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Studying the Effect of Doping in Some Physical Properties of Copper Oxide Thin Film

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ABSTRACT

Thin films of pure copper oxide and doped copper oxide have been prepared by chemical spray pyrolysis. The films were doped with Manganese (Mn) by 2% & 4% ratios. X-ray diffraction show that all prepared films have The two strong peaks of the CuO films appear at 35.74^o and 38.95^o which correspond to diffraction from planes (-111) and (111) respectively. The absorption coefficient was calculated from transmission spectra range (450 – 950 nm) , the absorption coefficient increase by doping, the allowed direct optical band gab energy has been evaluated from absorption coefficient and the energy band gab increased by doping.

Keywords: Thin film, Pyrolysis, Copper Oxide, Absorption Coefficient

دراسة تأثير الاشابة على بعض الخصائص الفيزيائية لغشاء اوكسيد النحاس

الخلاصة

تم تحضير الأغشية الرقيقة لأوكسيد النحاس النقية والمشابة بطريقة الرش الكيميائي. تم تشويب الاغشية بالمنغنيز بالنسب 2% و 4%. حيود الاشعة السينية اظهر ان جميع الأغشية المحضرة تتبلور عند الزاويتين 35.74^o و 38.95^o والتي تقابل مستويات حيود (111-) و (111) على التوالي. تم حساب معامل الامتصاص من طيف النفاذية للمدى (450 – 950 nm)، يزداد معامل الامتصاص بالاشابة، كذلك تم حساب فجوة الطاقة البصرية للانتقال المباشر المسموح بالاعتماد على معامل الامتصاص واتضح ان فجوة الطاقة تزداد بالاشابة.

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INTRODUCTION

Black copper oxide (CuO) appears to be a good candidate as a solar selective coating because it is inexpensive and easy processable. Furthermore, it was demonstrated to have the desirable optical properties for solar photothermal conversion, such as a high absorptance ($\alpha \geq 0.90$) and low emittance ($\varepsilon \leq 0.2$) .However, earlier studies demonstrated that CuO was susceptible to degradation , which has hindered for a more extended application (1).

CuO has received much attention due to a wide range of potential applications such as photoconductive, catalysis, superconductive devices and gas sensor (2, 3)

Copper oxide- based materials are of interest on account of their potential uses in many technological fields. CuO and Cu_2O materials are known to be p- type semiconductors in general and hence potential useful for constructing junction devices such as pn junction diodes. Moreover, their use in power sources has received special attention. Thus, in addition to photovoltaic devices (4).

Recently, it was studied as a novel anode material with high capacity and good capacity retention meeting the needs of further development of lithium ion batteries since it is nontoxic and abundant in nature (5)

Spray pyrolysis is useful tool for large – scale or small- scale production of particles with controlled particle size because the final product properties can be controlled through the choice of precursor and solution concentration or by changing aerosol decomposition parameters. Generally, in a spray pyrolysis process reaction temperature and carrier gas composition are basic operating variables.(6)

J. Morales & others were prepared CuO thin films by spray pyrolysis of aqueous copper acetate solution at temperatures over 200 – 300^{o}C range. The heating temperature was found to have little limited effect on the particle size and thickness of the films which however increased significantly increasing time.(4)

F.Atay & others were deposit undoped & Mg doped (at the Mg percentages of 1, 3 & 5) copper oxide films at substrate temperature of 300 ^{o}C by ultrasonic spray pyrolysis technique. The spraying solution was prepared by dissolving $Cu(CH_3COO)_2.2H_2O$ (0.1M) & $Mg(CH_3COO)_2.2H_2O$ (0.1M) in distilled water. Undoped films have amorphous structure & high background intensities. But, Mg doped copper oxide films have polycrystalline structures, & background intensities decreased. Absorption coefficient increase for 1% & 3% Mg thin films. The optical direct band gaps increase for 1% & 3% Mg thin films.(7)

The aim of this work is to observe the effect of Mn incorporation on the optical, structural and of pyrolysis sprayed copper oxide films and to investigate the feasibility of the films for solar cell devices as absorbing layers and gas sensor.

EXPERIMENTAL DETAILS

Firstly, a spray pyrolysis method was used to prepare the CuO thin film. $CuCl_2.2H_2O$ in the form of aqueous solution of concentration 0.1 M was used as precursor.

This was sprayed pneumatically over a heated clean glass substrate using compressive air as carrier gas in normal air ambient.

Substrate temperature was 523K with 1ml/min of spray rate could be appropriate for good quality polycrystalline films. The distance between the nozzle and the substrate was maintained at 25 cm.

