A Study the Calculation of the Urbach Energy of ZnO Thin Films Using Different Precursor Molarities

Said Benramache[*‡], Okba Belahssen[*], Hachemi Ben Temam[*]

*Physic Laboratory of Thin Films and Applications (LPCMA), University of Biskra, 07000, Algeria
(saidbenramache07@gmail.com, belahssenokba@gmail.com, ha_bentemam@yahoo.fr)

‡Corresponding Author: Said Benramache, e-mail: saidbenramache07@gmail.com

Received: 21.08.2014 Accepted: 08.11.2014

Abstract– The Urbach energy is playing a role important in the absorption mechanism. In the present work, we have studied a new approach to the description of calculation of the Urbach energy by varying the optical gap energy with precursor molaritie. This calculation based on experimental data of our study published previously in the international journal, which were prepared by ultrasonic spray method at different precursor molarities on glass substrate at 350 °C. The measurement of the Urbach energy of undoped ZnO thin films were realized at different model proposals; these measurements shows that the Urbach energy of the films can be estimated by varying the optical gap energy and the concentration of ZnO solution. The best estimated results are measured by first proposed model with minimum relative errors values were limited to 2 %.

Keywords—ZnO; Thin films; Urbach energy; Optical gap; Correlation.

1. Introduction

Zinc oxide (ZnO) which is one of the most important binary II–VI semiconductor compounds has a hexagonal wurtzite structure and a natural n-type electrical conductivity with a direct energy wide band gap of 3.37 eV at room temperature, a large exciton binding energy (~60 meV) [1–3]. The resistivity values of ZnO films may be adjusted between 10^{-4} Ω cm and 10^{-3} Ω cm by changing the annealing conditions and doping [4]. In solar cells, ZnO thin films are used as an anti-reflective coating (ARC) and transparent conductive oxide (TCO) due to its high optical transmittance in the visible light region, ZnO has a wider band gap (Eg~ 3.3 eV) compared to CdS (2.42 eV)., optimum refractive index (n ~ 2.0) and natural n-type electrical conductivity [5,6].ZnO can be used as a heat mirrors, piezoelectric devices [7], thin films [8] chemical and gas sensing [9].

Zinc oxide based coatings are of much interest in science and technology due to their interesting applications such as in microelectronic devices, light emitting diodes, thin films, antireflection coatings, transparent electrodes in solar cells [10], gas sensors surface acoustic wave devices [11], varistors, spintronic devices and lasers [12]. ZnO thin films can be produced by several techniques such as molecular beam epitaxy (MBE), chemical vapor deposition, electrochemical deposition [13], pulsed laser deposition (PLD) [14], sol-gel process [15], reactive evaporation, magnetron sputtering technique and spray pyrolysis [16].

The aim of this work is study the possibility of the correlation with the optical properties in the ZnO thin films with precursor molarity. Benramache et al. [17] studied the correlation for crystallite size in undoped ZnO thin film with the band gap energy – precursor molarity – substrate temperature; we found that the correlation between the structural and optical properties suggests that the crystallites sizes of the films are predominantly influenced by the band gap energy of the thin films. In this paper, we have studied the possibility to estimate the Urbach energy by varying the band gap energy and the precursor molarities.

Table 1. The variation of the Urbach energy and optical gap energy of the ZnO thin films as a function of concentration [18].

M	$Eu_{exp.}$	$Eg_{Exp.}$
0.050	0.9221	3.08
0.075	0.3186	3.22
0.100	0.0850	3.37
0.125	0.1757	3.15

2. Methods and Model

The optical parameters such as E_g is the band gap energy and the Urbach energy E_u of ZnO thin films were taken from measurements in our publication [18], where we studied the effect of precursor molarity on the structural and optical parameters of ZnO thin films [18] (see Table 1). Here, the ZnO samples were deposited on glass substrates using the ultrasonic spray technique. The films were deposited at a substrate temperature of 350 °C with 2 minutes of deposition time.

In this study, we will show the evolution of the precursor molarity on the Urbach energy and band gap energy, we tried to establish correlations for each model proposed. In our calculations, the Urbach energy can be calculated from precursor molarity and band gap energy of undoped ZnO thin films; the ZnO exhibit a single crystals exhibit n-type semiconductor with a high crystallinity.

3. Theoretical Calculations

We have descript previously the experimental data (see Table 1); one can be seen from this data, the Urbach energy of ZnO thin films change in the form nonlinear with the band gap energy and precursor molarity. We have used different models proposals in this study to estimate the Urbach energy, these models were discussed in the follow steps.

