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Short communication

Highly textured ZnO thin films: An economical fabrication, doping by Mn^{2+} and Sn^{2+} and approachment for optical devices

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Abstract

Fabrication of high quality zinc oxide thin films and analysis on its physical, chemical properties have applications in opto-electronic devices, UV laser, microelectronics and micro-machining schemes. Highly textured ZnO thin film with a preferred (0 0 2) orientation was prepared by two-stage chemical deposition (TSCD) using an aqueous solution containing zinc complex on a soda-lime glass substrate. From the results obtained, it can be shown that the preferred orientations of the film microcrystal changes with the doping process. The film was characterized by X-ray diffraction (XRD), SEM, EDAX, optical technique, Fourier transform infrared spectroscopy (FTIR) in order to qualify its suitability for application in commercial devices. Effect of number of dipping on growth rate and properties of the undoped and doped-thin film was investigated. XRD patterns revealed the formation of polycrystalline textured thin films containing nano-grains. The chemical compositions of the thin films were determined by EDAX and FTIR methods. SEM reveals the presence of uniform adherent thin film. Increasing in grain size (R_x) of undoped and doped thin films were observed, while increasing the number of dipping. Optimized films allowed a 96% average transmission in the visible range. The mean band gap measured from the transmission spectrums of the undoped samples was 3.25 eV. The transmission curves of doped samples fluctuated with increasing the wavelength and this is due to interference of the light in the film itself. Feasibility of the prepared films for application in optical and UV laser devices was assessed by optical systems.

Keywords: Zinc oxide thin films; Two-stage chemical deposition; Optical transmission; Doped samples

1. Introduction

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 [1,2]. 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 in the field of photovoltaic solar energy conversion [3,4]. Bulky ZnO is quite expensive now a days. It is not usually available as a large wafer. Thin ZnO films are therefore desirable as a substitute.

ZnO thin films can be produced by numerous methods. Sputtering, electron beam evaporation [5], spray pyrolysis [6], MOCVD [7], electroless bath deposition [8], PLD [9] and chemical deposition [10] 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.

Two-stage chemical deposition (TSCD) is used here to produce ZnO thin films. The substrate was first immersed into a cold aqueous solution containing a complex com-

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pound consisting of Zn^{2+} ions. The substrate was first covered with a layer of the complex. It was then dipped into a distilled boiling water bath to facilitate the decomposition of the complex into the desirable ZnO layer. This paper gives details of composition, structure, optical and infrared properties, surface morphology and PL properties of ZnO thin films deposited via TSCD method on soda-lime substrates.

2. Experimental procedure

Soda-lime plates with $25 \times 15 \times 1$ mm dimensions were used as the solid substrate for film growth. After degreasing, the plates were washed with deionized water and dried in a steam of hot air. Aqueous solution containing $(NH_4)_2ZnO_2$ were prepared by mixing concentrated NH_4OH with 0.5 M $ZnCl_2$ until white $Zn(OH)_2$ was precipitated. Further addition of NH_4OH resulted in dissolving of the precipitate. The solution was diluted up to appropriate concentration of Zn^{2+} 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 300 °C for 30 min. Film doping with Sn^{2+} and Mn^{2+} was performed during the growth process by adding 10 cc of 0.1 M Na_2SnO_2 or $SnCl_2$ and 0.5 M $MnCl_2$ to the solution containing Zn^{2+} complex, respectively.

Crystalline structure of the film was determined by X-ray diffraction (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/cm^3. 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. ZnO thin films produced at different dipping numbers were characterized by an Fourier transform infrared spectroscopy (FTIR) and their optical properties were determined by UV–Vis spectrophotometer model V-530 Jasco.

3. Results and discussion

Effect of addition of Mn^{2+} and Sn^{2+} dopant and increasing of the dipping number on the thickness of the deposited ZnO film is presented in Fig. 1. It is seen that the doping process decreases the average deposition rate. The deposition rate per dipping was averaged to 0.012, 0.01 and 0.008 μm for undoped, Mn-doped and Sn-doped films, respectively. Fig. 1 shows that the thickness variation vs. dipping number is linear and that the rate of increasing of the thickness is constant. Unchanged solution concentration during the growing process seems to be responsible for this effect.

