



# Formation of CuInSe<sub>2</sub> films from metal sulfide and selenide precursor nanocrystals by gas-phase selenization, an in-situ XRD study



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## ABSTRACT

In this work phase pure CuInSe<sub>2</sub> thin films were obtained by selenization of ternary CuInSe<sub>2</sub> and CuInS<sub>2</sub> nanocrystals and mixtures of binary nanocrystals such as CuS, In<sub>2</sub>S<sub>3</sub>, Cu<sub>2</sub>Se and In<sub>2</sub>Se<sub>3</sub>. The temperature of the selenium source was kept at 400 °C during selenization. Monitoring the process using in-situ x-ray diffraction, the effect of selenization on the phase formation and grain growth in the precursor film was investigated. Whereas CuInSe<sub>2</sub> and CuInS<sub>2</sub> nanocrystals exhibit little grain growth, we found that mixtures of binary nanocrystals can show significant sintering depending on the reaction conditions. For the mixture of CuS and In<sub>2</sub>S<sub>3</sub> nanocrystals, the crystallinity and the morphology of the obtained films strongly depends on the Cu/In ratio, with a Cu excess strongly promoting grain growth. With mixtures of Cu<sub>2</sub>Se and In<sub>2</sub>Se<sub>3</sub> nanocrystals the selenium partial pressure plays a crucial role. Selenium evaporation from the mixed compounds results in CuInSe<sub>2</sub> films composed of relatively small crystallites. Higher selenium partial pressures however resulted in improved sintering. Incomplete propagation of the selenization reaction through the layer was observed though, only leading to a well sintered CuInSe<sub>2</sub> top layer above a fine grained bottom layer.

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## 1. Introduction

CuInGaSe<sub>2</sub> (CIGS) and CuInSe<sub>2</sub> (CIS) are used as light absorbers in thin-film solar cells. Due to their direct band gap and high absorption coefficient CIGS and CIS are the most promising materials in this field. Highest efficiencies for CIGS solar cells are generally obtained by vacuum co-evaporation using elaborate multistage growth processes [1]. Despite the high efficiency of state-of-the-art thin film solar cells, the high production cost of these vacuum based deposition methods remains a main obstacle to the widespread use of CIGS solar cells. Therefore colloidal nanocrystals of solar absorber materials have attracted much attention in order to reduce process complexity and cost [2,3]. This non-vacuum based approach involves the printing of a precursor layer followed by a sintering step. The transformation step is typically based on annealing, often in combination with selenization [4]. As particulate precursors different materials have been explored such as metallic compounds [5], metal oxides [6] and CI(G)S nanocrystals [7,8]. Transformation of these particulate layers into dense films is not always achieved due to limited sintering at the maximum working temperatures of low-cost substrates [9,10].

Here, we report on a systematic study of the selenization behaviour of different types of nanocrystals including CuInSe<sub>2</sub> and CuInS<sub>2</sub> as well as mixtures of binary colloidal nanocrystals such as CuS, In<sub>2</sub>S<sub>3</sub>, Cu<sub>2</sub>Se and In<sub>2</sub>Se<sub>3</sub>. Different approaches to introduce additional reactivity into the as deposited layer in order to improve the sintering were investigated. In-situ XRD has been used as a tool to determine the effect of annealing and selenization on the phase formation and grain growth in the precursor films.

## 2. Experimental

### 2.1. Synthesis and deposition

CuInS<sub>2</sub> nanocrystals (NCs) are synthesized according to the following procedure. 1 mmol Cu(acac)<sub>2</sub> (0.262 g, Aldrich, 99.99%) 1 mmol In(acac)<sub>3</sub> (0.412 g, Aldrich, 99.99%) and 2.1 mmol elemental S (0.067 g, Merck, 99.999%) are combined in 15 ml of 1-octadecene (Alfa Aesar, Tech. 90%) using a three-neck flask. This flask is then attached to a Schlenk line, after which the heterogeneous mixture is flushed with nitrogen for 1 h. Next, 2 ml oleylamine (Acros, Tech. 80–90%) is injected, followed by increasing the temperature to 240 °C. Upon reaching 240 °C, the reaction is allowed to continue for 1 h. After this period, the flask is cooled down using a water bath, and the CuInS<sub>2</sub> NCs are washed using toluene and ethanol. The NCs are then

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collected by centrifugation and the brown-red supernatant is discarded. The NC pellet is redissolved in toluene and the resulting clear black solution is stored in the fridge.

