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Low temperature sintering and performance of aluminum nitride/borosilicate glass

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Abstract: Aluminum nitride (AlN)/borosilicate glass composites were prepared by the tape casting process and hot-press sintered at 950 °C with AlN and SiO_2-B_2O_3-ZnO-Al_2O_3-Li_2O glass as starting materials. We characterized and analyzed the variation of the microstructure, bulk density, porosity, dielectric constant, thermal conductivity and thermal expansion coefficient (TEC) of the ceramic samples as a function of AlN content. Results show that AlN and SiO_2-B_2O_3-ZnO-Al_2O_3-Li_2O glass can be sintered at 950 °C, and $ZnAl_2O_4$ and Zn_2SiO_4 phase precipitated to form glass-ceramic. The performance of the ceramic samples was determined by the composition and bulk density of the composites. Lower AlN content was found redounding to liquid phase sintering, and higher bulk density of composites can be accordingly obtained. With the increase of porosity, corresponding decreases were located in the dielectric constant, thermal conductivity and TEC of the ceramic samples. When the mass fraction of AlN was 40%, the ceramic samples possessed a low dielectric constant (4.5~5.0), high thermal conductivity (11.6 W/(m·K)) and a proper TEC (3.0×10^{-6} K^{-1}, which matched that of silicon). The excellent performance makes this kind of low temperature co-fired ceramic a promising candidate for application in the micro-electronics packaging industry.

Key words: Aluminum nitride (AlN), Borosilicate glass, Low temperature sintering, Performance
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INTRODUCTION

Low temperature co-fired ceramics (LTCC) allow the miniaturization of multilayer devices, consequently rendering wide applications in the wireless communications, automobile electronics, medical treatment and computer fields (Goebel and Shoefer, 2004; Peterson *et al*., 2005; Kemethmüller *et al*., 2006). To meet the requirements for desired microelectronics packaging, LTCC substrates should have a low dielectric constant, high thermal conductivity, and a thermal expansion coefficient (TEC) matching that of silicon substrates. General performance of some typical LTCC substrate products are given in Table 1 (Yang *et al*., 2005), showing that the thermal conductivity of present LTCC substrates is very low (about 2~4 W/(m·K)), which restricts their application in high-power devices. Besides, their TEC is higher than that of silicon (3.0×10^{-6} K^{-1}). Generally, the performance of LTCC substrates is determined by raw materials and process flow. Low thermal conductivity of borosilicate glasses existing in LTCC substrate can yield low thermal conductivity of the whole substrate. A common method to increase the thermal conductivity of LTCC substrates is thus to use ceramic powders with high thermal conductivity as the main constituent. Because of its excellent thermal conduction and low dielectric constant, and the proper TEC that matches that of silicon, aluminum nitride (AlN) is being considered as an ideal packaging material. AlN/borosilicate glass-ceramic composites have been extensively investigated and regarded as a potential material in LTCC substrates. AlN/borosilicate glass co-fired ceramics for LTCC substrates were prepared by tape casting and hot-press sintering at 850~1000 °C (Zhang *et al*., 2003a; 2003b; 2003c), reaching the thermal conductivity as high as 10 W/(m·K). However, this kind of composite faces restricted applications owing to its poisonous lead compound contained.

Table 1 General performance of some typical LTCC substrate products

Parameter	Dielectric constant	Density (g/cm^3)	Thermal conductivity (W/(m·K))	Thermal expansion coefficient (×10^{-6} K^{-1})
DuPont951AT	7.8 (3 GHz)*	3.10	3.3	5.8
ESL 41010	7.0~8.0 (1 MHz)	3.16	2.5~3.0	7
HeraeusCT2000	9.1 (1 kHz)	3.05	3	5.6
FerroA6-M	5.9±0.15 (10 MHz)	2.45	2 (with thermal vias)	7

* The data in parenthesis is the frequency when dielectric constant is measured

In the present study, lead free LTCC were prepared by the tape casting process and hot-press sintered at 950 °C with AlN and SiO_2-B_2O_3-ZnO-Al_2O_3-Li_2O glass as starting materials. The ceramic samples possessed a low dielectric constant (4.5~5.0), high thermal conductivity (11.6 W/(m·K)) and a proper TEC (3.0×10^{-6} K^{-1}, matching that of silicon).

