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Investigation of UV photoresponse property of Al, N co-doped ZnO film

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ABSTRACT

Al, N co-doped zinc oxide thin films were prepared using sol–gel assisted spin coating method with a range of nitrogen (N) doping ($x = 0, 1, 2$). The deposited films were characterized through X-ray diffraction, UV–visible spectroscopy, photoluminescence spectroscopy and hall measurements to find structural, optical and electrical properties. The X-ray diffraction pattern was confirmed the existence of polycrystalline nature with wurtzite structure. The strong band emission and green emission peaks have been observed in Al, N co-doped films. The nitrogen undoped film demonstrated n-type conductivity and nitrogen doping brings p-type conductivity with maximum hole concentration of 8.111×10^{16} cm^{-3}, carrier mobility of 9.965 cm^2/V.s for higher nitrogen doped film ($x = 2$). The UV photo responsivity (7.17×10^{-5} A/W) and gain (724.36×10^{-5}) of photo detector has been improved by a one order of magnitude in low nitrogen doping and decay time has been reduced drastically from 58.27 s to 10.32 s. These results demonstrated that the improved responsivity and decay time by 1 at% of nitrogen doping.

1. Introduction

The direct and wide band gap semiconductor materials gained more interest due to its potential application in electronic and optoelectronic applications such as short wavelength light emitting, laser diodes and UV photodetector. Due to large wide band gap (3.4 eV) and higher free exciton energy (60 meV) of ZnO have gained much attention towards those applications [1–4]. The fabrication of ZnO based light emitting and laser diodes needed both n-type and p-type ZnO. The n-type conductivity in ZnO was achieved without any doping and further carrier concentration improved with doping. The commercialization of ZnO based optoelectronic device is inadequate due to difficulties in the fabrication of stable p-type conductivity. This difficulty arises due to self-compensation effect of native defects, limited solubility and inactivation of the acceptor dopant in ZnO films. The existence of native defects such as zinc interstitials (Zni^{2+}) and oxygen vacancies (V_0^{2+}) show n-type conductivity in as prepared film [5]. In recent years, numerous growth and post-treatment techniques were used to fabricate stable p-type ZnO with different dopant [6] such as group V elements such as N, P, As, and Sb [2,6–10] or group I elements like Ag [11], Li [12], as well as co-doping group III–V elements like Al–N [10], In–N [13] and Ga–N [14]. Among these, nitrogen doping is a promising one to substitute for oxygen in ZnO because of similar ionic radii [15]. Recently researchers have used co-doping technique to achieve stable and higher hole concentration by simultaneously doping of nitrogen with reactive group III donor elements. The doping of the reactive donor element has increased the solubility of nitrogen in ZnO crystal. Aluminum is more suitable than Ga and In because of the superior stability due to strong Al–N and Al–O bonds and low cost, abundant [16].

Ultraviolet (UV) photo detector has received interest in recent years due to their potential application in space, flame detection, ozone monitoring, military and medical diagnostic applications [17]. For several decades, the semiconducting materials such as TiO_2, ZnO, SnO_2, ZnS, Nb_2O_5 and GaN, GaAs, Si were used to fabricate the UV photodetector. The visible and infrared response of small band gap materials like silicon and GaAs hinders their application in UV detector which was rectified by using a wide band gap semiconducting materials such as III–V nitrides, zinc oxide, silicon carbide, diamond. The ZnO based photodetector attract huge interest because of wide band gap, large exciton binding energy, high radiation hardness and higher visible blindness at room temperature. The optical and electrical property of the ZnO thin film was changed from pure ZnO by doping. Basak and Dutta reported the Al, N co-doped p-type ZnO/n-Si heterojunction photo detector, which showed rectification ratio of 10 at 4 V [18]. Huang et al. reported the p–n ZnO homojunction based photodetector with that report they prepared Al, N co-doped ZnO thin film on Al doped ZnO surface by RF reactive magnetron sputtering method. The fabricated homojunction photo detector showed good rectification at lower voltage [19]. The previous reports on Al, N co-doped ZnO and ZnO based p–n homo/hetro junction device also not showing any photo response characteristics of co-doping. Therefore, in this

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paper, we report the influence of nitrogen doping concentration on photo response characteristics of co-doped ZnO films.

In this report, we fabricated Al and N co-doped p-type ZnO thin film by simple and cost effective sol–gel assisted spin coating method. The effects of nitrogen doping on structural, optical, electrical and optoelectronic properties of p type ZnO thin films were studied in detail.

2. Experimental details

Al, N co-doped ZnO thin film was deposited on a glass substrate by sol–gel and spin coating method [20]. Zinc acetate dihydrate ($C_4H_6O_4Zn{\cdot}2H_2O$), aluminium nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$) and ammonium acetate ($C_2H_7NO_2$) were used as a source for Zn, Al and N respectively. In this experiment, nitrogen doping was varied with fixed Al and Zn atomic ratio by changing the amount of ammonium acetate. A sol was prepared by mixing stochiometric amount of zinc acetate, aluminium nitrate and ammonium acetate in isopropyl alcohol with constant stirring at 60 °C for 30 min in a hotplate and then diethanolamine ($C_4H_{11}NO_2$) was added into that solution as a stabilizer. The atomic ratio of Zn/N/Al was varied by 1:x:0.02 (x = 0, 1, 2). After adding the stabilizer solution turns into transparent and sol was aged for 1 day at ambient condition. The transparent sol was spin coated on the cleaned glass substrates and dried at 100 °C in the air for 5 min. This process was repeated for 10 times in order to obtain desired thickness of 250 nm. The spin coated samples were annealed at 450 °C for 1 h in a muffle furnace at temperature gradient of 5 °C/min.

