

UNIVERSITY OF SOUTH FLORIDA 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 15.8%, 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

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

Progress Summary

Over the past year progress has been made in all subtask areas. Upgrading of the pilot line lab in the IDRB building with the infrastructure to handle an operation of this scope was completed. The lab was officially turned over to the project, and plans for equipment installation are underway. The design and construction of the deposition system underwent a significant re-direction. This was driven by the formation of a partnership with Mustang Solar, a division of Mustang Vacuum Syatems(MVS) which is located in the Sarasota area. The partnership has three components: a licensing agreement developed in co-ordination with the USF Patents and Licensing Division, joint sponsorship in the construction and operation of the deposition system, and a FHTCC project to further support operation of the facility. MVS's experience in developing and selling large vacuum deposition systems had a significant impact on the design of the pilot line system. We jointly determined to pursue a roll-to-roll(RTR) format rather than the batch format of our original design. Substantial cost sharing by MVS in construction of the machine also made this transition possible. The deposition system is currently being built and is expected to be in operation in the first quarter of next year.

Progress on several fronts is also being made with our ongoing lab-scale experiments that are needed to support the pilot line. The substrate to be used in the RTR processing configuration for the line is stainless steel. All of our experience with $CuInGaSe_2$ (CIGS) processing has been on glass substrates, so this redirection has triggered the need for development of the stainless steel substrate and concomitant modification of the CIGS deposition process. Initial experiments on this task are underway.

Scaling up from a lab-scale process to a pilot level operation also requires significant modifications to processing approaches. Issues such as materials utilization, yield and throughput are not normally addressed with lab-scale efforts, but are critical to success of a commercial operation. The lab-scale experiments that we have undertaken under this project have targeted these concerns. A specific area in which we have promising results is materials utilization. All vacuum based deposition processes for CIGS suffer from excessive Se use, and loss of Ga. These losses are due to the thermodynamics and kinetics of film growth from vapor sources. The processes used fall into two general categories. In one case, referred to as co-deposition, all of the constituent atoms are deposited simultaneously. In the other, referred to as deposition/selenization, the metals are deposited first, and then they are subsequently selenized. Co-deposition can also include two or three steps for purposes of optimizing grain structure and





profiling of the atoms, particularly Ga. We have developed a novel process that falls between these two categories. Our results thus far are predominantly for the first step of an intended 2-step process. What we are able to do with this process is span the range in materials incorporation between the two endpoints of co-deposition and the deposition/selenization process. Within this range we discovered an important interaction between Se and Ga incorporation. This mechanism allows us to selectively tune the behavior of these components and thus better optimize their utilization. The experiments are being extended to the second step of the 2-step process which will then lead to the fabrication and evaluation of finished devices. With further work we expect this process to be upscaled for use in the pilot line system.

THIN FILM PILOT LINE

Industry Participation

The primary object of this project is to foster the development of a PV solar manufacturing industry in the state. While PV manufacturing has outstanding attributes as a business opportunity, it has become increasingly difficult for new investors to identify legitimate prospects to pursue. There are many who claim to have laboratory technology that can be scaled up to successful commercial manufacturing, but there is little in the public domain to help with this critical transition from lab-scale to manufacturing. This is largely because the incumbent PV companies hold this information close, since it is, after all, that which gives them a competitive advantage. Under this project we are proposing to conduct the development work from lab-scale to pilot-scale in an open academic environment. We believe that this will help stimulate potential investors to pursue PV manufacturing by providing them with access to operations and data that is more objective.

Over the second year of the project we had the good fortune to interact with a local company that specializes in the production of large-scale vacuum coating equipment. In pursuing a vendor to build our pilot line deposition system, we contacted Mustang Solar, a division of Mustang Vacuum Systems(MVS) located in Sarasota. During discussion of our plans with MVS it became apparent that we had common interests. Mustang Solar's business plan centered on it becoming a supplier of turnkey thin film PV manufacturing systems. It became clear that by joining the significant thin film expertise at USF and within the FESC community with MVS's vacuum equipment capabilities we would both significantly advance our agendas. An official partnership with MVS is now in place. It consists of three components: a licensing agreement, a cost sharing agreement for the construction of the deposition system, and a FHTCC project. The bottom line is that the addition of MVS as a partner will significantly enhance the resources of this project and amplify our efforts to accomplish our goals and objectives.

Deposition System

Thin film PV panels are manufactured in two basic formats. In one case glass is used as the substrate, and the process is considered as a batch process because each part is handled individually. The other approach uses a flexible substrate and a roll-to-roll(RTR) process feed mechanism. The product is a roll of material that then needs to be cut up and reconfigured into a module format. The substrate is either a metal like stainless steel or plastic. Both processing approaches are in common use in the thin film PV industry. Prior to our partnership with MVS we had been pursuing the glass substrate, batch approach. Most of our lab-scale experience has been with glass, and a batch type process offers greater flexibility in deposition machine configurations to better accommodate the limited resources available to the project. However, MVS has been developing RTR processing units and wished to pursue that option. They backed this up with significant cost sharing for the construction of the deposition system, so that is the path we are now pursuing. Our previous reports provided details for the design of a batch type deposition system as well as for setting





up the lab infrastructure to support glass based processing. Needless to say, we have had to revisit and modify those plans. While this has taken some additional time, we are confident that in the long run the benefits of this new approach will far outweigh the necessary delays in our original schedule. We have jointly designed the RTR deposition system with MVS and it is being constructed. While we wait for its delivery and installation, there are ongoing lab-scale experiments that are needed to put together the process recipes and to finish the fabrication of working cells and modules.

