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Growth temperature controlled shape variety of ZnO nanowires

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Abstract

ZnO nanowires array has been synthesized via a simple physical vapor deposition method at low growth temperature without using any catalyst. By controlling different growth parameters, the nanowires exhibit different shapes: needle-like with sharp tips or rod-like with flat tips. All the nanowires are single crystal with a growth direction along *c*-axis. The rod-like nanowires are well vertical aligned to the substrate surface with *c*-axis preferred orientation. The morphology difference of ZnO nanowires is believed originated from different growth mechanisms.

1. Introduction

One-dimensional (1D) nanostructures have attracted great interest in recent years, due to their unique and fantastic optical, electrical, and mechanical properties as compared with bulk materials. They have great potential in fundamental studies and applications in nanodevices and functional materials. Up to now, many kinds of 1D semiconductor nanostructures have been synthesized, such as Si [1], GaN [2], ZnS [3,4], ZnSe [5], ZnO [6–12]. Among them, ZnO nanostructrues are intensively studied, due to the wide band-gap of 3.37 eV and large binding energy of 60 meV, which makes it a promising material for UV photonic devices, sensors and piezoelectric devices [13]. Different-shaped ZnO nanostructures have been fabricated by various synthesis methods, including chemical vapor deposition [9,14], thermal evaporation [15,16], aqueous solution deposition [17] and pulsed laser deposition [18]. By now, people put much attention to the synthesis of the nanostructure and their optical and electrical properties. Fewer papers consider the growth mechanism of ZnO nanostructures. In this Letter, we have synthesized needle-like and rod-like ZnO nanowires array without using any metal catalyst. It was found under different growth temperature nanowires grow following different mechanism, which induces the tips of nanowires are sharp or flat.

2. Experimental

The growth was carried out in a horizontal tube furnace by vapor transport process for 30 min. Zinc powder (99.99%) was loaded in a quartz boat served as source material. Si (1 1 1) substrates with smooth face downward were laid above the source material with a vertical distance of 4 mm. Before being loaded, the Si (1 1 1) substrates were cleaned by organic solvent, etched by HF acid and washed with deionized water.

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The furnace was heated up to the desired temperature (430 and 520 °C, respectively) under a constant flow (150 sccm) of pure Ar. The temperature was detected by a thermal couple close the substrate. When the temperature reached, pure Ar was replaced by normal nitrogen gas at the same flow rate to start the ZnO growth. The oxygen is unintentionally introduced by the residual O_2 in the nitrogen gas. The pressure during the growth process was kept at 1 torr. After deposition, each substrate surface was covered with a white gray layer. The as-grown samples were then investigated by the field-emission scanning electron microscopy (FESEM), the energy-disperse X-ray (EDX) attached to the SEM, the X-ray diffraction (XRD) and the transmission electron microscopy (TEM). Photoluminescence (PL) measurement was performed using a He–Cd laser line of 325 nm as excitation source.

3. Result and discussions

Fig. 1a,b shows the FESEM images of the ZnO nanowires array synthesized at 430 and 520 °C, respectively. The samples grown at different temperatures have different morphologies. In Fig. 1a, high-density needle-like ZnO nanowires are obtained at low temperature of 430 °C, in which the length of the nanowires ranges from 2.8 to 3.2 μm with a top diameter of 30 nm and root diameter of 100 nm. While for the nanowires grown at 520 °C, the shape is rod-like with a homogeneous diameter from top to root (Fig. 1b). The rod-like ZnO nanowires are well vertically aligned to the substrate surface. The diameters range from 40 to 120 nm (most of the nanowires have diameters of 120 nm) with an equal length of 1 μm. The inset of Fig. 1b shows an amplified top image of a single nanowire, which indicates the top of rod-like nanowire is flat with a hexagonal structure. EDX analyses present both the needle-like nanowires and the rod-like nanowires consist of zinc and oxygen element only (figures not given). By careful observation, these rod-like nanowires seem growing on a thin layer. But the needle-like nanowires are directly grown on the substrate surface.

