Supplementary Information

Insights into interface and bulk defects in a high efficiency kesterite-based device

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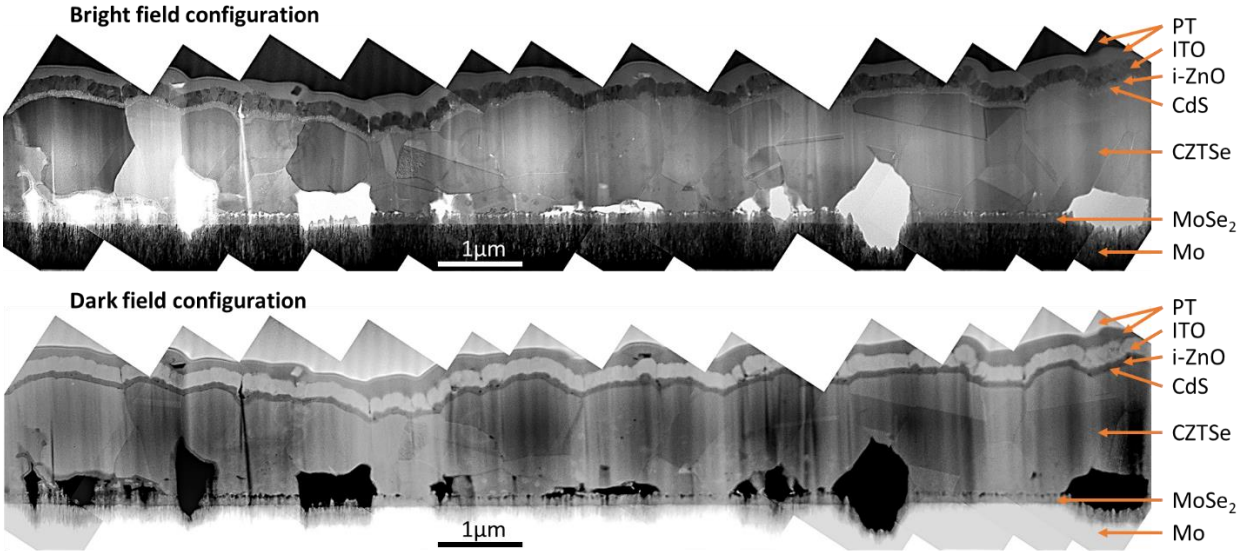

Fig. S1 Collage image of a series of cross-sectional STEM images of a CZTSe-based solar cell in both bright field and dark field configurations. Each image is acquired as de-magnified as possible. The different observed layers of the device are indicated, including the platinum layers added during FIB sample preparation.

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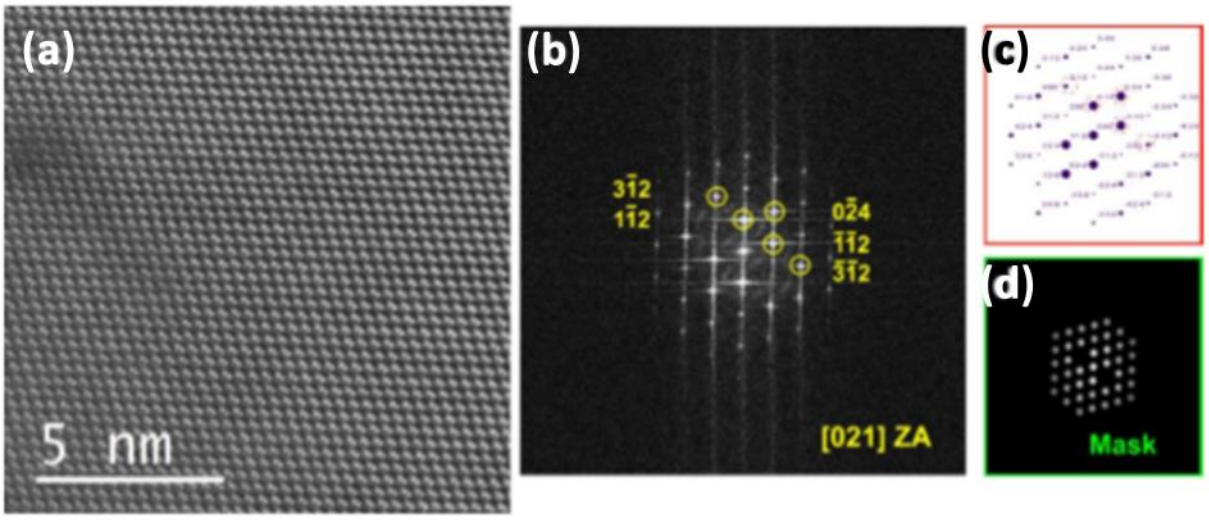

