The structure and optical properties of CdSe:Cu Thin Films

Eman M.N.Al-Fawadi*  Tariq. J. Alwan**  Ikbal S. Naji*

Date of acceptance 3/6/2008

Abstract:
A polycrystalline CdSe thin films doped with (5wt.)% of Cu was fabricated using vacuum evaporation technique in the substrate temperature range($T_s$=RT-250)$^\circ$C on glass substrates of the thickness(0.8$\mu$m). 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)$^\circ$C, while at higher substrate temperature($T_s$=150-250)$^\circ$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 amorphosity 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$^\circ$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 polycrystalline 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$^\circ$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

* Physics Dept./ Science College/ University of Baghdad
* Physics Dept./ College of Education/ Al-Mustansiriya University
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(5wt.%) 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]:

\[ \alpha = \frac{2.303 A}{d} \]  
\[ n = \left( \frac{4R}{(R-1)^2 - k^2} \right)^{1/2} - \frac{R+1}{R-1} \]  
\[ k = \frac{\alpha \lambda}{4\pi} \]  

where R is the reflectance, and the real and imaginary part of dielectric constant (ε₁ and ε₂) respectively can be calculated by using equations[9]:

\[ \varepsilon_1 = n^2 - k^2 \text{ (real part)} \]  
\[ \varepsilon_2 = 2nk \text{ (imaginary part)} \]

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\%\%) at RT, CdSe:Cu (5w\%\%) at b- T_s=50 °C, c- T_s=100 °C, d- T_s=150 °C, e- T_s=200 °C, f- T_s=250 °C

3-2 Optical Properties

Fig. (2a,b and c) shows the transmission, absorption and reflection spectrum for CdSe:Cu (5w\%\%) thin films at the substrate temperature range (T_s=27, 100, 150, 200, 250°C) for wavelength between (400-1200)nm. It was shown that the absorption edge for CdSe:Cu (5w\%\%) 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 crystallinity 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 gap. 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.

![Graphs](image_url)

Fig.(2)The T, A, R, (αhν) 1/2, α and lnα for CdSe:Cu thin films at different Ts.
Fig.(3) The $\alpha h^\nu^{1/2}$ as a function of $h\nu$ for CdSe:Cu thin films at different $T_s$.

Fig.(4) The $k, n, \varepsilon_1$ & $\varepsilon_2$ as a function of $\lambda$ 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 \( \text{CdSe:Cu} \) is a direct band gap semiconductor, this agreement with[11] , the absorption coefficient near the band edge is related to \( E_g \) by[3]:

\[
(\alpha h\nu)^2 = B (h\nu - E_g) \tag{6}
\]

The linear intercept of plot of \((\alpha h\nu)^2\) versus \( h\nu \) yields values of (1.65, 1.68, 1.7, 1.75, 1.8, 1.84)eV for \( \text{CdSe:Cu} \) thin films prepared at ( \( T_s=RT, 50, 100, 150, 200,250^\circ C \)) as shown in Fig.(2d)and Fig.(3) which agree well with result of [5-13], they found that the \( E_g \) ranged between (1.05-1.75)eV with increased \( T_s \) from RT to 250\(^\circ C \). 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 \( \text{CdSe} \) 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 amorphosity 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) \( \times 10^4 \)eV\(^{1/2}\)/cm as shown in Table (1). which mean that the amorphosity decreases with increasing substrate temperatures due to the improvement in the structure[2].

Fig.(2e) shows the absorption coefficient \( (\alpha) \) as a function of wavelength for \( \text{CdSe:Cu} \) at \( T_s=RT-250 \)\(^\circ C \) respectively which calculated from the equation(1). From this figure the value of \( \alpha \) decreases with increasing substrate temperature from 0.94X10\(^4\)cm\(^{-1}\) to 0.42X10\(^4\)cm\(^{-1}\) for \( T_s=RT-250 \)\(^\circ C \), 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 \( \alpha \) decreases with \( T_s \).

