The structure and optical properties of CdSe:Cu Thin Films

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Abstract:

A polycrystalline CdSe thin films doped with ($5w_t$%) of Cu was fabricated using vacuum evaporation technique in the substrate temperature range(T_s=RT-250)^{o}C on glass substrates of the thickness(0.8μm). The structure of these films are determined by X-ray diffraction (XRD). The X-ray diffraction studies shows that the structure is polycrystalline with hexagonal structure, and there are strong peaks at the direction (200) at (T_s=RT-150) ^{o}C, while at higher substrate temperature(T_s=150-250) ^{o}C the structure is single crystal. The optical properties as a function of T_s were studied. The absorption, transmission, and reflection has been studied, The optical energy gap (E_g)increases with increase of substrate temperature from (1.65-1.84)eV due to improvement in the structure. The amorphousity of the films decreases with increasing T_s. The films have direct energy gap and the absorption edge was shift slightly towards smaller wavelength for CdSe:Cu thin film with increase of substrate temperature.it was found that the absorption coefficient was decreased with increasing of substrate temperature due to increases the value of(E_g). The CdSe:Cu films showed absorption coefficient in the range (0.94 x10^4-0.42x10^4)cm^{-1}at T_s=RT-250 ^{o}C. Also the density of state decreases with increasing of substrate temperatures from (0.20-0.07)eV, it is possibly due to the recrystallization by the heating substrate temperatures.. Also the extinction coefficient, refractive index and dielectric constant have been studied.

Key Words: CdSe thin films, optical properties, structure properties poly crystalline CdSe.

1-Introduction

Of the II-VI compound semiconductors, CdSe is a promising candidate because of its applications in photoconductive thin films transistor electrography and lasers[1] . It has a direct intrinsic band gap of 1.74eV .The II-VI compound semiconductors thin films give photoconductivity only if it is doped and crystalline[2]. The electrical properties of these films depends mainly on the impurity concentration and sensitization of the films. Extensive studies have been carried out on the photoconducting properties of copper doped CdSe films[3]. The latter authors found that the absorption coefficient was increased with an increase of Cu impurity concentration and the absorption edge was shifted towards longer wavelength for Cu doped film with heat treatment (350^{o}C). An increase in the photosensitivity of pure CdSe under 600W/m^2 illumination was reported by Nair[4]. Al-Ani et al [5] has studied the optical properties of CdSe at different substrate temperatures, they found that the energy gap was increased as the

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substrate temperature increased. Also the same authors[6] 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[7] and Narayaandass et al[8] 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 [5,6]. In this paper we reported the optical properties of CdSe:Cu thin films at different substrate temperatures.

2-Experimental

Films of Cu doped CdSe (0.8µm thick) were prepared by vacuum evaporation technique (BALZERS) in the substrate temperature range(T_s=RT-250)°C on glass substrates. Pure CdSe mixed with solution of CuCl(5w_t%) and dried were taken as source materials. The structures of these films are determined by X-ray diffraction (XRD). The optical measurements were made at room temperatures(RT) using a Perkin- Elmer Spectrophotometer.

The absorption coefficient (α),refractive index(n) and extinction coefficient(k), has been calculated from the equations respectively[9]:

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

$n=(\frac{4R}{(R-1)^2}-k^2)^{1/2}-\frac{(R+1)}{(R-1)}$-------*(2)*

$k=\alpha\lambda/4\pi$---------------(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[9]:

$\varepsilon_1 = n^2 - k^2$ *(real part)*-------*(4)*

$\varepsilon_2 = 2nk$ (imaginary part)-------(5)

The doping of CdSe films showed similar characteristic to CdSe single crystal doped with impurity atoms.

3- Results and Discussions

3-1 Structure properties

The X-ray diffraction for CdSe:Cu thin film show polycrystalline structure and there are strong peak at reflecting from(002) plane and small peaks at (110) and (102) plane as presented in Fig.(1) with hexagonal structure at(T_s=RT-1250)°C and at (T_s=150-250) °C the structure are single crystal with only reflecting surface at (002) and this is an agreement with [10].

