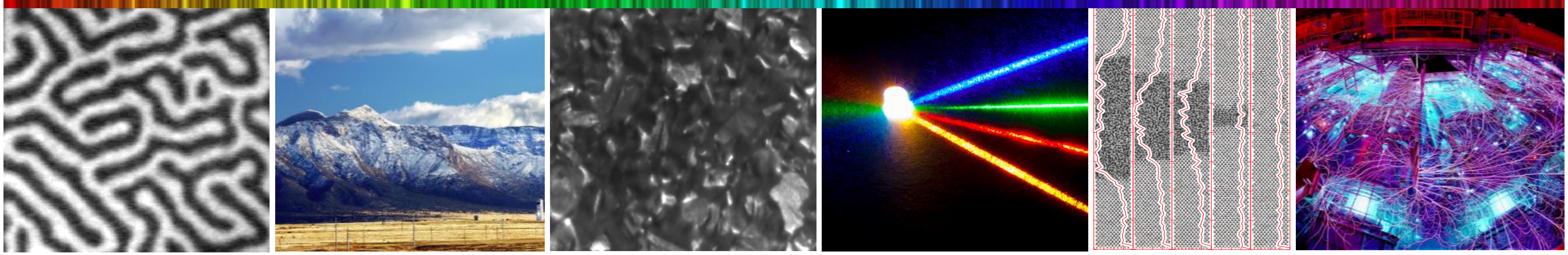
SAND2014-4778C

Photoemission and Low-energy Electron Microscopy (PEEM and LEEM) Studies of $Cu(In,Ga)Se_2$ Photovoltaic Materials



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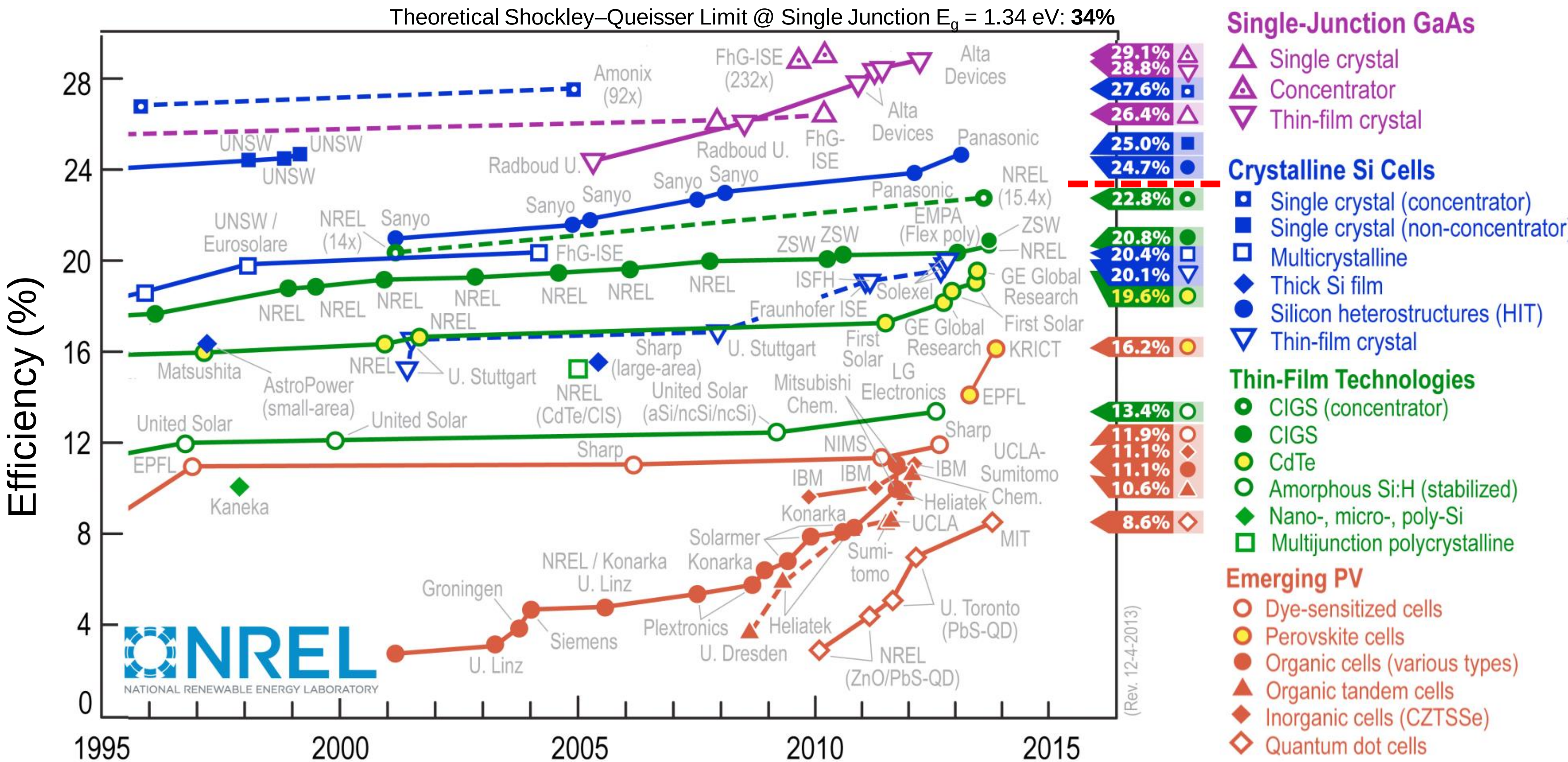
Best Thin-Film Research Cell Efficiencies

