# Metallurgical Reactions at the Interface of Sn/Pb Solder and Electroless Copper-Plated AlN Substrate

Bi-Shiou Chiou, Jiann-Haur Chang, and Jenq-Gong Duh

*Abstract*— Intermetallic formation between electroless-plated copper and Sn/Pb solder is investigated. An interlayer is formed between copper and solder, and segregation of Pb-rich and Sn-rich phases are observed. X-ray diffraction and EDX analysis results suggest that the major intermetallic formed in the interlayer is $Cu_6Sn_5$. For the as-plated sample, the adhesion strength of Cu to the AlN substrate after 150°C aging is affected by both the recrystallization and the creep of copper. For the soldered specimen, the presence of intermetallic compound causes cracks to propagate along the intermetallic/Cu interface and results in a decrease of the adhesion strength.

## I. INTRODUCTION

ALUMINUM NITRIDE (AlN) has received much interest in the electronics industry in recent years. The high thermal conductivity, adequate mechanical strength, good insulation resistance and a thermal expansion coefficient close to that of silicon have rendered AlN an excellent candidate for a substrate material in the application for high voltage, high power devices [1]–[4]. Direct-bonded-copper (DBC) substrates have been used for high power application because of the extremely low electrical resistance of copper [5]. Electroless Cu plating provides an excellent approach to metallize the ceramic substrate, because of its low operational temperature, no requirement of applied current and low cost [6]–[16]. Previous works by Chiou, Chang, and Duh reported that the AlN surface could be etched with NaOH to produce anchoring holes which rendered a mechanical interlocking between electroless Cu and the AlN substrate, and, consequently, increased the adhesion strength of electroless Cu. The adhesion strength of the electroless-plated Cu is much larger than 2 kg/mm², which is generally needed for the mounting of circuit devices [17], [18].

Tin/lead solders are commonly used in the electronic industry as interconnects and bonding pads for microcircuits. During the soldering operation and subsequent joint life, intermetallic compounds form and grow. The formation of the intermetallic compound may cause mechanical failure during thermal or power cycling [19]–[24]. Microcircuit performance and lifetime are then degraded as these intermetallics grow. For soldered electroless copper plated $Al_2O_3$, the copper–tin intermetallic dominated the mechanical performance due to
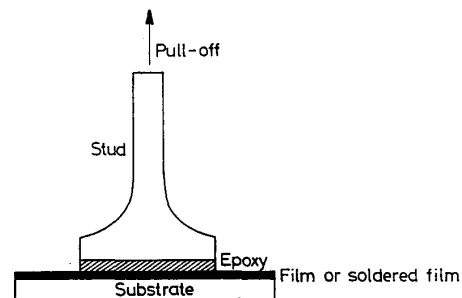
Fig. 1. Schematic diagram of the pull-off test.

crack initiation in the intermetallic region formed during high temperature exposure [25], [26]. However, kinetics of the intermetallic growth and the effect of the intermetallic compounds on the physical and mechanical properties of soldered electroless copper plated AlN system are not well understood.

The purpose of this research is to study the metallurgical change in the interface of Sn/Pb solder and electroless copper plated AlN. The microstructural evolution of the interfacial morphology is probed with the aid of electron microscopy and X-ray diffraction.

## II. EXPERIMENTAL PROCEDURE

Aluminum nitride substrates with 25.4 mm × 25.4 mm× 0.635 mm in size was abraded sequentially with 120, 400, 600, 1000, 1200 grits SiC papers. After abrading, the substrate was polished through 6-, 3-, and 1-$\mu$m diamond pastes. The polished aluminum nitride substrate was first cleaned with ultrasonic rinsing in water for 5 min at room temperature, followed by ultrasonic cleaning in ethyl alcohol. The sample was then cleaned ultrasonically in water. After cleaning, the substrates were etched in 4% NaOH solution at room temperature for 80 min. The etched sample was then cleaned ultrasonically in water. A surface roughness of ~0.13 $\mu$m was obtained for the etched substrates [18].

