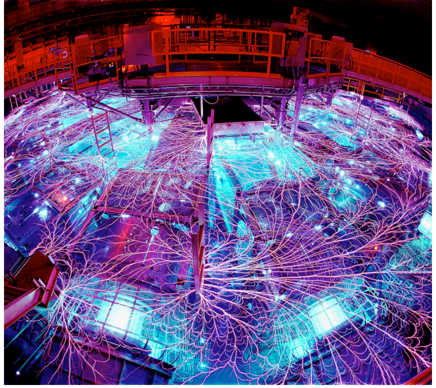
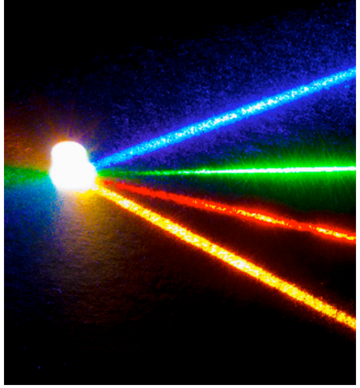
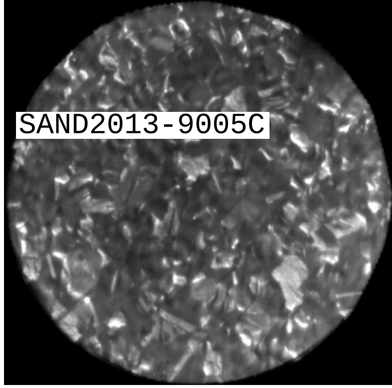





SAND2013-9005C

U.S. Department of Energy | SunShot Initiative

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

Spectroscopic Low-Energy & Photoemission Electron Microscopy Characterization of CIGS

Calvin K. Chan (PI), Sandia National Laboratories
Gary Kellogg, Center for Integrated Nanotechnologies
Rommel Noufi, National Renewable Energy Laboratory
Brian Korgel, The University of Texas at Austin
Daniel Dwyer, Photovoltaics Manufacturing Consortium

2nd DOE Thin-Film Workshop
09-10 October 2013, NREL, Golden, CO

BRIDGE Project Overview

- **Goal:** Develop new metrology tool to measure nanoscale chemical and electronic structure of PV materials and devices with high fidelity and in real time.
- **Collaborative Research Team**

Sandia National Laboratories

Calvin Chan (PI), Taisuke Ohta, 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

Gary Kellogg, Distinguished 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

Rommel Noufi, Principle Scientist, 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

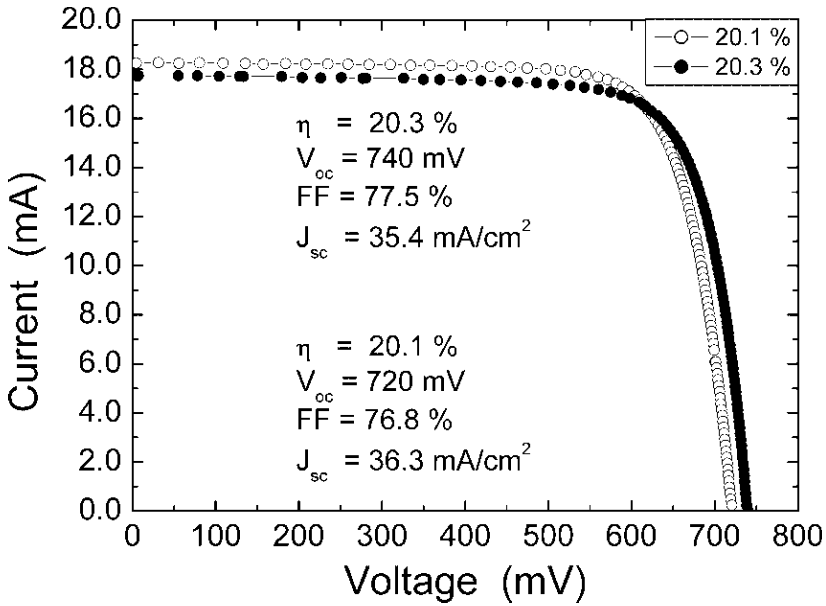
U.S. Photovoltaic Manufacturing Consortium PVMC

Daniel Dwyer, Senior Process Engineer
CIGS pilot line, commercialization

CIGS: The Promise and Problem

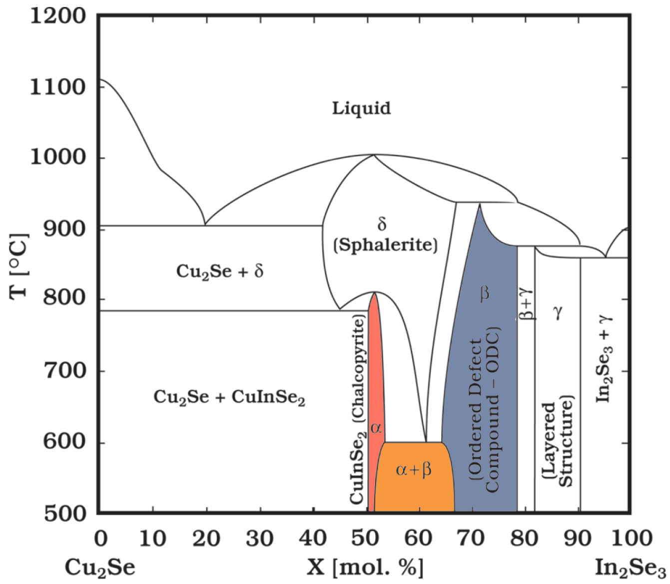
- **Highest performing thin-film PV**
  - ≳ 20% efficiency (ZSW, NREL)
  - Potentially low cost and flex
  - Good outdoor performance and stability
  - Radiation hard
- **Growing, but limited understanding**
  - Complicated phase diagram
  - Difficult to control phases over large areas
  - Role of surfaces and interfaces still debated
  - “Improvements by design” is limited

I-V of Record CIGS Cells from ZSW
(Certified by Fraunhofer ISE)



Jackson et al, *Prog. Photovolt: Res. Appl.* **19**:894 (2011).

Pseudobinary Phase Diagram of CIGS



Stanbery, *Crit. Rev. Sol. State Mater. Sci.* **27**:73 (2002).

