

## DIFFUSION IN CDS/CDTE THIN-FILM COUPLES

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**Abstract:** An analysis is presented of CdS diffusion into CdTe films that occurs during thermal and chemical post-deposition treatments used to fabricate CdS/CdTe thin-film solar cells. Cylindrical CdTe grains were used to model bulk and grain boundary diffusion assuming a constant diffusant source, reflecting back surface, and isolated grain boundaries. Using measured grain size distributions and grain boundary width, 3-dimensional CdTe<sub>1-x</sub>S<sub>x</sub> alloy distributions were calculated and used to generate x-ray diffraction line profiles. The modeled profiles were regressed with measured profiles, using the bulk and grain boundary diffusion coefficients as the only fitting parameters. For the CdCl<sub>2</sub>:O<sub>2</sub>:Ar treatment ambient typically used to fabricate high performance solar cells, the bulk and grain boundary diffusion coefficients were  $D_B = 2.4 \times 10^7 e^{-(2.8/kT)}$  and  $D_{GB} = 3.4 \times 10^6 e^{-(2.0/kT)}$ , respectively. The model is used to generate the spatial distribution of the CdTe<sub>1-x</sub>S<sub>x</sub> alloy in individual grains and throughout the film which can provide a basis for a more complete device model.

Keywords: CdTe – 1: Thin Film – 2: Diffusion – 3

### 1. INTRODUCTION

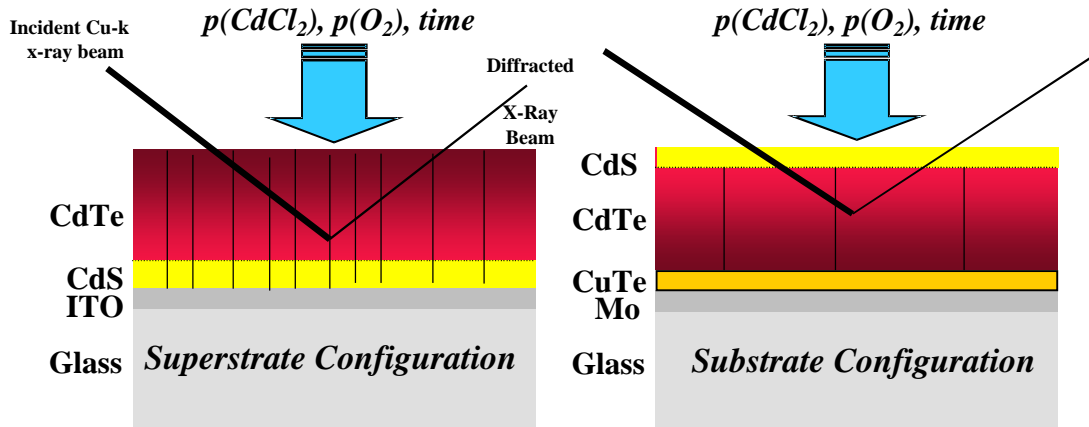
Processes used to fabricate high efficiency CdTe-based solar cells typically include a high temperature ( $T > 500^\circ\text{C}$ ) step, either during or after CdTe growth, followed by exposure of the CdS/CdTe films to cadmium chloride and oxygen at  $350^\circ\text{C}$  to  $450^\circ\text{C}$ <sup>1,2,3</sup>. This treatment promotes recrystallization, grain growth, diffusion between the CdS and CdTe layers, enhances p-type conductivity in the CdTe layer, and passivates defects<sup>4,5</sup>. Quantifying the interaction between CdS and CdTe layers that occurs during processing of superstrate configuration solar cells is critical for understanding the relationship between processing conditions and device operation, particularly in the high absorption and junction regions. The compositional distribution of sulfur and tellurium on each side of the interface depends on the chemical equilibrium at the processing temperature, the treatment time, and on the grain size distribution and crystallographic defect density of the films. In prior work, it was shown that treatment with CdCl<sub>2</sub>:O<sub>2</sub>:Ar does not change the thermodynamic miscibility limits in the CdS-CdTe system, but enhances the kinetic processes governing alloy formation<sup>6</sup>. Treatment of the CdS layer prior to CdTe deposition increases CdS grain size and limits diffusion of CdTe into the CdS film, limiting the present discussion to unidirectional diffusion<sup>7</sup>. In high efficiency cells where ultra-thin CdS is required for high photocurrent, diffusion of CdS into CdTe has a critical influence on final CdS thickness and uniformity. This paper quantitatively addresses diffusion of CdS into CdTe, resulting in 3-dimensional compositional distribution and sensitivity to treatment temperature and chemical ambient composition.

