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Effects of $CdCl_2$ treatment on the local electronic properties of polycrystalline CdTe measured with photoemission electron microscopy

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Abstract — **To investigate the effects of $CdCl_2$ treatment on the local electronic properties of polycrystalline CdTe films, we conducted a photoemission electron microscopy (PEEM) study of CdTe films in a superstrate configuration, with and without $CdCl_2$ treatment. We observed that individual grains vary in work function, regardless of whether or not films received $CdCl_2$ treatment. Surface photovoltage measurements indicated type inversion of exposed CdTe grain interiors from p-type to n-type upon $CdCl_2$ treatment, potentially altering the band alignment of the CdTe film with metallic contacts. Additionally, grain boundaries display lower work function than the grain interior after an air exposure, consistent with previous scanning Kelvin probe force microscopy studies. These results suggest that $CdCl_2$ treatment changes both the interface and bulk electronic structure of CdTe to facilitate carrier separation and collection in photovoltaic devices.**

I. INTRODUCTION

CdTe thin-film photovoltaics generate more than 2 GW annually, with the efficiencies of commercial CdTe-based solar cells (21.5%) having recently caught up with those of laboratory devices. As such, CdTe-based solar cells are a serious alternative to silicon-based photovoltaics for commercial production and deployment. A key component of manufacturing efficient CdTe photovoltaic devices is an activation process where the polycrystalline CdTe absorber layer is treated with $CdCl_2$ [1]. The effect of $CdCl_2$ treatment on the electronic properties of CdTe-based devices has been extensively studied but is not completely understood.

One effect of $CdCl_2$ treatment is a change in the microstructure of the CdTe layer, resulting in larger and more uniform grains, and increased minority carrier lifetimes [1]. Presumably, fewer grain boundaries lead to reduced scattering and recombination of photogenerated carriers. However, the performance of single crystal CdTe photovoltaics is known to be inferior to that of polycrystalline films.

This apparent contradiction is often explained in the context of preferential doping of grain boundaries during $CdCl_2$ treatment. The prevailing description is that Cl from the $CdCl_2$ treatment segregates to grain boundaries, depleting or even inverting them with respect to grain interiors. Junctions between grain interiors and grain boundaries are expected to repel holes and conduct electrons to the back contact more efficiently. Consequently, individual grain boundary properties have been a subject of intense study, and they have been measured using an array of techniques including scanning probe microscopy [2]- [3], electron beam-induced current [4], time-resolved photoluminescence [5], and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) [6]. The electrical conductivity type (n- or p-type) is often inferred from relative differences in local carrier distributions measured by these techniques. In this respect, photoemission spectroscopy is invaluable for determining electronic structure. For example, ultraviolet photoelectron spectroscopy (UPS) is routinely used to measure Fermi level positions, estimate doping levels, and determine relative band alignment among thin-film components in semiconductor devices. However, because UPS is an area-averaged technique, lateral variation of electronic properties smaller than the beam spot size (typically 1 mm to tens of microns) cannot be resolved.

In the work reported here, we used spectroscopic modes of photoemission electron microscopy (PEEM) to measure the effect of $CdCl_2$ treatment on the local electronic properties of CdTe films in a superstrate configuration. We observed grain-like domains and saw little change in microstructure between $CdCl_2$-treated and untreated films. We found that individual grains vary in work function for both $CdCl_2$-treated and untreated films. More surprisingly, our results indicate that $CdCl_2$-treatment alone does not alter the electronic structure at grain boundaries in a manner consistent with previous reports [2], [3]. With surface photovoltage (SPV) measurements, we demonstrate that $CdCl_2$-treatment inverted exposed CdTe grain interiors from p-type to n-type. These results run contrary to the common description of p-type CdTe with inverted/depleted grain boundaries. Further SPV measurements showed that air exposure after the hole dopes the CdTe surface. It is this air exposure following $CdCl_2$-treatment that activates grain boundaries. Measuring the electrical conductivity type of the surface is important to precisely predict how CdTe films interface with adjacent electrodes and buffer layers in devices.

