The Interfacial Reaction between Sn-Zn-Ag-Ga-Al Solders and Metallized Cu Substrates

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The interfacial interaction between the Sn-8.55Zn-0.5Ag-0.5Ga-0.1Al solder and three kinds of metallized substrates (Cu, Cu/Au, and Cu/Ni-P/Au) does not form the Cu-Sn intermetallic compound (IMC). Continuous Cu-Zn and discontinuous Ag-Zn interfacial IMC layers formed between the Cu and Sn-Zn-Ag-Ga-Al solder, while Cu-Zn and Au-Al-Zn IMCs formed on the Cu/Au substrate. Only the Au-Al-Zn IMC formed at the interface when the electroless Ni-P deposit was the diffusion barrier between Cu and the Au surface layer.

Key words: Intermetallics, Pb-free solder, Sn-Zn alloy, metallization

INTRODUCTION

Various kinds of Sn-based alloy systems have been developed for replacing the Sn-Pb eutectic solder.[1–4] Among these, Sn-Ag- and Sn-Zn-based Pb-free solders show great potential for practical application. The Sn-Ag solder provides better mechanical properties, creep resistance, thermomechanical fatigue behavior, and solderability on copper and copper alloys than the Sn-Pb solder.[1,4,5–8] The melting temperature of the Sn-Zn eutectic solder approaches that of the Sn-Pb eutectic solder, i.e., 199°C for Sn-8.9wt.%Zn.[9] However, a number of issues must be addressed for this solder to be used in electronic packaging applications. These issues are melting temperature, wetting property, interfacial intermetallic compound (IMC) growth, etc. The corporation of additional elements may address these issues and improve the Sn-Zn intrinsic characteristics.

During soldering, the formation of an interfacial IMC can assist in the bonding between the solder and substrate.[10] However, fracture can occur at these interfacial IMCs because they are brittle. The interfacial IMC formed between Sn-Ag- and Sn-Zn-based solders and various metallized substrates has been investigated during soldering or high-temperature aging. Previous studies[11–13] indicated that Cu_6Sn_5 with a scallop shape and Ni_3Sn_4 with a short rod shape were the major IMCs formed between the Sn-Ag-based solder and the Cu and Ni substrates, respectively.

The Sn-Zn-based solders reacted with Cu substrates to form a continuous interfacial Cu-Zn IMC layer with no Sn content.[14–16] Zinc, rather than Sn, reacts with Cu during soldering. The aging of a soldered Cu/Sn-9Zn specimen at 125°C results in the growth of the Cu-Zn IMC,[17] while the Cu-Zn IMC dissolves upon aging at 150°C, providing a channel for Sn to diffuse into the Cu substrate and form the Cu-Sn IMC. It was shown[18] that two layers of IMC formed between Cu and the Sn-Zn-Ag solder: a continuous, Cu-Zn IMC layer near Cu and a nodular Ag-Zn IMC layer near the solder. The morphology of the Ag-Zn IMC changed from scallops to nodules as the Ag content in the solder increased from 0.3 wt.% to 2 wt.%. A fractional addition of Al into the Sn-Zn and Sn-Zn-Ag solders gave rise to congregation of Al at the interface to form a Cu-Al-Zn IMC layer.[19,20] The Cu-Al-Zn IMC layer acted as a diffusion barrier that retards interdiffusion between Sn and Cu.

It was shown[21] that the Sn-8.55Zn-0.5Ag-0.5Ga-0.45Al solder possessed excellent mechanical and oxidation resistance properties. However, this range of Al content in the Sn-Zn solder induces grain-boundary deterioration and degrades the mechanical strength.[22] Accordingly, it was attempted to further lower the contents of Al to 0.1%. The present study investigated the interfacial-reaction behavior between the Sn-Zn-Ag-Ga-Al solder and various

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metallized substrates, Cu, Cu/Au, and Cu/Ni-P/Au, at the low Al content of 0.1 wt.%.

