# Unveiling Defect-Mediated Charge-Carrier Recombination at the Nanometer Scale in Polycrystalline Solar Cells

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## Abstract

Solar cells made of polycrystalline thin-films can outperform their single-crystalline counterparts despite the presence of grain boundaries (GBs). To unveil the influence of GBs, high spatial resolution characterization techniques are needed to measure local properties in their vicinity. However, results obtained using single technique may provide limited aspects about the GB effect. Here, we employ two techniques, near-field scanning photocurrent microscopy (NSPM) and scanning transmission electron microscope based cathodoluminescence spectroscopy (STEM-CL), to characterize CdTe solar cells at the nanoscale. The signal contrast from the grain interiors (GIs) to the GBs, for high-efficiency cells where CdTe is deposited at a high substrate temperature (500 °C) and treated by CdCl<sub>2</sub>, is found reverse from one technique to another. NSPM reveals increased photocurrents at the GBs, while STEM-CL shows reduced CL intensity and energy redshifts of the spectral peak at the GBs. The results are attributed to the increased non-radiative recombination and the band bending mediated by the surface defects and the shallow-level defects at GBs, respectively. We discuss the advantages of sample geometry for room-temperature STEM-CL, and present numerical simulations as well as analytical models to extract the ratio of GB recombination velocity to minority carrier diffusivity that can be used for evaluating the GB effect in other polycrystalline solar cells.

KEYWORDS: near-field scanning photocurrent microscopy, cathodoluminescence, scanning transmission electron microscope, CdTe, grain boundaries, nanoscale electronic structure

#### Introduction

Thin film solar cells such as cadmium telluride (CdTe)<sup>1-3</sup>, copper indium gallium selenide (CIGS)<sup>4</sup>, and organometal-trihalide perovskites are attractive for photovoltaic applications due to the low manufacturing costs and the high power conversion efficiency (PCE). Considerable efforts have been made to understand the recombination mechanisms that limit cell performance<sup>5-7</sup>. Despite recent improvements in PCE, the lack of characterization techniques that probe the inhomogeneity of polycrystalline materials inhibits further understanding of the origin of carrier recombination in these systems. In particular, the contribution of grain boundaries (GBs) to the cell performance still remains unclear<sup>8</sup>.

Macroscale measurements, *e.g.* current-voltage characteristics<sup>9-10</sup> and X-ray diffraction<sup>11-12</sup>, have been performed to determine the reliability of the devices. However, these techniques, lacking the nanoscale mapping capability, typically provide limited information regarding the inhomogeneity or the spatial distribution of recombination centers in individual devices. The approaches to nanoscale characterization can generally be categorized into two groups. The first group is based on large area photoexcitation and local signal detection, *e.g.* using scanning probe microscopy techniques. Among them, Kelvin probe force microscopy (KPFM) is commonly used to investigate film heterogeneities, especially GBs, by probing the contact potential difference<sup>13-17</sup>. Also, conductive atomic force microscopy (c-AFM) has been used to measure the local photocurrent<sup>14, 18-21</sup>. The second group of approaches uses a local excitation, such as an optical or electron beam<sup>22</sup>, and subsequently detects the overall photocurrent or luminescence<sup>23-24</sup>. Despite the advances, all techniques with high spatial resolution are inevitably sensitive to the sample surface and the measurements may reflect the predominant surface/interfacial response but not the

actual "bulk" property. Reliable modelling and interpretation of the experimental data is rather challenging in most cases, with issues specific to each measurement technique.

