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DEFECT CHARACTERIZATION OF HIGH THERMAL CONDUCTIVITY CaF_2 DOPED AlN CERAMICS BY RAMAN SPECTROSCOPY

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Calcium fluoride additive was used to produce high thermal conductivity AlN ceramics which has no grain boundary phase. Thermal conductivity of AlN is determined by the point defect, represented as oxygen related defect, within the AlN grain. The defect density characterization of high thermal conductivity CaF_2 doped AlN ceramics after heat treatment was conducted by Raman spectroscopy. As measure Raman linewidth broadening, the point defect density variation after heat treatment and corresponding thermal conductivity change was investigated.

Keywords: Raman spectroscopy; thermal conductivity; aluminum nitride; heat treatment.

1. Introduction

The high thermal conductivity of AlN makes it a very promising material for many device application coupled with its unique physical and chemical properties. AlN has attractive thermal and electrical properties, which are high thermal conductivity, high electrical conductivity and thermal expansion coefficient similar to Si. Its wide band gap has led to many investigations for the development of optoelectronic devices operating near the short-wavelength end of the visible spectral range. These properties make AlN an excellent material to replace alumina (Al_2O_3) and berilia (BeO) used for the manufacture of semiconductor devices.[1–3] An understanding of the nature of native defects in materials is needed for the applications because the defect-induced electronic states in the band gap significantly affect the thermal properties.

The intrinsic thermal conductivity value of pure AlN single crystal has been known to be 320 W/mK at room temperature. The thermal conductivity of sintered AlN was found to be reduced to 40 W/mK in early 1980s. With improved processing, increased thermal conductivity values of up to 285 W/mK have been

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reported.[4] AlN is a covalently bonded material and complete densification is very difficult. In order to achieve full density, high sintering temperature and sintering additives are required.[5,6] The most commonly used sintering additives are Y or Ca compounds. In particular, Yttria is one of the best additives to enhance densification by the liquid phase sintering process.[7] These additives react with the Al_2O_3 layer on the surface of the AlN particles forming second-phases that promote the particle rearrangement and densification. Accordingly, the addition of sintering additives is essential to obtain highly thermal-conductive densifed AlN ceramics, but it leads to residual grain-boundary phases which will adversely affect the thermal conductivity.[8] In order to obtain high thermal conductivity, it is needed to remove residual grain-boundary phase. Calcium fluoride is known as one of the sintering aids which did not leave residual grain-boundary phases because of its high volatility at high temperature.[9] The effect of calcium fluoride on microstructural development and related thermal conductivity of AlN ceramics is not fully understood.

A defect free AlN crystal is a very good insulator and phonons are exclusively the heat carriers in insulators. The thermal property, which is governed by phonons, is greatly influenced by defects in crystals. In AlN crystals, the most influential defects are oxygen-related defects consists of oxygen substitutions for nitrogen (O_N), aluminum vacancies (V_{Al}), and O_N–V_{Al} complexes.[10,11] These defects become phonon scattering sources and thus can be causes of thermal conductivity deterioration. Raman spectroscopy is a very useful tool for studying phonon dynamics and interactions which are affected the thermal conductivity of materials, as well as the factors influencing them. Anharmonic decay which determines the intrinsic linewidth and point defect scattering make the broadening of the Raman linewidth. The width of a Raman line can always be correlated with a phonon mean free path.[12,13] If there are no strong stress gradients in the material, the measured linewidth can be associated with point defect scattering. McCullen *et al.*[14] showed that the broadening of Raman lines is related to oxygen concentrations in the AlN film. Grains in ceramic samples are characterized by defects, similar to their single crystal counterparts. Oxygen-related defects in AlN grain can be characterized through investigation of Raman mode on each grain.

In this study, calcium fluoride additive was used to produce high thermal conductivity AlN ceramics which has no grain boundary phase. The microstructure of CaF_2-doped AlN ceramics was improved through co-additives and sintering conditions. Heat treatment at different atmosphere was conducted to enhance the thermal conductivity and change the defect density in AlN grain. We show how high resolution Raman spectroscopy can be used to characterize defects in AlN grain by investigating the broadening of Raman lines caused by phonon scattering. We show that the width of the E_2 (high) phonon Raman lines are correlated with the thermal conductivity measured by the laser flash method.

