

The Effect of the Thickness of Polycrystalline CdS film on the Efficiency of Cu₂S/CdS Solar Cell

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Abstract

In this paper, Cu₂S/CdS solar cells were prepared with different thickness of CdS layer, these layers were prepared by using chemical spray pyrolysis technique. The chemical spray solution was prepared by mixing cadmium chloride CdCl₂ and thiourea CS(NH₂)₂ of molar concentration 0.1 M/L, the CdS layer was formed after the solution was sprayed on hot Aluminum substrate at temperature 400°C. Experimentally the type of CdS film was found as n-type depending on the results of Hall Effect, the value of the Hall factor (R_H) is about $-1.348 \times 10^{-6} \text{ m}^3/\text{C}$ and the density of the majority charge carriers (N) is about $4.64 \times 10^{18} \text{ cm}^{-3}$.

The prepared film was tested by using X-Ray diffraction; the result shows that the film was CdS with a polycrystalline structure.

The Cu₂S layer was prepared by using Chemical dip process; this layer was formed on the surface of the CdS film and it is always p-type. The heat treatment was utilized to form the p-n junction.

The current-voltage characteristics of p-Cu₂S/n-CdS solar cells was studied, the efficiency of the prepared cells of different thickness; (2.19, 2.52, 3.64, and 5.55) μm of CdS layer was calculated at 85.4 mW/cm² light intensities, the results show that the thickness of the polycrystalline CdS film is an important parameter affecting the cell efficiency.

Introduction

Semiconductors materials like II-VI compounds have become more important in making photovoltaic devices, photoconductors, and infrared detectors and solar cells (1, 2). The Cadmium Sulfide (CdS) is an interesting material for the direct conversion of sun light in to electricity, it is characterized by a self-generated electromotive force (e. m. f), and it was identified as a potential material for low cost terrestrial photovoltaic energy conversion. CdS is a direct band gap semiconductor and it is a good absorber for sunlight with high optical absorption coefficient. Cadmium Sulfide /Copper Sulfide solar cell is one of the important thin films heterojunction types (3, 4).

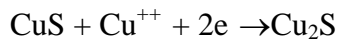
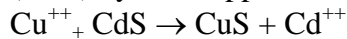
The chemical spray pyrolysis technique was used to prepare CdS layer, it is a simple and low cost thin film technology and it is utilized to form wide area film and it is capable to produce high thickness of CdS film, which leads to an accepted efficiency (5).

The necessary thickness of the CdS film seems to be a function of the relative physical perfection of the film. Most of high efficiency CdS cells were made from films with thickness of 5–20 μm. In thick film (more than 1 μm); there is an increase in the production of pairs (Electron– Hole) that leads to increase the photocurrent at the illuminated cell, but in thin CdS layer, the number of defects in the active region will probably increase and the conversion efficiency will deteriorate.

The behaviour of Cu₂S–CdS solar cell as a function of the thickness is somewhat more involved than for Si devices, this reason argues that the CdS layer can be reduced to the order of micron without a harmful effect; this would be true in a single crystal device,

polycrystalline CdS usually made thick to prevent such problems (6, 7).

The dipping process is the most often used method for the formation of the Cu₂S layers for Cu₂S–CdS solar cell. The reaction consisting in the displacement of one cadmium ion (Cd²⁺) by two copper ions (2Cu⁺) is according to the following reaction:



The Cu₂S was formed on the CdS layers, it is a very thin layer and it is always p-type and highly conductive.

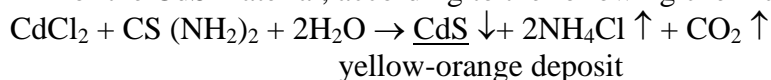
The p–n junction should be formed to get a photovoltaic device; generally, a "heat treatment" is used to form the junction. The conditions for the heat treatment depend on the CdS and Cu₂S fabrication method (8).

The annealed films may be attributed to the structure improvement and the decrease of the degree of amorphosity leading to decrease the localized states (9). This increasing of the mobility and concentration is due to the reduction of scattering of the carrier from the surface and the ionized impurities scattering gradually takes over, which agree with Kasmarski (10) Ohmer (11) and Jeong and Park (12) as well as the elimination of defects in films, and to the increasing in crystalline size which would decrease the number of the grain boundaries. The CdS film which was tested by X-ray diffraction (Nakamura et al (13).has a hexagonal structure.

