

## Tape Casting of $\text{Si}_3\text{N}_4$ Sheets for Potential Use as Circuit Substrate for Power Devices

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### Abstract

$\text{Si}_3\text{N}_4$  ceramics exhibit superior mechanical and electrical properties and potentially high thermal conductivity (200–320 W/m·K) at room temperature. They are an excellent prospective circuit substrate for power electronic devices. The literature reports that a great deal of work has been conducted on  $\text{Si}_3\text{N}_4$ , and  $\text{Si}_3\text{N}_4$  ceramics with thermal conductivity as high as 177 W/m·K have been realized. One of the main barriers for the application of  $\text{Si}_3\text{N}_4$  is the high cost of their fabrication. Tape casting is a flexible technique for the preparation of ceramic sheets with well-controlled composition and dimensions, and presents a prospective route for the development of  $\text{Si}_3\text{N}_4$  substrate at reduced cost.

In this study,  $\text{Si}_3\text{N}_4$  substrate was prepared by means of tape casting and the sintered reaction-bonded silicon nitride (SRBSN) technique. Initially, silicon green tapes were prepared by means of organic-solvent-based tape casting. The influences of binder content, plasticizer/binder ratio and solid loading on the tape properties were investigated and optimized. Subsequently, the nitration and sintering process was optimized. The microstructure and thermal properties of the  $\text{Si}_3\text{N}_4$  ceramics were investigated. Results showed that the preparation of  $\text{Si}_3\text{N}_4$  ceramics by means of tape casting and the reaction-bonded silicon nitride (SRBSN) technique is feasible.

*Keywords:* Silicon nitride, tape casting, thermal conductivity

### I. Introduction

Silicon nitride with high strength, high toughness, high wear and corrosion resistance, etc. has found a wide range of applications in the aerospace, nuclear power plant, automotive, industrial sectors, etc. as structural ceramics. In 1995, Haggerty and Lightfoot calculated the thermal conductivity of  $\text{Si}_3\text{N}_4$  to be as high as 320 W/m·K<sup>1</sup>, Hirotsuki *et al.* further calculated the thermal conductivity of  $\beta\text{-Si}_3\text{N}_4$  based on the molecule dynamic method. On the basis of their results, the thermal conductivity of  $\beta\text{-Si}_3\text{N}_4$  along a and c axis were approximately 170 and 450 W/m·K respectively<sup>2</sup>. Watari predicted that the thermal conductivity of  $\text{Si}_3\text{N}_4$  can reach 450 W/m·K based on the experimental results<sup>3</sup>. The combination of high mechanical properties with prospective high thermal conductivity makes  $\text{Si}_3\text{N}_4$  ceramics an attractive candidate for substrate materials in power electronic devices. For this reason, as described in the literature, a great deal of work has been conducted on improving the thermal conductivity of  $\text{Si}_3\text{N}_4$ <sup>4–7</sup>. A great advance was reported by You Zhou, based on the sintering of reaction-bonded silicon nitride (SRBSN) method, high thermal conductivity of 177 W/m·K can be obtained thanks to the low oxygen content<sup>8</sup>.

The main problem for the application of  $\text{Si}_3\text{N}_4$  substrates is currently the high price. For the typical preparation of  $\text{Si}_3\text{N}_4$  ceramics, a high sintering temperature and a long

holding time with high nitrogen pressure are always required, which will effectively increase the manufacturing cost. In addition, long-time sintering at high temperature will also inevitably lead to grain growth and reduced mechanical properties, which is also undesirable for application. From the industrial point of view,  $\text{Si}_3\text{N}_4$  ceramics with lower thermal conductivity in the range of 70–90 W/m·K are acceptable. Because  $\text{Si}_3\text{N}_4$  ceramics exhibit excellent mechanical properties, the substrate can be made much thinner than with AlN while achieving similar performance, thus the overall thermal resistance can be reduced. In the literature,  $\text{Si}_3\text{N}_4$  substrate with thermal conductivity of 70 W/m·K has been tested in an IGBT device and demonstrated satisfactory performance<sup>9</sup>. Therefore, a low-cost processing method for developing  $\text{Si}_3\text{N}_4$  substrate with thermal conductivity in the range of 70–90 W/m·K may be acceptable for commercial use.