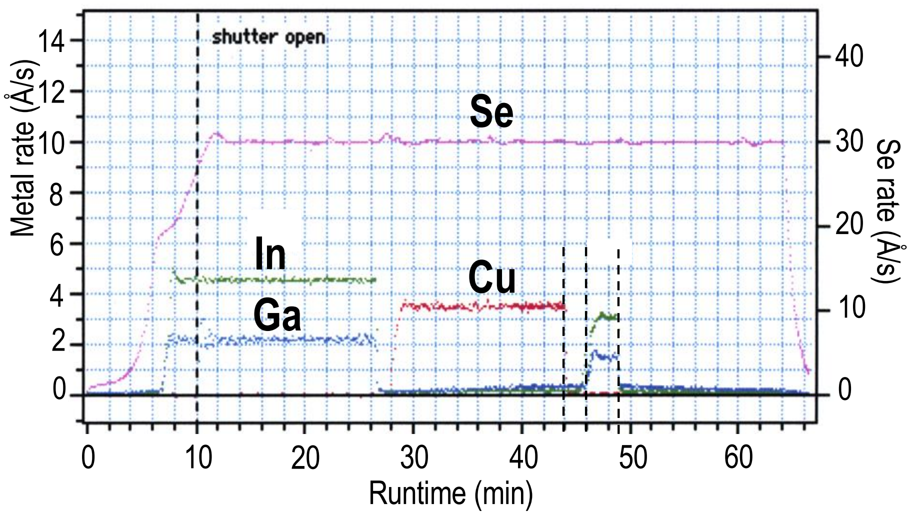
- **Thin-Film PV efficiencies approaching that of wafer-based Si technologies.**
  - Pilot modules ~ 0.85 x η_{max}, Production modules ~ 0.75 x η_{max}.

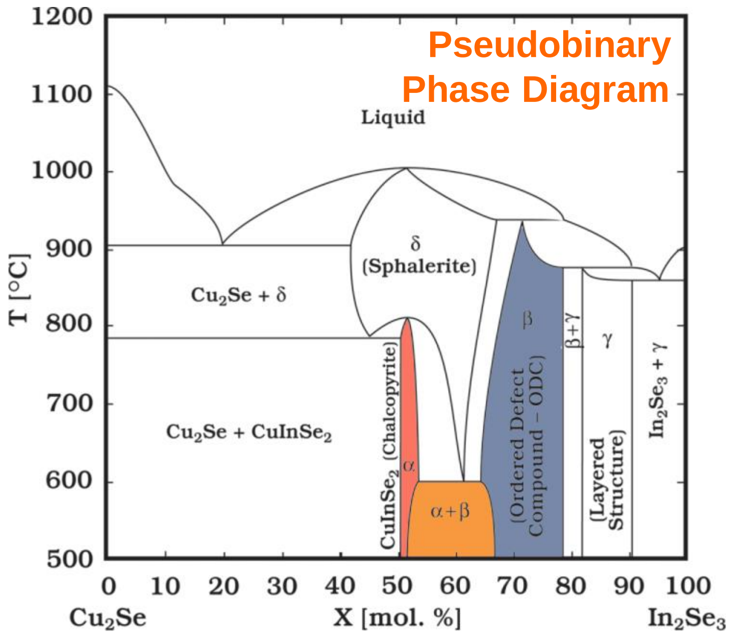


$Cu(In_{1-x}Ga_x)Se_2$ Photovoltaic Cells

- **Highest efficiency thin-film PV cell.**
  - "NREL 3-stage process" gives η_{lab} = 20%.
  - Good outdoor performance and stability.
- **Growing, but limited understanding.**
  - Difficult to control many different phases.
  - Role of defects and interfaces debated.

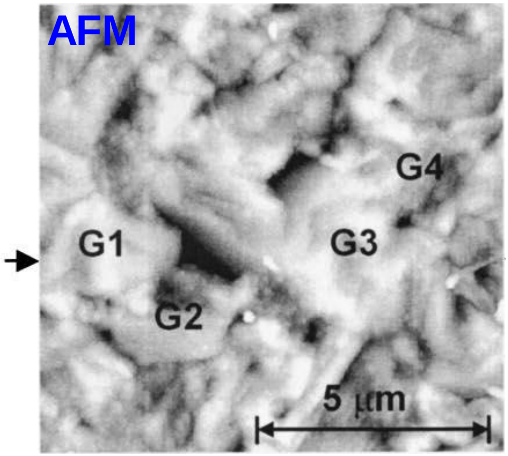
Deposition Profile for "NREL 3-Stage" Process