Secondly, Mn doped CuO thin films were deposited on glass substrate at a fixed substrate temperature 523K using a spray pyrolysis method. The precursor solution was prepared by dissolving 0.1M of CuCl2.2H2O and different volume rate of 0.1M of MnCl2.4H2O (2%,4%). The solution flow rate was kept at 4ml.min^{-1}, & the gas flow rate was kept at 28 L.min^{-1}.(4,7)

It is expected that the various concentration of Mn in CuO may affect the structural, optical properties of the films.

The films thickness was measured via laser interferometer method. All films had nearly equal thickness (200 and 300) nm.

$$t = \frac{l}{2} \times \frac{\Delta x}{x} \qquad ....(1)$$

Where : t : thickness of films, λ : the wavelength of laser, Δx ; the difference between the light and dark fringes ,x: light fringes

after thickness is measured, structural Tests conducted on thin-films by using X-Ray diffraction to make sure Type of thin films material and to predict the diffraction planes.

As well as optical properties were measured to deduce the absorption coefficient, extinction coefficient and the energy gap of the prepared films.

The structural studies of thin films were analyzed using x-ray diffractometer (Shimadzu XRD-7000) with CuKα radiation (Rigaku model, λ=1.5406 Å).

Optical measurements on the thin films are carried out using a recording uv-visible double beam spectrophotometer (Phoenix-2000v UV-VIS spectrophotometer) in the range (450-950)nm. Absorption coefficient is determined by the well- known relation ship :

$$\alpha = 1/d \ln 1/T \qquad .... (2)$$

Where d and T represent the film thickness and transmission coefficient, respectively.(8)

The extinction coefficient (k) was calculated from the relation :

$$k = \alpha\lambda/4\pi \qquad .... (3)$$

where λ represent the wave length. (8)
The spectra were analyzed by plotting $(\alpha h\nu)^2$ vs hν, based on eqation (2)

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad \ldots (4)$$

Where α is absorption coefficient, A constant (independent from ν) and n the exponent that depends upon the quantum selection rules for the particular materials.(9)

RESULTS AND DISCUSSION

XRD investigation

X-ray diffraction (XRD) patterns of the films prepared at substrate temperatures (523K) with thickness (300) nm. The graph between 2θ versus diffracted ray intensity is shown in figure (1)

The two strong peaks of the CuO films appear at 35.74 and 38.95 which correspond to diffraction from planes (-111) and (111) respectively were indentified using standard (ASTM) XRD pattern of the pure CuO material. These results agree with P.samarasekara.(3)Structural analysis results demonstrate that the pure CuO on glass substrate is of high a crystalline structure with a dominant in (-1 1 1) & (1 1 1) orientations.

The film of Mn doped Copper oxide with concentration (2% ,4%) can be analyzed By X-ray diffraction, see figures (2,3) . Peak intensities, and hence crystallinity increased with increasing the concentration of Mn.

Optical measurement

The transmittance spectra of the thin films were obtained in the range (450-950) nm. The values for the transmittances of CuO, CuO:2%Mn, CuO:4%Mn samples at 950 nm were 76.9%, 73%, 67%, respectively, at 450 nm the transmittances were 14.5%, 1.6%, 2% respectively As can be seen with increasing the dopant concentration, the transmittance of the films is decreased. The films with lower Mn concentration have higher transmittance. As shown in figure (4), it was determined that all films behaved as transparent materials at about (800-950) nm wavelength range.

These results agree with **F. Atay et al.,** who found that optical transmissions of the Copper oxide films were approximately 60% in the visible region, and these high transmission values decreased for Mg incorporated copper oxide (at 1 %) and Mg incorporated copper oxide (at 3 %) films . these results explained due to the effect of Mg incorporation on the transmission of the copper oxide films may be due to the structural properties, surface smoothness and defect density.(7)

The calculated absorption coefficient is found to increase with increase the Mn ratio as shown in figure (5) , the behavior of absorption coefficient can demonstrated in figure (6) at 450 nm & 950 nm.

In figure (7) we can see the behavior of extinction coefficient (k) wavelength (λ).

This indicates a likely dependence of the optical transmittance, structure as well as stoichiometry of the deposited films on the parameters during deposition & doping rates.

In order to better understand the changes in optical transmittance as a function of doping rate, we computed the direct optical band gap values using results based on the optical transmission measurements in the wavelength range (450-950) nm, the band gap values are obtained by extrapolating the linear portion of the plots of $(\alpha h\nu)^2$ versus $(h\nu)$ to $(\alpha h\nu)^2 = 0$, The variations are given in figure (8), The Mn doped CuO thin films have higher band gap, these results due to increased in crystallinity.

