International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.11 pp 497-501, 2015

Aluminium Doped Zinc Oxide (ZnO) Thin Film Fabricated for Semiconductor by Spray Pyrolysis Technique

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Abstract: Undoped and Aluminium (Al) doped ZnO thin films were fabricated by spray pyrolysis technique. The compound identification was confirmed by XRD analysis. The crystalline size of the film was determined by XRD analysis and the crystalline size was found to decrease when the film is doped with Al. Photoluminescence study shows undoped ZnO thin films emits in UV region and aluminium doped ZnO thin films in UV and visible region. Transmittance was decreased with increasing doping level and band gap energy also decreased. Film thickness was calculated using Profilometer in range in 0.3 to 1.6 μm. The four probe method was using to measured electrical resistivity. The electrical resistivity was increased when 0.01N Al doped ZnO thin film and it was decreased when 0.03N Al doped ZnO thin film.
Key Words: ZnO, Al-doped, band gap, electrical resistivity.

1. Introduction

Pure and doped ZnO thin film have attracted a lot of attention because of their physical, chemical, electrical, optical properties like low resistivity,wide band gap, transparent electrodes for solar cell [1,2]. The doping elements since (group III-A Al, B, Ga, In) have been used to increase the electrons density for conductivity of ZnO films [3-7]. Among transparent conductive oxide films, Al-doped ZnO thin films are being considered for manufacturing transparent electrodes due to their important properties such as low cost, nontoxic natures, good electrical conductivity, good adhesion to substrate, high luminous transmittance stability [8-11]. Aluminium was doped with metal oxides thin films for production of n-type semiconductor [12-17]. The ZnO thin film resistivity is reduced by doping with group III elements Al, Ga. Thin films are of particular interest for the fabrication of large area arrays, solar selective coating solar cell, photoconductors, sensors, antireflection coatings, interferences items, polarizer, narrow band filters, IR detectors, magnetic and superconducting films [19-22]. Binary metal oxide thin films (ZnO, CdO and SnO_2) properties like electrical, optical are modifying by doping process.

The spray pyrolysis, among the various deposition techniques, is the well suited for the preparation of doped zinc oxide thin films because of its simple and economic experimental arrangement, ease of adding various doping material, reproducibility, high growth rate and mass production capability for uniform large area coatings, which are desirable for industrial and solar cell applications.

2. Experimental

The ZnO solution was prepared with 0.1N using zinc acetate [$(CH_3 COO)_2$ Zn. $2H_2O$] as a precursor salt and deionised water as a solvent (50 ml). Zinc oxide thin films were fabricated on glass substrate using spray pyrolysis technique. The temperature of the substrate was maintained around 350°C. The spray rate was kept constantly by 0.25 to 0.5 ml/s using air as a carrier gas. The each spray time was 3 seconds continuously and time interval between each spray was 90 seconds. The solution was deposited onto the substrate through a nozzle fixed at 30 Cm from the substrate. Undoped ZnO thin film sample was coated with 30 ml solution and Aluminium doped ZnO thin film with doping concentration 0.01, 0.03N.

3. Result and Discussion

3. 1. Structural studies of undoped and doped ZnO thin film

The XRD patterns of undoped ZnO and Al-doped ZnO films are shown in Fig. 1. The figure shows the number of peaks and the prominent peaks are assigned namely (110), (002), (101), (102) and (103). The films deposited are polycrystalline in nature and the positions of X-ray diffraction peaks fit well with the hexagonal structure of ZnO (JCPDS card Zinc oxide, 89-1397). As seen from Fig. 1, the preferred orientation is (002) plane for ZnO film. In the present study, the most conspicuous feature observed in the XRD analysis of the films is orientation along the (002) plane. By doping the crystalline size was decreased this changes observed through peak broadening. The crystallite size for crystallites with the (002) plane was calculated by Scherer's formula, $D = 0.9\lambda/(\beta \cos\theta)$.

