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Molarities Effect on Structural Optical and Electrical Properties of Nanostructured Zinc Oxide deposited by Spray Pyrolysis Technique

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Abstract: ZnO thin film were synthesized by spray pyrolysis on glass substrates, using zinc chloride as precursor with different molarities 0.05M,0.1M and 0.15 M. The XRD patterns showed that the films deposited are polycrystalline with hexagonal structure and a preferred orientation of the along (002) plane. Increasing of solution molarity caused the increase the crystallite size of the films from37.01nm for 0.05M to 45.79 for 0.1M and it is slightly reduced for 0.15M. XPS studies indicates clearly the formation of the ZnO films. The optical study showed that the average transmittance enhancement when the molarity increases and reaches the maximum of about 80% for 0.1M. Further it exhibits increase in the optical band gap from 2.71 eV to 3.04 eV as the molarity increment. The room temperature electrical resistivity of ZnO films decreases when the molarity increases and reaches the optimum value of $1.92 \times 10^{+2}$ (Ωcm) for 0.1M
Keywords: ZnO, thin films, XPS study, optical properties, spray pyrolysis.

1 Introduction

Transparent conductive oxide (TCO) thin films occupy an important place in the domain of the photovoltaique and the optoelectronics. Zinc oxide (ZnO) is a versatile semiconductor which has attracted considerable attention due to their high stability, non-toxicity and excellent optical and electrical characteristics [1, 2]. ZnO presents hexagonal wurtzite structure with a direct wide band gap of 3.37 eV and high exciton binding energy of 60 meV at room temperature. However, ZnO is transparent semiconductor compound of type II–VI with natural n-type conductivity [3, 4]. Many techniques were used to deposit ZnO thin films on glass substrates, including hydrothermal method [5] sputtering [6], sol–gel processes [7] and spray pyrolysis method [8, 9]. Transparent conductive oxide thin films are used in the production of several components and devices, like as solar cells [10], gas detectors [11], transparent electrodes, UV photo-detectors and piezoelectric transducers [12, 13].
The main purpose of this work is to deposit ZnO films with suitable proprieties for PV cells. The ZnO thin films deposited by spray pyrolysis technique on the glass substrate with different molar concentrations 0.05M, 0.1M and 0.15M., in order to study the effect of variation of aqueous solution molarity on physical properties of ZnO thin films, so we can obtain good quality of the crystallinity, high transparency and conductivity, serve to reduce the losses during photovoltaic conversion.

2 Experimental Details

ZnO thin films were synthesized using spray pyrolysis technique onto microscope glass substrates of (75×25) mm^2 at 350°C for various molarities 0.05M, 0.1M and 0.15M. The solution was prepared by dissolving the $ZnCl_2$ powder in 100 ml deionized water. The substrates were first cleaned in a water bath, followed by dipping in con. HCl, acetone and ethanol successively. Compressed air at a pressure (2 bar) has been used as a carrier gas. Solution flow was 8 ml/min and spray nozzle to heating plaque distance was fixed to 29 cm. Moreover, the prepared solutions were immediately sprayed to avoid any possible chemical changes with time [9].
X-ray diffraction (XRD) patterns of the deposited films were recorded by Philips 1830 system using Cu Kα radiation (λ=1.546 Å) with 2θ in the range 20 – 65°. The XPS measurements were carried out on a Kratos Axis Ultra using Al Kα (1486.6 eV) radiation. High resolution spectra were acquired at 20 eV pass energy with energy resolution of 0.9 eV. The C 1s line of 284.5 eV was used as a reference to correct the binding energies for charge energy

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shift. The optical measurements were carried out at room temperature in the wavelength range 250–2500 nm using an UV-Vis-NIR JASCO type V-570 double beam spectrophotometer. The electrical resistivity, carrier concentration and mobility were measured using an Automated Hall Effect System (ECOPIA HMS-5000) at room temperature and silver lacquer as contact.

3 Results and Discussion

3.1 Structural Properties

The structural quality of deposited ZnO nanostructured films were examined using XRD analysis. **Fig.1** exhibits the XRD pattern of the ZnO thin films with various molarities grown on glass substrate at 350 ˚C. It observed that there are six orientations identified as (100), (002), (101), (102), (110), (103) planes respectively for the samples with molarity 0.1M and 0.15M.

All the films were crystallized in the wurtzite hexagonal phase and present a preferential orientation along the c-axis with preferred orientation in the (002) direction perpendicular to the substrate, which is consistent with the standard card (JCPDS card no: 65-3411 with lattice parameters a=3.249A° and c=5.20 A°). By increasing the molar concentration of precursors from 0.05M to 0.1M, the intensity of preferential orientation (002) was increased (**Fig.2**) showing the improved crystallinity. A slight decrease in the intensity of the pic was observed with increasing molar concentration to 0.15M.

