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Thin-Film Reactions during Diffusion Soldering of Cu/Ti/Si and Au/Cu/Al_2O_3 with Sn Interlayers

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The multilayer thin-film systems of Cu/Ti/Si and Au/Cu/Al_2O_3 were diffusion-soldered at temperatures between 250°C and 400°C by inserting a Sn thin-film interlayer. Experimental results showed that a double layer of intermetallic compounds (IMCs) η-$(Cu_{0.99}Au_{0.01})_6Sn_5$/$\delta$-$(Au_{0.87}Cu_{0.13})Sn$ was formed at the interface. Kinetics analyses revealed that the growth of intermetallics was diffusion-controlled. The activation energies as calculated from Arrhenius plots of the growth rate constants for $(Cu_{0.99}Au_{0.01})_6Sn_5$ and $(Au_{0.87}Cu_{0.13})Sn$ are 16.9 kJ/mol and 53.7 kJ/mol, respectively. Finally, a satisfactory tensile strength of 132 kg/cm^2 could be attained under the bonding condition of 300°C for 20 min.

Key words: Diffusion soldering, die attachment, intermetallic compounds, kinetics analysis, bonding strength

INTRODUCTION

Diffusion soldering (also known as solid-liquid interdiffusion bonding) is a novel joining technique based on the principle of isothermal solidification. A low-melting, metallic thin-film interlayer is employed in the process, which melts at low temperatures and reacts rapidly with both high-melting (HT_1 and HT_2) layers or with substrates to form intermetallic compounds (IMCs). Because the IMCs formed at the interfaces possess much higher melting points than the original low-melting interlayer, a special feature of bonding at lower temperatures and usage at higher temperatures can be achieved.[1] Such a superior characteristic enables diffusion soldering to broaden its application potentials in the electronics industry.[2–4]

For the manufacturing of a ceramic multichip modulus, Si dice are attached to multilayer ceramic substrates.[5] The bonding temperature for this die attachment process must be lower than 400°C to avoid any damage to integrated circuit chips. Polymer adhesives, glass bonding, metallic soldering, and Au-Si eutectic bonding are the traditional methods applied for this purpose. However, this causes strength degradation in the joining interfaces when the integrated circuit chips are functioning at elevated temperatures. Given the advantage of the diffusion soldering technique in pairing high operation temperature with low bonding temperature, its applicability in die attachment for high-density ceramic packages is, hence, examined.

According to the underlying principle of the diffusion soldering process, it is obvious that interfacial reactions play a key role in the joining efficiency of this technique. The effort of this study is thus concerned with the IMCs formed at the interfaces and their growth kinetics during the diffusion soldering of the multilayer thin-film systems bonded onto Si wafers and Al_2O_3 substrates. In addition, the tensile strengths of the diffusion-soldered specimens are evaluated.

EXPERIMENTAL

For the diffusion soldering of Si with Al_2O_3 substrates, Ti (20 nm), Cu (6 μm), and Sn (4 μm) were sputter-deposited sequentially on a Si wafer. A Cu layer (4 μm) and an Au layer (6 μm) were also deposited on an Al_2O_3 substrate by sputtering. The specimens with dimensions of 4 mm × 4 mm were cut with a diamond saw. The surfaces of the specimens were stripped with a deoxidized agent prior to diffusion soldering to remove any oxide film. The multilayer thin-film specimens were then sandwiched, as shown in Fig. 1, and heated at various temperatures

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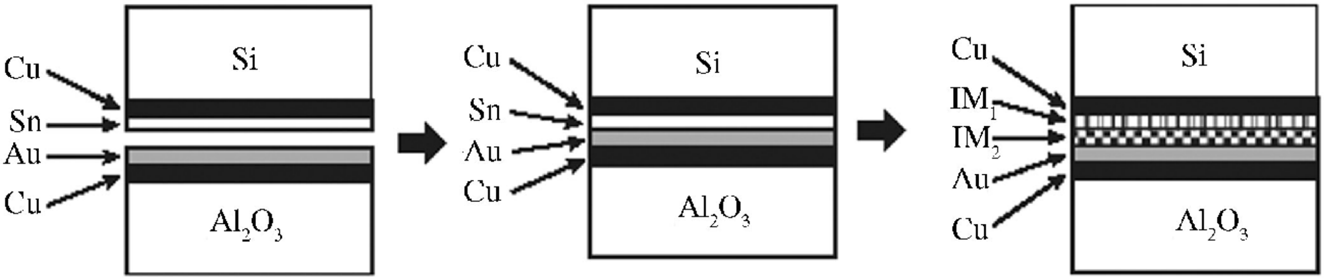

