Isothermal Solidification of Cu/Sn Diffusion Couples to Form Thin-Solder Joints

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Isothermal solidification of conventional Cu/Sn diffusional couples was performed to form thin (30 μm) joints consisting of Cu-Sn intermetallics. During initial stages of isothermal solidification, both Cu_6Sn_5 and Cu_3Sn phases grow, even though the former is the dominant. After consumption of all available Sn, the Cu_3Sn phase grows reactively at the expense of Cu and Cu_6Sn_5. Finally, we obtain solder joints that consist of only Cu_3Sn. Indentation fracture-toughness measurements show that Cu_3Sn is superior to Cu_6Sn_5. Furthermore, indentations of Cu_3Sn exhibit the presence of shear bands, which are not observed in Cu_6Sn_5, implying that the former is more ductile than the latter. Ductile intermetallic-based joints formed by isothermal solidification are promising candidates to form thin (as thin as 5–10 μm or less) solder joints, as they are thermally and thermodynamically stable compared to conventional solder joints. Excess copper in the interconnect provides ductility to the interconnect.

Key words: Cu/Sn, diffusional couples, solder joints

INTRODUCTION

Joining of dissimilar metals using solders is very common in electronic packaging. The primary functions of solder interconnects in electronic devices are to provide mechanical and electrical connections between components. The International Technology Roadmap for Semiconductors[1] predicts that, because of the advancement of complementary metal-oxide semiconductor technology, the maximum chip size may increase from 20 mm^2 to 25 mm^2 by 2005, and the power consumption will increase from 115 W to 160 W. At the same time, to meet higher input/output requirements, the size of the solder will decrease by about 55%, and the peak operating temperature of high-performance chips will increase from 155°C to 175°C. Besides Joule heating, another source of higher operating temperature is the proximity of an electronic device to another heat source, such as the engine in automotive applications. The advances in semiconductor technology and higher operating temperature of devices demand significant advances in packaging technology. Of particular importance is the ability for small, thin, and highly reliable solder joints. Furthermore, for environmental reasons, the electronics industry is moving toward lead-free electronics and, thus, lead-free interconnects. A particular problem is replacing the high-lead solder used for chip-to-chip carrier interconnects in C4 packages. If the chip-carrier to printed-circuit-board interconnects are made with Sn-Ag and Sn-Ag-Cu eutectic solders, the processing temperature is about 250°C, and there is no solder replacement for the high-lead solder that will withstand that reflow temperature. An intermetallic interconnect that can be formed at a low temperature but withstand much higher temperatures during subsequent processing may be a good solution for this need.

Recently, several attempts have been made to make thin-solder joints (10–20 μm) using thin-film metallurgy.[2–4] These attempts use the principles of isothermal solidification or transient liquid-phase bonding (TLP) to form very thin, intermetallic-solder junctions based on copper and tin. Although TLP[5–7] has been traditionally used to bond dissimilar materials for structural applications, it has recently been shown to offer a promising route to very thin, electronic interconnects.[2–4] Bader et al.[2] sputtered Sn and Cu, or Sn and Ni, on Si followed by a diffusion anneal in the temperature range of 240–300°C. Venkatraman et al.[3] attempted to form 10-μm-thick solder joints through isothermal solidification at 295°C using electroplated

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Au (6 μm) and Sn (2 μm) on Cu foils (17.5 μm). Cain et al.[4] performed diffusional modeling of TLP in the Au/Sn/Au system.

The present application of isothermal solidification is to sandwich molten tin between two substrates and isothermally react the molten tin with both substrates, forming an intermetallic interconnect that melts at a much higher temperature. A central idea is to fabricate thin-solder joints, employing a ductile intermetallic. Because copper is widely used in the electronics industry, we have chosen copper as the substrate material. Investigation of intermetallic growth and morphological development will help determine the feasibility of such interconnects for industrial applications.

EXPERIMENTAL PROCEDURES

Pure tin (99.999%) was used to form joints (approximately 50-μm thick) between two 0.25-mm-thick copper foils (99.9999%). The couples were processed at temperatures between 275–325°C. The reaction between liquid Sn and the two Cu substrates forming the sandwich was allowed to continue for times ranging from 15 min to 48 h. After the sample was removed from the furnace and cooled to room temperature in air, it was cross-sectioned for observation. The cross-sectioned pieces were mounted in Lapmaster Fast Cure Acrylic and ground and polished for metallographic examination in a Nikon Epiphot microscope. Finally, the mounted samples were studied with the use of a Hitachi 3500 scanning electron microscope (SEM), operating in backscatter mode, and compositions of the different phases were confirmed with electron dispersive spectroscopy.

