The electrical and optoelectronic properties of materials are determined by the chemical potentials of their constituents. The relative density of point defects is thus controlled, allowing to craft microstructure, trap densities and doping levels. Here, we show that the chemical potentials of chalcogenide materials near the edge of their existence region are not only determined during growth but also at room temperature by post-processing. In particular, we study the generation of anion vacancies, which are critical defects in chalcogenide semiconductors and topological insulators. The example of CuInSe₂ photovoltaic semiconductor reveals that single phase material crosses the phase boundary and forms surface secondary phases upon oxidation, thereby creating anion vacancies. The arising metastable point defect population explains a common root cause of performance losses. This study shows how selective defect annihilation is attained with tailored chemical treatments that mitigate anion vacancy formation and improve the performance of CuInSe₂ solar cells.
toms in a crystalline structure align in a regular lattice, but due to off-stoichiometry, thermal energy, reactions or phase changes, some of the atoms leave their lattice sites or fail to occupy them, generating point defects. The density of these defects (such as vacancies, antisites and interstitials) and their charge state (positive, negative and neutral) depend on the (electro)chemical potentials of the constituent atoms and electrons. These potentials are usually controlled by the elemental compositions during the growth of a material and are vital in shaping its properties.

Indeed, significant property changes can be observed with slight modifications of the synthesis conditions, especially when crossing the boundaries of phase homogeneity regions, as epitomized by the ablated realm of steels. Therefore, a deliberate positioning along the edges of single-phase existence regions during growth can be exploited to benefit from the characteristics of the different phases involved, such as a superior native doping or microstructure.

However, these advantages may come at a cost. The growth-dependent (electro)chemical potential of the constituent atoms is a source of interface instability. Different interface reactivity manifests itself as undesirable chemical reactions affecting the material obtained on either side of the phase boundary. Furthermore, the detrimental nature of the reactions may spring from the formed secondary phase or from the altered defect population at the interface or both.

Understanding the nature of the defects involved, their concentration and mobility during the growth and after subsequent interface reactions is essential for the advancement of many technologies. For example, it is valuable for the control of the physical properties and functionality of chalcogenides in today’s optoelectronic and future spintronic devices based on two-dimensional (2D) and three-dimensional (3D) semiconductors and topological insulators. Likewise, progress in the performance stability of perovskite-based photovoltaics (PVs) relies on strategies aimed at minimizing the formation, mobility or reactivity of anion vacancies.

Here, the case is made for CuInSe₂ (CIS), a 3D chalcogenide belonging to the adamantine family of materials with a wide single-phase existence region (Fig. 1a). CIS is a suitable proxy for the successful Cu(In,Ga)(S,Se)₂ (CIGS) PV technology and will become increasingly important for the third-generation concepts, e.g., future tandem cells in combination with wider-gap chalcogenides or halide perovskites.

Realizing today’s highly efficient CIGS, solar cells require a carefully conceived fabrication process, one that derives from a decades-long research endeavour. One key innovation in CIGS fabrication was enabled in the 1990s by crossing the phase homogeneity boundary during growth from ‘Cu-poor’ to ‘Cu-rich’, then back again to Cu-poor compositions (known as the three-stage process).

The strategy received widespread success, because it allows combining the superior microstructure of Cu-rich material (cf. cross-sections in Fig. 1b) and the superior performance typical for Cu-poor compositions.

However, besides showing larger grains, Cu-rich CIS displays a more ideal luminescence signature than Cu-poor CIS, a prerequisite for high efficiency potential (Fig. 1d). This fact has puzzled the community for a long time, because it is at odds with the worse performance of Cu-rich CIS devices.

It is well known that during CIGS solar cell manufacturing, exposure of the absorber surface to ambient air, alkali metal fluorides or chemical etchants before buffer deposition influences heavily the device’s optoelectronic properties. It is likely, but has never been investigated, that CIGS grown under different conditions displays different resilience to point defect formation during and after growth. It is unknown how the altered defect populations influence the PV performance in commonly processed CIGS absorbers from this fundamental viewpoint.

Here we identify the root causes of chemical instability of CIS when crossing the edge of its existence region and relate them to device’s performance losses. Three thin-film compositions with increasing Cu concentration are investigated as bare absorbers, after surface treatments and as PV cells. These are identified
Table 1 Sample identification legend.

| CIS growth compositions |
|-------------------------|
| Details | Naming |
| Cu-poor, red colour | P (as Poor) |
| Nearly stoichiometric, black colour | S (as Stoichiometric) |
| Cu-rich, blue colour | R (as Rich) |

| CIS surface post deposition treatments (PDts) |
|-----------------------------------------------|
| Details | Naming |
| Unetched, as grown | U (as Unetched) |
| 30 s KCN 5 % wt. at room temperature | W (as Weak etch) |
| 300 s KCN 10% wt. at room temperature | B (as Bold etch) |
| ≤480 s under Se flux ≤250 °C, ref. 60 | Se-only |
| ≤480 s under Se and KF fluxes ≤390 °C, ref. 70 | Se/KF |
| ≤480 s under Se and In fluxes ≤300 °C ref. 57,58 | Se-In |
| Thiourea-rich chemical bath deposition (CBD) of Zn(O,S) onto the surface of CIS, ref. 60 | CBD-Zn(O,S) |

Combinations of CIS types and surface treatment type are indicated by combining P, S or R with U, W or B, accordingly.

Table 1 Sample identification legend.

according to the naming in Table 1 with associated colour coding in Fig. 1b and throughout the figures. The films are grown via a one-stage co-evaporation process at 530 °C, followed by unforced cooling to room temperature (as for conventional lab-scale thin-film processing). Our results show that amphoteric selenium-copper divacancies can form at the surface of both Cu-poor and Cu-rich CIS at room temperature, albeit at different extent. In Cu-poor material, whereas wet chemical bath processing may be amphoteric selenium-copper divacancies can form at the surface of both Cu-poor and Cu-rich CIS at room temperature, albeit at different extent. In Cu-poor material, whereas wet chemical bath processing may be amphoteric selenium-copper divacancies can form at the surface of both Cu-poor and Cu-rich CIS at room temperature, albeit at different extent. In Cu-poor material, whereas wet chemical bath processing may be amphoteric selenium-copper divacancies can form at the surface of both Cu-poor and Cu-rich CIS at room temperature, albeit at different extent. In Cu-poor material, whereas wet chemical bath processing may be amphoteric selenium-copper divacancies can form at the surface of both Cu-poor and Cu-rich CIS at room temperature, albeit at different extent. In Cu-poor material, whereas wet chemical bath processing may be...
in light of the APT compositional results on stoichiometric CIS post-deposition etchants is investigated to solve this conundrum.

properties, is yet to be understood. Here, the composition-

Simsek Sanli et al.30 has revealed the presence of interspersed

grains obtained under Cu-rich conditions display lower densities

of the two scenarios occurs in reality.