EXPERIMENTAL PROCEDURE

The Pb-free solder investigated was Sn-8.55Zn-0.5Ag-0.5Ga-0.1Al, and the metallized substrates investigated were Cu, Cu/Au, and Cu/Ni-P/Au. The Au and Ni-P were electrolessly plated on a Cu rod (1-mm diameter) with a purity of over 99.9%. Before dip soldering, the substrate was degreased with 5wt.%NaOH at 70°C for 3 min, cleaned in 10 vol.% HNO_3 for 5 sec, and then dipped in a rosin mildly activated flux. A laboratory-prepared flux was used for dip soldering in the Sn-Zn-Ag-Ga-Al solder. The specimen was rinsed in deionized water for 5 sec after every step of the precleaning. The dipping temperature of the liquid solder was controlled at 230–270°C, and the immersion time was 15 sec. The as-soldered specimens were heat treated in a furnace at 150°C for the desired time to study the formation of interfacial IMCs upon aging. The cross sections of soldered specimens were polished with 0.3-μm Al_2O_3 prior to investigation by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and electron probe microanalysis (EPMA).

EXPERIMENTAL RESULTS

Wetting Properties

Table I lists the wetting data of different metallized substrates when reacting with the Sn-8.55Zn-0.5Ag-0.5Ga-0.1Al solder. The wetting time with Cu is less than 1 sec at and above 250°C, while it is 2.05 sec at 230°C. The results show good or acceptable wetting behavior with Cu. However, Cu/Au and Cu/Ni-P/Au substrates do not exhibit wetting with this solder at temperatures below 230°C. The wetting time is in the range of 1–2 sec at 250°C and above. The wetting forces are within 0.78–1.21 mN for all soldered specimens. In general, these data show that the solder exhibits better wetting ability of the Cu substrate than with the Cu/Au and Cu/Ni-P/Au substrates, and the wetting properties are improved by raising the dipping temperature.

Interfacial Reaction upon Dipping

Figure 1a shows that there are two IMC layers formed between the Sn-Zn-Ag-Ga-Al solder and the Cu substrate. Elemental mapping reveals that the inner layer (near Cu) is a Cu-Zn IMC, and the outer layer (near the solder) is a Ag-Zn IMC. The EDS analysis shows that the Ag:Zn atomic ratio of the Ag-Zn layer is 1:3. However, the electroless Au plating or electroless Ni-P/Au plating on Cu significantly varies the interfacial-reaction mechanism. Figure 2a presents a cross-sectional SEM image of the as-dipped specimen at 250°C for 15 sec. The corresponding elemental profiles (Fig. 2b) show that the interface consists of Au, Zn, and Al. The Au seems to form two separate layers with Zn (inner) and Al (outer), respectively. It is also possible that Zn forms a compound with Cu. The Cu and Sn are not in contact. The Au-Al-Zn region acts as a barrier layer to inhibit the interaction between Cu and Sn. The coexisting Au-Al-Zn region was also observed in the soldered Cu/Ni-P/Au specimen (Fig. 3). The electroless Au was deposited on the electroless Ni-P layer. The elemental profiles reveal that Al and Zn exhibit segregation behavior right next to the Au layer. The Sn and Cu are well separated from each other by the Ni-P layer.

Interfacial Evolution upon Thermal Aging

Figure 4 shows that a Cu-Zn layer of 2 μm formed after thermal aging at 150°C for 625 h. The Cu-Zn layer may grow up to 4 μm in some areas, as shown in Fig. 5. The EDS composition analysis of the IMC layer of Fig. 5 shows that this IMC consisted of Cu:Zn = 44.8:54.7, corresponding to the Cu_5Zn_8 IMC. The area detected in Fig. 5 does not show the Ag-Zn compound. Nevertheless, the elemental analysis of Fig. 4 indicates that a discontinuous nodular Ag-Zn compound formed in certain areas. The Cu and Sn are far from this area.

Thermal aging of the Cu/Ni-P/Au/solder specimen at 150°C up to 1,000 h indicates barrier behavior of the Ni-P layer, as seen in Fig. 6. The interfacial region contains Au, Al, Zn, and Ag. Gallium is distributed throughout the solder. The Au and Al form

Table I. Wetting Behaviors of the Sn-8.55Zn-0.5Ag-0.5Ga-0.1Al Solder on Cu, Cu/Au, and Cu/Ni-P/Au Substrates

(a) Wetting Time

Solder Bath Temperature	Substrate	Cu	Cu/Au	Cu/Ni-P/Au
	230°C	2.05	NA	NA
Wetting Time (sec)	250°C	0.99	1.35	1.80
	270°C	0.48	1.01	1.02

