Journal of ELECTRONIC MATERIALS, Vol. 30, No. 9, 2001

Interfacial Reactions in the Sn-Ag/Au Couples

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Ag-Sn alloys are one of the most promising lead-free solders. Their reactions with Au substrates have been examined by using the reaction couple technique. Sn-3.5wt.%Ag/Au and Sn-25wt.%Ag/Au couples have been prepared and reacted at 120, 150, 180 and 200°C for various lengths of time. Three phases, δ-AuSn, ε_2-$AuSn_2$, and η-$AuSn_4$, are found in all the couples. The thickness of the reaction layers increases with higher temperatures and longer reaction time, and their growth rates are described by using the parabolic law. Arrhenius equation is used to describe the temperature dependence of the growth rates. The activation energy of the growth of the intermetallic layers in both kinds of the reaction couples is similar and is determined to be 76.74 KJ/mole. Based on the reaction path knowledge and interfacial morphology, it is concluded that Sn is the fastest diffusion species in the couples.

Key words: Sn-Ag/Cu couples, interfacial reactions, lead-free solder

INTRODUCTION

Sn-Ag alloys are one of the most promising lead-free solders.[1–6] For the development of optimized processes of using Ag-Sn solders and reliability assessment of products made thereof, knowledge of interfacial reactions between Ag-Sn solders with prominent substrates are essential.[1,7] The interfacial reactions between Ag-Sn solders and Cu and Ni substrates have been examined previously;[8–10] however, those between Ag-Sn and Au have not been investigated.

Shimoyashiki et al.[11] studied the effect of Cu addition to the Sn-3.5wt.%Ag alloy upon the wettability and peel strength on a Au leadframe. They found the formation of $AuSn_4$ phase at the interface. Their work is the only available literature discussing the intermetallic formation in the Ag-Sn/Au system. This study was carried out to obtain an understanding of the interfacial reactions between Sn-Ag alloys and Au substrate. A reaction couple technique was used. Formation of intermetallic compounds, growth rates of the intermetallic layers, and the growth mechanisms of layers were investigated.

EXPERIMENTAL PROCEDURES

The alloys were prepared with Ag and Sn shots of 99.99 wt.% purity. A total mass of 10 g of proper amounts of Ag and Sn were weighed and encapsulated in a quartz tube of 8 mm inner-diameter under 10^{-3} torr of vacuum. The sample capsules were put into a furnace at 900°C, held for 12 h, removed from the furnace and quenched into icy water. Except for the preparation of the Ag_3Sn, the quenched alloys were cut into circular disks of 1.5 mm thickness. The Ag_3Sn alloys were homogenized at 360°C for 12 days prior to cutting.

The Ag-Sn alloys prepared as mentioned above and 100 μm thick Au foils of 99.99 wt.% purity were used in this study for the preparation of reaction couples. Two Ag-Sn disks and one Au piece were sandwiched together by two stainless screws as shown in Fig. 1. Boron nitride (BN) powders were sprayed on the screws to prevent possible reactions between the screws and Ag-Sn alloys. The Ag-Sn/Au/Ag-Sn sandwich was encapsulated in an evacuated quartz tube and placed in a furnace at 120, 150, 180, and 200°C for various lengths of time. The reaction couples were then removed from the furnace and quenched in water.

The interfacial reactions in these couples were first examined metallographically. The couples were mounted and polished carefully, so the cross-sectional interface exactly perpendicular to the Au foil was exposed. Optical microscopy and scanning electron microscopy (SEM) were used to examine the microstructures of reaction couples. Electron probe

(Received February 1, 2001; accepted April 20, 2001)

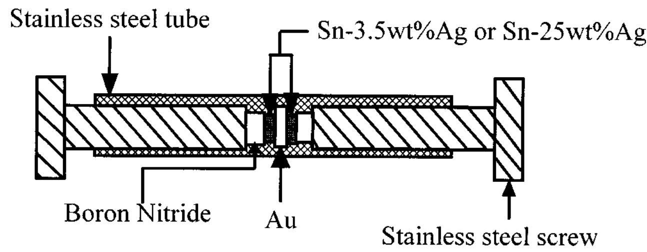

Fig. 1. Schematic diagram of the Sn-Ag/Au reaction couple.

