

Characteristics Study of ZnO Thin Films by Rapid Thermal Oxidation Treatment Technique

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ABSTRACT

In this paper preparation of good quality transparent conductive ZnO thin films by post-oxidation of vacuum evaporated Zn, on glass and silicon (p-type) as substrates, the oxidation was achieved in a short time (90 sec) which is known as rapid thermal oxidation. One growth parameter has been considered to specify the optimum conditions the film thickness are (200, 300, 400 & 500 nm).

The XRD spectra revealed a high oriented grain in the (002) lattice system which is hexagonal wurtzite and proved that the ZnO films have a polycrystalline structure. Also, the morphological properties of ZnO films show that all films have a homogeneous surface morphology and it appears, to change significantly as a function of thickness. The energy gap of ZnO films decreases as the thickness increases. The FTIR spectra indicate the existence of the distinct characteristic absorption peak at 472.56cm^{-1} for Zn-O stretching mode.

Study of effect I - V and C - V measurements of ZnO films with the increase thickness. The photovoltaic properties confirmed that the photovoltaic depends strongly on the bias voltage and the amount of current produced by a photovoltaic device which is directly related to the number of photons absorbed. C - V results demonstrated that the fabricated heterojunction is of abrupt type. Also, the width of the depletion layer (w) follows the same behavior (V_{bi}) decreased while the charge carrier density (N_d) was increased with the thickness increase.

Keywords: ZnO; Thin film; XRD; FTIR; Morphological; Electrical Properties.

دراسة خواص اغشية اوكسيد الزنك الرقيقة بتقنية المعاملة بالاكسدة الحرارية السريعة

الخلاصة

في هذا البحث تم تحضير نوعية جيدة من اغشية اوكسيد الزنك الرقيقة الموصلة الشفافة بتقنية الاكسدة السريع لاغشية الزنك المرسبة بالتبخير بالفراغ، على قواعد اساس من الزجاج حيث جرت

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الاكسدة بزم من قصير 90 ثانية ودرجة حرارة 300 سيليزية ويعرف هذا النوع من الاكسدة بالاكسدة الحارية السريعة. تم اعتماد احد معلمات الانماء لتحديد افضل الظروف وهو سمك الغشاء (200، 300، 400 و 500) نانومتر.

دراسة حيود الاشعة السينية تشير الى تمحور حبيبات غشاء اوكسيد الزنك باتجاه (002) لنظام شبكي سداسي واثبتت ان تركيب اغشية اوكسيد الزنك هي متعددة التبلور. ايضا، اظهرت طوبوغرافية اغشية اوكسيد الزنك ان كل الاغشية تمتلك سطوح متجانسة وتظهر تغير ملحوظ مع تغير السمك. تشير اطياف تحويل فورير للاشعة تحت الحمراء الى وجود خاصية قمة للامتصاص عند 472.56 cm^{-1} (لاوكسيد الزنك هي نمط تمدد).

تم دراسة تأثير قياسات تيار- جهد وسعة - جهد لاغشية اوكسيد الزنك مع زيادة السمك. اكدت الخصائص الفولتائية الضوئية ان التيار الضوئي يعتمد بقوة على فولتية الانحياز وكمية التيار الناتجة في النبيطة الفولتائية الضوئية التي ترتبط مباشرة بعدد الفوتونات الممتصة. اما نتائج سعة - جهد تشير الى ان نوع المفرق الهجين المصنع من النوع الحاد. ايضا لاحظنا عرض منطقة النضوب تتبع نفس سلوك جهد البناء الداخلي تقل بينما كثافة حاملات الشحن كانت تزداد مع زيادة سمك الاغشية.

INTRODUCTION

Zinc oxide (ZnO) is an important wide energy gap with a direct energy gap of 3.4 eV, which is greater than the thermal energy at room temperature [1]. It has attracted intensive research effort for its unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors and spin electronics [2]. The semiconducting properties of ZnO are in general similar to those of conventional semiconductors; its defect chemistry seems to be quite different [3]. Many investigations on the synthesis of ZnO in the nanoscale with additives were studied in relation to sintering temperature and time, additive contents and different properties by using different synthesis method such as soft chemical method, sol gel, coprecipitation, ion exchange or hydrolysis [4]. Thermal evaporation is used for preparation ZnO thin films in this research. The deposition by thermal evaporation method is simple, very convenient and most widely for producing thin films [5].

It is reported that the crystallite sizes in the film could be controlled over a nm range by varying the film thickness, deposition method and post deposition annealing [6].

Zinc oxide is not a new semiconductor. It has a long history of studies of its growth techniques and characterization of its material properties. For example, lattice parameters of ZnO are known from 1935, whereas detailed values of optical parameters were available in mid 50s. Even though good quality thin films (by chemical vapour deposition) were prepared in 1970, only recently ZnO attracts an increasing attention [7].

