

FULL PAPER

# Low temperature and fast growth of one-directionally grown aluminum nitride film by atmospheric pressure halide CVD method

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Aluminum Nitride (AlN) shows high thermal conductivity, high electrical resistivity, and chemical stability and expected as a candidate for a substrate of  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  based thin films for LEDs. In the present study, we demonstrate low temperature (800°C) and fast growth (9.2  $\mu\text{m}/\text{h}$ ) of one-directionally grown AlN film by atmospheric pressure halide CVD method, in which AlN films grow under air pressure without any requirement of vacuum systems. For obtaining uniaxial AlN films, seeding layer prepared at the initial stage of the growth plays an important role. Growth mechanisms and effects of the seeding layer is discussed based upon optical and microstructural analyses.

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## 1. Introduction

Aluminum Nitride (AlN) is one of III-V group materials with Wurtzite structure and is attracting much interest because of its high thermal conductivity, high electrical resistivity, and chemical stability.<sup>1,2)</sup> AlN is also expected to be used as a substrate for growing  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  based thin film UV LED owing to a small lattice mismatch between AlN and  $\text{Al}_x\text{Ga}_{1-x}\text{N}$ .<sup>3)</sup> There have been many reports for fast growth of AlN films, but most of the setup for growing AlN requires sophisticated setup for multiple reacting zone,<sup>4,5)</sup> high vacuum, and high temperature above 1000°C.<sup>4)</sup>

We have been studying an environmentally friendly process for preparing nitride materials. Atmospheric Pressure Halide CVD (APHCVD) method is a simple film growth method under atmospheric pressure, where halide sources of the group-III elements are thermally evaporated in  $\text{N}_2$  gas flow atmosphere and the sources react with  $\text{NH}_3$  at a growing temperature.<sup>6)</sup> As the reaction occurs under atmospheric pressure, the setup for the APHCVD method only requires silica glass tube and tube furnaces, etc.

In the present study, we prepared AlN films on an  $\text{Al}_2\text{O}_3$  (c-plane sapphire) substrate by the APHCVD method using  $\text{AlI}_3$  as an aluminum source. In comparison with the use of  $\text{AlCl}_3$  as a source of aluminum, which is mostly used in the other studies of halide CVD method for AlN film growth,  $\text{AlI}_3$  has lower chemical bond energy than  $\text{AlCl}_3$  and is expected to result in lowering reaction temperature to produce AlN.<sup>7)</sup> We also made another attempt in the present study; for investigating a nucleation behavior on the substrate, we used two different heaters, i.e. an outside heater (a tube furnace) and inside heater (a ceramic plate heater for heating the substrate).

## 2. Experimental

The experimental setup of the APHCVD method was schematically shown in **Fig. 1**. Starting materials of  $\text{AlI}_3$  and  $\text{NH}_3$  were used as sources for Al and N of AlN, respectively. First, the  $\text{AlI}_3$  powder lightly ground using agate mortar was placed on a silica glass boat and inserted into a tube reactor made of silica glass. The c-plane sapphire substrate (after annealed in air at 1000°C for 10 h for preparing step structure) placed on a ceramic plate heater was inserted into the glass tube reactor. The source and the substrate were placed at the center of the tube furnaces I and II, respectively.  $\text{N}_2$  carrier gas was introduced as it flows from the source side to the substrate side.  $\text{NH}_3$  reaction gas preliminarily mixed with  $\text{N}_2$  gas was introduced onto the substrate.

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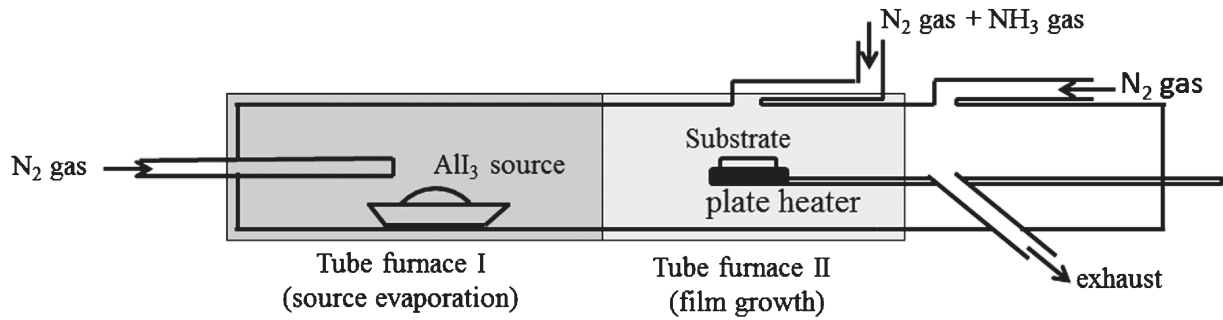


Fig. 1. Schematic of the setup of APHCVD method.

