

## **Thrust Area 4: Solar (Low Cost PV Manufacturing)**

### ***Solar Photovoltaic Manufacturing Facility to Enable a Significant Manufacturing Enterprise within the State and Provide Clean Renewable Energy***

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**Description:** The primary goal of this project is to enable the establishment and success of local solar photovoltaic manufacturing companies to produce clean energy products for use within the state and beyond and to generate jobs and the skilled workforce needed for them. Thin film technologies have shown record efficiencies of 20%, and present tremendous opportunities for new Florida start-up companies. USF, UCF, and UF are collaborating to develop a pilot line facility for thin film solar technologies, which will serve as a test bed for making ongoing improvements in productivity and performance of solar modules, develop advanced manufacturing protocols, and help train a skilled workforce to ensure the success of new companies.

**Budget:** \$1.6M

**Universities:** USF, UCF, UF

**External Collaborators:** Mustang Solar, a Division of Mustang Vacuum Systems

## **Progress Summary**

During the reporting period we continued progress in both thrust areas of the project. Development of the thin Film Pilot line is awaiting completion and delivery of the deposition system. The components are being assembled at Mustang Solar, and delivery is expected by June 1. Meanwhile we have been conducting extensive laboratory experiments as part of our preparations for the pilot line. These experiments address both near-term and long term issues. Since the line will be processing CIGS technology, main emphasis is in that direction.

We are using our 25 year processing experience with CIGS to develop new pathways for processing. These pathways are a compromise between those that produce the best laboratory cells and those that are necessary for commercial success. The process that we are developing is termed 2SSS, “2 Step Solid State” processing. The advantages are that the process uses solid Se as the Se source instead of the highly poisonous gas  $H_2Se$ , and simultaneous control of multiple deposition sources is relaxed. Our primary focus initially is in controlling the material composition with the new process. A particular concern from a manufacturing perspective is the effective utilization of source materials. We discovered an interrelationship between the selenization of the metal layers and the loss of Ga. This issue was observed in applying the 2SSS process to the first step of the two step process that we are developing. In this step we form a Cu-rich CuGaSe layer which provides a larger grain platform for growth of the second step layer containing all four elements. For the simplified 2SSS process we found that in order to achieve full selenization Ga was being lost from the precursor layer. This led to development of a modified 2SSS process that overcame this difficulty. Through further development of the process we demonstrated that the film composition using this process is the same as that produced by the highly controlled co-deposition process that produces 20% cells. This new approach is now being utilized in both steps of the 2 step process and initial results are indicating that we can produce the same film quality as with co-deposition while keeping the process time the same. We also have reduced Group III loss to the same level as co-deposition.

An important longer term issue for CIGS technology is the potential for scarce and expensive In. Efforts are underway in many labs to find a solution to this problem. A new material,  $\text{Cu}_2\text{ZnSnSe}_4$  holds promise. In is replaced by the Zn/Sn couple and both are earth abundant. The new material structure (kesterite) is similar to CIGS, but adds additional complications. There is ongoing debate as to what the bandgap is, and cell efficiencies are only about 5%. We have developed a new fabrication pathway for the material that may lead to improved performance. By judicious tuning of the kinetics and thermodynamics of film growth we are able to produce films with the same properties as those produced under more tightly controlled deposition conditions. This is again an attempt to find a manufacturable pathway for this material. Our results are also contributing important insights to the structure of the material and its ensuing electronic properties. If these can be understood and controlled, the material could replace CIGS as a more sustainable material for large scale application.

**Funds leveraged/partnerships:** A new collaboration has been initiated with a small company, Teleos Solar. A pre-proposal has been submitted to the DOE Innovative Manufacturing Initiative FOA.

## 2011 Annual Report

### Thin Film Pilot Line

#### Deposition System

As has been discussed in previous reports we have formed a partnership with a local company, Mustang Solar (MVS), to build and develop the thin film deposition system that is the key piece of equipment in the thin film pilot line. The machine is currently being assembled at Mustang and is scheduled for delivery by June 1. A description of the machine and the approach that we are taking was provided in our last report. Because the design of the machine is based upon USF proprietary processing information and upon MVS proprietary hardware details about the machine cannot be provided in these reports. However, once the machine is operational, we will be providing results on its performance. Meanwhile, we are conducting ongoing laboratory experiments that are directed toward defining the processes that will be transferred to the pilot line machine. Results from these experiments are provided in the next section.

