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Optical properties of ZnO thin films deposed by RF magnetron

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We have grown ZnO thin films on glass substrate by RF magnetron sputtering using metallic zinc target. The influences of some parameters on thin film optical properties were assessed. They exhibited extremely high resistivity of 10^{12} Ω.cm, an energy gap of 3.3 eV at room temperature. It was found that a RF power of 50 W, a target to substrate distance of 70 mm, very low gas pressures of 3.35×10^{-3} Torr of argon and oxygen mixed gas atmosphere gave ZnO thin films with a good homogeneity and a high crystallinity. All the films are transparent in the visible region (400 to 800 nm) with average transmittance above 80%. The optical transmittance and refractive index, calculated from the spectra of optical absorbance, show a significant dependence on the growth parameters. As for the sample grown at 100°C, the average transmittance is about 80% in the visible wavelength range and the refractive index is estimated to be 1.97.

Key words: ZnO, RF sputtering magnetron, X-ray diffraction, transmittance, refractive index.

INTRODUCTION

Zinc oxide is one of the most interesting II–IV compound semiconductors with a wide direct band gap of 3.3 eV (Meng and Dos Santos, 1994; Inukai et al., 1995; Han and Jou, 1995; Craciun et al., 1995; Subramanyam et al., 1999; Sanchez-Juarez et al., 1998; Sourdi et al., 2012; Yang Ming Lu et al., 2007). It has been investigated extensively because of its interesting electrical, optical and piezoelectric properties making suitable for many applications such as transparent conductive films, solar cell window and MEMS waves devices (Craciun et al., 1995). The thermal stresses were determined by using a bending-beam Thorton method (Han and Jou, 1995) while thermally cycling films. ZnO has hexagonal Wurtzite structure and some properties are determined by the crystallite orientation on the substrate. For example, for piezoelectric applications, the crystallite should have the c-axis perpendicular to the substrate. According to the literature, the reactive sputtering technique has received a great interest because of its advantages for film growth, such as easy control for the preferred crystalline orientation, epitaxial growth at relatively low temperature, good interfacial adhesion to the substrate and the high packing density of the grown film. These properties are mainly caused by the kinetic energy of the clusters given

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*Corresponding author. E-mail: roger.ondo_ndong@yahoo.fr by electric field (Molarius et al., 2003; Lin et al., 2008; Kim et al., 1997). This energy enhances the surface migration effect and surface bonding state.

In previous work, we investigated the effect of the substrate temperature and the oxygen-argon mixture gas on the properties of ZnO films. It has been found that the structural properties of ZnO films depend very much on the substrate temperature. Indeed, a ZnO hexagonal wurtzite structure and properties are determined by the orientation of the crystallites on the substrate. FWHM of the (002) X-ray rocking curve must be less than 0.32 for an effective electromechanical coupling (Ondo-Ndong et al., 2003). In continuation of this work, the optical properties of ZnO structures have been investigated based on the deposition parameters.

EXPERIMENTAL

Zinc oxide films were deposited by RF magnetron sputtering using a zinc target (99, 99%) with diameter of 51 and 6 mm thick. Substrate is p-type silicon with (100) orientation. The substrates were thoroughly cleaned with organic. Magnetron sputtering was carried out in an oxygen and argon mixed gas atmosphere by supplying RF power at a frequency of 13.56 MHz. The RF power was about 50 W. The flow rates of both the argon and oxygen were controlled by using flow meter (ASM, AF 2600). The sputtering pressure was maintained at $3.35.10^{-3}$ torr controlling by a Pirani gauge. Before deposition, the pressure of the sputtering system was under 4.10^{-6} torr for more than 12 h and were controlled by using an ion gauge controller (IGC – 16 F).

Thin films were deposited on silicon, substrate under conditions listed in Table 1. These deposition conditions were fixed in order to obtain the well-orientation zinc oxide films. The presputtering occurred for 30 min to clean the target surface. Deposition rates covered the range from 0.35 to 0.53 μm/h. All films were annealed in helium ambient at 650°C for 15 mn. Measurements of transmittance in the range from 300 to 900 nm are made using a UV-Visible CARY spectrometer.

The device has a pulsed xenon lamp, which produces only a flash in each acquisition of a measurement point. A quartz bulb, not glass, let's UV radiation through. The emerging beam is then a cylindrical diverging beam that will cover the entire surface of the mirror M1. A mirror allows the orientation and focus of the useful part of the beam emerging from the input to the network and then diffracted by the latter towards a beam exit slot gap. The assembly constituted by the entrance slit and the first mirror is called collimator. A blade placed on the path L of monochromatic radiation is used to reflect a portion of the intensity of the wave to a photoreceptor which measures the intensity of radiation which will pass through the vessel containing the sample to take into account small fluctuations the intensity of the light source. The rough surface materials with in homogeneities or imply low volume detected signal. Thus, we must make an adjustment, before any measurement: The 100% for power transmission Pyrex substrate as a reference. Piloting, digital capture and processing of data is performed by a microcomputer.

