EFFECT OF ZN CONCENTRATION ON STRUCTURAL AND OPTICAL PROPRIETIES OF ZNO THIN FILMS DEPOSITED BY SPRAY PYROLYSIS

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ABSTRACT

ZnO thin film were deposited by spray pyrolysis on glass substrates, using zinc nitrate as precursor with different molar concentrations varying from 0.05M to 0.2 M. To study the structural proprieties of the film , the different technique was used as the X-ray diffraction, atomic force microscopy (AFM), Raman scattering , and FTIR . The optical properties were explored by transmission, reflectivity and Photoluminescence techniques. The ZnO thin films obtained in this paper are polycrystallines, the grain size increases when the molar concentration of Zn precursor was increasing. The films are transparent in visible region, this transmission values decreases when the molar concentration increase caused by the increasing of surface roughness

KEYWORDS:

ZnO thin films; spray pyrolysis ; roughness.

1. INTRODUCTION

The increasing demand for energy made the solar cells as a new source of energy [1,2] for replace the conventional sources. However , despite the concentrated efforts to develop the PV systems , the high cost of the generated electricity prevents that PV systems are more widely spread, to reduce these cost, efforts to improve efficiency and the searches was concentrating on cheaper materials and structures are undertaken .Thin film nanostructure is an attractive solution due to their unique properties.

Zinc oxide (ZnO)[3] is one of the most extensively studied materials as an alternative photo anode to TiO_2[4].ZnO thin film has high transparency[5], piezoelectricity[6], room-temperature ferromagnetism[7], and huge magneto-optic[8] effect , it can be grown into many different nanoscale forms, thus allowing various novel devices to be achieved , also doping can improved some proprieties of ZnO [9], like conductivity which may change at will from metallic to insulting (including n-type and p-type conductivity. It has wide band gap energy of 3.37 eV, high

exciton binding energy of 60 meV, a wide range resistivity, high electron Hall mobility (200 cm2.V.s^{-1}) and high transparency at room temperature.

Some techniques was used to fabricate the ZnO thin film such as magnetron sputtering[10] spray plasma [11], sol gel spin coating[12] , pulsed laser deposition[13], metal-organic chemical vapor deposition and spray pyrolysis[5].

Spray pyrolysis is a versatile technique for deposition of metal oxides because of its cheapness and easy process control which gives the possibility of obtaining films with the required properties for different applications [5].

Different authors reported on the preparation of ZnO thin films by spray technique. In fact, E. Bacaksiz et al. [14] prepared ZnO thin film starting with different solution precursors such as zinc chloride, zinc acetate and zinc nitrate, at 0.1M concentration on glass substrate and at 550°C. It was observed that the nature of precursor affected the structural and optical proprieties of ZnO thin films. The higher value of transmittance was observed in ZnO thin films prepared with zinc nitrate precursors. Mazabala Banto et al [5] studied the effect of precursor concentration on structural, morphological and opto-electric properties of ZnO thin films starting by ZnCl2 dissolved in ethanol and deionized water with different molar concentrations increasing from 0.05M to 0.2M on glass substrate at 400°C and annealing or 5h,in air at 500°C. In this work it was shown that the molarity of precursors affected the properties of ZnO thin film. The film present high transmission (95%) at molar concentration 0.05M. E.U. Masumdar et al. [15] studied the effect of molarity on structural and opto-electric properties of ZnO thin films elaborated by using a precursor solution of zinc acetate in a mixed solvent of 75% methanol and 25 % distilled water. The films were grow with different molar concentration varied from 0.1M to 0.75 M on glass substrate and 450°C, the average transmission of the films varied from 75% to 88%.

The main purpose of this work is to obtain ZnO film with suitable proprieties for PV cells to can be used as a transparent conductive oxide (TCO) thin film, to reduce the losses during photovoltaic conversion [28].

In this study, the ZnO films deposited on the glass substrate was fabricated by zinc nitrate by varying molar concentration from 0.05M to 0.2M. To reduce the fabrication cost, the ZnO thin film was prepared without annealing temperature, so we could obtain high transparent, good morphology and high quality of the crystal.

