

The Effect of Cu Doping on the Physical and Structural Properties of CdSe Thin Films

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Abstract:

Pure Cadmium Selenium (CdSe) films were prepared on glass wafers using Chemical Bath Deposition (CBD) technique. Copper thin films with various thicknesses (100 Å, 200 Å and 300 Å) were deposited on the upper surface of (CdSe) by thermal vaporization technique. After that, prepared samples were annealed at a temperature of 250°C for 1 hour in order to diffuse Cu inside the CdSe and get the required sample.

Key words: CdSe thin films, CBD, Cu coated CdSe

الملخص:

تم تحضير أغشية الكاديوم سيلينيوم (CdSe) النقية على ارضيات من الزجاج باستخدام تقنية الترسيب في الحمام الكيميائي (CBD). رسبت أغشية رقيقة من النحاس ذات سماكات مختلفة (100Å, 200 Å, 300 Å) على السطح العلوي لأغشية (CdSe) بتقنية التبخر الحراري. بعدها تم تلدين النماذج المحضرة عند درجة حرارة (250°C) لمدة (1h)، لغرض انتشار النحاس داخل CdSe والحصول على النموذج المطلوب.

الكلمات المفتاحية: أغشية الكاديوم سيلينيوم، CdSe المطعمة بالنحاس، الترسيب بالحمام الكيميائي.

Introduction

The II-VI group compound semiconductors have gained a large extent of attention in the last decades because of their wide applications [1,2]. These semiconductors have assumed a basic job in solar cells because of their widely applications. Cadmium selenium is appeared one of the prevalent competitors, which has the band gap (E_g) of 1.70 eV, and its conductivity appears always n-type [3]. Indeed, these properties the conductivity and band gap are considered the good factors for formation solar cells. There are various deposition techniques have been widely used to prepare CdSe thin films such as Electro-deposition [4], successive ion layer adsorption and reaction [5], chemical bath deposition (CBD) [6], molecular beam epitaxy [7], thermal evaporation [8], metal oxide chemical vapor deposition [9], spray pyrolysis [10]. Among these, CBD is an important deposition technique compound semiconductors due to its simplicity and it is a slow process [11] this means ion by ion or cluster by cluster condensation in an aqueous solution that leads to control the deposition of the compound on the substrate in the presence of a suitable assistance agent. The researchers tried to add impurity with different applications in CdSe to enhance the

physical properties of Cadmium selenium thin films. when CdSe is employed to make the absorbed layer, the thin film conductivity of the solar cells should be p-type. Therefore we must convert CdSe from (n-type) to (p-type) by doping Cadmium selenium with acceptor elements such as Cu and Mg. where n-type doping is much less complicated than p-type doping in II-VI group due to self-compensation effects of group VI vacancies[12]. To correct the modalities, the reasonable deposition parameters should improve. However, when the acceptors penetrate into the lattice, they cannot effectively diffuse into the sites of crystal, even if they, the concentration of these acceptors will not be completely arranged inside the films [13]. In general, the copper ended up being a quicker diffuser, along these lines it has now been picked as a reasonable dopant.

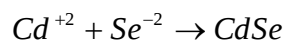
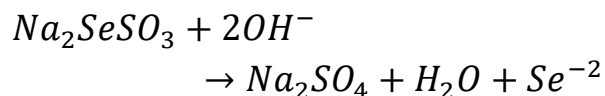
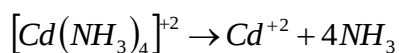
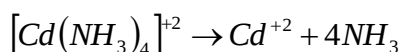
In the present work, we demonstrated the effect of Cu thickness on the structural, optical and electrical properties of CdSe films.

Experimental part

The substrate cleaning is vital in the deposition of CdSe thin films. where glass slides are used with a size of (7.5cm ×1 cm)which is Commercially

available. The glass slides were washed utilizing solution of soap and then put in hot chromic acid for 10 min and then rinsed with distilled water to be rinsed by acetone. For the deposition of CdSe thin films, we used chemical bath deposition technique (CBD). The sources Cd^{2+} and Se^{2-} ions are found from Cadmium Chloride symbol and Sodium selenosulphite respectively.