At this point, it is not possible to resolve with certainty which of

the Cu-rich domains are accumulations of Cu defects within the lattice of the metastable phase at room temperature, formed by focused ion beam (FIB)-induced aggregation and chemical reduction to elemental copper. Another possibility (ii) could be that the domains result from segregation of the excess Cu2Se at extended defects during cool down (Fig. 1c). Recent high-resolution TEM evidence from Simsek Sanli et al.30 has revealed the presence of interspersed Cu2Se domains within CIS grains, to which they attributed a topotactical grain growth effect during the three-stage process31. At this point, it is not possible to resolve with certainty which of the two scenarios occurs in reality.

Regardless of the actual mechanism of grain growth, the larger grains obtained under Cu-rich conditions display lower densities of detrimental planar defects36, which is the reason why highly efficient CISG is grown by deliberately crossing the edge of the homogeneity region during the so-called three-stage process13. Why then Cu-rich CIS consistently yields worse device performance than Cu-poor CIS, even after the removal of the excess Cu2Se phase14 and despite the proven superior transport properties, is yet to be understood. Here, the composition-dependent reactivity of CIS towards atmospheric oxygen and post-deposition etchants is investigated to solve this conundrum in light of the APT compositional results on stoichiometric CIS and the possible existence of the supersaturated metastable αm phase in CIS thin films.

Thermochemistry and defect population metastability. The thermodynamic stability of CISG against reactions at interfaces has been assessed in finished devices32-34 and on bare absorbers35,36. Kazmerski et al.37 revealed the formation of In2O3, SeO2 and Cu2Se on the CIS film surface above 150 °C38, with Hauschild et al.36 and Lehmann et al.39 finding In2O3 to be the most prominent oxide in air-exposed Cu-poor films. Figure 3a shows the computed Gibbs free energy of bulk In2O3 formation, respectively, out of In2Se3 [Eq. (1)] and CIS [Eq. (2)], as well as the alternative formation of Cu2O out of CIS [Eq. (3)].

\[
\text{In}_2\text{Se}_3(s) + \frac{3}{2} \text{O}_2(g) \Leftrightarrow \text{In}_2\text{O}_3(s) + \frac{3}{2} \text{Se}_n(s, g) \quad (1)
\]

\[
2\text{Cu}_2\text{Se}(s) + \frac{3}{2} \text{O}_2(g) \Leftrightarrow 2\text{Cu}_2\text{O}(s) + \frac{3}{2} \text{Se}_n(s, g) \quad (2)
\]

\[
2\text{CuInSe}_2(s) + \frac{3}{2} \text{O}_2(g) \Leftrightarrow \text{In}_2\text{Se}_3(s) + \text{Cu}_2\text{O}(s) + \frac{1}{2} \text{Se}_n(s, g) \quad (3)
\]

Conversion of In2Se3 to In2O3 and elemental selenium formally corresponds to oxidation of selenide anions and is very favourable in air (negative ΔG, solid red line). The positive slope of ΔG is consistent with the decreased degrees of freedom of the gas species, implying an even stronger thermodynamic driving force for conversion at room temperature.

Clearly, the Gibbs free energy of CIS formation is insufficient to stabilize the compound34 (dashed red line); hence, unprotected CIS is intrinsically unstable against oxygen (cf. Supplementary Fig. 4 for detailed point defect reaction energetics). The thermodynamic driving force is a necessary but insufficient condition for a reaction to happen (cf. Supplementary Note 1). Nevertheless, Eq. (2) is confirmed to occur at room temperature (Supplementary Fig. 3) and—thermodynamically speaking—cannot be reverted even under exposure to a static atmosphere of metastable Se2 molecules generated hypothetically by a cracker effusion cell (black dotted line). Stronger reagents, such as H2, are needed to reduce In2O340.

Equation (3) leading to Cu2O is only barely favourable, so the formation of In2O3 is thermodynamically more likely, in agreement with Hauschild et al.36 and Lehmann et al.39.

The presence of humidity was shown to accelerate further the oxidation of the related GaSe 2D compound41, so it is very likely that exposure of CISG samples to (moist) air during processing affects the CISG surface chemistry and the physics of the subsequent solar cell device.

To corroborate these considerations, a Cu-poor epitaxial CIS film, i.e., a proxy for CIS bulk (free from grain boundaries), was subject to a graded oxidation. The resulting library was characterized by scanning electron microscopy (SEM)/energy-dispersive X-ray spectroscopy (EDS) at low acceleration voltage and by photoluminescence (PL) along the macroscopic gradient, as shown in Fig. 3b. The regions closer to the O2 source result in a
higher In/Cu ratio (full red dots) and O content (hollow dots), consistent with the outgrowth of an In-O phase. Concomitantly, the PL yield (black curves) is lower and a shoulder peak appears, as shown more clearly in Fig. 3c.

To gain mechanistic insights into the CIS surface reactions, it is useful to relate the thermochromy at macroscopic level to the physics and chemistry of point defects in the material. The shoulder peak at ca. 0.9 eV is ascribed to the transition from the conduction band minimum to the ion vacancy (V\textsubscript{In}) in CIS\textsuperscript{43}. It is hypothesized that the formation energy of V\textsubscript{In} in CIS (ca. 2.5 eV/V\textsubscript{In}\textsuperscript{44,45}) results from the reaction between indium atoms and gas-phase oxygen is offset energetically by the large Gibbs free energy gain associated to Eq. (2) (ca. 2.9 eV/In atom).

The formation of V\textsubscript{In} under kinetic control implies that the outgrowth of In-O does not occur entirely as per Eq. (2), but leads at least partially to a defected CIS lattice without the segregation of Cu-Se phases, as per Eq. (4).

\[ 2[\text{Cu}_{(1-x)}\text{In}_{x}]_2\text{V}_{\text{Cu}}\text{Se}_2 + \frac{3x}{2}\text{O}_2(g) \rightarrow x\text{In}_2\text{O}_3(s) + 2[\text{Cu}_{(1-x)}\text{In}_{x}]_2\text{V}_{\text{Cu}}\text{Se}_2 + \frac{3x}{2}\text{O}_2(g) \]

From the phase diagram viewpoint, Eq. (4) is ensured by the Cu solubility range (Fig. 1b), entailing an increase of the Cu/In ratio of the underlying Cu-poor CIS without Cu\textsubscript{2}Se ejection. Under thermodynamic equilibrium, the increased Cu\textsubscript{In} eventually translates into a lower share of (In\textsubscript{Cu} + V\textsubscript{Cu})\textsubscript{2}Se\textsubscript{2}, but from a kinetic standpoint V\textsubscript{In} defect formation is justified: given the relatively high energy barrier for In migration in CIS (ca. 1.1 eV\textsuperscript{46}), once V\textsubscript{In} is formed it is not easily dissolved.

