مجلة كلية التربية للعلوم الصرفة- جامعة ذي قار
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المجلد 8، العدد 1، اذار 2018

Manufacture and deposition of Copper oxide nanoparticles on quartz glass substrate for study of structural and Optical properties

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Abstract

In this article, thin films of copper oxide are prepared by synthesis of CuO nanoparticles using different solvents by a low cost sol-gel method. Chemical bath deposition (CBD) method is used on substrates of quartz glasses are dried in oven at 150 ℃ for 3 hours. Finally these quartz glass pieces are annealed at 500℃ for 1 hour. The structural and optical properties of the samples have then been tested by XRD, SEM, FTIR and UV-Visible spectrophotometer. The crystallite size and strain are higher for the CuO nanoparticle synthesized using propanol as solvent that shown by XRD analysis. The blue shift of direct band gap and the red shift of indirect band gap indicated by UV-Visible spectrophotometer Optical absorption analysis. So, the blue shift is due to the quantum confinement effect seen for nanoparticle systems while the red shift is associated with the formation of surface defects.

Keywords: propanol ; ethanol ; quartz

Journal of College of Education for pure sciences(JCEPS)
Web Site: http://jceps.utq.edu.iq/ **Email:** jceps@eps.utq.edu.iq
Volume 8, Number 1, March 2018

تصنيع وترسيب جسيمات أوكسيد النحاس النانوية على قاعدة من زجاج الكوارتز لدراسة الخصائص التركيبية والبصرية

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الخلاصة

في هذه البحث، تم تحضير أغشيه رقيقة من اوكسيد النحاس من خلال تحضير دقائق اوكسيد النحاس النانويه باستخدام محاليل مختلفة بطريقة sol-gel منخفضة التكلفة على قاعدة من زجاج الكوارتز بطريقة ترسيب الحمّام الكيميائي (CBD) ومن ثمّ تجفيف المحلول الجيلاتيني في الفرن بدرجة حرارة 150 °C لمدة 3 ساعات. وبعد ذلك لدن غشاء اوكسيد النحاس عند درجة حرارة 500) لمدة ساعة واحدة. الخصائص التركيبية والبصرية للعينات إختبرت من قبل XRD، SEM، FTIR وجهاز المطياف UV . دقائق النحاس النانويه المحضرة باستخدام البروبينول كمذيب كان الحجم وإلاجهاد البلوري اكبر كما ظهر واضح في تحليل XRD . الزحف باتجاة الطيف الأزرق لفجوة الطاقه المباشرة والزحف باتجاة الطيف الأحمر لفجوة الطاقه الغير مباشرة أشارا إليه تحليل طيف إلامتصاص من قبل جهاز المطياف المرئي البصري. في هذه الحالة، الزحف باتجاة الطيف الأزرق ناتج عن تأثير الحجز الكمّي للأنظمة الدقائق النانوية بينما الزحف باتجاة الطيف الأحمر يرتبط بتشكيل العيوب السطحيّة.

1. INTRODUCTION

Nanoscale metal oxides have attracted a great deal of research interest because of both fundamental and technological point of view. Among all the metal oxides, cupric oxide (CuO) has attracted considerable attention because of its peculiar properties. CuO has been used as a basic material in cuprate High-TC superconductors as the super-conductivity in these classes of systems is associated with Cu-O bondings [1,2].

CuO thin film can also be used in p-type field effect transistors and CO gas sensors [3]. A wide range of deposition techniques such as chemical vapor deposition[4] electrodeposition[5], thermal evaporation [6], sol gel techniques[7], spray pyrolysis[8], pulsed laser deposition[9] and plasma based ion implantation and deposition [10], besides that magnetron sputtering, all these techniques have been used for preparation of cu films [11, 12].

Experimental Methods

For the synthesis of CuO nanoparticles in sol-gel process, 2.5 gm of $Cu(NO_3)_2.H_2O$ is dissolved into 10 ml of ethanol. In order to see the effect of solvent, we use propanol instead of ethanol for the synthesis of another CuO nanoparticles. $Cu(NO_3)_2.H_2O$ dissolved in two different solvents separately stirred for 1 hour to obtain the homogenious solutions. These solutions are kept for 2 day for gel formation. Then the quartz pieces are placed in glass containers. The gels are put in glass containers and then the gels are dried in oven at 150 ℃ for 3 hour. The obtained thin film for CuO deposited into quartz glass pieces. Finally these quartz glass pieces are annealed at 500℃ for 1 hour. The structural and optical properties of the samples have then been tested by XRD, SEM, FTIR and UV-Visible spectrophotometer.

2.2 Film thicknesses

The deposited CuO thin film on quartz glass substrate has been calculated by weight difference method(BALANCE MODEL KERN ALJ220-4NM) using formula:

$t = m/ A. \rho$ …… (1)

where t is a film thickness of the deposited CuO thin film on substrate, m is the actual mass of CuO deposited on substrate, A is area of the film (ρ = 6.31 g/ cm^3) [13]. The calculated thickness of the deposited CuO film was 19 μ m.

