Studying the optical properties of (Cr_2O_3:I) thin films prepared by spray pyrolysis technique

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Abstract

Undoped and Iodine (I)–doped chrome oxide (Cr_2O_3)thin films have been prepared by chemical spray pyrolysis technique at substrate temperatures(773K) on glass substrate. Absorbance and transmittance spectra have been recorded as a function of wavelength in the range (340-800 nm) in order to study the optical properties such as reflectance, Energy gap of allowed direct transition, extinction coefficient refractive index, and dielectric constant in real and imagery parts all as a function of wavelength. It was found that all the investigated parameters affect by the doping ratios.

Key words

Cr_2O_3 thin film, optical properties of Cr_2O_3, spray pyrolysis.

Article info

Received: Sep. 2010

Accepted: May. 2011

Published: May. 2012

دراسة الخصائص البصرية للاغشية الرقيقة (Cr_2O_3:I) المحضرة بطريقة الرش الكيميائي الحراري

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الخلاصة

حضرت أغشية رقيقة من اوكسيد الكروم المشوبة باليود باستخدام تقنية الرش الكيميائي الحراري عند درجة حرارة القاعدة (773K). سجل طيف الامتصاصية والنفاذية كدالة للطول الموجي ضمن المدى(340nm-800) وذلك لغرض دراسة الخواص البصرية المتمثلة بالانعكاسية، فجوة الطاقة للانتقال المباشر المسموح ، معامل الخمود، ومعامل الانكسار،ثابت العزل بجزئه الحقيقي والخيالي. لقد وجد بأن جميع المعلمات قيد الدراسة قد تأثرت بنسب التطعيم.

Introduction

Chromium oxide Cr_2O_3 thin films are of great interest due to their wide variety of technological applications. This oxide exhibit high hardness and high wear with corrosion resistance which are important properties for protective coating applications[1], it has already found several applications as protective coatings on read–write heads in digital magnetic recording units and in gas-bearing applications, It has been studied for optical and electronic uses such as selectively absorbing films for solar energy conversion, solar energy shielding films for windows, and electrode material for electro chromic windows [2]. The most stable phase is the corundum structured Cr_2O_3. This form of oxide has important industrial applications, for instance in catalysis and solar thermal energy collectors. Chromium oxide is an insulating antiferromagnetic material it is also suitable as a tunnel junction barrier [3]. On the other hand, despite its intrinsic insulator nature, Cr_2O_3 films can either p-type or n-type as semiconductor behaviors, depending on the growth present either p-type or n-type semiconductor behaviors, depending on the growth conditions. The confluence of all these properties in a single material makes Cr_2O_3 a key material for the development of a broad range of industrial applications [4]. In this research we are intend to improve the optical properties of Cr_2O_3 component by doping with different ratio of Iodine (I).

The aim of research is to study the optical properties of Cr_2O_3 thin film and improve its optical properties by doping the component with different ratios of Iodine(I).

Experimental work

The method of chemical spray pyrolysis utilized in this paper to prepare thin films of Chromium oxide (Cr_2O_3). The subsequent reaction on the heated substrates produces the Cr_2O_3 thin films products. By using the chromium chlorine hydrate ($CrCl_3.6H_2O$) as a powder material with blue green color and its equivalent weight (88.816) and purity 97% to produce thin films of chromium oxide, prepare the solution of chromium chlorine hydrate with Concentration (0.1M) by solute (0.888816 gm) from the material in (100ml) of water in order to arrive the perfect solution use the Magnetic stirrer. The following relation used to get the weight of solution within the above molarty:

$$M = (W_t / M_{wt}) .(1000/V) \quad (1)$$

M: concentration molarty . W_t: volume of water. V: weight of solution.,

M_{wt}: molecular weight of ($CrCl_3.6H_2O$) material

After the solution is cooling locate in the spray system to spray on the glass substrate at (773K) we can get the (Cr_2O_3) thin films according to the chemical equation :

$$2Cr\,Cl_3 + 2H_2O \xrightarrow{\text{Heat}} Cr_2O_3 + 6HCl$$

to prepare thin films of Chromium oxide (Cr_2O_3) doped with 3% and 5% of Iodine (I) used the NH_4I material its molecular weight(144.95gm) and with concentration (0.1M) by solute (1.4495 gm)from the material in (100ml) of water in order to arrive the perfect solution use the Magnetic stirrer.

$$NH_4I \rightarrow NH_3 + HI$$

It has been found that the following deposition parameters give films at:

(1) Substrate Temperatures are 773k

(2) Spray rate 10 cm^3/min.

