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Realization and study of ZnO thin films intended for optoelectronic applications

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Abstract :

The objective of this study is the realization of zinc oxide (ZnO) thin films intended for optoelectronic applications. For this purpose, thin films were prepared by spray pyrolysis technique from zinc acetate solutions of different molarities (0.025 M, 0.05 M and 0.1 M) used as precursors on Si and glass substrates heated between 200 and 500 °C. The nozzle to substrate distance was varied between 20 and 30 cm. Structural, optical and electrical properties of the films have been studied. The results indicated that the films deposited were transparent in the visible region, well adherent to the substrates and presented surface roughness. All samples were polycrystalline in nature, having hexagonal würtzite type crystal structure. A (002) preferred orientation was observed at 450°C and a 0.025M molarity. The optical energy gap measured was about 3.3 eV. The refractive index values presented small variations with the deposition conditions and were located between 1.8 and 2.0. The electrical properties showed that the samples are natively n-type semiconductor and the electrical conductivity at room temperature varied between 10^{-5} *and* 10^{-2} $(\Omega.cm)^{-1}$.

Keywords : *thin films, semiconductor, band-gap, refractive index, electrical conductivity, optoelectronic.*

1. Introduction

Zinc oxide (ZnO), a II-VI type semiconductor with a large direct band gap of 3.4 eV, belongs to the family of transparent conducting oxides (TCO). It is a potential candidate for transparent front face electrodes on solar cells and flat panel displays owing to its electrical conductibility along with its high transparency [1-4]. Spray pyrolysis deposition (SPD), used here to prepare ZnO films, consists of spraying a Zn-containing precursor solution onto a heated substrate. The film forms as the solution's atomized aerosol droplets vaporize on the heated substrate leaving behind a dry precipitate for thermal decomposition. SPD has the advantages of set-up easiness vacuum-less, cost-effective, and flexibility over the plasma film deposition methods [5]. Large surface ZnO films can thus be deposited under atmospheric conditions on substrates from low-priced chemicals, while monitoring the preparation process step by step [6]. However, the physical and chemical properties of the films thus prepared depend on the process parameters such as the substrate temperature, the precursor concentration of the starting solution, the gas pressure, the solution flow rate, the deposition time and the nozzle-substrate distance [7-8]. The aim of this work is to study the structural, optical and electrical properties of ZnO thin films prepared by SPD under different substrate temperatures, precursor molarity values and spraying gun nozzle-substrate distances in order to optimize the deposition conditions yielding ZnO films with desired physical properties for particular applications. X-ray diffraction (XRD), transmittance measurements under UV-Visible, ellipsometry and electrical measurements were used to evaluate these properties. The evolution of the properties of the sprayed ZnO films is discussed and correlated to the deposition conditions.

2. Experimental Details

A. Sample preparation

The zinc oxide films were deposited by spraying a solution of zinc acetate dihydrate ($Zn(CH_3COO)_2$, $2H_2O$) dissolved in doubly distilled water onto silicon and glass substrates. The substrate temperature was varied between 200 and 500°C and measured via a Chromel–Alumel thermocouple. Precursor concentrations of 0.025M, 0.05M and 0.1M were used. The distance between the substrates and the spray gun nozzle was varied between 20 and 30 cm.

B. Sample Characterization

The structural properties of films were studied by X-ray diffraction, using Cu-K$_\alpha$ radiation of wavelength $\lambda = 1.5405$ Å. The size D of the crystallites was calculated from the Scherer's formula [9]. The thickness and the index of refraction were determined from ellipsometric measurements performed on ZnO films deposited onto Si substrates. The transmittance of the layers deposited on glass was measured in the UV-Visible region using a double beam spectrophotometer (Shimadzu 3101PC). The gap energy E_g of the ZnO films deposited on glass substrates was determined from their transmittance $T(\lambda)$. The absorption coefficient $\alpha(\lambda)$, in the spectral region of absorption of the light, was deduced from the Beer-Lambert law [10]. According to the Tauc's theory for the direct allowed transitions such as those occurring in the direct gap of ZnO, $\alpha(h\nu)$ close to the band edge is :

$$\alpha \cdot h\nu = A\sqrt{h\nu - E_g}$$

where A is a constant of proportionality and $h\nu$ is the energy of the incidental light photons. E_g can be estimated by extrapolating to the $h\nu$- axis the linear part of the $(\alpha h\nu)^2$-

curve. The limit of absorption below E_g can be described, empirically, by :

$$\alpha(h\nu)=\alpha_0\, \mathbf{exp}\left(\frac{h\nu}{E_{Urb}}\right),\ h\nu\langle E_g$$

The E_{Urb} parameter was determined by the variation of $log(\alpha)$ with $h\nu$. The electrical properties of the layers were determined using the $I(V)$ characteristics measured by the two points technique for a coplanar structure with two gold electrodes deposited by pulverization.

