

The physical characteristics of $\text{Cu}_2\text{S}/\text{CdS}$ thin-film solar cell

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$\text{Cu}_2\text{S}/\text{CdS}$ heterojunction has been prepared and characterized by using the vacuum evaporation technique on glass substrate. The Cu_2S layer was obtained by the dry method, i.e. by evaporation of a CuCl film followed by heat treatment. The photovoltaic properties including I-V characteristics, short-circuit current (I_{sc}), open-circuit voltage (V_{oc}), fill factor (ff), efficiency (η) of $\text{Cu}_2\text{S}/\text{CdS}$ heterojunction cells have been examined after formation. Heat treatment improved the photovoltaic cells. High resistivity of CdS thin film, high series resistance and the poor design of the grid have lead to low efficiency.

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1. Introduction

In recent years, efforts on the development of thin film solar cells have been more and more concentrated on $\text{Cu}_2\text{S}/\text{CdS}$ cells with a p-n heterojunction. During the past decades, thin film photovoltaic cell of $\text{Cu}_2\text{S}/\text{CdS}$ was the most promising solar energy conversion (optoelectronic) device due to the high conversion efficiency more than 9.1%, easy fabrication and low cost [1]. However, it has generally been considered that the formation of p-type CdS is very difficult, because of the strong self-compensation effect due to sulphur vacancies [2] and the depth of the acceptor level in CdS (~ 1 eV) [3], despite the fact that there have been some reports on p-type CdS [4]. Cadmium sulphide/copper sulphide solar cells are clearly heterojunction cell with CdS having energy gap of 2.42 eV and Cu_2S having an energy gap of 1.2 eV. Considering the nature of sunlight, it is clear that the Cu_2S layer is responsible for the bulk of photocurrent generation [5].

The interested method of fabrication of $\text{Cu}_2\text{S}/\text{CdS}$ solar cells is to vacuum evaporated CdS followed by wet dipping to form Cu_2S [6,7]. Several techniques such as dry process [8], vacuum evaporation [9], sputtering [10] and spray pyrolysis [11] have been applied for the production of Cu_2S films.

In this work, a simple structure for the $\text{Cu}_2\text{S}/\text{CdS}$ heterojunction based on a range of experiments made on cells has been investigated.

2. Experimental details

A schematic cross section of the cell with the configuration glass/Ag/CdS/ Cu_2S /Au with a surface area of about 1 cm^2 is shown in Fig. 1. The back electrode was obtained by deposition of silver layer of 150 nm thick on glass substrate under vacuum of 10^{-3} Pa. The silver layer acts an ohmic back contact with the deposited CdS layer [12]. The CdS layer approximately 1500 nm in thickness was deposited by vacuum evaporation of pure CdS

powder. The CdS layer must be thick layer to prevent shorting during drying method process due to the diffusion of the highly mobile copper ions through imperfections in the CdS layer. The deposition rate was 15 nm/s, and the substrate was held at about 200°C during the deposition. To increase the absorption and to obtain a smooth CdS surface before evaporating the CuCl , the CdS-layer is etched. The solution of etching is $\text{HCl}:\text{H}_2\text{O}=1:1$ at a temperature of 60°C for about 10 sec. This etching process results in a surface roughness due to the pyramidal structure [13] of the CdS surface.

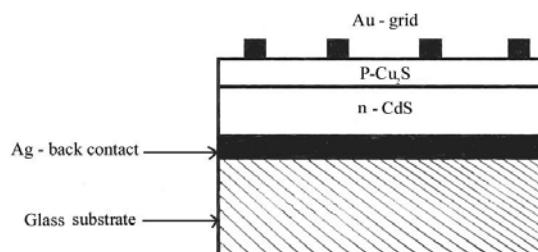
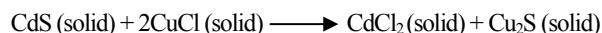


Fig. 1. Schematic diagram of a cross-section of $\text{Cu}_2\text{S}/\text{CdS}$ solar cell.