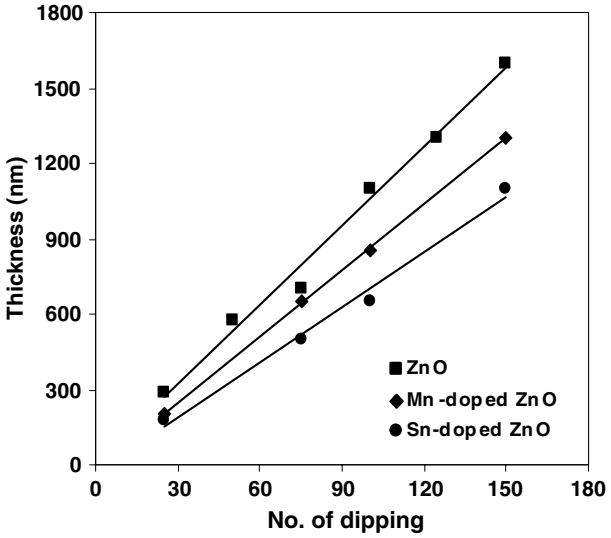

Fig. 1. The variation of film thickness vs. the number of dipping.

4. Phase evaluation and particle size of the samples

XRD patterns of (a) undoped, (b) Mn-doped and (c) Sn-doped zinc oxide thin films are shown in Figs. 2–4. 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 $2\theta = 34.3$ (in Fig. 2) and $2\theta = 36.2$ (in Figs. 3 and 4) with standard ones show that the preferred orientations of the microcrystals of the film are along the c axis normal to the surface of the substrate, (0 0 2) and (1 0 1) crystal planes. From the recorded spectrums, one can understand that the degree of crystallinity improves with the number of dipping. From this result, it can be shown that the preferred orientations of the film microcrystal changes with the doping process.

The crystallite sizes (R_x) of the undoped and doped films were calculated from the XRD peak broadening of the (0 0 2) peak for the undoped film and the (1 0 1) peak for the doped films at a diffraction angle $2\theta \sim 34.3$ and 36.2, respectively. Using Scherrer's equation:

$$R_x = (0.9\lambda)/(\beta \cdot \cos\theta),$$

where λ is the wavelength (1.5406 Å for Cu Kα radiation) and β 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). As it is indicated in Table 1, the crystallite size of the doped films is less than that of the undoped films.

The crystallite size of the Sn-doped films is considerably less than that of the Mn-doped films. The Sn-doped films are, therefore, considered as suitable candidates for manu-

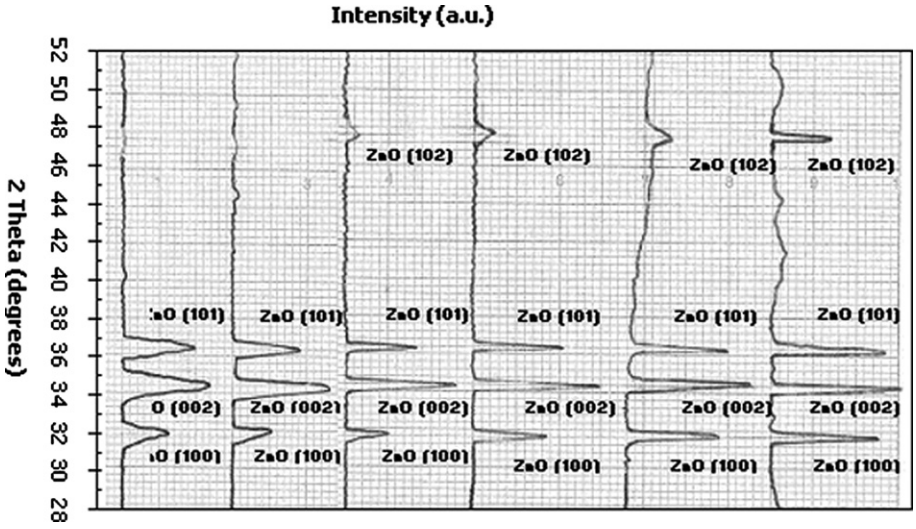

Fig. 2. X-ray diffractograms of undoped ZnO thin films.