(3) Distance between sprayer nozzle and substrate of 30 $\pm$ 1 cm.

The glass substrates are placed on the hot plate fan about (30) min before spraying process, so the glass substrates are nearly at the same temperature as the hot plate. Each spraying period lasts for about (15 s) followed by about (5) min waiting period to avoid excessive cooling of the hot substrates due to the spraying. The samples thickness was measured using the weighing method. The samples thickness was in the range (2000 $\pm$ 20A°). The Absorbance and transmittance spectrum were recorded for wavelengths interval in the regions (340-800) nm by using (UV-1650 PC, Shimadzu spectrophotometer).

Results and Discussions

1-Reflectance(R) and Transmittance (T)

The Reflectance calculated from the spectrum of absorption (A) and transmission (T) According to the law of energy conversation [5].

$$R + T + A = 1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

The Absorbance, Transmittance and Reflectance spectra of the films are shown in Fig. (1-a), (1-b) and (1-c) respectively. The doping and incorporation Cr_2O_3 thin films by Iodine (I) increases the Absorbance with increase the ratio of doping in the visible region due to increase the donor state levels; therefore it is clear from Fig. (1-b) and (1-c) and according to equation (3) the

Transmittance and Reflectance are decrease in the this region, this mean the band gab is decrease due to increase the donor state levels by processing of doping.

2-Absorption Coefficient (α) and optical energy band gab (E_g)

Absorption Coefficient (α) represents the ration of decreasing in intensity of radiation Through the material by following relation[6]:

$$\alpha = \frac{1}{t}\ln\frac{1}{T} \quad (4)$$

where:

(t) is the thickness of the thin film, and (T) is the transmittance.

Fig. (2) shows the Absorption coefficient against wavelength for the undoped and I–doped (Cr_2O_3) thin films, The samples show a high coefficient of absorption ($\alpha > 10^5$ cm^{-1} for λ< 400 nm) and (10^4 cm^{-1} for λ> 400 nm) , the values of Absorption coefficient (α) increases with increasing photon energy and as shown the Absorption coefficient increase with increase the ration of doping(Cr_2O_3) thin film with Iodine (I), this behavior of Absorption coefficient due to increases the Absorbance with increase the ratio of doping where the band gab decrease, because the increase the donor state levels by processing of doping.

As direct band gap semiconductors, the incident photon energy (h*v*), absorption coefficient (α), and optical energy gap (E_g) are related by the following relation [7]:

$$h\nu\alpha = A^{-}(h\nu - E_g)^n \quad (5)$$

It was found that n=1/2 is the best fit for our result (allowed direct transition) get:

$$(h\nu\alpha)^2 = A^{-}(h\alpha - E_g) \quad (6)$$

where (A^{-}) is a constant.

The variation of $(\alpha h v)^2$ versus photon energy for the undoped and I–doped (Cr_2O_3) thin films are plotted in Fig. (3) to determine the optical gap. The optical band gap (E_g) can be evaluated by extrapolation of the liner part to be (3.30eV, 3.23eV, and 3.14eV) for pure (Cr_2O_3) and with ratio 3% and 5% I–doped (Cr_2O_3) respectively. It is clear that the increase in ratio of doping increase the Absorption coefficient which leads to decrease the optical band gap, this effect is frequently observed in n–type semiconductors. The increase of carrier concentration in doped thin film will cause the Fermi level to move into the conduction band.

2-Extinction Coefficient (*k_o*)

Extinction Coefficient is the absorption energy in the thin film and it also represent the imaginary part of refraction index according to the relation [7]:

$$n = \frac{c}{v} = n_0 - ik_0 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

where:

(v) Is the velocity of light in the thin film,

(c) is the velocity of light in the vacuum and

(n_o) is the real part of refractions index.

Also the extinction coefficient is related to absorption coefficient (α) by the relation [8]:

$$k_0 = \frac{\alpha\lambda}{4\pi} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(8)$$

where the wavelength (λ) in cm unit if absorption coefficient (α) in (1/cm).