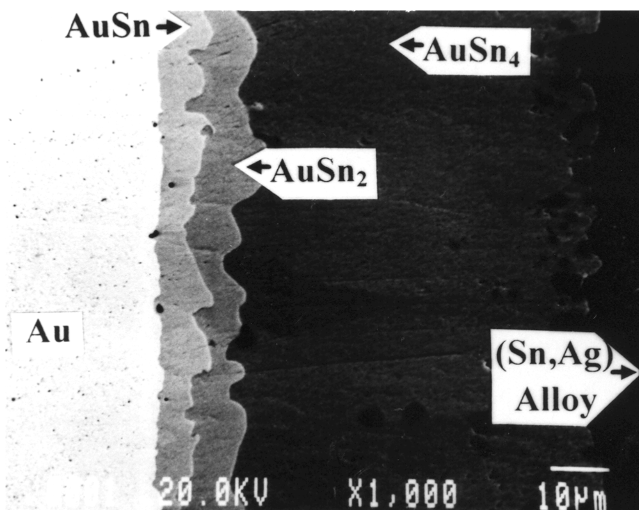

Fig. 2. Back-scattered electron image of the Sn-3.5wt.%Ag/Au couple reacted at 200°C for 30 h.

microanalysis (EPMA) operated at 30 kV was used for compositional determination. The thickness of the reacted layers was determined by using an image analysis system attached to an optical microscope. The layer thickness was determined by dividing the area of the reacted layers to the linear length of the interface. Thus, the determined thickness was an average value of that in the selected area. Each thickness data reported in this study was an average of at least measurements of three different areas.

RESULTS AND DISCUSSION

Figure 2 is a back-scattered electronic image (BEI) of the Sn-3.5wt.%Ag/Au reaction couple reacted at 200°C for 30 h. The brightest phase on the left-hand side is the Au foil, the darkest region on the right-hand side is the Sn-Ag alloy, and three intermetallic layers can be found at the interface. Compositions of the three layers determined by using an EPMA from the left-hand side to the right-hand side are Sn-0.01 at.% Ag-49.44 at.% Au, Sn-0.01 at.% Ag-32.92 at.% Au, and Sn-0.18 at.% Ag-19.50 at.% Au, respectively. Figure 3 is the EPMA line-scan compositional profile across the reaction layers. It can be noticed that all the phases formed in the Sn-3.5wt.%Ag/Au couples have very little solubility of silver. By comparing the compositions of the three layers with those of binary Au-Sn compounds,[12] it is concluded that the brighter and thinner phase adjacent to the Au phase is the δ-AuSn phase, the darker phase adjacent to the Sn-Ag

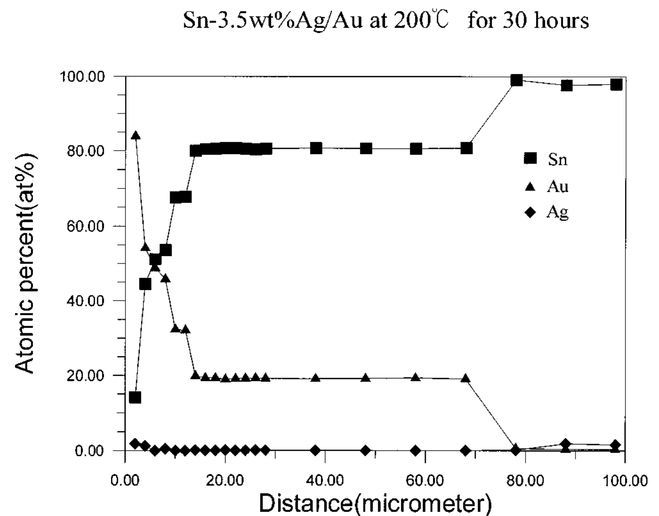

Fig. 3. EPMA line-scan compositional profile across the intermetallic layers in the Sn-3.5wt.%Ag/Au couple reacted at 200°C for 30 h.

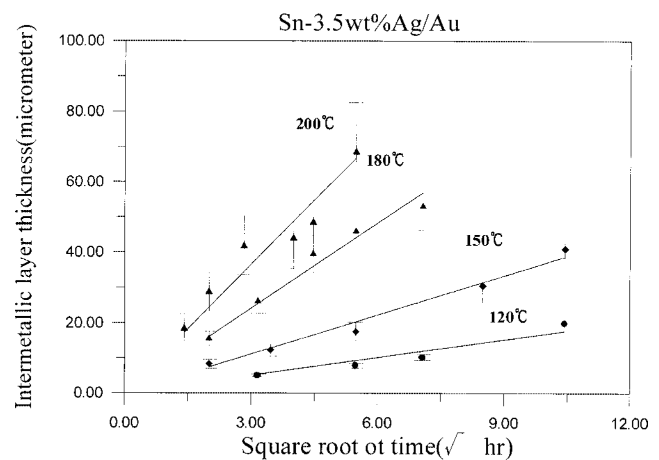

Fig. 4. Thickness of the intermetallic layers in the Sn-3.5wt.%Ag/Au couples.

alloy is the η-$AuSn_4$ phase, and the gray phase between the δ and η phases is the ε_2-$AuSn_2$ phase.