2.3 Characterization

X-ray diffraction (XRD) of the product has been carried out on Shimadzu XRD-6000 X-ray diffractometer equipped with Cu Kα radiation (λ = 0.15406 nm),employing a scanning speed of 12°

min-1 and 2θ ranges from 20° to 60° . The morphology of the produced films was investigated using Scanning Electron Microscope – SEM (Tescan Vega II- Cheek). Fourier Transform Infrared –FTIR Spectrophotometer (Shimadzu / ARAffinity-1) was used, optical properties have been carried out on UV-VIS spectrophotometer (metertech sp8001).

3. Results and Discussion

3.1 XRD Analysis

Figure (1A) shows the XRD pattern of CuO nanoparticles of thin film synthesized by sol-gel method using ethanol whereas in Figure (1B) it has been used propanol as solvent. In both solvent cases all the obtained peaks in the XRD pattern are well matched with the monoclinic phase of CuO bulk crystals and well consistent with the JCPDS card. No impurity peak related to any other phases of Cu like $Cu(OH)_2$, Cu_2O or Cu are seen in the observed XRD pattern. Our XRD results thus confirm synthesis of pure and well crystalline CuO nanoparticles without any impurity. The obtained results are well consistent with the previously reported literature [14].

The XRD peaks broaden and shift to higher angles for the CuO sample prepared when propanol used as solvent. The peak shift could be due to strain generation in the materials medium during synthesis. Since two different batches CuO nanoparticles were synthesized using ethanol and propanol as solvent. The solvent might be influencing the microstructure of resultant CuO nanoparticle [15].

The mean crystallite sizes of CuO grown on quartz glass substrate was calculated using Debye-Scherrer equation 2 [16].

$$L = 0.9\lambda / \beta . \cos\theta \ldots\ldots . (2)$$

where, L is the mean crystallite size (nm), λ is the wavelength of Cu Kα (0.15406 nm), β is the full width half maximum (FWHMXπ/ 180 rad.), and θ is the Bragg angle .The average crystallite size of CuO nanoparticales was calculated using sherrer = 29 nm

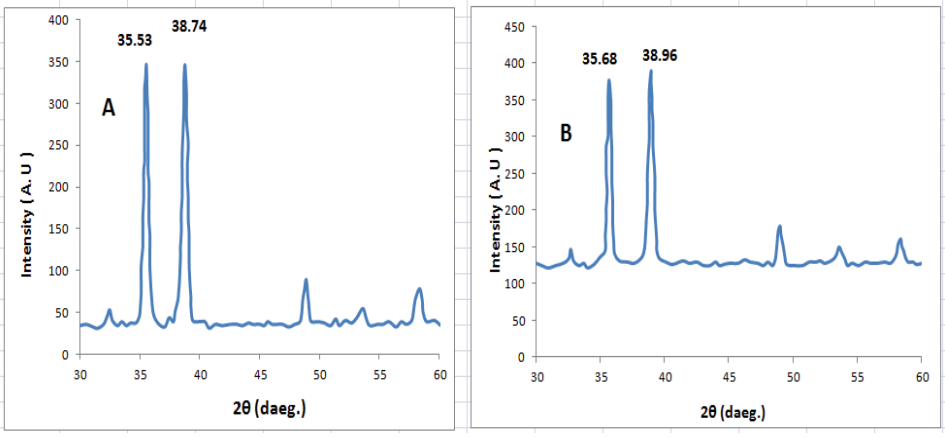

Figure (1) shows the XRD pattern of CuO nanoparticles thin film synthesized by sol-gel route (A) using ethanol and (B) propanol as solvent respectively.

3.2 FTIR analysis

The FTIR spectrum for CuO nanoparticales thin film using ethanol as solvent as shown in figure (2A) where bands at around 601,508 and 487 cm^{-1}, which can be assigned to the vibrations of Cu(II)-O bonds. There is a peak observed at 601 cm^{-1} in the spectrum CuO nanoparticles which is the characteristics of Cu-O bond formation. The broad absorption peak at around 3430cm^{-1} is caused by the adsorbed water molecules since the nano crystalline materials exhibit a high surface to volume ratio and thus absorb moisture.

The FTIR spectrum for CuO nanoparticales thin film using propanol as solvent in figure (2B) shows the two broad absorption bands at 601, 529 and 489 cm^{-1} are associated with Cu–O stretching modes [17]. Thus, the FTIR result suggests the presence of Cu–O bonds. Thus, the formation of copper oxide compound is confirmed from FTIR study the 437, 480, 503, 517, 606 and 650. The FTIR results of our work compare with previous reports, from the figure (2B) that our work approximately match with reference [18].

