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

Contract Number: **RD4-7** Milestone Number: **M2** Report Date: **6/12/2018**

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Congressional District: **26**

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 Milestone 2 goal was to develop the next module in building the R2R turnkey line for deposition of device quality CISe compounds in-line, targeting 2 main objectives:

(1) Devise the most efficient, compatible process that could be integrated with our R2R-SSE process

(2) Provide the most economical, safe, practical annealing tool suitable for in-line R2R operation.

The R&D effort tested and evaluated three alternate approaches: (a) selenization, (b) pulsed laser annealing (PLA) and (c) rapid thermal processing (RTP) for annealing CISe films. All three annealing methods were successfully advanced to accomplish objective 1. However, only the RTP method could meet the requirements of objective 2. This report provides a brief experimental evaluation of all 3 approaches as they relate to advancing the goals of Milestone 2 and for future expansion of the CISe PV technology scope. Based on the outcomes and cost considerations, the RTP method was selected for R2R thermal processing of CISe films. An inexpensive programmable RTP tool was designed, assembled constructed and implemented in-line for R2R processing.

Recent studies revealed exceptionally high-quality CISe films that are appropriate for novel nanostructured 3rd generation devices. Such devices offer performance, cost and processing advantages over standard planar thin film devices and hence, greater potential for commercial success. Thus, the R&D is striving to elucidate the operation mechanism and the unusual properties observed for the nanocrystalline CISe films. It is pursuing the development of new solar cell configurations, offering higher performance potential. The CISe technology has been evolving in new directions, taking advantage of new collaborations with various universities that have specialized nanomaterial characterization facilities.

Realizing the importance of the CISe PV project and the magnitude of its potential, we continue to launch and expand the roster of our national/international technical collaborations. We also seek broader exposure to our technology via technical publications and conference talks, and attracting business partnerships to expand the scope and speed up the technology commercialization.

TECHNICAL PROGRESS

To accomplish the M2 objectives originally proposed for Milestone 2, we tested alternate thermal processing modalities focusing on:

1. The effectiveness of the annealing method and its compatibility with SSE-made CISe films.
2. The complexity of the process relative to CISe chemistry and its amenability to R2R processing.
3. The economics, practicality and safety of the annealing tools that need to be custom developed.

The SSE method allows uniform coating of large foil surfaces with homogenous, stoichiometric CISe films. Thermal processing methods allow further manipulation of the film composition, grain size, and conductivity type. It allows creating different morphologies from the same SSE made CISe films for use in alternate device structures *DI* and *DII*, Fig. M2-1.

Although both *DI* and *DII* can be made with low cost R2R-SSE method, the *DII* type provides specific advantages in terms of ease of fabrication and performance potential because it can use as-deposited nanocrystalline films. *DI* needs polycrystalline *p*-CISe or *n*-CISe absorber, for use in bilayered *pn* and *np* junction, while *DII* can use nanocrystalline CISe bulk homojunction (BHJ) absorber. Thus, the *DI* device requires an additional step to recrystallize the SSE-made nano-grained CISe films into micro-grained polycrystalline films.

A number of thermal annealing methods were explored for CISe films. Successful outcomes were obtained with: (A) Furnace selenization, (B) Pulsed Laser Annealing (PLA), and (C) Rapid Thermal Processing (RTP). Characterization methods such as X-ray diffraction (XRD), scanning electron micrographs (SEM), photoelectrochemical (PEC) output, and resistance measurements were used to evaluate the crystallization extent and electronic quality of films produced by each annealing method and associated processing conditions.

A) Furnace Selenization

This approach adapts conventional selenization method to create the polycrystalline CISe morphology for *DI* device, Fig. M2-1a. It uses a high temperature furnace in a Se atmosphere to melt and recrystallize the CISe films. The selenization experiments were tested under various processing conditions that include: a sealed tube furnace under Se vapor pressure, temperature range from 350–500°C, duration of 10–30 min, substrates of stainless steel (SS), Mo foil, glass/Mo, etc. Selenization in a conventional sealed tube furnace leads to complete crystallization, producing sharp large-grained polycrystals that grow into each other to form a very tight crystalline CISe layer without pinholes, as seen in the SEM and XRD in Fig. M2-2a. However, the processing variables need to be controlled within narrow limits to avoid the issues that were initially encountered, such as film detachment and Se condensation.

