Original Article

The effect of Cu-doping on CdS thin films deposited by the spray pyrolysis technique

Ahmed A. Aboud\textsuperscript{a,}\textsuperscript{∗}, Ayan Mukherjee\textsuperscript{b}, Neerish Revaprasadu\textsuperscript{c}, Ahmed Nagaty Mohamed\textsuperscript{a}

\textsuperscript{a} Department of Physics, Faculty of Science, Beni-Suef University, Beni-Suef, Egypt
\textsuperscript{b} Department of Physics, RRS COLLEGE, PATLIPUTRA UNIVERSITY, PATNA, INDIA
\textsuperscript{c} Department of Chemistry, University of Zululand, Kwadlangezwa, South Africa

\begin{abstract}
Pure CdS and Cu-doped CdS thin films were deposited using the spray pyrolysis technique and characterized using XRD, XPS, AFM, UV-VIS spectroscopy and two probe DC-conductivity measurements. 2\%, 4\% and 6\% Cu-content was used for doping. The particle size was found to decrease from 28 nm to 25.4 nm upon Cu-doping. The influence of Cu-doping on the stress and dislocation per unit volume has been estimated from the XRD data. AFM images of the annealed films show changes in morphology with increase in surface roughness from 25 nm to 31 nm with Cu-6\% doping. Reflectance and transmission measurements were studied in the spectral range of 200–1100 nm to extract the optical properties variation upon copper doping. Also the band gap was found to decrease from 2.43 to 2.39 eV with increase in copper content. The electrical conductivity was measured by direct record of the resistance against temperature. All films show a semiconducting behavior and incorporation of Cu on CdS increases its activation energy.
\end{abstract}

© 2019 Brazilian Metallurgical, Materials and Mining Association. Published by Elsevier Editora Ltda. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

CdS thin film has drawn a large attention among researchers in the field of transistors [1], FET, LEDs [2], photonicss [3], photocatalysis [4], NIR-detectors [5], energy storage systems due to its high stability, excellent physical, chemical and optical properties which are different from bulk. Among the different metal sulphide chalcogenides, wide availability and ease of preparation have made CdS thin films popular for future applications [6]. Recently, CdS thin films have been used as a gas sensing material [6]. It is also widely used as window layer in thin film solar cells along with different absorbers such as CdTe [7], SnS [8], CdSe [9], CIGS and PbS [10].

The properties of CdS thin films can be precisely controlled by the doping process. It is well known that the conduction of pure CdS is attributed to the native defects or sulphur vacancies and cadmium interstitials [11]. Accordingly it is feasible to control the conductivity of CdS by introducing a suitable dopant. Several efforts have been made to prepare metal sulphide thin films doped with transition metals or rare earth ions. The doping of CdS with metallic ions such as In\textsuperscript{3+} [12],

\begin{correspondingauthor}
E-mail: isolarcell@yahoo.com (A.A. Aboud).
\end{correspondingauthor}
Al$^{3+}$ [13], Ni$^{2+}$ [11], Cu$^{2+}$ [14] and B$^{3+}$ can improve both the structural and electrical properties of CdS. Some authors found that Cu$^{2+}$ doping has an effect of deterioration of crystallinity [6]. However, detail reports on Cu doped CdS thin films are very scarce.

CdS thin films can be deposited by different techniques such as spray pyrolysis [15], chemical bath deposition (CBD) [16], successive ionic layer adorption and reaction (SILAR) [17] and spin coating [18] techniques. Among all of these processes, the spray pyrolysis is advantageous due to its simplicity, low cost, good film-substrate adhesion and relatively low temperature of deposition. It gives uniform, well-adherent and stoichiometric thin films.

In this work, we have prepared pure and Cu-doped CdS thin films using the spray pyrolysis technique. For this method, cadmium chloride and thiourea were used as precursors for pure CdS films. The Cu-content in the obtained films was regulated by adding a controlled amount of cupric acetate with a desired weight percentage with respect to cadmium chloride. The influence of Cu-content on structural, optical, morphological and electrical properties of CdS thin film was studied in detail.

2. Experimental details

The main advantage of spray pyrolysis process is its simplicity and low cost. We can design it in our laboratory. An adapted homemade spray pyrolysis system has been used to deposit both pure and Cu-doped thin films. Amorphous glass substrate were placed in a hot plate at fixed temperature $450^\circ$C with a fixed air flow rate at 25 L/min. A solution of 0.05 cadmium chloride hydrated (CdCl$_2$·H$_2$O, MW = 201.32 g/mol) and 0.05 M of thiourea (CH$_3$N$_2$S, MW = 76.12 g/mol) were used as cadmium and sulphur sources, respectively. In the case of doping with Cu, a calculated amount of cupric acetate (CH$_3$COO)$_2$Cu·H$_2$O MW = 199.65) was added as dopant (0–6%), dissolved in the same solution.

