Preparation and properties of Nanostructure Zinc Oxide Thin Films

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Abstract

Zinc Oxide (ZnO) is probably the most typical II-VI semiconductor, which exhibits a wide range of nanostructures. In this paper, polycrystalline ZnO thin films were prepared by chemical spray pyrolysis technique, the films were deposited onto glass substrate at 400 °C by using aqueous zinc chloride as a spray solution of molar concentration of 0.1 M/L.
The crystallographic structure of the prepared film was analyzed using X-ray diffraction; the result shows that the film was polycrystalline, the grain size which was calculated at (002) was 27.9 nm. The Hall measurement of the film studied from the electrical measurements show that the film was n-type. The optical properties of the film were studied using measurements from VIS-UV spectrophotometer at wavelength range (300-1100) nm; the optical characterization shows that the films have an average transmittance 55% in the VIS regions. The refractive index was calculated as a function of the photon energy, also the calculated optical energy gap was 3.3 eV and 3.1 eV for direct and indirect allowed transition respectively.

Keywords
Zinc oxide
Spray pyrolysis

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تحضير ودراسة خواص التركيب النانوي لأغشية أوكسيد الخارصين الرقيقة

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الخلاصة

يعتبر أوكسيد الخارصين (ZnO) نموذج من إحدى أشباه الموصلات ضمن المجموعة II-VI والتي لها مدى واسع في التركيب النانومتري (Nanostructures). في هذا البحث, تم تحضير أغشية رقيقة من أوكسيد الخارصين المتعدد التبلور على أرضية زجاجية بدرجة حرارة أساس 400 °C وذلك باستعمال تقنية الرش الكيماوي الحراري, تم تحضير محلول الرش من كلوريد الخارصين بمولارية مقداره 0.1 M/L.

تم دراسة ومناقشة خواص وتركيب الأغشية المحضرة حيث تم فحص الأغشية المحضرة بواسطة حيود الأشعة السينية ومن تحليل النتائج تبين أن جميع الأغشية المحضرة هي نوع متعددة التبلور. (Polycrystalline), تم حساب الحجم الحبيبي لها عند الأتجاه (002) وكانت قيمته 27.9 nm. ومن دراسة الخواص الكهربائية (والتي شملت قياسات تأثير هول والتوصيلية الكهربائية) تبين بأن الغشاء نوع n - type

تم دراسة الخواص البصرية لأغشية ZnO باستعمال مطياف يعمل ضمن الأطوال الموجية المرئية وفوق البنفسجية VIS-UV. إشتملت دراسة الخواص البصرية على تسجيل طيفي الامتصاصية والنفاذية للأغشية المحضرة لمدى الأطوال الموجية 300-1100 nm, أظهرت الدراسة البصرية بأن معدل النفاذية يقترب من 55% عند المدى المرئي. تم حساب معامل الإنكسار كدالة لطاقة الفوتون عند للأطوال الموجية المذكورة. تم أيضا حساب قيم فجوة الطاقة البصرية وكانت قيمتها للانتقال الإلكتروني المباشر المسموح 3.3 eV وللإنتقال الإلكتروني الغير مباشر المسموح 3.1 eV.

Introduction

II – VI semiconductors compound, such as Zinc oxide, is well known for application in a wide range of optoelectronic devices, it is one of transparent conducting oxide (TCO) materials whose thin films attract much interest due to its typical properties such as high chemical and mechanical stability and high optical transparency in the visible and near-infrared region. ZnO is one of the transparent conducting materials so it can be used as an anti-reflecting coating layer and as transparent conducting for solar cells [1].

Zinc oxide (ZnO) is emerging as an important material for ultraviolet and visible optoelectronic applications; this material has been proposed to be used as blue-violet optical emission devices, and in the same time it can be used as wide band gap high power devices, and surface acoustic devices [2].