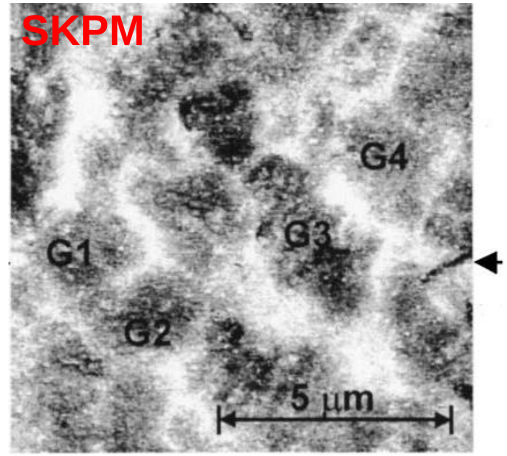


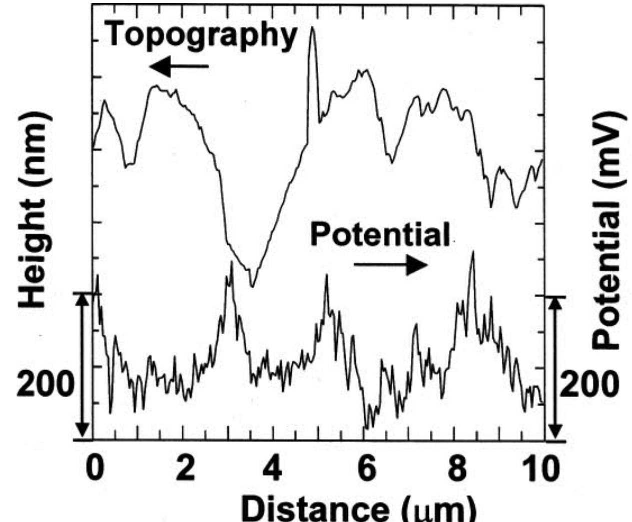


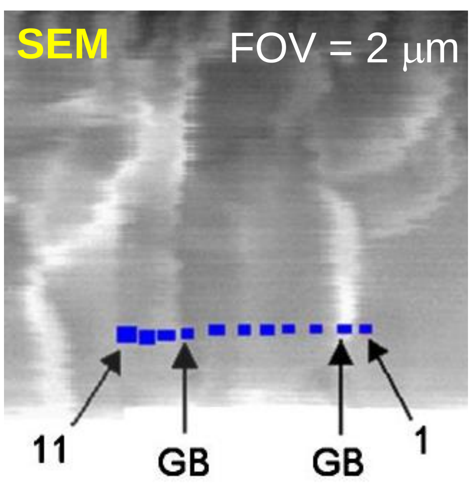
Stanbery, *Crit. Rev. Sol. State Mater. Sci.* **27**:73 (2002).

