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Efficient particle size control and purification of AlN powder using thermocyclic process, for use in crystal growth

Seong Min Jeong[a], Kang Hyuk Lee[a], Myung Hyun Lee[a], Won Seon Seo[a], Jonghee Hwang[a], Seung Min Kang[b] and Younghee Kim[a]*

[a]*Korea Institute of Ceramic Engineering and Technology, Seoul, Korea*

[b]*Department of Advanced Materials Science and Engineering, Hanseo University, Seosan, Korea*

A thermocyclic process was introduced to increase the particle size and purification of AlN powder for use as a source in growing single crystals. The particle size increase that occurred during thermocyclic process was theoretically verified by thermodynamic analysis. Thermodynamics-driven process conditions were experimentally optimized for producing large particles. The thermocyclic process not only caused particle growth but also improved the purity of the AlN powder. During repetitive sublimation and condensation cycles, the low-boiling, non-condensing impurities were eliminated by vaporization. Chemical analysis confirmed that the amounts of free carbon, oxygen, and metallic impurities were reduced after thermocyclic process. With non-purified and purified AlN powders, we grew bulk crystals of AlN and compared the chemical purity of crystals by SIMS measurement. The experimental result confirmed that AlN crystal grown by purified AlN powder having ~30 mm particle size and 99.999% purity exhibited improved crystal quality.

Key words: AlN powder, Particle size control, Purification, Thermocyclic process, Crystal Growth.

Introduction

Nitrides such as GaN, InN, and AlN are wide-bandgap materials that are suitable for optical devices, especially in the region from blue to ultraviolet light. These nitrides are generally fabricated by heterogeneous growth on sapphire substrates. However, AlN single crystals have recently been commercialized as a next-generation substrate for optical devices [1-2]. AlN has a small mismatch with GaN in the lattice parameter and coefficient of thermal expansion, which remarkably increases its performance and the durability of ultraviolet light emitting diodes (UV-LEDs).

The most feasible fabrication method for single-crystal AlN is physical vapor transport (PVT), which uses high-quality AlN powder as the source [1-5]. However, commercially available AlN powder contains a significant amount of detrimental oxygen, carbon, and metallic impurities. In particular, nitrogen vacancies, boron, carbon, and silicon impurities affect the optical properties of single-crystal AlN [6]. Oxygen impurities cause oxynitrides to evaporate prior to AlN at low temperature, which negatively affects the nucleation process [6]. Other metallic impurities are suspected to form stacking faults in the AlN single crystal. Therefore, in order to grow high-quality single-crystal AlN, it is first necessary to purify commercial AlN powder [6]. Prior to its application in growing single-crystal AlN, the PVT method has been used to produce single-crystal SiC for several decades. The similarity in the synthesis of AlN and SiC is significantly advantageous, as it facilitates the development of AlN growing techniques [7]. To grow SiC single crystals by the PVT method, both the particle size and the packing density of the SiC powder are crucial factors that determine the sublimation rate [8]. Considering the similarity in the sublimation-condensation mechanism in the crystal growths of SiC and AlN, the particle size of AlN powder is also a significant determining factor in the sublimation rate of AlN. The particle size of AlN powder should be carefully controlled. This is especially important in increasing the permeability of vaporized species when AlN crystals are grown using the PVT method, since high-purity AlN powder with a large particle size is required. AlN powder has been synthesized by various methods such as carbothermal reduction [9], self-propagating high-temperature synthesis (SHS) [10], chemical vapor deposition (CVD) [11], and plasma synthesis [12]. However, the resultant AlN powder usually has a particle diameter smaller than 10 μm [10]. Considering the SiC powder used for crystal growth has diameters on the order of 30-300 μm, this particle diameter is too small [13-14]. Granulated AlN powders larger than 100 μm are commercially available. However, these materials are inadequate for crystal growth because they contain Y_2O_3 as a sintering additive. Recently, Kim *et al*. [14] reported quality improvement of single-crystal 4H SiC grown with a

*Corresponding author:
Tel : +82-2-3282-2472
Fax: +82-2-3282-2430
E-mail: yhkokim@kicet.re.kr

purified β-SiC powder source using a thermocyclic process. The micropipe and dislocation density of the single-crystal 4H SiC grown by using the purified β-SiC powder were reduced in comparison to the single-crystal 4H SiC grown from non-purified powder [14]. In this study, we prepared high-purity AlN powder with a large particle size by a thermocyclic process from commercially available powder.