In this work, we introduce two different nanoscale characterization techniques both using a local excitation to probe the optoelectrical property near grain boundaries of polycrystalline CdTe solar cell to demonstrate the need of a reliable model for interpreting the experimental data. First, we use near-field scanning photocurrent microscopy (NSPM)<sup>25-29</sup> to characterize the relative change in local photo-responses with local illumination source. In NSPM, an atomic force microscopy (AFM) probe, consisting of a tapered fiber with a small aperture at the tip, functions as a local light source, and a photocurrent map is obtained by AFM scanning. NSPM is combined with a novel transmission implementation of scanning electron microscopy (STEM) based cathodoluminescence spectroscopy (STEM-CL)<sup>30-33</sup> to measure the radiative recombination that occurs within a nanometer-sized area using thin lamellae prepared by focused ion beam (FIB) milling process. The interaction volume, in which electron-hole pairs are generated by a convergent electron beam operated at 80 kV and later recombine to generate CL signals, is determined by the beam size and the lamella thickness. We demonstrate that this measurement procedure is conducive to quantitative modelling, and physical values, such as grain boundary recombination velocity  $(S_{GB})$ , can be determined. The combination of the qualitative NSPM mapping and room-temperature STEM-CL spectroscopy provide complementary information of the local charge carrier generation, recombination and collection within grain interiors (GIs) and at GBs in CdTe thin-films. The established protocol will advance the optoelectrical characterization at nanometer resolution and provide guidelines to drive device processing optimization toward improvements in cell performance. The model presented will find applications for other polycrystalline thin-film solar cells.

## **Results and Discussion**

The current density (J) – voltage (V) characteristics of four different types of CdTe/CdS cells processed at selected representative temperatures of 310 °C (hereafter low-temperature sample) and 500 °C for CdTe layer deposition (hereafter high-temperature sample), either with or without chlorine activation treatment (see Methods for details), are displayed in Figure 1a and Table 1. The uncertainty reported here is one standard deviation of J-V measurements of at least six devices. The low-temperature cell achieved a PCE of  $(9.1 \pm 0.09)$  % after chlorine activation treatment with a dramatically higher short-circuit current density ( $J_{SC}$ ) of (20.80 ± 0.22) mA/cm<sup>2</sup>, indicating an improved photocurrent collection. This can result from the recrystallization of CdTe grains during the chlorine activation treatment<sup>34</sup>. The high-temperature cell with chlorine activation treatment achieved the highest PCE of  $(11.1 \pm 0.07)$  % through the improvement of open-circuit voltage (V<sub>OC</sub>) and fill factor (FF), while the slightly reduced J<sub>SC</sub> may result from a wider bandgap of the cell (confirmed by the STEM-CL measurements). Previous works have hypothesized that the improved PCE of the high-temperature cell with chlorine activation treatment are accounted for the homogenized CdTe grains and the passivated GBs<sup>35-36</sup>. However, this proposition remains unverified due to the lack of information regarding local charge carrier recombination along with photocurrent collection near the GBs.



**Figure 1.** CdTe/CdS thin-film solar cell characterizations. (a) Current density (J) – Voltage (V) curves of the CdTe/CdS solar cells with/without chlorine activation treatment and using different substrate temperatures during CdTe deposition (310  $^{\circ}$ C, and 500  $^{\circ}$ C) during deposition. (b) Crosssectional SEM image of a high-temperature CdTe/CdS solar cell with chlorine activation treatment. (c) Schematic of NSPM technique. A tapered optical fiber with a small aperture (200 nm) in the metal coating mounted on a quartz tuning fork illuminates the sample (top of the CdTe layer).

Figure 1c depicts a schematic of NSPM technique. Light passing through the aperture of the NSPM probe locally illuminates the sample, and the induced photocurrent is measured. Since the CdTe thin-film surface is relatively rough ( $\approx 450$  nm, peak to peak) due to the grain morphology, a smooth surface (less than 30 nm height variation) with a wedge angle of 9.5° was sculpted using FIB (Figure S1a). The AFM topography image acquired simultaneously with NSPM image shows the smooth surface where no contrast in height is related to grain boundaries. (Figure S1b). For a direct correlation between grain morphology and photocurrent, the scanning electron microscopy (SEM) image at the same location was obtained (Figure 2a,d).

T <sub>Substrate</sub> (°C)	Activation treatment	J <sub>SC</sub> (mA/cm <sup>2</sup> )	V <sub>OC</sub> (V)	PCE (%)	FF (%)
310	No	$1.3\pm0.04$	$0.48\pm0.012$	$0.2\pm0.03$	$26\pm0.4$
500	No	$13.7 \pm 0.13$	$0.57\pm0.015$	$3.2\pm0.05$	41 ± 1.1
310	Yes	$20.80\pm0.22$	$0.76\pm0.009$	$9.1\pm0.09$	$58\pm0.9$
500	Yes	$20.10\pm0.15$	$0.80\pm0.011$	$11.1\pm0.07$	$69\pm1.3$

