

Microstructure and aging resistance of the joints between SAC305 solder and thermoelectric materials with different diffusion barriers

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Abstract

The microstructure and aging resistance of SAC305 soldering joints with different diffusion barriers in thermoelectric application were investigated in this paper. Results indicate that the SACPNi joints (SAC305 solder and p-type (Bi,Sb)₂Te₃ thermoelectric materials with Ni diffusion barrier) exhibit more defects when increasing the aging temperature and time. However, there were less defects observed in the SACPSB joints (SAC305 solder and p-type (Bi,Sb)₂Te₃ thermoelectric materials with Sn-58Bi alloy diffusion barrier) when aging temperature and time increased. This result indicated that, for p-type (Bi,Sb)₂Te₃ thermoelectric materials, the diffusion barrier of hot-dipping Sn-58Bi alloy was more preferable than electroless plating nickel in the application of joining p-type thermoelectric materials and the Cu substrates with SAC305 solder.

Key words: thermoelectric materials, soldering joints, aging resistance

1. Introduction

Since the increasing public awareness in environmental problems in recent years, the applications of thermoelectric modules are becoming widespread. Many investigations were conducted on thermoelectric power generators and thermoelectric coolers [1–5], these research works indicate that the efficiency of the thermoelectric modules depends on their thermoelectric figure-of-merit, which can be expressed as:

$$ZT = S^2 T \sigma / k, \quad (1)$$

where S is Seebeck coefficient, σ is electrical conductivity, k is thermal conductivity and T is average absolute temperature of hot and cold plates of the thermoelectric module. The larger the value of ZT , the more effective the thermoelectric module is. Therefore, it can be deduced that increasing the value of T would be an effective way to improve the effectiveness of the thermoelectric module.

The highest operating temperature of the thermoelectric module is usually limited by the melting point of the solder, which joins the thermoelectric material with the conductive substrate. Sn-Bi eutectic alloy is currently one of the most widely used lead-free solders in thermoelectric modules [6]. However, the melting point of this solder alloy is only 139°C, which significantly suppresses the efficiency of the thermoelectric modules. In order to improve the efficiency of the thermoelectric modules, the applied solders with higher melting point are desirable. The melting temperature of Sn-Ag-Cu ternary alloy is 217°C, and it is widely considered as one of the most promising lead-free solders in electronic packaging application [7–9]. Therefore, the Sn-Ag-Cu solders can serve as the potential alternatives for Sn-Bi eutectic solder in thermoelectric modules.

Bismuth telluride families are the most commonly used thermoelectric materials [10–12], and they are usually identified as p-type and n-type based on their different function. The Sn and Te are primary ele-

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ments in the lead-free solders and bismuth telluride thermoelectric materials, respectively. It is well-known that Sn tends to react with Te to form a very thick intermetallic compound SnTe in the interface of the solder joints [13]. The undesirable SnTe IMCs usually affect the performance and reliability of the thermoelectric modules because they are usually brittle [14]. Liao et al. reported that Sn was preferable to react with p-type thermoelectric materials at cathode junction (hot side) due to electromigration and asymmetrical heating [15]. It indicated that the joint at the side of the p-type thermoelectric material was the weakest section in the thermoelectric module. Therefore, the interfacial reaction between the solder and the p-type thermoelectric material is well-advised to be investigated preferentially.

It is crucial to have a diffusion barrier to prevent the rapid-growing SnTe IMCs. It is reported that adding a small amount of silver and copper to the tin can effectively suppress the formation of SnTe compounds by forming layers of Ag-Te and Cu-Te IMCs [16, 17]. From this perspective, Sn-Ag-Cu solders also could be competent for the application in thermoelectric modules. Nickel is widely considered as an effective diffusion barrier in many research works [18, 19]. In commercial Peltier devices, in order to avoid the diffusion of Sn from the solder and Cu from the connectors into the thermoelectric materials, nickel is always used as the diffusion barrier [20]. In present study, nickel was also used as the diffusion barrier in a certain group of samples. According to the previous investigation we have conducted, there were few defects observed in the interface between the Sn-58Bi eutectic solder and the p-type thermoelectric material. Therefore, Sn-58Bi solder alloy was chosen as the diffusion barrier in another group of samples as the comparison for nickel.