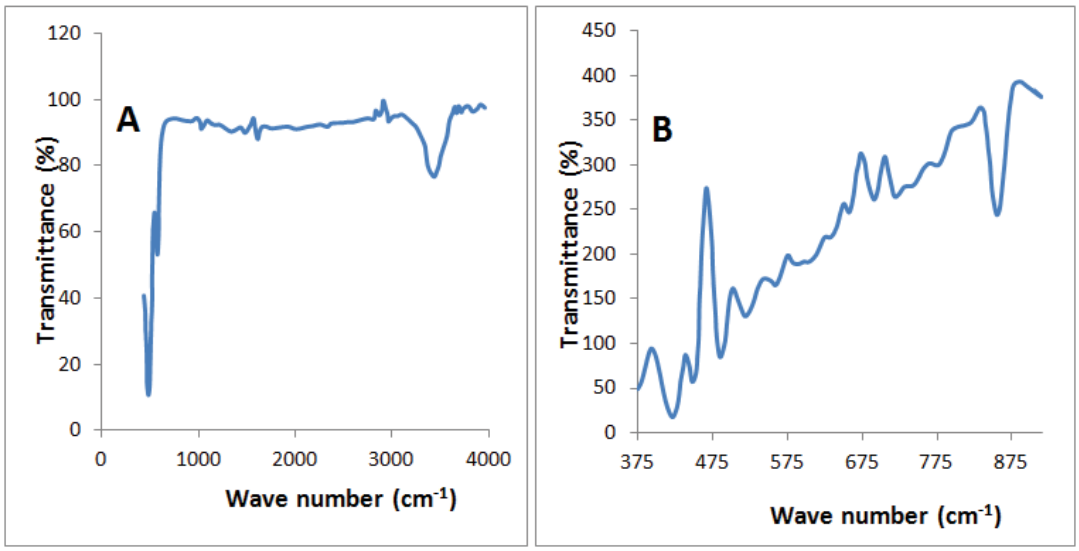

Figure (2) shows the FTIR spectrum of CuO nanoparticles thin film synthesized by sol-gel route (A) using ethanol and (B) propanol as solvent respectively.

3.3 Morphology analysis

The morphology of CuO nanoparticales thin film is shown in figure (3). This figure shows the SEM images of CuO as thin film synthesized by sol-gel route using ethanol as solvent in different magnifications(2.5kx,5kx,10kx,20kx),the images show that the grains are not highly homogeneous in shape and size there are shape cubic , spherical and others. The average grain diameter, as determined from figure (3) is about 65nm, which is to some extent higher than the value of the

crystallite diameter (29nm) as obtain from XRD pattern analysis, which is obvious, since, the crystallites clustered together to form grains with larger size.

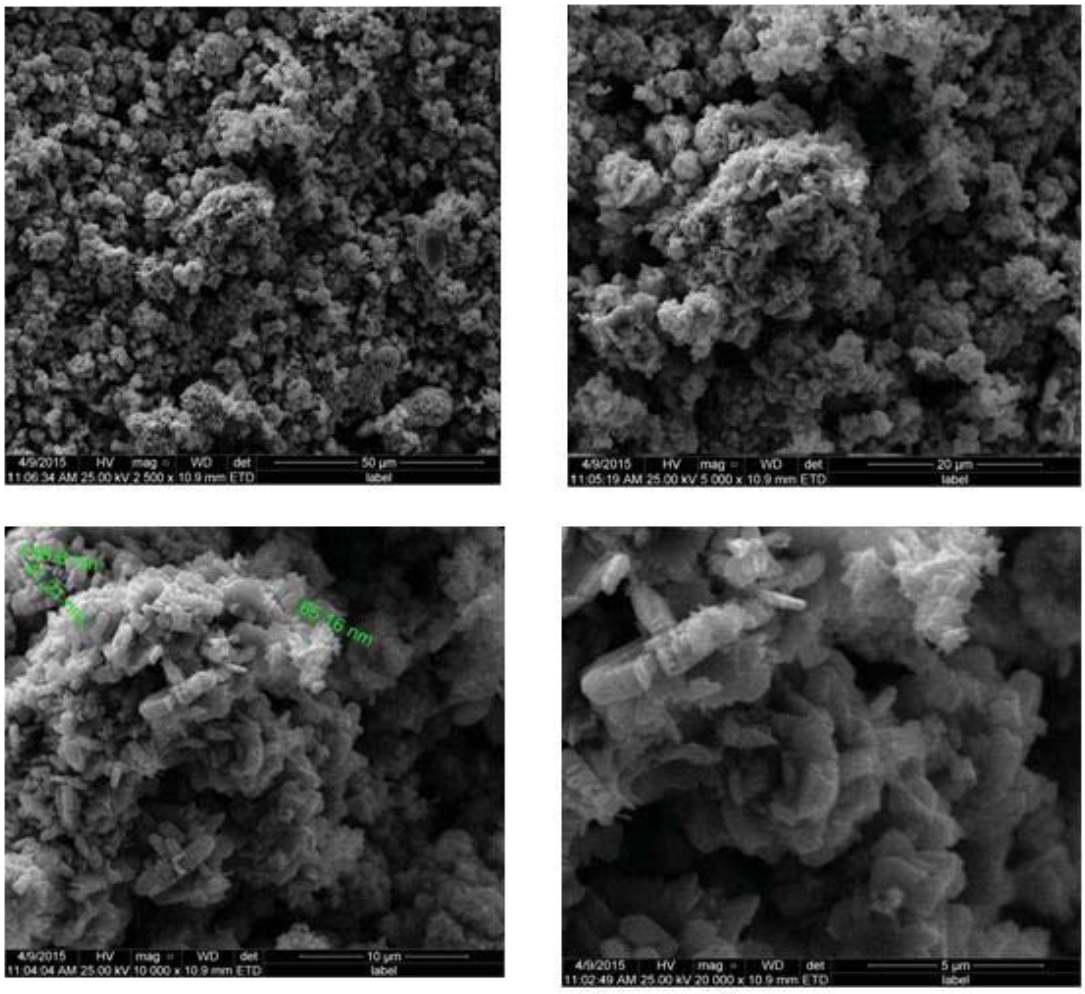

Figure (3) shows the SEM images of CuO as thin film synthesized by sol-gel route using ethanol as solvent in different magnifications(2.5kx,5kx,10kx,20kx) respectively.

