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Zn²⁺ COMPOSITIONAL DEPENDENCE ON STRUCTURAL, MICROSTRUCTURE AND OPTICAL PROPERTIES OF ZnO NANOSTRUCTURE

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KeyWords

CBD method, ZnO nanorods, XRD, SEM, UV-VIS Spectroscopy.

ABSTRACT

Uniformly distributed ZnO nanorods with several micrometers long have been successfully grown at low temperature by using two steps chemical bath deposition (CBD) method. In this mechanism of the ZnO nanorod films growth, the effects of Zn²⁺ concentration on samples were prepared with different molarities of zinc acetate dihydrate in the solution. Structural, diameter in size and morphology of ZnO nanorod films were investigated in detail by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The optical properties of ZnO nanorod films were also studied by UV-Vis spectroscopy. From the results, it was observed that Zn²⁺ ion concentration play a key role during the process of regulating the growth rate and forming the ZnO nanorod films by CBD. By investigation on growth characteristics of ZnO with different molarities, these kinds of structure were useful in solar cell application.

INTRODUCTION

In recent years, one-dimensional (1D) nanostructures such as nanotubes, nanowires, nanorods, nanobelts, nanocables, and nanoribbons have stimulated a considerable interest for scientific research due to their importance in fundamental physics studies and their potential applications[1-4]. Among various 1D nanostructural materials, zinc oxide (ZnO) is one of the most versatile materials. On account of its various remarkable properties such as a wide band gap of 3.37eV at room temperature, large exciton binding energy of 60meV, excellent chemical and thermal stability, transparency, biocompatibility, and wide electrical conductivity range, ZnO materials are global interest currently and has a variety of applications in an emerging area of nanotechnology[3-9]. For the technological applications of ZnO nanorods, rational synthesis and fundamental understanding about their properties are essential. Up to now, numerous experimental attempts have been reported to fabricate ZnO nanoscale materials, such as molecular beam epitaxy(MBE), pulsed laser deposition (PLD), chemical vapor deposition (CVD), sputtering, electrochemical deposition and thermal evaporation[10-18]. Compared with the methods mentioned above, the wet chemical bath deposition(CBD) method as a high performance growth technique for ZnO nanorods/ nanowires has recently received increasing attraction due to its obvious advantages of its simple, low cost, low temperature operation, easy coating of large surfaces and environmental friendliness. In this research, the wet CBD method was employed to fabricate ZnO nanorod films with special attention paid to the effect of Zn^{2+} concentration on the structure, morphology and optical properties of as-grown ZnO nanorod films.

EXPERIMENTAL PROCEDURE

To investigate the effect of Zn^{2+} concentration on the properties of ZnO nanorods, a sequence of experiments were performed for different molarities of zinc acetate. All the aqueous solutions were prepared using deionized water. Before ZnO nanorod films deposition, commercial glass (2cm×2cm) were thoroughly cleaned. For CBD growth process, the aqueous solutions of zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$, 99.9% purity] and hexamethyltetramine (HMT) ($C_6H_{12}N_4$, 99.9% purity) were used as precursor source for the growth of ZnO nanorods. Different molarities such as 0.02M, 0.04M, 0.06M of zinc acetate dihydrate and HMT were mixed together with deionized water and stirred with magnetic stirrer, aqueous solution was obtained. In this experiment, the synthesis process of ZnO nanorods contains two steps, i.e seed layer formation and nanorod growth. In the first step the glass substrates were immersed into the aqueous solution for 1h at a required temperature 80°C to form seed layer. In the second step seed layer coated glass was tilted against the wall of the aqueous solution beaker. Then the beaker was heat treated for 4h at a constant temperature of 80°C. After growth, the substrate was removed from the solution, rinsed with deionized water and then dried at room temperature. The sample was annealed at 500°C for 1h, ZnO nanorod film was obtained. X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM, JSM-5610) were used to characterize the crystalline state and morphology of the films. To investigate the optical properties, UV-Vis spectra were recorded on a UV-1800 Spectrophotometer.

