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Photoconducting and photoresponse studies on multilayered thin films of aluminium doped zinc oxide

T. Ganesh[1*], S. Rajesh[2] and Francis P. Xavier[3]

[1]*PG & Research Department of Physics, Presidency College, Chennai-600 005, India*
[2]*PG & Research Department of Physics, A.M Jain College, Chennai- 600 114, India*
[3]*LIFE, Loyola College and Loyola-ICAM College of Engineering and Technology (LICET), Chennai-600 034, India*
ntganesh@yahoo.co.in*

Abstract

Aluminium doped zinc oxide ($Zn_{1-x}Al_xO$) thin films were deposited by sol-gel spin coating technique onto a glass substrate (x=0-5wt%). The films were characterized by UV-Visible spectroscopy, SEM and were subjected to photoconductivity, temperature dependant conductivity and photo response measurements. The film with Al-1.5wt% showed the maximum absorption in UV and had a good optical transmission (~75%) in the visible regions respectively. The SEM images showed crack free films with little grain boundaries with decrease in grain size at higher aluminium concentration. The photoconductivity measurements reveal that there is a phenomenal increase in the photocurrent upon doping compared to undoped ZnO. The photocurrent reaches its maximum value (25μA) at 10V which is nearly 50 times more than the dark current (0.44μA) for Al-1.5wt% doped ZnO. The photocurrent then decreases for further increase in Al concentration. The photoresponse study gives the measure of rise and decay time. The rise time was found to be shorter for Al-1.5wt% among the doped film but longer than undoped ZnO. The temperature dependant conductivity shows that the thermal activation energy for the film decreases at Al-1.5wt% aluminium concentration and then increases for other concentrations in the temperature range 300-400K. The optimum conditions for maximum photoconductivity and photoresponse have been studied for photoconductive applications and the results presented.

Keywords: Sol-gel, spin coating, photoconductivity, activation energy.

Introduction

Zinc Oxide (ZnO) is a versatile material with a wide range of applications. Due to the excellent property of Zinc Oxide with high electrical conductivity and high transmittance (Gümü *et al.,* 2006) considerable attention is being given to this material. Zinc Oxide as thin films finds applications in electronic and opto-electronic devices (Ghosh *et al.,* 2006). Zinc Oxide finds potential application as UV photo detectors (Monroy *et al.,* 2003), gas sensors (Gao & Wang 2005), solar cells (Chen *et al.,* 2008; Ghaida, 2011), organic light-emitting displays (Plain *et al.,* 2005), surface Acoustic Wave (SAW) devices, heat mirrors (Elmer, 2000; Arshak & Gaiden 2005), photo-voltaic devices (Punniamorthy *et al.,* 2006) and as transparent electrodes (Lv *et al.,* 2008). ZnO is a wide bandgap (3.3eV) n-type semiconductor which can be produced by pulsed laser deposition (Sans *et al.,* 2004), chemical vapor deposition (Kashiwaba *et al.,* 2000), magnetron sputtering (Paraguay *et al.,* 1999), spray pyrolysis (Caglar *et al.,* 2006) and sol-gel process (Suping Huang *et al*., 2009; Mohammadi *et al.,* 2010). Among the above methods sol-gel spin coating technique is a simple deposition technique with cost effectiveness. Aluminium doped ZnO films have attracted attention due to their better optical transmittance, higher conductivity and low cost fabrication (Benouis *et al.,* 2007). Aluminium doped ZnO have been investigated for the use as low-cost TCO's. In the present study, we report the optical, surface and electrical properties of different concentration of aluminium doped zinc oxide thin films by sol-gel spin coating technique. Enhancement of photoconductivity and photoresponse are reported.

Material and methods

The precursor solution was deposited on glass substrate of 25mm x 25mm x 1mm dimension by sol-gel spin coating. The glass substrates were sonicated with acetone, methanol and isopropyl alcohol prior to deposition. The starting material was Zinc Acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$]. 2-Methoxy ~~-~~methanol and MEA (monoethanolamine) were used as solvent and stabilizer respectively. The dopant source was aluminium nitrate [$Al(NO_3)_3.9H_2O$] (Al 0-5wt%).

