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Bonding behavior of copper thick films containing lead-free glass frit on aluminum nitride substrates

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Abstract

The present work indicates through thermodynamic considerations that the calcium, barium-borosilicate glass, which was selected as the bonding agent in copper paste, is chemically compatible to aluminum nitride (AlN) substrate. Meanwhile it implicates the scarce of reactivity which results in poor adhesion strength between the copper thick film and the AlN substrate. However after pre-oxidized treatment on AlN substrate, the adhesion strength was improved significantly by about 1 kg/mm^2 (at 20 vol.% glass frit) than that of the untreated AlN substrate, due to the improved reactivity of the glass frit. The adhesion strength is also demonstrated being affected by frit content and firing temperature. The optimum value (1.85 kg/mm^2) was obtained when the copper paste (containing 20 vol.% glass frit) was printed on the pre-oxidized AlN substrate and subsequently fired at 850 °C.

Keywords: E. Substrates; Adhesion strength; Aluminum nitride; Copper thick films

1. Introduction

Aluminum nitride (AlN) substrate, because of its excellent thermal conductivity, has attracted a keen interest as heat sink material in electronic devices. Much effort has been devoted to develop techniques for the application of AlN substrate in microelectric circuits [1,2]. Metallization is one of them. For the thick-film hybrids that utilize AlN as a base substrate, layers of conductor are deposited onto the substrate followed by firing at elevated temperatures for improved film-substrate adhesion [3–5].

However, most conventional thick-film materials cannot be directly applied on AlN substrates since the glasses in thick-film materials easily react with AlN, producing bubbles at the interface between the thick films and AlN [6–8]. Therefore, it is very difficult to apply AlN for thick-film substrates because of its poor adhesion mentioned above. However, there are two possible ways regarding its use as substrates in thick-film circuitry. The first is to develop a new glass system as the bonding agent of thick-film conductors which would have good adhesion to AlN substrates [9–11]. The second is to develop a surface treatment method for AlN substrates, by which good adhesion with conventional thick-film conductors is obtained [12,13].

In this paper, a new method was present which combined the use of a new glass system as the bonding agent of copper thick film which did not react with AlN to produce bubbles and the application of pre-oxidized surface treatment for AlN substrate, by which the adhesion strength of the copper thick films was improved significantly. The wetting behavior of the selected glass frit to the AlN substrate was studied. The effects of frit content and firing temperature on the behavior of copper thick films were investigated, with special emphasis on the effect of surface treatment on AlN substrate.

2. Experimental procedure

Commercially available AlN powder, and 3 wt.% Sm_2O_3 and 2 wt.% Dy_2O_3 as sintering aids were used to fabricate AlN materials through pressureless sintering. The detailed process has been described in previous work [14]. The main properties of AlN substrate sintered were shown in Table 1. All the substrates were then ultrasonically cleaned in acetone prior to the printing process. Some of the bare AlN substrates

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Table 1
The main properties of aluminum nitride substrate sintered

	Density (g/cm^3)	Thermal conductivity (W/m K)	Dielectric constant (1 MHz)	Resistivity (Ω cm)	Coefficient of thermal expansion ($°C^{-1}$)
AlN	3.31	150–170	8.9	3.6×10^{-13}	4.36×10^{-6}

Table 2
Composition and properties of glass frit added in copper paste

Component	SiO_2	B_2O_3	CaO	BaO	Al_2O_3	Others (Na_2O, K_2O)
Content (wt.%)	18	30	22	25	3	2
Thermal expansion coefficient ($\times 10^{-6}\,°C^{-1}$)				9.8		
Density (g/cm^3)				2.7		
Softening temperature (°C)				709		

were pre-oxidized at 900 °C for 60 min before being printed with the conductor. This introduced a very thin oxide layer on AlN surface typically ∼2 μm in thickness.

The metal paste was formulated from copper powder of average particle size 3.4 μm, glass frit, and screening agents. The paste was ground to the required consistency in a three roll mixer. The glass frit added to the metal paste was smelted at 1450 °C and fritted to an average particle size of 4–5 μm. Table 2 shows the detailed composition and properties of the frit. The amount of frit content in the metal paste varied from 0 to 50 vol.% of copper powder. The paste was then screened onto AlN substrates using test patterns. One test pattern was a 10 mm × 10 mm square, and the others were six 2 mm-diameter circles. After that, the screened copper thick films were dried at 100 °C in vacuum for 20 min, followed by fired at peak temperatures ranging from 650 to 950 °C in a nitrogen atmosphere for 30 min.