In order to observe the thin layer clearly, we have grown some samples for a very short time. An initial stage of nanowires growth was detected. The images in Fig. 2 record the samples grown at 520 °C for 1, 5 and 30 min, respectively. For the sample just grown for 1 min, a thin film with a rough surface is obtained. This thin layer is consisted of ZnO nanoclusters. When extending the growth time to 5 min, some short nanorods appear on the thin film surface. These nanorods are almost vertical to the substrate surface. The diameter is around 50 nm and the length is 200 nm. With further increasing the growth time, nanorods grow larger and longer. Finally, rod-like nanowires array is formed with a length of 1 μm. The estimated longitudinal and transverse growth rates at the first 5 min are 40 and 10

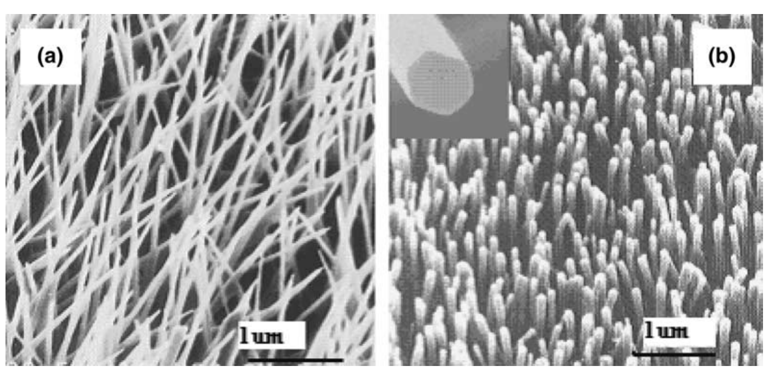

Fig. 1. FESEM images of the (a) ZnO nanowires synthesized at 430 °C and (b) rod-like ZnO nanowires synthesized at 520 °C.

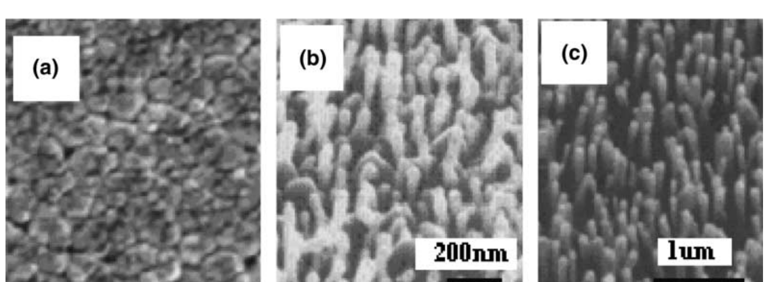

Fig. 2. FESEM images of the ZnO nanowires grown at 520 °C: (a) for 1 min, (b) for 5 min, and (c) for 30 min.

nm/min, respectively. When the total growth time (30 min) is concerned, the estimated longitudinal and transverse growth rates are 30 and 4 nm/min, respectively. Indicating a faster growth rate along the longitudinal direction.

The X-ray diffraction spectra (XRD) in Fig. 3 show the as-synthesized samples are ZnO wurtzite structure with lattice parameters of $a = 0.325$ nm, $c = 0.521$ nm. And both samples are c-axis oriented. In Fig. 3b, except [0 0 2] diffraction peak no other peaks are observed, which indicates the orientation of rod-like nanowires is higher than the needle like ones. The analysis is in well agreement with the FESEM images.

Fig. 4 shows the TEM images of the needle-like and rod-like ZnO nanowires. From the top image of Fig. 4a, the needle-like ZnO nanowire is found to have a smooth surface and a sharp tip (the inset in Fig. 4a is an enlarged image of the nanowire). The diameter of the nanowire decreases along the length. The rod-like nanowire has a uniform diameter distribution from the root to the tip part (Fig. 4b). The SAED patterns in both cases illuminate each nanowire is a single crystal with hexagonal structure and the nanowires grow along c-axis.

