

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

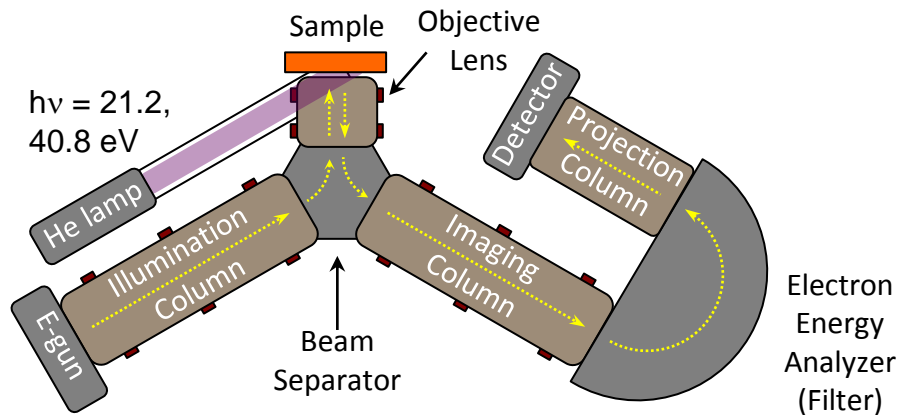


Daniel Dwyer, Senior Process Engineer
CIGS pilot line, commercialization

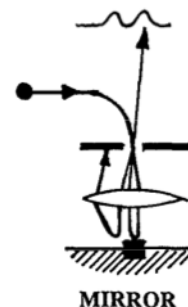
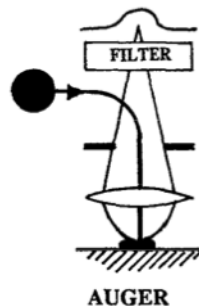
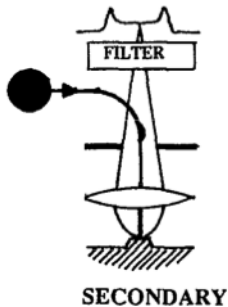
Technical Approach: Spectros. PEEM/LEEM

■ 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



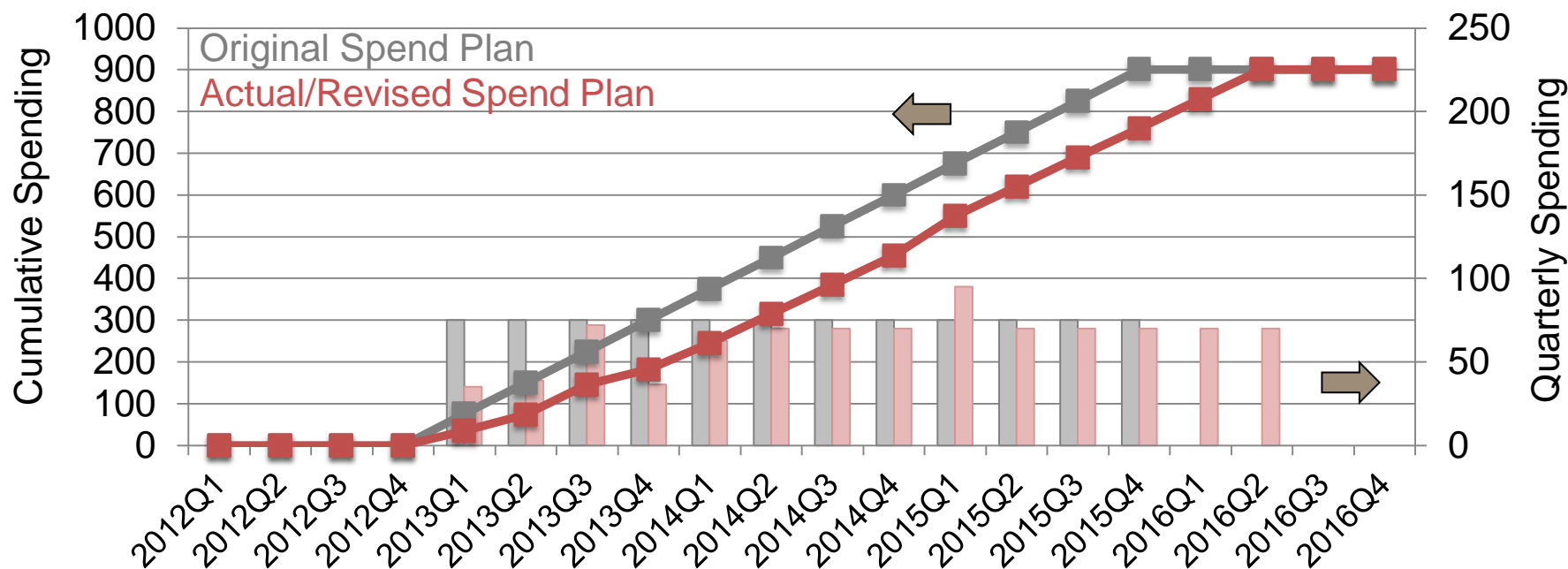
Veneklasen, *Rev. Sci. Instrum.* **63**:5513 (1992).

