

SAND2014-15643PE

**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**  
**07 May 2014**

**Agreement #25859**

# 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

**Kannan Ramanathan** (formerly Rommel Noufi), Group Manager

**Lorelle Mansfield**, Scientist

Thin-film PV materials and devices, record-setting vacuum-deposited CIGS

**Brian Korgel**, Professor, Chemical Engineering

**Doug Pernik, Taylor Harvey, C. Jackson Stolle**, Graduate Students

Solution-deposited thin-film PV materials and devices, nanoparticle synthesis

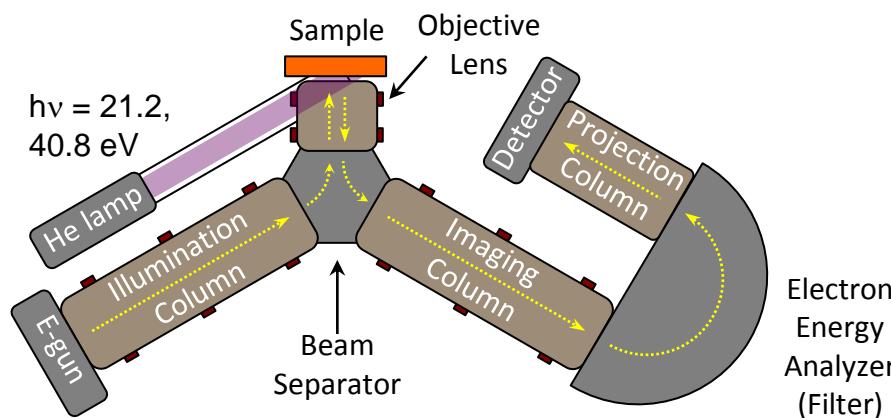
**Daniel Dwyer**, Senior Process Engineer

CIGS pilot line, commercialization

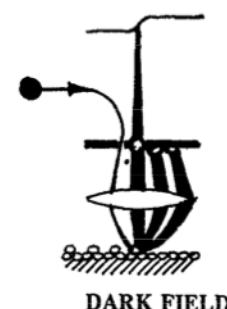
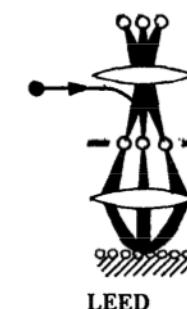
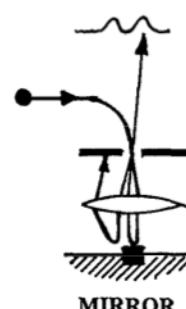
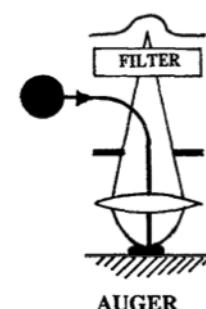
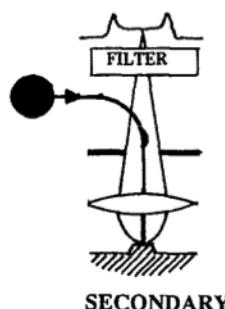


# Technical Approach: Spectros. PEEM/LEEM

- **Developing and Applying Photoemission / Low Energy Electron Microscopies (PEEM / LEEM) 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).

