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Influence of substrate temperature on the optical properties of ZnO thin films

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ABSTRACT

The ZnO thin films were deposited at different substrate temperatures by ultrasonic spray and spray pyrolysis techniques. In this paper we present a new approach to control the optical gap energy of ZnO thin films by varying the substrate temperature. The model proposed to calculate the band gap energy with the Urbach energy was investigated. The relation between the experimental data and theoretical calculation suggests that the band gap energies are predominantly estimated by the Urbach energies, film transparency and substrate temperatures. The measurements by these proposals model are in qualitative agreements with the experimental data, which the correlation coefficients values were varied in the range 0.96 – 0.99999, indicating high quality representation of data based on Eq. (2), so that the relative errors of all calculations are smaller than 4%.

1. Introduction

Zinc oxide (ZnO) is a very important material for many applications like gas sensors, microelectronics, optoelectronic devices, UV/violet/blue solid state emitters (LEDs), laser diodes (LDs), Schottky diodes, antireflection coatings, transparent electrodes in solar cells, heat mirrors, piezoelectric devices, thin films, chemical and gas sensing [1–4]. 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) [5,6].

The above discussion has been about ZnO nanostructures, but the same features are seen in the case of ZnO-based microcavities, which are generally used as active layer facilitate in polariton injection [7]. It is known that ZnO films prepared by the spray pyrolysis technique can have a wide band gap between 3 and 3.37 eV [8,9]. Ton-That et al. [10] estimated the direct correlation between the band gap and crystal structure suggests that the band-edge optical properties of Mn-doped ZnO are predominantly influenced by the amount of Mn atoms substituting Zn on the lattice sites. However, Benramache et al. [11] studied the correlation for crystallite size in undoped ZnO thin film with the band gap energy, precursor molarity and 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, found that the crystallite size could be estimated by the optical gap energy. The aim of this work is to study the possibility of estimated the optical band gap energy by varying the Urbach energy and film transparency in undoped ZnO thin films; this calculation was studied as a function of the precursor molarity and substrate temperature. These correlations between the optical gap energy and Urbach energy were based on experimental data using ultrasonic spray and spray pyrolysis methods were published in the international journals [12–34].

In this paper, we have studied the possibility to estimate the optical gap energy with Urbach energy of undoped ZnO thin films by varying the substrate temperatures and film transparency.

2. Materials and methods

The ZnO samples were deposited on glass substrates by ultrasonic spray and spray pyrolysis techniques (see Table 1). The films were deposited at various substrate temperatures and precursor molarities. The optical properties of undoped ZnO thin film such as the optical gap energy, Urbach energy and film transparency were taken from various papers [12–34]; they have studied the effect of substrate temperature and precursor molarity on structural, optical and electrical properties of undoped ZnO thin films, these experimental data are shown in Table 2, which used for studding the correlation between optical gap energy and Urbach energy with

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Table 1
The parameters conditions were used in this paper.

Method	Ultrasonic spray or spray pyrolysis
Oxide	Zinc oxide thin films
Zn reactants	Zn acetate or $ZnCl_2$
Solvents	Ethanol – methanol – water
Substrate	Glass
Molarity (M)	0.01 – 0.02 – 0.05 – 0.075 – 0.1 – 0.125
Temperature (°C)	300, 350, 400, 450, 500

Table 2
Summary of experimental data for the optical properties of undoped ZnO thin film.

