• *Research Articles*

Microstructure Characterization of Single-crystal ZnO Nanorods Synthesized by Solvothermal at Low Temperature

Chunna YANG, Ying LI, Ge XU and Xiuliang MA†
Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

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Single-crystalline ZnO nanorods have been synthesized by a simple solvothermal process at low temperature. Transmission electron microscopy (TEM) observations have confirmed that the as-synthesized products have rod-like morphologies with diameters ranging from several nanometers to 30 nm and lengths from 100 nm to 2 μm. Such hexagonal ZnO nanorods are structurally uniform and the growth direction is identified to be [0001]. Growth mechanism of the ZnO nanorods was proposed.

KEY WORDS: ZnO nanorod; Transmission electron microscopy

1. Introduction

Nanostructured materials have superior properties than their bulk counterpart because the scale of these nanomaterials is comparable to the de-Broglie wave length of carriers. Therefore, one-dimensional (1D) nanostructures, such as nanotubes, nanowires and nanorods[1–5], have attracted extraordinary attention for their potential applications in gas sensors[6], lightemitting diodes[7], data storage[8], and catalyst supports[9]. One-dimensional ZnO nanoforms have been widely investigated as electronics and optoelectronics materials[10–12] owing to its wide band-gap (3.37 eV at 298 K) and large exciton binding energy (60 meV). For example, Wang *et al.*[13] recently assembled piezoelectric nanogenerators using ZnO nanowire arrays. A number of nanoforms of ZnO, such as nanowires[14], nanodots[15], nanobelts[16], nanoneedles[17], nanoflowers[18] and nanorods[19] have been reported. And, various synthetic techniques have been applied to synthesize these ZnO nanoforms, such as anodic alumina template (AAM)[20], metalorganic chemical vapor deposition (MOCVD)[21], chemical vapor deposition (CVD)[22], electrochemical deposition (ECD)[23], laser ablation[24] and hydrothermal method[25,26]. Among these methods, the hydrothermal method is appealing because it has the advantage of simplicity, low temperature, low cost, and can be easily controlled. In this paper, we report the synthesis of single-crystalline ZnO nanorods *via* a simple solvothermal process at low temperature. Growth mechanism has been proposed on the basis of detailed observation of transmission electron microscopy.

2. Experimental

All chemicals are commercial reagent with analytical grade without further purification. Polyvinylpyrrolidone-k30 (PVP-k30) 1.25 g and absolute ethanol 60 ml were added into a vessel, and the solution was magnetically stirred for 20 min; after that, 0.25 g $Zn(Ac)_2{\cdot}2H_2O$ was slowly added into the solution and stirred for another 20 min; then 1.5 g NaOH was added into the vessel and continuously stirred for 30 min; in the end the solution was heated up to 80°C and maintained at this temperature for 30 h, and then cooled to room temperature naturally. The final white precipitates were washed with absolute ethanol and distilled water several times. The TEM samples were prepared by dispersing some products in absolute ethanol and immersing them in an ultrasonic bath for 60 min. Drop of the resulting suspension was placed onto a copper grid with carbon film, and dried in air at room temperature. A JEOL 2010 transmission electron microscope was used for lattice imaging and electron diffraction. A Tecnai G^2 F30 transmission electron microscope, equipped with high-angle-angular-dark-field (HAADF) detector, Gatan imaging-filter (GIF) and X-ray dispersive spectroscopy (EDS) system was used for Z-contrast imaging and composition analysis.

3. Results and Discussion

Figure 1 is a low-magnification TEM image showing the morphologies of the as-synthesized products. It is shown that the product contains of rod-like crystals with diameters of several nanometers to several

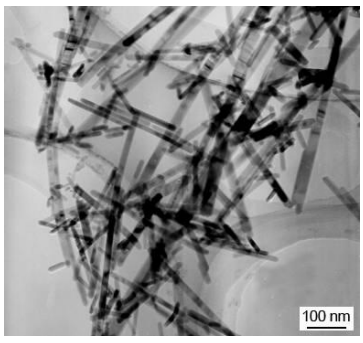

Fig.1 A low magnification TEM image showing that the as-synthesized products are nanorods

† Prof., Ph.D., to whom correspondence should be addressed, E-mail: xlma@imr.ac.cn.