To synthesize CuS nanocrystals, 3 mmol Cu(acac)<sub>2</sub> (0.786 g) is flushed with nitrogen together with 3.05 mmol S (0.0978 g) in 20 ml 1-octadecene at room temperature. After 1 h, 10 ml of oleylamine is injected and the reaction mixture is heated to 130 °C. After 1 h, the flask is cooled down to room temperature using a water bath. Then, the CuS nanocrystals are collected using toluene and precipitated using ethanol. Following centrifugation, the brown red supernatant is discarded while the nanocrystals are dispersed using toluene. In a typical In<sub>2</sub>S<sub>3</sub> nanocrystal synthesis, 2 mmol InCl<sub>3</sub> (0.465 g, Aldrich, 99.999%) is stirred and flushed with nitrogen after adding 8 ml octadecene at 110 °C. Meanwhile, 3.6 mmol S (0.1538 g) is dissolved in 6 ml octadecene in a nitrogen-filled glovebox at 150 °C. After the injection of 4 ml OLAm in the flask with the In precursor and raising the temperature to 170 °C, the S-octadecene solution is injected in this flask. The reaction is allowed to stir for 1 h at 170 °C, followed by cooling down to room temperature using a water bath. The In<sub>2</sub>S<sub>3</sub> nanocrystals are separated by adding toluene and ethanol, and are redissolved in toluene.

CuInSe<sub>2</sub>, Cu<sub>2</sub>Se and In<sub>2</sub>Se<sub>3</sub> nanocrystals are obtained according to procedures we described earlier [11].

Thin films of different nanocrystal precursor combinations of approximately 1 μm thickness were deposited on silicon substrates for the analysis of annealing conditions. The as-synthesized nanocrystals are washed first and dispersed in chloroform. Their approximate concentration was measured and calculated by UV-VIS-NIR spectroscopy [12], using the bulk optical constants of the respective materials. These values were used to calculate the amount of nanocrystal solution to be drop casted on the silicon substrate. All thin films were drop casted from chloroform solutions and dried in air at room temperature.

## 2.2. In-situ XRD and selenization

Several in-situ XRD studies have reported on the mechanism of Cl(G)S formation during selenization. Most of these studies focus on the selenization of sputtered CuIn precursor films [13–17]. For non-vacuum based methods only a few investigations have been reported [18,19]. Here, annealing was performed in an experimental stainless steel heating chamber, mounted in a Bruker D8 Discover, dedicated for in-situ x-ray diffraction ( $\lambda = 0.15406$  nm) was used as the x-ray source, while a linear detector recorded the diffraction pattern providing information on the crystallinity of the film. The diffraction patterns were collected every 10 s. Gas-phase selenization was carried out in a heated graphite box which could be inserted into the stainless steel heating chamber. The samples were placed in this graphite box together with 1 g selenium powder (Aldrich, 99.5%) that was put in a well inside the graphite box a few centimeters away from the sample. The sample inside the box rested onto a separately controlled heater, allowing independent control of the sample temperature (if higher than the graphite box temperature). After filling the outer stainless steel chamber with helium, the graphite box was heated to 400 °C creating Se vapor inside the graphite box. Subsequently the sample was annealed to 550 °C with a ramp rate of 0.5 °C/s by the other heater inside the graphite box while the box itself remained heated at 400 °C to provide a constant supply of selenium vapor.