Fig. 3 demonstrates XPS survey spectra of the ZnO thin films prepared with molarity 0.1M. The observed peaks of Zn 3d, Zn3p, Zn3s and O 1s peaks were observed, indicating the presence of Zinc and oxygen on the surface of the deposited ZnO films. In addition, strong peak of C 1s has been observed which can be attributed to surface contamination with hydrocarbon after transportation in air. Similar result was reported in the pieces of literature [14] for ZnO films grown by microwave method.

Table 1 illustrates the effect of solution molarity on the structure parameters evaluated from the XRD data. The structural parameters, such as crystallite size (D), microstrain (ε), stress (α*) and texture coefficient (TC) were calculated using the following relations [9, 15].

$$D = (0.9.\lambda)/(\beta.cos\theta) \quad (1)$$

$$\varepsilon = \frac{\beta.\cos\theta}{4} \quad (2)$$

$$\sigma^* = -453.6 * 10^9 \left(\frac{c-c_0}{c_0}\right) \quad (3)$$

$$TC_{(101)} = \frac{I_{(002)}/I^0_{(002)}}{(1/N)\sum_n I_{(hkl)}/I^0_{(hkl)}} \quad (4)$$

Where: **λ** is the wavelength of Cu-Ka radiation, θ is the Bragg angle and β is defined as the full width at half maximum (FWHM) of the most intense diffraction peak (002). c_o is the parameter of Bulk ZnO. I (hkl) is the measured relative intensity of a plane (hkl). I° (hkl) is the standard intensity of the plane (hkl) taken from the JCPDS data, N is the reflection number and 'n' is the number of diffraction peaks.

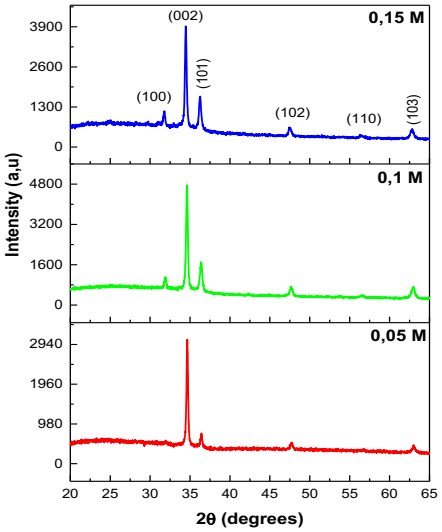

Fig 1: XRD patterns of the deposited ZnO thin films for different molarities.

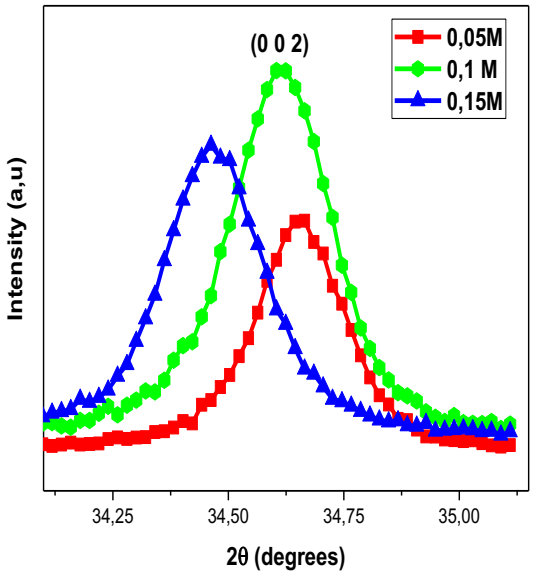

Fig.2: (002) peak position of the ZnO films for different molarities.

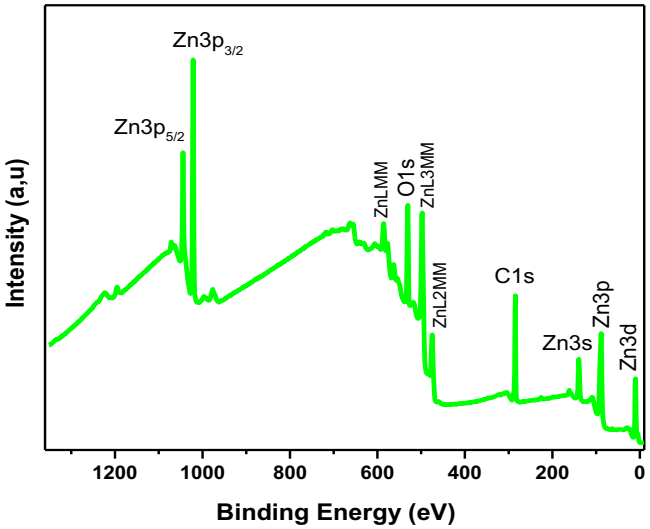

Fig. 3: XPS survey spectrum of ZnO thin films prepared with molarity 0.1M.

