Etching process

CuS segregates at the surface which can be removed by KCN

Vacancies and In

Reducing temperature profile as shown in Fig. 1(a). It is known, that

Of 1.4 to 1.6. in a rapid thermal process (RTP) featuring a

Sulfurization of metallic CuIn-

Reduced CuInS2 doped CuInS2 phases, obtained by Cu

S (x=1,2) phases, obtained by Cu

Formation thereby effectively reducing donor-like defects which are basically sulfur vacancies and In0.5-antisites [11],[10],[9],[4],[5]. The excess CuS segregates at the surface which can be removed by KCN etching.

Avoiding the segregation and thereby the ex-situ KCN etching process would enable an in-line process including the deposition of the TCO-layer completely under vacuum conditions. To end up with an CuS free absorber surface, it is necessary to sulfurize samples with only a small amount of Cu surplus just sufficient to ensure the intrinsic p-type-doping. However, the absence of a large copper surplus impacts the structural and crystal quality which must be compensated [6],[4],[5].

Therefore the experiments below have been designed in order to achieve a small amount of CuxS formation and its benefits during the low-temperature part of the sulfurization in spite of using near-stoichiometric precursors with reduced copper surplus. This is feasible regarding the Cu-In-quantities of the compounds involved below 300°C. Completing the final stage of the sulfurization and adding a post-growth heat treatment yields an absorber without CuS.

**Experimental:**

Sulfurization, thermal treatment and the XPS/UPS characterization of the samples were performed in a dedicated ultra high vacuum system. The Cu/In-precursors were prepared on molybdenum substrates. Prior to the precursor layer deposition the Mo-substrate was coated with a sputtered Mo-layer of 500 nm to provide an uncontaminated and smooth surface akin to those commercially prepared on glass substrates. A metallic bi-layer of industrial standard thickness consisting of 352nm Cu and 648nm In was deposited by sequential sputtering, performed at the HZB baseline at a base pressure of 6x10^-5 mbar. The Cu/In ratio of 1.2 is significantly closer to stoichiometry than the Cu/In ratio of >1.4 commonly used. The samples were transported ex-situ and cleaned after introduction into the UHV-system by annealing at 550°C for 2h. After thermal cleaning the CuIn-precursor consists mainly of Cu1In5 alloy coexisting with a crystalline In phase [14], [4],[5]. The sulfurization of the CuIn-precursor was performed in a dense sulfur atmosphere attained by evaporation of elementary sulfur at about 120°C. In contrast to the common rapid thermal process (RTP) a thermocouple controlled resistance heating system allowed for a controlled thermal process with several sophisticated temperature profiles. The temperature profile was adjusted to exploit the reactive phase transitions of the sulfurization process involving CuS. To facilitate grain boundary diffusion by thermal strain the ascending slopes were run at a rate of 15°C per minute. After the sulfurization process the samples were annealed for another hour at 550°C in the absence of sulfur. This post-sulfurization heat-treatment completes the process by enabling additional phase transitions, diffusion and an improvement of the structural properties as reported in various studies [15], [16].

The samples were investigated in-situ by photoelectron spectroscopy using a Phoibos 150 analyzer with a MCD-9 detector, a XR-50 X-ray source Mg K alpha (1253.6 eV) and He-I lamp (21.2 eV). In order to supplement the surface-sensitive data, ex-situ volume-sensitive x-ray diffraction measurements (XRD) and energy dispersive x-ray analysis (EDX) were carried out. The crystal structure and phase composition were investigated with standard XRD measurements in a theta-2theta geometry performed in a D8 Advance (Bruker AXS) diffractometer with excitation by Cu-K-alpha1,2. The diagrams were recorded in the range of 10° to 120° with an increment of 0.005°. The chemical composition of the volume was analyzed by EDX. Elemental mappings
were obtained from an area of 40x50 µm² and a depth of 500 nm (10 kV measurements). Scanning electron microscopy analysis (SEM) was performed to gain further knowledge of the surface morphology as well as the grain size. The electron beam energy was 25 kV while the scanned area shown in Fig. 4 was 30x40 µm².

Results and discussion:
Three groups of samples were prepared.

Sample I
For reference a sample was sulfurized utilizing a temperature profile well-established at commercial baselines (Fig. 1(a)). This profile consists of a temperature slope up to about 500°C while the sample is exposed to the S atmosphere. After a dwelling time of 10 min the sample is cooled down.

Sample II
To avoid the formation of InS from superficial In and S which is considered to be a precursor of the unwanted CuInS₂ phase, sample II was heated to a starting temperature prior to exposure to the sulfur atmosphere as shown in Fig. 1(b). The start temperature of 175°C was chosen well above the melting point of In at vacuum conditions (160°C). At this temperature segregated In agglomerates have been liquefied and have completely reacted with Cu forming Cu₁₁In₉ alloy [4], [5].

