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Observation of [V_{Cu}^{1-} In_i^{2+} V_{Cu}^{1-}] Defect Triplets in Cu-Deficient $CuInS_2$

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ABSTRACT

Copper indium disulfide ($CuInS_2$) is a semiconductor with a direct energy band gap of 1.53 eV, an optimal value for highly efficient thin-film solar cells. But it has reached only ~ 11 % power conversion efficiency, far less than the theoretically achievable value of ~ 30 %. The cause of this low performance is not understood. A single crystal grown from 1 mol% Cu-deficient melt was studied, using atomic resolution high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) and electron dispersive spectroscopy (EDS). While the bulk crystal is exactly stoichiometric $CuInS_2$, it contains nanometer-thick, structurally coherent, Cu-deficient interphases that form along rotational twin boundaries in the {112} plane. Transition zones from bulk crystal to interphase are observed, where In is seen to move from its normal site In_{In} in the chalcopyrite structure to a tetrahedral interstitial site In_i, while Cu remains in its normal Cu_{Cu} position. Two In_{In} rows of the bulk crystal merge into one row of In_i, causing excess In_i in the

interphase. The concentrations of Cu_{Cu} and In_i reflect a ratio of Cu vacancies, V_{Cu}, to excess In_i of ~ 2. Their relative lattice positions, and the high electrical resistivity of the crystal, suggests that V_{Cu} and excess In_i 'precipitate' as self-compensating, electrically neutral, $[V_{Cu}^{1-}\ In_i^{2+}\ V_{Cu}^{1-}]$ defect triplets. This is the first atomic-level observation of the ordered defect that has been invoked as the basic structural modifier in chalcopyrite compound homologs. The interphases introduce an optical gap of 1.47 eV. Electron trapping in band tail states, evident from a photoconductivity exponent of 0.54, is the likely cause of an unusually low electron mobility of 0.1 $cm^2V^{-1}s^{-1}$. The overall result is that making $CuInS_2$ slightly copper-poor inserts nanometer-thick layers of the interphase into the bulk crystal. This study shows that apparently conflicting results of the effect of Cu deficiency on $CuInS_2$ thin-film solar cells may be resolved by analyzing structure and composition at nanometer spatial resolution.

1. INTRODUCTION

1.1 $CuInS_2$ thin-film solar cells. $CuInS_2$ is a diamond-like semiconductor with the crystal structure of chalcopyrite that was first synthesized to explore the applicability to ternary compounds of the Grimm-Sommerfeld valence rules for tetrahedral coordination.[1–4] The chalcopyrites have the diamond-like zincblende structure but with two cations ordered on sublattices. The Bravais lattice of the chalcopyrite is body centered tetragonal, belonging to space group $I\bar{4}2d$. The first crystals of $CuInS_2$ were grown to evaluate its suitability for semiconductor device applications, and for its piezoelectric and non-linear optical properties.[5–7] The direct energy band gap of $CuInS_2$ makes it a strong light absorber, with a value of 1.53 eV that lies at the optimum for efficient single-junction solar cells.[8,9] Therefore $CuInS_2$ has been explored for polycrystalline thin-film solar cells,[10] beginning with a 3.6% efficient homojunction cell,[11] then *n*-CdS/*p*-$CuInS_2$ heterojunction solar cells first reaching 7.3%,[12] and later 11.4% power conversion

efficiency.[13] What has kept the $CuInS_2$ efficiency substantially lower than the 15% reached with $CuInSe_2$ is not understood.[14] Much higher efficiencies have been reached with alloys of $CuInS_2$: 15% by alloying with Ga_2S_3 in $Cu(In,Ga)S_2$,[15] and the highest efficiency achieved in any inorganic thin-film solar cell of 23.35% with a compositionally graded $Cu(In,Ga)(S,Se)_2$ alloy absorber layer.[16]

CdTe and $Cu(In,Ga)Se_2$ thin-film solar panels are deployed on large scales. The commercial successes of these solar cells made of polycrystalline thin films are the result of primarily empirical research and development. Controlling electrically active defects and carrier lifetimes remains an art. Stoichiometry, point and line defects, grain boundaries, and interfaces affect conductivity type, carrier mobility and recombination lifetime, and thereby solar cell efficiency. Overall, the quantitative understanding of the electronic properties of polycrystalline thin-film compound semiconductors is far from that of polycrystalline silicon,[17,18] which grew from an exhaustive grasp of the properties of single-crystalline silicon. To the device physics community, it is a given that the quantitative understanding of single-crystal chalcopyrite semiconductors is indispensable for reaching maximum thin-film solar cell performance. Therefore, soon after initial exploration,[5–7] raising solar cell efficiency became the principal motive for studying $CuInS_2$ single crystals.[19–28] An exemplary single-crystal result is the measurement of electron mobilities as high as 338 cm^2/Vs,[22] providing an important yardstick for assessing the device quality of polycrystalline $CuInS_2$ films. The goal of the present study was to resolve a long-standing debate in polycrystalline $CuInS_2$ solar cells, namely the existence and presumed effects of Cu-deficiency, by clearly identifying the phase(s) and defects in a $CuInS_2$ single crystal grown from a slightly copper-deficient melt.

1.2 Stoichiometry of $CuInS_2$. Chalcopyrite crystals can be homogeneous at non-stoichiometries of up to several atomic percentages.[1,29] A finite range of sulfur-content is evident from the ability to make $CuInS_2$ crystals *n*-type by annealing under minimum sulfur pressure, and *p*-type when annealed at high pressure.[6,9] That allowed the fabrication of an *n*-on-*p* type homojunction thin-film cell, made by changing the sulfur pressure from high to low during film growth.[11] Indeed, adjusting composition instead of substitutionally doping remains the means of controlling carrier type and magnitude of the electrical conductivity in $CuInS_2$. But the role of Cu non-stoichiometry in setting the efficiency of polycrystalline thin-film $CuInS_2$ solar cells remains controversial. The search for high efficiency initially explored Cu-poor material,[30] as employed in $CuInSe_2$ cells,[31] then moved to Cu-rich $CuInS_2$,[10,13,30] and then back again to Cu-poor $Cu(In,Ga)S_2$.[15] Several reports describe depositing $CuInS_2$ absorber films with excess Cu, and then removing that excess by etching in KCN solution prior to heterojunction fabrication, insinuating substantial solubility of Cu in $CuInS_2$.[10,13,30,32] A recent study illustrates the challenge of identifying the solar-optimal stoichiometry of $CuInS_2$. Lomuscio et al.[32] prepared $CuInS_2$ polycrystalline films with either copper excess or copper deficiency, set by either single or two-step vacuum deposition under five different temperature protocols. Surprisingly, the quasi-Fermi level split measured in the films (a gauge of achievable open-circuit voltage) did not correlate with the open circuit voltage of $CuInS_2$ solar cells made from these films. The observation by Klenk et al.[10] that films with copper-poor compositions exhibit very Cu-deficient free surfaces points to the possibility of phase separation between $CuInS_2$ and a Cu-poor phase. Such phase separation may also occur at interfaces, as is suggested by the formation of a $CuIn_5S_8$ interlayer by Cu out-diffusion from a $Cu(In,Ga)Se_2$ absorber near the heterojunction into the overlaying In_xS_y buffer, which depletes the absorber of Cu.[33] By changing the energy band alignment or the conductivity

type at the heterojunction, such depletion can have drastic effects on solar cell efficiency.[34–37] Therefore, to design the optimal solar cell material it is clearly important to know where the Cu-poor boundary of $CuInS_2$ lies, and what the crystal properties at that phase boundary are.

1.3 Phase diagram of $CuInS_2$. Observations made during the first growth of single crystals[5] suggested that the tetragonal γ-phase of $CuInS_2$, which is the stable modification below 980 °C,[23,38] has a narrow homogeneity range, as was also suggested by the In_2S_3 and $Cu_{2-x}S$ admixtures detected in evaporated $CuInS_2$ thin films.[12] While Binsma et al.[38] extrapolated to a narrow Cu-rich and a wider Cu-poor homogeneity range at room temperature, in the course of a study of the In-$CuInS_2$ phase diagram Fearheiley et al.[23] found no appreciable solubility of In (suggesting no appreciable Cu-deficiency) in $CuInS_2$. Verheijen et al.[39] identified a homogeneity range from 50 to 52 mol% In_2S_3 (i.e., Cu deficiency) in the Cu_2S-In_2S_3 binary system. Crystals grown from stoichiometric melts under temperature gradients > 10 °C/cm contained lamellar structures of stoichiometric $CuInS_2$ separated by the highly Cu-deficient thiospinel $CuIn_5S_8$.[24–26,40] The authors suggest that Cu-deficient $CuInS_2$ is not stable, and surmise that the formation of $CuIn_5S_8$ from stoichiometric melts indicates that constitutional supercooling is enabled by the dissolution of Cu_2S in $CuInS_2$ (i.e., $CuInS_2$ can absorb excess Cu_2S). The summary of this group of investigations is that stoichiometric $CuInS_2$ can take up Cu_2S but not lose it. A crystallographic study of the compositions of polycrystalline films in the Cu_2S-In_2S_3-Ga_2S_3 ternary system with focus on Cu-poor compositions,[41] also concluded that the Cu-poor homogeneity range must be very narrow; all Cu-poor compositions did result in two-phase mixtures of essentially stoichiometric $CuInS_2$ and $CuIn_5S_8$.[42–44]

A detailed theoretical study of point defects in $CuInSe_2$ by density-functional theory by Zhang et al.[45] suggests that Cu-deficiency is accommodated by the formation of stable, electrically

neutral [V_{Cu}^{1-} In_{Cu}^{2+} V_{Cu}^{1-}] defect triplets; these enable the self-compensation of Cu vacancy acceptors, V_{Cu}, by moving In to Cu sites where it becomes the antisite donor In_{Cu}. The defect triplets are the basic structural constituent of group-I deficient ordered defect compounds (ODC). Wasim et al.[46] verified these theoretical findings with a combined experimental and theoretical study of a group of chalcopyrites and their ODC derivates. It is important to keep in mind that Cu-deficiencies introduced in phase diagram studies, or in crystal and thin-film growth, are large by the standard of electronic substitutional doping. While a 1 at.% deficiency in composition may produce mostly electrically neutral defects like [V_{Cu}^{1-} In_{Cu}^{2+} V_{Cu}^{1-}], it still might leave a minor (e.g., 10^{-4} at.%) concentration of electrically active dopant defects, enough to dominate charge transport in solar cells.