It is shown that the film at (200-250)°C have better structure than the CdSe:Cu films which prepared at RT due to improvement in films structure by the increasing of substrate heating compared with films at RT. The light intensity increases with increasing substrate temperatures from (T_s=RT-250)°C and decreases for the other peaks due to improvement in the structure as shown in Fig.(1) and this is agreement with [11], they found that the films are polycrystalline and have a hexagonal structure and highly oriented with the (002)planes.

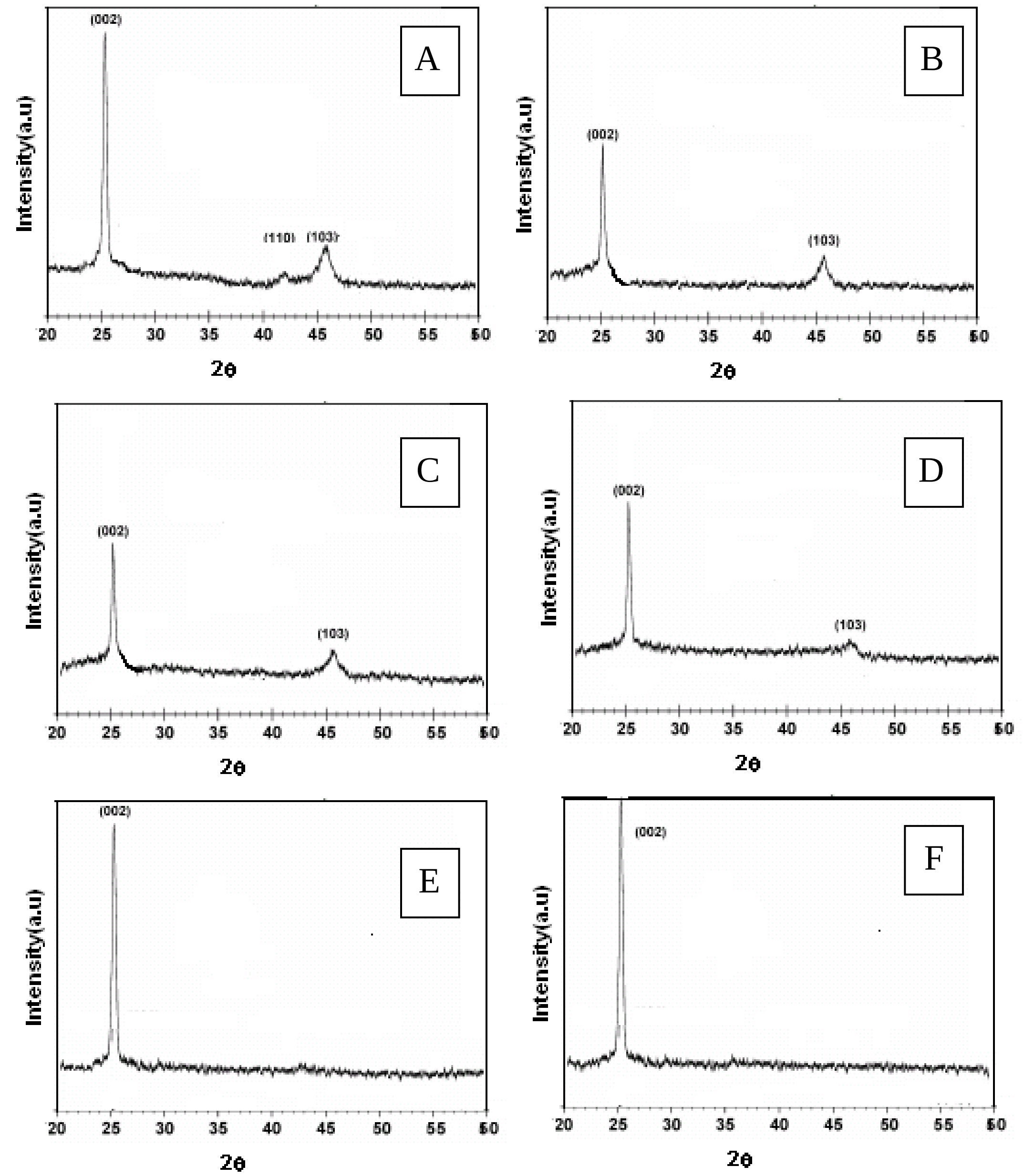

Fig.(1)X-ray diffraction for CdSe:Cu thin film for a- CdSe:Cu(5w_t%)RT, CdSe:Cu (5w_t%) at b- T_s=50 ^{o}C, c- T_s=100 ^{o}C, d- T_s=150 ^{o}C,e- T_s=200 ^{o}C, f- T_s=250 ^{o}C

3-2 Optical Properties

Fig.(2a,b and c) shows the transmition , absorption and reflection spectrum for CdSe:Cu(5w_t%) thin films at the substrate temperature range(T_s=27, 100, 150, 200, 250^{o}C for wavelength between (400-1200)nm. It was shown that the absorption edge for CdSe:Cu(5w_t%) thin films is shifted towards smaller wavelength with the increase of T_s and this is due to improvement the structure by heating.

The absorption, transmission, and reflection has been studied, also energy gap and optical constant has been determined. In general, our results showed nearly a decrease in transmission spectra with increasing substrate temperatures. The observed decrease in the optical transmission spectra can be related to the improvement in the crystalinty of the films, a similar decrease in the optical transmission spectra was observed by Nair et al[4] in the chemically deposited CdSe thin films. The band gap energy should decrease with annealing if the effect was indeed a quantum size effect Gray et al[11].

The absorption edge shifting to smaller wavelength and this may be attributed to the improvement in the structure and decreases the localized state in the band gab. Also we are studied the spectrum of absorptance and reflectance as in Fig.(2b&c). It is obvious that it behavior is opposite to that of transmittance spectrum.

