Effect of Thickness on Some Physical Properties of α-Fe_2O_3 Thin Films Prepared by PLD

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Abstract
The effect of thickness variation on some physical properties of hematite α-Fe_2O_3 thin films was investigated. An Fe_2O_3 bulk in the form of pellet was prepared by cold pressing of Fe_2O_3 powder with subsequent sintering at 800°C. Thin films with various thicknesses were obtained on glass substrates by pulsed laser deposition technique. The films properties were characterized by XRD, and FT-IR. The deposited iron oxide thin films showed a single hematite phase with polycrystalline rhombohedral crystal structure .The thickness of films were estimated by using spectrometer to be (185-232) nm. Using Debye Scherrerś formula, the average grain size for the samples was found to be (18-32) nm. Atomic force microscopy indicated that the films had smooth surfaces, with a lateral grain shape. The optical absorption of the films was determined from spectrophotometric measurements.

Keywords: Fe_2O_3 thin films; PLD; XRD; AFM; Absorption Spectra

تأثير السمك على بعض الخواص الفيزيائيه لأغشية α-Fe_2O_3 المحضره بالترسيب بواسطة الليزر النبضي

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الخلاصه
تمت دراسة تأثير تغير السمك على بعض الخصائص الفيزيائيه لأغشية α–Fe_2O_3 الرقيقه . حضر قرص من Fe_2O_3 بالكبس على البارد لمسحوق Fe_2O_3 ثم تم تلبيدها بدرجة حرارة $800\ ^oC$. تم الحصول على أغشيه رقيقه بأسماك مختلفه على قواعد زجاجيه بتقنية الترسيب بالليزر النبضي. و قد ظهر أن أغشية أوكسيد الحديد الرقيقه نقيه و تمتلك تركيب بلوري معيني متعدد التبلور وبحجم حبيبي nm (32- 18). تم قياس سمك الأغشيه (185-232) nm بواسطة المطياف. تشير نتائج مجهرية القوة الذريه الى أن الأغشيه تمتلك سطوح ناعمه مع حجم حبيبي جانبي. تم قياس الأمتصاصيه البصريه للأغشيه بواسطة القياسات الطيفيه.

الكلمات المفتاحيه: أغشية Fe_2O_3 الرقيقه، PLD، AFM،XRD، طيف الأمتصاصيه.

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1. Introduction

Iron can form several oxides of different stoichiometry and crystalline phases. These oxides are wustite (FeO), maghemite (Fe_3O_4), hematite (α-Fe_2O_3), and maghemite (γ-Fe_2O_3). Hematite is the thermodynamically stable phase of Fe_2O_3.This material is a semiconductor that is characterized by good thermodynamic stability at high temperatures, non-toxicity, low cost and abundance [1]. α-Fe_2O_3 has a bandgap energy of 2.1 eV which enables it to absorb considerable amount of visible light (40% of incident solar radiation) [2]; additionally, it exhibits a chemical stability over a broad PH range [3]. These characteristics make it attractive for many applications, such as solar energy conversion, electrochromism, photocatalysis, interference filters, photo-oxidation of water, gas sensitive material [4, 5]. Moreover, it has recently been reported that nanostructured α-Fe_2O_3 thin films are suitable for developing multi-junction hybrid photoelectrodes for hydrogen production [6].

α-Fe_2O_3 thin films may be prepared by a variety of techniques such as sol-gel, reactive magnetron sputtering, aerosol/spray pyrolysis[2], metal-organic deposition, electro-deposition, pulsed laser deposition [4] and chemical vapor deposition [7].

The aim of this work is to study the influence of thickness on some physical properties of α-Fe_2O_3 thin films prepared by pulsed laser deposition.

2. Procedure

Hematite α-Fe_2O_3 thin films were deposited onto ultrasonically cleaned glass substrates by pulsed laser deposition technique using Nd-Yag laser source with 1064 nm wavelength. The number of pulses was 300 and 900 for the films with thickness (185, 232) nm, respectively. The laser source energy was 700 mJ for all films. A high purity (99.99%)(WLIAMS LTD, England) Fe_2O_3 powder was cold pressed in the form of a pellet with 13 mm diameter and 3.5 mm thickness. The pellets were sintered at 800 ℃ for 5h in an atmospheric environment and used as source material.