Experimental

Thermocyclic treatment of AlN powder

Thermocyclic treatment was carried out to purify and grow the AlN particles. A sample of 20 g of a commercial AlN powder (H.C. Starck, Germany) was annealed using a thermocyclic process in a graphite crucible under low pressure in a N_2 (10 Torr) atmosphere. The powder was heated to 1750 °C with a heating rate of 15 °C /min, and held for 10 to 120 min. Then, the temperature was increased up to 1950 °C at 2 °C/min and held again. Subsequently, the sample was cooled down to 1750 °C, and then heated up to 1950 °C again for each cycle (Fig. 2). This was repeated three times. High-purity AlN powders with increased particle sizes were obtained as a result. Thermodynamic calculations were carried out using the FactSage^{TM} 6.4 software with the FactPS database [15] to evaluate the atmospheric effect on sublimation at various working pressures.

Crystal growth experiment

The AlN bulk crystals were grown by a PVT process from AlN powder and ultrahigh-purity nitrogen gas at growth temperatures of 2000-2200 °C, and pressures of 0.1760 Torr.

Characterization

X-ray powder diffraction analysis was carried out using an X-ray diffractometer (P/MAX 2200V/PC, Rigaku Corp.) with a Cu target (K_α = 1.54) to identify the crystalline phase of the powder. The shapes and sizes of the particles were observed by a scanning electron microscope (JSM-6700F, JEOL, Japan) and particle size analyzer (Beckman Coulter, Model LS230). The chemical bonding states of the constituent elements before and after purification were analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5000 VERSA PROBE) with monochromatic Al Kα (hν = 1486.6 eV) excitation radiation using a 25 W source power at a 15 kV acceleration voltage. The metal ion contents in the AlN powder after thermocyclic annealing were analyzed by glow discharge mass spectrometry (GDMS) with Ar as the discharge gas. To analyze the metal ion contents in the AlN crystal, time-of-flight secondary ion mass spectrometry (TOF-SIMS, ionTOF, TOF-SIMS-5) was performed with a Cs^+ primary ion source.

Results and Discussion

It is well known that AlN completely dissociates in the vapor phase to N_2 and Al through following reaction [15]:

$$AlN(s) = Al(g) + 1/2N_2(g) \quad (1)$$

The sublimation of AlN typically occurs at temperatures much higher than 2000 °C under atmospheric pressure [15]. At such high temperatures, the chemical reaction is strongly governed by thermodynamics rather than reaction kinetics and mass transport. Therefore, a thermodynamic analysis could reveal the influence of process conditions on vapor-solid equilibrium, especially at high temperatures, which is advantageous in identifying optimal process conditions.

In order to evaluate the atmospheric effect on sublimation at various working pressures in this study, thermodynamic calculations were carried out using the FactSage^{TM} 6.4 software with the FactPS database [16]. It was assumed that the gaseous species in the initial conditions were Ar or N_2. As a result, the sublimation of AlN at 1 atm was estimated to be complete at 2360.6 °C under Ar and 2412.7 °C under N_2. With decreasing

