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Preparation and Study the Structural and Optical characteristics of Zinc Oxide (ZnO) Thin Films.

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ABSTRACT

thin films of Zinc Oxide (ZnO) They were created with the Thermo Chemical Spray Pyrolysis (CSPT) method on glass substrates at 350 oC. Zinc chloride salts. XRD and AFM were used to characterise the ZnO thin films' structural characteristics and surface morphology.. All of the produced films had a polycrystalline hexagonal structure with various peaks and angles, with a preferential orientation along the (002) direction, according to the XRD examination. The XRD results also showed that a rise in solution concentration caused the ZnO film's intensity to significantly increase and its crystallite size to somewhat increase. AFM investigate was done to look at the films' surface topography. The findings demonstrated that surface roughness, root mean square (RMS), and particle size roughness all increased with molarity. The produced films, however, can still be utilised as windows in solar cells in spite of these variances in surface roughness. Using a UV-Visible Spectrophotometer to measure the absorbance spectrum between 300 and 1100 nm in wavelength, the optical properties as a transmittance, absorption coefficient, and band gap energy were ascertained. The ZnO-prepared films showed transmittance values ranging from around 71% to 42%, with un direct transitions occurring. The films' band gap energies varied from 3.16 eV to 3.28 eV. The transmittance was found to drop and the absorption coefficient spectrum to rise with concentration, suggesting a tighter band gap energy.

Introduction

Zinc oxide (ZnO) is one of the transparent conductive oxides (TCOs), which are metal oxides combining with oxygen. i.e., they are semiconductors oxides such as (In_2O_3) and (SnO_2) [1]. It belongs to the group of binary compounds (VI-II) in the periodic table and exhibits unique properties used in various industrial applications. Zinc oxide is classified as an n-type semiconductor and possesses a large direct bandgap of approximately 3.3 eV, making it economically advantageous compared to other materials like SiC, In_2O_3, $CdSnO_4$, SnO_2 and GaN [2-6]. It has high optical transparency in the visible region and excellent chemical and mechanical stability. Zinc oxide crystallizes in the hexagonal wurtzite structure with lattice constants (c=0.525 nm) and (a=0.325 nm) [7].

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Due to its distinct characteristics, zinc oxide finds numerous applications in precise electronic devices, optical instruments, light-emitting diodes (LEDs), transparent conductive electrodes for solar cells [8], gas sensors, and temperature sensors [9]. and many others [10].Moreover, zinc oxide exhibits a high binding energy (electron-hole pair) of approximately 60 M eV [11]. It can be synthesized in its pure form or doped using various methods includes electrochemical deposition [12]. chemical bath deposition technique [13]. facile chemical route [14], combined sol-gel/hydrothermal/SILAR method [15]. chemical precipitation method [16]. sonochemical synthesis [17], and the Spray Pyrolysis Technique [18]. In order to manufacture (ZnO) thin films, our study used the thermal chemical decomposition process, which is inexpensive in terms of equipment, simple to use, and capable of producing large-area films with high adhesion and uniformity. Moreover, this method allows the mixing of two or more materials with different melting points [19]. The chemical decomposition technique (CSP) presents a valuable alternative to widely-used conventional methods for over two decades. In this process, salts of the compound materials are dissolved in a solution and then sprayed onto heated substrates in small defined droplets generated by a spraying device (Nozzle). The heated substrates promote the formation of a well-crystalline structure during the deposition [20].The objectives of this work is to obtain the best film by changing the molarityconcentrations, and its use in optical applications.

Preparation of Spray Solutions

Zinc chloride, which is provided by Chemical Ltd., Poole, England, with a purity of 99.6%, is dissolved in distilled water of a certain purity, as shown in Table (1), to create spray solutions with different concentrations. The following equation is followed in the preparation of each solution. [21].

$$W_t=M_{wt}\times M_t\times V/1000 \quad (1)$$

Where:

Wt: weight required to be dissolved (g).

Mt : Molar Concentration (M).

MWt : Molecular Weight (g/mol).

V: Distilled water Volume (ml).

Then, the salts were dissolved in distilled water 100 ml, then the solution was mixed with a device on the magnetic stirrer for a period of 20 min in order to ensure complete homogeneity of the solution, then the process of spraying the solution on glass substrates in order to prepare a (ZnO) film.

Table (1): Salts used in preparation of (ZnO) thin films

The molar concentration (M)	Net weight ($ZnCl_2$) (g)	Water used for dissolving Salt (ml)
0.04	0.5450	100
0.05	0.6813	100
0.07	0.9538	100

Equal amounts of zinc chloride ($ZnCl_2$) solutions were taken after the solution was prepared in order to create a (ZnO) thin film. One hundred millilitres of the solution were sprayed onto glass substrates set on an electric heater set to 350±10°C, with a spray rate of 5 s, a stoppage time of 20 s, and a spray device height of 30±2.