Theoretical model for complex index

To calculate the optical constants, are often used to model on a volume of isotropic and homogeneous material. In reality, the behavior of thin films obtained from the ideal model overflows due to the inhomogeneity of layers and the dispersion of the refractive.

Table 1. ZnO sputtering conditions.

Sputtering pressure	3.35×10^{-3} Torr
Mixture gas	$A_r + O_2$ = 80 – 20%
Power RF	50 W
Sputtering time	6 h
Substrate temperature	100°C
Target-substrate distance	7 cm

These optical constants are represented by the index of refraction that is, in the general case, depends on the complex wavelength dependence $\tilde{n} = n(\lambda) + ik(\lambda)$. Is the real part of the refractive index. The complex index $\tilde{n} = n(\lambda) + ik(\lambda)$ is very important for the dielectric characterization of materials. $\tilde{n}$ Provides, at infinity, the complex permittivity $\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$ through:

$$\varepsilon_1 = n^2 - k^2$$

$$\varepsilon_2 = 2n \cdot k$$

And also, the relative permittivity ε_r and electrical conductivity to the required frequency σ through:

$$\varepsilon_r = \varepsilon_1$$

$$\sigma = \varepsilon_2 \cdot \omega \cdot \varepsilon_0$$

The measurement of light transmission through a parallel plate dielectric film, in the working range considered, is sufficient to determine the real and imaginary parts of the complex refractive index and thickness. Wales and Lyashenko developed a method using the successive approximations and interpolations for calculating these three quantities (Wales et al., 1967; Lyashenko and Miloslavskii, 1964).

Manifacier et al. (1976) have developed a method, like in the same range of applicability but differs from Lyashenko and Miloslavskii (1964) accuracy by: Firstly, the calculation processing and the data is easier, and secondly it provides an explicit expression for n, k and thickness. This last method we have used to characterize our samples of zinc oxide thin film prepared. Figure 1 shows a thin layer complex refractive index $\tilde{n}$, linked by two transparent media n_1 and index n_0. With n_0 the index of air ($n_0 = 1$) and n_1 the index of the substrate.

In the case of normal incidence, the amplitude of the transmitted wave length is given by Wales et al. (1967) and Lyashenko and Miloslavskii (1964):

$$A = \frac{t_1 t_2 \exp\left(-2i\pi nd/\lambda\right)}{1 + r_1 r_2 \exp\left(-4i\pi nd/\lambda\right)} \tag{1}$$

Where t_1, t_2, r_1, r_2, n and d are respectively the transmission and reflection coefficients of the front and rear faces of the sample, the refractive index and the thickness of the material.

The transmission of the layer is given by:

$$T = n_1/n_0 \mid A \mid^2 \tag{2}$$

In the case of low absorption along with,

$$k^2 << (n - n_o)^2 \text{ et } k^2 << (n - n_1)^2 \tag{3}$$

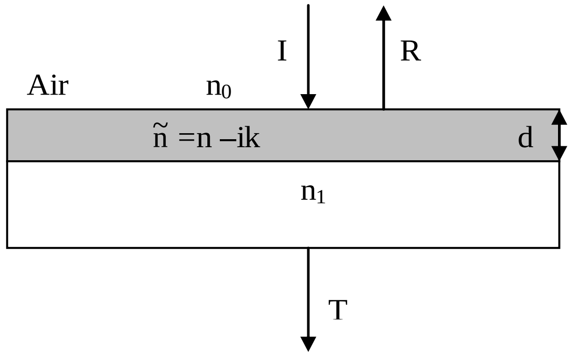


Figure 1. Optical transmittance on the sample.

