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Correlation with annealing temperature of pure and doped ZnO thin film

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Abstract

Transparent conducting pure and doped zinc oxide thin films with cobalt and indium were deposited on glass substrate using the ultrasonic spray method. The thin films were deposited at 350°C and annealed at 500°C. The direct correlation between the difference in crystallite size (ΔG) and the difference in Urbach energy (ΔE_u) suggests that the crystallite sizes of the films are predominantly influenced by the disorder of the thin films. The crystallite sizes in the thin films depend on the disorder (fewer defects), where minimum disorder confirmed high crystallinity. The correlation of the conductivity before and after the annealing temperature also indicates that the measurement of the electrical conductivity of the films by the optical band gap was equal; it is predominantly influenced by the transition tail width of undoped and doped ZnO thin films. It will be shown that the conductivity of undoped and doped ZnO correlates directly with the band gap of the host material. The model proposed of pure and doped ZnO thin film with annealing temperature was investigated.

Keywords: ZnO, Semiconductor doping, Thin films, 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, characterized by two interconnecting sublattices of Zn^{2+} and O^{2-}, such that each Zn ion 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 and a high exciton binding energy (~60 meV) [3, 4]. The resistivity values of ZnO films may be adjusted between 10^{-4} Ω cm and 10^{-4} Ω cm by changing the annealing conditions and doping [5].

In general each existing and prospective application of polycrystalline films requires specific optical, electrical, chemical, mechanical, or structural properties, which almost all strongly depend on the surface quality of the film [6]. It is well-known that the physical properties of these surfaces are improved after annealing, as that engenders a change in the physical properties with fewer defects such as oxygen diffusion (or oxygen vacancies) created during the deposition process. For this reason, this work focuses on the correlation between these physical properties in ZnO, ZnO:Co and ZnO:In films such as: (i) crystallite size and Urbach energy, and (ii) electrical

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conductivity and the optical band gap; when they are correlated before and after the annealing temperature of all films.

In this paper, we study and evaluate the relationship between the difference in crystallite size (ΔG) and the difference in Urbach energy (ΔE_u) of the deposited films, and also study the possibility to estimate the correlation between electrical conductivity and the optical band gap before and after the annealing temperature. It will be shown that the conductivity of undoped and doped ZnO is directly correlated with the band gap of the material.

2. Method

The ZnO, ZnO:Co and ZnO:In samples were deposited on glass substrates using the ultrasonic spray technique. The doped films with indium and cobalt concentration of 3 and 2 wt. %, respectively were deposited at 350°C with 2 minutes of deposition time. The thin films were annealed at 500°C. The physical properties of undoped and doped thin film such as crystalline structure, optical gap energy and electrical conductivity were taken from measurements in our publications, where we studied the effect of various parameters such as substrate temperature, annealing temperature, growth times, cobalt and indium concentrations of ZnO thin films [7–10] (see Table 1).

The direct correlation between the structural and optical properties were studied for the difference in crystallite size (ΔG) and the difference in Urbach energy (ΔE_u) of the ZnO, ZnO:Co and ZnO:In films. The correlation of the thin films between the electrical and optical properties before and after the annealing temperature was also studied to measure electrical conductivity and the optical band gap. The model proposed of pure and doped ZnO thin film with annealing temperature is discussed.

3. Results and discussion

3.1. Correlation between the structural and optical properties

The aim was to study the correlation between the structural and optical properties of undoped and doped ZnO thin films. Previously reported relationships between the band gap and the lattice parameters (a and c) showed very large variations from linearity [11] and plotted the band gap as a function of lattice constants a and c.

