

## Sulphurisation of gallium-containing thin-film precursors analysed *in-situ*

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### **Abstract**

It has been demonstrated that rapid thermal sulphurisation of sputtered Cu/In precursor layers is suitable for industrial production of thin-film photovoltaic modules. The process is relatively straightforward and the underlying fundamental aspects, such as phase formation sequence and reaction rates, have been studied intensively. Using lab-scale preparation technology, incorporation of gallium is known to improve transport properties of the absorber and to enable the fabrication of wide-gap cells. In this work we have used energy dispersive *in-situ* x-ray diffraction to study the sulphurisation of sputtered Cu:Ga/In precursors. It is the necessary basis for the future development of an industrially feasible production of Cu(In,Ga)S<sub>2</sub> films. Precursor stacking sequence and sulphur partial pressure in relation to precursor temperature have been varied. In many cases, in particular when establishing sulphur partial pressure already at low precursor temperature, we observe a severe reduction of reaction rates after going from pure Cu to Cu:Ga in the precursor. In consequence, single phase films cannot be prepared within the feasible range of times and temperatures. Adhesion failure and at least intermediate formation of CuIn<sub>3</sub>S<sub>8</sub> are other problems frequently encountered. In spite of these problems, promising pathways to single phase Cu(In,Ga)S<sub>2</sub> films prepared from sputtered Cu:Ga/In precursors have now been identified.

## Introduction

CuInS<sub>2</sub> is an attractive absorber for thin film chalcopyrite-based photovoltaic modules. Its main advantage is currently seen in the availability of a self-adjusting, fast and robust sulphurisation process [1]. Industrial implementation is already on its way [2]. Its wide band gap of 1.5 eV implies that it is perfectly feasible to work with the pure ternary compound which contributes to the robustness of its preparation. However, it has been shown that incorporating gallium into the material increases its performance potential [3]. The majority of investigations concerning this topic have been using lab-scale approaches which cannot be integrated easily into the industrial process due to the use of evaporation and/or time-consuming annealing steps. In this work we aim for a straightforward modification, replacing the Cu target by a Cu:Ga alloy target and restricting further modifications of the process to a minimum. This also implies the use of sulphur vapour for rapid thermal annealing even though H<sub>2</sub>S gas appears to have some advantages especially in connection with the introduction of gallium [4,5]. Two-step preparation of chalcopyrite thin films is governed to a large extent by phase formation kinetics which have to be known in detail to optimise the process. This scientific foundation has been established by *in-situ* x-ray diffraction and other methods for the gallium-free baseline process [6]. In this contribution we report on the extension of the previous work for precursor films sputtered from a Cu:Ga alloy target.

## Experimental

Samples used for this work were prepared by DC magnetron sputtering from metallic targets onto Mo covered soda-lime glass. Ga was incorporated by sputtering from a Cu:Ga alloy target with 14 at.% Ga. Nominal layer thicknesses for the Cu:Ga alloy layer and the In layer were 559 nm and 492 nm respectively. These proportions lead to a Cu excess of  $\text{Cu}/(\text{Ga}+\text{In}) = 1.5$ . The layer sequence of the precursor stacks had been varied (Cu:Ga/In or In/Cu:Ga). In experiments with annealing prior to the sulphurisation experiment the annealing was carried out at a pressure of 10<sup>-3</sup> Pa with 10 min. at 675 K.

The sulphurisation processes were carried out in a vacuum chamber with a pressure ranging from 10<sup>-3</sup> Pa to 10<sup>-2</sup> Pa depending on the sulphur partial pressure during annealing time. For the *in-situ* x-ray diffraction spectroscopy we used white synchrotron radiation at the beamline F3 at HASYLAB (DESY). The energy range for the spectra shown in this study is from 6 keV to 57 keV with a nominally fixed diffraction angle of  $\theta = 3.7^\circ$ . The angle varies slightly between the different experiments. The precise diffraction angle was determined by means of an Au powder reference sample and is given individually in the figure captions. Spectra were taken every 5 to 20 seconds. Elemental sulphur was evaporated in a Knudsen source at a temperature of 455 K. The Sample and the sulphur source could be heated up individually. For a detailed description of the set-up see [7]. Heating rates were chosen to be 0.3 K/s in favour of good resolution of the intermediate phases occurring during the sulphurisation processes. Samples were heated up to 825 K and held at constant temperature for 10 to 25 minutes. Additionally, *ex-situ* x-ray spectroscopy was used to determine phases present in the precursors, the vacuum annealed, and the reactively annealed samples. All spectra were normalized to the intensity of the Mo K $\alpha$  fluorescence signal which lies within the observed energy range.

