Synthesis and Study of Nanostructure Fe_2o_3 Film by Laser Assisted Spray Pyrolysis

Bahaa T. Chiad*, Zainab S. Sadik*, Dunia K. Mahdi*and Fatin H. Mohammed**
*Department of Physics, College of Science, University of Baghdad.
** Department of Physics, College of Science, Al-Mustansiriya University.

Abstract

Films of hematite (α-Fe_2O_3) were deposited by using laser assisted spray pyrolysis technique (LASP). The films were deposited on heated substrates with temperature 400℃, once with using laser and other without laser, Structural analysis, using X-ray diffraction, verified the phase of the films and revealed that the films had a polycrystalline structure composed of nano-crystallites. Atomic force microscopy indicated that the films which deposited by laser assisted had smooth surface with smallest lateral grain size compared with the films deposited without laser, where the average grain size for the film deposited without laser about 146nm,while the average grain size for the film deposited with laser about 77nm.

Keywords: Spray pyrolysis; Iron oxide; Ultrasonic spray; CO_2 laser.

1. Introduction

During few decades, iron oxides have been widely studied; more recently, these oxides have been developed in the form of nanopowders and films. This is due to the wide variety of applications in various areas of science and technology. These applications include, drug delivery vehicles [1], solar filter [2], spinvalves [3], recording media [4], among others. The Fe_2O_3 phases include hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), δ-Fe_2O_3, and ε-Fe_2O_3 [5]. Hematite is the thermodynamically stable phase of Fe_2O_3, and is the subject of this work. This material is a semiconductor that is characterized by good thermodynamic stability at high temperatures, non-toxicity, low cost and abundance [6].

In this work, α-Fe_2O_3 films were prepared by the ultrasonic spray pyrolysis, once with assisted of laser and other without laser the structural properties were investigated to verify the phase of the material and study the affect of laser on structure properties and grain size of the α-Fe_2O_3 films.

By using Scherrerr equation (1) [7] was calculated the grain size for the films prepared with and without laser.

$$\delta=\kappa\lambda/\beta\cos\theta. \quad (1)$$

where:

δ is grain size, κ is shape factor=0.89, λ is wavelength=1.5405Å from Cu-Kα, β is full-width at half maximum peak intensity (FWHM)), θ isthe Bragg angle.

2. Experimental Procedure

The spray pyrolysis by laser-assisted set-up consists mainly of the following parts: a spraying and a liquid feeding unit, a 3W continuous wave CO_2 laser with wavelength 10.6 µm. We have used ultrasonic atomizer in the spraying unit. Fig.(1) show the schematic diagram of the experimental apparatus of LASP technique.

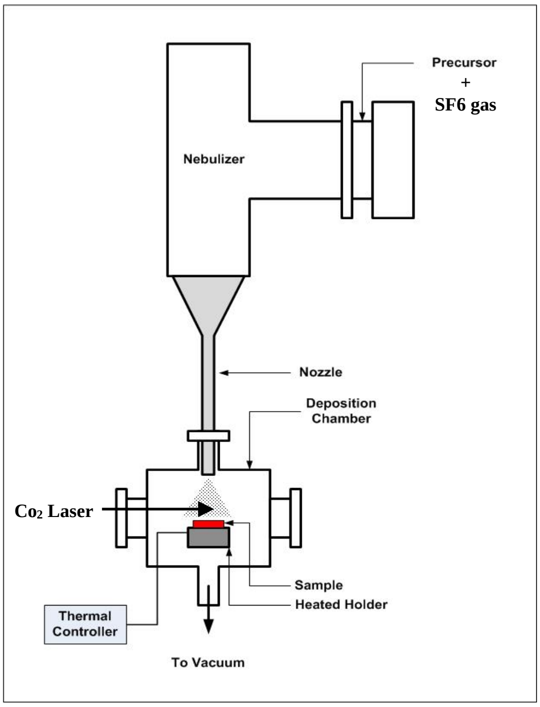

Fig.(1) Schematic diagram of the experimental apparatus of LASP technique.

