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The effect of annealing and the influence of Gamma-ray on the optical properties of nanostructure Zinc Oxide Thin Films

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Abstract

The semiconductor ZnO is one of II – VI compound group, it is prepare as thin films by using chemical spray pyrolysis technique; the films are deposited onto glass substrate at 450 °C by using aqueous zinc chloride as a spray solution of molar concentration 0.1 M/L. Sample of the prepared film is irradiating by Gamma ray using CS ^{137}, other sample is annealed at 550°C.

The structure of the irradiated and annealed films are analyzed with X-ray diffraction, the results show that the films are polycrystalline in nature with preferred (002) orientation. The general morphology of ZnO films are imaged by using the Atomic Force Microscope (AFM), it constructed from nanostructure with dimensions in order of 77 nm.

The optical properties of the prepared films are studied by using measurement from UV-VIS-NIR spectrophotometer at wavelength within the range (300-900) nm. The optical results show that the absorption of the prepared films are decreases after annealing and increases after irradiation. The optical constants such as the refractive index and the photoconductivity are calculated before and after annealing as a function of the photon energy. Also the values of the optical energy gap are calculated, it is 3.3 eV and 3.1 eV for the direct and indirect allowed transition respectively; these values are reduced after annealing.

Keywords
ZnO nanostructure
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تأثير التلدين والتشعيع بأشعة كاما على الخواص البصرية لأغشية اوكسيد الخارصين الرقيقة ذات التركيب النانوي

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الخلاصة:

يعتبر اوكسيد الخارصين (ZnO) احد أشباه الموصلات ضمن المجموعة II – VI، تم تحضير هذا المركب بشكل أغشية رقيقة على أرضية زجاجية بدرجة حرارة أساس 450 °C وذلك باستعمال تقنية الرش الكيماوي الحراري، تم تحضير محلول الرش من كلوريد الخارصين بمولارية مقداره 0.1 M/L، تم تعريض نموذج من الأغشية المحضرة لأشعة كاما (γ-ray) باستعمال المصدر المشع CS ^{137} وتم أيضا تلدين بعض النماذج المحضرة من أغشية ZnO عند درجة حرارة 550 مئوي.

تم فحص الأغشية الملدنة والمشععة بواسطة حيود الأشعة السينية ومن تحليل النتائج تبين أن جميع الأغشية المحضرة هي نوع متعددة التبلور. (Polycrystalline). تم دراسة تركيب الغشاء بإجراء فحوصات بواسطة المجهر Atomic Force Microscope (AFM) وتبين أن الغشاء ذو تركيب نانوي بمعدل للحجم البلوري 77 nm .

درست الخواص البصرية للأغشية المحضرة باستعمال مطياف يعمل ضمن الأطوال الموجية الفوق البنفسجية- المرئية- والقريبة من تحت الحمراء (UV- VIS- NIR) لمدى الأطوال الموجية 300-900 nm، أظهرت الدراسة البصرية بان الأمتصاصية تقل بعد التلدين و تزداد عند التشعيع. تم حساب بعض الثوابت البصرية والتي شملت حساب معامل الانكسار ،التوصيلية الضوئية قبل وبعد التلدين كدالة لطاقة الفوتون عند للأطوال الموجية المذكورة وقد تبين أن للتلدين أثر واضح على قيم الثوابت البصرية . تم ايضا حساب قيم فجوة الطاقة البصرية وكانت قيمتها 3.3 eV, 3.1 eV لكل من الانتقال الإلكتروني المباشر المسموح والانتقال الإلكتروني الغير مباشر المسموح على التوالي وقد تبين أن قيم فجوة الطاقة البصرية تقل عند التلدين.

Introduction

Zinc oxide is one of transparent conducting oxide (TCO) materials whose thin films attract much interest. It is important material due to its typical properties such as high chemical and mechanical stability and high optical transparency in the visible and near-infrared region, it can be used as antireflection coating layer for solar cells [1].

Zinc oxide (ZnO) is emerging as an important material for optoelectronic applications, it 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, surface acoustic devices [2].

