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RESEARCH ARTICLE

STRUCTURAL AND OPTICAL CHARACTERIZATION OF PVP/ZnO NANOCOMPOSITES PREPARED BY SOL-GEL DIP-COATING METHOD

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ABSTRACT

The effects of Polyvinylpyrrolidone (PVP) on ZnO thin films prepared by sol-gel dip-coating method were investigated by X-ray diffraction (XRD), Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectrometer (FTIR) studies. The optical absorption and transmittance spectra of ZnO thin films have been recorded using UV Spectrophotometer. In addition, the Photoluminescence (PL) has also been obtained to investigate the optical properties of ZnO and PVP/ZnO thin films. The XRD patterns exhibited that, the films were formed in the preferred orientation along c-axis as a function of polyvinylpyrrolidone (PVP) concentration and which also confirms the formation of Wurtzite structure. The crystallite size was calculated using the Scherrer's formula. The SEM images of ZnO, PVP/ZnO (0.05M) and PVP/ZnO (0.07M) prepared films have depicted a fairly uniform distribution of particle size, such as, 1.2 μ m, 0.7 μ m and 1.1 μ m respectively. The FTIR spectra confirm the presences of ZnO and PVP/ZnO peaks. A remarkable increase in the band gap of PVP/ZnO was observed by UV Spectrophotometric analysis, further it was noticed that, the band gap values were larger than the optical band gap of bulk ZnO material. Whereas, the PL excitation spectra have depicted a strong UV emission and blue emission.

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INTRODUCTION

Zinc oxide has many unique physical properties, such as, an excellent electronic and photonic material having a wide band gap ($E_g=3.37$), a large excitation binding energy of 60MeV, high chemical stability, good piezoelectric properties, non-toxicity and bio-compatibility. Therefore, ZnO has attracted considerable attention of many researchers especially for its potential applications including gas sensors, photo-detectors, light emitting diodes, piezoelectric devices and spin electronics (Khare, 1995; Khare, 1994; Narsimba Rao and KPalatha 1987; Wohrle, 2005). Generally the polymers are the material of great interest because of their low cost, easy processability, low weight, high quality surfaces and easy fabrication of thick and thin samples. The most valuable property of polymer is that they have the capacity to inhibit electrical conductivity as an insulator. In addition to these, the PVP is known to have pharmaceutical importance and also possesses good electrical storage capacity, dopant-dependant electrical and optical properties (Prescott, 1965); due to these remarkable characteristic features it has drawn a special attention among the conjugated polymers. Many techniques have been

employed for the deposition of high quality ZnO thin films like, chemical vapour deposition (CVD) (Natsume *et al.*, 1992), magnetron sputtering (Wang *et al.*, 2007; Singh *et al.*, 2007), spray pyrolysis (She *et al.*, 2005) and sol-gel method (Maiti *et al.*, 2007). Among these methods, sol-gel technique has gained worldwide interest since it offers several advantages, such as, high chemical homogeneity, low processing temperature, possibility of controlling size and morphology of particles. The aim of the present study is to investigate the effects of PVP on structural and optical properties of ZnO thin films.

MATERIAL AND METHODS

Nanocrystalline ZnO thin films were deposited from sol-gel of zinc acetate (Himedia 99.5%), ethanol and monoethanolamine (MEA) (Himedia 99.99%) using dip coating apparatus on glass substrate. The nanocrystalline thin films of ZnO were prepared by dissolving 0.3M of Zinc acetate dehydrate in 10ml of ethanol, by mixed both together, stirred well and kept at room temperature for 15 minutes. The clear solution obtained was heated at 60°C using magnetic stirrer for 1 hour and kept for 24 hours at room temperature. Meanwhile, the MEA (0.3M) was added drop by drop into the mixtures of Zinc acetate dihydrate and ethanol solution. Thin films of PVP/ZnO nanocomposites were synthesized by sol-gel dip-coating

