Study the effect of CdCl₂ heat treatment on CdS/CdTe photovoltaic Heterojunction properties

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Abstract:
CdS/CdTe heterojunction has been fabricated by thermal evaporation technique. Polycrystalline CdTe and CdS films have been prepared by thermal evaporation technique on glass substrate with heating substrate of 423 K of 1 and 0.1 μm thicknesses respectively. The heterojunction annealed at 573 K. The current – voltage under illumination showed that the photocurrent increased with increasing the incident illumination intensity for CdS/CdTe heterojunction, and no photovoltaic effect was observed.
The CdS/CdTe heterojunction has been heat treated after evaporated CdCl₂ film at 573 K under vacuum for 30 min., the heterojunction has better photovoltaic properties. The open circuit voltage (V_{oc}) and the short circuit current (I_{sc}) increased with increasing the incident illumination intensities, and the efficiency is 1.24 % at 78 mW/cm².

Experimental Work:
Preparation of CdS/CdTe Heterojunction Solar Cell:
All films and ohmic contacts have prepared by thermal evaporation technique by using Edward E306A coating system under vacuum of about 10⁻⁶ mbar (in thin films laboratory - college of science - university of Baghdad),the polycrystalline structure of CdS and CdTe films have tested by X-ray diffraction measurements.
There are three steps to prepare CdS/CdTe heterojunctions as the following and it is illustrated in Fig. (1)

I- Corning glass used as a substrate, coated by the gold of 0.15 μm thickness as back ohmic contact, CdTe as an absorber layer (the p-type layer which found from Hall measurements) with thickness of about 1μm with deposition rate of about 7.5 Å/sec, then CdS as a window layer (the n-type Layer) with thickness of about 0.1μm with deposition rate of about 1.6 Å/sec, it annealed at 573 K for 30 min. under vacuum.
II- Indium Tin Oxide (ITO) was used as antireflecting and transparent conducting oxide which represented the front contact with thickness of about 0.1 μm.
III- The grid ohmic contacts the aluminum of 0.2 μm thickness. The following scheme shows the basic structure of the cell.

Preparation of CdS/CdTe Heterojunction Solar Cell with CdCl₂ Film:
In fabrication CdS/CdTe solar cell, there is post deposition heat treatment in the presence of CdCl₂ or chloride. The CdCl₂ improves the overall performance of photovoltaic properties of the heterojunction and appears to improve the yield and uniformity of device [1]. Typically, CdS/CdTe solar cell prepared as mentioned in the previous item, but before evaporating ITO, it followed by CdCl₂ film heat treatment consists of the following steps:

I- Coating the surface of CdS/CdTe with CdCl₂ film by thermal evaporation technique with 0.1 μm thickness [1, 2].
II- Annealing the coated CdS/CdTe with CdCl₂ film HJ at 573 K for 30 min. under vacuum of about 10⁻² mbar.
III- The residual CdCl₂ film removed by etching the surface of CdS/CdTe HJ by using nitric acid (HNO₃) 1%; phosphoric acid (H₃PO₄) 60% : water (H₂O) 39% [2,3,4].
Results and Discussions:

Optoelectronic Measurement:

Current-Voltage Characteristic for CdS/CdTe Heterojunction without CdCl₂ Film:

Figure (2) shows the photocurrent of CdS/CdTe heterojunction annealed at 573 K under different illumination intensities. The photocurrent is considered as the important parameter, which plays an effective role in solar cells. The prepared heterojunction strongly depends on the illumination intensities as shown in this figure. The photocurrent increases with increasing the depletion region width as shown in the relation below [5]

\[ I_{ph} = qaG_{ph}(w + L_p + L_n) \]

Where \( G_{ph} \) generation of photocarriers, \( L_p \) and \( L_n \) are the diffusion depth of holes and electrons carriers respectively. The influences of built in voltage (\( V_{bi} \)) which led to separate the electron-hole pairs and then increases the photocurrent [5,6], photocurrent increased by 3 times with increasing the illumination intensities. The reverses bias photocurrent is a function of the generation and diffusion carriers.

![Fig. (2): The I-V characteristics for HJ CdS/CdTe heterojunction at forward and reverse bias voltage at different illumination intensities.](image Url)

The performance characteristics of the HJ were very poor. This was properly due to the high resistive CdTe layer, some leakage current through pin holes and the grain boundaries, defects at the CdS/CdTe interface on non-optimum back contact formation [7], the midgap states that act as recombination centers may arise either from states created as a result of junction fabrication or lattice mismatch between CdTe and CdS [8,9], or may be due to many nonuniformities caused by the contribution of grain size variations, thickness variations of one or more layers, interfacial oxides, contamination and other weaknesses [10, 11].

