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Controlled growth of ZnO nanorods by polymer template and their photoluminescence properties

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A large amount of one-dimensional ZnO nanorods with diameters in 15－50 nm aligned in radial cluster were successfully synthesized by polar polymer polyvinyl alcohol (PVA) as soft-template. The growth of ZnO nanorods was controlled by changing annealing temperature. The evolution of the morphology and microstructure was investigated by scanning electron microscope, transmission electron microscope and X-ray diffraction. It is shown that ZnO nanorods tend to be uniform and the crystallization is gradually improved with the temperature increasing from 400℃ to 700℃. The photoluminescence spectra of products show a strong ultra violet emission and relatively weak defect emissions. The sharp strong emission peak at 354 nm owing to the inter-band transition indicates the extraordinary photoluminescence property of ZnO nanorods.

ZnO nanorods, polymer soft-template, PVA, photoluminescence spectrum

1 Introduction

Quasi-one-dimensional nanometer materials such as nanowires, nanorods and nanobelts have attracted much attention due to their remarkable morphology-dependent properties and potential applications in nano-optoelectronics devices[1]. As a wide band gap semiconductor (3.37 eV), ZnO is one of the most promising materials for photo-catalysis[2], ultraviolet/blue emission devices[3] and field emission devices[4].

Among the various growth techniques for nanostructure ZnO such as hydrothermal method[5], chemical vapor deposition[6], self-assembly method[7] etc., soft-template has some advantages including simple and facile technique, mild condition and low energy consumption. Polymer coils of polyvinyl alcohol (PVA) insert each other in the semidiluted solution and form crosslinking network template whose meshes size can be adjusted from nanometer to micron. The steric hindrance of polar polymer PVA can control ZnO nucleation. In this paper, a large amount of 1D ZnO nanorods with diameters in 15－50 nm aligned in radial clusters were successfully fabricated by PVA as soft template. In the case of 1D nanostructure[8,9], the formation process and photoluminescence property of ZnO nanorods aligned in radial cluster has not been investigated before. The unique geometrical structure of ZnO exhibits a particular ultraviolet emission peak at 354 nm.

2 Experiment

In a typical synthesis, PVA (the alcoholysis degree ⩾ 97%, the average degree of polymerization 1750 ± 50) was first dissolved in deionized water. $Zn(CH_3COO)_2 \cdot 2H_2O$ (99%, Aldrich) and the homogeneous PVA aqueous solution were mixed by mass ratio of 2∶1 under

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magnetic stirring in water bath at 60℃ for 1—2 h. Glass substrate was cleaned using acetone and ethanol in ultrasonic cleaning machine, and then washed thoroughly with distilled water. The substrate was coated with the uniformly dispersed mixed solution by spin coating at 3000—3500 rpm, and then dried in infrared ray. The products were obtained by annealing at 400℃—700℃ for 3 h in the muffle furnace with a constant air flow.

The crystal structure of the products was investigated by X-ray diffraction (XRD, D/MAX-2500). The morphology of the products was analyzed by scanning electron microscopy (SEM, JEOL/JEM-6700F) and field emission gun transmission electron microscope (TEM, TECNAI G^{2}F-20). Photoluminescence spectrum was performed at room temperature using F-4500 spectrofluorometer (Hitachi) with a Xe lamp as the excitation light source.

3 Results and discussion

3.1 X-ray diffraction analysis

The XRD patterns of bare glass substrate and the samples annealed at different temperatures are shown in Figure 1. The diffraction peaks of the samples are all in good agreement with the typical wurtzite-type ZnO crystals according to JCPDS card (36-1451) except the minor peaks from ~ 15° to ~ 25° in Figure 1(curve 2) which are attributed to PVA incomplete decomposed products. It is also noted that the XRD curves turn to be sharp and clear continuously, which shows that the crystallinity is improved with the annealing temperature increasing from 400℃ to 700℃.