From above relation the extinction coefficient is calculated. Fig (4) show the extinction coefficient (k_o) against wavelength for the undoped and I–doped (Cr_2O_3) thin films, it is seen that the Extinction coefficient (k_o) increases with increase the ratio of doping ratio than other pure (Cr_2O_3), The behavior of extinction coefficient (k_o) is like the behavior of absorption coefficient (α) according to the equation (5).

3-Refractive Index (n_o)

Refractive index associated with the reflectance of thin film by the relation [9]:

$$n_0 = \left[\left(\frac{1+R}{1-R} \right)^2 - (k^2{}_0 + 1) \right]^{\frac{1}{2}} + \frac{1+R}{1-R} \text{..............(9)}$$

From above relation the Refractive index (n_o) are calculated.

As shown in the Fig (5) the Refractive index against wavelength for the undoped and I–doped (Cr_2O_3) thin films, the behavior of Refractive index is like the reflectance (R) according to equation(9). as shown in the Fig (5)the increasing of doping ratio lead to decrease the refractive index.

4-The Dielectric Constant (ε)

The reaction between the light and the charges of medium occur by presses of the absorption of energy in material and that lead to polarized of the medium's charges, this polarization decrypted by the complex dielectric constant for the medium by the relation[10]:

$$\varepsilon = \varepsilon_r - i\varepsilon_i \qquad (10)$$

where:

ε_r is the real part of the dielectric constan.

ε_i is the imaginary part of the dielectric constant

$$\varepsilon_r - i\varepsilon_i = (n_0 - ik_0)^2 \qquad (11)$$

From the last relation the real and imaginary parts of the dielectric constant are calculated as following:

$$\varepsilon_r = n_0^2 - k_0^2 \qquad (12)$$

$$\varepsilon_i = 2n_0k_0 \qquad (13)$$

Figures (6) and (7) show the dielectric constant against wavelength for the undoped and I–doped **(**Cr_2O_3**)** thin films for real and imaginary parts respectively, Where real part (ε_r) is the normal dielectric constant which represents the amount of actual saving of electrical energy and the imaginary part (ε_i) represents the absorption losing associated with free carriers two parts of complex dielectric constant were calculated using the equations (12 and 13). The curves for both parts are found to be oscillatory in nature depending upon the crystal structure and the thickness of the film [11]. Where the values of real part undergoes rising and falling and its behavior is similar to the behavior of refractive index(n_o) according to equation (12) where the effect of extinction coefficient(k_o) is very lightly or may be neglected. While the behavior of imaginary part is similar to the extinction coefficient (k_o) according to equation (13).

Conclusions

The results show that the optical energy gap for allowed direct transition of (Cr_2O_3)thin films decreases from (3.30 eV to 3.14 eV) when doping ratio increases from (0% to 5%). The increase the ratio of doping increase the absorption coefficient (α). The extinction coefficient and imaginary Part of the dielectric constant increase with increase the ratio of doping while the refractive index and real Part of the dielectric constant decrease with increase the ratio of doping.

