Effects of sol concentration on structural, morphological and optical waveguiding properties of sol-gel ZnO nanostructured thin films

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Abstract. Nanostructured ZnO thin films with different precursor concentrations (0.5–0.8 M) have been deposited on glass substrates by sol-gel dip coating technique. X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), UV-visible spectrophotometer, and m-lines spectroscopy have been employed to investigate the effect of solution concentration on structural, morphological, optical and waveguiding properties of the ZnO thin films. XRD spectra have shown that all the films are polycrystalline and exhibit the wurtzite hexagonal structure. SEM micrographs and AFM images have revealed that morphology and surface roughness of the thin films depend on sol concentration. The UV-visible transmittance results show a high transparency in the visible range and a shift of the maximum transmittance to the higher wavelength with increasing sol concentration. Waveguiding properties such as refractive index, number of propagating modes and attenuation coefficient measured at 632.8 nm wavelength by m-lines spectroscopy indicate that our ZnO slab waveguides are single mode and demonstrate optical losses estimated around 1.5 decibel per cm (dB/cm) for the thin film prepared with a sol concentration of 0.7 M.

1 Introduction

Recently, zinc oxide (ZnO) has attracted intensive investigations due to its important advantages including good transparency, material stability, wide band gap (3.37 eV) and high exciton binding energy at room temperature (60 meV). In thin film form, ZnO is a promising candidate for application in many areas such as room temperature UV lasers [1], solar cells [2,3], field-effect transistors [4], light-emitting diodes [5], chemical sensors [6] and optical waveguides [7,8].

ZnO thin films have been prepared using different fabrication methods such as molecular beam epitaxy (MBE) [1], pulsed laser deposition (PLD) [9], metal-organic chemical vapor deposition (MOCVD) [10], magnetron sputtering [11], electron beam evaporation [12], spray pyrolysis [13], electrochemical deposition [14,15], hydrothermal method [16] and sol-gel route [17–21]. The sol-gel method, has emerged as one of the most promising processing route as it is particularly a low-cost and versatile technique to produce thin, transparent and homogeneous films of many compositions on silicon and glass. However, the properties of the prepared films by sol-gel can be affected by several factors. These factors include sol aging time [22,23], nature of the precursor and its concentration [24–33], type of solvent [34], stabilizer agents [35], preheating temperature [36] and post-annealing temperature [37]. Moreover, the optical waveguiding properties of the film strongly depend on the microstructure of the material, surface roughness, porosity and grain size which are connected to the fabrication process parameters such as dip-coated speed, sol concentration, treatment temperature and number of coating layers. Although many works about the influence of solution concentration on the properties of ZnO thin films has been reported, there are still some discrepancies between them.

For example, effect of sol concentration on c axis orientation was studied by several groups. Some studies have shown that the best c axis orientation is obtained from the films deposited at 0.3 M [27,28,30]. These authors have...
demonstrated that further increase in sol concentration causes the random orientation. However, Liu et al. [33] in a recent work reported that the c axis orientation increase with increasing sol concentration. Other works have indicated that the highest c axis orientation is obtained for the films deposited at 0.7 M [36]. Influence of sol concentration on optical transmittance in UV-visible range and optical band gap was also investigated. Kamaruddin et al. [32] found that the transmittance increase with increasing sol concentration from 0.3 to 0.7 M while other studies found the opposite behavior [25,27,33]. Xu et al. [27] and Malek et al. [29] found that the optical band gap decreases as the sol concentration increases while Lee et al. [26] reported that the band gap increases. However, to the best of our knowledge, the effect of sol concentration on optical waveguiding properties has not been reported yet.

In this paper, ZnO thin films were prepared by sol-gel process and deposited on glass substrates by the dip-coating technique using different sol concentrations (0.5–0.8 M). The effects of the precursor concentration on structural, morphological, optical and waveguiding properties of the prepared ZnO thin films are investigated.

