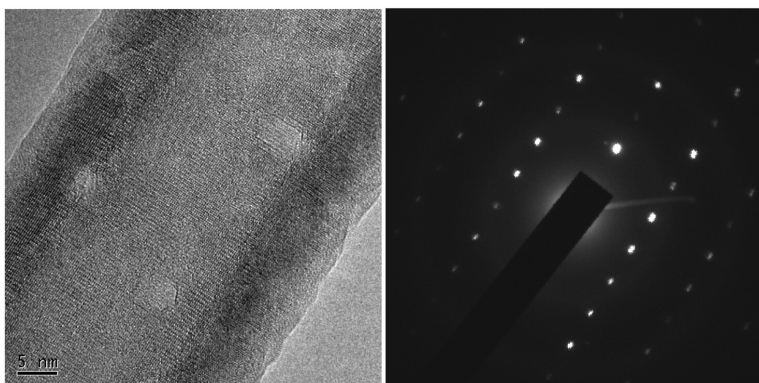Communication

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Synthesis and Characterization of Faceted Hexagonal Aluminum Nitride Nanotubes

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Since the discovery of carbon nanotubes by Iijima,[1] their unusual properties and wide potential applications,[2] resulting from their unique tubular nanostructures, have stimulated intensive exploration to the nanotubular geometries of other systems. Examples are the nanotubes of $B_xC_yN_z$ composites, some metal chalcogenides such as WS_2, MoS_2, VO_x and TiO_2, the halogen compound of $NiCl_2$, as well as GaN for group III nitrides.[3–8] Among these systems, group III nitride nanotubes are particularly interesting because the wurtzite nitrides form a continuous alloy system with adjustable direct band gaps from 6.2 eV in AlN through 3.4 eV in GaN to 1.9 eV in InN. Hence, ultimate nanoscale optoelectronic devices for a wide range of wavelengths with many advanced features such as high thermal conductivity and superior stability may be realized by using this nanotubular system. Despite of the scientific and technological importance and the great endeavor devoted, the progress in this aspect is still limited.[8,9] GaN nanotubes have recently been synthesized by an "epitaxial casting" approach using hexagonal ZnO nanowires as the templates.[8] This progress has given us intense interest and confidence to extend the nanotubular geometry to the other group III nitrides of the third-generation semiconductors,[10] due to their structural similarity. Very recently, the stability of the AlN nanotubes has been theoretically predicted.[9] In this contribution, our special attention is paid to the AlN nanotubes because the lattice mismatch between AlN and GaN is only about 2%, which permits great range and flexibility in heterostructure design.[10] The synthesis and characterization of the faceted single-crystalline hexagonal aluminum nitride (h-AlN) nanotubes are reported here.

This novel morphology was found in the product by simply nitriding the aluminum powder, which was impregnated with cobalt sulfate (1.0 mmol Co per gram of Al) in advance, with NH_3/N_2 (NH_3 4 vol %). The reaction was carried out in a horizontal tubular furnace. The furnace was first heated at a rate of 10 °C/min to 900 °C under flowing Ar of 100 sccm. Then, the flowing gas was switched to NH_3/N_2 of 300 sccm, and the furnace was continually heated to 1100 °C and maintained at this temperature for 90 min. After this, the furnace was cooled to ambient temperature, and a black product was obtained.

