

# Synthesis and Infrared Study of Nanosized Aluminum Nitride Powders Prepared by Direct Current Arc Plasma

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Nanosized hexagonal wurtzite aluminum nitride (AlN) powders have been synthesized by the direct current (DC) arc plasma method using mixed gas of ammonia and nitrogen ( $\text{NH}_3\text{--N}_2$ ). The growth of the crystals is affected by the thermal stability of their nitric surface, and the average size of the particles varies slightly according to reaction gas pressure. Fourier transform infrared (FT-IR) transmission measurements were carried out at room temperature on the nanosized powders in different mediums. The IR spectra show an intense and broad absorption peak at about  $770\text{ cm}^{-1}$  ( $\epsilon_m=2.36$  of KBr) or  $800\text{ cm}^{-1}$  ( $\epsilon_m=1.0$  of in air) attributed to the Fröhlich mode of the nanostructured AlN crystals. Some bulk modes also appear as shoulders or peaks in the spectra simultaneously.

## I. Introduction

Aluminum nitride (AlN) is an extensively studied nitride system due to its desirable optical, electrical, dielectric, and acoustical properties.<sup>1,2</sup> In recent years, ultrafine AlN powder has been paid attention to as an important ceramic material. Compared to the study of synthesis and sintering properties, the study of vibrational modes of nanocrystalline AlN is deficient.<sup>3–6</sup> Gonsalves et al.<sup>3,4</sup> reported that the AlN powder with size of 60 nm has a characteristic band at  $690\text{ cm}^{-1}$  in IR spectra, corresponding to the Al–N absorption. An absorption band of Al–N at  $740\text{ cm}^{-1}$  was obtained in the IR spectrum of AlN–BN nanocomposite crystals.<sup>5</sup> Ramesh and Rao<sup>6</sup> reported an Al–N absorption at  $683\text{ cm}^{-1}$  in the nanosized AlN crystals. In an early IR transmission study,<sup>7</sup> analyzed by multiphonon combination, the small AlN crystals have intrinsic vibrations: LO at  $737\text{ cm}^{-1}$ ,  $\text{TO}_1$  at  $665\text{ cm}^{-1}$ , and  $\text{TO}_2$  at  $630\text{ cm}^{-1}$ . The vibrations of AlN films including nanocrystalline thin films have been determined by IR measurements in many literature papers.<sup>8–12</sup> The data are transverse optical (TO) mode at  $660\text{--}670\text{ cm}^{-1}$  and longitudinal optical (LO) mode at  $880\text{--}915\text{ cm}^{-1}$ .

To our knowledge, no reports of the vibration bands mentioned above have been discussed associated with small size effect. Based on the idea of Fröhlich<sup>13</sup> and following discussions of some researchers,<sup>14,15</sup> when ionic microcrystal size is reduced smaller than the wavelength of the light in the crystal, in the limit of  $k_{\text{TO}}R \rightarrow 0$ , where  $k_{\text{TO}}$  is the wavenumber of the TO mode and  $R$  is the radius of the sphere, there are a series of absorption peaks lying in the reststrahlen band between the  $\omega_{\text{TO}}$  and  $\omega_{\text{LO}}$  near  $q = 0$  ( $q$  is the wave vector), called surface modes.

The vibration mode in the spherical ionic microcrystal has frequencies obtained from

$$\omega_n^2 = \frac{\epsilon_0 + (n+1)/n\epsilon_m}{\epsilon_\infty + (n+1)/n\epsilon_m} \omega_{\text{TO}}^2 \quad (n = 1, 2, 3, \dots) \quad (1)$$

where  $\omega_{\text{TO}}$  is the transverse optic mode frequency,  $\epsilon_0$  and  $\epsilon_\infty$  are the static and high-frequency dielectric constants of the crystal, respectively, and  $\epsilon_m$  is the dielectric constant of the medium surrounding the specimen. The lowest frequency of the series modes ( $n = 1$ ) is called the Fröhlich mode. The theory has been used to deal with the vibration modes of some small ionic crystals including some nanostructured materials.<sup>16–19</sup>

