# Molarities effect on structural and optical properties of ZnO prepared by spray pyrolysis

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**Abstract**
In these paper describes the ZnO thin film deposition by spray pyrolysis technique with different molarities ( 0.05 , 0.1 , 0.15 , and 0.2 ). The studies were focused on the effect of variation of aqueous solution molarity on physical of the ZnO thin films. Increasing of solution molarity caused the Decrease the smoothing and homogeneity of the films and shape factor , further it exhibits increase in intensity of the peak preferred orientation (002) plane ( from about 1700 to 4000 ) , integral breadth ( from 0.015 to 0.016 ) deg. Decreased transmission especially in the NIR region at 800 nm (from 90% to 55%) and band gap (from 3.12 to 3.02) eV. It is more suitable for acoustic applications, due to the scattering effect recorded.

**Key wards:** ZnO thin films, molarities effect, spray pyrolysis, structure properties and optical properties, Integral Breadth ,shape factor, energy gap.

## 1. Introduction

Zinc oxide is a versatile semiconductor which has attracted considerable attention because of its catalytic, electrical and optical properties. These properyies find wide technological applications. For instant, ZnO based materials have been used in solar cells, transparent conducting films, ultraviolet protection films, chemical sensors, varistors, light emitting diodes, laser diodes, etc. [1, 2]. Different techniques were used to prepare ZnO thin films such as pulsed laser deposition [3,4,5], molecular- beam epitaxy, sputtering, vacuum evaporation, chemical bath deposition [6,7,8], successive ionic laser adsorption and reaction (SILAR), and chemical spray pyrolysis(CSP) technique [9,10,2,11]. Out of these, chemical spray pyrolysis (CSP) is an inexpensive low technology and safe method for producing highly transparent and conductive zinc oxide film.

## 2. Experimental

The substrate used for deposits of ZnO thin films in this work is the microscopic glass slides (boro-silicate glass) with dimensions (76 × 21× 1) mm . It was cleaned by diluted HF, ethanol and distilled water, then dried and wept by optical cleaning paper. The ZnO films were prepared by using an aqueous solution of Zinc Chloride ($ZnCl_2$ $2H_2O$) with different molarities (0.05, 0.1, 0.15, 0.2) M. The aqueous solution was diluted in distilled water and mixed by a magnetic stirrer, and in each deposition the volume used was (100 ml) . The ZnO thin films were deposited by spray pyrolysis technique. The deposition method involves the decomposition of an aqueous solution of zinc chloride. The spray solution of different molarities were sprayed onto heated substrates held at (573 ± 5 $^oK$) . Compressed air was used as a gas carrier and it was fed with the solution into a spray nozzle at a pre-adjusted constant atomization pressure.The nozzle-to-substrate distance was 25 cm and the spraying period was (5 s) with flow rate as ( 3 ml/min ) . Aluminum electrodes were evaporated on the surface of ZnO thin films using thermal evaporation equipment through a mask giving sensitive area (0.5×0.5) $cm^2$. Film thickness is measured by optical interferometer method. The method is based on interference of the light beam reflection from thin film surface and substrate bottom. He – Ne Laser (632 nm) is used and the thickness is determined using the formula:-

$$d = \frac{\Delta x}{x}.\frac{\lambda}{2} \qquad (1)$$

Where: x is fringe width, $\Delta x$ is the distance between two fringes and $\lambda$ is the wave length of laser light.

## 3. Measurement

### 3.1. Structure measurement

The topography of the ZnO surface was inspected with optical transmission – microscope (OTM) type Nicon – 73346 of 270X. A digital camera was mounted on the microscope and connected to the computer in order to store surface image .To determine the nature of the growth films and the structural characteristics of ZnO films, X – ray diffraction measurement has been done and compared with the ASTM (American Society of Testing Materials) cards, using Philips PW 1840 X – ray diffractometer of $\lambda$ = 1.54 $^{\circ}A$ from Cu - Kα. The average grain size (GS) of the polycrystalline material can be calculated from the X – ray spectrum by means of Full Width at Half Maximum (FWHM) method (Scherrer relation) [12].

$$GS = \frac{A\lambda}{\Delta\theta\cos\theta} \qquad (2)$$

Where $\Delta\theta$ is the full – width at half maximum of the XRD peak appearing at the diffraction angle $\theta$, A the shape factor, the value of which depends on the crystalline shape, and generally it is 1.The Integral Breadth ( β ) is given by :[13]

$\beta$ = Area / $I_o$ (3)

Where: Area = area under peak.