# Project Updates and Proposed Revisions

## ■ Timeline and Budget

### Extend Project by 2 Quarters:

- **Budget Period 1 (January 2013 – June 2014): \$450k**

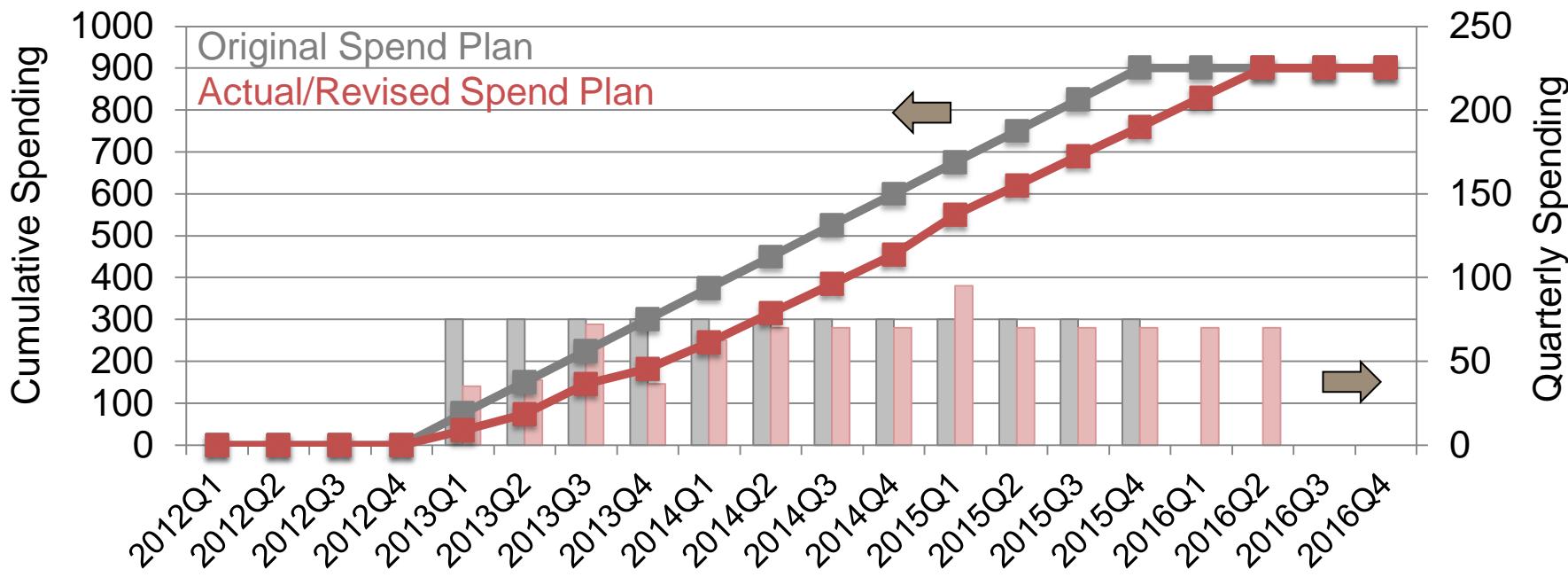
December 2014

\$245k spent (54% spent over 83% BP1)

- **Budget Period 2 (July 2014 – December 2015): \$450k**

January 2015 – June 2016

- See next slide for added task.



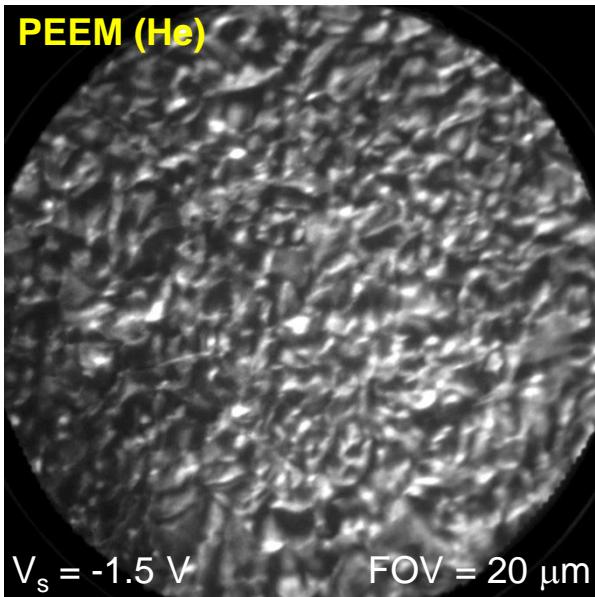
# Project Updates and Proposed Revisions

