

AlN nanorings

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Received 1 March 2005; received in revised form 30 May 2005; accepted 2 June 2005

Available online 25 July 2005

Communicated by M. Schieber

Abstract

Aluminum nitride nanorings with hexangular crystal structure were first synthesized by evaporating of aluminum alloy in ammonia/nitrogen atmosphere at 1100 °C. The products were characterized by transmission electron microscopy, scanning electron microscopy, FT-IR absorption and Raman scattering. Nanorings with the diameter of about 3 μm are formed by bending nanowires. HRTEM and electron diffraction studies revealed that nanorings are single crystal and the *c*-axis of the AlN crystal directs along the radial direction of the nanoring. The electrostatic polar charge model is employed in the explanation of the AlN nanoring formation.

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Keywords: A1. Crystal morphology; B1. Nanomaterials; B1. Nitrides

1. Introduction

Research on the growth and properties of quasi-one-dimensional (1D) nanomaterials has increased steadily over the last decade, largely due to their potential applications in nanoscale devices as interconnects or functional components [1]. 1D nanomaterials have been demonstrated as building blocks for nanocircuits [2–4], nanosystems [5] and nanooptoelectronics [6,7]. A variety of 1D systems

have been synthesized, including nanotubes [8,9], nanowires [10–12], coaxial nanocables [13] and nanobelts [14]; and they have been fabricated for a wide range of materials from metals [15–17], semiconductors [18,19] and oxides [20] to polymers [21,22]. AlN is a highly thermally and chemically stable III–V semiconductor, which is gaining interests as an excellent candidate for high-power, high-temperature electronics and base of wide band-gap diluted magnetic semiconductor [23,24]. A variety of 1D AlN nanostructures, such as nanowires, nanotubes and nanobelts, have been synthesized [25–27]. Very recently, it has been shown that 1D nanomaterials grow in a variety of

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geometry configurations ranging from nanobows [28], nanohelices/nanosprings [29–31] to nanorings [32,33]. In this study, AlN nanoring is presented which is prepared by evaporation of aluminum alloy in ammonia/nitrogen atmosphere at high temperature.

2. Experimental procedure

The sample preparation was carried out in a horizontal tubular furnace. Two grams of aluminum alloy, in which aluminum content account for 95 at% while manganese 5 at%, were put into an alumina vessel. Then, the whole vessel was slipped in a two open-end straight quartz tube with diameter of 2 cm. Inserted into a horizontal tubular furnace; the quartz tube was flushed with ammonia/nitrogen (5:100) atmosphere to remove the remaining air in the tube. The furnace was then heated at a rate of 60 °C/min to 1100 °C under ammonia/nitrogen flow at 100 sccm. Subsequently, the furnace was kept 1100 °C for 1 h and then cooled down to room temperature in the flow of ammonia/nitrogen atmosphere. After reaction, a gray product was obtained at the position where the aluminum alloy had been placed. The prepared

sample was characterized by transmission electron microscopy (TEM Philips Tecnai F20), scanning electron microscopy (SEM Philips XL30), FT-IR absorption (Nexus 870) and Raman scattering (JY HR800).

3. Results and discussion

TEM is employed for the studies of the nanorings. A successive loop is viewed in Fig. 1(a). The diameter of the nanowire is about 45 nm while the diameter of the nanoring is about 3 μm . The diameter of the nanoring is much greater than that of the nanowire. High-resolution transmission electron microscopic (HRTEM) image of the marked part on the main body of the nanoring is shown in Fig. 1(b). The measured d-spacings of the crystal are 0.487 and 0.269 nm correspondingly, which are consistent with the standard values of $c = 0.4978$ nm and $a = 0.2694$ nm for hexangular AlN (JCPDS Card: 76-0565). The inset of Fig. 1(b) is the electron diffraction pattern of the corresponding part that can be indexed as a hexangular phase of AlN recorded from $[0\ 1\ \bar{1}\ 0]$ zone axis. On the studies of the HRTEM image and electron diffraction pattern of the nanoring, it is worth to note that

