
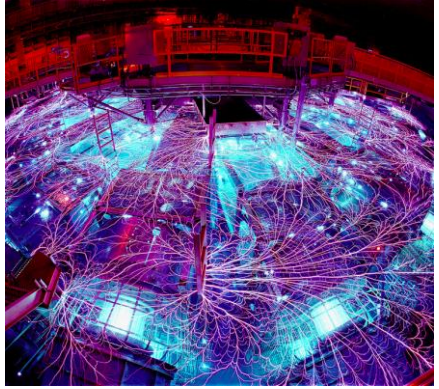
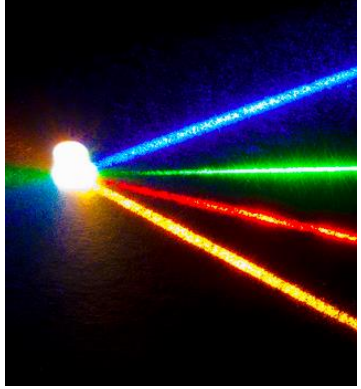
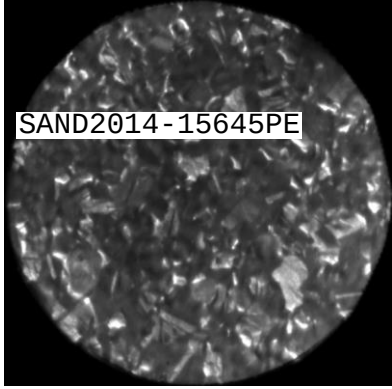

U.S. Department of Energy SunShot Initiative

Bridging Research Interactions through collaborative Development Grants in Energy (BRIDGE)

Spectroscopic Photoemission Electron Microscopy (Spec-PEEM) for Imaging Nanoscale Variations in the Chemical and Electronics States of Thin-Film Photovoltaics

Calvin K. Chan, Sandia National Laboratories
Kannan Ramanathan (Rommel Noufi), NREL
Brian Korgel, The University of Texas at Austin
Taisuke Ohta (Gary Kellogg), Center for Integrated Nanotechnologies
Normand Modine, Center for Integrated Nanotechnologies
Daniel Dwyer, Photovoltaics Manufacturing Consortium

Quarterly Update
20 February 2014

Agreement #25859

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BRIDGE Project Overview

- **Objective:** Develop and apply new metrology tool (spec-PEEM) to measure nanoscale chemical and electronic structure of PV materials and devices.
- **Collaborative Research Team**

Sandia National Laboratories

Calvin Chan (PI), Senior Research Staff
C. Bogdan Diaconescu, Post-doc
Low-energy and photoemission electron microscopy, electron spectroscopy, electronic/chemical structure, interfaces, materials/device physics

The Center for Integrated Nanotechnologies

Taisuke Ohta (formerly Gary Kellogg), Senior Research Staff
Normand Modine, Brian Swartzentruber, Principle Research Staff
Low-energy electron microscopy, theory and simulation of nanoscale phenomena, nanoscale electronic transport, nanomanipulation

NREL NATIONAL RENEWABLE ENERGY LABORATORY

Kannan Ramanathan (formerly Rommel Noufi), Group Manager
Lorelle Mansfield, Scientist
Thin-film PV materials and devices, record-setting vacuum-deposited CIGS

THE UNIVERSITY OF TEXAS AT AUSTIN

Brian Korgel, Professor, Chemical Engineering
Doug Pernik, Taylor Harvey, C. Jackson Stolle, Graduate Students
Solution-deposited thin-film PV materials and devices, nanoparticle synthesis