$I_o$ = maximum intensity. The shape factor of the line profile resulting from the XRD patterns could be calculated from the relation: [13]:

$\Phi = \Delta / \beta$ (4)

The number of crystallite layer ($N_\ell$) which could be calculated due to the percolation theory, and it depends on the film thickness (t) as the relation:

$t = g * N_\ell$ (5)

Where: g is a mean crystallite size or average grain size [14].

### 3.2. Optical Measurements

UV-VIS, Phoenix-2000V device was used to record the optical transmission for CdO/glass thin films before and after annealing in the range (300 – 1100 nm). The data from transmission spectrum can be used in the calculation of the absorption coefficient (α) for CdS films, according to the following equation [15]:

$$\alpha = \frac{1}{d}\ln\frac{1}{T} \qquad (6)$$

Where d is the thickness of thin film, and T is the transmission. In the direct band gap structure or direct transition semiconductors (present case), the absorption coefficient and optical band gap (Eg) are related by [16].

$$\alpha = (h\upsilon - Eg)^{1/2} \qquad (7)$$

Where h is Plank's constant and υ is the frequency of the incident photon.

## 4. Results

### 4.1. Structures properties

Surface topography was studied by means of reflection microscope. Figure (1) shows the influence of solution molarity on the homogeneity and smoothness of the films. From these photos it is clear that the smoothness and homogeneous of the films are decreasing with increasing the aqueous solution molarity . That the surface roughness is increased with thickness increasing, this result is in a good agreement with those in the literature [17] The X-ray diffraction patterns of ZnO thin film deposited at 573 K are shown in figure (2) for different molarities. Polycrystalline ZnO thin films show a preferred orientation in the (002) direction perpendicular to the substrate. This plane is strongly dependent on the deposition conditions; diffraction patterns preliminary recorded on the film indicated that all investigated films were polycrystalline. Diffraction pattern was recorded for a range of 2θ from 20$^o$ to 80$^o$ at

$2^{o}$glancing angle. The film was crystallized in the wurtzite phase and presents a preferential orientation along the c-axis , the strongest peak observed at $2\theta = 34.43^{o}$ ( d = 0.260 nm ), the (100) , (101) ,(110) and (004) peaks were also observed at $2\theta = (31.83^{o})$ , $(36.489^{o})$, $(57.15^{o})$ and $(72.66^{o})$respectively with lower intensity than that of (002) peak .These results are close to those reported in the literature [10] . Table (1) shows the effect of solution molarity on the structure parameters evaluated from the diffrograms shown in figure (1). The integral breadth of the samples were obtained from the XRD pattern sheets and using the relation (3) , our results indicate that increasing the molarity leads to increasing in the integral breadth , they are recorded in the table (1)below . The shape factor was calculated using the relation (4), the results show that the shape factor had decreased with increasing molarity of the aqueous solution, and they decreased with increasing film thickness**.** The average grain size was calculated using Scherrer's formula (2), the valus of average grain size listed in the Table (1) show increases with molarity of the solution and such increment will represent an increasing of the deposited films thickness. Increasing of solution molarity are cause to increase the average grain size, as shown in figure (3). It may be due to the combined effect of increase in Zn incorporation, increase in growth rate and reorientation effect. The number of layers was evaluated by using the relation (5) . In table (1) the variation of layer number varies with molarity in a random way. It is thought that the substrate temperature varies and the quantity of drops plays a great role in these random changes.

