A Study the Calculation of the Optical Gap Energy and Urbach Energy in the Semiconductor Doping

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

*Physic Laboratory of Thin Films and Applications LPCMA, University of Biskra, Algeria

belahssenokba@gmail.com, saidbenramache07@gmail.com

‡Corresponding Author: Said Benramache, Tel-+213779276135, e-mail: saidbenramache07@gmail.com

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Abstract– We investigated the optical properties of pure and Aluminum doped zinc oxide thin films as the n-type semiconductor. In this paper we have focused our attention on the creation of a new approach to calculate the optical gap and Urbach energies, these correlations based on experimental data were published previously in the literatures. The thin films were deposited at different precursor molarities by ultrasonic spray and spray pyrolysis techniques. The calculation by these proposal models of the band gap and the Urbach energies of undoped and doped ZnO thin films were studied. The relation between the experimental data and theoretical calculation with precursor molarities suggests that the band gap and/or the Urbach energies are predominantly estimated by the band gap and/or the Urbach energies and the concentrations of ZnO solution and Al doping. The measurements by these proposals models are in qualitative agreements with the experimental data that have been reliable in this work, at this point the correlation coefficients value was estimated of 0.99, and thus we have found that the relative errors of all calculation are smaller than 4 % for optical band gap and 20 % for Urbach energy. The best estimated results were obtained for Al doped ZnO thin films; with minimum relative errors values were limited to 3.6 and 8.3 % for the band gap and the Urbach energies, respectively. This is the approach adopted to improve the band gap energy for less disorder of ZnO thin films after doping. Stoichiometric Al doped ZnO films are highly transparency and good optical band gap.

Keywords: ZnO; Thin film; Semiconductor doping; Correlation.

1. Introduction

Zinc oxide (ZnO) has a wurtzite (WZ) structure, this is a hexagonal crystal structure (lattice parameter: a = 0.325 nm, c = 0.521 nm), belonging to the space group P63mc, and is characterized by two interconnecting sublattices of Zn^{2+} and O^{2-}, such that each Zn ions is surrounded by a tetrahedral of O ions, and vice-versa [1,2]. 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 (60meV) [3,4].

Semiconducting transition metal oxide (such as ZnO) based glasses have gained much interest in science and technology due to their interesting applications such as transparent conductive, ferromagnetism, semiconductors, piezoelectric and solar cells, as the doped thin films have low resistivity and good optical gap energy at low deposition, and transparent in the visible region such as in Al and doped ZnO thin films discussed by [5–8].

ZnO thin films can be produced by several techniques such as reactive evaporation and thermal annealing [9], molecular beam epitaxy (MBE) [10], magnetron sputtered technique [11], pulsed laser deposition (PLD) [12], the low-temperature solution method [13], potentiostatic electrodeposition [14], the sol-gel technique [15], chemical vapor deposition, electrochemical deposition [16] and spray pyrolysis [17], have been reported to prepare thin films of ZnO. Among these, we will focus more particularly in this paper on the spray technique because of its simplicity and suitability for large-scale production, it has several advantages in producing nanocrystalline thin films, such as, relatively homogeneous composition with fine and porous microstructure, a simple deposition on glass substrate because of the low substrate temperatures involved, easy control of film thickness [18].

In this paper, we have studied the possibility to estimate the optical gap energy E_g and Urbach energy E_u of undoped

and Al doped ZnO thin films by varying the precursor molarities and doping level of doped films.

2. Experimental and Methods

In this study, the undoped and Al doped ZnO samples were deposited on glass substrates using the ultrasonic spray and spray pyrolysis technique. In general the depositions were performed at a substrate temperature of 350 °C. The optical parameters such as the band gap energy and the Urbach energy of undoped and Al doped ZnO thin films were taken from our previous papers, where studied the effect of precursor molarity, doping level on structural, electrical and optical parameters of ZnO thin films. However, the optical parameters of the thin films were also taken from [19–28] studied the effect of precursor molarity, doping level and substrate temperature on undoped and Al doped ZnO thin films. The data is obtained from publications, most of which used zinc as a precursor (see Table 1). From these data it can be derived that the differences shown in Tables 2 and3 can be partially ascribed to differences in the deposition circumstances, such as reactor geometry, substrate temperature, deposition time, flows, concentration of ZnO solution, annealing temperature, etc. The variations of optical gap energy and Urbach energy of undoped and doped ZnO thin films varied in the form nonlinear (see Tables 2 and 3). The model proposed of thin films with precursor molarity and doping concentration is discussed.

