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Synthesize of ZnO Nanorods on Quartz Substrates with Seed Layer via Hydrothermal Method: Influence of Solution Concentration

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Abstract

Vertically oriented ZnO nanorods have been synthesized by hydrothermal method on quartz substrates with a seed layer. The influence of solution concentration on the morphology, structural and optical properties was analyzed. Results indicated that with the increase of solution concentration, the diameter and uniformity of ZnO nanorods increased. And the preferred orientation is obviously which shows better crystal quality. Typically, when the solution concentration is 0.03 mol/L, the nanorods exhibit a stronger UV emission peak located around 380 nm. In the visible region, all synthesized samples demonstrate more than 80% of optical transparency.

Keywords

Hydrothermal Method, ZnO Nanorods, Solution Concentration

1. Introduction

With a large direct band gap of ~3.3 eV and a large exciton binding energy of ~60 meV, ZnO semiconductor is still withstanding separately in the field of material research. Especially, ZnO has been considered as one of the most promising nanomaterials for many applications in optoelectronics [1] [2], piezoelectricity [3], gas sensors [4], photocatalysts [5], and so on. Depending on the application, ZnO was synthesized in several morphological forms: nanocrystals, nanoring, nanodisk, nanowires, nanorods and quantum dots [6] [7] [8]. And there are many methods to prepare ZnO nanomaterials, such as pulsed laser deposition (PLD), chemical vapour deposition (CVD), electrochemical deposition and hydrothermal method [9] [10] [11] [12]. Compared with other nano morphology, the nanorod array has attracted much attention due to its excellent electrical and optical properties. Due to the simple preparation process, stoichiometry control, fast growth rate, low production cost and low temperature, hydrothermal method is the most commonly used method to prepare ZnO nanorods [13]. However, due to low temperature, the prepared ZnO nanorods by hydrothermal method have poor orientation and uniformity limiting the output efficiency and lifetime of practical devices. In order to obtain ZnO nanorods with high crystallization quality, uniform arrangement and fast growth rate, in this paper, a layer of ZnO film was prepared by RF sputtering technique as the seed layer, and then ZnO nanorods were grown on the quartz substrate with ZnO seed layer by hydrothermal method. The effects of the seed layer and different solution concentrations on the morphology, structural and optical properties of ZnO nanorods were studied.

2. Experimental

2.1. ZnO Seed Layer

ZnO seed layer was deposited by RF magnetron sputtering system with a ZnO target (99.999%, purity). 1 cm × 1 cm Quartz glasses were used as substrates. Before loading into reaction chamber, substrates were cleaned in an ultrasonic cleaner using acetone, ethanol, and deionized water for 20 min, and dried with nitrogen gas. The flow rate of Ar was kept at 10 sccm (standard cubic centimeter per minute), and the pressure during deposition was 0.5 Pa. The RF power was fixed at 100 W. The seed layer was about 50 nm thick.

2.2. ZnO Nanorods

Zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$] and hexamethylenetetramine [$(CH_2)_6N_4$, HMT] were used as precursors. Aqueous solutions of $Zn(NO_3)_2$ and HMT with equivalent molar concentration were prepared individually (range 0.01 - 0.04 mol/L). Then, the two solutions were mixed together and transferred into Teflon-lined autoclave. The substrates were then placed on the special holder of the boxes, facing downward, and suspended in the solution. The solutions and the substrates were then placed in a drying oven and heated to a constant temperature of 90˚C for 12 h. Finally, the substrates along with the products were taken out from the solution, cleaned in alcohol, deionized water, and dried with nitrogen at 300˚C.

The morphologies of the ZnO nanorods were evaluated with a field emission scanning electron microscopy (FESEM, JEOL-JSM-6700F). The structural and optical properties were characterized using an X-ray diffraction (XRD, Advanced D8, Germany), a UV/vis spectrometer (Hewlett-Packard, 8453), and a PL spectroscopy (He-Cd laser, 325 nm) in turn. The surfaces of the seed layers were observed by atomic force microscope (AFM, AJ—IIIa) in tapping mode.

