

Communication

Strong Anisotropic Effects of p -Type Bi_2Te_3 Element on the $\text{Bi}_2\text{Te}_3/\text{Sn}$ Interfacial Reactions

SHAN YE, JEN-DONG HWANG,
and CHIH-MING CHEN

The p -type Bi_2Te_3 thermoelectric materials made by zone-melting method exhibit high anisotropy in the mechanical/thermoelectric properties due to unidirectional crystal growth. This unidirectional crystal structure also has a strong effect on the $\text{Sn}/p\text{-Bi}_2\text{Te}_3$ interfacial reactions. Stripe-like Sn_3Sb_2 phase precipitated in the SnTe phase in a direction approximately perpendicular or parallel to the $\text{Sn}/p\text{-Bi}_2\text{Te}_3$ interface depending upon the $p\text{-Bi}_2\text{Te}_3$ crystal orientation. Such anisotropic growth behavior of the Sn_3Sb_2 phase significantly affected the SnTe phase growth.

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Thermoelectric (TE) materials have attracted much attention for a long period of time due to their unique Seebeck (or Peltier) effect. Commercial TE modules have been successfully used as a cooler for mobile or microprocessor applications.^[1] Besides, TE modules can be potentially used as a power generator in factory by converting waste heat to electricity. Bismuth telluride (Bi_2Te_3)-based compounds are well-known TE materials for low-temperature applications below 473 K (200 °C).^[2] They can be produced using different methods such as zone melting,^[3] mechanical alloying,^[4] and spark plasma sintering.^[5] Among these growth methods, zone melting is widely used because it can produce the TE ingots with the most excellent performance along the crystal growth (pulling) direction.^[3] This can be attributed to the fact that the growth of the atomic layers in the solidified Bi_2Te_3 hexagonal cells preferentially aligned in a direction parallel to the pulling direction. In other words, the c -axis of the Bi_2Te_3 hexagonal cell is approximately perpendicular to the crystal pulling direction.

Solder joint, which is formed by joining the TE elements to the Ni/Au-plated ceramic plate using solder, also plays an important role in the module performance.

Many efforts have been devoted to the investigation of the interfacial reactions between TE materials and selected solders to provide useful information for the reliability evaluation of the solder joints.^[6–11] However, the TE materials used for investigation were either fabricated by simple casting or simplified as a single Te element, and no reports emphasized on the Bi_2Te_3 compounds made by zone melting. In this study, the interfacial reactions between the Bi_2Te_3 compounds made by zone melting and pure Sn were investigated. A surprising phenomenon was found that the direction of the atomic layers in the Bi_2Te_3 elements had a strong anisotropic effect on the growth behavior of the SnTe intermetallic compound formed at the $\text{Sn}/\text{Bi}_2\text{Te}_3$ interface. It has been shown that the Bi_2Te_3 compounds exhibit strong anisotropic characteristics in the mechanical,^[12] electrical,^[13] and thermal^[14] properties due to its directional crystal structure. However, to the best of our knowledge, the anisotropic effect originated from the Bi_2Te_3 element on the SnTe growth was observed for the first time.

