Research Article

Growth of ZnO Nanowires in Aqueous Solution by a Dissolution-Growth Mechanism

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A novel methodology based on the dissolution-growth mechanism was developed to prepare ZnO nanowire films. The film morphology and structure were investigated by using field emission scanning electron microscopy, high-resolution transmission electron microscopy, and X-ray diffraction analysis methods. The results show that the ZnO nanowires are single crystalline *c*-oriented wurtzite. The ZnO rod crystals were eroded to provide the growth primitive of ZnO nanowires, which formed on top of the rod crystals when the erosion reaction got the equilibrium. The length of the resultant nanowires is rather large because the successive erosion of the rod crystals maintains the low concentration of $\text{Zn}_2\text{O}(\text{OH})_{2n-2}$ in the aqueous solution.

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1. INTRODUCTION

One-dimensional zinc oxide represents an important basic material due to its low-cost, large-band [1], and luminescent properties and has wide applications in photocatalyst [2], gas sensor [3], varistor [4], transparent conductive coating [5], and solar cells [6]. The fabrication of one-dimensional zinc oxide has been widely studied by different methods. For example, vapor-liquid-solid epitaxial (VLSE) mechanism [7], thermal evaporation [8], hydrothermal methods [9], template-based growth [10], chemical vapor deposition [11], and pulsed laser deposition [12] have been successful in creating 2D-oriented arrays of ZnO rods. Among these methods, solution process has been demonstrated to be a facile method for synthesizing ZnO due to its own advantages such as simplicity, reproducibility, non-hazardousness, cost effectiveness, being suitable for producing large-area thin films. Various morphologies have been achieved by aqueous solution method, for example, rod-like [13], tube-like, flower-like crystals [14], and so on.

But up to now, growth of nanowire with large length has not been achieved by aqueous solution method. The diameter of ZnO nanocrystals is dependent on the concentration of the solution [13, 15]; nanorods can be obtained when the concentration is relatively low, but nanowires cannot because the concentration of the solution will decrease greatly with

the crystal growth. So it is essential to maintain the concentration of the solution during the whole growth process to get nanowires with larger length. In this paper, a novel method was developed to obtain large-scale ZnO nanowires based on the basic dissolution-growth mechanism. The successive erosion of rod crystals was used to maintain the zinc concentration in the solution.

2. EXPERIMENTAL

ZnO rod films were fabricated in aqueous solution using the method in [13, 16]. To prepare ZnO nanowires, 1 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ aqueous solution was added in a 25 mL beaker, and stirred for several minutes. Then ZnO rod films (2×1 cm) were inserted in the solution and the beaker was sealed. After the beakers were kept in an oven at 80°C for 2–6 hours, the films were removed from the solution and dried under vacuum at 80°C . The pH value of the initial solution was 11.5, and it decreased slightly to 11.2 after the erosion for 6 hours.

The ZnO nanowires were characterized by using field emission scanning electron microscopy (FESEM, JEOL 6700, 200 kV), high-resolution transmission electron microscopy (HRTEM, PHILIPS TECNAI G2 F20, 300 kV). X-ray diffraction was recorded by Rigaku D/max-2500 X-ray diffractometer (30 kV, 20 mA) with copper targets ($\lambda = 0.154059$ nm).

FIGURE 1: FESEM photographs of ZnO films eroded for different periods: (a) 0 hour, (b) 2 hours, (c) 4 hours, and (d) 6 hours.

FIGURE 2: XRD pattern of ZnO film obtained after erosion for 6 hours in the ammonia solution.