2 Experiments

ZnO thin films were prepared by the sol-gel process. As a starting material, zinc acetate dihydrate (Zn(CH$_2$COO)$_2$·2H$_2$O) was dissolved in a mixture of ethanol and monoethanolamine (MEA, C$_2$H$_7$NO) solution at room temperature with a concentrations ranging from 0.5 to 0.8 M. The MEA to zinc acetate molar ratio was fixed at one. The resulting ZnO sol was stirred at 50 °C for 1 h, and then aged at room temperature for 36 h to get a clear and transparent homogeneous ZnO aqueous solution. The glass substrates were washed with a liquid detergent, rinsed with distilled water, and then immersed in 4 M nitric acid for 15 min. Then they were rinsed under ultrasound with ethanol and distilled water, and then immersed in 4 M nitric acid for 24 h. Then they were rinsed under ultrasound with ethanol and distilled water during 15 min at T = 60 °C and, finally, were dried at T = 100 °C for 24 h. The deposition was carried out using a KSV dip-coater with a constant withdrawal speed of 30 mm/min. The deposited films were preheated at 200 °C for 10 min after each coating. This procedure was repeated five times to increase the thickness. The films were subsequently heated up to 500 °C for 1 h in order to obtain crystallized ZnO.

The samples were characterized by X-ray diffraction (XRD) with a Panalytical diffractometer operating at 40 kV and 30 mA using Cu Kα radiation at a grazing incidence (ω = 0.54°). The characterizations by scanning electronic microscopy (SEM) and atomic force microscopy (AFM) were performed with a Raith Pioneer system and a Nanosurf easylime 2 AFM. The optical transmittance spectra were obtained using a Safas UVmc$^2$ UV-visible spectrophotometer. Optical waveguiding characterization of the films has been carried out using m-lines spectroscopy [38,39]. The refractive indices and the film thickness of the single mode waveguides were determined from the measured effective indices and a Veeco Dektak 150 surface profiler.

3 Results and discussion

3.1 Structural and morphological characterizations

Figure 1 represents the XRD patterns of the ZnO thin films obtained from solutions with concentrations of 0.5–0.8 mol/L. The results showed that all the diffraction peaks correspond to a polycrystalline ZnO with hexagonal wurtzite-structure. All diffraction peaks are broad. We also notice the overlapping of the (002) and (101) peaks indicating that ZnO particle size values are less than 10 nm. The intensity of the (002) peak indicates that all the films exhibit preferential orientation growth along (001), that is, perpendicular to the substrate surface. It is clearly seen that the peak intensities of the ZnO thin films increase when the precursor solution concentration were increased from 0.5 to 0.8 M. This feature indicates that the crystallinity of the samples is enhanced when sol concentration was increased. Xu et al. [27] have also attributed the increase in the peak intensities to the film thickness increases caused by the increase of the sol concentration.

The crystallite size ($D$) and lattice constants are calculated from Rietveld refinement using Maud software. Analysis of the obtained data shows that the crystallite size increases with increasing sol concentration, while the lattice parameters $a$ and $c$ appear to be constant. This increase in particle size with increasing precursor concentration has been also reported by several authors [24,25,27,31].

Figure 2 represents a high-magnification scanning electron micrographs of ZnO thin films obtained from solutions with precursor concentrations of 0.5 M, 0.6 M, 0.7 M and 0.8 M. An abrupt change in the surface morphology of the films can be observed as the precursor concentration of the solution increases. For the case of the films deposited at 0.5 and 0.6 M concentrations, the morphology seems to be consisted of interconnected nanowires with the presence of large pores. These pores are filled slightly for the concentration of 0.6 M, however, the diameter of these
nanowires is greater than those of the 0.5 M. The SEM micrographs of ZnO thin films deposited at 0.7 M concentration show a more compact morphology and film deposited at 0.8 M revealed uniform morphology with spherical aggregate grains. The change of the morphology can be explained by the growth mechanisms. It is well-known that the growth rate increases with increasing concentration. Hence, for higher concentrations, film growth is faster and the possibility to the positioning of the growth species in a more well-defined structure is decreased. Furthermore, the empty space between the grains is reduced, causing a more compact morphology and leading to a decrease in the number of pores and their sizes.

AFM images of the surface morphologies of ZnO thin films at different sol concentrations are shown in Figure 3. The films exhibit different surface roughness which seems to be dependent on the sol concentration (see Tab. 1). The lowest value of the root mean squared roughness ($R_{rms}$) is obtained for the film deposited at 0.7 M and the highest one is recorded for the film deposited at 0.6 M.

### 3.2 Optical characterizations

#### 3.2.1 UV-visible transmittance

Figure 4 displays the optical transmittance of ZnO films deposited at different precursor concentrations. The results show a significant dependence of the transmittance on the sol concentration. The lower transmittance observed in the UV region (less than 350 nm) for 0.5 M and 0.6 M concentrations is due to the presence of pores in the ZnO films. This result was confirmed by the SEM images. The average transmittance in the visible wavelength region (400–700 nm) varies from 70 to 90% and in the infrared one the transmittance exceeds 80%. The maximum transmission exceeds 90% for all the films and shifts to longer wavelengths with increasing concentration. It can be observed that for 0.5 M and 0.6 M concentrations, the maximum transmittance is in the visible region whereas for 0.7 M and 0.8 M concentrations it is in the infrared one. The interference phenomenon can be noticed for the films deposited at 0.7 and 0.8 M indicating a smooth and homogeneous surface.