II. EXPERIMENTAL DETAILS

CdTe samples were fabricated using closed-space sublimation (CSS) at Colorado State University's Advanced Research Deposition System [7]. Prior to film deposition, The

TCO layer was cleaned using a standard ultrasonic detergent rinse, an ultrasonic deionized water rinse, and an isopropyl alcohol wash, and then treated using a plasma cleaning process. CdTe was deposited directly onto a sputtered $Mg_xZn_{1-x}O$ (MZO) layer. During CSS growth and $CdCl_2$ treatment, substrate temperatures were in the range of 425–500˚C and source temperatures were 435–610˚C. To reduce topographical artifacts in PEEM measurement, samples were mechanically polished using a 1 μm diamond polish. Samples were subsequently sputter-cleaned with 50 eV Ar^+ ions for 10–20 min. with a fluence of ~0.1-0.15 $\mu A \bullet cm^{-2}$ to remove surface contaminants. The composition of the CdTe surface before and after sputtering was verified using x-ray photoemission spectroscopy (XPS). After sputter-cleaning and XPS measurement, samples were transferred for PEEM measurement without air exposure. Figure 1 shows a general schematic of the sample and PEEM electronic structure measurement configurations.

PEEM measurements were conducted in a LEEM-III system (Elmitec Elektronenmikroskopie GmbH) equipped with a hemispherical electron energy analyzer and coupled to a tunable DUV light source composed of a pressurized Xe lamp (Energetiq, EQ-1500 LDLS), a Czerny–Turner monochromator (Acton research, SP2150), and refocusing optics. The spectral width of the DUV light was set to 50-100 meV throughout the wavelength range used for the measurement (λ = 175–350 nm, $h\nu \cong$ 3.6–7 eV). We collect photoemission spectra (PES) at each pixel in a PEEM image using a typical electron energy step size of 10 meV. Similar to conventional analysis of XPS/UPS spectra, fits to the spectra specified the locations of the vacuum level and the valence band edge. SPV measurements with PEEM were performed by illuminating the sample with additional light from a 3 mW, 403 nm ($h\nu \cong$ 3.1 eV) continuous-wave laser. The laser is focused to a roughly 1mm diameter spot. The field of view (FOV) for photoemission images and spectral maps was 48 µm with a diameter of 600 pixels, corresponding to a pixel size of ~80 nm/pixel.

III. RESULTS & DISCUSSION

Representative PEEM intensity images (FOV = 48 µm) of $CdCl_2$-treated and untreated samples are shown in Fig. 1. In each case, the electron kinetic energies at which the images were acquired were close to the vacuum level edge of PES. These images highlight local variations in the vacuum level, where lower vacuum levels have higher photoemission intensity than regions with higher vacuum levels. Microcrystalline grains in CdTe are clearly evident in Figs. 1(a) and 1(b).

Differences in surface microstructure between $CdCl_2$-treated and untreated samples appeared to be minimal. Grains in $CdCl_2$-treated CdTe (Fig. 1(a)) seemed to be 1-2 times larger than grains in untreated CdTe (1(b)).

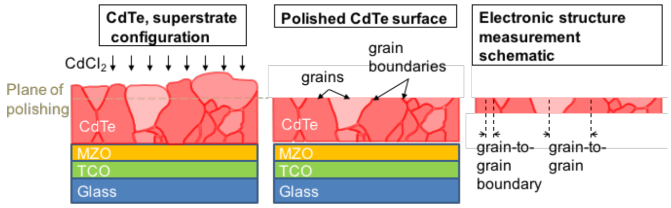

Fig. 1. Schematic of the CdTe sample in superstrate configuration, denoting grain interiors and grain boundaries and illustrating grain-to-grain and grain-to-grain boundary designations for electronic structure measurements with PEEM.

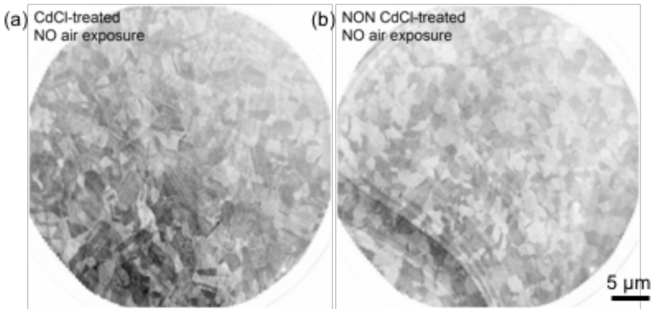

Fig. 2. PEEM intensity images due to local variations in the work function of (a) $CdCl_2$-treated and (b) untreated CdTe. Images were obtained at an electron kinetic energy on the vacuum level edge of PES that were obtained using λ = 190 nm light.

