Effect of Cu doping on optical properties of Mn_2O_3 films prepared by spray pyrolysis

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Abstract

Thin films of Mn_2O_3 doped with Cu have been fabricated using the simplest and cheapest chemical spray pyrolysis technique onto a glass substrate heated up to 250 ^oC. Transmittance and absorptance spectra were studied in the wavelength range (300 -1100) nm. The average transmittance at low energy was about 60% and decrease with Cu doping, Optical constants like refractive index, extinction coefficient and dielectric constants (ε_r), (εi) are calculated and correlated with doping process.

Key words

Thin films,

optical properties,

spray pyrolysis

technique.

Article info

Received: Dec. 2011

Accepted: May. 2012

Published: Oct. 2012

تأثير التشويب بالنحاس على الخواص البصرية لأغشية أوكسيد المنغنيز المحضرة بطريقة التحلل الكيميائي الحراري

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الخلاصة

حضرت أغشية رقيقة من اوكسيد المنغنيز و اوكسيد المنغنيز المشوب بالنحاس بطريقة التحلل الكيميائي الحراري البسيطة والواطئة الكلفة على قواعد زجاجية مسخنة لغاية 250 ^oC. سجلت قيم الامتصاصية والنفاذية في مدى الأطوال الموجية nm (300-1100). كان معدل النفاذية عند الطاقات الواطئة بحدود 60% ويقل بالتشويب CuO، الثوابت البصرية كمعامل الانكسار، معامل الخمود و ثوابت العزل (ε_r),(ε_i) حسبت وربطت مع نسبة الاشابة.

Introduction

Semiconductor thin films have produced and studied in polycrystalline form for many decades. Indeed, most new semiconducting materials produced in polycrystalline form before techniques developed for producing single crystals[1].

(Mn_2O_3) transparent conducting oxide is a n-type semiconductor with direct band gap around 3.2 eV that is used in Gas Sensors Devices, optical memory, and as solar energy converters [2]. Spray pyrolysis is a useful alternative to the traditional methods for obtaining manganese oxide thin films, because of its simplicity, low cost and minimal waste production, the spray pyrolysis process allows the coating of large surface and it is easy to include in an-industrial production line. This technique is also compatible with mass production systems [3] . Mn_2O_3 has been prepared by various methods such as chemical vapor deposition [4], sol- gel method [5], vacuum thermal evaporation [6], and chemical spray pyrolysis [7]. The aim of this work to fabricated $(Mn_2O_3)_{1-x}(CuO)_x$ thin films and studied the effect of CuO doping on the optical properties of Mn_2O_3 thin films prepared by chemical spray pyrolysis deposition technique on glass substrate at a temperature of (250)°C.

Experimental details

Thin films of $(Mn_2O_3)_{1-x}$ $(CuO)_x$ have been prepared by chemical pyrolysis technique. The spray pyrolysis was done with a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at temperature of 250°C, the chemical solution was achieved by adding 1.979 gm of $(MnCl_2.4H_2O)$ on 100 ml of deionized water , and adding of 1.704 gm of $(CuCl_2.2H_2O)$ on 100 ml, achieved by taking 0.1 M of dissolve in distilled water , homogeneous mixture was achieved by using magnetic stirrer. The optimized conditions were the following parameters, spray time (15 sec) , average deposition (10 cm^3/min) , distance between nozzle and substrate (30 $\pm$1cm) and the carrier gas (filtered compressed air) was maintained at a pressure of 10^5 Nm^{-2} . Thicknesses of the samples were measured using the weighting method, The accuracy of thickness measurements was 200 nm, with x takes the values 0.03, 0.05. Optical transmittance and absorbance were recorded in the wavelength range (300-1100nm) using UV-visible spectrophotometer (Shimadzu Company Japan).

Results and discussions

Fig.1 shows the spectral distribution of transmittance for $(Mn_2O_3)_{1-x}(CuO)_x$ films in the wavelength range (300-1100) nm.

