

# Investigation of the Microstructure of $\text{Cu}(\text{In,Ga})\text{Se}_2$ Thin Films Used in High- Efficiency Devices

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R. Noufi, Y. Yan, K. Jones, M. Al-Jassim,  
B. Keyes, J. Alleman, and K. Ramanathan  
*National Renewable Energy Laboratory*

J. Abu-Shama  
*Colorado School of Mines, Department of Physics*

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# Investigation of the Microstructure of Cu(In,Ga)Se<sub>2</sub> Thin Films Used in High-Efficiency Devices

Rommel Noufi, Yanfa Yan, Jihad Abu-Shama\*, Kim Jones, Mowafak Al-Jassim, Brian Keyes, Jeff Alleman, and Kannan Ramanathan  
National Renewable Energy Laboratory, Golden, CO 80401  
\*Colorado School of Mines, Dept. of Physics, Golden, Colorado

## ABSTRACT

We examined the microstructure of Cu(In,Ga)Se<sub>2</sub> (CIGS) films, as it transitioned from Cu-rich to In-rich composition, by transmission electron microscopy, and energy-dispersive X-ray spectroscopy. We find that the Cu-rich samples have larger grains than the In-rich samples, and they contain two structurally different forms of the Cu<sub>x</sub>Se secondary phase. These samples also show sub-interfaces about 0.2 μm below the surface. The In-rich samples were almost void of these sub-interfaces.

## INTRODUCTION

In our laboratory, we have demonstrated confirmed efficiency of 18.8% for the ZnO/CdS/CIGS/Mo/glass solar cell. The efficiency of this device can still be improved to greater than 20%. Two areas of improvement may be pursued. The first is optimizing CdS/ZnO properties to enhance short-circuit current; the second is reducing defect density (and hence recombination) in the space-charge region and, more specifically, in the top 0.2 μm of the CIGS absorber. The latter will enhance both the open-circuit voltage ( $V_{oc}$ ) and the short-circuit current density ( $J_{sc}$ ). To achieve the latter, our strategy is to investigate the microstructure evolution during film growth and to

identify the location, density of defects, and mechanisms that create the defects. Based on this study, we hope to develop a fundamental understanding of why this device operates at the current level of performance, and further modify the growth process to greatly minimize defects. In this study, we focus on the second approach because it has a more far-reaching impact.

## EXPERIMENTAL

CIGS thin films were deposited by physical vapor deposition in a multisource bell jar system. A 3-stage growth process is used for this deposition (Fig. 1). In this process, a precursor of (In,Ga)<sub>2</sub>Se<sub>3</sub> is reacted with Cu+Se to produce Cu(In,Ga)Se<sub>2</sub> plus Cu<sub>x</sub>Se as a secondary phase, followed by the addition of In+Ga+Se to adjust the composition to slightly Cu-poor. The film growth is then interrupted at predetermined points along the reaction pathway and the films are analyzed. The thin-film samples used in this study are labeled a through d and are indicated in Fig. 1. These samples represent the transition of the film from Cu-rich to In(Ga)-rich, and hence, the near-surface region that is susceptible to defect formation. The films are characterized using an electron probe for micro-analysis, transmission electron microscopy (TEM), scanning electron microscopy, energy dispersive spectroscopy (EDS).

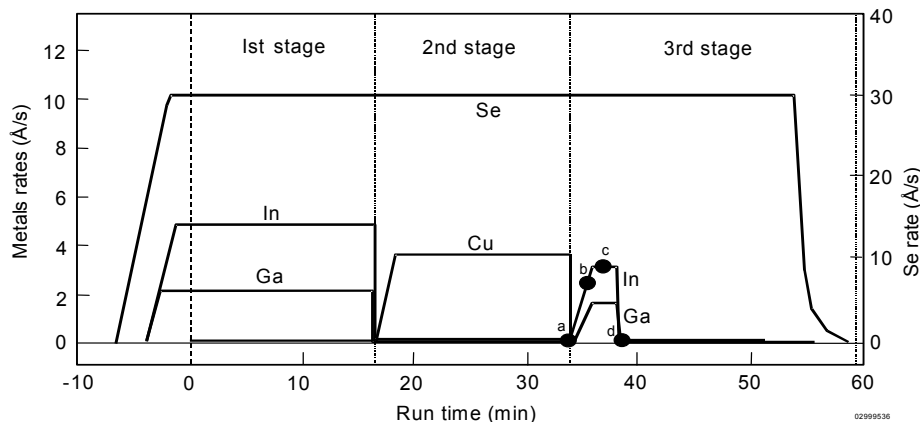
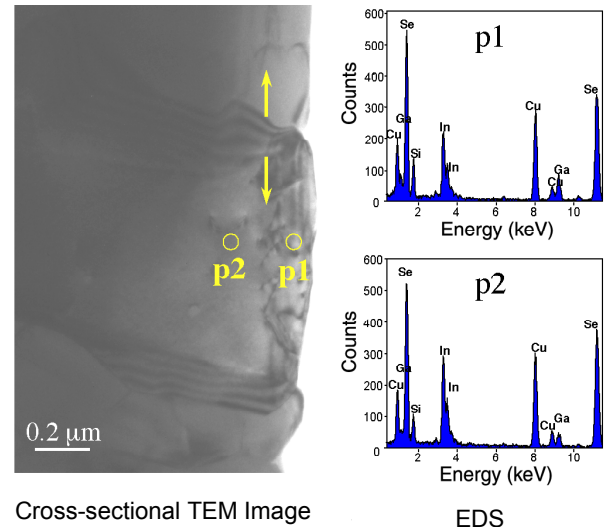