3. Results and Discussion

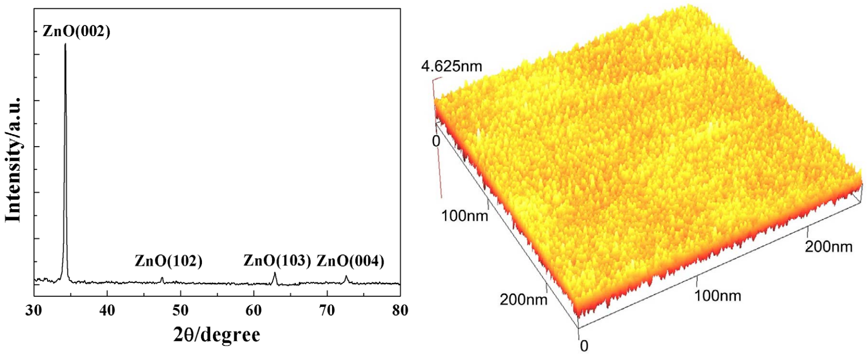
3.1. Structure and Morphology of ZnO Seed Layers

The XRD pattern of the ZnO seed layer is shown in **Figure 1(a)**. It can be seen that the ZnO (002) peak is observed at around 34.4˚, and indicate that the seed layer exhibit a strong c-axis preferred orientation and reveal the wurtzite structure.

To evaluate the surface morphology of ZnO films, AFM scans were performed. Result is shown in Figure 1(b). The surface is smooth and uniform, and is suitable to the growth of nanorods in the next step.

3.2. Structure and Morphology of ZnO Nanorods

Figure 2 shows the XRD patterns of ZnO nanorods which grew on the ZnO seed layer with different solution concentrations. The exhibited diffraction peaks at 2θ values 32.10˚, 34.78˚, 36.73˚, 47.88˚, 63.39˚ are attributed to the (100), (002), (101), (102), (103) crystallographic planes respectively. This result is well matched with the standard ICDD file no 36-1451 and indicates the formation of hexagonal wurtzite structure. The appearance of sharp peaks indicates that as-grown ZnO nanorods are highly crystalline in nature.



(a) (b)

Figure 1. XRD pattern (a) and AFM (b) of ZnO seed layer.

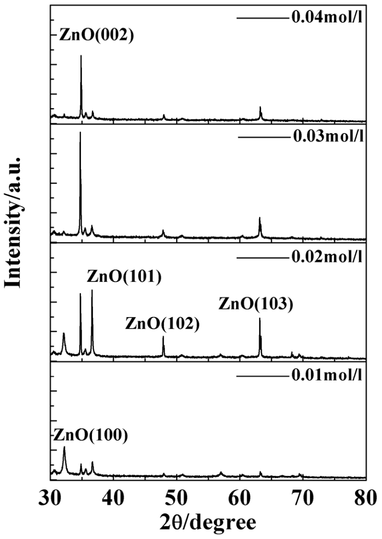


Figure 2. XRD patterns of ZnO nanorods with different solution concentrations.

Furthermore, when the solution concentration was increased above 0.02 mol/L, strongest intensity of the diffraction peak corresponding to (002) plane indicates that the samples have a c-axis preferential orientation at this time. Albeit the intensity of ZnO (002) diffraction peak decreased slightly when the solution concentration is 0.04 mol/L.

To identify the surface morphology of the synthesized ZnO nanorods, FESEM analysis was performed. **Figure 3** represents the FESEM images to show the effect of the solution concentration on the ZnO nanorods. The results reveal the nanorods-type morphology which is perpendicular to the substrate surface for all the samples synthesized using different solution concentrations. Furthermore, with the increase of solution concentration, the diameter of nanorods increases, the interstice between nanorods decreases, and the uniformity of nanorods becomes better in turn. However, there is slight agglomeration taking place in ZnO nanorods which may be due to the higher concentration of zinc ions in the solution. It is thought that when the concentration of zinc ions in the solution is too low, and the nucleation rate and growth rate of ZnO nanorods are slow, resulting in smaller diameter of ZnO nanorods and larger interstice between nanorods. As increase the solution concentration, the zinc ions in solution increased, so the diameter of nanorods increases, the interstice between nanorods decreases, and the uniformity of nanorods become better in corresponding, while higher concentration of zinc ions in solution will lead to rapid crystallization and resulting in large bulk particles with severe agglomeration finally.

3.3. Optical Properties of ZnO Nanorods

PL spectroscopy can be used to probe the electronic band gap, impurity levels and defects, quality of material and recombination mechanisms. **Figure 4** displays the PL spectra of ZnO nanorods synthesized with different solution concentration. When the solution concentration is 0.01 mol/L, the spectrum of ZnO nanorods can be divided into the UV and the visible light parts. Normally, the UV emission located at 380 nm is attributed to an exciton transition [14]. In visible region, a broad blue emission band is observed between 400 - 500 nm with two centers at 418 nm and 437 nm respectively.

