The optical Properties of Fe_2O_3 Thin Film Prepared By Chemical spray pyrolysis Deposition (CSP)

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Abstract

In this work, Fe_2O_3thin films have been prepared on glass substrate by chemical spray pyrolysis (CSP) technique at temperature 450^{o}C. Structural and optical properties of Fe_2O_3 thin films have been investigated and analyzed extensively with respect to deposition time.
The XRD results indicate that the structure of all prepared thin films from aqueous solutions $FeCl_3$ were polycrystalline in nature and has a rhombohedral (hexagonal) phase with preferred orientation along (104) plane.
The average grain size values for all prepared films have been found in the range from 76.543 to 83.258 nm , which indicates that all films have been Nano crystalline .The absorbance and transmittance spectra have been recorded in the wavelength range 300-600 nm, which showed that the absorption edges of Fe_2O_3 thin films differed at different deposition times. The optical band gap for allowed direct transition has been decreased from (2.4813 to 2.449)eV and with increasing deposition time. Moreover, the effect of deposition time on optical constants (absorption coefficient, reflectance, extinction coefficient, and refractive) has been investigated.

Keywords :

Fe_2O_3 thin film , chemical spray pyrolysis deposition (CSPD), Structure and optical properties .

الخلاصة

في هذا البحث حضرت أغشية Fe_2O_3 الرقيقة على أرضيات من الزجاج بتقنية الرش الكيميائي الحراري وبدرجة حرارة 450 درجة مئوية. تم دراسة وتحليل الخصائص التركيبية والبصرية لأغشية Fe_2O_3 بتأثير تغير زمن الترسيب نتائج حيود الأشعة السينية (XRD) تشير إلى ان تركيب الأغشية الرقيقة المحضرة من محلول $FeCl_3$هي متعددة التبلور وتمتلك طور معيني قائم ((Rhombohedral (Hexagonal) وبإتجاه سائد على طول المستوي (104). وجد ان قيم متوسط الحجم الحبيبي لجميع لأغشية المحضرة هي في المدى من 76.543 nm إلى 83.258nm ، والتي تعطي مؤشرا إلى أن جميع الأغشية هي نانوية التبلور. سجلت أطياف الامتصاصية والنفاذية في مدى الطول الموجي 300-600 nm، والتي أظهرت أن حافات الامتصاص لأغشيةFe_2O_3 الرقيقة تتغير بتغيير زمن الترسيب . وان طاقة الفجوة البصرية للانتقال المباشر المسموح انخفضت من 2.481 eV إلى 2.449 eV بزيادة زمن الترسيب بالإضافة إلى ذلك تم دراسة تأثير زمن الترسيب على الثوابت البصرية [معامل الامتصاص (α) والانعكاسية (R) ومعامل الانكسار (n) ومعامل الخمود (k)].

الكلمات المفتاحية: غشاء رقيق Fe_2O_3 ، الرش الكيميائي الحراري، الخواص البصرية والتركيبية

Introduction:

Iron oxide thin film (Fe_2O_3) can be used in several fields. It can be employed as, for example: Gas sensors[1,2] due to its great sensitivity for flammable gases, its fast speed of response and its long-term stability. Photo electrochemical solar cell for solar energy conversion [3,4] due to its optical band gap (Eg = 1.9 eV), its high optical absorption coefficient (a = $10^5 cm^{-1}$) for $\lambda > 600$ nm and its ability to present both conductivity type by using an appropriate doping element. ferromagnetic films have many applications for microwave devices as well as high-density recording media [5,6].

Experimental:

The chemical spray pyrolysis method has been used intensively lately for the preparation of different types of thin films, especially of oxides of many metals and semiconductors [7]. The thin films of hematite Fe_2O_3 were prepared from a solution of 4.055g $FeCl_3$ in 250 ml doubly distilled water. The clear yellow solution was sprayed on preheated glass substrates. This solution was passed through a pneumatic nebulizer with a nozzle diameter 0.7 mm. The spraying process lasted for about 15s. The period between spraying processes was about 3 min; this period is enough to avoid excessive cooling of the glass substrates.

