Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of the European Ceramic Society 25 (2005) 2791–2794
www.elsevier.com/locate/jeurceramsoc

Effects of MgO addition on the density and dielectric loss of AlN ceramics sintered in presence of Y_2O_3

Shoichi Kume *, Masaki Yasuoka, Naoki Omura, Koji Watari

National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Anagahora, Shimoshidami, Moriyama-ku, Nagoya 463-8560, Japan

Available online 18 April 2005

Abstract

In the present work, effects of sintering additives on dielectric loss tangent of AlN ceramics were explored. Different amounts of Y_2O_3 and MgO were respectively added as sintering additives to AlN powder, and pressureless sintering was performed in a nitrogen flow atmosphere at 1850 °C or 1900 °C for 2 h. The resulted AlN ceramics became denser due to addition of MgO, and a full dense sinter was obtained at a relative density of 0.998. Tan δ decreased with increasing MgO amount when kept Y_2O_3 content and the sintering temperature at 1 mol% and 1900 °C, respectively.

Keywords: AlN; Y_2O_3; MgO; Dielectric properties; Sintering

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 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 and high insulation properties and a small dielectric loss tangent (tan δ). For a microwave window, 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 silicon nitride.[7] Alumina and sapphire have however relative low thermal conductivity, and as the ability of silicon 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 property 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 sinters or the relationship between porosity and tan δ for AlN sinters,[1] the effects 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 effects 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 a SEM image of the powder. Although the grain diameter is only approximately 1 μm, this powder is very pure and contains only very little oxygen. As shown in Table 2, 0.5 or 1 mol% Y_2O_3 and 0.5 or 1 mol% MgO were added as sintering additives. Above

* Corresponding author. Tel.: +81 52 736 7158; fax: +81 52 736 7405.
E-mail address: s.kume@aist.go.jp (S. Kume).

0955-2219/$ – see front matter
doi:10.1016/j.jeurceramsoc.2005.03.141

Table 1
Characteristics of AlN powder

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

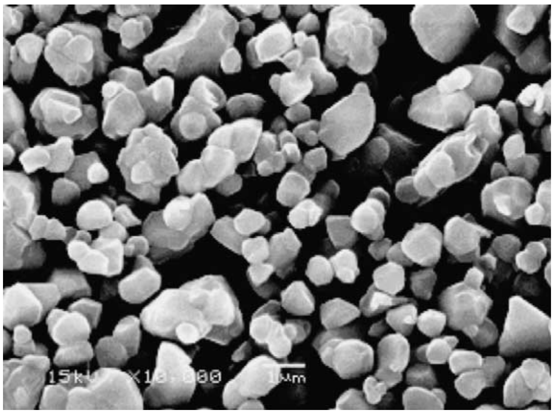

Fig. 1. SEM photograph of AlN powder.

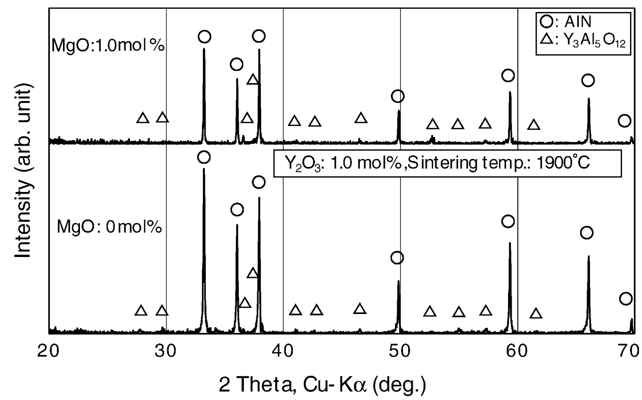

Fig. 2. XRD profiles of sintered AlN.

Table 2
Composition of starting powders

Number	Composition (mol%)		
	AlN	Y_2O_3	MgO
1	99.5	0.5	0.0
2	99.0	1.0	0.0
3	99.0	0.5	0.5
4	98.5	1.0	0.5
5	98.5	0.5	1.0
6	98.0	1.0	1.0

powders were mixed in ethanol, and after drying, were CIP formed at 100 MPa, sintered at 1850 °C or 1900 °C for 2 h with a nitrogen flow. The bulk density of the AlN sinter was measured by the Archimedes method. The crystal phases of AlN sinters were analyzed using a Rigaku Corporation RINT-2500/PC(450mA)L XRD device. To measure the dielectric losses of the AlN sinter, machining and polishing were performed on a rectangular parallelepiped. Dielectric losses were measured within the range of 26.5–40.0 GHz at room temperature using an HP 8722ES, S-Parameter Network Analyzer.