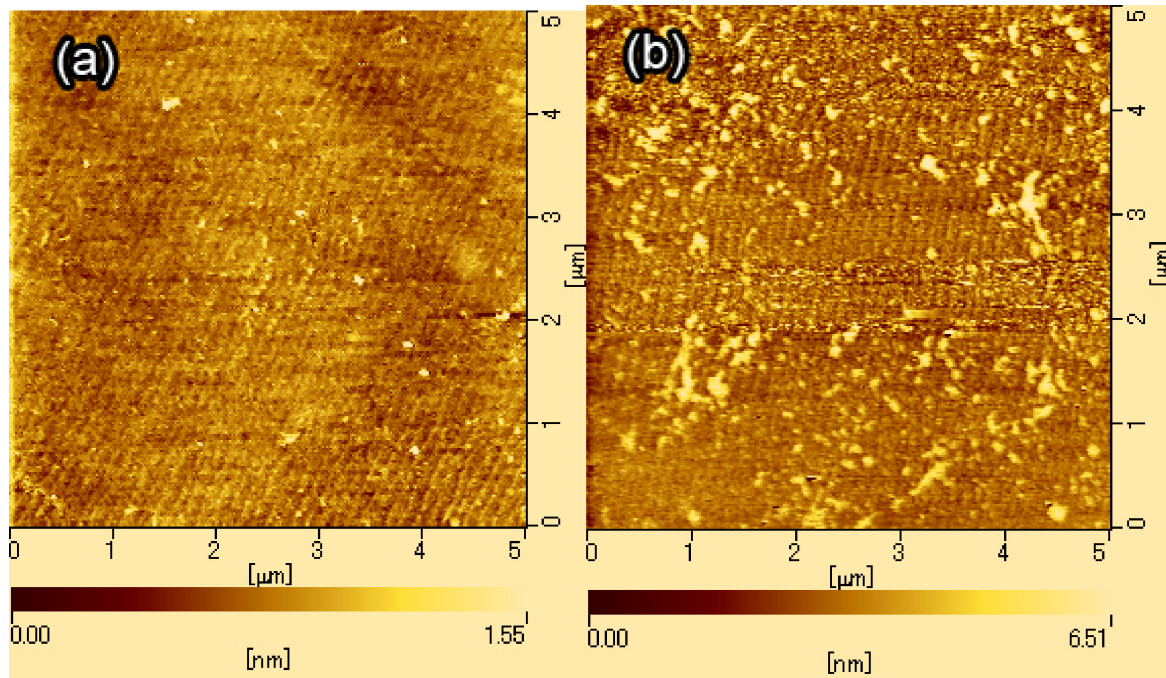
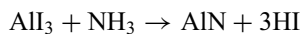


Fig. 2. AFM images of the surface morphology of the c-sapphire substrate (a) before and (b) after preparing the seeding layer by the 1st step growth for 10 min.

The expected reaction in this method is



In order to remove the second product HI and non-reacted  $\text{NH}_3$ , which are toxic and highly reactive with water vapor, the gas outlet was connected to a tightly sealed tube and sent to a fume hood after bubbling in a water trap two times.

In the present study, the AlN film was prepared in a two-step temperature profiles. At the first step, small amount of the  $\text{AlI}_3$  vapor was supplied to the substrate in order to generate nuclei on the substrate. At the second step, larger amount of the  $\text{AlI}_3$  vapor was supplied to the substrate in order to obtain rapid AlN growth. Details of the experimental conditions were shown in **Table 1**.

### 3. Results and discussion

#### 3.1 Preparation of the seeding layer (1st step growth)

**Figure 2** shows Atomic Force Microscopy (AFM) images of the surface morphology of the c-sapphire sub-

Table 1. Optimized AlN growing conditions by APHCVD

	1st step	2nd step
Temperature of furnace I/ $^{\circ}\text{C}$	140	250
Temperature of furnace II/ $^{\circ}\text{C}$	800	800
Source carrier gas flow rate/sccm	350	350
$\text{NH}_3$ gas flow rate/sccm	20	40
Growth time/min.	10	30
V/III ratio	1715	14.9

strate before and after preparing the seeding layer by the 1st step growth for 10 min. By the 1st step growth, random hill structures about 7 nm height were generated and the RMS value increased from 0.17 to 0.87 nm. The size of the hill structures on the substrate was ca. a few tenth to a few hundred nm. We tried to analyze the hill structure by X-ray Photoelectron Spectroscopy (XPS), but no obvious peak related to N 1s was observed which might be due to the small coverage area of the hill structure on the surface. In order to cover the larger area of the substrate, we increased the growth time of the 1st step from 10 to 120 min and analyzed by XPS. **Figure 3** shows XPS spectra of the film

