

March 17, 2004

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Re: Twenty-Seventh Monthly Report #NDJ-2-30630-11

Dear Harin,

This letter comprises the monthly technical status report for ITN's subcontract # NDJ-2-30630-11, "Plasma-Assisted Coevaporation of S and Se for Wide Band Gap Chalcopyrite Photovoltaics", under the Thin Film Partnership Program. The reported work was performed during the third month of phase 3 for this contract (twenty-sixth month overall), which is February 7, 2004 through March 7, 2004. This report describes activities performed by ITN, as well as those performed by lower-tier subcontractor Colorado School of Mines (CSM), under the direction of Dr. Colin Wolden.

## 1. Program Goals and Approach

Our primary objective under this program is to determine if the chalcogen in CIGS co-evaporation can be delivered more effectively by activation with a plasma. Possible advantages of plasma-assisted co-evaporation (PACE) are

- increased utilization of chalcogens,
- decreased deposition temperatures,
- decreased deposition times, and
- increased ability to tailor S/Se ratio.

University researchers at CSM are developing and testing the fundamental chemistry and engineering principles. Industrial researchers at ITN are adapting PACE technology to CIGSS co-evaporation and validating PACE process for fabrication of thin film PV.  $\text{In}_2\text{Se}_3$  films, which are used as precursor layers in high-efficiency CIGS depositions, were used as the first test case for the examining the advantages of PACE listed above, and significant advantages were demonstrated. Presently, the examination is being extended to the complete high-efficiency three-stage CIGS co-evaporation process.

## 2. Incorporation of PACE Sources Into Three-Stage Deposition

This month, a preliminary installation of the PACE source in the three-stage CIGS bell jar was completed. The source was installed in the location it will be used for CIGS deposition. Rate control and uniformity were verified. RF circuitry has not yet been added to the current location.

In previous months, Se from the PACE source in a test chamber was observed to follow the expected  $\cos^3\theta$  flux distribution. This month, the same flux distribution was confirmed with the PACE source installed in the three-stage bell jar. Expected flux profile was generated from the  $\cos^3\theta$  flux distribution, in combination with chamber and source dimensions and orientation. This prediction is shown in Figure 1a. For experimental verification, Se from the PACE source was deposited on glass witness slides placed across the area used for substrates in CIGS depositions. As expected from earlier tests, PACE source Se rate control was acceptable in the bell jar. Multiple thickness measurements were performed across the witness slides via mechanical profilometry. The measured flux distribution is shown in Figure 1b. Two thickness measurements near some Se-coated fixturing were omitted, as some coating appears to have originated from inadvertent heating of the fixturing. There is reasonable agreement between Figure 1a and Figure 1b, considering that there are several degrees of uncertainty in the angles between the source axis and substrate.

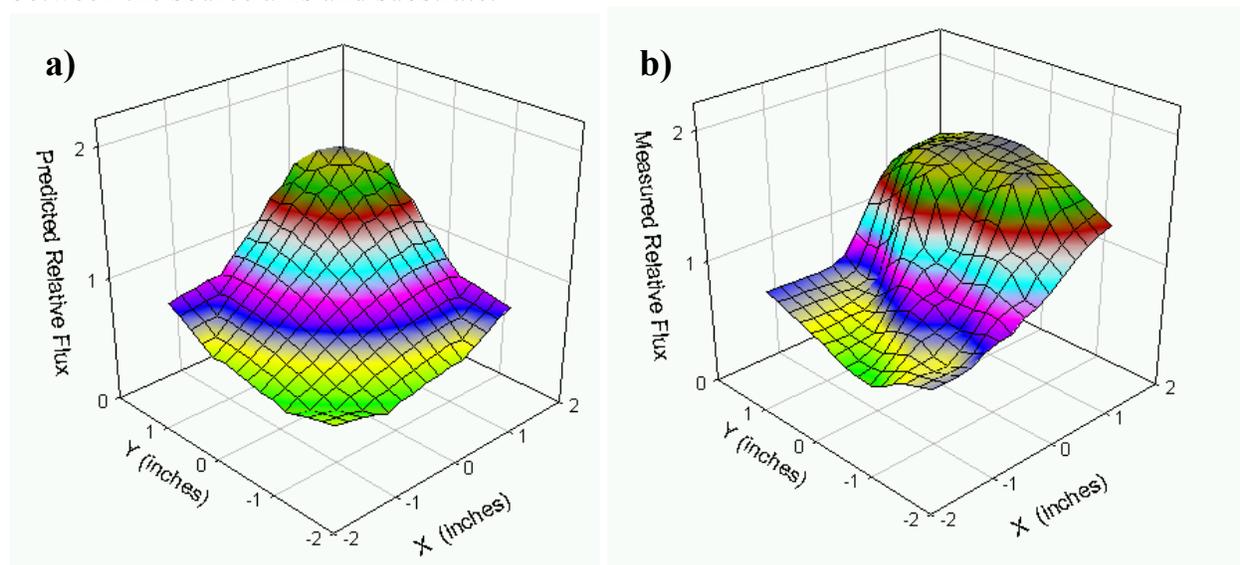


Figure 1: a) Predicted and b) measured flux distributions from PACE source in CIGS three-stage bell jar.