Results and discussion

1. X-ray test

The X-ray (XRD) findings of the (ZnO) film at molarities of 0.04, 0.05, and 0.07 M are shown in Figure (1). Diffraction peaks that match to crystallographic planes can be seen, suggesting a polycrystalline structure. The crystal planes (100), (002), (101), and (004) are represented by the observed diffraction peaks, which have corresponding diffraction angles of 32.761°, 34.097°, 35.778°, 47.027°, 62.545°, and 72.294°. The (002) plane exhibits the prevailing preferred orientation, suggesting a hexagonal crystal structure. These outcomes align with the JCPDS: 65-3411 International Card. We see that a minor increase in the concentration of the solution caused the intensity and crystal size of the film made from (ZnO) to slightly rise.

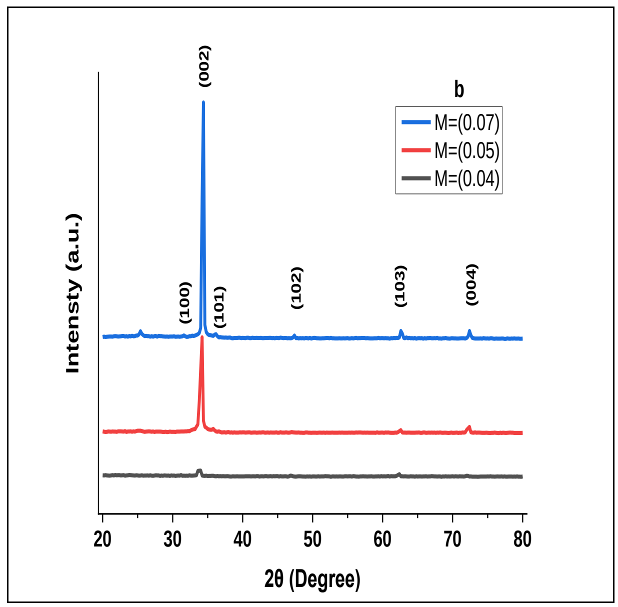

Figure (1): ZnO thin-film XRD anlysise with (0.04, 0.05, 0.07)M.

Table (2) provides the diffraction angles, crystalline size, and crystallographic planes that were determined using the Debye-Scherrer equation [22]. for (0.04, 0.05, 0.07) M molarities.

$$D=(k\lambda)/(\beta \cos\theta) \quad (2)$$

D: Crystal size. , β: Full Width Half maximum (FWHM) in radian.

K: Scherer's constant (0.94) , λ : X-Ray Wavelength (Å).

θ: Diffraction Angle (Bragg's Angle

Table (2): ZnO thin-film XRD results with (0.04, 0.05, 0.07) M.

Type of film	Molarit (M)	(hkl) Hexag	2θ (deg)	θ (deg)	d (nm)	FWH (deg)	β (rad)	D (nm)	Average D (nm)
ZnO	0.04	(100) (002) (101)	33.838 35.752 37.766	16.919 17.876 18.883	0.2646 0.2509 0.2380	0.667 0.818 1.339	5 0.01442 7 0.02335	13 11 6	10
ZnO	0.05	(100) (002) (101)	31.72 34.097 36.21	15.86 17.048 18.105	0.2731 0.2627 0.2507	1.052 0.409 0.795	0.018304 0.007116 0.03833	8 22 11	13.66
ZnO	0.07	(100) (002)(101)	27.899 34.337 47.386	13.949 17.168 23.693	0.3195 0.2609 0.1917	1.79 0.324 0.545	0.03122 0.005652 0.00950	5 28 17	16.66

The structural parameters shown in Table (3) were calculated from the following equations:

Dislocation Density (δ)[23]is:

$$\delta=1/D^2 \quad (3)$$

Where:

δ: Dislocation Density in (mm^{-2}).

Number of Film Layers (N_L)[24] is:

$$N_L= t/D \quad (4)$$

Where:

t: film thickness (mm).

Number of Crystals (N_o) [25]:

$$N_o=t/D^3 \quad (5)$$

Micro Strain (ε) [23]:

$$\varepsilon =(\beta \cos\theta)/(4) \quad (6)$$

Where:

β: Full Width Half maximum (FWHM) in radian.

θ:Angle of Diffraction (Bragg's Angle).

