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Nanoscale Imaging and Spectroscopy of Band Gap and Defects in Polycrystalline Photovoltaic Devices

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Abstract

Improving the power conversion efficiency of photovoltaic (PV) devices is challenging because the generation, separation and collection of electron-hole pairs are strongly dependent on details of the nanoscale chemical composition and defects which are often poorly known. In this work, two novel scanning probe nano-spectroscopy techniques, direct-transmission near-field scanning optical microscopy (dt-NSOM) and photothermal induced resonance (PTIR), are implemented to probe the distribution of defects and the bandgap variation in thin lamellae extracted from polycrystalline CdTe PV devices. dt-NSOM provides high-contrast spatially-resolved maps of light transmitted through the sample at selected wavelengths. PTIR provides absorption maps and spectra over a broad spectral range, from visible to mid-infrared. Results show variation of the bandgap through the CdTe thickness and from grain to grain that is spatially uncorrelated with the distributions of shallow and deep defects.

Solar cells can provide an important contribution in transitioning to a low carbon economy.¹ In particular, polycrystalline thin film photovoltaic (PV) materials such as cadmium telluride (CdTe),^{2,3} copper indium gallium selenide⁴, and organometal-trihalide perovskites,⁵ have shown great promise for solar energy harvesting due to their lower fabrication costs and power conversion efficiencies, in excess of 20 %.⁶ Because efficiency is a strong driver for reducing PV production and deployment costs, considerable efforts have been devoted⁷ to understand the physical mechanisms limiting cell performance, as a pathway to approach the maximum theoretical efficiency for a single junction cell given by the Shockley-Queisser limit. PV devices typically consist of a light absorbing layer, p-n junction and contacts that control the generation, separation and extraction of charge carriers, respectively. Although such architecture is conceptually simple, improving the PV efficiency is an engineering challenge, which requires understanding and controlling the chemical composition and defects ranging from point defects that are intrinsic to the constituent materials or derived from inter-layer diffusion, to extended defects such as dislocations and grain boundaries.^{8,9} Knowledge of the nanometer-scale details of electrical and optical properties correlated with the compositional, structural and defect mapping is required to fully unleash the potential of these technologies.

The techniques that are commonly used to investigate film heterogeneities include electron beam induced current (EBIC),^{10, 11, 12} photoluminescence (PL)^{13, 14} and cathodoluminescence (CL).¹⁵ EBIC yields nanoscale carrier collection efficiency maps,^{11, 16} however, it typically provides limited insights regarding the origin of the inhomogeneity or the carrier recombination process. Conventional PL does not provide the desired nano-scale resolution. Furthermore, both PL and CL probe radiative recombination processes that yield only indirect information on the Shockley-Read-Hall (SRH) recombination assisted by deep defects, often the dominant loss.¹⁷ Other techniques that in principle could probe deep energy traps directly, such infrared spectromicroscopy¹⁸ and deep level transient spectroscopy,¹⁹ are not suitable for nanoscale mapping because of insufficient spatial resolution and limited charge sensitivity, respectively. Therefore, new nanoscale characterization techniques are desirable to unveil the nature of heterogeneities and defects limiting the efficiency of polycrystalline PV devices.

In this work, two complementary atomic force microscopy (AFM)-based optical techniques, the photothermal induced resonance (PTIR)^{20, 21, 22} and a novel implementation of near-field scanning optical microscopy (NSOM),^{23, 24, 25} are leveraged to characterize CdTe polycrystalline solar cells with nanoscale resolution. In PTIR, a sample placed on an optically transparent prism, is illuminated in total internal reflection geometry over a relatively large area, while an AFM tip acts as a local detector for measuring absorption spectra and maps. In direct-transmission NSOM (hereafter dt-NSOM), an AFM probe, consisting of a tapered fiber with a small aperture at the tip, functions as a local light source, and a photodetector in direct contact with the sample measures the light transmitted through the sample. For these measurements, lamellae were extracted from a CdTe photovoltaic device and from a reference CdTe single crystal using focused ion beam milling. PTIR and dt-NSOM maps across CdTe grains and across the p-n junction display spatial variations of the band gap and of the distribution of both shallow and deep defects with a resolution comparable to the lamella thickness (≈ 300 nm), 4-times smaller than the average CdTe grain size (≈ 1200 nm).