The biggest impact of changing to RTR processing is in handling the substrate. Our initial substrate will be stainless steel. The thin film material will remain CuInGaSe₂ (CIGS). While we have undertaken some processing of CdTe on stainless steel, all of our CIGS processing has been on glass. We are planning experiments to start our development work for deposition of CIGS on stainless steel. Some of the more important issues that need to be resolved are developing an effective barrier for impurity control, developing a source of Na, and assuring good adhesion of all of the component layers. These are all ongoing topics of R&D in the CIGS community as well.

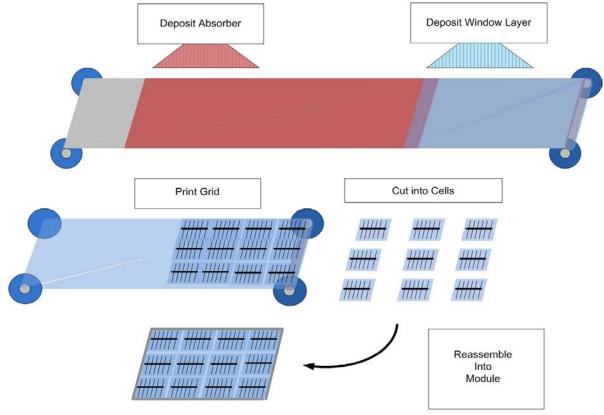


FIGURE 14. ROLL-TO-ROLL THIN FILM CELL PRODUCTION.

The overall impact of these changes is illustrated in figures 1. The substrate is a web of stainless steel about 14" in width. The absorber, CIGS, and junction/window layer partners are deposited in a continuous in-line manner in the deposition system. Metal-based collection grids are then printed on the top surface. The web can then be cut into individual cells which can then be tested much in the same manner as for Si solar cells. The cells are then wired into module format and encapsulated to form a finished module. This configuration will provide a versatile test bed for developing the processes and the





component delivery systems and for optimizing throughput and yield. Operation of a line with these capabilities will significantly enhance the confidence level for investing in a manufacturing line.

Lab Scale Experiments

There are several pathways for CIGS deposition that are being actively pursued by the thin film PV community. We have participated in the development of these as well, but now need to choose and develop an approach that will be competitive at a commercial level. We have identified a couple of favored pathways and must now address the key issues associated with scale-up. An issue that is common to all pathways is efficient materials utilization. In particular, vacuum based CIGS processes suffer from loss of Ga and excessive use of Se. Some results from experiments addressing this topic are provided below.

Selenium Incorporation

To first order CIGS is a material that comes together with good electronic properties. The phase diagram indicates that if the four constituents are brought together at the right temperature, single phase CIGS will form. Theoretical calculations also indicate that defects do not readily form states in the gap. And indeed if co-deposition is used to place the atoms together at the right rate for an acceptable substrate temperature, high quality films are produced which can be made into 20% devices. The best devices made by co-deposition use a multi-step process in which the components are deposited at different stages in the deposition cycle. While this is the ideal approach on a scientific basis, there are issues that have kept it from becoming a practical reality at a manufacturing level. This has given rise to numerous alternatives for deposition. Among these are the 2-step processes, the most successful of which is that in which metal precursors are selenized with H₂Se gas. Another approach is what we designate as 2SSS which is an acronym for 2-step solid selenization and which employs evaporated Se(solid) as the source of selenium. The base case for this approach is that in which the metals are deposited sequentially followed by the selenization step. Variations include deposition of metal selenides and all permutations of the order of deposition followed by selenization. We have focused our efforts primarily on the 2SSS approach, but are also using co-deposition to enhance our understanding of the key underlying mechanisms. We have explored a large subset of the 2SSS deposition space and are making progress in understanding the controlling mechanisms.