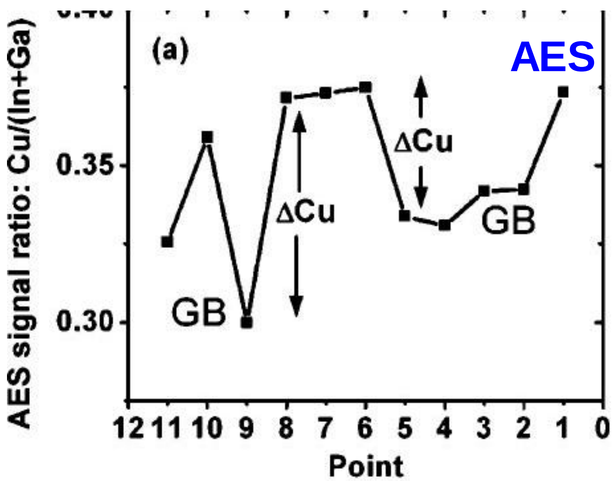
Examples of Microscopy on CIGS

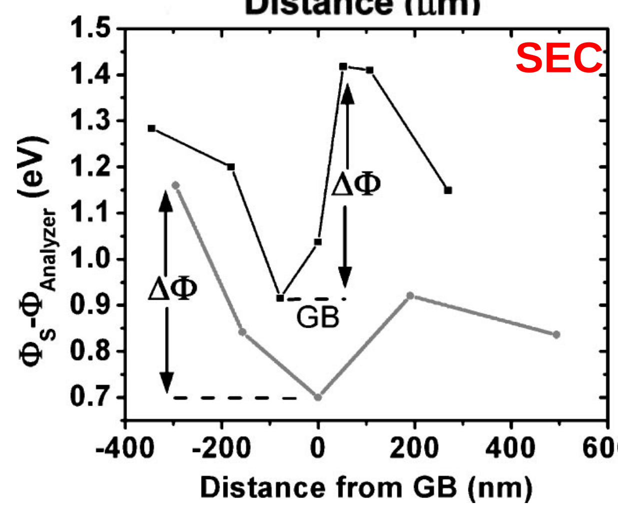






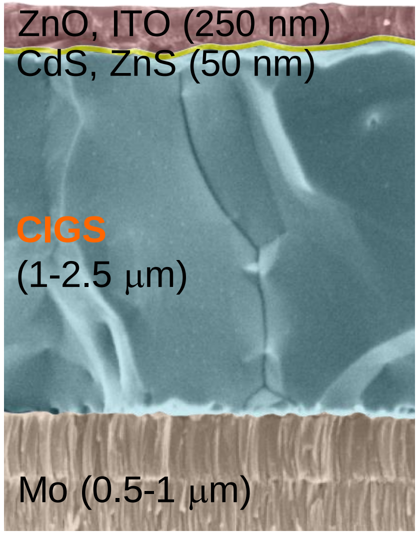


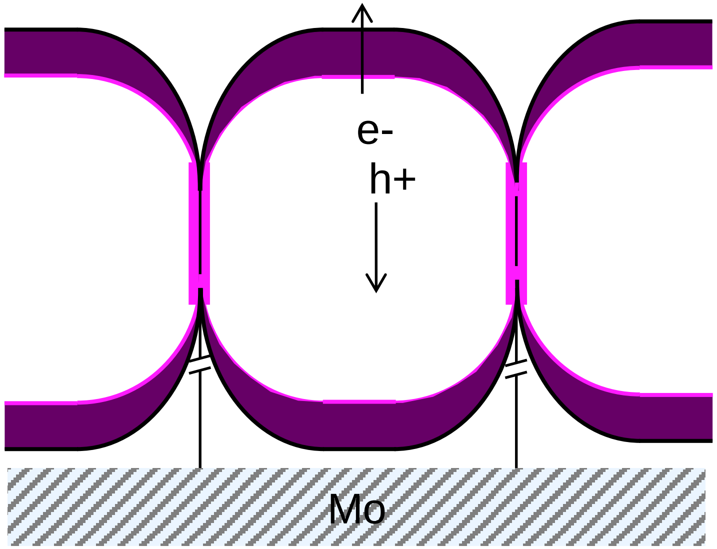




Current Understanding of CIGS

- **Foundation to advance processing techniques and PV materials (e.g. CZTS).**





Interface Layer:
Cu-poor (β)
E_g = 1.6 eV
n-type?

Grain Interior:
Stoichiometric (α)
E_g = 1.1 eV
p-type

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

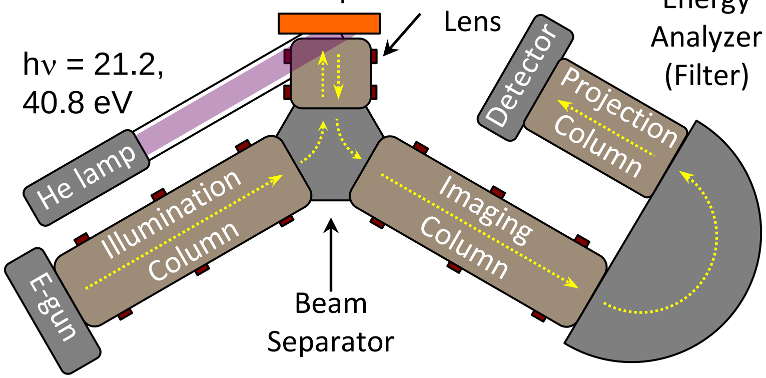
- **Open questions: *Electronic Structure***
  - Interface layer depleted or inverted?
  - Band alignment at p-n junction?
  - Size of the space-charge region?
  - Any hole/electron barriers?
  - How do holes get out?
  - Nanoscale phase segregation?
  - Chemical/Electronic structure variations?
  - Contacts?

Hetzer et al, *APL* **86**:162105 (2005) | Azulay et al, *PRL* **108**:076603 (2012) | Abou-Ras et al, *PRL* **108**:075502 (2012) | Li et al, *IEEE J. Photovolt.* **2**:191 (2012) | Bär et al, *APL* **93**:244103 (2008) | Jiang *et al.*, *APL* **84**:3477 (2006) | Yan *et al.*, *APL* **87**:121904 (2005) ...