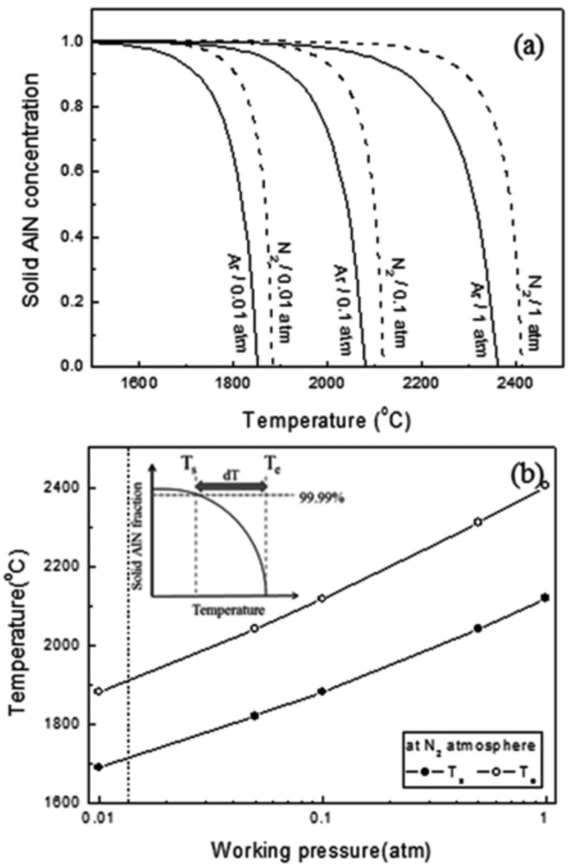


Fig. 1. (a) Solidus line for AlN under various atmospheres (b) Change in vaporization temperature with working pressure under a N_2 atmosphere.

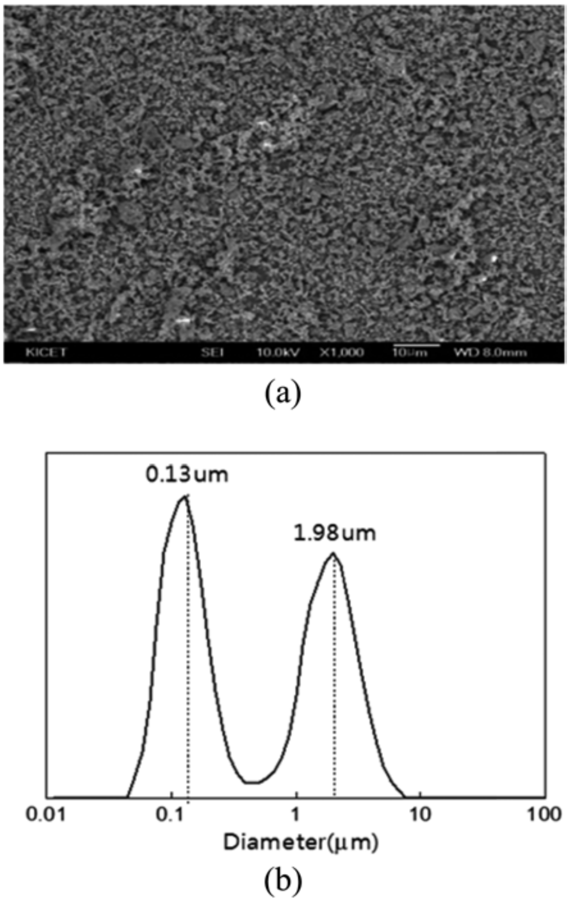


Fig. 2. (a) SEM image (b) particle size distribution of AlN raw material.

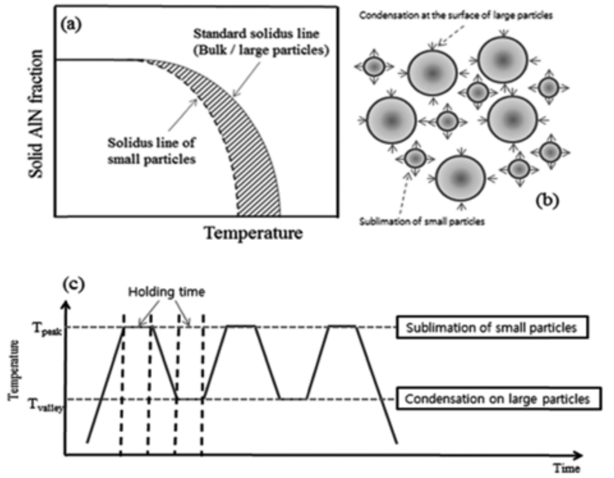


Fig. 3. (a) Schematic diagram of the effect of particle size on the vaporization temperature. (b) Schematic diagram of simultaneous processes of sublimation and recondensation. (c) Schematic diagram of temperature control in thermocyclic annealing.

