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Spectral response of CdS/CdTe solar cells obtained with different S/Cd ratios for the CdS chemical bath

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Abstract

In this work, the influence of the variation of chemical bath thiourea concentration in the solution for depositing CdS layers upon the spectral response of chemical bath deposition (CBD)-CdS/CdTe solar cells is studied. Although changes in the short and long wavelength range for the spectral response of the cells were observed in dependence of the thiourea concentration, no significant changes were observed in the diffusion length of minority carriers in the CdTe layer, as determined from the constant photocurrent method, when the thiourea concentration is increased in the CdS deposition solution.

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1. Introduction

It is well known that the growth kinetics and the properties of CdTe solar cells are affected not only by the CdCl₂ treatment but also by the deposition method and the morphological features of the CdS window layers [1,2]. The efficiency of solar cells not

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only depends on the grain size of CdTe, but is influenced also by the CdS–CdTe interatomic intermixing [3,4], the series and shunt resistances, etc. Recently we have found that chemical bath deposition (CBD) of CdS thin films grown with increasing thiourea concentration in the CBD solution affects the photovoltaic performance of CdS/CdTe solar cells [5]. The important solar cell parameters such as short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and efficiency (η) improve when the CdS layers are prepared with increasing thiourea/CdCl₂ ratios (R_{tc}). Improvement in J_{sc} , V_{oc} , FF and η was observed when R_{tc} varied from 1 to 5, with a maximum value of efficiency of 12.34% [5,6], but when the cells were fabricated with CBD-CdS layers having R_{tc} values higher than 5 a drop in the above parameters was obtained. Changes in the photoconductivity properties of the layers and a possible modification of the interfacial CdS_{1-x}Te_x compound were assumed as the important mechanisms in order to explain these results. However, a full interpretation is difficult due to other phenomena present in this type of devices.

In order to see the effect that the S/Cd ratio in the CdS growth solution has on the quantum efficiency of solar cells, in this work we present a study of the spectral response of CdS/CdTe solar cells fabricated with different thiourea/CdCl₂ ratios in the CdS-CBD solution.

2. Experimental

CdS layers were deposited on conducting glass substrates (SnO₂:F) by the CBD method, from an aqueous solution containing cadmium chloride, ammonium chloride, ammonium hydroxide and thiourea (here after referred to as “thio”), which were mixed in proper proportions to obtain different nominal $c(\text{thio})/c(\text{CdCl}_2)$ ratios (R_{tc}). The concentration of thio in the bath solution was varied as listed in Table 1. The volume of the total bath solution was kept constant. The experimental set-up for the chemical bath of CdS consisted of a temperature controlled (± 1 °C) water bath, in which a 100 mL beaker containing the reactants in a solution magnetically stirred is immersed. Concentrations of NH₃ (2.3 mol/L), NH₄Cl (2×10^{-2} mol/L) and CdCl₂ (2.4×10^{-3} mol/L) are kept constant in every experiment. The films were grown at 75 °C. The deposition time was varied, according to our previous knowledge of the growth kinetics, with the purpose of obtaining films with similar thickness in all cases [7].

Solar cells were prepared by depositing CdTe thin films on SnO₂:F/CBD-CdS substrates by the CSVT-hot wall (HW) technique using CdTe powders (of 99.99% purity). The atmosphere used during the CdTe deposition was a mixture of Ar and O₂, with an O₂ partial pressure of 50%. In all cases, the total pressure was 0.1 Torr. Prior to all

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

S/Cd R_{tc}	C (thiourea) in the bath (mol/l)	Deposition 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

Table 2

Short circuit current (J_{sc}) and efficiency (η) for CdS/CdTe solar cells with different S/Cd ratio (R_{tc}) in the CdS bath

S/Cd	J_{sc} (mA/cm ²)	η (%)
1	20.8	7.1
2.5	21.8	8.3
5	23.8	12.3
10	22.7	5.4

These parameters were measured under AM1.5 illumination.

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 and 650 °C, respectively. Under these conditions, CdTe layers of approximately 2 μ m were obtained. The CdTe thin films were then coated with a 200 nm CdCl₂ 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 cm², onto the CdTe and annealed at 180 °C in Ar.

Table 2 shows the values of J_{sc} and η of the solar cells obtained with different S/Cd ratio (R_{tc}) in the CdS bath. Spectral response measurements for the solar cells were made illuminating the CdS side and detecting the signal on the copper–gold and SnO₂:F contacts. The photocurrent was measured as a function of the wavelength on each solar cell and on a calibrated Si solar cell (with known spectral response) used as a reference. The external spectral response was obtained illuminating each solar cell with a He–Ne laser and measuring the photocurrent. Calculations of the quantum external efficiency were made by measuring the calibrated power of the laser beam and the corresponding photocurrent of the solar cell. Then, an estimation of the internal quantum efficiency was obtained taking a 13% reflection loss correction in all cases [8].

3. Results and discussion

Fig. 1 shows the estimated internal quantum efficiency spectrum for the different CdTe/CdS solar cells as a function of the R_{tc} ratio. The short wavelength cutoff of the spectral response is defined by the absorption edge of CdS, while the long-wavelength edge is limited by the collection of photocurrent from the CdTe layer (including CdTe_{1-x}S_x).