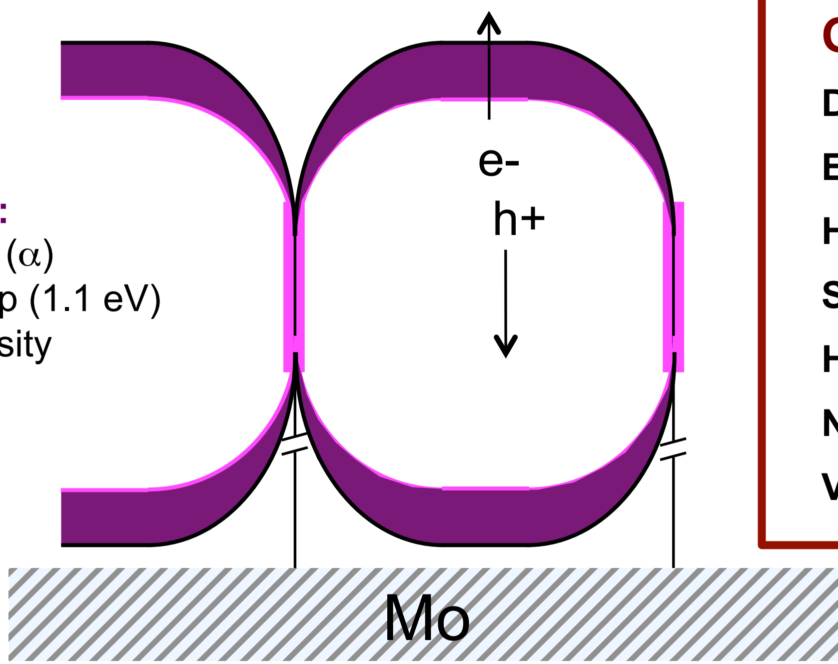
Microscopy of CIGS

- **Many efforts to correlate processing-structure-property relationships**
  - Scanning (Auger) Electron Microscopy [e.g., Hetzer et al, *Appl. Phys. Lett.* **86**:162105 (2005)]
  - Scanning Tunneling Microscopy and Spectroscopy [e.g., Azulay et al, *Phys. Rev. Lett.* **108**:076603 (2012)]
  - (Scanning) Transmission Electron Microscopy [e.g., Abou-Ras et al, *Phys. Rev. Lett.* **108**:075502 (2012)]
  - Functional Scanning Probe Microscopies [e.g., Li et al, *IEEE J. Photovolt.* **2**:191 (2012)]
  - Depth Sensitive Spectroscopy [e.g., Bär et al, *Appl. Phys. Lett.* **93**:244103 (2008)]

Interface Layer:
Cu-depleted ODC (β)
Higher bandgap (1.6 eV)
Higher e- density

Grain Interior:
Stoichiometric (α)
Lower bandgap (1.1 eV)
Higher h+ density
p-type

Junction:
Built-in potential, ϕ
(~0.5 eV?)



Open Questions

Depletion or inversion?

Energy level (band) alignment?

Hole/electron barrier?

Space charge region?

How do holes get out?

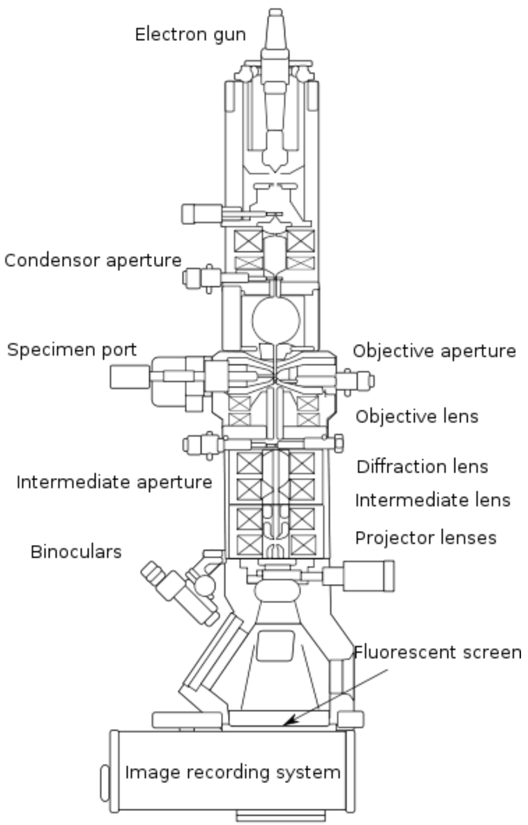
Nanoscale phase segregation?

Variations?

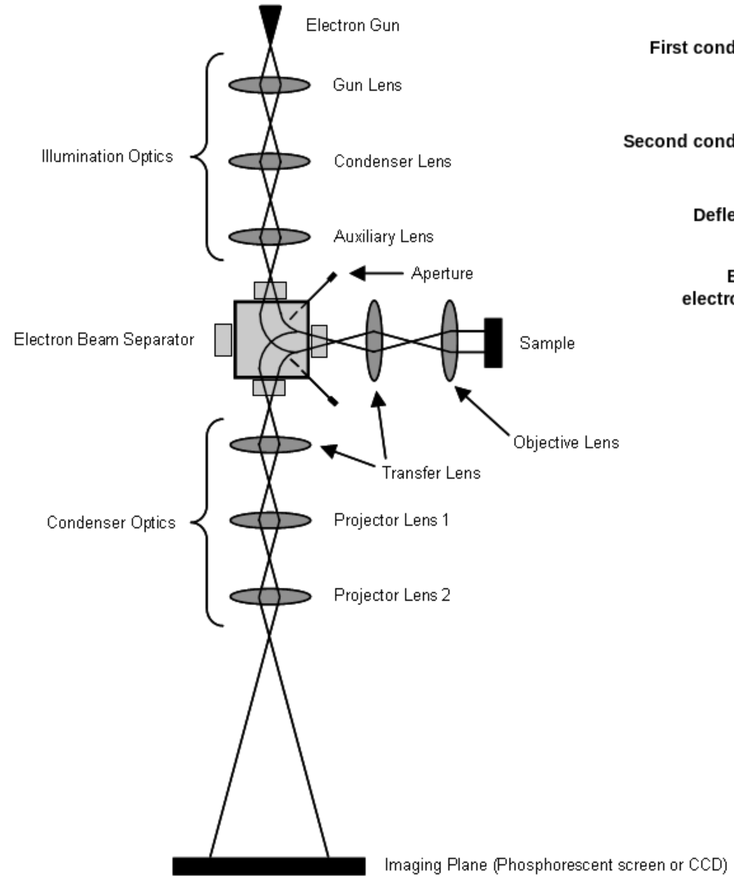
Our Approach: LEEM / PEEM

- **Low Energy / Photoemission Electron Microscopies (LEEM / PEEM)**
  Similar to TEM and SEM, but uniquely different.

