Metallization of Aluminum Nitride Substrates by Electroless Copper Plating

By Bi-Shiou Chiou, J.H. Chang and Jenq-Gong Duh

The metallization of AIN substrates by electroless Cu plating was investigated for as-received unpolished and mechanically polished AIN substrates. Four-percent NaOH aqueous solution was employed as the chemical etchant before plating to create sites for mechanical interlocking. For the unpolished substrates, the adhesion increased from 1.3 kg/mm^2 for the sample with an average surface roughness of 0.2 µm to 2.3 kg/mm^2 for those with an average surface roughness of 0.82 pm. Mechanical interlocking is suggested as the major cause for adhesion in the Cu-unpolished AIN system. The adhesion strength of Cu with respect to the mechanically polished AIN substrate increases to a value larger than 7.6 kg/mm^2. This makes electroless Cu plating a good candidate for AIN metallization. Nevertheless, the mechanism that causes the increased adhesion strength for the mechanically polished case needs further investigation.

Aluminum nitride (AIN) has been the subject of much interest in the electronics industry in recent years. Its high thermal conductivity, good mechanical strength, good electrical properties and a thermal expansion coefficient close to that of silicon have rendered it an excellent candidate for a substrate material in high-voltage, high-power devices.[1-4]

Surface metallization is necessary for the application of electronic circuits to ceramic substrates. One such application is thin film metallization with multiple metal layers, such as Ti-Pd-Au. Another is printed thick-film refractory-metal molybdenum-manganese (Mo-Mn) or tungsten (W). The limited availability of compatible thick-film material systems has restricted the production of hybrid circuits based on AIN to low-volume applications. Several thick-film formulations have been successfully coated on AIN with reasonable adhesion, such as Ag/Pd paste,[a] copper paste,[b] and a tungsten paste for multilayer AIN substrates.[3,5,6] Among the metallization material systems, copper, with its superior conductivity, high solder-leach resistance, and remarkable cost-saving potential, is gaining wide acceptance as the conductor material. Direct-bonded copper (DBC) looks promising, although it has not been optimized.[7]

This paper describes the metallization of AIN surfaces by electroless Cu plating. This method has been widely used for the metallization of plastics.[8] Metallization of ceramic substrate surfaces by electroless plating, with sufficient adhesion, is more difficult than with plastics because of the difficulty of etching ceramic surfaces.[9-12] The electroless method Possesses advantages, such as mass production capability and cost-effectiveness. The application of Cu electroless plating on AIN substrates will make them more practical and feasible.

Experimental Procedure

Aluminum nitride substrates[c] were cleaned ultrasonically in ethyl alcohol for 5 min. Some of the substrates were mechanically polished with 400, 600, 1000, and 1200 grit SiC and 0.05 µm Al_2O_3 sequentially before cleaning. The sensitization/activation process is shown in Table 1. The basic bath compositions and operating conditions of electroless Cu plating are given in Table 2. Among the chemicals employed for the bath composition, HCHO acts as the reducing agent for copper, derived from $CuSO_4 \cdot 5H_2O$, back to elemental Cu. Sodium potassium tartrate is used as a completing agent, rendering part of the copper as complexes. The control of pH around 12.5 is through the application of Na_2CO_3 and NaOH. During plating, $SnCl_2 \cdot 2H_2O$ plays the role of sensitizer, such that the surface of the substrate is coated with a layer of Sn. Also, $PdCl_2$ is applied in the activation process, in which Pd^{2+} is reduced to Pd° on the substrate surface by adsorbed Sn^{2+} (i. e., $Pd^{2+} + Sn^{2+} \rightarrow Pd^\circ + Sn^{4+}$). Then catalytic Pd° promotes the reaction in Cu electroless plating.

The AIN substrate is etched by NaOH solution. The etching process is as follows:[11]

$$AlN + NaOH + 4H_2O \rightarrow NH_4OH + NaAl(OH)_4 \quad (1)$$

The average surface roughness, R_a, was measured with an a-step. The adhesion strength between substrate and metal film was measured with a pull tester. The surface morphology of the specimens was examined with a scanning electron microscope (SEM).

Results and Discussion

Figure 1 shows the typical effect of etching time on the surface roughness of AIN substrate. The average surface roughness,

[a] 9601, Electro-Science Laboratories, Inc., King of Prussia, PA.
[b] 9029D, Cermalloy Div., Heraeus Inc., W. Conshohocken, PA.
[c] "SHAPAL" AIN by Tokuyama Soda Co., Japan.

