

September 17, 2003

Dr. Harin Ullal, MS3212
National Center for Photovoltaics
National Renewable Energy Laboratory
1617 Cole Blvd
Golden, CO 80401

Re: Twenty-First 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 ninth month of phase 2 for this contract (twenty-first month overall), which is August 7, 2003 through September 7, 2003. 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. In_2Se_3 films, which are used as precursor layers in high-efficiency CIGS depositions, are the first test case for the examining the advantages of PACE listed above. Gradually, this examination is being extended to the complete high-efficiency three-stage co-evaporation process.

2. ICP Source Development

As reported in previous months, plasma-activated chalcogen delivery in the co-evaporative environment is being investigated using two approaches. In the first approach, chalcogen flux delivered to the plasma is controlled mainly by the effusion source temperature. Advantages of this first approach include large source capacity and capabilities for high Se pressures. In the second approach, chalcogen flux is controlled mainly by the temperature of a hot carrier gas that flows over Se-coated plates. Advantages of the second approach include reduced thermal time constants and reduction of condensation between the Se source and the ICP device. This month, progress was made in the implementation and testing of both source designs.

At CSM, calibration of the delivery and efficacy of the ICP selenium source using hot carrier gas has begun. Preliminary screening of variables indicated that plasma power and pressure are not critical within the range examined as long as a stable plasma is achieved. These variables were fixed at 60 W and 100 mtorr, respectively. Two substrates were used in all experiments: sputtered Cu and evaporated In thin films. The thin films contained the amount of Cu or In that would be found in a typical $\sim 2 \mu\text{m}$ CIGS film. In this first round of experiments, the substrates were at room temperature. The primary variable of interest was Se source temperature, reflecting the exponential vapor pressure dependence. Heating and PID control were refined to provide very accurate and real-time control over this parameter. The goal is to provide sufficient Se flux to accomplish selenization, but not so much as to excessively coat the ICP device and compromise the plasma. This is in part why Cu substrates were used: since Cu is readily susceptible to selenization, it is a very sensitive detector to the presence of active selenium.

Source action was examined as a function of carrier gas temperature, operation time, and substrate type. Figure 1 displays the result of varying selenium source temperature on Cu selenization. No selenization occurs for source temperatures less than 120 °C. The degree of selenization is much more significant at 130 °C. Figure 2 shows a progression of x-ray diffraction (XRD) patterns as a function of time at 130 °C. Significant selenization is observed at 30 minutes, and the copper peak is nearly gone at 90 minutes. The conversion of polycrystalline Cu to selenides appears to proceed through amorphous phases: the background level increases steadily. The temperature of 130°C is likely close to optimal, as it provides sufficient selenium to selenize the Cu in a reasonable time period, and the ICP device itself remains free of deposit in the region of the plasma, allowing long-term stable ICP operation. To further refine Se delivery, a high-temperature (375 °C) metering valve will be incorporated next month. Indium substrates did not convert to In_2Se_3 , as was observed previously when placing the substrates inside the ICP device. XRD revealed a two-phase system attributed to oxide formation some time after the initial In deposition. Future with regard to In sample storage and handling will be modified to minimize oxidation.

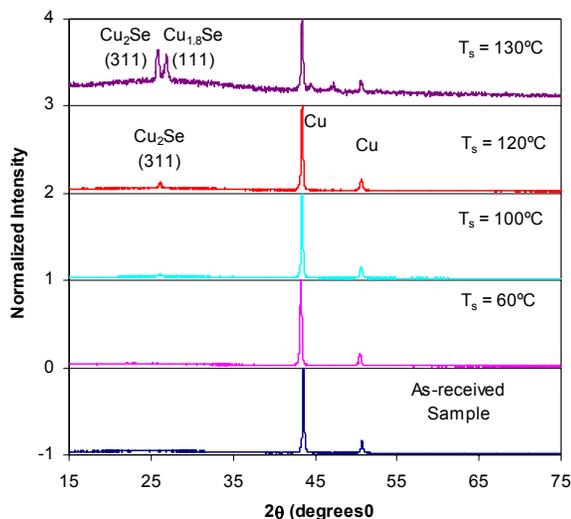


Figure 1: Copper selenization as a function of Se source temperature.

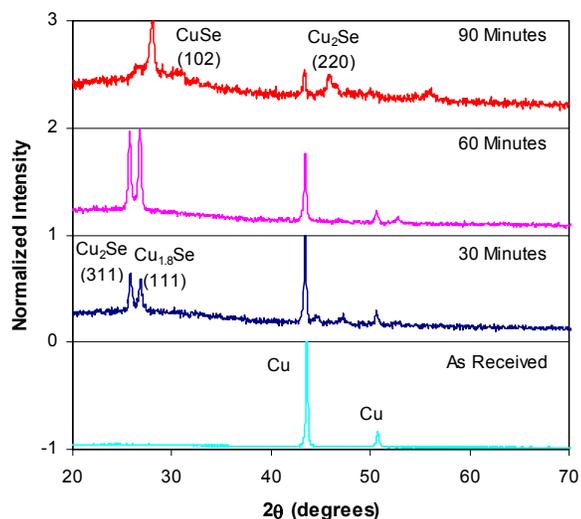


Figure 2: Copper selenization as a function of time at $T_s = 130^\circ\text{C}$.

