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Synthesis and characterization of Sb doped ZnO thin films for photodetector application

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ABSTRACT

We report properties of metal–semiconductor–metal (MSM) photoconductive UV detectors based on Sb-doped ZnO thin films. Highly *c*-axis oriented Sb-doped ZnO thin films were prepared by spray pyrolysis technique onto glass substrates. Optical properties and photocurrent measurements were carried out to study optoelectronic properties of Sb-doped ZnO thin films. These films are highly transparent in visible region and exhibit a steep absorption edge at 365 nm. The electrical resistivity measurement showed semiconducting behaviors of Sb-doped ZnO thin films. All Sb-doped ZnO thin films exhibit n-type electrical conductivity. *I–V* characteristics of photodetector devices were analyzed by applying 5 V bias. The 3% Sb doped ZnO photodetector shows higher responsivity of 5.1 A/W at 365 nm under 10 μW/cm^2 photo-illumination. In order to check the maximal (for the rise) or minimal (for the fall) level of photocurrent, the results on photodetector for 30 s ON and OFF cycles of illumination have been reported.

1. Introduction

The wide band gap semiconductors have various applications such as optoelectronic devices, ultraviolet (UV) light-emitting diodes (LEDs) [1], UV detector [2], gas sensor [3], transistor [4], solar cell [5] and water purification [6]. ZnO-based materials are more important for visible-blind ultra-violet (UV) photon detection because of their higher optical transmittance in visible region and superior UV photosensitivity. To tailor the properties of the ZnO photodectros, several doping elements have been used and reported in the literature viz. Ga, In, P, Sn especially for achieving *p*-type doping. But native donor defects in non-stiochiometric ZnO and impurity compensation is hurdle for *p*-type conductivity. There are few reports on the growth of Sb-doped ZnO for UV photodetectors. Therefore, it is crucial and highly desired to develop photodetectors based on novel materials like Sb doped ZnO to effectively detect UV irradiation. Limpijumnong et al. [7] observed that both As and Sb have low acceptor-ionization energies to obtain *p*-type ZnO. Palani et al. [8] have reported on the influence of Sb as a catalyst in the growth of ZnO nano wires and nano sheets. It was observed that Sb ion is substituted on the Zn site without change in the hexagonal wurzite structure. Mandalapu et al. [9] have fabricated homo-junction photodiodes based on Sb-doped ZnO for ultraviolet detection. They observed that the photo carriers were generated from 250 nm and steadily increased up to 350 nm. Xiu et al. [10] have prepared high-mobility Sb-doped *p*-type ZnO thin films on *n*-Si substrates by molecular-beam epitaxy system.

Several thin film deposition techniques, viz. pulsed laser deposition technique (PLD) [11], RF sputtering technique [12], spin coating method [13], chemical vapor deposition method [14], hydrothermal process [15], sol–gel method [16] have been employed to obtain Sb doped ZnO thin films. Many researchers have successfully achieved *p*-type ZnO by mono-doping group V elements such as N, As, P and Ag [17–20].

Among the abundant deposition methods, spray pyrolysis technique is a useful method for obtaining Sb doped ZnO thin films because of its low cost, eco-friendly nature and large area deposition capabilities. It is well known that undoped ZnO have *n*-type conductivity and it is associated with native defects like oxygen vacancies, zinc interstitials, zinc vacancies, and oxygen interstitials etc. [21,22]. This is in contrast Sb shows an effective dopant to often minimized native defects such as V_O and Zn_i and from shallow acceptor complex $Sb_{Zn} - 2V_{Zn}$ [7,23,24]. Therefore, there are only few reports about Sb doped ZnO based UV detectors.

In the present work, we have synthesized undpoed and Sb doped ZnO (SZO) thin films by spray pyrolysis technique. The effect of Sb doping onto structural, morphological, optical and electrical properties has been studied. The photoconductive UV detectors based on a metal–semiconductor–metal (MSM) structure of Sb-doped ZnO thin films was studied.

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2. Experimental

The ZnO thin films were deposited onto the preheated glass substrates using spray pyrolysis technique. The precursor solution was prepared by mixing of 0.1 M zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$) dissolved in a solution containing double distilled water, acetic acid and methanol (25:10:65) and 0.1 M antimony chloride ($SbCl_3$) dissolved in a acetic acid. The resultant precursor solution was sprayed onto preheated glass substrates at optimized substrate temperature of 450 °C [25] for different doping concentration (0%, 2%, 3%, 3.5%). Other preparative parameters viz. spray rate (5 ml/min.), total quantity of sprayed solution (100 ml) and nozzle to substrate distance (32.5 cm) were kept constant for all experiments.

