The Effect of the Doping Levels on Urbach Energy of the Zinc Oxide Thin Films

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Within the proposed model, the calculated Urbach energy of the undoped and Bi-, Sn- and Fe-doped ZnO thin films is studied as a function of doping levels. The Bi-, Sn- and Fe-doped ZnO films were deposited by spray depositions at various conditions such as ZnO-based solution molarity and doping levels. The measurements by means of this proposed model are found to be in a qualitative agreement with the experimental data with high correlation coefficients of 0.92–0.98. The Urbach-energy calculations for doped films are improved to maximum enhancement corresponding to minimum error, which is found for the Sn- and Fe-doped ZnO films to be 5.5 and 5.1%, respectively.

У рамках запропонованого моделю, розраховану енергію Урбаха нелеґованих і леґованих Бісмутом, Станумом і Ферумом тонких плівок ZnO вивчено як функцію рівнів леґування. Леґовані Бісмутом, Станумом і Ферумом плівки ZnO були нанесені осадженнями матеріялу, що розпорошується, за різних умов типу молярности розчину на основі ZnO та рівнів леґування. Міряння за допомогою цього запропонованого моделю, як виявляється, перебувають у якісній згоді з експериментальними даними з високими коефіцієнтами кореляції у 0,92–0,98. Обчислення енергії Урбаха для леґованих плівок поліпшено аж до максимального підвищення, що відповідає мінімальній помилці, яку знайдено для плівок ZnO, леґованих Станумом і Ферумом, рівною 5,5 і 5,1% відповідно.

В этой работе, в рамках предложенной модели, рассчитанная энергия Урбаха нелегированных и легированных висмутом, оловом и железом тонких плёнок ZnO изучена как функция уровней легирования. Легированные висмутом, оловом и железом плёнки ZnO были нанесены осаждениями распыляемого материала в различных условиях типа молярности раствора на основе ZnO и уровней легирования. Измерения посредством этой предложенной модели, как обнаруживается, находятся в качественном согласии с экспериментальными данными с высокими коэффициентами

корреляции 0,92−0,98. Вычисления энергий Урбаха для легированных плёнок улучшены вплоть до максимального повышения, соответствующего минимальной ошибке, которая найдена для плёнок ZnO, легированных оловом и железом, равной 5,5 и 5,1% соответственно.

1. INTRODUCTION

In past years, the investigation of new materials for photovoltaic applications was depended and related to the experimental and modelling parameters of any properties. However, zinc oxide is one of the most important semiconductor materials for its semiconducting characteristics. It is an inorganic compound with the formula ZnO, which has a wurtzite structure. This is a hexagonal crystal structure; ZnO is available as large bulk single crystals [1−4]. Transparent conducting oxides (TCO) (such as ZnO) based glasses have gained much interest in science and technology; they are a unique class of materials based on metal oxides that exhibits both optical transparency, low resistivity, and good optical-gap energy due to their interesting applications such as transparent conductive, ferromagnetism, semiconductors, piezoelectric and solar cells [1−3]. However, in the past years, ZnO was used as primary films for a gas sensing due to their high optical transmission and high electrical conductivity. So far, ZnO as a thin film can be used with verity of investigated application for optoelectronic, piezoelectric, and photovoltaic applications such as sensors [4], thermoelectric devices [5], catalysis [6], fuel-cell electrodes [7], dye-sensitized solar cells (DSSCs) [8], and electrochromic material for displays [9].

ZnO is one of the most important binary II−VI semiconductor groups. The native doping of the semiconductor due to O vacancies or Zn interstitials is of n-type. ZnO has a wide-band gap of 3.37 eV at room temperature and a large exciton binding energy (60 meV) [9, 10].

ZnO thin films can be produced by some techniques such as reactive evaporation, thermal annealing, molecular beam epitaxy, magnetron sputtered technique, low-temperature solution method, potentiostatic electrodeposition, sol−gel technique, pulsed laser deposition, chemical vapour deposition, electrochemical deposition, and spray pyrolysis

[11−18], which have been reported to prepare thin films of ZnO.