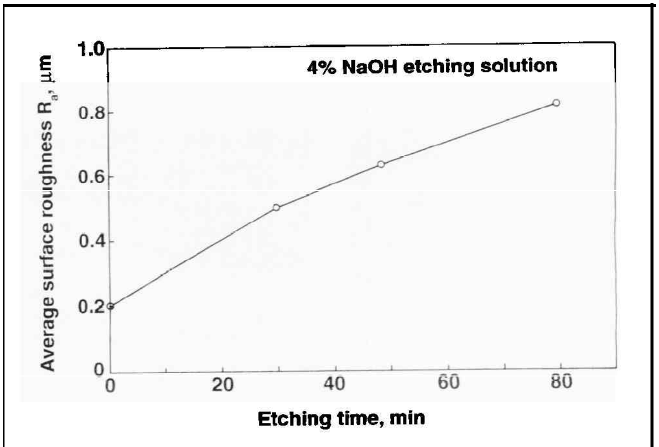

Fig. 1—Effect of etching time on the average surface roughness of the as-received AIN substrates.

Table 1
Sensitizer/activator Pre-treatment Process

Process	Chemical	Concentration	Time
Ultrasonic cleaning	ethyl alcohol	—	5 min
Rinse	DI water		
Etching	NaOH	40 g/L	30 min 50 min 80 min
Rinse	DI water	—	—
Sensitization	$SnCl_2 \cdot 2H_2O$ HCl	10 g/L 40 mL/L	10 min
Rinse	DI water	—	—
Activation	$PdCl_2$ HCl	1 g/L 20 mL/L	10 min
Rinse	DI water	—	—
Electroless plating			

Table 2
Basic Bath Composition and Conditions for Electroless Cu Plating

Chemicals	Concentration	Operating Condition
$CuSO_4 \cdot 5H_2O$	5 g/L	pH 12.5
NaK tartrate	20 g/L	adjusted with NaOH
NaOH	4 g/L	bath temperature 25 °C
Na_2CO_3	5 g/L	plating time
HCHO (37%)	30 mL/L	10–120 min

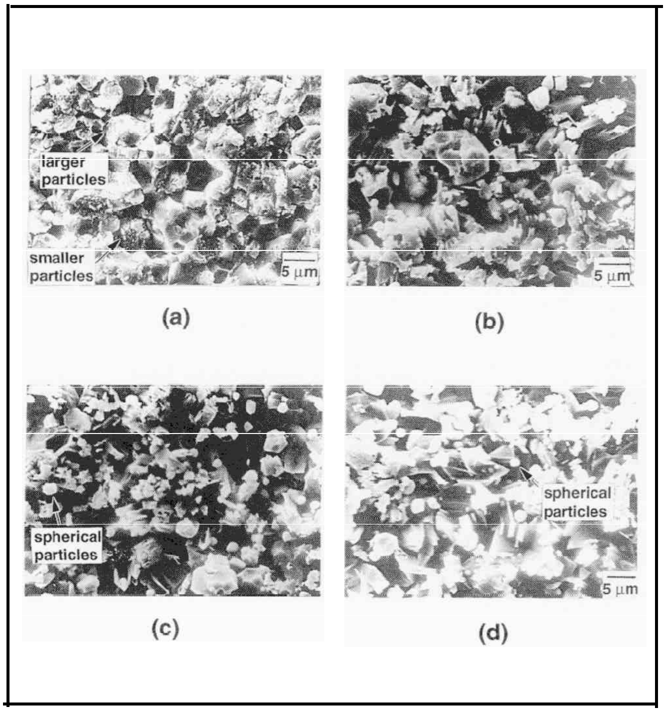

Fig. 2—SEM surface morphology of as-received AIN substrates after (a) O min,)30 min. (c) 60 min, and (d) 80 min etching time in 4-percent NaOH solution.

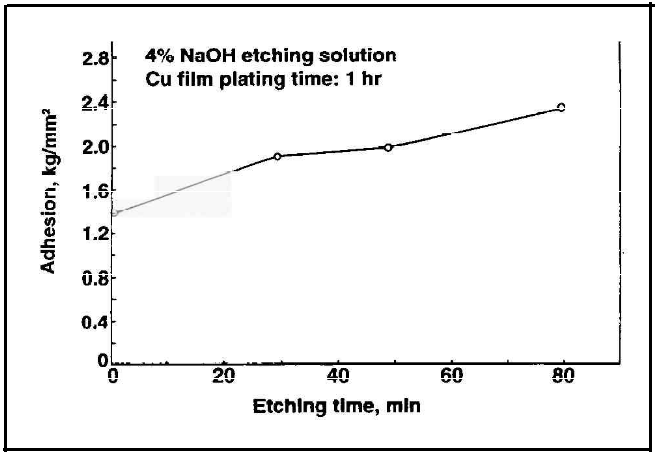

Fig. 3—Adhesion of Cu film to AIN as a function of etching time for Cu film plated for 1 hr.

