The effect of thickness on the optical properties of Cu_2S thin films

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Abstract

In this work, the optical properties of Cu_2S with different thickness (1400, 2400, 4400) Å have been prepared by chemical spray pyrolys is method onto clean glass substrate heated at 283 °C ±2. The effect of thickness on the optical properties of Cu_2S has been studied. It was found that the optical properties of the electronic transitions on fundamental absorption edge were direct allowed and the value of the optical energy gap of Cu_2S (E_g) for direct transition decreased from (2.4-2.1) eV with increasing of the thickness from (1400 - 4400)Å respectively. Also it was found that the absorption coefficient is increased with increasing of thicknesses. The optical constants such as extinction coefficient, refractive index and the imaginary part of the dielectric constant have similar termed of variation for the absorption coefficient.

Key words
Cu_2S thin films, optical properties, chemical spray pyrolys method.

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تأثير السمك على الخصائص البصرية لاغشية Cu_2S

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الخلاصة

في هذا البحث تم دراسة تأثيرالسمك على الخصائص البصرية لاغشية كبريتيد النحاس والمحضرة بطريقة التحلل الكيميائي الحراري بأسماك مختلفة (4400,2400,1400) انكستروم على قواعد زجاجية وبدرجة حرارة 283±2 درجة سليزية. تم راسة تأثير السمك على الخصائص البصرية لاغشية كبريتيد النحاس. لقد بينت نتائج القياسات البصرية للانتقالات الالكترونية ان هذه الاغشية تمتلك فجوة طاقة مباشرة وتقل من 2.4- 2.1 الكترون فولت بزيادة السمك من 1400-4400 انكستروم بالتعاقب، الامتصاصية تزداد بزيادة السمك معامل الامتصاص، اماالثوابت البصرية معامل الخمود، معامل الانكسار والجزء الخيالي لثابت العزل الكهربائي فيسلك سلوك معامل الامتصاص أي يزداد بزيادة سمك الغشاء.

Introduction

Copper sulfides (Cu_xS, 1≤x≤2) are interesting materials due to their special physical and chemical properties. Cu_xS (x=1-1/2) thin films have recently received considerable attention due to numerous technological applications in achievement of solar cells [1-3], in photo thermal conversion of solar energy (as solar absorber coatings) [4], as selective radiation filters on architectural windows (for solar control in the warm climates) [3,5], as electro conductive coatings deposited on organic polymers[6].

The copper sulfur system (Cu_xS) has five stable phases that exist in nature: chalcocite (Cu_2S), djulerite ($Cu_{1.97}S$), digenite ($Cu_{1.8}S$), anilite ($Cu_{1.75}S$) ($Cu_{1.4}S$) and yarrowite ($Cu_{1.12}S$) this are referred to as blaubleibender covellite [3].

Among them, cuprous sulfide (Cu_2S) is considered as an ideal absorber in photovoltaic conversions due to its high absorption coefficient (10^4 cm^{-1}) and narrowband gap (1.2 eV) [7,8]. Chalcocite, Cu_2S, is a p-type semiconductor that is an attractive absorber for solar energy conversion because of its band gap (E_g=1.2eV), its nontoxicity and the abundance of its constituent elements [4].

Thin films can be fabricated in various ways. The techniques can be divided into physical and chemical methods. In physical methods, the film material is moved from a target source with some form of energy to the substrate This method is widely used in one-compound films, like metal films. Under physical methods we have vacuum evaporation and sputtering, where the deposition has been transferred to gaseous state either by evaporation or an impact process. Chemical film fabrication method involves chemical reaction and the precursors are mostly components undergoing reaction at the substrate surface or in the vicinity of the substrate. Under chemical methods we have the gas phase chemical processes such as conventional chemical vapour deposition (CVD), laser CVD, metal organochemical deposition (MOCVD) and plasma enhanced chemical vapour deposition. Liquid phase chemical techniques include electrodeposition, chemical bath deposition, electroless deposition, anodization, spray pyrolysis etc. [9,10,11].

