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Synthesis, Structural and Electrical characterization of codoped p-type ZnO Thin Films

Pathak, Trilok Kumar[1]; Pal, Pankaj K.[1]; Gupta, Himanshu[1]; Matta, Gagan[2]; Kumar, Ajendra[3]; Kumar, R.[1] and Purohit, L. P.[1]

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Abstract

The fabrication of p-type ZnO is very difficult due to its self compensation of shallow accepter resulting from various naturally occurring donor defects such as oxygen vacancies or interstitial zinc. Al-N codoped ZnO thin films were fabricated on glass substrate by sol-gel method. The sol is prepared with $Zn(CH_3COO)_2.2H_2O$, CH_3COONH_4, $Al(NO_3)_3.9H_2O$, 2 methoxyethanol and monoethanolamine (MEA). The resistivity, mobility and carrier concentration were investigated using Hall measurement (HL-5500PC). The p-type Al-N codoped ZnO thin films were deposited on glass substrate by sol-gel method. The carrier concentration decreased 4.72×10^{19} to 3.03×10^{18} for 0.1 to 0.3 Al concentration, hall mobility also decreased and resistivity increased. These thin films are used in optoelectronic devices and solar cell. The current-voltage characteristics are also discussed.

Keywords: Thin films | analytical instrumentation | solar energy

For correspondence:

[1]Department of Physics;
[2]Department of Zoology and Environmental Science;
[3]Department of Mathematics and Statistics,
Gurukula Kangri University, Haridwar, India
Email: **tpathak01@gmail.com**

Introduction

ZnO has potential to provide the key for many future applications due to its optical and electronic properties (Pathak *et al.*, 2015). ZnO has a wide band gap (3.37 eV) and a large excitation binding energy (60 meV). It shows a native n-type conduction resulted from its non-stoichiometry and can be easily doped to obtain a high conductivity with group III elements such as Al, Ga *etc*. The high doping levels are difficult due to the background n-type doping orienting from the presence of H-impurity, 'O' vacancies, Zn interstitials and

due to the large accepter activation energies or low solubility of commonly used N, P, As, Sb. Codoping with two potential acceptors N and As or N and Al are used due to higher solubility of the forming N-Al-N complex. ZnO thin films can be obtained by different methods such as spray pyrolysis, chemical vapour deposition (CVD), RF magnetron sputtering, Sol-gel techniquehas 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. The sol-gel method is therefore prevalent today and ideal for exploratory research.

In this work we have deposited codoped Zn:N:Al (1:3:0.1, 1:3:0.2, 1:3:0.3) thin films on glass substrate by sol-gel technique using spin coater and demonstrated that dual codoping is a promising method to produce low resistivity and stable p-ZnO thin films with high hole concentration.

Experimental Details

All the reagents used in the present work for the chemical synthesis were of analytical grade. ZnO co-doped with Al (Zn:N:Al) thin films were formed for different precursor solution by varying the atomic concentration. Zinc acetate dehydrate [$Zn(CH_3COO)_2.2\ H_2O$, Alfa Aesar], ammonium Acetate [CH_3COONH_4, Alfa Aesar] and aluminum nitrate [$Al\ (NO_3)_3.9H_2O$, 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 (1:0.1 to 0.3 at %). The resultant solution was stirred for 2 h, then temperature was increased to 60°C and kept in stirrers for 1 h. Resultant clear and homogeneous solution was filtered using filter paper and kept for 72 h. Now using 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 furnace to evaporate the solvent and then annealed at 450°C for 1.5 h in microprocessor controlled muffle furnace.

The crystalline structure of the undoped and codoped thin films was analyzed using X'pert Pro diffractometer. The surface morphology was recorded by using EVO-40 ZEISS. The Optical transmittance spectra were collected using a UV-VIS-IR spectrophotometer (Schimadzu-3600, Japan). Hall measurement was done using HL-5500. Current-Voltage characteristic was study by semiconductors characterization system (SCS-4200, Keithley). All measurements were carried out at room temperature.

Results and Discussion

X-Ray diffraction (XRD) analysis

The XRD was used to analyze the growth orientation and crystallite size of ZnO thin films. The XRD graph of the thin films synthesized by sol-gel method on glass substrate is shown in Fig.1. Three diffraction peaks (101), (002) and (101) of ZnO belonging

to a hexagonal wurtzite crystal structure (JCPDS card No. 36-1451) were observed for the undoped thin films. Three diffraction peaks (101), (002) and (101) was again observed for co-doped sample (Zn:N;Al) at Al at % 0.3. Therefore, the structure same for codoped ZnO as undoped due to the internal defects of ZnO. The amorphous ZnO thin films were obtained after codoping of N and Al. Strong peak was observed (002), satisfying the hexagonal equation;

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

The c/a ratio is 1.65. Hence the structure of ZnO and N doped is hexagonal wurtzite. The particle size was determined by Scherer's equation [19].

$$D = \frac{K\lambda}{\beta\cos\theta} \qquad (2)$$

where K is the constant taken to be 0.94, λ is the wavelength of X-Ray used (λ_{Cu} =1.54 A$^{\circ}$) and β is full width half maxima (FWHM). The crystallite size of undoped ZnO is 21 nm, while it is 30 nm for 0.3 at% co-doped ZnO.

