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Substrate Temperature Effects on Some Optical Constants of Cobalt Oxide Thin Films

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Abstract:
Cobalt oxide thin films has been deposited onto different glass substrate temperature ranging (350-500) ^oC by spraying an aqueous solution of cobalt chloride using chemical spray pyrolysis. Absorbance spectra were recorded in order to calculate the optical constants. In general all these parameters were affected by increasing the substrate temperature . The optical energy gap was calculated by Tauc relation indicate that its value were decrease upon increasing substrate temperature from1.91 eV for 350 ^oC substrate temperature to 1.82 eV for 500 ^oC substrate temperature.

Keywords: Co_3O_4, thin film, Chemical spray pyrolysis, optical properties.

Introduction
With a chemical formula AB2O4, spinel ferrites and cobaltites consist of a cubic close-packed arrangement of oxygen ions, with A^{2+} and B^{3+} ions located at two different crystallographic sites [1]. At room temperature, the most stable form of cobalt oxide is Co_3O_4, a semiconductor with a modest band gap of less than 1.6 eV, as compared to the 2.4 eV gap of charge-transfer insulator CoO [2, 3, 4]. The supported catalysts containing cobalt in the metallic, oxidc, or sulphided state are very important in heterogeneous catalysis [5, 6]. Cobalt oxides are well-known electrochromic materials that have attracted a lot of attention for applications in smart windows [7], solar cells [8], heterogeneous catalysts [9], gas sensors [10], electrode materials [11], energy storage [12], and magnetic materials [13,14].

Cobalt oxide films are obtained by wet processes such as thermal decomposition, electrodeposition [15,16,17] and sol–gel [18]. Dry processes are also employed such as PVD [19,20], ALD [21,22,23,24] and metalorganic CVD (MOCVD) [25, 26, 27, 28]. Chemical spray pyrolysis method used successfully to prepare metal oxides [29,30,31,32,33]. In this work, the chemical spray pyrolysis method was used to prepare Co_3O_4 thin film and study the effect of substrate temperature on its optical properties.

Experimental Part

The Co3O4 thin films were prepared by spraying an aqueous solution of Cobalt chloride (CoCl2.6H2O) and a few drops of HCl were added to make the solution clear. A total volume of 100 ml was used in each deposition. The spray pyrolysis was done by using a glass atomizer, which has an output nozzle of 1 mm. The optimized conditions that concern the following parameters: spray time was 10 sec, the stopping period 3 minutes to avoid excessive cooling of glass substrate. The carrier gas (filtered compressed air) was maintained at a pressure of 105 Pascal, distance between nozzle and substrate was about 30 cm, solution flow rate 5 ml/min. Thickness of the sample was measured using the gravimetric method and was found to be 340 ± 20 nm. The optical properties are calculated from recording the absorbance spectra via UV-Visible spectrophotometer in the wavelength range (450-900) nm.

Results and discussion

The optical properties of Co_3O_4 films by means of optical absorption in the UV-Vis region of (450–900) nm have been investigated. The absorbance spectra versus wavelength are represented in Fig.1. From the figure, the absorbance are decreased with the increasing of wavelength and increased with increasing of substrate temperature, this behavior attributed to the arrangement of atoms with the increasing of substrate temperature.

