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Aging and Cu concentration effects on Sn–9Zn–xCu/Au couples

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ABSTRACT

Aging and Cu concentration effects on the interfacial reactions between Sn–9 wt%Zn–*x* wt%Cu (SZ–*x*Cu) alloys and the Au substrate were investigated in this study. The Au_3Zn_7/$AuZn_2$/AuZn and Au_3Zn_7/AuZn phases were formed in the SZ/Au and SZ–1Cu/Au couples aged at 160 °C for 24 h. Only the AuSn phase was found in the SZ–4Cu/Au couple aged at 160 °C for 24 h. When the aging time was extended to 800 h the Sn atoms became the dominant diffusion element. Binary Au–Sn phases and the metastable Au–Zn–Sn ternary phase were formed at the interface in the SZ–*x*Cu couples when the Cu content was 1–4 wt%. When the Cu content was increased to 7–10 wt% AuSn and (Cu, Au)Sn phases were observed at the alloy/Au interface aged at 160 °C for 24 h. After 800-h heat treatment the SZ–*x*Cu systems were transformed completely into the Cu–Sn/Au systems. The (Cu, Au)SnAuSn and Cu_6Sn_5/AuSn were formed in the SZ–7Cu/Au and SZ–10Cu/Au couples. The results indicate that the evolution of intermetallic compounds (IMCs) was very sensitive to the Cu concentration in the SZ solders and the heat treatment period.

1. Introduction

Gold (Au) is a very important material in electronic packaging. For example, an Au layer is electroplated onto a Ni surface in the under bump metallization (UBM) multilayer structure and printed circuit board (PCB). The Au stud-bump bonding (SBB) technology has recently developed as a very attractive solution for a low-cost flip-chip technology. The function of Au layer is to provide protection against oxidation and enhance the wettability [1]. Because of the toxicity of lead, Sn–Pb solders are forbidden in electronic devices and products [2,3]. The liquidus temperature of a Sn–9 wt%Zn (SZ) solder is close to that of Sn–Pb solders, giving SZ solder the potential to replace Sn–Pb solders. However, the poor wettability of SZ solder is a serious problem restricting its use in the electronic industry.

Yu et al. investigated the SZ/Cu system and revealed that the addition of Cu to SZ solder could improve its poor wettability and enhance its anti-oxidation properties [4]. Kao et al. studied the interfacial reactions of Sn–*x*Zn/Cu systems and reported that the Zn concentration strongly influenced the interfacial reactions [5]. Suganuma and Kim found that the formation of Cu–Zn intermetallic compounds (IMCs) was unstable when the reaction temperatures were above 150 °C in the SZ/Cu system [6]. Yen et al. discovered that the IMC formation in the SZ–*x*Cu/Ni, SZ–*x*Cu/Ag and SZ–*x*Cu/Au systems dramatically changed with the Cu concentration in the SZ solder [7–9]. We also mentioned that the IMC evolution in Sn–*x*Zn/Au couples aged within 1 h was very sensitive to the Zn content in Sn–Zn alloys in our previous studies [10]. This current work does address the matter in a more systematic way, by varying the Cu content in the solder from 0 to 10 weight percent at 160 °C for 6–800 h. We hope to obtain a reasonable explanation for the change in IMC evolution caused by the substitution of dominant diffusion elements due to aging and Cu concentration effects.

2. Experimental procedure

Sn–9 wt%Zn alloys containing 0, 1, 4, 7, and 10 wt% Cu were prepared from high purity Sn, Zn and Cu shots above 99.0 wt% purity. Each alloy was encapsulated in a quartz tube in a vacuum (0.13 N/m^2) and placed in a furnace at 900 °C for 48 h for homogenization. The sample tube was quenched in icy water after the aging process. The small alloy ingot was removed from the tube and dissected into disk-shaped specimens with a diameter of 6.0 mm and a thickness of 1.0 mm. The interfacial reaction between the solder and substrate was carried out using the solid/solid reaction couple technique. Two SZ–*x*Cu alloy disks and one Au foil with 3.5 mm × 3.5 mm × 100.0 μm dimensions were sandwiched together using two stainless steel screws. Boron nitride powders were sprayed onto the screws to prevent them from reacting with the SZ–*x*Cu alloys. The SZ–*x*Cu/Au/SZ–*x*Cu sandwich was encapsulated into an evacuated quartz tube and placed in a furnace to age at 160 °C for 6–800 h. After the aging reaction couple was quenched in icy water. The reaction couple schematic diagram is similar to that in a previous work [10].