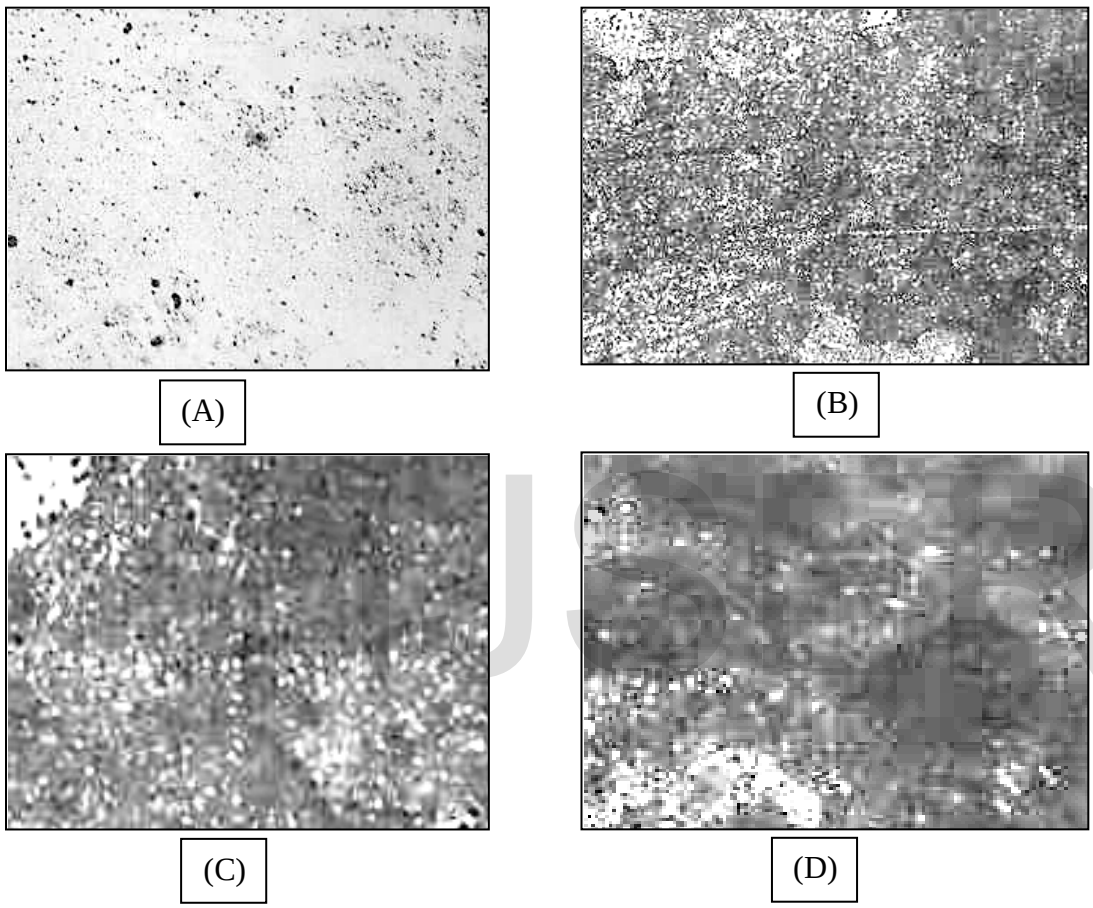



Fig. (1) Photos of ZnO thin film surface prepared at different molarities, (a) 0.2M , (b) 0.15M , (c) 0.1M and (d) 0.05M .

