Study of the optical and structural properties of the (ZnO) membrane, which is prepared by the method of thermal steaming by using the closed oven

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ABSTRACT

This study investigated the optical and structural properties of the (ZnO) membrane, which is prepared by the method of thermal steaming in the vacuum by using the closed oven on glass platforms at room temperature. The crystallization of the membranes prepared by X-ray diffraction pattern was diagnosed. The membranes were found to be polymorphic with hexagonal structure and crystal direction (002), the membranes were annealed for (5,15,25) min at (510°C),the results showed the increased height of peaks with their intensity and decreases in the optical gap energy. The study of optical properties also included the recording of both the absorption spectra and the permeability spectrum of the prepared membranes at the wavelength range (250-1100) nm, Also, the rest of the optical constants were calculated as functions of the photon energy, including (absorption coefficient, extinaction cofficient), Where the value of the absorption coefficient for ZnO thin films varies from (1.4 cm^{-1} to 2.09cm^{-1}), and the value of extinaction coefficient varies from (0.6 to 0.38). Transmission spectra showed highly transparent films with band gap energy varies ranging from 3.47ev to 3.3 eV.

Introduction

Thin membranes are referred to a layer or several layers of atoms of a specific substance with a thickness of one micron (1M) [1,2].Thin membranes are of great importance as they are used in a large number of optical fields such as normal, cold and heat mirrors as well the sensitive panels of electromagnetic waves, also used in the manufacture of dry films for imaging and photocopying, and used in the manufacture of electricity switches, resistors and micro-connections and integrated circuits and some compon ents of the circuit. It also contributed to the current development in the field of building digital computers because of its small size and light weight, in addition to the development of space research equipment and others [3].

Zinc Oxid is an inorgnic Compound with the formula ZnO.It is awhite powder that is insolube in water. ZnO is present in the Earth's Crust as the mineral zncite. That being side, most ZnO used Commercially is synthetic. Zinc Oxid is Commonly found in medical ointments Where it used to treat Skin irritiations. In more recent times zinc oxid has transceded to use in semiconductors, Concrete use, Ceramic and glass Compositions and even Cigarette filters .Zinc Oxide is also used in Cigarette filters, Lazer diodes and paint coatings. The band gap of zinc oxide is (3.3 eV) [3]. The methods of preparation of thin films have been varied, there are complex and simple as the cost of the devices used, The most important of these methods are [4]:

1.Electrical Deposition
2.Sol_Gel Deposition
3.Chemical Vapor Deposition
4.Sputtering
5.Spin Coating
6.Thermal Evaportion in the vacuum

In this study we used the method of thermal evaporation in the vacuum, This method is to heat the boat, which contains the thin film material to be prepared until the material turns to the boiling point and become hot vapor collides with the substrat and then deposited the material on it. The process is under low pressure and the pressures used in the deposition

process vary according to the material used to prepare the membrane.

Theoretical:

1. X-rays:

it is electromagnetic waves with wavelengths between ultraviolet rays and gamma rays, whose wavelengths do not exceed a few extras and range from (0.1-10) A°.Diffraction depends on the crystal structure and wavelength of the radiation used, where the wavelength must be equal to the constant of the lattice so the relationship between wavelength, frequency and photon energy can be described as follows [5].

$$E = h\nu = \frac{hc}{\lambda} \quad ------ (1)$$

Where E: photon energy

λ: wave length

ν : The frequency

When the constants are compensated, equation (1) is as follows:

$$\lambda(A°) = \frac{12.4}{E(kev)} ------ (2)$$

It is also noticeable when a single wavelength radiation is projected onto the surface of the recorded membrane, peaks will appear as a result of (Bragg) reflections on the parallel crystal surfaces it then receives the constructive interference of the reflected X-ray waves.The (Bragg's Law) is adopted as the calculation of the distances between the levels in the chain through the following relationship [6]: -

$$n\lambda = 2dsin\theta ------ (3)$$

Where n represents: the number of diffraction rank

λ: Wavelength of Falling Radiation

d: Inter-level distance

θ: Bragg's angle

Where *hkl* are Miller indices

Hexagonal structure:

$$\frac{1}{d^2} = \frac{4}{3}\frac{h^2 + h\,k + k^2}{a^2} + \left[\frac{l}{c}\right]^2 \ldots\ldots\ldots\ldots (5)$$

2. Atomic Force Microscope (AFM):

Is one of the types of scanner probe microscopes (SPM) based on the technique of scanning tunnel microscopy (STM), which is usually used to measure the surfaces of conductors and also insulators, and can provide us with very accurate information about the roughness of the surface (RMS) and also the size and numbers of granules [7].

