EXPERIMENTAL STUDY ON STRUCTURAL AND OPTICAL PROPERTIES OF ZnO THIN FILMS PREPARED BY SPRAY PYROLYSIS TECHNIQUE

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In this work, thin films of the ZnO material were deposited on glass substrates using spray pyrolysis technique. The obtained films are good in quality, adhere well to the substrate and do not present any apparent visual defect. The structural study by X-ray diffraction (XRD) presents a spectrum with very fine peaks, proof of a good crystallization. The study of this spectrum shows a privileged orientation (002) and indicates the presence of structure wurtzite, the cell parameters found are respectively about 3.245 and 5.189 Å. These results are in very good agreement with ASTM card No. 36-1451. The grain size measured at the most important peak (002) is about 263 Å. Moreover, an optical study using (UV-VIS-NIR Jasco V-570) spectrometer was undertaken on these films. A new approach for evaluation thickness is proposed. All the optical constants were given. The direct gap is evaluated at 3.27 eV, value in good agreement with the literature.

Keywords: structural materials, photoelectric cells, spray technique; thin films

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Introduction

The zinc oxide (ZnO) is among the most transparent oxides in the visible range. In its aspect, it looks as glass. In addition to its character semiconductor, it seems to be a good protective agent against corrosion. Judiciously doped, the ZnO can give a good conducting and transparent product, like a conducting glass. So its use is irreproachable as windows in the solar cells.

However, the problem of suitable doping remains posed; many attempts, like doping with aluminum, fluorine or lithium gave promising results [1, 2]. This compound which belongs to the II-VI group, offers varied applications; In addition to its employment like gas-detector, it can be also used like pressure sensor; it has also the quality to be piezoelectric.

ZnO compound is a semiconductor with a large gap; all the optical studies give a direct gap whose value is in the interval: 3.22-3.32 eV [3]. ZnO presents also two possible phases of crystallization; rocksalt structure and wurtzite one, the latter is the most frequent in nature [4-6].

Experiments

ZnO thin films were prepared using the spray pyrolysis technique. Used solution is 0.1 M of molarity; it is prepared with zinc nitrate $Zn(NO_3)_2$-$6H_2O$ and bidistilled water as solvent. The obtained solution is pulverised on glass substrates with compressed air (2 bars) as carrying gas. The solution flow is adjusted at 5 ml/min. The substrate temperature is regulated at 350 °C; it is controlled by a chrome-nickel thermocouple. The distance from the spray nozzle to the heater is kept approximately at 30 cm. Under these deposit conditions, good films are obtained. They are uniform, very adherent to the substrates and do not present apparent visual defects.

The structural characterisation of these films is undertaken, at the ambient temperature, using Rigaku Miniflex diffractometer. This equipment utilize the Bragg-Brentano assembly in the θ-2θ configuration. The X-ray source is a monochromatic beam with $\lambda_{K\alpha 1}$ = = 1.5406 Å as wavelength and 1 kW as power. All the

optical measurements were carried out using a Jasco model V-570 (UV-VIS-NIR) spectrophotometer. The apparatus has a double beam and covers the interval: (200-2500 nm).

Results and discussions

Structural properties

Fig. 1 represents the experimental spectrum diffraction obtained for the as deposit film. It presents very fine peaks, proof of a good crystallization. Moreover, according to the existence of a dominant peak, the material presents necessarily a privileged orientation.

