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Effect of precursor structure on Cu(InGa)Se_2 formation by reactive annealing

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ABSTRACT

Precursor structures of Mo/CuGa/In, Mo/In/CuGa, Mo/In/CuGa/In and Mo/CuGaIn were prepared on thin sodium-free glass by the sputtering of CuGa and In targets. *In-situ* phase evolution of precursors with temperature was investigated by a high-temperature X-ray diffraction system, which verified the existence and transformation of several intermetallics: Cu_2In, $Cu_{11}In_9$, Cu_3Ga, Cu_7In_3, Cu_9Ga_4 and $Cu_{16}In_9$ as well as elemental In. $MoSe_2$ layers produced during selenization were detected by scanning electron microscope and X-ray diffraction, with their thicknesses varying by precursor structure. Adhesion strength of Cu(InGa)Se_2 to each Mo layer was assessed by applying CdS chemical bath deposition process to each sample.

1. Introduction

The reactive annealing of metallic Cu–Ga–In precursors under Se or H_2Se is a likely method of producing effectively large area Cu(InGa)Se_2 (CIGS). However, Ga accumulation near the Mo side of substrate/Mo/CIGS structure is often observed during the selenization of Cu–Ga–In precursors yielding phase-separated $CuInSe_2$ (CIS) and $CuGaSe_2$ (CGS) which subsequently lead to lower open-circuit voltages [1]. To improve Ga depth uniformity within the CIGS layer, Alberts et al. [2] successfully employed a two-step selenization/sulfization by H_2Se and H_2S. Kim et al. [3] reported that a homogeneous through-film Ga profile was achievable by simultaneous H_2Se/H_2S reaction of metal precursors.

CIGS films formed by selenization of metal precursors are readily delaminated from Mo layers during CdS chemical bath deposition due to their poor adhesion. It has been suggested that a $MoSe_2$ layer may affect the adhesion at the interface of CIGS and Mo [4,5]. In particular, a $MoSe_2$ layer oriented parallel to the surface of the Mo layer shows poor adhesion because hexagonal $MoSe_2$ compounds are stacked by weak Van der Waals interactions.

Bilayer metal structures, such as $Mo/Cu_{0.7}Ga_{0.3}/In$, have been widely used as precursors for two-step sputter-selenization processes [1,6]. This paper reports the use of various precursors with different stacking sequences of intermetallic CuGa and elemental In to investigate the phase evolution of the metal precursors and the characteristics of the CIGS layer selenized by reactive annealing, with particular attention paid to the formation of $MoSe_2$ and compositional depth profiles.

2. Experimental details

Various types of mono- and multi-layer precursors (CuGa/In, In/CuGa, In/CuGa/In and CuGaIn) were prepared on Mo-coated thin sodium-free Corning 7059 glass (SFG) of 0.7 mm thickness by sequentially or simultaneously sputtering CuGa alloy with 24 wt.%Ga and elemental In targets. Total thicknesses of precursors were intended to be 600–700 nm. The atomic compositions of the precursors were confirmed to be Cu/(In + Ga) = 0.9–1.0 and Ga/(In + Ga) = 0.27–0.31.

The phase evolution of the metal precursors with temperature was observed by an *in-situ* high-temperature x-ray diffraction (HT-XRD) system composed of Panalytical X'pert Pro MPD and Anton Paar HTK16 furnace. Precursor samples were mounted on the strip heater and the chamber was evacuated to remove oxygen. Initially, samples were heated to 50 °C at a rate of 100 °C/min under flowing He environment, and XRD data were then collected over the 2θ range of 20 to 60° for around 3 min while maintaining this temperature. This XRD scan was repeated every 10 °C during subsequent heating to 550 °C.

The reactive annealing of metal precursors was performed in a rapid thermal process (RTP) system consisting of a quartz tube reactor with an inner diameter of 62 mm, quartz sample tray and infrared (IR) heater. The quartz sample tray held up to six 1 cm × 1 cm samples. The IR heater ramped temperature rapidly, requiring only 1 min to reach 1000 °C from room temperature. The Cu–Ga–In metal precursors were selenized during annealing, by a Se layer thickness of 30–50 nm being deposited on them with additional Se vapor supplied from a quartz sample cover coated by a 3–4 μm Se layer while minimizing the

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re-evaporation loss of Se from the selenized CIGS samples. The Se-coated sample cover and samples' surfaces were separated by approximately 4 mm.