It is well known that the thickness, grain boundary and grain size have been found to increase with the solution concentration [17]. Therefore, the visible light will be absorbed by more quantity of ZnO molecules and scattered by more grain boundary, which leads to gradual change in optical properties of ZnO thin films at different solution concentrations.

In addition, it is clear from the adsorption edges that concentration does affect much the band gap energy of the ZnO thin films. The optical band gap, $E_g$, for the different films deposited at different sol concentration was estimated from the spectra using the method of the first derivative of the transmittance [40]. The results shown in Table 1 indicate that $E_g$ is minimum for the film deposited at 0.8 M and is maximum for the one at 0.7 M. The films deposited at 0.5 and 0.6 M have a band gap of 3.3 eV. This behavior may be related to the grain size and morphology of the films. The SEM images have revealed that the morphology of the films deposited at 0.5 and 0.6 M consists of interconnected nanowires while the films deposited at 0.7 and 0.8 M are formed by spherical like grains.
Table 1. Crystallite size ($D$), lattice constants and roughness root mean square for different sol concentrations.

<table>
<thead>
<tr>
<th>Sol concentration</th>
<th>0.5 M</th>
<th>0.6 M</th>
<th>0.7 M</th>
<th>0.8 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystallite size (nm)</td>
<td>3.1</td>
<td>3.5</td>
<td>4.3</td>
<td>4.5</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>5.210</td>
<td>5.210</td>
<td>5.210</td>
<td>5.220</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>3.266</td>
<td>3.262</td>
<td>3.261</td>
<td>3.265</td>
</tr>
<tr>
<td>$R_{\text{rms}}$ (nm)</td>
<td>8.07</td>
<td>11.15</td>
<td>6.81</td>
<td>7.89</td>
</tr>
<tr>
<td>Band gap, $E_g$ (eV)</td>
<td>3.30</td>
<td>3.30</td>
<td>3.35</td>
<td>3.24</td>
</tr>
</tbody>
</table>

3.2.2 M-lines measurements

To investigate the waveguide optical properties of the nanostructured ZnO thin films, we have used m-lines spectroscopy [38,39]. This technique is a useful method to determine the optogeometric parameters of waveguiding thin films, such as thickness and refractive index. It uses a prism coupling method to input the laser light into the optical film. In optical planar waveguides, light propagation can occur within a thin film of a transparent material when its refractive index is higher than that of surrounding layers and when the film has sufficient thickness to support at least one guided mode.

A well-characterized rutile prism is mounted onto a precise rotary stage ($0.001^\circ$), which can be turned by a feedback-controlled DC motor. The mode profiles in both the TE (transverse electric) and TM (transverse magnetic) polarizations are obtained by measuring the reflected intensity of a (He-Ne) laser beam operating at a 632.8 nm wavelength, as a function of the incidence angle. The measurements were carried out on the film deposited on glass substrate. Figures 5a and 5b show the typical TE and TM guided modes spectra of 5-layer ZnO thin films prepared with a sol concentration of 0.7 M and 0.8 M, respectively. The results show that our slab waveguides support only the fundamental TE$_0$ and TM$_0$ modes.
Fig. 5. Typical fundamental guided mode spectra of 5-layer ZnO thin film with a sol concentration of 0.7 M and 0.8 M (a) TE (b) TM.

From the angular position of the reflectivity dips we compute the effective mode indices. These last ones serve to calculate the refractive indices and the thickness of the film. These parameters are related to the effective mode indices using equation (1). At least two modes are generally needed. Because our slab waveguides are single mode, we use the measured value of the effective indices and that of thickness obtained by the Veeco Dektak 150 surface profiler. The results of the calculation are reported in Table 2.

The results show that increasing the sol concentration lead to an increase of the thickness and the refractive index of the thin films for both TE and TM polarizations. The slight increase of the refractive index may be due to higher densification of the film. These results are in agreement with the transmittance spectra already discussed in the previous section. The sharpness of the reflectivity dip of the ZnO thin film with a sol concentration of 0.7 M is more significantly enhanced indicating a good optical confinement of the light beam into the waveguide structures compared to the one with concentration of 0.8 M. Measurements of the losses will bring more information about this point.

