Studying the effect of thickness' variation on some optical properties of Iron Oxide Thin Films

Reem Saadi Khaleel, Mohammad Hameed abdulla, Mustafa shakir Hashim,

Physics Department, Education College, Al-Mustansirya University , Physics Department, Science College, Diala University

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Abstract

We have studied the effect of thickness' variation on some optical properties of (Fe_2O_3)thin films deposited on preheated glass substrates at a temperature of (420 °C) by chemical pyrolysis technique. The optical transmission (T %) in the wavelength range (400-900)nm of films was measured. Optical conductivity, band tail width and skin depth are calculated and correlated with the variation of film's thickness. The change in optical properties due to scattering by acoustic or optical phonons is investigated. The carrier concentration N_{opt} was obtained using Drude's theory of dielectrics .

Introduction

Among magnetic materials, iron oxides, such as (α-Fe_2O_3) and (Fe_3O_4), are the most popular materials and possess many advantages in technological applications .

Iron oxide thin film (Fe_2O_3) can be used in several fields . (α-Fe_2O_3) is the most stable iron oxide compound material and is widely used in photoelectrodes, gas sensing, catalysts, magnetic recording, and medical fields.[1] due to its great sensitivity for flammable gases, its fast speed of response and its long-term stabilities; Photo electrochemical solar cell , due to its optical band gap, its high optical absorption coefficient; Negative electrode in rechargeable batteries. It is also used for water electrolysis in the presence of sunlight [2-3]. (α–Fe_2O_3)has been prepared by various methods such as chemical vapor deposition , sol- gel method , pulsed laser deposition , sputtering and chemical spray pyrolysis [4-8].

The aim of this work is to study the effect of thickness' variation on some optical properties of Iron Oxide thin films which was prepared by chemical pyrolysis technique.

Experimental details

Thin films of iron oxide have been prepared by chemical pyrolysis technique. The spray pyrolysis was done with a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at temperature of (420 °C) (because we obtained the best homogeneous film at this temperature),the chemical solution was achieved by adding (4.0402 gm) of ($Fe(NO_3)_3.9H_2O$) on 100 ml of deionized water , homogeneous mixture was achieved by using magnetic stirrer. The optimized conditions were the following parameters, spray time (15 sec) , average deposition (10 cm^3/min) , distance between nozzle and substrate (30 cm) and the carrier gas (filtered compressed air) was maintained at a pressure of 10^5 Nm^{-2} . Thicknesses of the samples were measured using the weighting method. Optical transmittance and absorbance were recorded in the wavelength range (300-900nm) using UV-visible spectrophotometer (Shimadzu Company Japan).

Results and discussion

In Figure (1) the optical transmittance (T%) of(Fe_2O_3) films with three thicknesses (100,300 and 500) nm are shown.

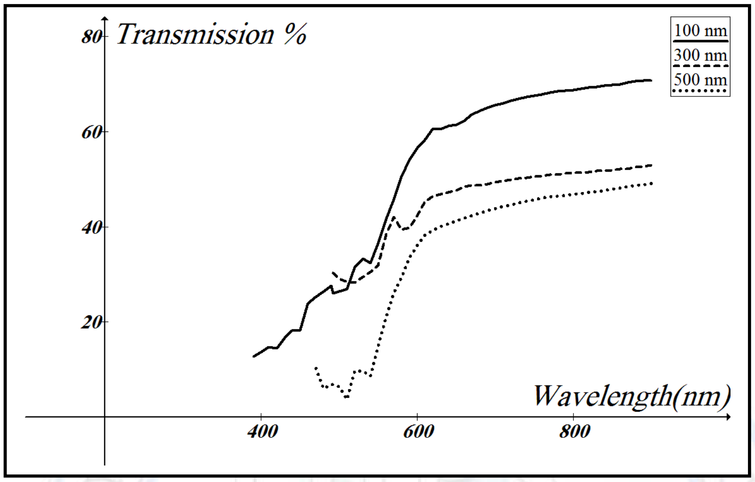


Figure (1) Transmittance against Wavelength for Fe_2O_3 thin films with different thicknesses.

