

**XRD and AFM Analysis of Iron Oxide (Fe<sub>2</sub>O<sub>3</sub>) Thin Films Prepared by Chemical Spray Pyrolysis Method :The Effect of Substrate Temperature**

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**Abstract**

Iron Oxide (Fe<sub>2</sub>O<sub>3</sub>) thin films were prepared by Chemical Spray Pyrolysis technique, on glass substrates at (400,450,500)°C , XRD analysis reveals that all the prepared films were polycrystalline and Hexagonal with a preferred orientation a long (104) plane, The increase in temperature cause an increase in the crystallization of film and homogeneity in addition to increase the grain size, It has been found that an increase in temperature leads to an increase in the crystalline grain size and working to improve the crystal structure. Moreover, the results showed an atomic force microscope (AFM) an increase in the values of the square root of the mean square roughness (RMS), an increase of temperature.

**Keywords:** Fe<sub>2</sub>O<sub>3</sub> thin films, Chemical Spray Pyrolysis, Structural properties, XRD, AFM.

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تحليل صور الاشعة السينية ومجهز القوة الذرية لأغشية أكسيد الحديدك ( $Fe_2O_3$ )  
المحضرة بطريقة التحلل الكيميائي الحراري: تأثير درجة حرارة القاعدة

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### الخلاصة

حضرت أغشية أكسيد الحديدك ( $Fe_2O_3$ ) بدرجات حرارة مختلفة باستخدام طريقة التحلل الكيميائي الحراري على قواعد زجاجية عند ( $400,450,500\text{ }^{\circ}C$ )، وأظهرت نتائج فحوصات الاشعة السينية (XRD) ان كافة الاغشية المحضرة ذات تركيب متعدد التبلور من النوع السداسي وبالاجاه السائد للمستوي (104). وقد أدت الزيادة بدرجات الحرارة الى زيادة في تبلور الغشاء وتجانسه فضلا عن زيادة الحجم الحبيبي، وقد وجد أن زيادة درجة الحرارة تؤدي إلى زيادة في حجم الحبيبات البلورية وتعمل على تحسين التركيب البلوري. فضلا عن ذلك فقد أوضحت نتائج مجهر القوة الذرية (AFM) زيادة في قيم الجذر التربيعي لمتوسط الخشونة (RMS) بزيادة درجة الحرارة.

**الكلمات المفتاحية:** أغشية أكسيد الحديدك الرقيقة، التحلل الكيميائي الحراري، الخواص التركيبية، الاشعة السينية، مجهر القوة الذرية.

### Introduction

The Iron (hematite) is considered as one of the most important transition elements oxides and the ferric oxide is most stable one among all other iron oxides. The ferric oxide is one of the thermodynamic phases of iron and one of trivalent iron compounds, which can be obtained from the intense heating of ferrous sulfate or from the oxidation of ferrous when adding alkali to ferrous sulphate solution. Ferric oxide is an n-type semiconductor which adopts hexagonal crystalline structure [1]. This material is characterized of its good thermal stability at relatively high temperatures, non-toxic, low-cost, abundant, has energy gap of (2.5eV) which lies within the range of visible spectrum, has a relatively high refractive index, high resistance against corrosion, has environmentally friendly properties, has good

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conductivity as well as a high absorption in the short wavelength region and high chemical stability. The ferric compounds show high paramagnetic properties, which means that the electrons remain unpaired [2]. Ferric oxide thin films can be used as radiation filters in the visible region and near-infrared of the electromagnetic spectrum. Ferric oxide thin films own high efficiency to convert light into electrical energy when used as photo-electrode and it also used in solar systems [3]. To investigate the effect of substrate temperature on the structural properties of the prepared thin films.

### **Experimental**

For the purpose of preparation of (Fe<sub>2</sub>O<sub>3</sub>) thin films iron chloride (FeCl<sub>3</sub>) powder of (162.21 g / mol) molecular weight was used.

The solution was prepared at room temperature with a concentration of (0.1 M) by dissolving (1.6221 g) of the iron chloride powder in (100 ml) of distilled water, and to ensure full solubility magnetic stirrer was used. The solution was left for an appropriate period to make sure that there are no deposits and the powder is dissolved in the distilled water completely. The resultant solution was sprayed on glass substrates to get the required thin films. The optimized deposition conditions such as spray nozzle substrate distance (29±1 cm), spray time (8 s), spray interval (2 minutes), spray rate (2.5 ml/min.) and pressure of the carrier gas (10<sup>5</sup> N/m<sup>2</sup>) were kept constant for each substrate temperature (400, 450 and 500 °C). The X-ray diffraction patterns for the prepared films were obtained in a (Shimadzu XRD-6000) goniometer using copper target (Cu K $\alpha$ , 1.5418 Å). 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. The thickness of the prepared thin films was obtained by the gravimetric method and it was in the range of (400±20) nm.

