Optical Properties of Pure Zinc Oxide Thin Films Prepared by Sol-Gel Method

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Abstract:

Thin films of pure ZnO have been prepared on glass substrate using the Sol–Gel spin coating technique. Transmittance and absorbance spectra have been measured by using double beam UV-Visible 1800 spectrophotometer in the wavelength range (300-800)nm. It was found that the absorbance decreases with increasing the wavelength, while the transmittance increases with rising the wavelength. The transmittance exceeds 90% in the visible light region and in the near-infrared. The obtained results have shown that intrinsic ZnO is a semiconductor of wide optical energy band gap estimated to be 3.33eV. Furthermore, some optical properties and optical constants have been calculated from absorption and transmission measurements such as absorption coefficient, Urbach energy, extinction coefficient, refractive index and dielectric constant.

Key words: TCO- Semiconductor- Thin Film- Transmittance- Absorbance-The optical energy band-gap- Optical properties.

الخواص البصرية لأغشية أكسيد الخارصين الرقيقة والمحضرة بطريقة المحلول الغروي

الملخص:

تم تحضير أغشية رقيقة من أكسيد الخارصين النقي باستخدام تقنية المحلول الغروي والترسيب الدوراني. تم قياس طيف كل من الامتصاص والنفاذية للأغشية المحضرة باستخدام مطياف الأشعة الفوق بنفسجية – المرئية ذو الحزمة المضاعفة في مدى طول موجي (300nm–800). ولقد بينت الدراسة أن الامتصاصية تقل بزيادة الطول الموجي بينما تزداد النفاذية بزيادة الطول الموجي. كما أن النفاذية تتجاوز الـ 90% في منطقة الضوء المرئي

وبالقرب من منطقة الأشعة تحت الحمراء. وبينت النتائج المتحصل عليها أن أكسيد الخارصين الغير مطعم هو شبه موصل ذو فجوة طاقة واسعة قيمتها في حدود (3.33eV). كما تمت دراسة العديد من الخواص البصرية والثوابت البصرية باستخدام طيفي الامتصاص والنفاذية مثل معامل الامتصاص، طاقة أورباخ، معامل الخمود، معامل الانكسار بالإضافة الى ثابت العزل.

الكلمات المفتاحية: أكاسيد التوصيل الشفافة، شبه موصل، غشاء رقيق، نفاذية، امتصاصية، فجوة الطاقة البصرية، خواص بصرية.

Introduction:

Transparent conducting oxides(TCOs) such as ZnO and SnO are one of the most important compound semiconductors and became one of the most promising material in many applications and commercial devices due to their unique properties, such as low resistively and high transmittance in the visible light region[1],. ZnO is the material composed of cheap and abundant elements, and is readily produced for large scale coatings[2]. The interest in ZnO is fueled and fanned by its prospects in optoelectronic applications owing to its direct wide band gap Eg~3.3eV at 300K[3]. Some optoelectronic applications of ZnO overlap with that of GaN, another wide-gap semiconductor Eg~3.4eV at 300K which is widely used for production of light-emitting devices. However, ZnO has some advantages over GaN among which are the availability of high-quality ZnO thin film and a large exciton binding energy (60meV). ZnO also has much simpler crystal-growth technology, resulting in a potentially lower cost for ZnO-based devices[4]. Therefore, ZnO is a good candidate for many device applications, such as transparent electrode, flat panel display, organic light emitting diode, solar cells, field emission device, sensors, ultrasonic oscillators, transducers, photo-protective coating, surface acoustic wave device and laser diodes[5-17].

Besides the previous unique properties, ZnO-based semiconductors can present ferromagnetic behavior at room temperature when doped with transition metals such as Co and Mn[18, 19]. Therefore these systems become very attractive for both fundamental and technological point of view.