The etched substrate was immersed in sensitization solution for 10 min; rinsed with deionized (D.I.) water; immersed in activation solution for 5 min; and then rinsed in D.I. water before electroless copper plating. The deposition rate for Cu plating in this study is about 4.7 $\mu$m/h. Copper films of 10-$\mu$m thickness were deposited on etched AlN substrate. The detailed plating procedure was described previously [18]. The compositions of the sensitization, activation, and plating bath

TABLE I
COMPOSITION OF SOLUTIONS EMPLOYED IN ELECTROLESS CU PLATING

| | Chemical | Concentration |
|---|---|---|
| Sensitization | $SnCl_2$ $2H_2O$ | 16 g/l |
| | HCl | 30 ml/l |
| Activation | $PdCl_2$ | 0.1 g/l |
| | HCl | 8 ml/l |
| Electroless Cu | $CuSO_4$ $5H_2O$ | 30 g/l |
| | $KNaC_4H_4O_6$ $4H_2O$ | 50 g/l |
| | EDTA | 10 g/l |
| | HCHO (37%) | 30 ml/l |
| | pH = 12.5 | |
| | (adjusted by NaOH) | |
| | T =25C | |



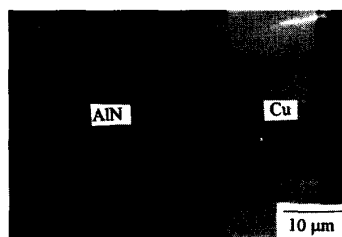Fig. 2. Surface morphology of the AlN substrate before plating.



Fig. 3. Cross-sectional view of electroless Cu on AlN substrate.

solutions as well as the plating conditions are summarized in Table I.

The electroless copper-plated specimens were cleaned in deionized water in an ultrasonic cleaner for 10 min, and then dipped into the RMA-type (4381 RMA-type, multicore, Herfordshire, England) flux. The solder was a 63Sn/37Pb eutectic alloy (SN63 eutectic, Multicore, Hertfordshire, England), and the solder bath was hold at 230°C. The substrate was vertically dipped into the bath for five seconds. The soldered specimen was then cleaned with a cleaning agent (PC81 cleaner, Multicore, Hertfordshire, England) in an ultrasonic cleaner for 20 min. The as-plated and/or soldered samples were then stored at 150°C for various times before investigation.
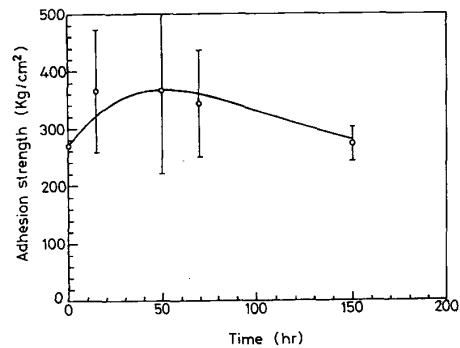


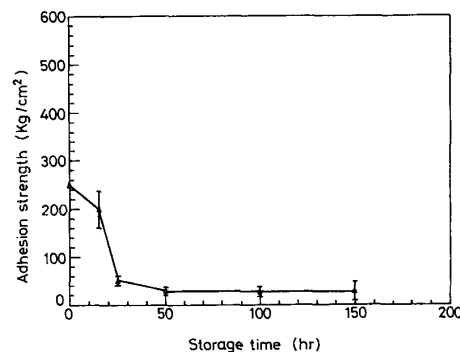Fig. 4. Adhesion strength of electroless-plated Cu on AlN substrate as a function of storage time at 150°C.



Fig. 5. Adhesion strength of soldered samples after various storage time at 150°C.

TABLE II
COMPOSITION OF THE INTERLAYER ANALYZED BY EDX

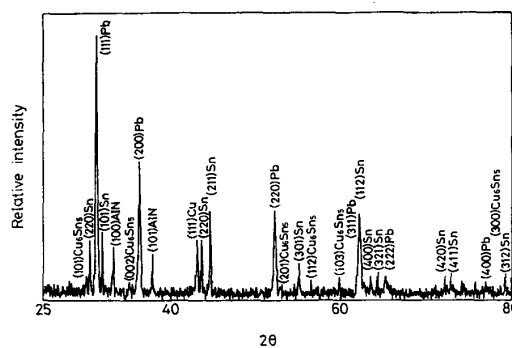| Element | Cu | Sn | Pb |
|---|---|---|---|
| Atom % | 52.2 | 46.7 | 1.1 |
| Modified Atom % | 53.8 | 46.2 | 0 |



Fig. 6. The X-ray diffraction pattern of the soldered sample after 150-h thermal storage at 150°C.

