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The Concentration Effects On Preparation Of (Fe_2O_3) Nanoparticle By Chemical Spray Pyrolysis (CSP) Technique

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***Abstract*—In this research (Fe_2O_3) thin film which prepared by Chemical Spray pyrolysis (CSP) technique and deposited on glass substrate for three concentrations (0.05, 0.075 and 0.1)M.**

The structural and optical properties have been investigated.

X-ray diffraction (XRD) measurements indicate that all the prepared films were polycrystalline and Hexagonal with a preferred orientation a long (104) plane, in addition to the results of the measurements of an atomic force microscope (AFM) showed decrease in the values of the roughness average and Root Mean Square (RMS) an increase the concentration. UV-Vis measurements reveal that the energy gaps of (Fe2O3) thin films were found (2.3 , 2.48 and 2.5)eV.

***Keywords*—Fe_2O_3, thin film , chemical spray pyrolysis deposition (CSPD), Structure and optical properties**

1. Introduction

Iron oxide thin film (Fe_2O_3) found in nature as hematite, is one of the most important oxides of transition elements, which is the most stable among all other iron oxides.[1]. This material is characterized of its good thermal stability at relatively high temperatures, non-toxic, low-cost , numerous, has environmentally friendly properties , The ferric compounds show high paramagnetic properties, which means that the electrons remain unpaired [2] Iron oxide thin film (Fe_2O_3) , is can be used in several fields. It can be used as, for example: Gas sensors [3,4] due to its great sensitivity for flammable gases, its fast speed of response and its long-term stability, magnetic recording materials, catalysis, optical devices and pigments.[5] . Photo electrochemical solar cell for solar energy conversion [6,7] due to its optical band gap (Eg = 2.3 , 2.48 and 2.5 eV)

2. Experimental

In a typical procedure , (0.811, 1.2165 and 1.622) g of iron (III)chloride anhydrous ($FeCl_3$), 162.2 g/mol Molar mass (purity 97.0% , Sinopharm Chemical Reagent Co. , Ltd) were dissolved in 100ml of distilled water. The solution was added into a round-bottom flask with stirring.

The color of the solution was brown. A nanopowder suspension was formed as shown in figure 1 . The suspension was kept at 75 °C for fifteen minutes. The resultant solution was sprayed on glass substrates at temperature (375˚C) to get the required thin films. To get a good deposition was put slot nozzle at an height (40 cm) from the surface of the substrate , spray time (8 s), spray interval (1.5 minutes) and pressure of the carrier gas (10^5 N/m2) were kept constant for each concentration used.

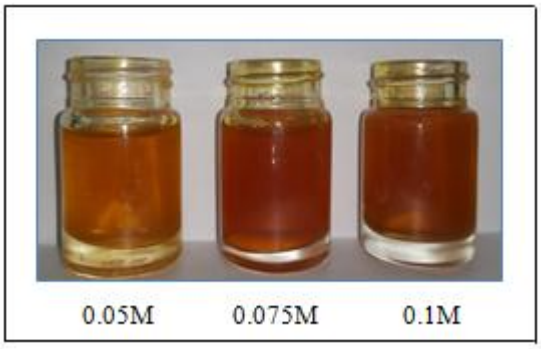


Fig.1: (Fe_2O_3) freshly colloidal nanoparticles which are prepared by mixing 100 ml of distilled water on the ferric chloride powder for three concentrations (0.05 , 0.075 and 0.1)M

Glass substrates lifted from the surface of the heated and cooled after it reaches a temperature to room temperature

Thickness of the samples was measured using the weighting method , by using the relationship

$$t = \frac{\Delta W}{\rho \times Area} \qquad (1)$$

Where (t) is the thin film thickness , (ΔW) is the change in weight (The difference between the substrate weight before and after the deposition) , (ρ) The density of the thin film material (Ferric oxide material density equal to 5.24g /cm^3) and Substrate surface area equal (625cm^2).

where the use of the thickness of (350 nm) .

The crystal structure of the prepared films has been examined by X-ray diffractometer (XRD-6000 Shimadzu). The morphology of the thin films was examined by Atomic Force Microscopy (AFM) micrographs which were recorded by using scanning

probe microscope type (SPM-AA3000), contact mode, supplied by Angstrom Advanced Inc. To find out optical measurements and study the electronic transfer, use the spectrometer (UV- Visible-NIR Spectrophotometer) equipped of the company (Shimadzu) Japanese.

