Photoluminescence Study of Hydrothermally Grown ZnO Nanostructures

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Abstract

In this work, the hydrothermally grown ZnO nanostructures were successfully prepared using the aqueous solution of zinc nitride dehydrate ($Zn(NO_3)_2$). The effect of solution molarity on the optical and structural properties of ZnO nanostructures were studied by temperature dependent photoluminescence (PL) measurements. The intensity ratio of the ultraviolet emission to the visible emission is calculated. It is found that the calculated results are also dependent on the solution molarity and consistent with the crystal quality of ZnO nanostructures.

Keywords: zinc oxide, hydrothermal, precursor concentration, photoluminescence

1. Introduction

Zinc oxide (ZnO) has been extensively investigated due to its unique properties such as wide direct bandgap energy (3.36 eV), large exciton binding energy (60 meV), and thermal stability. These characteristics make this material interesting for many applications such as solar cells, optoelectronic and nanowave devices [1-3]. The role of the nanostructure size, impurities, and morphology is very important to these applications. Various methods have been utilized to synthesize ZnO nanostructures, such as metal-organic chemical vapor deposition (MOCVD), sol-gel methods, and the low temperature hydrothermal method [4-5]. The hydrothermal method has been widely used to ZnO structures on ZnO-seeded substrate because of its advantages including low-cost, low-temperature, nanoelectronic compatible, and suitable for large area substrates [6]. The properties of ZnO produced by the hydrothermal method are dependent upon preparation parameters such as growth temperature, precursor concentration, and growth time [7]. In this work, the hydrothermally grown ZnO nanostructures were prepared with different aqueous solution molarities and different deposition time. The effects of solution molarity on the optical and structural properties of ZnO nanostructures were studied by temperature dependent PL measurements. It is found that the PL emission intensity increases and then decreases with the increasing solution molarity.

2. Experiment

A thin film of zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) was spin coated onto an indium-tin-oxide (ITO) glass substrate and annealed at 300 °C in oxygen for 20 min. The hydrothermal method was used to grow ZnO nanostructures on ITO glass using an aqueous solution of zinc nitrate ($Zn(NO_3)_2$) and ammonium hydroxide (NH_3OH). The solution molarity increases from 10 to 50 mM. PL measurements were performed to examine the structural and optical properties of the ZnO nanostructures. The temperature dependent PL spectra were measured using a He-Cd laser operating at a wavelength of 325 nm and the average excitation intensity was 30 mW. The samples were mounted in a closed-cycle He cryostat where the temperature (T) was varied from 10 to 300 K.

3. Results and Discussion

Fig. 1 shows the XRD patterns of ZnO nanostructures fabricated with solution-molarity 20 mM and deposition time 1 hour. The detected XRD peaks are characteristic of the ZnO with hexagonal wurtzite type crystalline structure. The strongest (002) peak indicates that the fabricated ZnO is grown along the c-axis direction.

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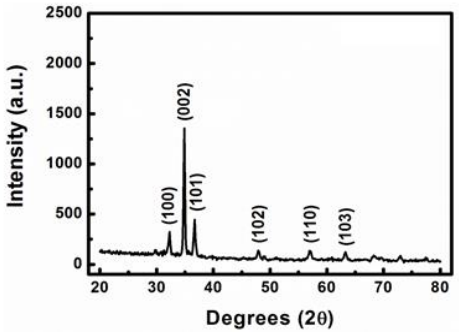

Fig. 1 XRD patterns of ZnO nanostructures

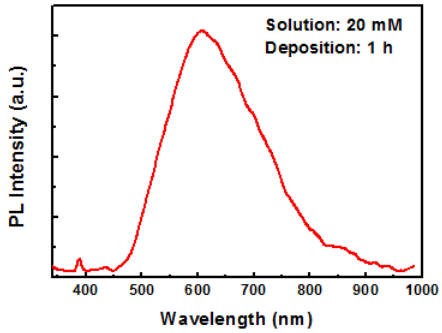

Fig. 2 PL spectrum of ZnO nanostructures measured at room temperature

The room temperature PL spectrum of this sample is shown in Fig. 2. Observing the measured result, the PL spectrum shows a strong yellow-orange emission peak at ~610 nm in the visible region and a weak peak in the ultraviolet (UV) region at ~390 nm. Room-temperature PL spectra of ZnO usually exhibit a broad peak in the visible region. The origin of this emission peak can be attributed to the defect in ZnO, such as oxygen vacancies located in ZnO surfaces [8]. The UV peak is attributed to free-exciton recombination corresponding to the near-band-edge transition in ZnO.

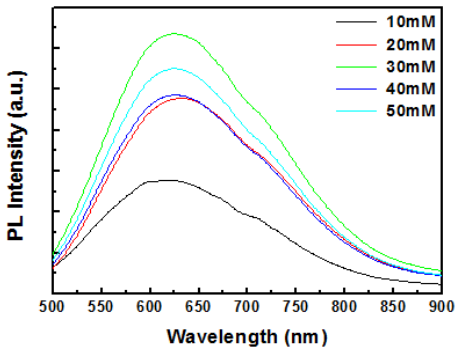

Fig. 3 Visible emission of PL spectra for the ZnO nanostructures with various solution molarities

Fig. 3 presents the visible emission of PL spectra for the samples prepared at deposition time 3 hours, with various solution molarities. It is clearly seen that the emission intensity increases as the solution molarity increased from 10 to 30 mM, and then decreases as the solution molarity is higher than 30 mM. We suppose that the increase in emission intensity could be associated with the increasing concentration of the oxygen vacancies [9]. The obtained results are similar for the sample with 1-hour deposition time.

The relative PL intensity ratio of the emission in the UV region (I_{UV}) to the emission in the visible region (I_{vis}) is shown in Fig. 4. It can be seen that the ratio increases with the molarities for the samples, and decreases as solution molarity greater than 50 mM. The I_{UV}/I_{vis} is one of the main factors that usually used to compare the optical properties of samples [10]. The higher PL intensity ratio means fewer structural defects in the samples. Too higher solution molarity leads to the disorder of ZnO structures, and deteriorate the crystal quality.

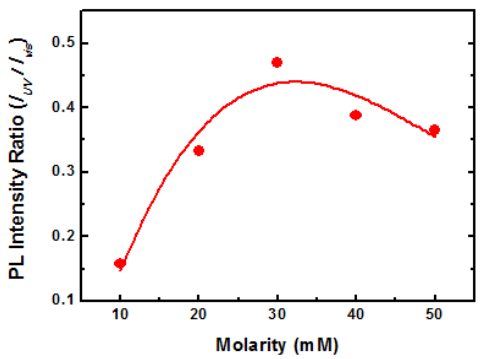

Fig. 4 Variation of I_{UV}/I_{vis} values with different solution molarities

4. Conclusions

In this paper, the hydrothermally grown ZnO nanostructures were prepared with different aqueous solution molarities and different deposition time. The temperature dependent PL measurements were carried out to investigate the effects of solution molarities on the optical and structural properties of ZnO nanostructures. It is found that the visible emission intensity of PL spectra increases and then decreases with solution molarities. Moreover, the PL intensity ratio of the emission in the UV region to the emission in the visible region is calculated. The values of ratio increase as the molarity varying from 10 to

40 mM, and decrease at molarity 50 mM. It is concluded that the optical property and crystal quality of ZnO nanostructures are improved by an appropriately increasing solution molarity. However, too higher solution molarity leads to the disorder of ZnO structures, and deteriorate the crystal quality.

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