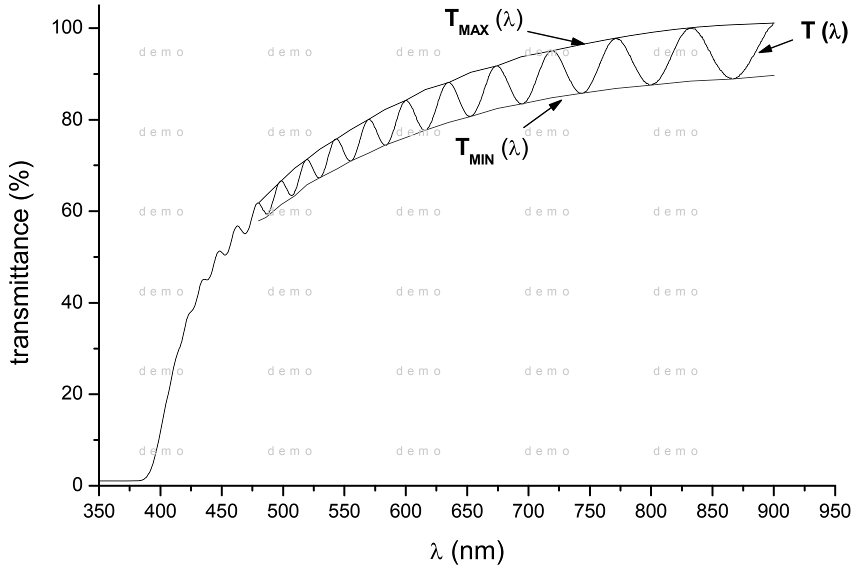


Figure 2. Optical transmittance spectra Example on the sample.

$$T = \frac{16 n_0 n_1 n^2 \alpha}{C_1^2 + C_2^2 + 2C_1 C_2 \alpha \cos 4n\,\pi d/\lambda} \quad (4)$$

Where $C_1 = (n + n_0)(n_1 + n)$, $C_2 = (n - n_0)(n_1 - n)$ (5)

And $\alpha = \exp(-4\pi k d/\lambda) = \exp(-\beta d)$ (6)

β is the absorption coefficient of the thin film, k is the extinction coefficient and the percentage absorption α.

Generally, outside the region of the fundamental absorption or free carrier absorption (for higher wave lengths), the dispersions of n and k are large. The maxima and minima of transmission in Equation (4) to occur:

$$\frac{4\pi n d}{\lambda} = m\pi \quad (7)$$

Where m is the wave number.

In corresponding to a thin layer of transparent semiconductor substrate non-absorbent, $C_2 < 0$ usual cases, the extreme values of the transmission are given by the formula:

$$T_{max} = \frac{16 n_0 n_1 n^2 \alpha}{(C_1 + \alpha C_2)^2}, \quad T_{min} = \frac{16 n_0 n_1 n^2 \alpha}{(C_1 - \alpha C_2)^2} \quad (8)$$

Combining Equations (8) relationship Lyashenko developed an iterative method for the determination of n and α, and using Equations (6) and (7), determining k and d. We propose a major simplification of this method. Indeed, we consider T_{min} and T_{max} as continuous functions of n (λ) and α (λ). Indeed, the two envelopes of the measured transmittance form a non-linear system of two equations in two unknowns n (λ) and α (λ), which can be solved by iteration. These functions, which are envelopes of the maxima T_{max} (λ) and the minimum T_{min} (λ) in the transmission spectrum are shown in Figure 2. α coefficient is given by the ratio of Equations (8).

$$\alpha = \frac{C_1\left[1 - (T_{max}/T_{min})^{1/2}\right]}{C_2\left[1 + (T_{max}/T_{min})^{1/2}\right]} \quad (9)$$