These films were subsequently subjected to thermal annealing at 550^{o}C in an atmospheric environment for 2h.The thickness of the films was measured using a (BLACK-CXR-SR-25 spectrometer). The structure of the films was investigated by X-ray diffraction (XRD) using a (Shimadzu XRD-6000) diffractometer, employing CuKα (1.54Å) radiation. The surface morphology of the films was examined by atomic force microscopy (AFM) (SPM-AA 300, Angstrom Advanced Inc., USA).Optical absorbance was performed over the wavelength range (400-1000) nm using UV-visible spectrophotometer (Shimadzu UV-1800). The FT-IR spectrum was recorded in the range (400-1000) cm^{-1} as KBr discs on a Shimadzu FT-IR-8400F Spectrophotometer.

3. Results and Discussion

Figure - 1 shows X-ray diffraction pattern of α-Fe_2O_3 thin films. From these patterns it is clear that all films have a single phase. The films are polycrystalline and fit well with the rhombohedral crystal structure. These films are in correspondence with data from the International Center for Diffraction Data (ICDD file No.01-071-5088). The average grain size is calculated employing Scherrer's equation [8].

$$D=\frac{0.9\lambda}{ß COS\Theta} \qquad (1)$$

Where D is grain size, λ is wavelength of X-ray, ß is the full width at half maximum in radian, and Ɵ is Bragg angle. The average grain size was found to be (18-32) nm and it is nearly agrees with Balouria et al. [9].The thicknesses of the films were estimated to be (185,204,210,232) nm by spectrometer measurements.

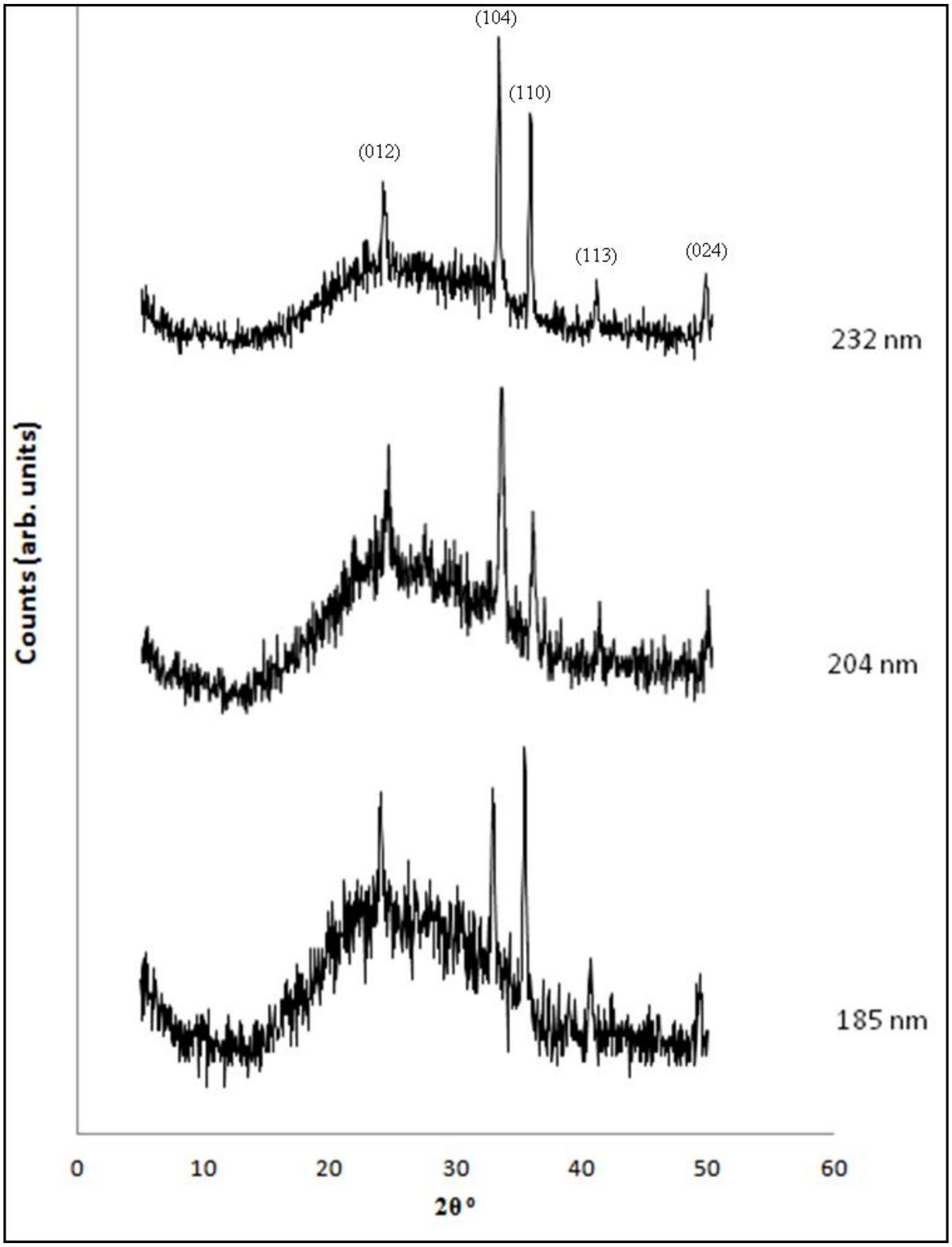

Figure 1- XRD patterns of α-Fe_2O_3 thin films with different thicknesses.