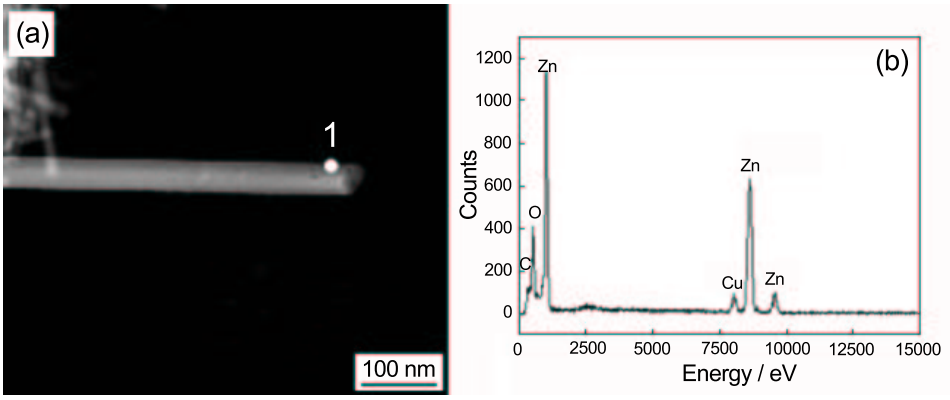

Fig.2 (a) A low magnification HAADF image of one ZnO nanorod, (b) EDS spectrum from the point 1 which is mark in (a) confirming that the nanorod is composed of zinc and oxygen

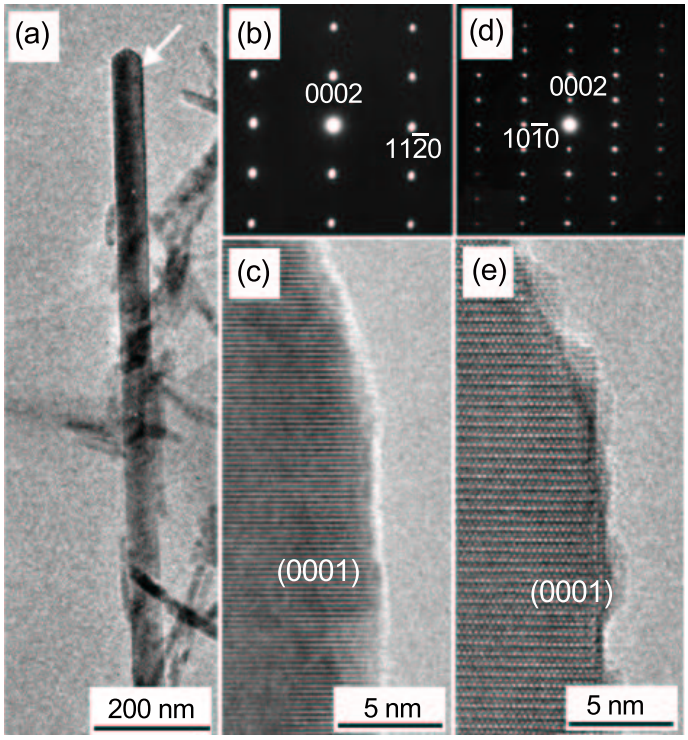

Fig.3 (a) A low-magnification image of one nanorod; (c) HRTEM image taken along [1$\bar{1}$00] from the area marked by white arrow in (a); (e) HRTEM taken along [1$\bar{2}$10] from the area marked in (a); (b) and (d) shows the corresponding SAED pattern of (c) and (e)

tens of nanometers. The length of these rod-like crystals ranges from several hundred nanometers to micrometers. The yield of the product was high and free from other nanoforms. Figure 2(a) is a low magnification HAADF image of single ZnO nanorod, and Fig.2(b) is the EDS spectrum from the point 1 which was marked in Fig.2(a). It is seen that the nanorod is composed of zinc and oxygen. The C and Cu peaks are from the copper grid.

Figure 3(a) is a low-magnification TEM image of a ZnO nanorod showing that the rod has a uniform diameter. Figure 3(b) and (d) are EDPs of the two low-index zone axis, which indicate that the nanorod is single-crystallized. Figure 3(c) and 3(e) are HREM images corresponding to the above two low-index directions. It is seen that the growth direction of the nanorod is paralleled to [0001]. Such a growth direction can be simply explained in terms of "lowest energy" argument, since (0001) plane of ZnO with hexagonal structure is the closest packed plane in the crystal and stacking along the [0001] direction is energetically favorable[27]. Electron diffraction and high-resolution experiments in variant areas along the nanorod confirm that the nanorod is single-crystallized and free from defects of stacking faults and dislocations.