(b) Wetting Force

Solder Bath Temperature	Substrate	Cu	Cu/Au	Cu/Ni-P/Au
	230°C	0.78	NA	NA
Wetting Force (mN)	250°C	1.13	0.99	0.88
	270°C	1.16	1.21	1.10

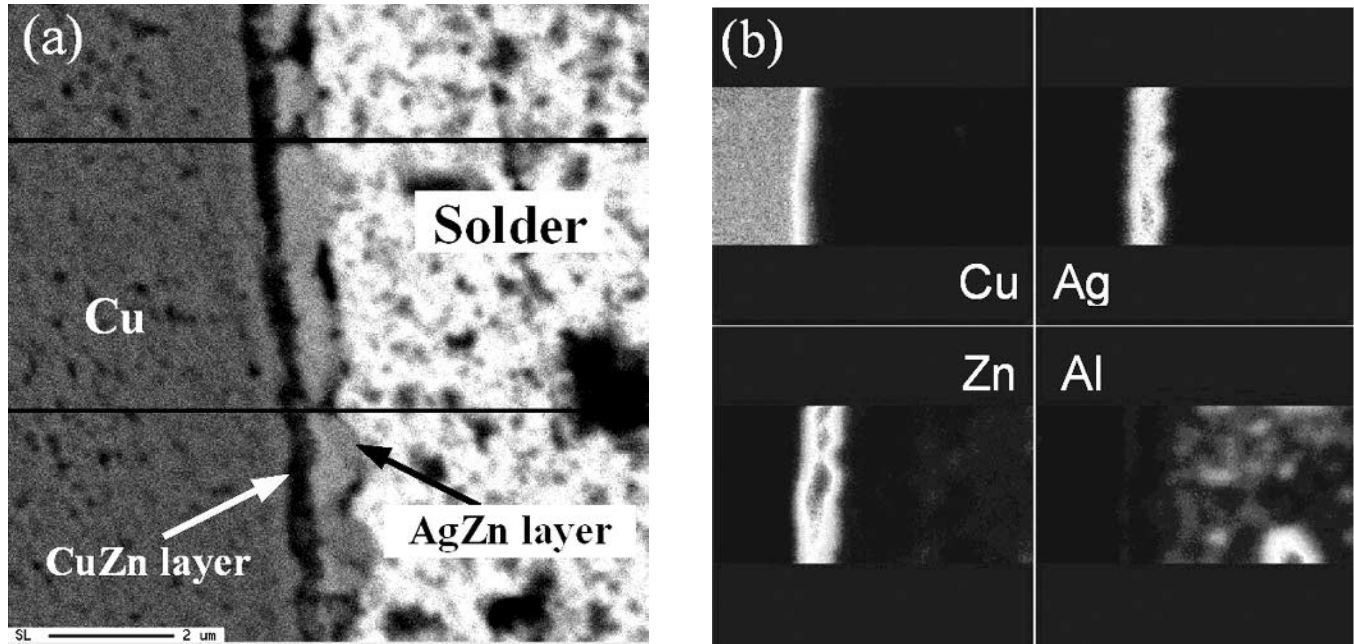

Fig. 1. The elemental distribution at the interfacial area of the as-dipped Cu/Sn-8.55Zn-0.5Ag-0.5Ga-0.1Al specimen: (a) backscattered electron image and (b) elemental distribution; dipping condition: 250°C for 15 sec; mapping area: between two straight lines.

