Thickness Effect on the Structure and Electrical Properties of ZnO Thin Films

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Abstract

The objective of this research is studing the effectes of the thickness on the structur ,the d.c. conductivity and the activation energies for ZnO films Thin films of ZnO were deposited by spray pyrolysis technique on glass substrates. The thickness of the films (t) was determined using the weighing-method. Crystal structure were investigated by means of a X-ray diffraction XRD, it was found that all films have three peaks located at $2\theta \approx 31.8^{o}$, 34.4^{o} and 36.3^{o} with hkl{(100), (002), and (101)} respectively and that the crystallinety increasing with increasing the thickness(t) .The d.c. conductivity for ZnO films has been studied as a function of T for different thicknesses (900, 1400 and 4000 nm) From all samples we noticed that the d.c. conductivity increases with increasing the temperature Also we can be seen the increasing of (σ) with the increasing of film thickness , we noticed the decreasing of activation energies with the increasing of the film thickness.

تأثير السمك على التركيب والخواص الكهربائية لأغشية ZnO الرقيقة

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الخلاصة

يهدف البحث دراسة تا ثير السمك لاغشية ZnO الرقيقة على التركيب البلوري والتوصيلية المستمرة .d.c وبالتالي على طاقة التنشيط .

حضرت اغشية ZnO الرقيقة بطريقة الرش الحراري على اساس من الزجاج , سمك الغشاء t تم ايجاده بالطريقة الوزنية . اما التركيب البلوري تم فحصه باستخدام حيود اشعة -X- ووجدنا ان جميع الاغشية ذات تركيب متعدد التبلور لها ثلاث قمم عند الزوايا (31.8 ,34.4 و36.3)وقيم معاملات ميلر المقابلة {(101),(002),(100)}hkl على التوالي ,ووجدنا ان التبلور يزداد مع زيادة السمك . التوصيلية d.c لاغيشة ZnO درست كدالة لدرجة الحرارة T لمختلف الاسماك (900, 1400 and 4000 nm) ووجدنا ان التوصيلية .d.c تزداد مع ازدياد درجة الحرارة وكذلك لاحظنا ان التوصيلة تزداد ايضا مع ازدياد السمك للغشاء ونعلم ان طاقة التنشيط تقل مع ازدياد التوصيلة وهذا ما حصلنا عليه.

1- INTRODUCTIO

ZnO film has been received increased attention for various microelectronic applications. It has potential uses in photo detectors , solar cells, and light Emitting diodes (LEDs)[1,2] . ZnO is a II–VI compound n-type semiconductor with a wide direct band gap of 3·3 eV (at room temperature) and has a hexagonal wurtzite structure with space group [3-6], cell parameters of a =0·3250 nm, c = 0·5206 nm fig (1) . It has a large exciton binding energy of 60 meV s[6,7] .To produce the electronic devices using ZnO films, it is essential to study the electrical and other properties such as structural

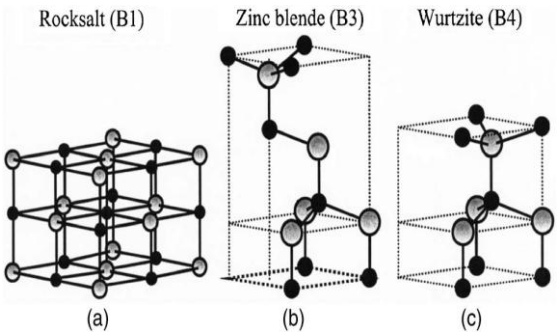


Fig (1)
Stick and ball representation of ZnO crystal structures: (a) cubic rocksalt (B1), (b) cubic zinc blende (B3), and (c) hexagonal wurtzite (B4). The shaded gray and black spheres denote Zn and O atoms, respectively(9)

In this study, ZnO thin films were deposited by the spray pyrolysis technique on glass substrates. The crystallinity and structure of these films were analyzed by X-ray diffraction.

