

Effect of Thickness on Some Optical Properties of Fe₂O₃ Thin Films Prepared by Chemical Spray Pyrolysis Technique

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Abstract

The paper reports the influence of the thickness on the some optical properties of Fe₂O₃ thin films, which were prepared by chemical Spray pyrolysis technique on glass substrate heated to 400°C. The thickness of thin films (250, 280, 350) nm were measured by using weighting method. The optical properties include the absorbance and reflectance spectra, extinction coefficient, and real and imaginary part of the dielectric constant. The result showed that the optical constant ($k, \epsilon_r, \epsilon_i$) decreased with the increase of the thickness.

Keywords : Fe₂O₃, Spray pyrolysis technique, Optical properties

Introduction

Fe_2O_3 is one of the most important transition metal oxides with a bandgap of 2.2 eV. It received an extensive attention due to its good intrinsic physical and chemical properties, such as its low cost, stability under ambient conditions, and environmentally friendly properties [1]. Due to these properties, Fe_2O_3 nanostructures can have wide applications in many fields including magnetic recording materials, catalysis, optical devices, gas sensors, photochemical and pigments.[2].

Thin films of Fe_2O_3 were prepared using many deposition techniques such as Aerosol – assisted chemical vapor deposition (AAC-VD) which is simple to operate and very versatile.[3] and of Fe_2O_3 were prepared using technique pulsed laser deposition (PLD)[4], Sol-gel[5], Sputtering [6,7] and from aim of research Rajendra N.Goyal et al[8]. reported the preparation and characterization of iron oxide nanocrystalline thin films by ultrasonic spray pyrolysis technique iron oxide films were grown on quartz substrate at different deposition temperatures varying from (400-700)°C. So the notice of both orientation and the size of the crystalline thin films revealed the magnetite to hematite phase transformation with an increase in substrate temperature and they showed the deposited thin films exhibited the estimated direct band gap (E_g) in range 2-2.2eV, in addition to that, the films deposited on quartz substrate at different temperatures had low conductivity and thus are not suitable for electrochemical sensing. While Qing Wei et al.[9] were reported the different morphologies of α – Fe_2O_3 films including particles, porous, granular and nanosheets, which have been prepared by directly oxidizing the as-deposited Fe films in air, also the effect of the heating temperature, duration of time and rate of heating were reported by adjusting the rapidly oxidation condition. They noticed that, one can easily control the morphology of α - Fe_2O_3 films from clusters of particles to porous films, in addition, through the oxidation process at the low heating rate, α - Fe_2O_3 nanosheets can easily be fabricated on the Si substrate.

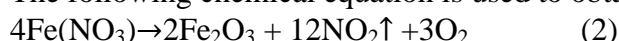
Experimental

Thermal Spray pyrolysis method is basically a chemical process, which consists of a solution that is sprayed into a substrate held at high temperature, where the solution reacts forming the desired thin film. Fe_2O_3 films were grown onto glass substrates, using a typical spray pyrolysis system. The spray solution was prepared by mixing the appropriate volumes of ferrite nitrate dehydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) (molecular weight 404.02 g/mol) which is a solid material with white color when it is completely dry while it has an orange color when it is dissolved in the water. The solution was prepared with (0.2 mol/L) by mixing (8.0804 gm) from ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) with (100ml) deionized water in magnetic stirrer to facilitate the complete dissolution of the solute in the solvent to obtain clear solution. Finally, the solution was sprayed into a spray pyrolysis deposition chamber. The following equation is used to obtain the required weight according to the calibration above:

$$M = \left(\frac{Wt}{M_{wt}} \right) \cdot \left(\frac{1000}{V} \right) \quad (1)$$

Where :M is the concentration molar, V is the volume of water, Wt is the required weight and M_{wt} is the molecular weight of ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$).