Experimental

The fabricated samples were prepared by vacuum evaporation technique using Balzer unit model (BL-510) as a coating system. The system was pumped down to a vacuum of 10^{-5} mbar, with constant deposition rate equal to 5.4 Å/sec. thin films of ZnO were deposited on glass and silicon substrates with different thickness.

The crystal structure dependence on the rapid thermal oxidation (RTO) treatment was characterized by X-ray diffraction (XRD) using Philips X-ray diffractometer system which records the intensity as a function of Bragg's angle with Cu K α as the line source ($\lambda=1.542\text{ Å}$). Atomic Force Microscope (AA3000 Scanning Probe

Microscope SPM, tip NSC35/AIBS) from Angstrom AD-Vance Inc. FTIR Affinity-1 Fourier Transform Infrared Spectrophotometer SHIMADZU.

Results and discussions

The X-ray Diffraction (XRD) investigation has been carried out for the prepared films of ZnO. The following figures show the XRD patterns for samples grown at RTO temperature 300°C and oxidation time 90 sec for Zn films depositing on glass substrate with difference thicknesses. One peak could be recognized in Figure (1) the film is crystalline structure with a hexagonal structure (Wurtzite phase)[8]. The strongest peak, observed at $2\theta = 34.3646^\circ$, can be attributed to the (002) plane of the hexagonal ZnO the intensity of the ZnO (002) diffraction peaks becomes more intense and sharper.

Table (1): The experiment and the standard value of d, FWHM and Intensity of ZnO films.

Thickness (nm)	hkl	$2\theta_{Exp.}$ (deg.)	$2\theta_{Std.}$ (deg.)	$d_{Exp.}$ (Å)	$d_{Std.}$ (Å)	FWHM (deg.)	Intensity (a.u)
200	002	34.40	34.42	2.604	2.603	0.1378	362
300		34.45		2.601		0.1724	900
400		34.35		2.608		0.0973	2360
500		34.43		2.604		0.2520	5032

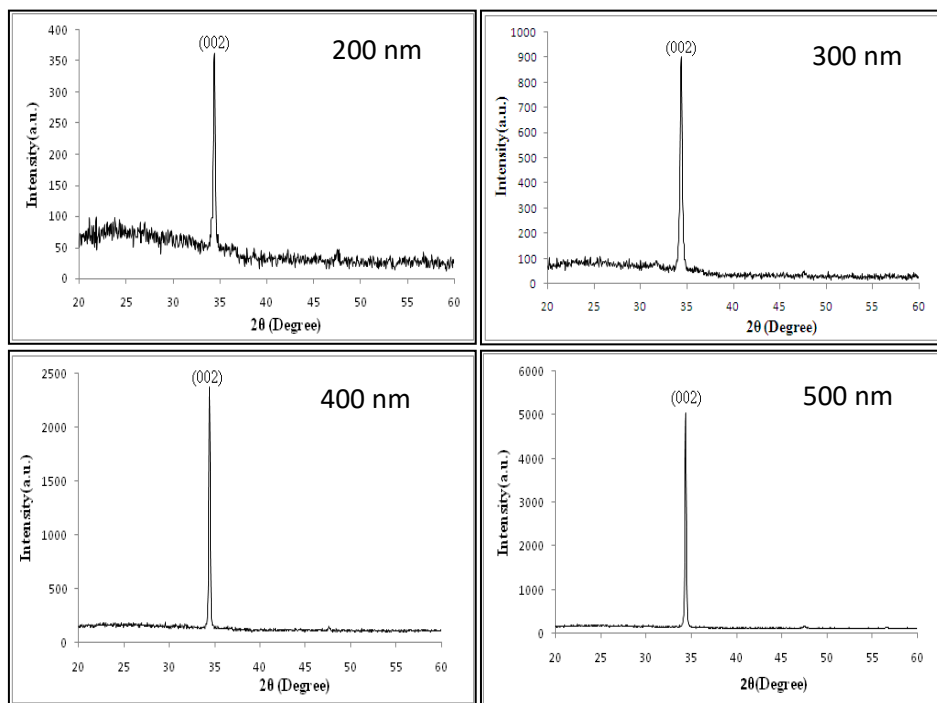


Figure (1): shows the X-Ray diffraction pattern of ZnO thin film at oxidation time 90 sec, with different thicknesses

The energy gap decrease with the increasing in film thickness. This is attributed to the increase in average grain size, this lead to decay island and formation continuous film (as shown in AFM measurement). Table (2) shows the energy gap with different thickness of ZnO films.

