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Formation reactions of chalcopyrite compounds and the role of sodium doping

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Abstract

The selenisation of the thin film precursors indium, Cu–In and Cu–In–Ga has been studied by in-situ X-ray diffraction. The influence of sodium doping on the kinetics of the solid-state reactions observed agrees with the predictions derived from a phenomenological model presented earlier. In this model a layer of sodium polyselenide is assumed to form at the surface of the precursor, or around each crystal grain. This layer might be responsible for impeded ion exchange in certain solid-state reactions.

Keywords: Chalcogenides; Thin films; Crystal growth; X-ray diffraction

1. Introduction

Sodium doping (abbreviated below as “Na”) during rapid thermal processing of stacked elemental layers (RTP-SEL) is known to increase the grain size of the absorber material in Cu(In,Ga)Se_2 thin film solar cells [1]. One important mechanism involved might be the compensation of copper vacancies by Na^+ cations on the surface of the crystallites [2]. Discussing the effect of Na on the chalcopyrite absorber it is helpful to distinguish between the influence of Na on 1.) the reaction kinetics of the formation of $CuInSe_2$ during RTP-SEL, 2.) the grain size, and 3.) the electronic properties.

In this article we will discuss the first two points. We have investigated the selenisation of metallic precursors with different amounts of Na by in-situ X-ray diffraction (XRD). With this method the chemical solid-state reactions for the absorber formation can be identified and the influence of Na becomes obvious.

2. Experimental

The selenisation reactions of the following four types of samples (Table 1) have been investigated: a) elemental indium, b) the intermetallic compound $Cu_{11}In_9$, c) a Cu–In and a Cu–In–Ga precursor (d). The metal layers were deposited in a laboratory dc magnetron sputter coater, the selenium cover layer was evaporated. In order to study the influence of Na on the reaction kinetics, the selenisation of sodium-free samples was compared to that of Na doped precursors. Samples a) and b) were annealed in selenium vapour provided from an evaporation source. The formation of binary selenide compounds is limited by the amount of selenium provided by evaporation. Despite an evaporated Se excess of 20% prior to the annealing process this selenisation condition will be referred to as “selenium deficient” in the following, because Se had the possibility to easily evaporate from the sample upon heating. In contrast, samples c) and d) were tempered in selenium excess conditions, which was realised by covering the sample with a polyimide foil to keep the selenium on the precursor [3]. The crystalline solid-state phases occurring during the annealing process were detected by real-time XRD. The phase evolution was determined by Rietveld refinement.

Table 1
Overview of investigated samples (thickness of the metallic layer: 0.6 μm)

Sample	Precursor type	[Na] [%] (*)	[Se]÷([Cu]+[In]+[Ga])
a)	In/Se	0, 100, 200	1.2
b)	$Cu_{11}In_9$/Se	0, 50, 100, 200	1.2
c)	$Cu_{0.9}In$/Se	0	≈10
d)	$Cu_{0.9}In_{0.7}Ga_{0.3}$/Se	0, 100	≈10

(*) 100% Na corresponds to a sodium concentration of [Na]÷[In] much smaller than 10^{-2} and can therefore not be considered as a matrix component.

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3. Results

3.1. The influence of Na on the reaction kinetics in the binary system In–Se

There is no influence of Na on the phase sequence of the binary compounds formed in type a) samples. The first selenide compound is always In_4Se_3 which begins to form at temperatures of about 200 °C. At higher temperatures we observe reactions resulting in InSe and β-In_2Se_3. Finally the slightly selenium deficient phase β-In_2Se_3 is transformed into stoichiometric γ-In_2Se_3. The evolution of the molar fractions determined by Rietveld refinement demonstrates a change in the reaction kinetics of the transition from In_4Se_3 to β-In_2Se_3: addition of 200% Na delays this reaction by 40 K towards higher temperatures (Fig. 1).