U.S. PHOTOVOLTAIC MANUFACTURING CONSORTIUM PVMC

Daniel Dwyer, Senior Process Engineer
CIGS pilot line, commercialization

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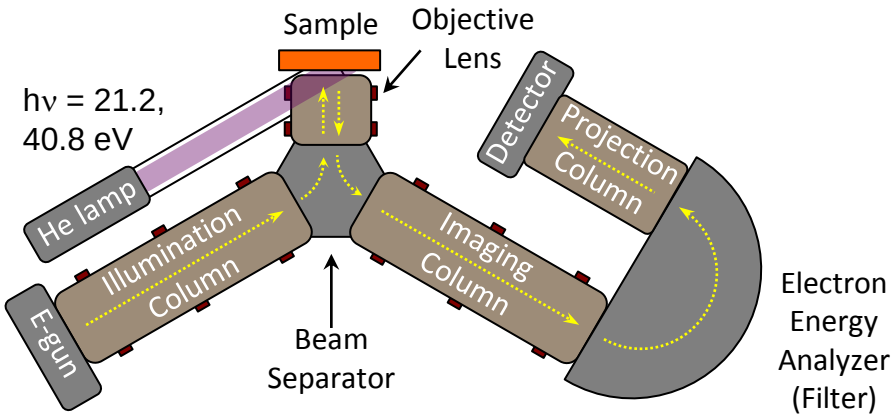
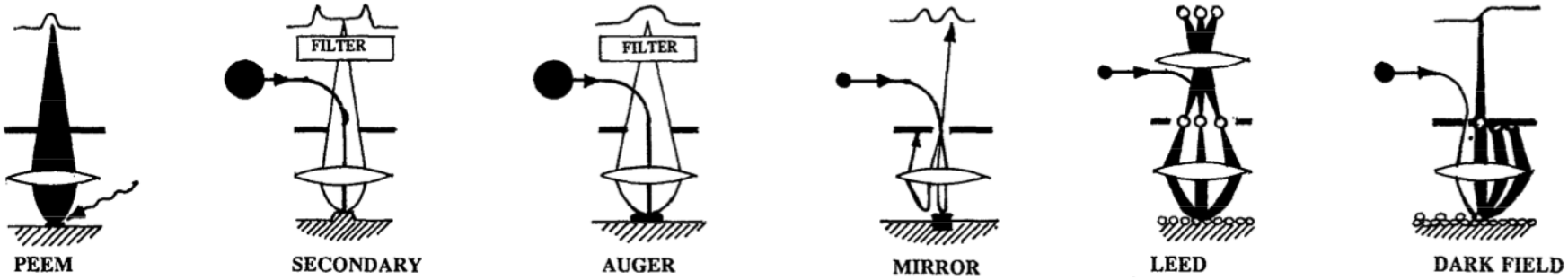
Technical Approach: Spectros. LEEM/PEEM

- **Developing and Applying Low Energy / Photoemission Electron Microscopies (LEEM / PEEM) to Photovoltaic Materials and Devices**

  Spatially-resolved electronic and chemical structure (PES, EELS, AES, SES, LEED, etc.)



- **5-10 nm spatial resolution**
- **50-100 meV spectral resolution**
- **Live-time imaging of:**
  - Surface topology and crystallography
  - Electronic and chemical structure
  - Carrier/field distribution
  - Fermi-level/surface
  - Interfacial band alignment



Veneklasen, *Rev. Sci. Instrum.* **63**:5513 (1992).

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Project Updates

- **Timeline and Budget**
  - **Budget Period 1** (January 2013 – June 2014): **$450k**
    $183k spent (41% spent over 67% BP1)
  - **Budget Period 2** (July 2014 – December 2015): **$450k**

- **Milestones for BP1**

Date	Task/Milestone	Status
Ongoing	Fabricate PVD-CIGS and NP-CIGS samples and devices; Deliver to SNL.	**Ongoing**
12/2013	Demonstrate nm-resolved chemical/electronic states in NP-CIGS films.	**Postponed/Cancelled.** NP-CIGS too rough. Focus on PVD-CIGS.
06/2014	Observe mesoscale Cu segregation at PVD-CIGS grain boundaries.	**Completed 09/2013**
06/2014	Demonstrate nm-resolved chemical/ electronic states of PVD-CIGS.	**In Progress**
06/2014	Demonstrate feasibility of dynamics studies.	**In Progress.** *In situ* real time grain growth observed. Pending analysis.
06/2014	Identify industrial partner.	**In Progress**

