

## Optimization of Binder Burnout for Reaction Bonded Si<sub>3</sub>N<sub>4</sub> Substrate Fabrication by Tape Casting Method

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(Received August 29, 2015; Revised October 7, 2015; Accepted October 7, 2015)

### ABSTRACT

It is a challenge from an industrial point of view to fabricate silicon nitride substrates with high thermal conductivity and good mechanical properties for power devices from high-purity Si scrap powder by means of thick film processes such as tape casting. We characterize the residual carbon and oxygen content after the binder burnout followed by nitridation as a function of the temperature in the temperature range of 300°C - 700°C and the atmosphere in a green tape sample which consists of high-purity Si powder and polymer binders such as polyvinyl butyral and dioctyl phthalate. The optimum condition of binder burnout is suggested in terms of the binder removal temperature and atmosphere. If considering nitridation, the burnout of the organic binder in air compared to that in a nitrogen atmosphere could offer an advantage when fabricating reaction-bonded Si<sub>3</sub>N<sub>4</sub> substrates for power devices to enable low carbon and oxygen contents in green tape samples.

**Key words** : Silicon nitride, Silicon, Tape casting, Reaction bonding, Thick films

### 1. Introduction

Ceramic materials having high electric insulation and thermal conductivity are excellent as a thermal medium for rapidly diffusing the heat generated from a device and have been used as substrate materials for the devices for transportation vehicles, substrate materials for integrated electronic circuits, heat sink parts for laser oscillator, reaction container parts for semiconductor manufacturing apparatuses and precision machine parts, etc.<sup>1-5)</sup> Particularly, ceramic heat sink substrates for high-power devices with a recently increasing importance in industrial areas require high insulation, withstanding voltage, thermal conductivity, strength, toughness along with low permittivity and similar thermal expansion coefficient to those of Si chip and metal joining materials, while aluminum nitride (AlN), alumina (Al<sub>2</sub>O<sub>3</sub>), silicon nitride (Si<sub>3</sub>N<sub>4</sub>), etc. have been studied as the ceramic materials suitable for such requirements.<sup>6-9)</sup>

Although aluminum nitride has been much studied leading to commercialization as a ceramic heat sink substrate for high-power due to its high thermal conductivity (100 ~ 270 W/mK), it has problems such as reliability degradation and short life, etc. with vulnerable characteristics of thermal fatigue resistance caused by a low strength (250 ~ 450 MPa), a difference in thermal expansion coefficient from that of Si (4.5 ~

4.6 × 10<sup>-6</sup>/K, Si: 2.6 × 10<sup>-6</sup>/K). Meanwhile, silicon nitride is a material capable of manifesting a high strength (500 ~ 800 MPa), high toughness (5 ~ 8 MPa m<sup>1/2</sup>), excellent matching in thermal expansion coefficient (2.7 ~ 3.4 × 10<sup>-6</sup>/K) to that of Si, and high thermal conductivity (70 ~ 170 W/mK) comparable to that of AlN, and shows excellent thermal fatigue resistance, making it to be a material suitable for next-generation high-power devices.

However, since Si<sub>3</sub>N<sub>4</sub> has a low price competitiveness due to high costs of the raw material powder, it is not yet commercialized as a heat sink substrate.<sup>10)</sup> Recently, to solve such problems, studies are in progress where high-quality sintered body of silicon nitride is obtained through reaction sintering<sup>11-12)</sup> using the raw material of high-purity Si powder obtained as the byproduct of manufacturing process when jigs for semiconductor processes or wafers are manufactured. Reaction sintering is a method where Si<sub>3</sub>N<sub>4</sub> is obtained by reacting of Si green body with nitrogen gas, where manufacturing of elaborate shapes is possible because of low shrinkage rates after nitriding reaction.<sup>13-16)</sup>

