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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 basis for the future development of an industrially feasible production of $Cu(In,Ga)S_2$ 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 ranges of time and temperature. Adhesion failure and at least intermediate formation of $CuIn_5S_8$ are other problems frequently encountered. In spite of these problems, promising pathways to single phase $Cu(In,Ga)S_2$ films prepared from sputtered Cu:Ga/In precursors have now been identified.

Keywords: Chalcopyrite; Gallium; Energy dispersive XRD; $Cu(In,Ga)S_2$; Solar cell

1. Introduction

$CuInS_2$ 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 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 that 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_2S 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.

2. 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. The amount of material actually deposited on the substrate was determined by weighing. This confirmed a ratio of $Cu/(In+Ga)=1.5\pm0.05$. The layer sequence of the precursor stacks was varied (Mo/Cu:Ga/In or Mo/In/Cu:Ga). In experiments with annealing prior to the sulphurisation experiment

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the annealing was carried out at a pressure of 10^{-3} Pa for 10 min at 675 K.

The sulphurisation processes were carried out in a vacuum chamber with a pressure ranging from 10^{-3} Pa to 10^{-2} 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 to 57 keV with a nominally fixed diffraction angle of $\theta = 3.7°$. 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 s. Elemental sulphur was evaporated in a Knudsen source at a temperature of 455 K. The sample and the sulphur source could be heated individually. For a detailed description of the set-up see Ref. [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 to 825 K and held at constant temperature for 10 to 25 min.

Additionally, ex-situ X-ray spectroscopy was used to determine phases present in the precursors, and in the vacuum annealed and the reactively annealed samples. All spectra were normalized to the intensity of the Mo Kα fluorescence signal to cancel out overall intensity variations. They mainly stem from a decreasing primary beam intensity during a process and changes

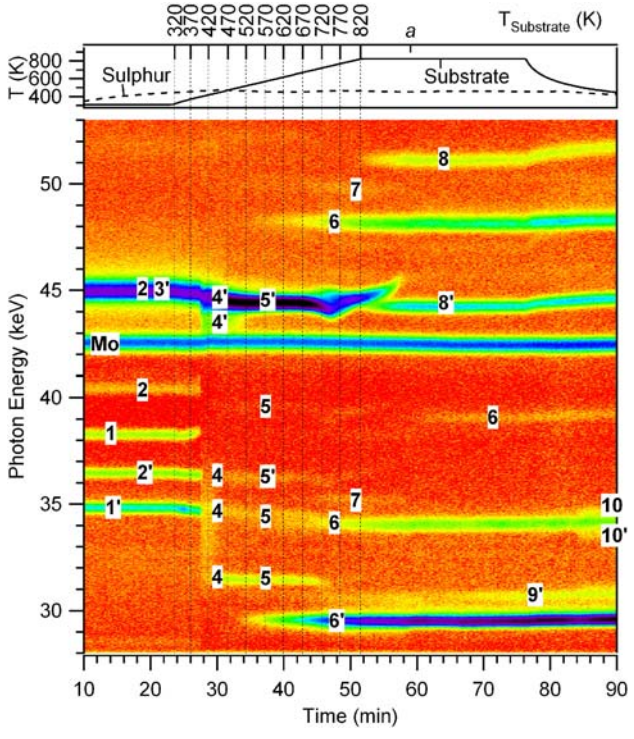

Fig. 1. In-situ X-ray diffraction spectra acquired during the sulphurisation of a Mo/Cu:Ga/In precursor layer. The signal intensities are expressed as different colours. The maxima have been attributed to the phases: 1-In, 2-$CuIn_2$, 3-Cu:Ga, 4-$Cu_{11}In_9$, 5-$Cu_9(In,Ga)_4$, 6-$CuInS_2$, 7-$CuIn_5S_8$, 8-Cu:Ga, 9-$CuGaS_2$, 10-CuS. The apostrophes after the numbers mark the maxima used for Fig. 2. Diffraction angle: $\theta = 3.705 \pm 0.002°$. The upper part of the figure shows the temperature profiles of the sample and the sulphur source.