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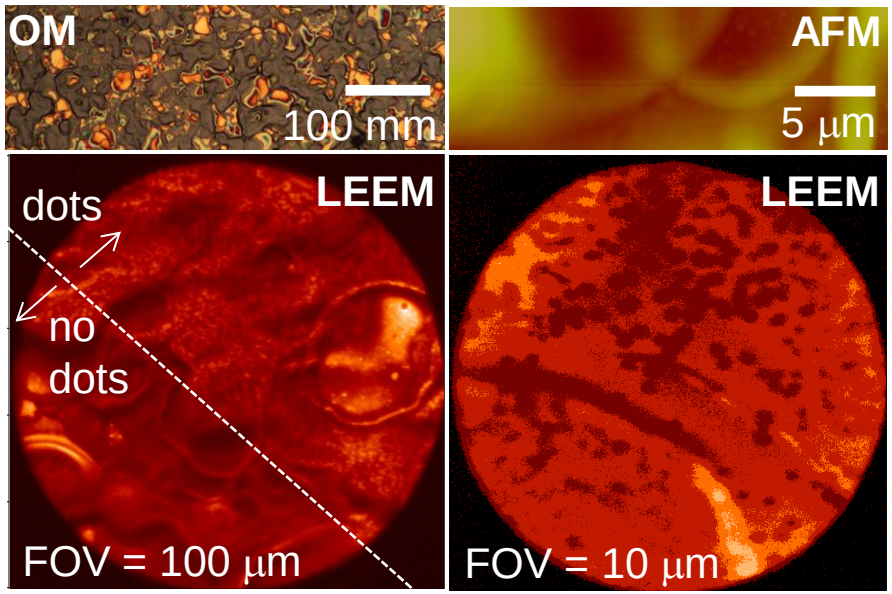
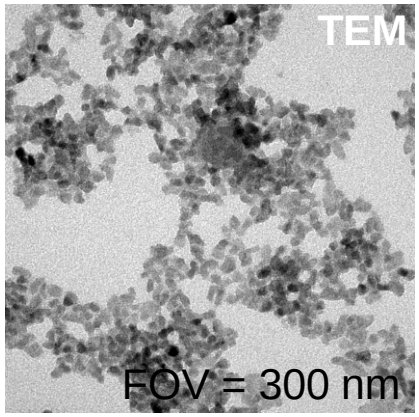
Research Highlight (Presented CY13 Q1,Q3)

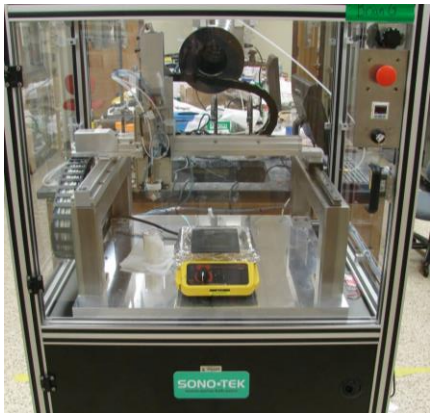
- **NP-CIGS Films**
  - OLA-capped CIGS-NC, Ga/(In+Ga) = 0.3
  - Spray deposited with Iwata hand sprayer

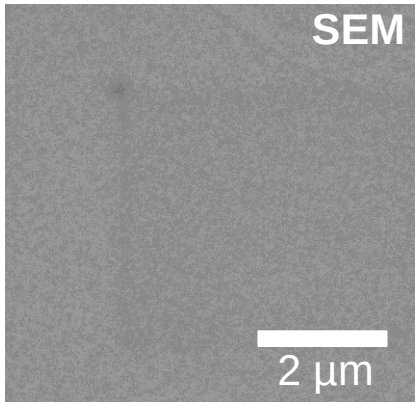


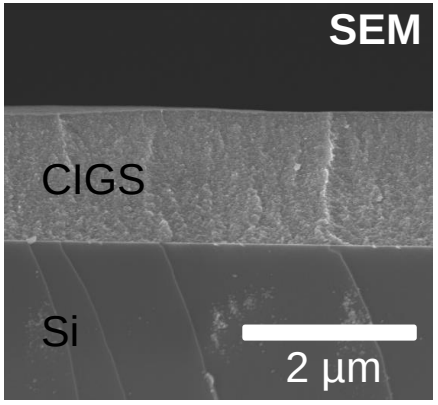
- Uneven films due to high liquid flow rates and large droplet sizes.

- Sono-Tek automated ultrasonic sprayer installed and operational at UTA (Q3).









- Smooth, crack-free, uniformly thick films.
  In queue for spec-LEEM/PEEM experiments.