Many researches done on zinc oxide by using of various film growth techniques such as thermal vacuum evaporation, sputtering technique, chemical bath deposition, and spray pyrolysis [3].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. Very limited work has been reported on the preparation of ZnO using chemical bath deposition technique [4].

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 [5]. 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) [6].

. 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.

The optical properties of 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 [7].

ZnO 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 [8].

Experimental details

ZnO films are prepared 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 450 °C, the solution is sprayed directly onto the hot glass substrate.

One sample of the prepared films is irradiating for two week by gamma radiation by using radioisotope CS ^{137} of activity 2µCi (half life time of the radioisotope is 30.17 y, the manufacture date is 1982), other sample is annealed at 550°C for about three hours.

Two experimental methods are 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× 10^{-3} gm) is used for weighting the needed materials and for measured the thickness of the prepared films. He-Ne laser of wavelength 632.8 nm was used for measured the thickness of the films by optical interference fringes method, the thickness of all the prepared films are varied between 380-400 nm.

The X-ray diffraction technique is used to determine the crystalline structure the films before and after annealing and irradiated. X-ray has the following information: source Cuk$_\alpha$ radiation of wavelength $\left(\lambda = 1.54060\, A^\circ\right)$, Current =30 m A, Voltage =40 kV, Scanning angle (20° to 60°). The surface morphology of the prepared films is tested by Atomic Force Microscope (AFM).

The optical properties of ZnO films are carried out from IR-VIS-UV spectrophotometer at wavelength within the range (300-900) nm before and after annealing and irradiation.

Results and Discussions:

1. X-ray analysis

The X-ray diffraction patterns of ZnO thin films are obtained, the prepared film at 450°C have only one sharp peak and three small peaks, as shown in fig. (1). The highest peak observed at $2\theta = 34.38°$ ($d = 0.2604$ Å) can be attributed to the (002) plane of the hexagonal ZnO. The (100), (101) and (102) peaks are also observed at $2\theta = 31.58°$, 36.14° and 47.45° respectively, as listed in table (1), these peaks are much lower intensity than the (002).

The XRD pattern shows that the film is polycrystalline, crystallized in the hexagonal phase and presents a preferential orientation along the c-axis. The result is in agreement with the literature of American Standard of Testing Materials (ASTM).

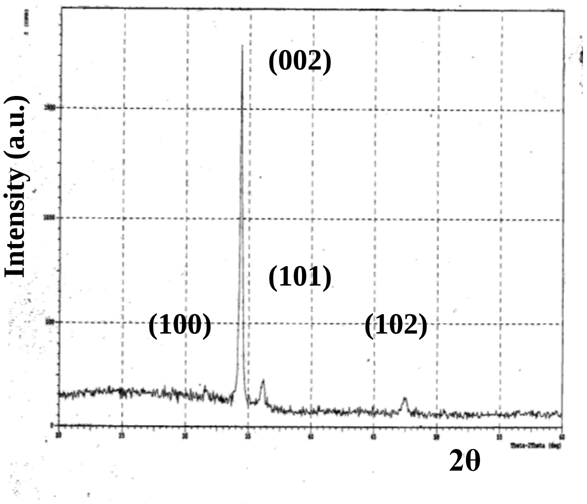

Fig. (1):* X-ray diffraction pattern *of ZnO thin film

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

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

(hkl)	(2θ) Degree	d ASTM (Å)	d *(XRD)* (Å)
(100)	31.58	2.816	2.830
(002)	34.38	2.602	2.604
(101)	36.14	2.476	2.483
(102)	47.45	1.911	1.914

The lattice constant for ZnO thin films is calculated at (002) by using the fallowing relation [9]:

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

The lattice constant (c_o) is 5.19 Å.

Two peaks (101), (102) are very low after annealing and the peak (103) is disappeared, as show in fig. (2).

Cs^{137} radioisotope is used to investigate creation of defects at ZnO thin films by gamma radiation, the peaks (100), (002), (102) of low intensity can be observed at $2\theta = 31.8°$, $2\theta = 34.9°$ and $2\theta = 47.2°$ respectively, as show in fig. (3).

