

Synthesis and Optical Characterization of Aluminum Nitride Nanobelts

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Aluminum nitride nanobelts with hexagonal structure were successfully synthesized by evaporating aluminum powder in ammonia/nitrogen atmosphere at 1200 °C. The as-prepared AlN nanobelts have a rectangular cross section with a width of 30–500 nm and length of about 100 μm . The optical characterization indicates that the vibration modes of the AlN nanobelt agree well with those of AlN film despite its nanobelt geometry. This nanobelt geometry of AlN could be important for the construction of GaN-based nanoheterostructures in future nanoelectronics.

1. Introduction

Group III nitrides are the most promising semiconductors with a direct band gap from 1.9 eV (InN), 3.4 eV (GaN), to 6.2 eV (AlN). Their one-dimensional (1D) quantum confinement geometries such as nanowire and nanotube are particularly important not only for understanding fundamental concepts underlying the observed optical, electronic, and mechanical properties of materials, but also for the wide potential applications.^{1–7} As a newcomer of the nanoworld, nanobelts have attracted increasing attention since their discovery in 2001,⁸ because of the novel geometry as well as the promising properties relating to, e.g., field emission, field-effect transistors, and gas sensors.^{9–11} To date, most of the studies on nanobelts have dealt with oxide nanobelts. Extending the synthesis of this kind of objects to non-oxide systems is no doubt an interesting topic. With the lithium-assisted self-assembly process, Zhang et al. reported the serendipitous synthesis of aluminum carbide (Al_4C_3) nanobelts and suggested similar nanostructures of other carbides and nitrides.¹² GaN nanobelts were synthesized by a thermal CVD method.¹³ As an important member of group III nitrides, AlN is a perfect substrate for the epitaxial growth of the GaN-based heterostructure due to its small lattice mismatch with GaN and its superior properties such as high melting point, excellent thermal conductivity, high resistance to chemicals, and high electrical resistivity, hence is widely used in today's electronic industry.¹⁴ It is expected that AlN nanobelt could be important for the construction of GaN-based nanoheterostructures in future nanoelectronics. A similar configuration has been demonstrated by the multifunctional $\text{TiO}_2/\text{SnO}_2$ nanotapes.¹⁵ Here, we report the synthesis and characterization of AlN nanobelts. The experimental results indicate that AlN nanobelts could be produced in gram scale and they are very similar to AlN films in nature despite the nanobelt geometry.

2. Experimental Methods

AlN nanobelts were prepared by evaporating metallic aluminum at 1200 °C under the ammonia/nitrogen atmosphere. In a typical run, the aluminum powder (99%) with the particle size of 100–200 mesh was dipped into the CoSO_4 solution. The solvent was first volatilized at room temperature and then the cobalt-containing Al powder (0.5 mmol Co per gram of Al) was obtained after drying at 100 °C for 2 h. The precursor was placed in a quartz tube located in a horizontal tubular furnace. This system was flushed with Ar several times to remove the oxygen and moisture. Finally, the furnace was heated to the temperature of 1200 °C at the rate of 12 °C/min. As the temperature reached 860 °C, the flow of argon was replaced by NH_3/N_2 of 300 sccm. After allowing the reaction to proceed for 1.5 h, the furnace was cooled to ambient temperature under the flowing Ar. A gray powder covered by a thin layer of black powder was obtained at the position where the precursor was placed.

The gray product was characterized by various methods. X-ray diffraction (XRD) experiments were carried out on a Philips X'pert Pro X-ray diffractometer with $\text{Cu K}\alpha$ radiation of 1.5418 Å. The morphology and structure of the product were analyzed by scanning electron microscopy (SEM, JEOL JSM-6300, 20 kV), transmission electron microscopy (TEM, JEOL-JEM-1005 at 100 kV), and high-resolution transmission electron microscopy (HRTEM, JEM2010 at 200 kV). The optical properties of the product were studied by ultraviolet–visible spectroscopy (UV–vis, UV-2401PC spectrometer), infrared spectroscopy (IR, BRUKER VECTOR22), and Micro-Raman spectroscopy (T64000 laser Raman spectrometer). All the measurements were performed at room temperature.

