Thermoelectric Characteristics of the Thermopile Sensors with Variations of the Width and the Thickness of the Electrodeposited Bismuth-Telluride and Antimony-Telluride Thin Films

Min-Young Kim* and Tae-Sung Oh

Department of Materials Science and Engineering, Hongik University, Seoul 121-791, Korea

Thermopile sensors were processed on glass substrates by using successive electrodeposition of p-type Sb-Te and n-type Bi-Te thin films, and their thermoelectric characteristics were measured. The thermopile sensor, consisting of the p-n legs of 2 μm-thickness and 50 μm-width, exhibited the sensitivity of 24.8 mV/K. By changing the width of the p-n thin-film legs from 50 to 100 μm, the sensitivity decreased to 15.4 mV/K because of less pairs of the p-n thin-film legs in the thermopile. With increasing the thickness of the thin-film legs from 2 to 5 μm, the sensitivity was improved to 36.5 mV/K due to higher Seebeck coefficients of the 5 μm-thick Bi-Te and Sb-Te films than those of the 2 μm-thick films.

Keywords: thermoelectric thin film, thermopile sensor, bismuth telluride, antimony telluride, electrodeposition

1. Introduction

Thermoelectric devices utilizing Seebeck effect and Peltier effect have been widely investigated for applications to thermoelectric power generation and thermoelectric cooling.11 Recently, various works have been conducted to apply thermoelectric thin films to micro-devices such as thermopile sensors and micro-coolers.2–6 Thermopile sensors processed with thermoelectric materials convert heat energies generated by various physical signals and chemical reactions into electrical signals.7–9 With advantages of high sensitivity, no offset, and no need for biasing, they can be utilized to various applications such as infrared sensor, microcalorimeter, psychrometer, RMS converter, EM-field sensor, flow meter, vacuum sensor, and accelerometer.7–9 As the responsibility of a thermopile sensor is given by the ratio of the voltage out of a sensor to the absorbed radiation power, thin films of large Seebeck coefficients are required to get a high responsibility.10 As Bi₂Te₃ and Sb₂Te₃ are narrow band-gap semiconductors with superior thermoelectric characteristics at room temperature, various works have been performed to utilize thin films of Bi₂Te₃ and Sb₂Te₃ for thermopile sensors.2,6,11,12 While various processing techniques such as evaporation, metal-organic chemical vapor deposition, molecular beam epitaxy, and electrodeposition can be used for thermoelectric thin-film fabrication, electrodeposition is attractive because it is a rapid and low-cost method as well as a low-temperature process.2,5,6,12–16

While various works were carried out for thermopile sensors of cross-plane configuration,5,17–19 a thermopile sensor of in-plane configuration has its advantage in fabrication because of easy formation of in-plane thin-film legs by using electrodeposition. In this study, the n-type bismuth telluride (Bi-Te) and the p-type antimony telluride (Sb-Te) thin films were electrodeposited to fabricate thermopile sensors composed of the Bi-Te and the Sb-Te thin-film legs. Thermoelectric characteristics of the thermopile sensors were measured with variations of the width and the thickness of the p-n thin-film legs of the thermopile sensor.

2. Experimental Procedure

Bi-Te films of 2 μm and 5 μm-thicknesses were electrodeposited from a nitric-acid aqueous solution containing 50-mM Bi-Te in 1M HNO₃ at a constant potential of −50 mV. Bi₂O₃ and TeO₂ were successively dissolved in 1M HNO₃ to obtain an electrodeposition solution with the Bi/(Bi + Te) mole fraction of 0.5. As a seed layer for electrodeposition, we sputter-deposited an 1 μm-thick Ti onto a glass substrate. A three-electrode electrochemical cell system was employed with a Ti/glass substrate as a cathode, a Pt mesh electrode as an anode, and an Ag/AgCl electrode as a reference electrode.

Sb-Te films of 2 μm and 5 μm-thicknesses were electrodeposited from an aqueous solution containing 70-mM Sb-Te electrolytes. To make the Sb-Te electrodeposition solution, we successively dissolved TeO₂ and Sb₂O₃ into a mixed solution of 3.5 M perchloric acid and 0.35 M tartaric acid at 160°C with the Sb/(Sb + Te) mole fraction of 0.9. A three-electrode electrochemical cell system was employed to electrodeposit the Sb-Te films on a Ti/glass substrate at a constant potential of 20 mV relative to the Ag/AgCl reference electrode. Compositions of the Bi-Te and the Sb-Te films were analyzed by energy dispersive spectroscopy (EDS). The Seebeck coefficients (α) of the Bi-Te and the Sb-Te films were evaluated using a relationship of \( \alpha = \Delta V / \Delta T \) after measuring the Seebeck voltage (ΔV) generated in the in-plane direction of a film at a temperature difference (ΔK) of 20 K. A sub-heater, located at the hot end of a film, was used to make the temperature difference of 20 K across both ends of a film. During the Seebeck-coefficient measurements, the temperature of the cold end of a film was kept at room temperature by using a Cu cold block.