2. EXPERIMENTAL DETAILS

2.1. Materials and preparation

ZnO thin films were prepared by spray pyrolysis process from a solution with different molar concentrations of $Zn(NO_3)_2,6H_2O$ precursor (0.05 M, 0.1M, 0.15 M and 0.2M) in 25 ml of deionized water. The spray system used in this work was fully described and schematically presented in [16]. The $Zn(NO_3)_2,6H_2O$ solution was sprayed with a solution spray rates of 2 ml/min onto a preheated glass substrate at 500°C during 10 min, using compressed air as a carrier gas. The nozzle to substrate distance was about 45 cm. The obtained ZnO thin Films are transparent, exhibiting a good adherence to the substrate surfaces.

2.2. Measurements

The structural characterization was carried out by X-ray diffraction (XRD) technique using a Bruker D 8 advance X-ray diffractometer with CuK_α(k=1.5418˚A) radiation for 2θ values in the range of 25–60°.Film surface morphology was investigated using Atomic Force Microscope(AFM) in tapping mode configuration by a nanoscope III microscope, and Raman spectra were recorded in the 300-700 cm^{-1} range using a Jobin-Yvon spectrometer (T64000 model) equipped with an Ar^+ laser (632.8 nm exciting line) and a CCD detector in a back-scattering geometry. Transmittance spectra were recorded using a UV–vis spectrophotometer in the 350–1200 nm range. The reflectivity spectra of the ZnO thin films surfacewere measured using a LAMBDA 950 UV/Vis/NIR spectrophotometer equipped with an integrating sphere. The composition of as-formed and treated ZnO thin film was analyzed by means of Fourier transform infrared spectroscopy (FTIR).The optical properties were analysed by photoluminescence technique PL) in the range 340-500 nm using a 299 nm line of an Ar laser as an excitation light source.

3. RESULTS AND DISCUSSION

3.1. Structural properties

Fig. 1 Demonstrates the XRD patterns of ZnO thin films for different zinc nitrate precursors. The films are polycrystallines with hexagonal Wurtzite structure and no parasite phase is observed. All the graphs of ZnO thin films shown a orientation along the (002) so the c-axis of the crystallites is perpendicular to the substrates, due to the minimization of internal stress and surface free energy [5,17].

By increasing the molar concentration of precursors, the intensity of preferential orientation was increased indicating that the films crystallinity has been improved, small peaks of (001) and (101) orientation also appeared in concentration 0.15 and 0.2M.
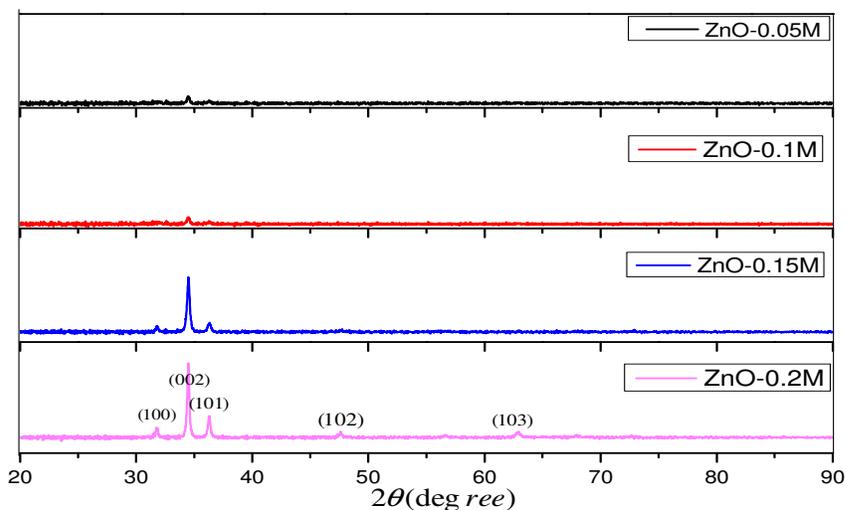

Figure 1: XRD patterns of ZnO films prepared with different molar concentration of precursor

The crystallite size was calculated from the (002) diffraction peak using Scherer formula:

$$D = \frac{0.9\lambda}{\beta\cos\theta} \ (1).$$

D is the grain size in a particular orientation, λ is the X-ray wavelength, θ is the diffraction angle corresponding to the particular orientation, β is the width at half maximum intensity (FWHM) of the peak.