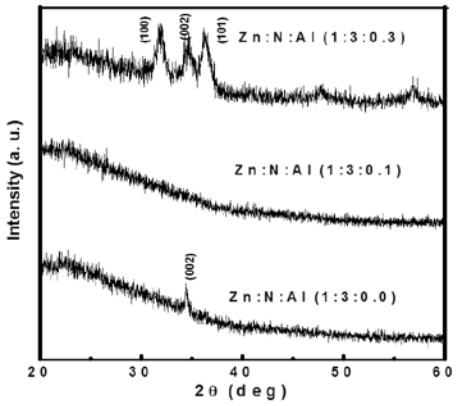

Fig. 1: XRD pattern of co-doped ZnO films

Surface morphology and component analysis

SEM was used to determine microstructure of thin films. SEM image of undoped, and codoped ZnO thin films are shown in Fig. 2. From micrograph it is observed that there is growth of small square shape crystallites. The grain size increases continuously for undoped, codoped ZnO samples.

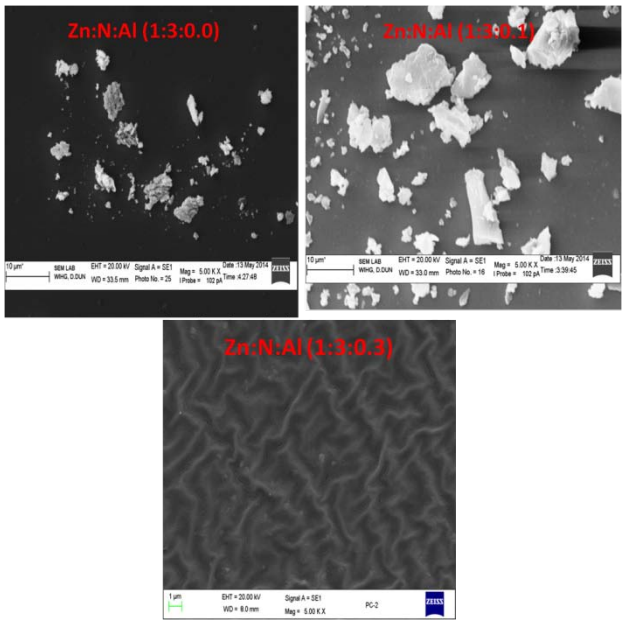

Fig. 2: SEM image of co-doped ZnO films

Electrical properties

The variation in resistivity (ρ), carrier concentration (n) and Hall mobility (μ) of ZnO films with codoping is shown in Fig.3. The resistivity of films decreases as the doping concentration increases, correspondingly carrier concentrations are found to increase. The increased carrier concentration is attributed to the free electrons/hole donated by doping ions in ZnO. Hence, the presence of two donors improved the carrier concentration of the ZnO films. The minimum resistivity

with maximum carrier concentration is observed for N and Al codoped ZnO with p-type conductivity. The Hall mobility of ZnO films is strongly dependent on doping concentration and decreases with increase in doping concentration. The mobility decreases gradually with the increases in doping concentration in the films from 9.80 $cm^2 V^{-1} S^{-1}$ to 1.54 $cm^2 V^{-1} S^{-1}$. The decrease in mobility is due to the increase in the ionized impurity scattering mobility. The ionized impurity scattering mobility is inversely proportional to carrier concentration. If the value of carrier concentration increases, the value of mobility decreases. For undoped ZnO, n-type conductivity is observed, while p-type conductivity is observed for doped and codoped ZnO thin films.

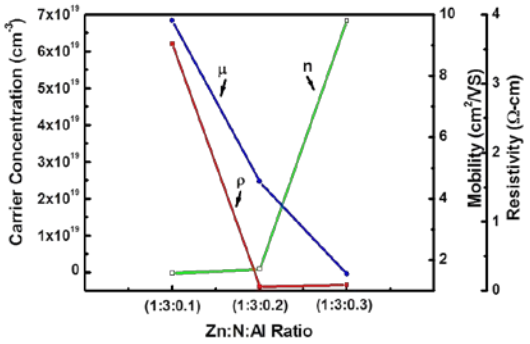

Fig.3: Hall probe result of co-doped ZnO films

To confirm the carrier type of thin films current voltage characteristics are carried out using semiconductors characterization system (SCS-4200, Keithley). The effect of doping and codoping on I-V results of ZnO films is shown in the Fig 4. The ohmic behavior is confirmed by the fairly linear I-V curve for all thin films. The symmetry of I-V characteristics with ZnO structure shows that ZnO film has n-type conduction as shown by hall measurement results. On the other hand the I-V measurements of codoped film show consistent polarity with low resistance which confirms p-type conductivity. It is obvious that conductive type of ZnO thin films depends on N_2 atoms concentration.

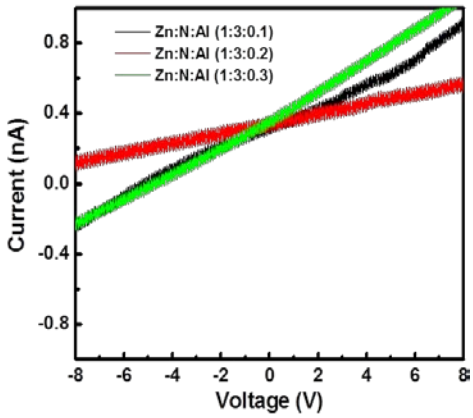

Fig.4: I-V results of co-doped ZnO films

Conclusion

Al-N codoped p-type ZnO films were successfully synthesized by sol-gel technique on glass substrate. The structure of the film was wurtzite hexagonal crystalline structure. The crystallinity of thin films is decreased with increased Al concentration. The transmittance of the film is 80 % on an average with respect to air and the band gap decreases on N_2 doping and N:Al codoping of ZnO. The minimum resistivity is observed to be 0.825Ω -cm for N and Al codoped ZnO films. The current voltage characteristics of doped and codoped films show consistent polarity with low resistance which confirms p-type conductivity. These highly transparent and conducting p-type ZnO thin films can be used as a window layer in solar cells as well as in other optoelectronic devices.

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