The wetting behavior of glass frit to AlN substrate was observed by using high-temperature optical microscopy (MHO-2). The sheet resistance of the copper thick films was measured by a semiconductor resistivity meter (BD-86A) on samples which have 10 mm × 10 mm square metal film patterns. The adhesion strength test was performed by applying loads perpendicular to the adhesion surface as same as that in reference [15]. The surface morphologies of the fired copper films were observed using scanning electron microscope (SEM).

3. Results and discussion

3.1. Background for search of glass frits

The glass frit, which improves the sinterability and bonding of the metal film to the substrate, was added to the metal paste in order to study the behavior of adhesion strength by frit bonding. However the following information has been pointed out in previous papers [6–8]. When glasses contain some oxides, typically PbO, the oxidation reactions between AlN and the glass occur, producing blisters either in the conductor layer or at the interface between the conductor layer and AlN. The oxidation reactions of AlN ceramics with oxide are described by the following equations:

$$\frac{4}{3}\mathrm{AlN(s)} + b\mathrm{M}_x\mathrm{O}_y(\mathrm{s,l}) \rightarrow \frac{2}{3}\mathrm{Al_2O_3(s)} + \frac{2}{3}\mathrm{N_2(g)} + a\mathrm{M(s,l)} \quad (1)$$

Here, M is the metal, and M_xO_y is metal oxide. Reaction (1) is conducted by subtracting reaction (3) from reaction (2).

$$\frac{4}{3}\mathrm{AlN(s)} + \mathrm{O_2(g)} \rightarrow \frac{2}{3}\mathrm{Al_2O_3(s)} + \frac{2}{3}\mathrm{N_2(g)} \quad (2)$$

$$a\mathrm{M(s,l)} + \mathrm{O_2}(g) \rightarrow b\mathrm{M}_x\mathrm{O}_y(\mathrm{s,l}) \quad (3)$$

The possibility of reactions between AlN and various metal oxides is characterized by the change in standard Gibbs free energies, ΔG_2° and ΔG_3° for reactions (2) and (3), respectively. The condition to suppress oxidation of AlN during firing is indicated in the expression $\Delta G_2^\circ > \Delta G_3^\circ$ while the condition promoting oxidation of AlN is indicated in the expression $\Delta G_2^\circ > \Delta G_3^\circ$.

The formation of free energy of several oxides was calculated from published data [16], and summarized as a function of temperature in Fig. 1. The position of ΔG° against T curves for the oxidation relations allows to predict the stabilities of various combinations of materials. At a given temperature any oxide whose free energy lies above that for the oxidation of AlN will oxidize the AlN, meanwhile itself being reduced by the AlN. Any oxide whose free energy lies below that for the oxidation of AlN at a given temperature will be stable in contact with AlN. As can be seen from Fig. 1, the main constituents (SiO_2, B_2O_3, CaO and BaO) of the glass frit used in this experiment lie below the line for AlN oxidation, indicating that this glass frit is a chemically compatible glass to AlN substrate.

However, in practice, reactions may be very complex in such mixed oxide systems. There is also possibility for the formation of other than pure metal forms and free nitrogen in reaction (1) [6]. But it has been demonstrated and well accepted that reaction (1) at the interface between AlN and glass is the main factors which worsen the properties of thick films [6,8]. Therefore, to simplify the influence factors, a simple Ellingham diagram was used as shown in Fig. 1.

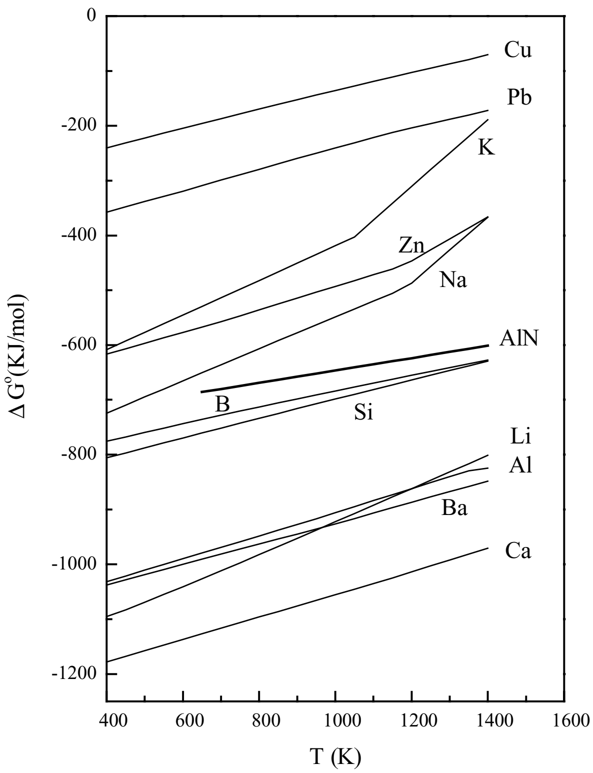

Fig. 1. Gibbs energies for selected reactions as a function of temperature.

