

# Formation Mechanism of Aluminum Nitride Powder via Organic Precursor Prepared from Anhydrous Aluminum Chloride and Ethylenediamine

by

Masataka KANO\*, Takeo HYODO\*\*, Yasuhiro SHIMIZU\*

and Makoto EGASHIRA\*\*

Synthesis of AlN powder via an organic precursor prepared from anhydrous aluminum chloride and ethylenediamine has been investigated to establish a simple and low-cost process. A brownish white solid product precipitated rapidly by simply mixing anhydrous aluminum chloride into ethylenediamine at room temperature in flowing dry N<sub>2</sub>. Any crystallized compounds were not formed from the resulting organic precursor after calcination at 800°C for 5 h in flowing dry N<sub>2</sub>, but formation of amorphous AlN was suggested from the FT-IR spectroscopic analysis. Crystallized AlN powder could be synthesized from the precursor after calcination at 1200°C for 5 h in flowing dry N<sub>2</sub>. The crystallite size of AlN powder was less than 25 nm, but the particle size was in the range of 60-100 μm due to agglomeration of fine particles under the present synthesis conditions.

## 1. Introduction

Recent progress in technology for integrated circuits and power supply units has increased demand for silicon-compatible substrates with the thermal conductivity superior to that of conventional alumina substrates. Besides aluminum nitride (AlN), beryllium oxide and silicon carbide are possible candidates from the viewpoint of thermal conductivity. But, the use of these two materials is limited from potential toxicity in case of beryllium oxide and from high dielectric constant for silicon carbide relative to that of AlN. In addition to the high thermal conductivity, high electrical resistivity and thermal expansion coefficient comparable to that of silicon make AlN a more attractive material for the substrates, and therefore the application of AlN substrates has been expanding into various fields.

AlN powder is now prepared commercially either by direct nitridation of metallic aluminum or by carbothermal reduction-nitridation of alumina. However, grinding process is indispensable for the former, resulting in an increase in oxygen content in the powder. The increase in

the oxygen content is the main cause for a decrease in thermal conductivity of AlN ceramics<sup>1), 2)</sup>, and therefore new preparation process to reduce oxygen content in the resulting powder is highly requested. On the other hand, the latter requires high-purity alumina powder and reactions in the temperature range of 1500-2000°C, both of which lead to a rise in fabrication cost.

Thus, numerous efforts have so far been directed to developing new preparation methods of fine AlN powder. Typical examples are synthesis of fine AlN powder from Al powder by combined nitridation in fluidized- and packed-bed around 1400 °C in pure N<sub>2</sub><sup>3)</sup> and nitridation of Al powder in the microwave-induced N<sub>2</sub> plasma generated from SiC ceramics under atmospheric pressure<sup>4)</sup>. Various organic precursors have also been utilized to reduce temperatures for the synthesis of AlN powder. AlN powder was synthesized by the calcination of the polymeric precursor prepared from triethylaluminum and ethylenediamine (H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, ED) at 1000 °C in an ammonia atmosphere<sup>5)</sup>. The use of hydrazine as a nitridation agent and lithium metal as a reductive agent

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\*Department of Materials Science, Graduate School of Science and Technology

\*\*Department of Materials Science and Engineering

for aluminum chloride reduced successfully the calcination temperature to 800°C for the synthesis of AlN powder even in an argon atmosphere<sup>6</sup>. In addition, organic precursors prepared from the following binary and ternary systems have been studied for the synthesis of AlN powder:  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O} \cdot (\text{NH}_2)_2\text{CO}$ <sup>7</sup>,  $\text{AlCl}_3$ -glucose<sup>8</sup>,  $\text{LiAlH}_4$ - $\text{PrNH}_2$ <sup>9, 10</sup>,  $\text{LiAlH}_4$ - $\text{EtNH}_2 \cdot \text{HCl}$ <sup>9, 10</sup> and  $\text{LiAlH}_4$ - $\text{CH}_3\text{NH}_2 \cdot \text{HCl} \cdot (\text{CH}_3)_2\text{NH} \cdot \text{HCl}$ <sup>11</sup>. Another interesting method is the formation of an AlN polymer precursor,  $[\text{Al}(\text{NH}_2)(\text{NH})]_n$ , by electrolysis in a cell containing a  $\text{NH}_4\text{Br}/\text{NH}_3$  electrolyte and Al electrodes at room temperature. AlN powder was then prepared by the calcination of the precursor above 600°C in flowing  $\text{NH}_3$ <sup>12</sup>. However, most of these methods are characterized by their rather complicated procedure for the preparation of precursors. In addition, inflammable and expensive aluminum sources and ammonia as a nitrogen source are used in some cases, whereas simple and low-cost process is favorable from the viewpoint of industrial application.

