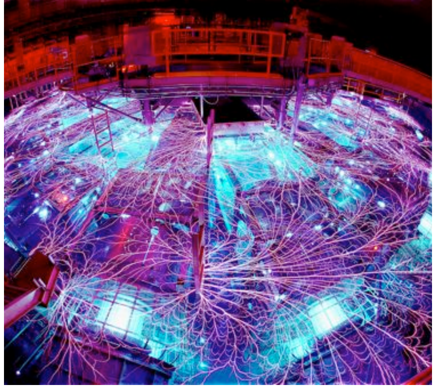

Large Built-in Potential Variations Observed at $Cu(In_{1-x}Ga_x)Se_2$ Grain Boundaries Using Low Energy Electron Microscopy

Calvin K. Chan*, Sandia National Laboratories
Rommel Noufi, National Renewable Energy Laboratory
Lorelle Mansfield, National Renewable Energy Laboratory
Gary Kellogg, Center for Integrated Nanotechnologies

MRS Workshop on Photovoltaic Materials and Manufacturing Issues III
10-13 September 2013, Golden, CO

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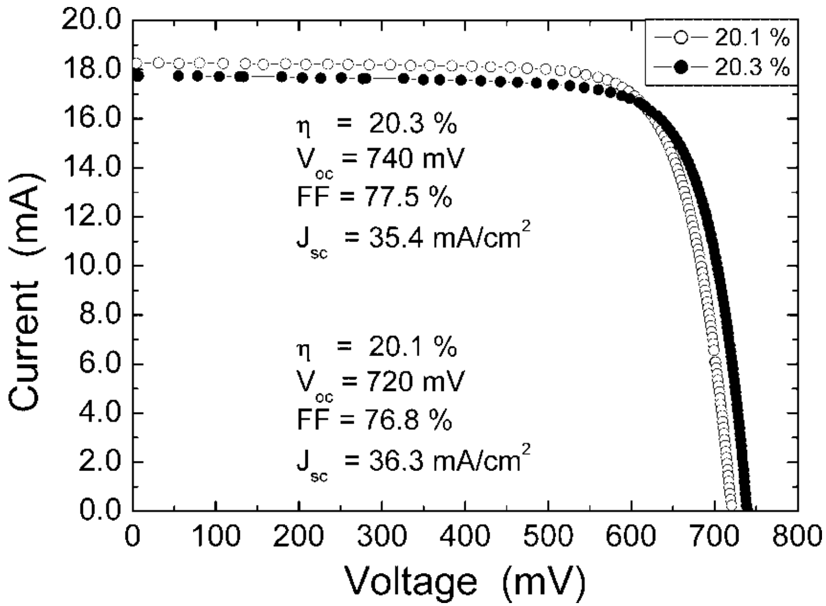
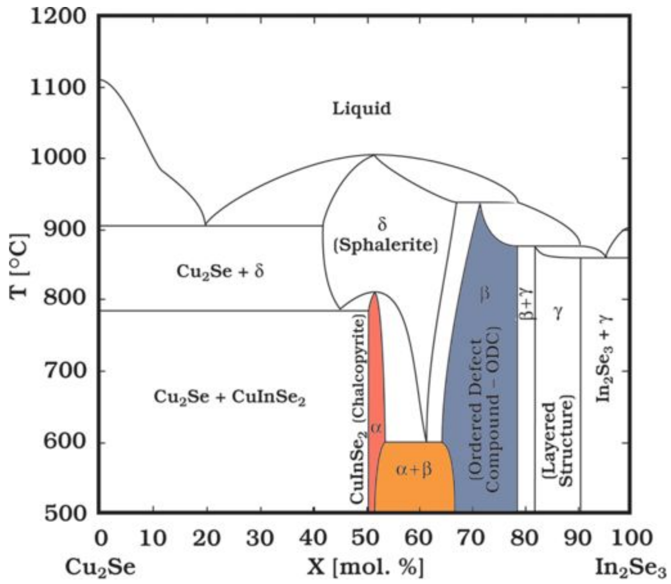
CIGS: The Promise and Problem

- **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)



Pseudobinary Phase Diagram of CIGS



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

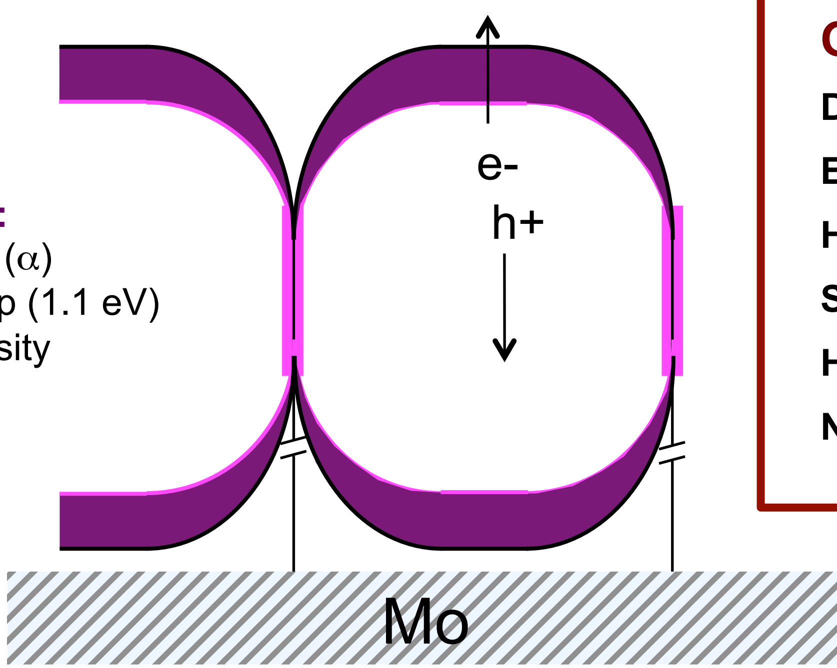
Stanbery, *Crit. Rev. Sol. State Mater. Sci.* **27**:73 (2002).