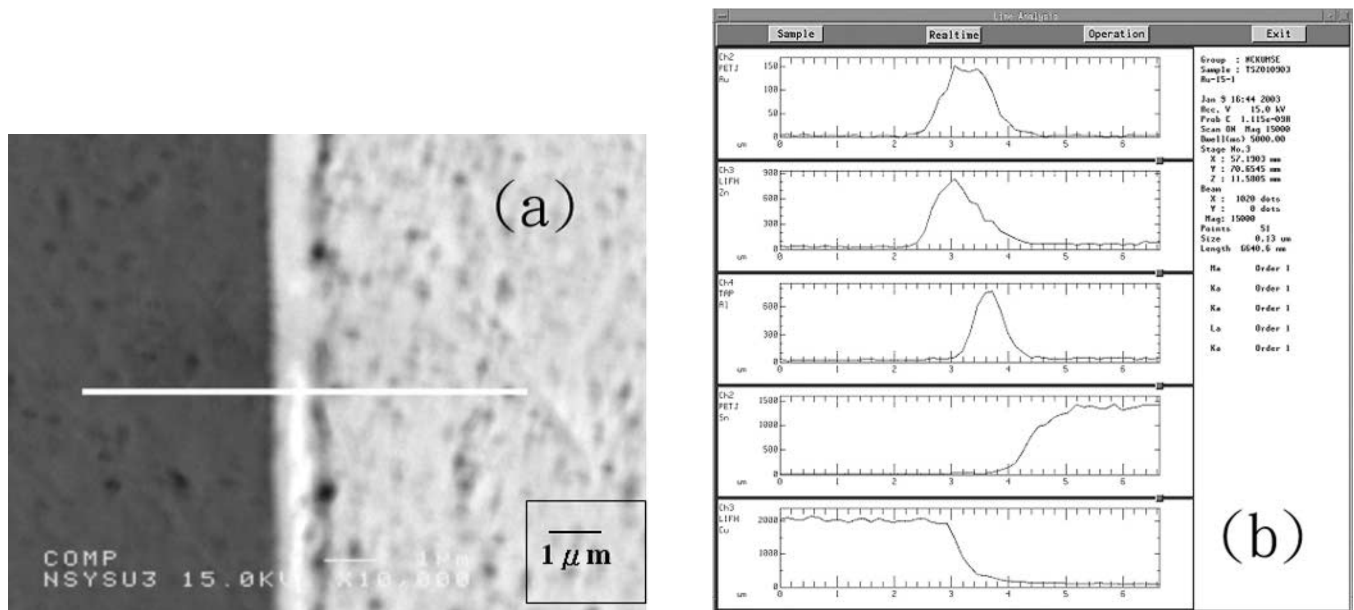

Fig. 2. The elemental profiles at the interface of the as-dipped Cu/Au/Sn-8.55Zn-0.5Ag-0.5Ga-0.1Al specimen: (a) backscattered electron image and (b) elemental distribution; dipping condition: 250°C for 15 sec.

a thin continuous layer (about 1–2 μm), while the Ag-Zn is a discontinuous layer. The edge of the Sn and Ni regions does not match with each other, showing evidence of no direct contact. The Cu and Sn are not interacting upon the thermal aging at 150°C up to 1,000 h.

The phenomenon of noninteraction between Cu and Sn with the solder was investigated for the Cu/Au/solder specimen. The thermal aging at 150°C up to 1,000 h results in the diffusion of Zn through the Au layer to form an IMC with Cu, as seen in Fig. 7. The EDS analysis of the Cu-Zn coexisting layer gives rise to a composition of Cu:Zn:Al = 45.95:53.1:0.96. This is also likely a Cu_5Zn_8 layer that contains Al. The Au layer exists between the solder and the Cu-Zn layer. There is no contact between Cu and Sn.

DISCUSSION

Wetting Properties

The wetting of the Sn-8.55Zn-0.5Ag-0.5Ga-0.1Al solder on the Au metallization surface is more difficult than that on the Cu substrate, as shown in Table I. This tendency is different from many other

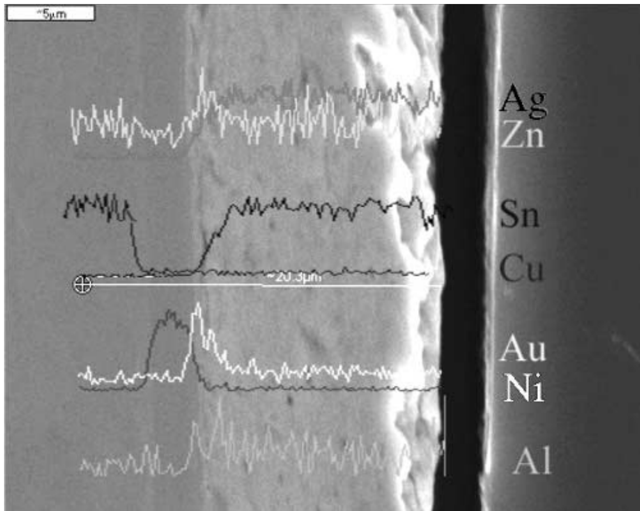

Fig. 3. The elemental profiles of the as-dipped Cu/Ni-P/Au/Sn-8.55Zn-0.5Ag-0.5Ga-0.1Al specimen; the dipping condition is 250°C for 15 sec.