Table (3): Structural parameters for CdS thin film with (0.04, 0.05, 0.07) M

Type of film e	Molarity (M)	Thickness (t) (nm)	D (nm)	β (rad)	θ (deg)	(ε)	N_o (nm^{-2})	N_L	δ (nm^{-2})
ZnO	0.04	(400)	13 11 6	0.011635 0.014427 0.005525	16.92 17.876 18.883	0.00278 0.003432 0.0045475	0.1820 0.3 0.0138	30.4 36 66.6	0.00591 0.0082 0.0277
ZnO	0.05	(400)	8 22 11	0.018304 0.007116 0.03833	15.86 17.048 18.105	0.0044018 0.0017008 0.0091080	0.78125 0.037565 0.231481	50 18.18 36.36	0.015625 0.002066 0.008264
ZnO	0.07	(400)	5 28 17	0.03122 0.005652 0.00950	13.949 17.168 23.693	0.007574 0.00135 0.002174	0.182066 0.14577 0.097656	3.2 0.019 0.0002	0.04 0.001275 0.0034

2. AFM results

Figure (2) shows the three-dimensional (3D) grain size distribution atomic force micrographs and the (ZnO) film formed at 350 oC using the chemical spray pyrolysis (CSP) process with various molarities (M) of (0.04, 0.05, 0.07). It is clear that the root mean square (RMS), grain size value, and surface roughness all rise with increasing molarity. The greater molar concentration, which marginally increases the droplet size, is responsible for this. In spite of this, the produced film (ZnO) has a flat surface and high homogeneity, which decrease reflectance and increase transmittance, making it suitable for use as windows in solar cells. The molarity of 0.04 M produced the greatest film. The comprehensive AFM testing findings for the (ZnO) film are shown in Table (4).

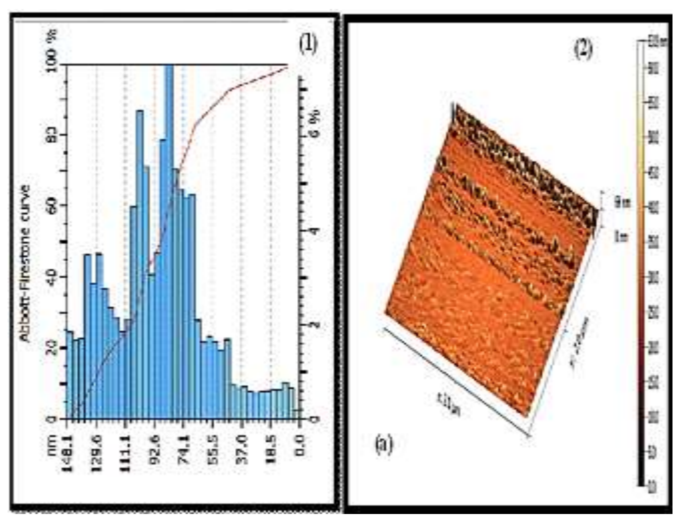

Figure (2-a): results of AFM for ZnO film with (0.04) M.
1. Grain size distribution **2.** (3D) Analytical Micrograph.

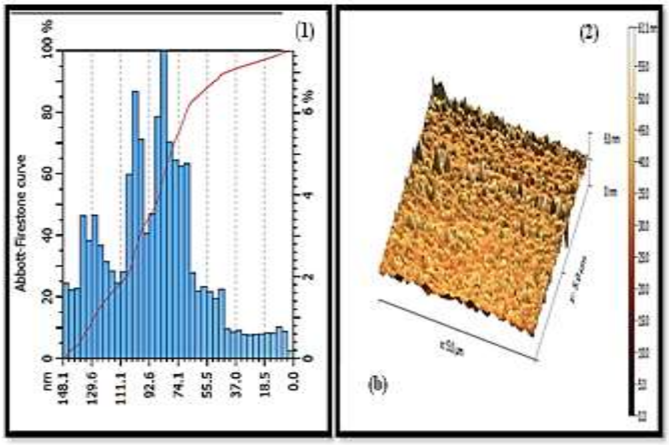

Figure (2-b): results of AFM for ZnO film with (0.05) M.
1. Grain size distribution **2.** (3D) Analytical Micrograph.

