A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

NREL National Renewable Energy Laboratory

Innovation for Our Energy Future

Project Title: Inkjet Direct Write Solar Cells FOR PUBLIC RELEASE		
Contract Number: RD-93	Report Number: 36	Report Date: 11/9/2008
Reporting Period: 10/8/2005 – 10/8/2008		
Progress Summary: Task 1: Substrate Preparation (complete) Task 2: Investigate MOD/nanoparticle precursors (complete) Task 4: ZnO precursor development (complete) Task 5: Inkjet system development (complete) Task 6: Solar cell processing (complete)		
Principal Investigator: David S. Ginley 303-384-6573 ph david_ginley@nrel.gov	Contract Contact : Jennifer Schofield 303-384-7424 ph Jennifer_schofield@nrel.gov	

Executive Summary: Copper Indium Gallium Diselenide is one of the most attractive thin film photovoltaic materials with potential efficiencies up to 20%. Historically the potential for CIS has not been fully realized in part because most of the manufacturing approaches have required a selenization step utilizing H_2Se or Se vapor. This project was focused on the development of an atmospheric and direct write ink based approach to CIS solar cells. The ultimate goal was to replace conventional processing with solution based processing for all key layers as shown in Figure 1. We have succeeded in this for many of the layers.

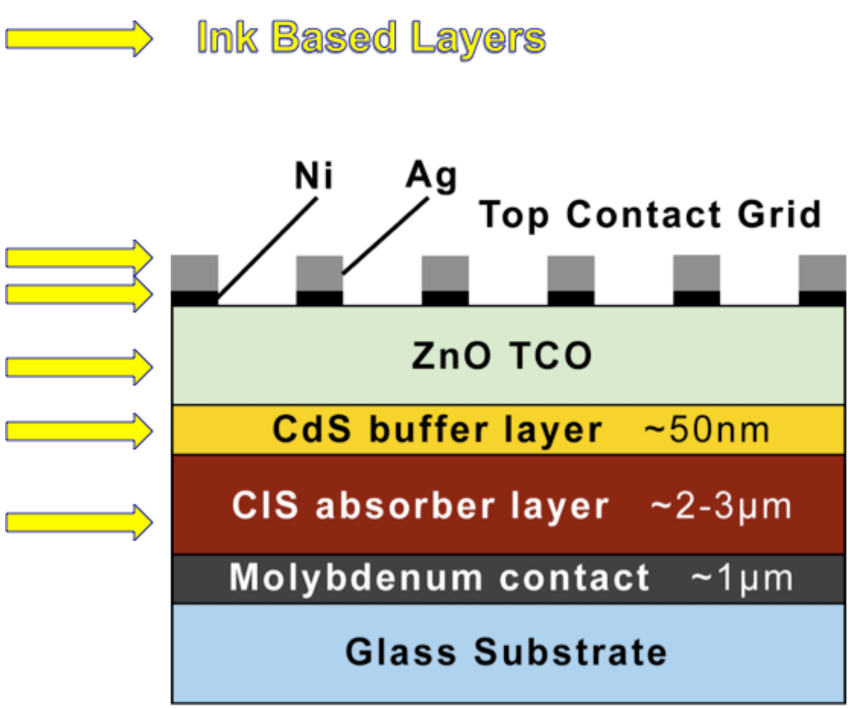

Figure 1 schematic of a CIGS solar cell showing the layers that have been successfully produced by solution precursors as show by the yellow arrows.

The approach is based on the fact that non-vacuum processing can have much lower capital investment costs, can build in the proper Se concentration and can be highly reproducible. The project was performed with funding from XCEL, the DOE PV program and Heliovolt Corporation. Work was performed in a collaboration between NREL, Heliovolt, the University of Minnesota and the Colorado School of Mines. To be able to accomplish this ambitious goal, a multistage process of developing precursor inks for the various components of the cell and then integrating them via inkjet printing and rapid thermal processing into actual devices was pursued. Initial work produced a set of binary inks that could be used to produce the binary selenides as well as in combination CIS. Later work developed Ga based precursors and a second and third generation of CIS precursors. Work is now focusing on developing ink chemistries that are more manufacturable, lower cost, greener and produce the same quality films. We have also begun to develop partnerships for the production of the inks.

