Synthesis of zinc oxide nanopowder and nanolayer via chemical processing

Tolou Shokuhfar*

Centre for Mechanical Technology and Automation,
Department of Mechanical Engineering,
University of Aveiro,
3810-193 Aveiro, Portugal
E-mail: tshokuhfar@mec.ua.pt
*Corresponding author

M.R. Vaezi and S.K. Sadrnezhad

Advanced Materials Research Center,
Materials and Energy Research Center, MERC Karaj, Iran
E-mail: Vaezi9016@yahoo.com
E-mail: sadrnezh@sharif.edu

A. Shokuhfar

Advanced Materials and Nanotechnology Research Center,
Department of Materials Science and Engineering,
K.N. Toosi University of Technology, Tehran, Iran
E-mail: shokuhfar@kntu.ac.ir

Abstract: In the present research work, the newest economic method for synthesis of ZnO nanopowder has been carried out via solochrome processing from an aqueous solution of a zinc-containing complex. The results obtained from XRD and TEM show that the nanoparticles are single crystals and have elongated particulate shape with a narrow size distribution. Solochrome processing can thus be an attractive method for industrial production of the nanopowders. The highly textured ZnO thin film with a preferred (002) orientation was also prepared by Two-Stage Chemical Deposition (TSCD), using an aqueous solution containing zinc complex on a soda-lime glass substrate. The films were characterised by XRD, SEM, EDAX, optical spectrophotometer and FTIR to justify the suitability for commercial device quality.

Keywords: zinc oxide; Two-Stage Chemical Deposition; TSCD; nanograins; optical transmission; doping.


Biographical notes: T. Shokuhfar is currently Principal Investigator and continuing her PhD studies at the Centre for Mechanical Technology and Automation University of Aveiro and is Principal Investigator of the
1 Introduction

Zinc oxide has a wide range of applications in the functional devices, catalysts, pigments, optical materials, cosmetics, nanostructure varistors, UV absorbers, gas sensors and industrial additives (Hingorani et al., 1993; Sakohara et al., 1998; Zhao et al., 1997). Different methods for production of ZnO nanopowders have already been investigated (Hingorani et al., 1993; Sakohara et al., 1998; Zhao et al., 1997; El-Shall et al., 1995; Lin et al., 1998). Mechanochemical processing is an example Tszuuki et al. (1997), Ding et al. (1995, 1996a, 1996b, 1997), Schaffer and McCormick (1990) and
Leite et al. (1996), but it needs milling; therefore, it can not be economically feasible to be applied as a nanopowder mass production process.

Solochemical (SC) processing is a new zinc oxide nanopowder production method that involves preparation of a solution containing zinc complex and subsequent decomposition of the complex into the zinc oxide nanopowder. Another name for this method is Two-Stage Solochemical (TSSC) method. TSSC method can also be used for production of other oxides such as Mn2O3 and NiO. Pouring of a limpid chemical (containing zinc complex) onto a second chemical leads to the formation of a nanoscale powder.

The solochemically formed nanopowders can further be doped with other oxides. The product materials can form a new type of nanocomposites. Nanocomposite particles are usually used as varistors with nanostructure morphology.

Zinc oxide thin films offer a variety of applications. Highly oriented low-conductivity film can be used as an ultrahigh-frequency electroacoustic transducer because of its piezoelectric properties (Jin et al., 2000; Lin et al., 2001). High-conductivity ZnO thin films with high visible spectrum transparency coefficient can be used as a transparent electrode in the field of optoelectronic display and the field of photovoltaic solar energy conversion (Studeniki et al., 1998; Joeph et al., 1999). Bulky ZnO is quite expensive nowadays. It is not usually available as a large wafer. ZnO thin films are, therefore, desirable as a substitute.

ZnO thin films can be produced by numerous methods. Sputtering, electron beam evaporation (Kuroyanagi, 1989), spray pyrolysis (Gopalaswamy and Reddy, 1990), MOCVD (Kim et al., 1992), electroless bath deposition (Ristov et al., 1987), PLD (Ramamoorthy et al., 2001) and chemical deposition (Mitra et al., 1998) are some examples. Chemical deposition is an advantageous technique for formation of a largely surfaced thin film. Deposition of ZnO films with controllable thickness and conductivity is made possible by using this method. Deposition is performed onto any substrate nonreactive with the chemicals used for deposition.