3. Results and discussion

Fig. 2 shows the XRD profiles of AlN sinters with or without 1.0 mol% MgO and without one when Y_2O_3 of 1.0 mol% was added and the sintering temperature was 1900 °C. In both sinters, AlN and $Al_5Y_3O_{12}$ ($5Al_2O_3/3Y_2O_3$: YAG) were detected. However, no other crystal phases could be identified. In addition, there was no significant difference in the above results even when Y_2O_3 was 0.5 mol% and sintering temperature was 1850 °C. 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 second phase in the AlN sinter changes to YAM–YAP–YAG with increasing sintering temperature.[14] This is thought to be related to the re-release of oxygen in solid solution which dissolved in AlN crystals in the AlN solution—precipitation step due to formation of the liquid phase, which increases the purity of the AlN.[14,17,18] The fact that YAG was detected in this experimental result is thought to be related with the material passes through a liquid phase formation—oxygen solid solution—re-release process. This result is agree with the past reports,[14,17,18] at the same sintering temperature as high as 1850 °C or 1900 °C.

Fig. 3 shows the relationship between the amount of MgO addition and the relative density of the AlN sinters. In the figure, 0.5 and 1.0 are the Y_2O_3 addition amounts, and 1850 °C

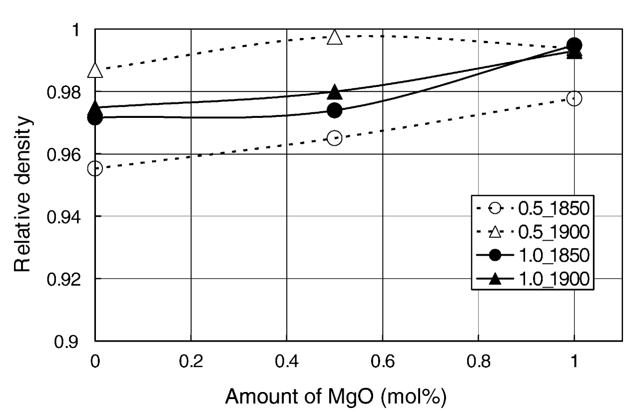

Fig. 3. Relationship between relative density and amount of MgO.

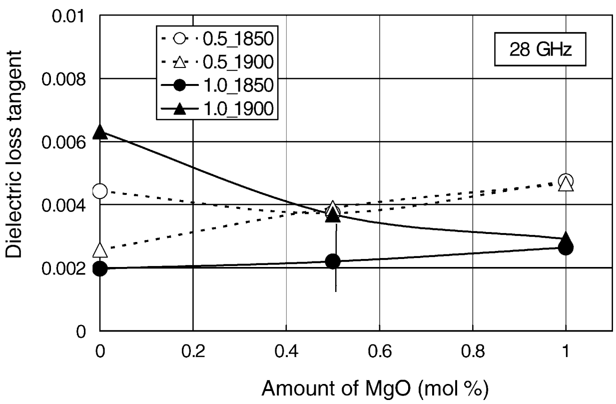

Fig. 4. Relationship between dielectric loss tangent and amount of MgO.

and 1900 °C are the sintering temperatures, respectively. Theoretical density was estimated with the Rule of Mixtures. The relative density was calculated from the ratio of the bulk density and the theoretical density. When no MgO was added, the relative density was between 0.955 and 0.985. The densification is thought to be related to liquid phase mentioned above and YAG formation. Due to the addition of MgO, densification was further increased. The highest value at 0.998 was obtained at a sintering temperature of 1900 °C when adding 0.5 mol% Y_2O_3 and 0.5 mol% MgO. For addition of 1.0 mol% 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 ± 0.125 GHz for each specimen. An error bar shows typical standard deviation in the figure. Values of 0.5, 1.0 and 1850, 1900 are identical to those in the description of Fig. 2. Although the reason was unclear, tendency of tan δ with increasing MgO amount for the AlN sinters differed depending on Y_2O_3 content and sintering temperature. Tan δ decreased with increasing MgO amount when Y_2O_3 content and the sintering temperature were 1 mol% and 1900 °C, respectively. The tan δ in this study was 2.3×10^{-3} when MgO amount was 1.0 mol%. This value is not minimum in this study but is effectively one order of magnitude less than 11×10^{-3} and 22×10^{-3} reported by I.P. Fesenko and M.A. Kuzenkova,[4] and that is of the same order as from 2.4×10^{-3} to 4.1×10^{-3} where the values of tan δ were successfully reduced by 1/3 from their previous study due to the effect of post-sintering,[8] between 2.2×10^{-3} and 4.8×10^{-3} in the report by R. Heidinger and S. Nazare,[1] or approximately 2.5×10^{-3} for AlN sinters.[3] Extrinsic loss degenerates due to crystal imperfections such as defects, dislocations, pores, microcracks, grain boundaries, second phases and impurities.[4] The reasons why dielectric loss tangent of the sinter was almost 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 phases were not only AlN but also YAG which has a dielectric loss of 1×10^{-4} or less,[16] and was sufficiently densified.

