Electrochemically deposited thermoelectric n-type Bi\textsubscript{2}Te\textsubscript{3} thin films

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Abstract
Electrochemically deposited n-type Bi\textsubscript{2}Te\textsubscript{3} alloy thin films were grown from nitric acid baths on sputtered Bi\textsubscript{x}Te\textsubscript{y}/SiO/Si substrates. The film compositions, which varied from 57 to 63 at.% Te, were strongly dependent on the deposition conditions. Surface morphologies varied from needle-like to granular structures depending on deposited Te content. Electrical and thermoelectric properties of these electrodeposited Bi\textsubscript{2}Te\textsubscript{3} thin films were measured before and after annealing and compared to those of bulk Bi\textsubscript{2}Te\textsubscript{3}. Annealing at 250 °C in reducing H\textsubscript{2} atmosphere enhanced thermoelectric properties by reducing film defects. In-plane electrical resistivity was highly dependent on composition and microstructure. In-plane Hall mobility decreased with increasing carrier concentration, while the magnitude of the Seebeck coefficient increased with increasing electrical conductivity to a maximum of \(-188.5\) μV/K. Overall, the thermoelectric properties of electrodeposited n-type Bi\textsubscript{2}Te\textsubscript{3} thin films after annealing were comparable to those of bulk Bi\textsubscript{2}Te\textsubscript{3} films.

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1. Introduction
Thermoelectric devices generate an electric potential gradient from a thermal gradient, or vice versa, without any actuating parts. Thermoelectrics can be utilized as electric generators or coolers in several applications, such as power generation systems, microcoolers, CCD technologies, and infrared detectors. To improve the efficiency of thermoelectric devices, the appropriate thermoelectric materials having the best performance at a specific operating temperature must be selected. The thermoelectric figure of merit, ZT, can be expressed as \(\alpha^2 \sigma T / \kappa\), where \(\alpha\) is the Seebeck coefficient, \(\sigma\) the electrical conductivity, \(T\) the temperature, and \(\kappa\) the thermal conductivity. Among the various thermoelectric materials, Bi\textsubscript{2}Sb alloys have superior performance at low temperatures (<200 K) [1], whereas SiGe has the highest ZT at higher temperatures (1100–1200 K) [2]. Bismuth telluride (Bi\textsubscript{2}Te\textsubscript{3}) has been a main focus of research because of its superior ZT near room temperature [3].

Bi\textsubscript{2}Te\textsubscript{3} alloy is a V\textsubscript{2}-VI\textsubscript{3} compound semiconductor, which can be tailored as n-type or p-type by varying the composition with slight deviations from its stoichiometric composition. In addition to bulk Bi\textsubscript{2}Te\textsubscript{3} materials, which are processed by solidification methods or powder metallurgy, Bi\textsubscript{2}Te\textsubscript{3} films varying from sub-micron to several micron thick have been studied, because of their potential applications in miniature thermoelectric devices. Various methods such as evaporation [4-5], sputtering [6,7], MOCVD [8] and electrodeposition [9-13] have been developed for the deposition of Bi\textsubscript{2}Te\textsubscript{3} films. Of these processes, electrodeposition is widely investigated because of its many advantages, including it cost-effectiveness, rapid deposition rates, and relative ease in controlling film thickness from the nanoscale to a few millimeters.

In an early study, Takahashi et al. [9] successfully demonstrated electrodeposition of intermetallic compounds of Bi\textsubscript{2}Te\textsubscript{3} and confirmed their structures by XRD analysis. A systematic investigation of the electrochemical reactions and
compositional changes as a function of applied potential in a nitric acid bath containing Bi$^{3+}$ and HTeO$_2^+$ was performed by Martin-Gonzalez et al. [10]. They proposed several electrochemical processes for forming Bi$_2$Te$_3$ intermetallic compounds at different potential ranges. Miyazaki and Kajitani [11] also used an acidic bath and reported that the deposition of either n-type or p-type bismuth telluride could be controlled by controlling the deposition potential. n-Type Bi$_2$Te$_3$ could be obtained above 20 mV versus saturated calomel electrode (SCE), whereas p-type Bi$_2$Te$_3$ was deposited below 20 mV versus SCE. They proposed that changes in the majority charge carrier concentration of Bi$_2$Te$_3$ is caused by decreasing the applied potential and enhancing the deposition of Bi. This compositional shift to the Bi-rich side introduces p-type semiconductor characteristics in Bi$_2$Te$_3$. This change in behavior with compositional changes is well matched with the results of the study by Martin-Gonzalez et al. [10], even though the potential range reported for the specific Bi$_2$Te$_3$ composition is not similar. This difference is primarily due to differences in the concentrations of Bi$^{3+}$ and HTeO$_2^+$ in the electrochemical baths. Besides simple baths which consisted of Bi$^{3+}$, HTeO$_2^+$, and HNO$_3$, complex baths of Bi$^{3+}$ complexed with EDTA (ethylenediaminetetraacetic acid) have been suggested by other researchers [12]. These researchers proposed that the formation of bismuth hydroxide (Bi(OH)$_3$) could be suppressed by complexing Bi$^{3+}$ with EDTA.

