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Synthesis of hexagonal monocrystal AlN microtubes and nanowires at low temperature*

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This paper reports that pure hexagonal aluminium nitride microtubes and nanowires growing along the [0001] direction have been successfully synthesized by directly reacting $AlCl_3$ with NaN_3 at low temperature (450°C) under condition of non-solvent system. The grey–white powder of reacting product was characterized by high-resolution transmission electron microscope (HRTEM), which shows that the powder is long straight-wire morphology with outer diameter from 40 nm to 300 nm and length up to several micrometres. The results of both electron diffraction (ED) and x-ray diffraction (XRD) indicate that the AlN microtubes have a pure hexagonal monocrystal tubular structure with the combination of the curled AlN nanobelts. Room-temperature photoluminescence spectrum of the synthesized sample showed an emission peak, which is closely related to the small size of the microtubes.

Keywords: *h*-AlN, microtubes, nanowires
PACC: 8120, 7855, 7280E

1. Introduction

As one of the III-nitrides, AlN is of direct band gap, and the band gap is 6.2 eV,[1] near to be dielectric. Its electrical resistivity ($>10^{11}\Omega\cdot$m) is very high, while its dielectric constant (8.6) is very low. Due to these properties, AlN is ideal to be electron substrate material and integrated circuit encapsulation material.[2] Its high heat conductivity ($320\,\mathrm{W\cdot m^{-1}\cdot K^{-1}}$),[3] three times as high as Al_2O_3, and low coefficient of thermal expansion ($4.3\times 10^{-6}\mathrm{K^{-1}}$) can well solve the problem of thermal matching between substrate and semiconductor and solve the cooling problem of high power electronic device caused by the integration and micromation. The ternary alloy AlGaN and AlInN, whose band gap can be controlled from 0.7 eV to 6.2 eV, are very suitable to make photoluminescence[4] and detective devices covering from infrared to ultraviolet. It can be used in pressure sensor, thermal radiation detector, field effect transistors[5,6] and catalyst in chemical reaction.[7] Because of its excellent optical and acoustic properties, it can also be used in surface acoustic wave device as well. Recently, randomly oriented AlN nanowires[8,9] and nanotubes[10] have been fabricated, while well-aligned nanowires are very important in future application.[11] Aligned AlN nanowires have been synthesized by using anodic alumina membrane templates.[12] Up until now, fabrication of high-quality and well-aligned AlN nanowires arrays has remained as one of the foremost challenges in comparison with the similar system of GaN nanowires arrays.[13]

The most widely used methods for producing AlN are ion beam evaporation,[6] direct current electric arc and so on. In these procedures aluminium is compellingly separated from its precursor under extreme conditions, then react with ammonia or nitrogen.[14] Another approach to compose AlN is to make carbon separate out from hydrocarbon, then react with Al_2O_3 in ammonia or nitrogen environment at high temperature (>1600 °C), The procedure usually lasts for several hours.[15] Under a high pressure (>1000 atm) and at a high temperature (>1900°C), AlN is also successfully composed by reacting aluminium powder with atomic nitrogen or NaN_3.[16] However, the equipments used in the above methods are expensive and the experimental condition is very rigorous, which is hard to reach in most laboratories.

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2. Experimental results and discussion

This paper reports that, in a homemade stainless-steel autoclave, by directly reacting anhydrous $AlCl_3$ and NaN_3 without dissolvent and any catalyst, the monocrystal AlN nanowire and microtubes are successfully produced.[17] The reacting temperature is 450°C and the reacting time is about 24 hours. Thus AlN nanowires and microtubes are produced according to the following reactions:

$$NaN_3 \rightarrow N_2 + Na + N, \quad (1)$$

$$AlCl_3 + 3Na \rightarrow Al + 3NaCl, \quad (2)$$

$$Al + N \rightarrow AlN. \quad (3)$$

The product is examined by high-resolution transmission electron microscope (HRTEM) (JEOL, JEM-3010) to observe the microform, which is shown in Fig.1, most samples show non-branched morphology and in the shape of long straight tubes. The tube

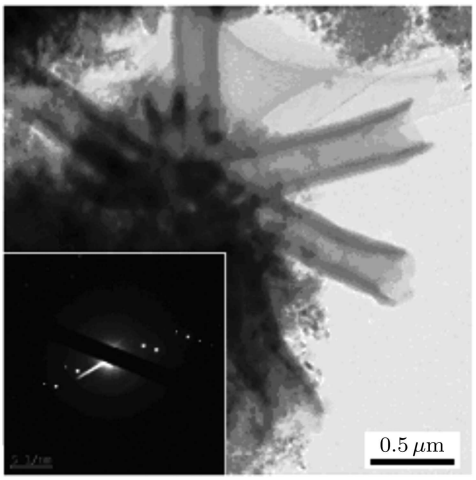


Fig.1. The HRTEM pictures of AlN microtube. The inset figure is the ED pattern of the microtube, which indicated that the microtubes are monocrystal structure.