Firstly, we have used the relationships in the form nonlinear to calculate the Urbach energy from the band gap energy and precursor molarity. We suppose that the band gap energy was dependant with the precursor molarity in ZnO thin films. For this raison can be realized three different proposals models to compare the best one, which were evaluated in the following relationships:

$$E_u = a \times E_g + b \times M + c \times M^4 \tag{1}$$

where E_u is the correlate Urbach energy (see Table 2), E_g is the band gap energy and M is the precursor molarity, a, b and c are empirical constants as $a \approx 0.8992$, $b \approx -38.006$ [eV.mol^{-1}.L] and $c \approx 8574.6$ [eV.mol^{-4}.L^4]. However, can be obtained other formula as expressed as:

$$E_u = \frac{a + E_g}{b + c \times M^2} \tag{2}$$

where a, b and c are empirical constants as $a \approx -3.472$, $b \approx -0.14604$ and $c \approx -111.81$ [mol^{-2}.L^2]. And:

$$E_u = a \times \exp\left(b \times E_g + c \times M^2\right) \tag{3}$$

where a, b and c are empirical constants as $a \approx 26571000$ eV, $b \approx -5.4977$ and $c \approx -97.15$.

Secondary, we have compared the different relationships with the experimental data using the relative error, this letter can be calculated by following formula:

$$\varepsilon = \left|(Eu_{Exp} - Eu_{Corr}) / Eu_{Exp}\right| \times 100 \tag{4}$$

The correlation coefficients in this calculation are present in Table 2, it was related to relative errors via:

$$R^2 = 1 - \frac{\sum_i^N \varepsilon_i}{N} \tag{5}$$

where N is the number of measurement and ε is the relative error.

4. Results and Discussion

The variation of the correlate Urbach energy from Eq.(1) is shown in Figure 1, significant correlations were found between the Urbach energy experiment and theoretical calculations values of the ZnO thin films with precursor molarities (ZnO concentration), This correlation indicate that the measurement of Urbach energy of our undoped films by the proposed model; it is equal to the experimental data. From Eq.(2), the Figure 2; show that the Urbach energy of the ZnO thin films is predominantly estimated by the band gap energy and the concentration of ZnO solution (see Table 2).

Table 2. The variation of the correlates Urbach energy in the ZnO thin films as a function of concentration.

M	$E_{u\ exp.}$	$E_{g\ Exp.}$	$E_{u\ c}$ (Eq.1)	$E_{u\ c}$ (Eq.2)	$E_{u\ c}$ (Eq.3)
0.050	0.9221	3.08	0.922827	0.921128	0.922691
0.075	0.3186	3.22	0.316279	0.325173	0.315457
0.100	0.0850	3.37	0.087164	0.080687	0.090408
0.125	0.1757	3.15	0.175138	0.170094	0.175451
Correlation coefficients			0.981720	0.948515	0.962582

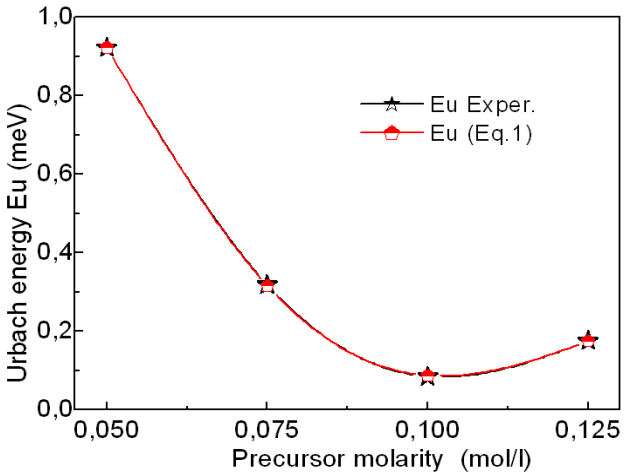

Figure 1. The variation between the experimental and theory of Urbach energy in ZnO thin films evaluate by Eq.(1) at different precursor molarity.

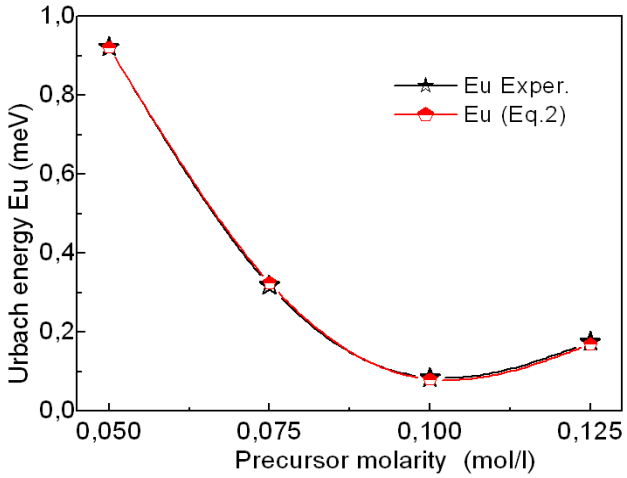

Figure 2. The variation between the experimental and theory of Urbach energy in ZnO thin films evaluate by Eq.(2) at different precursor molarity.

