Dramatic Recrystallization During $CdCl_2$ Treatment of Evaporated CdTe Thin Films

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***Abstract* — In this work, we report the different effects of $CdCl_2$ treatment on CdTe films deposited by thermal evaporation onto CdS and MgZnO (MZO) buffer layers. The main finding, which is relevant for understanding recent advances in CdTe device efficiency, is that few-µm thick CdTe films deposited on MZO can be induced to completely recrystallize forming a film consisting of grains that span the film thickness and are up to 30 µm laterally. On CdS buffer layers, the changes in microstructure with Cl treatment are much less pronounced and the final microstructure is less ideal for thin film photovoltaics. We propose a thermodynamic framework for understanding the microstructural changes during $CdCl_2$ treatment which can assist in understanding the wide range of behaviors observed across the many CdTe thin film solar cell fabrication procedures.**

***Index Terms* – cadmium telluride, thermal evaporation, microstructure, grain size, thin film.**

I. Introduction

Cadmium telluride (CdTe) is the most successful thin film solar module technology with total installed capacity >10 GWp which is nearly 5 times that of CIGSe and a-Si combined [1]. Advancements in the last 10 years in both efficiency and manufacturing cost have enabled CdTe to be the first to reach $1/Wp and to maintain cost parity with mc-Si since then [1]. There are still further opportunities for improvement, as even the lab cell record falls well short of the theoretical efficiency because of non-radiative recombination, material parameters, and device implementation losses [2]. Since no grain boundary passivation process has ever completely eliminated recombination/generation activity, the elimination of any horizontal grain boundaries and maximization of grain size remain key goals for high efficiency. The requirement of large grain size only becomes more important as the bulk lifetime improves and devices move towards the limit of higher doping and carrier collection dominated by diffusion rather than drift.

Mass production of CdTe device stacks utilizes vapor transport deposition (VTD) to deposit the CdTe based absorber layer which yields high deposition rate. Close-spaced sublimation (CSS) can also deliver high deposition rate and is utilized in many research labs. Sputtering from CdTe targets, electrodeposition, solution deposition, nanoparticle deposition, and thermal evaporation have also each been investigated [3]. Each of these deposition processes result in different stoichiometry and microstructure.

After deposition, there is a cadmium chloride ($CdCl_2$) heat treatment which fixes many electronic defects and enables grain growth. Historically, the microstructure of CdTe films has been limited to grain sizes on the order of 1-5 µm in diameter at thicknesses of 2-6 µm [4], [5]. Devices made from active layers with small grain sizes have suffered from low lifetime and high recombination rates [2], [6]. Larger grains are often preferred so as to prevent recombination at grain boundaries and to promote effective carrier transport through the thickness of the active layer. The $CdCl_2$ post deposition treatment step is critical for all known processes to fabricate CdTe thin film solar cells. The effects of this treatment vary depending on the details of how it is carried out and critically on the microstructure and defects present in the CdTe film stack [3].

Changes occurring during $CdCl_2$ treatment include: grain growth at the expense of small grains (Ostwald ripening), complete recrystallization of grains, elimination of stacking faults and twins, inter-diffusion of cadmium sulfide (CdS) and CdTe, partial passivation of grain boundaries (lowering but not eliminating their recombination velocities), formation of acceptor A centers (donor-double acceptor pairs acting as single acceptors), and reduction in defects such as Te antisites and Te vacancies [6], [7]. The changes at the level of microstructure and inter-diffusion are the most dependent on the as-deposited microstructure.

The final microstructure of a thin film of CdTe following $CdCl_2$ treatment will be determined by the kinetics and thermodynamics associated with the as-deposited microstructure including other materials in the device stack. Free surfaces and the interface with the buffer layer contribute to the total energy of the film, as do the strain and chemical energies of point defects, dislocations, twins, stacking faults, grain boundaries, 2nd phases, and voids. All these factors can be combined in equation form for the total Gibbs free energy of a film, given by (1) where SA denotes surface area, γ surface interface energy, ss solid-solid interface, sv solid-vacuum interface, dis dislocation, etc.

$$G_{Tot} = SA_{ss} * \gamma_{ss} + SA_{sv} * \gamma_{sv} + V * \Delta G_V + G_{dis} G_{\dots} \quad (1)$$

During deposition of CdTe on different substrates, the only difference in the total free energy of the film is the different surface energies of the substrates. This difference has the potential to create different film morphologies, affecting grain size, grain boundary density, dislocation density, and other properties.

When films which were deposited on different substrates are annealed, the residual film energy as well as the CdTe/substrate interface energy govern final film morphology. Film morphologies will form which have the lowest free energy for the associated substrates and starting energy state.