The fracture toughness and hardness of the ε- and η-phase intermetallics were measured using a Vicker's indenter on polished cross-sectioned samples. For hardness determination, the loads were applied for 5 sec and were low enough so as to not initiate a crack in the intermetallic. Generally, a 10-g load was used on the η phase and a 100–200-g load was applied to the ε phase. Hardness values were calculated directly from the Vicker's indentation.

Fracture toughness of the intermetallics was determined by the Vicker's-indentation method,[8] using loads ranging between 25–100 g for the η phase and 300–1,000 g for the ε phase. In this measurement, the loads applied were greater than for the hardness measurements such that a penny-type crack developed within the intermetallics, at the corners of the indents. After testing, the samples were examined in the SEM to determine the average lengths of the induced cracks.

RESULTS

Microstructure of Solder Joints

In the following, we present the dynamics of interfacial microstructure during isothermal solidification of Cu/Sn diffusion couples at 275°C and 325°C. Liquid tin reacts with a solid-copper substrate to form a scalloped η-(Cu_6Sn_5) terrain. Beneath the η phase, a relatively planar, slightly undulating layer of ε-(Cu_3Sn) phase also develops. Both phases are stable, as seen in the Cu-Sn phase diagram. The results for various times at 325°C reaction temperature are illustrated in Fig. 1a–f. Figure 1a and b shows the η-phase scallops, growing into liquid tin from both solid-copper substrates. The η scallops have rounded ends, and there are considerable differences in their heights. At least some of this difference arises because the sections are taken through an array of scallops. In Fig. 1a and b, a complete layer of ε phase underlies the η phase. This phase is undulated with the "wave" heights corresponding to the η-scallop peaks, as previously observed on reaction of molten sn with a single cu surface.[9] Note there are open channels of molten tin very close to and, at times, touching the ε layer.

Figure 1d shows η scallops in contact with each other. Scallops brush into each other from the opposing sides and combine, leaving small pockets of Sn. The η scallops grow in the direction of these pockets because it is the only way to continue consumption of the remaining Sn. Scallop contact is also shown in Fig. 2c, which was heated at 275°C for 5 h.

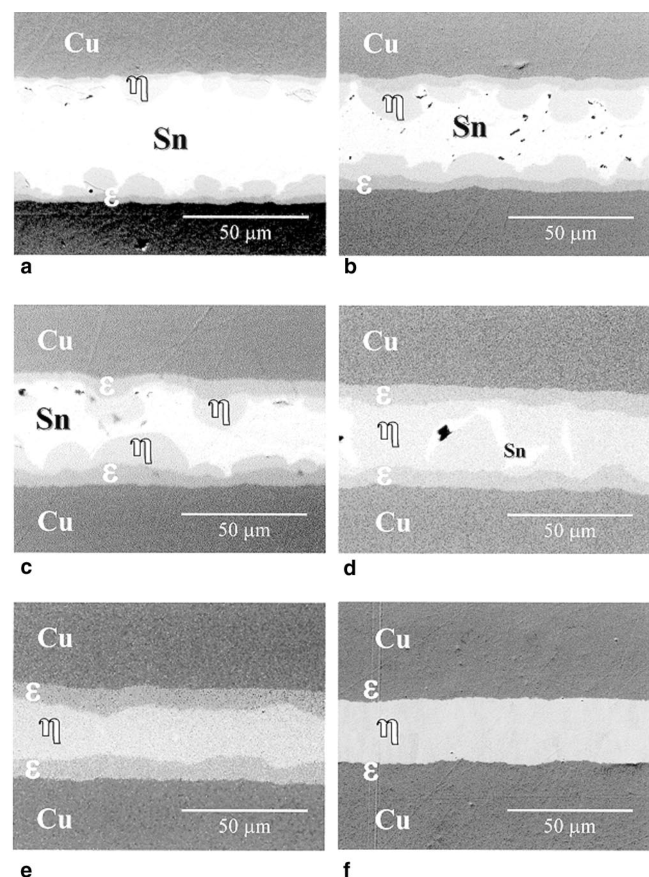


Fig. 1. Progression of intermetallic formation in similar samples at 325°C resulting in a thin solder joint 30–50-μm thick. The figures illustrate reactions times for (a) 15 min, (b) 1 h, (c) 2 h, (d) 3.5 h, (e) 3.5 h, and (f) 5 h. In each micrograph, η and ε represent Cu_3Sn and Cu_6Sn_5, respectively.

