Development of the Environmental Friendly Non-Aqueous Tape Casting Process for High-Quality $\text{Si}_3\text{N}_4$ Ceramic Substrates

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Abstract. A cheap and environmental friendly non-aqueous tape casting process for preparing high quality $\text{Si}_3\text{N}_4$ ceramic substrates was explored. A ternary solvent mixture of ethanol, ethyl acetate and butyl acetate-based formula was developed by using castor oil, polyvinyl butyral and dibutyl phthalate as the dispersant, binder and plasticizer, respectively. The influence of dispersant content, binder content and solid loading on the rheological properties of $\text{Si}_3\text{N}_4$ slurries was firstly investigated. It was found that the optimized formulation for dispersant, binder and solid loading was 1.6 wt%, 12 wt% and 51 wt%, respectively. The flat, flexible and uniform green tapes with a thickness of 400–500 $\mu$m and high-quality including high bulk density, uniform pore distribution and low porosity were obtained. After drying and debinding, the green sheets were sintered at 1900 °C for 2 h, where $\text{Si}_3\text{N}_4$ ceramics with a thermal conductivity being 85.79 W m$^{-1}$ K$^{-1}$ can be achieved. The sintered samples were one of the most attractive substrate materials for high power electronics applications.

1. Introduction
With the rapid development of modern society, energy and environment problem are brought to worldwide attention. In order to save energy and reduce carbon dioxide emissions, the sources of energy tend to shift from fossil raw materials to electrical energy. Therefore, efficient and rational utilize of electrical energy is becoming more and more important. Power electronics are the key technology to solve the problem, and it is widely used in various fields, such as industrial robots, hybrid vehicles, advanced electric vehicles, and so on. Nowadays, power device technology is developing for high voltage, current and power density. In the near future, silicon will be replaced by wide-bandgap semiconductors (WBGS). However, the high power will cause the higher thermal stress on the device. For devices and packaging materials, especially the key challenge in preparing brittle ceramic substrates with electrical insulation and heat dissipation [1,2]. Therefore, good mechanical reliability and high thermal conductivity of ceramic materials are necessary for high power electronic devices.
Ceramic substrate is a basic material used in high-power electronic circuit structure technology and interconnection technology. At present, AlN is used as the main ceramic substrate materials, it exhibits high thermal conductivity (more than 200 W m⁻¹ K⁻¹) for power devices, but its mechanical properties are not very high (Flexural strength: 300-400 MPa, Fracture toughness: 3-4 MPa m¹/²), and Si₃N₄ ceramic has a theoretical thermal conductivity similar to that of AlN and good mechanical properties, which is one of the most attractive ceramic substrate materials for high power electronics applications[3,4].

Silicon nitride (Si₃N₄) has been regarded as a promising insulating substrate material for high-power electronic devices and advanced structural components because of its excellent mechanical properties (high hardness, strength and fracture toughness) and high thermal conductivity[5,6]. However, the low sinterability and poor processability limit the wide commercialization of Si₃N₄ ceramics [7]. Besides, it is difficult to fabricate complex shaped components by traditional forming methods [8-10]. Ceramic processing techniques, such as slip casting, freeze casting, gel casting and injection molding, have been applied for the preparation of Si₃N₄ components [11,12]. The toxic available binder systems are usually used for the above processing techniques, and the low density and strength of the products is difficult to optimize. Thus, the selection of the molding process is important for the preparation of ceramic materials with environmentally friendly and good properties.

Tape casting is of high efficiency and low cost in fabricating ceramics substrates [13], which is widely used in electronic industry and complex shaped components with high quality [14-16]. Nowadays, organic casting is mostly used in a typical industrial production. The use of a binary mixed solvent containing toluene and alcohol [17], which causes serious environmental pollution and high cost. Tape casting is divided into aqueous and non-aqueous. However, the aqueous tape casting is sensitive to parameters [18], which is due to the reactions may take place between the ceramic powders and water for non-oxide materials (AlN, SiC and Si₃N₄) [19,20].

