Electrodeposition of Ni on Bi₂Te₃ and Interfacial Reaction Between Sn and Ni-Coated Bi₂Te₃

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Bismuth-telluride (Bi₂Te₃)-based compounds are common thermoelectric materials used for low-temperature applications, and nickel (Ni) is usually deposited on the Bi₂Te₃ substrates as a diffusion barrier. Deposition of Ni on the *p*-type (Sb-doped) and *n*-type (Se-doped) Bi₂Te₃ substrates using electroplating and interfacial reactions between Sn and Ni-coated Bi₂Te₃ substrates are investigated. Electrodeposition of Ni on different Bi₂Te₃ substrates is characterized based on cyclic voltammetry and Tafel measurements. Microstructural characterizations of the Ni deposition and the Sn/Ni/Bi₂Te₃ interfacial reactions are performed using scanning electron microscopy. A faster growth rate is observed for the Ni deposition on the *n*-type Bi₂Te₃ substrate which is attributed to a lower activation energy of reduction due to a higher density of free electrons in the *n*-type Bi₂Te₃ material. The common Ni₃Sn₄ phase is formed at the Sn/Ni interfaces on both the *p*-type and *n*-type Bi₂Te₃ substrates, while the NiTe phase is formed at a faster rate at the interface between Ni and *n*-type Bi₂Te₃ substrates.

Key words: Electroplating, Ni, thermoelectric, intermetallic compound

INTRODUCTION

Thermoelectric (TE) materials receive considerable attention in recent decades due to their unique renewable characteristics that can convert waste heat to useable electricity.^{1–3} The TE materials can be classified into several groups depending upon the application temperature. Bismuth-telluride (Bi₂Te₃)-based compounds belong to the group of low-temperature TE materials because of their application temperature around 200°C.^{4–6} To offer the TE power, the *p*-type (Sb-doped) and *n*-type (Se-doped) Bi₂Te₃ elements need to assemble in pairs between two ceramic substrates to form a module. One of the key processes in the module assembly is joining of Bi₂Te₃ elements and metallizations on the ceramic substrates using solders. The soldering reactions at the solder/Bi₂Te₃ joints play an

important role in the reliability performance of a TE module.

Many previous reports have pointed out that direct contact of Bi₂Te₃ and Sn-based solder results in the formation of the SnTe phase.^{7–11} The brittle SnTe phase shows a fast growth rate,¹² so a thick SnTe phase can easily form at the solder/Bi₂Te₃ joints which degrades the solder joints mechanically. To suppress the SnTe formation, a Ni diffusion barrier is usually deposited on the Bi₂Te₃ elements prior to soldering.^{13,14} Therefore, the study of interest becomes the reaction between solder and Ni.^{12,15,16} The electroplating technique is commonly used to form a Ni layer on different substrates as the diffusion barrier.^{17,18} In this study, electrodeposition of Ni on the *p*-type and *n*-type Bi₂Te₃ elements was investigated, including electrochemical analysis of the Ni deposition, microstructural characterizations of the Ni plated layer, and growth rate of the Ni-plated layer. The intermetallic compound formation and growth at

the Sn/Ni joints on the *p*-type and *n*-type Bi₂Te₃ elements were also investigated.

EXPERIMENTAL PROCEDURES

Two types of Bi₂Te₃ TE materials were prepared using a typical zone-melting method,¹⁹ and one was the *p*-type Bi₂Te₃ doped with Sb and the other was the *n*-type Bi₂Te₃ doped with Se. The as-prepared Bi₂Te₃ ingot was sliced into several discs, encapsulated with tape, and cut into cuboids ($0.2 \times 0.2 \times 0.5 \text{ cm}^3$), as shown in Fig. 1. Encapsulation of tape is to protect brittle Bi₂Te₃ materials from fracture due to mechanical cutting. The surface of the Bi₂Te₃ cuboids was roughened by grinding using SiC powders to improve adhesion between Bi₂Te₃ and Ni. A Ni layer was then deposited on the roughened surface of the Bi₂Te₃ cuboid using electroplating which was performed at 50°C with an operation voltage of 2 V. It should be noted that the Bi₂Te₃ ingot made by zone-melting technique possesses a highly anisotropic structure with crystal planes (atomic layers) stacking layer by layer and parallel to the growth direction.^{20,21} The roughened surface for Ni electrodeposition is either parallel to or perpendicular to the atomic layer, as shown in Fig. 1. After Ni electrodeposition, Sn shots (Alfa Aesar, 99.8%, MA, USA) were placed on the Ni-coated Bi₂Te₃ cuboid and put into a tube furnace filled with nitrogen. To remove the native oxide layer on the reactant surface for better wetting of the molten Sn on the Ni surface, the Ni surface was covered by a thin flux layer (Magna 51 flux) prior to the Sn placement. The joining reaction between Sn and the Ni-coated Bi₂Te₃ cuboid was performed at 250°C for 1 min during which the molten Sn shots joined the Ni-coated Bi₂Te₃ cuboid through a liquid/solid reaction. After joining, the Sn/Ni/Bi₂Te₃ samples were put into an oven at 200°C for various lengths of time to perform the solid/solid reaction.

