Enhancing CZTSSe solar cells through electric field induced ion migration

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Figure S1 – Unbiased 10nm NaF TOF-SIMS

Figure S1 – TOF-SIMS measurements of 10nm NaF device





Figure S2 - Difference of element concentrations between the positively biased sample labelled +10V (positive voltage at cell surface) and the negatively biased sample labelled -10V.





Figure S3 - TOF SIMS measurement of Na, Se, Zn and Mo concentration in bare CZTSSe with 30nm NaF layer. The Black line refers to a positive bias applied, and red refers to a negative bias applied to the samples.

The measured samples were not part of the same absorber, but belonged to the same batch, so some changes to Se levels can be seen. In spite of this, the relative distribution is quite similar. It is evident that after application of a negative bias voltage (sample surface charged negative) the Na and Se ion locations and dispersions in the absorber change, as they are pushed away from the surface. All the TOF-SIMS data was normalized in accordance with the Molybdenum substrate signal strength, as all samples were deposited on the same Mo foil.

Figure S4 KPFM setup:

Figure S4 - Illustration of KPFM setup. (a) 1^{st} pass - Capturing topography and applying a bias voltage between tip and sample. (b) 2^{nd} scan the tip is raised 30nm above the surface and the contact potential difference is recorded.

The CZTSSe device is based on a flexible Molybdenum foil, the KPFM scan has two parts:

The first part involves scanning the surface topography while applying a positive or negative voltage bias between the tip and the sample. A surface topography image is produced as the tip scans line by line. In the second part the bias voltage is stopped, the tip is raised 30nm above the surface and the 1st scan topography line is traced keeping a 30nm distance from the surface. At this point the charge difference between the tip and surface will cause a deflection of the tip, the deflection is negated by applying a DC voltage to the tip. The voltage that nullifies the potential difference between the tip and sample is recorded and referred to as Contact Potential Difference (CPD).

Figure S5 shows an enlarged image of the 30nm NaF layered sample exhibiting a clear change to GB-GI contrast as well as surface features becoming more prominent.



Figure S5 - Enlarged images of 30nm NaF layered sample (a) Biased at +1V (b) unbiased (c) Biased at -1V

Evidence of Ionic motion:

To verify the changes to the images are not caused by a measuring artifact that occurs during biasing process (such as charged particles that stick to the tip, thus changing the tip work function), images were taken of surface topography after applying an external bias to the samples. The bias was applied by placing the samples between two conducting plates and connecting the later to a 10V voltage source. Figure S6 shows that changes in grain boundaries are reproduced:



Figure S6 – Contact potential differences [mV] of CZTSSe with 30nm layer of NaF. (a) +10V bias applied externally. (b) no bias applied. (c) -10V bias applied externally.

In addition, Temporal kinetics measurements were conducted, the AFM tip was placed at a point on a grain boundary, a bias voltage (+/-1V) was applied to the tip and the CPD was measured over time. The results can be seen in Figure S7:



Figure S7 – Kinetics measurements showing CPD change over time when a bias is applied. (a) No Na (b) 10nm NaF (c) 30nm NaF

To obtain the difference between grain boundaries and grain interior, 10-line scans going across the grain boundary, as well as the entire grain, were extracted - as seen in Figure S8. Each line is 5 pixels thick, averaging 5 data points, to increase measurement accuracy. The grain boundary was found visually, and the length extracted was between 20-40nm, depending on the line scan length and corresponding data points acquired. Standard deviation method was used to calculate the errors.



Figure S8 - Example of line scans extracted from AFM data to obtain grain boundary-grain interior difference.





Figure S9 – I-V measurements of CZTSSe solar cells with different Na concentrations, normalized to the pre bias values. (a) Normalized Voc no Na sample (b) Normalized Voc 10nm NaF (c) Normalized Voc 30nm NaF (d) Normalized Jsc no Na sample (e) Normalized Jsc 10nm NaF (f) Normalized Jsc 30nm NaF (g) Fill factor (FF) no Na (h) FF 10nm NaF (i) FF 30nm NaF (j) Efficiency no Na (k) Efficiency 10nm NaF (l) Efficiency 30nm NaF.



Figure S10 – XRD measurements of CZTSSe absorbers – No NaF (Black), 10nm NaF (Orange).



EDS measurements show no contaminations are present according to the elemental peaks:



Figure S11 – EDS measurements of CZTSSe absorbers – (a) No NaF layer (b) 10nm NaF layer

Many reports have been made showing changes in depletion width and carrier concentration as one of the effects of Na doping. [*Adv. Sci.* **2020**, 7, 1903085, *Nat. Commun.* **2019**, 10, 2959] Our samples also confirmed that there were such effects through C-V measurements. The depletion width (W_d) can be determined by using $\varepsilon \varepsilon_0 A/C$ at zero bias.

$$C = \frac{\varepsilon \varepsilon_0 A}{x} \tag{1}$$

As a result of applying this calculation, it was found that the No NaF sample had W_d of 103 nm, and the 10 nm NaF sample increased it to 132 nm. ε_0 is the vacuum permittivity, ε is the dielectric constant of kesterite, A is the cell area, and x is the distance from the junction interface. ($\varepsilon_0 = 8.85 \times 10^{-12} F \cdot m^{-1}$, $\varepsilon = 8.6$, $A = 0.3 \ cm^2$) In addition, carrier concentration was calculated using the following equation.

$$N_A = \frac{-2}{q\varepsilon\varepsilon_0 A^2 [\frac{d\left(\frac{1}{C^2}\right)}{dV}]}$$
(2)

The carrier concentration of the No NaF sample was $2.27 \times 10^{16} cm^{-3}$, and the 10 nm NaF sample showed a smaller value of $1.34 \times 10^{16} cm^{-3}$. Additionally, defect level and defect density were confirmed through AS measurement. Both factors showed a tendency to decrease when Na was doped. TR-PL results confirmed that the carrier life-time increased due to the decrease in defect level and defect density due to the Na doping effect.

The results can be seen below:







Figure S12 – (a) carrier concentration vs. distance from the junction for CZTSSe w/o NaF and w/10 nm NaF (b) Arrhenius plots for the inflection frequencies for the no NaF CZTSSe from the derivative of the admittance spectra. (c) Arrhenius plots for the inflection frequencies for the 10 nm NaF CZTSSe from the derivative of the admittance spectra (d) TR-PL decay curves of the no NaF CZTSSe and 10 nm NaF CZTSSe (e) Defect density of states for the no NaF CZTSSe TFSC extracted from the results of admittance spectra. (f) Defect density of states for the 10 nm NaF CZTSSe TFSC extracted from the results of admittance spectra. (g) admittance spectra No na. (f) admittance spectra 10nm NaF.