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

August 8, 2008

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

Re: NREL Subcontract #ADJ-1-30630-12
D.5.33

Dear Bolko,

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period of February 1, 2008 to February 29, 2008, under the subject subcontract. The report highlights progress and results obtained under Task 2 (CIS-based solar cells).

Task 2 – CIS-based solar cells

Composition Control for Increased V_{OC}

In this task we are investigating processes to increase V_{OC} in $Cu(InGa)(SeS)_2$ solar cells using absorber layers formed by the reaction of precursors in H_2Se / H_2S which is typically low due to accumulation of Ga at the back of the reacted film. A two-step reaction of Cu-Ga-In precursors with partial reaction in H_2Se at 400° – 450°C followed by completion in H_2S at 550°C has been used to form $Cu(InGa)(SeS)_2$ films with uniform incorporation of the Ga.[1] To provide a basis for improvements in device performance, efforts are being undertaken to improve the IEC H_2Se/H_2S baseline process to improve reproducibility. Current studies into the effect of sulfization temperature on Ga homogenization have yielded several possible approaches to improve process reproducibility.

$Cu_{0.8}Ga_{0.2}$/In precursor bi-layers were selenized at 450ºC for 15 minutes, followed by sulfization at temperatures ranging from 450° – 550ºC for 30 minutes. Two samples were processed side-by-side for each run in an "upstream" and "downstream" orientation. Samples were characterized by SEM/EDS, XRD, and AES depth profiling.

Figure 1 shows Ga/(Ga+In) ratios measured by EDS for sulfization temperatures over the range 450° – 550ºC. Since EDS is sensitive to the top 0.5 – 1 µm of the 2 µm film, it is useful for characterizing the degree of Ga homogenization in a sample. If the Ga/(Ga+In) ratio measured by EDS is equivalent to the known ratio based on precursor sputter thicknesses, it can be

reasonably concluded that a uniform Ga profile exists in the sample. Figure 1 shows that a sulfization temperature of ~500ºC is necessary, but not sufficient, to achieve a uniform Ga profile.

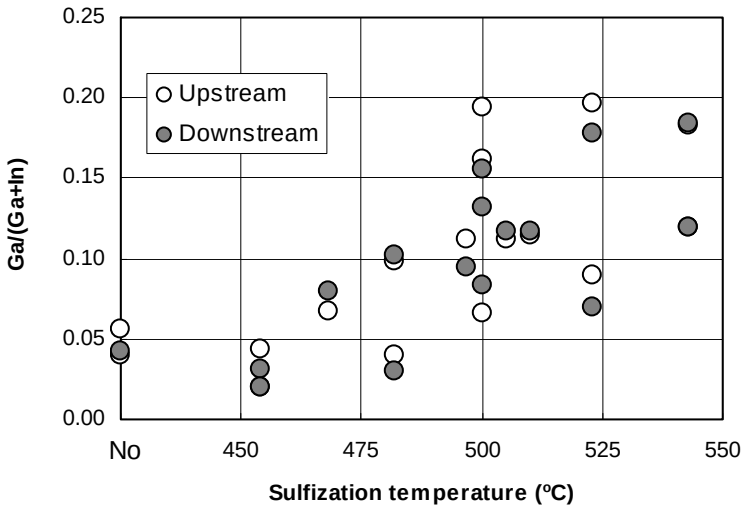


Figure 1. Ga/(Ga+In) ratio in H_2Se/H_2S-reacted precursor films measured by EDS over a range of sulfization temperatures.

Figure 2 shows (112) d-spacings of the same samples, and indicates an abrupt decrease in d-spacing, indicating a higher degree of either Ga or S incorporation into the chalcopyrite lattice, at temperatures of 500ºC and above. As with the EDS data, there is a wide range of d-spacings observed at temperatures above 500ºC. However, there is an additional result of interest in that upstream and downstream samples processed side-by-side at temperatures between 500° – 510ºC repeatedly exhibit d-spacings on either side of the apparent "gap" between ~3.318 Å and ~3.301 Å. This suggests a high sensitivity to process conditions in this temperature range.

