The effect of optical gap energy on crystallite size in the Al, Co and In Doped ZnO thin films: by correlation

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Development of novel nanomaterials as a semiconductor depends on the size and structure. Undoped and doped ZnO with aluminum, cobalt and indium were deposited by ultrasonic spray technique on glass substrate at 350 °C. This paper is to present a new approach to the description of estimate of the crystallite size of doped ZnO with Al, Co and In. The correlation between structural and optical properties of doped films suggests that the crystallite size of the films is predominantly estimated by the band gap energy and the concentration of Al, Co and In. The measurement in the crystallite size of doped films with proposed model it is equal to the experimental. The maximum of relative error value was estimated in the indium and cobalt doped ZnO thin films. Thus result indicates that such Co doped ZnO thin films have many fewer defects and less disorder.

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1. Introduction

Zinc oxide is an oxide of group II metal Zinc that belongs to P63mc space group. Zinc is in the transition metal row which has $3d^{10}$ moments and hence it does not have any unpaired electron orbiting around the nucleus [1,2]. Ilican et al. [3] observed that the best a/c ratio which agreements with JCPDS standard data belongs to ZnO film at 3000 rpm. Zinc oxide is a semiconductor material with a hexagonal wurtzite (lattice parameter: a=0.324 nm, c=0.519 nm) [4]. It has been reported that ZnO has very large exciton binding energy of 60 meV and wide direct band gap (3.37 eV) [2-8] at room temperature which makes it a promising candidate for short-wavelength optoelectronic applicat-ions, such as light-emitting diodes (LEDs) [10], ultravi-olet lasers [11], ultraviolet photodetectors [12], etc.

ZnO thin films can be doped with variety of semiconductors to meet the demands of several application fields. Stoichiometric ZnO films are highly resistive. Conducting films can be made either by creating oxygen vacancies, which act as donors or by doping with various dopants such as Ga^{3+}, Mn^{4+}, Al^{3+}, Co^{2+} Cu^{2+}, V (2+, 3+, 4+ or 5+), Ni^{2+}, Mn^{2+} and Fe^{3+} [12 21]. Many attempts were reported about doped ZnO films, but most of them are related with Al doping. There are several works that us the doping such as Co, In or Al in ZnO to enhance the optical and electrical conductivity of ZnO. Moreover, The doped films can be using for various applications such as transparent electronics, piezoelectronic devices, gas sensors, and the transparent electrode window layer of thin film solar cells [14-22].

In this work, the objectives were applied in order to study the possibility of the correlation between the optical and structural properties of ZnO thin films with precursor molarity. Cuong Ton-That et al [23]. Estimated the direct correlation between the bandgap and crystal structure suggests that the band-edge optical properties of Mn-doped ZnO is predominantly influenced by the amount of Mn atoms substituting Zn on the lattice sites. Bensouyad et al [24]. They descript the relation between structural and optical properties of TiO_2: ZnO thin films, which considerate experiment study, and controlled the variation of crystallite size by modifying the annealing temperature, film thickness and doping. Therefore, Ramana et al [25]. They found that the grain size of V_2O_5 thin films produced by pulsed laser ablation strongly influences their optical characteristics. However, some works have been performed according to the settings of conditions such a temperature, the thickness, the oxidizing conditions, the nitrogen addition and doping to improve physical properties of ZnO films [26–38].

The objective of the paper is to present a new approach to calculate the crystallite size by the optical gap energy, precursor molarity and doping level of doped ZnO thin film.

Table 1 The band gap energy E_g and crystallite size G of ZnO, ZnO:Al, ZnO:Co and ZnO:In as a function of Al concentration [39–44].

	ZnO:Al		ZnO:Co		ZnO:In	
Doping, %	E_g (eV)	G (nm)	E_g (eV)	G (nm)	E_g (eV)	G (nm)
0	3.10	29.76	3.25	33.28	3.25	33.28
1	3.15	17.35	3.295	35.25	/	/
2	3.19	18.93	3.362	55.46	3.158	41.60
3	3.26	32.05	3.30	40.19	3.185	45.78
4	3.13	16.02	/	/	3.066	32.002
5	3.15	14.36	/	/	/	/

2. Methods and model

The ZnO, ZnO:Al, ZnO:Co and ZnO:In samples were deposited on glass substrates by ultrasonic spray technique at a temperature of 350 °C with 2 min of deposition time. The optical gap energy and crystallite size of the films measured with doping level in the our papers, there we have studied the effect of various parameters such as doping level, growth times, substrate temperature, annealing temperature of the ZnO thin films. However, these dopants ZnO with Al, Co and In were studied in our published papers, usually the experimental results Œ[39–44] to evaluate a correlation for the optical gap energy and crystallite size (see Table 1).