The main object of this work is to present a new-proposal model to calculate the Urbach energy of Bi-, Sn- and Fe-doped ZnO thin films; these estimations were studied by varying the precursor molarities and doping level of doped films.

2. MATERIALS AND METHODS

In this work, we have investigated a correlation to be used for study the relation between the Urbach energy and the preparing conditions of ZnO thin films, which were studied, the influence of evolution of the precursor molarity, doping level and the band-gap energy on Urbach energy. The optical properties of ZnO such as band-gap energy and the Urbach energy of undoped and doped films were taken from the literature [19−34] (Tables 1 to 4) to study the

TABLE 1. Experimental data [29]. Undoped ZnO thin films with $a \approx 3.28711$ and $b \approx 0.0184683$.

Ref.	Molarity M, mole·l^{-1}	Temperature T, °C	Optical gap $E_{g(e)}$, eV	Urbach energy $E_{u(e)}$, eV	Urbach energy, $E_{u(c)}$, V	Relative error e, %
[19]	0.05	350	3.08	0.9221	0.938	1.72
[19]	0.075	350	3.22	0.3186	0.281	11.80
[19]	0.1	350	3.37	0.085	0.069	18.82
[19]	0.125	350	3.15	0.1757	0.201	14.39
[20]	0.1	350	3.10	0.2734	0.279	2.05
[21]	0.1	350	3.267	0.108	0.108	0
[22]	0.02	350	3.19	0.08	0.071	11.25
[23]	0.1	350	3.25	0.064	0.074	15.62
[24]	0.1	350	3.304	0.1139	0.101	11.32
[25]	0.1	350	3.317	0.0983	0.097	1.32
[26]	0.1	350	3.27	0.17	0.165	2.94
[27]	0.1	350	3.25	0.209	0.203	2.87
[28]	0.1	350	3.23	0.490	0.444	9.39

Note: $E_{g(e)}$—experimental optical-gap energy; $E_{u(e)}$—experimental Urbach energy; $E_{u(c)}$—correlate Urbach energy.

TABLE 2. Experimental data and the Urbach energy correlate for Bi-doped ZnO thin films with 0.02 mole·l^{-1}, $A \approx -1.37139$ and $B \approx -39.00365$.

Doping level [X]/[Zn], %	Temperature T, °C	Optical gap $E_{g(e)}$, eV	Urbach energy $E_{u(e)}$, eV	Urbach energy $E_{u(c)}$, eV	Relative error, %	Ref.
0	350	3.19	0.08	0.071	11.25	
1	350	3.195	0.011	0.035	—	
2	350	3.21	0.08	0.081	1.25	[22]
3	350	3.21	0.095	0.102	7.37	
4	350	3.225	0.52	0.487	6.34	
5	350	3.239	0.53	0.498	6.04	
0	450	3.250	0.2527	0.281	11.19	
1	450	3.240	0.4159	0.454	9.16	[30]
3	450	3.200	0.4573	0.465	1.68	
5	450	3.120	0.4954	0.462	6.74	

effect of precursor molarity, doping level and substrate temperature on physical properties of undoped and doped ZnO thin films with Bi, Sn and Fe. The thin films were deposited on glass substrates by chemical spray ultrasonic and pyrolysis techniques. The proposal model to calculate the Urbach energy of Bi-, Sn-, and Fe-doped ZnO thin films was based on estimation for the undoped films that is found in nonlinear format as expressed in Ref. [29].

2.1. The Urbach Energy Evaluated

The Urbach energy for ZnO thin films was calculated by Eq. (1) [29]:

$$E_u = \exp\left(\ln M + \frac{1}{b}\ln\frac{a}{E_g}\right) \pm \Delta E_u, \text{ if } X_0 = 0, \tag{1}$$

where E_u—Urbach energy [meV]; a, b—empirical constants for undoped film; M—concentration molarity (mole/l); ΔE_u is the resulting error for Urbach energy; E_g is the optical-band gap, and X_0 is the doping concentration.

