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EFFECT OF GROWTH LAYER SOLUTION CONCENTRATION ON THE STRUCTURAL AND OPTICAL PROPERTIES OF HYDROTHERMALLY GROWN ZINC OXIDE NANO RODS

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The paper reports on the effect of growth layer solution concentration on the properties of ZnO nano rods. The ZnO nano rods were grown through hydrothermal process, in which growth layer solution were prepared in three different concentrations. The prepared ZnO thin films have been annealed at 500°C temperatures in air atmosphere. The growth layer molar concentration of the sol-gel thin film plays an important role on the growth of ZnO nano rods. The phase and morphology were investigated by using X-ray diffraction technique and scanning electron microscopy. Also, absorbance spectra were measured by using UV-Vis spectrophotometer and the Band gap was calculated. This hydrothermal method represents a new, low-cost, time efficient and scalable method for synthesizing ZnO nano rods. Experimental results revealed that the hydrothermally grown ZnO nano rods have higher absorption spectra. The PL spectra of ZnO nano rods show UV emission and visible PL emission.

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Keywords: ZnO nano rod, growth layer solution concentration, hydro thermal method, band gap

1. Introduction

Zinc oxide is an eminent semiconductor with a wide direct band gap (3.37eV) and a large exciton binding energy of 60meV at room temperature [1]. It is used in many applications such as surface acoustic wave devices (SAW), gas sensor devices, laser and optoelectronic devices [2-4]. Numerous methods for fabricating the ZnO nanostructures have been investigated, including metal-organic chemical vapor deposition [5], atomic layer deposition [6], and thermal evaporation [7]. However, most synthesis methods require high temperatures (400°C –1300°C) [8], complex processes and vacuum systems [9]. Hence, an efficient and economical method for growing ZnO nano rods is desired for a diverse range of applications.

The sol-gel method is more fashionable because of its cheapness, reliability, repeatability and simplicity [10]. In addition, the nano rods which are produced by this route, confirm good optical properties. But this can be achieved only by good control of the size and morphology of the nano rods [11]. One of the ways that this can be done is by providing good absorption of the surfactant onto the surface of the nano rods [12]. Recently, a solution-based approach was developed to achieve highly oriented nano rods film with high surface area on substrate, which has the advantages of mild synthetic conditions, simple manipulation and large scale-up production. The hydrothermal process as one of the solution phase routes is simple process that can be

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performed at low temperatures [13, 14]. It opens a door for future optoelectronic devices based on ZnO nanostructure arrays [15]–[19].

2. Experimental

Seed layers were deposited on the substrates by the conventional dip coating method and thermal treatment. All the reagents used were analytically pure and it was used without further purification. Prior to deposition, the glass substrates were thoroughly cleaned. The seed layer solution concentration of Zinc acetate dihydrate in the ethanol solution was assigned to 0.1mol. Then 0.25ml of distilled water was introduced drop by drop to adjust the hydrolysis of Zinc acetate. Under stirring, the solution was transferred into a clear homogeneous solution. The above solution was stirred continuously for 2 hours at room temperature. The seed solution was dip coated on well cleaned glass substrates for 5 times at regular intervals of 1 minute at room temperature. The 5 layer films were annealed in a furnace at the temperature of 200°C for 1 hour.

ZnO nano rods were grown on well cleaned glass substrate by hydrothermal technique. Zinc Nitrate hexa hydrate Zn $(NO_3)_2.6H_20$ and hexamethylenetetramine (HMT) $C_6H_{12}N_4$, were employed as precursors. Well-aligned ZnO nano rods can be controlled *via* adjusting the preparation parameters, such as precursor concentration, growth temperature and time. Here we report the effect of three different precursor concentrations on the grown ZnO nano rods with constant annealing temperature of 500 C. 0.02mol of Zinc Nitrate dihydrate Zn $(NO_3)_2$. $6H_20$ and 0.1mol of hexamethylenetetramine (HMT) $C_6H_{12}N_4$, were taken in the ratio of 1:5. The other two molar ratios were 1:10 and 1:15. ZnO nano rods were grown in above three concentrations and annealed at same temperature of 500°C for 1 hour.