Commercially available p-CdTe/n-CdS solar cells (3500 nm and 50 nm thickness, for the CdTe and CdS layers, respectively) were used in this study. The cell back contact (CdTe side) consisting of aluminum and Cr/Mo layer was removed together with the sealing glass. The characteristic optical lengths of dt-NSOM and PTIR do not match the CdTe absorber thickness and are wavelength-dependent. For example, for bulk CdTe, the light penetration depth in transmission ranges from sub-micron (just above band gap) to many microns (below the bandgap).²⁶ In contrast, for the PTIR illumination geometry, the penetration depth is smaller than the absorber thickness in a working solar cell. Therefore, thin lamellae were extracted using focused ion beam (FIB) milling to achieve a spatial resolution adequate to map both bandgap and defects with the two AFM techniques. Two types of lamellae were used: a cross sectional solar cell lamella (average thickness: $335 \text{ nm} \pm 10 \text{ nm}$) as determined by AFM, containing the CdTe/CdS/ITO/glass layers (hereafter cross-sectional lamella) and a lamella containing only the CdTe layer cut-out $0.5 \text{ }\mu\text{m}$ above p-n junction with a thickness of $350 \text{ nm} \pm 10 \text{ nm}$ (hereafter in-plane lamella). Uncertainties in this paper represent a single standard deviation. As reference, a lamella with thickness $340 \text{ nm} \pm 10 \text{ nm}$ was extracted from a CdTe single crystal (hereafter single-crystal lamella).

PTIR is a composition sensitive scanning probe technique that combines the lateral resolution of AFM with the chemical specificity of absorption spectroscopy.^{20, 21, 27} In PTIR, a pulsed wavelength-tunable laser illuminates the sample and a contact AFM tip locally transduces the sample thermal expansion induced by light absorption into mechanical cantilever motion. The cantilever oscillation is detected by reflecting a diode laser off the cantilever into the AFM four-quadrant detector (figure 1a). PTIR absorption spectra and maps are obtained by plotting the amplitude of the cantilever deflection as a function of wavelength and location, respectively. Because the cantilever contact resonance oscillation amplitude is proportional to the absorbed energy in the sample,²⁸ the PTIR spectra can be directly compared with IR spectral databases enabling material identification.²⁹ The ability for quantifying the chemical composition^{28, 30} with a spatial resolution down to 20 nm²⁷ has earned this technique considerable popularity for analyzing thin organic^{31, 32, 33} or metal-organic materials.^{30, 34, 35} However, because the PTIR signal is also proportional to the sample linear expansion coefficient, inorganic samples are typically challenging to measure. Here we show that CdTe, an inorganic (and mechanically rigid) material is also amenable to PTIR characterization. Recently, the PTIR spectral range was extended to the visible and near-IR²⁷ enabling the determination of the local optical band gap in organo-metal trihalide perovskites.³⁰ Further details of our PTIR setup are available elsewhere.^{27, 36}

The PTIR absorption spectrum of the reference CdTe single-crystal lamella is shown in figure 2a. In this work, the bandgap values were estimated as the onset of the linearly extrapolated PTIR absorption. The bandgap obtained from the CdTe single crystal lamella was $1.521 \text{ eV} \pm 0.007 \text{ eV}$. This value is in agreement with previous reports ($1.50 \text{ eV} \pm 0.05 \text{ eV}$; $\approx 827 \text{ nm}$).^{37, 38} The uncertainty of the bandgap throughout the paper was determined by the fitting procedure and should not be interpreted as an absolute uncertainty of the bandgap.

The PTIR spectra (Fig. 2a) measured at four marked locations (1-4 in Fig. 2c) on the cross-sectional lamella show that the CdTe optical band gap (E_g) monotonically increases from the CdTe device top surface (location 1, E_g of $1.424 \text{ eV} \pm 0.004 \text{ eV}$) toward the p-n junction and CdS layer ($E_g = 1.457 \text{ eV} \pm 0.005 \text{ eV}$ at location 4). The overall variation ($\approx 33 \text{ meV}$) for the sample analyzed here (absorber thickness: $3.5 \mu\text{m}$) is quite small and should have a minimal impact on the cell efficiency. In fact, to significantly impact the transport of minority carriers, the magnitude of the drift field (bandgap gradient / absorber thickness, $9.43 \text{ meV}\cdot\mu\text{m}^{-1}$) must be larger than the characteristic field associated with diffusion, carrier thermal energy ($kT = 25.7 \text{ meV}$) over the minority carrier diffusion length ($1 \mu\text{m}$)¹¹, ($\approx 25.7 \text{ meV}\cdot\mu\text{m}^{-1}$ for our samples), which is not the case here.

