Effect of additives on dielectric loss of AlN ceramics

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Abstract

We investigated dielectric loss tangent of AlN sintered bodies. Y_2O_3 and MgO were respectively added in the proportions of 0.5 or 1.0 mol% as sintering additives to AlN powder, and pressureless sintering was performed in a nitrogen flow atmosphere at 1850 °C or 1900 °C for 2 hours. The AlN sintered body became denser due to addition of MgO, and sufficient densification was achieved at a relative density of 0.955 - 0.998. The dielectric tangent at 28 GHz was 2.0×10^{-3} - 6.3×10^{-3} for no addition of MgO, and a satisfactory value of 2.3×10^{-3} - 4.5×10^{-3} was obtained for 1 mol% addition of MgO.

1. Introduction

In recent years, large-scale integrated circuits (LSI) have become more advanced and more intricate, and plasma devices using microwaves above 1×10^9 Hz (1 GHz), e.g., plasma etching devices and plasma CVD devices, are now necessary to machine them[1-4]. Plasma devices include devices wherein members such as microwave permeation windows, protective plates, and clamps and electrostatic chucks are exposed to plasma. To perform their functions, these members must be able to withstand fluorinated reaction gases, and they must have high heat dissipating properties, high insulation properties and a small dielectric loss tangent (tan δ). For microwave permeation windows, a material having an excellent dielectric loss wherein tan δ is of the order of 3×10^{-3} or less is required[5]. Materials having a low tan δ include alumina[6], sapphire[6] and silicone nitride[7]. However, alumina and sapphire have low thermal conductivity, and as the ability of silicone nitride to withstand fluorinated reaction gases is low, these materials cannot be used in the above applications.

On the other hand, AlN offers high thermal conductivity (320 W/m·K at room temperature[8,9]), has high insulating properties and is able to withstand fluorinated gases, so it may be described as promising[10]. Previously, as regards dielectric loss tangent of AlN in frequency bands above the GHz level, the measurement results of tan δ for commercial AlN sintered bodies or the relation between porosity and tan δ for AlN sintered bodies[1], the effect of eliminating N vacancies by annealing[2], and the improvement of dielectric loss tangent by reheating in a carbon reducing atmosphere after sintering[11], have been reported. However, there have been practically few reports so far on dielectric losses at GHz and higher frequencies when a third substance is added to an AlN - Y_2O_3 system as a further additive.

It is therefore an object of this study to clarify the effect on tan δ of adding small amounts of MgO as a third substance.

2. Experimental method

The AlN starting material powder was Mitsui chemicals, Inc. Grade MAN-2. Table 1 and Fig. 1 respectively show the characteristics and SEM image of the powder. Although the grain diameter is only approximately 1μm, this powder is very pure and contains only very little oxygen. As shown in the composition table of Table 2, 0.5 or 1 mol% for Y_2O_3, and 0.05 or 1 mol% for MgO, were added as sintering additives. These were mixed in ethanol, and after drying, were CIP formed at 100 MPa, sintered in a current of nitrogen at 1850 °C or 1900 °C for 2 hours, and cooled to obtain an AlN sintered body. The bulk density of the AlN sintered body was measured by the Archimedes method. The crystal phase was measured using a Rigaku Corporation RINT-2500/PC(450mA)L XRD device. To measure the dielectric losses of the AlN sintered body, machining and polishing were performed on a rectangular parallelepiped. Dielectric losses were measured within the range of 26.5 GHz - 40.0 GHz at room temperature using an HP 8722ES, S-Parameter Network Analyzer.

3. Results and discussion

Fig.2 shows the XRD profiles of an AlN sintered body when Y_2O_3 of 1. 0 mol% was added and the sintering temperature was 1900 °C. In this experiment, AlN and $Al_5Y_3O_{12}$ ($5Al_2O_3/3Y_2O_3$: YAG) were found. However, no other crystal phases could be identified. Also, there was no significant difference in the above results even when Y_2O_3 of 0.5 mol% was added. In the AlN-Al_2O_3-Y_2O_3 system, the phases which can be obtained at 1800 °C or above are AlN, 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, Al_2O_3 and a liquid phase[12,13]. The crystal phase of second phase in the AlN sinter body changes to YAM-YAP-YAG[14] with increasing sintering temperature. This is thought to be related to the re-release of oxygen in solid solution which dissolved in AlN in the AlN solution - precipitation step due to formation of the liquid phase, which increases the purity of the AlN[14]. The fact that YAG was detected in this experimental result is thought to be because, as the sintering temperature is as high as 1850 °C or 1900 °C, as in the case of this report[14], the material passes through a liquid phase formation - oxygen solid solution - re-release process, and the AlN becomes purer due to this process.