The crystal structure and morphology of ZnO nano rods were investigated by X-ray diffraction (XRD) on XPERT-PRO X-ray diffractometer with Cu K_radiation (λ = 1.54060 nm) at a scanning rate of 0.05◦ s−1in the 2θ range from 10◦ to 80◦ and scanning electron microscope (SEM) on HITACHI S-4800. To investigate the optical properties, the absorption and transmittance spectra were recorded by UV–Vis spectra on a JASCO Corp., V-570 spectrophotometer at room temperature. The PL spectra of the grown ZnO nano rods have been recorded using a HORBIA JOBIN YVON-Fluorolog at an excitation wavelength of 350 nm.

3. Results and discussion

Fig 1 gives the XRD patterns of the ZnO nano rod arrays corresponding to the different growth layer concentrations (1:5, 1:10, 1:15). The detected (h k l) peaks are at 2θ values of 31.7647°, 34.4227° and 36.2520° corresponding to the lattice planes (100), (002) and (101) respectively. They are in agreement with the standard JCPDS 036-1451 card for hexagonal wurtzite ZnO. The intensity of the peak is found to vary with the different growth layer concentrations. It is found that no other characteristics peaks corresponding to impurities of the precursors such as Zinc Nitrate hexa hydrate and Hexamethylenetetramine are observed in XRD patterns. At the growth concentration of 1:5 only weak (002) diffraction peak is observed. At the growth concentration of 1:10 a strong (002) diffraction peak and very weak (100) and (101) peaks are observed indicating that the ZnO samples are all of high c-axis orientation. It is noticeable that for the samples grown at 1:15 concentration, the XRD pattern shows very strong (002) diffraction peak and very weak (100) and (101) peaks. In addition, the intensity of (002) diffraction peak is strongest, compared to other samples.

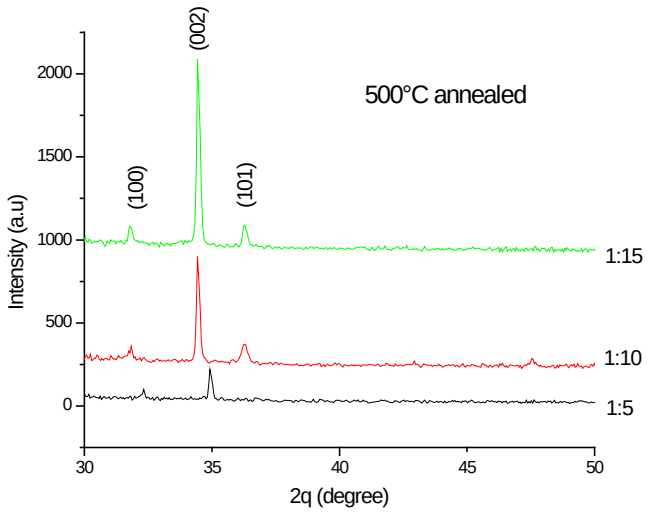

Fig.1 XRD pattern of ZnO nano rod array at three different growth concentrations

From the above XRD patterns it is clearly seen that, as the growth concentration increases the diffraction peaks were oriented strongly along the (002) peak. This implies that the grown nano rods at 1:15 concentration show perfect c-axis orientation which is in accordance with SEM images. This nano rods orientation is determined by the nucleation and agglomeration of the zinc nitrate and hexamethylenetetramine particles on the nucleation sites. The average size of the ZnO particle is calculated using Debye Scherer formula, $d_{avg} = 0.9\lambda / \beta \cos\theta$. Where d_{avg} = Average crystal size. λ= Wavelength of incident beam (1.5406Å). β= FWHM in radians. θ= Scattering angle in degree. The grain sizes of the nano particles are found to be 1.17nm, 1.72nm and 2.01nm for growth concentrations of 1:5, 1:10 and 1:15 respectively.

Fig.2 (a-c) show the SEM images of ZnO nano rods grown under different growth layer concentrations of 1:5, 1:10 and 1:15 respectively. They show the dense arrays of hexagonal ZnO nano rods having different diameters that are formed under different molar ratios. In Fig.2a, it is observed that the nano rods are grown in all directions. It is clearly seen that from Fig.2b and 2c, as the molar ratio increases the ZnO nano rods are oriented towards the vertical direction.

