The effect of Doping Ratio on the Opical Properties of CdSe Film

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Date of acceptance 2/6/2005

Abstract

The films of CdSe pure and doped with copper of ratio (0.5, 1.5, 2.5, & 4wt%Cu) have been prepared by evaporation technique of thickness 1μm onto clean glass substrate. The effect of Cu concentration on optical properties of CdSe pure and doped with copper has been studied. It s found that they have direct energy gap. The absorption edge was shift slightly towards higher wavelength for Cu- doped films and energy gaps(E_g) decrease with increasing of Cu concentration from 1. 83eV to 1.79eV for CdSe pure and doped with 4wt% respectively, due to increasing of impurity levels in the band gap. It was found that the absorption coefficient is increased with increase of Cu concentration from $7X10^3 cm^{-1}$ at 0.75μm for pure CdSe to the $1.15X10^4 cm^{-1}$ for 4wt% Cu at the same wavelength. The amorphousity of the films decreases with increasing of Cu concentration due to improve the structure of the film by adding the Cu. And the density of state increases with increasing copper from (0.119-0.15)eV for CdSe pure and doped with 4wt% respectively. The refractive index, extinction coefficient and dielectric constant were also studied.

1-Introduction:

Cadmium selenide is an important member of this group of binary compounds. It has a direct intrinsic band gap of 1.74eV, which makes it an interesting material for various applications. This material has been grown in bulk single crystalline form and has been used as an efficient photoconductor. There are two main methods for preparing semiconductors thin films, the first method is involves electrochemistry to deposit the thin films on a solid surface and this procedure provides materials such as CdTe, CdSe and CdS which are used in solar cells, and the second method is chemical spray[1]. In recent years much attention has been shown in semiconducting II-VI compounds because of their optoelectronic properties and applications. CdS and CdSe films which grown by evaporation technique have been used as gas sensors for detection of oxygen[2]. Al-Ani et al [3]has studied the optical properties of CdSe at different substrate temperatures, they found that the energy gap was increased as the substrate temperature increased. Also the same authors[4] have prepared CdSe:Cu by vacuum evaporation technique. And they found that the energy gap was decreased as the copper content increased. Mahmoud et al[5] and Narayaandass et al[6] have prepared CdSe film by hot wall deposition technique onto glass substrate, they are studying the X-ray diffraction and found that the films exhibit preferential orientation along the (103) direction and changes to the (002) direction as the thickness increases. The optical absorption coefficient exceeds $5X10^4 cm^{-1}$ for all wavelength less than 0.7 μm [3,4]. Materials films depend mainly on the impurity concentration and sensitization of the films. Extensive studies have been carried out on the

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photoconducting properties of Cu-doped CdSe[4,10,11].The nature and rule of defects in CdSe, and the part played by copper have still been well-established[12,13]. As will most of the II-VI compounds, accidental trace contamination with copper is quite common. This is particularly importance in the Cu_2 Se-CdSe heterojunction solar cell device where copper may diffuse readily across the junction. On the other hand, copper is widely used as a counter dopant in the preparation of photoconductive CdSe[14]. This paper presents the results of a study the optical properties of pure CdSe and doped with copper at different concentration, and calculate all the optical constants.

2-Experimental:

The pure cadmium selenide (CdSe)(99.999)% were doped with copper by chemical diffusion by mixed it with solution of CuCl(0.5, 1.5,2.5, 4wt%) and dried at 100°C for one hour and were taken as a source materials. CdSe:Cu films were deposited onto glass by vacuum evaporation with thickness(1μm). Annealing was made for all films at 350°C in vacuum with argon atmosphere. Lambda 9 Spectrophotometer from Perkin-Elmer Co. Has been used to carry out the absorptance(A) and transmittance(T) spectrum in the wavelength(λ) range (0.4-1)μm region for pure CdSe films and doped with copper. The absorption coefficient (□refractive index(n) and extinction coefficient(k), has been calculated from the equations respectively[15]:

$$\alpha = 2.303A/d \text{------------------------} (1)$$

$$n = \left(\frac{4R}{(R-1)^2} - k^2\right)^{1/2} - \frac{(R+1)}{(R-1)} \text{——} (2)$$

$$k = \alpha\lambda/4\pi \text{——————————} (3)$$

where R is the reflectance, and the real and imaginary part of dielectric constant (ε_1 and ε_2)respectively can be calculated by using equations[15]:

$$\varepsilon_1 = n^2 - k^2 \quad (\textit{real part}) \text{———} (4)$$

$$\varepsilon_2 = 2nk \quad (\text{imaginary part}) \text{-------} (5)$$

3-Results and Discussion:

Fig.(1) shows the transmittance and absorptance spectra for pure CdSe films and doped with different copper concentration (0.5, 1.5, 2.5, & 4wt%) and annealed at temperature 350°C under argon atmosphere. The absorption, transmission, and reflection has been studied, also energy gap and optical constant has been determined. In general, our results showed a decrease in transmission spectra with increasing Cu concentration. The absorption edge shifting to higher wavelength and this may be attributed to the creating levels at the energy band by adding the more of Cu concentration, which leading to shifts to smaller energies and this may be indicate that doping with Cu leads to an increasing new states in the energy gap, visualized as an increase in the width of concentration tail leading to a shift of Fermi level towards the valance or conduction band[16].Also we are studied the spectrum of absorptance as in Fig.(1). It is obvious that it behavior is opposite to that of transmittance spectrum. The pure CdSe films have highest transmission(9%) at 0.7μm , while other films which doped with4wt% Cu showed lowest transmission(2%) at the same wavelength. These results agreed with Rao et al[17] and with the researcher who prepared CdSe films by laser induced evaporation[18].

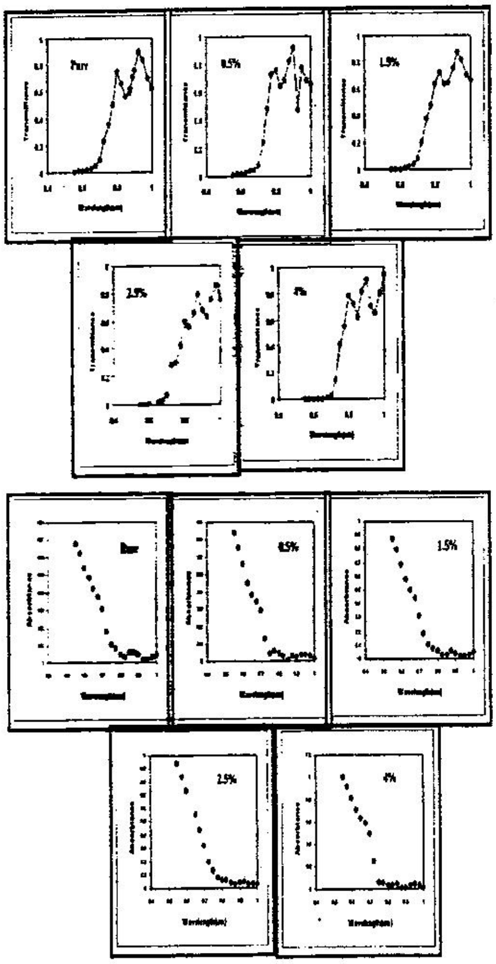

Fig.(1)The transmittance and absorptance spectra of pure CdSe films and doped with different Cu concentration (0.5, 1.5, 2.5, & 4wt%)

The reflectivity decreased from 0.605 to 0.48 at pure CdSe and 4wt% Cu respectively. Fig.(2) shows the absorption coefficient (α) of pure CdSe and doped with (0.5, 1.5, 2.5, 4wt%), which calculated from the equation(1). From this figure the value of α increases with increasing Cu concentration from $7X10^3cm^{-1}$ at 0.75μm for pure CdSe to the $1.15X10^4cm^{-1}$ for 4wt% Cu at the same wavelength(see Table(1). This is related to the increase of Cu metal concentration, this none stoichiomeric in the films leads to increase the impurity levels or the density of localized state which leads to increase the absorption coefficient. The dominate feature of the energy (hυ) dependence of the absorption coefficient(α) is the onset of absorption near the region of interband transitions from valence band to conduction band .

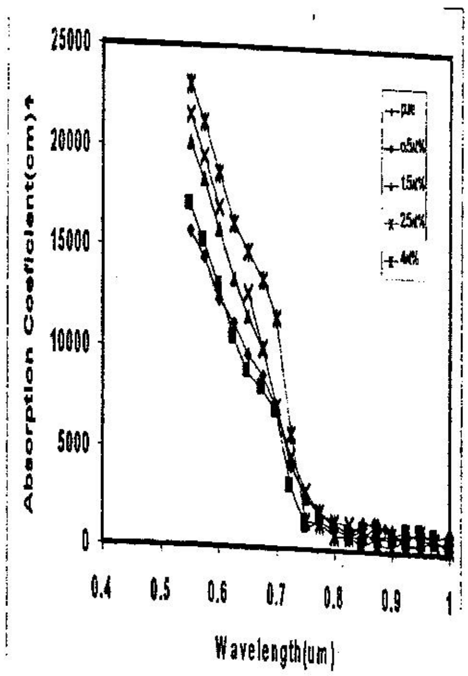

Fig.(2)The absorption coefficient of pure CdSe films and doped with different Cu concentration (0.5, 1.5, 2.5, & 4wt%)