Among manufacturing methods for the green body, tape-casting process is a low-cost process to manufacture ceramic sheets of a small thickness widely used in the industry.<sup>17)</sup> While uniform and highly filled green sheets are manufactured by addition of organic materials to obtain a high-density sintered body through tape-casting method, the organic materials contained in this green sheet must be completely removed through binder burnout.<sup>18)</sup> Meanwhile, SiO<sub>2</sub> is generally present on the surfaces of Si powder as the starting raw material, while oxygen may be additionally contained

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upon slurry blending, tape casting, binder burnout, etc.<sup>6)</sup> When SiO<sub>2</sub> film is formed on the surface of Si powder in this way, nitriding reaction is delayed so as to leave residual Si, and the nitriding rate should be increased by controlling the SiO<sub>2</sub> to be as low as possible since the residual Si remaining in the sintered body has effects on mechanical characteristics, particularly, fracture toughness and high-temperature characteristics of the sintered body.<sup>19)</sup> Also, thermal conductivities of silicon nitride substrate can be lowered when a large quantity of oxygen is dissolved in the silicon nitride crystals after sintering as a result of inadequate binder burnout.<sup>20-21)</sup>

In the present study, manufacturing conditions for thick-film substrates for heat sink were to be derived through tape-casting method with high-purity Si powder used as the starting raw material. The contents of residual oxygen and carbon were measured after temperature and atmosphere conditions of binder burnout were changed as well as after the nitriding process subsequent to the binder burnout to investigate how oxygen and carbon were changed in the follow-up process, and the binder burnout conditions advantageous to the final properties of heat sink substrates were presented.

## 2. Experimental Procedure

Si powder (Grade 4, > 98.9%, VESTA Si Co., USA) had an average particle size of about 3 μm. For additives as a sintering aid, Y<sub>2</sub>O<sub>3</sub> (Grade B, > 99.9%, H.C. Starck Co., Germany) with an average particle size of about 2 μm and MgO (magnesium oxide, > 99%, High Purity Chemical Co., Japan) with an average particle size of about 8 μm were used. As a solvent, ethanol and toluene mixed by 50 vol% each was used, while PVB (BMSZ, > 97%, SEKISUI Chemical Co., LTD, Japan) for the organic binder, DOP (Diocetyl phthalate, 99%, SAMCHUN Chemical, Korea) for the plasticizer, copolymer series (DISPERBYK®-111, Altana Co., Germany) for the dispersant were employed.

An overall process flow for preparation of green sheets is shown in Fig. 1. To obtain the optimum green sheet, slurries were prepared by changing the binder contents in comparison with the powder to the conditions of 5.5 ~ 9.5%, the representative formulation of which is shown in Table 1. Si powder along with Y<sub>2</sub>O<sub>3</sub> and MgO as the sintering aids were subjected to the first mixing in a 3D Mixer using zirconia balls, followed by ball milling together with organic materials and solvent for 24 h, with the final slurry being obtained after undergoing aging for 24 h. We characterized the flow behavior using a rheometer (HAAKE MARS III). The shear rate dependency of the viscosity was measured in the shear rate range of 10 - 300 s<sup>-1</sup> at a constant temperature of 25°C. Tape casting was conducted by pouring the slurry in a doctor blade set at the dam height of 300 μm, and moving the film at the velocity of 2.0 m/min, from which 100 μm-thick green sheets were finally produced. For the density of the green sheets, the mean density and the standard deviation

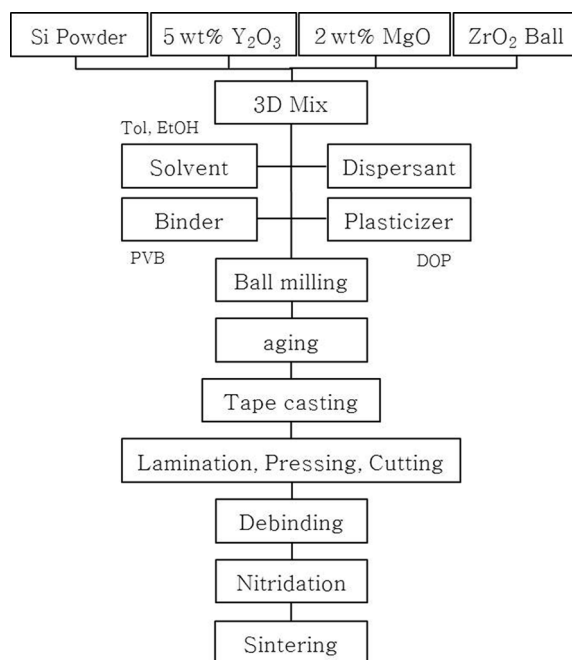


Fig. 1. Flow diagram of experimental procedure.