3. Results and Discussion

3.1. Structure and Morphology of the AlN Nanobelts.

Figure 1 is the XRD pattern of the as-prepared gray product. The diffraction peaks with miller indices marked above can be indexed to the hexagonal AlN (h-AlN), indicating that the gray

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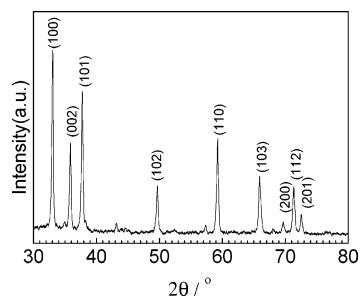


Figure 1. XRD pattern of the as-prepared AlN nanobelts. Miller indices of hexagonal AlN are placed above the corresponding peaks.

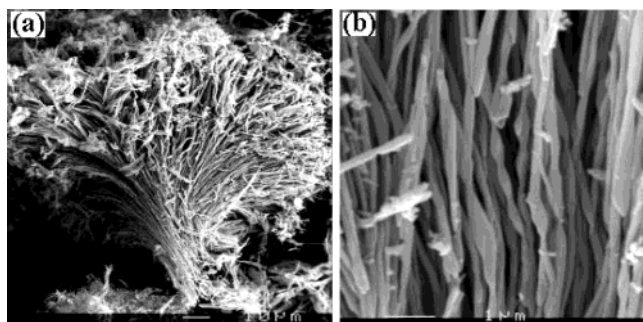


Figure 2. SEM image of (a) the AlN nanobelts bundle, and (b) the enlarged image with quasi-aligned nanobelts.

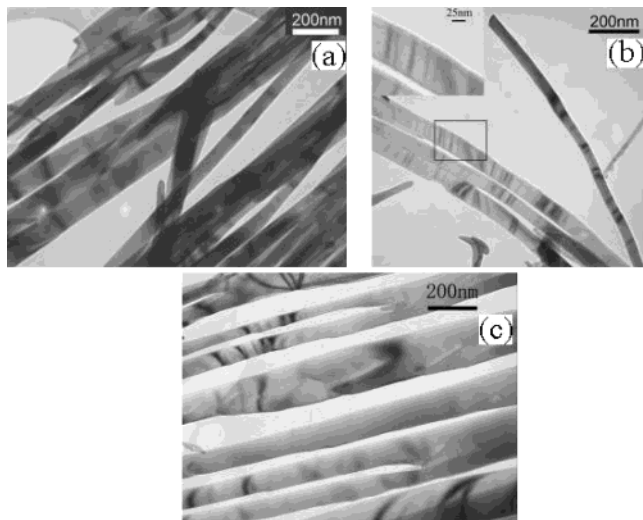


Figure 3. TEM images of AlN nanobelts. (a) Regular AlN nanobelts. (b) Cross-section of AlN nanobelts showing the thickness of about 20 nm. Inset is the enlargement of the boxed region, displaying the rectangular geometry of the AlN nanobelt. (c) Branched AlN nanobelts.

product is h-AlN. SEM observation reveals that the product is composed of nanobelts and is partially in the form of nanobelt bundles with the length up to 100 μm as shown in Figure 2a. The enlarged SEM image in Figure 2b clearly indicates that the nanobelts are quasi-aligned, most of which twist with different period. The width-to-thickness ratio of these nanobelts is estimated to be 4–10.

TEM image could provide more geometric details about the AlN nanobelts and several different morphologies were observed as typically shown in Figure 3. The ripple-type contrast implies the presence of strain in the AlN nanobelts.^{8,12} The width for different nanobelts varies from 30 to 500 nm. The enlargement of the cross-sectional TEM image in the inset of Figure 3b indicates the rectangular geometry of the nanobelt with the thickness about 20 nm. The width-to-thickness ratio for this

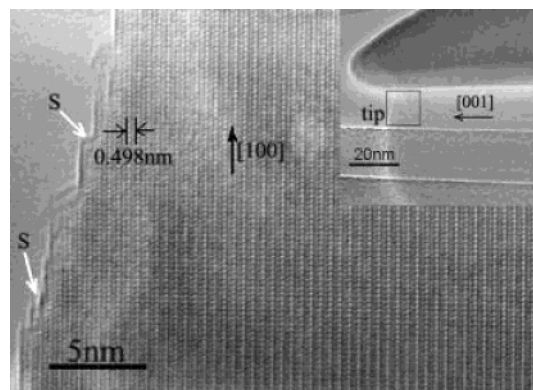


Figure 4. HRTEM image of the AlN nanobelt from the boxed tip part of the nanobelt shown in the inset. The tips of the AlN nanobelts are hemi-elliptic.