At \( 1<\alpha<10^4 \)cm\(^{-1}\) the value of width of tails(\( \Delta E_i \)) of localized state in the gap is obtained from Fig.(2f), where \( \ln \alpha \) is plotted as a function of \( h\nu \), in accordance with Urbach relation[9]:

\[
\alpha = \alpha_e \exp (h\nu/\Delta E_i) \tag{7}
\]

where \( \alpha_e \) is constant. The value of \( \Delta E_i \) 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 \( \text{CdSe:Cu} \) at ( \( T_s=RT, 50, 100, 150, 200,250^\circ C \)) 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 \( \alpha \). 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 \( \text{CdSe:Cu} \) at ( \( T_s=RT, 50, 100, 150, 200,250^\circ C \)) respectively (see Table(1)).Eya[16] found that the refractive index at this
films which prepared by (CBD) has the value of 2.64 , Fig(4c&4e) and Table(1) show the variation of real and imaginary part of dielectric constant (ε₁ and ε₂) respectively as a function of Tₛ which calculated from the equations(4 and 5). The behavior of ε₁ is similar to refractive index because the smaller value of k² comparison of n², while ε₁ is mainly depends on the k values, which are related to the variation of absorption coefficient. It is found that ε₁ and ε₂ decreases with increasing Tₛ as shown in Table(1), and this is nearly agreement with[10].

<table>
<thead>
<tr>
<th>Tₛ</th>
<th>E₀(eV)</th>
<th>BX10⁷ eV/V²/cm</th>
<th>ΔE₀eV</th>
<th>α cm⁻¹x10⁶</th>
<th>n</th>
<th>k</th>
<th>ε₁</th>
<th>ε₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>1.65</td>
<td>18.4</td>
<td>0.20</td>
<td>0.940</td>
<td>4.018</td>
<td>0.0447</td>
<td>16.142</td>
<td>0.359</td>
</tr>
<tr>
<td>50</td>
<td>1.68</td>
<td>32.8</td>
<td>0.17</td>
<td>0.863</td>
<td>3.833</td>
<td>0.0507</td>
<td>14.520</td>
<td>0.386</td>
</tr>
<tr>
<td>100</td>
<td>1.70</td>
<td>25.3</td>
<td>0.12</td>
<td>1.010</td>
<td>3.811</td>
<td>0.5820</td>
<td>14.690</td>
<td>0.441</td>
</tr>
<tr>
<td>150</td>
<td>1.75</td>
<td>26.8</td>
<td>0.12</td>
<td>0.970</td>
<td>3.197</td>
<td>0.0550</td>
<td>10.980</td>
<td>0.333</td>
</tr>
<tr>
<td>200</td>
<td>1.80</td>
<td>28.2</td>
<td>0.08</td>
<td>0.620</td>
<td>3.195</td>
<td>0.0320</td>
<td>10.660</td>
<td>0.280</td>
</tr>
<tr>
<td>250</td>
<td>1.84</td>
<td>31.9</td>
<td>0.07</td>
<td>0.420</td>
<td>3.190</td>
<td>0.0252</td>
<td>10.220</td>
<td>0.160</td>
</tr>
</tbody>
</table>

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(E₀) increases with increasing of substrate temperatures. All the other optical constant are strongly influenced by the heating substrate.

References:


الخواص التركيبية والبصرية للأغشية الرقيقة \text{CdSe}:\text{Cu}

الخواص:

حضرت الأغشية الرقيقة \text{CdSe}:\text{Cu} المطعمة بالنحاس بنسبة (5\% \text{w/w}) باستخدام تقنية التخمير الفراشي بمدى درجة حرارة أساس (T_s=RT-250\degree C), حيث تكرب تلك الأغشية بواسطة الفحص بالأشعة السينية (XRD). تم التحصي بدرجات حرارة بين (200) درجة قوية للإطاحة (150-250\degree C) عند (T_s=RT-250\degree C). التحول التركيب إلى البلورة المرفعة. درست الخصائص البصرية كدالة لدرجة حرارة الأساس (T_s=RT-250\degree C). وترتفع الطاقة الزائدة بزيادة درجة حرارة الأساس من (1.84-1.65) eV. وتقل العشوائية نتيجة التحسين بالتركيب البلوري. تمتلك الأغشية فجوة طاقة تزداد بزيادة درجة حرارة الأساس (0.94 \times 10^{-4} - 0.42 \times 10^{-4}) cm^{-1} at T_s=RT-250\degree C, وذلك نتيجة لعدم نشأة حزمة طاقة درجة حرارة الأساس. كذلك تقل كثافة الحالات بزيادة درجة حرارة الأساس من (0.94 - 0.07) eV. وذلك نتيجة لعدم نشأة حزمة طاقة درجة حرارة الأساس. كذلك درس معامل الأكسس ومعامل الأكسس ومعامل الأمتصاص وثوابت العزل كدالة لدرجة حرارة الأساس.

كلمات مفتاحية: أغشية الرقيقة والخصائص البصرية، الخصائص التركيبية \text{CdSe}

المتعدد البلورات.