In the present investigation, Two-Stage Chemical Deposition (TSCD) process was applied to produce ZnO thin films. The substrate was first immersed into a cold aqueous solution containing a complex compound consisting of Zn⁺⁺ ions. It was then covered with a layer of the complex and dipped into a boiling distilled water bath to facilitate the decomposition of the complex into the desirable ZnO layer. Results of the most recent studies carried out in our laboratory on synthesis of ZnO nanopowders via two-stage solochemical reaction \((\text{NH}_4)_2\text{ZnO}_2 + \text{H}_2\text{O} \rightarrow \text{ZnO} + 2\text{NH}_3\text{OH}\) are reported in this paper. Also, this paper gives details of composition, structure, optical and infrared properties and surface morphology of ZnO thin films deposited via TSCD method on soda-lime substrates.

2 Experimental

2.1 Preparation of zinc oxide nanopowder

Anhydrous ZnCl₂ powder (Merk, 99.5%), ammonia and an appropriate additive were used to produce the initial zinc-containing solution. ZnCl₂ powder was dried in air at 150°C overnight prior to use and milled simply in a ceramic mortar. It was then added to a beaker containing NH₄OH aqueous solution to produce the complex.
Concentrated NH₄OH was gradually poured into the beaker until a white precipitate of zinc hydroxide was formed. Further addition of NH₄OH resulted in dissolution of the precipitate, indicating the time for addition of the additives. The transparent solution was diluted with de-ionised water. It was then dropped into the second solution containing the additive at 100°C to produce zinc oxide nanopowder.

Nanopowders were then washed with ethanol and collected in a glass case. The powder was subsequently dried at 60°C in an oven, holding the sample for several hours. It was then characterised by X-ray diffraction (XRD) (Cu-Kα radiation), Transmission Electron Microscopy (TEM), simultaneous Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA).

2.2 Preparation of zinc oxide thin film

Soda-lime plates with 25 × 15 × 1 mm³ dimensions were used as the solid substrate for film growth. After degreasing, the plates were washed with deionised water and dried in a steam of hot air. Aqueous solution containing \(\text{NH}_4\text{Cl}_2\text{ZnO}_2\) was prepared by mixing concentrated NH₄OH with 0.5 M ZnCl₂ until white Zn(OH)₂ was precipitated. Further addition of NH₄OH resulted in dissolution of the precipitate. The solution was diluted up to appropriate concentration of Zn²⁺ complexes. This was found to be the most convenient concentration for production of a good-quality film on the substrate. Cleaned glass substrates were first immersed into a cold (15°C) complex-containing solution and then in hot water (90–115°C) for 2 s. After a required number of dipping, the substrate with the deposited ZnO film was annealed at 250°C for 30 min.

Crystalline structure of the film was determined by XRD method. XRD diffractograms were obtained using Cu-Kα radiation beams produced by a Philips PW1390 apparatus. Knowing the surface area of the substrate and the deposited mass of the layer, the thickness of the film was determined by assuming a precipitate density of 5.606 g/cm³. SEM was used to study the surface morphology of the thin layer. Semi-quantitative analyses of the grown layers were determined with a Kevex model EDAX system. Optical properties of ZnO thin films were determined by UV–Vis spectrophotometer model V-530 Jasco.

3 Results and discussion

3.1 Zinc oxide nanopowder

3.1.1 X-ray diffraction

Figure 1 depicts the X-ray diffraction spectrum of the nanopowder sample produced by SC method. The experimental values obtained for the lattice parameter \(d\) of the powder were comparable with those given by ASTM (card number 3-0888). These values indicated a hexagonal crystal system with wurzite structure of ZnO, having the prominent diffraction peaks from such crystal planes as (100), (002) and (101). A mean particle size of 35 nm was calculated for (101) crystal planes by Scherrer’s formula. This value agreed well with TEM micrograph of the ZnO powders.
3.1.2 Transmission Electron Microscopy (TEM)

A typical TEM micrograph of the ZnO powder processed by SC method at different magnifications is shown in Figure 2. The powder consisted of 20–60 nm particles having two morphologies:

- equiaxed particulates
- elongated grains.

These morphologies are related to the SC processing nature.
The particles appeared to be well separated from each other. Figure 3 shows the Diffraction Pattern (DP) imaging of the produced nanopowder. Sharp diffraction rings appear in the diffraction pattern, and strong diffraction spots exist in these rings. The diffraction pattern corresponds with zinc oxide. As shown in Figure 3, no amorphous phase can be detected in the diffraction pattern. Dark field imaging revealed that each particle was a single crystal. As is shown in Figure 2, each elongated particle contained some porosity. This was related to the nature of the SC processing. Due to the difference between the temperatures of the two chemical solutions, the formation of ZnO nanopowder was accompanied with a thermal shock, which resulted in production and increase of porosity in powders, especially the elongated and the large particles that sensed greater shock effects.