**Table 1.** Photovoltaic performance of CdTe/CdS solar cells with/without chlorine activation treatment and annealed at different temperatures (310 °C and 500 °C)

The regions of the low- and high-temperature CdTe/CdS samples with chlorine treatment for the NSPM measurement are shown in the SEM topography images (Figure 2a,d), respectively, and the corresponding NSPM images (Figure 2b,e) are obtained with a laser wavelength of 635 nm. In the low-temperature cell, the NSPM image displays strong grain-to-grain variations in photocurrent (Figure 2b). The line-scan profile extracted from the black dotted line in Figure 2b shows the photocurrent measured at the centers of the GIs (G1 to G3, Figure 2c) are generally greater than that of the grain boundaries (GBs). Interestingly, in the high-temperature cell, a strong increase in photocurrent at the GBs and a reverse spatial distribution of photocurrent is revealed by the NSPM image (Figure 2e). The line-scan profile (Figure 2f) extracted from the black dotted line in Figure 2e shows that the photocurrent is peaked at all the three GBs (GB 1 to GB3) without any correlation to the line-scan profile of surface topography (red curve, Figure 2f). The observation suggests an enhanced collection of charge carriers excited by the near-field light source at the GB is in agreement with the previous results obtained using electron beam induced current (EBIC)<sup>37</sup>.



**Figure 2.** NSPM imaging and line-profiling of CdTe thin-films. (a) Top-view SEM image and (b) NSPM image at the same location with a laser wavelength of 635 nm for the low-temperature CdTe/CdS solar cell with chlorine treatment. (c) line profiles of the height (red) and the NSPM intensity (blue) corresponding to the black dotted line in (b). G1 to G3 denote three different grains. (d) Top-view SEM image and (e) NSPM image at the same location with a laser wavelength of 635 nm for the high-temperature CdTe/CdS solar cell with chlorine treatment. (f) line profiles of the height (red) and the NSPM intensity (blue) corresponding to the black dotted line in e. GB1 to GB3 denote three different grain boundaries. The NSPM pixel sizes are 19.5 nm × 19.5 nm. All scale bars are 1  $\mu$ m. The image quality in panel a was affected by the charging effect particularly observed for the low-temperature sample. Because the same sample was used for the correlative NSPM measurement in panels b and c, a thin conductive coating for mitigating the charging effect could create shunts for NSPM measurements, and therefore, was not adopted here.

As we know that the absorption length  $(l_{ab})$  of light in CdTe is a function of wavelength, the use of diode lasers at various wavelengths can change the excitation volume for NSPM measurements. Two additional NSPM images obtained from the same area of each sample, using 405 nm and 850 nm lasers, are shown in Figure S2 in comparison to Figure 2. For both LT and HT samples, the NSPM images, using wavelengths of 405 nm ( $l_{ab} \approx 40$  nm) and 635 nm ( $l_{ab} \approx 200$  nm), show similar photocurrent distributions. The reduced signal to noise ratio (SNR) at 405 nm (Figure S2a,c) is a caused by the increase in surface recombination due to a shallower penetration depth. In contrast, a different photocurrent distribution is observed with the 850 nm excitation (Figure S2b,d). Although the absorption length ( $l_{ab} \approx 1 \ \mu m$ ) is within the CdTe thickness ( $\approx 4.5 \ \mu m$ )<sup>37</sup>, the external quantum efficiency at this wavelength decreases drastically due to the close proximity to CdTe bandgap (approximately 830 nm). This leads to decreases in photocurrents (Figure S2b,d) compared to that when using 645 nm (Figure 2b,e) source. In general, for the high temperature sample, which shows the best cell performance among the samples measured (Table 1), the photocurrent at the GBs measured by NSPM is greater than the adjacent gain interiors. Such behavior is similar to the EBIC measurements in high-efficiency cells<sup>37-38</sup>, where GBs can counterintuitively display similar photocurrents as GIs within the space-charge-region.

