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Dielectric and thermal properties of AlN ceramics

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Abstract

The effects of slow-cooling and annealing conditions on dielectric loss, thermal conductivity and microstructure of AlN ceramics were investigated. Y_2O_3 from 0.5 to 1.25 mol% at 0.25% increments was added as a sintering additive to AlN powder and pressureless sintering was carried out at 1900 °C for 2 h in a nitrogen flowing atmosphere. To improve the properties, AlN samples were slow-cooled at a rate of 1 °C min^{-1} from 1900 to 1750 °C, subsequently cooled to 970 °C at a rate of 10 °C min^{-1} and then annealed at the same temperature for 4 h. AlN and YAG ($5Al_2O_3/3Y_2O_3$) were the only identified phases from XRD. AlN doped with 0.5 and 0.75 mol% Y_2O_3 had a low loss of <2.0×10^{-3} and a high thermal conductivity of >160 W m^{-1} °C^{-1}.

Keywords: Sintering; Dielectric properties; Nitrides; Thermal conductivity

1. Introduction

Recent advances in substrate and packaging material machining for integrated circuits (ICs) require more intricate plasma devices such as plasma etching devices and plasma CVD devices operating at microwave frequencies above 1×10^9 Hz (1 GHz).[1–4] In plasma devices, components such as microwave windows, protective plates, clamps and electrostatic chucks are regularly exposed to plasma. To function properly, these components must not only be able to withstand fluorinated reaction gases, but they must also have high heat dissipation and insulation properties and a low dielectric loss tangent ($\tan\delta$). For example, for a microwave window material, a very low $\tan\delta$ on the order of 3×10^{-3} or less is required.[5] Materials having low $\tan\delta$ include diamond,[6,7] alumina,[8] sapphire[8] and silicon nitride.[9] However, diamond is very expensive, alumina and sapphire have relatively low thermal conductivity, and corrosion resistance of silicon nitride to fluorinated reaction gases is low. Hence, these materials cannot be used effectively for the above-mentioned applications.

AlN is found to be a good candidate material for plasma environments, since it offers high thermal conductivity (~270 W m^{-1} °C^{-1}),[10–13] high insulating properties and high withstanding capacity to fluorinated gases.[14] On the other hand, $\tan\delta$ of known AlN ceramics are around 1×10^{-2} at 3 GHz.[15] Hence, lowering of $\tan\delta$ while maintaining high thermal conductivity is required as mentioned above.

The $\tan\delta$ is affected by intrinsic and extrinsic losses. The intrinsic loss depends on the crystal structure and is minimum in a pure and perfect single crystals. On the other hand, the extrinsic losses are associated with imperfections in the crystal structure, such as the grain boundary, impurities, vacancies, dislocations and residual stresses in a polycrystal ceramic.[16] Therefore, reducing these imperfections in the microstructure is necessary to decrease $\tan\delta$.

In general, annealing is well-known approach to decrease vacancies, dislocations and residual stresses in crystals. The dihedral angle of AlN grains was found to be enhanced further with slow-cooling,[17] which means slow-cooling enhances purification of AlN grains. Hence, decrease in $\tan\delta$ can be expected by the annealing and the slow-cooling processes. It has been reported that the processes of annealing and slow-cooling were effective in lowering $\tan\delta$ of AlN ceramics.[18,19]

By reducing intrinsic defects is effective in not only decreasing $\tan\delta$ but also maintaining high thermal conductivity.[15,17] The

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purpose of this study was to evaluate the effect of the annealing and slow-cooling processes on regenerative index[15] as a function of dielectric loss and thermal conductivity.

2. Experimental procedure

AlN powder (TOYALNITE JB, TOYO ALUMINIUM K.K., Japan) was used as the starting material. Y_2O_3 (Daiichi Kigenso Kagaku Kogyo Co. Ltd., Japan) at 0.5, 0.75, 1.0 and 1.25 mol% was used as a sintering additive. These powders were mixed in ethanol using a planetary ball milling device (Pulverisette 6, Fritsch Japan, Japan), dried and made into pellets of 16 mm in diameter and 5 mm in thickness by uniaxial molding, followed by cold isostatic pressing at a pressure of 200 MPa. The cold isostatically pressed AlN–Y_2O_3 compacts were pressureless-sintered at 1900 °C for 2 h in a flowing nitrogen atmosphere. Following sintering, AlN samples were cooled at a rate of 1 °C min^{-1} from 1900 to 1750 °C, then further cooled at a rate of 10 °C min^{-1} to the annealing temperature of 970 °C and annealed for 4 h and then cooled at a rate of 10 °C min^{-1} to room temperature (RT). The bulk densities of the AlN samples were measured using Archimedes' method. To measure tan δ of the AlN samples, machining and polishing were performed on the disk shaped solids (ϕ 10.0 × h 5.0 mm). The dielectric constants and the quality factors were measured by the Hakki–Coleman method.[20]

