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Project Title: **New CIS Solar Cells with All-Solution-Based Roll-to-Roll Processing**

Contract Number: **RD4-7** Milestone Number: **M1** Report Date: **8/12/2017**

Reporting Period: **July 13, 2017 – August 12, 2017**

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Congressional District: **26**

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MILESTONE REPORT

EXECUTIVE SUMMARY

The project research aims to advance the roll-to-roll (R2R) manufacturing process for the copper indium selenide (CISe) thin-film technology that was developed through prior RDF efforts, to the next stage. The principal goal for Milestone M1 is to 'Design and develop a new fast flow plating cell to improve the CISe film quality and the R2R system operation, speed and application range". This goal has been successfully accomplished during this period, with the development of a new efficient flow cell and its integration into the R2R system for CISe deposition.

The fast flow plating tank was proposed, to enable high-rate R2R single-step electrodeposition (SSE) while maintaining the special features of CISe films resulting from this process. It also aimed to streamline the manufacturing-line design. As it was the first-of-its-kind tool for deposition of semiconductor compounds, the R2R-SSE flow cell system required significant research effort to investigate the relationship between various process parameters. By design, this tool included many re-adjustable features and parts to facilitate this investigation. As anticipated, this flow plating system, along with ancillary modules for storage and overflow tanks, required several iterations of design, construction, assembly and testing to achieve a satisfactory prototype. The RDF4 research has now launched a new flow cell system that can deposit CISe films via R2R-SSE with the desired thickness and composition.

Simultaneously, the project R&D has initiated Milestone M2 and M3 work, to evolve the CISe solar cell design and operation to maximize its performance. Substantial effort was devoted to unravel the opto-electronic properties of the SSE made CISe film and test new device configurations with alternate contact materials. Realizing the value and magnitude of the CISe PV project, we have sought and established quite a few technical collaborations and partnerships aiming to expand the scope and chart a path to speedy commercialization of the technology.

Project funding is provided by customers of Xcel Energy through a grant from the Renewable Development Fund.

TECHNICAL PROGRESS

The principal objective for Milestone M1 was to reconfigure R2R SSE system into a single, compact integrated tool to deposit CISe absorber with new efficient tools for improved operation, speed and application range.

A new fast flow cell was designed and configured, to:

- allow pumping the plating solution at high speeds through a narrow channel
- obtain strong, laminar solution flow over the substrate, and
- promote homogeneity in composition and thickness of the CISe film.

The R2R-SSE process was designed to simultaneously include the steps of: rewinding the foil; pumping the heated Cu/In/Se plating solution through the flow cell in a counter direction; and applying a fixed potential to carry out the deposition.

Our previous R2R SSE process was carried out in a large volume plating tank with stationary solution, pumped and agitated with spargers. The transition from the previous version to the flow cell version was expected to present some challenges because it involved deposition of CISe compounds. Unlike standard metal deposition, the SSE mechanism for CISe compounds requires controlling several deposition parameters. The kinetics of the processes involved in the CISe compound formation are strongly affected by the solution flow speed, the flow cell geometry and a number of other process parameters. Although CISe formation is thermodynamically driven, multiple reaction paths exist that determine the final film composition, Fig. M1-1. CISe film formation takes place through a combination of chemical (C', C'', C_n) and electrochemical (E_1, E_2) reactions which can create multiple solid phases [1, 2]. The following sequence of reactions is the most desirable path for our solar cell application:

E_1: CuSe (In) $\rightarrow E_2$, C': $CuInSe_2 \rightarrow C_3$: $CuIn_3Se_5$

Thus, the new R2R-SSE system was planned with substantial flexibility in design, assembly and operation to allow testing different cell and electrode configurations and geometries, each of which offered specific advantages. For example, the flow cell allows adjusting pumping speed and volume to change the solution flow rate and deposition speed. Cell elements (anode, spacer/holder plastic bars) are designed to be removable and re-arrangeable into different configurations to alter the solution flow patterns, the rate of solution transport and the geometry of current distribution.