### 2. DIFFUSION MODEL

A cylindrical representation of CdTe grains was adopted to model bulk and grain boundary diffusion of CdS into CdTe films. The analytical solution developed by Gilmer and Farrell for polycrystalline films was employed using a constant diffusant source, reflecting back surface, and isolated grain boundaries<sup>8</sup>. Using measured grain size distributions and grain boundary width, 3-dimensional CdTe<sub>1-x</sub>S<sub>x</sub> alloy distributions were determined for individual grain sizes and integrated to generate x-ray diffraction line profiles. The modeled x-ray diffraction line profiles were regressed with measured profiles, using the bulk and grain boundary diffusion coefficients as the only fitting parameters. The diffusion coefficients were determined at fixed temperatures for times ranging from 10 to 40 minutes. The bulk and grain boundary diffusion coefficients determined for each treatment time were within 20% indicating the uniqueness and validity of the method. Details of the model will be presented in a forthcoming paper.<sup>9</sup>

### 3. EXPERIMENTAL

Superstrate and substrate CdS/CdTe couple configurations were examined (Figure 1). For the superstrate configuration, which is that used for high efficiency devices, 1.5 - 2.0  $\mu\text{m}$  CdTe films were deposited at  $250^\circ\text{C}$  to  $340^\circ\text{C}$  and 3.0 nm/s onto CdS/ITO/7059 superstrates. For the substrate configuration, CdTe films were deposited onto a CuTe film on Mo/7059 substrates, which result in large grain as-deposited films. In all cases, 200 nm thick CdS films were evaporated at  $220^\circ\text{C}$  at 0.3 nm/s.



**Figure 1.** Schematic diagrams of superstrate and substrate CdS/CdTe couples.

Reactive treatments were carried out in CdCl<sub>2</sub>:O<sub>2</sub>:Ar vapor at temperatures from 375°C to 450°C at different partial pressures of the CdCl<sub>2</sub> and O<sub>2</sub> species<sup>10</sup>. Multiple treatment times were employed for each treatment condition to ensure uniqueness in determination of bulk and grain boundary diffusion coefficients. In some cases, a high temperature anneal was used to obtain large grains in superstrate samples. For this, the samples were treated in argon at 1 atmosphere at 580°C for 15 minutes following CdTe deposition.

Atomic force microscopy (AFM) and scanning electron microscopy (SEM) were used to determine grain size distributions, based on shape averaging of the surface grain morphology. Transmission electron microscopy (TEM) has shown that, for the most part, the surface grain size extends to the interface; in as-deposited superstrate films, this is due to heteroepitaxial growth condition<sup>2</sup>. After treatment, the grain boundaries remain perpendicular to the interface and exhibit widths on the order of 2 nm.

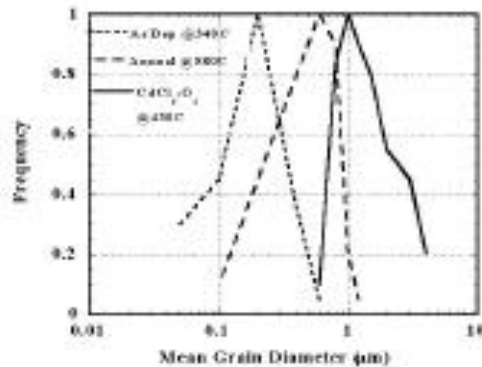
X-ray diffraction analysis was carried out for the (511)/(333) reflection using Bragg-Brentano parafocusing diffractometer with Cu-k radiation. This reflection was selected because it is an order of the (111) texture exhibited by the films and is at high enough angle to yield good instrumental resolution and low asymmetry.

#### 4. RESULTS

##### Grain Size Distribution

CdTe deposition temperature and CdS film grain size affect the as-deposited CdTe grain size distribution, and post-deposition heat treatment can dramatically change the distribution. Figure 2 shows the measured grain size distribution function for superstrate films after: deposition at 340°C; annealing at 580°C for 15 minutes in argon; and

after treatment in CdCl<sub>2</sub>:O<sub>2</sub>:Ar vapor at 430°C for 20 minutes. As-deposited CdTe grains in superstrate films have a high thickness to lateral aspect ratio and coalesce upon post-deposition treatment. In modeling time-progressive treatments of superstrate structures, it was therefore necessary to obtain the grain size distribution corresponding to each treatment time and temperature. In contrast, substrate device structure yielded CdTe grains with low lateral to thickness aspect ratio that did not change during subsequent treatments.