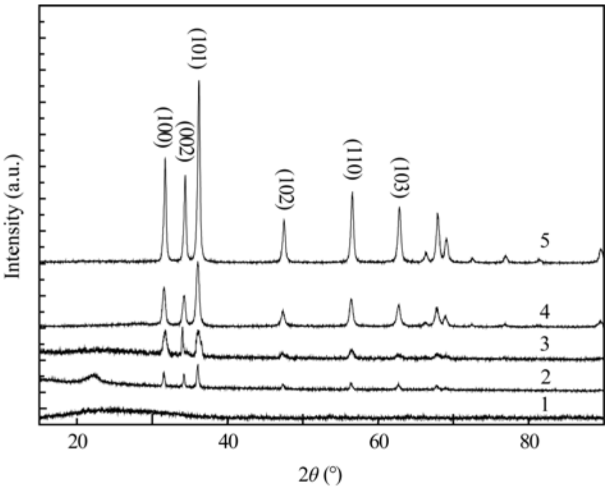

Figure 1 X-ray diffraction patterns for glass substrate (curve 1), samples annealed at 400℃ (curve 2), 500℃ (curve 3), 600℃ (curve 4), and 700℃ (curve 5).

3.2 SEM and TEM morphology and possible formation mechanism of ZnO nanorods

In the SEM images of the sample annealed at 400℃, there are numerous ZnO prisms with an unequal rectangular-like cross-section area. They are conglutinated together to form a cluster-shaped structure with the average size of ~ 20 μm (Figure 2).

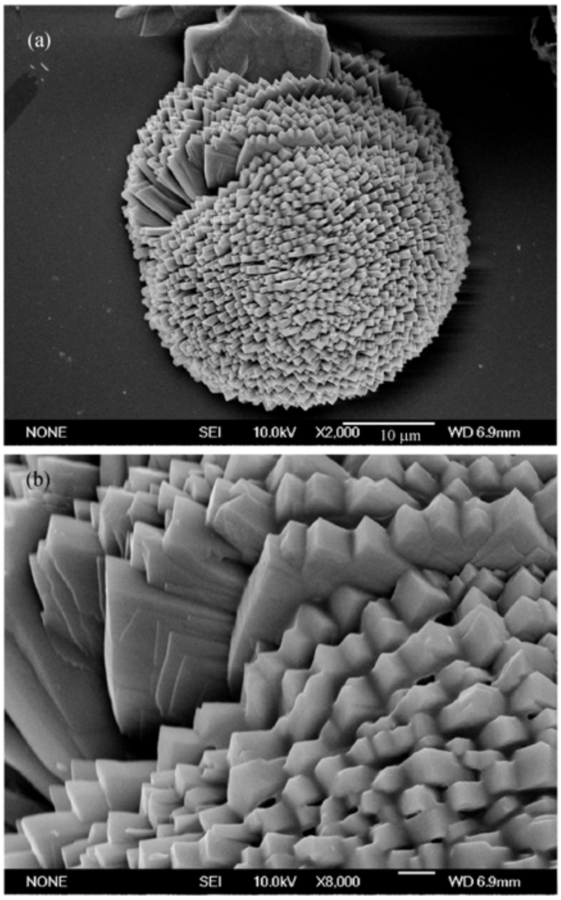

Figure 2 SEM images of samples prepared at 400℃. (a) Low-magnification; (b) high-magnification.

The effect of the annealing temperature on the morphology evolution of ZnO nanorods is shown in Figure 3 (a)—(l). It can be observed that the length-diameter ratio of ZnO nanorods is significantly increased from 500℃ to 700℃ and the nanorods morphology becomes more uniform with diameters in 15—50 nm finally.

Figure 4 shows TEM images of local morphology of nanorods at 700℃ and corresponding fast Fourier transform (FFT) patterns as in the insets. It can be seen that nanorods are structurally uniform with lattice fringes spacing of 0.52 nm, which confirms that the grown nanostructures are preferentially oriented in the

