Investigation of Lattice Defects in Aluminum Nitride with High Thermal Conductivity by Positron Annihilation Lifetime Measurement

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It is important to investigate lattice defect structure in AlN crystal to improve the properties of AlN ceramics. Positron annihilation lifetime measurement (PAL) was carried out to investigate lattice defects in high thermal conductivity AlN ceramics. PAL measurement can detect atomic vacancy type defects like point defect in crystal with non-destruction and high sensitivity. Two positron lifetime components were observed at 230 and 132 ps, which were assigned to lifetime components of aluminum-site vacancy (V\text{Al}) and AlN perfect crystal, respectively. There was a good correlation between positron mean lifetime and thermal conductivity of AlN ceramics. Also, it was found that there was a good agreement between V\text{Al} concentration calculated from thermal conductivity and positron lifetime analysis. On the other hand, V\text{Al} concentration calculated from dissolved oxygen concentration in AlN grain was two orders higher. It was suggested that aluminum octahedrally coordinated to oxygen structure formed below 0.75 at% and they were not affect to phonon scattering.

Key words: aluminum nitride, positron annihilation lifetime, lattice defect, thermal conductivity

1. Introduction
Aluminum nitride (AIN) has excellent properties such as high thermal conductivity, high electrical resistivity and so on [1]. Therefore, AIN is expected to the heat dissipative material of high power devices and light emitting diode (LED) etc. Furthermore, AIN filler is now attracting attention in the resin composite material field from the aspect of thermal conductivity [2]. Properties of AIN ceramics are influenced by grain boundaries and lattice defects in AlN crystal. Especially, thermal conductivity of AIN is decreased by phonon scattering caused by distortion, dislocation, lattice defects, and secondary phase in grain boundaries. Relationship between the lattice defect structure and properties of AIN has been studied widely by many researchers so far [3]-[8]. Harris et al. proposed oxygen related defects structures of aluminum octahedrally coordinated to oxygen in AIN, and the structure changes to an inversion domain boundary with aluminum octahedrally coordinated to oxygen over 0.75 at% oxygen concentration [4].

However, research on behavior in the atomic vacancy concentration is not directly carried out so far. In this work, we have investigated the relation of the lattice defects and properties of AIN in detail using positron annihilation lifetime measurement (PAL). This analysis method can detect atomic vacancy type defects like point defect in crystal with non-destruction and high sensitivity.

2. Experimental
High purity AIN powder produced by Tokuyama Corp. (average particle size of 1.25 μm, Oxygen 0.85 wt%, Carbon 300 ppm, Ca 10 ppm, Si 9 ppm, Fe 5 ppm) was used as starting material. Ca3Al2O6 (average particle size of 1.54 μm) was used as sintering additive. The amount of additive was changed from 0.0 to 4.8 wt% of AlN powder. Mixing of AlN powder and the sintering additive was carried out by a planetary ball mill for 90 min using ethanol as solvent. Plastic pot and Al2O3 ball (diameter 10 mm) was used to mill. After mixing and drying, the uniform particle size of the mixed powder was obtained by sieve method. Disks of 30 mm in diameter and 5 mm in thickness were prepared using a cold isostatic press of 250 MPa. Sintered disks of 30 mm in diameter and 4 mm in thickness were obtained at 2153 K for 30 hours in reduced N2 atmosphere and an AIN container.

Thermal conductivity was measured by laser flash method using Rigaku LF/TCM-FA8510B. A commercial hot gas extraction analyzer was used to evaluate the amount of oxygen. The microstructure was analyzed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). PAL measurements were performed using a conventional fast-fast coincidence system with a time resolution of FWHM = 200 ps and FW(1/10)M = 400 ps [9]. The positron source was about 600 k Bq 22NaCl deposited between two Kapton films of 7.5 μm in thickness. The positron source was sandwiched between a pair of AIN specimens, and these specimens and the positron source
were wrapped with an aluminum foil which was grounded to avoid the effects resulting from a charge-up of the AlN specimens by positron irradiation. Nearly $4 \times 10^5$ counts were accumulated at room temperature for each lifetime spectrum. The source component in a lifetime spectrum was composed of two lifetime components at room temperature, and the values of lifetimes and intensities of these components were 1990 ps and 1.7 % for the longer source component and 365 ps and 22.5 % for the shorter source component. After subtraction of these source components one-component (mean lifetime) and two-components analyses were performed using a nonlinear least-square fitting.

3. Results and discussion

Fig.1 shows the relation between thermal conductivity of six AlN specimens and positron mean lifetime, and oxygen concentration in AlN grain. Positron mean lifetime was good correlation to thermal conductivity of AlN as well as oxygen concentration. Therefore, positron mean lifetime can detects the vacancy in AlN crystal related to thermal conductivity.

Furthermore, from the lifetime fitting analysis, two lifetime components were detected in AlN specimens under 211 W/mK as shown in Fig.2. Two components lifetime fitting suggested the presence of aluminum-site vacancy type lattice defect ($V_{Al}$) produced by dissolved oxygen during sintering [10]. Longer lifetime components of 230 ps ($\tau -2$) and shorter lifetime of 132 ps ($\tau -1$) were assigned to components of $V_{Al}$ and perfect crystal of AlN, respectively. Intensity of longer lifetime components ($\tau -2$) assigned to $V_{Al}$ was decreased with increasing of thermal conductivity.