Figure 3  The diffraction pattern imaging of ZnO nanopowder

TEM studies indicated a mean particle size of 45.3 nm, with a standard deviation of 9.8 nm. This was as good as the nanopowders produced by the mechanochemical method measured by TEM analysis (Tsuzuki and McCormick, 2001). The nanopowders produced in this research can be used in gas sensors for air pollutant’s detection. These nanopowders incorporate innovative specifications obtained for the first time.

3.1.3 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectrum is an important record, which provides information about the structure of a compound. Almost all functional groups in a molecule characteristically absorb within a definite range of frequency in this technique (Kalsi, 1985). Transmission of IR radiation in this technique causes the various bonds in a molecule to stretch and bend with respect to one another. In the present study, infrared transmission spectrum of the solochemically synthesised zinc oxide nanopowder was recorded to be in the range of 4000-400 cm$^{-1}$. The result is a transmittance infrared spectrum, which is shown in Figure 4.
The aim of the present IR spectral analysis on the synthesised ZnO nanopowder includes:

- assessment of the formation of the material
- the absence of un-reacted starting materials in the synthesised ZnO nanopowder.

A systematic interpretation of the IR spectrum can be of great help to determine whether a reaction occurs and to give the possible products. The absorption region from 650 cm$^{-1}$ to 1500 cm$^{-1}$ represents generally the fingerprint region of the materials, which are unique in characteristic. As reported in the literature (Kalsi, 1985), Zn–H vibrations (both symmetric and asymmetric) are indexed around 150 cm$^{-1}$ and O–H stretching is observed around 3500 cm$^{-1}$. The presence of Zn–H vibration may be attributed to the adsorption of hydrogen during SC processing, while the presence of O–H vibration may probably be attributed to the residual Zn(OH)$_2$ present in the powder.

### 3.1.4 TG/DT analysis

Figures 5 and 6 show TG/DTA curves of the nanopowder produced by SC method. The TGA curve shows that the weight loss occurs in three stages:

- A weight loss of 6.411 occurring in the temperature range 21.7–402$^\circ$C.
  This weight loss attributes to the adsorption of humidity on the exterior surface of the nanopowders, which can be desorbed from the surface during heating the sample by the TG analyser.
The second stage occurs in the temperature range of 402.1–563°C, corresponding to a weight loss of 10.01%, attributed to the adsorption of humidity in the interior pores of the nanopowder desorbed from the pores during the TGA processing.

The third stage is related to evolution of the additional humidity from pores, which cannot exit during heating of the sample. No appropriate exo- or endothermic peaks are evident in the DTA curve.

Figure 5  TGA curve of ZnO nanopowder obtained from SC processing

![TGA curve of ZnO nanopowder](image)

Figure 6  DTA curve of ZnO nanopowder obtained from SC processing

![DTA curve of ZnO nanopowder](image)

3.2 Zinc oxide thin film

Effect of increasing of the dipping number on the thickness of the deposited ZnO film is presented in Figure 7. The deposition rate per dipping was averaged to 0.012 µm. Figure 1 shows that the thickness variation vs. dipping number is linear and that the rate of increase of the thickness is constant. Unchanged solution concentration during the growing process seems to be responsible for this effect.
Figure 7 The variation of film thickness vs. the number of dipping

![Graph showing the variation of film thickness vs. the number of dipping.](image)

3.2.1 Phase evaluation and particle size of the samples

X-ray diffraction patterns of zinc oxide thin films are shown in Figure 8. Crystal structure and chemical composition of the phases are determined from these graphs. It is concluded that the deposited thin film is pure ZnO. Other materials such as impurities are below limits of detection. Comparing the peaks pronounced at $2\theta = 34.3$ (Figure 8) with standard ones shows that the preferred orientations of the microcrystals of the film are along the $c$-axis normal to the surface of the substrate (002) crystal plane. From the recorded spectrums, one can understand that the degree of crystallinity improves with the number of dipping.

