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Annealing effect on dielectric property of AlN ceramics

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Abstract

Effects of slow-cooling at high temperatures and annealing at intermediate temperatures on dielectric loss tangent of AlN ceramics were explored. Y_2O_3 was added as a sintering additive to AlN powders, and the powders were pressureless-sintered at 1900 °C for 2 h in a nitrogen flow atmosphere. In succession to the sintering, AlN samples were slow-cooled at a rate of 1 °C/min from 1900 to 1750 °C and/or annealed at 970 °C for 4 h. $Al_5Y_3O_{12}$ was detected in the AlN ceramics obtained by the slow-cooling and $AlYO_3$ was found in the ceramics cooled at a rate of 30 °C/min. AlN ceramics with a relative density of 0.986 were obtained by the slow-cooling method. On the other hand, very low $\tan\delta$ values between 2.6 and 4.6×10^{-4} were obtained when the AlN ceramics were annealed at 970 °C for 4 h.

Keywords: Sintering; Dielectric properties; Nitrides; Annealing

1. Introduction

In recent years, since substrate and package materials for integrated circuits (ICs) have become more advanced and more intricate plasma devices using microwaves above 1×10^9 Hz (1 GHz) (e.g., plasma etching devices and plasma CVD devices) are now necessary for machining.[1–4] In plasma devices, members such as microwave windows, protective plates, and clamps and electrostatic chucks are regularly exposed to plasma. To perform their functions, these members not only must be able to withstand fluorinated reaction gases, but they must also have high heat dissipation and insulation properties and a small dielectric loss tangent ($\tan\delta$). For a microwave window, a material with an excellent dielectric loss where $\tan\delta$ is of the order of 3×10^{-3} or less is required.[5] Materials having a low $\tan\delta$ include alumina,[6] sapphire[6] and silicon nitride.[7] However, alumina and sapphire have relative low thermal conductivities, whereas the ability of silicon nitride to withstand fluorinated reaction gases is low. Hence, these materials cannot be used in the above applications.

On the other hand, AlN offers a high theoretical thermal conductivity (320 W/m K at room temperature[8,9]), has high insulating properties and is able to withstand fluorinated gases; therefore, AlN is a good candidate material for the above applications.[10,11] $\tan\delta$ is affected by intrinsic and extrinsic losses. The intrinsic loss depends on the crystal structure and sets the lowest value of the loss in a pure and perfect single crystal. On the other hand, the extrinsic loss is associated with imperfections in the crystal structure, such as the grain boundary, impurities, lattice defects, dislocations, residual stresses in its polycrystal and so on. Therefore, reducing these imperfections of the microstructure decreases $\tan\delta$. However, there have been very few reports so far on dielectric losses at GHz and higher frequencies. Previously, as regards to $\tan\delta$ of AlN in the frequency bands above the GHz level, the effects of eliminating N vacancies by slow-cooling,[2] and the improvement of $\tan\delta$ by reheating in a carbon reducing atmosphere after sintering[11] have been studied but no satisfactory results were reported. Hence, the objective of this study is aimed at clarifying the effect of cooling schedule on $\tan\delta$ of AlN ceramics.

2. Experimental procedure

The AlN starting material powder was from Mitsui chemicals, Inc. of grade MAN-2. Y_2O_3 of 1 mol% was added to this material as a sintering additive. These were mixed in ethanol, and after drying, were formed into a cylinder with 16 mm in diameter and 5 mm in thickness using uniaxial molding and then CIPed at 100 MPa. The formed sample was sintered under nitrogen flow atmosphere at 1900 °C for 2 h. Following sintering, four

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Table 1
Cooling conditions

Sample number	Slow-cooling 1900–1750 °C 1 °C/min	Annealing 970 °C 4 h
1	○	○
2	○	–
3	–	○
4	–	–

different kinds of cooling schedules were performed as shown in Table 1 and Fig. 1. Bulk densities of the AlN sinters obtained were measured using the Archimedes' method. To measure tan δ of the AlN sintered ceramics, machining and polishing were performed on the rectangular solids (7.0 mm × 5.0 mm × 3.5 mm). Dielectric loss was measured each 0.125 GHz within the range of R band (26.5–40.0 GHz) at room temperature by using HP 8722ES, S-Parameter Network Analyzer. Crystal phases in AlN sintered ceramics were identified by XRD analysis. Fracture surfaces of AlN ceramics were observed using SEM.

3. Results and discussion

3.1. XRD analysis

Fig. 2 shows the XRD profiles of AlN sinters obtained through four different kinds of cooling schedules. In both sinters of No. 1 and No. 2, AlN and $Al_5Y_3O_{12}$ ($5Al_2O_3/3Y_2O_3$: YAG) were detected. However, no other crystal phases could be identified other than the peaks of Al sample holder. On the other hand, $AlYO_3$ was recognized in both No. 3 and No. 4 sinters. It was found that YAG was formed if AlN sinter was cooled slowly at high temperature and YAP (Y_2O_3/Al_2O_3) was generated in AlN ceramics without the slow-cooling. This could be related to the re-release of oxygen in solid solution which dissolved in AlN crystals in the AlN solution–precipitation step, increasing the purity of the AlN crystals[12–14] during the slow-cooling.