Agreement between measured and predicted PACE source flux profiles is significant because it indicates that the sources continue to function as expected, and because it provides guidelines for upcoming adjustments to sources. Activities for next month will include adjusting the PACE source position to center the flux distribution and maximize uniformity, controlling the PACE source using the same automatic recipes used for CIGS deposition, and beginning the

installation of RF components. These activities are proceeding on or ahead of the schedule specified in the January monthly report.

### 3. Plasma-Assisted Film Kinetics

The CSM benchtop source provides a novel and time-efficient method to map the temperature, Se, and plasma parameter dependence of film formation. Because changes were being made to the RF matching network in CSM's in-situ PACE source, most progress this month at CSM was achieved using the benchtop setup. Recent conclusions from the benchtop source are

- + Se flux is stable and well-controlled;
- + Optical monitoring of the plasma in the PACE source provides a good indication of the Se rate;
- + CIGS forms in the plasma at the minimum temperature examined, 300 °C; and
- + CIGS formation under the conditions currently examined is limited by Se exposure, not temperature.

The data leading to these conclusions are discussed in the following paragraphs.

Several upgrades were made to the inductively coupled plasma (ICP) configuration and the selenium source, which resulted in stable, well-controlled selenization experiments. The current benchtop set-up is shown schematically in Figure 2. The components involved and the experimental procedure used are the following:

- Argon enters through a needle valve that is adjusted to establish a total pressure of 100 mTorr in the system
- The stainless steel line is heated using heater H1 to a temperature of ~285 °C (T2) to prevent premature selenium condensation.
- Substrates coated with metals precursors are placed in 3 positions (S1, S2, and S3). A long foil is attached to the substrate susceptor. The susceptor is supported in the plasma by a thermocouple probe and a heating element probe. In all experiments described here, the susceptor heater was not used: The plasma itself did all heating.
- Substrate 1 (S1) is directly on the susceptor, which is placed just downstream of the ICP coil.
- Substrate 2 (S2) extends off the susceptor into the center of the ICP coil.
- Substrate 3 (S3) is placed on the pyrex tube just upstream of the ICP coil
- At this point the plasma is ignited and the system is allowed to reach steady state.
- Substrate temperatures reported here are measured by the thermocouple in the susceptor (T1). Because the susceptor is thermally isolated and surrounded by plasma it is expected to be an accurate measurement of the substrates themselves, particularly S1. By moving the susceptor, it is estimated that S2 is ~20 °C hotter, while S3, which is in contact with the Pyrex tube, is ~20 °C cooler.
- Optical emission spectroscopy (OES) measurements are taken throughout. The OES fiber optic probe is directed at the spot above S3 just upstream of the coil.
- After the susceptor temperature reaches steady state, the selenium source is heated slowly using H2 and measured by a sheathed thermocouple in direct contact with the selenium itself (T3).

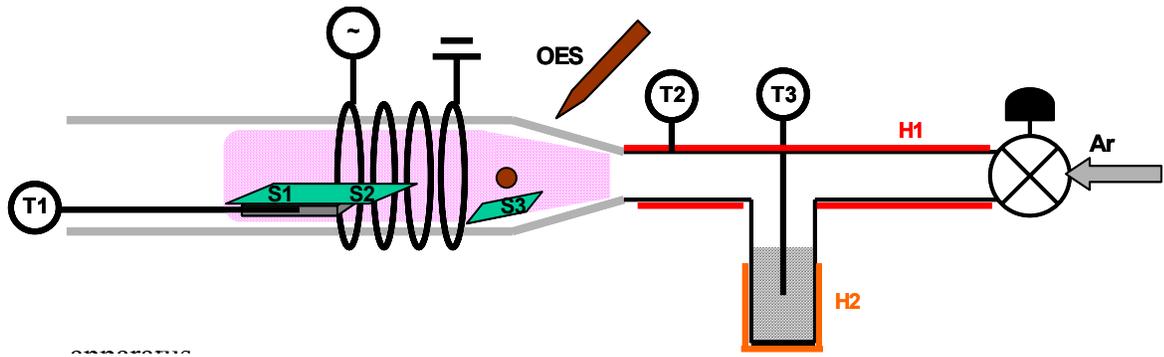


Figure 2: Benchtop selenization apparatus.

