Effect of Microstructure on Dielectric Properties of Si$_3$N$_4$ at Microwave Frequency

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Abstract. Silicon nitride (Si$_3$N$_4$) has been researched intensively because of superior mechanical properties up to high temperature. The mechanical properties of Si$_3$N$_4$ are strongly related to microstructure. The microstructure control of silicon nitride is well known to be a key issue for tailoring the mechanical properties of structural ceramics. This work was performed to reveal the effect of microstructure on dielectric properties at microwave frequency. Three starting powders were used: fine, course $\alpha$-Si$_3$N$_4$ and $\beta$-Si$_3$N$_4$. Sintering additives, 5 wt.% Y$_2$O$_3$, 2 wt.% Al$_2$O$_3$, and 1 wt.% MgO were mixed with each starting powder. Si$_3$N$_4$ ceramic with different $\beta/\alpha$ phase specimen were obtained by hot pressing. The post-resonator method was used for the measurement of dielectric properties, dielectric constant ($\varepsilon'$) and dielectric loss (tan$\delta$), at microwave frequency range. Silicon nitride ceramics show dielectric constant of 8.1 – 8.6 and dielectric loss $1.1 \times 10^{-3}$ – $5.6 \times 10^{-3}$. The effect of grain size and the role of phase on microwave dielectric properties are discussed.

Introduction

Silicon nitride is the important structural ceramic. The good mechanical and thermal properties of silicon nitride (Si$_3$N$_4$) make it useful as structural material[1-3]. The silicon nitride possesses the best mechanical and thermostructural properties for high temperature radome application. The mechanical and thermal properties have been studied widely, but a few reported on dielectric properties[4,5]. Silicon nitride is strong covalent chemical bond and has two forms, $\alpha$ and $\beta$ phases.[6,7] The unit cell of the $\alpha$-Si$_3$N$_4$ is twice as length as the $\beta$-Si$_3$N$_4$. The stacking sequence of $\alpha$ -Si$_3$N$_4$ is ABCDABCD···, and $\beta$-Si$_3$N$_4$ is ABAB···. Because of stacking sequence, $\alpha$ -Si$_3$N$_4$ is harder than $\beta$ - Si$_3$N$_4$, but $\beta$ - phase is more stable at high temperature. The $\beta/\alpha$ phase ratio of polycrystalline silicon nitride changes during the sintering processing. The mechanical properties of silicon nitride are determined by not only $\beta/\alpha$ phase ratio, but also by their grain size, aspect ratio of $\beta/\alpha$ phase, and composition of second phase.

The dependencies of the mechanical properties of Si$_3$N$_4$ on $\beta/\alpha$ phase and microstructure have been reported[3]. The elongated grain structures provide enhanced long-crack toughness. The $\beta/\alpha$ phase ratio was increased, the hardness decreased.

To reveal the microstructure effect on dielectric properties, the contents of the sintering additives are fixed and different starting powders are used for fabricating different microstructures. The present of glass phase influences the dielectric properties of silicon nitride. In this study, the effect of intergranular glass phase is eliminated using the same amount of sintering additives. The post-resonator method is used for dielectric properties measurement. The post-resonator method is
well known method for microwave range measurement application. This method has 2% error for measurement result[8]. This paper investigates the specific roles of $\beta/\alpha$ phase ratio and grain size on dielectric properties of Si$_3$N$_4$. The goal of this study is to obtain as clear a correlation as possible between the microstructure and the dielectric properties of poly crystalline silicon nitride.

**Experimental Procedures**

**Materials processing and preparation.** Three starting silicon nitride powders were used: relatively coarse $\alpha$-Si$_3$N$_4$ (UBE-SN-E3, mean particle size 1.0µm, Ube Industries, Tokyo, Japan), relatively fine $\alpha$-Si$_3$N$_4$ (UBE-SN-E10, mean particle size 0.3µm, Ube Industries, Tokyo, Japan), and $\beta$-Si$_3$N$_4$ (SN-F1, mean particle size 3.0µm, Denki Kakagu, Tokyo, Japan). Sintering additives, 5 wt.% Y$_2$O$_3$ (Fine grade, H.C. Starck GmbH, Goslar, Germany), 2 wt% Al$_2$O$_3$ (AKP50, Sumitomo Chemical Co.Ltd., Tokyo, Japan), and 1wt% MgO (Baikowski Co., NC), were mixed with each starting powder. The powder mixtures were ball milled in a plastic jar using high purity 2-propanol for 24 h, and subsequently dried and sieved through a 120-mesh screen. These resulting mixes were designated according to the Si$_3$N$_4$ starting powders: $\alpha$-fine (E10 powder, $\alpha$-phase, fine); $\alpha$-coarse (E3 powder, $\alpha$-phase, coarse); $\beta$ (SN-F1, $\beta$-phase).

Hot-pressing of sample blocks was performed in N$_2$ gas at 1 atm under uniaxial compression 25 MPa in a BN coated graphite die, at 1600°, 1700°, and 1800° for 1 h.

Microstructures of sintered samples were observed on polished and etched sections. Specimens were etched by plasma in CF$_4$ and O$_2$ gas for 10 min. The etched specimens were examined by scanning electron microscopy (SEM). X-ray diffraction (XRD) was used to determine the $\beta/\alpha$ phase ratio for each specimen. Density was measured using Archimedes method.

**Dielectric measurements.** Dielectric constant and dielectric loss were measured at room temperature, frequency near 8 GHz by post-resonator method using the TE$_{011}$ mode[8]. The conducting plates were made of OFHC (oxygen free high conductive copper) and were mirror-polished. The copper plates were the diameter of 100 mm. The measured specimens were approximately 20 mm in diameter and 9 mm in thickness disks. TE$_{011}$ mode was examined using a vector network analyzer (HP8510C) with resolution of 1Hz. The calculation of complex permittivity was used Newton-Raphson method.