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

Table 1. The parameters conditions were used in this paper.

Method	ultrasonic spray and spray pyrolysis
Oxide	zinc oxide thin films
Zn reactants Solvents	Zn acetate or $ZnCl_2$ ethanol– methanol– water
Substrate	glass
Molarity (M)	0.02–0.05–0.075–0.1–0.125
Temperature C°)	350
dopant	Al
[X]/[Zn] (%)	1 to 15

3. Theoretical Calculations

3.1. Undoped ZnO Thin Films

Firstly, for undopedZnO thin films, we have used the relationship in the form nonlinear to calculate the optical gap energy by the Urbach energy, precursor molarity. Thus, we found the following relation:

$$E_g = a\left(\frac{M}{E_u}\right)^b \tag{1}$$

where E_u is the Urbach energy, E_g is the band gap energy correlate and M is the precursor molarity (see Table 2), and a and b are empirical constants as $a \approx 3.28711$ and $b \approx 0.0184683$

$$\begin{cases} E_g = \left(3.28711 \times (1+AX_0)\right) \times \left(\frac{M}{E_u}\right)^{\left(0.0184683 \times (1+BX_0)\right)} & if \quad X_0 \succ 0 \\ E_g = \left(3.28711\right) \times \left(\frac{M}{E_u}\right)^{0.0184683} & if \quad X_0 = 0 \end{cases} \tag{2}$$

3.2. Doped ZnO Thin Films

For the Al doped ZnO films, here we have studied the correlation with Al doping levels, which were deposited at different precursor molarities(see Table 2), to perform the correlation in this step the optical parameters were measured with doping level. In this section the optical gap energy was estimated with undoped ZnO thin film (0 wt. %). The correlation can be written in another form:

where A and B are empirical constants and X_0 is the concentration of Al doped ZnO films, which were presented in Table 3.

Table 2. Summary results of experimental data, the correlate optical gap energy, the correlate Urbach energy and relative errors for the Undoped ZnO thin films.

Undoped ZnO thin films $a \approx 3.28711$ and $b \approx 0.0184683$									
S.N.	M ($mol.l^{-1}$)	T (°C)	$E_{g\,(Exp.)}$ (eV)	E_u (eV)	$E_{g\,(Corr.)}$ (eV)	Error (%)	$E_{u\,(Corr.)}$ (eV)	Error (%)	Ref.
1	0.05	350	3.08	0.9221	3.115	1.136	0.938	1.72	[19]
2	0.075	350	3.22	0.3186	3.200	0.590	0.281	11.80	[19]
3	0.1	350	3.37	0.085	3.297	2.166	0.069	18.82	[19]
4	0.125	350	3.15	0.1757	3.266	3.682	0.201	14.39	[19]
5	0.1	350	3.10	0.2734	3.212	3.612	0.279	2.05	[20]
6	0.1	350	3.267	0.108	3.273	0.183	0.108	0	[21]
7	0.02	350	3.19	0.08	3.204	0.439	0.071	11.25	[22]
8	0.1	350	3.25	0.064	3.314	1.969	0.074	15.62	[23]
9	0.1	350	3.304	0.1139	3.279	0.757	0.101	11.32	[24]
10	0.1	350	3.317	0.0983	3.288	0.874	0.097	1.32	[25]
11	0.1	350	3.27	0.17	3.255	0.458	0.165	2.94	[26]
12	0.1	350	3.25	0.209	3.243	0.215	0.203	2.87	[27]
13	0.1	350	3.23	0.490	3.192	1.176	0.444	9.39	[28]

Table 3. Summary results of experimental data, the correlate optical gap energy, the correlate Urbach energy and relative errors for the Al doped ZnO thin films.