Ammonia(NH_3) is utilized as a complex factor in the preparation of CdSe thin films. For the preparation of Sodium seleno-sulphite (Na_2SeSO_3), mixture of Na_2SO_3 (0.5M) and Se metal(0.5M) was added in 10 ml a distilled water and then heated at temperature ($100^\circ C$) for (2-4 h). Cadmium Chloride was dissolved in 10 ml distilled water and then added in 1 ml ammonia solution. After that glass substrates were kept in reaction mixture for 24 h at room temperature. The solution temperature was ($35^\circ C$). The time of the deposition was about (20-24 h). After the deposition, the substrates dried in air and put in a desecrator [11]. The chemical reaction is explained as[14]:



The thickness of CdSe was calculated by the equation:

$$t = \frac{\Delta w}{\rho A} \dots \dots \dots (1)$$

Where (t) is thin film, (Δw) is the difference between the substrate weight before and after the deposition, (ρ) is thin films density (5.8 gm/cm^3), and (A) is the area of sample surface. CdSe films were observed to be homogenous with thickness about $0.6 \mu m$, well adherent to the glass substrate and orange red in color.

The deposited CdSe thin films were annealed in vacuum (10^{-6} torr) for 1 h at $250^\circ C$. After that the samples of CdSe were deposited with Cu layer with various thicknesses (100, 200, 300 Å). The resulted samples had been also annealed in 1 h at $250^\circ C$, thin films thickness was ($\sim 0.6 \mu m$) from the eq.(1). The optical properties of the pure Cadmium selenium and Cu/CdSe thin films were characterized by using UV–

VIS–NIR spectrophotometer in the range (320–1000 nm). Electrical resistivity of the doped and undoped CdSe thin films were also measured by four probe method. The type of charge carriers were known by using the Hall effect with magnetic field 600 G. The CdSe thin films were measured by technique X-ray diffraction patterns (XRD, Bruker/D8-advance with wave length $\lambda = 1.54178 \text{ \AA}$, Germany) at 40 kV and 20 mA employing in 2θ range from 20° to 80° . The surface morphology and particle sizes were determined by Scanning Electron Microscopy (SEM) (JEUM-JSM-6754 F) operating at a voltage of 10 kV.

Results and Discussion

X-ray diffraction

Fig.1. (a-c) appears XRD patterns of the Cu/CdSe samples. The distinct diffraction peaks position corresponding to the (002), (110), (103) planes of hexagonal blend CdSe. It can be seen that dominant diffraction peaks match well with the wurtzite CdSe reported in the JCPDS Powder Diffraction File no.(8-459). The large number of peaks in XRD measurements

proves that the films are polycrystalline in the nature from Fig.1a. It was also observed that at Cu thickness of (100 Å), the most serious reflection top at $2\theta = 25.79^\circ$ relating to a hexagonal structures, which has the plane (002) as the desired orientation[15,16]. The intensity of the peak (002) has increased with thickness hence the crystallinity of CdSe increased. As it is seen, there has been an increase in the intensity of two peaks (110) and (103) when they are compared with Fig1.b & c. With increasing the thickness (Fig.b), the intensity of two peaks (110) and (103) and the intense (002) peak have decreased. Also we observed that the shift in the intense (002) peak and (110), (103) peaks towards the lower diffraction angle as compared to Fig 1.a . For Cu thickness (200 Å) which be because of the substitution of Cadmium by Copper in the hexagonal lattice. The increase in Cu thickness from 100 to 300 Å prompts decline in the crystallinity of the Cu/CdSe samples and the intensity of three peaks (002), (110) and (103) have decreased compared to pure CdSe: Cu thin films at 100 Å and 200 Å as shown in Fig.1.

The grains volume are calculated by the

Scherrer eq.(2) [17]:

$$D = \frac{K\lambda}{\beta \cos \theta} \dots \dots \dots (2)$$

where (β) is the width of angular peak at half maximum in radian, (λ) is the wavelength of X-ray ($\text{\AA}$), and (θ) is the angle of Bragg's diffraction.

