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, extinction coefficient), Where the value of the absorption coefficient for ZnO thin films varies from (1.4 cm$^{-1}$ to 2.09 cm$^{-1}$), and the value of extinction 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 components 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 Oxide is an inorganic compound with the formula ZnO. It is a white powder that is insoluble in water. ZnO is present in the Earth’s Crust as the mineral znite. That being side, most ZnO used commercially is synthetic. Zinc Oxid is Commonly found in medical ointments Where it used to treat Skin irritations. In more recent times zinc oxide has transcended 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 Evaporation 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 substrate 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) Å. 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].

   \[ E = h\nu = \frac{hc}{\lambda} \]  

   Where \( E \): photon energy 
   \( \lambda \): wave length 
   \( \nu \): The frequency

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

   \[ \lambda(A) = \frac{12.4}{E(kw)} \]  

   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]:

   \[ nd = 2d\sin\theta \]  

   Where \( n \) represents: the number of diffraction rank

   \( \lambda \): Wavelength of Falling Radiation 
   \( d \): Inter-level distance

   \( \theta \): Bragg’s angle

   Where \( hkl \) are Miller indices

   **Hexagonal structure:**

   \[ \frac{1}{a^2} = \frac{4h^2 + k^2 + k^2}{a^2} + \frac{(l-\frac{1}{3})^2}{c^2} \]  

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]:

      \[ A_3 = \frac{I_o}{I} \]  

      Where \( I_o \): The transmitted radiation intensity 
      \( I \): The incident radiation intensity 
      \( A_3 \): 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 \((I_t)\) to the intensity of the incident radiation \((I_o)\) is called transmittance \((T)\) [9]:

      \[ T = \frac{I_t}{I_o} \]  

      Where \( I_t \): The transmitted radiation intensity 
      \( I_o \): The incident radiation intensity 
      \( T \): The transmittance

   The phenomenon of absorption 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 excite the electron which moving from a lower energy of level to a higher energy level and this process can happen in two 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 \( \Delta k = 0 \), 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 \( \Delta k = 0 \). This transition is described by the following relation[11]:

   \[ \Delta h\nu = B (h\nu - E_p) \]  

   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 \( \Delta k = 0 \), 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

   \[ \Delta h\nu = B (h\nu - E_p) \]  

   Where \( E_p \) 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 \( r = 3 \).

   \[ \Delta h\nu = B (h\nu - E_p) \]  

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

   \[ \Delta h\nu = B (h\nu - E_p) \]
In general, the electronic transition type and the optical energy gap can be found from the following equation:

\[ \alpha (\nu t) = B (h\nu - E_{opt}) \] .......................... (12)

Where \( h \): is the plank constant.
\( \alpha \): is the absorption coefficient.
\( h\nu \): 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.
\( E_{opt} \): is optical energy gap.

**K_o**: The coefficient of extinction.

The real part \( \varepsilon_r \) of the Dielectric constant is describ by the following relation:

\[ \varepsilon_r = n^2 - K_o \] .......................... (17)

The imaginary part \( \varepsilon_i \) of the Dielectric constant is describ by the following relation:

\[ \varepsilon_i = 2nK_o \] .......................... (18)

Where \( \varepsilon_r \): The real part of the Dielectric constant
\( \varepsilon_i \): 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 (2.8x10^-3)Torr. The substrates were cleaned by soap solution, Methoxy ethanol, distilled water, 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. 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 annealed ZnO membrane for (5,15,25) min. The membrane intensity decreased significantly with increased annealed 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 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

**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 (\( \alpha \)) and the extinction coefficient (\( K_o \)) [11].

**a. Absorption coefficient (\( \alpha \))**
The absorption coefficient (\( \alpha \)) 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:

\[ I = I_0e^{-\alpha t} \] .......................... (13)

When compensating constants we get the following equation:

\[ \alpha = 2.303 \frac{A}{t} \] .......................... (14)

Where : \( I_0, I \) are the incident and the transmitted photon intensity respectively \( t \): The thickness of the material \( \alpha \): The absorption coefficient

**B. Extinction coefficient (\( K_o \))**
Extinction 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]:

\[ K_o = \frac{\alpha\lambda}{4\pi} \] .......................... (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:

\[ N = n_o - iK_o \] .......................... (16)