Soon after the intermetallic layers meet, η-phase scallops grow to consume all of the remaining pockets of Sn. Thus, the joint is left with a single uniform layer of η, two growing layers of ε, and the surrounding Cu substrates. Figure 1e is an illustration of this stage.

Figure 1a–e also shows the progressive growth of the ε phase with longer reaction times. The ε layers grow thicker with increasing reaction time and, in doing so, consume the η as well as copper, as shown in Fig. 1e. At extremely long reaction times, only the ε phase is present (Fig. 1f). Once the ε phase has developed to encompass the entire volume of the joint, no further changes in phase appear to occur after still longer reaction times. It should be noted that the ε developed with an unequiaxed, columnar-grain structure, as shown in Fig. 3. These grains are approximately 15–25 μm in width (parallel to the copper surface) and greater than 50 μm in length (perpendicular to the copper).

When pure Cu and Sn are sandwiched together, as in our experiments, upper and lower layers of intermetallic appear to develop simultaneously. While the intermetallics growing from either substrate share the same tin source, their copper supplies are initially independent. When the shared Sn source becomes scant, the growing η scallops from either copper substrate advance upon each other vertically. However, Fig. 1c shows that each η-scallop's crest does not meet with another scallop in direct alignment from the opposite side, but it, instead, shifts its direction of growth. Figure 2a–c exemplifies the occurrence of relatively misaligned, η growth at 275°C for 18 h and 48 h.

Figure 4a and b illustrates two distinct short-circuit interdiffusion paths. In Fig. 4a, liquid Sn is in contact with a thin layer of η phase adjacent to the Cu substrate. In contrast, Fig. 4b shows that liquid Sn is in contact with a thin layer of ε adjacent to the Cu substrate. While the local equilibrium between liquid Sn/η is consistent with the phase diagram, the observation of liquid Sn in contact with the ε phase contradicts the equilibrium phase diagram at 275°C. Perhaps, it represents a transient effect associated with the dissolution of the η phase.

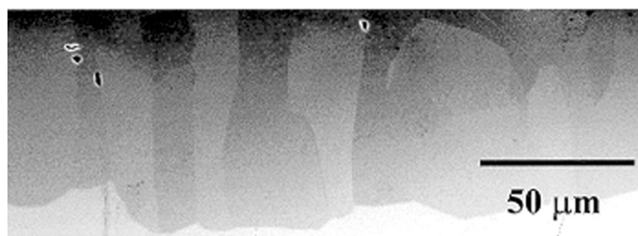


Fig. 3. SEM micrograph showing columnar grains of Cu_3Sn formed at 325°C.

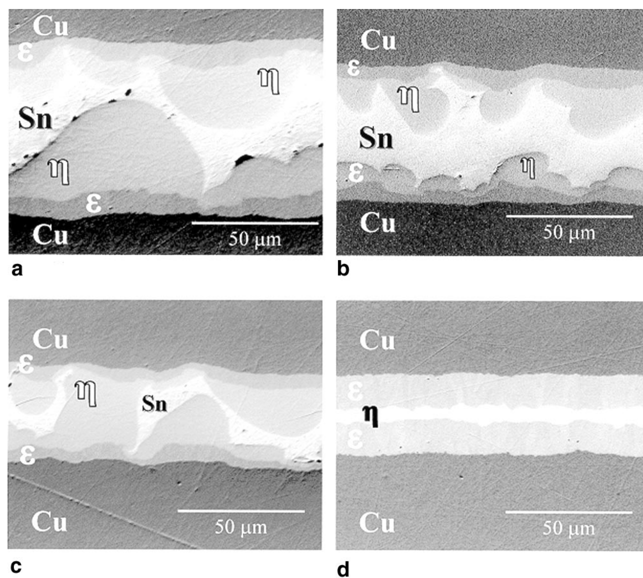


Fig. 2. Reaction times of (a) 18 h, (b) 48 h, and (c) 5 h for intermetallic joints reacted at 275°C show staggered η scallops. (d) Complete intermetallic η-phase joint and growing ε-phase layers reacted at 325°C for 5 h.