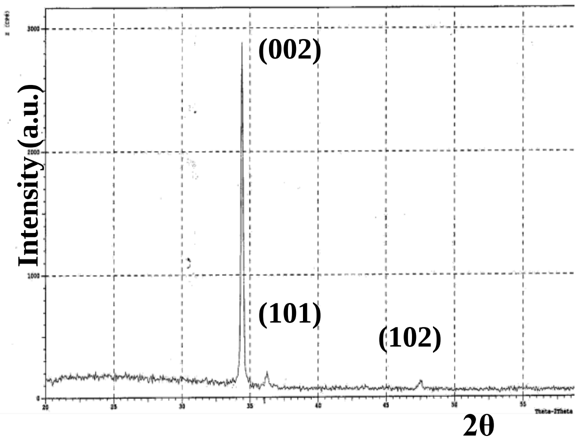

Fig. (2): The X-ray diffraction pattern of ZnO thin film after annealing

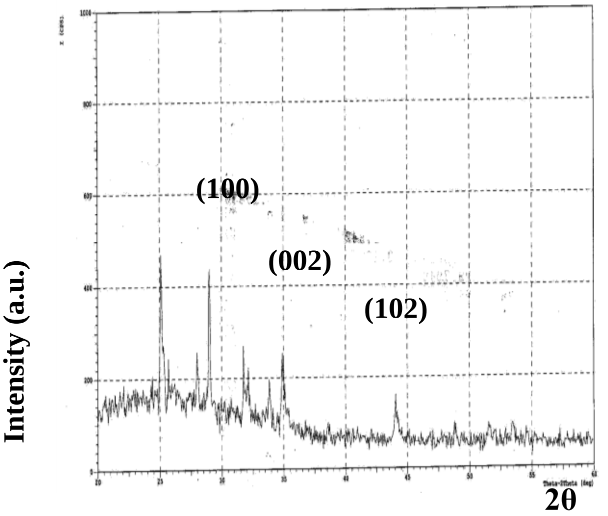

Fig. (3): The X-ray diffraction pattern of ZnO thin film after irradiation

3-2 Surface morphology

The general morphology of the ZnO film was imaged by using the Atomic Force Microscope (AFM), as shown in fig. (4). The figure shows that the prepared film was constructed from nanostructure with dimensions in order of 77 nm.

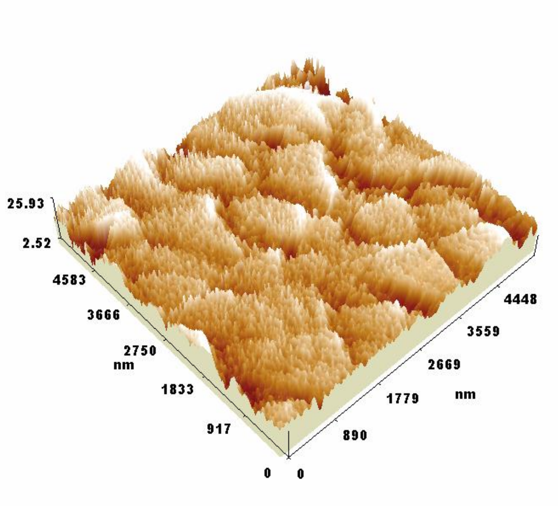

Fig. (4): The Surface Morphology of ZnO thin film takes from Atomic Force Microscope

3. The transmission and the absorption spectrum

The transmission spectra of ZnO thin films are estimated at wavelength within the range (300-900) nm before and after annealing, the films have highly transparent in the visible region of the electromagnetic spectrum and present a sharp ultraviolet cut-off at approximately 380 nm, as shown in fig. (5). the transmission is increase from 55% to 85% after annealing, it is fairly agrees with the deposited film using chemical bath deposition technique and spray pyrolysis technique [11].

The moderately high transmission of the film throughout the UV-VIS regions makes it as good material for optoelectronic applications as antireflection thermal control coating material [12, 13].

