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Blue Shift of Luminescence of Sol-Gel Derived Zno And $Zn_{0.95}Li_{0.05}O$ Nanostructures

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Abstract:

The influence of Lithium doping on PL spectra and optical properties were studied in this report. Morphology of sol-gel derived zinc oxide thin films was also studied. 5 at% doping concentration were used in the solution. The XRD measurement exhibits single phase wurtzite structure along the (002) plane. The average particle size of pure ZnO and ZnLiO was found to be 36nm and 49.5 nm respectively. Incorporation of Lithium influenced the particle size. Films exhibits average transmittance more than 85%. Band gap increases with Li doping. FESEM reveals the uniform chromosome type structure. The PL spectra showed near band edge emission of ~399nm and deep level emission peaks of around ~468nm. The PL peak intensities were found to increase with doping of Lithium and shifting of peak was also observed.

Keywords: nanostructures; ZnLiO; sol-gel; XRD measurement.

Introduction:

ZnO nanostructures have attracted much interest of researchers due to its useful optical and structural properties. ZnO as a wide band gap material with transparent properties found to be applicable such as thin film transistors [1-3], solar cell [4, 5], light emitting devices [6] and photo detectors [7]. These nanostructures can be synthesized by various kinds of deposition methods, such as sol-gel process [8], chemical bath deposition [9], spray pyrolysis [10] and molecular beam epitaxy [11]. While the sol-gels based deposition of films offers reduction in the cost of deposition and excellent compositional control [12]. In the present study, sol-gel deposition process is used for deposition of nanostructures. The change in property of ZnO had been observed with change in deposition condition and doping parameters. The doping of Li in ZnO films could improve their properties and preferential orientation growth. Present study reveals that the doping of Li changes band-gap of ZnO and grain size. The optical and structural parameters of ZnO and ZnLiO films were studied.

Experimental:

ZnO and ZnLiO nanostructures were deposited using sol-gel spin coating method. Solution of Zinc acetate, Lithium acetate was prepared for 0.4 moles of 5 at% Lithium. The solution was stirred on hot magnetic plate at 60 °C. After aging of solution it was used for spin coating deposition. With constant speed of rotation films were coated. The films were coated repeatedly for six times to get desired thickness. Samples were Pre and post heated after each coating and cooled down at room temperature. Samples were characterized for structural and optical properties. The crystal structures of thin films were investigated by XRD analysis. FESEM was carried out for surface morphology. The optical transmittance and optical absorption were investigated by using double beam Shimadzu UV-2600 spectrophotometer. The room temperature photoluminescence spectrum was measured.

Results and Discussion:

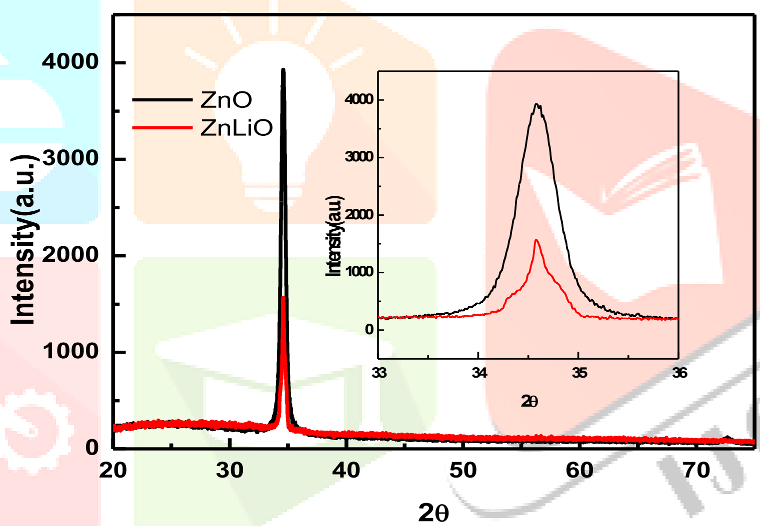

Fig. 1 XRD pattern of ZnO and ZnLiO nanostructures. (Inset: Intensity of peak)

ZnO and ZnLiO nanostructures were characterized using X-ray diffractometer. Fig. 1 shows the XRD plot of ZnO and ZnLiO nanostructures. Analysis clearly indicates single dominant peak corresponding to (002) plane at the 2ϴ value of 34.58º. The doping of Lithium does not deteriorate the crystal structure. The average crystalline size of ZnO and ZnLiO thin films has been estimated from Debye Scherrer equation [13].

$$D = \frac{0.9\lambda}{\beta\cos\theta} \qquad (1)$$

Where, D is the average crystalline size of the film. λ is the wave length of X-ray source (1.54059 Å), θ is the Bragg diffraction angle and β is the full width at half maximum intensity (FWHM) in radians.

