

# Ultraviolet emission from high-quality crystalline ultra-long AlN whiskers

Sibin Zuo,<sup>1</sup> Haiyun Zhang,<sup>1</sup> Jun Wang,<sup>2</sup> and Wenjun Wang<sup>2,a)</sup>

<sup>1</sup>Research Center for Applied Finance, School of Banking and Finance, University of International Business and Economics, Beijing 100029, China

<sup>2</sup>Research and Development Center of Functional Crystal, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100190, China

(Received 3 June 2013; accepted 14 August 2013)

We report here the fabrication and characterization of ultra-long AlN whiskers by physical vapor transport method. The obtained whiskers are 1–3  $\mu\text{m}$  in diameter and up to millimeters in length. The whiskers grow along the [0001] crystallographic direction and are well crystallized. They exhibit a strong ultraviolet emission at 345 nm, the shortest wavelength reported in AlN whiskers or nanowires. Our results indicate that these large scales of AlN whiskers are less contaminated by oxygen and other impurities compared with the previously reported ones, which may find wide applications in fabricating ultraviolet optoelectronic devices. © 2013 International Centre for Diffraction Data. [doi:10.1017/S0885715613000687]

Key words: AlN, whiskers, physical vapor transport, VS mechanism

## I. INTRODUCTION

As one of the important III–V semiconductors, AlN has wide applications in field emission, high-power, and high-frequency electronic devices owing to unique properties such as high thermal conductivity, good electrical resistance, low dielectric loss, and ideal thermal expansion (Monemar, 1999; Han *et al.*, 2004). Among the III-nitride compounds, AlN exhibits the largest direct band gap (6.2 eV) and the shortest wavelength ultraviolet emission near the band gap. This makes AlN an ideal material for fabricating short wave light-emitting diode (LED) as the solid-state light sources (Morkoç *et al.*, 1994), which has been regarded as an excellent alternative to replace the conventional lighting sources such as gas lasers and mercury lamps. Compared with the AlN bulks, one-dimensional (1D) structured AlN has a compact size and a high aspect ratio, making AlN exhibit a much better performance in field emission, reinforcement in ceramic-matrix composites, and potential applications for nano scaled optoelectronic devices (Tang *et al.*, 2007; Liu *et al.*, 2011). Therefore, the synthesis of high purity 1D structured AlN is of particular interest.

Quasi-1D AlN whiskers or nanowires have been produced by different methods including carbothermal reaction of aluminum oxide (Jung and Joo, 2005), direct nitridation of aluminum powder (Liu *et al.*, 2010), chemical vapor deposition (Wu and Liang, 2009), and silica-assisted catalytic growth method (Tang *et al.*, 2001). Generally, the prepared 1D AlN often exhibit different photoluminescence (PL) characterizations. A wide emission band ranging from 600 to 400 nm centered at 426 nm was observed by Lei *et al.* (2007). They reported that oxygen impurity was a key factor leading to the wide blue band, and a similar phenomenon was also observed by Xu *et al.* (2003). Byeun *et al.* (2010)

reported the band with a maximum at 500 nm from the 1D single-crystalline AlN nanostructures and the emission band was attributed to the vacancy of Al or O impurity. PL spectrum of AlN whiskers was composed of two emission bands located at 405 and 510 nm, attributed to the nitrogen vacancy, was reported by Jiang *et al.* (2011). Recently, Li *et al.* (2012) reported a sharp ultraviolet emission at 358 nm from well-aligned wurtzite-structured AlN nanorods. Summing up from the former studies, it is still a challenge to achieve ultraviolet emission approaching the band gap in 1D AlN nanostructures because of O impurity, vacancy defects, and excessive surface defects.

In this study, high-quality crystalline AlN whiskers with ultraviolet emission at 345 nm were produced by PVT method. This method has advantages of high yield, low contamination, and the diameter or length of the whiskers can be easily controlled (Bao *et al.*, 2009). To the best of our knowledge, the 345-nm emission is the shortest wavelength observed in 1D AlN materials. This ultraviolet emission will make AlN whiskers a more promising material in AlN-based nanodevices, especially solid-state lighting source, ultraviolet LED, and lasers.

