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Effects of thiourea concentration on CdS thin films grown by chemical bath deposition for CdTe solar cells

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Abstract

We study the effects of thiourea concentration on CdS thin films deposited by chemical bath deposition (CBD), submitted to post-thermal treatments of $CdCl_2$, and its effect on the characteristics of CdS/CdTe solar cells. We compare these cells with similar ones fabricated with CdS-films grown by Close Space Vapor Transport (CSVT). The CBD-CdS cells shows higher open circuit voltage (V_{oc}) and fill factor (FF), while the short circuit current remains with little change, as the ratio of S to Cd in the CBD solution goes from 1 to 5. This dependence changes when there is a variation of the CBD-CdS layer thickness. We have obtained cells with more than 12% efficiency when the CdS layers are deposited by the best CBD condition (S/Cd=5) as compared to the best cells with CdS layers prepared by CSVT that had 11% efficiencies. Other measurements such as spectral response were performed and their results were correlated to the I–V characteristics of the solar cells so that the best performances of CBD-CdS solar cells are explained in terms of the chemical composition of this layer.

Keywords: CdS/CdTe solar cells; Thiourea; Cell efficiency

1. Introduction

Among the II–VI semiconductor compounds, CdS is a representative material with many applications such as large area electronic devices and solar cells. We are particularly interested in the latter because it is a good window layer for CdTe and chalcopyrite-based solar cells. In fact, the best efficiency (16.5%) for a CdTe solar cell has been achieved [1] with a CdS window layer grown by chemical bath deposition (CBD), although CBD gives poor crystalline quality for CdS layers in comparison with other deposition techniques. As we have already shown in a previous paper [2], CBD gives the best photoconductivity and morphological properties such as roughness and pinhole density when compared to films processed by other techniques.

A good window layer must fulfill several characteristics: low carrier recombination, low resistivity, and being a good match to CdTe. It is the purpose of this work to study CdS films processed by CBD using different thiourea concentrations in the bath solution with post-thermal treatments using $CdCl_2$. These films were used to make CdS/CdTe solar cells and compare these devices with those with CdS layers grown CSVT with similar characteristics (film thickness, post thermal treatments, etc.). The results show that those devices with CdS grown by CBD are better possibly due to a higher photo-

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Table 1
Thiourea to $CdCl_2$ ratio and bath time used to process the several CBD samples

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

conductivity that causes a smaller series resistance in the cells.

2. Experimental details

For the deposition of the CdS films by chemical bath, a 150-ml beaker containing the reactants in a solution magnetically stirred was immersed in a temperature controlled (±1 °C) water bath. The concentrations of NH_3 (2.3 mol/l), NH_4Cl (2×10^{-2} mol/l) and $CdCl_2$ (2.4×10^{-3} mol/l) were kept constant in every experiment. In order to change the S to Cd ratio in the solution, the $CS(NH_2)_2$ (thiourea) concentration was varied. All the films were grown on SnO_2/F conducting glasses (10 Ω cm) at 75 °C, which is assumed as the substrate temperature. The deposition time was also varied, according to our previous knowledge of the growth kinetics [3], with the purpose of having films with similar thickness. The thiourea concentration and deposition time for each S/Cd relation are listed in Table 1.

The CdS films grown by CSVT have been already described elsewhere [4], and had similar thickness to those grown by CBD. Deposition times of 100, 120 and 140 s were used obtaining thickness of the order of 130 to 150 nm. The chamber pressure was kept at 13.33 Pa in Ar ambient, using source and substrates temperatures of 725 and 450 °C. Thermal treatment of $CdCl_2$ was provided after the deposition by CBD and CSVT during 30 min at 400 °C in air.

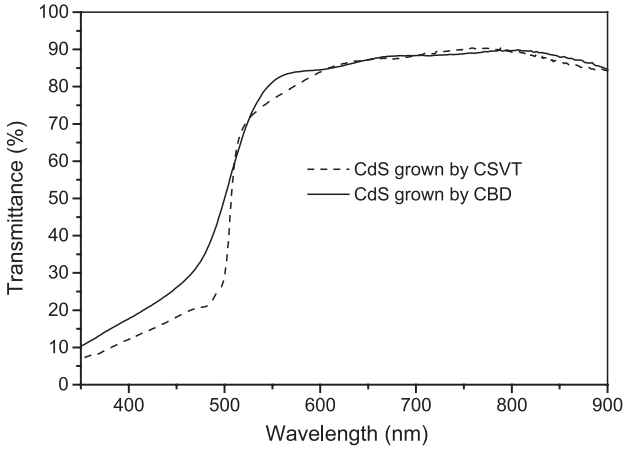

Fig. 1. Optical transmission of CBD and CSVT-CdS samples processed in this work.