3. Results and discussion

X-Ray Diffraction:

The results of tests X-ray diffraction showed that the thin films of ferric oxide (Fe_2O_3) is multi-crystallizing (Polycrystalline) nature of the type hexagon and the prevailing direction (104), and peaks in the X-ray diffraction diagrams for the films prepared apply and dramatically with the international card (Joint committee on powder diffraction standards) (JCPDS) for ferric oxide (Fe_2O_3) with serial number (00-033-0664).

Table (1) illustrates the portion of the card (JCPDS) and the results obtained from X-ray diffraction of the thin films of (Fe_2O_3) prepared at a temperature (375°C) and three concentrations (0.05,0.075 and 0.1) M

Sample	2θ (deg)	d_{hkl} (Å)	Into. (a.u.)	hkl
(STEM)	24.1378	3.684	22	012
	33.1522	2.7	100	104
	35.6112	2.519	76	110
	54.0892	1.6941	72	116
(0.05 M)	33.1880	2.69724	100	104
	35.6773	2.51455	38	110
(0.075M)	24.1792	3.67788	22	012
	33.1833	2.69761	100	104
	35.6673	2.51523	28	110
	54.1031	1.69374	31	116
(0.1 M)	24.1784	3.678	22	012
	33.1689	2.69875	100	104
	35.6478	2.51656	34	110
	54.0756	1.69454	29	116

The lattice constant (a_0) and (c_0) can be calculated according to the formula [8]:

$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2} \qquad (2)$$

It can be noted that the values of the lattice constants (a) and (c) well agreed with the values obtained from the standard cards (JCPDS) for all thin films prepared at three concentrations (0.05, 0.075 and 0.1)M. Where the values of the constants in the search are

(a = 5.0356°A) and (c = 13.752°A) While their values in the standard cards (JCPDS) are (a = 5.036°A) (c = 13.749°A).

The figure.2 shows that the intensity of Fe_2O_3 thin film which deposited from the higher concentration increasing indicated that the crystallization defects.

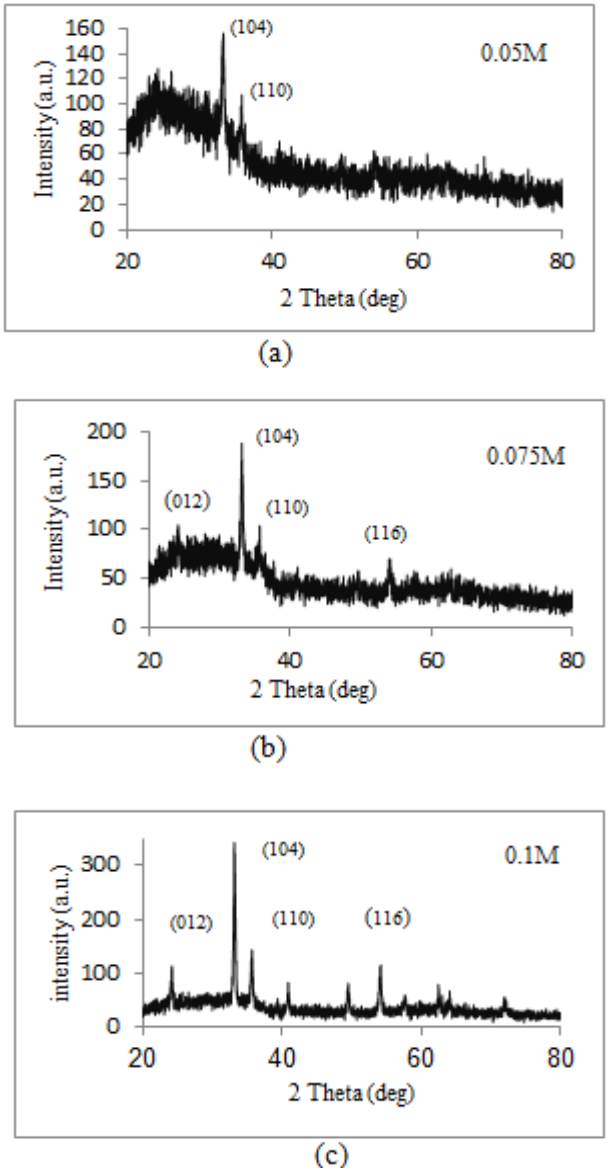


Fig.2: XRD patterns of (Fe_2O_3) thin films prepared by Chemical Spray pyrolysis (CSP) technique and deposited on glass substrate for three concentrations (0.05, 0.075 and 0.1)M.