The correlation between the structural and optical properties first was studied with precursor molarity; secondary in the aim of this study we have estimated a correlation with the doping level, which the precursor molarity of ZnO is fixed at 0.1 M.

The correlation between the structural and optical properties were studied for the crystallite size (G) as a function of the band gap energy (E_g), precursor molarity M and doping level X0 of doped ZnO thin films. These parameters correlates were resulting from the following equation Eq. 1:

where $G_{(e)}$, $E_{g(e)}$, $M_{(e)}$ and $X_{0(e)}$ are the experimental data; $G_{(e)Max}$, $E_{g(e)Max}$, $M_{(e)Max}$ and $X_{0(e)Max}$ are maximal experimental values and $G_{(*)}$, $E_{g(*)}$, $M_{(*)}$ and $X_{0(*)}$ are the first values have been consisted in the correlate relationships. Table 2 The variation of empirical constants estimated by Eq. (3) of ZnO:Al , ZnO:Co and ZnO:In.

$$\begin{cases} G_{(*)} = \dfrac{G_{(e)}}{G_{(e)Max}} \\ E_{g(*)} = \dfrac{E_{g(e)}}{E_{g(e)Max}} \\ M_{(*)} = \dfrac{M_{(e)}}{M_{(e)Max}} \\ X_{0(*)} = \dfrac{X_{0(e)}}{X_{0(e)Max}} \end{cases}, \tag{1}$$

3. Results

We have estimated the relationships between the crystallite size and the band gap energy with the precursor molarity in ZnO thin films. We have obtained the following empirical relationships:

$$G_{(c)} = a \times b^{E_{g(*)}} \times M_{(*)}{}^{c}, \tag{2}$$

where $G_{(c)}$ is the correlate crystallite size; a, b and c are empirical constants as $a \approx 0.0001558$, $b \approx 6627$ and $c \approx 0.3399$.

The doped ZnO thin films were deposited for the precursor molarity equal to 0.1 M, the letter has been indicated in doped ZnO thin films with the parameters a, b and c are constants. For this reason we have found the following empirical relationships, Eq.(3):

$$G_{(c)} = ((\exp(d \times X_0) \times (1.558 \times 10^{-4} \times 6627^{E_{g(*)}} \times M_{(*)}{}^{0.3399}))^{(1+e \times E_{g(*)} \times X_0)} + f \times X_0), \tag{3}$$

ZnO :Al $\quad G_{(c)} = ((\exp(0.3279 \times X_0) \times (1.558 \times 10^{-4} \times 6627^{E_{g(*)}} \times M_{(*)}{}^{0.3399}))^{(1+1.014 \times E_g \times X_0)} - 0.4876 \times X_0)$

ZnO :Co $\quad G_{(c)} = ((\exp(0.3322 \times X_0) \times (1.558 \times 10^{-4} \times 6627^{E_{g(*)}} \times M_{(*)}{}^{0.3399}))^{(1+1.517 \times E_g \times X_0)} - 0.6446 \times X_0)$

ZnO :In $\quad G_{(c)} = ((\exp(1.211 \times X_0) \times (1.558 \times 10^{-4} \times 6627^{E_{g(*)}} \times M_{(*)}{}^{0.3399}))^{(1-0.5167 \times E_g \times X_0)} - 0.7096 \times X_0)$

where d , e and f are parameters constants dependences of dopant and doping level. These parameters are collected in Table 2, estimated as a function of dopant element.

Table 2 The variation of Empirical constants estimated by Eq.(3) of ZnO:Al , ZnO:Co and ZnO:In

Dopant element	Al	Co	In
Empirical constants			
d	0.3279	0.3322	1.211
e	1.014	1.517	-0.5167
f	-0.4876	-0.644	-0.7096

4. Results and discussion

As shown in Figs 1, 2 and 3. Significant correlation was found between the crystallite size and the optical gap values of the doped ZnO thin films as a function of Al, Co and In concentration, respectively. The measurement in the crystallite size of doped films by these proposals models are in qualitative agreements with the experimental data, thus the relative error of this correlation is smaller at doping levels of 0 and 3 wt. %. The minimum error value was estimated in the cobalt and indium doped ZnO thin films (see Fig. 4). Thus result indicates that such ZnO:Co and ZnO:In 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.

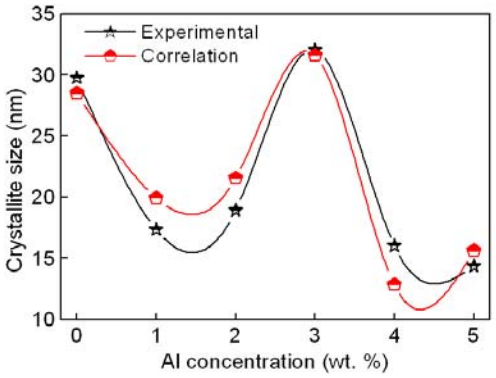

Fig. 1. The experimental crystallite size and correlation of ZnO:Al thin films as a function of the Al concentration.

