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Pressure-dependent real-time investigations on the rapid thermal sulfurization of Cu– In thin films

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ABSTRACT

Rapid thermal processing (RTP) under high sulfur partial pressure of copper rich Cu–In alloy thin films is investigated using in situ energy dispersive X-ray diffraction (EDXRD). Cu–In precursors are sulfurized at S vapor pressures in the 1 mbar range. Diffraction of white synchrotron light and recording of EDXRD spectra every 10 s at the EDDI beamline of the BESSY facility is used to monitor in situ the solid phases during the sulfurization and the subsequent cool-down. Ternary $CuInS_2$ forms via the binary InS and CuS and the ternary $CuIn_5S_8$ phases. The concentration of copper in the secondary $Cu_{2-x}S$ phase, which segregates on the surface of the $CuInS_2$, shows a strong dependence on the maximum sulfur pressure during the RTP-like process.

1. Introduction

Polycrystalline $CuInS_2$ (CIS) thin films used as absorber layers in thin film solar cells [1] are on the verge to large-scale industrial production. $CuInS_2$ has an almost ideal band gap (1.5 eV) for a single gap solar cell. Its fabrication process is rather inexpensive as compared to conventional silicon-based cell technologies and carries still a high potential for further cost reduction. State of the art $CuInS_2$ thin films are obtained by a rapid thermal processing (RTP), where copper-rich Cu–In films sputtered on Mo coated glass are placed in a sulfur vapor atmosphere for a few minutes at temperatures around 550 °C [2]. The average power conversion efficiencies (8–10%, $60\times120\,cm^2$ module) of CIS-based solar modules are promising; yet further improvements are expected. This inspires the use of techniques that permit a detailed understanding of the formation process, with the perspective of its further optimization.

Previous work has already treated the sulfurization of metallic Cu–In precursors under constant low sulfur pressure conditions similar to physical vapor deposition (PVD) like processes with a maximum pressure in the 10^{-3} mbar range [3,4]. It was found that $CuInS_2$ grows directly from the Cu–In intermetallic phases, and that in the Cu-rich case the $CuInS_2$ film is covered with $Cu_{2-x}S$ during the high temperature period. The present work investigates processes in a significantly higher pressure range (~1 mbar). Table 1 summarizes the main differences of the PVD, RTP and RTP-like (as used in this work) process parameters. Since the appearance of the binary sulfide phases like CuS, $Cu_{2-x}S$, InS and In_2S_3 is known to be pressure dependant [5], investigations of the influence of the sulfur partial pressure on the formation of the $CuInS_2$ thin film and the binary sulfide phases are highly desirable.

The detection of crystalline phases during film formation in almost real time is possible, thanks to the in situ recording of energy dispersive X-ray diffraction (EDXRD) spectra. The current investigation summarizes the first experiments of a novel in situ EDXRD setup, where the influence of the *S* pressure on the growth of $CuInS_2$ in a closed space reactor is studied.

2. Experimental procedure

2.1. The reaction chamber

The experiments were realized in a custom-made vacuum chamber, which fits the XRD goniometer available for diffraction experiments at the EDXRD beamline (EDDI) at BESSY (Berlin,

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Table 1
Typical parameters of PVD and RTP processes for the sulfurization of Cu/In thin films

Process	Heat-up ramp (°C/s)	Top temperature (°C)	Annealing time (min)	Max. sulfur pressure (m bar)	Reference
PVD	0.3–0.4	550	5–15	1.0×10^{-4}	[3,4]
RTP	5–15	550	0–3	1.0×10^{0}	[2,11]
This work	1	550	15	3.0×10^{0}	–

Germany). The base pressure of the setup is below 1×10^{-4} mbar, and a liquid nitrogen filled trap is placed between the vacuum chamber and the high vacuum pumping station. The actual reaction chamber has a reaction volume of 107 cm^3. Two sets of lamp heaters are placed on top and on bottom of the reactor. The heaters allow heating rates up to 8.6 K/s as measured by thermocouples located near the radiating lamps. The chamber is equipped with two 1-mm thick aluminum windows through which the X-rays can be coupled in and out of the chamber. The hard X-rays (10–100 keV) can pass the reaction chamber without significant losses in signal intensity due to absorption.

2.2. Process details

During the experiments the heating program was set to a ~1 °C/s ramp to 550 °C followed by a 15-min annealing period. The cool down followed without any external cooling. The exact temperature at the sample position is difficult to determine because of the high temperatures and corrosive sulfur environment. As a calibration method, the evolution of the lattice constant of gold powder placed at the sample position was followed and translated in a temperature transient. All the temperatures from now on will be referred to the gold calibration if not otherwise stated. During cool down the temperature readings converge as the time proceeds.