## ▪ Summary of Budget Period 1 Milestones

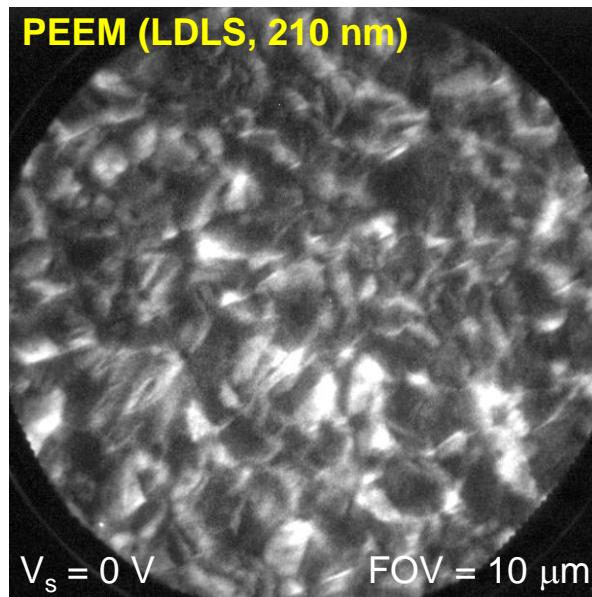
Date	Task/Milestone	Status
12/2013	<b>M (ST-3.4).</b> Demonstrate nm-resolved chemical/electronic states in NP-CIGS films.	Completed 12/2013.
06/2014	<b>M (ST-3.5).</b> Observe mesoscale Cu segregation at PVD-CIGS grain boundaries.	Completed 09/2013.
06/2014 12/2014	<b>M (T-3).</b> Demonstrate nm-resolved chemical/electronic states of PVD-CIGS.	On-track. Electronic states demonstrated. Chemical states TBD.
12/2014	<b>ST-3.6.</b> Add and evaluate sample cleaning capabilities, e.g. sputter gun, H <sub>2</sub> cracker.	On-track. ST added 2013 Q4. Installed and prelim. studies begin.
12/2014	<b>ST-3.7.</b> Add and evaluate high intensity monochromated laser-driven light source.	On-track. ST added 2013 Q4. Unit installed. Prelim. studies begun.
12/2014	<b>ST-3.8.</b> Develop image analysis software to perform statistical analysis of data.	Not yet started. ST added 2014 Q1. See next slides for details.
06/2014 12/2014	<b>G/NG-1</b> Dynamic growth studies feasible?	On-track. Preliminary data on grain ripening observed, pending analysis.
06/2014	Identify industrial partner.	At-risk. Landscape changing quickly. Will continue efforts at meetings.
06/2014	Compute band structure of CIGS GB	At-risk. Lack of personnel. Previous efforts by Yan. Will discuss with Yan.

# Progress Report for CY14 Q1

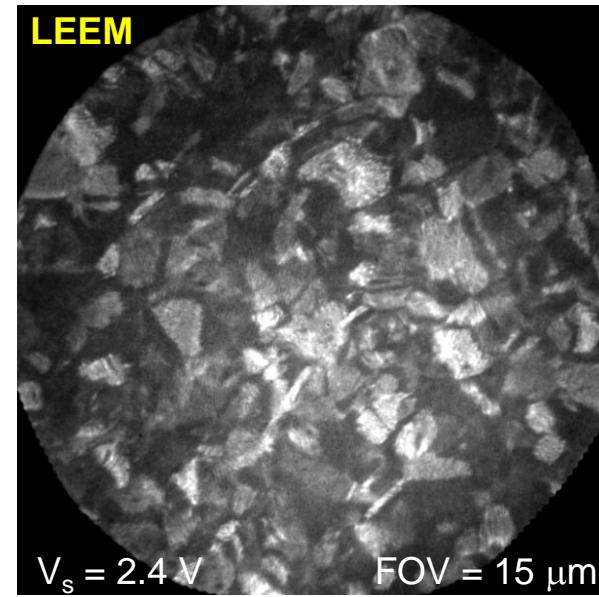
- **Comparison of Results Using New Laser-Driven Xenon Plasma Lamp System**
  - ~10x higher intensity for Laser-Driven Light Source (LDLS,  $h\nu = 6$  eV) vs He lamp (He I,  $h\nu = 21.2$  eV).



