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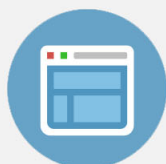
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Synthesis of monocrystal aluminum nitride nanowires at low temperature

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Hexagonal monocrystal aluminum nitride (*h*-AlN) nanowires are synthesized through the direct reaction of AlCl₃ with NaN₃ in a nonsolvent system at low temperatures. The *h*-AlN nanowires are characterized by the high-resolution transmission electron microscope, electron diffraction, x-ray diffraction, and photoluminescence spectra. The analysis shows that the nanowire has a long straight-wire morphology with a diameter ranging from 40 to 60 nm, the longest one up to several micrometers, and they are of pure monocrystal hexagonal or face center structure which has a relatively narrow emission peak, centered at 413 nm (3.00 eV). In addition, a possible growth mechanism for *h*-AlN nanowire is discussed. © 2007 American Institute of Physics.

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I. INTRODUCTION

With the integration and micromation of high power electronic components, the heat produced in a unit area is largely increased. Therefore, it becomes difficult to cool high power electronic device and is urgent to search for ascendant thermal conductive material. AlN is a very promising material for electron substrate and integrated circuit encapsulation¹ because its heat conductivity (320 W m⁻¹ K⁻¹) (Ref. 2) is three times as high as that of Al₂O₃, which is of the highest value among the ceramic materials ever found. AlN semiconductor, one of the III nitrides, holds a direct band gap of 6.2 eV (Ref. 3) and high electrical resistivity (>10¹¹ Ω m), while featuring low dielectric constant (8.6) and coefficient of thermal expansion (4.3×10⁻⁶ K⁻¹) and better chemical stability.⁴⁻⁷ Recently, though randomly oriented AlN nanowires^{8,9} and nanotubes¹⁰ have been fabricated and aligned AlN nanowires have been synthesized usually by anodic alumina membrane templates,¹¹ fabrication of high-quality and well-aligned AlN nanowire arrays has remained as one of the foremost challenges compared to the similar system of GaN nanowire arrays.¹² Well-aligned nanowires have spurred interests in future application.¹³

AlN semiconductor is traditionally produced by means of ion beam evaporation and direct current electric arc.¹³ In the process, aluminum is compelled to separate from its precursor under extreme conditions and then reacts with ammonia or nitrogen.¹⁴ Another approach to synthesize AlN is to separate carbon from hydrocarbon and make it react with Al₂O₃ in ammonia or nitrogen environment at high temperatures (>1600 °C) for several hours.¹⁵ Either under a high pressure (>1000 atm) or at high temperature (>1900 °C), AlN is produced by reacting atomic nitrogen or NaN₃ (Ref. 16) with aluminum powder. There are two obvious disadvantages

in this method: the experimental equipment is expensive, and experimental condition is relatively rigorous and difficult to achieve in most laboratories.

Hereby, an easier method for the synthesis of the superior-quality AlN semiconductor is introduced through a series of experiments. The resultant powder obtained in the experiments is examined by high-resolution transmission electron microscope (HRTEM), electron diffraction (ED), and x-ray diffraction (XRD) and is ascertained to be hexagonal aluminum nitride monocrystal nanowires through these examinations.

II. EXPERIMENTS

AlN nanowires are synthesized in a stainless-steel autoclave. Put anhydrous AlCl₃ (1.4 g) and NaN₃ (2.0 g) into the autoclave under a dry and pure nitrogen environment, and put the well-airproofed autoclave into a conventional furnace to heat. Adjust the temperature controller so that the furnace temperature rises to 450 °C within an hour and stays there for 24 h, and take the autoclave out of the furnace and cool it naturally down to room temperature. Wipe off the by-product NaCl and other residual impurities with de-ionized water, and then dry the product, the white-gray powder is the final product in the experiments. The powder is taken to be examined by high-resolution transmission electron microscope (JEOL, JEM-3010), electron diffraction (JEOL, JEM-3010), photoluminescence spectra (Ocean Optics, HR2000), and x-ray diffraction (JEOL, XRD-7000S, Cu: 1.545 620 Å).