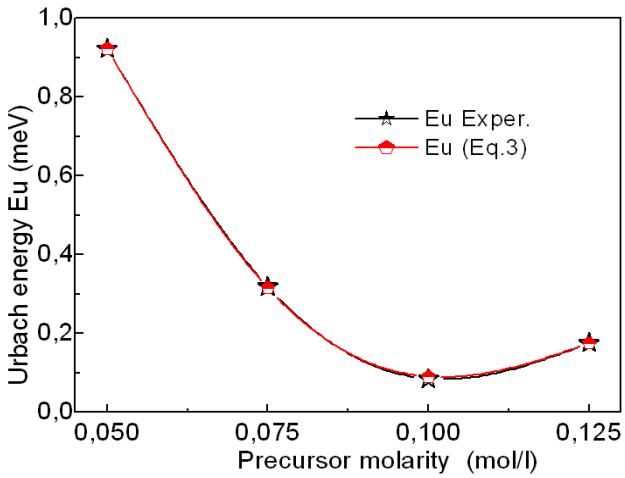

Figure 3. The variation between the experimental and theory of Urbach energy in ZnO thin films evaluate by Eq.(3) at different precursor molarity.

Figure 3, present the results of the variation of calculate optical band gap energy from Eq.(3), in our experience there was no evidence for significant changes in Urbach energy with correlation upon varying the band gap energy by modifying the precursor molarity. This correlation also indicates that the Urbach energy of the films is predominantly influenced by the band gap energy and the precursor molarity of the thin films.

At some points, the measurement in the Urbach energy of ZnO films by the model proposed; it is equal to the experimental data, thus the relative error of these correlations are varied between 0 to 6.4 %, can be calculated Eq. (4) (see Figure 4). Good agreement was found between the calculated and experimental values. The best calculated results are achieved in Eq. (1) with minimum relative errors values were limited to 2 %. Thus the correlations between the Urbach energy and the band gap energy with the precursor molarity were investigated.

The correlation coefficients are presented in Table 2. From Table 2, it can be seen that the proposed model in Eq. (1) is good and achieved results obtaining from highest the correlation coefficients, this is the approach we have adopted in the enhance of Urbach energy and less disorder of ZnO thin films. Thus results indicate that the ZnO thin films are chemically purer and have many fewer defects and less disorder owing to an almost complete chemical decomposition.

5. Conclusion

In summary, the ZnO thin films were prepared with different precursor molarities by ultrasonic spray method on glass substrate at 350 °C. In this paper we have presented a new approach to the description of estimation of the Urbach energy of undoped ZnO. We have obtained that the Urbach energy of the doped films can be estimated by varying the band gap energy and the concentration of ZnO solution. The calculate Urbach energy was investigated with three different proposals models, the obtain measurements are in qualitative agreements with the experimental data. The measured of relative errors values were changed between 0 and 6.5 %, the

best estimated results was given from equation (1) with minimum relative errors values were limited to 2 % corresponding to highest the correlation coefficients. Thus result indicates that the ZnO thin films are chemically purer and have many fewer defects and less disorder owing to an almost complete chemical decomposition.

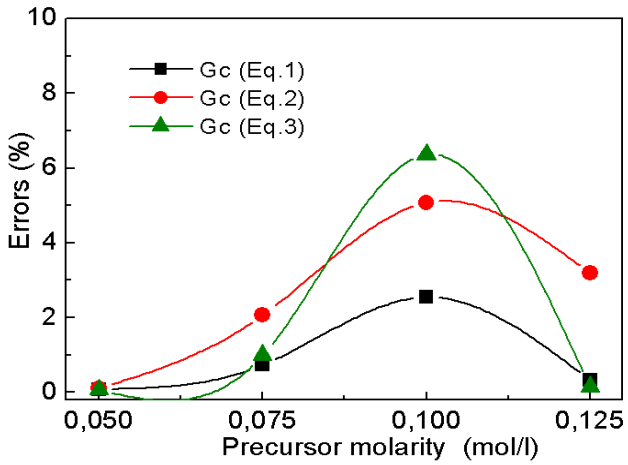

Figure 4. Relative errors of the Urbach energy calculate of ZnO thin films with precursor molarity for all proposed models.

