The Influence of Dopants (CD and Al) On the Physical Properties of ZNO

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Abstract - Zinc oxide and doped (Cadmium,Aluminium) zinc oxide thin films have been deposited on glass substrates by simple sol-gel spin coating technique. The structure of the deposited ZnO films was determined by powder X-ray diffraction (XRD) and it exhibits wurtzite structure along c-axis orientation. The surface morphology of the undoped and doped ZnO thin films has been examined by SEM. The optical absorbance of the deposited films was recorded using UV-Vis-NIR spectrometry. The optical band gap of deposited films was found to be 3.13 eV for pure ZnO, 3.21 eV and 3.22 eV for 1% cadmium (Cd) and 1% Aluminium (Al) doped ZnO respectively. The photoluminescence spectra of the films show prominent peaks between 382 to 385nm.

Index Terms - ZnO, doped ZnO, XRD, absorbance, photoluminescence

1. Introduction

ZnO is both a piezo-electric and electro-optic (EO) material and a semiconductor possessing a wide band gap of 3.37eV [1]. The most unique property of ZnO is its large exciton binding energy of 60 meV [2], which is much larger than those of GaN (24.7 meV)[3], ZnSe (21 meV)[4] and ZnS (36 meV) [5]. Due to this large binding energy, the exciton is stable at room temperature even in bulk crystals. Owing to these properties, ZnO is considered as a promising material for light-emitting devices[6] and semiconductor lasers with low thresholds in the ultraviolet (UV) region. Generally, the PL spectra obtained from ZnO thin films shows UV NBE emission around 380 nm, which strongly depends upon the preparation methods. Recently, it has been demonstrated that doping with cadmium and aluminium decreases the intensity of photoluminescence(NBE) emission[7]. In this paper we report on the preparation of high-quality ZnO thin films by the solgel deposition process. The solgel deposition technique is an easy and very cheap method to prepare metal oxide films.

2. Experimental

ZnO films were prepared by sol-gel method on glass substrate. For preparing undoped films, Zinc acetate dihydrate was used as the precursor and a sol was obtained by dissolving the precursor in a solution of ethanol and diethanolamine (DEA). The molar ratio of DEA to zinc acetate was maintained as 1.0 and the concentration of zinc acetate was 0.5 M. For doped films, cadmium nitrate and aluminium nitrate were used along with the precursor,zinc acetate dihydrate. The value of dopant concentration was 1 wt% for both dopants. The solutions were stirred

at 50°C for 1 h by a magnetic stirrer to yield a clear and homogeneous solution. In all cases the solution was allowed for aging at room temperature for one day before used for coating process. The final sol was used to prepare films by spin coating technique.

Glass substrates which were used for deposition were sonicated in dilute HCl for five minutes and then rinsed with acetone and distilled water. The prepared sol was dropped onto glass substrate which was rotated at a speed of 3000 rpm for 30 seconds using a spin coater. After each deposition, the film was dried at 200°C for 1minute to remove the organic residuals. The process was repeated eight times to get film of desired thickness. The film was then annealed in air at 450°C for 1 hour.

The structure of undoped and doped ZnO films was analyzed by X-ray diffractometry with Cu K_α radiation. Surface morphology was observed by scanning electron microscopy. The optical absorbance of all ZnO films was measured at room temperature using UV-Vis NIR spectrometer(JASCO,V-570) and the optical band gap energy was further determined. UV-fluorescence (CARY ECLIPSE) was used to study the luminescence property of the films at room temperature.

