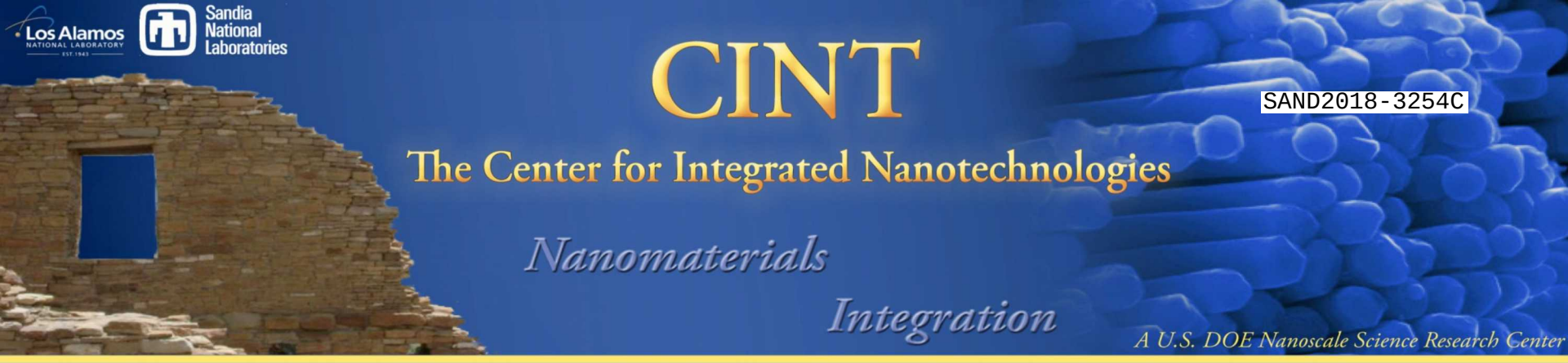


SAND2018-3254C

Photoemission electron microscopy as a new tool to study the electronic properties of an inhomogeneous semiconductor for photovoltaics

Morgann Berg[1,2], Jason M. Kephart[3], Amit Munshi[3], Walajabad S. Sampath[3], Taisuke Ohta[1,2], & Calvin Chan[1]

[1] Sandia National Laboratories, Albuquerque, New Mexico, United States
[2] Center for Integrated Nanotechnologies, SNL & LANL, New Mexico, United States
[3] Department of Mechanical Engineering, Colorado State University, Fort Collins, Colorado, United States

Work published online in ACS Applied Materials & Interfaces, "Local Electronic Structure Changes in Polycrystalline CdTe with $CdCl_2$ Treatment and Air Exposure"

April 6, 2018 9:30 AM to 9:45 AM
MRS, Symposium EN19: Novel Inorganic Semiconductors for Optoelectronics and Solar Energy
PCC North, 100 Level, Room 124 B

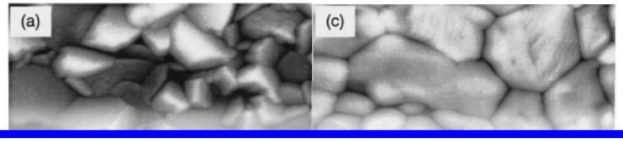
Los Alamos NATIONAL LABORATORY

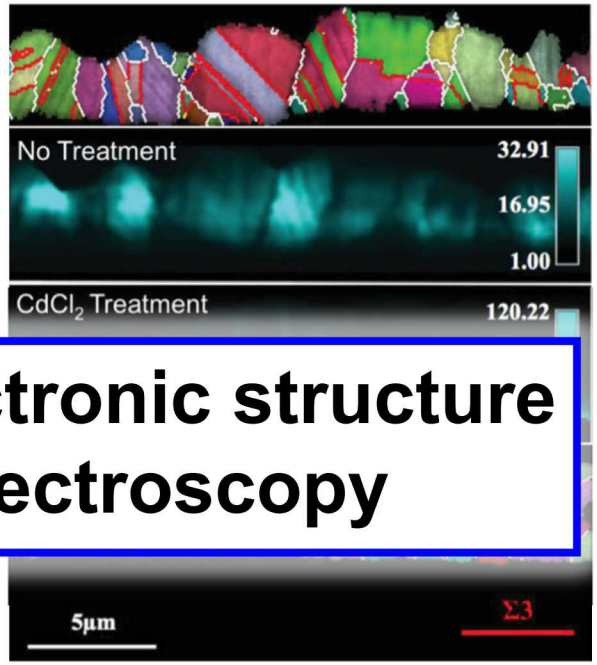
U.S. DEPARTMENT OF ENERGY | Office of Science

Sandia National Laboratories

$CdCl_2$ "activation" is a well known processing step to improve the grain size & PV efficiency of CdTe

- Polycrystalline CdTe photovoltaics reaching 21.5% efficiency
  - Competitor with silicon-based photovoltaics

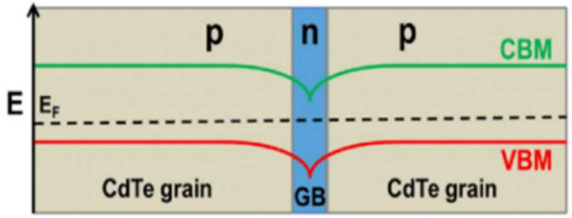




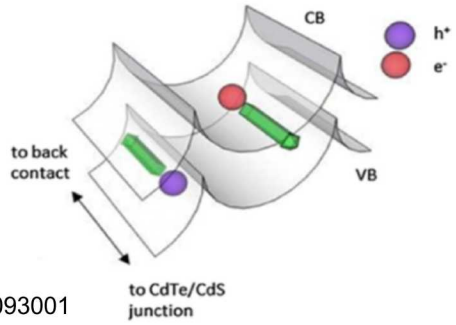
Poplawsky et al., Adv. Energy Mater. 4 1400454 (2014)

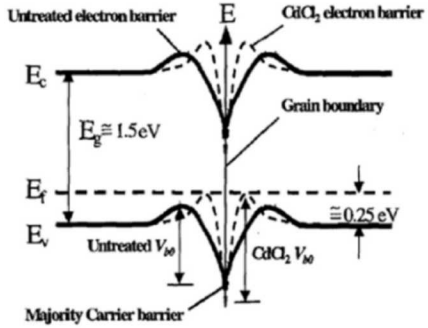
Our approach: probing local electronic structure based on photoemission spectroscopy

- Limited understanding of local processing-structure-performance relationship
  - Why polycrystalline CdTe outperforms single crystals?