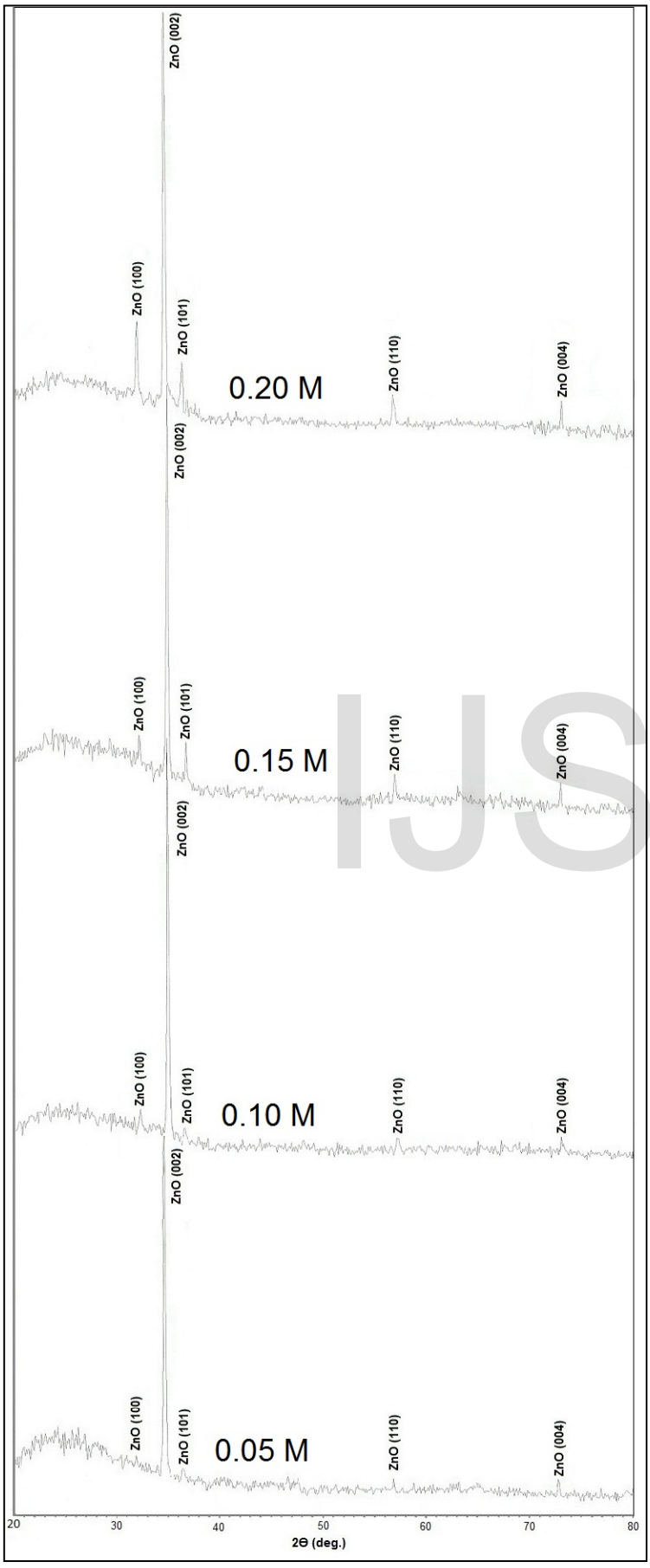



Fig. (2) XRD patterns of ZnO thin films prepared at different molarities , (a) 0.2M , (b) 0.15M , (c) 0.1M and (d) 0.05M .

