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Faster photoresponse, enhanced photosensitivity and photoluminescence in nanocrystalline ZnO films suitably doped by Cd

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ABSTRACT

Faster photoresponse, enhanced photosensitivity and photoluminescence are obtained in Cd doped nanocrystalline ZnO films obtained by sol-gel method. The rise and decay times decrease for 0.56 at% Cd doping and the photosensitivity increases by approximately 20% rendering the sample very useful for switching and UV detector applications. Comparatively larger surface to volume ratio occurs for this sample. Consistent switching behavior is obtained throughout. The films are optically transparent with crystallite size less than 22 nm. Optical band-gap is tuned between 3.22 and 3.15 eV by increasing the Cd doping slightly which compares favorably well with earlier reports. The NBE emission in the ultraviolet at 386 nm, from 0.51 at% Cd doped sample, is remarkably good with suppressed defect-emissions and six-fold higher intensity as compared to that from undoped sample. The surface roughness decreases with increase in dopant concentration.

1. Introduction

ZnO nanostructures such as nanorod, nanowires and thin films etc. are widely studied as they are prospective candidate for application in optoelectronic devices such as UV–blue light-emitting diodes, solar blind UV-photodetectors, laser diodes, phototransistor and resonant tunneling devices. Large exciton binding energy of 60 meV at room temperature, much larger than those of ZnSe (19 meV), GaN (24 meV) and ZnS (39 meV) is unique to ZnO [1–5]. The large binding energy facilitates stable formation of excitons thereby enhancing the efficiency of luminescence and sensitivity of photoresponse which are a requirement for nano scale optoelectronic devices [6]. For fabrication of earlier mentioned devices and the development of spintronic systems and quantum well structures, smooth control on the band gap of ZnO is essential [5,7,8]. Although cadmium doped ZnO is one of the promising candidates for optoelectronics and other ZnO based devices, study of the various properties of Cd doped ZnO is not extensively investigated. ZnO possesses a wide direct band gap of ~3·37 eV while cadmium oxide possesses a narrower direct band gap of ~2·4 eV [7]. The relative difference in the melting points of ZnO and CdO, may be useful to fabricate Cd–ZnO nanostructure. Further, tuning of the emission from ZnO in the visible region may make it useful to transparent self-emitting display devices [9]. Substitution of Zn by Mg/Ca and Cd respectively enhances and diminishes the optical band gap of ZnO thin films [8,10–12]. Dopants also affect the photoluminescence (PL) properties and photoresponse of ZnO films [9,13]. PL study reflects upon the crystalline quality and the presence of unintended impurities in the sample as well as exciton fine structures [14]. During photoexcitation of ZnO with suitable energy, excitons which are excited electron-hole pairs can be generated. These excitons may recombine radiatively providing ultraviolet PL emission. However, the presence of defect states modifies the emission mechanism [15]. Since the photoconductivity in zinc oxide is governed with surface related processes besides those related with bulk, role of dopants on surface morphology becomes important. The rate of oxygen adsorption and photodesorption depends on the availability of free electrons from n-type ZnO and photogenerated holes which in turn depends on surface states and surface to volume ratio [16–18]. The photoconductivity studies for non-metal doped sample i.e. for N:ZnO film, deposited on alumina [19] and glass [20] substrates, by spray pyrolysis technique had also been reported where the dark and photo currents are of the order of micro- and milli-ampere, respectively. Out of several methods for depositing ZnO based thin films such as magnetron sputtering [21], pulsed laser deposition (PLD) [8,10,22],

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metal organic chemical vapour deposition [23], spin coating [11,12,24–28], spray pyrolysis [7,29–33] etc., we have adopted sol-gel spin coating method which is simpler besides producing good quality films. It allows homogenous mixing of the chemicals at atomic level, thus reducing the possibility of undetectable impurity phases [24,28]. In this paper, Cd doped ZnO films have been successfully prepared by sol-gel spin coating and large decrement in optical band gap of nanocrystalline ZnO based films is reported, with very small amount of doping as compared to earlier reports. The effect of Cd dopant on photoluminescence, photoconductivity and switching behavior are also presented which compare favorably well with literature.

2. Experimental

2.1. Sample preparation

Zinc acetate dihydrate and cadmium chloride are the starting chemicals for the preparation of undoped and Cd doped thin films by sol-gel method. The undoped, 1, 2 and 3 at.% doped precursor solutions of 0.2 M are prepared in ethanol. Diethanolamine is used to control the viscosity of precursor solution which has been stirred magnetically at 60 °C for 30 min to get homogeneous solution. All the precursor solutions are aged for 5 days which are then used to spin coat thin films on properly cleaned glass substrate at a spinning speed of 3000 rpm for 30 s. After each coating, the sample is heated to 400 °C for 60 min and then cooled back naturally to room temperature. The process is repeated 25 times for obtaining appreciable thickness and finally all the films are annealed at 450 °C for 4 h. The prepared samples are named as Z0, Z1, Z2 and Z3 which are deposited for 0, 1, 2 and 3 at% Cd concentration in precursor solutions, respectively.

