

STRUCTURAL AND CHEMICAL STUDIES ON CdTe/CdS THIN FILM SOLAR CELLS WITH ANALYTICAL TRANSMISSION ELECTRON MICROSCOPY

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ABSTRACT: CdTe/CdS thin film solar cells have been grown by closed space sublimation and high vacuum evaporation at different temperatures. After the growth, a standard CdCl₂ treatment was applied for 30 min at 430°C. The microstructure of the cells was studied by cross-sectional transmission electron microscopy. A recrystallization after the CdCl₂ treatment was observed not only for CdTe but also for CdS. For all cells, diffusion of S into CdTe and Te in CdS were studied. The presence and distribution of Cl at the interface and at grain boundaries was also investigated. The lattice parameter as an indicator for a compositional change in the CdTe absorber layer after the CdCl₂ treatment was determined from convergent beam electron diffraction. The results were cross-checked with X-ray diffraction and compared with results obtained for a Cd₅₀S₅Te₄₅ polycrystal. The chemical composition at the interface of the cells was studied directly with energy dispersive X-ray spectroscopy mapping. The diffusion of S is found to depend on the extent of CdCl₂ treatment. While a diffusion of Te at the interface was not observed, segregation of Cl and Te at the CdTe/CdS interface was clearly revealed. Based on these results, a formation of a Te-Cl compound is proposed to explain the catalytic role of Cl for the CdTe/CdS recrystallization.

Keywords: CdTe - 1: Diffusion - 2: Electron Microscopy-3

1. INTRODUCTION

Treatments with CdCl₂ during annealing of CdTe/CdS solar cells after deposition and their effects on the structure and composition of the cells have been the subject of various studies (an overview has been given by Durose et al. [1]). Yet, no conclusive picture of the role of Cl or of the extent to which S and Te interdiffuse has been obtained. In the following, the authors present some new results on the diffusion of S and the role of Cl and propose, based on these measurements and the phase diagrams for CdTe, CdS and CdCl₂, a mechanism for the recrystallization of CdTe, which involves the formation of a liquid Te-Cl phase during annealing.

2. EXPERIMENTAL DETAILS

CdS layers approximately 700 nm thick were grown at a substrate temperature of 150°C by use of high vacuum evaporation (HVE) onto SnO_x:F coated soda lime glass substrates. A 4 μm thick layer of CdTe was deposited by means of HVE at a substrate temperature of 150 or 300°C. For the CdCl₂ treatment, vacuum evaporated layers of different thicknesses were deposited on the CdTe layer. The thick-

ness of the CdCl₂ layer was measured with a quartz crystal thickness monitor. The stacks were then annealed in air at 430°C for 30 min. The cells exhibit an efficiency of 12.4 % with a short circuit current density of 23 mA/cm² and an open circuit voltage of 800 mV. For transmission electron microscopy (TEM) studies, cross sectional samples were prepared by mechanical cutting and polishing, dimple grinding and ion milling. The TEM studies were performed on a Philips CM30 electron microscope equipped with an energy dispersive X-ray spectroscopy (EDS) detector, and on a Tecnai F30 electron microscope equipped with a Gatan Image Filter. For comparison with the results obtained on the cells, a Cd₅₀S₅Te₄₅ polycrystal was prepared from CdS and CdTe. The two compounds were powdered and sealed in a quartz tube to avoid any loss by evaporation. The quartz tube was placed in a furnace at 1150°C. The homogeneity and composition were verified with analytical TEM.

3. RESULTS AND DISCUSSION

Fig.1 shows a comparison of the CdTe/CdS interface before and after a CdCl₂ treatment and the recrystallization of both the CdTe and the CdS layers. Especially the recrystallization of CdS suggests that