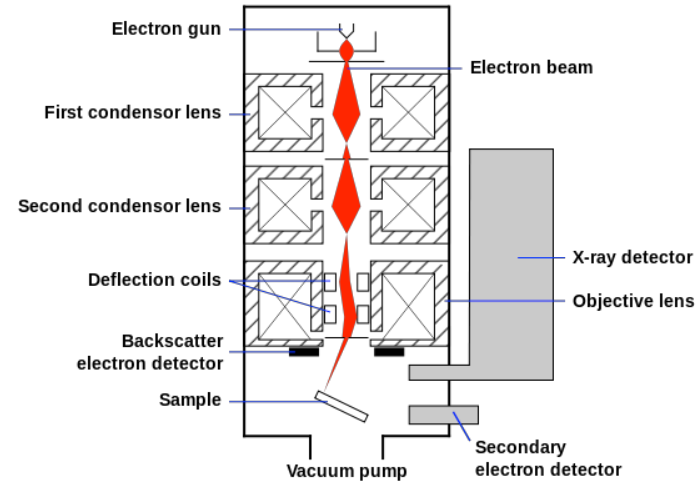
TEM



LEEM / PEEM



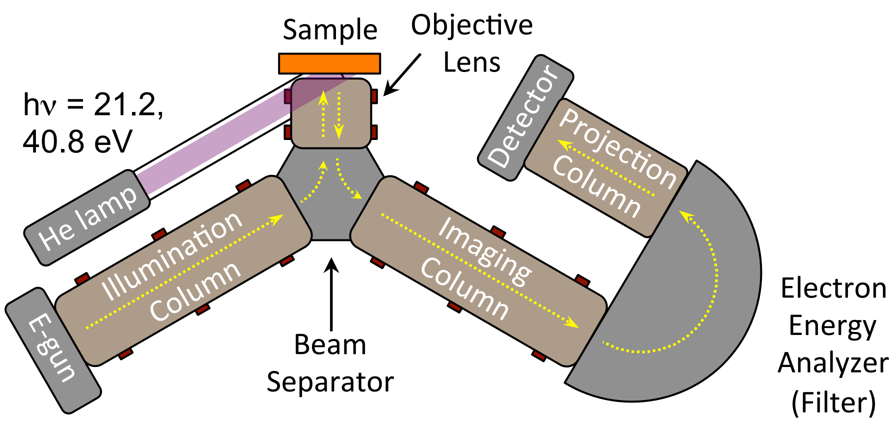
SEM



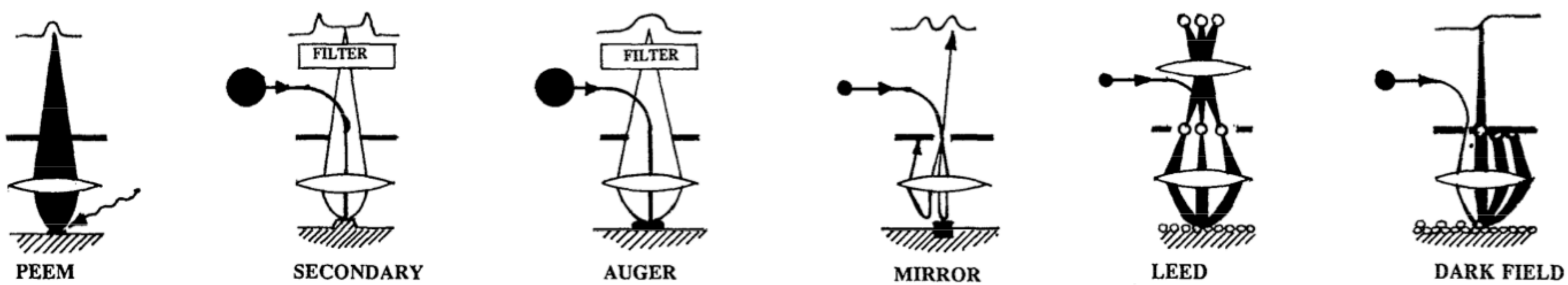
cchan@sandia.gov

Our Approach: LEEM / PEEM

- **Low Energy / Photoemission Electron Microscopies (LEEM / PEEM)**
  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

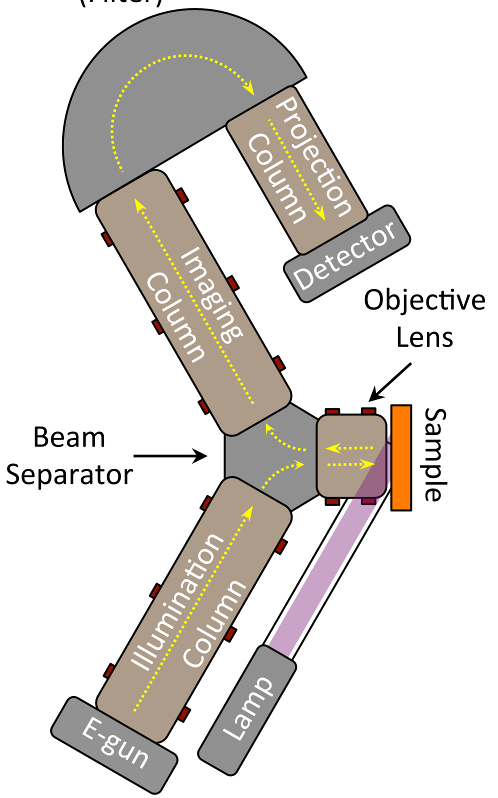


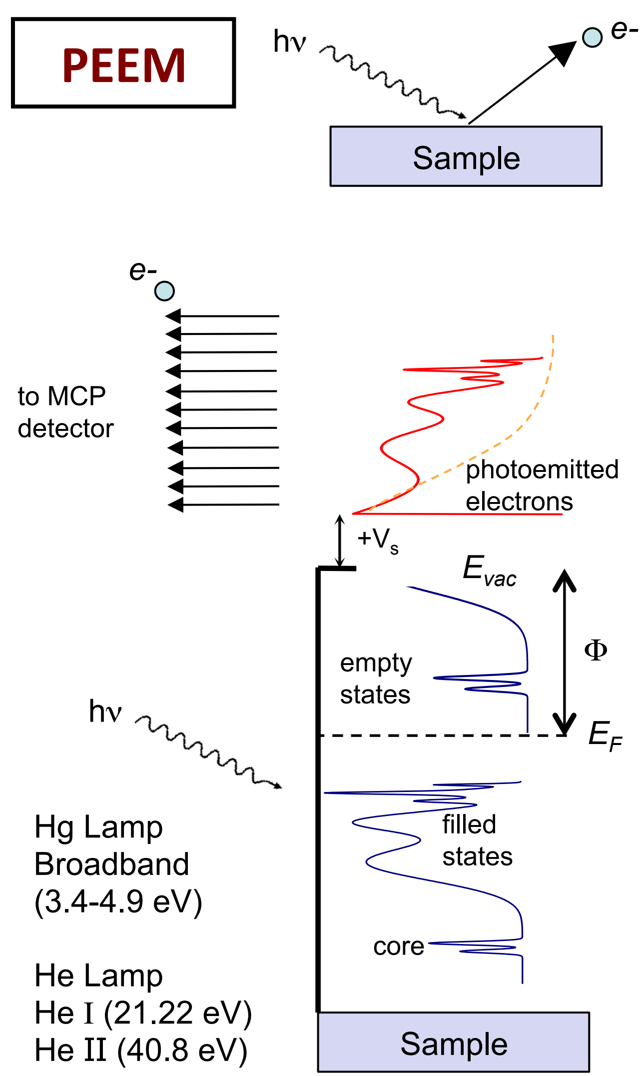
- **Sandia is a leader in the development and application of LEEM / PEEM.**
  3 PEEM / LEEM systems, 6+ FTE with 150+ years expertise, 5+ external "users" per year, studying a variety of materials systems