FOV = 20  $\mu\text{m}$   
 $V_{\text{MCP}} = 1.5$  kV  
 $t_{\text{exp}} = 5$  sec  
Avg Counts = 1000



FOV = 10  $\mu\text{m}$   
 $V_{\text{MCP}} = 1.4$  kV  
 $t_{\text{exp}} = 0.5$  sec  
Avg Counts = 300



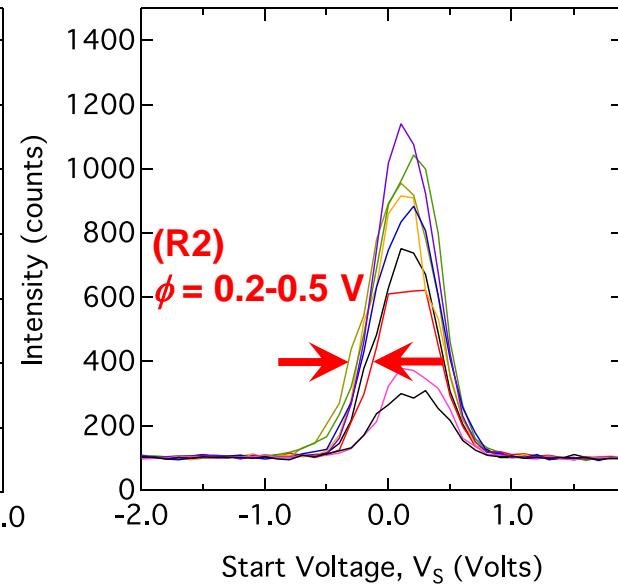