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.



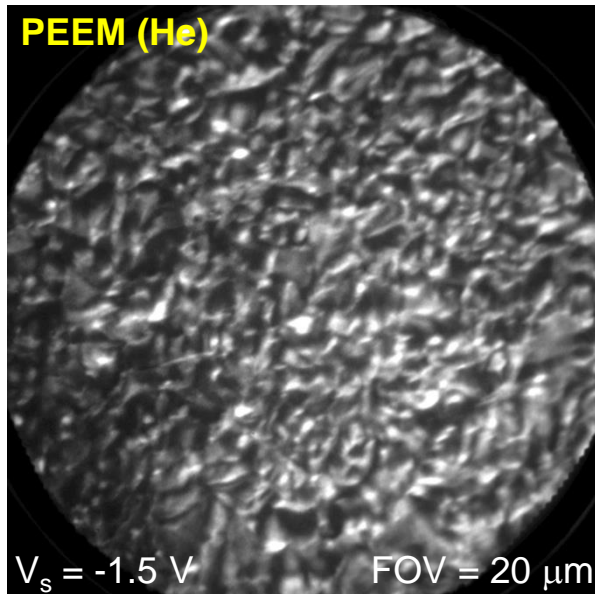
Project Updates and Proposed Revisions

■ Summary of Budget Period 1 Milestones

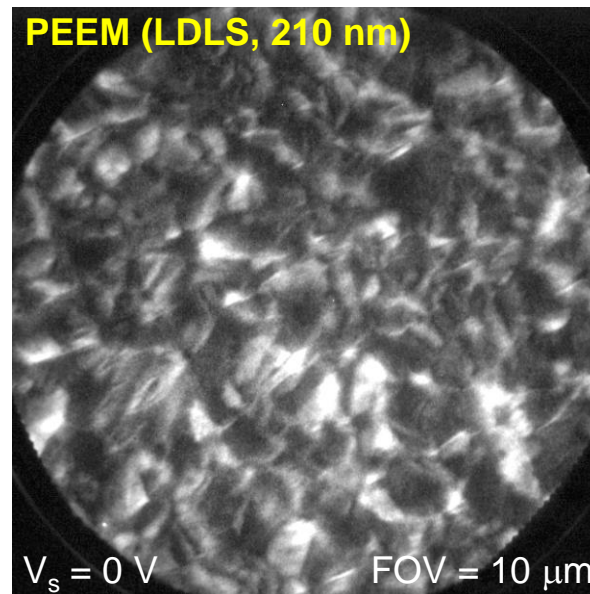
Date	Task/Milestone	Status
12/2013	M (ST-3.4). Demonstrate nm-resolved chemical/electronic states in NP-CIGS films.	Completed 12/2013.
06/2014	M (ST-3.5). Observe mesoscale Cu segregation at PVD-CIGS grain boundaries.	Completed 09/2013.
06/2014 12/2014	M (T-3). Demonstrate nm-resolved chemical/electronic states of PVD-CIGS.	On-track. Electronic states demonstrated. Chemical states TBD.
12/2014	ST-3.6. Add and evaluate sample cleaning capabilities, e.g. sputter gun, H ₂ cracker.	On-track. ST added 2013 Q4. Installed and prelim. studies begin.
12/2014	ST-3.7. Add and evaluate high intensity monochromated laser-driven light source.	On-track. ST added 2013 Q4. Unit installed. Prelim. studies begun.
12/2014	ST-3.8. 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	G/NG-1 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

