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Growth of ZnO Nanowires with unusual growth directions

ZHEN FANG*, XIU LIN, KAIBIN TANG[a], XIANWEN WEI, FENG TAO[b]
Anhui Key Laboratory of Functional Molecular Solids, College of Chemistry and Materials Science, Anhui NormalUniversity, Wuhu 241000, P. R. China
[a]*Nanomaterial and Nanochemistry, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei, 230026, P. R. China*
[b]*Department of Mechanical Engineering, Anhui University of Technology and Science, Wuhu 241000, P. R. China*

We report the synthesis of zinc oxide nanowires with unusual $[10\bar{1}0]$ growth direction via a simple chemical vapor transport method by direct oxidation of zinc powder at 850 ^oC. Morphology of the nanowires was characterized by field emission scanning electron microscopy. The lengths of the nanowires were up to several hundred microns and the diameters were about 100 nanometers. The growth habit of ZnO nanowires was investigated by high resolution transmission electron microscopy and selected area electron diffraction. The detail composition of ZnO nanowire was determined by X-ray energy dispersive spectrometer. This synthetic route is versatile and can be used in fabricating other one dimension metal oxide nanowires.

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1. Introduction

Among the known one-dimensional semiconductor nanomaterials, zinc oxide has two distinguished characteristics. One is its many charming physical properties, such as room temperature near-ultraviolet emission, field emission, transparent conductivity, piezoelectricity, and gas sensitivity [1-4]. The other is its abundant morphologies, including nanowires, nanobelts, nanotubes, nanosprings, nanoflowers, nanotetrapods, nanorings, nanodisks, and other complex nanostructures [5-13]. Since Yang and co-workers had successfully demonstrated room temperature ultraviolet lasing in ZnO nanowires array on sapphire substrates [14], synthesis of different forms of ZnO nanostructures and investigation of its novel properties have been widely explored. Recently, zinc oxide nanowires arrays were used as piezoelectric nanogenerators by Wang et al [15, 16]. This discovery has the potential of converting mechanical, vibrational, and hydraulic energy into electricity for powering nanodevices.

Usually, one dimensional ZnO nanostructures adopt [0001] growth habit because of the polarity along this direction. Controlling growth of ZnO with unusual growth direction is crucial now for scientific and technological research, however, for the outstanding properties may bring by the unusual crystalline side surface. Many efforts had been made to synthesize one dimensional ZnO nanostructures, the preparation method used including chemical vapor deposition, laser ablation, and solution-base routes [17-20]. Among these methods, the vapor transport and condensation process proved to be an effective route to synthesize ZnO nanostructures. Our previous works confirm that the growth direction of single-crystalline SnO_2 zigzag-like nanobelts can be controlled via this chemical vapor transport (CVT) method [21]. In this letter, we report using this simple CVT method to fabricate ZnO nanowires, the nanowires with unusual $[10\bar{1}0]$ growth direction could be fabricated easily under ambient pressure. To the best of our knowledge, this growth habit of one-dimensional ZnO nanostructures was scarcely reported [22, 23].

2. Experimental procedure

The experimental apparatus used for the synthesis of ZnO nanowires consists of a horizontal tube furnace, a quartz tube, a gas supply system, and a temperature controlling system. In a typical process, analytical grade zinc powder (2 g) was loaded into an alumina boat, which was covered with a copper foil above 5 mm. The boat was placed in the center of the quartz tube. Then the furnace was heated to 850 ^{o}C at the rate of 10 ^{o}C/min and kept at this temperature for 2 hours under pure argon flow rate of 200 sccm. After that, the furnace was cooled to room temperature naturally. White fuzzy-like products are found on the surface of the copper substrate. The morphologies of the sample were examined by field emission scanning electron microscopy (FESEM, JOEL JSM-6700F and Hitachi S-4800). High resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) images were obtained from a JEOL-2011 transmission electron microscope using an accelerating voltage of 200 kV. For X-ray energy dispersive spectrometer (EDS) analysis, the samples were deposited on thin amorphous carbon films supported by molybdenum grids.