Atomic force microscopy images of the films are shown in figure - 2, which were recorded in contact mode. The surface morphology of the films showed columnar microstructure.

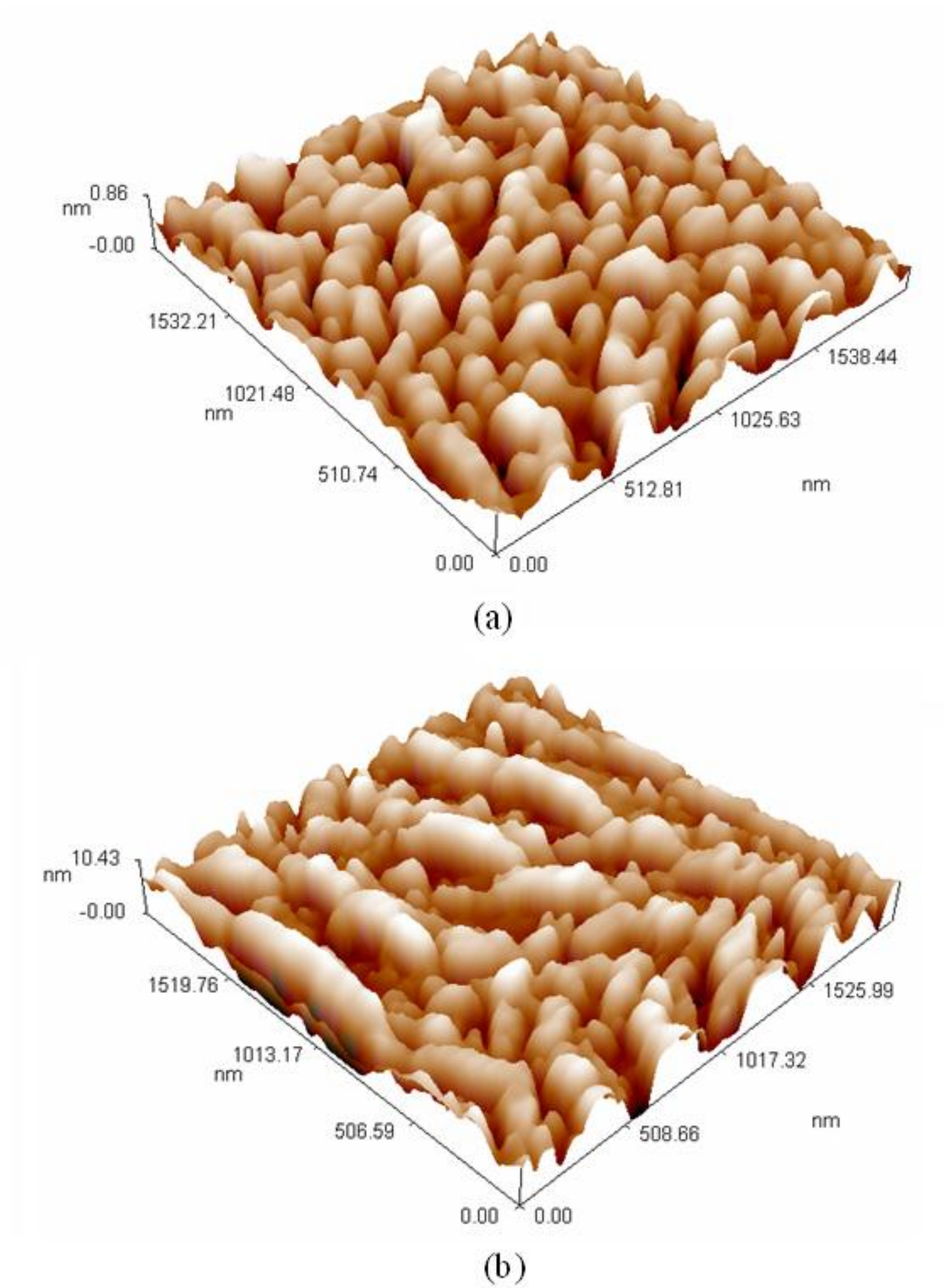

Figure 2- AFM images (a) for 185 nm thickness (b) for 232 nm thickness

Statistical analysis of the images was performed to obtain the root-mean-square surface roughness RMS. The average roughness was 0.159 nm and 1.91 nm for the films with thickness (185, 232) nm, respectively. Table-1 shows the values of average roughness, RMS and grain size.The films were translucent and reddish brown in color, which is an indication of the formation of α-Fe_2O_3 phase. Similar results have been pointed by schwertmann et al. [10].

Table1-The values of average roughness, RMS and grain size of α-Fe_2O_3 films.

Thickness (nm)	Average roughness (nm)	RMS (nm)	Grain size (nm)
185	0.159	0.19	18
232	1.91	2.29	32

The optical absorption spectra of Fe_2O_3 films with different thickness in the wave length range of (400-1000) nm are shown in figure -3. It is clear from this figure that the spectral characterization is affected