In this work, the estimate of the Urbach energy for doped ZnO thin films was investigated by the following Eq. (2):

$$E_u = \exp\left(\ln M + \frac{1}{b\left(1 + BX_0\right)} \ln \frac{a\left(1 + AX_0\right)}{E_g} \right) \pm \Delta E_u, \text{ if } X_0 > 0, \quad (2)$$

where A, B—empirical constants for doped film; E_g—optical-gap energy [eV]; X_0—concentration of doping [%].

The resulting errors for Urbach energy (ΔE_u) can be measured from Eqs. (1), (2) by the following relationships as expressed in Eqs. (3), (4) [35]:

$$\ln E_g - \ln\left(a\left(1 + AX_0\right)\right) = \left(b\left(1 + BX_0\right)\right)\left[\ln M - \ln E_g\right], \quad (3)$$

$$\left(b\left(1 + BX_0\right)\right)\left(\frac{dE_u}{E_u} - \frac{dM}{M}\right) + d\left(b\left(1 + BX_0\right)\right)\left(\ln E_u - \ln M\right) =$$
$$= \frac{d\left(a\left(1 + AX_0\right)\right)}{\left(a\left(1 + AX_0\right)\right)} - \frac{dE_g}{E_g}. \quad (4)$$

The difference found about the doping concentration of doped thin films was limited, so we have $d(a(1 + AX_0)) = 0$ and $d(b(1 + BX_0)) = 0$.

Equation (4) can be written in the following form of Eqs. (5), (6):

$$\left(b\left(1 + BX_0\right)\right)\frac{\Delta E_u}{E_u} = \frac{\Delta E_g}{E_g}, \quad (5)$$

$$\Delta E_u = \frac{1}{\left(b\left(1 + BX_0\right)\right)}\frac{\Delta E_g}{E_g}E_u. \quad (6)$$

2.2. The Relative Error Measurement

The relative error value was measured between the experimental data and correlate values by the following Eq. (7):

$$\varepsilon = \left|\left(E_{u\ exp} - E_{u\ corr}\right) / E_{g\ exp}\right| \cdot 100. \quad (7)$$

The correlation coefficient R depends on both relative errors and doping *via* Eq. (8):

$$R = 1 - \frac{\sum_{i=1}^{N} \varepsilon_i}{N}. \quad (8)$$

TABLE 3. Experimental data and the Urbach energy correlate for Sn-doped ZnO thin films with 0.2 mole·l^{-1}, $A \approx -1.91294$ and $B \approx 33.62015$.

Doping level [X]/[Zn], %	Temperature T, °C	Optical gap $E_{g(e)}$, eV	Urbach energy $E_{u(e)}$, eV	Urbach energy $E_{u(c)}$, eV	Relative error, %	Ref.
0	450	3.37	0.055	0.052	5.00	
1	450	3.26	0.054	0.053	1.85	[31]
3	450	3.25	0.058	0.058	0.83	
5	450	3.18	0.058	0.089	1.02	
0	400	3.125	0.301	0.411	–	
1	400	3.03	0.675	0.655	2.90	[32]
	400	2.985	1.143	1.161	1.56	
2	400	2.88	1.352	1.427	5.53	

TABLE 4. Experimental data and the Urbach energy correlate for Fe-doped ZnO thin films with $A \approx -13.92950$ and $B \approx -941.53779$.

Molarity	Doping level [X]/[Zn], %	Temperature T, °C	Optical gap $E_{g(e)}$, eV	Urbach energy $E_{u(e)}$, eV	Urbach energy $E_{u(c)}$, eV	Relative error, %	Ref.
	0	300	3.29	0.073	0.074	1.37	
0.2 mole·l^{-1}	1	300	2.67	0.136	0.131	3.67	[33]
	2	300	2.75	0.136	0.129	5.14	
	0	410	3.255	0.081	0.085	4.93	
		410	3.115	0.164	0.165	0.61	
0.01 mole·l^{-1}	1.5	410	3.135	0.197	0.196	0.51	[34]
	2	410	3.105	0.219	0.215	1.82	

Table 1 presents the summary results of experimental data, which were obtained from published papers and the correlated Urbach energy and relative error for undoped ZnO thin films [19].

3. RESULTS AND DISCUSSION

Figure 1 shows the variation of experimental and correlate Urbach energy for undoped ZnO thin films.