EXPERIMENTAL PROCEDURE

AlN and borosilicate glass were used as raw materials. Commercial AlN powders (particle size of 0.5 μm, Hefei Nanotech Co., Ltd., China) and SiO_2-B_2O_3-ZnO-Al_2O_3-Li_2O system borosilicate glass powders were mixed at different mass ratios (*m*(AlN):*m*(glass)=30:70~70:30). Ethanol (EtOH) was employed as solvent, while polyvinyl butyral (PVB) and dibutyl(*o*-)phthalate (DBP) were introduced as binder and plasticizer, respectively. The mixture was ball-milled for 24 h to obtain slurry. Tapes were cast on a glass surface by using a blade to level the slurry and later dried at air atmosphere. The dried tapes were cut into 30 mm×30 mm squares, then stacked to the thickness of 1.5 mm (15 layers) to 3 mm (30 layers) at 80 °C and 20 MPa, and burned out at 550 °C. Finally, the green laminates of the AlN/glass composites were hot-press sintered at nitrogen atmosphere and 950 °C for 1 h.

X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (D/max-IIIA, Japan) using standard Cu K_α radiation. The microstructure was analyzed via a scanning electron microscopy (S-3000N, Japan). The porosity and bulk density were measured by mercury intrusion porosimetry (AutoPore IV 9510, Micromeritics, USA). The dielectric constant was recorded through a dielectric frequency and temperature spectrum analyzer (HP3458A, USA). The thermal conductivity was checked using a laser flash apparatus (Netzsch LFA 427, Germany), and the TEC by a GP-2 type optical dilatometer.

RESULTS AND DISCUSSION

Microstructure, porosity and bulk density

The XRD patterns of glass powder, AlN and ceramic samples sintered at 950 °C with different AlN contents are shown in Fig.1. Results show that glass powder tended to crystallize at 20° to 40°, zinc oxide (ZnO) easily reacted with aluminum and silicon, and two crystalline phases crystallized during sintering. The crystalline phases of ceramic samples after sintering were mainly composed of AlN, $ZnAl_2O_4$ and Zn_2SiO_4. The crystallite sizes of $ZnAl_2O_4$ and Zn_2SiO_4 (about 279 and 236 nm, respectively) were calculated through the Scherrer formula. The AlN/glass composites were transformed to glass-ceramic after sintering. It is also shown that the intensity of crystallite grew with the increase of glass concentration.

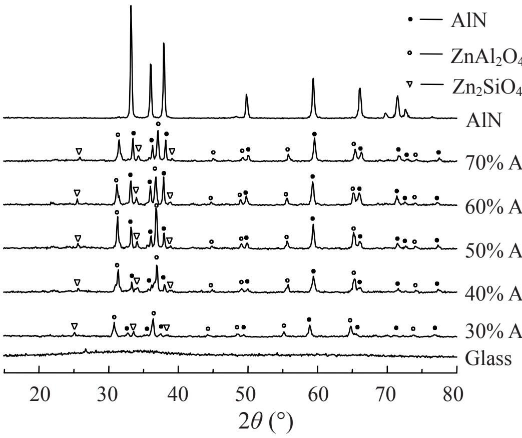

Fig.1 XRD patterns of glass, AlN and ceramic samples sintered at 950 °C with different AlN content

The microstructures of cross section for the AlN/SiO_2-B_2O_3-ZnO-Al_2O_3-Li_2O glass ceramic samples are shown in Fig.2. There existed liquid phase flowing when AlN and SiO_2-B_2O_3-ZnO-Al_2O_3-Li_2O glass was sintered at 950 °C, thereby the composites possessing a high bulk density. In the matrix glass, aluminum oxide could react with AlN at high temperature and produce AlON ceramic phase, which would increase the adhesion strength between the glass composites and AlN powders and better combine the matrix glass with AlN. Lithium oxide is known to help decrease the softening point of matrix glass and advance liquid phase sintering of ceramic samples (Northwest University of Light Industry, 2006). Liquid phase proportion of the composites decreased while the AlN content of batch composition increased from 30% to 70% (in mass fraction, the same below). AlN can be soaked by liquid glass phase when its content is 30%. With the increase of AlN content, the proportion of liquid glass phase descended and could not reach the whole area of ceramic samples, leaving some pores unfilled.