## Results

The spectrum of a film sputtered from the Cu:Ga target exhibits a single, somewhat broadened maximum. Annealing at 490 K results in decreasing peak width and the appearance of a second maximum. This spectrum can be assigned to the solid solution [8]. We assume that the maximum at 44.9 keV in the initial spectrum of a Cu:Ga/In precursor is due to the same phase, albeit with poor crystallinity. (The maximum coincides with a small CuIn<sub>2</sub> diffraction signal.) With this assumption,

the precursor phases of the sulphurisation experiment shown in Fig. 1 are Cu:Ga, CuIn<sub>2</sub>, and In. At a temperature of about 400 K the maxima assigned to the latter phases disappear and Cu<sub>11</sub>In<sub>9</sub> appears to be present for a short period. After that metals are transforming into a phase which we assume to be Cu<sub>9</sub>(In,Ga)<sub>4</sub> [9, 10]. This is followed by the formation of CuInS<sub>2</sub>. As its signal increases in intensity (Fig. 2) and at substrate temperature above 720 K the maximum of the Cu<sub>9</sub>(In,Ga)<sub>4</sub> phase shifts to higher energies indicating a decrease of the lattice constant and an increasing Ga/(In+Ga) ratio in the Cu<sub>9</sub>(In,Ga)<sub>4</sub> phase. A phase transition back to Cu:Ga coincides with the appearance of CuGaS<sub>2</sub>. The most significant result of this experiment, however, is the fact that the reaction comes to an almost complete stand-still 10 minutes after reaching the top temperature (marked *a* in Fig. 1 and 2) with significant amounts of Cu:Ga remaining. This was surprising in view of initial experiments that showed that Cu:Ga by itself can be sulphurised easily enough (Fig. 3). Fig. 4 shows a contrasting experiment where the metal phases disappear rapidly already during the initial ramp-up of substrate temperature. In contrast to the experiment in Fig. 1, the precursor had been annealed without sulphur at 675 K before the experiment and the layer sequence was In/Cu:Ga. The set sulphur source temperature curve was the same as in the first case. Depending on substrate temperature, CuS or Cu<sub>2</sub>S are present in significant amounts throughout the process.

## Discussion

The data of numerous experiments can be categorized into two typical cases, similar to the ones described in the previous section. The first case is characterised by a slow and incomplete reaction, the absence or low intensity of maxima of Cu<sub>x</sub>S binary phases, at least intermediate presence of CuIn<sub>5</sub>S<sub>8</sub>, and the formation of CuInS<sub>2</sub> prior to the formation of CuGaS<sub>2</sub>. In the other case the reaction proceeds rapidly, with clear signatures of Cu<sub>x</sub>S binaries, the absence or low concentration of CuIn<sub>5</sub>S<sub>8</sub> and much earlier formation of CuGaS<sub>2</sub> (or Cu(In,Ga)S<sub>2</sub>). It is evident that in this second case the reaction is much closer to the thermodynamic equilibrium: formation of Cu<sub>x</sub>S is expected from the Cu-excess in the precursor, and CuGaS<sub>2</sub> (being more stable than CuInS<sub>2</sub>) forms early. On the other hand, the first case clearly indicates a kinetic limitation where the transport of Cu (absence of Cu<sub>x</sub>S, presence of CuIn<sub>5</sub>S<sub>8</sub>) and Ga (CuInS<sub>2</sub> forms first) hampers the reaction. In terms of experimental conditions, the first case is more likely to occur when the precursor is deposited in the sequence Cu:Ga/In, is not pre-annealed, and when the sulphur pressure is significant already during heating. It is commonly accepted [11], and easily understood [12] from the diffusion coefficients, that the reaction front during sulphurisation of metal films in vapour is located at the surface. This correlates with our *ex-situ* analysis of the incompletely reacted samples where the remaining Cu:Ga is found at the back with the chalcopyrite on top of it. In SEM graphs we see two clearly distinct layers largely separated by cavities. These two layers are easily separated by applying a sticky tape. We speculate that this ill-defined interface between the Cu:Ga and the chalcopyrite layer blocks the transport of Cu and Ga to the reaction front. In some cases we could observe during the *in-situ* experiment a detachment of the chalcopyrite layer followed by rapid sulphurisation of the underlying Cu:Ga. We cannot presently explain the correlation between experimental conditions and the blocking effect. We note that the effect described here is different from the one observed in previous work [13, 5] where the kinetic limitation occurred within the (evaporated) precursors.