Phase identification of as-prepared Bi₂Te₃ materials was carried out using x-ray diffraction (XRD, MAC MXTIII, Japan). A typical metallographical methodology was used to examine the reaction behavior of the Sn/Ni/Bi₂Te₃ samples. Firstly, the Sn/Ni/Bi₂Te₃ samples were mounted in epoxy resin. Then, the cross-sections of the Sn/Ni/Bi₂Te₃ interface were exposed by sequentially grinding and polishing using SiC sandpapers and Al₂O₃ suspensions, respectively. Field-emission scanning electron microscopy (FESEM, JSM-6700F, JEOL, Japan) was used to observe the microstructures of the Sn/Ni/Bi₂Te₃ interface. X-ray energy dispersive spectroscopy (EDS) and an electron probe x-ray microanalyzer (EPMA) were used to determine the elemental compositions of the reaction products formed at the Sn/Ni/Bi₂Te₃ interface. The cross-sectional area and interfacial linear length of the reaction product were calculated using image software, and the average thickness of the reaction product was determined by dividing the cross-

sectional area by the interfacial linear length. The cyclic voltammetry (CV) analysis was performed to characterize the Ni deposition using a potentiostat (PGSTAT30, Auto-Lab) with a three-electrode cell. Tafel measurement was carried out using a three-electrode system, using a Ni piece as the counter electrode, SiC-polished Bi₂Te₃ with a mask as the working electrode, and Ag/AgCl as the reference electrode. The scanning rate was 10 mVs^{-1} from 0.4 V to -1 V at a temperature of 50°C. All faces of the tested Bi₂Te₃ cuboid were masked by a sticker except the target face. A window with a size of $2 \times 1.5 \text{ mm}$ was opened on the target face.

RESULTS AND DISCUSSION

Phase Identification of Bi₂Te₃ Made by Zone Melting

It is known that the zone-melting method produces a Bi₂Te₃ ingot with a highly anisotropic structure due to directional crystal growth along the pulling direction.^{21,22} Quintuple building blocks, each consisting of five monoatomic sheets of Te⁽¹⁾-Bi-Te⁽²⁾-Bi-Te⁽¹⁾, join to each other by weak van der Waals forces. So, cleavage occurs easily along the van der Waals gap between two neighboring quintuple building blocks when the Bi₂Te₃ crystal was subjected to mechanical exfoliation.²³ As shown in Fig. 1, the right-hand side SEM image shows the van der Waals gaps on the roughened surface. This surface is the reaction face for Ni electrodeposition and Sn joining, which is designated as the “perpendicular” interface due to the perpendicular relationship between the crystal planes and reaction face. In contrast, the left-hand side SEM image shows a flat surface with three crystal planes being partly exfoliated. This reaction face is designated as “parallel” because it has a parallel relationship with the crystal plane direction.

Figure 2a and b show the XRD patterns of as-prepared *p*-type and *n*-type Bi₂Te₃ cuboids, respectively. The detection regions include the perpendicular (perp) and parallel (para) sides for both *p*-type and *n*-type Bi₂Te₃ cuboids. Basically, the characteristic peaks correspond to the crystallographic planes of *p*-type (JCPDS 49-1713) and *n*-type Bi₂Te₃ samples (JCPDS 50-0954), confirming that the as-prepared ingots by zone melting are indeed the Bi₂Te₃ phase. However, the characteristic peaks are different for the “para” and “perp” sides of the same Bi₂Te₃ samples. The texture coefficients (TC) of all crystallographic planes can be calculated using the following Eq. 1²⁴:

$$TC_{(hkl)} = \frac{I_{(hkl)}/I_{0(hkl)}}{\frac{1}{N} \sum I_{(hkl)}/I_{0(hkl)}} \quad (1)$$

where I and I_0 are measured and standard intensity, respectively, of the characteristic peaks. N is the number of crystallographic planes of interest. In general, the crystal has a preferred orientation