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method using polyvinylpyrrolidone (PVP) (Himedia 99.999%). Zinc acetate dihydrate 0.3M was dissolved in 10ml of ethanol and the subsequent addition of 90 ml distilled water to which the mole ratio between PVP and $Zn(CH_3COO)_2 \cdot 2H_2O$ at (0.05M) and (0.07M) respectively. Both the solutions were continuously stirred for 24 hours at room temperature before using as starting sol in dip-coating process. The glass substrates were soaked in a mixture solution of HCl and HNO_3 (1:2) for a duration of 10 minutes, then they were rinsed with distilled water and subsequently with ethanol for several times, and dried before dipping into starting sol. Each layer of as-prepared films was dried at $80^\circ C$ in hot air for 15 minutes. The dipping process was carried out for 5 times, after the formation of each layer it was cooled down to room temperature. Finally, all ZnO & PVP/ZnO films were calcined at $550^\circ C$ in air for 1½ hour to ensure that, all organic species were expelled from the films. The X-ray Diffraction (XRD) spectra were recorded using Bruker D8 advanced X-ray diffractometer with $CuK_{\alpha 1}$ (1.54060\AA) as a source. The SEM micrographs of all the samples have been obtained using Scanning Electron Microscope (Hitachi Model S-3000N) and photoluminescence excitation spectra were also recorded with (Shimadzu RF 5301) Luminescence spectrophotometer. A pulsed xenon lamp was built in the spectrophotometer as the excitation source (excitation wavelength – 315 nm). In addition the thickness of the films was also determined by Stylus Profilometer (Mitutoyo SJ-301).

RESULTS AND DISCUSSION

Structural Properties

SEM studies

Surface morphological studies of ZnO and PVP/ZnO nanocomposite films at different concentrations have been carried out with a Scanning Electron Microscope and images were recorded. The particle size distribution data were shown in Figure 1(a-c) & 2. The SEM images of ZnO resemble a granular surface which showed fairly uniform distribution of grains. The SEM image depicted (Fig -1a) a high degree of orientation with fairly elliptical and flower shaped grains of relatively larger in size which more or less uniformly distributed.

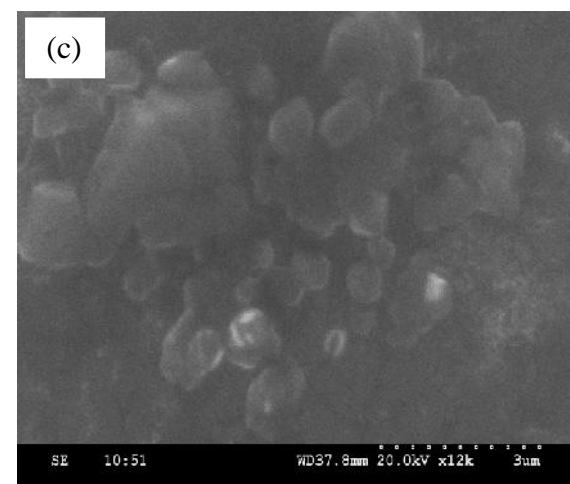
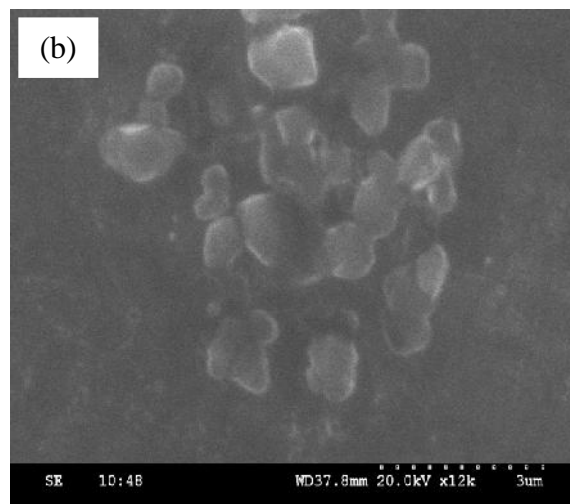
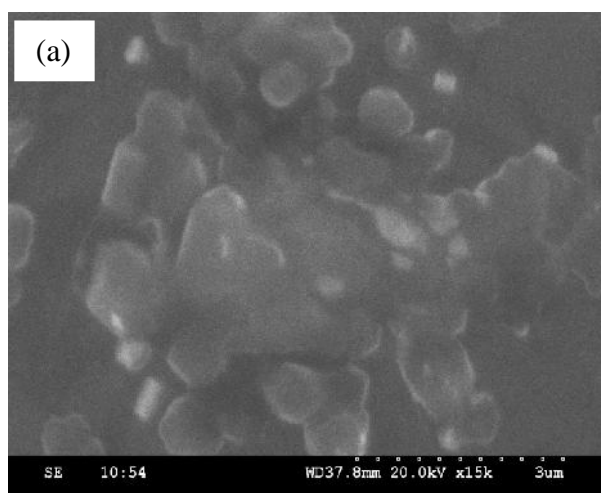
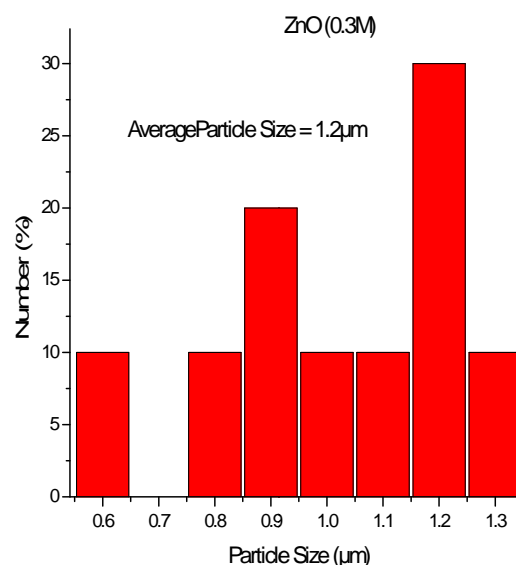