In order to get uniform thin films, the height of the spraying nozzle, solution molarity and the rate of the spray process are kept unvaried during the deposition process at 30 cm, 0.1 M and 10 cm3/ min, respectively. The formed thin films were red brown to black in color. A temperature controller was used to measure the substrate temperature and control the resistance heater via a thermocouple. The films were prepared by spraying onto glass substrates that were heated at 450°C. The crystal structure of the prepared films has been examined by X-ray diffractometer (XRD-6000 Shimadzu). The source of X– ray radiation was Cukα radiation, the scanning angle varied in the range (20-60)° with wavelength 1.5405Å, speed 5deg/min, current 30 mA, and voltage 40 KV.

The optical measurements were included transmittance and absorbance spectra in the wavelength range (200-1100) nm using UV-1650 PC UV- VIS spectrophotometer Shimadzu.The value of absorption coefficient (α) has been calculated by using eq. A: Absorbance , d: thickness of films [8]

$$\alpha = \frac{2.303A}{d} \quad \text{.........(1)}$$

The extinction coefficient (K) was calculated using the eq. α: absorption coefficient [9]

$$K = \frac{\alpha\lambda}{4\pi} \quad \text{...........(2)}$$

The refractive index was determined by the relationship, R: reflectance [9]

$$n = \frac{\sqrt{1+R}}{\sqrt{1-R}} \quad \text{.........(3)}$$

The average grain size of Fe_2O_3 thin films, the has been determine by using Scherer's formula.

$$g.s = \frac{K'\lambda}{B\cos\theta} \quad \text{..........(4)}$$

Results and discussion:

X-Ray Diffraction:

Fig.(1.1) show that the X-ray diffraction patterns of Fe_2O_3 thin film prepared from aqueous solution of ($FeCl_3$) at deposition time 3 minutes sharp peaks at 2θ equal to 24.0794^0, 33.2796^0, 35.877^0 and 54.2464^0 referred to (012),(104),(110) and(116) direction respectively. Also this figure confirm that the preferential orientation is in the (104) direction. While Fig.(1.2) show diffraction patterns aqueous solution of ($FeCl_3$) at deposition time 7minuts sharp peaks at 2θ equal to 24.3523^0,33.1497^0, 35.5724^0, $40.7533^0$and 54.1465^0 referred to (012),(104) ,(110), (113) and(116) direction respectively. Also, this figure confirms that the preferential orientation is in the (104) direction. From the figures the intensities of the Fe_2O_3 thin films diffraction peaks increases with the increase of deposition time, moreover a diffraction peak from the direction (113) was appear in the deposition time 7minuts. The increasing of the deposition time lead to increase in the film thickness and improvement the crystallincity of the films. The increase in the intensity of the peaks may be attributed to grain growth associated with larger thicknesses[7,10]. The grain size for all thin films has been found to vary from (76.543 to 92.335) nm. For aqueous solution of (FeCl3) at deposition time 3 minutes the average grain size of prepared has been 76.543 nm. Increasing deposition time to 7 minutes the average grain size increased to 83.343nm.

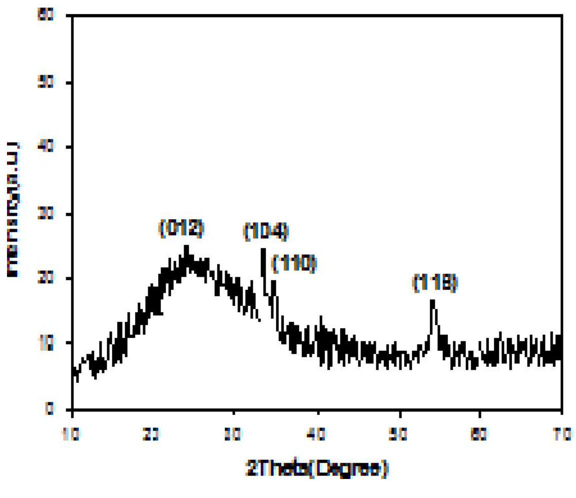

Fig.(1.1).The (XRD) for Fe_2O_3 Thin Films from $FeCl_3$ Aqueous Solution at Deposition Time 3 mints.