The experimental work

The chemical spray pyrolysis system was used in preparing the CdS film on pure Aluminum substrate of 3×3 cm² area and 1mm thickness. A metal substrate was used since it is already conducting.

The spraying solution was prepared by mixing 18.34 gm of cadmium chloride (CdCl₂) and 7.612 gm thiourea {CS(NH₂)₂} of molar concentration 0.1 Mole/Liter., then they were used as starting materials. The CdS film was formed on a hot Aluminum substrate at the temperature of 400 °C after 2-3 minutes from the beginning of the spray operation from the atomizer, as shown in fig. (1).The temperature of the substrate was controlled by a digital readout temperature controller unit of ±0.1°C accuracy. The spraying operation is continued for several times then the yellow–orange deposit layer would appear on the substrate, it was a film of the CdS material, according to the following chemical reaction (8, 14):

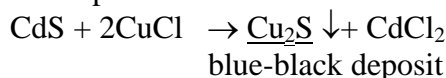


The thicknesses of the prepared films were measured by using the "Weight method".

The Cu₂S layer was formed by dipping the CdS film into a hot solution containing cuprous ions for 30 sec. The dipping solution was prepared by adding copper chloride (CuCl) with NaCl and hydrazine (2NH₂.HCl), the materials concentration of the dipping solution are:

6 gm/L CuCl, 2 g/L NaCl, and 1 ml/L hydrazine. Adjusted with HCl, PH=3.5. The reaction is generally performed in an aqueous solution, and it takes place at a temperature around 90 °C.

The replacement reaction is:



By using the dipping method; a thin layer of about 0.1–0.3 μm of Cu₂S was formed on the surface of CdS film and it is in a very intimate contact with it (4, 14).

The heat treatment is the required method to form the p-n junction, the layers of CdS and Cu₂S are dried and heated in an oven at 180°C for 3-5 minutes.

The ohmic contact made by evaporation Aluminum under vacuum using coating system type "Edwards E306A", the Aluminum mesh used as an upper electrode with the help of the mask, the evaporation condition was done in the pressure of 2×10⁻⁵ bar.

By using Hall Effect; the type of CdS film was found as n-type, depending on the value of Hall Factor (R_H.) as shown in figure (2). Electromotive force (e. m. f) was supplied on both

sides of the solar cell, and then two digital electrometers were used to calculate the output voltage and the output current. Visible light was used as the input power P_{in} , the intensity of the light was determined by changing the position of the light (up or down) with a suitable step.

Result and Discussion

1. The properties of Cu_2S/CdS solar cell

Sample of CdS thin film, which was prepared by using chemical spray technique, was tested by X-ray diffraction. The output results of these measurements shows that the film was CdS material with polycrystalline structure, as shown in fig. (3).

Cu_2S/CdS solar cell was classified as a "frontwall cell" when illuminated from the above (from the Cu_2S side). The energy gap of CdS material is mostly higher than the energy gap of Cu_2S material, for this reason, the responsivity of the Cu_2S film for the incident photons is higher than the responsivity of CdS film, therefore Cu_2S film has a high ability of the absorption for the photons of energy between 1.2–1.5 eV; where the value of the energy gap of Cu_2S film is 1–1.2 eV (14, 15).

Substrate choosing has an important effect in preparing solar cell where it affects the cell properties; the best substrate is that material which reduces the contact resistance for both layers; p-type, and n-type⁽⁸⁾. Experimentally; the type of CdS film was found as n-type, depending on the value of Hall Factor (R_H) which was calculated by using the equation(8):

$$R_H = \frac{V_H \times t}{I \times B}$$

R_H was about $-1.348 \times 10^{-6} \text{ m}^3/\text{C}$, this value was measured for the film of thickness $t = 1.203 \mu\text{m}$ (the film of this thickness has Hall electrode), $(V/I)_H = -0.282 \text{ Volt/Amp}$ and $B = 0.257 \text{ Tesla}$.

