

## Study the Effect of Thickness on the Electrical Conductivity and Optical Constant of $\text{Co}_3\text{O}_4$ Thin Films

**Bushra K. H. Al-Maiyaly**

Dept. of Physics/College of Education For Pure Science(Ibn Al-Haitham) /  
University of Baghdad

**Received in: 1 April 2012 , Accepted in: 21 May 2012**

### Abstract

In this research the Cobalt Oxide ( $\text{Co}_3\text{O}_4$ ) films are prepared by the method of chemical spray pyrolysis deposition at different thicknesses such that  $(250, 350, 450, \text{ and } 550) \pm 20$  nm.

The optical measurement shows that the  $\text{Co}_3\text{O}_4$  films have a direct energy gap, and they in general increase with the increase of the thickness. The optical constants are investigated and calculated such as absorption coefficient, refractive index, extinction coefficient and the dielectric constants for the wavelengths in the range (300-900) nm.

The electrical conductivity ( $\sigma$ ) and the activation energies ( $E_{a1}, E_{a2}$ ) have been investigated on ( $\text{Co}_3\text{O}_4$ ) thin films as a function of thickness. The films contain two types of transport mechanisms, and the electrical conductivity ( $\sigma$ ) increases whereas the activation energy ( $E_a$ ) would decrease as the films thickness increases.

**Key words** :Cobalt Oxide, Optical Constant, Electrical Conductivity, chemical spray pyrolysis

## Introduction

A glass with a Co or Fe oxide film on its surface is generally called a semi-reflective glass, because it partially reflects the solar spectrum. The glass reflects solar energy which reduces the cost of air-conditioning. In recent years the glass has become of interest with the rise in the cost of energy. The oxide films, mainly composed of Co, are widely employed for semi-reflective glasses, not only because of their energy saving effect but also because of their good durability as a glazing of building. [1]

Cobalt Oxide films that are highly protective against localized corrosion and depicting a wide variety of bright and uniform colors due to light interference, have been successfully electro generated on polycrystalline cobalt disk electrodes under potentiostatic. [2] Several methods have been developed for  $(\text{Co}_3\text{O}_4)$  films preparation, such as sputtering pyrolysis [3, 4], chemical vapor deposition [5], electro deposition [6, 7], pulsed laser deposition [8], electro chemical techniques [9], etc. In this research thermal chemical spray technique was used.

Experiment

### a-Preparation of the samples

Cobalt Oxide ( $\text{Co}_3\text{O}_4$ ) thin films in molarity (0.1) at different thicknesses were prepared by the method of chemical spray pyrolysis. They are prepared by spraying a solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  on preheated glass substrates at (663) °K.

A diluted (2.9104) gm of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in (100) ml water as molarity (0.1) was used in accordance with the following equation: [10]

$$M = (W_t / M_{wt}) \cdot (1000 / V) \dots\dots\dots (1)$$

Where M = molarity,  $W_t$  = weight of sample,  $M_{wt}$  = molecular weight, V = water volume.

The obtained solution is used for the preparation of  $(\text{Co}_3\text{O}_4)$  based on the reaction:-



The thin films of  $\text{Co}_3\text{O}_4$  are prepared by spraying the solution on glass substrates which are placed on the hot plate for 25 min before the spraying process; each spraying period lasts for about 15 sec followed by 2 min waiting period to avoid excessive cooling of the hot substrate due to the spraying process. It has been found that the following deposition parameters give good stoichiometric films:-(i) substrate temperature at (663) °K, (ii) distance between sprayer nozzle and substrate of (30) cm, (iii) spray rate of (15 ml / min). The films were clear, dark colored and having good adhesive properties .

### b-Measurement

The thickness of the sprayed samples (250, 350, 450, and 550) nm was measured by using the weighing method according to the following relation: [11]

$$t = (m / \rho \cdot A) \dots\dots\dots (3)$$

Where t= thickness of film, m= mass of film,  $\rho$ = density of films, A= area of film. Using a sensitive balance whose sensitivity is of the order ( $10^{-4}$ ) gm.