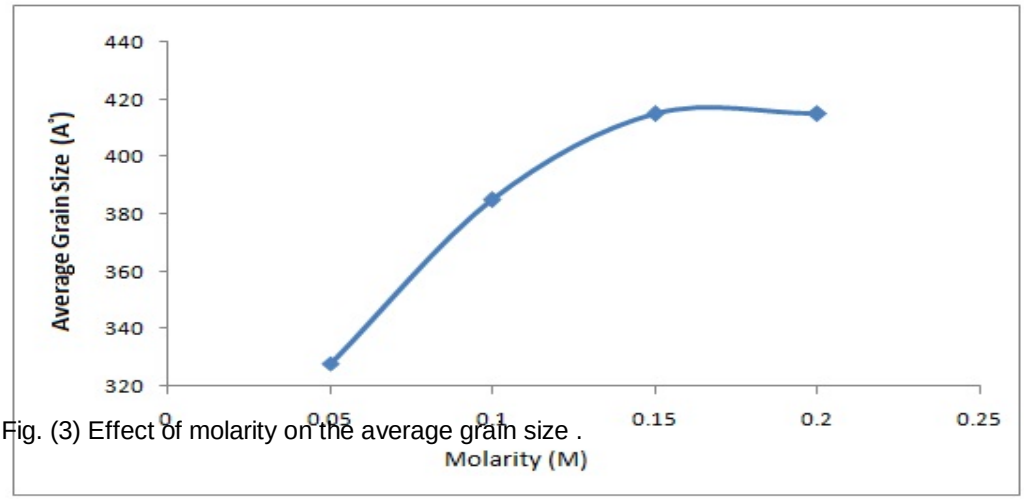



Fig. (3) Effect of molarity on the average grain size .

Table (1) effect of solution molarity on the structure parameters.

| Φ | $_{(deg)}\beta$ | $N_L$ | g (A°) | $_{(deg)}\Delta$ | $d_{X\text{-}Ray}$ (A°) | $d_{ASTM}$ (A°) | $2\theta_{X\text{-}Ray}$ | $2\theta_{ASTM}$ | orientation | sample |
|---|---|---|---|---|---|---|---|---|---|---|
| 0.021 | 10 | 11 | 378 | 0.210 | 2.810 | 2.810 | 31.835 | 31.819 | (100) | |
| 0.016 | 15.5 | 13 | 328 | 0.241 | 2.600 | 2.610 | 34.460 | 34.330 | (002) | |
| 0.016 | 13.5 | 11 | 376 | 0.209 | 2.465 | 2.460 | 36.489 | 36.494 | (101) | |
| 0.022 | 9.5 | 12 | 348 | 0.209 | 1.614 | 1.610 | 57.150 | 57.166 | (110) | **0.2** |
| 0.020 | 10.5 | 13 | 318 | 0.209 | 1.298 | 1.300 | 72.660 | 72.672 | (004) | |
| 0.022 | 9.0 | 8 | 446 | 0.193 | 2.809 | 2.810 | 31.829 | 31.819 | (100) | |
| 0.016 | 14.5 | 10 | 385 | 0.225 | 2.609 | 2.610 | 34.449 | 34.330 | (002) | |
| 0.015 | 12.5 | 8 | 452 | 0.193 | 2.459 | 2.460 | 36.478 | 36.494 | (101) | **0.15** |
| 0.023 | 8.5 | 8 | 488 | 0.193 | 1.608 | 1.610 | 57.139 | 57.166 | (110) | |
| 0.020 | 9.5 | 7 | 533 | 0.193 | 1.310 | 1.300 | 72.649 | 72.672 | (004) | |
| 0.020 | 9.0 | 7 | 487 | 0.177 | 2.807 | 2.810 | 31.813 | 31.819 | (100) | |
| 0.014 | 14.5 | 8 | 415 | 0.209 | 2.601 | 2.610 | 34.438 | 34.330 | (002) | |
| 0.014 | 12.5 | 7 | 493 | 0.177 | 2.448 | 2.460 | 36.467 | 36.494 | (101) | |
| 0.021 | 8.5 | 6 | 532 | 0.177 | 1.604 | 1.610 | 57.128 | 57.166 | (110) | **0.1** |
| 0.019 | 9.5 | 6 | 582 | 0.177 | 1.305 | 1.300 | 72.638 | 72.672 | (004) | |
| 0.018 | 9.0 | 5 | 535 | 0.161 | 2.810 | 2.810 | 31.811 | 31.819 | (100) | |
| 0.015 | 14.5 | 7 | 414 | 0.209 | 2.601 | 2.610 | 34.437 | 34.330 | (002) | |
| 0.014 | 12.5 | 6 | 492 | 0.177 | 2.467 | 2.460 | 36.456 | 36.494 | (101) | |
| 0.021 | 8.5 | 5 | 532 | 0.177 | 1.614 | 1.610 | 57.117 | 57.166 | (110) | **0.05** |
| 0.019 | 9.5 | 5 | 581 | 0.177 | 1.300 | 1.300 | 72.670 | 72.672 | (004) | |