Where; I is the current flow through the film, V_H is the generated voltage on both sides of the film, and B is the magnetic field. The density of the major carriers of the CdS film can be relatively calculated from the following relation (8, 16, 17)

$$N = \frac{1}{e \times R_H}$$

Where; (N) is the density of the majority carriers, (e) is the Charge of the electron. The experimental result of N value for CdS film of thickness $t = 1.203 \mu\text{m}$ was:

$$N = 4.64 \times 10^{18} \text{ cm}^{-3}.$$

2. Study the I–V characteristics of Cu_2S/CdS solar cell

The I–V characteristics of the prepared p- Cu_2S/n -CdS solar cell were studied at different light intensities, as shown in table (1).

At the illuminated cell; the short circuit current depends on the intensity of the incident lights as shown in figure (4a), and there is logarithmic relation between V_{oc} and the incident light for the prepared Cu_2S/CdS solar cell, as shown in figure (4-b).

One of the main reasons of low short circuit current is the absence of anti-reflection coating layer that can affect on the cell efficiency; other factors such as impurities could be important (18).

The electrical properties of four p- Cu_2S/n -CdS solar cells were studied for different numbers of thickness (2.19, 2.52, 3.64, and 5.55) μm of CdS layer at 85.4 mW/cm^2 light intensities, as shown in table 2. The results show that layer thickness of the solar cell has an effect on the cell efficiency, as shown in figure (5).

3. Calculation the efficiency and Fill Factor of the Cu_2S/CdS solar cell

The conversion efficiency (η) of the solar cell was calculated by using the equation (8):

$$\eta = \frac{FF \times I_{sc} \times V_{oc}}{P_{in}}$$

Where Fill factor (FF) is equal: $FF = \frac{I_m \times V_m}{V_{oc} \times I_{sc}}$

The maximum efficiency of Cu₂S/CdS solar cell of area 6.25 cm² under 85.4 mW/cm² light intensity was 2.8 % for 5.55 μm thickness of CdS layer.

In a thick film, there is an increase in the photocurrent at the illuminated cell, so the best efficiency was registered in cell with a thick CdS layer.

Fill Factor which is defined as the ratio of the maximum power to the (I_{sc}×V_{oc}) was equal to 0.70, as shown in fig. (6).

In the illuminated cell there is the best absorption of the incident light occur in the solar cell of thick CdS layer. Improving the present setting of the used spray technique can be capable to produce a high thickness of CdS layer, which leads to an acceptable efficiency.

Much more work is required on annealing and doping studies before high efficiencies would be observed (5, 19).

Conclusions

The prepared Cu₂S/CdS solar cell by using simple technique was good; it can operate in an acceptable efficiency. The CdS layer was easily fabricated by using a chemical spray pyrolysis technique. The spray technique is utilized to produce a wide area solar cell and it is required for such a thick film.

The thickness of the polycrystalline CdS layer is an important parameter affecting the cell efficiency.

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Table (1): Performance of Cu₂S–CdS Solar cell at different light intensities of 5.55 μm thickness of CdS layer

t (CdS) Thick. (μm)	Intensity (mW/cm ²)	Isc (mA)	Voc (mVolt)
5.55	38.4	22	400
	56.5	31	420
	69.1	41	430
	85.4	47	450

Table (2): Performance of four Cu₂S–CdS Solar cells of different thickness of CdS layer at 85.4 mW/cm² light intensity

t (CdS) Thick. (μm)	Isc (mA)	Voc (mVolt)	V max. (mVolt)	I max. (mA)	FF % Fill Factor	η % Efficiency
2.19	39	400	320	29	0.63	1.78
2.52	38	420	330	31	0.64	1.90
3.64	43	430	330	36	0.66	2.30
5.55	47	450	340	44	0.70	2.80



Fig. (1): The Setup arrangement of the spray system

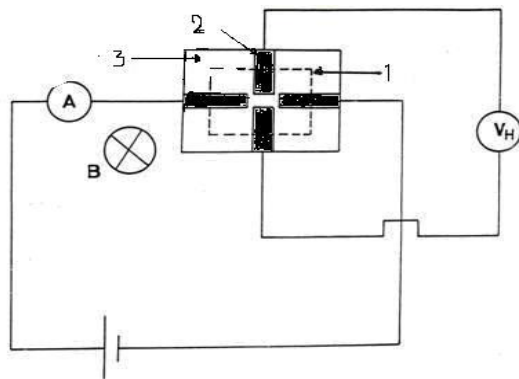


Fig. (2): The electrical circuit to measure the Hall Factor
 1-The dotted square is CdS films, 2-The dashed lines represent the masks, 3- The Aluminum substrate