The correlate values were scaled parameter values according to Eq. (1), as represented in Table 1, which were estimated as a function of solution molarity and optical energy. As can be seen, all estimated values are proportional to the experimental data. Thus, the calculations by the proposed equations are in qualitative agreement with the experimental data, so it is found that the correlation coefficient is of about 0.92, *i.e.* the maximum agreement of the estimation was found to be minimum error.

Table 2 presents the summary results of experimental data and the Urbach energy correlate for Bi-doped ZnO thin films, which are calculated from Eq. (2).

Table 3 presents the summary results of experimental data and the Urbach energy correlate for Sn-doped ZnO thin films, which are calculated from Eq. (2).

Table 4 presents the summary results of experimental data and the Urbach energy correlate for Fe-doped ZnO thin films, which are calculated from Eq. (2).

As shown in Fig. 2, the doping evolution of Bi-, Sn-, and Fe-doped ZnO thin films influence on the estimation of Urbach energy with doping levels and their optical-gap energy; here, the investiga-
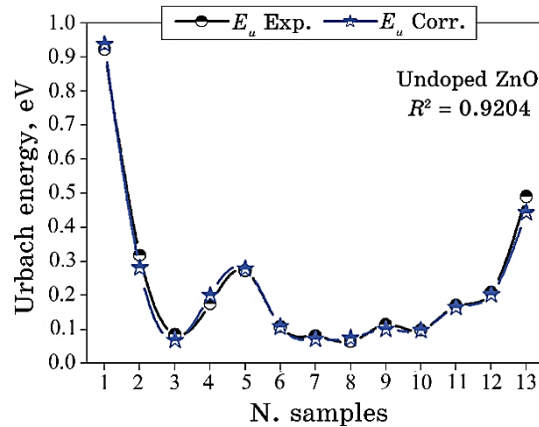

Fig. 1. The variation of Urbach energy experimental.
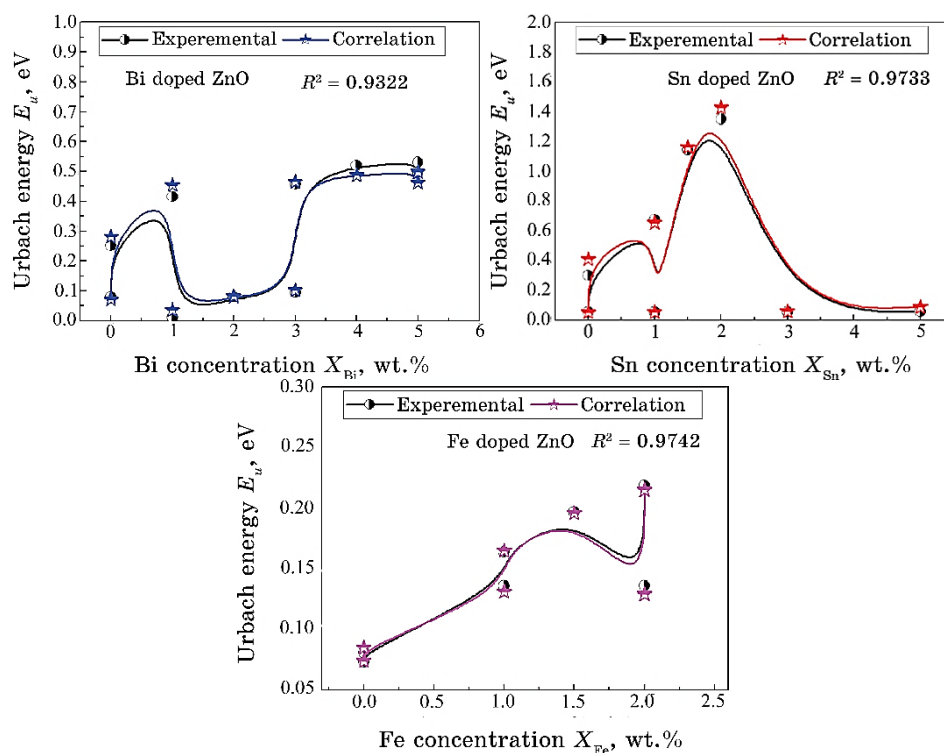
Fig. 2. The variation of Urbach energy experimental and correlate of Bi-, Sn-, and Fe-doped ZnO thin films.

tions were carried out on the basis of Eq. (2).