The X-ray diffraction (XRD) pattern shows that the product is composed of h-AlN and a little non-nitrified Al residues. Figure 1 shows the transmission electron microscopic (TEM) images of the as-prepared product. It is seen that the product is a mixture of nanotubes and nanowires. The nanotubes are typically a few micrometers in length with the diameters from 30 to 80 nm. Most AlN nanotubes have both ends open. It is observed that the open ends have the pseudohexagonal morphology. In addition, more than five distinguishable contrast regions can be seen for the nanotube in Figure 1b, while there are only three for the nanotube in Figure 1c. These indicate that the AlN nanotubes are faceted with
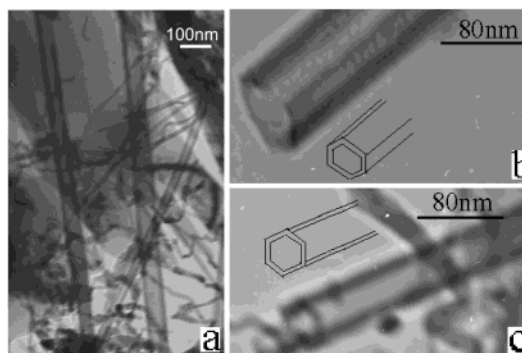
Figure 1. (a) TEM image of the AlN product containing nanotubes and nanowires. (b, c) Pseudohexagonal open ends of two AlN nanotubes in different lying fashions as schematically shown in the figures. For faceted tubular structure, different lying fashions will result in different numbers of distinguishable contrast regions as seen here.
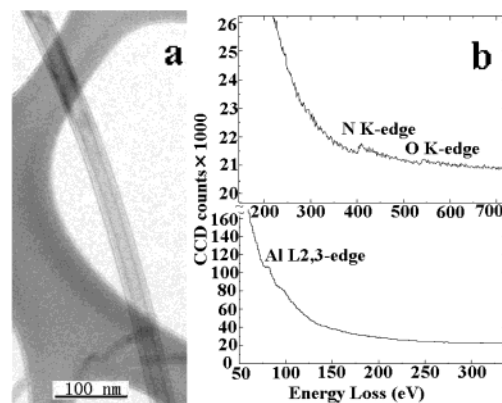

Figure 2. (a) TEM image of an AlN nanotube. (b) Corresponding EELS spectra exhibiting the distinct K-edges at 401 and 540 eV in the upper curve for N and O species. The absorption peak at 73 eV in the lower curve is the characteristic L2,3-edge of Al.

hexagonal cross section as schematically shown in Figure 1 b and c. Such faceted tubes were reported for GaN[8] and ZnO[11] with the same hexagonal structure but a completely different growth mechanism.

A nanotube shown in Figure 2a possesses the outer diameter of 33 nm and the inner diameter of 17 nm. The corresponding EELS spectra (Figure 2b) of this nanotube contain the absorption peaks of Al L2,3-edge at 73 eV and N characteristic K-edge at 401 eV, again indicative of AlN nanotube. The trace peak of O K-edge at 540 eV indicates the surface oxidation of the AlN nanotubes.

High-resolution TEM is employed to characterize the AlN nanotubes in detail. The nanotube in Figure 3 has an outer and inner diameter of ca. 42 and 21 nm, respectively. The local enlarged images of the tube wall (left and middle insets) indicate that the two sets of fringes are perpendicular to each other with the spaces
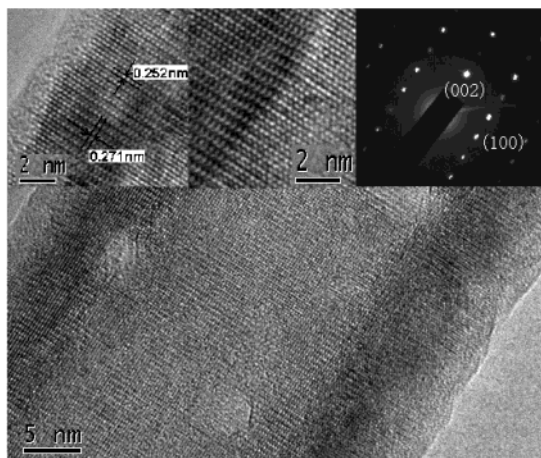
Figure 3. HRTEM image of the h-AlN nanotube with the growth direction of [0001]. The enlarged images of the tube wall close to the outer and inner surface are shown in the left and middle inset, respectively. The right inset is an SAED pattern of the nanotube.