The PTIR image at 1.45 eV (855 nm , Fig 2c) corresponding to the band transition onset, clearly shows that the absorption occurs predominantly close to the CdTe solar cell top surface (i.e. back contact). Because the PTIR signal is proportional to the sample thickness²⁸ and the thickness variation here is much smaller ($\approx 2 \%$ not including the sample edges, see figure S1) than the PTIR signal variation (up to 800%), the bandgap contrast is unambiguously assigned to local compositional or stoichiometric heterogeneities. At 1.55 eV (800 nm , Fig 2d) approximately corresponding to the peak of the band transition, the PTIR image shows that light absorption occurs throughout the CdTe layer up to immediate

vicinity of the CdTe/CdS *p-n* junction. The signal variation over the 1.55 eV map ($\approx 20\%$) is consistent with the spectral intensity variations at 1.55 eV (Fig. 2a) for the spectra obtained at four marked locations (1-4 in Fig. 2c).” At 1.62 eV (above the bandgap, Fig. 2e), the PTIR signal variation is below 5% throughout the map, indicating homogeneous absorption.

Next we analyze the in-plane CdTe lamella sample which was etched by Ar⁺ milling after the PTIR measurements to aid the data interpretation. The etched surface reveals the underlying grain morphology (Fig 3a) due to the orientation-dependent etching rate. Figure S2 provides a comparison of the sample topography obtained before Ar⁺ milling and measured simultaneously with the PTIR maps. The PTIR image obtained by illuminating the sample at 870 nm (1.425 eV, Fig 3b), close to the onset of band transition, shows a spatial pattern correlated with the grain pattern. In contrast, for excitation energy larger than the optical bandgap, the PTIR absorption images are fairly uniform as expected (Fig 3d). The PTIR spectra (Fig 3e) obtained at different grains (marked locations in Fig 3a) contain rich information. First, the band gap of the polycrystalline CdTe absorber is smaller than the one in the single crystal CdTe and varies noticeably from grain to grain up to $19\text{ meV} \pm 6\text{ meV}$ (from $1.443\text{ eV} \pm 0.004\text{ eV}$ to $1.462\text{ eV} \pm 0.005\text{ eV}$). Second, the band transition is sharper (steeper slope) for the CdTe single crystal than that for the polycrystalline sample suggesting lower concentration of shallow impurity states in the CdTe single crystal. Third, the absorption intensity in the band tail differs significantly from grain to grain and it is significantly stronger with respect to the single crystal (see inset of Fig 3e). Interestingly, the tail absorption does not follow the exponential decay according to the Urbach rule^{39, 40} which, in contrast, is commonly observed for large-area measurements.

It has been reported that the deep defect states located in the mid-gap are responsible for the SRH recombination¹⁷. Here we show that such deep level defects can be successfully probed by PTIR measurements. Because of the relatively low concentration of deep energy states and their correspondingly weak absorbance, the laser power was increased 50-fold to obtain a measurable PTIR signal in the 954 nm to 1653 nm spectral range. Although the single crystal sample does not provide a detectable PTIR signal in this region (Fig. 3f), the polycrystalline CdTe sample displays an absorption onset corresponding to a deep level defect state ($0.44\text{ eV} \pm 0.02\text{ eV}$ less than the conduction band minimum). This feature can be attributed to Cd vacancies (V_{Cd})⁴¹ as suggested by other macro- and micro-scale studies based on photo-induced current transient spectroscopy⁴², CL⁴¹, and deep level transient spectroscopy⁴¹. The PTIR image at 1.25 eV (see Fig. S2d) does not show strong intensity variation.

We note that the grain boundaries do not display any special contrast. It is commonly accepted that grain boundaries can be either sites of recombination⁴³ or carrier collection,^{16, 44} or present distinct compositions. For example, the grain boundaries in CdTe can assist the diffusion of S⁴⁵ and other impurities; however, grain boundary passivation⁴⁵ can impede such effect and typically leads to highly efficient CdTe devices.⁴⁶ The PTIR resolution can be a complex function of the sample thermo-mechanical properties,^{21, 47} thickness and material interphases.⁴⁸ Although for thin and mechanically soft samples the spatial resolution can be better than the sample thickness (down to 20 nm, limited by the tip size);²⁷ for the mechanically rigid samples studied here, the PTIR resolution may be limited

by the sample thickness⁴⁷ and may not be sufficient to resolve the details at the grain boundaries.