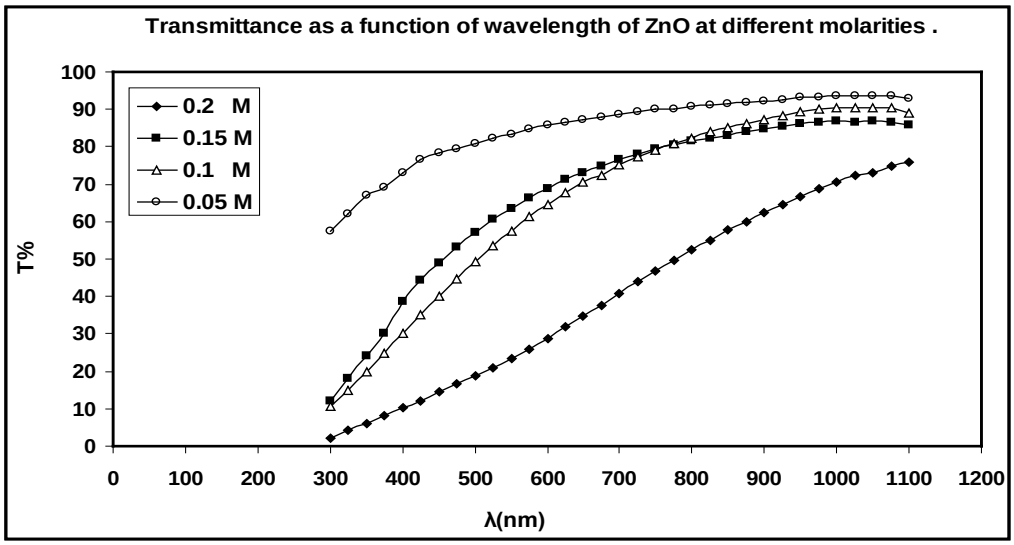


**4.2. Optical properties**

Figure (3) shows the optical transmittance and absorption spectrum of ZnO thin films in the wavelength range from [(300) to (1100) nm] . The films are not highly transparent in the visible range of the electromagnetic spectrum with the maximum value of about (90%) recorded for film with lower molarity (0.05M), and the transmittance decreased with increasing molarities . In returning to figure (1) where the smoothing of the films decreased with molarity increasing , one could attribute the low transmission to the scattering that takes place at the surface , and when increases with surface roughness . Figure (4) shows the absorption coefficient (α) of ZnO films with different molarities, determined from transmittance measurements using equation (6). From this figure, the absorption coefficient of ZnO thin films decreased sharply in the UV / VIS boundary and depends directly on the cut-off wavelength, and then decreased gradually in the visible region because it is inversely proportional to the transmittance. The optical energy gap was determined by using the absorption coefficient values, figure (5) shows the plot of $(\alpha h\nu)^2$ vs. hν . The energy gap ($E_g$) was estimated by assuming a direct transition between valance and conduction bands from the relation (7) : Energy gap is determined by extrapolating the straight line of the spectrum to αhν = 0 , from this drawing , the energy gap was narrowing with increasing molarity , and

their values were ( 3.12 to 3.02 ) eV . Increasing molarity causes increase in the density of charge atoms and then every electron is effectively surrounded by an exchange and correlating hole that lowers the energy of the electron, and the conduction band is shifted downwards.

For ZnO films deposited at higher substrate temperature (above 300$^{o}$C) then these films was polar semiconductors and they displace off charge from one atomic species to the other. Then the charged particles move in the crystal, they create a displacement polarization. An electron attracts the positively charged ions and repels the negatively charged ions, thus a cloud of positive charge surrounds an electron and the valance band holes are surrounded by negative charges. The increased molarities may cause increase of the charged atoms. The variation of energy gap with molarities is shown in figure (6). This figure shows that the increasing in molarity will decrease the energy gap (narrowing):



