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RESEARCH ARTICLE

ZnO nanorod arrays: Dependence of morphology upon ammonia

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Well-aligned ZnO nanorod arrays were prepared on FTO substrate by hydrothermal method at low temperature for 5 h. The effect of ammonia on the length of ZnO nanorod was studied in detail. The resulting materials were extensively characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and UV-visible absorption spectra (scatter mode). With the increase of ammonia, the length of ZnO nanorod increases.

Keywords ammonia, ZnO nanorods, length

1 Introduction

ZnO has wide direct band gap (3.37 eV) and large exciton binding energy (~60 meV), which makes it an excellent optoelectronic material [1,2]. It has been recognized as one of the promising nanomaterials and for many high-technology applications, e.g., surface wave filters, photonic crystals, varistors, sensors, solar cells [3–7], and so on. So far, many nanostructures have been developed to obtain higher properties of ZnO, including nanoparticles, nanowires, nanorods, nanotips, nanocone, nanosheets, nanobelts and nanoneedles [8]. Recently, ZnO nanoforest with the efficiency of DSSC, which was 5 times higher than before, was synthesized by Ko et al. [9], because of the larger internal surface area, better stability, and higher electron mobility provided by the special nanostructures. Those structures can be obtained through sol-gel synthesis [10], chemical vapor deposition [11], electrochemical deposition [12], physical vapor deposition [13], low-temperature aqueous growth [14], hydrothermal growth [15] and chemical bath deposition [16]. For the reasons of lower temperature, easier operation and less costs, hydrothermal growth becomes one of the favorite methods.

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In this paper, ZnO nanorod arrays were synthesized by hydrothermal method. In the process of preparation, the content of ammonia tremendously affects the growth of ZnO nanorod. Our work is mainly focused on the dependence of the length of ZnO nanorod arrays upon ammonia content. We found that the length of nanorod inceases with the increase of ammonia content from 5 to 10 mL. ZnO nanorod with a length of 6 μm was obtained after 5 h. And surprisingly, we found that the top of the nanorod changed to needle.

2 Experiment

2.1 Pre-treatment of the substrates

Fluorine doped tin oxide (FTO) glass were used as substrate. The FTO were cleaned with ethanol, acetone and isopropanol, respectively. The solution was dip-coated on the cleaned FTO substrates with a concentration of 5 mmol/L zinc acetate dehydrate at 15 mm/min for three times. Finally, the substrates were annealed at 350°C for 1 h to obtain the ZnO seed layer.

2.2 Hydrothermal deposition

The precursory solution was prepared by mixing Zn $(NO_3)_2 \cdot 6H_2O$ (0.04 mol/L), methenamine $(CH_2)_6N_4$ (0.02 mol/L), PEI (molecular weight is 800, 0.005 mol/L) and ammonia ($NH_3 \cdot H_2O$, 3 mol/L). The content of ammonia was changed in the range of 5 to 10 mL. Then the precursor and substrate with ZnO seed layer were sealed in reactor at 90°C for 5 h. The sample was rinsed with DI water and dried by N_2.

2.3 Characterization

The morphology, crystalline quality and optical characteristics of ZnO products were investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD), and UV-visible absorption spectra. XRD patterns were recorded on a Rigaku RINT D/Max-2500 powder diffraction system using Cu Kα radiation of 0.15406 nm wavelength. SEM was undertaken on a JEOL JSM-6360 scanning electronic microscope operating at an acceleration voltage of 20–30 kV. UV-absorption spectra was taken by scatter mode using Varian Cary 5000.

3 Results and discussion

3.1 Morphology

Figure 1 is the SEM cross section of ZnO nanorod arrays in different conditions. Figs. 1(a)–1(f) are ZnO nanorod arrays