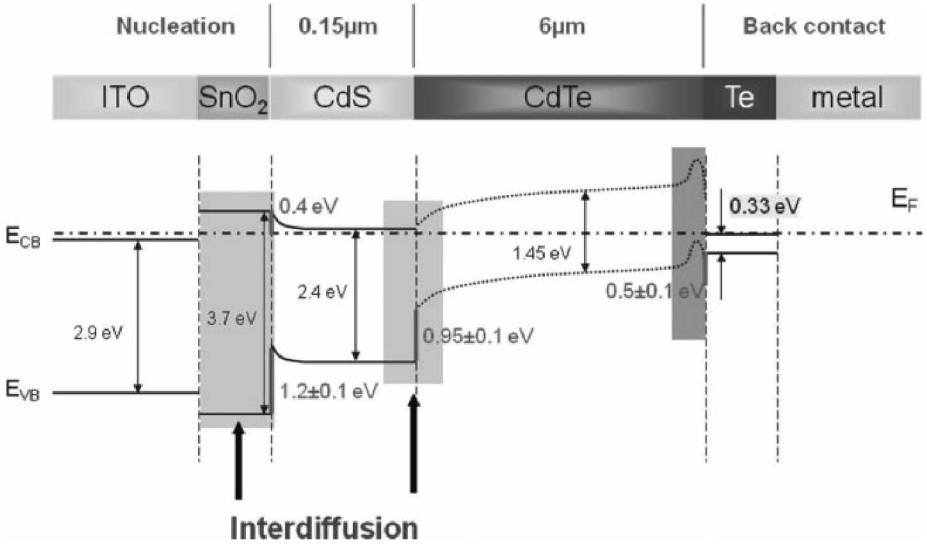


Major, Semicond. Sci. Technol. 31 (2016) 093001



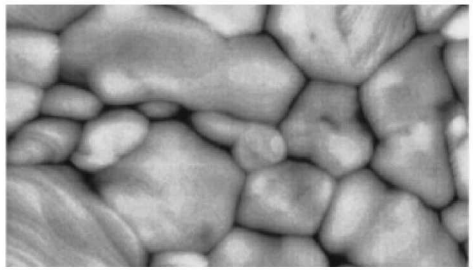


Photoemission spectroscopy is an electronic structure probe

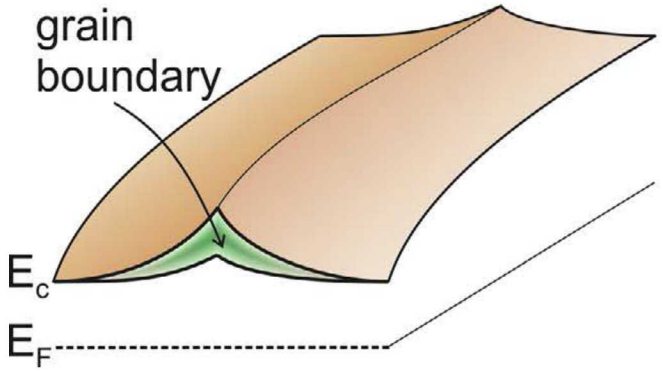


Jaegermann, et al., Adv. Mater. 2009, 21, 4196

- Conventional: depth profiling of electronic structures



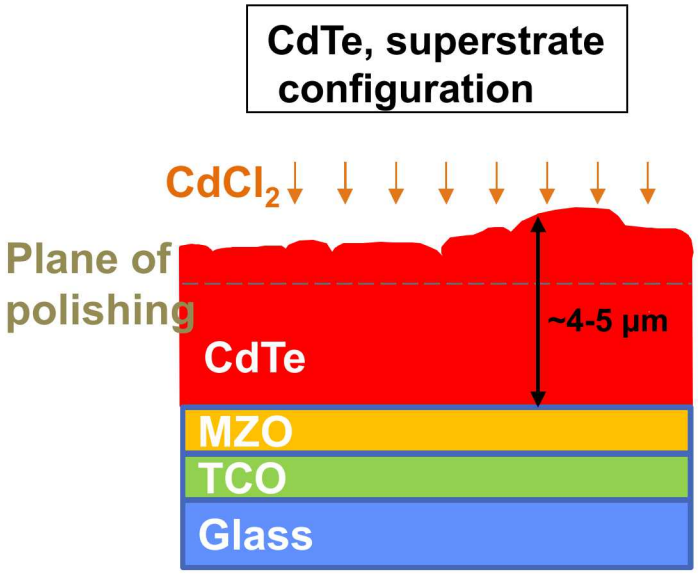
Moutinho, et al., J. Vac. Sci. Technol A, 16, 1251 (1998).

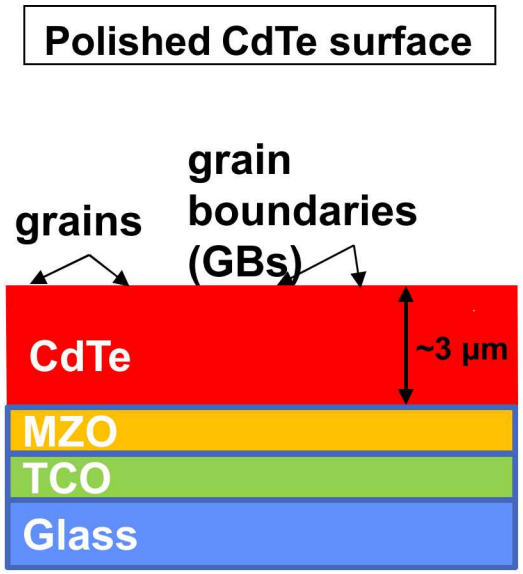


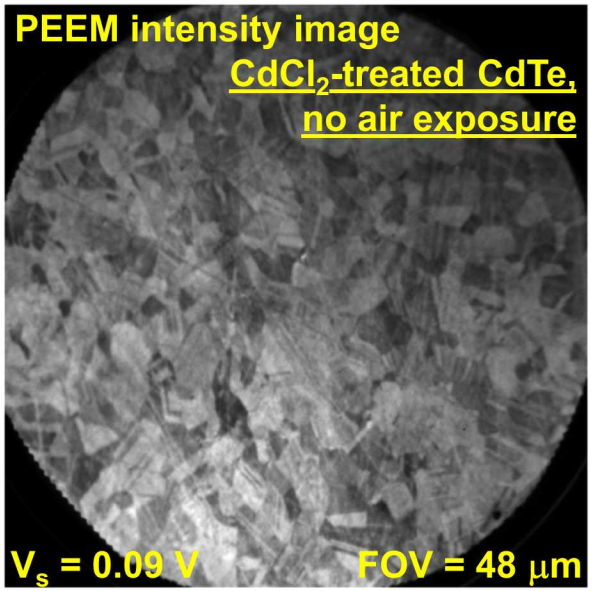
Nicoara, et al., Scientific Reports, 7, 41361 (2017)

- Unconventional: **spatially-resolved profiling** of electronic structures (i.e. *potential landscape*)

We polished the sample surface to expose the grain interiors and grain boundaries







Grain size ~3 μm

- Colorado State Univ. superstrate CdTe
  - Closed-space sublimation deposition of CdTe on $Mg_{0.23}Zn_{0.77}O$(MZO)/NSG TEC 10, no rear contacts (~15% efficient with contacts)
  - X-ray Photoelectron Spectroscopy, Cd:Te ratios ~5:6 for untreated CdTe, ~11:10 for $CdCl_2$-treated CdTe
  - Low-energy sputter-cleaning step
    - 50 eV Ar^+ ions, 10–20 min, ~0.1-0.15 μA•cm^{-2} fluence
  - **Inert environment sample transfer**
  - 30 min air exposure step