Having demonstrated stable control of selenium vapor delivery using hot carrier gas, the next step is to look at selenization as a function of increased substrate temperature and in the presence of co-evaporated indium.

At ITN, improvements were made to the ICP source based on Se effusion temperature. Level of effort in this area was low, however, due to replacements for the broken quartz reactor tube unexpectedly requiring over four weeks fabrication time at the vendor. The Se effusion source lid was re-machined for ease of removal and better sealing. Improvements to the positioning of the effusion source heater and the ICP source Ar feed lines were also made. Installation of a quartz crystal microbalance (QCM) for rate-monitoring over the source is underway.

3. Team Activities

ITN and CSM participate in CIS team activities. At ITN, a follow-up investigation to the absorber sub-team's examination of transport parameters was completed. Admittance spectroscopy and capacitance-voltage were measured on the team devices. Results were compared among devices and with previous measurements made by the team. Data, analysis, conclusions, and recommendations were documented and distributed to the team in report format. Perhaps most significant is an apparent correlation between the defect density measured by admittance spectroscopy and the voltage shortfall (i.e. the difference between voltage predicted by the bandgap profile and that actually measured). This correlation is illustrated in Figure 3, as graphed in the report to the team.

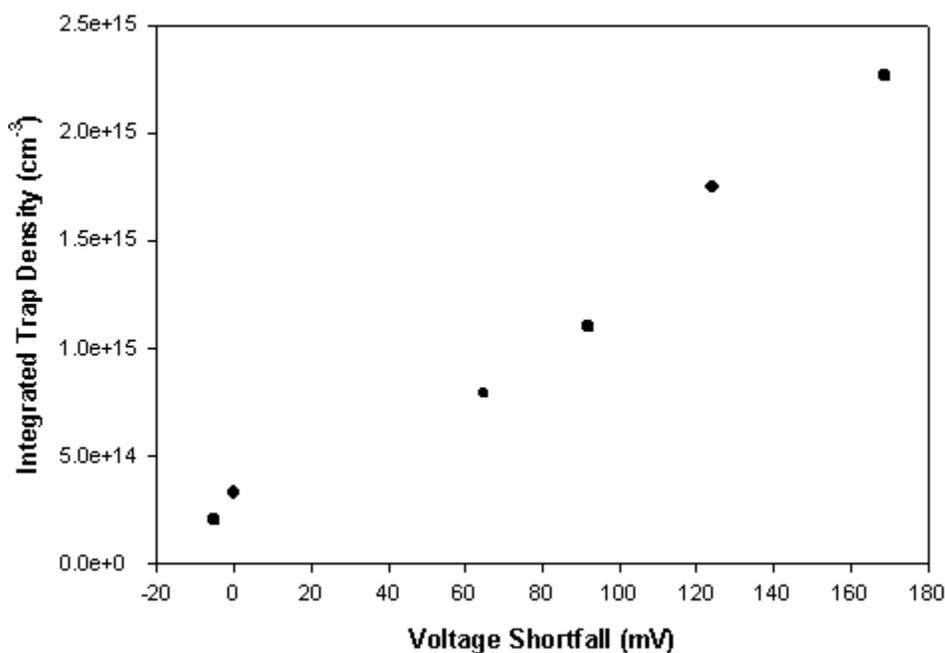
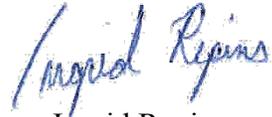


Figure 3: Integrated admittance spectroscopy trap density as a function of voltage shortfall for all team devices.

At CSM, in conjunction with team interests in both microstructure and stability, initial imaging of CIGS devices in the presence of water vapor, using CSM's Environmental Scanning Electron Microscope, has begun. The goal of using this instrument is to observe morphological or chemical changes that may occur to chalcopyrite photovoltaic structures during exposure to moisture and heat. Microscope operating conditions that provide good imaging in the presence of water vapor have been established. To date, only the top surface of devices have been imaged, which is a nanocrystalline transparent conducting oxide. There is no significant difference between images taken in the presence of inert gas or water vapor. Device cross sections are expected to be more interesting. Techniques are being developed to prepare samples for cross-section, eliminating problematic delamination from the edge of the break.

Best Wishes,

A handwritten signature in blue ink that reads "Ingrid Repins". The signature is written in a cursive style with a large initial 'I'.

Ingrid Repins
Principal investigator
ITN Energy Systems

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