The project initially focused on preparing the research laboratory to carry out the RDF7 project R&D. The laboratory was outfitted with new exhaust systems, platforms to house the R2R modules and other processing equipment. Experimental setups were tested and updated, and new tools were procured. Several holding and processing tanks were constructed and fitted with appropriate electrodes, heating and pumping systems. Alternate versions of the fast flow cell were considered, constructed and tested to obtain the desired tilting for fast uniform, laminar solution flow over the foil, while minimizing pumping and turbulence.

The first version of the flow cell configured the R2R system with the pre-process and post process systems stacked in a 2-tier R2R-line design. Two tier platforms were constructed to house the post deposition sections above the pre-deposition and flow cell sections. While this design reduced R2R system footprint, it increased the complexity of design, which would not be easily adaptable to a future modular R2R system for depositing additional device layers. The design was revised to construct a linear R2R system to conform to our originally proposed linear flow cell R2R system design. This new version was compatible with future expansion. It allowed adding more processing modules at either end of the R2R-SSE system to deposit other device layers. The flow cell tilt was obtained by placing the post process modules on an elevated platform, relative to the pre-process modules. This offered more uniform solution flow over the foil. It also offered cost and manufacturing advantages for future expansion of the R2R system for fabricating devices. Several parts of the system were tweaked to optimize the fluid dynamics, fine tune the foil position in the horizontal plane, and maintain continuous solution contact to the entire surface of the foil during the operation. The system was initially tested by circulating heated water (60°C) from the solution reservoir through the flow cell into the overflow tank and back to the reservoir. The first runs showed that the flow cell functioned well, producing continuous smooth solution layer flowing over the substrate. A few leaks were detected at the joints in the flow cell after the modifications. These were readily sealed with additional silicon glue. Final inspection of the tool components confirmed that the system works properly for several hours and that the solution heating, circulation, and overflow tanks were leak-free.

The next tests involved SSE of CISe film with the flow cell and evaluation of the film composition and thickness using X-ray Fluorescence (XRF) analysis. The composition data revealed crucial information regarding the relationship of the tilt angle and the current distribution, and thus, the coverage and composition of the CISe coating. As noted, the formation of the ternary CISe compound occurs through successive reactions, Fig. M1-1. The slow kinetics of the chemical reactions C' and C_3 were found to be incompatible with very high solution flow rate. The latter tends to direct the path to the less desirable reaction for Se^0 formation *via* reaction C", as was evidenced by the large excess of Se found in the films. We took advantage of the built-in flexibility in the flow cell system to modify the cell geometry, tilt angle, electrode configurations, solution composition, flow rate, etc.

The next few iterations of the R2R plating cell/electrode configuration included successive modifications and testing of the system operation and the film composition to:

- optimize the total system design and configuration
- adjust the tilt angle of the flow cell; front side and back side dams were installed to maintain a relatively thick (>1") layer solution above the foil and enable smoother solution flow
- improve current distribution in the plating cell with new electrodes and their placement, and
- modify the flow cell design to confine the solution into a narrower area to optimize the current distribution, accommodate the top anode, and prevent back flow of solution into the other chambers.

With these adjustments, the SSE process can successfully coat the entire foil. System leak inspection and film composition evaluation was carried out after each modification of flow cell and the other components of the R2R system. The needed adjustments to both the system and deposition parameters were made to achieve leak free operation and the desired film composition. Final test runs of the complete system showed satisfactory operation of the pre-cleaning, SSE of CISe, rinsing and rewinding sections of the R2R system, Fig. M1-2. Further optimizing the process parameters and cell design produced the desired CISe film stoichiometry and good adhesion to the foil. Milestone 1 has thus achieved the proposed performance goals. Nonetheless, this tool optimization will continue as we proceed through the next milestones to optimize the process efficiency, speed and reproducibility of the total R2R system.

