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Interfacial reaction between n- and p-type thermoelectric materials and SAC305 solders

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ABSTRACT

Sn96.5Ag3.0Cu0.5 (SAC305) is one of the most promising lead-free solder alloys and bismuth telluride-based compounds are the best known thermoelectric materials. Interfacial reactions of the SAC305/$Bi_{0.5}Sb_{1.5}Te_3$ and SAC305/$Bi_{1.8}Sb_{0.2}Se_{0.15}Te_{2.85}$ couples at 260 °C are studied to investigate the effect of reaction on the efficiency and reliability of thermoelectric device. Initially, the major products in SAC305/$Bi_{0.5}Sb_{1.5}Te_3$ couple reaction for a short time are a strip-type Ag-rich IMC layer and a dense SnTe–SbSn mixture layer. With the reaction time increasing, a two-phase layer, which is SnTe–SbSn mixture with pores with 200–500 nm size which are occupied by solder originally, appears next to the dense layer. However, the reaction products do not change significantly. It is observed that the growth rate of reaction phase layer is about 4.05 μm/min. As for the SAC305/$Bi_{1.8}Sb_{0.2}Se_{0.15}Te_{2.85}$ couple reaction, besides SnTe phase, Bi–Te phase is also formed at the solder/$Bi_{1.8}Sb_{0.2}Se_{0.15}Te_{2.85}$ interface. As the reaction time increases, the morphology of IMC layer becomes rough, and then the stable scallop-type IMC appears; the growth rate of reaction phase layer is about 0.39 μm/min.

1. Introduction

Currently, thermoelectric (TE) device have attracted much attention due to a wide range of applications in solid-state cooling and power generation, which will benefit from its unique features such as friendliness to the environment, highly reliable with no moving parts, and noiseless operation [1–3]. The efficiency and reliability of TE device are determined basically not only by the materials with high figure of merit [4,5], but also by the fabrication factors [6]. And the most popular failure in TE device is found to be the solder joint between the thermoelectric element and electrode [7]. In general, the failure of the solder joint in commercial devices is always caused by the consumption of the nickel layer, which is plated with 3–5 μm thickness to sever as a diffusion barrier preventing diffusion of the solder material into the TE elements [8,9]; however, it has been found that the tin in the solder often consumes Ni to form Ni_3Sn_4 and penetrate through the layer to react with TE material [10–12]. Thus, Interfacial reaction between solder and TE material is fundamentally important to the efficiency and reliability of thermoelectric devices [13]. Bismuth telluride families such as the p-type material, $Bi_{0.5}Sb_{1.5}Te_3$, and n-type material, $Bi_{1.8}Sb_{0.2}Se_{0.15}Te_{2.85}$, are the most commonly used thermoelectric materials due to their good thermoelectric properties [14–16]. The lead-free solder Sn96.5Ag3.0Cu0.5 (SAC305) is commonly employed in assembling electronic modules [17,18].

Recently, interfacial reactions between different molten solders and Te substrate have been studied [19–23]. Chen and Chiu [20] have reported that the product of Sn/Te couple reaction is SnTe, which has an extremely fast growth rate, about 1.7 μm/min. It is interesting that the reaction layer SnTe will evolve into a unique cruciform pattern when surrounding a rectangular Te substrate. A recent study by Liao and Huang [21] reveals that when the solder containing a small addition of Ag reacted with Te substrate, a thin layer of Ag–Te compounds at the interface would suppress the growth rate of SnTe IMC layer. Lee et al. [22] have carried out the investigation concerning the effect of Sb addition in Sn solder on the kinetics of interfacial reaction of Sn–xSb/Te couples and found that Sb element expedite the growth rate of reaction layer due to SbSn enhanced SnTe nucleation rate. In most of those reports, the Te substrate is a substitute for bismuth telluride based compounds and the research focus is the effect of alloying elements on the formation and kinetics of intermetallic compound.

However, the interfacial reactions in molten solder /TE materials couples are different from that of molten solder/Te substrate, and few previous results are available in the literature to study the evolution of IMC morphology and formation phase, which will affect the mechanical and electrical properties of the joint.

Accordingly, in the present study the interfacial reactions in the SAC305/$Bi_{0.5}Sb_{1.5}Te_3$ and SAC305/$Bi_{1.8}Sb_{0.2}Se_{0.15}Te_{2.85}$ couples will

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be investigated at 260 °C to provide a further understanding of their effect on the reliability in TE device.

2. Experiment procedure

Both p-type $Bi_{0.5}Sb_{1.5}Te_3$ and n-type $Bi_{1.8}Sb_{0.2}Se_{0.15}Te_{2.85}$ thermoelectric materials were obtained from a commercial supplier and were cut into small specimens with a dimension of 5 × 5 × 1 mm using a diamond saw. To obtain a high-quality surface, the specimens were polished to remove surface oxide and cleaned consecutively with acetone and deionized water in an ultrasonic bath. The commercially available solder paste SAC305 (Sn96.5Ag3.0Cu0.5) was printed on a Cu foil using stencil printing with the thickness of 0.2 mm, and then the copper foil was put on a hot plate that was maintained at the temperature 260 °C (above about 30 °C above nominal melting point of solder) with a variation of ±1 °C. When the solder paste was melted, the n-type or p-type thermoelectric materials were put onto the molten solder and remained still for different reaction time of 1 min, 2 min, 5 min and 10 min before being removed from the hotplate. The samples were then mounted in an epoxy, metallographically polished and etched for a few seconds using a CH_3OH (92 vol%)–HCl (8 vol%) solution to reveal their interfacial microstructures. Some of the samples were intentionally etched away solder by HNO_3 (10 vol%) to reveal the morphology of IMC. The morphologies of IMCs by solders/TE materials couples were observed under OLYMPUS GX51 optical microscopy (OM) and Hitachi S4800 scanning electron microscope (SEM), and the compositions of the reaction products were also analyzed using an energy-dispersive X-ray spectrum (EDS). And the phases were confirmed by using Bruker Advanced D8 X-ray diffraction analysis (XRD) after the solder was completely etched. The average thickness measurement of the interfacial IMC was performed using the image analysis.