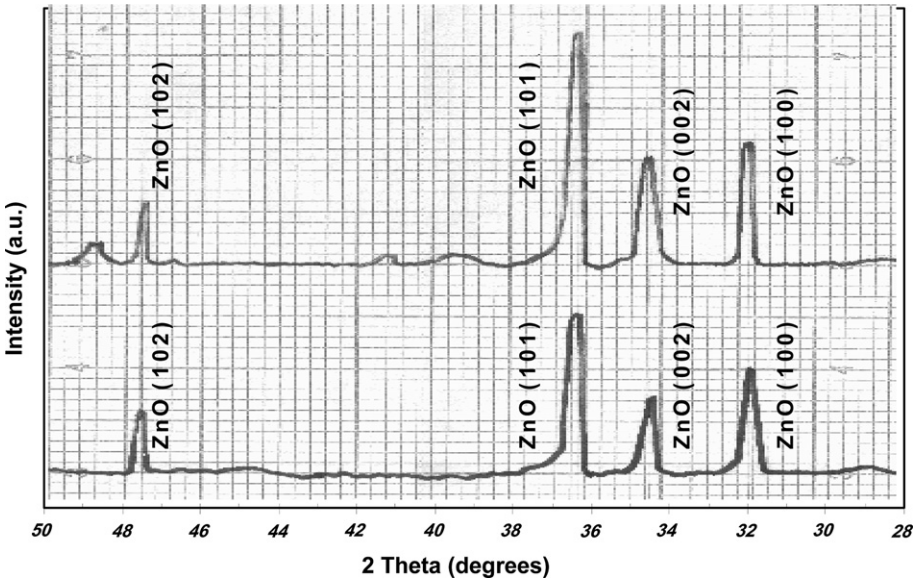

Fig. 3. X-ray diffractograms of Mn-doped ZnO thin film.

facturing of the thin film gas sensors due to their better sensing power.

5. Optical transmission

Effect of dipping number on transmission spectrum of the undoped ZnO film measured with fluorescence spectrophotometer is presented in Fig. 5. 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.

As is seen in Fig. 5, there is a high transmission region exceeding 90% with a sharply defined absorption edge at 320 nm. This region corresponds to an energy band gap of 3.25 eV determined from extrapolation of $(\alpha h\nu)^2$ vs. $h\nu$ to zero energy. This value agrees well with the reported band gap values given for bulk undoped ZnO before [11]. 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 [4].

The transmission spectra of Mn-doped and Sn-doped ZnO films are presented in Fig. 6. These spectra show the same fundamental absorption edge but not so sharply defined. The undulating shape of the transmission curves is caused by interference of the light in the film itself. Sn-

