Synthesis of morphology controllable aluminum nitride by direct nitridation of γ-AlOOH in the presence of N₂H₄ and their sintering behavior

Angga Hermawan, HyoungWon Son, Yusuke Asakura, Takao Mori and Shu Yin

ABSTRACT
Direct nitridation process has been performed to synthesize morphology controllable aluminum nitrides (AlN). Three different morphologies of γ-AlOOH were treated under NH₃ flow at 1400°C for 4 h. Hydrazine (N₂H₄) was employed in this study as a nitriding agent to promote nitridation reaction. In the presence of hydrazine, a high purity of aluminum nitride (AlN) could be achieved with less than 5 wt.% of oxygen impurities. Interestingly, after being exposed to elevated temperatures, the initial morphology was still retained. Whereas the TEM measurement indicated surface roughening due to the release of H₂O. The investigation of sintering behavior of the prepared AlN powders revealed that plate-like morphology had the lowest shrinkage completing temperature (1574°C).

1. Introduction
In area of industrial ceramics, aluminum nitride (AlN), especially in form of powder, has been recognized as attractive material for applications on electronic packaging, opto-electronic device and substrate for high-integrated electronic circuit, because of its excellent physicochemical properties, including high thermal conductivity (280 W/m.K), high electrical resistivity (>$10^6$ Ωm), low thermal expansion coefficient (4.6 × 10⁻⁶/K at 20–500°C), wide band gap (6.02 eV), high thermal stability in inert atmosphere and chemically stable [1,2]. There are several established methods to synthesize AlN powder, such as direct nitridation of Al source under N₂ and NH₃ gas flow [3], carbothermal reduction nitridation (CRN) [4], self-sustain high-temperature synthesis (SHS) [5], gas-reduction nitridation [6], etc. Among them, direct nitridation is the most frequent method to synthesize AlN powder, considering the low cost and simple nitridation technique. Hence, due to the low melting temperature of most metals, the metal aggregation greatly occurred resulting uncompleted nitridation process because of the lack diffusion access of nitridation gases [7–9]. It is well agreed that the final morphology of AlN could induce some novel properties. Therefore, the selection of precursor is a critical factor to synthesize morphology controllable and well-distributed AlN powder.

Furthermore, there are many precursors have been utilized to produce high-purity AlN, such as Al₂O₃ [3], Al₂S₃ [10], (NH₄)₃AlF₆ [11], aluminum citrate [12],...
and Al(OH)₃ [13]. It was reported that starting materials influenced the nitridation reactivity. To the extent of our best knowledge, only a few studies about the use of boehmite (γ-AlOOH) as a nitridation precursor have been reported. Whereas, the boehmite has larger Gibbs free energy compared to that of alumina at the same temperature, indicating its higher reactivity [14] and also economically profitable since alumina production is derived from γ-AlOOH. Additionally, various unique morphologies of γ-AlOOH have been realized by using hydrothermal treatment [15–18], so that production of AlN powder with controllable morphology may be possible using γ-AlOOH as a precursor. Nitridation agent is next extensive factor to boost up nitridation reactivity thus lowering the nitridation temperature and shortens the nitridation time. The ammonium halide mineralizers, i.e. NH₄X (X = F, Cl, Br, I) were studied to increase both yields of the obtained GaN and thermal activation of starting materials under NH₃ flow [19]. Nonetheless, the solid-solid-gas reaction between starting material and mineralizer could break the initial morphology led to the change in final particle size. Therefore, a solid-liquid reaction may solve for retaining the morphology of starting materials. One of the candidates is hydrazine as it can compromise the largely negative standard Gibbs energy owned by the starting materials due to its highly positive standard Gibbs free energy and its decomposition products such as NH₂· radicals is very reactive [20]. Understanding the sintering behavior of AlN is essential for product commercialization. A high density of AlN sintering body may only be achieved by applying high sintering temperature above 1900°C [21], and sintering aids are added to accelerate the sintering process [22,23]. The newly developed Spark Plasma Sintering (SPS) exhibits rapid densification of many ceramics at low temperatures. Basically, the applied direct pulsed current generates spark discharge and plasma in particle interfaces, lead to particle diffusion and consequently result in the fully densified sintering body [24]. In this paper, we reported the study of the synthesis of AlN with controllable morphology using direct nitridation method from the γ-AlOOH precursor in the absence and presence of hydrazine. The large chemical energy of hydrazine improved the nitridation rate, leading to lower oxygen contents. The possible nitridation mechanism of the present study and sintering behavior of the controllable morphology of AlN were also investigated.