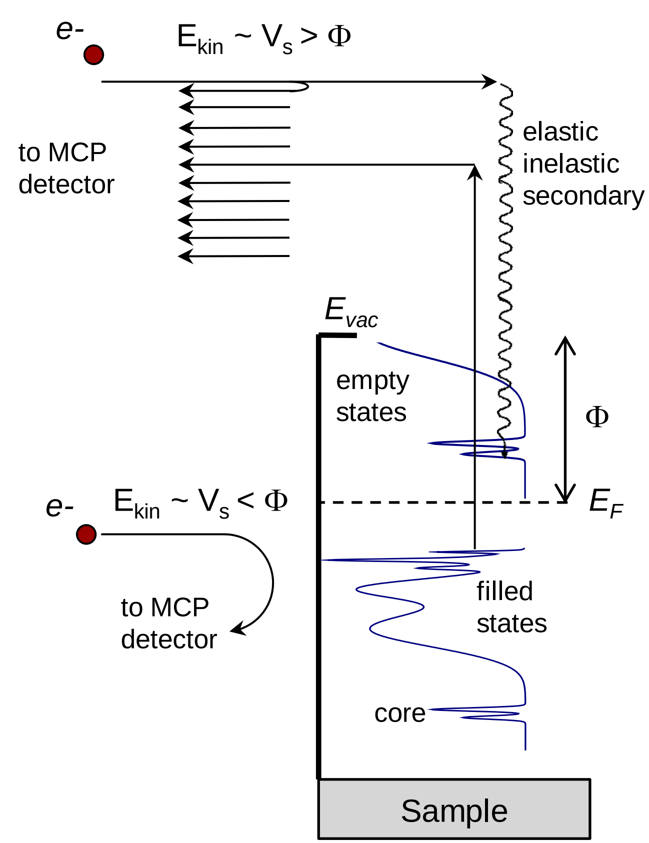
Our Approach: LEEM/PEEM

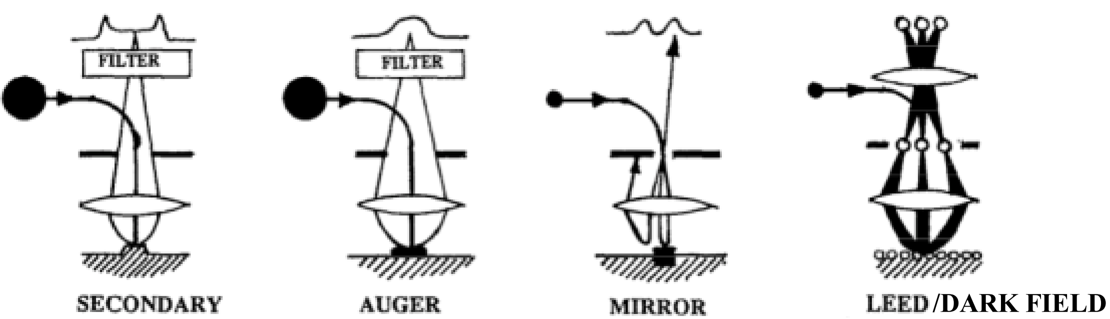
- **Low Energy / Photoemission Electron Microscopies (LEEM / PEEM)**
  Spatially-resolved electronic and chemical structure (PES, EELS, AES, SES, LEED, etc.)

Elmitec LEEM III/ SPELEEM



LEEM





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

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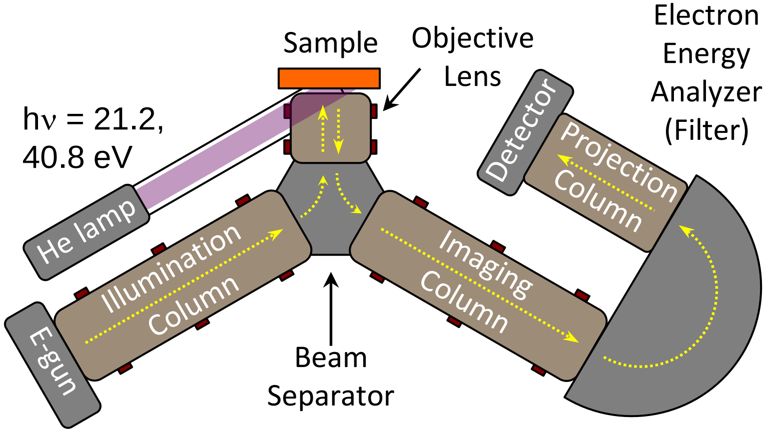
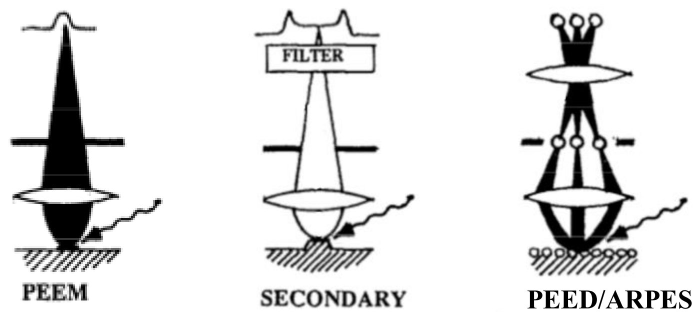
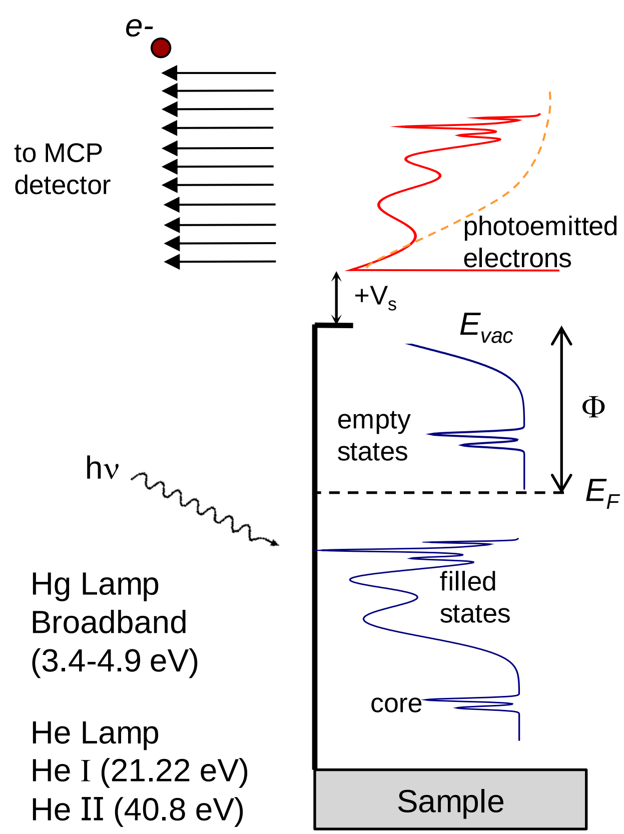




PEEM



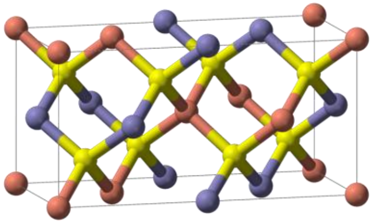
Hg Lamp
Broadband
(3.4-4.9 eV)

