



Investigation of structural, optical and luminescent properties of sprayed N-doped zinc oxide thin films

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ABSTRACT

N-doped ZnO (NZO) thin films are synthesized via spray pyrolysis technique in aqueous medium treating zinc acetate and N,N-dimethylformamide as precursors. Influence of N doping on structural, optical and luminescence properties have been investigated. Films are nanocrystalline having hexagonal crystal structure. Raman analysis depicts an existence of N–Zn–O structure in NZO thin film. XPS spectrum of N 1s shows the 400 eV peak terminally bonded, well screened molecular nitrogen (γ -N₂). Lowest direct band gap of 3.17 eV has been observed for 10 at% NZO thin film. The UV, blue, and green deep-level emissions in photoluminescence of NZO films are due to Zn interstitials and O vacancies.

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1. Introduction

Zinc oxide is having a huge impact on materials science because of its high exciton binding energy (60 meV), wide band gap (3.25 eV) and high transparency. It is a promising material that could be applied in many fields such as transparent conductive contacts, solar cells, laser diodes, ultraviolet lasers, thin films transistors, piezoelectric devices and photocatalyst [1–4]. Nature provides a multiplicity of materials, architectures, systems and functions with many inspiring properties such as sophistication, miniaturization, hierarchical organizations, adaptability and environment-response. Mimicking the elaborate architectures and basic principles to design and make more reliable and efficient materials or systems is highly appealing. One of the most promising materials that has been synthesized is N-doped ZnO (NZO). Since its pioneering work, NZO has received a lot of attention because the implantation of nitrogen modifies the electronic structure by introducing localized states to the top of the valence band, narrowing the band gap.

Transparent conducting oxide (TCO) materials are naturally n-type degenerate semiconductors and the lack of a high quality p-type TCO always has been the main obstacle before the fabrication of a fully transparent devices. Among the candidates of shallow acceptors, nitrogen is the most tried one due to its nearest-neighbor bond length of 1.88 Å that is similar to the Zn–O

bond length of 1.93 Å [5]. Although successful reports have been made in the preparation of ZnO by nitrogen using various deposition methods such as sputtering [6], chemical vapor deposition, MOCVD [7], PLD [8] and spray pyrolysis [9,10], some doubts emerge since most of the reported data refer to high resistive films. Moreover, it is difficult to find a metal with a work function high enough to make the proper ohmic contact. So, it is very difficult to prepare a high quality N-doped ZnO due to self compensation effect and inactivation of the acceptor dopants in the ZnO films [11]. Among the abundant deposition methods, spray pyrolysis is a viable method to prepare stable and conductive films, due to its low density of oxygen vacancy and consequently limited hydrogen compensation after film formation [9]. Spray parameters such as substrate temperature, solution concentration, solution quantity, doping concentration play important role on the film properties. It provides easy way to dope any element in any proportion into the host lattice with a meager quantity of solute. Doping concentration enhances the electrical conductivity due to generation of degenerate semiconductors, incorporation of defect states etc. In this paper, the influence of nitrogen doping on the structural, morphological, compositional, optical, luminescence properties of spray deposited NZO thin films in aqueous media have been discussed.

2. Experimental

Nitrogen doped zinc oxide thin films were prepared onto the corning glass substrates by using chemical spray pyrolysis technique in aqueous medium. To deposit NZO thin films, zinc acetate

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($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, AR grade, 98.8% pure) supplied by HIMEDIA and N,N-dimethylformamide ($\text{HCON}(\text{CH}_3)_2$, AR grade, 99% pure) supplied by THOMAS BAKER were used as initial ingredients. To attain nitrogen doping, N,N-dimethylformamide ($\text{HCON}(\text{CH}_3)_2$) was mixed in to the solution. The $[\text{N}]/[\text{Zn}]$ ratios calculated on atomic percent used in the starting solution were 1%, 5%, 10%, 15% and 20%. It was observed that the $[\text{N}]/[\text{Zn}]$ ratios higher than 20% resulted in degraded films probably due to a reaction of the solution with excess nitrogen. The actual $[\text{N}]/[\text{Zn}]$ ratios in the film were relatively less than in the solution. The resulting 100 cc precursor solution was sprayed onto the preheated corning glass and fluorine doped tin oxide (FTO) substrates of size $0.125 \text{ cm} \times 2.5 \text{ cm} \times 7.5 \text{ cm}$ held at optimized substrate temperature of 450°C through a 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.

