



## Effect of molarity on the structural and optical properties of ZnO thin films deposit by CSP

**Nadir F. Habubi\*, Ziad M. Abood, Ahmed N. Algamel**

Department of Physics, College of Education, Al-Mustansiriyah University, Baghdad, Iraq

\*E-mail address: [nadirfadhil@uomustansiriyah.edu.iq](mailto:nadirfadhil@uomustansiriyah.edu.iq)

### ABSTRACT

ZnO thin films have been prepared by chemical spray pyrolysis technique CSP. XRD pattern reveals that the preferred orientation was varied with concentration, topography analysis was done by AFM micrograph which confirm the existence of nonstructural films. The optical properties was done by recorded the transmittance and absorbance which were affected by an increase in concentration. The values of optical energy gap obtained from Tauc relation were 3.17, 3.18 and 3.19 eV for 0.05, 0.1 and 0.5 M respectively. Urbach energy confirms the decrease in band tail as the concentration increase.

**Keywords:** ZnO, ZnO thin films, structural properties, optical properties, Urbach energy

### 1. INTRODUCTION

ZnO has been chosen to be one of the most used metal oxide in many applications due to its unique properties such as: high transparency and conductivity, chemical stability, wide band gap, non toxic material, strong piezoelectric effect, large exciton binding energy ( $\sim 60$  meV)<sup>[1-6]</sup>.

ZnO is used extensively as a component in many applications, solar cells<sup>[7]</sup>, organic light emitting diode<sup>[8]</sup>, plasma hydrogenated ZnO films<sup>[9]</sup>, transparent electrode<sup>[10]</sup>,

photodiodes<sup>[11]</sup>, photocatalysis<sup>[12]</sup>, optoelectronic<sup>[13]</sup>, nanostructured solar cell<sup>[14]</sup> gas sensor<sup>[15,16]</sup>, and diluted magnetic semiconductors for spintronix<sup>[17]</sup>.

Different growth methods were used to fabricate ZnO thin films ,including chemical bath deposition<sup>[18]</sup>, R F magnetron sputtering<sup>[19]</sup>, pulsed laser deposition<sup>[20]</sup>, dc magnetron sputtering<sup>[21]</sup>, electrodeposition<sup>[22]</sup>, molten salt method<sup>[23]</sup>, pulsed laser ablation in liquid<sup>[24]</sup>, and chemical spray pyrolysis<sup>[25]</sup>. This paper focused on the investigation of molarity variation effects on structural and optical properties of ZnO thin films prepared by chemical spray pyrolysis.

## **2. EXPERIMENTAL**

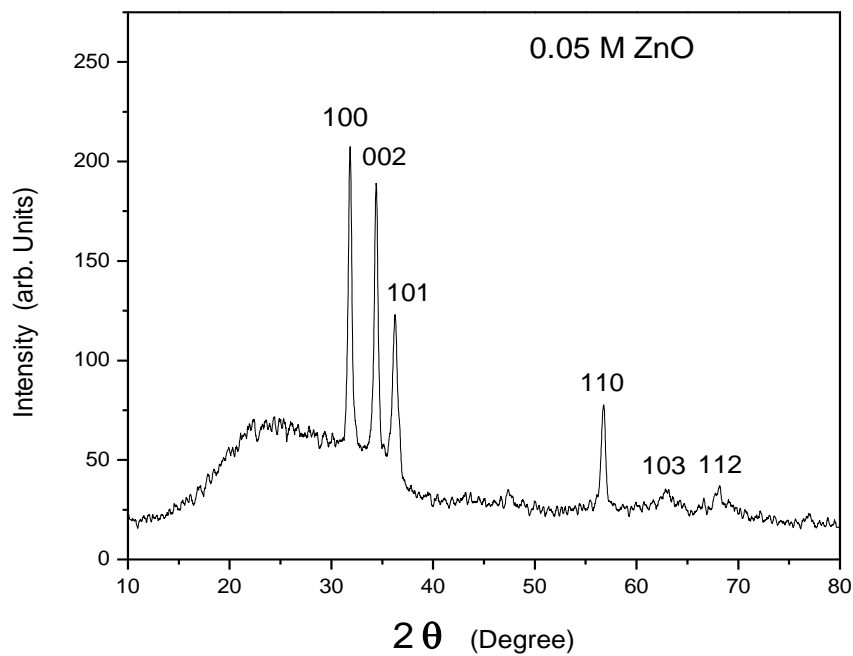
Zno thin films were prepared by chemical spray pyrolysis technique. Different molarties (0.05, 0.1, 0.15) M solution of zinc acetate was dissolved in re-distilled water with a few drops of acetic acid to improve the solubility of zinc acetate. This aqueous solution was sprayed on to glass substrate heated at 400 °C monitored by a temperature controller using chromel-alumel thermocouple.

After many repeated observations, we arrived at the following optimization conditions: solution flow rate was 5 ml/min , spraying cycle 10 S followed by 60 wait to avoid excessive cooling, distance between nozzle and substrate were  $28 \pm 1$  cm, Nitrogen gas was used as a carrier gas.

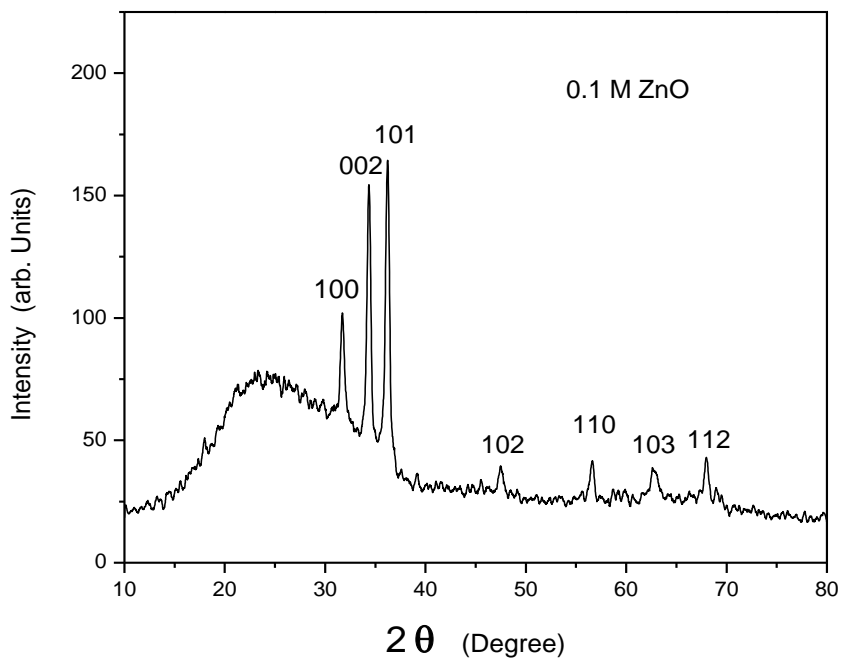
Structural characterization was carried by X-Ray Difffractometer (Shimadzu XRD 600 Japan) using  $K_{\alpha}$  radiation with the wavelength 1.541 Å. The morphology of the films was held by AFM (Digital instrument, Inc Nanoscope III and dimension 3100). Optical measurements were calculated using double beam spectrophotometer (Shimadzu UV Probe 1650 Japan) in the wavelength range (380-900) nm.