The phase and crystal structure were identified with X-ray diffractometer (D/MAX-B, Rigaku, Japan) with a wavelength of Cu $K\alpha$ (1.5406 A). The surface morphology and cross section view morphology were analyzed with a scanning electron

(a)                                              (b)
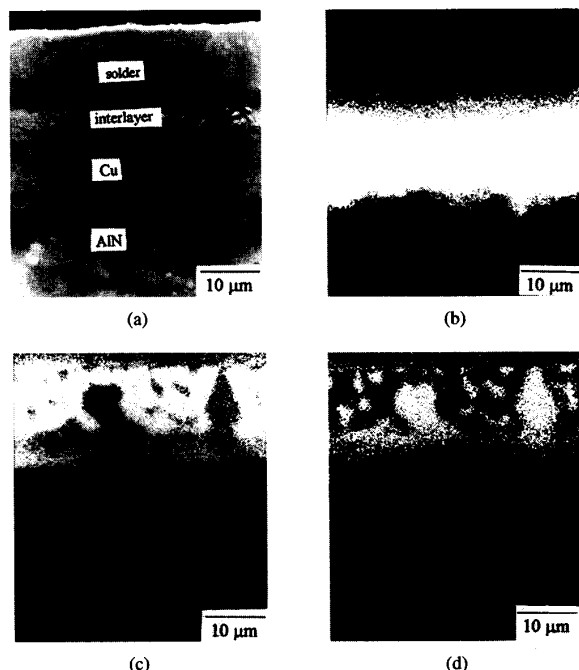
(c)                                              (d)

Fig. 7. Cross-sectional view of the soldered sample after 25 h storage at 150°C. (a) SEM micrograph. (b) Cu X-ray mapping. (c) Sn X-ray mapping. (d) Pb X-ray mapping.

microscope (SEM) (250 MK3, Cambridge, UK) equipped with EDX (Excel, Link, England).

The adhesion strength of Cu deposited on the AlN substrate is evaluated with a direct pull tester (SEBASTIAN FIVE, QUAD Group, USA). A stud was bonded perpendicularly to the coating surface with epoxy by holding it in contact through a spring mounting chip designed especially for the stud. The assembly was cured at 150°C for one hour. The stud was inserted into the platen and gripped. The tester pulled the stud and samples down against the platen support ridge until the coating or epoxy failed. The schematic diagram of the pull-off test is represented in Fig. 1. The force was increased slowly until failure occurred at $F$ (kg). For the area, $A$ (cm$^2$) of the circular section of the stud, the pull strength, $\sigma_a$(kg/cm$^2$), is defined as $\sigma_a = F/A$.

## III. RESULTS AND DISCUSSION

Fig. 2 shows the surface morphology of the AlN substrate before plating. The micro-etching holes, as seen in Fig. 2, provide mechanical interlocking sites for the bonding of electroless copper to the AlN substrate. The cross-sectional view of electroless Cu on AlN substrate is given in Fig. 3. It is observed that the electroless Cu tends to smooth the surface morphology of the substrate. This suggests that electroless copper plating is a potential approach for conformal via hole coating.