Se flux is stable, well-controlled, and monitored by OES. Figure 3 shows OES spectra as a function of source temperature ( $T_3$ ). The strong emission at wavelengths greater than 600 nm is due to argon. The prominent selenium bands located around 500 nm are only detected for source temperatures greater than about 160 °C. The Se band intensity increases monotonically with source temperature while the argon emission remained unchanged. Source temperatures  $> 260$  °C are not included in the current data, since above 260 °C the tube becomes coated with selenium and the plasma becomes unstable. The selenium density as measured by OES actinometry was found to increase exponentially with source temperature as expected. The Arrhenius plot is shown in Figure 4.

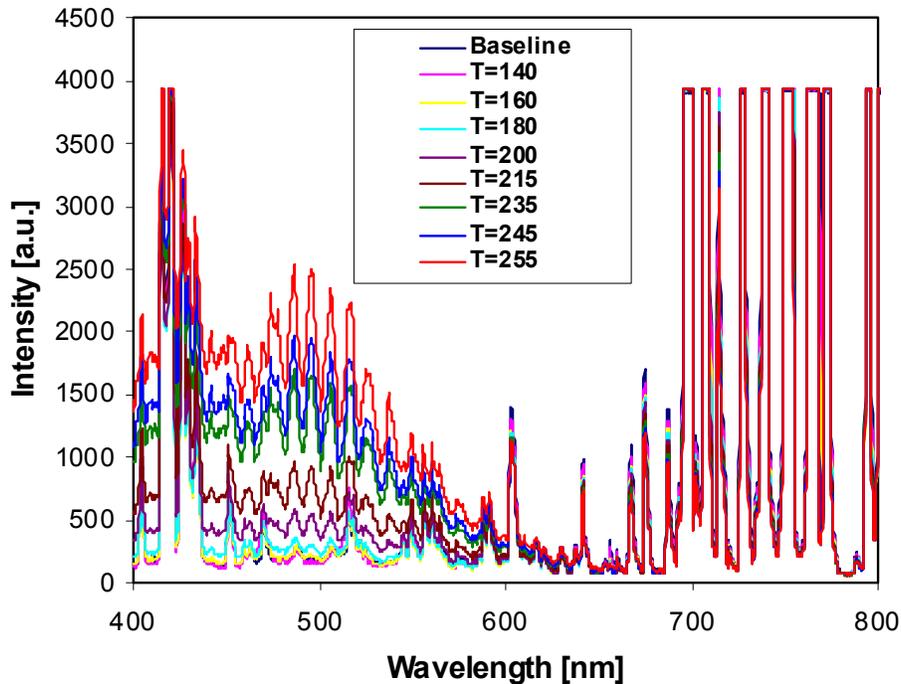


Figure 3: OES spectra as a function of selenium source temperature. Pressure = 100 mTorr, RF power = 80 W.

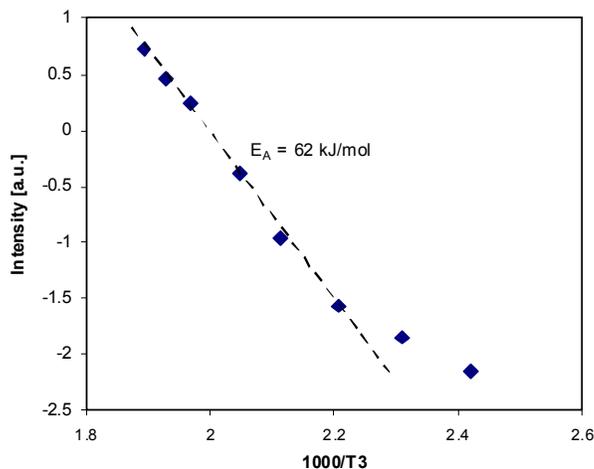


Figure 4: Arrhenius plot of selenium density as a function of source temperature. Actinometry lines are  $\lambda = 496 \text{ nm}$  for selenium, and  $\lambda = 604 \text{ nm}$  for argon.

Sputtered thin films of uniformly mixed Cu, In, and Ga were converted to CIGS when exposed to plasma-activated Se and mildly elevated temperatures. X-ray diffraction (XRD) patterns demonstrating this conversion are shown in Figure 5. The film of Figure 5 resulted from a treatment with a substrate temperature  $T_1 = 300 \text{ }^\circ\text{C}$  (RF plasma power = 80 W), a selenium source temperature of  $T_3 = 220 \text{ }^\circ\text{C}$ , and a process time of 2 hours. This is the lowest substrate temperature explored to date. In Figure 5, the top XRD patterns are from samples placed at S1, S2, and S3. The bottom pattern is from the unreacted metal precursor. All the major peaks in the reacted samples are from chalcopyrites or the Mo back contact. A careful examination of the smaller peaks has not yet been performed. Major chalcopyrite and Mo peaks are labeled on the top (S3) pattern. In some cases, splitting of the peaks indicates the existence of both CIS and CIGS, as noted in the second (S2) scan.