The difference in shapes of nanowires is considered originated from different growth mechanisms under two temperatures. Although the difference between these two temperatures is small (90 °C), it is enough to affect the growth process. Because both the Zn vapor partial pressure and reaction activity of zinc and oxygen are determined by temperature. And during the growth process no catalyst was used. For the nanowires grown at 430 °C (this temperature is only slightly higher than the melting point of metal zinc 419 °C), small amount of zinc gas was transported to the substrate surface. Because of low reaction activity, the Zn atoms can only stay on the substrate with forming a liquid Zn or ZnO_x ($x < 1$) droplets. When this liquid phase saturated with being further oxidated, crystalline ZnO presents. This is the nucleation process of nanowires. Due to a liquid phase participating into the growth process, ZnO nanowires grow at this temperature follows a vapor–liquid–solid (VLS) mechanism [19,20]. The diameter of the nanowire is determined by the size of liquid ZnO_x drop. And this liquid zinc sub-oxide phase is always on the tip of nanowires. Therefore, when the sample is cooled to the room temperature a sharp tip is formed [18].

For the sample synthesized at 520 °C, nanowires with a flat top were observed on the thin layer of ZnO. This phenomenon can be explained by the vapor solid (V–S) growth mechanism. Before nitrogen gas is introduced into the quartz tube, the substrate surface is covered with a thin Zn film (the temperature of 520 °C is much higher than the melting point of Zn). Then, with nitrogen gas being transported in the reaction tube, metal Zn is oxidated by the residual O_2 in nitrogen gas. During

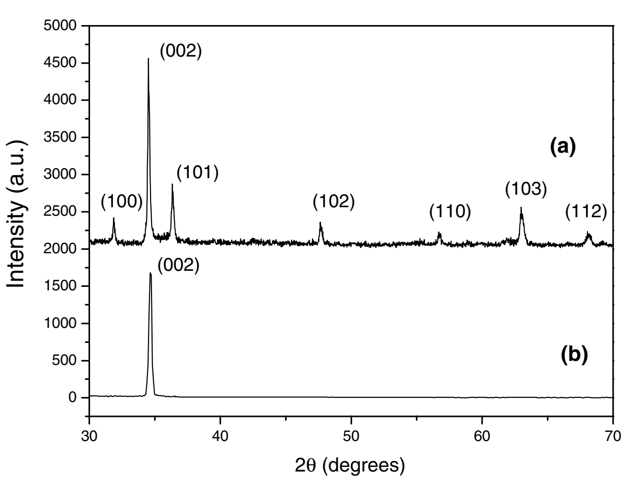

Fig. 3. XRD analysis of: (a) needle-like ZnO nanowires and (b) rod-like ZnO nanowires.