Thermal aging was employed to evaluate the Cu metallization. Fig. 4 exhibits the adhesion strength of electroless-plated Cu to AlN substrate after various times at 150°C. The adhesion strength after thermal storage for various time increases
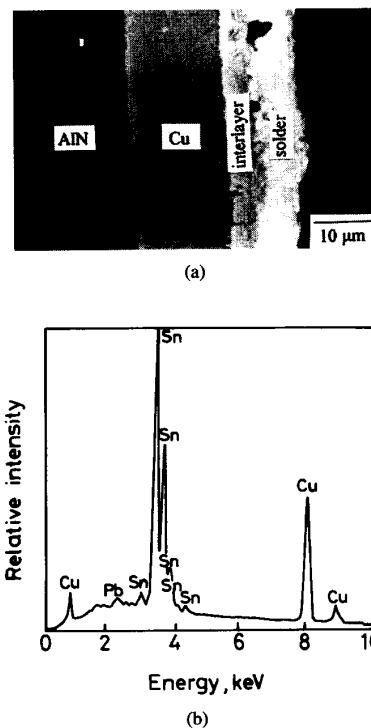


(a)



Energy, keV

(b)

Fig. 8. EDX analysis for the interlayer. (a) SEM cross-sectional view and (b) X-ray spectrum.

initially and then slightly decreases, as shown in Fig. 4. The mechanical properties of the electroless copper would affect the adhesion strength between electroless Cu and substrate. The temperature used for thermal storage test, 150°C, is the recrystallization temperature of copper [27]. As is well known, a metal undergoing recrystallization experiences a great deal of ductility increase as well as a decrease in strength. Okinaka and Nakahara [28] argued that hydrogen is trapped in bubbles during deposition of electroless copper. They correlated the ductility of the electroless copper film with the cavity density and hydrogen baked out during annealing at 150°C. Pedraza and Godbole [27] reported that recrystallization of electroless copper resulted in a ten fold-increase in ductility and 40% decrease in tensile strength. Thermal aging the electroless copper plated substrate at 150°C results in recrystallization of electroless copper, and the ductility of the electroless copper is increased. It is rather difficult to form cracks at the electroless copper on the top of interlocking as the ductility of electroless copper prevails. Since the ductility of electroless copper tends to blunt crack propagation introduced during the pull-off test, the observed adhesion strength is then increased. The increase of strength during thermal storage is not appreciable, as indicated in Fig. 4. The adhesion strength, however, decreases slightly after 150°C storage because the elevated temperature (150°C) may cause deterioration on the electroless copper. Creep in the copper itself might be one of the possibilities. The adhesion strength of soldered samples as a function of storage time at 150°C is given in Fig. 5. There is a drastic drop in the adhesion strength after 25 h aging, where the
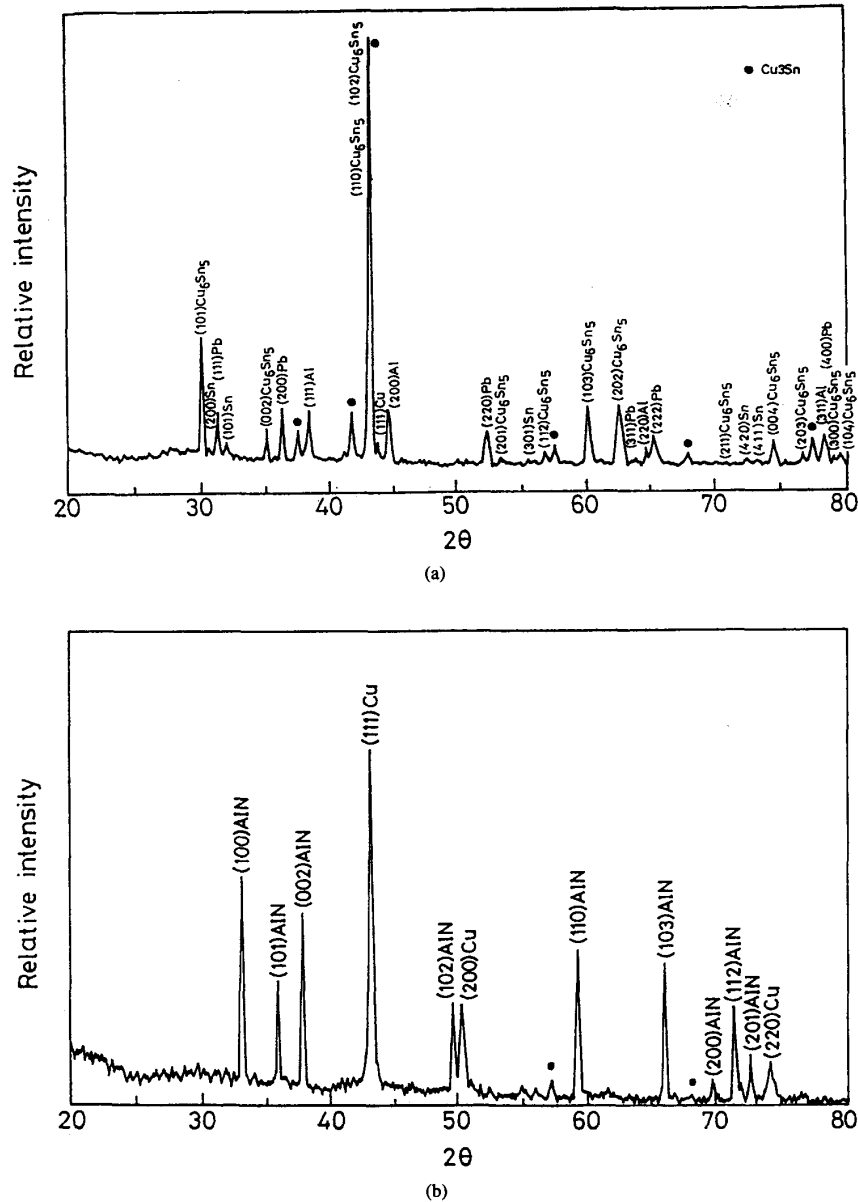
Fig. 9.   X-ray diffraction pattern of the fracture surface of soldered sample (a) top fracture surface and (b) bottom fracture.
Sample aged at 150°C for 25 h.