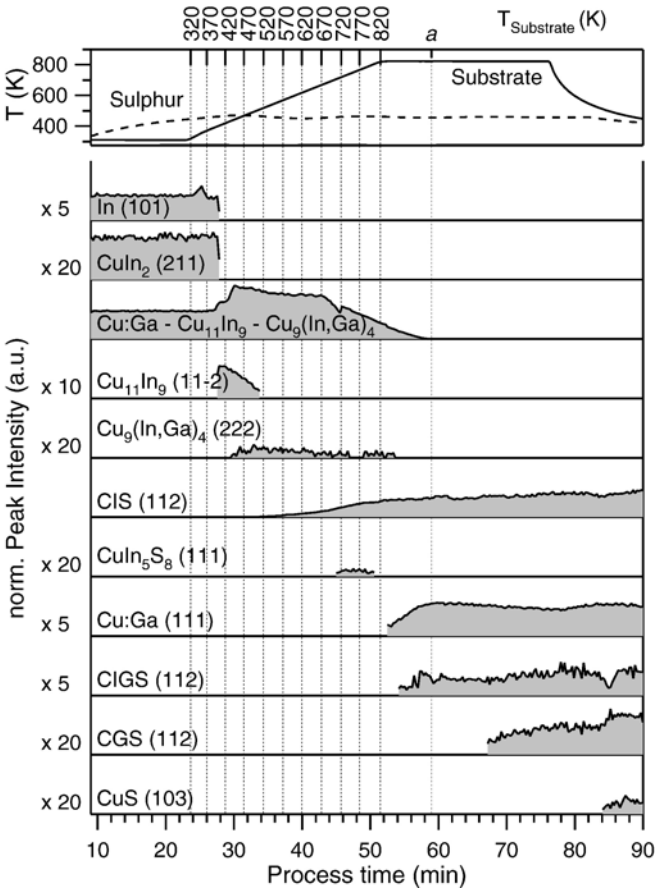

Fig. 2. Signal intensity of in-situ X-ray diffraction spectra acquired during the sulphurisation of a Mo/Cu:Ga/In precursor layer. The plot shows the intensity of the maxima marked with an apostrophe in Fig. 1. The maximum of the phase Cu:Ga in the precursor spectra cannot be clearly separated from the maxima of the subsequent phases $Cu_{11}In_9$ and $Cu_9(In,Ga)_4$. Therefore the intensity of these signals are plotted as a single curve.

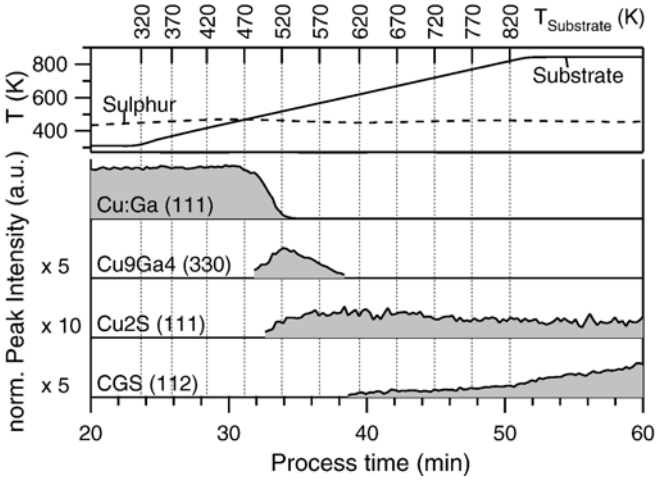

Fig. 3. Signal intensity of in-situ X-ray diffraction spectra acquired during the sulphurisation of a Cu:Ga precursor layer. The plot shows the intensity of the strongest maximum of each phase.