In the present study, tape casting and the conventional sintered reaction-bonded silicon nitride (SRBSN) method was utilized to prepare  $\text{Si}_3\text{N}_4$  substrate. The dispersion of Si in azeotropic ethanol/methyl ethyl ketone systems was investigated and the effect of binder and plasticizer on the properties of the tape casting slurries was studied. The nitridation process and the gas-pressure-sintered  $\text{Si}_3\text{N}_4$  ceramics were also investigated. A relatively low sintering temperature and short holding time are proposed with the aim of reducing the cost.

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## II. Experimental Procedure

### (1) Starting materials

Si powder (HAOXI Research Nanomaterials, Inc) with the particle size  $D_{50}$  at 1.48  $\mu\text{m}$ , the specific surface area and oxygen content as 2.34  $\text{m}^2/\text{g}$  and 0.88 wt% respectively was used for this study.  $\text{Y}_2\text{O}_3$  and  $\text{MgO}$  with the final molar ratio of  $\text{Si}_3\text{N}_4:\text{Y}_2\text{O}_3:\text{MgO} = 91:6:3$  were selected as sintering additives. An azeotropic mixture of alcohol/methyl ethyl ketone (MEK) at 34/66 was selected as the solvent. Castor oil, phosphate ester (PE), glycerol trioleate were selected for the dispersion of the Si powder. For the preparation of the tape casting slurries, a polyvinyl butyral with higher molecular weight (B98, Monsanto, USA) was used as a binder and butyl benzyl phthalate (Santicizer 160, Solutia, Inc., St. Louis, USA) as a plasticizer. The slurry preparation process was as follows: the ceramic powder and sintering additives were dispersed in the solvent mixture in the presence of a dispersant. After ball-milling for 24 h, the binder and plasticizer were added and the slurries were further ball-milled for 24–48 h to ensure a homogeneous structure was obtained. After any trapped air bubbles had been removed, the slurries were tape-cast on ProCast Precision Tape Casting Equipment (Division of HED International, Inc., Ringoes, NJ, USA) at a speed of 100 mm/min with a gap height fixed at 300 mm. Once they had dried, the green tapes could be subsequently characterized and sintered. The binder was removed in a graphite furnace with a slow heating rate of 1  $^\circ\text{K}/\text{min}$  up to 800  $^\circ\text{C}$  and holding time of 1 h based on the TG-DTA data. The tapes were sintered at 1850  $^\circ\text{C}$  with 1 h holding at 0.6 MPa  $\text{N}_2$  pressure.

### (2) Measurement of the slurry properties

30 vol% Si slurries were prepared using an azeotropic EtOH/rMEK (34 : 66) mixture as a solvent with different dispersant, the concentration of which was kept as 2 wt% of the solid to ensure all the suspensions were well stabilized. The slurries were ball-milled for another 24 h to allow the equilibrium adsorption of dispersants on to the powder surface. After rheological measurement, binder and plasticizer were added with different content. The slurries were further ball-milled for 48 h before further rheological measurement.

The rheological behavior was characterized using a Universal Stress Rheometer SR5 (Rheometric Scientific, USA) at 25  $^\circ\text{C}$ . Shear-dependent behavior of the examined suspensions was evaluated by ascending and descending shear rate ramps from 0.01 to 1000  $\text{s}^{-1}$  in 5 min, and from 1000 to 0.01  $\text{s}^{-1}$  in 5 min respectively.