Experimental

The Copper Sulphide films were prepared by spray pyrolysis method on glass substrates at temperatures (Ts) of 283±2 °C. The effective area of the substrates was approximately 2.5 cm^2. The deposition parameters such as solution flow rate; and nozzle to substrate distance were kept constant at 5 ml/min, and 30±1 cm, respectively. The starting solution was prepared using $CuCl_2.2H_2O$ and thiourea. Firstly, thiourea was dissolved in a minimum amount of deionized water while Copper Chloride ($CuCl_2.2H_2O$) was dissolved in Water. Secondly, both solutions were mixed and diluted with deionized water, so that the final concentration was 0.1 M, which were then sprayed onto the heated substrates.

The substrates were ultrasonically cleaned, first with trichloroethylene and then with acetone and methyl alcohol followed by rinsing in distilled water. The spray nozzle was moved in the x–y plane. Moving the spray nozzle is just an option, so, it is possible to work in a stationary position too with the same setup. In a typical experimental procedure, Copper sulphide was prepared from $CuCl_2.2H_2O$ `and thaurea.

Results and discussion

The optical properties of the films deposited on glass substrates are determined from the absorption (A), and transmission (T) measurements in the range of 310–1100 nm. The transmission spectrum of Cu_2S thin films for different thickness (1400, 2400 and 4400)Å was shown in Fig. 1. The variation of the transmission of Cu_2S thin films with the wavelength is very important because this variation will limit the transmitted wavelengths which play an important role in determination the category/type of the optical filters. The results agree with Fuwei Zhugeet al, Ashour et al. [1,11]. Fig. 1 shows that the spectrum reveal very pronounced interference effects for photon energies below the fundamental absorption edge [12]. It is clear from the same figure that the transmittance decreases with increasing of thickness which can be also deduced from the changing in the films' colore, from grey color for thickness(1400)Å to dark grey for thickness(4400)Å. The absorbance spectrum of (Cu_2S) thin films with different thickness (1400, 2400 and 4400)Å was shown in Fig.2. It is clear that as the thickness increases the absorption of (Cu_2S) thin films. This increasing in the absorption is attributed to the increasing of thickness which results in an increase of the depth of donor levels associated with these vacancies and these levels will be available for the photons to be absorbed therefore the absorbance of Cu_2S thin films increase with increasing of thickness.

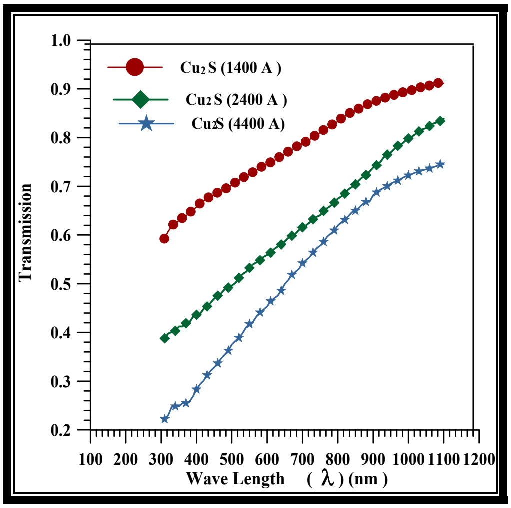

Fig. 1: Transmission spectrums of Cu_2S thin films.

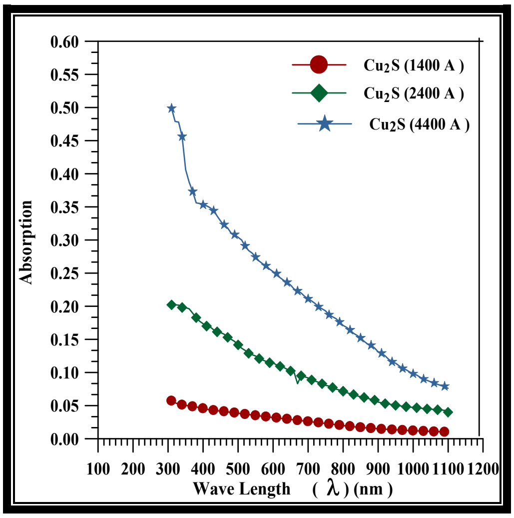

Fig. 2: Absorption spectrums of Cu_2S thin films.

The absorption coefficient (α) of Cu_2S thin films was determined by using Eq.(2).

$$\alpha = 2.303\,\frac{A}{t} \quad \text{………………} \quad (1)$$

where (A) : is the absorption ,(t): is the thickness of the film.