PTIR can deliver valuable spectroscopic information, however, achieving a high signal to noise ratio in inorganic materials requires a relatively long imaging time. This also limits the ability to study the correlation between the microstructure or the device structure and the absorption in a statistically meaningful way. Therefore, to independently determine the spatial variation of absorption we have developed dt-NSOM (Fig. 1b), a complementary near-field technique that provides maps with a high signal to noise ratio and that is not affected by thermo-mechanical properties of the sample. In these measurements, the light passing through the aperture of the NSOM probe locally illuminates the sample, and a high efficiency Si photodetector, in direct contact with the sample, measures the light transmitted through the sample as a function of the tip location. The dt-NSOM method developed here does not conceptually differ from the illumination mode NSOM⁴⁹ but offers significant practical advantages. First, dt-NSOM can be directly implemented in a typical high-end AFM and does not require integrating the AFM with an inverted microscope (as for illumination mode NSOM). Second, the solid angle for light collection in dt-NSOM is significantly higher than what can be practically achieved with a typical inverted microscope. The same setup used in dt-SNOM could also be used for other related NSOM experiments such as scanning photocurrent microscopy.²⁵ However, illumination mode NSOM has other unique advantages; for example, it can provide broadband near-field PL spectra in each pixel.²⁴ The dt-NSOM transmitted signal (T) is normalized to the background light intensity (I_{bkg}) measured by positioning the NSOM tip in contact with the photodetector (see experimental for details):

$$T(\lambda)(\%) = \frac{I_{\text{sample}}(\lambda)}{I_{\text{bkg}}(\lambda)} \cdot 100 \quad (1)$$

where λ is the wavelength used in the measurement. This background normalization does not take into account possible differences in the tip-sample and tip-detector near-field interactions which preclude the use of dt-NSOM data for quantitative determination of material properties such as the absorption coefficient.

Figure 4 displays the topography and the corresponding dt-NSOM images of the in-plane lamella sample obtained by illuminating the sample with photon energies above the band edge (2.38 eV, 1.53 eV), close to the band edge (1.46 eV) or sub-band gap (1.37 eV, 1.27 eV). At 2.38 eV (520 nm, Fig. 4b), the signal is homogeneous because the absorption depth (≈ 100 nm) is smaller than the sample thickness (≈ 350 nm). Similarly, at 1.53 eV (810 nm, Fig. 4c, just above the band gap) light transmission is still relatively uniform with the pixel to pixel intensity variation $\approx 10\%$, which is consistent with Fig. 2d. The largest transmission contrast ($\approx 25\%$) was observed at 1.46 eV (850 nm, Fig. 4d) where the dt-NSOM maps displays strong spatial variation, similar to the PTIR image at 1.425 eV (Figure 3b). The grain boundary positions observed in the topography image are overlaid for reference on the dt-NSOM images (white lines). Interestingly, the dt-NSOM images corresponding to the

bandgap absorption edge (1.46 eV, Fig 4d) and to the shallow impurities in band tail (1.37 eV, Fig 4e), show a very different spatial distribution of bright (transparent) and dark (opaque) spots. Finally, the dt-NSOM map at 980 nm (≈ 1.27 eV Fig 4f), shows a high transmission ($T\% > 96\%$) and approaches 100 % for most locations which is attributed to the relatively low concentration of deep energy levels. Line scan profiles extracted from figure 4 clearly show the absence of correlation between dt-NSOM and surface topography (see figure S3 of the supporting information).

Many features in the dt-NSOM transmission maps show some degree of correlation with the grain structure. In a map at a particular wavelength, some grains are homogeneously (similar to the PTIR data in Fig. 3b) or partially dark or bright with the contrast edges markedly correlating with the grain boundaries (see areas delimited by the blue circles in Fig. 4d-f). Other common case is a bright or dark spot centered along a grain boundary and extending partially inside neighboring grain interior (examples encircled by red in Fig. 4d-f). This could be explained by assuming that the spatial distribution of impurities determines the contrast of the dt-NSOM maps, and that the impurities diffuse preferentially along and from the grain boundaries.