### (3) Characterization

The green density of the tapes was measured with the Archimedes method. The pore size and porosity of the green tapes were characterized by means of Hg porosimetry. After sintering, specimens for thermal conductivity measurement were machined into disk-like shapes (10 mm in diameter and 2 mm in thickness). Thermal diffusivity ( $\alpha$ ) measurements were performed at 25  $^\circ\text{C}$  on laser-flash apparatus (LFA427 Nano ash, NETZSCH Instruments Co. Ltd, Selb, Germany). Specific heat ( $C_p$ ) was measured with

a differential scanning calorimeter (DSC; PerkinElmer DSC-2 C, USA). Thermal conductivity ( $\kappa$ ) could be calculated based on bulk density, thermal diffusivity and specific heat capacity using the following equation:

$$\kappa = \rho c_p \alpha \quad (1)$$

The phase composition of the samples was measured by means of X-ray diffraction (XRD, D/Max-2250V, Rigaku, Japan). The microstructure was characterized with a scanning electron microscope (FESEM, JSM-6700F, JEOL, Tokyo, Japan).

## III. Results and Discussion

### (1) Tape casting

The dispersability of the slurries is the key factor for obtaining high-quality and homogeneous green tapes, which is also important for the subsequent nitridation and sintering process. In this work, three typical dispersants, castor oil, phosphate ester (PE) and glycerol trioleate were tested and compared. Based on the measurement of the rheological properties, phosphate ester was found to be better for obtaining well-dispersed slurries. Then 30 vol% Si slurries with different phosphate ester were prepared and the rheological properties were measured. As shown in Fig. 1, all the slurries showed a well-dispersed state. With the increase in dispersant content, the viscosity of the slurries decreased initially, reaching a low point at the dispersant content around 1.8 wt%, and increased slightly thereafter. This might suggest that the dispersant content of 1.8 wt% could help to develop well-dispersed slurries. At low dispersant content, before the saturation adsorption, there is not enough dispersant to stabilize the ceramic powder, so the slurry viscosity decreases continuously with the increase in the dispersant content; after reaching the saturation adsorption, excess dispersant would have an adverse effect on the dispersion of the slurries and lead to a slight increase in viscosity<sup>10</sup>. Based on this result, the content of phosphate ester was kept as 1.8 wt% for the subsequent slurry preparation.

Subsequently, PVB was added and the slurry properties were characterized. The addition of PVB was able to effectively increase the slurry viscosity owing to its high molecule weight. The binder content should not usually be so high as long as the green sheets are crack-free with adequate strength<sup>11</sup>. In our study, it was found that at the binder content of around 8 wt%, the sheets showed tensile strength at around 0.6 MPa and a not so significant decrease in green density based on the characterization of the green tape properties. The plasticizer content was further optimized in term of plasticizer/binder mass ratio. On the basis of the rheological properties and also on the green tape strength and density characterization, a plasticizer/binder mass ratio at 1.2 was found to be suitable for tape casting. It was found that the slurries with binder and plasticizer showed shear thinning behavior, suitable for tape casting.

Next, the influence of the solid loading on the slurry properties was characterized. Results showed that with the increase in the solid loading, the slurry viscosity increased clearly at the low shear rate range. At high solid

content, the slurry was not so homogeneous. Therefore, in our work, the solid content was set at 33 vol% for tape casting.

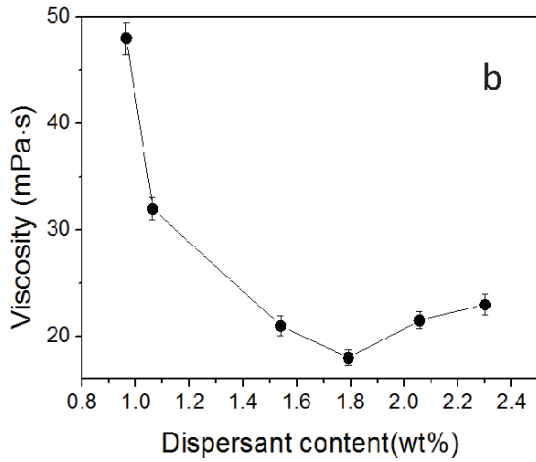
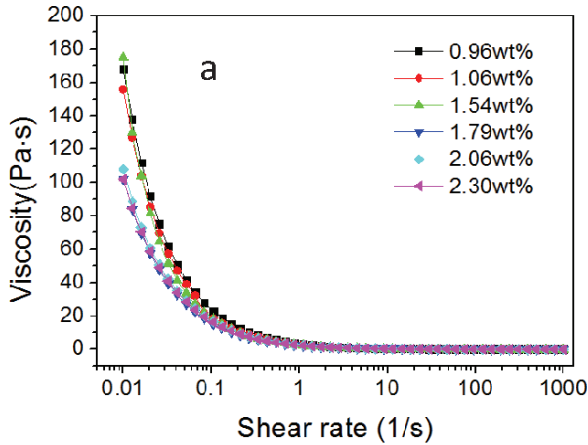