Fig. 1. Flowchart of sample preparation of Bi_2Te_3 cuboids and Sn/Ni/ Bi_2Te_3 reaction couples.

when the $\text{TC}_{(hkl)}$ value of the crystallographic plane is larger than 1. In Fig. 2, the preferred orientations are identified as (0 0 15), (1 1 0), (0 0 9), and (1 1 0) for $p\text{-Bi}_2\text{Te}_3$ (para), $p\text{-Bi}_2\text{Te}_3$ (perp), $n\text{-Bi}_2\text{Te}_3$ (para), and $n\text{-Bi}_2\text{Te}_3$ (perp), respectively, and their corresponding $\text{TC}_{(hkl)}$ values are 2.14, 1.02, 1.42, and 2.84, respectively. It is found that the preferred crystal plane on the parallel sides of the $p\text{-Bi}_2\text{Te}_3$ and $n\text{-Bi}_2\text{Te}_3$ is (0 0 15). The (0 0 15) basal plane is perpendicular to the c -axis, and its relatively stronger intensity indicates that the as-received TE substrates possess a classical layered structure as shown in Fig. 1. In contrast, the preferred crystal plane on the perpendicular sides of the $p\text{-Bi}_2\text{Te}_3$ and $n\text{-Bi}_2\text{Te}_3$ becomes (1 1 0), which is parallel to the c -axis of the crystal. The above-mentioned results concerning the preferential crystal planes were also observed in the TE samples prepared by mechanical alloying and plasma-activated sintering.²⁵ A preferentially orientated microstructure with the (1 1 0) plane was formed along the pressing direction during plasma sintering; however, the basal planes of (0 0 l), including (0 0 6), (0 0 15), and (0 0 18), became preferentially orientated on the sections perpendicular to the pressing direction.²⁵ Besides, the compositions of the p -type and n -type Bi_2Te_3 materials are also determined using EPMA and they are 13.1 at.% Bi-58.4 at.% Te-28.5 at.% Sb and 48.3 at.% Bi-45.8 at.% Te-5.9 at.% Se, respectively, which are approximately represented as $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ and $\text{Bi}_2\text{Se}_{0.3}\text{Te}_{2.7}$.

Fig. 2. XRD patterns of as-prepared (a) p -type and (b) n -type Bi_2Te_3 cuboids.

Fig. 3. SEM micrographs of surface morphologies of (a) p -type Bi_2Te_3 (para) substrate before Ni electrodeposition, (b) p -type Bi_2Te_3 (para) substrate after Ni electrodeposition, (c) n -type Bi_2Te_3 (para) substrate before Ni electrodeposition, and (d) n -type Bi_2Te_3 (para) substrate after Ni electrodeposition.

Microstructural Characterization and Deposition Rate of Ni

Surface roughening of the Bi_2Te_3 substrates is a strategy commonly used to improve adhesion between an electroplated Ni layer and Bi_2Te_3 substrate. As shown in Fig. 3a and c, the surface morphologies of the $p\text{-Bi}_2\text{Te}_3$ (para) and $n\text{-Bi}_2\text{Te}_3$ (para) substrates become very rugged after SiC grinding. After electrodeposition of Ni, the Bi_2Te_3 surfaces are covered by a uniform Ni layer with a fine-grained microstructure, as shown in Fig. 3b and d. Similar results are also observed for the electrodeposition of Ni on the $p\text{-Bi}_2\text{Te}_3$ (perp) and $n\text{-Bi}_2\text{Te}_3$ (perp) substrates. The results are not shown here due to high similarity to Fig. 3. The interfacial adhesion between the electroplated Ni layer and Bi_2Te_3 substrate looks good, as shown in Fig. 4. The electroplating time for deposition of Ni is 60 min. Basically, the electroplated Ni layers adhere closely to the Bi_2Te_3 substrates, meaning that roughening pretreatment is helpful for interfacial adhesion. Noteworthy is the thickness of Ni; the Ni layers on the $p\text{-Bi}_2\text{Te}_3$ substrates have a thickness of 12–14 μm , while the Ni layers on the $n\text{-Bi}_2\text{Te}_3$ substrates grow to a much greater thickness of 20–21 μm . Similar results are also observed for the other reaction times, as shown in Fig. 5, which depicts the relationship between the thickness of Ni and reaction time. Overall, the direction of the crystallographic plane (perp versus para) has a negligible

effect on the deposition rate of Ni, while the TE type (p -type versus n -type) shows a significant effect.