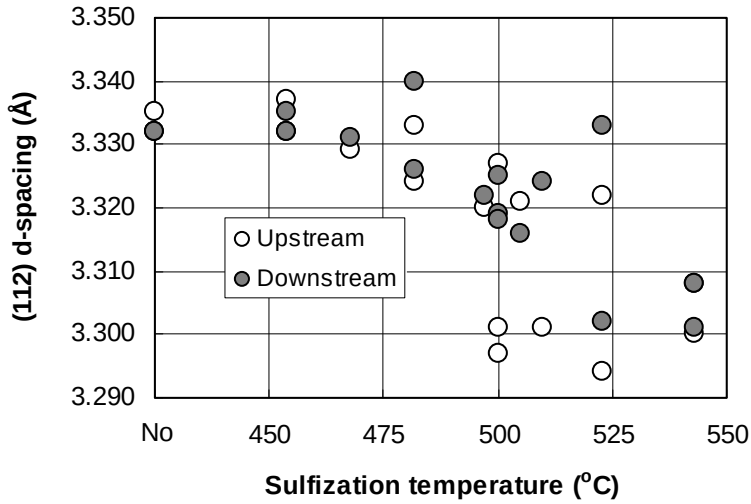


Figure 2. Chalcopyrite (112) d-spacing for H_2Se/H_2S-reacted samples over a range of sulfization temperatures.

The samples in Figure 1 exhibiting Ga/(Ga+In) < 0.12 at sulfization temperatures exceeding 520ºC, and the samples in Figure 2 exhibiting d > 3.320 in the same temperature range suggest that there are variables in the existing baseline H_2Se/H_2S process that are not fully understood. It is already known that the degree of selenization influences the degree of Ga homogenization that occurs during sulfization.[1,2] It is further known that thermal characteristic times in the existing chalcogenization system are on the order of minutes.[3] Therefore, the samples are heating up for a substantial fraction of the 15-minute reaction time. It is therefore suggested that the baseline H_2Se/H_2S process be modified to utilize a reduced selenization temperature. This will slow down the reaction rate, allowing longer selenization times of which thermal transients represent a much smaller fraction of the reaction time. It is expected that this will result in more reproducible degrees of selenization.

Based on the high degree of (112) d-spacing sensitivity during sulfization at temperatures in the range 500° – 510ºC, it is contemplated that the Ga homogenization and sulfization mechanisms may be in competition with one another. It can be inferred that Ga is substantially immobile once is has been incorporated in the chalcopyrite lattice – this is based on the reduced Ga homogenization as degree of selenization increases. As sulfur reacts with Ga-bearing intermetallics, it is driving its incorporation into the chalcopyrite lattice, reducing its mobility. Thus, the homogenization of Ga may be dependent on both temperature and S concentration. A second suggestion for improving the baseline H_2Se/H_2S process is to incorporate an inert anneal at temperatures between 500° – 550ºC before the introduction of sulfur. This also suggests the possibility of reduced Ga homogenization with increased H_2S concentration. This approach has the further benefit making a fundamental determination of whether temperature or sulfur is the driving force for Ga homogenization. It should be noted that Marudachalam found that Ga could be homogenized in fully selenized films by an inert anneal at temperatures above 500ºC.[4]

A second approach to increase V_{OC} using films formed by the reaction of precursors is to control the relative through-film Ga composition by circumventing the formation of Cu-Ga-In

intermetallic phases using mixed metal/metal-selenide precursors. Formation of a relatively stable Cu_9Ga_4 phase was identified as a cause of the Ga segregation to the back of the film.[5]