High quality ZnO thin films can be grown at relatively low temperature less than 700ºC[4], by a number of methods including; pulsed laser deposition, DC reactive magnetron sputtering, atomic layer deposition, RF magnetron sputtering, metal organic chemical vapor deposition and chemical spray

pyrolysis, pulsed laser deposition, dc reactive magnetron sputtering and sol–gel spin coating technique[20-24], which have been applied in this work.

Due to the importance of studying the optical behavior of ZnO thin films, where what can be expected of ZnO properties would provide an effort to position it for future device applications. This work is focused on the optical properties investigation of the pure ZnO thin films. The most important optical properties are the absorbance and transmittance of the thin films as a function of the photon wavelength. The other optical properties and optical constants can be concluded from absorption and transmission measurements.

The reflectance (R) as a function of the wavelength can been calculated according to the relation;　　　　$R = 1-A-T$　　　(1)

　　where A represents absorbance and T is transmittance.

The absorption coefficient (α) can be determined using Bouger Lambert law;

$$\alpha = \ln (100/ T\%)/t \qquad (2)$$

Furthermore, the spectral dependence of the absorption coefficient (α) and photon energy (hν) can be evaluated by using Urbach empirical rule, which is given by the following equation;

$$\alpha = \alpha_0 e^{\frac{h\nu}{E_u}} \qquad (3)$$

where (α_0) is a constant and (E_u) denotes the energy of the band tail or Urbach energy which is considered one of the important optical parameters in thin films which indicates the degree of crystalline in the structure due to the formation of localized states energies at the boundaries of the energy band gap. According to the previous equation, Urbach energy can be obtained from the slope of the straight line of plotting $\ln(\alpha)$ against the incident photon energy in the linear region of the exponential curve, it is usually below the fundamental absorption region. The inverse of the slope is the Urbach energy.

The fundamental absorption edge, which corresponds to the electron excitation from valence band top to conduction band bottom is used to determine the value of direct optical band gap using the Tauc relationship[25];

$$(\alpha h\nu)^2 = c (h\nu - Eg) \qquad (4)$$

where c is a constant which is inversely proportional to amorphousity and Eg is the optical energy band gap.

The extinction coefficient (K_0) which represents the imaginary part of the refractive index of the thin films can be calculated by the relation[26]:

$K_0 = \alpha\lambda/4\pi$　　　(5)

The refractive index (n_0) can be calculated by using the equation[26]

$$n_0 = \left[\left(\frac{(1+R)}{(1-R)}\right)^2 - (K_0^2 + 1)\right]^{1/2} + \frac{(1+R)}{(1-R)} \qquad (6)$$

Photon interaction with material may causes charge polarization. The polarization normally described by the complex dielectric constant(ε), whereby $\varepsilon = \varepsilon_r + \varepsilon_i$. Both real part ($\varepsilon_r$) and imaginary part ($\varepsilon_i$) can be calculated according to the following equations respectively;

$$\varepsilon_r = n_0^2 - K_0^2 \quad , \quad \varepsilon_i = 2n_0 K_0 \qquad (7)$$

Where, ε_r represents the measure of polarizibilty and ε_i represents value of the loosing energy due to movement of polarized dipoles as a heat.

In this work, we report on the growth of pure ZnO thin films at room temperature on glass substrates by sol-gel spin coating technique in order to investigate their optical properties.

Experimental details:

Intrinsic ZnO thin films were fabricated using the Sol–Gel spin coating technique. The starter solution was prepared from Zinc Acetate Dehydrate $Zn(CH3OO)_2.2H_2O$ of purity 99.5% and Isopropanole CH3CH(OH)CH3, at 0.1M concentration at room temperature. This solution was stirred on a magnetic stirrer with a hot plate for an hour. Some drops of Diethanol amine (DEA) C_2H_5-OH were added drop by drop to obtain a clear transparent solution with a continues rotating for two hours. The growth was performed with a slow rate on a circular well cleaned glass substrate of 10mm diameter and 1mm thickness. The thickness of the obtained films was measured by the gravimetric method~(300±20)nm. The optical properties of ZnO thin films were carried out with a double beam UV–Visible 1800 Spectrophotometer, which is made in England. Absorbance and transmittance measurements were collected by using the spectrophotometer in the wavelength (300-800)nm. While, the other optical properties and optical constants have been concluded from absorption and transmission measurements .

