Infrared and Thermoelectric Properties of Bi<sub>x</sub>Te<sub>y</sub>-Based Alloyed Thin Films

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We studied the infrared (IR) and thermoelectric properties of (Bi<sub>x</sub>Te<sub>y</sub> + Cd) and (Bi<sub>x</sub>Te<sub>y</sub> + InSb) alloyed thin films prepared on SiO<sub>2</sub> glass substrates by electron beam evaporation (EB). Cd was used in terms of the enhancement of sensitivity to IR radiation because CdTe is known to be highly sensitive to IR radiation. The voltage sensitivities were 0.71 and 43.9 mV for Bi<sub>2</sub>Te<sub>2.4</sub> and Bi<sub>2</sub>Cd<sub>2.6</sub>Te<sub>5.5</sub>, respectively, at a bias current of 10 mA and a blackbody furnace temperature of 1000°C. The maximum values of the power factor (P<sub>f</sub>) were 1.15×10<sup>-3</sup> W/mK<sup>2</sup> at 450 K for Bi<sub>2</sub>Te<sub>2.4</sub>, 2.46×10<sup>-4</sup> W/mK<sup>2</sup> at 550 K for Bi<sub>2</sub>Te<sub>3.6</sub>+InSb<sub>6</sub>, and 8.90×10<sup>-6</sup> W/mK<sup>2</sup> at 550 K for InSb<sub>2.2</sub>.

1. Introduction

Bi<sub>2</sub>Te<sub>3</sub> has been mainly used as a Peltier-type cooling device and sometimes as a Seebeck-type thermoelectric power generator because Bi<sub>2</sub>Te<sub>3</sub> has the highest efficiency of conversion from electric energy to heat energy (or vice versa) among materials in practical use.<sup>(1–5)</sup> On the other hand, it is not widely recognized that Bi<sub>2</sub>Te<sub>3</sub> is a narrow-gap semiconductor and has an energy band gap of 0.15 eV (the cutoff wavelength is approximately 8 μm), which corresponds to the far-infrared spectral region.<sup>(6,7)</sup> We have recently focused on this fact and have studied the possibility of using Bi<sub>2</sub>Te<sub>3</sub> in a far-infrared detector.<sup>(8)</sup> Infrared sensors such as those containing InSb and PbS are fabricated on the basis of bulk crystals.<sup>(9)</sup> Sensors based on thin films can have higher sensitivity than those based on bulk crystals. Moreover, the processes used in the fabrication of various semiconductor electronic devices can be applied.

We previously studied the infrared properties of Bi<sub>x</sub>Te<sub>y</sub> binary alloys. In this study, we aim to improve the sensitivity of an infrared sensor using alloyed (Bi<sub>x</sub>Te<sub>y</sub> + Cd) or (Bi<sub>x</sub>Te<sub>y</sub> + InSb) thin films. In addition, we also examine the photoconductive effect.

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and evaluate the possibility of using (Bi<sub>x</sub>Te<sub>y</sub>+Cd) and (Bi<sub>x</sub>Te<sub>y</sub>+InSb) alloyed thin films in infrared detectors. Moreover, we have fabricated a thermoelectric material using (Bi<sub>x</sub>Te<sub>y</sub>+Cd) or (Bi<sub>x</sub>Te<sub>y</sub>+InSb) thin films.

2. **Experiment**

(Bi<sub>x</sub>Te<sub>y</sub>+Cd) and (Bi<sub>x</sub>Te<sub>y</sub>+InSb) alloyed thin films were prepared on SiO<sub>2</sub> glass substrates by electron beam evaporation (EB). The substrate temperature was 250°C. The EB system current was varied from 2 to 10 mA, and the voltage was set at 3.9 kV. The compositions x and y of the thin films were measured by energy-dispersive X-ray spectrometry (EDX), where the values of x and y for a specimen were obtained by averaging the data measured five times for the specimen. In addition, to examine the sensitivity (voltage change) of the samples, we used a blackbody furnace. The peak wavelength of the blackbody furnace was calculated using the Vienna displacement rule. The Hall mobility and carrier concentration of the samples were measured by the Van der Pauw method. Using the data obtained by these measurements, we evaluated our samples in terms of the following three quantities: (1) voltage sensitivity $R_v$, (2) noise-equivalent power NEP, and (3) specific detectivity $D^*$.  