The variation of the absorption coefficient of Cu_2Sthin films with the photon energy for different thickness (1400, 2400 and 4400)Å is shown in Fig.3. It can be noticed that the value of the absorption coefficient of Cu_2S thin films is of the order of (10^4) cm^{-1} which supports the direct band gap nature of the semiconductor [17]. Our result agrees with [1,11]. It is also clear that the absorption coefficient of the films increases with the increasing of thickness. This is attributed to the increase in the absorbance of films with increasing of thickness causing an increment in their absorption coefficient.

The values of optical energy gap (E_g) for Cu_2Sthin films prepared by spray pyrolysis method have been determined from the region of the high absorption at the fundamental absorption edge of these films by using Tauc equation [13]:

$$(\alpha h\upsilon) = B_o(h\upsilon - E_g)^r \quad \text{……………} \quad (2)$$

where α is the absorption coefficient, hυ is the incident photon energy in eV, B_0 is a constant depends on the nature of the material (properties of its valence and conduction band) [14] and r is parameter depends on the nature of the transition between the top of the valence band and bottom of the conduction band [15].

This equation is used to find the type of the optical transition by plotting the relations $(\alpha h\upsilon)^2$, $(\alpha h\upsilon)^{2/3}$, $(\alpha h\upsilon)^{1/2}$and $(\alpha h\upsilon)^{1/3}$ versus photon energy (hυ) and select the optimum linear part. It is found that the first relation yields linear dependence, which describes the allowed direct transition, then E_g was determined by the extrapolation of the portion at α=0 as shown in Fig. 4. It illustrates the variation of the optical energy gap for Cu_2S thin films with different thickness.

It is clear that the optical energy gap for Cu_2S thin films decreases as the thickness of films increased. This is attributed to the decrease the depth of donor levels which is associated with the vacancies and causing a reduction in the optical energy gap for Cu_2S thin films [16]. The value of optical energy gap varied from 2.4-2.1 eV, when thickness of the film increased from 1400-4400Å respectively. It can be observed that the optical energy gap for Cu_2S thin films varies smoothly but not linearly with the increasing in thickness. Fig.5 shows the variation of energy gap with the thickness.

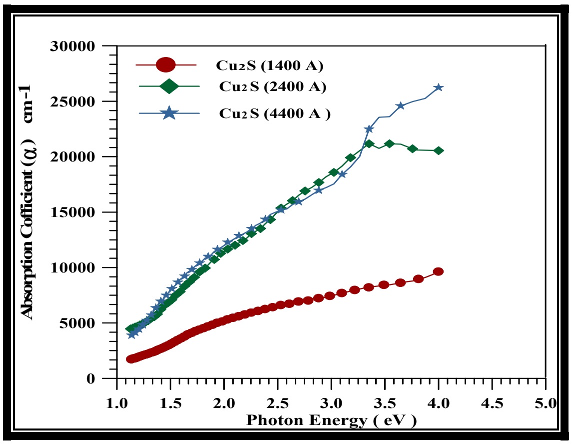

Fig. 1:Transmission spectrums of Cu_2S thin films.

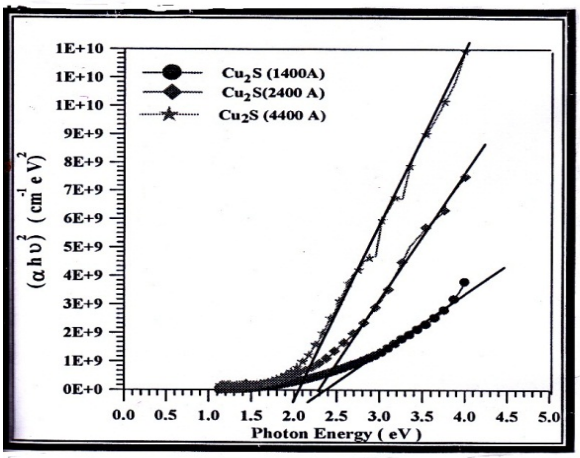

Fig. 4: $(\alpha h\upsilon)^2$ as a function of hυ for Cu_2S thin film of the photon energyCu_2Sthin film.