## II. EXPERIMENTAL

The growth of AlN whiskers was achieved by the physical vapor transport (PVT) method in a radio frequency (RF)-heated furnace capable of maintaining a temperature of up to 2400 °C. High-purity AlN (99.9%) powder was used as the reactant source. The source was first placed into the TaC crucible loaded in a graphite crucible, then the graphite crucible was placed inside the induction heating furnace. A sketch of the experimental configuration of the crucible and growth assembly was illustrated by Zuo *et al.* (2012). AlN whiskers were grown in a temperature of 1800 °C, under a nitrogen (99.99%) pressure of 0.6 atm and a distance of 15 mm between the source and crucible lid. After 6 h growth,

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: wjwang@aphy.iphy.ac.cn

large quantities of white AlN whiskers were deposited on the TaC lid. Crystalline phase identifications were performed on an X-ray diffractometer (X'Pert ProMRD) with  $\text{CuK}\alpha$  radiation at 40 kV and 40 mA. The composition of the samples was determined from X-ray photoelectron spectra (XPS), which was recorded on an X-ray photoelectron spectrometer, using monochromatized Al X-rays as the excitation source. The morphologies and microstructures of the samples were observed by a scanning electron microscope (SEM, FEI, XL-30) and a high-resolution transmission electron microscope (HRTEM, JEOL, JEM-2010), respectively. Raman scattering measurement was performed at room temperature by a Raman system (JY-HR800) using the 532-nm line of a solid-state laser as an excitation source. PL spectra were conducted at room temperature with a Hitachi F-7000 spectrofluorometer using an Xe lamp as an excitation light source.

### III. RESULTS AND DISCUSSION

Figure 1 presents the photograph and a typical X-ray diffraction (XRD) pattern of the as-prepared samples. Large quantities of cotton-like white wires are deposited on the TaC lid. XRD diffraction peaks with miller indexes marked above can be indexed as hexagonal AlN ( $a = 3.114 \text{ \AA}$  and  $c = 4.981 \text{ \AA}$ ), agreeing well with the standard reference diffraction pattern (ICDD-PDF No. 25-1133). In addition, no characteristic peaks of impurities such as  $\text{Al}_2\text{O}_3$ , AlON, and other compounds were found. XPS was applied to determine the element composition and corresponding chemical states of the sample. Figure 2(a) shows the measured spectrum of the sample, indicating the presence of elements Al, N, C, and O. The presence of carbon might have come from the sample handling and the oxygen may arise from the AlN surface oxidized layer when exposed to the atmosphere. No other impurity elements were detected in the XPS resolution limitation. The binding energies of  $\text{N}_{1s}$  and  $\text{Al}_{2p}$  centered at 396.5 and 73.5 eV, as shown in Figures 2(b) and 2(c), respectively, are in good agreement with the values of aluminum nitride films deposited by plasma source molecular beam epitaxy (Rosenberger *et al.*, 2008). The  $\text{Al}_{2p}$  is assigned to aluminum bound to nitrogen and the  $\text{N}_{1s}$  is assigned to nitrogen bound to aluminum in wurtzite AlN.

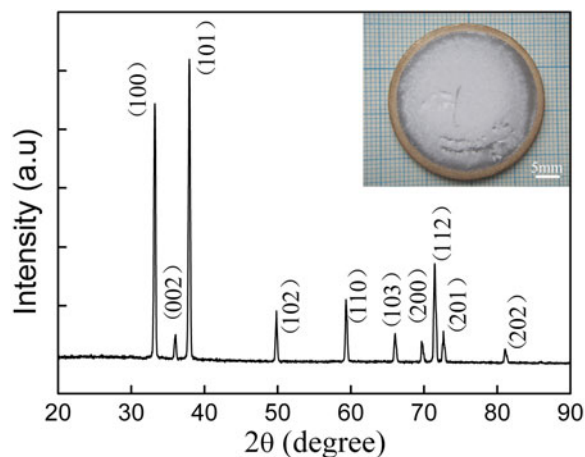


Figure 1. (Color online) Typical XRD pattern of an as-prepared sample, and the insert gives the photograph of the sample.