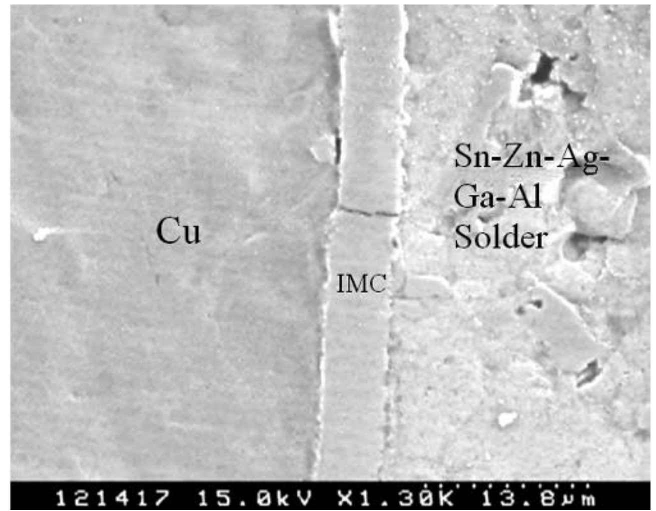

Fig. 5. An IMC layer (4 μm) formed in Cu/Sn-8.55Zn-0.5Ag-0.5Ga-0.1Al after thermal aging at 150°C for 625 h.

solder systems where the Au metallization generally improves wetting behavior. The degradation in wetting performance by Au metallization is ascribed to the different interfacial-reaction mechanism, as observed in Figs. 1–3. Gold dissolves into the solder rapidly when in contact with Sn-Pb solders. However, in the present study, Au reacts with Al and Zn of the solder to form a thin Au-Al-Zn IMC layer at the interface. Gold can form varieties of IMCs with Al and Zn. The Au-Al interaction is a very fast reaction. Accordingly, the interaction among Au, Al, and Zn is responsible for the poor wetting behavior.

Fig. 4. The elemental analysis at the interfacial area of long-time aged Cu/Sn-8.55Zn-0.5Ag-0.5Ga-0.1Al specimen; aged at 150°C for 625 h.