We have worked on the development of other than the absorber layer with solution precursors as well. We have obtained some success recently on the development of TCO precursors for ZnO and InZnO. We have also worked on developing inks for metallizations. To replace the conventionally vacuum deposite metallizations. We have developed high quality Ni and Ag inks that can produce contacts as good as or better than those by conventional means.

Technical Progress:

- Task 1: Substrate Preparation

This task was specifically focused on developing precursors to be able to make the substrates for CIS solar cells. The key part of this was to develop precursors for Mo and then make CIS compatible Mo layers. While we in fact did develop initial precursors for Mo it turns out this is a very difficult task and was decided to not be critical to the project as commercial Mo coated glass is readily available. Ultimately, we would like to develop alternatives to Mo even an inverted cell design potentially.

- Task 2: Investigate MOD/nanoparticle precursors

This task has represented the major portion of the project. The initial focus was just to develop metal organic based Se containing inks that decomposed into the correct binary phases. This would be enabling for the ultimate success of the approach. Initial work was on the development of an InSe based precursor. The results of this are shown in Figure 2. As can be seen in Figure 2 the initial precursor decomposes with a rapid anneal at 500ºC to phase pure In_2Se_3. The desired phase.

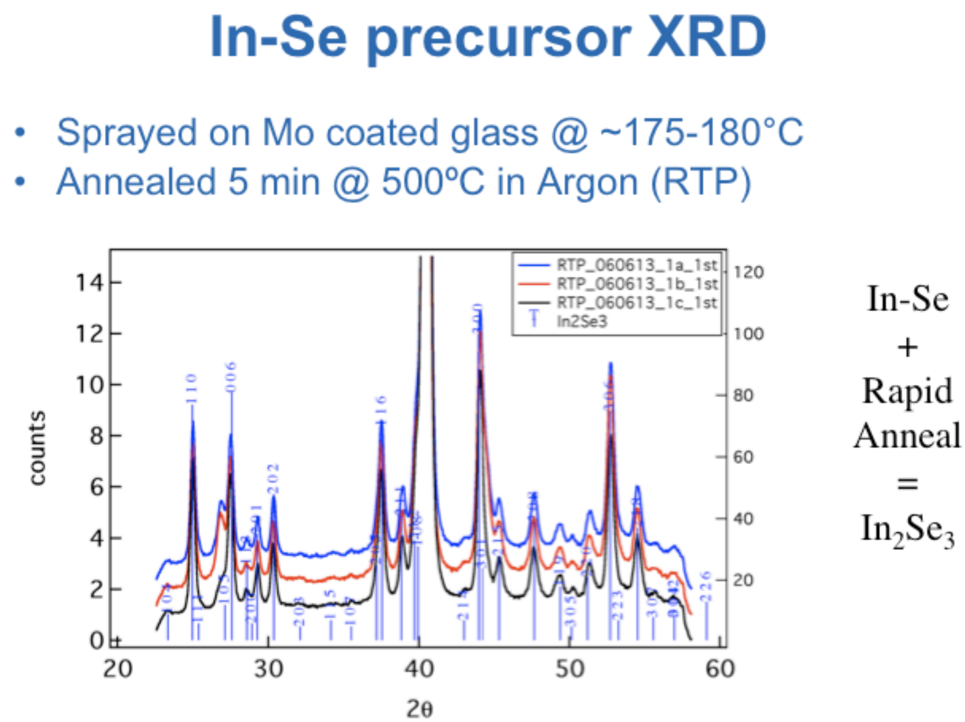

Figure 2 shows the decomposition of the InSe based precursor to get the desired In_2Se_3 phase.

Given the initial success with the In-Se the next step was to develop a Cu-Se ink to enable CIS based materials. This turned out to be more difficult than that for the In but was accomplished as shown in Figure 3.

