Indian Journal of Pure & Applied Physics
Vol. 47, January 2009, pp. 24-27

Effect of solvents on the particle morphology of nanostructured ZnO

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Received 14 May 2008; revised 25 August 2008; accepted 13 October 2008

Nanostructured ZnO thin films have been prepared by simple sol-gel dip coating technique. Zinc acetate, ammonium hydroxide, sodium hydroxide and ethanol are used as precursors. As prepared nanostructured films are annealed at 500°C and characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive analysis of X-rays (EDAX). The shapes of the particles are found spherical in nature having particle sizes in the range of 30 nm. With the change of solvent from ammonium hydroxide to sodium hydroxide, particle shapes have been changed from spherical to nanowires having average diameter of 60 nm.

Keywords: Nanostructured ZnO, Spherical nanoparticles, Nanowires, Sol-gel

1 Introduction

The synthesis and characterization of the nanostructured ZnO thin films is an active area of research for nearly half a century. ZnO exists in variety of nanostructures, therefore, it is expected that it will be the next most important nanomaterial after the carbon tubes[1-4]. Zinc oxide is a wide band gap semiconductor with a band gap of 3.37 eV and large binding energy 60 meV. Nonstoichiometric pure ZnO is *n*-type semiconductor. Its optical and electrical properties are not very stable at high temperature[5]. ZnO based materials have been widely used as dielectrics, ceramics, pigments, catalyst and sensing materials[6-8].

A variety of techniques have been applied so far for fabricating ZnO thin films, such as plasma-enhanced molecular beam epitaxy (MBE)[9,10], sputtering[11,12], pulsed laser deposition[13,14] and the sol-gel method[15-17]. Sol-gel technique has the advantages of being non-vacuum, low substrate temperature deposition and low cost technique. At present, sol-gel technique is one of the well-known procedures for deposition of metal oxide (ZnO, WO_3, SnO_2) thin films.

In the present study, nanostructured ZnO thin films are prepared by sol- gel dip-coating technique. The effect of preparative parameters, such as, *p*H of the sol, number of coats and solvents used, on the shape and morphology of the particles are studied. These films are employable in gas sensing. Improved gas sensing performance is expected from these nanostructured films.

2 Experimental Details

Two routes (Figs 1 and 2) were employed to synthesize ZnO thin films and powder.

In first route, sol was obtained from GR grade zinc acetate [$(CH_3COO)_2$ $Zn.2H_2O$], ethanol and ammonium hydroxide (NH_4OH) solutions. The *p*H of the sol was set at 7.2 by varying the quantity of ammonium hydroxide. The gel was obtained by adding 5 gm of polyethylene glycol (PEG) in water. The sol was mixed into gel. The so obtained sol-gel was allowed for aging for 5 hrs. The ZnO thin films were then obtained by dipping the substrates using ETCL –01 dip coater. The sol-gel was dried, washed and annealed at 500°C for 2 h to obtain the ZnO powder.

In second route, zinc acetate, ethanol and sodium hydroxide (NaOH) solutions were used. The solution pH was varied with the use of NaOH. The gel was obtained by dissolving polyethylene glycol into water. The sol was slowly mixed into gel. After aging for 2 h sol-gel was obtained. The ZnO thin films were then obtained by dip coating technique. Remaining sol-gel product was dried, washed and annealed at 500°C to obtain the ZnO powder.

ZnO powders obtained from routes 1 and 2 were examined by Philips X-ray diffractometer (model PW 1730). The surface morphologies of the films were studied by JEOL6300(LA). The quantitative elemental analysis of the films was carried out by JEOL-energy dispersive spectrometer (model JED-2300).

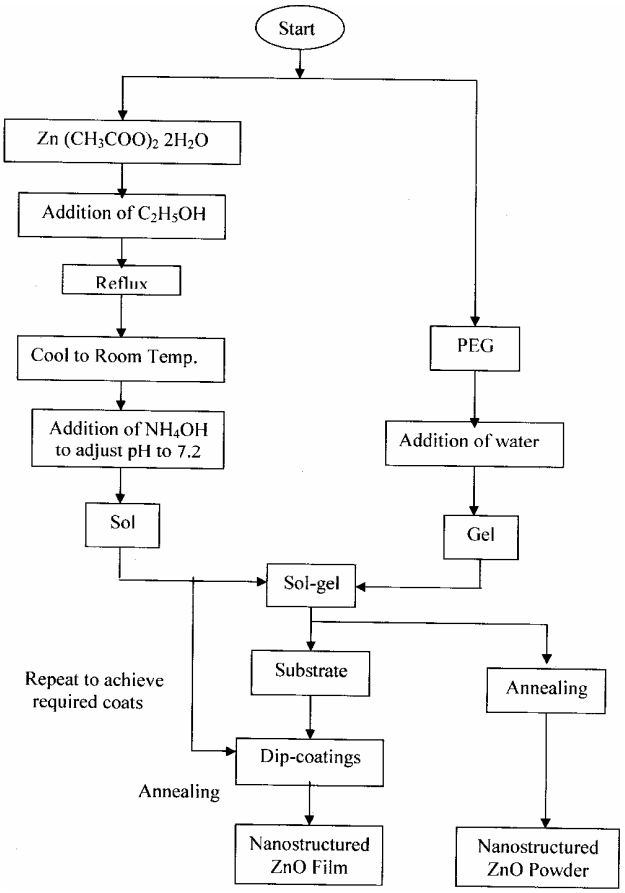

Fig. 1 — Synthesis of nanostructured ZnO films / powder by using ammonium hydroxide as a solvent