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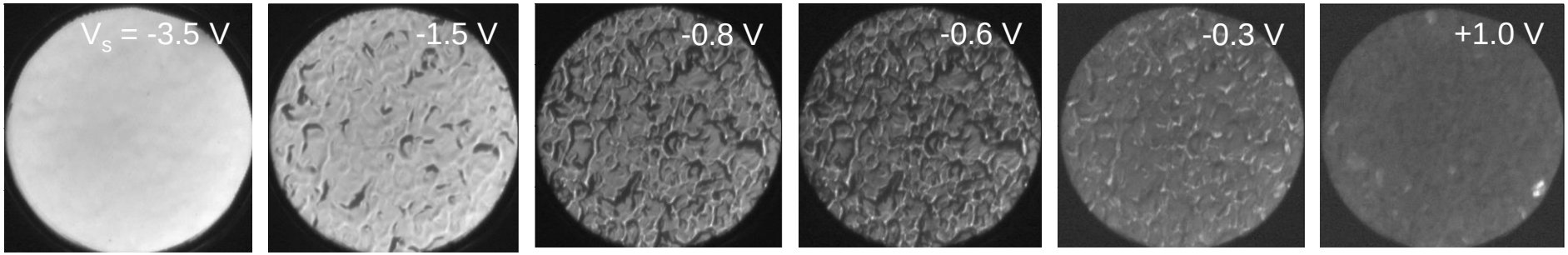
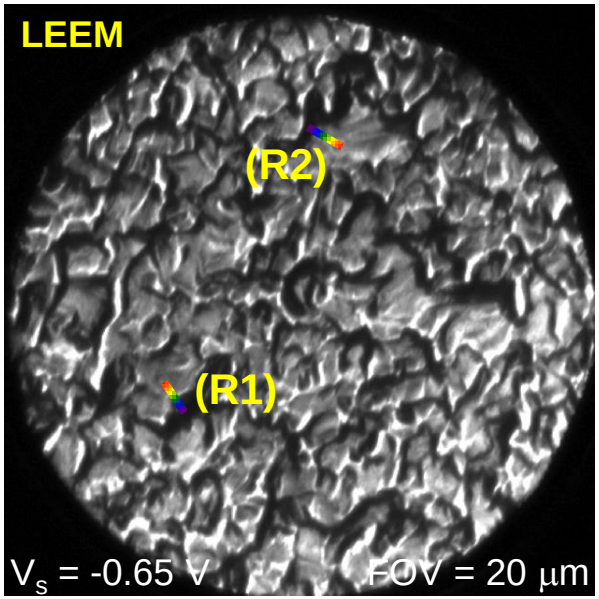
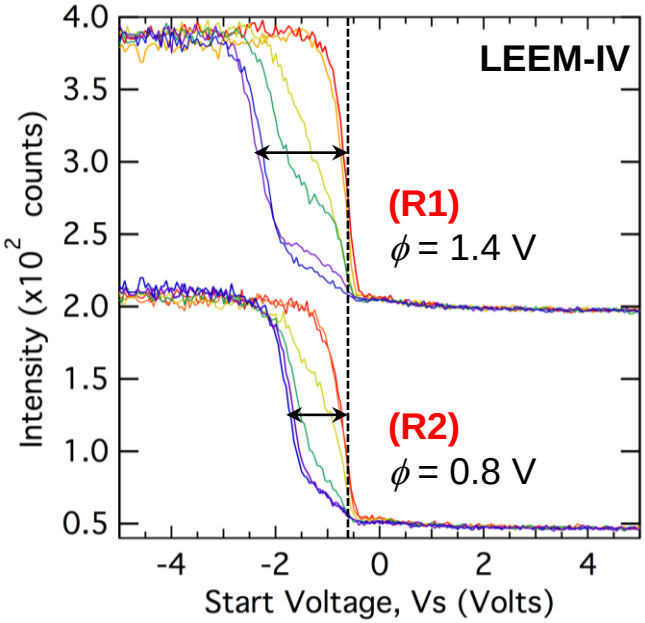
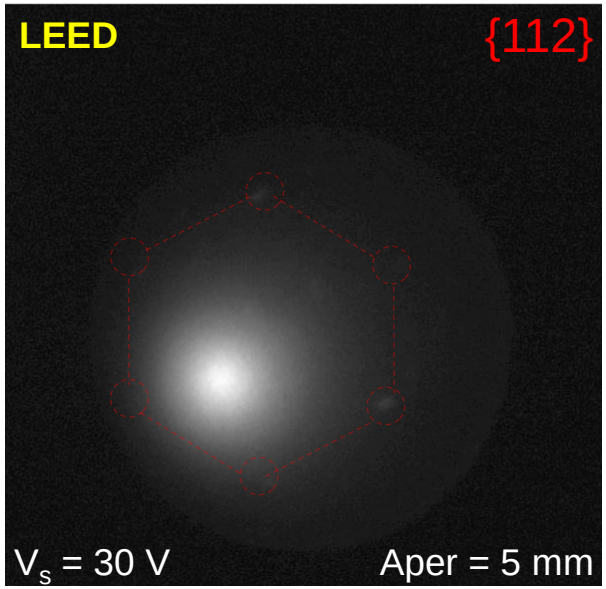
Research Highlight (Presented CY13 Q2)