The aim of the present study was to establish a simple and low-cost AlN synthesis process via an organic precursor prepared from anhydrous aluminum chloride and ethylenediamine in a  $\text{N}_2$  atmosphere. A possible mechanism for the precursor formation and the AlN synthesis from the precursor has also been discussed based on the X-ray diffraction and fourier-transform infrared spectroscopic analyses of the products in each step of the synthesis.

## 2. Experimental

Anhydrous  $\text{AlCl}_3$  (Wako Pure Chemical Industries, Ltd., reagent grade) and ED (Wako Pure Chemical Industries, Ltd., reagent grade) were used as an aluminum source and a nitrogen source, respectively, without further purification. The liquid ED was placed in a three-neck flask, and the atmosphere inside the flask was purged with flowing dry  $\text{N}_2$  (99.99%). Anhydrous  $\text{AlCl}_3$  was then added slowly to the liquid ED up to a molar ratio of  $\text{AlCl}_3 : \text{ED} = 1 : 10$  at room temperature while stirring and flowing dry  $\text{N}_2$ . The resulting suspension smoked along with a rise in its temperature during the addition, and then a brownish white solid product was precipitated rapidly. The solid product was dried at 150°C for about 2 h in flowing dry  $\text{N}_2$  to remove excess ED, subsequently treated in vacuo at 100°C for 3 h.

The precursor powder thus obtained was calcined at

800 or 1200°C for 5 h in a tubular-type electric furnace in flowing dry  $\text{N}_2$ . Carbon fibers were placed at the upper stream in a reaction tube and was used to eliminate trace  $\text{O}_2$  in flowing dry  $\text{N}_2$  during the calcination.

The powders before and after the calcination were characterized by X-ray diffraction (XRD, Rigaku, RINT-2200), fourier-transform infrared spectroscopy (FT-IR, Perkin Elmer, System 2000) and scanning electron microscopy (SEM, Hitachi, S-2250N).

## 3. Results and Discussion

### 3.1 Characterization of As-dried Organic Precursor

Figure 1 shows an XRD pattern of the as-dried organic precursor synthesized from  $\text{AlCl}_3$  and ED. The XRD pattern of the precursor was completely different from that of  $\text{AlCl}_3$ , and could not be identified with the available JCPDS (Joint Committee on Powder Diffraction Standards) cards. This implied the formation of a new compound by the reaction of  $\text{AlCl}_3$  with ED. Therefore, FT-IR spectroscopic analysis was carried out to get information on the chemical bonds involved in the precursor based on the data in Ref. 13. Since the peaks around 3500 and 3400  $\text{cm}^{-1}$  generally stand for

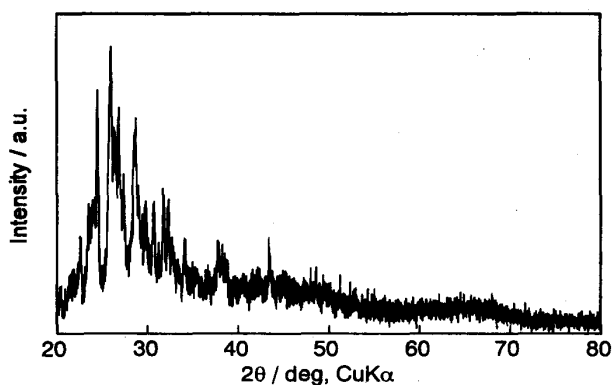


Fig. 1 XRD pattern of the as-dried organic precursor synthesized from  $\text{AlCl}_3$  and ED.