3. Results and Discussion

3.1. Structural characterization

The crystal structure and orientation of the undoped and doped ZnO thin films were investigated by taking X-ray diffraction (XRD) patterns The XRD spectra for ZnO thin films shown in Fig. 1 have diffraction peaks corresponding to (100), (002), (101), (102), (110), (103), (112) and (201) planes and these are observed in both bare and doped ZnO films. Cadmium doped films are less crystalline compared to bare and aluminium doped films which is revealed based on the intensity of peaks observed. Aluminium doped ZnO thin film is more crystalline than the other two films as the dominant (002) peak is having the hi ghest intensity. Again in Al doped ZnO, other prominent peaks are also more intense compared with the corresponding peaks of the bare and Cd doped ZnO thin films. Basically all films exhibit good crystallinity and the peaks are indexed for a hexagonal ZnO lattice. The calculated 'd' values are in good agreement with the standard 'd' values which is the interplanar spacing between the planes. All the strong peaks are assigned to the pure hexagonal phase of wurtzite ZnO. The XRD patterns of all samples indicated enhanced intensities for the peaks corresponding to (002) plane, indicating preferential orientation along the c-axis. The full width at half maximum (FWHM) of ZnO thin films for (002) plane are given in Table 1. FWHM values of Cd and Al doped ZnO thin films are more compared to the bare ZnO film indicating that the grain size decreases on doping. The grain size, *D* of crystallites has been calculated using the well-known DebyeScherrer's formula [8].

$$D = \frac{K\lambda}{\beta COS\theta} \text{----------(1)}$$

where K = 0.9 is the Scherrer constant, λ = 0.15405 nm is the x-ray wavelength, β is the peak width of half maximum and θ is the Bragg's diffraction angle.

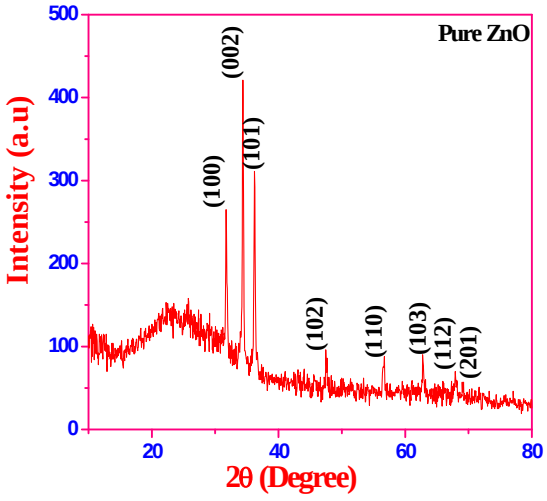
The dislocation density δ which represents the amount of defects in the film was determined using the formula[9]

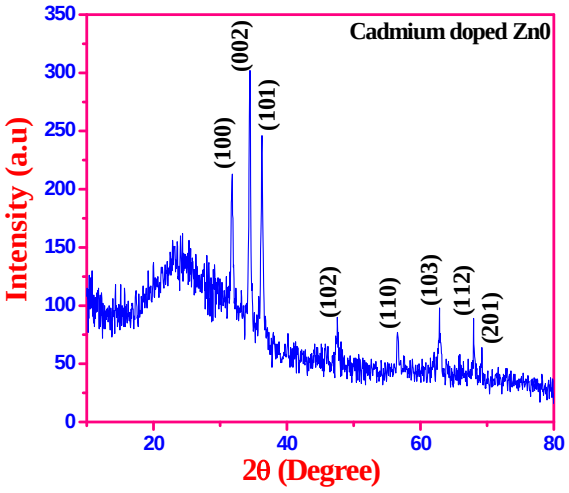
$$\delta = \frac{1}{D^2} \qquad \text{----------(2)}$$

The calculated values of particle size and dislocation density are given in Table 1. The larger *D* and smaller FWHM values indicate better crystallization of the film. It is observed that the grain size of the ZnO crystallites deposited on glass substrate decrease with doping.

Table.1: 2θ, FWHM, d-spacing, particle size and dislocation density of bare and doped ZnO films.