The deposited films were characterized by X-ray diffraction with Cu Kα radiation ($\lambda = 1.542$) on a DX-2500 diffractometer. The surface morphology of the films was studied by a Bruker Atomic Force Microscope. The optical transmission and reflection spectra in the spectral range 200–1100 nm were recorded using PG-T700 equipment. Film thickness was measured by the Tolansky’s method of multiple beam Fizeau fringes [19]. Finally the electrical conductivity was measured by the direct measurement of the electrical resistance and temperature using a two-probe method with silver paste used as contact.

3. Results and discussion

3.1. Structural characterization

Fig. 1 shows the XRD pattern of pure CdS thin films. The XRD results confirm the formation of pure hexagonal phase of CdS (ICDD card number 06-0314) with (101) as the preferred orientation. The same plane has been recorded as the main direction of growth in spray pyrolysis deposited CdS by Shaban et al. [15] and Rmili et al. [11]. In the current work no new peaks are recorded due to copper doping which indicates the phase remain same as previous. Peaks related to CdO were recorded by Ziabari et al. [14] at Cu-doping level of 3%. At higher values of Cu-doping, 6%, Shaban et al. [15] received CdO peaks upon annealing the Cu-doped CdS at 400 °C and 500 °C. In all films the peak related to (101) plane was observed as the main peak. The peak intensity of (101) plane decreases with increase in Cu concentration. But the peak intensity of the other planes remains approximately constant except for the (100) plane which also increases. Xie et al. [20] noticed the preferred orientation changes from (200) to non-preferred orientation structure with increase in the Cu-content. In the same work the intensities of other planes such as the (100), (101), (110) and (112) increases upon doping which is in contrast to our observations. The diffraction peaks shift to higher.
Table 1 – (a) The lattice constant, band gaps, grain size, thickness and lattice constants for all films. (b) Some recorded values from other authors.

(a)

<table>
<thead>
<tr>
<th>Cu-content (%)</th>
<th>Lattice constants</th>
<th>Band gap (eV)</th>
<th>Refractive index</th>
<th>Grain size (nm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a , (\text{Å}))</td>
<td>(c , (\text{Å}))</td>
<td>Minimum</td>
<td>Maximum</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>4.129</td>
<td>6.74</td>
<td>2.43</td>
<td>2.16</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>4.123</td>
<td>6.741</td>
<td>2.4</td>
<td>1.9</td>
<td>2.2</td>
</tr>
<tr>
<td>4</td>
<td>4.1177</td>
<td>6.762</td>
<td>2.4</td>
<td>1.65</td>
<td>2.17</td>
</tr>
<tr>
<td>6</td>
<td>4.1156</td>
<td>6.773</td>
<td>2.39</td>
<td>1.73</td>
<td>1.95</td>
</tr>
</tbody>
</table>

(b)

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Crystallite size (nm)</th>
<th>Doping level</th>
<th>Band gap (eV)</th>
<th>Preparation method</th>
<th>(E_a) (eV)</th>
<th>Lattice parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure</td>
<td>Cu-doped</td>
<td>Pure</td>
<td>Cu-doped</td>
<td>Spray pyrolysis</td>
<td>Pure</td>
<td>Cu-doped</td>
</tr>
<tr>
<td>[6]</td>
<td>56</td>
<td>54–53</td>
<td>1–5%</td>
<td>Decrease</td>
<td>0.45</td>
<td>&gt;0.45–0.96</td>
</tr>
<tr>
<td></td>
<td>~12.5</td>
<td>~5.6</td>
<td>3% and 5%</td>
<td>Decrease</td>
<td>CBD</td>
<td>**</td>
</tr>
<tr>
<td></td>
<td>3.6–4.735</td>
<td>3.808–3.00</td>
<td>0.56</td>
<td>Decrease</td>
<td>CBD</td>
<td>**</td>
</tr>
<tr>
<td></td>
<td>**</td>
<td>**</td>
<td>~17.96 at%</td>
<td>Vacuum evaporation</td>
<td>0.69</td>
<td>**</td>
</tr>
<tr>
<td></td>
<td>**</td>
<td>0.34 ppm</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>43–26.4</td>
<td>**</td>
<td>0</td>
<td>2.21 to 2.34</td>
<td>**</td>
<td>CBD</td>
<td>0.48–0.06</td>
</tr>
</tbody>
</table>

where \(d\) and lower \(d\)-spacing, upon copper doping. This shift may indicate the substitution of cadmium (Cd\(^{2+}\), 0.096 nm [15]) with copper which have a lower atomic volume (Cu\(^{2+}\), 0.072 nm, and Cu\(^+\), 0.096 nm [15]).