In this study we identify the phase(s), the structural, and the opto-electronical properties of a $CuInS_2$ crystal grown from a 1 mol% Cu-deficient melt. We describe crystal growth and basic crystal properties, then the crystal's atomic structure as seen by scanning/transmission electron microscopy (STEM), plus its fine structure atomically mapped in conjunction with atomic scale electron dispersive spectroscopy (EDS) for analysis of composition. The crystal's optoelectronic properties are evaluated by measuring electronic transport and photoconductivity. The results are fascinating: we discovered a Cu-deficient phase *in statu nascendi*, including the gradual displacement of In from its normal site in the chalcopyrite to a new site that, while interstitial in the chalcopyrite, is the dominant position of In in the Cu-deficient phase.

2. INSTRUMENTATION & METHODS

Powder X-ray diffraction analysis was performed on a Bruker D8 Advance Eco with Cu Ka radiation and a LynxEye-XE detector. The scan parameters were 0.02°/step with 0.085 s/step, for a total scan time of 8 min. A Quanta 200 field emission gun environmental scanning electron

microscope (SEM) equipped with an integrated Oxford System was employed for energy dispersive X-ray (EDS) analysis, for routine evaluation of chemical constituents. X-ray photoelectron spectra (XPS) were collected under 10^{-9} Torr using a ThermoFisher K-Alpha X-ray photoelectron spectrometer. All spectra were recorded using Al Kα radiation (1487 eV) with a survey and pass energy of 100 and 20 eV, respectively. Measured peaks were fit using Casa XPS software and a Shirley background. The C 1s peak at 284.5 eV of adventitious hydrocarbon was used as an internal binding energy reference. The optical bandgap was measured with the Agilent Technologies Cary 5000 UV-Vis-NIR spectrometer equipped with a Universal Measurement Accessory (UMA) with incident light from 200 to 1300 nm wavelength.

Photoconductivity measurements were performed on the same instrument as the electronic transport measurements, a Quantum Design Physical Property Measurement System, using a custom dark-room setup. Ohmic contact was made with Pt wires connected to the (112) surface with InGa eutectic. Current-voltage curves were plotted in real time as the potential was swept between -10 and 10 V at varying LED light intensities with each wavelength tested (365 nm, 395 nm, 462 nm, 537 nm, 640 nm, 780 nm, 850 nm, 940 nm, and 1050 nm). These measurements were performed at room temperature.

The resulting, symmetric I-V curves demonstrate ohmic behavior at both wire contact points showing that non-ohmic contacts are not the origin of the observed effects. The linear slope of the I-V curves indicate that the system's free electron lifetime remains constant, given the relationship: $\mathrm{I} = \mathrm{e}\frac{F\mu\tau}{L^2}\mathrm{V}$ where e is the electron charge, F is the free electron generation rate, μ is the mobility, τ is the free electron lifetime, and L is the spacing of electrodes.

3. EXPERIMENT & RESULTS

3.1 Single crystal growth and initial characterization. Polycrystalline $Cu_{0.99}In_{1.00}S_{2.00}$, (i.e., 1 mol% Cu deficient) was synthesized from the elements Cu (99.99%), In (99.999%), and S (99.99%) in an evacuated quartz tube at T = 1100 °C.[47] After ascertaining the chalcopyrite structure by powder X-ray diffraction, and composition by energy-dispersive X-ray spectroscopy (EDS), ~ 20 g were ground into large grains and sealed under vacuum in a carbon-coated quartz tube. The $CuInS_2$ single crystal was grown in a vertical Bridgman furnace set to 1140 °C. The quartz tube was held in the hot zone for 24 hours, then lowered through the length of the furnace at 0.1 mm/hour, and finally annealed at T = 400 °C for 24 hours. This annealing temperature approximates the substrate temperatures in films deposited by thermal evaporation of the elements.[32,41] The four independent variables—stipulated by the phase rule for setting the composition of a ternary compound—are temperature, total pressure, sulfur partial pressure and copper-to-indium ratio.[23,48–50]

During extraction from the quartz tube, the 38 mm long single crystal ingot cleaved along the (112) plane into six pieces (Fig. 1a). All further measurements were made on the section IV piece, ~ 14 mm from the tip of the ingot. We cleaved four different samples for evaluating optical, X-ray, TEM, and photoconductivity characteristics. The freshly cleaved samples were not chemically etched prior to measurement. The material's optical transmission spectrum (Fig. 1b) exhibits the steep absorption edge of a direct-gap semiconductor, from which we extract an optical band gap of 1.47 eV. Figure 1c shows the XRD patterns of the (112) face of a $CuInS_2$ crystal and of a powder sample prepared from the crystal boule, and the corresponding database pattern. The diffraction lines are not broadened, as they might be by small domains. Laue diffraction identifies the crystal's natural cleavage plane as (112) (inset to Fig. 1c), powder XRD confirms the tetragonal chalcopyrite structure (space group $I\bar{4}2d$). X-ray photoelectron spectroscopy (XPS) confirmed

Cu^{1+} and In^{3+} oxidation states as well as an S^{2-} sulfide peak (SI, Fig. S1). With scanning electron microscopy (SEM) we found that the crystal's perimeter—which had been in contact with the carbon-coated quartz wall—exhibits pronounced (112) terraces, i.e., along the natural cleavage plane (Fig. 1d and e).[23]

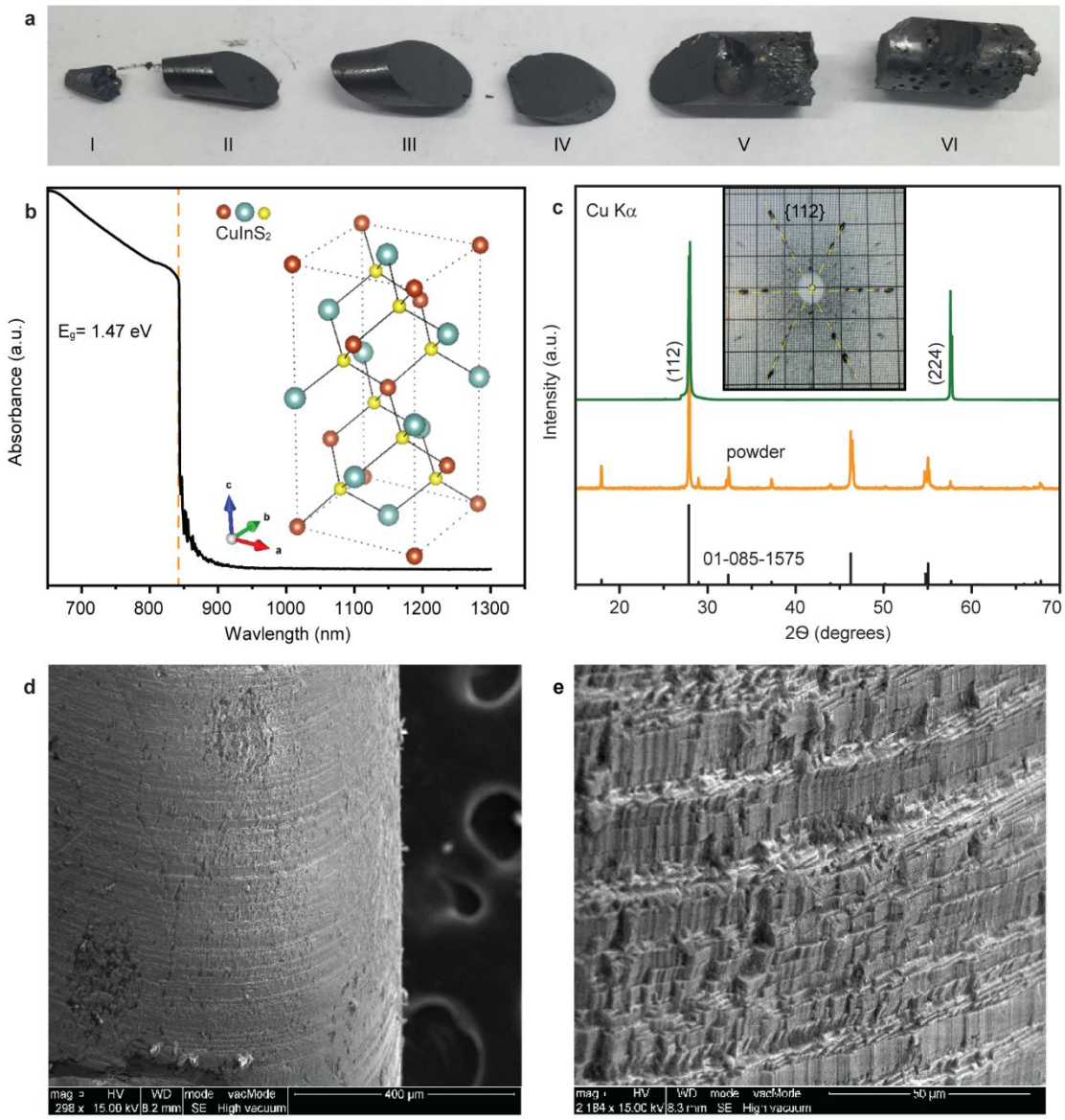

Figure 1. Structural and optical characterization of 1 mol% Cu-deficient $CuInS_2$ single crystal. a, The single crystal boule cleaved along the (112) in six sections upon extraction from the growth ampoule. All measurements in this work were performed on crystals extracted from section IV. **b**, Optical absorption spectrum of $CuInS_2$, showing a sharp onset of absorption at 1.47 eV. A freshly cleaved (112) slab (0.3 mm thick) was exposed for this measurement. The inset shows the tetragonal chalcopyrite structure of $CuInS_2$. **c**, XRD pattern of the single crystal face (green), powder form (orange), and database pattern match (black). The inset shows a Laue diffraction pattern of the (112) crystal surface. SEM imaging of section IV is presented at magnification **d**, 250x and, **e**, 2000x, revealing the pronounced (112) terraces on the perimeter of the crystal boule.

