Carrier Modulation in Bi$_2$Te$_3$-Based Alloys via Interfacial Doping with Atomic Layer Deposition

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Abstract: The carrier concentration in Bi$_2$Te$_3$-based alloys is a decisive factor in determining their thermoelectric performance. Herein, we propose a novel approach to modulate the carrier concentration via the encapsulation of the alloy precursor powders. Atomic layer deposition (ALD) of ZnO and SnO$_2$ was performed over the Bi$_2$Te$_{2.7}$Se$_{0.3}$ powders. After spark plasma sintering at 500 °C for 20 min, the carrier concentration in the ZnO-coated samples decreased, while the carrier concentration in the SnO$_2$-coated samples increased. This trend was more pronounced as the number of ALD cycles increased. This was attributed to the intermixing of the metal ions at the interface. Zn$^{2+}$ substituted for Bi$^{3+}$ at the interface acted as an acceptor, while Sn$^{4+}$ substituted for Bi$^{3+}$ acted as a donor. This indicates that the carrier concentration can be adjusted depending on the materials deposited with ALD. The use of fine powders changes the carrier concentration more strongly, because the quantity of material deposited increases with the effective surface area. Therefore, the proposed approach would provide opportunities to precisely optimize the carrier concentration for high thermoelectric performance.

Keywords: carrier modulation; atomic layer deposition; Bi$_2$Te$_3$

1. Introduction

Bi$_2$Te$_3$-based alloys have received a great deal of attention for thermoelectric applications operating at room temperature, because Bi$_2$Te$_3$-based alloys have superior thermoelectric performance near room temperature for both n- and p-type conduction [1–5]. It includes two typical applications such as solid-state coolers and power generation. Since the thermoelectric cooler has no moving parts, it is favorable for cooling systems requiring low noise and non-vibration [6]. Electricity can also be generated by the thermoelectric Bi$_2$Te$_3$-based alloys from areas where there is a temperature difference on each side. Human bodies can be a good energy source to scavenge the waste heat near room temperature. Therefore, much efforts have been dedicated to the development of wearable energy harvesting using the thermoelectric Bi$_2$Te$_3$-based alloys [7–10]. The thermoelectric performance of the materials is defined by the figure-of-merit, $zT = S^2\sigma T/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, and $\kappa$ is the thermal conductivity. The parameters $S$, $\sigma$, and $\kappa$ are each a function of the carrier concentration, and these parameters are strongly coupled with...
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each other. Therefore, carrier concentration is regarded as one of the critical parameters for optimizing the thermoelectric performance of a material.

The most common strategy for tuning the carrier concentration of Bi$_2$Te$_3$-based alloys is to uniformly incorporate impurity atoms with different valence states. Single elements have been commonly used as doping materials for this purpose. Some elements including Br [11], I [12], Ge [13,14] were reported as a donor, and the other elements such as Sn [15,16], Pb [17,18], Sb [19] were proposed as an acceptor in Bi$_2$Te$_3$-based alloys. However, these elements are often distributed non-uniformly in the matrix, and even partially activated as a dopant. Therefore, the carrier concentration is often not proportional to the amount of the dopants. In addition, some elements show amphoteric behavior in Bi$_2$Te$_3$-based alloys. In cases of the elements such as Ag and Cu, some groups reported Ag [20,21] and Cu [22–25] as a donor, while the others reported the p-type behavior of Ag [26] and Cu [27–29]. This amphoteric behavior results from the existence of various types of lattice defects [30], which are significantly dependent on the process conditions. Thus, this could be implicated in the large scattering for the reported carrier concentrations.

Compound dopants [31–34], such as CuBr and SbI$_3$, have also been used as doping materials. However, these halides can be partially decomposed in the synthesis process of thermoelectric Bi$_2$Te$_3$-based legs [35]. This makes it difficult to have precise control of the carrier concentration. Indeed, it was reported that the carrier concentration for Bi$_2$Te$_3$-based alloys was required to be modulated within a very narrow range of 2–6 × 10$^{19}$/cm$^3$ for optimizing the thermoelectric performance [36]. Therefore, it is imperative to develop a new doping method that can precisely control the carrier concentration in such a narrow range.

