

The optical properties of $2(\text{CdS})\text{X}(\text{CuInS}_2)_{1-\text{X}}$ thin film systems.

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ABSTRACT

The optical properties of $2(\text{CdS})\text{X}(\text{CuInS}_2)_{1-\text{X}}$ (CCIS) thin film systems grown by chemical spray pyrolysis on glass slides were studied .The obtained results of X-ray diffraction (XRD) structure analysis were polycrystalline for all values of $\text{X}= 0,0.1,\dots,0.4$, and have many phases with new phase (CCIS) .The optical characteristics of the prepared thin films have been investigated by UV-VIS spectrophotometer in a wavelength ranging (300-1100) nm . The prepares films have a direct energy gap (E_g) its value varied between (1.4 - 1.8) eV depending on X value . The optical constants such as refractive index (n) ,extinction coefficient (k) ,real and imaginary dielectric constants (ϵ_1 & ϵ_2) also discussed .It is found that the prepared films are promising in thin film solar cell.

Introduction

Chalcopyrite thin film solar cell with high efficiencies are prepared using CdS buffer layers on CuInS₂ surface . Their is a tendency to substitute CdS for an other , Cd – free material, although the efficiency of solar cells with alternative buffers is still inferior [1-3]. In this respect the investigation of phase relation involving CuInS₂ and CdS is important to assess possible element interdiffusion at the p- n hetrojunction and to extend the knowledge about solid solutions and possible intermediate phases .

Physical properties of many systems are investigated some of them are ,quasi – ternary Cu Ga S₂- CuInS₂-2CdS system was investigated using differential thermal analysis and phase X-ray diffraction [1] ,photocatalysts (CuIn)XCd₂(1-X) S₂ was synthesized by a low temperature hydrothermal method and characterized by XRD ,SEM ,and BET[4] and phase equilibria in the CuInSe₂ –CuGaSe₂ - 2CdSe system are studied using thermal analysis and phase X-ray diffraction [5] . CdS – Cu In S₂ system prepared by spray pyrolysis method does not found in litriture ,and its optical properties not have been studied . In the present study we prepared $2(\text{CdS})\text{X}(\text{CuInS}_2)_{1-\text{X}}$ thin film system by spray pyrolysis method and investigated the optical properties of the prepared thin films for using as thin film solar cells.

Experimental

The $2(\text{CdS})\text{X}(\text{CuInS}_2)_{1-\text{X}}$ thin film systems prepared by chemical spray pyrolysis were $\text{X} = 0,0.1,\dots,0.4$. The films deposited on micro glass slides were first cleaned with detergent water and then dipped in acetone . Spray solutions are prepared by mixing 0.1M aqueous solution of CdCl₂, CuCl₂ ,InCl₃ and thiourea [CS(NH₂)₂] in the ratio of Cd: Cu: In: S (2x:1-x:1-x:2) respectively then mixing the amount of solution for each experiment by a magnetic stirrer . Automated spray solution is transferred to the hot substrate kept at the normalized deposition temperature of $350 \pm 10^\circ\text{C}$ with the help of carrier gas. Filtered air is used as carrier gas, the flow rate of which is normalized to ~2 ml/min . To avoid excessive cooling of substrate, spraying was achieved in periods was about 10sec followed by 15sec wait [6]. To deposit films of uniform thickness the distance between the substrate and spray nozzle was kept at 58 cm. Thickness measurement of the films has been carried out using optical method (Pezos fringes)which equal to 200 ± 20 nm. To determine the nature of the growth and structural characteristics of the prepared thin films, an X-ray diffraction (XRD) obtained for diffractometer type (Philips PW1840 with target Cu-K α). The (UV-Vis-Spectrophotometer) type Jenway (6800UV / Vis) was used to measure the absorbance and transmittance in the wavelength range 300 - 1100 nm, and from these measurements, the optical parameters were calculated. The topography of CCIS thin film surface was inspected with optical reflected-

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microscope type (Polarizing microscope Eclipse - 50ipol Nikon)

Results and Discussion

The structure of the prepared thin films was examined by XRD as shown in fig .(1) .The patterns of X= 0.1 and X=0.3 obtained that the films have CuInS2 ,CdS and In2S3 peaks as well as (CCIS) peak . Structure of CuInS2 compound is hexagonal at X=0.1 and cubic at X=0.3 . The amount of CCIS increased in the film with increasing X .