3.2 Microstructure of the bulk chalcopyrite $CuInS_2$. Samples for transmission electron microscopy were prepared by focused ion beam cutting in a FEI Helios NanoLab™ 600 dual beam system (FIB/SEM). Conventional TEM imaging, atomic resolution high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) imaging, and atomic-level EDS

mapping were performed on a double Cs-corrected FEI Titan Cubed Themis 300 scanning/transmission Electron Microscope (S/TEM) equipped with an X-FEG source operated at 300 kV and a Super-X EDS system. Relative compositions were determined with EDS by integrating the area of the elemental peaks. The stated compositions are average values over selected areas or pixels (making image resolution important); their estimated accuracy is ±0.5 at.%. The TEM elemental signal at a given atom position is produced by a whole column of atoms that are superposed in the ~ 100 nm thick sample. Therefore, the signal intensity combines the electron density (Z number) of the particular atom (or atoms when viewing in directions where Cu and In are superposed—see Fig. 4c) with the occupation of the column. While the EDS signal does not directly tell us the number of occupied sites in an atomic column, line scans or area scans do trace *changes* in occupation, and hence, composition; maximal intensity reflects complete occupation of a column, as in bulk $CuInS_2$.

The TEM image in Figure 2a taken in the $\langle 1\bar{1}0 \rangle$ direction shows that the $CuInS_2$ crystal has a lamellar structure. The lamellae are alternating pseudo-twins that form a herringbone pattern. The thickness of the lamellae ranges from several nm to hundreds of nanometers. The corresponding composite diffraction patterns from the pseudo-twins are shown in the bottom panels of Fig. 2a. They are taken from the $\langle 1\bar{1}0 \rangle$ and $\langle \bar{1}\bar{1}1 \rangle$ zone axes, respectively, and identify the pseudo-twin plane as {112}. The pseudo twins are separated by a rotational-twin boundary (a 180° rotation)[24] that has been theorized to be the most energetically favored twin boundary in chalcopyrites, as it avoids the reconstruction that would be inevitable in anion- and cation-terminated twin boundaries.[51,52] Pairs of twins are imaged at the tops and bottoms of each frame of Fig. 2b and c.

Periodic interfacial structures ("interphases") are seen to be inserted into the pseudo-twin

boundaries. In Fig. 2b and c these structures are viewed by aberration-corrected scanning transmission electron microscopy (STEM) from the $\langle 1\bar{1}0\rangle$ and $\langle \bar{1}\bar{1}1\rangle$ directions, respectively. The interphases at the pseudo-twin boundaries, shown schematically in Fig. 2d, contain a single (top frames of Fig. 2b and c) or a double (bottom frames) layer. In Fig. 2c the bulk chalcopyrite exhibits alternating pairs of bright (In stack) and faint (Cu stack) spots. As seen in the top frames, the single-layer interfacial structure includes two bright atomic planes but with interplanar spacings different from those of the chalcopyrite $CuInS_2$ bulk. The bulk twins sandwich the interfacial

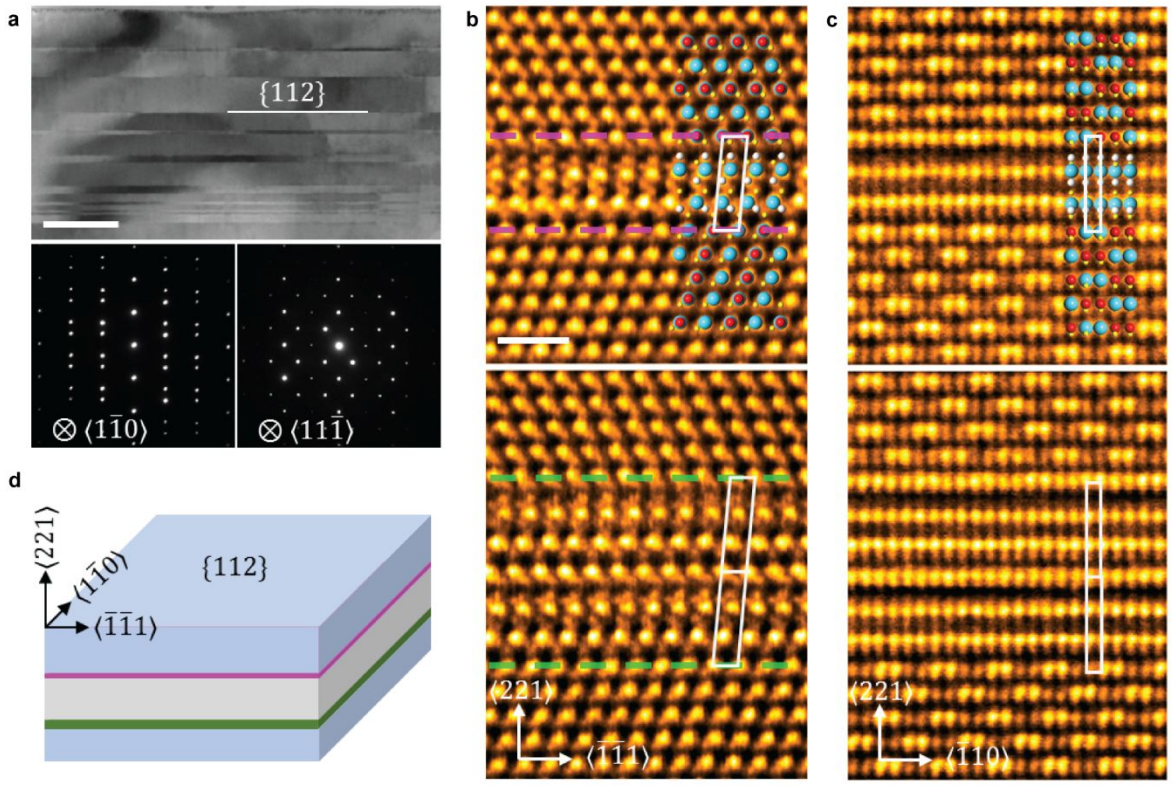

Figure 2. Microstructure of chalcopyrite $CuInS_2$. a, Bright-field TEM image showing lamellar pseudo-twins. The pseudo-twin plane is {112}. Scale bar, 500 nm. The corresponding composite diffraction patterns of the bottom panels were taken along the $\langle 1\bar{1}0\rangle$ and $\langle \bar{1}\bar{1}1\rangle$ zone axes, respectively. **b**, **c**, High-resolution STEM HAADF images showing parts of chalcopyrite $CuInS_2$ pseudo-twins above and below single (top frames) and double layers (bottom), viewed from the $\langle 1\bar{1}0\rangle$ and $\langle \bar{1}\bar{1}1\rangle$ directions, respectively. A color-coded chalcopyrite structure (Cu, red; In, blue; S, yellow) is overlaid on the TEM images to identify atoms. In Fig. 2c, atomic-column pairs of Cu and In can be seen—note the alternation of bright (In) and faint (Cu) pairs in the bulk crystal. Scale bar, 1 nm. **d**, Schematic illustration of (blue or gray) bulk $CuInS_2$ pseudo-twin lamellae separated by a single (magenta) and a double (green) interphase, all stacked in the $\langle 221\rangle$ direction.

phase. Note, again, that in the atomic resolution images, changes in spot size or intensity reflect changes of the type and/or the number of atoms in the stack at that position.

3.3 Composition of bulk crystal and of interfacial structures. The chemical compositions of bulk and interphases were determined by mapping the three elements by atomic-level STEM energy-dispersive X-ray spectroscopy. Figure 3a and b show STEM-HAADF images of bulk chalcopyrite $CuInS_2$, and the corresponding elemental maps of Cu (red), In (green), and S (blue), viewed along the $\langle 1\bar{1}0\rangle$ and $\langle \bar{1}\bar{1}1\rangle$ directions, respectively (see more details of single-element mappings in the SI, Fig. S2). The bulk composition is 25.2 at.% Cu, 24.3 at.% In and 50.5 at.% S, (SI, Table S1), which is, within accuracy, the stoichiometry of $CuInS_2$. The chalcopyrite unit cell is delineated to identify the atomic positions. While in the $\langle 1\bar{1}0\rangle$ projection (Figs. 3a and 4c) Cu and In atoms lie on top of each other, in the $\langle \bar{1}\bar{1}1\rangle$ projection of Fig. 3b they alternate (bright, In; weak, Cu).