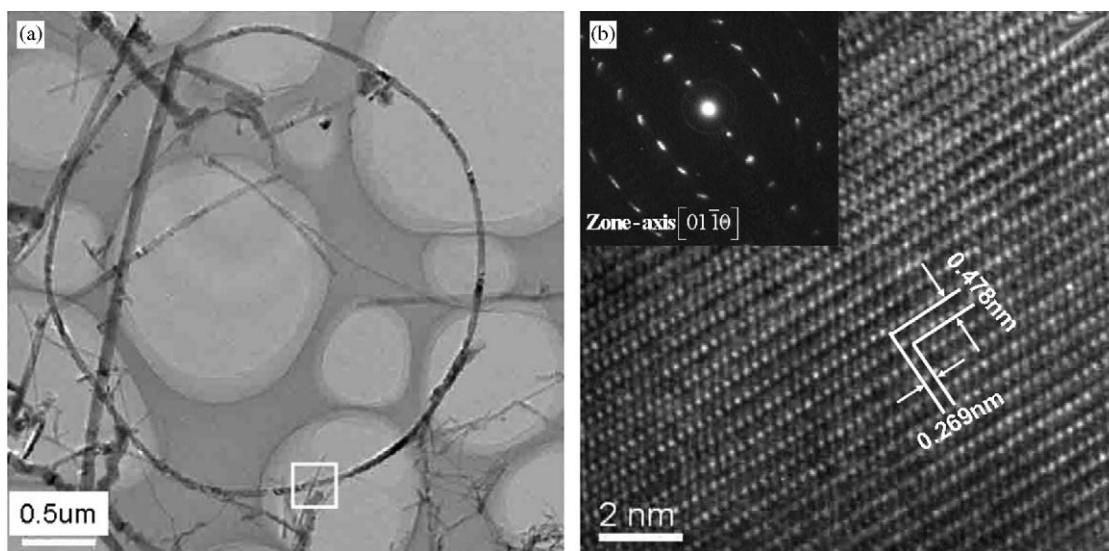


Fig. 1. TEM image of a single nanoring. (a) A nanoring with seamless structure. (b) HRTEM image of the marked part in the main body of the nanoring, the inset is the corresponding electron diffraction pattern.

the nanoring is in good crystal structure with its *c*-axis along the radial direction of the nanoring. As the charges are polarized in *c*-axis direction of AlN, this structure leads to the positive (or negative) charge on the inner surface and negative (or positive) charge on the outer surface of the nanoring as reported in ZnO [28,32,33]. The crystal structure and geometry of the AlN nanoring reveals the possibility of the formation of the nanoring which will be discussed later.

For illustration of the looped structure of the nanoring shown in Fig. 1(a), high magnification of the joint is presented. Fig. 2(a) shows the TEM image focused on the joint of the nanoring with the inset of the electron diffraction pattern for the marked part. No gaps can be observed between the two parts of the nanowire at the joint, which reveals the complete looped ring in the nanostructure. The electron diffraction pattern gives single crystal property at the joint that reveals the excellent sintering seal for the adjacent parts of the nanowire. Fig. 2(b) shows the HRTEM image of the part near the joint highlighted in Fig. 1(a) by an arrow. In this image, two white lines are used for eye guide of the gap between two adjacent parts of the nanowire near the joint. On the up-right part, an amorphous area can be observed

which reveals the difference from the nanoring. From up-right to down-left, the gap becomes smaller and smaller which join into each other finally. It is worthy of pointing out that, when the two adjacent parts seaming a joint, the crystal structure shows the same orientation property as the main body of the nanoring shown in Fig. 1(b). That is to say, the *c*-axis of the joint as well as the other parts of the nanoring is along the radial direction of the nanoring. This bending nature of the nanoring reveals its possible mechanism related to the polar charged property of the AlN for the formation of the nanoring.