Fig. 1. The scheme of diffusion soldering for Cu/Ti/Si and Au/Cu/ Al_2O_3 with Sn interlayers.

ranging from 250°C to 400°C in a vacuum furnace of 5.3×10^{-4} Pa. After diffusion soldering, the specimens were cross-sectioned, ground with SiC paper, and polished with 1-μm and 0.3-μm Al_2O_3 powders. Morphology observations and growth rate measurements of the IMCs were mostly conducted via a scanning electron microscope. Chemical compositions of the IMCs were analyzed using an electron probe microanalyzer (EPMA). For the evaluation of bonding strengths of the diffusion-soldered specimens, tensile tests were conducted using a microforce tester at a crosshead speed of 0.01 mm/s.

RESULTS AND DISCUSSION

The typical morphology of the diffusion-soldered joints for the bonding of Cu/Ti/Si and Au/Cu/Al_2O_3 with Sn interlayers is shown in Fig. 2. The EPMA line profiles for Au, Sn, and Cu elements across the multilayers of the diffusion-soldered specimen (Fig. 2) are plotted in Fig. 3. The Sn interlayer after diffusion soldering is eliminated and replaced by bilayered IMCs between Cu/Ti/Si and Au/Cu/Al_2O_3. The IMCs adjacent to the Cu layer have a chemical composition (at.%) of Cu:Au:Sn = 54.8:0.2:45, i.e., $(Cu_{0.99}Au_{0.01})_6Sn_5$, which corresponds to the η-Cu_6Sn_5 phase on the Cu-Sn phase diagram. The η-Cu_6Sn_5 intermetallic phase has often been reported on in studies of Cu/Sn interfacial reactions.[6] During the Cu/Sn soldering reactions, η-Cu_6Sn_5 has been found to react further with Cu to form the ε-Cu_3Sn IMC, which might be too thin to be observed in this diffusion-soldering study.

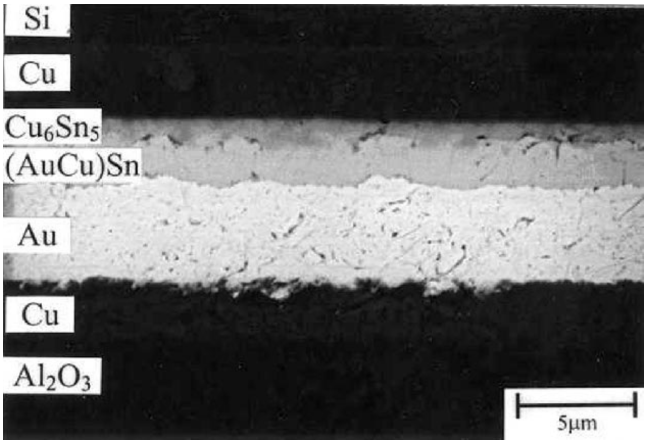

Fig. 2. The morphology of IMCs formed after diffusion soldering between Cu/Ti/Si and Au/Cu/Al_2O_3 at 300°C for 20 min with Sn interlayers.

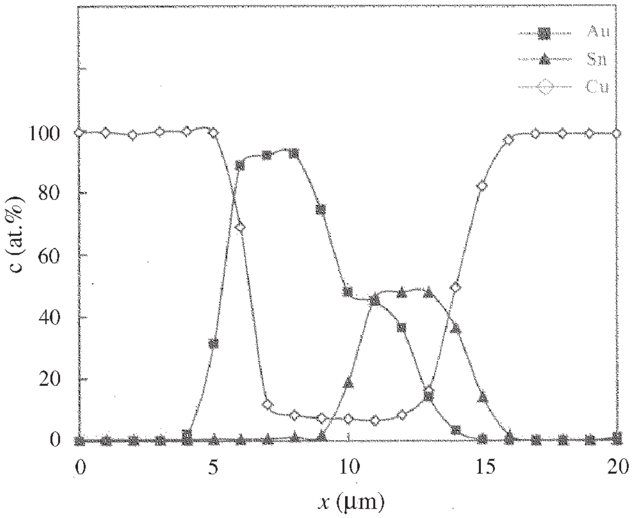

Fig. 3. The Au, Sn, and Cu concentrations across the multilayers of the diffusion-soldered specimen (Fig. 2).