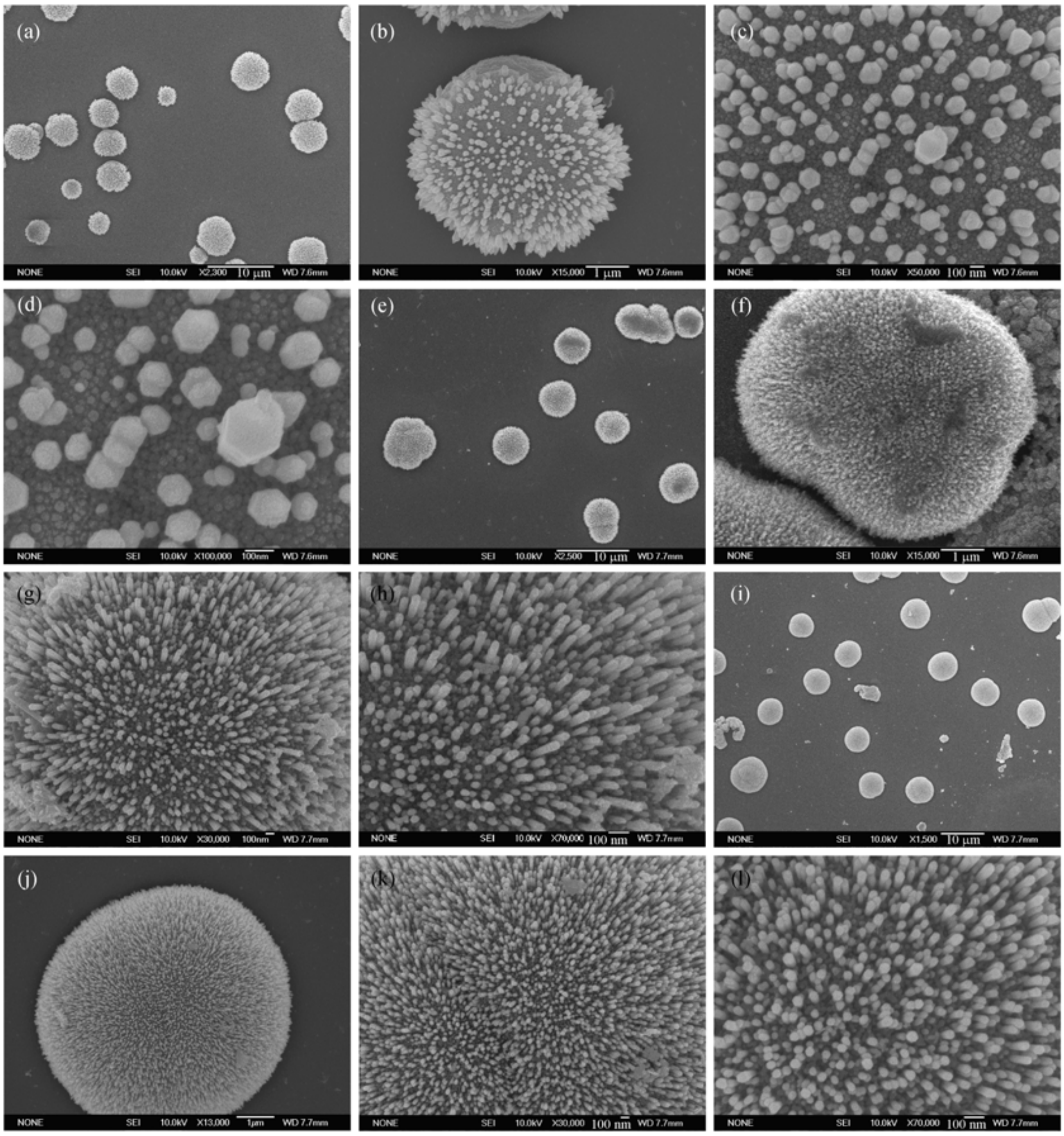

Figure 3 SEM images of ZnO nanorods with different morphologies obtained at (a)－(d) 500℃; (e)－(h) 600℃; (i)－(l) 700℃, respectively.

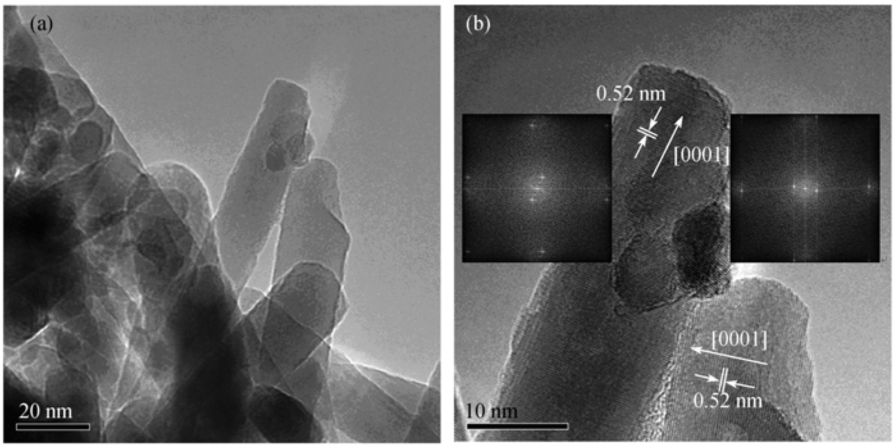

Figure 4 TEM images and Fast Fourier Transform (FFT) patterns of ZnO nanocolumn at 700℃. (a) Low-magnification; (b) high-magnification.