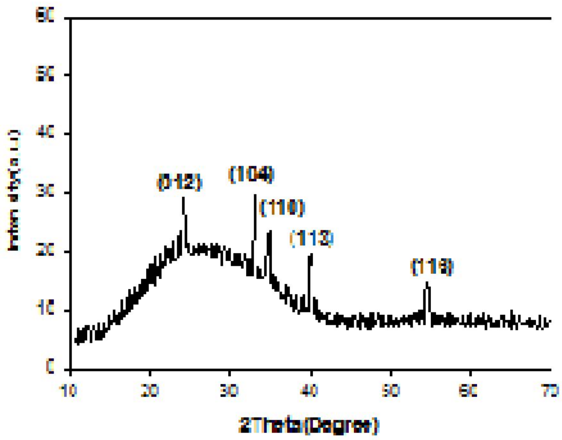

Fig.(1.2).The (XRD) for Fe_2O_3 Thin Films from $FeCl_3$ Aqueous Solution at Deposition Time 7 mints.

Optical Properties

Transmittance:

Figs.(1.3),shows the optical transmittance of Fe_2O_3 thin films prepared from the two aqueous $FeCl_3$, as a function of wavelength optical transmission spectra depends on the chemical and crystal structure of the films, the film thickness and the surface morphology.

From the figure the transmission in the visible region is found to be higher than 65% and 55%with sharp cut-off wavelength value approximately 540 nm. This indicates that the film has good absorption of the UV and near visible-light, that decreases in transmittance with an increase in the deposition time are shown in the figures, which are due to the thickness effect.[11 ,12] This behavior is attributed to the increase the number of atoms with the thickness that leads to the increase of the number of collision between incident atoms, which in turn, leads to the increase of absorptance and decreasing transmittance [13].

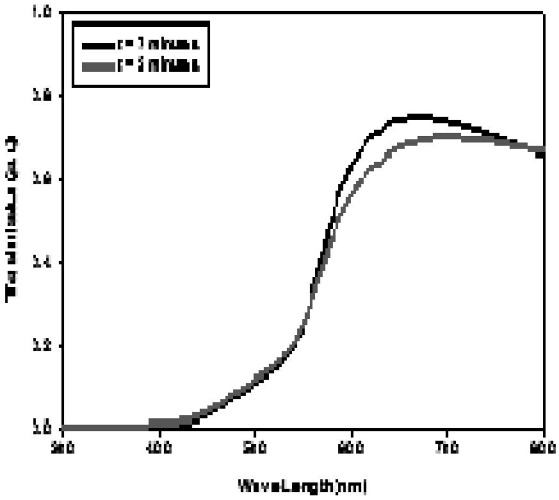

Fig.(1.3).The Transmittance Vs. Wavelength of Fe_2O_3 Thin Films from $FeCl_3$.Aqueous Solution at Different Deposition Time.

Absorbance:

The optical absorption spectrum of Fe_2O_3 thin films shows high absorption in the UV-Visible region of wavelength rang (300-600 nm) , where as in the visible region above 600 nm the transmittance of the films increases. Fig.(1.4) show absorptance spectrum of Fe_2O_3 thin films prepared from $FeCl_3$ aqueous solution in two deposition time (3and 7)min. It is clear from the Figure that increasing deposition time from 3minute to7 minute lead to an increase the absorption of the films ,which were refer to the increasing in the thickness of the films. At the visible region the absorbance of the prepared films was decreases with the increaseing of wavelength that it is suitable to be antireflection coating.[14]