Fig. 1: Influence of the dispersant content on the rheological properties of Si slurries.

Based on the study above, an optimized tape casting slurry was proposed with the dispersant, binder, plasticizer/binder ratio and the solid loading at 1.8 wt%, 8 wt%, 1.2 and 33 vol% respectively. An optical photograph and microstructure of the cast green tape are shown in Fig. 4. The obtained green tapes showed a smooth surface, with no obvious defects. Moreover, they had good flexibility for free bending and cutting. The microstructure of the heat-treated green bodies showed that the ceramics powders and pores were homogeneously distributed.

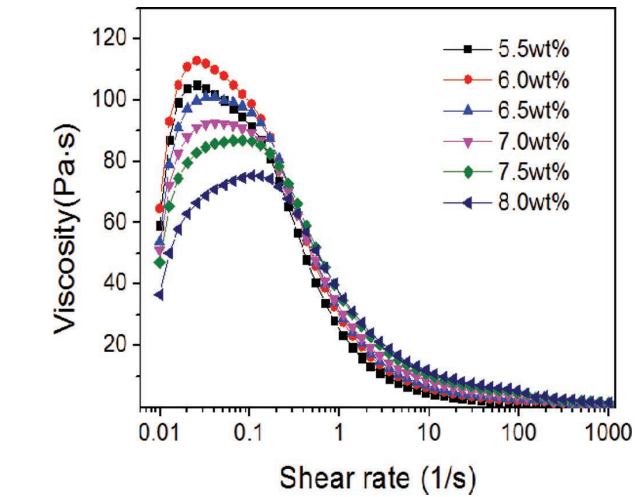
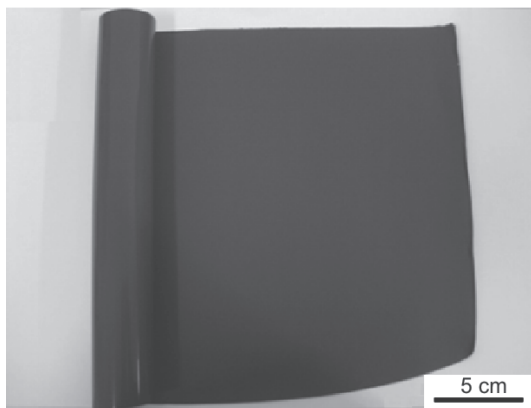


Fig. 2: Influence of the binder content on the rheological properties of 30 vol% slurries with the plasticizer binder ratio at 1:1.

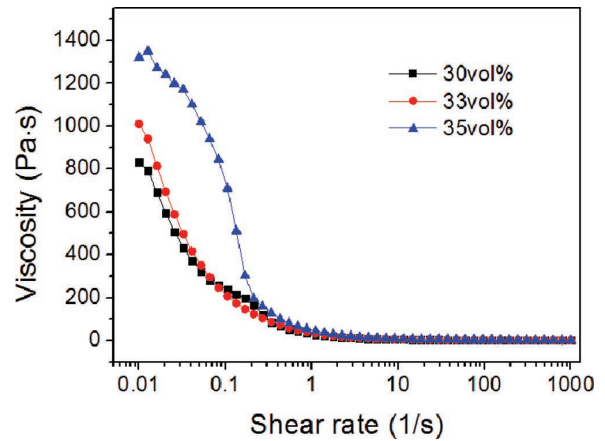


Fig. 3: Influence of the solid loading on the rheological properties of the slurries.