Average crystalline size estimated from XRD pattern and found to be 36.30 nm and 49.5 nm for ZnO and ZnLiO thin films respectively. Crystalline size increased by Li doping. The diffraction angle of peak (002) is 34.58º and 34.58º for ZnO and ZnLiO thin films respectively. Inset of fig. 1 shows the decrease in intensity with Li doping. The structural parameters of ZnO and ZnLiO thin films were summarized in the table 1.

	Compound	2 θ (°)	FWHM (°)	Max. Intensity	Grain size D(nm)
Deposited samples	ZnO	34.58	0.23	3946.31	36.30
	ZnLiO	34.58	0.168	1580.46	49.50

Table 1: Structural parameters of ZnO and ZnLiO nanostructures.

Fig. 2 presents the FESEM images of ZnO and ZnLiO thin films. Images of the films were taken at the scale of 50µm with magnification of 5,000 for ZnO and ZnLiO nanostructures. Uniform chromosome type structure is retained for both the films with change in crystal size. The films show denser morphology without visible voids and defects overall the surface.

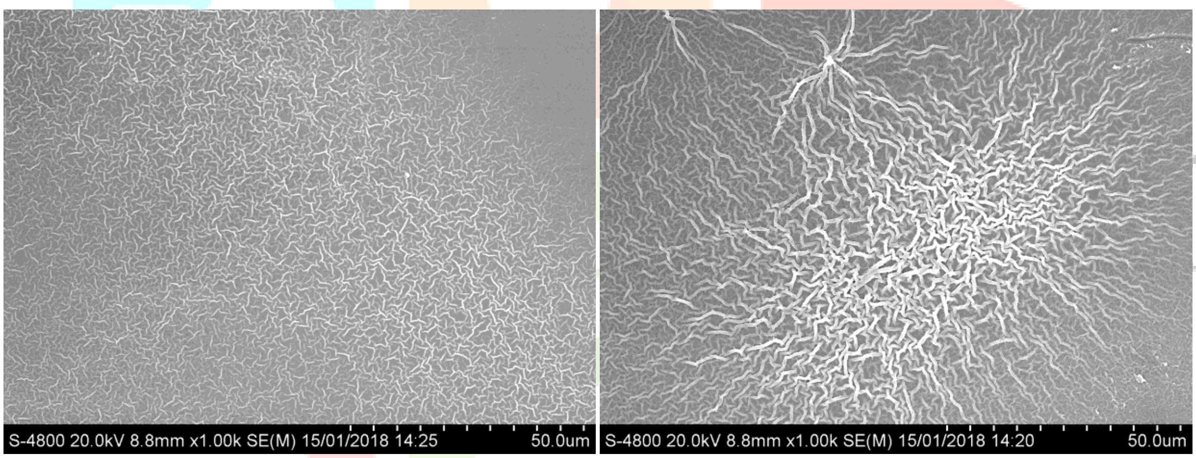

Fig.2 FESEM images of ZnO and ZnLiO nanostructures.

Optical properties were characterized by UV-Vis spectrophotometer. As ZnO is a transparent conducting oxide, it is essential to study effect of Li doping on transmittance. Fig. 3 a) explores the optical transmittance of ZnO and ZnLiO nanostructures. The films exhibit good transparency. The transmittance value of ZnO and ZnLiO thin films was found 86.50% and 85.60% respectively. The optical band gap (E_g) of ZnO and ZnLiO nanostructures was determined by using the absorption coefficient and extrapolation method. Fig. 3 b) showed plot of photon energy verses absorption coefficient for ZnO and ZnLiO nanostructures. The graph showed the optical band gap energy value 3.283 eV and 3.3 eV for ZnO and ZnLiO thin films respectively. Doping of Lithium showed broadening in the band gap.