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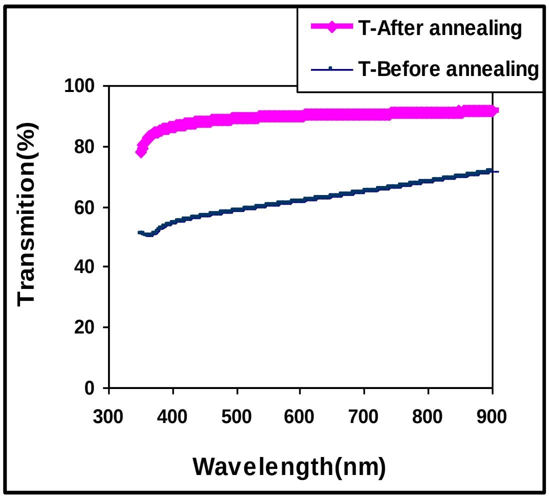

Fig. (5): The transmission spectra of ZnO thin films before and after annealing

ZnO films have good absorption at short wavelength region, and then the absorption spectra decreased with increasing of the wavelength, as show in fig. (6), the annealed films showed lower absorption in same wavelength region.

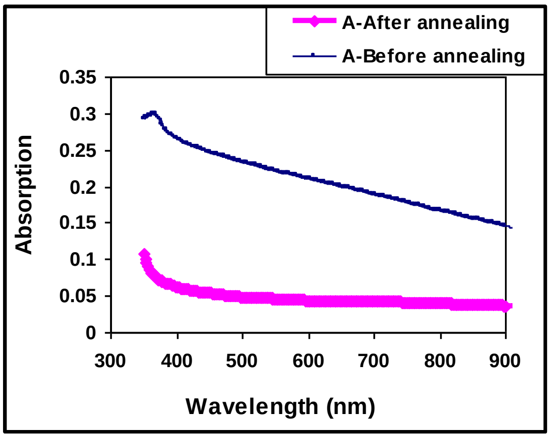

Fig. (6): The absorption spectra of ZnO thin films before and after annealing

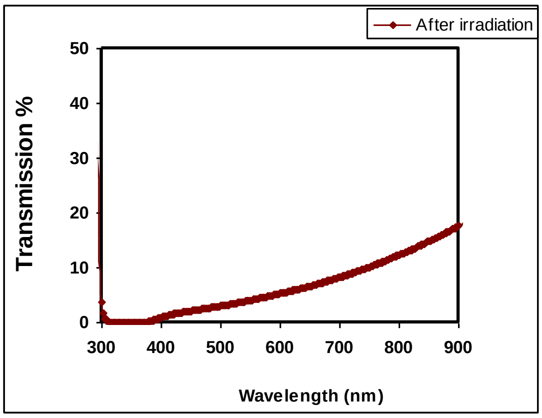

Fig. (7): The transmission spectra of ZnO thin films after irradiation

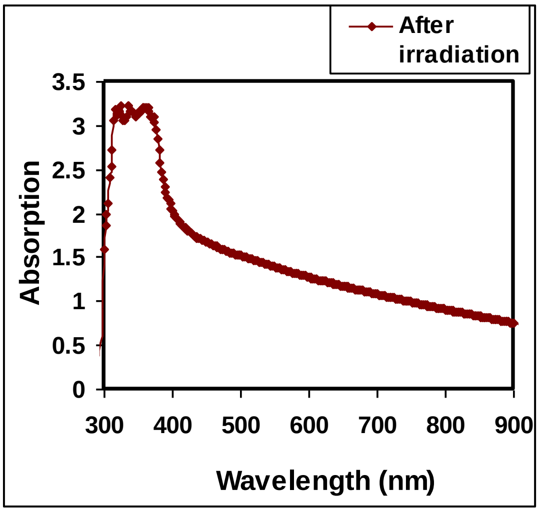

Fig. (8): The absorption spectra of ZnO thin films after irradiation

The transmission of irradiated ZnO films is decrease in the visible range, the absorption of the films is increase after irradiation, as show in fig. (7, 8).

4. The Optical Energy Gap

The value of the energy gap *(Eg)* of ZnO compound as a bulk is equal 3.31 eV but as thin film it is depend on the manufacturing techniques [4, 11].