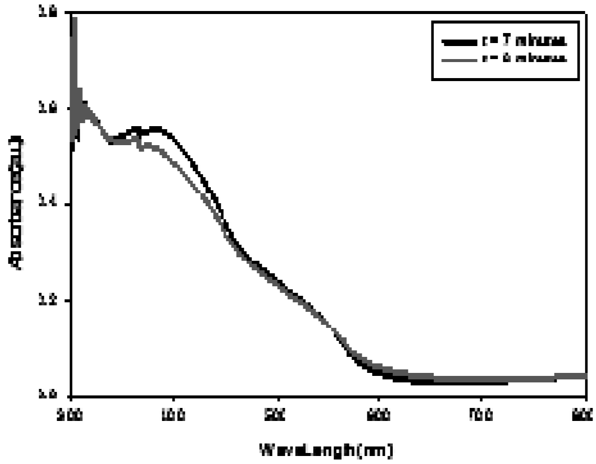

Fig.(1.4).The Absorptance Vs. Wavelength of Fe_2O_3 Thin Films from $FeCl_3$ Aqueous Solution at Different Deposition Time .

Absorption Coefficient:

Absorption coefficient is calculated by using equation $\alpha = (2.303 A) / t$ .The variation of absorption coefficient (α) as a function of photon energy of deposited Fe_2O_3 thin films from two different aqueous solutions at different deposition time is shown in the Figure.(1.5). The values of the absorption coefficient (α) larger than (10^4 cm^{-1})which gives an indicate that the electronic transitions was direct transitions. It is absorbed that the absorption coefficient (α) increases with decreasing of the deposition time, because of the thickness effect . The absorption coefficient decrease with decreasing photon energy, this can be linked with increase in grain size and density of layers and it may be attributed to the light scattering effect for its high surface roughness.

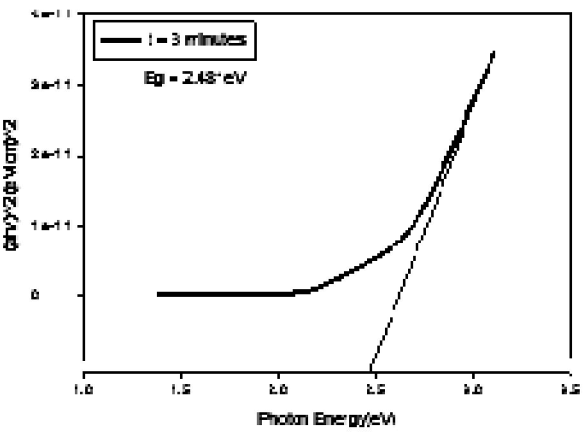

Fig.(1.5). The Absorption Coefficient Vs. Photon Energy of Fe_2O_3 Thin Films from $FeCl_3$ aqueous Solution at Different Deposition Time .

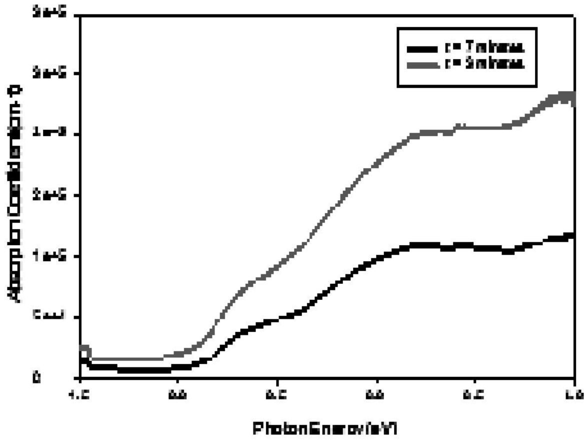

Fig.(1.6).The Direct Optical Energy Gap for Fe_2O_3 Thin Film from $FeCl_3$ Aqueous Solution at Deposition Time 3mints.

