Structural, microstructural, and optical properties of ZnO thin films prepared by spray pyrolysis

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ABSTRACT

The thin films of zinc oxide were deposited by the ultrasonic spray technique on glass substrates. Our interest consists in the study of structural and microstructural properties. The X-ray diffraction analysis of the samples shows that the thin films crystallize in the hexagonal structure of the Wurtzite type. With a preferential orientation along the c-axis perpendicular to the substrate surface. The average size of the crystallites of the order of 49 nm. The microstructures/nanostructures of thin films are characterized by the presence of nano pedals. The chemical composition of the films was analyzed by EDS which revealed the formation of the ZnO phase. The synthesized layers showed a transmittance value of 90%. The optical band gap and the refractive index values are in good accordance with available studies in the literature.

I. Introduction

Metal oxides are widely present in the environment, they have interesting properties, and they are used separately in very diverse areas such as pharmaceutical, electronic, cosmetic, and medical industries, etc. ... Among these oxides is zinc oxide[1].In recent years, zinc oxide (ZnO) has become an interesting research topic because it has many applications in everyday objects, and it has demonstrated the best properties.

ZnO is a semiconductor with a large optical gap of 3.37eV, high exciter energy of 60meV, and transmittance of 0.9 in the visible, ZnO crystallizes in the wurtzite structure under normal conditions. Due to its particular optoelectronic properties, it has been used to evaluate new theoretical or computational approaches as well as in many technological applications, such as transparent electronics, field emitters, gas sensors or solar cells [2,3]. Various techniques have been used for their elaboration in thin layers, among which we can mention chemical vapor deposition (CVD)[4], physical vapor deposition (PVD), laser ablation[5,6], pneumatic sputtering, and cathodic sputtering[7,8]. These methods allow to make good quality deposits but they require an important financial investment for the installation and for maintenance of the infrastructures. However, other methods of elaboration less expensive and easy to implement have been developed recently: the sol-gel method[9] and the pyrolysis spray process[10].

The aim of this study is to investigate the structural, microstructural, and optical properties of ZnO thin films, elaborated by the pyrolysis process. Pyrolysis is a deposition technique used to prepare thin and thick films, ceramic coatings, and powders. Unlike many other film deposition techniques, spray pyrolysis is a very simple and relatively cost-effective method (especially with respect to equipment costs) and offers an extremely easy technique for preparing layers of any composition. Spray pyrolysis does not require high-quality substrates or chemicals. The method has been used for the deposition of dense films, and porous films, and for the production of powders. Even multilayer deposits can be easily prepared using this technique [11]

II. Experimental part

1. Films preparation

The spray pyrolysis process, which is an intermediate deposition technique between air spraying and chemical vapor deposition (CVD), seems to be very simple and relatively cost-effective, especially with respect to the equipment cost. The latter allows us to successfully prepare ZnO thin films. Starting from zinc acetate solution [$C_4H_6O_4Zn$. 2 H_20] (1.2g, purity 90~99%) dissolved in absolute methanol (30ml, purity 99. 5%), the solution was stirred with a magnetic stirrer for 30 minutes, then a few drops of acetic acid were added to prevent the formation of hydroxides. the thin films were deposited on glass substrates heated at a temperature of 450°C, at a deposition time of 30min, and a flow rate of 20ml/h.

2. Characterization techniques

We characterized the structure of the films by X-ray diffraction first (Rigaku Ultima IV equipped with Cu-Kα radiation, 0.15418 nm). The morphology of the films was verified by scanning electron microscopy (Quanta™ 250 FEG-SEM from FEI) equipped with energy dispersive X-ray spectroscopy (EDS) for chemical analysis. Finally, the optical properties are verified by measuring the transmittance of the films using a SpectroScan 80D UV-vis spectrophotometer in the 190-1100 nm spectral range.

III. Results and discussion

1. Structural properties

In figure.1. the XRD spectra of ZnO thin films deposited on glass substrates are presented. From the spectra it can be noted that four diffraction peaks are recorded at angles 2θ = 31, 34, 36 and 47 ° respectively reflecting the crystallographic planes of indices (hkl): (100), (002), (101), and (102) of the würtzite hexagonal structure of ZnO (JCPDS 00-036-1451)[12,13]. This is confirmed by the preferential orientation along the direction (002) direction which is confused with the crystallographic axis (c). Results that are like ours, in which films are aligned with the parameter ($\vec{c}$) perpendicular to the substrate plane, were observed by other research teams on analogous structures [12-15].