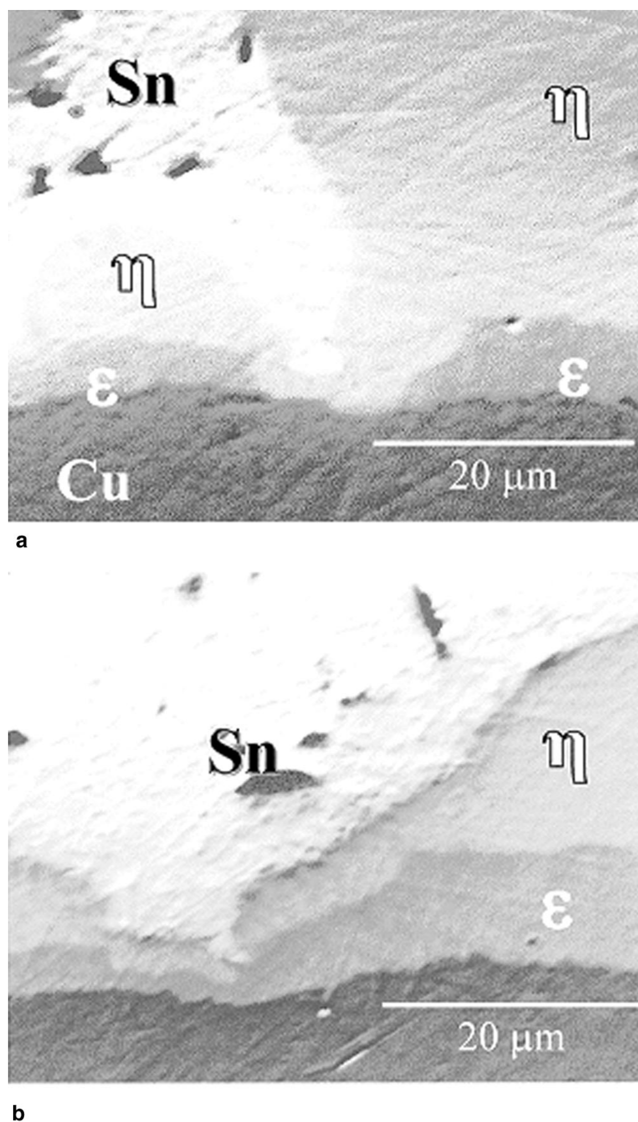


Fig. 4. (a) Cu diffusion channel through η layer in sample reacted for 18 h at 275°C. (b) Cu diffusion channel through ε layer in different region of joint shown in (a).

Indentation Hardness and Fracture Toughness of Cu_6Sn_5 and Cu_3Sn

The indentation fracture toughness was estimated from Vicker's-indentation cracks using the following formula:[8]

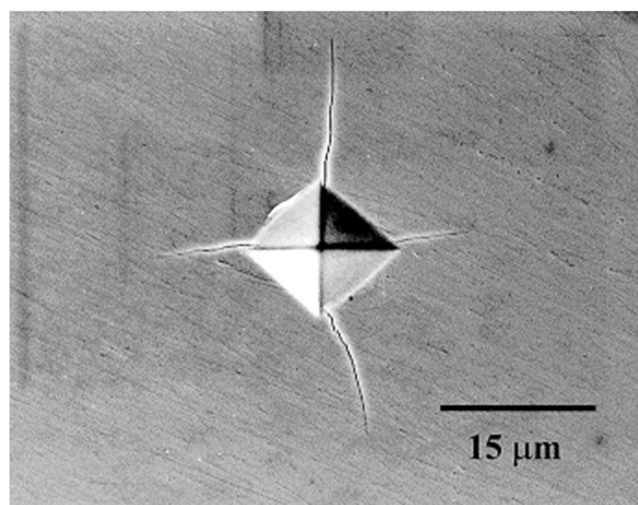
$$K_{IC} = 0.016\left(\frac{E}{H}\right)\left(\frac{F}{C^{1.5}}\right)$$

where E is Young's modulus, H is the hardness, F is the indentation load, and C is the indentation crack length measured from the center of indentation. The E of η and ε phases are taken from Fields et al.[10]

Figures 5a and 4b show characteristic features of indentation cracks in η and ε phases, respectively. In the case of the η phase, the cracks propagate freely from all four corners. On the other hand, because of insufficient thickness of the ε layer, the cracks propagate freely from only two corners and from the other two corners the cracks are stopped at the ε/Cu interface (Fig. 5b). The Vicker's hardness of η and ε phases is 450 ± 21 kg/mm^2 and 430 ± 15 kg/mm^2, respectively. These are in good agreement with those reported by Fields et al. Based on the maximum crack lengths, the calculated indentation fracture toughnesses for η and ε phases are 0.402 ± 0.08 MPa $\sqrt{m}$ and 0.961 ± 0.14 MPa $\sqrt{m}$, respectively. Using the average crack length, the calculated fracture-toughness values for η and ε are 0.481 ± 0.09 MPa $\sqrt{m}$ and 1.230 ± 0.31 MPa $\sqrt{m}$, respectively. In both cases, these values differ significantly from Fields et al., who reported fracture-toughness values of 1.4 ± 0.3 MPa $\sqrt{m}$ for η and 1.7 ± 0.3 MPa $\sqrt{m}$ for ε.