2. Experimental

2.1. Synthesis of precursors

Two different morphologies of boehmite (nest-like and plate-like) were synthesized by a simple hydrothermal method. Nest-like AlOOH was prepared by dissolving 0.1 M of Al(NO₃)₃ · 9H₂O in 50 mL of distilled water. After stirring for 15 min, 0.02 M of CTAB (cetyltrimethylammonium bromide) was introduced into the solution, then stirred again until a homogeneous solution was obtained. The solution was transferred into a Teflon-lined autoclave and heated in a furnace at 200°C for 12 h.

Synthesis process of plate-like AlOOH was quite similar with nest-like AlOOH. First, 0.1 M of Al(NO₃)₃ · 9H₂O was dissolved into 50 mL of distilled water and stirred for 15 min. 0.5 M of Na₂CO₃ was slowly added into the solution to give a lactic solution, and the mixture was introduced into 50 mL Teflon-lined followed by heating at 200°C for 24 h. After cooling down to room temperature, the product was washed and dried at 60°C for 12 h.

In addition, a commercially available AlOOH with needle-like morphology from Mitsubishi Gas Chemical (Code: BMI 090314) was also utilized.

2.2. Synthesis of aluminum nitride powders

As-prepared AlOOH (nest-like and plate-like) and as-received needle-like AlOOH were used as precursors to synthesize aluminum nitride powders. 0.2 g of precursors were placed in an alumina boat and nitridated in an electrical furnace at 1400°C for 4 h with 200 mL/min of NH₃ flow. N₂ gas was introduced at 200°C upon cooling process until the temperature reached to room temperature to remove the excess NH₃. To understand the effect of nitriding agent, 0.6 mL of hydrazine (N₂H₄) was also subsequently mixed with the precursors in prior to the nitridation process.

2.3. SPS sintering

Densification of AlN powder was performed using spark plasma sintering (SPS, FUJI DENPA KOKI SPS-1080). The SPS sintering of as-prepared AlN was carried out at 1600°C for 20 min with the heating rate of 100°C/min and pressure constantly kept at 80 MPa. Packing of AlN powders to graphite die was carried out inside a glove box under Argon atmosphere at 1 atm to prevent oxidation of the AlN. In addition, N₂ gas was purged twice before the sintering to remove excessive moisture and oxygen.

2.4. Characterizations

X-Ray diffraction analysis (XRD, Bruker D2 PHASER) with CuKα radiation (λ = 0.1542 nm) was used to identify the crystalline phase of the samples. The morphology of products before and after nitridation was observed by scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, JEM-2010). The specific
surface area was determined by BET method using \( \text{N}_2 \) adsorption measurement (Quantachrome, NOVA 4200e). Oxygen content was measured by oxygen/nitrogen analyzer (HORIBA EMGA 920), after correcting calibration curve of Si\(_3\)N\(_4\) (JCRM R006, O content is 1.18 wt.% and N content is 38.98 wt.% ) as a standard sample.

3. Results and discussion

3.1. Synthesis of precursors

Figure 1 shows the XRD patterns of \( \gamma \)-AlOOH precursors. It was clearly found that all diffraction peaks from three different morphologies could be indexed to boehmite (\( \gamma \)-AlOOH), based on JCPDS no. 21–1307. Additionally, no impurity peaks were observed in the needle-like and nest-like particle, indicating the precursors were pure \( \gamma \)-AlOOH. However, the appeared impurity peaks in plate-like morphology at 13°, 16°, 26.5°, 32°, 34° were corresponded to NaAl(OH)\(_2\)(CO\(_3\)) as the result of the reaction between Al\(^{3+}\), OH\(^-\) and Na\(_2\)CO\(_3\). Sharp peaks indicated the good crystallinity of the samples. The plate-like possessed the highest crystallinity and in the opposite, nest-like had the lowest crystallinity.

