

University of South Florida Solar Photovoltaic Manufacturing Facility to Enable a Significant Manufacturing Enterprise within the State and Provide Clean Renewable Energy (Progress Report)

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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

Summary of Annual Progress

Over the past year progress has continued to be made on the two main task areas of the project, development of the Thin-Film Pilot Line deposition system and development and advancement of laboratory scale processes for CIGS related materials and devices. As a result of the changing landscape related to CIGS manufacture the Pilot Line System was modified to focus on the key elements currently controlling commercialization of the technology. Simulation tools that address cost factors as well as technology were developed and utilized to guide the redirection of the design. It was determined that deposition rates of 20 Å/s and above were needed to hit the targeted cost factors for capital equipment utilization. The design of the deposition machine and the process recipes will allow attainment of these rates.

The key factor for machine and process design on the technology side is the arrival rate and sequence of the CIGS constituents. Simulation tools have been developed and utilized that allow determination and control of these species. The deposition tool set utilizes two pair of metal deposition sources and several Se sources distributed over the deposition zones. The twodimensional deposition profile of the components are individually simulated and then combined to simulate the overall two-dimensional profile. Imbedded in the simulations is the ability to control the evolution of the metal ratios across the deposition zone. And, simulation of the Se/metal profiles within a targeted range completes the capture of the entire deposition process. The insights provided from these simulations have guided the design of the deposition system. It will be versatile enough to enable access to a large range of deposition space that contains the

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Florida Energy Systems Consortium optimum parameters for performance and cost control. The machine components have been delivered, and it is currently being assembled.

Based upon CIGS laboratory scale experimentation that has been underway two process recipes have been chosen to implement in the Pilot Machine. The initial configuration of the machine will be directed toward determining which of these has the most potential for success. On a longer timeframe we have also been developing CuZnSnSe(CZTS) as a sustainable substitute for CIGS. With increasing production volume the availability of In may drive up its cost. CZTS uses earth abundant materials and has demonstrated efficiency in the 10% range. We have been developing the material, and with new insights gained from use of Raman spectroscopy have made significant progress in improving material quality. Initial results from devices made with the upgraded material are also promising.

3.0 Thin Film Pilot Line

As progress is being made in the manufacture of CIGS solar panels new challenges and opportunities are emerging for ongoing growth of the technology. Champion large area module efficiencies of 16% are being reported, and average production efficiencies are catching up. So it is clear that performance parameters for large scale applications can be met. What remains is to demonstrate that costs are competitive and have a pathway to remaining so. The key to cost is throughput and materials utilization. These translate to fast deposition rates and management of In and Ga utilization. From the beginning of our research endeavors at USF we have always pursued deposition technologies that would be able to pass commercialization muster while avoiding those that allowed fast pathways to high efficiency, but had no chance at commercialization. There has been a series of companies that failed by trying to commercialize the easy high efficiency technologies. With this backdrop we have designed our new deposition system to accommodate the commercialization drivers. The system will incorporate tools to evaluate deposition approaches that have not been reported in the literature. Our objective is to demonstrate that one of these surpasses commercialized technologies in performance and cost.



FIGURE 5. PROJECTED CAPITAL EQUIPMENT COST IN \$/W FOR CIGS DEPOSITION AS A FUNCTION OF DEPOSITION RATE



Cost Simulation

Throughout the project we have developed and used simulation tools to guide our technology development. Of particular importance to the design of the deposition system is the projected capital cost/Watt for the deposition tool. The drivers for this cost factor are the capital cost of the equipment, the throughput, the efficiency and the yield. There are also variations for series and parallel target configurations that have various cost tradeoffs. An example of results for a few of these configurations is shown in Fig. 1. This component for the cost of a finished module should be about 20%, which for a selling price of \$0.60/W should be around \$0.12/W. As can be seen in the figure, this threshold can be reached for deposition rates of 20 Å/s and higher.

At this point it is necessary to bring another technical factor into the cost discussion. Deposition rates of 20 Å/s can be attained by both sputtering and thermal evaporation of the source materials. While thermal evaporation is the technology that has been used to progress efficiencies to the 20% level, it has not proven to be a successful technique for large area manufacturing. Sputtering is considered the technology of choice for large area manufacture because of its ability to deposit uniformly and reproducibly over large areas. Ideally one would like then to just sputter from a CIGS target or maybe a combination of CuSe, In₂ Se₃ and Ga₂ Se₂ targets. These approaches have not worked largely because of loss of Se, but even if they did, sputter rates of 20 Å/s and higher are not realistic for "ceramic" targets. Thus sputtering of metals is what must be pursued, and that is what we, and others, are working at. Depositing Cu, In and Ga at these rates is not the problem, it is rather how to selenize the metal layers. This is where innovations are needed to enable the emergence of this technology and what is guiding our efforts and the design of our deposition tool.