Table 1: the measurements of X-ray results are

Cu diffusion thickness	hkl	2 θ	FWHM	D ($\text{\AA}$)
100 $\text{\AA}$	002	25.79	0.2	7.14
100 $\text{\AA}$	110	42.34	0.35	4.24
100 $\text{\AA}$	103	46.23	0.4	3.76
200 $\text{\AA}$	002	25.7	0.22	6.46
200 $\text{\AA}$	110	42	0.5	3
200 $\text{\AA}$	103	45.8	0.48	3.2
300 $\text{\AA}$	002	25.4	0.23	6.17
300 $\text{\AA}$	110	42.4	0.46	0.14
300 $\text{\AA}$	103	46	0.42	0.143

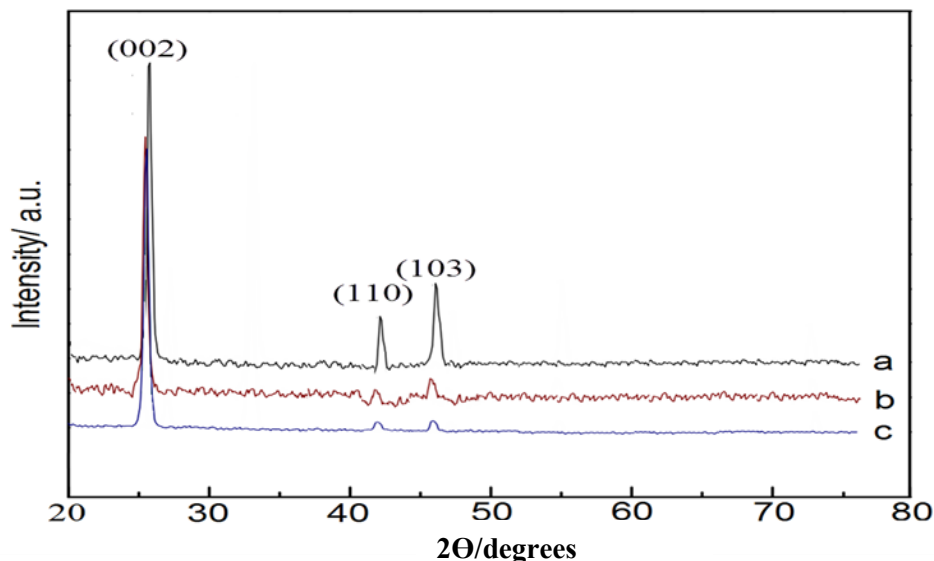


Fig.1:X-ray diffraction patterns of CdSe films as a function of Cu diffusion thickness
(a)100 Å, (b)200 Å (c) 300 Å.

Scanning Electron Microscope (SEM)

Fig. 2 appears the (SEM) images of (a, b, c, and d) CdSe/Cu samples. The (Fig. 2.a) films appeared the combinations of many from nano size grains to gathers. The mean grain sizes of the thin films are approximately 20 Å [18]. The (Fig. 2.b) films additionally demonstrate thickness populated and all around created grains with various shapes such as quasi- spherical having

different sizes. Fig. 2.c shows the films (Cu=200 Å) have a partial crystallinity and an amorphous nature with various dislocations, and the appearance of the voids on the sample surface. In spite of the fact that the shapes of the grains in the (Fig. 2.d) thin films are nearly similar sizes are not as much as that of (Fig. 2.c) films, which implies that a portion of the grains are not well developed and good covered to

the substrate of glass. The previous results prove that Fig. 2.a thin films created on the substrate at room temperature cannot have acquired sufficient thermal energy for them to create the same size as shown in Fig. 2.b

films [18]. Whereas Fig. 2.c samples showed an amorphous nature and partial crystallinity. Finally Fig. 2.d shows that the size of grain decline as the Cu diffusion thickness was increased and this result is agree with XRD pattern.

