

A comparative study of silver-epoxy and tin-lead solder in their joints with copper, through mechanical and electrical measurements during debonding

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A comparative study of silver-epoxy and tin-lead solder in their joints with copper was made through simultaneous mechanical and electrical measurements during debonding. Silver-epoxy joints to copper abruptly increased in contact electrical resistivity upon completion of shear debonding, whereas tin-lead soldered joints to copper did not, due to the higher ductility of solder compared to silver-epoxy. The contact resistivity before debonding was higher for silver-epoxy than solder. Cleansing of the copper surface was essential for silver-epoxy, but not for solder. Acetone washing of copper surface helped silver-epoxy joints, but not soldered joints. Acid washing helped soldered joints more than acetone washing, but helped silver-epoxy joints to the same extent as acetone washing.

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1. Introduction

Electrical connections using solders (e.g., tin-lead) and conductor filled polymers (e.g., silver particle filled epoxy, abbreviated silver-epoxy) [1–4] as the joining media are widely used in electronic packaging. Solders are more conventional and well accepted than conductor filled polymers, but the environmental problems associated with solder use and the thermal fatigue problem associated with soldered joints are causing the use of conductor filled polymers to grow rapidly. A conductor filled polymer is a composite material in which the matrix (polymer) is non-conducting and the conductivity of the composite is derived from that of the filler. In contrast, a solder is a metal alloy, the entirety of which is conducting. Moreover, a conductor filled polymer is much less conducting than a solder. In addition, joining with solders involves heating, but joining with conductor filled polymers may or may not involve heating. These differences between a conductor filled polymer and a solder suggest differences between joints made using these two media. This paper addresses the differences in terms of the contact resistivity, shear bond strength, effect of surface treatment of the adjoining copper, and change in contact resistivity upon debonding for joints with copper. A low contact resistivity and a high bond strength are obviously desirable. The absence of change in contact resistivity upon debonding is also desirable, as this means that a debonded joint is still good electrically and the joint is thus more reliable electrically. Intuition suggests that a debonded joint is bad electrically, but recent work has shown that the contact resistivity of a soldered joint essentially does not

change upon debonding, but only upon physical separation [5, 6]. Whether this is also the case for a joint made with a conductor filled polymer has not been previously investigated. This work extends previous work from soldered joint to silver epoxy joint, thereby providing a comparative study.

2. Experimental methods

The solder used was eutectic tin-lead; its volume electrical resistivity was $10^{-5} \Omega \cdot \text{cm}$; its coefficient of thermal expansion was $25 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$; its melting temperature was 183°C ; it was used without flux. The conductor filled polymer used was silver particle filled epoxy (CW2400 Circuit Works Conductive Epoxy, from Chemtronics Inc., Kennesaw, GA); its volume electrical resistivity was less than $10^{-3} \Omega \cdot \text{cm}$; its coefficient of thermal expansion was $120 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ at $25\text{--}100^\circ\text{C}$ (as measured in this work); it was cured at $80\text{--}90^\circ\text{C}$ for 10–15 min during use. The interface between each of these two joining media and copper wire (2 mm diameter, unless stated otherwise; coefficient of thermal expansion $17 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) was investigated by simultaneous measurement of the contact electrical resistivity and the shear stress during pull-out of a copper wire from the joining medium in which it was embedded at an end. The shear force was applied by using a Sintech 2/D screw-type mechanical testing system under displacement control at a displacement of 1.0 mm/min. A copper wire was embedded at both ends in the joining medium, but exposed in the middle, such that the embedment length was larger at one end than

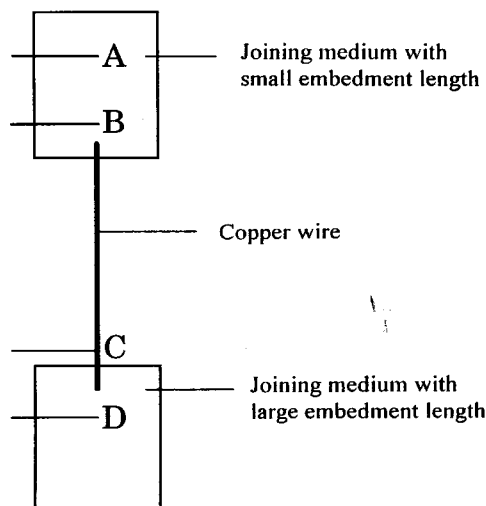


Figure 1 Sample configuration for simultaneous measurement of shear stress and contact electrical resistivity between copper wire and joining medium.