We next use STEM-CL measurements at room temperature to characterize the same CdTe/CdS solar cells. STEM-CL has important differences from NPSM, and provides complementary information about the system. For example, in NPSM, the signal is acquired by carrier collection and requires both electron and hole reaching the electrical contacts. The signal therefore depends on features of the system related to the path traversed by the carriers, and therefore possesses a "non-local" element. In contrast, photon generation from radiative recombination in CL is strongly localized at the excitation position, where the density of nonequilibrium electrons and holes is maximized. We show that under experimentally relevant conditions for CdTe, the radiative recombination is directly related to the non-radiative recombination. STEM-CL, therefore, serves as a direct, local probe of spatially resolved non-radiative recombination. CL has previously been employed for determining grain boundary recombination velocity in various photovoltaic materials using a SEM<sup>39</sup>. However, the enlarged interaction volume using a SEM presents a number of challenges in quantitative interpretation of the data, primarily due to the influence of

the sample topography. The measurement probes sample properties within the enlarged interaction volume that contains sample surface, sample bulk, and grain boundaries. Disentangling the contributions from each typically requires numerical simulation<sup>39</sup> and depends on numerous system parameters. However, using STEM-CL, the lamella thickness is required to be sufficiently thin so that the electron beam can transmit through the sample. This substantially simplifies the analysis. Additionally, the surface properties can be determined independently by varying the sample thickness. Although the electron beam generates a multitude of excitations (*e.g.* secondary electrons) in addition to electron-hole pairs at the band edges, the time scale for the thermalization of these higher energy excitations is vastly shorter than for the decay of electron-hole pairs<sup>40</sup>. Therefore, STEM-CL can be used to measure the radiative recombination of the long-lived electron-hole pairs, which can be understood with the use empirical expressions that relate the beam current properties to the generation of electron-hole pairs<sup>41</sup>.

A custom-built system<sup>42</sup> was used to collect STEM-CL spectroscopy data at room temperature. CdTe samples were extracted from the high- and low-temperature CdTe/CdS solar cells with a similar wedge angle shown in Figure S1a, and further thinned into lamellae using FIB milling process. The CdTe microstructure of the low temperature cell is revealed in an annular dark field (ADF) image (Figure 3a) acquired in STEM mode. Point measurements of CL spectra are shown in Figures 3b, and c from multiple neighboring grains and GBs (marked in Figure 3a). Spectra acquired from GIs and GBs have a prominent spectral line consistently at  $\approx 1.5$  eV (Figure 3b,c), which is primarily due to band-to-band transitions during charge carrier recombination. The spectral line can be fitted using a Gaussian profile. The peak position and full width half-maximum (FWHM) are related to the bandgap, sub-bandgap states, and quasi-Fermi level splitting<sup>43</sup>. We leave a systematic analysis of these factors for future study, and here present the extracted peak positions as a function of electron beam position. The mean value of peak centers among nine different grains of the low-temperature cell is 1.5068 eV  $\pm$  0.0089 eV (the uncertainty here is determined by the single standard deviations of the fit parameters). This peak center value is in good agreement with previously reported bandgap values (1.50 eV  $\pm$  0.05 eV;  $\approx$  827 nm)<sup>44-45</sup>. However, the CL spectra show strong grain-to-grain variations, suggested by the standard deviation. Interestingly, the CL peak center and intensity obtained at the GBs are not distinct from the GIs, which is consistent with the NSPM image in Figure 2b. Also, any red or blue shifts of spectra peak position at GBs compared to those of GIs are not found. The lack of peak shifts between GBs and GIs suggests that the low-temperature cell is dominated by grain-to-grain fluctuations with respect to the density variation of non-radiative recombination centers, which can be related to structural defects and/or impurities.



**Figure 3.** STEM-CL of a low-temperature CdTe solar cell. (a) Scanning transmission electron microscopy annular dark field (STEM-ADF) image of the low-temperature cell using a minimum collection angle of  $\approx 82$  mrad, whereas the inset showing another ADF image of the marked area using a minimum collection angle of  $\approx 21$  mrad that enhances diffraction contrast to reveal a grain boundary between two grains aligned to various directions. (b) CL spectra at GI 1, GI 2 and GB 1 between the two grains. (c) CL spectra at GI 1, GI 3 and GB 2 between the two grains.