It is then revealed that interface reactions can lead to a chalcopyrite material with metastable defect populations at temperatures as high as 550 °C.

**Composition-dependent CIS reactivity against O\textsubscript{2}**. Equation (2) is assessed at room temperature as a function of the Cu content in CIS. Figure 4a shows the X-ray photoemission spectroscopy (XPS) signature of Cu-poor, stoichiometric and Cu-rich CIS after air exposure of the single-phase films for 24 h (i.e., films previously subject to removal of the excess Cu\textsubscript{2}Se by surface chemical etching with potassium cyanide (KCN)).

The surface composition of air-exposed Cu-poor CIS is consistent with In-O outgrowth, at least partially compatible with Eq. (4), although Cu-Se segregation is not excluded considering that atomic redistribution at room temperature is slower than at 550 °C. Stoichiometric CIS shows a similar behaviour.

Conversely, the surface composition of air-exposed Cu-rich CIS reveals a higher Cu-Se concentration, which is compatible with larger Cu-Se outgrowth. A reaction pathway alternative to Eq. (4) should then be invoked to account for the XPS data in this case. If Cu-rich CIS is a Cu supersaturated \( \alpha \)\textsubscript{In}, solution, the Cu-Se outgrowth may proceed by consumption of Cu interstitial atoms and formation of V\textsubscript{Se}, as per Eq. (5), where indium oxide formation leads to In subtraction from a material already oversaturated with Cu.

This can exclusively be compensated by the formation of the Cu-Se secondary phase in Cu-rich material, unless the limit of Cu equilibrium solubility in CIS is exceeded.

\[ 2[\text{In}(1-z)\text{Se}_{1-z}/2]_2\text{In}_{(1-z)/2} + \frac{3x}{2}\text{O}_2(g) \rightarrow x\text{In}_2\text{O}_3(s) + y\text{Cu}_2\text{Se}(s) + 2[\text{Cu}(1-z)\text{Se}_{1-z}/2]_2\text{In}_{(1-z)/2} + \frac{3x}{2}\text{O}_2(g) \]

Figure 4b, c exemplify the extreme cases of interface reactions from the perspective of CIS point defects under Cu deficiency and Cu excess, as inferred from the experimental evidence. The formation of indium oxide provides most of the thermodynamic driving force for Eq. (5) to happen, but the Cu excess in Cu-rich CIS appears to increase the reaction rate compared with Cu-poor CIS, which can be represented by a lowering of the reaction energy barrier, as suggested in Fig. 4d.

It is proposed that the nucleation and growth of the Cu\textsubscript{2}Se phase in the Cu-rich film is eased either by the large pool of Cu interstitials present in the Cu supersaturated \( \alpha \)\textsubscript{In} solution and/or by the pre-existence of Cu\textsubscript{2}Se domains acting as seeds.
It is then established that interface reactions can have profound consequences for the underlying defect chemistry of chalcopyrite even at room temperature without any liquid phase being involved. Furthermore, the defect reaction pathways can be markedly diverse if the substrate phase happens to occur near the edges of its existence region, which can have fundamental implications for further processing and ultimately for device performance.

**Composition-dependent CIS stability against cyanide.** Cu-Se phases are very conductive and reduce severely the shunt resistance of copper-based chalcogenide solar cells. Whether they occur as residues of absorber fabrication or following exposure to ambient air, they are effectively removed by aqueous cyanide (CN\(^{-}\)) solutions, presumably following Eq. (6) or Eq. (7).

\[
\text{Cu}_2\text{Se}_{(s)} + 7\text{KCN}_{(aq)} + \frac{1}{2}\text{O}_2(g) + \text{H}_2\text{O}_{(l)} \rightarrow 2\text{K}_2[\text{Cu}(\text{CN})_3]_{(aq)} + \text{KSeCN}_{(aq)} + 2\text{KOH}_{(aq)} \tag{6}
\]

\[
\text{Cu}_2\text{Se}_{(s)} + 6\text{KCN}_{(aq)} \rightarrow 2\text{K}_2[\text{Cu}(\text{CN})_3]_{(aq)} + \text{K}_2\text{Se}_{(aq)} \tag{7}
\]

KCN etching is also known to restore, at least partially, the original optoelectronic properties of aged absorber layers even after oxidation by strong agents such as hypochlorite; hence, PV device fabrication baselines may include a cyanide etching step, enabling a diode-like electrical behaviour. However, unlike widely accepted, cyanide is unable to chemically remove the In\(_2\)O\(_3\) phase formed as a result of CIS oxidation, i.e., any removal of such a phase upon cyanide etching is consequential to the chemical dissolution of interspersed Cu-Se phases, as per Eq. (6) or Eq. (7) (cf. Supplementary Fig. 3).

Having established the composition-dependent reactivity of CIS towards ambient air, it is important to understand whether the classical KCN etching also alters the defect population near the interface differently, depending on the CIS bulk composition and etching conditions. To this end, unetched films (KCN-U) are compared with films subject to two etching conditions: a 'weak' (KCN-W) etch (5 wt.% KCN for 30 s duration) and a 'bold' (KCN-B) etch (10 wt.% KCN for 300 s duration) on selected samples of Cu-poor, stoichiometric and Cu-rich CIS. The sample naming in the following figures is attributed combining the CIS chemical composition ('Poor', 'Stoichiometric' or 'Rich') with the KCN etching condition ('Unetched', 'Weak etch' or 'Bold etch'), e.g., yielding PW for Cu-poor with weak KCN etch (cf. Table 1 for full naming convention).

SEM/EDS analysis shows the morphological and compositional effects of KCN etching near the CIS surface and deeper in the films (Figs. 5a, b). Figure 5a is the corresponding matrix of top views. The small clusters identified at the surface of Cu-poor unetched and Cu-rich weakly etched CIS films are attributed to remnant Cu-Se phase, as they are clearly removed with further etching. EDS yields compositional information that is reasonably free from roughness convolution. At 7 kV acceleration voltage, the beam interacts approximately with the topmost 200 nm of film, whereas at 20 kV the interaction reaches at least 800 nm depth. It follows that Cu-rich CIS after bold etch shows a more pronounced surface Cu depletion than Cu-poor after bold etch, which is striking considering that the bulk composition is by far the opposite (consistent with the growth conditions and with APT analysis in Supplementary Fig. 1).