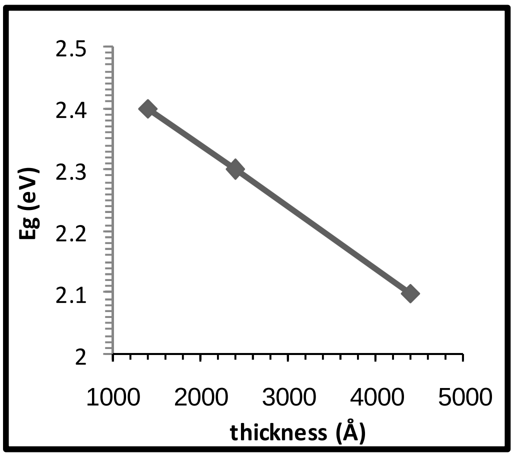

Fig. 5: Variation of the optical energy gap Cu_2Sthin films.

with the thickness.

The refractive index (n_o) of Cu_2S thin films has been determined by using the following equation [18]:

$$n_o = \sqrt{\frac{4R}{(R-1)^2} - k_o^2} - \left(\frac{R+1}{R-1}\right) \qquad (3)$$

where, R : is the reflectance of the films and k_o : is the extinction coefficient.

The variation of the refractive index as a function of the photon energy for Cu2S thin films was illustrated in Fig. 6. It is clear from this figure that the refractive index increases with the increasing in the photon energy of the incident photon. Also it can be observed that the refractive index of Cu_2S thin films increases with the decreasing in the thickness of Cu_2S thin films. Where (n_o) varies according to the grain size even if the crystalline structure is itself of the material.

The extinction coefficient (k_o) has been determined by using the following equation [18]:

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

It is clear from this equation that k_o depends on α and has a similar behavior to α. Fig. 7 illustrates the variation of the extinction coefficient of Cu_2S thin films with the photon energy. It can be noted From this figure that k_o varies slightly with the increasing in the photon energy and the decreasing in the absorption coefficient. Then k_o increases highly at the absorption edge region and this increasing is attributed to the increasing of the absorption coefficient due to the direct electronic transitions then after k_o reaches to its maximum value at the high absorption region corresponding to the increment in the photons' energy and the increasing in the absorption coefficient with the decreasing in the wavelength. In addition, it is clear from this figure that with the increasing in the thickness the extinction coefficient k_o increases. This is attributed to the increasing in the absorption coefficient due to the increasing of the depth of donor levels associated with sulfur vacancies and these levels will be available for the photons to be absorbed causing an increment in the absorbance and leads to increase in the absorption coefficient. Therefore k_o will increase with increasing in the thickness, since it has a similar behavior to α and are depended on it.

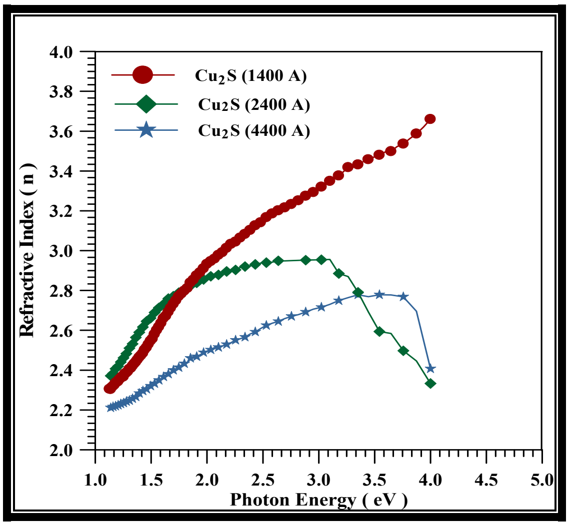

Fig. 6: The variation of the refractive index as a function of the photon energy for Cu_2S thin films.