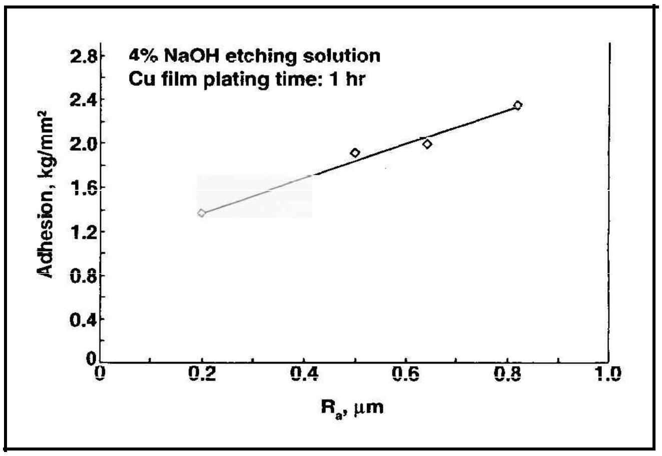

Fig. 4—Adhesion strength as a function of average surface roughness for electroless Cu on AIN substrate.

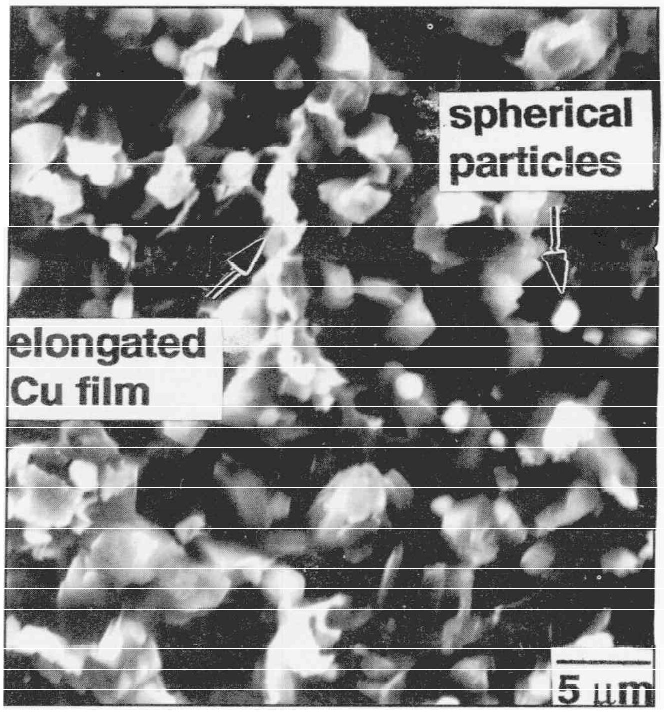

Fig. 5.—Typical fracture surface of the electroless Cu-AIN system.

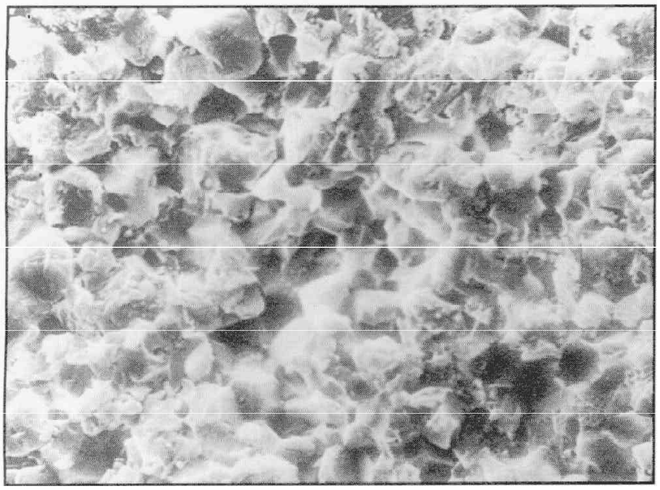

Fig. 6.—SEM surface morphology of the AIN substrate polished with 0.05 µm Al_2O_3.

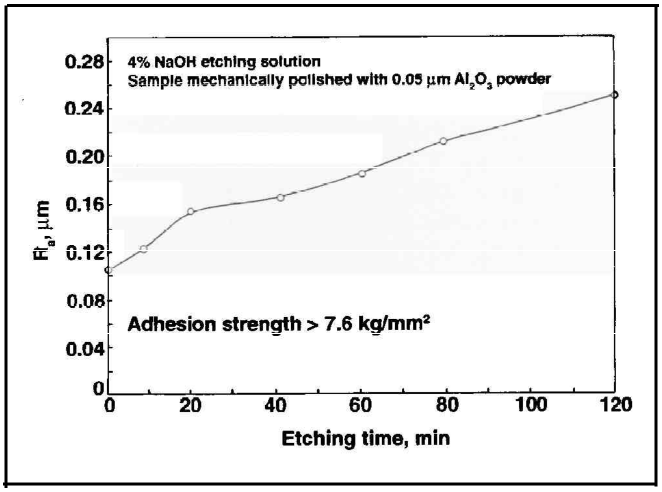

Fig. 7.—Average surface roughness as a function of etching time for the polished AIN substrate.