It has been postulated in previous work (without Ga) that various phase transitions during the heating of the precursor lead to Cu<sub>16</sub>In<sub>9</sub> (symmetry group P6<sub>3</sub>mmc (hexagonal)) as the last sulphur-free phase being formed. In this work we suggested the existence of a Cu<sub>9</sub>(In,Ga)<sub>4</sub> phase (symmetry group P $\bar{4}$ 3m (cubic)). This is a somewhat ambiguous postulate in view of the XRD spectra of both phases being almost identical. However it is supported by the following arguments: A Cu-Ga phase of the symmetry P6<sub>3</sub>mmc is not reported to exist under equilibrium conditions whereas Cu<sub>9</sub>Ga<sub>4</sub> (P $\bar{4}$ 3m) is stable in a very wide temperature range according to the binary phase diagram. The latter phase has been clearly identified in our experiments done without indium. It is conceivable

that the stability of  $\text{Cu}_9\text{In}_4$  (normally a high-temperature phase,  $T > 890 \text{ K}$ ) extends to lower temperature when gallium is incorporated. The position of the maxima of our assumed phase is between the maxima of  $\text{Cu}_9\text{In}_4$  [9] and  $\text{Cu}_9\text{Ga}_4$  [10], respectively. Its variation is consistent with the assumption of changes in the Ga/In+Ga ratio. Finally, we observe two, albeit low intensity maxima in our spectra at 34.6 keV and 39.5 keV which cannot appear for the ideal  $\text{P6}_3\text{mmc}$  structure but are allowed for the cubic lattice of  $\text{P}\bar{4}3\text{m}$  symmetry.

## **Conclusions**

We have investigated the sulphurisation of precursors including a layer sputtered from a Cu:Ga target. We postulate the occurrence of a cubic  $\text{Cu}_9(\text{In,Ga})_4$  phase during the reactions. Furthermore, we find two distinctly different types of reaction. In one case there is a severe obstruction of the transport of Cu and Ga to the reaction front, presumably caused by the already reacted part of the material losing contact to the Cu:Ga layer in the back. Without being able to exactly describe the reasons for this phenomenon at this point, we have identified process parameters which reproducibly circumvent the problem. These parameters result in fast and complete reaction producing the phases expected from thermodynamic considerations and should form the basis of further development.

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## **List of figure captions**

**Fig. 1:** In-situ x-ray diffraction spectra acquired during the sulphurisation of a Cu:Ga/In precursor layer. The signal intensities are expressed as different colours. The maxima have been attributed to the phases: 1-In, 2-CuIn<sub>2</sub>, 3-Cu:Ga, 4-Cu<sub>11</sub>In<sub>9</sub>, 5-Cu<sub>9</sub>(In,Ga)<sub>4</sub>, 6-CuInS<sub>2</sub>, 7-CuIn<sub>5</sub>S<sub>8</sub>, 8-Cu:Ga, 9-CuGaS<sub>2</sub>, 10-CuS. The apostrophes after the numbers mark the maxima used for Fig. 2. Diffraction angle:  $\theta=3.705^\circ \pm 0.002^\circ$ . The upper part of the figure shows the temperature profiles of the sample and the sulphur source.