At $\alpha > 10^4cm^{-1}$ the optical energy gap of material E_g may be obtained from the equation near the band edge:

$\alpha h\upsilon = B(h\upsilon - E_g)^r$-------------------(6)

where B is constant represent amorphousity factors. Which has been obtained from the root square of the straight line slope in the Fig.(3). From this figure the value of B is increased with increasing Cu concentration .We know that B is inversely proportional to amorphosity and the width of the band tails [15]. Equation (1) is applied for allowed direct transitions as shown in Fig.(3) which present the $(\alpha h\upsilon)^2$ as a function of hυ in accordance with equation(1) and the extrapolation of the linear regions give value of E_g(1.83, 1.8, 1.8, 1.82, 1.79)eV for pure CdSe and doped with (0.5, 1.5, 2.5, 4wt%)Cu respectively(see Table(1)) and this attributed to the increase the density of localized state in the energy gap which cause shift in E_g to smaller energy gap with increasing Cu concentration. These value of E_g are agreement with Ichimura et al[19], they obtained E_g about (1.84-1.9)eV before annealing and (1.75-1.85)eV after annealing. Also Shreekanthan et al[9] have found that the value of E_g equals to 1.88eV for CdSe which prepared by hot wall method at room temperatures, And Philip et al[20] found that the E_g shifts towards higher wavelength with increasing pressures.

At1< α <$10^4 cm^{-1}$ the value of width of tails(ΔE_t) of localized state in the gap is obtained from Fig.(4)where Ln α is plotted as a function of hv, in accordance with Urbach relation[15]:

$$\alpha = \alpha_o \exp(h\nu / \Delta E_t) \text{------------} (7)$$

where α_o is constant. The value of ΔE_t extracted from the reciprocal slope of the linear part are equals to (0.119, 0.12, 0.13, 0.149, 0.15)eV for pure CdSe and doped with (0.5, 1.5, 2.5, 4wt%)Cu respectively(see Table(1)), and this attributed to the increasing of Cu concentration in the E_g which lead to create localized state in the E_g . The value of extinction coefficient(k) which calculate from the equation(3) are shown in Table(1). The behavior of k is nearly similar to the corresponding absorption coefficient. We can see from this figure that the value of k increased by increasing Cu concentration and this is due to the same reason which mention previously in α. The values of the refractive index(n) which which calculated from the equation(2) are equals to (3.8, 3.7, 3.36, 2.78, 1.592) for pure CdSe and doped with (0.5, 1.5, 2.5, 4wt%)Curespectively (see Table(1)),

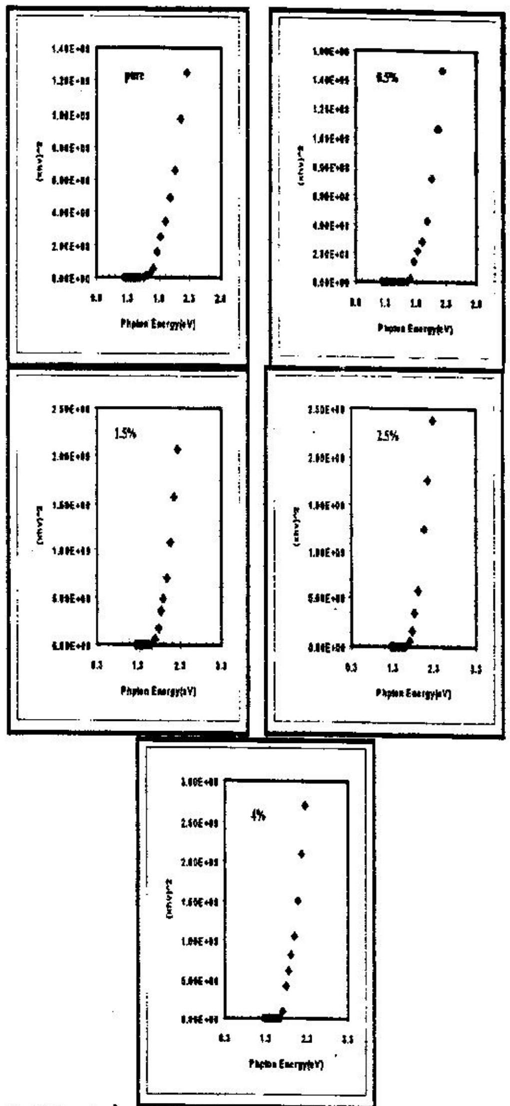

Fig.(3) the $(\alpha h\nu)^2$ as a function of hv of pure CdSe films and doped with different Cu concentrations (0.5, 1.5, 2.5, 4Wt%).