Sample	2θ Value along (002) plane	FWHM	d-spacing(Å)	Particle size (nm)	Dislocation density δ x 10^{14} (lines/m^2)
Pure ZnO	34.3510	0.1757	2.60854	47	4.52
Cd doped ZnO	34.4077	0.2696	2.60437	31	9.76
Al doped ZnO	34.5648	0.3297	2.59289	25	16.00





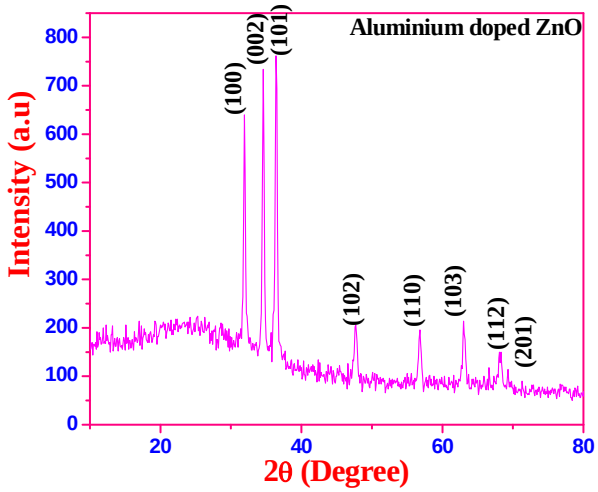
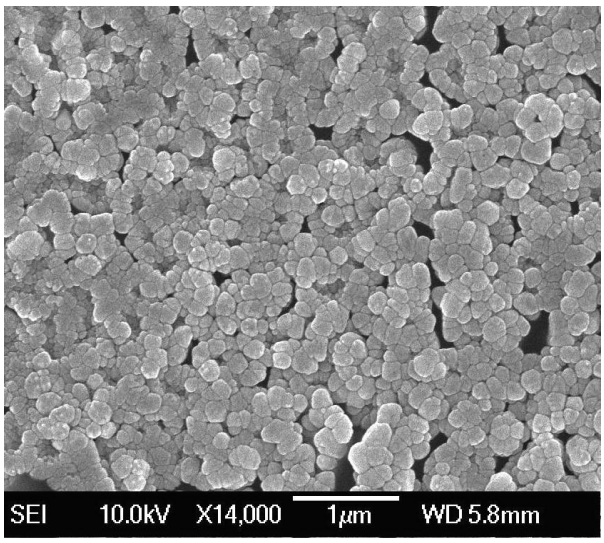
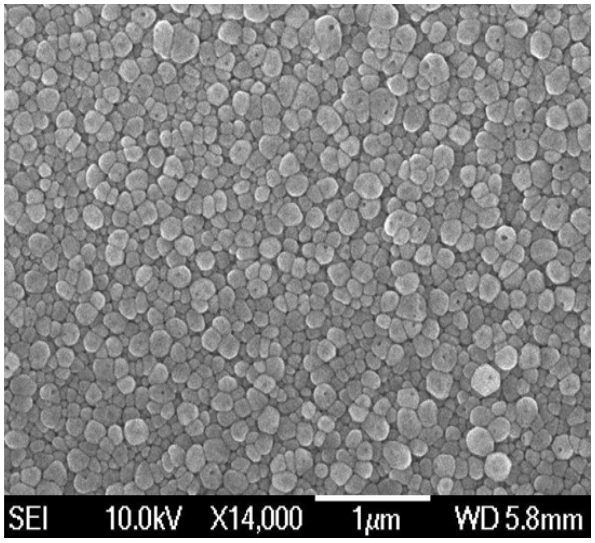