The electrical and electrochemical analyses were performed to gain insight into the substrate effect (p -type versus n -type) on the Ni deposition. As shown in Fig. 6a, the output current for the Ni deposition with increasing plating time was recorded with the plating voltage being fixed at 2 V. The output current is larger for the Ni deposition on the n -type Bi_2Te_3 substrate than on the p -type Bi_2Te_3 substrate. This implies that a higher concentration of Ni^{2+} ions from the plating solution can be reduced for the growth of the Ni layer, and, therefore, increases the deposition rate of Ni. The reduction behavior of the Ni^{2+} ions can be characterized by CV measurement.²⁶ Figure 6b shows the CV response of the deposition of Ni on the two substrates. The on-set voltage of the reduction reaction is similar for the p -type and n -type Bi_2Te_3 substrates, indicating similar charge transfer resistance on the two Bi_2Te_3 surfaces. However, the n -type Bi_2Te_3 substrate exhibits a higher current response at the reduction peak, showing that a higher concentration of electrons on the n -type Bi_2Te_3 surface contributes to the reduction reaction and, therefore, enhances the deposition rate of Ni.

Figure 7 shows the Tafel plots of Ni electrodeposition on both p -type and n -type Bi_2Te_3 substrates with the deposited surfaces parallel to and perpendicular to the crystal plane direction. Table I summarizes the equilibrium potentials and exchange

Fig. 4. Cross-sectional SEM micrographs of electroplated Ni layers on (a) *p*-type Bi₂Te₃ (perp), (b) *p*-type Bi₂Te₃ (para), (c) *n*-type Bi₂Te₃ (perp), and (d) *n*-type Bi₂Te₃ (para).

Fig. 5. Relationship between thickness of Ni electroplated on *p*-type and *n*-type Bi₂Te₃ substrates and reaction time.

currents obtained from Fig. 7. Both curves obtained from *n*-type Bi₂Te₃ give more positive equilibrium potentials than those obtained from *p*-type Bi₂Te₃. The reduction rate of the redox reaction is considered in the electrodeposition of Ni.²⁷ The more positive equilibrium potential implies there is a larger cathodic region with a higher cathodic rate and lower activation energy for reduction. Hence, the Tafel plots prove that electrodeposition of Ni occurs more readily on the *n*-type Bi₂Te₃ substrate. This can be explained by the difference in electron density between *n*-type and *p*-type Bi₂Te₃. The

Fig. 6. (a) Variation of output current for Ni electrodeposition with increasing plating time (The plating voltage was fixed at 2 V.). (b) Cyclic voltammetry (CV) response of Ni electrodeposition on *p*-type and *n*-type Bi₂Te₃ substrates.

Fig. 7. Tafel plots of Ni electrodeposition on *p*-type and *n*-type Bi_2Te_3 substrates along parallel and perpendicular directions. The resistance data²⁷ are also shown at the bottom of the plot for comparison.

Table I. Equilibrium potentials and exchange currents of Ni electrodeposition on *p*-type and *n*-type Bi_2Te_3 substrates along parallel and perpendicular directions

Substrate	E_{eq} (V)	I_0 (μA)
<i>p</i> - Bi_2Te_3 (perp)	-0.171	10.47
<i>p</i> - Bi_2Te_3 (para)	-0.235	10.23
<i>n</i> - Bi_2Te_3 (perp)	-0.043	10.62
<i>n</i> - Bi_2Te_3 (para)	-0.096	10.26

major charge carrier in *p*-type Bi_2Te_3 is the electron hole which inevitably consumes electrons due to charge recombination and builds up a higher energy barrier for cathodic electrodeposition. In contrast, the major charge carrier in *n*-type Bi_2Te_3 is the electron, so it has a higher electron density which makes the Ni ions easily reduced on the surface. Besides, the trend of the ease of electrodeposition of Ni on different Bi_2Te_3 substrates can be arranged in the descending order as follows: *n*-type (perp) > *n*-type (para) > *p*-type (perp) > *p*-type (para). This trend is consistent with the results from the resistance data²⁸ shown in Fig. 7. The above-mentioned trend also implies that the Ni electrodeposition occurs more easily on the perpendicular face than on the parallel face for both *n*-type and *p*-type substrates. However, the effect of crystal plane direction (perp versus para) on the Ni deposition is insignificant (Fig. 5). The root cause is still unclear and needs further investigation.