- **"Work Function" Mapping with LEEM-IV on PVD-CIGS ($CuIn_{0.6}Ga_{0.4}Se_2$)**
  - Intensity (I) vs. Start Voltage (V) ⇒ Stack of images as a function of V_s ⇒ Spectrum for each pixel.
  - Varying kinetic energy of incident electrons.









Variations in the grain boundary potential: ϕ = 0.5-1.4 V (larger than other reports).

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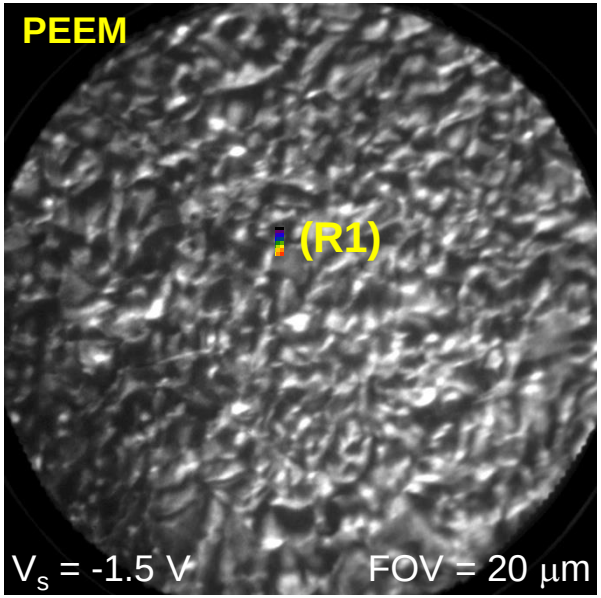
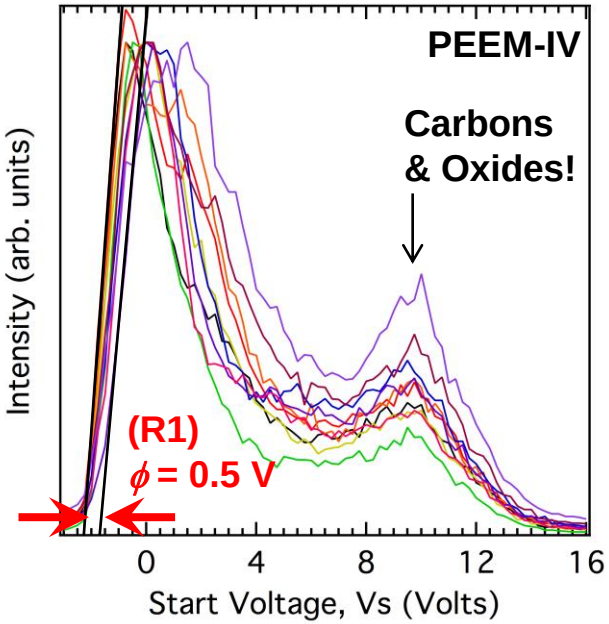
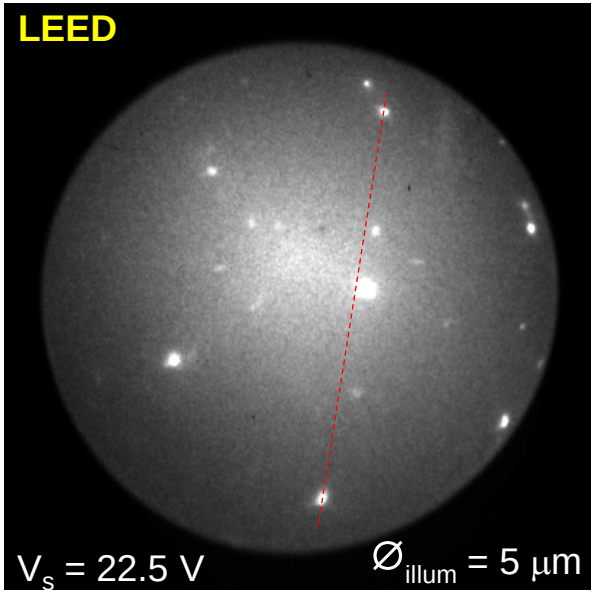
Research Highlight (Presented CY13 Q3)