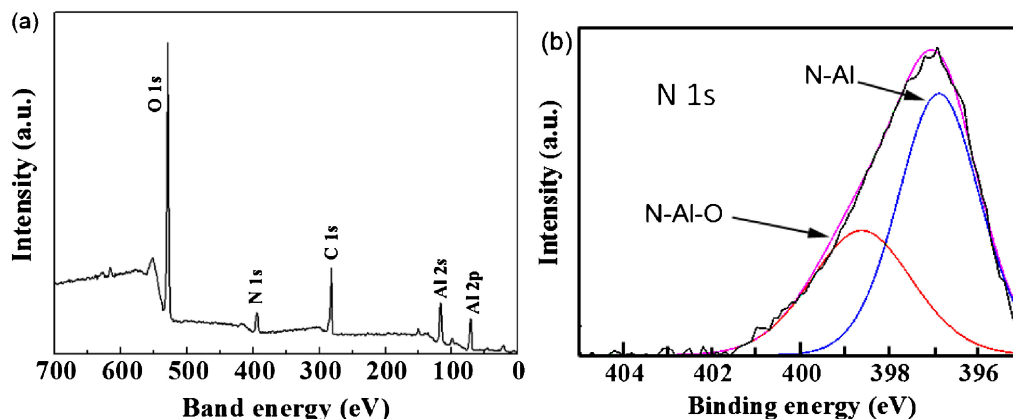


Fig. 3. XPS spectra of the film prepared by the 1st step growth (growth time was increased to 120 min. for obtaining thick film).

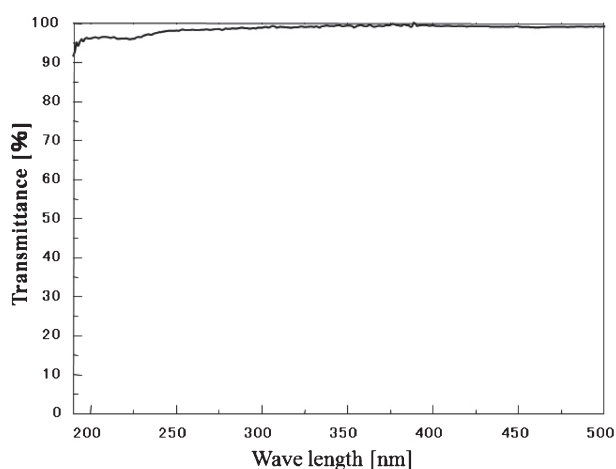


Fig. 4. UV-Vis transmittance spectra of the film prepared by the 1st step growth (growth time was increased to 120 min. for obtaining thick film).

prepared by the 120 min. growth, where an N 1s peak indicating nitride related bonds appeared at about 397 eV. By peak deconvolution, two peaks of N-Al ( $396.4 \pm 0.3$  eV) and N-Al-O ( $398.0 \pm 0.3$  eV) bonds were assigned.<sup>8)</sup> Similar XPS spectra (not shown here) were also obtained on the thick film after the 2nd step growth, which may imply the AlN film contains impurity of oxygen on the surface or in the structure of the AlN. The film prepared by the 120 min. growth was also analyzed by UV-Vis transmittance spectra as shown in Fig. 4. The transmittance spectrum of the film showed a slight decrease at a UV region below 250 nm, which is supposedly caused by AlN and/or AlN containing impurities such as oxygen etc. Although we tried to exclude contamination of oxygen and water in the process, small amount of oxygen might be contaminated due to the inner surface of the silica glass tube and/or silica glass boat etc. Further investigation about the oxygen contamination will be studied in the future.

### 3.2 Fast growth of AlN on the seeding layer (2nd step growth)

After depositing the seeding layer by 10 min. growth as explained above, a subsequent fast growth of AlN film

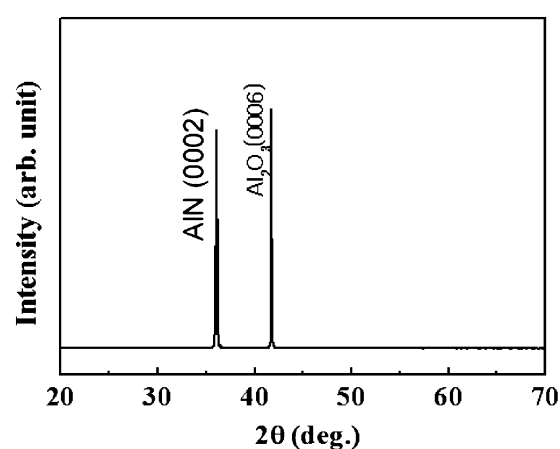


Fig. 5. XRD of the film prepared by the 1st and 2nd steps.

for 30 min. was demonstrated by increasing the supplying amount of aluminum and nitrogen sources.