Fig. 1. SEM images showing surface morphology of (a) ZnO (0.3) (b) PVP/ZnO (0.05) (c) PVP/ZnO (0.07)

Figures 1b and 1c have indicated the changes in the surface morphology and uniform distribution of grains with smaller grain size in PVP/ZnO nanocomposites at different concentrations, such as, 0.05M and 0.07M respectively.



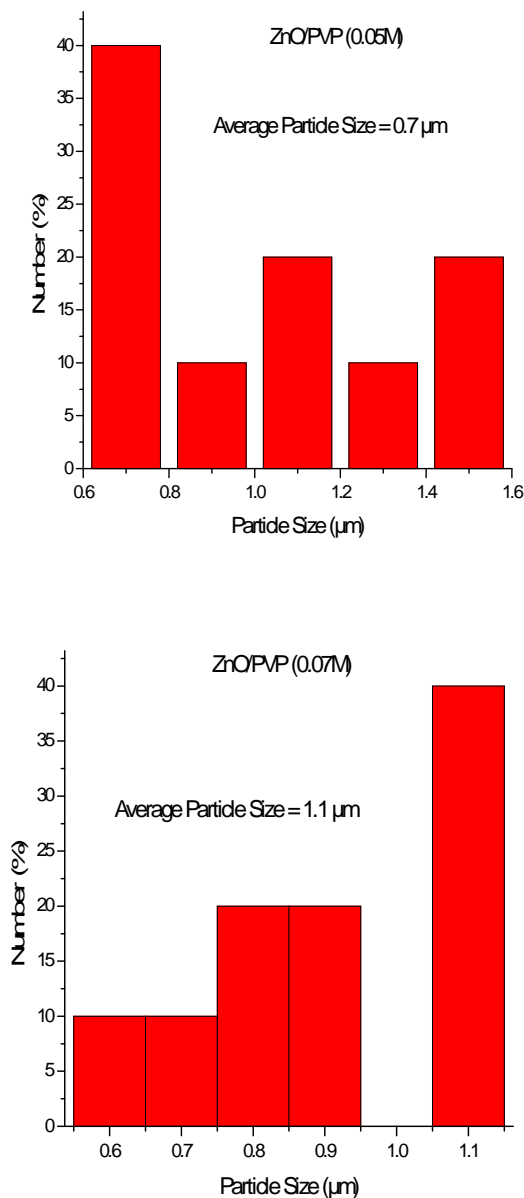


Fig.2. The particle size distribution of ZnO, PVP/ZnO from SEM images

The gradual change in the crystalline nature of films was mainly due to the enhancement of PVP. Both the ZnO, ZnO/PVP (0.05M) and ZnO/PVP (0.07M) were estimated as average particle size, such as, 1.2 μm , 0.7 μm and 1.1 μm are respectively.

XRD Studies

The X-ray diffractograms of ZnO thin films deposited on glass substrate showed a dominating (002) peak indicating high preferential c-axis oriented wurtzite type crystalline nature

(Fig - 3). The dependence of PVP concentrations on crystallinity of ZnO thin films were also analysed by XRD technique in (Fig-3). In all the samples (100) and (002) peaks were observed. According to the above samples, the intensity of their (002) peaks declines in sequence. The peak intensity (100) increases with respect to the addition of polymer concentration, which indicated that, the quality of the films gradually falls off. The crystallite sizes were calculated using Debye-Scherrer's formula (Khranovsky *et al.*, 2006) for the most prominent orientations of the ZnO films and shown in Table - 1.

$$D = \left(\frac{0.9\lambda}{\beta \cos\theta} \right)$$

Where,

D - The diameter of the crystallites forming the film.

- The wavelength of $\text{CuK}\alpha$ line (0.15406 nm).

- Full width at half maximum (FWHM) in radian.

- Bragg angle.

The crystallite size of PVP on ZnO thin films gave a value of 54nm and 53nm. PVP capped ZnO thin films have a value in same range (Sumetha Suwanboon *et al.*, 2008). PVP concentration plays important role in grain size. When the polymer concentration increases the size of the grains began decreases, the grains were more densely packed in highly doped films as well as the surface reveals lower porosity then become roughly constant (Sumetha Suwanboon, 2008). However, the obtained crystallite size deviated from the real value in concordance with low peak intensity and large peak width. It also preferred orientation along the c-axis of the ZnO thin films due to creation of some hydroxyl ions (OH^-) by PVP when dissolved in solvent. These OH^- ions have promoted the hydrolysis reaction of zinc molecule with distilled water. This can be explained by the ZnO nanoparticles being capped by PVP molecule, so that the growth of ZnO was inhibited (Casswell *et al.*, 2003).

Optical Properties

FTIR Studies

The FTIR spectra of ZnO and PVP/ZnO thin films were obtained and the characteristic absorption of Zn-O bond has been indicated by the peak at 463cm^{-1} (Fig - 4a). In the FTIR spectrum of PVP/ZnO (Figure - 4b & 4c) several peaks were observed and located at 1655cm^{-1} , 1355cm^{-1} , 1210cm^{-1} , and 480cm^{-1} . The peak at 1655cm^{-1} obtained was in a distinct stretching mode whereas, the peak obtained at 1210cm^{-1} resulting from the stretching mode of C-N in PVP molecule. In the case of PVP/ZnO thin films, the ZnO peak was observed at 480cm^{-1} . A distinct stretching mode observed at the peak 1655cm^{-1} indicated the carbonyl group on the PVP molecule. Whereas, the peak at 1210cm^{-1} represented by the stretching mode of C-N was due to the addition of PVP in ZnO.

