

Optical, Structural, Electrical, and Morphological Properties of Nanostructured ZnO Thin Films Prepared by the Sol-Gel Dip-Coating Technique

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Abstract- Nanostructured zinc oxide (ZnO) thin films were deposited on ultrasonically cleaned glass substrates using a sol-gel dip-coating technique. Zinc acetate dihydrate, ethanol, and ammonium hydroxide were used as the starting materials. Films with different numbers of coating cycles were prepared and subsequently annealed at 500 °C for 1 h. The structural, morphological, elemental, electrical, and optical properties of the films were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), electrical conductivity measurements, and UV-visible spectroscopy. The crystallite/grain size increased with increasing number of coating cycles. The films exhibited nonstoichiometric ZnO composition and transparent surface morphology. The optical band-gap energy obtained from the absorption spectra was found to depend on the number of coating cycles. The electrical activation energy also increased with increasing grain size. These results demonstrate that the structural and optical properties of sol-gel-derived ZnO thin films can be modified by controlling the number of coating cycles.

Keywords— Nanostructured ZnO, Transparent conductive thin films, Sol-gel dip-coating.

I. INTRODUCTION

Zinc oxide is a transparent conducting oxide with a larger binding energy (60 meV) and wide band gap (3.37 eV).

ZnO has been extensively studied in recent years because of its wide range of technological applications. ZnO has attracted considerable attention for gas-sensing applications under atmospheric conditions.

ZnO has also been investigated for low-voltage phosphor applications and has been employed in vacuum fluorescent displays (VFDs) and field-emission displays (FEDs) [1]. ZnO has become one of the promising candidates for flat-panel displays (FPDs) and gas sensors [2], transparent conducting oxide electrode [3].

Several techniques have been used to prepare nanocrystalline ZnO thin films such as pulsed laser deposition (PLD) [4], spray pyrolysis [5,6], DC magnetron sputtering [7], molecular beam epitaxy

(MBE) [8], metal organic chemical vapor deposition (MOCVD) [9,10], hybrid beam deposition (HBD) [11] and Sol-Gel technique [12,13].

The nanometer sized building blocks (mostly crystallites) are assembled to form nanostructured materials. These blocks are microstructurally heterogeneous, consisting of crystallites and grain boundaries. This structure, on nanometer scale, is important for many of their properties as compared to their bulk materials.

II. EXPERIMENTAL

1. Preparation of nanostructured transparent ZnO thin films

Sol-gel dip-coating technique was used for deposition of nanostructured ZnO. Zinc acetate dihydrate $[Zn(CH_3COO)_2 \cdot 2H_2O]$, ethanol (C_2H_5OH), and ammonium hydroxide (NH_4OH) were used as the starting materials for the preparation of ZnO thin films. 0.2 M zinc acetate was dissolved in 50 ml ethanol and refluxed for three hours at temperature of 80 °C and then cooled at room temperature. Ammonium hydroxide solution was added drop-

wise. The pH of the solution was initially greater than 7. After vigorous stirring for 20 min, the pH was measured to be 7.1. After approximately 1 h, the sol became milky. The films were deposited before the sol became milky. Prior to the deposition of the films, glass substrates were cleaned with liquid detergent followed by ultrasonic cleaning and with methanol. ETCL-01 dip coater was used for coating the films. ZnO thin films were obtained by repetitive dipping and withdrawal of the substrate with speed of 50 mm/min for particular number coats. The films so obtained were dried in air at room temperature. This process was repeated for different number of coats (5,6,7 cycles). As obtained thin films were annealed at 500 °C for 1 hour.

2. Characterization of nanostructured thin films

X-ray diffraction patterns of the ZnO thin films annealed at 500 °C were recorded using CuK α ($\lambda = 1.5418 \text{ \AA}$) radiation. The average crystallite size was estimated from the broadening of the (101) diffraction peak using the Scherrer equation. Microtopographical and elemental analyses of the samples were carried out with a JEOL 6300 (LA) scanning electron microscope equipped with an energy dispersive x-ray analyzer. Optical absorption spectra were recorded with Simadzu 2450 UV-VIS spectrophotometer.