by thickness. The absorption gradually decreases as the wavelength extends toward the visible region. From (540 to 600) nm the absorption decreases significantly and becomes linear into the red region. The presence of an absorption tail between 540 and 600 nm probably indicates the existence of sub-bandgap states [1]. It is widely accepted that the band edge of Fe_2O_3 is located in the range of (580-620) nm [11].The threshold of absorption at 564 nm (2.2 eV) is in approximate agreement with the bandgap value of 2.2 eV for Fe_2O_3 [12]. It is obvious that the absorbance increases with the increasing of film thickness because in the case of thicker film, more atoms are present in the film so more states will be available for the photons to be absorbed.

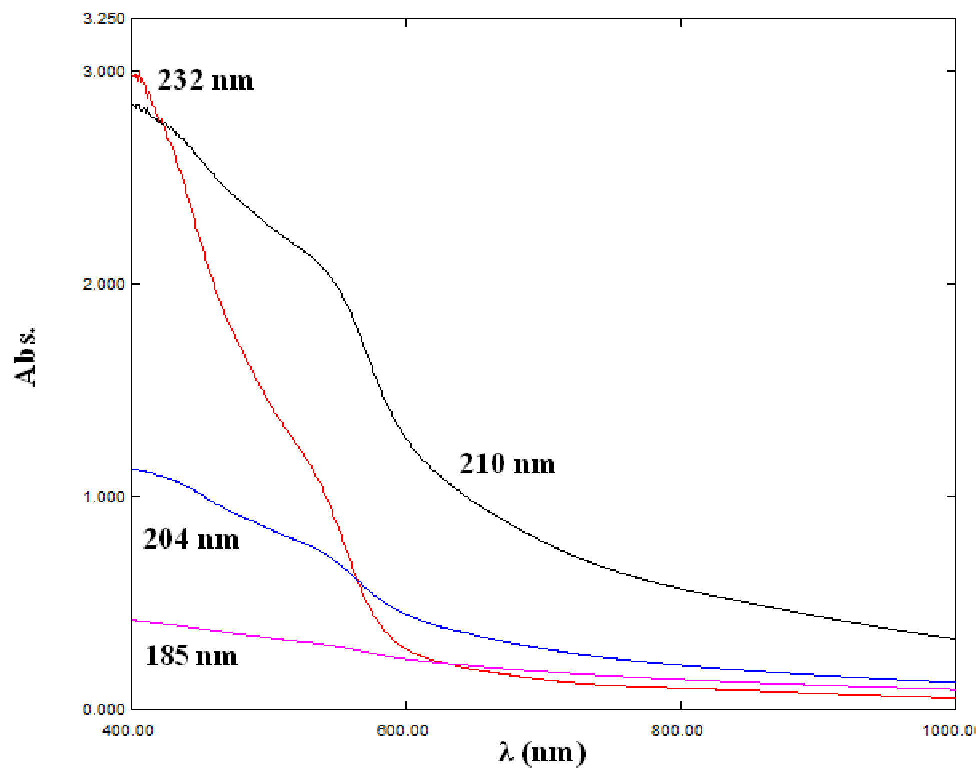

Figure 3- Absorption spectra of α-Fe_2O_3 thin films with different thicknesses

Table- 2 illustrates the values of optical constants, the refractive index (n), extinction coefficient (k), the real part (ε_r) and the imaginary part (ε_i) of dielectric constant.

Table 2- The values of optical constants of α-Fe_2O_3 films.