Al doped ZnO thin films with 0.1 $mol.l^{-1}$ $A \approx 0.09876$ and $B \approx 40.09027$									
S.N.	[X]/[Zn] (%)	T (°C)	$E_{g\,(Exp.)}$ (eV)	E_u (eV)	$E_{g\,(Corr.)}$ (eV)	Error (%)	$E_{u\,(Corr.)}$ (eV)	Error (%)	Ref.
1	0	350	3.10	0.2734	3.212	3.612	0.279	2.05	[20]
2	1	350	3.15	0.1861	3.218	2.158	0.176	5.42	
3	2	350	3.19	0.1503	3.224	1.065	0.158	5.12	
4	3	350	3.26	0.1257	3.255	0.153	0.128	1.83	
5	4	350	3.13	0.2120	3.139	0.287	0.214	0.94	
6	5	350	3.15	0.2549	3.111	1.238	0.267	4.75	
7	0	350	3.267	0.108	3.273	0.183	0.108	0	[21]
8	1	350	3.272	0.110	3.266	0.183	0.109	0.91	
9	2	350	3.275	0.106	3.280	0.152	0.103	1.83	
10	2.25	350	3.296	0.099	3.288	0.242	0.102	3.03	
11	2.5	350	3.311	0.103	3.283	0.845	0.109	5.82	
12	2.75	350	3.325	0.102	3.284	1.233	0.107	4.90	
13	3	350	3.305	0.098	3.290	0.453	0.107	4.08	
14	3.25	350	3.289	0.084	3.293	0.122	0.091	8.33	
15	3.5	350	3.283	0.095	3.274	0.274	0.101	6.31	

3.3. The Urbach Energy Evaluated

The Urbach energy of undoped and Al doped ZnO thin films were also correlated as the following relationships:

$$\begin{cases} E_u = epx\left(\ln M + \dfrac{1}{b(1+BX_0)}\ln\dfrac{a\,(1+AX_0)}{E_g}\right) \pm \Delta E_u & if \quad X_0 \succ 0 \\ E_u = epx\left(\ln M + \dfrac{1}{b}\ln\dfrac{a}{E_g}\right) \pm \Delta E_u & if \quad X_0 = 0 \end{cases} \tag{3}$$

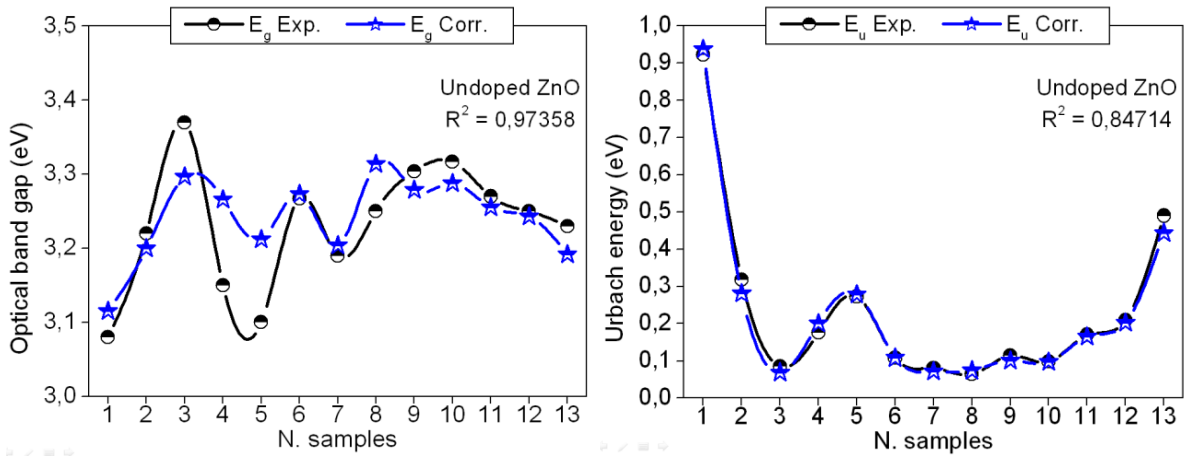

Figure 1. Summary results of experimental data, the correlate optical gap and Urbach energies in the Undoped ZnO thin films.