## **3. RESULTS AND DISCUSSION**

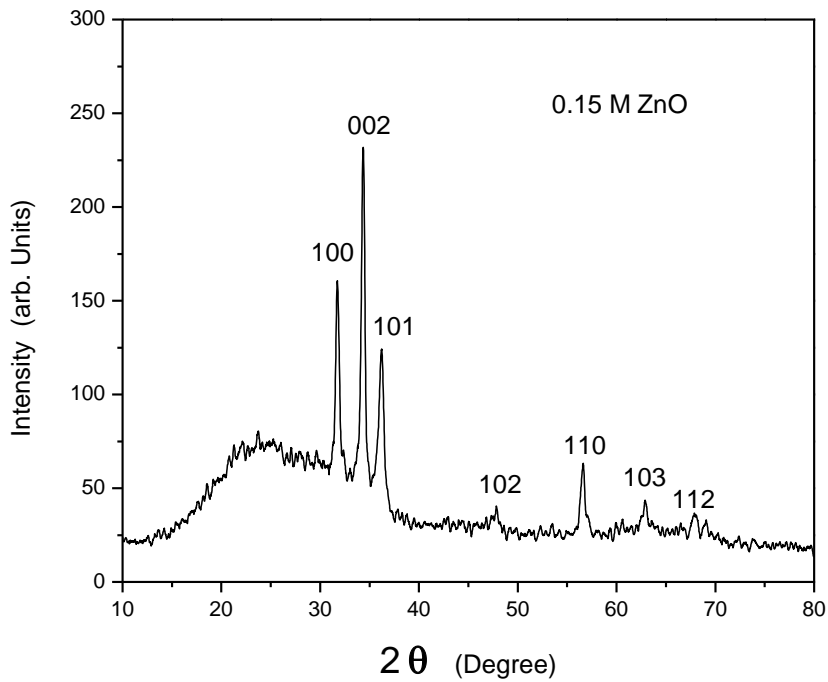
Figs. 1-3 represent the XRD pattern for the prepared ZnO with different molarties. All the films shows a hexagonal wurtzite structure which suit with (JCPDF card no. 36-1451) From these figures we can see that the preferred orientation was characterize with molarity these planes were (100), (101) and (200) for 0.05 M, 0.1 M and 0.15 N respectively. This may be related to the entropy solution when raising the concentration, the average solvation of species changes with the decrease of entropy therefore alternative orientation are possible due to slow growth formation which affected the lower surface energy<sup>[26]</sup>. The lattice parameters values obtained for different molarity are shown in Table 1 which were in good agreement with its bulk values. He average crystallite size was calculated using the Scherror formula<sup>[27]</sup> their values were shown in Table 1 indicating that the crystallite size increased via the increasing in concentration. The value was in the range of (20.60-22.63) nm which predict the existence of nanostructure. Tensile strain was calculated, their values were tabulated in Table 1which shows that strain value along c-axis orientation of ZnO thin films increase with the increase in concentration. Texture coefficient  $T_c$  along the preferred orientation of each pattern was calculated utilizing the equation of Barret and Massalski<sup>[28]</sup>.