Recently, we reported that the carrier concentration of ZnO/Bi$_2$Te$_3$ heterostructures changed with the intermixing of Zn$^{2+}$ and Bi$^{3+}$ ions at the interface [37]. This suggests that the carrier concentration can be modulated by coating Bi$_2$Te$_3$-based grains with a thin hetero-material layer. In this study, we demonstrate carrier modulation in Bi$_2$Te$_3$-based alloys via interfacial doping with atomic layer deposition (ALD). We further demonstrate that the carrier concentration of the alloy can be increased or decreased, depending on the valence states of the metal ions in the ALD-grown-material.

2. Materials and Methods

Bi$_2$Te$_{2.7}$Se$_{0.3}$ was prepared by melting the constituent materials in a rocking furnace at 800 °C for 6 h and subsequent quenching. The Bi$_2$Te$_{2.7}$Se$_{0.3}$ chunks were ball-milled with zirconia balls for 24 h under an Ar atmosphere, to produce a fine powder. ZnO and SnO$_2$ thin films were grown over the Bi$_2$Te$_{2.7}$Se$_{0.3}$ powders by ALD in a home-built vibrated chamber. Diethylzinc (DEZ) and Tetrakis(dimethylamino)tin (TDMASn) were used as the Zn and Sn sources, respectively. H$_2$O was employed as the oxygen source for the growth of ZnO and SnO$_2$. The film growth was performed at room temperature for ZnO and 65 °C for SnO$_2$, respectively. An ALD cycle consists of metal precursor injection-purge-H$_2$O injection-purge. The amount of the ALD-grown film was controlled by changing the number of ALD cycles. The detailed conditions for the ALD process are reported elsewhere [38,39]. The metal-oxide-coated Bi$_2$Te$_{2.7}$Se$_{0.3}$ powders were sintered by spark plasma sintering (SPS) (Elteck Korea Co., Anyang, Korea) at 500 °C for 20 min, under an applied pressure of 40 MPa.

The microstructure of the SPS Bi$_2$Te$_{2.7}$Se$_{0.3}$ material was examined with scanning transmission electron microscopy (STEM) (FEI, Hillsboro, Ore., USA). X-ray photoelectron spectroscopy (XPS) (ULVAC-PHI, Chigasaki, Japan) was employed to examine the chemical states of the coated materials. The Seebeck coefficient was measured using a standard four-probe method at room temperature. The carrier concentration and mobility were measured by the Hall measurement, using van der Pauw geometry.

3. Results and Discussion

Figure 1a illustrates the strategy used to modulate the carrier concentration via interfacial doping. For the interfacial doping, a very thin oxide layer was grown over n-type Bi$_2$Te$_{2.7}$Se$_{0.3}$ powders. ALD,
which is based on a self-limiting mechanism, was employed for the conformal growth of the metal oxide on the powders. The metal ions in the ALD-grown layer could intermix with the Bi$_2$Te$_3$-based alloys near the interface during the SPS process, and these metal ions were substituted for the Bi$^{3+}$ ions near the interface. In order to optimize the carrier concentration, the ALD-grown oxide layer should be able to act as either a donor or an acceptor for the Bi$_2$Te$_3$-based alloys. Hence, the selection of a proper growth material is a critical factor in modulating the carrier concentration. Here, we selected ZnO and SnO$_2$ as the materials used to decrease and increase the carrier concentration, respectively. The cations in both materials had valence states different from the Bi$^{3+}$ ions in the Bi$_2$Te$_3$-based alloys. It was expected that the ALD of ZnO and SnO$_2$ would decrease or increase the electron concentration in the n-type Bi$_2$Te$_{2.7}$Se$_{0.3}$, by the substitution of Bi$^{3+}$ with Zn$^{2+}$ or Sn$^{4+}$, respectively.

