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Dispersion Parameters and Morphology of Chemical Spray Pyrolysis Deposited Fe2O3 Thin Films Prepared at Different Thickness

KEYWORDS: Fe_2O_3 thin films , dispersion parameter , optical properties , chemical spray pyrolysis technique.

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ABSTRACT *Fe_2O_3 thin films have been prepared by thermal chemical spray pyrolysis (CSP) on glass substrate heated to temperature about 400 oC using solution of aqueous ferrite nitride dehydrate (Fe $(NO_3)_3$. $9H_2O_3$) at different thickness (250, 280 and 350) nm. The thickness of the films was measured using weighting method. The effect of thickness on the morphology , optical properties and dispersion parameters has been studies. AFM analysis shows that the roughness , root mean square (r.m.s) and the average diameter increase with increasing of thickness , Transmittance spectra of the films indicate that the films have high transparency about 90% in the visible region has been obtained at thickness of 250 nm. The optical transmittance has slightly decreased with increasing of thickness. The optical absorption studies reveal that the transition is direct with band gap value varied with the thickness. Also the refractive index dispersion curves obey to the single oscillator's model. The dispersion energy and single-oscillator energy varied with the thickness.*

1- Introduction

Metal oxide thin films have unique characteristics such as good magnetic properties and conductivity, high optical transmittance over the visible wavelength region, excellent adhesion to substrates and chemical stability and photochemical properties. Among magnetic materials, iron oxides, such as (α-Fe_2O_3) and (Fe_3O_4), are the most popular materials and possess many advantages in technological applications . Iron oxide thin film (Fe_2O_3) can be used in several fields . (α-Fe_2O_3) is the most stable iron oxide compound material and is widely used in photoelectrodes, gas sensing, catalysts, magnetic recording, and medical fields [1]. Due to its great sensitivity for flammable gases, its fast speed of response and its long-term stabilities ; Photo electrochemical solar cell , due to its optical band gap, its high optical absorption coefficient ; Negative electrode in rechargeable batteries. It is also used for water electrolysis in the presence of sunlight [2,3].

Fe_2O_3 is one of the most important transition metal oxides with a band gap of 2.2 eV. It is received an extensive attention due to its good intrinsic physical and chemical properties, such as its low cost, stability under ambient conditions, environmentally friendly properties and etc. [4]. For a typical sample of Fe_2O_3 the refractive index and extinction coefficient at 632.8 nm are 2.918 and 0.029 respectively.

(α-Fe_2O_3) has been prepared by various methods such as chemical vapor deposition , sol- gel method , pulsed laser deposition , sputtering and chemical spray pyrolysis [5-9]. While in this paper the influence of thickness on the optical dispersion parameters of Fe_2O_3 thin films prepared by spry pyrolysis technique characterized.

2 - Experimental

Thermal spray pyrolysis method is basically a chemical process, which consist of a solution that is sprayed into a substrate held at high temperature, where the solution reacts forming the desired thin film. Fe_2O_3 films were grown onto corning glass substrates, using a typical spray pyrolysis system. The spray solution was prepared by mixing the appropriate volumes of ferrite nitride dehydrate ($Fe(NO_3)_3.9H_2O_3$) (molecular weight 404.02 gm /mol) which is a solid material with white color when it is completed dray while it has an orange color when it is dissolved in the water. The solution is prepared with (0.2 mol/L) by mixed (8.0804 gm) from ($Fe(NO_3)_3.9H_2O_3$) with (100 ml) deionizer water in magnetic stirrer to facilitate the complete dissolution of the solute in the solvent to obtain clear solution. Finally, the solution was spray in to a spray pyrolysis deposition chamber. The flowing equation is used to obtain the required weight according to the calibration above:

$$M = \left(\frac{W}{Mwt}\right) . \left(\frac{1000}{V}\right) \qquad \text{.........................(1)}$$

Where: M is the concentration molars , Wt is the volume of water , V is the required weight and Mwt is the molecular weight of (Fe $(NO_3)_3$. $9H_2O_3$). The following chemical equation is used to obtain the Fe_2O_3 thin films:

$$4Fe(NO_3) \rightarrow 2Fe_2O_3 + 12NO_2 \uparrow + 3O_2 \qquad \text{...........(2)}$$

The substrate temperature was fixed at 400 °C and was controlled within ± 5 °C with carrier air pressure (105 N/m^2) , flow rate of solution (10 cm^3/min) and the substrate to nozzle distance is 30 cm. Spraying was done in short time intervals (15s) , subsequent the deposition is stopped about 5min in order to returned the temperature in to the original value to complete the crystal growth. Optical transmission data were obtained with an UV-Visible Shimadzu 3101 PC double beam spectrophotometer. The effect of the thickness on the optical properties was investigated.