The following chemical equation is used to obtain the Fe_2O_3 thin films:



The substrate temperature was fixed at 400°C and was controlled within ± 5 °C with carrier air pressure (10^5N/m^2), flow rate of solution ($10 \text{cm}^3/\text{min}$) and the substrate to nozzle distance is 30cm. Spraying was done in short time intervals (15sec), subsequent the deposition is stopped about 5min in order to return the temperature into its original value. Optical transmission

data were obtained with an UV-Visible Shimadzu 3101 PC double beam spectrophotometer. The effect of the thickness on the optical properties was investigated.

Weighting Method

Ground glass is weighted before and after deposition completion of the re-deposition process and weighted again, and weight difference, which represents the weight of film material and the density of the material deposited area of the film can be calculated by the thickness of the thin film of the following equation :

$$\text{The thickness of the thin film} = \frac{\text{weight film material}}{\text{The thickness of the thin film material} \times \text{area of the film}}$$

Results and Discussion

The absorption spectrum of Fe₂O₃ thin films in the spectral range (340-1100)nm was prepared at substrate temperature of 400C and different thickness is shown in Figs.(1). It is clear from this figure that the spectral characterization is affected by thickness. The optical absorption spectrum decreases as the wavelength extends toward the visible region. The absorption decreases significantly and from 590-1100 nm becomes linear into the infrared region. The presence of an absorption tail between 590 and 1100 nm indicates probably the existence of sub-band gap states [10].

Also, we can observe from Fig.(1) that the Absorbance increases with the increase of thickness and shifted to longer wavelengths. This may be attributed to the creation of levels at the energy band by increasing thickness and this leads to the shift of peak to smaller energies. Also we studied the spectrum of the reflectance as shown in Fig.(2). It is obvious that their behavior is increased up to 480nm and then decreases with increase of wavelength.

It can be observed that the reflectance increases with increasing of thickness this is attributed to the increase in the absorbance and decreases in the transmittance.

Optical constant of Fe₂O₃ thin films were studied with the help of Absorption spectra in the UV-Visible region. Fig (3) shows the extinction coefficient of Fe₂O₃ thin films recorded in the range(340-1100)nm at different thickness. We can observe from this figure that the extinction coefficient, in general, decreases with the increase of wavelength for all films. Also its value increases by the increase of thickness in the range(250,280,350)nm. This is attributed to the same reason mentioned previously in the absorption spectrum.

The fundamental electron excitation spectrum of the film was described by means of a frequency dependent of the complex electronic dielectric constant. The dielectric constant is defined as, $\epsilon(\omega) = \epsilon_r(\omega) + i\epsilon_i(\omega)$ and real and imaginary parts of the dielectric constant are related to the n and k values. The ϵ_1 and ϵ_2 values were calculated using the formulas [11]

$$\begin{aligned} \epsilon_1(\omega) &= n^2(\omega) - k^2(\omega) \\ \epsilon_2(\omega) &= 2n(\omega)k(\omega) \end{aligned}$$

The ϵ_r and ϵ_i values dependence of wavelength are respectively shown in Fig. 4 and Fig. 5. The ϵ_r values are higher than that of ϵ_i values. It is seen that the ϵ_r and ϵ_i values decrease with increasing of thickness.

Conclusion

Fe₂O₃ thin films were prepared using spray pyrolysis technique onto glass substrate at temperature equal to 400°C and different thickness (250,280&350)nm. From UV-Visible spectrometer, the absorption spectrum was measured. Also, the optical constant such as

extinction coefficient real and imaginary dielectric constant were determined and indicated that they decreased with the increase of the wavelength and the thickness.