III. RESULTS

1. Structural analysis

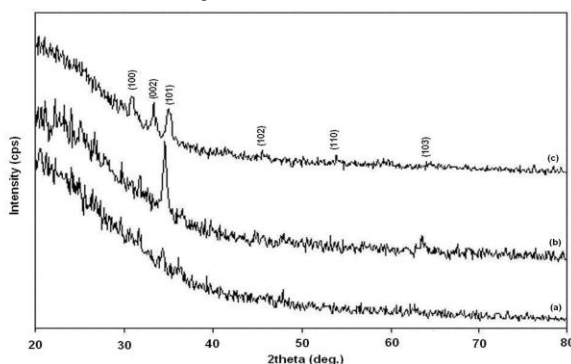


Fig. 1 X- ray diffractogram of ZnO thin films: (a) sample 1:[5 coats], (b) sample 2: [6 coats] and (c) sample 3: [7 coats].

Figure (a), (b) and (c) show the x-ray diffractogram of the ZnO films prepared with 5, 6 and 7 coats

respectively. The prominent peaks are matching with the standard ASTM data for ZnO [15]. The XRD peaks of the sample 1 are very weak. It may be due to amorphous nature of film material. X-ray peaks are observed to be broadened and broadening goes on increasing with increase in number of coats. Average particle sizes of sample 2 and 3 are calculated using Scherrer formula and represented in table 1.

Table 1: Crystallite size calculated from (101) peak for 6 and 7 coats

Sample	No .of coats	Average crystallite Size(nm)
S1	5	15
S2	6	21
S3	7	27

It is clear from table 1 that particle size goes on increasing with increase in number of coats. Amount of ZnO material deposited on the substrate would be larger if substrate would pass through larger number of coating cycles. It is, therefore, quite obvious to observe larger particle sizes with larger number of coats.

2. Elemental analysis by EDAX

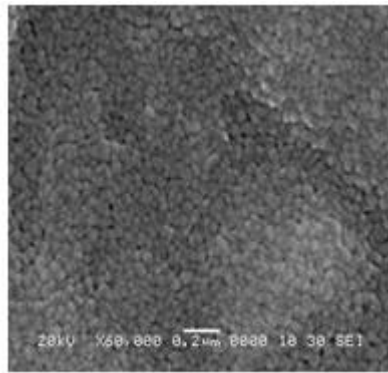
Table 2: Elemental compositions of ZnO thin films

Element	Sample 1		Sample 2		Sample 3	
	mass %	at. %	mass %	at. %	mass %	at. %
Zn	50.97	39.90	53.30	31.42	52.36	34.33
O	49.03	60.10	46.70	68.58	47.64	65.67
Total	100.00	100.00	100.00	100.00	100.00	100.00

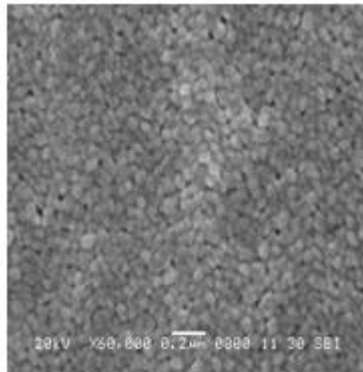
Theoretically expected mass % of Zn and O in stoichiometric ZnO are expected to be 80.3 and 19.7 respectively. The observed values of mass % of Zn and O, as represented in table 2, are not exactly matching with stoichiometrically expected mass %. The elemental compositions from table 2 clearly indicate that the films are nonstoichiometric in nature. The films are observed to be zinc deficient (oxygen rich).