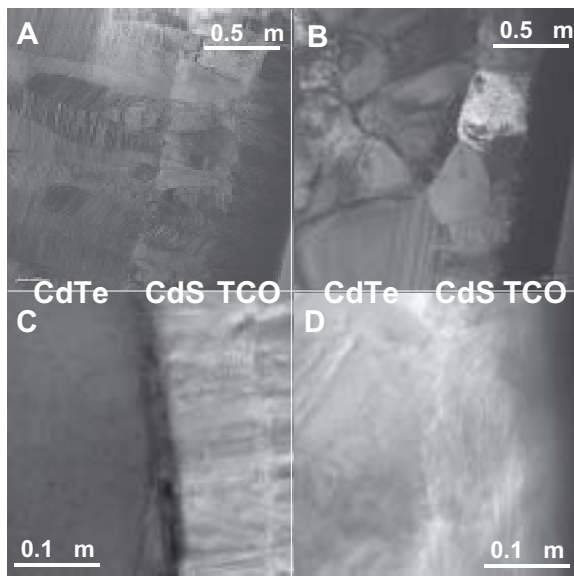


Figure 1: Micrographs of the CdTe/CdS interface region before and after the CdCl₂ treatment for HVE- (A and B) and closed space sublimation (CSS)-deposited (C and D) cells. A recrystallization and an increase in grain size not only in the CdTe layer but also in the CdS layer can be observed for both processes.

an extra CdCl₂ treatment of the CdS layer directly after its deposition is not required. A comparison with samples grown on a CdS layer pre-treated with CdCl₂ show no structural or electrical difference. For HVE-grown layers, a columnar grain growth in the CdTe and CdS layers and preferred [111] orientation of the CdTe layer, together with a high density of lattice defects (e.g. twins) are observed in the as-deposited condition. The recrystallization induced by treatment with CdCl₂ leads to increased grain size and random orientation in both the CdTe and CdS layers, and to a reduction in defect density. For CSS grown cells, the CdS layer exhibits a columnar structure with an increase in grain size after CdCl₂ treatment. In contrast to the HVE cells, the CdTe layer experiences no increase in grain size after annealing. Already as-deposited CdTe layers consist of large, rather defect-free grains.

3.1 CBED measurements

The incorporation of S into the CdTe absorber layer leads to a decrease in the lattice parameter of CdTe [2]. A decrease from the nominal lattice parameter of CdTe of 0.6481 nm with increasing S content has been observed with X-ray diffraction. To the authors' knowledge, all measurements of the lattice parameter to determine the extent of S diffusion have been performed with X-ray diffraction (XRD), suffering from the disadvantage of averaging over both the CdS and CdTe layers without giving any spatial reso-

lution at the interface. In the present work, convergent-beam electron diffraction (CBED) offers the advantage of being very sensitive to changes in lattice parameter as small as $\Delta a/a=10^{-3}$ in combination with high spatial resolution, defined by the spot size of the electron beam, which may be as low as a few nanometers. For a complete description of CBED see e.g. Ref. [3]. CBED patterns were dynamically simulated for various lattice parameters. From the simulation a linear dependence between the distance between the HOLZ lines marked in Fig. 2 and the lattice parameter was derived and compared with the recorded CBED patterns.

The results in Fig. 2 show a strong dependence of the lattice parameter of CdTe on the distance from the interface. The lattice parameters obtained for positions less than 0.5 μm away from the interface and more than 1 μm away from the interface (in Fig. 2 denoted as interface and bulk) were averaged separately and are shown together with the results for the Cd₅₀S₅Te₄₅ polycrystal. The lattice parameter of the latter has been determined from XRD and CBED. Both methods consistently yield a lattice parameter of 641 pm. Although the results obtained from the CBED measurements suffer from an inaccuracy inherent for CBED of these materials, they indicate a decrease in lattice parameter near the interface that suggests S diffusion to a depth of about 1.5 μm into the CdTe layer, leading to a S concentration of less than 5 at.% S.

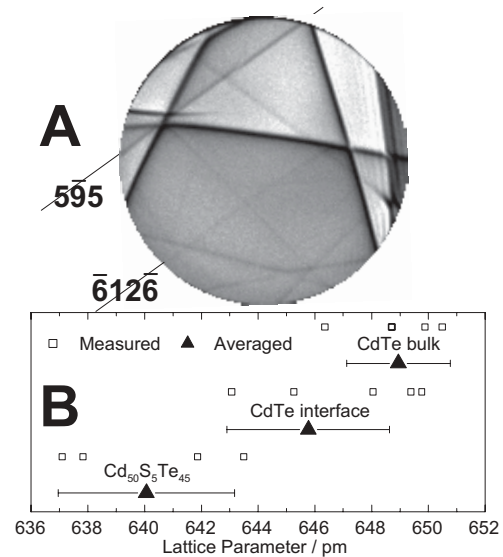


Figure 2: A) CBED pattern ([135] pole) obtained at 300 kV from the CdTe absorber layer. The HOLZ lines used to determine the lattice parameter are indicated. B) Lattice parameter at different distances from the interface, determined from CBED for a sample treated with a CdCl₂ layer of 4000 Å thickness. The lattice parameter for the Cd₅₀S₅Te₄₅ sample is shown for comparison.