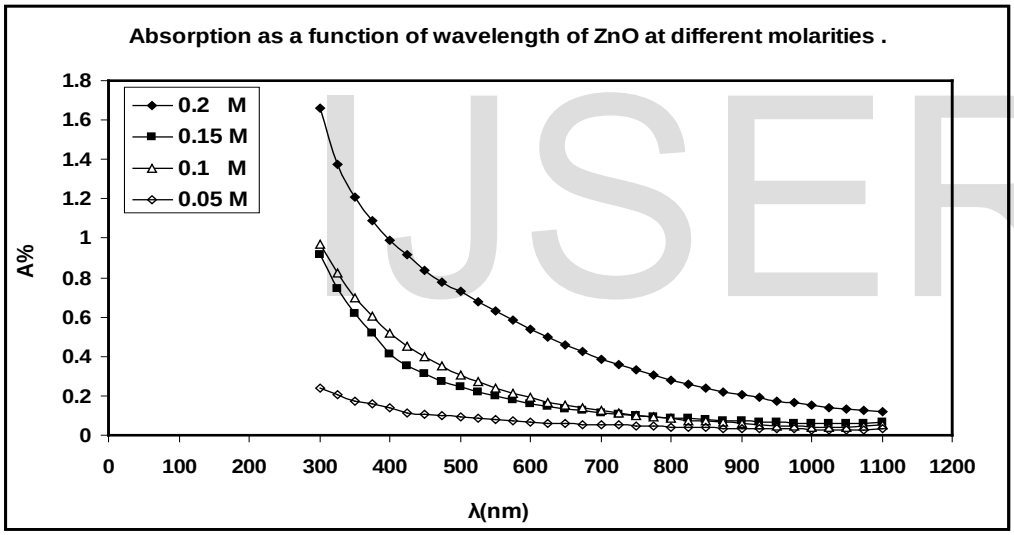




Fig. (4) transmittance and absorption spectrum of ZnO thin films prepared at different molarities .

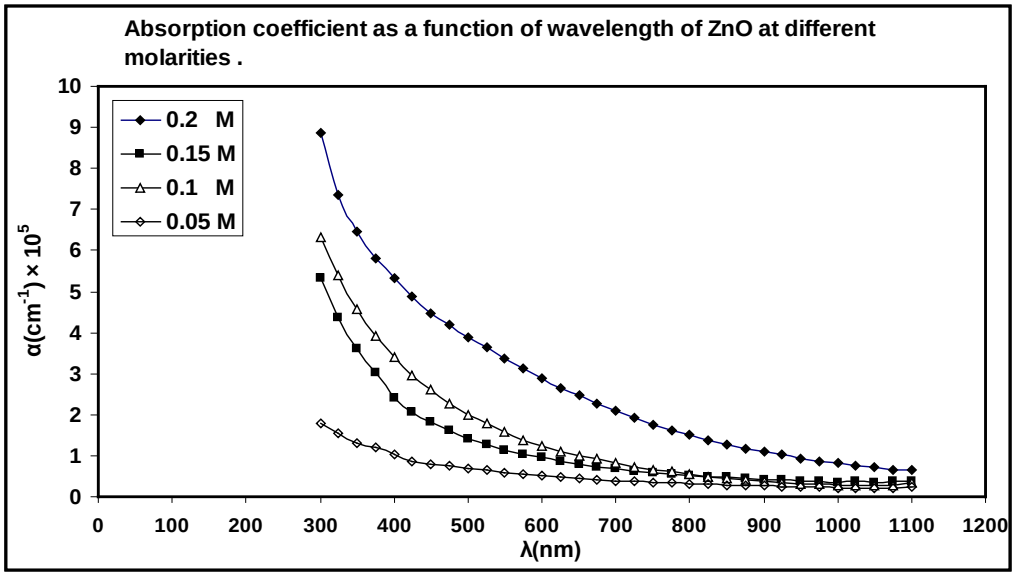



Fig.(5) Absorption coefficient as a function of wavelength of ZnO at different molarities .