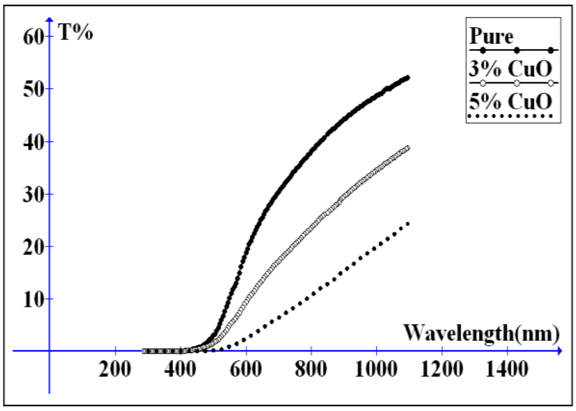

Fig.1: ***Optical transmittance versus*** **wavelength of $(Mn_2O_3)_{1-x}(CuO)_x$ films.**

In general the transmittance decreases when the doping concentration increases, the average transmittance of $(Mn_2O_3)_{1-x}(CuO)_x$ thin films in (600-1100) nm range increases. From 55% for pure sample to about 25% for sample doped with 3% CuO. Near the fundamental absorption edge all Films show a very sharp absorption edge. The transmittance is expected to depend mainly on three factors, [7] i.e., (1) oxygen deficiency, (2) surface roughness; surface scattering reduces the transmittance which depends on the grain size, and (3) impurity centers. We can assume that the higher transmittance of the film with a decrease of doping concentration is mainly due to the impurity centers.

The behavior of reflectance curves of all sample in Fig.2 can be discussed easily by divided these curves into two spectral regions before 500 nm and after it; in the first one the doping causes increasing reflectance, but in second one reflectance decreases with doping. The increase in reflectance for wavelength shorter than 500 nm indicates increased free carriers absorption and consequently higher carrier concentration for the CuO-doped film [8].

The refractive index of the thin films can be determined from the following equation [9]:

$$R= \{(n-1)^2+k^2\} / \{(n+1)^2+k^2\} \quad (1)$$

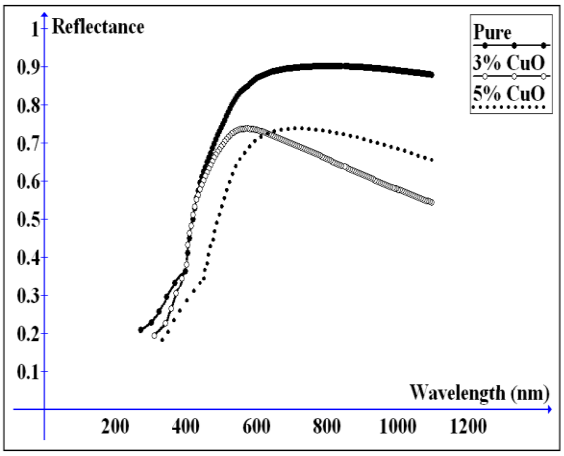

Figure (2) Reflectance versus wavelength of $(Mn_2O_3)_{1-x}(CuO)_x$ films.

where k ($k=\alpha\lambda/4\pi$) is the extinction coefficient[10], Fig.3 Shows the calculated values of the refractive indices for the $(Mn_2O_3)_{1-x}(CuO)_x$ films. This figure reveals a tendency for a decrease in refractive index with doping. The variation of (n_o) in investigated frequency range shows that some interactions take places between photons and electrons. (n_o) changes with variation of the photon

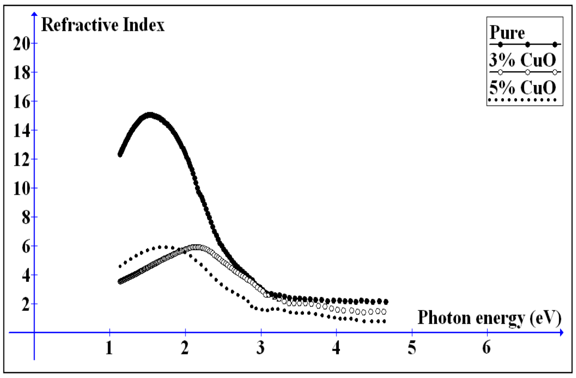

Fig.3: Refractive index versus Photon energy of $(Mn_2O_3)_{1-x}(CuO)_x$ films.

energy of the incident light beam are due to these interactions [11].

Fig.4 shows the (K_o) as a function of Photon energy, the behavior of (K_o) is (K_o) film (pure) < (K_o) doped (3,5%) because it has smaller absorption coefficient.