Fig. 3 shows the relation between the amount of MgO addition and the relative density of the AlN sintered body. In the figure, 0.5 and 1.0 are the Y_2O_3 addition amounts, and 1850 °C and 1900 °C are the sintering temperatures, respectively. The theoretical density was estimated with the Rule of Mixtures. The relative density was calculated from the ratio of the bulk density and theoretical density. When no MgO was added, the relative density was to approximately 0.955 - 0.985. The densification is thought to be related to the aforesaid liquid phase and YAG formation. Due to the addition of MgO, densification was further increased. It was highest for addition of 0.5 mol% Y_2O_3 and 0.5mol% MgO at a sintering temperature of 1900 °C, and was almost completely densified at a relative density of 0.998. For addition of 1.0mol% MgO, densification increased to a satisfactory level of 0.978 and 0.993 - 0.995. K. Komeya et al reported that when MgO is added to AlN, densification is more difficult than in the case of AlN alone[15]. The effect of MgO on densification in this study is unclear, but it appears to be due to the synergistic effect of the oxygen impurity Al_2O_3 and Y_2O_3 which was added as a sintering additive.

Fig. 4 shows the relationship between MgO addition amount and dielectric loss tangent (tan δ) at 28 GHz Gyrotron band. The values shown in the figure are average values for 12 points obtained by four measurements in the range of 28.00 ± 0.12 GHz for each specimen. The error bar shows the typical standard deviation. In the figure, 0.5, 1.0 and 1850, 1900 are identical to those in the description of Fig.2.

Tan δ for the AlN sintered body obtained in this study was 2.0 - 6.3 x 10^{-3} when MgO was not added and 2.3 x 10^{-3} - 4.5 x 10^{-3} when 1mol% MgO was added. These values are effectively one order of magnitude less than 11 x 10^{-3} - 22 x 10^{-3} reported by I.P.Fesenko and M.A.Kuzenkova[4], and they were of the same order as 2.4 - 4.1 x 10^{-3} where the value of tan δ was successfully reduced by 1/3 from their previous study due to the effect of post-sintering[8], 2.2 x 10^{-3} - 4.8 x 10^{-3} in the report by R.Heidinger and S.Nazare[1], or approx. 2.5 x 10^{-3} for an AlN sinter body[3]. Extrinsic loss degenerates due to crystal imperfections such as defects, dislocations, pores, microcracks, grain boundaries, grain boundary phases and impurities[4]. The reasons why dielectric losses tangent of the sintered body were generally satisfactory in this study, are thought to be that in the sintering step, the purity of AlN increased due to the liquid phase formation - oxygen solid solution - re-release process, while in addition, the detected crystal phase was not only AlN but also YAG which has a dielectric loss of 1 x 10^{-4} or less[16], and both are sufficiently densified.

4. Conclusions

We studied the effect of MgO addition on dielectric loss tangent in the 28 GHz Gyrotron band of an AlN sintered body obtained by pressureless sintering at 1850 °C or 1900 °C for 2 hours in a current of nitrogen, by adding a very small amount of MgO in addition to Y_2O_3 as an AlN sintering additives. As a result, the addition of small amounts of MgO was effective in increasing the densification of an AlN - Y_2O_3 system. Also, tan δ was 2.0 - 6.3 x 10^{-3} when MgO was not added, and increased to a satisfactory value of 2.3 x 10^{-3} - 4.5 x 10^{-3} when MgO of 1 mol% was added.

5. References

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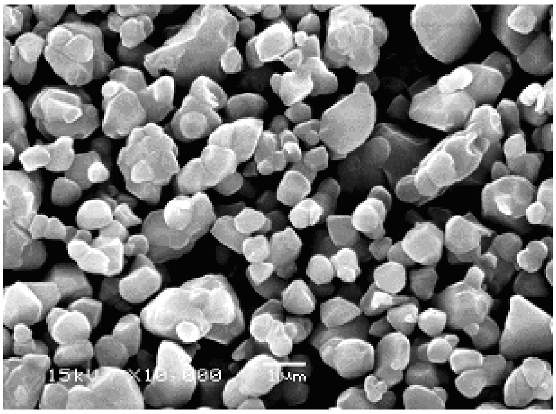

Fig. 1. SEM photograph of AlN powder.

