

Intermetallic Phase Formation in Thin Solid-Liquid Diffusion Couples

F. BARTELS and J.W. MORRIS, JR.

Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720

G. DALKE and W. GUST

Max-Planck-Institut für Metallforschung, Seestr. 75, D-70156 Stuttgart, Germany

Conducting joints with low fabrication temperatures and high thermal stability are useful in modern electronics. This paper discusses the potential use of intermetallic phases in making such joints. Thin interconnection layers that consist entirely of intermetallic phases have been produced by joining planar Cu substrates that are coated with thin films of Sn. Thin layers (1–5 μm) of intermetallic phase are produced at temperatures slightly above the melting temperature of Sn in a process similar to reflow soldering. Metallography and x-ray analysis are used to characterize the formation mechanism of the intermetallic. Cu dissolves into the liquid Sn by diffusion along narrow channels between grains of the growing $\eta\text{-Cu}_6\text{Sn}_5$ intermetallic phase. Tensile tests were used to measure mechanical properties. The joint strength increased with reaction time. The joint fails in a ductile mode as long as unreacted Sn is present, but fractures along interphase boundaries when the joint is completely intermetallic.

Key words: Diffusion, intermetallic compound, solder

INTRODUCTION

When microelectronic components are operated at moderately high temperature, as, for example, in automotive electronics or solid state heating elements, the common soft solders cannot be used because of their low thermal stability. New joining methods are needed to withstand such high temperatures. At the same time the bonding temperature should be as low as possible for technical and economical reasons.

One approach to meeting this need is to form joints with intermetallic phases (IP) produced by isothermal solidification. Using this method, joints can be produced at low temperatures (200–300°C) and can later be used at temperatures up to 200°C above the temperature at which they were formed.¹ To form intermetallic joints, substrates with relatively high melting points, such as Cu or Ni, are coated with thin layers of reactive metals with relatively low melting points, such as Sn or In. If coated substrates are

clamped together and heated above the melting point of the low-melting element, the liquid thin film reacts with the substrate to form intermetallic phases that have the desired high temperature and mechanical stabilities.

This study investigated the bonding of Cu plates coated with Sn. There are seven intermetallic phases in the binary Cu-Sn system, but only two of them are thermodynamically stable at room temperature: the orthorhombic $\epsilon\text{-Cu}_3\text{Sn}$ (whose melting temperature, $T_m = 675^\circ\text{C}$) and the hexagonal $\eta\text{-Cu}_6\text{Sn}_5$ -phase ($T_m = 415^\circ\text{C}$).² This system was chosen because both elements are commonly used in microelectronics, are widely available, and are nontoxic.

EXPERIMENTAL

Polycrystalline substrates of Cu with dimensions $4 \times 4 \times 2 \text{ mm}^3$ were prepared by rolling, cutting, and annealing 99.999% pure Cu. One $4 \times 4 \text{ mm}^2$ surface of the substrates was precision milled to reduce the roughness to less than 0.01 μm . Sn films of 1 μm thickness were deposited onto the milled surfaces of

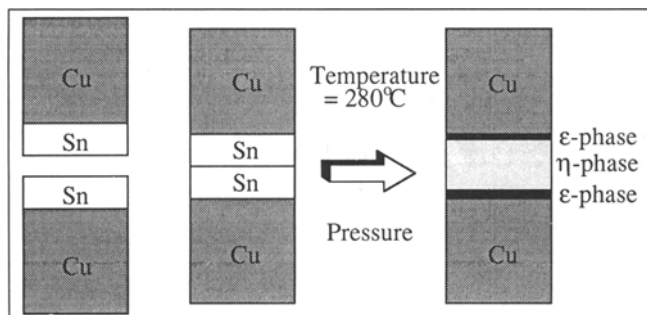


Fig. 1. Schematic diagram illustrating the isothermal solidification process.