Table 1: The variation in crystallite size, optical gap energy and electrical conductivity of ZnO, ZnO:In and ZnO:Co thin films experimental for with and without annealing temperature of 500°C

		G, nm	E_g, (eV)	E_u, meV	σ, $(\Omega{\cdot}\mathrm{cm})^{-1}$
Without	ZnO	33.28	3.250	209	7.5
	ZnO:Co	55.46	3.362	108	7.6
	ZnO:In	45.78	3.185	328	7.5
Annealed	ZnO	63.99	3.367	85	7.7
	ZnO:Co	59.42	3.319	40	8.3
	ZnO:In	55.47	3.226	230	9.5

Annealing at high temperature leads to the formation of oxygen diffusers, but not zinc interstitials since their formation energy is high [12]. Furthermore, zinc interstitials are very fast diffusers, and are mobile at temperatures as low as 200–350°C such as exist with deposited films. As we demonstrated above, the concentrations of these point defects decrease with increasing oxygen partial pressure and substrate temperature, leading to less conductive ZnO films. Moreover, since the crystallite sizes of the films are changed substantially in the oxygen, they anneal at 500°C as shown in Table 1. Annealing of the as-grown films in air resulted in complete elimination of the ZnO films, thus these point defects decrease; which means adequate temperature for less disorder (see Table 1).

We estimated the relationships between the difference in crystallite size (ΔG) and the difference in Urbach energy (ΔE_u) which are measured as a function of the with and without annealing temperature in all films as depicted in Fig. 1. One can observe that the difference in crystallite size (ΔG) reduces as the difference in Urbach energy (ΔE_u) of the thin films decreases. We found the following empirical relationships:

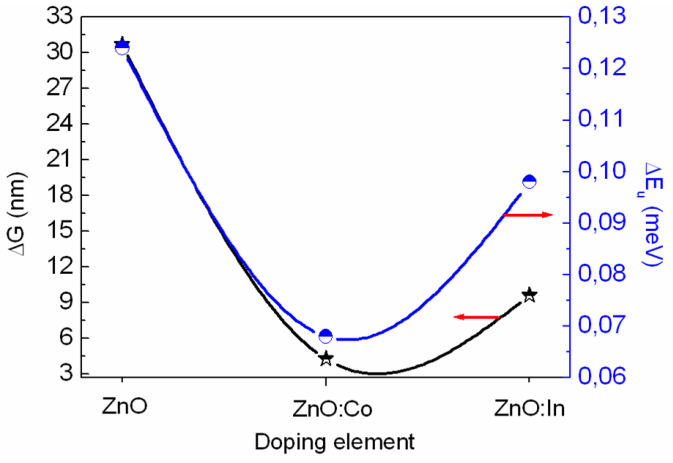

Figure 1: The variation of the difference in crystallite size (ΔG) with the difference in Urbach energy (ΔE_u) of ZnO, ZnO:In and ZnO:Co thin films

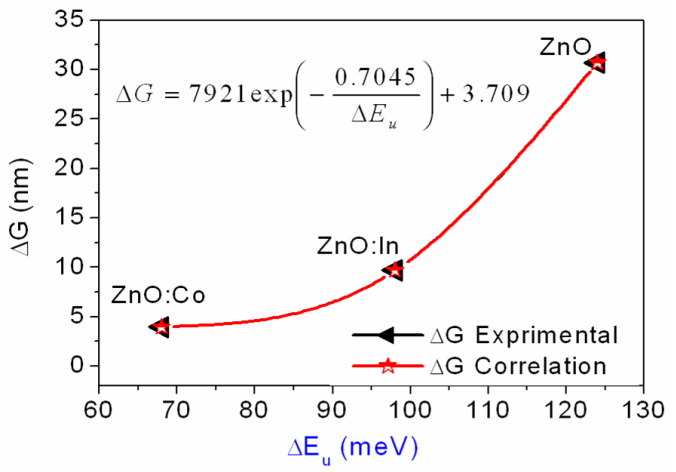

Figure 2: The correlation between the difference in crystallite size (ΔG) with the difference in Urbach energy (ΔE_u) of ZnO, ZnO:In and ZnO:Co thin films

Table 2: The variation of the difference in crystallite size (ΔG) experimental and correlated by the Urbach energy (ΔE_u) of ZnO, ZnO:In and ZnO:Co thin films with annealing temperature of 500°C

