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Preparation and Characterization of ZnO Thin Films By SILAR Method

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Zinc oxide (ZnO) thin films were prepared by the Successive Ionic Layer Adsorption and Reaction (SILAR) method. The structural, surface morphological and optical properties of the prepared films have been studied by using X-ray diffraction (XRD), scanning electron microscopy (SEM) and UV-VIS-spectrophotometer. The X ray diffraction analysis shows that the films are polycrystalline with zincite hexagonal structure. The study of surface morphology reveals that morphology of the prepared film has a good crystalline quality and the film surface has a generally rough and dense morphology. The prepared ZnO films exhibit a moderately high transmittance in visible band, and optical band gap of 3.56 eV which can be applicable for photovoltaic applications.

Keywords: *Zinc oxide, Thin film, Band gap, Crystalline structure, Spectrophotometer.*

Introduction

Thin film technology is stretching its hands in all its directions and thin film devices coming out of it play a dominant role in all walks of life. The need for new and improved optical and electronic devices have stimulated a new branch of solid state physics called thin film physics and technology which comprises the study and application of thin films of elements as well as binary and ternary systems with controlled compositions and specific properties. Any solid or liquid with one of its dimensions very much less than that of the other two may be called a thin film [1].Thin films can be considered to have two dimensions. The term thin film has often been loosely used in literature to imply not only a layer of solid material but also a liquid or gaseous phase [2].Thickness of thin films is usually discussed in terms of Angstrom (Å) units and is of the same order of magnitude as the dimension of a single atom [3]. There are neither any well-defined limits of its thickness to imply the end of the thin film stage nor one to indicate its transition to a thicker film region. Depending on the properties to be investigated and technological application thin film thickness can be varied from a few Angstrom (Å) to 10000 (Å) or even more [2].

There are different physical and chemical methods for the deposition of thin films from a variety of materials such as metals, insulators or dielectrics etc. [2]. Physical methods are easier to control where as chemical methods are more economical and utilize simple equipments. The application and properties of a selected material determines the suitable technique for the preparation of thin films [1]. Thin films are coated on different substrates such as alumina, glass, beryllia or beryllium oxide-based ceramic, aluminium nitride, silicon and metals [4]. During the last three decades, SILAR (Successive Ionic Layer Adsorption & Reaction) has emerged as a one of the solution methods to compound materials in thin film form. One of the newest solution methods for the deposition of thin film is SILAR method, which is also known as modified chemical bath deposition. SILAR was developed by Nicolau. SILAR method is inexpensive, simple and convenient for large area deposition.

ZnO thin film is an interesting wide band gap (3.3 eV)II-VI compound semiconductors and is composed of hexagonal wurtzite crystal structure. In recent years for developing highly oriented and transparent ZnO thin films has attractive potential application in transparent electrode in display, window layer in solar cells, field emitters, ultraviolet laser emission, photo detector and bio sensors. ZnO thin film considerable attention because of their size dependent properties and wide range of applications.

1. Experimental Details

Cleaning of the substrates

Substrates must be cleaned for durable and adherent coating with reproducible properties. Cleaning involves removal of contaminants without damage to the substrates. While cleaning the bond between the contaminants and the substrate molecules are broken and contaminants are set free from substrates.

The energy required to break these absorption bond could be supported by chemical, salvation and ion bombardment, thermal or mechanical process. The substrate cleaning procedure adopted in the present work involves three steps.

1.The substrates kept in the zig are cleaned in soap solution for 25-30 minutes.

2.The substrates are then cleaned in distilled water for 25-30 minutes.

3.The substrates are then dried in hot air oven for about 30 minutes.

