The Effect of the Annealing on the Optical Properties of Zinc Oxide Thin Films Prepared by Chemical Spray Pyrolysis Technique

Nada M. Saeed
Department of Physics, College of Science, University of Baghdad, 400 °C by using aqueous zinc chloride as a spray solution of molar concentration 0.1 M/L, then annealed at 550°C.

The crystallographic structure of the prepared film was analyzed with X-ray diffraction; the results shows that the film was polycrystalline in nature with preferred (002) orientation with grain size equal to 279 Å. The optical properties of the film were studied using VIS-UV spectrophotometer at wavelength within the range (300-1100) nm. The optical characterization shows that the films have an average transmittance 55% in the VIS regions and become 85% after annealing. The optical constants such as the refractive index (n), extinction coefficient (k), real and imaginary dielectric constants ($\varepsilon_r$, $\varepsilon_i$) were studied before and after annealing as a function of the photon energy at the mention wavelength, it was noted that the annealing affected on optical properties of the films. The optical energy gap was calculated to be 3.3 eV and 3.1 eV for the direct and indirect allowed transition respectively; these values are reduced after annealing.

Key words: Zinc oxide; Spray pyrolysis; semiconductor oxide.

ABSTRACT

Zinc Oxide (ZnO) is one of an important semiconductor material for its application in a wide range of optoelectronic devices. In this paper, ZnO was prepared as thin films by using 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 0.1 M/L, then annealed at 550°C.

The optical properties of the film were studied using VIS-UV spectrophotometer at wavelength within the range (300-1100) nm. The optical characterization shows that the films have an average transmittance 55% in the VIS regions and become 85% after annealing. The optical constants such as the refractive index (n), extinction coefficient (k), real and imaginary dielectric constants ($\varepsilon_r$, $\varepsilon_i$) were studied before and after annealing as a function of the photon energy at the mention wavelength, it was noted that the annealing affected on optical properties of the films. The optical energy gap was calculated to be 3.3 eV and 3.1 eV for the direct and indirect allowed transition respectively; these values are reduced after annealing.

Key words: Zinc oxide; Spray pyrolysis; semiconductor oxide.
INTRODUCTION

II – VI compound semiconductors, such as 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 is on the borderline between a semiconductor and the 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 stable with the wurzite structure (hexagonal symmetry) [6, 7, 8].

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 [9].

ZnO is suitable for an UV photodetector because of its direct wide band gap and large photoconductivity. ZnO epitaxial film-based photoconductive and Schottky type UV photodetector has been demonstrated [10].
MATERIALS AND METHODS

ZnO films were deposited onto glass substrates by spray pyrolysis technique using a 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 substrate; the films also were annealed at 550°C. 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 (± 0.1× 10⁻³ gm) was 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 were varied between 380-400 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 (\(\lambda = 1.54060 \text{ Å}\)), Current =30 mA, Voltage =40 kV, Scanning angle (25° to 50°).

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

RESULTS AND DISCUSSIONS

X-ray diffraction pattern for ZnO thin films

The X-ray diffraction pattern of ZnO thin films deposited at 400 °C, which was obtained with 2θ from 25° to 50 glancing angle, only with one sharp and three small peaks present, as shown in fig. (1). 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 literature of American Standard of Testing Materials (ASTM). The strongest 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 much lower intensity than the (002) peak.
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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, as listed in table (1).

![X-ray diffraction pattern (XRD) pattern of ZnO thin film before annealing](image1)

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

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>(2(\theta)) Degree</th>
<th>( d ) ASTM ((\AA))</th>
<th>( d ) (XRD) ((\AA))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>31.5</td>
<td>2.816</td>
<td>2.815</td>
</tr>
<tr>
<td>(002)</td>
<td>34.4</td>
<td>2.602</td>
<td>2.603</td>
</tr>
<tr>
<td>(101)</td>
<td>36.2</td>
<td>2.476</td>
<td>2.482</td>
</tr>
</tbody>
</table>

![X-ray diffraction pattern (XRD) pattern of ZnO thin film after annealing](image2)

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

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

\[
\frac{1}{d^2} = \frac{4}{3} \left[ \frac{h^2 + hk + k^2}{a_o^2} \right] + \frac{\ell^2}{c_o^2} \quad ----(1)
\]
The lattice constant \( (C_0) \) of the ZnO thin film was calculated at \( (002) \) as 5.19 Å, The grain size \( (G) \) can be calculated using the Scherrer’s formula [12]:

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

Where: \( (\lambda = 1.54060 \, \text{Å}) \) The grain size (crystallite size) is estimated about 279 Å at 002 before annealing. Two peaks are disappear after annealing; as showin fig. (2).

**The Transmission Spectra**

The transmission Spectra of ZnO thin films was estimated from VIS-UV spectrophotometer at wavelength within the range (300-1100) nm before and after annealing, the films have highly transparent in the visible range of the electromagnetic spectrum and present a sharp ultraviolet cut-off at approximately 380 nm, as shown in fig. (3). The transmission was increase from 55% to 85% after annealing, it is fairly agrees with the deposited film using chemical bath deposition technique and spray pyrolysis technique [13]. The moderately high transmission of film throughout the UV-VIS regions makes it a good material for applications as antireflection thermal control coating material.

