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Study of Optical properties of Copper Oxide (CuO) thin film prepared by SPD technique

Shymaa K. Hussian
Muthanna university/ Science college/ Physics department/ Samawa/ Iraq
Email: shymaahussen@mu.edu.iq
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Abstract:

This study is focused on the optical properties of thin films of p-type semiconductor CuO prepared by spray pyrolysis deposition technique. This film is grown at 350°C on glass substrate. The optical properties are considered because of its application as photovoltaic cells and solar energy conversion. These properties are evaluated from UV-VIS spectra. The results are shown high absorbance at UV region, which decreases rapidly in VIS-IR region whereas they show direct transition energy gap of 2.094 eV.

1.Introduction:

Thin film is a layer of material having thickness of the order of few nanometers[1]. In the past couple of decades, a large amount of research is carried out on semiconducting thin films for various device applications. A good amount of literature is available on the preparation and characterization of semiconductor chalcogenide materials [2].

The development of semiconductor thin films is one of the key technologies for pn-junction based devices such as diode, transistors, and light emitting diodes. Copper oxide (CuO) has unique features such as low cost, non-toxicity, the abundant availability of copper, high efficiency and relatively simple formation of the oxide layer, etc.

Copper oxides materials are known to be p-type semiconductors in general and hence potentially useful for constructing junction devices such as p-n junction diodes [3,4,5]. A part from the semiconductor applications, these materials have been employed as heterogeneous catalysts for several environmental processes [6,7], solid state gas sensor heterocontacts [8,9], and microwave dielectric materials [10]. Their use in power sources has received special attention. Thus, in addition to photovoltaic devices one of the important advantages of using CuO in device applications is that it is non-toxic and its constituents are available in abundance [11]. Because the chemical and physical properties of CuO are strictly dependent of its size and morphology thin films of copper oxide have been prepared by a number of techniques including spray pyrolysis [12], sol–gel synthesis [13] and electro deposition [14],sol-gel synthsis [15], chemical vapor deposition[16], pulsed laser deposition[17] and electro deposition[18].

In this study CuO thin films prepared by a spray pyrolysis technique , which is a well-known nanostructured thin film preparation method with excellent features such as the need for no sophisticated equipment, and quality targets or substrates, as well as film thickness and stoichiometry are easy to control and the resulting films are well compacted [19].

Here we have investigated the optical properties of CuO thin film deposited onto glass substrates using SPD technique.

2.Experimental part:

Copper chloride dehydrate ($CuCl_2.2H_2O$) is used in making the precursor solution for CuO thin films, to obtain 0.1 molarity concentrantion of $CuCl_2.2H_2O$ solution, an amount of 4.262 g of $CuCl_2.2H_2O$ that is dissolved in 250 ml of distilled water and the solution is stirred in a magnetic stirrer at room temperature for 10 minutes in order to get a transparent and well-dissolved solution.

Microscope glass slides are used as substrate cleand with organic solvents . The substrate temperature is fixed at 350 C°, the spray rate is usually in the range 2.1 ml/min, the distance between substrate to spray nozzle is 30 cm and air pressure 0.35 bar, respectively.

The optical measurements of the CuO thin films are calculated from the transmittance and absorbance spectrum at normal incidence over the range (190-1100)nm by using UV-VIS Spectrophotometer type (SHIMADZU) (UV-1650).

Thickness of the prepared thin film has been measured by using the optical interferometer method employing He-Ne laser 0.632 μm with incident angle 45°.This method depends on the interference of the laser beam reflected from thin film surface and then substrate. The film thickness (d) can be calculated using the following formula [14]:

$$d = \frac{\lambda}{2}\frac{\Delta x}{x} \qquad (1)$$

where λ is the wavelength of He-Ne laser.

From the absorbance data, the absorption coefficient α is calculated in the fundamental absorption region using Lambert law [20]:

$$\alpha = 2.303\frac{A}{d} \qquad (2)$$

where A is the optical absorbance and d is the film thickness.