The TE cylindrical ingots, p -type $(\text{Bi,Sb})_2\text{Te}_3$ and n -type $\text{Bi}_2(\text{Te,Se})_3$, were prepared using zone melting growth method. Their compositions were determined to be $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ and $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ (in at pct), respectively, for p -type $(\text{Bi,Sb})_2\text{Te}_3$ and n -type $\text{Bi}_2(\text{Te,Se})_3$ using electron probe micro-analyzer (EPMA) (JXA-8200, JEOL, Japan). As seen in Figure 1, the TE disk cut from a cylindrical ingot had a c -axis perpendicular to its longitudinal direction (atomic layer), namely, the pulling direction during zone melting growth. To prepare the TE element, the TE disk was cut into lots of cubes. It had been reported that cleavage occurred preferentially along the weak van der Waals gaps between two outer $\text{Te}^{(1)}$ atomic layers of two neighboring quintuple building blocks-five monoatomic sheets of $\text{Te}^{(1)}\text{-Bi-Te}^{(2)}\text{-Bi-Te}^{(1)}$ when the TE crystal was mechanically exfoliated.^[12] The cleavage planes could also be observed in the TE cube subjected to stronger cutting force as seen in Figure 1, and their direction was parallel to the atomic layers. This was an indication that we could easily divide the TE cubes into two groups according to their joining interface to the Sn solder. In the first group, the pure Sn was joined to the TE cubes where the joining interface was perpendicular to the atomic layers of the TE materials, which was named as “zm-perpendicular” hereafter. In the second group named as “zm-parallel” hereafter, Sn was joined to the TE cubes where the joining interface was parallel to the atomic layers of the TE materials. The joining was performed by placing the samples in a furnace (CDV-453, Smartlab, Taiwan) filled with nitrogen at 523 K (250 °C) for 1 minute. Then, the samples were heat-treated at 423 K (150 °C) for up to 240 hours.

The third group of TE elements was prepared using typical casting method. Proper amounts of elements of p -type $(\text{Bi,Sb})_2\text{Te}_3$ and n -type $\text{Bi}_2(\text{Te,Se})_3$ were weighed and encapsulated in a vacuum quartz tube. The quartz tube was placed in a furnace (F21100, Thermolyne, USA) at 1073 K (800 °C) and the elements were melted and mixed together. Heat treatment was performed at 773 K (500 °C) for 1 week to enhance compositional

SHAN YE, Graduate Student, and CHIH-MING CHEN, Professor, are with the Department of Chemical Engineering, National Chung Hsing University, Taichung 402, Taiwan ROC. Contact e-mail: chenm@nchu.edu.tw JEN-DONG HWANG, Manager, is with the Material & Chemical Research Laboratory, Industrial Technology Research Institute, Hsinchu 31015, Taiwan ROC.

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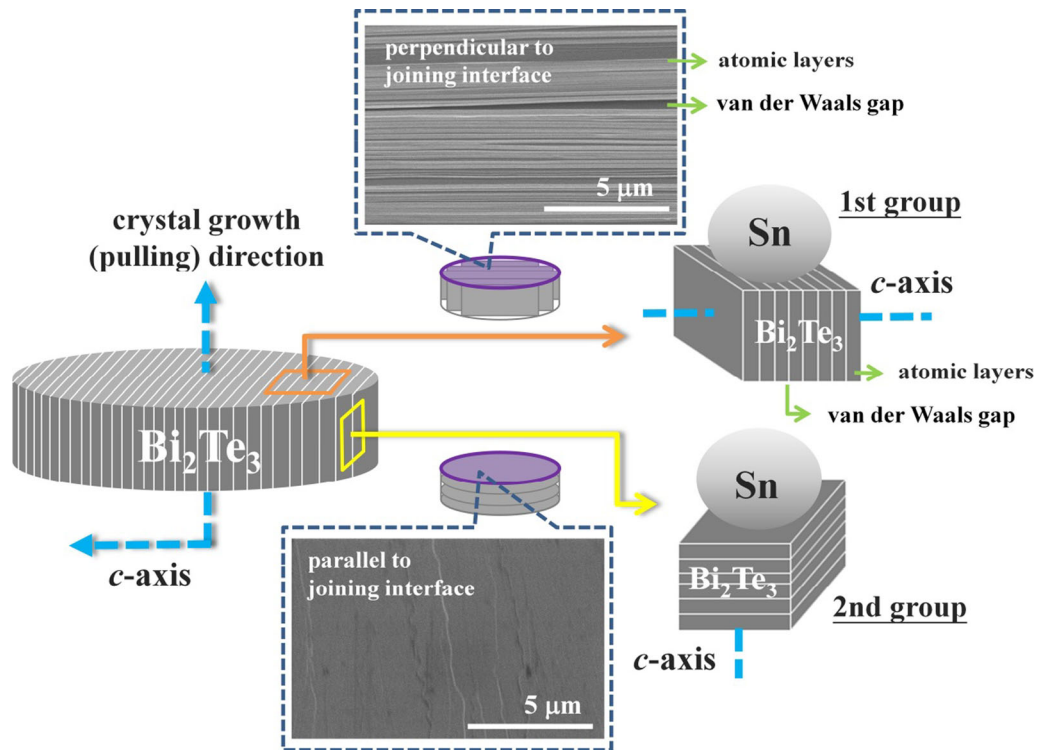