working pressure, the sublimation temperatures for AlN changed remarkably under Ar and N_2 atmospheres. As shown in Fig. 1(a), AlN could be sublimed, even at temperatures lower than 1900 ºC, if the working pressure was lower than 0.01 atm under both atmos-pheres. In all cases, as shown in Fig. 1(a), however, the sublimation of AlN under a N_2 atmosphere showed lower and narrower transition ranges compared to that under an Ar atmosphere. This result shows that the sublimation temperature for AlN is affected by the type of atmos-phere used. Furthermore, Fig. 1(a) also suggests that AlN should be sublimed and condensed with small temperature fluctuations under a N_2 atmosphere. With the same temperature change, a higher production yield would be thermodynamically expected under a N_2 atmosphere. Hence, we fixed the atmospheric gas as N_2 in subsequent thermodynamic calculations.

Fig. 1(b) shows that the sublimation temperature of AlN varies with the working pressure. In Fig. 1(b), the sublimation of AlN was quantitatively evaluated using the temperature for the start of the sublimation and the temperature for its completion. The starting temperature for the sublimation, T_s, was defined as the temperature where 99.99% of the AlN is present as a solid phase. The completed temperature of the sublimation of AlN was defined as T_e. Fig. 1(b) shows that both T_s and T_e increase in proportion to the logarithm of the working pressure. It was also interesting to note that the temperature gap between T_s and T_e increased slightly with increasing working pressure. From thermodynamic modeling, the working pressure was set as low as possible. This has the advantage of minimizing processing costs by lowering the sublimation temperature.

Considering the thermodynamic calculation results, thermocyclic annealing was conducted using a commercial AlN powder under a low pressure in N_2 (10 Torr) atmosphere. A sample of a commercial AlN powder was treated using thermocyclic process in a graphite crucible.

Fig. 2 shows the particle size distribution based on SEM images of AlN powder before the thermocyclic process. The raw AlN powder showed a bimodal particle size distribution comprised of a mixture of 0.13 mm and 1.98 mm sized particles. It is interesting to note that the bimodal powder with a mixture of small particles could be transformed into a powder comprised of uniform-sized larger particles (Fig. 2b). Since the vaporization of AlN particles is influenced by the particle sizes, the solidus line for a small AlN particle should be shifted to a lower temperature, as represented in Fig. 3(a). The sublimation of small particles and their condensation into large particles could occur simultaneously at a certain constant temperature, as illustrated in Fig. 3(b). Therefore, it can be concluded that the sublimed small particles act as sources and the stable large particles act as seeds for the growth of each particle.

Fig. 3(c) represents a schematic of the thermocyclic procedure with heating cycles used in this study. With this technique, more powders with small particle sizes could be vaporized at the "peak temperature, and then more vapor could be condensed on the large particles at