To measure thermal conductivity of the AlN samples, machining and polishing were performed on the disk shaped solids (10 mm in diameter, 5 mm in thickness). Thermal diffusivity was measured by a laser flash technique with a Laser Flash Thermal Constants Analyzer (TC 7000, ULVAC-RIKO, Japan) at RT. Thermal conductivity, κ was estimated using specific heat of 736.7 J kg^{-1} °C^{-1} and bulk densities. Crystalline phases in the AlN samples were identified by X-ray diffraction (XRD) analysis (RINT-2550, Rigaku Corporation, Japan). Fracture surface morphology of AlN samples was observed using scanning electron microscopy (SEM, JSM-5600M, JEOL, Japan).

3. Results and discussion

3.1. Phase analysis

Fig. 1 shows XRD profiles of AlN samples. In all samples, only AlN and $Al_5Y_3O_{12}$ ($5Al_2O_3/3Y_2O_3$:YAG) were detected. No other crystalline phases could be identified apart from the peaks from the Al sample holder (indicated as A). In addition, there was no significant difference in the given patterns, even when the amount of Y_2O_3 was different. From the Al_2O_3-Y_2O_3 system, the possible phases are Y_2O_3, YAM ($2Y_2O_3/Al_2O_3$), YAP (Y_2O_3/Al_2O_3), YAG ($3Y_2O_3/5Al_2O_3$), AlON (aluminum oxynitride spinel), Y_3O_3N and Al_2O_3.[14,16] The secondary phase in the sintered AlN changes to YAM–YAP–YAG with increasing sintering temperature.[21] The secondary phase in the AlN compact also changes to YAG–YAP–YAM with increasing the Y_2O_3/Al_2O_3 ratio.[22] These phase changes are thought to be related to the re-release of dissolved oxygen ion in solid solution with AlN crystals enhanced by the AlN solution-precipitation reaction in the presence of a liquid phase, which at the end increases the purity of the AlN grains.[15,17–23]

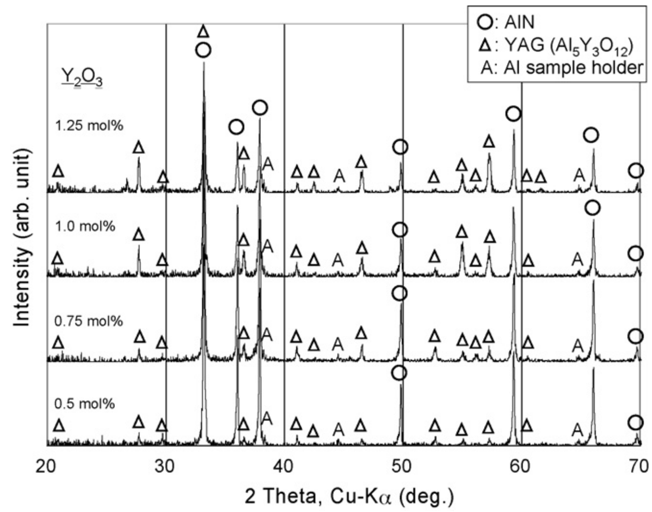

Fig. 1. XRD profiles of AlN samples.

3.2. Density

The AlN ceramic with 0.5 mol% Y_2O_3 is shown to have bulk density of 3.267 Mg m^{-3}. The bulk density of AlN ceramics increased with the increase of the amount of Y_2O_3. The relative density was calculated from the ratio of the bulk and theoretical density which was estimated using the Rule of Mixture. Based on the rough estimation used on calculating theoretical density of AlN ceramics, all AlN samples were almost fully densified to higher than 99%.

3.3. Microstructure

Fig. 2 shows SEM photographs of the fracture surfaces of the AlN ceramics. Y_2O_3 content is indicated in each photograph. Relatively brighter portions are secondary phase. The dihedral angle of the grains in the samples with more than 0.75 mol% Y_2O_3 seems to be higher than that of 0.5 mol% Y_2O_3. The increase of dihedral angle of the grains indicates the microstructural refinement mentioned above and in the previous report.[17] On the other hand, secondary phase is located not only at triple points of grains but also along the ridge lines of the grains when the Y_2O_3 content is more than 1 mol%. Relatively larger amount of YAG phase might affect thermal conductivity because of its drastically lower thermal conductivity which is 11.2 W m^{-1} °C^{-1}.[24]

3.4. Dielectric properties and regenerative index

Specific permittivity of all samples was between 8.4 and 8.6 as shown in Table 1. The values are almost the same as that of a static value.[25]

Fig. 3 shows the relationship between the dielectric loss tangent (tan δ), the thermal conductivity and the Y_2O_3 content of AlN ceramics. The values of tan δ and thermal conductivity in

