

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 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

We have maintained our efforts in the three areas of concentration, CIGS process development, $\text{Cu}_2\text{ZnSnSe}_4$ materials and device fabrication, and design and construction of the thin-film pilot system. In terms of timing, advancement of CIGS processing is the most urgent because it is guiding the development of our pilot line deposition system. Previously we reported progress on materials properties for the first step CGS layer deposited with our novel 2SSS deposition technique. We have extended those experiments to include deposition of Cu, In Ga and Se in the second step. Compositional analysis indicates that the films made with 2SSS are the same as standard co-deposition. In addition, we also find no evidence of loss of Ga or In in these films. This is important in terms of materials utilization at a manufacturing level. Having established good materials properties we proceeded to device fabrication. Initial experiments involved deposition of the first CGS layer by 2SSS and the second CIGS layer by conventional co-evaporation. The devices were similar in performance to those made entirely by co-evaporation. To evaluate at a more fundamental level we compared the quantum efficiency(QE) spectra of the devices and found the hybrid 2SSS/co-evaporated devices to have > 80% of the QE of the all co-evaporated devices. QE is particularly sensitive to material defects and a good indicator of material quality. We will report on extension of these studies to devices made entirely by the 2SSS process in upcoming reports.

While establishing the successful commercialization of CIGS is clearly the first priority, we and others are looking ahead to the stages of rapid growth for the technology. There is a body of evidence that suggests that the availability and cost of In and perhaps Ga will limit the growth of CIGS technology. To address this issue a new group of materials, the kesterites are being developed. These materials are derivatives of the CIGS family in which the In and Ga are replaced by a combination of Group II and Group IV elements. Efficiencies of order 10% have been reported. We have focused our efforts thus far on $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe). While the valency is preserved by replacing Group III elements with a combination of a II and a VI, these materials have the added complexity of the metals being able to

occupy alternate lattice sites. Thus the properties that one attains are a complex function of the fabrication pathway. A range of bandgaps have been reported in the literature. This is due not only to the complexity of alternate lattice sites but also to the presence of secondary phases. While the phase composition can normally be determined by XRD, that is not easily done in this case since the principal phases have nearly identical XRD signatures. To address this problem we have developed an optical model to determine the presence of secondary phases. We are currently using it to guide the fabrication of our materials to find the optimum pathway to single phase material. We have now attained materials that appear to be single phase, and we are moving forward with device fabrication and will provide results in our next report.

The key element of this project is the development of a deposition system and process methodology that can meet the requirements for successful commercialization. In designing and building this machine we have used the input from ongoing developments in the field as well as from our own lab-scale experiments. With large area module efficiencies of 16% being reported, the specific concern with scaling up to large areas has been relaxed. Consequently we are now focusing on throughput and yield as the key drivers for commercialization and modifying our machine design accordingly. The upgrades in machine capabilities that we are incorporating and that address these key issues will position us to have more impact on the drive to commercialization. We are currently working with vendors to incorporate these unique capabilities and expect to have the upgraded machine up and running by the first of the year.

Thin Film Pilot Line

Deposition System

The design and capabilities of the pilot line deposition system have been undergoing ongoing consideration as new information is generated by our own efforts and the field. When the project began, large area uniformity was a primary concern as module efficiencies were lagging significantly behind lab-scale efficiencies. Over the last year large area efficiencies of 16% have been reported. This existence proof has relaxed the concern for development of large area capability. Consequently we are now shifting priority in the design of our machine toward throughput and yield. The reduction in size of our stainless steel web substrate will facilitate the use of more advanced deposition tools and controls. The uniqueness of these capabilities will also enable the development of novel fabrication pathways that should enhance the potential for commercialization.