Preparation of ZnO thin films by SILAR technique

In the first step of a SILAR cycle solvated cationic precursor is adsorbing on the surface forming an electrical double layer. This layer is composed of two layers the inner (positively charged) and outer (negatively charged) layers. Positive layer consists of the cations and negative from the counter ions of the cations. Excess unabsorbed precursor is rinsed away from the diffusion layer. This results in a saturated electrical double layer. In the reaction phase the anion precursor is introduced to the system. Due to the low solubility of the material K_mA_n a solid surface is formed on the interface. The last step rinses the counter ions of both types of precursors as well as the reaction by product out of the system. By repeating these cycles thin layer of a material K_mA_n can be grown. If the measured growth rate exceeds the lattice constants of the material a homogenous precipitation in the solution could have taken place. The chemicals used in this experiment and the deposition parameters are tabulated in the tables 1 and 2.

In the present study very accurate electronic balance (SHIMADZU-AY220 digital electronic balance) is used for thickness measurements. Mass difference of the substrate before and after deposition gives the mass of the film 'm'. Knowing the length (1) and breadth (b) of the deposited film, area of deposition can be determined. If ρ is the density of the material of the film, then thickness (t) of the film is determined using the formula.

t = mass of the deposited film/area of the film x density of the film

$$t = \frac{m}{lb\rho} \qquad \text{-------------------} \quad (1)$$

[The density of 5.606 kg/m^3].

2. Results and discussion

XRD analysis of ZnO thin films:

Fig.1 shows the x-ray diffractogram of ZnO thin film prepared at room temperature. From the diffraction profile it has been found that the film is polycrystralline in nature with hexagonal structure. The XRD patterns has shows peaks at $2\theta=31.9^0$ with high intensity, weak intense at $2\theta=34.4^0$ and $2\theta=36.4^0$ are corresponding to (100), (002) and (101) planes respectively. From the XRD profiles (Fig 4.3) the lattice spacing 'd' has been determined and it has been found that it is in very good agreement with those of ASTM card, earlier researchers [5,6,7] and is presented in Table 3.

The individual crystalline size (D_c) of prepared film of thickness 510nm have been estimated and are in very good agreement with the reported values [7]. Using the size of the crystallites, the dislocation density, the number of crystallites per units surface area and strain have been determined and presented in Table 4.

SEM Analysis

Surface morphology of thin film is very important tool to investigate microstructure of thin films. Figure 2 Shows the surface morphology of the prepared film of different magnification. It reveals that film has a good crystalline quality and the film surface has a generally rough and dense morphology. The aggregation occurred probably during the process of drying.

In smaller magnification (Fig 2) the film shows a uniform and a rough morphology of the grown film containing an accumulation of small grains and here the deposit distribution is less porous [8,9]. Further magnification (Fig 2) shows that the film contains the larger grains and clusters. Due to such morphology, a very large surface area is required for ZnO thin films which can be applicable for high efficieny solar cells as an anti-reflection material [10,11].

Optical Analysis

The optical transmittance spectra of ZnO thin film is shown in Fig 3. Transmittance of the films increases with wavelength. The moderately high transmittances of the films throughout the visible region make it a good material for photovoltaic applications. The typical behaviour was observed by earlier researchers Sara and et al [12]. In the visible region of solar spectrum transmission spectra of ZnO thin show sinusoidal behaviour, this may be due to the layered structure of thin film [13,14]. The optical parameters such as absorption coefficient, extinction coefficient and band gap are estimated and are presented in Table 5. Important optical parameters such as type of transition, band gap etc. can be satisfactory analyzed on the basis of formulae derived for 3D and 2D models. By 3D crystal model, nature of transition in film composition can be obtained by plotting $(\alpha h\nu)^{1/2}$ versus ($h\nu$) for various values of r [α is the absorption coefficient, $h\nu$ is the photon energy and exponent r determines the type of transition and dimensionality of the bands]. ν

has values ½ (direct allowed), 3/2 (indirect allowed), 2 (direct forbidden). Extrapolation of straight-line portion of $(\alpha h\nu)^{1/2}$ versus (hν) plot at (hν > E_g; E_g = direct band gap) to zero absorption (hν-axis) gave the value of energy gap.