Optical Energy Gap :

The energy gap values depends in general on the films crystal structure. The arrangement and distribution of atoms in the crystal lattice also is affected by crystal regularity. The Figures. (1.6) and (1.7), illustrate allowed electronic direct transition. The optical energy gap values (E_g^{opt}) for Fe_2O_3 films have been determine by using Tauc relation , by plotting the ($\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$). It is found that the relation for r=1/2 yields linear dependence, which describes the allowed direct transition. E_g^{opt} is then determined by the extrapolation of the portionat (α=0). Figures.(1.6) and (1.7) show the value of energy gap of Fe_2O_3 thin films prepared from $FeCl_3$ aqueous solutions, at two deposition time .The energy gap of Fe_2O_3 thin films prepared from $FeCl_3$ aqueous decrease from (2.481 to 2.449)eV with increase deposition time from 3min. to 7 min., respectively . This is due to the increase in localized density of states near the band edges and in turn decreases the value of Eg with thickness. Also the decrease of direct band gap with the increase of thickness can be attributed to increase in crystallinity and an increase of crystallite(grain) size.[16] The results of energy gap value shown in the table(1.1).

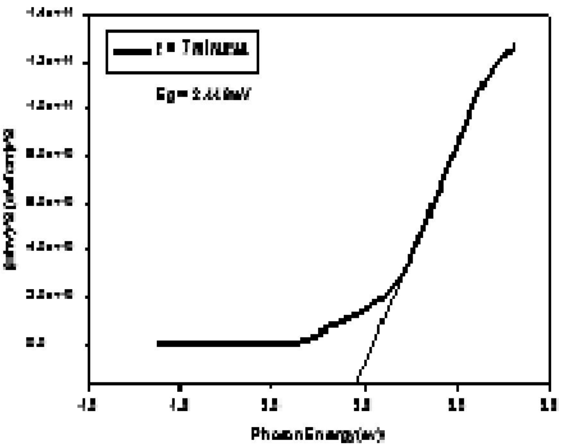

Fig.(1.7).The Direct Optical Energy Gap for Fe_2O_3 Thin Film from $FeCl_3$ Aqueous Solution at Deposition Time 7mints.

Table.(1.1).Direct Energy Gap for Allowed Transition for Different Thickness of Fe_2O_3 Thin Films.

Compound	deposition time	Thickness ±20nm	Energy gap(eV)
Fe_2O_3 from $FeCl_3$ aqueous solution	3min.	60	2.481
	7min.	118	2.449

Reflectance:

The reflectance (R) of Fe_2O_3 thin films is calculated from the absorption and the transmittance spectrum using the relation R + T + A = 1.

For all prepared thin films, the reflectance increase with the photon energy increasing ,and reach the maximum value ,in the photon energies corresponding to the energy gaps, where its value approximately equal to 65%. Then he value of R deceases at the higher energies of the incident photon, as shown in the Fig.(1.8).

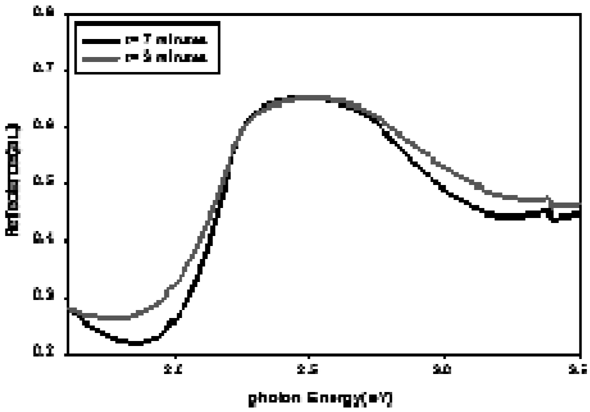

Fig.(1.8).The Reflectance Vs. Photon Energy of Fe_2O_3 Thin Films from $FeCl_3$ Aqueous Solution at Different Deposition Time

Refractive Index :