Sample III
For sample III further modifications of the sulfurization profile were based on the formation of CuInS₂ out of the Cu₁₁In₉ phase at temperatures of 200°C to 300°C [4], [5]. To extend the sulfurization process within this temperature range alternating increasing and decreasing low-temperature-slopes were performed (Fig. 1(c)). At 300°C the phase transition of Cu₁₁In₉ into Cu₂In₈ takes places [4], [5]. This is accompanied by the release of an amount of In which in our case cannot be bound by excess Cu. The formation of InS by unbound In becomes possible. Since the InS phase is the point of origin of an unfavourable reaction path its formation must be prevented [5], [8]. The variation of the temperature from 175°C to 250°C serves this purpose as it allows a sufficient amount of surface CuInS₂ and Cu₅S (x=1,2) to form shielding the In from the sulfur atmosphere.

pre treatment:
After thermal cleaning XPS investigations yield a negligible carbon signal and oxygen impurities below the detection limit of XPS. The XRD measurements of the metallic precursor exhibit a dominating Cu₁₁In₉ alloy signal accompanied with smaller signals of In crystallites. Taking into account the molecular factor of m⁻⁰.6 derived from XPS an In-rich surface can be assumed and In crystals at least partially reside on the surface. This corresponds to the results of Gossa [14].

Sulfurization and post-process heating
A VBM of about 0.7 eV - 0.8 eV is expected for stoichiometric CuInS₂ whereas a VBM of higher values indicate n-type CuInS₂ featuring donor-type defects like In₉Cu₈, V₅ or V₉Cu (Fig. 2(a)/(b)). The chalcopyrite structure is revealed by characteristic peaks at 27.9°, 32.3° and 46.4° corresponding to the (112), (004)/(200) and (204)/(220) reflections (Fig. 3). Moreover, this is backed up by CuInS₂ signals at 55.0°, 74.8° and 86.1° (not shown) referring to the (116)/(312), (316)/(332) and (228)/(424) reflections, which also correspond to CuInS₂. A distinct splitting of the (004)/(200) and (204)/(220) reflections indicates the chalcopyrite’s tetragonal distortion. Fig. 4(a) shows the SEM picture of sample II with the introduction of the start-temperature, while Fig. 4(b) documents the application of combined start-temperature and low-temperature-slopes of sample III.

Sample I:
After sulfurization, sample I (Fig. 2(a)) shows CuInS₂ valence band structure [20], [17]. However, the sample features a lower intensity of the Cu3d-DOS (density of states) and a VBM in the range of n-type CuInS₂. These observations match the Cu- and S-poor stoichiometry derived from XPS data. The Auger-parameter of Cu and In is in the range of CuInS₂. No phase transformation can be derived from the XPS/UPS spectra (Fig. 2(b)) after post-processing heating. However, taking into account the shift of the VBM a Cu-diffusion from the volume can be assumed. The shift is probably caused by less V₉Cu and In₉Cu defects and accompanied by the slightly increased Cu-states in the valence band respectively. Furthermore, the stoichiometry has changed to less Cu-poor values. The XRD-spectra of sample I indicate additional phases corresponding to Cu₅In₈-phases. Sample I exhibits a low reflection splitting due to CuAu-ordering which is caused by a high density of defects thus indicating a poor crystalline quality.

The elemental distribution measured by EDX shows a general Cu- and S-deficiency with small inhomogeneous spots of increased Cu and S deficiency. This deficiency is confirmed by XPS data implying an even more Cu- and S-deficient surface.

Sample II:
Sample II prepared with initial annealing shows the VB-structure of CuS with a VBM at the Fermi level according to the p-metal characteristic of CuS. The appearance of a second phase at the Cu2p and S2p XPS peaks indicates a superposition of CuInS₂ and CuS spectra. This assumption is supported by the binding energies of the identifiable sulfur phases and the Auger-parameters of Cu and In which correspond to CuInS₂ as well as CuS. With respect to the main Cu phase, the Auger-parameter indicates CuS whereas the Auger-parameter of In is in the range of CuInS₂. The stoichiometry is Cu- and S-rich. After post-sulfurisation heating sample II shows the typical VB-structure of CuInS₂. Furthermore, no secondary phases can be detected by XPS. Sample II features a VBM at 1.0 eV, low Cu-DOS and a more In-rich stoichiometry indicating n-type CuInS₂. The change from a Cu-rich to a Cu-poor surface implies that non-sulfurized residues of the metallic precursor have reacted with a small superficial amount of CuS. The XRD results reveal values between that of sample I and III. The secondary Cu₅In₈ phase is reduced and the CuInS₂ phase is increased but the crystalline quality remains poor compared to sample III described below. The SEM picture of sample II shows a
rough surface with a droplet-like appearance and a small grain size as indicated by the FWHM of the (112) XRD-reflex.