CONCLUSIONS

Undoped and Mn doped CuO thin films were prepared by spray pyrolysis. The concentration of Mn is (2%,4%). It is clearly shown from X-ray patterns that the doped films have higher Peak intensities (crystallinity) than the pure films. Absorption coefficient increase with increasing the concentration of Mn. observed value of band gap of doped films is greater than the pure film band gap (2.1eV) of CuO films.
The transmittance of films decreases with increases the concentration of Mn.

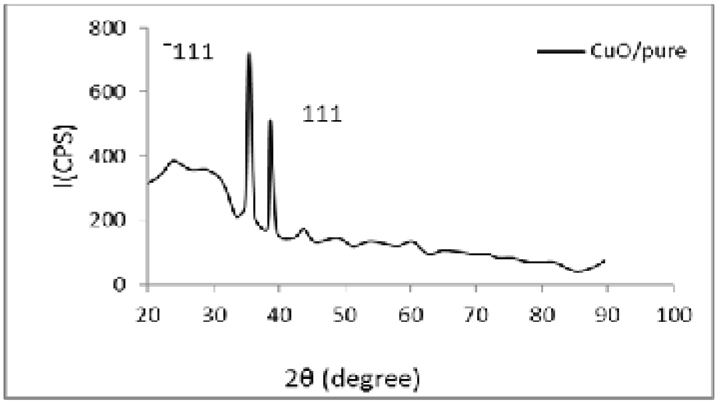

Figure (1) XRD pattern for CuO thin film.

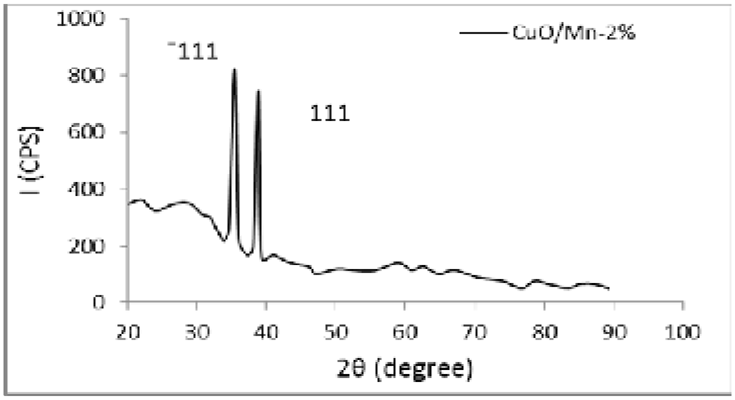

Figure (2) XRD pattern for CuO doped 2% of Mn.

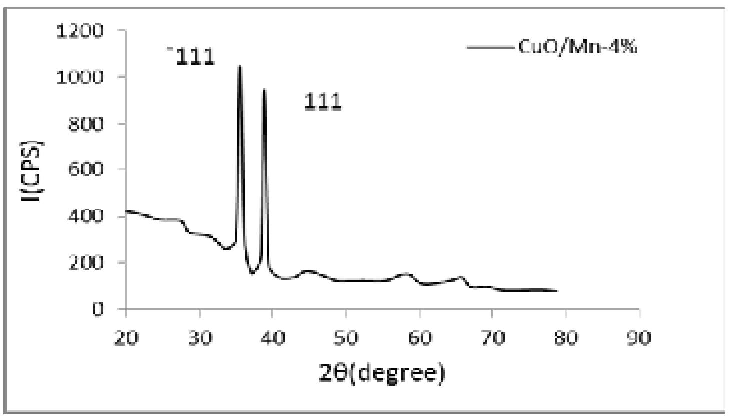

Figure (3) XRD pattern of CuO doped 4% of Mn.