Extinction coefficient (k) of prepared film is calculated by using the relation [21]:

$$k = \frac{\alpha\lambda}{4\pi} \qquad (3)$$

where λ is the wavelength of the incident photon.

The reflectance (R) has been found by using the relationship [22]:

$$R + A + T = 1 \tag{4}$$

Now, from the reflectance data, the refractive index (n) is calculated by the following relationship [23]:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \tag{5}$$

It has been calculated the optical conductivity σ [24]:

$$\sigma = \frac{\alpha n c}{4\pi} \tag{6}$$

Where c is the velocity of light.

The nature of transition (direct or indirect) is determined by using the relation[25]:

$$\alpha h\upsilon = a(h\upsilon - E_g)^r \tag{7}$$

where hv is the photon energy, E_g the band gap energy, a and r are constants. It is worth to note that for an allowed direct transition, r=1/2 and for an allowed indirect transition, r=3/2.

3. Results and Discussion:

The absorption spectrum of CuO film is as shown in Fig.(1). It can be noticed that high absorbance at UV region, then it decreases rapidly in the visible region near IR region, so the absorption studies revealed that the fabricated films are very low absorptive at the visible region and is more suitable for the fabrication of solar cells [7].

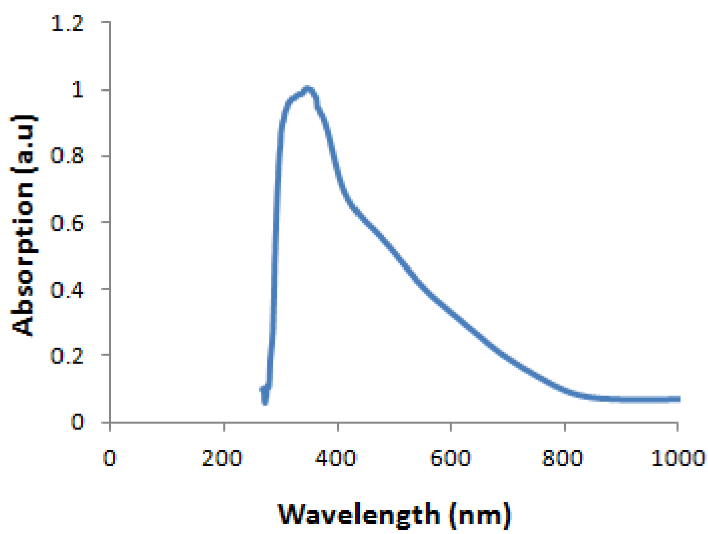

Fig. (1) Absorption spectrum of CuO thin film.

Fig. (2) shows the absorption coefficient of CuO film which is determined from equation(2). The absorption coefficient of this film increases rapidly beyond absorption edge region and then decreased gradually because its inversely proportional to the transmittance. One can evidently see that CuO thin film has high value of absorption coefficient ($\alpha \geq 10^4 cm^{-1}$) which is conducive to increasing the probability of direct transitions occurrence.

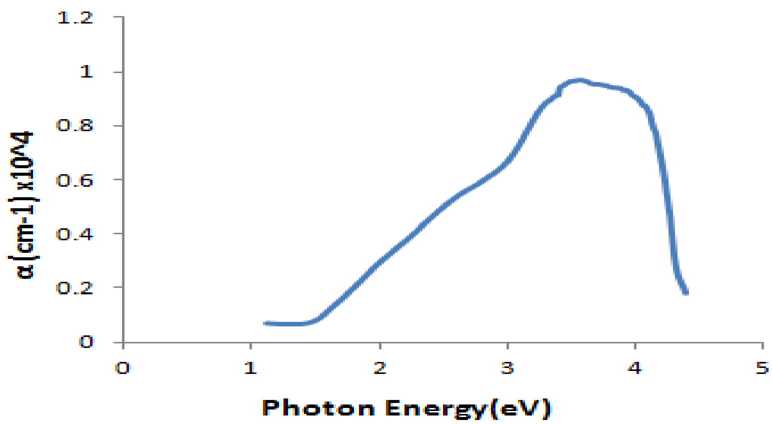

Fig. (2) Absorption coefficient as a function photon energy of CuO thin film.