We used EDS to also determine by how much the composition of the interphases deviates from bulk $CuInS_2$, along the trace marked in the HAADF image of Fig. 3c. The panel at its right shows the element maps of Cu (red), In (green) and S (blue). The lower left panel shows the EDS-determined concentration profiles along the trace in the STEM-HAADF image above. With respect to the bulk, the interfacial layers are depleted of Cu (down -7.9 at.% in the single layer and down -11.5 at.% in the double layer) and contain up to +8.6 at.% excess In and +3.0 at.% excess S. Thus, while the bulk contains 25.2 at.% Cu, the single and double interfacial phase layers contain only 17.1 at.% and 13.7 at.% Cu, respectively, but 32.9 at.% In (for sulfur see SI, Table S1). An additional example, analyzed along the $\langle \bar{1}\bar{1}1\rangle$ direction, is provided in the SI, Fig. S3. The copper deficiency of the interfacial phase suggests that the interfacial phase accommodates the copper deficiency of the overall crystal.

3.4 Structure of the Cu-deficient interphases, and the [V_{Cu} In_i V_{Cu}] triple point defect. The atomic occupations in the interfacial structures can be deduced from the atomic resolution STEM-

HAADF images of Fig. 2b and c. Figure 4 shows the corresponding atomic models of a single-layer interfacial structure (top frames of Fig. 2b and c), viewed from $\langle 1\bar{1}0 \rangle$ and $\langle \bar{1}\bar{1}1 \rangle$, respectively.

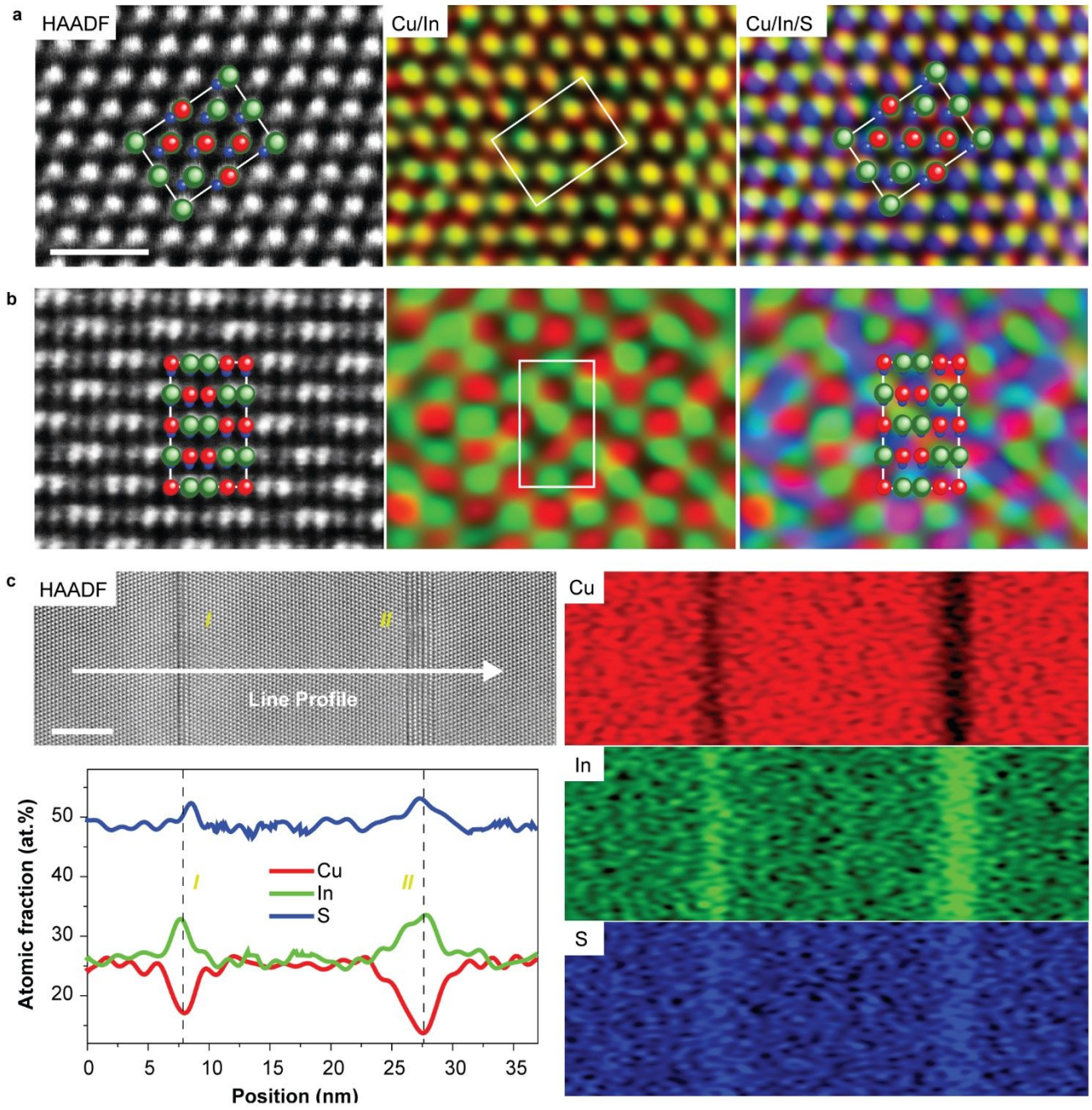

Figure 3. Quantitative analysis of composition. a,**b**, Atomic-level STEM-EDS maps showing the positions of Cu (red), In (green) and S (blue) in bulk chalcopyrite $CuInS_2$. The top row is viewed along the $\langle 1\bar{1}0 \rangle$ direction and the second row along $\langle \bar{1}\bar{1}1 \rangle$. The leftmost panels show HAADF-STEM images, the center panels the element mappings of Cu/In and the right panels of Cu/In/S. The chalcopyrite unit cell is delineated to highlight the positions of the three elements. In the $\langle 1\bar{1}0 \rangle$ projection Cu and In atoms are superposed; in the $\langle \bar{1}\bar{1}1 \rangle$ projection they are separate. Scale bar, 1 nm. **c**, STEM-EDS mapping of bulk $CuInS_2$ including one pseudo-twin boundaries with a single (***I***) and one with a double (***II***) interphase layer. The HAADF image shows the EDS trace across the bulk and the two interphases. The right panel combines the elemental maps of Cu (red), In (green) and S (blue) from multiple scans. The compositional profiles along a single scan, at bottom left, show Cu depletion and In and S enrichment in the interfacial layers. Scale bar, 5 nm. To improve the contrast in elemental maps, color coding in this Figure, and in Figs. S2 and S3, is red/green/blue, different from the red/blue/yellow in Figs. 1, 2, 4, and 5.

Note the color codes in Figs. 4 and 5, where In is coded blue and S yellow throughout; the Cu position, however, is coded red in the chalcopyrite structure but gray in the interphase, the latter because we cannot exclude partial occupation by In. In Fig. 4a, viewed along the $\langle 1\bar{1}0 \rangle$ direction, Cu and In overlap in the chalcopyrite bulk structure, as further illustrated in the unit cell of Fig. 4c. Viewed along $\langle \bar{1}\bar{1}1 \rangle$ in Fig. 4b, the Cu and In positions are separate. The black quadrangles in Fig. 4a and b delineate the minimal cells of the interphase structures.

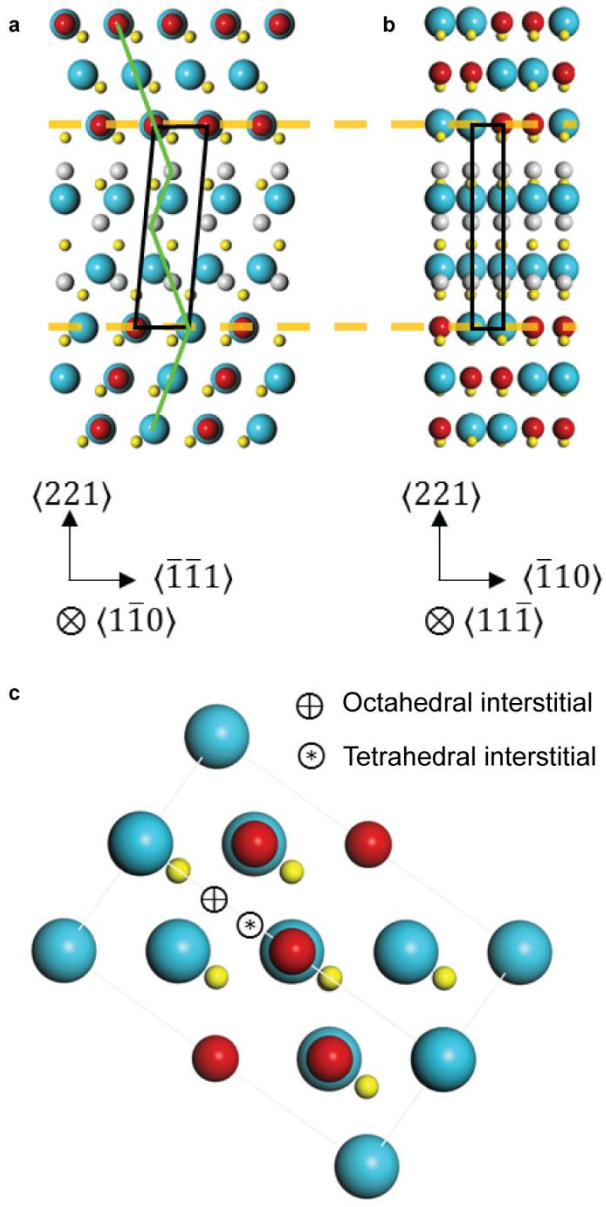

Figure 4. Schematic of the interfacial structure. a, b, Atomic model of the single-layer interfacial structure (top frames of Fig. 2b and c) viewed along the $\langle 1\bar{1}0 \rangle$ and $\langle \bar{1}\bar{1}1 \rangle$ zone axes, respectively. **c**, Chalcopyrite unit cell viewed in the $\langle 1\bar{1}0 \rangle$ direction, identifying the interstitial sites. Note the overlaid Cu (red) and In (blue) positions. The ball size qualitatively reflects the Z (= electron) number of a given atom.