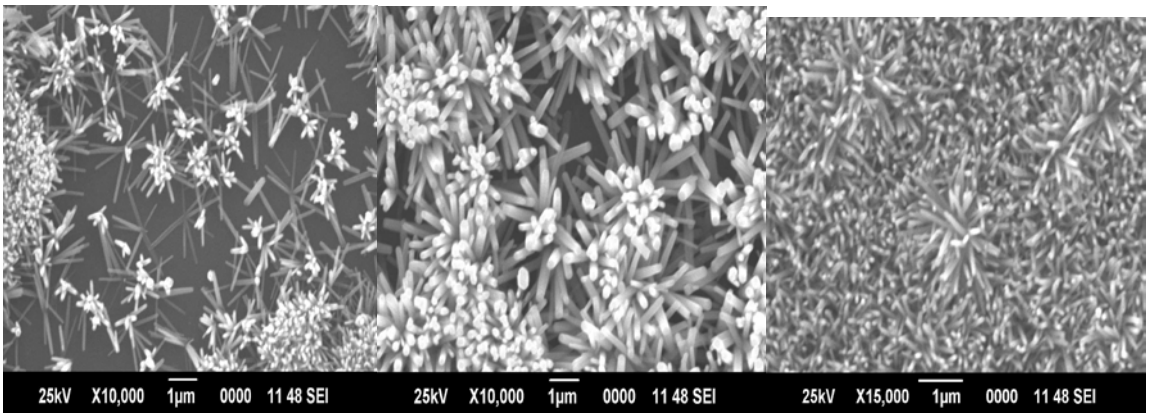

Fig.2 SEM images of nano rods grown on different growth solution concentration of 1:5, 1:10 & 1:15

The ZnO nano rods are grown at the same annealing temperature and for the same duration and their different lengths are likely to be a reflection of different growth solution concentration and in turn reflect in *c*-axis growth rates.

Optical properties of ZnO nano rods are important for many of their technological applications. In most cases the UV-Vis spectra of ZnO comprised of Absorption and Transmittance and the relationship between the two depends strongly on the preparation method and post-preparation treatment.

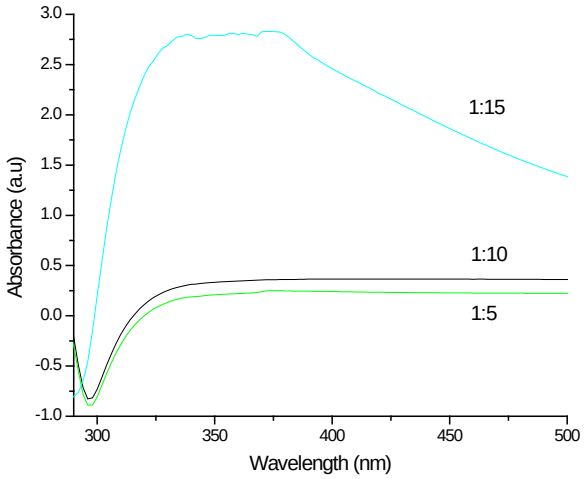

Fig.3 Absorption spectra obtained at three different growth solution concentrations

The optical absorption spectrum is shown in Fig.3. It clearly indicates that, as growth solution concentration increases the optical absorption edge shift to a higher wavelength. The intensity of the absorption spectra increases considerably as growth solution concentration increases from 1:5 to 1:15. It is well known that the optical absorption determines the optical band gap and ZnO films have a direct band gap. The optical band gap of ZnO films was found to decrease from 3.40 eV, 3.25 eV, to 3.10 eV, as growth solution concentration increases from 1:5, 1:10 to 1:15 respectively. The decrease in band gap of ZnO films may be attributed to the improvement in the crystalline quality of the films and increase of grain size.

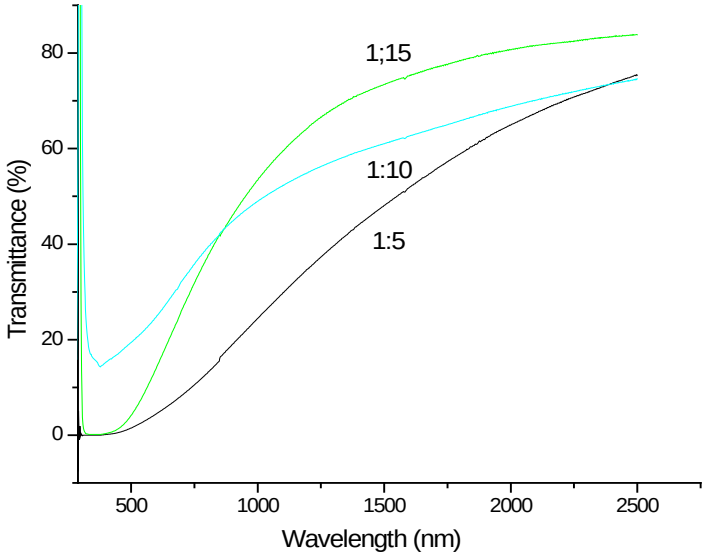

Fig.4 Transmittance spectra obtained at three different growth solution concentrations