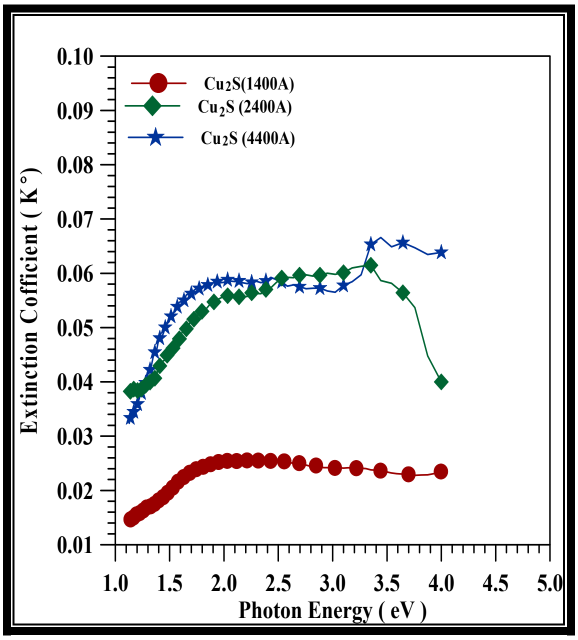

Fig. 7: Extinction coefficient as a function of the photon energy for Cu_2S thin films.

The dielectric constant (ε) consists from real part (ε_r) and imaginary part (ε_i) depend on the frequency of the electromagnetic wave. The variation of ε_r and ε_i versus photon energy in the range (1.1-3.2) eV at different thickness were shown in Figs. 8 and 9 respectively. The ε_r and ε_i increase with the increasing of the photon energy of the incident radiation and this is due to the change of reflectance and absorbance [19].The behavior of ε_r is similar to that of the refractive index because of the smaller value of k^2 compared with n^2, while ε_i mainly depends on the k value, which are related to the variation of absorption coefficient. ε_i represents the absorption of radiation by free carriers [20]. It is observed that ε_r increases with increasing of thickness, and this attributed to the same reason mentioned previously for the refractive index, while ε_i decreases with increasing of thickness and this is due to the similar interpretation discussed previously for the extinction coefficient.

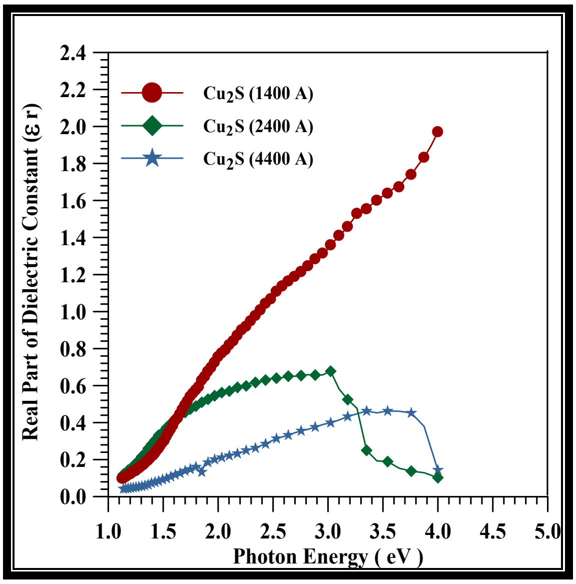

Fig. 8: Real part of the dielectric constant as function of the photon energy for Cu_2S thin films.

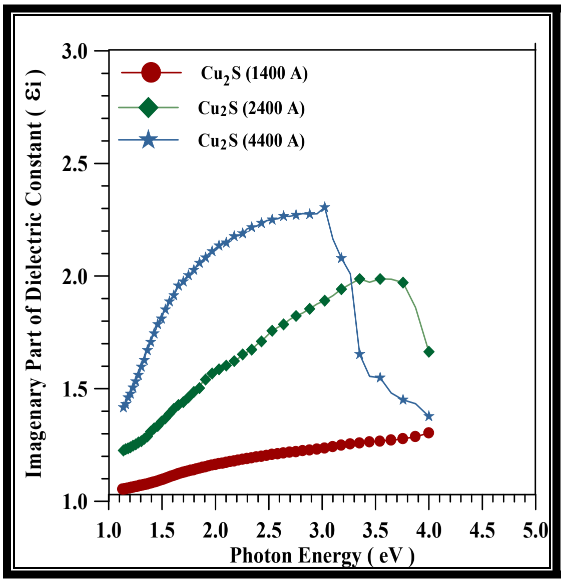

Fig. 9: Imaginary part of the dielectric constant as function of the photon energy for Cu_2S thin films.