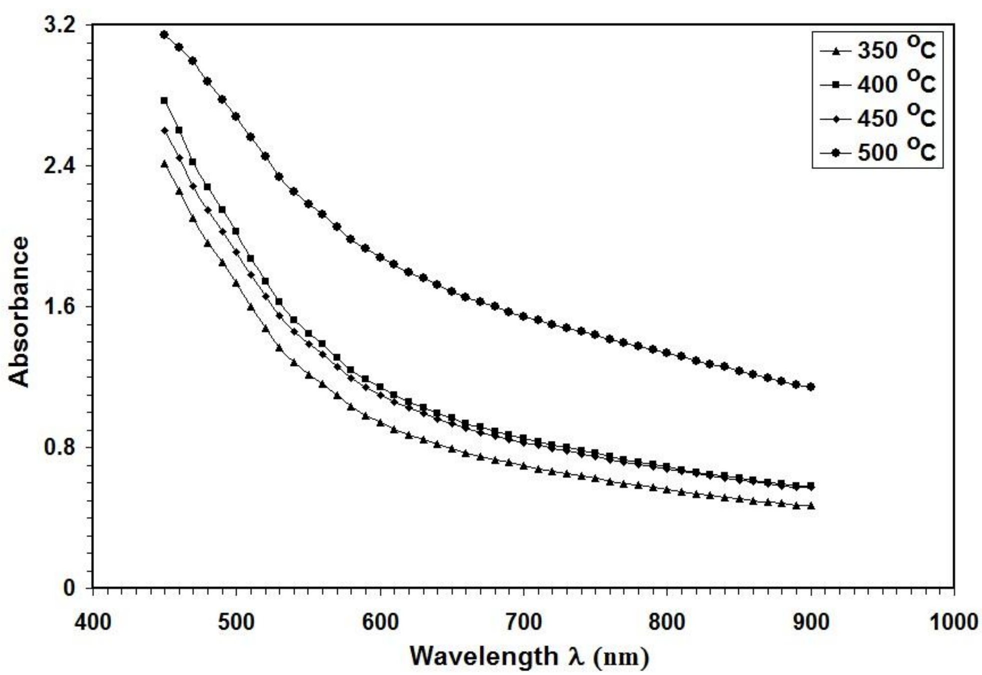

Fig.1: A plots of optical absorbance of the Co_3O_4 thin films for various annealing temperature.

The optical absorption coefficient (α) can be deduced from the absorption spectra (A) using the relation[17]:

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

where t is the thickness of the as deposited thin films. The absorption coefficient versus wavelength are presented in Fig.2. The absorption coefficient increased with the increasing of photon energy, this attributed to the increasing of number of electrons that passing from valence to conduction bands. From the figure, it can notice that the increasing of absorption coefficient with the increasing of substrate temperature and its values are greater than 10^{-4} cm^{-1} for all deposited Co_3O_4 thin films, which refer to the allowed direct energy gap.

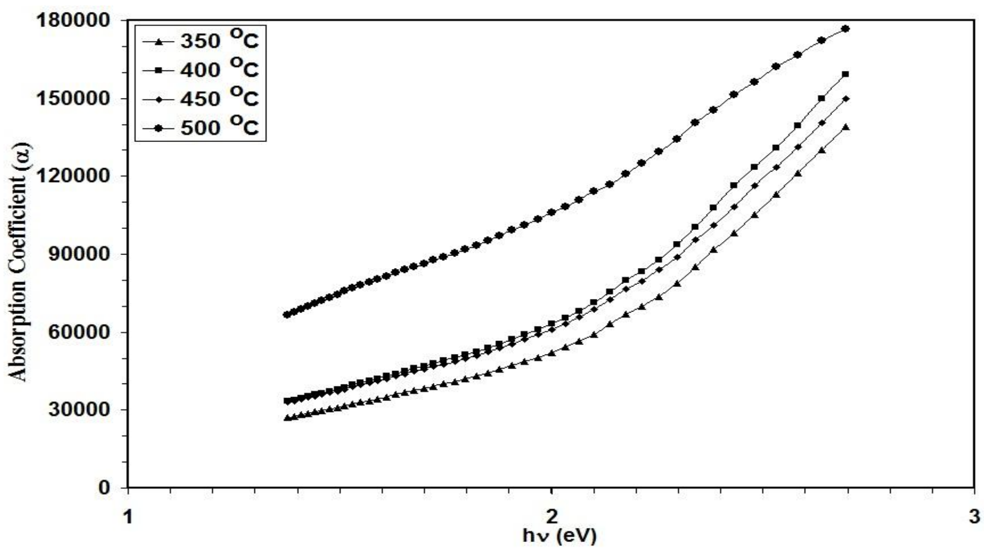

Fig.2: A plots of absorption coefficient of the Co_3O_4 thin films for various annealing temperature.