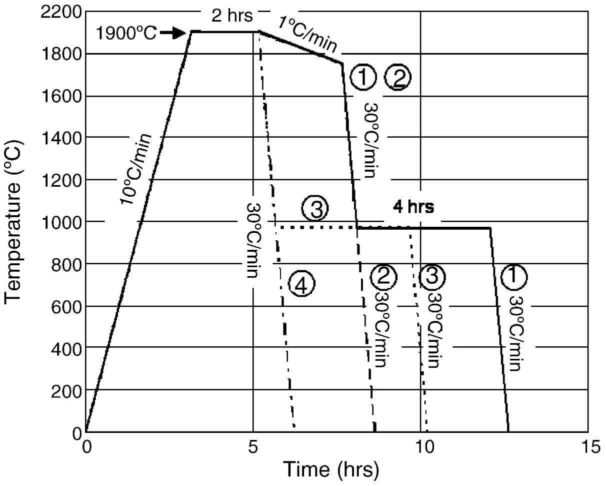

Fig. 1. Sintering and cooling profiles.

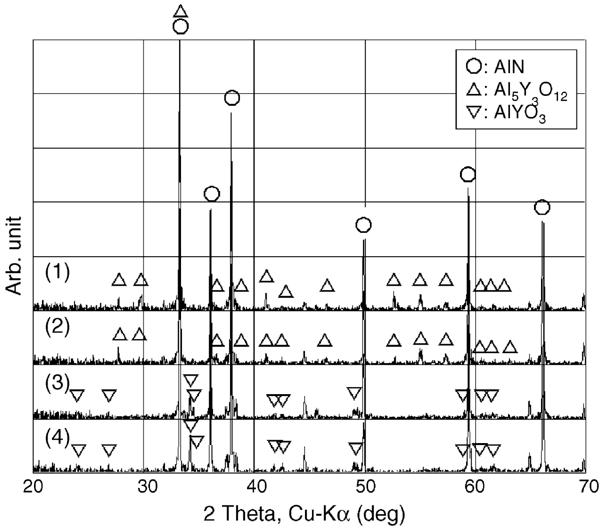

Fig. 2. XRD profiles of AlN sinters.

3.2. Density

Fig. 3 shows the relative densities of the AlN ceramics obtained by different cooling processes. Theoretical density was estimated using the Rule of Mixtures, while the relative density was calculated from the ratio of the bulk and theoretical densities. Relative densities calculated were in the order of 0.975–0.987 with a spread within roughly 0.01. The densities of both No. 1 and No. 2 samples were slightly higher than the other samples. It is assumed that the slow-cooling after sintering was effective in densification of the samples due to the development of their microstructures.

3.3. Microstructure

Fig. 4 shows the SEM photographs of fracture surfaces of the AlN ceramics obtained by different cooling processes. Dihedral

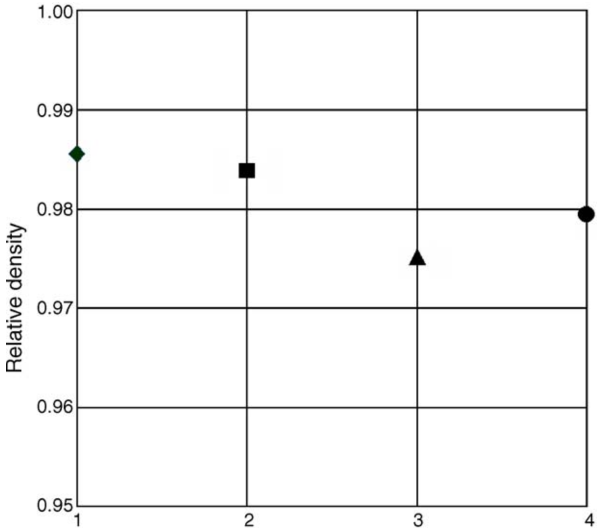

Fig. 3. Relative density of AlN ceramics obtained by four kinds of cooling conditions as shown in Table 1.

