

Photoluminescence characteristics of CdS layers deposited in a chemical bath and their correlation to CdS/CdTe solar cell performance

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Abstract

In this work, we study CdS films processed by chemical bath deposition (CBD) using different thiourea concentrations in the bath solution with post-thermal treatments using CdCl₂. We study the effects of the thiourea concentration on the photovoltaic performance of the CdS/CdTe solar cells, by the analysis of the I - V curve, for S/Cd ratios in the CBD solution from 3 to 8. In this range of S/Cd ratios the CdS/CdTe solar cells show variations of the open circuit voltage (V_{oc}), the short circuit current (J_{sc}) and the fill factor (FF). Other experimental data such as the optical transmittance and photoluminescence were obtained in order to correlate to the I - V characteristics of the solar cells. The best performance of CdS–CdTe solar cells made with CdS films obtained with a S/Cd ratio of 6 is explained in terms of the sulfur vacancies to sulfur interstitials ratio in the CBD–CdS layers.

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1. Introduction

Chemical bath deposited (CBD) CdS thin films are regularly n-type, mainly due to sulfur vacancies. The variation of the S/Cd ratio for the chemical bath solution used for the preparation of such CdS films will presumably modify the physical

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properties of the films, such as the morphology, the optical and the electrical conductivity of these films. The S/Cd ratio will also have an influence upon the structural and electrical properties of the CdTe layer itself in CdS/CdTe solar cells, in addition to the modification of the CdS–CdTe interface. The aim of this work is to investigate the influence of the variation of the S/Cd ratio in the bath solution for CdS thin films prepared by Chemical Bath Deposition upon the characteristics of CdS/CdTe solar cells in a superstrate configuration.

It must be mentioned that CdS thin films grown by CBD has produced conversion efficiencies for CdS/CdTe solar cells as high as 16.5% (Wu et al., 2001). Hence, CdS has become an important material for this kind of solar cells. We have demonstrated that CBD–CdS films have poor crystalline quality, but they give excellent results for photovoltaic applications because of their high relative photoconductivity, in addition to their better morphological properties, like the roughness and pinhole density, in comparison with CdS films as grown by other techniques (Morales-Acevedo et al., 2002). Recently, we have studied CdS/CdTe solar cells with variable S/Cd ratio in the CdS chemical bath solution and an optimum efficiency of 12.6% was obtained with S/Cd = 5 (Mendoza-Pérez et al., 2005). In this paper we do a detailed study by varying the S/Cd ratio between 3 and 8, and try to correlate the optimum ratio for solar cells with photoluminescence and optical properties of the CdS films.

2. Experimental details

The CdS thin films were prepared by CBD on a commercial conducting glass (0.5 μm thick $\text{SnO}_2\text{:F/glass}$ with 10 Ω/cm). For the chemical bath deposition of CdS, a beaker containing the reactants in a solution magnetically stirred was immersed in a temperature-controlled (± 1 $^\circ\text{C}$) water bath. The concentrations of NH_3 (2.0 mol/l), NH_4Cl (0.2 mol/l) and CdCl_2 (0.1 mol/l) were kept constant in each experiment. In order to change the S to Cd atomic ratio in the solution, the $\text{CS}(\text{NH}_2)_2$ (Thiourea) concentration was varied from 0.3 to 0.8 mol/l. The films were grown at 75 $^\circ\text{C}$ and the deposition times were also varied, accordingly to our previous knowledge of the growth kinetics, with the purpose of obtaining films with similar thickness in all cases. The solar cells were prepared by depositing CdTe thin films on $\text{SnO}_2\text{:F/CBD–CdS}$ substrates by the hot wall close spaced vapor

transport (CSVT–HW) 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 and prior to all depositions the system was pumped to 8×10^{-6} Torr as the base pressure. The 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 $^\circ\text{C}$ and 650 $^\circ\text{C}$, respectively. CdTe layers of ≈ 3.5 μm were obtained under these conditions. The CdTe thin films were coated with 200 nm of CdCl_2 and then annealed at 400 $^\circ\text{C}$ for 30 min in air. For the back contact, Cu and Au (2.0 and 350 nm, respectively) were evaporated successively onto the CdTe layer, with an area of 0.08 cm^2 , and annealed at 180 $^\circ\text{C}$ in Ar ambient.

