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Growth of threaded AlN whiskers by a physical vapor transport method*

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Threaded aluminum nitride (AlN) whiskers are grown by a physical vapor transport method in a radio-frequency induction heating furnace. The resultant whiskers are characterized by X-ray diffraction, Raman scattering, scanning electron microscopy, transmission electron microscopy and photoluminescence. The analysis shows that the whiskers are single-crystalline, wurtzite AlN. The threaded AlN whiskers are 0.5 μm∼100 μm in diameter and several millimeters in length in the fiber direction, and have lots of tiny sawteeth on the surface. The morphology of this threaded AlN whisker is beneficial for bonding when the whisker is used in composite. The growth of the whiskers is dominated by the vapor–solid (VS) mechanism, and the particular morphology might result from an oscillating condition produced in the radio-frequency induction heating furnace.

Keywords: AlN, whisker, threaded morphology, physical vapor transport

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1. Introduction

Aluminum nitride (AlN) is one of the most important and versatile semiconductors, featuring a direct wide band gap of 6.2 eV, excellent thermal conductivity, a low thermal expansion coefficient, high electrical resistivity, high resistance to chemicals, transparency in the ultra-violet (UV) range, and negative electron affinity. Consequently, AlN is promising for application to UV optoelectronic devices, radio-frequency (RF) power electronic devices, and field emission devices.[1,2] Recently, great efforts have been made to prepare low-dimensional inorganic semiconductors due to their unique properties and novel potential applications in nano/micro-scale devices as interconnects or functional components.[3,4] To fully realize their unique properties, it is important to tune the shapes, sizes, and surface morphologies of the microstructures.[5–8] As an important semiconductor, AlN one-dimensional (1D) structures with various shapes (straight, zigzag, ripple, etc.) have been prepared by different methods such as carbothermal reaction,[9,10] the nitridation of aluminum or its alloy powder,[11–14] chemical vapor deposition,[15,16] ammonothermal synthesis,[17,18] and the physical vapor transport (PVT) method.[19–24] Among these methods, PVT can avoid the introduction of impurities and can be used to produce AlN 1D materials with various sizes from nanometers to micrometers.[23] Hexagonal and triangular AlN microfibers have been reported by Bao *et al.*,[23] and Jiang *et al.*[24] In this paper, we report the threaded AlN whiskers grown by the PVT method for the first time. X-ray diffraction (XRD), Raman scattering, scanning electron microscopy (SEM), inductively coupled plasma-atomic emission spectrometry (ICP-AES), and transmission electron microscopy (TEM) are used to characterize the resulting novel AlN whiskers. The photoluminescence properties and probable growth mechanism for the particular morphology are also discussed.

2. Experimental procedure

The growth of threaded AlN whiskers was carried out by the PVT method in an RF induction heating furnace. In a typical growth run, commercial AlN (99.9%) powders were placed in a TaC crucible which was then placed into a graphite crucible before being loaded inside the RF induction heating furnace. The furnace system was evacuated to a vacuum of about 6.0×10^{-4} Pa, then filled with high-purity N_2 (99.999%) of 0.07 MPa. After that, the crucible was heated to 1850 °C and maintained for 5 h before the power of the furnace was shut off. In order to obtain the threaded AlN whiskers, a larger temperature gradient (about 20 °C/mm) between the source and crucible lid was designed. Deposited AlN whiskers were collected from the TaC crucible lid for further characterizations.

The phase and crystal structures of the as-grown products were identified by X-ray diffraction (XRD, Panalytical diffractometer with Cu Kα radiation). The morphologies and micro-structures were observed by scanning electron micro-

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scope (SEM, Hitachi, S-4800) and high resolution transmission electron microscope (HRTEM, JEOL JEM-2010), respectively. Elemental analysis of the whiskers was carried out by energy dispersive X-ray spectroscopy (EDX, EDAX Hitachi, S-4800) attached to the SEM instrument and inductively coupled plasma-atomic emission spectrometry (ICP-AES). Raman scattering measurement was performed at room temperature in a Raman system (JY-HR800) using the 532-nm line of a solid-state laser as the excitation source. The resolution of the Raman spectrometer was lower than 1 cm^{-1}, and the diameter of the incident light spot was about 1 μm. A photoluminescence (PL) spectrum was carried out at room temperature with a luminescence spectrophotometer using a He–Cd laser with 325-nm excitation.