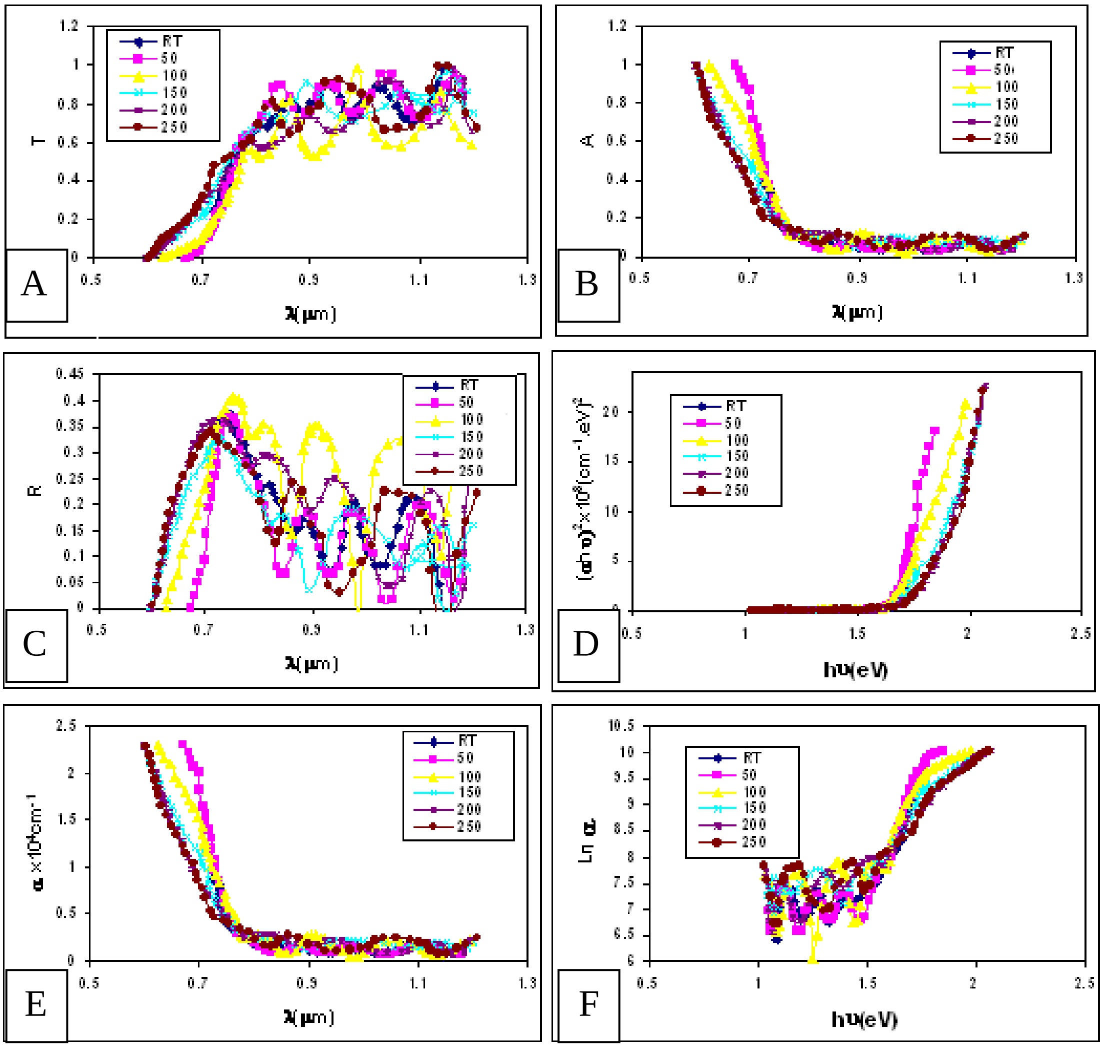

Fig.(2)The T, A, R, $(\alpha h\nu)^{1/2}$, α and lnα for CdSe:Cu thin films at different T_s.