Berg, et al., ACS Applied Materials & Interfaces, published online

We use photoemission microscopy & spectroscopy to evaluate the band alignment

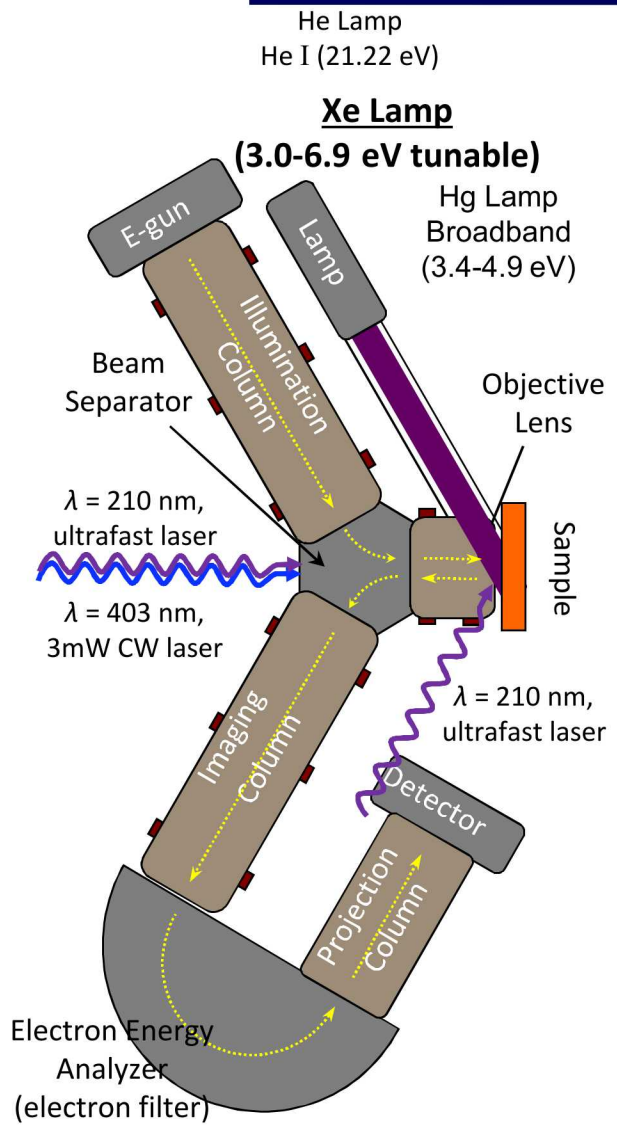
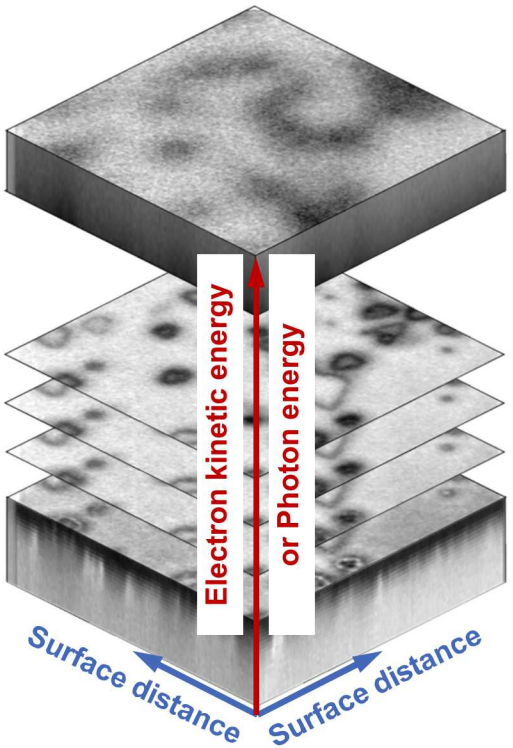
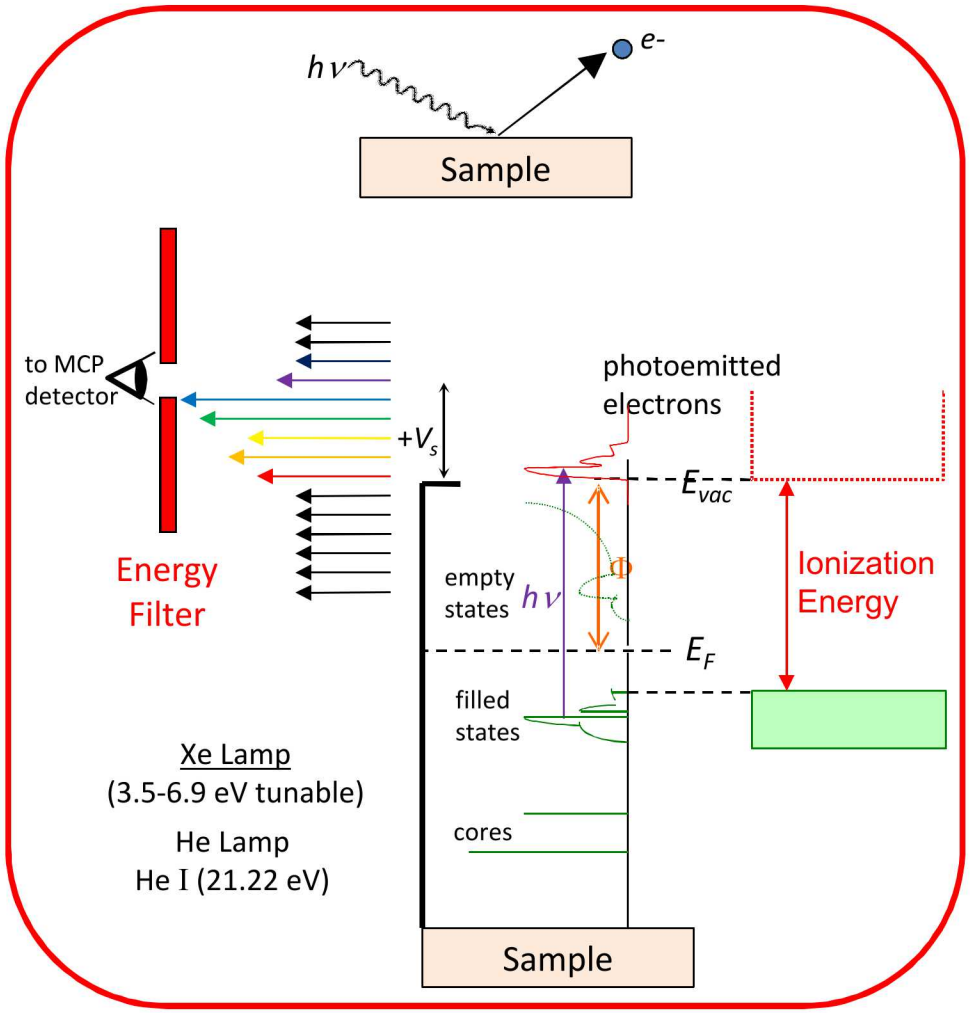


Figure courtesy: M. Berg

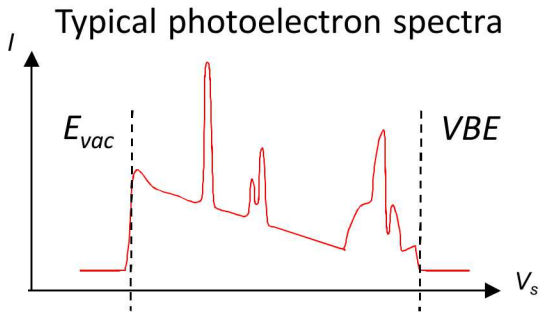
- Monochromatic light sources combined with an electron energy filter in photoemission electron microscopy (PEEM) to acquire electron spectra
  - Spatial resolution ~50 – 200nm
  - Energy resolution ~0.2 – 0.5eV
- Spectrum is extracted from each pixel in the image stack
- Deep UV CW source is used for the work presented here
  - λ = 180 – 350nm (hv = 3.54 – 6.89eV): tunable energy photon using the lab source