References

1. Wu, J. J.; Lee, Y. L.; Chiang, H. H. and Wong, D. K. P(2006). J. Phys. Chem. B110 18108.
2. yiroky' K. S ~ ;Jires'ova', J. and Hudec L. O. (1994), Thin Solid Films 245 211
- 3.Asif Ali Tahir , Upul Wijayan tha K.G., Sina Saremi-Yarahmadi,Muhammad Mazhar and Vickie Mckee, .2009,Nanostructured α - Fe_2O_3 thin films for photoelectrochemical Hydrogen Generation ,chem.mater,21,3763-3772,3763.
- 4.Krause. M.K., Esquinazi P., Ziese M., Hohne R., Pan A., Galkin A.and Zeldov E., (2002) J. Magn. Magn. Mater. 245 1097
5. Tang, N.J; Zhong.W.;Jiang, H.Y.; Wu.X.L, iu.W L, Du.Y.W, (2004) J. Magn. Magn. Mater. 282 92.
6. Ohta,S. andTterada, A. (1986) Thin Solid films 143 73.
7. Zhang, G.; Fan, C.; Pan, L.; Wang, F.; Wu ,P.; Giu, H.;Gub. Y .; Zhang.Y. Magn. Magn.J.
8. Rajendra, N. Goyal a,*, Davinder Kaurb, Ashish K. Pandeya (2009), Growth and characterization of iron oxide nanocrystalline thin films via low-cost ultrasonic spray pyrolysis, Materials Chemistry and Physics, 116, 638–644
9. Qing Wei, Zhengcao Li, Zhengjun Zhang* and Qin Zhou, (2009), Facile Synthesis of α - Fe_2O_3 Nanostructured Films with Controlled Morphology, Materials Transactions, 50: (6) 1351 to 1354
10. Beermann, N.; Vayssieres, L.; Lindquist, S.-E.and Hagfeldt, A. J. (2000) Electrochem. Soc., 147, 2456–2462.
11. Moss, S.;Burrell, G.J.and. Ellis, B. (1973), Semiconductor Opto-Electronics, Wiley, New York.

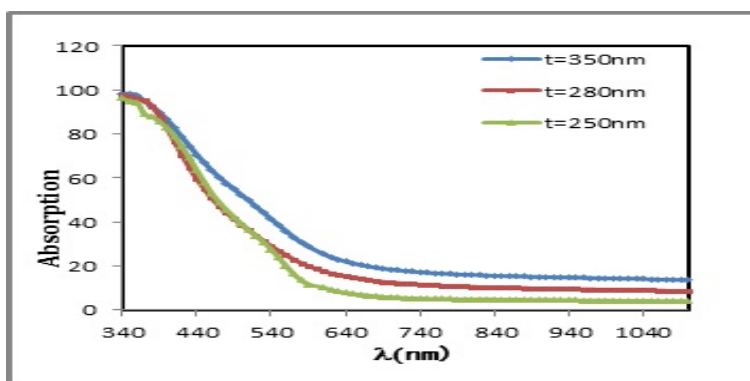


Fig.(1): Absorption spectrum as a function of wavelength for Fe_2O_3 films at different thickness

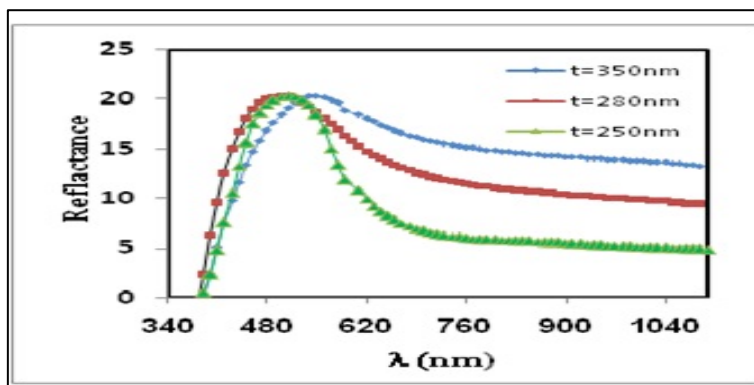


Fig.(2): Reflectance spectrum as a function of wavelength for Fe₂O₃ films at different thickness