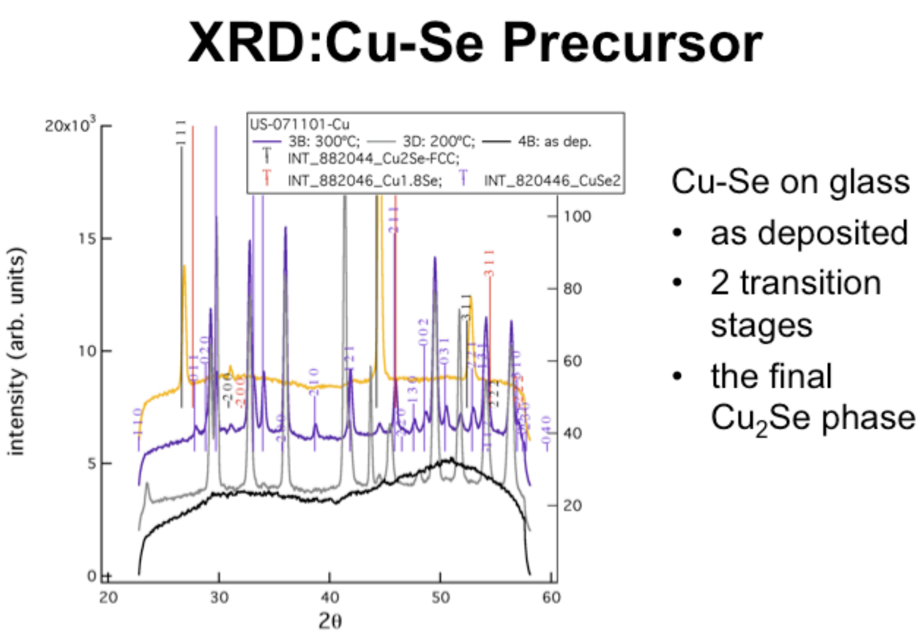

Figure 3 shows the decomposition of the CuSe precursor to the desired Cu_2Se phase. By tuning the precursor we can now get Cu_2Se, CuSe, and $CuSe_2$.

The initially Se rich precursor can be processed to phase pure Cu-Se phases with the ultimate phase being Cu_2Se.

Figure 4 shows two approaches to combining these precursors. They can be combined in binary layers or in a ternary ink.

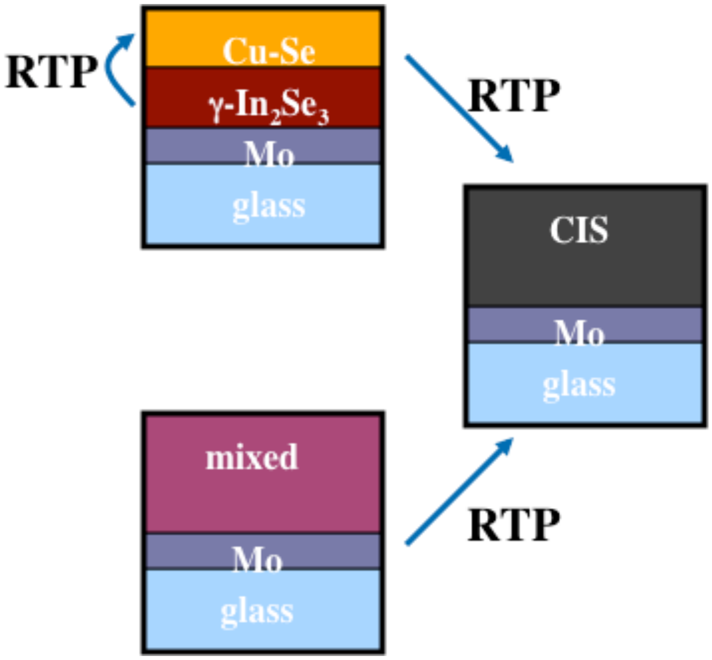

Figure4 shows the two main approaches to combining the Cu and In precursors to get CIS. We note that the Ga based precursor can be integrated similarly.

Figure 5 shows the binary approach which produces phase pure CIS directly.