Table 1. Composition of the Suspension for Tape Casting

Si powder (wt%)	solvent (wt%)	dispersant (wt%)	binder(PVB) (wt%)	plasticizer (DOP) (wt%)
53.93	40.45	0.16	4.05 (P/S = 7.5%)	1.41

were obtained for 10 samples per content by the dimension measurement, while the surface condition of the sheets was checked by using an optical microscope. 1 mm-thick stacked sheets were prepared by application of 12 ton of pressure for 10 seconds after setting the table temperature of Stacking Machine at 40°C and overlapping several layers of the green sheet. To increase the forming density through tighter adherence of the stacked sheets, the sheets were pressed for 10 minutes at 70°C under 20MPa using a WIP (Warm Isostatic Press), and then the substrates were cut into the size of 30 × 30 mm.

Thermogravimetric analysis of the green sheets was conducted using TG-DSC (SDT Q600) at the heating rate of 10°C/min under the flux of Air and N<sub>2</sub> gas at the rate of 100 ml/min. For quantitative analysis of the residual oxygen and carbon after binder burnout under various conditions, the N/O elemental analyzer (HORIBA EMGA-920) and the C/S elemental analyzer (LECO CS230) were used. The process of binder burnout under the oxidizing atmosphere was conducted in a box-type electric furnace, while binder burnout under the inert atmosphere was conducted in a tube-type electric furnace. As the N<sub>2</sub> gas employed for the inert atmosphere, 5N grade in purity was used, where the flux was fixed at the rate of 1L/min. Also, nitriding processing involved furnace cooling to room temperature after being held for 4 h at 1400°C and 1450°C, respectively. After nitrid-

ing, the samples also underwent the analysis of the residual oxygen and carbon contents by using the N/O elemental analyzer and the C/S elemental analyzer, while X-ray diffraction analysis was conducted for the analyses of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>,  $\beta$ -Si<sub>3</sub>N<sub>4</sub> and Si.

### 3. Results and Discussion

Shown in Fig. 2 is viscosity behavior of the slurry as a function of the ratio between PVB organic binder and the Si powders (=P/S ratio). When the P/S ratios were 5.5%, 7.5%, 9.5%, the viscosities were measured to be 2414, 616, 406 cP (shear rate = 100s<sup>-1</sup>), respectively. When the P/S ratio was 5.5%, thickness deviations for the center part and the left/right sides of green sheet were relatively large, while the thickness of the green sheet for the P/S ratio being 9.5% was so small that it was inefficient for preparation of the stacked substrates with the final thickness of 1 mm. Green sheet densities as a function of the P/S ratio are shown in Fig. 3. Although the average density values for the P/S ratio of 5.5%, 7.5%, 9.5% were 1.61, 1.63, 1.62 g/cm<sup>3</sup>, respectively, no difference for any particular composition was observed when the dispersion was taken into account. However, when the P/S ratio was 5.5%, the standard deviation for density was greater than that for other compositions so that it could be seen to be a disadvantageous condition for the actual process. Optical micrographs for the green sheet surface are shown in Fig. 4 as a function of the P/S ratio. In the green sheet with the P/S ratio of 5.5%, several agglomerates were discovered, while splitting was observed in the green sheet with the P/S ratio of 9.5%. The green sheet with the P/S ratio of 7.5% had an excellent surface condition as compared with other compositions, and the P/S ratio of 7.5% could be seen to be the optimum composition for green sheet preparation even when the viscosity and density characteristics were considered.