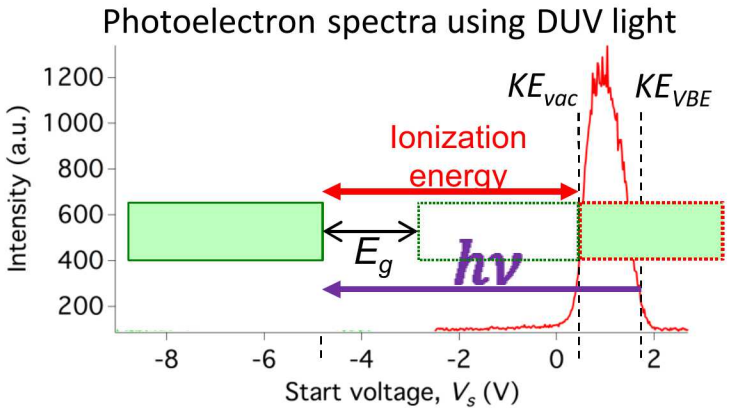


We extract E_{vac} from photoelectron (photoemission) spectra



Photoemission process

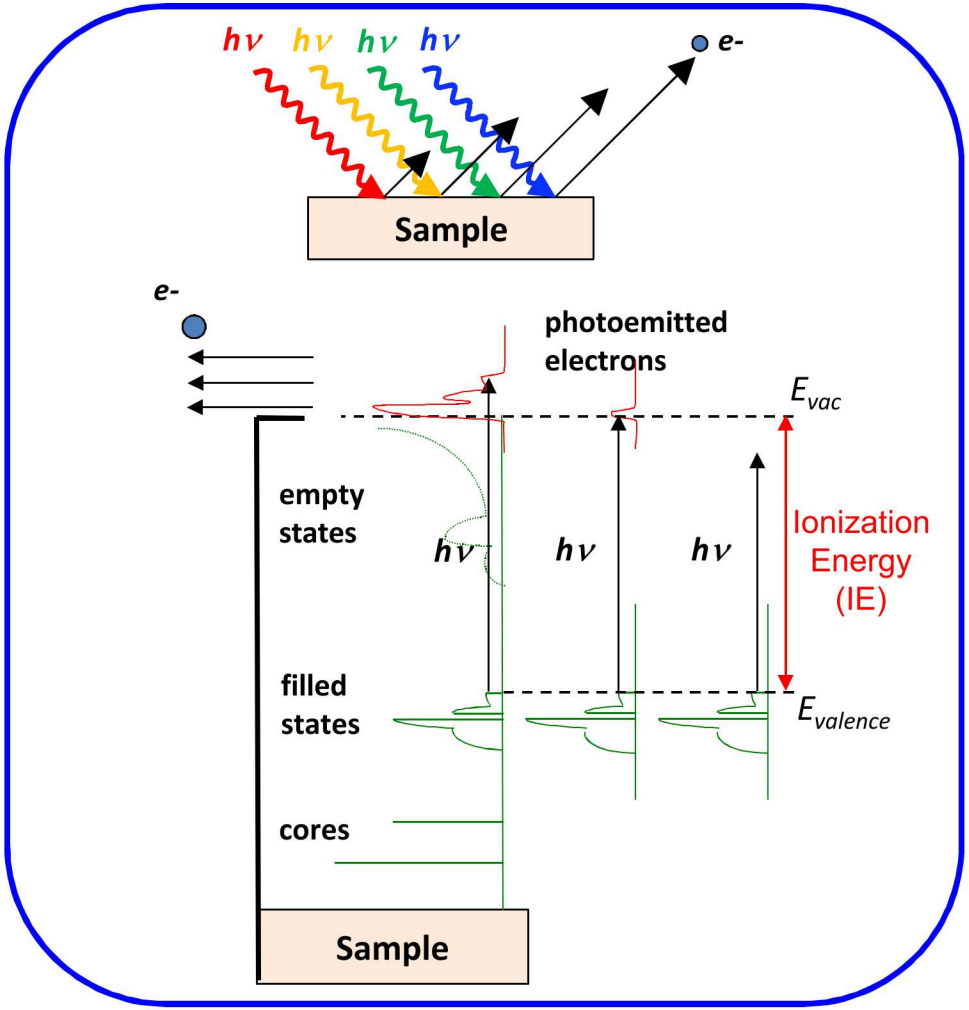




$$BE = KE - h\nu$$

Figure courtesy: M. Berg, C. Chan

We map *Ionization Energy (IE)* from photoemission yield spectra



Photoemission yield

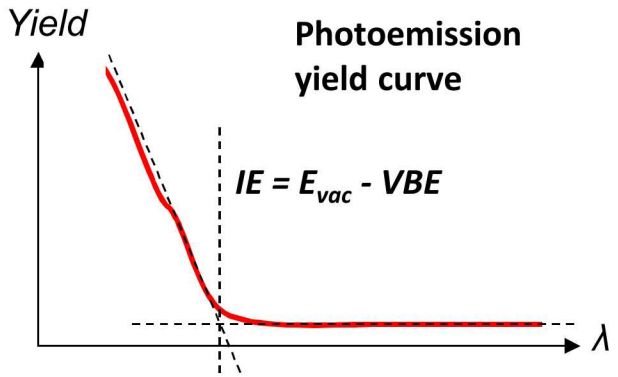
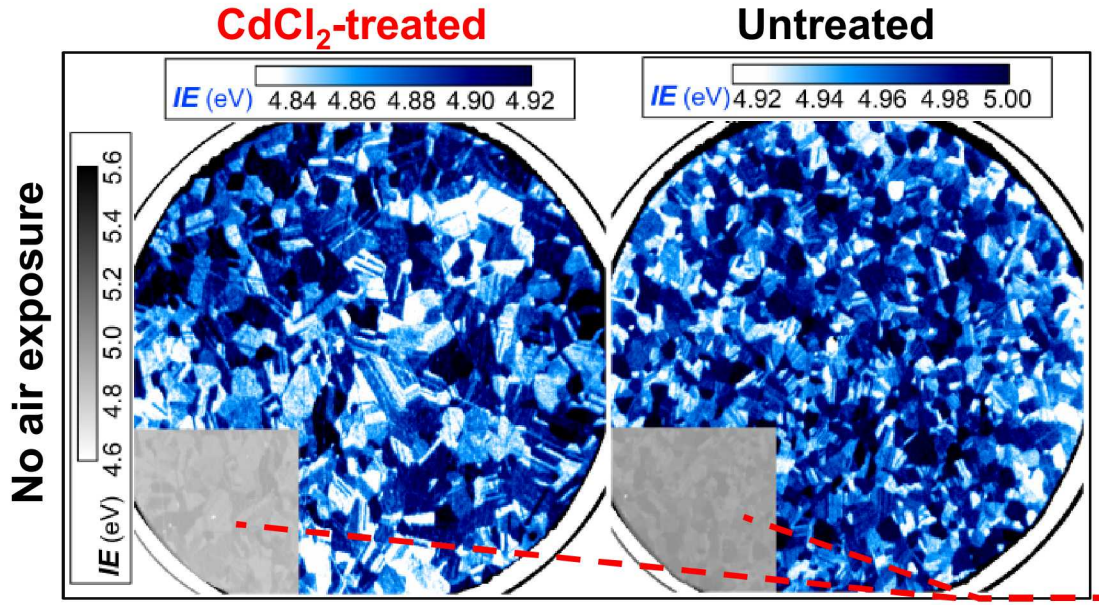


Figure courtesy: M. Berg, C. Chan

IE map did NOT show distinct potential at grain boundaries: WHY?