The Cu_2S -layer is produced by vacuum evaporation of a thin layer of CuCl powder (300 nm thick) onto the CdS film at room temperature. Then the sample was heated at 170°C for 5min in the same vacuum chamber at pressure of 10^{-3} Pa. In this case, a layer of Cu_2S is formed by the toptaxial conversion of CdS by CuCl into Cu_2S according to the following reaction:



After reaction, the film was taken out of vacuum, rised in distilled water or alcohol to remove the residual layer of CdCl_2 formed in the reaction. After dipping, a heat treatment for 5 minutes at approximately 180°C in air was required in order to complete the junction formation and

also to improve the cell efficiencies. The thickness of the Cu_2S layer on the surface of the CdS film was calculated from gravimetric method [14].

The structure of Cu_2S film was determined by X-ray diffraction (XRD). The front ohmic contact of $\text{Cu}_2\text{S}/\text{CdS}$ cell was achieved by thermal evaporation of gold grid (~ 100 nm) through a mask on the front side. The junction characteristics were analyzed in terms of current-voltage (I-V) measurements. The I-V characteristics in dark and under 100 mW cm^{-2} illumination by using a halogen lamp on Cu_2S side through the transparent grid of gold contact. The temperature variation ($270 - 343 \text{ K}$) on the I-V characteristics was studied under the dark condition. The cell parameters V_{oc} , I_{sc} , ff , and also the conservation efficiency (η) were calculated.

3. Results and discussion

Cadmium sulphide films deposited on glass at 200°C exhibit the wurtzite structure with two diffraction peaks, as shown in the XRD pattern of Fig. 2. The c-axis ((002) direction) of the hexagonal crystallites is being perpendicular to the substrate. The lattice parameters of $d(002) = 0.3398 \text{ nm}$, $d(004) = 0.1639 \text{ nm}$ and $c = 0.6676 \text{ nm}$ were determined from the diffraction pattern. These values are in close agreement with others [15, 16]. The well-oriented CdS layer was obtained, with an as-deposited roughness, which is shown in the scanning electron microscope of Fig. 3.

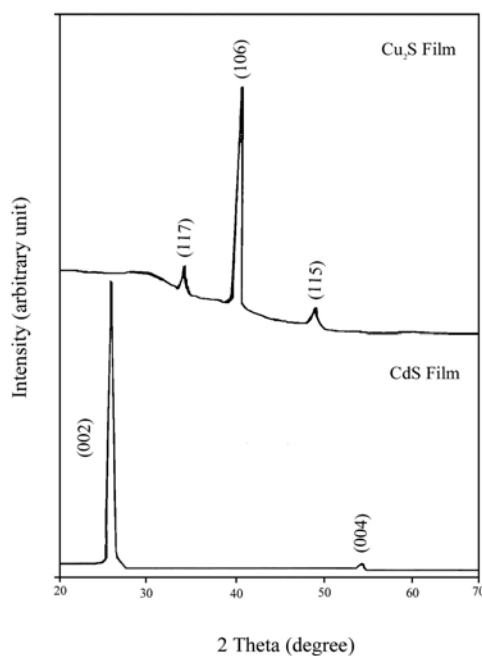


Fig. 2. X-ray diffraction diagram of CdS and Cu_2S thin films.



Fig. 3. Scanning electron microscope image of CdS film, ($t = 100 \text{ nm}$, $T_s = 200^\circ\text{C}$, $R = 15 \text{ nm/s}$).

The dry process starts with the deposition of a CuCl layer onto the surface of the CdS layer. During the heat treatment of CuCl , the ion exchange reaction takes place. Since in this case we have a homogeneous distribution but immobile Cu-source, the reaction cannot proceed down into grain boundaries. Also, the heat treatment after deposition of CuCl material, forces copper to diffuse into the adjacent CdS layer, thus resulting in an optimised Cu-deficiency (and p-type conductivity) of the Cu_2S layer. The Cu_2S films formed were investigated with X-ray diffraction as shown in X-ray diffraction allows the identification of the copper-sulphur phase present in the film; when the film consists of pure chalcocite (Cu_2S) with orthorhombic phase, the stoichiometry index x of the resulting Cu_xS film can be determined quantitatively [17]. The film grows preferentially with their (002) plane parallel to the substrate. Also, if the film contained copper deficient phases such as djurleite ($\text{Cu}_{1.75}\text{S}$), digenite ($\text{Cu}_{1.8}\text{S}$) or anilite ($\text{Cu}_{1.75}\text{S}$), the crystal structure was so bad that no clear X-ray diffraction peaks could be observed. The lattice parameters were calculated to be $d(115) = 0.18242 \text{ nm}$, $d(106) = 0.22539 \text{ nm}$ and $d(117) = 0.262188 \text{ nm}$.