Many researches have been done on zinc oxide by using of various film growth techniques such as thermal vacuum evaporation, sputtering technique, chemical bath deposition and spray pyrolysis technique. The spray pyrolysis is a useful alternative to the traditional methods for obtaining ZnO thin films, because of its simplicity, low cost and minimal waste production. The spray pyrolysis process allows the coating of large surface and it is easy to include in an industrial production line.[3].

The structure of ZnO is a mixture of cubic and hexagonal structure depending on the manufacturing conditions. The electronic transport mechanism in polycrystalline thin films strongly depends on their structure (i. e. grain size, grain boundaries, and structure defects). The X-ray diffraction technique was used to determine the crystalline structure and grain size of the thin films [4]. ZnO is on the borderline between a semiconductor and an ionic material. Under most growth conditions, ZnO is an n-type semiconductor, although p-type conductivity of ZnO has also been reported for growth under certain conditions. ZnO exhibits a wurzite structure (hexagonal symmetry) or rock salt structure (cubic symmetry), however, ZnO crystals most commonly stabile with the wurzite structure (hexagonal symmetry), as shown in fig. (1) [5, 6].

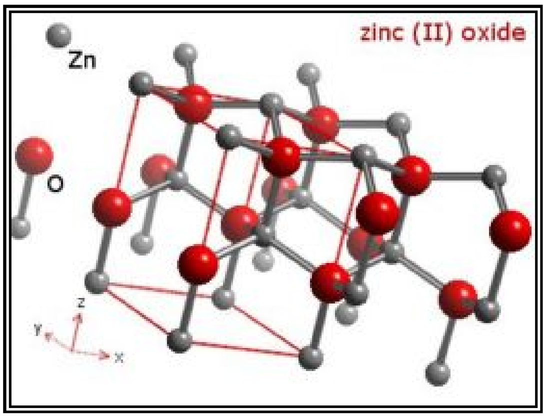

Fig. (1): The crystal structure of ZnO

Nanostructure development materials have received much attention because of their novel properties, which differ from those of bulk materials. Developing of II-VI based semiconductor nanostructures is of great interest. ZnO is probably the most typical II-VI semiconductor, which exhibits a wide range of nanostructures. The lattice parameters of the bulk ZnO are a = 0.32495 nm and c = 0.52069 nm at 300K, with a c/a ratio of 1.602, which is close to the 1.633 ratio of an ideal hexagonal close-packed structure [7, 8].

The optical properties of a thin film depend strongly on the manufacturing technique. Two of the most important optical properties; refractive index and the extinction coefficient are generally called optical constants. In many instances researches, the optical constants were measure by examining the transmission through a thin film of the material deposited on transparent substrate. The absorption of radiation that leads to electronic transitions between the valence and conduction bands is split into direct and indirect transitions [9].

ZnO has a high exciton binding energy of 60 MeV, much greater than the thermal energy at room temperature (26 MeV). Thus the exciton in ZnO could be stable even at room temperature, which facilitates efficient excitonic recombination. It is suitable for an UV photodetector because of its wide direct band gap and large photoconductivity, ZnO epitaxial film-based photoconductive and Schottky type UV photodetector has been demonstrated [10].

Experimental details

ZnO films were deposit onto glass substrates by spray pyrolysis technique using solution of Zinc Chloride, the molar concentration of the spray solution was 0.1 M/L, the flow rate of solution was 2 ml/Sec and the substrate temperature was held constant at 400 °C, with spray pyrolysis, the solution is sprayed directly onto the hot substrate.

Two experimental methods were used for thickness measurements; the "Weighting method" and the "Optical interference fringes method". The Weighting method gives an approximate value for the thickness of the thin films with an error 30 %. A digital balance with accuracy of ($\pm 0.1\times 10^{-3}$ gm) was used for weighting the needed materials to measure the thickness of the prepared films. He-Ne laser of wavelength 632.8 nm was used for measuring the thickness of the films by optical interference fringes method. The thicknesses of all the prepared films were varied between 280-300 nm.