The data of Figure 5, and similar experiments under other conditions, indicate that CIGS formation within the currently examined process space is limited by Se exposure, not temperature. One route to this conclusion is comparing the three samples from a given test. In all cases, the order of peak intensities (and presumably degree of film conversion) is  $S_3 > S_2 > S_1$ . It is expected that the selenium density is also ordered as  $S_3 > S_2 > S_1$ , since selenium is depleted as it moves down the tube. In contrast, the sample temperatures are ordered  $S_1 > S_2 > S_3$ . Comparison of tests made at different temperatures and treatment times also supports this trend.

A number of tasks related to the data of Figure 5 will be performed in the upcoming weeks. The influences of selenium flux and temperature in controlling plasma-assisted chalcopyrite conversion will be decoupled. XRD peak shifts and splits will be more closely examined. Very small XRD peaks will be carefully compared against those measured on the binary selenides to verify complete film conversion. Results will be compared against film treatment performed without plasma assistance, and the process space related to advantageous plasma-assisted chalcopyrite formation will be more fully explored.

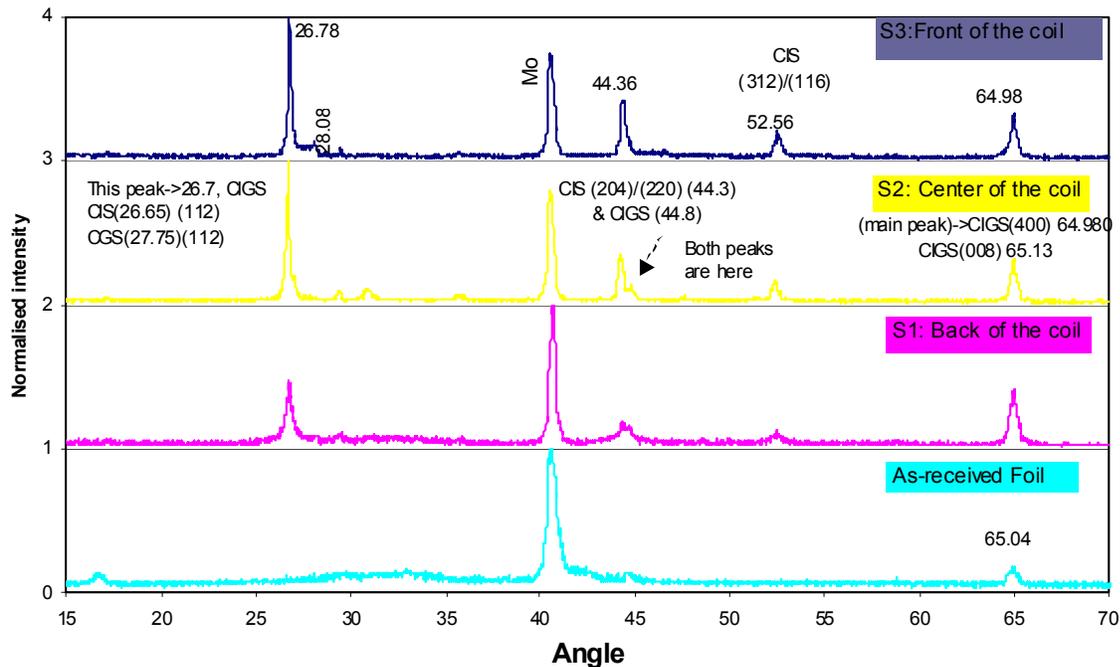


Figure 5: XRD patterns obtained at  $T_s = 300\text{ }^\circ\text{C}$  ( $rf = 80\text{ W}$ ), selenium  $T_3 = 230\text{ }^\circ\text{C}$ , and  $t = 2\text{ hrs}$ .

#### 4. Team Activities

ITN and CSM participate in CIS team activities. This month, revision of a draft outline with figures, for a possible publication describing the absorber sub-team’s study of transport-related absorber measurements, continues. Discussion of recent drive level capacitance data from NREL is also underway.

Best Wishes,

Ingrid Repins  
 Principal investigator  
 ITN Energy Systems

Cc: Ms. Carolyn Lopez; NREL contracts and business services  
 Dr. Colin Wolden; CSM technical lead