Fig 4 shows the optical transmittance spectra of samples with three different growth solution molar concentrations of 1:1, 1:10 and 1:15, annealed at constant temperature of 500°C for 1 hour. The transmittance spectra is in the visible range nearer to infrared wavelength region. The

effect of change in the growth layer molar concentration on the optical transmittance was investigated. A slight decrease in average transmission was observed with the increase of growth layer molar concentration and was attributed to the increase of surface roughness. The optical transmittance of ZnO films was found to decrease from 83%, 75%, to 70% with the increase of growth layer molar concentration. The results indicate that high optical quality ZnO nano rods can be successfully achieved *via* this low temperature chemical approach.

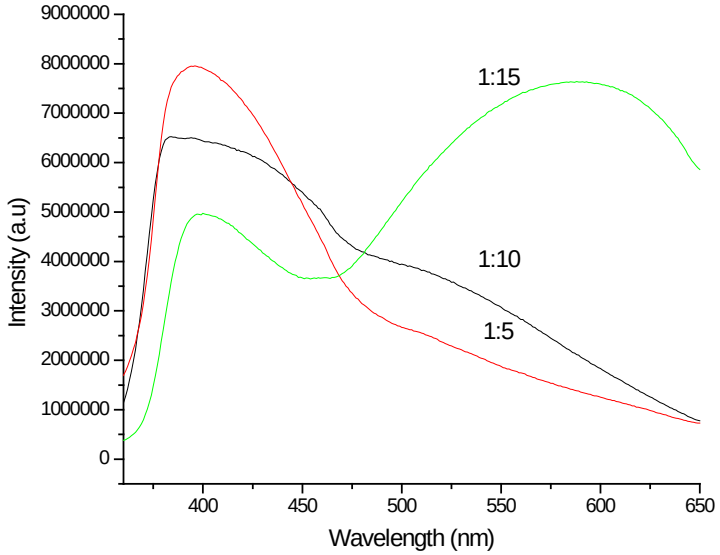

Fig.5 Room temperature Photoluminescence spectra obtained at three different growth solution concentrations

The Room temperature Photoluminescence spectra of ZnO samples obtained with an excitation wavelength of 350nm for three different growth solution concentrations of 1:1, 1:10 and 1:15 is shown in the fig.5. The Ultraviolet (UV) emission peak in the range of 380-410 nm dominates all the PL spectra, the only difference being the relative intensity of peaks. The UV emission also called the near band edge emission (NBE) may originate from free excitonic emission in the ZnO materials as ZnO has a high exciton binding energy of 60meV at room temperature. Besides the strong UV emission peak, PL spectrum covers the surface related visible PL emission in the wavelength range of 550-650nm. The intensity of this broad visible PL emission is highly sensitive to the environment and mainly depends on the surface to volume ratio of the nanoparticles. The obtained PL results of the samples indicate that the visible PL emission is enhanced while the UV emission is suppressed as growth solution concentration increases and particularly at the concentration of 1:15, due to large competition from the defect emission and increase in both the oxygen vacancies and zinc interstitials. The emission spectra of products synthesized under different growth solution concentration are different from each other, confirming that optical properties of ZnO are very sensitive to the preparation conditions.

5. Conclusions

ZnO nano rod arrays have been successfully synthesized on glass substrate by hydrothermal method. The orientation mechanisms were elucidated. The morphology evolution of the rods was monitored by XRD and SEM measurements. The nano rod growth, size and density were largely improved by changing the growth layer molar concentration. The nano particle size varies from 1nm to 2nm. The UV-Vis Absorption and Transmittance spectra measurements demonstrate that high optical quality ZnO nano rods array could be achieved by this low temperature, low cost chemical approach. The band gap of the grown rods decrease from 3.40 eV to 3.10 eV as growth solution concentration increases.. The results indicate that the change in growth solution concentration, play crucial role in the growth rate, size and density of the nano

rods. Rods with better morphologies are expected by further modifying the concentration of growth layer and annealing temperature.

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