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Photoluminescence and Photoconductivity Studies on Pure and Aluminium Doped ZnO Nanostructured Films

T. Ganesh^{1*}, S. Rajesh² and Francis P. Xavier³

¹Department of Physics, Presidency College, Chennai 600005, India

²Department of Physics, A.M. Jain College, Chennai 600114, India

³Department of Physics, Loyola-ICAM College of Engineering & Technology, Loyola Campus, Chennai 600034, India.

*Corres. Author: ntganesh@yahoo.co.in

Abstract: Thin films of pure zinc oxide (ZnO) and Aluminium doped ZnO (AZO) prepared by sol-gel assisted spin coating technique on glass substrates were characterized by fluorescence spectroscopy and its photo conductivity property was studied. The Texture Coefficient (TC) and crystallite size were calculated from the XRD. The photoluminescence (PL) spectra showed UV and defect related visible emissions. A model has been proposed to show the defect states existing between valence band (VB) and conduction band (CB) based from the observed PL spectra. The photoconductivity and photo response studies show the enhanced conductivity and increased rise and decay times due to Al doping onto ZnO. The defect states and trap depth determined were analysed and the results are discussed.

Keywords : sol-gel; spin coating; photoconductivity; photoluminescence.

1. Introduction and Experimental

ZnO is a versatile material having a band gap of 3.37 eV, large exciton binding energy of 60 meV and high electron mobility. It is a promising candidate for display panels, dye-sensitized solar cell, LED's, TCO and sensor applications. ZnO nanostructures have been synthesized by PLD, CVD, sputtering, MBE, ALD and sol-gel processing. The sol-gel has the advantage of fabricating the material over small as well as for large area application. The experimental details for preparing sol-gel assisted spin coating technique of undoped and Al doped ZnO films were previously reported [1]. In brief, Zinc acetate dihydrate, 2-methoxy ethanol and monoethanolamine were used to prepare sols. Aluminium Chloride was used for doping. We reported the effect of aluminium onto ZnO and studied their properties. To further investigate the effect of Al onto ZnO, we report the defect states obtained from PL characteristics and trap depth determined from photoconductivity studies in this research and their results are discussed.

2. Results and Discussion

From the XRD spectra [1], texture coefficient (TC), crystallite size was determined. The TC, crystallite size and specific surface area for the films were determined using the relations cited [2,3,4] and the data are listed in Table 1. The TC (hkl) = 1 indicates the randomly oriented crystallites of the film, while higher values

indicate abundance of crystallites oriented along the corresponding planes. Table 1 shows the highest TC value for undoped ZnO along (002) plane. This value decreased for all the Al-doped films. However, TC values for all the doped films along (100) and (101) has improved. The average crystallite size has decreased as the Al doping concentration increases when compared to ZnO. The PL spectra for the films are shown in Fig. 1. The spectra indicate emission peaks at 3.36, 3.13, 2.82, 2.75, 2.65, 2.57 and 2.33 eV respectively for ZnO. These values indicate the UV emission and defects related to visible region. The emission at 2.33 eV could be due to transition from conduction band to the edge of the oxygen antisites (O_{zn}) as reported in the literature [5]. Hence, this oxygen antisite an acceptor level may be located at 0.95 eV above the valence band. This value closely agrees with 0.97 eV as reported earlier [6].

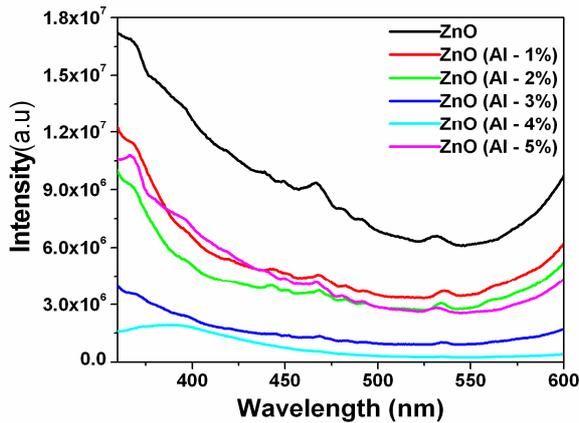


Fig. 1 Photoluminescence Spectra of Pure and Al doped Zinc Oxide Films

The doping of Al has resulted in quenching of relative intensities of UV and visible emission peaks. Hence, Al doping concentration and reduction in crystallite size might have contributed to the change in PL emission intensity peaks. But, the relative intensities of UV and visible emission peaks decreases with increase in Al concentration upto Al-4 wt%. However, the UV and visible emission intensity of Al-5 wt% ZnO film was more than the Al 2-4 wt% ZnO films. The variation of photo current with applied electric field under halogen lamp illumination is shown in Fig. 2. All the samples showed linear increase in photo current with increasing applied field. The photo current for undoped or pure ZnO at 100 and 150 V/cm, when compared to the current value at 50 V/cm increased by 1.4 times (an increase of 35%) and 1.3 times (an increase of 24%) respectively. The photo current at 50, 100 and 150 V/cm of Al-2 wt% film increased by 1.8, 2.5 and 3.3 times respectively, when compared to pure or undoped ZnO film at the same applied field. The magnitude of the photo current was more for Al 1-3 wt% when compared to pure or undoped ZnO film.