In which the peak broadening due to residual stresses in the films was neglected. Where D, β and λ are the size of the crystallite, the broadening of the diffraction line measured at half its maximum intensity in radians and the wavelength of X-rays (1.54060 Å), respectively.

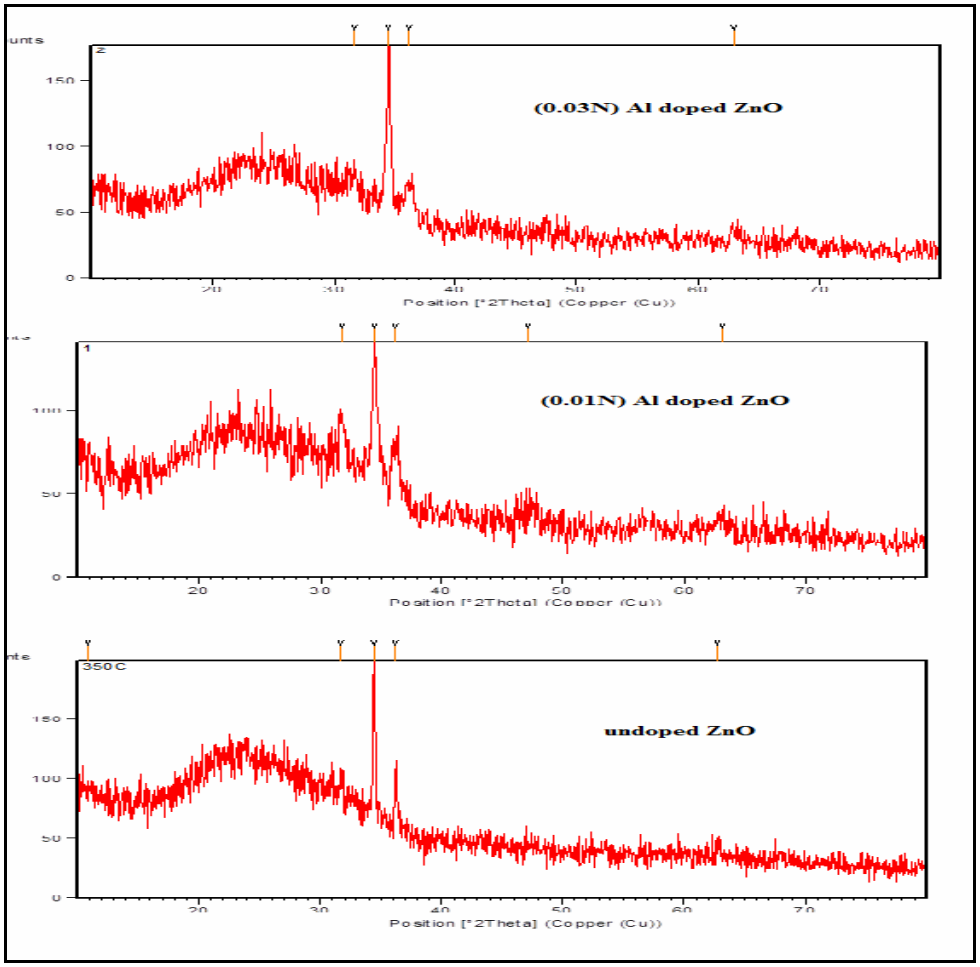

Fig. 1. XRD pattern of undoped and Al: ZnO film

3. 2. Photoluminescence of Al-doped and undoped ZnO

Photoluminescence spectra can be used to determine the band gap energy as well as some impurities having their energy levels in the band gap region in semiconductors. The strong emission was observed at 390 nm (3.2 eV) in UV region and low emission peaks are observed in visible region ZnO thin film. Intensity of the UV emission was related to the crystal quality of deposited materials with fewer structural defects and impurities. The ZnO thin film has good optical properties and promising candidate for the UV optical devices.