One of the shortcomings of vacuum based CIGS processing is that excessive quantities of Se are needed to grow stoichiometric films. This is not only costly, but produces rapid buildup of Se inside of reactors. At a manufacturing level this results in the need for frequent cleaning and hence adds to down time. The problem has its roots in the low sticking coefficient for Se on the growth surface. This in turn is due to two underlying causes, the tendency of Se to form chains and rings, and the kinetics and thermodynamics of surface interactions. In Fig. 2 we show Se incorporation as determined by EDS measurements for typical co-deposited CIGS films. The completed films have metal compositions characteristic of high electronic quality. The overriding factor is that excessive Se flux is needed to produce these high quality films. We show these results at two substrate temperatures because we are interested

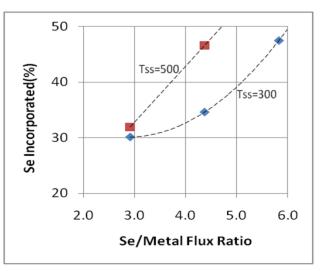


Figure 2. Se incorporated in co-deposited CIGS as a function of Se/metal flux ratio for two substrate temperatures.







in exploring these effects in the most favored two- and three-step processing pathways. In these multi-step processes the first layers are deposited at lower temperature and the finishing layers at the highest temperature in the range 500 - 550 °C. While the trend lines suggest different mechanisms at the two temperatures, the data is too limited to make that case. Rather, the more important point is that the incorporation mechanism is enhanced by temperature. While this is beneficial, the flux needed to reach stoichiometry is still four times the metal flux, and it is commonly found that better films are made by depositing the earlier layers at the lower substrate temperature. It is the case, however, that these results are for depositing a single step CIGS film, while the best devices are made using multi-step processes. Consequently we turn our attention to films made as part of a multi-step process. One of these that we have explored is the two-step process which uses a Cu rich CGS first layer. The theory behind this approach is that a Cu-rich environment enhances grain growth in the finished film by providing a large grained CGS platform for subsequent growth of CIGS. There is evidence to support this view, but it is also the case that additional factors come into play in the formation and success of these films. As the 2SSS acronym implies, we favor this approach and are building understanding of its underlying mechanisms. We have deposited and studied Cu-rich CGS made by conventional co-deposition as well as by selenization of metal precursors. In the latter the entire metal precursor is deposited and then it is selenized. There are also variations with this approach that include incorporation of some Se in with the metal precursors. In addition, we are also depositing these films using a novel proprietary approach. As will be discussed, these films have attributes that span the range between the two endpoints of codeposition and precursor selenization.

Incorporation of Se in Cu-rich CGS films showed similar low sticking coefficients to those of CIGS films in Fig. 2. In addition we found that the sticking coefficients were a function of the Cu/Ga ratio which had to be sorted out. In Fig. 3 we show Se incorporation as a function of Cu/Ga for the three categories deposition: co-deposition, precursor of selenization(PS), and proprietary deposition. As we are concerned with controlling Se loss, for this series we used a Se/metal flux level of about four which is at the boundary of the Sestarved region. The films were all made with equivalent quantities of Cu, Ga and Se incident on the substrate. The targeted composition was Cu/Ga of about 1.2. The substrate temperature for this series was 300° C. As can be seen, the co-deposited films attain the requisite Se of

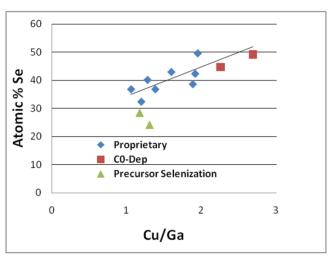


Figure 3. Dependence of Se composition on Cu/Ga ratio for step 1 Cu-rich CGS films in a 2SSS process.

about 50%, but have Cu/Ga ratios of about 2.5 which indicates a Ga loss of about 50%. Needless to say this is substantial and of concern at a manufacturing level. At the other end of the range the PS films have incorporated all of the incident Ga, but are substantially low in Se content. What needs to follow is whether the low Se in this layer is an issue in terms of the overall film composition and its performance. he amount of Se used later in the process is also far in excess of stoichiometry and may be able to make up for this shortfall. It is also the case that increasing the Se flux for the PS films can and does raise the Se content level. We do not yet have the data showing the effect on Cu/Ga, but the data from the proprietary films is illustrative of what one would expect.

Clearly there appears to be a tradeoff between Se and Ga incorporation as well. The proprietary films play into this tradeoff, and as can be seen fill the range between the co-deposition and PS endpoints. However, they do provide advantages. At the high end of the Cu/Ga range they are able to reach the stoichiometric mark for Se, but at lower Cu/Ga levels than the co-deposited films. A simple calculations





indicates a 33% loss of Ga relative to 50% for the co-deposited films. In the lower Cu/Ga range the proprietary films can also preserve all of the Ga while incorporating 35% Se relative to 25% for the PS films. So in terms of effective Ga and Se utilization these films are superior to both co-deposition and PS films.

A logical point for beginning to understand these mechanisms is to consider the species that can form. The literature provides numerous sources of phase diagrams and XRD data to guide thinking. Loss of Ga(and In) is commonly attributed to the formation of volatile species such as Ga₂Se, and we assume that is the case here. The Ga that remains and the Cu form various phases with Se as well as with each other to form CGS. Since Cu exceeds Ga, it is clear that it must form Cu_xSe_y species with the level of Se depending upon the level of Se and the temperature. Ga similarly forms Ga_xSe_y species. With ongoing experiments we expect to sort this out and develop a processing pathway with enhanced component utilization. This process will then be reformatted for transfer to the RTR pilot line deposition system. We expect this to provide a differential advantage to processing approaches currently in play.