The energy gap is estimated by assuming a direct and indirect allowed transition between valence and conduction bands using the fallowing equation [7]:

$$(\alpha h\upsilon)=A^{*}(h\upsilon-E_g)^{r} \text{.............} (2)$$

Where A^* is constant, α is the absorption coefficient, $h\upsilon$ is the incident photon energy, and r is 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. The energy gap is determined by extrapolating the straight line portion of the spectrum to $\alpha E = 0$. Fig. (9-a, b) shows the plot of $(\alpha h\upsilon)^2$ vs. $h\upsilon$ before and after annealing.

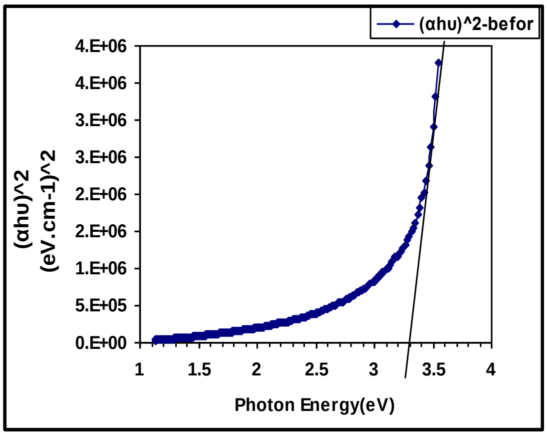

Fig. (9-a): The direct allowed transition energy gap of ZnO thin films before annealing

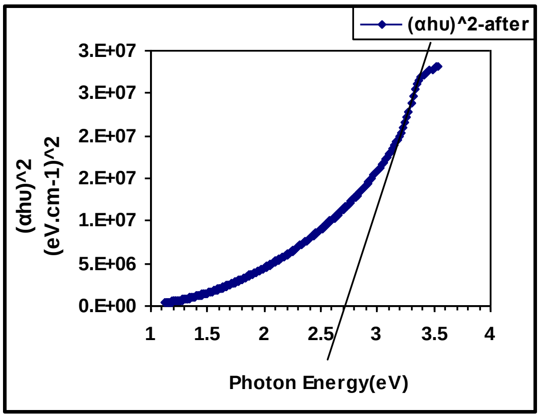

Fig. (9-b): The direct allowed transition energy gap of ZnO thin films after annealing

From these figures, the value of the optical energy gap of ZnO thin film is equal 3.3eV for the direct transition between valence and conduction bands before annealing and it become 2.7 eV after annealing; these values are in good agreement with previously reported value [1, 14].

The optical energy gap for the indirect allowed transition of ZnO thin films is calculated from equation (2) using r=2, it is 3.1eV before annealing, as show in fig. (10-a), it can be observed that the value of the energy gap for the indirect allowed transition is reduced after annealing to be 2.1 eV, as show in fig. (10- b).

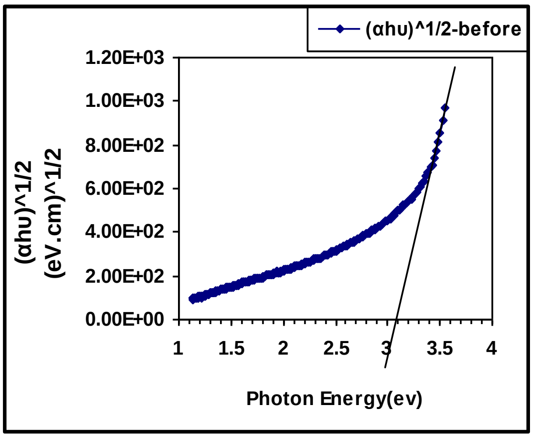

Fig. (10-a): The optical energy gap of ZnO films for the indirect allowed transition before annealing