The porosity has a remarkable effect on the performance of ceramic samples after sintering. The variation of porosity and bulk density as a function of AlN content is shown in Fig.3. When the AlN content was increased from 30% to 70%, the bulk density of the ceramic samples fell from 3.4 to 2.0 g/cm^3. The porosity was inversely proportional to the bulk density, going up with the increase of AlN content. When the AlN content was higher and the glass content was lower, less liquid phase was found at sintering. Thereby, the flow of liquid phase was insufficient to fill in all of the air pores in the composites. The bulk density would be lower whereas the porosity be higher.

Dielectric constant

Fig.4 shows the variation of the dielectric constant (ε') of ceramic samples at different frequencies as a function of AlN content. The dielectric constant ranged from 3.7 to 6.2 and the change trends for the dielectric constant of ceramic samples with different AlN content were similar. In the matrix glass, only

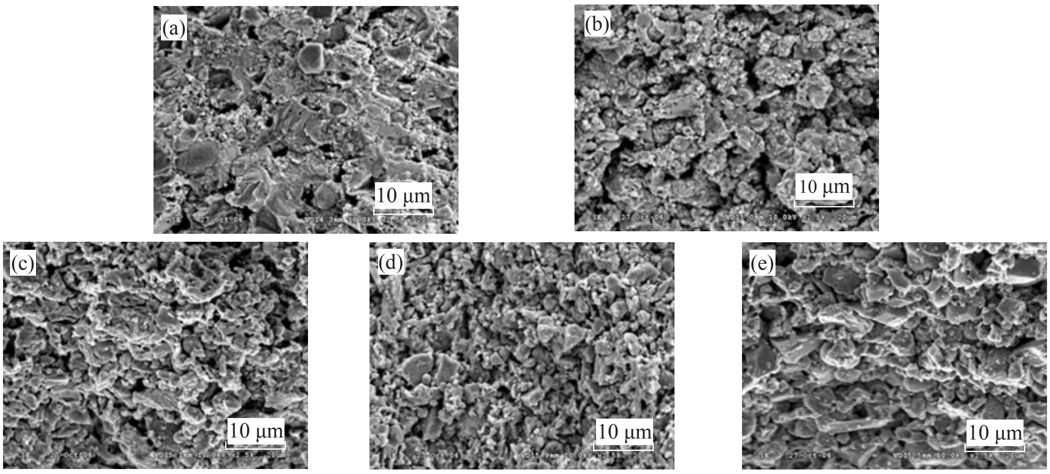

Fig.2 Microstructures of cross section for AlN/SiO_2-B_2O_3-ZnO-Al_2O_3-Li_2O glass composites. (a) When AlN content is 30%, AlN particles are soaked by liquid glass phase entirely; (b) When AlN content is 40%, most AlN particles are soaked by liquid glass phase and the pores increase; (c) When AlN content is 50%, some AlN particles emerge and liquid glass phase fails to envelop all AlN particles; (d) When AlN content is 60%, some AlN particles emerge and liquid glass phase fails to envelop all AlN particles; (e) When AlN content is 70%, many AlN particles are bare

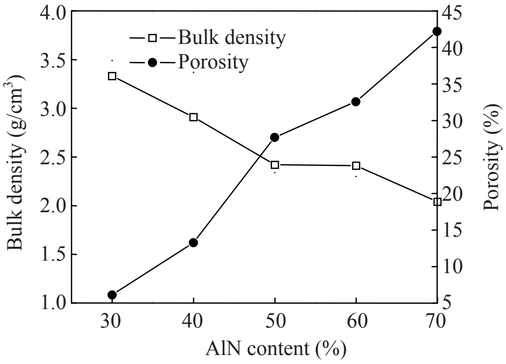

Fig.3 Variation of the bulk density and porosity of ceramic samples sintered at 950 °C as a function of AlN content (in mass fraction)