2-Experimental procedure

Various techniques have been used to synthesize ZnO. Low temperature deposition methods for thin film photovoltaic devices are of interest to enable the use of lightweight, flexible substrates. Such devices provide a higher power-to-weight ratio and significant cost savings compared to current technologies. The spray pyrolysis method is a well-known nanostructured thin-film preparation method with excellent features such as the need for no sophisticated equipment, and quality targets or substrates; also, film thickness and stoichiometry are easy to control and the resulting films are well compacted.

ZnO films have been produced by spraying the aqueous solution of (0.1)M of Zinc acetate $CH_3.COO)_2.Zn2H_2O \equiv 219.5$g/mol onto the microscope glass substrates ($1x25x75mm^3$) at substrate temperature of 370 ^oC. The substrate temperature was maintained to within $\pm 10^oC$. 50 ml alcohol was used for preparing the solutions. The used Zinc acitate mass was calculated using the following equation:

weight(g)=Molarity(mol/l)*Volume(l)*Molecular weight (g/mol)…….(1)

Prior to deposition, the substrates were cleaned in with cleaner solution, distilled water and followed by alcohol using ultrasonic bath.The schematic arrangement of spray pyrolysis set-up is shown in Fig. (2). Spray pyrolysis is basically a chemical process, that is the spraying of the solution onto substrate held at high temperature, where the solution reacts forming the desired film.The spray rate of the solution was adjusted to be five sprinkling in minute, the sprinkling time about ten second. The normalized distance between the spray nozzle and the substrate is 29cm. Nitrogen was used as the carrier gas. The temperature of the substrate was controlled by an Iron-Constantan thermocouple.The thickness of the films (t) was determined using the weighting-method.

$$T=\frac{\Delta m}{A\rho} \qquad \ldots(2)$$

Where Δm = the mass difference of slide after and before the deposition, A= area =2.5*7.5 cm^2 and ρ= ZnO mass density=5.6 g/cm^3.

Crystal structure were investigated by means of a X-ray diffraction XRD Shimadzu 6000 Japan using CuKα, λ=1.5405A^o). To study the electrical properties for the films Ohmic contacts for the prepared films were produced by evaporating (Al) electrodes of 300 nm thickness, by means of thermal evaporation methods, using Edward coating unit model (606) under high vacuum (10^{-5}m bar) which was provided by rotary and diffusion pumps, then the d.c conductivity (σ) have been studied using the electrical circuit which was consisting of oven type Herease and kethley, while fio the a.c conductivity A multi–frequency RLC meters model HP-R2C(4274A) have been used.

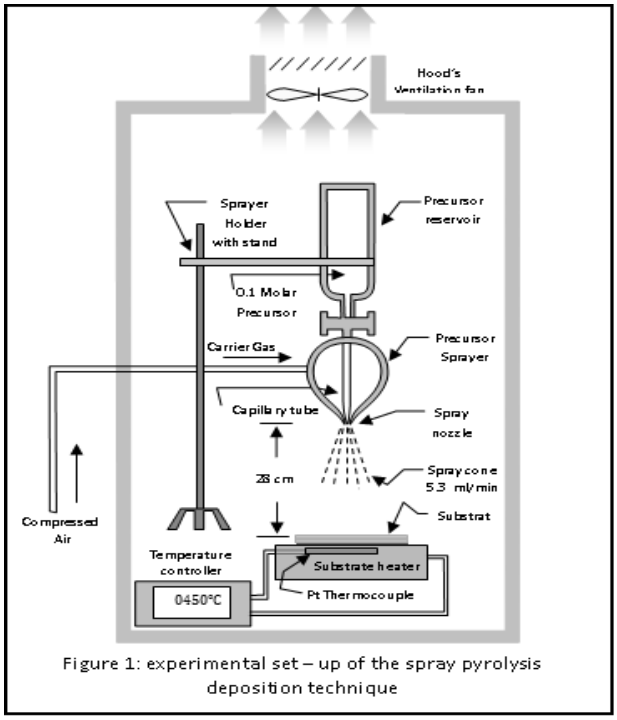


Figure 1: experimental set – up of the spray pyrolysis deposition technique

Figure (2). Schematic of the spray pyrolysis system.