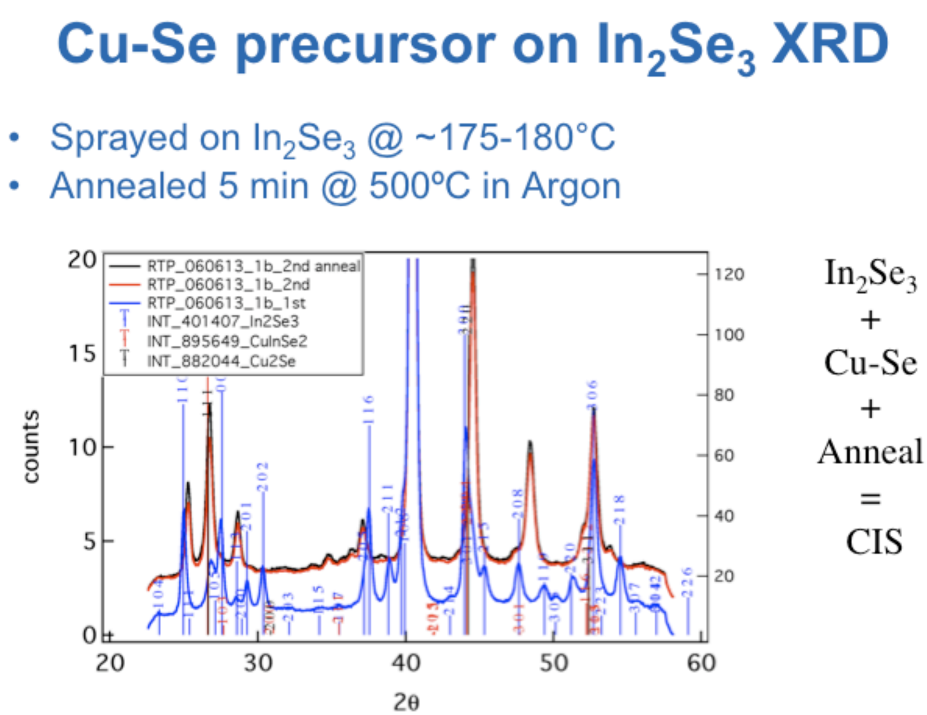

Figure 5 shows the bilayer combination of first producing the In_2Se_3 layer and then reacting it with the Cu-Se precursor to get phase pure CIS.

The combined ink also produces CIS directly. Nominally, the formation of the correct phase is an important first step but not sufficient. The key second step is the establishment of the correct morphology for solar energy conversion. This requires the formation of micron sized grains. A great deal of systematic work was required to be able to find the appropriate place in phase space to be able to get dense large grain materials. Figure 6 illustrates the morphology obtained.

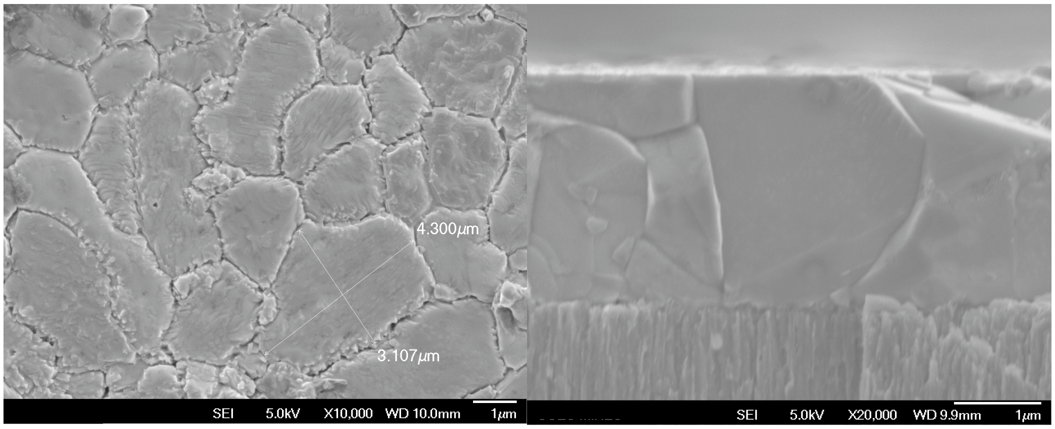

Figure 6 shows the morphology for an optimized combination using the bilayer approach. This morphology is comparable to that for the world record cell by PVD approaches.

Figure 6 shows the formation of very large grain materials with dense grains that are full thickness. These films have produced up to 5% cells. The lack of higher efficiencies is primarily due to the films being slightly off stoichiometry. To address this a second generation of binary inks has been produced and is currently under development to produce improved photovoltaic devices. The current inks are sufficient to be incorporated into production processes as binary materials. Finally Figure 7 shows that we have developed a Ga precursor as well that can be integrated with the precursors above to produce phase pure $Cu(InGa)Se_2$.