3. Results and discussion

3.1. Interfacial reactions in the SAC305/$Bi_{0.5}Sb_{1.5}Te_3$ couples

Figs. 1–4 are SEM micrographs of intermetallic compound (IMC) formed by SAC305/$Bi_{0.5}Sb_{1.5}Te_3$ couple reaction at 260 °C for 1, 2, 5 and 10 min, respectively, showing that there exist two typical microstructures.

The first type of microstructure, which occurs in reaction at 260 °C for shorter time (1 and 2 min), has a continuous and dense layer with a rugged interface (Figs. 1a and 2a). It is interesting to observe that a strip-type Ag-rich layer, which is determined by the EDS elemental mappings of element Sn and Ag (Figs. 1b and 2b), exists between the dense layer and TE material.

The second type of microstructure, which has a thick and porous reaction zone, occurs in reaction for longer time (5 and 10 min) shown in Figs. 3a and 4a, and the microstructure of couple reaction at 260 °C for 10 min is representative. From optical micrographs shown in Fig. 4b, the reaction layer formed at the interface consists of three adjoining layers with different morphologies: porous layer with a rugged interface (IMC1), dense layer with planar interface (IMC2) and thin strip-type layer (IMC3), and the IMCs thicknesses from solder to thermoelectric material are 10.87, 25.78 and 1.98 μm, respectively. To differentiate the IMCs in SEM micrograph, the EDS elemental mappings of Sn and Ag of reaction couples are performed (Fig. 4c). The reaction layer can be clearly distinguished due to the distinct differences of Ag and Sn concentration. It is noted that the location and morphology of IMC3 in optical micrographs (Fig. 4b) coincides with that of Ag-rich region in the elemental mapping SEM micrographs (Fig. 4c). It is concluded that IMC3 is an Ag-rich phase.

The composition of products by SAC305/$Bi_{0.5}Sb_{1.5}Te_3$ couples for different time determined by EDS are showed Table 1. And the XRD results are exhibited in Figs. 2c, 3c and 4d after the SAC solder was completely removed by chemical etching. It is observed that diffraction peaks correspond to the SnTe and SbSn phases as well as $Bi_{0.5}Sb_{1.5}Te_3$ substrates in these XRD patterns. It is concluded that the reaction products by SAC305/$Bi_{0.5}Sb_{1.5}Te_3$ couples are probably a mixture of multiphase compounds: SnTe and SbSn. Besides, the composition comparison between IMC1 and IMC2 indicates that there are more SnTe phase and less SbSn phase in the porous zone (IMC1), which have a great effect on the IMC growth.

The reaction products are formed by the dissolution and diffusion of element Te and Sb into molten solder. If Sn is the dominant diffusing species and diffuses into the thermoelectric material during the reaction, the composition ratio of Te/Sb/Bi in the reaction layer should be about 6:3:1. However, as are shown in the EDS results (Table 1), the actual ratio of three elements is extremely different from the expected one and the element Bi is very low. Thus, the dominant diffusing species are Te and Sb during the reaction. Besides, the standard Gibbs free energy of SnTe [24], Sb_2Te_3 [25], and Bi_2Te_3 [26] compounds are −60.2, −58, and −45.8 kJ/mol, respectively, so SnTe should be more thermodynamically

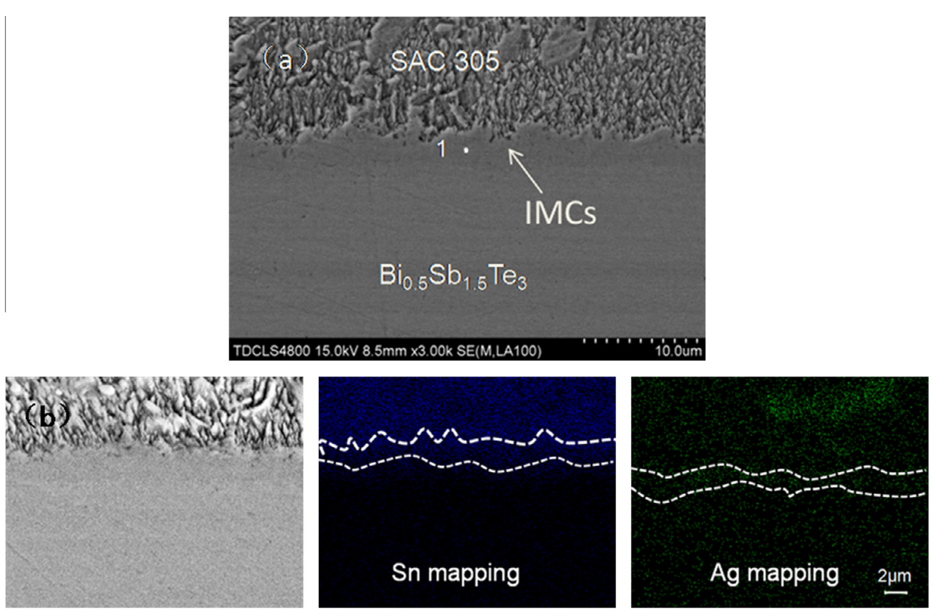

Fig. 1. The SAC305/$Bi_{0.5}Sb_{1.5}Te_3$ couple reacted at 260 °C for 1 min. (a) Cross-sectional SEM micrographs of the couple, (b) individual Ag and Sn elemental mappings of the couple.