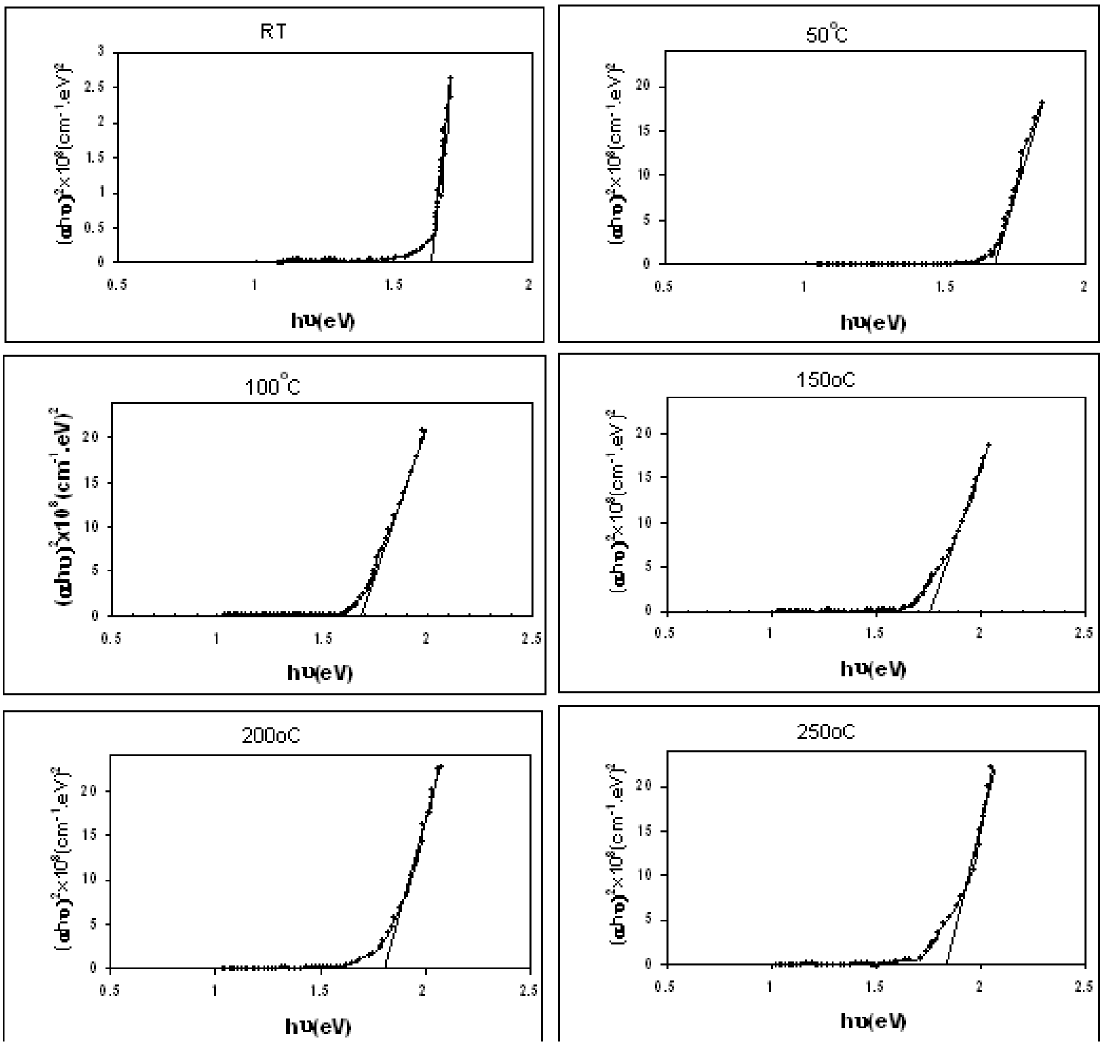

Fig.(3)The αhν)$^{1/2}$ as a function of hν for CdSe:Cu thin films at different T_s.

