



UNITED STATES DEPARTMENT OF ENERGY  
UNIVERSITY CENTER OF EXCELLENCE  
FOR PHOTOVOLTAIC RESEARCH AND EDUCATION

February 21, 2007

Bolko von Roedern  
National Renewable Energy Laboratory  
1617 Cole Boulevard  
Golden, CO 80401

Re: NREL Subcontract #ADJ-1-30630-12  
D.5.10

Dear Bolko,

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period of November 16, 2006 to December 15, 2006, under the subject subcontract. The report highlights progress and results obtained under Task 2 (CIS-based solar cells).

## **TASK 2: CuInSe<sub>2</sub>-BASED SOLAR CELLS**

### **Cu(InGa)(SeS)<sub>2</sub> Formation by H<sub>2</sub>Se/H<sub>2</sub>S Reaction**

Previously, we showed that a heat treatment (HT) of the Cu<sub>0.8</sub>Ga<sub>0.2</sub>/In precursor films prior to H<sub>2</sub>Se/H<sub>2</sub>S reaction improved the uniformity of the reacted films. Characterization of the effect of the HT at 250°C in flowing H<sub>2</sub>(4%)/Ar for 1 hour has been completed. SEM micrographs are shown in Figure 1 and compositional measurements on the nodules and on the smooth background are summarized in Table I. The as-sputtered film contains In nodules on a smooth Cu-Ga background. After the HT, the morphology does not change, but the composition has inverted, and the nodules are Cu-Ga rich.

XRD measurements of the precursors show that after the HT, they contain a single intermetallic phase identified as Cu<sub>9</sub>(In<sub>0.64</sub>Ga<sub>0.36</sub>)<sub>4</sub> along with elemental In. These results are the same as those previously reported for Cu<sub>0.8</sub>Ga<sub>0.2</sub>/In precursor films heat treated at 450°C [1].

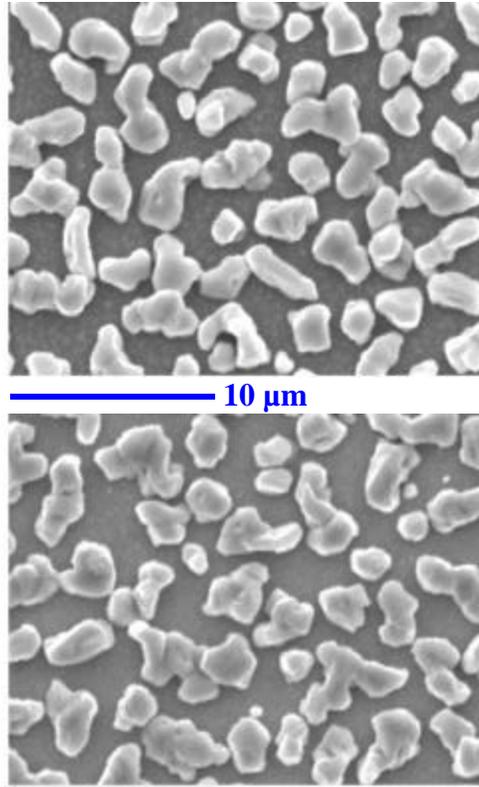


Figure 1.  $\text{Cu}_{0.8}\text{Ga}_{0.2}/\text{In}$  precursor: (top) as-sputtered, and (bottom) after heat treatment at  $250^\circ\text{C}$  for 1 hour in  $\text{AR}/\text{H}_2(4\%)$ .

Table I. Compositions of nodules and background surface on as-sputtered and heat treated precursor films.

Sample	Region	Cu	Ga	Mo	In
As-sputtered	nodule	5.3	1.7	0.3	92.7
	surface	60.2	16.8	12.8	10.2
Heat treated	nodule	57.1	14.3	0.2	28.4
	surface	7.8	2.7	26.1	63.5

Even with the heat treated precursors to provide a uniform and reproducible film state for reactions, spatial uniformity and reproducibility remain as ongoing concerns. To provide more uniform heating, the heating mantle around the quartz reaction tube was replaced and temperature calibration of the reaction zone completed.