3. Results and Discussion

A. Structural Characterization

X-ray diffractograms of ZnO thin films deposited on glass at various substrate temperatures and a concentration of 0.05M are represented on figure 1. The films are polycrystalline, made of only one hexagonal phase of würtzite type. They show a maximum intensity for the peaks (100), (002) and (101). The (002) peak appears in all the diffractograms and its intensity increases with the temperature.

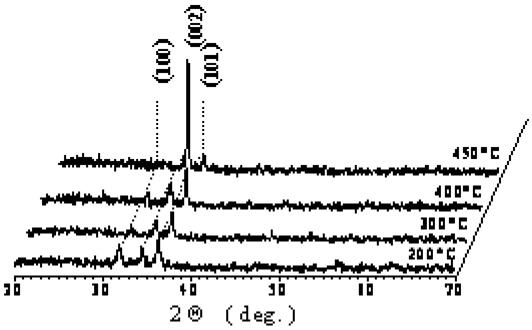

Fig. 1 XRD patterns of ZnO thin films with a molarity of 0.05M deposited by spray pyrolysis for various substrate temperatures.

The domination of this peak, at 450°C, indicates that the growth with the *c* axis perpendicular to the substrate is favored. This type of growth is especially important for piezoelectric applications. The orientations (100) and (101), corresponding to an *c* axis parallel to the surface, have as a basic plan formed of a mixture of zinc and oxygen atoms of equal numbers, which facilitate the arrangements between these atoms, and consequently requires less energy, and this explains their appearance at low temperature. The preferential orientation (002) is observed at 450°C. This result is critical for piezoelectric applications [11]. Krunks et al. have related this preferred orientation in sprayed films to the higher chemical purity of the layers grown at high substrate temperature. It was shown that the chemical purity of the films is controlled by the level of thermal decomposition of metalorganic complex compounds formed in the starting solutions [11-13].The variations of estimated grains size D with temperature are represented on figure 2. The size of the grains increases from 27 to 80 nm when the temperature of growth varies from 200 to 450°C. This evolution is normal because the increase in the temperature of deposition or treatment is always accompanied by an increase in the size of the grains whatever the technique of development used [14]. The samples deposited at high temperature grow more slowly, which is equivalent to an annealing of the layer in formation, involving an increase in the size of the grains. The results obtained here agree well with the works of Chopra and Roth et al. [15-17] that showed that the grains size increase with the films thickness.

(2)

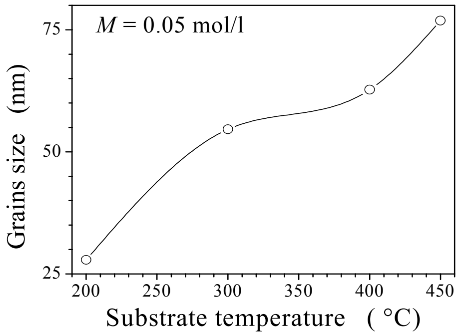

Fig. 2 Variation of the estimated grains size with the substrate temperature.

B. Optical Characterization

The transmittance spectra $T(\lambda)$ of ZnO films deposited on glass are shown on figures 3 and 4. Transmittance strongly depends on the temperature. As mentioned above, at low temperature, the reaction of decomposition of the droplets remains incomplete and the impurities are self incorporated in the material. Consequently, the mass deposited will be more important and, moreover, absorption will be stronger, which explains the low coefficient of transmission and its dependence on the wavelength in the visible region. On the other hand, at 450°C,

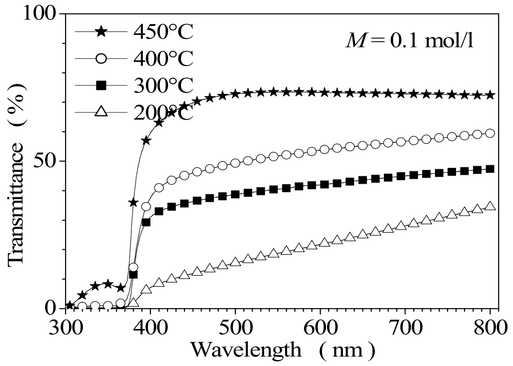

Fig. 3 Variation of the optical transmittance with the wavelength for different temperatures of deposition at 0.1M.

