RESEARCH PAPER

Studies on Sol-gel Dip-coated Nanostructured ZnO Thin Films

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ABSTRACT

Nanostructured ZnO thin films were prepared by sol-gel dip coating technique. Zinc acetate and ammonium hydroxide were used as precursors and ethanol was as solvent. Ammonium hydroxide (NH_4OH) solution was added drop-wise under vigorous stirring to obtain the sol-gel of different pH (varying from 6.9 to 7.2). ZnO thin films were obtained by dipping the glass substrates for few seconds and then dried in air at room temperature. This process was repeated for different number of coats for the typical sol. Different numbers of coating cycle was employed to obtain the films with varying thicknesses. These films were annealed at 5000C and were characterized by x-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive analysis of x-rays (EDAX). ZnO thin films obtained from sol-gel dip-coating technique were observed to nanostructured. Average particle size was observed to be smaller than 50 nm. The most of the particles were observed to be spherical in shape. ZnO films were observed to be nonstoichiometric (Zinc deficient) in nature. The results were discussed and interpreted.

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INTRODUCTION

Nowadays, research in the field of metal oxide nanoparticles is proceeding vigorously [1]. ZnO has attracted intensive research effort for its unique properties and versatile applications in ultraviolet (UV) light emitters, short-wavelength nano-lasers, and piezoelectric devices, ultrasensitive, spin electronics, field-effect transistors, and field emitters. ZnO is a typical n-type semiconductor, in which the density of holes in the valence band is exceeded by the density of electrons in the conduction band; the major charge carrier in ZnO semiconductors is electrons in the conduction band. Zinc oxide nanoparticles are used in various applications of catalyst [2], photocatalyst [3], U-V absorption and antibacterial treatment [4]. Zinc oxide is a wide band gap semiconductor with a band gap of 3.37 eV. Pure nonstoichiometric ZnO is n-type semiconductor. Its optical and electrical properties are not very stable at high temperature [5]. It is used for high power devices, ferroelectric memories, transparent conductive films used in displays, solar cells, various optoelectronic devices [6-8] and gas sensors [9- 16]. ZnO based material have been widely used as dielectric, ceramics, pigments, catalyst and sensing materials [17]. ZnO thin films have been grown using several deposition techniques, such as: spray pyrolysis [18], magnetron sputtering [19, 20], pulsed laser deposition [21, 22], chemical vapor deposition [23, 24] and sol-gel techniques [25].

Currently, there is a great interest in the methods of creating nanostructures on the surfaces for the next generation high performance

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nano-devices and for the number of molecular electronics applications. Therefore, synthesis and characterization of the nanostructured ZnO thin films and nanocrystalline powder have been an active area of research for nearly half a century and is still an active area of high priority research in nanoscale research [26-28]. ZnO exists in variety of nanostructures. Therefore, it is expected that it will be the next most important nanomaterial after the carbon tubes. In the present work, nanostructured ZnO thin films were prepared by sol- gel dip-coating technique and characterized by various analytical techniques.

MATERIALS AND METHODS

Zinc acetate [$(CH_3COO)_2$ $Zn.2H_2O$ GR grade] and ethanol was used as precursor materials. 0.2 M zinc acetate was dissolved in 50 ml ethanol under vigorous stirring at 800C. This solution was refluxed for 3 hours and then cooled to a room temperature as explain elsewhere [18]. Ammonium hydroxide (NH_4OH) was drop-wise added to obtain the sol-gel of different pH (varying from 6.9 to 7.2). ZnO thin films were obtained by dipping the glass substrates and then dried in air at room temperature. This process was repeated for different number of coats (dipping cycles) for the typical sol. ETCL –01 dip coater was used for coating the films. The films, so obtained were annealed at 5000C. The sol-gel was washed and dried at 5000C to obtain ZnO powder.

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

$$Zn(CH_3COO)_2 + 2NH_4OH \rightarrow 2CH_3COONH_4 + Zn(OH)_2 \quad (1a)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (1b)$$

Addition of ammonium hydroxide into zinc acetate would result into ammonium acetate and zinc hydroxide (Eq.1 (a)). Heat treatment would convert zinc hydroxide into ZnO (Eq.1 (b)).

The overall chemical reaction can be written as:

$$Zn(CH_3COO)_2 + 2NH_4OH \rightarrow ZnO + 2CH_3COO\,NH4 + H_2O \quad (2)$$

ZnO powder and films could therefore be obtained successfully prepared by sol-gel dip-coating technique.