Recently, research into the fabrication and characterization of nanowire structures of thermoelectric materials has received much attention due to the possibility of enhancing the figure of merit (ZT) by reducing the structural dimensions to a single dimension [14–17]. Hicks and Dresselhaus [18] calculated that the figure of merit for nanowires will be significantly improved by decreasing the diameter. They calculated a ZT of ~14 for a wire width of 5 Å, 28 times higher than that of Bulk Bi$_2$Te$_3$ (ZT=0.5). Previously, we have demonstrated methods to fabricate both thermoelectric micro- and nano-devices using electrodeposited thermoelectric films and nanowires, respectively [19,20,24–32]. In order to enhance the performance of nanowires and nanostructures, electrodeposition conditions must be further optimized.

Although there have been many publications on electrodeposited Bi$_2$Te$_3$ thin films or nanowires [9–17], most of these studies are confined to electrochemical studies for analyzing the relationship between composition or microstructure of deposited thin films and the effect of deposition conditions such as pH, applied potential, and bath composition.

In this study, we studied the thermoelectric properties and electrical characteristics of electrodeposited Bi$_2$Te$_3$ films systematically by using sputtered Bi$_2$Te$_3$ thin films on SiO$_2$/Si substrate as a seed layer. By using sputtered Bi$_2$Te$_3$ thin film as the seed layer, the lattice mismatch between substrate and deposit can be minimized to reduce defect formations. In parallel, the effects of film compositions on surface morphologies of BiTe alloys at different applied potentials were also investigated.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Electrical characteristics of the sputtered BiTe seed layer</th>
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<tbody>
<tr>
<td>In-plane resistivity ($\Omega$cm)</td>
<td>1.49</td>
</tr>
<tr>
<td>In-plane mobility (cm$^2$/V·s)</td>
<td>2.9</td>
</tr>
<tr>
<td>Carrier concentration ($cm^{-3}$)</td>
<td>1.40E21</td>
</tr>
</tbody>
</table>

2. Experimental

Bi$_2$Te$_3$ films were electrodeposited on a Bi$_2$Te$_3$ seed layer from an aqueous nitric acid bath at 23 °C. The bath was composed of 0.008 M Bi$^{3+}$ from Bi(NO$_3$)$_3$ and 0.01 M HTeO$_2^+$ from TeO$_2$ in 1 M HNO$_3$. The pH was maintained at pH 0.1, and a 1 μm thick Bi$_2$Te$_3$ seed layer was deposited on a SiO$_2$/Si wafer (lightly doped p-type, 2 in. diameter) by rf sputtering. The electrical properties of sputtered seed layer are listed in Table 1. Bi$_2$Te$_3$ films were deposited potentiostatically on the Bi$_2$Te$_3$ seed layer with strong agitation. The reference and counter electrodes were SCE and platinum mesh, respectively. The charge density was controlled to maintain the deposited film thickness at approximately 6 μm, which was considered thick enough, compared to the Bi$_2$Te$_3$ seed layer, to minimize the effect of the seed layer when measuring electrical and thermoelectric properties of each electrodeposited Bi$_2$Te$_3$ film. After electrodeposition, Bi$_2$Te$_3$ films were annealed in forming gas (7.2% H$_2$ in Ar) at 250 °C for 2 h. Annealing has previously been shown to improve the thermoelectric properties of as-deposited films [20].

Cyclic voltammograms were performed in unstirred solution containing three different concentration of Bi$^{3+}$ (0, 1, and 8 mM) with fixed HTeO$_2^+$ concentration using an EG&G Potentiostat/Galvanostat 273A with a scan rate of 10 mV/s. Surface morphologies of electrodeposited Bi$_2$Te$_3$ films were investigated using scanning electron microscopy (SEM) (LEO 1550 VP FESEM); with energy dispersive spectroscopy (EDS) (Oxford INCA Energy 300 X-ray Energy Dispersive Spectrometer System) was used for determining the bismuth and tellurium content in the electrodeposited films. Seebeck coefficients and transport properties were measured along the direction parallel to the substrates before and after annealing. Hall effect measurements were performed to determine the transport properties (i.e. electrical resistivity, carrier concentration, and carrier mobility) of the deposited films at room temperature.