In the η phase, cracking always initiated from all four corners of the indent and propagated along a straight-line path, as shown in Fig. 5a. Because each hardness indent was made within a single η grain (scallop), there were no grain boundaries to impede the propagation of the crack. The lack of grain boundaries may help explain the difference in fracture toughness reported here from that reported by Fields et al. In their study, polycrystalline Cu_6Sn_5 was used with a grain size of roughly 10–15 μm.

In contrast to the η, in the ε phase, cracks did not always initiate at all four corners, and the induced cracks generally spanned several grains and propagated primarily in a transgranular manner (Fig. 5b). In a few instances, however, cracking in the ε was noted to follow along a grain boundary. These cracks always initiated at the grain boundary and continued to propagate along the boundary for the entire length of the crack. In this case, the crack propagated along the long axis of the grain, perpendicular to the copper surface. Because the grain size of the ε in our study was roughly the same as that in the investigation by Fields et al. (roughly 30–40 μm in length), it is not likely that grain size is the source of the difference in calculated toughness values of the ε. Instead, the difference in the measured fracture toughness is likely a result of processing. Their bulk intermetallic was no greater than 99% dense and, therefore, contained a high concentration of voids, which would act to blunt the crack and thereby reduce the stress concentration at the tip.



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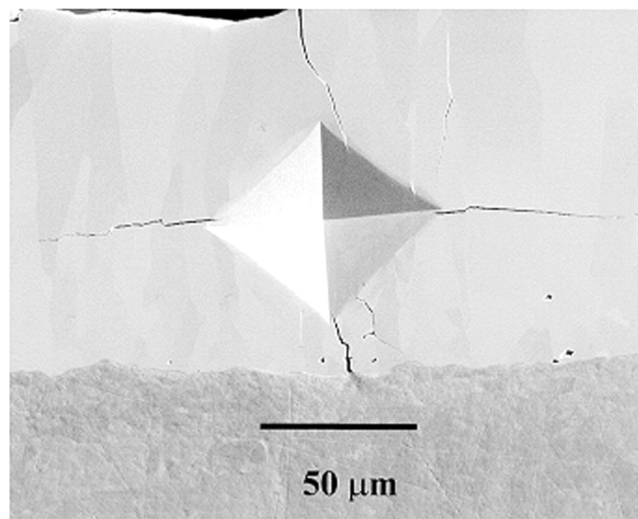

b

Fig. 5. SEM micrographs showing hardness indents and cracks at room temperatures: (a) Cu_6Sn_5 tested at a load of 50 g and (b) Cu_3Sn tested at a load of 1 kg.

Another important observation is the presence of slip bands around indentations in the ε phase; an example of which is shown in Fig. 6. However, slip bands were not observed in the case of the η phase. The slip bands form because of localized plastic deformation from the stress gradients around the indentations. The presence of slip bands demonstrates the ability of the ε phase to undergo plastic deformation prior to fracture. Its much higher fracture load, compared to the η phase, makes it the preferable intermetallic for interconnects.

DISCUSSION

An isothermal-solidification process may consist of four stages:[11] (a) dissolution of the base metal in liquid solder and the establishment of local equilibrium at the liquid/solid interface; (b) homogeniza-

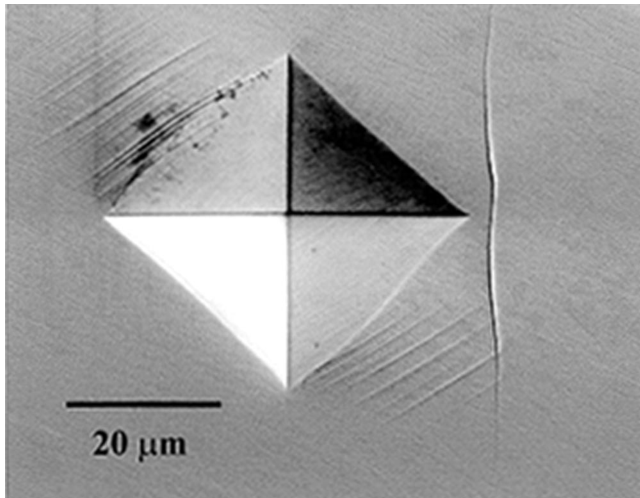

Fig. 6. SEM micrograph showing a hardness indent and slip bands in Cu_3Sn tested at a load of 500 g.

tion of the liquid; (c) isothermal solidification, in which the rate-controlling step is the interdiffusion in the new phases that may form at the interface; and (d) homogenization of the solidified joint.