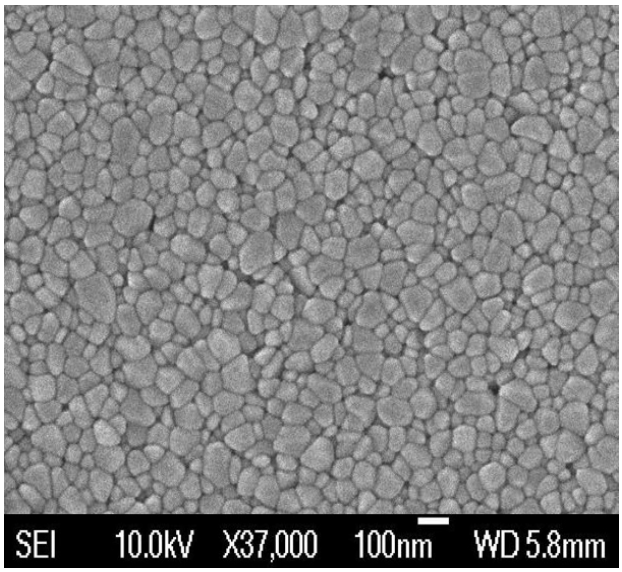
Figure 1. XRD patterns of pure and doped ZnO nanoparticles



(a)



(b)



(c)

Figure.2:SEM images of (a) Pure (b) Cd doped and (c) Al doped ZnO nanoparticles

SEM was used to examine the particle size, rough morphology and distribution of particles present on the surface of film. The result exhibits that the particle size of all samples are in nanometer scale. From Fig. 2 it is seen that the particles are spherical-liked or polygon in shape. Again it is observed that the grain size of ZnO particles decreases on doping with cadmium and Aluminium. This is in line with the XRD result given in Table 2 where the particle size decreases with doping. ZnO films doped with Aluminium has the smallest particle size.