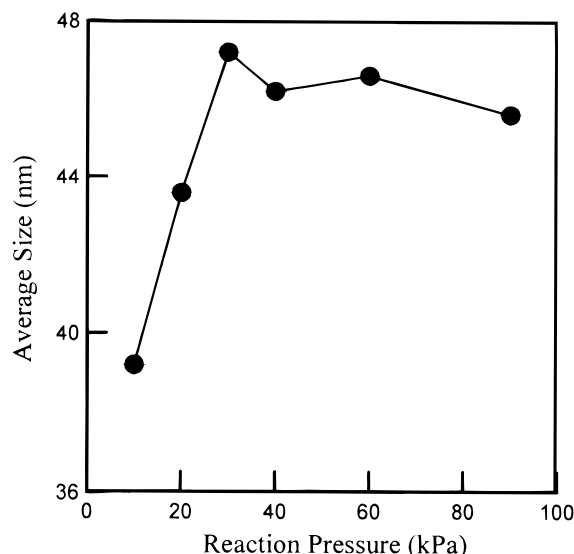
Nanocrystalline AlN and Al–AlN powders were synthesized via a plasma method. In this paper, by using SAXS (small-angle X-ray scattering), TEM (transmission electron microscope), and FT-IR (Fourier transform infrared) spectroscopy measurements, we examined changes of size and morphology as a function of the reaction pressure and vibrations of the pure nanoscale AlN crystals.

## II. Experimental Methods

The apparatus of the DC (direct current) arc plasma and the synthesis of precursor AlN nanocrystalline have been reported in detail in the previous literature.<sup>20</sup> In brief, the Al clusters evaporate from an Al ingot in the  $\text{NH}_3\text{--N}_2$  plasma, then react with the active chemical species (e.g.,  $\text{N}_2$ ,  $\text{NH}_3$ ,  $\text{NH}_2$ ,  $\text{NH}$ , or  $\text{N}$ ) to form AlN grains, and finally condense onto the cooling collection chamber.

X-ray diffraction experiments were performed on a Rigaku X-ray diffractometer. A  $\text{Cu } K_\alpha$  X-ray source was used. The average sizes of powders were measured by the SAXS method.

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**Figure 1.** Change of the average size as a function of the reaction pressure for nanosized AlN powder.

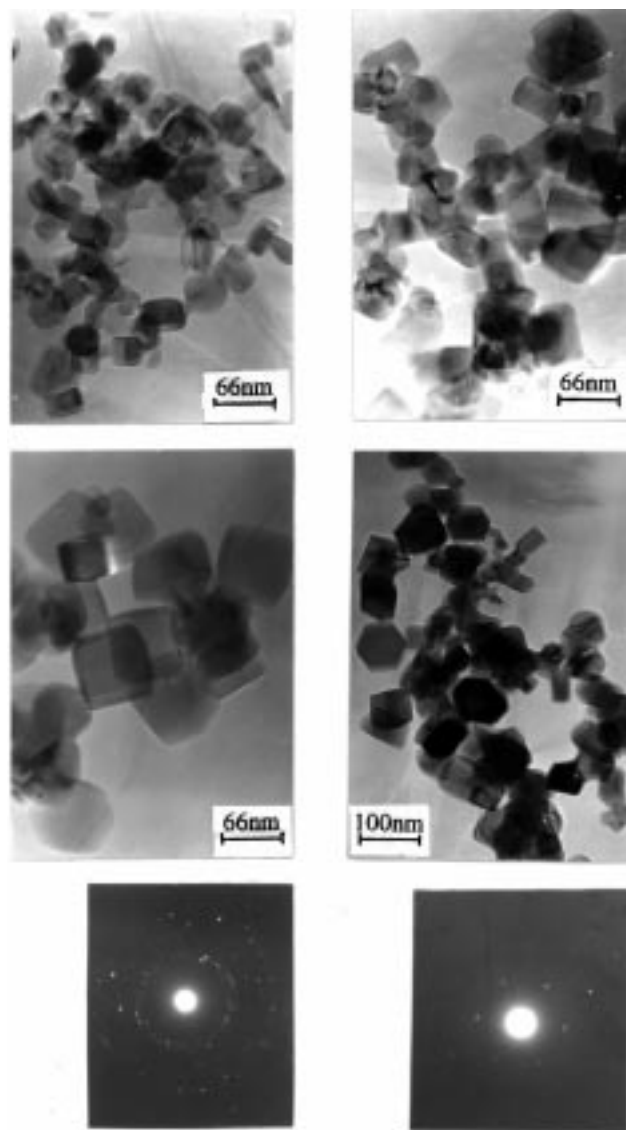
The AlN crystal morphology was studied by a Hitachi-8100 TEM. Selected-area electron diffraction patterns were used to analyze the crystal structure.