In this work, the anhydrous ethanol, ethyl acetate and butyl acetate were used as a ternary solvent mixture to fabricate Si₃N₄ ceramic substrates by non-aqueous tape casting. The rheological behaviors of slurries, microstructure and properties of the green tapes and as-sintered Si₃N₄ ceramic substrates were investigated.

2. Experimental

2.1. Starting materials

The α-Si₃N₄ powders (an average size of 745.9 nm and a specific surface area (BET) of 5.209 m²/g, P95H, VESTA Ceramics AB, Sweden) and the commercial Si₃N₄ powders (an average size of 804.0 nm and a specific surface area (BET) of 7.381 m²/g, JinSheng Ceramic Technology Co., Ltd., Jiangsu, China) were used in the fabrication of green tapes. Magnesium oxide (50 nm, 99.9% metals basis, Shanghai Macklin Biochemical Co., Ltd., Shanghai, China) and Yttrium oxide (99.99% metals basis, Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China) were used as sintering aids. The ternary mixture of ethyl acetate/butyl acetate/ethanol at a mass ratio 1/2/1.4 was selected as the solvent system. The dispersant used for stabilizing the Si₃N₄ slurries was castor oil (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China). Commercial Polyvinyl Butyral (PVB) and dibutylphthalate (DBP) were used as binder and plasticizer, respectively.

2.2. Experimental process

The Si₃N₄ slurry was prepared as follows: Firstly, Si₃N₄ powder, MgO and Y₂O₃ were mixed in a molar ratio of 93/5/2; a non-aqueous solvent was prepared by mixing ethyl acetate, butyl acetate and ethanol at a mass ratio 1/2/1.4; Subsequently, the pre-mixed solvent and the dispersant was added to Si₃N₄ powder containing the sintering aids by ball milling for 24 h; the binder (PVB) and the plasticizer (DBP, which are milled at least for 12 h to occur interaction effect) were added; the new slurry was ball milled for 24 h; Finally, the slurry was de-gassed by using a vacuum system for 30 min.
The gap height of the blade was controlled at 400-800 μm. The casting speed was 0.1 cm·s⁻¹. The tapes were dried at 27.5 °C for 12 h.

The dried tapes were cut into square pieces. The organic compound was removed at 500-600 °C for 5 h in order to exclude the residual carbon. The green bodies were sintered in nitrogen atmosphere. The sintering temperature, the holding time and pressure value were 1900 °C, 2 h and 2 MPa, respectively. The experimental process for tape casting is shown in Figure 1.

2.3. Characterization

The rheological properties of the slurries were performed using a shear controlled rheometer (DV II + Pro, Brookfield, Guangzhou, China). Mercury porosimetry (Auto Pore 9500, America) was used to determine the porosities and pore size distributions in the green tapes. The microstructures of the green bodies and sintered Si₃N₄ ceramics were observed by using a field emission scanning electron microscopy (SEM,Leo-1530, Zeiss, Oberkochen, Germany). The surface roughness of the green tape was measured using an atomic force microscope (AFM)(NTEGRA, NT-MDT, Russia) operating in the tapping mode regime. The Archimedes principle was employed to measure the bulk density of the sintered Si₃N₄ ceramics. The thermal conductivity of the sintered materials was measured by laser flash method using a heat conduction analysis meter (LFA 447 MicroFlash, Netzsch , Germany).

3. Results and discussion

3.1. Rheological properties of Si₃N₄ slurries

High solid content, good fluidity and stable dispersion of the slurry is the key to obtain a uniform, dense and defect-free green body. The rheological properties of the cast slurry depend mainly on the solids content of the powder, the dispersant content and the binder content, so the regulation of the cast slurry is particularly important.