3. Optical characteristics:

The electromagnetic spectrum falling on any material suffers from three physical phenomena: reflection, absorption, and penetration [8].

a. Reflectivity :

The reflectivity was obtained during the energy conservation law, which also combined permeability and absorption, where the phenomenon of reflection (internal and external) obtained from the surfaces of the material at the wavelength of the beam, which is greater than the crystal dimension of matter falling on the beam [8].

b. Absorption :

Absorption is the ratio between the intensity of radiation absorbed by the membrane and the intensity of the radiation falling on the material, and is given by the following relationship [8]: -

$$A_\lambda = \frac{I_A}{Io} ------ (6)$$

Where I_A: The transmitted radiation intensity

I_o: The incident radiation intensity

A_λ: The absorption

Where the phenomenon of absorption occurs when the reaction of the falling beam with the electronic cloud of the material.

c. Transmittance :

The ratio of the intensity of the transmitted radiation (I_A) to the intensity of the incident radiation (I_0) is Called transmittance (T_λ) [9]: -

$$T_\lambda = \frac{I_A}{I_o} ------ (7)$$

Where I_T : The transmitted radiation intensity

I_o: The incident radiation intensity

T_λ: The transmittance

The phenomenon of access occurs when a slight absorption of the falling rays on the membrane .The process of absorption occurs as a result of incident photon with energy and exicte the electron which moving from a lower energy of level to a higher energy level and this process can happen in t wo ways as shown in fig.(1)[10]:

1.Direct transition: The direct transition in general occurs between top of valence band and bottom of conduction band (vertical transition) at the same wave vector Δk = 0 , for conservation of momentum. The allowed direct transition refers to that transition which occurs between top of the valence band and bottom of the Conduction band when the change in the wave vector is equal to zero (Δk = 0) ,This transition is described by the following relation[11] :

αhυ =B $(h\upsilon - E_g)^r$………(8)

Where B: is constant depends on the nature of the material. If the transition occurs also between states of the same wave vector and still the change in the wave vector is equal to zero (Δk = 0), the transition is called forbidden direct transition:

2.Indirect transition : In indirect transition there is a large momentum difference between the points to which the transition takes place in valence and conduction bands, this means that the conduction band minima are not at the same value of k as the valence band maxima, then, assistance of a phonon is necessary to conserve the momentum, therefore

αhυ =B$(h\upsilon - E_g \pm E_P)^r$…………. (9)

Where Ep is the energy of an absorbed or emitted phonon, For an allowed indirect transition, the transition occurs from the top of the valence band to the bottom of the conduction band , When r = 2 , For forbidden indirect transition r = 3 .

αhυ=B $(h\upsilon - Eg \pm E_P)^2$ ……… (10)

While, the forbidden indirect transitions occur from any point near the top of V.B to any point other than the bottom of the C.B, Then we have

αhυ =B $(h\upsilon - E_g \pm E_P)^3$ ………. (11)

In general, the electronic transition type and the optical energy gap can be found from the following equation:

$$\alpha (h\upsilon) = B (h\upsilon - E_g opt)^r \ldots\ldots\ldots (12)$$

Where h: is the plank constant.

α: is the absorption coefficient.

hυ: is the incident energy.

r: is constant which takes the values (1/2, 3/2) depending on the material

and the type of the optical transition whether it is direct and indirect.
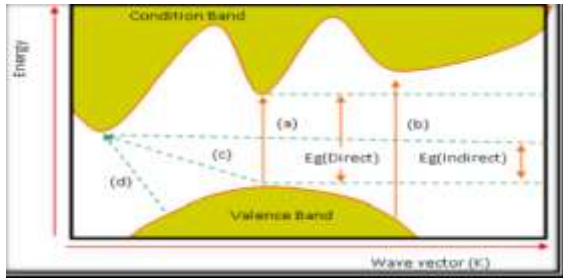
E_g opt : is optical energy gap.