Fig (2) shows the optical microscope image of the prepared thin film surfaces. From these micrographs, when X = 0, the surface of CuInS2 has rough surface and large grains, but when adding CdS as substitution the surface became smooth and their is a black line which may be related to the new phase of CCIS. The absorption coefficient(α) which is the decrement ratio of incident radiation relative to unit length in the direction wave propagation inside the medium, is relating with the absorbance (A) through the following relation [7].

$$\alpha = 2.303 A/t \dots\dots\dots (1)$$

Where (t) is the sample thickness.

The optical absorption coefficient (α) for the prepared thin films was calculated from eq. (1). The values of α for all thin films found to be greater than 104 cm-1 in the visible region , which means that the films have a direct optical energy gap [8], so that the value of r in the empirical

following equation equal to $\frac{1}{2}$ [9,10] .

$$(\alpha hv) = C (hv - Egopt) r \dots\dots\dots (2)$$

Where C is constant .

Fig(3) shows the absorption coefficient (α) of thin films vs photon energy $h\nu$.From this figure when the value of $h\nu$ equal to 1.4 eV which E_g of CuInS2 , α bigine increases and its increases changed with $h\nu$ depended on the value of X . Also fig(3) shows that the value of $\alpha > 104$ cm-1 in the visible region which means that the energy gap of these films are direct [8] . A direct optical energy gap (E_g) was calculated by using the following relation [11].

$$(\alpha hv)^2 = C (hv - Egopt) \dots\dots\dots (3)$$

Fig (4) Shows the energy gap values of (CCIS) thin film at different X values , which obtain

that energy gap increases with X ,i.e with increases CdS which ranged from 1.4 eV at X= 0 to 1.8 eV at X = 0.4. The change of the band gap for CdS – CuInS2 does not follow the rule for simply mixing two semiconductors together as shown in fig (5) , this behaviour also found by Lu Ren et al [12] for (Cu In)XCd2(1-X) S2 system .

The values of extinction coefficient (k) are calculated using the following relation [7] .

$$k = \alpha \lambda / 4\pi \dots\dots\dots (4)$$

Where λ is the wavelength of the light . The k values are plotted vs $h\nu$ for CCIS thin film for different value of X as shown in figure (6) , which shows that k increased in general with $h\nu$ from 1.4 eV which the energy gap of CuInS2 at X = 0, and its behaviour different from film to the other which may be related to the film structure. The k behaviour similar to α behaviour .

The refractive index (n) was calculated using the following relation [7] .

$$\frac{1+R}{n} = \frac{1}{1-R} + \left[\frac{4R}{(1-R)^2} - k^2 \right]^{1/2} \dots\dots\dots(5)$$

where R is the reflectivity .

The values of n vs $h\nu$ is shown in fig (7) . From this figure ,the maximum value of n at X = 0 is equal to 2.3 which is related to CuInS2 films, while the other films of X = 0.1 to X = 0.4 the value of n equal to 2.6 ,but its maximum peak was shifted toward higher energy as X increased , which is related to the E_g value of thin films , where after $h\nu \geq E_g$ the photon was absorbed and the refractive index (n) decreased as shown in fig (7) .

Real dielectric constant were determined using the equation (6) [7].

$$\epsilon_1 = n^2 - k^2 \dots\dots\dots (6)$$

The plots of ϵ_1 with $h\nu$ for different thin films are shown in fig. (8). This Figure shows that the behave of ϵ_1 with $h\nu$ similar to the refractive index (n) which have a maximum value which is about 6 for all films of $X \geq 0.1$ and then decreased with increasing $h\nu$.

Imaginary dielectric constants (ϵ_2) were determined using the relation [7].

$$\epsilon_2 = 2nk \dots\dots\dots(7)$$

Fig. (9) shows the behaviour of ϵ_2 vs $h\nu$ for films which indicate that ϵ_2 have two shapes the first one when $h\nu < E_g$, the behavior is similar to k shape and the second when $h\nu \geq E_g$ its behaviour is similar to n shape.

From the result presented here it can be concluded that a thin films of $2(\text{CdS})_x(\text{CuInS}_2)_{1-x}$ were prepared by chemical spray pyrolysis method .as polycrystalline structure with many phases for the first time . The films give a graded optical band gap of nonlinear behaviour between 1.4 - 1.8 eV . The optical constants k, n and (ϵ_1 & ϵ_2) are depending on X value . The results suggest that the prepared films using in industrialize thin film solar cell.