3. Results and discussion

The morphology of the product was checked using FESEM. Fig. 1a is the typical low magnification SEM image of large amounts of uniform nanowires grown on the copper foil. The length of nanowires is about several hundred microns and the diameter is about hundred of nanometers. The nanowires were shown more clearly in high-magnification SEM images in Fig. 1b. The cross section of nanowires is rectangle indicated by real line. TEM studies were carried out to examine the detail structure and composition of the nanowires. Fig. 1c is the low-magnification TEM image of the nanowires, which indicates that the diameter is about 100 nm in accordance with the FESEM observations. The poor TEM image of the surface is due to the dispersal of the nanowires in organic solvent before TEM observation. The EDS (Fig. 1c, inset) recorded from the central of the nanowire indicates the presence of Zn, O and a small quantity of Cu. EDS result indicated that the white fuzzy-like products are ZnO nanowires. The crystalline structure was also investigated by SAED and HRTEM. The clear diffraction spot of SAED in Fig. 1d (inset) illuminated the single crystalline structure of ZnO nanowire and can be indexed as the $[1\bar{2}1\bar{1}]$ zone axis of hexagonal ZnO (JCPDS No. 76-0704). The lattice space of HRTEM image (Fig. 1d) was about 0.28 nm, corresponding to the interplanar spacing of (100) planes for hexagonal ZnO. The HRTEM analysis together with the SAED pattern reveals that the growth direction of the nanowire is $[10\bar{1}0]$.

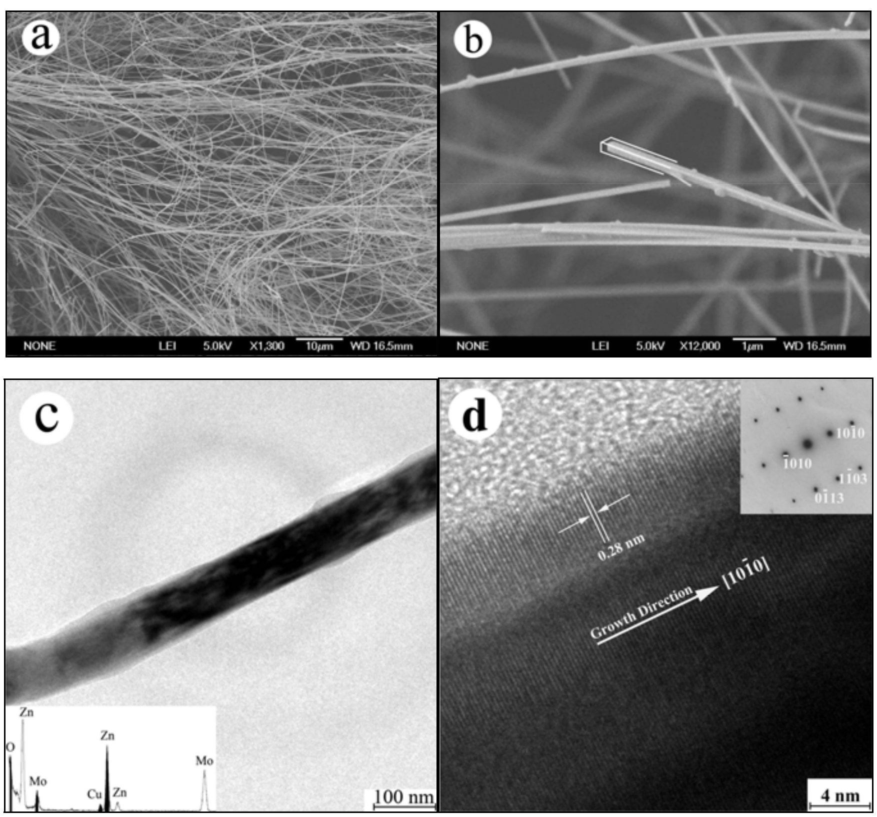

Fig. 1. (a) low-magnification SEM images of nanowires; (b) high-magnification SEM images of nanowires; (c) TEM image and EDS of single nanowire; (d) HRTEM and SAED of ZnO nanowire.