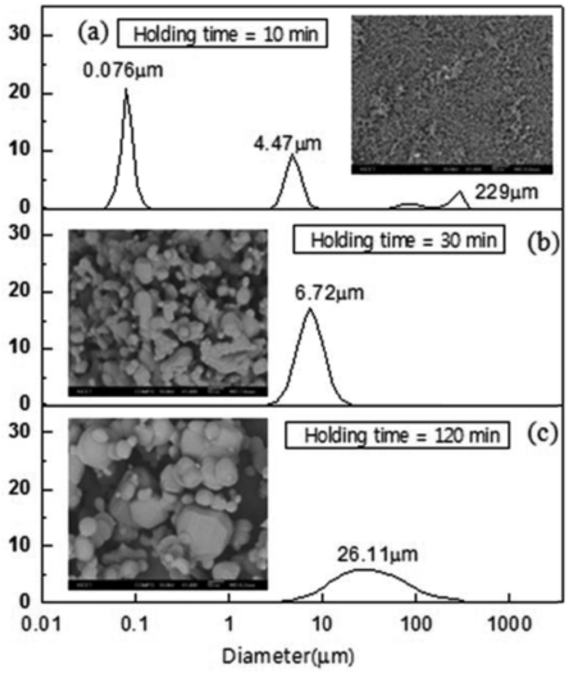
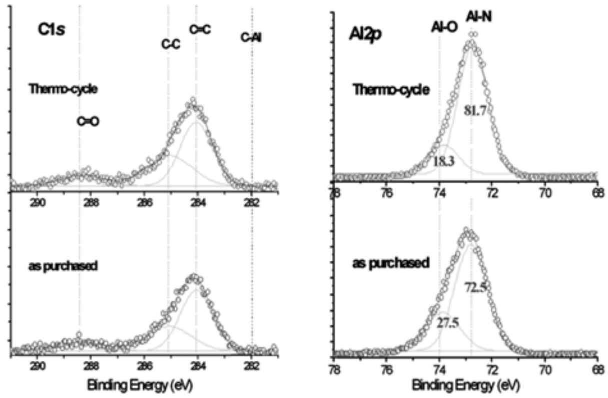


Fig. 4. SEM images showing particle size distribution of an AlN powder after thermocyclic annealing with various holding times. (a) holding time =10 min. (b) holding time = 30 min. (c) holding time = 120 min.



(a) (b)

Fig. 5. Fig. 4.Chemical state of the AlN powder analyzed by XPS: (a) Al2p XPS spectra and (b) C1s XPS spectra.

the “valley temperature. Therefore, the powder scale-up would be expected to proceed in a shorter time.

The peak and the valley temperatures in the thermocyclic process were initially set to T_e and T_s, respectively, which were obtained by thermodynamic modeling, as shown in Fig. 1(b). After several trial-and-error experiments, the peak and the valley temperatures were experimentally adjusted to 1750 ^oC and 1950 ^oC, respectively. The holding times at the peak and the valley temperature were set to be equal.

Figs. 4(a)-4(c) show the particle size distributions of the AlN powders with SEM images after thermocyclic process for various holding times of 10, 30, and 120 min. As shown in Fig. 4(a), the particles in the thermocyclically annealed powder still have a bimodal distribution.

The large particles of 229 mm in Fig. 4(a) were assumed to be agglomerated particles. Compared to the particle size distribution of the raw powder shown in Fig. 2(a), Fig. 4(a) confirms that 10 min of holding time was not sufficient to grow particle size. However, thermocyclic treatment using a longer holding time, as shown in Figs. 4(b) and 4(c), proved to be effective. In Fig. 4(b) with a 30 min holding time, the particle size of the powder ranged from ~ 2.5 to ~ 18 mm and the average value was 6.72 μm. The powder thermocyclically annealed with a holding time of 120 min had an even larger diameter of 26.11 μm, which could not be achieved using a normal annealing technique. However, the particle size distribution shown in Fig. 4(c) was quite large, and a sieving process was required to collect uniform

(a)

(b)

(c)

Fig. 6 (a) As purchased AlN powder (b) Purified AlN powder using themocyclic process (c) AlN bulk crystal grown on the graphite lid using purified AlN powder.

Table 1. GDMS analysis of AlN powders (all values in ppm wt.).

Elements / AlN Powder	B	Mg	P	S	Cr	Mn	Fe	Ni
Non purified	0.35	8.6	0.99	1.6	7.9	1.1	18	13
Purified	0.25	0.36	< 0.1	0.92	< 0.5	0.08	< 1	< 0.5

particles. In general, the particle size of the powder was enlarged through the thermocyclic process, which led to an enhanced sublimation rate of the AlN source powder. The AlN powder sublimed from the bottom of the crucible, which was kept at a relatively higher temperature with respect to the seed, forming gaseous species of Al and N_2. The large particle size can help to facilitate vapor-phase transport with large porosity to the top of the crucible, where the crystals grew by re-crystallization.

