Preparation of Aluminum Nitride Powder from Aluminum Chloride/Ethylenediamine Precursor

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塩化アルミニウム-エチレンジアミン系前駆体からの窒化アルミニウムの調製

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Aluminum nitride powder was prepared by calcination of an organic precursor, which was synthesized by adding aluminum chloride powder in an ethylenediamine solvent in a dry N_2 atmosphere. It was confirmed from X-ray diffraction analysis and Fourier transform infrared spectroscopy that amorphous and hexagonal AlN powders formed from the precursor after calcination at 800 and 1200°C for 5 h in flowing dry N_2 , respectively. Scanning electron microscopic observation revealed that the AlN crystallites obtained at 1200°C were less than 25 nm in diameter, though they easily agglomerated to form large grains of 60–100 μm . The particle size was comparable to the crystallite size (≈ 17.5 nm) calculated from the half width of the XRD (100) peak.

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1. Introduction

Aluminum nitride (AlN) is well known as an attractive material for silicon-compatible substrates with high thermal conductivity and low thermal expansion coefficient comparable to Si. AlN powder was commonly prepared by direct nitridation of metallic aluminum or carbothermal reduction of Al_2O_3 . However, grinding process is indispensable for the former, resulting in an increase in oxygen content in the powder, and highly pure Al_2O_3 and high temperature are needed for the latter. To avoid such problems, some more sophisticated methods of AlN synthesis have been suggested and developed. Typical examples are nitridation of floating metallic Al powder in flowing N_2 ¹⁾ or that of metallic Al powder in Ar- N_2 plasma induced by 2.45 GHz microwave²⁾ and reactions of metallic Al powder with various N-containing materials.^{3),4)} Various organic precursors have also been utilized to prepare fine AlN particles at lower temperatures. $AlCl_3 \cdot 6H_2O$ -urea,⁵⁾ $LiAlH_4$ - $iPrNH_2$ or $LiAlH_4$ - $EtNH_2 \cdot HCl$,^{6),7)} $AlCl_3$ -trimethylphenylammonium- NH_3 ,⁸⁾ $AlCl_3$ - N_2H_4 -metallic Li⁹⁾ and $AlCl_3$ -glucose systems¹⁰⁾ were investigated as the precursors for AlN synthesis. However, these methods are not easy to be practically used, since the preparation procedures of the precursors are rather complicated, except for Refs. 5) and 10). Ethylenediamine (ED) was also used for preparing an AlN thin film on an Si substrate by Jiang et al.¹¹⁾ However, they used inflammable and expensive trialkylaluminum as the Al source, and NH_3 is indispensable as the N source. The use of N_2 , instead of NH_3 , is undoubtedly favorable from the view point of industrial application. In the present study, we employed an organic precursor synthesized from $AlCl_3$ and ED, to fabricate fine AlN particles in a N_2 atmosphere.

2. Experimental

Anhydrous $AlCl_3$ (Kishida Chemical Co., Ltd., reagent grade) was added in an ED (Kishida Chemical Co., Ltd., reagent grade) solvent as an N-source at a molar ratio of $[AlCl_3]/[ED]=0.1$ in flowing dry N_2 (99.99%) at room temperature. The temperature of the suspension increased after the addition, and then a brownish white solid product was precipitated. The solid product was filtered off and was

dried at 130°C for about 2 h to remove unreacted ED. The solid product was then calcined at 800 or 1200°C for 5 h in flowing dry N_2 . The powders obtained 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

Figure 1 shows an XRD pattern of the organic precursor synthesized from $AlCl_3$ and ED. The XRD pattern of the precursor was completely different from that of $AlCl_3$, but the compound could not be identified from the available JCPDS (Joint Committee on Powder Diffraction Standards) cards, suggesting that a new solid material was synthesized by the reaction of $AlCl_3$ with ED. An FT-IR spectrum of the precursor is shown in Fig. 2. Since the peaks around ca. 3500 and 3400 cm^{-1} generally stand for asymmetric and symmetric stretching vibrations of amide and amine groups in diluted solutions,¹³⁾ the absorption peaks at 3515 and 3438 cm^{-1} can be assigned to residual ED in the precursor.

Fig. 1. XRD pattern of an organic precursor synthesized from $AlCl_3$ and ethylenediamine.