The inset of Fig. 1 shows the change in the main peak intensity in all films. The main peak intensity decreased as the copper content increased in the deposited films. The reduction in the (1 0 1) intensity is in contrast to the results of Shaban et al. [15] who observed an increase. Such a reduction in the peak intensity can be attributed to the replacement of cadmium ions with copper ions. Copper in its ionic states (Cu\(^+\) or Cu\(^{2+}\)) has smaller ionic radii as mentioned before. The replacement of cadmium with smaller volume atoms is expected to inhibit the growth in the same direction. This suggests that incorporation of Cu ions resulted in the enhancement of the degree of polycrystallinity, i.e. increase of amorphization of the film through suppression of grain growth.

The average particle size estimated from X-ray diffraction pattern using the main peak depending on Scherrer’s equation:

\[
D = \frac{0.9 \lambda}{\beta \cos \theta}
\]  

(1)

where \(D\) is the particle size, \(\lambda\) is the X-ray wavelength (1.5406 Å), \(\beta\) is the full width at half maximum (FWHM) in radian and \(\theta\) is the center of the diffraction peak angle value in radian. The FWHM value has been calculated using the X’Pert program.

The particle size values are obtained using Scherrer’s formula. The value obtained from Scherrer’s equation is smaller than the real sizes [21,22]. Generally the peak broadening in XRD analysis originates from the instrumental broadening and physical factors such as crystallite size and lattice strain [23,24]. In the case of physical factors, FWHM of each diffraction peak is expressed as a linear combination of the contributions from lattice strain and crystallite size determined using Scherrer’s equation and the actual crystallite size will be slightly higher than the measured value if instrumental and strain broadenings are taken into account.

The particle size was found to decrease from 28.03 nm to 24.56 nm by increasing the Cu-content. This indicates the deterioration of the crystallinity of the deposited films upon Cu-doping. Also the lattice parameters were calculated using the equation as follows:

\[
\frac{1}{d^2} = \frac{3}{4} \left( \frac{d^2 + k^2 + l^2}{a^2} \right) + \frac{t^4}{c^2}
\]  

(2)

where \(d\) is the inter-planer distance, \((h k l)\) are miller indices, and \(a\) & \(c\) are the lattice constants. Table 1 lists the changes in the lattice parameters as a function in the copper content where the lattice parameter \(a\) decreases constantly as the copper content increases. The value of \(a\) decreases with Cu content, this may be due to increase in microstrain. The recorded value is higher than that by Shaban et al. [15] for the as deposited films. That could be attributed to the higher deposition temperature in this work. The parameter \(c\) decreases when the copper content is 6%, followed by an increase. In all cases the values of \(a\) and \(c\) are lower than the corresponding values of the pure films or the reference ICDD card.

Fig. 2 shows the shift in the position of the (1 0 1) plane toward higher 2-theta values upon Cu-doping.

The distortion in the peak shape could be attributed to the non-uniform strain in the thin films. The micro-strain which is manifested in the peak shift in the XRD patterns is measured using the equation [11]:

\[
\text{Micro-strain } \epsilon = \Delta (\theta_{101}) \cot (\theta_{101})
\]  

(3)

This structural strain is caused by compressive stress \(\sigma_{st}\) that can be estimated by [11]:

\[
\sigma_{st} = 3\epsilon B
\]  

(4)
where $B$ is the average bulk modules of CdS which is about 69.44 GPa [25].

Fig. 3 exhibits the strain and dislocation lines per unit volume (dislocation density is the length of dislocation per unit volume), $Y = 1/D^2$, as a function of the Cu-content in the deposited films. We can see that the compressive stress remains approximately constant, no significant variation, up to 4% of Cu content and then decreases significantly at 6% of Cu. Also a constant increase in the dislocation per unit volume is observed with Cu-content increase which further enhances the deterioration of crystallinity upon Cu-doping. The number of crystallites per unit area, $N$, is determined using the following formula [26]:

$$N = \frac{t}{D^3}$$

(5)

where $t$ is the film thickness as measured and $D$ is the particle size estimated from Sherrer’s equation.

