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MILESTONE REPORT # 2

Project Title: **Cost-effective Pilot Line for Flexible PV Modules**		
Contract Number: RD3-53	**Milestone Number:** 2	**Report Date:** 10/22/2009
Reporting Period: April 23, 2009 to October 22, 2009		
Milestone Description: Scaled CIS Absorber		
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Congressional District: 24		

LEGAL NOTICE

PROJECT FUNDING WAS PROVIDED BY CUSTOMERS OF XCEL ENERGY THROUGH A GRANT FROM THE RENEWABLE DEVELOPMENT FUND

MILESTONE 2 SUMMARY REPORT

Executive Summary

The project leverages the results of InterPhases' RD-78 project to realize a commercially viable solar cell technology for large-scale renewable electricity generation. On the path to achieving a cost-effective manufacturing-oriented design for pilot production of PV modules, the new project seamlessly integrates the results of the completed RD2 project. The R&D is currently progressing along a dual path of process scale-up and simultaneous optimization, aimed at building a strong base for the pilot production. Along with process scale-up and pilot line development, we have been developing ways to improve device performance. Considering that the electronic and structural quality of the copper indium selenide (CIS) films is critical to the device performance, we continue to improve its deposition and recrystallization. The latter step exploits the emerging annealing technologies to increase the grain size of the CIS films.

In parallel, the research continues to simplify fabrication, increase device stability and further reduce costs of large scale solar cell production. Fruitful relationships have been established with equipment vendors to develop a reel-to-reel deposition system and other necessary processing and characterization tools. A detailed characterization task has been launched through various collaborations in order to better correlate the material and electro-optical properties with the PV performance. We have made considerable progress on the tasks, directed at achieving the Milestone 2 goal, for developing strip cell fabrication. The current research primarily focuses on:

- Developing solution-based method for efficient junction formation
- Depositing compatible buffers for efficient strip device
- Devising deposition process and equipment for a conducting transparent window
- Characterizing electro-optical properties of the films and junctions.

To make the next leap forward from the current level of performance, the project is drawing upon new developments in nanotechnology, taking advantage of the highly ordered nanocrystalline grains of our electrodeposited CIS films to produce super-efficient solar cells. Our unique results for electrodeposited CIS films present an excellent opportunity to combine nanotechnology concepts with 3rd generation (3G) PV device structures. Such devices can access a broad absorbance spectrum for maximum solar energy conversion as well as reduce many losses that typically occur in a conventional *n/p* based device. In conjunction with process scale-up, we also investigated the fabrication of advanced device structures, associated deposition parameters and interface and junction properties during this period.

Technical Progress

The project carried out further research on Tasks 1 and 2 and initiated Task 4 research. The research performed on several subtasks (1a-d) substrate/absorber processing, (2a) junction formation and (2c) characterization, extended the project results beyond the scope of Milestone 2. New subtasks, initiated this period include (2b) window deposition, (4a-c) R2R designs for absorber, RTP and buffer processes.

1. Absorber Processing and Analysis

Absorber deposition analysis showed excellent composition uniformity over large areas. To advance the R2R system design, further investigations were conducted to determine the effects of various parameters on the CIS film properties, and understand the relation between the parameters, the film morphology and the different mechanisms of film formation and decomposition. Effects of altering components of the processing equipment and deposition conditions on the properties of the electrodeposited films were investigated. For example, by using alternative lower-cost deposition schemes of CIS films on different substrates, we achieved interesting technical results with various degrees of practical success. The modifications invariably require re-adjustment of process parameters. A pre-requisite step to monitor the electrode/electrolyte reactions voltametrically was implemented. It can detect potential shifts resulting from altering system components before the deposition. Subsequent processing of the electrodeposited CIS films is proceeding via two alternate paths:

- **Path A** investigates new methods to re-crystallize the CIS into large grained crystalline films.
- **Path B** takes advantage of our unique nano-crystalline CIS films to advance PV technology to very high efficiency 3G PV cells.