Figure 5 shows the topography and the corresponding dt-NSOM images of a cross-sectional lamella that includes the Pt layer used in the FIB process. Consistently with Fig. 4c and Fig. 2d, the dt-NSOM image at 1.53 eV (Fig S4c, 810 nm, just above the band gap), shows almost uniform contrast with vanishing light transmission through CdTe layer. At 1.37 eV (Fig. 5c) and 1.27 eV (Fig. 5d, below the band edge), the NSOM images show strong grain-to-grain variations similarly to what observed for the in plane lamella sample (Fig 4e-f). At the bandgap absorption edge (1.46 eV, Fig 5b) the transmitted light is on average weaker (absorption is stronger) close to the CdTe solar cell top surface, in agreement with the PTIR image in Fig. 2c. These results confirm a band gap gradient through the CdTe absorber thickness superimposed to the grain-to-grain band gap variation.

Overall, the results from PTIR and from dt-NSOM are very consistent and complimentary. PTIR data enable the determination of the local band gap based on the absorption spectra. The difference between the bandgap value in the single crystal and the bandgap values of the polycrystalline CdTe absorber layer is significant, $\approx 4\%$. Additionally, the local band gap varies from grain-to-grain by $\approx 1.7\%$ for the in plane lamella sample and displays an average gradient of $\approx 2.2\%$ through the absorber thickness. Bandgap values of polycrystalline CdTe samples smaller than that for single crystals have been commonly reported in room-temperature macroscale absorption or reflection measurements.⁵⁰ This is probably caused by a deviation from stoichiometry or by an incorporation of multiple defects that are both intrinsic and extrinsic to CdTe as the growth conditions for polycrystalline CdTe films are typically much farther apart from the thermodynamic equilibrium than that for bulk single crystal or for epitaxial growth.

Possible deviations from the Cd:Te stoichiometry are typically small, not exceeding a few tens of parts per million,⁵¹ and it is unlikely that they could account for band gap changes at percentage level observed in this work. The stoichiometry and the band gap can be affected by ion inter-diffusion and alloying. The best known example of the latter is given by S

diffusion from the CdS layer that forms a $\text{CdTe}_{1-x}\text{S}_x$ alloy. The $\text{CdTe}_{1-x}\text{S}_x$ bandgap decreases as a function of the x for realistic x values (up to $x \approx 0.25$, bandgap minimum).^{15, 38, 46} In a previous work on a CdTe/CdS cell with a thick CdS layer (200 nm), S diffusing from the p-n junction was detected over $\approx 1 \mu\text{m}$ away from the junction in concentrations ranging from $\approx 1 \%$ to $\approx 7\%$.^{52, 53} TEM-based EDX measurements (Fig S5 in the supporting information) were performed to identify the presence and distribution of extrinsic elements in the CdTe layer. S was detected only in an area within $\approx 100 \text{ nm}$ from the p-n junction, in agreement with other studies.⁵⁴

Charged impurities cause fluctuations of electrostatic potential. While the conduction and valence band follow the same potential, optical transitions at energies below the band gap become allowed once tunneling effects are taken into account. The concentration of charged impurities that is required to lower the apparent band gap by a few tens of millivolt, is quite high, i.e. in the range of $10^{18}\text{-}10^{19} \text{ cm}^{-3}$.⁵⁵ This level of doping is rather common for chlorine (Cl).⁵³ Cl was the only other extrinsic element, other than S, that was detected in the film by EDX measurements (Fig S5 in the supporting information). EDX maps show Cl located either along grain boundaries or homogeneously distributed in specific grains. Annealing in the presence of CdCl_2 is an important step for achieving high efficiency CdTe solar cells. In that context, Cl provides several functions: it passivates some defects, it aids the redistribution of other defects and impurities and it promotes the re-crystallization of CdTe grains.⁴⁶ Cl ions show an amphoteric behavior and can provide either n-doping (typically at lower concentrations) or p-doping (typically at higher concentration) by forming shallow defect complexes with native CdTe defects.⁵⁶ The uncorrelated light absorption patterns at the band edge and within the gap suggest that multiple extrinsic species could be involved. The concentrations of other impurities are usually lower, in $10^{16}\text{-}10^{17} \text{ cm}^{-3}$ range^{53, 57}, which is below the detection limit of EDX, and we are unable to reliably identify their nature. However, because Cl facilitates the redistribution of neutral and charged defects and impurities and forms shallow defect complexes with native CdTe defects, it is likely that the observed absorption patterns are related to the distribution of Cl interacting with other extrinsic impurities.

