J. of university of Anbar for pure science : Vol.7:NO.2: 2013
2nd Conference For Pure Science - university of Anbar 20-22/11/2012

ISSN: 1991-8941

Formation and Characterization of Co2O3 and Co2O3(1-x):Cux Thin Films

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Abstract: Co_2O_3 and $Co_2O_{3(1-x)}$:Cu_x films have been deposited by using spray pyrolysis technique on a glass substrates. The optical properties of the cobalt oxide have been studied as a function of doping concentration with Cu. Changes in direct optical band gap energy of cobalt oxide films were confirmed after doping, Eg increased from 1.48 and 1.95 eV for the undoped Co_2O_3 to 1.55 and 2.05 eV with increasing the doping concentration to 5%. The effect of doping on the optical parameters of Co_2O_3 thin films such as transmittance, reflectance, absorption coefficient, refractive index, extinction coefficient, and real and imaginary parts of dielectric constant has been reported.

Keywords: Optical properties, Cobalt Oxide. Thin films, $Co_2O_{3(1-x)}$:Cu_x

Introduction

The optical properties of thin films are very important for many applications, including interference devices, such as antireflection coatings, laser mirrors and monochromatic filters, as well as optoelectronics, integrated optics, solar power engineering, microelectronics and optical sensor technology depending on the reflectance and transmittance properties of the films during their preparation.

Transparent conducting oxides (TCO) are well known and have been widely used in optoelectronics and transparent electronics as well as in different research fields. Most of the existing TCOs are n-type, whereas it is very difficult to prepare binary metal oxides with p-type conductivity [1]. Among the transition metals, copper and cobalt are the most active for the decomposition of nitrous oxide and removal [2, 3].

Cobalt oxide is an important functional material for a wide range of technological applications such as heterogeneous catalysts, anode materials in Li-ion rechargeable batteries, magnetism, and optical devices [4-7], gas and humidity sensors[8,9], solar selective absorber, pigment for glasses and ceramics [10], catalyst for oxygen evolution and oxygen reduction reaction [11, 12]. It is widely used as an electrochromic material [13], electrochemical capacitors for high power devices in energy storage systems (supercapacitors) [14, 15].

Owing to the influence of doping on the properties of materials, the controlled preparation of cobalt oxide of different doping materials and concentrations are always the researcher's purpose. This paper reports the influence of doping with copper on the preparation and properties of cobalt oxide (Co_2O_3) thin films by spray pyrolysis technique (SPT). The accurate determination of the optical constants of these materials is important, not only in order to know the basic mechanisms underlying these phenomena, but also to exploit and develop their interesting technological applications. Therefore, the optical absorption parameters, such as dielectric constant ε, have been evaluated.

Experimental details

Cobalt chloride $CoCl_2.6H_2O$ o.1 M as matrix material and Copper chloride Cu o.1 M as a doping agent with a concentration of 1%, 3% and 5% have been dissolved in de-ionized water and ethanol to form the final spray solution, a few drops of HCl were added to make the solution clear, a total volume of 50 ml was used in each deposition, these two starting solutions were used for deposition of Co_2O_3:Cu thin films. The spray pyrolysis was done by using a laboratory designed glass atomizer, which has an output nozzle of 1 mm. The films were deposited on preheated glass substrates at a temperature of 450°C. With the optimized conditions that concern the following parameters, spray time was 10 sec. The period between spraying processes was about 3 min, this period is enough to avoid excessive cooling of glass substrate. 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, solution flow rate 5 ml/min. Thickness of the sample was measured using the weighting method and was found to be around 0.3 μm. A thermocouple was fixed to the substrate surface and the temperature was measured at the four corners of the glass substrate surface, Optical transmittance and absorbance were recorded in the wavelength range (300-900nm) using UV-visible spectrophotometer (Shimadzu Company Japan).

Optical transmittance and absorbance were reported in order to find the effect of doping on the parameters under investigation.

