EFFECTS OF COBALT NANOPARTICLE ON MICROSTRUCTURE OF SN58BI SOLDER JOINT

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Abstract

Eutectic Sn–Bi alloy is acquiring significant observation in the electronic packaging industry because of its advantageous properties such as ductility, low melting temperature, and mechanical strength. Miniaturization of electronic devices requires solder paste having a low melting temperature for the fabrication of chips on printed circuit board (PCB). Surface mount technology (SMT) is a reliable technique for this purpose. This work focuses to find out the effects of cobalt nanoparticle (NP) addition into the Sn-58Bi solder joint. The reflow process was done on samples of 0%, 0.5%, 1% and 2% cobalt addition. Then thermal aging of 0% and 0.5% of cobalt addition were done at 70°C, 85°C, and 100°C. To characterize the specimen and determine intermetallic compound (IMC) growth, scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy were used. After the addition of Co-nanoparticles, the microstructure of Sn-58Bi was refined. The interfacial IMC thickness was also reduced after the addition of cobalt nanoparticles. Cu_6Sn_5 and Cu_3Sn were found in the IMC of Sn-58Bi but only $(Cu, Co)_6Sn_5$ was found in the IMC of Sn-58Bi-xCo nanoparticles. Growth of interfacial IMC of SN-58Bi-xCo was significantly controlled as compared to Sn-58Bi after thermal aging.

Keywords: Intermetallic compounds, Sn-58Bi solder alloy, Energy Dispersive X-Ray Spectroscopy (EDX), Diffusion, Thermal Aging.

1. INTRODUCTION

The trend of the electronics industry is driving to a smaller scale but with higher performance and lower cost. Consumers in this market are constantly looking for multi-functional and high-quality products. As the time comes, Moore's Law no longer continues since there is a limitation on materials and knowledge. An alternative to Moore's Law which is the "More-than-Moore" prediction is assumed. It predicted that the miniaturization of electronic devices might no longer be valid as stated in Moore's law; however, the performance should continuously increase [1]. After the fabrication of chips, they are then prompted to mount on the PCB by using surface mount technology (SMT). The solder materials that are used to attach the chips and PCB should have a lower melting point [2]. Lead-based solders are one of the best materials for this kind of bonding since the Pb-based alloys have a lower melting point of 183°C [3]. However, it has been found in the past that lead-based materials have been highly toxic since the 1970s [4]. As a result, lead-free solder materials are needed to replace the Pb-based solder [5].

To date, a number of Pb-Free solder materials have been found to replace the Pb-based solder and most of these are tin-based alloys [6]. One of the suggested solder materials is tin-bismuth (Sn-Bi) solder alloy with eutectic or near eutectic composition [7]. The reasons for replacing Sn-Pb with Sn-Bi solder alloy are due to both solder alloys having the same mechanical properties at a lower temperature and the melting point of the eutectic Sn-Bi alloys being much lower than the Sn-Pb solder alloy. It can reduce the thermal damage to the chips during the reflow process [8]. During soldering, the intermetallic compound (IMC) forms in the solder interface which attributes to the bonding. The morphology of the IMC can vary according to the soldering conditions. The heat generated by the chips can harm the solder joint when the electronic device is in use. The diffusion rate of atoms in solder increases as the homologous temperature rises, resulting in an increase in IMC layer thickness [9]. As the thickness of the IMC increases, it can cause reliability issues for the solder joint.

Many kinds of research have been carried out to find the solution to enhance the reliability of the Sn-Bi solder alloy such as the addition of alloying element [10], the addition of microparticles [11, 12], the addition of nanoparticles (NP) [13-18] and addition of carbon nanotubes [19]. Ni [20], Zn [21], and Mo [22] have been added to SAC in the past. Some researchers also added Ni into the Sn-Bi solder joint [23, 24]. They have found significant improvement in the reliability of the solder joint. Huang and Cheng found that when Co was added to Sn-57Bi solder as an alloying element, it suppressed the growth rate of Cu_3Sn and only Cu_6Sn_5 was observed in the solder alloy [25]. Bashir et al. added Co NP into Sn-58Bi solder joint and found the improvements in mechanical properties [16]. Less focus has been paid by the researchers on the effects of Co into Sn-Bi. Cobalt is one of the potential candidate and can be added to the Sn-Bi solder alloys to enhance the reliability of the solder [26]. To understand the Sn-Bi-Co system, information such as microstructure on interfaces, microstructure on solder matrix, the formation of intermetallic compounds after reflow and after aging, and the rate of growth of IMC after the addition of Co to the system are required. The major problem of the Sn-Bi solder alloy is the increment of IMC thickness when the electronic device is in service [23, 24]. There is a need to understand the effect of the addition of Co nanoparticles into the Sn-Bi solder alloy at high-temperature. As no research has been done to investigate the effects of cobalt nanoparticle addition into tin-bismuth solder alloy. In this study, different concentration of Co nanoparticle has been added into the Sn-58Bi solder alloy to obtain the information required.