2.2. Characterization

The crystal phase and crystallinity of the samples has been investigated using X-Ray diffractometer (Model – PANalytical X'Pert PRO X-ray diffractometer) for 2θ values ranging from 25 to 70° using CuK_α radiation ($\lambda = 1.54184$ Å). Transmittance and PL spectra have been recorded using UV–Vis spectrophotometer (Model- V670, Jasco) and fluorescence spectrometer (Model- LS-55, Perkin Elmer) respectively. The source of excitation wavelength is Xe discharge lamp. The surface morphology is obtained using FESEM (Model- ZEISS) and with the same equipment energy dispersive analysis (EDX) has also been done to ascertain the quantity of the cadmium dopant in the annealed films. All the measurements have been performed at room temperature.

2.3. Photoconductivity measurements

The photoconductivity characteristics of the samples, at room temperature, have been obtained by studying the current-voltage (I–V) characteristics and, rise and decay of photocurrent. Electrical contacts on the film were made using silver paste with electrode spacing of 10 mm. The area of illumination was 1 cm^2 and the photo-excitation source was a 300 W UV lamp. Dark current (I_{dc}) in absence of light and photocurrent (I_{pc}) under ultraviolet illumination of 365 nm were measured using multimeter (RISH Multi-18S) with adapter RISH Multi SI-232.

3. Results and discussion

3.1. X – ray diffraction

Fig. 1 shows the X-ray diffraction pattern of the samples in question. The XRD peaks correspond to the hexagonal wurtzite structure of ZnO showing preferred orientations along (100), (002) and (101). However, small peaks along (102), (110) and (103) also appear [9,23,25,34,35]. No impurity phase of Cd is detected. In case of pulsed laser deposition, Mishra et al. [8,34] have reported that the segregation starts at 8 at.% Cd doping in ZnO. The peak along c-axis i.e. (002) plane is prominent and occurs at $2\theta = 34.21°$, 34.57°, 34.77° and 34.33° for samples Z0, Z1, Z2 and Z3 respectively.

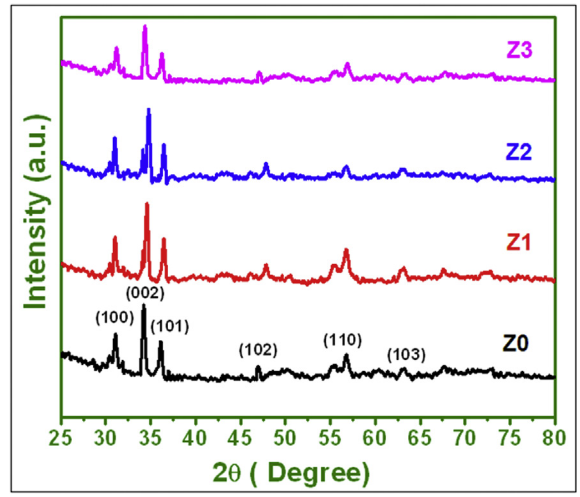

Fig. 1. XRD pattern of samples Z0, Z1, Z2 and Z3.

The orientation parameter [9] $\gamma_{(hkl)} = I_{(hkl)}/\Sigma(I_{(hkl)})$ varies from 0.082 to 0.312. Further it indicates that all the films are preferably oriented along (002) plane. The particle sizes along (002) plane lie in the range 18–21 nm which are estimated using Debye-Scherer (DS) formula [12]. Williamson and Hall (WH) plot (Fig. 2(a)) has been also performed to ascertain the cause of broadening of diffraction peaks [12]. The strain ε and particle size t_{WH} are determined, by comparing the trend line equation with $\beta\cos\theta = C\lambda/t_{WH} + 2\varepsilon \sin\theta$. Here C, the correction factor is taken equal to 1. The strain, Fig. 2(b), is least in sample Z2 and therefore the particle sizes t_{DS} and t_{WH} (13–31 nm) obtained by DS formula and that by WH plot are close to each other. The dislocation density ($= 1/t_{DS}^2$) which represents the amount of defects in the film [12] varies randomly from 22.15×10^{14} to 91.01×10^{14} lines/m^2 for the undoped and doped samples.

The c-lattice constant of ZnO thin film, Fig. 2(b), is larger than those of doped samples. It decreases as the Cd dopant is introduced i.e. for Z1 and Z2 and then again increases for further doping i.e. for Z3 while remaining smaller than that for undoped ZnO. Decrement in lattice constant c occurs in spite of the Cd^{++} ion being large (0.97 Å) as compared to Zn^{++} ion (0.74 Å) indicating that the Cd^{++} substitutes itself at or lodges itself at vacant, Zn site. With further increase in dopant concentration Cd^{++} appears to lodge itself in the interstitials. The Zn–O bond length lies between 2.013 and 2.006 Å and decreases monotonously with the increasing dopant concentration.

3.2. EDX analysis

The EDX spectra (figure not shown here) revealed the presence of Zn and O as the only elementary species in the sample Z0 i.e. undoped ZnO. For doped samples the presence of Cd is also confirmed, besides Zn and O. The amount of Cd in the solid films is found to be 0.45, 0.51 and 0.56 at.% which is lesser than those in the corresponding precursor solutions where it was 1, 2 and 3 at.%