



Photoelectrochemical properties of highly mobilized Li-doped ZnO thin films

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ABSTRACT

Li-doped ZnO thin films with preferred (002) orientation have been prepared by spray pyrolysis technique in aqueous medium on to the corning glass substrates. The effect of Li-doping on to the photoelectrochemical, structural, morphological, optical, luminescence, electrical and thermal properties has been investigated. XRD and Raman study indicates that the films have hexagonal crystal structure. The transmittance, reflectance, refractive index, extinction coefficient and bandgap have been analyzed by optical study. PL spectra consist of a near band edge and visible emission due to the electronic defects, which are related to deep level emissions, such as oxide antisite (O_{zn}), interstitial zinc (Zn_i), interstitial oxygen (O_i) and zinc vacancy (V_{zn}). The Li-doped ZnO films prepared for 1 at% doping possesses the highest electron mobility of $102 \text{ cm}^2/\text{Vs}$ and carrier concentration of $3.62 \times 10^{19} \text{ cm}^{-3}$. Finally, degradation of 2,4,6-Trinitrotoluene using Li-doped ZnO thin films has been reported.

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1. Introduction

The ever growing demand for high performance electronic devices that can be fabricated onto large-area substrates utilizing cost inexpensive techniques has given a boost to the development of alternative types of semiconductor materials, such as organics and metal oxides such as ZnO, SnO_2 , and In_2O_3 with desirable physical characteristics missing in their traditional inorganic counterparts. Zinc oxide is very attractive for implementation into optoelectronic devices mainly because of their high charge carrier mobility, high optical transparency, excellent chemical stability, large exciton binding energy, mechanical stress tolerance and processing versatility [1–5]. However, the fabrication of p-type ZnO, which is an essential step for p–n junction-based devices, is still a bottleneck because of a self compensation effect from native defects, such as oxygen vacancies and zinc interstitials [6,7]. The p-type ZnO is achieved by the doping of elements from group I (Li, Na, K) and V (N, P, As) dopants. The theoretical studies demonstrated, the group I elements might be better p-type dopants than group V elements for introducing shallowness of acceptor levels [8]. Fabrication of lithium doped zinc oxide is essential for improving the efficiency of quantum confinement structures from the point of view of band gap engineering. Reports indicate that incorporation of lithium into ZnO lattice is an effective way to enhance optoelectronic properties. In spite of the fact that the realization of p-type zinc oxide is difficult due to asymmetric doping limitations [9], many groups have successfully achieved p-type zinc oxide by

doping with arsenic [10], phosphorus [11], nitrogen [12] and lithium [13]. In Li doped zinc oxide, Li substituting zinc (Li_{zn}) possesses shallow acceptor levels [14].

Pure and Li-doped zinc oxide thin films are usually grown by using various techniques such as sputtering, pulsed laser deposition, chemical vapor deposition, sol–gel, molecular beam epitaxy, evaporation, and spray pyrolysis [15–19]. However, as far as film quality, deposition rate, adherency and transparency concerned spray pyrolysis is better deposition technique. Compared to other techniques, it has numerous advantages viz. low cost, easy-to-use, high growth rates, safety, easy to vary the doping concentrations with tailoring physical properties and can be implemented for large area depositions. Several authors have been reported LZO thin films by different methods, but very few reports are available on spray pyrolysis. Based on these facts, the synthesis of a LZO films with high electron mobility, transmittance and carrier concentration has been demonstrated. In this present report, the influence of lithium doping on to photoelectrochemical, structural, morphological, optical, luminescence, electrical and thermal properties has been investigated. Additionally, analysis of reflectance, refractive index and extinction coefficient from optical measurements has been studied. Finally, oxidative degradation of 2,4,6-Trinitrotoluene has been studied with mineralization analysis by COD and TOC measurements.

2. Experimental

Li-doped ZnO (LZO) thin films were synthesized by using chemical spray pyrolysis technique in aqueous medium onto the corning glass substrates using zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (AR grade,

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98.8% pure) supplied by HIMEDIA and lithium nitrate (AR grade, 99% pure) supplied by LOBA as an initial ingredients. To attain Li doping, lithium nitrate was mixed in to the solution. The [Li]/[Zn] ratios calculated on atomic percent used in the starting solution were 0.25%, 0.50%, 0.75%, 1.0% and 1.25%. It was observed that the [Li]/[Zn] ratios higher than 1.25% results degradation of films probably due to a reaction of the solution with excess lithium. No supplementary additives or complexing mediator is entailed to form precursor solution with proper equilibrium. The resulting 100 cc precursor solution was sprayed onto the preheated corning glass substrates of size $0.125 \times 2.5 \times 7.5 \text{ cm}^3$ held at optimized substrate temperature of $450 \text{ }^\circ\text{C}$ through specially designed glass nozzle. The compressed air (2.3 kg cm^{-2}) was used as carrier gas at a constant spray rate of 5 cc min^{-1} . While varying the doping concentration, other preparative parameters such as solution concentration (0.1 M), volume of solution (100 cc), nozzle-to-substrate distance (32 cm) were kept constant for all experiments. PEC reactor model and its experimental procedure for degradation of any organic impurities have been explained in previous report [20,21].