		ΔE_u, eV	ΔG_E, nm	ΔG_C, nm
$\Delta G =$ 7921	ZnO	0.124	30.71	30.71
$\exp\left(-\frac{0.7045}{\Delta E_u}\right)$	ZnO:Co	0.068	3.96	3.96
+3.709	ZnO:In	0.098	9.69	9.69

$$\Delta G = A \exp\left(\frac{B}{\Delta E_u}\right) + C \tag{1}$$

Where ΔG is the difference in crystallite size before and after the annealing temperature, A, B and C are constants as $A \approx 7921$, $B \approx -0.7045$ and $C \approx 3.709$; ΔE_u is the difference in Urbach energy before and after the annealing temperature. The results are set out in Table 2. and are obtained from the following relations: $\Delta G = G_{annealed} - G_{without}$ and $\Delta E_u = E_{u(annealed)} - E_{u(without)}$:

$$G_{annealed} - G_{without} = A \exp\left(\frac{B}{E_{u(annealed)} - E_{u(without)}}\right) \tag{2}$$

This correlation also indicates that the crystallite sizes of the films are predominantly influenced by the disorder of the thin films. The crystallite size in the thin films depends on the disorder (fewer defects), where minimum disorder confirmed high crystallinity. The correlation between the structural and optical properties was investigated. This is shown in Fig. 2 and Table 2. Significant correlation was found between the difference in crystallite size experimental and correlated as a function of the difference in Urbach energy.

3.2. *Correlation between the electrical and optical properties*

The deposition temperature is an important factor that affects the conductivity of the asdeposited ZnO thin films. The zinc interstitial defects, which are also often created during the deposition process [13, 14], with annealing temperature, undergo a change in physical properties with fewer defects such as oxygen diffusion (or oxygen vacancies) created during the deposition process, which will increase conductivity. This is due to the reaction between oxygen and electrons in the conduction band.

To examine the correlation of the thin films between electrical conductivity and band gap energy (see Fig. 3), we used the linear formula to estimate electrical conductivity from optical gap values; our study uses one formula with different constants of the films before and after annealing temperature.

3.2.1. *Correlation before annealing temperature*

From the optical and electrical properties, we obtained an increase in electrical conductivity with in-

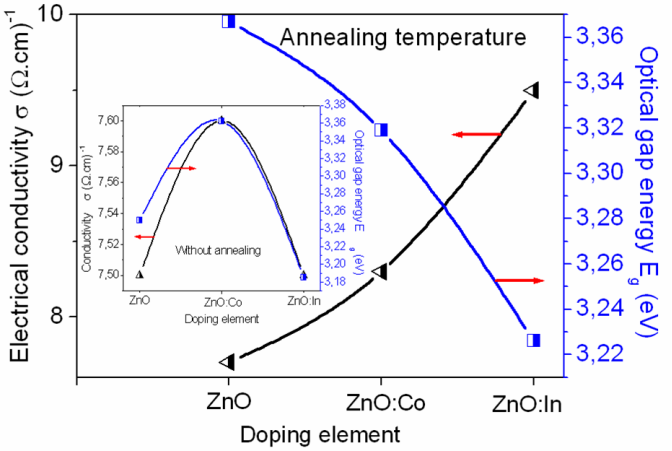

Figure 3: The variation of electrical conductivity σ before and after annealing temperature as a function of the optical band gap energy E_g for ZnO, ZnO:In and ZnO:Co thin films

creasing optical gap values; this is shown in Table 1. We found the following empirical relationships:

$$\sigma_0 = a\left(bE_g + c\right) \tag{3}$$

Where σ is electrical conductivity, E_g is band gap energy, a, b and c are constants as $a \approx 1.259$, $b \approx 0.4663$ and $c \approx 4.462$. These parameters are dependent of without annealing temperature. These results are set out in Table 3.

3.2.2. Correlation after annealing temperature

We used the above formula to estimate other constants for a model proposed between the optical and electrical properties. We estimated different constants which are dependent on the annealing temperature; they are shown in Table 1. We found the following empirical relationships:

$$\sigma_T = A\left(BE_g + C\right) \tag{4}$$

Where σ_T is electrical conductivity, E_g is band gap energy, A, B and C are constants as $A \approx 6.275$, $B \approx -2.058$ and $C \approx 8.16$. These results are set out in Table 3.