Fig. 1. Schematic Profile of the “3-Stage Process”

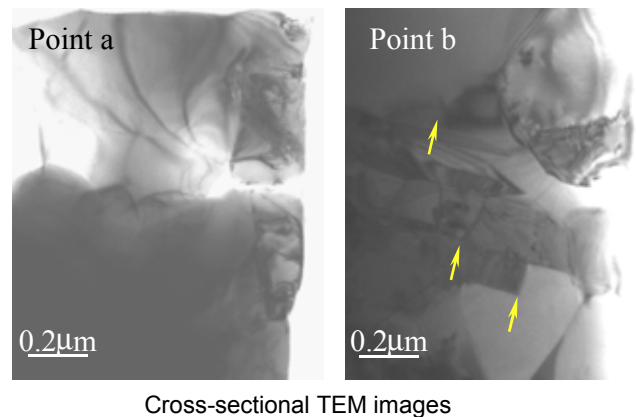
## RESULTS

In these proceedings, we enumerate select discoveries and, where appropriate, show the corresponding results graphically. The limited space precludes citing all the results to date.

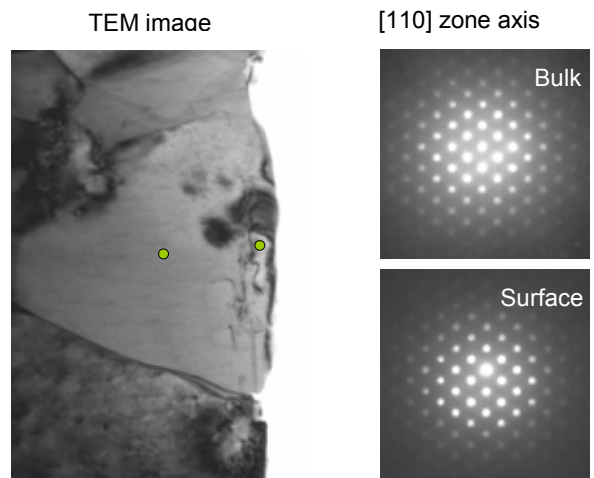
- At the Cu-rich stage (sample **a**), the film contains the  $\alpha$ -CuInSe<sub>2</sub> phase (as the primary phase) and Cu<sub>x</sub>Se as secondary phase. The grains of the two phases are coherent and appear as a large single grain by SEM. As the film transitions to In (Ga)-rich, the large grains appear to decompose into relatively smaller grains (samples **c** and **d**). See Reference 1.
- In the Cu-rich sample, two structurally different Cu<sub>x</sub>Se secondary phases exist with the CIGS major phase. A cubic phase exists on the CIGS crystallites (see Reference 2), and a tetragonal phase exists between the CIGS grains. We believe that the tetragonal Cu<sub>x</sub>Se is the first to form during the second stage of Figure. 1, and serves as the host lattice for In and Ga from the In(Ga)<sub>2</sub>Se<sub>3</sub> in stage one, resulting in the formation of the tetragonal lattice of the Cu(In,Ga)Se<sub>2</sub>. The cubic phase of Cu<sub>2-x</sub>Se forms at the point when Cu becomes in excess of stoichiometry, and nucleates on the already formed Cu(In,Ga)Se<sub>2</sub> crystallites. Figure 2 shows a cross-sectional TEM image of a CIGS grain from sample **a** showing dislocations that exist in the Cu-rich sample, about 0.2 to 0.1  $\mu\text{m}$  below the surface, with the near-surface region being higher in Cu concentration. A plan view TEM (not shown here) shows a planar network of dislocations (see Reference 3) in the film at this point of the growth.
- At the transition point from Cu-rich to In(Ga)-rich, sub-domain boundaries are formed, as indicated by the arrows in Figure 3. These sub-domain boundaries are conformal and coherent and cannot be seen by scanning electron microscopy (see Reference 3). These sub-boundaries are the precursors for grain-boundaries, which materialize when the film becomes In(Ga)-rich, and they also serve as stress (and thus defects) relief mechanism.
- Sample **d** represents the complete growth of the film. Figure 4 shows a cross-sectional TEM image and a selected-area electron diffraction (SAD) of the near surface (50 nm below surface) and the bulk. The CIGS grains contain minimal defects compared to the grains along the growth path (samples **a** and **b**), and for the first time, we show direct evidence that the surface region and the bulk are structurally similar and their composition is slightly different. Hence, we propose that the surface does not contain the ordered defect chalcopyrite (ODC). This conclusion is supported by the fact that SAD from the surface of sample **d** and that from bulk ODC material are different (see Reference 4).



**Fig. 2. Sub-interface in Surface Region of CIGS: Dislocations (Point a)**



**Fig. 3. Structural Changes in CIGS Film: Point a vs. Point b**



**Fig. 4. SAD of Surface and Bulk Showing Identical Structure**

## SUMMARY

The above results represent partial discoveries regarding the growth mechanisms of Cu(In,Ga)Se<sub>2</sub> using the "3-stage" process. These discoveries shed light on the grain growth, the point at which extended defects are formed, and then relieved. In an upcoming manuscript, we will describe in more detail the growth process illustrated by a mechanistic model.

## ACKNOWLEDGEMENTS

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