In accordance with the above-mentioned facts

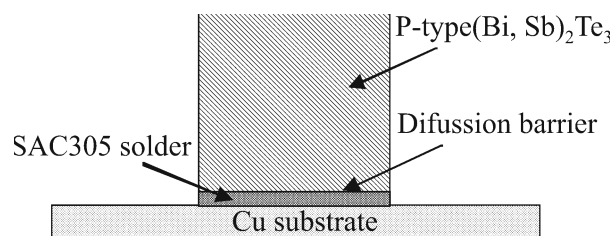


Fig. 1. The schematic diagram of the solder joint.

and analysis, the commonly used SAC305 (Sn-3.0Ag-0.5Cu) solder and p-type $(\text{Bi,Sb})_2\text{Te}_3$ thermoelectric materials with diffusion barriers of Ni or Sn-58Bi alloy were selected as the experimental materials in the present investigation.

Due to the thermoelectric modules usually performed in relatively high temperature for a long time, aging resistance of the joints is the critical property which should be evaluated. Thus, aging experiments were employed in present investigation as well.

2. Experimental procedure

Pure Sn granules (99.9 wt.% purity), Ag shots (99.9 wt.% purity) and copper sheet were used to prepare the SAC305 (Sn-3.0Ag-0.5Cu) solder. Precisely, pure Sn granules were mixed with 3.5 wt.% Ag and 0.5 wt.% Cu, sealed in evacuated quartz ampoules, and put into a furnace at 600°C for 3 h for alloying and homogenization. After air cooling, the SAC305 alloy was rolled into a 1 mm thick plate using a rolling machine, and then $4 \times 4 \text{ mm}^2$ solder plates were fabricated for subsequent experiments. The dimensions of the commercial p-type $(\text{Bi,Sb})_2\text{Te}_3$ thermoelectric materials (provided by Xianghe Orient Electric Co., Ltd.) were $4 \times 4 \times 4 \text{ mm}^3$. They were coated

Table 1. The scheme of the experiments

Specimen No.	Joints materials (thermoelectric material/solder/substrate)	Diffusion barrier	Aging temperature (°C)	Aging time (h)
1a	p-type $(\text{Bi,Sb})_2\text{Te}_3$ /SAC305 solder/ Cu substrate	Electroless	0	0
1b		Ni plate	150	2
1c			150	4
1d			200	2
1e			200	4
2a	p-type $(\text{Bi,Sb})_2\text{Te}_3$ /SAC305 solder/ Cu substrate	Hot dipping	0	0
2b		Sn-58Bi layer	150	2
2c			150	4
2d			200	2
2e			200	4