The UV photo detector device was fabricated by using spray deposited ZnO thin films based on metal–semiconductor–metal (MSM) structures. Spacing between the two contact electrodes was 10 mm. The ohmic contacts were made by silver paste onto the Sb doped ZnO layer. Identification of the phase and other related parameters of the Sb doped ZnO thin films were studies by Bruker X-ray diffractometer Model D2: phaser with Cu Kα (λ = 1.5406 A°) radiation in the span of 20–80°. The microstructure of the films was studied by using scanning electron microscopy (SEM) JEOL JSM-6360. Thickness of thin films on glass was calculated from the interference patterns of the reflection spectra measured using a Steller Net Inc. USA reflectometer equipped with UV–Vis light source and CCD detector. Absorption and transmission spectra of the film were recorded at room temperature by using a Shimadzu UV–Visible spectrophotometer. The electrical resistivity measurement of the film was carried out by using the two-point probe method in the temperature range 300–550 K. The type of electrical conductivity was determined from thermoelectric power unit in the temperature range 30–130 K. Current–voltage *I–V* characteristics were recorded with the AMEL instruments model-2059 potentiostat by sweeping the bias voltage from 0 to 5 V across the junction. The time response was measured by switching on and off UV light illumination at 30 s interval.

3. Results and discussion

3.1. X-ray diffraction studies

The X-ray diffractogram of undoped and Sb doped ZnO thin films in the 2θ range of 20–80° is shown in Fig. 1. All the films are polycrystalline and fit well with hexagonal (wurtzite) crystal structure (JCPDS card No. 075-1526). No extra peaks are observed corresponding to any other phases. The ZnO (002) diffraction peak shows the preferred orientation of the films along the c-axis direction. The intensity of the (002) plane (2θ = 34.74°) increases with increasing Sb concentrations up to 3%, which then decreased for higher doping concentrations. This may be due to the incorporation of Sb atom into ZnO lattice substitute for Zn site [26]. This result suggests that the Sb ion may be doped into ZnO crystals lattice without change in the wurtzite structure. The lattice constants *a* and *c* were calculated by the following relation [27].

$$\frac{1}{d_{(hkl)}} = \frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right) + \frac{l^2}{c^2} \tag{1}$$

where *d* is the interplanar spacing and *h*, *k*, *l* are crystal Miller indices respectively. The lattice parameters calculated from the XRD pattern for ZnO thin film (*a* = 3.23 A° and *c* = 5.21 A°) match well to the lattice constants *a* = 3.22 A° and *c* = 5.20 A° given in the standard data (JCPDS, 01-075-1526). The crystallite size of Sb-doped ZnO thin films was calculated by using Scherrer formula, [28].

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{2}$$

where *D* is crystallite size, λ is the of X- ray wavelength of Cu Kα line, β is the Full width at half maximum of the reflection peaks, θ is the Bragg angle. It is seen that the average crystallite size of ZnO thin film is of the order of 50 nm. No measurable change in the crystallite size is observed as all samples are deposited at same experimental conditions except Sb concentration.

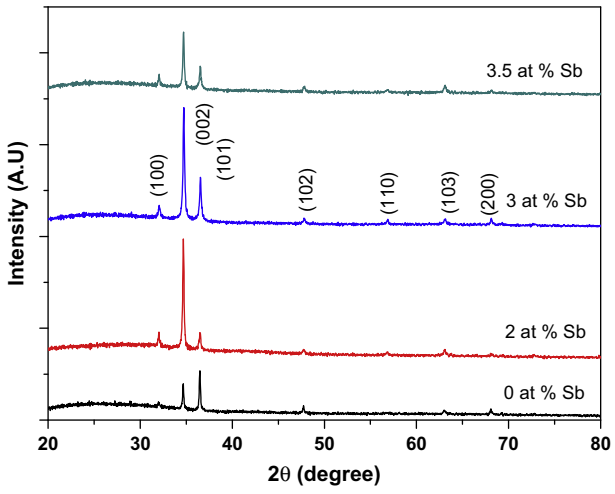

Fig. 1. X-ray diffraction patterns of pure and Sb-doped ZnO thin films.

3.2. Morphological studies

Fig. 2 shows surface morphology of Sb-doped ZnO thin films deposited at different Sb concentrations. SEM images depict that substrate is well covered with large number of compact grains which are uniformly distributed. As Sb doping concentration increases the grain size decreases and grain number increases due to increase of metal nucleation centers which confirms the enhancement in crystallinity. At 3 at.% Sb-doped ZnO film, compact and steeply organized grains are observed.

3.3. Optical properties

The optical transmission and reflectance spectra of undoped and Sb doped ZnO thin films are shown in Figs. 3 and 4 respectively. The films are highly transparent in visible region and highly absorbing in UV region. The average transmittance of the films in the visible region is about 90%. A steep absorption edge is observed at about 365 nm for all the films. Films are less reflecting and exhibit the interference in the spectra due to their specular nature. The average thickness calculated from reflectance spectra of deposited thin film is in the range 250–300 nm at different doping concentrations. The optical absorption of thin film was calculated by using following relation [29].

$$\alpha h\nu = A(h\nu - E_g)^n \tag{3}$$

where α is the absorption coefficient, *A* is the edge width parameter, '*hν*' is the incident photon energy, E_g is the energy difference between the top of the valence band and the bottom of the conduction band, $n = 1/2$ for direct transition and $n = 2$ for indirect transition. The Fig. 5 shows that variation of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for Sb-doped ZnO thin films. The direct band gap energy was determined by extrapolating the linear part of the plot to zero absorption coefficient ($\alpha = 0$) and is about 3.29 eV for undoped