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SAND2018-12078C

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

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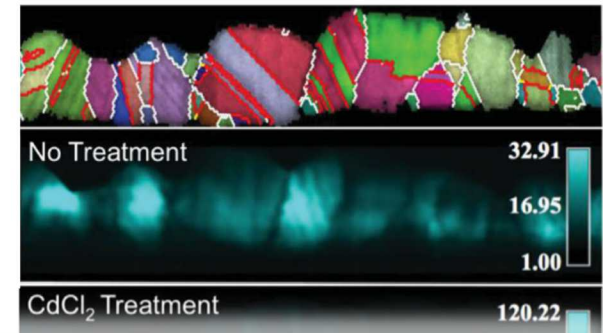
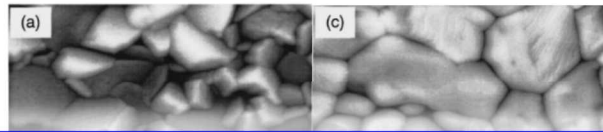
Work published online in ACS Applied Materials & Interfaces, "Local Electronic Structure Changes in Polycrystalline CdTe with CdCl₂ Treatment and Air Exposure"

October 23, 2018 3:00 PM

AVS, EM+2D+AN+MI+MP+NS-TuA3: Solar/Energy Harvesting and Quantum Materials and Applications
Room 101A

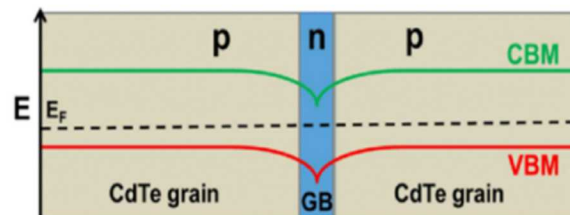
CdCl_2 “activation” is a well known processing step to improve the grain size & PV efficiency of CdTe

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

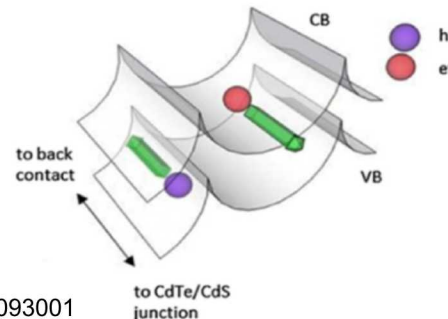


Our approach: probing local electronic structure based on photoemission spectroscopy

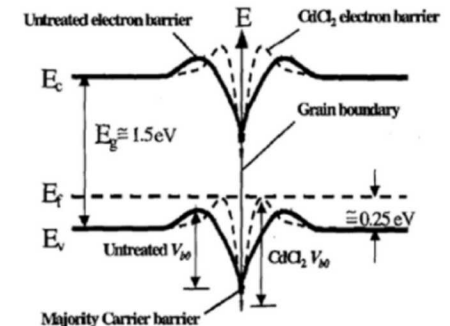
- Limited understanding of local processing-structure-performance relationship
 - Why polycrystalline CdTe outperforms single crystals?



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

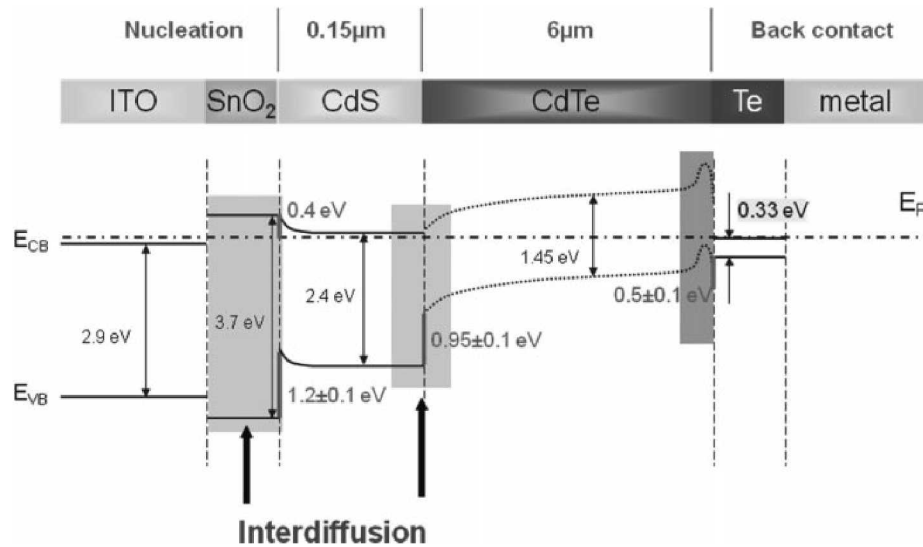


Poplawsky et al., Adv. Energy Mater. 4 1400454 (2014)