In summary, two novel spectroscopic techniques were leveraged to analyze the optical properties of CdTe solar cells with high spatial resolution. PTIR and dt-NSOM have complementary strengths and capabilities that are particularly useful in combination to analyze inorganic thin film materials. PTIR can provide spectra over a broad spectral range from the visible to the mid-IR directly, while dt-NSOM can currently provide light transmission images at selected wavelengths with superior signal-to-noise ratio due to more efficient data acquisition and better laser stability. The results obtained with these two methods are in good qualitative agreement providing model free and novel information. First, the band gap values in polycrystalline CdTe are smaller than for CdTe single crystal and display both grain to grain heterogeneity and a monotonic variation through the absorber thickness, implying an incorporation of a substantial number of charged impurities in the CdTe layer. Second, the bandgap gradient through the CdTe film is slightly larger than the in plane grain-to-grain variation which is likely related to a systematic compositional change either due to diffusion of extrinsic impurities from the back contact or other dynamics of impurities, e.g. evaporation, during the film growth. Third, both the impurities affecting the

bandgap values and the shallow impurities appear to be propagating along and from grain boundaries. As a result, each grain displays a specific spectrum and the absorption patterns at the band edge or just below the band gap are spatially uncorrelated. Fourth, we demonstrate here that the spatial variation of deep defects which are the most relevant for the SRH recombination process can be probed, however a more systematic assessment would benefit from further technical improvements. Specifically, the PTIR signal-to-noise ratio should be improved to adequately map the spatial distribution of mid gap defects, while the development of broadly tunable CW sources will enable the acquisition of local transmission spectra using dt-NSOM. Finally, we note that the grain boundaries do not display any special contrast in both PTIR and dt-NSOM images. However, the spatial resolution of dt-NSOM (and possibly of PTIR) is currently limited by lamella thickness and may be insufficient to capture details at the grain boundaries. We believe that the proof of concepts presented here are of broad applicability and will aid solar cell research, leading to a better understanding of a variety of photovoltaic materials and consequently help engineer them for greatest efficiency.

Experimental

A commercially available polycrystalline CdTe solar cell and (100) undoped p-type single crystalline CdTe wafer were used for this study. The CdTe solar cell consisted of a thin ($\approx 3.5 \mu\text{m}$) CdTe layer deposited by a close spaced sublimation process onto a layered structure of CdS (50 nm)/transparent conductive oxide (550 nm)/ glass (4 mm). The open-circuit voltage, short circuit current density, and fill factor are 820 mV, 23.3 mA/cm^2 , and 64.2 %, respectively, corresponding to a total area conversion efficiency of 12.2 %. The cell sealing glass was removed together with the back contact (Al + Cr/Mo) to expose the CdTe surface. After removing the back contact, thin CdTe lamellae were prepared by focused ion beam using 30 kV accelerating voltage, 0.79 nA current, and 4 mm working distance. The lamella samples were lifted out and transferred to right angle ZnS prisms to enable the PTIR measurement.

PTIR experiments were carried out using a modified commercial PTIR setup that consists of an AFM operating in contact mode and tunable pulsed laser source consisting of a nanosecond Q-switched diode pumped Nd:YAG pump laser (1064 nm) and optical parametric oscillator based on a beta barium borate non-linear crystal integrated into a single enclosure. The laser emits 10 ns pulses with $< 1 \text{ nm}$ line width at 1 kHz repetition rate in the range from 400 nm to 2300 nm. The low repetition rate of the laser assures that a new pulse will excite a sample and cantilever after they have returned to equilibrium, enabling the synchronous averaging of the signal. The typical laser spot size at the sample is $\approx 30 \mu\text{m}$. PTIR spectra were obtained by averaging the cantilever deflection amplitude from 256 individual laser pulses at each wavelength and tuning the laser at intervals of 50 cm^{-1} . The PTIR spectra were smoothed by Savitzky-Golay filter method (across 5 data points, 2nd polynomial order) to improve the signal to noise ratio. PTIR images were recorded by illuminating the sample with a constant wavelength while scanning the AFM tip. The AFM topography and the PTIR signal acquisition was synchronized so that for each AFM pixel the PTIR signal is an average over 32 laser pulses. Commercially available 450 μm long

silicon contact-mode AFM probes with a nominal spring constant between 0.07 N/m and 0.4 N/m were used.