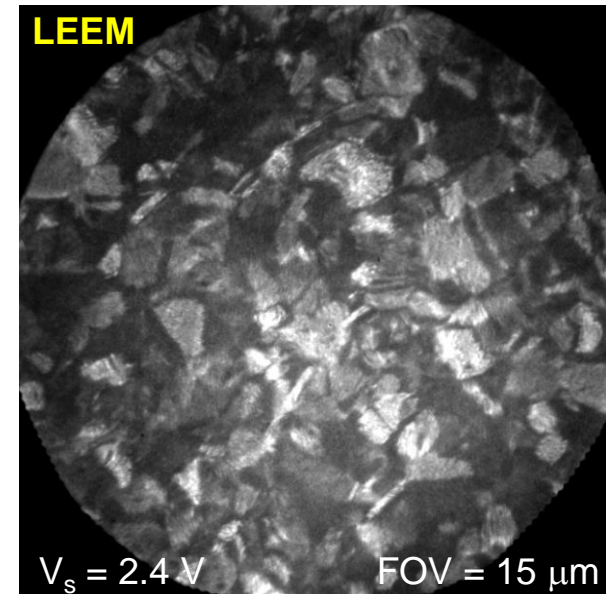
- **Comparison of Results Using New Laser-Driven Xenon Plasma Lamp System**
 - ~10x higher intensity for Laser-Driven Light Source (LDLS, $h\nu = 6$ eV) vs He lamp (He I, $h\nu = 21.2$ eV).