The crystalline structure of Al–N co-doped thin films was analyzed by X-ray diffractometer (XRD) operated at 40 kV and 40 mA with Cu Kα radiation in the range of 10–80° with a step of 0.02°. The optical properties like absorbance and transmittance of the Al–N co-doped ZnO films were measured by UV–visible spectrometer (UV2550, Shimadzu). Photoluminescence spectra of the films were measured by JASCO FP-6500 photoluminescence spectrometer with excitation wavelength of 325 nm at room temperature. The carrier concentration and Hall mobility were analyzed by DC Hall measurements (Lake Shore 7500, USA) at room temperature under a magnetic field of 5 kG using the Van der Pauw method. The photocurrent and dark current of the fabricated thin films were measured at probe station attached with semiconductor parameter analyzer (Agilent, 1500A).

3. Results and discussion

3.1. Structural analysis

The crystal structure and phase of the fabricated film was analyzed through X-ray diffraction pattern and resultant pattern was shown in Fig. 1. The fabricated film showed the polycrystalline nature and has a predominant orientation along the *c*-axis of the wurtzite structure for different nitrogen doping (x = 0, 1, 2 at%). The peaks are indexed on the basis of the JCPDS file (89-1397) and no other impurity peaks like AlN, Al_2O_3, Zn_3N_2 were detected in the XRD pattern. The peaks are observed at 2θ = 31.71, 34.33, 36.20, 47.58, 56.73, 63.08 and 68.12° which corresponds to the (100), (002), (101), (102), (110), (103) and (200) planes of the ZnO wurtzite structure respectively. The intensity of c-plane (002 peak) was gradually decreased with doping of aluminium and nitrogen compared to undoped film which indicates the reduce of crystallinity of the film. The crystallite size of the film was calculated for predominant peaks to analyze the doping effect using Debye Scherrer's formula (DS) [13]

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where λ, β, θ are the X-ray wavelength (1.54056 Å), full width half maximum (FWHM) and Bragg's diffraction angle respectively. The calculated crystallite size values are 13.62, 13.68, 15.62 nm for the doping level of x = 0, 1, 2 respectively. The crystallite size was increased with increasing nitrogen doping in the ZnO due to the stress related strain growth [21].

3.2. Optical studies

Fig. 2 shows the optical transmittance spectra of Al–N co-doped ZnO films with different doping level (x = 0, 1 and 2). The result showed that the all films have above 85% of optical transmittance in the visible region. We have calculated the band gap energy of films from absorbance spectrum using Tauc relationship [22].

$$\alpha h\gamma = A(h\gamma - E_g)^n \tag{2}$$

We assumed that the optical absorbance coefficient (α) corresponding to direct band of ZnO wurtzite structure, so n value is taken as 2. The calculated optical band gap was 3.166, 3.154, 3.103 for x = 0, 1, 2 respectively. The optical band gap was reduced by increasing the dopant level from 0 at% to 2 at% which is shown in Fig. 2 insets.

The photoluminescence spectra of the as prepared films are presented in Fig. 3. All samples clearly exhibited near UV emission around 3.12 eV and strong deep level emission (DLE) centered around 1.78 eV. The near UV emission is related to the near band emission (NBE) of ZnO which is originated from the transition of free exicton from the localized level below the conductance band to valence bond [23]. The localized level emerged due to lattice disorder created by free impurity atoms, various defects, surface and interface. The near UV emission peaks shift from 3.12 to 3.10 eV while increasing the nitrogen concentration. Because of

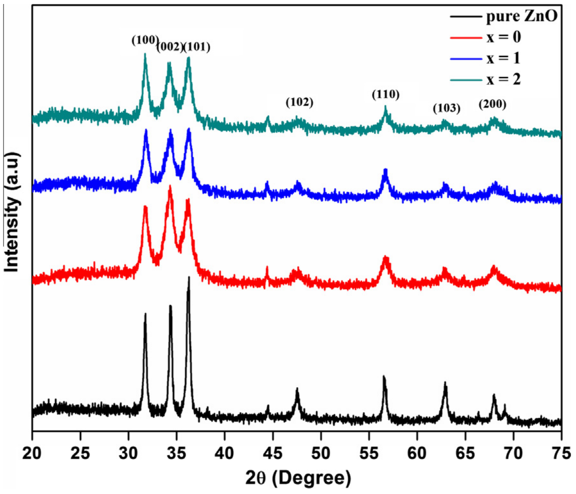

Fig. 1. XRD pattern of undoped and co-doped ZnO thin films with different nitrogen doping (x = 0, 1, 2).

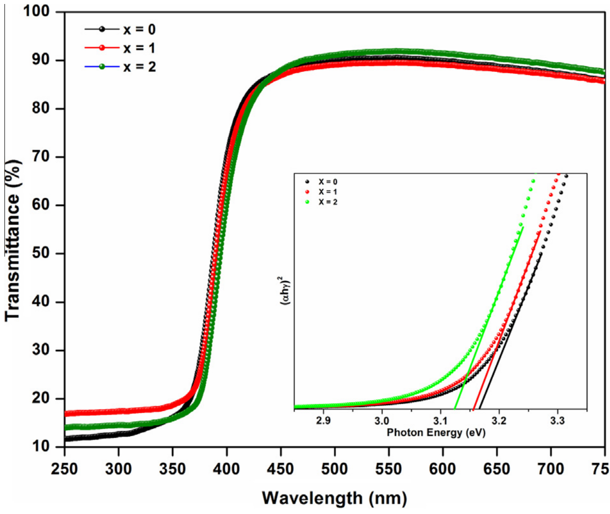

Fig. 2. Optical transmittance spectra of the co-doped ZnO thin films with different nitrogen doping. The inset shows the band gap calculation using Tauc model.