RESULTS AND DISCUSSION

Effect of Zn^{2+} Concentration on Structure Character of ZnO Films

X-ray diffraction analysis (XRD) was carried out for ZnO film to investigate phase assignment, crystallographic orientation and lattice parameters. Measurements were performed on a diffractometer (Rigaku RINI 2000) operating at 40 kV and 30 mA. The powder was scanned from 10° to 70° on 2θ with a step size of 0.02 using Cu- α radiation. The diffraction patterns of ZnO films were identified using JCPDS (Joint Committee of Powder Diffraction Standards) data file. Fig. 1(a-c) showed the XRD profile of ZnO nanorod films with different Zn^{2+} concentrations. In these figures there were nine different peaks appeared which matched with ZnO of JCPDS data library. In all reflection planes, (101) peak was one of the most intense peaks in all XRD spectra. Unfortunately, some coexisting peaks are form in figure 1(a) it was due to the other impurity. Lattice constant, hexagonality and average crystallite size of ZnO thin films were calculated and listed in table 3.1. From XRD results, fabricated ZnO films were entirely crystalline without changing the crystal structure of ZnO structure as wurtzite structure and hexagonal phase.

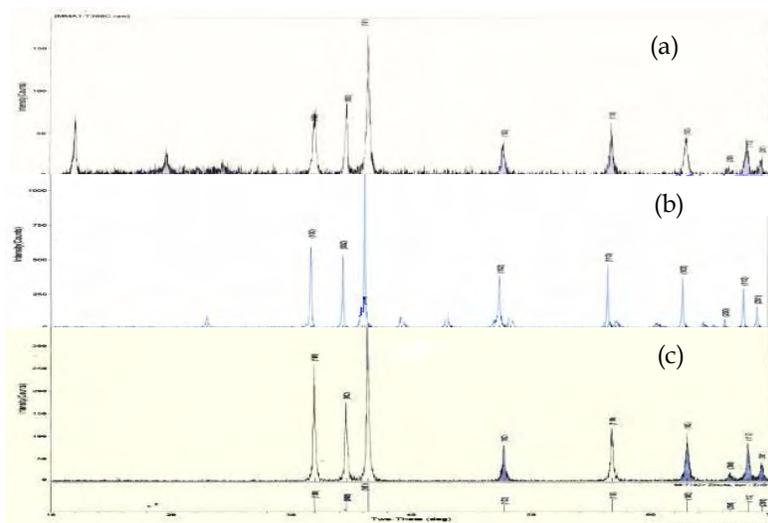


Fig. 1. XRD spectrum of (a)0.02M (b) 0.04M (c) 0.06M ZnO nanorod film

Table 1 Lattice parameters, hexagonality and crystallite size of ZnO nanorod films

Zn ²⁺ Concentration(M)	a(Å)	c(Å)	c/a	Crystallite size(nm)
0.02 (ZnO-1)	3.214	5.157	1.605	39.52
0.04(ZnO-2)	3.227	5.161	1.599	35.23
0.06(ZnO-3)	3.221	5.174	1.606	39.13

SURFACE MORPHOLOGY

Fig. 2(a-c) showed the evolution of the ZnO nanostructure as a function of Zn²⁺ concentration, and kept the other experiment condition constant. As can be seen from these figures, different structural and morphological changes were observed. Many rods like products exhibited diameter and the length in the range of (150-280 nm) and (1-2 μm). The ZnO nanorods were disorderly, and had a wide size distribution. It was convinced that some defects were formed in ZnO nanorods due to disengaged growth on the solution. Polycrystalline glass not provided the nucleation of ZnO and influence nanorods growth, which leads to disordered growth of nanorods. The result of SEM observation showed that the diameter and length increase with Zn²⁺ concentration increasing. Although network flake like structure was observed at the high Zn²⁺ concentration, all of ZnO nanorods exhibited hexagon cross section.

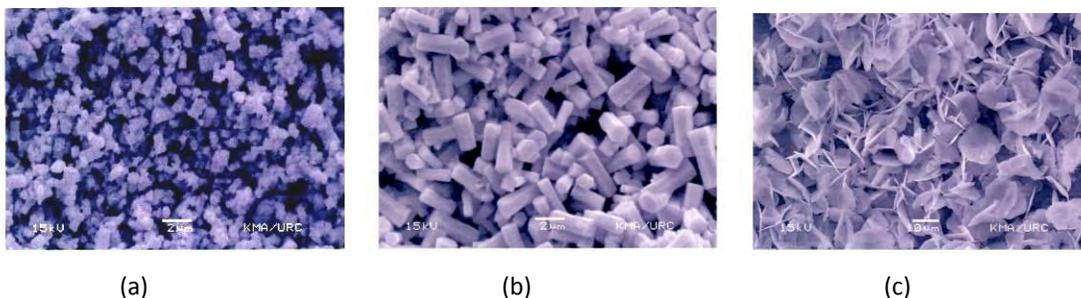


Fig. 2. SEM image of as-prepared ZnO nanorod grown on glass substrate with different solution concentration(a) 0.02M (b) 0.04M (c) 0.06M

