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Intermetallic Compounds Formed During Diffusion Soldering of Au/Cu/Al_2O_3 and Cu/Ti/Si with Sn/In Interlayer

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A Si wafer was sequentially sputter-coated with Ti (20 nm), Cu (6 μm), Sn (4 μm), and In (4 μm). The specimen was then diffusion-soldered at temperatures between 150 and 300°C with an alumina substrate deposited with Cu (4 μm) and Au (6 μm). Experimental results showed that a multilayer of intermetallic phases with the compositions of $(Cu_{0.99}Au_{0.01})_6(Sn_{0.52}In_{0.48})_5$/$(Au_{0.87}Cu_{0.13})(In_{0.94}Sn_{0.06})_2$/$(Au_{0.98}Cu_{0.02})$ $(In_{0.95}Sn_{0.05})$ formed at the Au/Cu interface. Kinetic analyses revealed that the growth of $(Cu_{0.99}Au_{0.01})_6$ $(Sn_{0.52}In_{0.48})_5$ and $(Au_{0.87}Cu_{0.13})(In_{0.94}Sn_{0.06})_2$/$(Au_{0.98}Cu_{0.02})(In_{0.95}Sn_{0.05})$ intermetallics were diffusion-controlled with activation energies of 21.5 and 31.3 kJ/mol, respectively. Sound tensile strengths of 42 and 48 kg/cm^2 have been obtained under the bonding conditions of 150°C for 40 min. and 200°C for 30 min., respectively.

Key words: Intermetallic compounds, diffusion soldering, Au/In/Sn/Cu interfacial reactions

INTRODUCTION

Diffusion soldering provides novel applications for high density and high power devices in meeting their requirements for heat-resistant joints.[1,2] This technique makes use of a low-melting metallic thin-film interlayer (LT) that reacts rapidly with both of the high-melting metallic layers or substrates (HT1 and HT2) that are to be bonded. The original thickness of the LT interlayer is less than those of the HT1 and HT2 layers or substrates, and the liquid/solid reactions contribute to exhaustion of the LT interlayer as well as the formation of interfacial intermetallic compounds between HT1 and HT2. Because the newly formed intermetallic phases possess melting points much higher than the original LT interlayer, the resulting joints can withstand considerably higher temperatures.[3]

On the basis of the underlying principle of the diffusion-soldering process, intermetallic reactions that occur at the LT/HT1 and LT/HT2 interfaces apparently play a key role in achieving joining efficiency for this technique. Bader et al. have investigated the intermetallic compounds along with their growth kinetics in diffusion-soldered Cu/Sn/Cu and Ni/Sn/Ni systems.[3] Sommadossi et al. further studied intermetallic reactions during the diffusion soldering of Cu/In-48Sn/Cu joints at temperatures between 180 and 400°C.[4] They reported on an ε-$Cu_{57}In_{16}Sn_{27}$ intermetallic phase that formed at temperatures below 200°C and an ε-$Cu_{77}In_{10}Sn_{13}$/η-$Cu_{57}In_{16}Sn_{27}$ double layer that formed at temperatures above 200°C. The growth kinetics of the ε-intermetallic phase between Cu and η-intermetallics was interfacially controlled with an activation energy of 121 kJ/mol. The intermetallic compounds formed at the diffusion-soldered interfaces between Cu/Ti/Si and Au/Cu/Al_2O_3 with pure Sn and pure In interlayers have been investigated by Liang et al.[5] and Tsao et al.,[6] respectively. In the wake of published studies on intermetallic reactions of liquid In-49Sn solder with solid Au and Cu substrates,[7,8] this present paper is concerned with thin-film diffusion soldering between Cu/Ti/Si and Au/Cu/Al_2O_3 using a near-eutectic In/Sn interlayer.