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



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

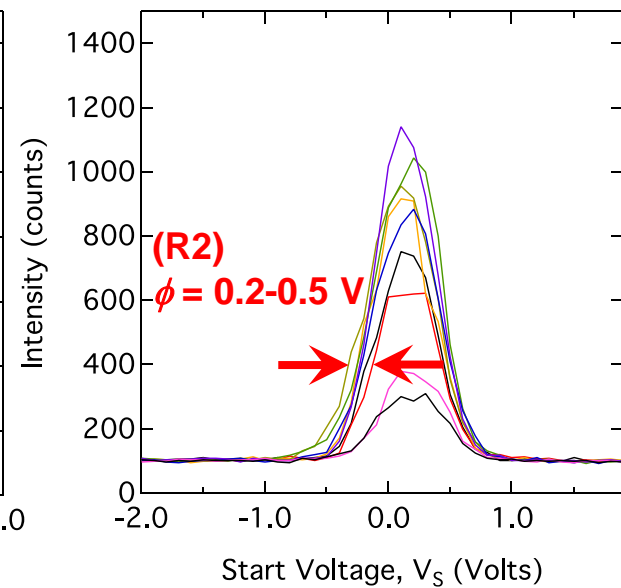
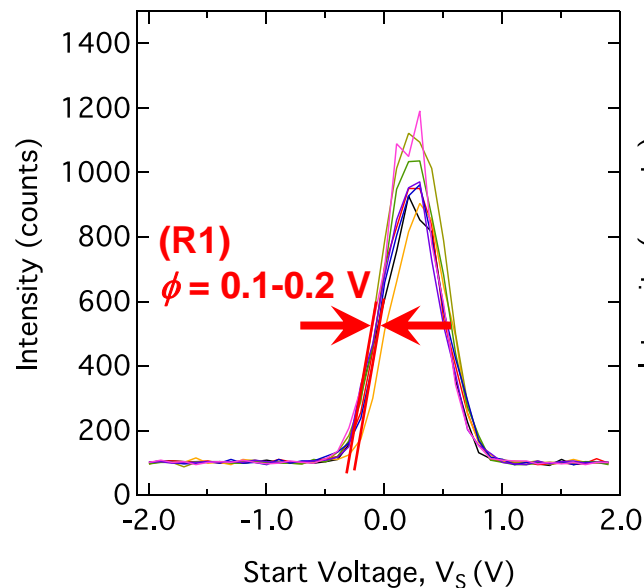
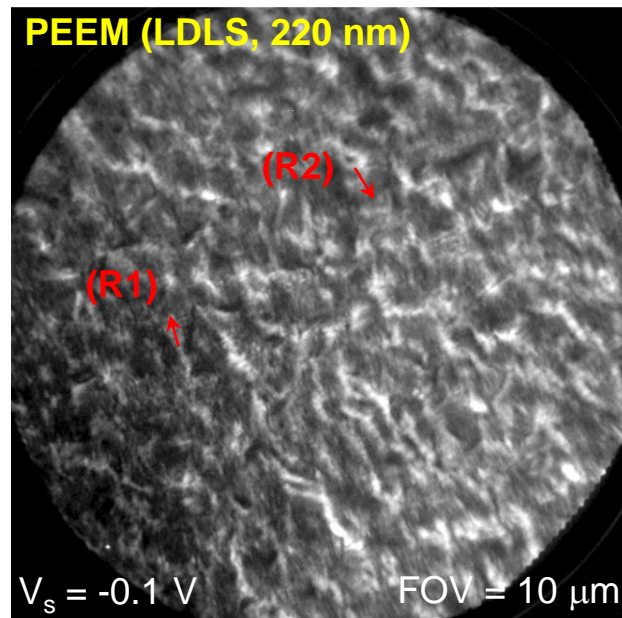
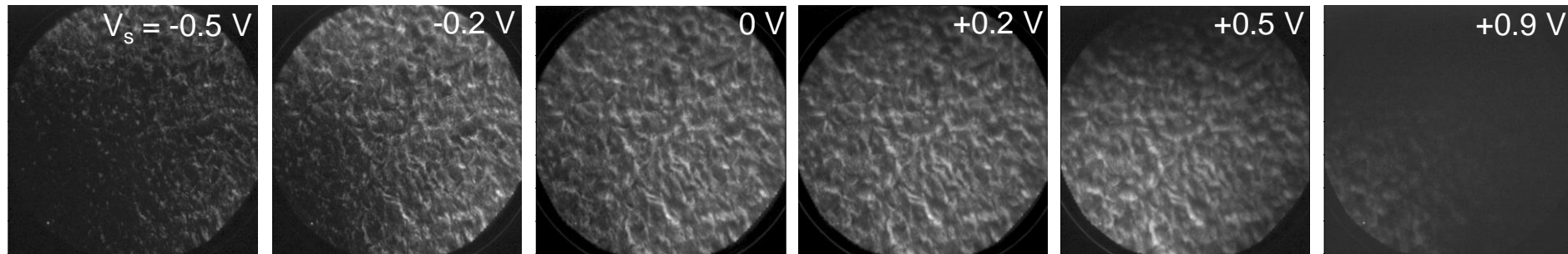