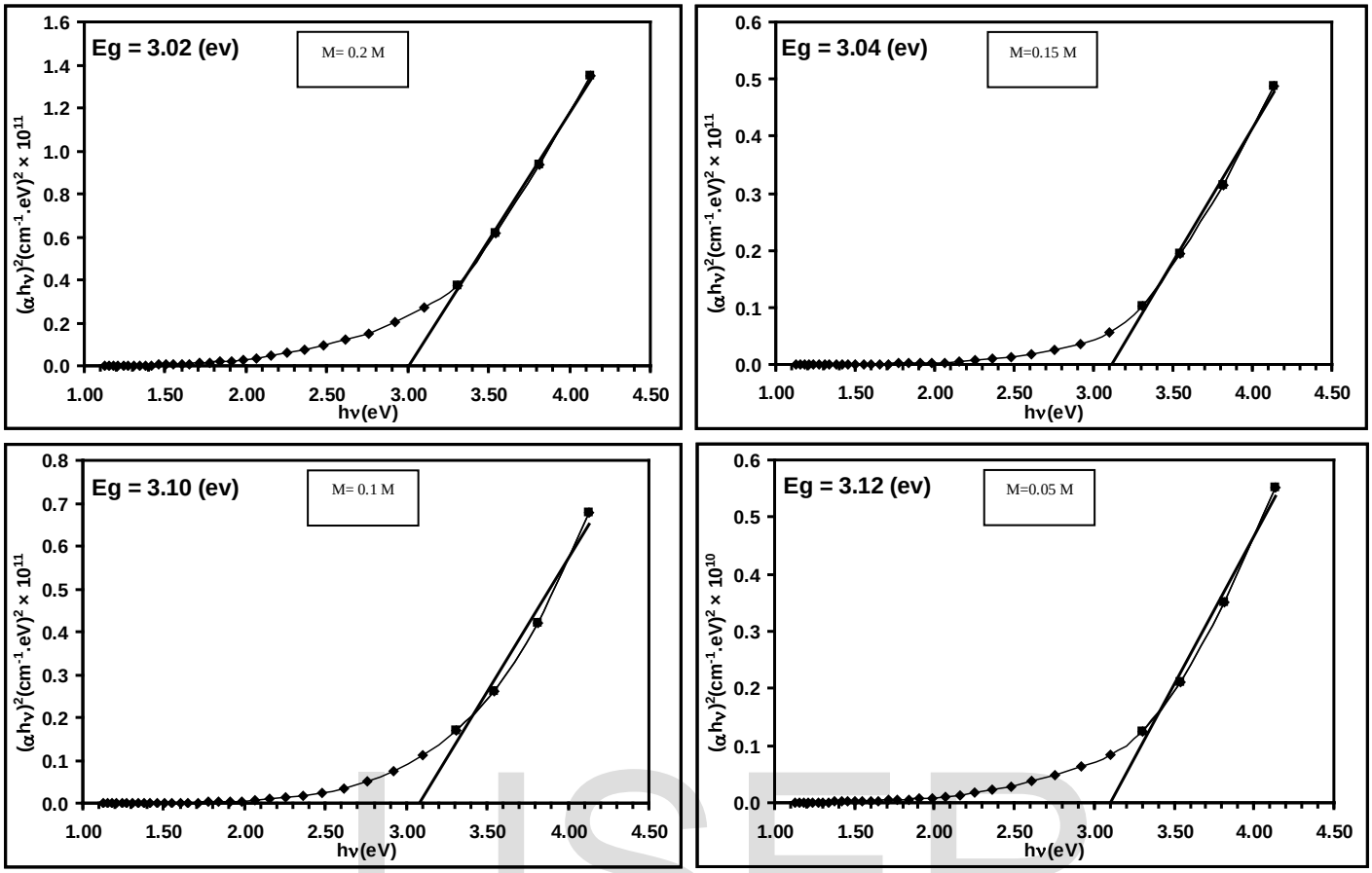



Fig. (6) Energy gap of ZnO thin film at different molarities, (a) 0.2M, (b) 0.15M, (c) 0.1M and (d) 0.05M.



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