EXPERIMENTAL PROCEDURES

The alumina ceramic substrate used for this study was sputter-coated with Cu (4 μm)/Au (6 μm) layers. Sn (4 μm) and In (4 μm) were then deposited on a Ti/Cu-coated Si wafer. The In/Sn/Cu/Ti/Si wafer and Au/Cu/Al_2O_3 substrate were cut in dimensions of 4 × 4 mm and assembled as shown in Fig. 1a. The specimens were heated at various temperatures ranging from 150 to 300°C in a vacuum furnace of 5.3×10^{-4} Pa for 10 to 40 min. In this case, Sn and In melted to form a near-eutectic Sn-In liquid layer

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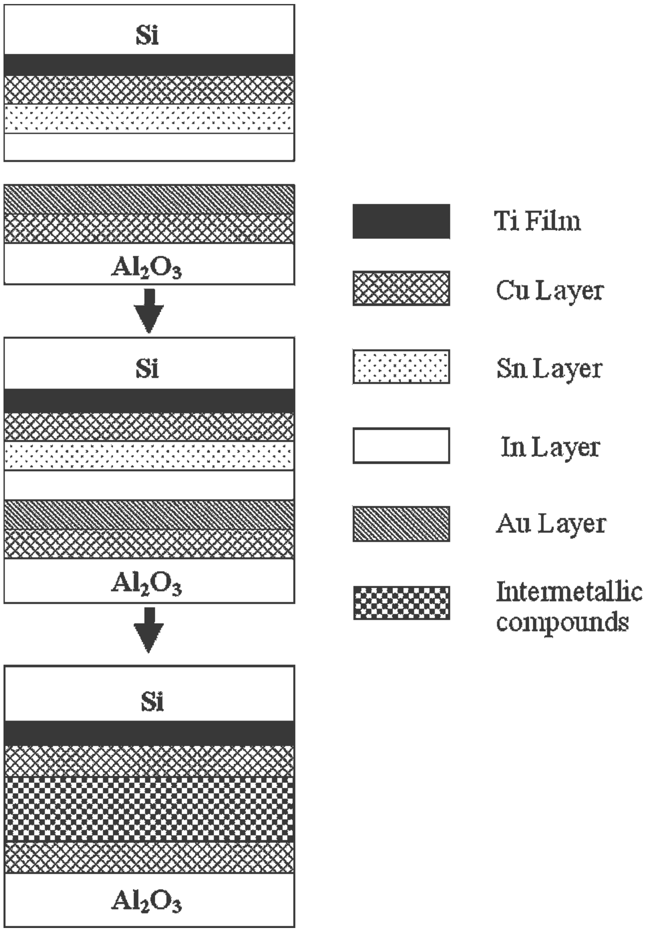

Fig. 1. Scheme of diffusion soldering for Cu/Ti/Si and Au/Cu/Al$_2$O$_3$ with In/Sn interlayers.

that reacted with the Cu and Au films (Fig. 1b). Diffusion soldering of the Sn-In layer with Cu and Au films resulted in the appearance of intermetallic compounds at the Sn-In(l)/Cu(s) and Sn-In(l)/Au(s) interfaces (Fig. 1c). After bonding, the specimens were cut along the cross section, ground with SiC paper, and polished with 1.0-μm and 0.3-μm alumina powders. The interfacial intermetallics were observed by scanning electron microscopy (SEM), and their chemical compositions were analyzed by an electron probe microanalyzer (EPMA). To evaluate the bonding strengths of the diffusion-soldered joints, both sides of the sandwiched specimens were gripped as shown in Fig. 2 and tensile-tested using an MTS-(Minneapolis, USA) Tytron 250 Microforce tester at a crosshead speed of 0.01 mm/s. The load and displacement ranges that can be measured with this equipment are 0.01–250 N and 0.1 μm–100 mm, respectively, which are suitable for this testing procedure.

RESULTS AND DISCUSSION

During the diffusion soldering between Au/Cu/Al$_2$O$_3$ and Cu/Ti/Si with In/Sn interlayers, the liquid Sn film (4 μm) reacted rapidly with the In film (4 μm) to form a liquid In-Sn alloy with a near-eutectic composition. The liquid In-Sn solder reacted further with the Au/Cu/Al$_2$O$_3$ and Cu/Ti/Si, which accounts for the appearance of a multilayer of intermetallic compounds at the interface, as shown in Figs. 3 and 4. Sound joints were obtained after diffusion soldering at 150°C for 40 min. (Fig. 3a) and at 200°C for 30 min. (Fig. 3b). The intermetallic layers broke into coarse particles with the increase in temperature or heating time, as revealed in Fig. 4a and b. EPMA analyses identified the Au, Sn, In, and Cu compositions across the multilayers of the diffusion-soldered specimens, which are plotted in Fig. 5. The composition (at.%) of the intermetallic layer adjacent to the Cu/Ti/Si is Cu:Au:Sn:In = 57.63:0.32:21.69:20.09, i.e., $(Cu_{0.99}Au_{0.01})_6(Sn_{0.52}In_{0.48})_5$, which corresponds to the η-Cu_6Sn_5 phase in the Cu-Sn equilibrium diagram. A similar intermetallic compound $(Cu_{0.99}Au_{0.01})_6Sn_5$ was found in the diffusion-soldered joint of Cu/Ti/Si and Au/Cu/Al$_2$O$_3$ with a Sn interlayer.[5] However, the change of the interlayer to pure In generated a different kind of intermetallic compound $(Cu_{0.99}Au_{0.01})In$.[6] For the soldering reactions between liquid In-49Sn and Cu substrates, Chuang et al. reported the formation of an intermetallic compound $Cu_6(Sn_{0.54}In_{0.46})_5$ at the In-49Sn(l)/Cu(s) interfaces.[8]