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

Principles of LEEM / PEEM

- For each pixel of the microchannel plate…



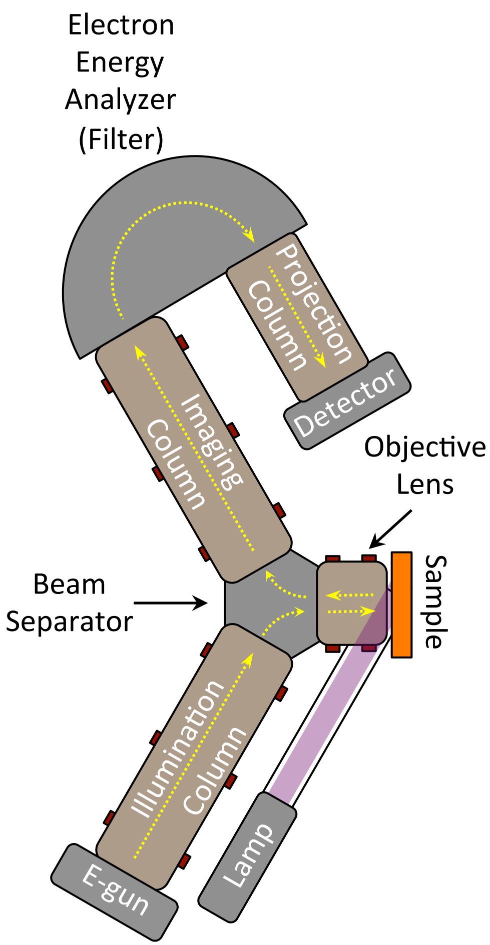


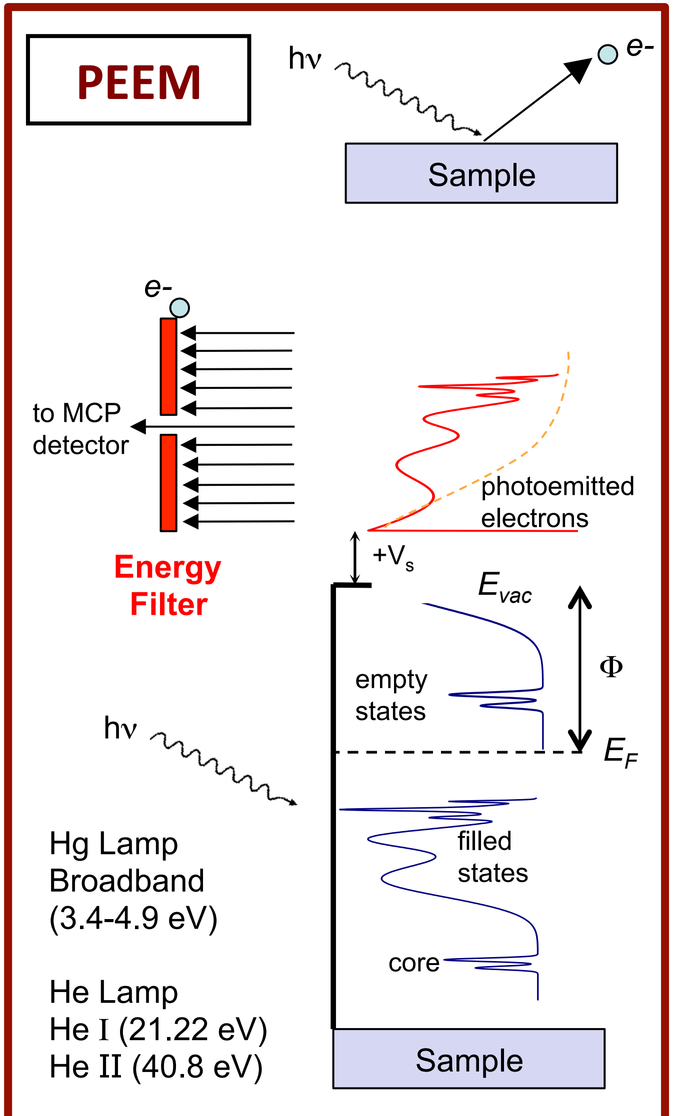
Hg Lamp
Broadband
(3.4-4.9 eV)

He Lamp
He I (21.22 eV)
He II (40.8 eV)

Principles of LEEM / PEEM

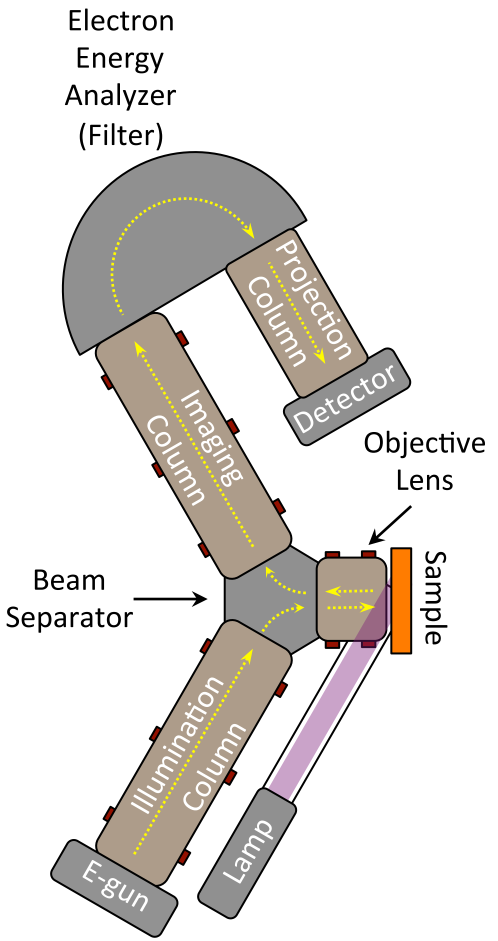
- For each pixel of the microchannel plate…

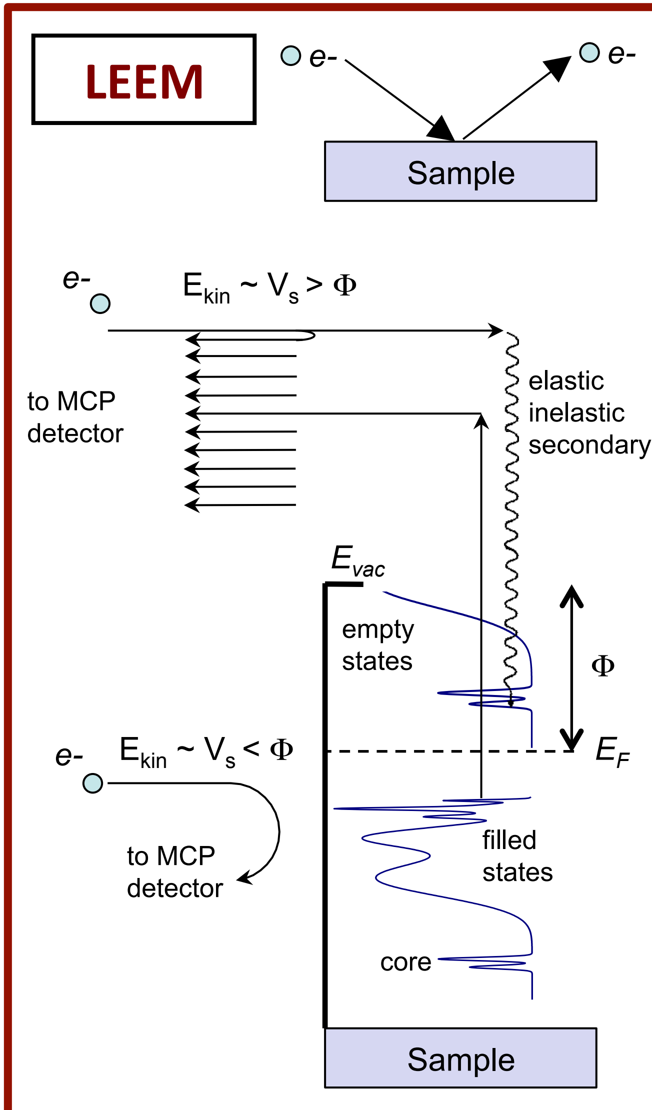




Principles of LEEM / PEEM

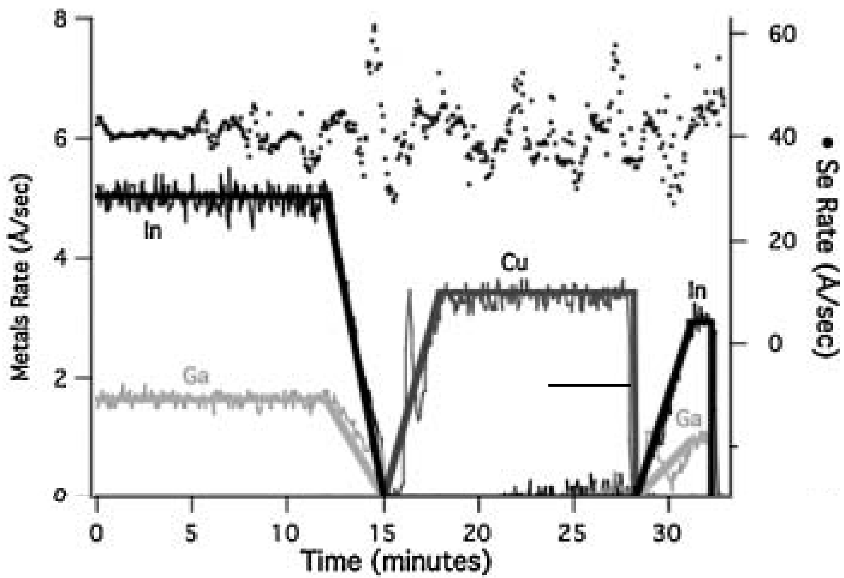
- For each pixel of the microchannel plate…