The STEM-ADF image (Figure 4a) of the high-temperature cell shows the electron beam positions where CL spectra (Figure 4b–d) are obtained from multiple neighboring grains and GBs. Compared to the low-temperature cell (Figure 3), the CL spectra here show higher peak intensity by one order of magnitude with a similar lamella thickness and strong GI-to-GB variations in the CL peak. The CL intensities at all GBs are suppressed compared to GIs. This reduction is due to either increased non-radiative recombination at GB, or to carrier separation at the GB, as we discuss in more detail below. The mean value of CL peak centers extracted from GIs (1.5143 eV  $\pm$  0.0019 eV) among six different grains of the high-temperature cell has a higher value with a lower standard deviation with respect to that of the low-temperature cell. Interestingly, the CL peaks at the GBs (red curves in Figure 4b–d) show an averaged redshift of 0.0025 eV  $\pm$  0.0006 eV compared to the GIs (blue and green curves in Figure 4b–d).



**Figure 4.** STEM-CL of a high-temperature CdTe solar cell. (a) STEM-ADF image of the high-temperature cell. (b) CL spectra at GB 1 and the two adjacent grains (GI 1 and GI 2). (c) CL spectra at GB 2 and the two adjacent grains (GI 3 and GI 4). (d) CL spectra at GB 3 and the two adjacent grains (GI 5 and GI 6). CL spectra at the three GBs show attenuated peak intensity and redshifts in the peak center. The spectral redshift is typically observed throughout the GBs in the high-temperature cells.

We resolve local variations in the CL peak by scanning the electron beam across a GB and into a neighboring grain in the high-temperature sample (Figure 5a). The CL peak area – integrated peak intensity within the peak width derived by a Gaussian fit – are measured as a function of the distance from the GB (Figure 5b). The CL peak area increases gradually and plateaus eventually when the electron beam is located at  $\approx 100$  nm away from the GB. The variations in CL intensity can be fitted using  $(1 - \exp(-x/L_D))$ , where a length parameter  $(L_D)$  of  $(93 \pm 8)$  nm results in an optimal fit. The uncertainty here is defined by the single standard deviation of the fit parameter.



Figure 5. STEM-CL line-profile across a GB and an adjacent GI. (a) STEM-ADF image and (b) CL peak area as a function of distance from the GB (yellow) and error bars represent the uncertainty of spectrum fitting using a Gaussian profile. The CL intensity profile is then fitted using  $(1 - \exp(-x/L_D))$ , where  $L_D = (93 \pm 8)$  nm gives an optimal fit.

The likely origin of the contrast at GBs in both NSPM and STEM-CL measurement is the change in chlorine (Cl) distribution with annealing temperature. Energy dispersive X-ray spectroscopy (EDX) line-scan profiles obtained in STEM mode revealed a small amount of Cl but its distribution was almost flat and even across a GB and the two adjacent CdTe grains in the low-temperature cell (Figure S4a). This suggests that the actual amount of Cl in the low-temperature sample may be below the EDX detection limit. Note that the composition at the GB is off from the stoichiometry and toward a slightly Te-rich and Cd-deficient condition. This may cause the GB to have a higher majority carrier concentration (more p-type) than the two adjacent grains<sup>46</sup>. We

found the slightly Te-rich and Cd-deficient composition as well as the flat-distributed Cl were consistent to any GBs and two adjacent grains throughout the entire sample. In contrast, Cl was found to segregate at the GBs in the high-temperature cell with a higher Cl concentration than the GIs (Figure S4b). This may result from the different average grain size observed in the low- and high- temperature samples. The high substrate temperature during CdTe deposition resulted in a distinct microstructure that has an increased average grain size in the high-temperature cell<sup>37</sup>, and the grain boundary area in the CdTe thin-film is therefore decreased. One assumes that an equal amount of CdCl<sub>2</sub> is incorporated into two CdTe thin-films with a varied average grain size, and the incorporated Cl is segregated at the grain boundaries during the activation treatment. The large average grain size should lead to a higher Cl concentration at the grain boundaries. A Cl concentration of 10<sup>18</sup> cm<sup>-3</sup> to 10<sup>19</sup> cm<sup>-3</sup> in CdTe has been reported to induce the donor-acceptorpair recombination that varies in energy up to a few tens of millielectronvolts from the band-toband recombination<sup>47</sup>, leading to a lower energy of the CL peak center. Therefore, we believe that Cl segregation is responsible for the energy redshift of the CL peak at the GBs. Furthermore, redistribution of the neutral and charged defects at GBs, caused by the excess Cl, possibly forms shallow defect complexes<sup>48</sup>. Cl atoms that occupy the Te sites at GBs may convert these GBs into n type, since the substitutional defects ( $Cl_{Te}$ ) create donor states that donate electrons<sup>46</sup>. The n-type GB can create a p-n-p junction with the two adjacent grains<sup>35</sup>, as illustrated in Figure S3. The builtin electric field within the GB depletion layer can drive the excess electrons toward the GBs while holes are repelled. The inversion at GBs is known to improve photo-generated carrier collection<sup>35,</sup> <sup>49</sup>, in good agreement with photocurrent enhancement at GBs observed in the NSPM images (Figure 2e). On the other hand, although this scenario may suggest that the reduced CL signal at the GBs is due to carrier separation, our numerical modeling shows that the high generation rate