Thickness (nm)	Energy gap (eV)
200	3.270
300	3.211
400	3.17
500	3.03

Figure (3) shows the typical FTIR spectra of a representative ZnO film with thickness (300) nm. One may observe the existence of distinct characteristic absorption peak at 472.56 cm^{-1} for Zn-O stretching modes. The peak at $\approx 1062.78\text{ cm}^{-1}$ may be attributed to aromatic C=C strength mode. The band at 1386.82 cm^{-1} is the C-

O stretching frequencies while the peak at $\approx 1768.72 \text{ cm}^{-1}$ is due to C=O band. The absorption in $\approx 2441.88 \text{ cm}^{-1}$ is because of the existence of CO_2 molecules in air. The band $\approx 3700 \text{ cm}^{-1}$ is due to O-H species in the film and those at 2800-3000 cm^{-1} is due to C-H stretching frequencies. No significant stretch mode of an N-H bond (about 3452.58 cm^{-1}) was observed, indicating that there are no physically absorbed NH_3 on the film surface of the samples. But a lower frequency peak of low intensity at $\approx 719.45 \text{ cm}^{-1}$ related to ZnO stretching modes was observed in the present spectra, this results agree with author's [8,9].

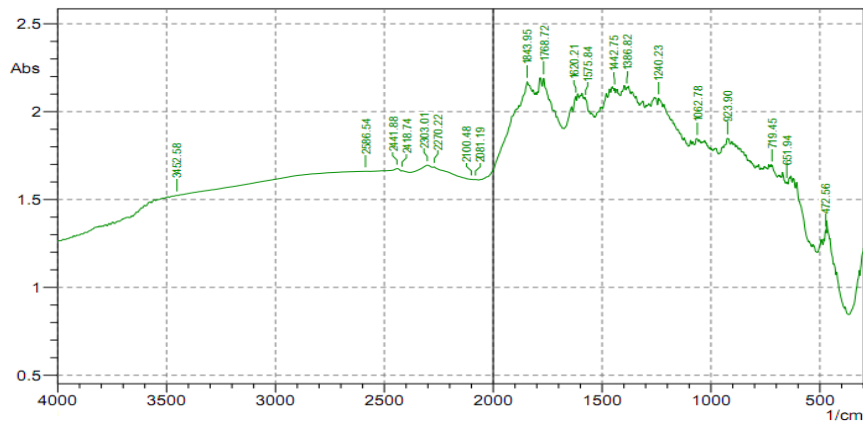


Figure (3): FTIR spectra of representative ZnO film with thickness 300nm

The experimental data concerning the Hall Effect of ZnO conducting at room temperature electrical measurements of the ZnO thin films grown on glass substrate noticed that the carrier mobility and contrition of carriers charge is found to increase with increasing thickness. This behavior is attributed to the increase of the growth crystalline with the thickness and decreasing of energy gap (E_g) as shown in table (2).

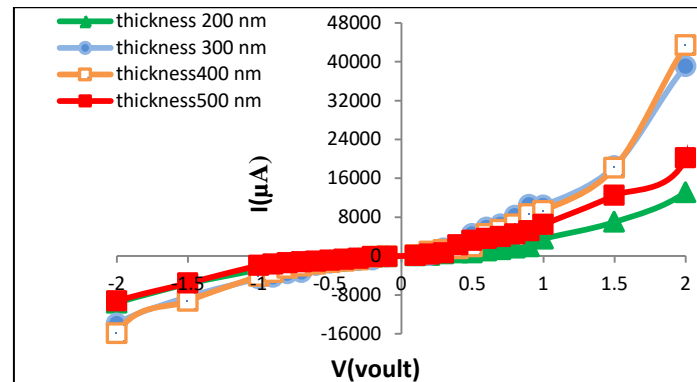
Table (3) shows the Hall coefficient (R_H), concentration (N_d) and mobility (μ_H) of carriers charge of ZnO films.

Thicknes s (nm)	Resistivit y ($\Omega \cdot \text{cm}$)	Conductivit y ($\Omega \cdot \text{cm}$) ⁻¹	R_H (m^2/C)	Type of conductivi ty	μ_H (cm^2/Vs)	N_d (cm^{-3})
200	2.281×10^{-4}	4.384×10^3	2.306×10^{-4}	n-type	1.011	2.707×10^{22}
500	1.198×10^{-5}	8.349×10^4	1.813×10^{-4}		15.130	3.444×10^{22}

ZnO/Si Heterojunction

One of the important parameters of diode measurement is a current-voltage characteristic which explains the behavior of the resultant current with the applied forward and reverse bias voltages. Figure (4) Shows I_d - V characteristics for ZnOheterojunction.

In general the forward dark current is generated due to the flow of majority carriers and the applied voltage injects majority carriers which lead to the decrease of the built - in potential (V_{bi}), as well as the width (W) of the depletion layer.