As can be seen in Fig. 2 with comparing with undoped films, the estimation of Urbach energy in the Bi-, Sn-, and Fe-doped films have a high correlation coefficient of 0.9322, 0.9733 and 0.9742, respectively. Besides, the calculation values are in qualitative agreement with the experimental data, *i.e.* the maximum agreement of the estimations was found to be with minimum relative error.

In Figures 3 and 4, we obtained that the relative errors of Urbach energy of undoped and doped thin films, respectively.

For undoped films, all calculations have errors smaller than 18%, however, we found after calculate that the relative error of the Urbach energy for doped films are improved, and the maximum enhancement of minimum errors was found for Sn- and Fe-doped ZnO thin films with 5.53 and 5.14%, respectively. It was confirmed that these models are suitable for calculation of optical properties with varying of some parameters. The decreases in the relative errors for undoped films to doped ones can be explained by the good optical properties, which can be observed with the fewer defects and less
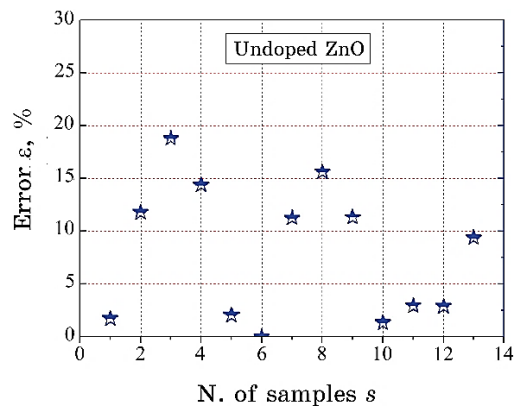
Fig. 3. The variation of error value of calculated Urbach energy for un-doped ZnO thin films.
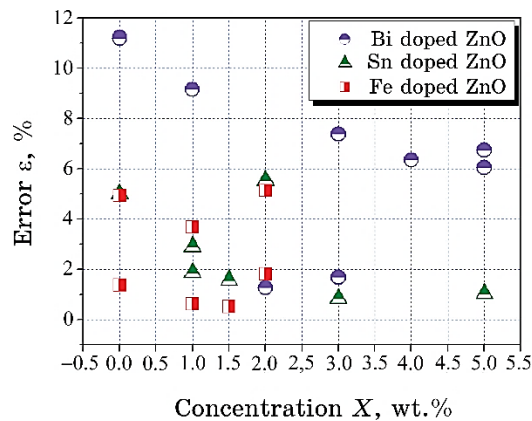

Fig. 4. The variation of error value of calculated Urbach energy for Bi-, Sn-, and Fe-doped ZnO thin films.

disorder.

4. CONCLUSIONS

In summary, the undoped ZnO and Bi-, Sn-, and Fe-doped ZnO films were chosen for studying the calculation of Urbach energy with same variations. Thin films were investigated by spray techniques such as ultrasonic and pyrolysis. The model proposed to calculate the Urbach energy of undoped and doped ZnO thin films were investigated. These relations suggest that the Urbach energy can be estimated by variations of optical-gap energy, concentration of ZnO

solution and doping level. The measurements by means of these proposed models are in qualitative agreement with the experimental data that has been reliable in this work, because of the high correlation coefficients, which were found to be in the range 0.92–0.98.

Thus, it is found that the relative errors for undoped ZnO films in all calculation are smaller than 18%. However, we found after calculate that the relative errors of the Urbach energy for doped films are improved with the maximum enhancement corresponding to minimum errors for Sn- and Fe-doped ZnO thin films, which are equal to 5.53 and 5.14%, respectively. As confirmed, these models are suitable for calculation of Urbach energy with variation of some parameters. The decreases in the relative errors of undoped ZnO to doped ZnO films can be explained by the good optical properties, which can be observed with the fewer defects and less disorder.

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