SEM is also applied to characterize the nanorings. Nanoring yield was estimated at about 2% of the total product. Nanowires grew from the Al alloy accompanied with nanorings among them that can be found in the SEM image of the prepared samples (Fig. 3(a)). Fig. 3(b) is a SEM image of a special nanoring. This image illustrates the complete loop property of the nanoring that is formed by bending upon the nanowire itself. A noteworthy characteristic of the nanoring is that there is a joint on the nanoring. It can be understood that the nanowires coiled and wrapped by themselves and formed looped structures in the growth process. At the crunode, sintering effect

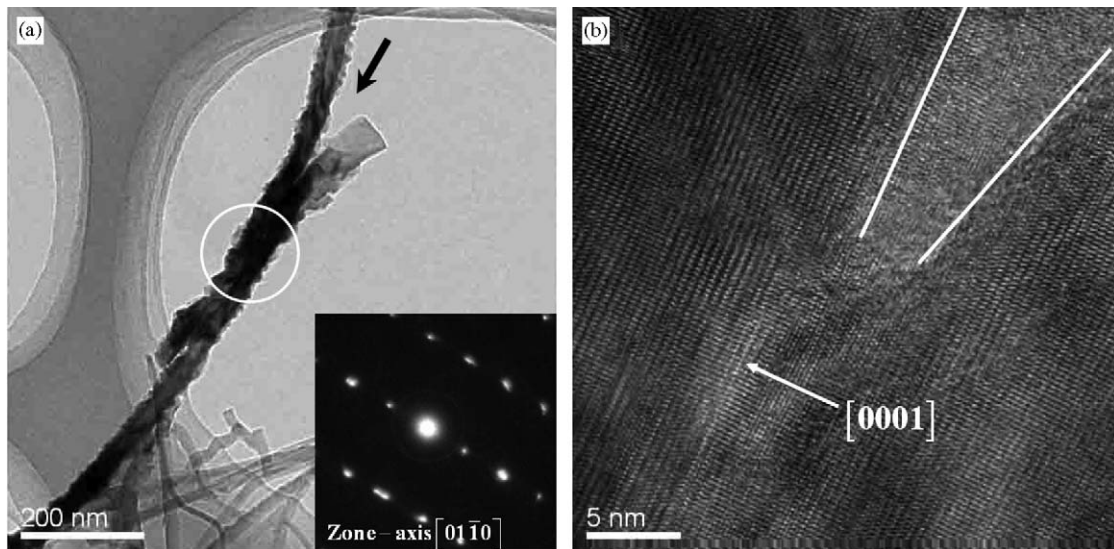


Fig. 2. TEM image at the joint of the nanoring. (a) Microphoto of the joint with the inset of the electron diffraction pattern of the circle marked part. (b) HRTEM image of the joint, the two white lines are the eye-guide of the two adjacent parts of the nanowire.