3. Results and discussion

Figure 1 shows the XRD pattern of the as-grown AlN whiskers. All the peaks in the XRD pattern can be well indexed to the hexagonal wurtzite phase of AlN with lattice constants of $a = 3.1131(5)$ Å and $c = 4.9843(11)$ Å (matching with JCPDS No. 76-0702). No other phase is seen in the XRD pattern. Figure 2 presents the room-temperature Raman spectrum of the threaded AlN whiskers. The Raman peaks

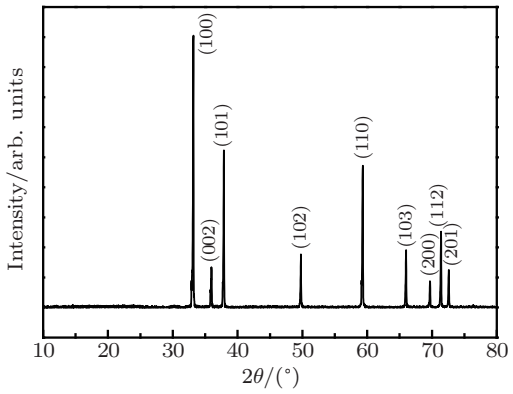


Fig. 1. XRD pattern of the threaded AlN whiskers.

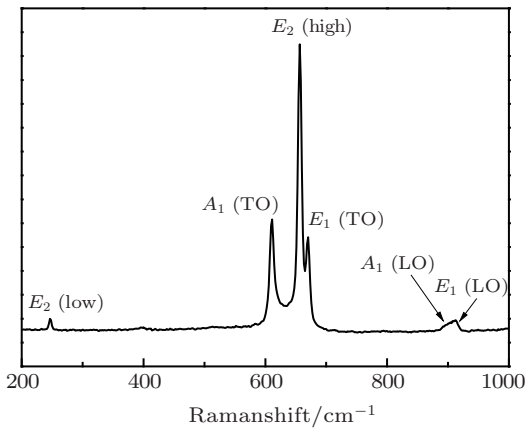


Fig. 2. Raman spectrum of the threaded AlN whiskers.

are sharp and well-defined, again indicating the good crystal quality of the AlN whiskers. Six phonon modes are observed at 246, 611, 656, 670, 895, 913 cm^{-1}, well matching the reported E_2 (low), A_1 (TO), E_2 (high), E_1 (TO), A_1 (LO), E_1 (LO) phonons.

The as-grown AlN whiskers are 0.5 μm∼100 μm in diameter and several millimeters in length in the fiber direction. The morphologies of the whiskers were first examined by SEM. Figure 3(a) shows a typical SEM image of the as-grown AlN whiskers. As can be seen, most of the whiskers are straight and have threaded morphology. There are also a few irregular 1D structures, possibly a result of the local fluctuation in temperature and growth thermodynamics. A magnified SEM image (Fig. 3(b)) presents that the AlN whiskers have screw thread structures. Obvious stripes can be observed in the SEM image of a single AlN whisker (Fig. 3(c)), of which the surface is not smooth. It should be noted that this particular morphology of AlN whisker is different from the ripple-like AlN nanowire[25] in that the diameter along the growth direction is the same, and yet different from the zigzag AlN nanowire[12] because the repeat segment length is too short with respect to the diameter. Nevertheless, the growth mechanism may share some similarities as those discussed below. Meanwhile, the threaded whiskers are different from the reported AlN whiskers which are straight with smooth surface and hexagonal or triangular cross sections.[23,24] Figure 3(d) shows the typical EDX spectrum, indicating that the whiskers are mainly composed of Al and N, and no any other elements were detected. The atomic ratio of Al/N obtained by inductively coupled plasma-atomic emission spectrometry (ICP-AES) is 0.96:1, revealing the formation of a slightly N-rich structure.

The morphologies of the threaded AlN whiskers are further investigated by TEM. Figure 4(a) shows a low-magnification TEM image of a single AlN whisker. The sawteeth on the edges are clearer than that in Fig. 3(c). Figure 4(b) shows two big sawteeth near the hump of the ripple-like edge (marked by a circle in Fig. 4(a)). The angle of the sawtooth is measured to be 125°, nearly the same as that associated with the hump of the ripple-like edge. The HRTEM image and the corresponding selected area electron diffraction (SAED) pattern of a single sawtooth are shown in Figs. 4(c) and 4(d), respectively. The lattice spacing is measured to be 0.498 nm, which accords well with the (0001) plane of hexagonal AlN. It is difficult to obtain the HRTEM image and the SAED pattern of the inner parts of the whisker since the whisker is too thick. However, according to the features of the TEM and HRTEM images, it is reasonable to believe that the growth direction of the whiskers is [0001].