3.4 Optical properties

3.4.1 UV-VIS (Absorption Spectra)

The optical absorption spectrum has been used to study the optical properties of the synthesized copper oxide nanoparticles thin films with 19 µm thickness deposited using ethanol and propanol solution as solvent are shown in figure (4A) and (4B) respectively; from this the band gap and the type of electronic transitions were determined. When a semiconductor absorbs photons of energy larger than the gap of the semiconductor, an electron is transferred from the valence band to the conduction band there occurs an surprising increase in the absorbency of the material to the

wavelength corresponding to the band gap energy. The relation of the absorption coefficient (α) to the incidental photon energy depends on the type of electronic transitions. When in this transition, the electron momentum is conserved, the transition is direct, but if the momentum does not conserve this transition it must be attended by a photon this is an indirect electronic transition [19]. Energy band gap studies of these materials have been reported using absorption spectra. The figure (4) describes the optical absorption spectrum of copper oxide nanoparticles thin films. The UV visible spectra displayed high excitonic absorption at 130 nm and135 nm when using ethanol and propanol solution as solvent respectively. It shows that the absorption edge at 420 nm and 389 nm for ethanol and propanol solution as solvent respectively. The material is reported as direct band gap material. For higher values of absorption coefficient, optical absorption shows a power load dependence on photon energy.

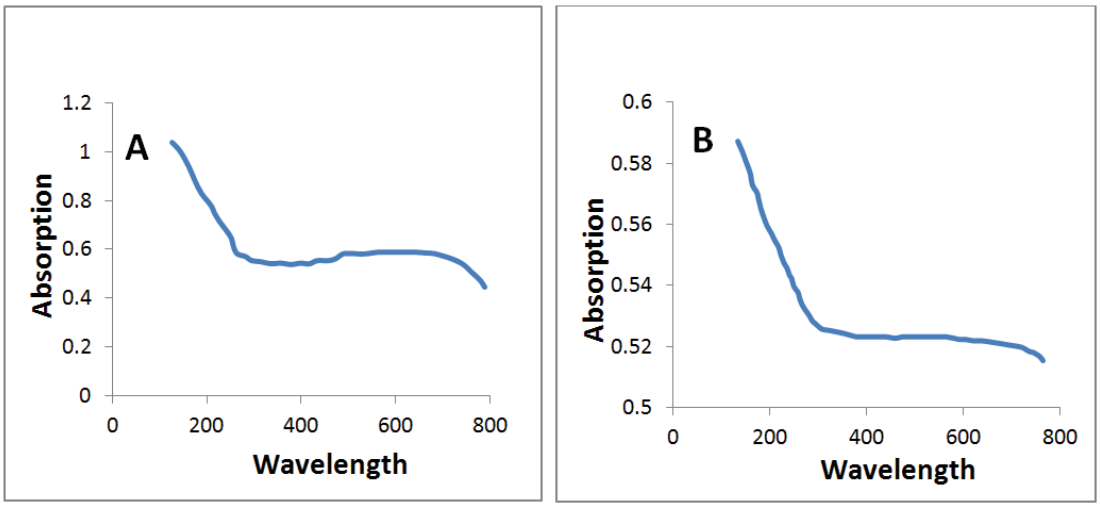

Figure (4) shows Variation of the absorption spectra against wavelength for CuO as thin film synthesized by sol-gel route (A) using ethanol and (B) propanol as solvent respectively.

3.4.2 UV-VIS (Transmittance spectra)

The optical transmittance spectra against wavelength for the tow samples of copper oxide nanoparticles thin films with 19 µm thickness deposited using ethanol and propanol solution as solvent are shown in figure 5A and 5B respectively. The presence of powdery deposit would cause scattering losses from the film surface, which would continuously reduce the transmittance with decrease in wavelength (λ) following an inverse power law, λ^{-n}. However, at the wavelength of about 500nm for 700nm the transmittance is reduced for coper oxide film using ethanol solution as solvent.