Undoped ZnO thin films emission energy in UV region and small emission energy in visible region with band gap energy is 3.2 eV (390 nm). After Al-doping with ZnO film the band gap energy was decreased from 3.2 eV to 2.3 eV. The emission energy was decreased by doping process in visible region. The blue-green emission was observed at 517 nm in visible region corresponding to the crystal defects. This green emission originated from the recombination of the holes with the electrons occupying the single ionized oxygen vacancies. It shows unfilled energy levels (they are holes) are created in band gap. Acceptor levels are defects formed above the valence band maximum in case of p-type conduction. Aluminium is a lesser oxidation state element it means cation deficiency and oxygen excess.

The values of energy levels obtained theoretically were 2.38 and 2.28 eV respectively for O_{Zn} and O_I. But, it was already proved that the acceptor levels due to oxygen interstitials were the origin for red emission in ZnO [18]. Hence it was presumed that, from the irradiation experiment and the annealing effect, the emission at 517 nm was due to the oxygen antisite. Transition was occurred from conduction band to the acceptor level of O_{Zn}

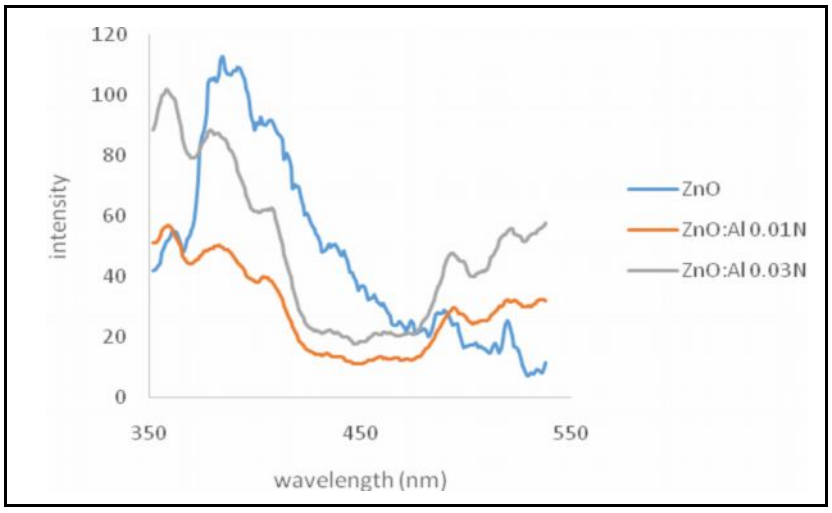

Fig. 2. Photoluminescence of undoped-ZnO and Al-doped ZnO thin film

3. 3.Transmittance spectrum of undoped ZnO and Al-doped ZnO thin film

Transmittance spectrum of undoped ZnO and Al- doped ZnO thin film was shown in Fig. 3. The undoped ZnO thin film transmittance was nearly 90% in visible region and absorption start at UV region. It shows ZnO film is a good semiconductor and its band gap energy is 3.3 eV. After Al-doped in ZnO film the transmittance was decreased by doping concentration increased. This transmittance decrease means absorption was increased.The optical band gap energy was reduced from 3.2 eV to 2.7 eV. The optical band gap of the film was calculated using the Tauc relation shown in fig.4.

