

Synthesis and Characterisation of Monolayer ZnO and Al:ZnO Thin Films Deposited by CBD Method

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Abstract: ZnO thin films are deposited on glass substrates by chemical bath deposition method. Zinc acetate dehydrate (ZAD) was used as the precursor. Dehydrated isopropyl alcohol was the solvent and the stabilizer used was monoethanolamine (MEA). Using dip coating method, a monolayer Zinc oxide film was coated on the glass substrates. XRD, FTIR, UV-Vis characterizations were obtained for the coated film. Then the solution was mixed with Aluminium Chloride to dope Al to the chemical. The procedure was repeated and the Al doped ZnO thin film was coated on the substrate. The particle size and the mechanical properties such as strain and dislocation density were studied from XRD analysis. Optical properties were studied from UV-Vis spectrum and FTIR analysis. It is seen that the average particle size for undoped ZnO is 43.55nm and it has been reduced to 27 nm for Al:ZnO, neglecting strain broadening.

Keywords: ZnO thin films, AZO, dip coating, CBD method, Al doping.

1. Introduction

An inorganic compound zinc oxide is a white powder; a wide band gap semiconductor of the II- VI semiconductor group is insoluble in water. ZnO is important for its multi-functional properties (semiconducting, magnetic, piezoelectric etc.) It is used as an additive in a number of products such as ceramics, cement, paints, batteries, adhesives and so on. It has various properties like wide band gap of 3.3eV, high electron mobility, good transparency and strong room-temperature luminescence. These properties of ZnO are used in current applications for transparent electrodes. ZnO thin films were prepared and coated by dip coating technique. Chemical techniques are relatively simpler and cost effective. Among various deposition techniques, chemical bath deposition yields stable, adherent, uniform and hard films with good reproducibility by a relatively simple process. The growth of thin films strongly depends on growth conditions, such as duration of deposition, composition and temperature of the solution and topographical and chemical nature of the substrate.

In the present work, an attempt has been made to synthesize ZnO and Al-doped ZnO by chemical dipping technique. The advantages of this method are its simplicity of working principle and low cost of apparatus. Zinc oxide possesses a unique position among semiconducting material owing to its superior and diverse properties such as piezoelectricity, chemical stability, biocompatibility, high catalytic activity in different gas ambient, optical transparency in the visible region and high voltage-current nonlinearity etc (Maiti *et al* 2007). Accordingly it has immense potential in different applications in photothermal conversion systems, heat mirrors, heterojunction solar cells, transparent electrodes, blue/UV light emitter device, solid state sensor, transducer (Maiti *et al* 2007; Sucheja *et al* 2007; Vijayalakshmi *et al* 2008) etc. The interest in doping ZnO is to explore the possibility of tailoring its physical properties (Aktaruzzaman *et al* 1991). Polycrystalline films of ZnO have been doped with various dopants (e.g. Al, Ni, Mn, Pd, Cu, Fe, Cd etc)

(Bedir *et al* 2006; Mandal and Nath 2006; Ghosh *et al* 2008; Kumar *et al* 2008; Yakuphanoglu *et al* 2010; Al-zaidi *et al* 2011) to obtain improved physical properties. AZO thin films were deposited on microscopic glass substrate by SILAR technique. XRD confirmed the incorporation of Al in ZnO lattice. [2] The effect of dopant concentration, heating treatment and annealing in reducing atmosphere on the microstructure as well as on the electrical and optical properties of the thin film is discussed. [9]

2. Experimental Techniques

The glass substrate was cleaned prior to deposition, by chromic acid followed by distilled water rinse and ultrasonic cleaning with equivolume of acetone and alcohol. Zinc acetate dehydrate (ZAD) was used as the precursor. 2.5 g of ZAD was dissolved in 30ml of 2-propanol isopropyl alcohol and this solution was stirred thoroughly on a magnetic stirrer for 3 hours. A milky solution was obtained. Then 2ml of monoethanolamine (MEA) as a stabilizer was added to the solution drop wise, until the solution becomes transparent. Again the solution was stirred using a magnetic stirrer at 100°C for about 3 hrs. To get a stable homogenous sol, this solution was kept undisturbed for about 24hrs at room temperature. Dip coating was applied thereafter by dipping the slides for 24 hours. The slides after deposition are heat treated on a hot plate at 100°C.