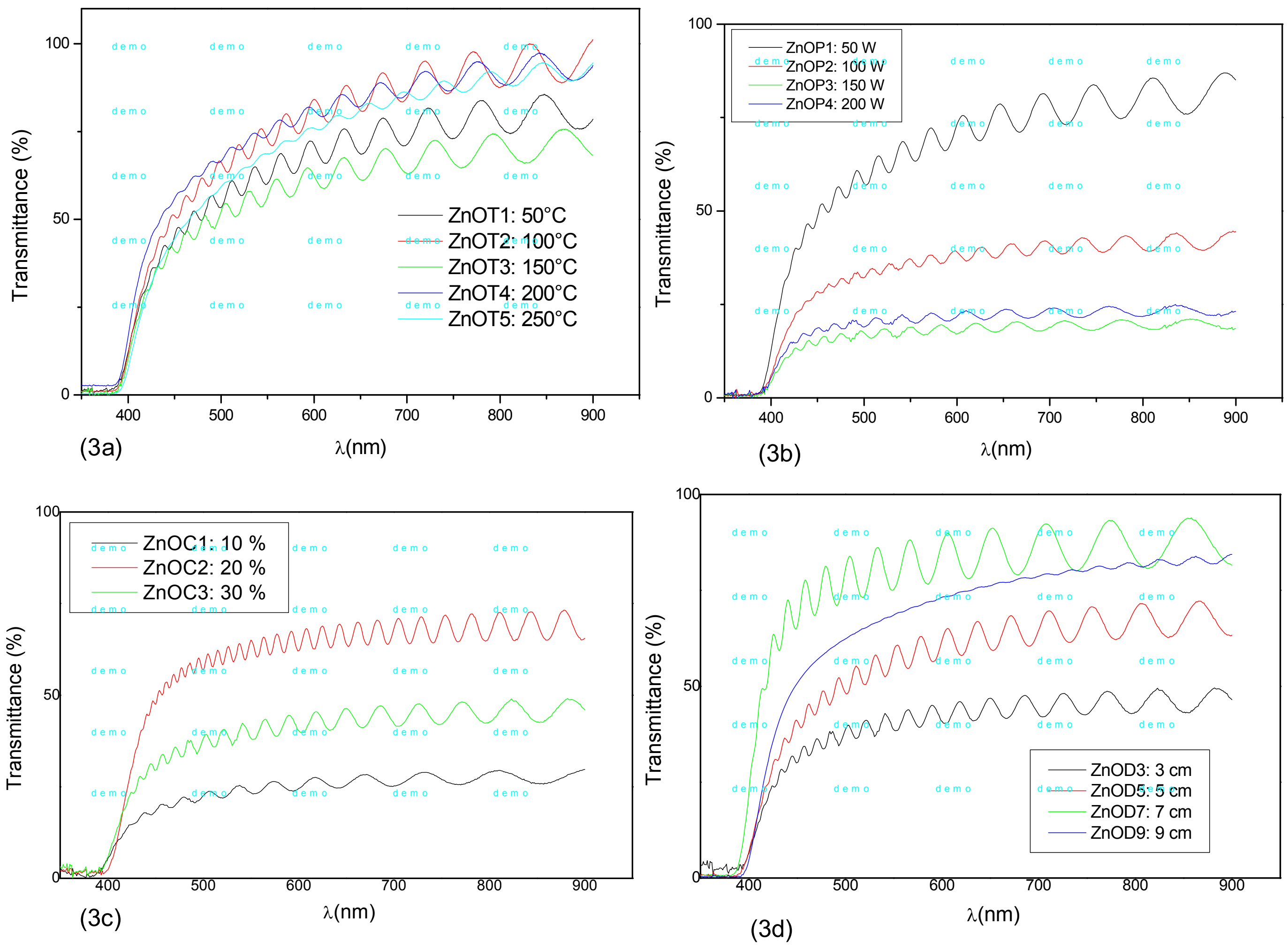


Figure 3. Optical transmittance spectra of ZnO thin films: a) at various substrate temperatures, b) at different power, c) based on the rate of oxygen, d) depending on the target-substrate distance.

Then we deduce Equation (8) the relationship of the refractive index of the thin layer.

$$n = \left[N + \left(N^2 - n_0^2 n_1^2\right)^{1/2}\right]^{1/2} \qquad (10)$$

With $$N = \frac{n_0^2 + n_1^2}{2} + 2n_0 n_1 \frac{T_{max} - T_{min}}{T_{max} T_{min}} \qquad (11)$$

N is a constant.

The Equation (8) shows that the refractive index n is determined explicitly.

Knowing n can be determined by the above equation α. The thickness d of the layer may be calculated by two maxima or minima using the equation below.

$$d = \frac{M\lambda_1\lambda_2}{2\left[n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1\right]} \qquad (12)$$

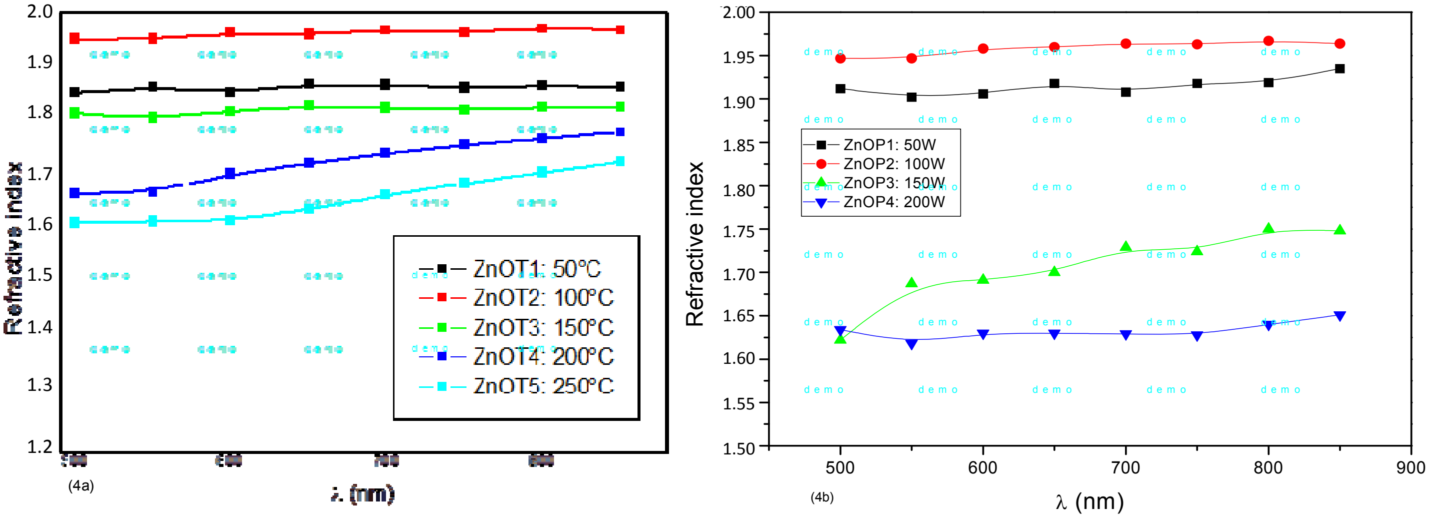
Where in M is the number of oscillations between two extreme points (M =1 between two consecutive minima or M=2 two consecutive maxima), λ_1, n (λ_1) and λ_2, n (λ_2) levels are matching wave the wavelength and the refractive index.