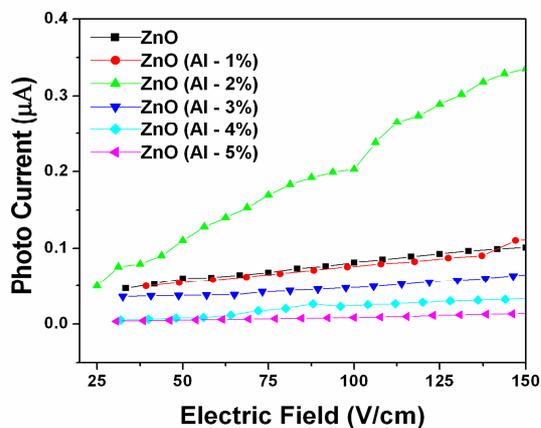


Fig. 3 Comparison of Photo Response of Undoped and Al-Doped ZnO Films

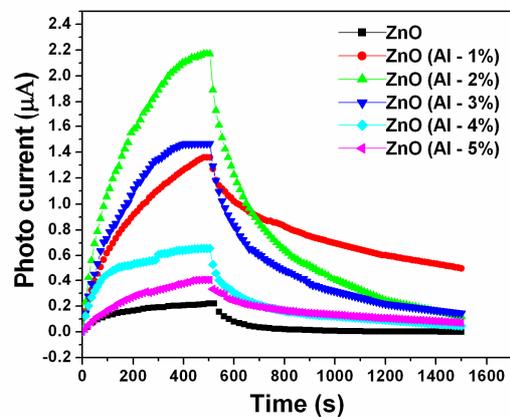


Fig. 2 Comparison of Photo Conductivity of Undoped and Al-Doped ZnO Films

Table 1 Structural and Photoresponse parameters of ZnO and Al doped ZnO

Samp. Code	Cryst Size (CS)	Texture Coefficient (TC)			Spec. Surf. Area (S _A)	Rise Time	Decay Time	Trap Depth		
	(nm)	100	002	101	$\times 10^4$ m ² /Kg	(s)	(s)	10 ¹³ (Hz)	10 ¹¹ (Hz)	10 ⁹ (Hz)
ZnO	19.6	0.56	1.99	0.35	5.4	112	246	0.98	0.91	0.79
AZ1	17.6	0.89	1.41	0.68	6.08	181	196	1.07	0.95	0.83
AZ2	15	0.94	1.35	0.69	7.13	151	156	1.05	0.93	0.81
AZ3	17.7	0.79	1.51	0.68	6.04	228	241	1.06	0.93	0.81
AZ4	12.5	0.56	1.68	0.74	8.5	245	327	1.04	0.92	0.80
AZ5	13	0.77	1.43	0.79	8.2	295	409	0.99	0.92	0.80

The time dependent photo current is shown in Fig. 3. The current increase as the light is switched ON and reaches a maximum value. Now, the light is switched OFF and the decrease in current is noted. The photocurrent for Al-2 wt% doped ZnO increased by 167 times (an increase of 2.15 μ A). The trap depth was calculated using the equations reported earlier [6]. From the graph the rise time and decay time are calculated using the equations [7] and listed in Table 1. The rise time was quicker for pure or undoped ZnO film, while the doped films showed slow response. The doped films took longer rise as well as decay time compared to pure or undoped ZnO. But, the ZnO films with Al 1-3 wt% showed quicker rise and decay times among the doped films. The time delay could be due to trap levels resulting in capture and release of charge carriers.

3. Conclusion

Pure and Aluminium doped zinc oxide thin films were characterized by photo luminescence spectra and its photo conductance behavior was studied. The PL spectra indicated the defect states and the presence of trap. The photoconductivity increased as the aluminium dopant concentration increases, upto Al-3 wt% and decreased for other concentration. The trap depth determined from photo response study agrees well with the earlier reported value and also is in agreement with the one determined from PL spectra. Hence, the PL characteristics and photo response study gives a clear insight on the defect states, trap depth, rise and decay time.

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