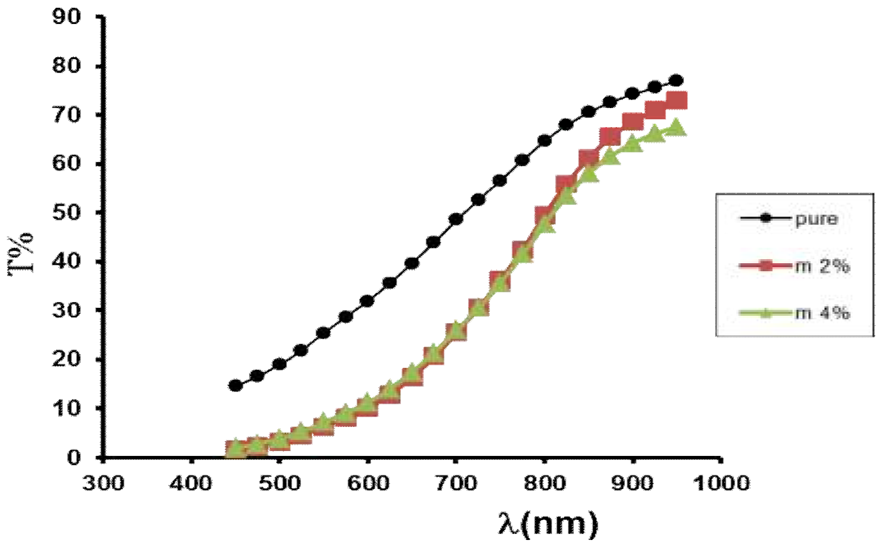

Figure (4) the transmission spectra of the CuO thin films

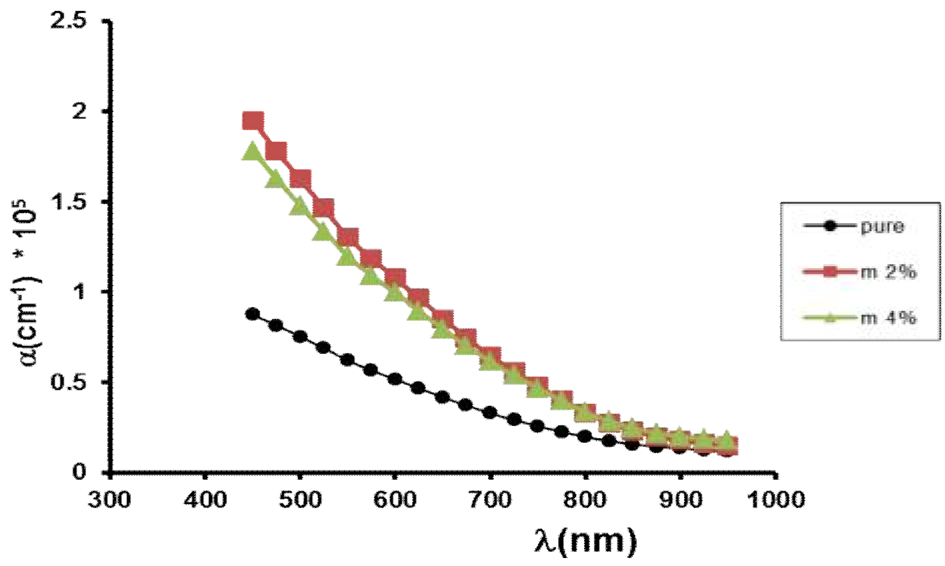

Figure (5) the absorption coefficient spectra of the CuO thin films

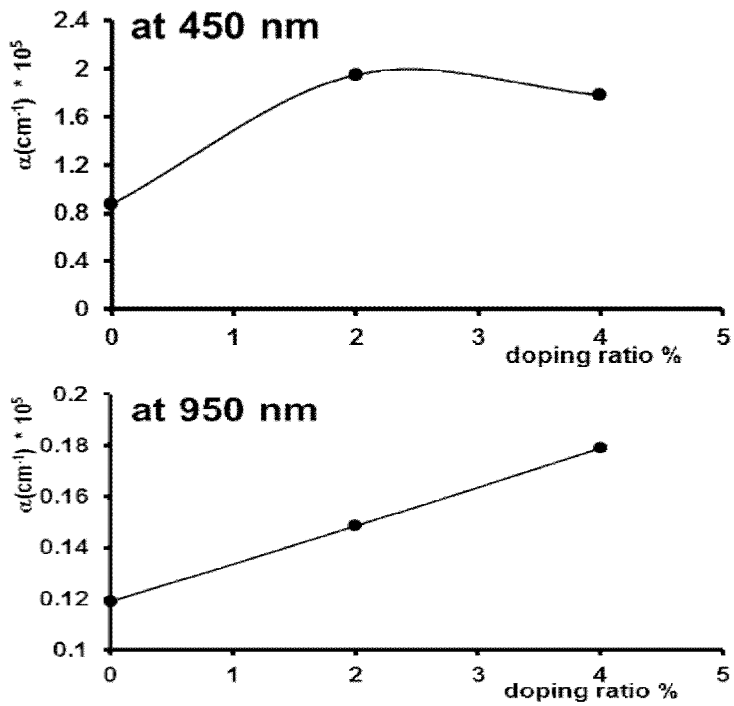

Figure (6) The behavior of absorption coefficient.