Table 1. The films peak position, grain size and Inter planer distance of ZnO and PVP/ZnO thin films, calculated for peak (002)

concentration	2 theta (deg)	Plane index (hkl)	Interplanar distance (A°)	FWHM degrees	Grain size D (nm)	Thickness (nm)
ZnO (0.3M)	34.44	002	2.601	0.141	63	158
PVP/ZnO(0.05M)	34.20	002	2.619	0.165	54	152
PVP/ZnO (0.07M)	34.34	002	2.608	0.165	53	145

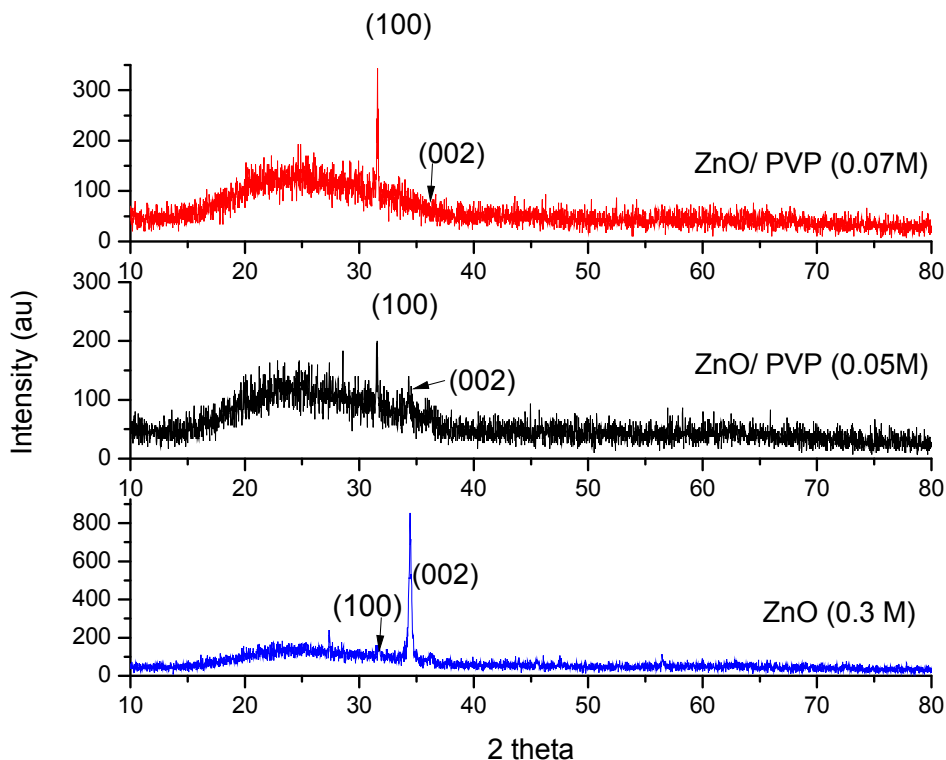


Fig. 3. X-ray diffraction patterns of ZnO (0.3M), PVP (0.05M), and PVP (0.07M)

From these observations, it has been confirmed that the presence of ZnO and Polymer PVP in the prepared ZnO and PVP/ZnO thin films.

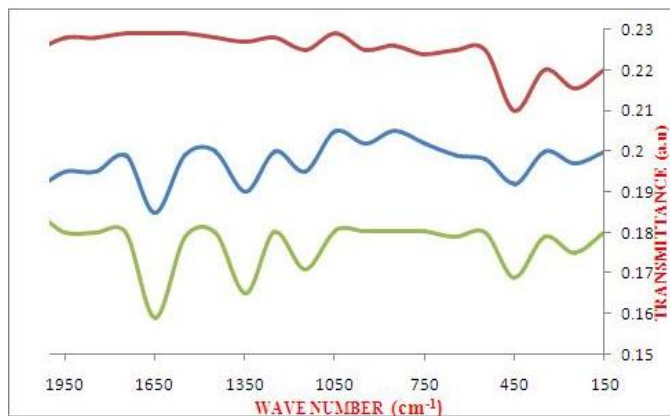


Fig. 4. FTIR Spectra of ZnO and PVP/ZnO thin Films

UV Studies

The transmittance spectra of ZnO and PVP/ZnO thin films were measured at a function of wavelength in the range of 300 - 800nm (Fig – 5). All the films showed that, the transmittance were higher than 80% in the visible region.