### Lab Scale Experiments

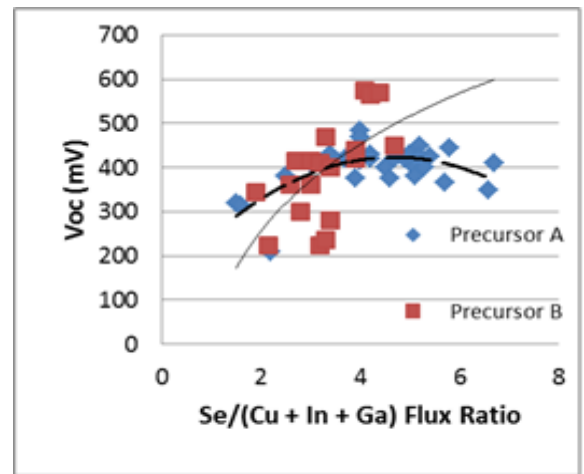
To support the design of the pilot line deposition system we are conducting ongoing experiments at the laboratory scale. These experiments address both near term and long term issues. The pilot line will be processing CIGS, and thus near term experiments are directed toward CIGS processing. Taking a longer view there is concern that at very high production levels the availability and cost of In may cause difficulties. To address this concern modifications of the basic CIGS design are being pursued. In particular we are endeavoring to replace In in CIGS with a combination of Zn and Sn, both of which are more sustainable than In. Further details are provided below.

### CIGS

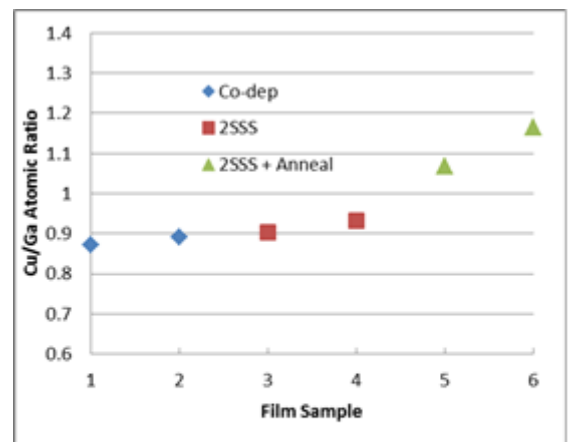
Commercial manufacture of CIGS technology has not yet met with success for a number of reasons. Among these are selection and use of the best deposition methodology. The world record 20% laboratory cells are made with a complex multi-step process that requires simultaneous tight control of three to four deposition sources. Scaling this up to a successful manufacturing level has been a

daunting task. We have pursued deposition methodologies that are more amenable to manufacture while admittedly not being able to produce the level of performance of complex processing. As we approached the institution of a pilot scale system it was apparent that we had to combine the best of these approaches to optimize performance within the demands imposed by commercial manufacturing. To this end we have taken our processes and modified them move toward more complex processing. In doing so we hope to find a manufacturing pathway that others have not pursued and that will be more successful. This has required changes to our processing hardware and recipes and the need to go up a different learning curve. However, we hope to shorten the time it takes by utilizing what we have learned over twenty years of CIGS studies. We use the acronym 2SSS for the new process. It stands for “2-Step Solid State” processing. Before moving on to more difficult device fabrication we first focus on developing processes that produce desired material properties. However, we are guided in this endeavor by device results from our current processing pathways.

Previously we reported results (Fig. 1) that showed different profiles of Voc dependence on Se flux for different precursors (1). To understand the underlying mechanisms we investigated the effect of Se flux on material properties and found interdependence between Ga and Se. Since Voc is largely driven by Ga, this mechanism is in part responsible for the profiles of Fig. 1. However, it is also the case that Ga introduces defects, and this also affects Voc(2). Here our concern was to understand this mechanism so that we could control it and thereby maximize performance while minimizing Ga and Se waste. The 2SSS process can be structured to mimic the 2-step and 3-step processes used with co-deposition. Here we focus on the 2-step process which we will then designate as 2S-2SSS. In this process the first step is to produce a Cu-rich CGS film (which may include some In) with large grain size. In Fig. 2 we show the Cu/Ga ratio for two samples of each type for this first layer produced by 2SSS and by co-deposition. In this case the 2SSS film was produced using the same deposition time and Se flux as the co-deposition film. While it has the same Cu/Ga ratio, its selenization level is only 27% compared with full selenization for the co-dep film. The 2SSS film can be fully selenized with a further anneal at 300° C for 30 minutes in Se flux, and this brings its Cu/Ga ratio to the desired level of about 1.1. However, this has required additional processing time and Se flux as well as the loss of Ga which is why the Cu/Ga ratio increases. The cause of this loss is that in order for Se to fully selenize a precursor layer it has to penetrate through the layers as they form. This gives rise to conditions that foster the formation of volatile  $Ga_xSe_y$  species. We have developed a modified 2SSS process that overcomes this problem. Fig. 3 shows a comparison of the selenization profile for films made by the standard and modified 2SSS process with that of co-dep films. The selenization profile is determined from the EDS peak amplitudes as a function of beam voltage.