In the case of Cu/Sn diffusion couples, it is well known that the local equilibrium at the interfaces is established quickly, leading to the formation of Cu_6Sn_5 and Cu_3Sn intermetallics. Experimental atomic-transport data[12] show that the diffusion of Cu in liquid Sn is very fast. Because both Cu_6Sn_5 and Cu_3Sn have a narrow homogeneity range, it is reasonable to assume that their compositions do not change significantly during the isothermal-solidification process. Therefore, the isothermal solidification, via the growth of Cu_6Sn_5 and Cu_3Sn intermetallics, and subsequent reactive homogenization (leading to only ε phase) are the key issues to understanding the fabrication of thin-solder joints involving Cu and Sn.

Isothermal solidification is primarily dominated by the reactive interdiffusion and growth (increase in volume fraction) of the η phase. A reactive interdiffusion in Cu/Sn couples is inherently complex as it involves many parallel processes, such as phase nucleation, lattice or grain-boundary diffusion in the η and ε, dissolution of η in the liquid, grain-boundary grooving (of η), grain coarsening, and creation or annihilation of point defects if any. As a result, the interpretation of the kinetic parameters evaluated from the reactive-diffusion experiments can be fairly complex.[13,14] Nonetheless, previous research[9,15,16] has shown that the development of the η-phase scallops takes place primarily by a nonconservative-coarsening/growth mechanism during which the number density of scallops decreases, while its volume fraction increases. The decrease in experimental number density of scallops in Figs. 1 and 2 qualitatively supports the prevailing coarsening mechanism. During the nonconservative coarsening process, the transport of copper into the molten tin and to the reaction sites may take place by more than one mechanism. In the case of the Cu/liquid-Sn interfacial reaction, the activation energies for interdiffusion in η and ε have been reported to be 36.4 kJ/mol and 46 kJ/mol.[17] Because of the presence of more than one type of short-circuit diffusion path, it is unlikely that the activation energy of the growth can be attributed to only one of the mechanisms that have been shown to occur.

Once all the liquid Sn is consumed, the homogenization of the solidified joint takes place by the reactive diffusion in the solid state where the ε phase grows at the expense of the phase. To obtain only ε phase in a joint, the supply of Cu must be sufficient. This process is expected to be inherently slow. For the solid-state reaction of Cu/Sn couples, the activation energy for interdiffusion in ε phase has been reported to be 70.7 kJ/mol,[18] 90 kJ/mol,[19] 43 kJ/mol,[20] 66.1 kJ/mol (fine grain),[2] and 81.6 (single crystal)[2] kJ/mol. The diffusion data of Bader et al.[2] suggest that a fine grain of the ε phase is highly desirable to accelerate its reactive-growth kinetics.

CONCLUSIONS

Isothermal solidification of tin between two layers of copper form interconnects having higher melting temperatures than interconnects used today because of η- and ε-intermetallic formation. The growth of the η phase in the intermediate stages of development of the process is influenced by interdiffusion between upper and lower intermetallic layers. Depending on the extent of reaction between Cu and molten Sn, a range of interconnects can be made from a fully ε interconnect to connected η grains with pools of Sn and a thin layer of ε. Isolated-Sn regions, even though molten during the second level of processing, may impart some needed ductility to the interconnect during operation of a device.

The ε phase is more ductile and tougher than the η phase. These properties are demonstrated by the presence of shear bands and indentation fracture-toughness values.

Ductile intermetallics are promising candidates to form very thin joints in electronic packages. The intermetallics may be chosen so that they are thermally and thermodynamically more stable than conventional solder joints, where the interfacial reaction and microstructural coarsening during service contribute significantly to the reliability of the device. The intermetallic layer connecting the two sides of the interconnect may be very thin so that the reaction time at temperatures currently used with high-lead solders in C4 joints may be sufficiently short so that current reflow furnaces can be used.

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