



# Effect of optical gap energy on the Urbach energy in the undoped ZnO thin films



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## ABSTRACT

The ZnO thin films were prepared with different precursor molarities by ultrasonic spray and spray pyrolysis techniques on glass substrate at 350 °C. The thin films were deposited at different substrate temperatures ranging between 0.02 and 0.125 M. In this paper we focused our attention on the present a new approach to correlate the Urbach energy, this correlation based on experimental data were published previously. 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 Eqs. (2) and (3) with minimum relative error value was limited to 20%. 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.

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## 1. Introduction

Zinc oxide (ZnO) is a very important material for many applications like microelectronics, short-wavelength light-emitting devices, lasers, field emission devices, solar cells and gas sensors [1–5]. It is a near-stoichiometric n-type semiconductor with low resistivity values of ZnO films may be adjusted between  $10^{-3} \Omega \text{ cm}$  and  $10^{-4} \Omega \text{ cm}$  by changing the annealing conditions and doping [6]. Zinc oxide (ZnO) is a II–VI compound semiconductors, most of the group II–VI binary compound semiconductors crystallize in either cubic zinc blende or hexagonal wurtzite (Wz) structure. It has a large exciton binding energy about 60 meV at room temperature and has a wide band gap energy 3.37 eV [7–10].

ZnO thin films can be produced by several techniques such as molecular beam epitaxy (MBE) [11], chemical vapor deposition [12], electrochemical deposition [13], pulsed laser deposition (PLD) [14], the sol–gel process [15], reactive evaporation [16], magnetron sputtering technique [17] and spray pyrolysis [18,19],

have been reported to prepare thin films of ZnO. Among these, we will focus more particularly in this paper on the spray ultrasonic 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.

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. [20] 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.

## 2. Methods and model

In this study, the ZnO samples were deposited on glass substrates using the ultrasonic spray and spray pyrolysis techniques.

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**Table 1**  
The Urbach energy, optical gap energy and correlates Urbach energy in the ZnO thin films were measured as a function of concentration.

Undoped ZnO thin films, $T_s = 350^\circ\text{C}$								
Ref.	$M$ ( $\text{mol l}^{-1}$ )	$E_{g(\text{Exp.})}$ (eV)	$E_{u(\text{Exp.})}$ (eV)	$E_{u(\text{Cor.})}^1$ (eV)	$E_{u(\text{Cor.})}^2$ (eV)	$E_{u(\text{Cor.})}^3$ (eV)	$E_{u(\text{Cor.})}^4$ (eV)	$E_{u(\text{Cor.})}^5$ (eV)
[17]	0.05	3.08	0.9221	0.326	0.923	0.911	0.645	0.771
[17]	0.075	3.22	0.3186	0.303	0.279	0.233	0.251	0.132
[17]	0.1	3.37	0.085	0.221	0.149	0.140	0.082	0.032
[17]	0.125	3.15	0.1757	0.005	0.146	0.155	0.197	0.240
[18]	0.1	3.10	0.2734	0.192	0.206	0.198	0.366	0.470
[19]	0.1	3.267	0.108	0.210	0.170	0.164	0.146	0.071
[20]	0.02	3.19	0.08	0.349	0.079	0.056	0.406	0.279
[21]	0.1	3.25	0.064	0.208	0.174	0.167	0.161	0.081
[22]	0.1	3.304	0.1139	0.214	0.163	0.156	0.119	0.051
[23]	0.1	3.317	0.0983	0.215	0.160	0.154	0.115	0.042
[24]	0.1	3.27	0.17	0.210	0.171	0.164	0.145	0.073
[25]	0.1	3.25	0.209	0.209	0.175	0.168	0.162	0.089
[26]	0.1	3.23	0.490	0.207	0.179	0.191	0.181	0.113

The films were deposited at a substrate temperature of  $350^\circ\text{C}$ . The optical properties of undoped ZnO thin film such a band gap energy and the Urbach energy were obtained from our previous paper [21], and various papers [22–30]; they have studied the effect of substrate temperature and precursor molarity on the structural and the optical properties of undoped ZnO thin films, these results are shown in Table 1

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. Results and discussion**

The calculated band gap of the films is in agreement with the expected value for ZnO thin films. It was shown that the band gap can be modified when using different solutions, this is important because the use of ZnO thin films for optoelectronic applications requires the control of the band gap. Both precursor solutions give good quality ZnO thin films.

We have described previously the experimental data; 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 following steps.

Firstly, we have used the relationships in the form nonlinear to calculate the Urbach energy from the band gap energy and precursor molarity. The following relationships are evaluated in this step:

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

where  $E_u$  is the correlate Urbach energy,  $E_g$  is the band gap energy and  $M$  is the precursor molarity (see Table 1),  $a$ ,  $b$  and  $c$  are empirical constants (see Table 2). The variation of the correlate Urbach energy is shown in Fig. 1, significant correlations were found between the Urbach energy and the band gap energy values of the ZnO thin films as a function of optical gap energy. However, can be used others formulas as expressed as:

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

And

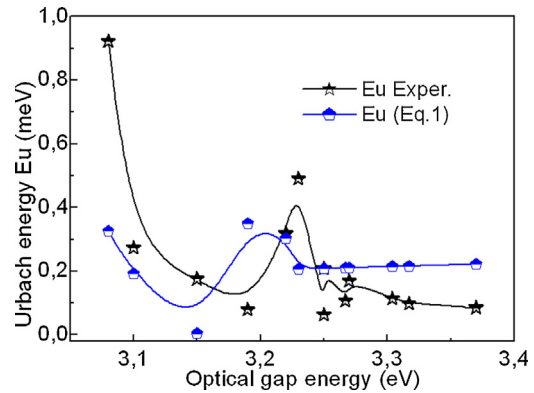
$$E_u = \frac{a + E_g}{b + c \times M} + d \ln M \tag{3}$$

where  $a$ ,  $b$ ,  $c$  and  $d$  are empirical constants were presented in Table 2. Figs. 2 and 3 show the variation the Urbach energy of the undoped ZnO thin films estimate by Eqs. (1) and (2), respectively. From these figures, we can note that the Urbach energy is predominantly estimated by the band gap energy and the concentration of ZnO solution. The variation in these estimates are less errors, we can be used also others estimations as expressed as:

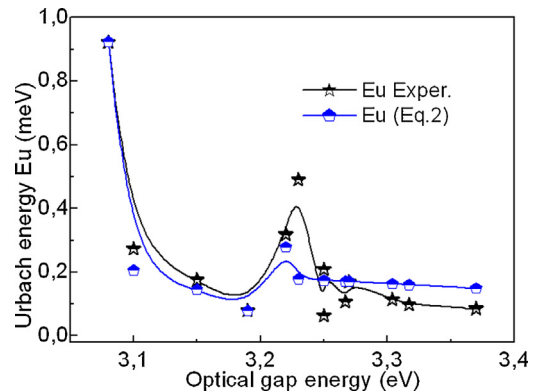
$$E_u = a \times \exp(b \times E_g + c \times M^2) \tag{4}$$

And

$$E_u = a \times M^b \times E_g^c \tag{5}$$



**Fig. 1.** The variation of Urbach energy experimental and correlations of ZnO thin films for the Eq. (1) as a function of the optical gap energy.



**Fig. 2.** The variation of Urbach energy experimental and correlations of ZnO thin films for the Eq. (2) as a function of the optical gap energy.

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