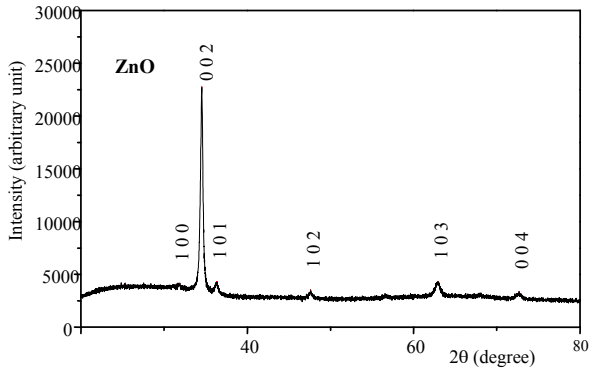

Fig. 1. *X-ray diffraction spectra of ZnO*

By using Bragg relation ($2d\sin(\theta) = \lambda$) on the one hand, and the ASTM diffraction card No. 36-1451 on the other hand, one can easily proceed to the indexing of the spectrum and the identification of the material. After indexing, the follow well solved peaks appear: (100), (002), (101), (102), (103) and (004). As seen on the Fig. 1, this material has the privileged orientation (002). This spectrum is obviously the signature of the ZnO material crystallising in the wurtzite structure where the distance $d_{(hkl)}$ is governed by the following law:

$$d_{hkl} = \frac{a}{\sqrt{\frac{4}{3}\left(h^2 + k^2 + hk + \frac{l^2 a^2}{c^2}\right)}}. \qquad (1)$$

This relation applied to the two most intense peaks, peaks (002) and (101), one can be able to determine the cell parameters (a and c). These parameters are estimated to be about: $a = 3.245$ Å; $c = 5.189$ Å.

One can note the good agreement by comparing our results with those given in the literature [6]. Certain results for comparison are given in Table 1.

Table 1

Cell parameters of ZnO

	Our results	Other results [6]	ASTM card of ZnO No. 36-1451
a (Å)	3.245	3.257	3.24982
c (Å)	5.189	5.219	5.20661

The estimated average grain size was evaluated using the well known Scherrer formula [7] given by the following relation:

$$G = \frac{K\lambda}{D\cos\theta}. \qquad (2)$$

In this relation, the different parameter means:

G: average grain size (Å), K: form factor, its value is in the interval: 0.7-1.7, λ: X-ray wavelength used in the handling (Å), D: half peak width of the considered peak (radian), θ: Bragg diffraction angle of the considered peak (radian).

The half peak width D is obtained by fitting the most intense peak to the Lorentz law given by the following equation:

$$y = y_0 + \frac{2A}{\pi}\frac{D}{4(x - x_c)^2 + D^2}. \qquad (3)$$

In this last relation, the different parameters represent:

y_0: initial ordinate or "offset"; A: surface under the peak; x_C: central x-coordinate; D: half peak width.

The fitting operation applied to the peak (002) gives a D value of about 0.352 rd (see Fig. 1). By taking form factor $K = 1$, it follows a grain size G of about: $G = 263$ Å.

Optical properties

Determination of the transmittance and the reflectance of the film

A thin film is not dissociable of its support, any optical measurement leads ineluctably to a complex result. The obtained result is always made up of the useful optical signal due to the film and the undesirable one coming from the substrate. Thus, we propose a measurement method to outline this difficulty and to isolate the useful signal of the film. For this purpose, we used the simplified diagram of a multiple reflection represented in the Fig. 2.

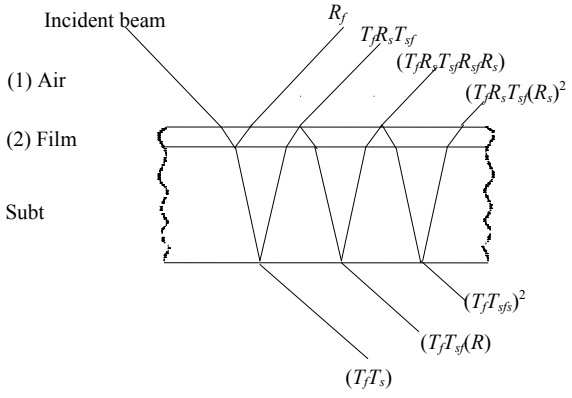

Fig. 2. *Simplified diagram of the multiple reflections phenomenon in a thin film according to [7]*