Table 1 shows the evolution of particle size with the molarity. The results indicated that the crystal quality of ZnO thin film was significantly improved with the increasing in molar concentration.
We could have more crystal quality information by use this formula [18]:

$$\delta = \frac{1}{D^2} \ \ (2).$$

With D is the average grain size. The dislocation density is the length of dislocation lines per unit volume of the crystal. Larger D and smaller δ values mean better crystallization of the films. Dislocation densities exhibit a decrease with increasing molar concentration, which indicates that the high molar concentration reduced the crystal lattice imperfections. The calculated c parameters were found to be 0.5211, 0.5201, 0.5198, and 0.5195 nm when the molar concentration varied from 0.05 M to 0.2M, compared to 0.5206 for a powder sample. The c parameter values decrease with molar concentration. This defect is related to the stress increases in the plane of the substrate surface.

The stress in the plane of the substrate surface, the c-axis strain (ε_{zz}) values has been calculated using the following equation [19]:

$$\varepsilon_{zz} = \frac{c-c_0}{c_0} \times 100 \ . \ (3)$$

where c is the lattice parameter of the strained films calculated from the X ray diffraction data and c_0 is the lattice parameter of bulk ZnO. Figure 2 shows the evolution of strain against the molar concentration (C).The strain is reduced when C increases.

For 0.05M the stress becomes positive ($\varepsilon_{zz}>0$) suggesting that the film is subjected to tensile stress in the plane of the substrate surface, and to compressive stress for the 0.1M, 0.15M and 0.2M concentrate samples.

Table 1: The particle size and dislocation with different precursor concentrations

Molar concentration (M)	2θ (degree) of (002)	FWHM (degree)	Crystallite size D (nm)	$\delta \times 10^{-3}$ (nm^{-2})
0.05	34.40	0.82	9.95	10,1007
0.1	34.47	0.30	27.40	1,3319
0.2	34.51	0.25	32.35	0,9496

In thin films, strains originate mainly from the mismatch between the polycrystalline film and the amorphous substrate and/or from the difference in the thermal expansion coefficients of the film and the substrate [20] The external stress parallel to surface of film were calculated from the DRX results using the following equation [21]:

(4) $\qquad \sigma = \left(2C^2{}_{13} - \dfrac{(C_{11}+C_{12})C_{33}}{2C_{13}} \right) \varepsilon_{zz}$

Where Cii are the elastic constants of ZnO bulk , its values are;

C_{11}= 208.8 GPa, C_{12} = 119.7 GPa, C_{13} = 104.2 GPa, C_{33}^{couche}= 213.8 GPa.

Table 2 shows the external stress with different molar concentrations. At 0.05 M the external stress was compressive, and became tensile for the three other concentrations, indicating a relaxation of the structure with the increase of the grain's size.
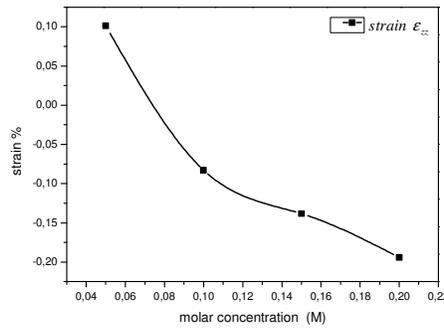

Figure 2: Evolution of strain vs the molar concentration

Molar concentration(M)	σ(GPa)
0.05	-23,6077906
0.1	19,31523402
0.15	32,25406444
0.2	45,28236113

Table 2: The external stress with different precursor concentrations

3.2. Morphological properties.

Fig 3 and 4 show the evolution of the grain size and the 2D. AFM surface morphology as a function of Figure 3 shows that increasing concentration influences the size grain. The grain present the spheres shape with uniform and homogenous distribution on the surface. It when increasing the molarity, a more random distribution of the grains on the surface is observed, which lead to a higher roughness. It is also observed that the particles agglomerated to form a porous structure.

The size measures of the particles from the AFM surface images are 13.3nm, 21.5nm, 44.9nm for molar concentration 0.05, 0.1and 0.2 M respectively. These values are higher than the values

calculated from XRD data. This could be explained by the fact that XRD data is an average over a large area (few mm^2), where AFM gives information about a micrometric area.