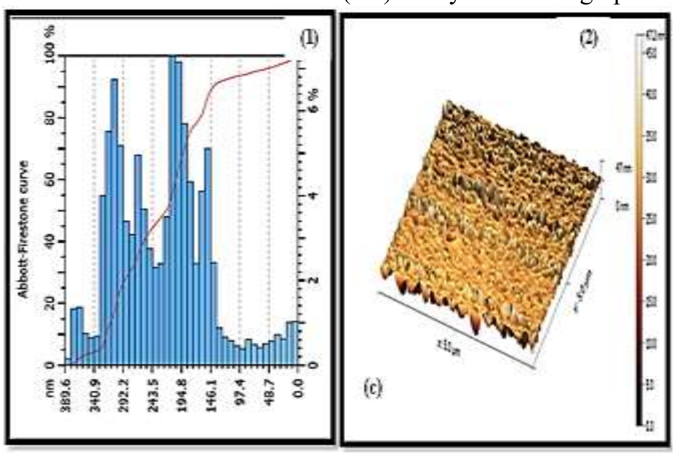

Figure (2-c): results of AFM for ZnO film with (0.07) M.
1. Grain size distribution **2.** (3D) Analytical Micrograph.

Table (4):AFM data for ZnO with (0.04, 0.05, 0.07) M.

Molarity (M)	Ave Diameter (nm)	RMS Roughness (nm)	Ave Roughness (nm)
0.04	94.23	25.11	18.59
0.05	137.9	43.82	38.32
0.07	259.9	76.84	62.29

3. Optical characteristics results

The transmittance and absorbance spectra were analysed as a function of wavelength in the 300–1100 nm range using a UV–Vis spectrophotometer to examine the optical properties of the generated (ZnO) films. Numerous optical characteristics, including the energy gap and absorption coefficient, may be computed from these spectra. The transmittance spectrum of zinc oxide is seen in Figure (3).Plotting the association between transmittance (T) and wavelength (λ) was done. At a visible spectrum wavelength of 550 nm, the transmittance was around 71%. The transmittance steadily drops to around 42% at the same wavelength as the molar concentration rises because to the increase in film thickness 0.07 M.

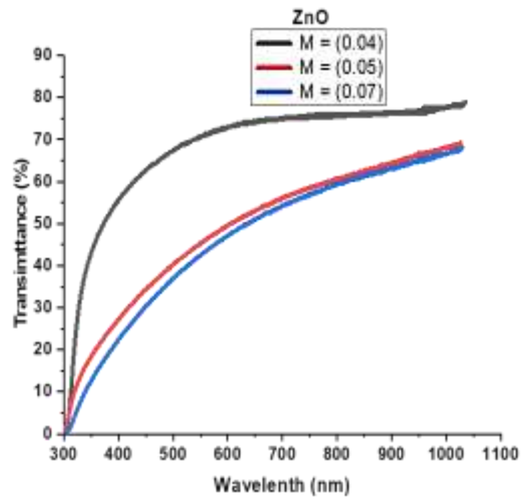

Figure (3): Transmittance spectra for ZnO film with (0.04, 0.05, 0.07) M.

The connection between the absorption coefficient (α) and wavelength (λ) is seen in Figure (4). At a wavelength of 550 nm, the absorbance was around 10^4 cm^{-1}, suggesting that undirect transitions were occurring.The absorbance progressively rises with an increase in molar concentration, and cause of the greater molar concentration, the absorption coefficient rises to around 4×104cm^{-1}.

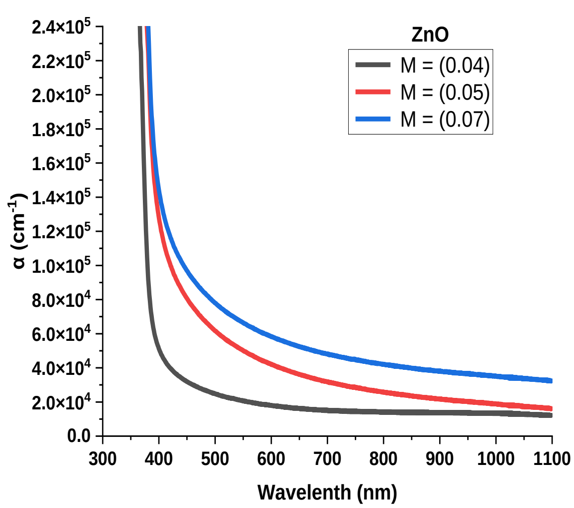

Figure (4): absorption coefficient for ZnO film with (0.04, 0.05, 0.07) M.

Equation (7) for the Tauc plot relation is used to display the energy gaps (Eg) for various concentrations in Figure (5) [26].

α=A/hv ((hv-E_g) $^{1/2}$) (7)

Where: α: is the absorption constant, h: is Plank's constan, A: is constant , v: is thefrequency of photon and E_g: enrge gap.According to the data, the films have energy gaps between 3.16 and 3.28 eV. An increase in molar concentration causes the energy gap to drastically reduce because it raises solution concentration, which in turn causes the film thickness to grow. For solar cell applications, it is therefore preferable to employ the produced (ZnO) film with a concentration of 0.04 M as the window layer.