The fundamental absorption which corresponds to the transition from valence band to conduction bands can be used to determine the optical band gap (E_g) by the equation

$$h = A (h - E_g)^{1/2}$$

Where,
 A - is a constant
 h - Planck's constant ($6.626 \times 10^{-34} \text{Js}$)
 - Frequency of incident photon.

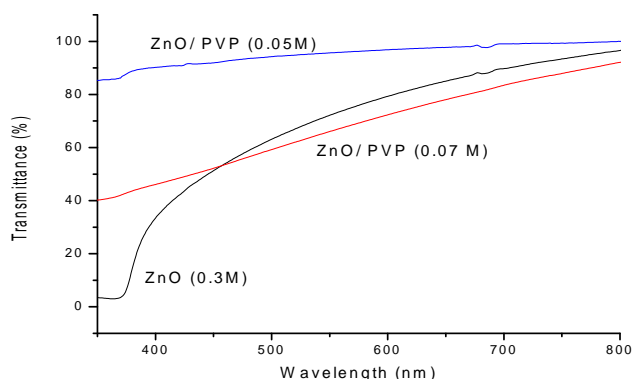


Fig. 5. Transmittance Spectra of ZnO and PVP/ZnO thin Films

The plots of $(h)^2$ versus Energy, at various ratios of PVP/ZnO are expressed in Figures - 6a and 6b. The values of direct band gap E_g were obtained from the linear portion of the curve by the extrapolation to zero of $(h)^2$ at energy intercept. The ZnO thin films gave the optical band gap of 3.2eV and PVP/ZnO thin films gave 4.02 and 4.04eV at the PVP concentrations of 0.05M and 0.07M respectively. These band gap values were larger than the optical band gap of bulk

ZnO material which was encapsulated by PVP in the study of Tang *et al.* (2006).

another (Kang *et al.*, 2003; Hsieh *et al.*, 2007; Zhang *et al.*, 2007).