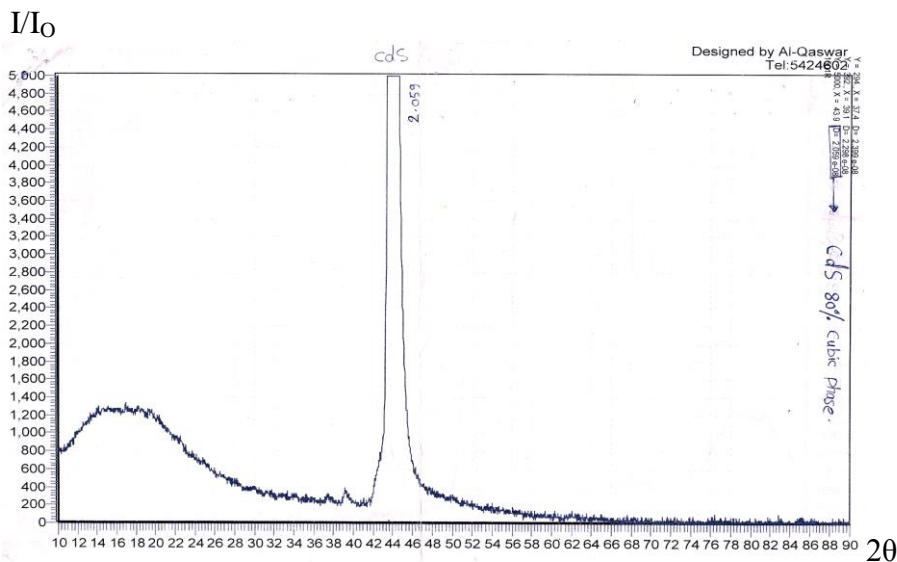


Fig. (3): Chart of X-Ray diffraction of CdS layer which was prepared by using chemical spray