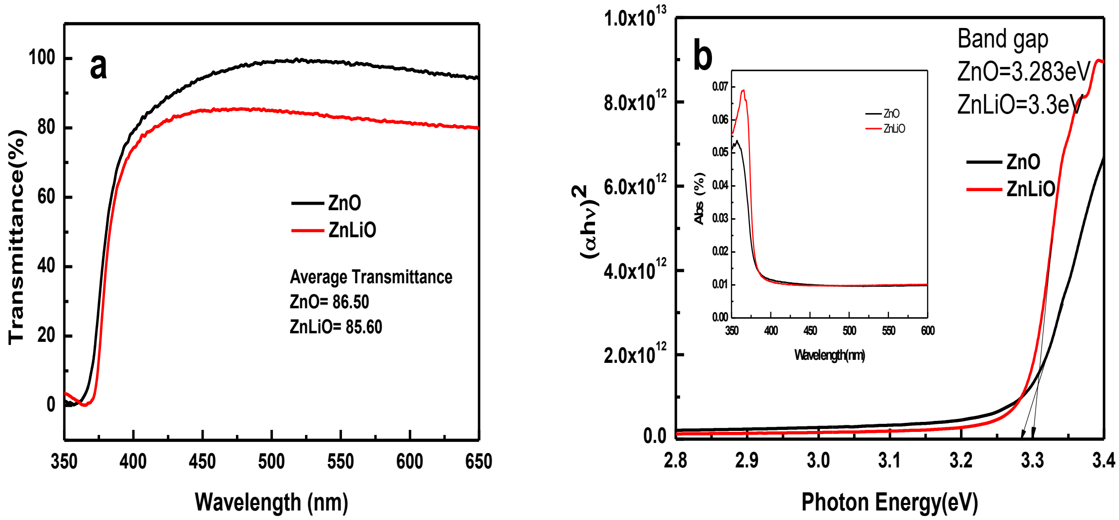

Fig. 3 a) Transmittance of ZnO and ZnLiO nanostructures b) Plot of absorption coefficient Vs photon energy.

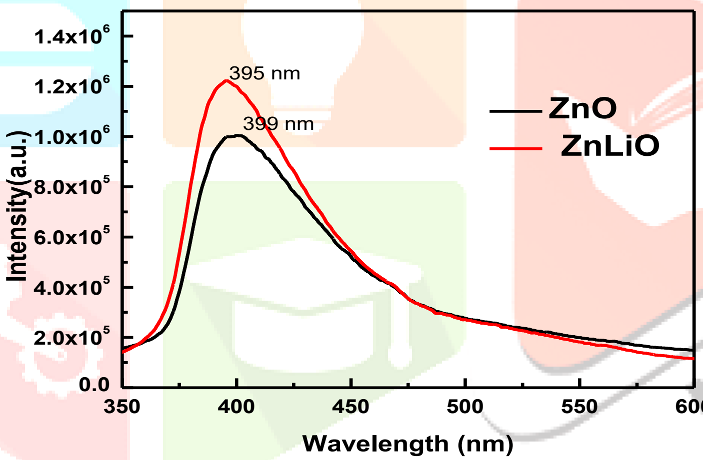

Fig. 4 PL Spectra of ZnO and ZnLiO nanostructures.

The room temperature Photoluminescence spectra are studied for investigation of the effects of lithium doping on ZnO thin films. Fig 4 shows the room temperature PL spectra of the ZnO and ZnLiO nanostructures.PL spectra of ZnO and ZnLiO nanostructures shows the strong peaks at 399 nm and 395nm respectively and blue emission low intensity peak at 468nm. Shifting of peak from 399 to 395nm indicates the blue shifting of luminescence. ZnLiO thin film shows a stronger peak than ZnO indicates that the ZnLiO films have higher optical quality than ZnO thin films.

Conclusion:

In summary, the ZnO and ZnLiO nanostructures were synthesized by simple and inexpensive sol-gel spin coating technique on glass substrate. The XRD spectra reveal the crystalline quality of ZnLiO thin films without any degradation of the wurtzite structure of the zinc oxide. The size of grains was found to increase with Li incorporation in the films. The FESEM reflects uniform chromosome type structure. Film showed more than 85% optical transparency in the visible range. Little increase in the band gap was observed with respect to doping of Li in ZnO nanostructures. The PL spectra of the ZnO and ZnLiO nanostructures contains two emission peaks dominated by a strong luminescence peak at 399 nm followed by blue visible emission peak at 468nm. The analysis and investigation lead successful incorporation of Li dopant in ZnO for transparent electrodes in optoelectronic devices.

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