Sample III:
After sulfurization, the UPS/XPS spectra of sample III are identical with sample II, but shows differences after post-sulfurisation heating. In contrast to sample I and II, sample III shows a valence band structure with well pronounced Cu3d-DOS combined with a VBM at 0.8 eV and stoichiometric composition derived from XPS-data. According to NIST data base [18] the derived Cu-Auger-parameter of 1849.4 lies between that of CuInS$_2$ (1849.9-1849.1) and Cu$_2$S (1849.6-1849.9). This either indicates Cu-rich CuInS$_2$ or a superposition of CuInS$_2$ and Cu$_2$S. The XRD spectrum corresponding to sample III shows a distinct single CuInS$_2$ signal.

The Cu$_{1}$In$_5$-signals were absent for sample III and phases like In$_5$S or CuIn$_5$S$_2$ can be excluded. Comparing sample I, II and III the intensity of the CuInS$_2$ (112) diffraction peak increases from sample I to sample III. An analysis of the (112)-CuInS$_2$ reflexes by Voigt profiles yields that sample III features the sharpest peaks. The reduction of the FWHM from 0.22°(sample I) via 0.18 (sample II) to 0.14° (sample III) can be attributed to an increased average grain size as deduced by the Scherrer formula [19] and is supported by the SEM images (Fig. 4). A distinct peak-splitting can be observed only on sample III.

The SEM picture reveals that the surface is dense and smooth with compact grains of sizes of 1-2 μm. Only few occasional residuals are segregated. EDX exhibits areas of relative Cu as well as Cu and S surplus. These larger inhomogeneous regions indicate Cu$_2$S or Cu$_2$S-residues. The surface morphology in general can be attributed to the CuInS$_2$ phase since a significant covering Cu$_2$S (x=1.2) phase can be ruled out by the XPS/UPS data.

The Cu$_{1}$In$_5$ phase can be regarded as an ideal start condition for sulfurization since its composition is close to the 1:1 stoichiometric ratio of the metallic components of the compound CuInS$_2$. However, agglomerations of In crystallites on the surface cause the undesirable formation of InS and must be therefore prevented during the sulfurization process.

Cu$_2$S is a potential fluxing agent for the sulfurization. We assume that the Cu$_{1}$In$_5$ phases revealed by the XRD spectra of sample I and II originate from an incomplete sulfurization process arising from the absence of Cu$_2$S during the process. Adding sulfur at start-temperature of 175°C where segregated In agglomerates are liquefied and have completely reacted with Cu forming Cu$_{1}$In$_5$ leads to an improvement but is not sufficient with regard to the absorber quality. However, sample III contained enough Cu$_2$S during the process to obtain stoichiometric CuInS$_2$ by post-process heating. The required Cu$_2$S is yielded by low-temperature-slopes prior to the high temperature part of the sulfurization. This could be shown by a precursor which was processed up to the low-temperature-slopes and subsequently cooled down without processing in the high temperature region. It yielded a thick (>500nm) initial Cu$_2$S-layer verified by XRD, EDX and XPS/UPS. Furthermore, the CuInS$_2$ formation in the low-temperature region could be proven by XRD (not shown) [21]. Since post-sulfurization heating was performed devoid of sulfur atmosphere, chemical reactions must be assumed to have been taken place between the surface and the bulk. The phase transition of Cu$_2$S to Cu$_2$S is known to take place at about 500°C while the reverse transformation Cu$_2$S to Cu$_2$S only takes place when sulfur is supplied [4]. It is likely that a transformation to Cu$_2$S is a minor side process during the post-processing of sample III. While a Cu$_2$S phase can be excluded by XRD, Cu$_2$S x-ray reflections are not easily distinguished from the CuInS$_2$ reflections and may be indiscernible in XRD spectra. Since Cu$_2$S is a semiconductor of similar band gap as CuInS$_2$, residuals of Cu$_2$S would be likewise indiscernible at the VBM, especially since the stoichiometry of the sample implies that the Cu$_2$S residuals are of a minor amount. Therefore Cu$_2$S-residues are an explanation for the Cu-rich areas revealed by EDX and probably match with the residuals seen in the SEM picture. The increased intensity of the (112) XRD-reflex and the absence of other phases at sample III indicate that the extent of CuInS$_2$ formation is improved by the afore mentioned start temperature of 175°C but mainly by the added low-temperature-slopes. The slopes allow CuInS$_2$ and Cu$_2$S formation by means of stress-induced growth while Cu$_2$S supports further formation of CuInS$_2$. Furthermore, the distinct reflection splitting and the narrowing of the FWHM indicate the formation of CuInS$_2$ with higher crystalline quality. Sample III yields a compact surface morphology and increased grain size which is supported by SEM and XRD. This improvement is the result of three effects: 1) the reaction path and the intermediate reaction products have an impact on aspects like augmented insertion of sulfur via Cu$_2$S leading to reduced sulfur vacancies, 2) the sulfurization progress is aided by the fluxing agent Cu$_2$S and impeded by InS and 3) the grain size is small along the In$_5$S-CuInS$_2$ reaction path and is increased along the CuS-CuInS$_2$ path [4],[6].