**Fig. 1.** XRD pattern of 0.05 M ZnO thin film



**Fig. 2.** XRD pattern of 0.1 M ZnO thin film.

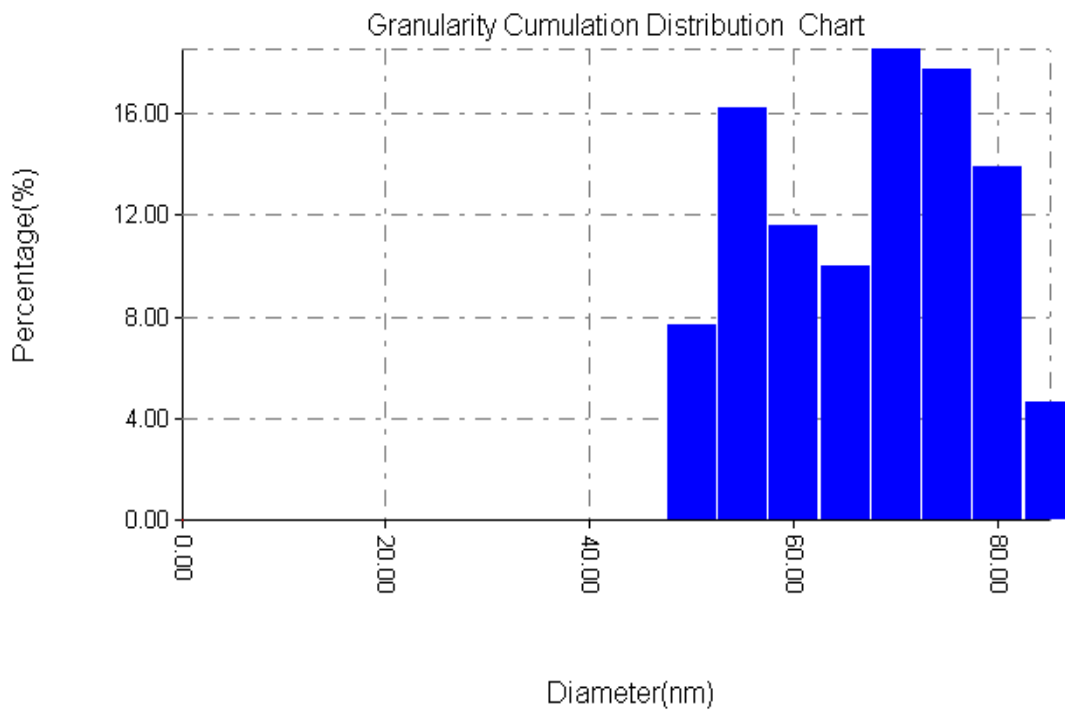
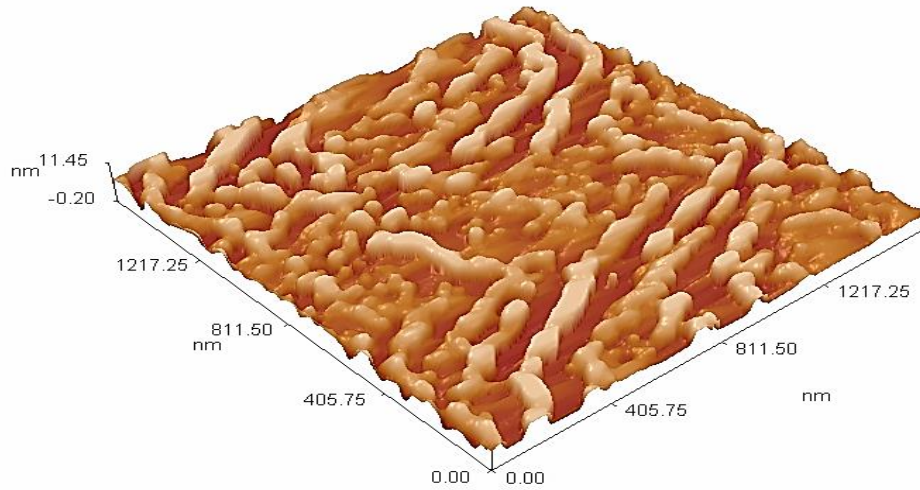


**Fig. 3.** XRD pattern of 0.15 M ZnO thin film.

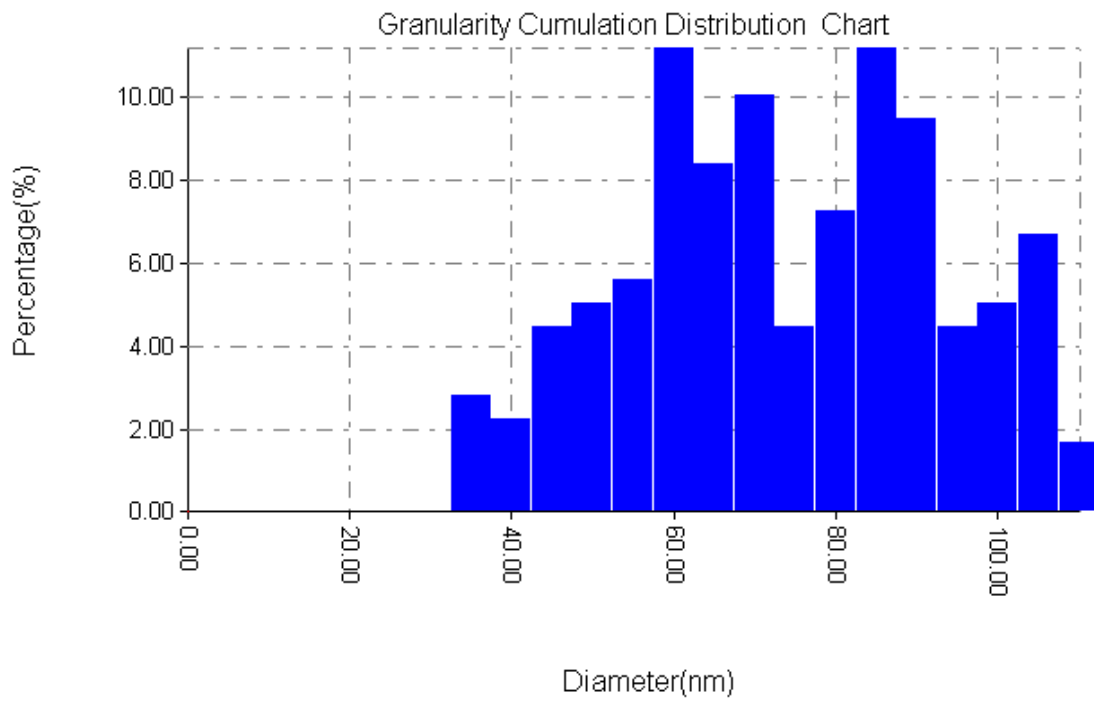
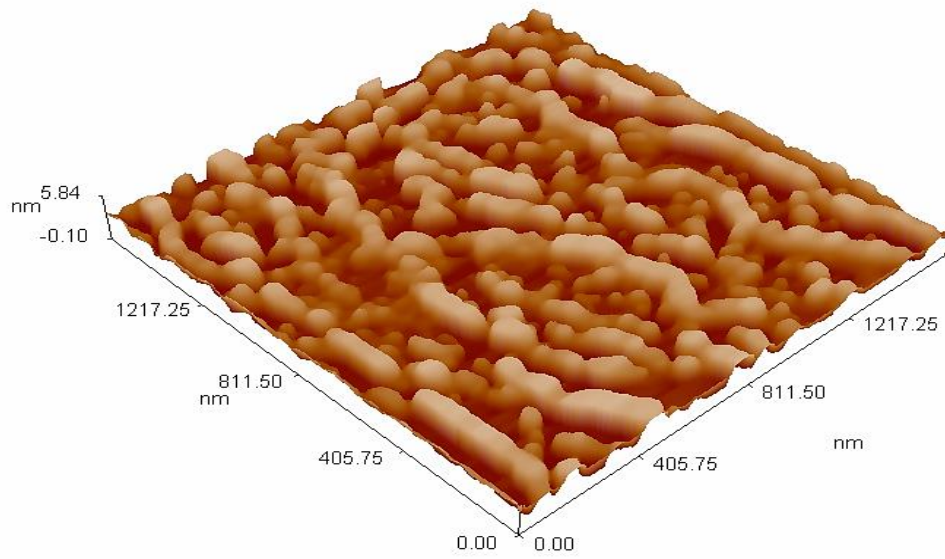
The increase in texture coefficients of the film with concentration refers to the large number of crystallites are oriented along the c-axis<sup>[29]</sup>. The dislocation density was also calculated via the inverse square of crystallite size<sup>[30]</sup> represents the defects of the film. These values were listed in Table 1 and show a tendency to decrease upon increase the concentration, this fact results in decreasing the lattice imperfection with molarity. The Number of crystallite size per unit is calculated and their value was shown in Table 1 indicating the decrease in no. of crystallite size upon increasing the concentration.