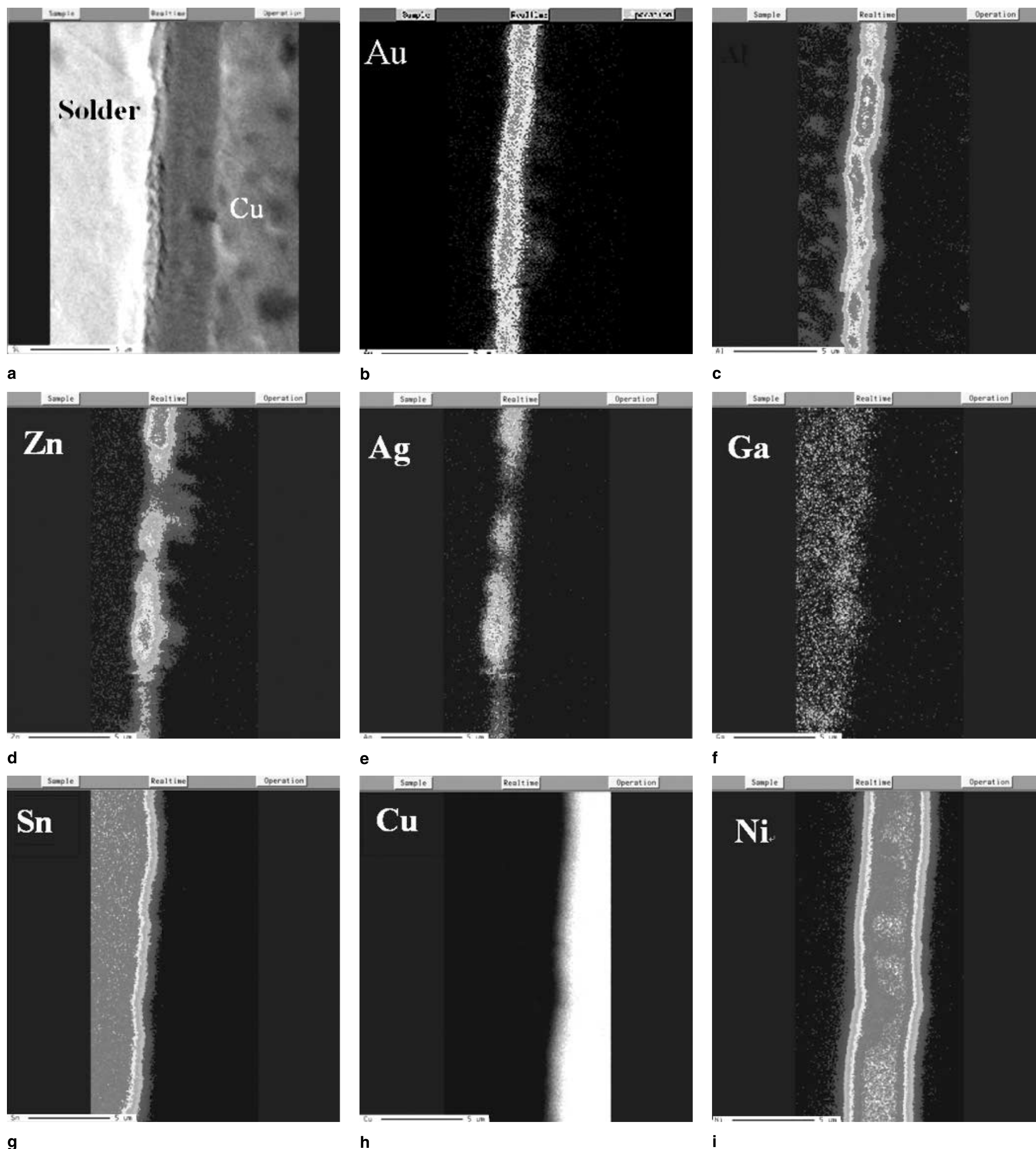

Fig. 6. The elemental distribution at the interfacial area of the long-time aged Cu/Ni-P/Au/Sn-8.55Zn-0.5Ag-0.5Ga-0.1Al specimen; aging condition: 150°C for 1,000 h.

Silver may also appear in certain areas because of the Ag-Zn interaction. These IMC formation reactions could result in fast wetting. Yet, it seems that the first-formed IMC layers with Au cease further interaction and, thus, degrade the wetting performance, in comparing with the wetting on Cu. On the other hand, the continuing reaction between Cu and Zn gives rise to good wetting performance in the wetting of Cu with the investigated solder.

The Interfacial Reaction

Based on the observation of the interfacial layer, the interfacial-reaction mechanism is described. Figure 8 is a schematic diagram of the interfacial

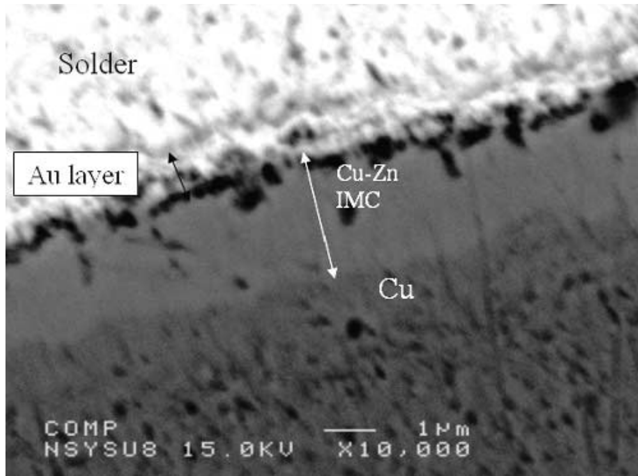

Fig. 7. The cross section of the aged Cu/Au/Sn-8.55Zn-0.5Ag-0.5Ga-0.1Al specimen; aging condition: 150°C for 1,000 h.

IMC formation between various metallizations and the Sn-Zn-Ag-Ga-Al solder. The Cu-Zn or Au-Al-Zn IMC layer was formed at the beginning of dip soldering. Afterward, the Ag-Zn IMC formed next to the previously formed IMC layer. It is likely that the Ag-Zn IMC is more difficult to nucleate on Au-Al-Zn (Fig. 3) than on the Cu-Zn IMC (Fig. 1) layer, and thus, only a very few $AgZn_3$ nodules were found. The Ag-Zn and Cu-Zn exhibit Ag_5Zn_8 and Cu_5Zn_8 compounds, respectively. Both compounds are of the same space group of $I\underline{4}3$(217) with the Pearson symbol of CI52. The Au-Al-Zn structure is not clear yet. But, it may belong to the Au-Al or Au-Zn compound. The Au-Zn compound may belong to tetragonal (Au3Zn), CsCl (AuZn), or cubic ($AuZn_3$). The Au-Al compound may belong to CaF_2 ($AuAl_2$) or hexagonal (Au_5Al_2).[23] All of the possible structures of Au-Al-Zn are dissimilar to that of the Ag-Zn compound. This may explain the easy nucleation of the Ag-Zn compound on Cu-Zn. Yet, the details of this mechanism need to be further explored. The detailed microstructure of the Au-Al-Zn layer remains to be investigated.

