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Charge Transport in CdTe Solar Cells Revealed by Conductive Tomographic Atomic Force Microscopy

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Polycrystalline photovoltaics comprising cadmium telluride (CdTe) represent a growing portion of the solar cell market, yet the physical picture of charge transport through the meso-scale grain morphology remains a topic of debate. It is unknown how thin film morphology affects the transport of electron-hole pairs. Accordingly this study is the first to generate three dimensional images of photocurrent throughout a thin-film solar cell, revealing the profound influence of grain boundaries and stacking faults on device efficiency.

The influence of microstructural defects on the device properties in CdTe and other polycrystalline photovoltaics remains largely unknown. This is partly because cross-sectional, surface, and bulk characterization techniques have been unable to image electrical pathways and interconnections through three-dimensional grains and grain boundaries with the requisite nanoscale resolution. Accordingly, this work employs a new conductive and tomographic variation of atomic force microscopy. Implementing a doped diamond-coated probe, active CdTe thin-film solar cells are progressively mechanically ablated through the full thickness, while photocurrents generated with in-situ illumination and biasing are simultaneously mapped. The resulting hundreds of current images through the thickness of these operating

solar cells clearly confirm that grain boundaries are preferential pathways for electron transport, partially explaining spatially dependent short-circuit and open-circuit performance. Uniquely, planar stacking faults consistent with wurtzite twinning are shown to enhance photocurrent, hypothesized as providing distinct channels for hole transport and thereby diminishing recombination. By comparison, such 3-dimensionally nanoscale results are also presented for specimens without high densities of stacking faults, and which are orders of magnitude less efficient at the macroscale. These results support an energetically orthogonal transport system of grain boundaries and stacking faults as being necessary for optimal solar cell performance, contrary to the conventional wisdom of the deleterious role of stacking faults on solar cell performance.

Cadmium telluride (CdTe) is a cost-efficient alternative to crystalline silicon for use in thin-film photovoltaics. Heterojunction solar cells of p-type CdTe/n-type cadmium sulfide (CdS) are extensively investigated because of suitable band-gap alignments and cost-effective methods of production [1]. However, experimentally attained efficiencies for thin films such as polycrystalline CdTe and silicon are consistently substantially lower than the theoretical efficiencies predicted by the Shockley-Queisser limit. Recombination at structural defects is often cited as the cause of reduced solar cell performance. These defects have been related to crystal twinning [2], stacking faults [3], interface passivation effects [4], impurity diffusion [1, 5], and other structural phenomena. To characterize the contribution of these effects to efficiency loss, it is necessary to image the electrical performance of individual CdTe grains and grain boundaries. Yet to date, no bulk, surface, or cross-sectional characterization technique has been able to image current pathways throughout a three-dimensional grain and its crucial surrounding microstructure. In this study, we tomographically image photocurrent in a commercial grade

CdTe/CdS thin film solar cell, and reveal that stacking faults in CdTe are surprisingly beneficial for hole transport.

As deposited CdTe solar cells generally do not perform well. Conventionally, a cadmium chloride (CdCl_2) activation process is employed to achieve high-efficiencies. Many studies have proposed that CdCl_2 treatment increases efficiency through recrystallization, by eliminating stacking faults and increasing grain size [4–7]. However, several cross-sectional transmission electron microscopy studies demonstrate the presence of stacking faults and crystalline twins after CdCl_2 treatment [2, 7–10]. Stacking faults present after treatment have been found to be planar, lamellar twins, with no dangling bonds [3]. High resolution TEM images have shown that closely packed stacking faults lead to local phase transitions, where hexagonal (wurtzite) structure is sandwiched between cubic (zinc-blende) structure. DFT Calculations predict that these sandwiched wurtzite structures have a lower ionization potential (electron affinity plus band gap) compared to surrounding zinc-blende CdTe [11]. These structures have thus been viewed as isolated hole traps, and hence deleterious to solar cell performance. This study, on the other hand, reveals a high density of electrically active planar defects throughout many micron-scale grains, such that these regions serve more as canals for hole transport, rather than as isolated traps. Despite CdTe photovoltaics being a billion dollar per year industry, this new insight provides a pathway for improving device performance through engineering stacking faults to further enhance charge transport.

3-dimensional visualization of these transport pathways is uniquely achieved via a newly developed Conducting Tomographic variation of Atomic Force Microscopy (CT-AFM), illumi-

Figure 1: Tomographic image of short circuit current. A slice of data is exposed from the rectangular solid, revealing stacking faults that extend approximately laterally on the order of microns. Bands of higher photocurrent exist intra-grain.

nated by 15 suns of full visible spectrum LED light through the substrate via a 40x objective. A heavily-doped, conducting diamond probe, with a nominal 50 nm radius of curvature, is implemented to map topography and photocurrents simultaneously at the surface of a CdTe/CdS photovoltaic cell. By applying forces on the order of microNewtons during scanning, the specimen is then ablated frame by frame, while maintaining a contact radius and hence local spatial resolution on the order of 10-20 nm. While it has been established that AFM techniques are able to remove surface material through thermal-mechanical micro-machining [12], few have combined milling with conductive probe imaging, due to the generally limited robustness of conductive AFM probes. The first conducting tomographic images have only recently been reported, applied for three-dimensional nano-scale images of conductance in resistive switching memories and carbon nanotube interconnects [13]. This work uniquely applies such tomographic concepts for solar cell investigations, implementing *in situ* illumination and correlating the results with TEM.