Transitioning the selenization for continuous R2R annealing process actually offers the benefit of high throughput; it avoids many batch processing issues, e.g. repeating steps for loading/unloading; alternating between heating and cooling; maintaining high Se pressure inside the sealed chamber. In collaboration with an industrial partner, we custom-designed a programmable furnace for continuous web annealing of CISe coated foil through a heated chamber in Se atmosphere. The Se-furnace can use alternate heating elements such as electric coil, infrared (IR) lamps and flash lamps. This approach, however, is severely constrained by stringent environmental regulations, the necessary but complex control systems, and scrubbers due to the toxicity of high temperature processing under hot, reactive Se/H_2Se atmosphere. Due to the high cost of the furnace and for sequestering the process, we decided to defer the development of the *DI* device and pursue the development of the *DII* device.

B) Pulsed Laser annealing (PLA)

Ultra-fast PLA provides an alternate route for creating polycrystalline morphology without the complexities of selenization. PLA uses radiant energy pulses in ambient atmosphere to locally melt and re-crystallize CISe films. PLA approach is appropriate for crystallizing CISe on metal foil also for large-scale atmospheric in-line R2R processing of solar cells.

We tested several laser systems, specifications and processing parameters; and characterized the morphology and opto-electronic properties of annealed CISe films. Unlike other methods, PLA with excimer and YAG laser enables complete melting without loss of material adhesion, even at high power. The molten films condense into an amorphous structure, depending on applied energies, SEM and XRD in Fig. M2-2b. This method limits the annealing to just the surface; thus it avoids decomposition, delamination or diffusion of the substrate elements. This laser could meet the specifications for increasing the grain size without structural damage to the CISe film in *DI* and *DII* devices. Table M2-I shows the effect on the crystallite size for the CISe films. The data was computed from multiple XRD measurements for the listed CISe samples made by SSE on Mo/glass (ML-#) and by R2R SSE on SS foil (R-#). The CISe films were exposed to laser pulses of varying total and instantaneous energies. The data shows significant (up to 75%) increase in grain size at fluence >70 mW/cm^2 and other listed conditions. Modest grain growth was observed with high pulsing even at 30 mW/cm^2. Optimized temperature/time profile can enable growth of crystalline, rather than amorphous CISe grains. Specific combinations of laser energy (mJ/cm^2), wavelength, pulse width, spot size, repetition rate and melt duration can enable creating the desired microstructure from the PLA melt.

We concluded that the cost and the complexity for in-line R2R thermal processing of CISe on metal foil would need a custom designed laser with capabilities to: ▪ partially overlap scanning lines, ▪ defocus beam spot for lateral crystallization, and ▪ prolong melt duration for adequate re-crystallization. Such a customized PLA system can be fabricated in collaboration with a laser manufacturer but would not offer significant cost-advantages over incumbent thin film or Si solar cells.

C) Rapid thermal processing (RTP)

RTP processing conditions studied include: ambient air, Se atmosphere, various temperature ranges, IR lamp power, pulsing profiles, automated MILA RTP equipment, etc. RTP under Se is needed for *DI*, but RTP in air is adequate for *DII* devices. RTP in air is a far simpler and cheaper process than the selenization or laser methods. Various degrees of crystallization can be obtained by changing the RTP pulse profiles. Using photocurrent rather than crystal size as a figure of merit, we concluded that RTP in air would be the most convenient and cost effective approach for *DII* devices.

