Investigation on the Interfacial IMCs Layer of Sn-58Bi/Cu Solder Joints

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Abstract. The interfacial intermetallic compounds (IMCs) layer of Sn-58Bi lead-free solder reacting with Cu substrate were explored at aging stage after soldering for 1 day, 3 days, 6 days, 8 days and 10 days, respectively. Results show that Bi doesn’t react with Cu atoms or Sn atoms. The IMCs layer is composed of Cu6Sn5 phase and Cu3Sn phase. The IMCs layer evolves from scalloped shape to layer shape with addition of aging time, meanwhile, Bi phase in matrix grows bigger. The growth kinetic equation of IMCs layer is obtained and described as \( X = 1.06 + 0.69t^{1/2} \), where 0.69\( \mu \)m/d\(^{1/2} \) is the growth coefficient. Compared with Sn-3Ag-0.5Cu lead-free solder, the growth coefficient of Sn-58Bi solder is much smaller. Accordingly, the growth of IMCs layer of Sn-58Bi solder is more slowly than that of Sn-3Ag-0.5 Cu solder.

1. Introduction
Solder interconnecting technology is used in various packaging applications such as ball grid array and flip chip technology, therefore reliability is undoubtedly an essential characteristic of any electronic device [1]. Cu is used extensively as the contact metallization in conventional electronics assemblies particularly on printed circuit boards (PCBs) and increasingly as the interconnection layer on semiconductor devices, while Sn-based alloys, especially, Sn-Pb alloys, are almost universally used as solders [2]. However, with the increasing demand of about environment and folks’ health, Sn-Pb alloy has attracted human’s increasing attention due to the toxicity of lead. As most of developed countries have legislated strictly to prohibit the use of Pb in most electronic components, scholars have dedicated tremendous efforts on lead-free solders as a replacement of Sn-37Pb eutectic solder [3]. Accordingly, Sn-Bi lead-free solder has been considered as one of the most promising lead-free products to replace conventional Sn-Pb solders in recent years. The eutectic alloy consists of a eutectic composition of 42 wt% Sn and 58 wt% Bi with a melting point of 138°C. Its low melting point makes it widely used in some special situation for soldering [4, 5].

Eutectic Sn-58Bi, was chosen as the basic solder alloy because it is cheaper than In-Sn solder, while the volume change on melting is negative. He [4] investigated the Bi layer formation with different current densities and obtained that the electromigration force and Joule heating took on the main driving forces for Bi diffusion and migration. Yen [6] researched interfacial reactions of Sn-58Bi and Sn-0.7Cu lead-free solders with alloy 42 substrate and found that no spalling IMCs observed at the solder/Alloy 42 interface as reflow temperature increased. As Sn-58Bi is low melting alloy, it can be widely used only the reliability meets the requirement of solder joints. Accordingly, the reliability
of Sn-58Bi/Cu solder joints is researched in this study, owing to the IMCs layer is the key to the reliability of solder joints, the aim of the paper is to explore the grows kinetics of IMCs layer.

2. Experimental procedures
The commercial copper plates with dimensions of 20 mm x 20 mm x 2 mm were used as the substrates in this study. The copper substrates were ground with silicon carbide paper and polished with 0.25µm diamond paste until a mirror surface was obtained. The prepared substrates were then dipped into 5% (by volume) nitric acid (HNO₃) to remove any oxide layer. Sn-58% Bi solder paste was then placed on the substrates with a diameter of 5 mm, and solder joints were formed with a F4N infrared reflow furnace. The specimens were reflowed at above liquidus temperature but the peak temperature wasn’t beyond 170°C for 250s.

After reflowing, the prepared solder joints were performed isothermal aging test in an vacuum drying oven at 120°C for 1 day, 3 days, 6 days, 8 days and 10 days, respectively. In order to investigate the formation and evolution of interfacial IMCs layer, specimens were sectioned perpendicularly to the solder/copper interface of the solder joint and mounted in Klarmount. The microstructure of solder joints after solid-state aging were observed using backscattered scanning electron microscopy (BSEM) and the elemental compositions of interfacial IMC layer were determined by energy dispersive X-ray spectroscopy (EDX) analysis.

Considering the reliable and repeatable accurate data of the mean thickness of IMCs layer, ten different BSEM images of a same magnification (2000x) for each specimen were used, SEM image analysis software was then employed to digitally measure the areas of the IMCs layers. The thickness of IMCs layers is determined by the area of the IMCs layers dividing its length. The mean thickness of IMCs layers was then calculated by averaging the above five data.