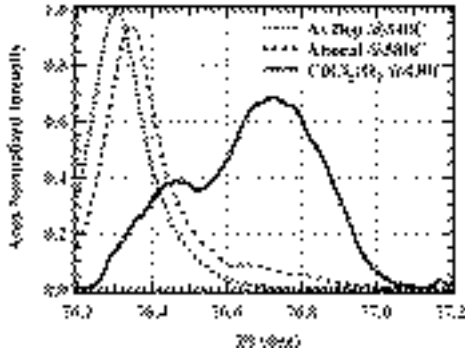


**Figure 2.** Grain size distributions: after deposition at 340°C; after annealing at 580°C for 15 minutes; after treatment in CdCl<sub>2</sub>:O<sub>2</sub>:Ar vapor at 430°C for 20 minutes.

##### X-ray Diffraction Line Profile

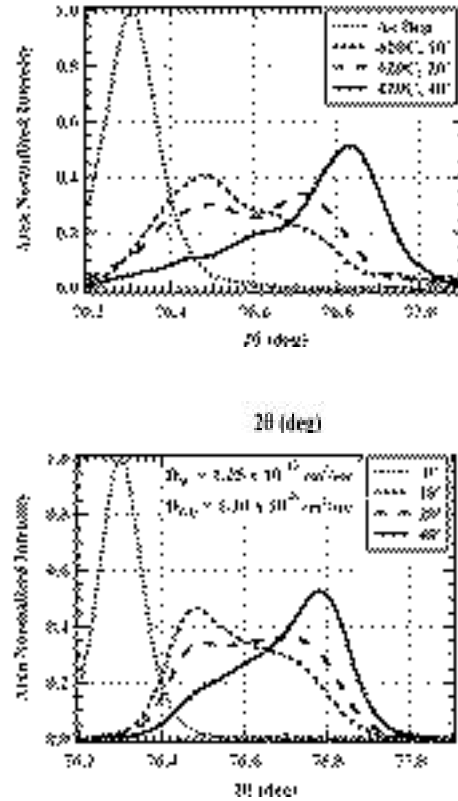
Figure 3 shows the (511)/(333) line profile for the superstrate structures of Figure 2 after: deposition at 340°C; annealing at 580°C for 15 minutes in argon; and treatment in CdCl<sub>2</sub>:O<sub>2</sub>:Ar vapor at 430°C for 20 minutes. The as-deposited reflection exhibits a slightly higher lattice parameter than that of pure CdTe, due to strain arising from

the CdS-CdTe lattice mismatch. Annealing at 580°C with no CdCl<sub>2</sub> relaxes this strain and produces a small quantity of CdTe<sub>1-x</sub>S<sub>x</sub> alloy, as seen in the high-angle tail of the line profile, corresponding to an equivalent CdS film thickness >10 nm. On the other hand, treating the as-deposited film in CdCl<sub>2</sub>:O<sub>2</sub>:Ar vapor at a lower temperature results in dramatic conversion of the CdTe film to a range of CdTe<sub>1-x</sub>S<sub>x</sub> alloys, corresponding to an equivalent CdS film thickness of ~50 nm. It is qualitatively concluded from this that the CdCl<sub>2</sub> and the O<sub>2</sub> species play a critical role in enhancing diffusion.



**Figure 3.** (511)/(333) x-ray diffraction line profile for the superstrate structures: after deposition at 340°C, after annealing at 580°C for 15 minutes; after treatment in CdCl<sub>2</sub>:O<sub>2</sub>:Ar vapor at 430°C for 20 minutes.

Time-progressive evolution of the diffraction line profile for superstrate films treated at 420°C in CdCl<sub>2</sub>:O<sub>2</sub>:Ar vapor is reasonably well modeled by a single bulk and grain boundary diffusion coefficient as shown in Figure 4. The measured (511)/(333) line profiles show a progression in the formation of CdTe<sub>1-x</sub>S<sub>x</sub> alloys extending to the solubility limit for 420°C, which is ~5.8 wt% and corresponds to  $2\theta = 76.85^\circ$ . After 10 minutes, an alloy tail is apparent, while after 20 minutes, a bimodal distribution is seen in the line profile. After 40 minutes, little or no pure CdTe remains, and the line profile maximum occurs at the angle corresponding to the solubility limit. This time progression was modeled using the actual grain size distributions for the films,  $D_B = 1.25 \times 10^{-13} \text{ cm}^2/\text{sec}$  and  $D_{GB} = 1.10 \times 10^{-8} \text{ cm}^2/\text{sec}$ . Application of the technique to superstrate and substrate structures treated from 380°C to 450°C and at constant  $p(\text{CdCl}_2) = 9 \text{ mTorr}$  and  $p(\text{O}_2) = 150 \text{ Torr}$ , bulk and grain boundary yielded diffusion coefficients with Arrhenius behavior and activation energies of 2.8 eV and 2.0 eV, respectively. The bulk diffusion coefficients obtained with the thin-film structures agreed within 20% of those obtained by Auger depth profiles of CdS diffused into CdTe single crystals. The diffusion coefficients can be expressed  $D_B = 2.4 \times 10^7 e^{-(2.8/kT)}$  and  $D_{GB} = 3.4 \times 10^6 e^{-(2.0/kT)}$ .