Because the atom positions in the interphases are largely derived from those in the bulk, we turn to inspecting the STEM-HAADF image of Fig. 5 taken along the $\langle 1\bar{1}0 \rangle$ zone axis (see Fig. 4a). Figure 5 shows a transition from a pseudo-twin boundary in the bulk, at left, to a single-layer interphase. Three In rows of the chalcopyrite bulk are seen to merge into two rows (blue) in the interphase. There, one row lies at the normally occupied chalcopyrite site In_{In} (e.g., 1/4, 1/4, 1/8). The other row of In is positioned as interstitial In_i at tetrahedral interstices (e.g., 3/4, 1/4, 1/8) in the chalcopyrite structure, identified in Fig. 4c. The additional occupation of tetrahedral sites forms an In-enriched interfacial layer. While in the transition from bulk to interphase the Cu atoms remain in their bulk Cu_{Cu} positions, Fig. 5a shows that their intensity fades in the transition from left to right. To remind the reader that in the interphase these positions remain normal Cu-on-In stacks (instead of Cu only) they are color-coded gray. However, their intensity becomes so small that we can be certain that in going from bulk to interphase many Cu_{Cu} sites in the stack are emptying out and become copper vacancies, V_{Cu}. Note that, as Cu fades, the In intensity increases going from left to right, a consequence of the merger of three rows in the bulk to two rows in the interphase. Thus, a dominant feature of the interphase is a fully occupied In stack (blue) placed between two stacks that, given their faint intensity, are highly deficient in Cu (gray). In the interphase, the EDS concentrations of Fig. 3c go down to a Cu deficiency of 11.5 at.% and up to an In excess of 8.6 at.%. Hence, the estimated atomic ratio of V_{Cu} to In_i is 11.5/8.6 = 1.34. Taken together, the atomic positions of two faint Cu stacks sandwiching the In_i stack, plus this ratio 1.34, are structural and compositional indicators for a high concentration of [V_{Cu} In_i V_{Cu}] defect triplets. In_{In} is an electron donor, and V_{Cu} is an electron acceptor. The defects will exchange charge, such that [V_{Cu} In_i V_{Cu}] triplets self-compensate to electrically neutral [V_{Cu}^{1-} In_i^{2+} V_{Cu}^{1-}].

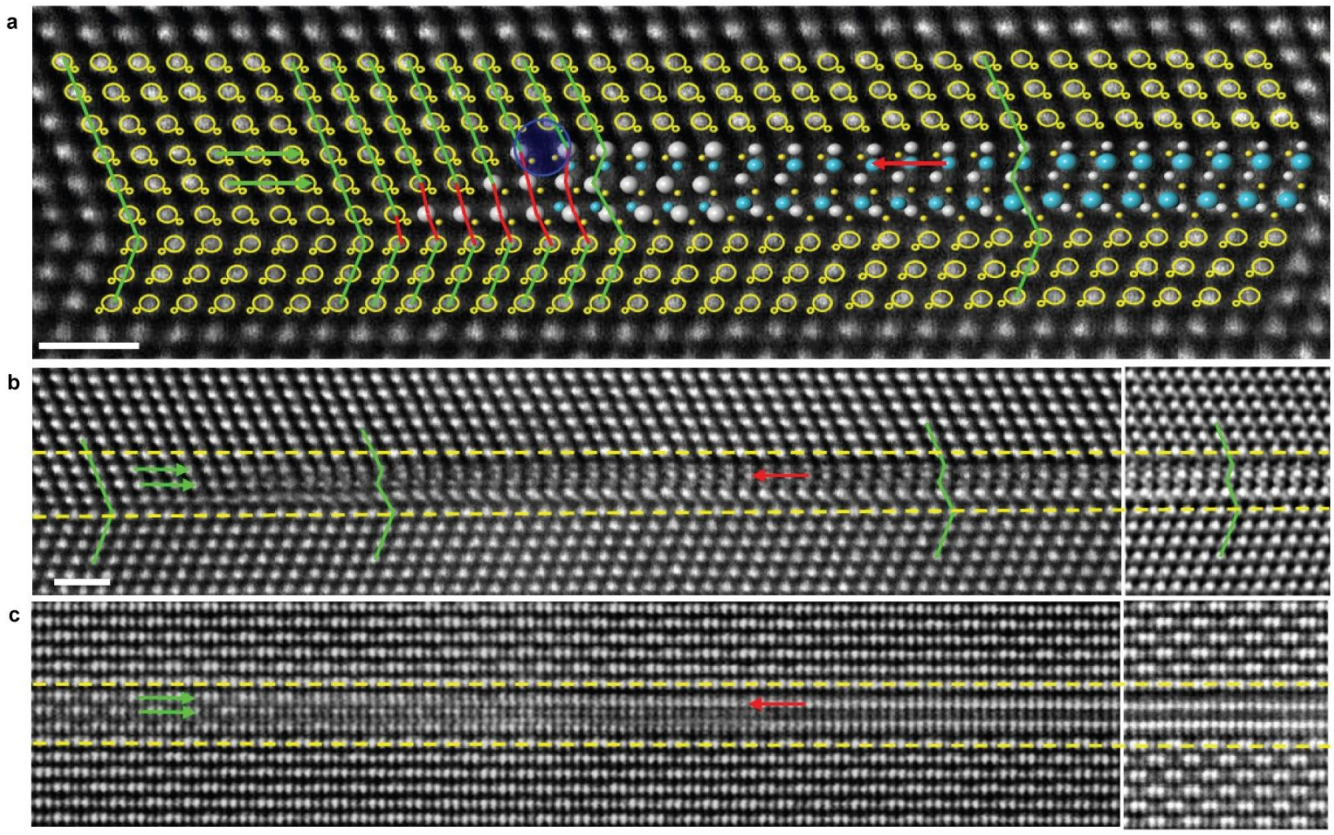

Figure 5. Transition from pseudo-twin boundary to interphase, observed going from left to right. a, Magnified STEM-HAADF image along the $\langle 1\bar{1}0 \rangle$ zone axis, with an overlaid atomic model to highlight the interfacial defect formed by the pseudo-twin boundary. The big and small open circles in the $CuInS_2$ bulk structure represent the occupations of Cu/In and S, respectively (see Fig. 2b). The In (blue) and S (yellow) atoms located in the interphase layer are color coded as in Figs. 1a, 2b, c, and 4. Cu is shown in grey (see text). The chalcopyrite phase at left has In and Cu atoms that lie on top of each other in their normal positions (grey). Going to the right, one can see that In (blue) has emerged from that stack by moving to a new position, which is the tetrahedral interstitial site of chalcopyrite. **b, c,** Original STEM-HAADF images, viewed along the $\langle 1\bar{1}0 \rangle$ and $\langle \bar{1}\bar{1}1 \rangle$ zone axes, showing how the interphase emerges from the pseudo-twin boundary. Sectioned off at right are images taken far from this transition. Scale bars, 1 nm.

The crystal contains planar, line and point defects. The interphase introduces a defect plane. This plane becomes apparent when counting from the meeting point of the herringbone pseudo-twin lattice planes in the bulk (green lines with elbows at the left of Fig. 5a and b) to equivalent planes separated by the interphase. There the equivalent bulk planes are offset, as illustrated in Fig. 5a and b (and Fig. 4a) by the jogs in the green lines that run from bulk to bulk across the interphase. This slip plane constitutes a planar defect that is contained in the interphase.

The transition from or to the pseudo-twin plane to interphase produces a line defect, which in Fig. 5a is surrounded by the blue circle. This is a partial dislocation, 1/6 $\langle \bar{1}\bar{1}1 \rangle$, which is similar to the 1/6 $\langle 112 \rangle$ in the face-centered cubic system. This dislocation compensates the displacement of interfacial atoms that is traced by the red lines. The blue circle around the positions of the atoms that surround the dislocation draws attention to the mispairing of coordinative bonds caused by the change of atomic stacking. As seen in the SI, Fig. S4, some of the interlayer phases form disks that are fully embedded in the crystal (instead of running from side to side), and therefore will be surrounded by a ring of these partial dislocations.

Thus, structural defects include the (112) pseudo-twin boundary of the bulk crystal, the (112) slip plane within the interphase, the 1/6 $\langle \bar{1}\bar{1}1 \rangle$ partial dislocation at the perimeter of the interphase, as well as In_i and V_{Cu} within the interphases. What are their opto-electronic consequences?

