ADVANCED FUNCTIONAL MATERIALS

Supporting Information

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Supplementary material for

Understanding the Beneficial Role of Grain Boundaries in Polycrystalline Solar Cells from Single Grain Boundary Scanning Probe Microscopy

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Further characterizations of grain boundaries

EBIC: Electron-Beam Induced Currents (EBIC) can reveal the location and direction of internal fields. EBIC showed contrast between GBs and grain bulk, when mapped under a Schottky (evaporated Au) contact. The EBIC signal is sensitive to the surface roughness, which could not be avoided by polishing without chemically modifying the surface to be measured. In addition, the resolution of EBIC is dictated by the diffusion length, which is (at room temperature) only slightly smaller than the grain size in p-CdTe,[1] making the distinction between fields related to different GBs difficult. EBIC will be useful for mapping flat CdTe, which can be obtained after removal of the glass and the SnO_2 layer from a cell, as done by Galloway et al.[2] To minimize the excitation volume low accelerating voltages are needed. To avoid high-injection conditions beam currents should be as low as possible. If both conditions can be met this can also circumvent electron-beam – induced surface reduction of the semiconductor.[3]

Remote-EBIC (REBIC)[4] was performed with bias applied between two remote contacts and EBIC measured in the area between them. REBIC did not show any distinct features at the GBs, probably due to the high lateral resistivity of PX CdTe, with the current having to cross many GB barriers.

Spatially resolved current-voltage (I-V) measurements: Lateral I-V measurements (across a given GB, parallel to the CdTe plane) can provide information about the electrical activity of the GB barrier. In analyzing the results, the contact-CdTe surface barrier should be taken into account, as well as the possible presence of sub-surface GB barriers that the current might have to cross.

I-V curves using a conductive AFM tip

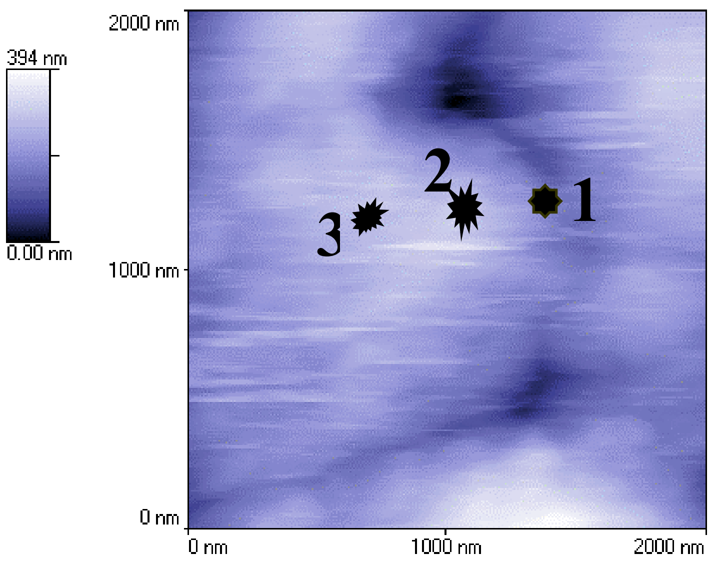
These were measured with the tip placed at different distances from a GB, on the CdTe grain surface, and with the SnO_2 electrode servinged as the other contact, as shown in Fig. S1. There I-V curves are shown as measured at varying distance from the GB. It is clear that the closer the spot is to a GB the higher the current at forward bias (i.e., the p-type CdTe sample positive). This means that the conductivity near the GBs is higher than farther away from them. This would not be possible if the GBs were purely depleted, but fits well with our model of an inverted core of the GBs.

In these types of measurements one has to consider the possibility that the tip–surface contact resistance, which is expected to be high with any metal contacting p-CdTe,[5] may control the measurement. Thus, one should be aware of changes in tip-resistance during measurements, which could lead to artifacts. For example, metal-coated tips showed rapid deterioration of the metallic coating, especially under large applied bias. Such wear has to be avoided to be able to compare measurements from different locations on the surface, and even more so if comparing different samples. Therefore, in the experiments shown here, frequent checks of the tip conductivity on a reference conductive sample were made and the tip was replaced when needed. We note that highly doped n-Si tips are unsuitable for work with samples such as p-CdTe. Highly doped p-type tips, if available, such as B-doped diamond tips, or sufficiently sharp full metal tips would be suitable.