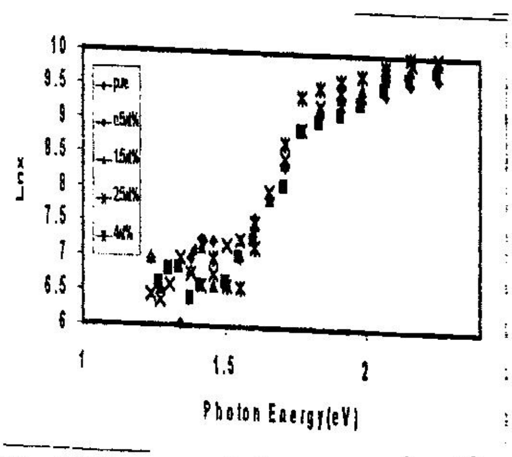

Fig.(4)Represents Ln α as a function of hυ of pure CdSe films and doped with different Cu concentration (0.5, 1.5, 2.5, & 4wt%)

which decreased with increasing Cu content, and this attributed to the increasing of Cu impurity inside E_g , which effect on the value of n[15]and this agreement with other researchers[21], they obtained on n equals to 2.63 and 2.43 at wavelength 0.75μm.Table(1) show the variation of real and imaginary part of dielectric constant (ε_1 and ε_2)respectively as a function of Cu content which calculated from the equations(4 and 5). The behavior of ε_1 is similar to refractive index because the smaller value of k^2 comparison of n^2, while ε_1 is mainly depends on the k values, which are related to the variation of absorption coefficient. It is found that ε_1 and ε_2 decreases with increasing Cu concentration as shown inTable(1).

Table(1) Represents the optical constants of CdSe and CdSe:Cu films with different Cu concentration

T_a	E_g (eV)	BX10^5 eV/cm^2	N at 0.675 μm	k at 0.675 μm	ε_1 at 0.675 μm	ε_2 at 0.675 μm	α (cm^{-1})x10^4	ΔE_e V
Pure	1.83	1.73	3.8	6.64	14.7	0.0635	0.70	0.119
0.5	1.80	1.73	3.7	4.25	14	0.0215	0.68	0.12
1.5	1.80	2.23	3.36	5.41	11.29	0.0577	0.72	0.13
2.5	1.82	2.23	2.78	5.41	7.76	0.0281	0.72	0.149
4	1.79	2.44	1.59	7.21	5.7	0.00456	1.15	0.15

Conclusions:

The pure CdSe and CdSe:Cu films were prepared on glass substrate by vacuum evaporation with thickness(1μm). Annealing was made for all films at 350°C with argon atmosphere. The effect of copper concentration on the optical properties of pure CdSe and doped with copper has been studied. Its found that:

1. The films have direct energy gapand the absorption edge was shift slightly towards higher wavelength for Cu-doped films.
2. The value of energy gaps(E_g) decrease with increasing of Cu concentration from 1. 83eV to 1.79eV for CdSe pure and doped with 4wt% respectively.
3. It was found that the absorption coefficient and extinction coefficient increased with increasing of Cu concentration.
4. The amorphousity of the films decreases with increasing of Cu concentration due to improve the structure of the film by adding the Cu.
5. The density of state increases with increasing copper from (0.119-0.15)eV for CdSe pure and doped with 4wt% respectively.
6. The values of the refractive index(n) are equals to (3.8, 3.7, 3.36, 2.78, 1.592) for pure CdSe and doped with (0.5, 1.5, 2.5, 4wt%)Cu respectivelywhich decreased with increasing Cu content.
7. It is found that ε_1 and ε_2 decreases with increasing Cu concentration.

References

1. ***File://B:\Michael Cosivera.htm(2002).***
2. Smyntyna,V.A., Gersutenko, V., Sashulies, S., et al, 1994,Sensors and Actuators B, 18-19:464.
3. .Al-Ani, S.K.J.,Mohammed, H.H., and Al-Ani, R.S., 2000, Fabricationof CdSePhotoconductive Detector, Iraqi J. Sci, 41C(4):192-211.
4. .Al-Ani, S.K.J.,Mohammed, H.H., and Al-Fawade, E.M., 2000, The Optoelectronic Properties of CdSe Photoconductive Detector, world Renewable Energy congress, VI Reading, U.K.,2026-2031.
5. Mahmoud, A.H., 1990, Cadmium SelenideThin Films Grown by Vacuum Deposition Technique, Crys. Res.Technol, 25:1147.
6. Narayandass, K. and Mangalaraj, D., 1998, Semiconducting science and technology, Electronic Journals, 641-46.