A thermopile sensor of in-plane configuration was designed as Fig. 1 to have 196 pairs of the Bi-Te and the Sb-Te thin film legs of 50 μm-width or 130 pairs of the p-n thin-film legs of 100 μm-width. Figure 2 represents the fabrication...
steps of a thermopile sensor test specimen. An 1 µm-thick Ti was sputtered on a glass substrate as a seed layer for electrodeposition. The p-type Sb-Te and the n-type Bi-Te thin-film legs were successively electrodeposited and patterned with photolithography. At this time, electrode pads to measure a Seebeck voltage (ΔV) of the thermopile sensor were also formed by electrodeposition of the Bi-Te. Then the Ti seed layer on the glass substrate was removed by etching at 10% HF solution. A 5.5 µm-thick photoresist was cured on the thermopile sensor as an insulation layer after exposing the sensor electrode pads. Then, a Ti/Cu/Ti thin-film heater was formed at the center region of the thermopile sensor by successive sputtering of 0.1 µm-thick Ti, 1 µm-thick Cu, and 0.1 µm-thick Ti through a metal mask.
A current was applied to the thin film heater to make a temperature difference across a hot end and a cold end of the thermopile sensor. As illustrated in Fig. 3(a), temperatures at the center (hot end) and an edge (cold end) of the thermopile were measured using thermocouples attached at each place. As temperature differences were less than 13 K, the temperature of the cold end was maintained at room temperature. The Seebeck voltage ($\mathcal{V}/\mathcal{C}$) of the thermopile sensor at a given temperature difference ($\mathcal{T}$) was measured using a digital multimeter.

### 3. Results and Discussion

Table 1 lists the thickness, composition, and Seebeck coefficient of the electrodeposited Bi-Te and Sb-Te films. The compositions of the Bi-Te films were close to the Bi$_2$Te$_3$ stoichiometry without depending upon the thickness of the film. However, the composition of the Sb-Te film changed with variation of the film thickness. As the reversible potential of the HTeO$_2^+/Te$ reaction is much more positive than the SbO$^+/Sb$ reaction, the electrodeposition rate of Te is faster than that of the Sb during electroplating at 20 mV. As the deposition rate of Sb was independent of the concentration of the SbO$^+$ and the HTeO$_2^+$ ions in the electrodeposition solution, the HTeO$_2^+$ ions would be consumed faster than the SbO$^+$ ions with progress of electrodeposition, resulting in gradual change of the film composition with increasing the film thickness.

In Table 1, the Seebeck coefficients of both the Bi-Te and the Sb-Te films, which were lower than those of the bulk alloys due to heavy doping inherent for the electrodeposition process, increased with the film thickness. The Seebeck coefficient of the Bi$_2$Te$_3$ thin films were reported to vary depending upon the reciprocal thickness of the films, in the effective mean free path model for the polycrystalline thin film developed by Tellier, the Seebeck coefficient of a thin film, $S_f$, is given by eq. (1).

$$S_f = S_b \left[ 1 - \frac{3}{8} (1 - p) \ell_f \frac{U_g}{1 + U_g} \right]$$

where $S_b = \frac{\pi e k T}{8m^*}$ is the Seebeck coefficient of the bulk, $k$ is the Boltzmann constant, $e$ is the electron charge, $E_F$ is the Fermi energy, $p$ is the specularity parameter, $\ell_f$ is the effective mean free path in the bulk, and $t$ is the thickness of the film. In eq. (1), the thickness dependence of the Seebeck coefficient of a thin film, $S_f$, is determined with the sign of $U_g$ which depends upon the scattering mechanism. While $U_g$ values for the Bi$_2$(Te$_{0.9}$Se$_{0.1}$)$_3$ thin films were calculated as negative, those for the Bi-Te thin films were reported to be positive, which would explain larger Seebeck-coefficient of the 5 µm-thick Bi-Te film than that of the 2 µm-thick film as listed in Table 1. With increase in the Seebeck coefficient with the film thickness, the sign of $U_g$ for the electrodeposited Sb-Te films could be also expected as positive.