The chemical composition of the IMC adjacent to the Au layer is Au:Cu:Sn = 44.4:6.9:48.7, i.e., $(Au_{0.87}Cu_{0.13})Sn$, corresponding to the δ-AuSn phase on the Au-Sn phase diagram. The relatively high Cu content of this δ-AuSn intermetallic phase is attributed to the rapid diffusion of Cu into the Au layer in Au/Cu/Al_2O_3, which simultaneously participates in the interfacial reaction between Au and the Sn interlayer during the diffusion soldering process. For the soldering reaction between liquid Sn and the Au substrate, the interfacial IMC most commonly formed is the $AuSn_4$ phase.[7] The appearance of the δ-AuSn phase can be attributed to a further reaction of $AuSn_4$ with the Au layer following the exhaustion of the Sn interlayer.

The average thickness (Δx) of the intermetallic layers formed at the interface was measured and listed in Table I. The data are plotted against the square root of reaction time (t) and shown in Figs. 4 and 5 for the $(Cu_{0.99}Au_{0.01})_6Sn_5$ and $(Au_{0.87}Cu_{0.13})Sn$ phases, respectively. In both cases, the growths of IMCs follow a parabolic rate law, implying that their reactions are diffusion-controlled. The growth rate constants ($k = \Delta x/t^{1/2}$) as calculated from Figs. 4 and 5

Table I. Thicknesses of Intermetallic Compounds Formed during Diffusion Soldering Between Cu/Ti/Si and Au/Cu/Al_2O_3 with Sn Interlayers

Temperature (°C)	Time (min)	$(Cu_{0.99}Au_{0.01})_6Sn_5$ (μm)	$(Au_{0.87}Cu_{0.13})Sn$ (μm)
250	10	0.51	0.89
	20	0.79	1.18
	30	1.05	1.38
	40	1.22	1.59
300	10	1.28	1.18
	20	1.63	1.46
	30	1.85	2.38
	40	2.08	2.50
350	10	1.78	2.17
	20	2.11	3.04
	30	2.46	3.68
	40	2.67	4.24
400	10	2.39	2.64
	20	2.84	3.47
	30	3.26	4.89

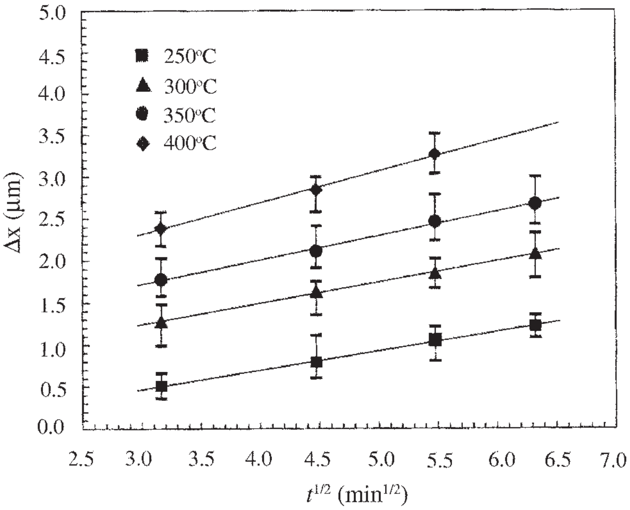

Fig. 4. The average thickness (Δx) of $(Cu_{0.99}Au_{0.01})_6Sn_5$ IMCs formed during diffusion soldering between Cu/Ti/Si and Au/Cu/Al_2O_3 with Sn interlayers.

are given in Table II. From the Arrhenius diagram of ln k versus 1/T, as shown in Fig. 6, the activation energies (Q) for the growths of $(Cu_{0.99}Au_{0.01})_6Sn_5$ and $(Au_{0.87}Cu_{0.13})Sn$ IMCs can be determined as 16.9 kJ/mol and 53.7 kJ/mol, respectively. The former value (16.9 kJ/mol) is quite consistent with the activation energy for the diffusion of Cu in liquid Sn (19.5 kJ/mol), as reported by Ma and Swalin.[8] It implies that the rate-limiting step in the growth of the $(Cu_{0.99}Au_{0.01})_6Sn_5$ intermetallic is the diffusion of Cu dissolved near the intermetallic reaction front into the surrounding liquid-Sn thin film.