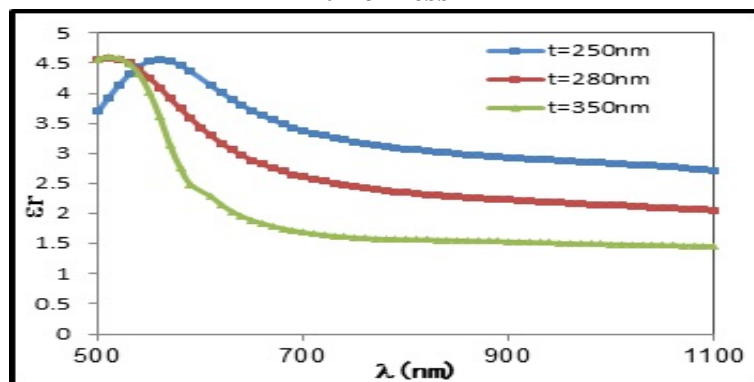


Fig. (3): Extinction coefficient as a function of wavelength for Fe₂O₃ thin films at different thickness

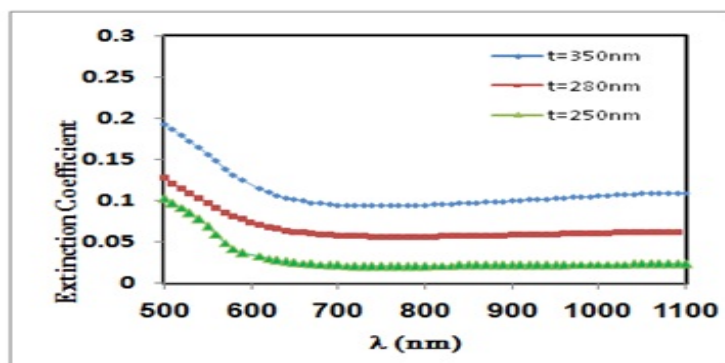


Fig.(4) Variation of ϵ_r as a function of wavelength for Fe₂O₃ films at different thickness

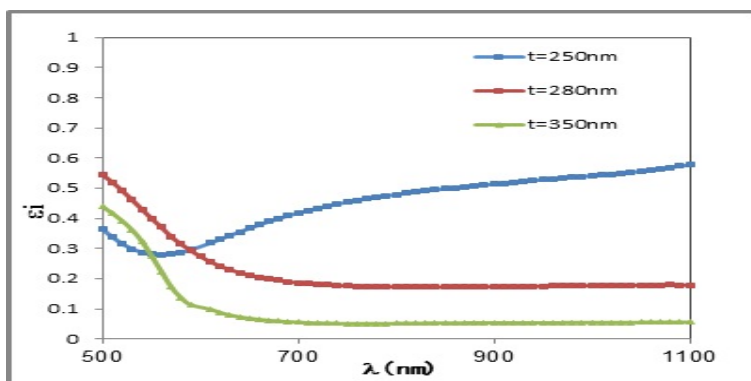


Fig.(5) Variation of ϵ_i as a function of wavelength for Fe₂O₃ films at different thickness

تأثير السمك في بعض الخواص البصرية لأغشية Fe_2O_3 الرقيقة المحضرة بطريقة التحلل الكيميائي

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الخلاصة

حضرت أغشية Fe_2O_3 الرقيقة بطريقة التحلل الكيميائي على أرضيات زجاجية وبدرجة حرارة $400^{\circ}C$ وبسمك متغير من $(250,280,350)nm$ وقيس سمك العينات المستخدمة بالطريقة الوزنية. الخواص البصرية تم تحديدها باستخدام المطياف الخاص بدراسة الخواص البصرية وللمدى من $(340-1100)nm$ كذلك درست الثوابت البصرية التي تتضمن معامل الخمود، ثابت العزل بجزئيه الحقيقي والخيالي. يحدد معامل الخمود من القياسات المباشرة للامتصاصية والانعكاسية. وتشير النتائج الى أن الثوابت البصرية للأغشية الرقيقة تقل بزيادة السمك.

الكلمات المفتاحية : ثلاثي أكسيد الحديدوز، التحلل الكيميائي، الخواص البصرية