

LOCAL MEASUREMENTS OF PHOTOCURRENT AND BAND GAP IN CdTe SOLAR CELLS

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ABSTRACT: Polycrystalline thin film technology has shown great promise for low cost, high efficiency photovoltaics. To further increase the power efficiency, a better understanding of microstructural properties of the devices is required. In this work, we investigate the inhomogeneous electrical and optical properties using local excitation techniques that generate excess carriers by a near-field light illumination or by a focused electron beam irradiation. The spatially-resolved photocurrent images of n-CdS / p-CdTe devices obtained by both techniques show high carrier collection efficiencies at grain boundaries. A novel and complementary technique, photothermal induced resonance (PTIR), is also used to obtain absorption spectra and maps in the near-field over a broad range of wavelengths. In PTIR a wavelength tunable pulsed laser is used in combination with an atomic force microscope tip to detect the local thermal expansion induced by light absorption. Sub-micrometer thick lamella samples of CdTe solar cells are measured, and the

variation of local band-gap is analyzed. We discuss the resolution and the sensitivity of the techniques in the range of photon energies close to the band gap.

Keywords: photothermal induced resonance (PTIR), CdTe solar cells, band-gap, scanning photocurrent microscopy (SPCM), near-field scanning optical microscopy (NSOM)

1 INTRODUCTION

Polycrystalline thin film photovoltaic (PV) technologies have shown great promise for solar energy harvesting using inexpensive PV materials, currently reaching a power conversion efficiency of $\approx 21\%$ for cadmium telluride (CdTe) and $\approx 22\%$ for copper indium gallium selenide (CIGS) solar cells [1]. To achieve the maximum efficiency of $\approx 30\%$ theoretically possible for these technologies, considerable efforts have been made to understand the physical mechanisms that limit cell performance. To further understand current limitations, the impact of inhomogeneous variation of grains and grain boundaries (GBs) on charge transport needs to be analyzed. In general, grain boundaries can act as recombination centers, even if they are passivated during the post-annealing process (e.g., CdCl₂ treatment) [2]. Inter-diffusion between CdTe and CdS can also induce additional recombination in the p-n junction or at the heterogeneous interfaces (e.g., grain to grain, grain to grain boundary) [3, 4]. In this work, we investigate the inhomogeneous electrical and optical properties using local excitation techniques that generate excess carriers by a near-field light illumination or by a focused electron beam irradiation. Furthermore, we present a complementary technique, photothermal induced resonance, which can directly measure the local variations of energy band-gap within CdTe grains and along the p-n junction.

2 EXPERIMENTAL

p-CdTe / n-CdS solar cells extracted from a commercial solar panel were used for scanning photocurrent microscopy electron beam induced current (EBIC) and photothermal induced resonance measurements. A thick 100 nm evaporated Au pad served as a top contact (Au / p-CdTe) and the common contact to the TCO layer was made using indium solder (indium / n-CdS / SnO₂). Cross-sections of the samples for SPCM and EBIC and the lamella samples for PTIR were prepared by a focused ion beam (FIB). To achieve high spatial resolution ($< 1\ \mu\text{m}$) in SPCM measurements, we adapted an optical fiber probe (200 nm in diameter) mounted on a tuning fork, typically used for near-field scanning optical microscopy (NSOM). EBIC measurements were performed in a scanning electron microscope (SEM) equipped with a nano-manipulator that was used to position an electrical probe on the contact to CdTe.

3 RESULTS AND DISCUSSION

3.1 Scanning photocurrent microscopy (SPCM)

Fig. 1 shows a cross-sectional SPCM (a; 405 nm illumination) and an EBIC image (b; 5 kV excitation) of CdTe devices prepared by a FIB milling process. As

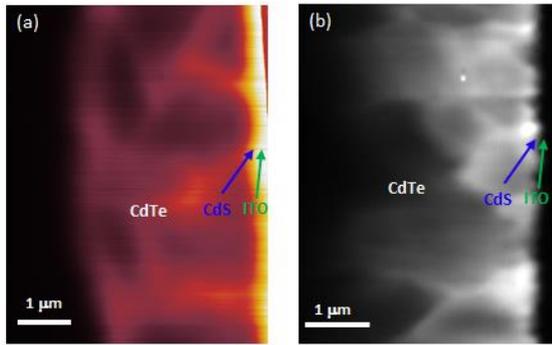


Fig. 1 Cross-sectional photocurrent images of FIB prepared p-CdTe/n-CdS devices. (a) SPCM image (laser wavelength: 405 nm, diameter of NSOM probe: 200 nm). The measured maximum photocurrent was 3.3 nA. (b) A 5 kV EBIC image (beam current: 300 pA).

expected, the measured photocurrent is large at the excitation near the p-n junction and decreases away from the junction [5]. Both images show that the grain boundaries are indeed more efficient photocurrent collectors than the grain interiors (GIs). This property can be associated with the local electric field at GBs, possibly induced by the accumulation of chlorine (Cl^-) [6] or by other charged defects. The band bending drives holes away from the grain boundary thus decreasing recombination. [7] Somewhat surprisingly, the photocurrent at GBs can be as strong or stronger than that at the p-n junction, making the identification of the depletion region difficult. We note that both a 405 nm laser beam and a 5 kV electron irradiation have similar shallow absorption depth in CdTe (≈ 100 nm), and thus the generated free carriers are subject to high recombination at the surface or within a layer modified / damaged by ion milling. The interaction volumes are increasing at longer laser wavelengths and at larger electron beam voltages, thus the contrast between GBs and GIs becomes weaker due to the averaging of photocurrent over the excitation volume. To extract quantitative parameters, an accurate modeling is required to de-convolute the responses at different beam energies and/or different wavelengths and to explicitly account for recombination at or near the surface, which is an on-going study.

