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Preparation and Study Energy gap of ZnO thin film nanostructure

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Abstract

In this work, Zno thin film and ZnO+nanoparticles ZnO have been derived by sol-gel using spin coating. The effect of adding nanoparticles has been studied. And the performance of thin film by using optical properties of the film has been worked out. The characteristics of the samples were analysed by using spectrometer, floursenmeter and an x-ray difractometers. The optical properties were studied by using a UV-vis spectrophotometer and a fluorophotometer. The result for x-ray diffraction shows that the ZnO thin film prepared by the sol-gel spin coating relatively poor crystalline quality, a little higher optical transmittance in the visible range than the one with nanoparticles and relatively a little weaker in emission performance. This film has less smooth surface compared to the one with nanoparticles .

1. Introduction

There is a lot of interest from our applied physics research group in working with alpha and gamma rays, in case of detection and application[1-4]. Now there is interest in studying the effect of this radiation in solar cell parameter, and the effect of this radiation on the efficiency of solar cell, in this work the performance of ZnO thin film should be checked first.

Zinc oxide (ZnO) is a prominent structure for a number of important and wide applications. The economic and ecological benefits of ZnO are low coast, available technology for films and Nano objects growth, nontoxicity and biocompatibility with human organism. ZnO attracted great interest as the material for ultraviolet and blue light emitting devices because of its wide band gap.

The application of Zno in photovoltaic is not limited to act as electron transport material (ETM) in dye sensitized solar cells (DSC) and hybrid solar cells (HSC)[5]. It can also be found applied as antireflection coating in inorganic solar cells [6,7] , or as optical spacer in polymer solar cells [8-11] .

The true consciousness about the potential impact of ZnO emerged once the simplicity of its synthesis was revealed together with its availability and low coast. opened up the opportunity for its application in a wide variety of devices, such as, solar cells, light emitting diodes, field effect transistors, electrochemical sensors, piezoelectric and thermoelectric devices, etc. Thus, there is a Synthesis need to study and understand how ZnO thin films characters change with changing some parameters in the preparation of the thin films.

2. Experimental

Materials used in this work to create ZnO thin film were Zinc acetate(1.65 gm) dehydrate (98% Merck), Isopropyl Alcohol (35ml) (99.5% , Fluka) , and Diethanol amine (2ml) (99% , BDH).
Glass substrates were cleaned with water and detergent. Then, they were cleaned with deionized water in an ultrasonic cleaner and washed with a mixture of acetone and alcohol. Spin coating was applied thereafter, by using the solution which was prepared for that. All Spinning time takes 30 sec , the spinning rate was 600 rpm for the first 8 sec, and then increased to 950 rpm for the last 22 sec.
A ZnO thin film was prepared by spin coating of sol-gel ZnO on top of the glass substrate . This process can be repeated many times to get film with desirable thickness . The ZnO sol-gel was prepared using the method previously reported [12,13] . By dissolving 1.65 gm of Zinc acetate dehydrate $[Zn(CH_3CO_2)_2.2H_2O]$ (Merck 99.98%) in 35 ml of dehydrated isopropanol alcohol (Merck 99.9%). The solution was stirred thoroughly on a magnetic stirrer for 30 min . A milky solution was obtained . Then 2 ml of dietrhanol Amin (Merck +99%) was added to the solution as stabilizer drop by drop until it became transparent , the solution was mixed by a magnetic stirrer at temperature of 60 C for about 120 min . The final solution was kept for 24 hr at room temperature before it was used . The yield was a stable, clear, and homogenous sol .The sol was deposited by the spinning coating technique. Once the ZnO by sol-gel was applied by spin coating the substrate was annealed at 600 c for 1 h . The procedure allows for the ZnO thin film used as buffer layer which permits a better contact between glass and ZnO and to evaporate some other unwanted materials from the film .
in case of ZnO thin film with ZnO nanoparticles, ZnO nanoparticles were add directly after preparation original solution, 0.25 mg nanoparticles of ZnO per 24 ml of solution have been add. Final mixture left for 20 min in an ultrasonic cleaner to get a better mixture for the solution due to the shaking produced by the machine. Spinning technique have been used to prepare the thin film directly from the final solution. This process can be repeated many time to obtain the required thickness. After each coating, thin film produced should be heated to 100 C for 30 min to dried up. And thin film required, placed at Furnace device at 600 C for about 1hr (18).
To obtain the optical constants of ZnO thin films , the optical transmittance measurements were carried out using a spectro SC, LaboMed.inc, made in USA. spectrophotometer, in spectral range between 300 to 800 nm at normal incidence.
Fluorescence spectra for samples were measured by using Perkin Elmer LS-3 spectrofluorometer. The excitation wavelength was set at 340 nm.
To identity the thin films, X-ray spectrum was measured for the samples,by using X'Pert Pro MPD by PANalytical company, with CuKα radiation.Manufactured by Netherlands.