2.3. The geometrical setup and the energy dispersive detector

A fixed θ–2θ Bragg geometry was adopted for the recording of EDXRD spectra. The source of the X-ray white beam (10–100 keV) is a 7-T multipole wiggler. The collimated primary beam has an intensity of $\sim10^{12}$ Photons/(s$*$mm^2) at 10 keV and of $\sim10^{10}$ Photons/(s$*$mm^2) at 100 keV for a 250-mA storage current. Details on the wiggler spectrum are given elsewhere [6]. The incoming X-ray beam has a rectangular shape of 2×1 mm^2 and its projection on the sample (3.7° tilt) leaves a footprint of 25-mm length on the sample. The angle between the white X-ray beam and the detector is $2\theta=7.4^\circ$ and is kept constant throughout the experiments. The sample tilt (θ) is 3.7° and is also fixed. Two high precision slit apertures collimate the diffracted X-rays before they enter a LN$_2$ cooled germanium detector (CANBERRA). The detector electronics allow differentiating the energy into 16,000 channels. The channel/energy calibration of the detector is done with radioactive ^{133}Ba, ^{57}Co and ^{241}Am as well as by means of fluorescence line positions of W, Au, Pb and Zr. The continuous channel/energy relationship is obtained by interpolation of a second-order polynomial function [6]. The detectors resolution is 160 eV at 10 keV and 420 eV at 100 keV. With an adequate optimization of the detector's electronics (rise time, flat top), complete spectra can be acquired within 4 s whereby the maximum intensity of the diffracted Mo-(1 1 0) peak of a 0.5-μm thick Mo thin film is in the order of ~500 counts. The resolution and signal to noise ratio are sufficient for qualitative phase analysis. The integration time of a single spectrum in the present study was chosen to be 10 s, which agrees with the time scale of the process (Table 1). The first and the last spectrum of the experiments were collected at room temperature with 240-s integration time. A detailed description of the experimental setup available for EDXRD at the EDDI beamline can be found in Refs. [6,7]. More general information on the EDXRD principle and similar experimental settings can be found in Refs. [8–10].

2.4. Diffraction pattern analysis

A 0.5-μm thick Mo thin film serves always as a back contact in the glass/Mo/CuInS$_2$ absorber stack. Mo is characterized by its low chemical reactivity and stability. Therefore the signal of the MoKα line at 17.44 keV was used for normalization as it is considered constant throughout the sulfurizations. This consideration introduces an error of only 3% taking into account the evolving absorption characteristics of the thin film (from Cu/In to CuInS$_2$). No other intensity normalization due to ring current decay is necessary. The background stems mostly from the amorphous underlying glass substrate and is subsequently subtracted. The observed diffraction peaks are then fitted with a Gaussian profile as it is usual for energy dispersive diffraction [9] leading to satisfactory results. Line energy position E, intensity and full width at the half intensity maximum (FWHM) are thereby obtained. Phase identification was made by overlapping the diffraction spectra to the Joint Committee of Powder Diffraction Standards (JCPDS) files knowing that the interplanar spacings, d, can be obtained by the Bragg equation $d=0.61993/[\sin(3.7^\circ)*E]\,\mathrm{nm\,keV}^{-1}$ [10].

2.5. Samples

All films were deposited on soda-lime glass by DC-sputtering as described in Ref. [11] in the following order: 500 nm Mo, 470 nm Cu and 648 nm In. The precursors are Cu-rich with a ratio of [Cu]:[In] = 1.6:1. Precursor dimensions are 12×22.5 mm^2. After some days of storage at room temperature the stack is transformed into Mo/Cu/CuIn$_2$ [3]. Three of these precursors are placed next to each other in the reactor together with well-determined amounts of elementary sulfur. The "standard process" was made with 0.9 mg S/sample, which corresponds to a nominal ratio of [S]:[In] = 2.4:1. Lower amounts of sulfur lead to incompletely sulfurized films, where rest copper is found at the back of the film.

A direct measurement of the sulfur pressure in the reactor is not possible. However, the sulfur pressure in the reactor depends on the initial sulfur quantity. The maximal pressure (p_M) inside the reactor is obtained at the highest temperature and has two extreme values corresponding to the case where none of the sulfur is consumed by the precursors (p_highest) and where the necessary sulfur for the formation of the stoichiometric phases (CuInS$_2$ and Cu$_2$S) has been consumed completely (p_lowest). Therefore $p_\mathrm{lowest}<p_\mathrm{M}<p_\mathrm{highest}$. In the case of the "standard sulfurization" in the given reaction volume we have that $p_\mathrm{lowest}=1.6\,\mathrm{mbar}<p_\mathrm{M}<p_\mathrm{highest}=11.5\,\mathrm{mbar}$. The experiments revealed that at the highest temperature the main phases present are CuInS$_2$ and Cu$_2$S, and that the maximum pressure, p_M, is therefore closest to p_lowest.

In order to investigate the influence of p_M, the initial sulfur quantity was doubled four times (2 ×, 4 ×, 8 ×, 16 ×).