Figure(4) I - V characteristics for ZnO heterojunction prepared at different thickness

Figure (5) the relation between the photocurrent density (J_{ph}) and bias voltage (V) of the ZnO/Si diodes at different thicknesses; observe that the photocurrent density increases with incident power densities.

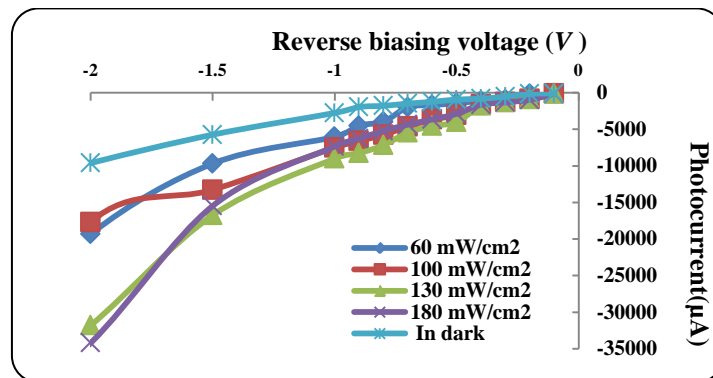


Figure (5) I_{ph} - V characteristics for ZnO heterojunction prepared at different thickness

Figure (6) gives the square of inverse capacitance is plotted against applied reverse bias voltage ($1/C^2$ - V) for ZnO/Si heterojunction prepared at different thickness. Results show that the device is “abrupt” which is confirmed by the relation between $1/C^2$ and reverse bias being a straight line.

The charge-carrier density (N_d) is seen to increase with the increasing of thickness due to increasing growth crystalline and decreasing the device capacitance with the increasing thickness.

Table (4): Values of W , V_{bi} and N_D for ZnO/Si heterojunction with different thicknesses

Thickness (nm)	V_{bi} (Volt)	N_D (cm ⁻³)	W (cm)
200	0.6	5.8×10^{17}	5.7×10^{-7}
300	1.5	12.3×10^{15}	3.4×10^{-5}
400	1.1	2.5×10^{14}	2.8×10^{-4}
500	1.5	7.2×10^{12}	1.1×10^{-3}

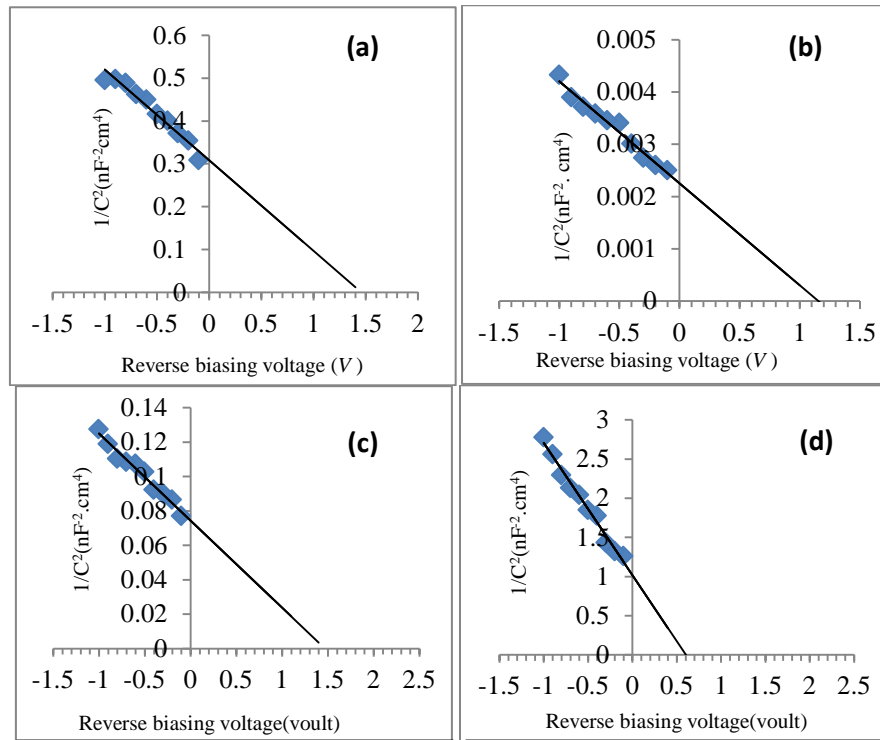


Figure (6): The variation of $1/C^2$ versus reverse bias voltage for ZnO/Si heterojunction at different thicknesses (a) 200 (b) 300 (c) 400 (d) 500 nm

Conclusion

The physical and photovoltaic properties are strongly dependent on the film thickness. Rapid thermal oxidation technique is very promising for photovoltaic application.

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