As shown in Figs. 4 and 5 significant correlation was found between the electrical conductivity and optical gap values of the ZnO, ZnO:Co and ZnO:In thin films. This correlation also indicates that the measurement of electrical conductivity of the films

Table 3: The variation in electrical conductivity σ of ZnO, ZnO:In and ZnO:Co thin films experimental and correlated by the optical band gap energy E_g for with and without annealing temperature of 500°C

		E_g, eV	σ_E, $(\Omega{\cdot}\mathrm{cm})^{-1}$	σ_C, $(\Omega{\cdot}\mathrm{cm})^{-1}$
Without $\sigma = 1.259\times(0.4663E_g +4.462)$	ZnO	3.250	7.5	7.53
	ZnO:Co	3.362	7.6	7.59
	ZnO:In	3.185	7.5	7.48
Annealed $\sigma = 6.275\times(-2.058E_g +8.16)$	ZnO	3.367	7.7	7.68
	ZnO:Co	3.319	8.3	8.33
	ZnO:In	3.226	9.5	9.49

by the optical band gap was equal; it is predominantly influenced by the transition tail width of undoped and doped ZnO thin films.

The direct correlation between electrical conductivity and band gap was investigated.

4. Conclusion

In conclusion, the direct correlation between the difference in crystallite size (ΔG) and the difference in Urbach energy (ΔE_u) suggests that the crystallite sizes of the films are predominantly influenced by the disorder of the thin films. The crystallite size in the thin films depend on the disorder (fewer defects), where the minimum disorder confirmed high crystallinity. The correlation of the conductivity before and after annealing temperature also indicates that the measurement of the electrical conductivity of the films by the optical band gap was equal; it is predominantly influenced by the transition tail width of undoped and doped ZnO thin films. It will be shown that the conductivity of undoped and doped ZnO is directly correlated with the band gap of the host material. The model proposed of pure and doped ZnO thin film with annealing temperature was investigated.

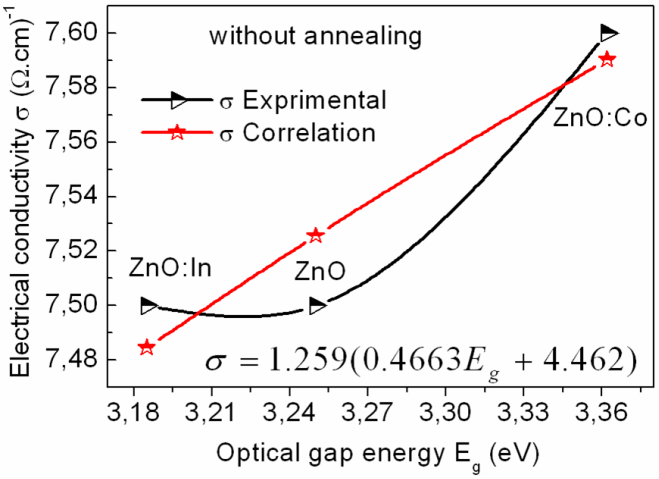

Figure 4: The correlation between electrical conductivity σ and optical band gap energy E_g for ZnO, ZnO:In and ZnO:Co thin films without annealing

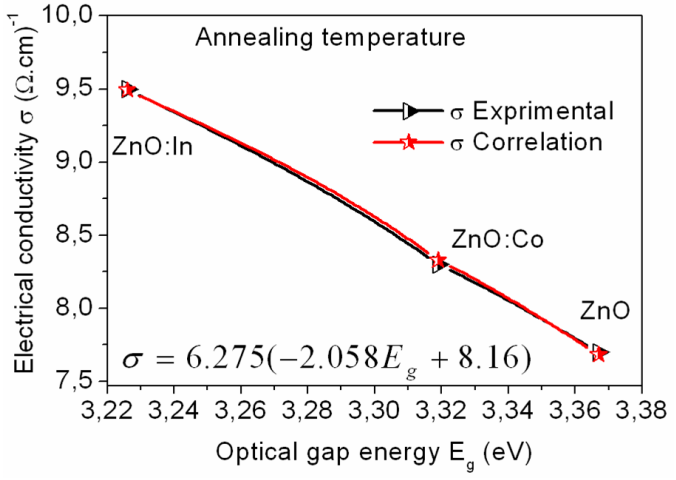

Figure 5: The correlation between electrical conductivity σ and optical band gap energy E_g for ZnO, ZnO:In and ZnO:Co thin films for annealing temperature at 500°C

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