Plot of $(\propto h\nu)^2$ versus (hν) (Figure 4) for ZnO thin film was plotted and the straight line portion is extrapolated to cut the x axis which gives the band gap. The estimated band gaps for found to be 3.56 eV (Table 5) and in agreement with the earlier researchers [14,15].

Plot of (hν) versus $(\propto h\nu)^{1/2}$, $(\propto h\nu)^{1/3}$ and $(\propto h\nu)^{2/3}$ shown in Figure 5 reveal that ZnO films did not have line above hν> Eg. Since extrapolation of it did not touch the zero absorption axis which confirms the fact that ZnO phase do not have indirect allowed direct forbidden and indirect forbidden transitions. The optical parameters such as absorption coefficient, extinction coefficient, reflectance, refractive index and band gap are estimated and are presented in Table 5.

3. Conclusion

The ZnO thin films are prepared by Successive Ionic Layer Adsorption and Reaction method. Thickness of the prepared films is calculated by Gravimetric method. The structure of the prepared films has been analyzed by XRD. It revealed that the prepared films are polycrystalline in nature with hexagonal structure. The characteristics peaks are identified and the structural parameters are calculated and presented. SEM micrograph showed that morphology of the prepared film as larger and clusters of grains higher magnification which can be act as an anti-reflection coating material for solar cell. The type of transition and band gap has been estimated from optical analyzed the band gap is found to be 3.56 eV. The optical parameters such as absorption coefficient, extinction co efficient are calculated and presented.

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Figure captions

Figure 1. X-ray diffractogram of ZnO thin film.

Figure 2. SEM micrographs of ZnO thin film.

Figure 3. Transmittance spectra of ZnO thin film.

Figure 4. Plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ of ZnO thin film .

Figure 5. Plot of $(\alpha h\nu)^{1/2}$,$(\alpha h\nu)^{1/3}$ and $(\alpha h\nu)^{2/3}$ vs.$(h\nu)$ of ZnO thin film.

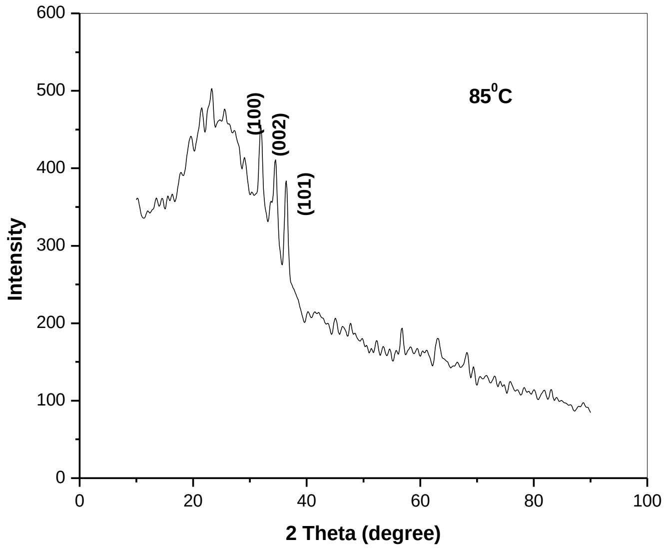


Figure 1. Nirmala et al.