FOV = 15 μ m
 $V_{MCP} = 1.35$ kV
 $t_{exp} = 0.1$ sec
Avg Counts = 1000

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

Progress Report for CY14 Q1

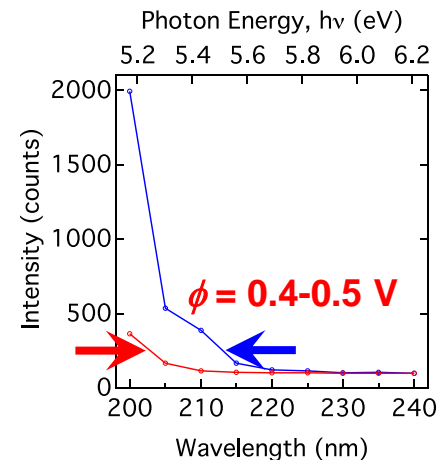
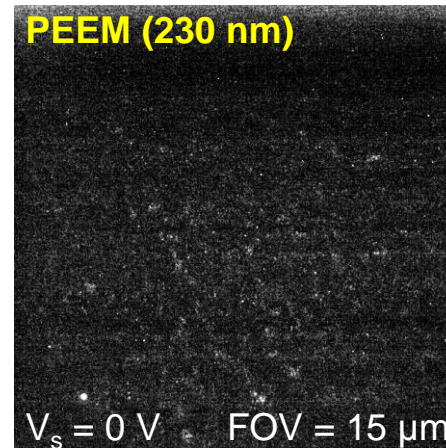
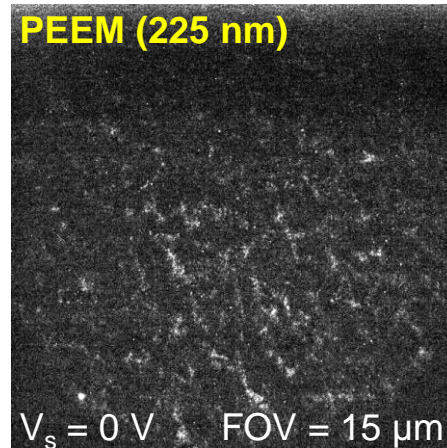
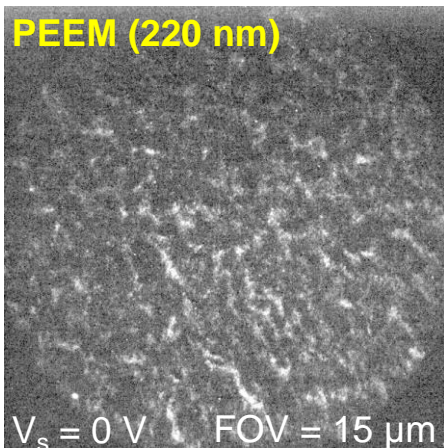
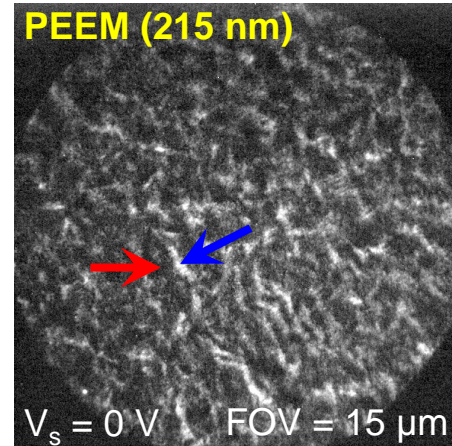
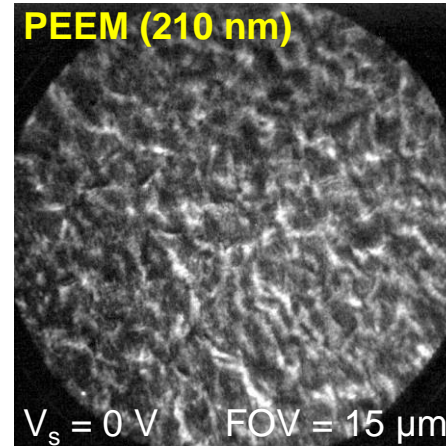
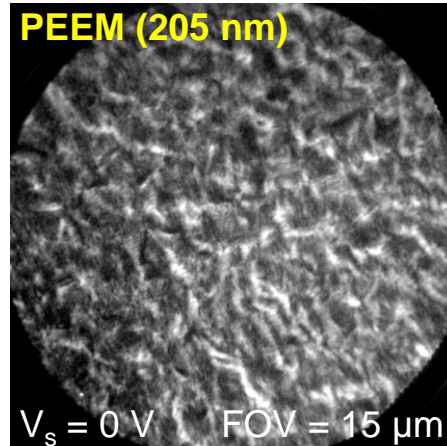
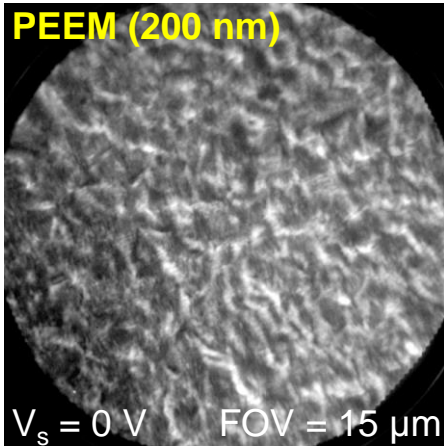
- Determining changes in local work function using PEEM-IV with new LDLS.



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

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 ~ 0.5 V.