2. Experiment

Polycrystalline AlN ceramics were sintered with calcium fluoride additives. Commercially available AlN powder (Grade F, Tokuyama Soda, Tokyo, Japan) was used as starting materials. CaF_2 (Calcium fluoride, Aldrich, USA) powder and Al_2O_3 (Aluminum oxide, Aldrich, USA) powder was added to the AlN powder as a sintering additives. These powders were mixed for 12 h in ethanol as a liquid medium using a ball mill. After ball milling, slurry was dried in an oven at 60°C. The dried powder was made into pellets of 20 mm diameter by uniaxial pressing, followed by cold isostatic pressing at 200 MPa. The cold isostatic pressed compacts were placed in a carbon crucible which contained a powder bed of BN. The prepared specimens were sintered by pressure-less sintering (Astro, Thermal Technology, Santa Babara, CA) at 1900°C for 3 h in flowing N_2 atmosphere. In order to enhance thermal conductivity, heat treatment at different atmosphere was carried out for 8 h. A reducing atmosphere of 95% nitrogen and 5% hydrogen and only nitrogen atmosphere was used.

The crystalline phases in the sintered samples were identified by X-ray diffractometry (XRD) with CuKα radiation. The fracture surfaces of sintered specimens were observed by scanning electron microscopy (SEM). Thermal conductivity values of the samples at room temperature were measured by the laser flash method. Typical samples dimensions were diameter of 12.7 mm and thickness of 2 mm, and both sides of the specimens were coated with carbon black. The micro Raman scattering measurements were performed at room temperature using 514.5 nm light from an Ar ion laser of 40 mW. A double monochromater was used to analyze the scattered radiation with a resolution of less than 1 cm^{-1}. The spot size on the crystallites was ~ 1 μm sufficient to measure one grain.

3. Results and Discussion

AlN ceramics were sintered with sintering additive of calcium fluoride at 1900°C for 3 h. The density of AlN sintered with 3 wt.% CaF_2 was 2.51 g/cm^3. CaF_2 cannot play a role as sintering additive at high temperature (1900°C) because CaF_2 is volatile above 1600°C, thus the specimen has relatively low density. Al_2O_3 powder was added to 3 wt.% in order to enhance densification. Al_2O_3 makes a solid solution with CaF_2 and it is expected that Al_2O_3 retard volatilization of calcium fluoride and the densification of AlN is enhanced. However, the addition of Al_2O_3 adversely affects thermal conductivity because oxygen atoms in Al_2O_3 diffuse into AlN lattice during sintering process15. The density and the thermal conductivity of the specimens as amounts of calcium fluoride were shown in Fig. 1. The density of specimen increases with the increase of the amount of Al_2O_3. It is clear that the addition of Al_2O_3 has a significant effect on densification. The density of 3.16 g/cm^3, corresponding to 98% of the relative density, could be achieved in the addition of 1.5 wt.% Al_2O_3. The thermal conductivity value of the specimen without the addition of Al_2O_3 is less than 100 W/mK owing to the low density.

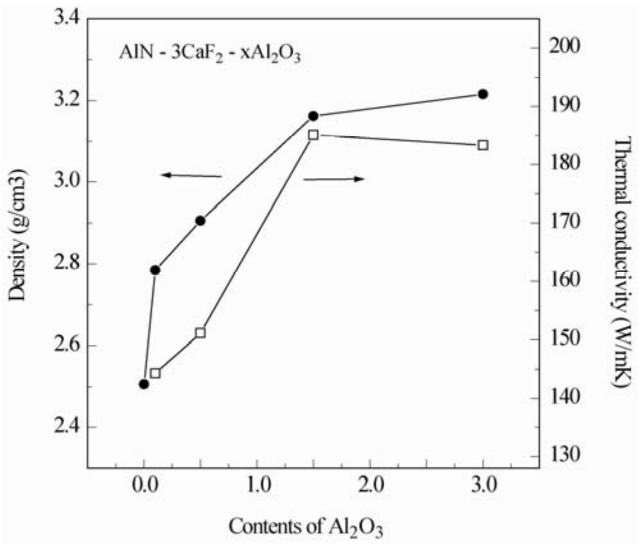

Fig. 1. Effects of Al_2O_3 content on density and thermal conductivity of AlN with 3 wt.% CaF_2 sintered at 1900°C for 3 h.