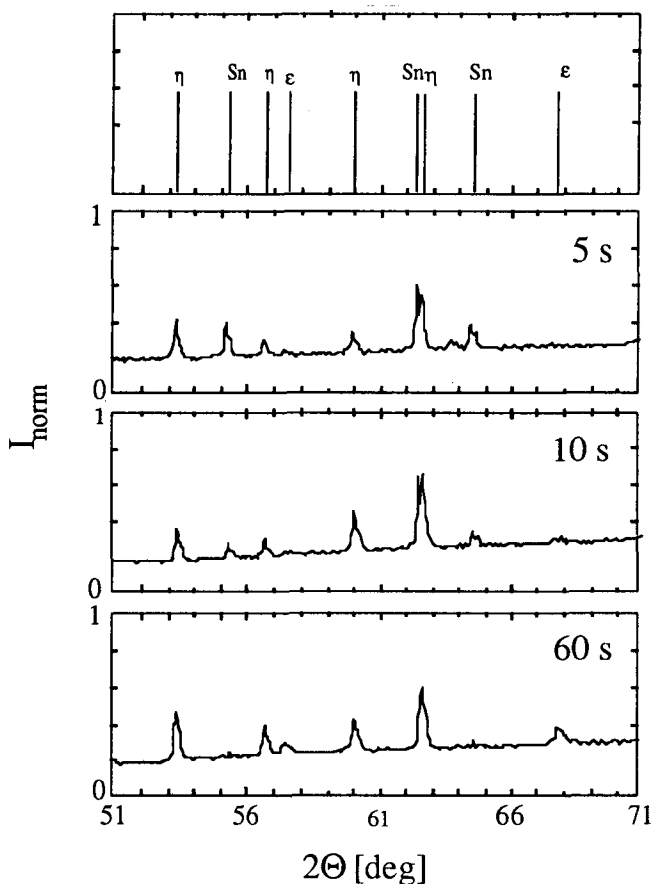


Fig. 2. Phase identification by x-ray diffraction. The chronological sequence shows the gradual decrease in the intensity of the characteristic Sn-peaks, accompanied by an increase in the intensity of the characteristic peaks of the intermetallic phases.

the substrates by electron-beam evaporation with a deposition rate of $0.02 \mu\text{m}/\text{min}$. During deposition, the substrates were water cooled to suppress the nucleation of intermetallic phases. Figure 1 illustrates the subsequent joining process. Two coated Cu substrates were stacked with the Sn layers in contact, and compressed in a custom made soldering press at a load of $0.05\text{--}0.1 \text{ MPa}$. The sample is held at 280°C to accomplish the isothermal reaction of liquid Sn and solid Cu to form the intermetallic. No flux was used, and the sample was reacted in ambient air.

Metallographic observations and x-ray diffraction measurements were used to identify the intermetallic

phases and estimate the reaction rates. In order to carry out x-ray diffraction measurements without changing the joining conditions, one of the coated substrates was replaced by a milled and oxidized Cu substrate with the same dimensions. After reaction, the two substrates could easily be separated due to the poor wetting of the oxide layer on the Cu by the liquid Sn.

Tensile tests were done to measure the mechanical properties of the joints. To accomplish these, the joints were glued onto stainless steel holders which could be fixed into a tensile testing machine by an universal joint.

RESULTS

Diffraction Measurements

X-ray diffraction was used to identify the intermetallic phases and to determine the sequential order of appearance of the phases. Since the presence of pure elements like Sn is also detectable, the diffraction method can also be used to measure the total liquid-solid reaction time. Measurements at the beginning of the reactions showed no indication of intermetallic phases.

Figure 2 shows portions of the diffraction patterns of an $1 \mu\text{m}$ thick Sn film on a Cu substrate after three different heating times. After reacting for 5 s, the diffraction pattern shows characteristic peaks of both pure Sn and the Sn-rich $\eta\text{-Cu}_6\text{Sn}_5$ -phase. No other intermetallic peaks are visible. On further reaction, the intensities of the Sn peaks gradually decrease until after 60 s no Sn peaks remain. The intensity of the characteristic peak of the η -phase increases monotonically, and peaks of the Cu-rich $\epsilon\text{-Cu}_3\text{Sn}$ -phase are also noticeable after 10 s reaction.

These results show that both the thermodynamically stable Cu-Sn intermetallics are formed in the joint, but the η -phase appears first and grows much faster than the ϵ -phase. The reaction is essentially complete after 60 s. Further reaction causes an increase in the intensities of the ϵ -phase peaks while the intensities of the η -phase peaks decrease. The increase in the fraction of ϵ -phase is expected since the substrates provide a reservoir of Cu.

Morphology

Cross-sectional micrographs were used to study the morphology of the intermetallic phases within the joint and to look for pinholes in the joint which could influence the joint quality. They were also used to investigate the reaction mechanism that leads to the short reaction times measured by x-ray diffraction. Figure 3 shows the cross sections after 10, 30, and 120 s reaction time at 280°C . Residual Sn was selectively etched away, which produces the black regions in the micrographs. After 10 s, almost the entire joining region is covered by large white rounded grains of the η -phase. At the bottom of the intermetallic layer a thin layer of the ϵ -phase is discernible by its darker color. This phase is grown by a solid-solid-reaction

between Cu and the η -phase. Each grain of the η -phase is still covered by unreacted Sn and between the grains the Sn reaches the Cu-substrate.

