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Improving the efficiency of CdS/CdTe solar cells by varying the thiourea/$CdCl_2$ ratio in the CdS chemical bath

O Vigil-Galán[1], A Arias-Carbajal[2], R Mendoza-Pérez[1], G Santana-Rodríguez[3,5], J Sastre-Hernández[1], J C Alonso[3], E Moreno-García[1], G Contreras-Puente[1] and A Morales-Acevedo[4]

[1] Escuela Superior de Física y Matemáticas-Instituto Politécnico Nacional, C P 07738, México D. F., México
[2] Facultad de Química-IMRE, Universidad de La Habana, 10400, La Habana, Cuba
[3] Instituto de Investigación en Materiales, UNAM, A.P. 70-360, Coyoacán 04510, México D.F., México
[4] CINVESTAV-IPN, Departamento de Ingeniería Eléctrica, Av. IPN No 2508, 07360 México D.F., México

E-mail: amorales@gasparin.solar.cinvestav.mx

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Abstract
In this work, the influence of the properties of CdS thin films grown by chemical bath deposition upon the characteristics of CdS/CdTe solar cells, when varying the thiourea concentrations in the CdS bath solution, is studied. The important solar cell parameters such as short circuit current (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and efficiency (η) were measured and it was noted that they improve for thiourea/$CdCl_2$ ratios (in the CdS deposition solution) up to 5, and drop for higher ratios in the range investigated. In addition, the ideal diode factor (n), saturation current (J_o) and series resistence (R_s) were studied under illumination and dark conditions. The results could be related to several factors, among them, the photoconductivity properties of the layers and the change of the $CdS_{1-x}Te_x$ layer at the CdS–CdTe interface.

1. Introduction

Cadmium telluride is one of the most promising semiconductor thin film materials for producing large area solar cells at low cost. The increasing interest towards this material has lead to a large number of studies on CdS/CdTe solar cells during the last few years [1–3]. The efficiency of the best CdTe-based devices has reached 16–17% [4, 5], far from the theoretical efficiency limit for cells with CdTe band gap (∼1.5 eV), around 30% [6]. CdS grown by chemical bath deposition (CBD) for CdTe solar cells has produced conversion efficiencies as high as 16.5% [4]. Hence, CdS has become an important material for this kind of solar cell. In a preceding paper, we have made a comparative study of the properties of CdS thin films grown by different methods like laser ablation, close space vapour transport, sputtering and CBD [7]. It was demonstrated that CBD-CdS films have poor crystalline quality, but they give excellent results for photovoltaics application because of their high relative photoconductivity, in addition to their better morphological properties (roughness and pinhole density) than CdS films grown by other techniques.

However, other aspects must be taken into account for processing of CdS/CdTe solar cells like the interdiffusion at the CdS–CdTe interface, the back contact in the p-type CdTe layer, the front contact of the solar cell, the bulk resistance of the layers, etc. In this regard, other developments have been made: for example, stable back and front contacts in order to obtain CdS/CdTe solar cells with low series resistance [8, 9]. Among all these open problems, the investigation of the

[5] Permanent address: IMRE, Universidad de la Habana, CP 10400, La Habana, Cuba.

Table 1. Thiourea concentration and deposition time for each S/Cd relation.

S/Cd R_{tc}	C (Thiourea) in the bath (mol l^{-1})	Time (min)
1.0	2.4×10^{-3}	120
2.5	6.0×10^{-3}	100
5.0	1.2×10^{-2}	120
10.0	2.4×10^{-2}	120

properties of the different layers, like their electrical resistivity, and their interface remains as one of the main issues for being able to improve efficiency.

The variation of S/Cd ratio for the solution used in the preparation of CdS films will modify the morphology, the deposition rate, the crystalline grain sizes, the resistivity and optical transmittance of these films and have an influence upon the structural and electrical properties of the CdTe layer itself, in addition to modifications of the CdS–CdTe interface. Hence the aim of this work is to investigate the influence of the S/Cd ratio in the solution for CdS thin films prepared by chemical bath upon the characteristics of CdS/CdTe solar cells with a superstrate structure.