The optical properties parameters including optical energy gab (E_g), absorption coefficient (α) and optical constants which include refractive index(n), extinction coefficient (k), real(ε_r) and imaginary part (ε_i) of the dielectric constant at the wave length (540) nm for Cu_2S thin films where thickness (1400, 2400 and 4400)Å deposited by chemical spray pyrolysis method on glass substrate at R.T 283±2C° are listed in Table 1. It is clear from this table that the optical energy gap decreases with the increasing in the thickness and other parameters.

Table 1: Optical properties parameters of Cu_2S films at different thicknesses at wave length (540) nm.

Thickness (µm)	**$\alpha \times 10^4$ (cm)$^{-1}$**	**E_g (eV)**	**n**	**k**	**ε_r**	**ε_i**
1400	0.606	2.4	3.075	0.02541	0.9485	1.1904
2400	1.3274	2.3	2.557	0.05627	0.61214	1.6621
4400	1.38707	2.1	2.415	0.05852	0.2554	2.2091

Conclusions

Chemical spray pyrolysis technique can be successfully employed for the deposition of uniform optical studied indicates that Cu_2Sthin films exhibit direct band gap which is slightly depends on the thickness almost cover the entire visible spectral that makes these films are suitable for optoelectronic devices especially for solar cell. The optical energy gap for Cu_2S thin films decreases as the thickness of films increased.

References

[1] Fuwei Zhuge, Xiaomin Li, Xiangdong Gao, Xiaoyan Gan, Fengling Zhou. Materials Letters, 63 (2009) 652–654.

[2] Sheng-Yue Wang, Wei Wang, Zu-Hong Lu, Materials Science and Engineering, B103 (2003) 184- 188.

[3] J. Santos Cruz, S. A. Mayen Hernanddez, J. J. Coronel Hernandez, R. Mejiarodriguez, R. Castanedo Pereza, G. Torres Ddelgadoa, S. Jamenez Sandovala Chalcogenide Letters, 9, 2 (2012) 85 - 91.

[4] Elijah Thimsen, Qing Peng, Alex B. F. Martinson, Michael J. Pellin, and Jeffrey W. Elam, Chem. Mater., 23 (2011) 4411–4413.

[5] H.M. Pathana, J.D. Desaib, C.D. Lokhandea, Applied Surface Science, 202 (2002) 47–56.

[6] J. Morales, V.C. Perez, J. Santos, L.J. Tirado, J. Electrochem. Soc. 143, 9 (1996) 2847.

[7]I.P. Parkin, Chem Soc Rev, 25, 3 (1996), 199-207.

[8] S. Schneider, J.R. Ireland, M.C. Hersam, T.J. Marks, Chem. Mater., 19, 11(2007) 2780–2785.

[9] H M Pathan and C D Lokhande, Mater. Sci., 27, 2, April (2004) 85–111

[10] S.D. Sartale, C.D. Lokhande, Materials Chemistry and Physics, 65, 1 (2000) 63-67.

[11] A.Ashour, Journal of Optoelectronics and Advanced Materials, 8, 4, August (2006) 1447-1451.

[12] Laila. I. Soliman, Alaa M. Ibrahim, FIZIKA A, 6, 4 (1997) 181–189.

[13] N. F. Mott and E. A. Davis "Electronic Processes in Non-Crystalline Materials", 2nd, Clarendon Press, oxford, 1979.

[14] S. O. Kasap, "Principle of electronic materials and devices", Snded, McGraw-Hill, New York, 2002.

[15] Z.R. Khan, M. Zulfequar, M.S. Khan, Chalcogenide Letters, 7, 6, (2010) 431-438.

[16] K. R. Murali, P. Elango, P. Andavan K. Venkatachalam, Journal of Materials Science, Materials in Electronics, 19, 3 (2008) 289-293.

[17] B. Ray, “II-VICompounds”, 1st Ed. Printed in Great Britain, 1969.

[18] S. O. Kasap, "Principle of electronic materials and devices," Snded, McGraw-Hill, New York, 2002.

[19] D. J. Roulston, “Bipolar Semiconductor Devices”, McGraw Hill, New York, (1990).

[20] S. M. Sze, K. Ng Kwok “Physics of Semiconductor Devices”, John Wily & Sons, New York, 2007.