The purpose of this study is to investigate the effect of cobalt NP in Sn-58Bi on the structural properties after reflow and after aging. Different reflow profiles were suggested in this work to obtain the sample with fewer voids. After the reflow process, the aging process under different temperatures was performed to obtain the effect of Co on the Sn-58Bi solder joint.

2. METHODOLOGY

The preparation of the copper substrate and solder paste are the initial steps. The copper substrate was cleaned and ground by using 3000 grit silicon carbide paper to remove the oxide layer. The copper substrate was dipped into the sulphuric acid and washed with distilled water, followed by drying to remove the remaining oxide and impurities. An appropriate amount of the eutectic tin-bismuth (Sn-58Bi) solder paste was mixed with 0.5% of cobalt nanoparticle. The initial cobalt NP size was 28 nm. The mixture was manually blended for 30 minutes. The mixture was then placed on a copper sheet through a mask with an opening of 6mm diameter and a height of 1 mm as shown in Figure 1 (a). It resulted in the solder paste having a cylinder shape. For solder paste with 1% and 2% of cobalt nanoparticle addition, the same procedure was repeated.

The solder paste was then reflowed in a reflow oven at 170°C for 45 seconds. The variation of temperature was kept at ±8°C. Another reflow sample was obtained at 180°C for 1 minute. The solder joints with 0 wt% Co and 0.5 wt% Co nanoparticle addition were subjected to high-temperature aging. The Aging Temperature (70, 85, 100) °C and Aging Time 504 Hour's used. Samples were cross-sectioned using the standard metallographic technique. The samples were placed vertically on a molding cup with an inner diameter of 30 mm and held using the sample holders as shown in Figure 1 (b). The microstructure and morphology analysis was carried out by using the (Phenom Pro X) scanning electron microscopy (SEM). For energy-dispersive X-ray spectroscopy (EDS), spot analysis was used. The thickness of IMC was assessed on multiple SEM images taken at a magnification of 5000x for each sample. By dividing the area of each IMC by its length, the average thickness of the IMCs was computed. Olympus Analysis Software was used to perform the measurements.

RESULTS AND DISCUSSION:

Microstructure after Reflow:

Figure 2 (a), (b), (c) and (d) shows the scanning electron micrograph images of Sn-58Bi, Sn-58Bi-0.5Co, Sn-58Bi-1Co and Sn-58Bi-2Co after reflow. The microstructure of Sn-58Bi-0Co has two distinct phases. The Bi-rich phase is the brighter phase, while the Sn-rich phase is the darkest phase. Similar results were found by the researcher in the past [23, 24]. The structure of tin and bismuth were broken down and grain size was reduced when Co nanoparticles were introduced to Sn-58Bi [27] as shown in Figure 2 (b), (c), and (d). Researchers have also found similar alterations in the structure of Sn-58Bi solder after Ni nanoparticles were added [23, 24]. Sakuyama et al. reported that the microstructure of the Sn-58Bi solder joint changed when a third element (Ag, Cu, Sb, and Zn) was added [27].

Figure 3 (a) and (b) show the BSE cross-sectioned image of the Sn-58Bi-2Co solder joint. When Co-nanoparticles were introduced to the solder, the coarsened Sn-rich phase was seen. The cobalt content at the chosen location 1 in Fig 3 (a) was 1.54 wt% or 3.89 at% as shown in

Table I, which means that the cobalt nanoparticles might be able to coarsen the Sn-rich microstructure. Yang et al. reported that when the Ni content in the solder matrix is low, the Ni3Sn4 grains disperse uniformly and appear as heterogeneous nucleation. However, as the wt% of Ni grows, the nucleation may become more concentrated in the solder. The grains coarsening is caused by the concentrated Ni3Sn4's inability to properly suppress grain growth. Due to this, the coarsened Sn-rich phase was observed in Sn-58Bi-2Co. The coarsening of the Sn-rich phase might be able to improve ductility slightly. From Table I, it was observed that the amount of cobalt added to the solder was not completely dissolved into the solder. The amount of Co dissolved into the solder was approximately 50% to 75% on the solder bulk. The rest of the nanoparticles were removed from the solder by the flux. The solder flux prevents the oxidation of metal at high temperatures and removes the oxides from the solder. The low density of solder flux at high temperatures will flow out from the solder due to the buoyancy force [28]. The oxidized cobalt particles might be removed by the flux from the solder to the surface, thus it cannot completely dissolve in the solder [29].