Morphology of particle can be tuned using surfactants since their chemical active surface is effective to control the particle orientation and particle growth. Figure 2 shows the SEM images of the AlOOH precursors consisted of three different morphologies, i.e. needle like, nest like and plate like. The latter two morphologies were obtained by the hydrothermal synthesis using different surfactants. For the preparation of hydroxide nanorods and nanotubes, CTAB was often be used due to its capping ability that could assist in rod formation and stabilizing the rod [25,26]. Therefore, in our sample, the nest-like particle was considered of consisting of several rod-like structures which bundled together. The possible formation mechanism of nest-like morphology might be explained as follow [27]:

\[
\text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \rightarrow \text{AlO}_2^- + 4\text{H}^+ + 3\text{NO}_3^- + 7\text{H}_2\text{O} 
\]

\[
\text{AlO}_2^- + \text{H}_2\text{O} \rightarrow \gamma - \text{AlOOH} + \text{OH}^- 
\]

When Al\((\text{NO}_3\text{)})_3 \cdot 9\text{H}_2\text{O} \) was dissolved in deionized water, followed by addition of CTAB, then treated by a hydrothermal process at 200°C, AlO\(_2^-\) nuclei started to be formed. At this stage, a positively charged cation surfactant (CTA\(^+\)) of CTAB with a long hydrophobic tail was adsorbed on the surface of AlO\(_2^-\) nuclei by electrostatic charge interaction [17,28]. Then, they assembled each other to form nanorod under hydrothermal condition. In final, each edge of nanorod attached to another edge of nanorod to form nest-like morphology.

Figure 1. XRD patterns of (a) needle-like; (b) nest-like and (c) plate-like AlOOH.

Figure 2. SEM images of (a) needle-like; (b) nest-like and (c) plate-like AlOOH.
In case of plate-like morphology, it was obtained in Na$_2$CO$_3$ aqueous solution. As reported by Alagappan et. al. [29], Na$_2$CO$_3$ played a role as mineralizer in the hydrothermal process. As Na$_2$CO$_3$ was introduced, OH$^-$ ions were continuously produced through the following process:

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCO}_3^- + \text{OH}^- \quad (3)$$

$$\text{HCO}_3^- + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 + \text{OH}^- \quad (4)$$

Since we also utilized Al(NO$_3$)$_3$·9H$_2$O as an aluminum source, the reactions (1) and (2) were supposed to occur during the hydrothermal process. To note, a milky solution that found after the addition of Na$_2$CO$_3$ indicated some chemical reactions may occur to AlO$_2^-$ ions to form larger species. The excess hydroxyl ions (OH$^-$) from reactions (3) and (4) caused the pH increment toward a basic condition. Besides, as investigated in the previous study [30], amount of OH$^-$ ions was effective to produce the plate-like of ZnO. Therefore, the same mechanism might be considered in the formation of plate-like AlOOH.

### 3.2. Synthesis of morphology controllable AlN

The XRD patterns of γ-AlOOH after nitridation process at 1400°C for 4 h in NH$_3$ flow are shown in Figure 3. Figure 3(a–c) represented the samples that nitridated without using hydrazine, meanwhile Figure 3(d–f) showed the nitridation samples in the presence of hydrazine. There was an enhancement in the XRD peaks intensity of AlN if hydrazine was introduced in the nitridation system, implying that small amount of hydrazine could increase the nitridation rate. The possible reason was that hydrazine has a positive Gibbs energy formation that could compensate the large negative Gibbs energy formations of hydroxide precursors, nitrides and water vapor [31] so that the Gibbs energy change ($\Delta G^o$) of the reaction became lower than those reactions without hydrazine addition. Additionally, the appearing peaks can be indexed to hexagonal aluminum nitride (JCPDS Card No. 25–1133) and no remarkable impurities peak was observed.

Figure 4(a–c) shows the TEM images of the samples without additive of hydrazine. Figure 4(d–f) shows the morphologies of the samples with the utilization of 0.6 ml of hydrazine. The shapes of morphology were still retained even after being exposed at 1400°C, indicating that various morphologies of nitride could be synthesized through the present method. However, the release of H$_2$O from
boehmite during the nitridation reaction led to a surface coarsening.