Current-Voltage Characteristic for CdS/CdTe Heterojunction with CdCl₂ Film:

The better photovoltaic properties obtained after CdCl₂ heat treated at 573 K for 30 min., as shown in figure (3). These were properly as a result of a better p-n junction formation with a fewer pin holes and lower interface state densities. CdCl₂ heat treatment is an activation step which enhances the performance improvement of CdTe/CdS solar cell by eliminating some defects [12]. Table (1) shows solar cell parameters. CdCl₂ film heat treatment causes chloride ion (\( Cl^- \)) moves via grain boundary diffusion through the CdTe layer. The accumulation of \( Cl^- \) near CdS interface is due to smaller grain boundary area in the greater grain CdS layer. This is due to the fact that \( Cl^- \) atomic radius of \( 167 \times 10^{-12} m \) is expected to substitute for sulfur (S) \( 170 \times 10^{-12} m \) in CdS over cadmium (Cd ) \( 97 \times 10^{-12} m \) [13,14,15], this accumulation improves the initial performance of CdS/CdTe solar cell.

![Fig. (3): The I-V characteristics for CdS/CdTe heterojunction solar cell at different illumination intensities.](image Url)

The net donors concentration near the interface is increased by increasing temperature of CdCl₂ heat treatment [14], but some negative side effect is strong n-doping of CdS layer, it would be serial resistance to ITO layer [12,16].

The interdiffusion of CdS and CdTe layers is believed to be responsible for overcoming the lattice mismatch between this two materials and reducing recombination at grain boundaries and also to be responsible for controlling intermixing between CdTe and CdS layers [4,9,12]CdCl₂ heat treatment enhances recrystallization and grain growth due to the large increase in the grain size and causes widening of grain boundaries [1,14].

The short circuit current (\( I_{sc} \)) and open circuit voltage (\( V_{oc} \)) are very important parameters because it can determine the range in which the device operates on it, and it can separate the generated pairs without need of applied external field. Figure (4) and Table (1) show the variation of \( I_{sc} \) and \( V_{oc} \) for the solar cell with different illumination intensities, \( I_{sc} \) and \( V_{oc} \) curves show a linear behavior at illumination intensities from 30 to 80 \( mW/cm^2 \) as a result of excitation and separation of electrons from their atoms by incident photons which leads to create electron-hole pairs and then increases of \( I_{sc} \) and \( V_{oc} \) [17]. Our prepared solar cell has filling factor (F.F.) of 0.624 and efficiency (\( \eta \)) of about 1.24 % at incident power intensity of 78 mW/cm².
Table (1): The variation of $I_{sc}$ and $V_{oc}$ with different illumination intensities for CdS/CdTe solar cell.

<table>
<thead>
<tr>
<th>Intensity (mW/cm$^2$)</th>
<th>$I_{sc}$ (mA.)</th>
<th>$V_{oc}$ (Volt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>2.719</td>
<td>0.459</td>
</tr>
<tr>
<td>60</td>
<td>1.778</td>
<td>0.448</td>
</tr>
<tr>
<td>50</td>
<td>1.599</td>
<td>0.442</td>
</tr>
<tr>
<td>40</td>
<td>1.429</td>
<td>0.433</td>
</tr>
<tr>
<td>30</td>
<td>1.226</td>
<td>0.425</td>
</tr>
</tbody>
</table>

Conclusions:
The photocurrent increased with increasing the incident illumination intensity for CdS/CdTe heterojunction, and no photovoltaic effect was observed. The CdS/CdTe heterojunction has been heat treated after evaporated CdCl$_2$ film and annealed at 573 K under vacuum for 30 min. The heterojunction has photovoltaic properties. $I_{sc}$ and $V_{oc}$ increased with increasing the incident illumination intensities, and the efficiency is 1.24 % at 78 mW/cm$^2$.

References:
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الملخص:
حضر المفرق الهجيني CdS/CdTe بتقنية التبخير الحراري. حيث حضرت أغشية متعددة البلورات من البلورات المختلطة الحلالية CdS/CdTe و CdTe و CdS بتقنية التبخير الحراري على ارضية من الزجاج عند درجة حرارة أساسية 423 مطلقة و 0.1 ميكرون للمادة على التوالي. عوامل المفرق حرارة بدرجة حرارة تذبذب (T_a) 573 مطلقة. وتبخير غشاء محتوى CdCl_2 بدرجة حرارة 573 مطلقة لمدة ثلاثعان من الكريستالات الفوتوفولتايكية. حيث نلاحظ تأثير التبخير الشفاف على جميع العناصر المذكورة، حيث يزيد من فولتية الدارة المفتوحة (V_{oc}) و تيار الدارة القصيرة (I_{sc}) مع زيادة شدة الإضاءة الساقطة. تمثل الخلايا الشمسية كفاءة تحويل قيمتها 1.24% للشدة الإضاءة ساقطة قيمتها 78 mW/cm^2.