## Fundamental Materials and Interface Characterization

*Cu(InGa)Se<sub>2</sub>/Mo Back Contact*

We have previously investigated the formation of  $\text{Mo}(\text{Se}_{1-x}\text{S}_x)_2$  layers on the surface of Mo films reacted in  $\text{H}_2\text{Se}$ ,  $\text{H}_2\text{S}$ , or a mixture of the two hydride gases and found that films reacted in the mixture formed a surface layer of only  $\text{MoSe}_2$ . In this report, we characterize the formation of  $\text{Mo}(\text{Se}_{1-x}\text{S}_x)_2$  at the interface between Mo and evaporated  $\text{Cu}(\text{InGa})(\text{SeS})_2$  using XPS and GIXRD measurements.

Four evaporated films were included in this study;  $\text{CuInSe}_2$ ,  $\text{CuInS}_2$ , and  $\text{CuIn}(\text{SeS})_2$  with 2 different relative  $[\text{S}]/[\text{Se}+\text{S}]$  ratios. Their compositions are listed in Table II. All films were deposited on soda lime glass substrates with a  $0.7 \mu\text{m}$  thick sputtered Mo contact.

$\text{Cu}(\text{InGa})(\text{SeS})_2$  films were deposited by elemental evaporation with uniform fluxes throughout the deposition at substrate temperature  $550^\circ\text{C}$ . The  $\text{Mo}/\text{CuIn}(\text{SeS})_2$  interface was exposed for direct characterization by peeling the  $\text{Cu}(\text{InGa})(\text{SeS})_2$  film from the substrate. This cleanly separates at the interface, leaving only  $\text{CuIn}(\text{SeS})_2$  on one side and reacted Mo on the other.

Table II. Compositions of  $\text{CuIn}(\text{SeS})_2$  films used for characterization of  $\text{Mo}(\text{Se}_{1-x}\text{S}_x)_2$  formation.

Type of Film	[Cu]/ [In+Ga]	[S]/ [Se+S]	Cu (at. %)	In (at. %)	S (at. %)	Se (at. %)
$\text{CuInSe}_2$	0.94	0	24.2	25.7	0.0	50.1
$\text{CuIn}(\text{S}_y\text{Se}_{1-y})_2$	0.82	0.24	21.8	26.6	12.0	39.6
$\text{CuIn}(\text{S}_y\text{Se}_{1-y})_2$	0.88	0.54	23.5	26.7	26.9	22.9
$\text{CuInS}_2$	0.96	1	25.2	26.1	48.4	0.3

Surface compositions measured by XPS on the reacted Mo are summarized in Table III. A typical XPS survey spectrum is shown in Figure 2. The surface always contains significant concentrations of C and O. To determine whether this is effected by exposure of the surface to air in the laboratory, an apparatus was added to the XPS system to enable an in-situ peel. Two films from the same run are compared in Table III and have nearly the same surface compositions. The interface layer for the  $\text{CuIn}(\text{SeS})_2$  samples both contained much more S than Se, indicating a preference for the reaction of Mo with S in this process. This is consistent with the equilibrium thermodynamics which show a more negative heat of formation for the reaction to form  $\text{MoS}_2$  relative to formation of  $\text{MoSe}_2$ . In addition to the elements listed in Table III, there was  $\sim 2\%$  In but no Cu in any film, and  $\sim 1\%$  Na for the in-situ peeled  $\text{CuInSe}_2$ .