The thin films deposition was again performed by dip-coating technique on glass substrate, using a sol prepared by the same procedure with $Zn(CH_3COO)_2 \cdot 2H_2O$, $AlCl_3 \cdot 6H_2O$, 2-methoxyethanol and monoethanolamine (MEA). The concentration of metal ions (Aluminium chloride) in the solution was 0.75 mol/l and the molar ratio of MEA to metal salts was 1.0M. The solution was stirred using a magnetic stirrer at 100°C for about 3 hrs. To get a stable homogenous sol, this solution was kept undisturbed for about 24hrs at room temperature. Dip coating was applied similarly thereafter by dipping the slides for 24 hours. These slides, after deposition are also heat treated on a hot plate at 100°C.

UV-VIS spectroscopy is mainly used to detect conjugated system. Because the promotion of electrons from ground state to excited state of system give rise to absorption in the region. UV VIS absorption usually corresponds to excite by the incident radiation to a higher molecular orbital.

3. Results and Discussion

3.1 XRD Analysis

The technique enables structural information for characterization of crystals. X-ray diffraction analysis investigates crystalline material structure, including atomic arrangement, crystallite size and imperfections. Fig. 1 shows XRD patterns of ZnO films prepared at 100°C. From the pattern, it is seen that the diffraction peaks are positioned at (7.09109) and (5.31356). The peak also shows that phase purity (i.e., no other secondary phases) of the sample.

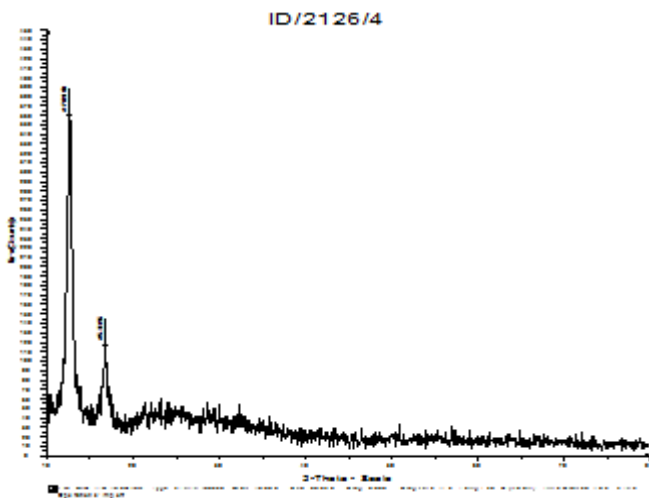


Figure 1: XRD pattern of ZnO dip coated at 100°C

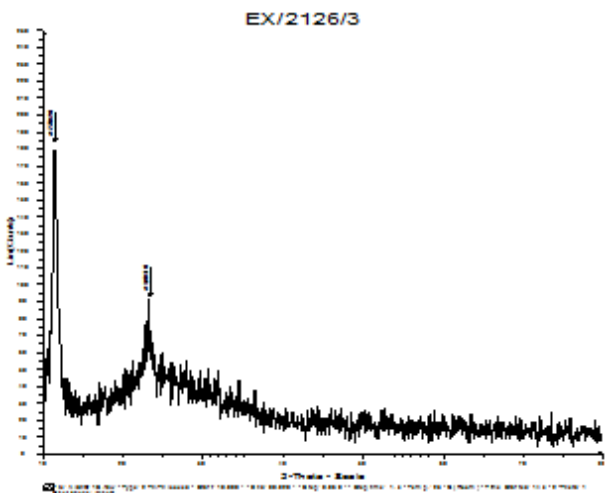


Figure 2: shows XRD patterns of Al:ZnO films prepared at 100°C. From the pattern, the diffraction peaks are positioned at (7.78128) and (3.81318).