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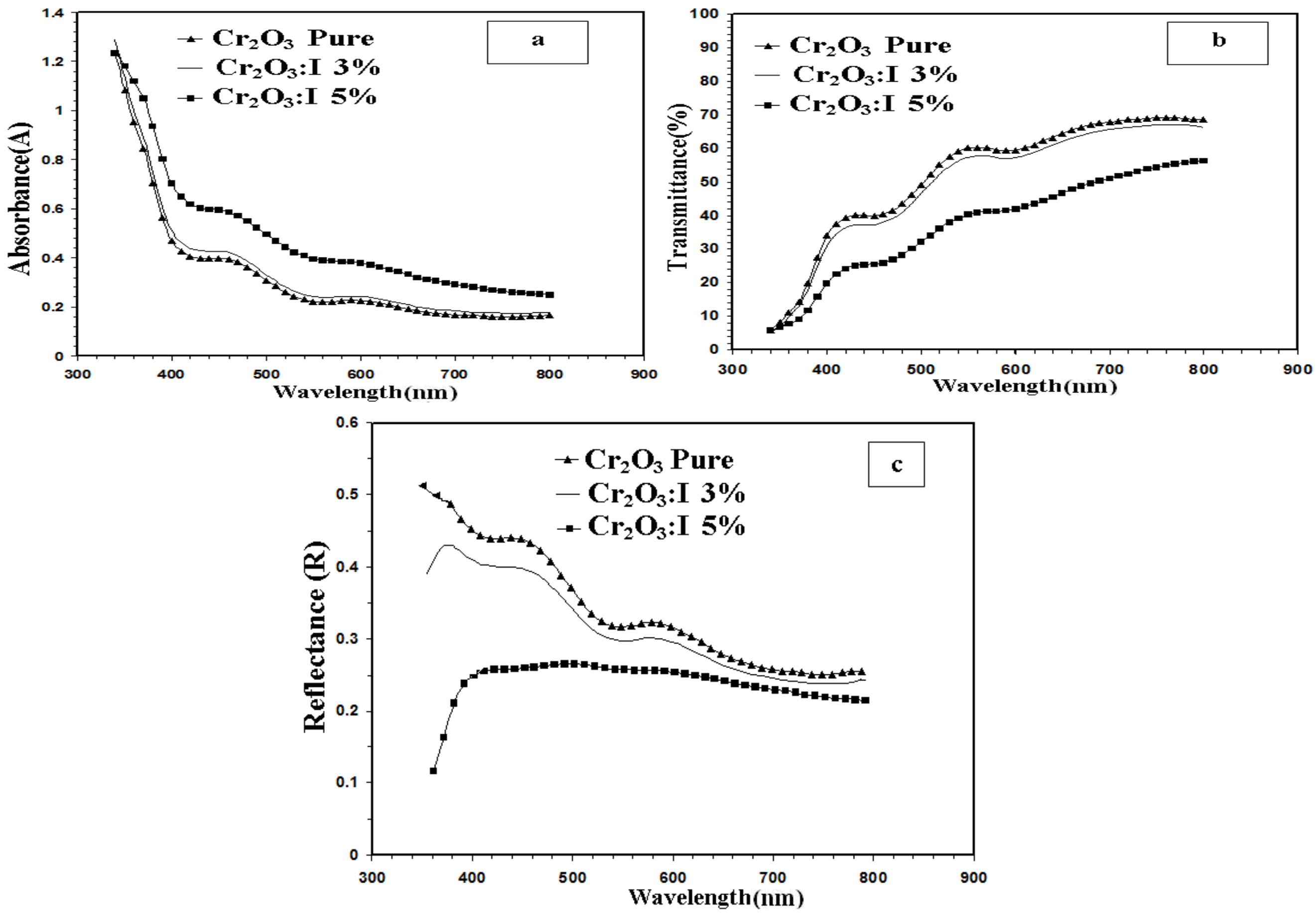

Fig(1):(a) Absorbance (b)Transmittance (c)Reflectance spectra against wavelength of the undoped and I–doped (Cr_2O_3) thin films .

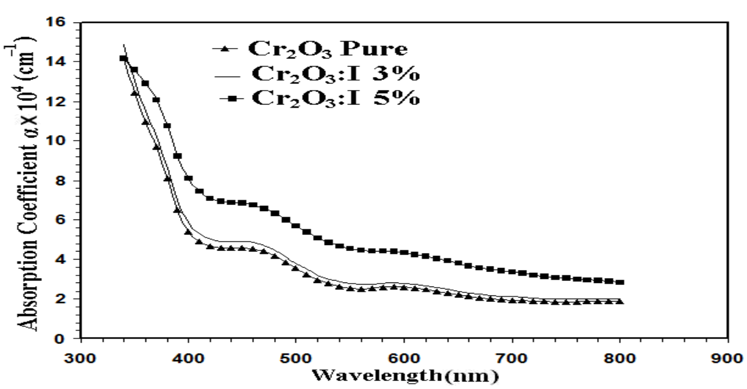

Fig (2): Absorption Coefficient (α) against wavelength for the undoped and I–doped (Cr_2O_3) thin films.