RESULTS AND DISCUSSION

Transmittance

To know the parameter values that seem to be making the best deposits from a structural point of view, we have undertaken, optical characterizations in order to identify the influence of the four parameters of deposits. And to avoid the effect of film thickness on the optical properties, we worked on samples of similar thicknesses of 2.8 to 2.9 µm.

Figure 3 shows the transmission spectra of ZnO films. We observe that the powers in Figure 3a transmission are high (80 to 90%) for all samples. It is also observed that the absorption front at a wavelength for which the transmission is reduced to 50% is set to 375 to 400 nm.



(4a)

(4b)

Figure 4. Refractive index as a function of wavelength: a) for different substrate temperatures; b) different powers.

The difference of the extreme of all samples was 100°C maximum in Figure 3a. Subramanyam et al. (1999) confirm these results. Indeed, they get a power transmission of the order 86% and observed a decrease in optical transmission with temperature in the range 300-400°C.

In the spectral range considered, we have represented in Figure 3b changing transmission thin zinc oxide layers for different powers. We note that the sample of ZnO prepared to 50 W has a maximum transmission of about 80%. By cons, for the other samples, the transmission spectra are of little use. These observations clearly confirm the results obtained by ray diffraction where we found that the samples are poorly crystallized and the grain size is unusually small compared to that obtained with the sample 50 W. The effect of oxygen on the transmission rate of the ZnO films showed in Figure 3c. A decrease in transmittance was observed to measure the percentage of oxygen in the gas mixture (Ar - O_2) increases in the region of short wavelength. The maximum transmission is observed for the oxygen content equal to 20% and the minimum transmission are higher. Moreover, the difference between the transmissions of the extrema (T_{max} - T_{min}) is greater for the sample. This reflects a higher refractive index.

We studied the influence of the target-substrate distance watching the optical transmission of the ZnO thin films. Figure 3d shows that the optical properties of zinc oxide are dependent of the target-substrate distance. Based on the experimental conditions, we can say that the target-substrate distance equal to 7 cm is ideal for making our ZnO films. Indeed, the power transmission of this sample was very high (95% λ = 600 nm). It is estimated to have homogeneous layer thickness minimum distance. Indeed, at this distance, the thermalization of the structure is efficient. The discharge (plasma) is maintained with a minimum of particle collision and the efficiency of the pulverization is effective.

Refractive index n

Changes in the refractive index as a function of wavelength at different substrate temperatures are shown in Figure 4a. The refractive index has a high dispersion to the layers developed to above 150°C temperatures. Figure 4b shows the variation of the refractive index as a function of wavelength at different powers. We see that the index decreases with power. It varies from 1.97 to 1.6 in from 50 to 200W at 600 nm. Figure 5 shows that a given wavelength, the refractive index increases from 1.87 to 1.97 when the substrate temperature ranges from 50 to 100°C. Above 100°C, the value of the refractive index decreases as the substrate temperature increases to 1.63. To highlight these observations, we have shown in Figure 6 changes in the refractive index as a function of oxygen concentration in the gas mixture at a given wavelength (λ = 600 nm). We find that the influence of the gas mixture on the refractive index is significant only when we have an oxygen level of 20%. In addition, we note a decrease in the index with increasing oxygen content in the gas mixture. We attribute this phenomenon, compared with the X-ray crystallographic disorientation of the structure. Indeed, the structural study showed that the optimum oxygen level, to develop well-crystallized films of ZnO was 20%.