III. FINDINGS AND DISCUSSION

A. The form and structure of AlN nanowires

In the experiments, about 70%–80% of the products are long straight wires and have nonbranched morphology of *h*-AlN monocrystal nanowires (as shown in Fig. 1). The relatively uniformed *h*-AlN monocrystal nanowires range in di-

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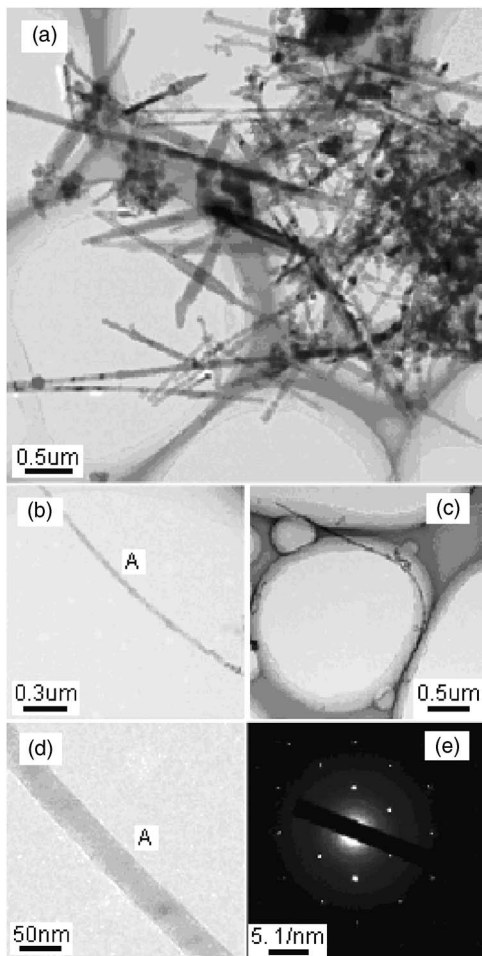


FIG. 1. (a), (b), and (c) are the HRTEM pictures of *h*-AlN monocrysal nanowire. (d) is an amplification of part A in (b). (e) Selected area electron diffraction (SAED) pattern of the nanowire in (d) indicating that the nanowire is a monocrysal structure.

ameters from 40 to 60 nm and most wires are as long as several micrometers. The rest of the products are nanometer particles and ribbons. The particles are subtransparent with diameters between 40 and 60 nm while the ribbons are very thin and long curled with widths about $0.1 \mu\text{m}$. Besides the three components mentioned above, there are also some fog-state materials composed of smaller particles, which may contain a little initial reactant that is not completely filtered.

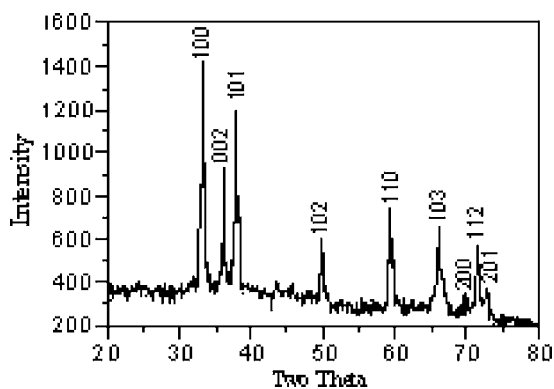


FIG. 2. The XRD pattern of *h*-AlN nanowire, the demarcated peaks indicate that the sample is hexagonal aluminum nitride.

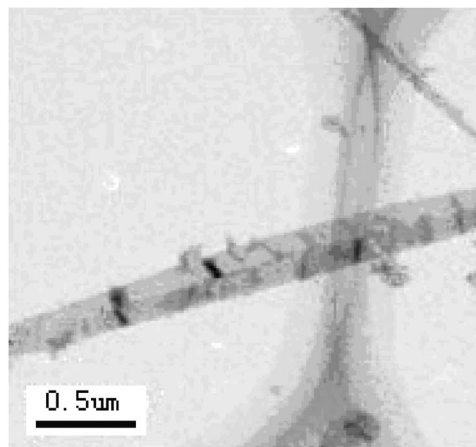


FIG. 3. The HRTEM pictures of *h*-AlN monocrysal face center structural AlN nanowire.