In a previous report, copper selenide was prepared by electrochemical deposition onto Mo-coated soda-lime glass substrates and annealing to form either $Cu_{2-x}Se$ or CuSe phases. Reaction in H_2Se gave $Cu(InGa)Se_2$ films that maintained a through-film Ga gradient even though no intermetallic phases were detected by XRD after short reaction times. In this report we show results with two additional precursor combinations. The first was formed by co-evaporation of Cu and Se with a substrate temperature of 520ºC followed by Ga and In layers deposited by electron-beam evaporation. The second was a $(In,Ga)_2Se_3$/Cu precursor formed with Ga and In layers sequentially deposited onto the substrate by e-beam evaporation and selenized for 60 minutes at 350ºC at atmospheric pressure followed by an e-beam evaporated Cu layer. As a control, $Cu_{0.8}Ga_{0.2}$/In precursors with a composition of Cu/(In+Ga) = 0.9 and Ga/(In+Ga) = 0.2 were prepared by sequential sputtering. All precursor types had Cu/(In+Ga) = 0.9 and Ga/(In+Ga) = 0.2 with thicknesses determined to yield 2 µm $Cu(InGa)Se_2$ films. The precursors were selenized for 5, 15 or 90 min (only 15 or 90 min for the $(In,Ga)_2Se_3$/Cu precursor) at 450ºC at atmospheric pressure in a quartz tube reactor using a 0.35at% H_2Se/0.0035at% O_2/Ar gas mixture.

XRD measurements were used to confirm the selenide phases in the as-deposited precursors and after the H_2Se reactions. The latter results are listed in Table I. With the precursors containing the selenide phases there were no intermetallic phases observed, unlike with the $Cu_{0.8}Ga_{0.2}$/Ga control.

Table I. Phases identified by XRD with different precursors.

Precursor structure	reaction time (min)	Identified phases
$Cu_{2-x}Se$/Ga/In	5	$Cu_{2-x}Se$, InSe, In_6Se_7
	15	$Cu(InGa)Se_2$
	90	$Cu(InGa)Se_2$
$Cu_{2-x}Se$/Ga/In	5	N/A
	15	InSe, GaSe, $Cu(InGa)Se_2$
	90	$Cu(InGa)Se_2$, $MoSe_2$
$Cu_{0.8}Ga_{0.2}$/In (control)	5	InSe, $Cu(InGa)Se_2$, Cu_3Ga, $\gamma 1$-$Cu_9(In,Ga)_4$
	15	$Cu(InGa)Se_2$, $\gamma 1$-$Cu_9(In,Ga)_4$
	90	$Cu(InGa)Se_2$, $MoSe_2$

Compositions were determined measured by EDS from the top and backside of the films using a film lift-off technique for the latter measurements. The [Ga]/[In+Ga] ratios after different selenization times are shown in Figures 3 and 4 for the two different mixed metal/metal-selenide precursors. Both cases showed Ga accumulation at the back of the $Cu(InGa)Se_2$ film, although the Ga gradient may be smaller with the $(In,Ga)_2Se_3$/Cu precursor.

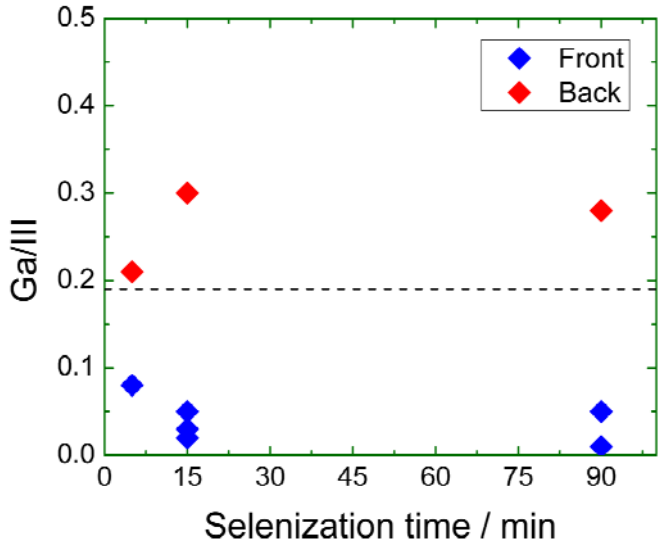


Figure 3. [Ga]/[In+Ga] ratios measured by EDS from the top and back sides of $Cu_{2-x}Se$/Ga/In precursor films selenized for different times. The dashed line shows [Ga]/[In+Ga] in precursor.