The deposition was carried out inside of deposition chamber, it made from stainless steel. The starting solution of precursor salt (aqueous solution of $Fecl_3$) was nebulized using ultrasonic nebulizer with frequency 1.7 MHZ, the solution droplets were transferred into deposition chamber, the substrate temperature was 400°C was controlled by a temperature control unit (Cnmon REX-C900), it was kept constant during the deposition time (5min). A 3W continuous wave CO_2 laser with wavelength 10.6 µm. Since the proposed precursor does not have resonance absorption with CO_2 wavelength, sulfurhexafluoride (SF6) is used as the carrier gas for aerosol transport. A CO_2 laser beam of wavelength 10.6µm was resonantly absorbed into the SF6 molecules through vibrational excitation. Therefore, the carrier gas was heated by the CO_2 laser as the aerosol/gas mixture was injected into the chamber.

In order to decrease the residual stress of the film, and the coated substrates were cooled slowly until reaching ambient temperature. 0.2 M aqueous solution of Iron (III) chloride was used in the preparation the iron oxide films. The crystalline structure of the films was determined by X-ray diffraction (XRD).

2.1 Synthesis of Fe_2O_3 films

2.1.1 Substrate cleaning

Substrate cleaning is an important factor to get reproducible films as it affects the smoothness, uniformity, adherence and porosity of the films. The substrate cleaning process depends upon the nature of the substrate; degree of cleanliness required and nature of contaminates to be removed, in this work a glasses substrates of dimensions 7.5 cm x 2.2 cm x 0.125 cm have been used as substrates for deposition of the coatings. The glass substrates were cleaned with an ultrasonic agitator in repeated baths of ethanol and acetone, then rinsed in distilled water prior to loading into the chamber.

2.1.2 Procedure of Fe_2O_3 coating deposition by USP (without laser)

The prepared substrate was set up on the substrate holder 10 cm away from the nozzle and the holder was heated to 400ºC. The nebulizer filled with precursor was setup as shown in Fig.(1) (but without laser). The chamber is connected to a vacuum pump to maintain the ambient pressure about 760 mmHg. The process was run for 5min to get a good layer of Fe_2O_3.

2.1.3 Procedure of Fe_2O_3 coatings deposition by USP (with laser)

All the parameters were kept as same as for ferrous oxide prepared without laser as the previous section, but in this procedure, a CW CO_2 laser of 3W was focused to a point just above the funnel tube orifice, while sulfurhexafluoride (sf6) which used as a carrier gas for aerosol transport at 3.5L/min flow rates. Also at the same time, the substrate was heated to promote film growth at the same conditions of procedure without laser with respect to concentration of precursor solution and substrate temperature.

2.1.4 Thickness measurement

Films thickness measurement by optical interferometer method. This method was based on interference of light beam reflected from film surface and substrate bottom. He-Ne laser of wavelength (632.8nm) was used and the thickness is determined using the formula:

$$d = \frac{\Delta x}{x} \times \frac{\lambda}{2} \quad \text{...} \quad (2.1.4)$$

Where x is fringe width, Δx is the distance between two fringes and λ is wavelength of laser light.

3. Result and Discussion

3.1 Structural properties

The XRD patterns of the films are shown in Fig.(3.1.a) and (3.1.b). The films had a polycrystalline structure. All of the observed peaks can be assigned to the α-Fe_2O_3 phase, in accordance with data from the ASTM (American Society of Testing Materials) cards**.** The Scans were performed over 2θ =20-60° for each sample.

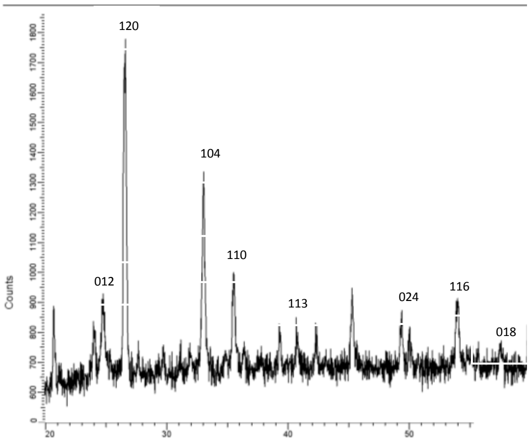

Fig.(3.1.a) X-ray diffraction pattern of a Fe_2O_3 nanograined film deposited by spray pyrolysis without laser heating.