Thickness (nm)	n	k	ε_r	ε_i
185	5.368	0.2937	28.731	3.153
204	3.369	0.426	11.170	2.877
210	5.706	0.168	32.535	1.922
232	2.413	0.025	5.822	0.123

FTIR spectroscopy is often used to identify iron oxide phase, and the α-Fe_2O_3 spectrum is distinctly different from that of common impurity phases such as Fe_2O_4 and γ-Fe_2O_3 [13]. The FT-IR spectrum of the α-Fe_2O_3 film is shown in figure - 4. The spectrum is typical of α-Fe_2O_3 phase showing peaks located at (412,495,612,660, and 830) cm^{-1}. All these FTIR lines closely match with the reported α-Fe_2O_3 phase of iron oxide [14].

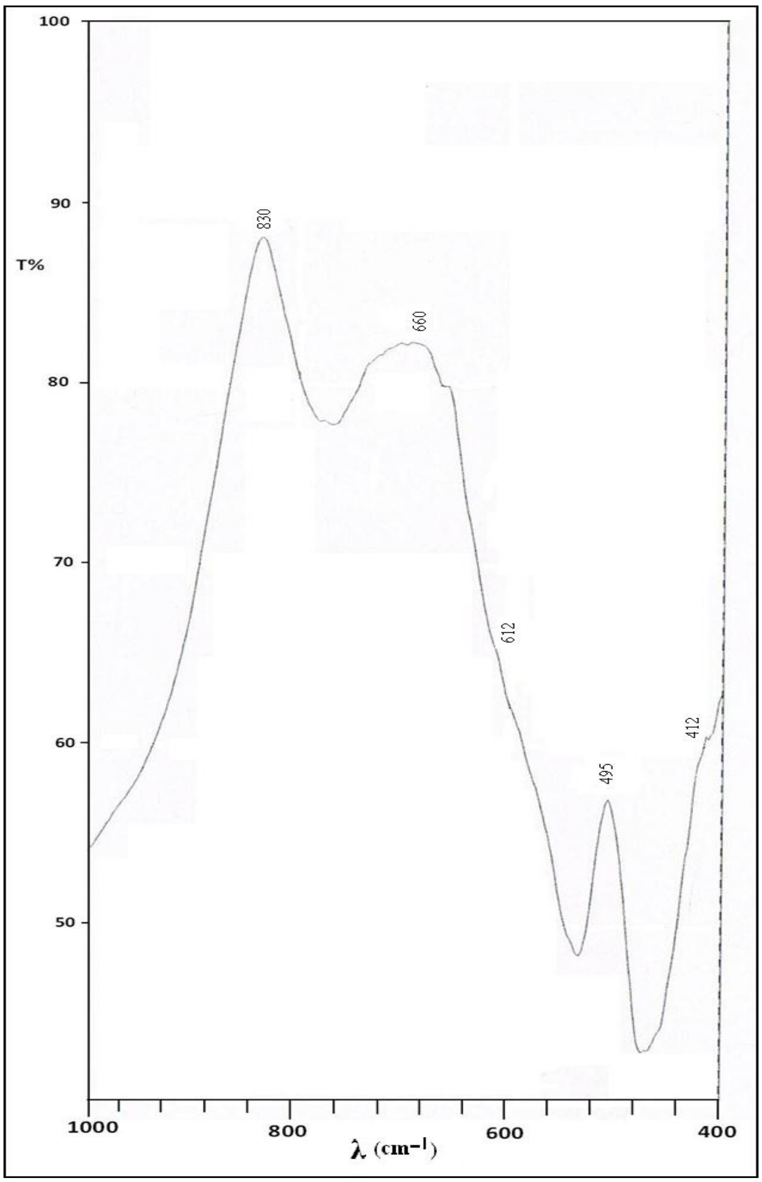

Figure 4 - FTIR spectrum of α-Fe_2O_3 thin film.

4. Conclusion

(α-Fe_2O_3) thin films with different thickness (185,204,210,232) nm were obtained on glass substrates by pulsed laser deposition technique followed by thermal annealing and were investigated by XRD, AFM, optical absorbance spectra and FT-IR. Based on the above results, the following conclusions can be drawn.

1. The films are polycrystalline, with nano-crystallite size increased with thickness. The crystalline phase is a pure α-Fe_2O_3. The average grain size was found to be (18-32) nm.
2. The average roughness was (0.159 nm and 1.91 nm) for the films with thickness (185,232) nm, respectively.
3. The spectral characterization was affected by thickness. The absorbance increased with the increase of film thickness.

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