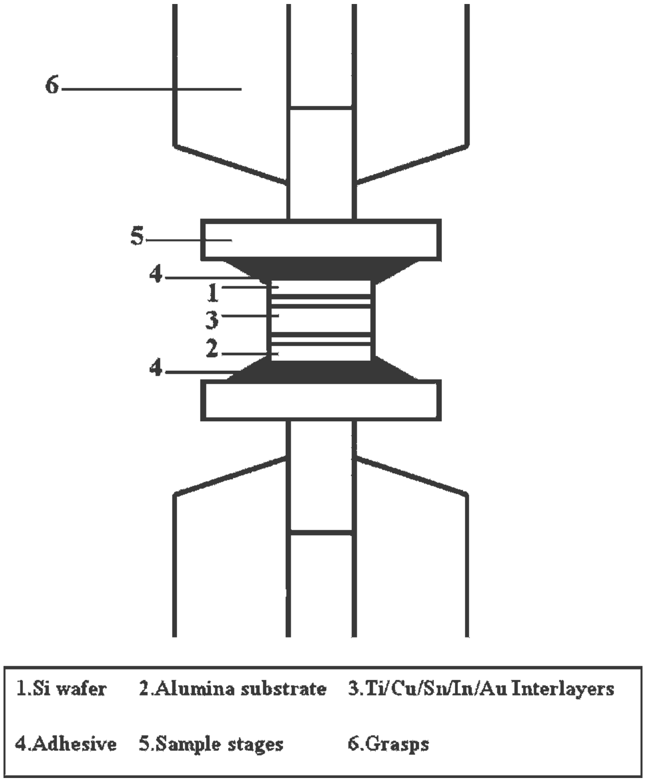

Fig. 2. Tensile test for the bonding strengths of the diffusion-soldered joints.

The intermetallic compounds adjacent to the Au/Cu/Al$_2$O$_3$ substrate were composed of two layers, $(Au_{0.87}Cu_{0.13})(In_{0.94}Sn_{0.06})_2$ and $(Au_{0.98}Cu_{0.02})(In_{0.95}Sn_{0.05})$, which correspond to the $AuIn_2$ and AuIn phases in the Au-In equilibrium diagram. For diffusion soldering between Cu/Ti/Si and Au/Cu/Al$_2$O$_3$