Fig. 1—Schematic drawing of the crystal orientation of a Bi_2Te_3 disk made by zone melting and the joining relationship between Sn and Bi_2Te_3 substrate.

homogenization. After homogenization, the sample was removed from the furnace and quenched in water. Phase identification of the as-prepared TE sample was carried out using powder X-ray diffractometer (D8 SSS, Bruker, USA), and the results indicated that the TE sample only contained the Bi_2Te_3 phase. The TE ingot was cut into cubic pieces and joined with Sn at 523 K (250 °C) for 1 minute. The joining process was carried out in a furnace filled with nitrogen. After joining with Sn, the Sn/ Bi_2Te_3 couples were heat-treated at 423 K (150 °C) for up to 240 hours. The third group was named as “hm” in terms of homogeneous melting.

Figures 2(a) through (c) show the cross-sectional images of the three Sn/ p -(Bi,Sb) $_2\text{Te}_3$ interfaces just after joining. The images were taken from a scanning electron microscopy (SEM) (JSM-6700F, JEOL, Japan). A new phase was formed at the interfaces and was identified as the SnTe phase according to the elemental analysis of EPMA. The thickness order of the SnTe phase was as follows: hm (50 μm), zm-perpendicular (28 μm), and zm-parallel (10 μm). It was found that the SnTe phase formed on the hm- Bi_2Te_3 substrate was thicker in comparison with the other two zm- Bi_2Te_3 substrates. However, after subsequent solid-state reaction at 423 K (150 °C) for 72 hours, the thickness order of the SnTe phase changed to the following order: zm-perpendicular, zm-parallel, and hm, as seen in Figures 2(d) through (f). The SnTe phase formed on the hm- Bi_2Te_3 substrate grew only to 67 μm , but the SnTe phase formed on two zm- Bi_2Te_3 substrates has grown over 200 μm . Figure 3 depicts the relationship between the SnTe thickness and

reaction time from 24 to 240 hours. It was found that the thickness order of the SnTe phase was the same for all reaction times, namely, zm- p -perpendicular > zm- p -parallel > hm- p -type. In Figure 3, the thicknesses of the SnTe phase formed at the interfaces between Sn and three groups of n - Bi_2Te_3 substrates (zm- n -perpendicular, zm- n -parallel, and hm- n -type) were also shown. The SnTe phase formed on the n - Bi_2Te_3 substrates was much thinner and their thickness difference among three group's substrates was insignificant in comparison with the p - Bi_2Te_3 case. Especially, the growth rates of the SnTe phase in the zm- n -perpendicular and zm- n -parallel cases were very close to each other, so their thickness curves almost superimposed to each other as seen in Figure 3.

Liao *et al.* also observed the asymmetric growth behavior of the SnTe phase at the p -(Bi,Sb) $_2\text{Te}_3$ and n - $\text{Bi}_2(\text{Te,Se})_3$ solder joints during soldering.^[7] They attributed the reduced growth rate of the SnTe phase to the Bi dissolution effect because a higher Bi content dissolved from the Bi-rich n - $\text{Bi}_2(\text{Te,Se})_3$ substrate into the molten solder.^[8] Based on the results presented in this study, we believed the Bi dissolution effect also played an important role in inhibiting the SnTe phase growth at the n - $\text{Bi}_2(\text{Te,Se})_3$ solder joint during solid-state reaction. Chen *et al.*^[11] systematically compared the reaction layer thickness in the Sn/Te, Sn/ Bi_2Te_3 , Sn/ Bi_2Se_3 , Sn/ Sb_2Te_3 , Sn/($\text{Bi}_{0.25}\text{Sb}_{0.75}$) $_2\text{Te}_3$, and Sn/ $\text{Bi}_{1-x}\text{Se}_x$ couples reacted at 523 K (250 °C). They found that the reaction layer thickness was dramatically reduced in the reaction couples with the addition of Se.