FT-IR spectra were recorded with a Nicolet 5DX spectrometer, which operates from 4000 to 400  $\text{cm}^{-1}$  with 7  $\text{cm}^{-1}$  resolution. The transmission spectra were obtained from the specimens in air or embedded in a KBr matrix. For the medium material of KBr, the sample was mixed up with the KBr powder and pressed into a pellet for the measurement. On the other hand, the AlN powder was dispersed in alcohol and then dipped onto a KBr substrate to obtain the IR spectra in air. All spectra were obtained at room temperature.

### III. Results and Discussion

In our experiments the synthesis of AlN powder at different reaction gas pressures was carried out in a mixed reaction gas (20%  $\text{NH}_3$ –80%  $\text{N}_2$ ). The gas pressure in the reaction chamber was controlled to determine the size of the powder. As shown in Figure 1, with increasing pressure, the average size of the particles increases from 39 nm at about 10 kPa to 47 nm at about 30 kPa and then remains almost unchanged up to 90 kPa.

It is known that the ultrafine metal particles synthesized by the vaporization method can grow large by a coalescence mechanism.<sup>21–23</sup> The vapor metal clusters with a lower melting point compared with the bulk material can easily grow into larger particles at a higher pressure. The formation of nanosized nitrides is not similar to that of the metal. Generally, nitrides have high thermal and chemical stability, so the nitric grains are not active enough to coalesce together for further growth as well as metal, even though their size is decreased to nanoscale and they are at higher temperature in plasma. At low reaction gas pressure, the generation rate of vaporized Al clusters is lower, which causes a small collision probability, so the original Al particles are nitrided into AlN grains in a small size. As pressure increases, the generation rate and collision probability of Al clusters increase, then the coalescence growth of the Al grains happens and leads to the AlN crystal growth. On the other hand, at a higher ambient pressure the rate of nitriding is enhanced simultaneously; the thermal stability of the as-synthesized nitric grains prevents growth during the coalescence process. Thus, at a lower pressure the sizes of the powders increase with the pressure and then remain almost unchanged at higher pressures above a critical pressure.

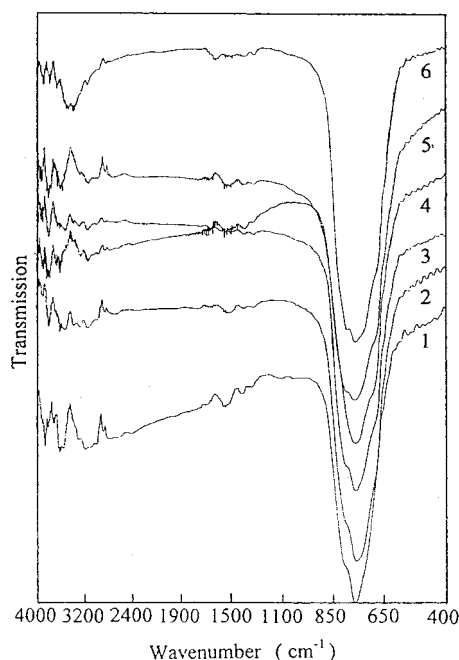


**Figure 2.** Typical TEM micrographs of the AlN powder synthesized at different reaction pressures: (a, upper left) 10 kPa; (b, upper right) 20 kPa; (c, middle left) 40 kPa; (d, middle right) 90 kPa, and electron diffraction patterns of (e, lower left) polycrystals and (f, lower right) a single crystal.

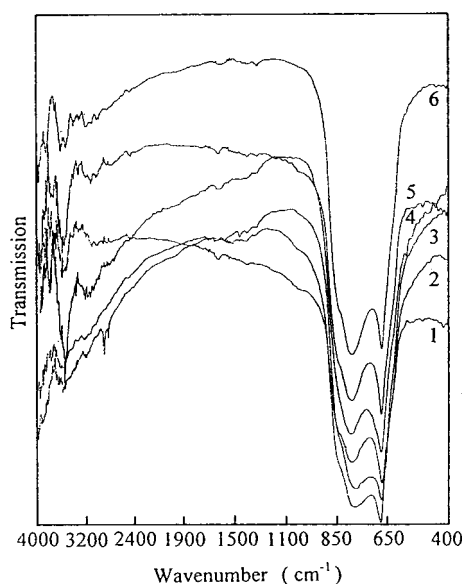
Typical images of the powders synthesized at different gas pressures are shown in Figure 2 (panels a–d). The nanosized particles have shapes reflecting the hexagonal structure for the AlN crystal habit, such as columns, hexagons, and cubes. Few spherical Al particles are found. The photographs illustrate that the particle size is slightly determined by the reaction pressure according to the above discussion. Selected-area electron diffraction patterns in Figure 2e,f indicate that the nanosized AlN crystals are in wurtzite structure and some particles are identified as single crystals from the diffraction spots as shown in Figure 2f.