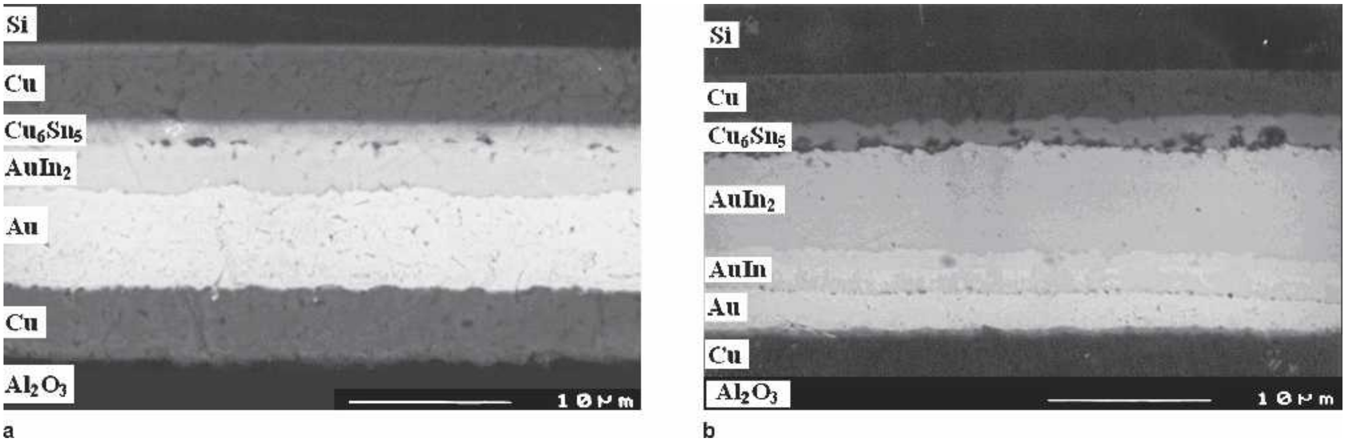

Fig. 3. Morphology of intermetallic compounds formed after diffusion soldering between Cu/Ti/Si and Au/Cu/Al_2O_3 using In/Sn interlayers: (a) 150°C, 40 min; (b) 200°C, 30 min.

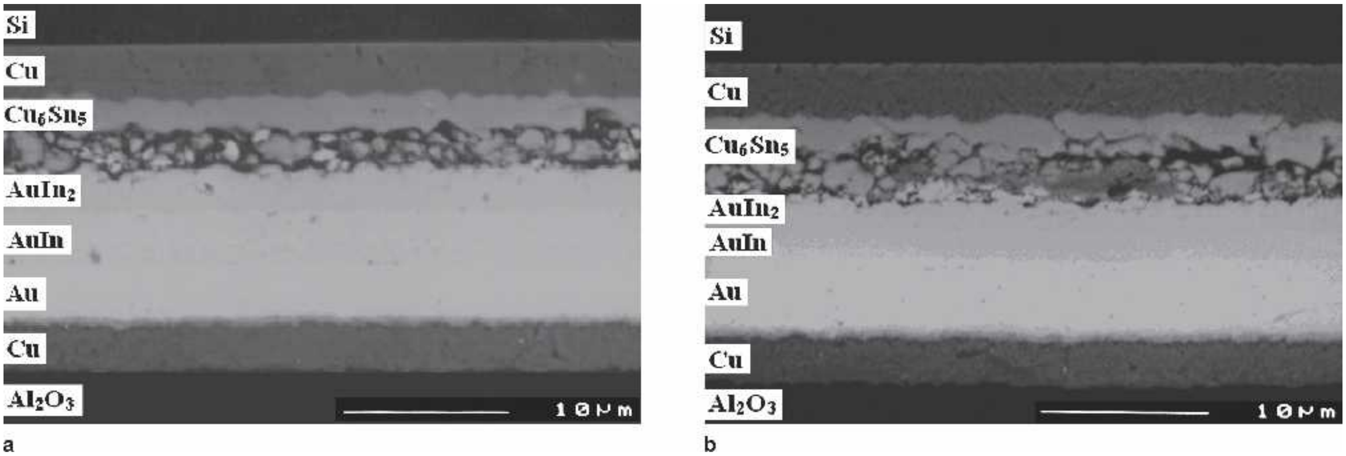

Fig. 4. Morphology of intermetallic compounds formed after diffusion soldering between Cu/Ti/Si and Au/Cu/Al_2O_3 using In/Sn interlayers: (a) 200°C, 40 min.; (b) 300°C, 30 min.

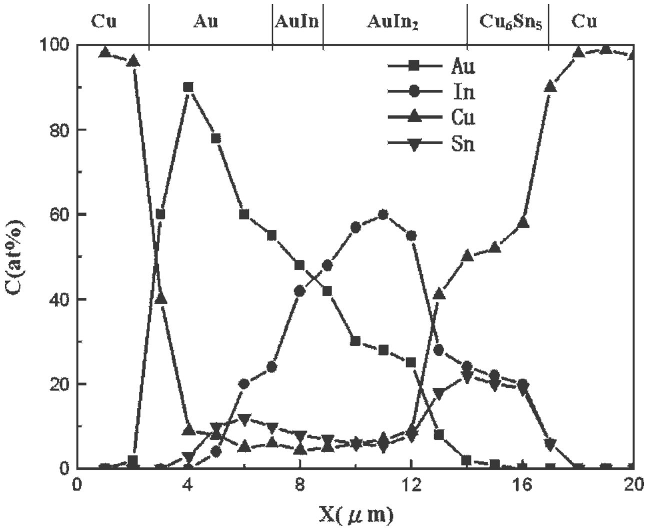

Fig. 5. Au, Sn, and Cu concentrations across the multilayers of a diffusion-soldered specimen (from Fig. 3b).