Figure 7 shows that the target distance of 7 cm substrate is ideal for obtaining zinc oxide layers of good quality, taking into account, of course, the deposition

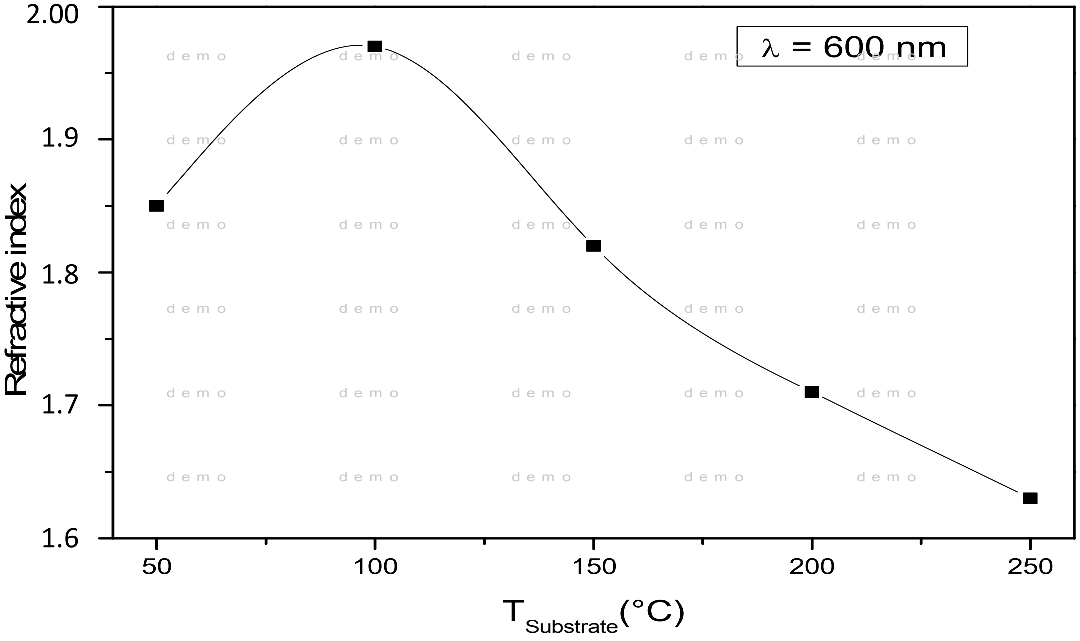


Figure 5. Refractive index as a function of the substrate temperature constant λ.

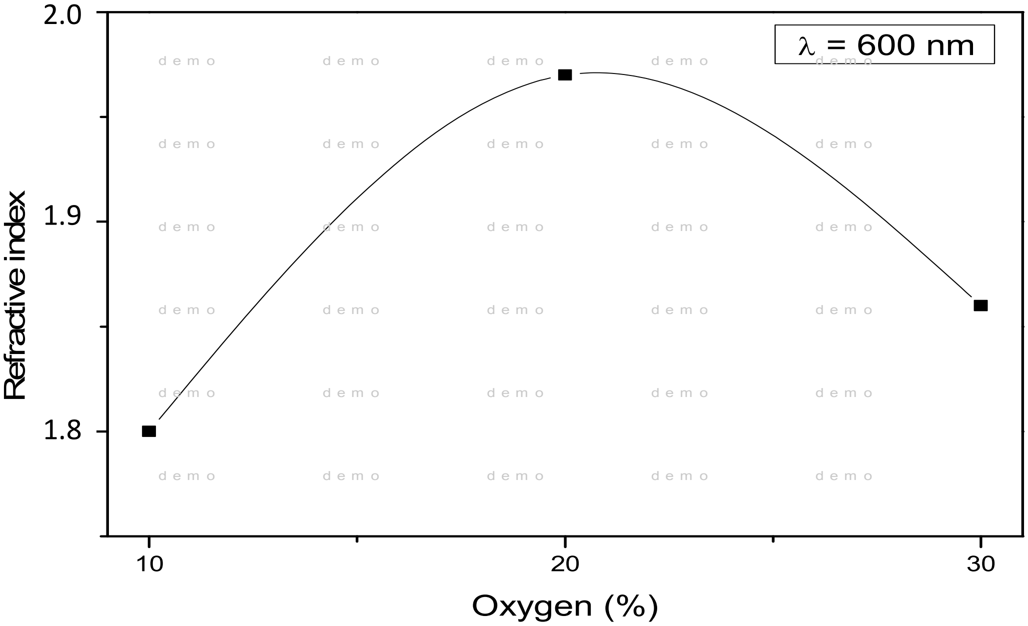


Figure 6. Refractive index as a function of oxygen concentration at constant λ.

conditions. Knowing that the optical properties of thin films depend on the thickness, we determined the thickness of our ZnO films by Equation (12) and we have compared to values determined by profilometry. Figure 8 shows the variation of the thickness of the ZnO thin film as a function of the launched power. We find that the thicknesses obtained by optical determination decrease as the power increases. This explains, perhaps, the low transmittance samples drawn over 50 W. In addition, the evolution of the diffraction peak as a function of RF power, shows that the samples prepared at most 50 W exhibit crystallization defects.