3.2 Optical characterization

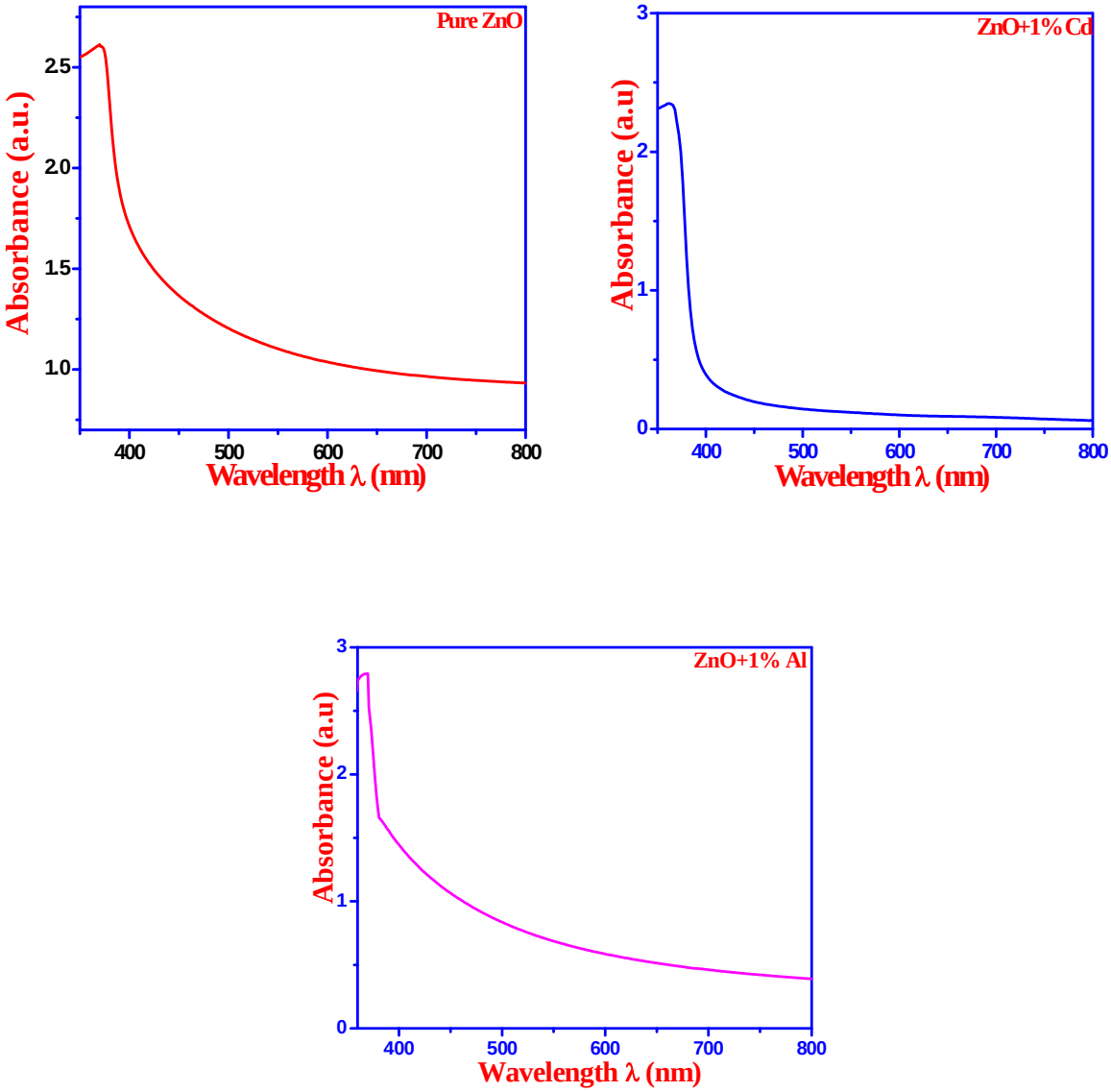


Fig.3. UV -Vis Absorption spectrum of ZnO and doped ZnO thin film

The variance of absorbance (A) as a function of wavelength of undoped and doped ZnO films was recorded using UV-Vis-NIR Spectrometer and is shown in Fig.3. The spectrum reveals that the deposited ZnO films have low absorbance in visible region which is the characteristic feature of ZnO material. From the theory of optical absorption, the absorption coefficient of the films is calculated using the expression[10],

$\alpha = 2.303\ A/\ t$ ---------- (3)