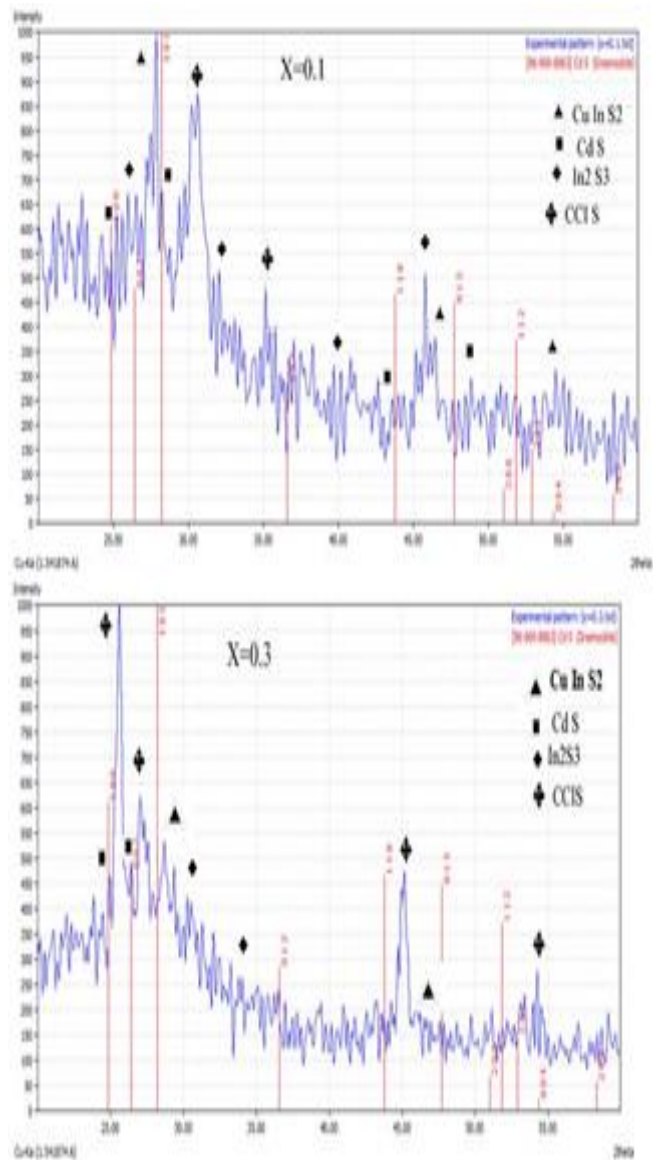
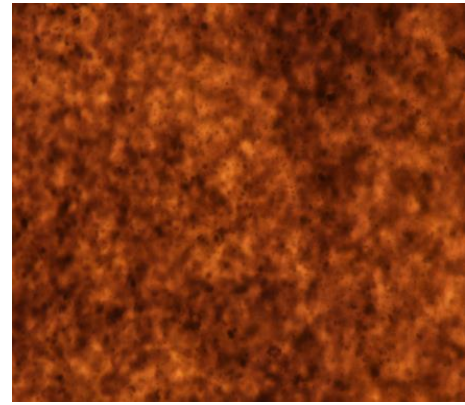
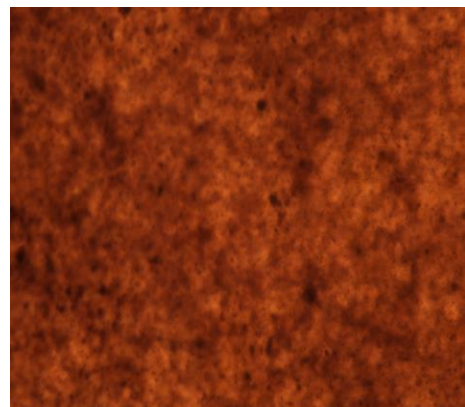


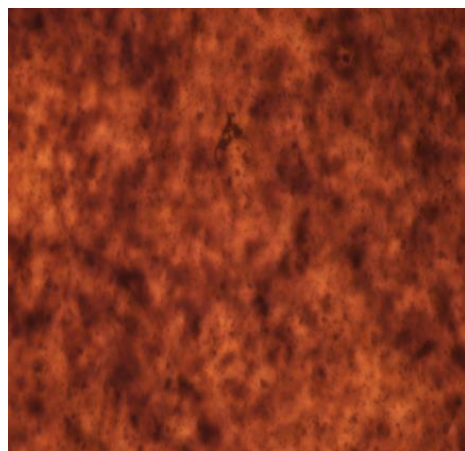
Fig.(1)The XRD Pattern of $2(\text{CdS})_x(\text{CuInS}_2)_{1-x}$ Thin films at X=0.1 and X=0.3.



