EFFECT OF CdCl₂ TREATMENT ON THERMALLY EVAPORATED CdTe THIN FILMS

K.S. RAHMANa, F. HAQUEa, N.A. KHANA, M. A. ISLAMb, M.M. ALAMc, Z.A. ALOTHMANa, K. SOPIANA AND N. AMINb,c,*

aSolar Energy Research Institute (SERI), Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia.
bDepartment of Electrical, Electronic and Systems Engineering, Universiti Kebangsaan Malaysia, Malaysia.
cAdvanced Materials Research Chair, Chemistry Department, College of Sciences, King Saud University, Riyadh 11451, Kingdom of Saudi Arabia.

The influence of CdCl₂ treatment on the properties of thermally evaporated CdTe thin film was investigated in this analysis to achieve high quality thin films. Thin films of CdTe were deposited on cleaned soda lime glass substrates at room temperature by thermal evaporation technique. Then the samples were treated by CdCl₂ and subsequently annealed at annealing temperature of 400ºC for 15 minutes. The structural, optical and electrical properties of the grown samples were investigated through XRD, AFM, UV-Vis spectrometry and Hall-effect measurement analysis. The as-deposited films prepared at 25A were found in polycrystalline form, whereas the films prepared at deposition current of 28A and 30A exhibit cubic crystallinity with (111) preferential orientation around 2θ = 23.8°. The crystallinity and the carrier concentration of the films were improved for all the CdCl₂ treated films. The surface roughness of the films was also highly affected by the CdCl₂ treatment as it was observed from AFM images. The bandgap has been found around 1.43 eV for the as-deposited films whereas the bandgap decreased to 1.4 eV after CdCl₂ treatment. The values of mobility, resistivity and Hall coefficient were observed to decrease after the CdCl₂ treatment.

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Keywords: Thermal evaporation, CdCl₂ treatment, CdTe thin film, XRD, AFM.

1. Introduction

Post deposition treatment is the most accepted method due to its inherent process flexibility [1-2]. Post deposition treatments are essential for obtaining larger grains as well as to improve the electronic parameters of devices. The properties of the deposited films can also be modified by various chemical, physical methods and post deposition treatments. Heat treatment with CdCl₂ is considered to be a major step for preparing high-quality CdS/CdTe solar cells [3–6]. Nowadays CdCl₂ treatment has become a standard and critical process for fabricating high-efficiency CdTe-based solar cell, regardless of the method used for depositing the CdTe layer. This treatment is needed to improve the performance of CdTe thin-film cells, which can eventually improve the cell efficiency to a factor of two or more [7-8]. Cadmium chloride treatment is a post-deposition treatment which has been carried out as a solution treatment. This treatment process is very simple and easy. CdCl₂ treatment is a process in which a specific amount of CdCl₂ is first dissolved in methanol. After that, grown samples are applied on CdCl₂ solution for 10-15 s by dipping or spraying techniques.

After the CdCl₂ application, the CdTe film undergoes air or vacuum heat treatment at 400° C to 420° C for 15-30 minutes which will be supportive for electrical, structural and optical modification of the films. For removing the excess CdCl₂, a hot water wash treatment is generally followed.
The CdCl$_2$ treatment usually results in grain growth in small grain films and improves device characteristics like open circuit voltage ($V_{oc}$) and Fill Factor (FF) [9]. Thin film CdTe based solar cells are regarded as a leading photovoltaic material for its low cost, easier deposition, high optical absorption coefficient and high chemical stability. CdTe has a band gap of $\sim$1.5 eV, which is very close to the ideal value for photovoltaic conversion efficiency. To fabricate the CdTe films, various preparation techniques have been employed such as vacuum deposition [10-12], electro deposition [13], molecular beam epitaxy [14], metal-organic chemical vapor deposition [15], closed-space sublimation [16] and screen-printing [17]. The thermal evaporation method has some benefits such as: the quantity of impurities included in the growing layer will be minimized, the trend of forming oxides will be significantly reduced and finally straight line propagation will occur from the source to substrate [18]. Thus thermal evaporation technique has been the most suitable method due to the very high deposition rate, low material consumption and low cost of operation [19]. Hence an effort has been made in this paper to enhance the structural, morphological, optical and electrical properties of thermally evaporated CdTe thin films by CdCl$_2$ treatment followed by heat treatment.