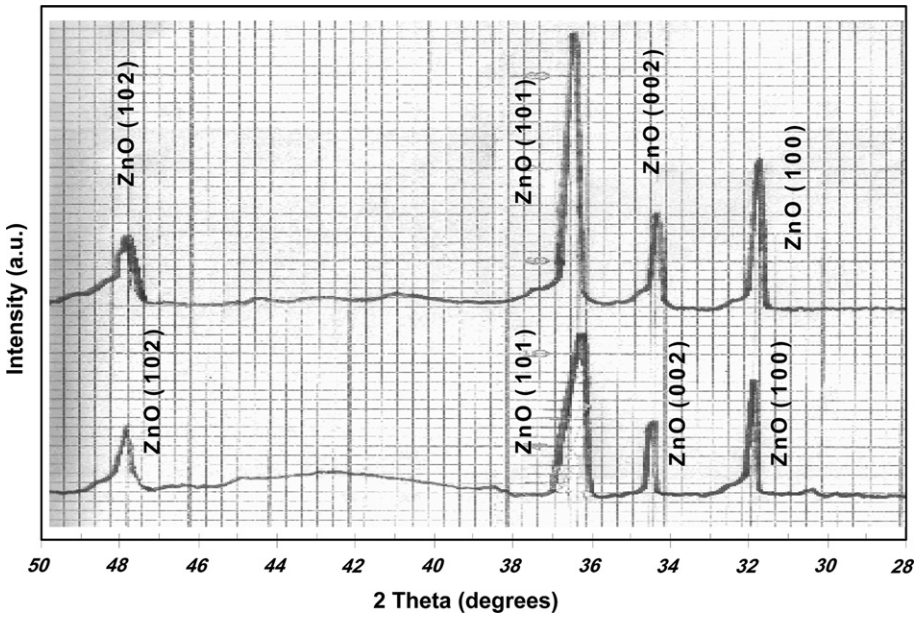

Fig. 4. X-ray diffractograms of Sn-doped ZnO thin film.

Table 1
Crystallite size (R_x) calculated from [002] (undoped films) and [101] (doped films) X-ray diffraction peaks

No. of dipping	R_x (nm) ZnO	R_x(nm) Mn-doped ZnO	R_x (nm) Sn-doped ZnO
25	10	8	5
50	13	–	–
75	15	–	–
100	22	–	–
125	26	–	–
150	32	25	20

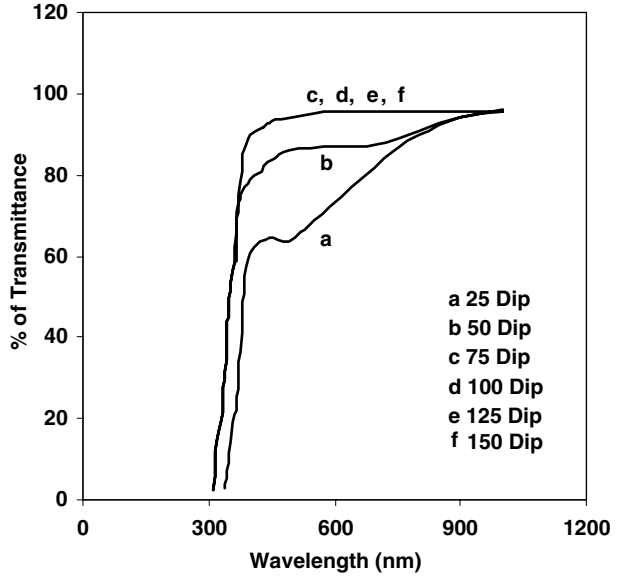

Fig. 5. Optical transmission spectrum of undoped ZnO thin films for different dipping numbers.

doped ZnO thin films display relatively higher optical transmission values than ZnO thin film doped with $MnCl_2$. It can therefore be concluded that the doping of the film with Sn^{2+} and Mn^{2+} decreases the resistivity and the conductivity of the film can be controlled by doping process.

6. Energy dispersive analysis by X-ray (EDAX)

Elemental composition of the sample was determined by EDAX analysis. Fig. 7 demonstrates the results of the undoped layer. Other peaks reveal the existence of Ca, Si and Cl. They belong to the substrate or come from the complex containing aqueous solution. High oxygen content indicates the existence of oxides of these elements.

7. Scanning electron microscopy (SEM)

Fig. 8 illustrates the scanning electron microscope image from the surface of the undoped 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 optimized experimental conditions, such as the molar concentration and the number of dipping.

8. Fourier transform infrared spectroscopy (FTIR)

Infrared spectrum is an important record, which provides information about the structure of a compound. In this technique, almost all functional groups in a molecule characteristically absorb a definite range of frequency [12]. Transmission of IR radiation causes various molecule bonds to stretch and bend with respect to one another.

