Effect of Experimental Condition on Properties of Zinc Oxide Films Prepared by Sol-Gel Deposition with Ammonium Hydroxide as an Additive

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Abstract
In this work, we report on the study of undoped zinc oxide (ZnO) thin films prepared by sol-gel spin coating technique using the ammonium hydroxide as an additive. The effect of the precursor concentration and the annealing temperature on the optical and structural properties of the produced films is analyzed; we changed the precursor concentration and the annealing temperature from 0.1 M to 0.2 M and 400°C to 500°C with steps of 0.1M and 100°C, respectively. X-ray diffraction (XRD) results show that ZnO thin films are polycrystalline with a hexagonal structure and preferred growth orientations along the a-axis (100) and c-axis (002) from the substrate surface. The elaborated films have shown a high transparency (more than 75%) in the spectral range from 400 nm to 2000 nm. The optical band gap energy values of the ZnO thin films elaborated are located around 3.22 eV. Room temperature photoluminescence is dominated by a strong luminescence peak around 378 nm and a low-intensity peak around 477 nm.

Keywords: Ammonium hydroxide; Sol-gel Method; Photoluminescence; Optical band gap; Process concentration and temperature

Introduction
The transparent conductive oxides (TCO) have attracted much attention for optoelectronic applications such as solar cells and light emitting diodes thanks to their interesting properties. In particular, in thin solar cells, in order to collect the maximum of carriers, a conductive layer covering the totality of the cell surface is essential. A trade-off between the conductor and the transparency of this layer must be obtained which is fulfilled by the TCO layers. The main used TCO as transparent electrodes for solar cells were for a long time the SnO2 and the ITO. Since the 1980s, a new TCO has been studied; it is the zinc oxide (ZnO) [1]. The ZnO is a II-VI wide bandgap semiconductor material with a direct band gap around 3.2-3.37eV at room temperature. The UV peak is justified by an exciton transition as reported by many authors [4,5], while the two broad visible bands are generally attributed to deep-level defects in ZnO crystal, such as vacancies and interstitials of zinc and oxygen [4,6].

ZnO thin films can be prepared by various techniques: Sputtering [7], Chemical Vapor Deposition (CVD) [8], Laser ablation [9], Sol-gel [10,11], Spray pyrolysis [12]. It has been reported that electronic transport, structural and optical properties of ZnO films, especially the photoluminescence, are very sensitive to the preparation method and deposition conditions [13-15].

In the present work, ZnO thin films were prepared by a sol-gel spin coating method and deposited on glass substrates. The Sol-gel process is chosen because it is simple and very cheap route to obtain transparent Zinc oxide films were used based on ammonium hydroxide as an additive thanks to its efficiency to obtain a transparent and homogeneous solution during a short time. The elaborated films were characterized by measuring optical, microstructural and photoluminescence (PL) characteristics. The effect of the precursor concentration and the annealing temperature on ZnO properties is investigated.

Experimental Details

Experimental procedure
Zinc acetate dihydrate (Zn(CH3COO)2.2H2O) with a different molarity (0.1 M and 0.2 M) and ethanol were used as starting materials. The solution with pH=10 was prepared by dissolving 0.10975 g of zinc acetate dihydrate in 4 mL of ethanol. In order to obtain a clear and homogeneous solution, 1 mL of ammonium hydroxide (NH4OH) was added and final step, the solution was filtered. The mixture was stirred by a magnetic stirrer at room temperature for 30 min and then was aged for 24 hours. The ZnO thin films were deposited by a spin-coating method on cleaned and dried glass substrates. The solution was spin-aged for 20, 2018

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coated on the substrates with the speed to 1000 rpm for the 30s. The samples were then heated 100°C for 10 minutes. This process of coating and heating was repeated 12 times [16]. Finally, ZnO thin films were annealed in a muffle furnace at two different temperatures at 400°C and 500°C for two hours under air. The entire process for preparing ZnO films is recapitulated in Figure 1.

**Characterization techniques**

The coated films have been characterized by different techniques. Microstructural properties were obtained at room temperature using X-ray diffraction (XRD) "PANalytical X’pert Pro MPD" diffractometer equipped with a copper Kα (λ=0.154 nm) radiation source. Optical studies were performed by measuring the transmittance and the reflectance for wavelengths in the range of 200-2000 nm at room temperature using a Shimadzu UV-Vis 900 spectrophotometer. Photoluminescence measurements were carried out at ambient temperature with a 300 nm laser.

**Results and Discussions**

**Structural properties**

The X-ray diffraction patterns of the ZnO thin films prepared by spin-coating with different Zinc acetate concentrations (0.1 M and 0.2 M) and different annealing temperature (400°C and 500°C) are presented in Figure 2. It is observed that elaborated ZnO thin films are polycrystalline with hexagonal wurtzite phase. The main X-ray diffraction peaks corresponding to (100), (002) and (101) planes were observed in all the ZnO films. In this case the two preferential orientations: a-axis (100) and c-axis (002) are present; this difference in orientation is attributable to chemical system utilized (the precursor concentration, the nature and the concentration of the additive) i.e., nature of the reactants as well as amorphous substrates such as glass and annealing temperature [17]. Znaidi et al. proposed that the different orientations observed, based on the particle-substrate versus particle-particle interactions [18]. The XRD patterns of the samples indicated enhanced intensities of (002) diffraction peak indicating preferential orientation along the c-axis for sample 0.1 M at 400°C and (100) for other samples.