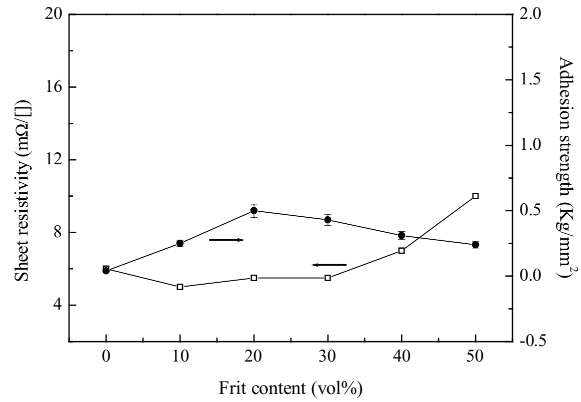

Fig. 3. Adhesion strength and sheet resistance of copper thick films sintered at 950 °C for 30 min on the untreated AlN substrates as a function of frit content.

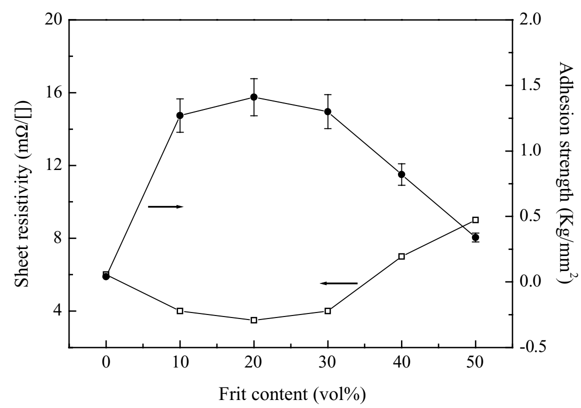

Fig. 4. Adhesion strength and sheet resistance of copper thick films sintered at 950 °C for 30 min on the pre-oxidized AlN substrates as a function of frit content.

3.2. Wetting behavior of glass to AlN substrate

To ensure the adhesion of metal film to substrates, the glass frit is also required to have suitable reactivity and wettability to AlN substrates. Fig. 2 shows the wetting behavior of the calcium, barium-borosilicate glass to AlN substrate from room temperature to 900 °C. It can be seen that the deformation point of the glass is 709 °C, indicating that liquid appears evidently and wetting of the glass starts at this temperature. The wetting angle of this glass then decreases with the temperature, presenting 90° at 826 °C and a low contact angle (<30°) at 878 °C, which indicates a higher wettability.

3.3. Effect of surface treatment of AlN substrate and frit content on the behavior of copper conductor films

As mentioned above, the glass frit used in this work is chemically compatible to AlN substrate while at the same time it implicates the scarce of reactivity. Fig. 3. shows the adhesion strength and sheet resistance of copper thick film on the untreated AlN substrate as a function of the frit content. It presents weak adhesions. The highest value (at 20 vol.% frit content) is only 0.5 kg/mm^2. However, the adhesion strength is improved significantly after the pre-oxidized treatment of AlN substrate (900 °C for 60 min) as shown in Fig. 4. As well known, calcium oxide reacts with alumina to form calcium aluminates at elevated temperature. The published standard formation Gibbs energies of these calcium aluminates from oxides [17], in the temperature range of 1000–1200 K, indicate the possibility of these reactions. It is thought that the evident increase of adhesion strength is attributed to these reactions between calcium oxide which is one of the main constituents of glass frit, and alumina which is induced to the surface of AlN

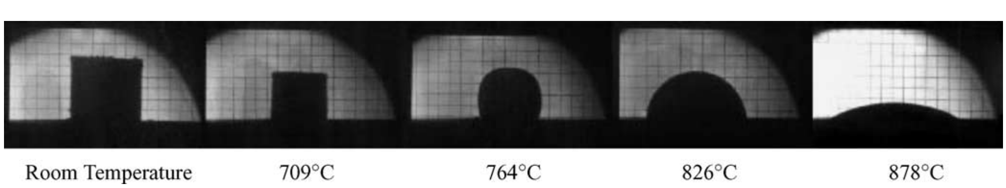

Fig. 2. Optical high-temperature micrographs of the calcium, barium-borosilicate glass on AlN substrate in an air atmosphere.