RTP needs to be limited to either low temperature or short duration to prevent the CISe decomposition. Within these conditions, CISe samples show increasing crystallinity with increasing annealing temperature, as seen in the XRD and SEM, Fig. M2-3. The grain size was estimated by using the Scherrer formula. It changes from near amorphous for as-deposited CISe to nanocrystalline grains of 4, 14 & 35 nm size for the annealed CISe samples. RTP at power of 550 W for 2.5 sec shows no visible damage to the film, SEM of Fig. M2-4a. Based on these results successful RTP temperature/time profiles were designed; these led to the high photocurrent output for both *n*-CISe and *p*-CISe films; it is in the range of state-of-the-art high efficiency vacuum deposited *p*-CIGS films, Fig. M2-4b. This result attests to the high electronic qualities of SSE made CISe films that include: nearly stoichiometric composition; compact shiny appearance; minimal composition change after RTP; and high photocurrent. Note that before RTP the as-deposited CISe films show negligible photocurrent. Thus the RTP step appears to improve the homogeneity of the charge carrier distribution without changing the grain size.

Due to the many cost and processing advantages, we developed the RTP method for R2R annealing. A stand-alone IR lamp based RTP system was constructed with the best available options to meet the listed Milestone 2 objectives, in terms of effectiveness, simplicity, economics and amenability to our R2R processing line. The tool provides unique timers to perform the required function and flexibility to:

(a) precisely select power level from 0 – 97% line voltage to create high intensity IR radiation
(b) vary variable distance from lamp to the target, and
(c) vary exposure time (1– 60 sec) and pulse frequency (15 sec –10 min).

This RTP tool was assembled and programmed for appropriate timing required for the annealing function. It was initially tested with a LED and then with an IR lamp. The system includes a power ON/OFF switch, power level control knob for IR annealing lamp, and a multi-function digital counter/timer/tachometer (CTT) with a LCD display, Fig. M2-5. Power level can be manually set and the phase angle fired Si control rectifier provides precise voltage to the lamp. The CTT can be programmed to control the exposure time with the Set 2 parameter, and the exposure repeat cycle with the Set 1 parameter. The 'MODE' key (blue) toggles between the two settings and the up and down arrow keys increase or decrease the values. Once power is ON and the two setting parameters are in place, a momentary contact switch labeled "RESET" starts the exposure time and shuts off at the end of the Set 2 parameter time. The process repeats based on Set 1 parameter. Pressing the "STOP" momentary switch stops the annealing process. All parameters are displayed on the CTT panel. Each lamp exposure cycle performs RTP.

This system provides flexibility for testing and programming the necessary functions to perform RTP for the CISe-coated foil. It was integrated in-line into the R2R system to process the CISe films exiting the plating/rinsing/drying modules, as shown in Fig. M2-6. The RTP tool was tested both on CISe films deposited by batch and continuous R2R process, using different combinations of pulse waveforms and lamp power. The film compositions were analyzed before and after the RTP. Representative data obtained for batch (B) and R2R (R) deposited CISe films are listed in Table M2-2. It shows that IR lamp power below 60% causes the minimal change in composition. At 80% power there is substantial Se ablation. Inserting diffusers or glass covers glass slide between the lamp and the sample reduces the annealing damage and allows prolonging the RTP or using higher IR power.

The project accomplished Milestone 2 objectives by providing a RTP tool that can easily, economically and successfully anneal SSE made CISe films on the R2R line. Processing parameters have been identified to produce space filling, columnar grain growth with no pin holes and photocurrent comparable to state-of-the-art co-evaporated CIGS films at a very small fraction (<5%) of the cost. RTP in air offers the advantages of higher speed, simpler processing and much lower cost relative to other recrystallization methods, including the InterPhases developed non-vacuum furnace selenization and PLA methods. These advantages for thermal processing SSE-made CISe films can easily transition into production scenario. Projected cost estimates indicate that RTP would cheaper by factors of 3 and 5 relative to our PLA and furnace selenization methods. RTP would be cheaper by an order of magnitude relative to the vacuum thermal processes of co-evaporation or selenization, used by the CIGS industry. Thus, the cost reduction by RTP far exceeds the 30% originally proposed goal. To date RTP in air is the only method that could effectively achieve all three objectives proposed for Milestone 2.

PROJECT STATUS

Project is on schedule and within budget.