R_a, increases from 0.2 µm for the as-received substrate to 0.8 µm after etching in 4-percent NaOH solution for 80 min. The SEM surface morphologies of substrates etched for various times is illustrated in Fig. 2. Apparent cavities are present on the surface of the as-received substrates, and AIN particles of various sizes are also observed, as indicated in Fig. 2a. As the etching proceeds, small AIN particles are selectively etched off and the cavities become deeper and wider for samples etched for longer periods of time. For samples etched over 60 min, long columnar structures of AIN are obtained. It appears that there exists a spherical particle on top of the column, as indicated in Figs. 2 c and d.

The adhesion of Cu film to AIN as a function of etching time is given in Fig. 3. There are two possible mechanisms for the adhesion. One, the formation of chemical bonding and, two, mechanical interlocking between the film and the underlying substrate. The bath temperature for the electroless copper plating, around 25 °C, is too low for chemical bonding to occur. Accordingly, it is generally accepted that mechanical interlocking is the major factor contributing to the adhesion strength of the electroless film with respect to AIN. Figure 4 exhibits a close correlation between the adhesion strength and the average surface roughness. The rougher the substrate surface, the more mechanical interlocking sites available. Consequently, adhesion increases with surface roughness, R_a, as expected. Figure 5 shows the fractured surface of the electroless Cu-AIN specimen after adhesion testing. Fracture occurs in the AIN side of the Cu-AIN interface and there is some elongated Cu film remaining on the surface. Also shown in Fig. 5 are the spherical particles on top of the AIN columns before plating. Further investigation is needed to identify the chemical nature of these particles.

In general, the adhesion strength should be more than 2 kg/mm² for the mounting of circuit devices. Adequate adhesion strength is obtained when substrate surface roughness is larger than 0.65 pm, as indicated in Fig. 4.

It has been reported that AIN will react with an oxidizing environment even at room temperature. Single crystals of AIN formed an Al_2O_3 oxide layer between 0.5 and 1 Å thick in one day at room temperature when exposed to air.[13] The Al_2O_3 ceramic is usually very difficult to etch. In order to eliminate the possible effect of Al_2O_3 formed on the substrate surface, some AIN substrates were polished with 0.05 µm Al_2O_3 powder before etching. The polished substrates, with an average surface roughness of -0.10 µm, are much smoother than the as-received substrates, as shown in Figs. 6 and 2a, respectively. Figure 7 exhibits the average surface roughness as a function of etching time for the polished AIN substrate. On comparing Figs. 1 and 7, it can be seen that the surfaces of the polished AIN, after various etching times, are much smoother than those of the as-received specimens.

It is interesting to note that very high adhesion strength is obtained for electroless Cu on the polished AIN substrates. The adhesion is greater than the strength of the epoxy used in the adhesion test (Le., 7.6 kg/mm²). For the polished substrates, fracture occurs at the epoxy instead of the Cu-AIN interface and, consequently, the correlation between real adhesion and surface roughness cannot be obtained. Probably, pre-etch polishing removes the Al_20_3 layer and provides afresh, uniform surface for subsequent etching and plating. The mechanism is, however, subject to further investigation. Nevertheless, it may be concluded at this point that polishing before etching raises the adhesion strength of Cu with respect to AIN to a value greater than 7.6 kg/mm². This makes electroless deposition of Cu a good candidate for the metallization of AIN substrates.

Conclusions

1. Metallization of AIN substrates can be achieved by electro-Iess plating of Cu on the substrates.
2. Adhesion of electroless Cu to the as-received AIN substrate increases as the substrate is etched for longer periods of time in 4-percent NaOH solution. The increase in the adhesion strength is attributed to the rough surface after etching, which provides sites for mechanical interlocking. Adhesion strengths larger than 2 kg/mm² are obtained for AIN with average surface roughness larger than 0.65 µm.
3. When the AIN substrate is mechanically polished before etching, the adhesion strength is further increased by about five times, to a value at least 7.6 kg/mm². This makes electroless Cu a good candidate for metallization of AIN.

Acknowledgment

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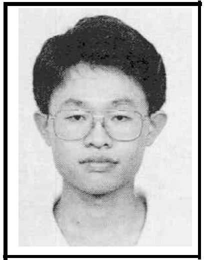
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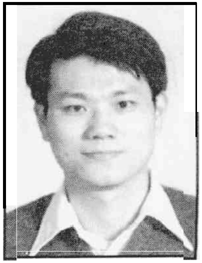
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