Fig.2 XRD pattern of Al doped ZnO (AZO) dip coated at 100°C

The particle size t , dislocation density ρ and strain η of both the films are calculated using the given formulae.

$$\text{Particle size } t = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

$$\text{Dislocation density } \rho = \frac{1}{t^2} / m^2 \quad (2)$$

$$\text{Strain } \eta = \left[\frac{\lambda}{t \cos\theta} - \beta \frac{\pi}{180} \right] \frac{1}{\tan\theta} \quad (3)$$

Table 1

Sample	Particle Size (nm)	Dislocation Density (/m ²)	Strain
ZnO	43.55	1.3001 X 10 ¹⁵	7.0730 X 10 ⁹
AZO	27	5.2725 X 10 ¹⁴	9.1788 X 10 ⁻³

3.2 UV-Visible Spectroscopy

In this study UV absorption spectra of the films are recorded at room temperature using JASCO (Model V-650) UV-Visible spectrometer. It is seen that in both the cases strong absorbance occurs in UV region in a wavelength of 358 nm.

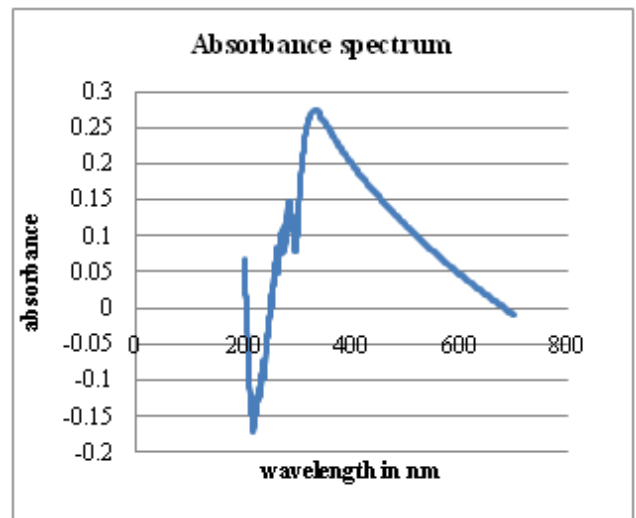


Figure 3: Absorbance spectrum of ZnO thin film

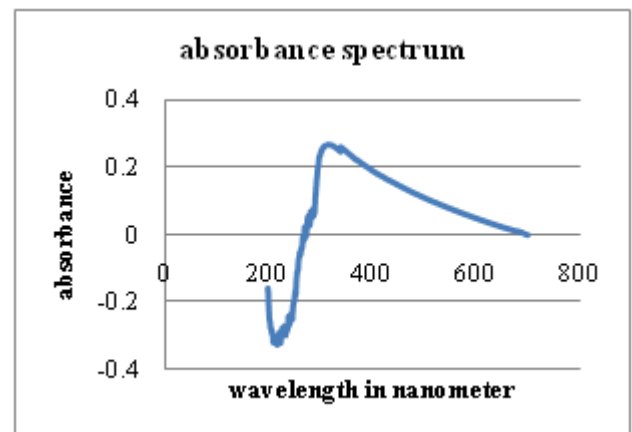


Figure 4: Absorbance spectrum of AZO thin film

The absorbance spectrum of Al doped ZnO thin films on the glass substrates are shown in Fig.4.

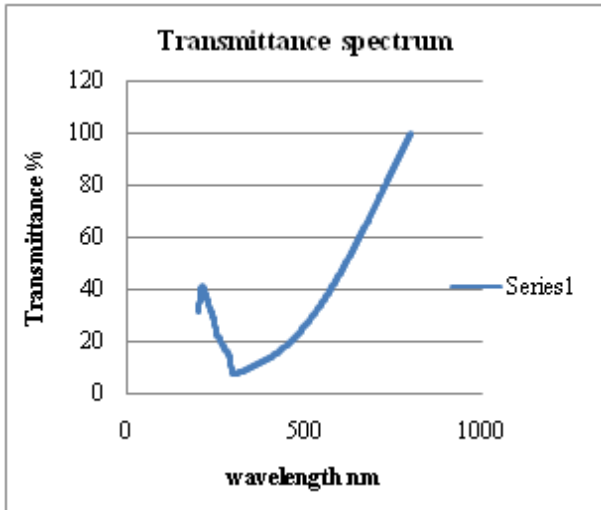


Figure 5: Transmittance spectrum of ZnO

The weak transmittance area covers almost the whole of the UV region ranging between 200 and 600 nm. It reveals that the transmittance of the film is above 80% in the visible region.