Notice that the behavior in the short and long wavelength regions depends on the R_{tc} values. A shift of the quantum efficiency to smaller wavelengths in the short wavelength range of the spectral response is observed, reaching its maximum for $R_{tc} = 5$. This shift is in correspondence with their respective transmission spectrum, shown in the inset. Notice also that in the long wavelength region there is no significant modification of the quantum efficiency. This behavior could be explained by a reduced optical absorption of the CdS layers formed with larger R_{tc} ratios up to $R_{tc} = 5$, as shown in the inset of Fig. 1. Also, sulfur diffusion into CdTe, causing the formation of a CdTe_{1-x}S_x ternary alloy, which exhibits a larger band gap than pure CdTe could help improve the short wavelength spectral response when the R_{tc} ratio in the CdS bath solution is changed.

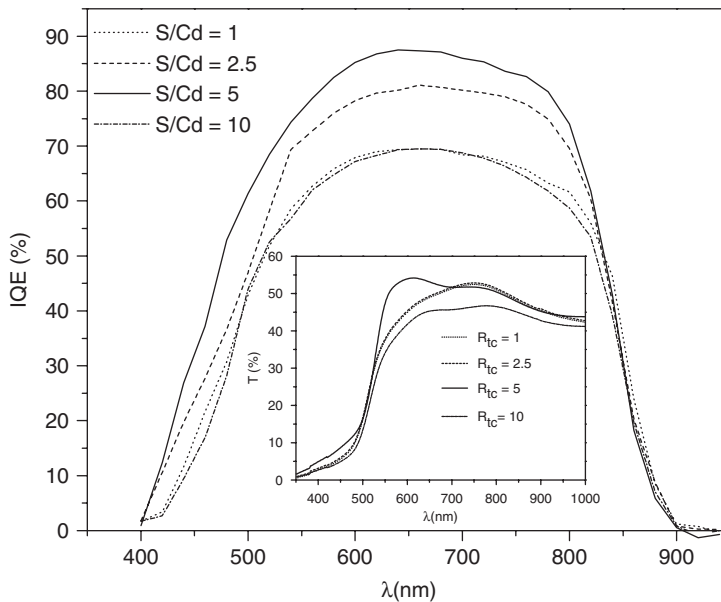


Fig. 1. Internal quantum efficiencies for CdS/CdTe solar cells with different R_{tc} ratios in the CBD-CdS deposition solutions.

On the other hand, photoluminescence measurements (not shown here) indicate that for R_{tc} values lower than 5, the sulfur goes into the CdS grain boundaries, while for R_{tc} values higher than 5, the amount of interstitial sulfur decreases due probably to the precipitation of sulfur in the solution. Therefore, R_{tc} near 5 is the optimal S/Cd concentration ratio in the CdS-CBD solution.

The diffusion length was determined using the steady-state short circuit or constant photocurrent method (CPM). This method is based on measuring the short-circuit current of a cell as a function of the wavelength of the incident light. In the range of wavelengths where the absorption coefficient is small such that the corresponding absorption length of the absorbed photons is within the CdTe layer, away from both the junction space charge region and from the back contact surface, the short circuit current contribution from the CdTe layer can be approximated [9] by

$$J_{ph} \sim q(1 - R)\Phi [L_n / (L_n + 1/\alpha)], \quad (1)$$

where R is the reflectance of the cell, α is the absorption coefficient and L_n is the electron diffusion length. In the CPM technique, the current is held constant by adjusting the photon flux density Φ as the wavelength is changed. The above equation then becomes

$$\Phi = C(L_n + 1/\alpha), \quad (2)$$

where C is a constant, and the electron diffusion length L_n is the intercept on the negative $1/\alpha$ axis when Φ is plotted against $1/\alpha$.

In order to evaluate the electron diffusion length, the CdTe absorption coefficient as a function of the wavelength must be known. Fig. 2 displays the spectral dependence

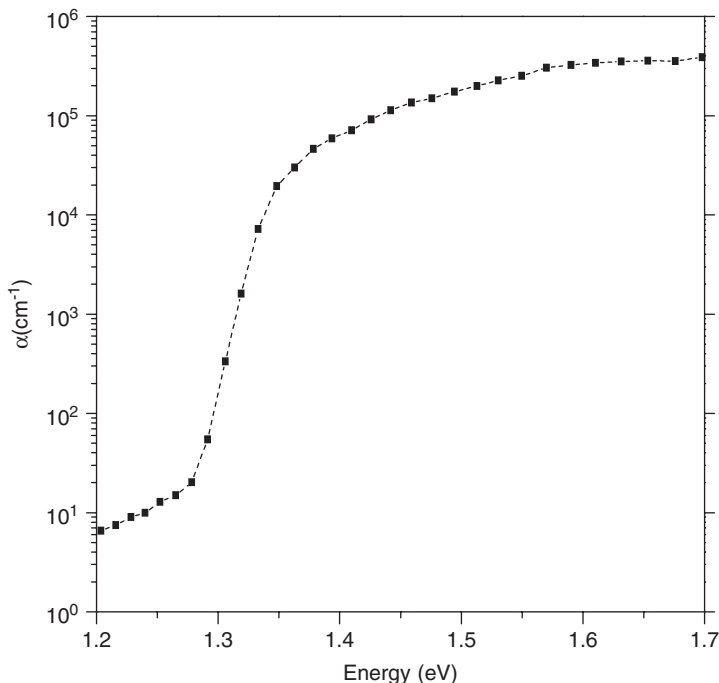


Fig. 2. Spectral dependence of the absorption coefficient in CdTe determined from photoacoustic spectroscopy measurements.