the other (Fig. 1). Subsequent debonding upon pull-out occurred at the end with the smaller embedment length. The contact resistivity (DC) was measured by the four-probe method. The four probes (labeled A, B, C and D in Fig. 1) were along a line, such that probe C was on the exposed copper wire, probes A and B (0.5 cm apart for silver-epoxy and 1 cm apart for solder) were on the joining medium embedding the wire by the smaller embedment length and probe D was on the joining medium embedding the wire by the larger embedment length. Current was passed through probes A and D; voltage was measured between probes B and C. The distance between probes C and D was 2–3 cm for silver-epoxy and about 1 cm for solder. The distance between probes B and C was 2–3 cm, depending on the sample. A Keithley 2001 multimeter was used. The measured resistance between the voltage probes consisted of the volume resistance of the copper wire, the volume resistance of the joining medium with the smaller embedment length and the contact resistance between copper and joining medium with the smaller embedment

length. The two volume resistances were separately obtained by measurement of the corresponding volume resistivities and then subtracted from the measured resistance in order to obtain the contact resistance.

The surface treatments applied on the copper wire prior to embedding in a joining medium were (i) acetone washing, (ii) 5% HCl acid washing, and (iii) 5% HCl acid washing followed by acetone washing. Treatments (i) and (ii) were applied to the solder case; treatments (i) and (iii) were applied to the silver-epoxy case. Treatment (iii) was not applied to the solder case because the heat during soldering was sufficient to remove any moisture that remained after acid washing. Scanning electron microscopy (SEM) showed that the surface contamination was less after acetone washing and the surface roughness was increased after acid washing (Fig. 2).

3. Results

Fig. 3 shows the shear stress and contact resistivity obtained simultaneously for as-received copper wire (1 mm diameter) embedded in solder to a length of 2.6 mm. The shear stress increased due to debonding. The maximum shear stress corresponded to the shear

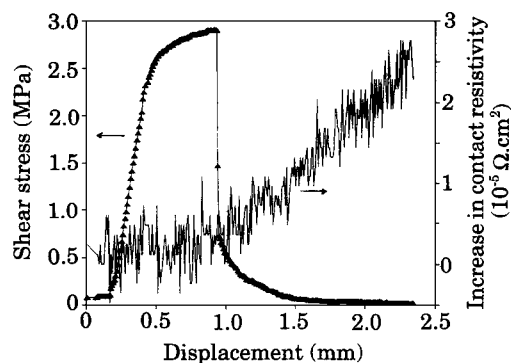


Figure 3 Variation of contact electrical resistivity and shear stress with displacement during pull-out of as-received copper wire from solder.