3. Result and Discussion

3.1 X-Ray Diffraction

X-ray diffraction was used for crystal phase identification for ZnO thin films which were prepared by sol-gel technique, Figure 1 shows the X-ray pattern of ZnO thin film prepared by using spin coating method.

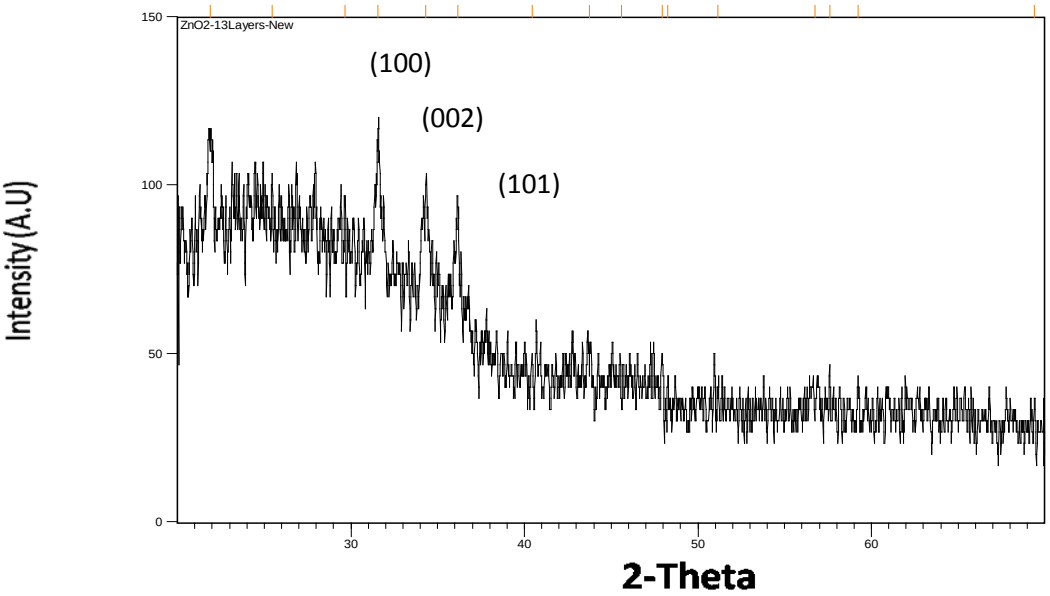

Figure1 X-ray diffraction spectra of ZnO thin film prepared by spin coating.

From figure 1 the film has amorphous structure with three noticeable ZnO diffraction peaks; (100), (002), and (101) appear at the "Bragg angle" of the diffraction $2\theta = 31.6^{o}, 34.3^{o}, and\ 36.2^{o}$ appear respectively, as listed in Table 1. These results are in agreement with the American Standard of Testing Materials (ASTM) and with [12] , as listed in Table 1.