Fig. S2 (a) H-Res HAADF image of a CZTSe grain. (b) FFT for the whole image in (a). [021] ZA is clearly resolved. (c) Theoretical computation for the reciprocal space of the modeled kesterite atomic cell (TEM-UCA software, University of Cádiz). (d) Mask generated to filter the noise in the HAADF image in (a).

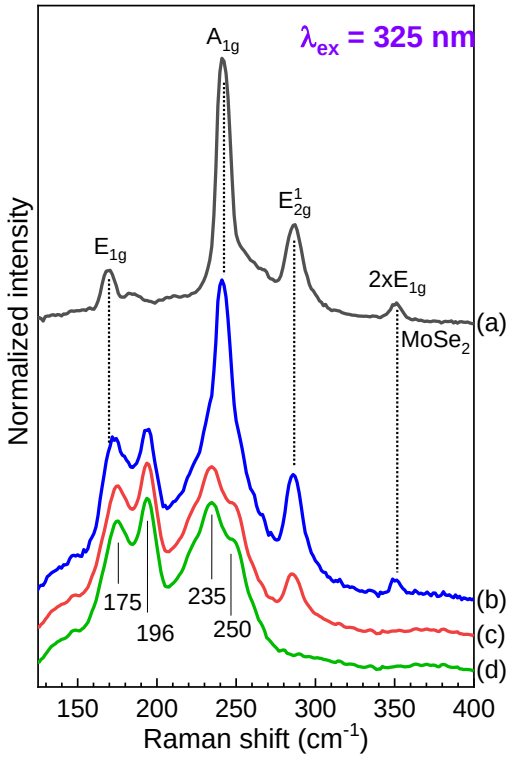

Fig. S3 Raman spectra measured under 325 nm excitation wavelength at the back interface from the (a) back contact side and (b) CZTSe side. Here (c) is CZTSe spectrum at back interface region obtained after subtracting the $MoSe_2$ spectrum (a); and (d) is CZTSe spectrum at back interface region obtained after subtracting the $MoSe_2$ peaks taking into account the different crystal texture.