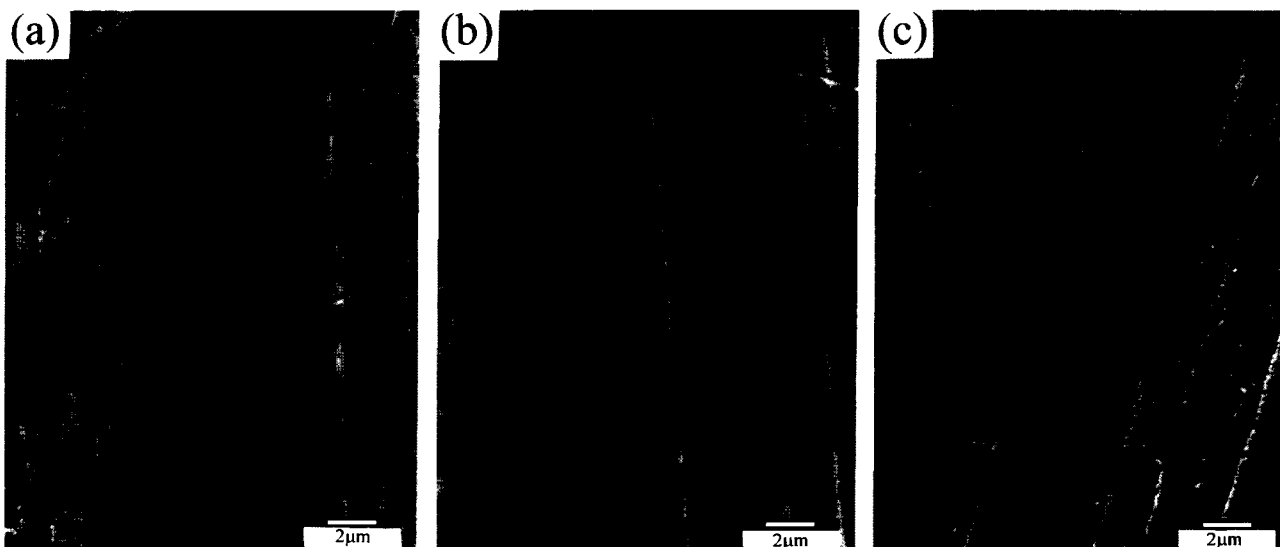


Figure 2 SEM micrographs of copper wire. (a) As received. (b) Acetone washed. (c) Acid washed.

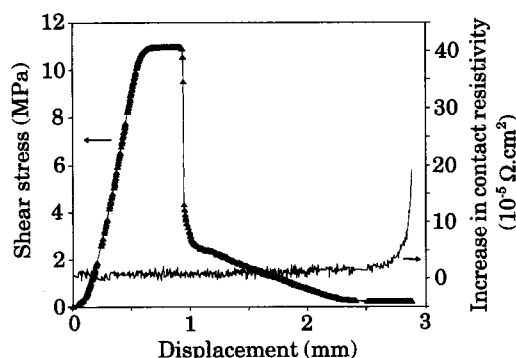


Figure 4 Variation of contact electrical resistivity and shear stress with displacement during pull-out of acid washed copper wire from solder.

bond strength (3 MPa, Fig. 3). The initial contact resistivity was $10^{-5} \Omega \cdot \text{cm}^2$; the absolute value could not be accurately measured due to its small value, so the increase in contact resistivity is shown in Fig. 3. After the completion of debonding, the shear stress dropped abruptly due to the pull-out of the wire from the solder. The contact resistivity increased only slightly at the completion of debonding; it increased significantly when the pull-out was extensive. Results for acetone washed copper wire and those for as-received copper wire (Fig. 2) are essentially the same; both bond strength and contact resistivity are similar.

Fig. 4 shows corresponding data for solder and acid washed copper wire. The embedment length was 2.5 mm. The shear bond strength was 11 MPa. The initial contact resistivity was $10^{-5} \Omega \cdot \text{cm}^2$. At the completion of debonding, the shear stress dropped abruptly, but the contact resistivity hardly changed. The high bond strength and low contact resistivity for acid washed copper compared to as-received copper is mainly due to the removal of the native oxide on the copper by the acid washing. The contact resistivity rose abruptly when the pull-out was almost complete.

Results for as-received copper wire and silver-epoxy shows a bond strength of 1.5 MPa, but the contact resistivity was too unstable to be measured.

Fig. 5 shows the corresponding data for acetone washed copper wire and silver-epoxy. The embedment length was 9.0 mm. The shear bond strength was 12 MPa. The initial contact resistivity was $2 \times 10^{-4} \Omega \cdot \text{cm}^2$. At the completion of debonding, the shear stress

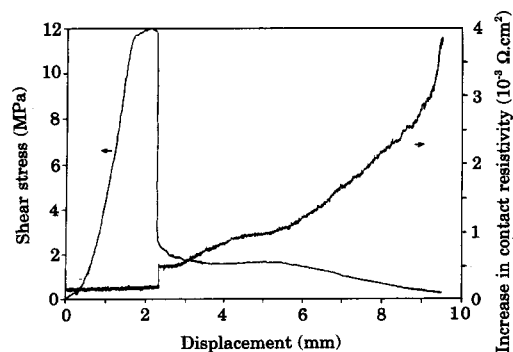


Figure 5 Variation of contact electrical resistivity and shear stress with displacement during pull-out of acetone washed copper wire from silver-epoxy.