All maps have 48 μm FOV

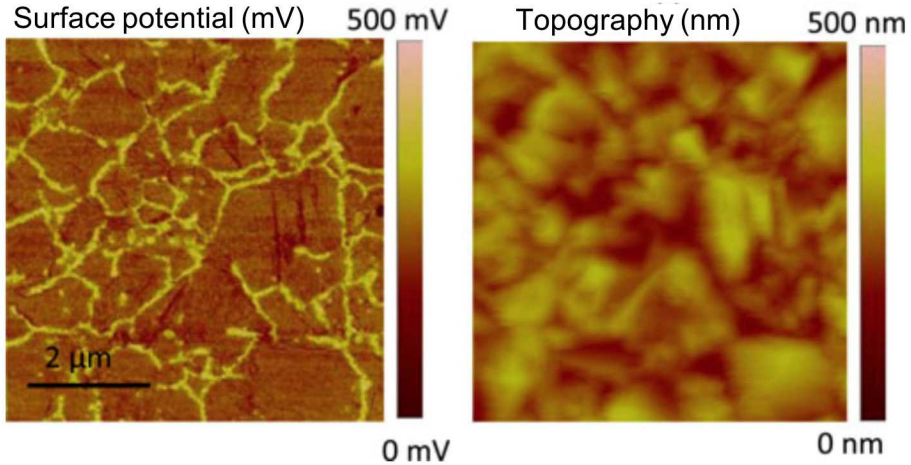
Grain-to-grain variation

Anticipated for polycrystalline films

$CdCl_2$ treatment decreases ionization energy

Consistent w/ electron doping by Cl through $CdCl_2$ activation

Scanning Probe Microscopy of $CdCl_2$-CdTe

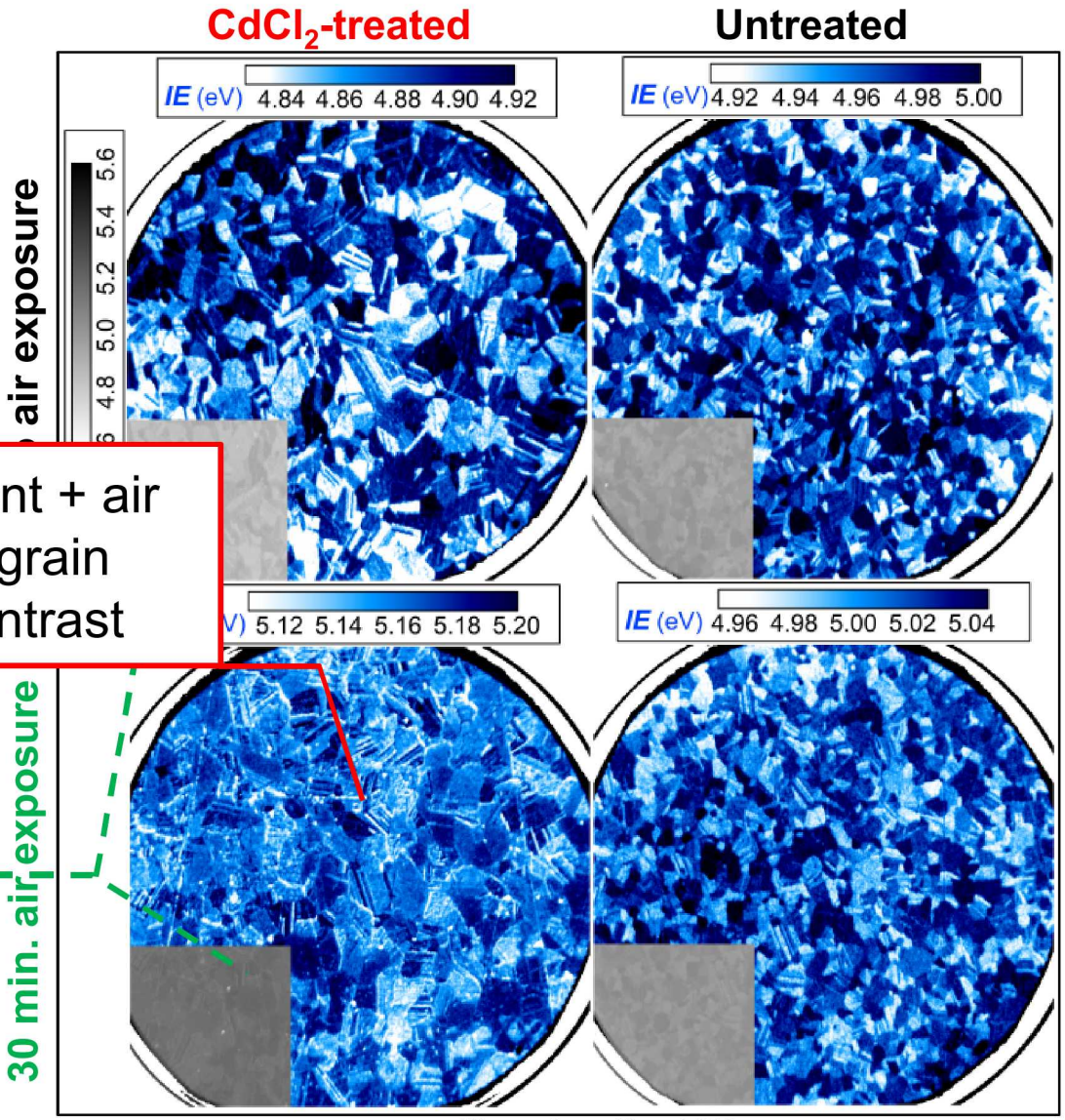


C.-S. Jiang et al., *IEEE J. of Photovolt.* 3 (4), 1383 (2013).

- No potential variation at grain boundaries?

Berg, et al., ACS Applied Materials & Interfaces, published online

Expected grain boundary (GB) contrast appeared <u>only after</u> exposing $CdCl_2$ activated CdTe to air