3. Results and discussion
Fig.1 shows the micrographs of Sn–58%Bi/Cu solder joints aged at 120°C for various times. As aged for 1 day, the IMCs is an extraordinary thin layer, Bi phase disperse randomly in the Sn matrix shown in Fig.1 (a), with aging time extended, the scalloped IMCs layer grows thicker, meanwhile, Bi phase coarsens to dendritic shape, as Sn has almost no solubility in Bi, Bi phase and Sn phase are separated in matrix. When the aging time increased to 8 days, the scalloped IMCs layer evolves to layer shape. In addition, the IMCs layer grows gradually thicker accompanied with larger Bi phase over time.

In order to identify the chemical compositions of solder matrix and the IMC phases based on the gray level in BSE micrographs in Fig.1, EDX analysis are used to confirm the phases. Fig. 2 (a) illustrates that the IMCs layer adjacent to the bulk solder which is pointed by slim arrow in Fig.1 (e) is Cu₆Sn₅, which is composed of 52.64 at.% Cu and 47.36 at.% Sn. Fig. 2 (b) shows that the IMCs layer adjacent to Cu substrate pointed by fat arrow in Fig.1 (e) is Cu₃Sn phase which is distinguished from the other IMC by its gray level, and it is composed of 79.05 at.% Cu and 20.95 at.% Sn. Hence, it can be confirmed that Bi can’t react with Cu substrate. While at soldering stage, Cu atoms diffuse to matrix and react with Sn, proceeding as

$$6\text{Cu} + 5\text{Sn} \rightarrow \text{Cu}_6\text{Sn}_5$$ (1)
Figure 1. Micrographs of Sn–58%Bi/Cu solder joints aged at 120°C for (a) 1 day, (b) 3 days, (c) 6 days, (d) 8 days and (e) 10 days.

At aging stage, as Cu$_6$Sn$_5$ is nonequilibrium, with the addition of aging time, to keep the balance of system and lower the free energy of the system, Cu atoms diffuse to matrix and react with Cu$_6$Sn$_5$, which follows

$$9Cu + Cu_6Sn_5 \rightarrow 5Cu_3Sn$$  \hspace{1cm} (2)
Figure 2. EDX analysis of IMCs layer: (a) slim arrow (b) fat arrow in Fig.1 (e).

As is known that the growth of IMCs layers follows diffusion controlled mechanism at aging stage[7, 8], the thickness of IMCs layers were measured and plotted with square root of time so as to explore the grows kinetics of IMCs layer. Fig.3 illustrates the thickness of IMCs layer is linearly growth with square root of aging time, which indicates it follows diffusion controlled mechanism. By linear fit, the growth equation of IMCs layer is obtained, which is described by

$$X=1.06+0.69t^{1/2}$$ \hspace{1cm} (3)

Where 0.69 is growth coefficient $k$, it reflect the growth rate of IMCs layer. Usually, smaller $k$ corresponds to thinner IMCs layer, which results in better reliability of solder joints. Compared with our previous study, the growth coefficient $k$ of Sn-3Ag-0.5Cu solder is 1.95 $\mu$m/d$^{1/2}$, therefore, it can be concluded that the growth of Sn-58Bi solder joint is much more slowly than that of Sn-3Ag-0.5Cu solder joint.

Figure 3. Average thickness of the IMC layers of Sn-58Bi/Cu joints with different aging time.

4. Conclusion

The interfacial reaction of eutectic Sn–58wt% Bi lead-free solder with Cu substrate aging for various times was investigated in this study. Bi doesn’t react with Cu atoms or Sn atoms, the IMCs layer are composed of Cu$_6$Sn$_5$ and Cu$_3$Sn phase. With aging time extended, the IMCs layer not only evolves from scallop shape to layer shape but also grows thicker, simultaneously, Bi phase in matrix grows larger. The growth kinetics equation of Sn–58wt% Bi solder is obtained by linear fit the thickness of IMCs layer with square root of aging time, the growth coefficient of IMCs layer is gained which is 0.69$\mu$m/d$^{1/2}$, it is illuminated that the growth of Sn-58Bi solder joint is much more slowly than that of Sn-3Ag-0.5Cu solder joint.
Acknowledgments

This work was financially supported by National Natural Science Foundation of China (NSFC) under grant No. 51604012 and 51575004, Foundation of Beijing outstanding talent training under grant No.201400020124G010, and Natural Science Foundation of Beijing (NSFB) under grant No.3162010.

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