II. Materials and Methods

The thin films reported were deposited by thermal evaporation at a pressure $<5x10^{-5}$ Torr on TEC 15 fluorine-doped tin oxide coated glass (FTO), or magnesium zinc oxide coated glass (MZO). The CdS buffer layer was deposited on sample 1 at room temperature. The films were annealed in a tube furnace with the films face-down, suspended above $CdCl_2$ beads, in a graphite boat. The parameters used for the deposition and annealing of the CdTe thin films are shown in Table I below.

Scanning electron microscopy (SEM) was used to obtain micrographs for grain size [8] and film thickness evaluation.

TABLE I
SUMMARY OF PROCESSING PARAMETERS

Sample Parameters	Sample 1	Sample 2
Substrate	FTO/CdS	MZO
Substrate Temp. (°C)	475	475
Deposition Rate (Å/s)	21 ± 4	21 ± 4
CdTe Thickness (µm)	6.0	6.0
Annealing Temp. (°C)	400	425
Annealing Time (min.)	30	30

III. Experimental Results

A. CdTe Deposited on FTO/CdS

The average grain size for sample 1 was (3.3 ± 0.5) µm before annealing, and (5.1 ± 0.5) µm after annealing respectively (see Fig. 1a-b). The grains transformed from faceted to flat morphology.

B. CdTe Deposited on MZO

The average grain size for sample 2 was (2.1 ± 0.3) µm before annealing and (10.8 ± 0.7) µm after annealing. The film deposited on MZO had the most dramatic grain recrystallization, transforming from small grains (see Fig. 1c) to very large, flat grains (see Fig. 1d). The grains extend throughout the thickness of the sample and the surface of the thin film is relatively flat (see Fig. 2).

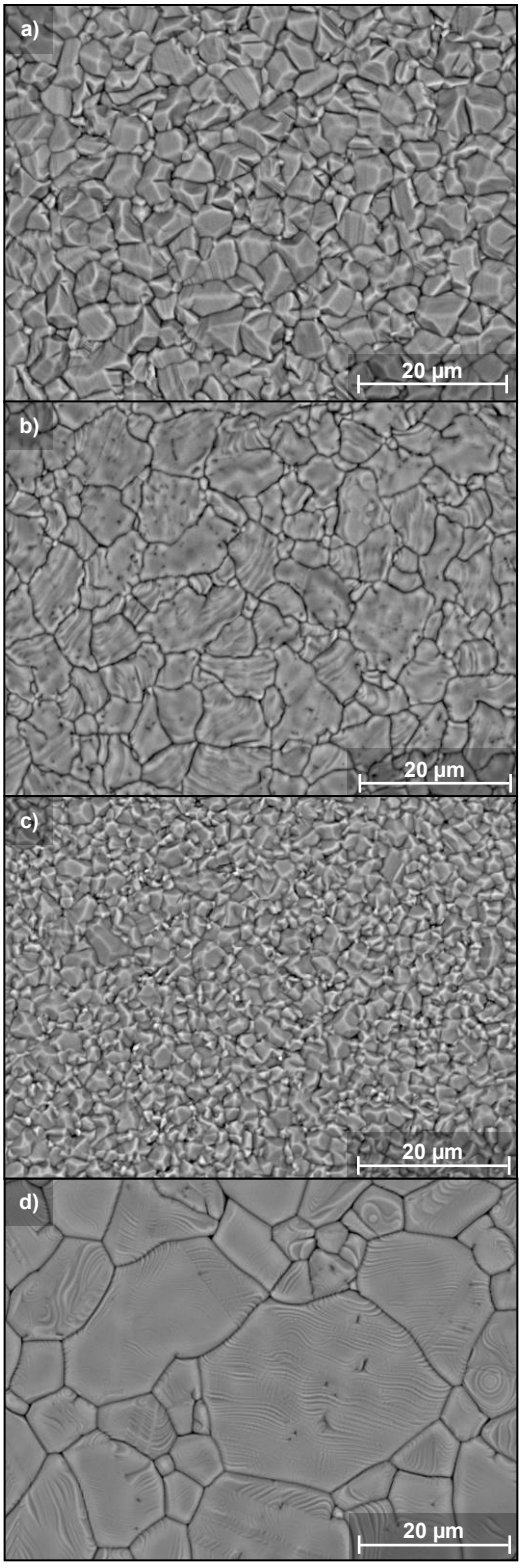

Fig 1. CdTe on a) FTO/CdS as deposited with large, faceted grains and a fairly rough surface, b) FTO/CdS annealed, with larger grains and flatter morphology, c) MZO as deposited with small grains, and d) MZO annealed with very large, flat grains.