Fig 5 shows the AFM images 3D of ZnO thin films, the grains are orthogonal to the film surface indicating that the film grows perpendicularly to the substrate. The fig 6 shows the average surface roughness (Rms). The Rms varies from 8.34 nm to 20.54 nm when molar concentration increases from 0.05 M to 0.2M. This evolution of the surface roughness is as a result of the grain size increasing.
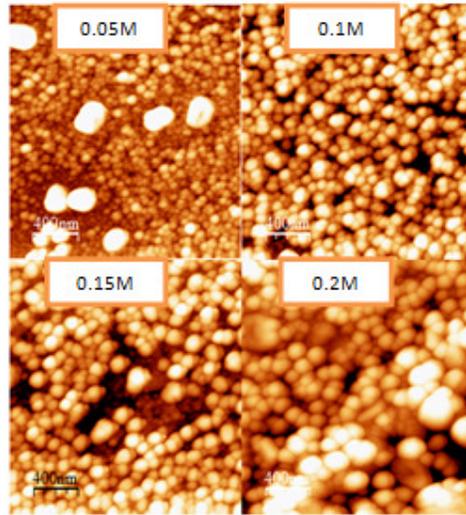
Figure3: AFM images 2D of ZnO thin film in different molar concentration
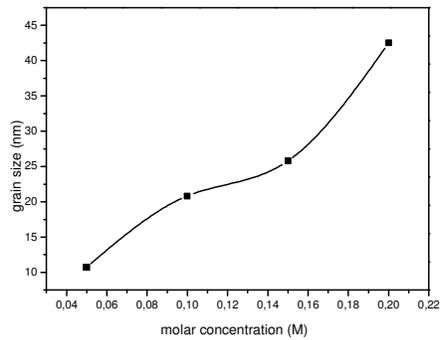

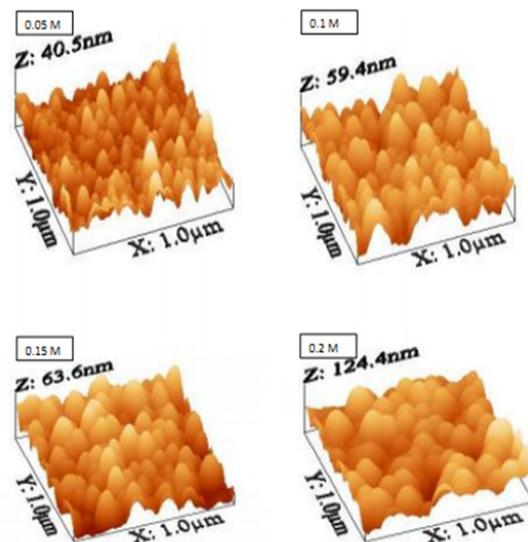Figure 4: Evolution of the grain size against the molar concentration

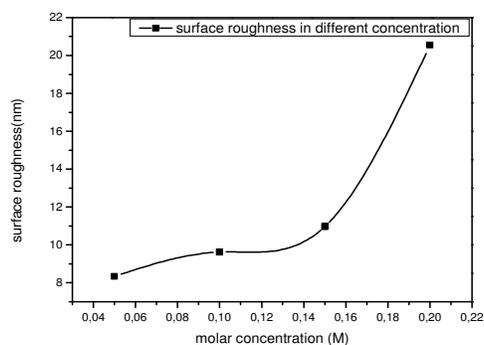Figure 1: The AFM images 3D of ZnO thin films in different molar concentration

Figure 6: Evolution of RMS according the molar concentration

3.3. FTIR

The FTIR analysis of ZnO thin film is shown in fig 7.The shoulder observed at 3556 cm^{-1} in all samples corresponds to the O-H moiety emanating from water [22].The very smalls peak for N-H stretching at 2940 cm^{-1} and 2450 cm^{-1}. The last peak illustrates the Zn-O at 500 - 400 cm^{-1} [23].

3.4. Raman

Raman spectra of the films were taken in order to confirm the presence of the Wurtzite phase in the ZnO thin films.

ZnO in the hexagonal structures with C_{6v}^4 symmetry each unit cell has 4 atoms and occupies 2b sites of symmetry. The group theory predicts eight sets of phonon normal modes at the Γ point, namely, 1A1 + 1E1 +2B1 +2E2[24].