2. Experimental procedure

The experimental set-up for the chemical bath of CdS consisted of a temperature controlled (±1 °C) water bath, in which a 150 mL beaker containing the reactants in a magnetically stirred solution is immersed. Concentrations of NH_3 (2.3 mol L^{-1}), NH_4Cl (2×10^{-2} mol L^{-1}) and $CdCl_2$ (2.4×10^{-3} mol L^{-1}) are kept constant in every experiment, but the $CS(NH_2)_2$ (thiourea) concentration was varied in order to obtain different S/Cd relations (R_{tc}) in the solution. The films were grown at 75 °C. Deposition times were also varied, according to our previous knowledge of the growth kinetics [10], with the purpose of obtaining films with similar thickness in all cases. The selected thiourea concentrations and deposition times for each S/Cd relation are shown in table 1.

Solar cells were prepared by depositing CdTe thin films on SnO_2:F/CBD-CdS substrates by the CSVT-HW (hot wall) technique using CdTe powders (99.99% purity). The atmosphere used during the CdTe was a mixture of Ar and O_2, with an O_2 partial pressure of 50%. In all cases the total pressure was 0.1 Torr. Prior to all depositions the system was pumped to 8×10^{-6} Torr as the base pressure. CSVT-HW deposition of CdTe was accomplished by placing a CdTe graphite source block in close proximity (1 mm) to the substrate block. The deposition time was 3 min for all the samples deposited with substrate and source temperatures of 550 °C and 650 °C, respectively. Under these conditions, CdTe layers of approximately 2 μm were obtained. The CdTe thin films were coated with a 200 nm $CdCl_2$ layer and then annealed at 400 °C for 30 min in air. For the back contact, two layers of Cu and Au (20 Å and 350 nm, respectively) were evaporated, with an area of 0.08 cm^2, onto the CdTe and annealed at 180 °C in Ar. For the front contacts, commercial conducting glasses were used (0.5 μm thick SnO_2:F/glass with 10 Ω/sq). The growth conditions of CdTe were maintained constant for all solar cells.

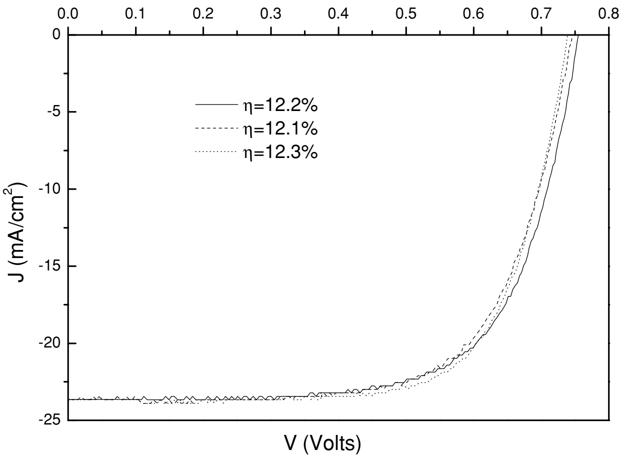

Figure 1. J–V characteristics of three CdS/CdTe solar cells made with CdS layers grown with $R_{tc} = 5$ during the CBD-CdS growth process.

3. Theoretical considerations

For high applied voltages, the dark diode equation can be approximated to

$$J \approx J_0 \exp\left(\frac{qV_{ef}}{nkT}\right) \quad (1)$$

where $V_{ef} = V - JR_s$. R_s is the total series resistance of the device. Hence, the plot of ln J versus V_{ef} yields slope $(q\,(nkT)^{-1})$ and intercept (ln J_0).

For low values of R_s, the applied voltage (V) falls at the junction and the values of ideal diode factor (n) and saturation current (J_0) correspond to the junction ones. However, for high values of R_s, the effective values of n and J_0 will be affected by the bulk resistance of CdS and CdTe layers and the contact resistance which constitute the total series resistance.