3.1.1. Viscosity of Si₃N₄ slurries varying with dispersant addition. Figure 2 shows the rheological properties of Si₃N₄ suspensions with different dispersant contents (0~3 wt%), in which the solids content of the suspension is 43 wt%. It can be seen from Figure 2(a) that the viscosity of the Si₃N₄ suspensions decreases with the increase of dispersant content in the range of 0-1.6 wt%. Due to the dispersant adsorbs to the surface of particles, the steric stabilization hinders the agglomeration among the particles, enhancing the fluidity of the suspension. However, the viscosity of the suspension increases continuously with the increase of dispersant content from 1.6 wt% to 3 wt%. Because the dispersant is saturated on the surface of the ceramic particles, the excess dispersant undergoes a cross-linking reaction between the particles, reducing the dispersibility of the particles. [21].
Figure 2(b) shows the relationship between the dispersant content and the viscosity of the suspension with the effect of the dispersant on the particles at a shear rate of 20 s\(^{-1}\). It can be seen that the viscosity of the suspension is high without the addition of dispersant. The viscosity of the suspension decreases gradually with the increase of dispersant content. When the dispersant content is 1.6 wt\%, the viscosity reaches a minimum value, so the optimum content of the dispersant is 1.6 wt\%.

![Figure 2. Rheological properties of Si\(_3\)N\(_4\) slurries with different dispersant contents (a); Relationship between the dispersant content and the viscosity of the suspension at shear rate of 20 s\(^{-1}\) (b).](image)

3.1.2. Viscosity of Si\(_3\)N\(_4\) slurries varying with binder addition. Figure 3(a) shows the effect of different binder contents on the rheological properties of Si\(_3\)N\(_4\) slurry. The solid content of the slurry is 45 wt\%, and the slurry composition is shown in Table 1. Apparently, the viscosity of the slurry increases continuously with the increase of binder content, exhibiting the shear-thinning behavior with the increase of shear rate. The analysis suggests that a network structure formed by macromolecular compound in the static slurry. When the shear rate increases, the network structure is continuously destroyed (viscosity drop), and the shear thinning rheological property of slurry can accurately control the shape of the wet bodies. Slurry with shear thinning rheological property can be characterized by viscosity value of low shear rate and high shear rate [22]:

\[
P = \frac{(R = 15s^{-1})}{(R = 10s^{-1})}
\] (1)
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(*\eta*; Viscosity of the slurry at different shear rate; \(R\); Shear rate; \(P = 1, \eta = c\), Newtonian behavior; \(P > 1\), Shear-thinning behavior)

The results show that it is difficult to obtain a defect-free green body with a slurry containing 11 wt% binder, while all other slurry is suitable for casting. For cast slurry, the content of organic additives should be as low as possible, which is due to the few organic additives can reduce the risk of defect formation. Therefore, the most suitable binder content of Si\(_3\)N\(_4\) slurry is 12 wt%.

**Table 1.** Composition of Si\(_3\)N\(_4\) slurry with different solid contents.

| No. | Solid content (wt%) | Dispersant (wt% of powders) | Binder (wt% of powders) |
|-----|---------------------|-----------------------------|-------------------------|
| 1   | 43                  | 1.6                         | 12                      |
| 2   | 47                  | 1.6                         | 12                      |
| 3   | 51                  | 1.6                         | 12                      |

**Table 2.** The properties of green tapes with different Si\(_3\)N\(_4\) powder.

| No.                  | Average Pore Size (nm) | Bulk Density (g/cm\(^3\)) | Apparent Porosity (%) |
|----------------------|------------------------|---------------------------|-----------------------|
| Sweden Si\(_3\)N\(_4\) | 164.76                     | 1.96                      | 19.06                 |
| Jinheng Si\(_3\)N\(_4\) | 188.49                     | 1.80                      | 24.60                 |

3.1.3. Viscosity of Si\(_3\)N\(_4\) slurries varying with solid content. Figure 3(b) shows the effect of solid content on the rheological properties of Si\(_3\)N\(_4\) slurry. It can be seen that the viscosity of the slurry increases with the increase of solid content, and all the slurry is a pseudoplastic fluid with the increase of the shear rate. After the test analysis, all the slurries except the slurry with a solid phase content of 55 wt% satisfy the rheological properties of tape casting. Based on the above test results, the porosity, pore distribution and density of the casting green body are studied by using the optimum slurry composition.