Optical transmission data were measured with a UV/Vis Shimadzu 3101 PC double beam spectrophotometer. The layer thickness was measured using a step profiler (Sloan Dektak III). For photoluminescence (PL) measurements, an Ar^+ laser ($\lambda = 457.9$ nm, 2.71 eV) was employed as the excitation source, focused on the sample through a cylindrical lens. The outgoing radiation from the sample was focused on the entrance slit of a 1403-SPEX double monochromator. The signal detection was carried out using an RCA-C31034 photomultiplier tube coupled to a photon counter thermoelectrically cooled in order to improve the signal-to-noise ratio. The PL spectrum was taken at room temperature.

3. Results and discussion

3.1. CBD–CdS thin films properties

The optical transmission spectra of the films grown for different S/Cd ratio are displayed in Fig. 1. High optical transmission and large bandgap values of the window material (CdS films) should improve the short circuit current of the solar cells. The highest average optical transmission is observed for S/Cd = 5, while for other films with smaller or higher S/Cd ratios, the optical transmission becomes lower in average. The thickness, the bandgap and the optical transmission of layers grown with different S/Cd ratios are listed in Table 1.

Fig. 2 shows the room temperature PL spectra for films with different S/Cd ratios in the solution. It is worth mentioning that the as-grown CBD–CdS films

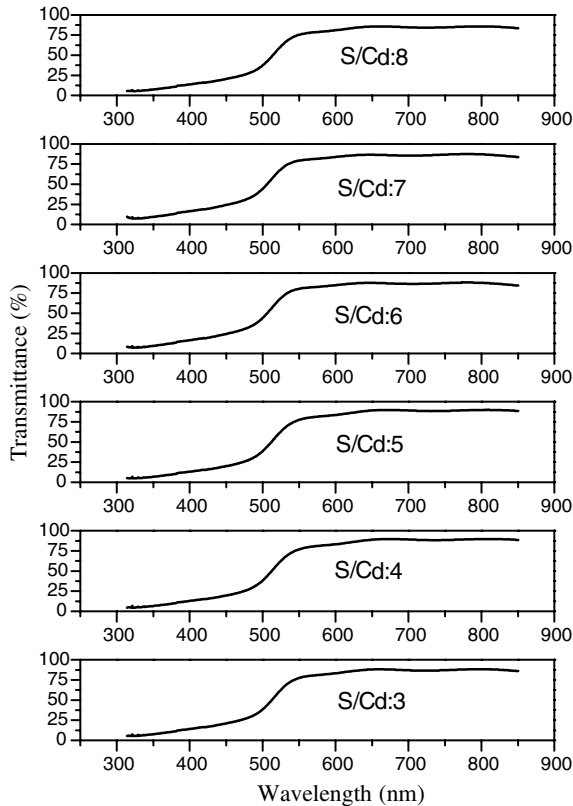


Fig. 1. Optical transmission characteristics of CBD-CdS films grown with different S/Cd ratios.

Table 1

Thickness (d), average transmission (T_{av}) and bandgap energy (E_g) of the CBD-CdS samples for different S/Cd ratios

S/Cd	3/1	4/1	5/1	6/1	7/1	8/1
d (nm)	145	140	130	110	111	109
T_{av} (%)	83	85	88	87	86	85
E_g (eV)	2.32	2.33	2.33	2.34	2.34	2.33

usually do not show any luminescence signal at room temperature possibly because of a high density of non-radiative defects with energy levels near the midgap. However, in this case, room temperature PL was detected for all the CdS samples, as can be seen in Fig. 2. All the samples showed two bands in the PL spectra, one localized at 2.30 eV and the other at 1.80 eV.