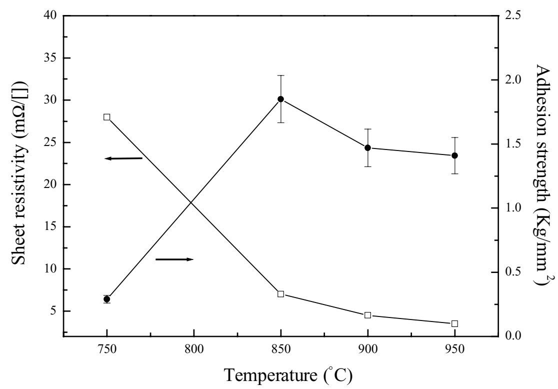

Fig. 5. The adhesion strength and sheet resistance of copper thick films containing 20 vol.% frit on the pre-oxidized AlN substrates as a function of firing temperature.

substrates through oxidation reaction. Moreover, in order to avoid the interfacial cracks that are believed result from the thermal expansion mismatch between the oxide scale and the AlN [18], the low oxidation temperature was employed. Therefore the oxide layer in this work is very thin (∼2 μm), implicating the low residual tension stress between oxide layer and AlN, which was demonstrated [18] to grow with the thickness of the oxide layer.

The effects of frit content on the adhesion strength and sheet resistance of the copper conductor were also shown in Figs. 3 and 4. In spite of the kinds of substrates (pre-oxidized or not), the adhesion strength increases with addition of frit, then decreases when the frit content is higher than about 20 vol.%. The sheet resistance of samples with small amount of frit is lower than that of the non-frit samples, but it increases considerably when the frit content is approximately over 30 vol.%. These results are well consistent with the results of Ishida et al. [19] and Chung et al. [20], which showed the effect of glass frit on the adhesion strength and sheet resistance, respectively.

3.4. *The influence of sintering temperature on the behavior of copper conductor films*

Since the wetting behavior of glass frit to the AlN substrate is considerably dependent on the temperature as shown in Fig. 2, the properties of the copper conductor will be correspondingly affected by the sintering temperature. The adhesion strength and sheet resistance of copper conductor films containing 20 vol.% frit on the pre-oxidized AlN substrates as a function of firing temperature are shown in Fig. 5. The changes of adhesion strength with temperature can be well explained by the wetting behavior of the glass frit to AlN