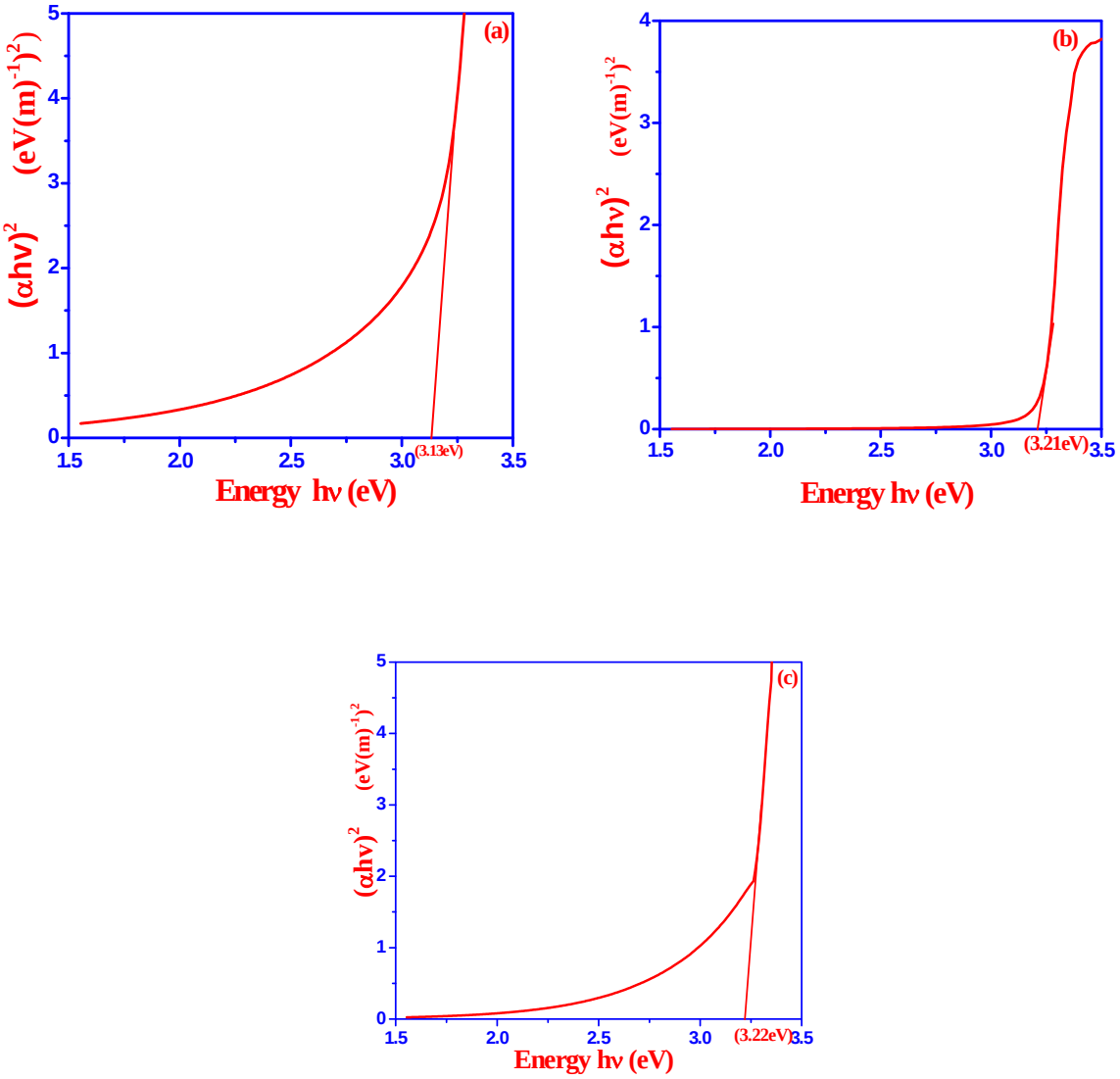


Fig.4 a-c: Tauc plot of (a) undoped (b) Cd doped (c) Al doped ZnO thin film through UV - Vis. absorption spectra of ZnO film

where, A is the absorbance and t is the thickness of film. The absorption coefficient α and the extinction coefficient k are related by the formula

$$k = \alpha \lambda / 4\pi \quad \text{---------- (4)}$$

The Optical energy gap E_g and absorption coefficient α are related by the equation

$$\alpha = (k/h\nu)(h\nu - E_g)^{\beta} \quad \text{---------- (5)}$$

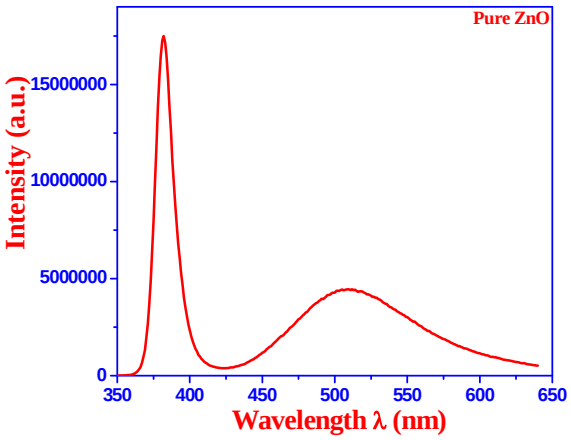
where, k is a constant, h is Planck's constant, hν is the incident photon energy and β is a number which characterizes the nature of electronic transition between valance band and conduction band. For direct allowed transitions, β =1/2 and it is

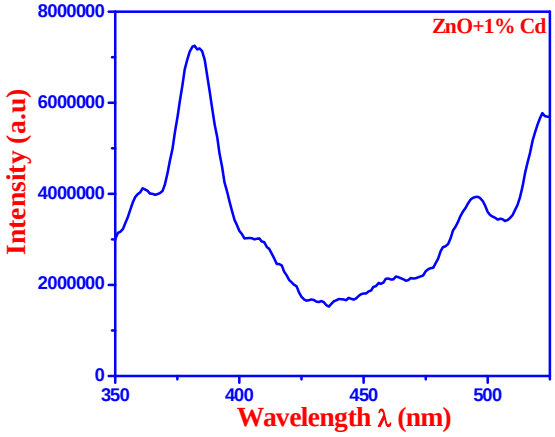
already known that ZnO is a direct bandgap semiconductor. Therefore the formula used for calculating energy band gap [11] is