The interplanar spacing \(d_{hkl}\) value of ZnO thin films was also calculated using Bragg equation [19]:

\[
2d_{hkl}\sin\theta = n\lambda
\]  

(1)

Both lattice parameters ‘a’ and ‘c’ for the hexagonal compact phase are calculated via the (002) and (001) orientations using the following relation [20,21]:

\[
\frac{1}{d_{hkl}^2} = \frac{4}{3\alpha^2\beta}\left(k^2 + \frac{k^2 + h^2}{c^2}\right)
\]  

(2)

Table 1 summarizes the calculated parameters of the zinc oxide thin films. The ‘a’ and ‘c’ values were in concordance with the standard values of ZnO single crystal indicating the good crystalline of ZnO films was good crystalline in nature [22]. Moreover, it can be seen that the interplanar spacing \(d_{hkl}\) decreases with the concentration and temperature increase showing that both of the concentration and temperature play an important role in improving the transparency of films.

On the other hand, the crystallite size of the ZnO films is estimated from the (002) and (100) diffractions peaks using Scherer’s formula [23]:

Figure 1: The adopted process for ZnO thin films preparation by sol-gel method.
The dislocation density (δ) is calculated using the following relation:

$$\delta = \frac{1}{D}$$  \hspace{1cm} (5)

Where δ is the dislocation density, D is the crystallite size, k=0.90 is the Scherer constant, β1/2 is the FWHM of the (002) and (100) peaks and θ is the Bragg angle. The dislocation density (δ) is calculated using the following relation:

$$\delta = \frac{1}{D}$$  \hspace{1cm} (5)

δ varied from 0.95 × 10¹⁵ to 1.5 × 10¹⁵ lines/m² depending on the precursor concentration and temperature. The dislocation density decreases when increasing the annealing temperature due to the effect of the temperature on the crystallization of the ZnO films. Furthermore, δ decreases with the increase in Zn concentration due to its role in grain size.

### Optical properties

**Study of films transparency:** The optical transmittance and reflection of undoped ZnO thin films in the UV-visible regions are presented in Figure 3. All prepared samples showed a high transmittance exceeding 75% within the visible and infrared region proving a high transparency of these films and their absorption are so weak. ZnO thin films in the visible range are efficient as windows layers for solar cells [26,27]. We notice also the absence of interference fringes in transmission spectra due to the surface roughness caused by the spin-coating process. Jlassi et al. have observed interference fringes in the transmittance spectra of undoped ZnO films elaborated by sputtering. They have obtained excellent results thanks to a post-etching process to roughen the ZnO surface [31].

**Fibres thickness:** We calculate the film thickness using the method of interference fringes. Using this method, one can determine the film thickness as follows [32]:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_1 - \lambda_2 n_2)}$$  \hspace{1cm} (6)

Where: n1 and n2 are the refraction indexes of the film for the wavelengths λ1 and λ2, respectively; we can calculate n1 and n2 from the total reflectance of the ZnO films (Tm2). Using this method, one can determine the film thickness as follows [32]:

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Where: n1 and n2 are the refraction indexes of the film for the wavelengths λ1 and λ2, respectively; we can calculate n1 and n2 from the following relation [32]:

$$r_{(1/2)} = \left( \frac{N_{(1/2)}}{N_{(2/1)}} + \left( \frac{N_{(1/2)}}{N_{(2/1)}} \right)^2 + 4 \right)^{1/2}$$  \hspace{1cm} (7)

Where: s is the refractive index of the substrate, which is typically 1.52 for the totally transparent glass substrate used in this study and N(1/2) can be obtained using this relation [32]:

$$N_{(1/2)} = 2s \left( \frac{T_M - T_m}{T_M T_m} \right) + \left( s^2 + 1 \right)$$  \hspace{1cm} (8)

Where: T(1/2) is the minimum transmittance corresponds with λ1(λ2) and TM is the maximum transmittance confined between T(1/2) and T(1/2).

From Table 2 the thickness d decreases when temperatures and concentrations increase, due to the increment of material density owing.
Table 2: Thickness, Optical band gap energies and Disorder (Urbach energy) E

| ZnO        | d (nm) | E_g (eV) | E_u (meV) | E_g/E_u |
|------------|--------|----------|-----------|---------|
| 0.2 M at T=500°C | 659.8  | 3.221    | 226       | 14.25   |
| 0.1 M at T=500°C | 437.79 | 3.21     | 220       | 14.59   |
| 0.1 M at T=400°C | 308.81 | 3.197    | 166       | 19.26   |

The optical band gap: The optical band gap of ZnO thin films was estimated through the determination of the absorption coefficient α calculated from the following expression [34-36]:

\[ \alpha = \frac{1}{d} \ln \left( \frac{1}{T} \right) \]  

Where T is the transmittance, d is the layer thickness.