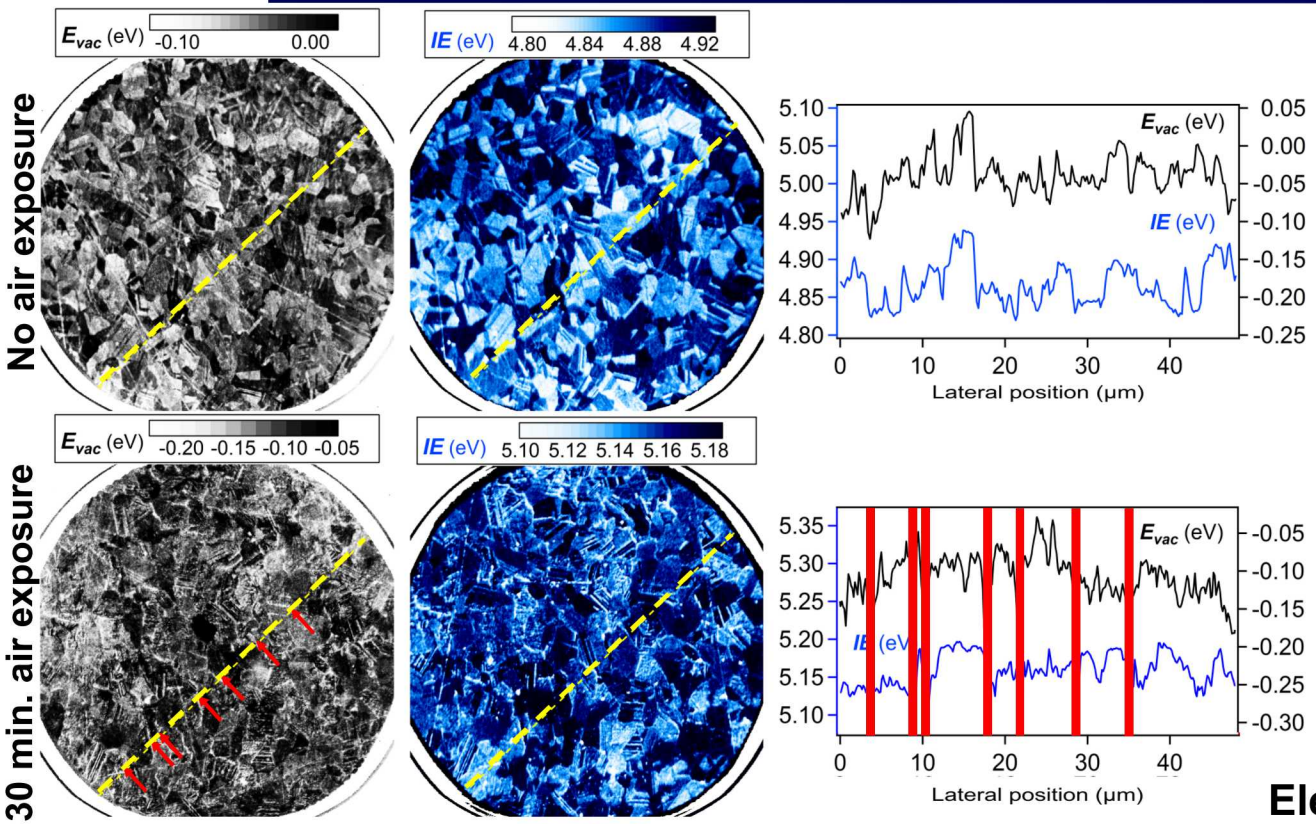


$CdCl_2$ treatment + air exposure = grain boundary contrast

Air exposure <u>increases</u> ionization energy

All maps have 48 μm FOV

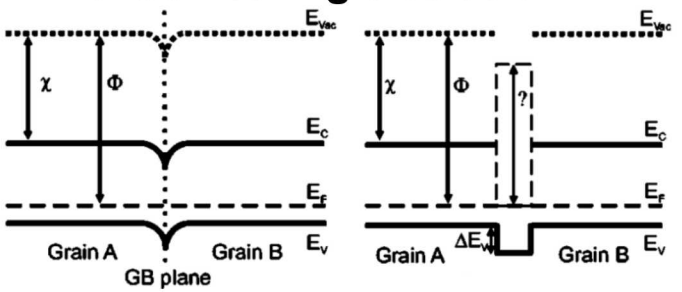
E_{vac} and *IE* maps elucidate grain boundaries with different electronic structures



- E_{vac} and *IE* closely match and vary in step-like fashion along with the grain

- E_{vac} and *IE* at the grain boundaries do not match closely

Electrostatic rigid band shift
or **something else** at GB?



- Analysis of GB band bending suggest net carrier density of ~10^{15}cm^{-3} and GB trap density of ~10^{11}cm^{-2} expected for undoped CdTe and the admittance spectroscopy measurement

Berg, et al., ACS Applied Materials & Interfaces, published online

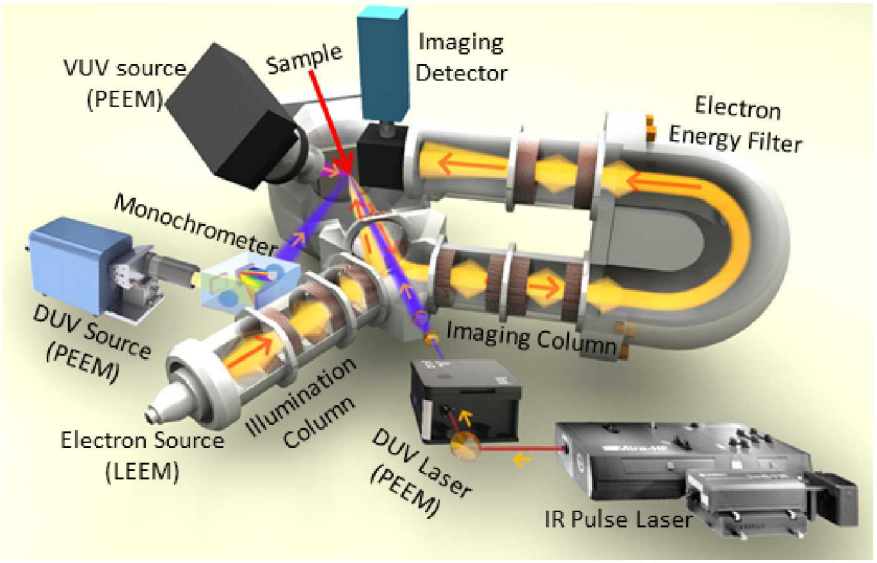
D. Fuertes Marrón et al. *Phys. Rev. B* 71, 033306 (2005).

Summary

- PEEM coupled to deep ultraviolet (DUV) light sources is an emerging analytical capability to explore the electronic properties of spatially inhomogeneous materials
  - We elucidated the electronic properties of grain and grain boundaries in polycrystalline CdTe

Visualization of the electronic structure variation in inhomogeneous semiconductor

- Berg, et al., ACS Applied Materials & Interfaces, published online



  - Other recent examples include:
    - TMDs (MoS_2, $MoSe_2$, WS_2): Keyshar, et al., ACS Nano 11, 8223 (2017); Berg, et al, Phys. Rev. B 95, 235406 (2017)
    - Graphene multilayers: Robinson, et al., Scientific Reports 8, 2006 (2018)
    - Polycrystalline metal films: Berg, Bussmann, et al., in preparation

Acknowledgements

- Financial support:
  - CINT, US DOE Office of Science (DE-AC04-94AL85000)
  - US DOE EERE SunShot Initiative (BRIDGE, DE-FOA-0000654 CPS25859)
  - National Science Foundation PFI:AIR-RA:Advanced Thin-Film Photovoltaics for Sustainable Energy award (1538733)
  - Sandia LDRD

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LEEM-PEEM contact:
Taisuke Ohta (tohta@sandia.gov)

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We have opportunities for higher resolution imaging and postdoc hiring