The X-ray diffraction technique was used to determine the crystalline structure and grain size of the films. X-ray has the following information: Source; Cu-Kα radiation of the wavelength $(\lambda = 1.54060\ A^{\circ})$, Current=30 m A, Voltage =40 kV, Scanning angle; 2θ (25° to 50°).

The optical properties were conveniently measured; the optical constants of ZnO films were carried out with VIS-UV spectrophotometer by examining the transmission through the film of ZnO material deposited on transparent glass substrate.

Results and Discussions

1. X-ray analysis

The X-ray diffraction pattern of ZnO thin films deposited at 400 °C, which was obtained with 2θ from 25° to 50 glancing angle appear only one sharp peak and three small peaks as shown in fig. (2). The XRD pattern of the film shows that the film is polycrystalline, crystallized in the wurtzite phase and presents a preferential orientation along the c-axis. The result is in agreement with the American Standard of Testing Materials (ASTM). The highest peak observed at 2θ= 34.4° (d = 0.2602 nm) can be attributed to the (002) plane of the hexagonal ZnO. The (100), (101) and (102) peaks were also observed at 2θ= 31.5°, 36.2 ° and 47.5 ° respectively, as listed in table (1), these peaks are of lower intensity than the (002) peak.

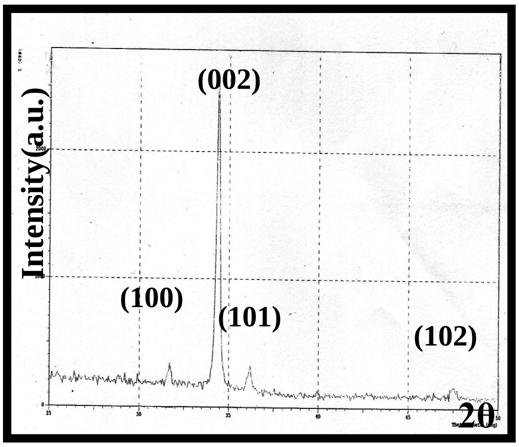

Fig. (2): X-ray diffraction pattern (XRD) pattern of ZnO thin film before annealing

The different peaks for ZnO film as well as the corresponding values of the interplanar spacing $d_{(h\ k\ l)}$ are in agreement with the standard values of ASTM data, as listed in table (1).

Table (1): The value of d for all peaks of ZnO X-Ray pattern

(hkl)	(2θ)	d	d *(XRD)*

	Degree	(ASTM) (Å)	(Å)
100	31.5	2.816	2.815
002	34.4	2.602	2.603
101	36.2	2.476	2.482
102	47.5	1.911	1.909

The lattice constant for ZnO thin films at 002 was calculated by using the following relation [11]:

$$\frac{1}{d^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a_o^2}\right] + \frac{\ell^2}{c_o^2} \quad \text{.........(1)}$$

The lattice constant (C_O) of the ZnO thin film was calculated at (002) as 0.519 nm, *a* =0.34 nm, c/a=1.52 which is nearly close to the ratio of an ideal hexagonal close-packed structure which was recorded as 1.633 [5].

The grain size *(G)* can be calculated using Scherrer's formula [12]:

$$G = \frac{0.9\,\lambda}{B\cos\theta} \quad \text{...................................... (2)}$$

Where: $\left(\lambda = 1.54060\ A^{\circ}\right)$

B is the FWHM

The grain size (crystallite size) is estimated about 27.9 nm at (002).

2. The transmission spectrum

The transmission of ZnO thin film was estimated from the UV-VIS spectrophotometer, it was about 55% in the visible region, as shown in fig. (3), It fairly agrees with the deposited film using spray pyrolysis technique but low when compared with the high transmission of about 85% in UV-VIS regions using chemical bath deposition technique [1].

The moderately high transmissions of the film throughout the UV-VIS regions make it a good material for photovoltaic applications as thermal control coating material [2, 3].

