

Annealing Effect on Some Optical Properties of Cr₂O₃ Thin Films Prepared by Spray Pyrolysis Technique

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Abstract:

Cr₂O₃ thin films have been prepared by spray pyrolysis on a glass substrate. Absorbance and transmittance spectra were recorded in the wavelength range (300-900) nm before and after annealing.

The effects of annealing temperature on absorption coefficient, refractive index, extinction coefficient, real and imaginary parts of dielectric constant and optical conductivity were expected. It was found that all these parameters increase as the annealing temperature increased to 550°C.

Key words: Cr₂O₃, Thin Films, Optical Properties, Spray Pyrolysis.

Introduction :

Chromia Cr₂O₃ has been extensively explored among the development of widespread industrial applications, due to the convergence of variety of mechanical, physical and chemical properties in one single oxide material.

Chromium oxide thin films are known as widely applicable in catalysis, solar thermal energy collectors and, as black matrix films, in liquid crystal displays [1, 2]. Other attractive usage of Cr₂O₃ thin films is as electrochromic material.

Various methods have been used for large area synthesis of Cr₂O₃ films such as chemical vapor deposition [3]. Remote plasma assisted pulsed laser deposition [4], plasma spraying [5], evaporation [6] and spray pyrolysis [7]. In the present investigation we used spray pyrolysis technique to prepare Cr₂O₃ thin films. Chromium, a 1st row transition metal, forms a number of oxides, one of these oxides is Cr₂O₃ which is the only solid chromium oxide that is thermodynamically stable at temperatures higher than 500 °C [8]. Also it is the hardest oxide, and

exhibits high hardness values and low friction coefficients [9, 10]. Some applications of Cr₂O₃ coatings have been found in tribological and wearing environment, as protective coatings on digital recording system [11] and in gas-bearing applications [12,13]. In the present investigation we report the effect of annealing on Cr₂O₃ thin films prepared by spray pyrolysis in order to study the optical constants, including refractive index, extinction coefficient, real and imaginary part of dielectric constant

Materials and Methods :

Thin films of chromium oxide have been prepared by chemical pyrolysis technique. The spray pyrolysis was done by using a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at temperature of 450°C, the starting solution was achieved by an aqueous solution of 0.1 M of CrCl₃ diluted with de-ionized water and ethanol, formed

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the final spray solution and a total volume of 50 ml was used in each deposition. With the optimized conditions that concern the following parameters, spray time was 10 s and the spray interval (3min) was kept constant. The carrier gas (filtered compressed air) was maintained at a pressure of 10^5 Nm^{-2} , distance between nozzle and substrate was about $29 \text{ cm} \pm 1 \text{ cm}$.

Thickness of the sample was measured using the weighting method and was found to be around $0.3 \text{ } \mu\text{m}$. Optical transmittance and absorbance were recorded in the wavelength range (300-900nm) using UV-visible spectrophotometer (Shimadzu Company Japan). The as deposited films were subject to annealing temperature at $550 \text{ }^\circ\text{C}$. Optical transmittance and absorbance were repeated after annealing in order to find the effect of annealing on the parameters under investigation.

Results and Discussions :

Fig. (1) Shows the optical absorbance of the Cr_2O_3 film annealed at temperature $550 \text{ }^\circ\text{C}$. It is evident that the optical absorbance increases in the visible region with increasing annealing temperature. In addition, we can see from this figure that the absorption edge has been slightly changed after annealing.

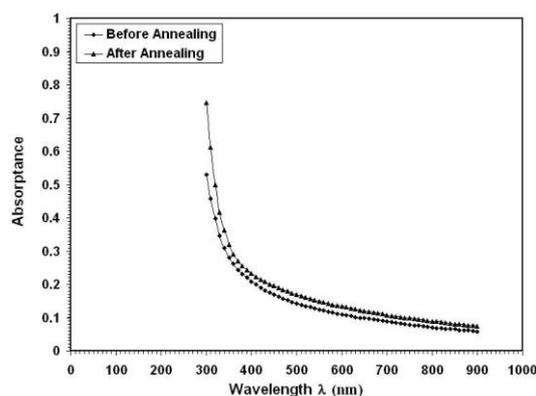


Fig. (1) Absorbance versus wavelength.

