



Phase stability in Ag-Cu-In-Ga metal precursors for (Ag,Cu)(In,Ga)Se₂ thin films



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ABSTRACT

The addition of Ag to Cu-Ga-In precursors for reaction to form (AgCu)(InGa)Se₂ has shown benefits including improved adhesion, greater process tolerance and potential for improved device performance. In this study, metal precursors were sputtered with a Cu-Ga/In/Ag-Ga sequence with Ag/(Cu + Ag) = 0.25 and (Ag + Cu)/(Ga + In) = 0.90. These precursor layers are shown to be unstable, with a phase evolution during storage at room temperature revealed by x-ray diffraction (XRD). This behavior was studied in samples annealed in the temperature range of 60–150 °C or stored for up to 90 days. XRD analyses indicated the formation of (Ag_{1-x}Cu_x)In₂ with Cu content of 28% and 36% for samples annealed at 100 °C and 150 °C, respectively. Energy dispersive x-ray spectroscopy and XRD analyses on selenized samples showed a uniform distribution of Ag and Cu through the films and a Ga accumulation near the back interface. Solar cells fabricated from the selenized films showed improved device performance in V_{OC} and FF as a result of the precursor anneal.

1. Introduction

Alloying silver (Ag) with Cu(InGa)Se₂ (CIGS) to form (AgCu)(InGa)Se₂ (ACIGS) has been investigated as a promising photovoltaic material, because of its lower melting temperature and wider bandgap than CIGS, which potentially leads to improved material properties [1] and superior performance as a wide-bandgap absorber. Co-evaporated films have shown reduced structure disorder [2], larger grain size [3,4] and enhanced device performance [5]. Recently, a 19.9% efficient ACIGS thin film solar cell with V_{OC} = 732 mV, with the absorber deposited by a three-stage co-evaporation process, was reported [6]. The formation of ACIGS films by the reaction of Ag-Cu-Ga-In precursors in H₂Se/H₂S has also been reported [7–9]. A 10 or 32 nm thick Ag layer in the precursor gave a significant improvement in film adhesion that enabled higher temperature reaction and improved device performance [7].

Complete investigation of Ag-containing precursors in the reaction (selenization and sulfization) process requires the development of stable and well-characterized precursors. In this work, Ag-Cu-Ga-In metal precursors have been deposited on Mo-coated soda-lime glasses as Mo/Cu-Ga/In/Ag-Ga stacked layers and were analyzed for changes in structure and phase composition of the (a) as-deposited metal precursor, (b) after room temperature storage in nitrogen and (c) after 60–150 °C anneal in argon. We show that the resulting variations in the phase composition directly affect the properties of selenized films and resulting device characteristics.

2. Experimental procedures

Ag-Cu-Ga-In metal precursors were deposited onto Mo-coated soda-lime glass substrates by DC magnetron sputtering at room temperature using 5 N purity Cu_{0.77}Ga_{0.23}, Ag_{0.77}Ga_{0.23}, and In targets. Samples were deposited with a Mo/Cu-Ga/In/Ag-Ga stacked layer structure, as described previously [8]. Sputtering parameters were determined to give Ag/(Cu + Ag) ≈ 0.25 and (Ag + Cu)/(Ga + In) ≈ 0.90 with an average total thickness ≈ 500 nm. To examine stability, precursors were stored at room temperature in a desiccator with nitrogen atmosphere for up to 90 days. Samples were also annealed in a vacuum oven under continuous Ar flow over a temperature range of 60 °C to 150 °C for 30 min and then cooled down to room temperature slowly in the oven. Annealing and storage conditions are summarized in Table 1. Then, the as-deposited, stored and annealed metal precursors reacted with H₂Se, at atmospheric pressure with 0.35% H₂Se/0.0035% O₂/Ar in a tubular quartz reactor at 450 °C for 50 min [10]. The reactor was first heated to 450 °C in 20 min with continuous 0.0035% O₂/Ar flow, while the metal precursors were kept in the cold zone. Then the H₂Se gas flow was started. After 10 min, samples were pushed into the hot zone using a push/pull rod and held for 50 min. Then the samples were pulled out from the heated zone and cooled down to room temperature in Ar flow.