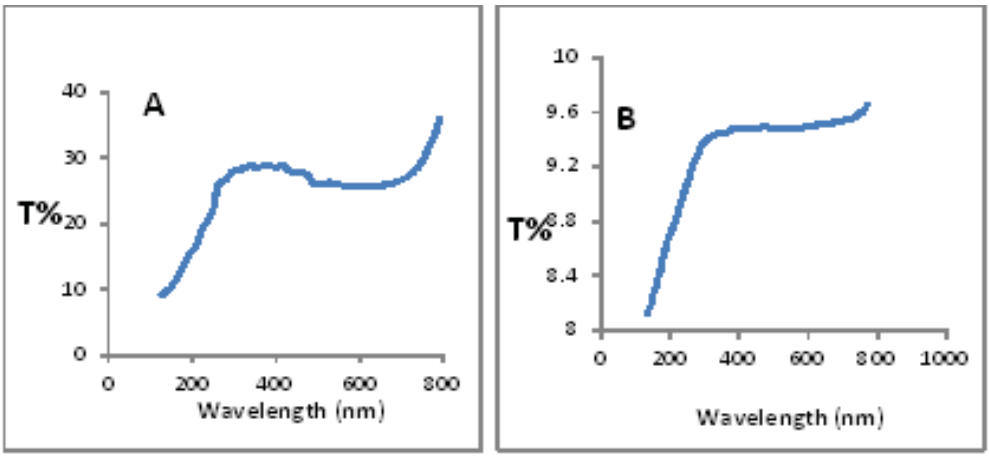

Figure (5) shows Variation of the transmittance spectra against wavelength for CuO as thin film synthesized by sol-gel route (A) using ethanol and (B) propanol as solvent respectively.

3.4.3 The optical band gap

The optical band gap of CuO nanoparticles thin film usual method of determining involves plotting $(\alpha h\nu)^{1/n}$ against photon energy, **hv**. Figure (6) and (7) show the variation of $(\alpha h\nu)^{1/n}$ against (**hv**) for CuO nanoparticles thin film with **n** values of **1/2** and **2** respectively. The indirect band gap of CuO nanoparticles synthesized using both the solvents show similar values and the values red shifted ~ 0.24 to 0.27 eV as compared to bulk value (1.45 eV) [20]. The increasing red shift with decreasing particle size suggests that the defects responsible for the intragap states are primarily of surface defects [21, 22]. Our results thus indicated that CuO nanoparticles prepared using ethanol as solvent show more surface defects as compared to the CuO nanoparticles prepared using propanol as solvent. Both the CuO samples show higher direct band gap as compared to bulk value (3.25 eV) [22, 23]. The blue shift in the direct band edges as seen in present case is due to the quantum confinement effect [22, 24].

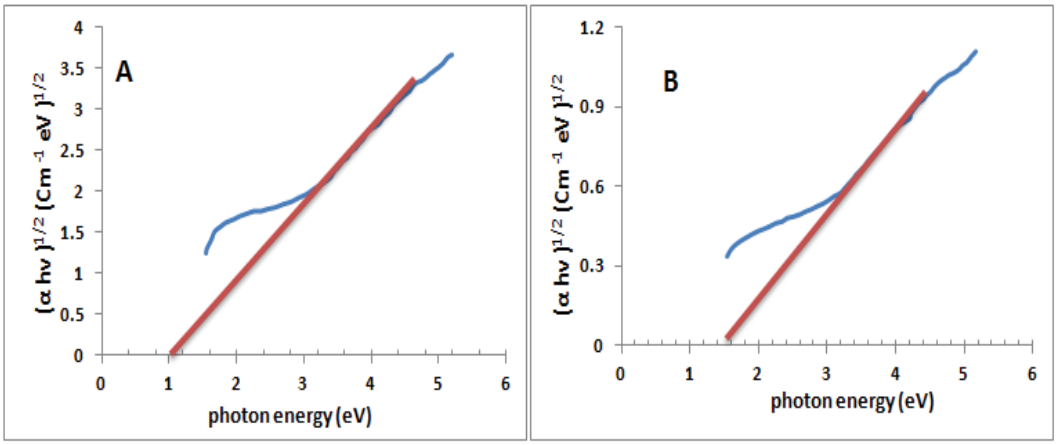

Figure (6) shows Variation of $(\alpha h\nu)^{1/2}$ vs. photon energy, for CuO as thin film synthesized by sol-gel route (A) using ethanol and (B) propanol as solvent respectively.

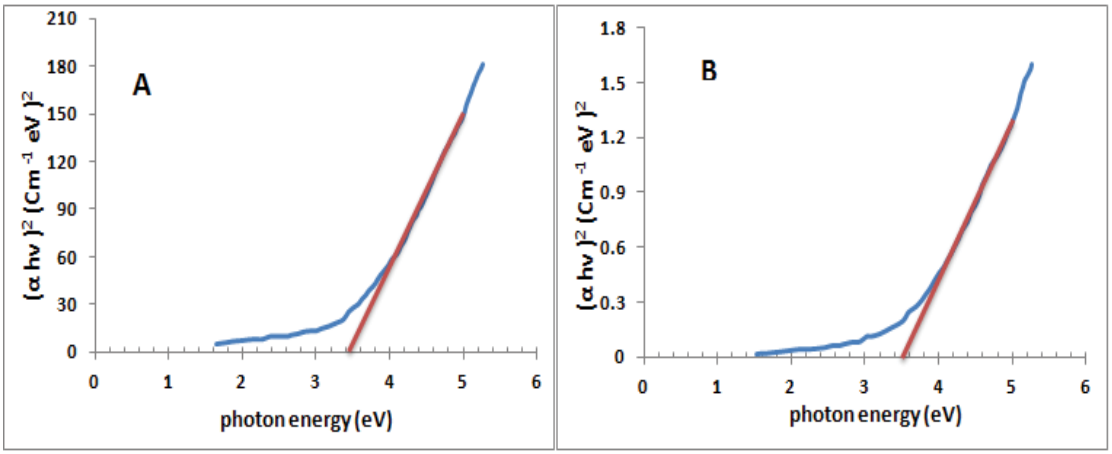

Figure (7) shows Variation of $(\alpha h\nu)^2$ vs. photon energy, for CuO as thin film synthesized by sol-gel route (A) using ethanol and (B) propanol as solvent respectively.