3- Result and Discussion

Atomic force microscopy (AFM) was employed to study the surface roughness of deposited Fe_2O_3 thin films. Figure (1a, b, c) shows an AFM study of the surface roughness of Fe_2O_3 thin films deposited at 400 °C on glass substrate at different thickness (250, 280 and 350 nm) in two and three dimensions, respectively. The root mean square (r.m.s) roughness is 0.226 nm for deposited film with thickness 250 nm, indicating uniform coverage and no tendency to agglomerate. The smoothness and continuity were cleared . As the thickness of the films increased to 280 nm (Fig. 1b) small islands, were formed on the Fe_2O_3 surface, which increased the r.m.s is 0.787nm . When film thickness 350 nm (Fig. 1c) the surface became much rougher and r.m.s becomes 0.875. From scanning probe microscopy, the granularity cumulating distribution chart is measured to determine the average diameter for Fe_2O_3 thin films at different thickness and the data is shown in Figure (2a , b ,c) and Table (1) .

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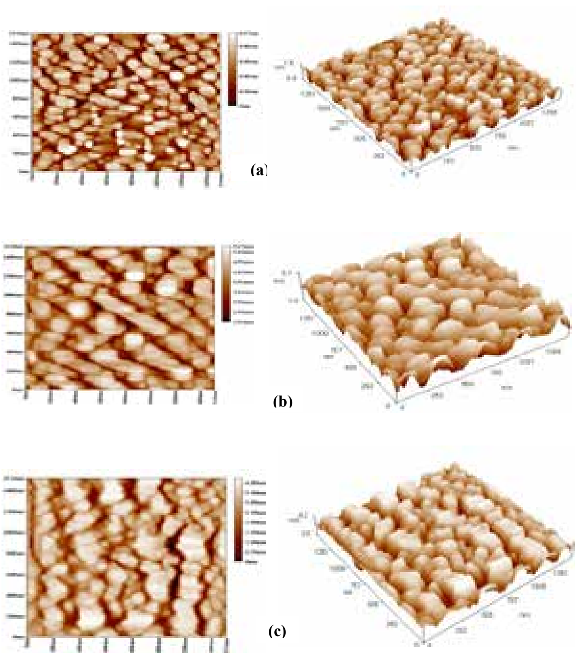
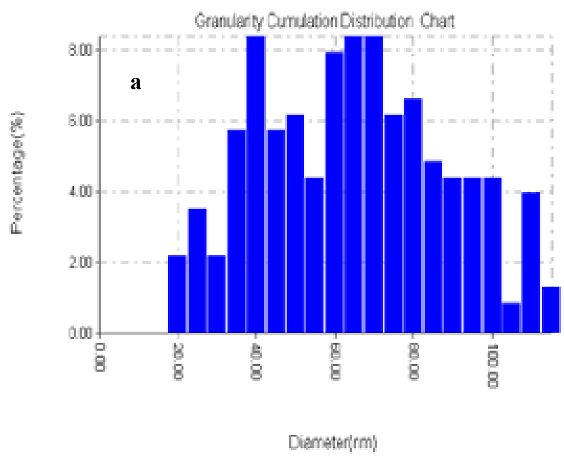
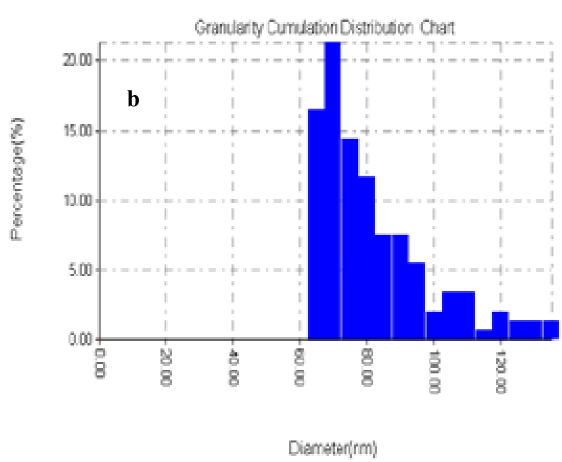


Fig. (1) AFM image for Fe_2O_3 thin films in two and three dimension at different thickness: (a) 250nm (b) 280nm (c) 350nm