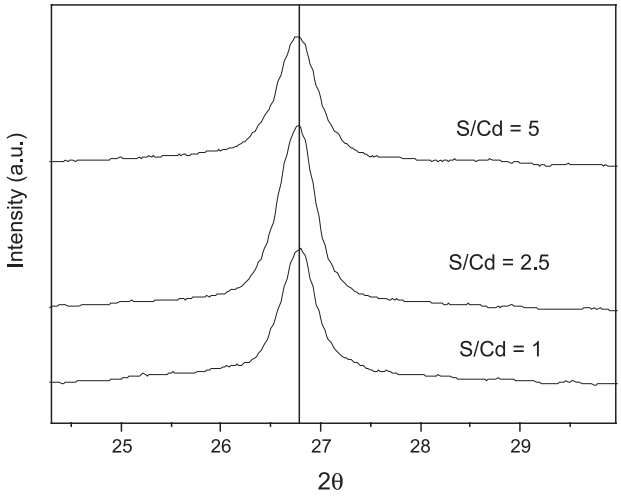

Fig. 2. X-ray diffraction spectra of the CBD-CdS film samples. They show preferential orientation in the (002) direction of the hexagonal structure.

We have not performed electrical measurements of the CdS films grown in this work by the CBD and CSVT techniques, but from our previous results [2] typical dark resistivity values are in the order of 1×10^6 and 1×10^7 Ω cm, respectively.

The solar cells for the CBD and CSVT-CdS films were made in the supersaturate configuration by depositing the CdTe thin films by CSVT on the CdS films, using 99.999% grade powders. The atmosphere used during the CdTe deposition was a mixture of Ar and O_2, with an O_2 partial pressure of 50%. Prior to all the depositions, the system was pumped to 1×10^{-9} Pa as the base pressure. The CSVT deposition of CdTe was accomplished by placing a CdTe source block in close proximity (1 mm) to the substrate. The deposition time was 3 min with substrate and source temperatures of 550 and 650 °C, respectively. Under these conditions, CdTe layers of approximately 3.5 μm were obtained. The CdTe thin films were coated with 200 nm of $CdCl_2$ and then annealed at 400 °C for 30 min in air. The metallic back contacts were Cu (2 nm) and Au (350 nm) evaporated with an area of 0.08 cm^2 onto the CdTe and annealed at 180 °C in Ar.

3. Results and discussion

3.1. Films characteristics

The optical transmission, in the visible region, for the best CdS layers grown by CBD (grown with a solution ratio

Table 2
Physical properties (optical and morphological) of the CdS film with S/Cd=5 processed by CBD and the best CdS film processed by CSVT

Film	Thickness d (nm)	Grain size (nm)	FWHM (°)	T_{av} above 500 nm (%)	BGE (eV)
CSVT	150	68.5	0.25	84.2	2.51
CBD	138	47.2	0.40	85.0	2.52

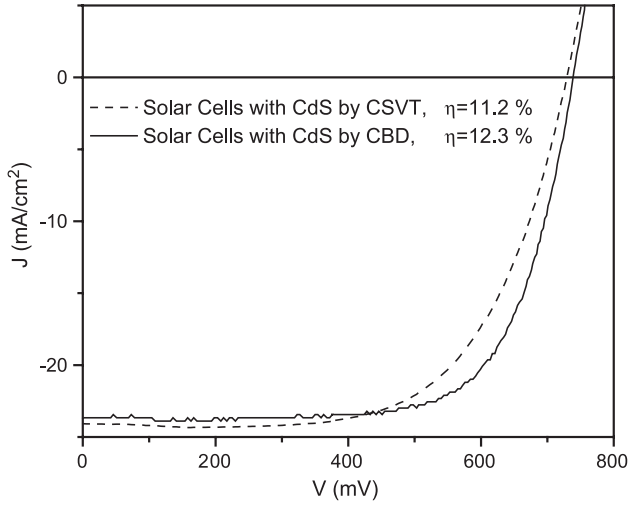

Fig. 3. I–V characteristics for the best solar cells with CBD and CSVT-CdS layers.

of S/Cd=5 and $CdCl_2$ annealing) and the best CdS layers grown by CSVT (grown for 140 s and $CdCl_2$ annealing) are shown in Fig. 1. We observe that for both samples the transmission is near 90% for wavelengths above 550 nm for films that had thickness between 138 and 150 nm. The band gap (BGE) was near 2.52 eV.

From X-ray diffraction measurements for the CBD-CdS layers as shown in Fig. 2, the lattice parameter of the sample with S/Cd=5 is larger than for the other two samples, possibly associated to a reduction of sulfur vacancies. The FHWM of the XRD peaks also increases as a consequence of smaller crystallites for this film. It has been shown in a previous paper [2] that the photoconductivity to dark conductivity ratios are higher for samples grown by CBD, in comparison with samples grown by other techniques like CSVT.