using pure Sn^5 and pure In^6 interlayers, the resultant interfacial intermetallics were δ-$(Au_{0.87}Cu_{0.13})Sn$ and $(Au_{0.67}Cu_{0.33})In_2$, respectively. On the other hand, soldering reactions between liquid In-49Sn and Au thick film, as reported by Liu,[7] resulted in the formation of a continuous $(Au_{0.96}Cu_{0.04})(In_{0.92}Sn_{0.08})_2$ intermetallic layer at the In-49Sn(l)/Cu(s) interfaces along with a great number of $(Au_{0.98}Cu_{0.02})(In_{0.94}Sn_{0.06})$ intermetallic blocks floating into the In-49Sn solder matrix.

The thicknesses (ΔX) of the intermetallic layers formed at the interfaces were measured and plotted vs. the square root of reaction time ($t^{1/2}$). Figures 6 and 7 show that the growth of the η-$(Cu_{0.99}Au_{0.01})_6(Sn_{0.52}In_{0.48})_5$ intermetallic layer and $(Au_{0.87}Cu_{0.13})(In_{0.94}Sn_{0.06})_2$/$(Au_{0.98}Cu_{0.02})(In_{0.95}Sn_{0.05})$ double layer exhibits a parabolic relation, implying that the interfacial reactions during the diffusion soldering of Cu/Ti/Si and Au/Cu/Al_2O_3 with the In/Sn interlayer were diffusion-controlled. The growth rate constants ($K = \Delta X/t^{1/2}$), as calculated from Figures 6 and 7, are listed in Table I. From the Arrhenius plots of growth rate constants in Fig. 8, the activation energies (Q) for the growth kinetics of η-$(Cu_{0.99}Au_{0.01})_6(Sn_{0.52}In_{0.48})_5$ and $(Au_{0.87}Cu_{0.13})(In_{0.94}Sn_{0.06})_2$/$(Au_{0.98}Cu_{0.02})(In_{0.95}Sn_{0.05})$ intermetallics are determined to be 21.5 and 31.3 kJ/mol, respectively. The former value (21.5 kJ/mol) is quite consistent with the activation energy for the diffusion

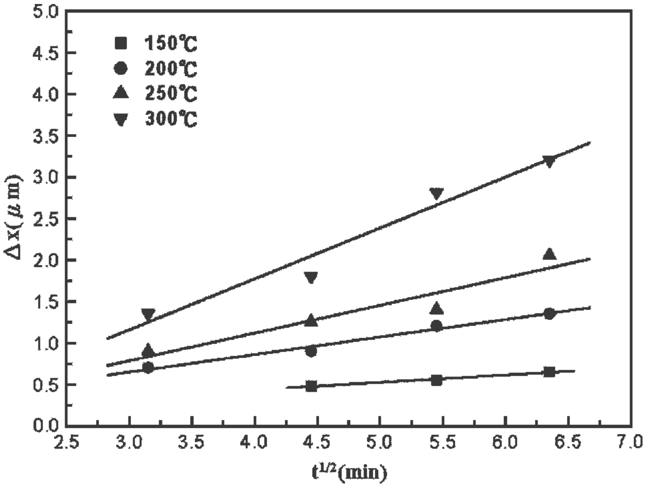

Fig. 6. Growth thickness (Δx) of $(Cu_{0.99}Au_{0.01})_6(Sn_{0.52}In_{0.48})_5$ intermetallic compounds formed during diffusion soldering between Cu/Ti/Si and Au/Cu/Al_2O_3 with In/Sn interlayers.