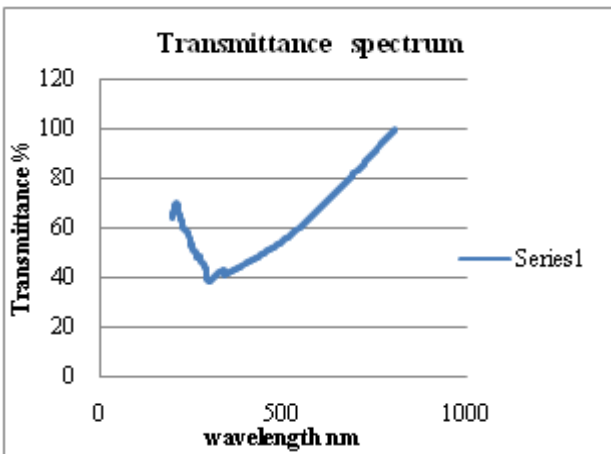


Figure 6: Transmittance spectrum of AZO

3.3 FTIR Spectroscopy

Infrared spectroscopy deals with the study of vibrational spectra of molecules. This spectrum originates from molecular vibrations which causes a change in the dipole moment of the molecule. FTIR is a powerful tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum.

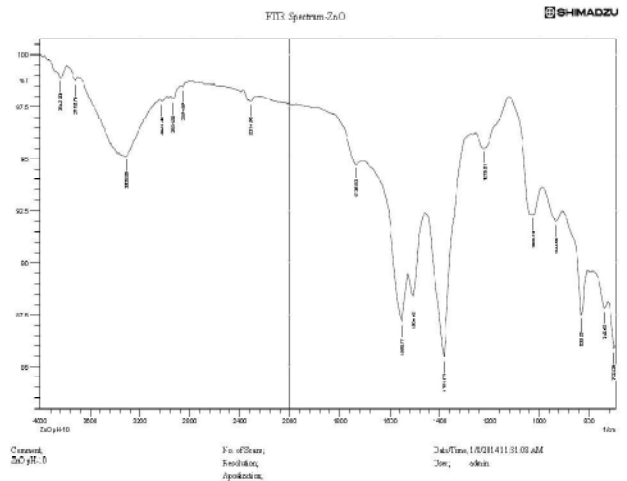


Figure 7: FTIR Spectrum of ZnO

Fig.7 shows the spectrum of ZnO films prepared at 100°C. Various bonds present in our sample were analysed. They are S=O bond, broad amide II band at 1504.48 cm⁻¹, C=O stretching vibration, asymmetric NO₂ stretching vibration and C-H stretching vibration.

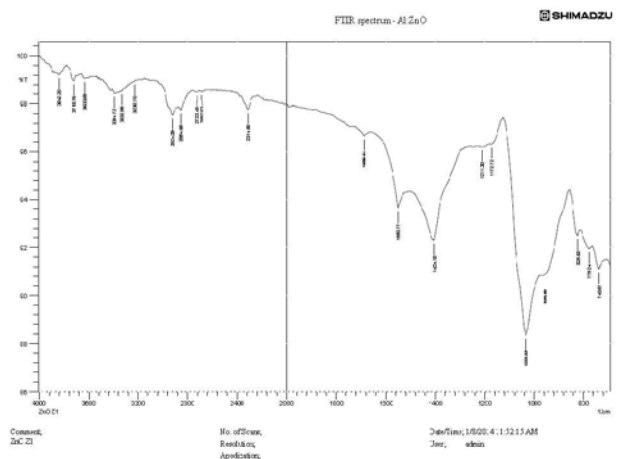


Figure 8: FTIR spectrum of AZO

From this spectrum the chemical bonds present in the Al doped sample was found. The strong N-H, C=C and C-H stretching vibrations are present. Very strong C=O and broad amide II band are also observed. In 1327 cm⁻¹ medium O-H deformation vibration was seen.

4. Conclusions

ZnO thin film and AZO were prepared by chemical bath deposition method. From XRD analysis it was observed that the particle size for ZnO is 43.55 nm and it has diminished to 27 nm. The strain as well as the dislocation density is found to be reduced for AZO when compared to ZnO. The functional and composition quality of the synthesized product was analysed by FTIR spectroscopy. UV-Vis spectroscopy is the measurement of the absorption of near and visible ultraviolet light using semiconductor zinc oxide thin film. From this, it is seen that the minimum transmittance % of ZnO thin film has been improved whereas the particle size has been diminished on doping of Aluminium to ZnO thin film.

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