DELIVERABLES

a) Milestone Report summarizing evaluation of the outcomes.
b) 1 x 1 cm annealed CIS film sample.

APPENDIX

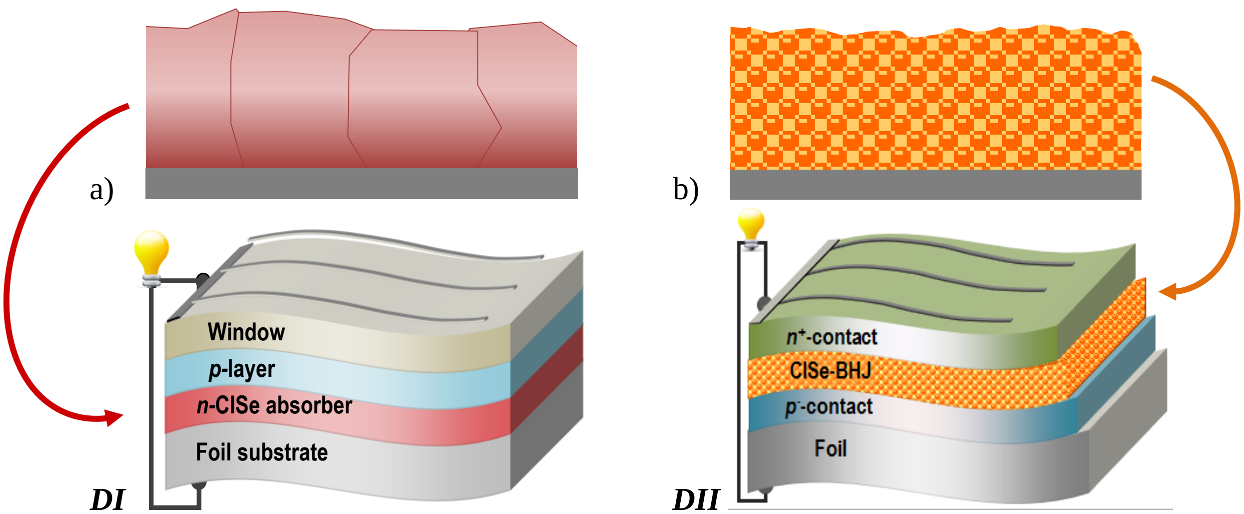

Figure M2-1. (a) Microcrystalline, and (b) nanocrystalline microstructure required for alternate thin film devices, *DI* and *DII* fabricated with R2R-SSE made CISe films.