density associated with electron beam excitation in the low injection level screens the built-in electric field in the vicinity of the GB thereby neutralizing the defect level. This screening precludes carrier separation from causing the reduced CL signal and therefore indicates that the GB acts as a recombination center under STEM-CL experimental conditions.

As we know, the STEM-CL geometry is more conducive to quantitative modeling than a traditional SEM-CL geometry for several reasons. First, the film thickness is much smaller than bulk length scales of the system (e.g. the bulk diffusion length). We can therefore assume that system variables are approximately uniform along the film thickness, which reduces the dimensionality of the problem to 2-D. Additionally, we expect the sample preparation leads to high surface recombination velocity S. The corresponding surface contribution to defect-mediated recombination rate is 2S/t, where t is the film thickness, and the factor of 2 comes from the presence of top and bottom surface. For t = 250 nm, the surface recombination contribution is much greater than bulk recombination for  $S\tau_{\text{bulk}} \gg 125$  nm. For  $\tau_{\text{bulk}} = 10$  ns, this corresponds to  $S \gg 10^3$  cm/s. We can therefore assume the bulk contribution can be neglected, and the effective defect-mediated recombination lifetime  $\tau_{eff}$  is determined by the film thickness,  $\tau_{eff}$  = t/(2S). This assumption can be verified by measuring the thickness-dependent CL peak area, as described in the Data Processing of STEM-CL section of the Supporting Information (Figure S7). Note that varying the lamella thickness (t) changes the effective bulk lifetime, providing another experimental knob. The CL peak area can be fit to a quadratic function  $A(t - t_{min})^2$ , and the offset  $t_{min}$  indicates the minimum lamella thickness that leads to an acceptable signal-to-noise ratio (SNR). The thinnest sample area for all our measurements has a thickness greater than the derived  $t_{min} - 1.6$  times of electron inelastic mean free path in CdTe<sup>50</sup>. Therefore, we believe that CL signal artifacts caused by transition radiation should not present in our measurements<sup>24</sup>.

Finally, the carrier generation profile from the high energy electron beam is uniform along device thickness and the beam spot size R is much smaller than other length scales of the problem. The beam can therefore be modeled as a delta-function excitation in 2-D. As described earlier, the geometry of the system removes the sample/surface distinction and substantially simplifies the analysis.

The CL intensity depends on the carrier generation rate (or beam current) and on the rates of radiative and defect-mediated recombination. The dependence of the CL intensity on beam current (*e.g.* linear vs. quadratic) can be used to determine the operating regime (*e.g.* low injection vs. high injection). We observe a linear dependence for beam currents ranging from 0.04 nA to 2.15 nA. This indicates that the experiment takes place in the low injection regime (see Supporting Information, section of Data Processing of STEM-CL for analysis details), where defect-mediated recombination dominates over radiative recombination and the maximum non-equilibrium carrier density is much less than the equilibrium carrier doping density.