3-Results and Discussion

Fig. (3) shows the XRD for ZnO thin films deposited on glass substrates at different thicknesses (900, 1400, 1450 and 4000 nm**).**

The patterns show that at all the films have three peaks located at 2θ ≈ 31.8^o, 34.4^o and 36.3^o with hkl{(100), (002), and (101)} respectively, in addition another peak appear at thickness 4000 nm located at 2θ ≈47.58^o with hkl (102), Table (1) shows all the peaks opserved in all films and the standard peaks from JSPDS and its intensities.

Our result declared a good coincidence with the reference data and declared that the film have a good crystalline with Hexagonal structure and the crystallinety increasing with increasing the thickness. The grain size was calculated by Scherrer's formula:

$$b = \frac{0.89\,\lambda}{\Delta(2\theta).\cos(\theta)} \quad \text{.....(3)}$$

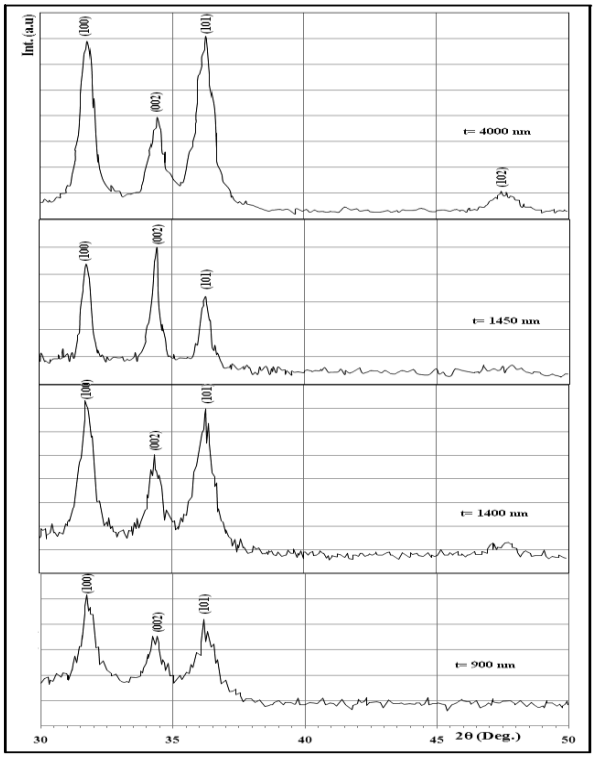


Fig. (3) XRD for ZnO thin films on glass at different thicknesses (900, 1400, 1450 and 4000 nm).

Thickness (nm)	Peak 2θ (deg.)	Exp. d_{hkl} (A^o)	Int. %	Stan. d_{hkl} (A^o) [49]	Int. %	Plane (h k l)
900	36.2922	2.47334	81	2.4759	100	101
	31.8361	2.8086	100	2.8143	57	100
	34.3635	2.6076	60	2.6033	44	002
1400	36.2534	2.4759	93	2.4759	100	101
	31.8213	2.8099	100	2.8143	57	100
	34.4064	2.6044	60	2.6033	44	002
1450	36.2651	2.47513	61	2.4759	100	101
	31.7932	2.81232	82	2.8143	57	100
	34.4054	2.60454	100	2.6033	44	002
4000	36.2526	2.47595	100	2.4759	100	101
	31.8167	2.81029	98	2.8143	57	100
	34.4142	2.60389	50	2.6033	44	002
	47.5794	1.90961	10	1.9111	23	102