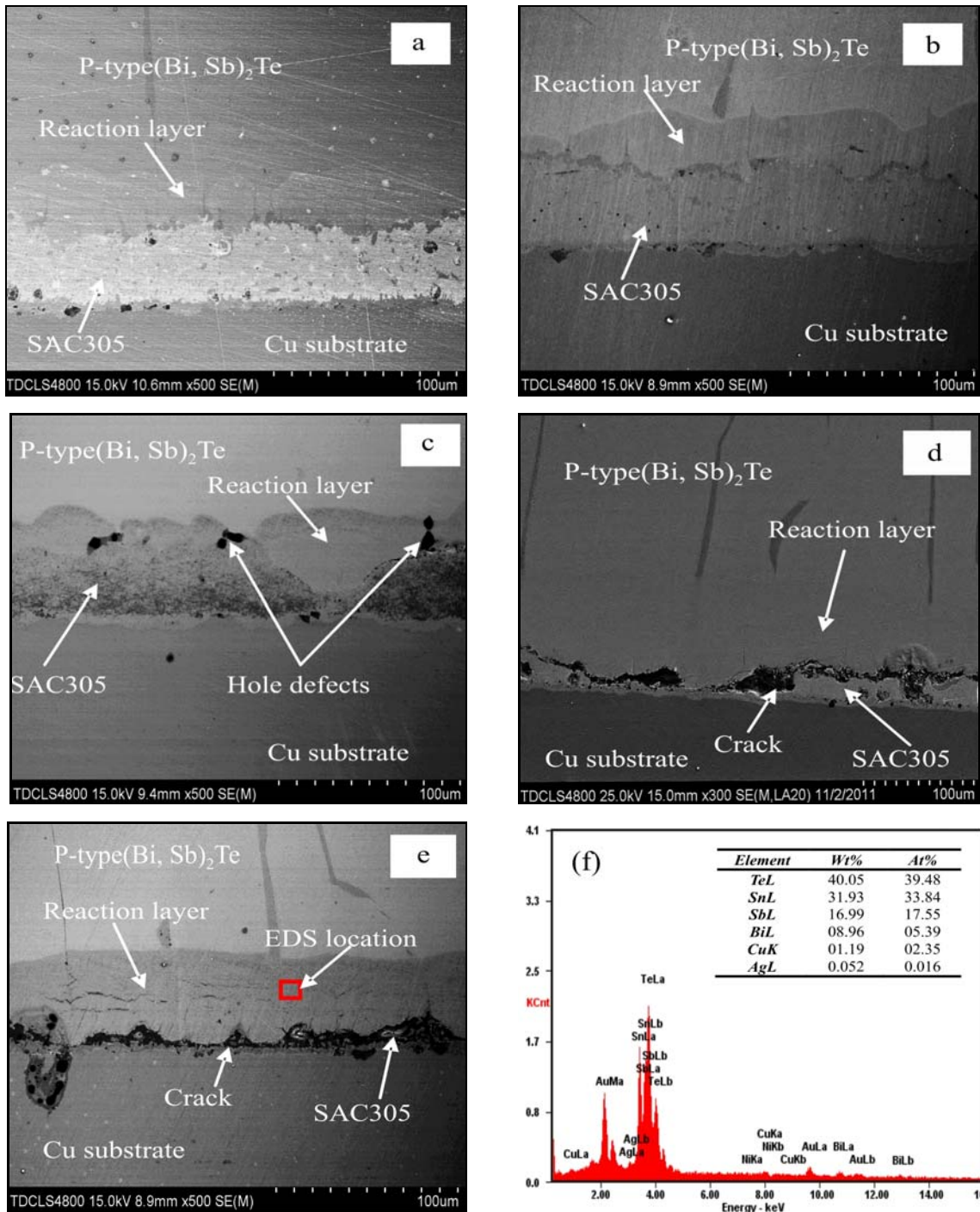


Fig. 2. SEM micrographs of SACPNi joints with aging treatments of (a) none, (b) 150°C for 2 h, (c) 150°C for 4 h, (d) 200°C for 2 h, (e) 200°C for 4 h, and (f) EDS profile and constituents of the interfacial compound.

with different diffusion barriers due to the reaction between Sn and Te that is detrimental to the properties of the solder joint. In practice, the surface of the p-type (Bi,Sb)₂Te₃ thermoelectric materials is usually without polish after wire-cutting, this coarse surface state could insure the coating materials be attached on the p-type (Bi,Sb)₂Te₃ thermoelectric materials strongly. In present experiments, Ni and Sn-58Bi

solder were coated on p-type (Bi,Sb)₂Te₃ thermoelectric materials by methods of electroless plating and hot dipping methods, respectively. The copper substrates used were machined with a dimension of 4 × 10 × 1 mm³.