3.4.4 UV-Visible (absorption coefficient)

Figure (8A) and (8B) are shown the absorption coefficient as a function of wavelength for CuO as thin film synthesized by sol-gel route using ethanol and propanol as solvent respectively. It is clearly seen from the figures that the absorption coefficient tends to decrease exponentially as the wavelength increases. This behaviour is typical for many semiconductors and can occur for a variety of reasons, such as internal electric fields within the crystal, deformation of lattice due to strain caused by imperfection and inelastic scattering of charge carriers by phonons[25, 26]. The absorbance of CuO sample synthesized with propanol solvent shows faster exponential decrease indicating more strain generation in this case.

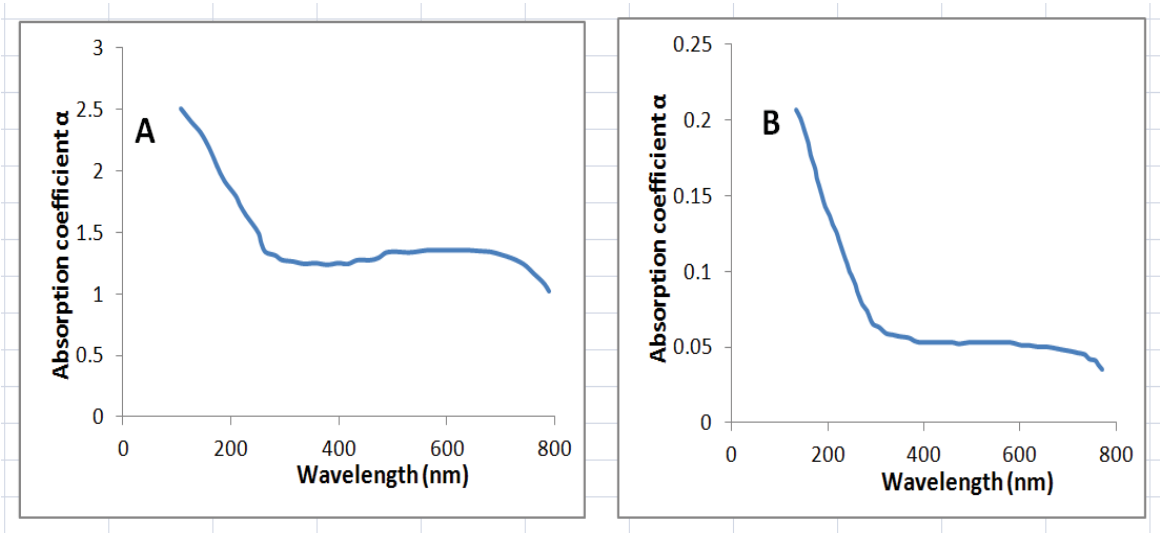

Figure (8) shows the absorption coefficient as a function of wavelength for CuO as thin film synthesized by sol-gel route (A) using ethanol and (B) propanol as solvent respectively.

3.4.5 UV-Visible (extinction coefficient)

The extinction coefficient (k_o) values against photon energy plot for CuO nanoparticles as thin film synthesized by sol-gel route using ethanol and propanol as solvent are shown in figure (9A) and (9B) respectively.

It is clear from figure (9A) and (9B) that the maximum value of the extinction coefficient were at (1.8 ev) and (1.9 ev) respectively then it decrease sharply with photon energy up to (4 ev). Furthermore, the extinction coefficient of CuO as thin film synthesized by using propanol as solvent is found to increases with increase in the photon energy, this might due to the effect of happening transition electrons between valance and conduction band. The extinction coefficient (k_o) of CuO nanoparticles thin films were calculated from the following expressions [27].