Where : \( N \) represents the complex refractive index. \( n_o \): True refractive index.
and the energy gap value of a membrane in the figure (3b) are equal (3.61 ev). These results are significant and there is a absorption function in the figure (3b) indicating that the time is not enough to annealing the membrane. In Figure [4], we observe an decreased in the value of the extinction coefficient. 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 2.09 cm\(^{-1}\)) and the value of extinction coefficient varies from (0.6 to 0.38). Transmission spectra showed highly transparent films with band gap energy varies ranging from 3.47 ev to 3.3 ev.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(2\theta) (Deg.)</th>
<th>FWHM (Deg.)</th>
<th>(d_{\text{hkl}}) Exp.((\text{A}^\circ))</th>
<th>G.S(nm)</th>
<th>hkl</th>
<th>(d_{\text{hkl}}) Std.((\text{A}^\circ))</th>
</tr>
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<tbody>
<tr>
<td>A Annealed for 5min</td>
<td>34.3136</td>
<td>0.4026</td>
<td>2.6113</td>
<td>20.7</td>
<td>(002)</td>
<td>2.6035</td>
</tr>
<tr>
<td>B Annealed for 15min</td>
<td>31.6779</td>
<td>0.2929</td>
<td>2.8223</td>
<td>28.2</td>
<td>(100)</td>
<td>2.8137</td>
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<tr>
<td></td>
<td>34.3136</td>
<td>0.3294</td>
<td>2.6113</td>
<td>25.3</td>
<td>(002)</td>
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<tr>
<td></td>
<td>36.1440</td>
<td>0.3660</td>
<td>2.4831</td>
<td>22.8</td>
<td>(101)</td>
<td>2.4754</td>
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<tr>
<td></td>
<td>47.5290</td>
<td>0.3661</td>
<td>1.9115</td>
<td>23.7</td>
<td>(012)</td>
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<td></td>
<td>62.7578</td>
<td>0.3661</td>
<td>1.4794</td>
<td>25.4</td>
<td>(013)</td>
<td>1.4772</td>
</tr>
<tr>
<td></td>
<td>72.4954</td>
<td>0.4027</td>
<td>1.3028</td>
<td>24.5</td>
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<td>C Annealed for 25min</td>
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<td>0.2197</td>
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<td>(100)</td>
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<td>0.2562</td>
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<td>(002)</td>
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<td>(101)</td>
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<td>47.4558</td>
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<td>(012)</td>
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<td>72.4588</td>
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<td>1.3033</td>
<td>26.9</td>
<td>(004)</td>
<td>1.3017</td>
</tr>
</tbody>
</table>

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 extinction 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

References

Figure (8) Image of the AFM-microscope of the surface of the membrane after Annealing for25(min) a. three dimension , b. two dimension.

<table>
<thead>
<tr>
<th>Time of annealing</th>
<th>Average Roughness</th>
<th>Root Mean Square</th>
<th>Average Grain</th>
</tr>
</thead>
<tbody>
<tr>
<td>5min</td>
<td>12.55 nm</td>
<td>16.1 nm</td>
<td>78.33 nm</td>
</tr>
<tr>
<td>15min</td>
<td>4.96 nm</td>
<td>1.41 nm</td>
<td>88.76 nm</td>
</tr>
<tr>
<td>25min</td>
<td>56.95 nm</td>
<td>3.61 nm</td>
<td>75.13 nm</td>
</tr>
</tbody>
</table>

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 annealed 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 annealed 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

Sn/Sb doped ZnO thin Films deposited by Sol-gel method, Optics & Laser Technology, 167(243).
دراسة الخواص البصرية والتركيبية لغشاء ZnO المحضر بطريقة التبخير الحراري وспособ الفرن

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الملخص

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

وتم تشخيص طبيعة تبلور الأغشية المحضر من خلال نمط جوهر الاضاءة السينية حيث وجد ان الأغشية ذات طبيعة متعددة التبلور وذات تركيب سداسي متراص وبالاتجاه البلوري (002)، كذلك تم تلدين الأغشية المحضر لمدة (5, 15, 25)min ودرجة حرارة (510)°C إذ اظهرت نتائج التلدين زيادة ارتفاع القمم مع حدوث انخفاض في فجوة الطاقة البصرية.

وتم فحص الخواص تناغمية للفة الأغشية المحضر وعند مدى الامتلاك (200-1100)nm، وايضا تم حساب نسب قياسية للفة الأغشية المحضر والتي تشمل معامل الإضاءة، معامل الخضارة، حيث ان قيمة معامل الإضاءة تتراوح بين (0.38-0.6)، بين فئة تناغمية للفة الأغشية اعلى قيمة للتنوع وفجوة الطاقة تتراوح بين (3.47-3.3 ev).