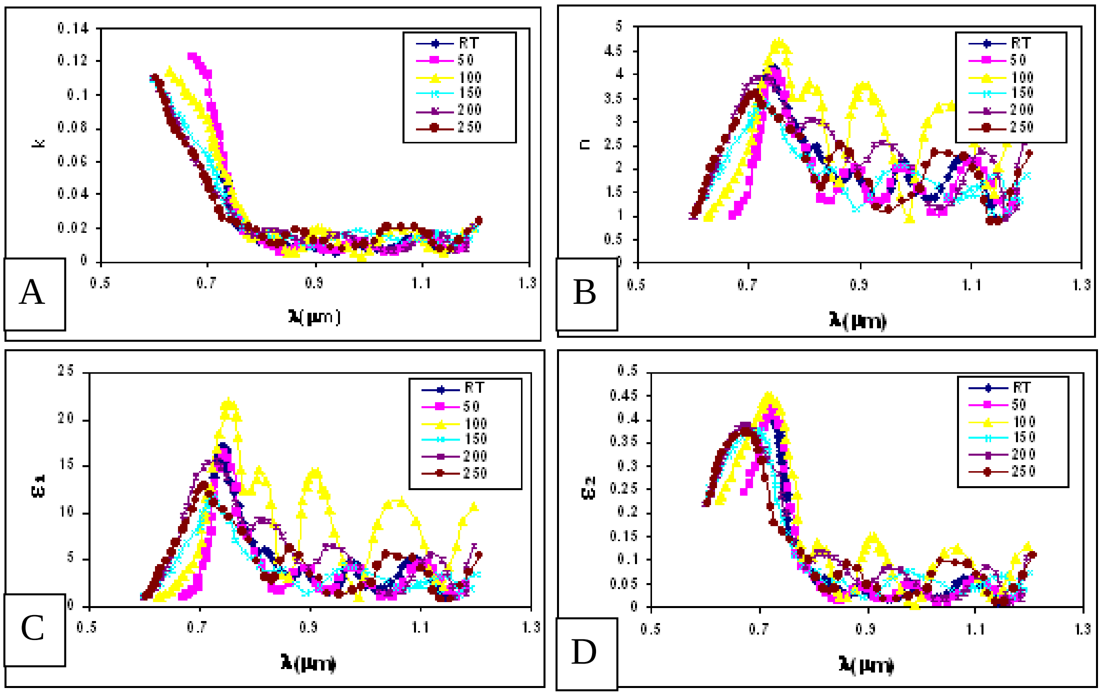

Fig.(4)The k,n ,ε_1 & ε_2 as a function of λ for CdSe:Cu thin films at different T_s.

In the region of the absorption edge the energy band gap E_g is determine. Since CdSe:Cu is a direct band gap semiconductor, this agreement with[11] , the absorption coefficient near the band edge is related to E_g by[3]:

$(\alpha h\upsilon)^2$=B (hυ- E_g)-------(6)

The linear intercept of plot of $(\alpha h\upsilon)^2$ versus hυ yields values of (1.65, 1.68, 1.7, 1.75,1.8, 1.84)eV for CdSe:Cu thin films prepared at (T_s=RT, 50, 100, 150, 200,250^{o}C) as shown in Fig.(2d)and Fig.(3) which agree well with result of [1-13], they found that the E_g ranged between (1.05-1.75)eV with increased T_s from RT to 250^{o}C. Also these value of E_g are agreement with Ichimura et al[14], they obtained E_g about (1.84-1.9) eV before heating and (1.75-1.85)eV after heating. Also Shreekanthan et al[12] 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[15] found that the E_g shifts towards higher wavelength, these results are attributed to the improvement in the structure of the films by the increases of substrate temperatures.
where B in the eq.(6) 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 substrate temperatures from (18.4-31.9) x10^4eV$^{1/2}$/cm as shown in Table (1). which mean that the amorphousity decreases with increasing substrate temperatures due to the improvement in the structure[2].
Fig.(2e) shows the absorption coefficient (α) as a function of wavelength for CdSe:Cu at T_s=RT-250)^{o}C respectively which calculated from the equation(1). From this figure the value of α decreases with increasing substrate temperature from 0.94X10^4cm^{-1} to 0.42X10^4cm^{-1} for (T_s=RT-250)^{o}C ,respectively.(see Table(1). This is related to the improvement in the structure by increasing T_s. This is an agreement with[10-13] which they found that α decreases with T_s.