Results and discussion

Optical measurements of transmittance of Co_2O_3:Cu thin films are shown in Fig. (1) These measurements have been taken in the wavelength range of 300-900 nm. It is observed that in the visible region all films have very low transparent, then transmittance is rapidly increased with increasing the wavelength to more than 800nm. This behavior may be attributed to perfection and stoichiometry of the films. Below 800 nm there is a sharp fall in the transmittance for all films, which is due to a strong absorbance of the films in this region while the structure tends to be more transparent in the long wavelengths region. Also it can be observed from the figure that the transmittance increased with increasing the doping concentration of Cu to 5%.

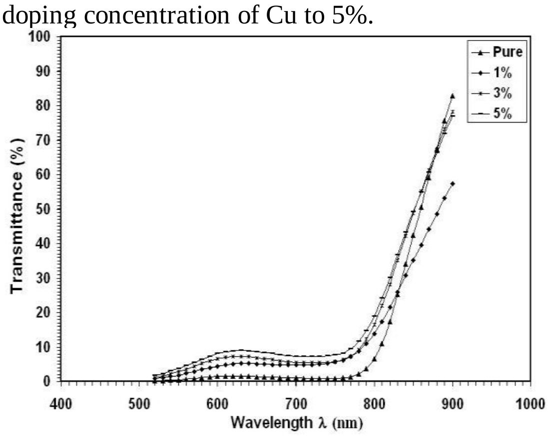

Fig. (1) The variation of transmittance with wavelength for Co_2O_3:Cu thin films.

Fig. (2) shows the optical reflectance spectra for undoped and doped Co2O3 thin films. The optical transmittance data may not be a necessary characteristic of valence to conduction band transitions in transition metal compound ,but it may also involve valence band to d-state and d-state to conduction band transitions , where the d-state/band lies between valence and conduction bands . The reflectance has been found by using the relationship:

$$R + T + A = 1 \quad ..... (1)$$

The overall reflectance of the films decreases as the doping concentration increases. As expected the reflectance of Co2O3:Cu thin films is extremely small in the visible region. The extremely small values of the reflectance and the absorbance in the visible region offered the most promise for realizing visible laser diodes (LD) and efficient light–emitting–diode (LED) displays, by using Co2O3:Cu thin films in these devices.

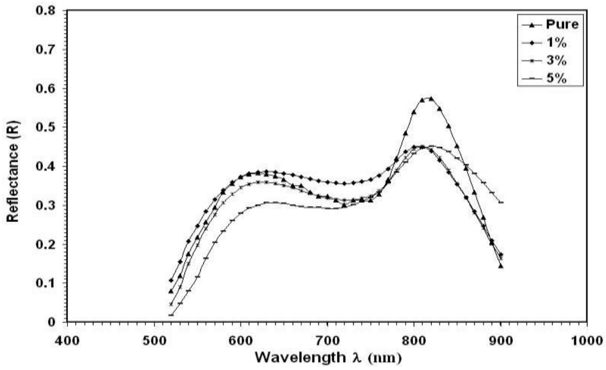

Fig. (2) The variation of reflectance with wavelength for Co2O3:Cu thin films.

The absorption coefficient (α) could be calculated by using the following relation [16]:

$$\alpha = \frac{2.303A}{t} \quad ....(2)$$

Where (A) is the absorption and (t) is the film thickness. Fig. (3) Shows the dependence of the absorption coefficient (α) on the wavelength. The absorption coefficient decreases with increasing the doping concentration of Cu. It can be seen from the figure that the absorption coefficient decreases up to wavelength 620 nm and then increases up to 750 nm and again decreases from 780 nm, depicting two regions of optical transitions. Similar type of results was reported by Shinde et. al.[17].

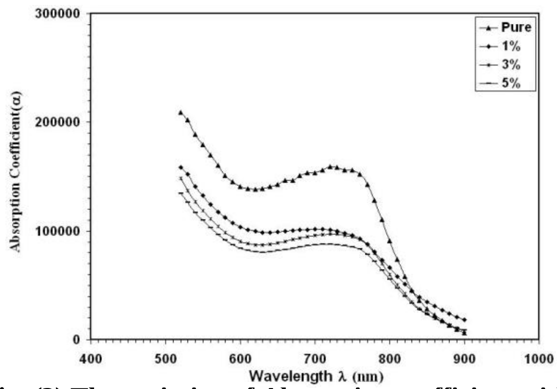

Fig. (3) The variation of Absorption coefficient with wavelength for Co2O3:Cu thin films.