The present experiments indicate that PVP plays an important role in the formation of ZnO nanorods, since we found that, in case of free from surfactant, the reaction of $Zn(Ac)_2{\cdot}2H_2O$ and NaOH ethanol solutions could easily result in ZnO nanoparticles. Zhong *et al.*[28] have proposed growth mechanism on ZnO nanocrystals which was synthesized by hydrothermal. They introduced the hypothesis that the growth unit is the complex formed by the attraction of cations and OH^- ions, whose coordination numbers

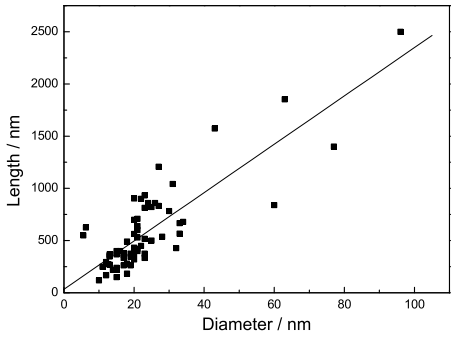

Fig.4 Plot of diameter *vs* length of the nanorods and their fitting

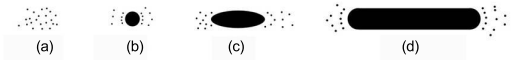

Fig.5 Schematic illustration showing a possible geometrical development of a nanorod during the growth: (a) some clusters of ZnO were first formed, (b) more small ZnO clusters form a bigger cluster, (c and d) schematic model illustrating the diffusion of ZnO clusters toward the two ends of a nanorod, growing along [0001]

is equal to that of the cation in the crystal to be formed. So the reactions can be considered as follows:

$$Zn(CH_3COO)_2 + 2NaOH = Zn(OH)_2 + 2CH_3COONa \quad (1)$$

$$Zn(OH)_2 + 2OH^- = Zn(OH)_4^{2-} \quad (2)$$

$$Zn(OH)_4^{2-} + Zn(OH)_4^{2-} = Zn_2O(OH)_6^{4-} + H_2O \quad (3)$$

$$Zn_xO_y(OH)_z^{(z+2y-2x)-} + Zn(OH)_4^{2-} = Zn_{x+1}O_{y+1}(OH)_{z+2}^{(z+2y-2x+2)-} + H_2O \quad (4)$$

$$2Zn_xO_y(OH)_z^{(z+2y-2x)-} + [2x-2y-z]Zn(OH)_4^{2-} = [4x-2y-z]ZnO + [4x-4y-z]H_2O \quad (5)$$

Due to the diffusion and movement of the ions, growth units $Zn(OH)_4^{2-}$ are bonded together through a dehydration reaction ($OH^- + OH^- = H_2O + O^{2-}$), when the $Zn_xO_y(OH)_z^{(z+2y-2x)-}$ cluster reach the critical size that was required for the formation of ZnO powder, the cluster $Zn_xO_y(OH)_z^{(z+2y-2x)-}$ was precipitated. $Zn_xO_y(OH)_z^{(z+2y-2x)-}$ is unstable and it will react with $Zn(OH)_4^{2-}$ as Eq.(5) and ZnO was formed. In the earlier studies of Ag nanowires[29,30], Xia *et al*. found that PVP macromolecules interacted more strongly with the {100} planes than with the {111} planes of silver, which resulted in [111] growth of silver nanowires. The PVP added in those experiments might coil around the nanoparticles first and the PVP seems to have stronger interaction with the $\{01\bar{1}0\}$ plane than with the {0001} planes of the nanocrystals. Figure 4 is a plot of length *vs* diameter of the nanorods. It is found that the length has a linear relation with its diameter. The imaginary line is its linear fitting curve and the corresponding equation is $l=23d+34$.

Figure 5 schematically illustrates the geometrical development of the nanorod. It is proposed that some small clusters of ZnO was firstly formed (Fig.5(a)). During its growth, the clusters with larger size will be growing at the expensive of the smaller ones (Oswald ripening)[31], then more small clusters bonded together to form a bigger cluster (Fig.5(b)). Because its side surface are tightly passivated by PVP, the growth velocity of [0001] direction is bigger than other directions. That is to say during its growth, the small clusters prefer to diffuse to the ends of a nanorod (Fig.5(c) and (d)). Following such a mode, it can easily grow into a longer one. The ratio of V[0001] and $V[01\bar{1}0]$ close to a constant, that means the aspect ratio of the nanorods will close to a constant.

4. Conclusion

At a low-temperature, large quantities of hexagonal ZnO nanorods with diameter from several nanometers to 30 nanometers and length up to 2 micrometers have been successfully synthesized by solvothermal method. Transmission electron microscopy and the associated techniques showed that the as-synthesized products are structurally uniform and the growth direction is identified to be [0001]. The present study indicates that PVP plays an important role in the formation of ZnO nanorods.

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