3.2. Characterization of Si\(_3\)N\(_4\) green tape

Figure 4 shows the optical photographs of high-quality green tapes obtained by casting with the optimum slurry composition. The Si\(_3\)N\(_4\) tapes with thickness of around 400-500 \(\mu\)m are prepared with a smooth, free of defects and good flexible. The bottom surface of green tapes will produce a reflection phenomenon in the case of illumination, indicating the bottom surface is smoother than the top surface, as shown in Figure 4(a). Due to the drying process of green tapes is one-side volatilization, the solvent migrates from the bottom surface to the top surface, and then it volatilizes from the top surface, resulting in an increase of the number of the pores and roughness on the surface of green tapes [23,24]. Figure 5(a) and (b) are AFM photographs of the top and bottom surface of the green tapes obtained by Swedish Si\(_3\)N\(_4\) powder casting; Figure 5(c) and (d) are AFM photographs of the top and bottom
surface of the green tapes obtained by Jinsheng Si$_3$N$_4$ powder casting, and the surface roughness (Ra) is 71 nm, 94 nm, 104 nm and 204 nm, respectively. It is suggested that the smaller the surface roughness of green tapes, the smoother and denser the surface, and the smaller the roughness difference between the top and bottom surface of green tapes, the more uniform the prepared green tapes. Therefore, the green tapes prepared by Swedish Si$_3$N$_4$ powder have good quality.

Figure 5. AFM images of the top (a) and the bottom (b) of Sweden Si$_3$N$_4$ green tape; AFM images of the top (c) and the bottom (d) of Jinsheng Si$_3$N$_4$ green tape.

Figure 6. (a) Microstructure, (b) EDX frame analysis and element distribution of Sweden Si$_3$N$_4$ green tape.
Figure 6(a) shows the microstructure of Si₃N₄ green tape surfaces dried at 60°C. It can be observed that the mixture of silicon nitride particles and a ternary organic solvent, dispersant, binder and plasticizer is uniformly distributed in the green body without agglomeration, increasing the density of the green body. EDX analysis and element distribution of microstructural frame (Figure 6b) show that nearly homogenous distribution of silicon and nitrogen element all through the microstructural frame with lesser extent of carbon and oxygen ions. The presence of C and O is due to the addition of organic additives, and the atomic ratio of Si and N is consistent with the structural composition of Si₃N₄.

3.3. Characterization and sintering properties of Si₃N₄ ceramic substrates

Figure 7(a) and (b) shows that the Si₃N₄ ceramic substrates are obtained by gas pressure sintering at 1900°C for 2 hours with 2 MPa. The sintered substrates have good quality, defect-free surfaces and a certain strength. The thermal conductivity was measured to be 85.79 W/(m·K). The fracture surfaces of Sweden Si₃N₄ samples are shown in Figure 7(c). It can be seen that some elongated β-Si₃N₄ grains with regular morphology dominate the microstructures of samples, and the pores are readily presented. Amount of β-Si₃N₄ grains linked the delaminated layers together and form inter-locked structure were found which can improve the toughness of the sintered samples [25]. In addition, Crack deflection, crack bridging and grain pullout of the rod-like β-Si₃N₄ grains by toughening mechanisms reinforce bending strength of the Si₃N₄ ceramics. The growth mechanism of β-Si₃N₄ grains can be attributed to the dissolution reprecipitation mechanism, which is related to the porous Si₃N₄ ceramic reported previously [26,27].

![Figure 7](image_url)

**Figure 7.** Photograph and Fractograph of sintered Si₃N₄ substrate, (a) (c) Sweden; (b) Jinhsheng.

4. Results and discussion

1. The optimum composition of Si₃N₄ slurry: Solid content of 51 wt%, dispersant content of 1.6 wt%, Binder content of 12 wt%, Plasticizer/Binder (weight ratio) = 0.7. At this time, the rheology of the slurry is most suitable for tape casting;

2. The green body obtained by the optimum slurry composition has good flexibility, smooth and defect-free, The roughness of bottom surface is lower than top surface, and the thickness is 400-500 μm;

3. After debinding and sintering, the flat, defect-free and uniform microstructure Si₃N₄ ceramic substrates are obtained, whose thermal conductivity is 85.79 W/(m·K);

4. Non-aqueous tape casting process not only maintains the performance of the ceramic substrates, but also contributes to environmental protection.

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