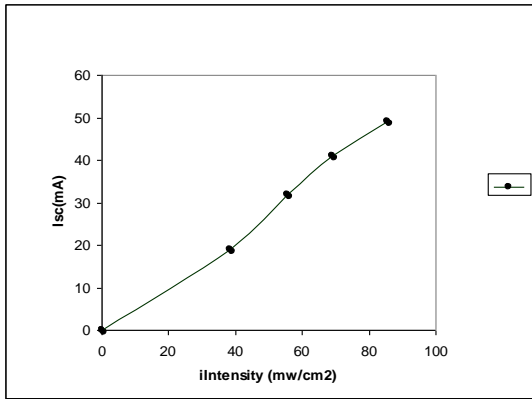


Fig.(4-a): The relation between Isc and the intensity of the incident light

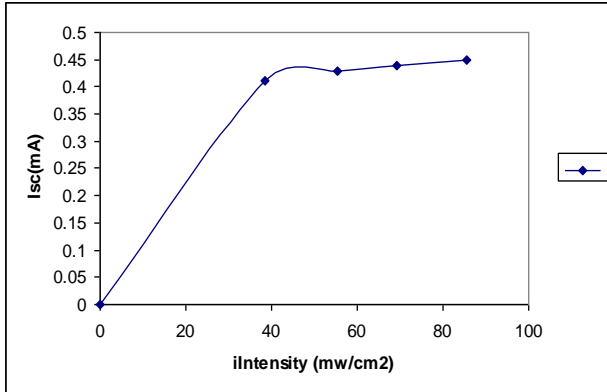


Fig. (4-b): The relation between Voc and the intensity of the incident light

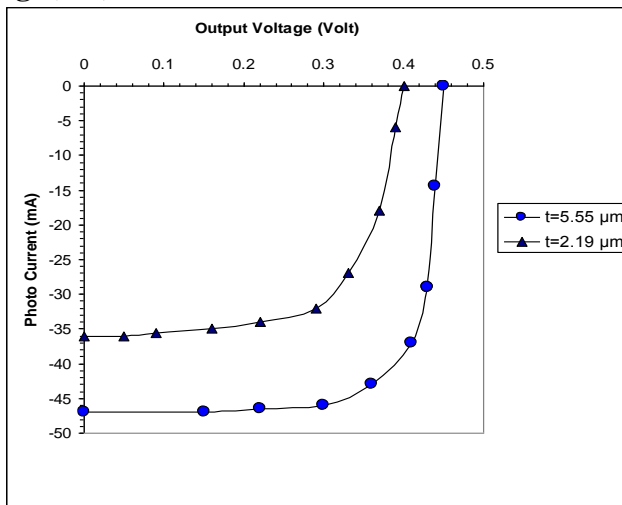


Fig. (5): The I-V plot of the prepared cells of minimum and maximum thicknesses of the prepared CdS layer at the same intensity

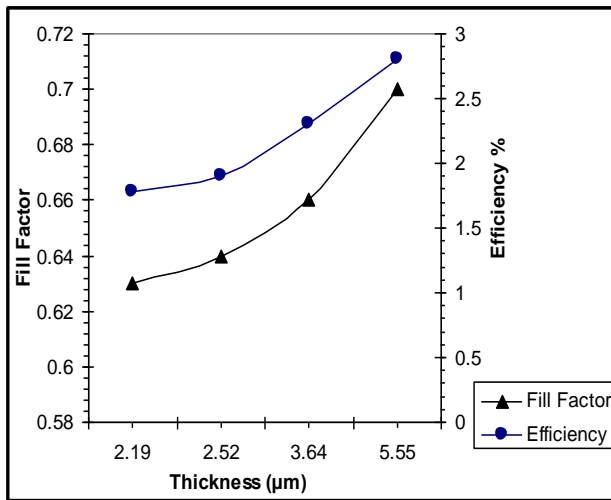


Fig. (6): The Efficiency and Fill Factor as a function of the thickness of CdS layer

دراسة تأثير سمك غشاء CdS المتعدد التبلور على كفاءة الخلية الشمسية نوع Cu₂S/CdS

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الخلاصة

في هذا البحث، حضرت خلايا شمسية نوع Cu₂S/CdS بعد تحضير أغشية مختلفة السمك لطبقة كبريتات الكاديوم CdS، تم تحضير هذه الطبقة باستخدام تقنية الرش الكيميائي الحراري. تم تحضير محلول الرش من خلط كلوريد الكاديوم والثايوريا بتركيز مولاري مقداره 0.1 M/L وتم رش المحلول على الطبقة الأساس المتكونة من شريحة الألمنيوم الساخنة لدرجة ٤٠٠ درجة مئوية.

تبين عمليا أن غشاء CdS هو من نوع n-type وذلك اعتمادا على نتائج تأثير هول Hall Effect، إذ كانت قيمة عامل هول $R_H = -1.348 \times 10^{-6} \text{ m}^3/\text{C}$ ومنه حسب تركيز حوامل الشحنات في غشاء CdS وكانت قيمتها $4.6 \times 10^{18} \text{ cm}^{-3}$. فحصت طبيعة تبلور الغشاء المحضر بطريقة الرش الكيميائي بالاعتماد على قياسات حيود الأشعة السينية، حيث وجد إنه يتكون من مادة كبريتات الكاديوم ذي تركيب متعدد التبلور

حضر غشاء Cu₂S باستخدام طريقة الغمس الكيميائي، إذ يتكون هذا الغشاء على طبقة كبريتات الكاديوم والذي ستمثل نوع p وقد استعملت المعالجة الحرارية للحصول على توصيلة p-n .

درست خواص تيار-جهد للخلايا الشمسية p-Cu₂S/n-CdS، و حسبت كفاية للخلايا المصنعة والمختلفة بسمك طبقة كبريتات الكاديوم μm (2.19, 2.52, 3.64, and 5.55) في حالة تسليط الضوء المرئي عليها بشدة 85.4 mW/cm² وتبين إن لسمك غشاء كبريتات الكاديوم المتعدد التبلور تأثير في كفاءة الخلية.