According to the last figure, it is easy to establish respectively the relationship relating to the transmittance T and reflectance R; that is as follow [7]:

$$T = \frac{T_F T_S}{1 - R_{SF} R_S}, \quad (4)$$

$$R = R_F + \frac{T_F R_S T_{SF}}{1 - R_{SF} R_S}. \quad (5)$$

In the previous relations, each parameter means: T_F: transmittance of the film; T_S: transmittance of the substrate; R_F: reflectance of the film; R_S: reflectance of the substrate; T_{SF}: transmittance of the system substrate-film; R_{SF}: reflectance of the system substrate-film.
It is clear that during a normal measurement; only the parameters T and R are accessible. The other parameters intervening in the relations (4) and (5) remain always unknown. So one proposes the measurement process schematized in the Fig. 3.

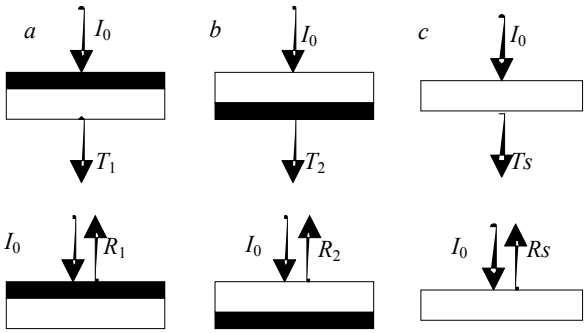

Fig. 3. *Schematic diagram of adopted measurements*

In this figure, one can note three steps of measurement:
− The sample being taken in the usual direction, one measures the transmittance T_1 and the reflectance R_1 of the film-substrate system; Fig. 3, *a*.
− The sample being taken in the opposite direction of the previous case, one measures the transmittance T_2 and the reflectance R_2 of the substrate-film system; Fig. 3, *b*.
− Finally, the substrate being taken alone, one measures the transmittance T_S and the reflectance R_S of the substrate; Fig. 3, *c*.
From all the previous stages, if the substrate is weakly absorbent, it is easy to see that the terms T_{SF} and R_{SF} are identified respectively with T_2 and R_2 ($T_{SF} \approx T_2$ and $R_{SF} \approx \approx R_2$) so that the relations (4) and (5) become:

$$T_1 = \frac{T_F T_S}{1 - R_2 R_S}, \quad (6)$$

$$R_1 = R_F + \frac{T_F R_S T_2}{1 - R_2 R_S}. \quad (7)$$

One can deduce in that case the required expression for T_F and R_F respectively the transmittance and the reflectance of the film lonely:

$$T_F = \frac{T_1}{T_S}\left(1 - R_2 R_S\right), \quad (8)$$

$$R_F = R_1 - \frac{T_F R_S T_2}{1 - R_2 R_S} = R_1 - \frac{T_1 R_S T_2}{T_S}. \quad (9)$$

Determination of the film thickness:
Let us suppose that $X = e^{-ad}$ in the transmittance formula of a layer with parallel faces which has a thickness d and an absorption coefficient α, it is always possible to write it in the form:

$$T_F = \frac{AX}{1 + BX^2 + CX\cos\varphi}. \quad (10)$$

A, B and C are constants and the parameter φ represents the dephasing given by the relation:

$$\varphi = \frac{4\pi nd}{\lambda}, \quad (11)$$

where n is the refraction index and λ *the* wavelength of the radiation used.
In the absence of any interference, the average transmittance T_m is obtained obviously when the term cos(φ) is null, in which case one will have:

$$T_m = \frac{AX}{1 + BX^2}. \quad (12)$$

Taking into account the equations (10) and (11), it is easy to establish the following relation:

$$T_F = \frac{T_m}{1 + K_C T_m + \cos\left(\frac{4\pi nd}{\lambda}\right)}. \quad (13)$$

In the previous equations, K_C is a constant.
If the refraction index n is approximately constant, that is always true in the transmitted part of the energy; it is possible to obtain the parameters n and d by fitting the experimental curve T_F to the equation (13) if the average T_m is available.