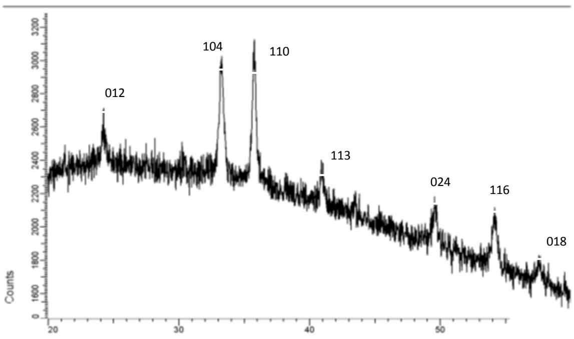

Fig.(3.1.b) X-ray diffraction pattern of a Fe_2O_3 nanograined film deposited by spray pyrolysis with laser heating.

Fig.(3.1.a and 3.1.b) show the comparison of the XRD patterns of the Fe_2O_3 deposited on glass substrate, which were made with and without a laser. Fig.(3.1.a) indicate crystalline peaks of α-Fe_2O_3 (012), (104), (110), (113), (024), (116) and (018), in addition of the peak α-FeOOH (110) and (120). Fig.(3.1.b) show the pure phase of α-Fe2O3. From this figures, we can find that the small amount of α-FeOOH which exit in the sample was prepared without laser converted to α-Fe_2O_3 with the sample was prepared with laser, where the thermal decomposition of the $Fe(OH)_3$ produced α-Fe_2O_3 with small amount of α-FeOOH Fig.(3.1.a)[8] and with affected of CO_2 laser produced high purity of α-Fe_2O_3 Fig.(3.1.b), Note that all parameters remained constant in both cases, so we believe that the laser heating is affecting on the structural of the film. The crystallite size was calculated using the Scherrerr equation, and was found to be 71 nm for the films deposited without laser heating, and 29nm for the films deposited with laser heating films. Thus, the films had a nano-crystalline structure. Table (1) and (2). illustrate the grain size of the prepared films with and without laser affect.

Table (1)
The experimental values of peaks, and grain size for prepared α-Fe_2O_3 film without Laser.

Thickness (nm)	*2θ (Degre)*	*d_{hkl} (Exp.) (Å)*	*hkl*	*FWHM (Deg.)*	*G.S (nm)*
214	24.4	3.66	012	0.2	71
214	33.2	2.712	104	0.5	28
214	35.8	2.56	110	0.5	29
214	41	2.207	113	0.1	149
214	49.6	1.8	024	0.6	25.66
214	54.1	1.71	116	0.4	38.9
214	57.4	1.63	018	0.1	159.3
214	21	4.21	110	0.2	70.7
214	26	3.384	120	0.2	71.4

Table (2)
The experimental values of peaks, and grain size for prepared α-Fe_2O_3 film with Laser.

Thickness (nm)	*2θ (Degree)*	*d_{hkl} (Exp.) (Å)*	*hkl*	*FWHM (Deg.)*	*G.S (nm)*
212	24.4	3.66	012	0.4	35.46
212	33.2	2.712	104	0.6	24
212	35.8	2.56	110	0.6	25.05
212	41	2.207	113	0.3	49.33
212	49.6	1.8	024	0.9	16.96
212	54.1	1.71	116	0.8	19.457
212	57.4	1.63	018	0.5	31.61

3.2 FTIR Analysis

Fig.(3.2) shows the FTIR spectra of iron oxide samples which prepared with laser. From the spectra it can be seen that two broad peaks at 555 and 466 cm^{-1}. These peaks may correspond to Fe-O stretching and bending vibration mode in α-Fe_2O_3 respectively [9], and the other peaks assigned to the O–H stretching vibration of absorbed water.

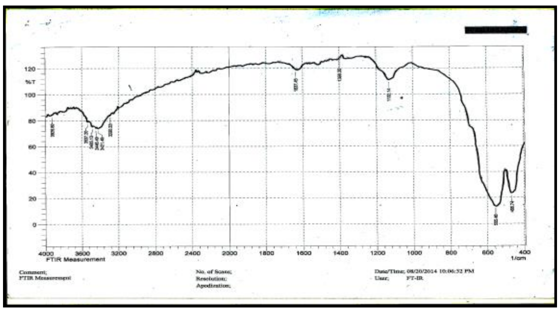

Fig.(3.2) FTIR spectra of iron oxide sample which prepared by laser assisted spray pyrolysis.

