Optical Properties of CUO Thin Films with Different Concentration by Spray Pyrolysis Method

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ABSTRACT

In this work, CuO thin films were prepared by spray pyrolysis method using different concentration of $CuCl_2$.$2H_2O$. X- ray diffraction (XRD) and UV-VIS transmission spectroscopy were employed to characterize the structure and optical properties of prepared films.XRD patterns show that the films are polycrystalline and monoclinic with (-111) and (111) crystalline orientations. The optical band gaps (2.05 to2.42eV) ,with high absorption coefficient change from $(3*10^5 - 1*10^5)$ cm^{-1} at 0.3M concentration , and excitation coefficient change from (0.85 – 0.7). These constants are found to be oscillatory in nature, which are attributed to the particular structure of films and their concentration.

Keywords: Cuo Films, Spray Pyrolysis, Optical Properties, Structure Properties.

الخصائص البصرية للأغشية الرقيقةCUOبتراكيز مختلفة بطريقة الرش الحراري

الخلاصه

في هذا البحث، تم تحضير غشاء اوكسيد النحاس بطريقه الرش الكيميائي الحراري باستخدام تراكيز مختلفه من المحلول المائي لملح كلوريد النحاس . حددت الخصائص التركيبه والبصريه للاغشيه المحضره باستخدام حيود الاشعة السينية والتحليل الطيفي للاشعه المرئيه وفوق البنفسجيه. تبين من نموذج حيود الاشعه السينيه ان الاغشيه ذات تركيب احادي و متعدد التبلور عند الاتجاهية البلورية (111-)و (111) . حددت فجوه الطاقه (2.42-2.05eV) و معامل الامتصاص عالي يتراوح بين $(3*10^5 - 1*10^5)$ cm^{-1} عند تركيز 0.3M ومعامل الخمود يترواح بين (0.7 – 0.85). وجد ان هذه الثوابت ذات طبيعيه متذبذبه والتي تعزى الى طبيعه الاغشيه من حيث التركيب والتركيز.

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INTRODUCTION

Copper oxides are semiconductors that have been studied for several reasons such as the natural abundance of starting material copper (Cu); the easiness of production by Cu oxidation; their non-toxic nature and the reasonably good electrical and optical properties by Cu_2O [1]. Copper forms two well-known oxides: tenorite (CuO) and cuprite (Cu_2O). Both the tenorite and cuprite were p-type semiconductors having band gap energy of 1.21 to 1.51 eV and 2.10 to 2.60 eVrepectively [2]. CuO have emerged as potentially powerful materials in various technological applications such as catalysis, magnetic storage media, batteries, solar energy conversion, gas sensing and field emission [3-7]. The films have been prepared by various techniques such as sputtering [8], chemical vapor deposition [1],spray pyrolysis [9] , pulsed laser deposition [10] thermal oxidation [11], electro deposition [12].

In this study, CuO thin films were prepared by a simple and cost effective chemical spray pyrolysis with different concentration at 250 C^o, to study the effect of changing the concentration on the structure and optical properties by using X-Ray diffraction and UV-VIS spectroscopy.

EXPERIMENTAL WORK

CuO thin films prepared by sprayingat different concentration (0.1, 0.2 & 0.3 M). Aqueous solutionof $CuCl_2.2H_2O$(Cupric chloride dehydrate, ~ 97% (RT), Fluka AG.) in distilled water where are deposited onto glass substrate at deposition temperature of 250 ± 10 C^o.The spray rate was maintained via compressed air carrier gas of the order ~ 3 ml/min. The nozzle was kept 30 cm apart from the substrate. To avoid excessive cooling of substrates, successive spraying process was used with time period of 3 sec between successive bursts. Substrate temperature was controlled by thermocouple fed to a temperature controller. The temperature on top side of the substrate is measured by placing a thermocouple on a reference glass substrate kept near the coating substrate so as to measure the exact temperature. Film thickness measured by laser interference according to fezo fringes was 0.2µm.