Lab Scale Experiments

The commercialization of CIGS technology is a dynamic field which is driven by many factors. In particular the scale up process has been daunting and has led to many failures because of the complexity of the technology and the constraints imposed by the market place. It is apparent that there are still fundamental issues that need to be resolved before one can proceed to commercialization with confidence. Key among these are yield, throughput and materials utilization. This project is addressing each of these. The key element in the project is development of the pilot machine as discussed above. The design and construction of this machine is a work in progress that will and must be adaptable to new knowledge as it is developed. Much of this input is coming from our own lab-scale experiments which are explicitly directed toward design of this machine. In our current CIGS reactor we are conducting experiments that simulate the approach that we will take in the pilot machine. Results from these experiments are presented in the last section. While we are endeavoring to optimize materials utilization for CIGS, we are also addressing the longer term issues relating to materials with our experiments on kesterites. The kesterite, $\text{Cu}_2\text{ZnSnSe}_4$, is a high potential replacement for CIGS which avoids the use of potentially expensive In and Ga. Results of our experiments with this promising material are also presented below.

Kesterite Solar Cells

As indicated above, $\text{Cu}_2\text{ZnSnSe}_4$ (CZTSe) is being developed as a replacement for CIGS. Replacing the Group III compounds with II-IV's adds additional complexity to the fabrication process. Nevertheless efficiencies in the 10% range are now being reported. One of the complications of this material is that the metals can occupy different lattice sites. A concern then is to determine the effect of metals location on optoelectronic properties. As such, the optical properties as manifested by the band gap of this material seem to have a range of values. Complicating the analysis is the potential for formation of secondary phases of metal selenides. The XRD profiles of these also happen to be nearly identical to that of CZTSe further complicating matters. We have undertaken development of an optical model to determine film composition to address this situation.

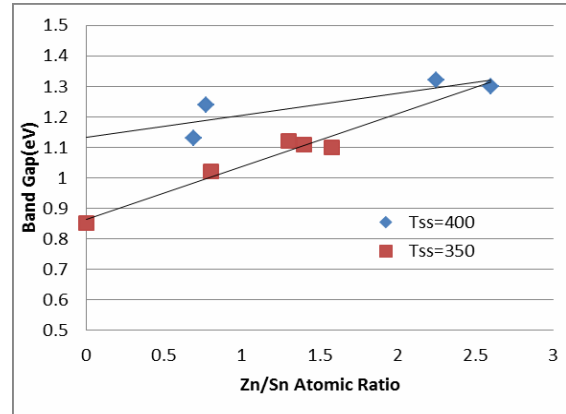


Fig 1. Band gap vs. Zn/Sn ratio for CZTSe films at two substrate temperatures

We have been investigating the effects on optical properties of deposition parameters and indeed see a rich phase space of properties. Previously we observed dependence of band gap on Zn/Sn as a function of substrate temperature. A key result, as shown in Fig.1, is that the band gap can be different for the same composition. This suggested that different phases were forming, even at the ideal stoichiometry, but we had no way of determining what they were. To address this issue we have been developing an optical simulation algorithm to analyze our optical data. The likely secondary phases to form are ZnSe, compounds of Cu and Sn selenide as well as CuSnSe . Of these the first and last are prevalent. Because ZnSe has a band gap of 2.6 eV, its direct influence on optical data would only occur at such high energies that the absorption of CZTSe would obscure it. However, it does act as a diluting medium for measuring absorption coefficients in that it contributes to the overall thickness of the film.

To determine the influence of the other compounds films of stoichiometric CuSnSe were deposited and the absorption coefficients measured (Fig. 2). Without knowing details of the phases formed the assumption is that the optical data adequately represents the aggregate effect of these in CZTSe films. Another assumption of the model is that CZTSe has first order optical properties that are the same as CIS. While Sn and Zn are adjacent neighbors to In in the periodic table, the same can be said of Ga, and replacing In with it causes dramatic changes in properties. Nevertheless, the best devices that are reported for CZTSe seem to have QE spectra very similar to CIS.