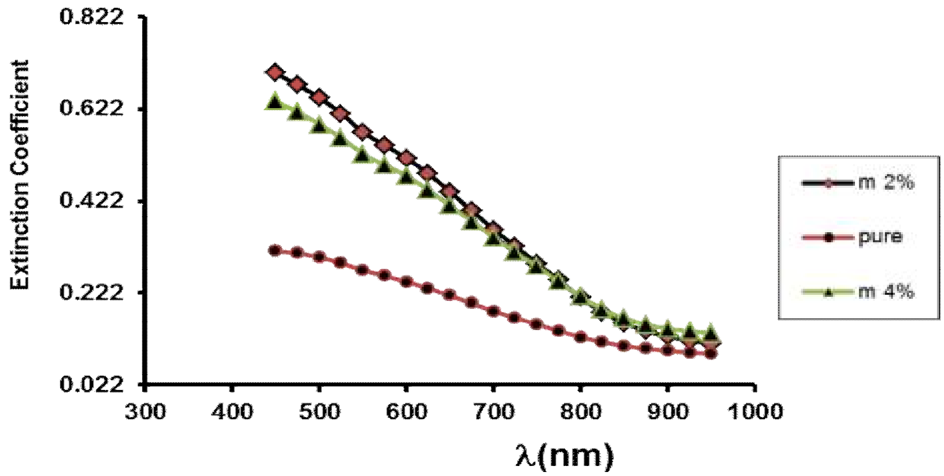

Figure (7) The behavior of Extinction coefficient.

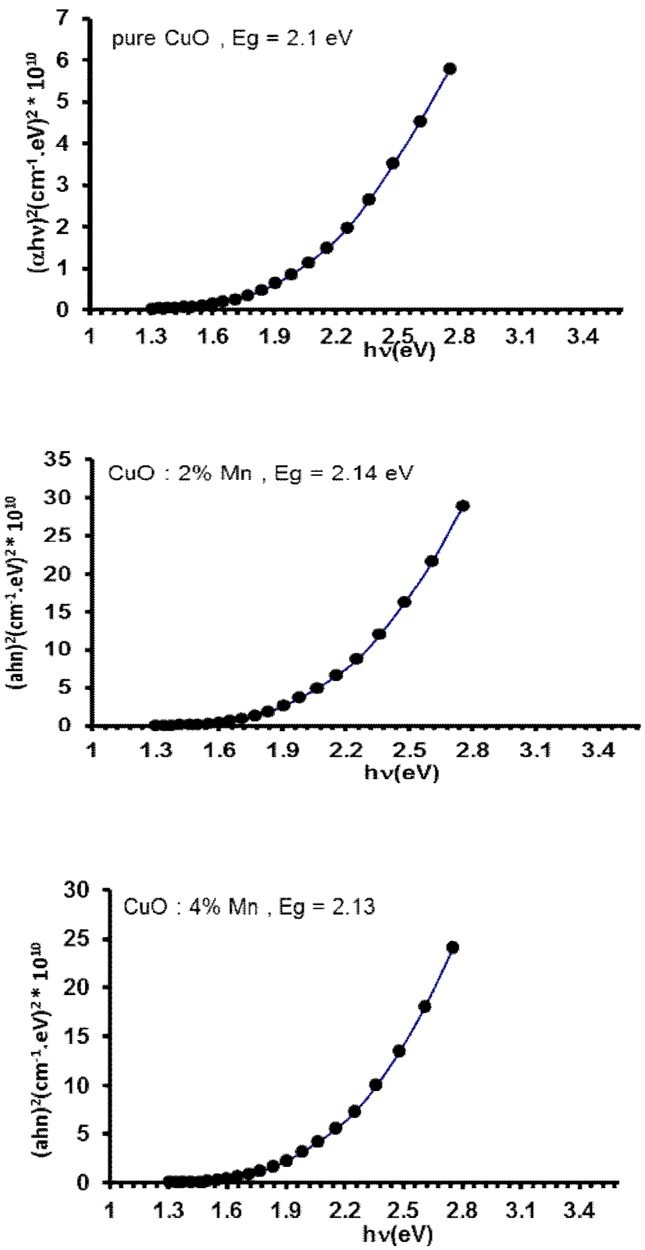

Figure (8) The plots of $(\alpha h\nu)^2$ versus (hν) of the CuO thin films

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