The crystal structure of thin film were determined by x- ray diffraction using the (Philips model, PW/ 1710) diffractometer , with monochromatic Cu Kα radiation (λ = 0.15418 nm at 40 KV and 30 mA). Optical analysis was done by optical transmission data were obtained with an UV/ VIS Shimadzu 3101 PC Spectrometer in the (200 to1100) nm range.

RESULTS AND DISCUSSION

Figure (1) shows the x-ray diffraction pattern of films prepared at different concentration of aqueous solution. The XRD patterns exhibit peaks at $2\theta \approx 32.5^\circ$, 35.68° & 38.78° corresponding to the (110), (-111) and (111) reflections of the CuO phase. The peak near $2\theta = 25.35^\circ$ which match reflection from (021) plane of Cu $(OH)_2$ phase. These data are compared with ICDD data. Peak intensities and increased with increasing concentration, the sharpness of the peaks shows that the films are polycrystalline and monoclinic in nature, these result were good agreement with literatures [9, 13, 14].

The optical transmissions of sprayed CuO thin films were measured at room temperature using UV-VIS Spectrometer. The transmission T was recorded in the range of 300 nm to 1100 nm of the incident beam as shown in Figure (2). The transmission in the visible region is found to increase with decreasing mole concentration of the solution. The maximum transmission behavior is observed for lower mole concentration and comparatively lower values are recorded for other concentrations. This is attributed to the increase of the film dens with increasing mole concentration of the films.

From the transmission data, the absorption coefficient α was calculated using Lambert law [15]:

$$\alpha = \frac{1}{t}\, In\left(\frac{1}{T}\right) \qquad \dots (1)$$

Figure (3) show the Variation of absorption coefficient of CuO films prepared at different concentration, the absorption ($\alpha \geq 10^5$ cm^{-1}) is related to direct band transitions [16].The energy gaps E_g of films were estimated using Tauc relation [17]:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \qquad \dots (2)$$

Where E_g is the band gap energy, A is constant and $h\nu$ is the photon energy. Figure (4) shows the variation of $(\alpha h\nu)^2$ as the incident photon energy ($h\nu$) of CuO films at different molar concentration. The optical band gap was determined by extrapolating the linear portion of this plot at $(\alpha h\nu)^2 = 0$ which indicates that the direct allowed transition dominates in the CuO films. The estimated E_g values are in the range 2.05 to 2.42 eV these results was agreement with reference [18]. The energy gap were decrease with increasing film concentration, this range is suitable to use this material for solar cell application.

The extinction coefficient k can be calculated by the following equation [17]:

$$K = \frac{\alpha\, \lambda}{4\, \pi} \qquad \dots (3)$$

The variation of extinction coefficient with wavelength are shown in Figure (5),the excitation coefficient related to attenuation value of electromagnetic wave where its passed through the medium, so that the high value of short wavelength related to the loss incident energy in absorption process or due to loss the wave in electron transit between the energy level but this result is revere in long wavelength this is may be related to appear another absorption process such as absorption by charge carrier. Also the excitation coefficient was increase with increasing films concentration.

CONCLUSIONS

CuO thin films prepared by spray pyrolysis method have been characterized using XRD and UV-VIS spectra to study the effect of solution concentration on structural and optical properties such as transmission; optical band gap, absorption coefficient and excitation coefficient. The structure of the films were monoclinic with (-111) and (111) crystalline orientations. The transmittance increases with decrease in concentration of the films. The optical band gap was also found to varyfrom2.05to 2.42eV, thus making the films suitable for solar cell applications. Variations in optical properties with wavelength are found to be oscillatory in nature, which are attributed to the particular structure of the films and their concentration.

REFERENCE

[1]. Johan, M. R. M. S. M. Suas, N. L. Hawar, H. A. Ching "Annealing Effects on the Properties of Copper Oxide Thin Films Prepared by Chemical Deposition" Int. J. Electrochem. Sci., 6, p. 6094 – 6104 **(**2011).

[2].Sekhar C.R., Solar energy mater. 68, 307 (2001).