First author	Methods	M (mol l^{-1})	T (°C)	E_g (eV)	E_u (eV)	T (%)
Benramache [12]	US	0.05	350	3.08	0.9221	20
Benramache [12]	US	0.075	350	3.22	0.3186	36
Benramache [12]	US	0.1	350	3.37	0.085	79.5
Benramache [12]	US	0.125	350	3.15	0.1757	38
Gahtar [13]	US	0.1	350	3.10	0.2734	67.4
kumar [14]	SP	0.05	450	3.25	0.2527	50
Prajapati [15]	SP	0.1	300	3.06	0.392	77
Chouikh [16]	USP	0.02	350	3.19	0.08	67
Benramache [17]	US	0.1	300	3.168	0.918	69.8
Benramache [17]	US	0.1	350	3.250	0.209	79.9
Benramache [17]	US	0.1	400	3.229	0.304	56.6
Zhu[18]	PL	0.1	350	3.27	0.17	72
Zhu[18]	PL	0.1	500	3.28	0.22	84
Rahal [19]	US	0.1	300	3.292	0.1128	39.8
Rahal [19]	US	0.1	350	3.317	0.0983	67.4
Rahal [19]	US	0.1	400	3.441	0.1003	65.4
Rahal [20]	US	0.1	350	3.27	0.108	81.7
Ilican [21]	US	0.2	450	3.29	0.088	83
Hafdallah[22]	US	0.1	350	3.42	0.3071	57
Ilican [23]	US	0.1	350	3.304	0.1139	67
Abed [24]	US	0.1	300	3.25	0.0765	53
Zebbar [25]	US	0.1	250	3.15	0.115	38
Zebbar [25]	US	0.1	300	3.222	0.075	67
Zebbar [25]	US	0.1	350	3.25	0.064	70
Zebbar [25]	US	0.1	400	3.275	0.056	72
Zebbar [25]	US	0.1	450	3.275	0.067	73
Yakuphanogl [26]	SP	0.2	450	3.285	0.5757	49
Kumar [27]	SP	0.05	450	3.25	0.2527	48
Swapna [28]	SP	0.1	450	3.277	0.1144	80
Kumar [29]	SP	0.05	450	3.29	0.377	38
Prajapati [30]	SP	0.1	400	3.125	0.301	77
Mhamdi [31]	SP	0.01	460	3.28	0.06773	80
Aksoy [32]	SP	0.2	450	3.37	0.055	79
Tokumoto [33]	SP	0.1	450	3.28	0.072	80
Prajapati [34]	SP	0.1	400	3.29	0.0734	77

varying the precursor molarity, film transparency and substrate temperature.

The resulting dataset for the optical gap energy of ZnO films comprises various substrate temperatures is presented in Fig. 1,

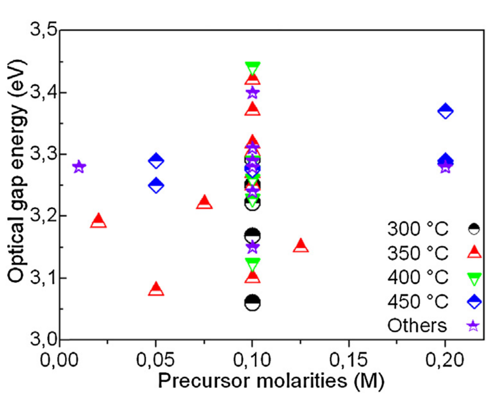

Fig. 1. Distribution as a function of precursor molarity of experimental data of the optical properties in undoped ZnO thin films at different substrate temperatures; these variations are presented in Table 1.

significant change the band gap energy with precursor molarity at different substrate temperature. From this data can be partially ascribed to differences in the deposition circumstances, such as reactor geometry, substrate temperature, annealing temperature, deposition time, flows, concentration of ZnO solution, etc. Nevertheless, the data suggests that across different authors, a common trend can be discerned. They are shown in Fig. 1 significant change the precursor molarity with substrate temperature because this is the relevant state variable for the correlation of optical properties. The graph indicates that the optical properties changed by varying the substrate temperature. The model proposed of thin films with substrate temperature is discussed.

3. Theoretical calculations

The film transparency was taken with the wavelength, which the transmission of film at 400 nm, the measurement of Urbach energy of the films from the slope of lnα vs in the range of 300 – 400 nm (3.1 – 4.1 eV), The Urbach tail energy in ZnO thin films can be determined by the following relation [35]:

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right) \quad (1)$$

where, α is the absorption coefficient, hν is photon energy ($h\nu = \frac{1240}{\lambda(\text{nm})}$(eV)), α_0 is a constant and E_u is the Urbach energy, the Urbach tail energy E_u is calculated from the slope of lnα vs. photon energy (hν) plot [36].