Results and Discussion:

The resulting spectra obtained of pure ZnO thin films are shown in figures(1) and (2). These figures are showing changes in absorbance and transmittance spectra respectively, as a function of photon wavelength. Figure(1) indicates that the absorbance decreases with increasing photon wavelength. Although the maximum absorbance is obtained in the range(300-350)nm, the incident photon energy could not excite the valence band electron to the conduction band whereas, its energy is about 2.17eV, i. e less than the optical energy gap.

Figure(2) shows a rise in the transmittance with raising the wavelength. Moreover, ZnO thin films show high transmittance exceeds 90% in the visible light region and in the near infra-red. In addition, a sharp increase in the

transmittance can be observed in the range (325-460)nm. Therefore, the fundamental absorption edge can be determined and it appears as has been shifted to a higher photon energy in a curve shape. The shift to higher energies proofs that ZnO thin film is a semiconductor of a wide energy band gap, while the curved shape confirms that the ZnO thin film under investigation is a polycrystalline structure.
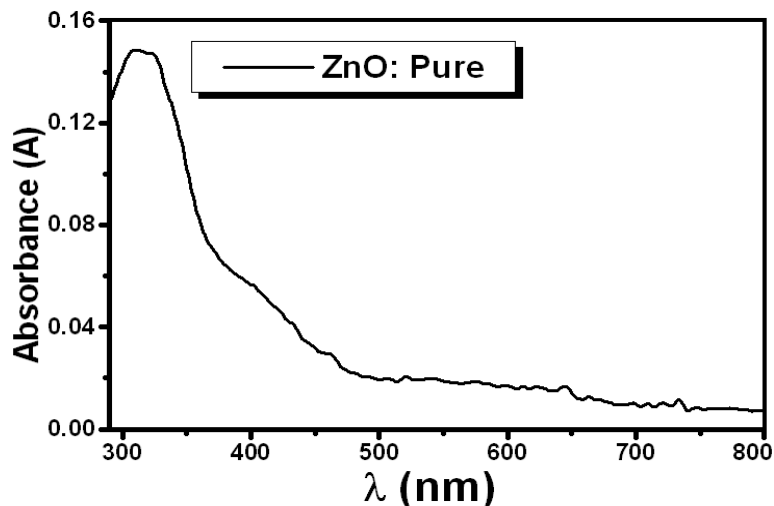

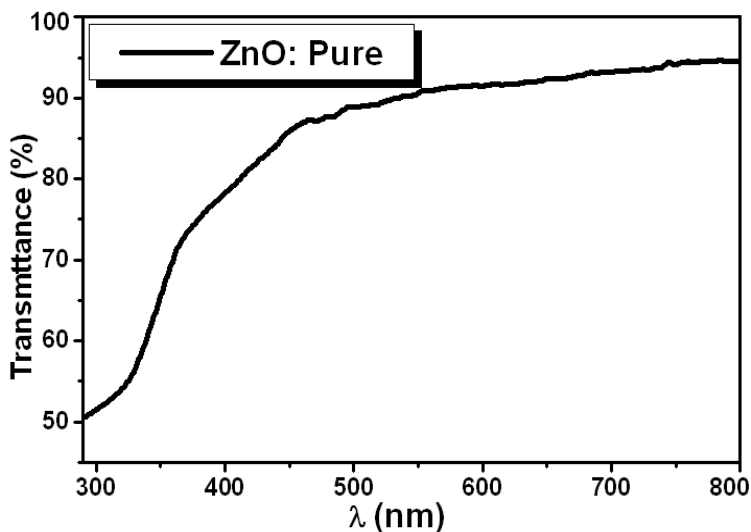Fig. (1) The absorbance spectrum of the pure ZnO thin film versus wavelength