Figure 4 shows the SEM image of IMC layer of the solder Sn-58Bi with addition of (a) 0%, (b) 0.5%, (c) 1% and (d) 2% of Co-nanoparticles. IMC layers on the substrate were found on all solder joints. The interfacial IMC thickness of Sn-58Bi, Sn-58Bi-0.5Co, Sn-58Bi-1Co, and Sn-58Bi-2Co after reflow were 1.37µm, 1.25µm, 1.17µm, and 0.62µm respectively as shown in Figure 5. Sn-58Bi solder had the highest interfacial IMC thickness of all the samples. The results proved that cobalt addition could suppress the growth of interfacial IMC thickness of the solder. Tay et al. [30] and Gain and Zhang [23] have found that adding Ni to SAC and Sn-58Bi solder can slow the formation of Cu_3Sn and reduce the thickness of the IMC. Through the reflow process, the Ni nanoparticle dissolved into the IMC and formed $(Cu, Ni)_6Sn_5$. Tay et al. also found a similar result where the Co-nanoparticle dissolved into the molten solder of SAC and formed $(Cu, Co)_6Sn_5$ IMC [29]. The current study also observed that the Co-nanoparticle addition formed the (Cu, Co)$_6$Sn$_5$ IMC which suppressed the growth of IMC thickness.

Table I shows the EDX analysis on the solder matrix of Sn-58Bi-xCo. The results show that the overall composition of the Co element in the solder matrix of Sn-58Bi-0.5Co was 0.24 wt% or 0.71 at%. The Co element in the solder matrix of Sn-58Bi-1Co and Sn-58Bi-2Co were 0.96 wt% or 1.87 at% and 1.54 wt% or 3.89 at%, respectively. This was because, during the reflow process, some of the cobalt nanoparticles were removed together with the flux [29]. So, in comparison to the concentration added to the Sn-58Bi, the Co element concentration was comparatively low. EDX analysis on the interfacial IMC layer of the Sn-58Bi-1Co solder joint in Table I shows that the composition of the IMC layer contains mainly copper and tin with a very low amount of cobalt. Based on the atomic concentration obtained as shown in Table I, the intermetallic compounds detected on the IMC layer were (Cu, Co)$_6$Sn$_5$. Bashir et al. found that (Cu, Co)$_6$Sn$_5$ IMC was formed when Co NP was added to SAC305 solder joint [15]. According to Cu-Sn alloying system, Cu_5Sn_6 and Cu_3Sn are the possible intermetallic compounds formed in the alloy. Tay et al. [29] reported that the Cu_6Sn_5 would form once it is reflowed, but the Cu_3Sn normally formed during the thermal aging or long reflow soldering process. Gain et al. also reported that during the reflow soldering, only a very thin layer of Cu_3Sn was found in the IMC of Sn-58Bi and also Sn-58Bi-0.5Co after holding for around 30 minutes at 160°C or 180°C. The interfusion of the Cu atom into the solder at such a shorter reflow time is not enough for the formation of Cu_3Sn. The cobalt nanoparticles added to the solder could hinder the formation of Cu_3Sn. Thus, the formation of Cu_3Sn was not found in the solder [23].

Microstructure after Aging:

Figure 6 (a), (b) before thermal aging and (c), (d), (e), (f), (g), and (h) after thermal aging, respectively, shows the interfacial IMC thickness at 504 hours along with the interface between the copper substrate and Sn-58Bi-xCo solder. From Table II, it can be seen that as the temperature was increased from 0°C to 100°C, the IMC layer thickness was also enhanced. After aging, both samples of Sn-58Bi and Sn-58Bi-xCo showed growth in the interfacial IMC layer. But the growth rate was controlled in the Sn-58Bi-xCo interfacial IMC layer as compared to the Sn-58Bi interfacial IMC layer. By this measurement, the addition of Co nanoparticles to the composite solder system hindered the creation and the following expansion of the IMC layer at their interfaces. Tay et al. reported that the cobalt nanoparticle in SAC solder causes the Cu_6Sn_5 to grow faster as compared to Cu_3Sn[29]. The authors thermally aged the sample at 150°C and found out that the addition of cobalt could suppress the growth of Cu_3Sn. Besides, the authors also found the Co composition on the Cu_6Sn_5 IMC layer but not the Cu_3Sn layer. During solidification, the production of fine Co-containing IMC particles in the solder matrix resulted in a high nucleation density, which impeded the IMC growth behaviour of composite solder connection [23].