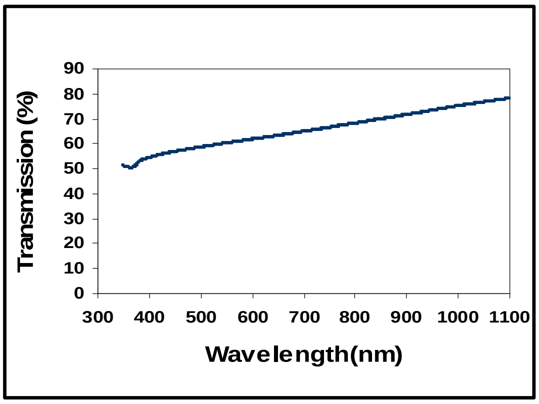

Fig. (3): The transmission spectra of ZnO thin films

3. The reflectance spectrum

The reflectance of ZnO film can be calculated from the absorption and the transmission spectra.

Fig. (4) show the reflectance of ZnO film as a function of the photon energy. R is almost constant in the range 1.6-3.1 eV then there is rapid reduction in the range 3.1-3.6 eV of the photon energy, this means that the absorbance of the film is very little amount at the photon energy less than the value of the energy gap; hυ< Eg.

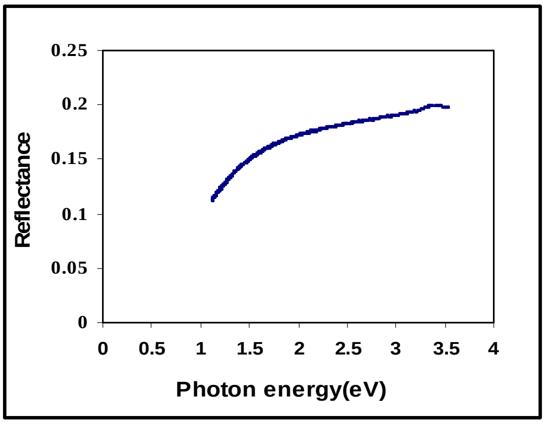

Fig. (4): The reflectance spectrum of ZnO thin films as a function of the photon energy

4. The optical energy gap

The value of the energy gap *(Eg)* of ZnO compound as a bulk is equal to 3.31 eV [13] but as thin film it depends on the manufacturing techniques, as show in table (2).

Table (2): The reported values of the direct energy gap of ZnO thin film for different manufacturing techniques

The researchers	year	E_g (eV)	Manufacturing techniques
Asomaza et al. [13]	2000	3.35	Chemical spray
C. GÜMÜ et al. [3]	2006	3.27	Chemical spray
Zheng et al [14]	2007	3.37	Sputtering
Suhail et al [15]	2009	3.15-3.25	DC-Sputtering
The present work	2009	3.30	Chemical spray

The energy gap *(Eg)* was estimated by assuming a direct and indirect allowed transition between valence and conduction bands using the following equation:

$$(\alpha h\upsilon) = A^{*}(h\upsilon - E_g)^{r} \ldots\ldots\ldots\ldots (3)$$

Where A^* is constant, α is the absorption coefficient, $h\upsilon$ is the incident photon energy, and r is a constant which takes the values (1/2, 3/2, 2, and 3) depending on the material and the type of the optical transition (whether it is direct or indirect). Fig. (5) shows the plot of $(\alpha h\upsilon)^2$ vs. $h\upsilon$, the energy gap is determined by extrapolating the straight line portion of the spectrum to $h\upsilon$= 0.

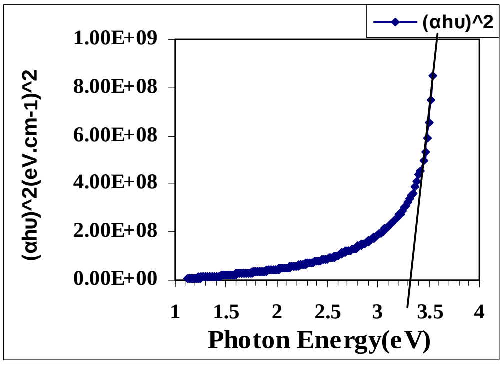

Fig. (5): The direct allowed transition energy gap of ZnO thin films

From this curve, the optical energy gap is equal 3.30 eV for the direct transition between valence and conduction bands; this value is in good agreement with the previously reported value for ZnO thin film [16]. This value of the direct energy gap for ZnO films make these films good material for solar device applications as antireflection coatings.