Figure 1 displays a volumetric representation of the photocurrent throughout the 2 μ m thickness of cadmium telluride processed with a CdCl₂ treatment following deposition, based on 147 consecutive conducting tomographic AFM images acquired during illumination. A movie of the complete dataset is included as Supplementary Figure 1. The images are collected from top-to-bottom, concluding at the buried transparent conducting oxide (anode), with the conductive probe acting as a positional top electrode (cathode). At zero bias applied to the specimen, i.e. short circuit conditions (I_{sc}), the probe collects p-Type (hole) electrical current. According to the I_{sc} CT-AFM dataset of Figure 1, only certain grains exhibit strong contrast at the surface. As is clearly apparent in any cross section of the data, though, numerous bands

of enhanced I_{sc} are present with 3-dimensional orientations dependent on grain orientation. This reveals that both inter- and intra- granular hole transport occurs as sketched in Figure 2b, and that this is substantially microstructurally dependent. In fact, regular series of planar stacking faults previously unreported in AFM-based studies are found to often correlate with the strongest measured photocurrents. Such defects are consistent with wurtzite twinning discussed in Yan et al. [11] and $\{111\}\Sigma 3$ twin boundaries discussed in Li et al. [2]. TEM images of an identical specimen as in Figure 1 reveal such wurtzite regions have a thickness of less than 10 nm (Figure 2b). These wurtzite pathways are often observed to extend across grains, and even to intercept at grain boundaries (Figure 3). Open-circuit voltage (V_{oc}) maps [14] (Figure 3a) from the same sample, and indeed the same location (but acquired before TEM sample preparation), reveal that regions between stacking faults have a higher open-circuit voltage compared to the mother grain. The enhanced measured photocurrent at these features therefore cannot simply be due to an increase in conduction or tip-injection.

In addition to uniquely characterizing photocurrents near planar stacking faults, conducting tomography also clearly resolves charge transport at grain boundaries. Other scanning probe techniques have been used with rare-earth photovoltaic systems to demonstrate hole-depletion near grain-boundaries [2, 15, 16]. Based on these surface measurements, researchers hypothesized that grain-boundaries serve as percolation pathways for electrons down to the PN junction interface. This effect is proven here in 3d via CT-AFM operated with a fixed tip-bias near the average open-circuit voltage for the specimen (Figure 4). In this quasi- V_{oc} regime, regions with more n-type character will have a lower or negative photocurrent (bright contrast

Figure 2: Schematic view of CT-AFM and charge transport in CdTe at short circuit current. Preferential pathways for holes include Wurtzite-structured CdTe periodically sandwiched between Zinc-Blende structure, as well as $\{111\}\Sigma 3$ twin boundaries discussed in Li et al. [2].

Figure 3: **a**, Planar AFM image of open-circuit voltage after 100 nm of tip ablation, as determined by IV curves at each pixel. Open-circuit voltage is highly dependent on grain. Cross-sectional TEM is performed. Grains with stacking faults are highlighted in green. Regions associated with stacking faults have higher open-circuit voltage compared to the mother grain. **b**, Cross sectional TEM of stacking faults. Wurtzite crystal structures extend to adjacent grains, which should aid in charge transport, as displayed by conductive tomographic AFM.

in figure). The strong signals localized at grain boundaries that are evident on the original surface or in the bulk (Figure S2), or in any cross-section of the data as in Figure 4a, all prove that many grain-boundaries in CdTe serve as primary pathways for electrons down to the cadmium sulfide, n-type, window layer.

Given the presence of an applied electric field and the often narrow spacing of stacking faults, hole current collection likely benefits from transport between wurtzite domains, in addition to simple conductivity along these intragranular pathways. Combined with the CT-AFM results from short-circuit current, charge transport for holes is concluded to be both inter and intra-granular, while electrons preferentially move along grain boundaries (Figure 4b). This is convenient for photovoltaic efficiency, as energetically and spatially different pathways will effectively decrease recombination. This picture is aligned with theory proposed by Li [2], and is opposite of the mainstream view [3, 9, 11] in which wurtzite regions act as hole traps and recombination centers. As directly observed here by CT-AFM, though, upon proper processing for high performance CdTe photovoltaics, a high density of wurtzite regions will interconnect to create a hole transport network, instead of remaining isolated and trapping photocarriers.

To confirm this hypothesis, CT-AFM results are also presented of I_{sc} during illumination for samples fabricated without the normal CdCl_2 treatment, as in Figure 5. Expectedly, minuscule macroscopic as well as nonoscale photocurrents are detected (note the scale is enhanced 6 times compared to Figure 1). In fact, the measured I_{sc} is essentially unchanged in light versus dark conditions for the full thickness specimens (Supplementary Figure 3). The grain morphology is nominally equivalent, though, confirming that improved device performance upon CdCl_2 treatment does not result from micron-scale recrystallization as some have claimed [9].