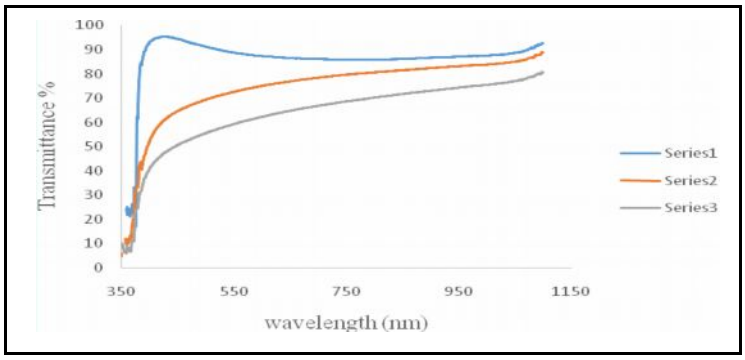

Fig. 3. Transmittance spectrum of Undoped and Doped ZnO thin films

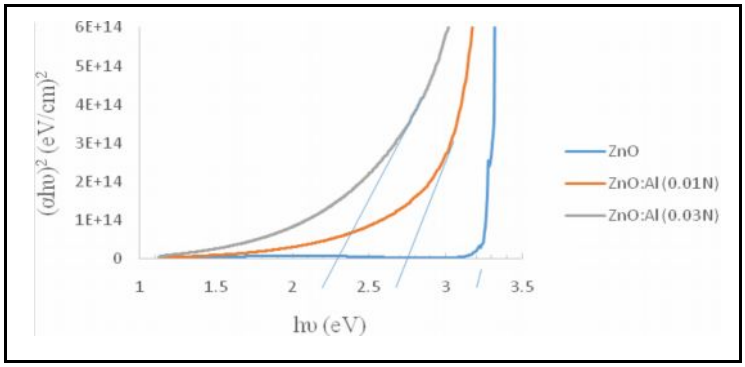

Fig. 4. Tauc graph of undoped and Al-doped ZnO thin film

3. 4. Thickness measurement

The film thickness was measured using stylus Profilometer. The temperatures on glass substrate and diffusion rate were not constant when spraying. According to this, the variation in film thickness was observed. The film thickness decreased with increase in substrate temperature is attributed to the increase in evaporation rate of initial product before reaching the substrate.The thickness ranges between 0.3 to 2.5 µm.

3. 5. Measurement of Resistivity

Electrical resistivity of pure and Al doped ZnO thin film was measured using four probe methods. The electrical resistivity of ZnO thinfilm decreases with 0.01N of dopant atom of Al^{3+}because of the coexistence of donors (intrinsic point defects such as oxygen vacancies and Zn interstitials) and acceptors in the films and Al atoms behave as acceptors. But it almost returns to its undoped behaviour when the doping level is increased to 0.03N and resistivity of ZnO thin film was increased. The increase in doping concentration as 0.03N, the sufficient disorder is produced in the lattice due to differences in the ionic radii of Zn^{2+} and Al^{3+}. This increases the efficiency of scattering mechanism such as phonon scattering and ionized impurity scattering which, cause the increasing in resistivity.

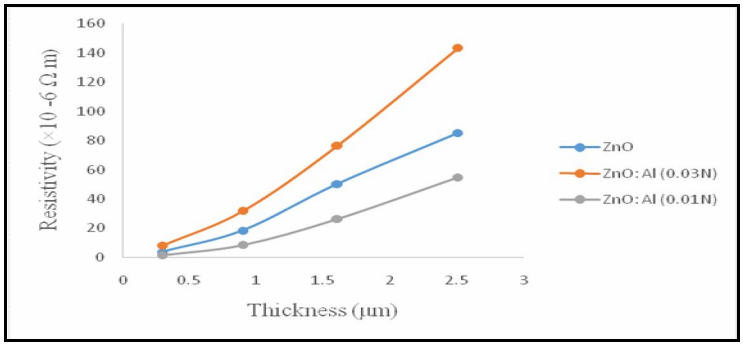

Fig. 5. The variation in resistivity of pure and Al doped ZnO thin films

4. Conclusion

The pure ZnO and Al:ZnO thin films were fabricated by spray pyrolysis technique with different Al-doping concentration at substrate temperature 350°C. The XRD studies, reveals that crystallinity nature of the film and grain size was decreased and the structure was not affected by Al-doping with ZnO film. The optical band gap energy was decreased by doping process, which was finding in photoluminescence spectrum of Al-doped ZnO film. In undoped ZnO film, the emission was strong in UV region only after Al-doping, weak peaks are available in visible region. The absorbance values increases while the transmittance value decrease when we used oxygen flow for thermal oxidation processes. Zinc Oxide films have high transmittance in the NIR region, which makes these films suitable for solar energy collection. The optical energy gap values decrease when we used oxygen flow for thermal oxidation processes.Electrical resistivity of undoped ZnO thin film was improved with 0.01N Al doping but it was increased beyond that it decreased with Al-doping 0.03N.

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