It is possible to calculate the concentration of lattice defects in AlN crystal from positron trapping model as shown in formula (1) - (4). The specific trapping rates of $5 \times 10^{14}$ s$^{-1}$ was used [11].

$$\lambda_1 = 1 / \tau_1 \quad (1)$$
$$\lambda_2 = 1 / \tau_2 \quad (2)$$
$$\kappa_d = I_2 ( \lambda_1 - \lambda_2 ) \quad (3)$$
$$C = \kappa_d / \mu \quad (4)$$

where $C$: concentration of lattice defects, $\kappa_d$: Trapping rate(s$^{-1}$), $\mu$: Specific trapping rate(s$^{-1}$), $I_2$: Intensity fraction of vacancy site component, $\lambda$: annihilation rate (s$^{-1}$) ($\lambda_1$: annihilation rate in...
bulk, $\lambda_2$: annihilation rate in vacancy site), $\tau$: positron lifetime (ps) ($\tau_1$: lifetime in bulk, $\tau_2$: lifetime in vacancy site)

From calculation by the positron trapping model, concentration of $V_{Al}$ was estimated $10^{-7}$ in 211 W/mK AlN specimen as shown in Fig.3.

On the other hand, thermal conductivity can describe as formula (5) from the kinetic theory.

$$\kappa = \frac{1}{3} C v l$$  \hspace{1cm} (5)

where $C$ is the heat capacity per unit volume, $v$ is the phonon velocity and $l$ is the phonon mean free path.

$l$ can be obtained using measured $\kappa$ and $C$, and calculated $v$ by Young’s modulus, Poisson’s ratio and density of the AlN specimen. Then the concentration of $V_{Al}$ can be roughly estimated by assuming that single vacancy is situated in a sphere of radius $1/2 l$, and by calculating number of sphere in the AlN unit cells.

Fig.4 shows relation between the thermal conductivity and mean free path of phonons in the AlN specimen. Concentration of $V_{Al}$ in AlN grain was calculated using measured thermal conductivity of AlN specimen. Circle (○) denotes the mean free path, diamond-shaped (◇) denotes the Al-vacancy concentration calculated by the thermal conductivity.

Fig.5 Relation between the thermal conductivity and $V_{Al}$ concentration estimated by three different methods. Circle (●) denotes the results estimated by positron annihilation lifetime measurement, inverted triangle (▼) estimated by thermal conductivity, and triangle (▲) estimated by oxygen concentration in AlN grain.

$V_{Al}$ concentration calculated from thermal conductivity and PAL has good agreement under 200 W/mK. But, in the region over 211 W/mK, $V_{Al}$ concentrations have small different results. It is supposed that this reason is issue of the measurement accuracy of PAL. On the other hand, the result obtained from oxygen concentration in AlN grain had a large different compared with the other results. It is assumed that issue of oxygen concentration measurement and effects of oxide in grain boundary. However, as there are two orders difference of $V_{Al}$ concentration in wide oxygen concentration range, and measurement accuracy of oxygen concentration of AlN is $\sigma < 0.02$ wt%, it is difficult to consider the effect of oxygen measurement. From the SEM and TEM observations, oxides were little or not present in grain boundary as shown in Fig.6 and Fig.7. Therefore, there is a high possibility that oxygen atom is dissolved to AlN crystal.
Grain boundary phase can’t be observed.

Thus, it has possibilities that excess oxygen atom in AlN crystal exists in a different structure from \( V_{\text{Al}} \) and they do not affect to phonon scattering. Also, these results suggest the possibility that aluminum octahedrally coordinated to oxygen structure forms below 0.75 at% oxygen concentration. Thermal conductivity of AlN around room temperature dominated by phonon scattering by coulomb attraction of \( V_{\text{Al}} \) and dissolved oxygen in nitrogen site of AlN crystal was suggested.

![TEM photograph of AlN specimen](image)

**Fig.7** TEM photograph of AlN specimen whose thermal conductivity is 211 W/mK. Oxides were little or no exist in grain boundaries.

4. Conclusion

Positron lifetime measurement was carried out to AlN specimens with high thermal conductivity. Two positron lifetime components were observed at 230 and 132 ps. They were assigned to lifetime components of aluminum site vacancy (\( V_{\text{Al}} \)) and AlN perfect crystal. There was a good correlation between positron mean lifetime and thermal conductivity of AlN. Also, there is a good agreement between the estimated \( V_{\text{Al}} \) concentration from thermal conductivity and positron lifetime analysis. On the other hand, \( V_{\text{Al}} \) concentration calculated from dissolved oxygen was two orders higher. It was suggested that aluminum octahedrally coordinated to oxygen structure formed below 0.75 at% by excess oxygen in AlN, they do not contribute to phonon scattering.

REFERENCES


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