The predominant difference is instead that very few active planar defects are observed without CdCl_2 treatment, as compared to samples with CdCl_2 treatment which display a much higher density and regular distribution of stacking faults and twins. Some recrystallization must therefore take place during CdCl_2 exposure [7, 17], along with the possibility of doping and/or grain boundary passivation, ultimately adding and/or activating stacking faults for enhanced p-type transport – ideal features to isolate in future research.

The role of stacking faults is further elucidated by investigating samples without CdCl_2 treatment. Expectedly, samples without treatment have minuscule photocurrent, with electrical current unchanged in light versus dark. Unlike to the treated samples, increased electrical current is measured when the CdTe layer is thinner than a micron, indicating a low shunt resistance across the p-n junction. As shown in Figure 5, grains in the untreated sample have similar size, shape, and vertical-morphology as the treated sample. This indicates that increased device performance is not due to larger grain-size through micron-scale recrystallization. While some planar stacking faults are observed in the untreated sample, samples with treatment display more uniform distribution of stacking faults, indicating that some recrystallization does take place [7, 17]. The addition of more stacking faults likely contributes to p-type transport, along with effects due to doping and grain boundary passivation.

In conclusion, a high density of planar hole transport pathways is directly reported throughout the volume of many grains in cadmium telluride photovoltaics, uniquely accessible via a new conductive tomographic variation of AFM (CT-AFM). These pathways are shown to extend laterally over microns within a grain, interconnect at grain boundaries, and correspond to closely spaced stacking faults, that create wurtzite-structures with a lower ionization potential

Figure 4: **a**, Tomographic view of CdCl treated sample with tip biased at 700mV, near open-circuit voltage. Near open-circuit voltage, regions with more n-type character will have lower current. **b**, Schematic view of CT-AFM and charge transport in CdTe at open circuit voltage. Grain boundaries in CdTe operate as electrical pathways for electrons.

Figure 5: Tomographic image of short circuit current in a CdTe photovoltaic without cadmium chloride treatment. Grain size and shape are similar to treated samples. Enhanced hole current is observed when CdTe thickness is below a micron, indicating a low shunt-resistance. Fewer wurtzite p-type pathways are observed in the untreated sample.

throughout the absorber material [11]. These channels provide an energetically and spatially orthogonal network of p-type conduction pathways to n-type corridors that are also confirmed to localize primarily at grain boundaries in CdTe [2, 9, 15, 16]. Contrary to previous research, instead of acting as hole traps, these planar defects are effective hole transport layers, beneficial to p-type conductivity by reducing recombination, and are thus important to engineer for future enhancements in the performance of polycrystalline solar cells.

Methods

Sample fabrication Samples were fabricated using closed-space sublimation, having market comparable device performance for open circuit voltage and efficiency (0.8V, 12.3%, respectively). 120 nm of n-Type cadmium sulfide was deposited on fluorinated-tin Oxide over a glass substrate. 2.7 microns of p-Type cadmium telluride was deposited on the cadmium sulfide layer, and serves as the bulk of light absorption. Additional samples were fabricated with and without cadmium chloride treatment. Samples without CdCl_2 treatment have very low efficiency (0.1%). Copper highly dopes the back surface of CdTe for use as a hole-blocking layer. The back electrode, consisting of a layer of carbon and nickel, is removed after macroscopic measurements in preparation for conducting tomography.

Conducting Tomography All CT-AFM measurements were performed using an Asylum Research MFP-3D AFM (Santa Barbara, CA, USA) operating in air. Current detection is achieved with an Asylum Research ORCA cantilever holder, featuring current resolution of 1pA up to a maximum of 20nA. Conducting diamond coated silicon probes (Nanoworld CDT-NCHR, Soquel, CA, USA) with a nominal 300 kHz resonant frequency and 40 N m^{-1} nominal spring constant

were used for all AFM images. Scanning tomography was performed with deflection set point of 30 nm, and a scan speed of $300 \mu\text{s}^{-1}$ per pixel. This system is built on an optical microscope (Nikon TE-2000, Melville, NY, USA) with a 40x objective lens, enabling simultaneous AFM imaging from the top during narrow depth-of-field (~ 500 nm) illumination from below. The sample is exposed from below through the transparent substrate and conducting electrode to a focused, unfiltered LED (CREE MK-R 12V, Durham, NC, USA) with an estimated illumination intensity of 1.5 W cm^{-2} (about 15 suns, as measured with a silicon reference cell which was previously tested with a 300 W Oriel Instruments Sol2A solar simulator). All experiments were performed in a dark room to avoid any influence of ambient light, though a ~ 5 mW IR super luminescent diode (860 nm) used by the AFM to detect probe deflection is active throughout the experiments. This negligibly influences the photoconductivity measurements, however, because the IR source emits above the primary absorption range of the CdTe (850 nm). Moreover, the overhanging cantilever and tip partially shadows the interrogated region of the specimen, which as a micron sized isolated island is totally independent of any surrounding material that might be incidentally illuminated.

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