Although there are four stable intermetallic phases, ζ, δ, ε_2, and η, in the Au-Sn system[12] at 200°C, the formation of ζ phase by interfacial reaction is not observed in this study. Buene et al.[13] and Nakahara et al.[14] studied the Au/Sn thin film couples, and they found the formation of δ, ε_2, and η phases. Although Nakahara et al.[14] in the abstract of their manuscript have mentioned that the ζ phase could be formed by subsequent transformations, the existence of the ζ phase has not been reported anywhere else in their manuscript. Hannech and Hall[15] and Kim and Tu[16] studied the reactions in the Pb-Sn/Au couples. Kim and Tu[16] reported only the existence of η phase in their wetting samples. Hannech and Hall[15] clearly identified the formation of ε_2 and η phases; however, the existence of ζ and δ was not confirmed. Shimoyashiki et al.[11] studied wetting characteristics between Sn-3.5wt.%Ag alloys (with addition of 0.5 wt.% to 1.5 wt.% Cu) and Au-coated leadframe, and they reported only the formation of η phase in their wetting samples. The same phenomenon is noticed in

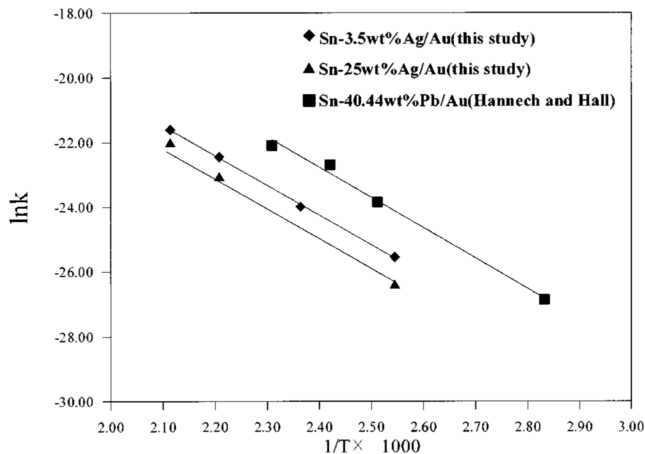

Fig. 5. Arrhenius plots for the formation of intermetallic phases in the Sn-Ag/Au couples.

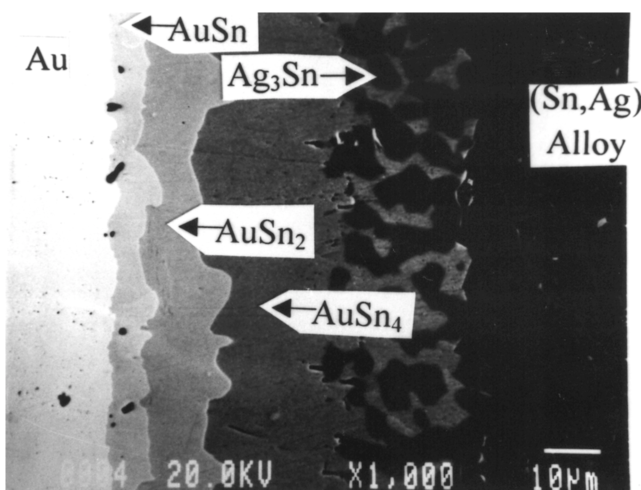

Fig. 6. Back-scattered electron image of the Sn-25wt.%Ag/Au couple reacted at 200°C for 30 h.

other systems that not all the stable compounds are found in the reaction couples.[17–19] Some of the missing phases might have not nucleated, and some of the missing phases might be just too thin to be detected.