Table 1: Summary of structural parameters of ZnO thin films deposited for various molarities.

Zn O Thin Films	Lattice constants c (Å)	d (0 0 2) (Å)	FWHM (0 0 2) Peak (2θ)°	Crystallite size (D) (nm)	Strain (ε) (10^{-4})	Stress (σ*) (10^9 N/m^2)	TC (0 0 2) texture coefficient
0.05M	5.1760	2.5880	0.25	37.01	10.13	2.56	2.41
0.1M	5.1768	2.5883	0.202	45.79	8.41	2.49	3.98
0.15M	5.2036	2.6018	0.272	34.02	11.52	1.54	3.02

The obtained values of the stress of the samples are positive sign demonstrating that the thin films are in a state of tensile stress. **Fig 4** shows the evolution of crystallite size (D), texture coefficient (TC), micro-strain (ε) and FWHM against the molar concentration. Our results indicate that increasing the molarity from 0.05M to 0.1M leads to increasing in the crystallite size from about 37.01nm to 45.79 nm and texture coefficient, and decreasing in the micro strain, indicating that the films crystallinity has been improved. Above 0.1M, the crystallite size (D) has been reduced to 34.02 for 0.15M caused by rising the disorder in the films.

3.2 Optical Properties

Optical transmission in the UV-visible-NIR spectral range is an important feature for evaluating the quality of deposited films. **Fig 5 (A, B)** shows the optical transmittance and reflectance for deposited ZnO thin films with various molar concentrations. It is well evident from the figure the average transmittance in the visible range increase from 61% for 0.05M to 75% for 0.1M, which can due to improving the crystallinity of the films when the molar concentration increase. Enhancement the transmittance of the films due to a reduction in grain boundaries **(see Fig 7)** (scattering photons by grain boundaries may result in a decrease in transmittance) caused by rising grain size. The size of grain affects the optical transmittance and reflectance spectra. A shift to low wavelength (blue shift) has been observed at the absorption edge of ZnO films when the molarity increase.

The optical direct band energy gap (Eg) of the films can be estimated using Tauc relation [16]

$$(\alpha h\upsilon)^2 = An\,(h\upsilon - E_g) \qquad (5)$$

Where: An is an energy independent constant. α is the absorption coefficient, h is the Planck constant, υ is the incident photon frequency, (h.υ) is the photon energy. The energy gap value of samples can be determined by the variation of the curve $(\alpha h\upsilon)^2$ versus photon energy (hν) as

shown in **Fig 6.** The optical energy gap was found to be 2.71, 3 and 3.04 eV for 0.05, 0.1 and 0.15 M respectively. The widening of optical band gap with the increase in molarity may be attributed to the crystal growth, which lead to an increase in the average grain size and reduction in grain boundaries (see **Fig 7**).

The width of tail of the localized state denoted by Urbach energy, which is directly related to the density of state, can be determined by following relation **[**17, 18**]**

$$\alpha = \alpha_0 \exp(h\upsilon/E_u) \quad (6)$$

Where: α_0 is a constant. The urbach energy (Eu) values are determined from the reciprocal of the slope of the linear portion of a plot of ln (α) versus photon energy (hν) (**Fig .7).** The obtained values of urbach energy are 0.81, 0.73 and 0.34 nm for 0.05M, 0.1M and 0.15M respectively.

This result is consistent with the values of the optical energy gap because there is an inverse relation between band tail and energy gap when the molarity vary from 0.05M to 0.15M.