<table>
<thead>
<tr>
<th>Sample</th>
<th>VBM</th>
<th>$W_f$</th>
<th>Δm=Cu/In-1</th>
<th>$\Delta s=2S/(Cu+3In)-1$</th>
<th>$\alpha Cu$†</th>
<th>$\alpha In$††</th>
</tr>
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<tbody>
<tr>
<td>Sample I</td>
<td>1.2 eV</td>
<td>4.8 eV</td>
<td>-0.63</td>
<td>-0.13</td>
<td>1849.1</td>
<td>825.4</td>
</tr>
<tr>
<td>Sample II</td>
<td>1.0 eV</td>
<td>4.9 eV</td>
<td>-0.40</td>
<td>-0.05</td>
<td>1849.1</td>
<td>852.5</td>
</tr>
<tr>
<td>Sample III</td>
<td>0.8 eV</td>
<td>5.3 eV</td>
<td>-0.05</td>
<td>-0.01</td>
<td>1849.4</td>
<td>852.5</td>
</tr>
</tbody>
</table>

Table I: Summary of the key data for sample I through III derived from XPS/UPS data.

† $\alpha Cu = binding energy (Cu2p$_{3/2}$) + kinetic energy (CuMM)
†† $\alpha In = binding energy (In3d$_{5/2}$) + kinetic energy (InMNN)

Conclusion
To expand the two-stage sulfurization process onto metallic precursors with a Cu/In ratio of 1.2, the process window in the temperature range below 300°C has been exploited. The results of the samples I, II and III, each sulfurized with identical CuIn-precursor set-up but different process modules, show the influence of the preparation process on the reactive formation of the crystal.
We have demonstrated that the crystalline and structural properties of the CIS absorber can be improved by inhibiting the growth path including InS as intermediate reaction product and simultaneously enhancing the initial CuS formation, known to be beneficial for the reactive process. Two new process modules avoid unbound In at the precursor surface and instead provide Cu for CuInS (\(x=1.2\)) formation. Firstly, we choose a start-temperature of 175°C which provides a precursor completely composed of the alloy CuIn$_2$S$_3$. Secondly, low-temperature-slopes exploit the formation of CuInS$_2$ from CuIn$_2$S$_3$ alloy creating a slight overrun of Cu and simultaneously avoiding the phase-transition from CuIn$_2$S$_3$ to CuIn$_2$S$_4$ In at 300°C. The released Cu is able to react at the surface with sulfur forming the beneficial CuIn$_x$S$_{2–x}$ (\(x=1.2\)) phase and CuInS$_2$ as proven by a sample processed only up to the low-temperature-slopes. Thus, the introduced modules provide Cu$_2$S even for Cu/In-ratio of 1.2. The formation of In-rich CuInS$_2$ or rather In-rich defect complexes, which normally take place in the range of small Cu/In-ratio, can be potentially augmented the solar cell efficiency.

The process adapted to 1.2 precursor leads to well-crystallized films of chalcopyrite ordered CuIn$_2$S$_3$, forming large grains and a smooth surface with only little Cu$_2$S residues remaining on the surface. The residues consist probably of Cu$_2$S$_3$. The post-sulfurization heat treatment causes recrystallization, thereby improving the crystallinity [15]. Moreover, it enables the reaction of segregated CuS with the volume thus converting superficial CuS into further CuIn$_2$S$_3$ and a small amount of Cu$_2$S residua. At the end of the process no CuS is left. Although it could not be shown whether the Cu$_2$S-residues have to be removed by KCN etching, the new process modules could be a promising way to produce CIS absorber for photovoltaic applications.

It is recommended that further studies using precursors with CuIn$_{x}$S$_{2-x}$ or 1.0 or 1.1 should be conducted in order to avoid Cu$_2$S-residues altogether. The results should enable to prepare the CuIn$_2$S$_3$ to buffer-layer heterojunction in a complete vacuum in-line process and therefore minimize impurities and potentially augment the solar cell efficiency.

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References