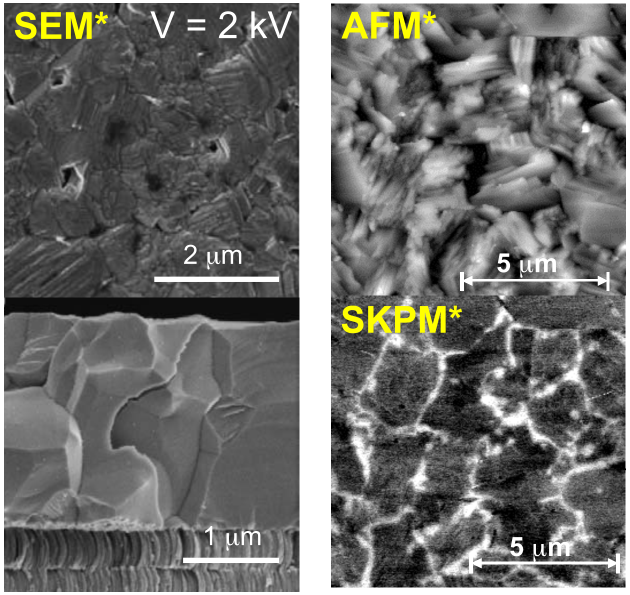




NREL 3-Stage CIGS Sample

- NREL $Cu(In_{0.6}Ga_{0.4})Se_2$ Samples*
  - 3-stage vacuum-deposition on SLG/Mo, no top contacts.
  - X-ray fluorescence: Cu(III) = 0.913, Ga(III) = 0.39.
  - Material would typically produce ~17-20% efficient devices.



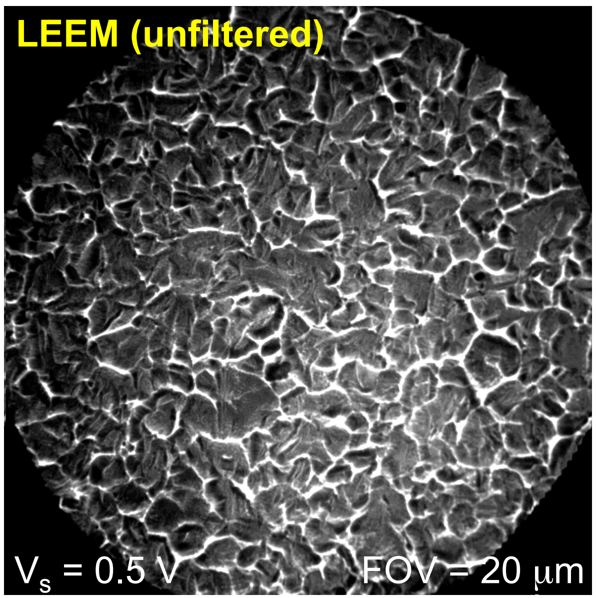


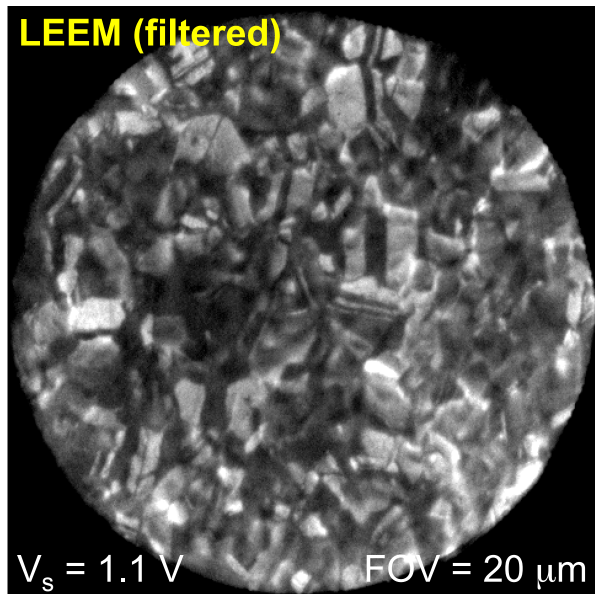
- **Microcrystalline, size ~1-2 μm**
- **Faceted surface**

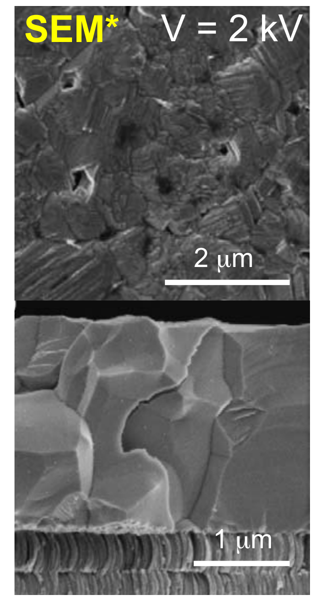
*Repins et al, *Prog. Photovolt: Res. Appl.* **16**:235 (2008). | Jiang et al, Appl. Phys. Lett. **84**:3477 (2004).

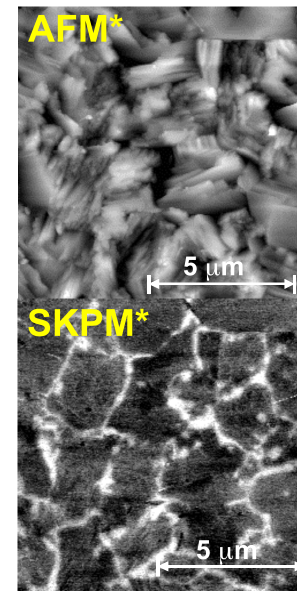
Imaging Morphology with LEEM

- NREL $Cu(In_{0.6}Ga_{0.4})Se_2$ Samples*
  - **PEEM / LEEM:** Samples annealed in situ at 300-400 °C for 12-48 hours.
  - Different highlights depending on various, well-controlled imaging conditions.







