix, are observed. There are only first reduction peak i (at 0.27 V) and its stripping peak vii (at 0.62 V) in the voltammogram, when the electrode scanned negatively to 0.20 V. In comparison with their counterpart peaks 1/7, in Fig. 4b, peaks i/vii occur at the same potentials. This suggests that i/vii peak pair is associated with Te upd. If potential of working



Fig. 5. Window opening cyclic voltammetry of the Au(111) electrode in 2.5 mM $Bi(NO_3)_3$, 2 mM TeO_2 , 0.3 mM SeO_2 and 0.1 M HNO_3 solution. The scanning rate is 100 mV/s.

electrode scanned more negative potentials through 0.10 V, a relatively broad reduction peak, labeled ii, (at about 0.14 V) and three oxidation peaks, labeled iv, vi and ix, appear. Since the oxidation peaks, labeled iv and vi, occur at the same potentials in comparison with their counterpart peaks (labeled 4 and 6 in Fig. 4b), these anodic peaks correspond to the oxidation of Bi upd and second Te upd, respectively. Another oxidation peak, labeled ix, occurs at the same potential in comparison with its counterpart peak (at about 0.91 V), in Fig. 1. These observations indicate that the peak ii is considered to be result of the second Se upd peak as well as both the second Te upd peak and Bi upd peak. When the potential is reversed from 0.0 V and scanned positively, oxidation peaks, labeled iv, vi and ix, become larger. When the potential is scanned negatively to -0.1 V, two anodic peaks, labeled v and viii, arise at 0.44 and 0.75 V. respectively. The relatively small oxidation peak, labeled viii, occurs at the same potential in comparison with the oxidative stripping of the Se bulk in Fig. 2. Another oxidation peak, labeled v, occurs at the same potential in comparison with the dissolution of Bi₂Te₃ bulk in Fig. 4b. If the potential is reversed from -0.15 V and scanned positively, current density of peak v increases. It can be seen that peak v is the oxidative stripping peak of Bi₂Te₃ bulk. However, the other anodic peaks (labeled iv, vi, vii and ix), which are the oxidative stripping peaks of Bi upd, Te upd and Se upd, do not change with prolonged polarization.

Based on the above results, for electrodeposition potential of Bi, Te and Se in upd range can be determined from Fig. 5. If we keep the potential of the electrode constant at a potential that is in the middle of the co-deposition region, as shown in Fig. 5, which stands for a region between the reductive Bi upd, Te upd and Se upd, theoretically, Bi, Te and Se will be deposited simultaneously at the electrode at this potential. Because the value of this potential is not enough for the bulk deposition of Bi, Te and Se, there was no deposition of Bi(III) on Bi, Te(IV) on Te or Se(IV) on Se. Therefore, it should promote the atom-by-atom growth of the mixture of Bi_2Te_3 and Bi_2Se_3 , or $Bi_2Te_{3-y}Se_y$ at the substrate. Electrochemical measurements indicate that the composition of $Bi_2Te_{3-\nu}Se_{\nu}$ films is influenced by the SeO₂ concentration in the co-deposition region between the reductive Bi upd, Te upd, and Se upd. In order to obtain the best stoichiometry of Bi₂Te_{2.7}Se_{0.3} compound, various SeO₂ concentrations were studied to optimize the stoichiometry of Bi, Te and Se elements in the films.



Fig. 6. EDS patterns of the $Bi_2Te_{3-y}Se_y$ films deposited at -0.02 V for 2 h from various deposition solutions: (a) 2.5 mM Bi(NO₃)₃, 2 mM TeO₂, 0.3 mM SeO₂ and 0.1 M HNO₃ solution and (b) 2.5 mM Bi(NO₃)₃, 2 mM TeO₂, 0.6 mM SeO₂ and 0.1 M HNO₃ solution.