The maximum enhancement of the crystallite size was found to be minimum error after doping at 3 wt. %, The amount of Al, Co and In doping contents are achieved in doped ZnO film with 3 wt. %. Based on the experimental and correlation values for the crystallite size were developed. Good agreement was found between the calculated and experimental values.

In our calculations the crystallite size for characterizing the doped ZnO thin films; the letter is a single crystals exhibit n-type semiconductors with a high crystallinity.

We will have estimated the crystallite size of the doped films by optical band gap with doping levels; it is predominantly influenced by the transition tail width of undoped and doped ZnO thin films. The correlation between the crystallite size and the band gap with the doping level was investigated.

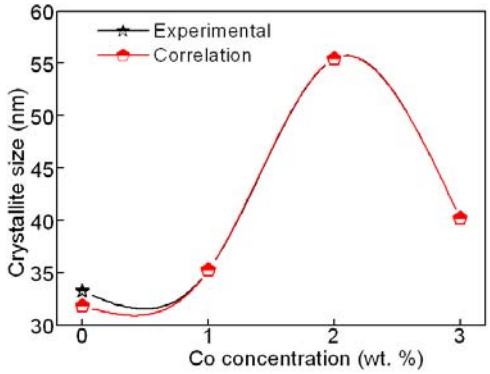

Fig. 2. The experimental crystallite size and correlation of ZnO:Co thin films as a function of the Co concentration.

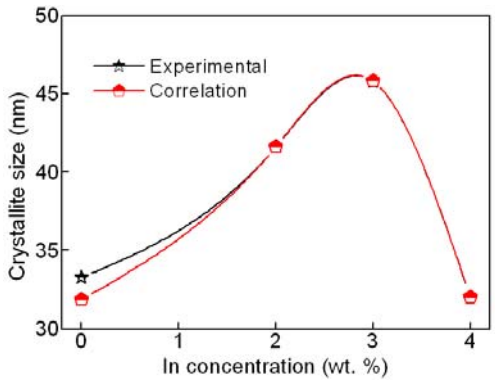

Fig. 3. The experimental crystallite size and correlation of ZnO:In thin films as a function of the In concentration.

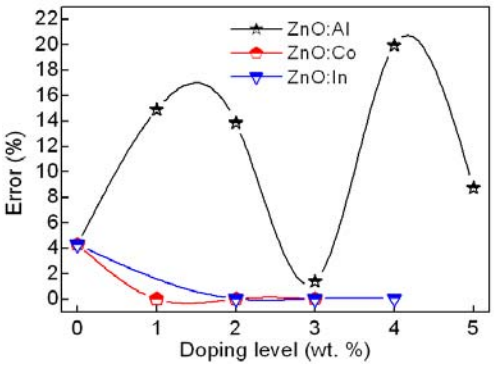

Fig. 4. The variation of errors of doped ZnO thin films as a function of the doping level.

Table 3 The experimental crystallite size G and correlation of ZnO:Al, ZnO:Co and ZnO:In as a function of doping level.

	ZnO:Al		ZnO:Co		ZnO:In	
Doping, %	G_c (nm)	G_e (nm)	G_c (nm)	G_e (nm)	G_c (nm)	G_e (nm)
0	28.48	29.76	31.85	33.28	31.85	33.28
1	19.93	17.35	35.25	35.25	/	/
2	21.55	18.93	55.46	55.46	41.61	41.60
3	31.61	32.05	40.18	40.19	45.79	45.78
4	12.82	16.02	/	/	32.01	32.002
5	15.62	14.36	/	/	/	/

G_c correlate value and G_e: experimental value.

5. Conclusion

In summary, high-quality transparent of undoped and doped zinc oxide thin films with aluminum, cobalt and indium were deposited by ultrasonic spray technique on glass substrate at 350 °C. The correlation between the crystallite size and the band gap with dopant concentration of Al, Co and In were investigated. In this paper we have presented a new approach to the description of estimation of the crystallite size of doped ZnO with Al, Co and In. we have obtained that the crystallite size of the doped films can be estimated by varying the band gap energy and the concentration of Al, Co and In. Some measurements in the crystallite size of doped films with proposed model it is equal to the experimental values. The measured of relative errors values were changed between 0 and 20 %, the cobalt and indium doped ZnO thin films having a maximum enhanced with maximum of relative error value of about 0.02 %. Thus result indicates that such Co doped ZnO thin films have many fewer defects and less disorder.

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