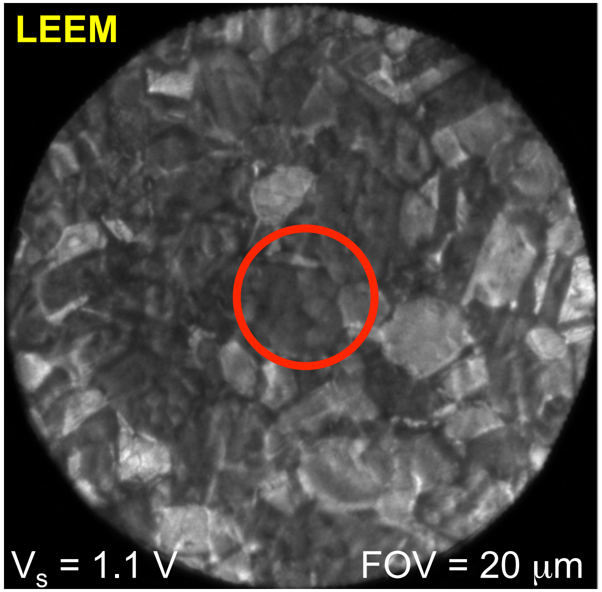


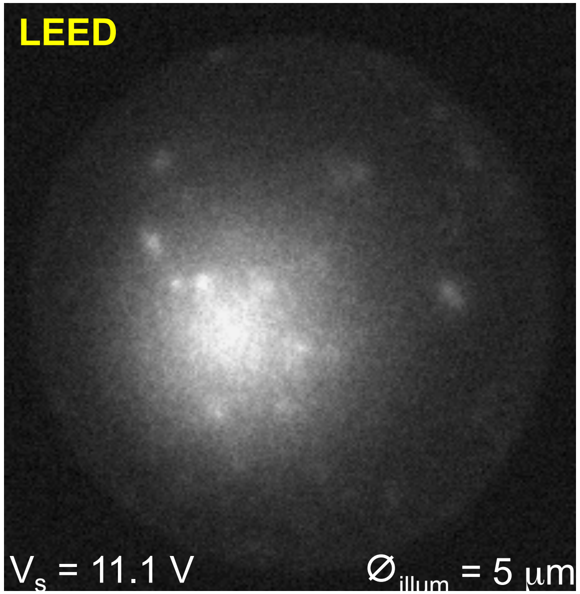
  - **Microcrystalline, size ~1-2 μm**
  - **Faceted surface**

*Repins et al, *Prog. Photovolt: Res. Appl.* **16**:235 (2008). | Jiang et al, Appl. Phys. Lett. **84**:3477 (2004).

Surface Structure with LEED

- NREL $Cu(In_{0.6}Ga_{0.4})Se_2$ Samples
  - Clean surface diffraction patterns difficult due to small grains and faceting.
  - Some grains ≳ 5 µm and relatively || to imaging plane.
  - **LEED:** 5 mm aperture over these grains.



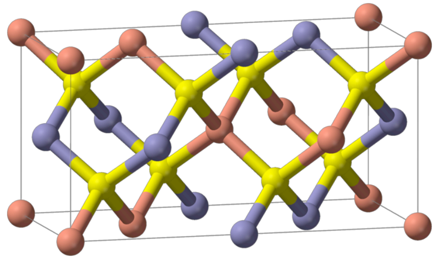


- **Microcrystalline, size ~1-2 µm.**
- **Faceted surface.**

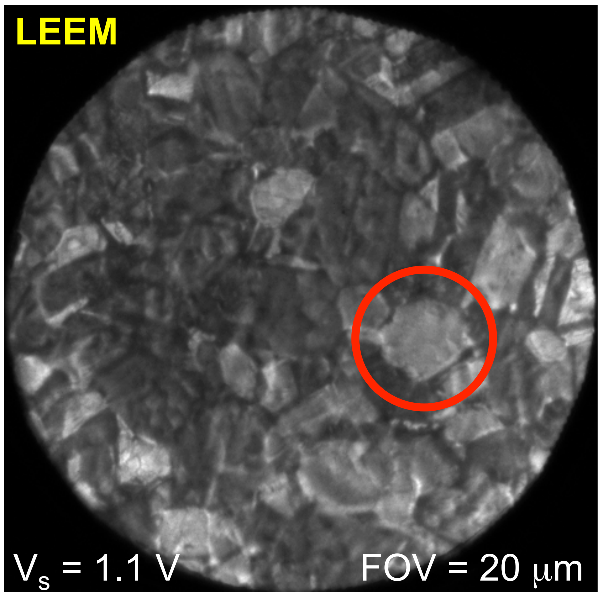
Contreras et al, *Thin Solid Films* **361**:167 (2000).

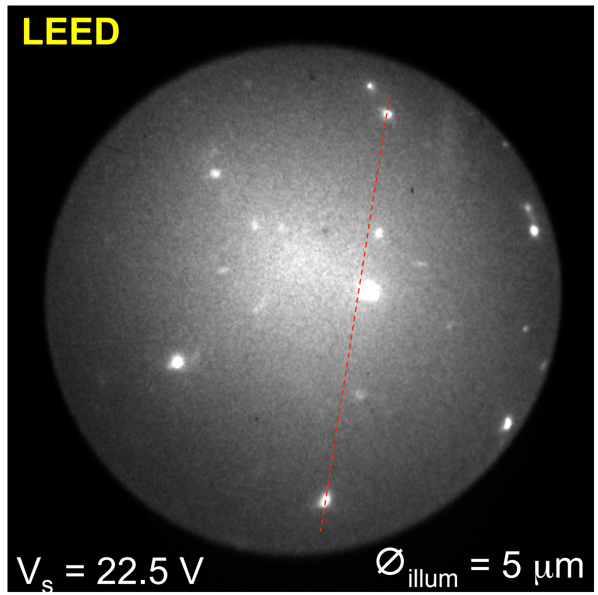
Surface Structure with LEED

- NREL $Cu(In_{0.6}Ga_{0.4})Se_2$ Samples
  - Clean LEED patterns difficult due to small grains and faceting.
  - Some grains $\gtrsim$ 5 μm and relatively || to imaging plane.
  - **LEED:** 5 mm aperture over these grains.