The preferred orientations of all films are estimated using the texture coefficient (TC), calculated from the X-ray diffraction patterns. The preferred orientation of the film will be $(k\ell)$ plane for the higher TC value [11]. The TC value is estimated using formula [27]:

$$TC(k\ell) = \frac{I(k\ell) / I_0(k\ell)}{\sum_l I(k\ell) / I_0(k\ell)}$$

(6)

where $TC(k\ell)$ is the texture coefficient of the $h k l$ planes, $I$ is the measured or normalized intensity, $I_0$ the corresponding standard relative intensity given in the ICDD card, and $N$ the number of diffracted peaks. Fig. 4 shows the variation of the texture coefficient of (1 0 1) and (1 0 0) in all films. As observed the TC of (1 0 0) increases as the Cu-content increase. On the other hand the TC of the (1 0 1) decreases as the Cu-content increases.

Three-dimensional AFM (10 $\mu$m × 10 $\mu$m) images of pure and Cu-6% CdS films are shown in Fig. 5. The surface of the films is found to possess peaks and valleys which reflects the rough nature of the surface. The images of the films appear as fine three-dimensional structures that decrease with increasing dopant content. The bright areas show the overgrown particles formed on the substrate. The doping with copper in CdS affects the surface morphology as shown in the images. The root mean square of the films was found to increase from 25 nm to 30 nm upon 6% Cu doping which signifies change in surface roughness due to copper doping.

### 3.2. XPS study

XPS measurements were done for pure and Cu-6% doped CdS films. The surface composition XPS analysis of the sample deposited from 6% Cu is shown in Fig. 6. The quantification of results exhibits the Cd:Cu weight percentage ratio of 4.1% lower than the solution weight percentage 6%. Considering the low signal of Cu around 934 and 976 eV, it may be linked to the segregation of copper inside the films, away from the surface. Strong peaks can be observed at 405 and 412 eV, relative to the Cd 3d doublet and peak around 530 eV relative to the O 1s signal. Peaks at the same values were recorded by others [14]. A small Na 1s signal in 1070 was recorded, probably due to
Fig. 4 – Variation of texture coefficient (TC) along the planes (1 0 1) and (1 0 0) of pure and Cu-doped CdS films.

Fig. 5 – AFM images of pure and Cu-6% doped CdS films.

Fig. 6 – Representative XPS survey spectrum for Cu-6% doped CdS thin films.

3.3. Optical characterization

3.3.1. Determination of the optical constants of the thin films

There is a particular interest in the refractive index ($n$) and extinction coefficient ($k$) values for semiconductors in the optical range higher than the band gap ($E_g$) value for opto-electronic applications. Owing to the different features of the $E$–$K$ diagrams, where $E$ is the energy and $K$ is the electron's wave-vector, the optical $n$ and the $k$ are depend on the wavelength value of the incident beam in the energies higher than the band gap. For non-transparent materials the refractive index expressed as a complex number as a result of the loss of the optical energy inside the materials during propagation. Accordingly the refractive index can be written as:

$$n^* = n - ik$$

Transmission ($T_{exp}$), with respect to air, and reflection ($R_{exp}$) of the spectra were recorded in the spectral range...
200–1100 nm. The measured data were corrected due to the substrate effect according to the formula [29]:

\[
T_f(\lambda) = \frac{T_{\text{exp}}T_{\text{sub}}(1 - R_{\text{exp}}R_{\text{sub}})}{T_{\text{sub}} - T_{\text{exp}}R_{\text{sub}}^2}
\]

(8)

\[
R_f(\lambda) = \frac{R_{\text{exp}}^2T_{\text{sub}}^2 - T_{\text{sub}}^2 R_{\text{sub}}^2}{T_{\text{sub}}^2 - T_{\text{exp}}^2 R_{\text{sub}}^2}
\]

(9)

where \(T_{\text{sub}}\) is the transmittance and \(R_{\text{sub}}\) is the reflectance of the glass substrate. Figure shows the transmission and reflection after correction using Eqs. (4) and (5) in the spectral range 200–1100 nm.