3. RESULTS AND DISCUSSION

Morphology of ZnO films obtained in ammonia solutions with different reaction times is shown in Figure 1. Figure 1(a) illustrates the FESEM image of the as-grown ZnO rod films, from which it can be seen that the substrate was covered with hexagonal rod crystals with the diameter of $0.2\text{--}0.6\text{ }\mu\text{m}$. The morphology evolution during the erosion process is shown in Figures 1(b), 1(c), and 1(d). As depicted in Figure 1(b), after 2 hours of reaction, hexagonal pits with the wall thickness of $\sim 30\text{ nm}$ formed on top of the rod crystals. This process is similar to the rod crystals growth, which we have found previously [15], namely, both erosion and growth begin from the center at (0001) plane of the rod crystals. As the period of the process was prolonged to 4 hours, nanowires appeared on surface of the films, of which the diameter was about $25\text{--}40\text{ nm}$ (as seen in Figure 1(c)). The nanowires became longer and thicker when the reaction time was increased to 6 hours (Figure 1(d)).

Figure 2 shows the XRD pattern of the ZnO film illustrated in Figure 1(d). The high (002) peak is indexed as the wurtzite structure of ZnO, indicating that the nanowires are highly *c*-oriented. An energy dispersive spectroscopic (EDS) analysis of the film (Figure 3) shows that the products are mainly composed of Zn and O elements, consistent with the result of XRD.

Figure 4 shows the HRTEM image of a part of a typical ZnO nanowire. The diameter and length of the nanowire are 30 nm and more than $5\text{ }\mu\text{m}$, respectively. So the aspect ratio

of the nanowire is more than 160, which is the typical characteristic of nanowire.

Figure 5 shows HRTEM and TEM (inset) images of a ZnO nanowire, demonstrating the single-crystalline structure of the nanowire. The lattice spacing of 0.28 nm shown in the HRTEM image of Figure 5 corresponds to a *d*-spacing of (100) crystal planes, confirming that the nanowire is *c*-oriented.

The growth of ZnO nanowire can be described based on the chemical equilibrium of dissolution-regrowth in the solution. Yamabi and Imai [17] and Peterson and Gregg [18] found that $\text{ZnO}_{(s)}$ only formed at small region in the phase diagram, thus suitable pH value and Zn species concentration is necessarily required. In aqueous solutions at $\text{pH} > 9$, Zn (II) soluble species in the form of hydroxyl complexes such as $\text{Zn}(\text{OH})_2(\text{aq})$ and $\text{Zn}(\text{OH})_4^{2-}(\text{aq})$ increase [16], the thermodynamic equilibrium for $\text{ZnO}_{(s)}\text{--H}_2\text{O}$ system can be represented by

As is well known, supersaturation is required for crystal growth in solution. In our system, the erosion should stop when the process achieves the equilibrium according to (1). However, the growth of nanowire indicates that the solution is supersaturated, which suggests that the erosion and growth proceed simultaneously when the reaction get the equilibrium.

When $\text{ZnO}_{(s)}$ is introduced into the basic solution, the equilibrium in (1) moves to the right because of the low $\text{Zn}(\text{OH})_n^{2-n}(\text{aq})$ concentration and H^+ consumption. Thus the $\text{ZnO}_{(s)}$ will be eroded. As the erosion time increases, the concentration of $\text{Zn}(\text{OH})_n^{2-n}(\text{aq})$ increases and approaches to the critical supersaturation. Peterson and Gregg [18] and Yamabi and Imai [19] have found that $\text{Zn}(\text{OH})_n^{2-n}(\text{aq})$ can form polyhydroxyl zinc complex, which was represented by

where $n = 2$ or 4 , $\text{Zn}_2\text{O}(\text{OH})_{2n-2}$ supplies the source of the heterogeneous nucleation and growth of ZnO nanowires. The concentration of $\text{Zn}(\text{OH})_n^{2-n}(\text{aq})$ and $\text{Zn}_2\text{O}(\text{OH})_{2n-2}$ increases with the erosion of the rod crystals and then the reaction achieves the equilibrium. The erosion process continues,

FIGURE 3: EDS picture of the ZnO film obtained after erosion for 6 hours.

FIGURE 4: HRTEM photograph of a typical ZnO nanowire.