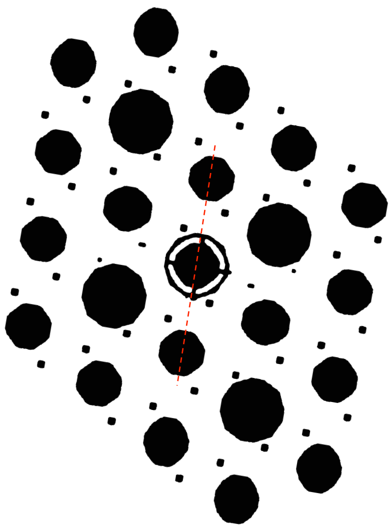


$Cu(In_{1-x}Ga_x)Se$





Modeled Reciprocal-Space Features of CIS {112} Plane

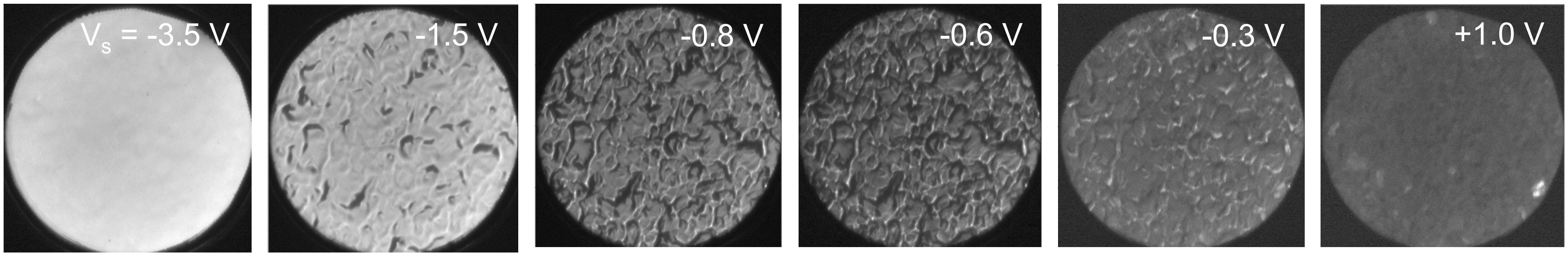


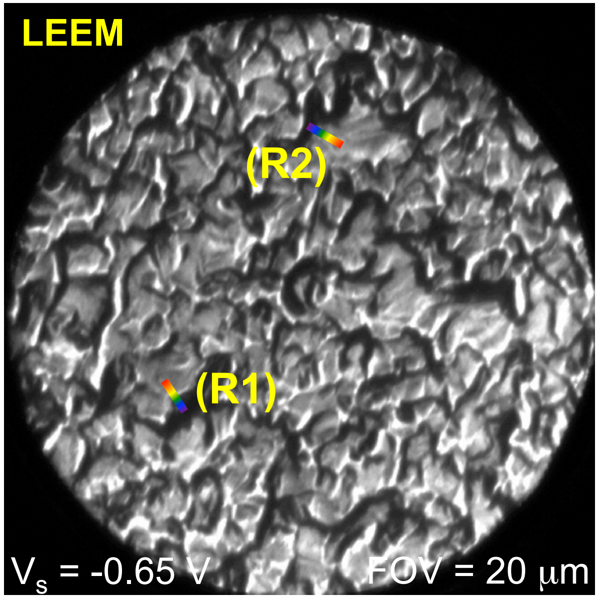
- **Hexagonal pattern consistent with CIGS {112} surface termination.**
- **Quantification of the lattice parameter is a work in progress.**

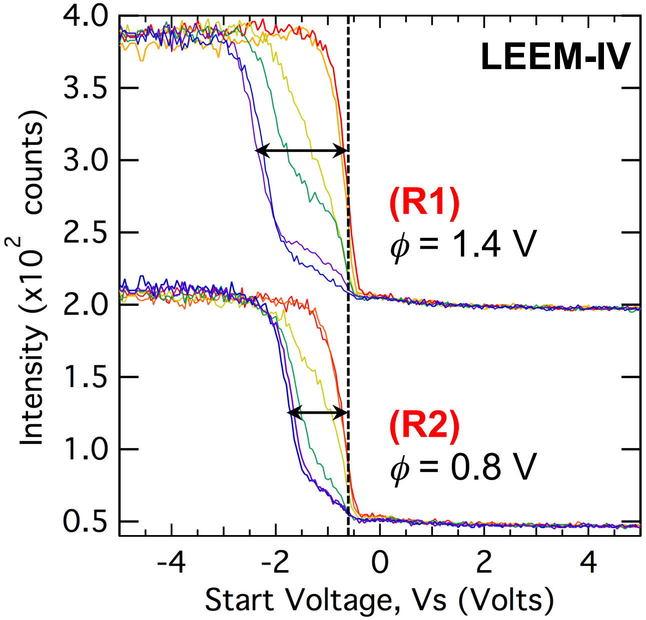
Contreras et al, *Thin Solid Films* **361**:167 (2000).

Work Function Mapping with LEEM-IV

- NREL $Cu(In_{0.6}Ga_{0.4})Se_2$ Samples
  - **LEEM-IV:** Intensity (I) vs. Start Voltage (V) ⇒ Stack of images as a function of V_s.
    Extract an IV spectrum for each pixel by tunneling through the stack.



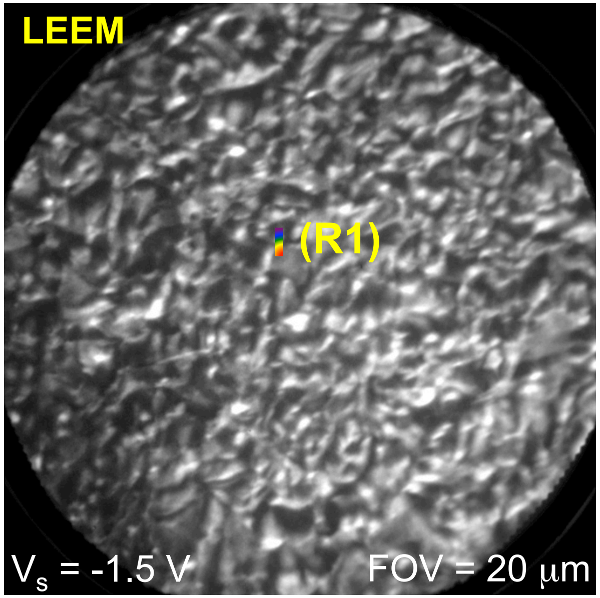


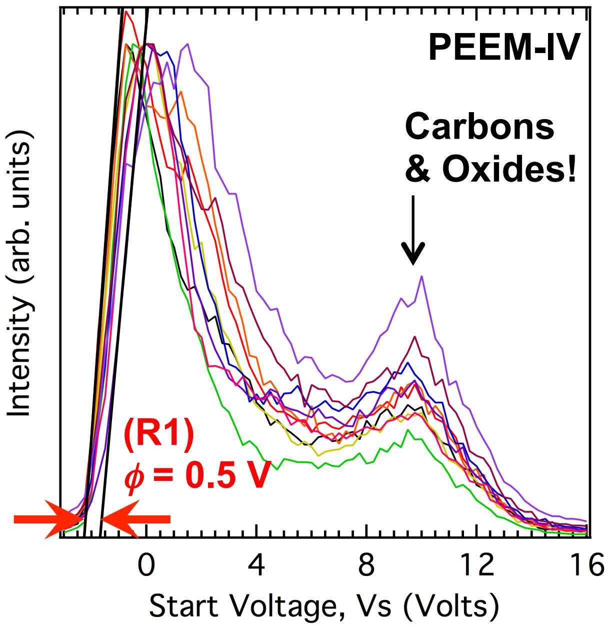


- **Significant variations in the grain boundary potential: ϕ = 0.1-1.4 V (larger than other reports).**

Electronic Structure Mapping with PEEM-IV

- NREL $Cu(In_{0.6}Ga_{0.4})Se_2$ Samples
  - **PEEM-IV:** He plasma discharge lamp (21.22 eV, 40.8 eV)
    Intensity (I) vs. Start Voltage (V) ⇒ Stack of images as a function of V_s.
    Extract an IV spectrum for each pixel by tunneling through the stack.
  - Very time-intensive experiment – 4 hours per dataset.