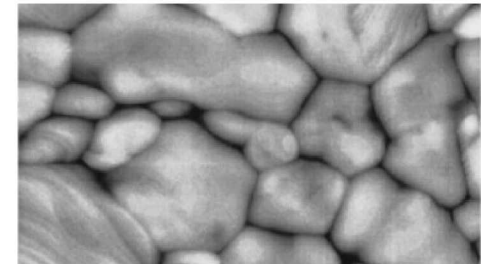


Photoemission spectroscopy is an electronic structure probe

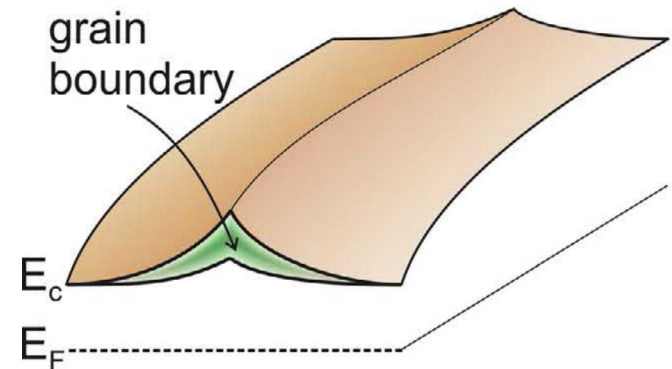


Jaegermann, et al., Adv. Mater. 2009, 21, 4196

- 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)

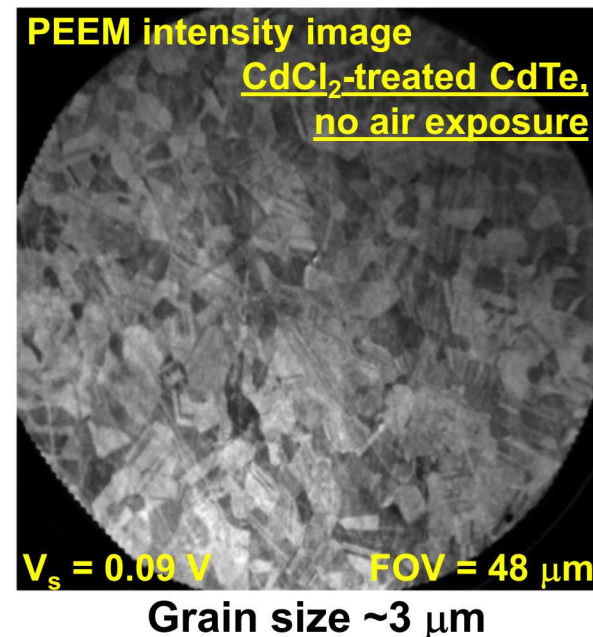
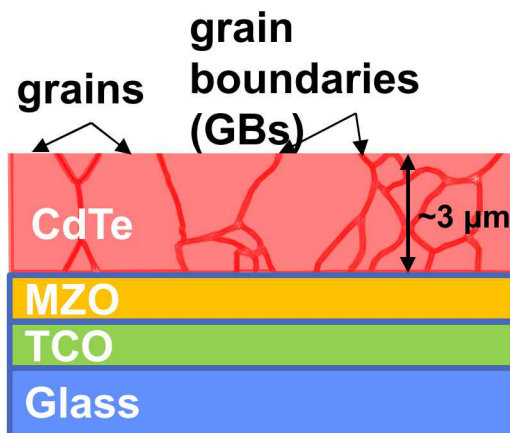
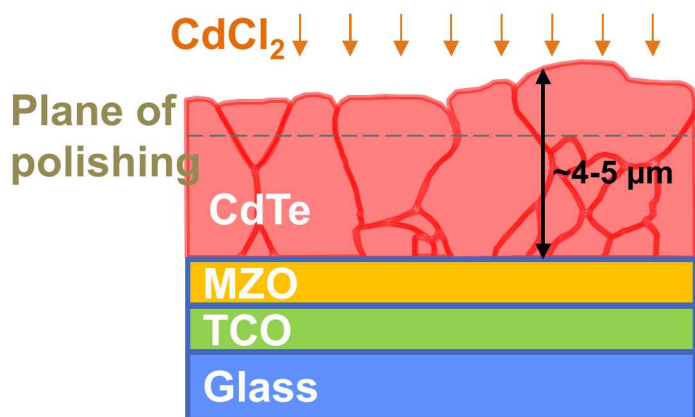
- Unconventional: **spatially-resolved profiling** of electronic structures (i.e. *potential landscape*)