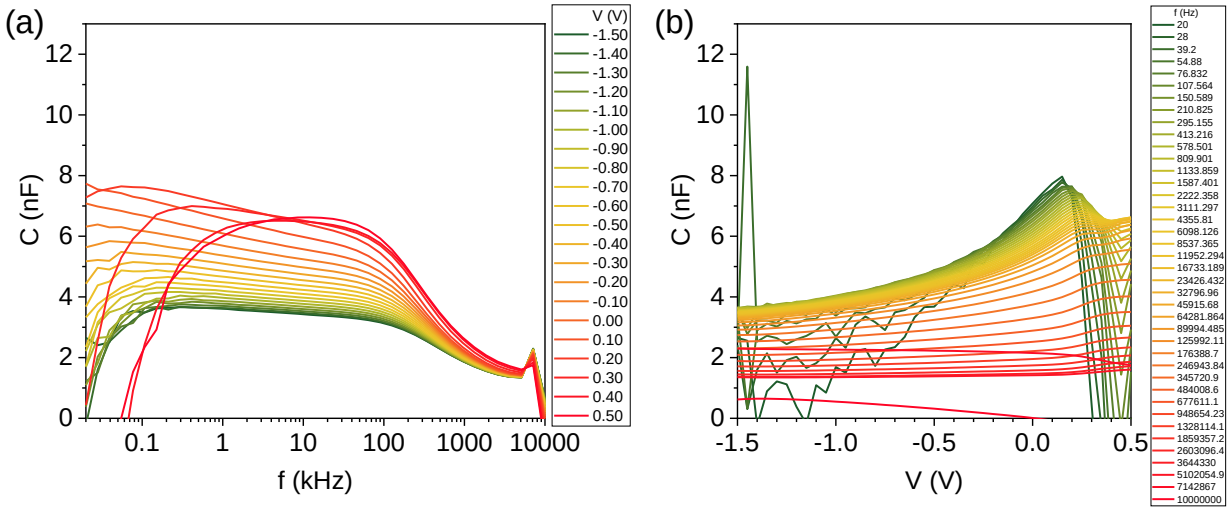

Fig. S4 (a) Measured capacitance of a CZTSe-based device in function of the AC frequency for different applied bias voltages. (b) Measured capacitance of a CZTSe-based device in function of the applied bias voltages for different AC frequencies. Capacitance values tending to zero are due to parasitic effects produced by the series resistance and the inductance which dominate at the corresponding AC frequencies and applied DC voltages.

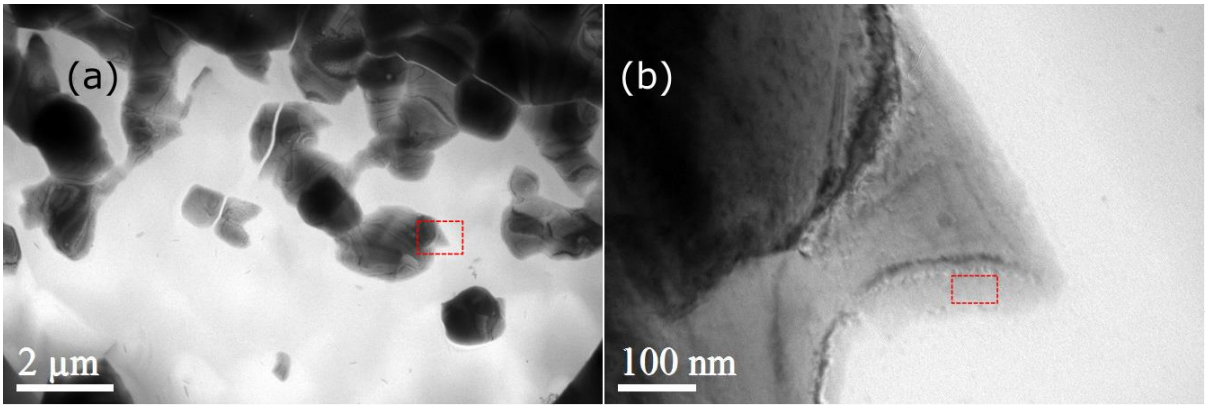

Figure S5. (a) Planar view TEM image of the front interface of a CZTSe absorber after removing the ITO/i-ZnO window layer and CdS buffer layer by HCl etching. Some grains delimited by bright boundaries can be distinguished. The grain boundaries are regular and narrow, so they should have a low impact on V_{oc} deficit. The large brighter areas correspond to empty regions that are produced during the ion milling, so they are not an intrinsic characteristic of the material (b) TEM image of the region indicated by a dashed rectangle in (a) with increased magnification. The dashed rectangle in this image indicates the region shown in Fig. 10a. Contrast differences are produced by thickness differences due to the low control of the ion milling by PIPS and rounded boundaries are also produced by material removing during ion milling.