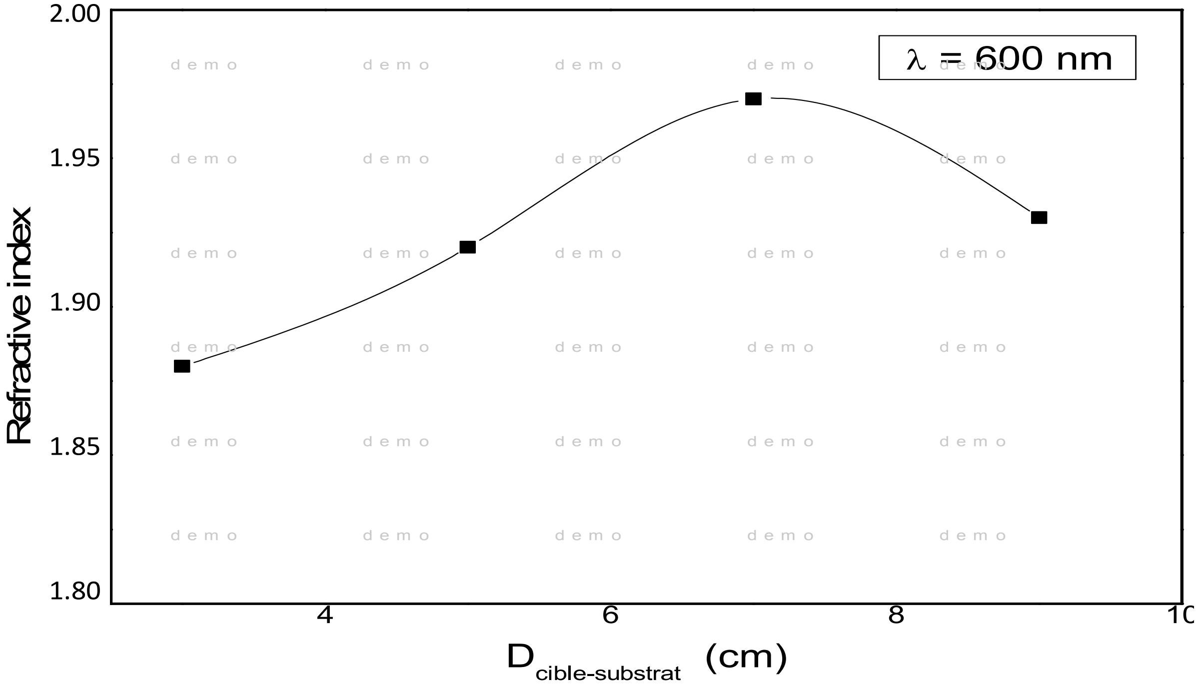


Figure 7. Refractive index as a function of the substrate-target distance constant λ.

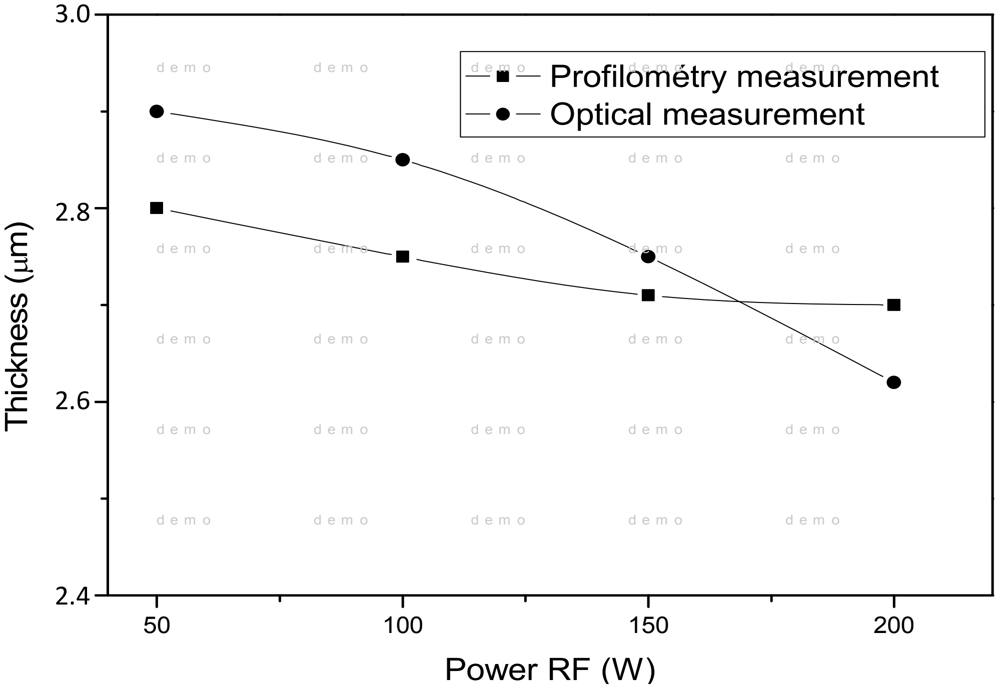


Figure 8. Evolution of the thickness of the ZnO film in function of the power RF.