Figure 5 shows X-Ray Diffraction (XRD) patterns of the film after the 2nd step. It showed only (0002) peak of AlN, which indicated the *c*-axis growth of the film. Crystallographic analyses about in-plane orientation of the film was also analyzed but there was no certain orientation in plane (not shown), therefore the film was considered to be one-directionally oriented film.

Figure 6 shows cross sectional Scanning Electron Microscopy (SEM) images of the film after the 2nd step growth (an AlN film prepared without 1st step was also shown for comparison). Drastic change in the microstructure was observed. The film obtained without the 1st step was a rough bundle like structure composed of rods and particles, on the other hand the film obtained by the two steps was composed of one-directionally grown film with smoother surface. From the cross sectional SEM image, average growth rate of the film at the 2nd step was calculated as  $9.2 \mu\text{m/h}$ . Figure 7 shows a top view of the film prepared by the two steps. It should be noticed that the AlN film was composed of rod shaped AlN crystals with ca. 100 to 500 nm in diameter and some of them coalesced each other. With comparing the microstructure of the nuclei shown in Fig. 2(b), the diameter of the rod crystal



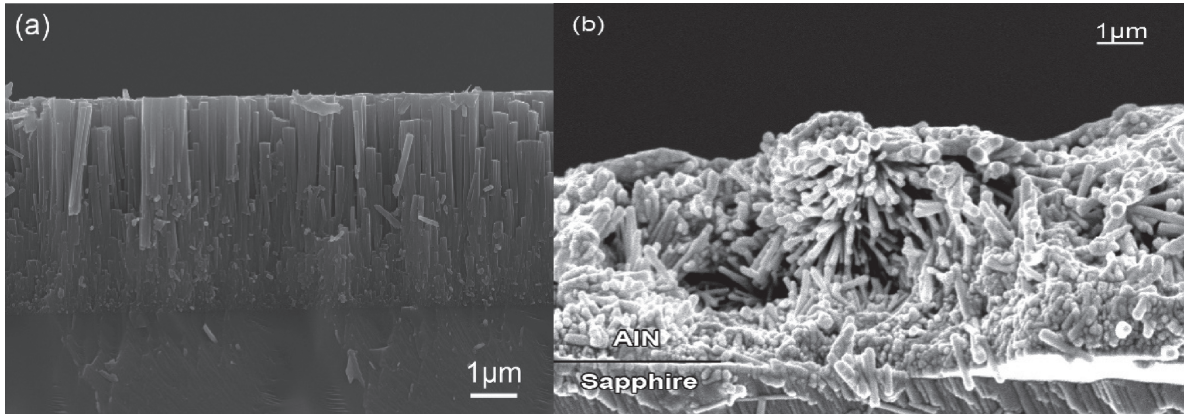


Fig. 6. Cross sectional SEM images of the film prepared by the 1st and 2nd steps (a) and a film prepared without the 1st step growth (b).

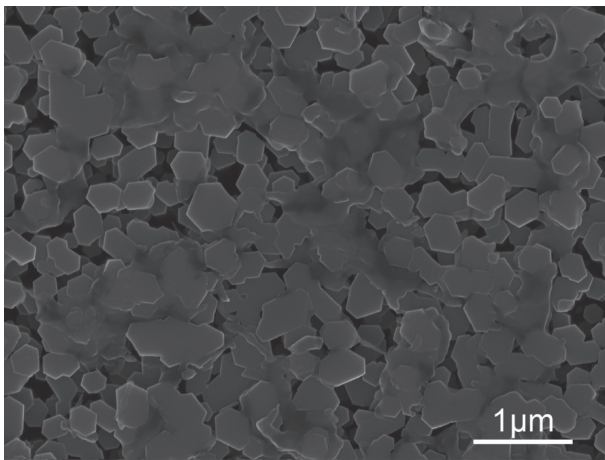


Fig. 7. Top view of the film prepared by the 1st and 2nd steps.