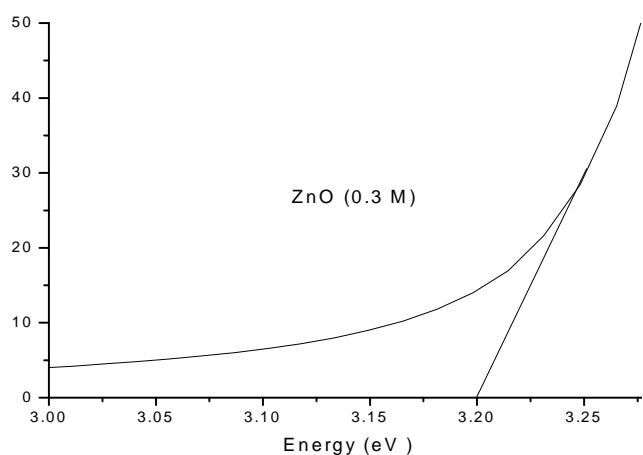


Fig. 6(a). Band gap of ZnO thin Film from UV spectrum

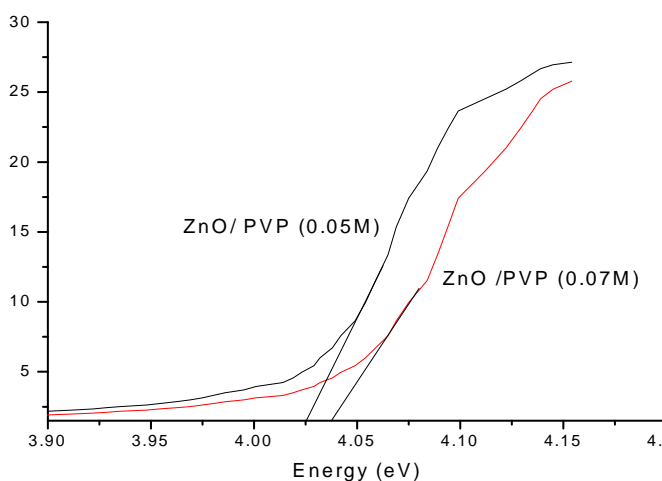


Fig.6(b). Band gap of PVP/ZnO thin film from UV spectrum

Photoluminescence studies of ZnO and PVP/ZnO thin films were carried out and depicted in Figure - 7. The ZnO thin films usually have two luminescent regions, such as, a strong ultraviolet emission peak and a weak blue emission peak (Fig - 7a). In PVP/ZnO thin films have ultraviolet emission intensity increased and visible blue emission decreases with increase in PVP concentrations were shown in (Fig - 7b and 7c). Usually the ultraviolet emissions have resulted from transition of electrons between the valence band and conduction band or/and a recombination of free exciton. However, visible blue emissions are connected with defects like oxygen vacancy, Zn interstitial and so on (Shan *et al.*, 2007). Many researchers have suggested that, the blue emission was related to oxygen vacancy (Kang *et al.*, 2003). Wei *et al.* (2003) have reported that, ZnO thin films prepared by pulsed laser deposition on sapphire substrates, found to have a blue emission centred at about 485nm, which were connected with Zn interstitial and Zn vacancies. There are many factors which affect the luminescence of ZnO thin films. Even though all the ZnO thin films used in this study were prepared by sol-gel method, their luminescent properties were different from one

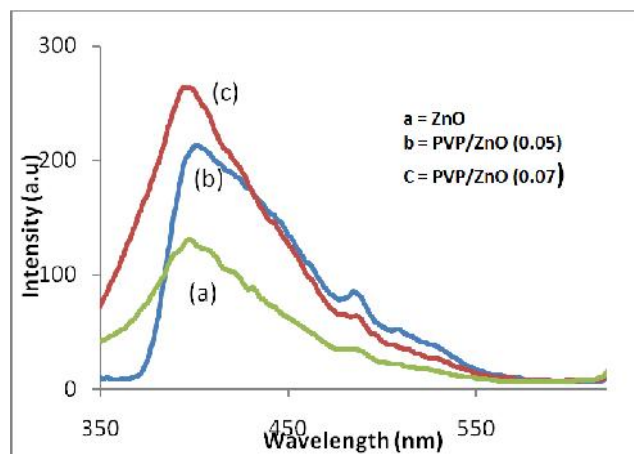


Fig. 7. PL spectra of ZnO and PVP/ZnO at different concentrations