To determine the optical parameters of the prepared thin film, we measured the transmission and the absorption spectrum in the range (200-900) nm using a double beam spectrophotometer (UV).

The optical absorption spectrum used to determine the optical energy gap ( $E_g^{opt}$ ) from the calculation of the variable absorption coefficient ( $\alpha$ ) for each wavelength from equation: [12]

$$\alpha = 2.303 (A / t) \dots\dots\dots (4)$$

Where A = absorbance.

Also incident photon energy ( $E=h\nu$ ) was calculated as a function of wavelength ( $\lambda$ ) according to equation:

$$E (\text{eV}) = (1240 / \lambda) \dots\dots\dots (5)$$

The energy dependence of absorption coefficient near the band edge for band to band and exciton transition could be described by Tauc formulas: [13]

$$(\alpha h\nu) = B (h\nu - E_g^{opt})^r \dots\dots\dots (6)$$

Where  $B'$  is a constant inversely proportional to amorphousity,  $r$  is constant and may take values 2,3,1/2,3/2 depending on the material and the type of the optical transition.

The optical constants including, the refractive index ( $n$ ), extinction coefficient ( $K$ ), and dielectric constant ( $\epsilon$ ), they are calculated from transmittance ( $T$ ) and absorbance ( $A$ ) spectrum in the range (200-900) nm.

The refractive index value can be calculated from the formula: [14]

$$n = \{ [4R / (R-1)] - K^2 \}^{1/2} - [(R+1) / (R-1)] \dots \dots \dots (7)$$

Where  $R$  is the reflectance which calculated by using equation:

$$R = 1 - T - A \dots \dots \dots (8)$$

The absorption coefficient ( $\alpha$ ) is related to extinction coefficient ( $K$ ) by: [14]

$$\alpha = 4\pi K / \lambda \dots \dots \dots (9)$$

The dielectric constant can be introduced by: [14]

$$\epsilon = \epsilon_1 - i \epsilon_2 \dots \dots \dots (10)$$

Where  $\epsilon_1 = n^2 - K^2 \dots \dots \dots (11)$

$$\epsilon_2 = 2nK \dots \dots \dots (12)$$

Where  $\epsilon_1$  = real part of dielectric constant,  $\epsilon_2$  = imaginary part of dielectric constant.

For D.C. measurement films deposited on the glass substrate with Al electrode Keithly models 616 have been used to measure the variation of electric resistance ( $R$ ) with temperature range (298- 473) °K, then calculated the resistivity ( $\rho$ ) by the formula: - [14]

$$\rho = \frac{R \cdot b \cdot t}{L} \dots \dots \dots (13)$$

Where  $t$  is film thickness,  $b$  is electrodes width;  $L$  is distance between two Al electrodes.

Then the conductivity ( $\sigma$ ) of the films was determined by using the relation:-

$$\sigma_{d.c} = \frac{1}{\rho} \dots \dots \dots (14)$$

## Results and Discussion

### a -Absorption Coefficient

Fig (1) shows the variation of the absorption coefficient ( $\alpha$ ) of ( $\text{Co}_3\text{O}_4$ ) films as a function of photon energy at various thicknesses (250, 350, 450, and 550) nm. It is observed that the absorption coefficient decreases the increase of thickness ( $t$ ) within the whole range of the spectrum; it is noticed that the absorption is not attributed to the free carriers only, but to impurities or localized electronic states. It is clear from this figure that all the films have high values of absorption coefficient ( $\alpha > 10^5 \text{ cm}^{-1}$ ) this means that the direct transition possible occurs. This result is in agreement with refs. [3, 15].