**Figure 1. Voc dependence on Se/metal flux ratio for two different precursors.**



**Figure 2. Cu/Ga ratio for CGS films produced by 2SSS and co-deposition.**

The EDS signal is made to sample increasing depths of the samples by increasing the beam voltage from 15 to 25 kV. Only the low voltage peaks are used for these ratios to accommodate the lowest beam voltage of 15 kV. The data is plotted as Se/(Cu+Ga) ratio in Fig.3. The co-dep film indicates, as expected, a ratio independent of beam voltage indicating uniform selenization of the entire sample. The standard 2SSS film, however, shows increasing Se content with decreasing beam voltage. As the beam voltage increases the selenization level decreases indicating that the top of the film is selenized more than the regions further in, an indication of the difficulty of Se penetrating the upper layers of the forming film. When this sample is subjected to a further anneal at 300 °C for 30 minutes in Se flux, as can be seen the selenization content increases and the profile becomes flatter. With further anneals the film can be made to rise further to match the profile of the co-dep film. However, of greater importance is the behavior of the film deposited with the modified 2SSS process. As can be seen, its selenization profile matches that of the co-dep film. It is also important to note that this film was made using the same deposition time and Se flux as the co-dep film. SEM images and XRD data also indicate comparable grain size and phase purity as co-dep films. Thus in terms of composition and structure these films are equivalent to co-dep films, and they incur minimal Ga loss.

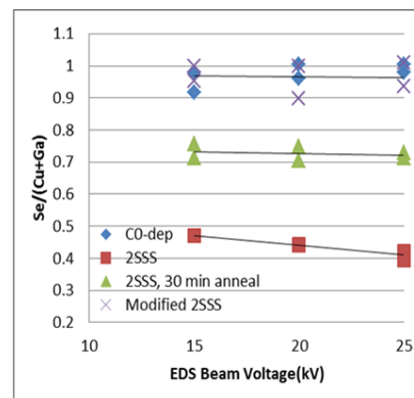


Figure 3. Se/metal ratio as a function of EDS beam voltage for CGS films made by co-deposition, 2SSS and modified 2SSS processes.

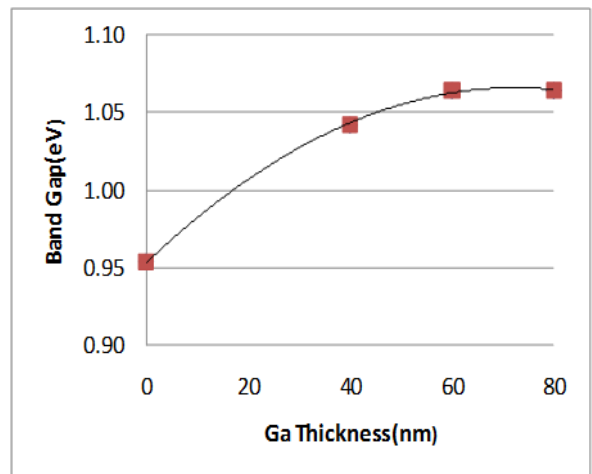
### Kesterite Solar Cells

A new material option that is being pursued is  $\text{Cu}_2\text{ZnSnSe}_4$ . Interest in this material stems from the potential shortage of In and that the Zn/Sn combination satisfies the valency requirements as a replacement for In. The structure that is formed is similar to that of CIGS and is termed “kesterite”. Thus far literature efficiencies are only at the 5% levels as it becomes increasingly clear that this is a complex material. We have turned to our extensive understanding of Ga incorporation in CIS to guide our efforts with this new material. Our first concern again is to understand and control the material properties before proceeding to devices.

We have developed considerable understanding and expertise in the development of CIGS solar cells that is guiding our development of kesterite –based solar cells. Because of the advantages at the manufacturing level discussed above our favored deposition process is 2-step processing using Se vapor, again designated as 2SSS. In using this approach to advance understanding and determine optimum deposition pathways the range we cover goes from co-deposition to selenization of individually deposited metal layers. Results attained thus far for kesterite solar cells are encouraging, but suggest that there are important fundamental issues that must be resolved if competitive performance with CIGS is to be attained. Although present focus is on demonstrating high efficiency, it is also important to build a basis for confidence in the stability of these compounds. Though the similarities to CIGS are many, there are important differences. For example, it seems that at higher temperatures anti-site occupancy is not at play for the sulfur based kesterites, but movement of the sulfur anion drives the phase transition from tetragonal to cubic(2). Although the phase transition is not completed until about 865 ° C, movement of the anion occurs at lower formation temperatures and suggests that the film properties will be a continuous function of processing temperature. This can be a problem with regard to stability, but it can also be an opportunity for optimization, if the controlling mechanisms can be understood. To this end the initial focus of our efforts is on understanding these mechanisms that drive materials properties.

