Surface Characterization of CulnS$_2$ with Lamellar Morphology

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ABSTRACT

Lamellar crystals of CulnS$_2$ grown in a steep temperature gradient have been characterized. Dispersive x-ray analyses show a predominant stoichiometry Cu/In/S = 1:1:2 and inclusions of Cu deficient phases. The cleaved surface is smooth, but after chemical etching a fine structure appears, with a great number of closely packed microcrystals of a dendritic shape. X-ray diffraction spectra of lamellae show the reflections of the CulnS$_2$ (112) and of the CuIn$_2$S$_3$ (111) lattice planes, indicating a strongly oriented structure. Depth profiles of CulnS$_2$ lamellae investigated with x-ray photoelectron spectroscopy show the presence at the cleaved surface of Cu deficient phases like CuIn$_2$S$_3$, which are a few tens of nanometers thick. The lamellar growth mechanism is discussed on the basis of these findings. X-ray photoelectron spectroscopy and secondary ion mass spectrometric investigations show that the oxidation behavior of the lamellar material resembles that of traditional CulnX$_3$ phases (X = S, Se).

Introduction

Efficient thin film solar cells require materials with high optical absorbptivity, $\alpha$, and suitable energy gaps, $E_g$. The theoretical efficiency is good for $E_g$ ranging between 1 and 2 eV, and it is maximum for $1.1 < E_g < 1.6$ eV. Due to their properties, the chalcogenides CulnX$_2$ ($\alpha \approx 10^3$ cm$^{-1}$, $E_g = 1.0$ and 1.5 eV) have been selected for solar energy conversion. CulnS$_2$-based thin film cells have already achieved efficiencies up to 13% under simulated AM 1.5 conditions. Development of CulnS$_2$ which has a bandgap in the optimum range, has lagged behind for a long time. However, a conversion efficiency exceeding 10% has been recently reported for a polycrystalline p-CulnS$_2$/CdS thin film junction under simulated AM 1.5 conditions.

Besides development of the thin film configuration, further investigation of bulk material growth appears justified both to extend the fundamental knowledge and to improve the quality of single-crystalline material for applications in efficient devices using concentrators. An intrinsic problem of CulnS$_2$, as compared with the se

Experimental

Lamellar CulnS$_2$ was prepared with the gradient freeze technique. Samples were fixed to suitable holders by means of conductive silver epoxy and fresh surfaces were obtained by peeling off crystal layers with adhesive tape. Investigations were performed both on samples peeled and transferred to the analysis chamber under an inert gas (N$_2$) and on samples previously exposed to oxygen.

Scanning electron microscopy (SEM) investigations were performed with a Philips Model XL 40 LaB$_6$ apparatus, equipped with a secondary electron detector (SE) and a solid-state detector for back-scattered electrons (BSE). Energy dispersive x-ray (EDX) analyses were performed using an EDAX PV99 spectrometer equipped with a thin beryllium window. Quantitative measurements were corrected taking into account the factors of atomic number Z, absorption A, and fluorescence F (ZAF correction). An electron beam energy of 25 keV was used, resulting in a sampling depth of about 2.5 μm. X-ray diffractograms were obtained on a Philips PW3710 instrument, using the Cu Kα radiation (40 kV and 30 mA, narrow divergence slit of 1/6 degree).

X-ray photoelectron spectroscopy (XPS) was run on a Perkin-Elmer PHI 5600c spectrometer with nonmonochromatized Mg Kα and Al Kα radiations (1253.6 and 1486.6 eV, respectively). The working pressure was less than 2 × 10$^{-7}$ Pa. The spectrometer was calibrated by assuming the binding energy (BE) of the Au 4f$_{7/2}$ line at 83.9 eV with respect to the Fermi level. The Cls line of adventitious carbon was assumed at 284.8 eV as internal reference for the peak positions. Survey scans (187.85 eV pass energy, 1 eV step, 0.5 s/step dwell time) were obtained in the BE range between 0 and 1200 eV. Detailed scans were recorded at 5.85 eV pass energy, 0.1 eV step, 1.0 s/step dwell time for the In 3d$_{5/2}$ and 3d$_{3/2}$ lines, Cu (2p$_{3/2}$ and 2p$_{1/2}$ lines), S (2p$_{3/2}$ line), Ols and C1s lines, together with the corresponding Auger lines for In and Cu. The chemical states of the various elements were in agreement with literature data.