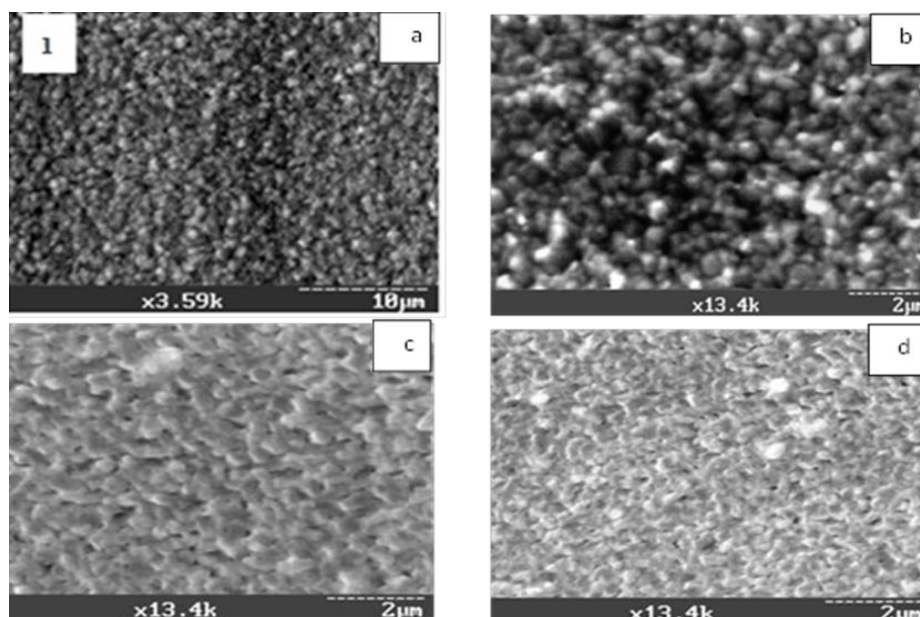


Fig.2: SEM images of CdSe films as a function of Cu thickness (a)0 Å (b)100 Å (c)200 Å, and (d)300 Å.

Optical properties

The transmittance spectra of the thin films were obtained in the range of 320-1000 nm. The average values for the transmittance of CdSe and Cu diffused CdSe films with the thickness of 100 Å, 200 Å & 300Å Cu samples in visible range (400-800 nm) were ~72.3%, ~43%, ~41.7% and ~30.3%, respectively.

As can be seen with increasing the thickness, the transmittance of the films is decreased (Fig.3). The transmittance declining might be because of losses of scattering at the thin film surface with the increasing Cu of thickness[19]. The films with lower Cu thickness have higher transmittances and sharper absorption edges. The peak position of CdSe:Cu

thin films slightly shifts towards the longer wavelength compared with the undoped CdSe thin films. When Cu ions were diffused into CdSe thin films, more defect states will be introduced. Therefore, it is reasonable that the peaks had appeared in the longer wavelength side [20]. The Comparison of the four spectra shows that the impurity (Cu) coated CdSe spectra was red shifted from the undoped CdSe.

The optical energy band gaps E_g of the films were derived assuming a direct transition between the edges of the valence and the conduction band, using the Tauc relationship as follows [21]:

$$\alpha h\nu = A(h\nu - E_g)^n \quad \text{.....(3)}$$

While (α) is the absorption coefficient, (A) is a constant, (h) is Planck's constant, (ν) is the photon frequency, and (n) is 1/2 for direct band gap semiconductor. An extrapolation of the linear region of a plot of $(\alpha h\nu)^n$ on the y-axis versus photon energy ($h\nu$) on the x-axis gives the value of the band gap energy (E_g). Since $E_g = h\nu$ when $(\alpha h\nu)^n = 0$, the direct band gap of the Cu coated CdSe films was estimated from the extrapolation of the linear portion of the graphs $(\alpha h\nu)^2 = 0$ as shown in Fig.4(a-d). The values of obtained band gap for Cu coated CdSe and pure Cadmium

selenium thin films were depicted in the Fig.4. where The E_g of CdSe thin film is calculated to be 2.22 eV. The value of band gap energy was found to decrease from 2.21 eV to 2.13 eV with corresponding increase in the Cu thickness from 0 Å to 300Å respectively, as shown in inset of Fig.4 (a-d).

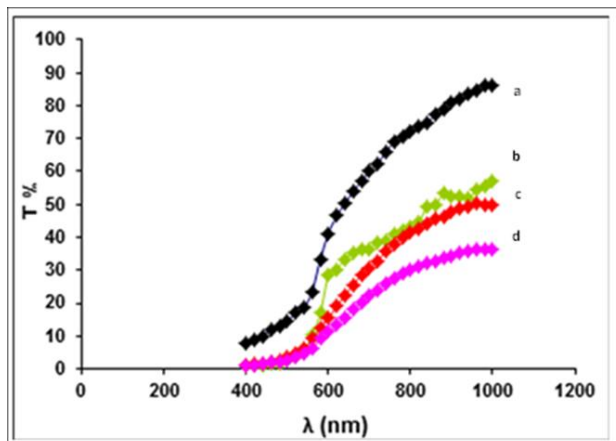


Fig.3: Transmittance spectra of CdSe films as a function of Cu diffusion thickness (a) 0 Å (b) 100 Å (c) 200 Å (d) 300 Å.