It is interesting that the ZnO nanowire growth plane is $(10\bar{1}0)$ in present work. Generally, the preferential growth plane of the ZnO crystal is (001), then $(\bar{1}0\bar{1})$, $(\bar{1}00)$, $(\bar{1}01)$, and $(00\bar{1})$ [9]. For the (001) crystal face is the corner of the coordination polyhedron present at the interface, which has the fastest growth rate (Fig. 2a) [24]. Formerly, we had reported the epitaxy on copper substrate could guided the SnO_2 zigzag nanobelts growing along [101] direction [21]. In current experiment condition, the copper substrate may also acts as the same rules in controlling the growth direction of ZnO nanowire. The growth along $(10\bar{1}0)$ plane under the controlling of the substrate made the unusual rectangular cross section of ZnO nanowires as indicated in Fig. 1b. The sketch map of ZnO crystal view along $(10\bar{1}0)$ plane further confirmed the reason for formation of rectangular cross section (Fig. 2b).

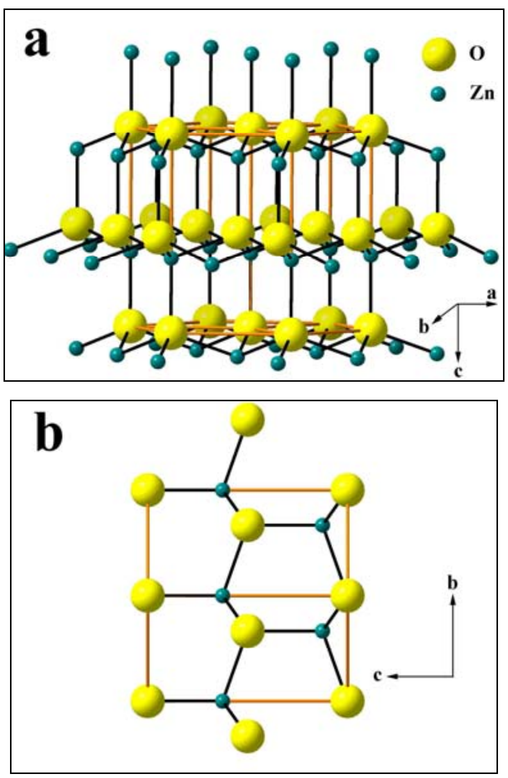

Fig. 2. (a) Structure model of wurtzite phase ZnO; (b) View along $(10\bar{1}0)$ plane of ZnO.

The whole CVT process can be express as following steps: I, zinc vapor sublimed under constantly heating and some zinc vapor liquefy on the copper substrate. II, the zinc liquid was oxided soon by the residual oxygen in the quartz tube [21]. III, ZnO nanowires with unusual growth direction were formed under the confine of copper substrate. By variation of the experimental temperature, we can get nanowires even the temperature reaches as high as 950 ^{o}C. The copper substrate will melt when the temperature is higher than 950 ^{o}C. Although the melting point of copper is 1084 ^{o}C, the Cu-Zn binary alloy formed easily under high temperature made the copper substrate melt. On the other hand, if the temperature is lower than 850 ^{o}C, the products were just zinc particles at the downstream of quartz tube.

4. Conclusions

In summary, ZnO nanowires with unusual $[10\bar{1}0]$ growth direction were obtained via CVT methods under 1 argon atmospheric pressure. Studies show that the rectangular cross section of ZnO nanowire was determined by the crystalline growth habit. This method is valid in guiding the growth of ZnO nanowires. We believe such synthetic route is versatile and can be adapted for the fabrication of nanowires of other one dimension metal oxide nanostructures.

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*Corresponding author: fzfscn@mail.ahnu.edu.cn