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Electrical and optical properties of p-type codoped ZnO thin films prepared by spin coating technique

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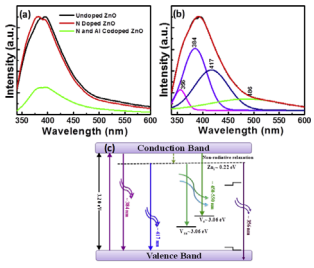
HIGHLIGHTS

- The p-type ZnO thin films synthesized by sol–gel method.
- The average transmittance of the ZnO films is observed 87%.
- A strong UV emission was observed for ZnO thin films.
- Maximum carrier concentration is observed $\sim 6.83 \times 10^{19}$ cm^{-3}.

GRAPHICAL ABSTRACT

Photoluminescence spectra of undoped, doped and co-doped ZnO thin film **(b)** De-convoluted PL curve of the undoped ZnO **(c)** A possible band diagram drawn from the fitted data.



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ABSTRACT

Undoped, doped and codoped ZnO thin films were synthesized on glass substrates using a spin coating technique. Zinc acetate dihydrate, ammonium acetate and aluminum nitrate were used as precursor for zinc, nitrogen and aluminum, respectively. X-ray diffraction shows that the thin films have a hexagonal wurtzite structure for the undoped, doped and co-doped ZnO. The transmittance of the films was above 80% and the band gap of the film varied from 3.20 eV to 3.24 eV for undoped and doped ZnO. An energy band diagram to describe the photoluminescence from the thin films was also constructed. This diagram includes the various defect levels and possible quasi-Fermi levels. A minimum resistivity of 0.0834 Ω-cm was obtained for the N and Al codoped ZnO thin films with p-type carrier conductivity. These ZnO films can be used as a window layer in solar cells and in UV lasers.

1. Introduction

Zinc oxide (ZnO) is one of the most attractive II–VI group semiconductors, a versatile material having a wide band gap (3.37 eV) and a large excitation binding energy (60 meV) [1,2]. The high electron mobility, high thermal conductivity, wide and direct band gap and large excitation binding energy make ZnO stable for a wide range of applications including sensing, photo detectors, light emitting diodes and laser diodes [1–7]. ZnO is considered to be a very promising material for optoelectronic devices [1–9], particularly in the case of the next generation of inorganic light-emitting diodes and lasers [10]. ZnO appears as a potential substitute for GaN and its derivatives whose production remains costly and polluting. Unfortunately, the advent of such an innovative technology suffers from the lack of easily obtainable p–n homojunctions. Until now, producing a stable p-type ZnO remains a great challenge, and the fabrication of reliable p-type thin films is really a bottleneck, which delays the launching of ZnO based

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optoelectronic devices in industry. Zinc oxide exhibits naturally an n-type conductivity that originates from the incorporation of "hidden" hydrogen atoms within the ZnO host lattice to give rise to a large amount of shallow donor levels [11]. The growth of p-type ZnO thin films is a very difficult task to perform but also a very important problem to solve. There is a number of possibilities accounting for the conductivity of ZnO thin films [12]. The suitable shallow acceptors may be less soluble than the lowest achievable concentration of donors. The impurities that yield shallow acceptors on one site may act as donors when on the other site or when at interstitials, and acceptors may have a natural tendency to pair with native defects or background impurities to form electrically inactive complexes. The doping of p-type doping materials (N, P, Sb) is difficult due to its low solubility of the dopants and the resistance to p-type doping is due to the self-compensation of shallow acceptors resulting from various naturally occurring or spontaneously generated donor defects such as oxygen vacancies or interstitial zinc [13–15]. Among the possible p-type doping agents, N is regarded as the most effective, considering its size, energy level and compensation effect [16,17]. Lots of literature is available on the growth of p-type ZnO. However, many of them reported unrealistically high hole mobilities and hole concentrations [18,19]. Theoretical treatment of this important subject has also appeared [20,21]. Several research groups have proposed a co-doping method to obtain p-type ZnO [22,23]. The co-doping method using acceptors and reactive donors simultaneously was proposed to increase the solubility of nitrogen in ZnO. ZnO thin films can be obtained by different methods such as chemical vapor deposition (CVD) [24], pulse laser deposition (PLD) [25], spray pyrolysis [26], magnetron sputtering [27] and sol–gel [28]. Sol–gel technique has many advantages in preparing ZnO films, such as strong *c*-axis orientation, ease of compositional modifications, large films, simplicity of working principle, low cost, and low annealing temperature [29,30]. The sol–gel method is therefore prevalent today and ideal for exploratory research.

In the present work undoped, N doped and Al–N codoped ZnO thin films were synthesized on plane glass substrates by the sol–gel method. The effect of doping and co-doping on structural, electrical and optical properties of ZnO were investigated.