Optical characterisations
The optical measurements of transmittance and reflectance were undertaken according to the procedure described before. All the range wavelengths offered by the spectrophotometer was explored (200-2500 nm). The obtained results are represented on the Fig. 4 and 5. The interference phenomenon is quite visible, mainly in the reflectivity spectrum.

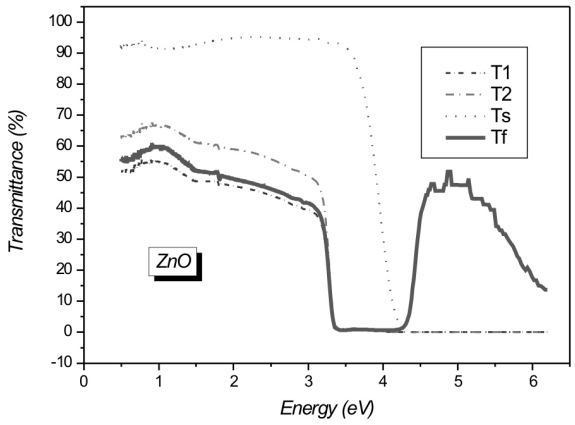

Fig. 4. *Transmittance spectra versus energy according to previous procedure*

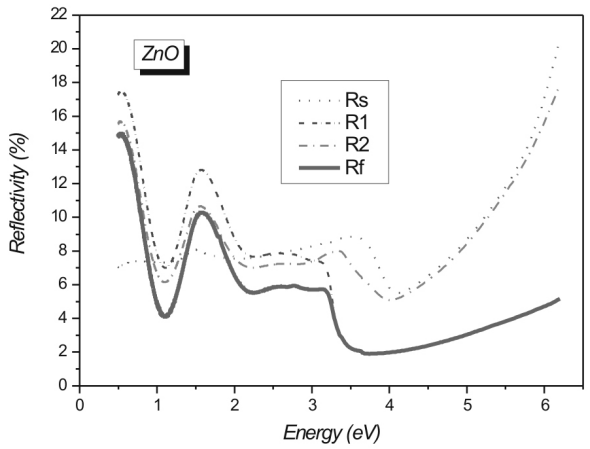

Fig. 5. *Reflectivity spectra versus energy according to previous procedure*

Because of the presence of interference, it is imperative to determine T_m and R_m; respectively average transmittance and reflectance of the film. Fig. 6 and 7, where the useful energy rang was limited between 0.5 and 4 eV, give a solution to this problem.