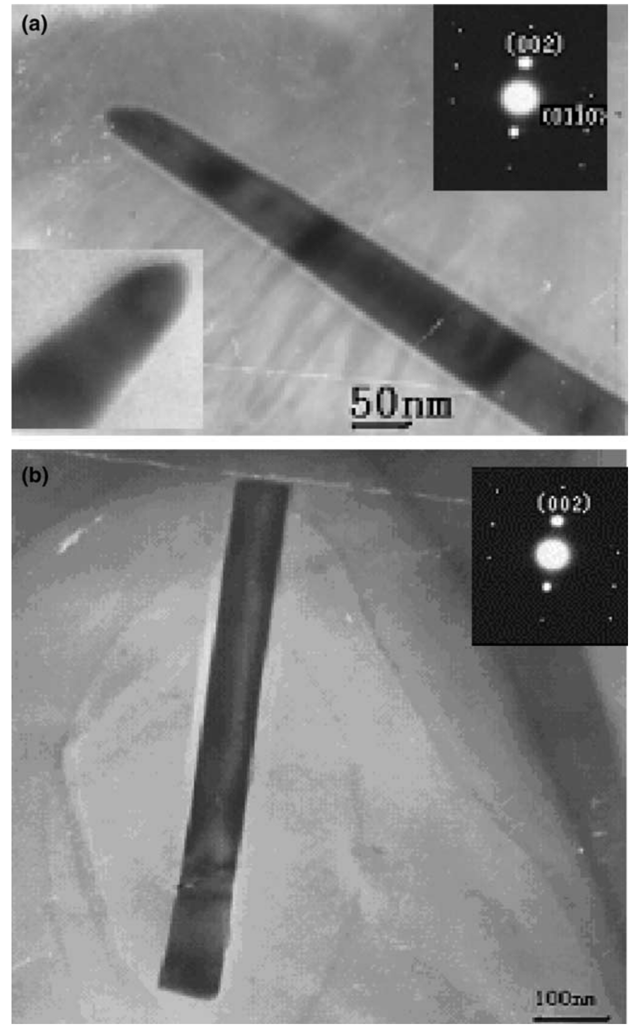

Fig. 4. TEM images of: (a) a needle-like ZnO nanowire and (b) rod-like ZnO nanowire.

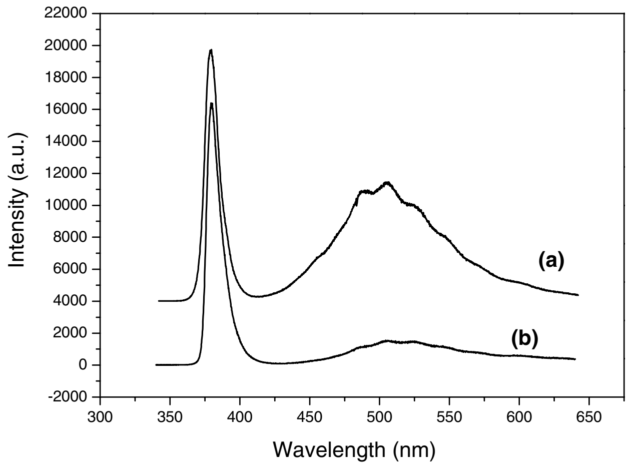

Fig. 5. PL spectrum of: (a) the needle-like ZnO nanowires and, (b) the rod-like ZnO nanowires.

this process, a thin layer of ZnO nanoclusters is formed on the substrate (as shown in Fig. 2a) with *c*-axis preferred orientation. This film could provide nuclei sites for the further growth of the nanowires through a self-catalyst process [21]. According to the 'low energy' principle [22], the [0 0 0 1] plane is the fastest growing crystallographic plane. Therefore, hexagonal-shaped ZnO nanowires are high orientation. But the nanowires grown at 430 °C have no oriented nuclei sites, they show divergence from the *c*-axis orientation.

Based on the above discussion, the density of oxygen vacancies is assumed higher for the sample grown at low temperature than the one grown at high temperature. This will influence the PL properties on these two samples. The PL spectra of the nanowires are illustrated in Fig. 5. In both cases, the emission bands are composed of a strong UV near-band-emission and a weak deep-level emission. The UV emission is considered originated from the radiative recombination of exciton. The deep-level emission is commonly regarded as coming from the singly ionized oxygen vacancies [23] or surface states [24]. The intensity ratio of the near-band-emission to the deep-level emission in rod-like nanowires is larger than that of the needle-like ones, which indicates there are more oxygen vacancies for the sample grown at low temperature. This result agrees well with our prediction above.

4. Conclusions

In summary, needle-like and rod-like ZnO nanowire arrays have been grown by simple vapor phase transport process under different temperatures of 430 and 520 °C, respectively. The nanowires have length of 2.8–3.2 μm with uniform diameter distribution of 100 nm at root parts and 30 nm at tip parts. The nanorod arrays have uniform length of 1 μm with diameter range from 40 to 120 nm. The different in structures and morphologies of the nanowires and nanorods are the results of the different growth mechanisms of VLS and S–V method respectively.

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