3. Microstructure using SEM

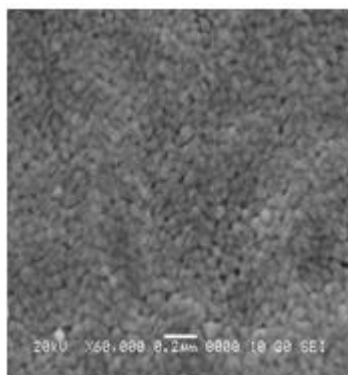
SEM micrographs of the as-prepared thin films were obtained to investigate their surface morphology and microstructure.



(a)



(b)



(c)

Fig.2 SEM images of as deposited ZnO thin films: (a) sample 1: [5 coats], (b) sample 2: [6 coats], and (c) sample 3: [7 coats].

Figure 2 (a),(b) and (c) show the microtopographs of the films obtained after 5, 6 and 7 coats respectively.

Both spherical and elliptical particles were observed, with a broad particle-size distribution.

In figure 2 (a) and (b) majority of particles are spherical as compared to elliptical. The majority of the particles in sample 3 were elliptical. The average grain/particle dimensions observed by SEM were estimated independently from the micrographs and observed be 30.6 nm, 34.6 nm and 37 nm respectively.

Table 3: Dependence of particle size on number of coats

Sample No.	No. of coats	Grain size (nm)	Shape of the grain		Remark
			Spherical	Elliptical	
1	5	30.6	Major	Minor	Transparent
2	6	34.6	about 50 %	about 50%	Transparent
3	7	37.0	Minor	Major	Transparent

From table 3, it is clear that all the samples are transparent and the grain size was observed to be increasing with the number of coats.

4. Electrical conductivity and activation energy

The electrical conductivity of the ZnO thin films was measured using a two-probe method over the temperature range of 358- 473 K

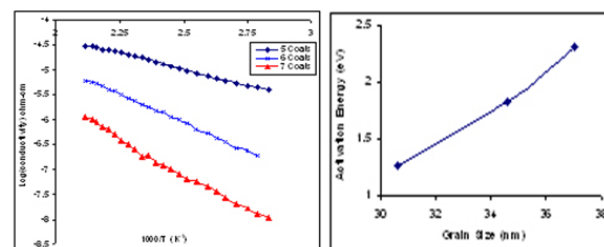


Fig. 3 (a) Variation of electrical conductivity with temperature and (b) Variation of activation energy (eV) with grain size (nm).

Figure 3 (a) shows the temperature dependence of d.c electrical conductivity of the samples. The activation energy of each sample was calculated from the slopes of the respective graphs. The activation energy is in the range 1.26 eV to 2.30 eV as tabulated in table 4. The activation energy increased with increasing grain size as indicated in figure 3 (b).

Table 4: Relationship between grain size, activation energy and number of coatings

Sample No.	No. of Coats	Grain Size (nm)	Activation Energy (eV)
1	5	30.6	1.26
2	6	34.6	1.83
3	7	37.0	2.30

It is clear from table 4 that activation energy goes on increasing with increase in grain size and number of coats.

5. Optical absorption

Optical absorption studies of zinc oxide thin films were carried out in the wavelength range 300.00 to 600.00 nm.

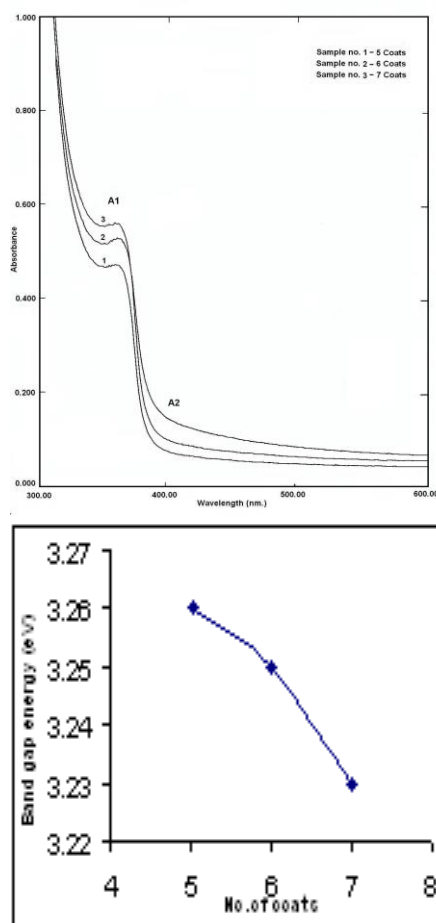


Fig. 4 (a) Plot of absorbance verses wavelength (nm) of thin films and (b) Variation of band gap energy (eV) verses number of coats.