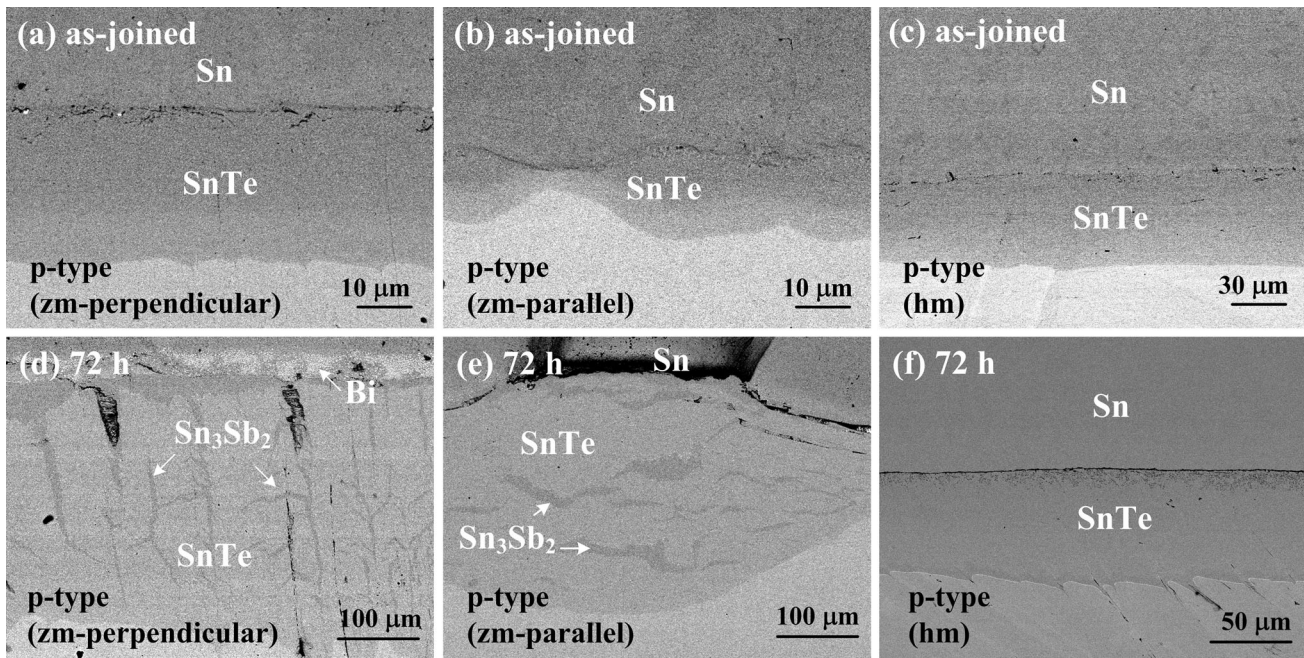


Fig. 2—SEM micrographs of the interfaces between Sn and three p - Bi_2Te_3 substrates: (a) through (c) as-joined, (d) through (f) after reaction at 423 K (150 °C) for 72 h.

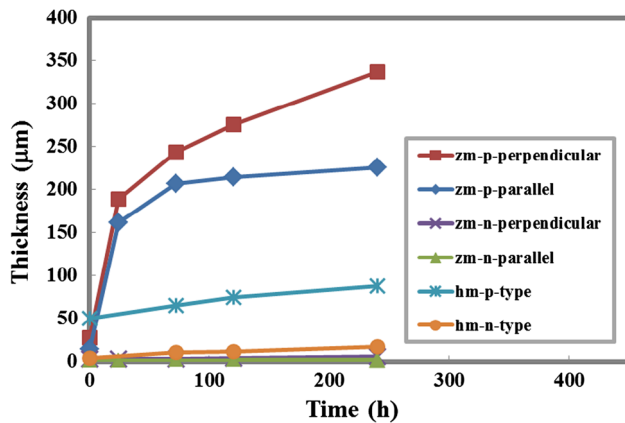


Fig. 3—Relationship between the thickness of the SnTe phase and reaction time, where the reaction temperature is 423 K (150 °C).