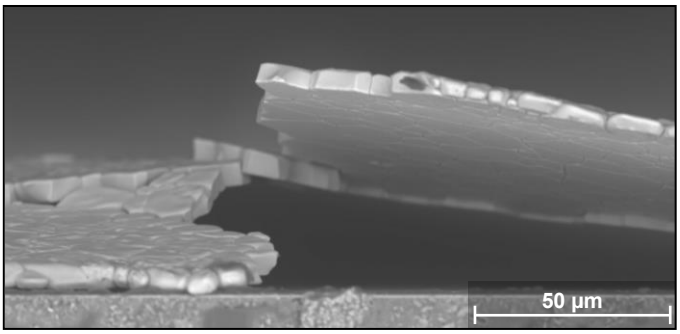

Fig. 2. Cross section of CdTe on MZO after annealing. The film is very flat and the grains are columnar, traversing the entire film thickness.

C. X-ray Diffraction

As deposited CdTe on both substrates was strongly textured towards (111). After the $CdCl_2$ treatment, both films showed significantly more reflections from the (311) and (200) crystallographic orientations. CdTe on MZO showed some (400) orientation after annealing, which is absent in the other films (see Fig. 3).

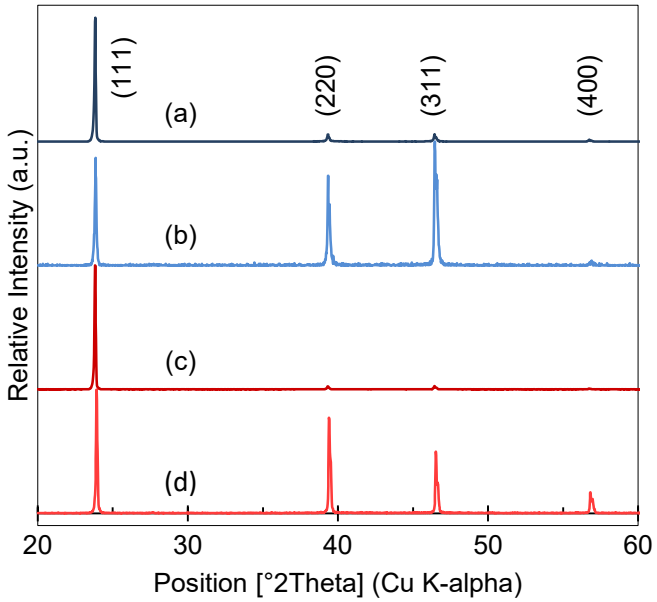

Fig. 3. X-ray diffraction patterns of (a) FTO/CdS/CdTe as deposited, (b) FTO/CdS/CdTe annealed, (c) MZO/CdTe as deposited, and (d) MZO/CdTe annealed.

IV Analysis of the Results

The experimental results of this research suggest that CdTe deposited on FTO/CdS behaves very differently than when it is deposited on MZO. For CdTe deposited on FTO/CdS the grain size starts out bimodal with largest grains up to a few µm. Deposition of CdTe on MZO, even at high substrate temperatures, resulted in tiny grains. The only difference in the deposition of these two films is the substrate, signifying that the energy of the CdTe/substrate interface differs for FTO/CdS and MZO. The small grains in CdTe on MZO have higher grain boundary density than CdTe on FTO/CdS. Other factors like dislocation density may be larger for the MZO film. CdS is traditionally used as a buffer layer in CdTe solar cell devices, providing an adequate lattice parameter match to decrease trap formation at the CdTe/substrate interface. This work suggests CdTe formation is more favorable on FTO/CdS than MZO.

Many changes occurred in each film after annealing in the presence of $CdCl_2$. These changes took place despite the annealing temperature (400-425 °C) being well below the deposition temperature (475 °C). $CdCl_2$ decreases the grain boundary energy and acts as a fluxing agent to promote recrystallization of grains [7]. This will only happen if the morphological change decreases the free energy of the film.

For CdTe on FTO/CdS, the annealed film had larger grains and flatter morphology. When the vapor phase above the film contained $CdCl_2$, (during annealing) instead of CdTe vapor (during deposition) the lower energy morphology was larger, flat grains. The annealed CdTe film on MZO has dramatically larger grains with flat tops. The large grain boundary density in the as-deposited film may provide the extra energy required to drive such drastic grain growth. CdTe on MZO substrate also promotes columnar grains after annealing, which eliminate grain boundaries through the thickness of the film. This is very desirable as high charge carrier mobility through the thickness of the film aids higher efficiency devices [7]. Both films exhibited a flatter morphology after annealing than as deposited. This signifies there is a higher energy penalty for surfaces of CdTe in the presence of $CdCl_2$ vapor than CdTe vapor.