The Se content is described by the (Cu + In)/Se ratio. Cu-poor CIS films display values around unity in the bulk and slightly above unity at the surface, irrespective of the KCN etching conditions. Conversely, the Se content of Cu-rich CIS films depends heavily on the type of KCN etching because of the large amounts of Cu\(_2\)Se in Cu-rich unetched and their partial removal by weak KCN etching. However, importantly, the value of (Cu + In)/Se at the surface of Cu-rich CIS after bold etch is above unity, indicative of surface Se deficiency, given that this film is surely free from Cu\(_2\)Se. The higher (Cu + In)/Se ratio in the bulk of Cu-rich CIS after bold etch may seem puzzling; however, it is explained by the presence of the Cu-rich domains identified by APT, in line with the higher Cu/In ratio at 20 kV.

Similar conclusions are drawn by means of secondary ion mass spectrometry (SIMS) depth profiling (Fig. 5c). However, when comparing SIMS with EDS, it should be borne in mind that SIMS is affected by film roughness, due to signal averaging (cf. Fig. 5a), and matrix effects. For example, the convolution of topography and matrix effects influences heavily the Cu and Se SIMS yields (hence, the SIMS profiles) of Cu-rich CIS after weak etch, where remnant Cu\(_2\)Se occurs.
Both EDS and SIMS show that stoichiometric CIS yields the smallest compositional change upon KCN etching. Overall, it is hypothesized that Cu atoms are removed selectively from the lattice of CIS by KCN; the more so, the higher the deviation from stoichiometry. Furthermore, Se depletion is apparent in Cu-rich CIS, leading to the formation of both Se and Cu vacancies. The extent of removal by the cyanide complexant is thermodynamically more favourable for Cu-rich than for Cu-poor CIS, possibly due to the abundance of Cu interstitial atoms in the supersaturated metastable phase, in line with the argument described in Fig. 4d (cf. Supplementary Fig. 4).

Optoelectronics of CIS metastability induced by cyanide. Having shown that KCN etching induces different chemical effects at the surface of CIS depending on the growth conditions, the next step is to investigate the effects of such surface alterations on the optoelectronic properties. To this end, photoelectrochemical (PEC), time-resolved surface photovoltage (TR-SPV), PL and thermal admittance (ADM) analyses were performed, giving complementary insights on the most relevant samples.

It is crucial to understand that the times constants discussed for PEC and SPV analyses are not carrier lifetimes, but time constants of electron transfer and of defect transformation/generation. A PEC current or photocurrent ($I_{ph}$) is defined as the difference between the electrochemical current recorded under illumination and under dark conditions. Negative values, such as those observed here, correspond to photocurrents driven by electron transfer (ET) into the redox couple that gives rise to a photovoltage $V_{ph}$.

The shape of the photocurrent transient in Cu-rich CIS after bold etch is very unusual, because $I_{ph}$ increases with time after the start of the light perturbation (note that the figure plots the measured current density that comprises dark current and photocurrent). Evidently, a different additional recombination or trapping pathway induced by the bold KCN etching must be invoked to account for this uncommon behaviour. The situation is explained by the presence of another defect(s) inside the absorber near the surface with a different lifetime (tens of seconds) and not immediately linked to the surface recombination (p-n junction).

The surface recombination (p-n junction) cannot be the only effect at play in this material, because the ratio of the surface to bulk recombination is too high ($k_{s,r}$ vs. $k_{b,r}$) for that to be the case. Another effect is likely at play, which is the ET of Cu into the redox couple (see Fig. 4) and the built-in electric field that is established at the surface of the CIS absorber.

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pathway apparent in Cu-rich CIS after bold etch (Supplementary Fig. 6). In fact, after bold etch, both Cu-rich and Cu-poor films display recombination pathways with long time constants (2.2 µs and 2.5 µs, respectively). However, the extent of recombination for Cu-rich is ca. one order of magnitude higher than for the Cu-poor case, such that the pathway is perceived in the time domain of the Cu-rich film, but not in that of the Cu-poor one.

TR-SPV measured by Kelvin probe force microscopy (KPFM) is used to analyse the effect of bold etching on the photogenerated carrier dynamics of Cu-poor and Cu-rich films (Fig. 6b, c). The SPV, defined as the difference between the contact potential difference (CPD) under illumination and the CPD in the dark, is measured as a function of the modulation frequency of a light source. Regions II of the SPV (time domain) transients show an initial fast response reaching a maximum SPV at the beginning of the illumination sequence (starting at 10 MHz), followed by a slow decay and an abrupt drop of the SPV signal at the end of the sequence (finishing at 100 Hz). Upon initial illumination, both samples show a positive SPV, consistent with a p-type material behaviour. However, Cu-rich CIS after bold etch yields an SPV of ~75 mV, which is approximately half the value obtained for the analogous Cu-poor film. A lower SPV is indicative of a smaller change of band bending at the surface, which can be related to a lower minority charge accumulation at the illuminated surface of CIS-RB. The average SPV spectra in the frequency domain (Fig. 6c) reveal decay times of $T_{\text{CIS-PB}} \sim 6.2 \pm 1.0$ µs and $T_{\text{CIS-RB}} \sim 0.75 \pm 0.2$ µs. This trend is consistent with a higher recombination rate for Cu-rich CIS after bold etch, in agreement with the relative $k_{\text{RB}}$ of Cu-rich and Cu-poor films subject to bold etch obtained from PEC.

During the illumination sequence, the average SPV of Cu-poor CIS after bold etch decays to ca. 50% of the initial value, indicating a full relaxation of the SPV (for sufficiently slow modulation above 10 kHz, the SPV is at the maximum and at 0 for half of the cycle, giving an average of 50%). In fact, when the light excitation is off after the modulation sequence, the CPD value in dark conditions is fully recovered. However, the CPD of Cu-rich CIS after bold etch does not drop to the dark value after finishing the modulation spectrum, but a finite SPV value is maintained at about 20% of the total SPV for at least ca. 26 min after switching the excitation light off (Region III). Thus, the average SPV decays only by 30% from the SPV maximum, indicating that the fast decay of the SPV does not lead to a full relaxation. The remnant SPV is attributed to the presence of charged trap states. This finding is consistent with the presence of additional recombination or trapping pathways in Cu-rich CIS after bold etch already identified by PEC.