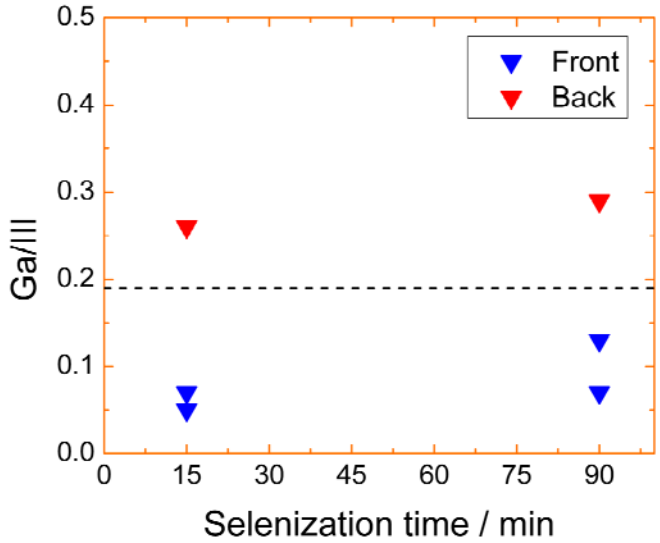


Figure 4. [Ga]/[In+Ga] ratios measured by EDS from the top and back sides of $(In,Ga)_2Se_3$/Cu precursor films selenized for different times. The dashed line shows [Ga]/[In+Ga] in precursor.

Device results of the solar cells made from the precursors following 90 min selenization reactions are shown in Table II. No increase in V_{OC} was obtained with either of the mixed metal/metal-selenide precursors compared to the sputtered metal precursor.

Table II. Device J-V parameters of the solar cells made from the selenized precursors.

Precursor	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	η (%)
$Cu_{2-x}Se/Ga/In$	0.439	37.2	62.4	10.2
$(In,Ga)_2Se_3/Cu$	0.332	32.9	38.1	4.2
control	0.474	36.8	50.5	8.8

In-Line Evaporation

Na Incorporation:

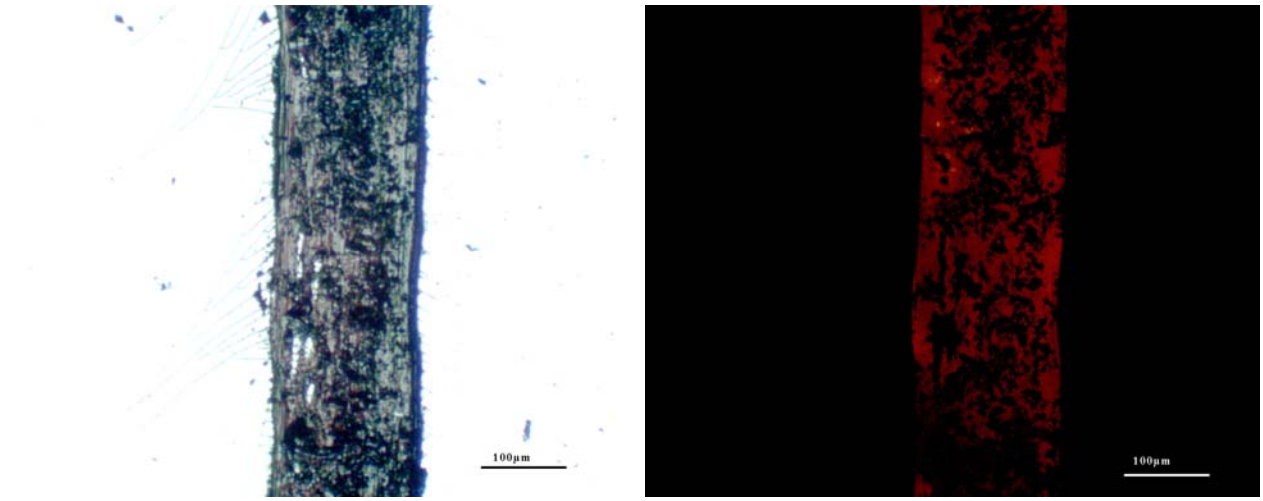
A NaF effusion source identical to other sources in the system was placed such that it would be 1st source in the direction of travel during the 2nd pass. The shield that forms the deposition zone partially covers effusion from the Na source. The initial Na source temperature was chosen to give an approximate effusion rate of 0.1% that of Cu. Since the sources are geometrically identical this temperature would correspond to NaF vapor pressure equal to 10^{-3} of the vapor pressure of Cu for the standard operating condition. For the Cu source temperature operating at 1400°C this gives a NaF source temperature of 685°C.