3.3 Electrical Properties

The Hall Effect measurements of the deposited ZnO thin films with various molarities have been investigated at room temperature. Electrical resistivity, mobility, Bulk concentration and Hall coefficient and sheet resistance are regrouped in **Table 2**. The negative sign of hall coefficient confirms n-type conductivity of the ZnO films. The increase of molar concentration from 0.05M to 0.1M causes a decrease in resistivity from $2.18 \times 10^{+2}$ to $1.92 \times 10^{+2}$ (Ωcm) and sheet resistance from $1.45 \times 10^{+7}$ to $9.63 \times 10^{+6}$ (Ω/sq), which could be due to the enhancement of the crystallinity of the ZnO films. Above 0.1M, they varied slightly inversely due to the rise structural disorder in the films (see **Fig 4**). The carrier concentrations of the ZnO films is in the order of 10^{+15} cm^{-3}

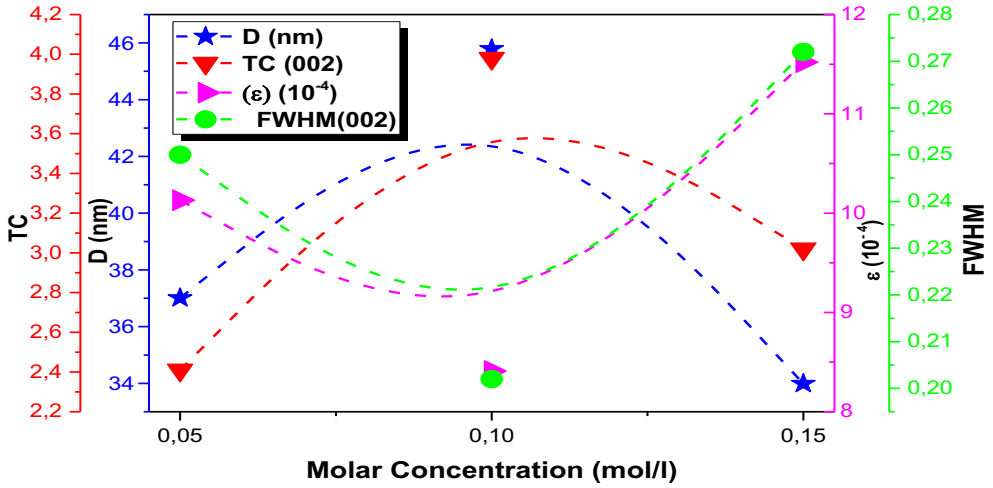

Fig 4: the average crystallite size (D), texture coefficient (TC), micro-strain (ε) and FWHM Of ZnO thin films prepared for different molarities.

Table 2: The Hall Effect results of the ZnO thin films deposited for different molarities

Molarity (M)	Resistivity (ρ) (Ωcm)	Mobility (cm^2/VS)	Carrier Concentrations (cm^{-3})	Hall Coefficient (cm^3/C)	Sheet Resistance (Rsh) (Ω/sq)
0.05M	$2.18 \times 10^{+2}$	3.28	$-8.71 \times 10^{+15}$	$-7.16 \times 10^{+2}$	$1.45 \times 10^{+7}$
0.1M	$1.92 \times 10^{+2}$	3.32	$-9.74 \times 10^{+15}$	$-6.40 \times 10^{+2}$	$9.63 \times 10^{+6}$
0.15M	$6.24 \times 10^{+2}$	3.21	$-3.10 \times 10^{+15}$	$-2.01 \times 10^{+3}$	$4.16 \times 10^{+7}$

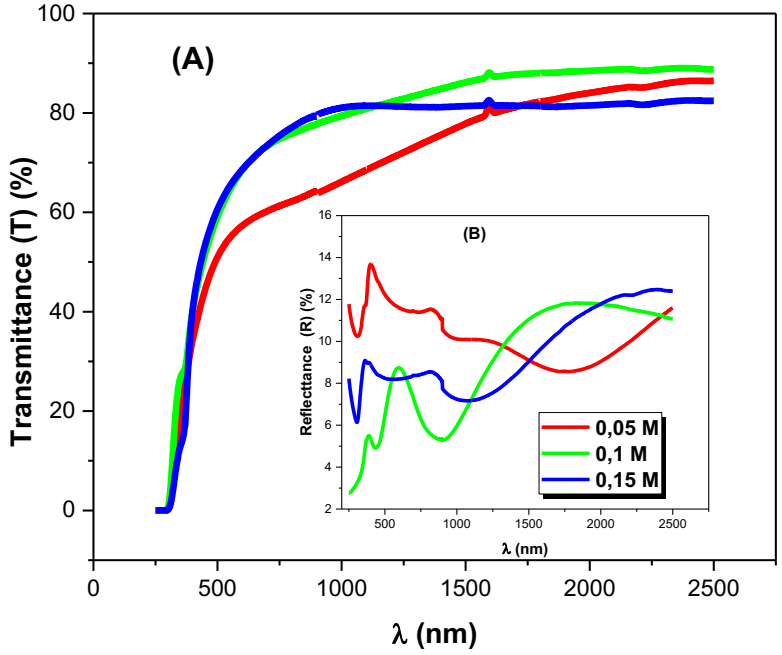

Fig 5 (A, B): Optical transmittance and reflectance of ZnO thin films for different molarities.