Progress Report for CY14 Q1

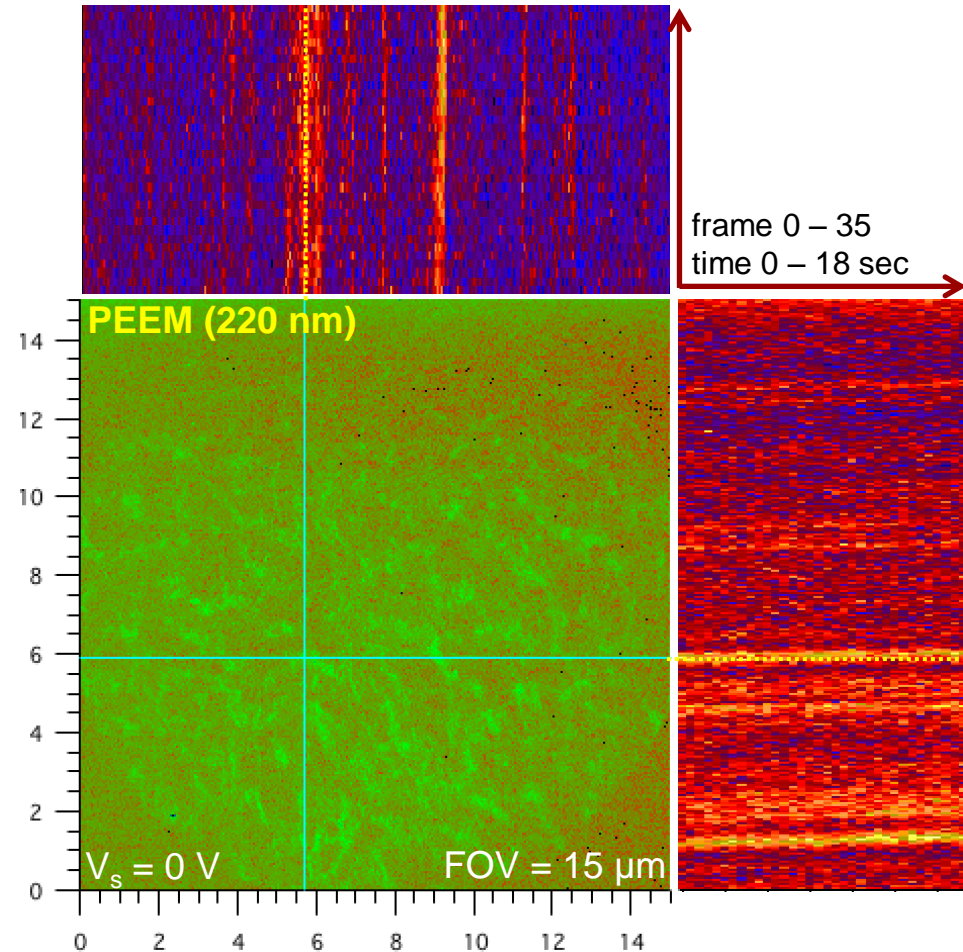
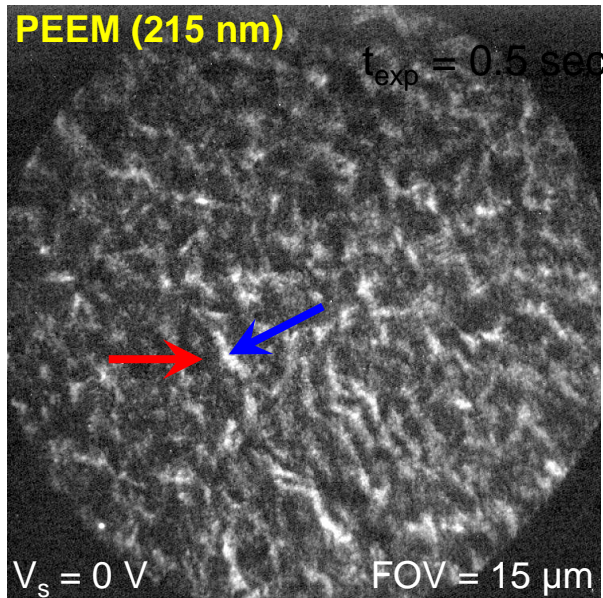
- Can we get better images/data by increasing acquisition time?

Higher t_{exp} ?

Higher frame averaging?

- Perform PEEM at 220 nm.

