

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

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Available online 2 December 2004

Abstract

We study the effects of thiourea concentration on CdS thin films deposited by chemical bath deposition (CBD), submitted to post-thermal treatments of CdCl₂, 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.

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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 CdCl₂. 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 ($\pm 1^\circ\text{C}$) 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 $\text{CS}(\text{NH}_2)_2$ (thiourea) concentration was varied. All the films were grown on SnO_2/F conducting glasses ($10\ \Omega\ \text{cm}$) 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.

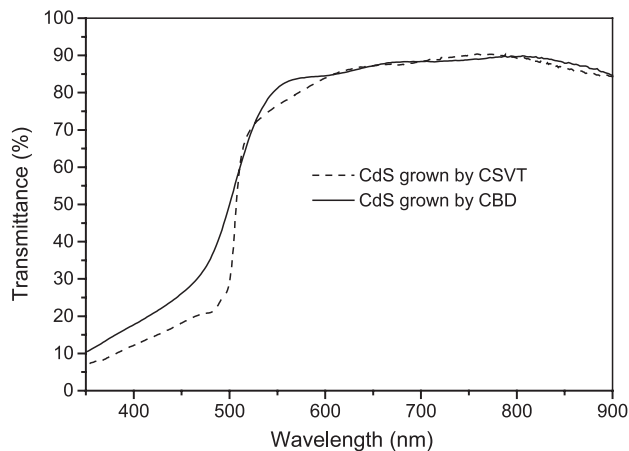


Fig. 1. Optical transmission of CBD and CSVT-CdS samples processed in this work.

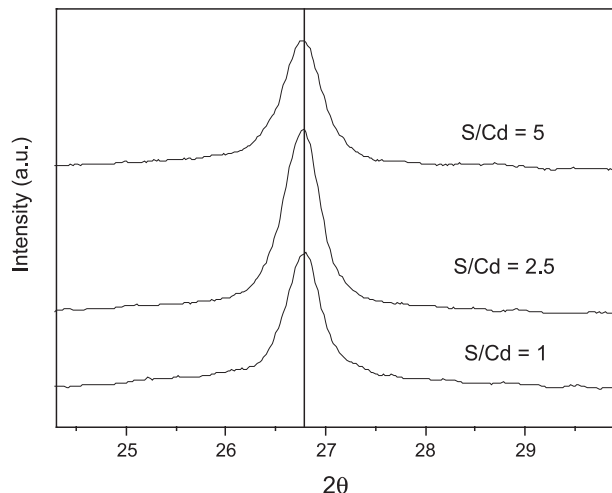


Fig. 2. X-ray diffraction spectra of the CBD-CdS film samples. They show preferential orientation in the (002) direction of the hexagonal structure.

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 $1 \times 10^7\ \Omega\ \text{cm}$, 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 $3.5\ \mu\text{m}$ 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 $0.08\ \text{cm}^2$ 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 ($^\circ$)	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

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