3.3 AFM analysis

The Fe_2O_3 films were analyzed by atomic force microscopy (AFM). An AFM image of a film deposited without laser heating is shown in Fig.(3.3.a). The average grain size is about (146)nm. Irregular particle shapes and size are visible in the three dimensional image. In comparison, a film deposited with CO_2 laser heating of the carrier gas with the same conditions which preparation of Fe_2O_3 films without laser .as shows a distribution of well-defined particles (Fig.3.3.b). The average grain size is about (76) nm.

In Fig.(3.3.a and 3.3.b), one can clearly see that in the presence of laser heating the grain sizes are much smaller than in absence of laser heating.

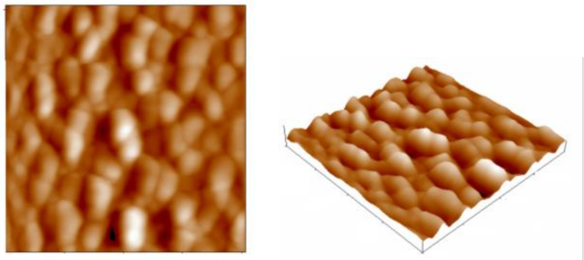

Fig.(3.3.a) 2D and 3D AFM image of a Fe_2O_3 film deposited by spray pyrolysis without the laser heating.

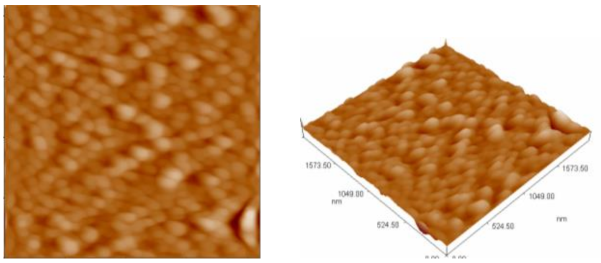

Fig.(3.3.b) 2D and 3D AFM image of a Fe_2O_3 film deposited by spray pyrolysis with the laser heating.

Without laser heating the average size of the grains is about 146nm in radius, while with laser heating, the grain size is reduced to about 76nm in radius. The reason for the change in particles size, with and without a laser, can be explained in terms of evaporation of the solvent. As a droplet comes out of the nozzle, the laser heating of SF6 results in the evaporation of solvent from the droplet, then the droplet becomes denser as compared to the base composition, which is used in the precursor [10]. The high density and smaller size reduce the possibility of droplet flattening when colliding with the substrate. This causes the deposited film to be consisting of well-defined particles as shows in the Fig.(3.3.b).

Conclusion

The iron oxide films obtained from aqueous solution of $FeCl_3$ via laser assisted spray pyolysis deposition have been studied with and without laser .Our experiments have shown that when the laser radiation in this process was absorbed into the carrier gas SF6, therefore the carrier gas was heated by CO_2 laser which is given the heat to the aerosol which was injected into the chamber, so that most solvent in the droplets is evaporated, leading to solid particles impinging on the substrate, film with much smaller grains have been grown by the laser heating the droplets than the grains have been grown without laser heating ,because that when the droplets were directly incident on the substrate , they initially flatten on the substrate, followed by evaporation of the solvent and decomposition , leading to large particles sizes.

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الخلاصة

رسبت اغشية من الهيماتايت (α-Fe_2O_3) باستعمال تقنية الانحلال الحراري بمساعدة الليزر. الافلام المترسبة على ركيزة بدرجة حرارة 400^o م, مرة باستعمال الليزر والاخرى بعدم استعمال الليزر. التحليل الهيكلي باستعمال حيود الاشعة السينية كشف ان طور الافلام لها بناء هيكلي متعدد التبلور مكون من بناء نانوي, مجهر القوة الذرية (AFM) يشير الى ان الاغشية المترسبة بمساعدة الليزر لها سطح املس مع حجم حبيبي اصغر مقارنة بالافلام المترسبة بدون الليزر, حيث ان معدل الحجم الحبيبي للغشاء المترسب بدون الليزر حوالي 146 نانومتر, بينما معدل الحجم البلوري للغشاء المترسب بمساعدة الليزر كان 77 نانو متر.