The band in the 1.60–1.85 eV range is associated to sulfur vacancies (V_S), whereas the peak around 2.3 eV is usually related to interstitial sulfur (I_S) (Mejía-García et al., 1999; Aguilar-Hernández et al., 2003). The enhanced PL signal is mainly due to sulfur enrichment, which gives rise to a

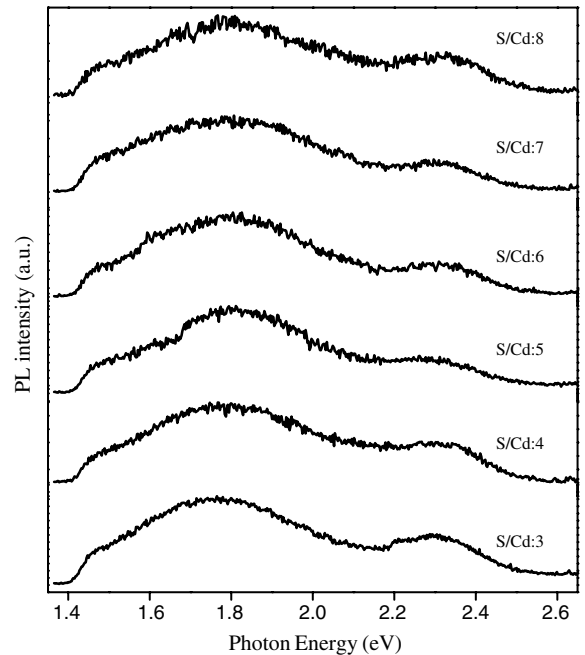


Fig. 2. Room temperature photoluminescence spectra of CBD-CdS films grown with different S/Cd ratios.

decrease of the trap density at the grain boundaries (Baccarani et al., 1978), decreasing in this way the density of non-radiative centers. In order to evaluate the effect of the sulfur enrichment we calculate the ratio of the relative intensities of V_S to I_S bands, respectively. Fig. 3, depicts the behavior as a function of the S/Cd ratio. As it can be seen, for S/Cd ratios of 3, 4 and 5 the quotient I_{V_S}/I_{I_S} increases as the S/Cd ratio increases, meaning that as more sulfur atoms are present in the bath solution more

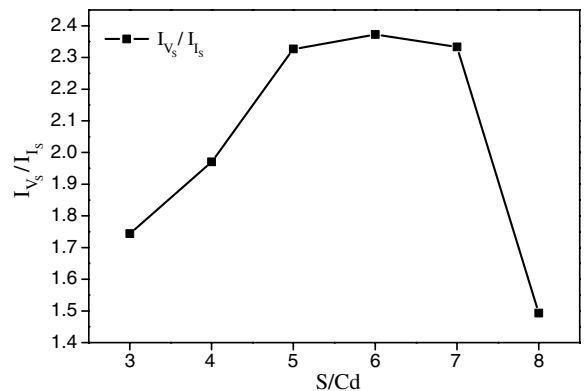


Fig. 3. Behavior of the relative sulfur vacancies (V_S) to sulfur interstitials (I_S) photoluminescence band intensities as a function of the S/Cd ratio.

sulfur vacancies are produced in relation to interstitial sulfur. For S/Cd ratios of 5, 6 and 7 an equilibrium between the introduction of sulfur atoms at interstitial sites and sulfur vacancies is achieved. For S/Cd ratios greater than 7, the sulfur atoms prefer to go into interstitial sites.

3.2. Solar cell performance

The I - V characteristics of CdS/CdTe solar cells under AM 1.5 illumination (normalized at 100 mW/cm^2) as a function of S/Cd are shown in Fig. 4. Table 2 summarizes the values of short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and efficiency (η) of the solar cells at different S/Cd R_{tc} . As it can be observed, the values of J_{sc} , V_{oc} , FF and η reach their higher values for S/Cd = 6.