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



Open Questions

Depletion or inversion?

Energy level alignment?

Hole/electron barrier?

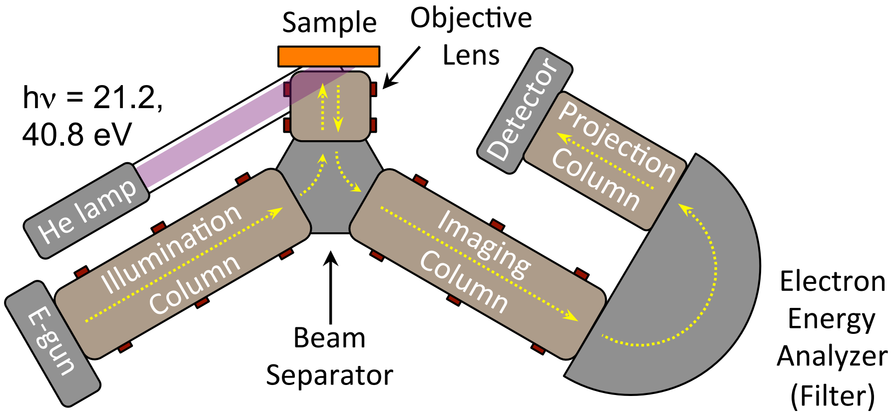
Space charge region?

How do holes get out?

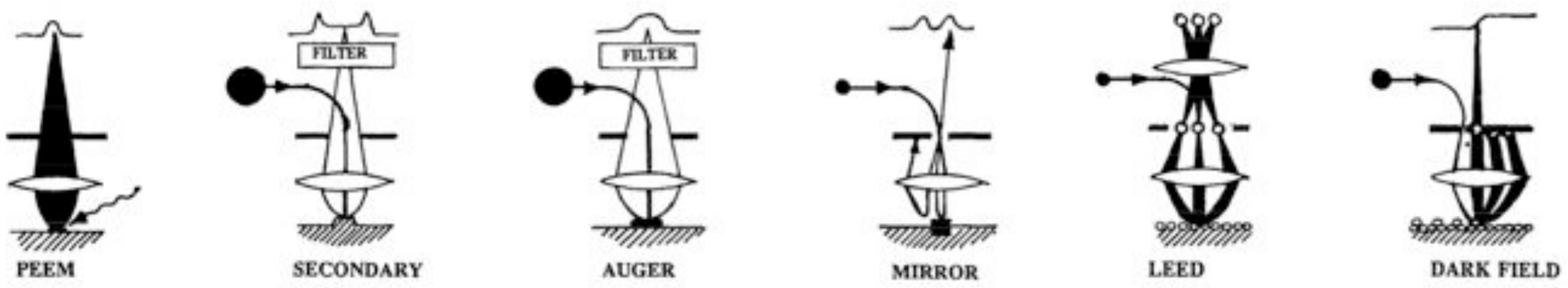
Nanoscale phase segregation?

Our Approach: LEEM/PEEM

- **Photoemission / Low Energy Electron Microscopies (PEEM / LEEM)**
  Spatially-resolved electronic and chemical structure (PES, EELS, AES, SES, LEED, etc.)



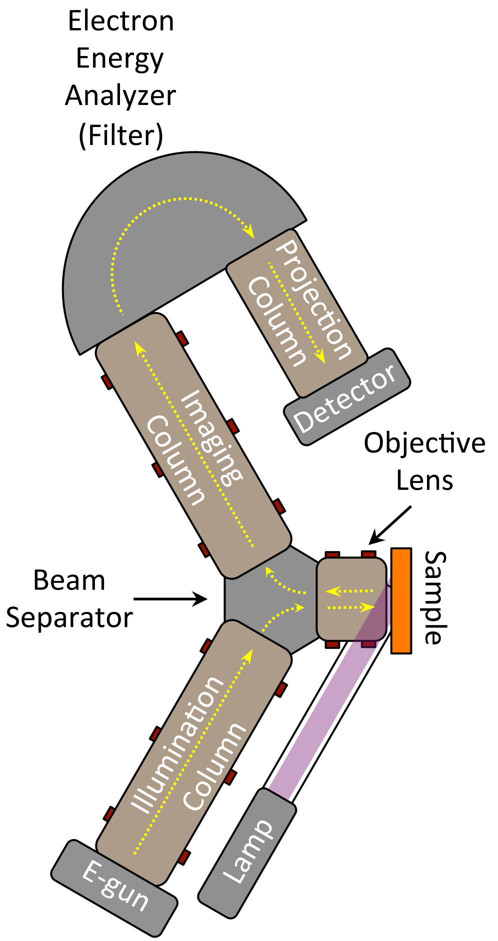
- **5-10 nm spatial resolution**
- **50-100 meV spectral resolution**
- **Live-time imaging of:**
  - Surface topology and crystallography
  - Electronic and chemical structure
  - Carrier/field distribution
  - Fermi-level/surface
  - Interfacial band alignment
  - Phonons/Plasmons