[3]. Muhammad, E.N. R. Irmawati, A.H. Abdullah, Y.H. Taufiq-Yap and S.B. Abdul Hamid "effect of number of washing on the characteristics of copper oxide nanopowders"Malaysian J.Analy. Sci., Vol 11, No 1, p. 294-301 (2007).

[4]. Zhou, K. R. Wang, B. Xu, Y. Li, Nanotechnology 17, p.3939 (2006).

[5]. Bao, X.P. Gao, J.C. G.L. Pan, D.Y. Song, J. Phys. Chem. B 108, p.5547 (2004).

[6]. Xiao,H.M. S.Y. Fu, Y.Q. Li, G. Yang, Eur. J. Inorg. Chem. 14 p.1966 (2007).

[7]. Zhao, T. Yu, X. Z.X. Shen, Y.H. Su, J. Cryst. Growth 268 ,590 (2004).

[8]. Ogwu,A.A. T.H. Darmab, E. Bouquerel" Electrical resistivity of copper oxide thin films prepared by reactive magnetron sputtering" j. Achiev. Mater. Manuf.Engin., vol.24 ,ISS 1,p.172 (2007).

[9]. Kumar, A. S. K. Perumala, P. Thirunavukkarasu "Structural and optical properties of chemically sprayed CuO thin films" Optoelec.Advan. Mater. –Rapid Commun. Vol.4, No. 6, p.831 – 833 **(2010).**

[10]. Kawwam, M. F. Alharbi, A. Aldwayyan, J. Kim, and K. Lebbou" Morphology Optimization of PLD-grown CuO Films for Solar Energy Devices" First Euro-Mediterranean Conference on Materials and Renewable Energies (EMCMRE-1) 21-25 November **(2011).**

[11]. Samarasekara, P. "Characterization of low cost P-Cu2O/N-CuO junction" Physics, No.2 (4), p.3 **(2010).**

[12].Y Li, J Liang, Z Tao and J Chen, Mater. Res. Bull, 43, p.2380 **(2008).**

[13]. Morales, J. L. Sanchez, F. Martin, J. R. Ramos-Barrado, M. Sanchez" Nanostructured CuO thin film electrodes prepared by spray pyrolysis: a simple method for enhancing the electrochemical performance of CuO in lithium cells" Electrochimica Acta 49, 4589–4597 **(2004)**.

[14]. Zhao, B. P. Liu, H. Zhuang, Z. Jiao, T Fang, W Xu, B. Lu, and Y Jiang "Hierarchical self-assembly of microscale leaf-like CuO on graphene sheetsf or high-performance electrochemical capacitors" J. Mater. Chem. A ,1, p. 367-373 **(2013).**

[15]. Banwell, C. N. "Fundamentals of Molecular Spectroscopy" MCGRAW-Hill Book Company (UK) Limited, 3rd ed., (1972), p. 25.

[16].Sze S.M.," Physical of semiconductor devices "Wiley –inter science publication, New York **(1983).**

[17]. Erdogan,I. Y. O. Güllü "Optical and structural properties of CuO nano film: Its diode application" J. Allo. And Compou. 492, p.378–383 **(2010)**.

[18]. Nixon Samuel Vijayakumar, G. M. Rathnakumari, P.Sureshkumar, "Synthesis, dielectric, AC conductivity and non-linear optical studies of electrospun copper oxide nanofibers", Archives of Applied Science Research, 3 (5), p. 514-525 **(2011)**.