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### Results and Discussion

Due to the importance of structural tests in giving information on the crystal structure of the material as well as the identification of the deposited material, X-ray diffraction (XRD) and atomic force microscope (AFM) have been employed, as follows:

#### **3.1. Results of X-Ray Diffraction**

Figure (1) shows the X-ray diffraction (XRD) patterns of the thin films deposited at (400, 450 and 500 °C) substrate temperature. The diffraction results show the presence of several peaks indicating that the nature of the thin films structure is Polycrystalline. At preparation temperature of (400°C), it is found that the thin film is polycrystalline and has hexagonal structure, and when comparing the positions, intensities and the interplanar spacings with the standard card (JCPDS) numbered (33-0664), it is found that the results are close to some extent as shown in tables (1) and (2).

The preparation of the thin films at substrate temperature of (450°C) has led to the emergence of additional peaks as well as the previous peaks obtained in the (XRD) pattern of the sample prepared at substrate temperature of (400°C), and the peaks increased intensity increased and became sharper. When matching new peaks with the standard card (JCPDS) numbered (33-0664), it was found that they were belong to ( $\text{Fe}_2\text{O}_3$ ) with a hexagonal phase. By increasing the temperature to (500°C), increase in the height and sharpness of the peaks was observed which can be attributed to the substrate temperature increase which has led to an increase in the crystallization of thin film material and this means that the crystalline defects are reduced as the temperature supplied the atoms with sufficient energy to restore their positions and arrange themselves in the lattice. The favorite direction trend for all prepared thin films is (104). Some of the structural characteristics obtained of X-ray diffraction were calculated as follows:

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### 1. Interplanar Spacing ( $d_{hkl}$ )

The spacing between the crystalline levels ( $d_{hkl}$ ) was calculated using the Bragg's law as follows:

$$n \lambda = 2d_{hkl} \sin \theta_B \dots \dots \dots (1)$$

Where:

( $\theta_B$ ) is the Bragg's angle,  $\lambda$  is the x-ray wavelength,  $n$  is an integer represents the diffraction order (1, 2,3, ..... etc.) and  $d_{hkl}$  is the interplanar spacing between two successive planes.

It was found that the interplanar spacing values for the prepared ferric oxide thin films depicted in table (2) are in agreement with that of the standard card (JCPDS).

### 2. Lattice Constants ( $a_0$ ) and $c_0$ :

The lattice constants for hexagonal structure can be calculated according to the formula [5]:

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a_0^2} \right) + \frac{l^2}{c_0^2} \dots \dots \dots (2)$$

Where ( $hkl$ ) are miller indices.

It can be noted that the values of the lattice constants ( $a_0$ ) and ( $c_0$ ) well agreed with the values obtained from the standard cards (JCPDS) for all thin films prepared at substrate temperatures of (400, 450, 500) °C as shown in table (2).

### 3. Texture coefficient ( $T_c$ )

The favorite direction of the planes in the polycrystalline thin films can be described using Joseph and Manoj relation [6]:

$$T_c(hkl) = \frac{I(hkl)/I_0(hkl)}{N_r^{-1} \sum I(hkl)/I_0(hkl)} \dots \dots \dots (3)$$

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Where  $I(hkl)$  is the measured intensity,  $I_0(hkl)$  the intensity values taken from the JCPDS data,  $(N_r)$  is the reflection number and  $(hkl)$  are Miller indices.

If it was found that the values of  $(T_c)$  for (104) direction are greater than one and the values of the remaining directions are less than one, which means that the plane (104) is the dominant direction for all thin films deposited at (400, 450 and 500) °C substrate temperature.

#### 4. Average crystallite size ( $D_{av}$ ):

The average crystallite size for all films is calculated for (104) direction by Scherrer formula [7]:

$$D_{av} = \frac{0.9 \lambda}{\beta \cos \theta_B} \dots \dots \dots (4)$$

Where  $(\beta)$  is full width of half maximum (FWHM) and  $(\lambda)$  is wavelength for Cu target of XRD instrument.

It was found that the crystallite size values for all thin films were in the range of 16-24.5 nm, as shown in table (2), where we note that the crystallite size increases with increasing temperature, while we note a decrease in the values of (FWHM), because it is known that an increase in temperature leads to an increase in kinetic energy of the deposited atoms and molecules making it easier for them to correct their occupancy in the lattice and then increase the size of the crystallites.