Precursor samples loaded on sample tray covered with a Se-coated quartz plate were then annealed in the center of the tube reactor. Prior to each run, the reactor was evacuated by a rotary pump for 10 min, with Ar then introduced to maintain a purged atmosphere. Precursor samples were pre-annealed at 250 °C for 30 min under flowing Ar to stabilize the stacked precursor. During reactive annealing, temperature was ramped to 550 °C from room temperature within 1 min, and maintained for 10 min, long enough to complete selenization.

Mono- and multi-layered precursor structures were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). Compositional depth profiles of the selenized films were measured by secondary ion mass spectrometry (SIMS).

3. Results and discussion

Fig. 1 illustrates the results of temperature ramp annealing experiments using precursors of different stacking sequences: such as Mo/In/CuGa, Mo/CuGaIn, Mo/In/CuGa/In and Mo/CuGa/In. The first scan at room temperature established the stable phases of the as-deposited precursors. The XRD pattern for precursor samples showed intermetallic Cu_2In, $Cu_{11}In_9$ and Cu_3Ga as equilibrium phases at room temperature. A pure In peak was found in precursors with an In surface layer (Mo/CuGa/In and Mo/In/CuGa/In). As temperature increased, the $Cu_{11}In_9$ phase, stable at low-temperatures, disappeared at around 100–120 °C. Elemental indium melted away evidenced by the abrupt disappearance of the In peak at its melting point of around 140 °C. Finally, at higher temperatures of 400–550 °C, Cu_9Ga_4, Cu_7In_3 and $Cu_{16}In_9$ phases were verified as phases possibly stable at high temperatures. In general, the co-sputtered CuGaIn precursor appeared to have homogenous and stable intermetallic compounds with no dramatic phase evolution during ramp heating.

Table 1
Equilibrium crystalline phases of as-deposited and pre-annealed precursors.

Precursor structures	Equilibrium crystalline phases (as-deposited)	Equilibrium crystalline phases (after pre-annealing under flowing Ar at 250 °C, for 30 min)
SFG/Mo/In/CuGa	Cu_2In, Cu_3Ga	Cu_2In, Cu_3Ga, $Cu_{11}In_9$, In
SFG/Mo/CuGaIn	Cu_2In, Cu_3Ga, In	Cu_2In, Cu_3Ga, $Cu_{16}In_9$, In
SFG/Mo/In/CuGa/In	Cu_2In, Cu_3Ga, $Cu_{11}In_9$, In	Cu_2In, Cu_3Ga, $Cu_{11}In_9$, $Cu_{16}In_9$, In
SFG/Mo/CuGa/In	Cu_2In, Cu_3Ga, $Cu_{11}In_9$, In	Cu_2In, Cu_3Ga, $Cu_{11}In_9$, $Cu_{16}In_9$, In

It is believed that the pre-annealing of precursors at 250 °C for 30 min under flowing Ar promotes the interdiffusion of stacked precursors making their morphology and structure more stable. The equilibrium crystalline phases of as-deposited and pre-annealed precursor samples, confirmed by XRD at room temperature, were listed in Table 1.

The SEM cross-sectional images of the as-deposited precursors and corresponding CIGS films produced by reactive annealing are compared in Fig. 2. It should be noted that the four precursors used here were loaded together into RTP trays and annealed simultaneously to ensure identical process conditions. The SEM images of precursors show that the thicknesses of Mo and metal precursors lie in the range of 600–700 nm and 600–1000 nm, respectively. It was also observed that the surface morphologies of precursors containing elemental In layers were relatively poor, probably due to the low melting temperature of In, while the co-sputtered CuGaIn precursor had a planar and relatively smooth surface. It is interesting to note that the samples selenized under the same RTP conditions had a variety of thicknesses depending upon the thickness of $MoSe_2$ formed during selenization. $MoSe_2$ layers were grown as a columnar structure and surprisingly the entire Mo layer of the SFG/Mo/CuGa/In precursor had been converted to $MoSe_2$.