$$k_o = \frac{\alpha\lambda}{4\pi} \quad \text{..... (3)}$$

where α is the absorption coefficient , λ is the wavelength

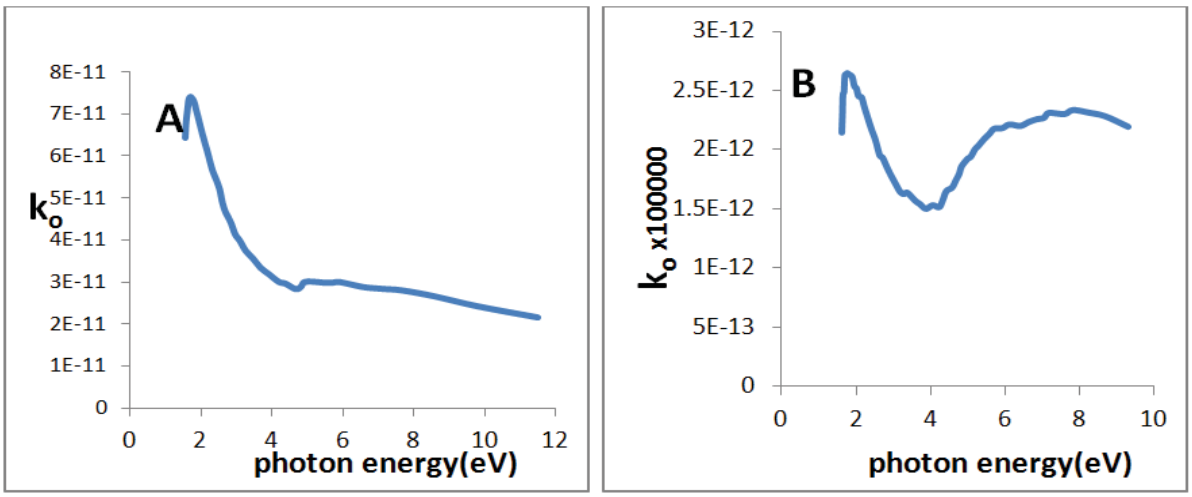

Figure (9) shows the extinction coefficient as a function of wavelength for CuO as thin film synthesized by sol-gel route (A) using ethanol and (B) propanol as solvent respectively.

3.4.6 UV-Visible (refractive index)

The figure (10A) and (10B) are shown the refractive index values against photon energy plot for CuO nanoparticles as thin film synthesized by sol-gel route using ethanol and propanol as solvent respectively.

It is clear from figures (10A) and (10B) that the maximum value of the refractive index were at (1.65 ev) and (1.68 ev) then it decrease sharply with photon energy up to (2 ev). Furthermore, the refractive index of CuO as thin film synthesized by using ethanol and propanol as solvent

respectively is found to decrease as the photon energy, this might due to the effect of particle size. The refractive index (n) of CuO nanoparticles thin films were calculated from the following expressions [27].

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

where R is the refraction , K_o is the extinction coefficient

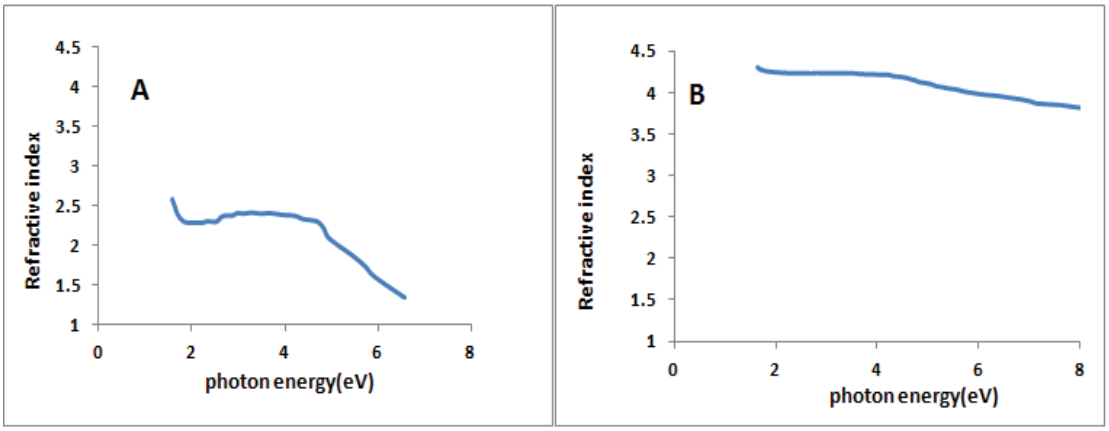

Figure (10) shows the refractive index as a function of wavelength for CuO as thin film synthesized by sol-gel route (A) using ethanol and (B) propanol as solvent respectively.

4. Conclusion

Thin films of copper oxide have been prepared by synthesis of CuO nanoparticles using different solvents by sol-gel method then the gels were dried on substrates of quartz glasses in oven at 150 ℃ for 3 hour. The quartz glass pieces were annealed at 500℃ for 1 hour.The crystallite size and strain are higher for the CuO nanoparticle synthesized using propanol as solvent that indicated by XRD analysis. The blue shift of direct band gap and the red shift of indirect band gap indicated by UV-Visible spectrophotometer Optical absorption analysis. In this case, the blue shift is due to the quantum confinement effect seen for nanoparticle systems while the red shift is associated with the formation of surface defects. The average crystal diameter derived from the XRD data analysis is found to be 29nm.

5. References

[1] F. Parmigiani and G. Samoggia, "Experimental Evidence of a Fluctuating Charge State in Cupric Oxide", Europhys. Lett. 7, 543(1988).

[2] X.G. Zheng, C.N. Xu, Y. Tomokiyo, E. Tanaka, H. Yamada and Y. Soejima, "Observation of Charge Stripes in Cupric Oxide", Phys. Rev. Lett. 85, 5170 (2000).