3.2.3 Optical losses

The determination of optical attenuation in waveguides is of great interest for designing integrated optical devices. Practical use of such structures directly depends on the measurement of this parameter. Several techniques have been used for losses measurement among which the endfire coupling [41] and the prism coupling methods [42].

In this work, we have used the prism-in coupling and the moving fiber methods (Metricon model 2010) in which the exponential decay of light is measured by a fiber probe scanning down the length of the propagation streak. A least squares exponential fit is then made to the intensity as a function of distance patterns and the losses are calculated in dB/cm. The overall losses measured are the combined total of both scattering losses from particles or other scattering centers, surface roughness and the inherent absorption of the waveguide material. The results of the optical attenuation measured in 5-layer ZnO thin films with a sol concentration of 0.7 M and 0.8 M are illustrated by Figures 6a and 6b. The optical losses have been estimated around \( \alpha = 1.5 \) and \( 2.7 \) dB/cm, respectively, using the following equation:

\[
\alpha = \frac{10}{\log L} \log \left( \frac{I_L}{I_0} \right) ,
\]

where \( I_0 \) is the initial light intensity, and \( I_L \) is the light intensity at the considered position \( L \), measured in centimeters.

Finally, it is noted that the ZnO thin film optical waveguides deposited at 0.5 and 0.6 M concentrations have shown reflectivity curves with broader line widths and wider resonance dips indicating the propagation of leaky modes with poor light confinement (spectra not shown). These two guiding structures have demonstrated high optical losses of 5 and 8 dB/cm, respectively. This can be
Table 2. Measured fundamental TE and TM effective indices, thickness and refractive indices of 5-layer ZnO thin films as a function of sol concentration.

<table>
<thead>
<tr>
<th>Sol concentration</th>
<th>0.5 M</th>
<th>0.6 M</th>
<th>0.7 M</th>
<th>0.8 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (nm), d</td>
<td>220</td>
<td>240</td>
<td>275</td>
<td>350</td>
</tr>
<tr>
<td>Polarization</td>
<td>TE</td>
<td>TM</td>
<td>TE</td>
<td>TM</td>
</tr>
<tr>
<td>Effective index, N₀</td>
<td>1.5622</td>
<td>1.5266</td>
<td>1.5774</td>
<td>1.5391</td>
</tr>
<tr>
<td>Refractive index, n</td>
<td>1.7155</td>
<td>1.7119</td>
<td>1.7211</td>
<td>1.7170</td>
</tr>
</tbody>
</table>

Fig. 6. Optical loss of the fundamental TE mode in 5-layer ZnO thin films: surface scattering measurement (dotted line), with exponential fit (in red): (a) C = 0.7 M, (b) C = 0.8 M.

XRD characterizations have shown that all the diffraction patterns are typical of the ZnO wurtzite hexagonal structure with a preferably c-axis orientation. Besides, the crystallinity of the thin films is improved and the crystallite size is increased with increasing sol concentration. SEM micrographs have revealed that the morphologies of the thin films deposited at 0.5 and 0.6 M concentrations are consisted of interconnected nanowires while the ones of the thin films with 0.7 M and 0.8 M concentrations show a more compactness and less porosity. The SEM images have indicated that the surface roughness dependent on the sol concentration with the lowest R<sub>rms</sub> value achieved for the film deposited at 0.7 M. The maximum transmittance exceeds 90% for all the deposited thin films. This maximum is shifted towards the longer wavelengths when precursor concentration is increased. It is also found that the band gap value (E<sub>g</sub>) is concentration dependent. The optical properties determined by m-lines spectroscopy have demonstrated that increasing the sol concentration lead to an increase of the thickness and the refractive index of the thin films for both TE and TM polarizations. The results have also shown from the mode spectra that the guided mode of the ZnO thin film waveguide deposited at 0.7 M is better confined and exhibit lower optical losses compared to the ones at 0.5, 0.6 and 0.8 M. Propagation loss as low as 1.5 dB/cm was found in the thin film with sol concentration of 0.7 M using a surface scattering measurement technique.

4 Conclusion

In this work we reported the investigation of ZnO thin films with different precursor concentrations (0.5–0.8 M) prepared by sol-gel method for photonics applications. The effects of sol concentrations on structural, morphological and optical wave guiding properties are studied. Related to their morphologies revealed by the SEM images (Figs. 2a and 2b) and discussed in Section 3.

References