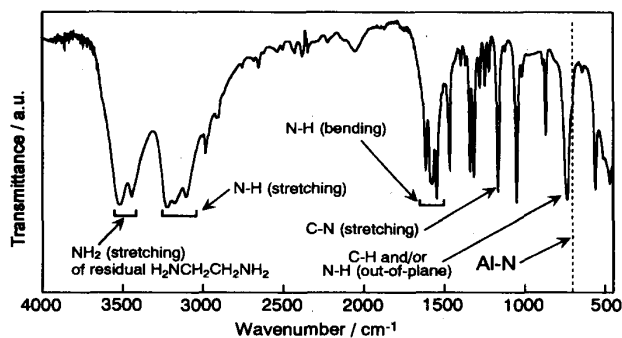


Fig. 2 FT-IR spectrum of the as-dried organic precursor synthesized from  $\text{AlCl}_3$  and ED.

asymmetric and symmetric stretching vibrations of amide and amine groups in diluted solutions, the adsorption peaks at 3515 and 3438  $\text{cm}^{-1}$  shown in Fig. 2 can be assigned to  $-\text{NH}_2$  groups in the precursor. The peaks at 3217, 3174 and 3101  $\text{cm}^{-1}$  are considered to be the stretching vibrations of N-H groups of different bonding structure involved in the precursor, such as asymmetric and symmetric stretching vibrations of secondary amines and amine salts, and multiple absorption of dimerized / oligomerized / polymerized amides. The peaks at 1616, 1589, 1578 and 1548  $\text{cm}^{-1}$  are assignable to N-H bending vibrations of amine groups ( $-\text{NH}_2$  and  $-\text{NH}$ ) and amine salts. The peaks at 1220 and 730  $\text{cm}^{-1}$  reflect C-N stretching and C-H and/or N-H out-of-plane vibration. These results suggest the existence of residual ED and very complicated bond states around N atoms in the precursor, although some peaks in Fig. 2 have not been identified yet. In addition, the existence of a weak shoulder peak at 700  $\text{cm}^{-1}$  suggested the formation of weak coordination bonds between Al and N and / or concrete Al-N bonds in the precursor<sup>7</sup>. Based on the FT-IR spectrum of the precursor, possible chemical reactions taking place during the synthesis are schematically shown in Fig. 3. The first step of the synthesis is considered to be the formation of coordination compounds between  $\text{AlCl}_3$  and ED. Thereafter, it is suggested that Al-N bonds form through partial or complete dissociation of Al-Cl bonds along with evolution of hydrogen chloride, and resulting compounds having terminal  $\text{NH}_2$  groups polymerize, leaving behind ED. Similar polymerization mechanism has been proposed for the precursor synthesized from an  $\text{AlCl}_3$ -hydrazine-Li system<sup>6</sup>.

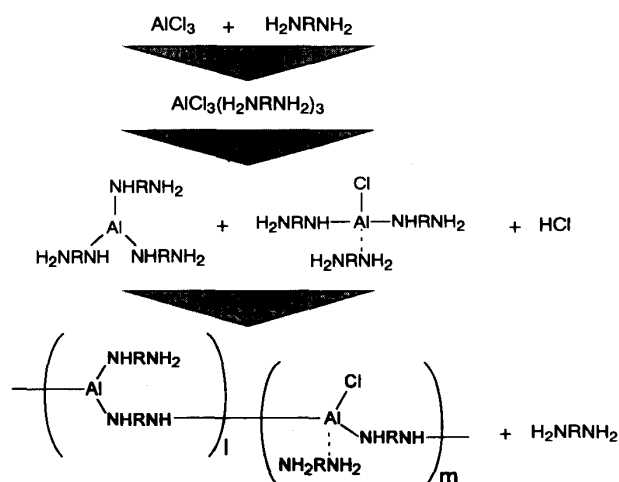


Fig. 3 Possible chemical reactions for the synthesis of precursor.

### 3.2 Characterization of AlN Powder after Calcination of Precursor

Figures 4 and 5 show XRD and FT-IR spectra of the resulting powders obtained after calcination at 800 and 1200  $^{\circ}\text{C}$  for 5 h in flowing dry  $\text{N}_2$ , respectively. The powder after calcination at 800  $^{\circ}\text{C}$  was black in color and showed a featureless XRD pattern as shown in Fig. 4(a). But, a small peak ascribed to Al-N bonds are observed in Fig. 5(a). In addition, absorption peaks around 3500 and 3150  $\text{cm}^{-1}$  almost disappeared, and those in the ranges of 1300-1600 (corresponding to N-H bending), 1000-1300 (C-N stretching) and 500-1000  $\text{cm}^{-1}$  (N-H out-of-plane vibrations) weakened significantly (compare Fig. 5(a) with Fig. 2). These results suggest decomposition and evaporation of organic groups in the precursor during the calcination at 800  $^{\circ}\text{C}$  in  $\text{N}_2$ , and the resulting powder seems to be a mixture of amorphous AlN and carbonaceous compounds.