Crystallite size measurements were determined from the full-width at half maximum (FWHM) of the strongest reflection of the (104) peak, using the Scherer approximation, as in equation (3)

$$G = \frac{K\lambda}{\beta \cos\theta} \qquad (3)$$

Where : (G) the Crystallite size ,

(K) the Scherer's constant it's quantity

(0.94) , (λ) the wavelength of the radiation, (β) the full width at half

maximum (FWHM) in radians , and

(θ) the Bragg angle.

Table 2: powder X-ray diffraction data (Fe_2O_3) thin film

Samples	Crystallite size (nm)	FWHM (deg)
(0.05 M)	19.0769	0.4167
(0.075 M)	24.89646	0.3193
(0.1 M)	29.48716	0.2696

It is noted from Table (2) that the increasing in the concentration of lead to an increasing in crystallite size. As well as observe the decrease (FWHM) with increasing in the concentration of values.

To calculate the Texture Coefficient we used the relationship (4), called the equation (Joseph & Manoj) where he describes the preferred direction of the level of the crystal (hkl) in a polycrystalline thin films.[9]

$$T_c = \frac{\frac{I}{I_\circ}}{\frac{1}{M_T}\sum\frac{I}{I_\circ}} \qquad (3)$$

Where (T_c) the Texture Coefficient

(I) the measured intensity, (Io) the intensity values taken from the JCPDS data,(M_T) the reflection number. Table (3) illustrates the composition the Texture Coefficient

where we note that it varies with concentration, and noted that the Texture Coefficient values for all samples that have been studied in the search for not less than one, this means that the films prepared used in the search of a one orientation along (104) plane , a (104) and there is no change of direction when changing the change concentration.

Table.3: powder X-ray diffraction data (Fe_2O_3) thin film with regard to the results of the Texture Coefficient for the three concentration.

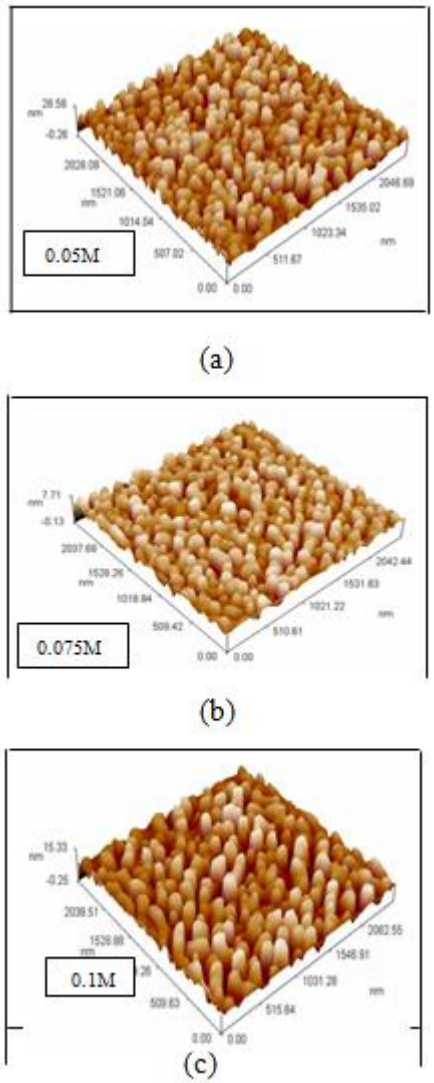
Sample	T_c
(0.05 M)	1.9
(0.075 M)	2.6
(0.1M)	3

In order to study the surface topography of the deposited thin films and the effect of the concentration at the same preparation conditions on it , Atomic force microscope (AFM) was used as it has the ability to produce micrographs and analyze the surface of the samples under investigation to give very precious statistical values of average crystallite size , Roughness average , and the values of the square root of the average square roughness as well as providing us with a lot of important information.