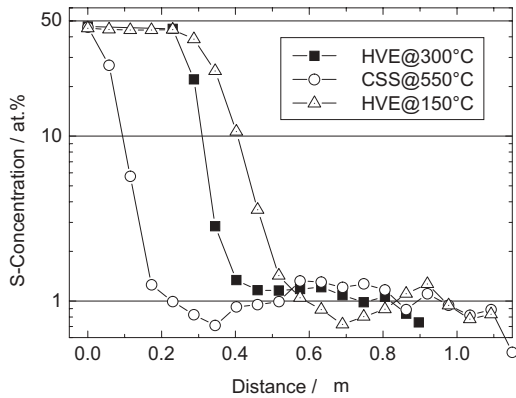


Figure 3: Concentration of S across the CdTe/CdS interface of as-deposited samples for various growth processes. The orientation of the interface is random. Hence the abscissa indicates the relative distance from the interface into the CdS (left) or CdTe (right) layer. None of the samples shows any significant diffusion of S into the CdTe layer. For better visibility, the locations of the interfaces are shifted relative to each other.

The chemical composition of all samples across the interface has been studied with EDS mapping, to corroborate the results from CBED measurements. Special care was taken to align the interface parallel to the electron beam. Thickness effects were eliminated by taking ratios of signals rather than their absolute values. For clarity, the composition across the interface is presented as a linescan taken perpendicular to the interface and averaged over a lateral width of 100 nm. All intensities measured were calibrated to concentrations using the $\text{Cd}_{50}\text{S}_5\text{Te}_{45}$ polycrystal. Concentrations of less than 1 at.% S are below the sensitivity of the method. Fig. 3 shows a comparison of the amount of S present in the untreated CdTe layer, deposited by CSS and HVE. For all samples, the S concentration is well below 1.5 at.%, at and beyond the interface. Neither the growth process nor the temperature of deposition had any influence on the diffusion of S. For all samples, CdCl_2 treatments of varying extent were applied and again, the S concentrations were measured.

Fig.4 shows results for a cell grown with HVE at 300°C. With increasing amounts of CdCl_2 applied during the annealing, a concentration profile of S develops into the CdTe absorber layer. Content of S up to 6 at.% at the interface and less than 1.5 at.% about 1.5 μm away from the interface were observed. Fig.5 shows that the S diffusion does not require any Te diffusion into the CdS layer. Te diffusion was not observed for any of the growth processes or CdCl_2 treatments. A lower solubility for Te in CdS compared with

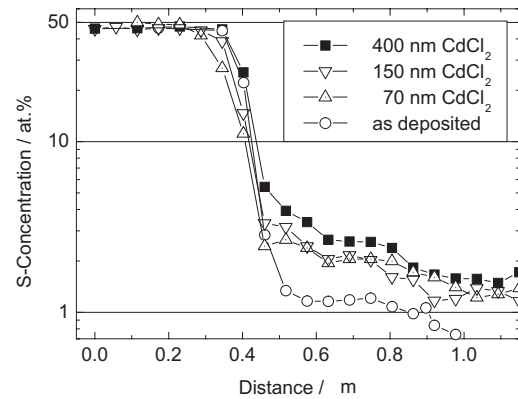


Figure 4: Dependence of the S concentration across the CdTe/CdS interface for a HVE ($T=300^\circ\text{C}$) grown layer. The stacks were treated with CdCl_2 layers of different thickness. The S diffusion increases with increasing amount of CdCl_2 . For better comparability, the CdTe/CdS interfaces are placed at the same position.