Fig. 5 shows the results of an analysis of the chemical components in powder before and after thermocyclic annealing, which was performed by narrow scanning of AlN's XPS main Al2p and C1s spectra. The Al2p XPS spectra of AlN powder in Fig. 5(a) show Al-N bonding with a binding energy of ~ 73 eV [17]. The analysis results of Al2p spectra confirmed that thermocyclically annealed and as-purchased powder had an Al-O binding energy of ~ 74 eV. XPS data of the as-purchased powder showed that the Al-O peak shifted toward the high-binding-energy side because of the high oxygen content. The results of XPS analysis confirmed the existence of Al_2O_3. However, thermocyclically annealed AlN powder had less Al-O content, and the Al-N bonding increased to more than 81%. This could be attributed to the evaporation of CO gas during the sublimation-condensation process. It is well known that carbon and oxygen react to form CO gas above 1600 °C. The C1s XPS spectra of both as-purchased and thermocyclically annealed powders in Fig. 5(b) showed C = O, C-C, and C = C peaks at binding energies of 288 eV, 285 eV, and 284 eV, respectively. From C1s peak analysis, the carbon impurity was identified as free carbon or graphite. No Al-C bond was found. The XPS analysis of the chemical components of AlN powder before and after thermocyclic treatment confirmed that the purity of the AlN increased during the purification process, as impurities such as carbon and oxygen, which can cause various defects, decreased. The thermocycling not only caused particle growth but also improved the purity to 99.999% based on the GDMS analysis data, which showed decreasing amounts of such metallic impurities as Mg, Cr, Fe, and Ni. During repetitive sublimation and condensation cycles, the residual oxygen reacted with extra carbon, and the metallic impurities were eliminated by vaporization (Table 1). Metallic impurities within the powder were reduced, which led to reduced parasitic nucleation on the seed during the crystal growing process.

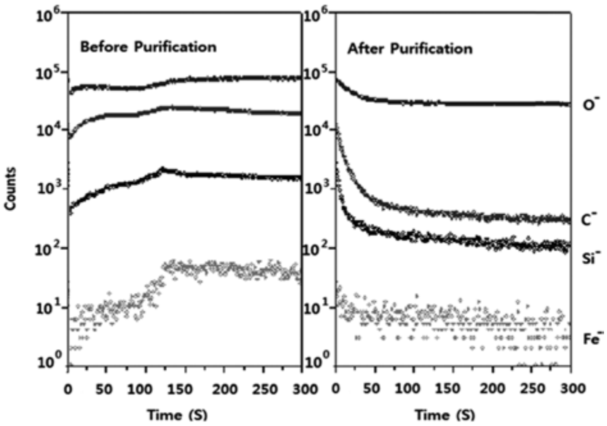


Fig. 7. SIMS analysis data of (a) As purchased AlN powder (b) Purified AlN powder using themocyclic process.

Figs. 7 (a) and (b) compare the impurities contents in AlN bulk crystals measured by TOF-SIMS. The AlN bulk crystal grown by purified powder using thermocyclic process showed much lower content of O, C, Si, and Fe impurities. The presence of Si atoms within the powder is especially problematic, as Si atoms can replace Al atoms in the lattice and produce a lattice dislocation. Also, various metallic impurities within the powder were reduced during the purification, which reduced parasitic nucleation within the seed and growth interface.

Conclusions

This study presents a successful thermocyclic annealing technique to control the particle size and purification of an AlN powder for use in AlN crystal growth. Thermodynamic modeling was shown to be effective method to find optimal process condition of AlN powder preparation. The purified AlN powder showed decreased oxygen, carbon and metallic impurities. The AlN crystals grown from purified AlN powder having ~ 30 mm particle size and 99.999% purity exhibited improved quality over crystals grown from as-purchased AlN powder. The results of this study suggest that thermocyclic annealing can be useful for efficient particle size control and purification of AlN powder for use in crystal growth.

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