### b- Optical Energy Gap

The optical energy gap ( $E_g^{\text{opt}}$ ) values were calculated from Tauc equation (6) which is used to find the type of the optical transition for ( $\text{Co}_3\text{O}_4$ ) films by plotting the relation  $(\alpha \text{ hv})^2$  versus photon energy ( $\text{hv}$ ) and select the optimum linear part, which describes the allowed direct transition, then we determined  $E_g^{\text{opt}}$  by the extrapolation of the portion at ( $\alpha = 0$ ) as shown in Fig (2). Fig (3) and table (1) show the optical energy gap as a function of thickness ( $t$ ), the noticeable remark is that the  $E_g^{\text{opt}}$  increased from (1.78 eV) to (2.1 eV) when the thickness increased. This behavior can be attributed to the increase of the density of localize states in the  $E_g$  which caused the energy gap seems large. The value of the optical energy gap agrees with ref. [4] which found it equals to (2.1 eV).

### c- Refractive Index

Fig (4) shows the variation of the refractive index values ( $n$ ) versus wavelengths in the range (300-900) nm, at different thicknesses (250, 350, 450, and 550) nm. We can notice from

this figure that the refractive index values increase with the increase of thickness, this behavior may be due to increase in packing density.[2]

The values of the refractive index of these films range from (2.69 to 3.38) at  $\lambda = 625$  nm, are in a good agreement with values reported in ref. [2]

#### d- Extinction Coefficient

The variation of the extinction coefficient (K) with photon energy for various thickness is shown in Fig (5), from this figure we can notice that the extinction coefficient values decrease with the increase of thickness, this behavior of the extinction coefficient values is similar for all the range of the wavelength spectrum to that of the absorption coefficients for the same reasons as we mentioned before.

#### e- The Dielectric Constants

Fig 6 (a, b) shows the variation of the real ( $\epsilon_1$ ) and imaginary ( $\epsilon_2$ ) parts of the dielectric constant values versus photon energy at different thicknesses.

From this figure we can deduce that the imaginary part of the dielectric constant ( $\epsilon_2$ ) decrease with the increase of thickness in all of the range of the spectrum while the real part of the dielectric constant ( $\epsilon_1$ ) increases with the increase of thickness because the variation of ( $\epsilon_1$ ) mainly depend on the value of the refractive index while the ( $\epsilon_2$ ) value mainly depend on the extinction coefficient values which are related to the variation of absorption coefficient.

#### f- D.C Conductivity

The plots of  $\ln\sigma$  versus  $10^3/T$  at different thicknesses for ( $\text{Co}_3\text{O}_4$ ) films are shown in Fig (7), the electrical conductivity ( $\sigma$ ) shows an increase behavior with the increase of (t). It is increased from (0.527)  $\text{ohm}^{-1}.\text{cm}^{-1}$  to (0.82)  $\text{ohm}^{-1}.\text{cm}^{-1}$ . This behavior is in an agreement with ref. [3]. The increase of trend in  $\sigma$  upon increase thickness can be attributed to the improvement in the films structure with the increase of (t), due to reducing dangling bonds, and defects like vacancy sites. We believe that the increases of film thickness (t) decreases the trapping centers of charge carriers, this is, perhaps, because of the decreased grain boundary scattering, moreover it yields more packing density. This figure also shows two mechanisms for electrical conductivity at lower and higher temperature with two values of activation energy ( $E_{a1}$ ,  $E_{a2}$ ) for all films, which means that there are two mechanisms of transport. Fig (8) shows the activation energies ( $E_{a1}$ ,  $E_{a2}$ ) of ( $\text{Co}_3\text{O}_4$ ) films as a function of thickness, it is clear from this figure that both  $E_{a1}$  and  $E_{a2}$  decrease with the increase of thickness (t) because of the decreased number of carriers available for transport, this behavior can be attributed to the decrease of the density of states in the gap, reducing of dangling bonds, and defects like vacancy sites in the films structure.

Table (2) shows the values of the electrical conductivity and the activation energies of deposited films.