### (2) Nitridation, sintering and properties of $Si_3N_4$ ceramics

After binder removal, crack-free green tapes can be obtained. Hg porosimetry showed a monomodal pore size distribution of the green sheets, suggesting a homogeneous microstructure, Fig. 5. The pore size was distributed in a narrow range of 100–200 nm, the porosity measured with the Hg porosimetry was around 50.6 vol%.

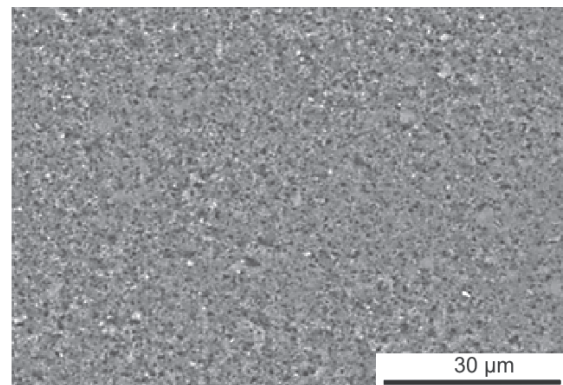


Fig. 4: Optical graph and micrograph of Si tape.

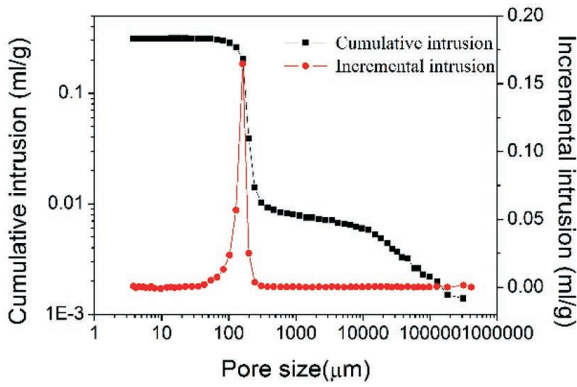


Fig. 5: Pore size distribution of the tape after binder removal.

Subsequently, the nitridation process was studied.



The nitridation reaction was quite simple as shown in Equation 1. However, owing to a large number of material parameters, such as temperature, pressure, gas composition, particle size, compact size, the heat generation and thermal diffusivity, etc., that can affect the nitriding process, the overall mechanism is quite complex<sup>12, 13, 14</sup>. In this study, only the influence of the temperature and holding time on the nitridation degree was investigated. Interestingly, the nitridation of Si tapes was different from that of Si powder dry compact. In pure nitrogen atmosphere, the variation of the nitridation degree with temperature and holding time was shown in Fig. 6. It was found that the prolongation of holding time and the increase in temperature could help to increase the degree of nitridation. High nitridation degree can be achieved at 1360 °C with 4 h holding time. In addition, it can be found that the Si powder with the particle size of 5 μm always shows a low nitridation degree compared with the powder of 1 μm in size. The influence of the solid content of the tape casting slurries on the nitridation degree was also studied. It was found that the solid content had a very limited effect on the nitridation degree in our experimental range. This nitridation process is similar to that reported in literature<sup>8</sup>. After nitridation, a homogeneous microstructure can be obtained, Fig. 7. XRD showed that it was a mixture of β and α phase.

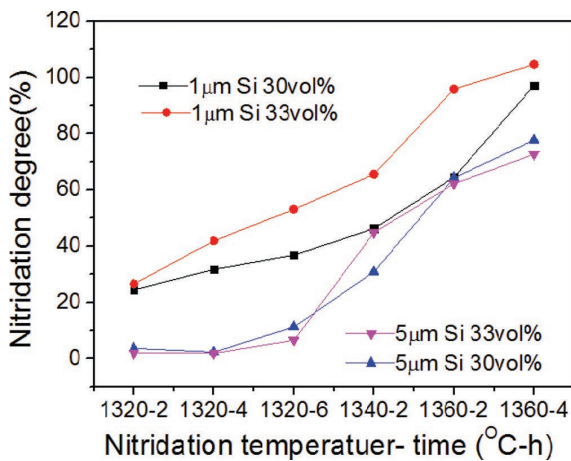


Fig. 6: Nitridation degree versus temperature.