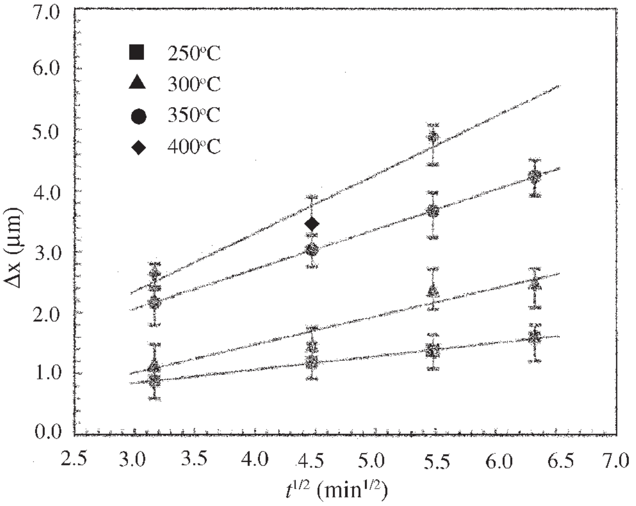

Fig. 5. The average thickness (Δx) of $(Au_{0.87}Cu_{0.13})Sn$ IMCs formed during diffusion soldering between Cu/Ti/Si and Au/Cu/Al_2O_3 with Sn interlayers.

Table II. Growth Rate Constants of Intermetallic Compounds Formed during Diffusion Soldering between Cu/Ti/Si and Au/Cu/Al_2O_3 with Sn Interlayers

Temperature (°C)	$(Cu_{0.99}Au_{0.01})_6Sn_5$ (μm/min$^{1/2}$)	$(Au_{0.87}Cu_{0.13})Sn$ (μm/min$^{1/2}$)
250	0.228	0.219
300	0.250	0.462
350	0.287	0.653
400	0.374	0.955

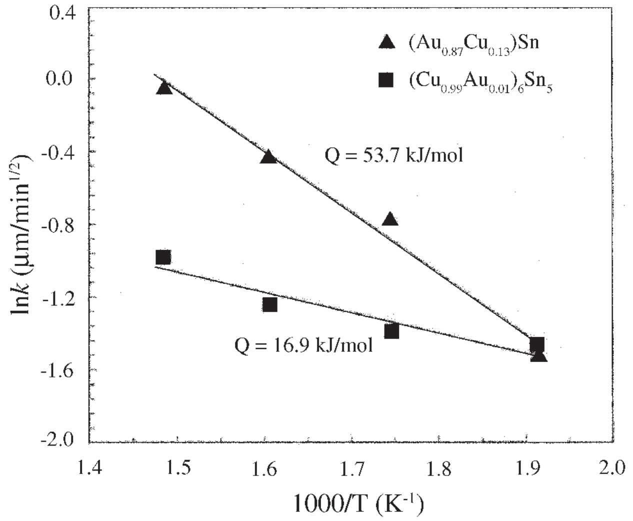

Fig. 6. The Arrhenius plots of growth rate constants (k) for $(Cu_{0.99}Au_{0.01})_6Sn_5$ and $(Au_{0.87}Cu_{0.13})Sn$ IMCs formed during diffusion soldering between Cu/Ti/Si and Au/Cu/Al_2O_3 with Sn interlayers.