To proceed we assume that there are three species contributing to absorption in these films, CZTSe, ZnSe and CuSnSe. The absorption due to CZTSe is modeled with a stoichiometric CIS profile from the literature, and that from CuSnSe from the measured absorption profile, both shown in Fig. 2. The effect of ZnSe will be to dilute the absorption due to the film volume taken up by its presence. The presence of the ZnSe phase thus rotates the absorption profile which would not change the band gap as determined by extrapolation of the $(\alpha h\nu)^2$ vs. $h\nu$ curve to the wavelength axis. Thus by mixing the contributions of these three we can simulate the effect on the absorption profile. Note that CuSnSe has a profile that would extrapolate to a lower band gap and that it has a steeper slope than CIS at increasing eV. So, a stoichiometric single phase film of CZTSe would have the profile of CIS shown in the figure. If that same film had 20% excess Zn which would form ZnSe, the profile would shift down as shown in the lower dashed curve. If, however it were lacking Zn, CuSnSe would form and shift the profile up as shown by the upper dashed curve. The central dashed curve is a combination of the two. Since they pull the profile in opposite directions, their combination almost again matches CIS. However, it clearly deviates at higher eV which is a telltale that the film is not single phase.

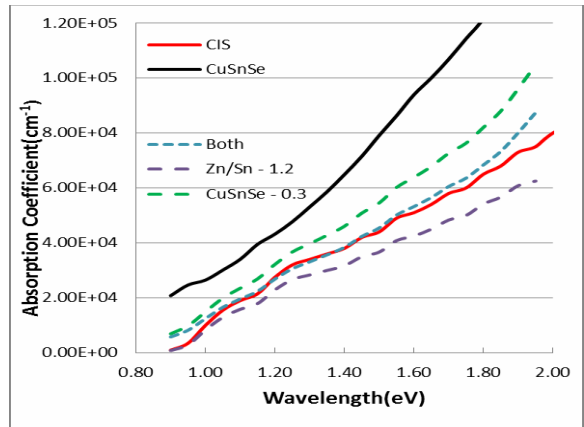


Figure 2. Simulation of absorption coefficient profiles as a function of film composition.

Since it is convenient to represent a film by its bandgap, we shift to plots used for such a determination. In Fig. 3 we plot $(\alpha h\nu)^2$ vs. $h\nu$ for CIS data (solid line) and for two variations of the model. The customary extrapolation of the fit to the curve to the axis results in a bandgap for CIS of about 0.97 eV which is typical of reported values. However, this determination is subject to the range of absorption data used. As can be seen here and in Fig. 2, there is a change of slope at higher wavelength energies the inclusion of which would result in a different value of bandgap. Nevertheless, since the range used here is closest to the wavelength axis, we will use it to determine our operational bandgaps.

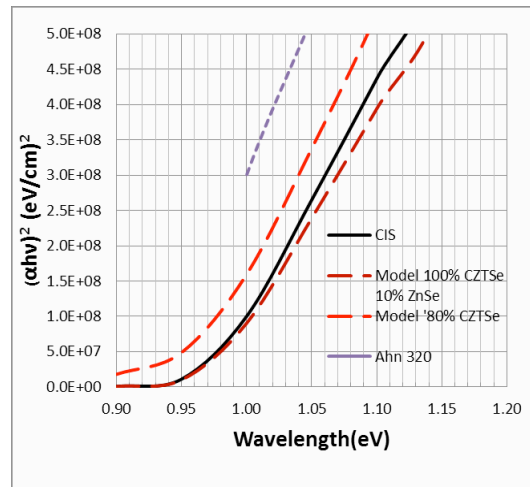


FIGURE 3. ABSORPTION VS. WAVELENGTH FOR THE OPTICAL

The model then uses the CIS absorption profile to represent CZTSe, and thus the CIS profile is what is expected for the absorption of single phase CZTSe. The two long-dashed curves indicate the effect on this profile due to secondary phases as discussed for Fig. 2. In this case the lower dashed curve is the profile for CZTSe containing 10% excess Zn, and the upper dashed curve is for a 20% Zn deficient film which results in the formation of CZTSe with the available Zn(80%), and CuSnSe with the remaining Cu and Sn. The effect of the film composition on the bandgap is shown in Fig. 4. Thus for Zn-deficient films there is a systematic downward shift in bandgap for increasing excess Cu/Sn which forms CuSnSe. For Zn-rich films there would be no change in bandgap, only a change in slope. Both the slope and bandgap of a film are used to