It was shown[19,20] that a thin and continuous Cu-Al-Zn IMC layer formed at the interface between the Cu and solder when 0.25% or more Al was added into the Sn-Zn or Sn-Zn-Ag solder. The phenomenon of Al segregated to the interface was not observed because of the low content (0.1%) of Al in the present study. Figures 2 and 3 show that Al was detected at the interface and reacted with Au and Zn to form an Au-Al-Zn or Au-Al IMC layer when the substrate was metallized with Au. The Gibbs free energy of compound formation of Au-Al, Au-Zn, Cu-Al, and Cu-Zn are −14.6 kJ/mole to −32 kJ/mole, −17.8 kJ/mole to −30.5 kJ/mole, −12.9 kJ/mole, and −11.5 kJ/mole to −12.3 kJ/mole, respectively.[24] The Gibbs free energy may not absolutely govern the interfacial reaction during dip soldering as the reaction does not reach equilibrium. However, the Au layer does react with Al upon dip soldering, while Al was

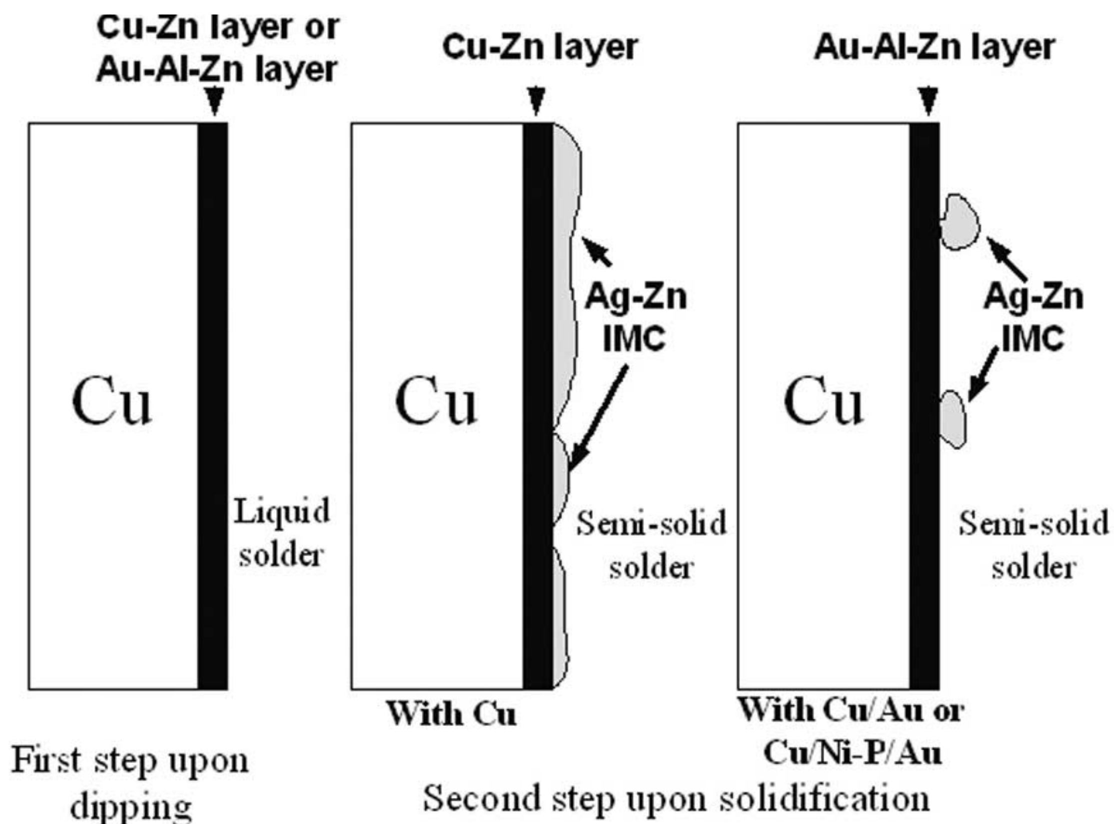

Fig. 8. A sketch of the interfacial IMC formation between Sn-Zn-Ag-Ga-Al and various metallized substrates.