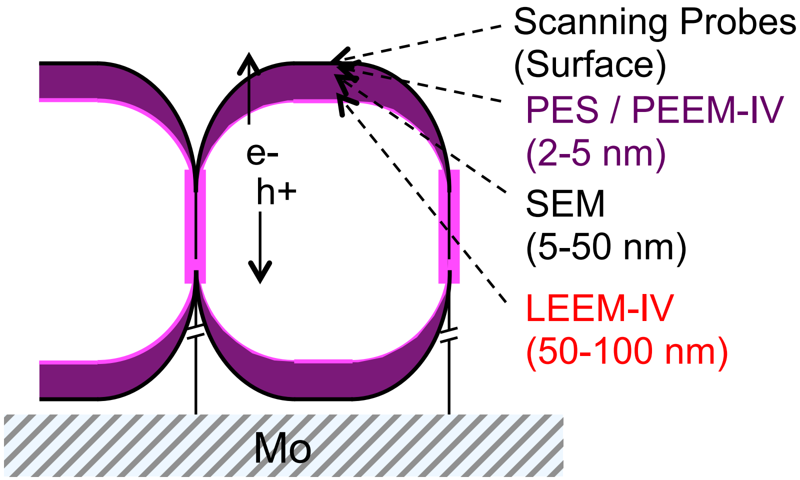


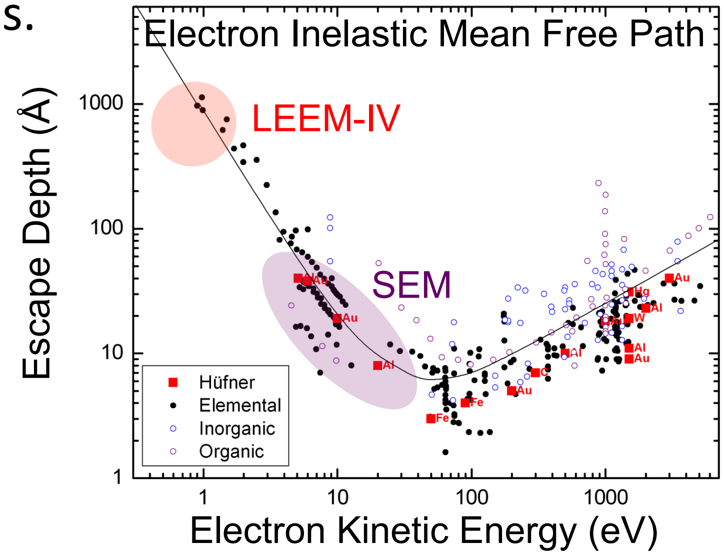


- **Work function from secondary electron onset: ϕ = 0.5 V (consistent with other reports).**
- **Lots of carbons and oxides based on feauture at V_s = 8-12 V.**

What’s the Difference Between LEEM / PEEM?

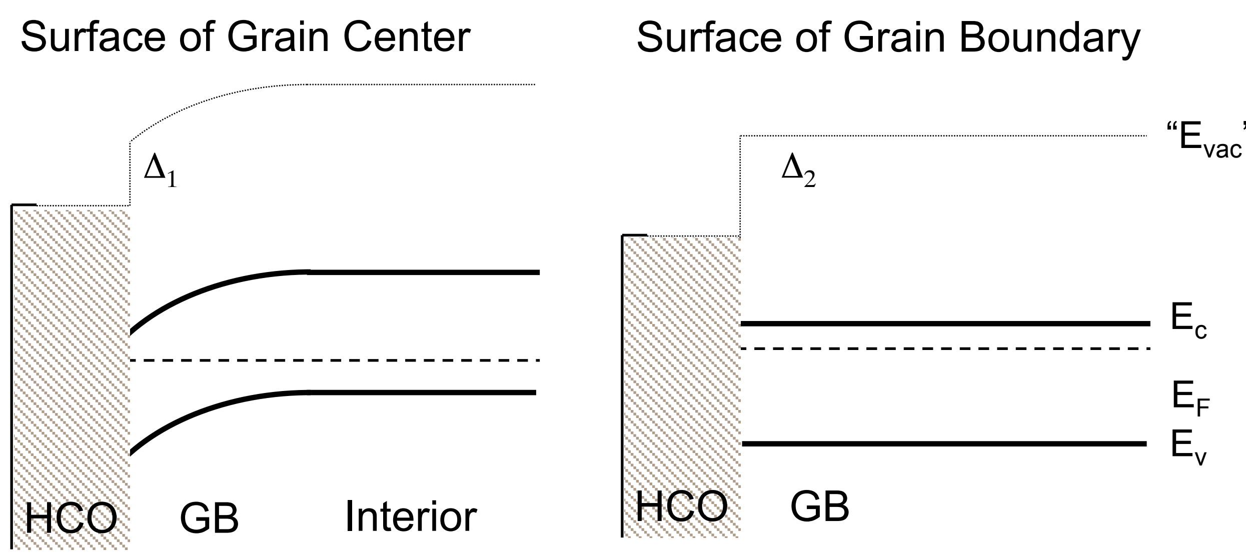
- Different probing depths of different techniques.





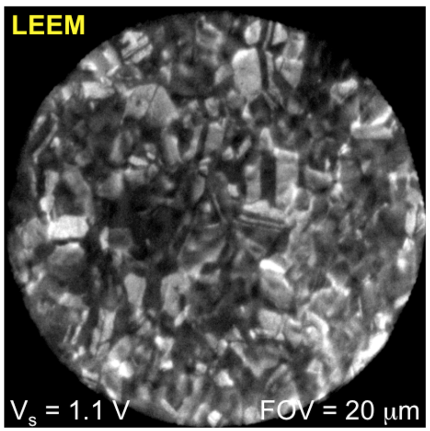
PEEM-IV measures **work function**.

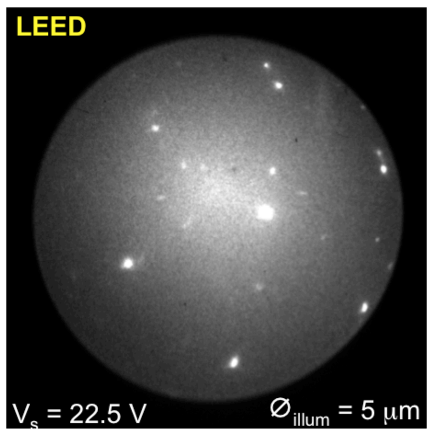
LEEM-IV measures **work function + electrostatic field** accessible within the mean free path of incident electrons.

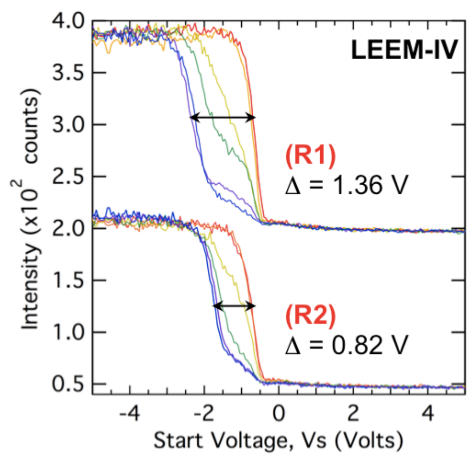


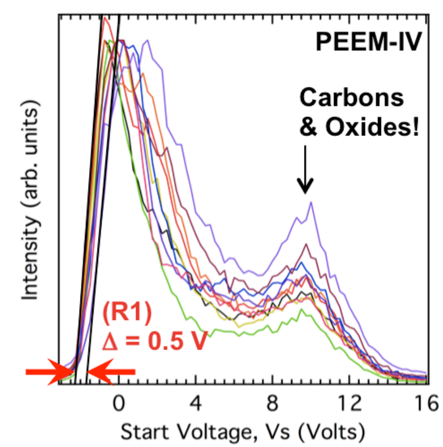
Conclusion and Next Steps

- **Conclusions**
  - LEEM / PEEM promising for characterizing chemical and electronic structure of CIGS.
  - Different contrast mechanisms highlight CIGS morphology, grain boundaries, etc.
  - Selective area LEED directly confirms {112} surface faceting of CIGS.
  - ϕ_{max} = 1.4 V or 0.5 V depending on measurement technique.









- **Next Steps**
  - Need to verify LEEM-IV results.
  - Sample processing: sputtering, focused ion beam milling.
  - New light sources to improve data collection efficiency in PEEM.
  - Correlate GB potentials with nanoscale charge transport.
  - Real time dynamical studies (e.g., selenization, ion migration, etc.)