Figure 8 shows a dominate mode centered at $437cm^{-1}$ which shifted to , the red shift ($2cm^{-1}$) for molar concentration of 0.15M. All samples present a peak with strong intensity corresponding to E2 (H)[25],E2(H) mode involving mainly Zn motion, which corresponds to band characteristic of Wurtzite phase the lowest E1(LO) for all the sample appears around 582 cm^{-1}. The high intensity of the E2 mode and lowest E1 (LO) mode indicate the higher quality of crystal in different concentrations.
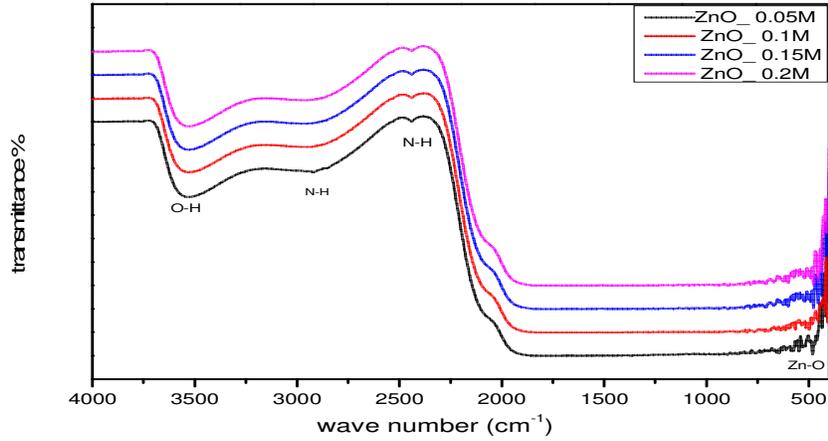

Figure7: The FTIR analysis of ZnO thin film synthesized with different molar concentrations
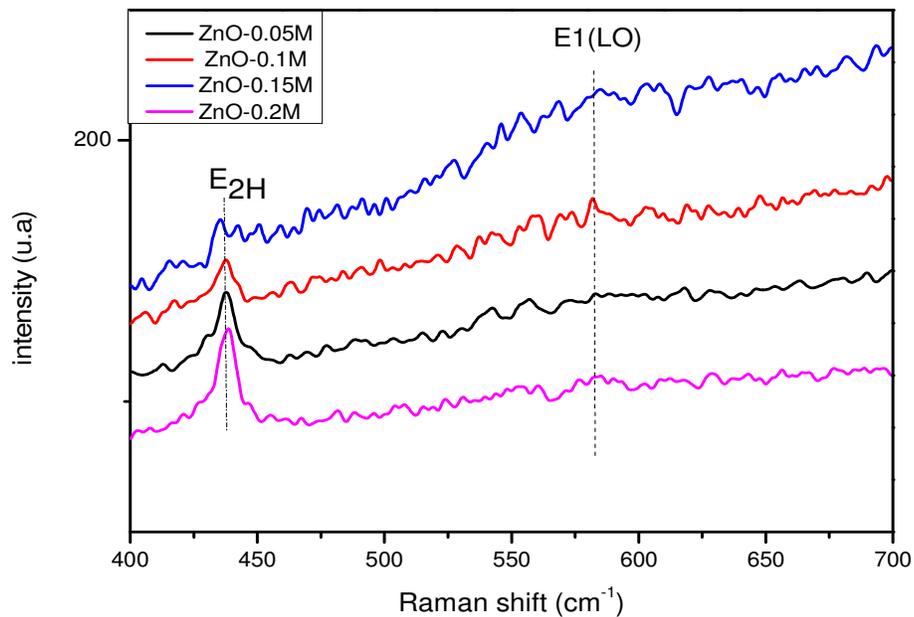

Figure 8: Raman spectra of ZnO prepared by spray pyrolysis with different molar concentrations

3.5. Optical properties.

3.5.1. Transmission

The optical transmission curves of ZnO thin films recorded as a function of wavelength in the range of 200 nm to 1200nm are shown in fig9.

All the films are mostly transparent in the visible region. However, the transmission goes down from 93% to 73% when the concentration increased from 0.05 M to 0.2M.All the films are highly absorbent in UV. The reduction of transmittance at higher molar concentration may be attributed to the increased scattering of photons by increase of the roughness of the surface morphology.

All the samples show a sharp absorption edge near to 375 nm in the UV region. This absorption edge was found to have a red shift when increasing the molarity.

The optical band gap was determined using method of Tauc [26];

$$(ah\nu)^2 = C(h\nu - Eg), (5)$$

C is a constant; $h\nu$ is the photon energy and Eg is the optical band gap. The optical absorption coefficient (a) was calculated using the following equation:

$$a = -\frac{\ln(T)}{D} \quad (6)$$

were the normalized transmission T was obtained from optical transmission spectra which has been normalized to the highest measured values by setting it to 100% , D the diameters values of the crystal
Table 3 shows the values of the energy band gap of ZnO thin films grows in different molar concentration of precursors.