The standard deviation in the BE values of the XPS lines was 0.1 eV. After a Shirley-type background subtraction, the raw spectra were fitted using a nonlinear least square fitting program adopting Gaussian-Lorentzian peak shapes for all peaks. The atomic compositions were...
evaluated using sensitivity factors as determined from theoretical photoionization cross sections and asymmetry parameters calculated within the Hartree-Fock-Slater one-electron central potential model.\textsuperscript{17}

The XPS spectra were recorded at a takeoff angle of 45°. Angle-resolved (ARXPS) investigations were performed comparing the spectra recorded at takeoff angles varying between 10° and 90°. The analysis chamber was equipped with a scanning electron microscopy/scanning Auger microscopy instrument, which was used in some cases for inspection of the area sampled by XPS technique. Depth profiles were carried out by Ar\textsuperscript{+} sputtering at 2.5 keV, 400 nA cm\textsuperscript{-2} beam current density with an argon partial pressure of 5 \times 10\textsuperscript{-6} Pa. The beam voltage and current were chosen to minimize preferential sputtering.\textsuperscript{18} Under these conditions we estimated a sputtering rate in the order of 3 nm min\textsuperscript{-1}. A bulk CuInS\textsubscript{2} crystal was analyzed before and after Ar\textsuperscript{+} etching for comparison. The quantitative analysis of the as-cleaved crystal surface was in agreement with nominal stoichiometry. After Ar\textsuperscript{+} sputtering S deficient stoichiometries CuInS\textsubscript{2} were observed (x = 1.8 \pm 0.1), indicating sulfur preferential sputtering.

SIMS spectra were taken on a custom-built instrument,\textsuperscript{19,20} based on a quadrupole mass analyzer. The samples were exposed to a rastered (3 x 2 mm), 3 keV, 650 nA Ar\textsuperscript{+} ion beam.

**Results**

**Lamellar morphology and crystal structure.**—The material has a peculiar lamellar aspect (Fig. 1a). The bulk of the lamellae is polycrystalline as suggested by spectroscopy\textsuperscript{7} and confirmed by SEM micrographs (Fig. 1). The cleavage surface, originally smooth to SEM inspection, shows after corrosion in acidic polyiodide\textsuperscript{8} a great number of closely packed microcrystals (Fig. 1c). The side view provided by a section of the lamellar crystal (Fig. 1b) indicates that the “bulk” of each lamella consists of a number of microcrystals, filamentous or dendritic in aspect, with a morphology also observed in thin films.\textsuperscript{21} The dendrites form an angle of 55° with the cleavage plane, corresponding to the angle between (112) plane and [110] direction in the chalcopyrite structure. Hence, the crystal is highly oriented despite its heterogeneity.

The XRD spectrum of powders (Fig. 2b) is that typical for a single-phase chalcopyrite CuInS\textsubscript{2}, as reported in JCPDS data files (Fig. 2a). Conversely, the spectrum of a lamellar crystal (Fig. 2c) only shows two major peaks at 2θ \approx 27.9° and 2θ \approx 57.6°, corresponding to (112) and (224) planes, respectively. This finding confirms a strong crystal orientation and was originally attributed to the presence of extended monocrystalline regions cleaving along (112) planes.\textsuperscript{22} Besides the dominant peaks of the chalcopyrite CuInS\textsubscript{2} phase (ch), Fig. 2c shows the reflections of the (111) lattice planes of the spinel CuInS\textsubscript{2} phase (sp).