We also studied the thermoelectric properties of (Bi<sub>x</sub>Te<sub>y</sub>+InSb) alloyed thin films using the power factor:\footnote{\cite{10}}

$$P_t = \frac{\alpha^2}{\rho},$$ \hspace{1cm} (1)

which is an important criterion; the value of $10^{-3}$ W/mK$^2$ is the standard for practical use, where $\rho$ is the electrical resistivity and $\alpha$ is the Seebeck coefficient. $\alpha$ and $\rho$ were measured in the temperature range from 300 to 600 K.

1. **Voltage sensitivity, $R_v$**

The voltage sensitivity of a sensor is defined as the output voltage divided by the incident luminous flux on its receptive surface:\footnote{\cite{11}}

$$R_v = \frac{V_o}{\Phi} = \frac{q\lambda\phi\eta\tau(\mu_+ + \mu_-)}{\sigma habd} I_s \frac{R_s R_e}{R_e + R_s} \text{ [V/W]},$$ \hspace{1cm} (2)

where $V_o$ is the output voltage, $\Phi$ is the incident infrared intensity, $\phi$ is the incident photon number per second, $\eta$ is the quantum efficiency, $\tau$ is the carrier lifetime, $\sigma$ is the electric conductivity (infrared irradiation), $habd$ is the element volume, $I_s$ is the bias current, $R_L$ is the load resistance, and $R_e$ is the element resistance.

2. **Noise-equivalent power, NEP**

NEP is defined as the incidence luminous flux that generates a signal voltage with the same value as the noise. It is used as the standard intensity of infrared rays that can be used for sensing without being buried in noise.
\begin{align}
\text{NEP} &= \frac{1}{D} = \frac{\Phi}{(V_n/\sqrt{\Delta f})^{3/2}} \quad \text{[W/Hz\textsuperscript{1/2}]} \\
\end{align}

Here, \(V_n\) is the noise voltage and \(\Delta f\) is the bandwidth.

(3) Specific detectivity, \(D^{*}\)

Specific detectivity is an unambiguous value by which the performance of various sensors can be evaluated regardless of their size.

\begin{align}
D^{*} &= \frac{R_s}{V_n \sqrt{\Delta f}} \sqrt{A_d} \quad \text{[cm \cdot Hz\textsuperscript{1/2} /W]} \\
\end{align}

Here, \(A_d\) is the receptive area.

2.1 Device

Figure 1 shows a photograph of our two types of device. The area of the upper device is \(5\times5\) mm\(^2\), the thickness is 0.5 \(\mu\)m, and receptive optical area is 12.5 mm\(^2\). The lower device is for Seebeck measurement. Its thickness is 0.5 \(\mu\)m. The thin films used in these devices were prepared on SiO\(_2\) glass substrates by EB.

2.2 Measurement system

Figure 2 shows a schematic of our measurement system. We used a blackbody furnace as the infrared source. The temperature of the furnace was changed between room temperature and 1000\(^{\circ}\)C. At 1000\(^{\circ}\)C, the thermal radiation peaks at approximately 3 \(\mu\)m, which is larger than the thickness of the samples studied here (0.5 \(\mu\)m), and thus, the thermal diffusion in a sample is not necessary to consider. The frequency of the optical chopper was 80 Hz. The voltage was set at 4 V.
3. Discussion

3.1 Amount of Cd in thin films

Figure 3 shows the amounts of Cd and Te in (Bi$_2$Te$_3$ + Cd) alloyed films provided that Bi$_2$Te$_3$ is a unit. With increasing amount of Cd, the ratio of Cd and Te to the total content in the films increased.

Figure 4 shows the amounts of In and Sb in (Bi$_2$Te$_3$ + InSb) alloyed films at Bi$_2$Te$_3$ = 1. With increasing amount of InSb, the ratio of In and Sb to the total content increased.

3.2 Evaluation using infrared system (biased current = 10 mA)

Figure 5 shows the voltage change for different samples under different ratios of Te and Cd. The voltage changes were 1.31 and 79.8 mV for Bi$_2$Te$_{2.4}$ and Bi$_2$Cd$_{2.6}$Te$_{5.6}$, respectively, at a bias current of 10 mA and a blackbody furnace temperature of 1000°C. As the ratio of Sb and Te to the total content in the sample increased, the voltage change increased and reached a maximum for Bi$_2$Cd$_{2.6}$Te$_{5.5}$. Then, as the ratio of Sb and Te increased further, the voltage change decreased.

Tables 1 and 2 show some properties for devices based on Bi$_x$Te$_y$ and (Bi$_x$Te$_y$ + Sb) alloyed thin films. These devices were evaluated using an infrared system.