Composition of the samples was measured by x-ray fluorescence

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Table 1
Storage and annealing conditions of the studied samples with the identified phases for each case.

| Sample | Condition | XRD phases |
|--------|--------------------|--|
| A1 | As-deposited | In; AgIn ₂ ; γ -(Ag,Cu) ₉ (In,Ga) ₄ ; Cu ₃ Ga |
| B1 | Stored 10 days | In; AgIn ₂ ; γ -(Ag,Cu) ₉ (In,Ga) ₄ ; Cu ₃ Ga, (Ag _{1-x} Cu _x)In ₂ , |
| B2 | Stored 50 days | In; AgIn ₂ ; γ -(Ag,Cu) ₉ (In,Ga) ₄ ; Cu ₃ Ga, (Ag _{1-x} Cu _x)In ₂ , |
| B3 | Stored 90 days | In; AgIn ₂ ; γ -(Ag,Cu) ₉ (In,Ga) ₄ ; Cu ₃ Ga, (Ag _{1-x} Cu _x)In ₂ , (Cu,Ag)In ₂ |
| C1 | Annealed at 60 °C | In; AgIn ₂ ; γ -(Ag,Cu) ₉ (In,Ga) ₄ ; Cu ₃ Ga, (Ag _{1-x} Cu _x)In ₂ , η -(Ag,Cu) ₁₆ (In,Ga) ₉ |
| C2 | Annealed at 80 °C | In; AgIn ₂ ; γ -(Ag,Cu) ₉ (In,Ga) ₄ ; Cu ₃ Ga, (Ag _{1-x} Cu _x)In ₂ , η -(Ag,Cu) ₁₆ (In,Ga) ₉ |
| C3 | Annealed at 100 °C | In; AgIn ₂ ; γ -(Ag,Cu) ₉ (In,Ga) ₄ ; Cu ₃ Ga, (Ag _{1-x} Cu _x)In ₂ , η -(Ag,Cu) ₁₆ (In,Ga) ₉ |
| C4 | Annealed at 150 °C | γ -(Ag,Cu) ₉ (In,Ga) ₄ ; Cu ₃ Ga, (Ag _{1-x} Cu _x)In ₂ , η -(Ag,Cu) ₁₆ (In,Ga) ₉ |

(XRF) and energy dispersive x-ray spectroscopy (EDS). XRF analyses were performed using Oxford Instrument X-Strata980. EDS was measured using an Amray model 1810T electron microscope with an Oxford Instruments PentaFET[®] 6900 EDS detector. The XRF measures the entire film thickness while EDS with electron voltage of 20 kV gives a composition value weighted toward the top of the film. The crystal structures of the films were evaluated using symmetric x-ray diffraction (XRD) and glancing incidence XRD (GIXRD) measured using a Rigaku D/Max 2500 with a Cu K α radiation source. Cross-section scanning electron microscope (SEM) images were obtained by a Zeiss Auriga 60 microscope. JADE software (Materials Data, Inc. (MDI) JADE 2010) was used to perform Rietveld refinements using the crystallographic information files (CIF) of AgIn₂ (PDF# 65-1552), In (PDF# 5-0642), Cu₃Ga (PDF# 44-1117), Cu_{1.8}In (PDF# 42-1475) and Cu₉Ga₄ (PDF# 2-1253) phases. Solid solubility of the phases with other elements was excluded from the refinements. All lattice parameters of the crystalline phases and their scale factors were refined. The 2 θ offset of the patterns was refined based on Mo peaks. The March-Dollase model [11] was used to refine the preferred orientation factors of the Mo, AgIn₂/(Ag_{0.72}Cu_{0.28})In₂, and Cu₃Ga phases with $\langle 110 \rangle$, $\langle 110 \rangle$ and $\langle 001 \rangle$ preferred orientation, respectively.