The variation of extinction coefficient (k) as a function of wavelength (λ) is shown in Fig.3, which can be calculated by the following equation[34]:

$$K = \frac{\alpha \lambda}{4\pi} \quad (2)$$

The extinction coefficient is decreased with the increasing of substrate temperature for the deposited thin films.

Refractive index (n) is one of the fundamental properties for an optical material because it is closely related to the electronic polarization of ions and the local field inside materials. The refractive index has been evaluated by the relation [34]:

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (3)$$

where k is the extinction coefficient. The refractive index versus wavelength was presented in Fig.4, which shows the increase of n with the increasing wavelength until 600 nm and then decreases for deposited films except the film that prepared at substrate temperature 500°C were increased with the increasing wavelength in the range 450-900 nm.

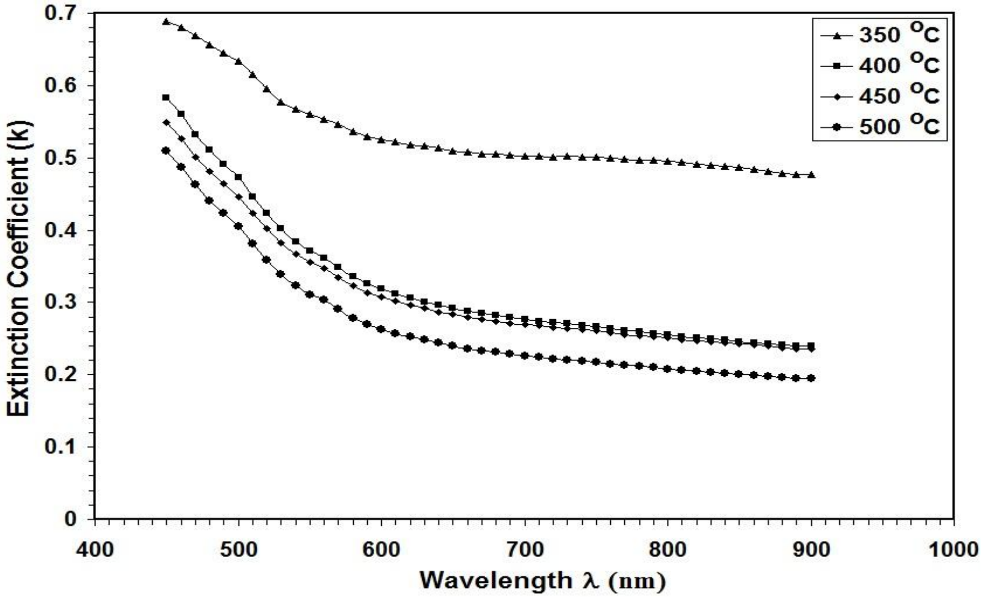

Fig.3: A plots of extinction coefficient of the Co_3O_4 thin films for various annealing temperature.