Determination of the optical gap E_g

The X-ray part presents a spectrum of electromagnetic radiation. The wave-particle duality of radiation is expressed by such a relation between the energy of a photon, and the wavelength λ.

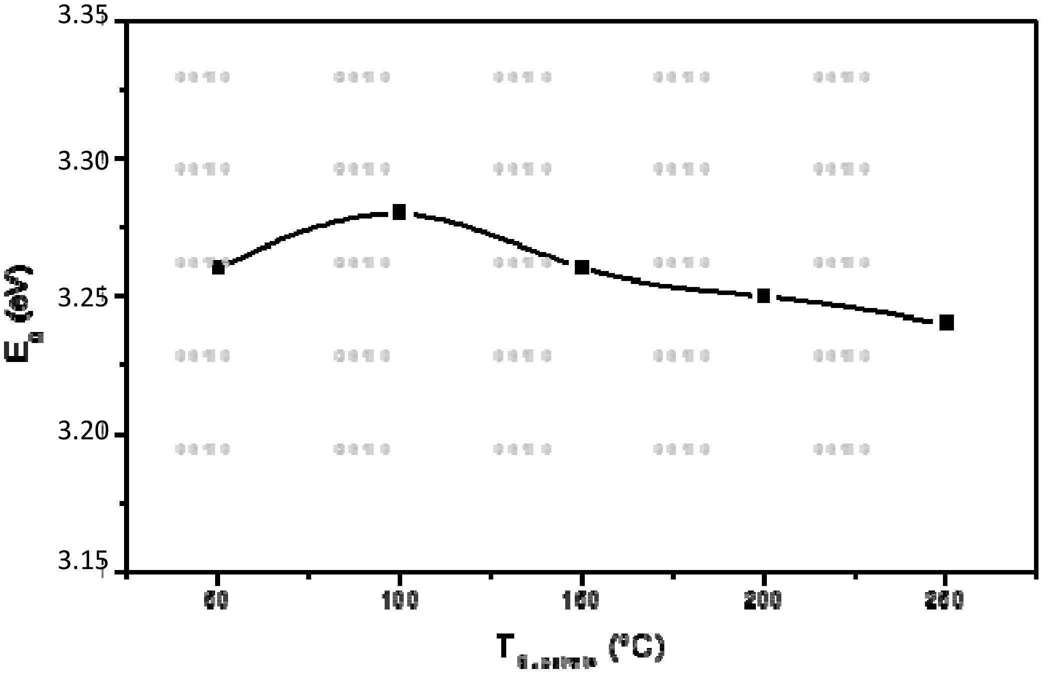


Figure 9. Dependence of the gap as a function of substrate temperature.

$$E = h\nu = \frac{hc}{\lambda} \quad \text{or} \quad \lambda = \frac{hc}{E} \qquad (13)$$

The simple and well-known formula is:

$$\lambda_{nm} = \frac{1{,}24}{E(eV)} \qquad (14)$$

It is from this relationship that we determine the energy of the band gap of our prepared by RF magnetron sputtering thin layers. In fact, we make a linear extrapolation at the absorption front of our power transmission layer. This straight line intersects the wavelength axis at a value of λ.For the different samples, we determined the optical gap from Equation (14). Indeed, the level of the linear variation of the absorption front, we drew a curve tangential to the front. This linear extrapolation, which cuts the axis of wavelengths, we can determine the optical gap. Figure 9 shows the evolution of the gap energy as a function of substrate temperature band. We find that the evolution of the energy of the forbidden band as a function of substrate temperature is almost constant. However, the sample prepared at 100°C gives an energy gap greater range compared to those given by the other samples.

Conclusion

Here, the effect on different experimental parameters on the growth and the properties of thin layers of zinc oxide has been studied. We performed several sets of samples we characterized optically. This systematic study led us to an area of very specific definition of manufacturing parameters for obtaining ZnO films of good quality. Indeed, the numerical parameters of the manufacturing balance sheet are as follows: 100°C for the substrate temperature, 50 W RF power injected into the discharge, 20% to the oxygen content in the gas mixture and 7 cm for the target-substrate distance.

These results, which are consistent with those found in the literature on zinc oxide prepared by RF magnetron sputtering, using a zinc target, will allow us to achieve the intended applications.

Conflict of Interest

The authors have not declared any conflict of interest.

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