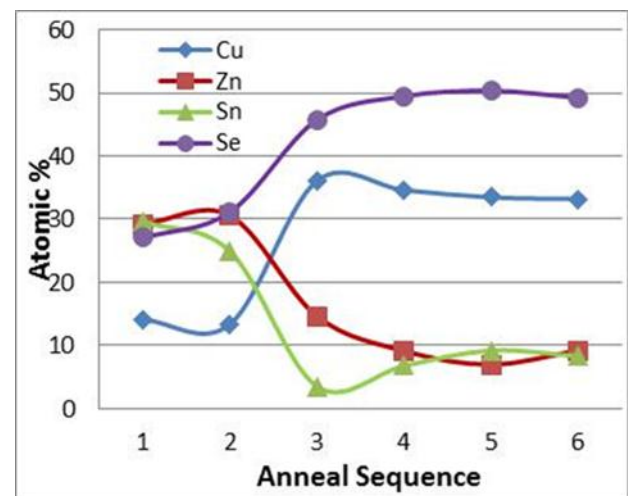


The literature suggests that the band gap of these materials has a range rather than a unique value. This is likely due in part to S migration, but the ability of the Cu and Zn cations to exchange locations is also a consideration(2). It is important then to understand the structural options that the material has, the dependence of electronic properties on those, and most importantly, to use that understanding to control film formation to effect optimum performance. We are applying our extensive experience with the I-III-VI<sub>2</sub> materials and devices to bring this about. A relevant issue that we have had success with is the proper incorporation of Ga. Ga is smaller and more electronegative than In and thus can easily incorporate into an In lattice site. This is the case for co-deposition in which the constituent atoms are all provided to the growth surface at the same time. In 2SSS processing the constituents are deposited in layers and must migrate together to form CIGS. In doing so they can also create an environment in which unfavorable secondary phases can form. In addition, we have also found it difficult for Ga to incorporate at all unless conditions are proper. If we deposit sequential layers of Cu and Ga on a Mo substrate followed by co-deposition of In and Se, we get a band gap of 0.95 eV which is that of CIS. The Ga has a tendency to migrate to the rear of the device where it forms high Ga content CIGS that is not in the space charge layer. By reversing the deposition order and depositing the In<sub>x</sub>Se<sub>y</sub> layer first followed by Cu/Ga we are able to effect Ga incorporation. The dependence of the band gap on the thickness of the Ga layer is shown in Fig. 4. As can be seen, there is a monotonic increase in bandgap with the Ga layer thickness up to about 55 – 60 nm. Voc also increases over this range, but with a slope less than that of the band gap. The implication is that incorporation of the Ga was not effective. Some of the incorporated Ga was creating defects that were competing with the band gap increase and holding Voc down.



**Figure 4. Dependence of CIGS bandgap on Ga layer thickness.**

Before addressing the effect of defects it is first important to understand and control the overall film formation process. The value of the bandgap itself has been the subject of ongoing debate. A recent paper by Ahn et al. (4) suggests that the bandgap of Cu<sub>2</sub>ZnSnSe<sub>4</sub>(CZTSe) is about the same as CIS if the material is made at a temperature of 320 °C. At higher temperatures there is phase separation of ZnSe. These findings suggest a phase instability which is worrisome. We have also addressed this same problem with CZTSe, but using 2SSS processing compared with co-deposition used by Ahn. In 2SSS processing diffusion plays an important role, and as we will show, can be used advantageously to control or limit secondary phase formation. In Fig. 5 we show the compositional dependence of the top layer of a 2SSS film on the anneal time at 400°C. The total film thickness is about three μm, and the composition is determined



**Figure 5. Film composition as a function of the number of anneal times for 40 minutes at 400 C.**

by EDS which just sees the top 0.5  $\mu\text{m}$ . In this case the Cu was deposited first and thus has to diffuse to the top. As can be seen, the Cu is initially low and then climbs to just over 30%. At the same time the Sn and Zn levels are adjusting from their initial values to a 1/1 stoichiometry. This suggests that in a proper environment Zn and Sn may collaborate rather than compete for lattice sites an important advantage to simplify processing.

### References:

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