The structural properties were studied by a Philips X-ray diffractometer PW –1710 (λ , 1.5406 Å) using Cu K α radiation in the span of $20\text{--}70^\circ$. Raman-scattering experiments were performed in air at room temperature with microRaman system from Jobin Yvon Horibra LABRAM-HR visible within $200\text{--}1400 \text{ cm}^{-1}$ using Argon 488 nm laser as an excitation source. The 600 and 1800 lines/mm gratings – Detector: CCD detector were used. The morphological characterization of the films was observed by using FE-SEM (Model: JSM-6701F, Japan). The surface topography of thin films was further analyzed from the AFM images taken by means of the atomic force microscopy (AFM, Digital Instrument, Nanoscope III) operated at room temperature, respectively. AFM images were collected in contact mode on a molecular imaging system using a silicon nitride cantilever. Optical transmission and reflectance measurements were carried out in the wavelength range $350\text{--}850 \text{ nm}$ using Spectrophotometer Systronic Model-119 & Spectroscopic Reflectometer StellerNet Inc., USA. The room temperature PL spectra were recorded using a Perkin–Elmer luminescence spectrometer (model: LS55) equipped with a Xenon flash lamp and a grating to select the source of excitation. The excitation and emission spectra were recorded in the fluorescence mode over the wavelength range $350\text{--}700 \text{ nm}$ using an excitation wavelength of 225 nm . The electrical conductivity, carrier concentration and Hall mobility were determined at room temperature using the Hall effect measurement setup supplied by Scientific Equipments, Roorkee, India. The specific heat capacity and thermal conductivity was measured by C-T meter made by Teleph Pvt. Ltd., France.

3. Results and discussion

3.1. Photoelectrochemical (PEC) characterization

Optimization of preparative parameters for deposition of good-quality adherent thin films is most essential. It is carried out by measuring the maximum values of I_{sc} and V_{oc} of the PEC cell formed with photoactive LZO films, 0.1 M NaOH was used as an electrolyte. Fig. 1 shows the variation of short circuit current (I_{sc}) and open circuit voltage (V_{oc}) with respect to lithium doping concentration. As we increase the Li doping concentration, both I_{sc} and V_{oc} increases gradually attaining a maximum value of $I_{sc} = 0.452 \text{ mA}$ and $V_{oc} = 0.472 \text{ V}$ up to 1 at% Li doping and then decreases. Because too much lithium is not soluble in ZnO lattice and segregates probably in the grain boundary. The decreased values are attributed to the replacement reaction of the Li interstitials as follows [22]:

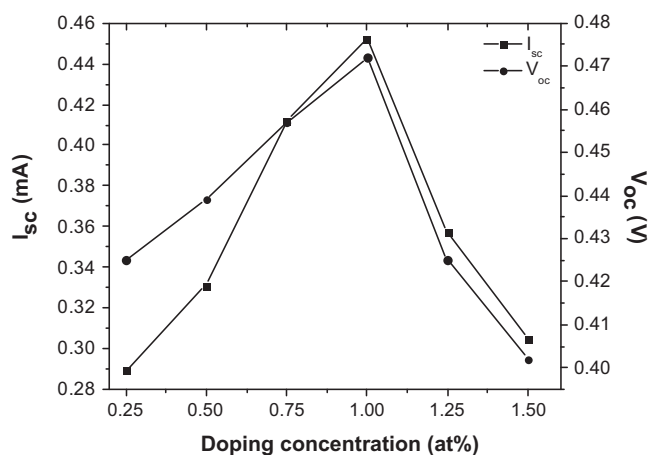


Fig. 1. Variation of I_{sc} and V_{oc} with Li-doping concentration.

3.2. X-ray diffraction (XRD) study

X-ray diffraction patterns of LZO thin films deposited for various Li doping concentrations at optimized substrate temperature $450 \text{ }^\circ\text{C}$ are shown in Fig. 2. Comparison of standard and observed 'd' values of LZO thin films is carried out using of Joint Committee for Powder Diffraction Standards (JCPDSs) card No. 05-0664. It is noticed that the films are polycrystalline and agrees with the hexagonal (wurtzite) crystal structure with strong orientation along the (002) plane. The intensity of diffracted plane increases with Li doping concentration up to 1 at% suggesting improvement in crystallite alignment along c -axis. In addition to that, the intensity of the diffraction peaks is seen to decrease with increasing doping concentration, implying the degeneration of film crystallinity at higher doping concentrations. Some weak reflections such as (100), (101), (102), (110), (103) and (112) have also been observed but with relatively small intensities. No extra secondary phases related to Zn or Li compounds are observed even at high [Li/Zn] content.

The crystallite size (D) is calculated from the full width at half maximum (FWHM) of the diffraction peaks with the Scherer's equation [23]. The average crystallite size of the LZO thin films is increases up to 1 at% doping concentration and then decreases as seen in Fig. 3. Average crystallite size varies from 46 to 59 nm.

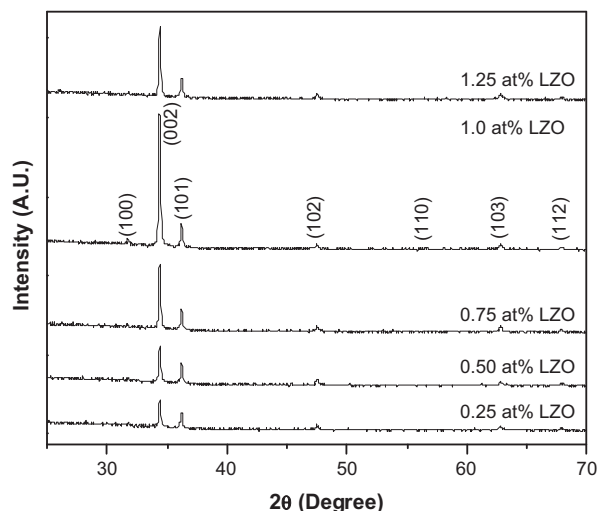


Fig. 2. X-ray diffraction patterns of Li-doped ZnO thin films.

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