The PL spectra (Fig. 6d) are acquired immediately after the etching (less than 3 min), to minimize surface degradation. For Cu-poor CIS, the highest PL yield is displayed by the film subject to weak etch, showing a fourfold increase compared with the unetched, consistent with the known CIS surface renewal by cyanide etching with the removal of Cu$_2$Se (Fig. 5a). However, bold etching appears to be detrimental for PL yield, suggesting the formation of detrimental defects.

For Cu-rich CIS films, bold etching leads to higher luminescence than weak etching. This is attributed to the fact that weak KCN etching is unable to remove the entire Cu-Se phases (cf. Fig. 5a) responsible for reduced photon absorption by CIS and the presence of defects that affect the different bandgaps of the absorbers and the different extent of electrostatic potential fluctuations.

The bar chart in Fig. 6d shows the relative activation energy ($E_a$) of the main capacitance step extracted from the slope of the Arrhenius plot of the ADM spectra of Schottky junctions formed with the bare absorbers (Supplementary Fig. 7). The activation energies provide information on the electrically active defects in the material. A value of 200 ± 20 meV is obtained if bold KCN etching is performed, regardless of the CIS composition and cyanide counterion (cf. Supplementary Fig. 7), twice as much as for Cu-rich CIS after bold etch.
poor after weak etching (100 ± 10 meV). No spectra could be recorded on unetched films and Cu-rich films after weak etching, due to the presence of the conductive Cu-Se phases at the surface.

A recent DFT study by Simsek Sanli et al.34 on the effect of CuIn antisites and Cu interstitials in CIS reveals the appearance of states at 270 meV above the valence band maximum and 210 meV below the conduction band minimum, respectively. However, it is not obvious why the population of these two defects would increase upon KCN etching. Instead, the 200 ± 20 meV defect could be related to the observed etching-induced depletion of Cu and Se from CIS. Besides, the CuIn and Cu have clear PL signatures (cf. Spindler et al.14) and do not correlate with the 200 ± 20 meV defect.

Passivation of metastable defects improves PV efficiency. To shed light on the Cu and Se depletion, and link it to the trap defect (s) identified by PEC and ADM, the surface chemical reactivity of Cu-rich CIS after bold etch is investigated as a function of air-exposure time (Fig. 7a, b). It is revealed that oxygen has a remarkable influence on the shape of its anomalous PEC transient (blue curves shown under illumination) and magnitude of photocurrent (inset). The recombination pathway induced by bold KCN etching appears to be slowly passivated by oxygen incorporation, leading to a transition from the anomalous type of transient observed for Cu-rich (Fig. 6a, cyan) to the classical transient typical of Cu-poor films (Fig. 6a, red) and simultaneous increase of photocurrent density (J_ph, inset). The photocurrent density reaches a maximum after 12 min of air exposure and then it decreases, due to interface deterioration caused by the outgrowing Cu-Se and In-O surface phases, as per Eq. (5).

Whatever the nature of the defect created by the bold KCN etching, oxygen appears to neutralize it, reducing the near-surface recombination pathway. It is plausible that oxygen passivates selenium vacancy donor defects, as proposed by Kronik et al.35. The Se vacancies formed during etching would effectively compensate or even type-invert the near-surface region of CIS, causing efficient capture of the photogenerated electrons, as observed within the PEC transient (k_0 lower than k_inf ~ k_s.e.g.). During subsequent air exposure, the vacancies would capture oxygen, forming compensating acceptors that remove the electron trap and restore p-type doping.

To provide a hint on the nature of such a defect and its effect on the performance of solar cells, the composition-dependent performance of CIS solar cells is now investigated with respect to the chemical reactivity towards surface treatments. Solar cells comprising Cu-poor and Cu-rich absorbers subject to either weak or bold etching were fabricated following a standard baseline (including CdS layer deposition by chemical bath (CBD)). The electrical characteristics of the devices under simulated sunlight are shown in Fig. 7c.

The different etching does not affect appreciably the performance of Cu-poor-based devices in terms of electrical characteristics (red curves in Fig. 7c). Conversely, no valuable electrical data could be extracted from devices based on Cu-rich unetched and weakly etched absorbers, due to the residual Cu2Se and resulting resistor-like behaviour (cf. RW dashed cyan curve). Only with bold KCN etch, it is possible to effect a diode curve out of an absorber with Cu-rich CIS composition (RB solid cyan curve).

However, it is clear that the device based on Cu-rich CIS subject to bold KCN etching is affected by a significant deficit of open circuit voltage (V_OC) compared with devices based on Cu-poor absorbers, regardless of the KCN etching type. In light of the PEC and ADM Schottky analysis, bold KCN etching could then be responsible for the formation of defects that cause recombination at the interface between the surface of Cu-rich CIS after bold etch and the buffer layer, hence the enduring V_OC deficit of Cu-rich compared with Cu-poor CIS-based devices36. A series of experiments was performed to test this hypothesis.

If the origin of the V_OC deficit is linked to the presence of Se vacancies, then post-deposition treatments (PDTs) performed on the absorber surface under Se-rich environments, should improve the V_OC. Three types of such PDTs were performed: Se-KF (selenium and potassium fluoride), Se-only and Se-In37,38.
effectively improve the $V_{OC}$ (cf. JV curves in Fig. 7c and ref. 55), strengthening the hypothesis that the detrimental defect introduced by bold KCN etching is indeed related to Se depletion (the changes observed after the PDTs are linked to the Se incorporation and are not merely due to the associated heating).

To link the solar cell performance to the electronic defects identified by PEC and ADM on the bare absorbers, the PV devices were also characterized by ADM. The activation energies extracted from the Arrhenius plots are shown by the bar chart in Fig. 7c.

ADM reveals that the $200 \pm 20$ meV defect of Cu-poor and stoichiometric CIS films after bold etch disappears after the absorbers are subject to device completion (Supplementary Fig. 7), consistent with the fact that the etching type has negligible effects on the performance of Cu-poor-based devices. The activation energies become $100 \pm 10$ and $130 \pm 10$ meV, similar to those of devices based on weakly etched absorbers with Cu-poor and stoichiometric composition, which are close to the common A2 ($100 \pm 10$ meV) and A3 ($130 \pm 10$ meV) acceptor defects found in PbS58.

The removal of the $200 \pm 20$ meV defect in the devices based on Cu-poor and stoichiometric absorbers is consistent with the passivation of Se vacancies via sulfur incorporation during the baseline deposition of the CdS buffer layer by CBD.