SEM micrographs of the cleavage surface taken with a BSE detector show regions of different brightness (Fig. 3, top). Whereas the predominant EDX stoichiometry is Cu/In/S = 1/1/2, in the brighter areas the material shows ratios Cu/In < 1, henceforth frequently referred to as Cu deficient, with Cu contents down to 7 to 8 atom percent (a/o). A variety of Cu/In/S stoichiometries between 1/1/2 and 1/5/8 is observed in the bright SEM regions, the figure 1/3/5 being the most common.\textsuperscript{23} Whereas there is no final evidence in the literature of a distinct CuInS\textsubscript{2} phase (see Ref. 10 and references therein), the spinel phase CuInS\textsubscript{2} is well known.\textsuperscript{22} The variability of EDX data can be attributed to the presence of Cu deficient phases thinner than the sampling depth of the technique, so that EDX apparent stoichiometries may include contributions from the CuInS\textsubscript{2} host phase. Cu deficient phases are seldom observed in sections like that of Fig. 1b, and are more common on the surfaces obtained by peeling off the crystal sheets, suggest-
ing that the crystal cleaves preferentially in correspondence of these foreign phases.

Surface composition of the as-cleaved crystal.—Angle-Resolved XPS analysis.—XPS investigations are performed on freshly peeled samples, transferred to the analysis chamber avoiding contact with air. After analysis, the samples are inspected by EDX to check the presence of Cu deficient phases, and only the XPS data relevant to samples with quite homogeneous “bulk” CuInS₂ composition are discussed in this section. XP spectra (not reported) show the peaks of Cu, In, and S elements at binding energies typical of chalcopyrites²−⁶. In 3d₆/₂ line at 444.3 eV, Cu 2p₃/₂ line at 932.5 eV, and S 2p₃/₂ line at 161.6 eV. The oxygen peak is negligible. A typical surface stoichiometry Cu/In/S estimated from XP spectrum is 1/3.6 ± 0.2/6.0 ± 0.4. Considering only ternary phases along the pseudobinary line Cu₆S-In₃S₈, this stoichiometry may represent the average of contributions from thin surface layers of CuIn₈S₁₈ (and possibly CuIn₆S₁₂), and the host phase CuIn₄S₈.

ARXPS experiments show a significant dependence of composition on detection angle, with the same qualitative trend in three examined samples. Some variation in the values and a nonmonotonous dependency of the composition on the sampling angle are observed, which may be accounted for by a nonhomogeneous surface stoichiometry, confirmed by XPS line scan experiments. The Cu content (7 to 9 a/o) and the ratio Cu/In ≈ 1/5 are minimum for grazing takeoff angles, corresponding to minimum sampling depths (≥1.8 nm for Cu 2p line). On increasing the takeoff angle the Cu content gradually increases and so does the Cu/In ratio. For perpendicular detection (sampling depth ≤0.4 nm for Cu 2p line) a Cu content of 11 to 13 a/o and a ratio Cu/In ≈ 1/2.5 or 1/3 are observed. These data show segregation of a phase with lower Cu content in the outermost layers close to the “fracture surfaces” exposed after cleaving. Considering only stoichiometries corresponding to the pseudobinary line Cu₆S-In₃S₈, the outermost layer composition approaches that of the spinel phase CuIn₄S₈.

Depth profile of the lamellae.—Surface analysis and depth profiles are performed in the two regions of the sample of Fig. 3 with different EDX composition. Accurate sample positioning is made possible by the SEM instrument in the analysis chamber, providing unequivocal identification of the regions with different composition on the basis of surface morphology. Exposure to air of the sample prior to XPS analysis cannot be avoided. However, XP spectra (Fig. 4) show a very small oxygen signal. The C and O peaks become negligible after the first sputtering cycle and the relevant signals are not reported in the depth pro-

![Fig. 2. X-ray diffractograms (Cu Kα radiation λ = 1.5406 Å): (a) reference file data for chalcopyrite (ch) CuInS₂ (JCPDS 27-159); (b) spectrum of powders of lamellar CuInS₂; (c) spectrum of a lamellar CuInS₂ crystal showing the main chalcopyrite (ch) peaks for (112) and (224) planes and peaks of the spinal phase (sp) CuIn₈S₁₈ (JCPDS 24-361).](image)

![Fig. 3. SEM micrograph (top) of a heterogeneous region of the lamellar material and relevant EDX microanalysis (bottom). The atomic ratios Cu/In/S are about 1/1/2 in the dark area and 1/3.9/6.2 in the bright area.](image)
files of Fig. 5 and 6, which may be considered representative of the pristine unoxidized material.