To prepare the precursor coating solution the concentration of Zinc acetate was 0.5 mol/l and the molar ratio of monoethanolamine to zinc acetate was kept at 1:1. The solution was stirred for 1 hour using a magnetic stirrer at room temperature to yield a clear transparent solution. Undoped and doped ZnO solutions were prepared and spin coated at 2500 rpm for 20 sec in air. After spin coating, the substrates were heat treated in two stages. First the substrates were heated at 623K for 20 minutes in air to evaporate the solvent. The above coating process was repeated 4 times. The films were subjected to second heat treatment at 773K for 1 h Thus, ZnO and aluminium doped ZnO thin films were fabricated.

Using CARY 5E UV-VIS-NIR high resolution spectrophotometer the optical absorption and transmittance of the films were measured in the spectral range of 300-2500nm. The surface morphology were observed using F E I Quanta FEG 200 - High Resolution SEM. For conductivity and temperature dependant conductivity measurements the experimental setup was similar to that reported earlier (Rajesh *et al.,* 2011). The

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Fig 1a .Optical Absorption and first derivative of absorption with photon energy of undoped and Al doped ZnO.

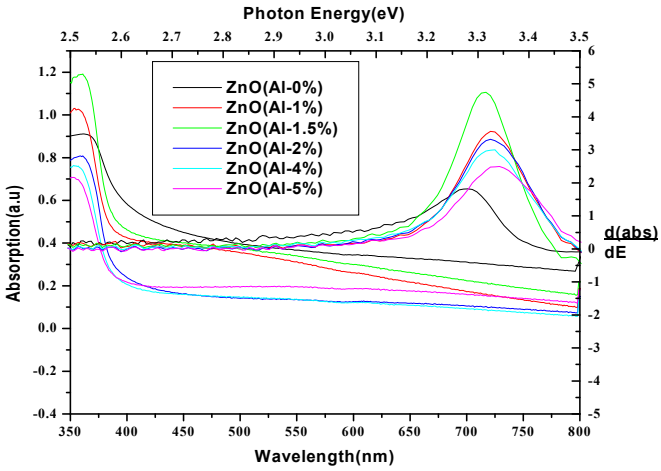
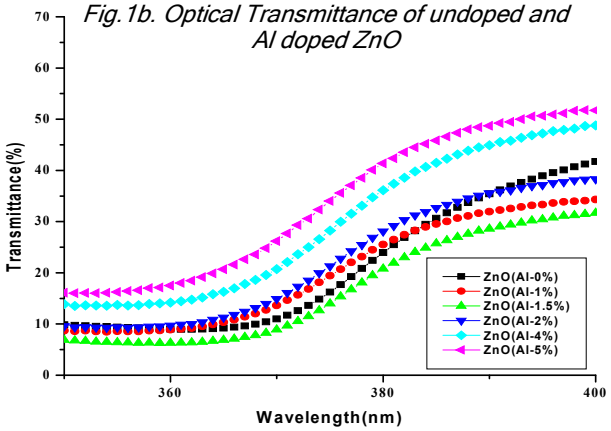


Fig. 1b. Optical Transmittance of undoped and Al doped ZnO



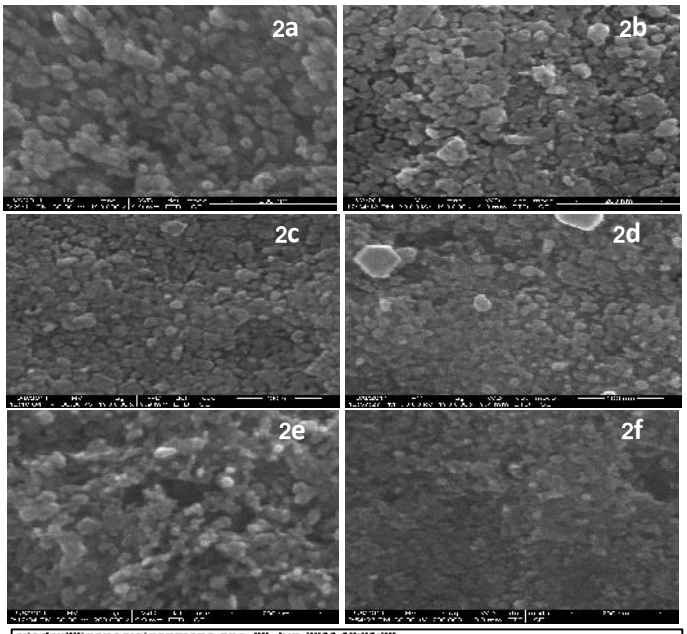
current was measured by connecting the electrodes in series with a DC power supply (0-500V) and a picoammeter (Keithley-6485). The applied field between the electrodes was increased from 0 to 300 V/cm and the current was measured in micro-ampere. For photoconductivity and photoresponse measurements the sample was illuminated with a halogen lamp. The intensity of light and the UV optical power was measured using luxmeter (Metravi 1330 light meter) and UV-340A light meter (Lutron Electronic) respectively. The intensity of light and the UV power was 4900 lux and 0.24W/m^2 for the halogen lamp.