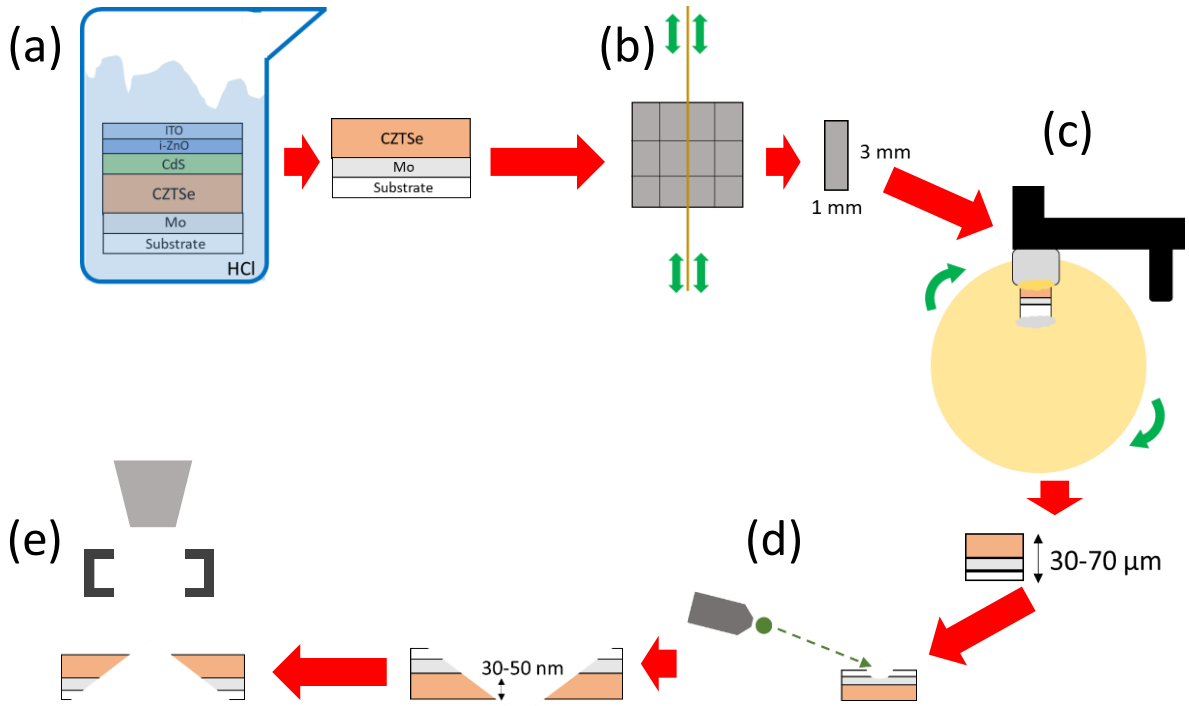

Fig. S6 Diagram of the sample preparation for planar view TEM study. (a) Removal of the ITO/i-ZnO window layer and the CdS buffer layer by HCl etching. (b) Etched sample cutting to obtain a piece with a CZTSe area of 2.5 × 2.5 mm^2 (with ~3mm thickness) (c) Polishing from the substrate side with a series of consecutively finer grain abrasive diamond films to obtain a sample thickness between 30 and 70 µm. (d) Final thinning by ion milling using a Precision Ion Polishing System (PIPS) to obtain a CZTSe region with thickness between 30 and 50 nm. (e) Planar view study of CZTSe absorber surface by TEM.

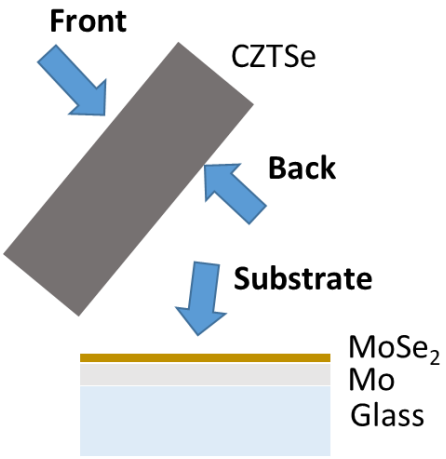

Fig. S7 Scheme representation about the mechanical lift-off for the interface Raman characterization.