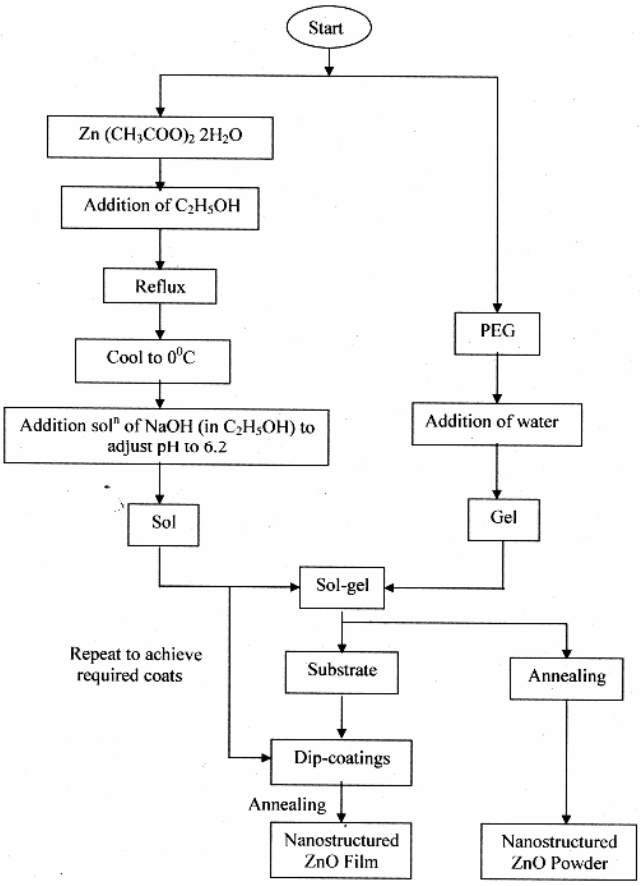

Fig. 2 — Synthesis of nanostructured ZnO films / powder by using sodium hydroxide as a solvent

3 Results and Discussion

3.1 Structural analysis

Figure 3 shows the X-ray diffractogram of the powder obtained from route 1. The diffraction peaks from various planes and *d* values are matching well with reported JCPDS data for ZnO[18], which confirms the formation of ZnO. By confirming the powder to be of ZnO, the material deposited on films would also be excepted as ZnO.

The grain size was determined using Scherer formula and was observed to be 27 nm.

Figure 4 shows the X-ray diffractogram of the powder obtained from route 2. Most of the diffraction peaks from various planes and *d* values are matching with reported JCPDS data for ZnO[18], which confirmed the formation of ZnO.

The average grain size was determined using Scherer formula and was observed to be 39 nm as calculated from the peak related to (110) plane.

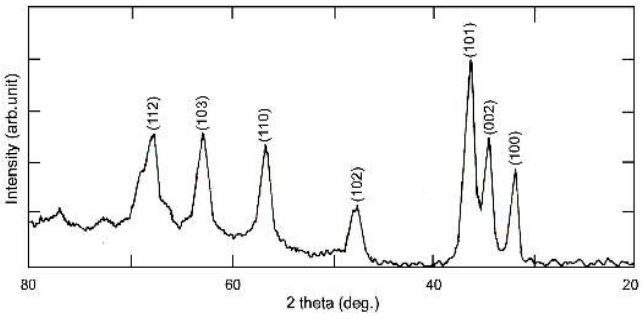

Fig. 3 — X-ray diffractogram of nanocrystalline ZnO by using NH_4OH as a solvent

3.2 Elemental analysis by EDAX

Theoretically expected stoichiometric mass % of Zn and O in ZnO are 80.3 and 19.7 respectively.

The elemental composition from Table 1 indicates that the films are nonstoichiometric in nature. The films obtained using NaOH solvent are nearer to stoichiometry.

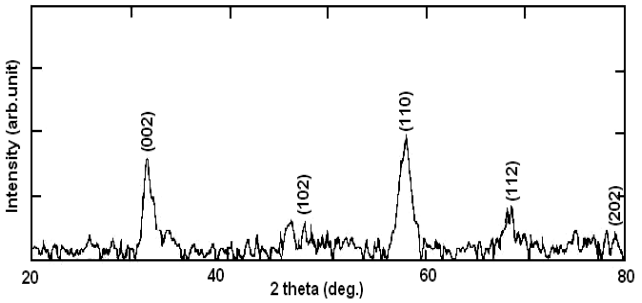

Fig. 4 — X-ray diffractogram of nanocrystalline ZnO by using NaOH as a solvent

Table 1 — Elemental compositions of ZnO films

Solvent	*p*H of Sol	mass %		at. %	
		Zn	O	Zn	O
NH_4OH	7.2	51.18	48.42	38.84	61.16
NaOH	6.2	70.41	29.59	36.65	63.35

3.3 Microstructure using SEM

Effect of solvents (NH_4OH or NaOH) on the particle morphology is shown in Figs 5 and 6.