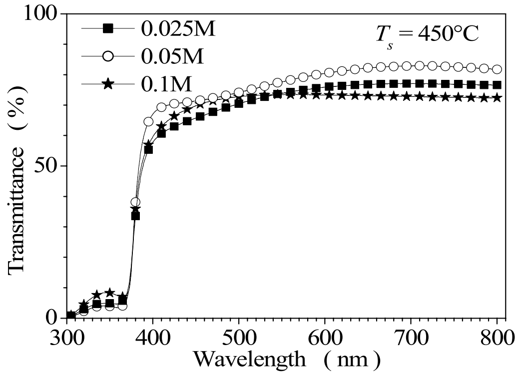

Fig. 4 Variation of the optical transmittance with the wavelength for different molarities at 450°C.

The transmittance is raised and depends slightly on the molarity. This indicates a complete thermal decomposition of the droplets involving the formation of a material close to the stoichiometry, which leads to layers of lower thicknesses. This is in good agreement with the results of Zaouk et al. who showed that at higher temperatures, there is enough energy available for the thermal decomposition, solvent evaporates before the droplets reach the substrate and only the solid precursor reaches the substrate where thermal decomposition occurs [11]. Consequently, the grown material is dense and the obtained films are relatively thin. Moreover the flat nature of the spectrum in the visible indicates that the material does not absorb in this region, which minimizes the thickness effect and thus the dependence on the molarity. That is also a consequence of the disappearance of the impurities following volatilization, at high temperature, of the secondary reaction products. The values found for the coefficient of transmission are about 70 to 85%, which gives the thin ZnO films the character of transparency in the visible region and makes this material a potential candidate for optoelectronic applications.

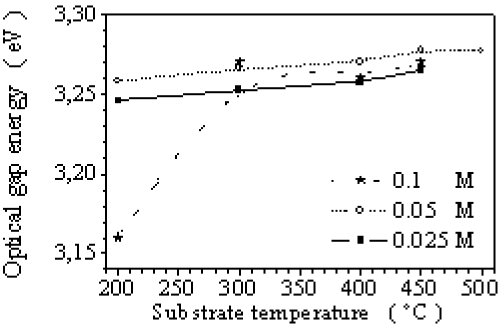

Fig. 5 Variation of the optical gap energy with the temperature of deposition for different molarities .

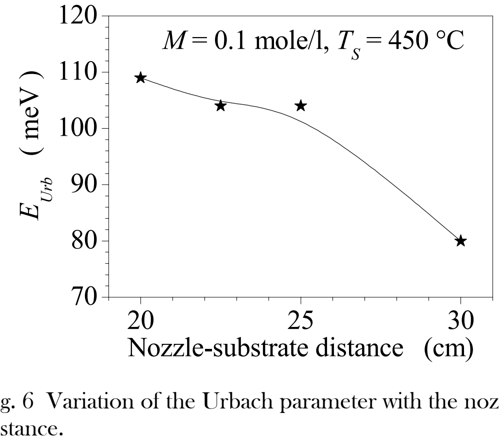

Fig. 6 Variation of the Urbach parameter with the nozzle-substrate distance.

The fundamental absorption region, due to the electronic inter-band transitions in ZnO films, is located in UV. According to (1), the value of the energy of the gap, E_g, is estimated by extrapolating to the $h\nu$-axis the linear part of the $(\alpha h\nu)^2$-curve. In figure 5, it can be seen that there is an influence of the conditions of deposition on the gap. In particular, this latter grows with the temperature. The energy of the forbidden band of our layers is approximately 3.3 eV which is lower than the value 3.37 eV of massive ZnO. Our results are in agreement with the work of Srikantand Lin et al. [18,19]. The increase in E_g can be correlated to the size of the grains which increases with temperature [14], this makes the value of E_g tend towards that of the massive ZnO. This point of view is similar to the observation of Ayouchi et al. [20], who had, on the contrary, obtained values of E_g higher than those of stoichiometric massive ZnO and thus observed a decrease of E_g with the temperature. This phenomenon was attributed to the reduced grains size in the thin layers of ZnO prepared by this technique and to the oxygen deficiency confirmed by XPS studies [20]. The low value obtained for the optical gap, for the film prepared with a molarity 0.1M at 200°C, is probably due to the incorporation of impurities and to structural defects which can be correlated with measurements of the refractive index. The low value obtained under these conditions indicates that the film is more porous than the others. From the variations of the refractive index with the deposition temperature, for various molarities, values situated between 1.7 and 2.0 are deduced, in agreement with the literature. The reduction of the refractive index with the raise of the concentration, observed, is compatible with the fact that the layer thickness increases with the molarity to the detriment of the density and, consequently, the drop of the index can be correlated to porosity.