Table 2 summarizes the growth parameters, the morphological characteristics and other properties for the best CBD-CdS sample with S/Cd=5 in the solution. In addition, in this table the parameters for the best CSVT-CdS sample are shown.

3.2. Solar cells devices characteristics

The CBD-CdS and CSVT-CdS solar cell I–V performances were measured under AM1.5 (100 mW/cm^2) illumination, and the results are graphed in Fig. 3. Table 3 shows the results obtained for the set of CBD-CdS solar cells, where we can notice that the best results are obtained for the

Table 3
Comparison of solar cell performances for CBD-CdS window layer

S/Cd R_{tc}	Rs (Ω cm^2)	Rp (Ω cm^2)	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	η (%)
1/1	6.8	318	617	20.8	0.55	7.1
2.5/1	4.4	800	690	21.8	0.56	8.3
5/1	2.9	757	740	23.8	0.70	12.3

Table 4
Comparison of solar cell performances for CSVT-CdS window layer

Samples (growth time in second)	Rs (Ω cm^2)	Rp (Ω cm^2)	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	η (%)
100	3.6	350	701	24	0.56	9.4
120	5.6	813	727	23.9	0.60	10.5
140	5.7	750	714	24	0.65	11.2

S/Cd=5 with an efficiency of 12.3%. In a similar form, Table 4 shows the results obtained for the set of CSVT solar cells. In Table 4, we can observe that the best results are obtained for solar cells made with CdS grown during 140 s.

From Tables 3 and 4, we can see the results for the best devices, i.e. those made with CdS grown by CBD and CSVT, whereas Fig. 4 displays the spectral response of these devices. From these tables, we can notice that the fill factor is better for the best CBD-CdS solar cell, while J_{sc} and V_{oc} are almost the same as for the CSVT-CdS solar cell with a difference of less than 3%, which is within the possible measurement error. Notice from these I–V curves of the CBD and CSVT solar cells that the main difference comes from the fill factor of the curves, a fact that can be associated to the larger series resistance (almost the double) for CSVT solar cells as compared to CBD cells. It has been shown that sulfur enrichment in CBD-CdS layers causes a decrease of carrier trap density at the grain boundaries. Hence, the difference in the FF values may arise from the larger photoconductivity for the CBD-CdS layers. The small difference shown in Fig. 4 for the spectral response of these cells in the short wavelength range indicates a better interface between the CBD-CdS and CdTe than for CSVT and the CdTe layers in this case, although the total short circuit current density is almost the same for both kinds of solar cells.

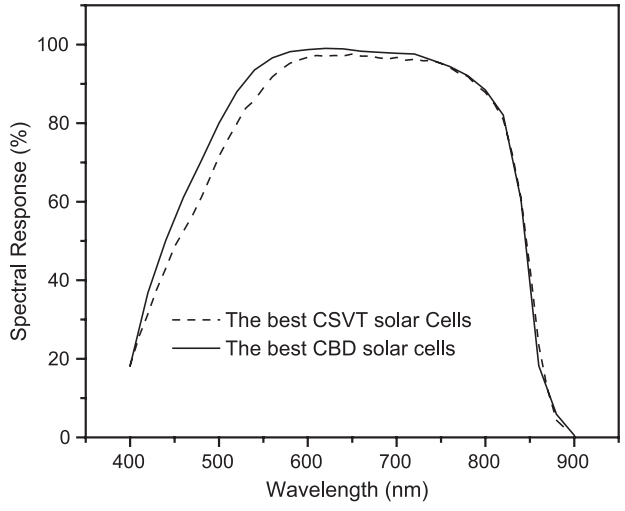

Fig. 4. Spectral response comparison for the best CBD and CSVT cells in the 400–900-nm wavelength region.

In summary, the main difference for CBD and CSVT-CdS layers for solar cells in this study is due to the higher resistivity (and smaller photoconductivity) associated to the CSVT-CdS layers. This fact gives a higher series resistance for cells done with CSVT-CdS layer than for CBD solar cells.

4. Conclusions

A set of CdS samples grown by chemical bath with different concentrations of thiourea in the solution were used as window layers for CdTe solar cells. It was found that varying the thiourea to $CdCl_2$ concentration solar cells present better performances for a larger S/Cd ratio in the CBD solution. On the other hand, we have found that the best performance as determined from the I–V curves corresponds to solar cells made with CdS window layers processed by CBD as compared to CdS grown by CSVT. This fact can be attributed to the best photoconductivity of the CdS layer. It has been observed that similar results have been obtained for the V_{oc} and J_{sc} values of solar cells with CBD and CSVT-CdS layers. The main difference for these cells is due to the higher series resistance of the latter, a difference that affects the fill factor and therefore the efficiency of the cells. Hence, it seems that CBD-CdS layers are slightly better than CSVT-CdS ones when used in solar cells, although both kind of materials can be used on CdTe for attaining high efficiency solar cells (above 11%), as shown in this paper.

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