In the case of direct transition, the optical band gap E_g is related to the absorption coefficient α via the eqn. (8) [37]:

\[ (\alpha h\nu)^2 = A (h\nu - E_g) \]  

Where A is a constant characteristic of the semiconductor and h\nu is the photon energy.

Figure 5a shows the plot of [αh\nu]² versus the photon energy h\nu for the different elaborated samples. The optical band gap values of the ZnO thin films elaborated are located around 3.22 eV which agrees with the values indicate in literature (3.2-3.3 eV) by many studies [16]. E_g increases partially for increase in microstrain along a-axis or c-axis. The larger optical band-gap was obtained for the ZnO thin film elaborated with 0.1 M at 500°C proving its high crystalline quality [37].

Urbach tailing features: Urbach law of the expression of the absorption coefficient is as follow [38]:

\[ \alpha = \alpha_e \exp \left( \frac{h\nu}{E_u} \right) \]  

The width of the located states (band tail energy or Urbach energy Eu) has been estimated from the slopes of (ln α (υ)) versus energy h\nu plots of the films:

\[ \ln(\alpha) = \ln(\alpha_e) + \frac{h\nu}{E_u} \]  

Figure 5b shows the plot of ln(α) versus the photon energy h\nu for the different elaborated samples. The Urbach energy is a parameter which reflects the power of photonics capture of a semiconductor, thus it changes in accordance with the optical band gap.

Optical and dielectric constants: The refractive index n and extinction coefficient k have been calculated using optical experimental measurements using Bathe and Patil method [39] and Belgacem method [40].

Figure 6 shows the variation of the refractive index n and the extinction index k as a function of the wavelength. The refractive index n presents a maximum at λg (corresponding to E_g value) then it decreases with the wavelength. The evolution of the refractive index is described by the Cauchy model (Figure 7) according to the equation (14) [41]:

\[ n(\lambda) = A + \frac{B}{\lambda^2} \]  

Where A and B are the Cauchy’s parameters (Table 3) and λ is the wavelength. The extinction coefficient values are lower than 0.1 attributed to the presence of structural defaults on film surface as well as in the bulk such as grain boundaries and dislocations as detailed in XRD analysis described above [42].
ZnO thin films exhibit two emission bands in UV region corresponding to the band-to-band transition known still by the excitonic emission and a second enough wide corresponding to the emission band visible around 378 nm indicative a reasonably good crystalline quality.

The UV emission peak intensity is diminished with the precursor molarity decrease. The shift of band gap energy is related to the structural property. Since ZnO thin film has a tensile built-in strain, the tensile strain in ZnO could be relaxed by providing sufficient thermal energy. If the tensile strain is relaxed, the band gap energy is decreased [42]. Furthermore, as the ZnO films were grown without any intentional doping, the origin of the weak PL emission at ~477 nm may be explained by the transition from the bottom of the conduction band to oxygen-related defects.

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We also notice that green-yellow PL intensity increases with increasing annealing temperature from 400 to 500°C. In fact, the annealing in the neutral atmosphere may remove the interstitial oxygen first and then generate singly ionized oxygen vacancy responsible for this emission [6]. Moreover, the broad green-yellow luminescence of ZnO thin films is related to the amount of non-stoichiometric intrinsic defects [43,44]. On the other hand, the observed red shift in UV emission peak and the little variation for the other emissions certainly due to the fact that, since there is increasing film thickness [11].

### Conclusion

The effect of experimental condition on physical properties of high transparent ZnO thin films using ammonium hydroxide as an additive by the low-cost sol-gel method with different precursor concentrations and annealing temperatures has been investigated. XRD study shows that all ZnO thin films prepared are in polycrystalline hexagonal wurtzite state with preferred growth orientations along the a-axis (100) and c-axis (002) planes. The grain size of crystallites decreases with the increase of Zn concentrations and with temperature decrease from 26 nm for 0.1 M at 400°C to 30 nm for 0.2 M at 500°C. All ZnO films are highly transparent with a transmittance more than 75%. The high quality of the films is confirmed by the low value of the extinction coefficient which was calculated from optical absorption curves. Finally, room temperature photoluminescence reveals that the UV peak positions are dominated by a strong luminescence peak at ~378-380 nm for different concentrations and temperatures is due to near band-edge excitonic emission of the wide band gap ZnO. We notice also a low-intensity peak at 477 nm.

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**Table 3:** Cauchy Model Parameters A and B used for different samples.

| ZnO Sid | A      | B (μm²) |
|---------|--------|---------|
| 0.2 M at T=500°C | 1.88 | 0.253  |
| 0.1 M at T=500°C | 1.62 | 0.21   |
| 0.1 M at T=400°C | 1.55 | 0.218  |

**Figure 7:** Dispersion of the refractive index (n) by Cauchy fitting for samples elaborated with (a) 0.1 M at 400°C (b) 0.1 M at 500°C (c) 0.2 M at 500°C.

**Figure 8:** Variation of the dielectric constant of ZnO thin films (a) real part (b) imaginary part.

**Figure 9:** The PL spectra of ZnO thin films of samples prepared (a) for different concentrations (b) for different annealing temperatures.