I-V measurements using SEM

Such experiments were conducted to measure the lateral current transport across a known number of GBs between the contacts. One electrode was an evaporated Au micro-contact, with a width of about 1 μm. A shadow mask was used since photolithography was not suitable due to remains of photo-resist material found on the rough CdTe surface. The second (mobile) contact was a W needle with a tip width similar to that of the microcontact. The sample was CSS-deposited CdTe on an insulating Al_2O_3 substrate, to prevent the measured current from passing through a conductive substrate. Bias was applied to the W probe. In the dark the conductivity was too low to be measured, probably due to large resistance at the W-CdTe contact. Therefore the measurement was conducted under visible illumination (W-Halogen lamp), installed inside the SEM chamber. The beam and detectors were turned off after locating the W tip in a given place and before the I-V measurement. A long waiting time was needed between turning off the e-beam and the I-V measurements, as deep traps in CdTe are charged by the beam electrons, and their discharge time can be rather long (in the scale of minutes).[6]

The I-V curves had the shape of a diode curve, with forward bias corresponding to negative bias applied to the W (Fig. S2). This may be explained by a relatively good contact between the evaporated Au and the p-CdTe, and a (Schottky) barrier at the W – p-CdTe contact. Measurements with a different number of GBs between the contacts showed increasing forward bias currents with decreasing number of GB’s. Naturally, also the distance between the contacts grows with the number of GB’s. Therefore, we calculated the resistivity per unit distance between the contacts (assuming constant contact area) from the slope of the I-V curve in forward bias. In this way we find increasing resistivity with increasing number of GB’s, as expected for an increasing number of barriers.



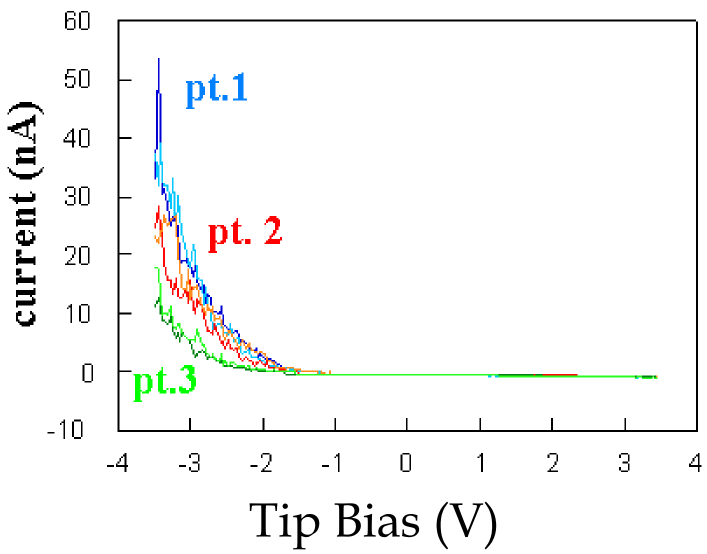


Figure S1: TOP: AFM image of PX CdTe surface using a Topometrix Discoverer microscope.

BOTTOM: I-V curves taken at the points indicated at the locations given on the topography image. For these measurements metal-coated tips were used.

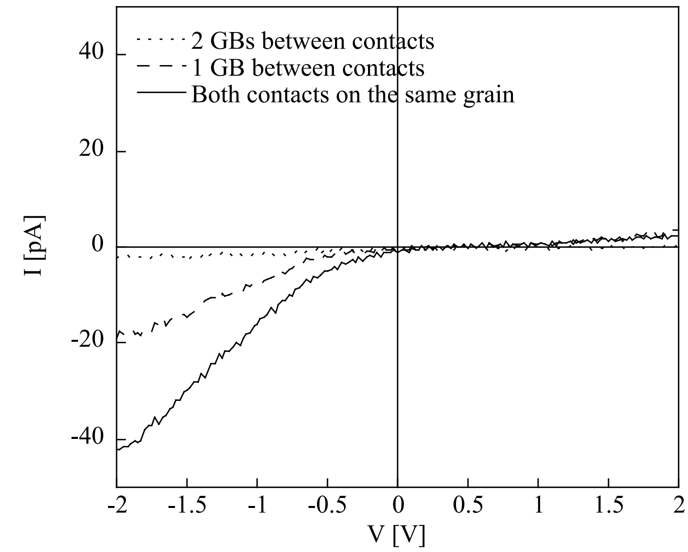


Figure S2: Current-voltage (I-V) curves measured with different numbers of GBs between the contacts (see text), in a 2-probe configuration in SEM under illumination in the visible range.

References:

[1] P. R. Edwards, S. A. Galloway, and K. Durose, *Thin Solid Films* **2000***, 361-362*, 364.

[2] S. A. Galloway, P. R. Edwards, and K. Durose, *Sol. Energy Mater. Sol. Cells* **1999**, *57*, 61.

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[5] K. D. Dobson, I. Visoly-Fisher, G. Hodes, et al., *Sol. Energy Mater. Sol. Cells* **2000**, *62/3*, 295.

[6] I. Lubomirsky, in *Ph.D. thesis, Materials and Interfaces* (Weizmann Inst. of Science, Rehovot, 1997).