$\alpha=(k/h\nu)(h\nu-E_g)^{1/2}$ ----------(6)

Using the graph of $(\alpha h\nu)^2$ versus $h\nu$, energy gap E_g of the sample is estimated by the straight line portion of $(\alpha h\upsilon)^2$ extrapolated to the x- axis, where $\alpha = 0$ and the intercept with the x-axis gives the band gap (E_g). From the Tauc plot (Fig. 4 a-c) the energy band gap of films was found to be 3.13 eV for pure ZnO, 3.21 eV for (1wt%) Cd doped ZnO and 3.22 eV for (1wt%) Al doped ZnO.

PL spectra of the synthesized samples were measured at room temperature. As shown in figure 5 (a-c), all the samples show a strong and sharp ultraviolet (UV) emission at about 383 nm (3.245eV), which is attributed to the near band edge(NBE)[12] emission of the wide band gap ZnO. Pure ZnO sample shows a weak blue-green emission (DLE) at 509 nm (2.442 eV) while Cd doped ZnO sample shows a strong blue-green emission peak at 521 nm(2.385 eV) with shoulder peak at 495 nm(2.511 eV). However, Al doped ZnO sample shows a relatively strong broad blue-green emission. These emissions were found to be extremely broad and this broadening may be due to phonon assisted by transition. The deep level emission might correspond to zinc vacancy and anti site defect as suggested by K Das et al [13]. The PL spectra reveal that the deposited ZnO thin films are of better quality as the band edge transition peak is intense and the sub-band transition peak is suppressed and diffused.





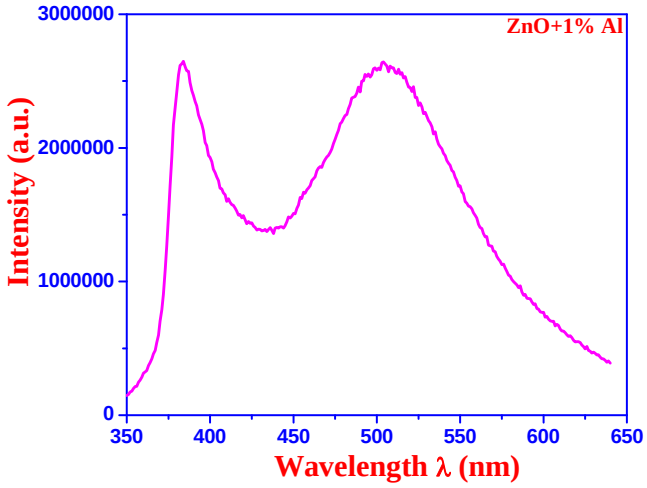


Fig.5. PL spectrum of ZnO and Cd-doped, Al-doped ZnO

4. Conclusion

Undoped and doped ZnO films having grain size of nanoscale were successfully deposited on glass substrates by sol-gel spin coating technique. The structural and optical properties of ZnO film are carefully investigated. All nanocrystals possess wurtzite hexagonal crystal structure of ZnO and show very good crystalline quality. SEM images revealed that the resulting ZnO nanostructures were single crystals that had grown along the c axis. All the samples show strong near band edge emissions, a signature of good optical quality. Room temperature PL spectra of the undoped and doped ZnO nanostructures show a strong UV emission band located at 383nm due to near band-edge emission. As the spin coated pure and doped ZnO thin films are of good quality, this method could be a promising one for fabricating optoelectronic nanodevices, such as LED and LD in future.

5. References

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