In general, the thin films of CdSe/Cu have good quality, and its band gap exhibits lower [22]. band gap in (Fig.4 d) appears smaller compared to other types of films in Fig.4. So it may be concluded that the (Fig.4 d) thin films indicated higher quality crystallinity. the crystallinity variation of grain sizes for

various kinds of doped samples at different concentrations in the CdSe/Cu thin films may be leaded to The changing of band gaps. This result agrees with [18], therefore it is evident that XRD measurements strongly proved that the variation of grain sizes were the same observation as with Cu thickness.

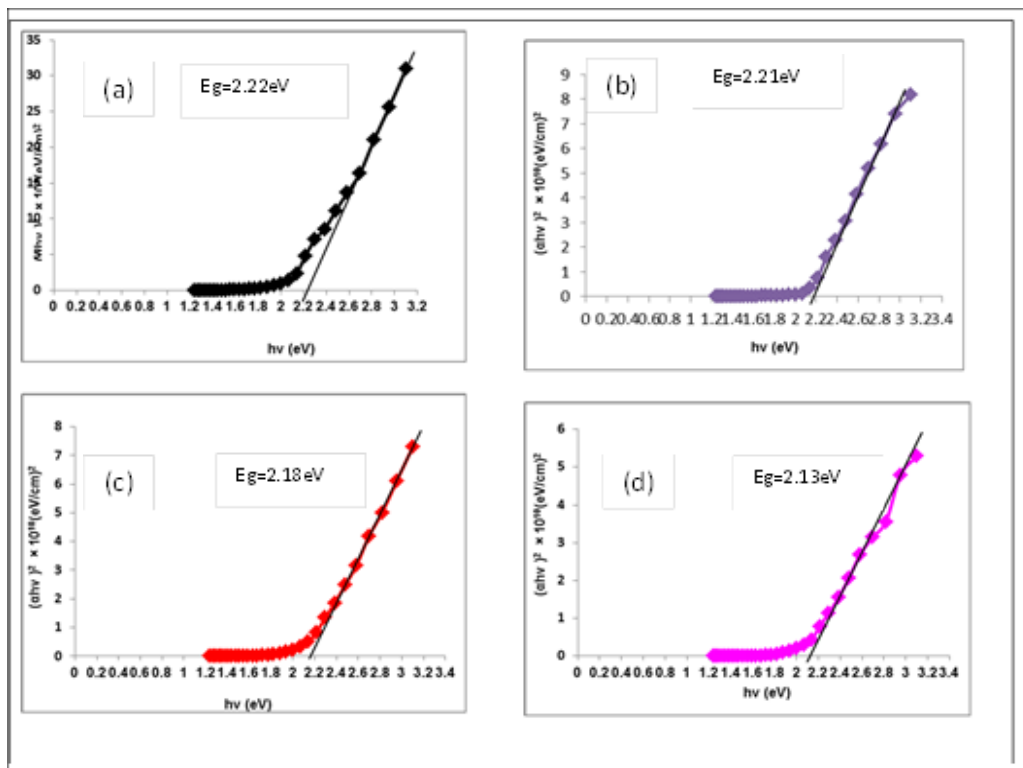


Fig.4:plots of absorption coefficient vs. photon energy of CdSe films as a function of Cu diffusion thickness (a) 0 Å (b) 100 Å (c) 200 Å (d) 300 Å.

Electrical Properties

The electrical properties were achieved on the pure CdSe and Cu coated CdSe thin films. Fig.5 indicates Electrical resistivity of CdSe films as a function of Cu thickness. The electrical resistivity of CdSe the thin films is (4.78 $\Omega \cdot \text{cm}$) at room temperature. It is found that the resistivity decline with an increasing Cu thickness indicating the nature of semiconducting of the uncoated and Cu coated CdSe samples. This may be due to the increase in the

charge carrier concentration. Electrical conductivity (σ) can be increased with the increasing of Cu thickness. Where the increase of free charge carriers for the Copper dopant atoms leads to the increase of electrical conductivity due to the copper atoms combined by substituting cadmium atoms. Similar observation has been made by [19].