Table 1 summarizes the oxygen and nitrogen contents of the nitridation products. It showed that oxygen content was much higher in the absence of hydrazine. Nevertheless, oxygen content was reduced as low as 4 wt. % when the hydrazine was introduced in the nitridation process. The low oxygen content was analyzed as the result of the high reactivity of NH\textsubscript{2}\textsuperscript{−} radical from hydrazine [20]. Furthermore, the lowest oxygen content was owned by nest-like morphology since it had low crystallinity that could be confirmed by XRD measurement in Figure 1. Amorphous phase and low crystallinity precursors were believed to have stronger nitridation reactivity than that of high crystalline one [32].

We proposed a possible nitridation mechanism based on the XRD analysis for the plate-like samples nitridated at 600–1400°C in the presence of hydrazine (Figure S1, Supplementary information). It was noticed that below 1000°C, γ-AlOOH transformed into γ-Al\textsubscript{2}O\textsubscript{3} with low crystallinity and there were no detectable peaks of an intermediate phase. There is a possibility that hydrazine may be dissociatively adsorbed by the γ-Al\textsubscript{2}O\textsubscript{3} surface as proposed by Lee [33]:

\[
2\text{AlOOH} + \text{N}_2\text{H}_4 \rightarrow \text{Al}_2\text{O}_3 + 2\text{NH}_2\cdot \cdot \cdot_{\text{ads}} + \text{H}_2\text{O} \tag{5}
\]

When the temperature reached 1000°C, NH\textsubscript{2}\textsuperscript{−} which adsorbed on γ-Al\textsubscript{2}O\textsubscript{3} reacted with NH\textsubscript{3} gas to form aluminum nitride, and ammonia (NH\textsubscript{3}\textsuperscript{+}) was subsequently formed by reaction between adsorbed species (H\textsubscript{ads} and NH\textsubscript{2}ads) as proposed by Pakdehi [34]:

\[
\text{Al}_2\text{O}_3 + \text{NH}_2\cdot \cdot \cdot_{\text{ads}} + \text{NH}_3 \\
\rightarrow 2\text{AlN} + 2\text{H}_2\text{O} + \text{H}_{\text{ads}} + \frac{1}{2}\text{O}_2 \tag{6}
\]

\[
\text{H}_{\text{ads}} + \text{NH}_2\cdot \cdot \cdot_{\text{ads}} \rightarrow \text{NH}_3\textsuperscript{+} \tag{7}
\]

Therefore, the overall reaction should be:

\[
2\text{AlOOH} + \text{N}_2\text{H}_4 + \text{NH}_3 \rightarrow 2\text{AlN} + 3\text{H}_2\text{O} + \text{NH}_3\textsuperscript{+} + \frac{1}{2}\text{O}_2 \tag{8}
\]

While for the nitridation reaction without the addition of hydrazine is as follows:

\[
\text{AlOOH} + \text{NH}_3 \rightarrow \text{AlN} + 2\text{H}_2\text{O} \tag{9}
\]

The small amount of hydrazine should be taken into account to predict that reactions 6, 7 and 8 might not sustainably occur. At the same point when hydrazine was completely decomposed, the direct reaction of alumina and ammonia might be taken place. It was also possible that the utilization of N\textsubscript{2}H\textsubscript{4} might play a role in reducing the required thermal energy for the nitridation due to its large Gibbs free energy, and therefore the nitridation process can be done in relatively low temperature [35]. However, the stoichiometry of the nitridation mechanism needed further investigations because in some cases the decomposition pathway may be different due to the nature of the substrate surface. Even though there were no evidence of the intermediate phase formation such as Al\textsubscript{2}O\textsubscript{3} during the treatment, it might still form before it was fully transformed to AlN [33]. Besides, as observed in Figure 1, the plate-like AlOOH also includes NaAl(OH)\textsubscript{2}CO\textsubscript{3} impurities, but the nitridation product was only a single phase of h-AlN. Based on the earlier study [36], NaOH evaporated at the temperature above 300 °C. Accordingly, the possible reaction of NaAl(OH)\textsubscript{2}CO\textsubscript{3} during the nitridation is clarified as follows:

\[
\text{NaAl(OH)}_2\text{CO}_3 + \text{NH}_3 \rightarrow \text{AlN}_{(s)} + 2\text{H}_2\text{O}_{(g)} \
+ \text{CO}_{2(g)} + \text{NaOH}_{(g)} \tag{10}
\]