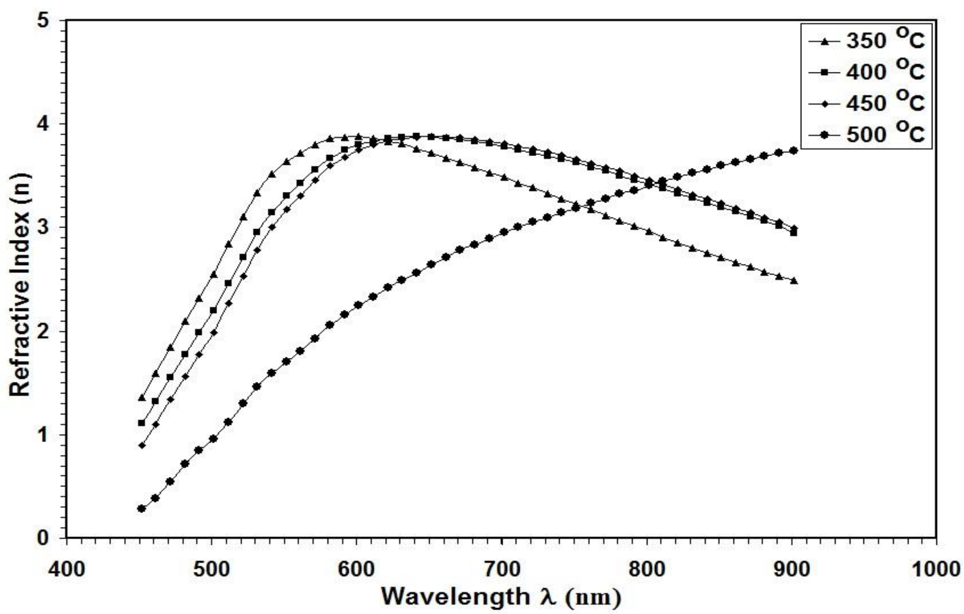

Fig.4: A plots of refractive index of the Co_3O_4 thin films for various annealing temperature.

The optical conductivity ($\sigma_{optical}$) could be calculated from the relation [35]:

$\sigma_{optical} = \frac{\alpha n c}{4\pi}$ (4)

where α is the absorption coefficient, n is the refractive index, and c is the speed of light in the space. The optical conductivity versus wavelength is represented in Fig. 5. From the figure, the optical conductivity was decreased with the increasing substrate temperature.

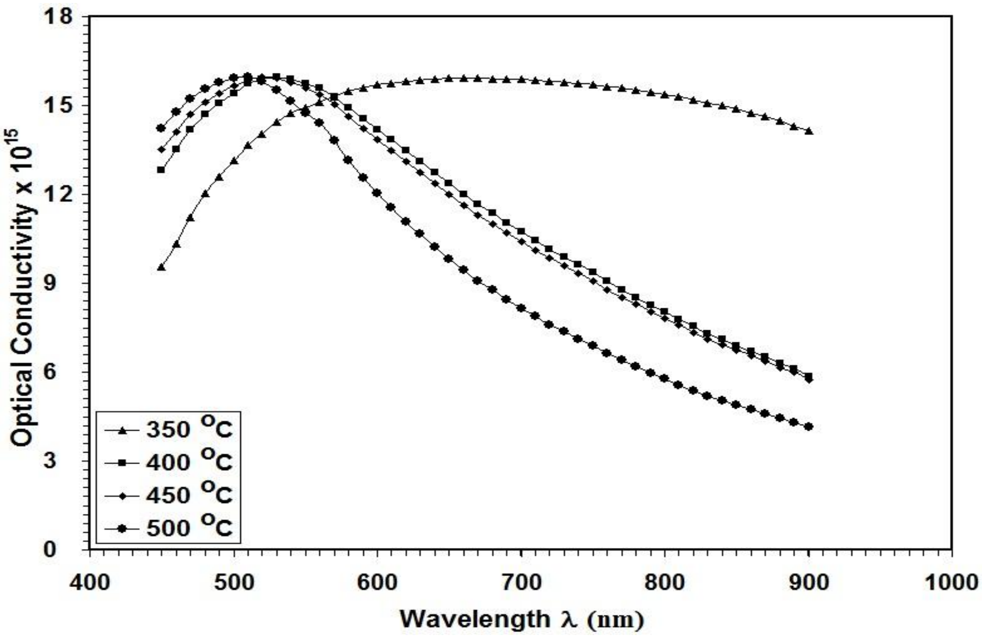

Fig.5: A plots of optical conductivity of the Co_3O_4 thin films for various annealing temperature.

The variation of optical density with wavelength is further analyzed to find out the nature of transition involved and the optical band gap. The nature of the transition involved is determined by using the relation[36]:

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

For allowed direct transition, n= 1/2. The plot of $(\alpha h\nu)^2$ versus hν is shown in Figs.6-9 is linear and indicates the presence of direct transition. The straight portion is extrapolated to energy axis at α =0 which gives the band gap energy (E_g). From the figures, the energy gap decreased from 1.91 eV for film prepared at substrate temperature 300 °C to 1.82 eV for film prepared at substrate temperature 500 °C.