At1< α <10^4cm^{-1} the value of width of tails(ΔE_t) of localized state in the gap is obtained from Fig.(2f), where Ln α is plotted as a function of hν, in accordance with Urbach relation[9]:

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

where α_o is constant. The value of ΔE_t extracted from the reciprocal slope of the linear part are equals to (0.2 0.17, 0.12, 0.12, 0.08, 0.07)eV for CdSe:Cu at (T_s=RT, 50, 100, 150, 200,250^{o}C) respectively (see Table(1)), and this attributed to the decreasing of Cu concentration in the E_g by increasing T_s which lead to reduce the localized state in the E_g .
The value of extinction coefficient(k) which calculate from the equation(3) are shown in Table(1) and Fig.(4a). The behavior of k is nearly similar to the corresponding absorption coefficient. We can see from this figure that the value of k decreased by increasing T_s from (0.0447-0.0252) and this is due to the same reason which mention previously in α.
Fig.(4b)represent the refractive index (n) of these films, it is decreases slightly with T_s due to decrease in the density of state as shown in Table(1).The values of the refractive index(n) which calculated from the equation(2) are equals to (4.018, 3.811, 3.833, 3.195, 3.190) for CdSe:Cu at (T_s=RT, 50, 100, 150, 200, 250^{o}C) respectively (see Table(1)),Eya[16] found that the refractive index af this

films which prepared by (CBD) has the value of 2.64 , Fig(4c&e) and Table(1) show the variation of real and imaginary part of dielectric constant (*ε_1* and *ε_2*)respectively as a function of T_s 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 T_s. as shown in Table(1), and this is nearly agreement with[10].