The XRD patterns of the selenized samples are shown in Fig. 3(a), demonstrating that the 600–700 nm-thick metal precursors were

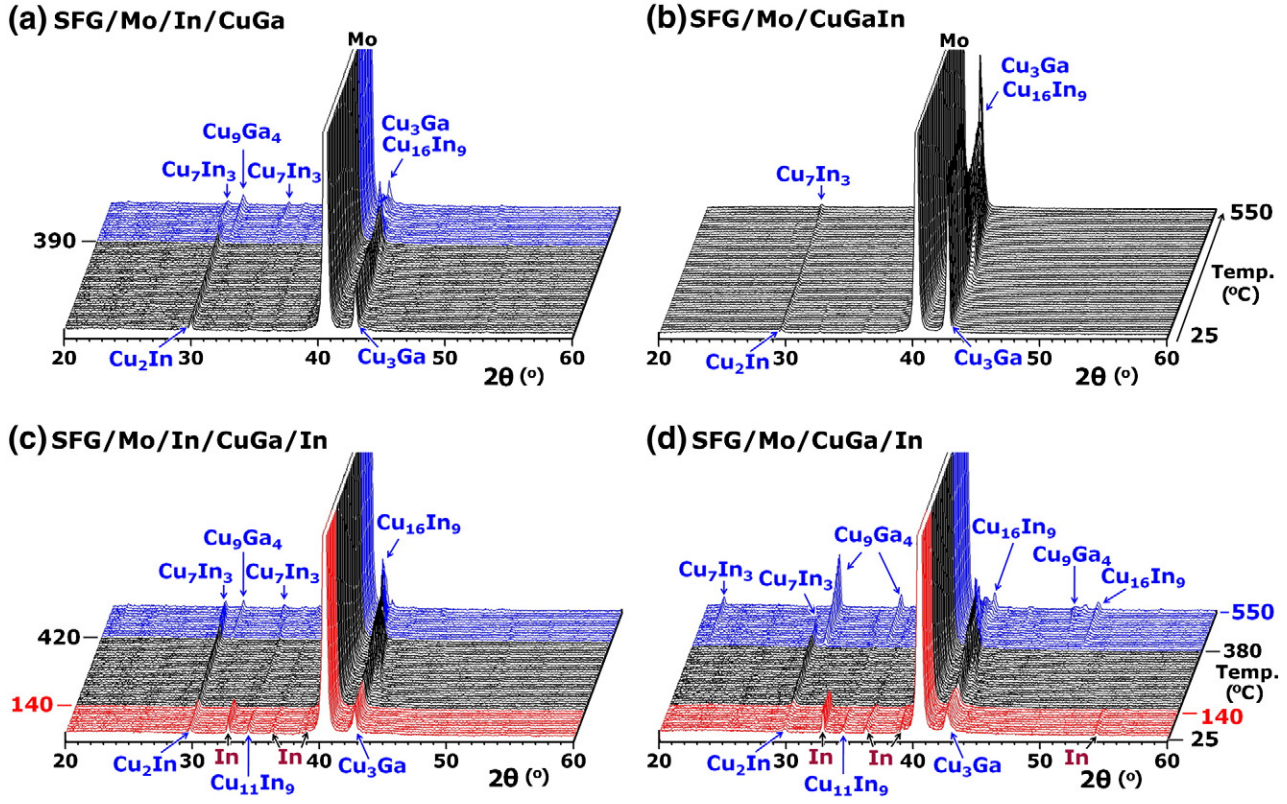

Fig. 1. *In situ* XRD scans during temperature ramp annealing of metal precursors: (a) SFG/Mo/In/CuGa, (b) SFG/Mo/CuGaIn, (c) SFG/Mo/In/CuGa/In, and (d) SFG/Mo/CuGa/In. *ICDD-JCPDF: In (03-065-9292), $Cu_{11}In_9$ (03-065-4963), Cu_7In_3 (03-065-2249), $Cu_{16}In_9$ (00-026-0522), Cu_9Ga_4 (01-071-0458), Cu_3Ga (00-044-1117).