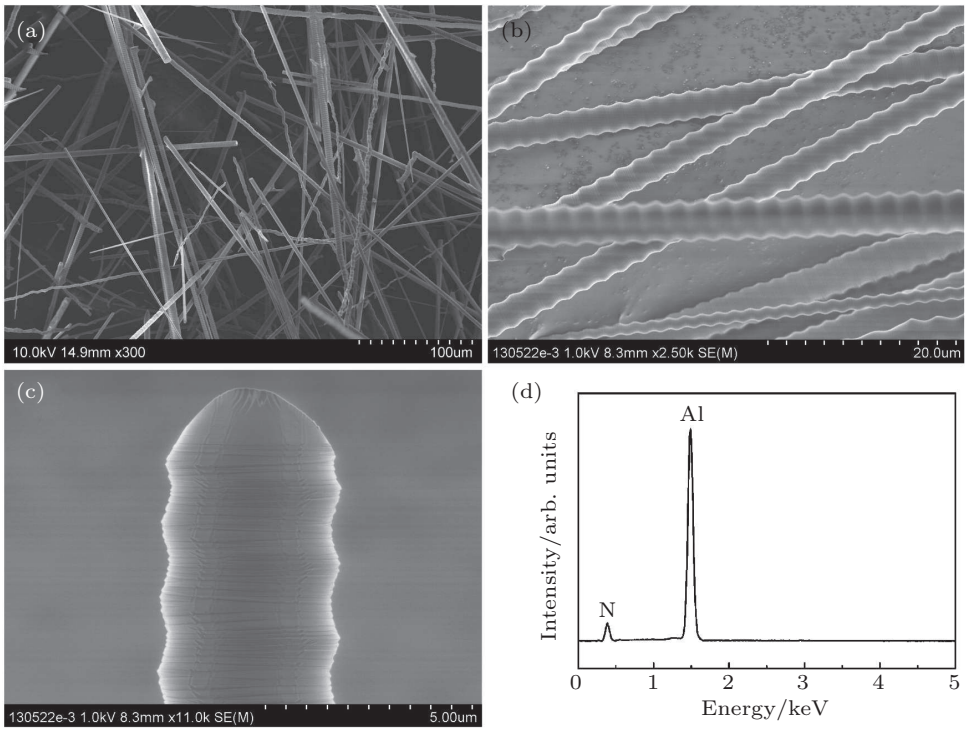


Fig. 3. (a) The SEM image of the threaded AlN whiskers; (b) a magnified SEM image of the threaded AlN whiskers; (c) the SEM image of a single AlN whisker; (d) the EDX spectrum of the threaded AlN whiskers.