ADDITIONAL MILESTONES

This period we also started working on Milestones M2 and M3 for the development of annealing tool, device processing and characterization, to address the requirements for as follows:

Milestone M2: We have designed and constructed some parts of the post deposition annealing system.

Milestone M3: We continue extensive research to improve the quality of CISe by depositing the films with a small benchtop plating system to reach this milestone. This task has been also exploring new device configurations by depositing and testing alternate contact layers for the CISe devices and investigating the properties with optoelectronic tools. A number of *n*-type and *p*-type materials have been tested for compatibility in terms of post processing and band alignment with the CISe absorber. The contact layers were processed using either solution or vapor phase deposition methods.

Various new collaborations, such as the SERIIUS/NREL consortium [3] and some equipment vendors have enabled access to characterization tools which led to some interesting AFM and photoluminescence (PL) data for our films. AFM provides spatial distribution of the CIS nanocrystals. PL provides information on the band gap, impurity levels, and defects, recombination mechanisms in the semiconductor film. PL also quantifies the amount of disorder in the CISe film, by measuring its purity and crystalline quality. Comparison of the PL data with other earlier electro-optical characterization results (from AFM, EER, EQE and EBIC analysis), is revealing new insights into the unique characteristics of SSE-made CISe nanostructures. The results indicate potential for new applications in addition to solar cells.

OTHER ACTIVITIES

Some of the interactions that were initiated at recent conferences and meetings have generated some useful leads for R&D collaborations at various national and international research institutes. Relevant information emerging from several conference papers, regarding nanostructured materials is helping interpret some of the unusual results obtained for our CISe films. Also new contact materials, particularly hole-selective contacts that were described in several papers are proving useful for our PV devices. We have identified potential candidates for a device physicist position from the pool of candidates interviewed at the Job Fairs at these conferences. Some business contacts were also launched at these meetings which could present future opportunities to manufacture the PV panels.

PROJECT STATUS

Project is on schedule and within budget.

DELIVERABLES 1

a) Design specifications of the new fast flow tank.
b) 3 x 6 in CISe film sample.
c) Task 1 Performance results.
d) Milestone Report summarizing the outcomes.

REFERENCES

1. S. Menezes, Materials Research Society Symposium Proc, 426, San Francisco, p. 189 (1996).
2. S. Menezes, Electrochemical & Solid State Letters, 5, C79 (2002).
3. www.seriius.org.

APPENDIX

Table M1-I. **System leak inspection and film composition**

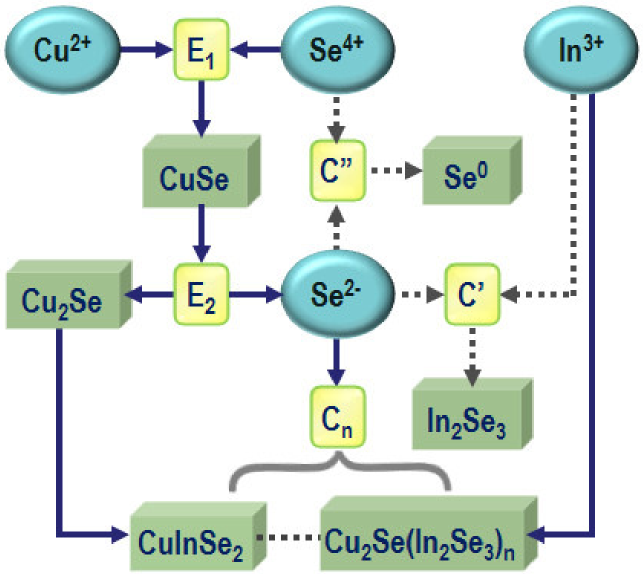

Figure M1-1. Reaction Mechanism leading to formation of ternary CISe compounds from Cu/In/Se ions. [E: electrochemical, C: chemical reactions]

Figure M1-2. R2R-SSE system with Fast Flow cell (middle) placed between pre-process (right) and post-process (left) modules.