From the transmittance data and according to Tauc [18] relation, (□h□)2 versus incident photon energy (h□), plots were obtained. The graphs are represented in Fig. (4) As cobalt oxide is a direct transition semiconductor, the estimated band gap energy values are found to be 1.48 and 1.95 eV for the undoped Co2O3 thin films, which is in consistent with the band gap energy of cobalt oxide films reported earlier for spray pyrolysis method [17]. After doping and increasing the doping concentration to 5% of Cu, the band gap energy values were increased to 1.55 and 2.05 eV. It can be notice from fig.4 that all the films have two different regions was put in evidence, corresponding to different phases. It was proved that Eg values, corresponding to these phases.the result of these thin films show the possibility of a threshold degeneracy of the valence band at k=o at the obtained energies[19] The activation energy calculated from the slopes of graphs represents the location of trap levels below the conduction band.

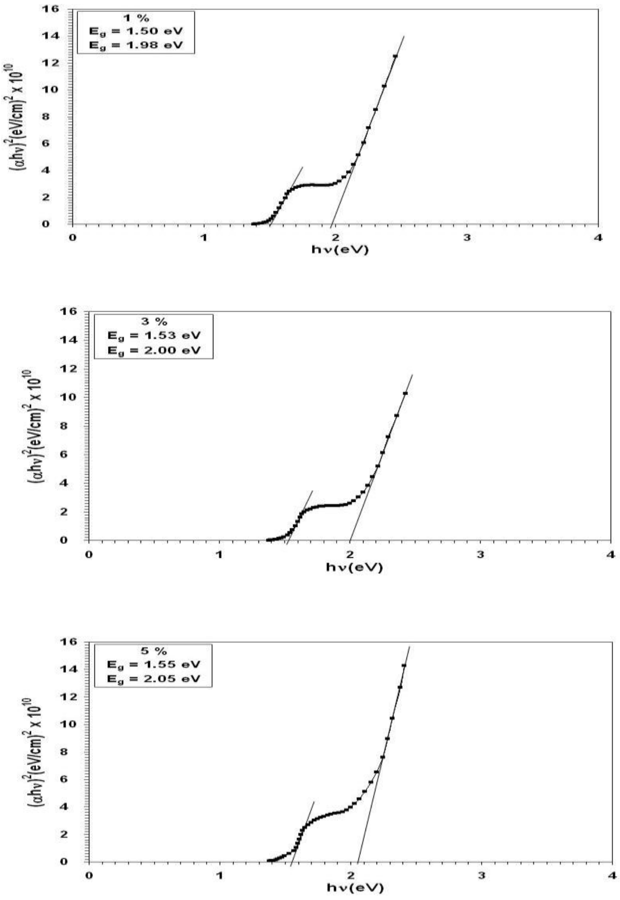

Fig (4) $(\alpha h\upsilon)^2$ for Co_2O_3:Cu thin films versus photon energy.

The refractive index is an important parameter for optical materials and applications. Thus, it is important to determine optical constants of the films. The refractive index of the films was determined from the following relation [20].

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

Where k is the extinction coefficient ($k=\alpha\lambda/4\pi$). The n and k values dependence of wavelength are shown in fig. (5) and (6) respectively. As seen in these figures, the n and k values decrease with increasing the doping concentration of Cu. Such behavior corresponds to the density of absorbing centers such as impurities absorption, excitation transition, and other defects in the crystal lattice dependent on the conditions of sample preparation.

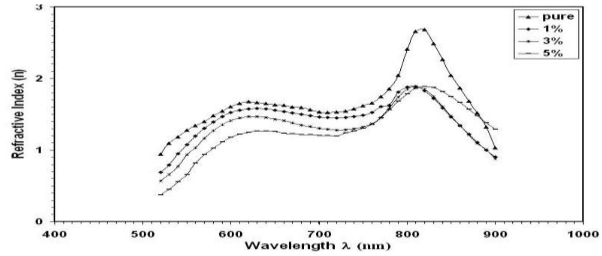

Fig. (5) The variation of refractive index with wavelength for Co2O3:Cu thin films.