SEM images of the as-prepared sample with different magnifications are shown in Figure 3. An overview of the samples [Figure 3(a)] reveals that ultra-long AlN whiskers with length up to several millimeters were obtained. The AlN whiskers are about 10–100 times longer than those previously reported (Wu and Liang, 2009; Liu *et al.*, 2010), and this ultra-long length will benefit tailoring and processing of the whiskers in electronic device applications. SEM image with higher magnification [Figure 3(b)] shows that the AlN whiskers are 1–3  $\mu\text{m}$  in diameter, and exhibit smooth surface and good toughness. SEM image of a single AlN whisker with smooth surface and six-sided prismatic morphology is presented as an insert in Figure 3(b). From the six-sided prismatic morphology, one can deduce the AlN whiskers belonging to the hexagonal phase, and this agrees well with the XRD analysis. No liquid droplets can be found at the tip, indicating that the growth mode does not involve the vapor–liquid–solid (VLS) mechanism, but rather direct growth from the vapor phase (VS mechanism).

In order to determine the microstructure of AlN whiskers, TEM and HRTEM images were conducted. From the corresponding HRTEM image [Figure 4(a)], it can be seen that the AlN whisker exhibits a typical crystalline characteristic and is structurally uniform with clear lattice fringes, no defects such as dislocation or stacking faults are found. The insert magnified fringe of the HRTEM shows the interplanar spacing of the AlN lattice planes to be 0.249 nm, which agrees well with the d-spacing of the (002) lattice planes of hexagonal AlN, confirming that the [0001] direction is the preferred growth direction of the AlN whiskers. The selected area electron diffraction (SAED) pattern of the whisker is presented in Figure 4(b), confirming that the whisker grows along the [0001] direction. Previous work also reported that the AlN nanofibers grown by the sublimation method grew along the [0001] direction (Jiang *et al.*, 2011).

The structural information of the AlN whiskers was also investigated by backscattering geometry Raman spectra, which was recorded at room temperature using a 532-nm solid-state laser as excitation source. Since the space group of wurtzite AlN is  $P6_3mc$  with all of the atoms occupying the  $\text{C}_{3v}$  sites, six first-order Raman active modes may be present:  $\text{A}_1(\text{TO})$ ,  $\text{A}_1(\text{LO})$ ,  $\text{E}_1(\text{TO})$ ,  $\text{E}_1(\text{LO})$ ,  $\text{E}_2(\text{high})$ , and  $\text{E}_2(\text{low})$  (Harima, 2002). In the Raman spectrum in Figure 5, two high-intensity peaks at 656.3 and 610.5  $\text{cm}^{-1}$  are indexed to the  $\text{E}_2(\text{high})$  and  $\text{A}_1(\text{TO})$  phonon modes, respectively. The peak at 670.5  $\text{cm}^{-1}$  is indexed to  $\text{E}_1(\text{TO})$ , whereas the two low-intensity peaks at 247.3 and 911.0  $\text{cm}^{-1}$  are assigned to the  $\text{E}_2(\text{low})$  and  $\text{E}_1(\text{LO})$ , respectively. It is also found that there are small shifts of about 2  $\text{cm}^{-1}$  to the lower wavenumbers (red shift) for  $\text{A}_1(\text{TO})$ ,  $\text{E}_2(\text{high})$ , and  $\text{E}_1(\text{TO})$  modes compared with the narrow peaks from bulk AlN data (Davydov *et al.*, 1998). Red-shift phenomenon is commonly observed in some AlN nanowire (Xu *et al.*, 2003), nanobelt (Wu *et al.*, 2003), and nano particle structures (Lan *et al.*, 1999; Cao *et al.*, 2000), as a result of decreasing microcrystal and impurity incorporation or the size confinement effect (Hayes *et al.*, 2000). The size confinement effect may be impossible for shift of the Raman frequency because the diameter of the AlN whiskers studied here are approaching micrometers size. Meanwhile, blue-shift of phonon frequencies of AlN nanowires was observed in other work because of the compressive stress in the lattice (Zhao *et al.*, 2005). It is well known that