In addition, a very little curled nanowire, with coarse surface or with smooth surface, is also found. The curled nanowire has a coarse surface probably because it has absorbed smaller particles, as is shown in Fig. 1(c). Figure 1(d) is an amplification of part A in Fig. 1(b). Figure 1(e) shows the ED pattern of the straight long nanowire in Fig. 1(d). Most nanowires have similar ED pattern except for the differences in brightness distribution and the angle of the parallelogram, which indicates that the straight long nanowire is monocrysal. Besides, by analyzing the ED patterns, most nanowires are found growing along the $[0001]$ direction. The product is also examined by XRD with the result shown in Fig. 2. Its pattern (as shown in Fig. 2) is compared with the standard XRD patterns, the sample is ascertained to be *h*-AlN with lattice constants of $a=3.109 \text{ \AA}$ and $c=9.979 \text{ \AA}$.

Other resultant powder obtained in the experiments is confirmed to be the face center structure AlN nanowires through the examination of HRTEM, ED, and XRD, as shown in Figs. 3 and 4. Compared with the standard XRD patterns, the 111, 200, 220, and 311 peaks in Fig. 4 testify the existence of face center structural AlN with a lattice constant of $a=4.045 \text{ \AA}$. Such long straight nanowires with square cross sections have seldom been reported so far.¹⁷

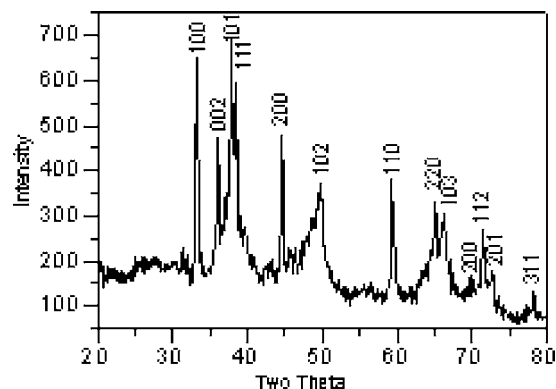


FIG. 4. The XRD pattern of unsegregated product. Besides the diffraction peaks of *h*-AlN, the 111, 200, 220, and 311 peaks belong to face center structure AlN.

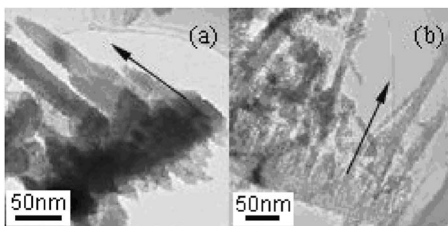


FIG. 5. The HRTEM image of the unsegregated product. The arrow shows the growth direction of nanowire. (a) The grown up *h*-AlN nanowire, the growth time is 24 h. (b) The growing nanowire shown is in bamboo shoot state, the growth time is 10 h.

B. The formation of monocrystal AlN

The above method for producing *h*-AlN is based on the metathetical reaction of AlCl_3 and NaN_3 . Because the reaction temperature is controlled at 450°C , which is higher than the subliming temperature of AlCl_3 (177.8°C) and the chemical decomposing temperature of NaN_3 (330°C),^{18,19} and because the binding energies of AlN and NaCl are higher than those of AlCl_3 and NaN_3 , AlN and NaCl molecules are more stable than AlCl_3 and NaN_3 and the reaction in the experiments must tend to produce AlN and NaCl. The NaCl is relatively stable and does not participate in other reaction again. Therefore, it crystallizes to microcrystal during the cooling process and appears in the product. It is then filtrated out as the by-product.