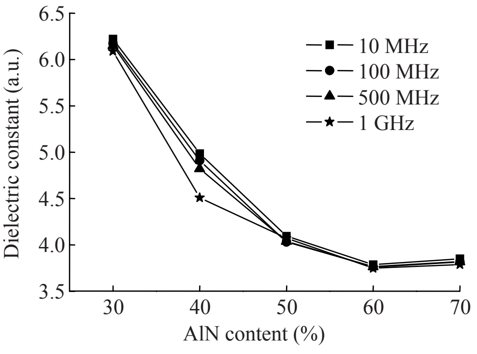

Fig.4 Variation of the dielectric constant (ε') of ceramic samples at different frequencies as a function of AlN content (in mass fraction)

Al_2O_3 possessed a dielectric constant corresponding to AlN; the dielectric constants of SiO_2, B_2O_3, and Li_2O were lower than that of AlN. However, the dielectric constant of ceramic samples dropped with the increase of AlN content. It is indicated that the contributions of glass composition and AlN were subdued and that the decline of the dielectric constant was mainly ascribed to the increase of porosity. When the AlN content was above 50%, the augment of porosity was gradual and the dielectric constant changed little. The formation of the dielectric constant was caused by various polarizations. Because of the frequency change, dipole reverse circumrotation followed the outer field. With the increase of the frequency, the reverse circumrotation of dipoles could not keep up with the frequency change and the dielectric constant accordingly decreased. At high frequency, some dipoles stopped reverse circumrotation and no longer contributed to the dielectric constant (Northwest University of Light Industry, 2006). Because the constitution was very complicated, there were several modes of polarizations in the ceramic samples and the frequency segment of each polarization was different. In general, the dielectric constant would decrease slightly by less than 0.4 with the increase of frequency.

Thermal conductivity

The thermal conductivity (λ) of ceramic samples is dependent on the composition and porosity of the ceramic samples. Due to its high thermal conductivity (319 W/(m·K) in theory of Tian and Shobu (2004)), AlN used as a ceramic matrix can improve the thermal conductivity of LTCC. Fig.5 shows the variation of thermal conductivity at room temperature of ceramic samples as a function of AlN content. The thermal conductivity of ceramic samples is as high as 4.7 to 11.6 W/(m·K). When the AlN content was below 40%, there would be enough liquid state glass at sintering to envelop most of the AlN particles and form dense ceramic composites. The heat conduction was ascribed to the passageway of interconnection among AlN particles; the thermal conductivity of ceramics rose with the increase of AlN content. When the AlN content was 40%, the thermal conductivity of the ceramic samples became as high as 11.6 W/(m·K). When the AlN content went above 40%, the liquid state glass would fail to envelop all AlN particles at sintering and the increase of porosity would become too quick to obstruct the heat conduction throughout the whole ceramic sample. Thus, the thermal conductivity of the ceramic samples dropped remarkably. When the AlN content exceeded 50%, the increase of porosity became gradual and the AlN content made the dominant issue for the thermal conductivity of all the ceramic samples. Therefore, it is believed that the thermal conductivity of the ceramic samples increases slightly with the growth of AlN content. Though the basic glass system was borosilicate glass, in which zinc oxide, aluminum oxide, and lithium oxide possessed fair thermal conductivity, the thermal conductivity of the matrix glass was still only about 1 W/(m·K). AlN made a main contribution to the thermal conductivity, and it is through the bulk density of ceramic samples that the matrix glass affected the thermal conductivity. Hence for improving the thermal conductivity, we should try our utmost to render ceramic samples with high density after sintering, meanwhile lessening adverse effects of the matrix glass.