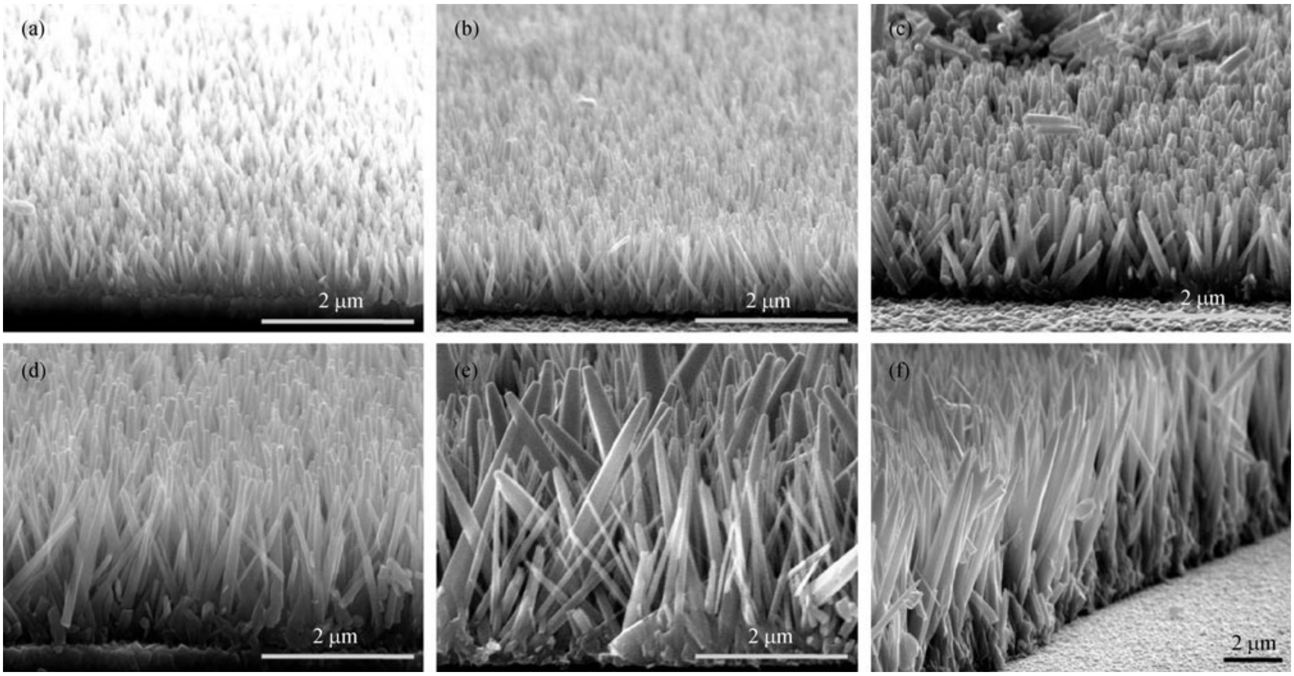

Figure 1 SEM images of ZnO nanorods arrays
(a) 5 mL $NH_3 \cdot H_2O$; (b) 6 mL $NH_3 \cdot H_2O$; (c) 7 mL $NH_3 \cdot H_2O$; (d) 8 mL $NH_3 \cdot H_2O$; (e) 9 mL $NH_3 \cdot H_2O$; (f) 10 mL $NH_3 \cdot H_2O$

with ammonia content being 5, 6, 7, 8, 9 and 10 mL. The results show that the length of ZnO nanorod increases with the increase of ammonia content. After calculated, the length of nanorod were obtained, about 700, 1000, 1300, 2200, 2800 and 6800 nm respectively. The structure of ZnO nanorod exhibits as hexagonal structure. The top of nanorod is circular when the ammonia content is lower. But with the addition of ammonia, the diameter of top rod got smaller and became needle.

3.2 Structure characteristics

The XRD of ZnO nanorod arrays are presented in Fig. 2. The lines from top to bottom of this figure correspond to the sample with ammonia content being 5, 6, 7, 8, 9 and 10 mL, respectively. The peaks with a star are the signal of SnO_2 from FTO. All of the ZnO nanorod arrays show five peaks located at 34.4°, 36.3°, 47.6°, 62.9° and 72.6°, corresponding to the (002), (101), (102) (103) and (004) directions of the ZnO hexagonal wurtzite structure. It indicates that the polycrystalline layer is formed. The peak at 34.4° (002) is intense and narrow, and the signal gets stronger as the ammonia increases. This indicates that ZnO nanorod were strongly *c*-axis oriented, which is well consistent with the SEM image results. It suggests that ZnO nanorod can be fabricated by this technique and exhibits as nice crystal.

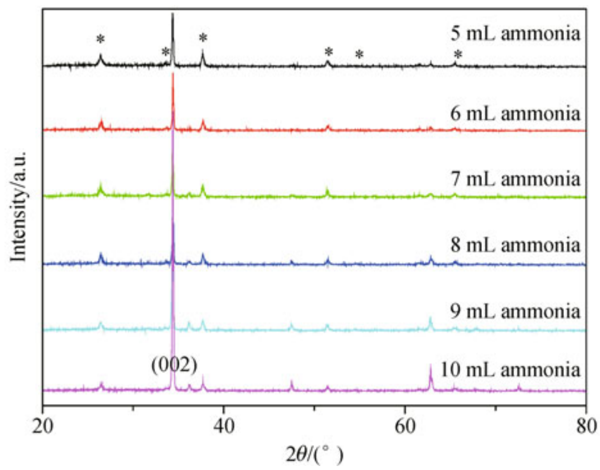

Figure 2 XRD patterns of ZnO nanorod arrays

3.3 Optical properties

Figure 3 shows the UV-visible absorption spectra (scatter mode) of the samples. When the ammonia content was changed from 5 to 7 mL, the band edge of ZnO nanorod arrays was around 380 nm and showed strong absorption. The strong absorption may be owed to the special ZnO nanorod arrays which are too short to scatter the light. When more ammonia was added, the ZnO nanorod arrays got longer and the band edge of ZnO

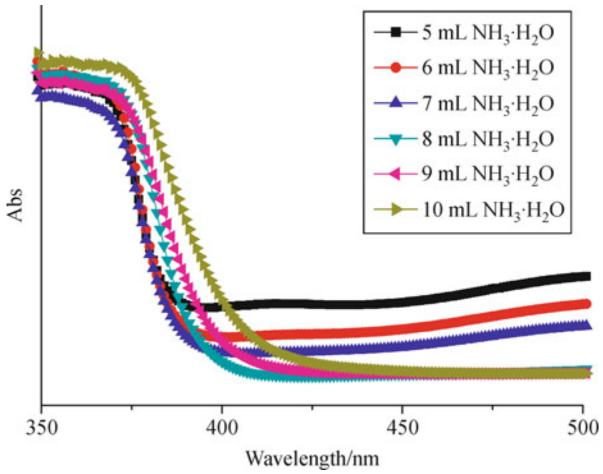

Figure 3 UV-visible absorption spectra (scatter mode) of ZnO nanorod arrays

appeared red shift obviously, which proved the narrower band-gap of ZnO.

4 Conclusion

In summary, ZnO nanorod arrays are synthesized by hydrothermal method at 90°C for 5 h successfully. It is worth mentioning that the ammonia content is an important parameter for the growth of ZnO nanorod arrays. The length of ZnO nanorod arrays increases with the increase of the ammonia content. When 10 mL ammonia is used in the precursory solution, the length of ZnO nanorod can reach 6 μm. It can also be deduced that with the length of ZnO nanorod arrays getting longer, the band gap gets narrower.

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