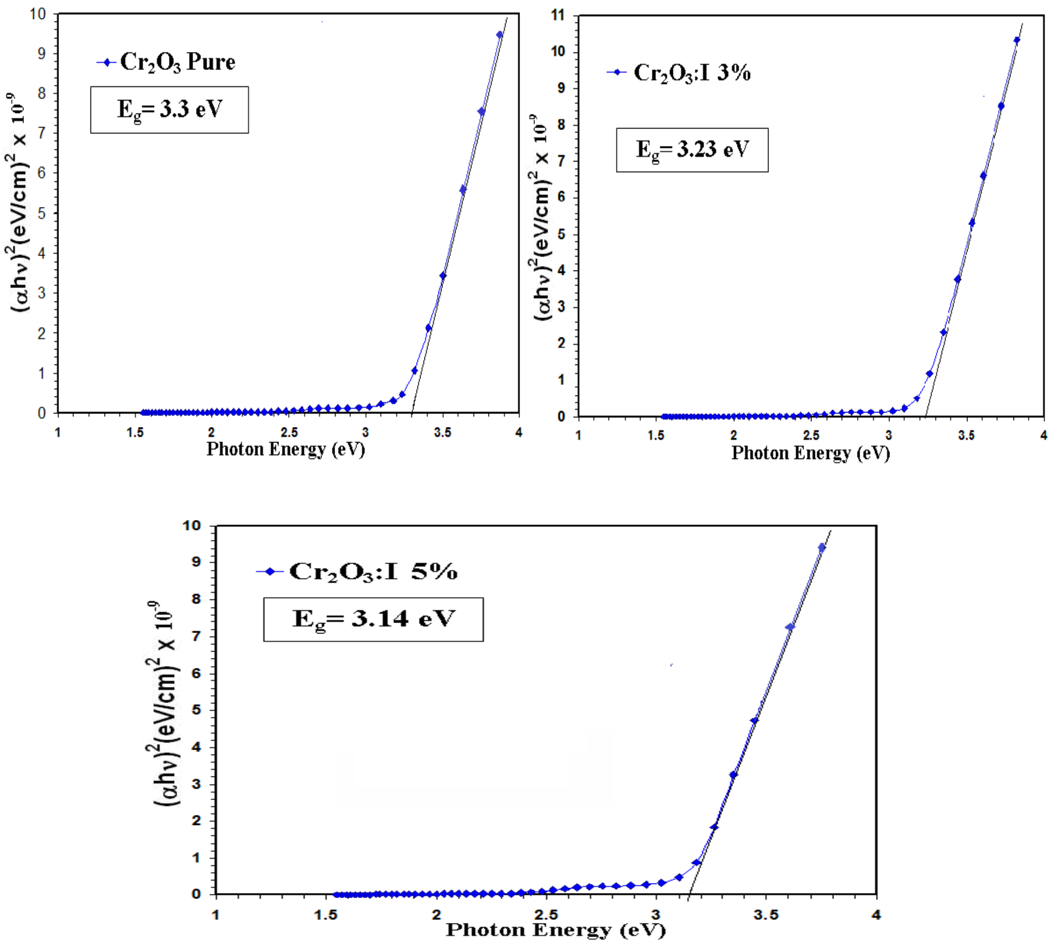

Fig (3): $(\alpha h\nu)^2$ for the undoped and I–doped (Cr_2O_3) thin films versus photon energy.

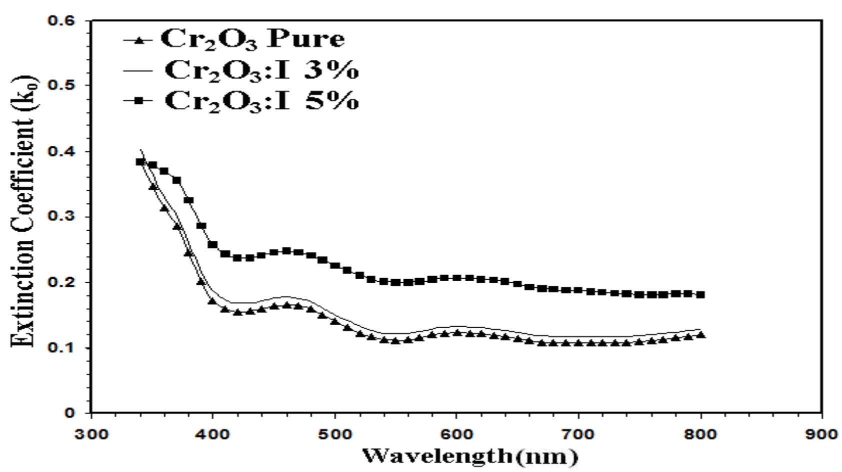

Fig (4): Extinction coefficient against wavelength for the undoped and I–doped (Cr_2O_3) thin films.