2. Methodology

Commercially available FTO coated soda lime glasses were cleaned in ultra-sonic bath degreased by methanol-acetone-methanol and de-ionized water for 5 minutes, respectively. Then the degreased glasses were dried out by dry N$_2$. The CdTe thin films of 1.5–2.0 $\mu$m thickness were deposited onto ultrasonically cleaned glass substrates by thermal evaporation using highly pure CdTe (99.99%). The chamber was emptied at a pressure greater than 10$^{-5}$ torr by the combination of rotary and diffusion pumps. When a vacuum of 10$^{-6}$ torr was attained in the vacuum chamber, the temperature of the boat was steadily raised to heat CdTe to temperatures greater than the melting point. This allowed the evaporation of CdTe material. The deposition time was fixed to 20 min. The typical conditions for thermal evaporation are listed in Table I.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>CdTe (99.99% pure)</td>
</tr>
<tr>
<td>CdTe thickness</td>
<td>1.5–2.0 $\mu$m</td>
</tr>
<tr>
<td>Substrate</td>
<td>Soda lime glass</td>
</tr>
<tr>
<td>Boat-substrate distance</td>
<td>4 to 6 (cm)</td>
</tr>
<tr>
<td>Magnitude of dc current</td>
<td>25 to 30 (Ampere)</td>
</tr>
<tr>
<td>Deposition time</td>
<td>20 to 30 min</td>
</tr>
</tbody>
</table>

After deposition, the treatment of samples was done with a saturated solution of 0.3 mole CdCl$_2$ in methanol. The samples were dipped into the solution for 10-15 s. After that, the samples were desiccated in air for 15 min. After the application of the solution on the film surface, samples were annealed in a vacuum furnace at 400$^\circ$ C for 15 min. The chamber pressure was maintained in the range 220-250 Torr during annealing. At the end of the annealing process, the samples were kept in the annealing chamber until the chamber temperature returned to room temperature. Then hot DI water was used to remove the CdCl$_2$ residues from the samples. The structural properties have been examined by the X-ray diffraction (XRD) method. Surface topography analysis of the samples was carried out by Atomic Force Microscopy (AFM) technique. The optical properties were measured by the double beam spectrophotometer in the wavelength range of 400 nm to 900
nm. The electrical properties were calculated from Hall-effect measurement system. The optical band gaps were calculated from their absorption edge extrapolated from the absorption spectra.

3. Result and discussions

3.1 Structural Analysis by XRD

X-ray diffraction (XRD) data taken by ‘BRUKER aXS-D8 Advance Cu-Kα’ diffractometer were used to find the crystallographic impact of CdCl₂ solution treatment on the properties of CdTe thin films. Fig. 1 shows the XRD pattern for the as-deposited and CdCl₂ treated CdTe thin film for various current flows (25A, 28A and 30A). The annealing temperature was kept at 400°C. From Fig. 1 it is clear that the films grown at 25A is polycrystalline in nature whereas the films deposited at 28A and 30A shows crystalline nature with a preferential orientation along the (111) cubic plane and found at 2θ=23.8°. CdCl₂ treatment influenced the film characteristics and consequently improved the cubic crystallinity as viewed from the figure. The existence of highly preferred orientation peak at 2θ=23.8° confirms a pure cubic zinc blende structure of the deposited CdTe films with preferential orientation along the (111) plane [20]. Other low intensity diffracted peaks were observed belonging to CdTe with positions at 2θ= 26.51°, 29.81°, 39.31°, and 46.51° correspond to (200), (102), (220) and (311) planes for current flow 25A. Another peak was observed for the same current flow at 2θ= 42.5° which does not match with the CdTe peaks. All the diffraction peaks are well matched with the JCPDS (00-015-0770) file and are in good agreement with the literature of CdTe cubic structure [21].