3. Results and discussion

Cyclic voltammetry (CV) analysis for the electrodeposition solution of 0, 1, and 8 mM Bi$^{3+}$ and with fixed HTeO$_2^+$ concentration (0.01 M) was carried out to determine the appropriate potential range for Bi$_2$Te$_3$ deposition. As shown in Fig. 1, a reduction peak around ~50 mV versus SCE developed when Bi$^{3+}$ was added. This peak can be identified as
Therefore, decreasing the potential from the peak potential is slightly more negative than that of Bi$_2$Te$_3$ reduction [10].

The applied potentials for depositing Bi$_x$Te$_y$ from 0, 1 and 8 mM, chosen from the CVs, are marked as short arrows on the inset of Fig. 1. The CV of Te electrolyte, second Te reduction peak potential. As applied potential became more cathodic, the deposited Te content increased to 62.4 at.% when the potential was $\sim$−60 mV, which is slightly more negative than that of Bi$_2$Te$_3$ reduction [10].

As applied potential was moved more negative than $\sim$−170 mV, deposited Te content in the films increased again, from 60.0 at.% (Bi$_2$Te$_3$) to 61.3 at.% (Bi$_{1.9}$Te$_{3.1}$) at $\sim$−400 mV. As shown in Fig. 1, the CV of Te electrolyte, second Te reduction peak occurred at $\sim$−500 mV, indicating it could be explained that Te content in the films increased again with applied potentials become more cathodic. Similar composition variation behavior was reported by Martin-Gonzalez et al. [10]. According to their results, within the potential range from $\sim$−120 to $\sim$−520 mV, Te content varied from 60.8 at.% ($\sim$−120 mV) to 43.6 at.% ($\sim$−260 mV), and increased again to 55.9 at.% ($\sim$−520 mV). Even though there are some differences, which could be explained by differences in substrate, deposited Te content follow a similar trend.

SEM images in Fig. 3 clearly show that the morphologies of electrodeposited Bi$_x$Te$_y$ films are strongly affected by the film compositions and deposition potentials. Bi$_x$Te$_y$ film which were deposited at $\sim$−10 and $\sim$−170 mV (57.0 and 60.0 at.% Te), having stoichiometric composition or Bi-rich BiTe films, show the granular structures. Whereas Te-rich BiTe films consisted with needle-like structure. The size of the needle-like structures of Te-rich Bi$_x$Te$_y$ films deposited at low cathodic potentials (i.e. $\sim$−60 and $\sim$−100 mV) were smaller than those of higher cathodic potential conditions ($\sim$−200 to $\sim$−400 mV). Significant morphology changing of BiTe thin films with composition might be related with the different roles of excess Bi and Te in the non-stoichiometric BiTe alloys.

Fig. 4(a) shows the carrier concentration obtained in Bi$_x$Te$_y$ films electrodeposited at different deposition potentials. Carrier concentration decreased from $\sim$5.6 $\times$ 10$^{20}$ to $\sim$1.8 $\times$ 10$^{20}$ cm$^{-3}$ as deposition potential decreased from 0 to $\sim$−180 mV, carrier concentration increased slightly as the deposition potential was further decreased. The carrier concentration of Bi$_x$Te$_y$ films before and after annealing are presented with different compositions in Fig. 4(b), where the carrier concentration for bulk Bi$_2$Te$_3$ is presented for comparison [33]. The carrier concentrations of electrodeposited Bi$_x$Te$_y$ films, where n-type charge carrier characteristics with Bi-rich Bi$_x$Te$_y$ films (Bi$_{1.9}$Te$_{3.1}$) are presented. The reason for n-type characteristics of Bi-rich electrodeposited BiTe thin film is not clear, but it is obvious that microstructures or structural imper-
Fig. 3. Surface morphology of Bi$_x$Te$_y$ films electrodeposited at different deposition potentials: (a) $-10$ mV, (b) $-60$ mV, (c) $-100$ mV, (d) $-170$ mV, (e) $-200$ mV, (f) $-300$ mV, (g) $-400$ mV.

Infections at different applied potential condition might affect the carrier concentration of electrodeposited Bi$_x$Te$_y$ films. On the other hand, Margi et al. [22] reported a linear relationship between film composition and carrier concentration, which does not match with our results. This discrepancy might be caused by differences in Bi$_x$Te$_y$ film composition. The range of film composition studied by Margi et al. was from 63.6 at. % Te (Bi$_{1.4}$Te$_{1.2}$) to 70.0 at. % Te (Bi$_{1.5}$Te$_{1.5}$), which means compositions were significantly shifted to Te-rich phases. As discussed above, the microstructure of electrodeposited Bi$_x$Te$_y$ films was considerably changed from near 60 at. % Te (Bi$_{1.7}$Te$_{0.3}$) to a Bi-rich phase (Bi$_{2.15}$Te$_{2.85}$), therefore it could be expected that, in the study of Margi et al., the microstructure change within Te-rich Bi$_x$Te$_y$ phases...
Fig. 4. Dependence of carrier concentrations of Bi$_x$Te$_y$ electrodeposits on (a) applied deposition potential and (b) Te deposit content.