After 30 s, the unreacted Sn is reduced to isolated pockets. There is no contact between the Sn pockets and no contact between unreacted Sn and Cu. Hence, further reaction must be controlled by diffusion through the intermetallic layer.³ The single grains of the η -phase are not visible in the micrographs because the grains adjoin and etching revealed only phase contrast, not grain contrast. The amount of ϵ -phase has increased and separates the η -phase from the Cu-substrate by an approximately 0.5 μm thick layer. The growth of the ϵ -phase is enhanced at high temperatures due to the higher interdiffusivity in the η -phase.⁴ On the formerly smooth Cu-surface, hollows appear on both sides of the residual Sn pockets. This indicates, that the main path of Cu transport up to this point is by diffusion through the unreacted Sn remaining between grains of the η -phase.

After 120 s, the microjoint consists entirely of the two intermetallic phases. There are only small pinholes left. Because of the small size of the pinholes, it could not be determined whether these holes were filled with residual Sn or if they are a consequence of the volume reduction during the reaction.

The examination of the cross sections confirmed that the reaction is finished in very short time, as

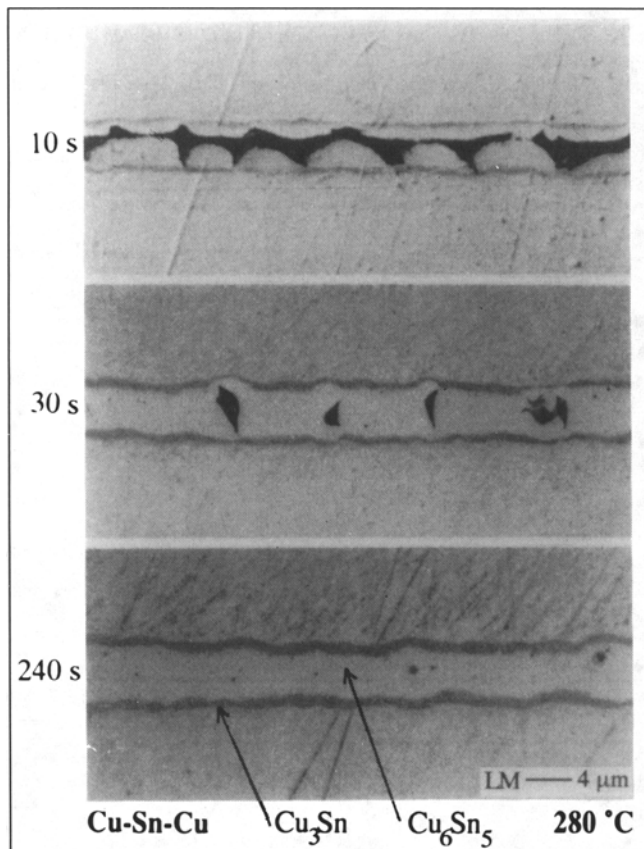


Fig. 3. Cross-sectional view of the joint after 10, 30, and 240 s reaction time at 280 °C. Residual Sn is selectively etched causing these areas to appear black.

indicated by the x-ray measurements, and that the final joint contains no or only small pinholes. The reason for the high reaction rate is the contact of unreacted liquid Sn and Cu between grains of the η -phase during the initial stage of the reaction. In the first 10 to 15 s of the reaction each grain of the η -phase is totally covered with unreacted Sn and between the grains there are deep channels in which the Sn reaches down to the Cu-substrate. Cu can dissolve in the liquid Sn and diffuse through the liquid phase to the top of the η -grains. The hollows in the substrate surface indicate the rapid dissolution of Cu at these sites. The probable reason for the residual Sn channels is an energetic advantage for the η -phase grains to be wetted by liquid Sn instead of forming grain boundaries.⁵ After all channels are closed, unreacted Sn remains in isolated pockets, separated from the Cu, and reacts at a much lower rate. Finally, the ϵ -phase grows by a solid-solid reaction between Cu and the η -phase and thus can only be seen after the η -phase has formed.

Mechanical Properties

The ultimate tensile strength was measured as a function of the reaction time to determine how the strength varies as the intermetallic fraction increases.