adhesion is lower than 50 kg/cm$^2$. Jones and Geckle reported the formation of intermetallic $Cu_6Sn_5$ and $Cu_3Sn$ between the solder and the plated Cu on $Al_2O_3$ during high temperature storage [25], [26]. The X-ray diffraction pattern of soldered samples after 150 h thermal storage is shown in Fig. 6, in which the $Cu_6Sn_5$ intermetallic compound is identified. The cross-sectional SEM micrographs and X-ray mapping of the soldered specimen after aging at 150°C for 25 h is given in Fig. 7. The SEM micrograph in Fig. 7(a) clearly indicates that a distinct layer is formed between the solder and the electroless Cu. The X-ray mappings of Sn and Pb, shown in

Fig. 7(c) and 7(d) respectively, reveal that segregation of both Sn-rich and Pb-rich phases occur after the sample is aged for 25 h. Fig. 8 shows a magnified view of the interlayer and the X-ray spectrum for the interlayer analyzed by EDX. The quantitative analyses of the interlayer is listed in Table II. It should be pointed out that the electron probe size in the EDX analysis in the order of several microns appears to be larger than the interlayer width as shown in Fig. 8(a). As a consequence, the neighboring solder is also scanned even through the electron beam is located within the interlayer. This explains the measured 1.1 at.% Pb in the EDX analysis
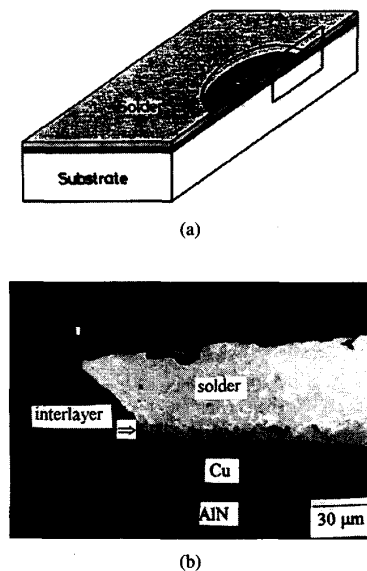
(a)



(b)

Fig. 10. Cross-sectional view of the fracture surface for the soldered sample after thermal storage at 150°C for 25 h: (a) schematic diagram and (b) SEM micrograph.