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

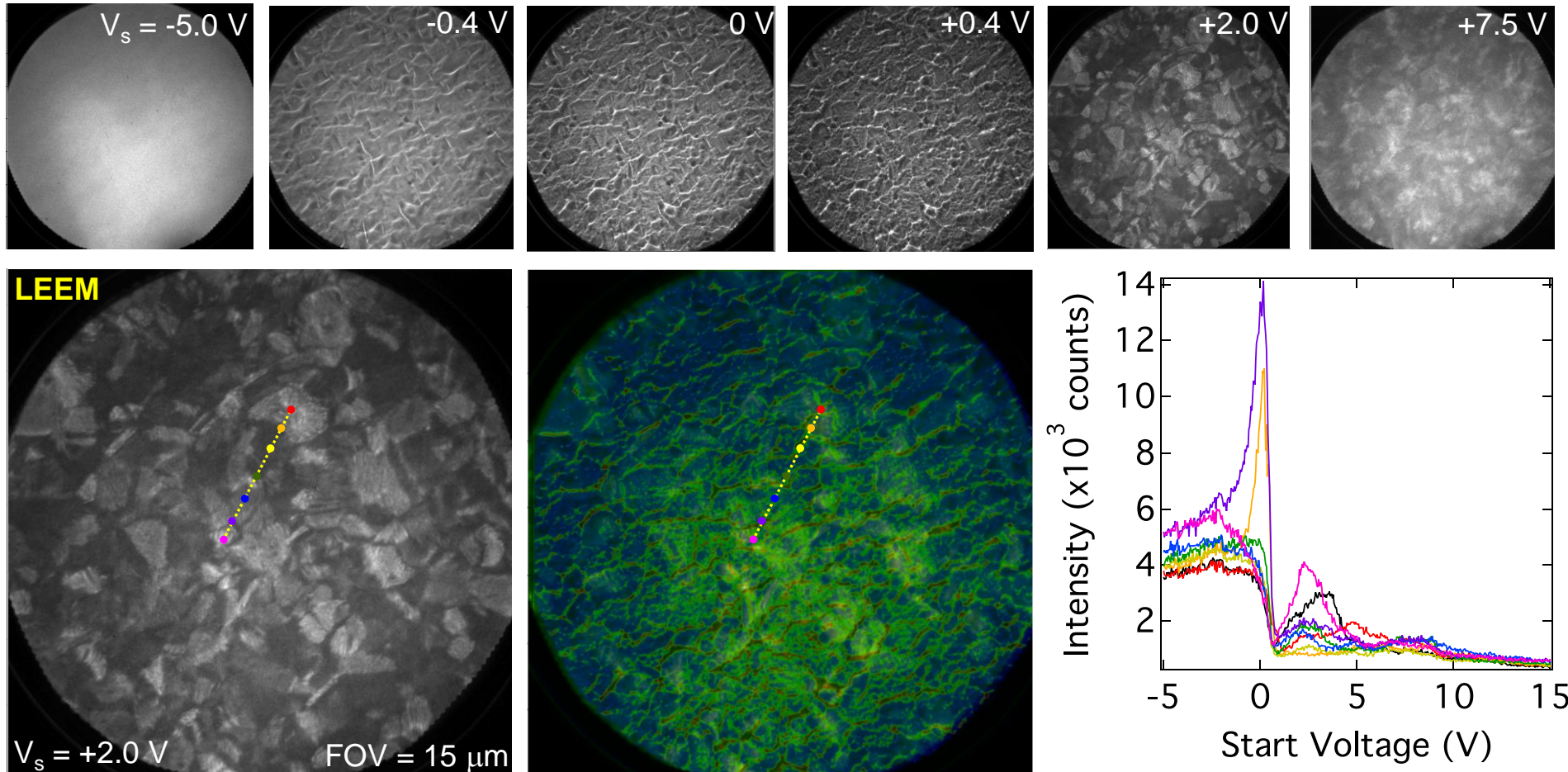


Noticeable drift is observed over ~5 min (35 images @ 0.5 sec, 16 frames each).

Need autocorrelation and thresholding algorithms.

Progress Report for CY14 Q1

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



G-GB variations show $\phi = 0.5\text{ V}$.

Origins of the fine details in the LEEM-iv spectra?