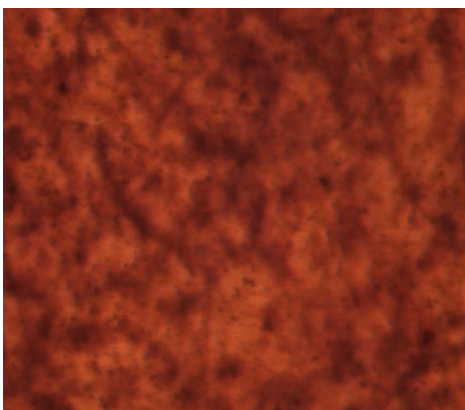
X=0



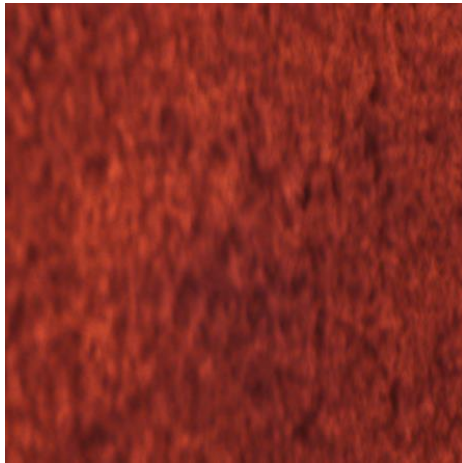
X=0.1



X=0.2



X=0.3



X=0.4

Fig.(2) The morphology of $2(\text{CdS})_x(\text{CuInS}_2)_{1-x}$ thin film surface.

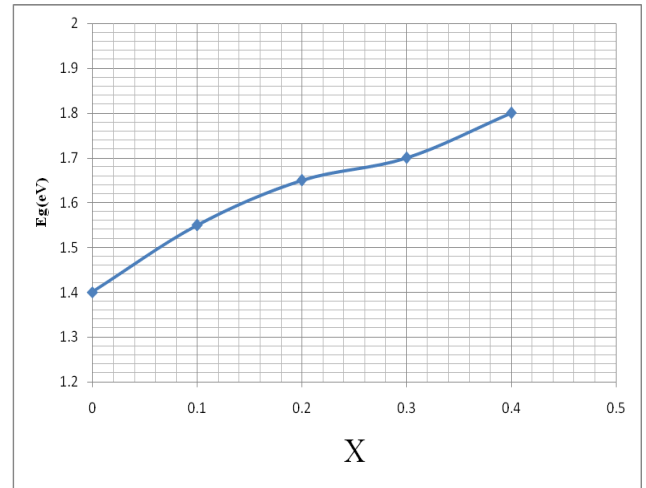


Fig.(5). The variation of E_g value with X for the CCIS thin film .

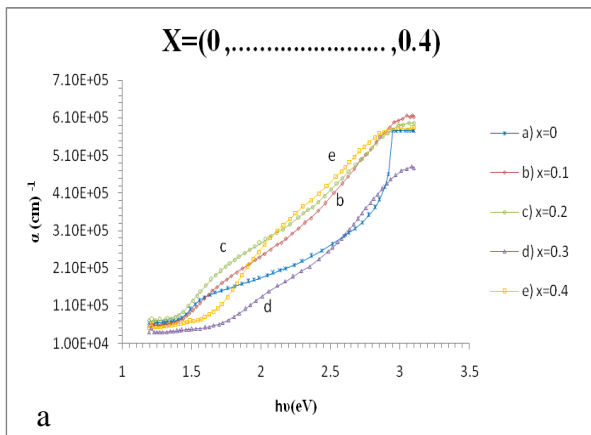


Fig .(3) The variation of absorption coefficient (α) with $h\nu$ for thin films of CCIS .

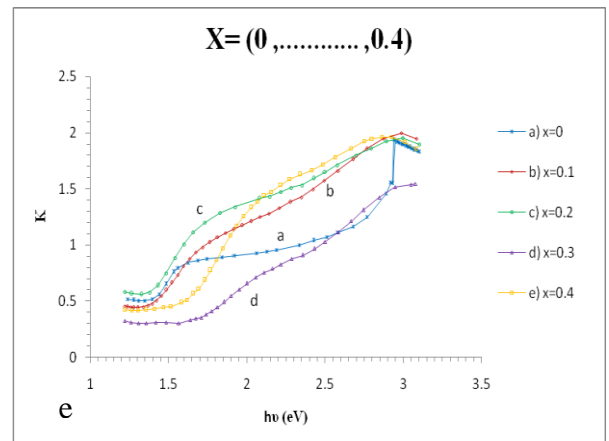


Fig.(6) . The extinction coefficient (k) with $h\nu$ for prepared thin films .