The blue emission of ZnO thin films have been reported by many authors (Lan *et al.*, 2007; Wei *et al.*, 2007; Peng *et al.*, 2008; Maity *et al.*, 2005; Linhua Xu *et al.*, 2008). The ZnO thin films prepared by the sol-gel method have a good stoichiometry. Therefore, the occurrence of blue emission in the present study was related to oxygen vacancy. This probably be due to some Zn interstitials and Zn vacancies in PVP/ZnO (0.05M) and PVP/ZnO (0.07M), which led to the weak blue emission. From the above analyses, it can be evident that PVP at different concentrations also have an effect on the optical properties of ZnO thin films prepared by the sol-gel dip-coating method.

Conclusion

The ZnO and PVP/ZnO thin films were successfully prepared by sol-gel dip-coating method. All films were dipped for five times and calcined at 550°C in air for 1½ hour. SEM micrographs showed uniform distribution of grain size particles for ZnO and PVP/ZnO thin films. ZnO thin films exhibited a preferred orientation along (002) and (100) plane which gave the grain size of 60nm and has a band gap of 3.2eV. The PVP concentration increased into solution of ZnO, which gave the grain size of 54nm and 53nm. Moreover, these ZnO thin films produced a large optical band gap of 4.02 and 4.04eV at PVP/ ZnO concentration of 0.05M and 0.07M respectively. When the addition of PVP concentration the crystallization quality dropped and grain size decreases. In PL spectra of PVP/ZnO thin films gave the strong ultraviolet emission and blue emission decreases with increase of PVP concentration. For the PVP capped ZnO thin films the strongest UV emission and weak blue emission centred at 485nm. Zinc Oxide with polymer thin films can be used to fabricate a low cost and efficient solid state solar cell, which contributes much to the field of material science.

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