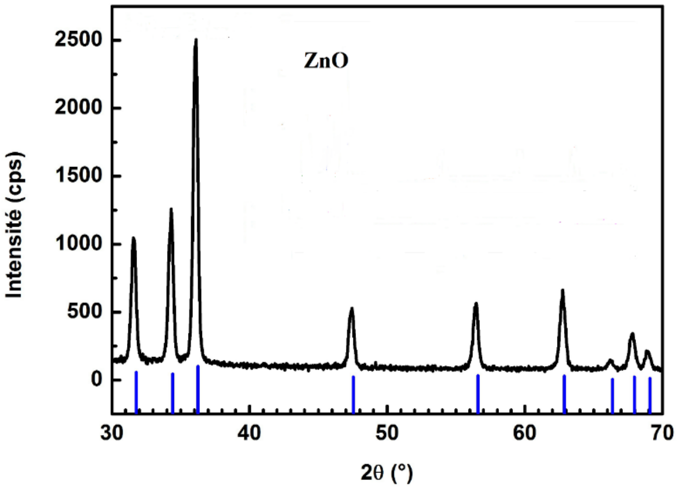

Figure 1 XRD patterns of ZnO films.

The values of the mesh parameter 'a', and 'c' of ZnO thin films are calculated from the X-ray diffraction spectrum, using the following relation [16]

$$a = \frac{\lambda}{\sqrt{3} sin\theta_{(100)}} \quad (1)$$

$$c = \frac{\lambda}{sin\theta_{(002)}} \quad (2)$$

Where λ is the wavelength of the radiation (1.54056 Å for Cukα radiation), and θ is the Bragg's diffraction angle. The values of the lattice parameters of the undoped ZnO thin films are lower than those reported in the literature; a = 3.2542 Å and c = 5.2129 Å compared to a = 3.2328 Å and c = 5.1952 Å, for the 357 nm thick ZnO thin films deposited on a glass substrate by spray pyrolysis from dehydrated zinc acetate ($Zn(CH_3COO)_2.2H_2O$) [12-15,17].

This difference could be caused by the low quality of the X-ray diffraction spectrum. In addition, it is important to mention that the recording of a XRD diffractogram of thin films in the powder mode is sensitive to the film thickness, may result in a certain trend of the position of peaks, thus leading to erroneous values of the mesh parameter. In our case, the measurements were performed using the grazing mode suitable for thin films, where the position of the sample is optimized before the spectrum is recorded.

The crystallite size (D) of ZnO thin films is calculated using the formula of Scherrer [16] :

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad (3)$$

The average strain (ε) is calculated using the following relationship [18]

$$\varepsilon = \frac{\beta}{4tan\theta} \quad (4)$$

With FWHM = βhkl (rad) is the width at the midpoint of the peak (hkl), presenting a crystallite size of about 49 nm and a strain value (ε= 0.229%).

2. Microstructural properties

Figures.2 (a and b) display the high-resolution observations from SEM at two magnifications × 10000 and × 20000. The ZnO microstructure is characterized by the presence of nano-petals which emerge perpendicular to the film surface [12].

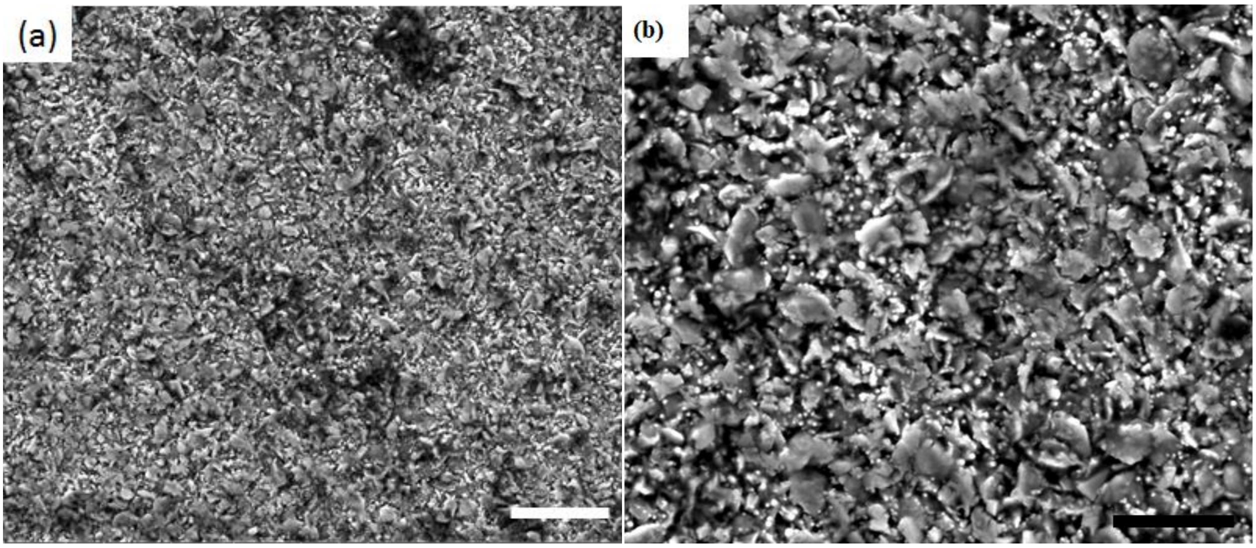

Figure 2 (a, and b) High–resolution SEM images of ZnO films, magnification of (× 10,000 and ×20,000)