After sintering at 1850 °C with 1 h holding time under 0.6 MPa N<sub>2</sub>, well-densified Si<sub>3</sub>N<sub>4</sub> ceramics were obtained.

Fig. 8 shows the fracture surface of the sample. A typical bimodal microstructure composed of large elongated β-Si<sub>3</sub>N<sub>4</sub> grains and small β-Si<sub>3</sub>N<sub>4</sub> matrix grains can be observed, similar to that reported in literature<sup>8</sup>. The relative density reached 99.1 % and the second phase was found to be Y<sub>2</sub>Si<sub>3</sub>O<sub>3</sub>N<sub>4</sub>. The thermal conductivity was in the range of 81 – 87 W/m·K, which is comparable to that reported in literature sintered at 1900 °C with 3 h holding<sup>15</sup>. Further improvement in the thermal conductivity can be achieved with the increase in sintering temperature and the prolongation of holding time to reduce the oxygen content in the β-Si<sub>3</sub>N<sub>4</sub> grains. However, the cost would then be increased as well. Work on an alternative route for improving thermal conductivity without high sintering temperature and long holding time is underway.

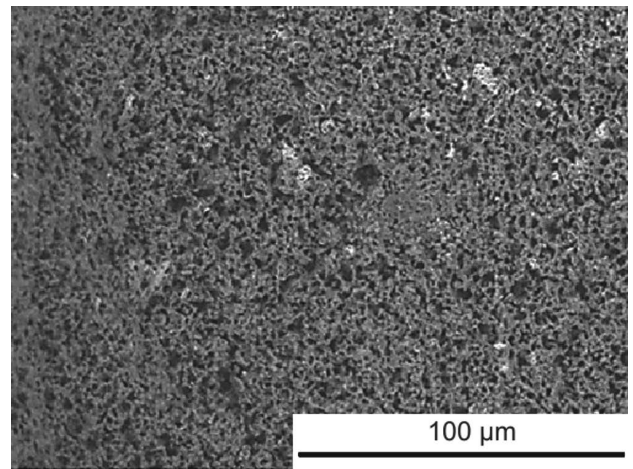


Fig. 7: Microstructure of the green tapes after nitridation.

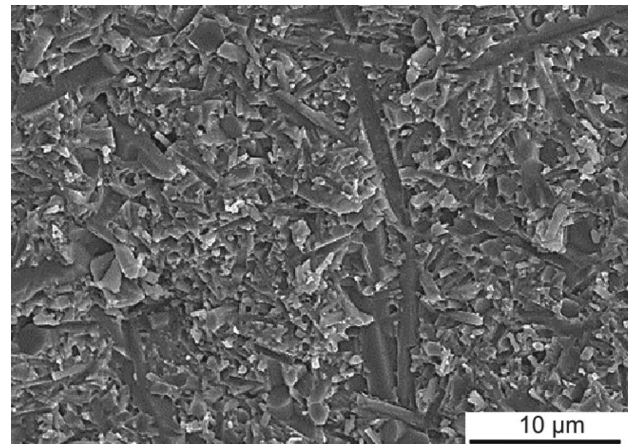


Fig. 8: Fracture surface of the Si<sub>3</sub>N<sub>4</sub> after sintering.

#### IV. Conclusions

Tape casting, nitridation and gas pressure sintering were proposed for the preparation of Si<sub>3</sub>N<sub>4</sub> ceramics. The dispersant, binder, plasticizer/binder ratio and the solid loading were optimized to be 1.8 wt%, 8 wt%, 1.2, 33 vol% respectively. The green tapes exhibited a homogeneous microstructure. After nitridation and gas pressure sintering, well-densified Si<sub>3</sub>N<sub>4</sub> ceramics were obtained with thermal conductivity at 81 W/m·K. Results showed that the proposed tape casting, nitridation and pressureless sintering is feasible for the preparation of Si<sub>3</sub>N<sub>4</sub> for potential use as circuit substrate for power electronic devices.

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