As shown in Fig. 7 the transmission of all films can be divided into two main regions: (i) above 500 nm where a regular reduction in the transmission value is observed upon increasing the copper content in the deposited films; (ii) strong absorption region below 500 nm. This cutoff at 500 nm is a familiar cut-off point for CdS thin films as recorded by many other authors [30,31]. Furthermore, the absorption edges are not fixed at the same value for all films, an indication the role of copper doping in tuning the band gap of the host CdS. The reflectance spectra show a regular reduction in the range below 700 nm. An interference in the reflectance spectra is observed in the spectral range 700–782 nm as shown in figure.

The dispersion spectra of the refractive index and the extinction coefficient are then calculated using the correct \(T_f(\lambda)\) and \(R_f(\lambda)\) using the following equation:

\[
R_f(\lambda) = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}
\]

(10)

\[
k(\lambda) = \frac{\lambda a}{4\pi}
\]

(11)

The variation of the refractive index and the extinction coefficient as a function of wavelength at different levels of copper doing is shown in Fig. 8 in the spectral range, 500–1100 nm. The refractive index shows a general reduction as the copper content increases which could be attributed to the reduction in the density of the film materials upon doping. Table 1 shows the minimum and maximum values of the refractive index with its corresponding wavelength. While the extinction coefficient shows a regular increase with both copper content and decrease as wavelength increases in all films in the high absorption part of the spectra, \(\lambda < 600\). In the high transparency region, away from the absorption edge, the extinction shows close to constant behavior as shown in Fig. 8. Table 1 shows the average value of \(k\) in the 600–1100 nm spectral range.

### 3.4. Optical absorption studies

The absorption coefficient \(\alpha\) of all thin films is calculated using the obtained measurements of transmission, reflection and thickness data according to the equation [32]:

\[
\alpha = \frac{1}{d} \ln \left( \frac{(1 - R)^2}{T} \right)
\]

(12)

where \(d\) is the films thickness, \(R\) is the reflectance of the film and \(T\) is the transmittance. In order to confirm the optical transition nature in the deposited thin films, the optical absorption coefficient obtained data were analyzed according to [33]:

\[
\alpha = \alpha_0 \left( \frac{\nu - E_g}{\nu} \right)^m
\]

(13)

where \(\alpha_0\) a constant, \(m\) is a constant depending on the nature of transition that dominates. The equation describes the allowed optical transitions, at \(m = 1/2\), and forbidden, at \(m = 3/2\).

As shown in Fig. 9, a single slope in the \((\alpha \nu)^2\) versus \(\nu\), a single straight line can be observed. This single straight
line confirms that the existence of a single CdS phase in the deposited films. The extrapolation of this straight line to meet the v axis gives the energy band gap value estimation at the intersection point. The energy gap values of all films are listed in Table 1. The band gap of the pure CdS thin film is found to be 2.437 eV. This value is lower than the recorded value of Khan et al. [26] where they estimate a value of 2.5 eV. But this value agrees with the result of Shaban et al. [15] for CdS films deposited by spray pyrolysis. This value also agrees with Mukherjee et al. [6] for the chemical bath deposition of pure and Cu-doped CdS thin films. By introducing Cu-to the inside of the CdS films, the band gap decreases. The band gap varies from 2.43 to 2.39 as a result of Cu-doping. A higher shift in the band gap value was recorded by Cortes et al. [33] with the grain size ranging from 85 to 205 nm. This blue shift in the energy gap value is attributed to weak quantum confinement dependence of the energy against the grain size. This weak correlation between the grain size and the band gap value could be attributed to a number of reasons: (1) high grain size value compared to the Bohr radius of the CdS, (2) agglomeration of the nanomaterials and (3) coulomb interaction between the charge carriers [32]. This reduction in the band gap could be attributed to intermediate or weak quantum confinement dependence of energy against the crystallite size.

Another reason for the band gap to decrease is the change in barrier height due to change in grain size in nanocrystalline films. The decreasing band gap with grain size as shown in Table 1 is a result of barrier height with increasing grain size. The variation of the grain boundary barrier height with grain size is given by Slater [25]:

$$E_g^2 = E_{bo}^2 + C(X - fD)^2$$

where $E_{bo}$ is the original barrier height, C is a constant depending on the density of charge carriers and dielectric constant of the material, X the barrier width, D the grain size and f is a fraction of the order of 1/15 to 1/50 depending on the charge accumulation and carrier concentration. Accordingly the decrease in the grain size causes the band gap to be reduced.