The thermal conductivity value increase to 144 W/mK with only a small Al_2O_3 addition of 0.1 wt.% and have the highest value of 185.1 W/mK with an addition of 1.5 wt.% Al_2O_3. This is a clear demonstration of the fact that the addition of Al_2O_3 improves the thermal conductivity. The increase in the thermal conductivity could be attributed to enhanced densification.

The morphology of fracture surface of samples with 3 wt.% CaF_2 and 0, 0.1, 1.5, and 3 wt.% Al_2O_3 sintered at 1900°C is shown in Fig. 2. In the specimen with only 3 wt.% CaF_2, it was seen that amounts of the liquid phase were not enough to consolidate the specimen by a liquid-solid diffusion because CaF_2 has been volatilized. Figure 2(a) shows that the edges of some grains were indistinct and many more pores could be observed in the specimen. A small amount of Al_2O_3 addition caused the green density to increase higher than in the case without the addition. This implies that Al_2O_3 impeded volatilization of CaF_2. As increase amounts of Al_2O_3, pores vanished gradually.

A heat treatment at different atmosphere was carried out in order to enhance the thermal conductivity of the fully densified AlN ceramics without a grain boundary phase. AlN ceramics sintered with 3 wt.% CaF_2 and 1.5 wt.% Al_2O_3 (sample CA15) at 1900°C for 3 h, which have the thermal conductivity value of 185.1 W/mK, were soaked at 1900°C for 8 h with nitrogen atmosphere and reducing atmosphere. Thermal conductivity values of each sample were 200.0 and 193.4 W/mK, respectively.

High resolution Raman spectroscopy experiments were conducted to characterize point defects which affect the thermal conductivity. Figure 3 shows a

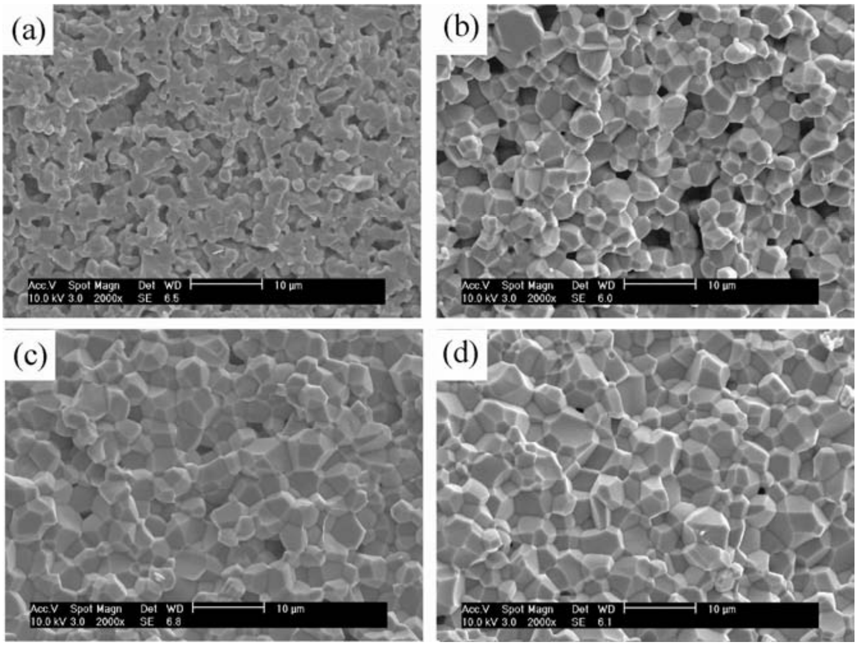

Fig. 2. SEM micrographs of fracture surface of (a) AlN-3 wt.% CaF_2 with (b) 0.1 wt.% Al_2O_3, (c) 1.5 wt.% Al_2O_3, (d) 3.0 wt.% Al_2O_3.The specimens were sintered at 1900°C for 3 h.