Two sets of experiments were performed at the Na source temperature of 685°C. Initially, NaF was turned on during the 1st pass where it was the last source seen by the substrate carrier traveling at 18”/min. Devices made on Upilex substrates did not show any improvements in V_{OC} or FF relative to our baseline. This could be the consequence of high speed substrate travel and low source temperature both of which tend to reduce NaF deposited on the substrate. As a result, a second set of runs were performed keeping the NaF source at the same temperature but moving the evaporation to the 2nd pass when substrate NaF is the 1st source and substrate travel is only 2”/min. Even under these conditions no effect was observed on the devices fabricated on Upilex substrates. The next set of experiments will follow the same protocol except for the NaF temperature which will be increased to give a vapor pressure of $5x10^{-3}$ that of Cu.

Monolithically Integrated Flexible Modules:

Scribing tests for monolithic integration by mechanical and laser scribing have been started. Initial attempts in mechanically scribing the molybdenum (Mo) layer (P1 scribe) with a programmable x-y mechanical scribing system resulted in tearing of the Upilex. Double stick tape was then used to secure the Upilex giving much improved results. However, the resulting scribe showed only partial removal of the Mo layer as can be seen in Figure 5 where the optical microscopy image of the mechanical scribe is shown both in reflection and in transmission. Note that even though the back side of the Upilex substrate is coated with 20 nm of Mo it does let enough light go through to have adequate observation in transmission.

In the case of scribing the $Cu(InGa)Se_2$ layer (P2 scribe) it was found that even the lightest pressure between the scribe tip and the sample would always remove the Mo from the Upilex. This was in contrast to the films on glass substrates where the P2 scribe left Mo film intact. As a result, the decision was made to test laser scribing for both P1 and P2 scribes.



A B

Figure 5. Optical microscope image of mechanically scribed Mo on Upilex viewed in reflection (A) and transmission (B).

Initial tests were made with the laser parameters that were successfully used for glass substrates. Figure 6 is the optical micrograph of the P1 scribe performed with the 532 nm laser. In this case, the Mo films were removed completely but there is substantial thermal modification to the Upilex at the center of the scribe.