In contrast, formation of a hexagonal and single AlN phase was confirmed after the calcination at 1200  $^{\circ}\text{C}$ , as shown in Fig. 4(b-1), whereas the resulting powder was still black in color. The color of the powder turned into gray after subsequent firing at 600  $^{\circ}\text{C}$  for 2 h in flowing air, but no oxide phase was induced by the firing, as shown in Fig. 4(b-2). The FT-IR spectrum of the powder after the firing shown in Fig. 5(b) exhibited a strong adsorption peak around 700  $\text{cm}^{-1}$  and quite resembled that of AlN powder supplied from Tokuyama Corp. (F-grade) in Fig. 5(c). In addition, absorption peaks assigned to N-H bending, C-N stretching or N-H out-of-plane vibrations were hardly observed after the firing. Thus, it is confirmed that the AlN powder after the calcination at 1200  $^{\circ}\text{C}$  in  $\text{N}_2$  still contains some carbonaceous compounds, but these compounds can be removed by the subsequent firing.

The crystallite size of AlN powder, calculated by Scherrer's equation, was 14.6 nm after the calcination at 1200  $^{\circ}\text{C}$  in  $\text{N}_2$  and remained unchanged after the subsequent firing. Owing to such fine microstructure of the synthesized AlN powder, its surface is likely hydrolyzed during handling. A broad peak at 3200-3600  $\text{cm}^{-1}$  and another around 1650  $\text{cm}^{-1}$  observed for the powder after the firing (see Fig. 5(b)) are, therefore, probably due to adsorbed water.

Deposition of a paste-like yellow material was observed at the outlet of the reaction tube after the

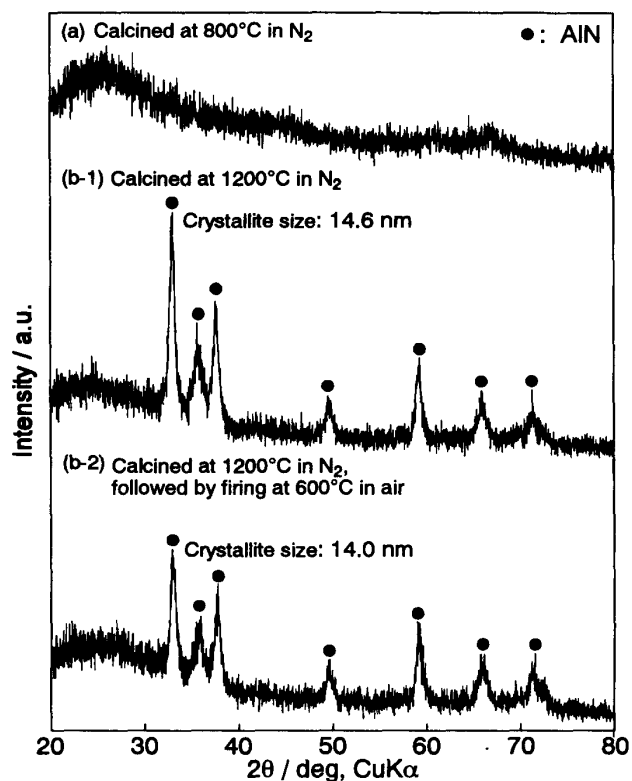


Fig. 4 XRD patterns of resulting powders after calcination of precursor.