The absorption coefficient of the annealed Cr_2O_3 film can be calculated by a simple method from absorption spectra [14]. The absorption coefficient, $\alpha(\lambda)$, is defined as:

$$\alpha = \frac{2.303A}{t} \text{ ----- (1)}$$

Where (A) is the absorption and (t) is the film thickness.

Calculated results are shown in Fig. (2) It shows that the absorption coefficient exhibits a function of the wavelength. The absorption coefficient decreases with the increasing of the wavelength. For a given wavelength, the absorption coefficient increases with increasing the annealing temperature. It is known that the absorption coefficient near the band edge shows an exponential dependence on photon energy [15]. We can estimate the energy gap from the absorption edge and their value were found to be 3.1 eV and 3.06 eV before and after annealing respectively.

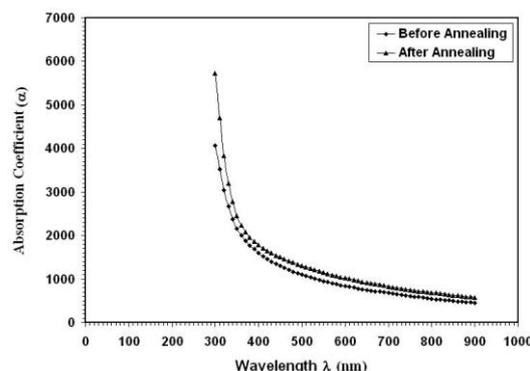


Fig. (2) Absorption coefficient versus photon energy

It is known that extinction coefficient and absorption coefficient can be related by [16]:

$$k = \frac{\alpha \lambda}{4 \pi} \text{ ----- (2)}$$

Where (α) is the absorption coefficient and (λ) is the incident wavelength.

From Fig. (3) One can easily obtain the extinction coefficient of Cr_2O_3 films, it can be seen that the extinction

coefficient increases as the annealing temperature increase.

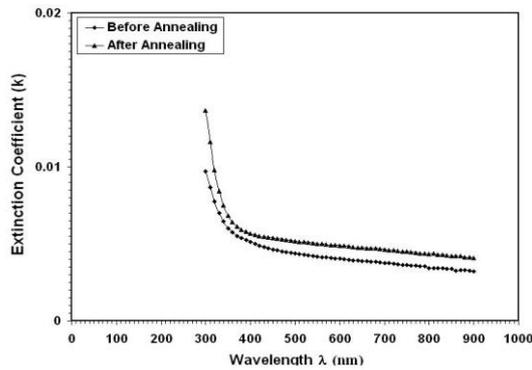


Fig. (3) Extinction coefficient versus wavelength.

The refractive index is an important parameter for optical materials and applications. Fig. (4) Shows the dependence of the refractive indices of Cr₂O₃ films on the wavelength. It can be seen that the refractive index decreases with the increasing of wavelength, i.e. anomalous dispersion. It can also be seen that the refractive index increases when increasing annealing temperature. The decrease and increase of refractive indices in the visible and ultraviolet region with increasing annealing temperature can be attributed to the variation of optical absorption in the visible region and ultraviolet region after annealing .

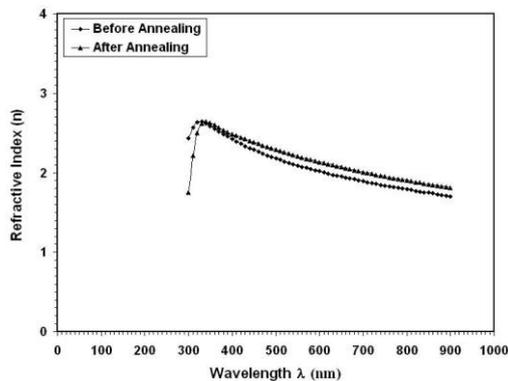


Fig. (4) Refractive indices versus wavelength.