T_a	E_g(eV)	BX10^4 $eV^{1\backslash 2}$/cm	ΔE_ueV	α cm^{-1}x10^4	n	k	ε_1	ε_2
RT	1.65	18.4	0.20	0.940	4.018	0.0447	16.142	0.359
50	1.68	32.8	0.17	0.863	3.833	0.0507	14.520	0.386
100	1.70	25.3	0.12	1.010	3.811	0.5820	14.690	0.441
150	1.75	26.8	0.12	0.970	3.197	0.0550	10.980	0.333
200	1.80	28.2	0.08	0.620	3.195	0.0320	10.660	0.280
250	1.84	31.9	0.07	0.420	3.190	0.0252	10.220	0.160

4-Conclusion:

From this research it has been shown that :

Structural and optical properties of CdSe:Cu films prepared by vacuum evaporation technique on different substrate temperatures have been studied , the films at low substrate temperatures are polycrystalline with hexagonal structure and heating the films at high substrate temperatures improve the crystallinity of films.

Optical studies reveal that CdSe:Cu films has a direct band gap energy and the value of absorption coefficient decrease with increasing substrate temperatures and the value of energy gaps(E_g) increases with increasing of substrate temperatures. All the other optical constant are strongly influenced by the heating substrate

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الخواص التركيبية والبصرية للأغشيةالرقيقة CdSe:Cu

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الخلاصة:

حضرت الأغشية الرقيقة CdSe:Cu المتعددة البلورات والمطعمة بالنحاس بنسبة ($5w_t\%$) بأستعمال تقنية التبخير الفراغي بمدى درجة حرارة اساس (T_s=RT-250)^{o}C على قواعد زجاجية. حدد تركيب تلك الاغشية بواسطة الفحص بالأشعة السينية (XRD) . بينت دراسات حيود الاشعة السينية بان التركيب يكون من النوع المتعدد البلورات السداسي، وهناك قمة قوية بالاتجاه (200) عند^{o}C (T_s=RT-250) بينما عند درجات حرارة الأساس العالية^{o}C (T_s=150-250) يتحول التركيب الى البلورة المفردة . درست الخصائص البصرية كدالة لدرجة حرارة الأساس(T_s) ودرست النفاذية والأمتصاصية والأنعكاسية. فجوة الطاقة تزداد بزيادة درجة حرارة الأساس منeV(1.65-1.84) وتقل العشوائية نتيجة للتحسن بالتركيب البلوري. تمتلك الأغشية فجوة طاقة مباشرة و تزاح حافة الأمتصاص بأتجاه الأطوال الموجية القصيرة لأغشية CdSe:Cu بزيادة درجة حرارة الأساس وجد بأن معامل الأمتصاص يقل بزيادة درجة حرارة الأساس من ($0.94\ x10^4$-$0.42x10^4$)cm^{-1}at T_s=RT-250 ^{o}C، كذلك تقل كثافة الحالات بزيادة درجة حرارة الأساس eV(0.20-0.07) ذلك نتيجة لاعادة التبلور بواسطة التسخين بدرجة حرارة الأساس..كذلك درس معامل الخمود ومعامل الأنكسار وثوابت العزل كدالة لدرجة حرارة الأساس .

كلمـات مفتاحيـة: أغشية CdSe الرقيقة والخصائص البصرية، الخصائص التركيبية CdSe المتعدد البلورات.