Transmittance measurements in the range of 500 nm to 1000 nm as shown in Fig. 4, were made on CdS and Cu_2S films. The CdS layer has the transmittance more than 90% at wavelengths longer than the absorption edge. The higher substrate temperatures shift the absorption edge to the higher energy side and increase the absorption near the band edge, also the colour of films will change from yellow to orange [16].

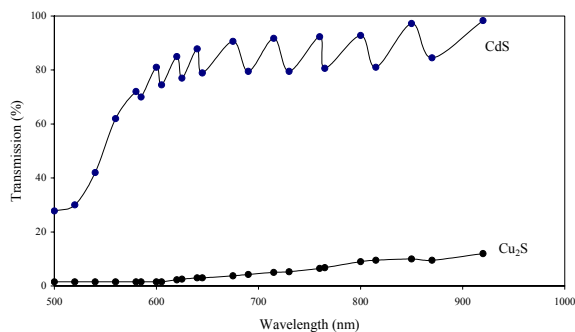


Fig. 4. Transmittance vs. wavelength for CdS and Cu₂S films.

The optical properties of Cu₂S film (Fig. 4) indicate that Cu₂S possesses a high absorption in the visible region of the spectrum and a high transmission in the infrared. The absorption coefficient (α) was calculated from the transmission (T) and reflection (R) data using the following formula [18]:

$$T = (1-R)^2 \exp(-\alpha t) \quad (1)$$

where, t is the film thickness. The dependence of absorption coefficient of Cu₂S film on the photon energy is shown in Fig. 5. The relation indicates the presence of band edges at 1.22 eV. The absorption edge is in agreement with Ramoin et al [19]. However this value is lower than those observed by Shiozawa et. al. [20], Eisenmann [21], Cusano [22] and Marshall and Mitra [23]. These difference in the values of energy gaps dependence on the preparation techniques.

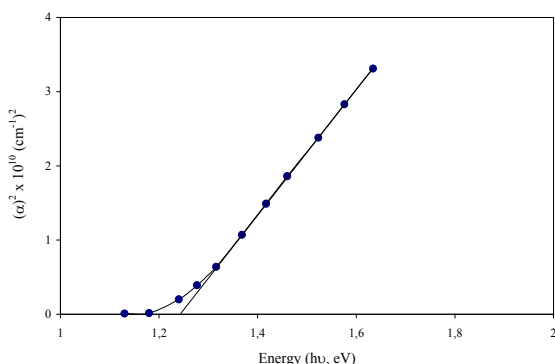


Fig. 5. Variation of $(\alpha)^2$ with photon energy for Cu₂S film.

Resistivity and Hall measurements on CdS film were made by the Van der Pauw technique. The resistivity of CdS film at 200 °C is 1.5 Ωm and has a carrier concentration equal 10^{21} m^{-3} and mobility $5 \times 10^{-4} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$. Similar studies of these parameters are reported by others [16,24]. With respect of Cu₂S, the carrier concentration is 10^{25} m^{-3} and mobility equal to $6 \times 10^{-4} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$.

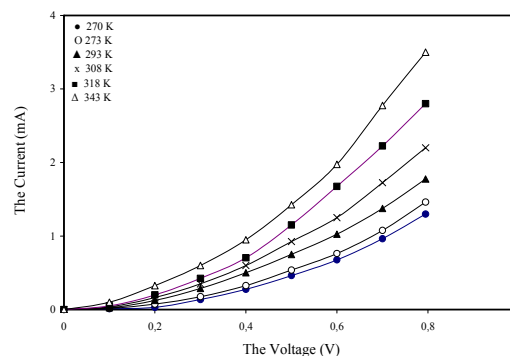


Fig. 6. $I - V$ characteristics of Cu₂S/CdS heterojunction in dark condition at different temperatures.