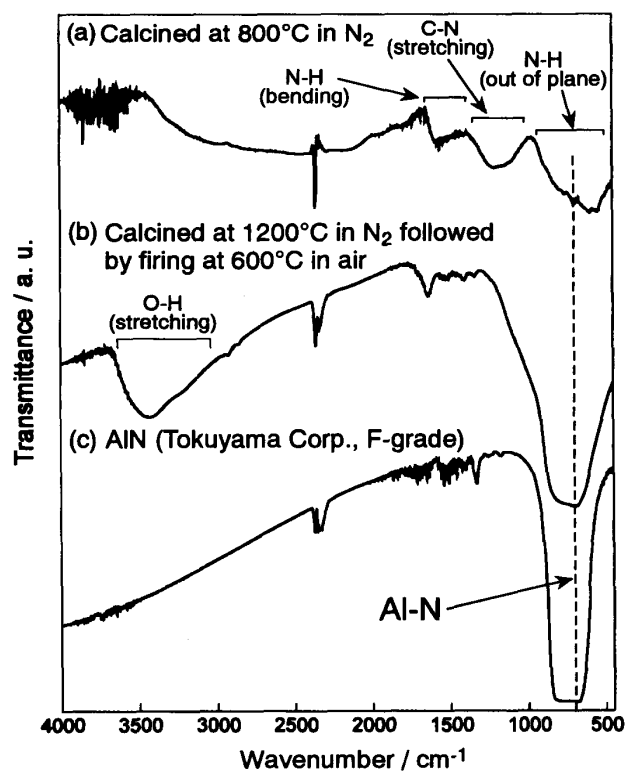


Fig. 5 FT-IR spectra of resulting powders after calcination of precursor and reference AlN powder (Tokuyama Corp., F-grade).

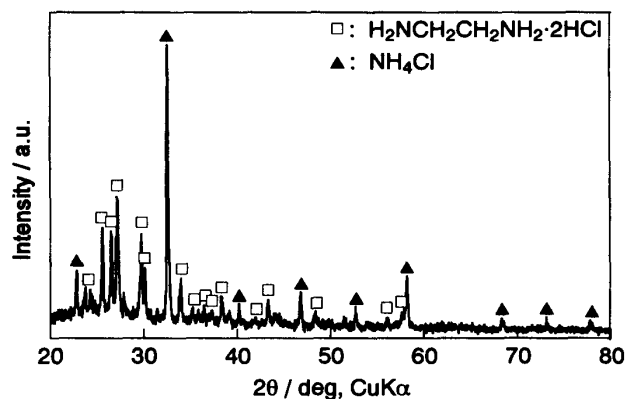


Fig. 6 XRD pattern of the material deposited at the outlet of the reaction tube after the calcination of precursor at 1200°C for 5 h in N<sub>2</sub>.

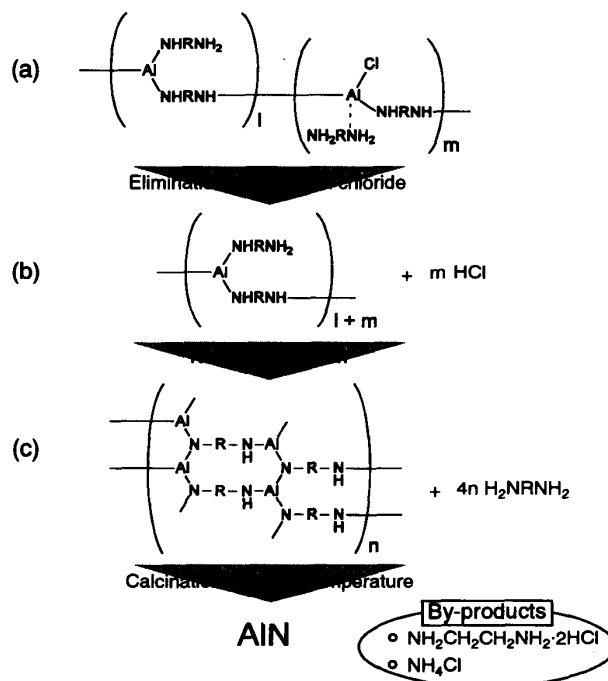


Fig. 7 Possible chemical reactions for the synthesis of AlN powder.

calcination of the precursor at both 800 and 1200°C in N<sub>2</sub>. XRD analysis of the compound revealed a mixture of H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>·2HCl and NH<sub>4</sub>Cl, as shown in Fig. 6. Then, it is confirmed that the thermal decomposition of the precursor proceeds by evolving ED and HCl. Based on the XRD and FT-IR analyses, possible chemical reactions taking place during the synthesis of AlN powder from the precursor are schematically shown in Fig. 7. The precursor is confirmed to have some Al-Cl bonds in the polymerized structure, as shown in Fig. 7(a). Polymerization is further accelerated upon heating, being accompanied with the evolution of HCl, as shown

in Fig. 7(b). Network formation shown in Fig. 7(c) is completed by the evolution of ED. The powder after the calcination at 800°C seems to have such network structure as shown in Fig. 7(c), since it exhibited absorption peaks assigned to N-H bending, C-N stretching or N-H out-of plane vibrations in the FT-IR spectrum. Heating at higher temperature, i.e. 1200°C in the present study, leads to the release and/or the decomposition of R-NH groups in the network structure, and results in the formation of AlN crystallites.  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \cdot 2\text{HCl}$  is undoubtedly formed by the reaction between the evolved ED and HCl, and  $\text{NH}_4\text{Cl}$  may be formed by the decomposition of  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \cdot 2\text{HCl}$  or by the reaction between R-NH groups and HCl. Some carbonaceous compounds are produced by the heating of R-NH groups in  $\text{N}_2$  and are the origin of the black-colored products after the calcination.