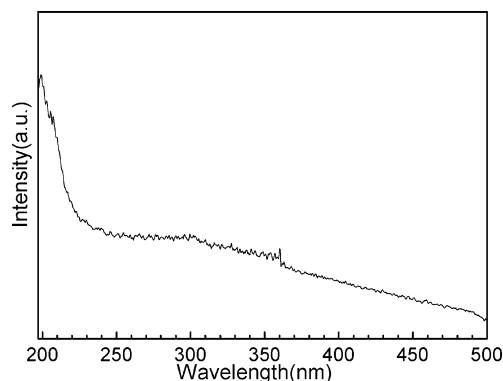


Figure 5. The UV-vis spectrum of as-prepared AlN nanobelts.

individual nanobelt is about 4 as measured from this image. The tips of the nanobelts are hemi-elliptic, different from the faceted tip morphologies of oxide nanobelts and Al_4C_3 nanobelts.^{8,12} Figure 3c shows some branched AlN nanobelts. The belt geometry could split to two branchlets. In some cases, one branchlet would cease growing, resulting in the significant decrease of the trunk width. The reason for such growth model has not been clarified yet. The yield of AlN nanobelts in the gray product is rather high (>90%) in addition to a small amount of nanowires and nanoparticles.

To further verify the structural characteristic of the AlN nanobelts, HRTEM image was obtained as typically shown in Figure 4. This individual image corresponds to the box in the tip part of the nanobelt as indicated in the inset of Figure 4. The distance of 0.498 nm between the two arrows is in agreement with the spacing d_{001} of h-AlN. This nanobelt is grown along [001] direction, which is different from the case for Al_4C_3 nanobelts growing within the basal plane.¹² Some steps are present on the tip surface of the nanobelts, as pointed out by the white arrows, accompanied with the formation of the hemi-elliptic end. From HRTEM results, it is seen that the AlN nanobelt is single crystalline and free from dislocations and defects.

3.2. Optical Characterization of the AlN Nanobelts. The as-prepared AlN nanobelts were further characterized by UV-vis spectroscopy to measure the excitonic or interband transitions (Figure 5). The absorption edge at 199.7 nm, corresponding to the band gap of 6.22 eV, could be well assigned to the optical transition of the first excitonic state of AlN.

Figure 6 shows the IR transmission spectrum of the AlN nanobelts, embedded in KBr matrix. The sharp peak around 631 cm^{-1} and the shoulder peak around 667 cm^{-1} are in good

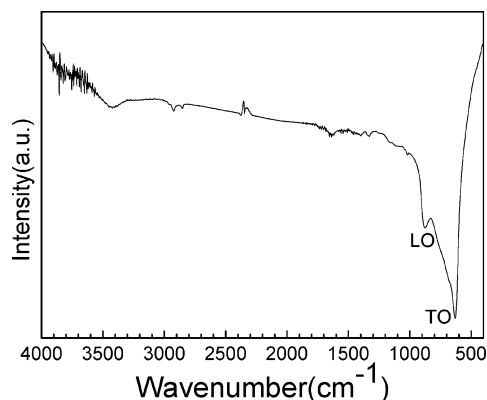


Figure 6. IR spectrum of as-prepared AlN nanobelts.

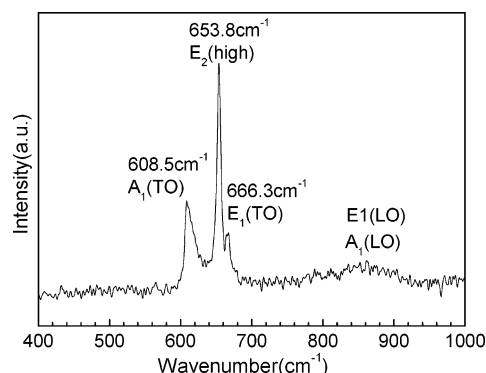


Figure 7. Raman spectrum of as-prepared AlN nanobelts.