3.5 Electronic transport and photoconductivity. Electronic transport properties were measured along the (112) plane of an 2x3x0.3 mm^3 sample with eutectic In-Ga contacts made on the (112) surface and Pt lead wires, using a Quantum Design Physical Property Measurement System (PPMS). In-plane resistivity vs. temperature data (plotted in Fig. 6) was collected from 395 K to 300 K—where we reached the measurement limit of our equipment. At T = 300 K, ρ_{xx} is 2.7×10^6 Ω·cm. From plotting log(ρ_{xx}) vs. 1/T (inset, Fig. 6a) we extract the thermal activation energy of 87 meV. Hall effect measurements performed at magnetic fields from $\mu_0 H$ = -3 to 3 T at 300 K gave the Hall resistivity ρ_{xy}, shown in Fig. 6b. The actual quantity plotted is ρ_{xy} with some admixture of ρ_{xx} because the Hall contacts were not made exactly orthogonal to the current and field directions. The negative slope reflects *n*-type conduction. The calculated electron concentration, *n*, is 2.3×10^{13} cm^{-3}, and the electron mobility, μ_n, calculated from ρ_{xy} and *n*, is 0.1

cm^2 V^{-1} s^{-1}. While high ρ and low n have been observed before, μ_n is unusually low.[6,9] Given that the (112) interphase layers embedded in the crystal may cause anisotropic conduction, we made a top-to-bottom ([112] direction) resistance measurement, from which we estimate $\rho_{zz} \approx 1x10^6$ Ω·cm, i.e., close to the ρ_{xx} measured laterally.

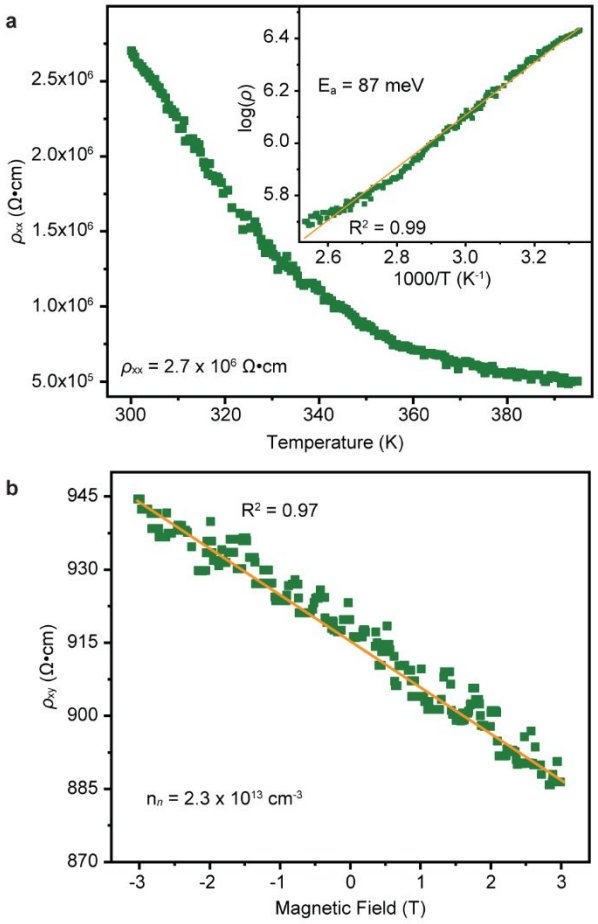

Figure 6. Electrical characterization of the 1 mol% Cu-deficient $CuInS_2$ single crystal. a, Resistivity (ρ_{xx}) vs. temperature profile from 300-395 K. The inset plots this data as log ρ_{xx} vs. 1/T from which an activation energy of 87 meV is extracted. **b**, Hall resistivity (ρ_{xy}) vs. magnetic field from μ_0H = -3 to 3 T at 300 K. The negative slope identifies electrons as the crystal's majority carrier. From this data we can calculate an electron concentration, *n,* of 2.3 x 10^{13} cm^{-3}.

Photoconductivity was measured in the configuration shown in the inset to Fig. 7a, with InGa eutectic and Pt wire contacts applied to the (112) face of the sample that had been characterized by TEM. LEDs of the eight different wavelengths (ThorLabs, FWHM ≈ 55 nm) shown in Fig. 7a illuminated the sample at irradiances ranging from 0.25 to 70 mW/cm^2, over voltages from +/- 10 V supplied by the PPMS. Illumination with LEDs enables high irradiance, at the expense of modest spectral resolution. Irradiances were measured using a digital handheld

optical power meter (model PM100D, Thorlabs) coupled with a Photodiode Power Sensor (model S120VC, Thorlabs).

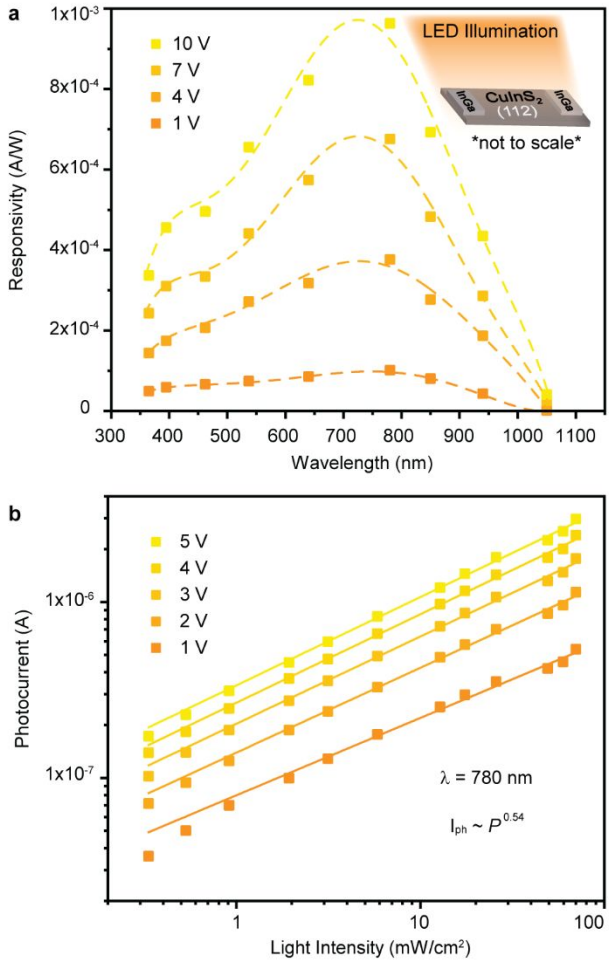

Figure 7. The photo-electric properties of the $CuInS_2$ crystal. a, Responsivity vs. wavelength for four applied voltages. Responsivity is highest at 780 nm. The inset shows the measurement geometry. **b**, Photocurrent vs. light intensity at 780 nm illumination for five applied voltages. A simple power law fit (solid lines) results in an exponent of 0.54.

In the responsivity vs. wavelength graph of Fig. 7a, for applied voltages ranging from 1 V to 10 V, dotted lines serve as guides for the eye. The responsivity peaks at 780 nm, corresponding to a photon energy of 1.59 eV (± 0.05 eV LED FWHM). The linear decrease in responsivity with wavelengths below 780 nm reflects a constant quantum efficiency. While SI, Fig. S5 shows the photocurrent vs. voltage plot for 780 nm irradiance from 0.25 to 70 mW/cm^2, Fig. 7b shows the log-log plot of the photocurrent vs. 780 nm irradiance. The dependence of log photocurrent on log light intensity is linear and fits a simple power law: $I_{ph} = AP^{\alpha}$ where I_{ph} is the photocurrent, A is a

scaling constant, P is the irradiance, and α is an exponent. The solid lines represent this fit. The slopes of these fits for 2V to 5V applied bias are identical at $\alpha = 0.54$.[53]

4. DISCUSSION

4.1 The [V_{Cu} In_i V_{Cu}] triple point defect. Electron microscopy of structure and composition at atomic resolution shows that introducing Cu deficiency in a $CuInS_2$ crystal results in exactly stoichiometric $CuInS_2$ bulk with intercalated sheets of a phase that is highly Cu deficient and In rich. These interphases lie in (112) planes, are nanometers thick, and contain either two or four In layers. Analysis of the transition from chalcopyrite-type bulk $CuInS_2$ to the interphase shows that three (or six) In_{In}-containing layers from normal sites in the bulk merge to two (or four) layers of interstitial In_i in the interphase, while the positions and number of the three (or six) corresponding Cu and S containing layers are preserved in the transition from bulk to interphase. There, the positions of Cu_{Cu} (and therefore V_{Cu}) on normal sites bracket interstitial In_i atoms. While the atomic positions in Fig. 5 do not reveal the actual occupation of sites within each stack, Coulombic attraction will make two V_{Cu}^{1-} become nearest neighbors of one In_i^{2+}. This positioning, the estimated Cu_{Cu}, V_{Cu} and In_i concentrations, and the high electrical resistivity of the sample taken together are conclusive indicators for the existence of electrically neutral [V_{Cu}^{1-} In_i^{2+} V_{Cu}^{1-}] triplets.[45] These are the basic structural modifier of ordered defect compounds in I-III-IV diamond-like semiconductors. The pronounced separation into stoichiometric $CuInS_2$ and a highly Cu-deficient interlayer phase confirms that the Cu deficient phase has high thermodynamic stability with respect to bulk $CuInS_2$. The cause of this stability is the reduction of Cu content, which diminishes the intensity of repulsion by the antibonding Cu d – S p hybrid states that form the top of the valence band.