2. Experimental details

All the reagents used in the present work for the chemical synthesis were of analytical grade. ZnO doped with Nitrogen (ZnO:N) and co-doped with Al (Zn:N:Al) thin films were formed for different precursor solution by varying the atomic concentration. Zinc acetate dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$, Alfa Aesar], ammonium Acetate [CH_3COONH_4, Alfa Aesar] and aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$, Alfa Aesar] were used as the source for Zn, N and Al respectively. Zinc acetate dehydrate was first dissolved in 2-methoxy Ethanol [$(CH_3)_2CHOH$, Qualigens] with mono ethanol amine (MEA) [$H_2NCH_2CH_2OH$, Alfa Aesar] which was used as a stabilizer. The molar ratio of MEA to zinc acetate was kept to 1:1, ammonium acetate and aluminum nitrate was mixed in required atomic ratios of Zn to N (1:3 at%) and Zn to Al (1:0.3 at%). The resultant solution was stirred for 2 h and then the temperature was increased to 60 °C and kept in the stirrer for 1 h. The resultant was a clear and homogeneous solution which was filtered using filter paper and kept for 72 h. Using a spin coater the films were deposited on ultrasonically clean glass substrates at rpm 2500 for 30 s. The films were preheated at 230 °C in a furnace to evaporate the solvent and then annealed at 450 °C for 1.5 h in a microprocessor controlled muffle furnace.

The crystalline structure of the undoped, doped and co-doped thin films was analyzed using a X'pert Pro diffractometer. The surface morphology was recorded by using a EVO-40 ZEISS. The Optical transmittance spectra were collected using a UV–vis-IR spectrophotometer (Schimadzu-3600, Japan). The photoluminescence (PL) data was recorded using a F-4600 FL spectrophotometer. Hall measurement was done using a HL-5500. All measurements were carried out at room temperature. All characterizations have been done at room temperature.

3. Results and discussion

3.1. X-Ray diffraction (XRD) analysis

The XRD was used to analyze the growth orientation and crystallite size of ZnO thin films. The XRD patterns of the thin films synthesized by the sol–gel method on glass substrates are shown in Fig. 1. Three diffraction peaks (101), (002) and (101) of the ZnO belonging to a hexagonal wurtzite crystal structure (JCPDS card no. 36-1451) were observed for the undoped thin films [31]. For the N doped ZnO thin films only the (002) peak is observed. Three diffraction peaks (101), (002) and (101) was again observed for the co-doped sample (Zn:N;Al). The N doped ZnO thin films have a hexagonal wurtzite structure and most of the crystallites were having a strong *c*-axis orientation along the (002) plane. It means with the N doping the stoichiometry of the films improved as well as the crystalinity quality. While for codoped ZnO thin films it shows a polycrystalline nature of the crystallites. The polycrystalline nature could be ascribed to the imbalance between the Al and N concentrations. The crystallite size was determined by Scherer's equation [32].

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

where, K is the constant taken to be 0.94, λ is the wavelength of X-Ray used (λ_{Cu}=1.54 Å) and β is full width half maxima (FWHM). The crystallite size of undoped ZnO was 21 nm, while it was 34 nm for N doped and 30 nm for co-doped ZnO. A strong peak was observed (002), satisfying the hexagonal equation;

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

The *c*/*a* ratio is 1.65. Hence the structure of ZnO and N doped is hexagonal wurtzite.

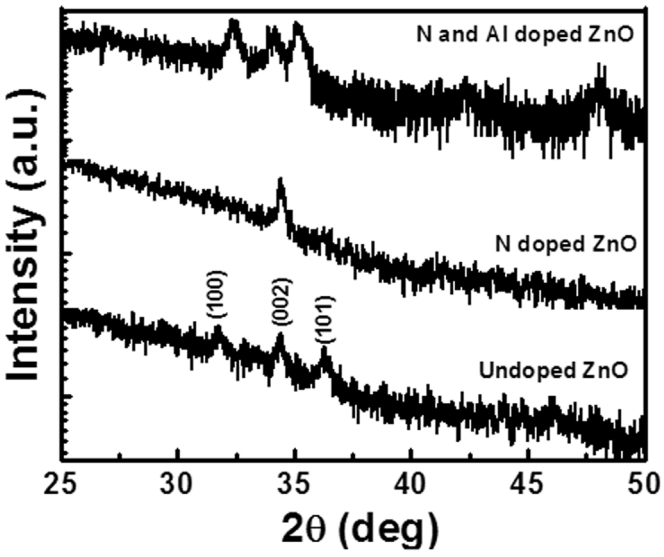

Fig. 1. XRD pattern of undoped, doped and co-doped ZnO thin films.