The refractive index n of (Fe_2O_3) thin films is measured by using the relation (3), It is shown in Figure.(1-9), as a function of photon energy. The variation of refractive index n with photon energy is similar to the behavior of reflectance because its dependence on the values of reflectance as shown by eq. (3). From the Figure. The values of n increases with the photon energy at the lower energies, then it reaches its maximum values at the energies corresponding to forbidden energy gaps of the films , where its value is approximately equal to 1.9. Then he value of n deceases at the higher energies of the incident photon. The explanation of this behavior may be related to the polarization of thin film because n depends on material polarization where with increasing polarization the velocity of light was decreased so n changed .The polarization depends on crystalinity and on grain size of thin film so these depend on the preparation conditions [17]. Also the refractive index values increases with deposition time (thickness) increasing, which may be attributed to higher packing density and the change in crystalline structure, this increase due to the enhancement of crystalline growth [18]

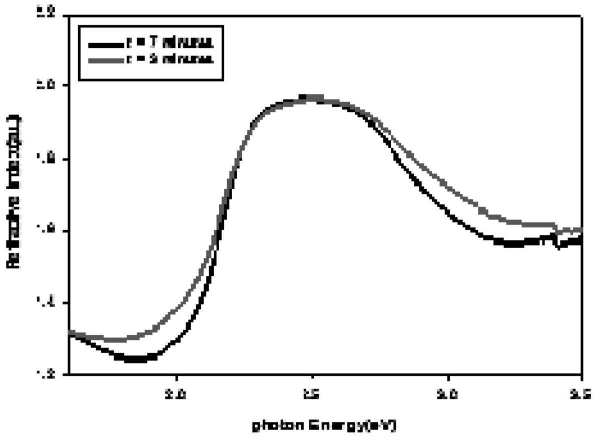

Fig.(1.9).The Refractive Index Vs. Photon Energy of Fe_2O_3 Thin Films from $FeCl_3$ Aqueous Solution at Different Deposition Time.

Extinction Coefficient:

The extinction coefficient (K) represents the amount of absorption energy in the thin film material, which means the attenuation of an electromagnetic wave that is traveling in a material. The values of (K) depends on the density of free electrons in the material and also on the structure defects . The extinction coefficient was evaluated using the relation $Ko = \alpha \lambda / 4\pi$, and through the relation the extinction coefficient is directly related to the absorption coefficient. Figure (1-10) show the variation of extinction coefficient as function of photon energy for all (Fe_2O_3) prepared thin films . It is obviously seen that k_0 behaves just like the absorption coefficient (α) because they are joined by previous relation. It is absorbed that the extinction coefficient decreases with increasing of the deposition time, which is due to thickness increasing and the enhancement of the crystallite growth. [17]

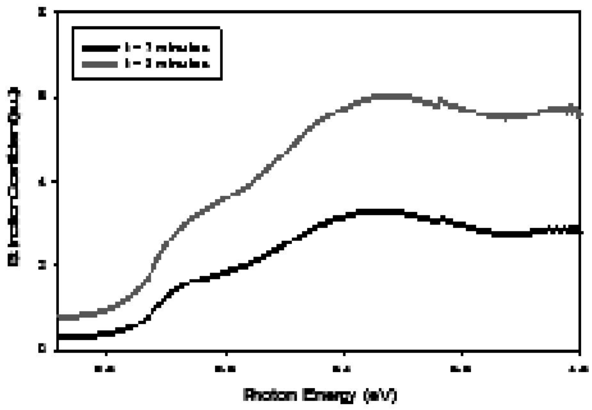

Fig.(1.10).The Excitation Coefficient Vs. Photon Energy of Fe_2O_3 Thin Films from $FeCl_3$ Aqueous Solution at Different Deposition Time.

Conclusion:

1-The XRD studies show that the Fe_2O_3 thin films has hexagonal (Rhombohedra) phase and the intensity of (104) direction is significantly increased with the increase of deposition time for the prepared films from $FeCl_3$ aqueous solution.