The optical energy gap for the indirect allowed transition of ZnO thin films was calculated from equation (3) using r=2, its value is 3.1eV, as show in fig. (6).

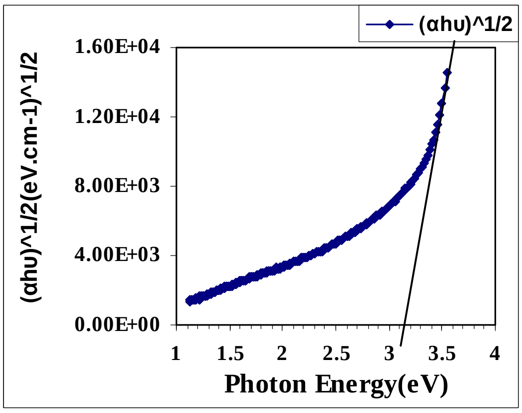

Fig. (6): The optical energy gap of ZnO thin films for the indirect allowed transition

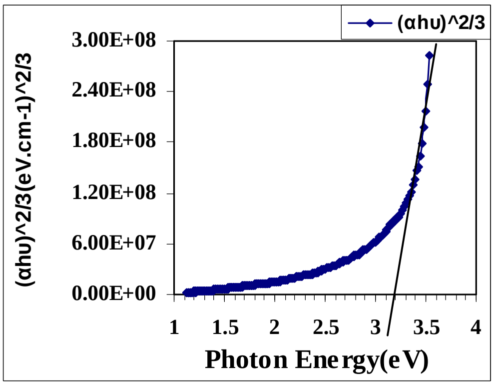

Fig. (7): The energy gap for direct forbidden transition of ZnO thin films

The direct forbidden energy gap was also calculated from equation (3) using r=3/2, its value is 3.15 eV, as shown in fig. (7).

5. Refractive Index and extinction coefficient *k*

The refractive index (n) and the extinction coefficient *k* are determined from the transmittance spectrum as a function of the wavelength within the range 300-1100 nm. The Refractive index can be determined from the following equation:

$$n=[(4R/(R-1)^2)-k^2]^{1/2}-[(R+1)/(R-1)] \ldots\ldots (4)$$

where R is the reflectance.

There is a little decrease in the refractive index in the visible range; it was estimated to be1.98 at 500 nm and 1.86 at 700 nm, as show in fig. (8). These values are nearly to the reported refractive index values which lies between 1.68 and 2.09 at 500 nm [17]. The refractive index changes slightly and steadily.

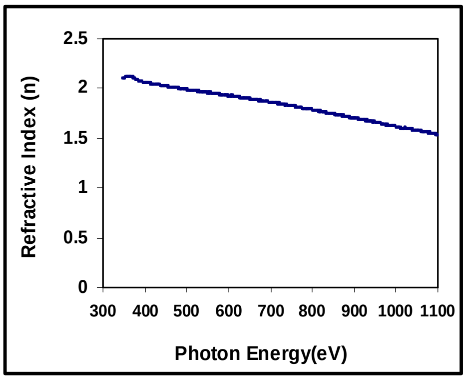

Fig. (8): The refractive index of ZnO thin films

The extinction coefficient *k* was calculated as a function of the photon energy using the relation: $k = \alpha\lambda / 4\pi$
The average value of *k* was within the range between 4.1×10^{-2} to 4.8×10^{-2} in the visible-near UV region, as show in fig. (9).