Fig. 2. FT-IR spectrum of an organic precursor synthesized from AlCl_3 and ethylenediamine.

On the other hand, the peaks at 3217, 3174 and 3101 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, or polymerized amides.¹³⁾ The appearance of several peaks between 1500 and 1650 cm^{-1} (1616, 1589, 1578 and 1548 cm^{-1}) are assignable to N-H bending vibrations of amine groups ($-\text{NH}_2$ and $-\text{NH}$) and amine salts,¹³⁾ suggesting that the bond states around N atoms in the precursor are complicated. The peak at 730 cm^{-1} is due to a CH and/or NH out-of-plane vibration. A weak shoulder peak of an Al-N stretching vibration at 700 cm^{-1} may be the evidence of the presence of Al-N bonds in the precursor.^{5),14)} Thus, two kinds of Al-N bonds may be suggested to exist in the precursor, as shown below.

1. Weak coordinate bond between Al and N (e.g., $\text{Cl}_3\text{Al}:\text{NH}_2-$).
2. Al-N bond formed by the reaction (e.g., $\text{AlCl}_3 + \text{NH}_2- \rightarrow \text{Cl}_2\text{AlNH}- + \text{HCl}$).

Tertiary amines, such as Al-N(Al)-C structure, may exist in the precursor, but it is difficult to confirm with FT-IR.

Figures 3 and 4 show XRD patterns and FT-IR spectra of the powders calcined at 800 and 1200°C for 5 h, respectively. The featureless pattern shown in Fig. 3(a) suggests that organic compounds involved in the precursor thermally decomposed or evaporated, to leave an amorphous residue after the calcination at 800°C. In the FT-IR spectrum (Fig. 4(a)), some absorption peaks were observed in the range of 1300–1600, 1000–1300 and 500–1000 cm^{-1} , which were corresponding to N-H bending, C-N stretching and N-H out-of-plane vibrations, respectively. In addition, a small peak of Al-N bonds was also observed around 700 cm^{-1} . Thus, it is very likely that amorphous AlN was formed together with carbonaceous materials by the calcination of the precursor at 800°C in flowing N_2 without using NH_3 . Surface hydrolysis of the formed amorphous AlN in the ambient air may be a cause of the appearance of the N-H bending and out-of-plane vibration.

The formation of hexagonal AlN was confirmed after the calcination at 1200°C with the XRD analysis, as shown in Fig. 3(b). Hashimoto et al. reported that AlN powder was prepared from the mixture of AlCl_3 and glucose by the calcination at temperatures above 1300°C in flowing N_2 .¹⁰⁾ In this case, N atoms in the prepared AlN powder should come from a gas phase and this require higher temperatures. In the present study, however, AlN powder could be prepared at a lower temperature of 1200°C, since Al-N bonds already

Fig. 3. XRD patterns of the products calcined at (a) 800°C and (b) 1200°C for 5 h in flowing N_2 .

Fig. 4. FT-IR spectra of the products calcined at (a) 800°C and (b) 1200°C for 5 h in flowing N_2 , and (c) reference AlN powder (Tokuyama Co., F-grade).

exist in the precursor. In addition, the FT-IR spectrum shown in Fig. 4(b) quite resembled that of AlN powder from Tokuyama Co. (F-grade) in Fig. 4(c), except for the very broad peak at 3200–3600 cm^{-1} due to adsorbed water.

SEM photographs of the AlN powder calcined at 1200°C for 5 h are shown in Fig. 5. The size of the agglomerated grains was in the range of 60 and 100 μm in diameter as shown in Fig. 5(a), but the size of the individual fine parti-

Fig. 5. SEM photographs of the product calcined at 1200°C for 5 h in flowing N_2 . (a) An agglomerated grain and (b) its surface.

cles was less than 25 nm in diameter, as shown in Fig. 5(b). This particle size was almost comparable to the crystalline

size of 17.5 nm calculated from the half-width of the XRD (100) peak.

Thus, the organic complex synthesized from $AlCl_3$ and ED was confirmed to be a novel precursor in preparing AlN powder. Further investigations are now in progress to modify the preparation and calcination conditions of the precursor to obtain fine AlN powder without agglomeration and to estimate the amount of impurities, especially oxygen.

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