determine its composition. Thus a single phase film with ideal stoichiometry would have the profile of CIS, while another film of ideal stoichiometry but in which ZnSe and CuSnSe are formed with the constituents would have a lower band gap and decreased slope. We have begun using the model to guide development of our films and have thus found pathways to single phase CZTSe. We will report results on devices made from these in our next report.

CIGS

There are many pathways for the deposition of CIGS. The most successful among these are the so called 2-step and 3-step processes used in physical vapor deposition reactors. Although the 3-step process has a small advantage in performance, we have focused on the 2-step because it is less complex. In addition, we have developed a variation of this process designated 2SSS which we expect to be more amenable to manufacturing. The 2-step process involves deposition of a CGS layer followed by deposition of Cu, In, Ga and Se in a second step to complete material formation. In our last report we presented results on our development of the first layer and demonstrated its equivalency to such layers deposited by the conventional 2-step process. In this report we provide results on the entire material stack as well as on preliminary device performance.

Materials Results

Similar results are obtained for the second step CIGS layer as were presented previously for the first step CGS layer. A difference is that a substrate temperature of 500° C is used for this layer, and the reaction rates are higher. Next the two layers were deposited in sequence using the modified 2SSS process for both. In this case the additional dimension of the process transition from the first to the second layer comes into play. This transition plus the higher temperature of the second step provide additional variables that also reach back to the first step deposition. We explored a region of this expanded deposition space and produced samples with a range of compositions. The selenization level extended from 43 to 58% which also provided a means of examining the Ga loss issue. The Cu/In and Cu/Ga ratios for these samples is plotted as a function of Se content in Fig. 5. Since it is safe to assume that Cu is not lost in the film formation process, the Cu/(Ga or In) ratio as a function of selenization should be a measure of the loss of either Group III component during film growth. As can be seen, in Fig. 5, there is little dependence of the Cu/metal ratio for either Ga or In on the selenization level. This indicates that neither Group III component is lost using the modified 2SSS deposition process. The data in Fig. 1 covers a large range of metal ratios including the targeted

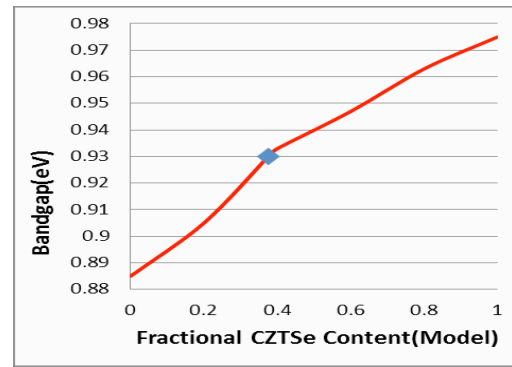


Figure 4. Bandgap dependence on the composition of CZTSe films.

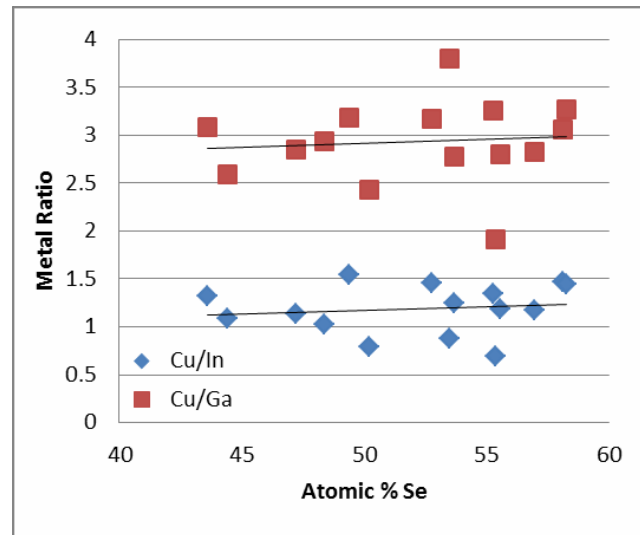


FIGURE 5. CU/ GROUP III RATIOS AS A FUNCTION OF SE CONTENT IN CIGS FILMS MADE BY 2SSS.