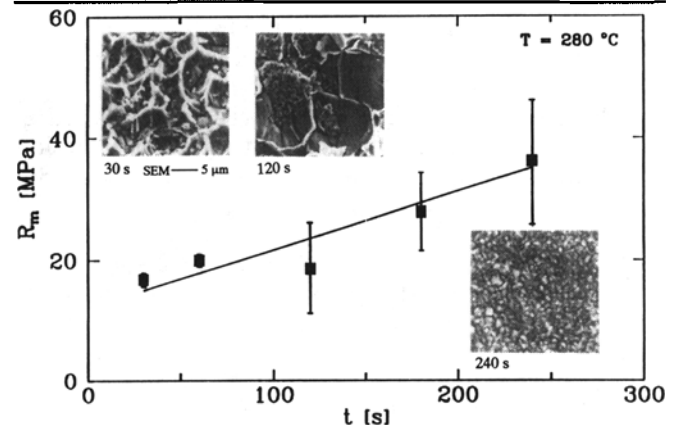


Fig. 4. Tensile strength as a function of the reaction time at 280 °C. Scanning electron micrographs of the fracture surface after 30, 120, and 240s are included in the plot.

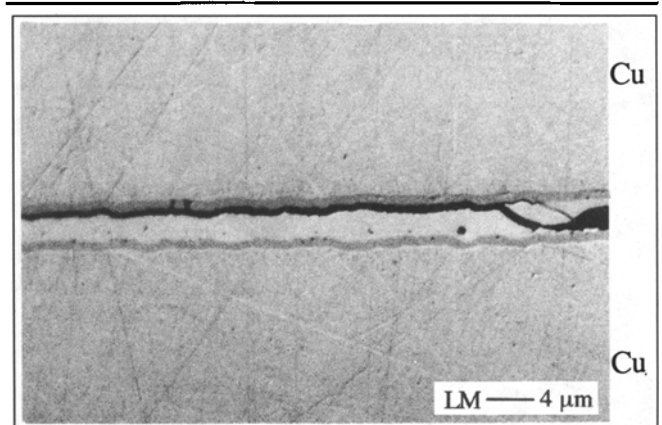


Fig. 5. Cross-sectional view of a crack in a sample tested in tension after 240 s at 280 °C.

Sets of four to six tests were done after 30, 60, 120, 180, and 240 s reaction time. The results are plotted in Fig. 4 and show that the tensile strength increases with reaction time. The strength after 30 s is approximately 18 MPa, which is approximately equal to the strength of pure Sn.⁶ It increases to almost 40 MPa after 240 s. As shown above, the reaction of liquid Sn and Cu is finished somewhere between 60 and 120 seconds. Note the increasing scatter of the experimental data at longer times. This demonstrates the brittleness of the intermetallic phases relative to metallic Sn.

Scanning electron micrographs of fracture surfaces after 30, 120, and 240 s reaction time are shown in Fig. 5. After 30 s, the fracture mode is ductile. This fracture surface indicates brittle particles embedded in a soft matrix. After 120 s reaction, a transition stage is reached in which the crack propagates partly at the interphase, as indicated by the rougher areas in the fracture surface, and partly in an intergranular mode, presumably between grains of the η -phase. After 240 s, the fracture mode appears to be entirely intergranular.

These SEM micrographs suggest that cracks tend to follow interphase boundaries after long reaction times. This hypothesis is confirmed by the result presented in Fig. 6, which shows a cross-sectional view of a crack in a sample heated for 240 s at 280°C. The crack propagates along the phase boundary between the η and the ϵ -phase. This interface is the weakest site in the joint after the reaction. Nevertheless the joints become stronger as the ϵ -phase fraction increases, and they are much stronger than pure Sn.

CONCLUSIONS

This study shows that microjoints consisting entirely of intermetallic phases can be produced at reasonable low temperatures (200–300°C) in short

reaction times (60–240 s). The reaction is rapid because a partially reacted intermetallic layer does not seal the Cu substrate; it contains narrow channels of liquid Sn between grains of the η -phase that provide rapid diffusion paths for Cu. This maintains a high rate of formation of the η -phase until the reaction zone is almost filled with intermetallic.

The integrity of the joints appears to be very good. The reaction zone is entirely filled with the two thermodynamically stable Cu-Sn intermetallic phases, and there are only a few very small pin holes ($<0.5\ \mu\text{m}$) in the reaction zone.

The tensile strength of the joints is high, and increases with reaction time. The fracture mode changes from the ductile, while pure Sn is present, to an interphase fracture mode in which the crack propagates at the interphase between the ϵ and η -phases. The scatter in the strength from sample to sample increases with reaction time, showing the more brittle character of the fracture mode.

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