The film deposited with thickness (100 nm) shows high transmittance compared to that of others; this behavior is a direct result to Lambert law. The shift in the absorption edge of thinner film clearly reveals that the (Fe_2O_3)Fe_2O_3 film with this thickness is of better quality.

It is seen that the absorption edge, which is a measure for the energy gap, is at lower wavelengths for the film with thickness (100 nm), indicating higher energy gap for it than that of the other films.[9]

The average transmittance for thinner film is approximately 70% in the region of the spectra above (600 nm), whereas for that with thickness (300 nm) and (500nm) are approximately 50% and 45% respectively.

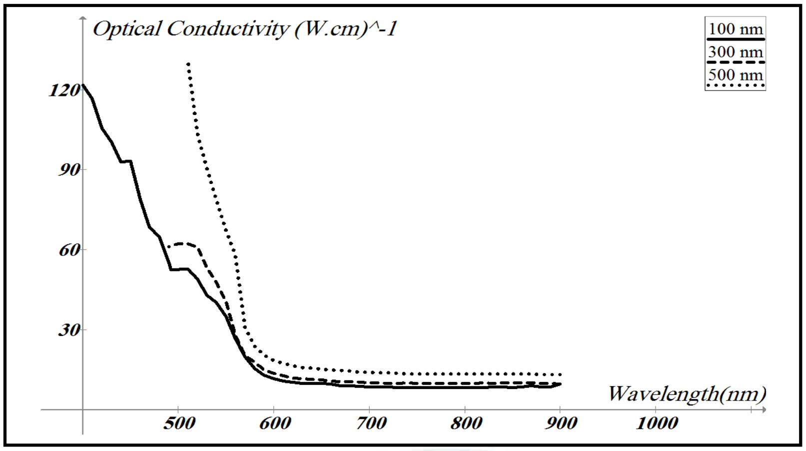


Fig. (2) Optical conductivity of Fe_2O_3 at different thicknesses .

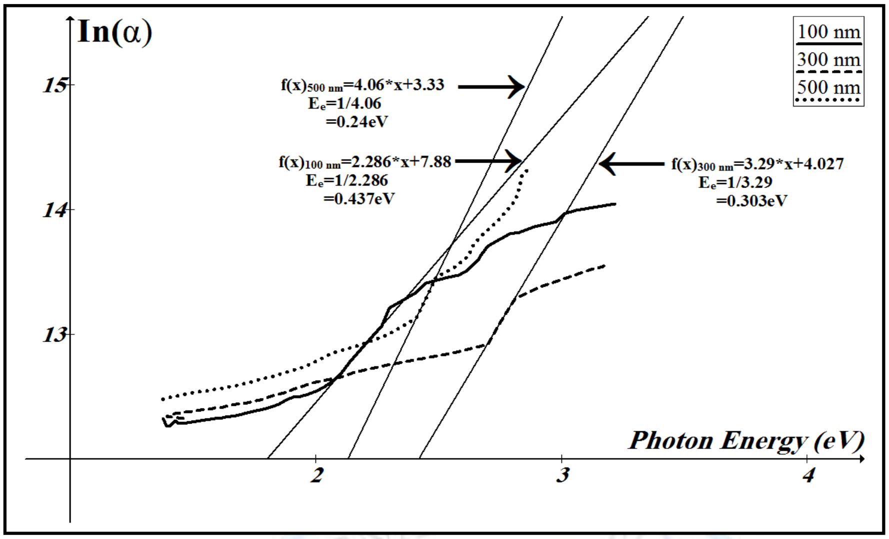
The optical conductivity (σ) of the films depends directly on the wavelength (λ) and absorption coefficient (α^2). With the aid of the Drude formula [10] :

$$\sigma = [\ \alpha^2 c\, \varepsilon_o \lambda / 4\pi\ ]$$

Figure (2) shows the variation of optical conductivity as a function of wavelength for different thicknesses. From the curves one can conclude:

• All curves show saturation in optical conductivity at visible spectrum.

• Under cut-off wavelength, high absorption of thin film behavior is due to the photon-atom interaction leading to higher carrier concentration. This effect increases the optical conductivity. [11]. Optical conductivity depends directly on the absorption coefficient (α^2) which depend inversely on the thickness of the films ,so optical conductivity decreases with increasing thickness.