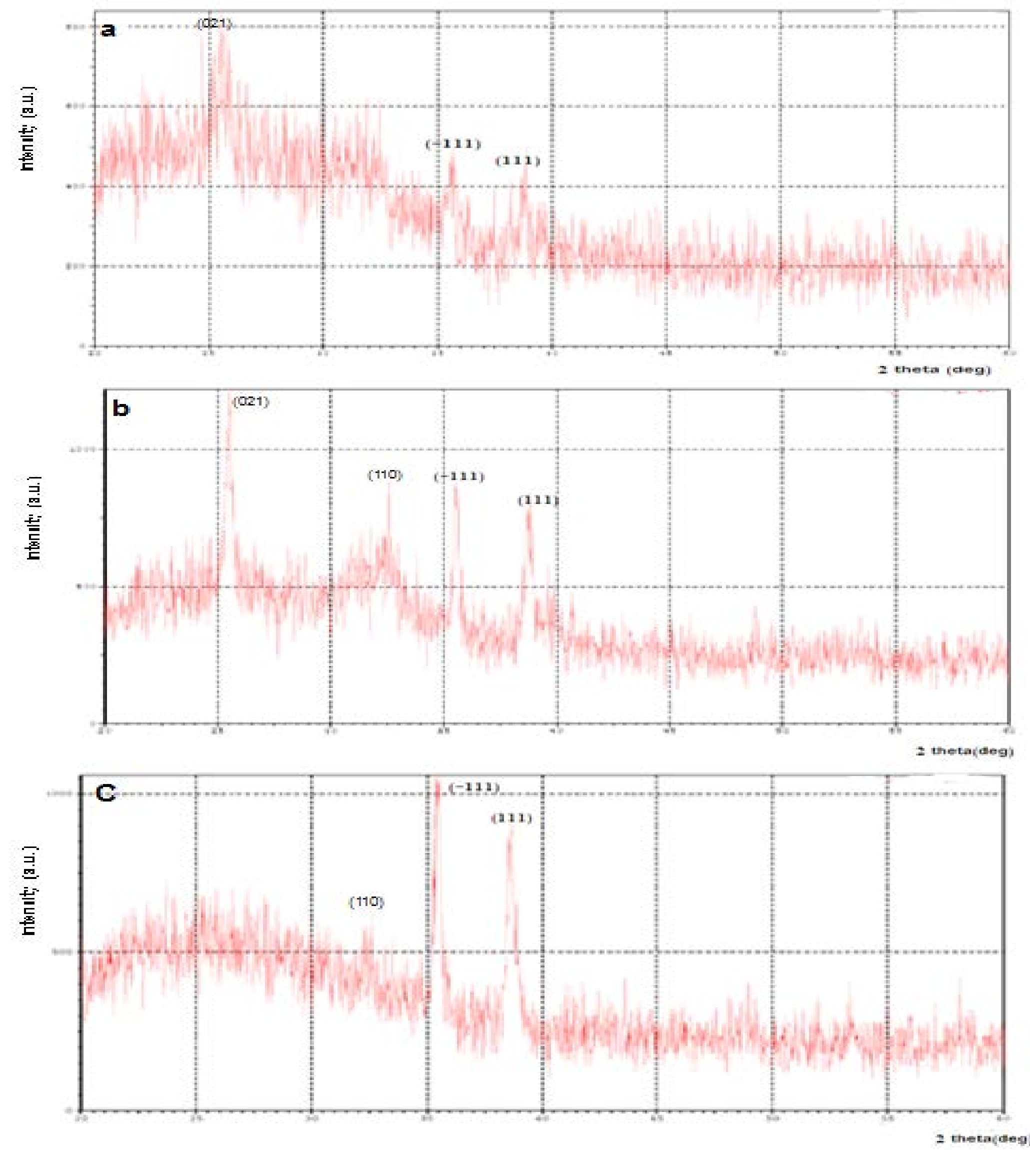

Figure (1) XRD pattern of CuO thin films prepared at different concentration: a)0.1M, b)0.2M ,& c) 0.3M.