## 2.3. Characterization and analysis

Before and after annealing the crystalline phases were characterized ex-situ using XRD (Bruker D8 Discover). The ex-situ XRD patterns were collected at a scan rate of 2°/min. The crystallite size of the nanocrystals has been estimated from the full width at half maximum (FWHM) of the (112) diffraction peak using the Scherrer equation. Instrumental effects have been taken into account by using lanthanum hexaboride to

calibrate instrumental broadening of the diffraction peaks. The evolution of the crystallite size and the d-spacing as a function of time was obtained by fitting the raw in-situ XRD data of the (112) diffraction peak. It should be noted that the obtained values are merely a qualitative estimate used to observe the evolution of the grain growth rather than very accurate values for the crystallite size. The morphology and composition of the films were determined by scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX), respectively using a FEI Quanta 200F FEGSEM.

## 3. Results and discussion

### 3.1. CuInSe<sub>2</sub> nanocrystals

Fig. 1 (blue) shows the XRD pattern of the as-deposited precursor film consisting of CuInSe<sub>2</sub> nanocrystals. For the as-synthesized nanocrystals the characteristic XRD peaks around 26.6°, 44.6° and 52.8° 2θ are observed corresponding to the (112), (220/204), and (116/312) planes of CuInSe<sub>2</sub>. The crystallite size of the nanocrystals is 16 nm as calculated using the Scherrer equation. No secondary phases could be detected indicating the formation of pure chalcopyrite nanocrystals. EDX measurements however showed a slightly In-rich composition with a Cu/In ratio of 0.9 for the precursor film.

The XRD pattern of these films after annealing in a helium atmosphere is shown in Fig. 1 (red). The films of CuInSe<sub>2</sub> nanocrystals were heated in helium for 10 min at 550 °C using a ramp rate of 0.5 °C/s. In addition to the increase in intensity of the main CuInSe<sub>2</sub> peaks other smaller characteristic peaks of the chalcopyrite structure are also observed. It demonstrates that the crystalline quality of the structure is improved by the thermal treatment. Nevertheless the crystallite size after annealing only increased up to 27 nm. In the annealed film we could also identify a secondary phase, indicated by (\*) in Fig. 1, as a Cu<sub>x</sub>In<sub>y</sub> alloy. Fig. 1 (black) also shows the XRD pattern for the films of CuInSe<sub>2</sub> nanocrystals after thermal treatment in a selenium atmosphere. The same temperature profile was used during selenization as for the inert annealing while the selenium source was kept at 400 °C. Similarly to the inert annealing the crystalline quality enhances after selenization although the crystallite size only increases up to 32 nm. In contrast no peaks related to a Cu<sub>x</sub>In<sub>y</sub> alloy are observed for the selenized sample. Hence it is likely that this secondary phase results from a loss of selenium during the thermal treatment in helium.

In situ XRD has been used to monitor the effect of annealing on the crystallite size of the nanocrystals constituting the precursor films. Fig. 2 shows the evolution of the CuInSe<sub>2</sub> (112) lattice spacing as a function of time during the thermal treatment in helium and selenium. Since

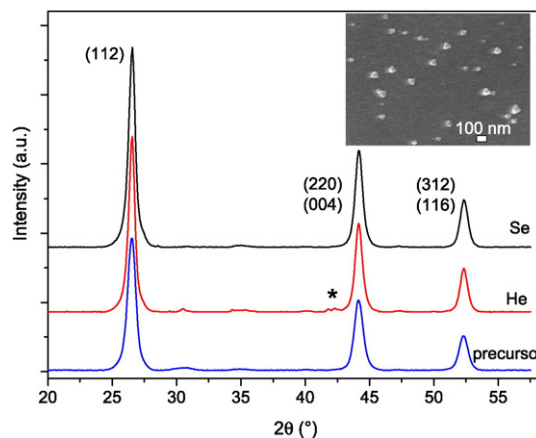


Fig. 1. XRD patterns of a CuInSe<sub>2</sub> nanocrystal thin film before (blue) and after annealing in helium (red) and after selenization (black). The insert shows a SEM image of the selenized sample.

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