The samples were treated using a standard metallographic process prior to inspection. Optical-microscopy (OM) and scanning electron microscopy (SEM) were used to observe and thoroughly examine the solder/substrate interface morphology. SEM with an energy dispersion spectrometer (EDS) and an electron probe micro-analyzer (EPMA) were used to precisely determine the IMC compositions formed at the interface between the solders and substrates.

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3. Results and discussion

3.1. SZ–xCu couples aged for 6 h

Fig. 1a presents a backscattered electron image (BEI) micrograph of the SZ/Au couple aged at 160 °C for 6 h. Two IMC layers are observed as shown in Fig. 1a. According to EPMA analysis and the binary phase diagrams of the Au–Zn and Sn–Zn systems [11], the dark layer was the Au_3Zn_7 phase with a composition of Au–43.5 wt%Zn. The gray layer is the $AuZn_3$ phase with Au–50.9 wt%Zn composition [11]. Fig. 1b shows a BEI micrograph of the SZ-1Cu/Au couple aged at 160 °C for 6 h. One IMC layer with a composition of Au–43.3 wt%Zn was formed and it was likely to be the Au_3Zn_7 phases [11].

A BEI micrograph of the SZ–4Cu alloy reacted with Au at 160 °C for 6 h is shown in Fig. 1c. Only an AuSn phase layer with a composition of Au–36.7 wt%Sn was found at the interface [11]. An irregular shaped Cu–58.0 wt%Zn region was observed in the solder and it was probably the Cu_5Zn_8 phase [11]. The surface morphology of the SZ–7Cu solder reacted with Au at 160 °C for 6 h is shown in Fig. 1d. The layered phase was composed of Au–37.0 wt%Sn, which was likely the AuSn phase [11]. An irregularly shaped region with Cu–49.3 wt%Zn composition was observed in the solder and it was likely the CuZn phase [11]. The surface morphology of the SZ–10Cu solder reacted with Au at 160 °C for 6 h is shown in Fig. 1e. The IMC layer composition was Au–36.9 wt%Sn, and it was the AuSn phase [11]. An irregularly shaped region observed in the solder was composed of Cu–49.6 wt%Zn. It was likely to be the CuZn phase [11]. Increasing the Cu content in the SZ alloys would influence the IMCs formed at the interface and cause them to segregate in the SZ–Cu alloys.

3.2. SZ–xCu couples aged for 24 h

Fig. 2a presents BEI micrographs of a SZ/Au couple aged at 160 °C for 24 h. Three IMC layers are found at the SZ/Au interface in Fig. 2a. The phase composition close to the Au side was Au–25.8 wt%Zn belonging to the AuZn phase [11]. The phase in the vicinity of the solder side was composed of Au–42.7 wt%Zn and was the Au_3Zn_7 phase [11]. The composition of the third phase between the Au_3Zn_7 and AuZn phases was Au–31.3 wt%Zn and it was likely the $AuZn_2$ phase [11]. The micro-island shaped phases spreading over the solder in Fig. 2a were also Au_3Zn_7 phases. Something different happened at the alloy/Au interface as the Cu addition into the SZ solder reacted with the Au. Fig. 2b shows a BEI micrograph of the SZ–1Cu/Au couple aged at 160 °C for 24 h. Two IMC layers with compositions of Au–31.7 wt%Zn (gray and thick) and Au–25.2 wt%Zn (bright and thin) were formed and determined to be the $AuZn_2$ and AuZn phases [11]. A phase shaped like a micro-island was also found in the solder. This phase had a unique composition of Au–9.2 wt%Cu–43.0 wt%Zn. It should be the Au_3Zn_7 phase with 9.2 wt% Cu solubility [11], which was labeled the $(Au, Cu)_3Zn_7$ phase. This result indicates that a considerable amount of Cu atoms were incorporated into the sub-lattice of the Au_3Zn_7 phase.