**Fig. 2:** Signal intensity of in-situ x-ray diffraction spectra acquired during the sulphurisation of a Cu:Ga/In precursor layer. The plot shows the intensity of the maxima marked with an apostrophe in Fig. 1. The maximum of the phase Cu:Ga in the precursor spectra cannot be clearly separated from the maxima of the subsequent phases Cu<sub>11</sub>In<sub>9</sub> and Cu<sub>9</sub>(In,Ga)<sub>4</sub>. Therefore the intensity of these signals are plotted as a single curve.

**Fig. 3:** Signal intensity of in-situ x-ray diffraction spectra acquired during the sulphurisation of a Cu:Ga precursor layer. The plot shows the intensity of the strongest maximum of each phase.

**Fig. 4:** In-situ x-ray diffraction of the sulphurisation of a In/Cu:Ga precursor layer. The precursor had been annealed without sulphur at 675 K before the experiment. The signal maxima have been attributed to the phases: 1-In, 5-Cu<sub>9</sub>(In,Ga)<sub>4</sub>, 6-CuInS<sub>2</sub>, 7-CuIn<sub>5</sub>S<sub>8</sub>, 9-CuGaS<sub>2</sub>, 10-CuS, 11-Cu<sub>x</sub>S. Diffraction angle:  $\theta=3.758 \pm 0.002^\circ$ .