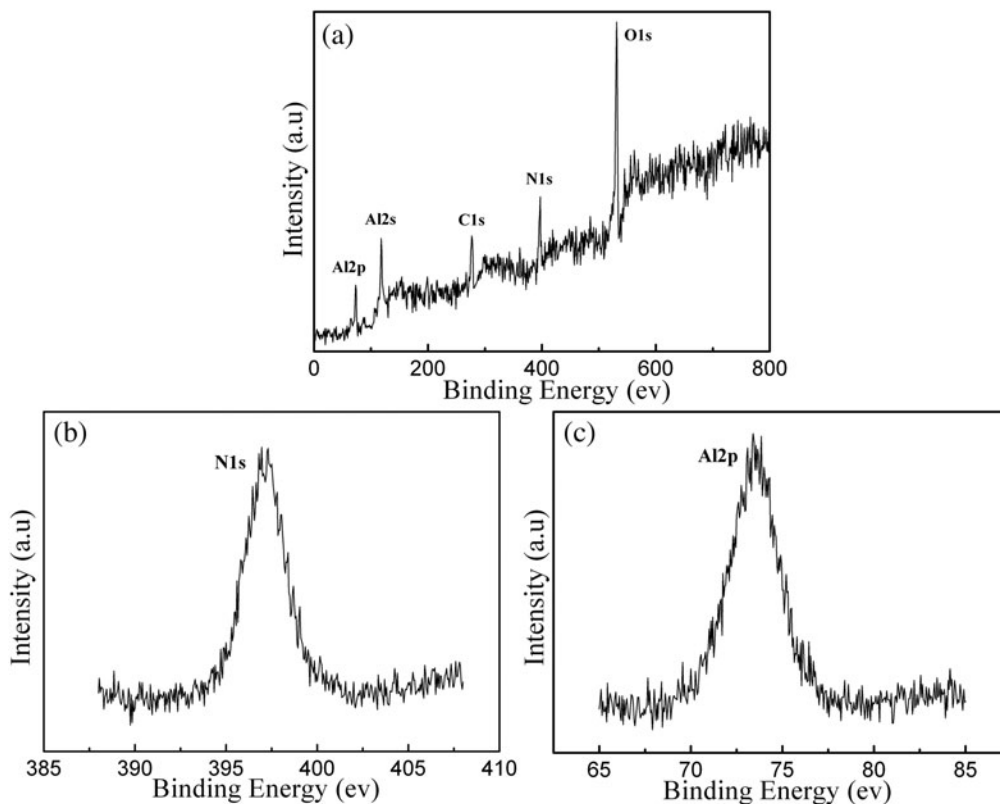


Figure 2. XPS spectra of an as-prepared sample: (a) survey spectrum, (b) N<sub>1s</sub> region, centered at 396.5 eV, and (c) Al<sub>2p</sub> region, centered at 73.5 eV.

impurities or stress in semiconductors significantly affect the Raman line width. The full-width at half-maximum of the A<sub>1</sub>(TO) and E<sub>2</sub>(high) are 7.9 and 7.0 cm<sup>-1</sup>, respectively, which are a little larger than those of the AlN crystallite (Bergman *et al.*, 1999), indicating low concentration of impurities and stress in the whiskers. In our study, the narrow Raman peaks with a less shift indicate a good crystalline quality and homogeneous structures of AlN whiskers were obtained.

PL measurements were conducted at room temperature at an excitation wavelength of 260 nm by using Xe lamp as the light source. As shown in the PL spectrum Figure 6, one can only observe a strong ultraviolet emission peak centered at 345 nm (3.59 eV), which is even 7 nm shorter than the shortest ultraviolet emissions of the AlN whiskers reported by Liu *et al.* (2010). The luminescence properties of AlN had been extensively studied in the past couple of decades and diverse luminescence mechanisms had been reported. Generally, nitrogen deficiency, aluminum vacancy, and oxygen point

defect were deemed to be the origin of the luminescence below band gap (Slack, 1973; Youngman *et al.*, 1989; Berzina *et al.*, 2002; Schulz *et al.*, 2011). Liu *et al.* (2010) pointed out that the UV emission (352 nm) of the AlN whiskers could be attributed to the transition between the deep impurity center (oxygen) and the valence band. Youngman *et al.* (1989) ascribed the broad band at 2.7 eV (457 nm) and 3.8 eV (326 nm) from AlN single crystals grown under nitrogen-deficient conditions results from the vacancy of N (V<sub>N</sub>). Schulz *et al.* (2011) investigated the optical properties in insulating, irradiation damaged bulk AlN crystals. An isolated transition, peaking about 3.3 eV (376 nm) was attributed to a donor–acceptor pair transition involving an unknown shallow donor and the isolated Al vacancy. Slack (1973) reported that the formation of O<sub>N</sub> (oxygen occupies a regular N site) accompanied by V<sub>Al</sub> for charge compensation. Thus, a state related to O<sub>N</sub>–V<sub>Al</sub> complex is formed inside the AlN band gap with a probable excited state close to the conduction band. According to the energy scheme proposed by Berzina