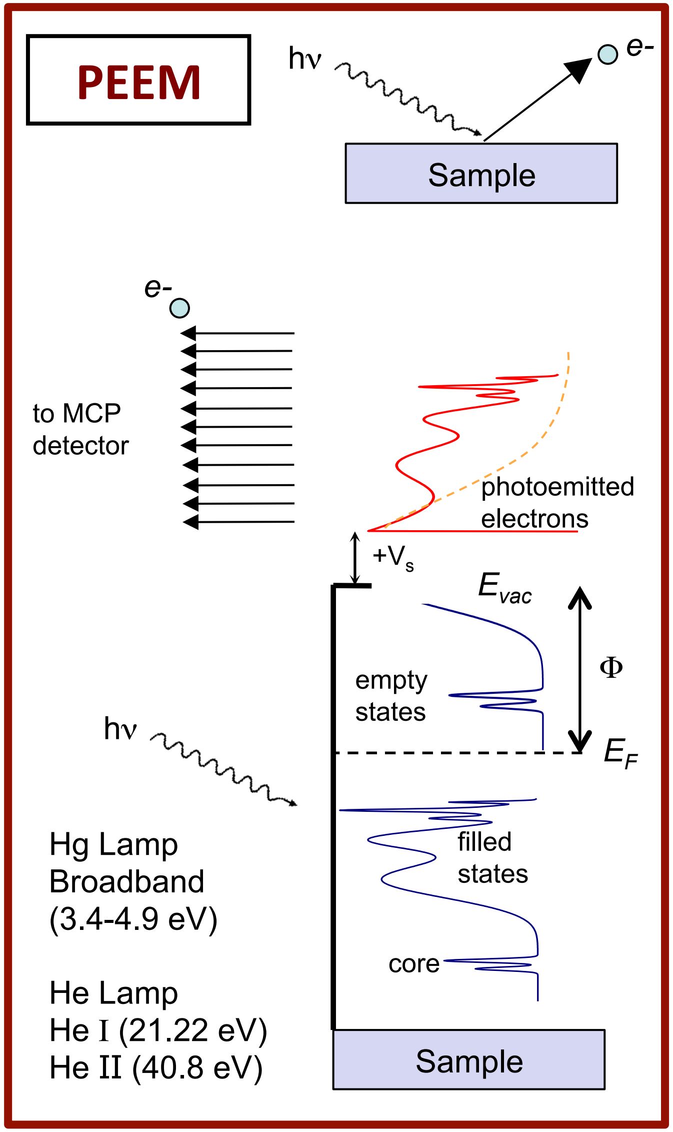


Veneklasen, *Rev. Sci. Instrum.* **63**:5513 (1992).

Principles of PEEM / LEEM

- For each pixel of the microchannel plate…





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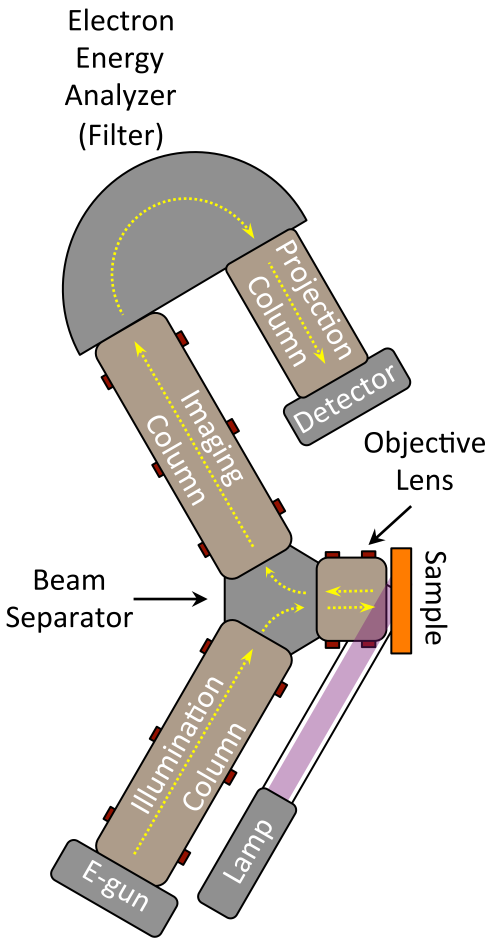

