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Reaction pathway analysis of $(Ag_xCu_{1-x})(In_{0.75}Ga_{0.25})Se_2$ with x = 0.75 and 1.0

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ABSTRACT

Reaction pathways during formation of $Ag(In_{0.75}Ga_{0.25})Se_2$ films were investigated by *ex-situ* characterization of time-progressive reactions using rapid thermal processing at 450 °C under 5% Ar/H_2Se atmosphere. Composition measurements using energy dispersive x-ray spectroscopy (EDS) and X-ray fluorescence (XRF) show that with Ag/(Ag + Cu) = 1.0, Ga grading and Se uptake occur gradually up to 20 min. With 7 min reaction, there was no sign of a $AgInSe_2$ phase and only a $Ag(In,Ga)_5Se_8$ chalcogenide phase formed. The reaction was completed with formation of $Ag(\underline{In},Ga)Se_2$ and $Ag(\underline{In},Ga)_5Se_8$ within 20 min. The addition of Cu to the precursor so that Ag/(Ag + Cu) = 0.75 speeds up the reaction and reduces the formation of the $Ag(\underline{In},Ga)_5Se_8$ phase. EDS and XRF analyses indicated that Ga grading and Se uptake were completed after 10 min. XRD analysis also shows formation of $CuInSe_2$ on the surface of the sample with Cu after 3.5 min reaction prior to other chalcogenide formation. On the other hand, a strong $Ag(\underline{In},Ga)Se_2$ (112) XRD peak appeared after 5 min reaction compared to 10 min reaction for 100% Ag films. EDS and Raman scattering measurements on the back-side of the films after delamination from the substrate indicated that Ga accumulated in $AgGaSe_2$ and Ga-Se phases at the back-side of films after 45 min reaction. XRD analysis showed that Ag tends to stay in the stable ζ-$Ag_3(\underline{In},Ga)$ phase during the reaction with Ag/(Ag + Cu) = 1.0, but not with 0.75, and this causes the longer reaction time and the non-uniformity.

1. Introduction

$Ag(In,Ga)Se_2$ (AIGS) has been studied as a promising material for nonlinear and near IR optical devices and spin-polarized electron sources [1–5]. It also has been recognized as a promising candidate for photovoltaic applications due to its wide bandgap and lower melting temperature compared to well-known $Cu(In,Ga)Se_2$ (CIGS) [6–8]. This wide-bandgap chalcopyrite material with high Ga content can potentially be used as the top cell in tandem solar cells.

AIGS materials have been synthesized with different techniques such as flash evaporation [9,10], non-vacuum solution coating [11] and co-evaporation [12–17]. Here, we investigate reaction pathways during formation of $(Ag_xCu_{1-x})(In_{0.75}Ga_{0.25})Se_2$ films with x = 0.75 and 1.0 using the two-step selenization method and compare them to formation of CIGS. In this process, Ag-Cu-In-Ga precursors were prepared in the first step [18], and then reacted with H_2Se to form the chalcogenide compound. We previously reported formation of $(Cu_{0.75}Ag_{0.25})(In_{0.75}Ga_{0.25})Se_2$ films using a similar process [19]. Ag addition in the precursor gave significant improvement in film adhesion that enabled higher reaction temperature and improved device performance [20].

The primary goal here is to determine reaction pathways during the formation of AIGS using *ex-situ* methods and to quantify the effect of Ag-alloying in the reaction. Knowledge of the growth process during the absorber formation is essential to develop a high quality absorber material and therefore high performance solar cells. This will lead to development of an advanced precursor reaction process with a controlled composition profile.

2. Experimental procedures

Ag-Cu-Ga-In metal precursors were deposited onto Mo/soda-lime glass (SLG) substrates by dc magnetron sputtering at room temperature using $Cu_{0.77}Ga_{0.23}$, $Ag_{0.77}Ga_{0.23}$, and In targets. Samples were deposited with Mo/Ag-Ga/In and Mo/Cu-Ga/In/Ag-Ga stacked layers, as described previously [8]. Sputtering parameters were determined to give Ag/(Cu + Ag) = 0.75, 1.0 and (Ag + Cu)/(Ga + In) ≈ 0.90 with thickness ≈ 500 nm. More information about precursors structure can be found in the Supplementary section (S1).