Figure (1): The optical transitions (a) Allowed direct, (b) Forbidden direct; (c) Allowed indirect, (d) Forbidden indirect[10].

4.Optical constants

These include the absorption factor (α) and the extinction coefficient (K_o) [11].

a. Absorption coefficient (α)

The absorption coefficient (α) is defined as the percentage of the decrease in the radiation energy of the falling beam. For the unit of distance toward the propagation of the wave within the medium, the absorption coefficient depends on the photon energy and the semiconductor properties [12].The absorption coefficient is given in the following relationship:

$$I = I_o e^{-\alpha t} - - - - - (13)$$

When compensating constants we get the following equation:

$$\alpha = 2.303 \, {}^A/_t - - - - - (14)$$

Where : I_o, I are the incident and the transmitted photon intensity respectively

   t: The thickness of the material

   α: The absorpition coefficient

B. Extinection coefficient (K_o)

Extinection coefficient (K_o) is the amount of attenuation obtained in the intensity of electromagnetic radiation due to the interaction of electromagnetic radiation with the particles of the thin membrane, and the coefficient of laxity is given by the following equation [12]: -

$$K_o = \frac{\propto \lambda}{4\pi} - - - - - (15)$$

When we observe the equation of the complex refractive index, we find that the coefficient of inertia represents the imaginary part of the equation as in the following relationship:

$$N = n_\circ - iK_o \ldots\ldots (16)$$

Where : N represents the complex refractive index.

$n_\circ$: True refractive index.

K_o : The coefficient of extinction.

The real part of the Dielectric constant is describ by the following relation:

$$\varepsilon r = n_o{}^2 - K_o{}^2 \ldots\ldots (17)$$

The imaginary part of the Dielectric constant is describ by the following relation:

$$\varepsilon i = 2n_\circ K_o \ldots\ldots (18)$$

Where εr: The real part of the Dielectric constant

   εi: The imaginary part of the Dielectric constant

Experimental Concepts

ZnO thin films were coated on glass substrates by thermal evaporation in the vacuum method, The pressure used in this process (2.8×10^{-4})Torr.The substrates were cleaned by soap solution,Methoxy ethanol , distilled water, acetone and finally with deionized water. Then the films were deposited on the glass substrates using thermal evaporation system . In order to evaporate the solvent and remove the organic residuals the films were preheated at 350°C for 15 minutes before each Coating. This process was repeated several times. Then the films were annealed at 510°C for (5,15,25)min after each Coating.. The structure and orientation of the ZnO thin films were analyzed by X-ray diffractometer with Cu-Kα radiation. The thickness of the films was determined by thickness profile meter. The surface morphology of the films was observed by Scanning electron microscope. The optical properties of the films were carried out by UV-Vis spectrophotometer.

Results and discussion

Figure(2) shows the x-ray diffraction of the annealied ZnO membrane for (5,15,25) min, The membrane intensity decreased significantly with increased annealied time. This result is consistent with the researcher[11], When given longer, the phase transformation process is good By observing Table (1) , the results of the examination of the X-rays of the membranes are shown after Annealing for (5, 15, and 25) min and comparing the results with the ASTM card no.(96-901-1663), the results showed that the ZnO membrane was polycrystalline and hexagonal and Figure (2) shows these membranes and the upper peaks. Where the results showed the increase in the duration of the Annealing increase in high levels of intensity for each of the three crystalline levels, especially the apparent level (200). The reason for the increase in the levels is that the increase in the time of the Annealing leads to the non-arrangement of the atoms within the crystalline lattice and thus lead to the divergence of the parallel and successive crystalline levels, As well as because of the crystalline construction of new angles of the compound (ZnO) ,and this indicates the oxidation of the element (Zn) to (ZnO) at a high rate where the crystalline grains begin to

become more regular, so appeared more than the peak of the compound (ZnO) and high intensity[12]. The figure(3 a) shows energy gap of the oxidized ZnO membrane for 5min times, The energy gap value(3,9

ev) and the energy gap value of a membrane in the figure (3b) are equal (3.61ev). These results are significant and there is a absorption function in the figure(3 b) indicating that the time is not enough to annealing the membrane. In Figure [4], we observe an decreased in the value of the extinaction coffcient. This indicates the occurrence of electron transitions.