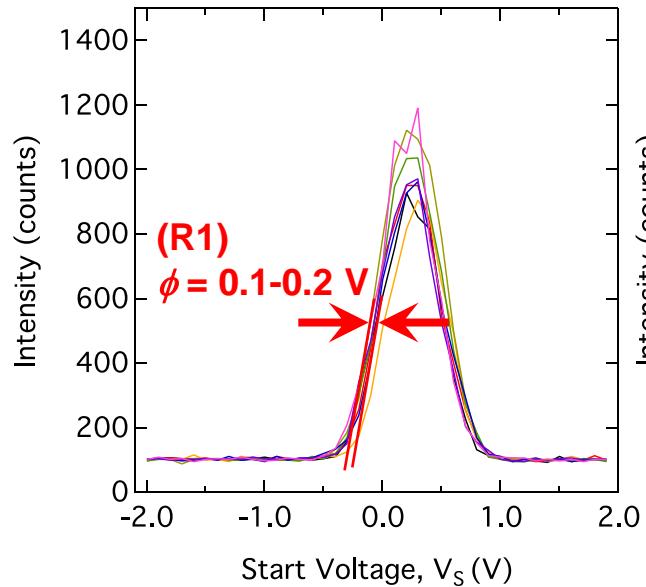
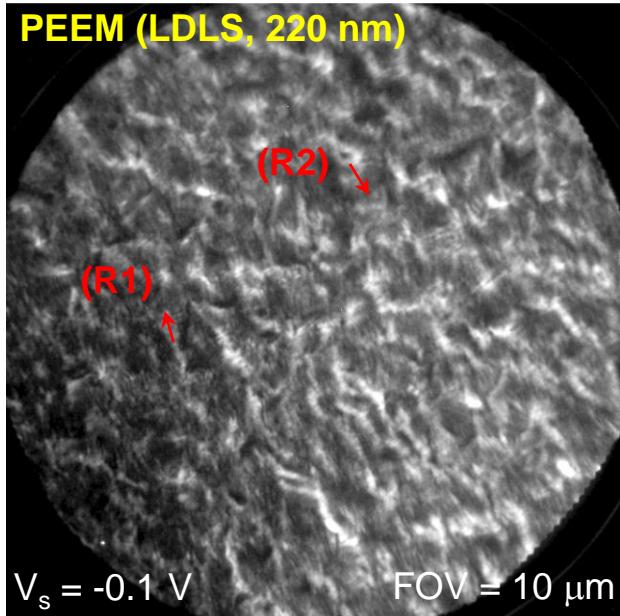
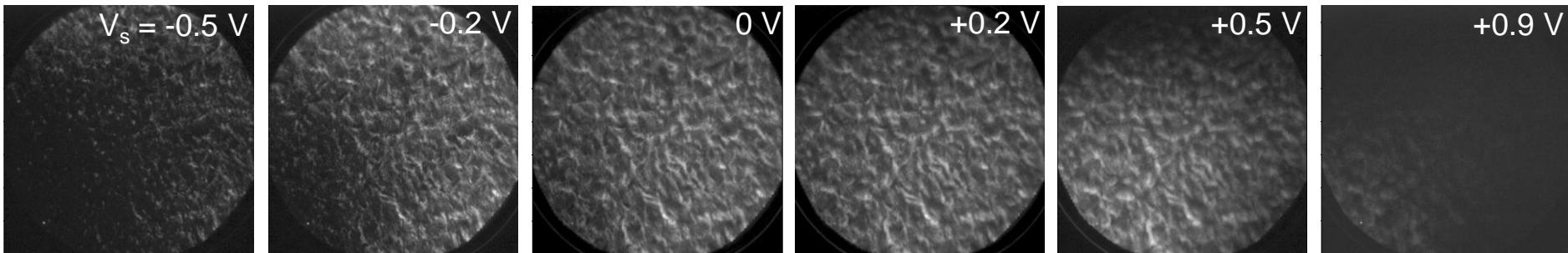
FOV = 15  $\mu\text{m}$   
 $V_{\text{MCP}} = 1.35$  kV  
 $t_{\text{exp}} = 0.1$  sec  
Avg Counts = 1000