The $I - V$ characteristic without illumination (in dark), the forward current of the cell increases slowly with increasing voltage is shown in Fig. 6 over the temperature range from 270 to 343 K. The heterojunction has rectification properties and the current increases with increasing temperature. Since the dark $I - V$ plots were similar to the diode characteristics. The values of the series resistance (R_s) in dark condition for the cell can be determined from the forward $I - V$ characteristics of Fig. 6 at higher voltage. The results given are R_s from 190 to 1200 Ω at different temperatures (270 - 343 K). The higher resistance may be responsible for decreasing the quality of the cell [25]. The current – voltage relation in heterojunction can be generally described by any of the diffusion model, the emission model or the recombination model from which the relation is represented by the standard diode equation [26, 27]:

$$I = I_0 \{ \exp (eV/nkT) - 1 \} \quad (2)$$

where e is the electronic charge, n is the diode quality factor, k is Boltzmann's constant, T is the absolute temperature and I_0 is the reverse saturation current.

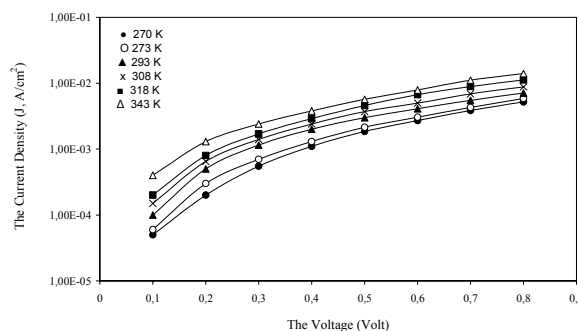


Fig. 7. Semilogarithmic relation of current voltage characteristic of Cu₂S/CdS heterojunction cell in dark condition at different temperatures.

The semi-log plot of forward $I - V$ characteristics of the heterojunction is shown in Fig. 7. The saturation

current density (J_0) was obtained by extrapolating the $J - V$ characteristics at low voltage, where the values were found to be in the ranges from 10^{-5} to 10^{-4} A cm $^{-2}$. Also, the diode factor, n , can be calculated from the slope of certain voltage interval. The values of n were found to vary from 2.59 to 3.6 at the different temperature range. The diode factor A (2.59 – 3.6) is greater than 2.0 (ideal value) [16,27,28].

The increase in n values (> 2 ideal value) indicates that the cells were non-ideal and most of the carriers (electrons and holes) were recombined at the junction (depletion) region [27, 29-31]. Hence, as the voltage increases, the current is limited by the carrier recombination. This could be due to the lattice mismatch of the CdS/Cu $_2$ S system, which may give rise to a large number of interface states [32]. Also, Ashour [16] and Ashour et al. [33] obtained higher values of n for CdTe/CdS and CuInSe $_2$ /CdTe devices and they indicated that due to generation – recombination processes.

The relation between the current (J_0) and the temperature (T) can be estimated from the following relationship [33]:

$$J_0 = J_{00} \exp (-\Delta E/kT) \quad (3)$$

where J_{00} is the constant determined by the particular type of the junction and ΔE is the activation energy. According to this equation, J_0 should change exponentially with temperature. On the other hand, the pre-exponential factor, J_{00} , which obtained by extrapolating the forward current curves shown in Fig. 7 to zero voltage is found to vary exponentially with $1/T$ as shown in Fig. 8. Therefore, plotting $\ln J_0$ vs. $1/T$ yields a straight line, where the activation energy of the charge carriers, ΔE , can be determined from the slope. The activation energy (ΔE) of the cell was estimated to be 0.7eV. Then due to conduction process, the hole in the valence band of Cu $_2$ S (p) flows from one localized state to another in CdS (n) located within an energy range of kT . This hole is recombined with an electron in the conduction band of CdS or it is emitted to the valence band of CdS.