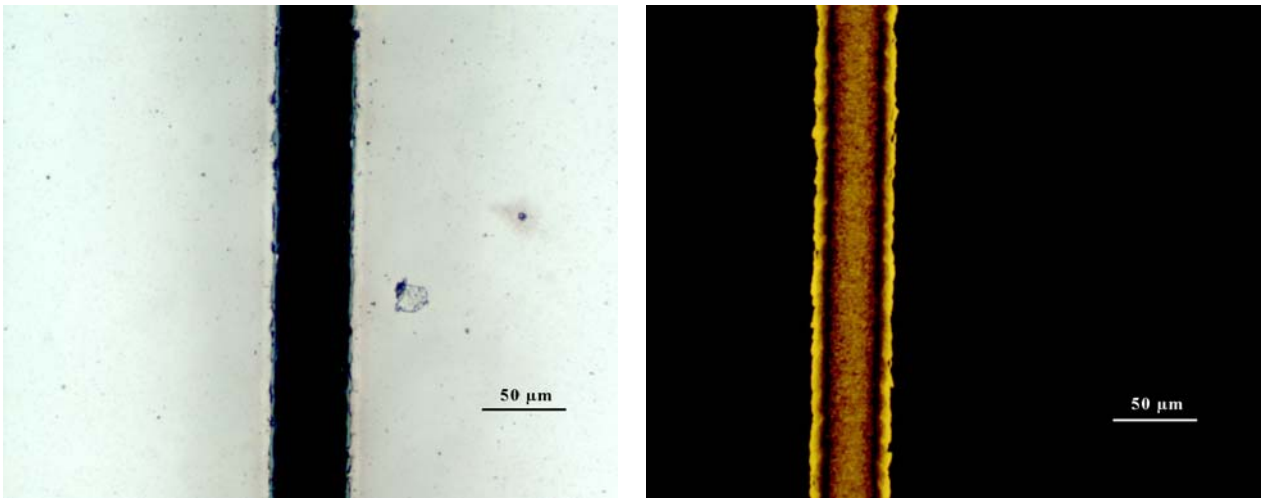


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Figure 6. Optical microscope image of laser scribed Mo on Upilex viewed in reflection (A) and transmission (B).

The P2 scribe on the films on Upilex is shown in Figure 7. The scribe was again made using the 532 nm laser based on the experience from the glass substrates. The micrographs are clear showing that the cut not only removes $Cu(InGa)Se_2$ but also the Mo layer and part of the Upilex substrate. From these tests it is clearly evident that much less aggressive laser scribing needs to be investigated.

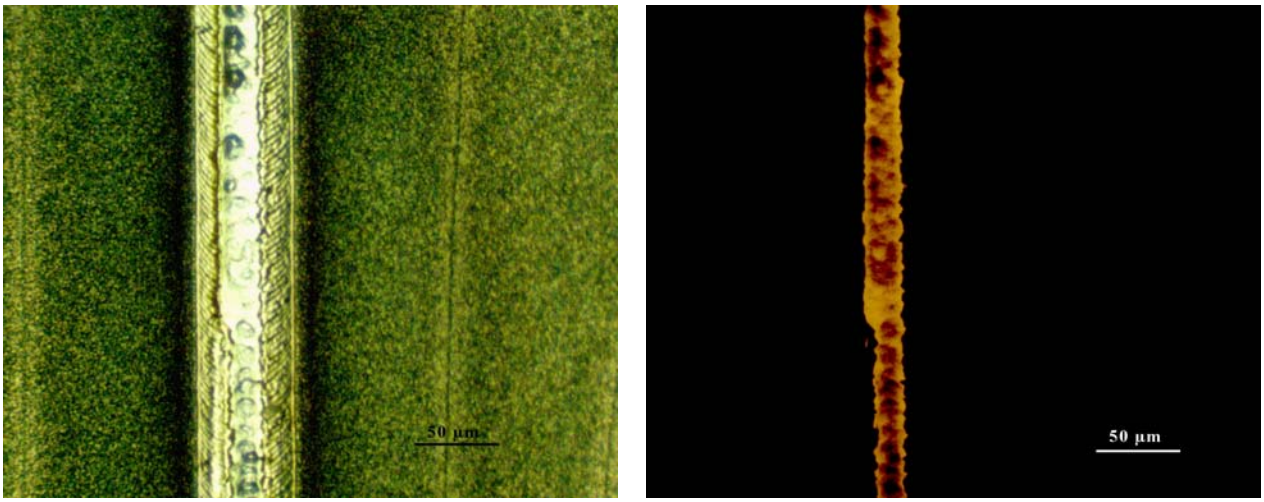

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Figure 7. Optical microscope image of laser scribed $Cu(InGa)Se_2$ on Mo coated Upilex viewed in reflection (A) and transmission (B).

Best regards,

Robert W. Birkmire
Director

References:

[1] V. Alberts, J. Titus, and R. W. Birkmire, *Thin Solid Films* **451-452**, 2004, pp. 207-211.
[2] G. M. Hanket, W. N. Shafarman, and R. W. Birkmire, *Proc. 2006 IEEE 4th WCPEC*, 2006, pp. 560-563.
[3] S. Verma, Ph.D. thesis, University of Delaware, 1993.
[4] M. Marudachalam, et al., *J. Appl. Phys.* **82**(6), 1997, pp. 2896-2905.
[5] G. M. Hanket, W. N. Shafarman, B. E. McCandless, and R. W. Birkmire, *J. Appl. Phys.* **102**(7), 2007, p. 074922.