**Table 1.** Structural parameters.

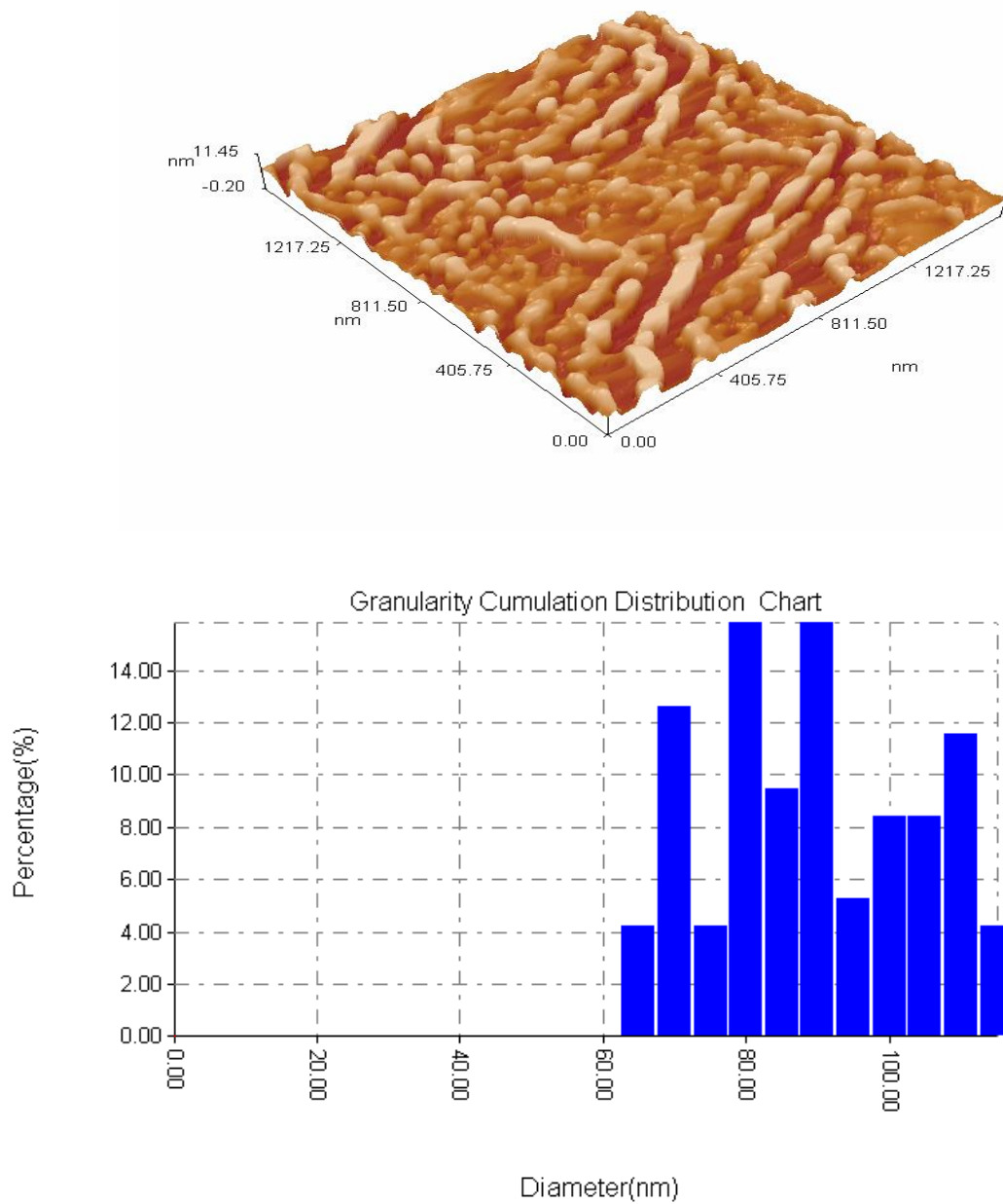
Molarity	$a_o$	$c_o$	<i>strain</i>	$D_{av}$	Dislocation density	No. of crystallite per unit area $\times 10^{12}$	$T_C$	hkl Preferred plane
0.05	3.242	5.209	0.0768	20.6	0.002356	3.43	1.977	100
0.1	3.252	5.215	0.1900	21.5	0.002160	3.01	1.574	101
0.15	3.250	5.217	0.2210	22.63	0.001950	2.58	2.826	002



(a)



(b)



(c)