From Figure 7 (a) & (b) low melting point as a function of response time, interfacial IMC layers differ between Sn-Bi solder connections and composite solder connectors created by adding Co NP in contact with Cu substrate. As reaction temperatures and time increased, the values of interfacial IMC layer thicknesses of all solder systems increased. (Fig 7, a and b). In Figure 7 (a) for plain Sn-58Bi, after a reaction period of 126 h (hours), the IMC layer thicknesses of plain Sn58Bi formed by reaction temperatures of 70°C, 85°C, and 100°C were about 0.6 µm, 0.62 µm, and 0.8 µm, respectively. After 504 h reaction time at temperatures of 70°C, 85°C, and 100°C, their IMC layers thicknesses were about 1.82 µm, 2.45 µm, and 3.2 µm, respectively. In Figure 5 (b) for Sn-58Bi-0.5Co, after 126 h reaction time at temperatures of 70°C, 85°C, and 100°C, their IMC layers thicknesses were about 0.35 µm, 0.55 µm and 0.58 µm, respectively. After 504 h reaction time at temperatures of 70°C, 85°C, and 100°C, their IMC layers thicknesses were about 1.69 µm, 1.77 µm, and 2.37 µm, respectively. A comparison of interfacial IMC growth of Sn-58Bi Sn-58Bi-xCo with the literature has been furnished in Table II. However, From Table II, we have seen that when temperature increases from 160°C to 200°C, the IMC growth for plain Sn-58Bi and Sn-58Bi-0.5Ni has increased, but the growth rate for Sn-58Bi-0.5Ni was slow as compared to plain Sn-58Bi[23]. The addition of Co NP to the interfaces hindered the development and growth of the IMC layer. During solidification, the production of fine Co-containing IMC particles in the solder matrix resulted in a high nucleation density, which impeded composite solder connections' IMC growth behaviour. It has been observed in the literature that rare-earth elements can obstruct the formation of an IMC layer in two ways: by changing the diffusion coefficient and the thermodynamics of elemental affinity.

CONCLUSION:

In this work, tin-bismuth with/without the addition of cobalt nanoparticles were analyzed. The microstructure of the solder matrix and interfacial IMC thickness before and after thermal aging has been investigated. The following conclusions can be drawn:

1. The image obtained from SEM showed that Co-nanoparticle addition has refined the structure of Sn-58Bi solder and reduced the grain size. EDX analysis results exhibit that the actual concentration of cobalt in the solder bulk and intermetallic compound layer is lower than the percentage added. The result shows that the addition of cobalt nanoparticles causes a small reduction in interfacial IMC thickness after the reflow process.

2. Sn-58Bi and Sn-58Bi-0.5Co were undergone thermal aging at 3 different temperatures 70°C, 85°C, and 100°C for 504 hours. Both samples showed interfacial IMC growth after increasing time and temperature. The growth of interfacial IMC of Sn-58Bi-xCo was significantly controlled as compared to Sn-58Bi.

3. From the EDX analysis results, Cu_6Sn_5 IMC was found at the interfaces of both Sn-58Bi & Sn-58Bi-xCo solder joints, but Cu_3Sn can only be found in the Sn-58Bi solder joint. It can conclude that the Co atom enhances the stability of Cu_6Sn_5 and suppresses the growth of Cu_3Sn.

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Compliance with Ethical Standards:

The authors followed the ethical standards during the experiments as well as during the preparation of the manuscript.

Author contribution:

All authors equally contributed to the conception and design, material selection, sample preparation, experiments, characterization, data collection, data analysis and manuscript preparation.

Competing Interests:

The authors have no relevant financial interests to disclose.

Research Data Policy and Data Availability:

The current study is based on experimental data. In the manuscript, the experimental data were correlated and discussed with existing studies done by other researchers (given in the references). The experimental data of the current study is unpublished and will be provided when required.

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