TABLE 1: Photon Modes of Nanobelts, Films, and Single Crystal of h-AlN

phonon mode	AlN nanobelts (cm ⁻¹)	AlN films (cm ⁻¹) ^a	crystal AlN (cm ⁻¹) ^b
A ₁ (TO)	608.5	607.3	610
E ₂ (high)	653.8	653.6	656
E ₁ (TO)	666.3	666.5	669
A ₁ (LO)	840~920	884.5	890
E ₁ (LO)		912	911

^a Ref 22. ^b Ref 23.

agreement with the TO₂ and TO₁ phonon modes of AlN film.^{16,17} The broad peak around 877 cm⁻¹ could be attributed to the longitudinal optical (LO) mode of AlN films.¹⁸ Some weak peaks appear from 1000 to 4000 cm⁻¹, which could be assigned to a very small amount of water, CO₂, and air in the spectrometer path or on the sample surface.¹⁷ Al–O peaks at 950 cm⁻¹ or 460 cm⁻¹,^{19,20} have not been detected, indicating that the h-AlN species in the sample is highly pure.

Raman scattering is a useful tool for the characterization of nanomaterials and could be used to probe the presence of lattice defects in these solids qualitatively, e.g., the crystalline quality could be judged from the peak shapes and the selection rules.²¹ The space group of wurtzite AlN is C_{4v}(P6₃mc) with all atoms occupying the C_{3v} sites. Six Raman-active modes may be present, i.e., 1A₁(TO) + 1A₁(LO) + 1E₁(TO) + 1E₁(LO) + 2E₂. The Raman spectrum of the as-prepared AlN nanobelts, shown in Figure 7, was recorded using the 514.5 nm line of an Ar⁺ ion laser as excitation source. For comparison, the phonon modes for our sample from Figure 7 and those for AlN film and AlN single crystal from the literature^{22–23} are summarized in Table 1. It is seen that, for our AlN nanobelts, A₁(TO), E₂(high), and E₁(TO) modes presented at 608.5, 653.8, and 666.3 cm⁻¹, respectively, are in good agreement with the results for

AlN film. The broadening and asymmetry of these phonon frequencies probably result from the size confinement effect and internal stress.²⁴ A rather broad peak centered around 870 cm⁻¹ may result from the modes of A₁(LO) and E₁(LO). The low intensity of longitudinal optical (LO) phonons probably resulted from the special angle between the wave vector of incident photons and axis direction [001] of hexagonal AlN nanobelts in the near backscattering geometry.²⁴ From the above optical spectroscopic results, it could be concluded that the as-prepared AlN nanobelt is similar to the AlN film in the optical properties, despite its nanobelt geometry.

The growth mechanism of the AlN nanobelts is still not clear enough at the moment. We have studied the influence of reaction temperature on the formation of nanobelts. It is found that only AlN nanowires were observed in the product when the temperature was below 1030 °C, which could be assigned to the extended vapor–liquid–solid mechanism,²⁵ and cobalt species functions in this case. AlN nanobelts became observable when the reaction temperature is higher than 1050 °C. For comparison, we also prepared AlN in a similar way, i.e., through direct reaction of Al powder and NH₃/N₂ at 1100 °C, but in the absence of other chemicals. Interestingly, AlN nanobelts can also be found (as shown in Figure 2b of ref 25). This implies that AlN nanobelts are self-assembled through vapor–solid reaction of the vaporized aluminum with NH₃/N₂ at high temperature due to the intrinsic properties of AlN such as the anisotropy of its hexagonal structure. In this case, the existence of cobalt could influence the growth conditions such as vapor pressure, which could be the reason for the high yield of AlN nanobelts in our preparation. Supporting evidence is that our TEM analysis on the black powder covering on the product shows the majority of AlN nanowires rather than nanobelts, which probably results from the low concentration of Al vapor on the surface due to the taking away by the flowing gas. Further study on this topic is still underway in our group.

4. Conclusions

Hexagonal AlN nanobelts with length about 100 μm and width from 30 to 500 nm are reported, which were synthesized through the reaction of aluminum and ammonia/nitrogen at an elevated temperature. The optical characterization results indicate that the AlN nanobelts are very similar to AlN thin films in nature despite the nanobelt geometry. Because of the important function of AlN in GaN-based electronics, the AlN nanobelt could be a promising substrate candidate for the construction of GaN-based nanoheterostructures in future nanoelectronics.

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