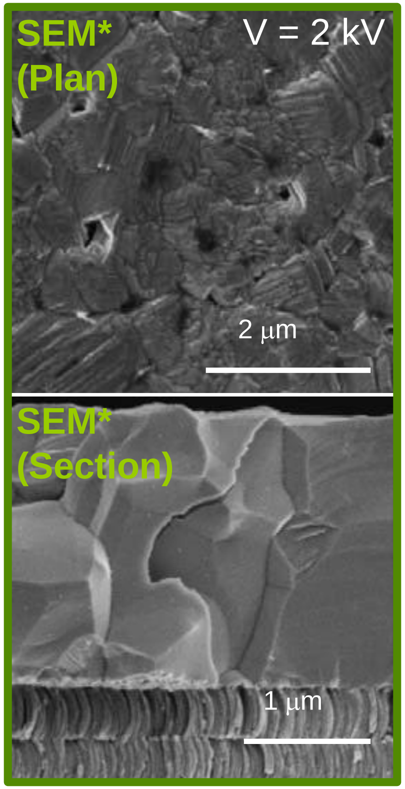
He Lamp
He I (21.22 eV)
He II (40.8 eV)

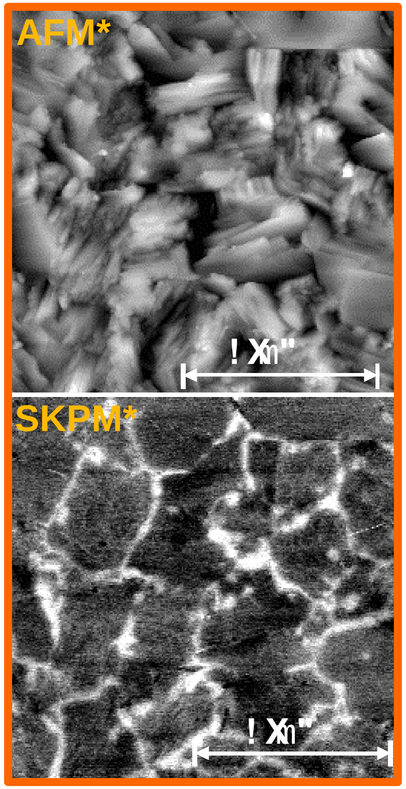
Veneklasen, *Rev. Sci. Instrum.* **63**:5513 (1992)

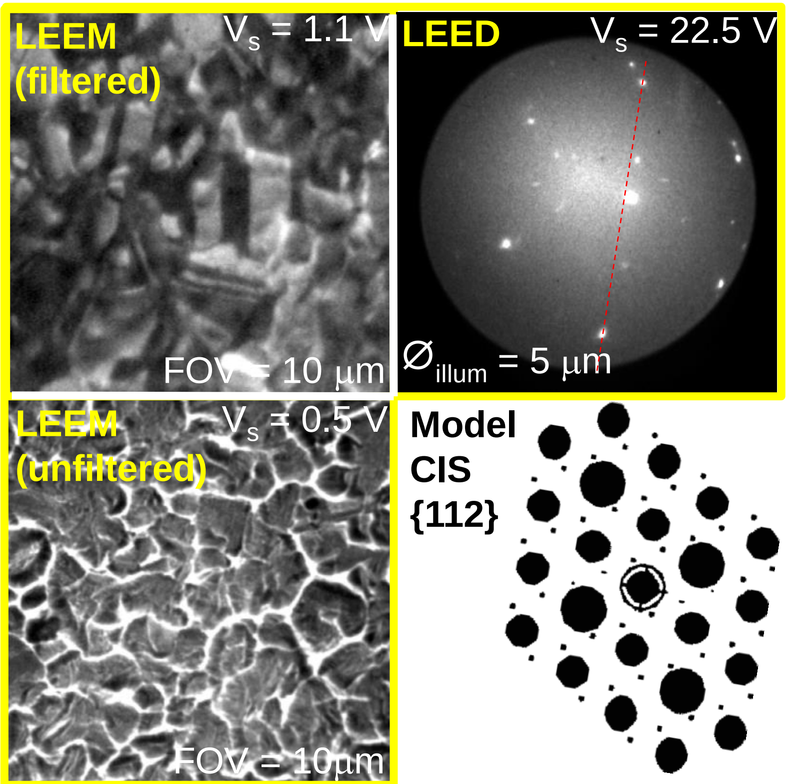
Morphology and Structure with LEEM

- **NREL 3-Stage $Cu(In_{0.6}Ga_{0.4})Se_2$ on Mo/SLG [no top contacts]**
  - Microcrystalline (1-2 μm)
  - Faceted {112} surface