Figure 4 (a) shows the variation of absorbance with wavelength of the thin film samples. Band gap energies calculated using edges A1 were observed to be varying from 3.64 to 3.75 eV [14]. These values are nearly matching with the reported value 3.37 eV. The variation in band gap energies may be due to nonstoichiometric nature of the films.

There are two absorption edges for each spectrum in figure 4 (a). The absorption edge on higher wavelength side (A2) may be due larger particles (following bulk properly) and the absorption edge on lower wavelength side (A1) may correspond to nanoparticles associated with the films.

Band gap energies calculated using edges A1 were observed to be varying from 3.64 to 3.75 eV. The higher values could be attributed to nanostructured ZnO.

Figure 4 (b) shows variation of band gap energy with number of coats. Band gap energy goes on decreasing with number of coats as tabulated in table 5.

Table 5: Relationship between grain size, Band gap energy and number of coatings

Sample No.	No. of Coats	Grain Size (nm)	Band gap energy (eV)
1	5	30.6	3.26
2	6	34.6	3.25
3	7	37.0	3.23

IV. DISCUSSION

The sol-gel process involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel).

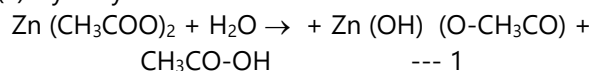
A fundamental requirement for the sol-gel chemistry is to form (network) a polymeric hydroxide. Since zinc belongs to the group which easily forms the polymeric hydroxide.

Dip-coating is simple, flexible and cost- efficient coating technique that in combination with the sol-

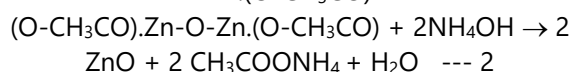
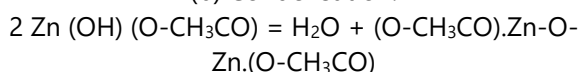
gel processing which allows the application of a variety of oxides on substrate. Thus good quality transparent, nanostructured zinc oxide thin films were successfully synthesized from sol-gel dip coating technique.

The possible chemical reactions responsible to form ZnO films could be as follows:

(a) Hydrolysis:



(b) Condensation:



In the process of hydrolysis, water molecule would react with zinc acetate and replace alkoxide group (CH_3COO) with hydroxyl group (OH). Subsequent condensation reaction would involve the $\text{Zn}(\text{OH})(\text{O}-\text{CH}_3\text{CO})$ group producing $\text{Zn}-\text{O}-\text{Zn}$ bonds plus by-product water and then further the production of ZnO .

V. CONCLUSIONS

Following statements can be made to summarize the results:

- Zinc oxide thin films were prepared by sol-gel dip-coating techniques.
- The films are nanostructured, transparent and nonstoichiometric in nature.
- The average crystallite sizes calculated using XRD for films prepared for 5, 6 & 7 coats are 15 nm, 21 nm & 27 nm respectively.
- The grain size observed from SEM is less than 50 nm.
- The EDX results indicate a deviation from the nominal stoichiometric composition, with an apparent oxygen-rich composition under the measurement conditions
- Number of grains goes on increasing and average grain size goes on increasing with number of coats.
- The band gap energy values are varying from 3.23 eV to 3.26 eV and from 3.64 to 3.75 eV.

- The activation energy values are varying from 1.26 eV to 2.30 eV.

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