Table 1. The values of (hkl) , 2Θ, and d for all peak of ZnO thin films

(hkl)	2Θ degree	d (A^0) (XRD) (ASTM)	d (A^0)
(100)	31.6	2.834	2.816
(002)	34.3	2.615	2.602
(101)	36.2	2.484	2.476

The lattice constant a_0 , c_0 for ZnO thin films can be calculated by using the following equation [13]

$$\frac{1}{d^2} = \frac{4}{3}\left[\frac{h^2 + hk + k^2}{a_0^2}\right] + \frac{l^2}{c_0^2} \qquad \text{-------- (1)}$$

Where h ,k , l Miller Indices
a_0 , c_0 lattice constants

the lattice constants c was calculated from (002) and a was calculated from (101) ,the ratio of the lattice constants c/a was calculated, and it was 1.61 which is nearly close to the ratio of an ideal hexagonal structure, which was recorded as 1.633 [14].

3.2 Absorption and Transmission

The absorbance of the prepared films are shown in Figure 2, there is a high absorbance in region up to 375 nm wavelength , then a sharp decrased in absoption, this property will give huge benifit for this thin film to be used in solar cell application. The absorbance of all samples were slightly decrease as the wavelength increases in the visible region. ZnO+nanoparticles ZnO thin film shows slightly less absorbance than ZnO thin film up to 375 nm wavelength, but above that shows a slight increase in absorbance.

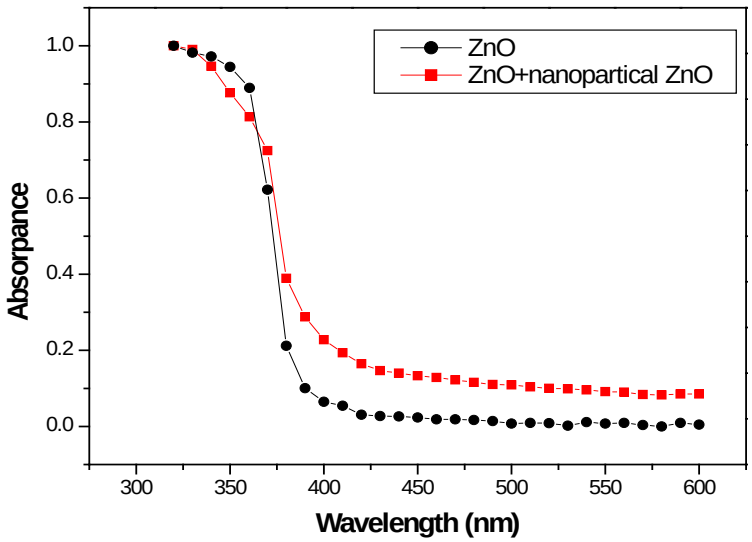

Figure 2 .Absorption spectrum of ZnO thin film and ZnO+nanoparticles thin film.

Transmitance specrum for those thin films, shows very low Transmitance in UV region, but in visable region, shows very high transmitance throughout the VIS. The regions compared to UV, as shown in Figure 3. That will give ZnO thin films a lot of application and previllage for using in photovoltaic polemer solar cells application.

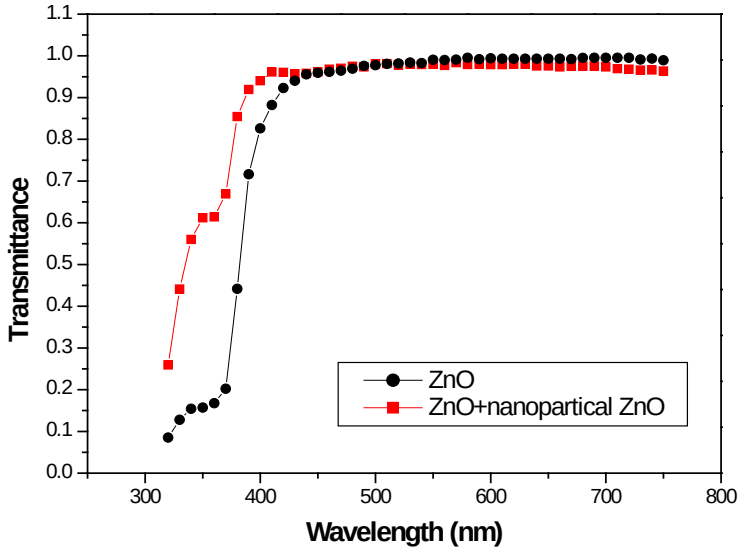

Figure 3. the Transmittance for ZnO thin film and the ZnO + nanoparticle ZnO thin film.