The value of the optical band gap is obtained by linearly extrapolating the linear portion to a=0 .

With increasing in molar concentration from 0.05M to 0.2M the energy band gap decreased from 3,64 to 3,16 eV, the decreased in band gap energy with increasing in molar concentration could be due to increase in carrier concentration and decrease in strain values. It has been demonstrated earlier the correlation between the direct band gap and the compressive stress of the ZnO thin films [27].
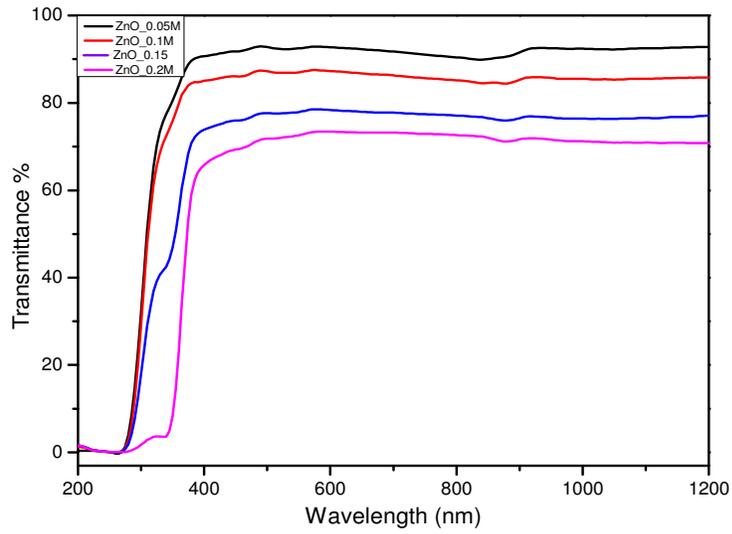
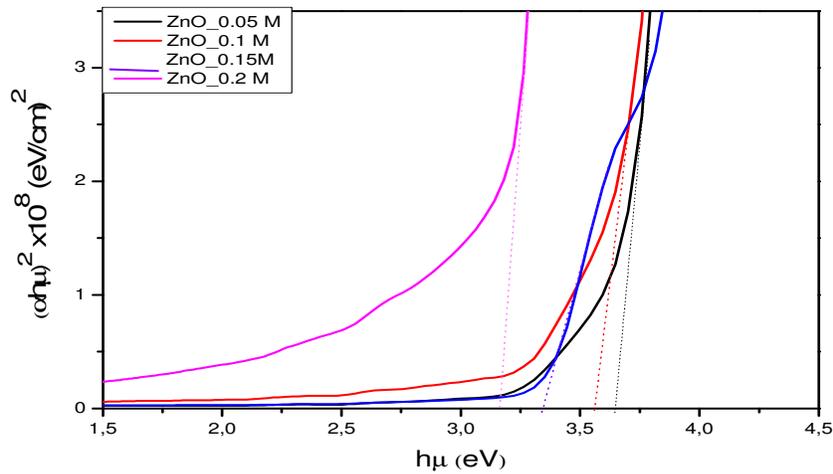Figure 9:Transmission spectra with different molar concentrations

Figure 10: (αhν)²vs hν plot of thin film with different molar concentrations

Table 3: Energy band gap in different molar concentration

Samplesmolar concentration (M)	0.05	0.1	0.15	0.2
Eg (eV)	3.64	3.56	3.34	3.15

3.5.2. Reflectance

These spectra show the excellent antireflection properties of the ZnO/Glass layer with different concentrations (fig 11). The total reflectivity had a low values in lower molar concentrations due to a lower values of RMS in the lower molar concentration this values increasing from 10% to 12%. Obviously, the increase of surface roughness causes the increase in scattering, reflection on the film surface[28], and thus the transmittance of the film decreases.

3.6.Photoluminescence proprieties.

PL spectra of ZnO thin films are shown in fig 12. It is clearly seen that the photoluminescence intensity depends strongly on the molar concentration of precursor.