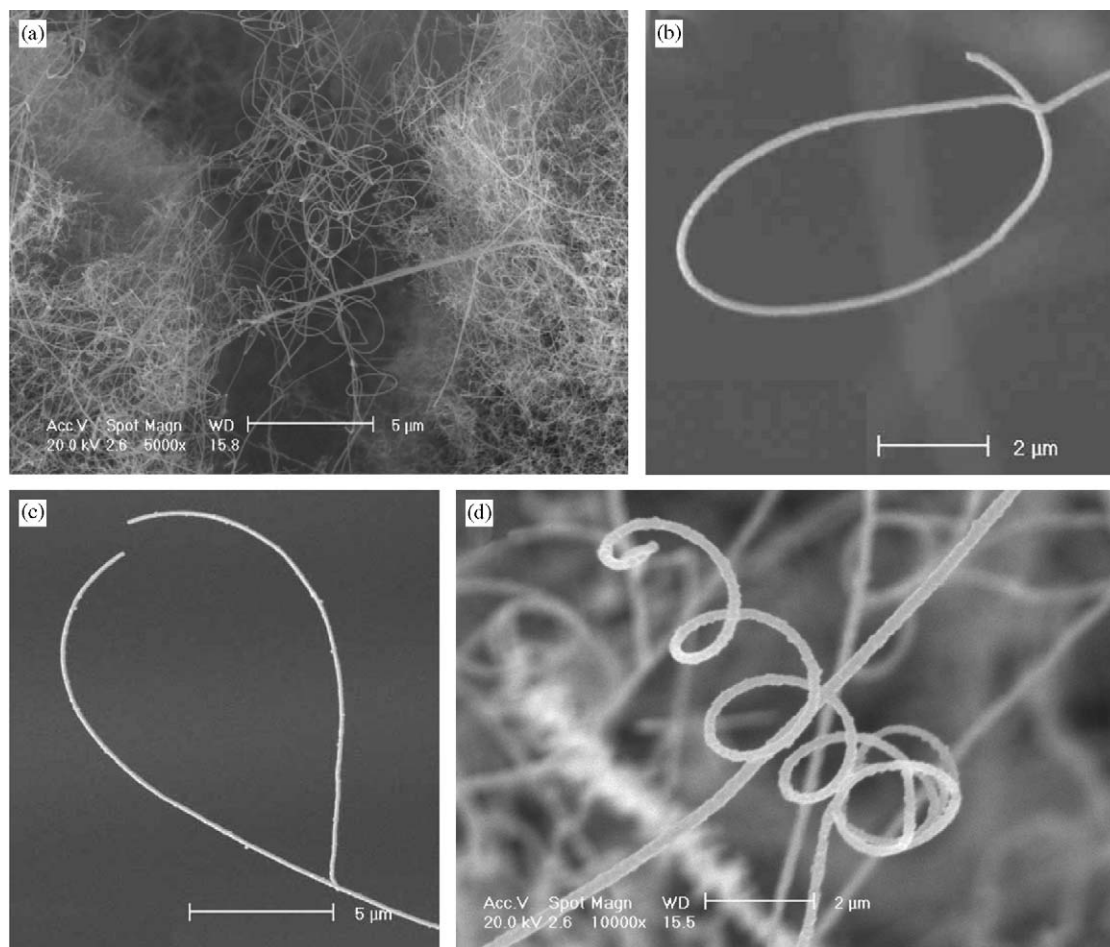


Fig. 3. (a) SEM images of nanorings. (b) A complete looped nanoring with a joint. (c) A nanoring with a broken hatch. (d) A SEM image of an AlN nanospring.

happened at high temperature leading to the joint of the nanowire. After the formation of the joint, a complete nanoring is formed. To support this hypothesis, a nanoring with characteristic structure is shown in Fig. 3(c). An obvious hatch is presented beyond the joint on the broken nanoring. As there is only one connection of the upper half ring to the main body of the nanowire, the crunode should have become a unitary by mass transport and diffusion at high temperature, otherwise the upper half nanoring should fall down without any other support.

Crunode of the nanowire is regarded as the crucial part in the nanoring formation. For some spiral nanowires with large gaps between the

adjacent segments of the nanowire, the gaps lead to the nanosprings rather than nanorings. Small amount of nanosprings have been observed in the prepared samples as shown in Fig. 3(d). In the nanosprings, the nanowires grow along screw direction with gaps between upper and lower segments of nanowires. With the gaps between the segments of the nanowire, no sintering seal can be realized at high temperature. We suggest that the close contact of the adjacent nanowire segments is the necessary condition for the formation of seamless nanorings.

The growth of the AlN nanoring can be understood on the basis of the electrostatic polar charge model [29]. The hexangular AlN crystal is

described schematically as a number of alternating planes composed of coordinated N^{3-} and Al^{3+} ions, stacked alternatively along the c -axis as shown in Fig. 4(a). The oppositely charged ions produce positively charged $(0001)_{\text{Al}}$ and negatively charged $(000\bar{1})_{\text{N}}$ polar surfaces. A dipole moment exists between the two surfaces along the c -axis. The dipole moment can be neutralized by symmetric charge distribution in the nanoring with the c -axis along the radial direction as shown in Fig. 4(b). As a result of bending, the electrostatic energy of the entire system is expected to decrease. On the other hand, the elastic deformation from forming a ring must be taken into account which will make the elastic energy increase. When the decrease of the electrostatic energy is larger than the increase of the elastic energy, the bending of the nanowire to form a nanoring takes place. The formation of the nanoring can be regarded to be driven by the minimization of the total energy as shown in the ZnO nanoring systems [29,32,33].

Fig. 5 shows the micro-FT-IR spectrum of the AlN nanorings. The sharp peak around 668 cm^{-1} is in good agreement with TO phonon modes, while the broad peak around 877 cm^{-1} could be attributed to the longitudinal optical (LO) mode as observed in AlN nanobelts [27]. Some weak peaks appear from 1000 to 4000 cm^{-1} , which could be assigned to a very small amount of water, CO_2 , and air in the spectrometer path or on the sample surface.