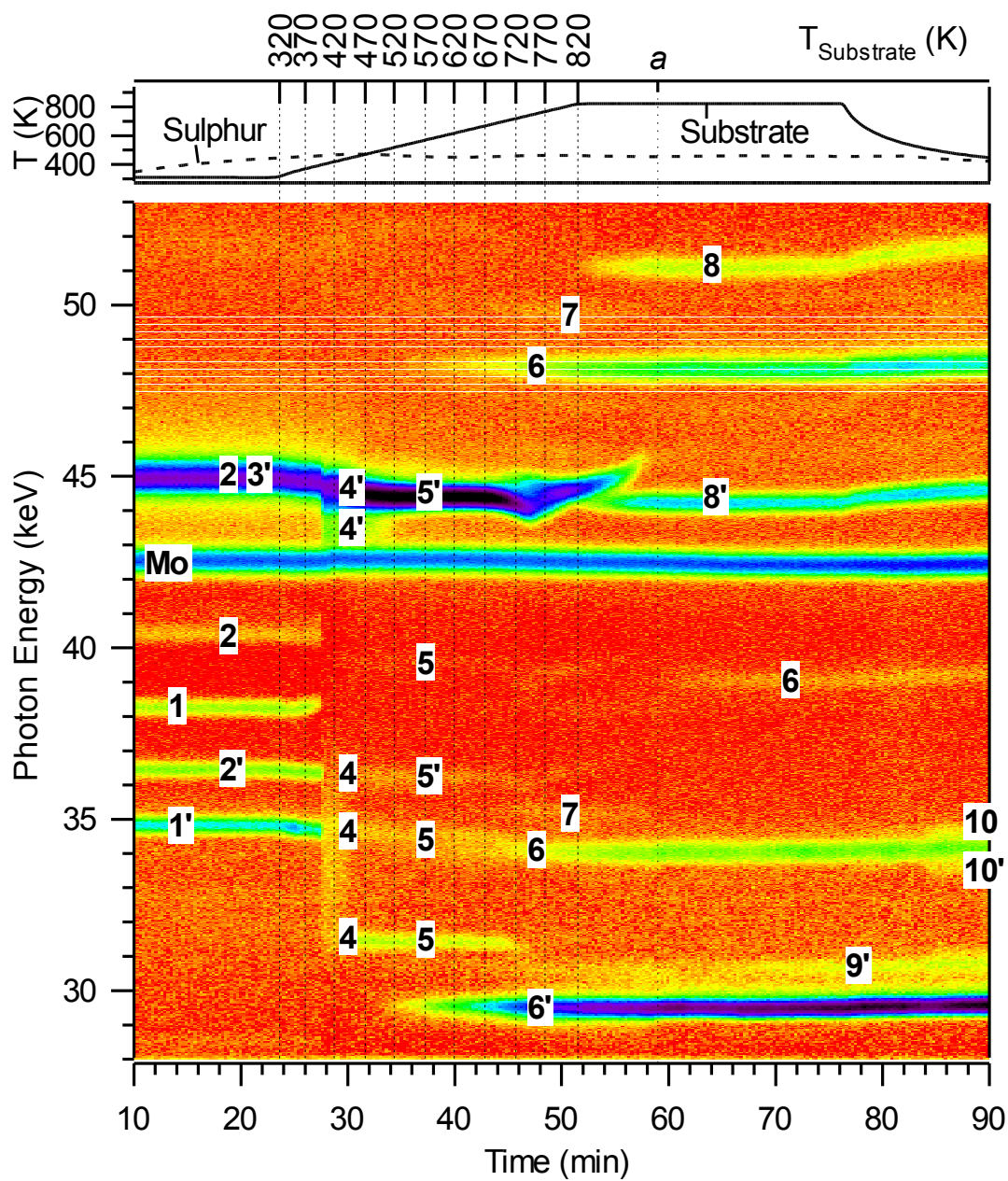


Fig. 1

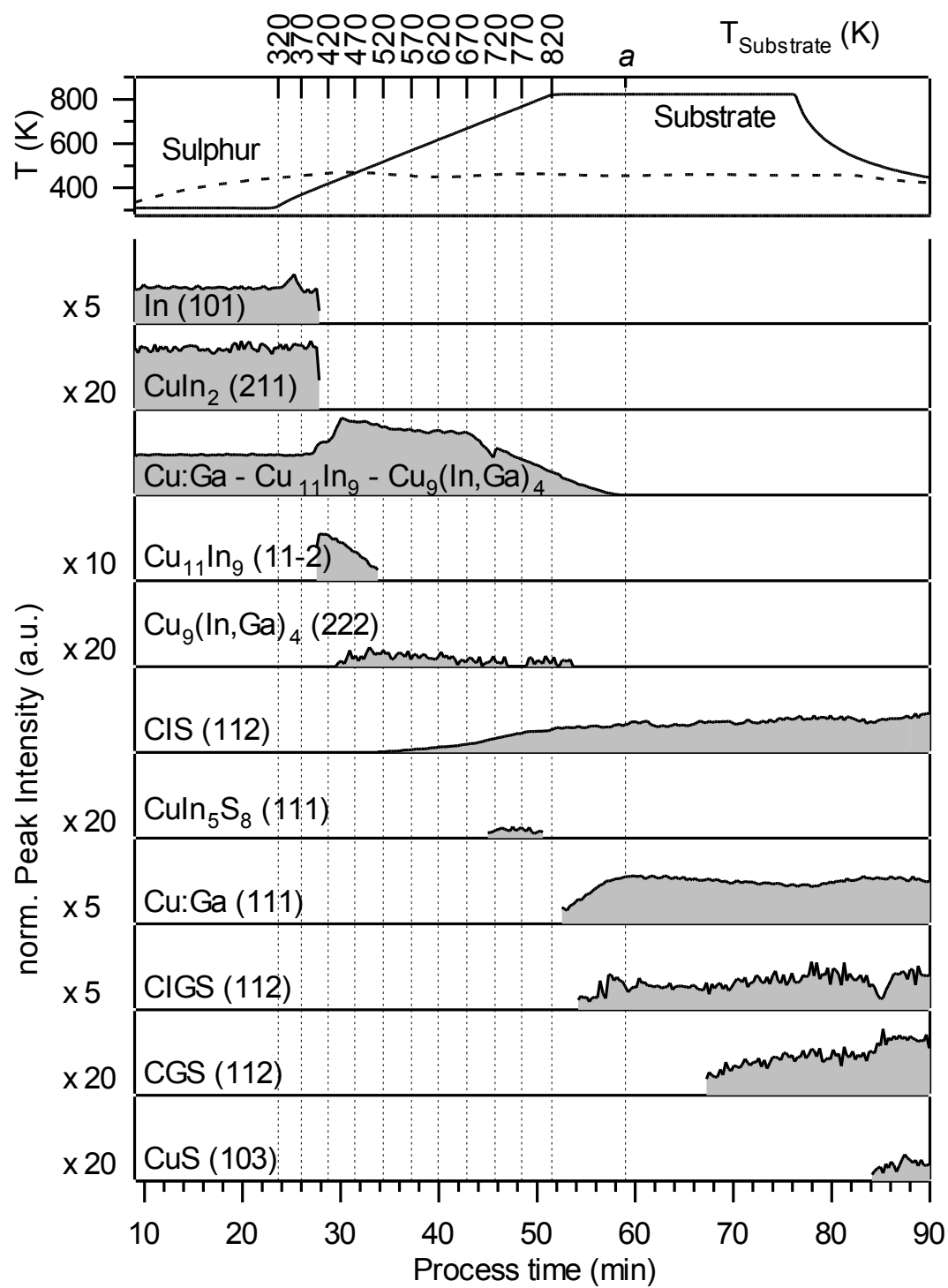