Figure(3) Relation between lnα and photon energy for Fe_2O_3 films deposited with different thicknesses.

The absorption coefficient α(f) in the low energy range follows the well known exponential law, i.e. the Urbach law tail which it is expressed by:[12]

$$\alpha(f) = \alpha_\eta \exp(\hbar f/E_e)$$

where E_e is interpreted as the width of the localized states in the band gap. E_e is estimated from the inverse slope of the linear plot between ln(α) vs. hf (eV) as in Figure(3) . One can observe decreasing of band tail width with thickness' increasing ($E_{e(100\ nm)}$=0.437 eV , $E_{e(300\ nm)}$=0.303 eV, $E_{e(500\ nm)}$=0.24 eV); this might due to decrease dangling bonds, defects and the trapping of the generated carriers as a result of increasing thickness. The increasing of thickness increases the homogeneity of the films and decreases the valleys which represented the source of dangling bonds and the defects.

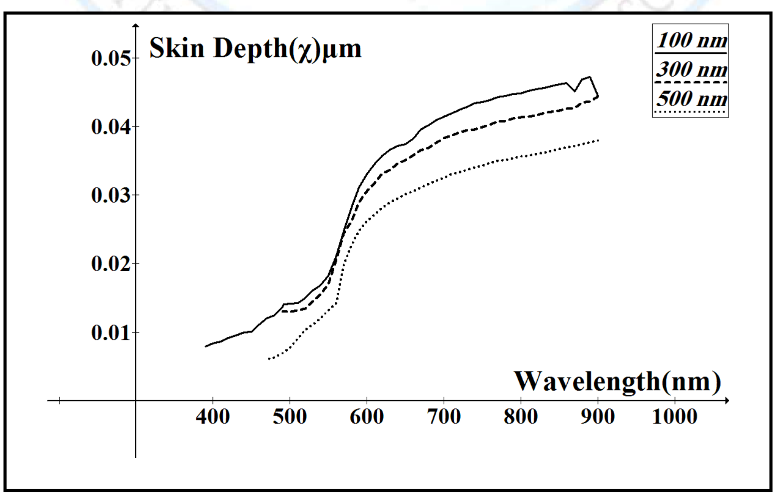


Figure (4) Skin Depth vs. Wavelength.

The electromagnetic wave will have amplitude reduced by a factor 'e' after traversing a thickness (called the skin depth) [13]. This skin depth is usually denoted by χ:

$$\chi = 1 / \alpha$$

Figure (4) shows skin depth as a function of wavelength , as wavelength increases , skin depth increases with thickness' increasing , this might be due to decrease the probability of absorption with thickness' increasing and the amplitude of the incident photons will be reduced by a factor 'e' through the short distance within the film thickness .[11].

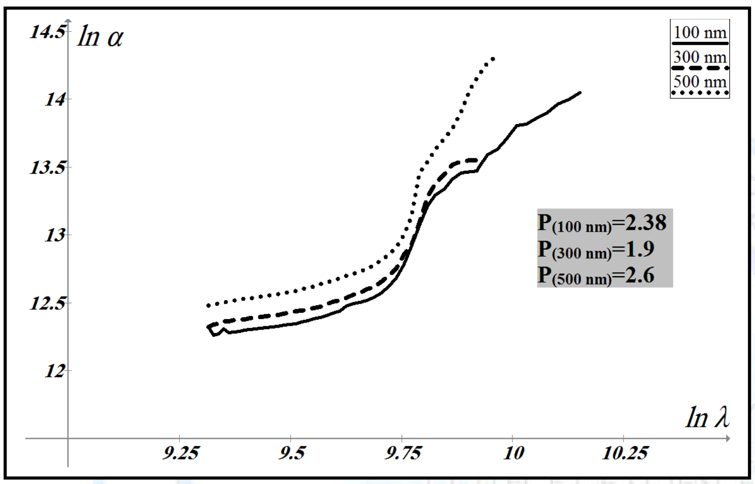


Figure (5) Photon scattering with the semiconductor lattice

Absorption due to free carriers is commonly written as $\alpha = k\,\lambda^{p}$, where k is proportional constant , the index *p* depends primarily on the scattering mechanism . In the case of lattice scattering one has to consider scattering from acoustic and optical phonons. For acoustic phonon scattering, $p \approx 1.5$; for optical phonon scattering, $p \approx 2.5$; and for impurity scattering, $p \approx 3.5$. Accordingly, the observed free-carrier absorption coefficient will then have all three contributions, as [14]

$$\alpha = A\lambda^{1.5} + B\lambda^{2.5} + C\lambda^{3.5}$$

where A,B,C are constants .