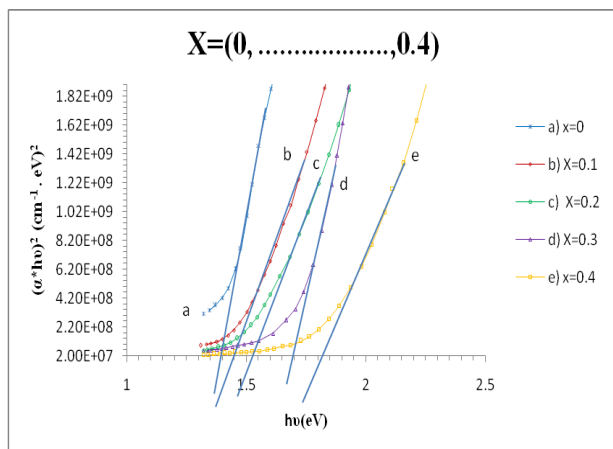


Fig.(4) . The optical energy gap (E_g) of film for X = 0,0.1,.....,0.4

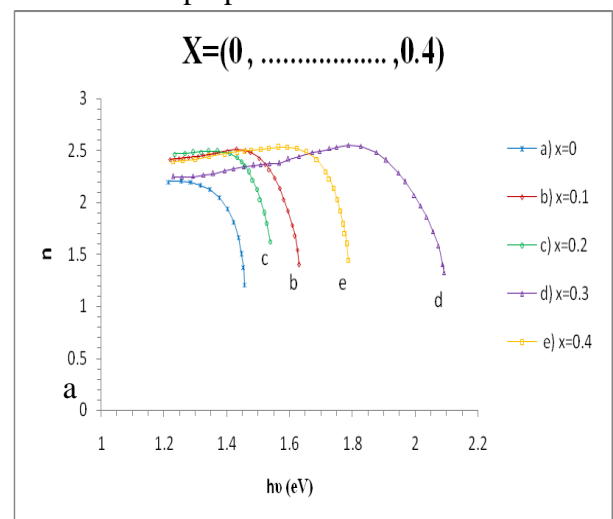


Fig.(7) . The variation of refractive index (n) with $h\nu$ for prepared thin films .

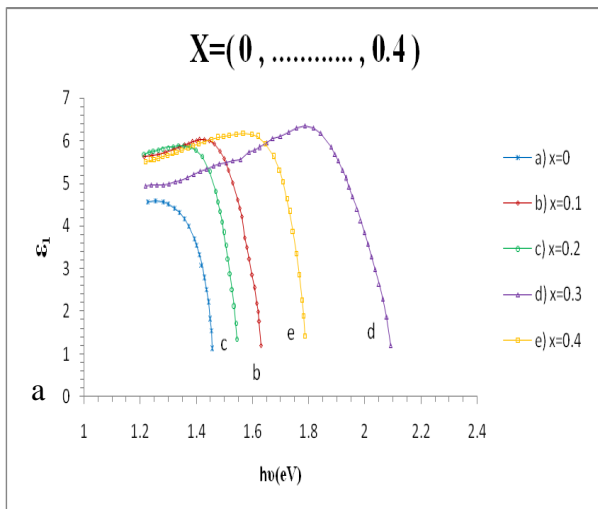


Fig.(8) .The real dielectric (ϵ_1) with $h\nu$ for CCIS thin films .