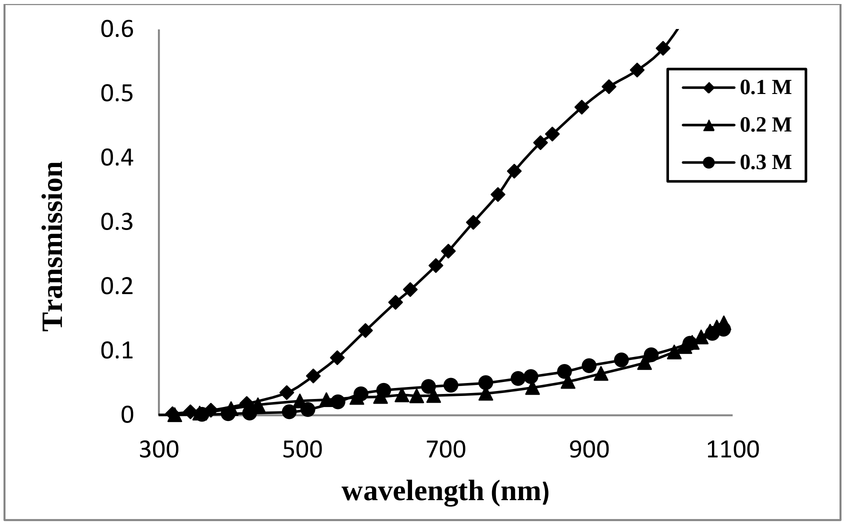

Figure (2) Optical transmission spectra of CuO films prepared at Different concentration.

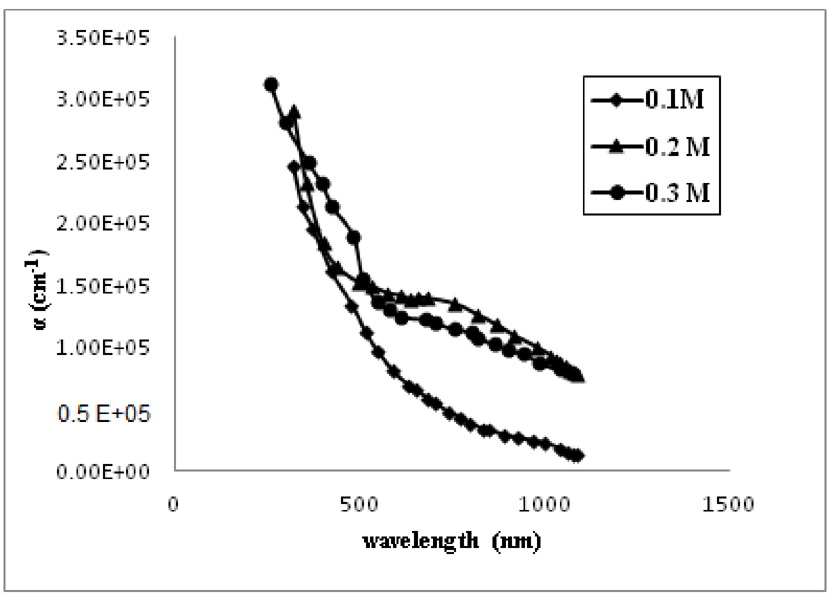

Figure (3) Variation of absorption coefficient of CuO films prepared at Different Concentration.

