Investigation of the effects of silica coating on the thermal conductivity and porosity of aluminum nitride after sintering

Ken’ichiro Kita and Naoki Kondo

Structural Materials Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Nagoya-shi, Aichi, Japan

ABSTRACT
This paper describes a method of applying a silica coating on aluminum nitride and investigations concerning the thermal conductivity between the coating layer and the aluminum nitride as well as the effect of the silica coating layer on the density of samples containing aluminum nitride and glass after sintering. The coating was carried out using polycarbosilane that was transformed into silica by pyrolysis under an airflow. The measured thermal conductivities of all the samples were within an error of less than 10 W/m·K. The porosity of a sintered sample containing the silica-coated aluminum nitride powder and glass powder was decreased by about 10% compared to that of a sintered sample comprising pure aluminum nitride powder.

KEYWORDS
Coating; glass; precursor polymer; surface modification; composite material

1. Introduction

The development of semiconductor chips for high voltage control and high-speed wireless communications is progressing, miniaturization of the package substrates contained in semiconductor chips is also required by industry [1–4]. These packages are usually manufactured using a low-temperature co-fired ceramic (LTCC) technology [5,6], the sintering temperature of which is approximately 1000°C due to the use of glass for the substrates. Packages derived from this technology can be sintered with low electrical resistance metals such as gold, silver, and copper. The technology is therefore suitable for making packages with high-frequency characteristics due to the low dielectric loss resulting from use of these metals [7,8]. It also enables the construction of multilayered packages and reduces the number of manufacturing irregularities occurring in the shrinkage strain of the packages during sintering. Packages derived from this technology can consequently achieve high accuracy and density.

The above semiconductor chips radiate large amount of thermal energy, the amount of which increases in proportion to the improvement of the chips. The ability of the packages to radiate heat is very important to make the chips work perfectly. Since downsizing of the packages is also required by industry to increase the heat density of the packages, an increase in heat radiation by the packages is in strong demand. This technology requires the use of glass as a substrate, however, and the thermal conductivity of glass is usually so low that thermal energy generated by the chips can hardly be radiated efficiently. Therefore, ceramic powders such as aluminum nitride and boron nitride, which have good thermal conductivity, are usually blended into the substrates to secure good thermal conductivity of the packages [9–11].

The wettability of the bonds between the glass and these ceramic powders is very low, however, and this poor wettability causes voids in the packages that reduce their thermal conductivity [12]. It has been reported that grinding these powders’ surfaces and using glass powders containing certain oxides facilitates the improvement of their wettability [13]. These methods require considerable skill and expense, because grinding the powder surfaces is highly skilled work. Since pure silica powder is one of the least costly oxides, therefore, we should invent a method of improving their wettability to provide more inexpensive packages.

To solve this problem, we considered methods of coating the surfaces of ceramic powders with silica using organometallic polymers. The wettability between an oxide ceramic and a molten glass is good [14], and some methods of surface modification of ceramic surfaces using organometallic polymers have already been reported [15–17]. The above LTCC technology requires good thermal conductivity, however, and there is no report on thermal resistance between the modified surface layer and the ceramics. An investigation of the thermal resistance between this layer and the ceramics is necessary for solving the afore-mentioned problem.

In this study, we tried to apply a silica coating to aluminum nitride boards using organosilicon polymers.
and to calculate the thermal resistance between the silica layer and the boards by measuring the boards’ thermal conductivities with and without the silica layer. In addition, we tried to produce mixed samples by sintering a mixed powder containing pure silica powder and aluminum nitride powder after applying a silica coating. We also measured the relative density of these samples to confirm the effect of the silica coating on the aluminum nitride powder.

2. Experimental procedure

2.1. Silica coating on aluminum nitride boards using an organosilicon polymer

To make the coating solutions, polycarbosilane (PCS; NIPUSI Type-A, Nippon Carbon, Japan), a type of organosilicon polymer, and pure toluene as a solvent were prepared. One coating solution contained 0.05 mol/L of PCS, and the other contained 0.1 mol/L of PCS. Both solutions were purified 3 times using membrane filters (As One Corporation, Japan).

Next, some mirror-finished aluminum nitride boards measuring 25 mm square and 0.4- or 0.25-mm thick were prepared. These were spin-coated using a spin-coater (SC-8001, AIDEN CO., LTD, Japan) and the above coating solutions. The spinning speed was fixed at 4,500 or 6,000 rpm when using the 0.1 mol/L solution and 6000 rpm when using the 0.05 mol/L solution. Finally, three kinds of coated samples were obtained. The sample coated at 4500 rpm using the 0.1 mol/L solution was named “Sample A”, the sample coated at 6000 rpm using the 0.1 mol/L solution was named “Sample B”, and the third sample coated using the 0.05 mol/L solution was named “Sample C”.