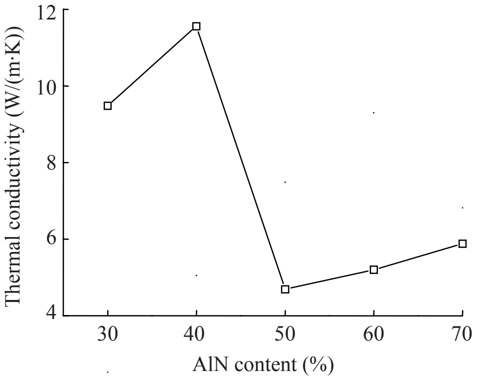

Fig.5 Variation of the thermal conductivity at room temperature of ceramic samples as a function of AlN content

Thermal expansion coefficient

The TEC of zinc oxide is 4.0×10^{-6} K^{-1}. After appropriate heat treatment, zinc borosilicate glasses have a relatively low TEC of 3.0×10^{-6} K^{-1} (Jia *et al.*, 2006). The matrix glass system used in this study was also zinc borosilicate glass. Fig.6 shows the TEC of ceramic samples with different AlN content vs temperature. Results show that the TEC of ceramic samples went up with the rise in temperature. The heat vibration of elementary particles (ions) in matrix materials increased with the augment of temperature and the space between elementary particles was enlarged, which would result in a higher TEC (Northwest University of Light Industry, 2006). Some potential energy must be overcome in order to enlarge the space between elementary particles. At low temperature, the heat vibrations of elementary particles were near the equilibrium position and the effects of electrovalent bonds or covalent bonds remained very strong, which means that the potential energy to be overcome was still very high. With the increase of temperature, the departure for heat vibrations of elementary particles from the equilibrium position was enhanced gradually. The functions of varied bonds were weakened and the potential energy to overcome reduced. Therefore, the TEC of the ceramic samples grew as the temperature rose. Fig.6 also shows that the TEC of ceramic samples always decreases with the increase of AlN content. As mentioned above, the porosity of ceramic samples increased as the AlN content mounted up. The increasing pores can "cushion" the thermal expansion of ceramic samples and this correspondingly reduced the TEC. When the temperature ranged from room temperature to 100 °C (the working temperature of LTCC substrates in applications), the TECs of the ceramic samples were between 1.8×10^{-6} and 3.1×10^{-6} K^{-1}, which matched those of silicon substrates.

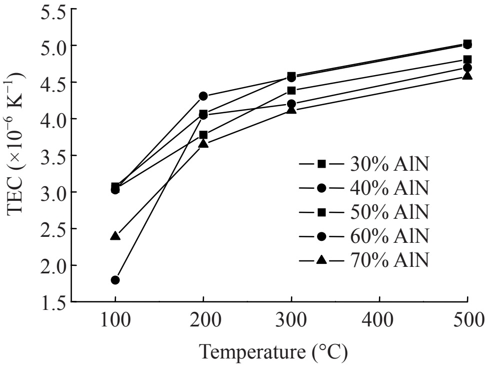

Fig.6 Thermal expansion coefficient of ceramic samples with different AlN content (in mass fraction) vs temperature

CONCLUSION

(1) AlN can be hot-press sintered with SiO_2-B_2O_3-ZnO-Al_2O_3-Li_2O glass at 950 °C to form dense ceramic materials.

(2) High glass concentration is conducive to liquid phase sintering, and the bulk density of ceramic samples increases with the glass concentration.

(3) The AlN content and porosity have a remarkable effect on the performance of ceramic samples. With the increase of AlN content, the thermal conductivity of ceramic samples rises at first and then descends when the AlN content is over 40%. With the augment of the porosity, the dielectric constant, thermal conductivity and TEC decrease.

(4) When the AlN content is 40%, ceramic samples possess a low dielectric constant (4.5~5.0), high thermal conductivity (11.6 W/(m·K)) and the proper thermal expansion coefficient (3.0×10^{-6} K^{-1}, matching silicon). The excellent performance makes this kind of LTCC a promising candidate for application in the micro-electronics packaging industry.

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