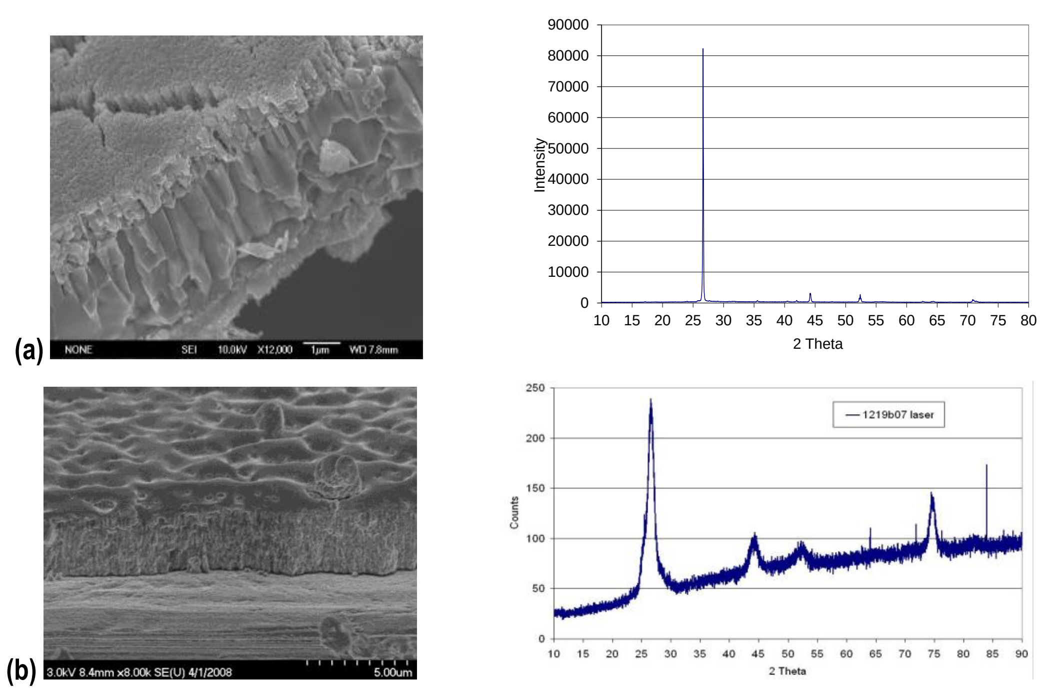

Figure M2-2. Cross-section of SEM images and XRD for CISe films by SSE: (a) selenized CISe at 500°C for 30 min (SEM), 20 min (XRD) (b) laser irradiated with 5 x 25ns 50 mJ/cm^2 pulses.

Table M2-I. CISe crystallite size (nm) increase as a function of laser irradiation parameters

Sample	Power	Time	Fluence	Total	Crystallite size (nm)		
	mW	Min	W/cm²	Pulses	As-made	Anneal	Incr
ML103	55	90	0.069	108,000	5.8(2)	10.1(1)	75%
R0109C2-2	65	40	0.080	48,000	8.3(2)	14.5(3)	75%
R0109a12-2	75	40	0.094	48,000	8.1(1)	12.6(2)	56%
ML101	70	40	0.088	48,000	8.1(5)	11.6(1)	44%
ML102	50	30	0.063	36,000	7.7(5)	10.5(1)	37%
R0109a12-1	45	120	0.056	144,000	7.9(9)	9.6(1)	21%
R0109a12-3	30	120	0.038	144,000	8.2(1)	9.8(2)	20%
R0109C12-2	50	30	0.063	36,000	5.6(6)	6.4(7)	14%
R0109C1-2	60	90	0.075	108,000	11.0(2)	11.7(3)	6%
ML105	20	120	0.025	144,000	5.5(4)	5.7(5)	3%
R0109C1-1	45	77	0.056	92,400	8.8(1)	9.1(1)	3%
ML104	40	77	0.050	92,400	4.9(6)	4.8(4)	-3%

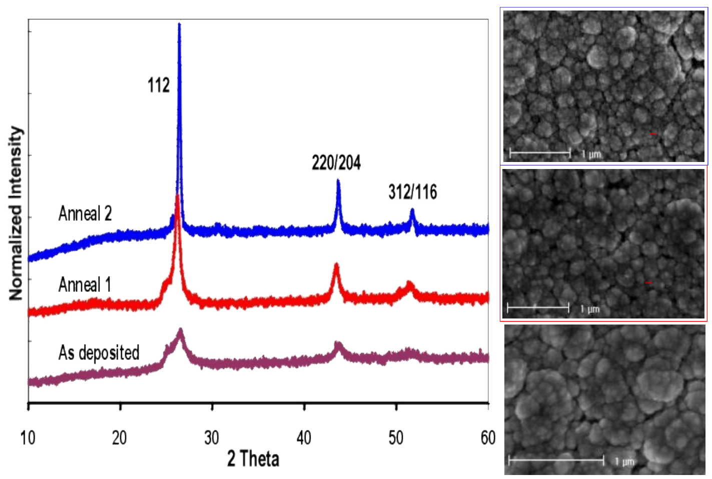

Figure M2-3. (a) XRD and (b) SEM for as-deposited CISe and after successive RTP steps.