Table (4) shows the values of roughness average, and the values of the square root of the average square roughness, and the average of crystallite size by measuring the atomic force microscope (AFM) to films prepared.

Fe_2O_3 concentration	Roughness average (nm)	RMS (nm)	Average diameter (nm)
(0.05 M)	4.18	5.08	67.56
(0.075 M)	1.04	1.25	86.83
(0.1 M)	2.42	2.92	107.33

Note from Table (4), the increase in concentration leads to increase crystallite size and also note the decrease in roughness average and the values of the square root of the average square roughness with the increase in concentration to 0.1 M.



0.075M

Fig.3: ***AFM images of (Fe_2O_3) thin films as a function of concentration .***

The figure (4) shows the transmition as a function the wavelength at a range (350-800) nm, also the figure relive that there is no transmittance at the range (350-550) nm. The transmittance started to appear above 550 nm, the increasing in concentration due to decreasing in transmition via that increasing at average grain size as show in AFM Image (3).

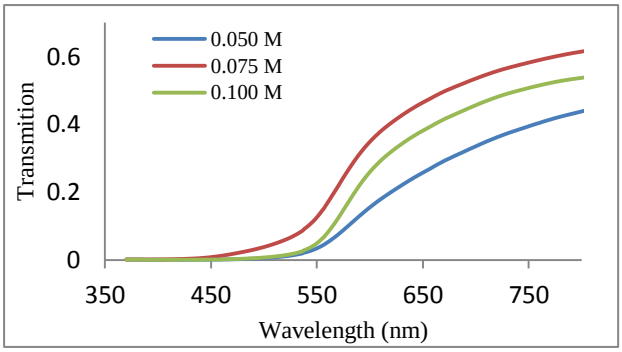


Fig.4: Transmittance spectrum of (Fe_2O_3) thin film which prepared by Chemical Spray pyrolysis (CSP) technique and deposited on glass substrate for three concentration (0.05 , 0.075 and 0.1)M

The reflection of the films has been found by using relationship :

$$R + T + A = 1 \qquad (4)$$

The reflection of the (Fe_2O_3) thin films increasing with increasing the wavelength until almost up to the top of the curve at 550 nm then begins to decline , so note from figure (5) the reflection spectrum of (Fe_2O_3) thin films increasing with increase concentration.

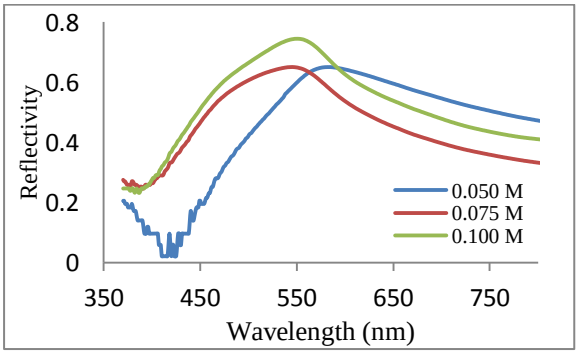


Fig.5: Reflection spectrum of (Fe_2O_3) thin film which prepared by Chemical Spray pyrolysis (CSP) technique and deposited on glass substrate for three concentration (0.05 , 0.075 and 0.1)M

From the reflection of the thin film, the refraction index can be calculated from the relationship

$$n_\circ = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (5)$$

Figure (6) illustrates the refractive index increasing with increasing concentration of the (Fe_2O_3) thin films.

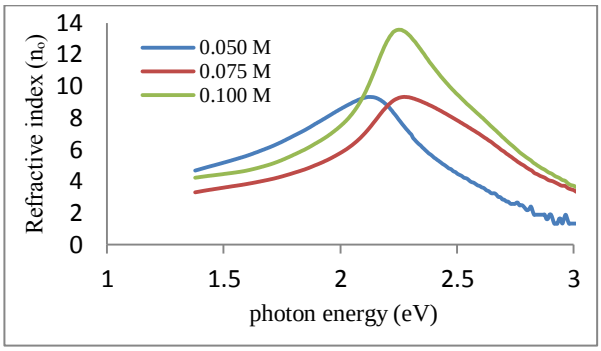


Fig.6: refractive index spectrum of (Fe_2O_3) thin film which prepared by Chemical Spray pyrolysis (CSP) technique and deposited on glass substrate for three concentration (0.05 , 0.075 and 0.1)M