7.Sebastian, P.J., 1994, Transport and Optical Properties of CdSe-CdTe Pseudo binary Thin Films, Cadmium Selenide , Thin Solid Films,245:123.

8.Waechter, D., Westcdff, M.R., Lin, F. and Hatalis, M.K., 1993, Properties of CdSe Thin Films as a function of Lateral Distance from Chromium Contacts, J. Electrochem.Soc., 140:10.

9. Shreekanthan, K.N., Regendra, B.V., Kasturi, V.B. and Shivakumar, G.K., 2003, Growth and characterization of semiconducting cadmium selenide films, Cryst.Res. Technol, 38(1):30-33/DOI.

10.Sathyalatha, K.C., Uthanna, S.M. and Jayarama, R.P., 1989, Electrical and Photoconducting Properties of Vacuum Evaporated Pure and Silver-Doped CdSe Film, Thin Solid Films, 174:233-238.

11.Svechnicov, S.W., Shtrum, E.L. and Klochov, V.P., et al, 1972, photoconducting properties of Copper- and Cadmium- Doped CdSe Films, Thin Solid Films,11:33.

12. 11.Robinnson, A.L. and Bube, R.H., 1971, Preparation of Photoconductive CdSe with Copper as a Counter Dopant, J. Appl. Phys., 42:5280.

13. Manfredotti, C., Rizzo, A., Vasanelli, L., et al , 1973, Defects in CdSe, J. Appl. Phys., 44:5463.

14. . Ture, I.E., Ressell, G.J. and Wood, J.,1985, Preperation of Cu2Se-CdSe Heterjunction Solar Cell Device, EEC Photovoltaic Conf., London

15 Alias, M.F.,1998, Optoelectronic Study of a-Si-Ge-Al(As):H Films, Ph.D. Thesis , Univers. of Baghdad , Dep. of Physics.

16. Madan, A. and Shaw, M., 1986, The Physics and Applications of Amorphous Semiconductors, Academic Press, ed.Madan, In. New York.

17.Rao, D.R. and Islam, 1993, Cadmium Selenide Thin Films, Thin Solid Films, 224:191.

18.Musa, G.M.,1997, Properties of CdSeFilms, Eng. And Technology, 16(5):333-342.

19.Ichimura, M., Sato, N., Nakeichi, A. and Arai, E., 2002, Properties of Photoconductivity Deposited CdSe, Phys. Stat.Sol. a, 193(1):132-138.

20.Phillip, X. and Quentin, W., 1996, Band Structure of CdS and CdSe at High Pressure, Phys. Rev. B, 54(24):17585.

21.Jeffery, P., Szabo and Cocivera, M., 1987, Effect of annealing atmosphere on the properties of thin filns CdSe, J. Appl. Phys.,61(10):4820.

تأثير نسب التطعيم على الخصائص البصرية لأغشية CdSe

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الخلاصة

حضرت اغشية CdSe النقية والمطعمة بالنحاس بالنسب (0.5, 1.5, 2.5, & 4wt%Cu) بطريقة التبخير الحراري في الفراغ وبسمك 1μm على قواعد زجاجية منظفة. تم دراسة تأثير تركيز النحاس على الخصائص البصرية لأغشية CdSe النقية والمطعمة بالنحاس ووجد بأن الأغشية تمتلك فجوة طاقة مباشرة وتزاح حافة الأمتصاص ازاحة طفيفة بأتجاه الأطوال الموجية العالية للأغشية المطعمة بالنحاس وكذلك تقل فجوة الطاقة (E_g) بزيادة تركيز النحاس من (1.38eV to 1.79eV) للأغشية النقية و المطعمة بالنحاس بالنسبة (4wt%Cu) على التوالي نتيجة ازبادة مستويات الشوائب داخل فجوة الطاقة. يزداد معامل الأمتصاص بزيادة تركيز النحاس من $7X10^3cm^{-1}$ عند 0.75μm للغشاء النقي الى $1.15X10^4cm^{-1}$ للنسبة 4wt%Cu عند نفس الطول الموجي. تقل العشوائية للأغشية بزيادة تركيز النحاس نتيجة للتحسن بالتركيب البلوري لتلك الأغشية. تزداد كثافة الحالات الموضعية بزيادة تركيز النحاس من(0.119-1.15)eV للأغشية النقية و المطعمة بالنحاس بالنسبة 4wt%Cu على التوالي. كذلك تم دراسة معامل الأنكسار، معامل الخمود وثوابت العزل.