![XRD Spectra](image)

Fig 1: XRD spectra of CdTe thin film deposited at current flows (a) 25 A (b) 28 A and (c) 30 A

The lattice parameter ‘a’ for cubic phase structure [hkl] for the films has been calculated from the Brag’s law and Vegard’s law [22-23]:

\[
d_{hkl} = \frac{\lambda}{2 \csc \theta}
\]  (1)
where, $d$ is the interspacing between the planes in the atomic lattice, $\lambda$ is the X-ray wavelength (0.15406 nm), $\theta$ is the angle between the incident ray and scattering planes and $a$ is the lattice constant.

To obtain more structural information, the mean crystallite sizes (D) of the films are calculated using Scherrer formula [24-25]:

$$D_{hk0} = \frac{0.9 \lambda}{\beta \cos \theta}$$

where, $\theta$ is the Bragg diffraction angle, $\lambda$ is the X-ray wavelength (0.15406 nm) and $\beta$ is the full width at half maximum [FWHM] of the film diffraction peak at 20. Crystallinity is highly correlated to FWHM values. The deterioration of the films crystallinity is determined by the higher values of FWHM, whereas the larger crystallite sizes indicate the enhanced crystallinity of the films [26-27]. The calculated values for different structural parameters of the as deposited and CdCl$_2$ treated CdTe thin films are shown in Table II.

The as grown films prepared at 25 A are polycrystalline in nature with random orientation. As a result, large number of grains with various relative orientations and positions create variations in the phase difference between the waves scattered by the grains. The total intensity scattered by all grains is equal to the sum of individual intensities scattered by each grain. The lattice strains are developed by varying displacement of the atoms with respect to their reference lattice positions. These phenomena can be described by micro-strain. Actually, the origin of micro-strain depends upon the deposition conditions of the film. The developed microstrain ($\varepsilon$) is calculated from the relation [28-29]:

$$\varepsilon = (\beta/4) \tan \theta$$

where, $\beta$ and $\theta$ has their usual significances. The larger value of $\varepsilon$ indicates the highly polycrystalline film whereas single crystalline nature exhibits lower micro-strain value. Determining the dislocations density is very important for analyzing the crystallographic properties of the thin film. Generally, dislocations are caused by an imperfection in a crystal caused by the miss registry of the lattice in one part of the crystal with respect to another part. The dislocation density of thin films is calculated by the Williamson and Smallman's relation [30]:

$$\delta = \frac{n}{D^2}$$

where, $n$ is a factor, which is considered almost equal to unity for minimum dislocation density and $D$ is the crystallite size or grain size. From Table II, it is observed that, the highest crystallite size (211.02 nm) is found for the (200)$^\text{cub}$ phase for as grown film which was deposited at 25A current flow whereas the (311)$^\text{cub}$ phase of CdCl$_2$ treated film grown at 25A shows lowest value of crystallite size. The lattice constant is found 0.65 Å for all the prepared films. However, the values of micro-strain and dislocation densities alter with the CdCl$_2$ treatment. The highest micro-strain of 0.83×10$^{-3}$ is obtained for (311) cubic phase for CdCl$_2$ treated and subsequently annealed film deposited at 25A which indicates the highest lattice misfit and dislocation in the film structure. The maximum value of dislocation density 2.58×10$^{11}$ is also found for the same sample.
Table 2. Calculated values of the structural parameters of CdTe thin films