The SEM images of the samples obtained respectively from route 1 and route 2 are shown in the figures. It is clear from images that as ammonium hydroxide (NH_4OH) solvent is replaced by sodium hydroxide (NaOH), the shape of the spherical ZnO nanoparticles is observed to be changed into ZnO nanowires.

It has been observed that when ammonium hydroxide is used as the solvent, the particles are spherical while the particles are wire like when sodium hydroxide is used as solvent (Table 2). The change in shape from spherical to nanowires could be attributed to one directional growth due to presence of Na^+ ions.

The overall chemical reaction responsible to form ZnO when NH_4OH is used as solvent is as follows:

$$Zn\ (CH_3COO)_2 + 2NH_4OH \rightarrow ZnO + 2CH_3COO\ NH_4 + H_2O$$

The overall chemical reaction responsible to form ZnO when NaOH is used as solvent is as follows:

$$Zn\ (CH_3COO)_2 + 2\ NaOH \rightarrow ZnO + 2\ NaCH_3COO + H_2O$$

Sodium acetate is water soluble and could therefore be removed from the end product. High purity ZnO nanopowders and films could therefore be obtained successfully by sol-gel dip-coating technique.

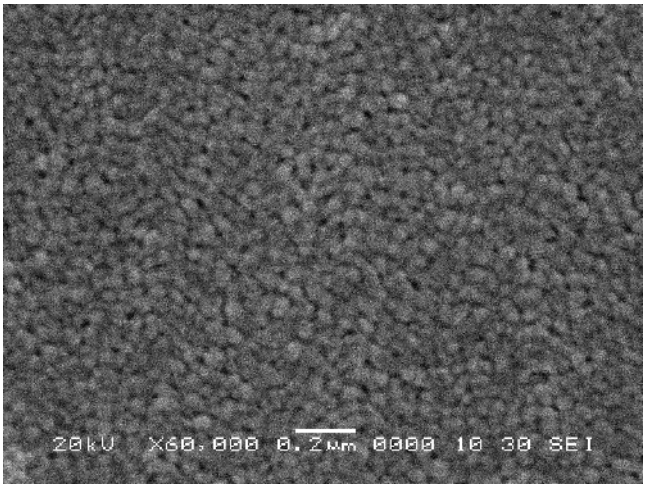

Fig. 5 — SEM image of sample obtained using ammonium hydroxide solvent

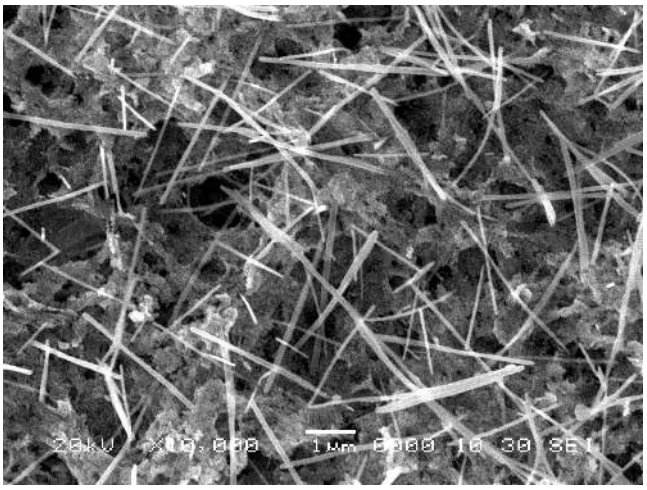

Fig. 6 — SEM image of sample obtained using sodium hydroxide solvent

Table 2 — Effect of solvents on shape of particles

Solvent	*p*H	Shape	Particle size (nm)
NH_4OH	7.2	Spherical	30
NaOH	6.2	Wires	60

4 Conclusions

The structural and microstructural characterization of sol-gel-dip-coated films indicate that they are nanocrystalline in nature. Most of the particles obtained from route 1 were observed to be spherical in shape. The particle size (obtained from route 1) was observed to be smaller than 50 nm. The particles obtained from route 2 were observed to be wire like which are having average diameter of 60 nm. ZnO films were observed to be nonstoichiometric in nature. Solvents affect the particle morphology of the nanostructured ZnO films.

Acknowledgement

The authors are thankful to the Head, Department of Physics and Principal, Pratap College, Amalner, for providing laboratory facilities for this work. The authors are also thankful to the Department of Information Technology, Govt. of India, New Delhi, for providing financial support.

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