**New light source provides higher resolution, more stable imaging.  
PEEM with LDLS resolution approaching parity with LEEM.**

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# Progress Report for CY14 Q1

- Determining changes in local work function using PEEM-IV with new LDLS.

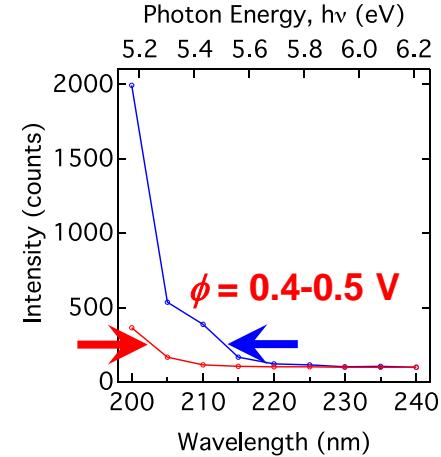
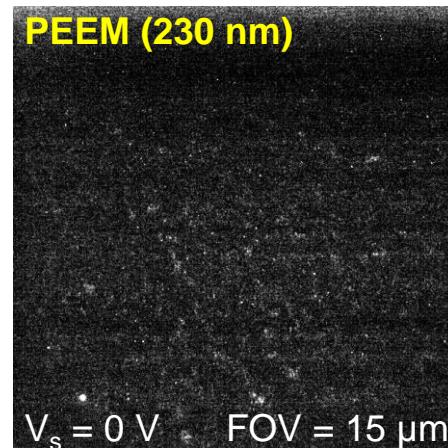
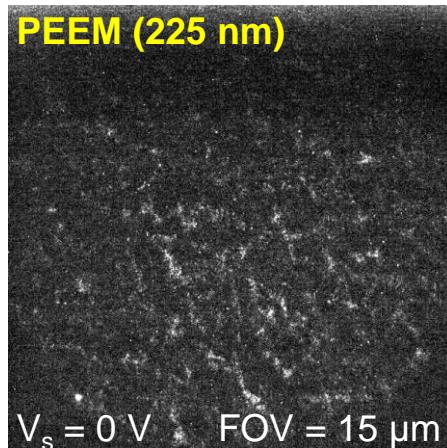
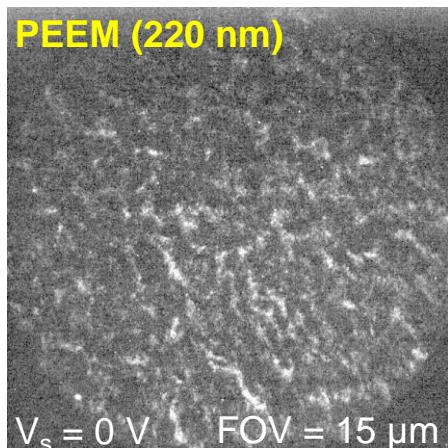
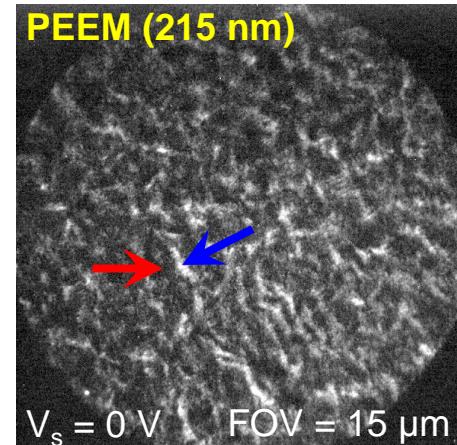
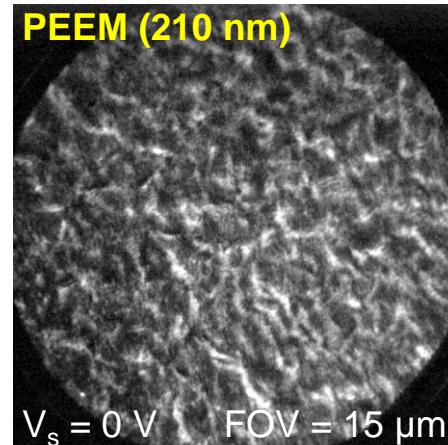
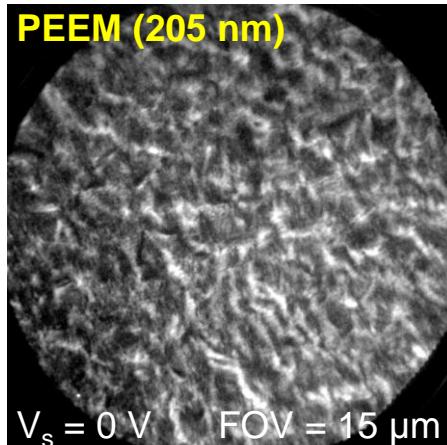
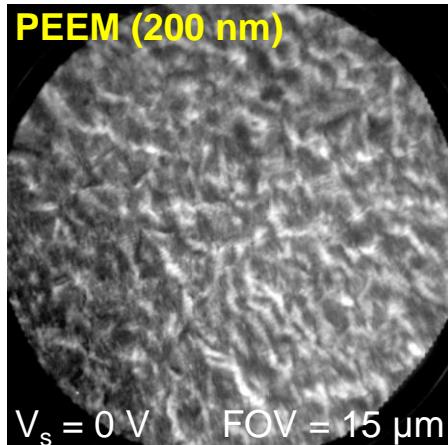