<table>
<thead>
<tr>
<th>Sample</th>
<th>hkl</th>
<th>( d_{hkl} ) (nm)</th>
<th>a (Å)</th>
<th>( \beta ) (deg)</th>
<th>( D_{hkl} ) (nm)</th>
<th>( \varepsilon ) ( \times 10^{-3} )</th>
<th>( \delta ) ( \times 10^{11} ) (cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Grown (25A)</td>
<td>(111)</td>
<td>0.37</td>
<td>0.65</td>
<td>0.04</td>
<td>203.05</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>(200)</td>
<td>0.34</td>
<td>0.65</td>
<td>0.12</td>
<td>68.04</td>
<td>0.12</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>(102)</td>
<td>0.30</td>
<td>0.65</td>
<td>0.04</td>
<td>205.67</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>(220)</td>
<td>0.23</td>
<td>0.65</td>
<td>0.04</td>
<td>211.02</td>
<td>0.06</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>(311)</td>
<td>0.19</td>
<td>0.65</td>
<td>0.08</td>
<td>108.16</td>
<td>0.15</td>
<td>0.08</td>
</tr>
<tr>
<td>CdCl(_2) Treated</td>
<td>(111)</td>
<td>0.37</td>
<td>0.65</td>
<td>0.36</td>
<td>22.56</td>
<td>0.33</td>
<td>1.96</td>
</tr>
<tr>
<td></td>
<td>(200)</td>
<td>0.34</td>
<td>0.65</td>
<td>0.08</td>
<td>102.07</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>(102)</td>
<td>0.30</td>
<td>0.65</td>
<td>0.08</td>
<td>102.84</td>
<td>0.09</td>
<td>0.09</td>
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<tr>
<td></td>
<td>(220)</td>
<td>0.23</td>
<td>0.65</td>
<td>0.08</td>
<td>105.49</td>
<td>0.12</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>(311)</td>
<td>0.19</td>
<td>0.65</td>
<td>0.44</td>
<td>19.67</td>
<td>0.83</td>
<td>2.58</td>
</tr>
<tr>
<td>As Grown (28A)</td>
<td>(111)</td>
<td>0.37</td>
<td>0.65</td>
<td>0.04</td>
<td>203.08</td>
<td>0.04</td>
<td>0.02</td>
</tr>
<tr>
<td>CdCl(_2) Treated</td>
<td>(111)</td>
<td>0.37</td>
<td>0.65</td>
<td>0.2</td>
<td>40.62</td>
<td>0.18</td>
<td>0.60</td>
</tr>
<tr>
<td>As Grown (30A)</td>
<td>(111)</td>
<td>0.37</td>
<td>0.65</td>
<td>0.08</td>
<td>101.54</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>CdCl(_2) Treated</td>
<td>(111)</td>
<td>0.37</td>
<td>0.65</td>
<td>0.2</td>
<td>40.61</td>
<td>0.18</td>
<td>0.60</td>
</tr>
</tbody>
</table>

3.2 Surface Morphology Analysis by AFM

Atomic Force Microscopy (AFM) gives microscopic information on the surface structure of the thin films and allows plotting topographies representing the surface relief [31]. In this work, we have used AFM to visualize the surface relief, identify the growth and determine the contribution of the deposition processes to the quality of the films. The surface topographical effects on CdTe thin films due to post deposition CdCl\(_2\) treatment were observed from AFM images as shown in Fig. 2.
Fig 2: AFM images for CdTe thin films for (a) as-deposited and (b) CdCl₂ treated films.

The calculated average roughness, $S_a$ and RMS roughness, $S_q$, for all the films are represented in Table III. The surface topography and roughness of the films were found by “NANOSURF EASYSCAN 2 AFM” (Atomic Force Microscopy) SYSTEM. Fig. 2(a) and (b) illustrate the topography (from 3D image) and grains (from 2D image) of CdTe thin films grown by thermal evaporation technique. For the as grown films, the average and root mean square (RMS) of the roughness is about 14.875 nm and 18.722 nm, respectively. For the CdCl₂ treated films, these values are 9.77 nm and 12.23 nm respectively. It has been observed that the average and root mean square value of the roughness drastically decreased after CdCl₂ treatment.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>$S_a$ (nm)</th>
<th>$S_q$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-grown</td>
<td>14.875</td>
<td>18.722</td>
</tr>
<tr>
<td>CdCl₂ treated</td>
<td>9.77</td>
<td>12.23</td>
</tr>
</tbody>
</table>