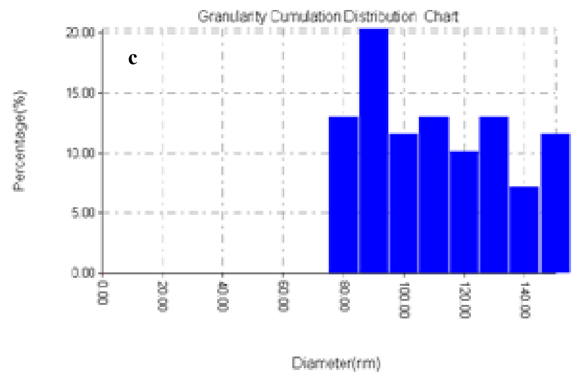


Fig. (2) The Granularity Cumulating Distribution for Fe_2O_3 thin films at different thickness: (a) 250nm (b) 280nm (c) 350nm

Table (1) shows roughness, R.M.S and the average diameter from AFM analysis for Fe_2O_3 thin films.

Thickness (nm)	Roughness (eV)	R.M.S (nm)	Average diameter (nm)
250	0.190	0.226	62.34
280	0.644	0.787	79.43
350	0.710	0.875	106.36

The transmittance and reflectance spectra of Fe_2O_3 thin films deposited on glass substrate by spry pyrolysis technique at different thickness (250, 280 and 350) nm measured in the range of wavelength (340-1100) nm have illustrated in figure (3). The film deposited with thickness (250 nm) shows high transmittance compared to that of others; this behavior is a direct result to Lambert law. The shift in the absorption edge of thinner film clearly reveals that the Fe_2O_3 film with this thickness is of better quality. It is seen that the absorption edge, which is a measure for the energy gap, is at lower wavelengths for the film with thickness (250 nm) indicating higher energy gap for it than that of the other films [10]. The average transmittance for thinner film is approximately 90% in the region of the spectra above (600 nm) whereas for that with thickness (280 nm) and (350 nm) are approximately 70% and 60% respectively. This result is agreed with Khaleel and et.al. [11]

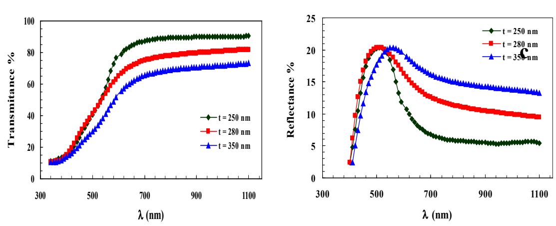


Fig. (3) The transmittance and reflectance spectra as a function of wavelength of Fe_2O_3 thin films deposited at different thickness.

The optical properties of Fe_2O_3 thin films by means of optical absorption in the UV-Visible region (300–1100) nm at different thickness have been investigated. The optical absorption coefficient (α) is dominated by the optical band gap of the semiconductor and could be calculated by using the following relation [12]:

$$\acute{a} = \frac{2.303A}{t} \quad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where (A) is the absorption and (t) is the film thickness.

Fig. (4) shows the dependence of the absorption coefficient (α) on the wavelength. The effect of thickness on the absorption coefficient of the films has been investigated.

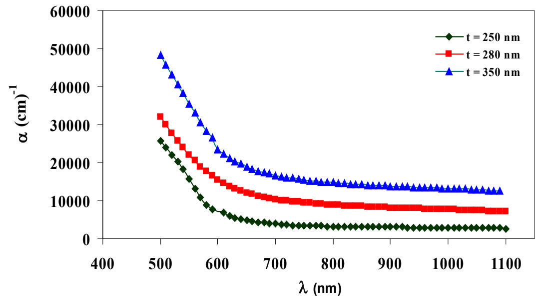


Fig.(4) The variation of absorption coefficient as a function of wavelength of Fe_2O_3 thin films deposited at different thickness.

The optical energy gap (Eg) of a semiconductor is related to the optical absorption coefficient (α) and the incident photon energy (αυh) by relation [13]:

$$áhõ = B(hõ - E_g)^r \quad ....(4)$$

Where B is energy independent constant and r depends on the kind of optical transition that prevails. Specially, r is 1/2 and 2 when the transition is directly and indirectly allowed, respectively. The Fe_2O_3 film is known to be a semiconductor with a directly allowed transition when r =1/2 , and its optical energy gap can be obtained by plotting the optical absorption versus the photon energy and extrapolating the linear portion of the curve to $(\alpha \upsilon h)^2 = 0$. In this transition process, the total energy and momentum of the electron –photon system must be conserved [14].