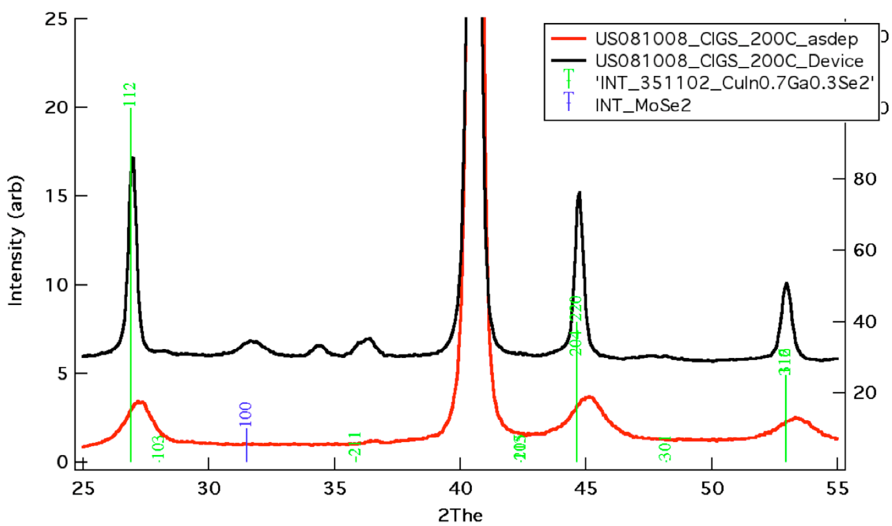

Figure 7 shows the development and incorporation of Ga to be able to get high quality phase pure CIGS.

This set of inks has fully achieved this task and provides a basis set for the development of future manufacturable CIGS solar cell processes.

- Task 3: Junction Formation Layer

This task was originally intended to develop alternatives to the existing CdS solution processed layer. Given that the existing layer is already solution processed it was decided to not extend this effort to other materials at present as optimization of all the layers simultaneously would have been too difficult. Recent work has shown that in fact CdS generally performs better than alternative layers. Alternative layers such as ZnSe, and ZnS are easily attainable by solution approaches.

- Task 4: ZnO precursor development

This task was focused primarily at the University of Minnesota but was also in the 3rd year initiated at NREL. Historically, it has been difficult to produce high quality conductive films comparable to those produced by PVD routes. This has turned out to be the case here as well. There have however, been some notable successes in this area, both with the synthesis of precursors and even the film formation. The focus at the University of Minnesota was both on the development of nanoparticle based and solution based precursors. They have attained probably the best control of ZnO nanoparticle synthesis to date producing high quality mono-disperse particles as shown in Figure 8.