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

CdTe, superstrate configuration

Polished CdTe surface



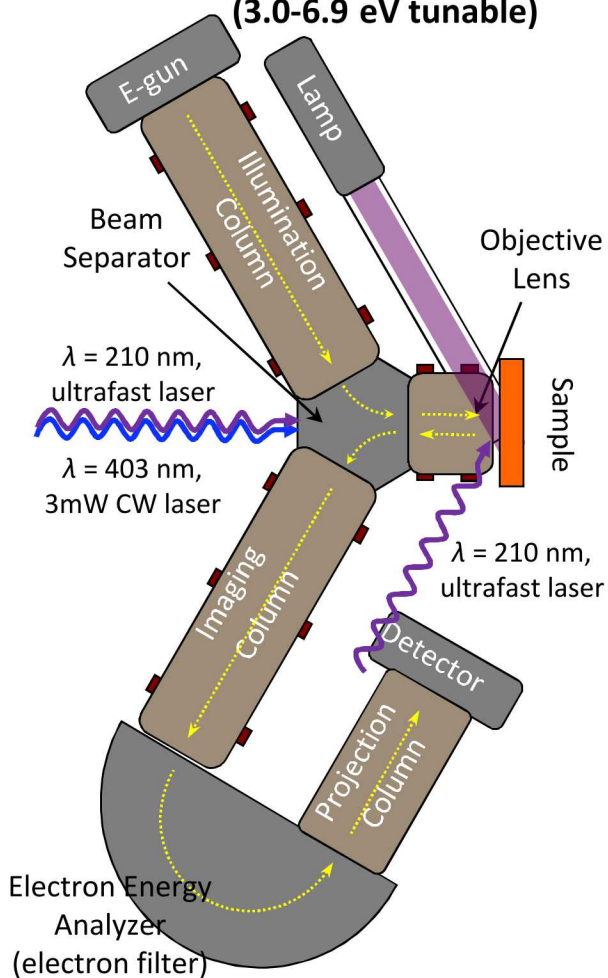
- Colorado State Univ. superstrate CdTe
 - Closed-space sublimation deposition of CdTe on $\text{Mg}_{0.23}\text{Zn}_{0.77}\text{O}$ (MZO)/NSG TEC 10, no rear contacts (~15% efficient with contacts)
 - X-ray Photoelectron Spectroscopy, Cd:Te ratios ~5:6 for untreated CdTe, ~11:10 for CdCl_2 -treated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



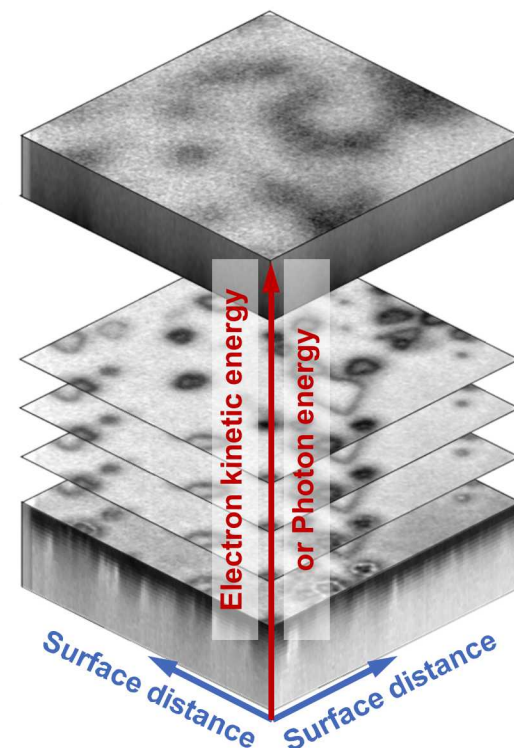
We use photoemission microscopy & spectroscopy to evaluate the band alignment

