Annealing Effect on Some Optical Properties of Cr_2O_3 Thin Films Prepared by Spray Pyrolysis Technique

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Abstract:

Cr_2O_3 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: Cr_2O_3, 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 $CrCl_3$ 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 cm ±1 cm.

Thickness of the sample was measured using the weighting method and was found to be around 0.3 µm. 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 ^oC. 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 ◦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.

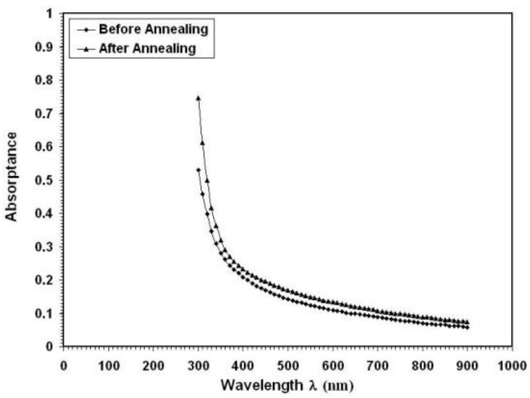

Fig. (1) Absorbance versus wavelength.

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:

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

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 wer found to be 3.1 eV and 3.06 eV before and after annealing respectively.

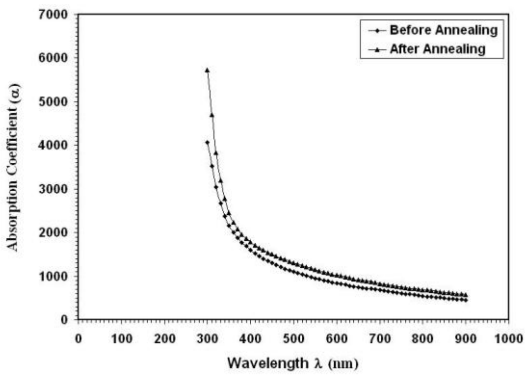

Fig. (2) Absorption coefficient versus photon energy

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

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

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.

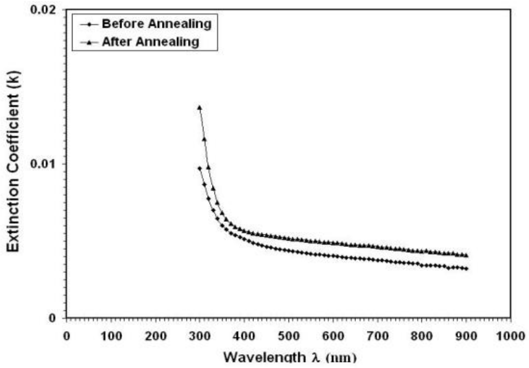

Fig. (3) Extinction coefficient versus wavelength.

The refractive index is an important parameter for optical materials and applications. Fig. (4) Shows the dependence of the refractive indices of Cr_2O_3 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 .

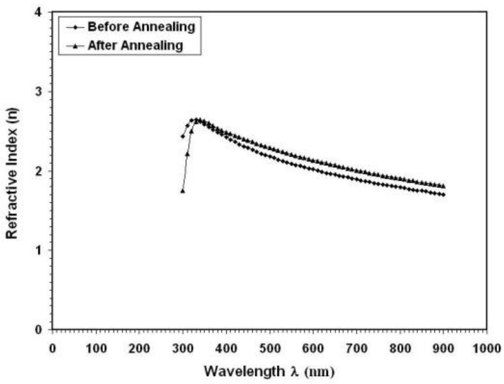

Fig. (4) Refractive indices versus wavelength.

The dielectric constant can be defined as [17]:

$\varepsilon(\lambda) = \varepsilon_1(\lambda) + i\varepsilon_2(\lambda)$ ------------- (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]:

$\varepsilon_1(\lambda) = n^2(\lambda) - k^2(\lambda)$ ------------- (4)

$\varepsilon_2(\lambda) = 2n(\lambda)\, k(\lambda)$ ------------- (5)

Figs. (5) and (6) present the dependence of the dielectric constant of the Cr_2O_3 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.

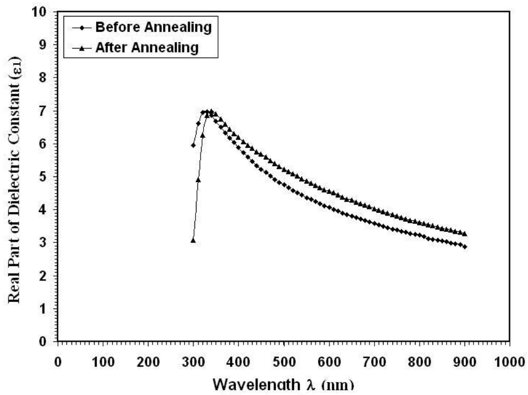

Fig. (5) Real part versus wavelength.

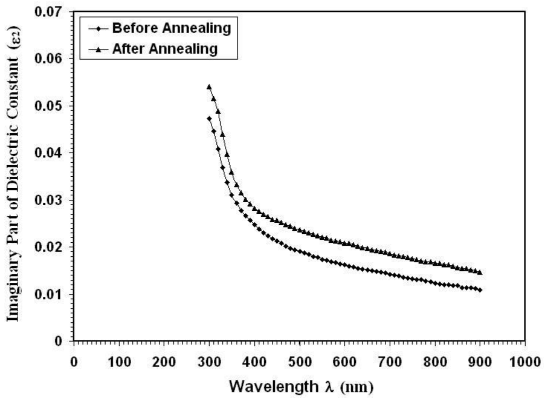

Fig. (6) Imaginary part versus wavelength.