Figure 3(a) illustrates an optical micrograph of the thermopile sensor consisted of the 196 pairs of the p-n thermoelectric legs of 50 µm-width and a Ti/Cu/Ti thin film heater, and Fig. 3(b) exhibits the optical micrographs of the
p-type Sb-Te and the n-type Bi-Te thin-film legs formed underneath the Ti/Cu/Ti heater. Because we fixed the total size of a thermopile sensor regardless of the leg width, as shown in Fig. 1, the thermopile sensor composed of 100 \( \mu \text{m} \)-wide legs was processed to have the 130 pairs of the p-n legs.

Figure 4 illustrates the typical curves of the temperature difference (\( \Delta T \)) across the center and the edge of the thermopile sensor and the Seebeck voltage (\( \Delta V \)) generated by the thermopile sensor vs. the applied heater-current (\( I \)). The thickness and the width of the thermoelectric legs were 2 \( \mu \text{m} \) and 50 \( \mu \text{m} \), respectively, for this thermopile sensor. A threshold existed in the applied heater-current, under which a temperature difference and a Seebeck voltage were not detected. Such a threshold in the applied heater-current could be attributed to the heating capacity of the photoresist layer used as an insulation layer between the thermopile sensor and the thin-film heater. As shown in Fig. 4, the temperature difference varied parabolically with the heater-current, indicating that the temperature difference across the hot and cold ends on top of the photoresist insulation layer was effectively formed by the Joule heating of the thin film heater.

Figure 5 reveals the dependence of the Seebeck voltage of the thermopile sensor consisting of the p-n thin-film legs of 2 \( \mu \text{m} \)-thickness and 50 \( \mu \text{m} \)-width as a function of the temperature difference across the hot and cold ends (leg thickness: 2 \( \mu \text{m} \)).

The sensitivities of the thermopile sensors with the p-n thin-film legs of 50 \( \mu \text{m} \)-widths are compared in Fig. 6. The thickness of the thin-film legs of these two thermopiles were fixed as 2 \( \mu \text{m} \). The thermopile sensor consisted of the 100 \( \mu \text{m} \)-wide thin-film legs exhibited the sensitivity of 15.4 mV/K smaller than 24.8 mV/K of the thermopile processed with the thin-film legs of 50 \( \mu \text{m} \)-width.

The thickness of the thin-film legs of these two thermopiles were fixed as 2 \( \mu \text{m} \). The thermopile sensor consisted of the 100 \( \mu \text{m} \)-wide thin-film legs exhibited the sensitivity of 15.4 mV/K smaller than 24.8 mV/K of the thermopile processed with the thin-film legs of 50 \( \mu \text{m} \)-width.

Such decrease in the thermopile sensitivity was caused by less pairs of the p-n legs in the thermopile of 100 \( \mu \text{m} \)-wide legs. As the sizes of two thermopile sensors were same, the thermopile sensor of 100 \( \mu \text{m} \)-wide legs had the 130 pairs of the p-n legs. If the thermopile of 100 \( \mu \text{m} \)-wide legs had 196 pairs of the p-n legs, it would have exhibited a sensitivity of 23.2 mV/K which was very close to 24.8 mV/K.

The sensitivities of the thermopile sensors with the p-n thin-film legs of 2 \( \mu \text{m} \) and 5 \( \mu \text{m} \)-thick films, respectively, are compared in Fig. 7. The widths of the thin-film legs of these two thermopiles were fixed at 50 \( \mu \text{m} \). The thermopile consists of the 5 \( \mu \text{m} \)-thick legs showed the sensitivity of 36.5 mV/K much higher than 24.8 mV/K of the thermopile consisted of the thin-film legs of 2 \( \mu \text{m} \)-thickness. For the thermopile of the 5 \( \mu \text{m} \)-thick legs, larger sensitivity could be expected from higher Seebeck coefficients of the 5 \( \mu \text{m} \)-thick Bi-Te and Sb-Te films in Table 1.
The thermopile sensor, consisted of the p-n legs of 2 of the p-n thin-film legs were processed on glass substrates.

4. Conclusions

Using successive electrodeposition of the p-type Sb-Te and the n-type Bi-Te films, thermopile sensors composed of the p-n thin-film legs were processed on glass substrates. The thermopile sensor, consisted of the p-n legs of 2 thickness and 50 thickness and 50 width, exhibited the sensitivity, i.e., the slope of the Seebeck voltage-temperature difference curve, of 24.8 mV/K. The measured sensitivity of the thermopile sensor was larger than the value estimated with the Seebeck coefficient of the Bi-Te and the Sb-Te films, which could be attributed to annealing effects during the thermopile processing.\textsuperscript{21)

Acknowledgements

This work was supported by the Seoul R&BD Program.


REFERENCES