Similar results are found for all the other Sn-3.5wt.%Ag/Cu couples reacted at 120, 150, 180, and 200°C, for various lengths of time (i.e., three Au-Sn intermetallic compounds, δ, ε_2 and η, are formed in the couples). As shown in Fig. 4, the thickness of the layers increased with higher reaction temperatures and longer reaction time. A linear relationship between the layer thickness and the square root of reaction time, $x = kt^{1/2}$, is used to describe layer growth, and the growth rate constant, k, can be determined from the slope. The activation energy of layer formation can then be determined from the Arrhenius equation,

$$k = k_o \times \exp(-Q/RT)$$

As shown in Fig. 5, the activation energy determined from the Sn-3.5wt.%Ag/Au couples is 76.74 kJ/mole. Hannech and Hall[13] determined the thickness of the Au-Sn intermetallic layers in the Pb-Sn/Au couples as

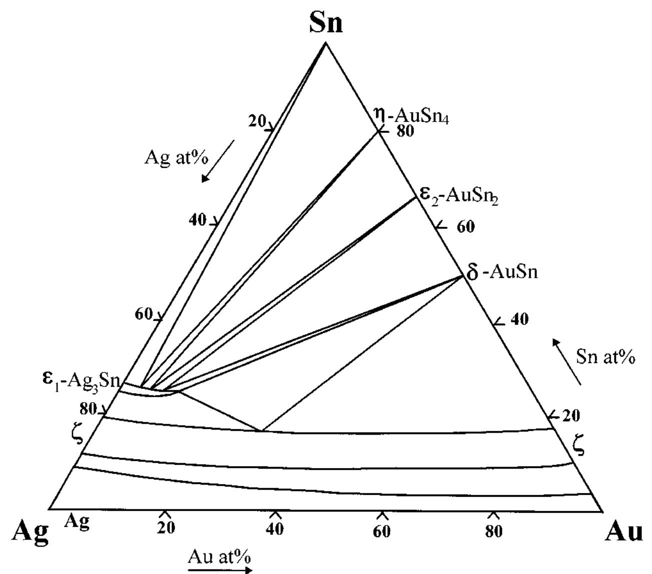

Fig. 7. Isothermal section of ternary Ag-Sn-Au system at 200°C.

a function of reaction time, they found the layer growth followed the parabolic law when it was thinner than 35 μm. Since Pb does not actively participate in the Pb-Sn/Au interfacial reaction, the reaction results determined in the Pb-Sn/Au system should be very similar to that in the Sn/Au and Sn-3.5wt.%Ag/Au systems. Most of layers in this study were thinner than 35 μm, and owing to the uncertainties of the thickness measurement, it is not sure if there is a changing of slope when the layer is thicker than 35 μm.

Figure 6 is the BEI micrograph of the Ag-25wt.%Ag/Au couples reacted at 200°C for 30 h. Similar to those observed in the Ag-3.5wt.%Ag/Au couples, three Au-Sn phases, δ, ε_2 and η, are found, but not the ζ phase. However, besides the formation of three Au-Sn compounds, the ε_1-Ag_3Sn phase is found mixing with the η phase. The ε_1 phase is formed during the solidification process of the Sn-25wt.%Ag alloy, and it exits as well in the solidified Sn-3.5wt.%Ag alloy as shown in Fig. 2. The ε_1/Au couples have been prepared and examined in this study, and no noticeable reaction was found. Since the ε_1 phase does not participate in the reaction, the solid Sn-Ag/solid Au couples should behave similarly to the Sn/Au couples. The ε_1 phase can be recognized as markers indicating the original position of the Sn-Ag/Au interface. Similar results have been found for all other Sn-25wt.%Ag/Au couples reacted at different temperatures for various lengths of time (i.e., δ, ε_2, and η are found and their thickness increases with higher reaction temperatures and longer reaction time).

A schematic isothermal section of the ternary Ag-Sn-Au system at 200°C is shown in Fig. 7. This isothermal section is proposed based on the phase equilibria of its three constituent binary systems[12,20,21] and the knowledge of phase equilibria ternary Ag-Sn-Au system.[22–24] Continuous solid solutions are formed between Ag and Au phases and between the two ζ phases of Ag-Sn and Au-Sn systems. The existence of the (Ag, Au) solid solution can be confirmed from the

binary Ag-Au phase equilibria data,[21] and that for the ζ phase is proposed based on the experimental observation that there is a continuous solid solution at 275°C.[23] The three binary Au-Sn compounds, δ, ε_2, and η, have almost no solubility of Ag. This has been found both in this study and that by Malhotra et al.,[24] the ε_1 phase is in equilibrium with most of the existent phases except the (Ag, Au) solid solution. Based on the isothermal section shown in Fig. 7, the Sn-3.5wt.%Ag and Sn-25wt.%Ag alloys are not in the single-phase region at 200°C. Both Sn-3.5wt.%Ag and Sn-25wt.%Ag alloys are a two-phase mixture containing Sn and ε_1 phases, and the solder/Au interfaces in the reaction couples contains two kinds of interfaces, Sn/Au or ε_1/Au. Since there is no noticeable reaction in the ε_1/Au and Sn has only very little solubility of Ag, the interfacial reactions in the Sn-3.5wt.%Ag/Au and Sn-25wt.%Ag/Au couples should be similar to those in the binary Sn/Au couples.