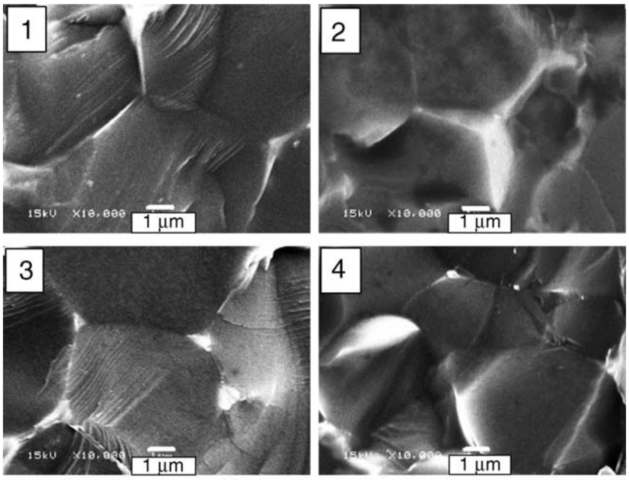

Fig. 4. SEM photographs of fracture surfaces of the AlN ceramics obtained by four kinds of cooling conditions as shown in Table 1.

angle of both the No. 1 and No. 2 samples seems to be increased clearly as compared to that of No. 4. This result is an evidence of microstructural development mentioned above and in a previous report.[15]

3.4. Dielectric loss

Fig. 5 shows the dielectric loss tangent (tan δ) at 28 GHz Gyrotron band for the AlN ceramics obtained by different cooling processes. 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 sample. The error bars show the standard deviation about the average values for each tan δ value. tan δ of the AlN ceramics obtained by slow-cooling was 1.8×10^{-3}. This value was roughly a half of that obtained with the No. 4 sample, which was not subjected either to slow-cooling or annealing. On the other hand, the tan δ values of No. 1 and No. 2 samples, which were obtained by annealing, were in the order of $2.6–4.6 \times 10^{-4}$. These values are roughly one tenth of that obtained with the No. 4 sample. These results mean that both the slow-cooling and annealing are effective processes in lowering of tan δ, annealing being more effective than slow-cooling. It should be noted that the value of tan δ obtained in this study is quite small, about one tenth of the previously reported values[3,4,8] between 2.2×10^{-3} and 4.8×10^{-3}.

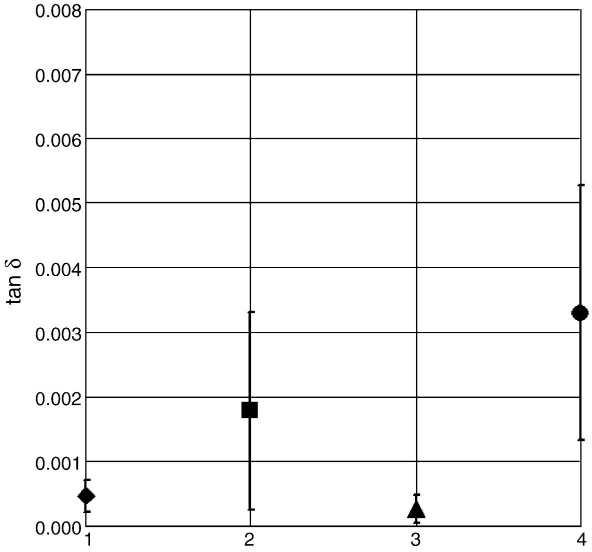

Fig. 5. Dielectric loss tangent of AlN ceramics obtained by four kinds of cooling conditions as shown in Table 1.

4. Conclusions

In order to clarify the effects of slow-cooling at high temperature and annealing treatments on the tan δ of AlN ceramics, AlN powder with 1 mol% Y_2O_3 was pressureless-sintered at 1900 °C for 2 h under nitrogen flow atmosphere. Following this, AlN sample was slow-cooled at a rate of 1 °C/min from 1900 to 1750 °C and/or annealed at 970 °C for 4 h. The results were as follows:

1 While $Al_5Y_3O_{12}$ was detected in the slow-cooled AlN ceramics, $AlYO_3$ was observed without the slow-cooling process.
2 The slow-cooling was relatively effective in densification of the AlN ceramics.
3 The dihedral angle of grains in the AlN ceramics generated by both the slow-cooling and annealing steps increased clearly when compared to those which were not subjected to slow-cooling.
4 It was shown that both the annealing and slow-cooling steps are useful in lowering of the tan δ of the AlN ceramics while the annealing is more effective in lowering of tan δ than the slow-cooling.

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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*, Toku-Kai2001-181049, July 3, 2001.
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*, Toku-Kai-Hei8-295567, November 12, 1996.
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*, Toku-Kai 2001-233676, August 28, 2001.
11. Koyama, T., Iguchi, M. and Ishii, M., Lowering of dielectric loss in AlN ceramics. *Taiheiyo Semento Kenkyu Hokoku*, 2002, **142**, 78–82.
12. Mizutani, N. and Shinozaki, K., Sinetring of AlN—densification, grain growth and removal of grain boundary phase. *Ceramics*, 1991, **26**, 738–743.
13. 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.
14. 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.
15. Kim, W.-J., Kim, D. K. and Kim, C. H., Morphological effect of second phase on the thermal conductivity of AlN ceramics. *J. Am. Ceram. Soc.*, 1996, **79**, 1066–1072.