Fig. 2

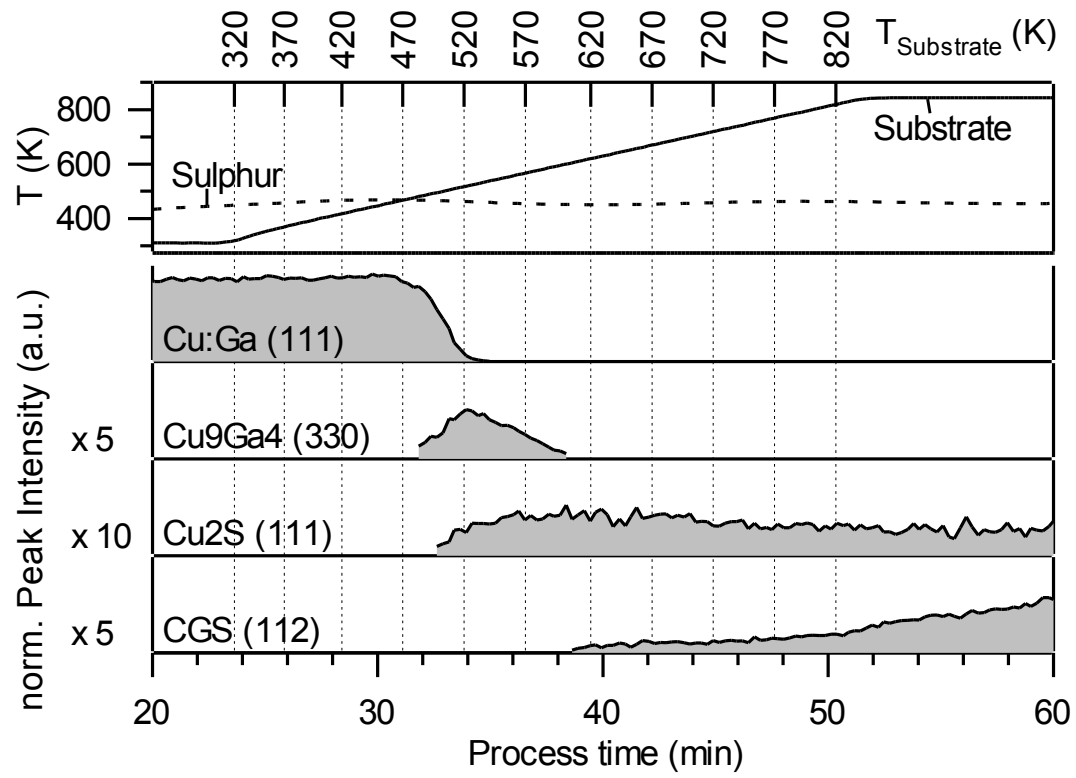


Fig. 3