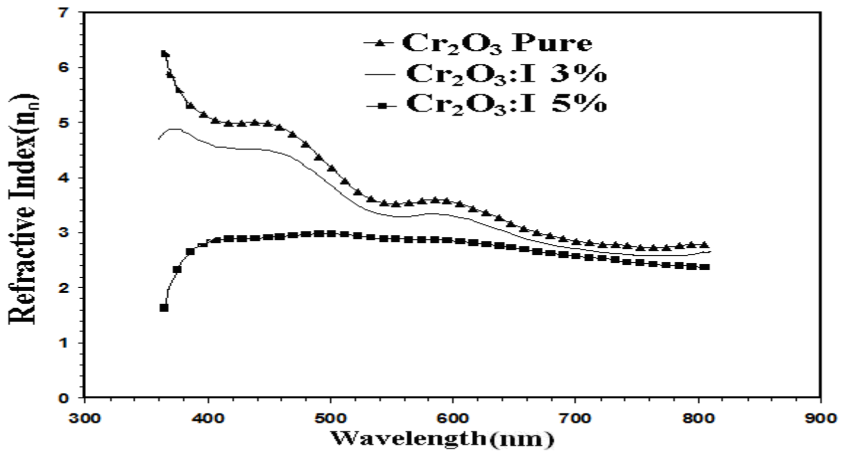

Fig (5): Refractive index against wavelength for the undoped and I–doped (Cr_2O_3) thin films.

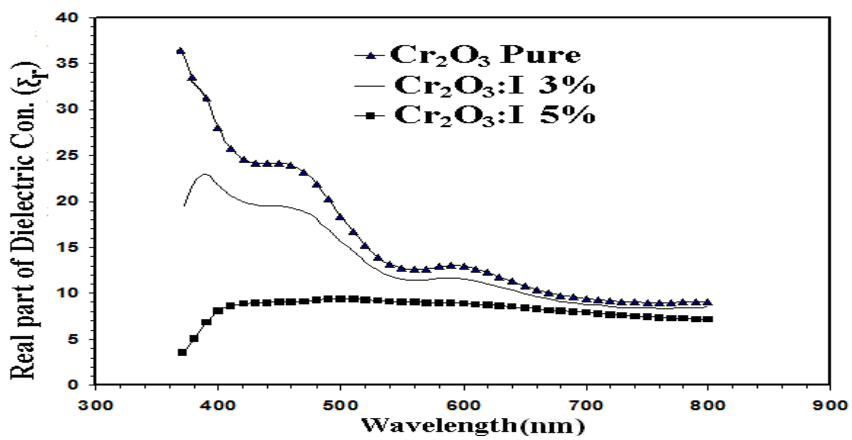

Fig (6): Real part of dielectric constant against wavelength for the undoped and I–doped (Cr_2O_3) thin films.

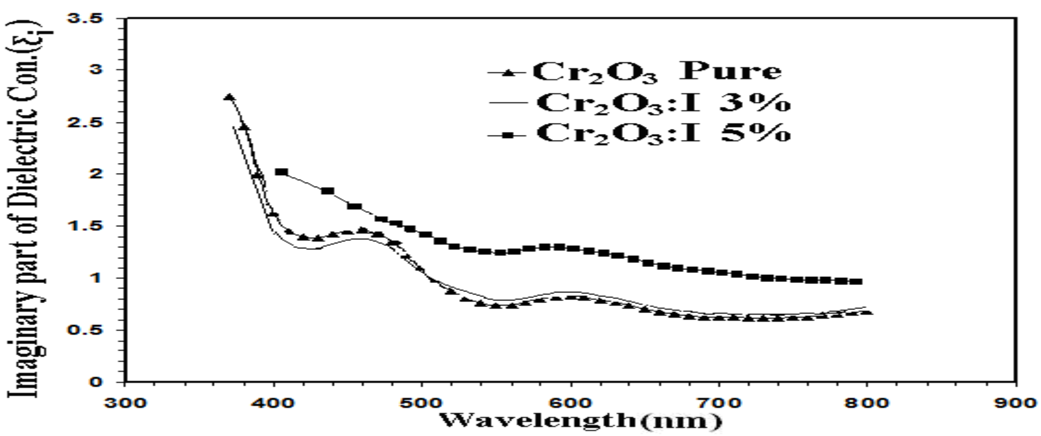

Fig (7): Imaginary part of dielectric constant against wavelength for the undoped and I–doped (Cr_2O_3) thin films.