In the previous research, a thin membrane of 99% purity was obtained during a period of 30 sec. In the current research, the best membrane was obtained during the period (25 min). This is due to the use of

the closed oven, this means that the amount of oxygen is limited inside the oven, it takes longer to obtain a thin membrane with 99% purity, this is due to the process of the reaction of oxygen gas with the atoms of (Zn), which takes longer time to become a compound (ZnO). Where the value of the absorption coefficient for ZnO thin films varies from (1.4 cm^{-1} to 2.09cm^{-1}) ,and the value of extinaction coefficient varies from (0.6 to 0.38). Transmission spectra showed highly transparent films with band gap energy varies ranging from 3.47ev to 3.3 ev

Table (1) The results of X-ray diffraction of the ZnO membrane after Annealing.

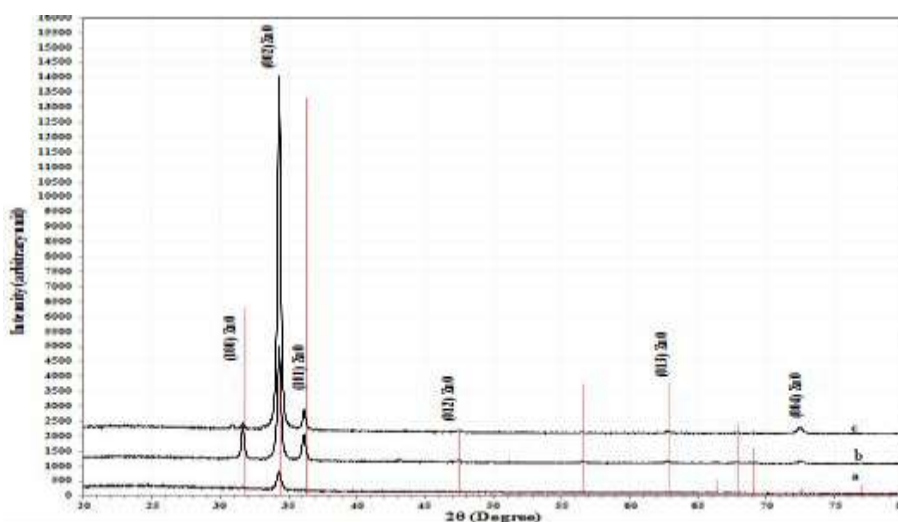| Sample	2θ (Deg.)	FWHM(Deg.)	d_{hkl} Exp.(A^O)	G.S(nm)	hkl	d_{hkl} Std.(A^O)
A Annealed for 5min	34.3136	0.4026	2.6113	20.7	(002)	2.6035
b Annealed for 15min	31.6779	0.2929	2.8223	28.2	(100)	2.8137
	34.3136	0.3294	2.6113	25.3	(002)	2.6035
	36.1440	0.3660	2.4831	22.8	(101)	2.4754
	47.5290	0.3661	1.9115	23.7	(012)	1.9110
	62.7578	0.3661	1.4794	25.4	(013)	1.4772
	72.4954	0.4027	1.3028	24.5	(004)	1.3017
C Annealed for 25min	31.6779	0.2197	2.8223	37.6	(100)	2.8137
	34.3136	0.2562	2.6113	32.5	(002)	2.6035
	36.1440	0.3294	2.4831	25.4	(101)	2.4754
	47.4558	0.2563	1.9143	33.9	(012)	1.9110
	62.7578	0.2196	1.4794	42.4	(013)	1.4772
	72.4588	0.3661	1.3033	26.9	(004)	1.3017