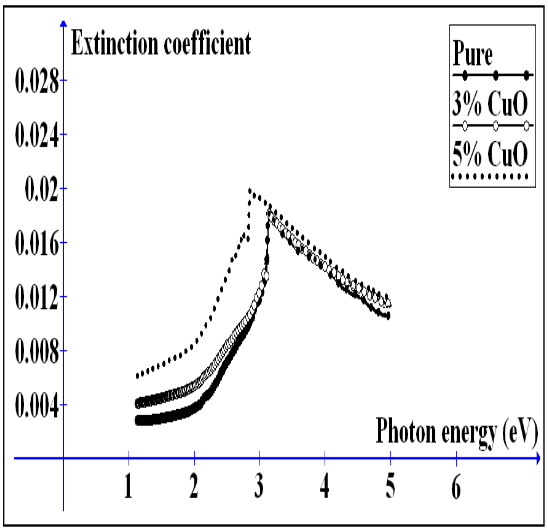

Fig.4: Extinction coefficient versus Photon energy of $(Mn_2O_3)_{1-x}(CuO)_x$ films.

The variation of the real (ε_r) and imaginary (ε_i) parts of the dielectric constant values versus Photon energy at doping concentration (Pure, 3%, 5%) are shown in Figs. 5 and 6. The behavior of ε_r is similar to that of refractive index because the smaller value of k^2 compared with n^2:

$$\varepsilon_r = n^2 - k^2 \quad (2)$$

While ε_i is mainly depends on the k values, which are related to the variation of absorption coefficient:

$$\varepsilon_i = 2nk \quad (3)$$

It is found that ε_r and ε_i decreasing with increases of doping. The real and imaginary parts of the dielectric constant indicate the same pattern and the values of real part are higher than imaginary part[12].

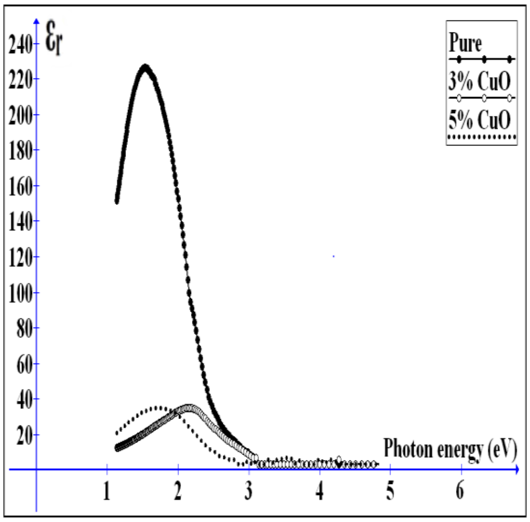

Fig. 5: Real Part Dielectric Constant versus Photon energy of(Mn_2O_3) $_{1-x}$(CuO) $_x$ films.

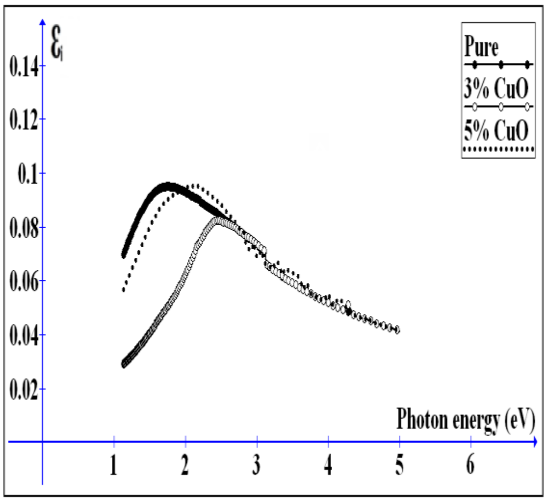

Fig.6: Imaginary Part Dielectric Constant versus Photon energy of(Mn_2O_3) $_{1-x}$(CuO) $_x$ films.

Conclusions

(Mn_2O_3) $_{1-x}$(CuO) $_x$ thin films were successively prepared by chemical spray pyrolysis. The doping affect of Mn_2O_3 on the optical properties were investigated. Optical measurements show that the film possesses transmittance over 60% in the visible region. The reflectance (R), refractive index($n_\circ$), and real (ε_r) and imaginary (ε_i) parts of the dielectric constant decreases with doping , and Extinction Coefficient (k) increases with doping.

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