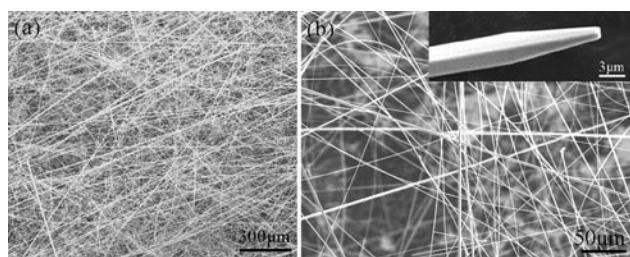


Figure 3. (a) Low-magnification SEM image of AlN whiskers with the length up to several millimeters, and (b) high-magnification SEM image of the AlN whiskers.

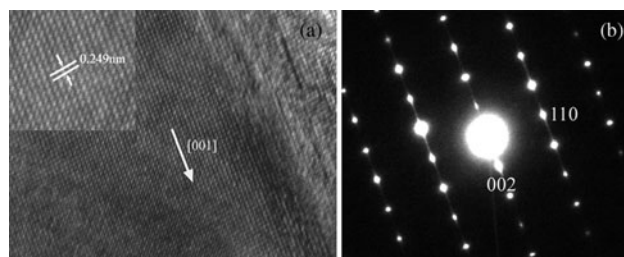


Figure 4. (a) HRTEM image of an AlN whisker, the insert is magnified fringes of the HRTEM. (b) SAED pattern of the AlN whisker.

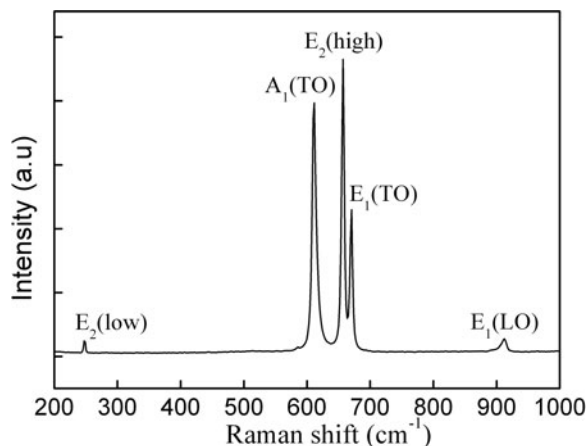


Figure 5. Raman scattering spectrum of AlN whiskers.

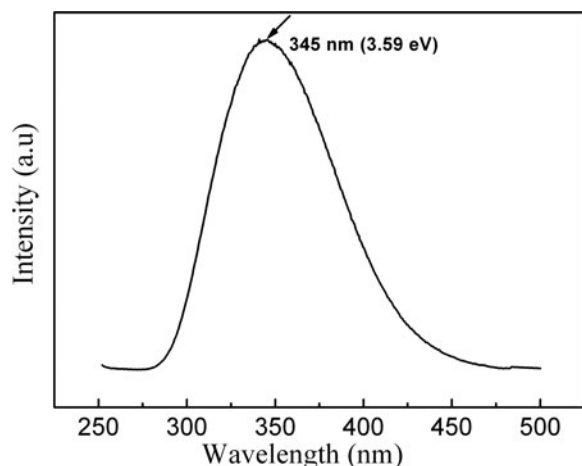


Figure 6. Room-temperature PL spectrum of AlN whiskers excited at 260 nm.