Tu and Thompson[9] reported that the growth of the Cu_6Sn_5 IMC during the solid-state reaction between Cu and Sn thin films at room temperature exhibited a linear rate. According to their discussion, the rate-limiting step should be the release of Cu atoms from the Cu film, rather than the diffusion across Cu_6Sn_5. In contrast to the thin-film reaction discussed by Tu and Thompson, Vianco et al.[10] studied the solid-state interfacial reaction between Cu and hot-dipped Sn at temperatures ranging from 70°C to 205°C. Parabolic growth kinetics for Cu_6Sn_5 IMCs was reported. The deviation of the reaction mechanism in Tu and Thompson's study[9] from the research of Vianco et al.[10] should be attributed to the ultra-thin-film specimens (Sn thickness under 0.5 μm) and the quite low reaction temperature (room temperature) adopted by the former study. For the solid-liquid interdiffusion between Cu and Sn thin films at 240°C and 300°C, Bader et al. showed that the growth of the Cu_6Sn_5 IMC did not follow the parabolic growth law.[1] As was explained by them, the deviation was attributed to the reduction of transport grooves resulting from the growth of the scallop-shaped Cu_6Sn_5 IMCs. Because the kinetic measurements obtained by Bader et al. were focused on the initial stage of reaction (reaction time: shorter than 2 min; intermetallic thickness: thinner than 2 μm), it is believed that once all the grooves along the interface have "closed" after a longer reaction time as similar for our study (reaction time: 10–40 min), the reaction-controlling step in the growth of Cu_6Sn_5 should turn out to be the diffusion through the continuous Cu_6Sn_5 intermetallic layer. Hayashi et al.[11] studied the soldering reactions between Cu and liquid Sn saturated with Cu and found that the growth of the Cu_6Sn_5 IMC was diffusion-controlled with an activation energy of 29 kJ/mol, a value quite near our own kinetic measurement (16.9 kJ/mol). In summary of the preceding results, it can be implied that the solid-liquid interfacial reactions in the Cu/Sn thin film case are carried out similarly to a "normal" soldering reaction.

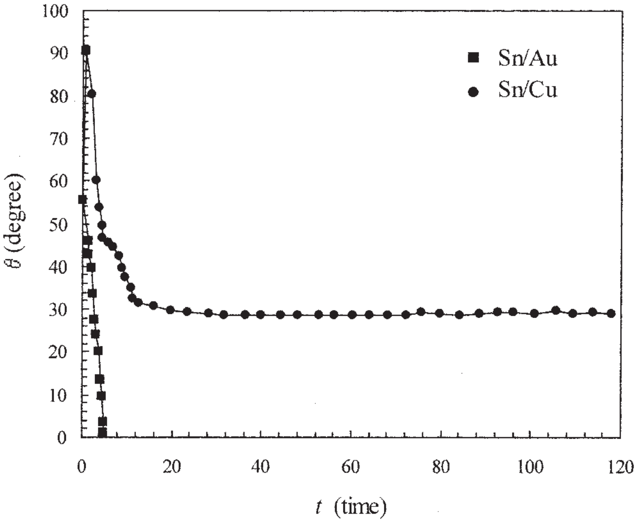

Fig. 7. The contact angles (θ) of liquid Sn on the surfaces of Au and Cu substrates at 350°C. $Sn_{(l)}/Au_{(s)}$ reacts much more quickly than $Sn_{(l)}/Cu_{(s)}$.

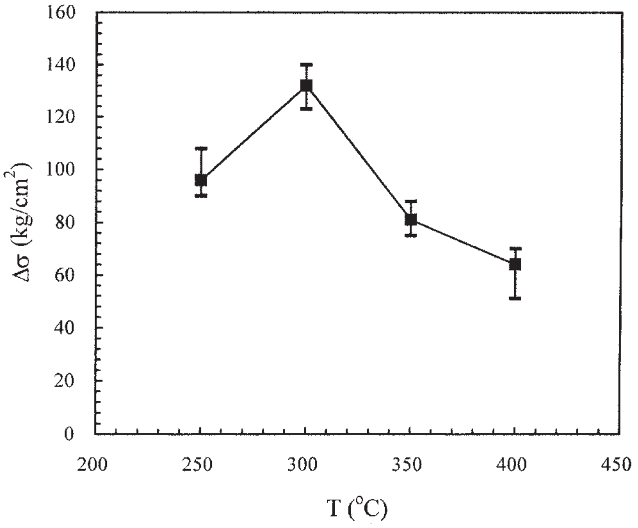

Fig. 8. The tensile strengths (σ) of Cu/Ti/Si wafer diffusion-soldered with Au/Cu/Al_2O_3 substrates at various temperatures for 20 min using a Sn thin-film interlayer.