[3]. Liao L., Zhang Z., Yan B., Zheng Z., Bao Q.L., TWu, CMLi, Shen Z.X., Zhang J.X., Gong H., Li J.C. and Yu T., Multifunctional CuO Nanowire Devices: p-type Field Effect Transistors and CO Gas Sensors. Nanotechnology, 20,085203, p.6., (2009)

[4]. Markworth, P. R., Liu, X., Dai, J. Y., Fan, W., Marks, T. J., Chang, R. P. H. J. Mater. Res "formation and kinetics study of cuprous oxide nanodots on LaAlO3 (0 0 1)" 16, 2408, (2001)

[5]. Golden, T. D., Shumsky, M. G.; Zhou, U., Vander Werf, R.A., Van Leeuwen, R. A. and Switzer, J. A. Chem. Mater" Electrochemical Deposition and Formation Mechanism of Single-Crystalline Cu_2O Octahedra on Aluminum" 8, 2499, (1996)

[6]. Özer, N. and Tepehan, F. Sol. Energy Mater. Sol. Cells 30, 13, (1993)

[7]. Ray, S.C. Sol. Energy Mater. Sol. Cells, 68, 307, (2001)

[8]. Kosugi, T.; Kaneko, S. J. Am. Chem. Soc., 81, 3117, (2004)

[9]. Chen, A., Long, H., Li, X., Li, Y., Yang, G. and Lu, P. Vacuum, 83, 927, (2009)

[10]. Ma, X., Wang, G., Yukimura, K., Sun, M. Surf. Coat.Technol., 201, 6712, (2007)

[11]. Prater, W. L.; Allen, E. L.; Lee, W. Y.; Toney, M. F.; Kellock, A.;Daniels, J. S. J. Appl. Phys. 2005, 97, 093301.

[12]. Pletea, M.; Bruckner, W.; Wendrock, H.; Kaltofen, R. J. Appl. Phys. 2005, 97, 054908.

[13] Charles kittel, solid state physics , eigthth edition , john wily and sons 2008.

[14] M. Abaker, A. Umar, S. Baskoutas, S.H. Kim and S.W. Hwang, "Structural and optical properties of CuO layered hexagonal discs synthesized by a low-temperature hydro-thermal process", J. Phys. D: Appl. Phys. 44, 155405 (2011).

[15] P. Mallick, S. Sahu " Structure, Microstructure and Optical Absorption Analysis of CuO Nanoparticles Synthesized by Sol-Gel Route" Nanoscience and Nanotechnology 2012, 2(3): 71-74

[16] P.H. Klug, L.E. Alexander, 1974, x-ray diffraction procedures for polycrystalline and amorphous materials, wiley, newyork, 618.

[17] K Santra, CK Sarkar, MK Mukherjee, B Ghosh. Copper oxide thin films grown by plasma evaporation method. Thin Solid Films; 213:226. 1992.

[18] N Papadimitropoulos, V Vourdas, EmVamvakas and D Davazoglou, Deposition and characterization of copper oxide thin filmsJournal of Physics: Conference Series 10 182–185, 2005.

[19] Rehman S., Mumtaz A Hasanain S.K., in: Size effects on the Magnetic and Optical properties of CuO nanoparticles", J. Nanopart. Res. 13 (2011), 2497.

[20] B.A. Gizhevskii, Y.P. Sukhorukov, A.S. Moskvin, N.N. Loshkareva, E.V. Mostovshchikova, A.E. Ermakov, E.A. Kozlov, M.A. Uimin, V.S. Gaviko, "Anomalies in the optical properties of

nanocrystalline copper oxides CuO and Cu2O near the fundamental absorption edge", JETP 102, 297(2006).

[21] S.G. Ovchinnikov, B.A. Gizhevskii, Y.P. Sukhorukov, A.E. Ermakov, M.A. Uimin, E.A. Kozlov, Y. Kotov and A.A.V. Bagazeev, "Specific features of the electronic structure and optical spectra of nanoparticles with strong electron correla-tions", Phys. Solid State 49, 1116 (2007).

[22] S. Rehman, A. Mumtaz and S.K. Hasanain, "Size effects on the magnetic and optical properties of CuO nanoparticles", J. Nanopart. Res. 13, 2497 (2011).

[23] F.P. Koffyberg and F.A. Benko, "A photoelectrochemical determination of the position of the conduction and valence band edges of p-type CuO", J. Appl. Phys. 53, 1173 (1982).

[24] S. Neeleshwar, C.L. Chen, C.B. Tsai, Y.Y. Chen, C.C. Chen, S.G. Shyu and M.S. Seehra, "Size-dependent properties of CdSe quantum dots", Phys. Rev. B 71, 201307(R) (2005).

[25] T.S. Moss, G.J. Burrell and B. Ellis, Semiconductor Op-to-Electronics, Butterworth & Co. Ltd, 1973.

[26] A. Sawaby, M.S. Selim, S.Y. Marzouk, M.A. Mostafa and A. Hosny, "Structure, optical and electrochromic properties of NiO thin films", Physica B 405, 3412 (2010).

[27] Sumangala D, Amma D, Vaidyan VK, Manoj PK Structural,electrical and optical studies on chemically deposited tin oxide films from inorganic precursors. Mater Chem Phy 93:194–201(2005).