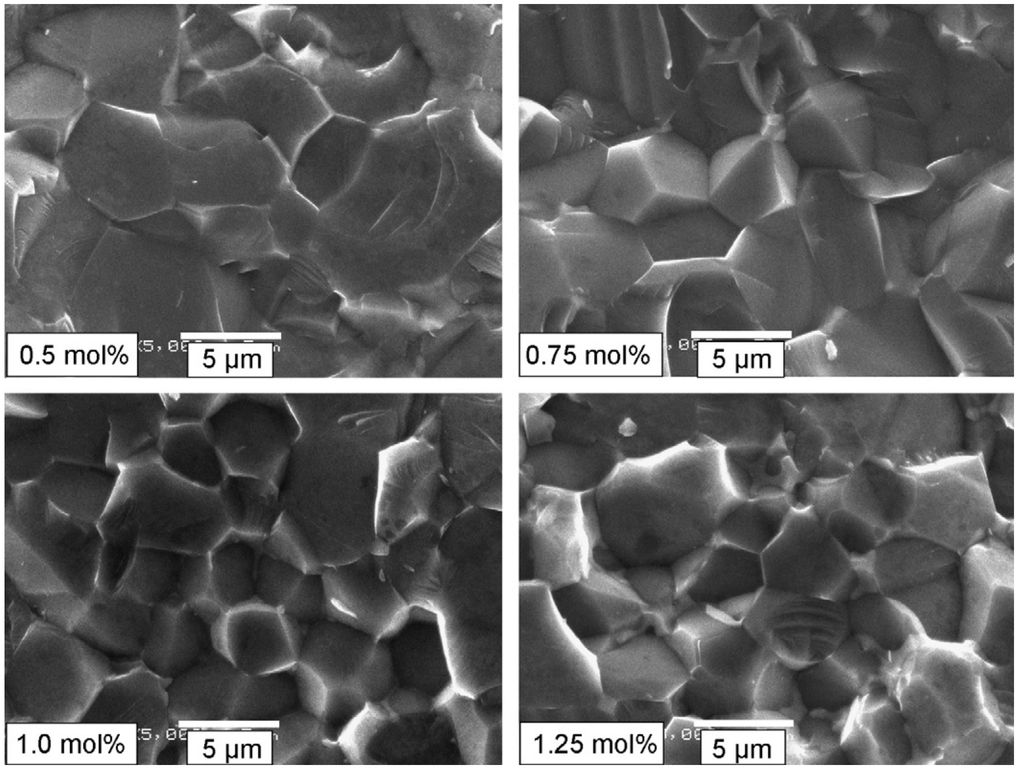

Fig. 2. SEM photographs of the fracture surfaces of the AlN ceramics.

Table 1
Specific permittivity of AlN samples

Y_2O_3 content (mol%)	Specific permittivity
0.50	8.5
0.75	8.6
1.00	8.4
1.25	8.5

this study, shown in the Fig. 3, are average values obtained by four and three measurements for each sample, respectively. The degrees of the standard deviation of tan δ are smaller than each symbol.

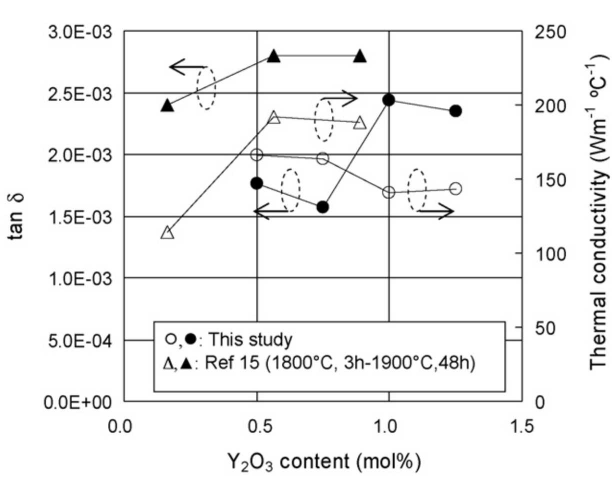

Fig. 3. The relationship between the dielectric loss tangent (tan δ), the thermal conductivity and the Y_2O_3 content for the AlN ceramics at 14 GHz.