*et al.* (2002), the  $O_N-V_{Al}$  complex level locates at about 1.2 eV above the valence band and the separated  $O_N$  ion level locates at about 4.3 eV. High-purity AlN source and nitrogen gas were used to grow AlN whiskers. Although some residual oxygen in the chamber would dissolve into the AlN lattice because of the high chemical affinity of aluminum and oxygen, the concentration oxygen in our sample is very low. Therefore, the emission at 345 nm (3.59 eV) could not be attributed to the  $O_N$  level or the  $O_N-V_{Al}$  complex level. It might be attributed to  $V_N$ . The oxygen element originating from surface absorption may also contribute to the emission. Of course, the exact PL mechanism of the AlN whiskers requires further investigation. Such a strong and uniform 345 nm ultraviolet emission will make the AlN whiskers ideal candidates for the application of ultraviolet optoelectronic nanodevices.

#### IV. CONCLUSION

Large quantities of ultra-long AlN whiskers were produced by the PVT method through the VS mechanism. The as-prepared samples were less contaminated by oxygen and well crystallized. A strong and uniform 345-nm ultraviolet

emission has been realized in the AlN whiskers. This emission is attributed to  $V_N$  and the surface defect states. Such extensive and uniform ultraviolet emission, as well as high crystal quality and ultra-long length, will make AlN whiskers ideal candidates for the application of nano- or micro devices in optoelectronics.

#### ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (grant numbers 51210105026 and 51172270), the National Basic Research Program of China (973 Program, grant no. 2013CB932901), and Chinese Academy of Sciences.

- Bao, H. Q., Chen, X. L., Li, H., Wang, G., Song, B., and Wang, W. J. (2009). "The sublimation growth of AlN fibers: transformations in morphology and fiber direction," *Appl. Phys. A* **94**, 173.
- Bergman, L., Alexson, D., Murphy, P. L., Nemanich, R. J., Dutta, M., Stroscio, M. A., Balkas, C., Shin, H., and Davis, R. F. (1999). "Raman analysis of phonon lifetimes in AlN and GaN of wurtzite structure," *Phys. Rev. B* **59**, 12977.
- Berzina, B., Trinkler, L., Sils, J., and Atobe, K. (2002). *Radiat. Eff. Defects Solids* **157**, 1089.
- Byeun, Y. K., Telle, R., Jung, S. H., Choi, S. C., and Hwang, H. I. (2010). "The growth of one-dimensional single-crystalline AlN nanostructures by HVPE and their field emission properties," *Chem. Vap. Deposition* **16**, 72.
- Cao, Y. G., Chen, X. L., Lan, Y. C., Li, J. Y., Xu, Y. P., Xu, T., Liu, Q. L., and Liang, J. K. (2000). "Blue emission and Raman scattering spectrum from AlN nanocrystalline powders," *J. Cryst. Growth* **213**, 198.
- Davydov, V. Y., Kitaev, Y. E., Goncharuk, I. N., Smirnov, A. N., Graul, J., Semchinova, O., Uffmann, D., Smirnov, M. B., and Mirgorodsky, A. P. (1998). "Phonon dispersion and Raman scattering in hexagonal GaN and AlN," *Phys. Rev. B* **58**, 12899.
- Han, S., Jin, W., Zhang, D., Tang, T., Li, C., Liu, X. L., Liu, Z. Q., Lei, B., and Zhou, C. W. (2004). "Photoconduction studies on GaN nanowire transistors under UV and polarized UV illumination," *Chem. Phys. Lett.* **389**, 176.
- Harima, H. (2002). "Properties of GaN and related compounds studied by means of Raman scattering," *J. Phys. Condens. Matter* **14**, R967.
- Hayes, J. M., Kuball, M., Shi, Y., and Edgar, J. H. (2000). "Temperature dependence of the phonons of Bulk AlN," *Jpn. J. Appl. Phys.* **39**, L710.
- Jiang, L. B., Zuo, S. B., Wang, W. J., Li, H., Jin, S. F., Wang, S. C., and Chen, X. L. (2011). "Role of Ni in the controlled growth of single crystal AlN triangular microfibers: morphology evolution, growth kinetics and photoluminescence," *J. Cryst. Growth* **318**, 1089.
- Jung, W. S. and Joo, H. U. (2005). "Catalytic growth of aluminum nitride whiskers by a modified carbothermal reduction and nitridation method," *J. Cryst. Growth* **285**, 566.
- Lan, Y. C., Chen, X. L., Cao, Y. G., Xu, Y. P., Xun, L. D., Xu, T., and Liang, J. K. (1999). "Low-temperature synthesis and photoluminescence of AlN," *J. Cryst. Growth* **207**, 247.
- Lei, M., Yang, H., Guo, Y. F., Song, B., Li, P. G., and Tang, W. H. (2007). "Synthesis and optical property of high purity AlN nanowires," *Mater. Sci. Eng. B* **143**, 85.
- Li, J. J., Song, B., Wu, R., Li, J., and Jian, J. K. (2012). "Preparation and optical properties of free-standing transparent aluminum nitride film assembled by aligned nanorods," *J. Am. Ceram. Soc.* **95**, 870.
- Liu, B. D., Bando, Y., Wu, A. M., Jiang, X., Dierre, B., Sekiguchi, T., Tang, C. C., Mitome, M., and Golberg, D. (2010). "352 nm ultraviolet emission from high-quality crystalline AlN whiskers," *Nanotechnology* **21**, 1.
- Liu, F., Su, Z. J., Mo, F. Y., Li, L., Chen, Z. S., Liu, Q. R., Chen, J., Deng, S. Z., and Xu, N. S. (2011). "Controlled synthesis of ultra-long AlN nanowires in different densities and *in situ* investigation of the physical properties of an individual AlN nanowire/Nanoscale," *Nanoscale* **3**, 610.
- Monemar, B. (1999). "III-V nitrides—important future electronic materials," *J. Mater. Sci. Mater. Electron.* **10**, 227.