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

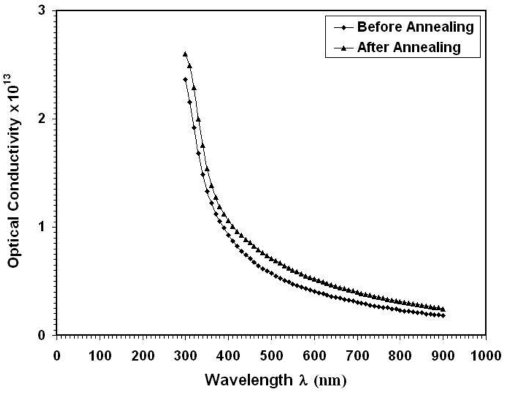

Fig. (7) Optical conductivity versus wavelength.

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.

References:

1. Ivanova, T., Gesheva, K., Cziraki, A., Szekeres, A., and Vlaikova, E. 2008. Structural transformations and their relation to the optoelectronic properties of chromium oxide thin films, J. Phys.: Conference Series, 113 : 012030.
2. Popovici, N., Parampes M. L, Da Silva R. C, Monnereau O, Sousa P. M., Silvestre A. J. and Conde, O. 2004. KrF pulsed laser deposition of chromium oxide thin films from Cr $_8$O $_{21}$ targets, Appl. Phys. A: Materials Science & Processing, 79 (4-6): 1409-1411.
3. Li, X., W., Gupta, A., McGuire, T. R. and Xiao, G. 1999. Magnetoresistance and Hall effect of chromium dioxide epitaxial thin films, J. of Appl. Phys., 85: 5585-5587.
4. Madi1, C., Tabbal1, M., Christidis1, T., Isber1, S., Nsouli, B., and Zahraman, K., 2007. Microstructural characterization of chromium oxide thin films grown by remote plasma assisted pulsed laser deposition, J. of Phys.: Conference Series 59: 600–604.
5. Ahn, H., S., Kwon, O., K. 1999. Tribological Behaviour of Plasma-Sprayed Chromium Oxide Coating, Wear 225–229: 814-824.
6. Cantalini, C. 2004. Cr_2O_3, WO_3 single and Cr/W binary oxide prepared by physical methods for gas sensing applications Original Research Article , J. Eur. Ceram. Soc. 24 (6): 1421-1424.

   Misho, R. H., Murad, W. A. and Fattahallah, G. H. 1989. Preparation and Optical Properties of Thin Films of CrO_3 and Cr_2O_3 Prepared by the Method of Chemical Spray Pyrolysis, Thin Solid Films, 169: 235_239.
8. Parkin, I. P. and Field, M. N. 1999. Atmospheric pressure chemical vapour deposition of chromium oxide films, J. Phys. IV (France) 9: 387-393.
9. Caro, G., Natali, M., Rossetto, G., Zanella, P., Salmaso, G., Restello, S., Rigato, V., Kaciulis, S. and Mezzi, A. 2005. A Comparative Study of Cr_2O_3 Thin Films Obtained by MOCVD using Three Different, Chem. Vapor Depos. 11: 375-380.
10. Hones, P., Levy, F., Randall, N., X. 1999. Influence of deposition parameters on mechanical properties of sputter-deposited

Cr_2O_3 thin films , J. Mater. Res. 14 (9): 3623-3629.

11. Bijker, M. D., Bastiaens, J. J., Draaisma, E. A., De Jong, L. A. M., Sourty, E., Saied, S. O. and Sullivan, J. L. 2003. The development of a thin Cr_2O_3 wear protective coating for the advanced digital recording system , Tribol. Int., 36 (2003) 227-233..

12. Bhushan, B., Theunissen, G. S. and Li, X. 1997. ribological studies of chromium oxide films for magnetic recording applications, Thin Solid Films, 311: 67-80.

13. Hones, P., Diserens, M. and Levy, F. 1999. Characterization of sputter-deposited chromium oxide thin films Original Research Article, Surf. Coat. Technol, 120–121: 277-283.

14. Kim, K. H., Park, K. C. and Ma, D. Y.1997. Structural, electrical and optical properties of aluminum doped zinc oxide films prepared by radio frequency magnetron sputtering, J. Appl. Phys., 81: 7764.

15. Urbach, F.1953. The Long-Wavelength Edge of Photographic Sensitivity and of the Electronic Absorption of Solids, Phys. Rev., 92:1324.

16. Wakkad, M. M., Shokr, E. Kh and Mohamed, S. H. 2000. Optical and calorimetric studies of Ge–Sb–Se glasses, J. of Non-Crystalline Solids, 265 (1-2): 157-166.

17. Dutta, S., Chattopadhyay, S., Sarkar, A., Chakrabarti, M., Sanyal, p. and Jana, D. 2009. Role of Defects In Tailoring Structural, Electrical and Optical Properties of ZnO, Progress in Material Science, 54: 89.

18. Buet, F., Olivier-Fourcade, J., Bensimon, Y. and Belougne, P. 1991. Complex Impedance Study of Chalcogenide Glasses , Solid State Communications ,77 (1): 29.

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

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الخلاصة:

تم تحضير أغشية رقيقة من أوكسيد الكروم Cr_2O_3 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, والتوصيليه الضوئية. وقد تبين ان جميع هذه الثوابت البصرية للأغشية المحضرة تزداد بزيادة درجة حرارة التلدين الى 550°C.