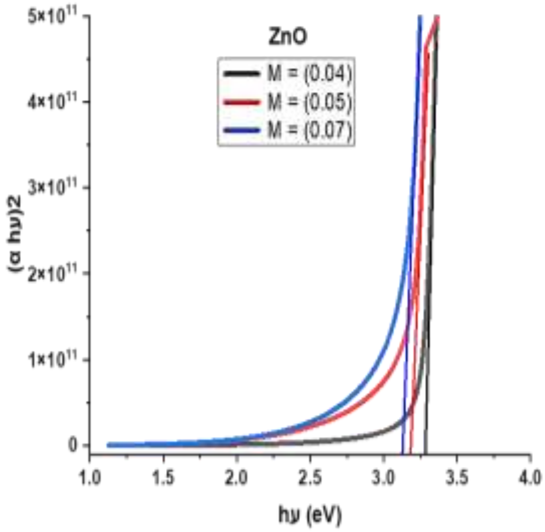

Figure (5): Energy gap for ZnO film with (0.04, 0.05, 0.07) M.

Conclusion

Based on the current investigation, zinc oxide (ZnO) films were produced on glass substrates at 350 °C and various molar concentrations using the Chemical Spray Pyrolysis technique (CSP). The concentrations of zinc chloride (0.04, 0.05, and 0.07) M were taken in a variable molar ratio to make (ZnO). X-ray diffraction (XRD) data indicates that the films are polycrystalline and have a hexagonal crystal structure. The prevailing favoured orientation was discovered at (002). For every molar concentration, several parameters related to structural characteristic were computed. Atomic force microscopy (AFM) studies showed that grainsize rate (RMS) and surface roughness increased with molar concentration. From the perspective of optical properties, the energy gap, transmittance, and absorbance spectra showed that as concentration increases, the absorbance spectrum increases while the energy gap, transmittance, and absorbance spectrum decrease. These analyses led to the conclusion that a molar concentration of 0.04 M yields the best-prepared (ZnO) film in terms of structural and optical findings. Because of its high homogeneity and smooth surface, this film may be utilised as a window layer in solar cells, resulting in decreased reflection, higher transmittance, and an energy gap.

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تحضير ودراسة الخصائص التركيبية والبصرية لأغشية أوكسيد الخارصين (ZnO) الرقيقة

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الخلاصة:

تم دراسة الأغشية الرقيقة لأوكسيد الخارصين(ZnO) المحضرة على قواعد زجاجية وبدرجة حرارة 350 ºC باستخدام تقينيه التحلل الكيميائي الحراري (Chemical Spray Pyrolysis) (CSPT)، من خلال استخدام املاح كلوريد الخارصين. تشير الفحوصات (XRD) ان جميع الأغشية المحضرة ذات تركيب متعدد التبلور وتركيب سداسي وتمتلك عدة قمم و زوايا وبالاتجاه السائد المفضل عند (002) ،كما بينت الفحوصات أن زيادة تركيز المحلول أدت إلى زيادة بالشدة بشكل ملحوظ وزيادة بسيطة بالحجم البلوري للغشاء المحضر لــ(ZnO)، كما بينت فحوصات (AFM) لمعرفة طبوغرافية السطح للأغشية، أن كلما زادت التركيز المولارية زادت خشونة السطح ومتوسط الجذر التربيعي (RMS) وكذلك معدل الحجم الحبيبي. وعلى الرغم من ذلك فأن الأغشية المحضرة يمكن استخدامها كنافذة في الخلايا الشمسية. أما الخصائص البصرية فقد تم احتساب كل من طيف النفاذية ومعامل الامتصاصية وفجوة الطاقة من خلال قياس طيف الامتصاصية ((Abso باستعمال مطياف UV-Visible Spectrotometer)) ضمن مدى الأطوال الموجية 300 nm -1100 nm. حيث وجد ان الأغشية المحضرة (ZnO) تمتلك انتقالات مباشرة و ذات نفاذية تصل إلى حوالي من1 % 7–42 كما لها فجوة طاقة تصل ما بين 3.28 - eV 3.16 eV و كلما ازداد التركيز أدى الى انخفاض النفاذية و زيادة معامل الامتصاص مع قلة فجوة الطاقة،

الكلمات المفتاحية: الاغشيه الرقيقة، اكاسيد اشباه الموصلات، تقنيه التحلل الكيميائي.