To assist in quantitative analysis of the CL data, we perform numerical simulation of the driftdiffusion-Poisson equation in 2-D using the numerical package Sesame. The system is modeled as uniform p-type CdTe with non-selective contacts and a single grain boundary. We considered a grain boundary with varying defect spectra (see Supporting Information for more modeling details). We find that for realistic values of beam current, the grain boundary defects in the vicinity of the beam are neutralized by non-equilibrium carriers, and that the electrostatic band-bending around the grain boundary is screened. The problem therefore maps to simple diffusion in 2-D with enhanced recombination at the grain boundary core. We find that the analysis of van Rooskbroeck<sup>51</sup> accurately describes the numerical solutions in both low and high injection regimes (see Supporting Information), so that we can reliably use the following result for the CL as a function of distance away from the grain boundary<sup>51-52</sup>:

$$CL(x) = CL_{\text{bulk}} \times \left(1 - \frac{S_{\text{GB}}}{S_{\text{GB}} + \nu_{\text{diff}}} \exp(-x/L_d)\right), \tag{1}$$

where  $CL_{\text{bulk}}$  is the signal in the GI, x is the distance away from the GB,  $L_d = \sqrt{D_n \tau_{\text{eff}}}$  is the diffusion length and  $D_n$  is the electron (minority carrier) diffusivity,  $v_{\text{diff}} = \sqrt{D_n / \tau_{\text{eff}}}$ . We find that the experimental data is well-described by Eq. (1) with  $L_d = (93 \pm 12)$  nm (Figure 5b). The short diffusion length is a consequence of the short effective lifetime caused by the sample surface recombination velocity. The short diffusion length is an advantage because the grain size is much greater than the small diffusion length, so that grain boundaries can be treated independently. The contrast of the CL signal at the grain boundary is included in Eq. (1), and is given by:

$$\eta = \frac{CL_{\text{bulk}} - CL(GB)}{CL_{\text{bulk}}} = \frac{S_{\text{GB}}}{S_{\text{GB}} + v_{\text{diff}}} = \frac{(S_{\text{GB}}/S)}{(S_{\text{GB}}/S) + (2L_d/t)}.$$
 (2)

The form of this equation can be motivated by noting that carriers may either diffuse away from the grain boundary or recombine at the GB core. The fraction of carriers recombining at the GB core is given by the relative rate of GB recombination. We again verify that Eq. (2) accurately describes the numerical simulation (see Supporting Information), and can confidently apply it to the experimental data. Some algebra leads to the following relation for the ratio of grain boundary recombination velocity to minority carrier diffusivity in terms of experimentally measured quantities:

$$\frac{S_{\rm GB}}{D} = \left(\frac{\eta}{1-\eta}\right) \frac{1}{L_D} \,. \tag{3}$$

Taking the experimental contrast value  $\eta = 0.5 \pm 0.05$  and  $L_D = (93 \pm 12)$  nm yields  $S_{GB}/D = (1.07 \pm 0.14) \times 10^5$  cm<sup>-1</sup>. Taking D = 5 cm<sup>2</sup>/s leads to  $S_{GB} = (5.35 \pm 0.70) \times 10^5$  cm/s, which is similar to values found in previous works.<sup>53</sup> The advantage of the TEM specimen geometry is the reliability and simplicity of Eq. (3). As discussed in the Supporting Information,

*a priori* knowledge of doping together with thickness-dependent CL measurements enables further quantitative analysis to determine  $S_{GB}$  and D independently. Obtaining these values based on the STEM-CL measurement at zero bias is useful to extrapolate device efficiency for typical p-n junction devices at the operating condition. This extrapolation relies on models, such as one-dimensional p-n junction model for J-V response. Such models have been recently developed for polycrystalline materials<sup>54-55</sup>.

## Conclusion

In summary, the nanoscale electrical and optical properties of CdTe solar cells were analyzed using two spectroscopic techniques using local excitations. NSPM and STEM-CL have complementary capabilities that enable us to observe the inhomogeneity of the samples with high spatial resolution. NSPM can provide photocurrent images with local light illumination in the near field at selected wavelengths that define the excitation volume/depth. On the other hand, STEM-CL provides the information of radiative recombination by observing luminescence excited by a fast (80 kV) and narrow (less than 10 nm) electron beam. The information obtained from the two complementary techniques includes multiple stages of evolution with a post-annealing of Cl treated solar cells deposited at different substrate temperatures, particularly the role of GBs, affecting the overall efficiency of the cells. First, photocurrent mapping in the low-temperature sample (310 °C) displays only grain to grain heterogeneity, while GBs become the major photocurrent collection path with higher substrate temperature (500 °C) during the deposition. We attribute this to reduced recombination at GBs due to p-n junction induced by Cl segregation as measured by STEM-EDX. Second, the red shift of the CL spectra peak and reduction of CL intensity at GBs in the high-temperature cell are attributed to Cl segregation to GBs, and enhanced recombination which occurs due to screening of the GB built-in potential. Third, we showed that the room temperature STEM-CL measurements are conducive to straightforward modelling and allow for quantitative determination of non-radiative recombination at GBs. We believe that the combination of two different techniques and the model presented here are of broad applicability and will lead to a better understanding of the role of GBs in CdTe and other polycrystalline thinfilm solar cells.