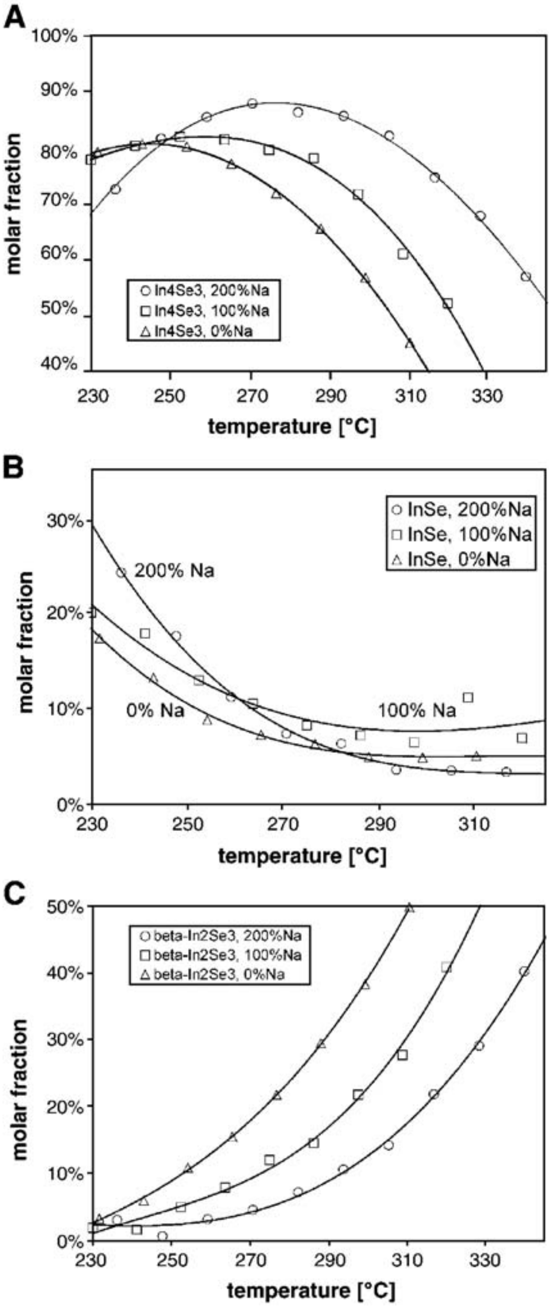

Fig. 1. Evolution of the indium selenide phases during selenising elemental indium. The heating rate was 0.5 K/s and selenium was evaporated from a heated source. The lines serve as guide-to the eye, only.

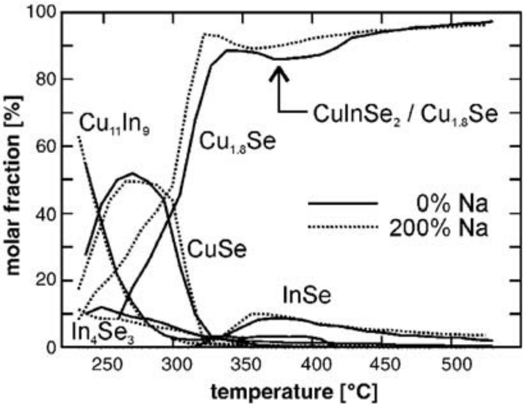

Fig. 2. Phase evolution while annealing of the intermetallic compound $Cu_{11}In_9$ with 0.5 K/s and evaporation of selenium from a heated source. The evolution of the molar fractions of the binary compounds is not significantly influenced. The formation of $CuInSe_2$ starts at 370 °C and is expressed by the minimum in the course of the $Cu_{1.8}Se$ fraction, which was simultaneously used to fit the reflections of $Cu_{2-x}Se$ and $CuInSe_2$. Although in this graphical representation there seems to be a difference in the formation temperature of $Cu_{1.8}Se$ and $CuInSe_2$ due to Na, there is no consistent trend with the data of 50% and 100% Na, which were omitted for clarity in Fig. 2. The contribution of InSe appears too small, which is caused by the fact that this phase is partly X-ray amorphous.

3.2. The influence of Na on the reaction kinetics of a $Cu_{11}In_9$ precursor

The first binary selenide compound formed upon heating sample b) is In_4Se_3 at a temperature of 215 °C, CuSe follows at 230 °C. After this, a selenium transfer reaction occurs. In_4Se_3 is selenised to InSe on the expense of CuSe, reacting to Cu_2Se by releasing selenium. Cu_2Se and InSe are the reactants for the formation of $CuInSe_2$ beginning at 370 °C. Rietveld refinement does not reveal any change in the formation temperatures and reaction rates due to Na (Fig. 2).

3.3. The influence of Na on Cu–In and Cu–In–Ga precursors

The general evolution of the selenide phases observed in samples c) and d) has been described earlier [3], here we will focus on the influence of Na. In all cases the first selenide compound formed is In_4Se_3 which is independent of Na for type d) samples. However, Na influences the selenisation kinetics of the metallic precursor. For the gallium containing precursor, 100% Na results in a linear consumption of the metallic compound $Cu_{11}In(Ga)_9$. Without Na the molar fraction of the intermetallics $Cu_{11}In_9$ (sample c) and $Cu_{11}(In,Ga)_9$ (sample d) decreases exponentially. This is caused by the decreasing selenium excess due to imperfect selenium inclusion by sample covering. The selenisation of $Cu_{11}In_9$ proceeds four times as fast as that of $Cu_{11}(In,Ga)_9$.