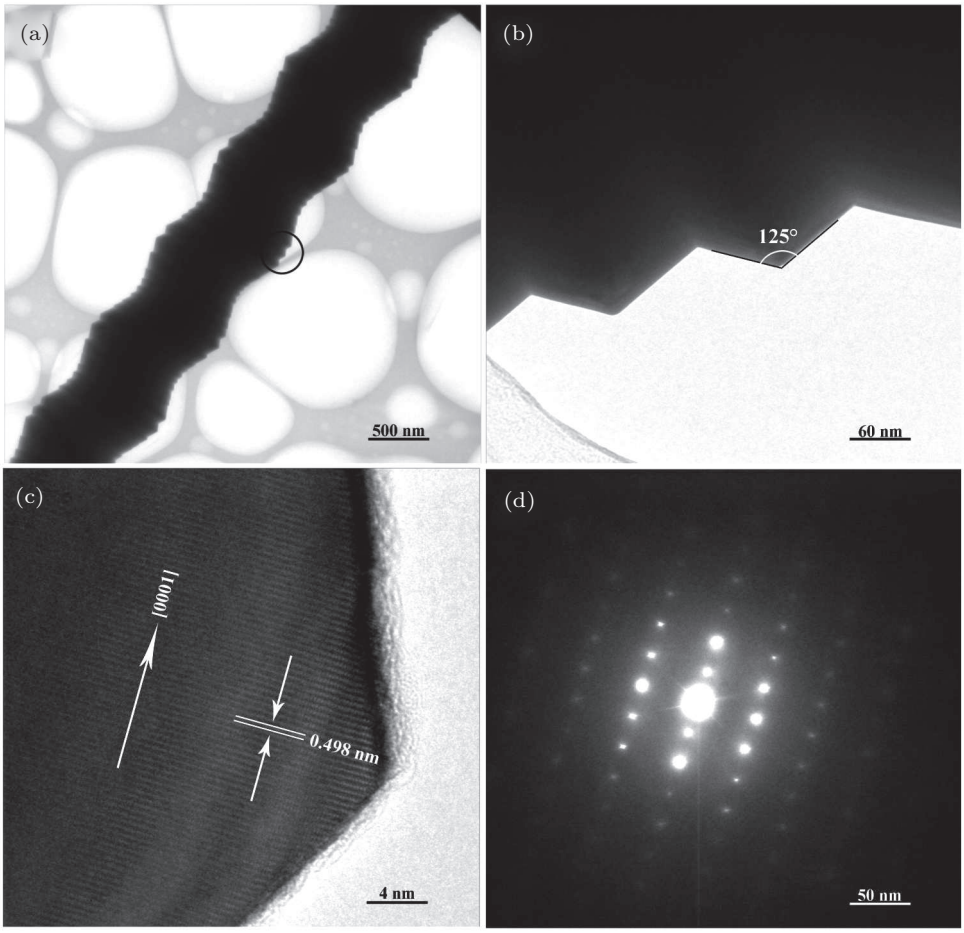


Fig. 4. (a) Low-magnification TEM image of the threaded AlN whisker; (b) enlarged TEM image of two big sawteeth marked by a circle in Fig. 4(a); (c) HRTEM image of a single sawtooth; (d) the selected area electron diffraction corresponding to Fig. 4(c).

The PL spectrum of the threaded AlN whiskers at room temperature is shown in Fig. 5. For a detailed analysis, the broad visible emission band is deconvoluted into two Lorentzian functions. As can be seen, the PL spectrum is composed of two emission bands located at 405.6 nm and 501.5 nm, possibly attributed to the native defects and the radiative recombination of a photogenerated hole with an electron occupying the nitrogen vacancy in AlN.[17,26] This similar emission band has also been observed previously in AlN nanowhiskers,[27] nanocones,[28] and nanowires.[29]

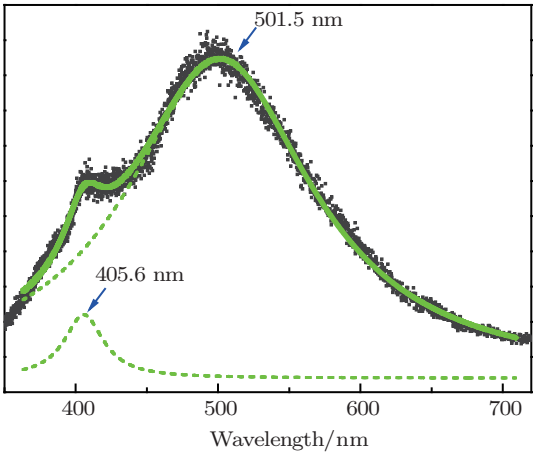


Fig. 5. (color online) Photoluminescence spectrum of the threaded AlN whiskers at room temperature. The emission band is deconvoluted into two Lorentzian functions for further analysis.

The threaded AlN whiskers have not been reported before, and the particular morphology is of great interest. The morphology of this threaded AlN whisker is beneficial for bonding when the whisker is used in composite. Since no catalyst is used and no spherical droplet is observed at the tip of the whisker, the growth of the threaded AlN whiskers should be dominated by a vapor–solid (VS) mechanism. Like the hexagonal AlN microfibers,[24] the threaded AlN whiskers may also grow layer by layer along the [0001] direction. As mentioned above, the angle of the sawtooth is 125°. Moreover, the HRTEM image and SAED pattern presented here are rather similar to those observed in zigzag AlN nanowires and ripple-like AlN nanowires,[12,25] so we speculate that the side faces of the whisker also belong to the equivalent $\{10\bar{1}1\}$ crystal faces, and the two sides of the sawtooth are along the $[2\bar{1}\bar{1}1]$ and $[\bar{2}111]$ directions, respectively. For the hexagonal crystal AlN, $[2\bar{1}\bar{1}1]$ and $[\bar{2}111]$ are crystallographic equivalent directions, which means there exist slight differences in anisotropic energy between them. A slight change in growth kinetics can change the growth direction from $[2\bar{1}\bar{1}1]$ to $[\bar{2}111]$ and from $[\bar{2}111]$ to $[2\bar{1}\bar{1}1]$. In the equilibrium state, the two sides of the sawtooth should be the same in length, but in an appropriate periodically varied growth condition with a large temperature gradient which is possible in the RF induction heating furnace, the lengths of the two sides may gradually and inversely evolve as can be seen in Fig. 4(a).

4. Conclusion

In this paper, we grow threaded AlN whiskers by the PVT method for the first time. The whiskers are 0.5∼100 micrometers in diameter and several millimeters in length in the fiber direction, and have asymmetrical tiny sawteeth on the surface. TEM results indicate that the threaded whisker grows along the [0001] direction, and the rough surface may result from both the equivalency of $[2\bar{1}\bar{1}1]$ and $[\bar{2}111]$ directions and a periodically varied growth condition in the RF induction heating furnace. Like other 1D AlN structures, the threaded AlN whiskers obtained here have potential applications in electronic packages and field emission.[30,31] Moreover, by virtue of the rough surface, the threaded AlN whiskers can be more promising for bonding in composites[32] than any other 1D AlN structures.

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