surfaces are smooth and almost without any deposit. The diameters range from 40 nm to 100 nm and they are relatively uniform. The lengths of most wires are up to several micrometers. Besides these tubes, there are many long straight-nanowires shown in Fig.3. The diameters of nanowires range from 40 nm to 60 nm, and their length is up to several micrometres. The inset in Fig.1 is the electron diffraction (ED) pattern of opened nozzle district, which shows that the microtubes are monocrystals. The microtubes are found growing along the [0001] direction by analysing the ED pattern. The product is also examined by x-ray diffraction (XRD) (JEOL, XRD-7000S, Cu: 1.5405620 Å), and the result is shown in Fig.2. The sample is ascertained to be h-AlN with lattice constants of $a = 3.109$Å and $c = 4.979$Å, which is in agreement with the data on JCPDS card No.65-0831 for wurtzite AlN.

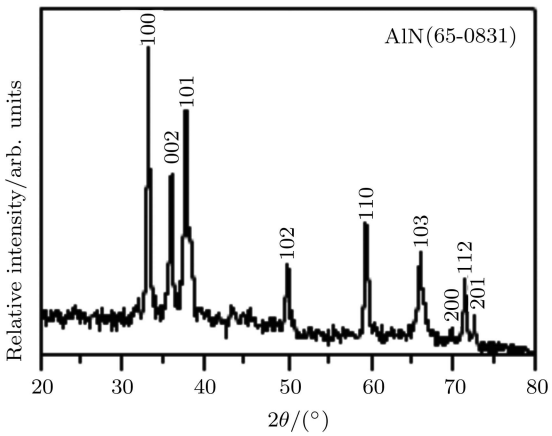


Fig.2. The XRD pattern of the product, the calibrated peaks indicated that the material is hexagonal monocrystal structure.

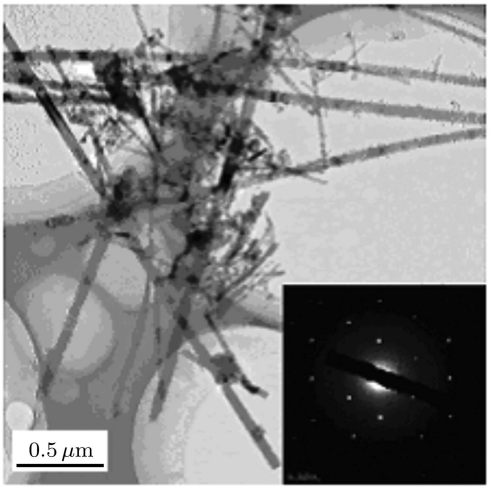


Fig.3. The HRTEM pictures of interlaced AlN nanowires.

The above method to produce AlN microtube is based on the metathetical reaction of $AlCl_3$ and NaN_3. In our experiments, 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).[18−20] Furthermore, the binding energy of AlN and NaCl are higher than those of $AlCl_3$ and NaN_3, which means that the former two molecules are more stable than the latter two. Therefore, the reaction in our experiments must tend to produce AlN and NaCl. The NaCl

is relatively stable, which does not participate in other reaction again. It crystallizes to micro-crystal during the cooling process and appears in the product. It is then filtrated out as the by-product.

About the growth mechanism of *h*-AlN, there are several hypotheses, such as 'vapour–solid',[21] 'liquid–solid', 'vapour–liquid–solid',[22] and so on. The AlN compound is very possibly generated via a vapour–solid mechanism in our experiments, since the NaCl melting point (801°C) is much higher than the reaction temperature (450°C) and liquidation is impossible. When the reaction temperature reaches up to 330°C, the $AlCl_3$ has sublimated before NaN_3 decomposes, the extricated neutral nitride and sodium atoms have been produced. Thus the reaction has begun. When the temperature reaches the set value of 450°C, the above reaction should end at certain time. The produced AlN, NaCl and other little residual material should exist as micro-crystal or molecular cluster, and spread in the high pressure environment which consists of N_2 and N in the later 20 hours. The temperature is kept at 450°C, and these AlN molecular clusters combine to be crystal nucleus or molecular chain. As the molecular clusters continue to deposit, the crystal nucleus grows up to micro-crystal with certain crystal orientation. Then the AlN micro-crystal grows up to nanowires abiding the preferential selection mechanism. Because the orientation of nucleus is stochastic, the orientation of nanowire is also stochastic, as shown in Fig.3. The molecular chains combine with each other and condense to be whisker and zone, which is shown in Fig.4(a). Because of high temperature and high pressure, the whisker and whisker, the zone and zone, the whisker and zone go on to combine and become thin film with large area. Under internal stress, the films become curled, and the microtubes come into being, which is shown in Fig.4(c). The microtubes may be monolayer (Figs.4(e)–4(f)) or multilayers (Fig.4(d)). The broken microtube in Fig.4(e) is examined by HRTEM and ED. The results are shown in Fig.4(b), which indicate that the microtubes are monocrystals. Based on the examination and analysis discussed above, we find that the nanowire obtained in this experiment can be ascertained to be hexagonal monocrystal AlN nanowire, and the microtubes obtained in this experiment can be ascertained to be hexagonal monocrystal AlN microtubes.