3. Energy dispersive spectroscopy (EDS) analysis

Figure 3 shows the results obtained by energy dispersive X-ray spectroscopy. From the EDS spectra, we can see the presence of Zn, O with foreign elements appearing as minor peaks belonging to the soda-lime glass substrate in the synthesized Si, Ca, Mg deposits [19]

Fig.3.

4. Optical properties

Fig.4. shows the transmittance spectra of ZnO thin films. All spectra show high transparency in the visible range (400-900 nm) with a T% around 90%. This indicates a better quality of the transparent layers, In the region between 370 and 400 nm, the transmittance has decreased dramatically due to the presence of fundamental absorption edge due to the transition between the valence band and the conduction band. This edge is used to determine the optical band Eg of films.

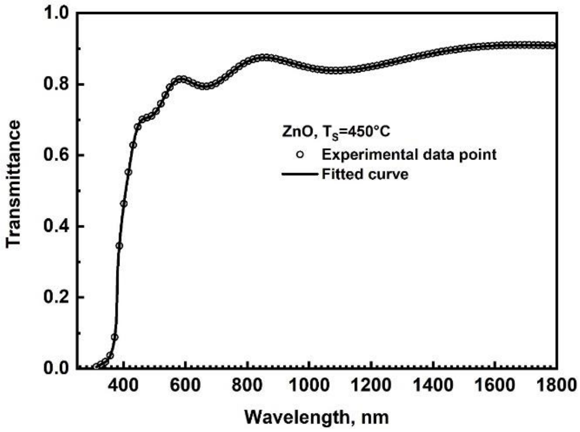

Figure 4 Transmission spectra of ZnO films. Measured (full circles) and calculated (solid lines) transmittance spectra of films

The film properties were estimated by means of a single-effect oscillator proposed by Wemple and DiDomenico [20]. Solid curves (Fig. 4) are the fitting curve, and the symbols are the experimental data. It can be seen from the figure a good correlation with the experimental data.

The values of d, Eg, and n at 598 nm were extracted by fitting [12,20]. The value of bandgap energy calculated is 3.26 eV. The thickness of the films is 486nm.

Figure 5 presents the calculated refractive indices [12] of ZnO films. It is observed that the values of refractive indices at 598 nm of the ZnO films are equal to 1.77.

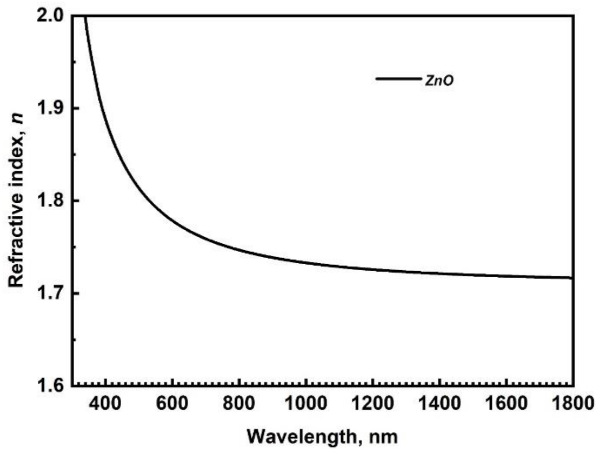

Figure 5 Refractive index of ZnO films.

IV. Conclusion

The ultrasonic spray technique was used to prepare ZnO thin films deposited on a glass substrate. The structural characterization was carried out using XRD, which shows that the thin films crystallize in the hexagonal structure of the Wurtzite type. With a preferred orientation (002) along the c-axis perpendicular to the surface of the substrate, with lattice parameters (a=3.2328Å,c=5.1952Å), a crystallite size of about 49 nm and a deformation value(ε= 0.229%). In the microstructure, the films are characterized by the presence of nano-petals arising from the surface of the films. The

EDS analysis of the chemical composition of the films confirmed the formation of the ZnO phase. The value of the optical bandgap is in agreement with the literature.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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