#### 5. Micro Strain (S):

The microstrain in the films is induced during the growth of thin films by varying displacements of the atoms with respect to their reference lattice position and for hexagonal structural system; it can be calculated using the following formula [8]:

$$S = \frac{|c_o( ASTM) - c_o( XRD)|}{c_o( ASTM)} \times 100\% \dots \dots \dots (5)$$

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Where (c<sub>o</sub>) (ASTM) is the value of the lattice parameter (c<sub>o</sub>) in the ASTM card, c<sub>o</sub>(XRD) is the lattice parameter (c<sub>o</sub>) calculated from the XRD patterns of the sample.

### 6. Dislocation Density (δ):

The dislocation density is defined as the number of dislocations lines pass through a unit area of (a) crystalline material and it can be represented by the ratio of the total length of the dislocations to the volume of the crystal and can be calculate using the formula given by Williamson and Smallmans [9]:

$$\delta = \frac{1}{D_{av}^2} \dots\dots\dots (6)$$

Where we note that the dislocation density decreases with increasing substrate temperature, as shown table (2) and decreases with increasing crystallite size because of the inverse relationship between them and this means improving the crystal structure.

### 7. Number of crystals per unit area (N):

The number of crystals per unit area can be calculated by the following relationship [10]:

$$(N = t/D_{av}^3) \dots\dots\dots (7)$$

Where( N) is the number of crystals per unit area and t is the thin film thickness.

Where it can be observed that the number of crystals per unit area decreases with increasing substrate temperature, as shown in table (2) and decreases with increasing crystallite size because of the inverse relationship between them and this means improving the crystal structure.

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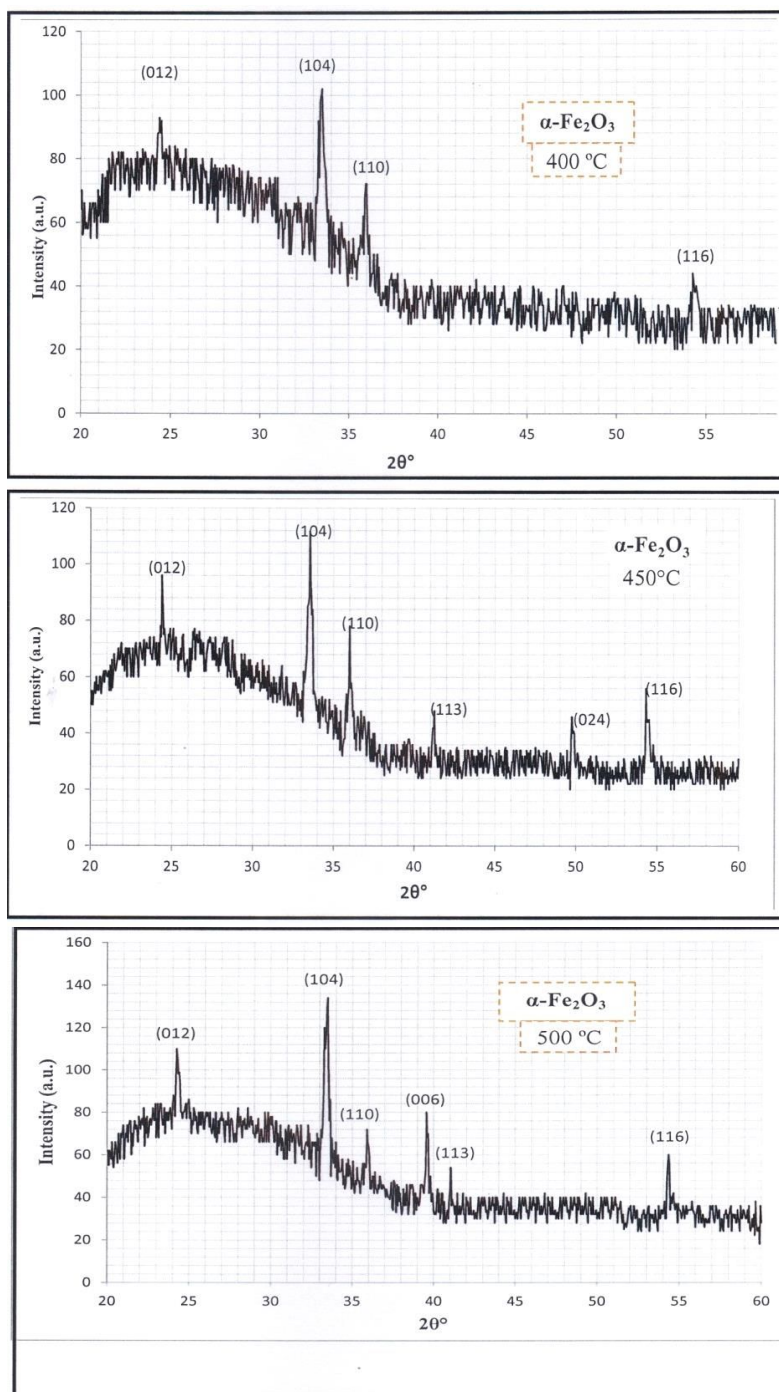
### **3.2. Results of Atomic Force Microscopy (AFM)**