Figure 5 shows the photoluminescence (PL) spectra of the synthesized sample at room temperature, the results obtained show that there is an emission peak with a full width at half maximum of about 5 nm centred at 413 nm. The peak grows with an increase in the intensity of the inclined light, and no red or blue shift is seen for the centre of the peak.

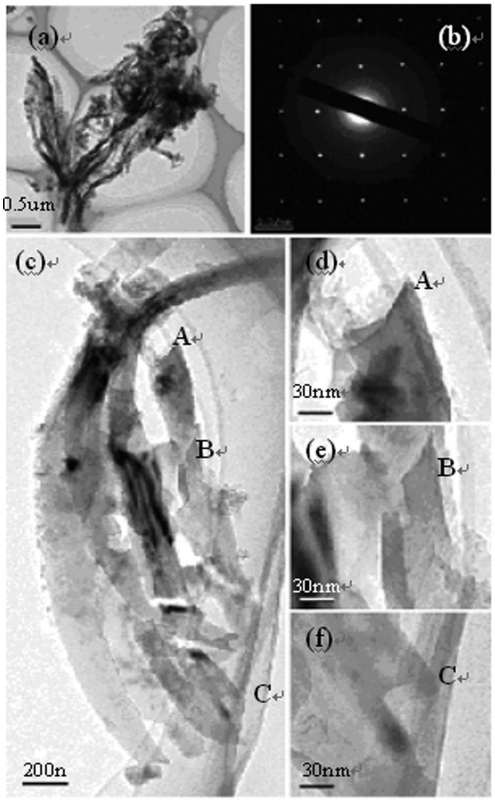


Fig.4. (a) The HRTEM full view of condensed AlN produced with 16 hours reaction. (b) The ED pattern of the broken microtube in (e). (c) The curled AlN film with 20 hours reaction. (d), (e), (f) are the amplificatory pictures of A, B, C areas in (c) respectively.

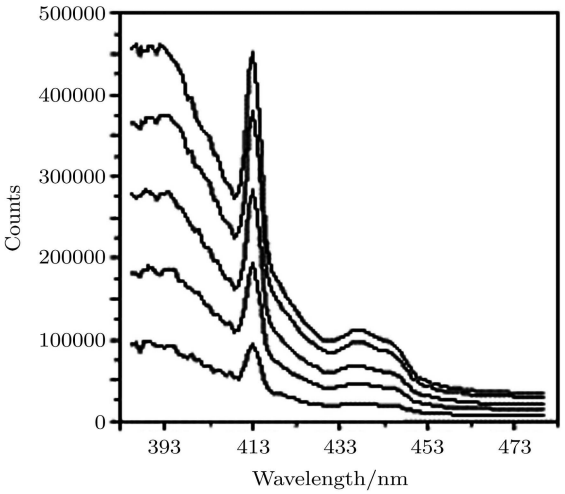


Fig.5. PL spectrum of the synthesized sample at room temperature.

In our experiment, the photon energy of the 355 nm laser (excitation light) is below the band gap (6.2 eV) of AlN, so the purple emission cannot be excited in

our experiment. The observed emission band could be assigned to deep level defects, such as the oxygen impurities[23−26] or nitrogen vacancy defect.

3. Conclusions

In conclusion, at low temperature, the hexagonal monocrystal h-AlN nanowires and microtubes have been successfully synthesized with a very cheap equipment by directly reacting anhydrous $AlCl_3$ and NaN_3. The reaction temperature is 450°C and the effective reaction time is about 24 hours. These are the first results of successful synthesis of hexagonal monocrystal h-AlN nanowire and microtube after nanometre AlN whiskers were produced by Wu C Z and his coworkers in 2004.[27] More importantly the growth mechanism of AlN nanowire and microtube is discussed.

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