The thermogravimetric analysis result for the green sheet with the P/S ratio of 7.5% is shown in Fig. 5. Under both oxidizing and inert atmospheres, mass reduction occurred near 200°C, which is considered attributable to the beginning of decomposition of the organic materials at this temperature. Under the oxidizing atmosphere, the behavior was observed where the weight was reduced up to 450°C followed by an increase again afterwards. In contrast, under the inert

atmosphere, weight increase did not occur even after 300°C, showing the behavior of continuous decrease. Here, the weight increase is considered to have occurred since the reaction rates between oxygen and Si under the oxidizing atmosphere were increased with formation of a considerable amount of SiO<sub>2</sub> film on the surface of Si powder. Under the inert atmosphere, weight increase is considered not to have occurred since such reaction was suppressed.

To consider specific effects of the binder burnout condi-

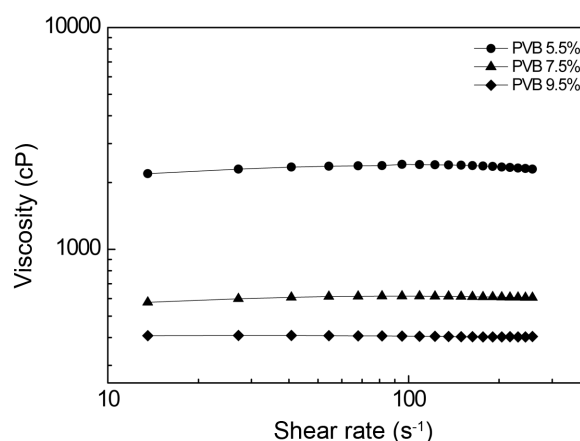


Fig. 2. Viscosity of slurry with the addition of PVB of 5.5, 7.5, and 9.5 wt% as a function of shear rate.

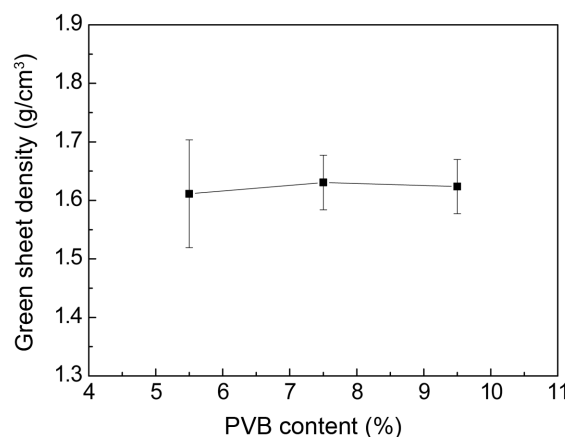


Fig. 3. Apparent density of green sheet with the addition of PVB of 5.5, 7.5, and 9.5 wt%.

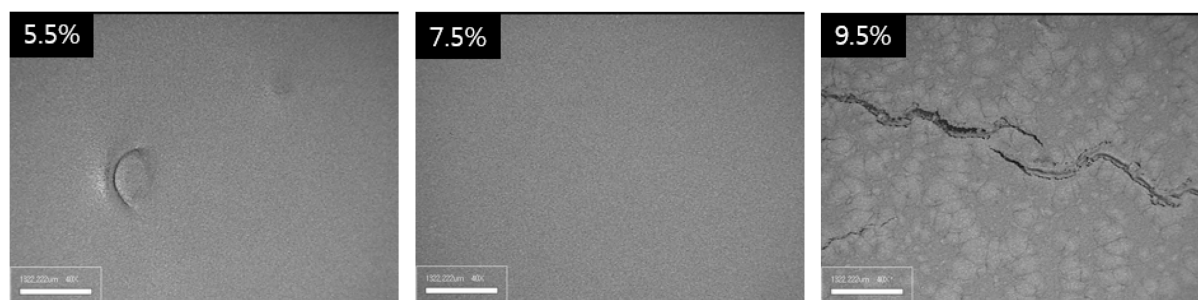


Fig. 4. Optical images of green sheet surfaces with the addition of PVB of 5.5, 7.5, and 9.5 wt%.

