

A Study of Aluminium Doped ZnO (AZO) Thin Film by SILAR Method

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Abstract: Al doped ZnO thin film (AZO) were deposited on cheap glass substrate by successive ion layer adsorption and reaction (SILAR) method at 0.1M concentration of zinc nitrate hexahydrate and 1% of aluminium chloride hexahydrate. The structural, morphological and optical characterization on the AZO thin film such as X ray diffraction, SEM and UV-visible spectrometer are taken respectively. From XRD study, the AZO thin film is polycrystalline in nature with hexagonal structure and the average crystallite size is 33 nm. The most prominent peaks corresponding to [100], [002] and [101] planes are found. SEM image of the thin film showing smooth and uniform flower grains on to the surface of the film. The transmittance of the film were as high as 80% in the visible range from 400-700 nm and the direct band gap value is 3.0eV. This technique is very simple and low cost to producing AZO thin film.

Key words: Al doped ZnO, SILAR, Structural, morphological and Optical measurements.

Introduction

In recent years, zinc oxide has become a particularly interesting metal oxide material because of its unique properties. ZnO is a semiconductor with a wide band gap (3.3 eV), large exciton binding energy, abundant in nature and environmentally friendly. this material attractive for many applications such as solar cells, photocatalysts, antibacterial activities, electrical devices, optical coatings, active medium in uV semiconductor lasers and in gas sensors [1]. Therefore polycrystalline ZnO thin films have been doped with group III and group II metal ions such as indium (In), gallium (Ga), aluminum (Al), cadmium (Cd), copper (Cu) to enhance their structural, optical and electrical properties [2]. Doping is particularly done to get high transparency, stability and high conductivity. Aluminium doped ZnO (AZO) thin films have high transmittance in the visible region, and a low resistivity, and the optical band gap can be controlled by using Al doping amount [3]. Among various chemical methods employed so far to deposit AZO films, Sol-gel requires costly chemicals and electro less deposition is characterized with poor coverage. Spray pyrolysis is a high temperature process and choice of suitable precursor solution is often not convenient. One of the less used and less studied chemical techniques is successive ionic layer adsorption and reaction (SILAR). The process can be carried out on any kind of substrate and the thickness can be easily controlled. Thus both thin and thick films can be prepared by this method.

Experimental condition

AZO thin film were deposited on glass substrates by the SILAR method. In the experiments, 0.1 M Zinc Nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), 1% of Aluminium chloride hexahydrate ($AlCl_3 \cdot 6H_2O$) and concentrated ammonia (NH_4OH) were used to prepare the solution. NH_4OH was added to adjust the pH of the solution to 10. The AZO thin film sample was grown by 20 cycle of deposition prior to testing of its crystallinity and nanostructure. In SILAR deposition of AZO thin film, two rinsing procedures is discussed as follows: (a) Dip glass substrates in the zinc complex solution for 10 s and (b) Dip glass substrates in hot water at $100^\circ C$ temperature for 10s. After deposition by SILAR dip-coating, the AZO thin film were annealed at $450^\circ C$ for 1hr.

Result and discussion

Figure 1 shows the X-ray diffraction (XRD) pattern of the AZO thin film deposited from SILAR. The material was scanned in the range $20-60^\circ$. Three XRD diffraction peaks can be found at 31.8° , 34.5° and 36.5° corresponding to (100), (002) and (101) planes in the AZO thin film, respectively. Table 1 shows the miller indices of the three planes and compared with d-spacing values to JCPDS for AZO thin film. The polycrystalline nature with hexagonal wurzite structure was preserved with (002) preferred crystal orientation on the glass substrate. From the Full Width at Half Maximum (FWHM) value of the peak obtained, the size of the crystallite formed in the AZO thin film is determined using Debye-Scherrer formula[4].

$$D = \frac{0.9\lambda}{\beta \cos \theta} \text{----- (1)}$$

Where, $k=0.9$ is the shape factor, β is full-width at half maximum (FWHM) values, θ is the Bragg's angle, λ is the X-ray wavelength (1.5406Å).

The crystallite size was found to (002) peak orientation, the average crystallite size is 33nm. The micro strain and dislocation density of AZO thin film were calculated using the following equations [5,6].

$$\epsilon = \frac{\beta \cos \theta}{4} \quad \text{----- (2)}$$

$$\delta = \frac{1}{D^2} \quad \text{----- (3)}$$

The AZO thin film with lower micro strain and dislocation density improve the crystallinity of the film which in turn increase the volumetric expansion of the film. The average microstrain and dislocation density value is 3.6×10^{-3} (lines⁻² m⁻⁴) and 9.308×10^{14} (nm⁻²) respectively.

Scanning electron microscopy is a convenient method for studying the nanostructure of thin film. The nanostructure SEM image of AZO thin film on glass substrate is shown in figure 2. The polycrystalline and flower shaped grains revealed from the SEM image. The SEM photograph clearly illustrates the formation of sub nanometer crystallites distributed more or less uniformly over the surface. Low deposition temperature in SILAR possibly results in large crystallites. The average particle size is 58 nm. Although no cracks could be detected, some holes indicating porosity is present.