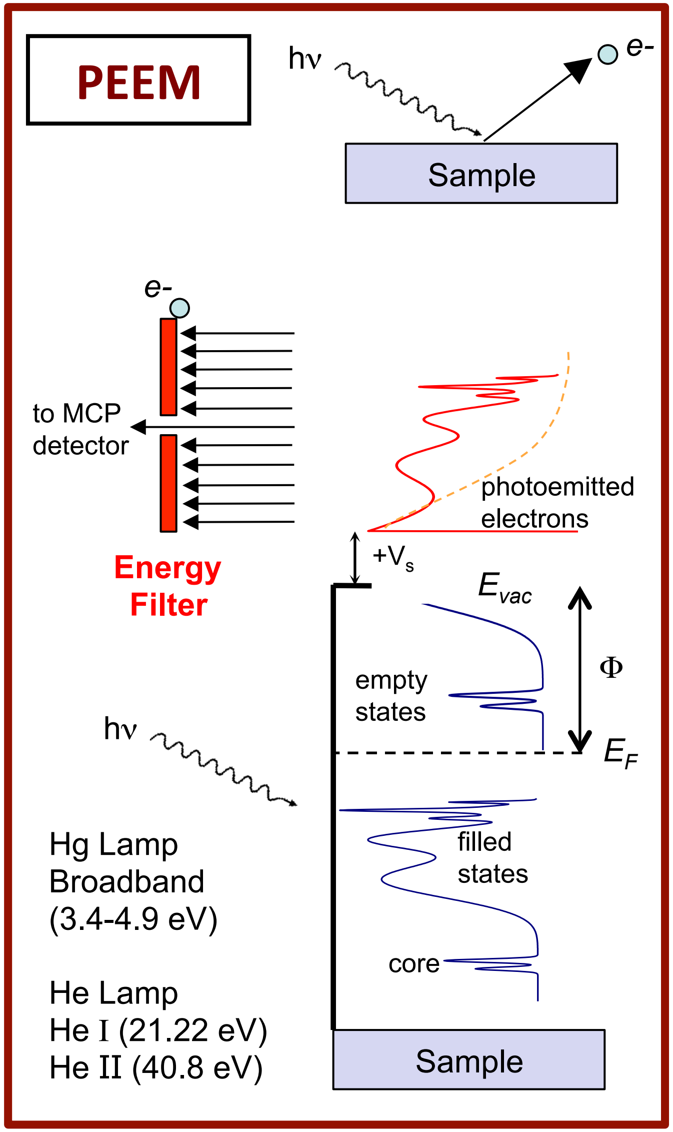

Principles of PEEM / LEEM

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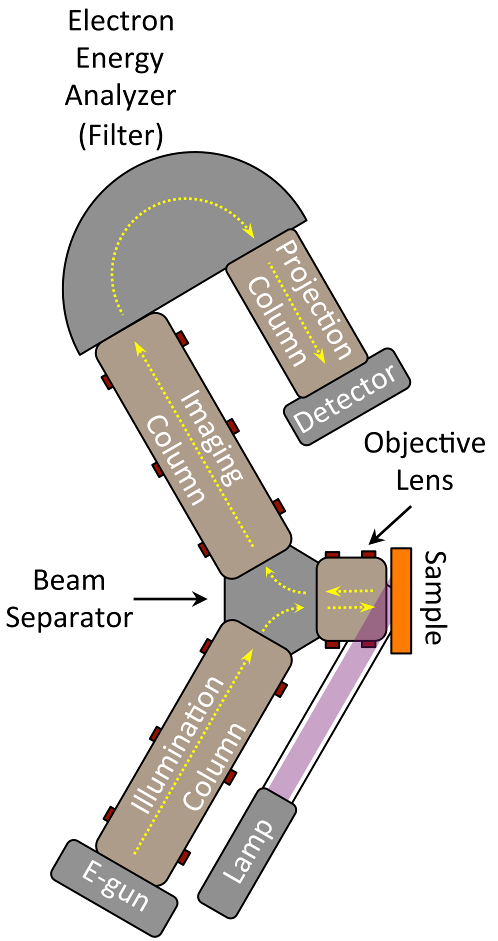
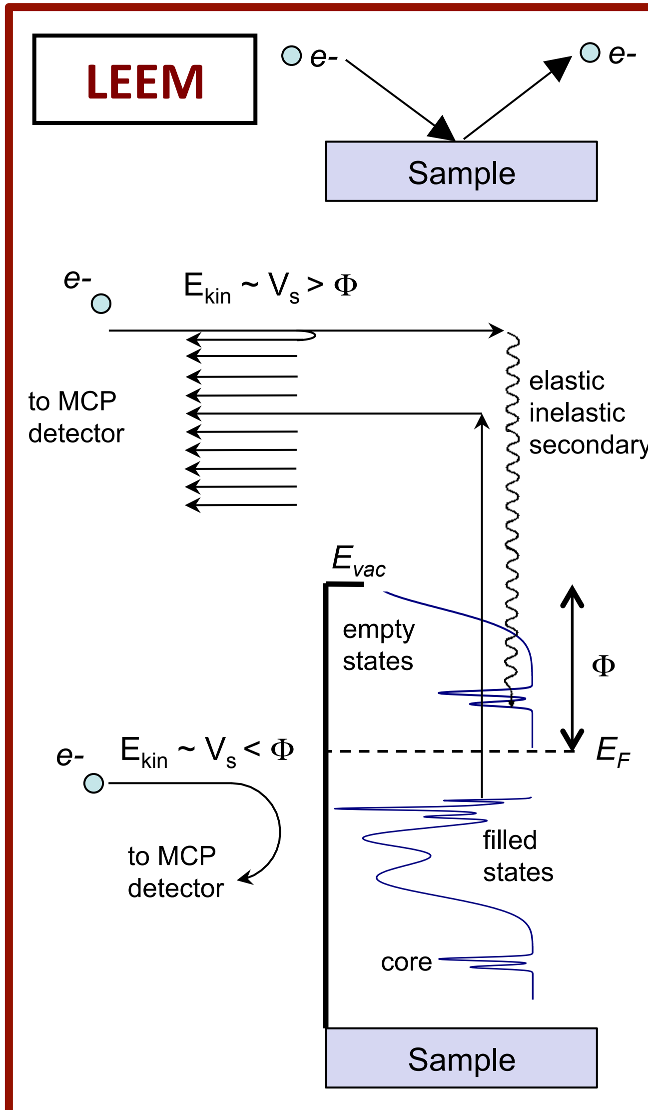
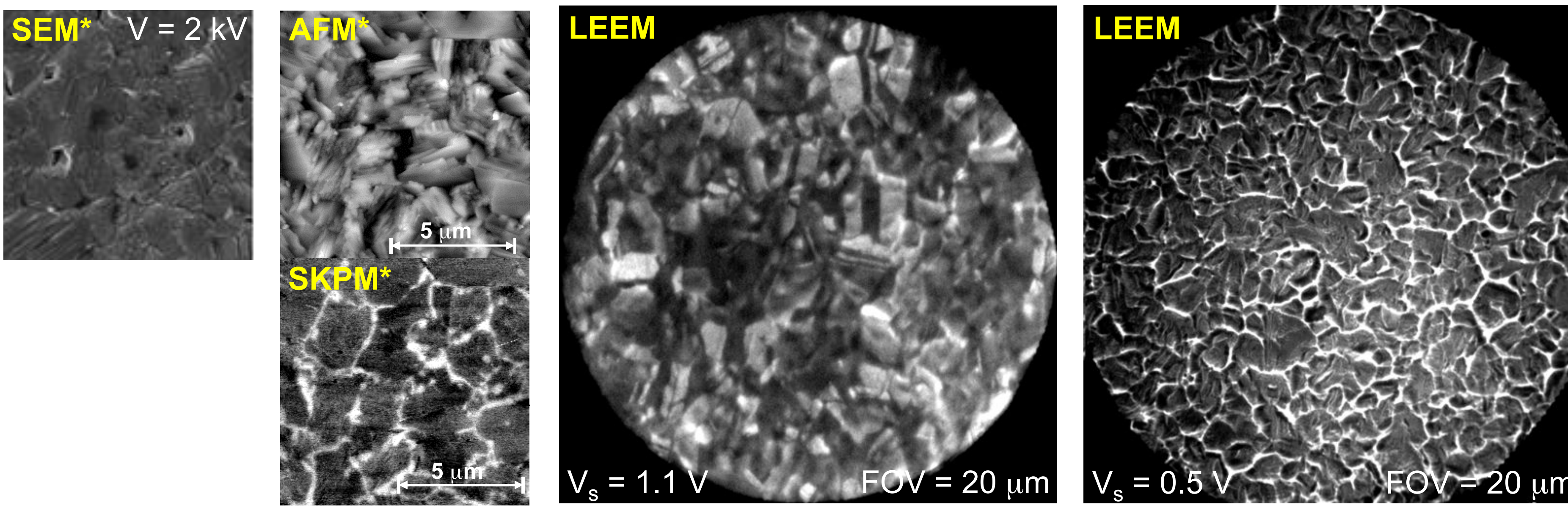




Imaging Morphology with LEEM

- NREL $Cu(In_{0.6}Ga_{0.4})Se_2$ Samples*
  - 3-stage vacuum-deposition on SLG/Mo, no top contacts (20% efficient with contacts).
  - X-ray fluorescence: Cu(III) = 0.913, Ga(III) = 0.39.
  - **PEEM / LEEM:** Samples annealed in situ at 300-400 °C for 12-48 hours.