It is possible to estimate the disorder existing in the layers by studying the variations of the absorption coefficient [20]. According to (2), the band tail width, E_{Urb}, is determined by the variations of $log(\alpha)$ with $h\nu$ The values found for the Urbach energy are comparable with those found by other authors [21]. The decrease in E_{Urb}, by increasing the deposition temperature or, as can be seen in figure 6, the nozzle-substrate distance, indicates that, under these conditions, the structural disorder and the defects decrease. Indeed, increasing the distance between the substrate and the spraying nozzle makes the layer to be formed at a longer time and, when the temperature is raised enough, that is equivalent to annealing the layer being formed.

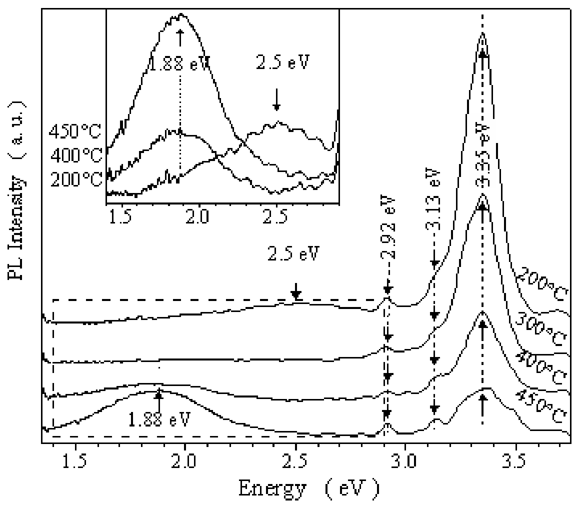

Fig.7. Photoluminescence spectra, at room temperature, of ZnO thin films deposited on Si substrates at different temperatures with a concentration of 0.025M. The inset is a magnification of low energy region (1.4-2.9 eV)

The photoluminescence (PL) was detected in all our ZnO samples and the shape of the spectra depends on the conditions of deposition (Fig. 7). In the ZnO film deposited at 200°C, a green luminescence band appears at about 2.5 eV (clearly seen in the inset of figure 7). It may be attributed to oxygen vacancies [22,23] due to an incomplete reaction when the film is deposited at low temperature. The green-yellow emission bands are usually assigned to one of the donor and acceptor mid-band-gap defect states such as oxygen vacancies, zinc interstitials, zinc vacancies, or antisite defects [24]. In the PL spectra of the samples deposited at 400 and 450°C the green luminescence band quenches and a red luminescence band appears at about 1.88 eV. The band is broad with a FWHM of about 0.5 eV. Its shape is Gaussian and the peak intensity increases with temperature. Even though the origin of red emission bands in ZnO remains an open question, this may be a result of an increase in the concentration of defects caused by oxygen interstitials [25-27]. Another peak seen for all films is located at 3.35 eV. Its intensity decreases with the deposition temperature. The bandgap of ZnO at room temperature found being about 3.3 eV, this suggests that this emission peak is excitonic in nature [28, 29].

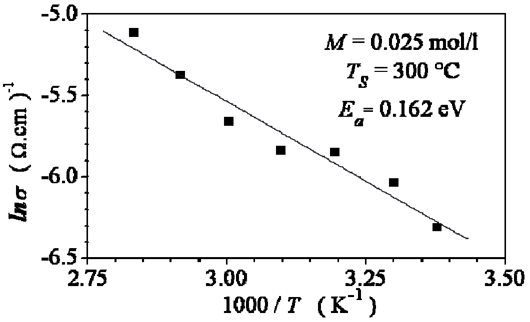

Fig. 8 Variation of the electrical conductivity of the ZnO thin layers with the heating temperature.