not seen to segregate at the surface of Cu (Fig. 1). These observations correspond to the thermodynamic trend. Meanwhile, long-time thermal aging at 150°C (Fig. 6) of the Cu/Ni-P/Au/solder specimen gave rise to a distinct layer of Au-Al. Gold does not dissolve into the solder. The formation of the distinct Au-Al layer can be described thermodynamically. In view of the observations on dip soldering and thermal-aging specimens, the formation of the Au-Al layer is so fast that a barrier formed to avoid further diffusion between Ni and Sn and retarded interaction between Ni and Sn.

On the other hand, it was shown that the thin Cu-Al-Zn interfacial IMC layer formed between Cu and the Sn-Zn-Al solder acts as a diffusion barrier to retard the elemental interdiffusion between Cu and Sn and, thus, the IMC growth upon aging.[19] Nevertheless, the Cu-Al-Zn layer does not exist at the interface between Cu and the solder. The Ag-Zn compound is not a continuous layer (Figs. 1 and 4). Zinc can diffuse across the Ag-Zn layer to react with Cu and form a Cu-Zn IMC layer between Cu and the Ag-Zn IMC layer (Fig. 4).

A comparison of the results of Figs. 1, 4, and 7 illustrates that the inner Cu-Zn IMC layer grew upon aging in the Cu/Sn-Zn-Ag-Ga-Al and Cu/Au/Sn-Zn-Ag-Ga-Al specimens. The diffusion of Zn across the Ag-Zn IMC and Au layers takes place during heating. It is also possible that the Ag-Zn layer supplied Zn for Cu-Zn IMC growth. However, a comparison between Figs. 3 and 6 indicates that, in the Cu/Ni-P/Au/Sn-Zn-Ag-Ga-Al specimen, the thickness of the interfacial IMC layer did not significantly vary after long-time aging at 150°C. This observation suggests that the reaction between the Ni-P layer and the Sn-Zn-Ag-Ga-Al solder is rather restricted. There was no interaction between Zn and Cu. The interdiffusion of Zn was stopped by the entrapment of Zn in the Ag-Zn and Au-Al-Zn IMCs. The Ni-P layer can be a desirable diffusion barrier to retard reaction between the solder and Cu. Experimental results have also been reported that[25] the Ni-P layer rarely dissolves into the Sn-Zn solder. This phenomenon may suppress the formation of the brittle Ni_3P phase in the Ni-P layer. The interaction between the Ni-P layer and the solder was found to enhance the formation of the Ni_3P phase. However, because there is no IMC formed with Ni, Ni was not consumed and, thus, did not result in the formation of Ni_3P in the present study.

One of the very important observations in this present study is the absence of the Cu-Sn compound formation. The Cu-Sn IMC or coexistence of Cu and Sn was not observed (Figs. 4–8). The extensive formation and growth of the Cu-Sn IMC in some Pb-free solder systems may result in gathering of thermal stress at the IMC/solder interface. Hence, the lack of the Cu-Sn compound and the slow growth rate of the IMC may be beneficial for the Sn-Zn-Ag-Ga-Al solder.

CONCLUSIONS

The Sn-8.55Zn-0.5Ag-0.5Ga-0.1Al solder has better wetting behavior with Cu than with an Au metallization layer. The Al tends to segregate at the interface between the Sn-8.55Zn-0.5Ag-0.5Ga-0.1Al solder and the Au metallization on Cu upon dipping of Cu/Au (plating) and Cu/Ni-P/Au (plating) substrates into the Sn-8.55Zn-0.5Ag-0.5Ga-0.1Al solder. The Cu-Zn IMC, which remains to be identified, was formed between the Cu substrate and the investigated solder. There is no Cu-Sn IMC formed between Cu and the solder. The IMC grows slowly upon aging at 150°C. The Ni-P metallized layer performs excellently as a diffusion barrier in the Cu/Ni-P/Au/Sn-Zn-Ag-Ga-Al specimen to retard the IMC growth.

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