He Lamp
He I (21.22 eV)

Xe Lamp
(3.0-6.9 eV tunable)

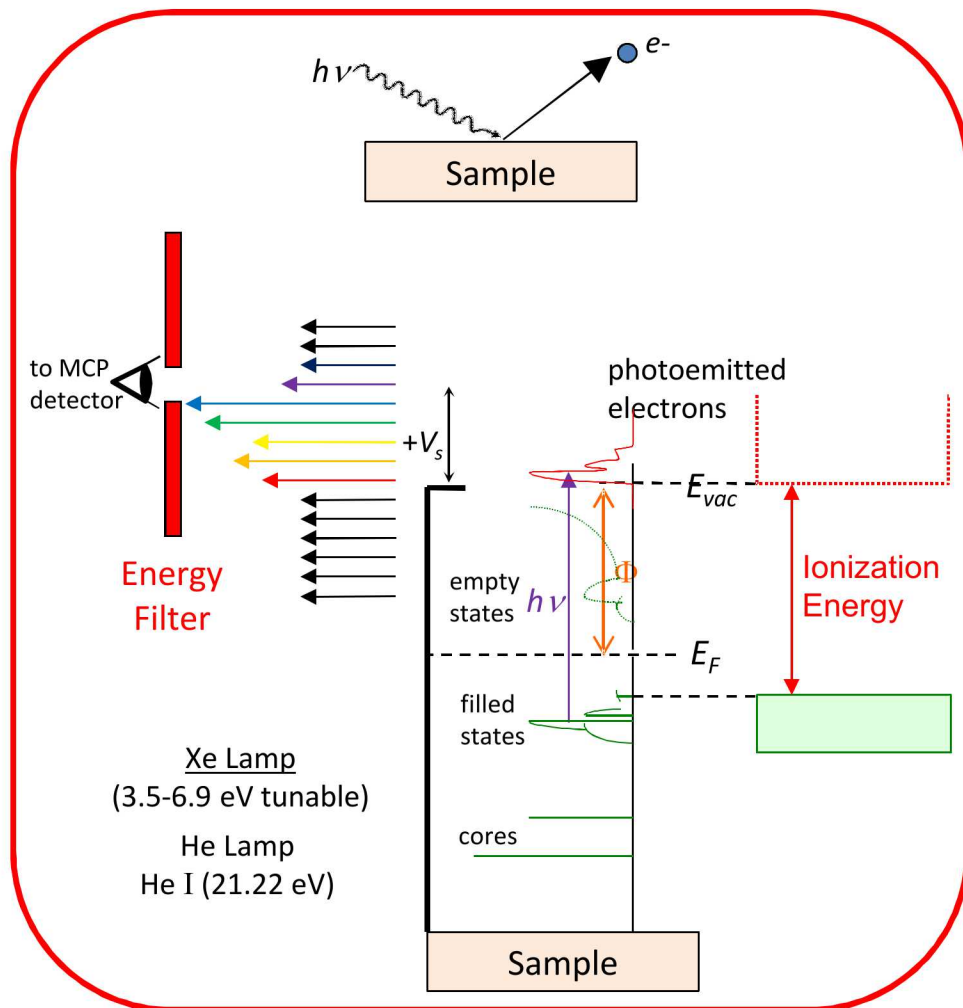


- Monochromatic light sources combined with an electron energy filter in photoemission electron microscopy (PEEM) to acquire electron spectra
 - Spatial resolution ~50 – 200nm
 - Energy resolution ~0.2 – 0.5eV
- Spectrum is extracted from each pixel in the image stack or data cube, and fitted to create maps
- Deep UV CW source is used for the work presented here
 - $\lambda = 180 - 350\text{nm}$ ($h\nu = 3.54 - 6.89\text{eV}$): tunable energy photon using the lab source