Despite fine structure detail in grains, “internal” variations (R1) show no  $\phi$ .  
G-GB variations (R2) show  $\phi = 0.5 \text{ V}$ .

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# Progress Report for CY14 Q1

- Local work function determined with PEEM using variable wavelength LDLS.



Observe photoemission onset/cutoff by varying incident photon energy.  
G-GB work function difference  $\sim 0.5$  V.

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# Progress Report for CY14 Q1

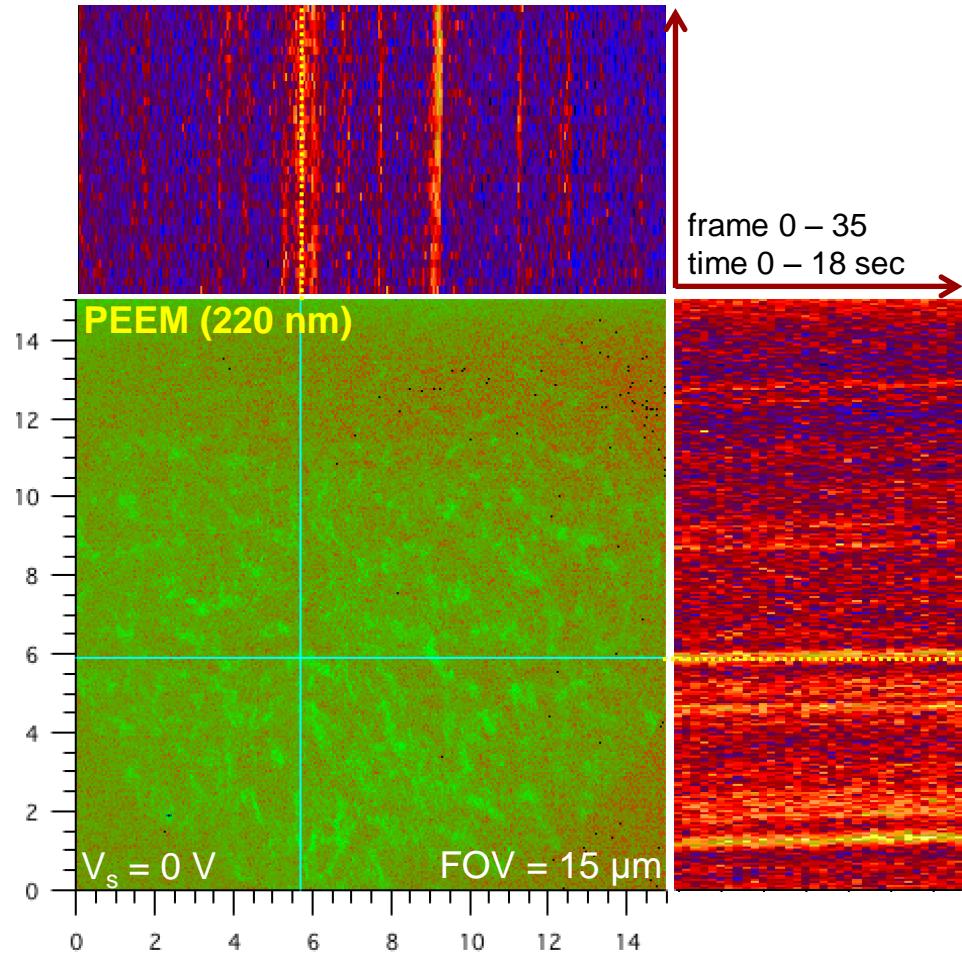
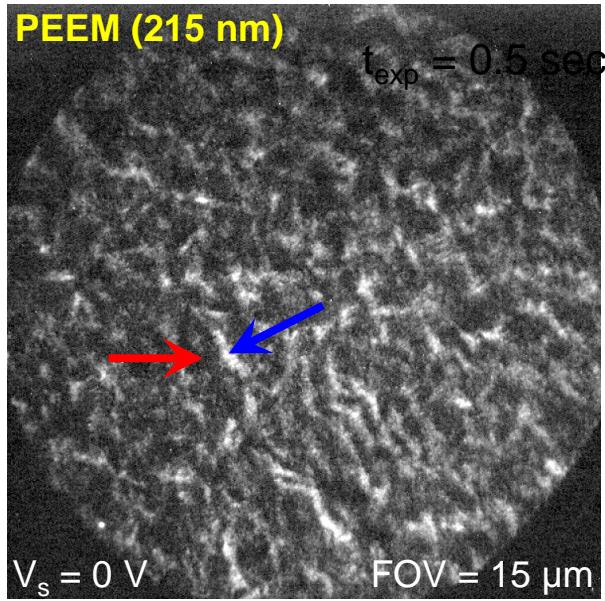
- Can we get better images/data by increasing acquisition time?

Higher  $t_{\text{exp}}$ ?

Higher frame averaging?

- Perform PEEM at 220 nm.