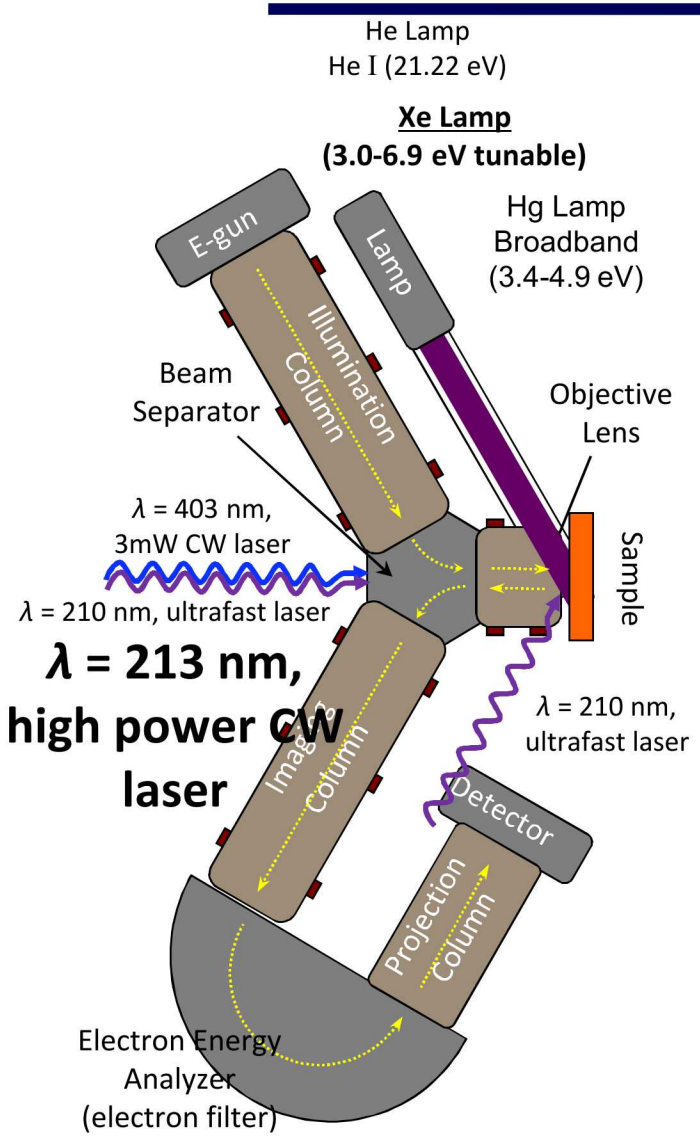
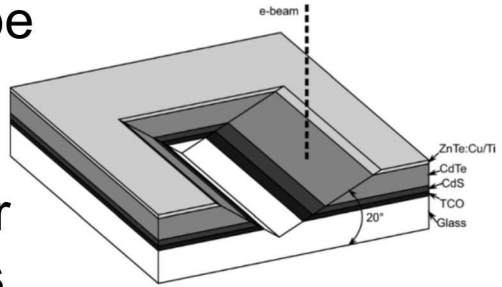


Figure courtesy: M. Berg

- ~10nm lateral resolution using λ = 213 nm, high power CW laser (future development)
- Postdoc opportunities (pending)
  - In-situ microscopy to probe potential landscape near solid electrolyte-battery electrode interfaces under voltage biasing conditions
    - Starting date: late summer 2018



J. Moseley et al., *J. Appl. Phys.* 120, 105704 (2016).

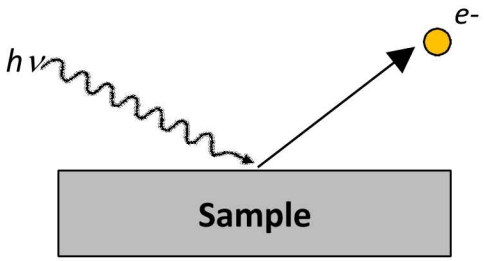
  - Imaging dielectrics/insulators and their defects using cavity mode-assisted photoemission process
    - Starting date: spring/early summer 2019

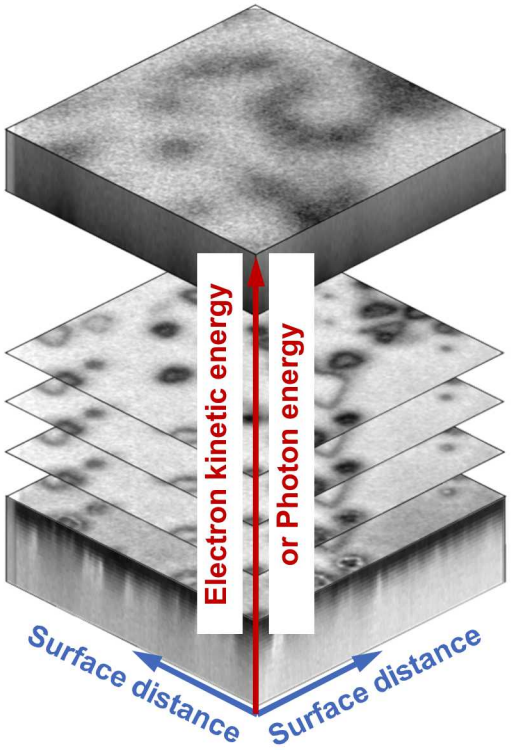
LEEM-PEEM contact:
Taisuke Ohta (tohta@sandia.gov)