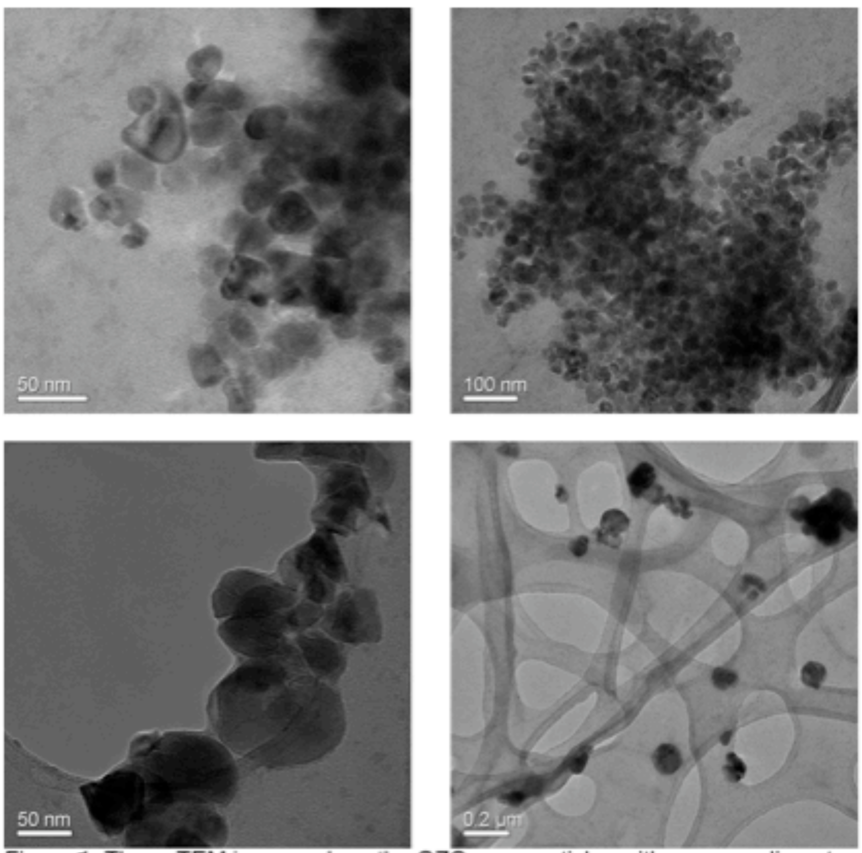

Figure 8: These TEM images show the GZO nanoparticles with average diameters of 30 nm (top images) and 50 nm (bottom images). The particle diameters were confirmed by x-ray diffraction (not shown).

Key has been the ability to produce both doped and undoped particles. Especially important has been the demonstration of Ga doped particles. These appear to be more processible than the conventional Al-doped materials. The actual device configuration employes an undoped and a thicker doped layer. While conductivities are not yet sufficient the approach is quite promising. One of the key elements is the ability to process at relatively low temperatures.

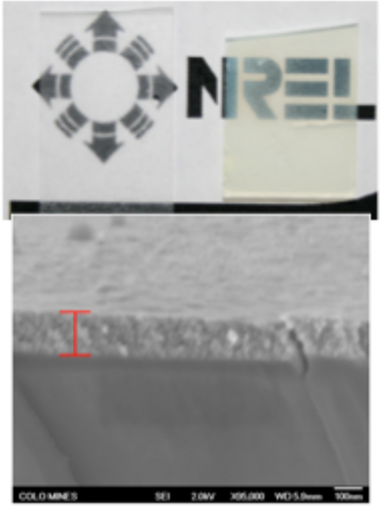

Figure 9 shows the transparency and mophology for an amorphous InZnO film from a binary precursor.

NREL has been investigating the InZnO amorphous oxide TCO system by solution means. Figure 9 shows an example of a film with 200 S/cm made with an NREL binary precursor containing the optimal In and Zn molecullarly. This is very exciting as the film are quite dense and transparent.

- Task 5: Inkjet system development

This task area was to develop a high throughput approach to the deposition of the precursor materials. The initial approach was to use ink jet printing. This proved not to be able to produce high quality films and to require far too much optimization of the ink formulation. This is primarily due to the fact that the small drops (picoliters) are delivered by drop on demand and this yields individual drying rings which do not integrate easily into a dense precursor film. As an alternative we developed ultrasonic spraying to deposit layers. In this approach a sonic transducer breaks up the precursor ink into picoliter droplets which are then deflected by an inert gas in a broad stream to the substrate as shown in Figure 10.

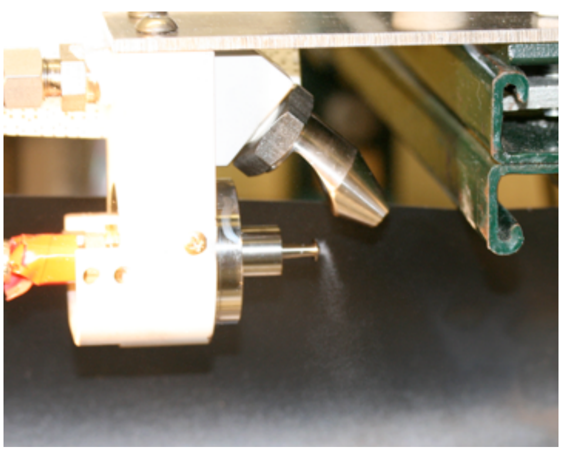

Figure 10 shows the ultrasonic spray head spraying a binary InSe precursor.

This technique has proven so successful that not only is it being looked at for this commercial application but it is being employed in 4 other technology areas.

- Task 6: Solar cell processing

Solar cell processing was initially problematic as the CIS group was moving it laboratories and we lost the capability completely for a significant amount of time. Eventually their capabilites were restored but in the interim we developed some of these capabilities and relied on Heliovolt for the remainder. Thus the device development did not advance as rapidly as possible. None-the-less we have been able to obtain over 5% cells by the binary multilayer approach and recently over 2% from the combined ink as is shown in Figure 11.