Figure 8 shows SEM photographs of the AlN powder prepared from the precursor by the calcination at 1200°C for 5 h in  $\text{N}_2$  and the subsequent firing at 600°C for 2 h in air. It is confirmed from the low and high reso-

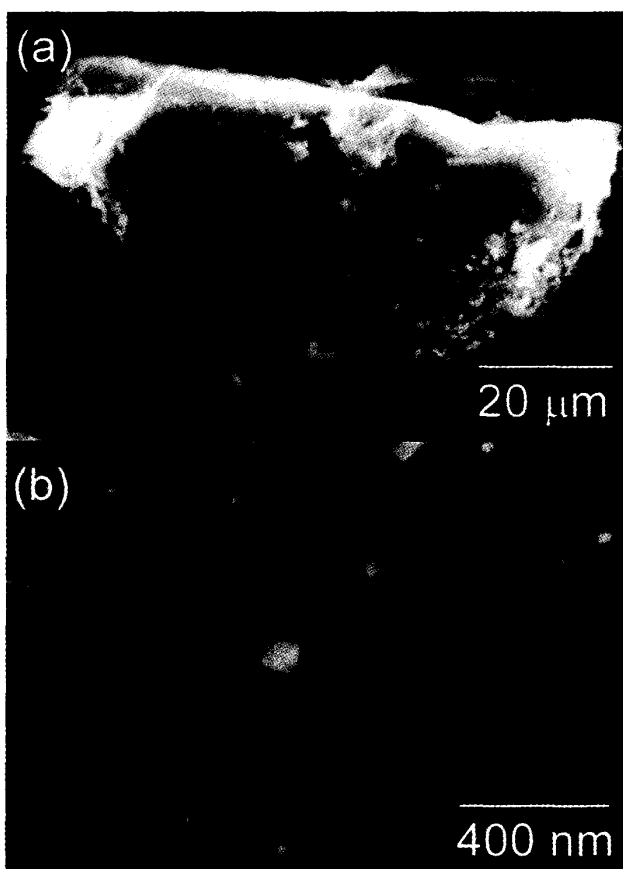


Fig. 8 SEM photographs of AlN powder prepared from the precursor by the calcination at 1200°C for 5 h in  $\text{N}_2$ , followed by the firing at 600°C for 2 h in air.

lution photographs that the powder consists of very fine primary particles less than 25 nm, and this particle size is almost comparable to the crystallite size calculated from the XRD data. However, it is obvious that these fine particles are agglomerated to form a secondary particle in the range of 60-100  $\mu\text{m}$ . Such feature may reduce the sinterability of the AlN powder. In this study, no grinding process of the precursor was adopted before the calcination, which is of course one reason for the formation of such large secondary particles. However, the rapid solidification of the precursor in ED solution is anticipated to be the main reason. To find milder reaction conditions for the preparation of the precursor, e.g. by employing a suitable solvent, and then to obtain finer secondary AlN particles are our next goal in future work.

#### 4. Conclusions

The organic precursor capable of producing AlN powder has been prepared by simply mixing anhydrous aluminum chloride into ethylenediamine at room temperature in flowing dry  $\text{N}_2$ . Calcination of the precursor at 1200°C for 5 h in flowing dry  $\text{N}_2$  led to a mixture of crystallized AlN powder and carbonaceous compounds, whereas amorphous AlN was formed after calcination at 800°C for 5 h. The carbonaceous compounds could be removed by subsequent firing at 600°C for 2 h in air, without any changes in crystal structure and crystallite size of the AlN powder. Possible chemical reactions during the formation of the precursor and AlN crystallites have been proposed based on the XRD and FT-IR spectroscopic analyses of both the products and by-products. The crystallite size of the AlN powder was less than 25 nm, but the particle size was in the range of 60-100  $\mu\text{m}$  due to agglomeration of fine particles under the present synthesis conditions.

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