of 0.271 and 0.252 nm, in good agreement with the $d_{1\bar{1}00}$ and d_{0002} spaces of h-AlN, respectively. From the left inset, it is seen that a rough amorphous layer with thickness about 1 nm surrounds on the outer surface of the AlN nanotube. Energy-dispersive X-ray analysis (EDX) shows that this amorphous layer consists of Al and O elements, which is assigned to the surface aluminum oxide species mentioned before. The contrast between the tube wall and the inside hollow region could be clearly identified from the middle inset. The selected area electron diffraction (SAED) pattern (right inset) indicates the h-AlN nanotube is single crystal with the growth direction of [0001], completely different from the proposed "polycrystalline and cubic AlN nanotube".[12]

From the above experimental results, it is seen that the faceted single-crystalline h-AlN nanotubes have been synthesized. Because of the importance of AlN in GaN-based electronics,[10] the nanotubular h-AlN could be an ideal substrate, e.g., to encapsulate GaN-based compounds, for the construction of GaN-based nanoheterostructures in future nanoelectronics.

By using first-principle methods, it was predicted that AlN nanotube is energetically favorable with a smooth tubular wall and a uniform diameter. The Al and N atoms should adopt sp^2 hybridization, and a layered (graphite-like) tubular structure was suggested.[9] However, the present HRTEM results provide an alternative AlN nanotube with Al and N atoms still arranging in hexagonal crystalline structure, similar to the case for bulk h-AlN, and the nonlayered structure is adopted. For such a structure, each atom on the surface has one dangling bond, and surface passivation such as oxidation is usually unavoidable. Hence, the oxygen signal is detected in EELS and EDX spectra for our AlN nanotubes. Of course, the hydrolysis of AlN[13] during the preparation of the TEM grid is also a possible reason.

While the template-confined synthesis of such GaN nanotubes, i.e., the epitaxial growth on the side {110} planes of the faceted ZnO nanowires,[8] is easily understood, the template-free growth mechanism for such AlN nanotubes is still not clear at the moment. It is generally accepted that the degree of supersaturation determines the prevailing growth morphology.[14] Hence, the occasion of the initial nucleation is crucial for the subsequent growth of the AlN nanotubes. We tried to change the conditions for the initial nucleation by altering the introducing temperature of the NH_3/N_2 gas. It is found that, when NH_3/N_2 was introduced at temperatures below 860 °C, no tubular structure could be detected. When the NH_3/N_2 gas was introduced at 950 °C, the AlN nanotubes with

rough walls could be prepared. The yield of nanotubes is about 5−30% in the product, depending on the temperature of the NH_3/N_2 gas introduced.

As known, for the hexagonal crystal structure, there is no center of inversion, and therefore, an inherent asymmetry along the c-axis is present which allows the anisotropic crystal growth along the [0001] direction.[11] For a bent h-AlN nanotube, the formation energy is high due to large elastic energy for the nonlayered structure, whereas the faceted nanotubular structure releases the general strain by introducing a finite number of twins, thus lowering the overall thermodynamical free energy. In fact, a close examination of the morphology of the AlN nanotube suggests that the hexagonal shape of the nanotube is consistent with the crystal symmetry of the bulk AlN; therefore, it might be formed without twin joints. Accordingly, it is speculated that some AlN species aggregate to form the hollow hexagonal seeds under certain conditions during the nucleating stage. Subsequent axial growth along the c-axis leads to the formation of the faceted nanotubes with hexagonal cross sections, while the lateral growth is prevented because the dangling bonds of the surface atoms are saturated by trace oxygen species in the reaction system.

In conclusion, faceted h-AlN nanotubes were first synthesized with the length of a few micrometers and diameters from 30 to 80 nm. This provides an ideal substrate for the construction of GaN-based nanoheterostructures in future nanoelectronics. Our experimental results also suggest the need for further extensive experimental and theoretical studies on the promising nonlayered nanotubular structures.

Supporting Information Available: XRD pattern of the product, EDX analysis of the outer surface of the AlN nanotube wall, HRTEM image of the open end of a h-AlN nanotube, TEM image of the product when NH_3/N_2 gas was introduced at 950 °C, and schematic elucidation for the characteristics of faceted nanotubes with hexagonal cross section in TEM (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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