values of $0.9 \leq \text{Cu}/(\text{In}+\text{Ga}) \leq 1$ and $0.2 \leq \text{Ga}/(\text{In}+\text{Ga}) \leq 0.3$ for good device performance. In the next section we report results for devices made with 2SSS processed films.

Device Results

With an established process for forming quality absorber layers we next turned to device fabrication. To proceed systematically our initial devices were made in a hybrid format. That is, the first layer consisting of Cu-rich CGS was deposited by the 2SSS process, while the second CIGS layer was deposited by co-evaporation. The format for these initial devices was an array of 0.1 cm^2 devices. The small device size is useful for early stage development because there is grading in the metal ratios across the array that can provide additional insights to device performance. The devices do not have metal grids, so fill factors cannot be determined. But comparisons can be made in terms of Voc's and Jsc's. Our reference co-deposition devices made under the same conditions as the 2SSS devices had Voc's in the low 500 mV range and Jsc's in the low $30 \text{ mA}/\text{cm}^2$ range. The initial hybrid

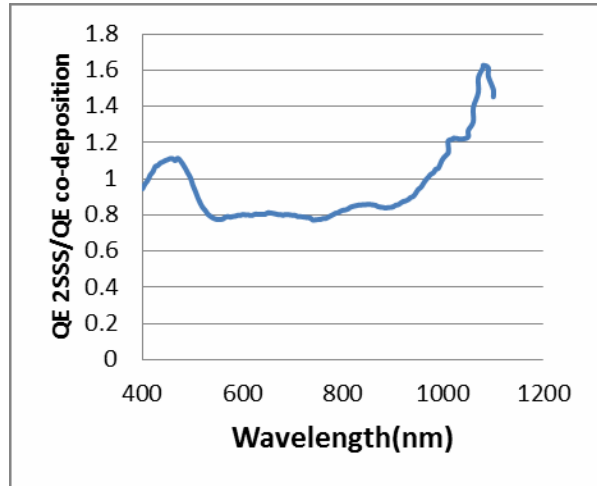


FIGURE 6. RATIO OF QUANTUM EFFICIENCIES FOR CIGS DEVICES MADE BY HYBRID 2SSS PROCESSING TO CO-EVAPORATION PROCESSING.

2SSS devices had Voc's in the same range and slightly lower Jsc's. Because of the nature of the 2SSS process we are particularly concerned with the transport properties of the absorber. Although our materials studies indicate that the 2SSS films have both compositional and macro-structural properties similar to co-deposition films, small differences at the point defect level can have significant influence on performance. Quantum efficiency is very sensitive to transport properties and is thus a good tool for evaluation. In Fig. 6 we show a comparison of QE for films grown with the hybrid 2SSS process and by co-deposition. As can be seen, the performance is at about 80% of that of co-deposition films with additional higher QE for the 2SSS films in the blue region of the spectrum. The increase in the ratio in the red region is attributable to a smaller bandgap for the 2SSS films. This is surprising since this would occur in the space charge region which is largely formed by co-deposition in these hybrid devices. It would seem that less Ga is supplied to the space charge region by the underlying CGS layer when it is deposited by the 2SSS process. We have experienced complex behavior of Ga in devices made using similar techniques in the past and have developed some understanding of the mechanisms with the help of device simulations. We will apply these techniques to 2SSS structures going forward to guide their future development. Having attained materials properties comparable to co-deposition we expect to achieve state-of-the art performance in devices.