ZnO thin film shows less transmittance than ZnO+ nanoparticles thin film up to 375 nm wavelength , but above that shows a slight increased in transmittance.

3.3 .Photoluminescence Spectrums

The photoluminescence (PL) is carried out at this work at room temperature, this will provide information of different energy state available between valence and conduction bands responsible for irradiative recombination. Figure 4 represents the photoluminescence spectrum of ZnO thin films and the ZnO+ nanoparticles ZnO . These films were excited at 340 nm.

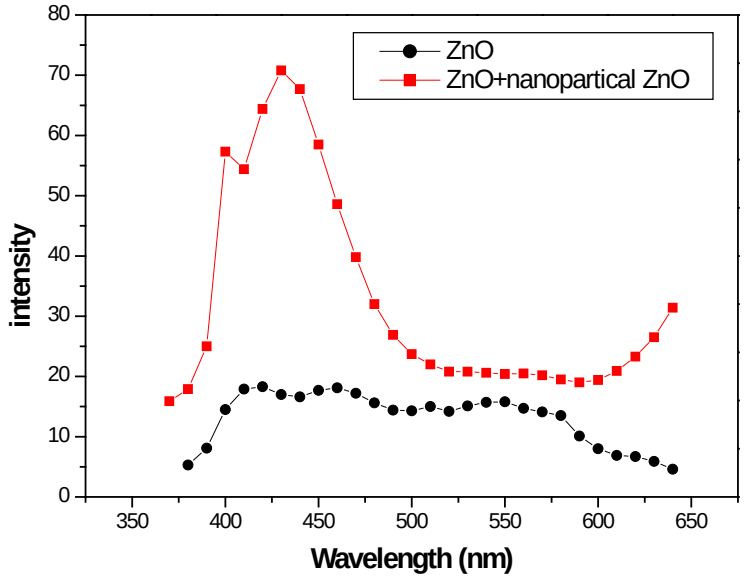

Figure 4 the photoluminescence spectrum of ZnO thin film and ZnO+nanoparticles thin films.

This figure shows that there an two peaks. The is first one fixed at 420 nm and the second one at 460 nm. Both of those peaks, have mostly the same intensity, in the case of ZnO thin film . But in the case of ZnO +nanoparticles ZnO those two peaks become a little bit clears with high intensity in general the spectrum of this thin film shows higher intensity than the previous one.The intensity of the first Peak at 400 nm, which represents band –to- band transition is lower than the intensity of the second one at 430 nm,

PL spectrum does not show a clear separation between the peaks, this may be attributed to the high speed of spinning, which was needed to get homogeneous sample , and non newtonian sols behaviour utilized by highly condensation rate of Zn:Ac. Slight broadening of band –to- band transition peak might be related to the existence of micro crack on the surface of the films.

3.4 Direct and Indirect Energy Gap

The value of the energy , E_g , of ZnO compound as a thin film depends on the manufacturing techniques, as mentioned by Ezama[16]. The optical energy gap can be estimated by calculating the absorption coefficient , α , which depends on the film thickness and absorbance , the following formula can be used for that,

$$\alpha = 2.303(\frac{A}{d}) \quad \text{----------} \quad (2)$$

Where A : is the absorbance , d : is the thickness .