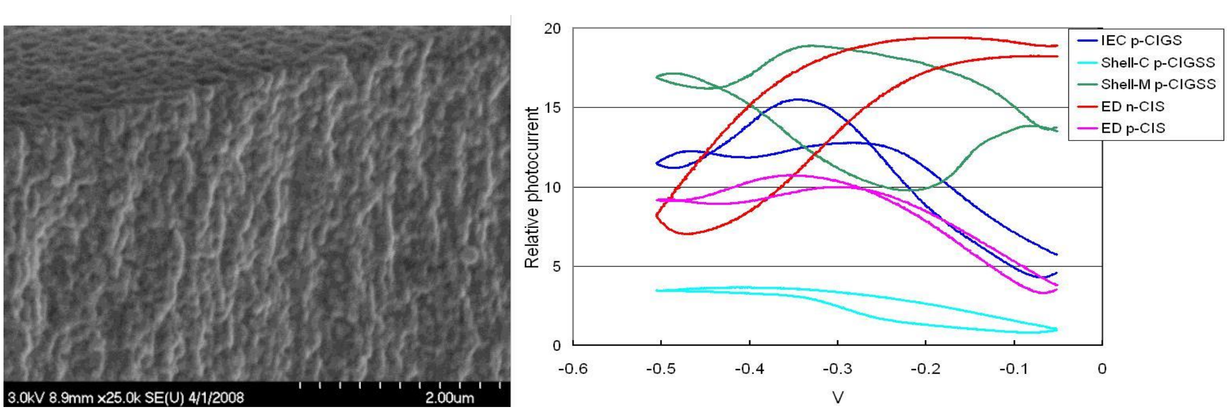

Figure M2-4. (a) SEM for RTP annealed at ~550°C for 2.5s, (b) photocurrent comparison for RTP annealed *n*-CISe and *p*-CISe films and vacuum deposited high efficiency CIGS films.

Figure M2-5. Photo of inline RTP system for roll-to-roll annealing features a multi-function controller and an IR lamp.

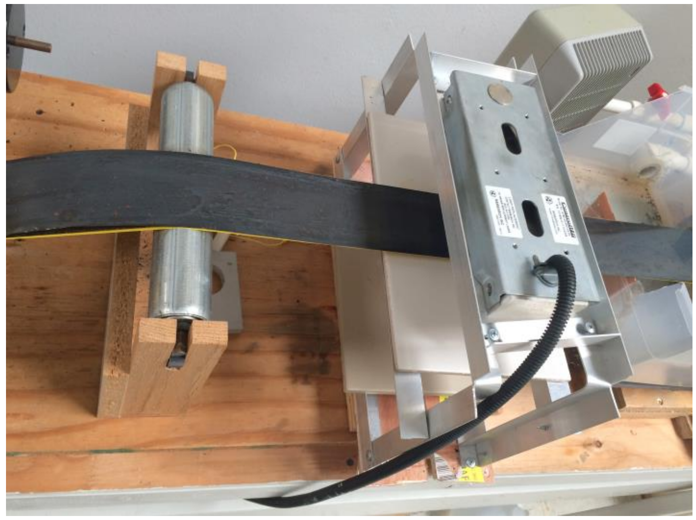

Figure M2-6. In-line rapid thermal processing with IR lamp, following R2R-SSE of CISe films on steel foil.

Table M2-2. Effect of RTP conditions on CISe composition

Sample ID	RTP conditions				As deposited	After RTP
	Pulses	On	Off	Power	Cu/In/Se	Cu/In/Se
B0514a	5	1	1	40%	1/1.7/3.6	1/1.6/3.6
R145a	7	1	1	40%	1/1.5/3.0	1/1.5/3.3
R145b	5	2	2	40%	1/1.4/3.3	1/1.6/3.5
R155a	5	3	3	40%	1/2.1/3.2	1/1.8/3.1
R155b	5	3	3	60%	1/1.9/3.7	1/1.8/3.6
R155c	5	3	3	80%	1/1.7/3.5	1/1.3/1.2
R155d	10	3	3	40%	1/1.3/3.2	1/1.6/3.4
R155e	10	3	3	60%	1/1.7/3.5	1/1.5/3.3
R155f*	5	3	3	60%	1/1.5/3.1	1/1.8/3.5

*deliverable sample