A rough estimate suggests that the interphase layers absorb much of the Cu deficiency introduced with the initially Cu-deficient charge used for crystal growth. Viewing the excess In in the interphases as the binding agent for Cu vacancies that have diffused out from the bulk $CuInS_2$, we calculate the concentration of V_{Cu} as approximately twice that of excess indium. EDS measures that the interphase with two rows of indium contains 8.6 at.% excess indium. This corresponds to (2 rows) x (2 V_{Cu} per In_i) x 8.6 at.% excess $In_i \cong 34$ at.% of Cu missing from that interphase. The interphase accommodates three rows of copper, just like the bulk. Therefore, the overall Cu deficiency in the interphase is 3 x 34 at.% = 102 at.%, equivalent to about one row of V_{Cu}. The average thickness of bulk $CuInS_2$ between the interphase layers is ~ 100 nm, which corresponds to ~ 300 layers of atoms. Following this argument, the original fraction of Cu vacancies in the hypothetical homogeneous, non-stoichiometric, crystal would have been ~ 1/300 ≅ 0.003, a value close to the targeted Cu deficiency of 1 mol% [0.25 – 0.003 = 0.247 at.%] of the starting material. This approximate agreement suggests that excess In_i is a titer for V_{Cu}, and that the interphases efficiently soak up V_{Cu} where they are thermodynamically quite stable.

Under the electron beam, the edge of an embedded interphase can be moved back and forth like a zipper. That observation implies fast movement of atoms. When zipping to extend the interphase, two rows of In_i can revert to three rows of In_{In} with minimal atomic displacement. S stays in its normal sites, as does Cu. However, a newly extended perimeter of the interphase needs stabilization by Cu vacancies. The observed zipper-like fluidity implies that V_{Cu} are supplied rapidly from the depth of the interphase to its growing edge. The electron beam likely provides the energy needed to dissociate the [V_{Cu}^{1-} In_i^{2+} V_{Cu}^{1-}] triplets, thereby supplying V_{Cu} to the advancing edge. Because of the high V_{Cu} concentration, Cu_{Cu} atoms will move easily between the Cu sites,

perhaps even functioning as a (112) confined sheet of Cu_{Cu} 'liquid'. Similarly, illumination has been observed to render [V_{Cu}^{1-} In_{Cu}^{2+} V_{Cu}^{1-}] triplets in $CuInSe_2$ nanocrystals high mobile.[54]

4.2 Crystallographic defects. While the existence of the [V_{Cu}^{1-} In_i^{2+} V_{Cu}^{1-}] triplet is made certain by a group of observations that prove the existence of a high concentration of V_{Cu} at the appropriate positions in the interphases, several crystallographic defects can be seen directly. They include the pseudo-twin boundary in the (112) planes, separating lamellae of $CuInS_2$ that are rotated 180° against their neighbors; 1/6 $\langle\bar{1}\bar{1}1\rangle$ partial dislocations that accommodate a bond mismatch at the periphery of the embedded interphase layers, and a one-bond offset with respect to the bulk, of lattice planes that terminate at interphase layers. Typically, such planar and line defects cause electronic defects, and indeed many point defects have been postulated for $CuInS_2$.[45,55–61] While no specific electronic defect has been identified in the present study, the observed photoconductivity exponent of 0.54 suggests that electronic defect levels do exist in the energy band gap, with a density of defect states decaying away from the band edges.[53,62] For a comprehensive overview of point defects in a chalcopyrite, the reader is referred to the discussion of $CuInSe_2$ by Zhang et al.[45]

The fully embedded interphase (SI, Fig. S4) demonstrates that pseudo-twin boundaries do exist in the absence of interphases. This suggests that at least some, and possibly all, of the interphases did form following the growth of a non-stoichiometric crystal. While Fig. 5 shows that the excess In in the interphases can be supplied by the merger of three In layers in bulk $CuInS_2$ to two layers in the interphase, V_{Cu}, however, must collect in the interphase by diffusion from the surrounding bulk. Figure 2a shows that the pseudo-twin boundaries, where the interphases are located, are spaced ~100 nm apart. It is instructive to compare the diffusion lengths of Cu and In under the crystal's annealing conditions of 400 °C for 24 hours, because that is the lowest

temperature at which a solid-state reaction might have proceeded in the present crystal. The diffusion coefficient of Cu^{1+}, determined from NMR line narrowing,[63] is $D(Cu^{1+}) = 5x10^{-3}$ x exp(-1.25 eV/ kT) ≅ $2x10^{-12}$ cm^2s^{-1} at 400 °C. The diffusion coefficient of In, determined with a radioactive tracer experiment at 650 °C, is $D(In) = 8.0x10^{-10}$ cm^2s^{-1};[50] the thermal activation energy was not measured. At 650 °C the calculated diffusion coefficient of Cu = $7x10^{-10}$ cm^2s^{-1} is essentially the same as that of In, surprisingly, given that Cu is considered to be less strongly bound in the chalcopyrite than In. Assuming the same activation energies for Cu and In diffusion, at 400 °C both diffusion coefficients, D, will be ~ $2x10^{-12}$ cm^2s^{-1}. For a 24-hours long diffusion time, *t*, the diffusion length $\sqrt{Dt}$ will be 4 μm, far longer than the ~ 100-nm spacing of the Cu poor interphases. Therefore, as far as Cu and In atomic and associated defect distributions are concerned, the crystal is equilibrated at 400 °C. While at high temperature the crystal may be homogeneous single-phase $CuInS_2$ with a high concentration of V_{Cu}, upon cooling it will segregate out V_{Cu} to interphases at temperatures down to 400 °C.

In the present case the Cu-poor interphases form along the (112) pseudo-twin boundary. Free surfaces of $CuInS_2$ can also become Cu poor.[44,64] At grain boundaries, to explain the passivation to recombination of photo-excited holes in polycrystalline thin film $CuInSe_2$ solar cells, Jaffe and Zunger argue that Cu depletion at grain boundaries sets up an electric field that repels holes.[65] Similar to this Cu depletion from free surfaces, grain boundaries and device interfaces,[10] the (112) pseudo-twin boundaries of the present crystal may function as nucleation sites for the Cu-poor interphases.

With the diffusion lengths of Cu and In being much larger than the spacing between the interphase layers, one may expect some interphases to grow at the expense of others due to Ostwald ripening. This might have occurred in the present crystal, because only single-thickness

interphases are found fully surrounded by bulk $CuInS_2$; these may be the first stage of V_{Cu} segregation. Single-thickness layers that extend through the entire crystal, and even more so, double layers, may already have benefitted from Ostwald ripening. The observations by Cattarin and Guerriero suggest that ripening may continue under appropriate crystal growth conditions.[25] The peculiar structural aspect of a filamentary $CuInS_2$ bulk observed by Cattarin et al.[26] was not seen in the present crystal.

4.3 Optical band gap. The optical gap determined from the transmission spectrum of 1.47 eV disagrees with the accepted band gap value for $CuInS_2$ of 1.53 eV.[8,9,28,66,67] It lies close to the 1.48–1.50 eV optical gaps reported by Cattarin et al.[40] in their work with photoanodes made of $CuInS_2$ that had filamentary morphology. The optical gap of 1.47 eV must originate in the interphase layers. As these occupy ~ 1% of the thickness of the 0.3 mm thick sample, the sum of their thicknesses is ~ 3 μm. If the joint valence band (VB) – conduction band (CB) states in the interphase layers remain localized on the Cu atoms,[66] they will absorb light as strongly as bulk $CuInS_2$ does. Then the reduction of the Cu concentration to ~ 2/3 of that in bulk $CuInS_2$ will reduce the strength of optical absorption in the interphase by only 1/3 from that of $CuInS_2$.

Analyses and computations highlight that the valence band maxima (VBM) in chalcopyrites lie at much higher electron energy (lower ionization energy) than in the equivalent II-VI semiconductors.[8,45,46,66] The antibonding Cu *d* – X *p* hybrid states in the valence band are the cause. Reducing the copper content reduces the antibonding repulsion, hence lowers the energy of the VBM. The conduction band minimum (CBM) is similarly displaced, but usually less strongly because of the compensating Coulombic attraction between the 2 V_{Cu}^{1-} and In_{Cu}^{2+} defects. Thus, band structure calculations suggest that the band gap will increase as the Cu content is reduced.[65]

Given the absence of experimental data for $CuInS_2$ that verify these theoretical predictions, we resort to relevant observations in its $CuInSe_2$ homolog. Experiments along the Cu_2Se – In_2Se_3 quasi-binary indeed agree with theory,[68] in that reducing Cu raises the bandgaps of Cu-In-Se compounds, from chalcopyrite $CuInSe_2$ (Cu:In = 1.00) at 0.99 eV, to $CuIn_3Se_5$ (Cu:In = 0.33) at 1.17 eV, to $CuIn_5Se_8$ (Cu:In = 0.20) at ~ 1.23 eV. As well, the corresponding electron affinities rise from 4.26 eV to 4.48 to ~ 4.62 eV. This rise in bandgap and electron affinity with Cu depletion was observed in CdS/$CuInSe_2$ solar cells.[34] Maeda et al.[68] found that within the $CuInSe_2$ homogeneity range, decreasing the Cu concentration does not change the gap, while the gap of the $CuIn_3Se_5$ phase does increase gradually, again, in agreement with theoretical prediction.

Returning to the sulfide, Shay, Neumann and Wasim[8,46,66] argue that the sensitivity of the bandgap value to Cu deficiency will be proportional to the degree of *d-p* hybridization, which is 34% in $CuInSe_2$ and 45% in $CuInS_2$.[8] This would mean that the energy positions of the VBM and the CBM in Cu-In-S compounds will exhibit a more pronounced drop with Cu depletion than of the Cu-In-Se compounds. In computations, this trend is borne out for the band gaps for $CuInS_2$ (1.45 eV) and $CuIn_5S_8$ (1.58 eV), and in the lowering of the CBM energy (i.e., increasing electron affinity) by 0.50 eV.[37] However, the experimentally measured values for thiospinel-structure $CuIn_5S_8$ do not agree. An indirect gap was detected at 1.29–1.31 eV and a direct gap at 1.51 eV, both lower than the $CuInS_2$ gap of 1.53 eV.[42,43,69] On the other hand, increased open-circuit voltage in $CuInS_2$/CdS solar cells is attributed to reduced interface recombination, caused by an increase of the band gap by Cu depletion.[10] While this observation deserves further analysis, the directly measured optical absorption edge of the present crystal agrees with neither the theoretical prediction for a Cu-deficient Cu-In-S phase, nor can it be linked to values observed for $CuIn_5S_8$. Likewise, currently available experimental data do not enable verification of the theoretically

predicted band edge offsets between $CuInS_2$ bulk and interphase layers, and further, of their possible consequences for barriers or quantum wells.[37] As an aside, our observation that the edge of interphase disks can be moved like a zipper by the electron beam of the microscope suggests that the coherent strain between bulk and interphase is small, hence may have little effect on band edge positions.