![Figure 1. Photograph of a post-resonator used in the measurement](image)
Results and Discussion

Materials characterization. Fig 2. shows SEM micrographs of the different Si₃N₄ microstructures for each starting powder:

1. **α-fine**: At 1600°C, the material contains mainly equiaxed α grains of mean grain size ≈0.3 µm, but some elongated β grains are already apparent. At 1700°C, the β phase is dominant and has continued their elongate growth. At 1800°C, the β grains enlarge further.

2. **α-coarse**: After hot pressing at 1600°C, this material reveals a microstructure with mainly equiaxed α grains of mean grain size ≈0.5 µm, but with minor β phase. At 1700°C, the β grains continue their elongated growth, but the α phase still dominates. Finally, at 1800°C, the β phase dominates, but the structure is predominantly equiaxed.

3. **β**: At 1600°C, the structure consists totally of equiaxed β grains, mean grain size ≈2.2 µm. On heating through 1800°C, the β phase persists, and the microstructures enlarge but remain predominantly equiaxed with just occasional elongate grains.

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Figure 2. SEM micrographs of polished Si₃N₄ specimen using hot press method sintered at 1,600 °C, 1,700 °C, 1,800 °C for 1h. Specimens plasma etched in CF₄ and O₂ gas for 10 min to reveal grain structures.

Mean grain sizes are plotted for the Si₃N₄ materials as a function of hot-pressing temperature in Fig. 3. Overall mean grain sizes increase steadily with temperature in all three materials. In **α-fine**, mean grain size changed 0.3 - 1.1 µm. The grain size of **α-coarse** increased 0.5 – 1.5 µm. The grain size of **β** were relatively large (2.2 – 3.5 µm).
Figure 4 plots volume percent α and β phase for the three Si$_3$N$_4$ starting powder types as a function of hot-pressing temperature. The β-phase ratio increase with sintering temperature. In α-fine, Si$_3$N$_4$ was transformed to β-phase completely at 1800 °C. But α phase remains in α-coarse even at 1800 °C. There is no detectable phase transformation at all in β. Density determinations indicate a porosity level < 0.1% except β at 1600 °C (7% porosity).

Dielectric properties measurement. The measurement results of dielectric constant at room temperature are shown in Fig 5. Dielectric constant of β at 1600 °C indicates unexpected low value (ε' = 7.7). This result causes by porosity. Dielectric constant and loss of β at 1650 °C were ε'= 8.5 and tanδ = 3.6 x 10^{-3} (<0.1% porosity). These results show similar trend to compare with other results of β. Dielectric constant increases slightly with sintering temperature. The amount of β-phase increases with sintering temperature. The band gap has a linear relation with dielectric properties. The band gap of β-phase Si$_3$N$_4$ is larger than α-phase Si$_3$N$_4$[9]. Dielectric constant is expected decreasing with increasing temperature, but the result is by contraries. Dielectric constant increases with increasing sintering temperature. Dielectric constant of β is slightly higher than α phase starting powder specimens. Fig 6, plots dielectric loss against sintering temperature.

Figure 3. Mean grain size of α-fine, α-coarse, β as a function of sintering temperature of Si$_3$N$_4$ specimens using hot press method for 1h.

Figure 4. XRD determination of volume fraction of α and β phases in α-fine, α-coarse, β as function of hot pressing temperature.

Figure 5. Measured dielectric constant as a function of sintering temperature of Si$_3$N$_4$.

Figure 6. Measured dielectric loss as a function of sintering temperature of Si$_3$N$_4$. 
Dielectric loss increases with sintering temperature. Dielectric loss of $\beta$ at 1600 °C is higher than $\beta$ at 1650 °C. This result is the same reason as dielectric constant. Dielectric loss of $\beta$ is significantly higher than $\alpha$-fine and $\alpha$-coarse.

The measured values do not exhibit a significant effect between dielectric properties and $\beta/\alpha$ phase ratio. From the figures it may be seen that dielectric properties are dependent of sintering temperature. Increasing the sintering temperature increases $\beta/\alpha$ phase ratio in $\alpha$ phase starting specimens.

Fig 7 and 8 plot dielectric properties against grain size. A small amount of change is observed in dielectric constant. Dielectric constant is changed from 8.0 to 8.6. Dielectric loss is varied $1.1 \times 10^{-3} - 5.6 \times 10^{-3}$. Dielectric loss increases with increasing grain size. The physical mechanism responsible for the grain size effect on dielectric constant and loss can be explained as the change of the crystal field caused by surface bond contraction. Decreasing the grain size increases the crystal field and subsequently decreases the dielectric properties[10]. This result is consistent with a previous studies of dense polycrystalline alumina which also have shown the strong dependency of grain size on dielectric loss of alumina[11].

Summary

The controlled microstructure specimens of $\text{Si}_3\text{N}_4$ are obtained from different starting powders and sintering temperature. The dielectric properties of $\text{Si}_3\text{N}_4$ are found to be strongly dependent on grain size. The grain size effect on the dielectric properties is explained as the change of the crystal field caused by surface bond contraction of the grain. No significant effect in dielectric properties is observed with the band gap difference of $\alpha$ and $\beta$ phase. Increasing the grain size causes an increase in dielectric properties. The grain size is more effective to dielectric loss. These results of dielectric properties provide useful information on optimum parameters to give the best performance in terms of mechanical and electromagnetic properties.

References