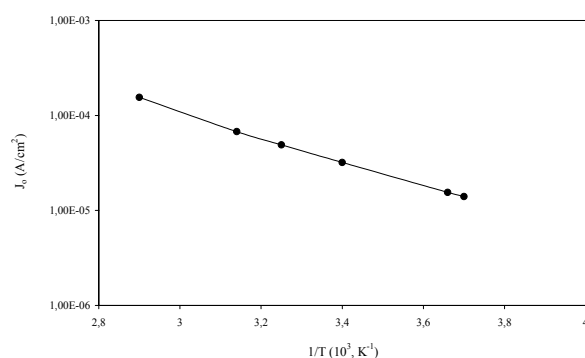


Fig. 8. The current density versus $1/T$ of Cu $_2$ S/CdS heterojunction solar cell in dark condition.

CdS/Cu $_2$ S solar cells are clearly heterojunction cells and by considering the nature of sunlight, it is clear that the Cu $_2$ S layer is responsible for the photocurrent generation [34]. In general, the heterojunction solar cells have a tendency towards multiple recombination centres located in the vicinity of the pn-junction. This leads to increase in the photocurrent in a non-linear manner as the light intensity is increased. This is the fact that with higher light intensities (if $h\nu \geq E_g$) there is an increased concentration of photo-generated charge carriers and they succeed in saturating the recombination centres.

The I-V characteristic under illumination of the cell is shown in Fig. 9. The short circuit current of the cell is substantially lower than the best cells in the literature. The cell exhibits the short circuit current (I_{sc} , 5.75 mA), but the open circuit voltage (V_{oc} , 0.5V) and the fill factor is about 63%. Efficiency in the fabricated cell measured about 7.2%. Obviously the weak value of this cell is the low value of the fill factor and the efficiency. This may be due to the higher series resistance [33] and to the poor design of the grid [35], which is determined by the mechanical mask for the deposition of the fingers. Also, Stanley and Ashour [36, 16] mentioned that the low efficiency of their CdS solar cells is due to the high CdS resistance. On the other hand Ibrahim and Ashour [27] concluded the small efficiency for their cell (ZnO/Si cell) might be due to a recombination of the charges at the depletion region between the two semiconductors.

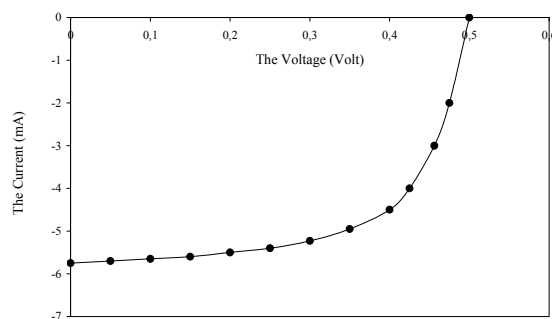


Fig. 9. I – V characteristic of Cu $_2$ S/CdS solar cell under illumination at room temperature.

It should be avoided by using a contact grid with a smaller finger spacing and decreasing the resistivity of CdS by doping it with indium.

4. Conclusions

A simple technique based entirely on vacuum evaporation and drying was used to fabricate Cu $_2$ S/CdS solar cell. The CdS film has been formed by vacuum evaporation and the Cu $_2$ S layer by drying techniques with the final cell being formed thermally. The CdS film has a hexagonal (wurtzite) structure with preferred orientation of the c-axis perpendicular to the substrate. The film exhibit

an optical absorption edge at 0.5 μm and has a carrier concentration is 10^{21} m^{-3} and mobility is $5 \times 10^{-4} \text{ m}^2 \text{ v}^{-1} \text{ s}^{-1}$.

The Cu₂S film prepared by the dry technique exist in the chalcocite (Cu₂S) phase. The film exhibits an absorption edge at 1.22 eV. The current-voltage under dark, illumination conditions are described. Efficiency of thin film CdS cell approached around 7.2%. The major limitations at present are the poor design of the grid and the CdS resistance, which is high, leading to a low fill factor. Work on improvement of the grid design and decreasing the CdS resistance is in progress.

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