Figures 3 and 4 show the FT-IR transmission spectra of the AlN powders, synthesized in various reaction atmospheres, embedded in KBr matrix and exposed to the air, respectively. In Figure 3, an intense and broad band centered at about 770  $\text{cm}^{-1}$  in the reststrahlen band of AlN crystal is observed in all the specimens. A broad peak at about 800  $\text{cm}^{-1}$  and a sharp peak at about 660  $\text{cm}^{-1}$  are shown in Figure 4.

There are some weak bands in the region of both 1000–1900  $\text{cm}^{-1}$  and 2400–4000  $\text{cm}^{-1}$  in Figures 3 and 4. They can be attributed to a very small amount of water,  $\text{CO}_2$ , and air



**Figure 3.** FT-IR transmission spectra of the nanosized AlN crystals embedded in KBr ( $\epsilon_m = 2.36$ ). Specimens 1–6 correspond to the powders synthesized at the reaction pressures of 10, 20, 30, 40, 60, and 90 kPa, respectively.



**Figure 4.** FT-IR transmission spectra of the nanosized AlN crystals measured with  $\epsilon_m = 1$  in air. Specimens 1–6 correspond to the powders synthesized at the reaction pressures of 10, 20, 30, 40, 60, and 90 kPa, respectively.

in the spectrometer path or on the surface of the samples.<sup>12</sup> Other bands attributed to the species of reactive  $\text{NH}_3$  gas coordinated to Al or  $\text{H}_2\text{O}$  in the samples can also be located in the two regions.<sup>9,24–26</sup> No obvious relative Al–O peaks appear in the spectra, especially the absorption of Al–O at  $950\text{ cm}^{-1}$ <sup>25</sup> or  $460\text{ cm}^{-1}$ ,<sup>27</sup> a series of Al–O bands reported in ref 28 and the infrared peaks of nanometer-sized  $\text{Al}_2\text{O}_3$  clusters.<sup>29</sup>

In the calculation of eq 1 with  $n = 1$ , the parameters are bulk parameters of the AlN crystal, where  $\epsilon_0 = 8.50$ ,  $\epsilon_\infty = 4.68$ , and  $\omega_{\text{TO}} = 663.6\text{ cm}^{-1}$ .<sup>8</sup> The dielectric constants of the medium are  $\epsilon_{\text{m(KBr)}} = 2.36$  and  $\epsilon_{\text{m(in air)}} = 1.0$ . The calculated Fröhlich frequencies of AlN nanosized crystals are at  $787\text{ cm}^{-1}$  in KBr

and  $832\text{ cm}^{-1}$  in air, respectively. We identified the 770 and  $800\text{ cm}^{-1}$  bands shown in Figures 3 and 4 as Fröhlich modes of the nanocrystalline AlN. When  $\epsilon_m$  decreases, the Fröhlich mode band shifts to a higher frequency according to eq 1. The absorption peak shifting from  $770\text{ cm}^{-1}$  for  $\epsilon_m = 2.36$  to  $800\text{ cm}^{-1}$  for  $\epsilon_m = 1$  in the experiments corroborates the existence of the Fröhlich mode in the nanoscale AlN crystals.