![Transmission Spectra of ZnO thin film before and after annealing](image)

**The Absorption Spectra**

ZnO films have good absorption at short wavelength region, then the absorption spectra decreased with increasing of the wavelength, as show in fig. (4), the annealed films showed lower absorbance in same wavelength region.
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The absorption coefficient \( (\alpha) \) of ZnO film was determined from the absorption measurements, \( (\alpha) \) was calculated using the relation; \( \alpha = \frac{2.303A}{t} \)

Where \( A \) is the absorption, \( t \) is the thickness of the film. The absorption coefficient \( (\alpha) \) of ZnO film was calculated to be \( 1.5 \times 10^4 \text{cm}^{-1} \) at wavelength equal 370 nm.

Fig. (5) show the absorption coefficient as function of the photon energy; \( (\alpha) \) decrease at low photon energy because the probability of the electrical transfer between valance band and the conduction band is very rare and it will increase in the edge of the absorption toward the high energy \( (h\nu>3\text{eV}) \) before and after annealing.

The Reflectance Spectra

The reflectance (R) of ZnO film can be calculated from the absorption and the transmission spectrum using the relation; \( R+T+A = 1 \)

Fig. (6) show the reflectance of ZnO film as function of the photon energy, \( R \) is almost constant in the range (1.2-3.1) eV then rapid reduction will appear in the range (3.1-3.6) eV of the photon energy, that mean the absorbance of the film will be very little amount at the photon energy less than the value of the energy gap; \( h\nu< E_g \).
The absorption will increase when the photon energy be equal the energy gap \((h\nu=E_g)\) that because of the electronic transfers between the valance band and the conduction band.

![Reflectance Spectra of ZnO thin films as a function of the photon energy before and after annealing](image)

**Fig. – 6**: The Reflectance Spectra of ZnO thin films as a function of the photon energy before and after annealing

The Optical Energy Gap
The value of the energy gap \((E_g)\) of ZnO compound as a bulk is equal 3.31 eV \([13]\) but as thin film it is depend on the manufacturing techniques \([4, 14]\). The energy gap was estimated by assuming a direct and indirect allowed transition between valence and conduction bands using the following equation \([9]\):

\[(\alpha h\nu) = A^* (h\nu - E_g)^r \] ............(3)

Where \(A^*\) is constant, \(\alpha\) is the absorption coefficient, \(h\nu\) is the incident photon energy, and \(r\) is constant which takes the values \((1/2, 3/2, 2, \text{ and } 3)\) depending on the material and the type of the optical transition whether it is direct or indirect. \(E_g\) is determined by extrapolating the straight line portion of the spectrum to \(\alpha E = 0\). Fig. (7-a, b) shows the plot of \((ah\nu)\) vs. \(h\nu\), before and after annealing.
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From these drawing, 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 value are in good agreement with previously reported value [14, 15].

The optical energy gap for the indirect allowed transition of ZnO thin films was calculated from equation (3) using r=2, it was 3.1eV before annealing, as show in fig. (8-a). It was observed that the value of the energy gap reduced after annealing to be 2.1 eV, as show in fig. (8- b).

Fig. -7 :
a : The direct allowed transition energy gap of ZnO thin films before annealing
b : The direct allowed transition energy gap of ZnO thin films after annealing
Fig. -8 :

a- The optical energy gap of ZnO films for the indirect allowed transition before annealing

b- The optical energy gap of ZnO films for the indirect allowed transition after annealing

**Refractive Index (n) and extinction coefficient (k)**

The refractive index (n) and extinction coefficient (k) were determined from a transmittance spectrum as a function of the wavelength within the range 300-1100 nm. The Refractive index can be determined from the following equation [9]:

\[ n = \left[ \frac{4R}{(R-1)^2} - k^2 \right]^{1/2} - \frac{(R+1)}{(R-1)} \] -----(4)

where; R is the reflectance.

There is a little decreasing in the refractive index in the visible range; it was estimated 1.98 at 500 nm to 1.86 at 700 nm, as show in fig. (9), these values are nearly close with the reported refractive index values which are lies between 1.68 and 2.09 at 500 nm [13]. The refractive index changes slightly and steadily, also it was observe that the refraction index decrease when film was annealed.
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The extinction coefficient \((k)\) was calculated as a function of the photon energy using the relation \([9]\):

\[
k = \frac{\alpha \lambda}{4\pi}\]

The average value of \(k\) was in the ranged between \(1.40 \times 10^{-2}\) and \(1.50 \times 10^{-2}\) after annealing where it was ranging between \(4.1 \times 10^{-2}\) to \(4.8 \times 10^{-2}\) before annealing at the same region, as show in fig. (10).

**Photo conductivity \((\sigma_{ph})\).**

The photo conductivity of ZnO thin films was calculated by using the equation \([9]\):

\[
\sigma_{ph} = \varepsilon_i \omega \varepsilon_0\]

Where: \(\omega\); are the angular frequency, \(\varepsilon_0\); the permittivity of the air, \(\varepsilon_i\); the imaginary part of dielectric constant.

The plots of the real and the imaginary parts of the dielectric constant against photon energy are shown in fig. (11-a), (11-b).
Fig. 11:
a-: The real part of dielectric constant of ZnO thin films before and after annealing
b-: The imaginary part of dielectric constant of ZnO thin films before and after annealing

The photo of conductivity of the film before and after annealing against the photon energy was show in fig. (12).

Fig. – 12 : The photo conductivity of ZnO thin films before and after annealing
Highly transparent ZnO thin films were successfully prepared by using spray pyrolysis technique onto hot glass substrate at 400 °C. The transmittance of the film improved after annealing, the film possesses high transmittance over 85% in the visible region and it has sharp absorption edge after annealing. It was observed that the prepared films has wide direct band gap, the wide band gap make these films good material for solar cell applications as antireflection coatings.

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REFERENCES