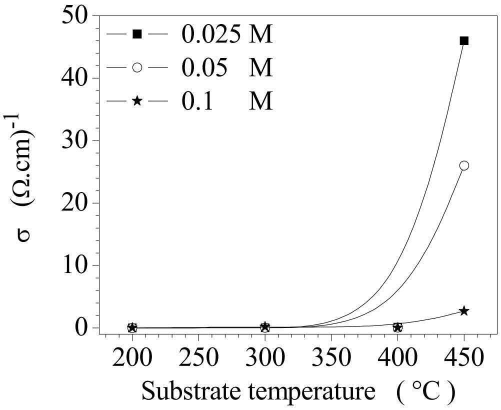

Fig. 9 Variations of the electrical conductivity with the temperature of deposition for various concentrations.

C. Electrical Characterization

The electrical properties of the ZnO thin layers are of a considerable interest, in particular in the photovoltaic applications. Fig. 8 represents the variation of the electric conductivity σ of the ZnO thin films with the heating temperature. It is expressed as a linear decrease of *log* (σ) with the reverse of the temperature. The behaviour is characteristic of a semiconductor. Fig. 9 shows the variations of σ with the deposition temperature T_s for various concentrations. At low deposition temperatures the conductivity remains low. This can be correlated to the structure of the films. Indeed, XRD results indicated the presence, at low temperature, of grains of small size. As the grain boundaries reduce the mobility of the carriers and since the conductivity is proportional to this parameter, this explains the low values of the conductivity of the prepared samples at low temperature. However, by increasing the temperature of the substrate beyond 400°C, the quality of films improves and the increase in grains size justifies the raise of the conductivity.

The activation energy informs about the position of the Fermi level E_F relatively to the bottom of the conduction band E_C. It is deduced from the measurement of conductivity σ at various temperatures by using (3), k_B being the Boltzmann constant :

$$\sigma = \sigma_0.\exp\left(\frac{-E_a}{k_B T}\right), E_a = E_C - E_F$$

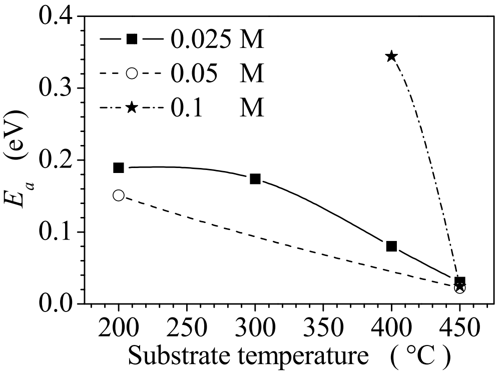

Fig. 10 Variation of the activation energy with the deposition temperature for different molarities.

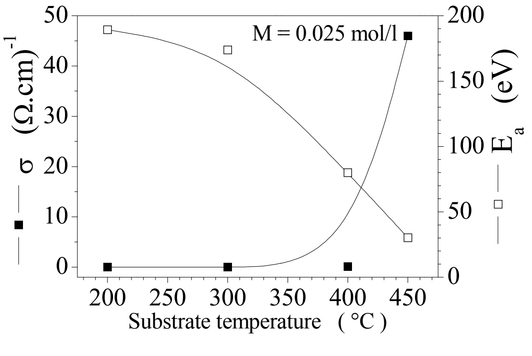

Fig. 11 Variation of the electric conductivity and the activation energy with the deposition temperature.

Fig. 10 shows variations of E_a with the deposition temperature for different concentrations of the starting solution. The maximum value of the activation energy found with our samples is about 0.35 eV. This value is lower than the half of the found energy gap which is about 3.3 eV. This indicates that the films are n-type semiconductors. This is in agreement with the literature since it is generally known that the ZnO thin layers are natively n-type. In Fig. 11, it is shown that at given measurement temperature the conductivity increases when the activation energy decreases. This is in agreement with (3) and confirms, again, the semiconducting behavior of the deposited layers.

4. Conclusion

In this work, ZnO thin films were prepared by the spray pyrolysis technique under various experimental conditions. Thus, various substrates (glass and silicon), several temperatures of deposition (from 200 to 500°C), various concentrations of a zinc acetate solution (0.025M, 0.05M and 0.1M) and spraying gun nozzle-substrate distances varying from 20 to 30 cm were used. The deposits were carried out in air. Several series of samples were prepared and their structural, optical and electrical properties studied. The analysis of the results showed that the deposited films characteristics depend on the experimental conditions. The correlation with the properties of the layers made it possible to optimize the parameters of deposition that lead to semiconducting ZnO thin layers having a great transparency. This makes ZnO thin films a serious candidate in optoelectronic applications. The highly orientated films obtained at a temperature of 450°C and a molarity of 0.025M show that this simple technique can be effective in piezoelectric applications for the manufacture of cheap ultrasonic oscillators and transducers devices.

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