All these samples were heated at 200°C for 1 h to remove the solvent and completely solidify the PCS. After heating, they were pyrolyzed at 900°C for 1 h under an airflow to transform the PCS into silica. After pyrolysis, cross-sections of all the samples were observed by scanning electron microscope (SEM; JEM-5600, JEOL, Japan), transmission electron microscope (TEM; JEM-2100, JEOL, Japan) and dispersive X-ray spectroscopy (EDS; JEM-2300, JEOL, Japan). In addition, the thermal conductivities of the silica layer on these samples were measured by the light pulse heating thermoreflectance method, and the thermal conductivities of samples and a mirror-finished aluminum nitride board without coating were also measured by the laser flash method.

2.2. Silica coating of aluminum nitride powder and sintering of the mixed powder containing the aluminum nitride powder and silica powder

Figure 1 presents the process of making the silica-coated aluminum nitride powder and the sintered samples containing aluminum nitride powder and silica powder. Aluminum nitride powders with an average diameter were approximately 5 µm (developed by Tokuyama Corporation, Japan) were dipped in a solution containing PCS and pure cyclohexane as the solvent. The weight of PCS in the solution was fixed at 2.23 g per 20 g of powder, because this weight enabled us to make a 500 nm coating layer on the powder numerically. The solvent on the dipped powder was removed by a freeze-drying method, and the dried powder was heated at 200°C for 1 h and pyrolyzed at 900°C for 1 h under airflow. Finally, aluminum nitride powder with a silica coating was obtained.

After the investigation of the powder by XRD, the aluminum nitride powder and glass powder (containing 85 wt% silica, 10 wt% boron oxide and 5 wt%...
alkali metal oxides) whose average diameter was approximately 2 µm were mixed well using an agate mortar. Aluminum nitride powder and silica powder were contained at a weight ratio of 7:10. Sample pellets derived from the mixed powders and measuring 15 mm in diameter and 10 mm thick were formed by a mold at 5 kN pressure. The pellets were sintered at 1000°C for 5 h under a N₂ flow and sintered sample pellets were obtained. These sintered sample pellets are called the ANc samples hereinafter. For purposes of comparison, sample pellets with the same shapes derived from the mixed powder containing aluminum nitride powder without a silica coating and silica powder were manufactured by the same method as the ANc samples. The comparison pellets are called as AN samples hereinafter.

The densities of the samples were measured by the Archimedean method and cross-sections of the samples were observed by SEM.

3. Results and discussion

3.1. Investigation of thermal resistance between aluminum nitride circuit boards and the silica layer on the boards

First, cross-sections of the coating layers of all the samples were observed. Figure 2 presents SEM images of the cross-sections. The lower areas of all the images present particle shapes revealing them to be aluminum nitride boards. The layers on the boards seemed to be coating layers, and each layer exhibited uniform thickness. In addition, each sample was coated with a gold layer for clear SEM observation, and this layer was observed on each coating layer. To clarify the thickness of the coating layers, arrows indicating the interface between the coating layers and other layers were added to each image. There was no exfoliation between the aluminum nitride boards and the coating layers. The thickness of each layer was changed by the concentration of the solution and the spinning speed during coating. The thickness of Sample A was approximately 450 nm, that of Sample B was approximately 380 nm and that of Sample C was approximately 150 nm.

Figure 3 presents a cross-section of Sample B observed by TEM and measured by EDS. As for the TEM image, three different areas were observed. One area at the bottom left was dark gray in color, another at the top right was fine gray, and the third was a layer between the dark gray and fine gray areas. Each area was measured by EDS point analysis. The strong peak of aluminum and the small peak of nitrogen were measured for the dark gray area, revealing it to be aluminum nitride. In the fine gray area, the strongest peak was carbon. Thus, this area seemed to contain resin-coated samples. The strong peaks of silicon and oxygen were measured for the layer between the dark gray and fine gray areas revealing this layer to be coating layer derived from PCS and indicating that PCS could be transformed into silica. A small peak of aluminum could be measured for this layer, and this layer seemed to be derived from the aluminum nitride layer. The probe diameter on this TEM was approximately 1 µm, which was larger than the thickness of the coating layer. It is therefore natural to assume that this layer was derived from aluminum nitride.
The thermal conductivities of all the samples, the aluminum nitride boards and the layers on all the samples were measured. The layers on the samples were measured using the light pulse heating thermoreflectance method, because this method enables measurement of layers which are thinner than 1 µm and low thermal conductive materials such as silica \[18\]. The average thermal conductivity of the layers on all the samples was 1.2 W/m·K, a value that is almost the same as that of pure silica. The other samples were measured using the laser flash method. The thermal conductivity of the aluminum nitride boards was 200 W/m·K.