## Conclusion

In conclusion, we studied in detail the influence of film thickness on the optical constant of ( $\text{Co}_3\text{O}_4$ ) films. Throughout our research we showed that:-

1. The absorption coefficient decreases with the increase of the thickness of prepared thin films.
2. All films prepared have high values of absorption coefficient ( $\alpha > 10^5 \text{ cm}^{-1}$ )  
We can use ( $\text{Co}_3\text{O}_4$ ) films as a window for wavelength ( $\lambda > 625$  nm) and as Filter for wavelength ( $\lambda < 625$  nm).
3. The optical energy gap values increases when films thickness increases.
4. The variation in films thickness resulted increase values of refractive index and decrease the extinction coefficient values.
5. The values of real part of the dielectric constant increase while the imaginary part of the dielectric constant decrease with the increase of films thickness.

6. The electrical conductivity shows as the increase of behavior with the increase of thickness, whereas the activation energies decrease as the thickness increases.

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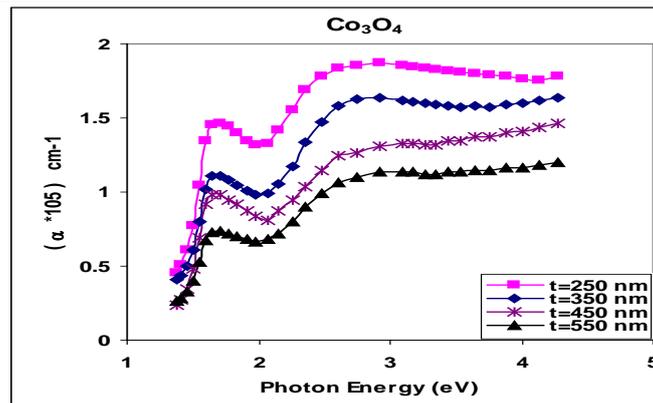
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**Table (1): The optical constant of (Co<sub>3</sub>O<sub>4</sub>) films at different thicknesses.**

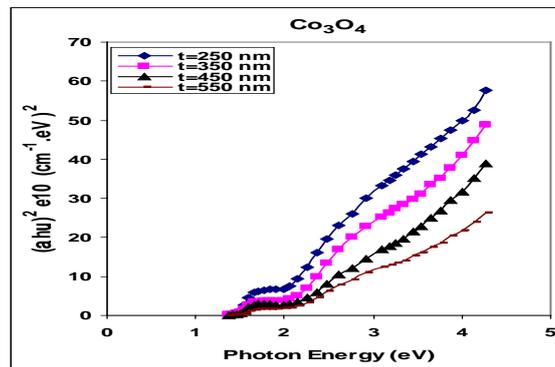
Films thickness (nm)	E <sub>g</sub> <sup>opt</sup> (eV)	Optical constant at λ =625 nm				
		α x 10 <sup>5</sup> cm <sup>-1</sup>	n	k	ε <sub>1</sub>	ε <sub>2</sub>
250	1.78	1.316	2.69	0.655	6.819	3.528
350	1.84	0.9808	2.82	0.488	7.72	2.75
450	1.96	0.838	3.09	0.417	9.41	2.58
550	2.1	0.666	3.38	0.331	11.32	2.24

**Table (2): The electrical conductivity and activation energies of (Co<sub>3</sub>O<sub>4</sub>) films at different thicknesses**

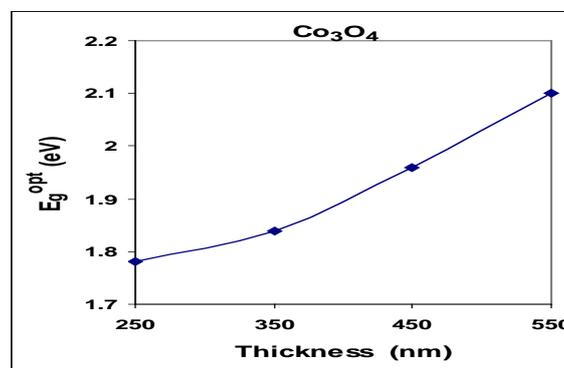
Films thickness (nm)	$\sigma$ at R.T ( $\Omega.cm$ ) <sup>-1</sup>	Ea <sub>1</sub> (eV)	Tem. rang (°K)	Ea <sub>2</sub> (eV)	Tem. rang (°K)
250	0.526	0.0985	303-363	0.254	373-473
350	0.625	0.0934	303-363	0.232	373-473
450	0.724	0.0897	303-363	0.204	373-473
550	0.82	0.0845	303-363	0.175	373-473