FIGURE 6. THICKNESS PROFILE OF A SPUTTERED FILM ON THE WEB.

Deposition Simulation

The process recipes that we will be developing are based upon sputtering of the metal components. We will pursue a couple of different approaches to Se delivery and determine which is most effective. The deposition system will be in a roll-to-roll configuration and will be able to handle "plastic" as well as stainless steel coils. The width of the substrate will be 4". Champion efficiency cells are made in deposition systems on small substrates onto which all four components, Cu, In, Ga and Se



FIGURE 3. CUMULATIVE THICKNESS AS A FUNCTION OF WEB POSITION.



FIGURE 4. METAL RATIO PROFILES FROM FOUR SPUTTERING SOURCES.





Florida Energy Systems Consortium are delivered to the substrate simultaneously and carefully controlled. This is not possible in a

manufacturing scale system based upon sputtering. In these systems the components are delivered to a moving substrate by multiple sputtering sources. Consequently there are time offsets in the arrival of the constituents. Given the complex phase space of CIGS and the potential for formation of unfavorable phases it is important to understand the formation chemistry and to design the deposition tools to be able to access the region of deposition space that produces high quality, single-phase CIGS. Throughout the years we have explored and studied many regions of this phase space and have designed the deposition tool to access regions that we know to be viable. To effectively use this understanding we have developed deposition simulation tools to guide design of the deposition tools. Figure 1 shows the instantaneous thickness profile, or equivalently the flux, of the deposition along the web for a sputter



FIGURE 5. FLUX RATIOS FOR TWO SPUTTER SOURCES AND SE SOURCES.

target located at 20". Fig. 3 shows the resulting thickness increase as the web moves over the sputtering source. There is a corresponding profile for a second sputter source adjacent to the first one. It has the same profile, but offset from the first source. Thus the instantaneous composition at any location on the web can be determined. Further, the composition can be changed by adjusting the separation distance between the sources, the sputter gun angle and the deposition rates. Fig. 4 is an example of the emergence of the metal ratio profile as a function of position for four sputtering sources resulting in targeted ratios of 0.9 for Cu/(In + Ga) and 0.4 for Ga/(In + Ga).

In addition to controlling the metal fluxes it is important to attain the proper delivery profile for Se. It is necessary to have an overpressure of Se to achieve full selenization of the films. A simulation result for one of the two pairs of sputter sources used for the Fig. 4 simulation is shown in Fig. 5. The targeted ratio of Se/metal is 3 - 5. The red(top) curve in the figure is this ratio and indicates that the desired range is achieved. The underlying curves are the contributions from the individual sources.







FIGURE 7. PILOT-LINE DEPOSITION SYSTEM.

The insights gained from the above analysis were used to guide the development of the Pilot-Line deposition system shown above which has a total length of 10 feet. This figure is before all of the operational hardware has been installed. We hope to report next time on installation and operation of the system and initial results.







One of the cost issues for CIGS is Indium. In is currently available and cost-effective, but going forward to large volumes this might not remain true. Consequently we and others have been pursuing alternative CIGS-related compounds. In particular we have focused our efforts on CuZnSnSe. Efficiencies of 5 - 10% have been reported for CZTS made with different techniques. We have chosen a deposition pathway that we believe will meet the requirements for large scale manufacture. Our efforts thus far have concentrated on attaining good materials properties. This material is more complex than CIGS because of the various locations that the metals can take in the lattice. These properties are also difficult to characterize by the usual techniques of XRD because of the similarities of the fingerprints for the relevant phases. We developed an optical technique which we reported previously and which was helpful in identifying the presence of ZnSe¹. Our attempts at making devices were being thwarted by the formation of ZnSe. Recently we started using Raman spectroscopy to gain further insights to the structural composition of our material. In Fig. 7 we show a Raman spectrum for a sample made at an annealing temperature of 300 °C. The main peak at just under 200 cm⁻¹ is that of CZTS with two satellite peaks on either side. The peak at 265 cm^{-1} , although identified to be ZnSe, is more likely CuSe. With additional processing at higher temperatures we find that this peak disappears. It is known that CuSe forms at lower temperatures and then reacts with the other constituents to form CZST. We are using these insights to guide further development of our material and believe that the electronic quality is now significantly better. However, the ultimate proof of material quality is in device performance. We have started making devices with the upgraded materials process and are seeing encouraging results. An IV curve of a device showing PV response is shown in Fig. 8. Once we advance the performance of CZTS at the laboratory level, we can also transfer the process to the Pilot-Line machine for further development.

¹ Y. Wang, S. Bendapudi, C. S. Ferekides and D. L. Morel, "*Optical Determination of Phase Composition and Processing Effects on Cu*₂*ZnSnSe*₄ *Film Quality and Device Performance*", Proceedings of the 38th IEEE PV Specialist Conference, Austin, June, 2012.