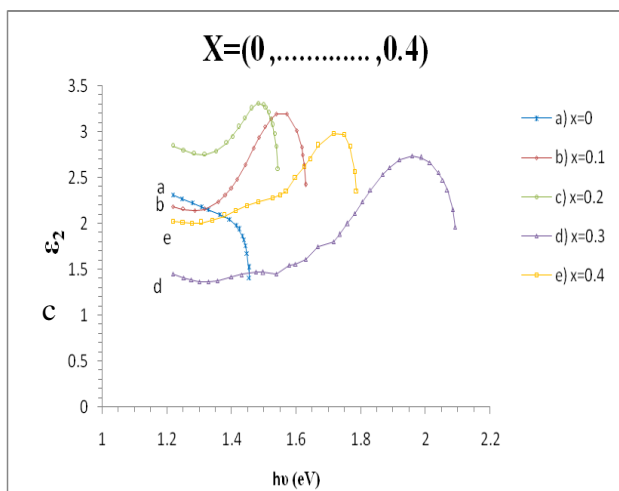


Fig .(9). The imaginary dielectric (ϵ_2) with $h\nu$ for CCIS thin film

References:-

- 1- Ramakrishna Reddy. K.T, Forbes .I, Miles. R.W, Carter. M.J , Dutta. P.K, (1998) . " Growth of high-quality CuInSe₂ films by selenising sputtered Cu–In bilayers using a closed graphite box ". Materials Letters 37, pp . 57–62 .
- 2- Puja Chawla , Geeta Sharma , lochab .S. P , and Nafa Singh (2010). " Effect of solvent-induced structural modifications on optical properties of

- CdS nanoparticles Bull ". Mater. Sci., Vol. 33, No. 5, pp. 535–541.
- 3- Bari. R.H, Pati . L .A. I, Soni. A and. Okram Bull G .S, (2007) . Mater Sci ; Vol .30, No.2, pp . 135-139.
- 4- Marushko . L.P , Romanyuk . Y. E , Piskach. L.V, Parasyuk . O.V, Olekseyu . I.D, Volkov . S.V, Pekhnyo . V.I, (2010). " The CuInSe₂–CuGaSe₂–2CdSe system and crystal growth of the γ - solid solutions ". Journal of Alloys and Compounds 505, pp. 101–107.
- 5- Djordjevic. J, Pietzker C, Scheer. R,(2003). J. Phys. Chem. Solids 64 p.1843.
- 6- Hamid . S. Al- Jumaili, (2003) . J. Al-Anbar University for pure science ,Vol. 1. No .3, pp .70 - 79.
- 7- Saliha Ilicaru Muhsin Zor ,Yasemin Cuglat , MujdatCaglar , (2006). Optica applicat 4 Vol. XXXVI No.1 .N , pp .29 – 37.
- 8- Ailes. N .C - Taylor , Bicknell. R . N , Blanks. D . K , Myens T. H, Schetzina. J. F (1985). J . Vace . Sci and Technol , A3 , 76.
- 9- Bem Rabeh. M, Kanzarian . M and Rezig. B,(2009). J. Optoelectronic and Biomedical Materials Vo l 1 , I, pp 70-78 .
- 10- Tauc. J, (1974). edition by J. Tauc, plenum press.
- 11-Thambidurai .M, murugan .N , muthukumaxasamy .N , Vasantha .S, balasundaraprabhu . R, agilan .S, (2009). " Chalcogenide Letters ". Vol. 6, No. 4 , pp. 171 -179.
- 12- Parasyulg .O.V , voronyuk . S.V, Gulay L.D, Davidyuk. G.ye and Halka V.O, (2003) . J .Alloys and compounds . Vol. 348, No.1-2, pp. 57-64 .

الخصائص البصرية لأنظمة أغشية $2(\text{CdS})\text{X}(\text{CuInS}_2)_{1-\text{X}}$ الرقيقة .

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الخلاصة

تم دراسة الخصائص البصرية لأنظمة أغشية $2(\text{CdS})\text{X}(\text{CuInS}_2)_{1-\text{x}}$ (CCIS) الرقيقة المحضرة بطريقة الرش الكيميائي الحراري على شرائح زجاجية . لقد بينت نتائج فحص حيود الأشعة السينية بان الأغشية متعددة البلورات لجميع قيم $X = 0, 0.1, \dots, 0.4$ وتمتلك عدة أطوار بالإضافة إلى الطور الجديد (CCIS) . إن الخصائص البصرية للأغشية المحضرة تم دراستها بمطياف UV-VIS ضمن مدى الأطوال الموجبة- (300-1100) nm وقد وجد بان الأغشية تمتلك فجوة طاقة بصرية نوع مباشر وان قيمتها تتغير بين (1.4 – 1.8) eV معتمدة على قيم X . لقد تم حساب ومناقشة قيم الثوابت البصرية والتي شملت معامل الانكسار (n) ومعامل الخمود (k) وثابت العزل الحقيقي (ϵ_1) والخيالي (ϵ_2) . إن نتائج البحث أظهرت بان الأغشية المحضرة تمتلك خصائص بصرية تؤهلها لتصنيع خلايا أغشية رقيقة شمسية .