Text

Text

We use photoemission microscopy & spectroscopy to evaluate the band alignment





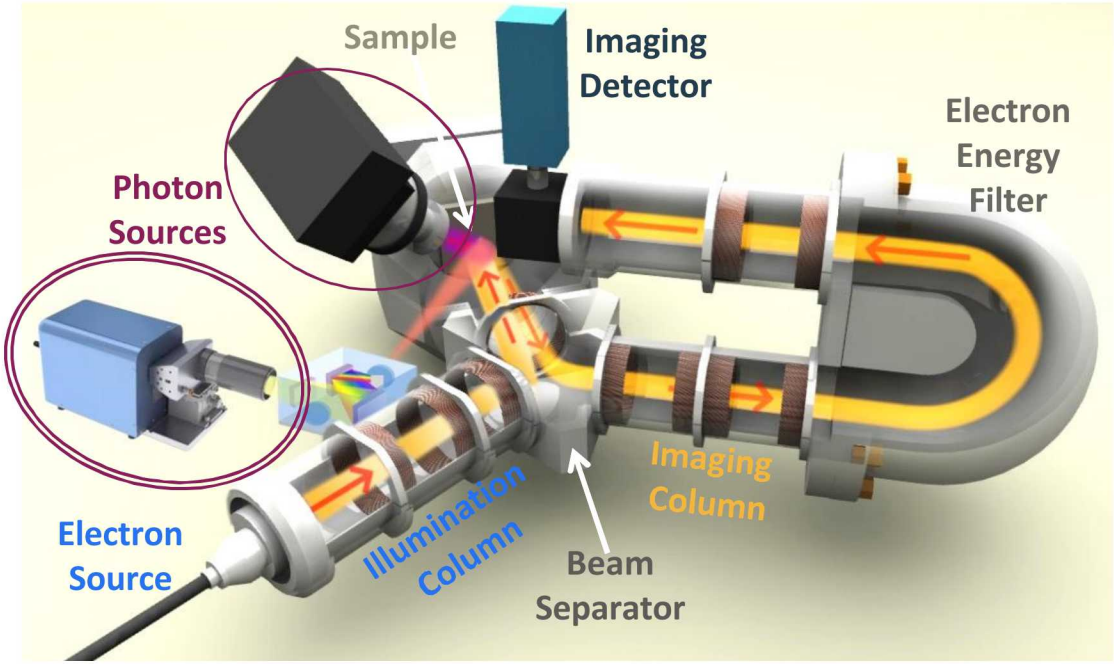


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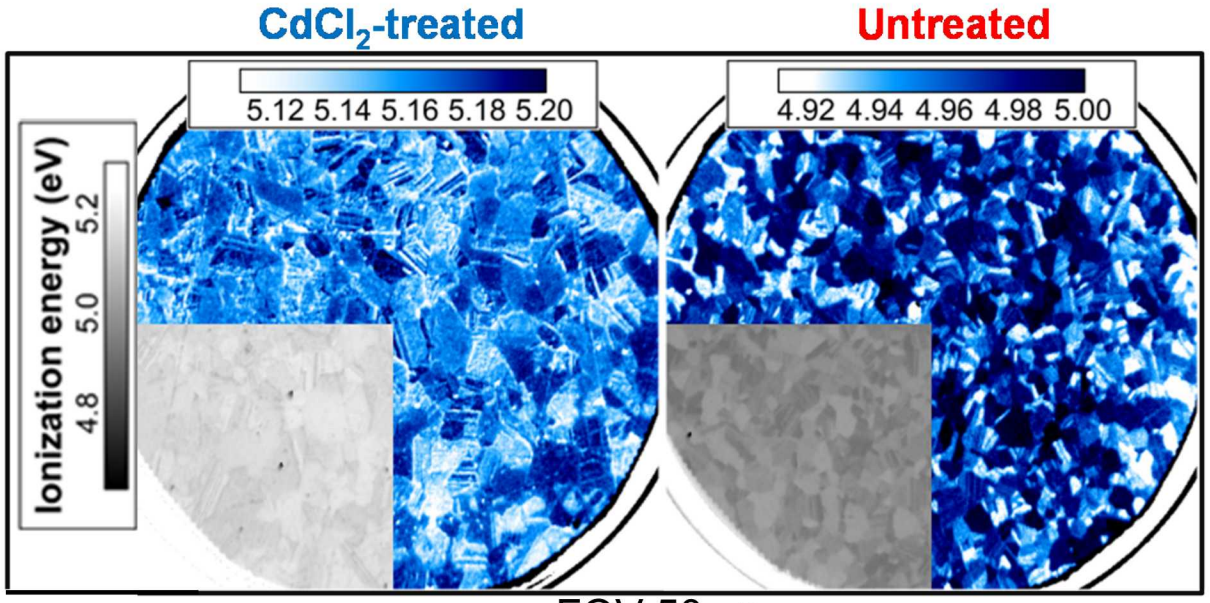
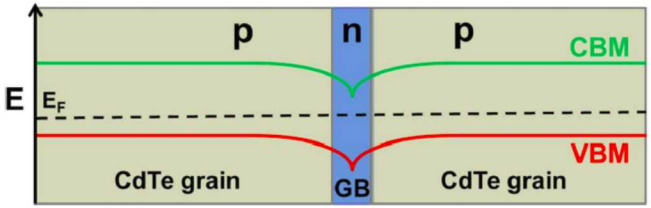
Figure courtesy: C. Chan

We observe the change of grain boundary energetics by $CdCl_2$ in polycrystalline CdTe



FOV 50μm

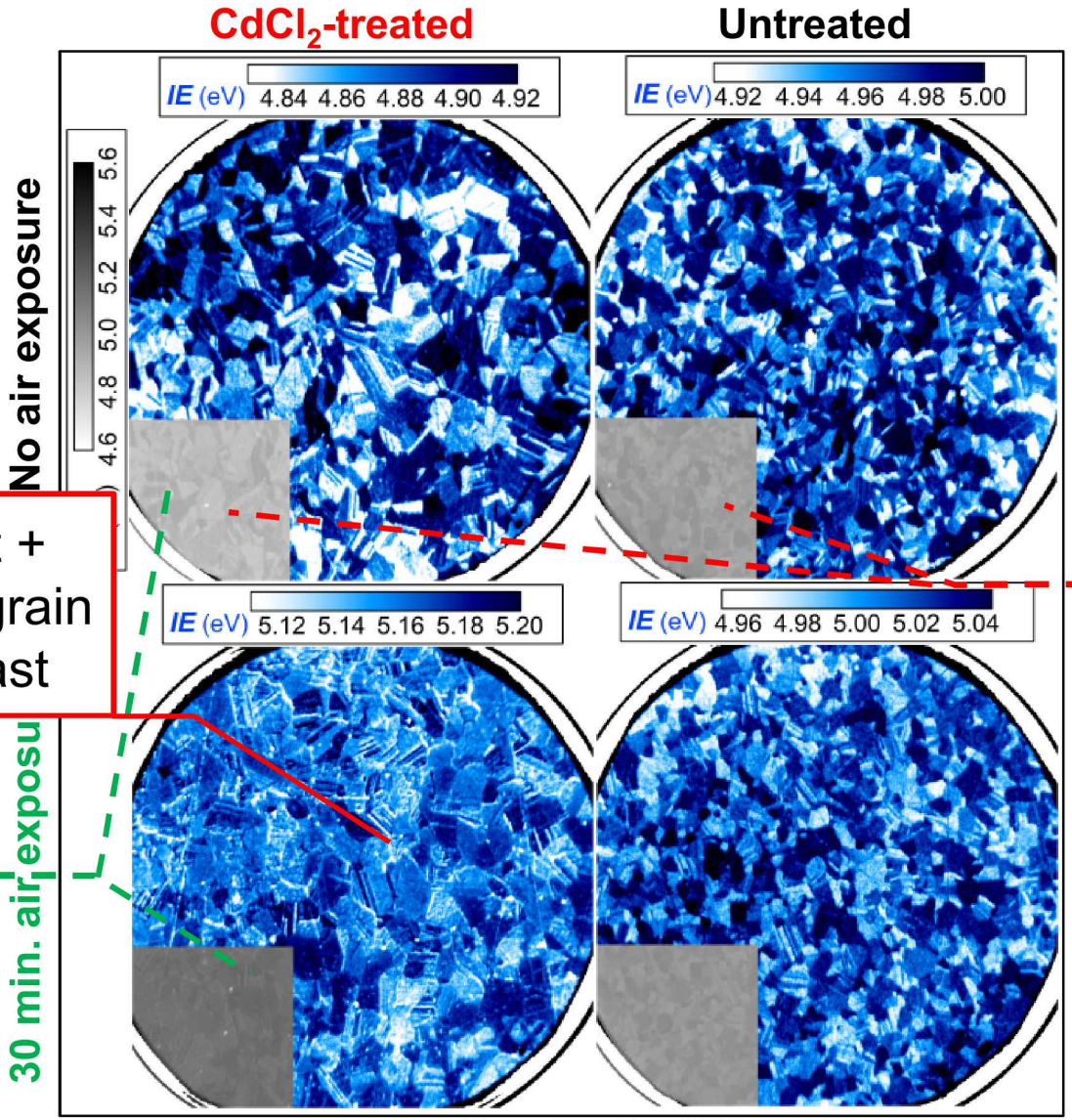


Li, et al., Phys. Rev. Lett. 112, 156103 (2014)

- $CdCl_2$ treatment has clear influence on the electronic properties of grain boundaries
  - Electronic properties not only vary between grain and grain boundaries, but also between grains
  - PEEM result is consistent with Electron Beam Induced Current study
- $CdCl_2$ treatment and air exposure have separate role in activating the grain boundaries

Berg, et al., ACS Applied Materials & Interfaces published online

We observe the change of grain boundary energetics by $CdCl_2$ in polycrystalline CdTe



Grain-to-grain variation

$CdCl_2$ treatment + air exposure = grain boundary contrast

$CdCl_2$ treatment <u>decreases</u> ionization energy

Air exposure <u>increases</u> ionization energy

All maps have 48 μm FOV