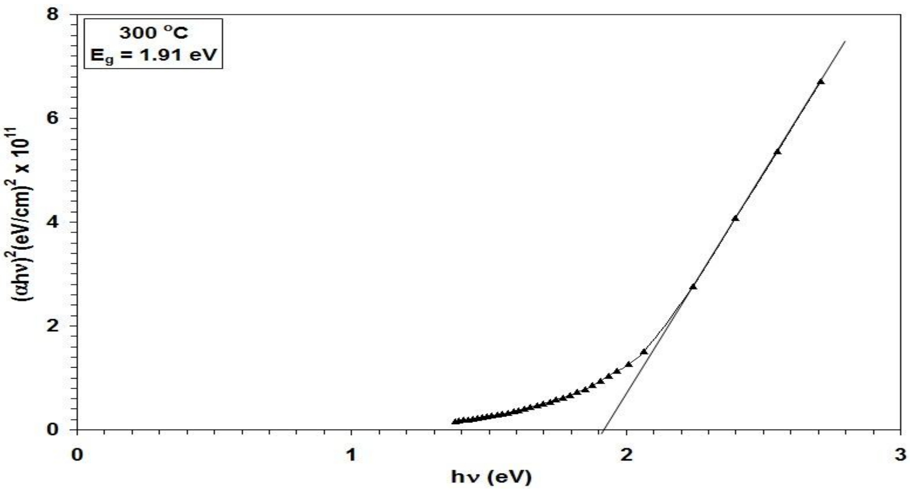

Fig.6: A plots of $(\alpha h\upsilon)^2$ versus hυ of the Co_3O_4 thin films at substrate temperature 300 °C.

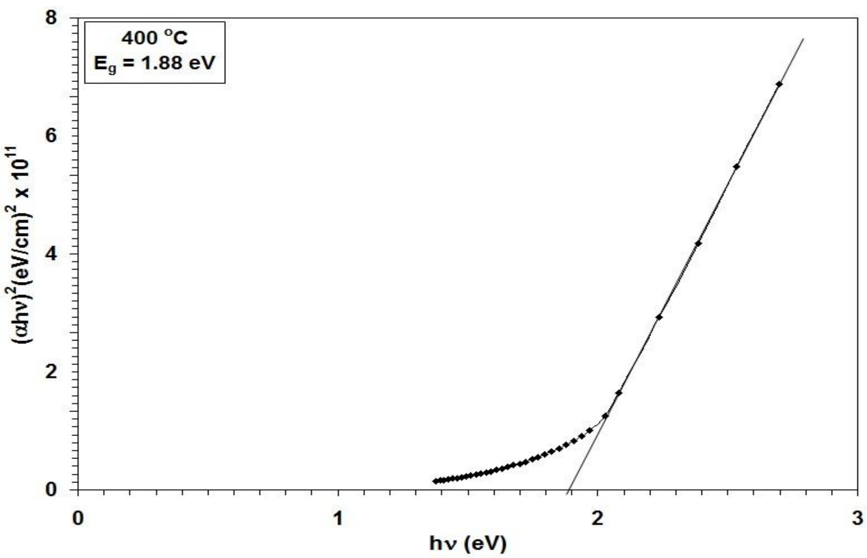

Fig.7: A plots of $(\alpha h\upsilon)^2$ versus hυ of the Co_3O_4 thin films at substrate temperature 400 °C.