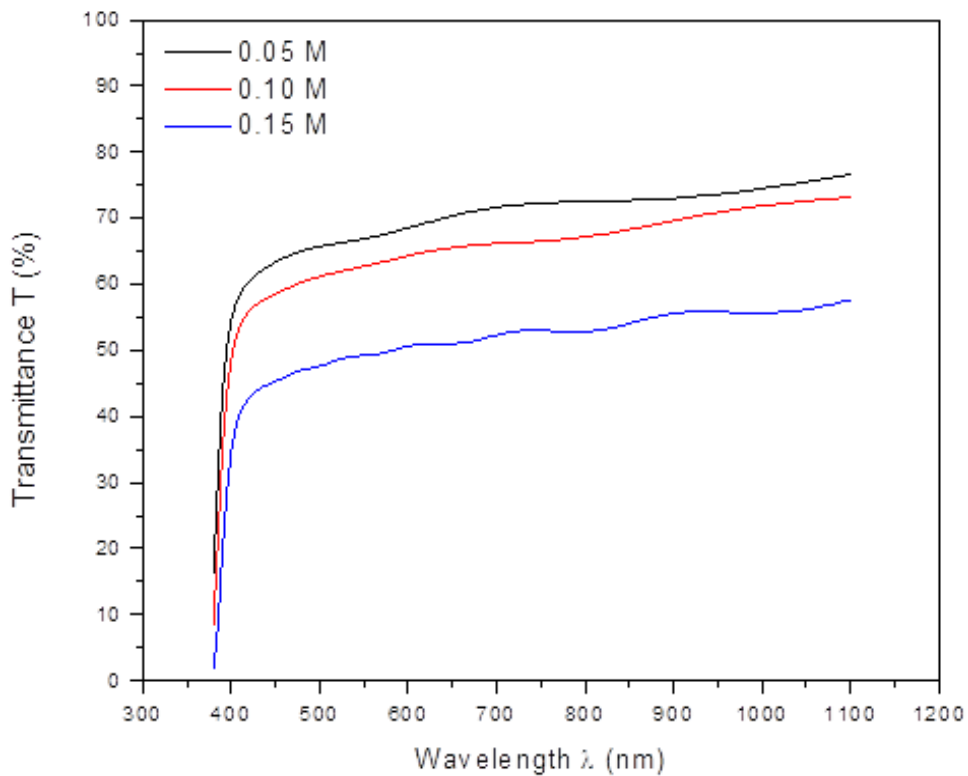
**Fig. 4.** AFM images and their distribution for ZnO thin film (a) 0.05 M, (b) 0.1 M and (c) 0.15 M.

**Table 2.** Surface roughness, RMS and estimated grain size.

Molarity	Surface roughness (nm)	RMS value (nm)	Average grain size (nm)
0.05	0.846	0.965	64.93
0.1	1.44	1.67	71.34
0.15	1.74	2.01	87.16

Figure 5 shows the optical transmittance in the visible – near infrared region for the deposited thin films with different concentrations. It is well evident from the figure that the transmittance decrease sharply near 380 nm, its value in the visible region remains nearly constant, we can also see from the figure a decrease in transmittance as the molarity increase.

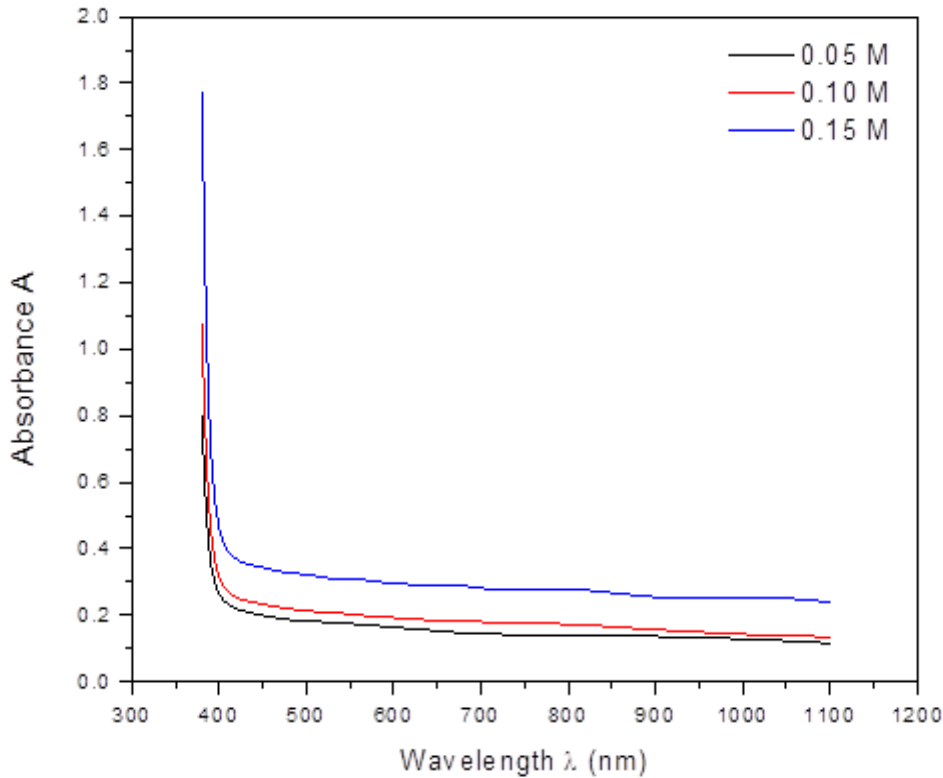
The absorption edge was shifted toward high wavelength (red shift).



**Fig. 5.** Transmittance versus wavelength of ZnO thin films with different molarity



The absorbance versus wavelength for ZnO thin films with different concentrations were shown in Fig. 6. The absorbance near 380 nm were sharp , the bend near the absorption edge confirms the polycrystalline structure of ZnO thin films. As we can see that the absorption in the visible and near IR remains almost constant.



**Fig. 6.** Absorbance versus wavelength of ZnO with different molarity.

The optical energy gap of ZnO thin films can be estimated using Tauc relation<sup>[32]</sup>. Since ZnO is a direct band gap , the value of the optical energy gap can be calculated from Figs. 7, 8 and 9 , which represents the relation between  $(\alpha h\nu)^2$  versus photon energy, by extrapolating the linear portion of the curve to  $\alpha h\nu = 0$ , the optical energy gap was found to be 3.17, 3.181 and 3.19 eV for 0.05, 0.1 and 0.15 M respectively. The increase in  $E_g$  could be attributed to the crystal growth, which lead to an increase in the average grain size. AFM images were recorded on  $(1.623 \times 1.623) \mu\text{m}$ .