Extinction coefficient (k) has been calculated using the Eq.(3), so the extinction coefficient of CuO film has been shown in Fig. (3).It is clear that the extinction coefficient increase rapidly in the UV range and then decreases. The increase and decrease in the extinction coefficient is directly related to the absorption of light which leads to nonzero value of extinction coefficient (k) for photon energies smaller than the fundamental absorption edge [20].

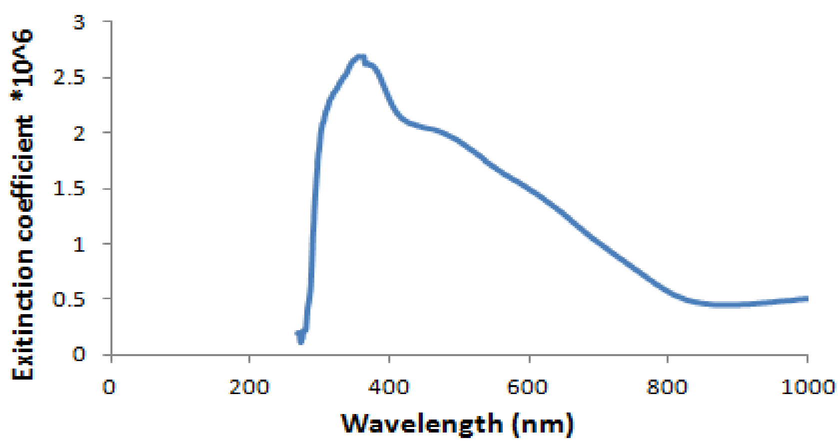

Fig. (3) Extinction coefficient against wavelength of CuO thin film.

Fig.(4) shows the reflectance spectrum for CuO thin film. It is clear that reflectance increases with increasing the wavelength and then it has a peak at the energies which is corresponding to the energy gap of the film, then decreases at the photon energy of larger values so this behavior is attributed to the very low absorbance of the film at the photon energies less than the forbidden energy gap , and when it becomes more than or equals to the energy band gap, a clear value of absorbance appears because the material electrons interaction with the incident photon has enough energy to make the electronic transition take place and this result which is in agreement with [24] .

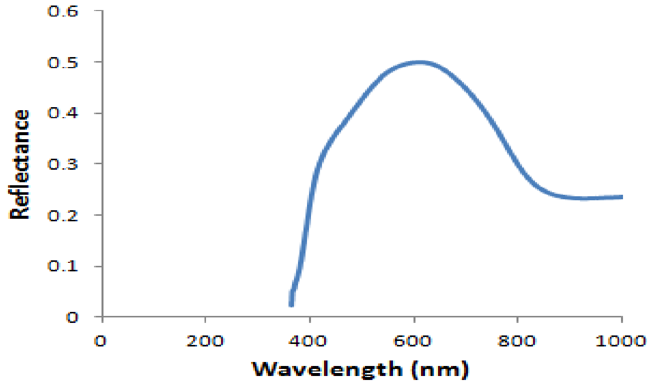

Fig. (4) Reflectance against wavelength of CuO thin film.

The refractive index of CuO thin film is determined from Eq.(5). Fig.(5) shows the variation refractive index of CuO film as a function of the wavelength, the values of the refractive index increases with increasing the wavelength in UV and the beginning of visible region . The results show that the maximum value of refractive index of prepared film is (1.665).