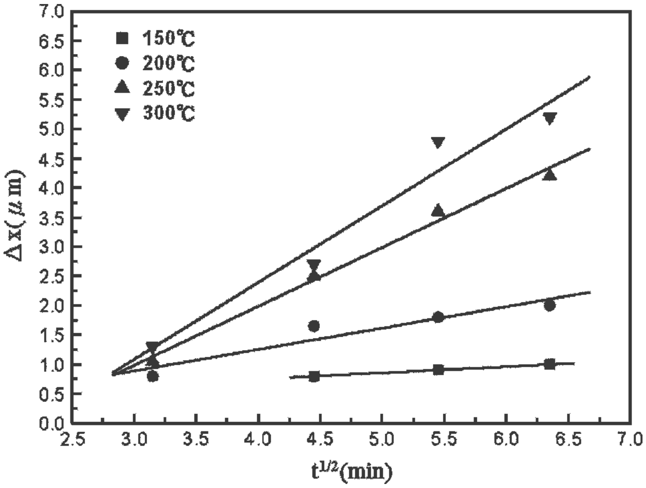

Fig. 7. Growth thickness (Δx) of $(Au_{0.87}Cu_{0.13})(In_{0.94}Sn_{0.06})_2$/$(Au_{0.98}Cu_{0.02})$ $(In_{0.95}Sn_{0.05})$ double layer formed during diffusion soldering between Cu/Ti/Si and Au/Cu/Al_2O_3 with In/Sn interlayers.

Table I. Growth Rate Constants (K) for the Intermetallic Compounds Formed during Diffusion Soldering between Cu/Ti/Si and Au/Cu/Al_2O_3 with In/Sn Interlayers

Temperature (°C)	$(Cu_{0.99}Au_{0.01})_6$ $(Sn_{0.52}In_{0.48})_5$ (μm/min$^{1/2}$)	$(Au_{0.87}Cu_{0.13})$ $(In_{0.94}Sn_{0.06})_2$ + $(Au_{0.98}Cu_{0.02})$ $(In_{0.95}Sn_{0.05})$ (μm/min$^{1/2}$)
150	0.124	0.147
200	0.253	0.392
250	0.273	1.022
300	0.641	1.371

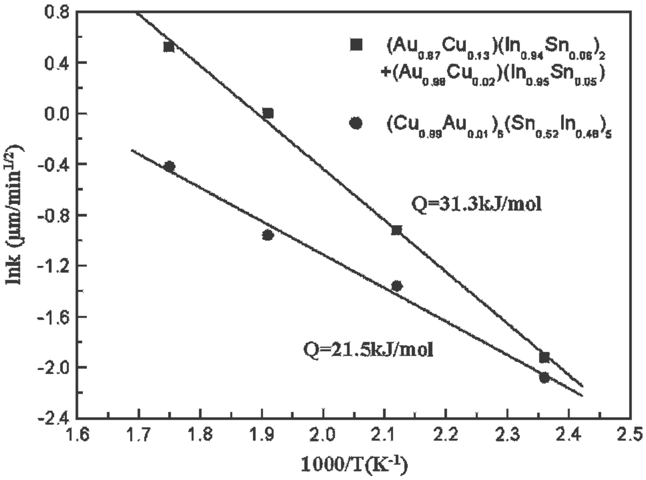

Fig. 8. Arrhenius plots of growth rate constants (k) for intermetallic compounds formed during diffusion soldering between Cu/Ti/Si and Au/Cu/Al_2O_3 with In/Sn interlayers.

of Cu in liquid Sn (19.5 kJ/mol), as reported by Ma and Swalin.[9] The rate-limiting step in the growth of the $(Cu_{0.99}Au_{0.01})_6Sn_5$ intermetallics should be the diffusion of Cu dissolved near the intermetallic reaction front into the surrounding liquid Sn thin film. Chuang et al.[8] calculated the activation energy for the growth of η-$Cu_6(Sn_{0.54}In_{0.46})_5$ intermetallics during the soldering reactions between liquid In-49Sn and Cu substrates and found it to be 28.9 kJ/mol, which, by comparison, was also nearly the same for the growth of η-$(Cu_{0.99}Au_{0.01})_6(Sn_{0.52}In_{0.48})_5$ adjacent to the Cu/Ti/Si during the thin-film diffusion-soldering reactions in this present study. The result implied that the growth mechanism of the η-Cu_6 $(Sn,In)_5$ intermetallic phase for thin-film diffusion soldering was not different from that for bulk soldering reactions. From the work of Liu,[7] the activation energy for the growth of the continuous $(Au_{0.96}Cu_{0.04})$ $(In_{0.92}Sn_{0.08})_2$ intermetallic layer was 51 kJ/mol, while the block-shaped $(Au_{0.98}Cu_{0.02})(In_{0.94}Sn_{0.06})$ intermetallic compounds were observed to float into the In-49Sn solder matrix. In this present study, the In-49Sn solder was exhausted throughout the diffusion-soldering process, with a greater number of $AuIn_2$-phase intermetallics reacting with Au to form the AuIn phase by a solid/solid diffusion mechanism. The calculated activation energy for the growth of ($AuIn_2$ + AuIn) during the thin-film diffusion-soldering reactions is therefore lower than that for the growth of $AuIn_2$ during the soldering reactions between liquid In-49Sn and Cu substrates.