Conversely, along with the significant $V_{OC}$ deficit, devices based on Cu-rich absorbers subject to bold etch also retain the $200 \pm 20$ meV defect, unlike cells based on Cu-poor CIS. It is important to note that both this defect and the $V_{OC}$ deficit are observed in all devices based on Cu-rich absorbers subject to bold etch regardless of the Cu/In ratio (above 1) or Se flux during absorber growth57. Crucially, Se-based PDTs succeed in passivating the $200 \pm 20$ meV defect, uncovering the $130 \pm 10$ meV A3 acceptor60 and improving $V_{OC}$. Therefore, a link is established between the $V_{OC}$ deficit, the $200 \pm 20$ meV defect and the bold KCN etching on Cu-rich CIS absorbers.

Moreover, devices comprising Cu-rich CIS absorbers subject to bold KCN etching and Zn(O,S) layers deposited by CBD with eight times the concentration of sulfur source compared with CdS CBD do not display the $200 \pm 20$ meV defect and also show a significant $V_{OC}$ improvement compared with standard CdS-based devices comprising Cu-rich films subject to bold KCN etching (Table 2). It is then clear that the longstanding $200 \pm 20$ meV defect is responsible for the $V_{OC}$ deficit of devices based on Cu-rich CIS subject to bold etch due to the preferential formation of Se vacancies induced by bold KCN etching on the metastable Cu-rich CIS phase. If Cu supersaturation of this phase is in the form of interstitial Cu atoms (cf. APT in Fig. 2), the coordination of Cu and Se by the cyanide ions in solution would be thermodynamically more favourable compared with Cu-poor CIS.

The hypothesis is consistent with the near-surface composition revealed by EDS and with positron annihilation studies by Uedono et al.54. Cu and Se vacancies can cluster to form Cu-Se divacancy defect complexes. These complexes can account for larger losses in open circuit voltage than mere Se vacancies. Indeed, the energy level of the divacancy complex occurs deeper in the gap than the Se vacancy alone62. It follows that the improved performance upon the various PDTs is in accordance with the replenishment of Se vacancies with Se, even if the Cu vacancy population remains unchanged. Based on these considerations, Fig. 7d shows a conclusive schematic illustration of the proposed metastable defect population in CIS subject to bold KCN etching and of the passivating effects of CdS CBD and Se-PDTs.

The impact of the findings on solar cell performance is summarized in Table 2, where the device parameters of the various samples are reported.

**Metastability is caused by amphoteric ($V_{SeV_{Cu}}$) divacancies.** The theoretical model published by Lany and Zunger in 200662 provides a final support to the hypothesis that the preferential Se and Cu depletion caused by cyanide etching is responsible for the appearance of the defect identified by ADM with an activation energy of $200 \pm 20$ meV.

Figure 8 illustrates a simplified model consistent with the experimental evidence gathered by PEC and TR-SPV (cf. Fig. 6), describing the sequence of events occurring from light perturbation to relaxation. Given that the $200 \pm 20$ meV defect is inaccessible by PL due to current detector limitations, the combined information from all the experimental techniques employed in this study and first-principle analysis sheds light on the chemical nature of this yet unidentified defect, i.e., complementing the recent review on CIGS electronic defects4 (cf. Supplementary Note 2 for a discussion on the energetic likelihood for the divacancy defect formation).

**Discussion**

The growth of CIS under Cu excess leads to the formation of domains having Cu concentration beyond stoichiometry within the bulk of the films. The domains may consist of Cu$_2$Se interpersed phase and/or Cu supersaturation in the form of Cu interstitials. Either way, this condition is compatible with previously reported metastable phase equilibria3,8 and affects the surface chemical reactivity of CIS towards air, etchants, PDTs and solar cell finishing processes.

Exposure of CIS to air at room temperature leads to the spontaneous formation of In$_2$O$_3$ and Cu$_2$Se. This reaction occurs at a higher rate on Cu-rich than on Cu-poor CIS, presumably catalysed by the high mobility of available Cu, or by interpersed Cu$_2$Se domains acting as seeds for further growth. KCN etching is needed to remove Cu$_2$Se, but it also imparts preferential leaching of Cu and Se from the underlying CIS lattice. The end result is a Cu and Se depletion from the CIS crystal lattice, responsible for the appearance of a $200 \pm 20$ meV defect from ADM measurements. The density of this defect is higher the higher the initial Cu/In ratio during CIS growth. Indeed, although standard CdS CBD is sufficient to remove the defect from Cu-poor material, the defect persists on Cu-rich material, where it causes front interface recombination and a large $V_{OC}$ deficit.

Specific chemical processes performed at the surface of (Cu and Se)-depleted Cu-rich CIS can eliminate the $200 \pm 20$ meV defect, hence reducing interface recombination and $V_{OC}$ deficit. These processes are typically associated to a high content of group

| Sample | Efficiency (%) | $V_{OC}$ (mV) | $J_{SC}$ (mA cm$^{-2}$) | FF (%) |
|--------|----------------|--------------|------------------------|--------|
| PW$^{71}$ | 12.8 | 446 | 42.0 | 68 |
| PB | 12.7 | 460.2 | 44.5 | 61.9 |
| SW$^{72}$ | 12.1 | 436.8 | 40.7 | 67.9 |
| SB | 11.7 | 434.5 | 38.5 | 69.7 |
| RW$^{60}$ | - | - | - | - |
| RB$^{60}$ | 7.0 | 355 | 42.1 | 46.8 |
| RB + Se-only$^{60}$ | 9.2 | 382 | 40.7 | 59.2 |
| RB + Se KF | 9.5 | 398 | 41.1 | 58.0 |
| PDT$^{70}$ | - | - | - | - |
| RB + Zn(O,S)$^{60}$ | 6.7 | 399 | 41.0 | 40.9 |

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(cf. Table 1 and ‘Methods’ section). All three treatments effectively improve the $V_{OC}$ (cf. JV curves in Fig. 7c and ref. 55), strengthening the hypothesis that the detrimental defect introduced by bold KCN etching is indeed related to Se depletion (the changes observed after the PDTs are linked to the Se incorporation and are not merely due to the associated heating).
VI elements of the periodic table (O and the chalcogens S and Se). Exposure of the absorbers to O₂ in the air at room temperature almost doubles the magnitude of electrochemical photocurrent recorded on semiconductor/electrolyte junctions with the distinct removal of a recombination pathway, as revealed by the shape of the photocurrent transient. Likewise, PDTs at higher temperature entails a sizable activation energy for the cleavage of the acceptor via capture of two holes, hence the time constant associated to the surface charge reconstruction is on the order of tens of minutes at room temperature, as observed in TR-SPV.