On the other hand, if the cell is illuminated

$$J_{sc} = J_0\left[\exp\left(\frac{qV_{oc}}{nkT}\right) - 1\right] \quad (2)$$

where J_{sc} and V_{oc} are the short circuit current density and the open circuit voltage, respectively. Hence

$$\ln J_{sc} = \ln J_0 + \frac{qV_{oc}}{nkT}. \quad (3)$$

From this equation, the values of n and J_0 can be determined from the measured values of J_{sc} and V_{oc} at different levels of illumination. For AM 1.5 illumination conditions R_s is determined directly from the J–V curve under illumination.

4. Results and discussion

4.1. Solar cells properties

Figure 1 shows the set of I–V characteristics for CdS/CdTe solar cells made with the same R_{tc} (S/Cd ratio = 5). As can be seen, according to our experimental conditions, the solar cells made with the same technological process have similar characteristics. The I–V characteristics of CdS/CdTe solar cells under AM 1.5 illumination (normalized to 100 mW cm^{-2}) as a function of R_{tc} are shown in figure 2. In table 2, the average shunt (R_p) and series (R_s) resistances,

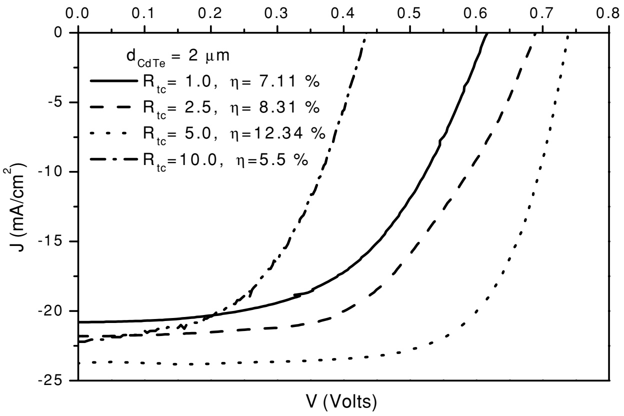

Figure 2. Typical J–V characteristics of CdS/CdTe solar cells under illumination at 100 mW cm^{-2}, having R_{tc} as a parameter.

Table 2. Average series resistance (R_s), shunt resistance (R_p), open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF) and efficiency (η) for CdS/CdTe solar cells with different S/Cd ratio (R_{tc}) in the CdS bath. These parameters were measured under AM1.5 illumination. The averages were taken from four samples for each R_{tc} ratio.

S/Cd R_{tc}	R_s (Ω cm^2)	R_p (Ω cm^2)	V_{oc} (volts)	J_{sc} (mA cm^{-2})	FF (%)	η (%)
1/1	6.8	318	0.617	20.8	55.2	7.1
2.5/1	5.4	800	0.690	21.8	55.5	8.3
5/1	2.9	787	0.740	23.8	70.5	12.3
10/1	5.9	135	0.435	22.7	52.0	5.4

the short circuit current density (J_{sc},), the open circuit voltage (V_{oc}), the fill factor (FF) and the efficiency (η) of solar cells fabricated with different R_{tc} are reported. As can be seen in table 2, η increases with R_{tc} up to $R_{tc} = 5$ and drops for $R_{tc} = 10$.

We believe that there are several factors directly or indirectly influencing the cell behaviour as mentioned in section 1. In particular, the amount of S in the CBD-CdS layers may influence the formation of the $CdS_{1-x}Te_x$ compound at the CdS–CdTe interface. CdTe films grown at high temperatures, such as those produced by CSVT, produce a sulfur enriched region due to S diffusion. The amount of S penetrating the bulk of CdTe from the grain boundary must be dictated by the bulk diffusion coefficient of S in CdTe and of course by the amount of S available in the CdS films. On the other hand, the recrystallization of CdTe could be affected by the morphological properties of the CdS layers grown with different S/Cd ratio. These facts have been studied by Lane *et al* [11] and Cousins *et al* [12]. From this point of view the formation of $CdS_{1-x}Te_x$ may be favoured when the R_{tc} is increased in the bath solution. This compound at the interface may cause a lower lattice mismatch between CdS and CdTe, and therefore a lower density of states at the CdTe interface region will be obtained, causing a lower value for the dark saturation current density J_o.