Therefore, the Se in the n - $\text{Bi}_2(\text{Te},\text{Se})_3$ substrate might also be a cause for the thinner SnTe phase. Another potential cause for the slower growth rate of the SnTe phase at the n - $\text{Bi}_2(\text{Te},\text{Se})_3$ solder joint was the lower availability of reactive Te from the n - $\text{Bi}_2(\text{Te},\text{Se})_3$ substrate.

It was noteworthy that the preparation methods for the p - Bi_2Te_3 substrates also had a strong effect on the SnTe phase growth. In summary, the SnTe phase formed on the p - Bi_2Te_3 substrate prepared by zone melting (zm-type) grew at a rate much faster than that on the p - Bi_2Te_3 substrate prepared by homogeneous melting (hm-type). Especially, the SnTe phase formed on the zm-perpendicular p - Bi_2Te_3 element grew much

faster than that on the zm-parallel p - Bi_2Te_3 substrate. As seen in Figures 2(d) and (e), stripe-like Sn_3Sb_2 phase was observed within the SnTe phase. The formation of the Sn_3Sb_2 phase was a result of precipitation of supersaturated Sb due to faster consumption of Te in support of the SnTe growth. No Sn_3Sb_2 phase was observed in the hm-type SnTe phase as shown in Figure 2(f), which was attributed to less Sb content in the thinner SnTe phase due to slower consumption of Te. It was found that the Sn_3Sb_2 phase had a preferential growth direction depending upon the atomic layer direction of the p - Bi_2Te_3 substrate. On the zm-perpendicular substrate, the Sn_3Sb_2 phase approximately grew in a direction perpendicular to the joining interface. However, the Sn_3Sb_2 phase grew in a direction parallel to the joining interface in the zm-parallel sample. Chen *et al.*^[10] also observed that the preferred growth direction of the Sn_3Sb_2 phase within the SnTe phase in the $\text{Sn}/(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ couple reacted at 523 K (250 °C). The mechanism still remained unsolved but the authors correlated this preferred growth direction with the preferred orientation of the SnTe phase.^[10] Because the p - Bi_2Te_3 substrate used by Chen *et al.* was not formed by zone melting, the anisotropic characteristic of the atomic layer direction in the p - Bi_2Te_3 substrate should not be so strong. Therefore, the Sn_3Sb_2 phase precipitated roughly in a direction parallel to or at a small included angle to the Sn/ p - Bi_2Te_3 substrate interface. By contrast, the Sn_3Sb_2 phase observed in the current study exhibited a strong anisotropic growth direction which was strongly related to the atomic layer direction of the p - Bi_2Te_3 substrate formed by zone melting. The details for such a strong anisotropic