The range of low photon energy the spectral dependence of the absorption edge follows Urbach’s empirical rule [6]:

$$\alpha(v) = \alpha_0 \exp \left( \frac{v}{E_u} \right)$$

where $\alpha_0$ is the constant and v is the photon energy, $E_u$ is an empirical parameter having the dimension of energy describing the distribution of the states in the band gap area but not their energy assignment [34]. It is also called the Urbach energy which gives the width of the band tail of the localized state of the band gap [6]. The Urbach tail was originally observed in ionic crystals having thermal disorder where lattice vibrations displace the atoms from their regular lattice positions [35]. The width of the band tail affects the optical band gap of
3.5. Electrical conductivity

The D.C. electrical conductivity ($\sigma$) of the sprayed films was measured as a function of temperature ($T$) in the range 453–573 K during cooling. Measurements were carried out using direct measurement of resistance in the presence of air in dark.

The variation of $\ln(\sigma)$ against $1000/T$ curves of the sprayed films with Cu content ranging from 0 to 6% as shown in Fig. 11. The conductivity is found to increase with temperature ensuring the semiconducting nature of the deposited films and decreases by increasing the Cu-content up to 6%. This behavior follows the Arhenius equation:

$$\sigma = \sigma_0 e^{E_a/kT}$$  \hspace{1cm} (16)

where $\sigma = 1/\rho$ (resistivity) and is the activation energy for electrical conduction and $v$ is Boltzmann’s constant. The values of the $\sigma$ are deduced from the slope of the Arhenius plot. The inset in figure shows the variation of the activation energy with respect to the Cu-content in the films. As shown the activation energy increases as the copper content increase.

The recorded reduction in the dc-electrical conductivity could be attributed to the structural changes brought in the films upon Cu-doping. As confirmed by RRD measurements the particle size decreased from 28 to 24 nm. This reduction in the particle size increases the grain boundary volume...
inside the deposited films which increases the grain boundary scattering for the moving free charge carriers. Also as revealed from the structural analysis by increasing the Cu-concentration the compressive strain and the dislocation per unit volume increases, which introduces more defects and increases the resistance of the films. Cu doping in CdS is known to produce acceptor levels which in turn tend to be of ‘p’ type [6]. During conduction there is a finite probability that these ‘p’ type carriers could undergo a recombination process at the grain boundary. This makes the grain boundaries more resistive and thereby contributes to the observed increase in resistivity upon Cu doping. Apart from the recombination of the carriers at grain boundaries, an added effect observed is the reduction of mean crystallite size with Cu concentration as shown in Fig. 11. This in turn results in an enhancement of charge carrier recombination and confinement effects [36].

The depth of the Fermi level below the conduction band, in N-type semiconductors, can be estimated from the following equation:

\[ E_g - E_F = kT \ln \left( \frac{2\pi m^* kT}{\hbar^2} \right) \]  

(17)

where \( E_g \) is the band gap, \( E_F \) is the fermi level energy, \( K \) is Boltzmann’s constant, \( T \) is the absolute temperature and \( n \) is the free electron concentration. Also the presence of Cu is known to introduce an acceptor level 0.34 eV above the valence band. This is accompanied by the down shift to the Fermi level away from the bottom of the conduction band which may explain the increase in the activation energy as shown in the inset of Fig. 11. Table 1 shows the recorded values of activation energy and other parameters which recorded by other researchers using different methods of deposition.

### 4. Conclusion

Thin films of CdS doped with Cu have been synthesized. The XRD analysis shows that the preparation of CdS hexagonal phases in all films with average grain size ranging from 28 to 24 nm. Also upon doping the stress was found to decrease significantly at Cu-6% and the same for the dislocation per unit volume in deposited films. AFM analysis show that the surface roughness changes with Cu-6% doping. The band gap shifts from 2.43 to 2.4 eV. Urbach’s tail is also calculated. Finally the conductivity is measured by direct record of the variation of resistance with temperature. The activation energy is estimated and is found to increase upon Cu-doping. In this work the increase in the band gap accompanied by an increase in the activation energy, i.e. the smaller the band gap the higher the activation energy. Such relations may suggest that the conduction mechanism follows the POOL-Grenkel mechanism where small polarons are responsible for the conduction process.

### Conflicts of interest

The authors declare no conflicts of interest.

### Acknowledgments

This work is partially supported by the Egyptian Academy for Scientific Research & Technology (Grant No. AERT/1200250) and the Faculty of Science BSU.

### References


[31] Ikhmayes SJ. S-rich CdS$_{1-x}$Te$_x$ thin films produced by the spray pyrolysis technique. Energies 2016:234.