as indicated in Table II. After extracting the undesired Pb and Sn due to the presence of Pb/Sn solder contents in the EDX quantitative results, one can normalize the measured Cu and remaining Sn and obtain a Cu/Sn ratio to be about 6:5. The derived $Cu_6Sn_5$ compound is in agreement with the X-ray diffraction pattern as indicated in Fig. 6. Because the crack propagates through the intermetallic/Cu interface, the major concern is the adhesion between solder and electroless copper, not between the electroless Cu and the substrate. The intermetallic compound $Cu_6Sn_5$ formed between electroless copper and the solder would introduce stress in the interface which causes the crack to propagate. The X-ray diffraction pattern of the fracture surface is shown in Fig. 9. Intermetallics of $Cu_6Sn_5$ and $Cu_3Sn$ are found on the top of the fracture surface, while only Cu and a small amount of $Cu_3Sn$ are identified on the bottom of the fracture surface. The top fracture surface is the one attached to the stud after fracture, while the bottom fracture surface is the one associated with the underlying substrate. This implies that the crack propagates along the $Cu_6Sn_5$, Cu interface. The cross section view of the fracture surface is represented in Fig. 10, which confirms the fact that the crack propagates along the Cu/intermetallic interface. The adhesion strength before thermal storage is above 200 kg/cm$^2$, while it decreases to below 50 kg/cm$^2$ after 25 h thermal storage. Thus, it is argued that the presence of the intermetallic compound results in the decrease in adhesion strength, as indicated in Fig. 5.

The formation and growth of intermetallics at the solder/substrate interface are factors affecting the solderability and reliability of solder joints. Research on intermetallic growth in Cu-solder joints has concentrated on growth into relatively thick solder layers. Sunwoo et al. studied the growth of Cu–Sn intermetallics at a pretinned copper-solder interface

and observed the $Cu_6Sn_5$ phase formation when Cu was wetted with eutectic solder at temperature below 400°C [29]. A recent study by Wu et al. revealed the diffusion behavior and microstructural evolution of Cu–Sn intermetallics at the composite solder/copper substrate interface [30]. The Cu-containing composite solder generally formed $Cu_6Sn_5$ layer. It was reported that $Cu_3Sn$ was never observed in any unaged sample using SEM due to the resolution limit, while it was only visible between the solder matrix and the copper substrate. This observation is similar to the one in this study in which no apparent $Cu_3Sn$ is found in the bulk soldered sample after 150 h thermal storage at 150°C as shown in Fig. 6. However, a small amount of $Cu_3Sn$ is barely detected only on the fracture surface of the soldered sample, as indicated in Fig. 9. For intermetallic formation and growth in the solder/substrate system, there exist diffusion through the growing intermetallic layer as well as an interfacial reaction. A more detailed investigation concerning the possible diffusion-controlled and/or interfacial reaction-controlled mechanism in the intermetallics formation between Sn/Pb solder and electroless Cu-plated AlN substrate will be reported in the near future.

## IV. CONCLUSION

1) Intermetallic formation between electroless-plated copper and Sn/Pb solder is evaluated. The electroless-plated copper tends to smooth the surface morphology of the AlN substrate. This makes electroless Cu plating a promising approach for conformal via hole coating.

2) The adhesion strength of Cu on AlN increases initially and then decreases after 150°C thermal storage. The increase in adhesion is attributed to the recrystallization of Cu at 150°C, the ductile Cu tends to blunt crack propagation introduced during the pull-off test. The lower adhesion strength for longer aging time is caused by deterioration of Cu, such as creep, at 150°C.

3) The adhesion strength of soldered samples decreases after 25 h at 150°C. Microstructural analysis of the soldered Cu/AlN assembly reveals the existence of an interlayer between solder and copper, and the segregation of Pb-rich and Sn-rich phases. X-ray diffraction and EDX analysis results indicate the formation of intermetallic $Cu_6Sn_5$ at the interlayer.

4) The intermetallic compound introduces stress concentrations in the interface which cause the crack to propagate along the intermetallic/Cu interface and results in the decrease in adhesion strength.

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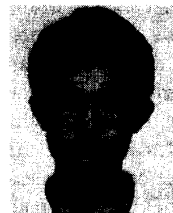
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