Fig. 5. Dependence of electrical resistivity of electrodeposited Bi$_x$Te$_y$ films on Te deposit content.

Structural effects on electrical properties also can be observed in the electrical resistivity of electrodeposited Bi$_x$Te$_y$ films. In semiconductor materials, the electrical resistivity is highly related to the carrier concentration, as is shown in bulk Bi$_2$Te$_3$. However, as shown in Fig. 5, the highest resistivity in electrodeposited Bi$_x$Te$_y$ films, 4.58 m$\Omega$ cm was measured at 61.3 at.% Te, deposited at $-400$ mV. Bi$_x$Te$_y$ films deposited at $-300$ mV had a resistivity of 2.95 m$\Omega$ cm. Films deposited at $-400$ and $-300$ mV have well developed needle-like structures, therefore the porosity of needle-like structure could be anticipated to enhance the resistivity of thin films. Bi$_x$Te$_y$ films electrodeposited at $-60$ mV also had needle structures, but the microstructure is smaller and more compact than the microstructures obtained at $-400$ or $-300$ mV, resulting in lower resistivity (1.80 m$\Omega$ cm).

Fig. 6(a) shows the relationship between Te content and Hall mobility and in electrodeposited Bi$_x$Te$_y$ films. Compared to bulk Bi$_2$Te$_3$, in which the in-plane Hall mobility varies from $\sim 31$ to $\sim 46$ cm$^2$ V$^{-1}$ s$^{-1}$, in-plane Hall mobilities of electrodeposited films were somewhat lower, and results were scattered. Hall mobility in Bi$_x$Te$_y$ films is affected by the electrical conductivity and carrier concentration, obtained from the Hall constant, expressed as following equation [23]:

$$\mu_e = \frac{\sigma_e R_e}{n e}$$

where $\mu_e$ is the mobility, $\sigma_e$ the electrical conductivity, $R_e$ the Hall constant, $n$ the carrier concentration and $e$ the electronic charge.

Here, electrical conductivity, the inverse of electrical resistivity, varies with temperature and other factors such as structural defects. The relationship between mobility and carrier concentration of electrodeposited Bi$_x$Te$_y$ films, is shown at $-300$ mV had a resistivity of 2.95 m$\Omega$ cm.
Fig. 7. Dependence of Seebeck coefficient of Bi$_x$Te$_y$ electrodeposits on (a) Te deposit content and (b) electrical conductivity.

in Fig. 6(b). The mobility data are scattered, but not because of carrier concentration, since the electrodeposited film and bulk material have similar levels of carrier concentration. The measurements were performed at the same temperature, so it is reasonable that the scatter in the measured Hall mobility of electrodeposited Bi$_x$Te$_y$ films could be caused by structural defects such as grain boundaries, which could decrease conductivity of thin films.

Seebeck coefficients of electrodeposited and bulk Bi$_x$Te$_y$ are presented in Fig. 7. As can be seen in Fig. 7(a), it is difficult to determine the relationship between the Seebeck coefficient and deposited Te content of electrodeposited samples. However, the relationship becomes clear when Seebeck coefficients are plotted against electrical conductivity (Fig. 7(b)). The Seebeck coefficient in electrodeposited Bi$_x$Te$_y$ films was significantly enhanced (larger negative value for n-type thermoelectric semiconductor) as the electrical conductivity increased from $\sim 0.2 \cdot 10^{-5}$ to $\sim 0.5 \cdot 10^{-5}$/Ωm. Seebeck coefficients of electrodeposited Bi$_x$Te$_y$ films can be further improved by optimizing electrodeposition conditions to obtain better electrical conductivity.

4. Conclusion

Bi$_x$Te$_y$ films were obtained by potentiostatic electrodeposition. These films had a range of 57.0–62.4 at.% deposited Te content, which is controlled by the deposition potential. The films exhibit n-type semiconductor characteristics. Surface morphologies of Te-rich Bi$_x$Te$_y$ films were needle-like structures, which were clearly distinguished from granular structures of stoichiometric (Bi$_2$Te$_3$) and Bi-rich Bi$_x$Te$_y$ films. Structural changes caused by variation of the film composition affected the electrical resistivity and carrier concentrations. The in-plane Hall mobility of electrodeposited films decreased with increasing carrier concentration, as expected, even though data were scattered. The Seebeck coefficient of electrodeposited Bi$_x$Te$_y$ films reached a maximum ($\sim 188.5 \mu$V/K) at the stoichiometric composition of Bi$_2$Te$_3$, deposited at $\sim 170$ mV. The Seebeck coefficient enhanced significantly with increasing electrical conductivity.

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References