The XP spectrum taken in the area of Fig. 3 with EDX composition Cu/In/S close to 1/1/2 is shown in Fig. 4, bottom. The oxygen signal represents a few a/o and the Cu/In/S atomic ratios are very similar to those recorded at the unoxidized samples, discussed in the previous section. Figure 5 shows the XPS depth profile. The copper content and the Cu/In ratio rapidly increase after the first sputtering cycle, up to 90 min of sputtering corresponding to an estimated depth of 70 nm, where Cu/In = 1/1/2. Peak shapes and positions do not vary significantly after sputtering. Proceeding in the depth profile, the Cu content increases further more slowly, and the Cu/In ratio attains the value of 1 by the estimated depth of 90 nm. In the latter condition, taking into account effects of sulfur loss discussed in the Experimental section, the XP analysis corresponds to the “bulk” EDX composition. Scanning Auger analysis of the area sampled by XPS (about 400 x 400 μm) before and after sputtering does not show local accumulations of elements resulting from the ion etching treatment, within the instrumental resolution of about 200 nm.

The XP spectrum taken in the area of Fig. 3 with EDX composition Cu/In/S = 1/1.9/6.2 is shown in Fig. 4, top. The surface stoichiometry evaluated from XP spectrum is about 1/1/1/3, with a Cu/In ratio not far from that of the CuInS₂ phase. Considering only compositions along the binary line Cu₅S-In₅S₅, the S content appears significantly below stoichiometric equivalence with the metals.

Inclusion of In-S phases like InS or In₅S₃ would better account for the observed stoichiometry; however, In₅S₃ and InS cannot be distinguished by their XPS spectra (see Ref. 31 and references therein), and this point could not be assessed further. Figure 6 shows the XPS depth profile recorded by sputtering this area. Even in this case the surface region is Cu depleted as compared to the bulk and the Cu content increases going deeper, but the variation is more gradual than that observed in Fig. 5. The Cu/In ratio, close to 1/10 at the surface, approaches 1/5 after removal of about 80 to 70 nm of material. Assuming that some sulfur preferential sputtering occurs also in this case, the “bulk” composition approaches that of CuInS₂.

Surface oxidation in the air—The XP spectra of the lamellar material exposed to air for a few days, at room temperature, show limited changes as compared to the spectra of the pristine material. No appreciable shift is observed in the positions of In and Cu lines. The absence of the Cu shake-up lines ensures that no significant amount of Cu(II) forms. The position and shape of the S lines is unaltered within experimental accuracy and no significant signal arises in the region typical of oxidized sulfur species like sulfate. A small O 1s peak is present, located at a binding energy of 531.8 eV, in a position typical of hydroxides. Since Cu(I) hydroxide is unstable and rapidly converts to Cu₂O, whose O 1s peak occurs at 530.3 eV, the observed O 1s position only fits literature values for In(OH)₃. The presence of In(OH)₃ is compatible with the observation of no energy shifts in the In lines. XP depth profiles indicate that exposure to atmospheric oxygen causes oxidation of a very thin surface layer. The XPS oxygen peak typically represents 10 to 20 a/o at the surface and disappears after 60 to 90 s sputtering (3 to 4.5 nm of material).

To better characterize the chemical bindings of the surface species we have also run SIMS spectra on an oxidized surface showing EDX composition close to CuInS₂. In the spectrum (Fig. 7), several peaks attributable to fragments containing the original atoms Cu, In, and S are observed. No significant peak can be accounted for by fragments containing both O and Cu, whereas at least three peaks correspond to fragments containing both O and In. The rapid decrease in time of the signal relevant to the ion with mass unit 246 (In₅O) confirms XPS indications of formation of a thin oxidized layer.