The optical absorption coefficient α was evaluated by the relation

$$\alpha h\nu = A(h\nu - E_g)^n \quad (6)$$

where

$$\alpha = 2.303 \frac{A}{t} \quad (7)$$

where (t) is the film thickness and (A) is the absorbency thin film , (hv) is the photon energy , it can be calculated from the relationship

$$E_g = \frac{1240}{\lambda_{(nm)}} \qquad (8)$$

and (n = 0.5) for allowed direct transition. Plotting the graph between $[(\alpha h\nu)^2]$ versus photon energy (hv) gives the value of direct band gap. By drawing a straight line touches the curve even goes a photon energy axis at the point $(\alpha h\nu)^2 = 0$, gives the value of band gap.

Shown in figure (7) the optical band gab is (2.3eV) for concentration (0.0.5M) , (2.48eV) for concentration (0.075M) and (2.5eV) for concentration (0.1M) . This means that whenever the increasing of concentration the value of energy gap increase.

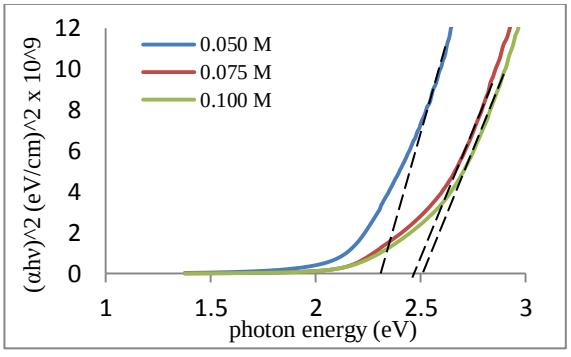


Fig.7: $(\alpha h\nu)^2$ versus photon energy plot of

spectrum of (Fe_2O_3) thin film which prepared by Chemical Spray pyrolysis (CSP) technique and deposited on glass substrate for three concentration (0.05 , 0.075 and 0.1)M

To calculate the optical conductivity used the following relationship

$$\sigma = \frac{\alpha n c}{4\pi} \qquad (9)$$

Where (σ) is the optical conductance , (c) is the velocity of the radiation in the space ,(n) is the refractive index and (α) is the absorption coefficient. Figure (8) shows the relation between the optical conductivity and photon energy for (Fe_2O_3) thin film. We note also that the optical conductivity increased with increasing concentration.

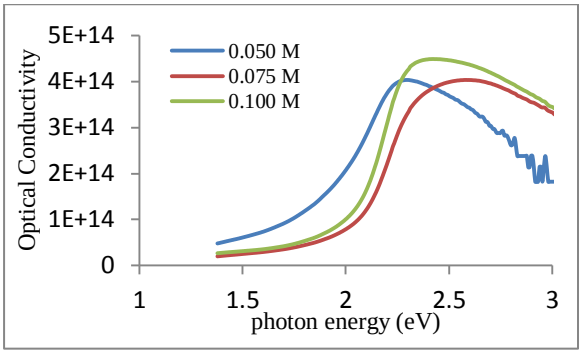


Fig.8: the optical conductance of spectrum of (Fe_2O_3) thin film which prepared by Chemical Spray pyrolysis (CSP) technique and deposited on glass substrate for three concentration (0.05 , 0.075 and 0.1)M

4. Conclusions

Preparation of (Fe2O3) thin films using chemical spray pyrolysis method at different concentration. The results of X-ray diffraction measurements showed that the thin films of ferric oxide prepared at three concentrations (0.05 , 0.075 and 0.1)M were polycrystalline and have hexagonal structure of the type (□-Fe2O3). The favorite crystal growth for all prepared thin films is (104). The increasing in the concentration of the solution leads to increase in the size of the crystalline grains and improves the crystal structure. The results of the atomic force microscope (AFM) show decrease in the square root of the mean square values of roughness (RMS) when an increase the concentration of the solution. The transmittance started to appear above 550 nm, the increasing in concentration due to decreasing in transmition. The reflection spectrum of (Fe_2O_3) thin films increasing with increase concentration. the refractive index increasing with increasing concentration of the (Fe_2O_3) thin films. Energy gap for direct transmission allowed an increase whenever increase concentration of the solution. The optical conductivity increased with increasing concentration.

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