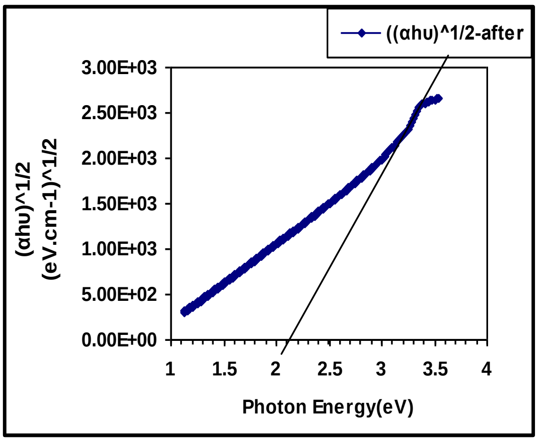

Fig. (10-b): The optical energy gap of ZnO films for the indirect allowed transition after annealing

5. Refractive Index *(n)*

The refractive index (n) is determined from a transmittance spectrum as a function of the wavelength within the range 300-900 nm. The Refractive index can be determined from the fallowing equation [7]:

$$n = [(4R/(R-1)^2) - k^2]^{1/2} - [(R+1)/(R-1)] \text{ ----(3)}$$

where: R is the reflectance, k is the extinction coefficient. There is a little decreasing in the refractive index in the visible range; it is estimated 1.98 at 500 nm to 1.86 at 700 nm, as show in fig. (11), these values are nearly close with the reported refractive index values which are lies between 1.68 and 2.09 at 500 nm [11]. The refractive index changes slightly and steadily, also it is observe that the refraction index decrease when the film is annealed.

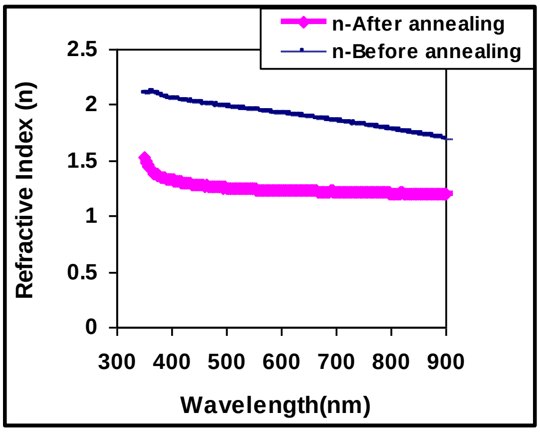

Fig. (11): The refractive index of ZnO thin films before and after annealing

6. Photo conductivity (σ_{ph}).

The photo conductivity of ZnO thin films is calculated by using the following equation [7]:

$$\sigma_{Ph} = \varepsilon_i \, \omega \, \varepsilon_o \text{----------------------------(4)}$$

Where ω are the angular frequency, ε_o is the permittivity of the air; ε_i is the imaginary part of dielectric constant.

Fig. (12) shows the photo of conductivity of the film before and after annealing against the photon energy.

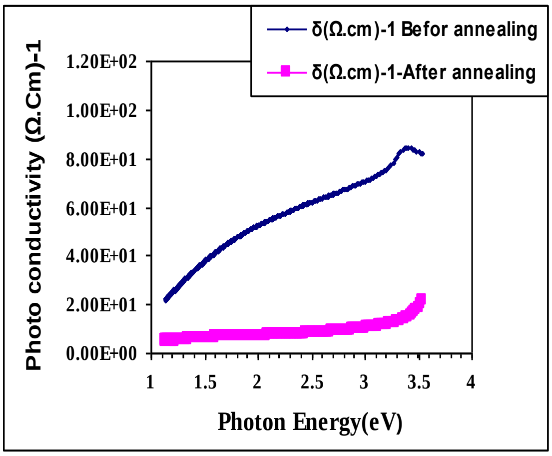

Fig. (12): The photo conductivity of ZnO thin films before and after annealing

Conclusions

Highly transparent ZnO thin films are successfully prepared by using spray pyrolysis technique onto hot glass substrate at 450 °C.

The transmission of the film improved after annealing, the absorption of the films is increase after irradiation and it decreases after annealing. The prepared films has wide direct band gap, the value of the energy gap is reduced after annealing. The wide band gap makes these films good material for solar cell applications as antireflection coatings and as UV photo detectors.

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