Methods

Absorbers and device preparation. Molybdenum coated soda lime glass was used as a substrate to fabricate polycrystalline CIS absorbers using physical vapour deposition in a molecular beam epitaxy (MBE) system. CIS was fabricated using a one-stage co-evaporation process at a substrate temperature of 350 °C, followed by unforced cooling to room temperature. The Cu/In ratio was varied through controlling the Cu and In fluxes. Absorbers grown under Cu deficiency were fabricated targeting a Cu/III ratio of <1 (CIS-P, ‘Cu-Poor’); conversely a Cu/III ratio of more than one was targeted for those grown under Cu excess (CIS-R, ‘Cu-Rich’). The elemental composition of the absorbers is determined by energy-dispersive X-ray spectroscopy with an acceleration voltage of 20 kV. This value represents the average composition of the absorber including Cu,Se if present. After growth, the absorbers are subjected to an etching step to remove copper selenide secondary phases and residual oxides. The absorbers were either immersed in KCN aqueous etching solutions or processed without etching (KCN-U, ‘Unetched’). Two types of KCN conditions were employed: a 30 s etch in a 5 wt. % KCN (KCN-W, ‘weak’) or a 300 s etch in a 10 wt. % KCN (KCN-B, ‘bold’). A CdS buffer layer was then deposited on top of the etched absorbers using cadmium iodide solution before sputtering both a nominally un-doped and a biased zinc oxide window layer. Lastly, nickel-aluminium contacting grids were evaporated by electron-beam deposition.

Solar cell analysis. The electrical parameters of the solar cells were extracted from the current–voltage (JV) measurements performed using a AAA Solar Simulator calibrated using a silicon reference solar cell, together with a JV source measure unit. JV analyses of CIS-RB devices were also measured as a function of annealing time at 60 °C and 80 °C. For this purpose, finished devices were annealed repeatedly on a hot plate for different durations, left to cool at room temperature and characterized in between each annealing period.

Epitaxial growths and deliberate oxidation. The growth of the 10 quintuple layer (QL) thick β-In₂Se₃ thin film was achieved by MBE on a c-sapphire substrate. The growth was performed at 550 °C under Se excess at rate of 1.5 QL min⁻¹. The thin film was left in air under dark conditions and its deliberate oxidation was studied by repeated Raman ex-situ analyses. The epitaxial CIS film was grown on a (100) GaAs wafer via metal-organic chemical vapour deposition by thermal decomposition at 470 °C of cyclopentadienyl-copper-triethyl phosphine, trimethyl- indium and diteriarybutyl selenide. The relative gas partial pressures were adjusted to achieve a Cu-poor CIS composition (Cu/In equals 0.87, as assessed by EDS). The epitaxial CIS film was subject to graded oxidation at 550 °C by placing the 2 cm-long specimen inside a tube furnace along a gradient of incoming oxygen partial pressure ensured by adjusting the aperture of the end valve such that the pressure attained by the rotary pump of the apparatus did not exceed 100 mbar.

Scanning electron microscopy. The morphology of the absorbers was assessed with a Hitachi SU-70 field-emission SEM. Top-view SEM images were taken before and after KCN etching, as well as after the post-deposition treatment and HCI etching, with a voltage of 7 and 20 kV with the intent to acquire compositional information at different depths. Cross-sectional SEM images were taken after removal of the excess Cu/Se phase, at a voltage of 7 kV.

Atom probe tomography. The cryo-FIB preparation was carried out using a Gatan C1001 LN₂ cold module and an in-house designed adapter holder for the APT specimen. APT experiments were performed with a local electrode atom probe (LEAP 3000X HR, Cameca Instruments), applying laser pulses of 532 nm wave-length, 15 ns pulse length and an emission of 0.1 nJ per pulse at a repetition rate of 100 kHz. The specimen base temperature was about 60 K. Atom probe specimens were prepared utilizing a dual-FIB (FEI Helios Nanolab 600i) using a lift-out procedure.

Raman spectroscopy. The Raman spectra of the β-In₂Se₃ epitaxial layers were acquired with an excitation wavelength of 532 nm on a confocal microscope at ×50 magnification. Given that in-situ oxidation of the β-In₂Se₃ can be largely accelerated by the laser beam, the laser power was limited to 1 mW and an average of 10 acquisitions of 4 s duration was found appropriate to maximize signal to noise.
ratio, while minimizing laser-induced oxidation. However, repeated exposure of the same spot over 5 min revealed clearly the decrease of signal. The intensity was normalized based on background signal.

X-ray photoemission spectroscopy. Surface chemical analysis of the absorbers was performed by XPS measurements using an ESCALAB 150Xi (Thermo Fisher Scientific) spectrometer and a monochromatic Al Kα radiation (1486.6 eV). Photoelectrons were detected parallel to the surface normal with a pass energy of 20 eV for the narrow scans. The XPS spectra were analysed using Avantage data processing software. Atomic concentration calculations and peak fitting were carried out after removing a Shirley-type background and by using the relative sensitivity factors provided by the Avantage library. The sputtering of the samples was performed with Ar+ ions (E = 4 keV) and with an angle of 45°.

Secondary ion mass spectrometry. SIMS depth profiling was performed with a Cameca SC-ULTRA instrument using 1 keV Cs+ ion bombardment. The analytical conditions used (primary ion beam, raster size) yield a sputtering rate of 0.20 nm s⁻¹. Secondary ion intensities were collected from an area of 60 µm in diameter. The SIMS profile data were normalized against the primary Cs+ flux to account for beam fluctuations⁴⁴.

Photoelectrochemical analysis. PEC films were recorded by holding the absorbers at −0.4 V vs Ag/AgCl reference in a 0.2 M aqueous EuCl₃ solution, employing a three-electrode setup described previously⁶⁶. Illumination was supplied by a 532 nm light-emitting diode (Thorlabs), subject to an asymmetric square-wave duty cycle. The PEC transients are described assuming three different kinetic constant of electron transfer: kₑ (electron transfer from semiconductor to electrolyte), kᵣ (surface recombination) and kₛ (bulk trap). The values of kₑ, kᵣ are obtained from each individual photocurrent transient by fitting the data, according to Eq. (8) and assuming a kₛ = 250 s⁻¹ for all samples⁴⁷.

$$J(\infty) = \frac{k_e}{k_e + k_r + k_s}$$

Intensity-modulated photocurrent spectroscopy. IMPS analysis was performed on CIS samples of various compositions subject to different etching and subsequently coated with Cds. The acquisition conditions consist of a negative polarization at −0.5 V vs. Ag/AgCl reference in a 0.2 M equimolar aqueous solution of K₂[Fe(CN)₄] and K₃[Fe(CN)₆]⁴⁷. The Cds/ferro-ferricyanide junction yields durable and highly ideal photocurrent transients. This ensures the reproducible acquisition of IMPS spectra, unlike the CIS/EuCl₃ junction that is subject to irreversible changes of interface properties, as described within this study. The Nyquist plot is obtained from the Bode plot by means of the phase angle information (ϕ), enabling the extraction of the real and imaginary photocurrents, as per Eq. (9).