3.3 Optical Properties Analysis

UV-Vis spectrometry is used to observe the optical properties such as transmission, absorption and optical bandgap of the prepared films. A blank FTO coated glass slide was placed in one of the beam directions during the scanning process while the glass slide with the deposited CdTe film was inserted in the other beam direction. In this way, the absorption and transmission spectra recorded by the spectrometer were obtained from the CdTe thin films deposited on the FTO coated glasses. The transmission spectra for as grown and CdCl₂ treated films are shown in Fig. 3 and Fig. 4, respectively, which was recorded for wavelengths ranging from 400 nm to 900
nm. The films exhibit a transmittance below 10% along the visible range which confirms that, the films are very suitable as a good quality absorber layer for photovoltaic applications. The band gap of CdTe thin films are calculated from the following equation [32-34].

\[ \alpha = A \frac{(h\gamma - E_g)^{1/2}}{h\gamma} \]  

(6)

where, \( \alpha \) is the absorption coefficient; A is constant; \( h\gamma \) is photon energy and \( E_g \) is the band gap.

Fig 3: Transmission spectra for as deposited CdTe thin films for deposition current flows (a) 25 A (b) 28 A and (c) 30 A.

Fig 4: Transmission spectra for CdCl₂ treated CdTe thin films for deposition current flows (a) 25 A (b) 28 A and (c) 30 A.

The graphs of \( (\alpha h\gamma)^2 \) vs \( h\gamma \) are plotted in Fig. 5. The bandgap found for as grown films for 25A, 28A and 30 A was 1.42, 1.41 and 1.43 eV, respectively. For CdCl₂ treated film, the bandgap decreased to 1.40, 1.39 and 1.38 eV, respectively. After the CdCl₂ treatment, the bandgap values decreased for all the current flows as compared with the as deposited films. Therefore, from the bandgap analysis, we can conclude that, CdCl₂ treatment has a significant effect on band gap values.
Fig 5: Graph of $(\alpha h \gamma)^2$ versus photon energy $h \gamma$ for as deposited and CdCl$_2$ treated CdTe thin films for deposition current flows (a) 25 A (b) 28 A and (c) 30 A.

3.4 Electrical Properties Analysis

Hall Effect measurement system can be used to find out a few material parameters, but the primary one is the Hall voltage ($V_{H}$). Other significant parameters such as carrier mobility, carrier concentration ($n$), Hall coefficient ($R_H$), resistivity, magneto resistance ($R$) and the conductivity type (N or P) can be derived from the Hall voltage measurement. Hall effect measurements are useful for characterizing every material used in producing semiconductors, such as silicon (Si) and germanium (Ge), as well as most compound semiconductor materials, including silicon.
germanium (SiGe), silicon-carbide (SiC), gallium arsenide (GaAs), aluminum gallium arsenide (AlGaAs), indium arsenide (InAs), indium gallium arsenide (InGaAs), indium phosphide (InP), cadmium telluride (CdTe), and mercury cadmium telluride (HgCdTe). These measurements can also be used in characterizing thin films of these materials for solar cells/photovoltaics, as well as organic semiconductors and nano-materials like graphene. They are equally useful for characterizing both low resistance materials (metals, transparent oxides, highly doped semiconductor materials, high temperature superconductors, dilute magnetic semiconductors, and GMR/TMR materials used in disk drives) and high resistance semiconductor materials, including semi-insulating GaAs, gallium nitride (GaN), and cadmium telluride (CdTe).