As prepared ZnO powder was examined by Philips X-ray diffractometer (Model PW 1730). The surface morphologies of the films were studied by JEOL 6300(LA). The quantitative elemental analysis of the films was carried out by using JEOL-energy dispersive spectrometer (Model JED-2300). The transmission electron microscopy of the film was studied by Tecnai 20 G2 (FEI make).

RESULTS AND DISCUSSION

Structural analysis

Fig. 1. shows the x-ray diffractogram of the powder after drying the gel. The diffraction peaks from various planes and d values, as represented in Table 1, are matching well with reported JCPDS data for ZnO which confirmed the powder to be

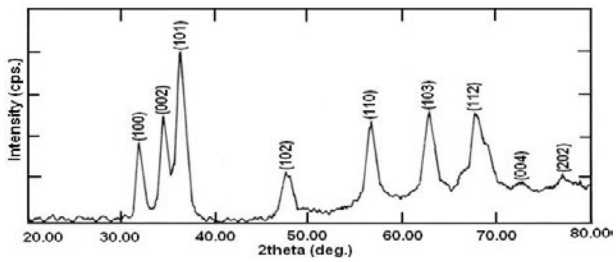

Fig.1. X-ray diffractogram of nanostructured ZnO.

Table 1: XRD data of ZnO

Peak No	*d* values Reported	*d* values Observed	Intensity Reported	Intensity Observed	Planes
1	2.816	2.811	71	50	100
2	2.602	2.604	56	67	002
3	2.476	2.479	100	100	101
4	1.911	1.916	29	37	102
5	1.626	1.624	40	63	110
6	1.477	1.478	35	67	103
7	1.379	1.384	28	68	112

of ZnO. The confirmation of the ZnO powder, in turn, would confirm that the material deposited on substrate to be of ZnO.

Scherrer's formula for grain size calculation

$$t = 0.9\ \lambda/\beta \cos\theta \quad (3)$$

Where, λ = Wavelength of X-ray, β = FWHM of peak, cos θ = Corresponding angle of the peak.

The average grain size calculated from Scherrer's formula was about 27 nm.

Elemental analysis by EDAX

Fig. 2 shows the energy dispersive spectra of the sample prepared with 5 coats and pH = 7.1. The mass% of Zn and O in stoichiometric ZnO (at% of each of Zn and O is 50) are expected to be 80.3 and 19.7 respectively. The observed values of mass % of Zn and O are represented in Table 2.

The elemental composition from Table 2, clearly indicates that the films are nonstoichiometric in nature. The films are observed to be zinc deficient.

Surface morphology using SEM

Effect of coating on particle size

Fig. 3(a), (b) and (c) are the SEM images of the thin films obtained after 5, 6 and 7 coats respectively from pH 7.1. The average particle sizes were observed from SEM image is presented in Table 3. The particle size distribution was observed to be reasonably narrow.

It is clear, from Table 3 that as the particle sizes increases with increase in number of coats.

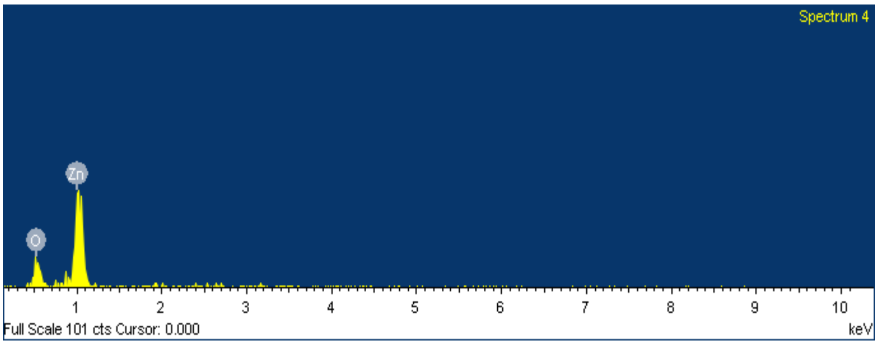

Fig.2. EDS spectra of sample prepared with 5 coats and pH = 7.1.