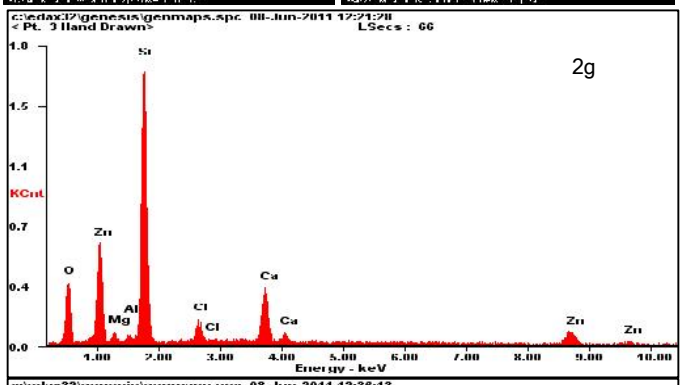
Results and discussion

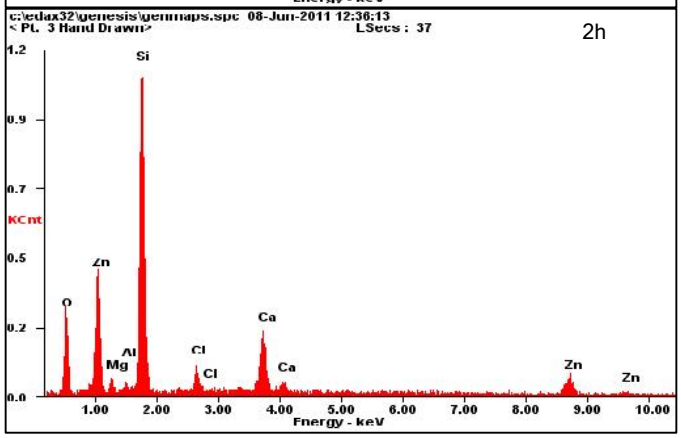
Optical Studies

The optical absorbance and transmittance were recorded for ZnO and aluminium doped ZnO thin films of various concentrations. The optical absorbance and the first derivative of the absorbance are presented in Fig.1a. It is found that the absorption increases up to Al-1.5% and then starts decreasing for further increase of concentrations. A common way of extracting band gap from absorption spectra is to get the first derivative of absorbance with respect to photon energy and finding the

Fig. 2a-2f SEM images of Al 0-5wt% ZnO films. Fig. 2g and 2h shows SEM-EDAX of Al-1 and 1.5wt%







maxima in the derivative spectra (Morales *et al.,* 2007). The derivative peak gives the absorption edge which is found to be 3.28eV, 3.32eV, 3.31eV, 3.32eV, 3.33eV and 3.34eV for Al 0-5wt% respectively. The plot of transmittance is shown in Fig.1b. The transmittance graph shows that there is a blue shift for the Al 1, 2-5wt% concentrations. This blue shift is because of the shift in

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Fig. 3a Variation of dark current with applied field.