[0001] (*c*-axis) direction.

ZnO crystal nucleuses form easily on the glass substrate with low surface barrier and tend to gather into cluster in the annealing process. In our work, uniformly distributed polar hydroxy groups of PVA can coordinate with Zn^{2+} to form stable and dispersive ZnO crystal nucleuses, and polymer network prevent ZnO nanoparticles from agglomeration efficiently at the same time.

PVA begins to decompose at 120℃ and disappears completely at 500℃[10]. With the samples annealed from RT to 400℃ for 3 h, polymer network gradually collapses. Incompletely decomposed products of PVA block the surface adsorption of ZnO nanocrystal, which leads to the different development of the same crystal facets and disproportion of the various crystal facets relative growth rate (see Figure 2). When the samples are annealed from RT to 500℃ for 3 h, polymer network is finally removed completely with the prolonging of reaction time. Amorphous ZnO nanoparticles begin to aggregate and form spherical shape. The surface energy of (0001) faces of the wurtzite structure ZnO is much larger than those of other faces, which finally results in progressive elongation along [0001] directions of the ZnO nanocrystals. Characteristic of ZnO crystals preferential growing is helpful for the orientation growth along radial direction anisotropically of ZnO nanoparticle aggregates and formation of one-dimensional nanorods in radial clusters (see Figure 3(a)—(d)).

When temperature increases to 600℃ or 700℃, sufficient energy accelerates the thermal motion of Zn and O ions and adatoms migration at ZnO surface. As a result, crystalline ZnO tends to be perfect and nanorods arrange more tightly in order.

3.3 PL spectrum

Room temperature PL spectra excited by 310 nm are shown in Figure 5. For comparison, PL spectrum of bare glass substrate is also given. There are two weak blue emission peaks centered at 411 nm (3.03 eV) and 434 nm (2.86 eV) respectively for the sample annealed at 400℃ (Figure 5(curve 2)). When temperature increases to 500℃, the intensities of the two blue peaks increase and an additional broad emission peak consisting of two weak ultraviolet emission peaks centered at 354 nm (3.51 eV) and 384 nm (3.24 eV) appears. At relative high temperature (600℃ or 700℃), the ultraviolet emission intensity increases significantly compared with that of the blue emission.

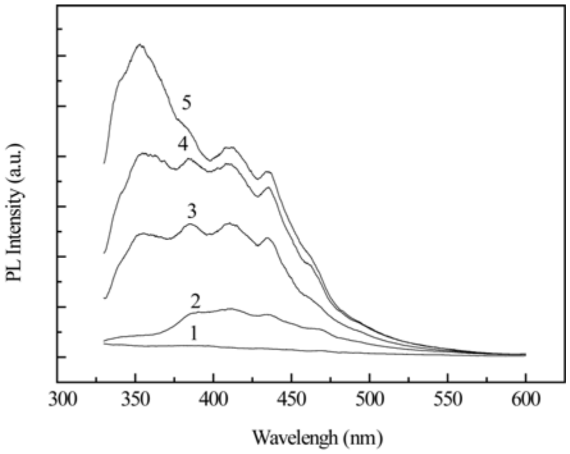

Figure 5 Photoluminescence spectra for bare glass substrate (curve 1), samples annealed at 400℃ (curve 2), 500℃ (curve 3), 600℃ (curve 4) and 700℃ (curve 5).

The spectra of ZnO nanostructures usually consist of a near band edge UV emission peak at ~ 380 nm (3.27 eV) which comes from the recombination of free excitons[11,12] and visible emission peak which is related to deep level structural defect or impurity[13,14,15]. However, the UV emission peak at 354 nm has been scarely observed. Ni YongHong et al. reported the UV emission peak at around 353 nm which was attributed to the ZnO surface partially passivated by CTAB as the surfactant[16]. Zhang et al.[17] observed a high-energy photoemission at 356 nm which was interpreted as quasi-Fermi level shift in the conduction band. In this work, the UV emission at 354 nm appears until PVA is completely descomposed at 500℃. We attribute it to the inter-band radiation combination of photogenerated electrons with high concentration in conduction band and holes in valence band. The improved crystallization of ZnO nanorods is helpful to reduce the density of surface state of ZnO nanoparticles and non-radiative recombination centers. Consequently, the UV emission intensity at 354 nm contributing to inter-band is improved greatly compared with the blue emissions coming from defects.