The structural properties were studied by a Philips X-ray diffractometer PW – 1710 (λ , 1.5405 Å) using Cu-K α radiation in the range of 20 – 70° . Raman-scattering experiments were performed in air at room temperature with micro Raman system from Jobin Yvon Horibra LABRAM-HR visible within 200 – 1400 cm^{-1} using Argon 488 nm laser as an excitation source. The 600 and 1800 lines/mm gratings – detector: CCD detector was used. XPS spectra were recorded by using an ESCA spectrometer (ULVAC-PHI 5600). The measurements were performed for a freshly cleaved sample surface. The energy resolution of the spectrometer was about 1 eV at pass energy 50 eV. Monochromatized X-ray (K α : 1486.61 eV) from an Al anode was used for excitation. An electron flood gun was employed to compensate for the sample charging under X-ray irradiation. The overall resolution was about 0.5 eV under our experimental conditions. The base pressure in the sample chamber was less than $6.0 \times 10^{-8} \text{ Pa}$ during the measurements. XPS core-levels were calibrated using C 1s peak. The deconvolution of the XPS peaks was performed using Lorentzian fitting. Zn 2p, O 1s, N 1s and valence band lines were systematically recorded. The morphological characterization of the films was observed by using SEM (Model: JEOL JSM 6360, Japan) and 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. All values for feature heights, root mean square (RMS) surface roughness, and surface area were calculated using digital instruments software. Optical transmission and reflectance measurements were carried out in the wavelength range 350 – 850 nm using Spectrophotometer Systronic Model-119 and 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 – 700 nm using an excitation wavelength of 225 nm .

The photoelectrochemical (PEC) cell was fabricated by using a standard two-electrode configuration (Fig. 1), comprising of n-type ZnO deposited onto the FTO substrate as an active photoanode and graphite as a counter electrode. Schematic experimental circuit diagram of PEC cell formed with n-ZnO photoelectrode is shown in Fig. 1. The aqueous 0.1 M NaOH was used as an electrolyte. These two electrodes are fitted in the bakelite holder having thickness 1 cm and diameter 3.5 cm and fixed in cylindrical corning glass cell with capacity 30 cm^3 . The distance between photoelectrode and counter electrode was 0.5 cm and exposed area of UV illumination

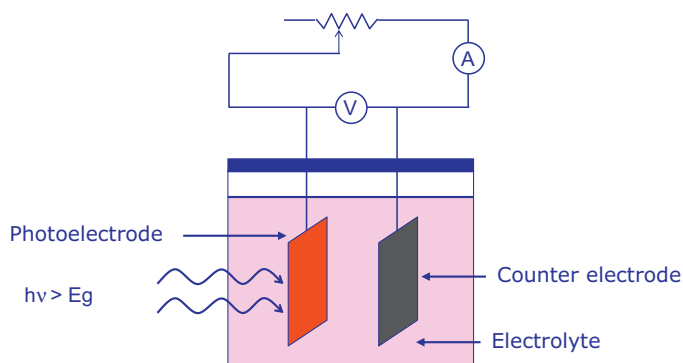


Fig. 1. Schematic diagram of PEC cell.

was 1 cm^2 . Then we measured the short circuit current (I_{sc}) and open circuit voltage (V_{oc}) between photoanode and counter electrode in dark and under illumination.

3. Results and discussion

3.1. Photoelectrochemical (PEC) characterization

The variation of short circuit current (I_{sc}) and open circuit voltage (V_{oc}) as a function of nitrogen doping concentration is as shown in Fig. 2. Both I_{sc} and V_{oc} increases gradually with doping concentration, attains a maximum value ($I_{\text{sc}} = 0.52 \text{ mA}$ and $V_{\text{oc}} = 0.562 \text{ V}$ respectively) at 10 at% N doping and then decreases for higher doping concentrations. This is attributed to the change in metastable N-on-O substitution (N_{O}), which may attract another N to form a (N_2) $_{\text{O}}$ donor or leave the O site to diffuse in the ZnO, at the same time, generate a V_{O} donor [12]. Generally, nitrogen can be substituted inside the ZnO in two forms: atomic nitrogen on oxygen sites (N_{O}) acting as acceptors and molecular nitrogen on oxygen sites (N_2) $_{\text{O}}$ acting as donors. Formation enthalpy of (N_2) $_{\text{O}}$ is lower than (N_{O}) which leads to n-type conduction of NZO thin films. The N–N atoms have strong bonding energy compared to N–Zn bonding energy [13,14]. The improvement in the PEC properties of the doped thin films is due to (i) morphological modifications that enhance the active surface area and (ii) quenching of the defect levels responsible for recombination losses, as compared to the pure ZnO. Upon illumination of junction, the magnitude of V_{oc} increases with negative polarity towards the NZO thin films, indicating cathodic behavior of photovoltage which confirms

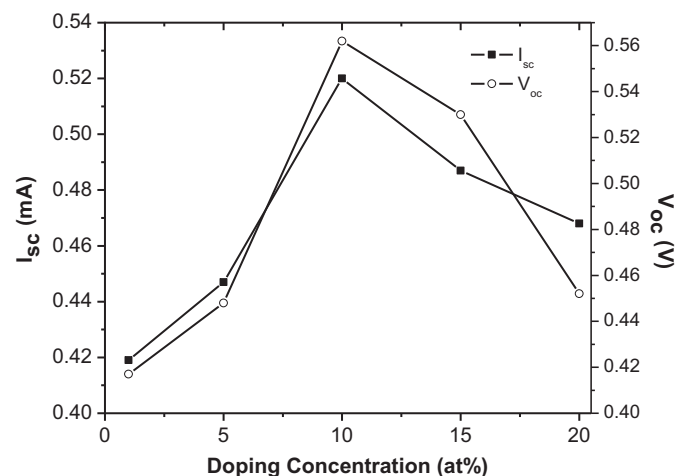


Fig. 2. Variation of I_{sc} and V_{oc} against doping concentration for N-doped ZnO thin films.

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