In order to study the surface topography of the deposited thin films and the effect of the substrate temperature 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 precise statistical values of average grain size and grains distribution, surface roughness and the root mean square (RMS) roughness as well as providing us with a lot of important information. Figures (2a, b and c) show the (AFM) micrographs of the samples deposited at different substrate temperatures (400, 450 500) °C. It can be observed that the values of average roughness (RMS) calculated using (Imager4.62) software attached with the (AFM) device, increase as the substrate temperature increases. The small values indicate the smoothness of the surface, which confirms the growth of small grains, as small values means that the surface is of densely packed grains.



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**Figure (1):** XRD patterns of  $\text{Fe}_2\text{O}_3$  thin films prepared at different substrate temperatures (400, 450 ,500) °C .

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**Table (1):** Peaks positions and interplanar spacings for Fe<sub>2</sub>O<sub>3</sub> JCPDS card and Fe<sub>2</sub>O<sub>3</sub> thin films deposited at different substrate temperatures (400, 450 ,500) °C.

Sample	2θ (degree)	d <sub>hkl</sub> (Å)	I	hkl Fe <sub>2</sub> O <sub>3</sub>
Fe <sub>2</sub> O <sub>3</sub> (33-0664)	24.138	3.6840	30	012
	33.152	2.7000	100	104
	35.611	2.5190	70	110
	54.089	1.6941	45	116
T= 400 C°	24.6226	3.61265	42	012
	33.4858	2.67393	100	104
	35.9536	2.49585	50	110
	54.3014	1.68802	42	116
T= 450 C°	24.5872	3.61777	65	012
	33.5621	2.66803	100	104
	36.0307	2.49069	50	110
	54.4180	1.68468	59	116
T= 500 C°	24.3822	3.64772	50	012
	33.4301	2.67826	100	104
	35.9287	2.49753	25	110
	54.3639	1.68623	34	116

**Table (2):** XRD results for Fe<sub>2</sub>O<sub>3</sub> thin films deposited at different substrate temperatures.

Sample	T=400°C	T=450°C	T=500°C	JCPDS	hkl
2θ (deg)	33.4858	33.5621	33.4301	33.152	104
d (hkl) (Å)	2.67393	2.66803	2.67826	2.7000	
FWHM(rad)	0.0088506	0.0065328	0.0059097		
(D <sub>av</sub> ) nm	16	22	24.5		104
δ × 10 <sup>11</sup> cm <sup>-2</sup>	3.7	2.0	1.6		
N <sub>o</sub> × 10 <sup>12</sup> cm <sup>-2</sup>	7.67	3.08	2.07		
Tc(hkl)	1.01	1.12	1.11		
Micro Strain S%	1.16	0.94	0.72		
Lattice constant a.	4.991	4.981	4.981	5.035	104
Lattice constant C.	13.61	13.58	13.64	13.74	104

The average roughness and root mean square (RMS) roughness for all samples are given in Table (3). It can be concluded also that the increase in substrate temperature has led to increase in the grain size and decrease in the grain boundaries which is in agreement with the results obtained from XRD analysis