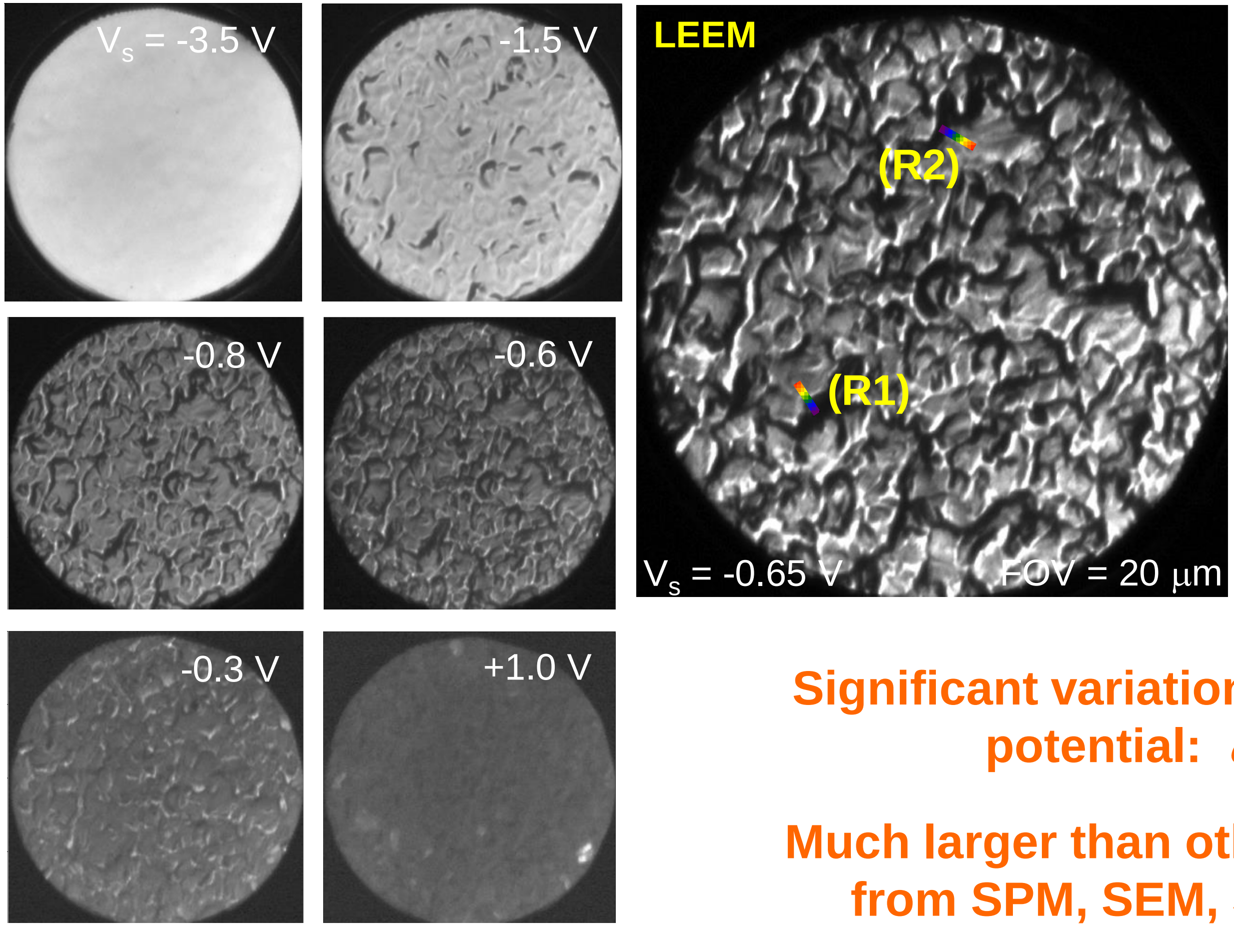


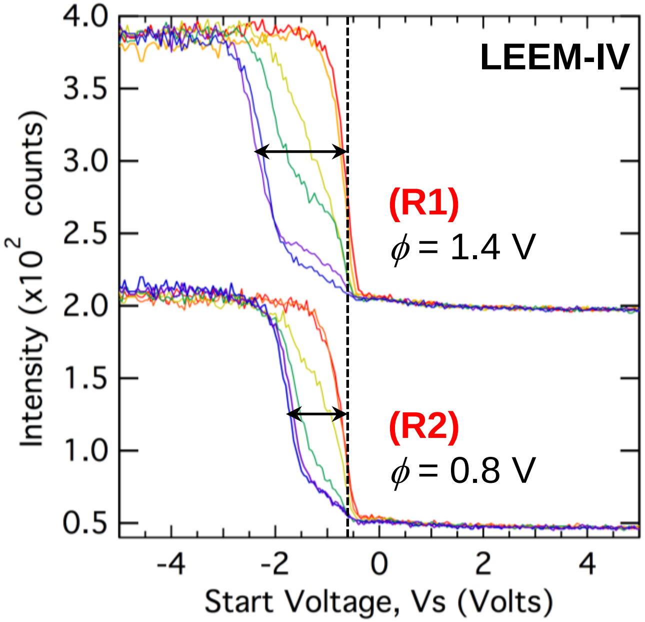


*Repins et al, *Prog. PV: Res. Appl.* **16**:235 (2008). | Jiang et al, *APL* **84**:3477 (2004). | Contreras et al, *Thin Solid Films* **361**:167 (2000).

Electric Field Mapping (LEEM-IV)

- **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.