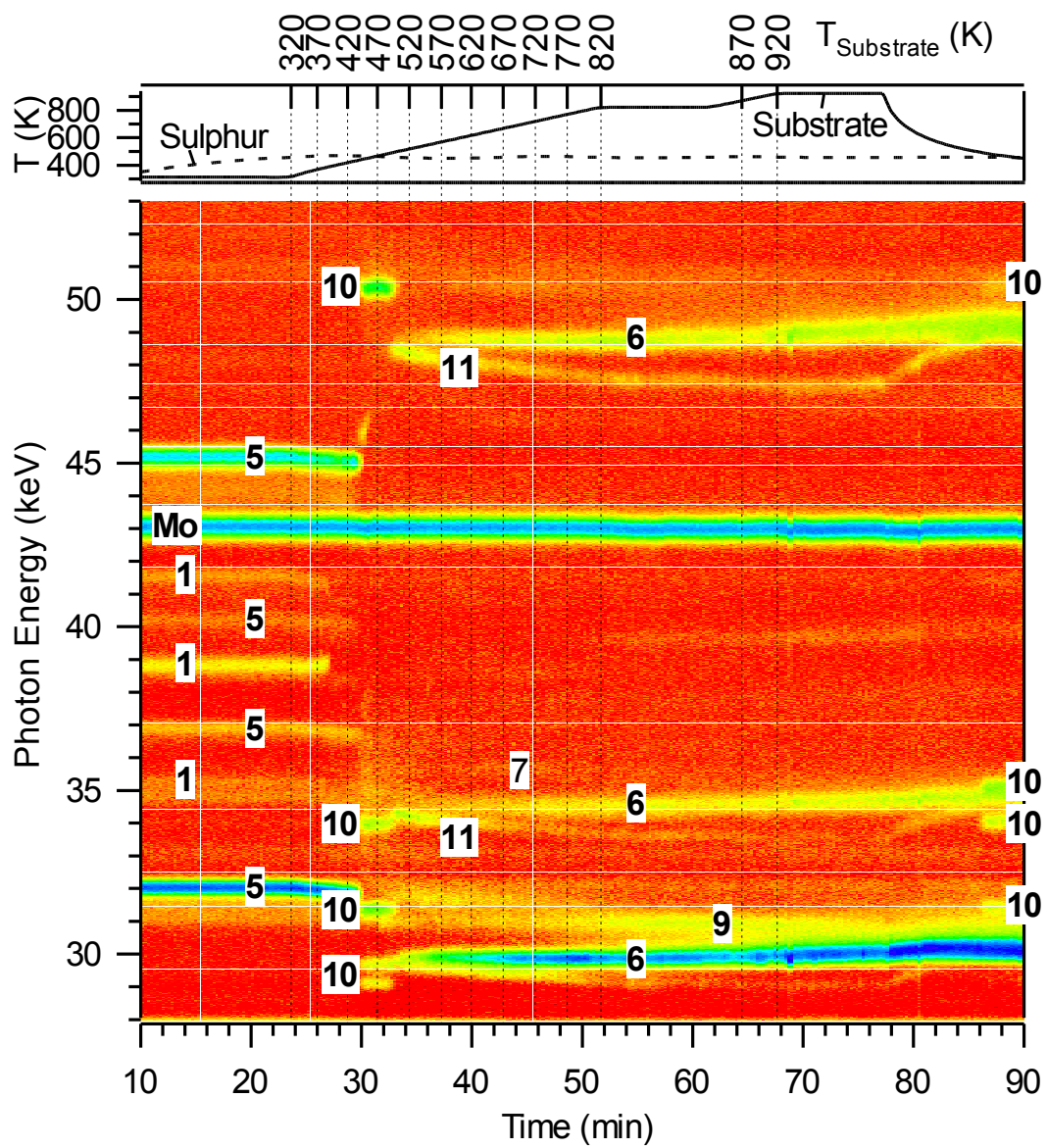


Fig. 4

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