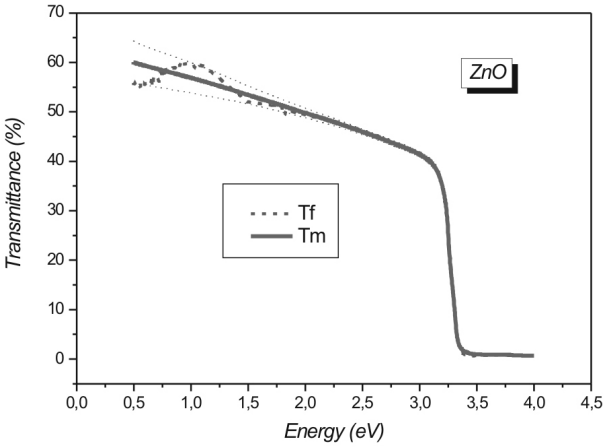

Fig. 6. *Average transmittance spectra T_m versus energy*

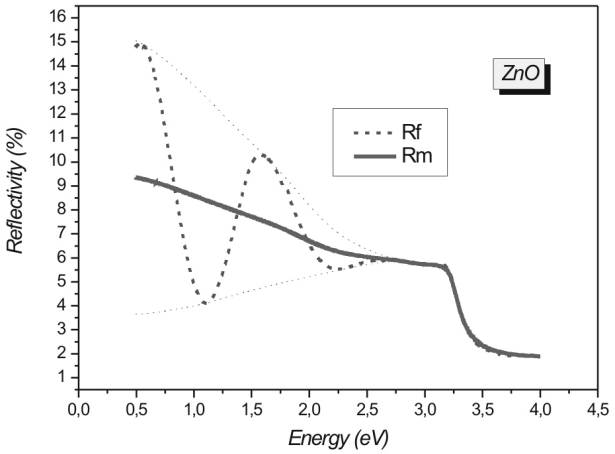

Fig. 7. *Average reflectance spectra R_m versus energy*

Once T_m and R_m determined, the thickness d is obtained by fitting the experimental result to the equation (13). As shown clearly in Fig. 8, the obtained thickness is evaluated to d = 486 nm.

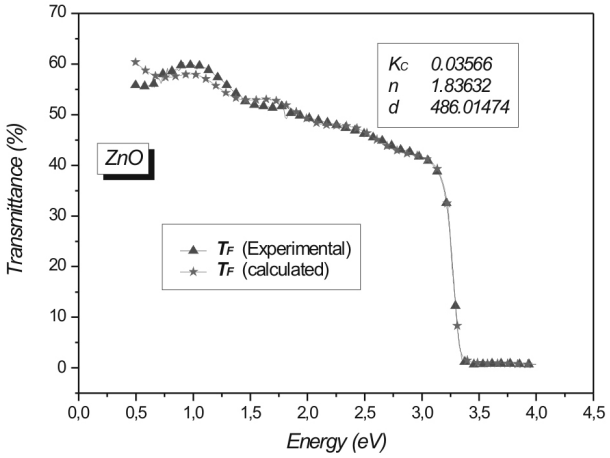

Fig. 8. *Determination of film thickness by fitting experimental transmittance T_F to equation (13)*

Transmittance T_F and reflectance R_F being now available, the film thickness d being determined, the absorption coefficient α is obtained using the well known relation:

$$\alpha = \frac{1}{d}\ln\left(1-\frac{R_F}{T_F}\right). \qquad (14)$$

Fig. 9 shows the absorption coefficient versus energy. It increases abruptly in the interval of the energy rang (3-3.5 eV), i.e. in the vicinity of a zone noted (zone A). The study of the curve $(\alpha h\nu)^2 = f(h\nu)$, in the vicinity of this zone, enables us to highlight the fundamental transition *Eg* (direct gap), characteristic of the ZnO material. Fig. 10 shows it clearly, the obtained value for *Eg* is about 3.27 eV.