Figure 8 X-ray diffractograms of the ZnO thin films for various number of dipping. (a) 25, (b) 50, (c) 75, (d) 100, and (e) 150 times of dipping

![X-ray diffractograms of ZnO thin films for various number of dipping.](image)
The crystallite sizes (R_x) of the films were calculated from the XRD peak broadening of the (002) peak at a diffraction angle 2θ = 34.3 using Scherrer’s equation:

\[ R_x = \frac{0.9\lambda}{\beta \cos \theta} \]

where \( \lambda \) is the wavelength (1.5406 Å for Cu-Kα radiation), and \( \beta \) is the Full-Width Half-Maximum (FWHM) of a peak in radians. The calculated grain size by Scherrer’s formula exhibits increasing grain size with the number of dipping (Table 1).

<table>
<thead>
<tr>
<th>Number of dipping</th>
<th>25</th>
<th>50</th>
<th>75</th>
<th>100</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_x ) (nm)</td>
<td>10</td>
<td>13</td>
<td>15</td>
<td>22</td>
<td>32</td>
</tr>
</tbody>
</table>

3.2.2 Optical transmission

Effect of dipping number on transmission spectrum of the ZnO film measured with fluorescence spectrophotometer is presented in Figure 9. Highest transmittance was attained at 550 nm wavelength, with a dipping number of 75 or higher. It was observed that annealing at 300°C, no matter periodic or continuous, causes better alignment of the textured films. This effect was increased with the number of dipping and finally led to reduction in free carrier absorption and low reflection loss, resulting in enhancement of the transmission percentage.

Figure 9  Optical transmission spectrum of the ZnO thin films for different dipping numbers

As is seen in Figure 9, there is a high transmission region exceeding 90% with a sharply defined absorption edge at 320 nm. To resolve whether the material has a direct or indirect band gap, plots of \((a hν)^2\) vs. \(hν\) and \((a hν)^{1/2}\) vs. \(hν\) were analysed. Better linearity was observed in the former case (Figure 10), from which the optical energy gap is obtained by extrapolating the linear portion of the absorption spectrum to \(ahν = 0\). Thus, an energy band gap of 3.28 eV was deduced. This value agrees well with the reported band gap values given for bulk undoped ZnO before (Yamamoto et al., 1980). The sharp
absorption onset and high transmission values of ZnO film at wavelengths above 400 nm exhibit the optical quality and low concentration of defects such as voids (Joeoph et al., 1999).

**Figure 10** Plot of \((ahv)^2\) as a function of the energy \((hv)\)

![Plot of \((ahv)^2\) as a function of the energy \((hv)\)](image)

3.2.3 *Energy dispersive analysis by X-ray (EDAX)*

Elemental composition of the sample was determined by EDAX analysis. Figure 11 demonstrates the results of the ZnO layer. Other peaks reveal the existence of Ca, Si and Cl. They belong to the substrate or come from the complex containing aqueous solution.

**Figure 11** EDAX elemental analysis of the undoped layer

![EDAX elemental analysis of the undoped layer](image)
3.2.4 Scanning Electron Microscopy (SEM)

Figure 12 illustrates the scanning electron microscope image from the surface of the zinc oxide layers produced by 100 times dipping process. As is seen in the figure, the uniformity of the film and the adherence nature is confirmed. This image reveals the presence of crystallites. The presence of spherical crystallites evidences the optimised experimental conditions such as the molar concentration and the number of dipping.

Figure 12  SEM micrograph of the surfaces of the oxide film produced after 100 times dipping process

4 Conclusions

High-quality nanopowders can easily be obtained by solochemical method. After preparation of a transparent solution containing zinc complex and gradual pouring of the solution into hot water, formation of ZnO nanopowder starts to take place. The mean particle size is 45.3 nm. This value agrees well with the result of the mechanochemical processing studied by other investigators, before. Elongated particles have a particulate morphology characteristic of the SC process with a noticeable amount of porosity. SC processing seems particularly suitable for a large-scale production of ZnO.

Very low-conductivity ZnO thin film can easily be deposited by successive immersions of the substrate

- in a cold ammonia complex solution
- subsequently in hot water.

The reaction that leads to form ZnO is as follows:

\[(\text{NH}_4)_2\text{ZnO}_2(\text{Complex}) + \text{H}_2\text{O}_{(aq)} \rightarrow \text{ZnO}_{(s)} + 2 \text{NH}_4\text{OH}_{(g)}\].

The thickness of the film is controllable with the help of successive immersion procedures. The optical transmission of the sample produced by 150 times dipping process shows a sharp absorption onset. High transmission values occur at wavelengths of 400 nm. Combination of sharp absorption onset and large transmittance percentage results in high-quality optical properties and low concentration defects.
Experimental results clearly indicate that ZnO thin films obtained by TSCD process introduced in this paper possess a sufficient quality adequate for industrial applications for making optical devices and UV lasers.

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