In summary, the observed value of the optical gap of 1.47 eV is ascribed to the Cu-poor interphase, in disagreement with theoretical predictions for Cu-poor bulk phases. The VBM and CBM positions of the interphase, and its band edge offsets to $CuInS_2$ remain to be determined.

4.4 Electronic transport and photoresponse. The electron mobility of 0.1 $cm^2V^{-1}s^{-1}$ is much lower than literature values, which range from 9 to 338 $cm^2V^{-1}s^{-1}$.[6,9,22,49,55] Only in *p*-type $CuInS_2$, made *p*-type by annealing in sulfur, a similarly low hole mobility of 0.1 $cm^2V^{-1}s^{-1}$ has been reported.[57] Early on, nearly complete donor-acceptor self-compensation was speculated to cause electron localization, hence low mobility, with the residual donor defects being In_{Cu} and V_S.[55] But charge carriers are scattered only weakly at highly symmetric grain boundaries like the (112) pseudo-twin boundary, and a free-carrier mobility of 0.1 $cm^2V^{-1}s^{-1}$ would imply a mean free electron path smaller than the interatomic distance. Therefore, the observed low electron mobility must be caused by trapping associated with the disk-like layers of the Cu-poor interfacial phase. An alternative interpretation, arising from the performance of lamellar $CuInS_2$ photochemical electrodes by Cattarin et al.,[25] invokes barriers to charge transport. These authors find that the $CuInS_2$ bulk is *n*-type while the interphase lamellae are either insulating or *p*-type, such that they may form *n*/*i*/*n* or *n*/*p*/*n* barriers in the conduction band. Because the interphase layers in our crystal are so thin, any barrier to electron transport may not be built up by a space charge, but instead may be caused by an offset in the CB edges and/or by interface dipoles. Unfortunately, around room

temperature the experimentally determined T-dependence of the mobility, $\delta\mu_n/\delta T$, is an unreliable guide to a physical mechanism, as the transition from impurity scattering to lattice scattering can change the value and even the sign of $\delta\mu_n/\delta T$.[27,49,55]

The electrical resistivity at room temperature (RT) of 2.7×10^6 Ω·cm is high because of the low electron mobility and the low electron concentration of 2.3×10^{13} cm^{-3}. High resistivities have been observed in as-grown crystals,[22,55,70] in crystals equilibrated with Zn (hence Cu-poor),[27] and in thin films prepared without excess Cu.[10,71] As nanometer-thick Cu-poor interphases cannot be detected by the routine X-ray diffraction analysis typically employed in thin-film solar cell work, some of the highly resistive material of earlier studies also may have been stoichiometric $CuInS_2$ with interphase inclusions. With the reservation that the thermal activation energy of the electrical resistivity includes both electron density and mobility, the value measured here of 87 meV is compatible with the donor ionization energies identified in $CuInS_2$, which range from 5 meV to 570 meV.[45,56–61]

The observations made on the present crystal agree with earlier work that invoked self-compensation due to the additional degree of freedom inherent in a two-cation structure of differing valency.[51,58,72–74] The widely accepted mechanism postulated by Zhang and Zunger[45] is the formation of electrically neutral [V_{Cu}^{1-} In_{Cu}^{2+} V_{Cu}^{1-}] defect triplets, which the present study confirms. Such self-compensation will raise the electrical resistivity. The sample's high resistivity also suggests that the atomic ratio of V_{Cu} to In_i, estimated from EDS data to be 1.34, likely lies very close to 2, as a large excess of relatively shallow In_i donors would greatly increase the concentration of free electrons.[56]

The spectral photoresponse, shown in SI Fig. S5, extends out to 1050 nm (1.18 eV) illumination, and agrees with the photoconductivity spectrum reported by Cybulski et al.[27] for *n*-

$CuInS_2$. The corresponding deep levels most likely lie in the interphases and the partial dislocations at their perimeters.

4.5 Implications for $CuInS_2$ thin films. The interphase layers segregate out on (112) pseudo-twin boundaries, which are planar defects with very small interfacial energies. Polycrystalline thin-film solar cells contain planar defects with substantially larger interfacial energies, which are more conducive to the segregation of planar second phases: free surfaces during film growth, grain boundaries, and device interfaces including heterojunctions and electrical contacts. While such planar defects will be stable locations for Cu-poor interphases, these can be detected only by high-resolution electron microscopy.[33] In the few-micrometer thick films employed for solar cells, the Cu deficient material will not be sufficiently thick to reduce the optical gap, and therefore won't be visible in optical absorption. However, in solar cell work to date, many electrical effects have been imputed to native compositional inhomogeneities. To establish reference samples, these electrical effects must be correlated once with structural and compositional analysis on the nanometer scale. After that, electrical techniques will remain the methods of choice for routine evaluation of device films. Electric fields associated with grain boundaries including polarity-induced band bending may confine photogenerated minority carriers, so that columnar grains will function as minority carrier conduits.[51] Using this argument, Cu-depleted grain boundaries have been inferred from high minority carrier lifetime. On the other hand, interphases at intra-grain boundaries may reduce the electron mobility as they do in the single crystal. Copper-depleted layers are likely to form at solar cell heterojunctions. These may favor or oppose the collection of photogenerated carriers. Indeed, $CuInS_2$ heterojunction solar cells have been made more efficient by using buffer layers that are impervious to Cu-in-diffusion. Pursuing a comparable goal on the Cu-rich side, $CuInS_2$ films have been deposited with excess Cu

and S to raise their chemical potentials above those in $CuInS_2$; the ensuing macroscopic cover of excess Cu_2S must be etched away before the heterojunction is formed.[13] Such empirical approaches have been central to the development of thin-film chalcopyrite heterojunction solar cells. Quantitative device design and simulation will require further experimental data, acquired on the nanometer scale, about the properties of $CuInS_2$ and of its interfaces with buffer and contact materials.

5. CONCLUSIONS & OUTLOOK

While the electrical transport properties of chalcopyrite-type semiconductors are adjusted by changing stoichiometry instead of substitutional doping setting the solar cell performance of $CuInS_2$ thin films by changing their Cu content has produced contradictory results. The present study of a single crystal shows that 'Cu-poor' $CuInS_2$ is bi-phasic on the nanometer scale. Cu deficiency segregates out readily along (112) pseudo-twin boundaries, where the deficiency organizes in the form of $[V_{Cu}^{1-}\ In_i^{2+}\ V_{Cu}^{1-}]$ defect triplets. These are electrically self-compensating and neutral. In polycrystalline thin-film solar cells Cu-deficiency will similarly segregate, because both Cu and In are fast diffusers at the substrate temperatures employed for solar cell fabrication. Therefore, designing $CuInS_2$ material for solar cells will need structural and compositional information at the nanometer scale, acquired after both film growth and cell fabrication, coupled with information on optical gap, band edge offsets and electrical transport properties. The present study suggests three directions toward obtaining the needed quantitative understanding of, hence better control over, this solar cell material. One is an exploration of type and magnitude of electrical conductivity achievable by varying the sulfur pressure along the Cu-poor phase boundary of $CuInS_2$. A second study would trace out the Cu-rich phase boundary in the same way. The result would enable the quantitative design of the $CuInS_2$ solar cell absorber layer. Coupled with these

material studies, values of the ionization energy and electron affinity of the interphases are needed to understand how they affect carrier transport properties as well as the open-circuit voltage of solar cells made with bi-phasic material. The electron states of the interphase of the present study may be quantum confined in the ⟨112⟩ direction. Current research on $CuInS_2$ (hence, non-toxic) nanocrystals[54] and quantum dots[75] may extend to exploring their ordered-defect, Cu-deficient, homologs, thereby helping to clarify band edge positions, quantized levels, and optical gaps.

ASSOCIATED CONTENT

Supporting Information. The supporting information is available free of charge at ###. Additional analysis and characterization of $CuInS_2$ single crystal including: XPS analysis of Cu 2p, In 3d, and S 2p (SI, Fig. S1); STEM-EDS mapping of Cu, In, and S (SI, Fig. S2); EDS-measured atomic percent composition of Cu, In, and S (SI, Table S1); STEM-EDS mapping of the single and double interphase layers in the $\langle\bar{1}\bar{1}1\rangle$ direction (SI, Fig. S3); STEM-HAADF image showing two interfacial phases (SI, Fig. S4); and, additional photoresponse data under 780 nm and 1050 nm illumination (SI, Fig. S5).

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Author Contributions

JJF and GC designed the experiments. JJF collected and analyzed electronic transport data with analysis assistance from RJC. JJF collected and analyzed photoconductivity data with analysis assistance from SW. GC collected and analyzed TEM data with analysis assistance from JJF and NY. JJF wrote the manuscript with assistance from GC, SW, and RJC. All authors have given approval to the final version of the manuscript.

Notes

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