SIMS and XPS data show that surface oxidation in the air proceeds with the formation of a thin passivating layer, a few nanometers thick, containing In(OH)₃ or related oxides and copper chalcogenides Cu₅S₃ or CuS, in which Cu is present as Cu(II). These findings resemble those reported...
for the oxidation of single crystals and polycrystalline CuInS$_2$ or CuInSe$_2$, in which the oxidation products had been identified as Cu$_x$X ($X = S, Se$) and In(OH)$_3$.

**Discussion and Conclusions**

The crystal bulk of lamellar CuInS$_2$ consists of closely packed, highly oriented, dendritic microcrystals. The lamellar morphology originates from a periodic interruption of their growth over a front that is very large in comparison with the section of a single dendrite. ARXPS and XPS depth profiles show segregation at the lamella surface of Cu depleted phase(s), with a prevailing stoichiometry close to that of the CuIn$_{59}$S$_{41}$ spinel phase, and a thickness estimated in the range of a few tens of nanometers. The presence of the CuIn$_{59}$S$_{41}$ phase is also confirmed by XRD evidence. Besides the predominant CuInS$_2$ phase, the material contains lamellar regions in which the EDX Cu/In/S atomic ratios are in the range between 1/3/5 and 1/5/8. Cu depletion at the surface (as compared to the bulk) is also observed in the latter regions.

The presence of a Cu deficient (spinel) phase in between the lamellae of chalcopyrite structure may explain the cleaving behavior. The [112] spinel face may epitaxially grow over the [111] face of the CuInS$_2$ matrix, but due to lattice mismatch strain is present. The easy crystal cleaving in correspondence of the surface phase results in the lamellar morphology.

The presence of a steep temperature gradient during crystal growth is essential to the appearance of the heavy twinned structure and the lamellar morphology. A tentative mechanism accounting for the periodic formation of a Cu deficient phase may be proposed assuming that in the given conditions the CuIn$_{59}$S$_{41}$ solid forms with a slight Cu$_{59}$S excess. Hence, the melt in contact with the solid is more and more depleted of the corresponding elements, until a critical composition is reached causing the crystallization of distinct Cu deficient phases like CuIn$_{59}$S$_{41}$ and, possibly, Cu$_x$S$_2$. This causes recovery of a nearly stoichiometric melt composition and epitaxial growth of solid CuIn$_{59}$S$_{41}$ starts again. The exact mechanism which allows this highly oriented growth of at least two phases is not fully understood at present and needs further investigations, assessing details of the growth process such as the excursions in the liquidus composition at the solid-liquid interface.

However, recent literature reports may indicate that the phenomena are not peculiar to the gradient freeze method. Formation of Cu deficient phases is even observed on top of CuInS$_2$ thin films prepared in an ultrahigh vacuum system by thermal co-deposition of the elements on a substrate kept at 500°C. For bulk cation ratios (Cu/In)$_{bulk}$ close to 1, the surface cation ratio is (Cu/In)$_{surface} = 1/3$ and the presence of a Cu$_x$In$_{1-x}$ phase has been proposed. The presence of a large temperature gradient in the conditions of film synthesis appears very likely, but it is not known whether the analogies with the lamellar material are a clue to a common growth mechanism.

The reported SEM, EDX, XPS characterization shows significant variability in the composition of lamellar CuInS$_2$, reflecting nonequilibrium growth conditions and complexity of the Cu-In-S phase diagram. Given the critical importance of stoichiometry in defining the electronic properties of ternary chalcopyrite semiconductors, this fact may account for the heterogeneous behavior of phototlodes, including presence of both n- and p-type conductivities, and for their low average performances. However, the observation of promising performance at selected samples calls for an additional effort in material synthesis. Investigations of lamellar crystal growth are currently in progress with the aim of preparing more homogeneous material end of clarifying the open questions on the growth mechanism.

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