4 Conclusion

In summary, ZnO nanocolumns clusters have been successfully synthesized on glass substrate via a novel polymer soft template method. As network template, PVA can control ZnO nucleation and crystal growth. The annealing temperature plays an important role to control the morphologies and photoluminescence of ZnO nanocolumns clusters. The intensity of UV emission peak at 354 nm increases by improved crystallinity at higher temperature.

1 Hu J T, Odom T W, Lieber C M. Chemistry and physics in one dimension: synthesis and properties of nanowires and nanotubes. Acc Chem Res, 1999, 32: 435—445
2 Xu F, Yuan Z Y, Du G H, et al. High-yield synthesis of single-crystalline ZnO hexagonal nanoplates and accounts of their optical and photocatalytic properties. Appl Phys A, 2007, 86: 181—185
3 Gao H Y, Wang Y F, Li J M, et al. Synthesis and characterization of ZnO nanorods and nanoflowers grown on GaN-based LED epiwafer using a solution deposition method. Phys D: Appl Phys, 2007, 40: 3654—3659
4 Lee C J, Lee T J, Lyu S C, et al. Field emission from well-aligned zinc oxide nanowires grown at low temperature. Appl Phys Lett, 2002, 81(19): 3648—3650
5 Choy J H, Jang E S, Won J H. Hydrothermal route to ZnO nanocoral reefs and nanofibers. Appl Phys Lett, 2004, 84(2): 287—289
6 Lee C Y, Tseng T Y, Li S Y. Growth of Zinc Oxide Nanowires on Silicon (100). Tamkang J Sci Eng, 2003, 6(2): 127—132
7 Gao P X, Wang Z L. Mesoporous polyhedral cages and shells formed by textured self–assembly of ZnO nanocrystals. J Am Chem Soc, 2003, 125: 11299—11305
8 Khan A, Jadwisienczak W M, Kordesch M E. Synthesis and luminescence properties of novel ZnO nanostructures: micro and nanospheres, polyhedral cages, tetra-pods, needles, tipped nanorods, nanowires and other “microphone-shaped” structures. Mater Res Soc Symp Proc, 2006, 900E(O06): 1—6
9 Lin T J, Guo J, Ding S L, et al. The growth mechanism of ZnO micro-nano spheres. Chinese J Inorg Chem (in Chinese), 2004, 22(4): 701—704
10 Zou Q, Zhang Z S, Li H Y, et al. Preparation process of ZnO nanobelts self-assembling generated via polymer. Chinese J Inorg Chem (in Chinese), 2006, 22(9): 1675—1678
11 Lyu S C, Zhang Y, Ruh H, et al. Low temperature growth and photoluminescence of well-aligned zinc oxide nanowires. Chem Phys Lett, 2002, 363: 134—138
12 Umar A, Karunagaran B, Suh E K, et al. Structural and optical properties of single-crystalline ZnO nanorods grown on silicon by thermal evaporation. Nanotechnology, 2006, 17: 4072—4077
13 Cheng W D, Wu P, Zou X G, et al. Study on synthesis and blue emission mechanism of ZnO tetrapodlike nanostructures. J Appl Phys, 2006, 100(054311): 1—4
14 Xu P S, Sun Y M, Shi C S, et al. Electronic structure of ZnO and its defects. Sci China A-Math Sci (in Chinese), 2001, 31(4): 358—364
15 Xu C X, Sun X W, Zhang X H, et al. Photoluminescent properties of copper-doped zinc oxide nanowires. Nanotechnology, 2004, 15: 856—861
16 Ni Y H, Wei X W, Hong J M. Hydrothermal preparation and optical properties of ZnO nanorods. Mater Sci Eng B, 2005, 121: 42—47
17 Zhang D H, Wang Q P, Xue Z Y. Photoluminescence of ZnO films excited with light of different wavelength. Appl Surf Sci, 2003, 207: 20—25