According to previous reports, the blue emission is ascribed to electrons transition from the shallow donor level (Vo) to the valence top or from the conduction bottom to the shallow acceptor level (Vzn) [15]. It is known that oxygen vacancy (Vo) can generate two defect levels, one is the deep donor level at 0.8 - 0.9 eV under the conducting band, and the other is the shallow donor level at 0.3 - 0.5 eV under the conducting band [16] [17]. So, it can be calculated that the energy gap from the shallow V_O donor level to the valence top is about 2.8 - 3.0 eV. This value is very close to the photon energy (2.96 eV and 2.83 eV) of the blue emission peak at 418 nm and 437 nm. Therefore, it can be considered that this blue emission band is mainly derived from the electrons transition from the shallow donor lever (Vo) to the valence top. When the solution concentration was increased above 0.02 mol/L, the blue emission band disappeared, only UV band can be observed, indicating the high purity with good crystallinity of the prepared ZnO nanorods.

The transmission spectra in the wavelength range of 300 - 800 nm for ZnO nanorods are given in **Figure 5**. A sharp absorption edge at ~360 nm denotes an UV sensitivity. The absorption of UV light is endorsed to the intrinsic band gap incorporation of ZnO nanorods due to the electronic transitions from the valence band to the conduction band. The average transmittance in visible region (400 - 700 nm) was about 80%. It can be concluded that ZnO nanorods are transparent for the visible light.

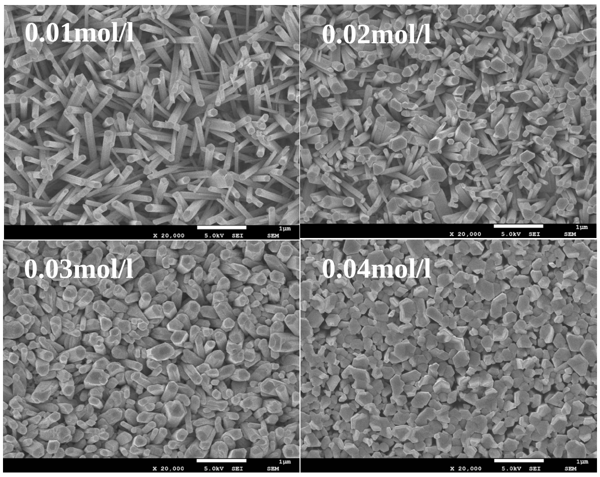


Figure 3. SEM images of ZnO nanorods with different solution concentration.

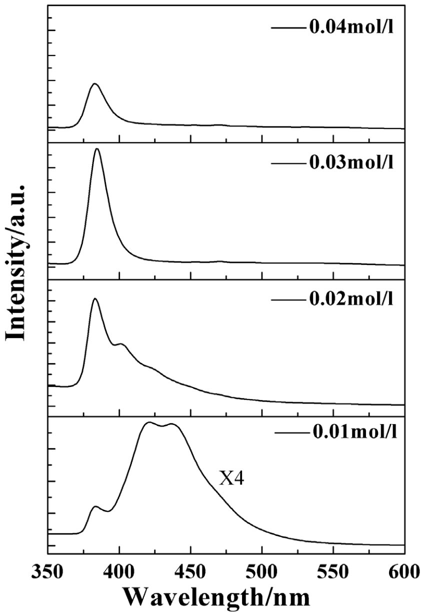


Figure 4. PL spectra of ZnO nanorods with different solution concentration.

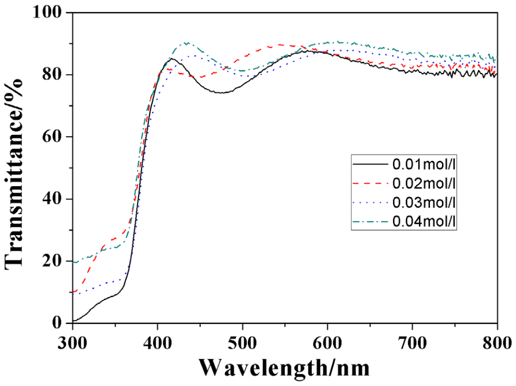


Figure 5. Transmittance spectra of ZnO nanorods with different solution concentration.

4. Conclusion

In conclusion, vertically oriented ZnO nanorods have been synthesized by hydrothermal method successfully. The influence of solution concentration on the morphology, structural and optical properties was analyzed. XRD analysis confirms the hexagonal wurtzite crystalline structure of the synthesized ZnO nanorods. SEM images indicate that with the increase of solution concentration, the diameter of nanorods increases, the interstice between nanorods decreases, and the uniformity of nanorods becomes better in turn. In PL spectra, UV emission band and visible emission band have been observed. The UV emission is attributed to an exciton transition. The blue emission band with center at 418 nm and 437 nm is mainly derived from the electrons transition from the shallow donor lever (Vo) to the valence top. For all samples, the average transmittance in visible region was about 80%. This work could be guiding the researchers who are utilizing hydrothermal method for film deposition towards various applications including optoelectronics, energy conversion and photocatalysts devices.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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