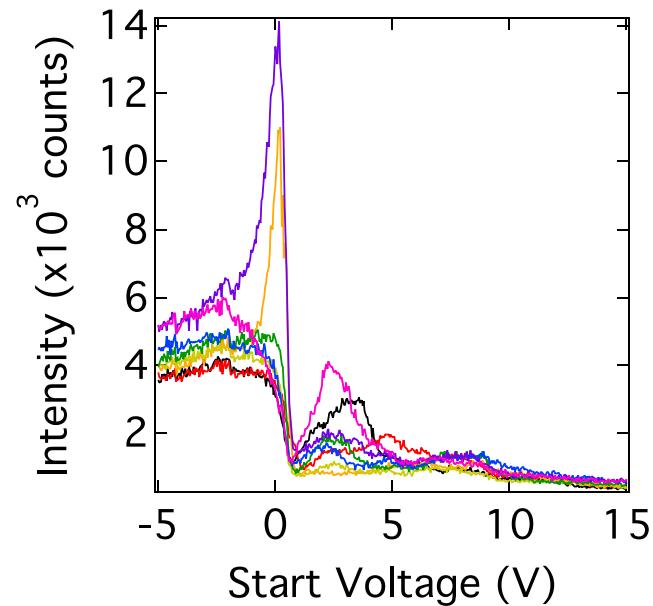
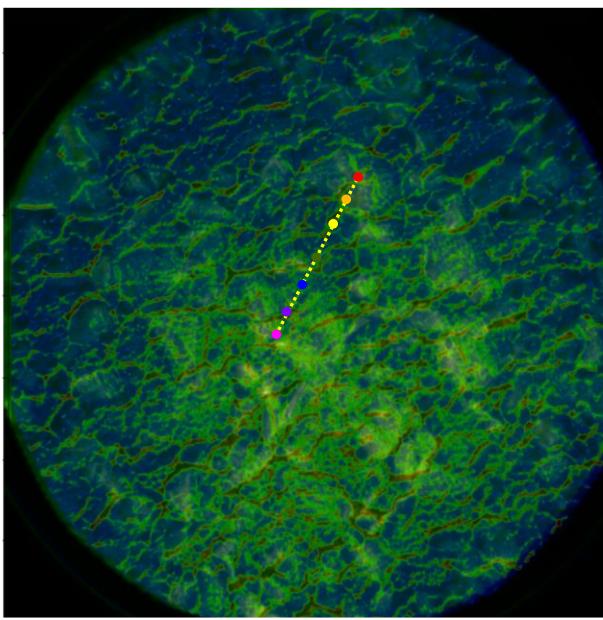
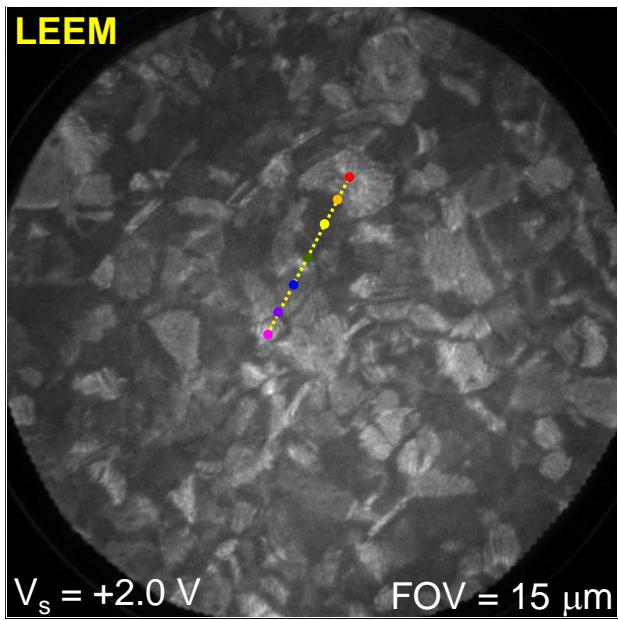
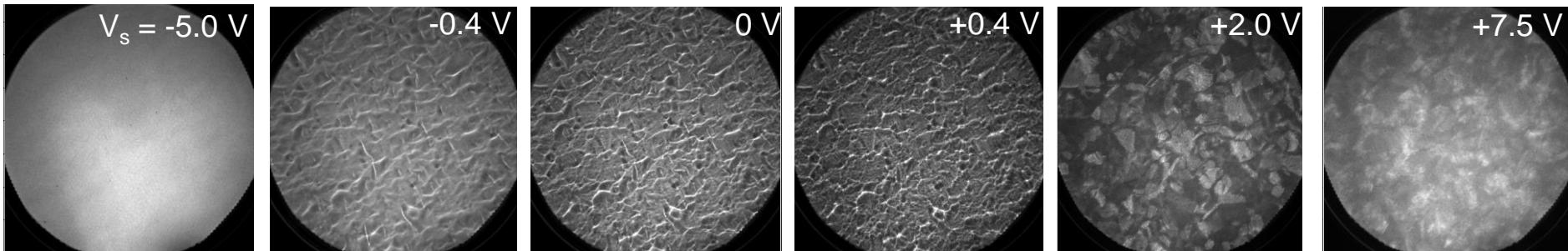
Take 35 images using  $t_{\text{exp}} = 0.5$  sec,  
16 frame average.



Noticeable drift is observed over ~5 min (35 images @ 0.5 sec, 16 frames each).  
Need autocorrelation and thresholding algorithms.

# Progress Report for CY14 Q1

- Determining changes in local work function using LEEM-IV.



**G-GB variations show  $\phi = 0.5$  V.**  
**Origins of the fine details in the LEEM-iv spectra?**

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