4. Conclusions

For applying AlN to a member for a plasma etching device, the material having high thermal conductivity and an excellent dielectric loss is required. We therefore studied the effects of MgO addition on the density and dielectric loss tangent in the 28 GHz Gyrotron band of an AlN sintered body obtained in presence of Y_2O_3 by pressureless sintering at 1850 °C or 1900 °C for 2 h in a current of nitrogen, by adding small amounts of MgO as an AlN sintering additive. Small amount MgO was effective for densification of AlN–Y_2O_3 system ceramics. AlN ceramics sintered with a density of 0.993 was obtained by sintering the 1 mol% Y_2O_3–AlN adding MgO of 1 mol% at 1900 °C. Tan δ of the AlN ceramic was 2.3×10^{-3}. It is therefore concluded that the AlN ceramic having high density and low dielectric loss is possible to produce by sintering AlN with both 1 mol% Y_2O_3 and MgO at 1900 °C for 2 h.

Acknowledgments

We greatly thank Dr. T. Shimada (NEOMAX) and Dr. W. Chen (AIST) for valuable discussion.

References

1. Heidinger, R. and Nazare, S., Influence of porosity on the dielectric properties of AlN in the range of 30 ... 40 GHz. *Powder Metall. Int.*, 1988, **20**, 30–32.
2. Enck, R. C., Harris, J. H., Youngman, R. A. and Nemecek, T. S., Process for making a low electrical resistivity, high purity aluminum nitride electrostatic chuck, *US Patent No. 6,017,485* (January 25, 2000).
3. Gonzalez, M. and Ibarra, A., The dielectric behavior of commercial polycrystalline aluminium nitride. *Diamond Relat. Mater.*, 2000, **9**, 467–471.
4. Fesenko, I. P. and Kuzenkova, M. A., Low dielectric loss ceramics of AlN fine and nanopowders. *Powder Metall. Met. Ceram.*, 2002, **41**, 567–569.
5. Nishizono, K. and Oh, U., Radio wave transmittal substance and production method thereof, *Japan Kokai Tokkyo Koho*, July 3, 2001 (Toku-Kai2001-181049).
6. Alford, N. M., Breeze, J., Wang, X., Penn, S. J., Dalla, S., Webb, S. J., Ljepojevic, N. and Aupi, X., Dielectric loss of oxide single crystals and polycrystalline analogues from 10 to 320 K. *J. Eur. Ceram. Soc.*, 2001, **21**, 2605–2611.
7. Tajima, K. and Uchimura, H., Microwave window substance, *Japan Kokai Tokkyo Koho*, November 12, 1996, (Toku-Kai-Hei8-295567).

8. Slack, G. A., Tanzilli, R. A., Pohl, R. O. and Vandersande, J. W., The intrinsic thermal conductivity of AIN. *J. Phys. Chem. Solids*, 1987, **48**, 641–647.
9. Watari, K., Hwang, H. J., Toriyama, M. and Kanzaki, S., Effective sintering aids for low-temperature sintering of AlN ceramics. *J. Mater. Res.*, 1999, **14**, 1409–1417.
10. Koyama, T. and Ishii, M., Corrosion-resistant substance for plasma and production method thereof, *Japan Kokai Tokkyo Koho*, August 28, 2001 (Toku-Kai 2001-233676).
11. Koyama, T., Iguchi, M. and Ishii, M., Lowering of dielectric loss in AlN ceramics. *Taiheiyo Semento Kenkyu Hokoku*, 2002, **142**, 78–82.
12. Sun, W. Y., Huang, Z. K., Tien, T. Y. and Yen, T. S., Phase relationships in the system Y–Al–O–N. *Mater. Lett.*, 1991, **11**, 67–69.
13. Medraj, M., Hammond, R., Thompson, W. T. and Drew, R. A. L., High-temperature neutron diffraction of the AlN–Al_2O_3–Y_2O_3 system. *J. Am. Ceram. Soc.*, 2003, **86**, 717–726.
14. Mizutani, N. and Shinozaki, K., Sinetring of AlN—densification, grain growth and removal of grain boundary phase. *Ceramics*, 1991, **26**, 738–743.
15. Komeya, K., Inoue, H. and Tsuge, A., Effect of various additives on sintering of aluminum nitride. *Yogyo-Kyokai-Shi*, 1981, **89**, 58–64.
16. Braginsky, V. B., Ilchenko, V. S. and Bagdassarov, K. S., Experimental observation of fundamental microwave absorption in high-quality dielectric crystals. *Phys. Lett. A*, 1987, **120**, 300–305.
17. Virkar, A. V., Jackson, T. B. and Cutler, R. A., Thermodynamic and kinetic effects of oxygen removal on the thermal conductivity of aluminum nitride. *J. Am. Ceram. Soc.*, 1989, **72**, 2031–2042.
18. Watari, K., Brito, M., Yasuoka, M., Valecillos, M. C. and Kanzaki, K., Influence of powder characteristics on sintering process and thermal conductivity of aluminum nitride ceramics. *J. Ceram. Soc. Jpn.*, 1995, **103**, 891–900.