**Fig. (1): Absorption coefficient behavior as a function of photon energy for (Co<sub>3</sub>O<sub>4</sub>) thin films deposited at different thicknesses.**



**Fig. (2): Variation  $(\alpha hv)^2$  & photon energy as a function of thickness for (Co<sub>3</sub>O<sub>4</sub>) films.**



**Fig. (3) : Variation optical energy gap as a function of thickness for (Co<sub>3</sub>O<sub>4</sub>) films**

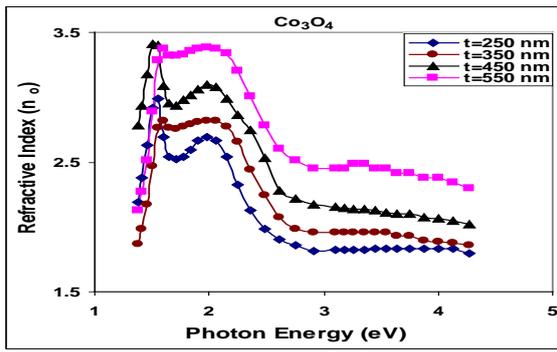


Fig. (4): Variation refractive index & photon Energy as a function of thickness for  $(Co_3O_4)$  films

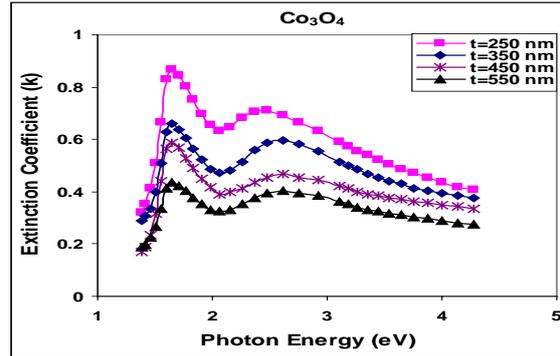
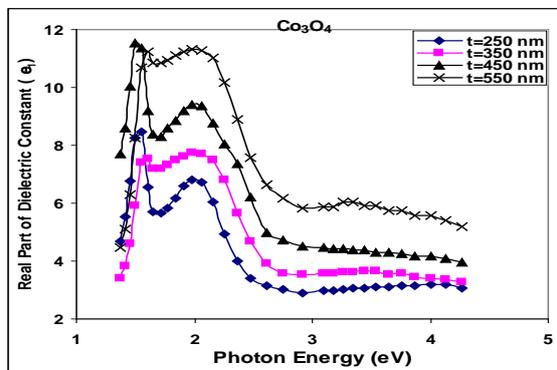
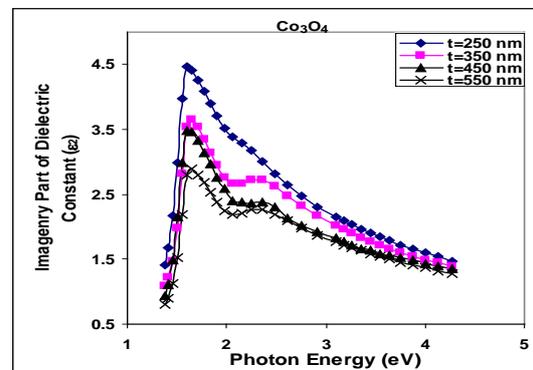


Fig. (5): Variation extinction coefficient & photon Energy as a function of thickness for  $(Co_3O_4)$  films



(a)



(b)

Fig. (6): Dielectric constant of  $(Co_3O_4)$  thin films & photon energy:-  
(a) Real part at different thicknesses. (b) Imaginary part at different thicknesses.