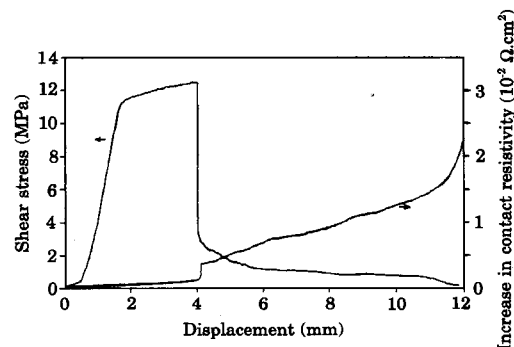


Figure 6 Variation of contact electrical resistivity and shear stress with displacement during pull-out of acid washed copper wire from silver-epoxy.

dropped abruptly, while the contact resistivity jumped up. The jump is in contrast to the absence of a jump in the case of the soldered joints (Figs 3 and 4).

Fig. 6 shows corresponding results for silver-epoxy and copper wire which had been washed by acid followed by acetone. The embedment length was 9.5 mm. The shear bond strength was 13 MPa. The initial contact resistivity was $2 \times 10^{-4} \Omega \cdot \text{cm}^2$. At the completion of debonding, the shear stress dropped abruptly, while the contact resistivity jumped up, as in Fig. 5.

4. Discussion

The coefficient of thermal expansion of copper was lower than those of solder and silver-epoxy, so compressive thermal stress was present on the copper after joining copper to either solder or silver-epoxy and subsequent cooling. The coefficient of thermal expansion of silver-epoxy was much higher than that of solder, though the joining temperature was higher for solder than silver-epoxy. Therefore, the thermal stress may be higher for silver-epoxy than solder. The probable difference in thermal stress between silver-epoxy and solder would have suggested that the contact resistivity would more likely jump up upon completion of debonding for solder than silver-epoxy. However, the opposite was observed, i.e., the contact resistivity jumped up upon completion of debonding for silver-epoxy, but not for solder. This is attributed to the greater ductility of solder compared to silver-epoxy and the resulting ability to conform to the topography of the copper wire during pull-out. Indeed, the tensile ductility is 0.7% for silver-epoxy (measured in this work) and is 1.38% for solder [7].

The contact resistivity between copper and silver-epoxy ($10^{-4} \Omega \cdot \text{cm}^2$) was higher than that between copper and solder ($10^{-5} \Omega \cdot \text{cm}^2$). This is attributed to the insulating nature of the epoxy matrix in silver-epoxy and the presence of a thin epoxy layer at the interface between copper and silver-epoxy.

Acetone washing of copper had essentially no effect for solder, but had a large positive effect for silver-epoxy. The soldered joint exhibited a stable contact resistivity for as-received copper wire, but the silver-epoxy joint exhibited an unstable contact resistivity for as-received copper wire. These observations mean that

cleansing of the copper surface was essential for silver-epoxy, but not essential for solder. This is probably because of the cleansing action of the hot liquid solder and the lack of cleansing action for epoxy.

The effectiveness of acid washing of copper on both soldered and silver-epoxy joints is due to the surface roughening and cleansing of the copper by the acid. For soldered joints, acid washing was more effective than acetone washing. For silver-epoxy joints, acid washing and acetone washing were similar in effectiveness. This difference between soldered and silver-epoxy joints is probably due to the high viscosity of the epoxy resin compared to liquid solder and the consequent limited ability of the epoxy to take advantage of the roughened copper surface.

5. Conclusion

Silver-epoxy joints to copper abruptly increased in contact resistivity upon completion of debonding, whereas soldered joints to copper essentially did not change in contact resistivity upon completion of debonding, due to the lower ductility of silver-epoxy compared to solder. The contact resistivity before debonding was higher for silver-epoxy than solder. Cleansing of the copper surface was essential for silver-epoxy, but not essential for solder. Acetone washing of the copper surface helped silver-epoxy joints, but had little effect on soldered joints. Acid washing helped soldered joints more

than acetone washing, but helped silver-epoxy joints to the same extent as acetone washing.

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