FIGURE 5: TEM (inset) and HRTEM photograph of a ZnO nanowire.

then new ZnO nuclei form on top of the ZnO rod because the solution is supersaturated. In previous work, we have found that the diameter of ZnO rods, which were fabricated by aqueous solution method decreased with the reduction of the zinc precursor concentration, due to the shift of chemical equilibrium in the solution [15]. As a result of the low zinc concentration in the solution, the diameter of the crys-

FIGURE 6: Nucleation and growth of the ZnO nanowire by dissolution-growth mechanism.

tals obtained in this work is in nanoscale [13]. The nanocrystals transform to nanowires with the increase of growth time for the successive erosion of ZnO rod, which maintains the rather low concentration of $\text{Zn}_2\text{O}(\text{OH})_{2n-2}$. Figure 6 gives the sketch of the growth mechanism.

In addition, the growth manner of the nanowires can be analyzed by the aid of TEM and HRTEM characterization. Three typical fractions of the ZnO nanowire were observed in the film eroded for 6 hours (Figure 7(a)). For the first fraction (as shown in Figure 7(b)), nanowire was composed of nanoparticles with the diameter of 5~8 nm, between which there are many mesopores. No crystalline fringe can be detected in these nanoparticles, suggesting the amorphous nature of the nanowire. As for the second fraction (Figure 7(c)), it can be seen that almost all of the nanoparticles are crystalline grains, and many of them begin to attach with each other along *c*-axis. The densification of the nanowire can be

FIGURE 7: (a) A typical TEM image of ZnO nanowire fractions, three kinds of fractions with different crystallinity were shown. (b) A typical HRTEM image of a ZnO nanowire fraction in the early growth stage and its TEM image (inset). (c) A typical HRTEM image of a ZnO nanowire fraction in the medium growth stage and its TEM image (inset), the arrowhead indicates the oriented attachment. (d) The HRTEM image of a typical crystallized ZnO nanowire fraction and its TEM image (inset).

FIGURE 8: Schematic disorder-order growth process of ZnO nanowire: (a) nanoparticle packing, (b) crystallization and oriented attachment of small grain domains, and (c) formation of single crystalline ZnO nanowire.

inferred according to disappearance of the pores. But the interfaces among the nanoparticle packing are still visible. A similar oriented attachment has also been found by Searson et al. [20] when preparing TiO_2 nanoparticles under hydrothermal condition. The driving force for the disorder-order assembly process is the reduction of surface energy, and this mechanism has been reported previously [21, 22]. The third kind of nanowire fraction is very smooth and compact (Figure 7(d) (inset)). Its HRTEM image shows that a large quantity of small grain domains has transformed into a single crystalline nanowire. According to these observed results, the proposed growth mechanism of ZnO nanowire can be illustrated in Figure 8. Based on the growth period, there are three different fractions in one nanowire, corresponding to three growing stages of the nanowire. Step (a) is nanoparticle packing process. Step (b) is the process of crystallization and oriented attachment. In Step (c), the single crystalline nanowire forms.

4. CONCLUSIONS

ZnO nanowires were synthesized in aqueous solution by a dissolution-growth mechanism. The nanowires are single

crystalline *c*-oriented wurtzite. The ZnO rod crystals were eroded to provide the growth primitive of ZnO nanowire. The nanowire formed on top of the rod crystals when the erosion reaction achieved the equilibrium. The growth manner of nanowires has been discussed based on the TEM and HRTEM results. The length of the nanowire is rather large because the successive erosion of the rod crystals maintains the low concentration of $\text{Zn}_2\text{O}(\text{OH})_{2n-2}$.

As we all know, ZnO nanowires have great application potential in the photoelectric field, such as luminescence, window and electrode material for solar cells, phosphors, piezoelectric transducers and actuators, surface acoustic coatings, varistors, and sensors. This strategy can provide a novel and simple route to obtain ZnO nanowires, even ultralong ZnO nanowires which may improve the properties of nanowire-based devices.

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