Consequently, the interfacial reactions in the two kinds of reaction couples examined in this study should be similar. The volume of ε_1 in the Sn-3.5 wt.%Ag/Au and Sn-25wt.%Ag/Au couples can be considered as diluent. Since the Sn-25wt.%Ag alloy has more ε_1 phase, it is expected that the growth rates of the intermetallic layers are slower. This expectation is confirmed experimentally, as shown in Fig. 5. The activation energy of the formation of the reaction layers in both kinds of the Sn-Ag/Au couples studied in this work is assumed to be identical and is determined to be 76.74 kJ/mole. A similar argument can be applied to the layer formation in the Pb-Sn/Au system.[15] As shown in Fig. 5, the activation energy of formation of the intermetallic layer calculated based on the data by Hannech and Hall[15] is 78.11 kJ/mole. Hannech and Hall used Sn-44.04wt.%Pb solders, which contain less Sn than those used in this study. The activation energy determined by Hannech and Hall[15] is in amazing agreement with that determined in this study, especially when the uncertainties of thickness measurements are considered.

Although the activation energy of compound formation is not changed by the existence of inert materials, the rate of compound formation is affected for sure. The growth rates of the intermetallic layers in the Sn-25wt.%Ag/Au couples are lower than those in the Sn-3.5wt.%Ag/Au couples, since the Sn-25wt.%Ag alloys have more inert ε_1 phase. As shown in Fig. 5, although the slopes are similar, the absolute values of growth rates are different, and such that the values of k_o for these three kinds of couples are different. The k_o for the Sn-3.5wt.%Ag/Au and the Sn-25wt.%Ag/Au couples are 0.123 and 0.054 cm^2/s, respectively. The amount of Sn in the Sn-3.5wt.%Ag and Sn-25wt.%Ag are 95.4% and 62.39%. A rough calculation indicates the k_o for Sn/Au is 0.133 cm^2/s. It should be pointed out that growth rates of the intermetallics may depend on various factors. Besides the contents of the inert phase as mentioned in the above, the liquidus temperatures of the alloys can be a factor as well. However, it is very difficult to quantify this effect. Although the liquidus temperature is the lowest for the Pb-Sn solders used by Hannech and Hall,[15] the difference from that of the Sn-3.5wt.%Ag alloy is not significant, and it is still not clear to the authors why the growth rates of intermetallic layers determined in their study are higher than those found in this work.

Nakahara et al.[14] discussed the possible diffusion mechanisms in the Sn/Au binary system. They have found that, at room temperature, gold is a faster bulk diffusion species, while grain boundary diffusion of tin is significant as well. Since the ε_1 phase does not react with Au and the Au-Sn intermetallic compounds contain a very small amount of Ag, the Ag element can be assumed to be immobile in the Ag-Sn/Au couples. As mentioned previously, the ε_1 phase can be considered as markers indicating the position of the original interface. It can be noticed in Fig. 6 that the intermetallic compounds grow on both sides of the original interface. The layer on the left-hand side is thicker than that on the right-hand side and suggests that Sn is a faster diffusion species than gold in the Ag-Sn/Au couples. Some voids can be found at the original interface as well; however, significant amounts of Kirkendall voids are not found, as indicated by Nakahara et al.[14] in their thin film couples.

CONCLUSIONS

At 120, 150, 180, and 200°C, Sn-3.5wt.%Ag and Sn-25wt.%Ag alloys contain Sn and ε_1 phases. Since the ε_1 phase does not react noticeably with the Au substrate, both the Sn-3.5wt.%Ag/Au and Sn-25wt.%Ag/Au couples are similar to Sn/Au couples at these reaction temperatures. Three binary Au-Sn phases, δ, ε_2, and η, but not ζ phase, are formed, and the total thickness of intermetallic layers increases with higher temperature and longer reaction time. The activation energy of the growth of the intermetallic layer in both kinds of couples is similar and is determined to be 76.74 KJ/mole. In these couples, Ag is not mobile, while Sn is the fastest moving species.

ACKNOWLEDGEMENT

The authors wish to acknowledge the financial support of National Science Council of Taiwan, ROC through the project NSC90-2214-E-007-002.

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