The decrease of point defects in AlN grains by removing oxygen impurities through heat treatment at high temperature improves not only thermal conductivity but also tan δ.[15,17] However, properties of the AlN samples in this study show much lower tan δ and relatively not so high thermal conductivity as compared to those obtained by post-sintering heat treatment at 1900 °C for 48 h.[15] Especially, tan δ of AlN samples doped with Y_2O_3 of 0.5 and 0.75 mol% is lower than 2.0×10^{-4} and the ratio of the tan δ values obtained in this study to those obtained at high temperature long time annealing is less than 0.6. On the other hand, thermal conductivity is higher than 160 W m^{-1} °C^{-1} and a ratio of it to those obtained by Koyama et al.[15] is roughly 0.85. The reason of these results is unclear. However, it is revealed that the slow-cooling with annealing at intermediate temperature is highly effective in lowering tan δ as compared with the high temperature long time annealing. Furthermore, even though 1.0 and 1.25 mol% Y_2O_3 doped samples had bigger dihedral angle than 0.5 and 0.75 mol% doped samples, not only thermal conductivity but also tan δ became relatively worse. The cause of aggravation of thermal conductivity is because of surplus YAG as mentioned above. However, the reason for the increase of tan δ is not clear because tan δ of YAG is very low 2×10^{-5}.[26]

Fig. 4 shows the relationship between the regenerative index, I_R and the amount of Y_2O_3. Koyama et al.[15] defined the regenerative index, I_R as an index of the degree of accumulation of heat in a component as follows:

$$I_R \equiv A\frac{P}{Q} \tag{1}$$

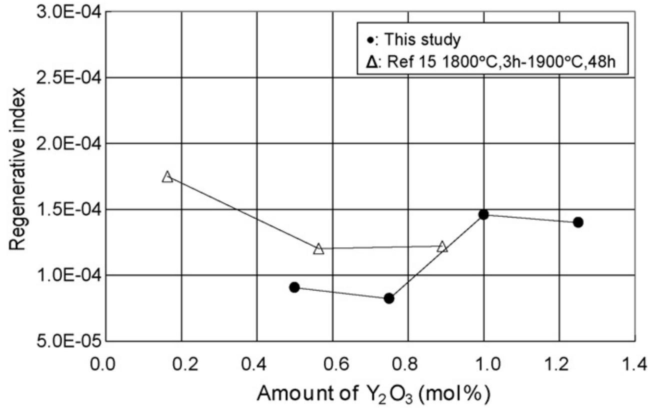

Fig. 4. Relationship between the regenerative index and the amount of Y_2O_3.

$$P = \frac{1}{2}\varepsilon_0\varepsilon''\omega E^2 V_s \tag{2}$$

$$Q = \kappa\frac{dt}{dx} \tag{3}$$

$$\kappa = \alpha \times \rho \times C_p \tag{4}$$

In the case where, dt/dx, ω, E and V_s are fixed, and $\varepsilon'' = \varepsilon' \tan\delta$,

$$\therefore\ I_R = A\frac{P}{Q} = \frac{\varepsilon' \tan\delta}{\kappa} \quad \left(A = \frac{2}{\varepsilon_0\omega E^2 V_s}\frac{dt}{dx}\right) \tag{5}$$

where P is the microwave absorption energy, Q the amount of heat flow, A the coefficient, ε_0 the permittivity of vacuum, ε'' the dielectric loss, ω the frequency, E the electric field, V_s the dielectric volume, κ the thermal conductivity, α the diffusivity of heat, ρ the density, and C_p the isopiestic specific heat, ε' is the specific permittivity.

The regenerative index of 0.5 and 0.75 mol% Y_2O_3 doped AlN samples are lower than 1.0×10^{-4}. These value are also lower than those of the AlN ceramics obtained by the high temperature long time annealing process (1900 °C–48 h).[15] As mentioned above, the ratio of $\tan\delta$ values of the samples obtained in this study to those obtained by high temperature long time annealing is 0.6. And that of thermal conductivity values is 0.85. ε' values of all samples are almost same (8.4–8.6: in this study, 8.2–8.4: Ref. [15]). The cause with these lower values is due to the lowering $\tan\delta$ rather than the enhanced thermal conductivity. Therefore, for keeping low regenerative index, slow-cooling and annealing at intermediate temperature condition is much effective as compared to high temperature long time annealing.

4. Conclusions

To clarify the effects of slow-cooling and annealing on the $\tan\delta$ and thermal conductivity of AlN ceramics, AlN powders with Y_2O_3 as a sintering aid were pressureless-sintered at 1900 °C for 2 h under a nitrogen flowing atmosphere. By XRD analysis, only YAG phase ($5Al_2O_3/3Y_2O_3$) was identified as the secondary phase in the AlN ceramics. By adjusting critical sintering parameters such as annealing and cooling rate, we found that slow-cooling at the rate of 1 °C min^{-1} and annealing at 970 °C for 4 h improved $\tan\delta$. By adding small amount of Y_2O_3, the $\tan\delta$ could be kept at lower than 2×10^{-3} while maintaining relatively high thermal conductivity at 160 W m^{-1} °C^{-1}. Hence, AlN samples having low regenerative index of lower than 1.0×10^{-4} could be obtained by slow-cooling and annealing at intermediate temperature process.

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