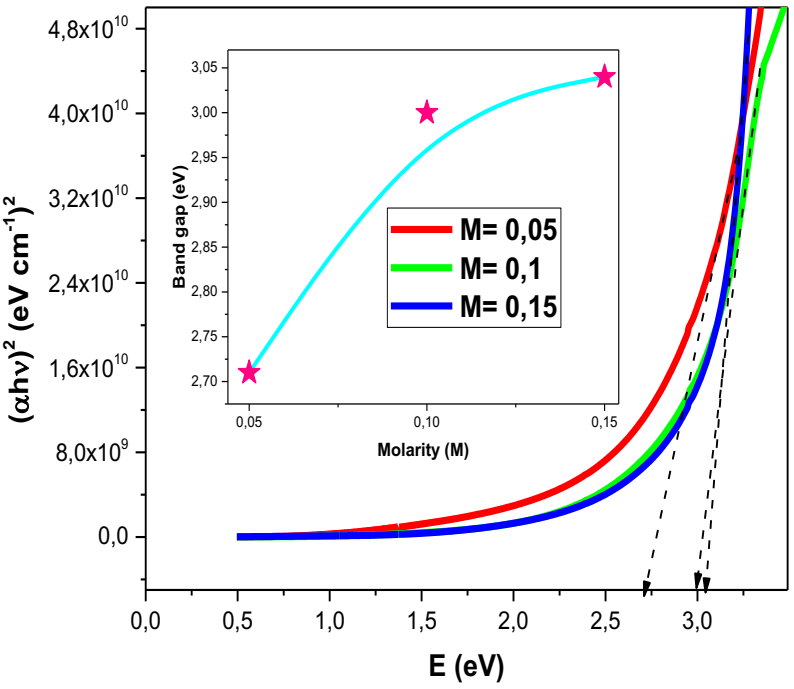

Fig 6: Variation of $(\alpha h\upsilon)^2$ against photon energy (hν).

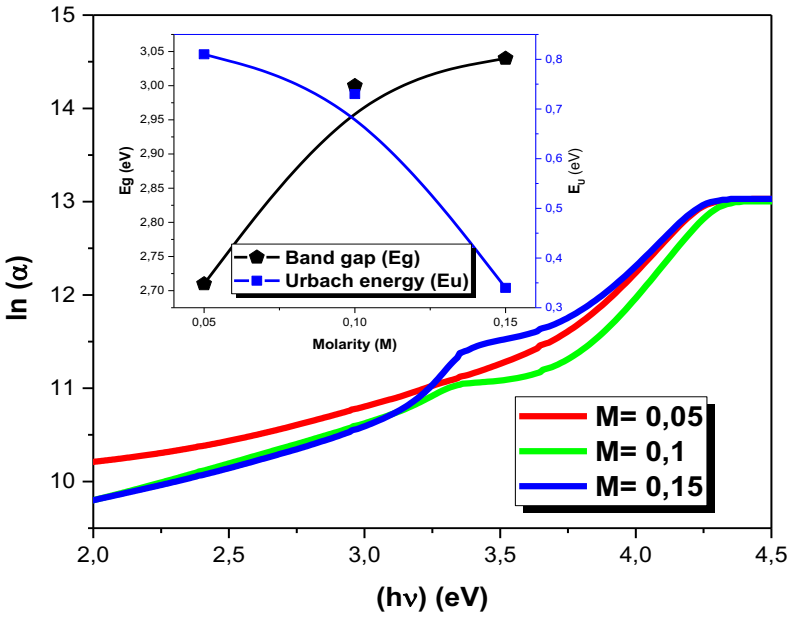

Fig 7: Variation of Urbach energy and optical Band gap of samples against molarity.

4 Conclusions

ZnO thin films were successfully deposited by spray pyrolysis method. The effect molarity was studied upon structural, optical and electrical properties. XRD analysis confirmed that the prepared ZnO thin films have a high quality Wurtzite hexagonal structure with a preferred orientation (002) direction. All the structural parameters were affected by changing molarity. The crystallinity of the films improve with varying molar concentration. XPS analysis indicates clearly the formation of the pure ZnO thin films. Highest transmittance is exhibited by the ZnO film with molarity 0.1M. The optical energy gap increased from 2.71 to 3.04 eV, proportionally with the molarity. Lowest resistivity is observed for ZnO films prepared with molarity 0.1M.

Therefore, we concluded that the synthesized of zinc oxide thin films with increased crystallite size, transmittance, band gap energy and conductivity requires adequate molarity.

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