The optical energy gap of the Fe_2O_3 film prepared at a different thickness and constant temperature substrate 400°C was range from (2.35-2.50) eV, as shown in Fig. (5), their values are given in Table (2). The values of the energy gap decreased as thickness increased because of decrease the disorder present in the structure occurring reorganization of the films [15]. The variation of the optical energy gap of the Fe_2O_3 films with various thickness is shown in Fig. (6).

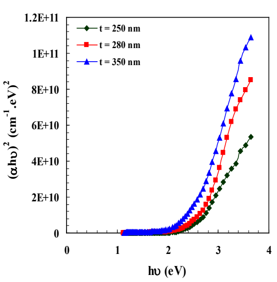


Fig.(5) The variation of $(\alpha h\nu)^2$ with photon energy of Fe_2O_3 thin films at different thickness.

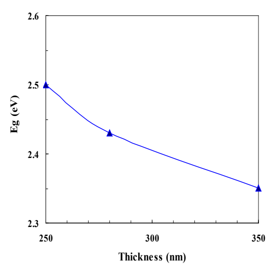
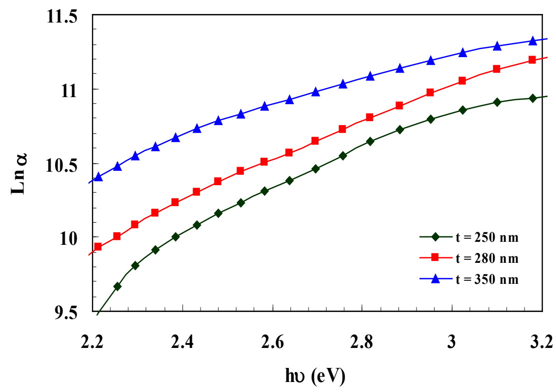


Fig.(6) The variation of energy gap of Fe_2O_3 thin films at different thickness.

The energy independent constant (B) has been obtained from the root square of the straight line in Tauc slope ($(\alpha h\nu)^{1/2}$ vs. photon energy). The B values are tabulated in Table (2). Our results show that B decreased with increasing of the thickness, B is inversely proportional to non-crystalline and width of tail states [15]. The decreasing of B suggests an increase of non-crystalline.

The width of the localized states available in the optical band gap of the Fe_2O_3 films affects the optical band gap structure and optical transitions and it is called as Urbach tail (EU). The Urbach tail of the films can be determined by the following relation [15]:

$$\alpha = \alpha_o \exp (h\upsilon / E_U) \quad .... (5)$$



Where α_o is a constant, E_U is the Urbach energy, which characterizes the slope of the exponential edge and it gives information about localized state in the band gap. Fig.(7) shows Urbach plots of the films. The value of E_U was obtained from the inverse of the slope of lnα vs. hυ and is given in Table (2). The E_U values change inversely with optical band gap of the films, E_U values have decreased with increasing of the thickness, as shown in Table (2).

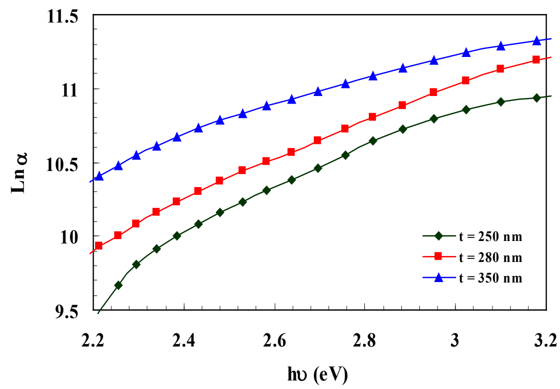


Fig. (7) The variation of Lnα as a function of photon energy for Fe_2O_3 thin films deposited at different thickness.

The dependence of the optical absorption coefficient with photon energy may arise from electronic transitions between localized states. The density of these states falls off exponentially with energy which is consistent the theory of Tauc [16]. Eq.(5) can be rewritten as:

$$á = á_o \exp\left(\frac{â}{k_B T} hí\right) \quad ....(6)$$

Where β is called steepness parameter, which characterizes the broadening of the absorption edge due to the electron–phonon interaction or exciton-phonon interaction. If the width of the edge, E_U , is related to the slope of Eq. (6), the β parameter is found as $\beta = k_B T/E_U$. The β values were calculated using this relationship and taking T = 300 K and are given in Table (2). The β values suggest that the absorption edge changes with thickness of the films. Because, the dispersion energy is related to the optical transition strengths and optical conductivity. Thus, in order to analyze the refractive index dispersion of the films, we used the single-oscillator model, developed by DiDomenico and Wimple. The single-oscillator model for the refractive index dispersion is expressed as follows [17]:

$$(n^2 - 1) = \frac{E_d E_o}{[(E_o)^2 - (hí)^2]} \quad ....(7)$$

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Where n is the refractive index , E_o is the average excitation energy known as the oscillator energy , E_d is the dispersion energy called oscillator strength , and hν is the incident photon energy . To evaluate the oscillator parameters , a graph of $(n^2-1)^{-1}$ against $(h\nu)^2$ was plotting in fig.(8) . Where (E_o/ E_d) represents the intercept on the vertical axis and $(E_oE_d)^{-1}$ is the slope of the plot . Hence, E_o, E_d , can be readily evaluated [18].

The moments of the optical dispersion spectra M_{-1} and M_{-3} can be derived from the following relations[17,18, 19]:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \qquad (8)$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \qquad (9)$$

The oscillator energy E_o , which was independent of the scale of ε_2 is consequently an average energy gap, whereas E_d depends on the scale of ε_2 and thus serves as an inter band strength parameter. The obtained M_{-1} and M_{-3} moments changes with thickness. The values obtained for the dispersion parameters E_o , E_d , M_{-1} and M_{-3} are listed in Table (2).

Table (2) Some optical and dispersion parameters of Fe_2O_3 thin films at different thickness.

Thick-ness (nm)	Eg (eV)	B×10^10 (cm^-2/eV)	E_U (meV)	β ×10^-3	E_o (eV)	E_d (eV)	M_{-1}	M_{-3} (eV)^-2	(n_o)
250	2. 50	3	695.41	37.2	2.825	4.269	1.509	0.189	1.584
280	2.43	2	767.46	33.7	2.576	2.154	0.836	0.126	1.355
350	2.35	1	1043.841	24.8	2.461	0.884	0.359	0.059	1.167

Thickness (nm)	Eg (eV)	B×10^10 (cm^-2/eV)	E_U (meV)	β ×10^-3	E_o (eV)	E_d (eV)	M_{-1}	M_{-3} (eV)^-2	(n_o)
250	2. 50	3	695.41	37.2	2.825	4.269	1.509	0.189	1.584
280	2.43	2	767.46	33.7	2.576	2.154	0.836	0.126	1.355
350	2.35	1	1043.841	24.8	2.461	0.884	0.359	0.059	1.167

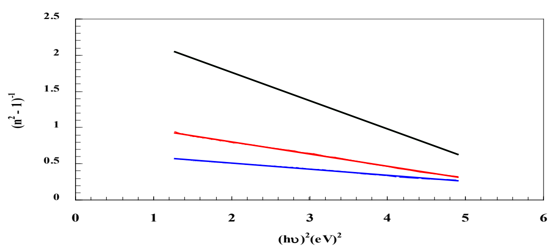

Fig. (8) The variation of $(n^2- 1)^{-1}$ as a function of square of photon energy for Fe_2O_3 thin films deposited at different thickness.

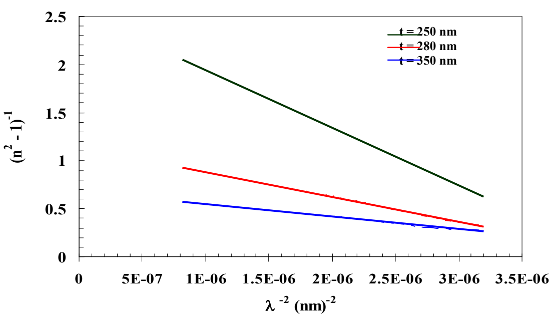

Fig. (9) Variation of $(n^2 - 1)^{-1}$ as a function of $(\lambda)^{-2}$ for Fe_2O_3 thin films deposited at different thickness.

Conclusions

Fe_2O_3 thin films were prepared by thermal pyrolysis technique at 400 °C and different thickness. AFM results show that the roughness and root mean square decreased with increasing of the thickness. Optical transmittance of (Fe_2O_3) films has been more than 90% transparency in the visible region at thickness 250 nm and decreases with thickness' increasing from approximately 70% to 60% in the region of the spectra about (600 nm). Optical energy gap decreased due to increase of thickness of the films. There is a decreasing in band tail width with thickness' increasing. The single–oscillator parameters were determined. It was shown that the dispersion parameters of the films obeyed the single oscillator model, the change in dispersion was investigated and its value decreased with increasing the thickness.

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