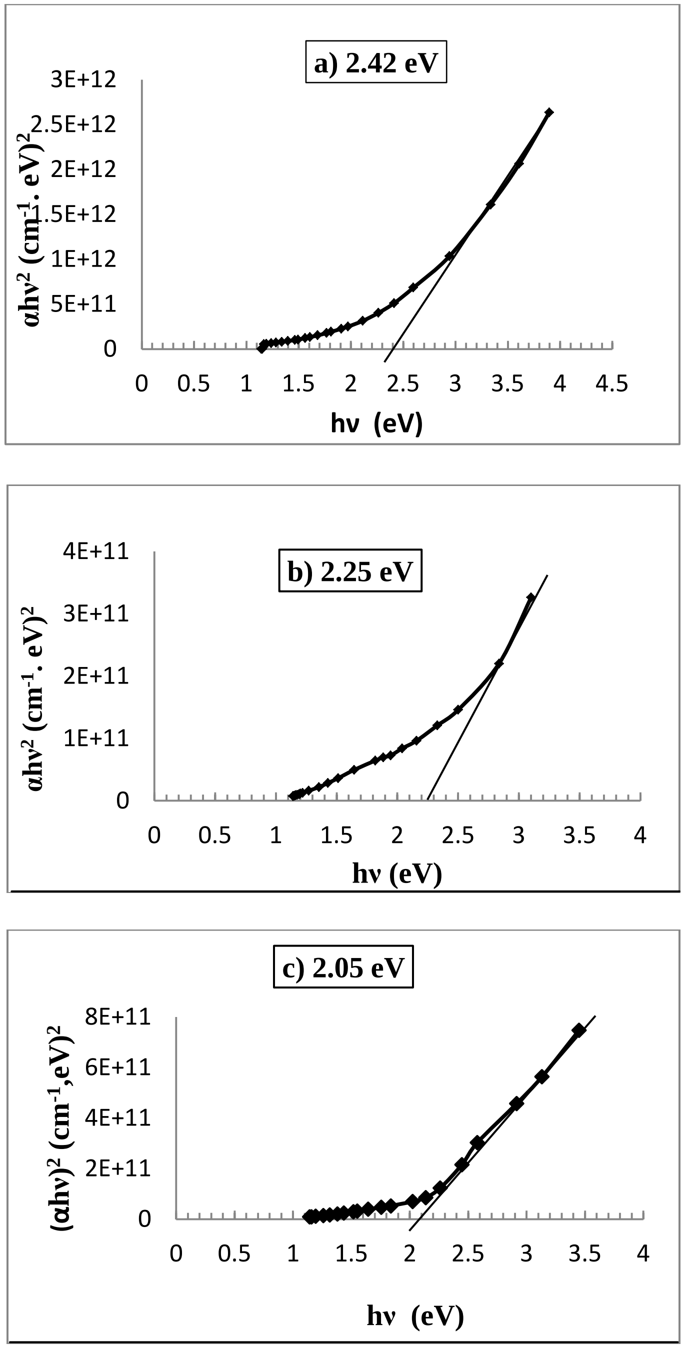

Figure (4) variation of $(\alpha h\nu)^2$ with photon energy($h\nu$) of CuO films Prepared at different concentration: a) 0.1M, b) 0.2M, & c) 0.3M.

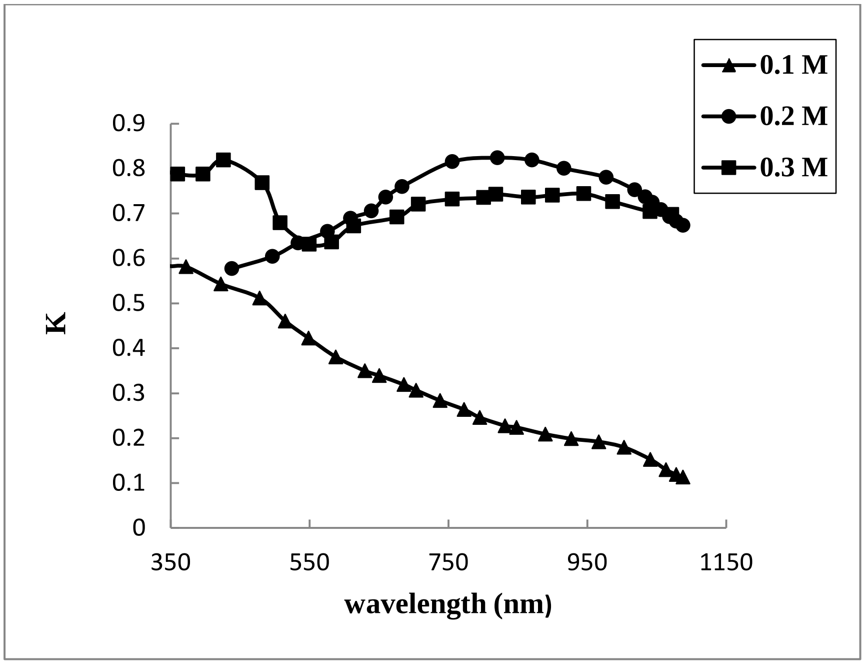

Figure (5) variation of excitation coefficient with wavelength of CuO films prepared at different concentration.