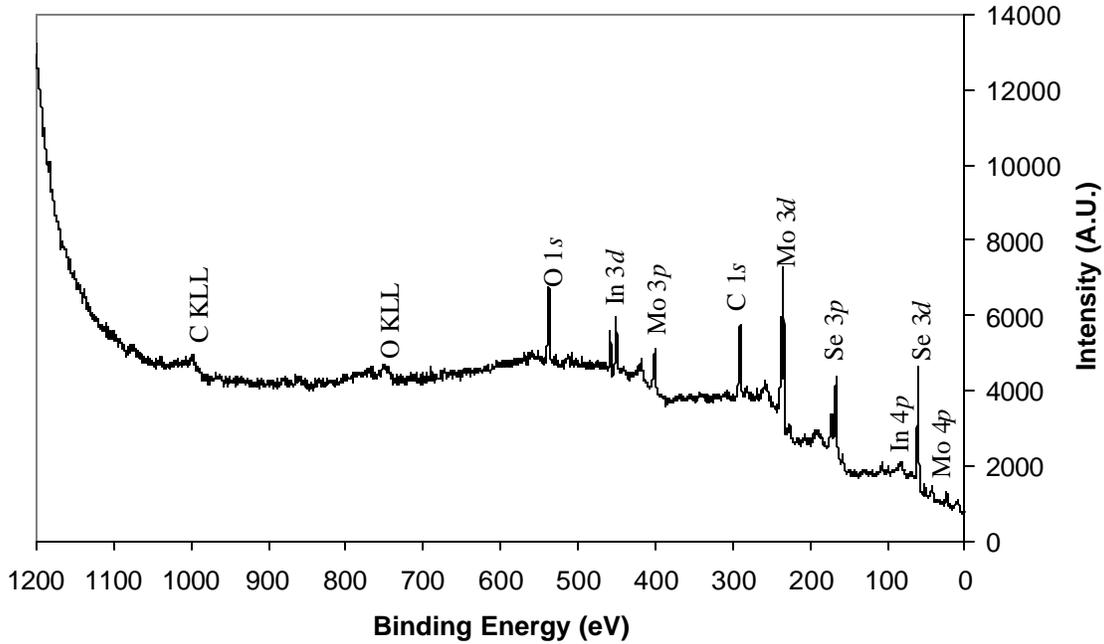


Figure 2. XPS survey scan of the Mo surface after the CuInSe<sub>2</sub> film was peeled off.

Table III. Summary of XPS atomic percentages for peeled Mo substrates exposed by peeling the CuIn(SeS)<sub>2</sub> films.

Type of Film	[S]/ [Se+S]	C (%)	O (%)	Mo (%)	S (%)	Se (%)
CuInSe <sub>2</sub>	0	41	19	12	0	25
CuInSe <sub>2</sub> in-situ peel	0	42	14	13	0	28
CuIn(S <sub>y</sub> Se <sub>1-y</sub> ) <sub>2</sub>	0.24	31	22	15	28	4
CuIn(S <sub>y</sub> Se <sub>1-y</sub> ) <sub>2</sub>	0.54	39	39	10	10	1
CuInS <sub>2</sub>	1	37	24	15	24	0

The interface layer was also characterized by glancing incidence XRD. In each case, the spectra only showed peaks from the Mo, the (002) reflection of the Mo(Se<sub>1-x</sub>S<sub>x</sub>)<sub>2</sub> and, in some cases, a small signal from residual CuInSe<sub>2</sub>. The Mo(Se<sub>1-x</sub>S<sub>x</sub>)<sub>2</sub> peaks are shown in Figure 3. The peak positions for the CuInS<sub>2</sub> and CuIn(SeS)<sub>2</sub> cases are similar and shifted from the CuInSe<sub>2</sub> peak position. However, the peaks are broadened sufficiently that precise peak positions cannot be used to calculate d-spacings and determine compositions. The GIXRD spectra were measured at 0.7° and 1° incident angles and in each case, there is no difference. This indicates that the Mo(Se<sub>1-x</sub>S<sub>x</sub>)<sub>2</sub> films are less than 150 – 200 nm thick, based on the XRD sampling depth at 0.7°.