The energy gap can be found out by taking into account a direct and indirect allowed transition between valence and conduction bands using the Tauc equation, as mentioned by Xuet. al. [15,17]

$$\alpha h\nu = B(h\nu - E_g)^r \quad \text{----------} \quad (3)$$

Where

hv : Is the incident photon energy , B : Is a constant , r : is constant

and r = ½ for direct transition
r = 2 for indirect transition
as given by Ghodsi [18]. Figure 5 shows the relation of, $(\alpha hv)^2$, and photon energy, from this relation , Eg , can be determined by extrapolating the straight line portion of the spectrum to $\alpha hv = 0$.

The value of the optical energy gap of ZnO thin film and ZnO + nanoparticles ZnO used in this work is equal to 3.2 eV and 3.21 eV for the direct transition between valence and conduction bands , as shown in figure 5 , and figure 6 respectively these values for energy gap are in good agreement with previously reported value by Alhamed et. al. and Yoshino[19,20].

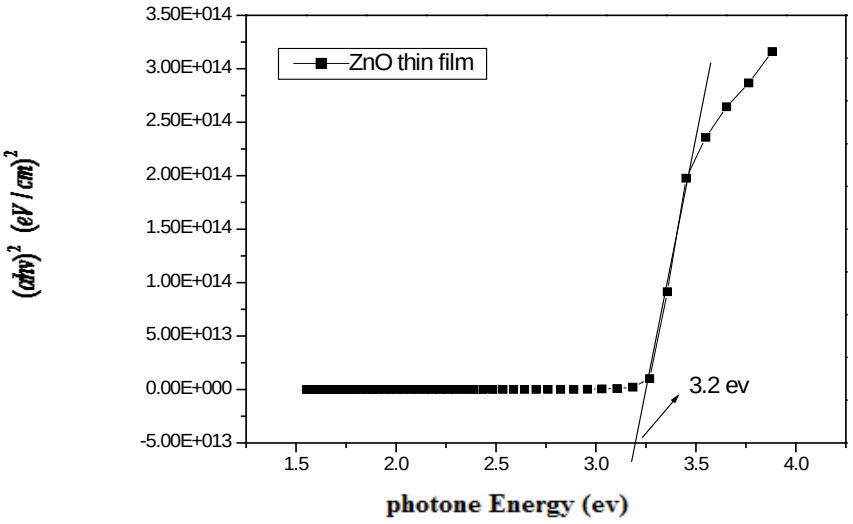

Figure 5 Direct allowed transition energy gap of ZnO thin films.

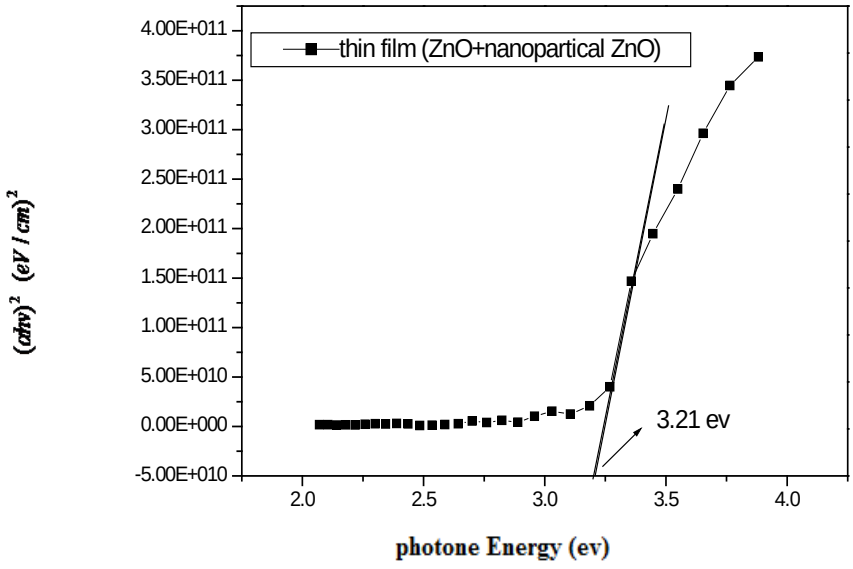

Figure 6 Direct allowed transition energy gap of ZnO + nanoparticles ZnO thin films.