The measurements of electrical resistivity of the same samples were conducted using a standard four-point probe method. The electrical resistivity

(ρ) is determined by loading a direct current (I) through the outer pair of probes and measuring the voltage drop, V, between the inner pair of probes which are positioned at a distance of $s = 2$ mm, using the following equation[23] :

$$\rho = \frac{\pi V}{\ln 2 I} d \dots \dots \dots 4)$$

Where is (d) the thickness of sample is ($\sim 0.6 \mu\text{m}$) and the electrical results are shown in table 2 and Fig.5.

:Table 2: The electrical calculations of pure & Cu coated CdSe films

Cu thickness($\text{\AA}$)	Resistivity ρ ($\Omega.\text{cm}$)	conductivity(σ) ($\Omega.\text{cm}$) ⁻¹
0	4.78	0.209
100	1.08	0.925
200	0.022	45.45
300	0.0033	303

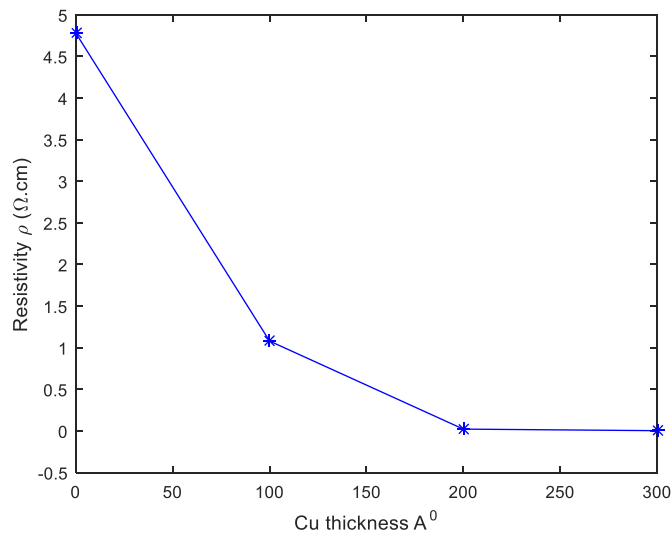


Fig.5:Electrical resistivity of CdSe films as a function of Cu thickness.

the Hall effect measurements were used to know type of the prepared thin films, and these measurements have proved that CdSe is n-type and Cu/CdSe is p-type as a result self-compensation effects of group VI vacancies[12], and the Hall coefficient decrease as increasing of Cu thickness, these calculations have executed by using eq.5 and the results have explained in the table3.

$$R_H = \frac{dV_H}{IB} = -\frac{1}{ne} \dots \dots \dots 5)$$

Where is (B) magnetic field, is (n) the density of free charge, and (I) is the current in the sample, is (e) electron charge, and (d) the thickness of sample.

Table 3: The Hall 's effect calculations for pure & Cu coated CdSe films:

Cu thickness(Å)	Hall coefficient (R _H) cm ³ /C	Hole Carrier concentration e/cm ³
0	56.8	1.1x10 ¹⁷
100	1.78	3.5x10 ¹⁸
200	1.33	4.7x10 ¹⁸
300	1.09	5.7x10 ¹⁸

Conclusion

The effect of Copper defusing on the structural, optical, electrical and properties of Cadmium selenium thin films have been achievement. (XRD) results have explained that Uncoated and Cu coated CdSe films are polycrystalline in nature with hexagonal crystal structure. SEM proved that the grain

sizes declined as the thickness of Cu diffusion was increased. We found that The optical band gap of doped CdSe has decreased from 2.22 eV to 2.13 eV this explain of the diffusion Cu in the CdSe matrix. The electrical resistivity of the prepared thin films changed from(4.78-0.0033)Ω.cm at room temperature. However, the conductivity was found

increases with the Cu thickness, which is related to the increase of number free charge carriers. The hall effect measurements have achievement on the samples, it has been found the thin films Cu/CdSe is p-type.

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