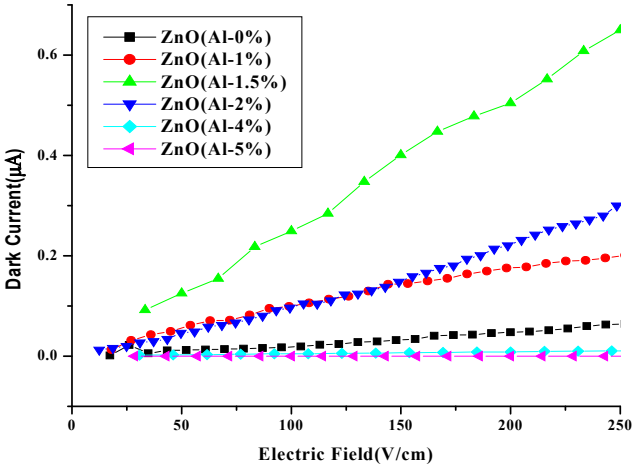


Fig .3b. Variation of Photo current with applied field. Inset shows variation of current with Al-concentration at 10V fixed voltage.

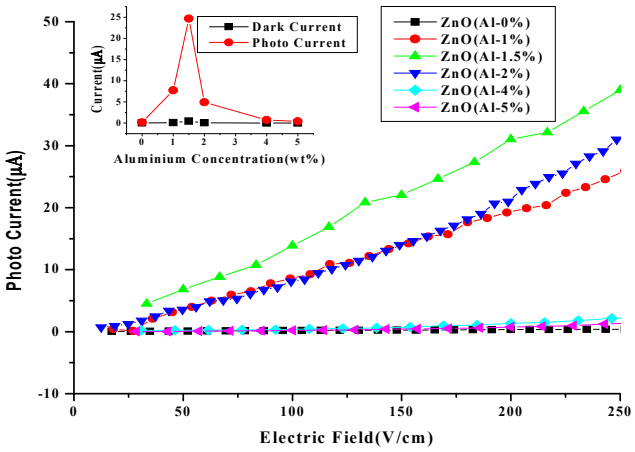
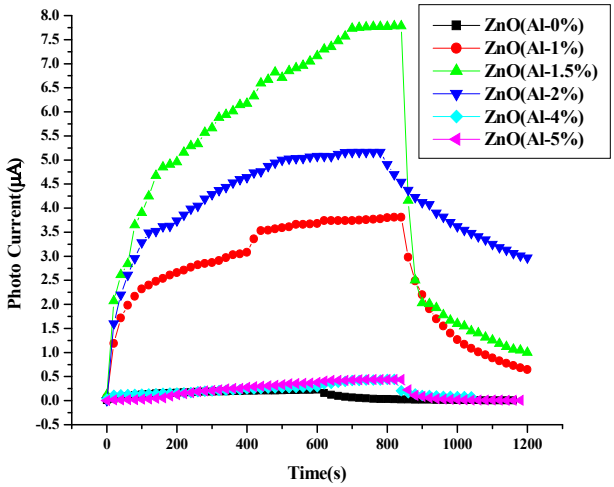


Fig. 4 Variation of photo current with time (Photoresponse)



the Fermi level within the conduction band which is known as Burstein-Moss effect (Burstein, 1954 & Moss, 1954). Zinc oxide with an aluminium concentration of 1.5wt% has the highest absorption in UV region and maximum transmission of about 70% in the visible region between 400 nm and 800 nm.

Surface morphology and compositional analysis

Fig. 2a -2f shows the SEM images of ZnO, ZnO-Al with various concentrations. It is found that the packing density is more in the case of Al doped zinc oxide (Al-1.5wt%) with little grain boundaries. The films are crack-free having nearly uniform distribution of grains for Al-1.5% indicating good quality of the film. Agglomerations of the grains are also visible at some regions. The incorporation of Aluminium onto zinc oxide is confirmed with SEM-EDAX (Fig.2g and 2h). The deterioration of the morphology is visible when the concentration of Al increases beyond 1.5%.The images indicated that the Al addition decreased the grain growth at higher doping concentration.