#### Methods

#### **Solar Cell Fabrication**

CdTe thin film solar cells were manufactured in the superstrate configuration on commercial fluorine doped tin oxide (FTO) coated float glass with a substrate size of 10 cm x 10 cm. The deposition of the CdS and the CdTe layers were carried out by close space sublimation technique (CSS) using an in-line pilot equipment installed at Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology (FEP). The raw materials CdS and CdTe granules were evaporated from heated crucibles in vacuum at a pressure of 0.1 Pa. Before coating, the substrates were heated to the selected substrate temperatures of 310 °C and 500 °C. The substrate temperatures were then stabilized to  $(310 \pm 10)$  °C for low temperature deposition and to  $(500 \pm 10)$  °C for high temperature deposition. The layer thickness was between 130 nm and 150 nm for the CdS window layer and between 4 µm and 5 µm for the CdTe absorber layer. The chlorine activation treatment was done by wetting the CdTe surface with a saturated methanolic CdCl<sub>2</sub> solution and subsequent heat treatment in a muffle furnace for 25 min at 400 °C in air atmosphere. The samples were etched with nitric and phosphoric acid in aqueous solution (NP-etch) to realize a tellurium enrichment which serves as a primary back contact. A secondary gold contact layer

with a thickness of 130 nm was deposited by DC magnetron sputtering. Laser scribing was used for preparation of 1 cm  $\times$  1 cm solar cells.

## **NSPM**

Light from a diode laser (635 nm) was coupled to an optical fiber (50  $\mu$ m core diameter / 125  $\mu$ m 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 measuring local photocurrent in non-contact mode AFM. A Lock-in amplifier was used to modulate laser power to improve the signal to noise ratio in the system. The photocurrent signal was amplified by a pre-amplifier with 10<sup>7</sup> V/A gain.

#### Cathodoluminescence in a STEM

STEM-CL measurements were performed at room temperature using a customized spectroscopy system attached to a monochromated scanning transmission electron microscope equipped with a Schottky field-emission gun and a wide spacing ( $\approx 5.5$  mm) between the objective lens pole-pieces. An aluminum parabolic mirror with a solid angle of 1.5 sr is placed underneath the sample to collect the CL signals.<sup>42</sup> Electron beam current can be controlled from 0.04 nA to 2.2 nA by adjusting the monochromator focus and the condenser lens current. CL peak characterization is conducted by fitting the peaks and background with a Gaussian profile and a 3<sup>rd</sup> order polynomial function, respectively to obtain CL intensities (amplitudes) and peak energies (centers).

#### ASSOCIATED CONTENT

#### Supporting Information.

SEM and AFM micrographs of CdTe sample morphology, NSPM data acquired using 405 nm and 850 nm wavelength excitations, illustrated band diagram near a n-type grain boundary in CdTe, STEM-EDX line-scan profiles revealing elemental distribution across grain boundaries in the lowand high- temperature cells, numerical calculations of minority carrier recombination in polycrystalline CdTe, quantitative analysis of STEM-CL data (PDF).

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## **Author Contributions**

Y.Y. and W.-C.D.Y. conceived the project and designed the experiments. Y.Y., D. Ha, and H.P.Y. performed the NSPM measurements, whereas Y.Y. and H.P.Y. prepared the CdTe samples. W.-C.D.Y. conducted the CL and EDX measurements in a STEM. The CdTe solar cells and device performance data are provided by D. Hirsch. All authors contributed to the data analysis. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. <sup>§</sup>Y.Y. and W.-C.D.Y. contributed equally to this work.

#### Notes

The authors declare no competing financial interest.

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#### NSPM Cond. Lens Obj. Lens Obj. Lens CdTe Lamella GB GB CB3 Obj. C. Optics

# SYNOPSIS (For Table of Contents Only)