of the absorption coefficient α determined from photoacoustic spectroscopy measurements for our CdTe films. For the application of the CPM method, the measurements were made in the 740–940 nm range for two constant values of the photocurrent measurements, in each solar cell. In this range, the absorption coefficient can be fitted to the expression

$$\alpha(\lambda)(\text{cm}^{-1}) = -5.79945 \times 10^6 + 23217.3649\lambda (\text{nm}) - 29.92841\lambda (\text{nm})^2 + 0.01257\lambda (\text{nm})^3. \quad (3)$$

Fig. 3 shows the plots of photon flux density vs. α^{-1} for $R_{\text{tc}} = 5$. A value of L_n of 0.49 μm was obtained independent of the I_{ph} value selected. Following the same procedure, the L_n values for the different solar cells were determined. Table 3 shows the values of L_n for the set of cells with different R_{tc} ratios. Taking into account the possible error for the determination of L_n we may conclude that the diffusion length is nearly constant and independent of R_{tc} . This result is expected since the CdTe layer should not be greatly modified in its properties except at the interface due to the variation of the CdS bath deposition conditions. In addition, due to the fact that surface recombination has an effect on carrier collection, the diffusion length measured is in fact an effective diffusion length. Therefore, for our CSVT CdTe layers, the effective diffusion length as given by the average of the values on Table 3 is $L_n = 0.52 \mu\text{m}$.

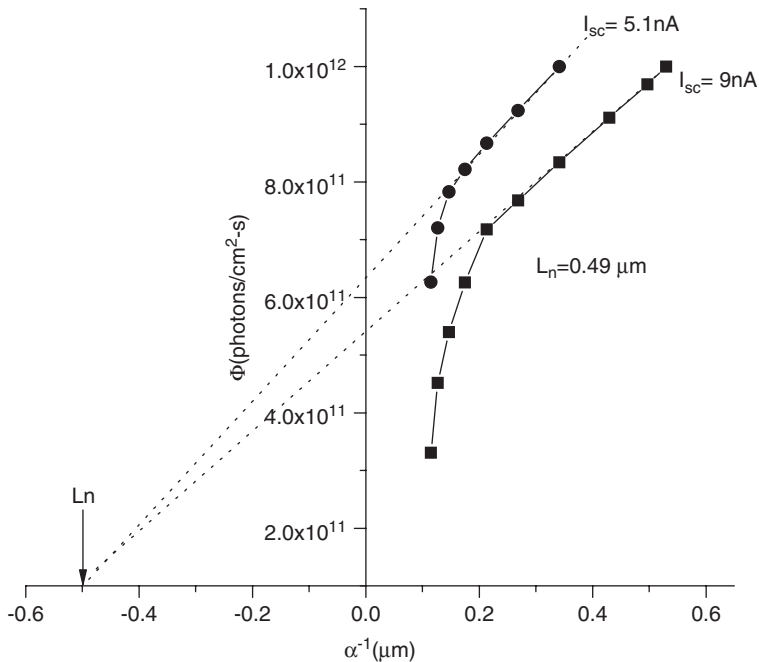


Fig. 3. Photon flux density versus α^{-1} for CdS/CdTe solar cells with $R_{tc} = 5$.

Table 3

Values of L_n obtained by the CPM method for different S/Cd ratios

S/Cd	L_n (μm)
1	0.61 ± 0.05
2.5	0.52 ± 0.05
5	0.49 ± 0.05
10	0.46 ± 0.05

4. Conclusions

In order to see if there is any effect due to the variation of the thiourea concentration in the CBD solution for depositing the CdS film on the spectral response of CdS/CdTe solar cells, we have studied this characteristic for solar cells where the S/Cd ratio in the CdS bath solution was changed. The spectral response is modified significantly only in the short wavelength range, associated to the CdS–CdTe interface. Solar cells fabricated with CBD-CdS layers having $R_{tc} = 5$ show optimum values both for the I - V characteristics under illumination and also for the spectral response. This spectral response variation shows that the CdS deposition bath solution affects mostly the characteristics of the interface between CdS and CdTe as well as the absorption coefficient of the CdS layer, but it does not modify the bulk properties of the CdTe layer in the solar cell. With these considerations, an electron effective diffusion length could be approximately measured by the constant

photocurrent method (CPM) technique, obtaining an average value around $L_n = 0.52 \mu\text{m}$ for the CdTe layers grown by CSVT.

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