Previous work [7] has shown when CdTe thin films are annealed above 385°C, significant grain reorientation occurs, favoring a reduction of (111) crystal orientations, for (220) and (311). Analysis of the XRD patterns of the films in this study reveal varying preferred orientation. The orientation parameters of each film were calculated according to the method of Harris, using a standard powder diffraction pattern for comparison [9]. The orientation parameter for each peak present in the XRD patterns was calculated according to (2) where p is the orientation parameter, N is the number of peaks in the analysis, I is the intensity of the pattern analyzed, and I_0 is the intensity of a standard powder pattern [5].

$$p(111) = N\left[\frac{I(111)}{I_0(111)}\right] \cdot \left[\sum \frac{I(hkl)}{I_0(hkl)}\right]^{-1} \qquad (2)$$

For this calculation, orientation parameters greater than one signify the film prefers orientation in that crystallographic direction. Values less than one indicate preference away from that direction. Values close to one signify the sample's orientation is random with respect to that direction [5]. The preferred orientation refers to the out of plane direction only.

The as-deposited CdTe on both substrates have preferred orientation towards the (111) axis with very little variation for other directions. After annealing, CdTe on FTO/CdS preferred (311) and (531) directions. After annealing, CdTe on MZO preferred (400) and (440) directions (see Fig. 4). The other crystallographic directions had very similar orientation parameters for annealed films on each substrate, much like the (111) peak. The differences and similarities in orientation parameters provide clues as to the CdTe crystal faces which have the lowest interface energy with FTO/CdS, MZO, CdTe vapor, and $CdCl_2$ vapor.

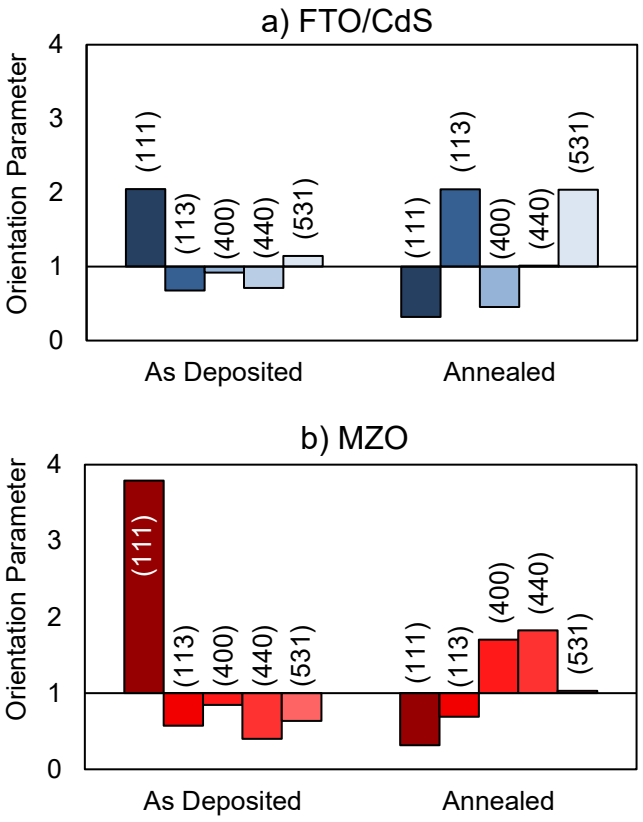

Fig. 4. Orientation parameters for several peaks of a) FTO/CdS/CdTe as deposited and annealed, and b) MZO/CdTe as deposited, and annealed.

V. Conclusion

The grain size in CdTe thin films is highly dependent on the substrate material and annealing method. The $CdCl_2$ treatment is integral to increasing the grain size, and it is especially effective when the initial grains are small. This improves the understanding of the effects of $CdCl_2$ treatments on CdTe thin films, as well as how substrate-film surface energies can affect microstructure and preferred orientation. As deposited film morphology affects the total energy of the film and thus the activation energy that must be overcome to reach a final desirable state

This work provides insight on how to achieve large grains in CdTe thin films. CdTe thin films were fabricated by thermal evaporation and $CdCl_2$ treatment, yielding a maximum grain size of 30 µm when deposited 6 µm thick on MZO. Large grains reduce unwanted recombination sites and increase the overall quality of the thin film towards crystalline perfection, optimized doping, and high minority carrier lifetime. Because these results were achieved within a small lab setting, the use of tighter controls and better equipment may allow for the development of even better film morphology.

Acknowledgement

This work was supported by funding from the Undergraduate Research Opportunities Program at the University of Utah awarded to Barrett Falbaum and Joshua Winger

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