After undergoing the SPS process, the microstructure of the ALD-coated Bi$_2$Te$_{2.7}$Se$_{0.3}$ was observed. Figure 1b shows a high-angle annular dark-field (HAADF) STEM image of the SPS pellet of ZnO-coated Bi$_2$Te$_{2.7}$Se$_{0.3}$. The Zn element map corresponding to the area observed in Figure 1b is presented in Figure 1c. These TEM results reveal that the Bi$_2$Te$_{2.7}$Se$_{0.3}$ grains were encapsulated by a very thin ZnO layer, even after SPS at a temperature of 500 °C. The heterogeneous interfaces were well-developed through the ALD technique. The appearance of the heterogeneous interfaces was attributed to the low solubility of the oxides in Bi$_2$Te$_{2.7}$Se$_{0.3}$ and the large differences in the melting points between the oxides (ZnO: 1975 °C and SnO$_2$: 1630 °C) and Bi$_2$Te$_{2.7}$Te$_{0.3}$ (approximately 606 °C). These heterogeneous interfaces were also observed in the SPS pellets of p-type Bi$_{0.4}$Sb$_{1.6}$Te$_3$ with an ALD-grown ZnO layer [38]. This suggests that a strategy based on this ALD technique is generally effective on Bi$_2$Te$_3$-based alloys, irrespective of the conduction type. The size of the Bi$_2$Te$_{2.7}$Se$_{0.3}$ grains was found to be small, generally below 1 µm. Given that the grains of Bi$_2$Te$_3$-based alloys generally grow to a larger size after SPS at high temperatures, such as 500 °C [40], this suggests that the ALD of a thin oxide layer effectively suppressed the grain growth during the sintering process. Indeed,
it has been previously reported that an extremely low $k$ value was obtained in the ALD-ZnO-coated Bi$_{0.4}$Sb$_{1.6}$Te$_3$, due to the formation of fine grains [38].

Figure 2a,b show the XPS spectra of (a) Zn 2p and (b) Sn 3d core levels in the SPS pellets of ZnO-coated and SnO$_2$-coated Bi$_2$Te$_{2.7}$Se$_{0.3}$, respectively. A single Zn 2p$_{3/2}$ peak was observed at 1021.5 eV, corresponding to the Zn$^{2+}$ valence state. The Sn 3d XPS spectra showed a single peak positioned at 486.5 eV, which corresponded to Sn$^{4+}$. No peaks corresponding to the other valence states were observed in either spectra. This means that the cations in the oxide layers preserved their own valence states, even after the high-temperature sintering process. This also suggests the possibility for these cations to act as an acceptor or a donor if the cations were substituted for Bi ions at the heterointerfaces.

![Figure 2](image.png)

**Figure 2.** XPS spectra of (a) Zn 2p and (b) Sn 3d core levels in the ZnO-coated and SnO$_2$-coated Bi$_2$Te$_{2.7}$Se$_{0.3}$, respectively.

The electrical properties of the SPS ALD-coated Bi$_2$Te$_{2.7}$Se$_{0.3}$ pellets were quantified, to verify the doping effects of the coating materials. Figure 3a shows the variation in the electron concentration of the ZnO- and SnO$_2$-coated Bi$_2$Te$_{2.7}$Se$_{0.3}$ pellets as a function of the number of ALD cycles. Interestingly, the two oxides, which are n-type semiconductors, exhibited opposite effects on the electrical properties of Bi$_2$Te$_{2.7}$Se$_{0.3}$. As the number of ALD cycles increased, the electron concentration in the ZnO-coated Bi$_2$Te$_{2.7}$Se$_{0.3}$ decreased, while the electron concentration in the SnO$_2$-coated Bi$_2$Te$_{2.7}$Se$_{0.3}$ increased. This indicates that the ALD-grown ZnO and SnO$_2$ layers could act as an acceptor and a donor, respectively, in Bi$_2$Te$_{2.7}$Se$_{0.3}$ through substitution for the Bi ions, which is consistent with the expectation proposed in Figure 1a. It was also found that the change in the electron concentration per ALD cycle was larger for the ZnO-coated Bi$_2$Te$_{2.7}$Se$_{0.3}$ than for the SnO$_2$-coated Bi$_2$Te$_{2.7}$Se$_{0.3}$. The difference resulted from the difference in the growth-per-cycle of the ALD processes of ZnO and SnO$_2$. Figure 4 shows the variation in the film thickness of ZnO and SnO$_2$ grown on Si substrate, as a function of the number of ALD cycles. The growth per ALD cycle of the materials is estimated from the linear fit of the graph. The growth per cycle of ZnO is 0.65 nm/cycle and the growth per ALD cycle of SnO$_2$ is 0.23 nm/cycle.