The in plane lamella sample and a cross sectional lamella sample were transferred to a high efficiency Si photodetector for dt-NSOM measurements. Light from different diode lasers (520 nm, 808 nm, 850 nm, 905 nm, and 980 nm) was coupled to an optical fiber (50 μm core diameter / 125 μm cladding diameter) which was glued on a quartz tuning fork and tapered down to 150 nm diameter. The tapered fiber probe was used to measure the sample topography as well as local light source for the transmission NSOM measurements in non-contact mode AFM. The dt-NSOM background signal (I_{bkg}) was obtained by averaging the signal intensity over $\approx 3.15 \cdot 10^6$ individual points on the bare Si photodetector. A Lock-in amplifier was used to modulate laser power to improve the signal to noise ratio in the system. The transmitted signal was amplified by a pre-amplifier with 10^8 V/A gain.

High-resolution element maps were obtained in a 200 keV scanning transmission electron microscope (STEM) equipped with ultrafast silicon drift detectors. The dual 100 mm² EDX detectors have a combined solid angle collection efficiency of 1.9 steradians, providing ultrafast data acquisition. All EDX data were collected with a 1 nm probe at a 512×512 pixel map (≈ 0.5 nm / pixel). EDX maps were processed using the Cliff-Lorimer correction method without absorbance correction.

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Figure 1. Schematics of PTIR and dt-NSOM techniques

(a) In PTIR a tunable (400 nm to 2300 nm) pulsed laser illuminates via total internal reflection a lamella sample (inset) placed on a ZnS prism. Light absorption in the sample induces thermal expansion which triggers the AFM cantilever oscillations. The cantilever deflection (which is proportional to light absorption) is detected by the AFM detector. (b) In dt-NSOM an optical fiber probe (aperture 150 nm in diameter, black) attached to a quartz tuning fork (white) illuminates the sample (CdTe lamella, dark grey) that is in direct contact with a high efficiency photodetector (blue). The photodetector measures the light intensity transmitted throughout the sample (represented by the red sphere) with respect to the light intensity measured when the tip is in direct contact with the detector.

Figure 2.

(a) PTIR spectra of a single crystal CdTe lamella (black) and CdTe polycrystalline cross sectional lamella sample cut from PV cell measured at four locations (1-4 in panel c) (b) Topography image of the solar cell cross section displaying the CdTe, CdS, ITO and glass. The PTIR absorption images at (c) 1.45 eV, (d) 1.55 eV, and (e) 1.62 eV confirm the band gap trend. The PTIR pixel sizes are 35 nm $\times$ 35 nm.

Figure 3.

(a) Topography image of the CdTe in plane lamella sample after Ar ion milling and corresponding PTIR images at 1.425 eV (b), 1.512 eV (c) and 1.60 eV (d). The PTIR pixel sizes are $15 \text{ nm} \times 15 \text{ nm}$. (e) PTIR spectra obtained from three different color-coded locations of the in-plane polycrystalline CdTe lamella (denoted in panel a) are compared with the spectrum of a single crystal CdTe lamella sample (black). The inset highlights the band tail absorption. (f) Sub bandgap PTIR absorption spectra of polycrystalline (red) and single crystal (black) CdTe lamella samples

Figure 4.

(a) Topography image of the CdTe in plane lamella sample (the red dotted line indicates the location of the line scans reported in figure S4 of the supporting information). dt-NSOM images at (b) 2.38 eV, (c) 1.53 eV, (d) 1.46 eV, (e) 1.37 eV, and (f) 1.27 eV. The grain boundary positions identified in the topography image are overlaid on the dt-NSOM images. The dt-NSOM pixel sizes are 19.5 nm $\times$ 19.5 nm. All scale bars are 2 μ m. Blue (red) circles are examples of the areas where the absorption contrast correlates with grain boundaries (grains).

Figure 5.

(a) Topography image of the polycrystalline cross sectional lamella sample and corresponding dt-NSOM images at (b) 1.46 eV, (c) 1.37 eV, and (d) 1.27 eV. The dt-NSOM pixel sizes are 19.5 nm × 19.5 nm.