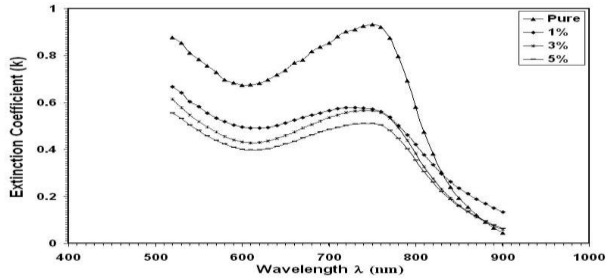

Fig. (6) The variation of extinction coefficient with wavelength for Co2O3:Cu thin films.

The dielectric constant is defined as ε (ω) = ε1(ω) + iε2 (ω) , real and imaginary parts of the dielectric constant are related to the n and k values. The ε1 and ε2 values were calculated using the formulas [21]:

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

$$\varepsilon_2 = 2nk \qquad \text{-- (5)}$$

The ε1 and ε2 values dependence of photon energy are respectively shown in fig. (7) and (8). The ε1 values are higher than that of ε2 values. It is seen that the ε1 and εi values decrease with increasing the doping concentration with Cu.

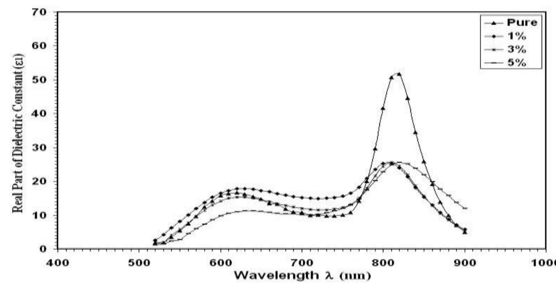

Fig. (7) The variation of real part of dielectric constant with wavelength for Co2O3:Cu thin films

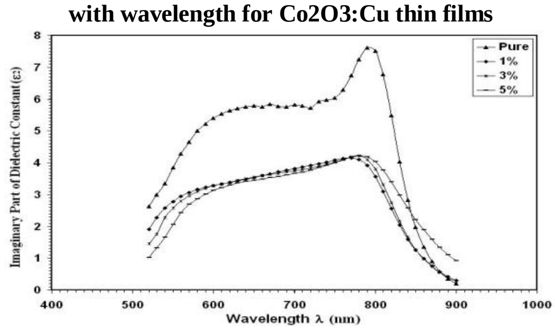

Fig. (8) The variation of imaginary part of dielectric constant with wavelength for Co2O3:Cu thin films

Conclusion

Co_2O_3 and Co_2O_3:Cu thin films were prepared by using chemical spray pyrolysis technique. Both doped and un-doped samples were characterized. Optical band gap increased due to doping. Similarly optical transmittance was affected for moderate doping. The extremely small values of the reflectance and the absorbance in the visible region offered the most promise for realizing visible laser diodes (LD) and efficient light–emitting–diode (LED) displays, by using Co_2O_3:Cu thin films in these devices.

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تحضير وتوصيف أغشية Co2O3 و Co2O3:Cu الرقيقه

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الخلاصه

تم ترسيب أغشية رقيقة من أوكسيد الكوبلت Co2O3 وأوكسيد الكوبلت المشوب بالنحاس Co2O3:Cu على قواعد زجاجية بأستخدام تقنية التحلل الكيميائي الحراري. تم دراسة الخواص البصرية لأغشية Co2O3 كدالـه لنسب التشويب بـCu. تم تأكيد التغييرات الحاصله في فجوة الطاقة البصريه بعد التشويب.حيث أزدادت Eg من 1.48 و1.95eV لغشاء أوكسيد الكوبلت غير المشوب الى 1.55 و2.05eV لغشاء أوكسيد الكوبلت المشوب بنسبة 5% من النحاس. تم دراسة تأثير التشويب على المعلمات البصريه لأغشية Co2O3 الرقيقة مثل: النفاذية، الانعكاسية، معامل الامتصاص, معامل الأنكسار، معامل الخمود، ثابت العزل الحقيقي وثابت العزل الخيالي.