For investigating the electrical properties of CdTe films, the resistivity and Hall Effect measurements with an incorporated resistivity/Hall measurement system (ECOPIA 3000) was used. For this purpose, the magnetic field was applied vertically to the surface of the sample and the magnitude and polarity of this were alternated periodically, while a direct current was passed across the sample using one diagonal pair of the four gold electrodes connected to a current source [21]. After that, by using a frequency response analyzer (HMS-3000), alternating Hall voltage induced synchronously with the ac magnetic field was detected via the other pair of electrodes. The magnitude of the magnetic field and the current source was 0.55 T at the maximum and 20 nA, respectively. The carrier concentration, mobility, resistivity and Hall coefficients were deduced from this study. The calculated bulk concentration, mobility, resistivity and Hall coefficients are presented in Table IV.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk Concentration ([\times 10^{11}] \text{(cm}^3\text{)})</th>
<th>Mobility ((\text{cm}^2/\text{Vs}))</th>
<th>Resistivity ([\times 10^4] \text{(\Omega}\cdot\text{cm}))</th>
<th>Hall Coefficient ([\times 10^5] \text{(cm}^3\text{/c}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited (25 A)</td>
<td>5.9</td>
<td>49.68</td>
<td>21.30</td>
<td>106.0</td>
</tr>
<tr>
<td>CdCl₂ treated (25 A)</td>
<td>5.8</td>
<td>18.80</td>
<td>4.70</td>
<td>107.0</td>
</tr>
<tr>
<td>As deposited (28 A)</td>
<td>7.4</td>
<td>150.50</td>
<td>4.58</td>
<td>84.7</td>
</tr>
<tr>
<td>CdCl₂ treated (28 A)</td>
<td>9.9</td>
<td>289.00</td>
<td>4.54</td>
<td>63.2</td>
</tr>
<tr>
<td>As deposited (30 A)</td>
<td>3.8</td>
<td>139.00</td>
<td>10.90</td>
<td>165.0</td>
</tr>
<tr>
<td>CdCl₂ treated (30 A)</td>
<td>6.9</td>
<td>19.24</td>
<td>4.72</td>
<td>19.6</td>
</tr>
</tbody>
</table>

The highest mobility was obtained for the CdCl₂ treated films deposited at 28 A current flows while it shows the lowest resistivity. The value of mobility decreased after CdCl₂ treatment for the films deposited at current flow of 25 A and 30 A, respectively. It is also observed that, bulk concentration of the films is in the order of \(10^{11}\text{cm}^3\), shows rising tendency with the increment of deposition current for the CdCl₂ treated films. The highest carrier concentration was found 9.9 \(\times 10^{11}\text{cm}^3\) for CdCl₂ treated sample which was grown at current flow of 28 A. The Hall coefficient value is lowest \((19.6 \times 10^5 \text{ cm}^3/\text{c})\) for the CdCl₂ treated films deposited at current flow of 30 A. From this analysis it is seen that, CdCl₂ treatment has an enormous impact on film properties as well as deposition current can also be an important factor for analyzing the films characteristics.

### 4. Conclusion

The structural, morphological, optical and electrical properties of CdCl₂ solution treated CdTe thin films grown by thermal evaporation has been investigated elaborately by XRD, AFM, UV-VIS spectrometry and Hall-effect measurement analysis. The XRD reveals that, the as grown films prepared at 25A are highly polycrystalline in nature, whereas the films prepared at 28A and 30A shows cubic crystallinity with (111) preferential orientation around \(2\theta=23.8^\circ\). The band gap has been found around 1.43 eV for the as deposited films whereas after CdCl₂ treatment, it decreased around to 1.4 eV. For the as grown films, the average and root mean square (RMS) of the roughness is about 14.875 nm and 18.722 nm, respectively. On the other hand, the average and
root mean square (RMS) of the surface roughness is about 9.77 nm and 12.23 nm, respectively, were found for the CdCl$_2$ treated films. It has also been seen that the average and root mean square value of the roughness decreased drastically after CdCl$_2$ treatment. The highest mobility was obtained for the CdCl$_2$ treated films deposited at 28 A current flows while it showed the lowest resistivity. The values of mobility, resistivity and Hall coefficient were observed to decrease after CdCl$_2$ treatment. Hence, it can be concluded that, a 0.3 M CdCl$_2$ solution for the CdCl$_2$ treatment with optimum annealing temperature range of 350 °C to 400 °C for subsequent annealing for 15 to 20 min. is suitable for 1.5–2.0 μm thick high quality CdTe thin film absorber layers.

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