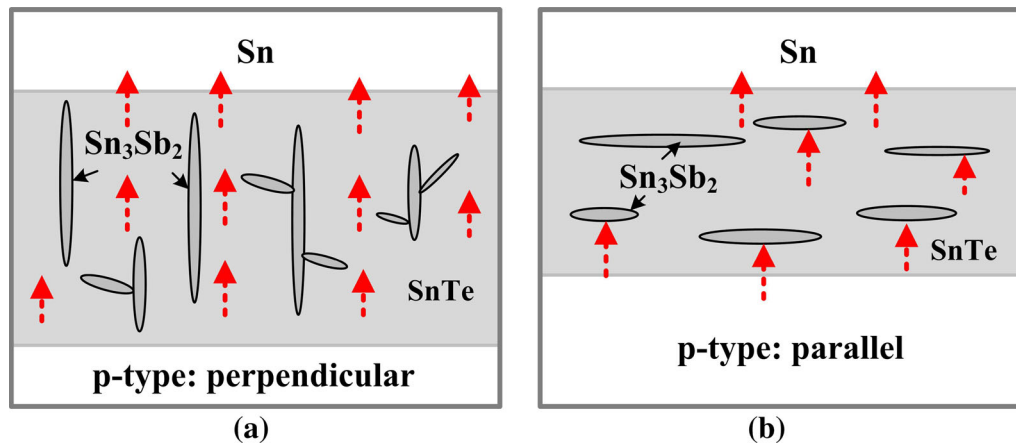


Fig. 4—Schematic drawing of stripe-like Sn_3Sb_2 phase precipitated in the SnTe phase formed on two $p\text{-Bi}_2\text{Te}_3$ substrates made by zone melting. (a) The stripe-like Sn_3Sb_2 phase precipitated in a direction perpendicular to the $\text{Sn}/p\text{-Bi}_2\text{Te}_3$ interface, so the atomic diffusion of element Te (dotted arrows) was not affected. (b) The stripe-like Sn_3Sb_2 phase precipitated in a direction parallel to the $\text{Sn}/p\text{-Bi}_2\text{Te}_3$ interface, which significantly hindered the atomic diffusion of element Te.

growth behavior of the Sn_3Sb_2 phase was still unclear, while we believed the atomic layer direction of the $p\text{-Bi}_2\text{Te}_3$ substrate should play a crucial role.

Although the anisotropic growth mechanism of the Sn_3Sb_2 phase needed further investigations, we believed its existence had a significant effect on the growth of the SnTe phase. As shown in Figure 4(b), the parallel-oriented Sn_3Sb_2 phase behaved like obstacles in the diffusion path for the dominant diffusion species, namely, Te.^[8] Therefore, the Te atoms were very likely to bypass the Sn_3Sb_2 phase when they met the parallel-oriented Sn_3Sb_2 phase, and this inevitably slowed down the atomic diffusion and the SnTe growth rate. By contrast, the perpendicular-oriented Sn_3Sb_2 phase had a negligible effect on the atomic diffusion, so the SnTe phase grew at a faster rate. Obvious precipitation of the Sn_3Sb_2 phase was observed approximately after 72 h reaction as Figures 2(d) and (e) shown. From Figure 3, it was found that the SnTe phase on the zm-parallel $p\text{-Bi}_2\text{Te}_3$ substrate grew rapidly in the initial stage of reaction but nearly stopped growing after 72 hours when the parallel-oriented Sn_3Sb_2 phase was formed. However, the SnTe phase on the zm-perpendicular $p\text{-Bi}_2\text{Te}_3$ substrate continuously grew with increasing the reaction time. Such a growth behavior revealed that the orientation of precipitated Sn_3Sb_2 phase indeed had a significant effect on the diffusion of Te atoms.

The SnTe phase was the primary reaction product in the $\text{Sn}/p\text{-(Bi,Sb)}_2\text{Te}_3$ interfacial reaction reacted at 423 K (150 °C), and its growth rate and microstructure strongly depended upon the crystal structures of the $p\text{-(Bi,Sb)}_2\text{Te}_3$ elements made by different methods. The SnTe phase formed on the $p\text{-(Bi,Sb)}_2\text{Te}_3$ element made by zone melting (zm) grew at a faster rate than that formed on the $p\text{-(Bi,Sb)}_2\text{Te}_3$ element made by homogeneous melting (hm). Especially, for the $p\text{-(Bi,Sb)}_2\text{Te}_3$ substrate made by zone melting stripe-like Sn_3Sb_2 phase precipitated within the SnTe phase in a direction perpendicular or parallel to the $\text{Sn}/p\text{-(Bi,Sb)}_2\text{Te}_3$ interface depending upon the crystal orientations of the

$p\text{-(Bi,Sb)}_2\text{Te}_3$ element. The parallel-oriented Sn_3Sb_2 phase retarded the atomic diffusion and reduced the SnTe growth rate accordingly. By contrast, the perpendicular-oriented Sn_3Sb_2 phase had a negligible effect on the atomic diffusion, so the SnTe phase grew at a faster rate.

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