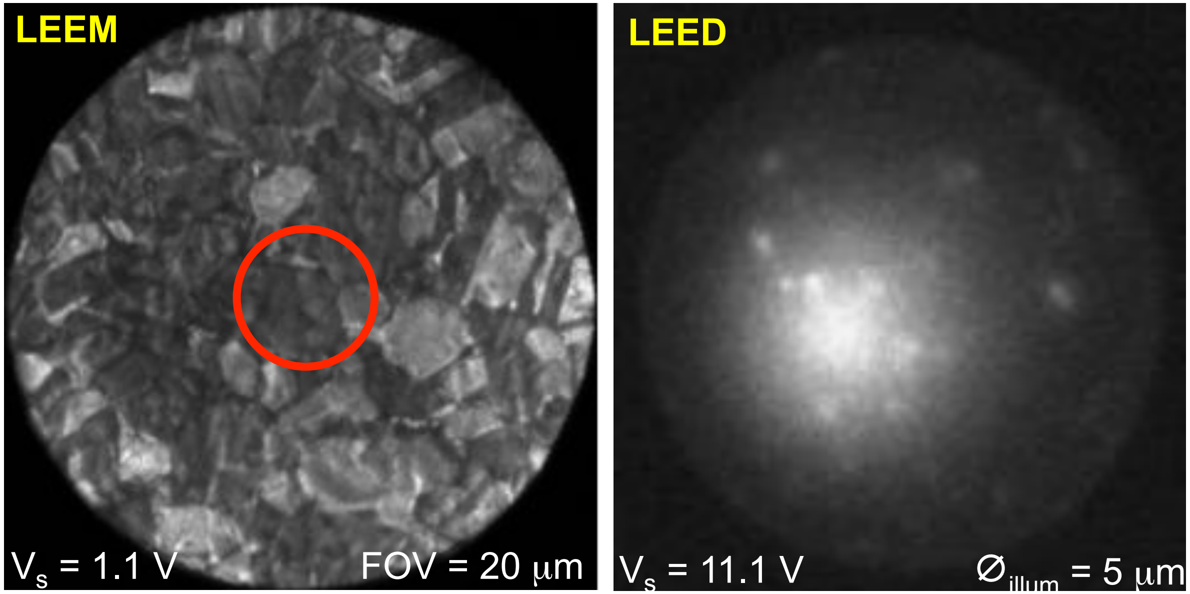


  - **Microcrystalline, size ~1-2 μm**
  - **Faceted surface**

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

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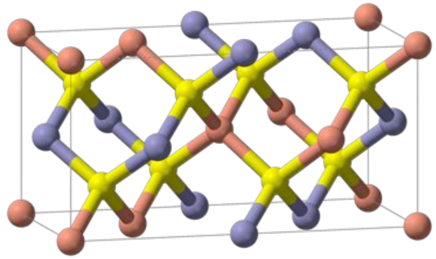
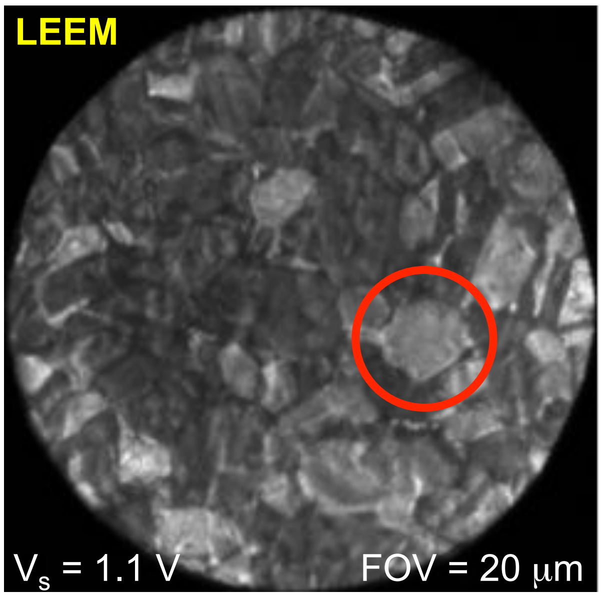
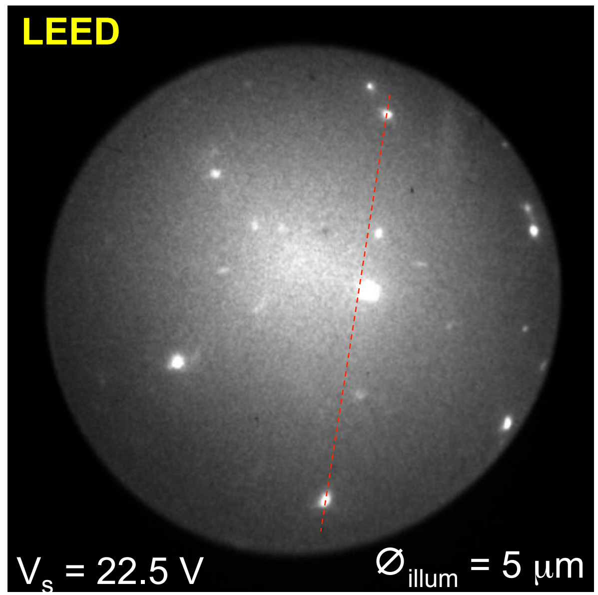
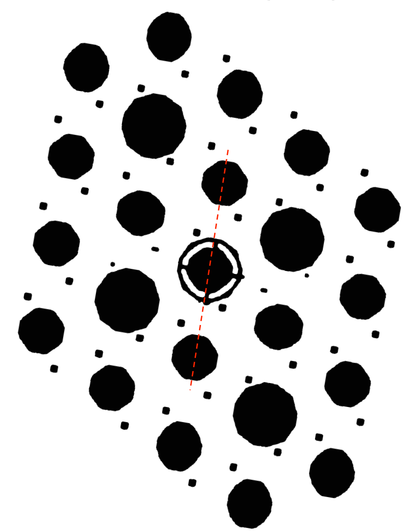