Path A. Effect of Process Parameters on Recrystallization

Various radiation sources such as IR, laser, flash lamp and thermal, were used to study ultra fast annealing effects and parameters. Special equipment was designed to improve the crystallinity and performance of the CIS precursors. Sharp XRD peaks indicate various degrees of crystallization as a function of source power, Fig. 1(top). Annealing leads to insignificant grain growth at low power, Fig. 1a but changes the surface morphology at high power, Fig. 1b. The sheet resistance drops by several orders of magnitude, indicating that the film undergoes sintering and particle agglomeration as it melts and compacts. Based on the flash lamp and laser anneal results, a wide range of pulse durations for ultra fast heating can also be applied without significant decomposition or grain growth. Controlled cooling and preheating, necessary to achieve further crystallization is being implemented.

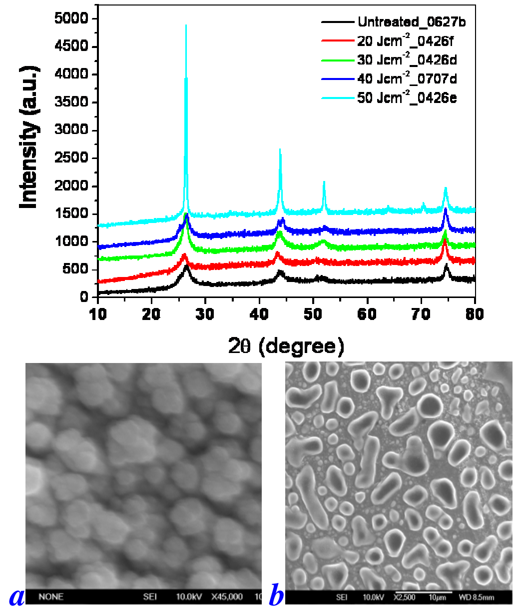

Figure 1. XRD (top) and SEM (bottom) of CIS surface (a) before and (b) after high power annealing.

Having established the standard annealing parameters such as time, temperature, atmosphere, cycles, this task has advanced to investigate RTP effects in conjunction with new process parameters. The results show:

- RTP of high quality CIS precursors produces very little composition change or Se loss. High quality CIS films, characterized by near stoichiometry and compact shiny appearance, tend to be thin and show high *n*-type photocurrent uniformly across the entire area of the sample. RTP of thick, Se-rich films leads to some Se and In loss, and *p*-type photocurrents, depending on film compactness. RTP under vacuum decreases Se content and the resistivity by an order of magnitude.
- Se minor phase that may present in Se-rich CIS films may be reacted with a thin layer of Cu to form Cu_xSe compounds which are known to promote large grain formation.

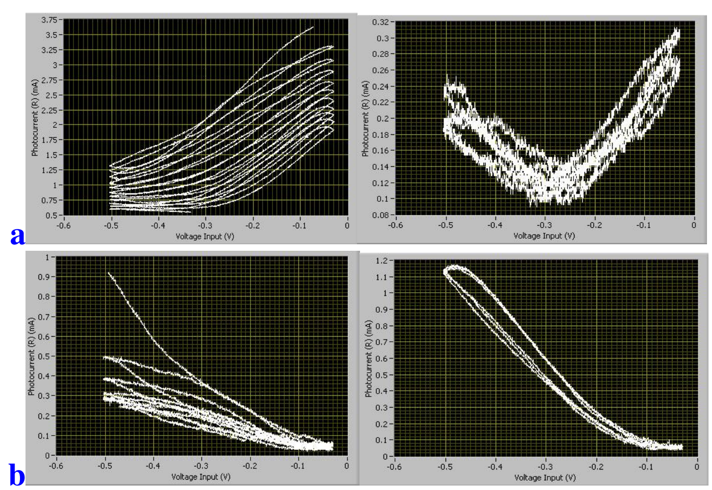

Figure 2. Photocurrent-voltage curves show (a) type conversion for *n*-section and (b) *p*-enhancement for *p*-section of CIS film after Na treatment.

- Na present in glass substrates is known to enhance crystal growth during CIGS formation. Notably Na doping has different effects on *n*- and *p*-type films. Na suppresses the photocurrent for *n*-CIS and enhances *p*-type photocurrent indicating that Na annealing induces *p*-type conductivity, Fig. 2.