C. The growth mechanism of monocrystal AlN nanowire

Talking of the growth mechanism of *h*-AlN, several hypotheses have been suggested such as “vapor-solid,”²⁰ “liquid-solid,” “vapor-liquid-solid,”¹³ etc. However, all these hypotheses still require more evidences to support. The reason of vapor-solid growth mechanism lies in the vapor of AlCl_3 that exists as dimer Al_2Cl_6 below 440°C and the reaction that begins at 330°C when the extricated neutral nitride and sodium atoms have been produced. Since the NaCl melting point (801°C) is much higher than the reaction temperature (450°C) liquidation is impossible and the AlN compound is likely to be produced via a vapor-solid mechanism. When the temperature reaches the setting value of 450°C , the above reaction should end at a certain time. The produced AlN, NaCl, and other little residual materials should exist as microcrystal or molecule cluster, and spread in the high pressure environment which consists of N_2 and N in the later 20 h. The temperature is kept at 450°C and the AlN microcrystal grows up to nanowire abiding the preferential selection mechanism. According to the examining results of ED and XRD, the AlN nanowires grow along the [0001] direction. Because the preferential orientation of crystal nucleus is stochastic, the orientation of AlN nanowire is stochastic. If the crystal nucleus is of hexagonal structure, the grown nanowire will show cylindrical long straight-wire morphology; this is also illustrated in Fig. 1(a). If the crystal nucleus is of face center structure, the grown nanowire will appear having a quadrangular long straight-wire morphology, as shown in Fig. 3.

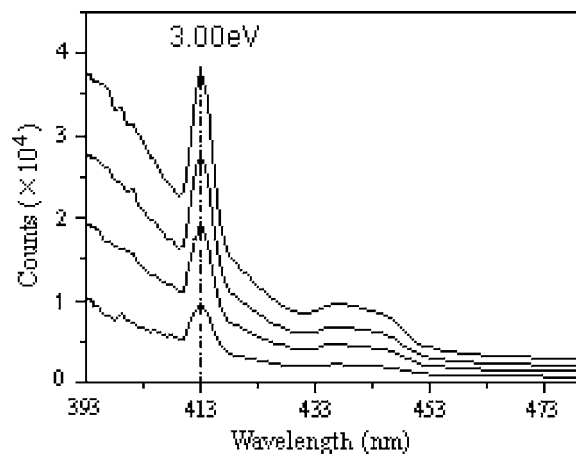


FIG. 6. PL spectrum of the synthesized sample with different excitation intensities at room temperature (laser emission wavelength at 355 nm).

The experiments indicate that the growth orientation of *h*-AlN is controllable. The *h*-AlN nanowires, growing on the silicon slice, as shown in Fig. 5, can be clearly seen to grow strictly along the arrow direction (viz., [0001] direction), as shown in Fig. 5(b). Even though the *h*-AlN nanowire shown in Fig. 5(a) is badly broken, the remaining parts and the three *h*-AlN nanowires still keep consistency in growth orientation. This means that the growth orientation can be controlled absolutely.

Figure 6 shows photoluminescence (PL) spectra of the synthesized sample at room temperature, which has a relative strong emission peak ranging from 410 to 416 nm, centered at 413 nm (3.00 eV). It is noteworthy that the energy of the 355 nm laser (exciting light) is below the band gap (6.2 eV) of AlN, so the purple emission cannot be excited in the experiment. The observed emission peak could be assigned to deep level defects, such as the oxygen impurities,^{13,21–23} nitrogen vacancy, aluminum vacancy, and N_{Al} or Al_{N} (antisite defects).²⁴

IV. CONCLUSION

The hexagonal monocrystal *h*-AlN nanowires can be synthesized through the direct reaction of anhydrous AlCl_3 with NaN_3 at a low temperature of 450°C for about 24 h. This is a simple method to synthesize hexagonal monocrystal *h*-AlN nanowires which has better morphology than the nanometer AlN whiskers produced by Wu. *et al.* in 2004.²⁵ More importantly, the growth orientation of AlN nanowires could be successfully controlled by substrate technique, and the growth mechanism of AlN nanowire is probably vapor-solid.

ACKNOWLEDGMENTS

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