Fig. 4 show the AFM images beside the Granularity distribution of the prepared ZnO with different concentrations. It can clearly see that all the values give a smooth surface, the surface roughness ant the root mean square values were increased with the increase of molarity. Table 2 illustrates the values of surface roughness, RMS and grain size, the increase in surface roughness assures that there is a grain growth, the value of the grain size confirmed the existence of nanostructure in the film

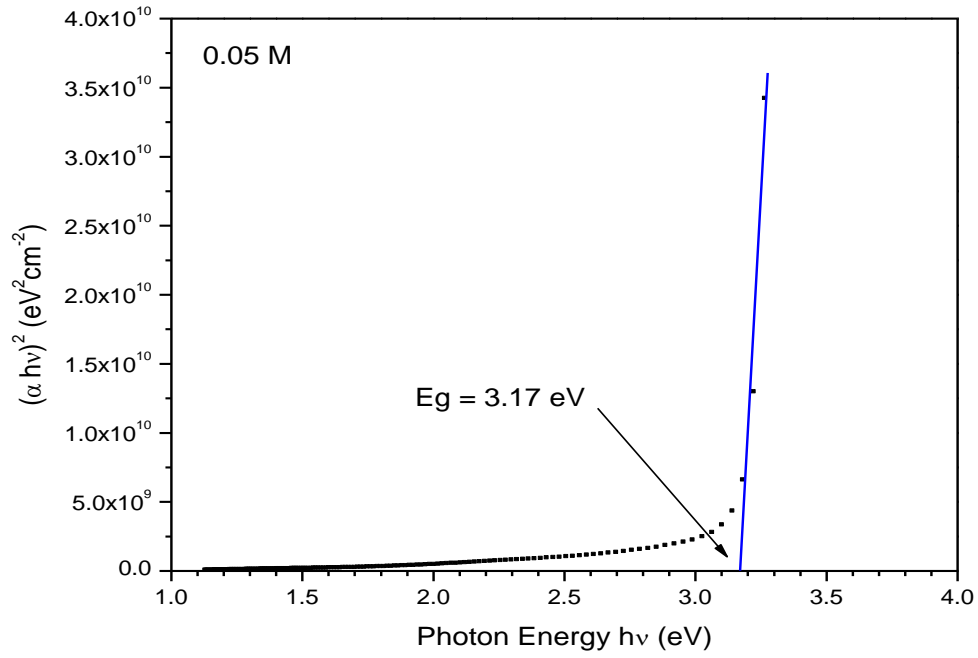


Fig. 7.  $(\alpha h\nu)^2$  versus photon energy for 0.05 M ZnO thin film.

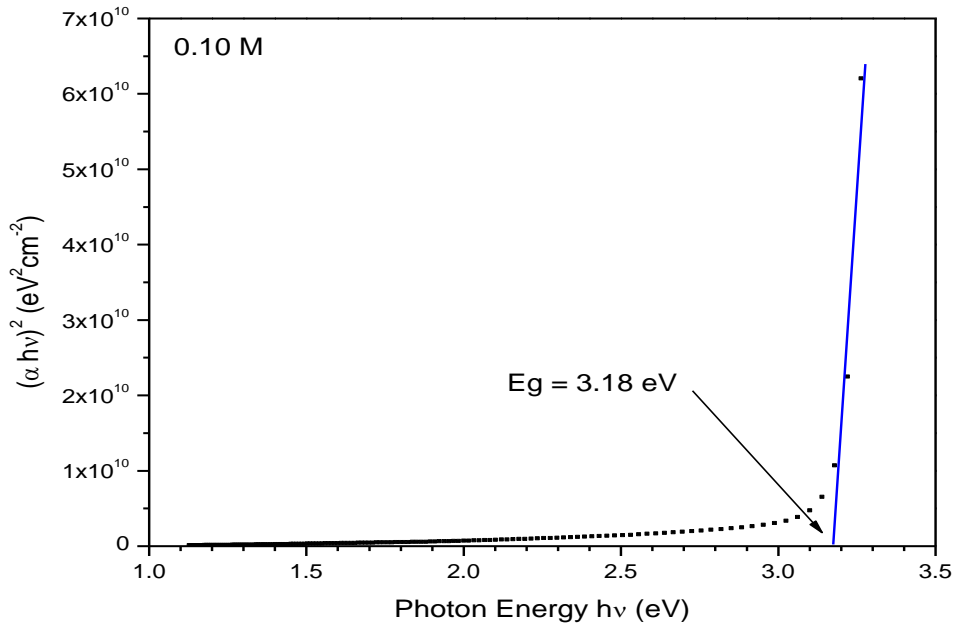


Fig. 8.  $(\alpha h\nu)^2$  versus photon energy for 0.1 M ZnO thin film.

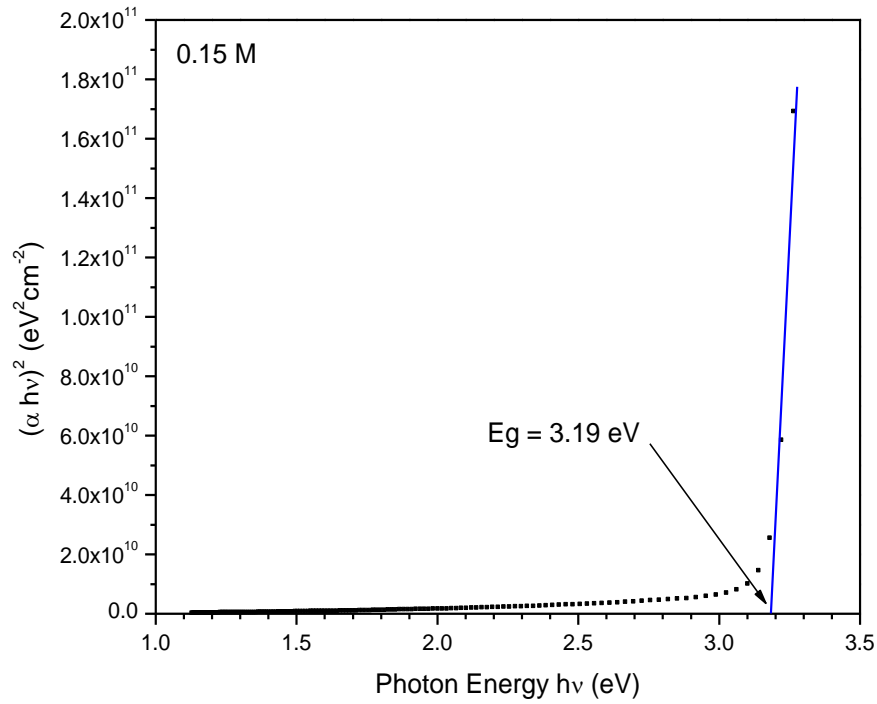


Fig. 9.  $(\alpha hv)^2$  versus photon energy for 0.15 M ZnO thin film.