Finally, the present method emphasized the possibility of the AlN powder synthesis with various unique morphologies at relatively low temperature by using morphology controllable γ-AlOOH as a precursor and hydrazine as a nitriding agent. Though experimentally promising, the hydrazine utilization may become a practical challenge, as it is toxic and flammable material. Thus, to increase the safety, the hydrazine solution can be supplied at a low concentration below the explosion limit.

\[\text{3.3. Sintering behavior of morphology controllable AlN}\]

The synthesized AlN powders using additional hydrazine and a commercial AlN (WAKO Chemical) were utilized in the SPS process without any sintering aids. Figure 5 shows the axial displacement of the AlN powder during the SPS sintering process. The minimum axial displacement indicates the initial shrinkage temperature. Table 2 summarized the shrinkage...
temperature of different morphology of AlN. It showed that nest-like AlN had the lowest initial shrinkage temperature (1099°C) and needle-like AlN had the highest one (1170°C). Still, these two morphologies required more than 1600°C to complete the densification, while for commercial AlN and plate-like AlN, the shrinkage was completed at 1579°C and 1574°C, respectively. In other words, the fully-sintered body of the additive-free commercial and plate-like AlN can be achieved under the pressure of 80 MPa below 1600°C. Interestingly, it was found that the shrinkage completing temperatures of these two AlN powders were lower than that of previous result [37]. The results suggested that particle size and morphology may influence the sintering behavior of AlN powders. Since the result also showed that the obtained density exceeded than the theoretical density (3.26 g·cm$^{-3}$), XRD measurement of sintering body was carried out to confirm the possibility of second phase existence. The result is shown in Figure 6. A noticeable peak of γ-AlON (3.67 g·cm$^{-3}$) could be observed in addition to the h-AlN phase, suggesting that the γ-AlON phase might be induced by the reaction between Al$_2$O$_3$ and AlN at a temperature of 1000°C or above improving the density of the sintered body. The effect of γ-AlON phase on the sample shrinkage is illustrated in Figure S2. At below 1300°C, the γ-AlON phase play a major role on shrinking the AlN powder; and above the 1300°C, the shrinkage is mostly governed by sintering temperature. But, it is difficult to clearly distinguish the effect of γ-AlON and sintering temperature on the AlN shrinkage since the formation and shrinkage of γ-AlON and initial shrinkage of AlN are probably occurred at the same time. Additionally, although oxygen amount in plate-like morphology is lower than that of the commercial sample, the peak intensity of the γ-AlON in the plate-like morphology is larger than that of a commercial one. This may suggest that the plate morphology facilitates the solid-state phase transformation. The interface contacts among the h-AlN particles provide the site for γ-AlON phase formation and thus the probability of contact among h-AlN particles regulates the rate of γ-AlON phase formation. In this study, plate-like AlN may have larger and more effective contact area than commercial AlN (proven by their specific surface area), led to the more γ-AlON phase in the sintered AlN body.

4. Conclusions
Aluminum nitride powders were successfully synthesized at relatively moderate temperatures with no notable change in the initial morphology of the precursors. N$_2$H$_4$ influenced the nitridation reactivity due to its decomposition product (NH$_2$·) is high active radical. Direct nitridation of the γ-AlOOH precursors in ammonia flow showed a promising method to fabricate low impurity aluminum nitride powders with controllable morphologies, which showed different sintering behavior, especially on the shrinkage temperature.

Acknowledgments
This research was partly supported by the JSPS KAKENHI Grant Number JP16H06439 and JP16H06441 (Grant-in-Aid for Scientific Research on Innovative Areas), and the Dynamic Alliance for Open Innovations Bridging Human, Environment and Materials, the Cooperative Research Program of “Network Joint Research Center for Materials and Devices”. The authors acknowledge the financial support from Hatano Foundation Scholarship.

Disclosure statement
No potential conflict of interest was reported by the authors.
Funding

This research was partly supported by the JSPS KAKENHI [Grant Numbers JP16H06439 and JP16H06441] (Grant-in-Aid for Scientific Research on Innovative Areas), and the Dynamic Alliance for Open Innovations Bridging Human, Environment and Materials, the Cooperative Research Program of “Network Joint Research Center for Materials and Devices”.

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