Before experiment, the p-type (Bi,Sb)₂Te₃ cubes, SAC305 solder plates and the copper substrates were cleaned consecutively with acetone, isopropyl alco-

hol, and deionized water in an ultrasonic bath to obtain the high-quality soldering surface. Each p-type $(\text{Bi,Sb})_2\text{Te}_3/\text{SAC305}/\text{Cu}$ joint was performed by laying a SAC305 plate between the p-type $(\text{Bi,Sb})_2\text{Te}_3$ cube and the copper substrate, then putting the whole specimen into the reflow furnace for reflowing. Each specimen only contained one joint. Figure 1 shows the schematic diagram of the solder joint.

In industry, the recommended peak temperature range for SAC305 is 235–255 °C, thus we chose 250 °C as the peak temperature in current experiments in order to study the joints reaction in relatively harsh circumstance.

In order to evaluate the reliability of SAC305 solder in the application of joining p-type $(\text{Bi,Sb})_2\text{Te}_3$ thermoelectric materials and copper substrates, the solder joints were aged with different time spans at different temperatures. All the samples were mounted by epoxy before grounding and polishing. The interfaces of the joints were examined by ESM and EDS. Table 1 presents the scheme of the experiments.

3. Results and discussion

Figure 2 shows the cross-sectional SEM micrographs of the specimens of No. 1 group, in order to simplify the name of this group, hereafter it was designated as SACPNi. Figures 2a–e are the SACPNi joints which were treated at different temperatures and different aging time spans. As shown in Fig. 2a, the as-soldered SACPNi joint was composed of two regions, the solder region and the interfacial reaction layer region. And no defect was obtained in the as-soldered SACPNi joint. After aging at 150 °C for 2 h, the joint experienced little change (Fig. 2b). But it can be clearly seen that the solder reduced significantly at certain position and there some holes appeared between the solder and the reaction layer region after the joint aging at 150 °C for 4 h (Fig. 2c). Figure 2d is the SACPNi joint aged at 200 °C for 2 h, large part of the solder region disappeared and the interfacial reaction layer region became larger, more apparently, there were more holes, or cracks were formed between the solder and the reaction layer region. This phenomenon was more obvious in the specimen which experienced aging time for 4 h (Fig. 2e), the major part of this joint was the compound region and almost none solder was left, cracks were more coherent and expanded. The interfacial reaction layer was identified as the SnTe compound by EDS (Fig. 2f).

In the micrographs of No. 1 group, no Ni diffusion barriers could be clearly seen in any of them. And it seems like the Ni diffusion barrier is ineffective in preventing the diffusion of Sn under these experimental conditions. In Fig. 3, the EDS line scan results of the 200 °C for 4 h specimen indicate that most of the Ni

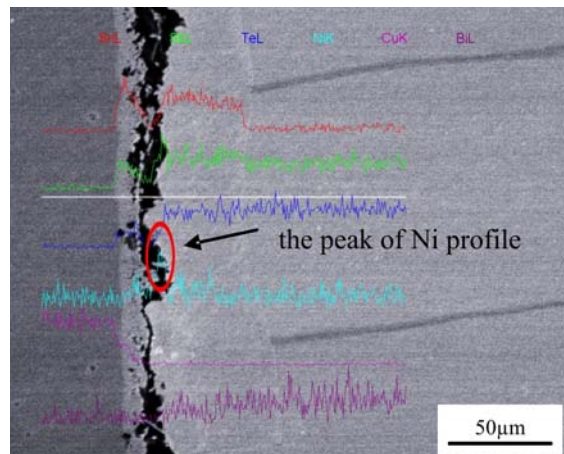


Fig. 3. EDS line scan of the SACPNi specimen (aging at 200 °C for 4 h).

diffusion barrier still attached on the surface of the p-type $(\text{Bi,Sb})_2\text{Te}_3$ specimen, and only certain portion of it diffused into the p-type $(\text{Bi,Sb})_2\text{Te}_3$ specimen. It also illustrates that there were Te and Sb diffused into the solder matrix corresponding to Sn diffusion. The ineffectiveness of Ni diffusion barrier is probably due to the final surface state of the thermoelectric materials and the inappropriate plating method for the thermoelectric materials. Specifically, the surface of the thermoelectric material was unpolished and nickel was plated on such curved surface by electroless plating method. Thus, nickel plate tends to be nonuniform and discontinuous, this inferior nickel plate rationally would be less effective for combat the diffusion of Sn.