References

[1] S. Benramache, B. Benhaoua, O. Belahssen, The crystalline structure, conductivity and optical properties of Co-doped ZnO thin films, Optik, Vol. 125, pp. 3864–3867, 2014.

[2] S. Benramache, A. Rahal, B. Benhaoua, The effects of solvent nature on spray-deposited ZnO thin film prepared from Zn (CH3COO)2, 2H2O, Optik, Vol. 125, pp. 663–666, 2014.

[3] Y. Zhang, C. Wu, Y. Zheng et al. Synthesis and efficient field emission characteristics of patterned ZnO nanowires. Journal of Semiconductors, Vol. 33, pp. 023001–5, 2012.

[4] S. Benramache, B. Benhaoua, Influence of annealing temperature on structural and optical properties of ZnO: In thin films prepared by ultrasonic spray technique, Superlattices and Microstructure, Vol. 52, pp. 1062–1070, 2012.

[5] M.Z. Pakhuruddin, Y. Yusof, K. Ibrahim, A. Abdul Aziz, Fabrication and characterization of zinc oxide anti-reflective coating on flexiblethin film microcrystalline silicon solar cell, Optik, Vol. 124, pp. 5397–5400, 2013.

[6] D.W. Kang, S.H. Kuk, K.S. Ji, H.M. Lee, M.K. Han, Effects of ITO precursor thicknesson transparent conductive Al doped ZnO film for solar cell applications, Solar Energy Materials and Solar Cells, Vol. 95, pp. 138–141, 2011.

[7] R. Mariappan, V. Ponnuswamy, A. Chandra Bose, A. Chithambararaj, R. Suresh, M. Ragavendar, Structural, optical and electrical characterization of nebulizer-sprayed ZnO nano-rods, Superlattices and Microstructures, Vol. 65, pp. 184–194, 2014.

[8] L. Castaneda, J. Moreno-Valenzuela, C. Torres-Torres, Chemisorptive detection by electrical and nonlinear optical absorption properties of a nanostructured ruthenium-doped zinc oxide film, Optik, Vol. 124, pp. 5209–5213, 2013.

[9] H. Yua, H. Fan, X. Wang, J. Wang, Synthesis and characterization of ZnO microstructures viamicrowave-assisted hydrothermal synthesis process, Optik, Vol. 125, pp. 1461–1464, 2014.

[10] H. Zhang, H. Liu, C. Lei et al. Low-temperature deposition of transparent conducting Mn–W co-doped ZnO thin films. Journal of Semiconductors, Vol. 31, pp. 083005–5, 2010.

[11] S. Benramache, B. Benhaoua, H. Bentrah, Preparation of transparent conducting of ZnO:Co and ZnO:In thin films by ultrasonic spray method, Journal of Nanostructure in Chemistry, Vol. 3, pp. 1–7, 2012.

[12] P. Prepelita, R. Medianu, B. Sbarcea, et al. The influence of using different substrates on the structural and optical characteristics of ZnO thin films. Applied Surface Sciences, Vol. 256, pp. 1807–1812, 2010.

[13] S. Benramache, B. Benhaoua, Influence of substrate temperature and Cobalt concentration on structural and optical properties of ZnO thin films prepared by Ultrasonic spray technique. Superlattices and Microstructures, Vol. 52, pp. 807–815, 2012.

[14] A.J. Hashim∗ , M.S. Jaafar, Alaa J. Ghazai, N.M. Ahmed, Fabrication and characterization of ZnO thin film using sol–gel method, Optik, Vol. 124, pp. 491–492, 2013.

[15] S. Benramache, B. Benhaoua, F. Chabane, Effect of substrate temperature on the stability of transparent conducting cobalt doped ZnO thin films, Journal of Semiconductors, Vol. 33, pp. 093001–4, 2012.

[16] Z.B. Bahs, A.Y. Oral, Effects of Mn and Cu doping on the microstructures and optical properties of sol–gel derived ZnO thin films. Optics Materials, Vol. 29, pp. 672–677, 2007.

[17] S. Benramache, O. Belahssen, A. Arif, A. Guettaf, A correlation for crystallite size of undoped ZnO thin film with theband gap energy – precursor molarity – substrate temperature, Optik, Vol. 125, pp. 1303–1306, 2014.

[18] S. Benramache, F. Chabane, D. Bensahal, O. Belahssen, F.Z. Lemmadi, Preparation and Characterization of Transparent Conductive ZnO Thin Films by Ultrasonic Spray Technique, Journal of Science and Engineering, Vol. 2, pp. 97–104, 2013.