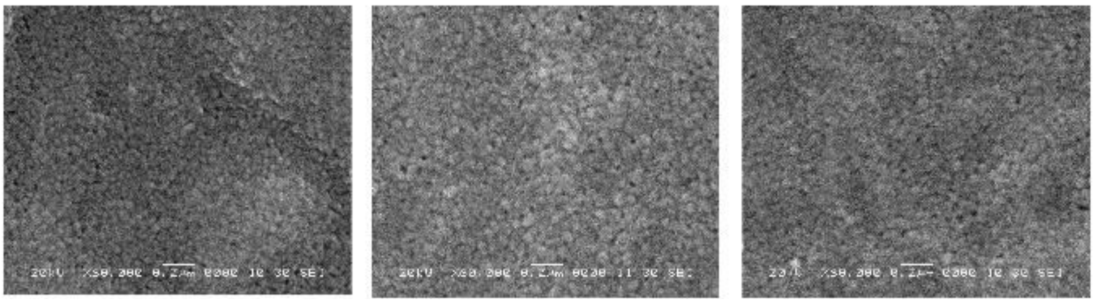

Fig.3. SEM images : (a) 5 coats, (b) 6 coats and (c) 7 coats

Table 2: Elemental compositions of typical ZnO thin films

Sample No.	No. of coats	mass %		at. %	
		Zn	O	Zn	O
1	5	50.97	49.03	39.90	60.10
2	6	53.30	46.70	31.42	68.58
3	7	52.36	47.64	34.33	65.67

Table 3: Variation of particle size with number of coats at pH = 7.1

No. of coats	5	6	7
Particle Size (nm)	30.6	34.6	37.0

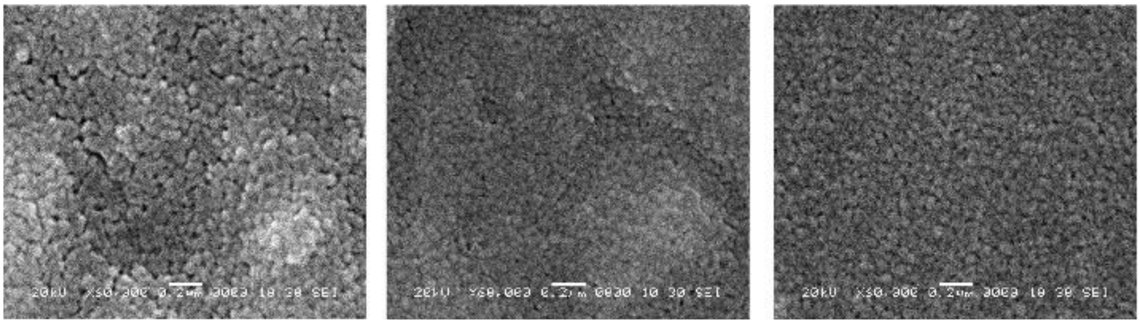

Fig.4. SEM images obtained from solutions with pH: (a) 6.9, (b) 7.1 and (c) 7.2

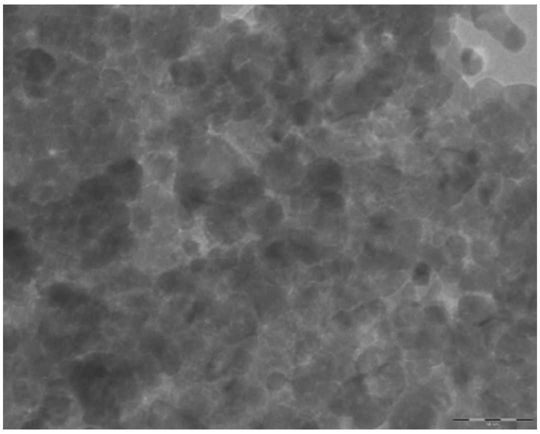

Fig.5. TEM image of sample prepared with 5 coats and pH = 7.1

Effect of pH on particle size and morphology

Fig. 4. (a), (b) and (c) show the SEM images of the film samples 1, 2 and 3 obtained from solutions with pH 6.9, 7.1 and 7.2 respectively. The average particle sizes of the films with pH 6.9, 7.1 and 7.2 were observed to be: 29.8 nm, 30.6 nm and 30.0 nm respectively. The particle size distribution seems to be reasonably narrow. The SEM images clearly indicate the elliptical or spherical shaped nanoparticles.

Microstructure using TEM

Fig. 5 shows the transmission electron microscopy image of the sample prepared with 5 coats and pH = 7.1. It is clear from TEM image that there are uniformly distributed spherical-shaped grains with the average grain size of 25 nm.

CONCLUSION

ZnO films obtained from sol-gel dip-coating technique were observed to nanostructured. The average grain size calculated from Scherrer's formula was about 27 nm. Average particle size was observed from SEM is to be smaller than 40 nm. The average grain size observed from TEM was about 25nm. The most of the particles were observed to be spherical in shape. ZnO films were observed to be nonstoichiometric (Zinc deficient) in nature. Number of coats used to synthesize the films was increase with increase in size of nanostructured ZnO.

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CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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