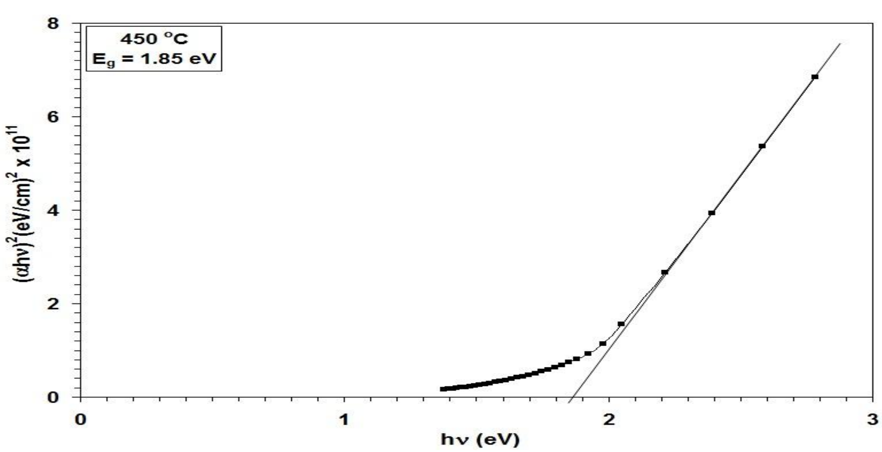

Fig.8: A plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$ of the Co_3O_4 thin films at substrate temperature 450 °C.

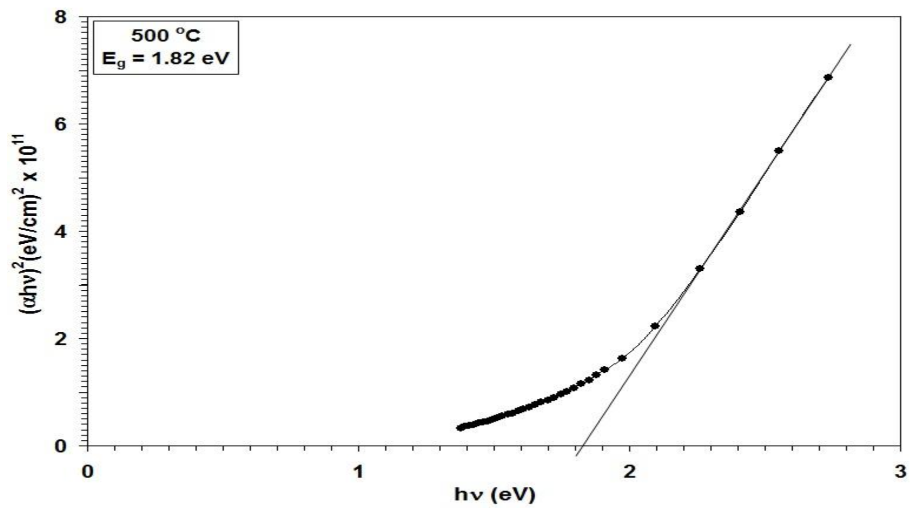

Fig.9: A plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$ of the Co_3O_4 thin films at substrate temperature 500 °C.

Conclusions

Thin films of cobalt oxide were studied in order to calculate the optical constants at different substrate temperatures. The results reveal that the substrate temperature play an important rule in the fabrication of cobalt oxide by varying the values of optical constant and decrease the value of the optical energy gap.

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تاثيرات درجة حرارة القاعدة على بعض الثوابت البصرية لاغشية اوكسيد الكوبلت الرقيقة

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الخلاصة:
حضرت اغشية رقيقة من اوكسيد الكوبلت بدرجات حرارة قاعدة مختلفة بمدى ^{o}C (350-500) بوساطة ترذيذ محلول كلوريد الكوبلت باستعمال طريقة التحلل الكيميائي الحراري. سجلت اطياف الامتصاصية لغرض حساب الثوابت البصرية. لقد وجد بشكل عام ان جميع الثوابت قد تاثرت بزيادة درجة حرارة القاعدة. حسبت فجوة الطاقة البصرية باستخدام علاقة تاوس والتي توصلت الى ان قيم فجوة الطاقة تتناقص بازدياد درجة حرارة القاعدة من 1.9 eV لدرجة حرارة قاعدة $350\ ^{o}C$ الى 1.82 eV لدرجة حرارة قاعدة $500^{o}C$.

الكلمات المفتاحية: Co_3O_4 ، اغشية رقيقة ،التحلل الكيميائي الحراري ،الخصائص البصرية.