- **Spectroscopic PEEM-IV Mapping on PVD-CIGS ($CuIn_{0.6}Ga_{0.4}Se_2$)**
  - Intensity (I) vs. Start Voltage (V) ⇒ Stack of images as a function of V_s ⇒ Spectrum for each pixel.
  - He lamp (21.22 eV, 40.8 eV): Very time-intensive experiment – 4+ hours per dataset.







- **GB potential from secondary electron onset: ϕ = 0.0-0.5 V (consistent with other reports).**
- **Feauture at V_s = 8-12 V: Superposition of Cu 3d, Se 4p, and Group III-oxides ⇒ Need surface cleaning procedure.**
- **Filtering out of secondary electrons ⇒ Clean CIGS {112} LEED pattern.**
- **Photoemission intensity is very low ⇒ Need higher intensity light source.**

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Future Work

- **Complete installation and verification of new high intensity light source.**
- **Perform variable photon energy spec-PEEM**
  - "Classic" photoemission method (Einstein)
  - Varies depth sensitivity
- **Meet BP1 Milestones**

Date	Task/Milestone	Status
Ongoing	Fabricate PVD-CIGS and NP-CIGS samples and devices; Deliver to SNL.	**Ongoing**
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06/2014	Demonstrate feasibility of dynamics studies.	**In Progress.** *In situ* real time grain growth observed. Pending analysis.
06/2014	Identify industrial partner.	**In Progress**

- **Think about undercosted funds: extend BP1 period/project or rollover into BP2?**

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Scientific Outputs

- **Presentations**
  - C.K. Chan, L. Mansfield, R. Noufi, "Large Built-In Potential Variations Observed at $Cu(In_{1-x}Ga_x)Se_2$ Grain Boundaries Using Low Energy Electron Microscopy," *Materials Research Society Workshop on Photovoltaic Materials and Manufacturing Issues III*, Golden, CO 09/10-13/2013 (Paper A4.08, ID 1748513).
  - C.K. Chan, G. Kellogg, R. Noufi, B. Korgel, D. Dwyer, "Spectroscopic Low-Energy & Photoemission Electron Microscopy Characterization of CIGS," *2nd DOE Thin-Film Photovoltaics Workshop*, Golden, CO 10/09-10/2013 (invited).
  - C.K. Chan, "Spatially Resolved Chemical and Electronic Structure of Thin-Film Photovoltaics," *Electronic Materials and Applications*, Orlando, FL 01/22-24/2014 (ID 1846592, invited).
  - C.K. Chan, L. Mansfield, T. Ohta, G.L. Kellogg, R. Noufi, "Evidence of p- to n-type inversion at CIGS grain boundaries: A depth-dependent surface electron microscopy study," *American Physical Society March Meeting*, Denver, CO 03/03-07/2014 (Abstract ID MAR14-2013-008781, Program Number F24.00011).
- **Program Highlights**
  - C.K. Chan, "Advanced Nanoscale Photovoltaic Materials and Device Characterization," *Sandia Research & Technology Showcase*, Albuquerque, NM 09/10/2013.
  - C.K. Chan, R. Noufi, B. Korgel, G. Kellogg, N. Modine, B. Swartzentruber, D. Dwyer, "Spectroscopic Photoemission Electron Microscopy (Spec-PEEM) for Imaging Nanoscale Variations in the Chemical and Electronic States of Thin-Film Photovoltaics," *Center for Integrated Nanotechnologies Program Review*, Albuquerque, NM 09/11-13/2013.

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