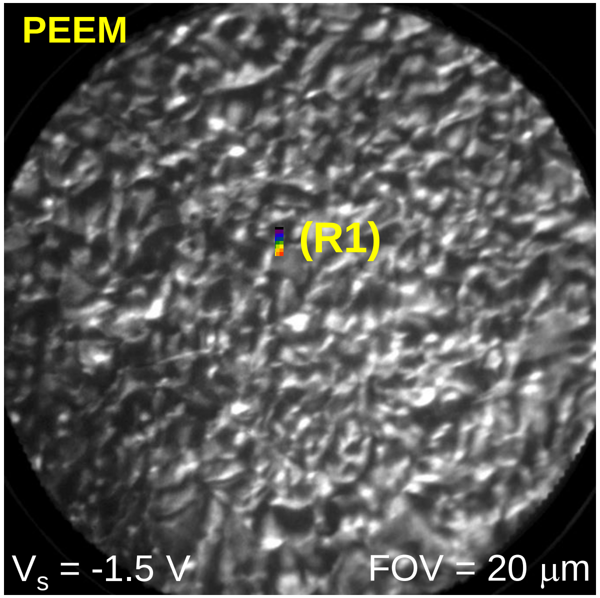


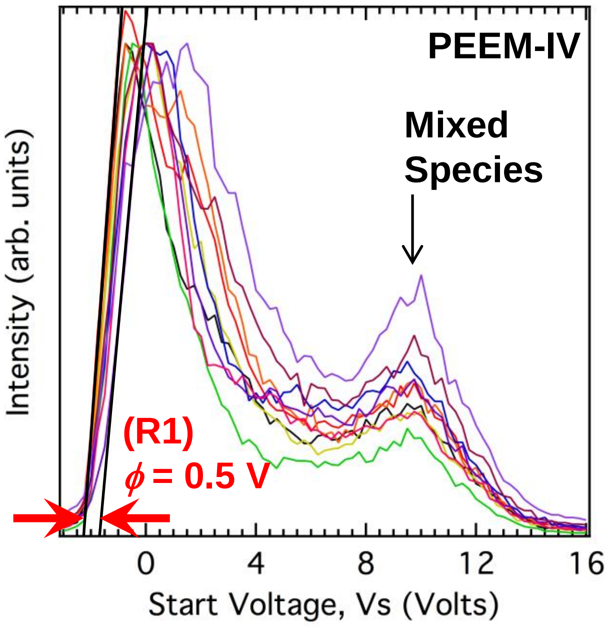
Significant variations in grain boundary potential: ϕ = 0.5-1.4 V

Much larger than other literature reports from SPM, SEM, STM: ϕ = 0.1-0.5 V

Electronic Structure Mapping (PEEM-IV)

- **PEEM-IV:** Similar to LEEM-IV, but using He plasma discharge lamp.





- Feature at V_s = 8-12 V: Superposition of Cu 3d, Se 4p, and Group III-oxides.
- **Grain boundary potential from 2º electron onset (work function): ϕ = 0.0-0.5 V.**
- **Rigid shift of valence features by similar potential: ϕ = 0.0-0.5 V.**

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Difference Between LEEM and PEEM?

- **PEEM measures work function and valence states (Photoemission)**
  - Very surface sensitive
  - Sensitive to surface contamination
- **LEEM measures Low Energy Reflected electrons (Backscatter)**
  - Internal electric fields and pn junctions

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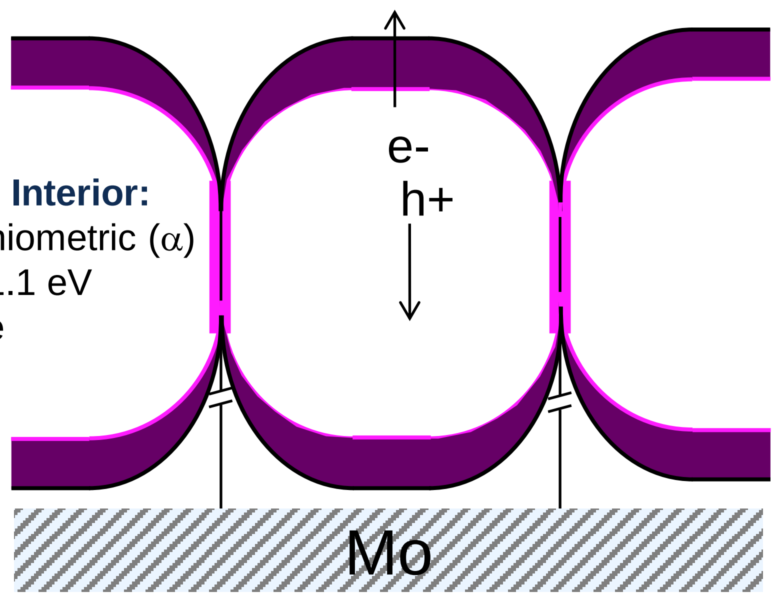
Cu-poor (β)
E_g = 1.6 eV
n-type?

Grain Interior:
Stoichiometric (α)
E_g = 1.1 eV
p-type

Junction:
Built-in potential, ϕ
(~0-0.5, 0.5-1.4 eV?)



Scanning Probes (Surface)

Work Function (Surface)

Auger e^- (1-2 nm, AEM)

Photoemission e^- (2-5 nm, PEEM)

Secondary e^- (5-50 nm, SEM)

Backscatter e^- (50-100 nm, LEEM)

X-rays (> 200 nm)

Transmitted e^- (N/A, TEM)

Acknowledgements

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Brian Korgel
Doug Pernik
Taylor Harvey
C. Jackson Stolle

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