A Spodumene Silicon Nitride Complex with Zero Thermal Expansion at Ambient Temperature

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1. Introduction

Ceramic materials have been applied to devices in the production process of integrated circuits (IC). Properties such as low thermal expansion, high stiffness, and chemical inertness are required for the materials used in the process. Jigs for supporting silicon wafers and tables for photolithography are the instances where ceramics are applied. Recent developments in semiconductor technology have provided highly integrated circuits, giving rise to the requirements of more accurate pattern printing on semiconductor chips in the photolithographic process and the required position accuracy as high as 0.1 nm.

The main factors governing position accuracy in the photolithographic process are the thermal expansion and the stiffness of materials used in photolithographic devices; cordierite- or spodumene-based glass ceramics have been adopted as the materials that satisfy the above-mentioned requirements. Spodumene and cordierite exhibit substantially anisotropic nature with respect to the thermal expansion coefficients of their crystallographic axes and ceramics consisting of either material exhibit negative thermal expansion at ambient temperature. These inconvenient thermal properties have been improved in spodumene-based glass ceramics and zero thermal expansion has been achieved by doping with oxides, such as MgO, Al₂O₃, and Fe₂O₃. Stiffness of oxide glass was increased by incorporating silicon nitride, which resulted in the formation of oxynitride glass ceramics consisting mainly of α-quartz solid solutions and β-spodumene solid solutions.

However, few published reports have dealt with the improvement of both properties, thermal expansion and stiffness in ceramics. The purpose of this study is to describe the influence of silicon nitride addition on Young’s modulus and the thermal expansion of ceramics based on spodumene. Both of these properties of a ceramic based on spodumene may be improved by incorporating silicon nitride.

2. Experimental procedures

Starting materials used for the fabrication of the ceramics were synthetic spodumene powder, which were commercially available (Marusui), and Si₃N₄ powder (Denki Kagaku Co., 99% purity), averaged grain sizes being 5 μm and 0.7 μm, respectively. The molar ratio of the principal components of the spodumene powder determined by inductively coupled plasma emission spectroscopy (ICP) was 0.98 : 1.00 : 4.21 for Li₂O : Al₂O₃ : SiO₂.

The powders were weighed and mixed at the ratios listed in Table 1. Each mixture was milled for 24 h, wetted by ethanol in a ball mill made of silicon nitride, subsequently dried in an evacuated chamber, and then in an oven at approximately 363 K. The dried powders were sieved by a screen with openings of 0.044 mm. Approximately 100 g of the sieved mixture was charged in a mould of 80 mm diameter, which was placed in a uniaxial hot press apparatus (Type FVHP–10, Fujidenka Co.). Sintering was performed by heating to 1523 K at a heating rate of 280 K/min, and holding for 2.5 h under a vacuum condition of less than 1 Pa; the pressure loaded on the specimens was 30 MPa.

Phase compositions were determined using an X-ray powder diffractometric (XRD) apparatus (RINT 2000, Rigaku-denki) equipped with a rotating Cu anode. The densities of the sintered specimens were measured by Archimedes’ method and Young’s modulus was evaluated by the ultrasonic pulse method using an apparatus (Type AT–500, Hitachi Ltd.) on the specimens cut into 10 mm samples.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>β -Spodumene</th>
<th>Silicon nitride</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>97.6</td>
<td>2.4</td>
</tr>
<tr>
<td>3</td>
<td>88.9</td>
<td>11.1</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>76.9</td>
<td>23.1</td>
</tr>
<tr>
<td>6</td>
<td>66.7</td>
<td>33.3</td>
</tr>
</tbody>
</table>
cubes.
The thermal expansion of the specimens was measured between 273 K and 323 K by the laser interference method with the aid of a dilatometer apparatus (LIX 1, Sinku-Riko).

3. Results and discussion

Figure 1 shows XRD profiles for the specimens. Each profile corresponds to a specimen described in Table 1. We identified the major constituent phases as β-spodumene and α-Si$_3$N$_4$ marked by squares and triangles, respectively. As the α-Si$_3$N$_4$ content increased in the starting mixtures, the peak intensities of the compound in the sintered specimens became prominent. Peaks for β-Si$_3$N$_4$ could be detected in the specimen doped with >11.1 mass% α-Si$_3$N$_4$, as marked by black circles, which existed as an impurity phase in the starting material of α-Si$_3$N$_4$ powder. Therefore, it was considered that most of α-Si$_3$N$_4$ was not transformed to β-Si$_3$N$_4$ under the sintering condition. It is possible that oxynitride glass was formed in the specimens by the reaction between α-Si$_3$N$_4$ and β-spodumene. However, the halo characteristic of the glass was not clearly observed in the XRD profiles.