Figures 6, 7, and 8 show the voltage sensitivity, noise-equivalent power, and specific detectivity of the samples, respectively. The voltage sensitivities were 0.71 and 43.9 mV for Bi$_2$Te$_{2.4}$ and Bi$_2$Cd$_{2.6}$Te$_{5.5}$, respectively, at bias current of 10 mA and a blackbody furnace temperature of 1000°C. The noise-equivalent powers were 5.76×10$^{-3}$ and 1.30×10$^{-3}$ W/Hz$^{1/2}$ for Bi$_2$Te$_{2.4}$ and Bi$_2$Cd$_{2.6}$Te$_{5.5}$, respectively, at 1000°C. The specific detectivities were 61 and 273 cm$\cdot$Hz$^{1/2}$/W for Bi$_2$Te$_{2.4}$ and Bi$_2$Cd$_{2.6}$Te$_{5.5}$, respectively, at 1000°C.

3.3 Evaluation using thermoelectric system

Figure 9 shows the temperature dependence of the electrical resistivity for (Bi$_2$Te$_{3.6}$ + InSb) and InSb$_{2.2}$ alloyed thin films. Their electrical resistivity decreased with
Fig. 3. Amounts of Cd in thin films (Bi$_2$Te$_3$ = 1) and in thin films (Bi = 2).

Fig. 4. Amounts of InSb in thin films (Bi$_2$Te$_3$ = 1) and amounts of In and Sb in thin films (Bi = 2).

Fig. 5. Voltage change for different samples.
Table 1
Physical properties of Bi$_2$Te$_3$.

| Property                        | Value   |
|--------------------------------|---------|
| Melting point [K]               | 860     |
| Electric conductivity [S/m]     | $120 \times 10^3$ |
| Thermal conductivity [W/mK]     | 1.5     |
| Thermoelectric power [µV/K]     | -300 (n) |
|                                 | +250 (p) |
| Figure of merit [10$^{-3}$/K]   | 2.2 (n) |
| Energy band gap [eV]            | 0.15    |
| Mobility [cm$^2$/V•s]           | -1140 (n) |
|                                 | +680 (p) |
| Lattice constant [Å]            | 4.38    |

Table 2
Device parameters.

| Thickness [µm] | Composition | Resistance [Ω] | Noise voltage [mV] |
|----------------|-------------|----------------|--------------------|
| 0.5            | Bi$_2$Te$_{2.4}$ | 213            | 0.008              |
| 0.5            | Bi$_{2.4}$Cd$_{1.6}$Te$_{5.5}$ | 3210         | 0.18               |

Fig. 6. Voltage sensitivity of the samples.
Fig. 7. Noise-equivalent power of the samples.

Fig. 8. Specific detectivity of the samples.

Fig. 9. Temperature dependence of electrical resistivity of alloyed thin films.
increasing temperature. Figure 10 shows the temperature dependence of the Seebeck coefficient of (Bi$_2$Te$_{3.6}$+InSb$_6$) and InSb$_{2.2}$ alloyed thin films. For InSb$_{2.2}$, the absolute value of the Seebeck coefficient decreased with increasing temperature. Figure 11 shows the temperature dependence of the power factor ($P_f$) for (Bi$_2$Te$_{3.6}$+InSb$_6$) and InSb$_{2.2}$ alloyed thin films, which was calculated using $P_f = \alpha^2/\rho$. The maximum values of $P_f$ were $1.15 \times 10^{-3}$ W/mK$^2$ at 450 K for Bi$_2$Te$_{2.4}$, $2.46 \times 10^{-4}$ W/mK$^2$ at 550 K for Bi$_2$Te$_{3.6}$+InSb$_6$, and $8.90 \times 10^{-6}$ W/mK$^2$ at 550 K for InSb$_{2.2}$.

![Fig. 10. Temperature dependence of Seebeck coefficient of alloyed thin films.](image1)

![Fig. 11. Temperature dependence of power factor.](image2)
4. Conclusion

We studied the infrared and thermoelectric properties of (Bi$_x$Te$_y$+Cd) and (Bi$_x$Te$_y$+InSb) alloyed thin films prepared on SiO$_2$ glass substrates by EB. In terms of infrared properties, the sensitivity of the (Bi$_x$Te$_y$+Cd) alloyed thin film as an infrared sensor was higher than that of the Bi$_x$Te$_y$ thin film.

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