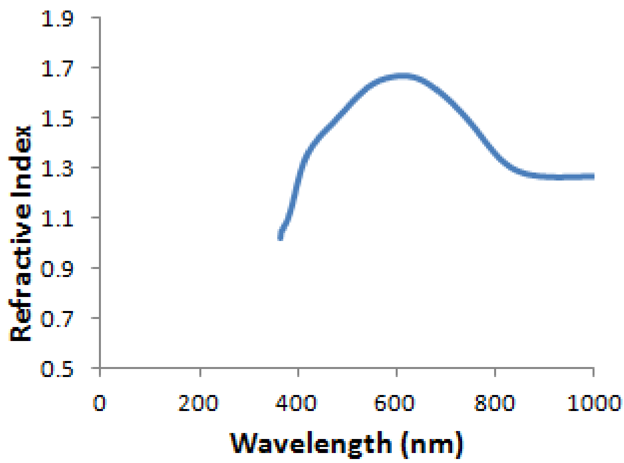

Fig. (5) Refractive index against wavelength of CuO thin film.

Fig.(6) shows the variation of optical conductivity for CuO film as a function of wavelength which using Eq.(6). It is clear that the optical conductivity decrease with increasing the wavelength.

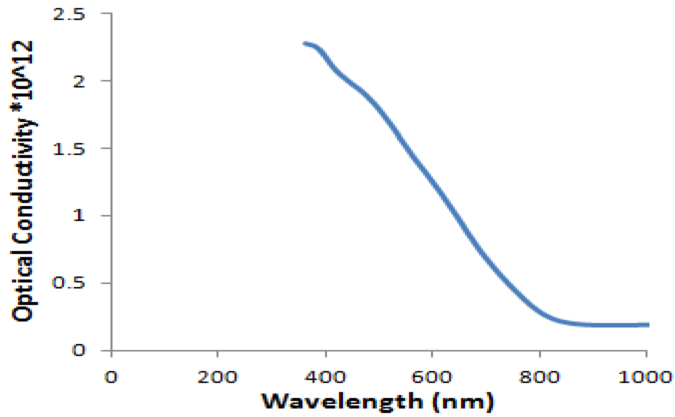

Fig. (6) Optical conductivity against wavelength of CuO thin film.

The plots of $(\alpha hv)^2$ versus the photon energy are shown in Fig. (7) of CuO film.

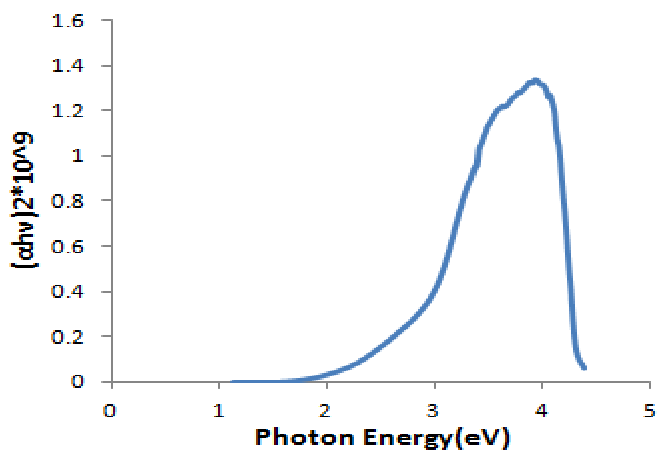

Fig. (7) Variation of $(\alpha h\upsilon)^2$ with photon energy for CuO thin film.

The linear behavior of the plot curve is shown in Fig. (7) indicates the existence of direct transitions. From the straight line obtained at high photon energy the direct allowed energy gap could be determined that equals (2.094 eV). This result is in a good agreement with the results mentioned in Refs. [9,17].