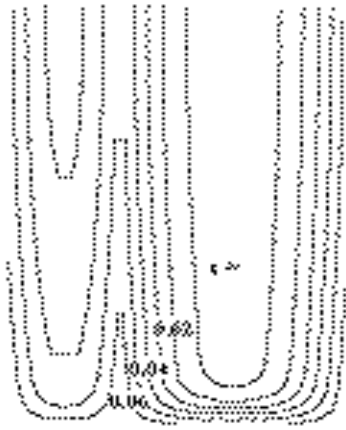


**Figure 4.** Measured (left) and modeled (right) x-ray diffraction line profiles: as-deposited and after treatment in CdCl<sub>2</sub>:O<sub>2</sub>:Ar vapor at 420°C for 10, 20 and 40 minutes with  $p(\text{CdCl}_2) = 9 \text{ mTorr}$  and  $p(\text{O}_2) = 150 \text{ torr}$ .

For fixed CdCl<sub>2</sub>:O<sub>2</sub>:Ar vapor treatment conditions, no difference in diffusion coefficients was found for CdTe films deposited at different temperatures, over the range from 250°C to 340°C. This demonstrates that the CdTe deposition temperature, while affecting grain size distribution and thus degree of alloy formation, does not fundamentally influence the diffusion mechanisms within the crystallites or the grain boundaries.

#### Spatial Distribution of CdTe<sub>1-x</sub>S<sub>x</sub> Alloys

Model calculations yield 3-dimensional distributions of S and Te and allow isocompositional contour plots of diffused regions to be represented (Figure 7). In the case shown, for two adjacent grains after treatment at 420°C for 40 minutes, using  $D_B = 1.25 \times 10^{-13} \text{ cm}^2/\text{sec}$  and using  $D_{GB} = 1.5 \times 10^{-8} \text{ cm}^2/\text{sec}$ , the differing grain size results in a different alloy profile in the junction and photocurrent generation regions. For the narrower grain, no pure CdTe remains at all, while the wider grain exhibits the entire range of alloy composition, from CdTe to CdTe<sub>0.94</sub>S<sub>0.06</sub> within the junction region.



**Figure 5.** Modeled isocompositional contour plot for 0.5  $\mu\text{m}$  and 1.0  $\mu\text{m}$  wide grains in 2  $\mu\text{m}$  thick CdTe film using  $D_B = 1.25 \times 10^{-13} \text{ cm}^2/\text{sec}$  and using  $D_{GB} = 1.5 \times 10^{-8} \text{ cm}^2/\text{sec}$ .

## 5. CONCLUSIONS

CdS diffusion into CdTe can be modeled by a combination of bulk and grain boundary processes. Compositionally broadened x-ray diffraction line profiles are sensitive to the diffusion process and allow quantitative evaluation of the diffusion coefficients. The CdTe grain size distribution, hence grain boundary volume, is the fundamental link between the deposition temperature and the observed diffusivity of CdS into CdTe. Without CdCl<sub>2</sub> and O<sub>2</sub> species present the diffusion that occurs during high temperature film growth or post-deposition treatment is very small. Treating films at lower temperatures but in CdCl<sub>2</sub>:O<sub>2</sub>:Ar ambient enhances the diffusion process without affecting the thermodynamic equilibrium solubility limits in the CdS-CdTe phase system. The primary effect of the ambient constituents is on the grain boundary diffusion coefficient, demonstrating the chemical role of halogen and oxygen species in creating mobile Te, and S species. A chemical basis for this may involve steady state reactions that produce SCl<sub>2</sub> and TeCl<sub>2</sub> and related compounds, which enhance transport of S and Te. The results show that CdS diffusion can be retarded by maximizing the as-deposited CdTe grain size, and by a suitable combination of treatment temperature and CdCl<sub>2</sub>:O<sub>2</sub>:Ar species concentrations during treatment. Finally, compositional distribution plots show that large variations in composition can exist parallel and perpendicular to the junction interface, depending on the grain size distribution. These distributions can provide the basis for 2-D device modeling of CdS/CdTe solar cells.

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