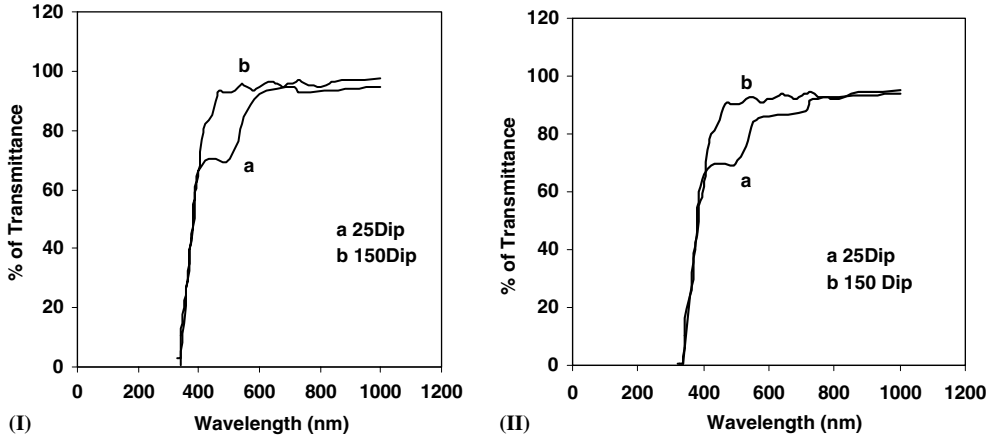

Fig. 6. Optical transmission spectrum of Mn-doped (I) and Sn-doped (II) ZnO thin films.

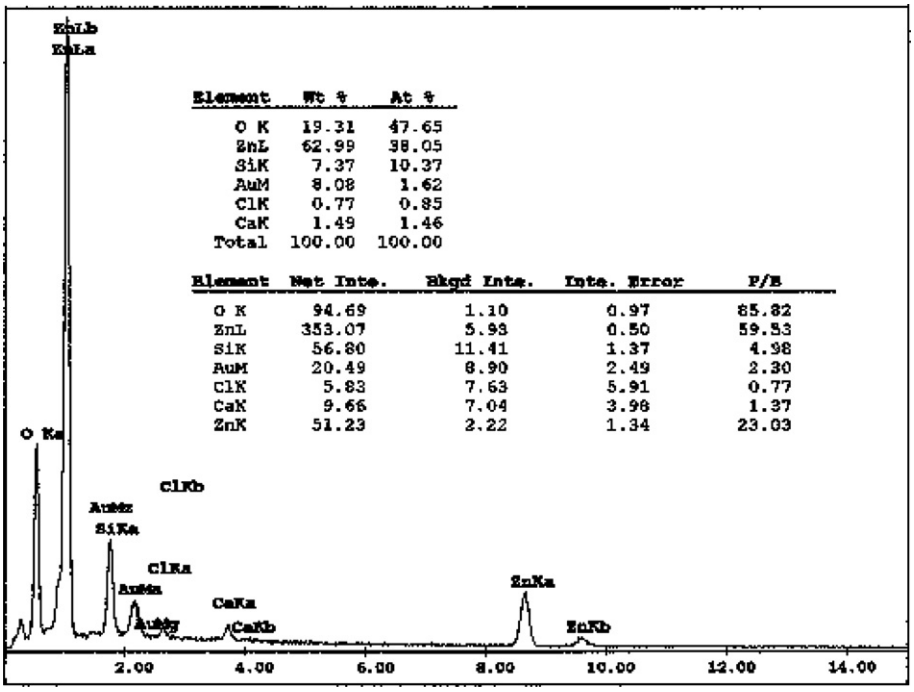

Fig. 7. EDAX elemental analysis of the undoped layer.

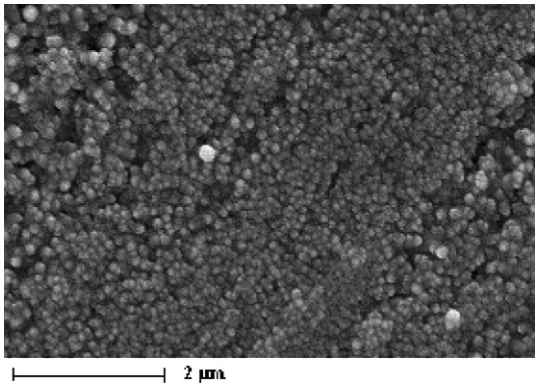

Fig. 8. SEM micrograph of the surfaces of undoped oxide film produced after 100 times dipping process.