From the I - V curves of the CBD-CdS based solar cells, one of the differences comes from the knee of the curves, which is partially associated to a change of the series resistance for the different samples. This feature can also be associated to a larger recombination ratio at the space-charge region

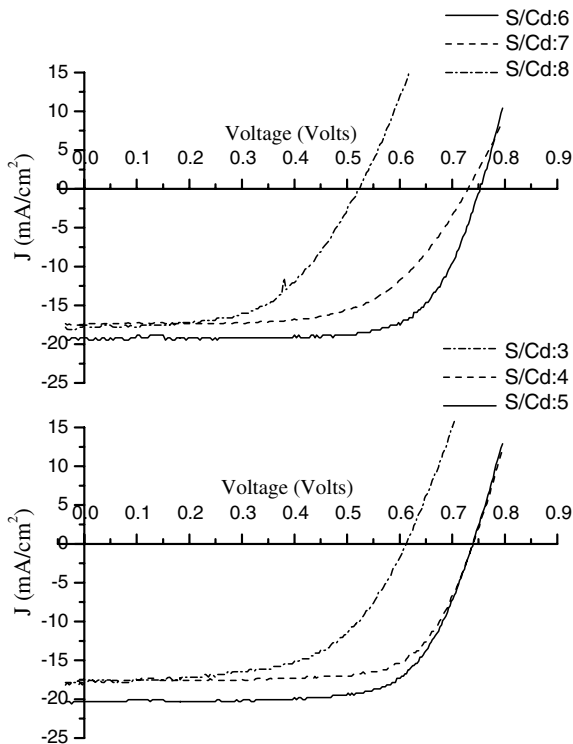


Fig. 4. J - V characteristics of the CdS/CdTe solar cells under illumination (100 mW/cm^2) as a function of the S/Cd ratio.

Table 2

Short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and efficiency (η) of the CdS/CdTe solar cells for different relative S/Cd concentrations

S/Cd	R_{tc}	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)
3/1		0.613	18.2	0.57	6.4
4/1		0.705	17.6	0.68	8.5
5/1		0.703	20.5	0.65	9.4
6/1		0.726	21.1	0.69	10.6
7/1		0.702	17.2	0.65	7.8
8/1		0.491	20.5	0.59	6.0

of the CdS/CdTe hetero-junction. It has been shown that sulfur enrichment in the CBD-CdS layers causes a decrease of carrier trap density at the grain boundaries (Baccarani et al., 1978). For samples with S/Cd ratios of 7 and 8 this enrichment could also take place, but probably at the expense of a ternary compound (CdSTe) at the CdS-CdTe interface with a larger polycrystalline disorder.

In summary, we have shown that the CBD-CdS thin films grown by varying the thiourea concentrations in the CdS bath solution cause a variation of the CdS/CdTe solar cells performance when the relative concentration of thiourea S/Cd is increased in the range from 3 to 8. We have found that the best characteristics are obtained for a S/Cd ratio of 6. This optimum value for the S/Cd ratio is related to the amount of sulfur vacancies in the films which possibly affect the amount of recombination at the CdS-CdTe hetero-junction.

4. Conclusions

We have found that CBD-CdS thin films grown under variable concentration of thiourea in the solution improve the CdS/CdTe solar cells performance when the relative concentration of S/Cd is increased from 3 to 8. The optimal conditions for CdS/CdTe solar cells performance are for CBD-CdS samples grown at 75°C with $\text{S(thio)/Cd(CdCl}_2\text{)} = 6$ in the bath solution.

We also have found that the best performance from the I - V curves corresponds to solar cells made with CdS window layers with a large sulfur vacancy band (at 1.8 eV) in the photoluminescence measurements. More sulfur vacancies seem to contribute to a decrease of the minority carrier recombination at the CdS-CdTe interface and at the grain boundaries, allowing solar cells processed with CBD-CdS emitters to have better V_{oc} , FF and efficiency.

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