2- The average grain size of the Fe_2O_3 increase with increase the deposition time.
3- The optical studies of Fe_2O_3/glass thin films show that the transmission spectrum is in the visible region and its values are higher than 55% and 65% with a sharp cut-off wavelength values approximately 540 nm.
4- The maximum value of reflectance for prepared films is 65% at the energies corresponding to the energy gaps . This means that the film is suitable to be antireflection coating material.

5-Absorption coefficient (α) of (Fe2O3) thin films is larger than 104 cm-1, this converts to a large probability that direct electronic transition will happen.
6-The forbidden energy gap for allowed direct transition decreased with the increase of the deposition time.

References:

[1] K. Siroky, J. Jiresova, L. Hudec, J.Thin Solid Films 245 PP.211–214 (1994).

[2] D.uk-D. Lee, Dong-H. Choi, Sens. Actuators 231 (1990).

[3] P.S. Patil, C.D. Lokhande, S.H. Pawar, Bull. Electrochem. 5 (1989).

[4] J.H. Kennedy, D.J. Dunnwald, Electrochem. Soc. 130 (1983) 2013.

[5] Alaa A. Akl," Optical properties of crystalline and non-crystalline iron oxide thin films deposited by spray pyrolysis", J. Applied Surface Science, 233 PP. 307–319,(2004).

[6] L. Dghoughi , B. Elidrissi , C. Bernede , M. Addou , M. Alaoui Lamrani , M. Regragui , and H. Erguig ,"Physico-chemical, optical and electrochemical properties of iron oxide thin films prepared by spray pyrolysis", J. Applied Surface Science, 253 PP. 1823–1829(2006).

[7] A. A. Akl, " Microstructure and electrical properties of iron oxide thin films deposited by spray pyrolysis ", J. Applied Surface Science 221 pp. 319–329, (2004).

[8] Uark Fox "Optical Properties Of Solid ", Published In The United States By Oxford University Press,(2001).

[9] J. Taucc, "Amorphous And Liquid Semiconductors", Edited By J.Taucc, Plenum Press, (1974).

[10] Y. H. Chen and K. J. Tu," Thickness Dependent on Photocatalytic Activity of Hematite Thin Films", J. International Journal of Photoenergy,2012, PP.1-6,(2012).

[11] I. Ojai, A. Mere, M. Krunks, R. Nisumaa, C. H. Solterbeck and M.Es. Souni, "Structural and electrical characterization of TiO2 films grown by spray pyrolysis", J. Thin solid films.,515, (2), PP. 674-677),(2006).

[12] S. S. Shariffudin, M. Salina, and S. H. Herman," Effect of Film Thickness on Structural, Electrical, an Optical Properties of Sol-Gel Deposited Layer-by-layer ZnO Nanoparticles", J. Trans. Electr. Electron. Mater,13, pp. 102-105, (2012).

[13] Peter Y. Yu Manual Cardona, "Fundamentals of Semiconductors", Springer_ verlag Berlin Heidelberg New York, (1996).

[14] B. G. Stereeman, "Solid State Electronic Devices", 2nd Ed, Practice Hall, Inc. Engle wood Cliffs, N.J. (1980).

[15] S. Karvinen, "The effect of trace element doping of TiO2 on the crystal growth and on the anatase to rutile phase transformation of TiO2", J. Solid State Sciences, 5, pp.811-819,(2003).

[16] M.F.A. Alias , R.M. Aljarrah , H.KH. Al-Lamy and K. A.W. Adem," Investigation the Effect of Thickness on the Structural and Optical Properties of Nano ZnO Films Prepared by d.c Magnetron Sputtering", J. *I.J.A.I.E.M.*,2 PP.198-203,(2013).

[17] Y. A. AL Shaabani," Studying Some Physical Properties Of Zn2xCu1-xIn1-xS2 thin Films Prepared by Chemical Spray Pyrolysis", of Applied Sciences University of Technology,(2009).

[18] J. Jiu, S. Isoda , M. Adachi and F. Wang," Preparation of TiO2 nanocrystalline with 3–5 nm and application for dye-sensitized solar cell", J. Science Direct, 189,pp.314-321,(2007).