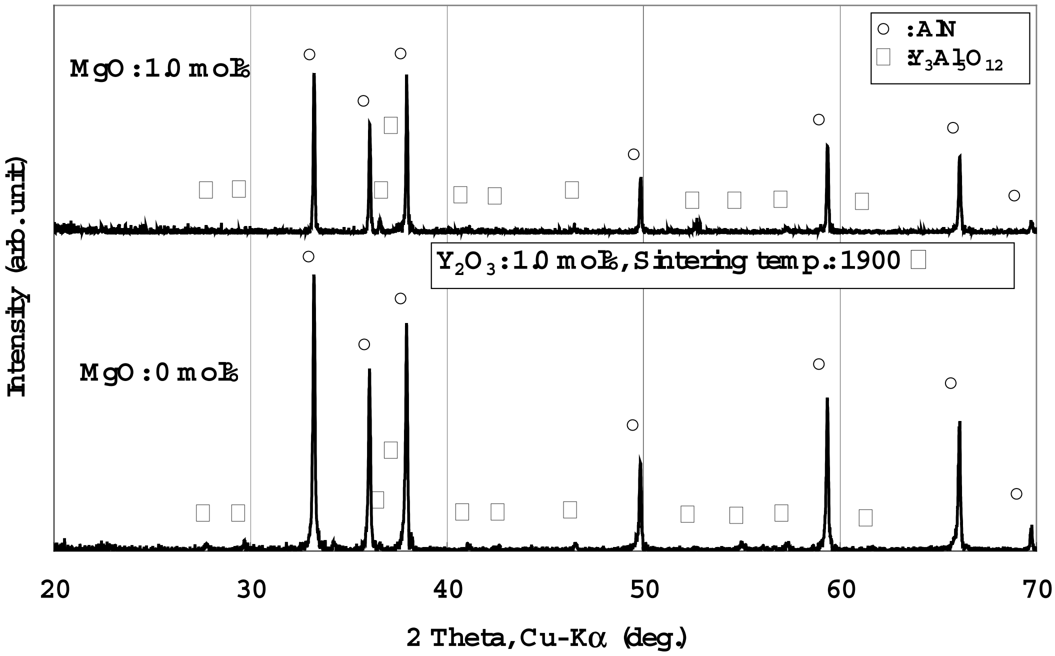

Fig. 2. XRD profiles of sintered AlN.

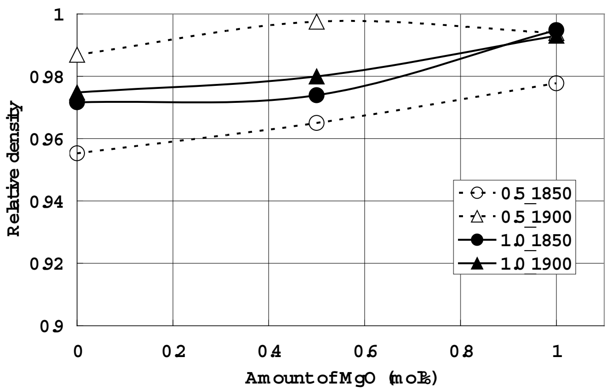

Fig. 3. Relationship between relative density and amount of MgO.

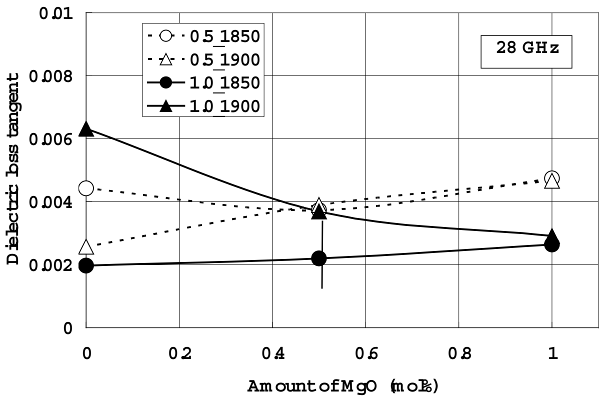

Fig. 4. Relationship between dielectric loss tangent and amount of MgO.

Table 1. Characteristics of used AlN powder.

Al	N	Impurities								Specific surface area	Particle size
		O	C	Ca	Mg	Cr	Fe	Si	Ni		
%		%		ppm						m^2/g	µm
65.7	33.9	0.3	0.04	< 10	< 10	< 10	15	23	< 10	1.9	0.9

Table 2. Composition of used powders.

	Composition (mol%)		
No.	AlN	Y_2O_3	MgO
1	100.0	0.5	0.0
2	100.0	1.0	0.0
3	100.0	0.5	0.5
4	100.0	1.0	0.5
5	100.0	0.5	1.0
6	100.0	1.0	1.0