Table (1) Comparison of observed and standard (d) values observed in films deposited in different thickness

Where θ is the Bragg angle, $\Delta(2\theta)$ the full half width in radiant and λ the X-ray wavelength. The values of grain size were shown in table(2), this table shows that the grain size decreased with increasing the film thickness .

t (nm)	$\Delta(2\theta)$ deg.	$\Delta(2\theta)$ Rad.	$2\theta^o$	θ^o	b (nm)
900	0.5432	0.0095	31.8361	15.92	15.19
1400	0.6396	0.0111	31.821	15.91	12.73
1450	0.6743	0.0117	34.4054	12.203	12.06
4000	0.7542	0.0132	36.2526	18.126	10.95

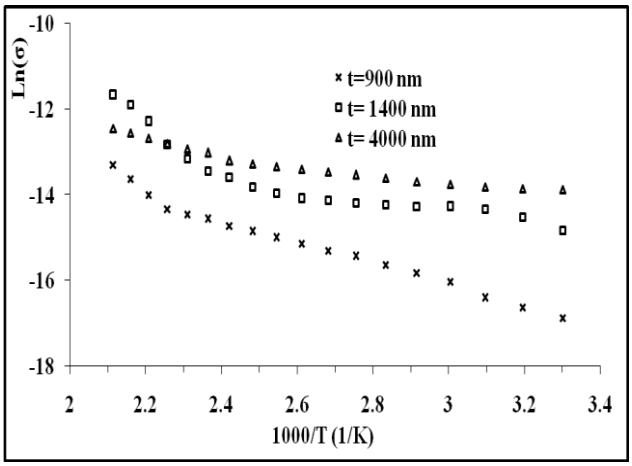
Table(2) The value of FWHM, Bragg angle and the grain size at different thicknesses

4-D.C Conductivity

The d.c. conductivity for ZnO films has been studied as a function of Ln(σ) versus reciprocal of T at different thicknesses (900, 1400 and 4000 nm) within the range of (303-473 K) as shown in Fig.(4). D.c conductivity (σ) of samples obtained using the following equation:

$$\sigma = l/R.\ t.\ d \quad \text{.....(4)}$$

Where, l: distance separated the electrodes, R: Resistance of film, t: film thickness, d: electrodes width.



Fig(4)The relation between Ln(σ) versus reciprocal of Temp.
for ZnO at different thicknesses

From all the samples we can noticed that the d.c. conductivity increases with increasing the temperature As seen from Fig.(4) function of lnσ versus reciprocal temperature for all samples has a relation closed to linearity . This figure declared that in all sample there are two stages of conductivity throughout the heating temperature range. The first activation energy (E_{a1}) occured at higher temperature

and this activation energy was due to conduction of the carrier excited into the extended states beyond the mobility edge, while the second activation energy (E_{a2}) occurs at low temperature and the conduction mechanism of this stage is due to carriers transport to localized states near the valence and conduction bands. Also it can be seen that the increasing of (σ) with the increasing of film thickness and decreasing of (σ) with the increasing temperature, this was caused by the decreasing of the grain size which lead to increasing the mobility and was caused by the increasing of the activation energies.

The activation energy (E_a) of the films can be deduced from multiplying Boltzman constant (k_B) by the slope of the plot of (ln σ) versus the reciprocal temperature in (K^{-1}).

Table (3) shows the E_{a1}, E_{a2} and temperature range for different film thickness. We can noticed from this table the decreasing of activation energies with the increasing the film thickness.

Thickness (nm)	Activation energy (eV)		**Temp. range (K)**
900	Ea1	0.590702217	443-473
	Ea2	0.197373973	303-443
1400	Ea1	0.550059354	443-473
	Ea2	0.085489332	303-443
4000	Ea1	0.195064368	443-473
	Ea2	0.065523551	303-443

Table (3)the E_{a1}, E_{a2} and temperature range
for different film thickness.

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