![Figure 3](image.png)

**Figure 3.** Variations in the (a) electron concentration; (b) Seebeck coefficient; (c) $zT$ of the ALD-coated Bi$_2$Te$_{2.7}$Se$_{0.3}$ as a function of the number of ALD cycles.
That is the reason why the electron concentration in Figure 3a changed with the number of ALD cycles. The zT value of uncoated Bi$_2$Te$_2.7$Se$_0.3$ pellets in terms of the powder size (Figure 5a). Despite the powders having the same composition value of the SPS pellets was also influenced by the ZnO and SnO$_2$ ALD coatings, as shown in Figure 3c. The zT value of uncoated Bi$_2$Te$_2.7$Se$_0.3$ was approximately 0.5. The zT value increased to 0.7 after the ALD of ZnO, because the electron concentration was moderated by the ALD coating. On the other hand, the ALD of SnO$_2$ further increased the electron concentration, resulting in the deterioration of the zT value down to 0.45. Therefore, coating Bi$_2$Te$_2.7$Se$_0.3$ with a very thin oxide layer through ALD could be a promising way to enhance the thermoelectric properties via carrier modulation.

The carrier modulation was closely related to the amount of oxide grown over the particles. That is the reason why the electron concentration in Figure 3a changed with the number of ALD cycles. In addition to cycle variation, the quantity of the grown oxide could change with the effective surface area of the Bi$_2$Te$_2.7$Se$_0.3$ powders. This suggests that the size of the powders was another factor that affected the carrier modulation. First, we examined the electrical properties of the uncoated Bi$_2$Te$_2.7$Se$_0.3$ pellets in terms of the powder size (Figure 5a). Despite the powders having the same composition and identical SPS conditions, the electron concentration decreased and the S value increased as the size of the powder increased. The increase in the electron concentration as the powders became finer was due to the increase in number of grain boundaries. A previous study has reported that grain boundaries in Bi$_2$Te$_3$ acted as an electron source [41].
For comparison, we examined the electrical properties of ZnO-coated Bi$_2$Te$_{2.7}$Se$_{0.3}$ with two different powder sizes of $<53$ µm and 75–180 µm. We chose ZnO as the ALD-grown material, because the ALD of ZnO improved the thermoelectric performance of n-type Bi$_2$Te$_{2.7}$Se$_{0.3}$, as previously shown in Figure 3c. Figure 5b shows the variation in the electron concentration of the ZnO-coated Bi$_2$Te$_{2.7}$Se$_{0.3}$, with different powder sizes, as a function of the number of ZnO ALD cycles. Although the electron concentration decreased with increasing the number of ZnO ALD cycles for both powder sizes, the electron concentration in the SPS pellet made from a powder with particle sizes of $<53$ µm decreased more abruptly than the electron concentration in the SPS pellet made from powder with particle sizes of 75–180 µm. The S values increased as the number of ZnO ALD cycles increased as well, due to the decrease in the electron concentration, as shown in Figure 5c. This indicates that the carrier concentration can be exquisitely tuned by the controlling in number of ALD cycles and the powder size.

4. Conclusions

We proposed a novel strategy to modulate the carrier concentration in Bi$_2$Te$_3$-based thermoelectric alloys via an ALD technique. The ALD of oxide layers grown over Bi$_2$Te$_{2.7}$Se$_{0.3}$ powders changed the carrier concentration by doping through intermixing metal ions at the interfaces. The electron concentration was found to be modulated depending on the valence state of the cations in the oxide layer; e.g., the ALD of ZnO with Zn$^{2+}$ decreased the electron concentration while the ALD of SnO$_2$ with Sn$^{4+}$ increased the electron concentration. Consequently, the carrier concentration can be precisely controlled, even in a very narrow range of $2\times10^{19}$/$\text{cm}^3$ for the optimized performance. It was also shown that the carrier concentration could also vary with powder size. This ALD-based approach provides the ability to optimize the thermoelectric performance of Bi$_2$Te$_3$-based alloys via explicit modulation of the carrier concentration.

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