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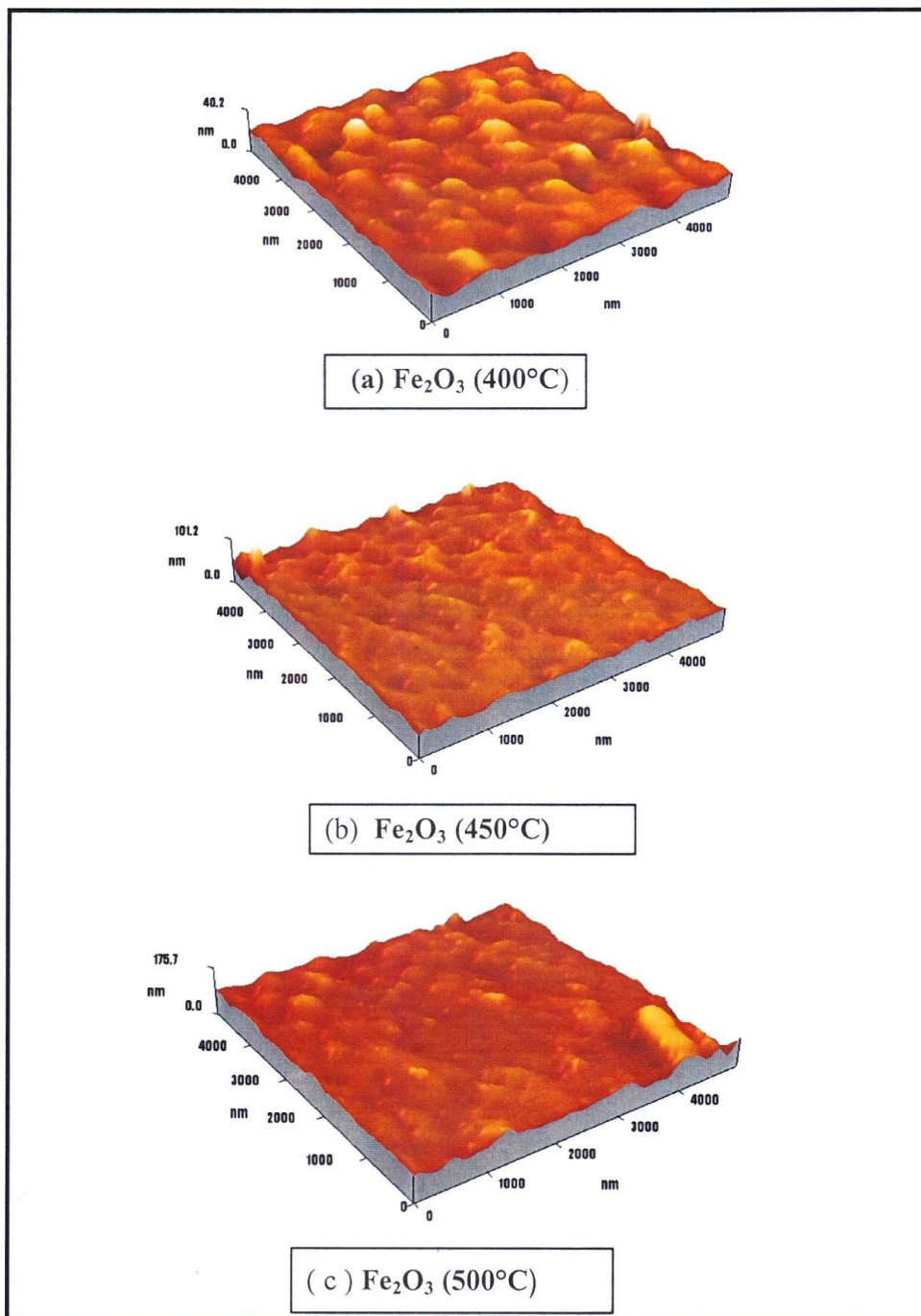


Figure (2): AFM micrographs of  $\text{Fe}_2\text{O}_3$  thin films prepared at different substrate temperatures (400, 450 , 500) °C.

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**Table (3):** The average roughness and root mean square (RMS) roughness measured by (AFM) for Fe<sub>2</sub>O<sub>3</sub> thin films prepared at different substrate temperatures (400, 450 , 500) °C.

Sample	Surface Roughness (nm)	RMS (nm)
Fe <sub>2</sub> O <sub>3</sub> (400°C)	2.37	3.12
Fe <sub>2</sub> O <sub>3</sub> (450°C)	3.58	4.88
Fe <sub>2</sub> O <sub>3</sub> (500°C)	6.82	9.55

### Conclusions

1. Preparation of (Fe<sub>2</sub>O<sub>3</sub>) thin films using chemical spray pyrolysis method at different substrate temperatures.
2. The results of X-ray diffraction measurements showed that the thin films of ferric oxide prepared at substrate temperatures of (400, 450, 500) °C were polycrystalline and have hexagonal structure of the type ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>).
3. The favorite crystal growth for all prepared thin films is (104).
4. The increase in the substrate temperature leads to an increase in the size of the crystalline grains and improves the crystal structure.
5. The results of the atomic force microscope (AFM) show an increase in the square root of the mean square values of roughness (RMS) as the substrate temperature increases.

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