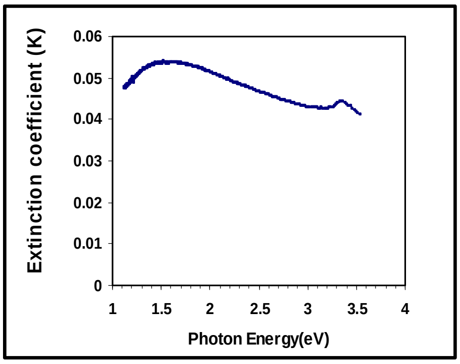

Fig. (9): The extinction coefficient of ZnO thin films

6. Photo conductivity (σ_{ph})

The photo conductivity is calculated using the equation:

$\sigma_{Ph} = \varepsilon_i \, \omega \, \varepsilon_o$ .... (5)

Where ε_i is the imaginary part of dielectric constant ω is the angular frequency and ε_o is the permittivity of the air. The Photo conductivity is calculated as a function of the photon energy, it increases at high energies, as shown in fig. (10).

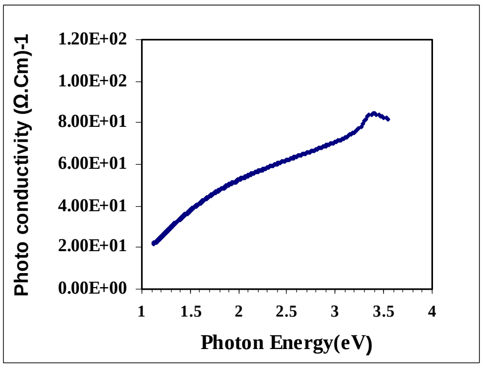

Fig. (10): The photo conductivity of ZnO thin films

7. Hall Effect and Hall Results

A magnetic field (B)is applied at right angles to current flow I, an electric field E_H is generated which is mutually perpendicular to the current and the magnetic field. The generated electric field (E_H) is called Hall field which is related to the Hall voltage (V_H) by the relation:

$V_H = E_H.w$

Where *w* is the distance between the two electrodes. By plotting Hall voltage as a function of current, the Hall coefficient (R_H) can be calculated using the relation:

$$R_H = \frac{V_H}{I} \cdot \frac{t}{B} \quad ....(6)$$

Where t is the film thickness; t= 280 nm, B=0.257 Tesla, the value of V_H/I, is calculated from the slop of fig. (11). Hall coefficient was estimated to be 10.89×10^{-6} m^3/C. From this result, the film was conduced that the film is n-type, as shown in fig. (11).
The thickness of the prepared films is one of the most important parameters which affect physical properties.

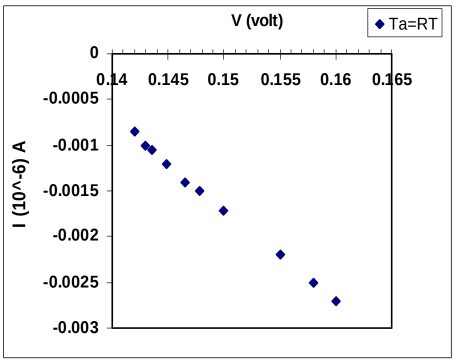

Fig. (11): The plot of Hall voltage versus the current for ZnO Thin Films

Carrier concentration (n) can be determined from Hall measurements of ZnO thin films; it is calculated using the relation:

$$n = \frac{-1}{e\ R_H} \quad \text{.......................................} \ (7)$$

Where: e is the charge of the electron which is equal 1.6×10^{-19} C.
Carrier concentration was estimated as 5.73×10^{17} cm^{-3}.

Conclusions

ZnO thin films were successfully prepared by the spray pyrolysis technique onto hot glass substrate at 400 ºC. The wide direct optical band gap of the prepared films makes these films good material for solar device applications as antireflection coatings.
The ratio of the lattice constant (c/a) which is nearly close to the previously reported value makes these films an ideal hexagonal nanostructures material.

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