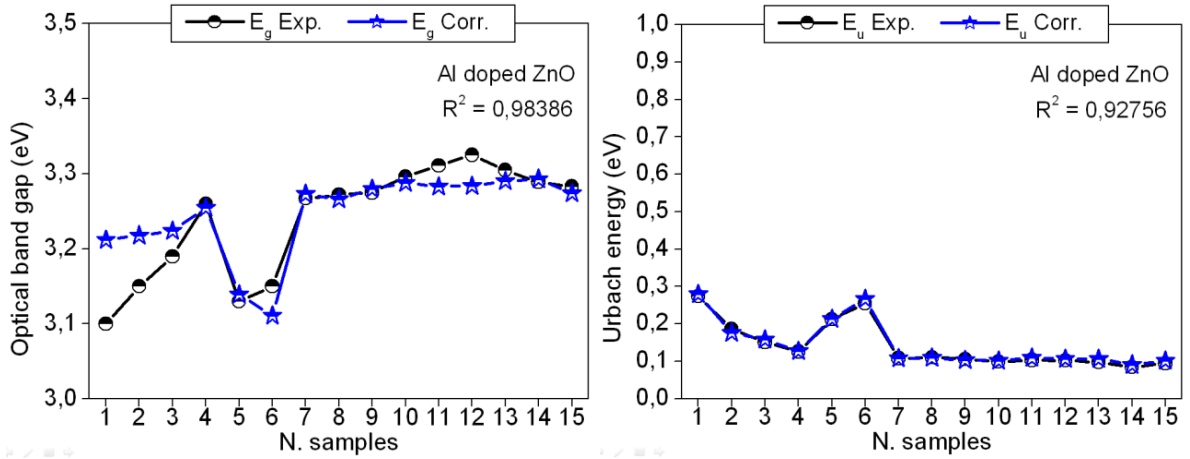

Figure 2. Summary results of experimental data, the correlate optical gap and Urbach energies in the Al doped ZnO thin films.

where a, b and A, B are empirical constants relates the undoped and Al doped ZnO thin films, respectively. These constants were measured in the section 3.1 and 3.2. The resulting errors (ΔE_u) were measured from Eq. (2) as described in the following formula:

$$\Delta E_u = \frac{1}{(b\ (1+BX_0\ ))}\frac{\Delta E_g}{E_g}E_u \qquad (4)$$

3.4. The Relative Error Measurement

The relative error value was measured between the experimental data and correlate values by the following relationship

$$\varepsilon = \left|(X_{Exp} - X_{Corr})/X_{Exp}\right| \times 100 \qquad (5)$$

where $X_{(e)}$ and $X_{(c)}$ are the experimental and correlate values, respectively, ε is the relative error.

4. Results and Discussion

In the present study an attempt is made to correlates optical gap energy with Urbach energy of undoped and Al doped ZnO thin films by varying the precursor molarity and doping concentration. Figure1 shows the calculations of the scaled parameter values according to Eq. (2) and Eq. (3) also are presented in Table 2. In the Figure 1 we investigated the estimation values of the optical gap energy and Urbach energy as a function of the samples numbers of undoped ZnO thin films. In our calculations the some points the optical energy gap found inversely proportional to the Urbach energy. As can be seen, the calculations by the proposed equations are in qualitative agreements with the experimental data. The correlation coefficient increased at the calculation of the optical gap energy, which the maximum agreement of the estimation was found to be minimum error.

As shown in Figure2 (see Table 3), significant estimation was found between the optical gap energy values and the Urbach energy values of the Al doped ZnO thin films as a function of Al concentration. The measurement in the optical gap energy and the Urbach energy values of Al doped films were also investigated by Eq. (2) and Eq. (3), respectively, found that the calculations values are in qualitative agreements with the experimental data, also the correlation coefficient increased at the calculation of the optical gap energy, which the maximum agreement of the estimation was found to be minimum relative error. The latter can be calculated from relationships:

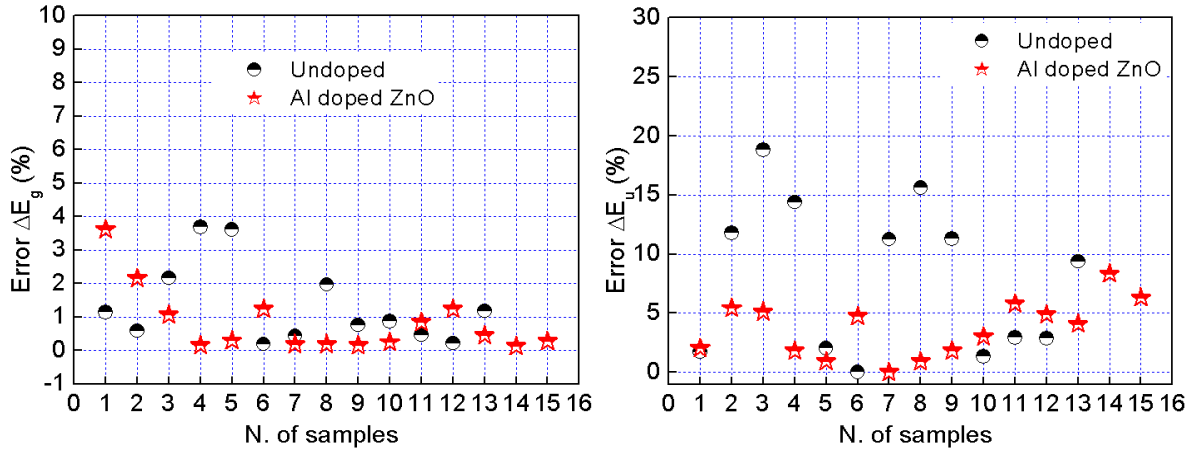

Figure 3. The correlation coefficients for optical gap energy and Urbach energy at different dopant's.

$$\left|(E_{g\ \ Exp} - E_{g\ \ Corr})/E_{g\ \ Exp}\right| \times 100 \quad (6)$$

and

$$\left|(E_{u\ \ Exp} - E_{u\ \ Corr})/E_{u\ \ Exp}\right| \times 100 \quad (7)$$

We obtained that the relative errors of all calculations are smaller than 4 % for the estimation of optical gap energy and 10 % in the Urbach energy (see Figure 3), the correlation coefficients in this correlation are also presented in Figures 1 and 2. The correlation coefficient depends on both relative errors and doping via:

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

where N is the number of measurement and ε is the relative error. The correlation coefficients are presented in Figures 1 and 2, it can be seen that the Al doped ZnO thin films are good and achieved results obtaining from increasing the correlation coefficients, this is the approach adopted to improve the band gap energy for less disorder of ZnO thin films after doping. The maximum enhanced of the correlation coefficients values were estimated for the optical gap energy values (see Figure 3).

In our calculations the optical properties for characterizing the undoped and Al doped ZnO thin films; Stoichiometric Al doped ZnO films are highly transparency and good optical band gap. We have estimated the optical band gap and the Urbach energies of the undoped and Al doped ZnO thin films by varying the precursor molarities and doping concentrations; it are predominantly influenced by the transition tail width of undoped and Al doped films. The correlation between the optical properties and the experimental conditions was investigated.

5. Conclusion

In summary, the undoped and Al doped ZnO thin films were deposited on glass substrates using the ultrasonic spray and spray pyrolysis technique. The model proposed to calculate the band gap and the Urbach energies of undoped and Al doped ZnO thin films were investigated. The relation between the experimental data and theoretical calculation with precursor molarities suggests that the band gap and/or the Urbach energies are predominantly estimated by the band gap and/or the Urbach energies and the concentration of ZnO solution. The measurements by these proposals models are in qualitative agreements with the experimental data that have been reliable in this work, because the high correlation coefficients, which were found in the range 0.84–0.99.Thus we have found that the relative errors of all calculation are smaller than 20 %.The best estimated results were obtained for Al doped ZnO thin, with minimum relative errors values were limited to 3.6 and 8.3 % for the band gap and the Urbach energies, respectively. This is the approach we have adopted in the enhance of band gaps energy and less disorder of ZnO thin films after doping. Stoichiometric Al doped ZnO films are highly transparency and good optical band gap.

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