The tensile strengths of Si/Ti/Cu/Sn/In/Au/Cu/Al_2O_3 specimens diffusion-soldered under various conditions are listed in Table II. At lower temperatures (<200°C) and for shorter times (<20 min.), the

Table II. Tensile Strength of Cu/Ti/Si Wafer Diffusion-Soldered with Au/Cu/Al_2O_3 Substrates at Various Temperatures and Times Using In/Sn Interlayers

Temperature (°C)	Bonding Strength (kg/cm^2)			
	10 min	20 min	30 min	40 min
150	—	—	12 ± 5	42 ± 9
200	—	29 ± 6	48 ± 8	21 ± 7
250	—	23 ± 6	16 ± 3	7 ± 4
300	—	8 ± 3	9 ± 4	4 ± 2

intermetallic reactions at the interfaces of Cu/In-Sn solder/Au were insufficient, and many cavities or even crevices appeared at the interfaces. In these cases, the specimens failed marginally to join. However, at temperatures above 250°C, the intermetallic layers broke into coarse particles, as shown in Fig. 4, which resulted in a drastic reduction of the bonding strengths, even to the values lower than 10 kg/cm^2. Sound tensile strengths of 42 and 48 kg/cm^2 have been obtained under bonding conditions at 150°C for 40 min. and at 200°C for 30 min., respectively.

CONCLUSIONS

Multilayer thin-film systems of Cu/Ti/Si and Au/Cu/Al_2O_3 were diffusion-soldered at various temperatures ranging from 150 to 300°C with an In/Sn double layer inserted between them. The In/Sn double layer melted at the outset of heating, forming a near-eutectic In-49Sn solder film, which reacted further with the Cu/Ti/Si and Au/Cu/Al_2O_3 substrates to form a trilayer of intermetallic compounds. The compositions of these intermetallics as determined by EPMA analyses were $(Cu_{0.99}Au_{0.01})_6(Sn_{0.52}In_{0.48})_5$/$(Au_{0.87}Cu_{0.13})(In_{0.94}Sn_{0.06})_2$/$(Au_{0.98}Cu_{0.02})(In_{0.95}Sn_{0.05})$, which can be simplified as $Cu_6(Sn,In)_5$/$AuIn_2$/AuIn. Kinetic analyses showed that the growth of intermetallics was diffusion-controlled. However, the growth rate of the η-$(Cu_{0.99}Au_{0.01})_6(Sn_{0.52}In_{0.48})_5$ was much lower than those of the Au-In intermetallics $(Au_{0.87}Cu_{0.13})(In_{0.94}Sn_{0.06})$/$(Au_{0.98}Cu_{0.02})(In_{0.95}Sn_{0.05})$. The activation energies as calculated from the Arrhenius plots of the growth rate constants for η-$(Cu_{0.99}Au_{0.01})_6(Sn_{0.52}In_{0.48})_5$ and $(Au_{0.87}Cu_{0.13})(In_{0.94}Sn_{0.06})$/$(Au_{0.98}Cu_{0.02})(In_{0.95}Sn_{0.05})$ were 21.5 and 31.3 kJ/mol, respectively. Sound tensile strengths of 42 and 48 kg/cm^2 have been obtained under bonding conditions at 150°C for 40 min. and at 200°C for 30 min., respectively. Heating at the temperatures above 250°C caused the $AuIn_2$ intermetallic compounds in front of the η-$(Cu_{0.99}Au_{0.01})_6(Sn_{0.52}In_{0.48})_5$ layer to break into coarse particles, and their bonding strength decreased drastically to values below 10 kg/cm^2.

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