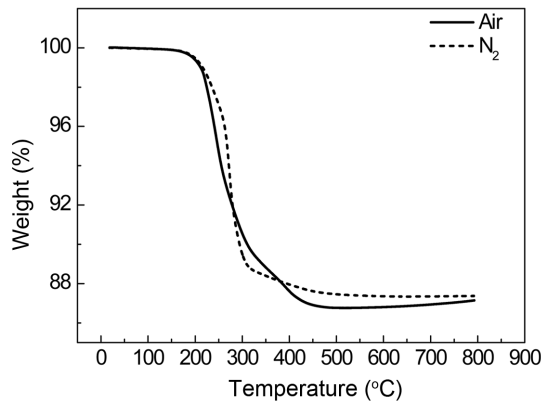
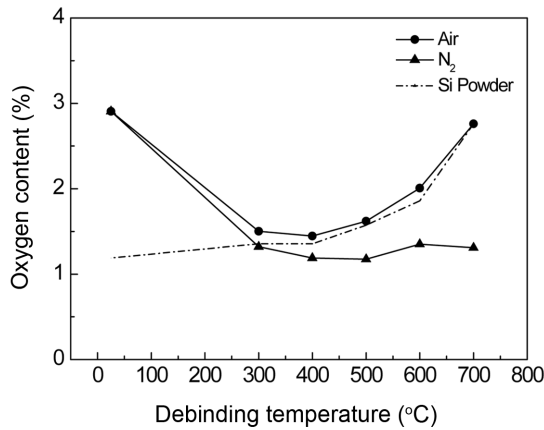
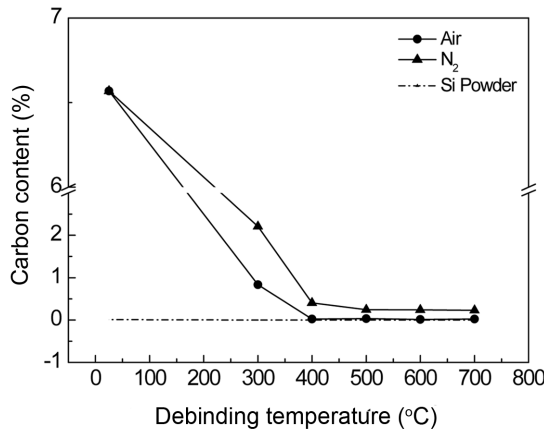


Fig. 5. Thermogravimetric analysis in Air and  $N_2$  atmosphere.



(a)



(b)

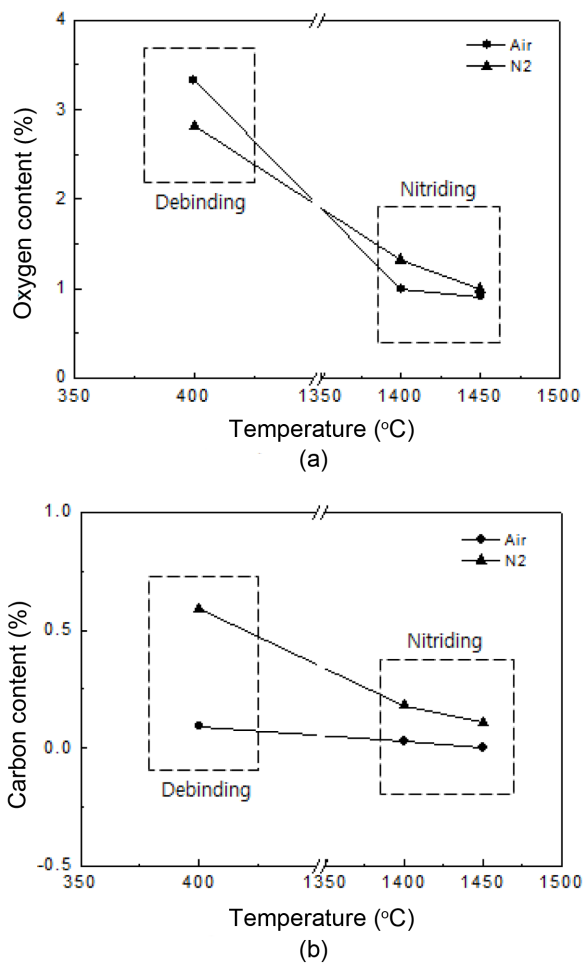
Fig. 6. The amount of residual (a) oxygen and (b) carbon in the substrate as a function of de-binding temperature and atmosphere. Note that no oxides are added to a substrate as a sintering aid for avoiding vagueness in residual oxygen and carbon measurement.