The change in grain size we observed with PEEM is consistent with observations of grain recrystallization for CdTe films grown at higher temperature [8]. These results suggest that grain size alone does not drive improvement in the performance of $CdCl_2$-treated samples. Therefore, we looked to changes in the electronic structure to better understand the influence of $CdCl_2$-treatment.

In both $CdCl_2$-treated and untreated samples, we observed grains that vary in work function. Analyzing local PES spectra, histograms show a similar distribution in the relative work function for $CdCl_2$-treated and untreated CdTe films. This source of local variation in electronic properties may be fundamental to polycrystalline CdTe as a solar absorber. Grain-to-grain variation in surface potential has been observed to some extent in scanning Kelvin probe microscopy (SKPM) [3] and ToF-SIMS [6] studies. Interestingly, ToF-SIMS showed Te-concentration variation amongst grains in CdTe, which could give rise to a grain-to-grain work function variation such as we observed.

In conjunction with the PEEM, SPV measurements indicated type inversion of the exposed CdTe grain interior from p-type to n-type with $CdCl_2$ treatment. Figures 2(a) and 2(b) show PES with and without additional 403 nm laser illumination for $CdCl_2$-treated and untreated CdTe, respectively. The presence of a surface photovoltage causes accumulation of photogenerated majority carriers at the surface, which reduces surface band bending. The direction of the shift allows the identification of the majority carrier type.

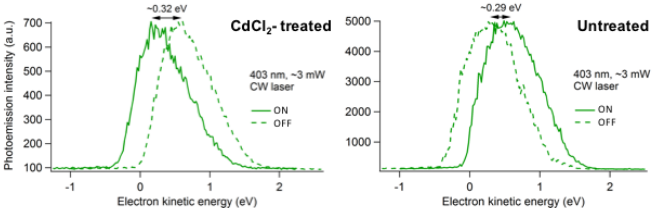

Fig. 3. Surface photovoltage measurements using a continuous wave 403 nm laser. Local photoelectron spectra are obtained for all samples with λ = 190 nm light while the CW laser is on and off.

The shift of the $CdCl_2$-treated CdTe spectra to lower energy in the presence of a surface photovoltage indicates that the surface of the exposed $CdCl_2$-treated CdTe grain is n-type. THe shift of spectra in untreated CdTe upward in energy with additional illumination suggests that its exposed surface is p-type. These results agree with ref. [9] which shows that $CdCl_2$ treatment tends to shift the Fermi level of both n-type and p-type CdTe films into the upper half of the band gap.

Reports have also associated $CdCl_2$ treatment with changes in the electronic environment of grain boundaries in CdTe. As before, we observed that variations in grain-to-grain work function were the main source of local electronic structure variation in our measurements; we did not observe grain boundary inversion or depletion with PEEM that would be consistent with previous studies. As our samples were not exposed to air, and PEEM measurement was conducted in UHV, we sought to determine whether grain boundary characteristics could be influenced by measurement conditions. We exposed the $CdCl_2$-treated CdTe sample to air for 30 minutes, then reintroduced the samples into PEEM. Grain boundaries appeared to be activated after air exposure in a manner consistent with previous SKPM studies. Preliminary SPV and photoemission yield measurements indicated that air exposure acted as a hole dopant. It appears that air exposure depletes the n-type CdTe surface of electrons and activates grain boundaries, which serve as conduits for electrons to reach the metallic contact.

In conclusion, our measurements using photoemission electron microscopy allowed us to fill in critical details for assessing the performance of CdTe films in photovoltaic devices. SPV measurements were especially useful to determine the surface type directly. PEEM measurement in UHV also enabled us to observe a crucial intermediate step toward activating grain boundaries in $CdCl_2$-treated CdTe, namely, air exposure. Our result suggests that PEEM is a powerful tool to characterize both surface-wide properties of CdTe films as well as properties of secondary junctions in CdTe (e.g. from grain-to-grain or grain boundary-to-grain) that impact carrier separation and collection.

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