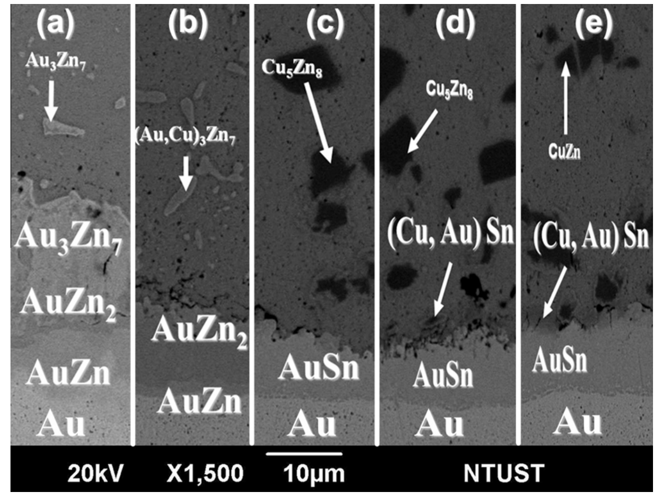

Fig. 2. BEI micrograph of the SZ alloy added (a) 0, (b) 1, (c) 4, (d) 7, and (e) 10 wt% Cu reacted with Au at 160 °C for 24 h.

A BEI micrograph of SZ–4Cu alloy reacted with Au at 160 °C for 24 h is shown in Fig. 2c. Only a flat AuSn layer with a composition of Au–36.9 wt%Sn was found at the interface [11]. In addition, an irregular shaped Cu–58.0 wt%Zn region was observed in the solder and it was should be the Cu_5Zn_8 phase [11]. Fig. 2d shows a BEI micrograph of the SZ–7Cu/Au couple aged at 160 °C for 24 h. A flat layer with a composition of Au–36.7 wt%Sn was found at the solder/Au interface and it was the AuSn phase [11]. Two kinds of irregular-shaped regions were also observed in the solder. One region had a composition of Cu–59.6 wt%Zn, and it was the Cu_5Zn_8 phase [11]. Another phase attached to the interface was analyzed with a composition of Cu–7.5 wt%Au–49.3 wt%Sn, labeled as the (Cu, Au)Sn phase [11,12]. Because Zn atoms were completely consumed, the Sn atoms became the dominate diffusion elements in this system. As more than 6 wt% Cu content was added into the SZ solder, the Cu atoms could rapidly react with Zn atoms to form the short-range-order (SRO) Cu–Zn IMCs in the solder [4,7,13]. The entire Zn element in the solder was completely consumed in forming the Cu_5Zn_8 phase. The excess Cu atoms moved and segregated onto the Au side and reacted with Sn and Au. The solder/Au interface then became the Sn–Cu/Au system and the (Cu, Au)Sn was observed spreading over the interface.

Fig. 2e shows a BEI micrograph of the SZ-10Cu/Au system aged at 160 °C for 24 h. Two kinds of IMC layers were observed at the interface. The thicker IMC layer was composed of Au–37.4 wt%Sn designated as the AuSn phase [11]. The composition of the thin IMC layer was Cu–13.7 wt%Au–49.9 wt%Sn, which was labeled the (Cu, Au)Sn phase [11,13]. An irregularly shaped region could be observed in the solder and with a Cu–49.6Zn composition belonging to the CuZn phase [11]. When the Cu content was increased to 10 wt%, enough Cu atoms reacted with Zn atoms to form Cu-rich Cu–Zn IMCs. The Au and Sn atoms were continuously inter-diffused toward interfaces with increasing aging time.

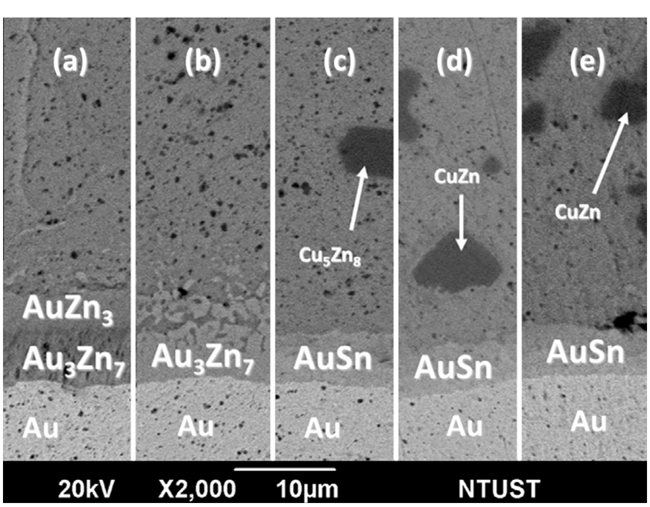

Fig. 1. BEI micrograph of the SZ alloy added (a) 0, (b) 1, (c) 4, (d) 7, and (e) 10 wt% Cu reacted with Au at 160 °C for 6 h.