The appearance of holes and cracks in aged specimen is mainly attributed to the diffusion of Sn into the p-type $(\text{Bi,Sb})_2\text{Te}_3$ specimen which is quicker than that of Te and Sb into the SAC305 solder matrix, especially under high temperature and at long aging time. These holes and cracks at the joints obviously will cause the thermoelectric modules ineffective early. Therefore, the life span of the thermoelectric module substantially depends on the diffusion rate of Sn. The precise measurements of Sn diffusion rate and the SnTe growth rate are ongoing currently.

Figure 4 shows the cross-sectional SEM micrographs of the specimens of No. 2 group. For simplicity, this group is referred as SACPSB. The only difference between the SACPSB and the SACPNi was their diffusion barrier, the diffusion barrier of SACPSB was the Sn-58Bi solder alloy rather than Ni. Compared with the SACPNi joints, it can be clearly seen that SACPSB joints experienced relatively little change after aging at 150 °C for 2 and 4 h (Figs. 4b,c), but there were large portions of compounds formed at the joints interface as well. After aging at 200 °C for 2 and 4 h (Figs. 4d,e), respectively, less severe crack defects were observed in the SACPSB joints than those in

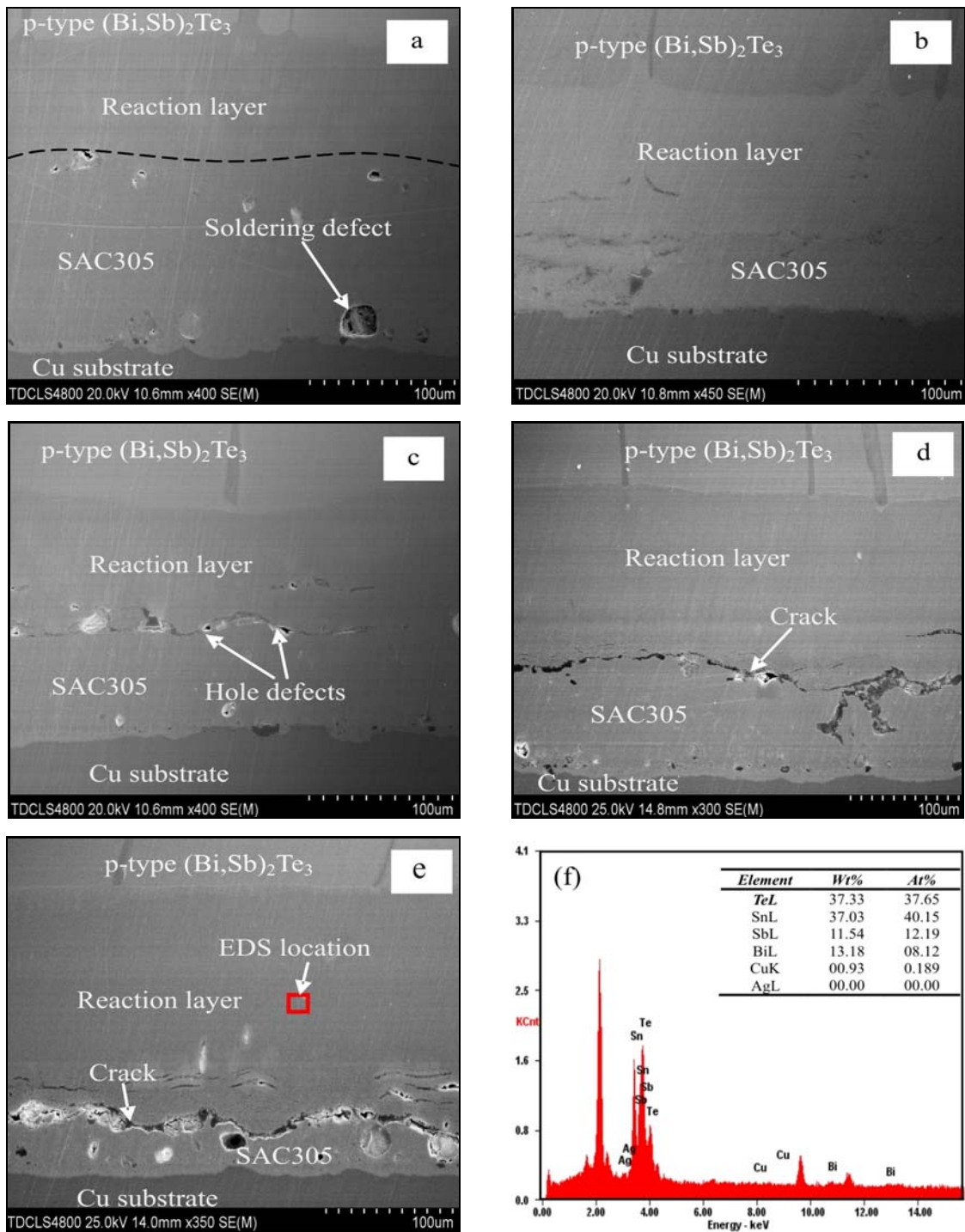


Fig. 4. SEM micrographs of SACPSB joints with aging treatments of (a) none, (b) 150 °C for 2 h, (c) 150 °C for 4 h, (d) 200 °C for 2 h, (e) 200 °C for 4 h, and (f) EDS profile and constituents of the interfacial compound.

SACPNi joints. EDS analysis also indicated that the interfacial reaction layer was SnTe IMCs (Fig. 4f). The favorable morphology of SACPSB joints can substantially contribute to their reliabilities, especially in high-temperature application.