It shows a very intense emission peaks around 378nm, the UV emission has been claimed to be due the near–band edge emission NBE or recombination of free exciton-exciton collision process[29], the intensity of this peaks was increased with the molar concentration , also the weak peaks appears in 432 nm only in the lower precursors concentration 0.05M and 0.1M attributed of the presence of defects in this films, this results confirm the next results obtained in DRX spectra , and RAMAN spectra, when the improvement of the quality the crystal is investigated with the increasing of precursor concentration.
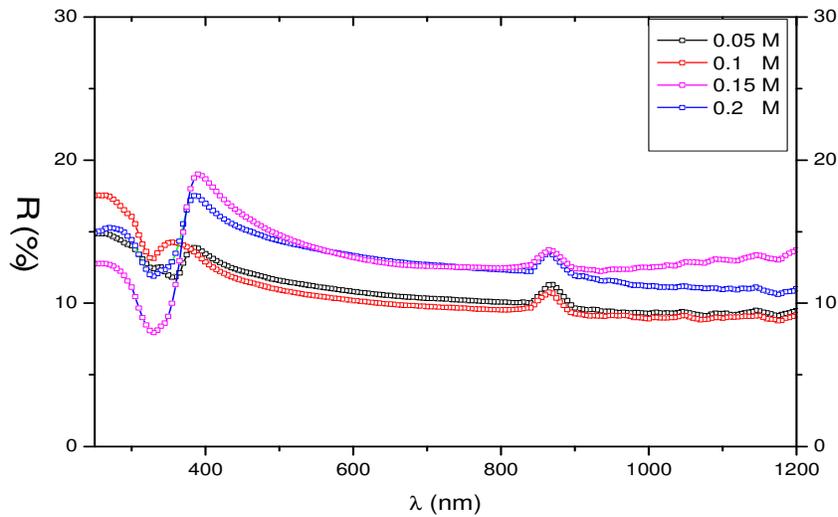

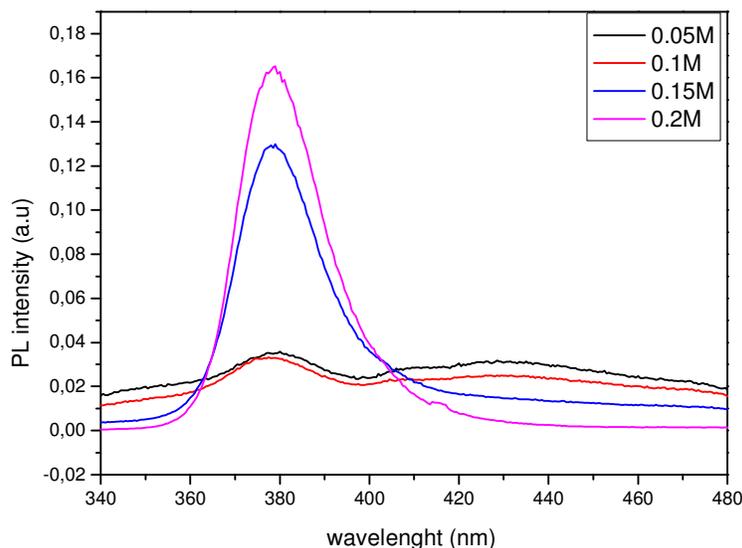Figure 11:Total reflectivity of ZnO thin film growth in different molar concentrations

Figure 12: The PL spectrum of the ZnO thin film

7. CONCLUSION

In the present work, ZnO thin films were deposited by a simple and cheap deposition technique, namely spray pyrolysis. The X-ray diffraction showed that films have a polycrystalline structure with an orientation according to the c-axis corresponding to the (002) crystallographic orientation. The intensity of this peak and grain size were increasing , With the increase in molar concentration .The Raman result confirms the high quality of the crystal. The FTIR shows the existence of the Zn-O band between 500-400 cm^{-1} and the O-H moiety emanating from water in 3556 cm^{-1}.

The optical measurements have shown a decrease in the transmission T (%) with an increase in the molarity dueto the surface roughness. The band gap values were decreased from 3.64 eV to 3.15 eV as molarity of the solution increased for 0.05 M to 0.2 M. The main results are a decrease of surface reflectivity from 12% to about 10%.

The PL spectra have shown the existence of different defects in the visible range of ZnO thin film of the lower molar concentration 0.05M and 0.1M.RAMAN spectra confirm the progress of the quality of the films in the higher precursor concentration 0.15M and 0.2M.

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