Path B: Alternate CIS Structures and Devices

This path takes advantage of the special morphology for our electrodeposited CIS to produce new device structures suitable for 3G concepts. Notably, nanocrystals tend to be perfect, pure phases because there are simply not enough lattice positions in the nano volume to accommodate any impurity atom. Any deviation from stoichiometry would destroy the nanocrystal structure. Unlike large crystals, the process of nanocrystal formation tends to exclude impurity atoms. Nanocrystals are also difficult to dope for the same reason that they do not like to accept impurity atoms that can destroy their crystal structure. Nanocrystal based 3G solar cells offer a potential route to utilize much of the solar spectrum to achieve super high efficiencies.

We have investigated a number of new device components and structures in order to adapt our technology to such devices. Various types of semiconductor films that meet the requirements for the 3G device components have been deposited. The deposition parameters were adjusted to achieve the desired CIS composition and conductivity type for each layer. Various device structures were fabricated by using sequential electrodeposition and RTP annealing steps for each layer to produce new multi-component configurations. Junction characteristics were evaluated to determine if they are blocking, rectifying, Schottky diode, ohmic or shunted. The results will be included in future reports after addressing appropriate patent issues.

2. Electrical Characterization of Device Components

Table I. Sheet resistance after various process steps

Process step	Resistance
As-deposited	0 - 20kΩ/sq
Anneal	0 - 5kΩ/sq
Surface treatment	2 - 7MΩ/sq
Device on foil	50 - 250Ω/sq
ZnO on glass	2 - 120kΩ/sq

Characterization of devices during various fabrication stages is necessary to assure high performance. Various cell components, junctions and devices were characterized by measuring
(a) photocurrents with electrolytic or solid state contacts, and
(b) sheet resistance using four point probe method.

Deposition of each device component was followed by an annealing step. The samples were analyzed after annealing, surface treatment, buffer deposition and window deposition. The photocurrent data indicates the conductivity type of the film and electronic quality of the junction, Fig. 2. Sheet resistance was mapped after deposition of each device component layer, e.g. absorber, junction, buffer, window to determine electrical uniformity across the sample. The as-deposited samples show relatively uniform resistance attributed to uniform growth. The sheet resistance decreases after a brief air-anneal, and increases after surface treatment, Table I.

3. Sputter deposition of conducting transparent ZnO window

ZnO window deposition, the final device component, currently requires a vacuum sputter deposition step. High transparency and low resistance are critical requirements to achieve high performance devices for this ZnO layer. The sheet resistance of as-grown ZnO:Al layers was measured and mapped to verify the

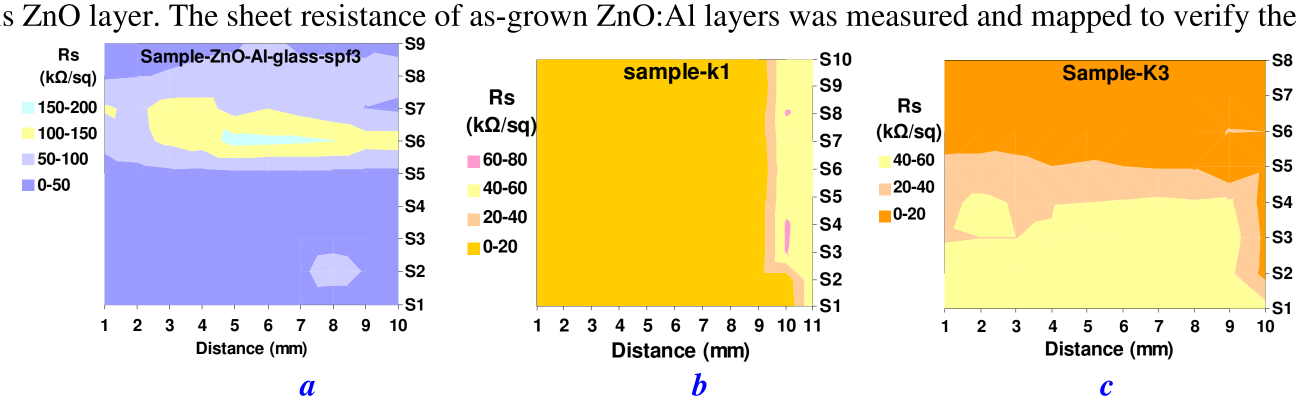

Figure 3. Sheet resistance mapping for outsourced (a) ZnO/glass, and in-house (b) ZnO/Si, (c) ZnO/glass