tions on the residual oxygen and carbon, the binder burnout conditions were varied in the temperature range of 300 ~ 700°C. Pure Si powder was heat treated under the oxidizing atmosphere and the residual oxygen content was

measured and shown as a dotted line in Fig. 6 (a). The residual oxygen content at room temperature corresponds to the content of residual oxygen formed during preparation process of Si powder as the raw material, amounting to about 1.0 wt%. As the heat treatment temperatures were raised, the residual oxygen content was continuously increased, and about 3.0 wt% was detected at the highest heat treatment temperature of 700°C.

To clearly distinguish the changes in the residual oxygen and carbon contents for binder burnout, the green sheets with addition of only Si and the organic binder were heat treated under the oxidizing, inert atmospheres with exclusion of the oxide sintering aids which could cause an ambiguity in analysis, followed by analysis of the residual oxygen and carbon contents, the results of which are shown in Fig. 6. According to the analysis results for the residual oxygen content, about 2.9 wt% of the residual oxygen was detected at room temperature irrespective of the atmospheres, which is considered to be caused by the oxygen contained in the organic binder (PVB,  $(C_8H_{14}O_2)_n$ ) and the plasticizer (DOP,  $C_6H_4(COOC_8H_{17})_2$ ) added to the green sheet. Around 400°C, the lowest content of residual oxygen was observed irrespective of the atmospheres, and the residual oxygen content was increased with an increase in binder burnout temperatures by the same amount as that for the case of pure Si powder in the case of oxidizing atmosphere. Under the inert atmosphere, no large change could be observed despite an increase in the binder burnout temperatures. According to the analysis results for the residual carbon content, the residual carbon content at room temperature was about 6.5 wt%, which appears to have been caused by the carbon contained in the organic binder and the plasticizer. Irrespective of the binder burnout atmospheres, a drastic reduction in the residual carbon content was observed in the process of temperature rise to about 400°C, followed by no large change even upon increase in the binder burnout temperatures. However, there was a difference in the absolute content of residual carbon depending on the atmospheres; about 0.242 wt% of residual carbon content was detected at 500°C under the inert atmosphere, while about 0.024 wt% of that was detected at the same temperature in the case of the oxidizing atmosphere, which is 10 times lower than the case of the inert atmosphere.

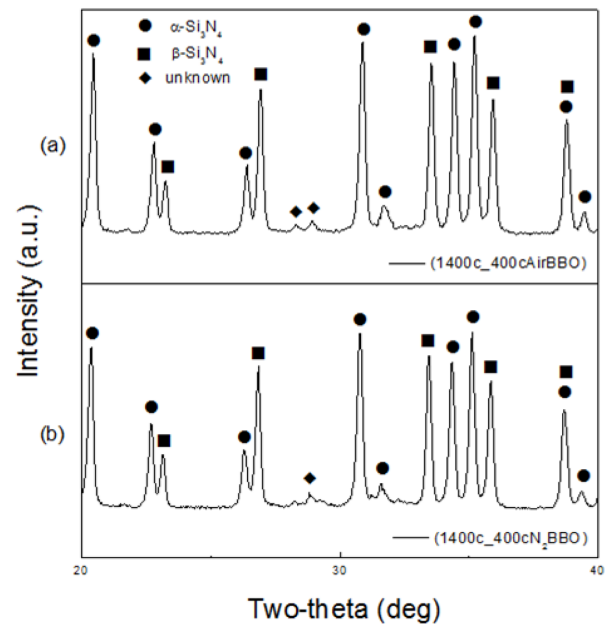
To optimize the binder burnout conditions considering the nitriding process, Si green sheets with oxides as sintering aids were prepared, followed by binder burnout at 400°C under the oxidizing and the inert atmospheres and nitriding processing at 1400°C and 1450°C, respectively, and then the contents of residual oxygen and carbon present inside the specimens were measured. As can be seen in Fig. 7, the contents of both residual oxygen and carbon present after binder burnout process were reduced as the nitriding process was implemented. In the case of residual oxygen, although the residual oxygen content in the specimens debinded under the oxidizing atmosphere was larger than that in the specimens debinded under the inert atmosphere,