- Morkoç, H., Strite, S., Gao, G. B., Lin, M. E., Sverdlov, B., and Burns, M. (1994). "Largebandgap SiC, IIIV nitride, and IIVI ZnSebased semiconductor device technologies," *J. Appl. Phys. Lett.* **76**, 1363.
- Rosenberger, L., Baird, R., Cullen, E. M., Auner, G., and Shreve, G. (2008). "XPS analysis of aluminum nitride films deposited by plasma source molecular beam Epitaxy," *Surf. Interface Anal.* **40**, 1254.
- Schulz, T., Albrecht, M., Imscher, K., Hartmann, C., Wollweber, J., and Fornari, R. (2011). "Ultraviolet luminescence in AlN," *Phys. Status Solidi b* **248**, 1513.
- Slack, G. A. (1973). "Nonmetallic crystals with high thermal conductivity," *J. Phys. Chem. Solids* **34**, 321.
- Tang, Y. B., Cong, H. T., and Cheng, H. M. (2007). "Synthesis and properties of one-dimensional aluminum nitride nanostructures," *Nano* **2**, 307.
- Tang, C. C., Fan, S. S., Chapelle, M. L., and Li, P. (2001). "Silica-assisted catalytic growth of oxide and nitride nanowires," *Chem. Phys. Lett.* **333**, 12.
- Wu, H. M. and Liang, J. Y. (2009). "Synthesis and luminescence properties of AlN nanowires," *Ferroelectrics* **383**, 95.
- Wu, Q., Hu, Z., Wang, X. Z., and Chen, Y. (2003). "Synthesis and optical characterization of aluminum nitride nanobelts," *J. Phys. Chem. B* **107**, 9726.
- Xu, C. K., Xue, L., Yin, C., and Wang, G. (2003). "Formation and photoluminescence properties of AlN nanowires," *Phys. Status Solidi a* **198**, 329.
- Youngman, R. A., Harris, J. H., and Chernoff, D. A. (1989). "Structural evolution of AlN nano-structure: nanotips and Nanorods," *Ceram. Trans.* **5**, 309.
- Zhao, Q., Zhang, H., Xu, X., Wang, Z., Xu, J., Yu, D., Li, G., and Su, F. (2005). "Optical properties of highly ordered AlN nanowire arrays grown on sapphire substrate," *App. Phys. Lett.* **86**, 193101.
- Zuo, S. B., Wang, J., Chen, X. L., Jin, S. F., Jiang, L. B., Bao, H. Q., Guo, L. W., Wei, S., and Wang, W. J. (2012). "Growth of AlN single crystals on 6H-SiC (0001) substrates with AlN MOCVD buffer layer," *Cryst. Res. Technol.* **47**, 139–144.