As the first step, we have descript previously the experimental data; one can be seen from this data, the band gap energy of ZnO thin films change in the form nonlinear with the Urbach energy and substrate temperature. In this part, we have studied the model proposal to estimate the band gap energy of undoped ZnO thin films. From Table 2, the variation of substrate temperatures were observed, in this section we established estimation in band gap energy by varying the substrate temperature such as 300, 350, 400 and 450 °C, as discussed in our published paper [11], we will used different model, the precursor molarity was fixed at 0.1 M. The final formula was evaluated in the following relationship:

$$E_g = C^{(1)}E_u + C^{(2)}\frac{T^0}{T^t} + C^{(3)}\exp\left(C^{(4)}E_u\right) \quad (2)$$

where, $C^{(1)}$, $C^{(2)}$, $C^{(3)}$ and $C^{(4)}$ are empirical constants measured as a function of substrate temperature, the variations of these constants are nonlinear for all the substrate temperature. Thus, we found the following relation:

$$C^{(n)} = \sum_{i=1}^{n} n^{N-i} f_i(T) \quad (3)$$

where, $C^{(n)}$'s are the empirical constants, n is the number of constant n = 1, 2,3 and 4 (see Eq. (5)) related of the substrate temperature T and N = 4 the total numbers of parameters. For j = 1.........4 (number of columns), the function $f_i(T)$ becomes:

$$f_1(T) = a_{11}T^3 + a_{12}T^2 + a_{13}T + a_{14} \quad (4)$$

$$f_i(T) = \sum_{j=1}^{4} a_{ij}T^{4-j} \quad (5)$$

where, a_{ij}'s are the empirical constants were measured as a function of substrate temperature (see Table 3).

4. Results and discussions

As shown in Figs. 2–5. Significant estimation was found between the optical gap energy values and the Urbach energy values of

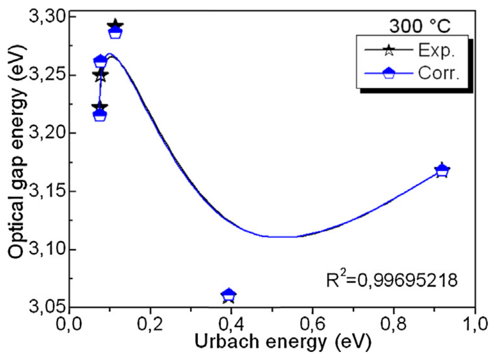

Fig. 2. Variation of the optical gap energy experimental and correlate from Eq. (2) of undoped ZnO thin films as a function of Urbach energy with 300 °C.

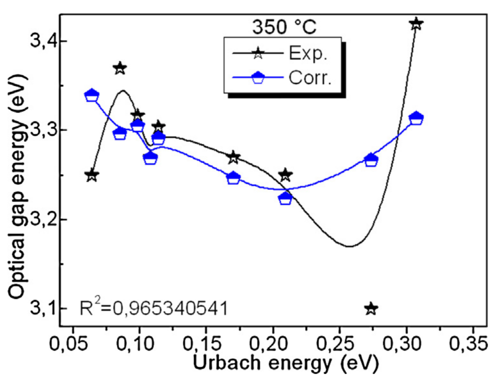

Fig. 3. Variation of the optical gap energy experimental and correlate from Eq. (2) of undoped ZnO thin films as a function of Urbach energy with 350 °C.

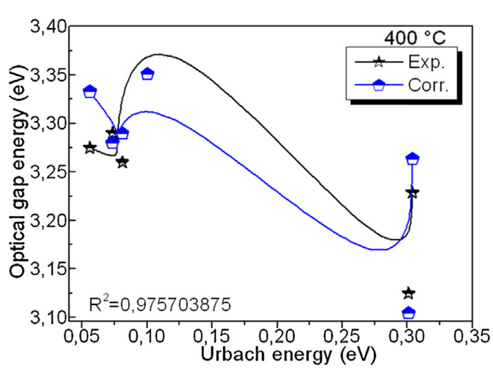

Fig. 4. Variation of the optical gap energy experimental and correlate from Eq. (2) of undoped ZnO thin films as a function of Urbach energy with 400 °C.