On the other hand, the dark resistivity of the CdS and CdTe layers, and their variation under illumination (photoconductive properties) also change the characteristics of the cell under dark and illumination conditions. In other words, a better photoconductivity implies smaller resistivity values under illumination, with the possible improvement of the solar cell properties.

Table 3. Average values for n and J_o in dark conditions and R_s under illumination conditions, for the different CdS/CdTe devices as a function of R_{tc}. The average values reported here are for four samples for each R_{tc} ratio.

S/Cd R_{tc}	n	J_o ($\times 10^{-6}$ mA cm $^{-2}$)	R_s (Ω cm^2)
1/1	2.9	3850	6.8
2.5/1	2.7	323	5.4
5/1	2.1	6	2.9
10/1	2.4	269	5.9

In this regard, the values of n and J_0 of the fabricated solar cells with $R_{tc} = 5$ were calculated under dark and illumination conditions. Under dark conditions the above parameters were 2.1 and 6×10^{-9} A cm^{-2}, respectively, but under illumination they were 1.4 and 9×10^{-11} A cm^{-2}, respectively. The dark values of these parameters are not representative of the measured solar cell open circuit voltage shown in table 2 for $R_{tc} = 5$, but agrees with these parameters under illumination, as expected.

In table 3, the dark n and J_0 and the R_s values under illumination (100 mW cm^{-2}) are shown. The R_s values were obtained from the J–V characteristics shown in figure 2. As expected, the dark diode properties (n and J_0) and R_s change with R_{tc}.

In addition, optical transmittance, thickness and morphological measurements of the CBD-CdS films showed the following characteristics when increasing R_{tc}:

(1) Band gap values are observed to increase (from 2.45 eV to 2.52 eV when changing R_{tc} from 1 to 10).
(2) Grain sizes become smaller (from 55.4 nm to 47.2 nm when S/Cd = 1 and 10, respectively).
(3) The optical transmission above threshold increases from 68% to 72% when R_{tc} is increased from 1 to 10.

Higher bandgap values of the window material improve the short circuit current of the solar cells. On the other hand, thin films with smaller grain sizes show fewer pinholes with a positive effect on the open circuit voltage and fill factor. In this regard, the properties of the CdS layers are correlated with the kinetic of the deposition process when the concentration of thiourea is changed. For instance, for high thiourea concentration, the reaction rate becomes large enough to promote a quick CdS precipitation which leads to the formation of agglomerates in the solution rather than nucleation on the substrate surface, while for low thiourea concentration a very slow growth process can be expected, leading to a thinner but more homogeneous layer.

Therefore, there are multiple factors influencing the improvement of the characteristics of CdS/CdTe solar cells when the S/Cd ratio in the CBD-CdS solution is increased up to 5. An optimum value for R_{tc} is expected and further investigation of the device and the CdS layers is necessary in order to better understand all the phenomena involved.

5. Conclusions

We have found that CBD-CdS thin films grown with variable thiourea concentration in the CBD solution improve the CdS/CdTe solar cells performance. The important solar cell parameters such as short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), efficiency (η), ideality factor n, J_0 and series resistance improve when the CdS layers are prepared from CdS layers with R_{tc} from 1 to 5. A relative efficiency increase of 73% is obtained for the cells when R_{tc} is changed from 1 to 5, without any other modification like the bulk resistance and thickness of the layers or the back contact formation on the p-type CdTe layer. Cells fabricated with CBD-CdS layers having $R_{tc} = 10$ show poor behaviour so that an optimum value for this parameter is between 5 and 10, and therefore a further optimization study is under way.

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