Fig. (2) The transmittance of the pure ZnO thin film versus wavelength

Figure(3) indicates the reflectance of the intrinsic ZnO thin film versus wavelength . It shows a reduction in the reflectance with increasing the photon wavelength. The maximum reflectance can be observed at lower wavelengths which equivalent to the fundamental absorption edge.
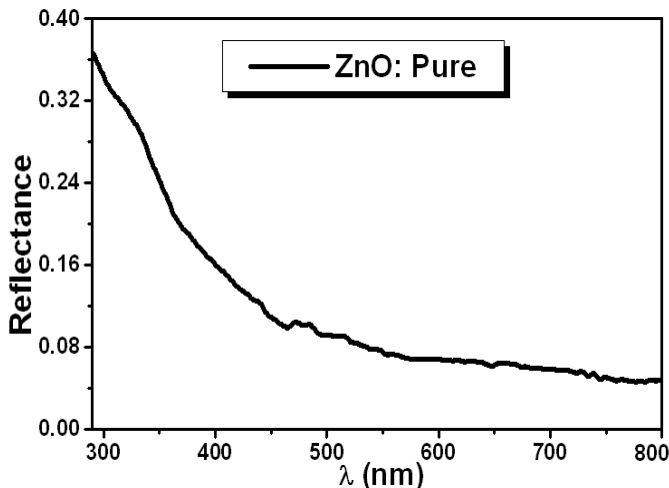

Fig. (3) The evaluated reflectance of the intrinsic ZnO thin film versus wavelength

Absorption coefficient spectrum as a function of photon energy is shown in figure(4). The spectrum is showing a gradual rise of (α) with increasing photon energy in the range[1.5-2.5]eV, followed by a sharp increase of (α) when photon energy exceeds 2.5eV.
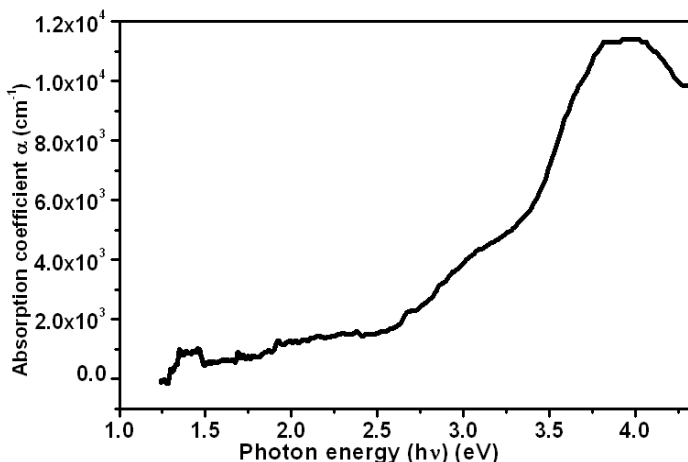

Fig.(4) Calculated absorption coefficient as a function of photon energy

The optical energy band-gap, which defined as the electron excitation energy from valence band top to conduction band bottom can be determined for the allowed direct electronic transitions by drawing the relationship between $(\alpha h\nu)^2$ versus $(h\nu)$ according to Tauc relation[25]. Figure(5) is showing the plot of $(\alpha h\nu)^2$ versus photon energy$(h\nu)$ for the pure ZnO thin film. As indicated the optical energy gap equals 3.33eV.
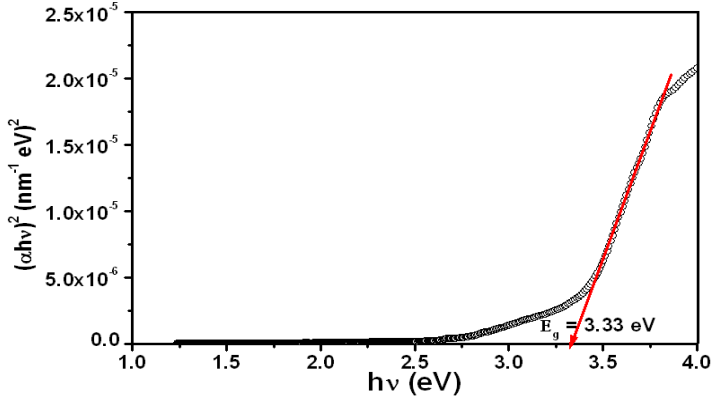