Infrared transmission spectrum of the ZnO thin film prepared by TSCD method used in this study is recorded to be in the range of 400–4000 cm^{-1}. The result is shown in Fig. 9.

IR spectral thin film analysis aims to assess (a) the formation of the material planned to form the layer and (b) the absence of un-reacted starting materials in the deposited ZnO thin film. A systematic interpretation of the IR spectrum can be of great help to determine whether a reaction occurs and the identity of the possible products. The absorption region from 650 to 1500 cm^{-1} generally represents the finger print region of those materials which are unique in character. As reported in the literature [12], Zn–H vibrations (both symmetric and asymmetric) are

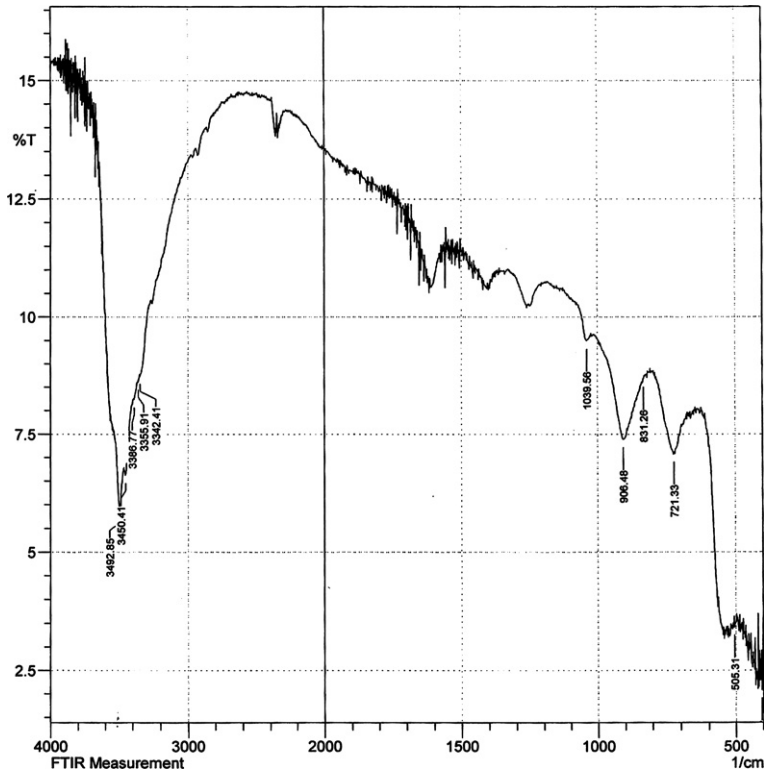

Fig. 9. FTIR spectrum of undoped ZnO thin film.

indexed to be around 150 cm^{-1}. O–H stretching is observed to be around 3500 cm^{-1}. The presence of Zn–H vibration may be attributed to adsorption of hydrogen during hot bath dipping. The presence of O–H vibration may, however, probably attribute to the residual $Zn(OH)_2$ present in the thin film.

9. Conclusions

Very low conductivity ZnO thin film can easily be deposited by (a) successive immersions of the substrate in a cold ammonia complex solution and (b) subsequently in hot water. The reaction that leads to form ZnO is as follows:

$$(NH_4)_2ZnO_{2(Complex)} + H_2O_{(aq.)} \rightarrow ZnO_{(s)} + 2NH_4OH_{(g)}$$

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.

SEM analysis confirms the presence of ZnO crystallites. The structural shape of these crystallites varies from non-spherical to spherical with increasing of the dipping number. $SnCl_2$ and $MnCl_2$ doping changes the preferred orientation of the crystallites grown and the film conductivity. 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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