3.2 Photothermal induced resonance (PTIR)

To independently determine a compositional variation over the polycrystalline absorber and across the overall device structure, we explore the potential of a novel optical spectroscopic microscopy, PTIR, based on the photothermal effect [8]. The local expansion of the sample induced by the absorption of pulsed light from a tunable laser is detected by an AFM tip instantaneously (see Fig. 2). PTIR was recently extended to the visible and near-IR ranges [9]. In this work, we employ the PTIR technique to measure the local band-gap of CdTe lamella obtained by FIB-sectioning of a CdTe photovoltaic device. The band-gap transition of bulk CdTe absorber is expected to be ≈ 1.45 eV, while the local absorption may vary at interfaces (e.g., grain boundaries, metallurgical junction) due to inhomogeneous local compositions. For this study, we use a range of the energies near the CdTe band gap transition (around of 1.45 eV) to determine local absorption variation due to compositional variation in CdTe layer.

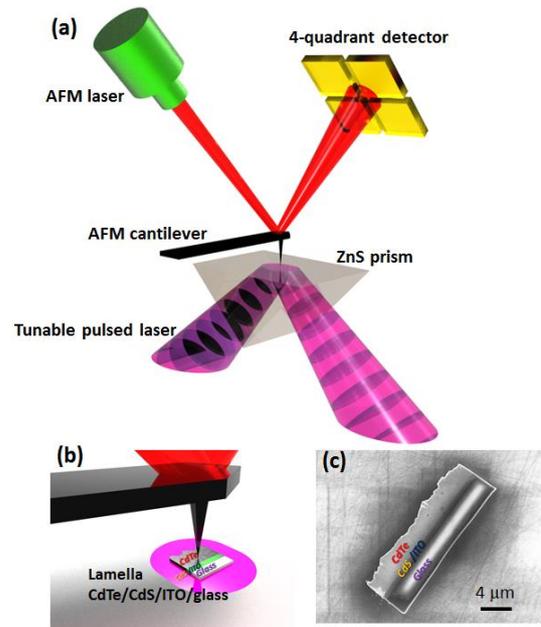


Fig. 2 Schematics of PTIR technique. (a) A visible laser illuminating from the side of the ZnS prism produces local expansion of the sample. (b) The local expansion induces the deflection of the AFM cantilever, which is detected by a 4-quadrant detector. (c) An SEM image of a FIB prepared lamella (CdTe/CdS/ITO/glass) on a ZnS prism.

We applied the PTIR technique to the FIB prepared lamella of CdTe sample that was transferred to a zinc sulfide (ZnS) prism by a glass needle using a micro-manipulator. Fig 3 shows the topography, PTIR images (1.45 eV, 1.55 eV), and PTIR spectra (1.2 eV to 1.7 eV) for the CdTe/CdS/ITO(indium tin oxide)/glass lamella sample. PTIR images and spectra were acquired in the range of the energies of laser excitation close to CdTe band gap to explore the compositional variation through the absorber. As seen in the maps, the intensity of the PTIR signal varies over CdTe area: a larger signal is seen near CdTe surface (Fig. 3b) and, in some areas, in the vicinity of the p-n junction (blue lines in each image).

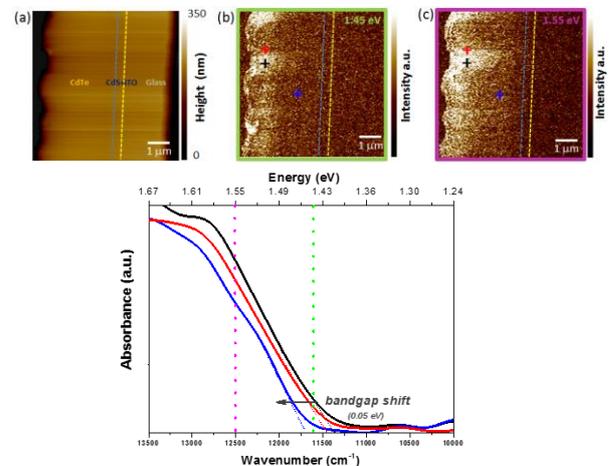


Fig. 3 PTIR data of a p-CdTe / n-CdS / ITO / glass lamella sample. (a) Topography, (b) 1.45 eV PTIR image, and (c) 1.55 eV PTIR image. (d) PTIR spectra collected at three different spots (color-coded locations denoted in the PTIR images)

Thus, the PTIR technique enables imaging heterogeneous and homogeneous domains in CdTe with submicron spatial resolution. We interpret the origin of PTIR contrast as the variation of absorption caused by a band gap variation. The PTIR spectra in Fig. 3d clearly show a band gap shift (0.045 eV) at the color-coded locations denoted in the PTIR images. The extrapolation lines (dashed lines) indicate optical band-gaps (E_g) of ≈ 1.412 eV, ≈ 1.426 eV and ≈ 1.457 eV for black, red, and blue lines, respectively. A possible reason for the band gap variation is sulfur diffusion from the CdS to the CdTe, resulting in the formation of CdTe_{1-x}S_x [10]. Other possibility is that CdCl₂ treatment affects the interior of CdTe grains via potential incorporation of electrically active impurities.

4 CONCLUSIONS

In summary, we have analyzed functional and structural properties of CdTe solar cells with two different techniques. In high-resolution photocurrent maps of cross-sections of CdTe devices obtained by SPCM and EBIC techniques, grain boundaries showed higher carrier collection properties than grain interiors, and the photocurrent decreases away from the p-n junction. Spectroscopic PTIR measurements showed a variation of local absorption in a range of wavelengths near the CdTe band gap, implying an inhomogeneous composition of the CdTe absorber layer although the PTIR images don't show the contrast between GIs and GBs.

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