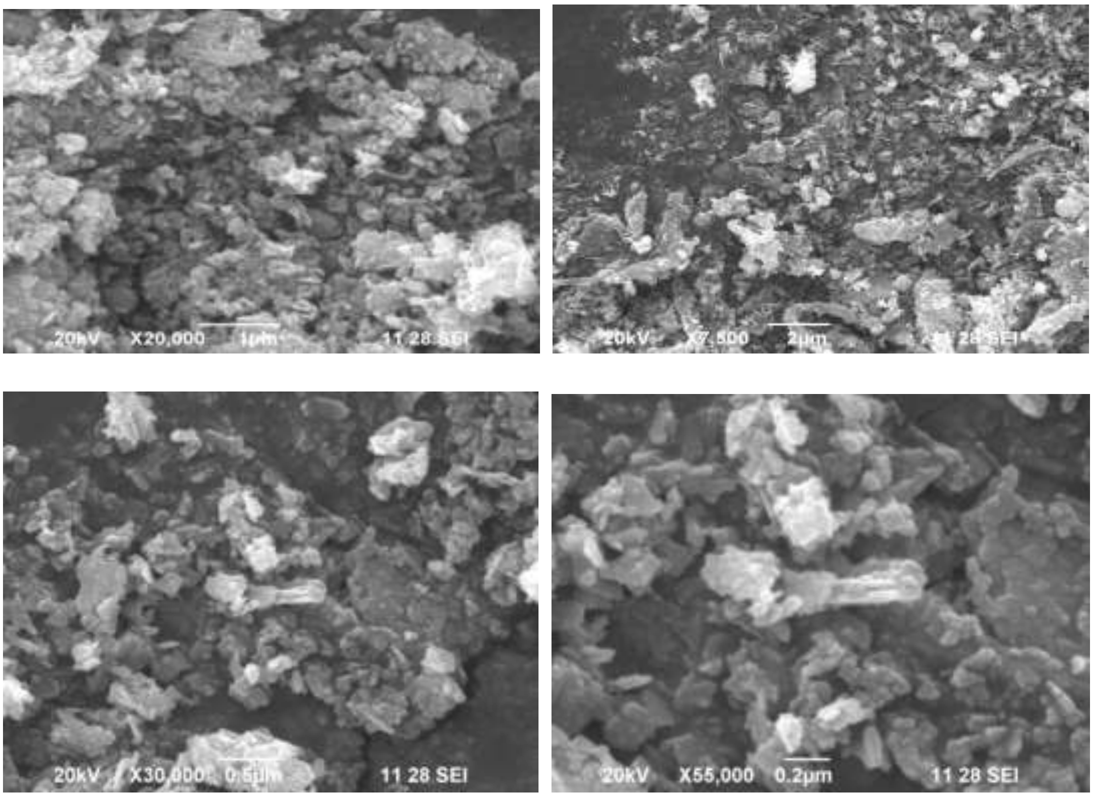


Figure 2. Nirmala et al.

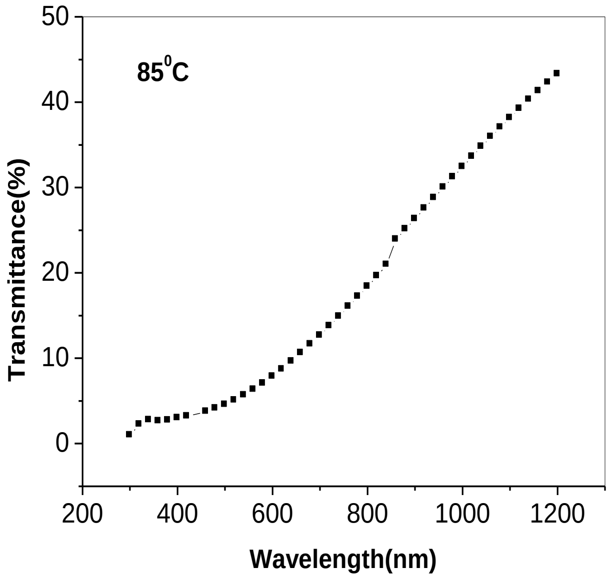


Figure 3. Nirmala et al.