The optical transmittance spectra of the SILAR deposited AZO thin film is presented in Fig.3 for the wavelength range of 350–1000 nm. It has been suggested that the optical transmittance in the visible range is 80%. The sharp ultraviolet absorption edges occurred at approximately 350 nm.

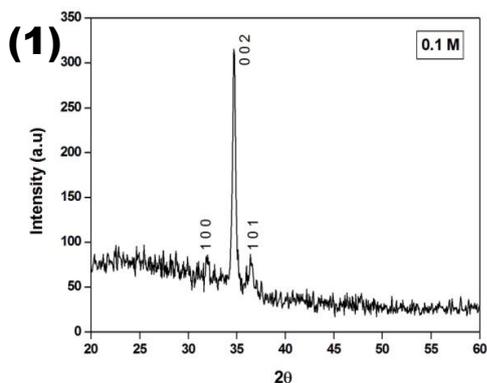
The direct allowed optical band gap of tin disulfide thin films has been determined from relation between the absorption coefficient (α) and the incident photon energy ($h\nu$) can be written as [7].

$$\alpha h\nu = B(h\nu - E_g)^n \quad \text{----- (4)}$$

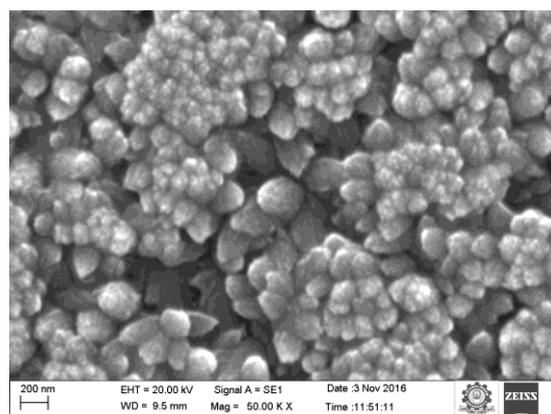
Where B and E_g are constant and optical band gap, respectively. The optical band gap of the AZO thin film is shown in fig.4. The energy band gap was estimated at 3.0eV.

Conclusion

Al doped ZnO (AZO) thin film were prepared by simplifying SILAR method. From XRD analysis it was observed that the polycrystalline nature with hexagonal structure. The average crystallite size is 33 nm. The lower microstrain as well as the dislocation density are also observed for AZO thin film. SEM image of the thin film showing smooth and uniform flower grains on to the surface of the film. The average particle size is 58nm. The transmittance value of the AZO thin film were as high as 80% in the visible range and the direct band gap value is 3.0eV. This is the method is very simple and low cost to producing AZO thin film.



(2)



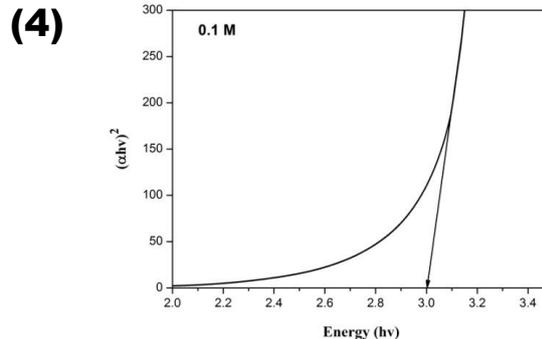
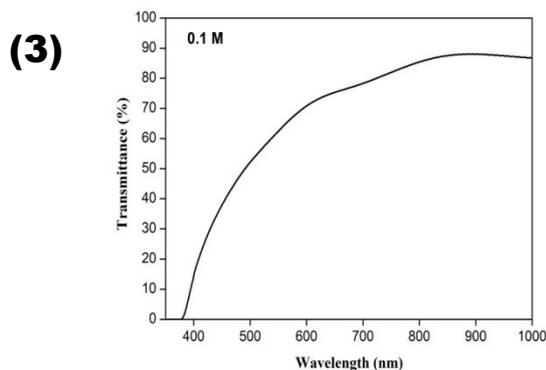


Figure.1. XRD pattern of AZO thin film at 0.1 M.

Figure.2. SEM image of AZO thin film at 0.1 M.

Figure.3. Transmittance spectrum of AZO thin film at 0.1 M.

Figure.4. Band gap value of AZO thin film at 0.1 M.

Table 1: 2θ and d-spacing value compared with JCPDS file.No: **89-0510**

Concentration (M)	2θ Values		d-Spacing (Å)		Miller indices (hkl)	Structure
	Observed Value	JCPDS Value	Observed Value	JCPDS Value		
0.1 M (Zinc) 1% (Al)	31.8227	31.779	2.81210	2.813	1 0 0	Hexagonal
	34.5767	34.43	2.59417	2.602	0 0 2	
	36.3559	36.26	2.47119	2.475	1 0 1	

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