The space group of wurtzite AlN is $\text{C}_4^6\text{V}(\text{P}6_3\text{mc})$ with all atoms occupying the $\text{C}_{3\text{V}}$ sites. Six Raman-active modes may be present, i.e., $1\text{A}_1(\text{TO}) + 1\text{A}_1(\text{LO}) + 1\text{E}_1(\text{TO}) + 1\text{E}_1(\text{LO}) + 2\text{E}_2$. The Raman spectrum of the as-prepared AlN

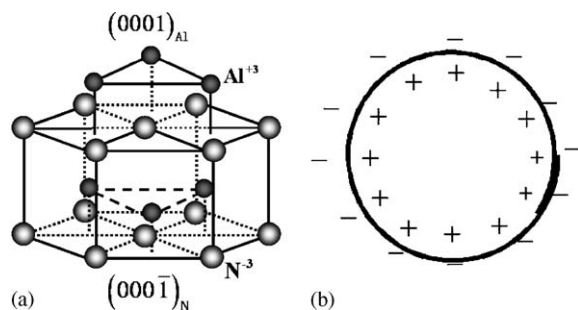


Fig. 4. Schematic of (a) the charge polarization in AlN and (b) the formation of a nanoring.

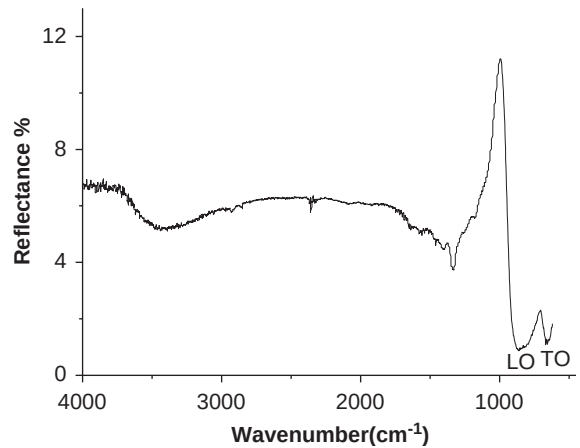


Fig. 5. FT-IR spectrum of the prepared sample.

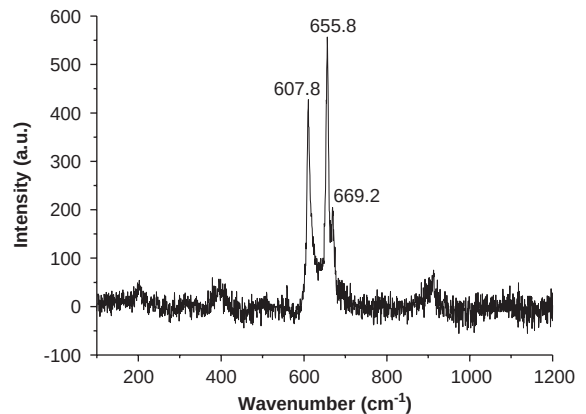


Fig. 6. Raman scattering spectrum of the prepared sample.

nanorings, shown in Fig. 6, was recorded using the 488.0 nm line of an Ar⁺ ion laser as excitation source. In Fig. 6, the Raman shift peaks around 607.8, 655.8 and 699.2 cm^{-1} are attributed to the $\text{A}_1(\text{TO})$, $\text{E}_2(\text{high})$ and $\text{E}_1(\text{TO})$ vibration modes, respectively. This Raman shift peaks are signatures for wurtzite AlN as reported previously for bulk, nanobelts and nanotips structure [27,34,35].

4. Conclusions

Aluminum nitride nanorings with hexagonal crystal structure were successfully synthesized by

evaporating of aluminum alloy in ammonia/nitrogen atmosphere at 1100 °C. TEM and SEM studies illustrated the ring-like structure and seamless property in the nanostructure. HRTEM and electron diffraction studies revealed the *c*-axis of the AlN crystal directs along the radial direction of the nanoring. The electrostatic polar charge model is employed in the explanation of the AlN nanoring formation. The FT-IR and Raman spectra of the AlN nanorings are in good agreement with the wurtzite AlN nanobelts. The AlN nanorings are expected to find novel applications in the nanotechnology area.

Acknowledgments

This work was supported by the Natural Science Foundation of China (No. 60390072) and The National Key Project for Basic Research (No. G1999064508).

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