It should be noted that the experimental results are smaller than the calculation, because the Fröhlich mode is very sensitive to the crystal size and shape and the dielectric constant of the medium. In the above calculation, the specimens are assumed to be isotropic ionic crystals with spherical shape of a uniform size. It has been described that the Fröhlich absorption of cubical particles has a lower frequency than that of the spheres.<sup>16</sup> As observed from the TEM photographs in Figure 2a–d, the particles have typical hexagonal shapes; thus the shape effect in nanocrystalline AlN should be considered as the reason for the discrepancy. Another significant factor in interpreting the discrepancy is the differences in the selected optical parameters,<sup>17,30</sup> especially for the AlN crystal. The vibration frequency of the TO phonon and dielectric constants have been reported with different values by many researchers, for example,  $\epsilon_0 = 9.14$ ,  $\epsilon_\infty = 4.86$ ,<sup>7</sup> and  $\omega_{\text{TO}} = 650\text{ cm}^{-1}$ .<sup>31</sup> AlN crystal has tetragonal  $sp^3$  chemical bonds, but it is not completely covalent; it is partially ionic with 47% ionicity.<sup>32</sup> Despite this, the surface mode theory is applicable to nanocrystalline AlN as well as other wurtzite structured covalent semiconductor materials, such as  $\beta\text{-SiC}$ <sup>19</sup> (12% ionicity<sup>32</sup>) and  $\text{ZnO}$ ,<sup>17</sup> but the frequency of the mode will be different from that of completely ionic crystals. Thus the discrepancy between the theoretical values and experimental ones exists reasonably.

The broadness of the Fröhlich absorption peaks in the IR spectra can be explained as follows: (i) the existence of a size and shape distribution, (ii) the appearance of higher order modes predicted by eq 1 with  $n$  larger than 1, and (iii) the effects of defects and interfaces of the nanostructured crystals.

In Figure 3 (with KBr), it should be noted that there are two shoulders at about  $690$  and  $810\text{ cm}^{-1}$  on both sides of the  $770\text{ cm}^{-1}$  mode band, respectively. The absorption at  $690\text{ cm}^{-1}$  belonging to the Al–N band of nanostructured AlN crystal has been reported in some literature,<sup>3–6</sup> which is close to the bulk mode at  $660\text{ cm}^{-1}$ . The shoulder at  $810\text{ cm}^{-1}$  is uncertain and it may be the absorption of the vibration of  $\gamma$  or  $\delta$  (Al–N<sub>2</sub>) at  $840\text{ cm}^{-1}$  as reported in films.<sup>9</sup> Synthesized in the nitric atmosphere of plasma, the surface of the particles easily coheres with some nitric species in the condensation process and then forms some rich nitrogen nonsaturated bands, such as N–Al–N. The shoulders at about  $840\text{ cm}^{-1}$  appearing in Figure 4 can also be attributed to the rich nitrogen bands.

In Figure 4, there is an intense band at  $660\text{ cm}^{-1}$  that can be attributed to the similar AlN bulk absorption (TO phonon).<sup>8,24–26</sup> The appearance of the Fröhlich mode with bulk modes in one IR spectrum has been reported in other literature.<sup>16–18</sup> The authors tended to explain it as the presence of some large particles with sizes comparable to or larger than the length of an internal wavelength, on the order of micrometers. The as-synthesized powder in our experiment has a size of nanometer order ( $<100\text{ nm}$ ), so the assumption of existing large particles is not acceptable. According to the reports in previous literature,<sup>33</sup> the existence of bulk mode can be attributed to the aggregation (especially to form the chainlike structure in the experiment with  $\epsilon_m = 1$  in air) of the particles. In addition, the variations of the intensity ratio of bulk mode and surface mode shown in Figure 4 are also caused by the aggregation

effect; here the smaller particles tended easily to form the chainlike structure.

Finally, we will notice the difference between our results of nanocrystalline AlN and those in other literature<sup>3,4</sup> that did not explain an existing shoulder at about 800 cm<sup>-1</sup> appearing at the high wavenumber side of the 690 cm<sup>-1</sup> peak. According to the above discussion, the shoulder may be attributed to the Fröhlich mode of 800 cm<sup>-1</sup> observed in our experiment.

#### IV. Summary and Conclusion

The synthesis process and vibrational spectra of nanostructured AlN crystals prepared at different ambient pressures were studied by SAXS, TEM, and FT-IR analyses. On the basis of the results in this paper, we conclude that (i) the size of the nanoscale AlN crystals can be controlled by the reaction ambient pressure, because the nitric nanocrystal has a thermal stability surface and the variation of the crystal size is small, and (ii) the nanostructured crystals have an obvious Fröhlich mode due to the size effect. Further detailed study on the effects of the shape, size, aggregation, ionicity, and defects related to the vibration modes of nanocrystalline AlN will be discussed in other papers.

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