Figure (2) The results of x-ray diffraction of ZnO films were annealed at 510˚C for(a (5min), b(15min), c(25min).
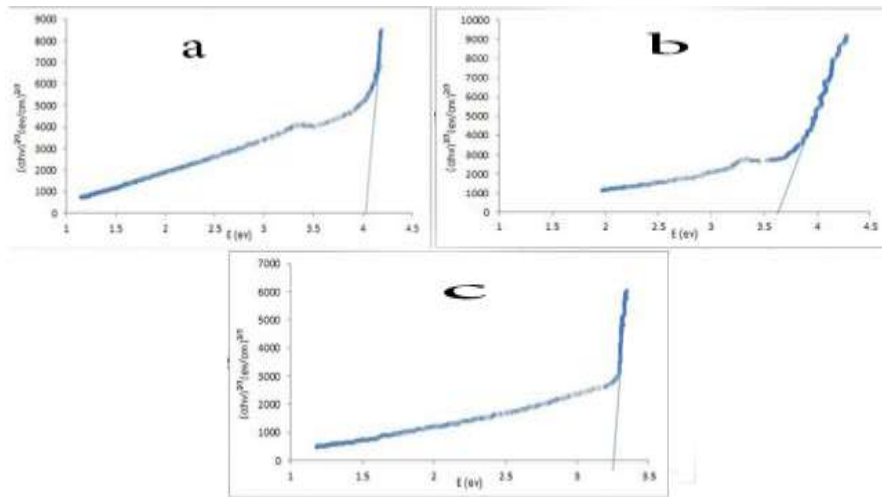
Figure (3) The results of energy gap of ZnO films were annealed at 510°C for(a (5min), b(15min), c(25min).
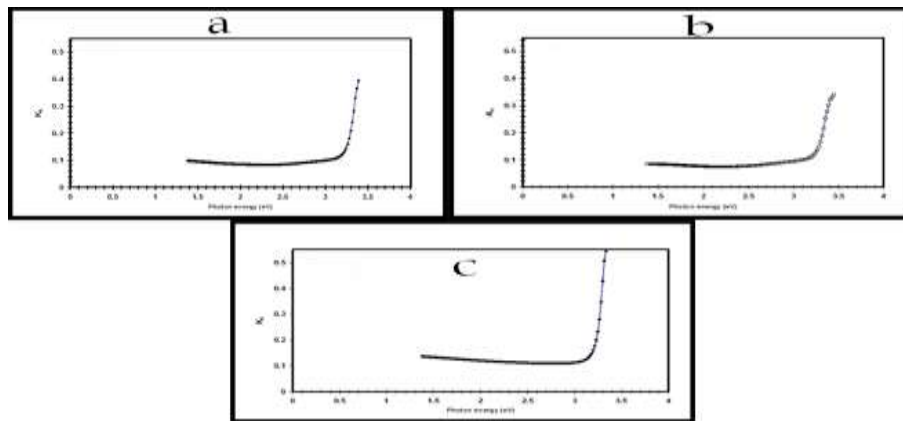

figure (4) The results of extinaction coefficient of ZnO films were annealed at 510°C for(a(5min), b(15min), c(25min))
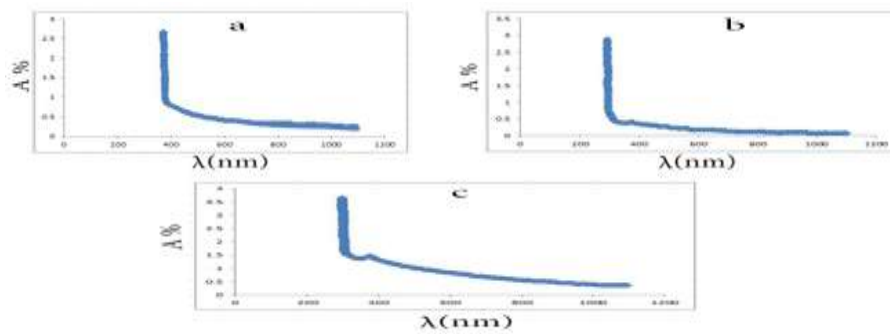

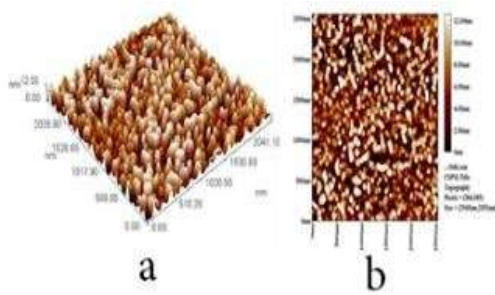**figure (5) The results of Absorption of ZnO films were annealed at 510°C for (a(5min), b(15min), c(25min))**