Solar cells were fabricated with a structure of glass/Mo/(Ag,Cu)

Table 2
Lattice parameters (Å) of primary AgIn₂, secondary (Ag_{1-x}Cu_x)In₂ and Cu₉Ga₄ phases, derived from Rietveld analyses.

| Sample | Condition | AgIn ₂ | (Ag _{1-x} Cu _x)In ₂ | Cu ₉ Ga ₄ |
|--------|--------------------|------------------------|---|---------------------------------|
| A1 | As-deposited | a: 6.8752 c: 5.6151 | – | a: 8.6674 |
| B1 | Stored 10 days | a: 6.8724 c: 5.6143 | a: 6.8251 c: 5.5235 | a: 8.7327 |
| B2 | Stored 50 days | a: 6.8664 c: 5.6093 | a: 6.8053 c: 5.5373 | a: 8.7488 |
| B3 | Stored 90 days | a: 6.8689 c: 5.6095 | a: 6.8132 c: 5.5348 | a: 8.7547 |
| C1 | Annealed at 60 °C | a: 6.8681 c: 5.6102 | a: 6.8184 c: 5.5483 | a: 8.7273 |
| C2 | Annealed at 80 °C | a: 6.8671 c: 5.6083 | a: 6.8144 c: 5.5488 | a: 8.7410 |
| C3 | Annealed at 100 °C | a: 6.8536 c: 5.6014 | a: 6.8114 c: 5.5495 | a: 8.7520 |
| C4 | Annealed at 150 °C | – | a: 6.7889 c: 5.5278 | a: 8.7601 |

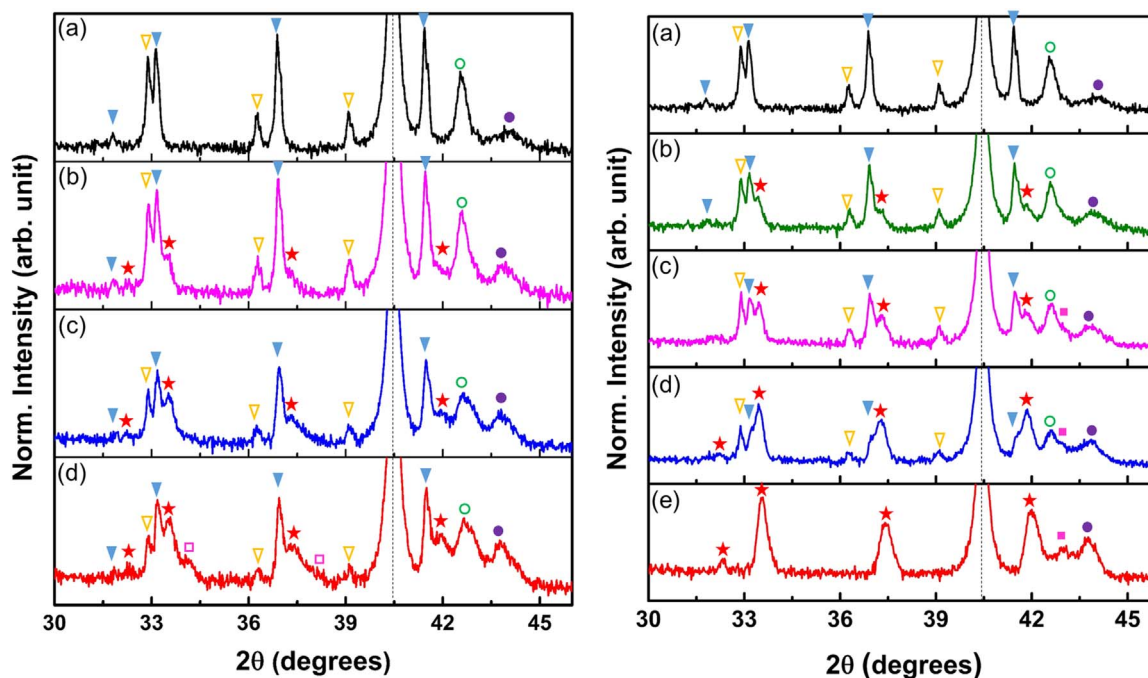


Fig. 1. (left) XRD patterns of precursors (a) as-deposited and stored for (b) 10, (c) 50 and (d) 90 days in N₂ controlled desiccator and (right) (a) as-deposited and annealed at (b) 60 °C, (c) 80 °C, (d) 100 °C and (e) 150 °C. Phases were identified as; \blacktriangledown : AgIn₂, \triangledown : In, \circ : Cu₃Ga, \bullet : γ -(Ag,Cu)₉(In,Ga)₄, \square : (Cu,Ag)In₂, \star : (Ag_{1-x}Cu_x)In₂. The Mo peak is shown by the dashed line. The diffraction data is plotted in a square root scale (y-axis).

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