Synthesis and Study of Nanostructure Fe₂O₃ Film by Laser Assisted Spray Pyrolysis

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Abstract
Films of hematite (α-Fe₂O₃) were deposited by using laser assisted spray pyrolysis technique (LASP). The films were deposited on heated substrates with temperature 400°C, 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; CO₂ 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], spin valves [3], recording media [4], among others. The Fe₂O₃ phases include hematite (α-Fe₂O₃), maghemite (γ-Fe₂O₃), δ-Fe₂O₃, and ε-Fe₂O₃ [5]. Hematite is the thermodynamically stable phase of Fe₂O₃, 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-Fe₂O₃ 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-Fe₂O₃ films.

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

\[ \delta = \frac{\beta}{k \cos \theta} \]

where:
\( \delta \) is grain size, \( k \) is shape factor=0.89, \( \lambda \) is wavelength=1.5405Å from Cu-Kα, \( \beta \) is full-width at half maximum peak intensity (FWHM), \( \theta \) is the 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 CO₂ 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.](image)
The deposition was carried out inside of deposition chamber, it made from stainless steel. The starting solution of precursor salt (aqueous solution of FeCl₃) 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 (Cmon REX-C900), it was kept constant during the deposition time (5min). A 3W continuous wave CO₂ laser with wavelength 10.6 µm. Since the proposed precursor does not have resonance absorption with CO₂ wavelength, sulfurhexafluoride (SF6) is used as the carrier gas for aerosol transport. A CO₂ laser beam of wavelength 10.6μm was resonantly absorbed into the SF6 molecules through vibrational excitation. Therefore, the carrier gas was heated by the CO₂ laser as the aerosol/gas mixture was injected into the chamber.

In order to decrease the residual stress of the film, 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 Fe₂O₃ 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 Fe₂O₃ 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 400°C. 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 Fe₂O₃.

2.1.3 Procedure of Fe₂O₃ 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 CO₂ 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:

\[
d = \frac{\Delta x \times \lambda}{2x} \tag{2.1.4}
\]

Where \(x\) is fringe width, \(\Delta x\) is the distance between two fringes and \(\lambda\) 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-Fe₂O₃ 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.
laser heating films. Thus, the films had a nanocrystalline 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-Fe₂O₃ film without Laser.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>2θ (Degree)</th>
<th>d_hkl (Exp.) (Å)</th>
<th>hkl</th>
<th>FWHM (Deg.)</th>
<th>G.S (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>214</td>
<td>24.4</td>
<td>3.66</td>
<td>012</td>
<td>0.2</td>
<td>71</td>
</tr>
<tr>
<td>214</td>
<td>33.2</td>
<td>2.712</td>
<td>104</td>
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<td>28</td>
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<tr>
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<td>110</td>
<td>0.5</td>
<td>29</td>
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<tr>
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<td>0.1</td>
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<tr>
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<tr>
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<td>0.2</td>
<td>71.4</td>
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**Table (2)**
The experimental values of peaks, and grain size for prepared α-Fe₂O₃ film with Laser.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>2θ (Degree)</th>
<th>d_hkl (Exp.) (Å)</th>
<th>hkl</th>
<th>FWHM (Deg.)</th>
<th>G.S (nm)</th>
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</tr>
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</table>

**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-Fe₂O₃ respectively [9], and the other peaks assigned to the O–H stretching vibration of absorbed water.
3.3 AFM analysis

The Fe$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ film deposited by spray pyrolysis without the laser heating.](image)

![Fig.(3.3.b) 2D and 3D AFM image of a Fe$_2$O$_3$ film deposited by spray pyrolysis with the laser heating.](image)

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 pyrolysis 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.

**Reference**


[8] Wenqing Qin, 1, 2 Congren Yang, 1, 2 Ran Yi, 1, 2 and Guanhua Gao, 1, 2 "Hydrothermal Synthesis and Characterization of Single-Crystalline \( \alpha \)-Fe\(_2\)O\(_3\) Nanocubes" Journal of Nanomaterials, 2011Article ID 159259, 2011 ages, 2011
[9] Index of Vibrational Spectra of Inorganic and Organometallic Compounds vol.3.

الخلاصة

رسبت اغشية من الهيماتايت (\( \alpha \)-Fe\(_2\)O\(_3\)) باستعمال تقنية الانحلال الحراري بمساعدة الليزر، الأفلام المترسبة على تركيزة 1 درجة حرارة 400\( ^\circ \)C، مرة باستعمال الليزر الأخر، بعدم استعمال الليزر، التحليل الهيكي باستعمال جيود الاشعة السينية كشف ان طور الأفلام لها بناء هيكي متبعد التبلور مكون من بناء نادي، مجهر القوة الذرية (AFM) يشير إلى ان الأغشية 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 نانومتر.

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