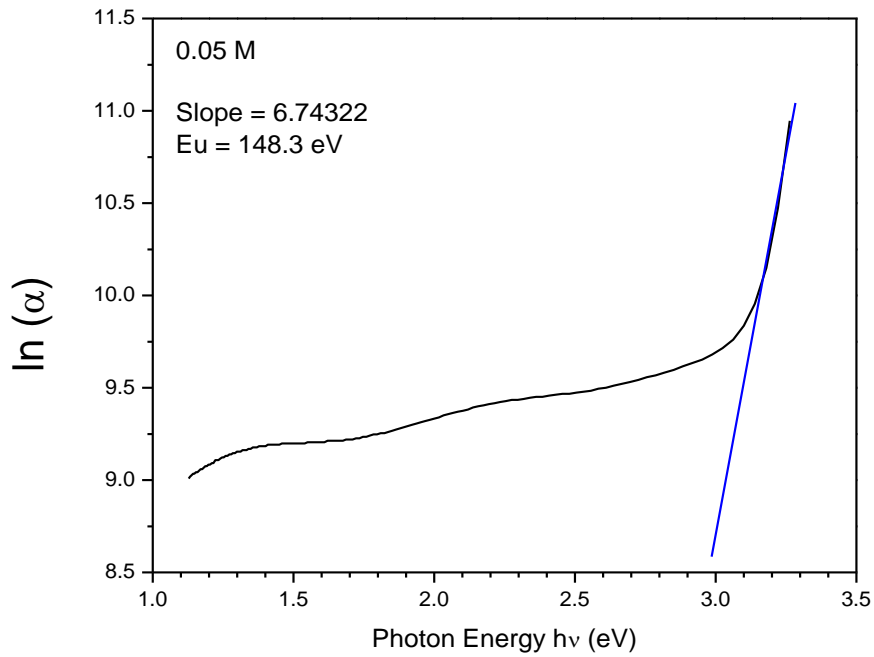
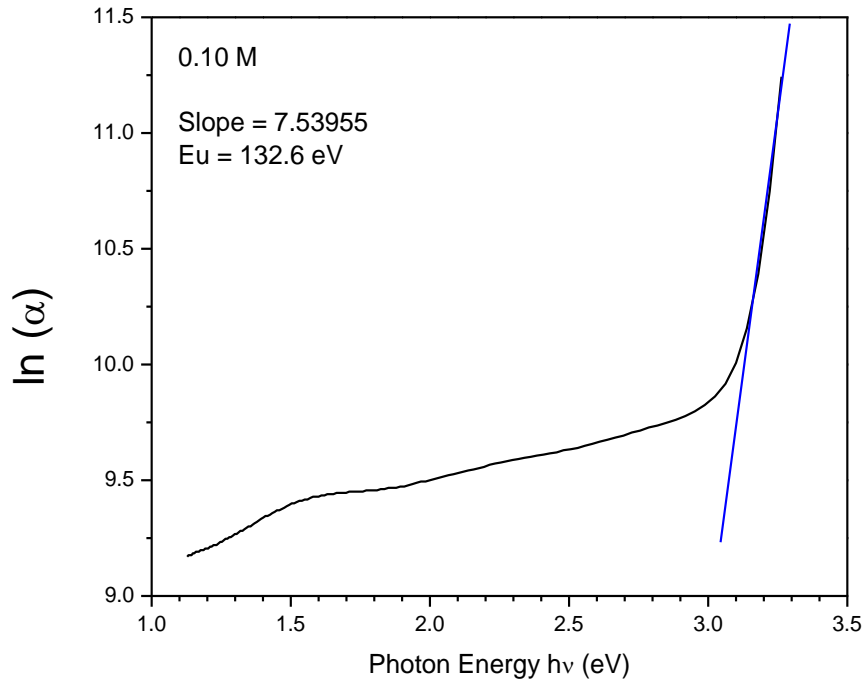
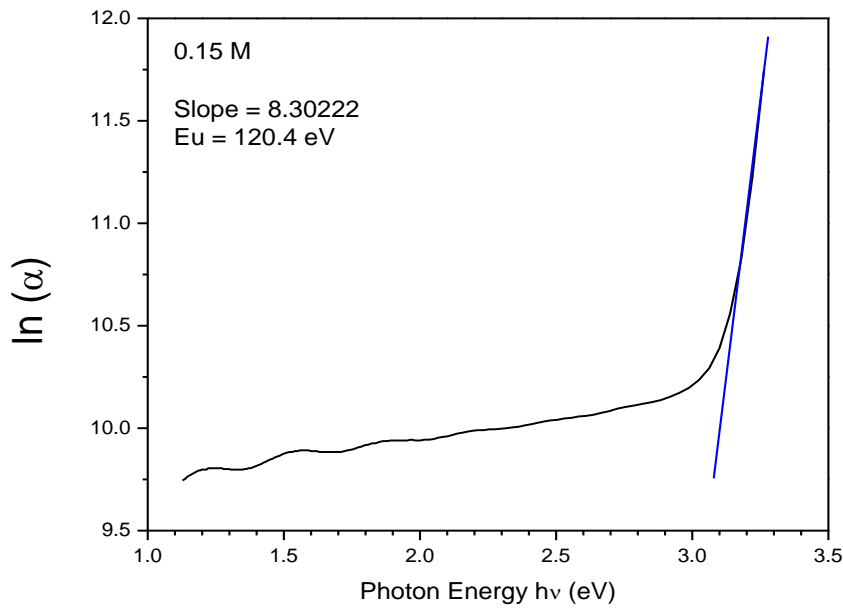


Fig. 10.  $\ln(\alpha)$  versus photon energy for 0.05 M ZnO thin film.



**Fig. 11.**  $\ln(\alpha)$  versus photon energy for 0.1 M ZnO thin film.



**Fig. 12.**  $\ln(\alpha)$  versus photon energy for 0.15 M ZnO thin film.

The particle size of ZnO thin film, which was calculated by AFM is greater than the values of XRD, this fact could be attributed to the widening of the full width at half maximum of ZnO that is because the effect of strain and defect of the film<sup>[31]</sup>.