$Cu(In_{1-x}Ga_x)Se$





Modeled Reciprocal-Space Features of CIS {112} Plane

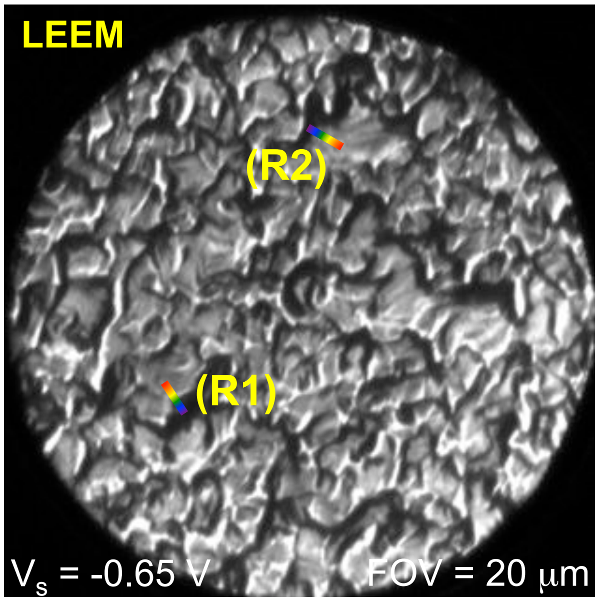


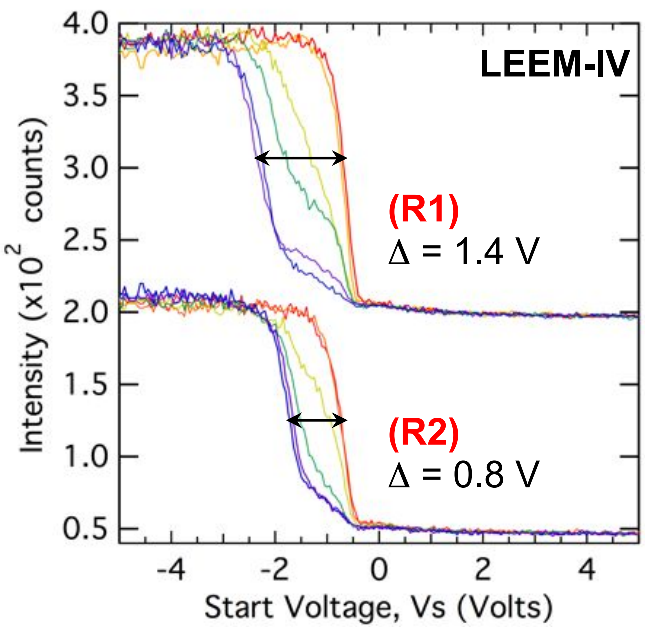
- **Hexagonal pattern consistent with CIGS {112} surface termination.**
- **Quantification of the lattice parameter is a work in progress.**

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

Electronic Structure with LEEM-IV

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



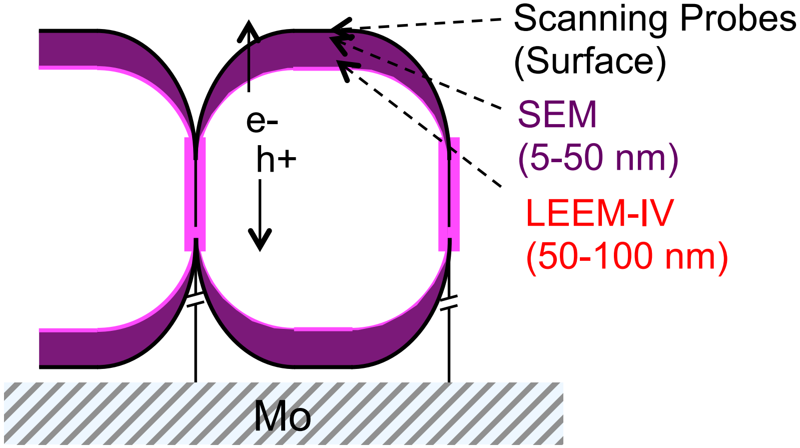


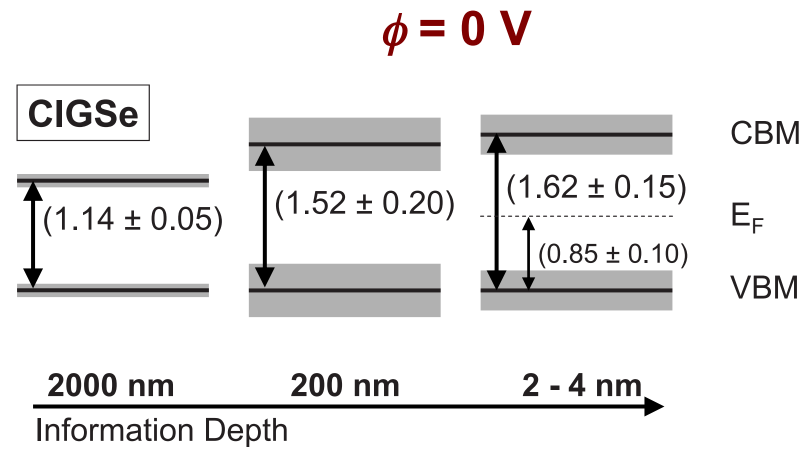
- **Significant variations in the grain boundary potential: ϕ = 0.1-1.4 V.**
- **GB potential difference much larger than reported with other techniques (50-100 meV).**

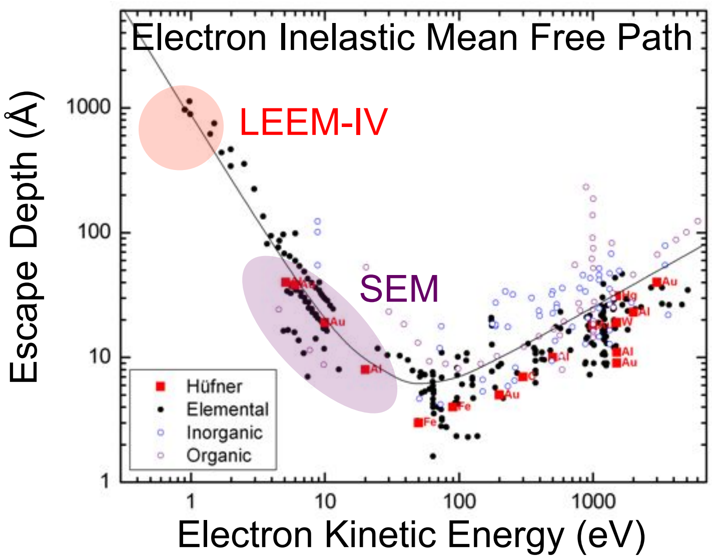
Why are GB Potentials Larger in LEEM?