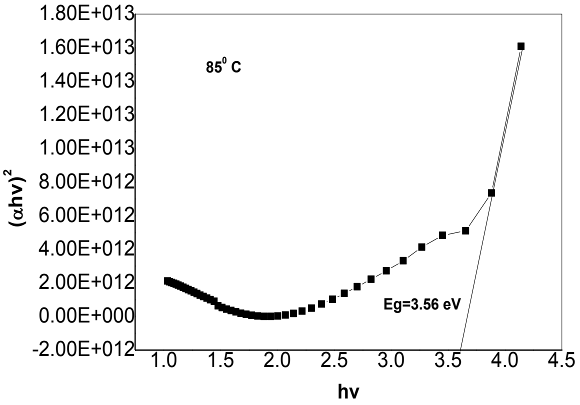
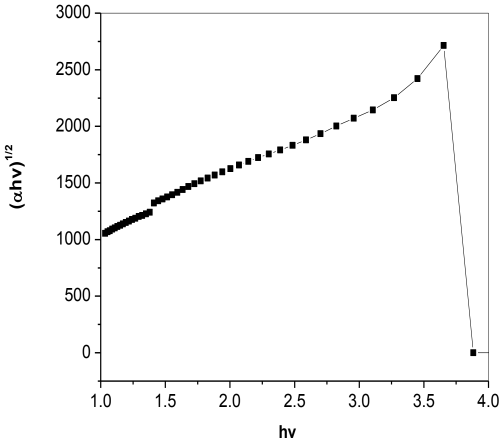
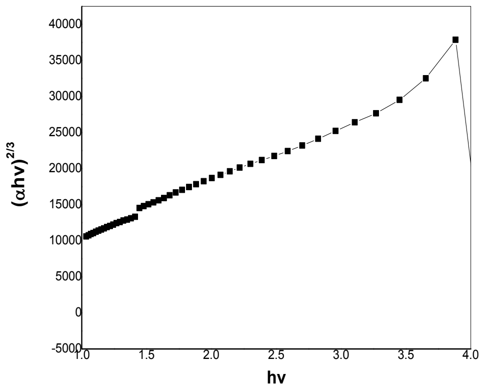


Figure 4. Nirmala et al.





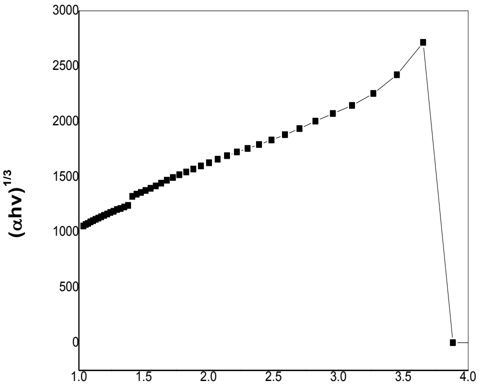


Figure 5. Nirmala et al.

Table 1. Details of chemicals used for the deposition of ZnO thin film

$ZnSo_4$	NaOH	Distilled water	Stirring Time	Deposition Time
0.1 mol	4 pellets	100ml	1hr	2hrs

Table 2. Optimised deposition parameters

Parameter	Variation range	Optimized value
pH	10 -11	11
Temperature	Room temperature -100^0 C	85˚C
Time	1hr	20 min
cycle	50-200	150

Table 3. XRD data of ZnO thin films

Plane (hkl)	2θ degrees		d (Å)	
	Observed	JCPDS	Observed	JCPDS
(100)	31.9024	31.777	2.8029	2.813
(002)	34.4407	34.432	2.6019	2.601
(101)	36.36533	36.264	2.4685	2.475

Table 4. Structural parameters of ZnO thin films

Film thickness (nm)	Lattice constant a (Å) Obs	Lattice constant a (Å) ASTM	Lattice constant c (Å) Obs	c (Å) ASTM	Crystallite size Nm	Volume V	DiDislocation density (10^{14}/lines/m^2)	No. of crystallite per unit area (10^{15} m^{-2})	Strain $\varepsilon \times 10^{-3}$
720	3.23	3.2648	5.2059	5.2194	10.1158	33.6982	9.72	0.4926	3.425
					10.007		9.986	0.5089	3.4625
					11.8508		7.12	0.3064	2.9238

FilmThickness (nm)	α (10^6 m^{-1}) [λ = 1000 nm]	K [λ = 1000 nm]	E_g(eV)
720	1.209316	0.096	3.56

Table 5. Optical parameters of ZnO thin films