**Fig. 7.** The amount of residual (a) oxygen and (b) carbon in the substrate as a function of gas nitriding temperature. Note that gas nitriding process is performed under only  $\text{N}_2$  atmosphere, not air.

a drastic reduction was observed in the temperature of nitriding process so that the amount of residual oxygen in the specimens debinded under the oxidizing atmosphere became rather smaller than that in the specimens debinded under the inert atmosphere. In the case of residual carbon, the residual carbon content in the specimens debinded under the oxidizing atmosphere was much smaller than that in the specimens debinded under the inert atmosphere, and such difference was also maintained in the temperature of nitriding process to the extent that the residual carbon content was not detected by the C/S analyzer in the specimens debinded under the oxidizing atmosphere after completion of the nitriding processing at 1450°C. Thus, the corresponding residual carbon content can be seen to be remarkably smaller than that of 0.108 wt% in the specimens debinded under the inert atmosphere.

Shown in Fig. 8 are the XRD patterns for the specimen subjected to nitriding process at 1400°C following debinding at 400°C under the oxidizing and inert atmospheres. In view that the specimens debinded under both oxidizing and inert



**Fig. 8.** XRD patterns of substrates after gas nitriding at 1400°C for 4 h. Substrates underwent the process of binder burnout at 400°C in (a) air and (b)  $\text{N}_2$  atmosphere before gas nitridation. ●:  $\alpha\text{-Si}_3\text{N}_4$  ■:  $\beta\text{-Si}_3\text{N}_4$  ◆: unknown)

atmospheres show similar peaks of  $\alpha\text{-Si}_3\text{N}_4$  and  $\beta\text{-Si}_3\text{N}_4$ , the atmosphere for binder burnout process is considered not to be related to the fraction of phase transformation. In conclusion, it may be seen that implementation of binder burnout for green sheets under the oxidizing atmosphere near 400°C with consideration of the residual oxygen and carbon contents is effective for the minimization of the residual oxygen and carbon contents which can affect thermal and mechanical properties upon manufacturing of the reaction sintered  $\text{Si}_3\text{N}_4$  substrates through the tape-casting process with the high-purity Si powder as the starting raw material.

#### 4. Conclusions

In the present study, stacked substrates were prepared by tape-casting method with high-purity Si powder as the starting raw material. To obtain slurry formulation for preparation of green sheets, the P/S ratio were varied and the viscosity of slurry as well as the density and the surface condition of the green sheets were evaluated, allowing the optimum composition to be obtained.

The residual oxygen and carbon contents were measured after the temperature and the atmosphere conditions for the binder burnout were varied, and the residual oxygen and carbon contents were also measured after nitriding process for investigation of what levels the amounts of residual oxygen and carbon present before sintering were at. Although the smallest content of oxygen was left in substrates after binder burnout under the inert atmosphere at

400°C, there was no difference in the residual oxygen content in the case of implementation through the nitriding process as the follow-up process according to the difference in the binder burnout atmospheres. Rather, the residual carbon content was much smaller in the case of the specimens through the binder burnout under the oxidizing atmosphere at 400°C than the specimens through the binder burnout under the inert atmosphere, demonstrating the former case to be more advantageous to the final material properties of heat sink substrates.

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