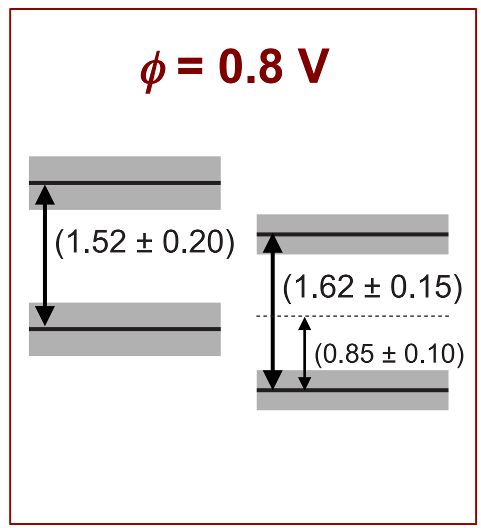
Bär et al, *Appl. Phys. Lett.* **93**:244103 (2008).

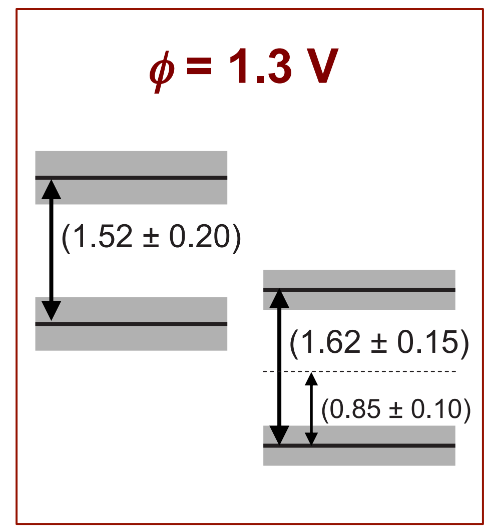
- Different probing depths of different techniques.





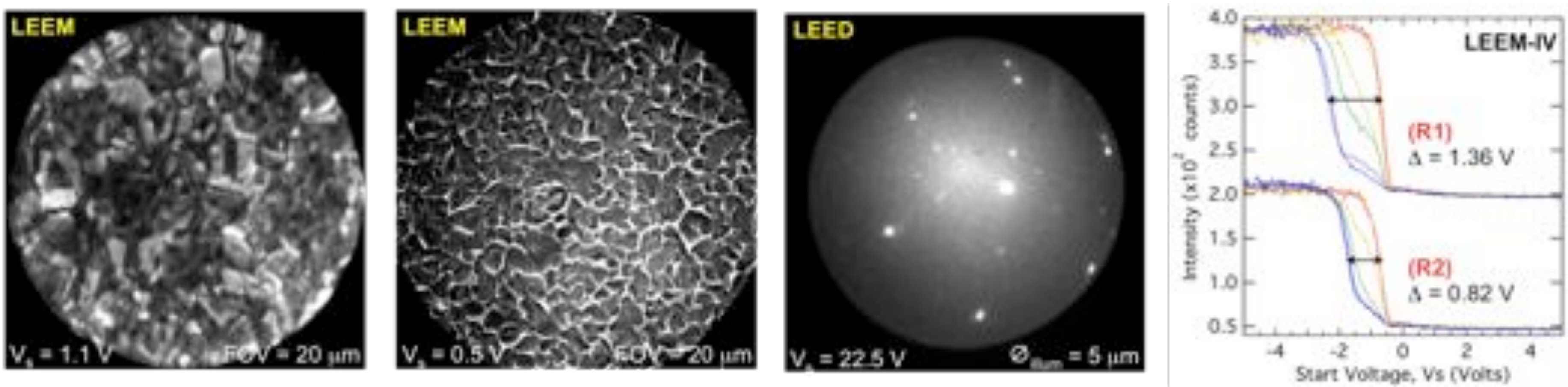






Conclusion and Next Steps

- **Conclusions**
  - PEEM / LEEM: powerful tool for concurrently characterizing physical and electronic structure.
  - Different contrast mechanisms highlight CIGS morphology or grain boundaries.
  - Selective area LEED directly confirms {112} surface faceting of CIGS.
  - Significant variations (0.1-1.4 V) in the pn junction potential at CIGS grain boundaries.



- **Next Steps**
  - Investigate which nanoscale physicochemical properties determine magnitude of GB potential.
  - Investigate how GB pn junction potentials impact nanoscale charge transport.
  - Extend studies to more problematic materials and interfaces (e.g., higher Ga content CIGS, alternative buffer layers and contacts, CZTS, nanocrystals).

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