Variation of current with applied field

The variation of dark current with applied field is presented in Fig 3a which shows that the dark current increases up to Al-1.5wt% and decreases for other concentration. The variation of photocurrent with applied field is presented in Fig. 3b. It shows that the photocurrent values first increases to a maximum value for 1.5wt% Al doping and then decreases for other concentration. This is because of Al^{3+} ions replaces Zn^{2+} which results in the free electron for every zinc atom. This increases the carrier concentration which results in the decrease of resistivity of doped zinc oxide film. The variation of current with aluminium concentration for a fixed voltage (10V) is shown in Fig.3b (inset).

Table I. Photoresponse and temperature dependent conductivity values

Al wt%	Rise Time (s)	Decay Time(s)	Activation Energy(eV)
Al-0	112	246	0.027
Al-1	223	305	0.031
Al-1.5	161	266	0.029
Al-2	199	342	0.036
Al-4	210	469	0.065
Al-5	223	583	0.069

Variation of photo current with Time

Fig 4 shows the photoresponse of the ZnO films under halogen lamp illumination. The lamp was switched on to measure the growth of current with time at a fixed applied voltage (5V). Once the photocurrent reaches maximum value, the light is switched off to measure the decaying current. The exponential dependence of current on time is given by the equations $I_t = I_o (1-e^{-t/\zeta_r})$ and $I_t = I_o e^{-t/\zeta_d}$ for rise and decay respectively, where I_t-current at the time t, I_o-maximum photocurrent, ζ_r, ζ_d-time constants. Table I shows the rise and decay time determined from the above equation. The magnitude of the photocurrent for the Al-1.5wt% has increased considerably compared to other doped concentrations. The decay time is larger all the films compared to the rise time showing that the decay process takes place very slowly.

Variation of current with Temperature

Fig 5 shows lnI vs 1/kT for the aluminium doped and undoped ZnO films. The value of the activation energy is found out from the slope of the plot. The thermal activation energies are listed in Table I. In region (300-400K) the thermal activation energy for the doped film first decreases at Al-1.5% and starts to increase for other concentrations. The increase may be

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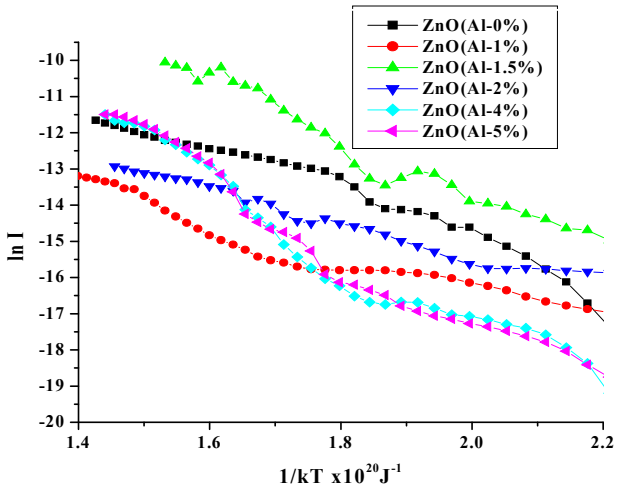
Fig .5. lnI vs 1/kT for undoped and Al doped ZnO films



because of more Al replacing Zn which leads to the increase in activation energy.

Conclusion

ZnO and doped ZnO thin films with various concentrations of aluminium were prepared employing spin coating technique. The Al-1.5wt% doped ZnO thin film compared to other concentration showed highest absorption in the UV and good optical transmission in the visible regions respectively. With further optimization of this film with regard to increased transparency in the visible region will make it a suitable candidate for solar cell application. The surface morphology showed decreased grain size beyond Al-1.5wt% confirming the blue shift arising due to smaller size of grains which will result in the increase in band gap of the material. SEM-EDAX confirms the incorporation of Al onto ZnO. The photoconductivity revealed the conductivity increases upon Al doping upto an optimum of 1-1.5wt%, but decreases beyond this concentration under illumination. The increase in Al content might create more trap levels thereby reducing the photoresponse. The rise time is found to be least for the 1.5% Al concentration among the doped films, but greater than the undoped ZnO. The decay time which is usually larger than the rise time is observed for all the films. The thermal activation energy showed the thermal activation energy is least for the 1.5wt% aluminium doped ZnO film. The samples prepared by sol-gel method indicate that they could be promising candidates for photoconductive applications.

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