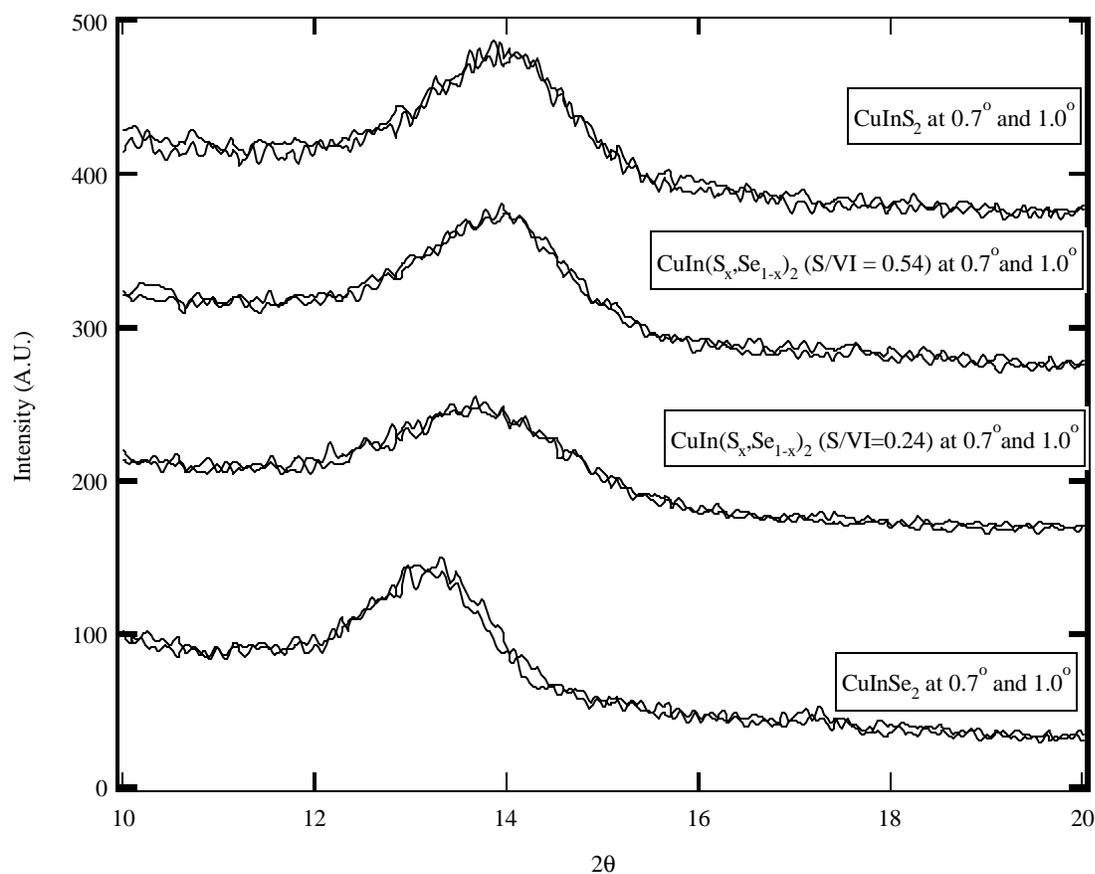


Figure 3. GIXRD spectra for the  $\text{Mo}(\text{Se}_{1-x}\text{S}_x)_2$  (002) peaks on the peeled Mo substrates.

## Collaborations

University of Oregon IEC and Oregon continue to collaborate closely to characterize opto-electronic properties of solar cells with  $\text{Cu}(\text{InGa})\text{Se}_2$  as a function of absorber alloy composition, sodium incorporation, and other processing conditions, with IEC providing sample sets with different compositions or substrates for analysis.

University of Toledo IEC provided  $\text{Cu}(\text{InGa})\text{Se}_2$  device samples for piezoelectric measurements.

Case Western Reserve University IEC provided  $\text{Cu}(\text{InGa})\text{Se}_2$  samples with different compositions and deposited on different substrates for TEM analysis.

Purdue University IEC has reacted novel precursor films in  $\text{H}_2\text{Se}$  to help Purdue's effort to develop alternative processes for  $\text{Cu}(\text{InGa})\text{Se}_2$  formation.

Ascent Solar, DayStar, Miasolé, Nanosolar, SoloPower, Solyndra

IEC has leveraged its expertise, baseline processes, and characterization facilities to assist these companies by, for example:

- reacting precursor films to form  $\text{Cu(InGa)(SeS)}_2$  and characterizing the resulting materials.
- fabricating cells to validate their cell fabrication processes.
- analysis of materials and devices supplied by the companies.
- supplying films or devices for comparison to their materials or calibration of their measurements.

**Reference:**

1. G. Hanket, W. Shafarman, R. Birkmire, Proc. WCPEC-4, 560 (2006).

Best regards,



Robert W. Birkmire  
Director

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RWB/eak

Cc: Paula Newton, IEC  
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