Figure 2 shows the change in bulk densities as α-Si$_3$N$_4$ was added. The bulk densities of the specimens did not increase linearly as α-Si$_3$N$_4$ was added, and the values reached about 2.6 g/cm$^3$ in the specimen doped with 33.3 mass% α-Si$_3$N$_4$. Since the bulk density of the raw specimen was 2.18 g/cm$^3$, the value was 92% of the theoretical density. However, the bulk density of the specimen doped with 33.3 mass% α-Si$_3$N$_4$ corresponded with the theoretical density of a composite consisting of 66.7 mass% β-spodumeme and 33.3 mass% α-Si$_3$N$_4$. The mechanism how α-Si$_3$N$_4$ behaves in the densification process is still ambiguous; however, it should be emphasized that α-Si$_3$N$_4$ acted effectively as a sintering aid.

Figure 3 displays the temperature dependence of thermal expansion coefficients for each specimen. Thermal coefficients depended not only on temperature, but also on the composition, and increased almost linearly when temperature rose except for the specimen doped with 20 mass% α-Si$_3$N$_4$, whose curve exhibited a slight inclination as temperature increased. The thermal expansion coefficients for the specimens doped with more than 20 mass% α-Si$_3$N$_4$ tended to have positive values in the higher temperature region. The specimen doped with 23.1 mass% α-Si$_3$N$_4$ reached the zero thermal expansion coefficient value at room temperature.

Figure 4 shows the effect of the amount of α-Si$_3$N$_4$ addition on the averaged thermal expansion coefficients between 293 K and 300 K. The averaged values were improved markedly by α-Si$_3$N$_4$ addition, achieving a minimal value of −0.032 × 10$^{-6}$/K in the specimen doped with 23.1 mass% α-Si$_3$N$_4$. The minimal value in the temperature range is sufficiently small to use the material in practice. The thermal expansion coefficient estimated by averaging the values for α-Si$_3$N$_4$ and β-spodumene was consistent to that determined experimentally.

Figure 5 shows the change in Young’s modulus of the specimens with α-Si$_3$N$_4$ addition. As in the case of the thermal expansion coefficients, the Young’s modulus values increased nonlinearly with the increase in the amount of α-Si$_3$N$_4$ addition. For the specimens doped with more than 23.1 mass% α-Si$_3$N$_4$, the Young’s modulus values are higher than that of the nondoped specimen. The increase in Young’s modulus was attributable to the concurrent increase in bulk densities.

Many investigations have been carried out on systems containing oxides and nitrides, which have recently been reviewed by Riley. An example is the study of a
spodumene-based Li–Si–Al–O–N glass ceramic, whose properties and microstructure with a substantial amount of AlN were clarified. The dominant phases were α-quartz solid solutions, with β-spodumene solid solutions and silicon oxynitrides also reported as minor phases. The system consisting of Li, Si, Al, O and N has been investigated by Jack, who described α'-sialons with a variation in cell dimensions that were produced when different proportions of LiAlO₂ and Si₃N₄ were reacted. The compositions of the ceramics in the present study were similar to those studied previously. Oxynitride glass might be formed in the ceramics, but no crystalline oxynitrides were found, suggesting that the sintering temperature used in this experiment was not sufficiently high to form crystalline oxynitrides. The bulk densities and Young’s moduli of the Si₃N₄-doped specimens improved significantly.

4. Conclusions
The influence of Si₃N₄ addition to ceramics based on spodumene has been investigated and the following results were obtained.

(1) Dominant phases of the ceramics were β-spodumene and α-Si₃N₄.
(2) Bulk density and Young’s moduli of the ceramics improved significantly when Si₃N₄ was incorporated.
(3) The averaged thermal expansion coefficient of the ceramics was $-0.032 \times 10^{-6}/\text{K}$ between 293 K and 300 K for the specimen doped with 23.1 mass% Si₃N₄.

References