The width of the localized state denoted by Urbach tail, which, is directly related to the density of state, can be obtained by Urbach relation<sup>[33]</sup>. Figs. 10, 11 and 12 shows the relation between  $\ln(\alpha)$  as a function of photon energy for ZnO thin films with different molarities. The Urbach energy can be obtained by taking the inverse slope of the curve. The width of the localized state decreases as the concentration increases, their values were 148.3, 137.6 and 120.4 meV for 0.05, 0.1 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, the values of the grain size assure this result, by the increase of crystal growth leading to an increase in the band tail.

#### 4. CONCLUSIONS

ZnO thin films were successfully prepared by CSP. The effect of molarity was studied upon structural and optical properties. XRD analysis obtained from the pattern shows that the preferred plane was changed by changing molarity, all the structural parameters were affected by changing molarity. The AFM results assure the existence of nanostructure. The optical energy gap values were increased as the concentration increases, which is due to the increase in crystal growth leading to an increase in the average grain size.

#### References

- [1] Nadir Fadhil Habubi, Reem Saadi Khaleel and Sami Salman Chiad, *AL- Mustansiriya J. Sci* 21 (2010) 41.
- [2] Ali A. Yousif, Adawiya J. Haider, Nadir F. Habubi, *Int. J. Nanoelectronics and Materials* 5 (2012) 47.
- [3] Yaodong Liu, Lei Zhao, Jianshe Lian. *Vacuum* 81 (2006) 18.
- [4] M. Bouderbala, S. Hamzaoui, M. Adnane, T. Sahraoui, M. Zerdali, *Thin Solid Films* 517 (2009) 1572.
- [5] Raid A. Ismail, Nadir F. Habubi, Hussam R. Abid *International Letters of Chemistry, Physics and Astronomy* 4 (2014) 37.
- [6] N.F. Habubi, S.S. Chiad, S. Jabbar, and W. Jabbar, *Journal of the Arkansas Academy of Science* 66 (2012) 82.
- [7] N. Hirahara, B. Onwona-Agyeman, M. Nakao, *Thin Solid Films* 520 (2012) 2123.
- [8] Sang-Hee Ko Park, Jeong-Ik Lee, Chi-Sun Hwang and Hye Yong Chu, *Japanese Journal of Applied Physics* 44 (2005) L 242.
- [9] Hooyoung Song, Jae-Hoon Kim, Eun Kyu Kim, Sung-Min Hwang, *Thin Solid Films* 517 (2009) 3927.

- [10] E. Chikoidze, M. Nolan, M. Modreanu, V. Sallet, P. Galtier, *Thin Solid Films* 516 (2008) 8146.
- [11] Lei Luo, Yanfeng Zhang, Samuel S. Maob, Liwei Lin, *Sensors and Actuators A* 127 (2006) 201.
- [12] T. Pauporte, J. Rathousky, *Microporous and Mesoporous Materials* 117 (2009) 380.
- [13] Maja Šćepanović, Mirjana Grujić-Brojčinić, Katarina Vojisavljević and Tatjana Srećković *Journal of Applied Physics* 109 (2011) 034313.
- [14] M. Krunk, A. Katerski, T. Dedova, I. Oja Acik, A. Mere *Solar Energy Materials & Solar Cells* 92 (2008) 1016.
- [15] Huarong Tang, Yaming Li, Chengbin Zheng, Jun Ye, Xiandeng Hou, Yi LV *Talanta* 72 (2007) 1593.
- [16] Radu Ionescu, *Sensors and Actuators B* 48 (1998) 392.
- [17] P. Sharma, A. Gupta, K.V. Rao, F.J. Owens, R. Sharma, R. Ahuja, J.M.O. Guillen, B. Johansson, G.A. Gehring, *Nat. Mater.* 4 (2003) 173.
- [18] Y. Lare, A. Godoy, L. Cattin, K. Jondo, T. Abachi, F.R. Diaze, M. Morsli, K. Napo, *Applied Surface Science* 255 (2009) 6615.
- [19] Minhong Jiang, Xinyu Liu, *Applied Surface Science* 255 (2008) 3175.
- [20] Lei Zhao, Jianshe Lian, Yuhua Liu, Qing Jiang, *Applied Surface Science* 252 (2006) 8451.
- [21] Shingo Suzuki, Toshihiro Miyata, Makoto Ishii, Tadatsugu Minami, *Thin Solid Films* 434 (2003) 14.
- [22] Jesus Cembrero, David Busquets-Mataix, *Thin Solid Films* 517 (2009) 2859.
- [23] Ah Reum Han, Seong-Ju Hwang, Yongnan Zhao, Young-Uk Kwon, *Journal of Magnetism and Magnetic Materials* 320 (2008) 1591.
- [24] Haibo Zeng, Weiping Cai Jinlian Hu, Guotao Duan, Peisheng Liu, and Yue Li, *Applied Physics Letters* 88 (2006) 171910
- [25] H. Mondrago'n-Sua'rez, A. Maldonadob, M. de la L. Olvera, A. Reyes,R. Castanedo-Pe'rez, G. Torres-Delgado, R. Asomoza, *Applied Surface Science* 193 (2002) 52.
- [26] Zuraida Khusaimi, Mohamad Hafiz Mamat, Mohamad Zainizan Sahdan, Norbani Abdullah, Mohamad Rusop, *Defect and Diffusion Forum* 312-315 (2011) 99.
- [27] C. Gümüs, O. M. Ozkendir, H. Kavak, Y. Ufuktepe, *Journal of Optoelectronic and Advanced Material* 8 (2006) 299-303
- [28] C. S.Barret, T. B. Massalski (1980) *Structure of metals* (Oxford: Pergamon Press)
- [29] P. Sagar , M. Kumar, R.M. Mehra, *Materials Science-Poland* 23 (2005) 685.
- [30] Saliha Ilcan, Yasemin Caglar, Mujdat Caglar, Fahrettin Yakuphanoglu. *Applied Surface Science* 255 (2008) 2353.

- [31] Huiming Huang, Yangjun Ou, Sheng Xu, Guojia Fang, Meiya Li, X.Z. Zhao, *Applied Surface Science* 254 (2008) 2013.
- [32] J. Tauc, R. Grigorovichi, A. Vancu, *Phys. Status Solidi* 15 (1966) 627.
- [33] F. Urbach, *Phys. Rev.* 92 (1953) 1324.

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