4. Conclusion:

CuO thin film was deposited on to glass substrate at temperature (350°C), has been prepared using SPD technique with a solution of $CuCl_2.2H_2O$. The film exhibits high absorbance values at ultraviolet region which they decrease rapidly in the visible/ near infrared region, the film shows a direct transition which was (2.094eV) for allowed energy gap. The film has high values of absorption coefficient($\alpha \geq 10^4$ cm^{-1}). The spray pyrolysis method for the production of thin solid films is a good method for the preparation of thin films which are suitable for scientific studies and for many applications in technology and industry, equally.

References:

[1] Xiaoming Huang, Zhexun Yu, Shuqing Huang, Quanxin Zhang, ongmei Li, Yanhong Luo, Qingbo Meng, Preparation of fluorine-doped tin oxide (SnO_2:F) film on polyethylene terephthalate (PET) substrate, Materials Letters 64 (2010) 1701– 1703.

[2] T. Serin, A. Yildiz. Ș. H. Șahin, N. Serin, Muliphonon hopping of carriers in CuO thin films, Physica B 406(2001) 3551-3555.

[3] V. Dhanasekaran, T. Mahalingam, R. Chandramohan, Jin-Koo Rhee, J. P. Chu, Electrochemical deposition and characterization of cupric oxide thin films, Thin solid Films 520(2012) 6608-6613.

[4] Bushra. K. H. al-Maiyaly, I. H. Khudayer, Ayser. J. Ibraheim, Effect ambient oxidation on structural and optical properties of copper oxide thin films,International Journal of Innovative Research in Science, Engineering and Technology,Vol.3 (2014) 2319-8753.

[5] A. A. Ogwu, T. H. Darma, E.Bouquerel, Electrical resistivity of copper oxide thin films prepared by reactive magnetron sputtering, Journal of Achievement in Materials and Manufacturing Engineering, Vol. 24 (2007) 172-177.

[6] F. Bayansal, S. Kahraman, G. çankaya, H. A. çetinkara, H. S. Gṻder, H.M. çakmak, Growth of homogenous CuO nano-structured thin films, Journal of Alloys and Compounds 509(2011) 2094-2098.

[7] Onah D. u., Ugwu E. I., Ekpe J. E., Optical properties of nanocrystalline Tio_2/CuO core-shell thin films by thermal annealing, American Journal of Nano Research and Applications,3(3) (2015) 62-65.

[8] P.K. OOI, C.G. Ching, M.A. Ahmad, S.S. NG, M.J. Abdullah, H. Abu Hassan , Z. Hassan, Characterizations of cupric oxide thin films on glass and silicon substrates by radio frequency magnetron sputtering, Sains Malaysiana 43(4)(2014) 617–621.

[9] Riyam A. Hammoodi, Assist. Prof. Dr. Ahmed K. Abbas ,Prof. Dr .Abdul hussein K. Elttayef, Structural and optical properties of CuO thin films prepared via R.F.magnetron sputtering, International Journal of Application or Innovation in Engineering &

Management, Volume 3, Issue 7(2014) 2319 – 4847.

[10] J. Morales, L. Sánchez, F. Martín, J.R. Ramos-Barrado, M. Sánchez, Use of low-temperature nanostructured CuO thin films deposited by spray-pyrolysis in lithium cells, Thin Solid Films 474 (2005) 133– 140.

[11] Takahiro Itoh, Kunisuke Maki, Growth process of CuO(1 1 1) and Cu2O(0 0 1) thin films on MgO(0 0 1) substrate under metal-mode condition by reactive, Vacuum 81 (2007) 1068–1076.

[12] Sakhar C. Ray ,Preparation of copper oxide thin film by the sol-gel-like dip technique and study of their structural and optical properties ,Solar Energy Materials &Solar cells 68(2001)307-312.

[13] Dattarya Jundale1, Shailesh Pawar, Manik Chougule, Prasad Godse, Sanjay Patil, Bharat Raut, Shashwati Sen, Vikas Patil, Nanocrystalline CuO Thin Films for H_2S Monitoring: Microstructural and Optoelectronic Characterization, Journal of Sensor Technology,1(2011) 36-46.