Figure (6) Image of the AFM-microscope of the surface of the membrane after Annealing for(5)min a.three dimension , b.two dimension.
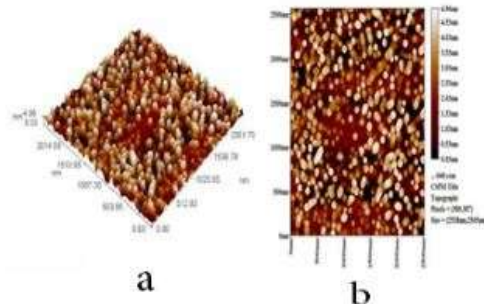

Figure (7) Image of the AFM-microscope of the surface of the membrane after Annealing for(15)min a.three dimension , b.two dimension.

During the observation of Figure (8) of the Annealing membrane for (25 min) which shows the image of the membrane in three dimensions and two dimension of the AFM-microscope showed that surface roughness and average square root were increasing the value of the thermal treatment is due to the crystalline development of the particles perpendicular to the surface and the type of membrane of the type of needle, As well as because of the increase in the proportion of the particle ,and the shape of the form

to the columns instead of the ball shape , and thus the appearance of the membrane in the form of columns or spindle.
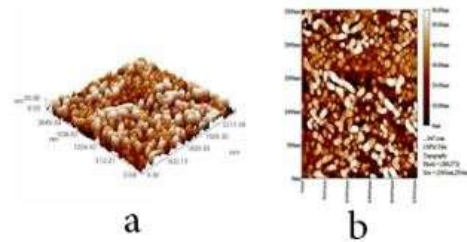

Figure (8) Image of the AFM-microscope of the surface of the membrane after Annealing for(25)min a. three dimension , b.two dimension.

Table (2) The results of AFM - microscope of the surface of the ZnO membrane after Anneaking

Time of annealing	Average Roughness	Root Mean Square	Average Grain
5min	12.55 nm	16.1 nm	78.33 nm
15min	4.96 nm	1.41 nm	88.76 nm
25min	56.95 nm	3.61 nm	75.13 nm

Conclusion

1. The results showed that the ZnO membrane was polycrystalline and hexagonal.
2. The results show that the appropriate time to annealing ZnO membranes in the case of a limited amount of oxygen is 25 min.
3. The results showed that the annealied leads to increased peaks intensity and their unity and thus lead to increased crystallization and stability of the crystal.
4. The results show that the annealied process of the ZnO membrane leads to a decrease in the energy gap.
5. The study showed that the optical properties of ZnO membrane have a energy gap equal to(3.3 eV) at 510°C

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دراسة الخواص البصرية والتركيبية لغشاء ZnO المحضر بطريقة التبخير الحراري وبأسلوب الفرن تام الغلق

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الملخص

تم في هذا البحث دراسة الخواص البصرية والتركيبية لغشاء ZnO المحضر بطريقة التبخير الحراري في الفراغ وبأسلوب الفرن التام الغلق على قواعد زجاجية تكون في درجة حرارة الغرفة.

وتم تشخيص طبيعة تبلور الأغشية المحضرة من خلال نمط حيود الاشعة السينية حيث وجد ان الأغشية ذات طبيعة متعددة التبلور وذات تركيب سداسي متراص وبالاتجاه البلوري (002)، كذلك تم تلدين الأغشية المحضرة ولمدة (5, 15, 25)min وبدرجة حرارة (510°C) إذ اظهرت نتائج التلدين زيادة ارتفاع القمم مع حدتها والنقصان في فجوة الطاقة البصرية. كذلك اشتملت دراسة الخواص البصرية تسجيل كل من طيف الامتصاصية وطيف النفاذية للأغشية المحضرة وعند مدى الاطوال الموجية (250-1100)nm، وايضا تم حساب بقية الثوابت البصرية كدوال لطاقة الفوتون والتي تشمل (معامل الامتصاص، معامل الخمود)، حيث ان قيمة معامل الامتصاص تتراوح ($2.09cm^{-1}$ _ $1.4\ cm^{-1}$)، وقيمة معامل الخمود (0.38_0.6). بين طيف النفاذية للغشاء اعلى قيمة للنفاذية وفجوة الطاقة تتراوح بين($3.47\ ev$_3.3).