$$I_{ph}(w) = I_{ph}(w) \cdot \left(\cos(\phi(w)) - i \sin(\phi(w))\right)$$

Time-resolved surface photovoltage. KPFM was used to locally probe the photogenerated carriers by monitoring the CPD behaviour under illumination. KPFM experiments were performed in an ultra-high vacuum scanning probe microscope, Omicron Nanotechnology GmbH, controlled by Nanonis electronics and using a PtIr-coated cantilever (f₀ = 167 kHz). Amplitude modulation was used for the detection of the CPD with an ac bias of 400 mV at the second oscillation mode of the cantilever. Real-time KPFM measurements are not always suitable to characterize the carrier dynamics, since the KPFM controller time constant, of few tens of ms, is much slower than the time scale at which charge generation, separation and relaxation processes take place. Region I of the time domain response obtained on CIS-Pb (in Fig. 6b) exemplifies this behaviour. Upon switching on and off a continuous-wave (cw) radiation source (635 nm laser, Thorlabs), the CPD shows a sharp increase followed by an abrupt decrease, but no information related to the time constants of the raise and decay can be extracted. Therefore, a time-dependent study of the SPV is performed by measuring an average SPV as a function of the frequency of a modulated light source⁶⁷. The surface photovoltage is defined as: SPV = CPD under illumination − CPD under dark. For the modulated light, a fast switched diode laser (PicQuant FSL500) was externally triggered with user-defined signal patterns, avoiding any frequencies which could lead to artifacts due to frequency mixing. The light sources have an optical power of ~4.5 mW (with an intensity of ~100 mW cm⁻²) and an illumination angle of 28°, to ensure illumination of the sample under the tip and cantilever beam. The decay time (τ) values are obtained from each individual frequency spectrum by fitting the data according to Eq. (10)⁶⁷.

$$V_{spv}(f) = V_{dark} + SPV \cdot D + \tau \cdot SPV \cdot \left(1 - e^{-\frac{(1 - D)}{\tau \cdot f}}\right)$$

Photoluminescence. A home-built calibrated setup is used for the determination of PL properties. A continuous monochromatic illumination (660 nm) from a solid-state laser is used for excitation. The emitted PL is collected by an off-axis mirror, guided into a grating monochromator by an optical fibre and detected by an InGaAs-detector array.

Admittance spectroscopy. The temperature- and frequency-dependent ADM measurements were performed in the dark, after keeping the sample mounted in the dark at room temperature for one night, with a Precision LCR meter using a closed-cycle helium cryostat in a temperature range of 320–50 K. ADM measurements are performed to study the electronic defect states in the semiconductor junction. The finite capture/emission time constants of such a defect level result in distinct steps in the ADM spectrum. The inflection frequency (fᵢ) of a capacitance step at a given temperature is determined by the defect response time and the thermal activation energy of the defect can be obtained from the slope of an Arrhenius plot of the temperature-dependent inflection frequencies (presented in Supplementary Fig. 7c). It is noteworthy that fᵢ is commonly scaled with a factor T⁻¹ to account for implicit temperature dependences of the thermal velocity and effective density of states⁵⁸,⁵⁹.

Thermochemical computation. The thermochemical treatment in Fig. 3a was elaborated using tabulated data⁹. The chemical potential of CuIISe₂ is determined assuming the reported enthalpy of formation from the elements at 298 K ²,³,²,⁴ and an entropic contribution of ideal mixing (ΔSN₁₉₅ equals R ln(5)), as per Eq. (11), and is consistent with previous studies³⁸.

$$G_{\text{CuIISe}_2}(T) = \frac{G_{\text{CuIISe}_2}(298) + G_{\text{EuSe}}(298) + G_{\text{CuSe}}(298) - T \Delta S_{\text{N}}_{195}}{2}$$

Data availability

The datasets generated and/or analyzed in the present study are available from the corresponding author on reasonable request.

Received: 18 April 2019; Accepted: 27 June 2020; Published online: 20 July 2020

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Acknowledgements
This contribution has been enabled by the Luxembourgish Fonds National de la Recherche (FNR) in the framework of the GALDOCHS project (Gas-phase alkali doping of chalcogenide semiconductors, C14/MS/830276) and CURi-K project. INL and the European Commission are acknowledged for funding the Nano Train for Growth II project number 713640 through the Marie Curie Cofund programme. S. Sadewasser, N.N. and M.W. acknowledge funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement number 641004 (Sharc25). We acknowledge the Luxembourg Institute of Science and Technology (LIST) for SEM use and Mr. Brahim El Abb (LIST) for his skilful technical assistance in the SIMS analysis. Uwe Tezins, Andreas Sturm, and Christian Bross are acknowledged for their constant support in running the atom probe facilities at MPIE. T.S. acknowledges the support by the German Research Foundation (DFG) (Contract Number GA 2450/1-1). Lifeng Liu and Pedro Alpuim are acknowledged for giving access to the IMPS and Raman instruments. Professor Alberto Credi (Alma Mater Studiorum University of Bologna) is gratefully acknowledged for his insightful suggestions as chair of the 47th Conference of Inorganic Chemistry of the Italian Chemical Society held in Bari in September 2019, where part of this work was presented.

Author contributions
D.C., H.E. and S. Siebentritt designed the research and experiments. H.E. and F.B. fabricated the absorbers and performed the post-deposition treatments. H.E. performed the JV and ADM characterizations. D.C. performed the defect chemical analysis, the PEC and IMPS characterizations. M.C. deposited the ten-layer In₂Se₃ stack by MBE and assisted during the Raman analyses. C.S. deposited the epitaxial CIS by MOVPE. N.N. and D.S. performed the TR-SPV analysis. T.S. performed cryo-FIB and APT analysis, and processed the 3D data. M.M. performed the baseline process of the cells and performed SEM and EDX characterization. M.S. performed solar cell characterization on devices subject to low-temperature annealing for different durations. M.W., F.B. and C.S. performed the PL characterizations. D.C., H.E. and S. Siebentritt wrote the paper. All authors (including S. Sadewasser, P.I.D. and D.R.) contributed to interpretation of measurement results and discussions for the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41467-020-17434-8.

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Peer review information Nature Communications thanks Takeaki Sakurai and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. Peer reviewer reports are available.

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