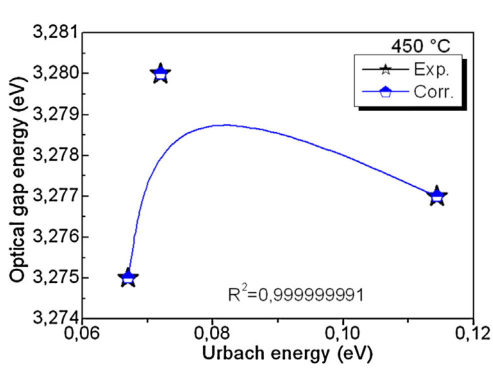

Fig. 5. Variation of the optical gap energy experimental and correlate from Eq. (2) of undoped ZnO thin films as a function of Urbach energy with 450 °C.

Table 3
The variation of the empirical constants according to Eq. (5).

	a_{i1}	a_{i2}	a_{i3}	a_{i4}
a_{1j}	−0.01205	23.12481	−14732.3195	3.12E+06
a_{2j}	0.01904	−36.53676	23275.5082	−4.92E+06
a_{3j}	−0.00801	15.37471	−9794.16499	2.07E+06
a_{4j}	0.001	−1.92161	1224.11307	−258991.664

the undoped ZnO thin films as a function of substrate temperature of 300, 350, 400 and 450 °C, respectively. The measurement in the optical gap energy values with the Urbach energy values of undoped films by Eq. (5) are in qualitative agreements with the experimental data, from these figures, we can obtain that the correlation coefficient of all calculation are higher than 0.96, can be calculated from relationship

$$R = 1 - \frac{\sum_{i}^{n} \varepsilon_i}{n} \tag{6}$$

where, n is the number of measurement and ε is the relative error, it is the difference between the experimental data and theoretical calculation as $\left|\frac{(E_{g\ Exp} - E_{g\ Corr})}{E_{g\ Exp}}\right| 100$, it can be seen that the correlations with substrate temperature are good and achieved results obtaining from increasing the correlation coefficients, this is the approach we have adopted in the enhance of band gaps energy and less disorder of ZnO thin films in the high temperature. The maximum enhanced of the correlation coefficients values were estimated for the substrate temperature of 450 °C (see Fig. 5). Thus result indicates that undoped ZnO thin films are chemically purer and have many fewer defects and less disorder owing to an almost complete chemical decomposition and contained higher optical band gap energy. The same phenomena are carried out by Mariappan et al. where they have observed with increasing the film transparency of ZnO nano-rods that the band gap energy increased from 2.97 to 3.19 eV 400 °C with increasing the substrate temperature from 300 to 400 °C, respectively [37], Mani and Rayappan [38] found the optical gap of sprayed ZnO thin films decreased from 3.30 to 3.26 eV as a function of annealing duration (0 to 24 h).

In our calculations the optical properties for characterizing the undoped ZnO thin films; Stoichiometric ZnO films are highly transparency and good optical band gap. We have estimated the optical band gaps energy with the Urbach energies of the undoped ZnO thin films by varying film transparency and substrate temperature; it are predominantly influenced by the transition tail width of undoped films. The correlation between the optical properties and the experimental conditions was investigated.

5. Conclusion

In summary, the undoped ZnO thin films were deposited on glass substrates using the ultrasonic spray and spray pyrolysis technique. The model proposed to calculate the band gap energy with the Urbach energy was investigated. The relation between the experimental data and theoretical calculation suggests that the band gap energies are predominantly estimated by the Urbach energies, film transparency and substrate temperatures. The measurements by these proposals models are in qualitative agreements with the experimental data, we found that the correlation coefficients values were varied in the range 0.96 – 0.99999, which show high quality representation of data based on Eq. (2).

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