was larger than the size of the nuclei. On the other hand, the number density of the rod crystals in a unit area was smaller compared to that of the nuclei. This may indicate that the 2nd step AlN growth occurs not only along the  $c$ -axis of the AlN but also grow along the perpendicular direction of the  $c$ -axis of AlN. It is interesting that each rod seems to have hexagonal facets on the side and flat plane at the top surface, which may indicate that each rod is a single crystalline of AlN and the facets of it appears. The facet has significant meaning from a view point of optical application since the crystal planes of AlN perpendicular to the  $c$ -axis, i.e.  $m$ - or  $a$ -planes (so-called “non-polar” planes), are expected as high efficiency light emitting plane.<sup>9),10)</sup> The AlN rod structure implies a possibility of application as a substrate for high efficiency light emitting device if  $\text{Al}_x\text{Ga}_{1-x}\text{N}$  based quantum well is prepared on the side of the rods.

Figure 8 shows Transmittance spectra of the AlN film after the two step growth. Due to light scattering by the surface of the rod like shape film, transmittance at the visible light region, ca. 400–700 nm, was at most 70%. Estimated bandgap energy of the film was 5.7 eV as shown in Fig. 9. Although the theoretical bandgap of AlN is reported as 6.2 eV, the film showed lower bandgap. This

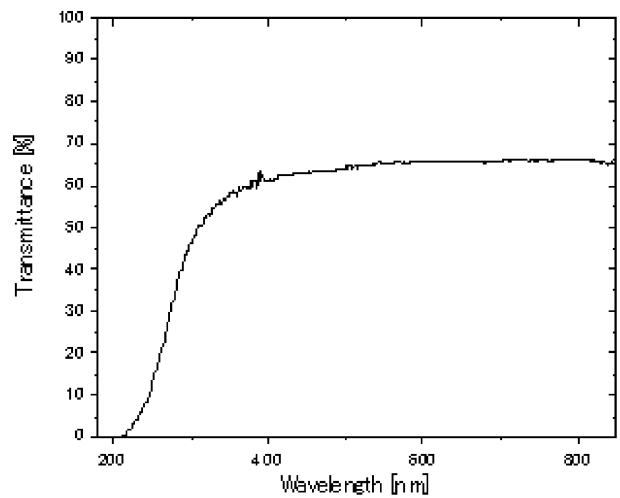


Fig. 8. Transmittance spectra of the film prepared by the 1st and 2nd steps.

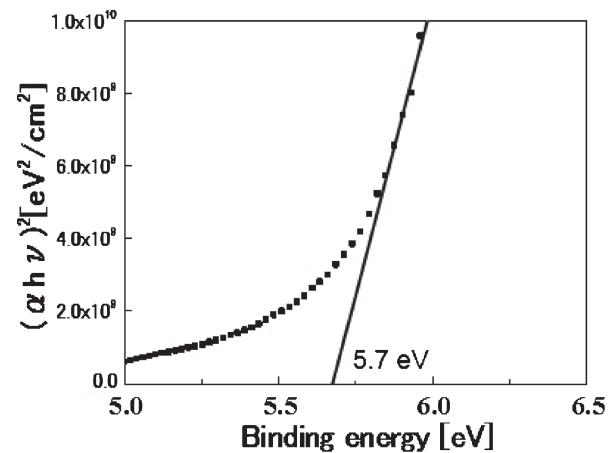


Fig. 9. Bandgap energy calculated from the transmittance spectra shown in Fig. 8.

might be caused by the oxygen contamination and/or a dislocation in the crystal.

A growth mechanism of the AlN film by the two step growth could be considered as follows. At the 1st step, quite small amount of the Al source is supplied onto the

substrate owing to the lower heating temperature of the  $\text{AlI}_3$  source and only the small hill structures are prepared on the sapphire substrate (heterogeneous nucleation on the substrate). At the 2nd step, large amount of the Al source was supplied owing to the higher heating temperature of the Al source, and rapid AlN growth started from the hill structure (crystal growth from the seeds on the substrate). If the 1st step was omitted, homogeneous nucleation in the atmosphere and a random growth on the particles as well as the on the substrate took place and resulted in the rough structure.

#### 4. Conclusion

One-directionally grown AlN film composed of single crystalline like rod structure was synthesized by APHCVD method at low temperature of  $800^\circ\text{C}$  using  $\text{AlI}_3$  as an aluminum source. The film was grown by two steps: 1. seeding layer was generated on the sapphire substrate by supplying small amount of Al source, and 2. subsequent rapid AlN growth ( $9.2\ \mu\text{m}/\text{h}$ ) by increasing Al source supply. The seeding layer played an important role for the one-directional growth from which it could be considered that the seeds act as a nucleation site for the AlN growth.

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