

Real-time investigations on the formation of CuInSe_2 thin film solar cell absorbers from electrodeposited precursors

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Abstract

In this article, we present results of a detailed real-time X-ray diffraction (XRD) study on the formation of CuInSe_2 from electroplated precursors. The solid-state reactions observed during the selenisation of three different types of precursors are presented. The first type of precursors (I) consists of the nanocrystalline phases Cu_{2-x}Se and InSe at room temperature, which react to CuInSe_2 starting at 470 K. The second type of precursor (II) shows an inhibited CuInSe_2 formation out of the initial phases Cu_{2-x}Se and $\gamma\text{-In}_2\text{Se}_3$ starting at 400 K. The third precursor type (III) shows completely different selenisation behaviour. Starting from the intermetallic compound $\text{Cu}_{11}\text{In}_9$ and amorphous selenium, the formation of the binary selenides In_4Se_3 and CuSe is observed after the melting point of selenium at 494 K. After selenium transfer reactions, the compound semiconductor CuInSe_2 is formed out of Cu_{2-x}Se and InSe . This type (III) reaction path is well known for the selenisation of SEL precursors (stacked elemental layers of sputtered copper and indium and thermally evaporated selenium).

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1. Introduction

Thin film solar cells based on the compound semiconductor CuInSe_2 (CIS) have proven to be a promising low-cost alternative to polycrystalline silicon technology. One possibility for a further reduction of production costs of this semiconductor material is to replace the cost-intensive high-vacuum deposition process, used for the production of SEL precursors [1], by the simultaneous electrodeposition of the elements copper, indium and selenium on top of a molybdenum-coated substrate. Conversion efficiencies of up to 11.5% have been demonstrated using precursors with simultaneously deposited copper, indium and selenium [2]. Thinking of a technological implementation into a large-scale production line, the simultaneous deposition process is, of course, the preferable technology as compared to a

sequential deposition process. The simultaneous deposition process enables to influence the initial phase composition of the samples by changing various parameters of the electrochemical deposition process.

As the reaction path and the CuInSe_2 formation temperature have an extensive influence on the crystalline quality of the resulting semiconductor, a knowledge and understanding of the mechanisms happening while annealing is mandatory for an optimisation of the production process. For this reason, we performed angle-dispersive in situ X-ray diffraction (XRD) measurements to monitor the solid-state reactions happening while annealing. The results of these investigations may lead to an improvement of the applied annealing profile as well as to an optimisation of the electrochemical deposition process itself. The in situ experiments have been performed to learn about the mechanisms, which led to the observed differences of the morphology and structural quality of absorbers processed from precursors deposited with different parameters. We have compared the observed reaction paths and give

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recommendations of a deposition technique resulting in CuInSe₂ with high structural quality.

2. Experimental methods and data evaluation

Angle-dispersive real-time XRD experiments were performed using a laboratory X-ray source with a power load of 3.3 kW (parallel beam, monochromatic CuK α radiation) in combination with a CCD area detector (for details see Ref. [3]) and an especially designed beam-stop arrangement [4]. Measurements were realised in transmission geometry, with the CCD detector mounted in a position, that the primary beam hits the detector in the middle of the active area perpendicular to its surface.

The sample surrounding [3] consists of an evacuated reaction chamber ($p = 10^{-2}$ Pa), equipped with two X-ray transparent polyimide windows with a thickness of 75 μ m for the primary and diffracted beam to enter and exit, respectively. The sample heating was realised by a PID controlled (Eurotherm) mica heater (Minco). The applied heating profile consisted of a ramp from room temperature to 923 K with a heating rate of 0.8 K/s, followed by an isothermal line at 923 K with a duration of 450 s. The sample cooling was passive, initiated by switching off the heating unit.

The samples consisted of thin polycrystalline films (thickness of about 1 μ m) of simultaneously electrodeposited copper, indium and selenium. As the in situ experiments were performed in transmission geometry, X-ray transparent polyimide foil with a thickness of 75 μ m has been used as a substrate. An electrically conductive layer of molybdenum (thickness of 0.5 μ m) has been deposited by DC magnetron sputtering in advance of the electrodeposition, in order to enable the electrochemical deposition process.