Interfacial Reactions at the Sn/Ni/ Bi_2Te_3 Interface

Figure 8 shows the cross-sectional SEM micrographs of the Sn/Ni/ Bi_2Te_3 interfaces after thermal aging at 200°C for 360 h. An intermetallic compound is found at the Sn/Ni interface on the four Bi_2Te_3 substrates. Its composition is determined to be 43.2 at.% Ni-56.8 at.% Sn based on the EDX analysis and is identified as the Ni_3Sn_4 phase. The phase formation of Ni_3Sn_4 is consistent with previous studies regarding the Sn/Ni interfacial

Fig. 8. Cross-sectional SEM micrographs of Sn/Ni/ Bi_2Te_3 interfaces after thermal aging at 200°C for 360 h. The inset micrographs show the Sn/Ni/ Bi_2Te_3 interfaces before thermal aging (as-joined). (a) *p*-type Bi_2Te_3 (perp), (b) *p*-type Bi_2Te_3 (para), (c) *n*-type Bi_2Te_3 (perp), and (d) *n*-type Bi_2Te_3 (para).

Fig. 9. Thickness variation of Ni₃Sn₄ on *p*-type and *n*-type Bi₂Te₃ substrates with increasing reaction time.

reactions.^{29,30} Figure 9 shows the thickness of the Ni₃Sn₄ phase on the four Bi₂Te₃ substrates for all reaction times. The thickness data shown in Fig. 9 are the averages determined by dividing the cross-sectional area of the Ni₃Sn₄ phase layer by the linear Sn/Ni interfacial length. It is found that the thickness data are approximately similar for the Ni₃Sn₄ phase formed on the four Bi₂Te₃ substrates, meaning that the type and crystal plane direction of the Bi₂Te₃ substrate has an insignificant effect on the growth rate of the Ni₃Sn₄ phase. Besides, the growth behavior of the Ni₃Sn₄ phase shows a parabolic trend which corresponds to the diffusion-controlled growth. In addition, the NiTe phase formed at the Ni/*n*-Bi₂Te₃ interface shows a greater thickness, as shown in Fig. 8. This can be explained by the diffusion behavior of Ni in different Bi₂Te₃ substrates. Lan et al.³¹ investigated the effect of Ni diffusion barrier at the solder/Bi₂Te₃ interface. They found that the Ni diffusion barrier effectively suppressed the diffusion of Sn from solder to Bi₂Te₃, whereas Ni diffused into Bi₂Te₃. The diffusion length of Ni into the *n*-type Bi₂Te₃ substrate reached 3.5 μm which was much longer than that (120 nm) into the *p*-type Bi₂Te₃ substrate.³¹ Based on Fick's law, the diffusion coefficients of Ni in the *n*-type and *p*-type Bi₂Te₃ substrates was calculated to be $3.1 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ and $1.8 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$, respectively.³¹ Therefore, a thicker NiTe phase was formed at the Ni/*n*-Bi₂Te₃ interface due to faster diffusion of Ni in the *n*-type Bi₂Te₃ substrate.

CONCLUSIONS

Electrodeposition of Ni on the *p*-type and *n*-type Bi₂Te₃ substrates with the crystal plane direction perpendicular to or parallel to the deposition face was investigated. Thickness measurement of the Ni layer based on cross-sectional SEM observation shows that the deposition rate of Ni on the *n*-type Bi₂Te₃ substrates is faster than on the *p*-type Bi₂Te₃ substrate, but is independent on the crystal plane direction. CV and Tafel analyses indicate that the

n-type Bi₂Te₃ material shows a lower activation energy for reduction due to a higher density of free electrons. Only the Ni₃Sn₄ phase was formed at the interfaces between Sn and Ni-coated Bi₂Te₃ substrates no matter the Bi₂Te₃ type and crystal plane direction. The growth rate of the Ni₃Sn₄ phase is also independent on the Bi₂Te₃ type and crystal plane direction. However, the NiTe phase was formed at the Ni/*n*-Bi₂Te₃ interface as a result of the faster diffusion of Ni in the *n*-type Bi₂Te₃ substrate.

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