Fig.(5) Dependence of $(\alpha h\nu)^2$ on the photon energy for pure ZnO thin film

The absorption spectrum has been used to evaluate Urbach energy of the prepared ZnO thin film, which is considered as one of the important parameters in thin films. According to equation(3) and by taking the inverse of the slope, Urbach energy value of the prepared pure ZnO thin film is~ 0.38eV as shown in figure(6).
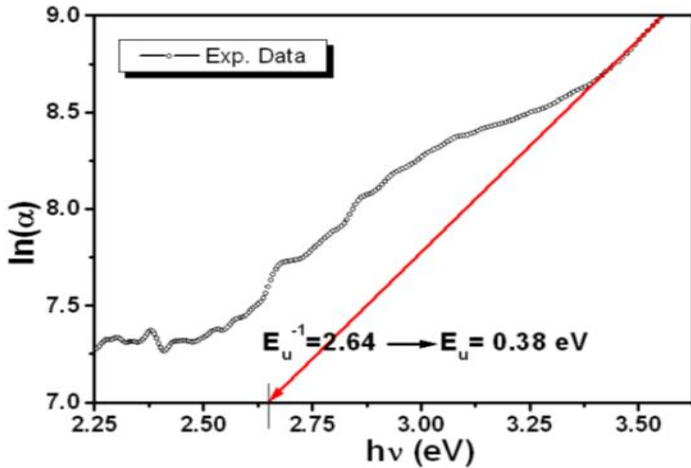

Fig.(6) Urbach energy of the pure ZnO thin film

Table(1). Optical energy band-gap values of intrinsic ZnO thin films according to some previous studies

Reference	Preparation method	Eg(eV)	year
عبدالله محمد فارع[28]	Chemical Thermal deposition	3.12	2001
Ansari[29]	Sol-Gel	3.9	2002
S.H. Jeong , et al[30]	Sputtering method	3.2	2003
Joseph , et al[31]	Chemical Spray Pyrolysis	3.24	2005
S. Larcheri , et al[32]	Chemical Vapor Deposition	3.2	2006
Mi and Bai[33]	DC Magnetron sputtering	3.12	2007
Wang, et al[34]	DC Magnetron sputtering	3.30	2008
Xing, et al[35]	DC Magnetron sputtering	3.18	2010
Wu, Bor-Tsuen, et al[36]	Are Evaporation in vacuum	3.35	2011
S. F. Oboudi, et al[37]	Chemical Spray Pyrolysis	3.36	2013
Lin, et al[38]	Sol-Gel	3.295	2013
A. A-K. Hussain, et al[39]	Pulsed Laser Deposition	3.2	2014
M. J. Jasim and U. M. Nayef[40]	Chemical Thermal Evaporation	3.27	2015
H. Sutanto, et al[41]	Sol-Gel	2.98	2016
Present study	Sol-Gel, Spin Coating	3.33	2020

The extinction coefficient of the prepared thin film as a function of photon wavelength is shown in figure(7).
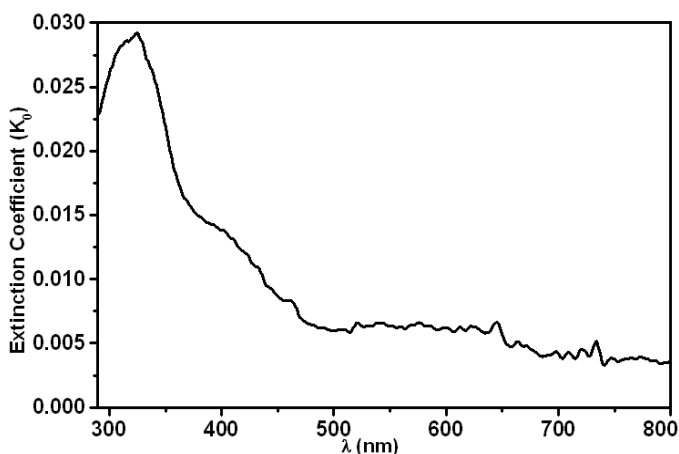