S in CdTe is a possible explanation [4]. Based on these observations, the S diffusion may be described assuming a constant source surface model. The phase diagram of CdS-CdTe [4] does not predict a content of S of more than 6.5 at.% for a $\text{CdS}_x\text{Te}_{1-x}$ layer without phase separation. This is in accordance with the present observations and the model applied for the S diffusion that requires a maximum solubility of S in CdTe of roughly 7 at.% to account for the concentration profile observed. A segregation of S along the

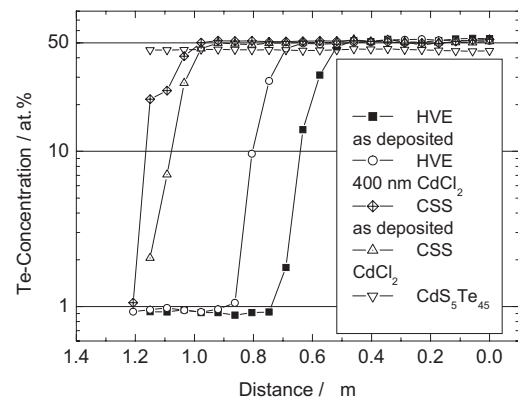


Figure 5: Diffusion of Te for various samples. As in Fig. 3, the positions of the interfaces are shifted. Both the growth process as well as the thickness of the CdCl_2 layer were varied. Yet no Te diffusion above the detection limit is observable for any of the cells.

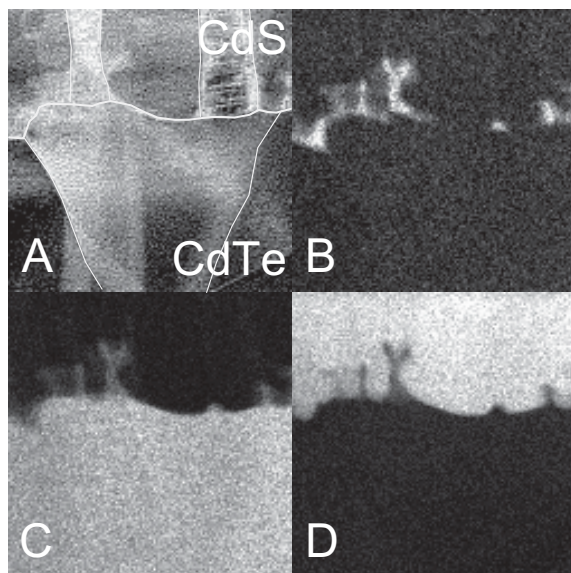


Figure 6: EDS maps of the CdTe/CdS interface for a cell treated with 4000 Å of CdCl₂. A) Greyscale image with highlighted grain boundaries B) Cl map C) Te map D) S map. The maps represent an area of 1.47 by 1.47 μm². Note that both in the CdTe and in the CdS layers only Cl segregation leads to a change in chemical composition at the grain boundaries.

CdTe grain boundaries is often expected or postulated for grain boundary enhanced diffusion. However, with micro probe EDS mapping no enrichment of S along the grain boundaries in the CdTe layer was found. If the cells are treated with an excess amount of CdCl₂, in the present case more than 1500 Å, Cl starts to segregate along the CdTe/CdS interface with a bias towards the CdS layer. Fig. 6 shows that this segregation coincides with a reduced S and an increased Te concentration. The phase diagrams of CdTe-CdCl₂ and CdS-CdCl₂ [5, 6] do not show any solubility of Cl exceeding 10¹⁸ cm⁻³ in CdTe or CdS at the temperatures studied [7]. Hence the appearance of Cl at the interface can not be explained by regular diffusion processes. The results suggest instead the formation of a Te-Cl phase [8]. As any of these phases will be liquid at 430°C, this could explain the importance of CdCl₂ for the recrystallization of the CdTe layer as well as the observation of Cl at the interface. No assumption of exceptionally large diffusion constants would be necessary. The X-ray diffraction results obtained from the region of Cl segregation are presently being evaluated and should help to identify the Te-Cl compound involved in the process (Te₃Cl₂ or TeCl₄).

4. CONCLUSION

At the CdTe/CdS interface, S is shown to diffuse

into CdTe under the influence of a CdCl₂ treatment. The extent of diffusion increases with the amount of CdCl₂ deposited, but owing to the limited solubility of S in CdTe, does not exceed 7 at.% and saturates for CdCl₂ layers of more than 1500 Å thickness. No diffusion of Te into CdS is observed. After the CdCl₂ treatment, a segregation of Cl and Te at the CdTe/CdS interface is found. This suggests that a Te-Cl phase forms at the early stage of the annealing. This phase could explain the role of Cl as a flux agent during the CdCl₂ treatment.

5. ACKNOWLEDGEMENTS

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