OPTICAL CHARACTERIZATION

Fig. 3(a) showed the optical absorption spectra for ZnO nanorod films with different Zn²⁺ concentration. In this figure all of optical absorption spectra were well accepted and the absorption bands were observed at about 370nm. The theory of optical absorption provide the calculation of the band gap from $(\alpha h\nu)^2$ was plotted with $h\nu$. When the linear portion of $(\alpha h\nu)^2$ versus $h\nu$ plot was shown in Fig.3(b) extrapolated to $\alpha=0$, the band gap of sample was obtained. The estimated band gaps of ZnO nanorod films with different Zn²⁺ concentration were 3.23, 3.28 and 3.32 eV respectively. The optical band gaps of ZnO nanorod films were found to increase with an increase in Zn²⁺ concentration. It might be attributed to the improvement of the crystalline quality of ZnO nanorod films at lower Zn²⁺ concentration. The optical transmission spectra of ZnO nanorod film was pictured in Fig. 3(c). The transmittance spectra was within the UV nearer to visible wavelength region that is maximum 85%, which revealed the superior optical properties in the ZnO films produced by CBD method. The transmittance of ZnO films increased with the increasing in Zn²⁺ concentration and was observed that to decrease in surface roughness. The optical transmittance was found to increase 75%, 80% and 85% with the increase in Zn²⁺ concentration.

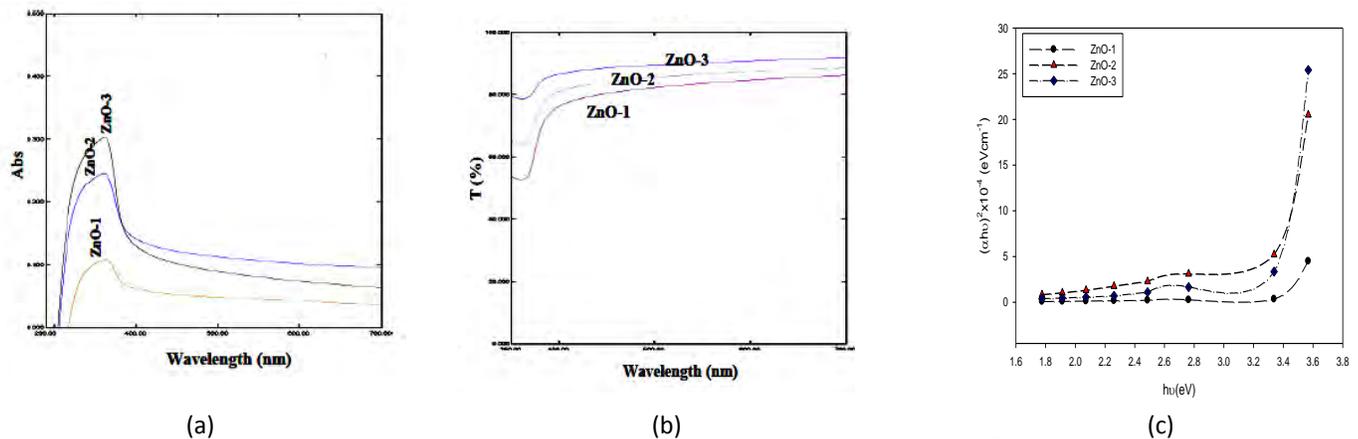


Fig. 3(a) The optical absorption spectra (b) the optical transmission spectra (c) the plot of $(\alpha h\nu)^2$ vs $h\nu$ for ZnO Films

Conclusion

Uniformly distributed ZnO nanorods with submicron diameter have been successfully grown at low temperature by using chemical bath deposition. The mechanism of the nanorods growth on the different molarities was proposed XRD results demonstrated that ZnO nanorod films with the hexagonal wurtzite structure growing along with (002) crystallographic orientation. The morphology of ZnO nanorod films changed from rods to flake like structure after increasing in Zn²⁺ concentration but hexagonal phase remained the same. The optical band gap of ZnO nanorod films increased from as the increasing in Zn²⁺ concentration, which could be related to grain variation. As the increase in Zn²⁺ concentration, the surface roughness was decreased because of superior optical transmittance (85%). From the results, Zn²⁺ ion concentrations played a key role during the process of regulating the growth rate and forming the ZnO nanorods semiconductor films by CBD. Thus the present research allowed more economical coating, easily adoptable and technically simplicity thereby making products that were more compact.

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