The calculated activation energy for the growth of the $(Au_{0.87}Cu_{0.13})Sn$ intermetallic (53.7 kJ/mol) is close to the activation energy for the lattice diffusion of Au in Sn ($\|$C: 46.1 kJ/mol, $\perp$C: 74.1 kJ/mol), as reported by Dyson.[12] The growth of the $(Au_{0.87}Cu_{0.13})Sn$ intermetallic is, therefore, believed to be controlled by the lattice diffusion of Au through the solid IMC. The discrepancy in growth rate-controlling mechanisms for $(Cu_{0.99}Au_{0.01})_6Sn_5$ and $(Au_{0.87}Cu_{0.13})Sn$ intermetallics may be attributed to the much quicker liquid/solid reaction for $Sn_{(l)}/Au_{(s)}$ than that for $Sn_{(l)}/Cu_{(s)}$. This explanation can be validated by the quite different wettability of liquid Sn on Au and Cu substrates. Figure 7 shows that the contact angle of liquid Sn on an Au substrate decreases rapidly and vanishes at complete wetting (~0°), while the contact angle in the case of a Cu substrate remains at about 30°, implying that it is much easier for liquid Sn to react with Au than with Cu. In other words, $Au_{0.87}Cu_{0.13}$ reacts rapidly during diffusion soldering with Sn to form $(Au_{0.87}Cu_{0.13})Sn_4$. After the thin-film Sn is exhausted, a further solid/solid interfacial reaction takes place: $(Au_{0.87}Cu_{0.13})Sn_4 + 3(Au_{0.87}Cu_{0.13}) \rightarrow 4(Au_{0.87}Cu_{0.13})Sn$. Because the reaction efficiency is governed by the slow mode of the latter reaction, the rate-controlling mechanism for the growth of $(Au_{0.87}Cu_{0.13})Sn$ is, therefore, the diffusion of Au in this solid intermetallic phase. The solid/solid interfacial reaction in the Au/Pb-Sn solder system has been studied by Hannech and Hall.[13] They found that an $AuSn_4$ IMC was formed under diffusion control during the reaction. The activation energy was 40 kJ/mol, similar to the value of our measurement for the solid/liquid thin-film reaction of the Au/Sn system (53.7 kJ/mol). Their results sustain the view held by this present study that the growth of $(Au_{0.87}Cu_{0.13})Sn$ is controlled by a solid/solid interfacial reaction as discussed previously.

Tensile strengths of the specimens after diffusion soldering at various temperatures for 20 min are shown in Fig. 8. A maximum value of 132 kg/cm^2 is attained at the bonding temperature of 300°C. As Table I indicates, such an optimized bonding condition (300°C, 20 min) is conducive to the growth of $(Cu_{0.99}Au_{0.01})_6Sn_5$ and $(Au_{0.87}Cu_{0.13})Sn$ intermetallic layers to the thicknesses of 1.63 μm and 1.46 μm, respectively.

CONCLUSIONS

To evaluate the applicability of the diffusion-soldering technology in the die attachment process for ceramic packages, the multilayer thin-film systems of Cu/Ti/Si and Au/Cu/Al_2O_3 were bonded with Sn interlayers at various temperatures ranging from 250°C to 400°C. The IMCs formed after diffusion soldering as analyzed by EPMA are η-$(Cu_{0.99}Au_{0.01})_6Sn_5$ and δ-$(Au_{0.87}Cu_{0.13})Sn$ on the respective sides of Si and Al_2O_3. The growth of both IMCs is diffusion-controlled but with different rate-limiting steps. The activation energy for the $(Cu_{0.99}Au_{0.01})_6Sn_5$ intermetallic is 16.9 kJ/mol, which is near that for the diffusion of Cu in liquid Sn (19.5 kJ/mol). The growth of the $(Cu_{0.99}Au_{0.01})_6Sn_5$ intermetallic is controlled by the diffusion of dissolved Cu into the liquid-Sn thin film. The growth of $(Au_{0.87}Cu_{0.13})Sn$ presents an activation energy of 53.7 kJ/mol, a result in agreement with that for the lattice diffusion of Au in Sn ($\parallel$C: 46.1 kJ/mol, $\perp$C: 74.1 kJ/mol), thus revealing that the rate-limiting step in the growth of $(Au_{0.87}Cu_{0.13})Sn$ is the diffusion of Au through the IMC. Tensile tests for the specimens diffusion-soldered at various temperatures for 20 min give a maximal value of 132 kg/cm^2 at the bonding temperature of 300°C, corresponding to the growth thicknesses of 1.63 μm and 1.46 μm for $(Cu_{0.99}Au_{0.01})_6Sn_5$ and $(Au_{0.87}Cu_{0.13})Sn$ intermetallic layers.

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