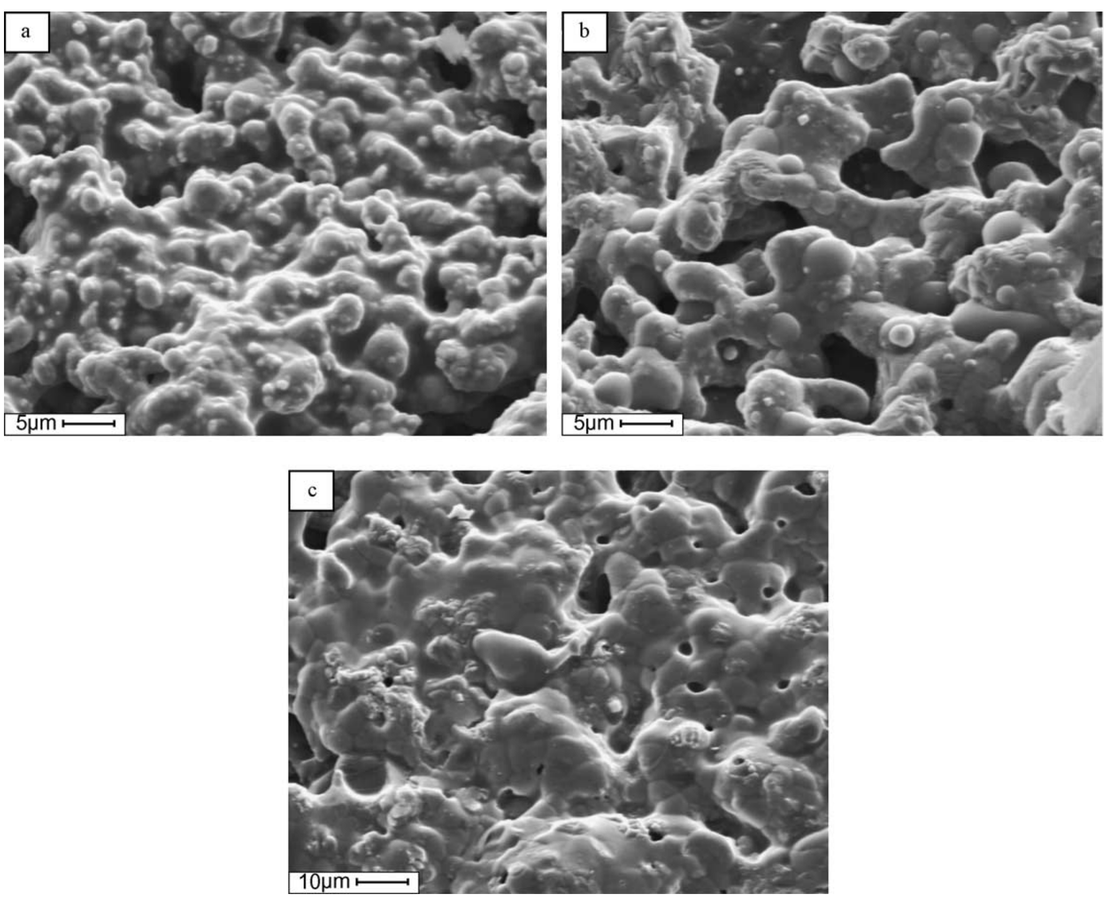

Fig. 6. The surface micrographs of the copper thick films sintered at peak temperature (a) 750 °C, (b) 850 °C, and (c) 950 °C on the pre-oxidized AlN substrates for 30 min.

substrate as shown in Fig. 2. At low temperature (750 °C), the adhesion strength presents the lowest value (0.3 kg/mm^2) due to the large wetting angle (>90°, see Fig. 2) of the glass frit. With the increase of temperature, the wettability of the glass frit is improved, resulting in the rapid increase of adhesion strength. When the specimen is fired at 850 °C, the adhesion strength presents the highest value (1.85 kg/mm^2). However with the subsequent increase of temperature, the adhesion strength decreases slightly. It might be due to the high wettability (<30°, see Fig. 2) of the frit which causes the excessive concentration of the frit to the surface of AlN substrate, and then result in the delamination of the copper thick film.

The sheet resistance of above specimens is consistent with its surface morphologies as shown in Fig. 6. A liquid phase of glass frit can be observed for all the specimens. For the specimen sintered at 750 °C, it is found that the copper particles are isolated by the insulative glass phase (see Fig. 6a). That is why the sheet resistance of this specimen is higher. With the increase of firing temperature, the copper grain grows up and gradually forms interconnected reticulate structure as shown in Fig. 6b, which causes the considerable declination of sheet resistance. After that, when the temperature is increased to 950 °C, the reticulate structure almost disappears, and a denser microstructure can be observed in Fig. 6c. It leads to the subsequent slight decrease of sheet resistance.

4. Conclusions

In order to find a compatible glass frit, the thermal stability of AlN substrate in the presence of metal oxide was evaluated. Since CaO, BaO, B_2O_3 and SiO_2 do not induce oxidation of AlN and release gases during firing, a calcium, barium-borosilicate glass was employed as the bonding agent of the copper paste. Based on using of this glass frit, a series of experiments was performed in order to study the effects of surface treatment of AlN substrate, frit content and firing temperature on the bonding behavior of copper thick films. The adhesion strength between the copper thick films and untreated AlN substrate presented low values due to the scarce of reactivity of this glass frit. However for the pre-oxidized AlN case, the adhesion strength was found being improved considerably, by about 1 kg/mm^2 (at 20 vol.% glass frit) than that of the untreated AlN substrate. It is due to the improved reactivity of the glass frit which is result from the possible reactions between calcium oxide (one of the main constituents of glass frit) and alumina (formed from the oxidation of AlN) during firing. The adhesion strength is also demonstrated being affected by frit content and firing temperature. The optimum adhesion strength (1.85 kg/mm^2) was obtained when the copper paste (containing 20 vol.% glass frit) was printed on the pre-oxidized AlN substrate and subsequently fired at 850 °C.

Acknowledgements

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