The variation of ln(λ) and ln(α) is shown in figure (5) , the slope is the value of (P) . It is clear from the values of P that the scattering in films with thicknesses (100 nm and 500 nm) is due to optical phonon , but it's due to acoustic phonons in the film with thickness (300 nm).

The carrier concentration N_{opt} can be obtained using Drude's theory of dielectrics, using the following equation[15].

The real dielectric constant ε', which results due to the contribution from the free carrier electric susceptibility, can be written by the following relation

$$\varepsilon' = \varepsilon_i - [(e^2/4\pi^2 c^2 \varepsilon_0)(N/m^*)]\lambda^2$$

where ε' is real part of dielectric constant , ε_i is the residual dielectric constant due to the ion core , e is the electronic charge, c is the velocity of light, ε_o is the permittivity of free space ($\varepsilon_0 = 8.85 \times 10^{-12}$ C/N.m^2) and N/m* is the ratio of carrier concentration to the effective mass ($m^* = 9.10956 \times 10^{-31}$ kg). According to the free electron Drude model [16], ε_1 should be a linear function of λ^2 as it shown in figure (8).

The values of carrier concentration N_{opt} for the three films are

{ $N_{opt(100\ nm)} = 3.28*10^{28}$ m^{-3} , $N_{opt(300\ nm)} = 0.95*10^{28}$ m^{-3}, $N_{opt(500\ nm)} = 2.16*10^{28}$ m^{-3}}.This variation might be attributed to the existence of trapping centers which have not equal numbers in three films due to cleaning processes before the deposition.

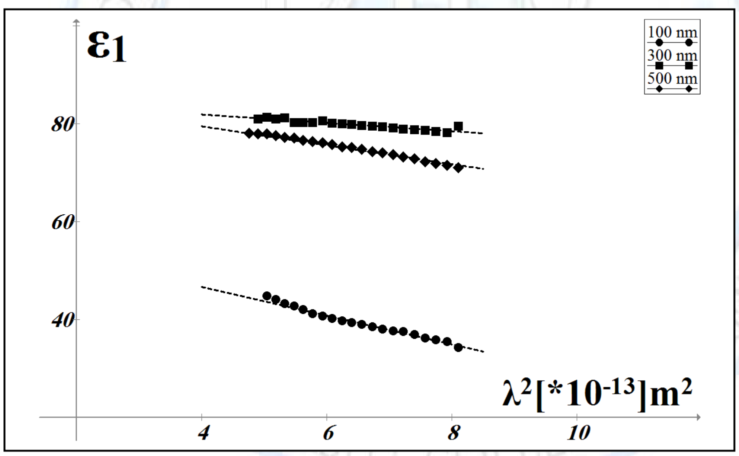


Figure (8) dielectric constant vs. $(\lambda)^2$ for Fe_2O_3 thin films.

Conclusions

Optical transmittance (T %) of (Fe_2O_3) films decreases with thickness' increasing from approximately 70% to 45% in the region of the spectra above (600 nm). All curves show saturation in optical conductivity at visible spectrum. There is a decreasing in band tail width with thickness' increasing. As wavelength increases, skin depth increases with thickness' increasing. Scattering in films with thicknesses (100 nm and 500 nm) is due to optical phonon, but it's due to acoustic phonons in the film with thickness (300 nm). The values of carrier concentration N_{opt} for the three films are{ $N_{opt(100\ nm)}=3.28*10^{28}\ m^{-3}$, $N_{opt(300\ nm)}=0.95*10^{28}\ m^{-3}$, $N_{opt(500\ nm)}=2.16*10^{28}\ m^{-3}$}.

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