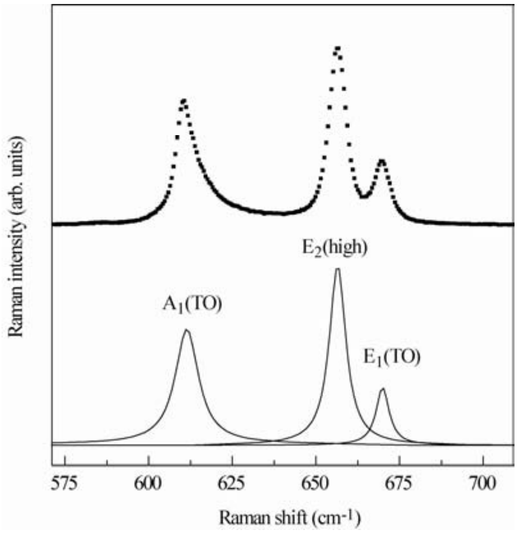

Fig. 3. High resolution Raman spectrum of AlN-CaF_2-Al_2O_3 ceramics (upper figure). The deconvoluted spectra are presented at the lower figure.

Table 1. Grain sizes, Raman linewidths and thermal conductivities of samples CA15 (AlN-3 wt.% CaF_2-1.5 wt.% Al_2O_3) and CA15 with heat treatment at different atmosphere.

Sample	Heat treatment	Atmosphere	Grain size (μm)	Thermal conductivity (W/mK)	Raman linewidth (cm^{-1})
CA15	—	—	3.15	185.1	5.90 (23)
CA15-N	1900°C, 8 h	N_2	4.50	200.0	5.77 (11)
CA15-NH	1900°C, 8 h	95% N_2–5% H_2	4.02	193.4	5.82 (22)

representative Raman spectrum along with the deconvoluted spectra of the AlN grain. The experimental peak was fitted using a Lorenzian function. Peaks at about 612, 658, and 666 cm^{-1} were observed for all experimental points, and each peak corresponded to the A_1 (TO), E_2 (high), and E_1 (TO) modes of AlN, respectively.[16] AlN has a wurtzite structure and belongs to space group C_4^{6v} crystal symmetry. Among the many active Raman modes of AlN, nonpolar E_2 (high) mode, the strongest of the allowed modes in this experiment represented the vibrations of the Al and N atoms. The broadening of E_2 (high) mode were observed to characterize oxygen-related defects. When oxygen atoms substitute for N atoms, an Al vacancy is created for every three oxygen atoms by the charge neutrality constraint. These substitutions make broadening of Raman line for phonon scattering by defects.[11,17] The width of the Raman line is affected when oxygen occupies an N site.

The qualitative information about the point defects in the AlN grain and of its thermal conductivity is obtained by the E_2 (high) mode Raman linewidth measurements. A broadening of the Raman linewidth corresponds to higher point defect concentration. Table 1 shows the Raman linewidths, thermal conductivities and grain sizes of samples CA15 and CA15 with heat treatment at different atmosphere. Since point defects of the AlN lattice produce an increase of the Raman linewidth,[18] Raman linewidth decrease of the samples with heat treatment implies that the purification of AlN lattice occurred and defect concentration decrease in AlN lattice. Compared with the thermal conductivity of each sample, high thermal conductivity samples have small Raman linewidth. It implies that Raman linewidth shows the oxygen-related defect concentration which affects thermal conductivity. As shown in Table 1, each sample has different grain size. Since there is no second phase in a grain boundary, grain size effect is negligible. The Raman linewidth of the sample with heat treatment at nitrogen atmosphere is smaller than that of the sample with heat treatment at reducing atmosphere. This implies that the heat treatment at nitrogen atmosphere can remove oxygen related defects in AlN lattice more effective than the heat treatment at reducing atmosphere.

4. Conclusions

(1) Adding Al_2O_3 as a sintering aid promotes densification and enhances the thermal conductivity of AlN-CaF_2 system. Samples with density 3.16 g/cm^3, corresponding to 98% of the relative density, and 185.1 W/mK of the thermal conductivity as measured the laser flash method were obtained, when the samples was added 1.5 wt.% CaF_2 and pressure-less sintered at 1900°C for 3 h.

(2) Additional heat treatment at different atmosphere helps to increase thermal conductivity. AlN with 3 wt.% CaF_2 and 1.5 wt.% Al_2O_3 samples with heat treatment at nitrogen atmosphere and reducing atmosphere have the thermal conductivity of 200.0 W/mK and 193.4 W/mK, respectively.

(3) Raman experiments were conducted in order to characterize oxygen related defect in AlN samples. The width of E_2 (high) mode was measured using a Lorentzian function. Samples with heat treatment have small E_2 (high) mode Raman linewidth and high thermal conductivity. It implies that Raman linewidth shows oxygen-related defect concentration and heat treatment makes purification of AlN samples.

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