[14] A. Tombak, M. Benhaliliba, Y.S. Ocak, T. Kiliçoglu, The novel transparent sputtered p-type CuO thin films and Ag/p-CuO/n-Si Schottky diode applications, Results in Physics 5 (2015) 314–321.

[15] Mohd Rafie Johan, Mohd Shahadan Mohd Suan, Nor Liza Hawari,Hee Ay Ching, Annealing Effects on the Properties of Copper Oxide Thin Films Prepared by Chemical Deposition, Int. J. Electrochem. Sci., 6 (2011) 6094 – 6104.

[16] Khawla S. khashan , Dr.Jehan A. Saimon ,Dr.Azhar I. Hassan, Optical Properties of CuO Thin Films with Different Concentration by Spray Pyrolysis Method, Eng. &Tech.Journal, Vol. 32 (2014) Part (B), No.1.

[17] Xiaojun Zhang, Dongen Zhang, Xiaomin Ni, Huagui Zheng, Optical and electrochemical properties of nanosized CuO via thermal decomposition of copper oxalate, Solid-State Electronics 52 (2008) 245–248.

[18] Abdul Hai Alami, Anis Allagui, Hussain Alawadhi, Microstructural and optical studies of CuO thin films prepared by chemical ageing of copper substrate in alkaline ammonia solution, Journal of Alloys and Compounds 617 (2014) 542–546.

[19] Kajal Jindal, MonikaTomar, VinayGupta, CuO thin film based uric acid biosensor with enhanced response characteristics, Biosensors and Bioelectronics 38 (2012) 11–18.

[20] Adel H. Omran Alkhayatt, Shymaa K. Hussian, Fluorine highly doped nanocrystalline SnO2 thin films prepared by SPD technique, Materials Letters155(2015)109–113.

[21] S. S. Roy, A. H Bhuiyan, J. Podder, Optical and Electrical Properties of Copper Oxide Thin Films Synthesized by

Spray Pyrolysis Technique, Sensors & Transducers, Vol. 191, Issue 8(2015) 21-27.
[22] Julián Morales, Luis Sánchez, Francisco Martín, Jose R. Ramos-Barrado, Miguel Sánchez, 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 (2004) 4589–4597.
[23] J. Joseph, V. Mathew, J. Mathew, K. E. Abraham," Studies on Physical Properties and Carrier Conversion of SnO_2: Nd Thin Films", Turk J Phys., 33 (2009) 37 – 47.
[24] M.N. Nnabuchi ," Optical and Solid State Characterization of Optimized Manganese Sulphide Thin Films and Their Possible Applications in Solar Energy", The Pacific Journal of Science and Technology, 7 (1) (2006) 69-76.
[25] D.D.O. Eya, A.J. Ekpunobi, and C.E. Okeke, FAS," Optical Properties of Cuprous Oxide Thin Film Prepared by Chemical Bath Deposition Technique", The Pacific Journal of Science and Technology, 6 (2) (2005) 98-104.

دراسة الخواص البصرية لغشاء اوكسيد النحاس CuO المحضر بطريقة الرش الكيميائي الحراري

م.م شيماء كريم حسين

الخلاصة:

ركزت هذه الدراسة على الخواص البصرية لغشاء CuO شبه الموصل نوع p-type والمحضر بطريقة الرش الكيميائي الحراري عند درجة حرارة $350^{\circ}C$ على قواعد من الزجاج، تم النظر بالخصائص البصرية بسبب تطبيقاتها كخلايا كهروضوئية، هذه الخواص حسبت من طيف UV-VIS وأظهرت النتائج امتصاصية عالية في المنطقة فوق البنفسجية وبعدها تنقص في المنطقة المرئية والقريبة من المنطقة تحت الحمراء وبينت أن فجوة الطاقة الانتقالية المباشرة هي 2.094 eV.