As shown in Figure 2, each coating layer exhibited uniform thickness. The samples can therefore be regarded as laminated materials containing aluminum nitride boards and coating layers of uniform thickness. The ideal thermal conductivity of laminated materials can be calculated if the thickness and thermal conductivity of each layer comprising the materials are known. The volume fraction of the coating layer, \( v_c \), can be calculated by Equation (1):

\[
v_c = \frac{t_c}{t_c + t_d}
\]

where \( t_c \) is the thickness of the coating layer and \( t_d \) is the thickness of the aluminum nitride board. The ideal thermal conductivity of the laminated material, \( k_{eq} \), can be calculated with Equation (2) using \( v_c \) from Equation (1), \( k_c \), the thermal conductivity of the coating layer, and \( k_d \), the thermal conductivity of the board \[19\].

\[
k_{eq} = \frac{1}{\frac{v_c}{k_c} + \frac{(1-v_c)}{k_d}}
\]

The differences between the values of the calculated and that of measured thermal conductivities indicated the thermal resistance between them. Table 1 presents the thickness of the aluminum nitride board, that of the coating layer, and the calculated and measured thermal conductivities of all the samples. The measured thermal conductivities of all the samples were almost the same as the calculated value and were in error by less than 10 W/m·K. It was therefore accepted that there was no strong thermal resistance between the coated silica layer and the aluminum nitride board.

| Sample | Thickness of silica layer (µm) | Thermal conductivity of the silica layer (W/m·K) | Thickness of aluminum nitride board (µm) | Thermal conductivity of the board (W/m·K) | Calculated thermal conductivity (W/m·K) | Measured thermal conductivity (W/m·K) |
|--------|--------------------------------|-----------------------------------------------|------------------------------------------|------------------------------------------|--------------------------------------|----------------------------------|
| A      | 0.45                           | 1.2                                           | 250                                      | 200                                      | 154.1                               | 149.8                            |
| B      | 0.38                           | 1.2                                           | 400                                      | 200                                      | 172.8                               | 162.9                            |
| C      | 0.15                           | 1.2                                           | 400                                      | 200                                      | 188.3                               | 183.6                            |

Figure 3. TEM images of sample B and the results of EDS point analysis.
3.2. Investigation of density modification by the mixture containing aluminum nitride powder with the surface modification and glass after sintering

After making aluminum nitride powder with surface modification by the method described above, sintering of the mixed powder containing aluminum nitride powder and silica glass was carried out to investigate the effect of the surface modification for improving the density of the sintered sample derived from the mixed powder. For purposes of comparison, a sintered sample derived from mixed powder including pure aluminum nitride powder was also prepared. The detailed process followed to produce these samples is shown in Figure 1.

Figure 4 presents XRD patterns derived from the aluminum nitride powder with surface modification and pure aluminum nitride powder. The strong peaks of 33°, 36°, 38°, 50°, 60°, 66° and 70° are derived from aluminum nitride, and the broad peak from 15° to 30° was derived from amorphous particles. This broad peak originated with the surface modification by PCS and could be observed by amorphous silica [20,21]. As shown in Figure 3, this amorphous material derived from PCS consisted of Si and O atoms. It was therefore considered that aluminum nitride powder with the surface modification was covered by an amorphous silica layer.

Figure 5 presents images of these samples. The sample in the image at left is an AN sample, and the image at right shows an ANc sample. There is no distinct difference between them in this image, because their shapes and colors are almost the same. Figure 6 presents SEM images of the samples. The left image shows an AN sample and the image at right shows an ANc sample. Many pores with diameters of approximately 10 µm can be observed in the AN sample. The number of pores in the ANc sample has clearly decreased, however, compared with the AN sample.

Table 2 shows the densities of these samples measured by the Archimedean method and the calculated ideal densities and porosities. The measured density of the AN sample is 2.06 g/cm³ and the porosity of this sample was approximately 23.4%. As for the ANc sample, the measured density was 2.31 g/cm³ and the porosity was 13.5%. These results were consistent with the SEM images, revealing that the silica coating on the aluminum nitride powder enables it to increase the density of sintered samples containing the powder and silica powder.