Fig.(7) Extinction coefficient as a function of wavelength of the pure ZnO thin film

Figure (8) represents refractive index variations as a function of wavelength. It can be noticed that n_0 decreases with rising (λ), and (n_0) curve is similar to the reflectance curve.
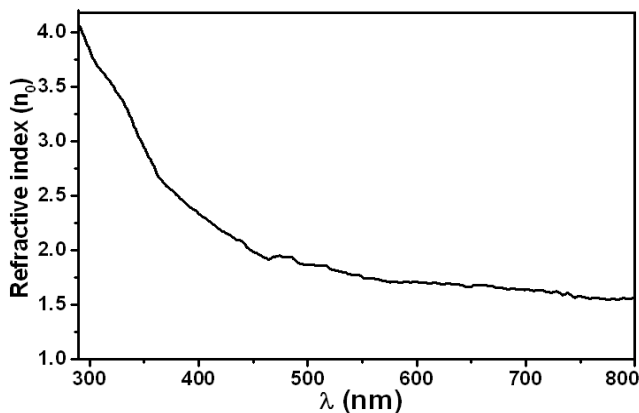

Fig.(8) Refractive index as a function of wavelength of the pure ZnO thin film

The occurred polarization through the thin film due to its interaction with incident photons has been estimated by calculating the two components of the dielectric constant(ε). Figures(9-a,b) show changes in real part and imaginary part values of dielectric constant as a function of photon energy, whereas both ε_r and ε_i of the prepared thin film increase with rising hν.
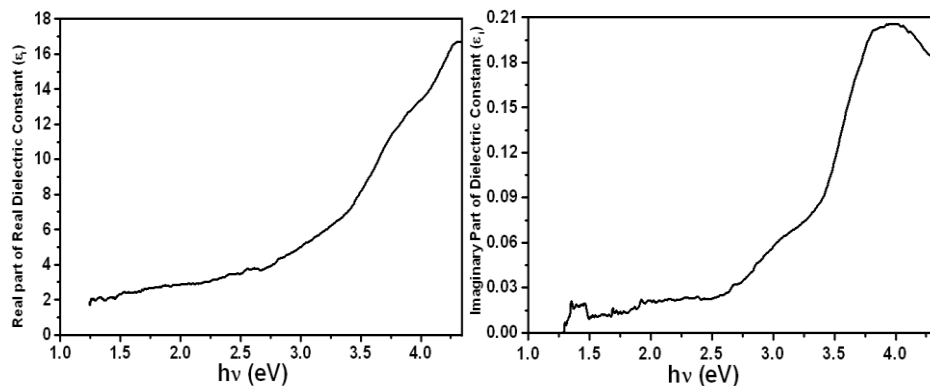

Fig.(9) Real part (left) and imaginary part (right) of dielectric constant of the pure ZnO thin film versus incident photon energy

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Conclusion:

We have successfully synthesized the ZnO thin films by Sol-Gel spin coating technique. The analysis of UV-visible spectra has shown that increasing wavelength leads to a rise in transmittance. On the other, it causes a reduction in absorbance. The transmittance of the film is very high and exceeds 90% in the visible light and infra-red region. This makes ZnO good candidate to be used as antireflection coating within this spectral region. In addition, it causes a shift of the fundamental absorption edge to higher photon energy value. It has been shown that the pure ZnO thin film is a semiconductor of a wide optical energy band gap estimated to be 3.33eV.

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