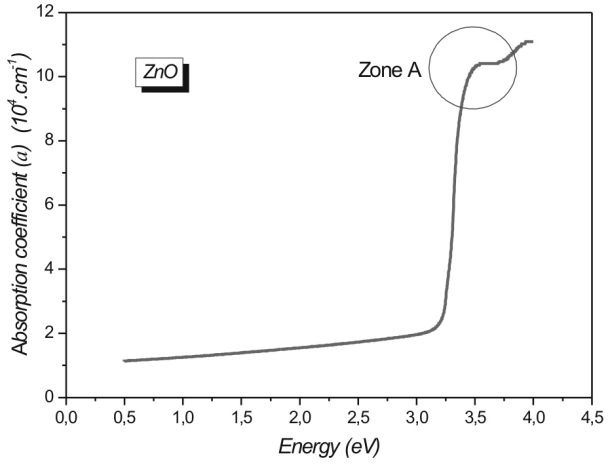

Fig. 9. *Absorption coefficient α versus energy (hν)*

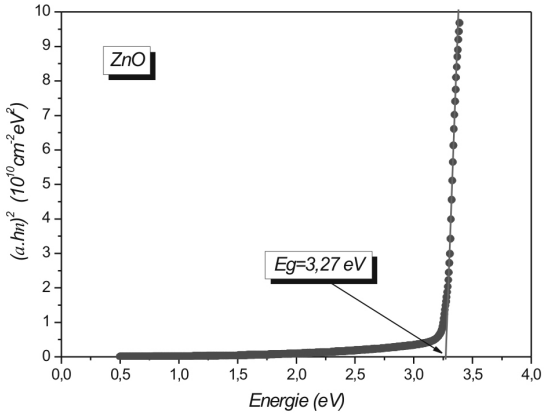

Fig. 10. *Curve $(\alpha h\nu)^2$ versus energy (hv) in the vicinity of zone A*

Table 2 which contains empirical values is given for comparison. The direct gap found is in a great agreement with the literature [3].

Table 2

Direct gap *Eg* of ZnO

Direct gap *Eg* (eV)	
Our results	**Other results [3]**
3.27	3.22-3.32*

(*) Values found for ZnO doped with boron.

From the following equations (15) and (16) we can reach easily the extinction coefficient k and the refraction index n.

$$\alpha = 4\pi\frac{k}{\lambda} \Rightarrow k = \frac{\alpha\lambda}{4\pi}, \qquad (15)$$

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2}\ . \qquad (16)$$

The coefficients n and k are also linked to the real and imaginary part of the dielectric function. The real part ε_1 as well as the imaginary part ε_2 are easily obtained using the following equations:

$$\varepsilon_1 = n^2 - k^2, \qquad (17)$$

$$\varepsilon_2 = 2nk. \qquad (18)$$

Fig. 11 shows the variations of n and k, Fig. 12 shows those of ε_1 and ε_2.

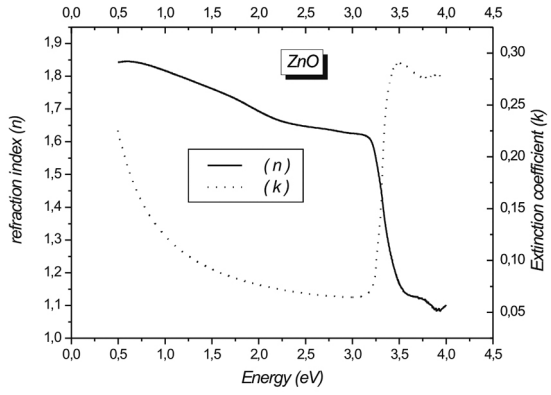

Fig. 11. *Curves n and k versus energy (hv)*

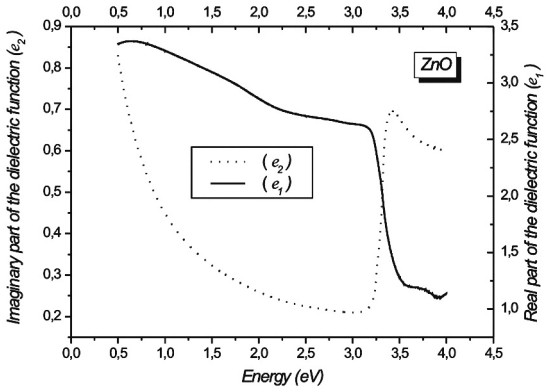

Fig. 12. *Curves ε_1 and ε_2 versus energy (hv)*

Conclusion

This work shows in a clear way the possibility of manufacturing thin films of ZnO by the spray technique. This simple and economic technique proves to be easy to implement. It allows the realisation of compound like oxides or sulphides. The ZnO object of this study is found to be polycrystalline, crystallises in a wurtzite structure and shows a privileged orientation (002). The cell parameters are evaluated respectively at (a = 3.245 and c = 5.189 Å). The optical study shows that the material is very transparent in the visible region and that it is a semiconductor with large gap. This study reveals the existence of a direct fundamental transition; the optical gap determined is about 3.27 eV. Moreover all the optical constants were given.

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