The dielectric constant can be defined as [17]:

$$\varepsilon(\lambda) = \varepsilon_1(\lambda) + i\varepsilon_2(\lambda) \quad \text{----- (3)}$$

The real (ε_1) and imaginary (ε_2) parts of the dielectric constant are related to the n (refractive index) and k (extinction coefficient) values. These values can be calculated using the following formulas [18]:

$$\varepsilon_1(\lambda) = n^2(\lambda) - k^2(\lambda) \quad \text{----- (4)}$$

$$\varepsilon_2(\lambda) = 2n(\lambda)k(\lambda) \quad \text{----- (5)}$$

Figs. (5) and (6) present the dependence of the dielectric constant of the Cr₂O₃ films on the wavelength. The real and imaginary parts follow the same pattern and the values of real part are higher than imaginary part. It can be seen that the real and imaginary parts of the dielectric constant decreases with increasing wavelength. On the other hand both of them are increases with increasing annealing temperature.

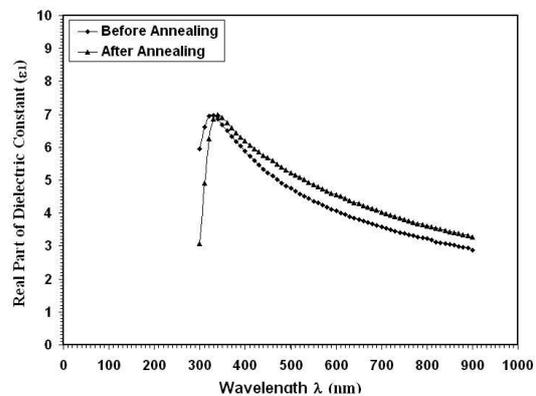


Fig. (5) Real part versus wavelength.

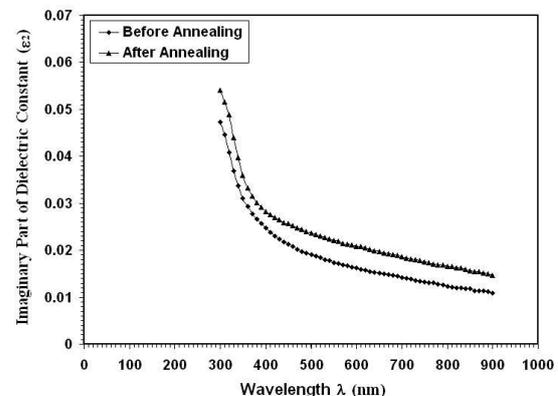


Fig. (6) Imaginary part versus wavelength.

Fig. (7) Shows the dependence of the optical conductivity of Cr_2O_3 films on wavelength, it can be seen that the optical conductivity increases as annealing temperature increased.

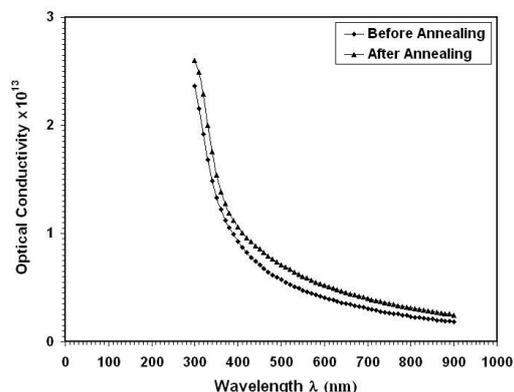


Fig. (7) Optical conductivity versus wavelength.

Conclusions:

The produced films of chromium oxide were thermodynamically stable at temperatures higher than 500 °C and this result is in a good agreement with Parkin et al. results. The detailed study of annealing effect on some optical parameters of Cr_2O_3 has shown that absorption coefficient, refractive index, extinction coefficient, real and imaginary parts of dielectric constant and optical conductivity increases as the annealing temperature increased to 550 °C.

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تأثير التلدين على بعض الخصائص البصرية لأغشية أكسيد الكروم المحضرة بطريقة الرش الكيميائي الحراري

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الخلاصة:

تم تحضير أغشية رقيقة من أكسيد الكروم Cr₂O₃ على قواعد من الزجاج باستخدام طريقة التحلل الكيميائي الحراري. سجل طيفي النفاذية والامتصاصية في مدى الأطوال الموجية (300-900) نانومتر قبل وبعد التلدين. درس تأثير التلدين على كل من معامل الامتصاص، معامل الانكسار، معامل الخمود، ثابت العزل بجزأيه الحقيقي والخيالي، والتوصيل الضوئية. وقد تبين ان جميع هذه الثوابت البصرية للأغشية المحضرة تزداد بزيادة درجة حرارة التلدين الى 550°C.