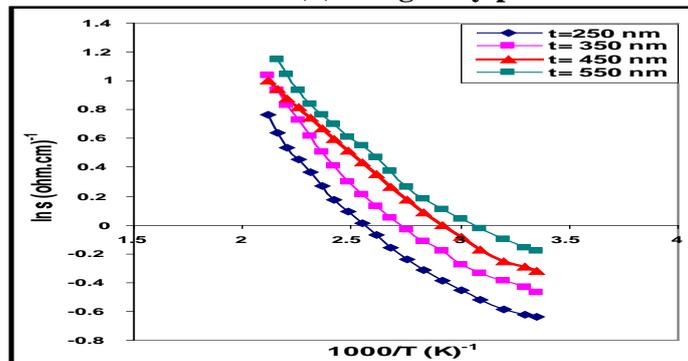


Fig. (7): Variation  $\ln \sigma$  versus  $10^3/T$  as a function of thickness for  $(Co_3O_4)$  films

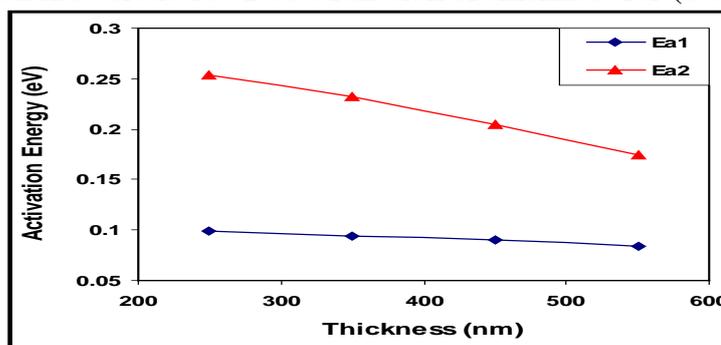


Fig. (8): Variation activation energies as a function of thickness for  $(Co_3O_4)$  films.

## دراسة تأثير السمك في التوصيلية الكهربائية والثوابت البصرية لأغشية الرقيقة $\text{Co}_3\text{O}_4$

بشرى كاظم حسون الميالي

قسم علوم الفيزياء / كلية التربية للعلوم الصرفة (أبن الهيثم) / جامعة بغداد

أستلم البحث في : 1 نيسان 2012 ، قبل البحث في 21 أيار 2012

### الخلاصة

في هذا البحث حضرت أغشية أكسيد الكوبلت ( $\text{Co}_3\text{O}_4$ ) بطريقة الرش الكيميائي الحراري وعند أسماك مختلفة من خلال القياسات البصرية تبين ان لأغشية ( $\text{Co}_3\text{O}_4$ ) فجوة طاقة مباشرة وتزداد قيمتها بصورة عامة بزيادة السمك. ولقد حسبت الثوابت البصرية، مثل: معامل الامتصاص، ومعامل الخمود، وثابت العزل الكهربائي ضمن مدى الاطوال الموجية (300-900) nm. وحسبت التوصيلية الكهربائية ( $\sigma$ ) وطاقات التنشيط ( $E_{a1}, E_{a2}$ ) لأغشية ( $\text{Co}_3\text{O}_4$ ) كدالة لتغير السمك ، وقد أظهرت الاغشية أليتين للانتقال الالكتروني ولوحظ زيادة التوصيلية الكهربائية مع نقصان طاقات التنشيط بزيادة سمك الاغشية المحضرة.

**الكلمات المفتاحية :** أكسيد الكوبلت ، الثوابت البصرية، التوصيلية الكهربائية ، الرش الكيميائي الحراري .