4. Conclusion
Silica coating of an aluminum nitride board using polycarbosilane could be carried out by heating it to 1000°C under airflow. The all thermal resistance between the silica coating layer and the board was very small. In addition, the density of sintered samples containing glass powder and aluminum nitride powder could be increased, and the porosity of the
samples could be decreased by applying a silica coating to the aluminum powder. The silica coating on aluminum nitride could maintain both good thermal conductivity and reduce the porosity of sintered samples containing aluminum nitride and glass.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**References**

[1] Takai M. Applications of nuclear microprobes to semiconductor process developments. Nucl Instrum Methods Phys Res B. 1995;104:301–507.

[2] Liu A, Jones R, Liao L, et al. A high-speed silicon optical semiconductor capacitor based on a metal-oxide-semiconductor capacitor. Nature. 2004;427:615–618.

[3] Li X, Ni Z, Gu L, et al. Micromachined high-performance RF passives in CMOS substrate. J Micromech Microeng. 2016;26:113001–113006.

[4] Chidambaram V, Jing T, Yang RB, et al. Novel solution for high-temperature dielectric application to encapsulate high-voltage power semiconductor devices. IEEE Trans Compon Packag Manuf Technol. 2016;9:3–9.

[5] Jantunen H, Kangasvieri T, Vähäkangas J, et al. Design aspects of microwave components with LTCC technique. J Euro Ceram Soc. 2003;23:2541–2548.

[6] Zitani MK, Ebadzadeh T, Banijamali S, et al. High quality factor microwave dielectric diopside glass-ceramics for the low temperature co-fired ceramic (LTCC) applications. J Non-Cryst Solids. 2018;487:65–71.

[7] Vitriol WA, Steinberg JI. Development of a low-temperature cofired multilayer ceramic technology. Int J Hybrid Micro-Electron. 1983;6:593–598.

[8] Shimada Y, Utsumi K, Suauki M, et al. Low firing temperature multilayer glass–ceramic substrate. IEEE Trans Compon Hybrid Manuf. 1983;6:382–388.

[9] Chen GH, Tang LJ, Cheng J, et al. Synthesis and characterization of CBS glass/ceramic composites for LTCC application. J Alloys Compd. 2009;478:858–862.

[10] Zhang Q, Luo X, Li W, et al. Tape casting of AlN/glass composites for LTCC substrate. J Mater Sci. 2003;38:1781–1785.

[11] Yuan L, Liu B, Shen N, et al. Synthesis and properties of borosilicate/AlN composite for low temperature co-fired ceramics application. J Alloys Compd. 2014;593:34–40.

[12] Sobocinski M, Teirikangas M, Peräntie J, et al. Decreasing the relative permittivity of LTCC by porosification with poly(methyl methacrylate) microspheres. Ceram Int. 2015;41:10871–10877.

[13] Tarnovsky R, Diffy J. Influence of temperature and glass composition on aluminum nitride contact angle. IOP Conf Ser Mater Sci Eng. 2016;156:012041.

[14] Shen P, Fuji K, Nogi K. Wettability of some refractory materials by molten SiO$_2$–MgO–TiO$_2$–Fe$_2$O$_3$ slag. Matel Chem Phys. 2009;114:681–685.

[15] Bill J, Heimann D. Polymer-derived ceramic coatings on C/C-SiC composites. J Euro Ceram Soc. 1996;16:1115–1120.

[16] Kita K, Kondo N, Izutsu Y, et al. Study of modification on alumina surface by using of organosilicon polymer. J Ceram Soc Jpn. 2011;119:378–381.

[17] Barroso G, Li Q, Bordiab RK, et al. Polymeric and ceramic silicon-based coatings – a review. J Mater Chem A. 2019;7:1936–1963.

[18] Baba T. Development of thin film reference material for thermal diffusivity. Proceedings of the 1st International Symposium on Thermal Design and Thermophysical Property for Electronics; 2008 June 18–20; Tsukuba, Japan.

[19] Aktay KSC, Tamme R, Müller-Steinhagen H. Thermal conductivity of high-temperature multicomponent materials with phase change. Int J Thermophys. 2008;29:679–692.

[20] Shabir Q, Pokale A, Loni A, et al. Medically biodegradable hydrogenated amorphous silicon microspheres. Silicon. 2011;3:173–176.

[21] Jaya RP, Bakar BHA, Johari MAM, et al. Strength and permeability properties of concrete containing rice husk ash with different grinding time. Cent Eur J Eng. 2011;1:103–112.