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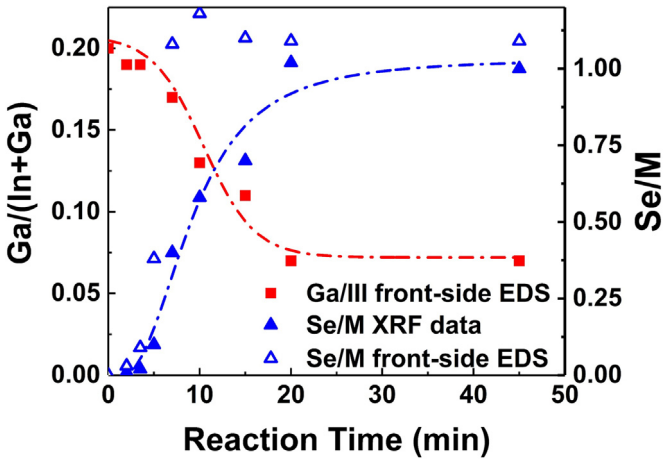
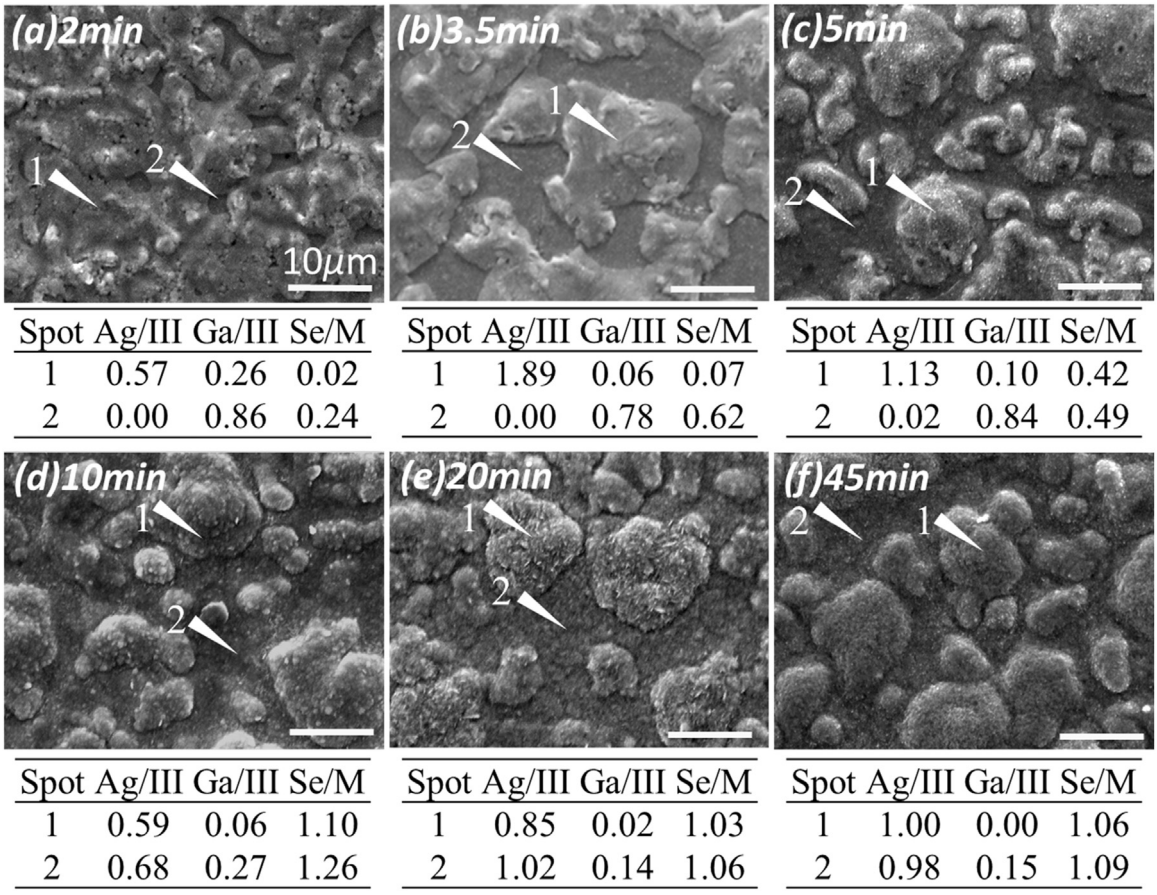


Fig. 1. Se/Metals and Ga/(Ga + In) versus reaction time measured by EDS and XRF for as-deposited and reacted Ag/(Ag + Cu) = 1.0 films. Lines are a guide to the eye.

Selenization was done using rapid thermal processing (RTP) at atmospheric pressure in a tubular quartz reactor [21]. For each run, a precursor was first loaded into the reactor which was then charged with 5% H_2Se in Ar. The reaction temperature was 450 °C and the reaction time varied from 2 to 45 min. The temperature ramp time was set to ~ 1 s. At the end of the reaction, the lamp was turned off and Ar was flown into the tube. The cooling time of the sample surface temperature was ~ 30 s to 250 °C with temperature measured and controlled using a



Spot	Ag/III	Ga/III	Se/M
1	0.57	0.26	0.02
2	0.00	0.86	0.24

Spot	Ag/III	Ga/III	Se/M
1	1.89	0.06	0.07
2	0.00	0.78	0.62

Spot	Ag/III	Ga/III	Se/M
1	1.13	0.10	0.42
2	0.02	0.84	0.49

Spot	Ag/III	Ga/III	Se/M
1	0.59	0.06	1.10
2	0.68	0.27	1.26

Spot	Ag/III	Ga/III	Se/M
1	0.85	0.02	1.03
2	1.02	0.14	1.06

Spot	Ag/III	Ga/III	Se/M
1	1.00	0.00	1.06
2	0.98	0.15	1.09

Fig. 2. Plan-view SEM images and point-EDS analysis of the reacted Ag/(Ag + Cu) = 1.0 films for different reaction times. Point-EDS analysis results are shown under each figure. In the tables, Ag/(In + Ga) and Ga/(In + Ga) were shown by Ag/III and Ga/III, respectively.