The surface image of ZnO and ZnO + nanoparticles ZnO thin films is shown in figure 7 and figure 8. These two figure are for two different techniques of preparation, are imaged by using microscope. Figure 7 shows that ZnO+nanopartical ZnO thin films clearer than the one without nanoparticles ZnO.

Figure 7 microscope image of ZnO+ nanoparticle ZnO thin film.

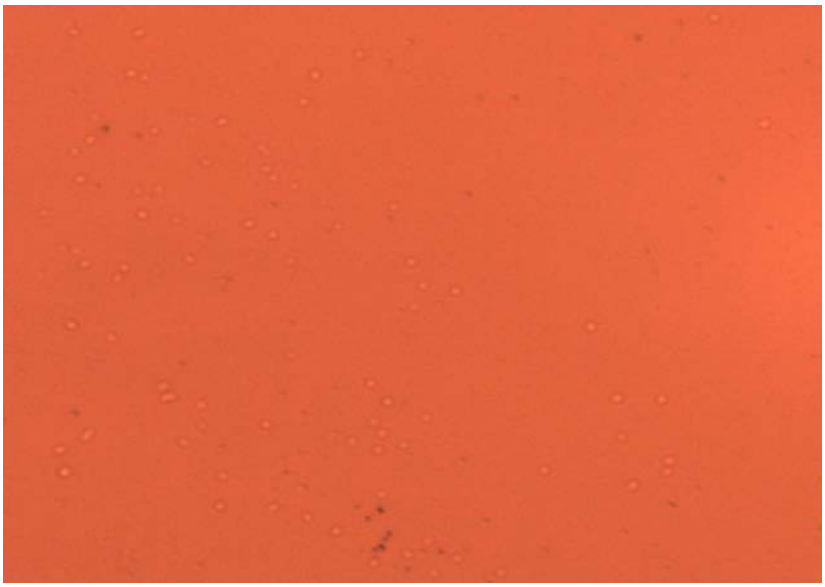

Figure 8 .microscope image of ZnO thin film

The image in figure 8 was for ZnO thin film without nanoparticles, this image shows more spot in it compare to image in figure 7. That will show differences in morphology.

4- Conclusion

The following conclusion can be drawing from this work.

- ZnO thin film shows a good transmittance in visible region if it compared with UV region. That will make this type of thin film ideal for protecting solar cell.
- Efficiency of the foil is not going to change much, if the nanoparticles added to original foil.
- There are some micro cracking in the surface of the thin film which causing broadening in photoluminescence peak.
- ZnO thin film with Nano particles shows more clearance with better morphology.

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إعداد ودراسة فجوة الطاقة لغشاء أكسيد الزنك الرقيق النانوي التركيب

الخلاصة

في هذا العمل , قد حضرت الاغشية الرقيقة لمركب الزنك اوكسايد ومركب الزنك اوكسايد المضاف اليه جزيئات نانوية من الزنك اوكسايد التي من السائل الهلامي باستخدام طريقة طلاء البرم . لقد تمت دراسة تاثير اضاقة الجسيمات النانوية وقد تم استنتاج استجابة الاغشية باستخدام الخواص الضوئية للفلم .وقد تم تحليل صفات النماذج باستخدام جهاز قياس الطيف الضوئي وجهاز قياس الفلورة وجهاز الاشعة السينية . اظهرت نتيجة التحليل باستخدام الاشعة السينية بان غشاء الزنك اوكسايد المحضر بهذه الطريقة يكون ضعيف التبلور, ويظهر نفوذية عالية في منطقة الضوء المرئي اكثر بقليل من الغشاء المحتوي على الجزيئات النانوية لكن مورفولوجية الغشاء المحتوي على الجزيئات النانوية افضل بكثير من الغشاء الغير محتوي على الجزيئات النانوية.