The superior morphology of the SACPSB joints is mainly the result of the Sn-58Bi alloy diffusion barrier. It was reported that the SnTe compound growth

rate would decrease with increasing Bi concentration in Sn-Bi solder when a piece of Te was immersed in this melted solder [6]. Because of that, the Sn-58Bi diffusion barriers were coated on the p-type specimens, the density of Bi at the interface between the solder matrix and the p-type specimens increased significantly, the growth rate of SnTe compound and diffusion rate of Sn were less severe correspondingly. Additionally,

hot-dipping method for plating the Sn-58Bi alloy on the surface of the thermoelectric material could be beneficial to form thick and continuous plate, which contributes to preventing the Sn diffusion. Therefore, the Sn-58Bi diffusion barrier could extend the life-span of the solder joints in the application in harsh circumstance.

4. Conclusions

1. The investigation of SACPNi joints indicates that SAC305 solder tends to react with the p-type $(\text{Bi,Sb})_2\text{Te}_3$ thermoelectric materials severely. With an increase of aging temperature and aging time, there are more holes or cracks emerged in the joint interface. These results show that electroless plating Ni diffusion barrier cannot prevent the Sn diffusion effectively, it is probably due to inferior final state of thermoelectric materials surface and inappropriate electroless plating method.

2. The hot-dipping diffusion barrier of Sn-58Bi solder on the p-type $(\text{Bi,Sb})_2\text{Te}_3$ thermoelectric materials can significantly restrain the diffusion rate of Sn and suppress the formation of SnTe, that benefit the reliability of the SACPSB joints. This desirable result ought to be ascribed to the advantage of Sn-58Bi solder alloy and the appropriate hot-dipping plating method.

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