3.2. Compositional, structural and morphological characterization of $Bi_2Te_{3-y}Se_y$ films

In order to investigate the effect of SeO₂ concentration in the solution on the composition of the films, Bi₂Te_{3-y}Se_y films were prepared on Au(1 1 1) substrates by changing only SeO₂ concentration. The representative EDS pattern of Bi₂Te_{3-y}Se_y with $y \sim 0.3$ deposited from 2.5 mM Bi(NO₃)₃, 2 mM TeO₂, 0.3 mM SeO₂ and 0.1 M HNO₃ solution is shown in Fig. 6a. When the concentration of SeO₂ in the deposition solution was elevated to 0.6 mM, the atomic percentage of Se element in the film was increased (see Fig. 6b). The results indicate that the content of Se in electrodeposited Bi₂Te_{3-y}Se_y films is strongly dependent on the concentration of SeO₂ in the deposition solution. These results could mean that the film is a mixture of Bi₂Te₃ and Bi₂Se₃ or that the Te_{1-x}Se_x alloy is



Fig. 7. Powder XRD diffractogram of $Bi_2Te_{2.7}Se_{0.3}$ film grown at -0.02 V for 2 h.

formed instead of elemental Te and one phase has formed. These findings are in agreement with the results in a Bi–Te–Se system as reported by previously workers [7,30].

XRD pattern of the film electrodeposited on Au(1 1 1) electrode at -0.02 V in a solution of 2.5 mM Bi(NO₃)₃ + 2 mM TeO₂ + 0.3 mM SeO₂ + 0.1 M HNO₃ is shown in Fig. 7. The diffraction peak observed at 2θ = 38.18 is due to the Au substrate. All the other diffraction peaks could be indexed to the hexagonal Bi₂Te₃ compound (JCPDS, 15-863), indicating that a single phase had formed. The peaks are slightly shifted to smaller d spacings compared to standard Bi₂Te₃. In other words, the peaks are slightly shifted to larger 2θ /degree values compared to standard Bi₂Te₃. Nevertheless, there is only one set of peaks for every plane; we can confirm that the formation is of a single phase. In addition, no diffraction peaks from the elemental Bi and Te are detected. Consequently, the XRD result suggests that an electrodeposition carried out at the co-deposition region is able to induce a single-phase ternary alloy formation can be described as [7]:

$$2Bi^{3+} + (3-y)HTeO_2^{+} + (y)H_2SeO_3 + (9+y)H^{+} + 18e^{-}$$

$$\rightarrow Bi_2Te_{3-y}Se_y + (6+y)H_2O$$
(1)

The surface morphologies of the films prepared at -0.02 V for various deposition times were investigated with SEM and shown in Fig. 8. The SEM image in Fig. 8a, recorded for a 1 h deposition time, reveals a surface containing smooth granular crystallites with an average size of 0.5 µm. These granular crystallites become larger as the deposition time increases to 2h and their surfaces are covered by thorn-like nanostructures (see Fig. 8b). These nanostructures may have potential applications in enhancing the thermoelectric performance. By increasing the deposition time, these crystallites become peach pit-like crystallites with average size of 2 µm (see Fig. 8c). However, the films in Fig. 8b and c are shown 3D growth characteristics. Accordingly above analyses for Fig. 3, there is not a big difference in the upd and bulk deposition potentials and that there would be a tendency for the Bi to deposit by a 3D nucleation and growth mechanism in parallel with any upd. Due to the 3D nucleation of Bi, some new Bi₂Te₃ or Bi₂Se₃ crystal nuclei will grow dominantly. Consequently, these results



Fig. 8. SEM images of $Bi_2Te_{2.7}Se_{0.3}$ films deposited at -0.02 V for various deposition times: (a) 1 h, (b) 2 h, and (c) 3 h.

show that the morphologies of electrodeposited $Bi_2Te_{3-y}Se_y$ films are strongly affected by the deposition times.

4. Conclusions

 $Bi_2Te_{3-y}Se_y$ thin films have been successfully prepared by an electrochemical co-deposition method, which based on the upd of Bi, Te and Se from a solution of Bi(III), Te(IV) and Se(IV) in 0.1 M HNO₃. The cyclic voltammetry and EDS analyses indicated that the composition of the films can be controlled by using different concentrations of SeO₂ in the deposition solution. Consequently, the best stoichiometry of $Bi_2Te_{2.7}Se_{0.3}$ films was obtained by a co-deposition method. The films are polycrystalline and exhibit a single phase. SEM studies indicate that the surface of the substrates is covered by granular crystallites with the average size of 2 μ m.

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