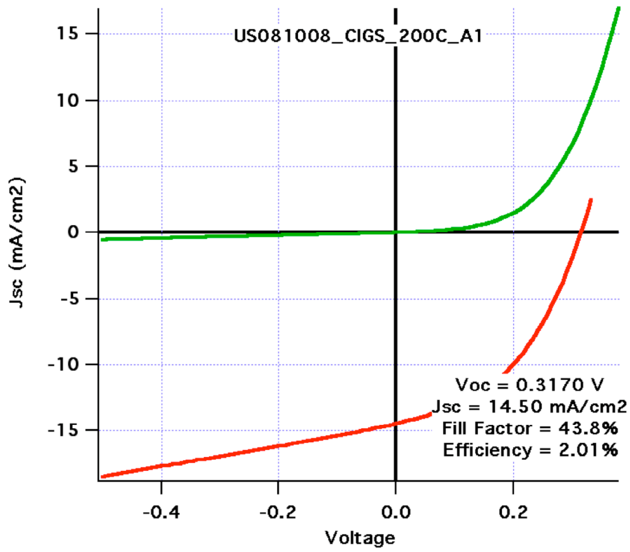

Figure 11 shows very recent results for a solar cell produced from the ternary Cu-In-Se ink. This has produced a 2% cell.

These results have shown that viable devices can be made from a solution based, all atmospheric approach with no selenization step. This was the key objective of this project. Analysis of materials and devices has shown that a key focus is to improve the stoichiometry of the films to the optimum for CIGS, to maintain the film morphology, and to improve the ink formulation to be manufacturabe.

Other outcomes:

- Heliovolt – we have through-out continued to work with Heliovolt, who have been very supportive both financially and with staff and technical support. This relationship has been crucial to the success of this project and has clearly benefited both and has been very successful in developing a transferable technology. This has also led to subsequent relationship with printer and ink companies that is leading to a consortium for the development of this technology.
- Students – this program has clearly been instrumental in supporting students at both the Colorado School of Mines and at the University of Minnesota. Especially Jennifer Nekuda, who did her whole thesis as part of this project and she did successfully defend her PhD work in June and is now a postdoc at Imperial College in England. This work has resulted in two publications, one IEEE and one JMR, there were also 6 presentations at national meetings. Due to the very high interest in IP, publishing papers was not the highest priority. Three students were also supported at the University of Minnesota and there are two papers coming out of this work as well.
- Patents – there have been 4 patents applied for from this program and there are also 4 more disclosures in process that will be applied for this year. These are already being negotiated for by Heliovolt and will be also made available to our new partners in printer and ink technologies.

- Papers – as above there are 2 publications and 8 patent applications from NREL/Heliovolt and 2 publications from the University of Minnesota
- Awards – the program has been awarded a number of awards based predominately on the development of the Hybrid CIGS Technology jointly with Heliovolt. These include: an R&D 100 Award, an Editors Choice R&D100 Special Award and a Federal Laboratory Consortium Technology Transfer Award.

Future Directions:

Despite the end of the XCEL funding, which we will truly miss as it was enabling for the development of the program, we will be continuing this effort with both DOE-PV and Heliovolt Funding. As Heliovolt moves into commercialization, we will need to continue to optimize the inks and process parameters for the absorber layers. This has now resulted in two new generations of optimized inks with less waste, greener constituents and lower cost. This is now being augmented by new partnerships with printer and ink/chemical companies for the inks supply side. We will continue to research the development of TCO's by solution processes. In many ways this is the "holy grail" of solution processes. Nominally, it is possible to get transparent moderately conductive films, but historically is has been very difficult to get very conductive films. We believe that the other cell components are relatively well under control. We have very high quality metallizations and we have the good interface layers. We have not and may not be able to do the Mo layer, however, to date people have had great success at using stainless steel substrates. Our major thrust over the next year, will be a clear focus on facilitating technology transfer and pilot line success.

LEGAL NOTICE

1617 Cole Blvd. • Golden, CO 80401-3393 • (303) 275-3000
NREL is operated by Midwest Research Institute • Battelle