homogeneity of the samples in terms of doping and thickness uniformity. Since this ZnO deposition step has been outsourced to date, it was important to determine its homogeneity. We have now set up an in-house sputtering system to provide better control of the window layer. System parameters are being investigated to deposit suitable TCO and metal contacts to the CIS cell.

Sheet resistance mapping for outsourced and in-house deposited ZnO films is compared in Fig. 3. Wide variations in resistance from 2–120kΩ/sq were found for the ZnO/glass control sample, Fig. 3a. Better uniformity was obtained if the same ZnO was coated on device structures, Table 1. Even the initial films deposited in-house indicate better uniformity in the sheet resistance. The ZnO films deposited on Si substrates appear more uniform than that on glass substrates, Figs. 3b and 3c. The resistance of the initial ZnO layers was in the kΩ/sq range. Subsequent films obtained by varying the RF power, chamber geometry and pressure improved the conductivity for *n*-ZnO films by ~ orders of magnitude.

i-ZnO films were also grown under the same conditions except for introducing oxygen into the sputtering system. The oxygen doped ZnO layers show very high sheet resistance in the high MΩ/sq. After annealing in air at 350°C for 6 hours, the sheet resistance of the samples increased to the MΩ/sq range, due to oxidation of ZnO:Al layers. No physical damage is observed, indicating mechanically strong layers.

4. Module Fabrication and Pilot line Development

Investigation into materials and equipment requirements for module design and pilot line development are being pursued in order to transition our CIS PV technology to a mature production state. Many industrial equipment manufacturers and custom tool designers are just starting to develop manufacturing equipment for non-Si PV technologies. The recent Intersolar North American conference in San Francisco provided a wealth of information on new developments in the PV industry which we have been pursuing. We have investigated into competitive module designs and visited module material and equipment vendors. Collaborative discussions have been initiated with thin film module developers to determine optimum materials and designs for maximum durability and flexibility. Test houses have been contacted for standard analysis of module performance, reliability and environmental testing.

The Pilot development effort has been initiated by evaluating and developing measuring equipment, thermal processing systems, and R2R continuous plating system designs. Collaborative partnerships with the equipment developers are in progress to determine preliminary functional requirements for electroplating and annealing systems and to develop blueprints for customized systems.

5. Other Activities

The PI presented an invited talk "New Concepts for Manufacturing High Efficiency Flexible Solar Cells" at the special Lockheed Martin symposium at the 2009 Cleantech/Nanotech conference. Participation in this and other conferences and workshops led to new collaborations with technical specialists and equipment vendors. InterPhases has established new collaborations with the *California Nanosystems Institute* and *UCLA* faculty to access the comprehensive metrology and characterization services; the *University of Notre Dame* group, widely recognized for nanocrystalline structures; and pilot system developers to design custom equipment. We have recruited a *UCLA* grad student and a Post doc to carry out processing and characterization work. Various sales representatives for production equipment manufacturers visited InterPhases to determine our equipment needs. We continue to interact with potential investors and manufacturing companies that approach us to move our technology into the next phase.

Deliverable 2:

A 10cm strip sample of CIS cell has been prepared and submitted with this Milestone Report.

Milestone	Name	% Completed
1	Scaled fabrication for absorber CIS and cell	100%. Research continues to optimize and scale up the deposition and post thermal treatments for CIS films.
2	Scaled strip cell	100%. Research continues to optimize strip cell fabrication and concurrently investigate alternate materials and device configurations.
3	Module Fabrication	5%. Design module assembly and encapsulation technology.
4	R2R equipment design	15%. Designs for plating and thermal processing systems

Project Status:

Pilot development tasks for achieving low cost PV electricity with CIS solar cells are progressing on schedule.