The bath contained Cu²⁺ and In³⁺ ions with a suitable corresponding anion and selenous acid (H₂SeO₃) as metal sources. Furthermore, it comprises an organic additive in different concentrations and a supporting electrolyte.

The deposition was carried out using an electroplating cell comprising of a molybdenum-coated float glass serving as the cathode, an inert anode and an Ag/AgCl reference electrode. The electrolyte was agitated using a circulating pump and a spray nozzle array. The cathode was placed in front of the spray nozzle array to grant a homogenous hydrodynamic towards the molybdenum surface. The deposition was performed using an Autolab PGSTAT 30 system (Metrohm) under potentiostatic regime. The pH was adjusted to 2.2 (± 0.2). The deposition potential was varied between -0.75 and -1.0 V vs. Ag/AgCl to adjust the proper [Cu]/[In] ratio of being copper rich and copper poor, respectively (see Table 1). A brightening agent was used to give dense and adherent depositions. The as-deposited selenium content of the samples was adjusted by the additive content of the bath. The stoichiometry of type (I), (II) and (III) precursors was adjusted by increasing ppm amounts of the additive.

Table 1

Composition and initial phases of the three investigated precursor types

Type	[Cu]/[In] ^a	[Se]/[In] ^a	[Se]/[In] ^b	Initial phases
I	0.88	2.04	—	Binary selenides InSe, Cu _{2-x} Se
II	1.07	1.65	—	Binary selenides γ -In ₂ Se ₃ , Cu _{2-x} Se
III	0.75	0.70	2.33	Intermetallic Cu ₁₁ In ₉ and elemental Se

^aatomic composition after the electrodeposition process, determined by XRF

^batomic composition after additional evaporation of selenium (only done for type III)

The atomic composition after the electrodeposition process was determined by X-ray fluorescence measurements (Table 1). The investigated type (I) samples were slightly copper deficient and selenium rich with [Cu]/[In] = 0.88 and [Se]/[In] = 2.04. Type (II) precursors were copper rich and selenium poor with a stoichiometric ratio of [Cu]/[In] = 1.07 and [Se]/[In] = 1.65. The deposition parameters of the third type of samples (III) led to copper-poor and selenium-deficient precursors with [Cu]/[In] = 0.75 and [Se]/[In] = 0.70, respectively. In order to enable a complete conversion to CuInSe₂ of this precursor type, the missing amount of selenium has been deposited after the electrodeposition by thermal evaporation of elemental selenium, resulting in [Se]/[In] = 2.33.

The described experimental setup leads to rotationally symmetrical powder patterns (recorded 2θ range between 10° and 50°), which simplifies the necessary incidence-angle dependent intensity correction from two dimensions to one dimension. Besides this, the raw data are rectified for sample absorption and corrected for flat field and spatial distortion. The two-dimensional diffractograms are integrated along the azimuth angle ϕ using the software Fit2D [5–7]. The one-dimensional diffraction patterns are used for a time-resolved qualitative (using Jade 6.1, MDI) phase analysis. Additionally, the powder patterns were refined by the Rietveld method [8] to obtain a time- and temperature-resolved phase evolution of present polycrystalline phases during the heating profile. The diffractograms were refined in the 2θ range between 20° and 48°, the background has been fitted with a third-order polynomial. As the polyimide substrate delivers a broad diffraction signal within the considered 2θ range, an additional Gaussian peak at $2\theta = 26.3^\circ$ has been included in the fit. The position, intensity and width of this peak have been determined considering a room temperature diffractogram and kept constant for the refinement of subsequent powder patterns. The temperature factors of all contributing phases (Table 2) have been constrained to one common refinable value. Three observed phases show preferred orientations, the orientation directions of these phases are InSe $\langle 110 \rangle$, γ -In₂Se₃ $\langle 001 \rangle$, $\langle 111 \rangle$ and Cu₁₁In₉ $\langle 010 \rangle$. The lattice parameters of the contributing phases have been refined,

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