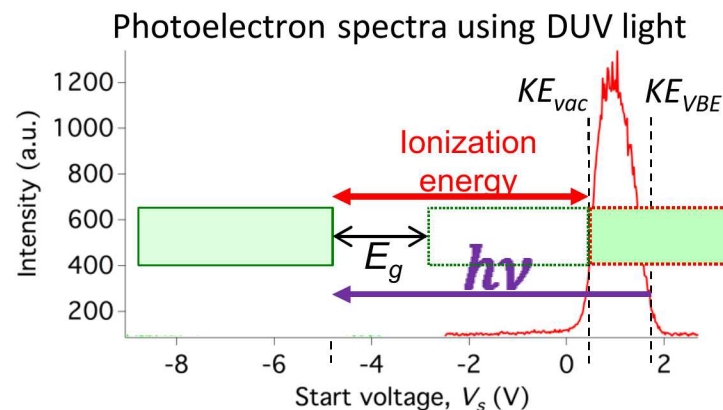
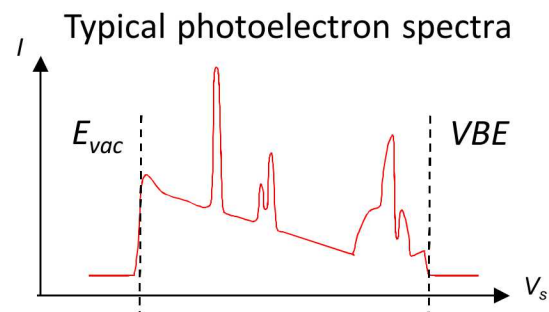




We extract E_{vac} from photoelectron (photoemission) spectra



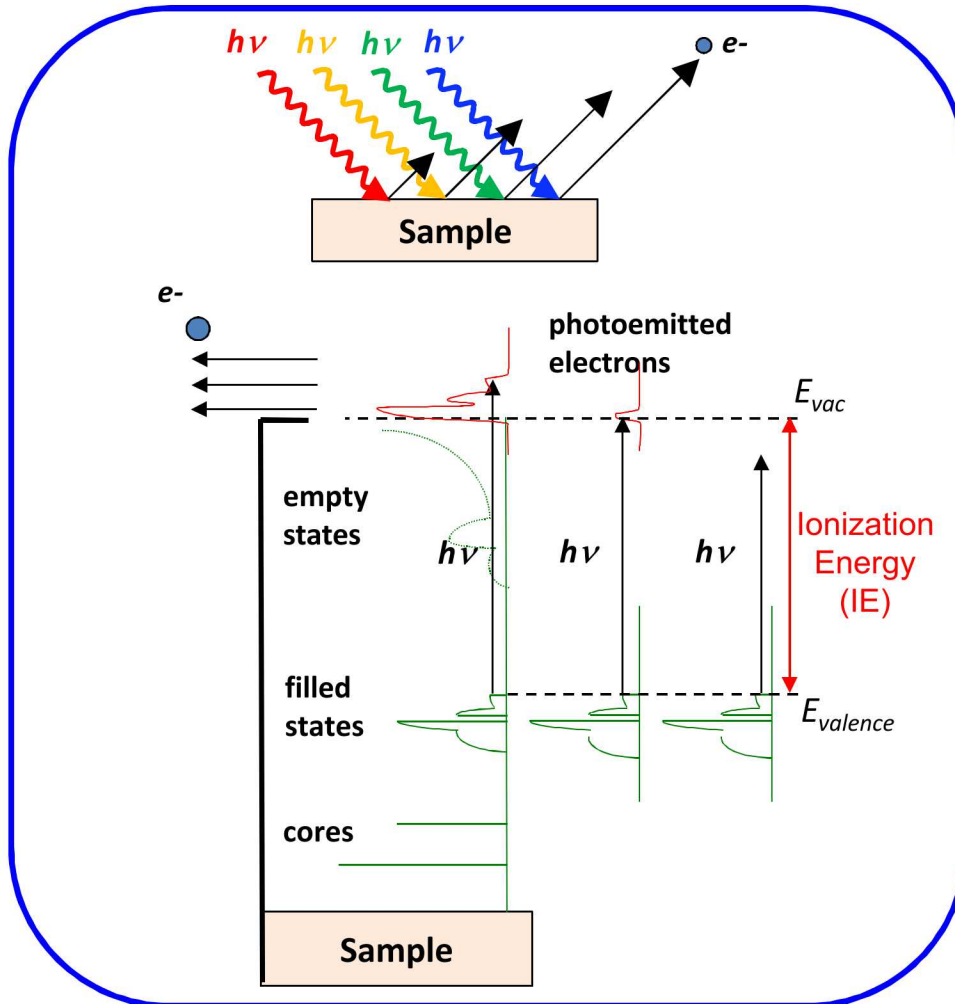
Photoemission process



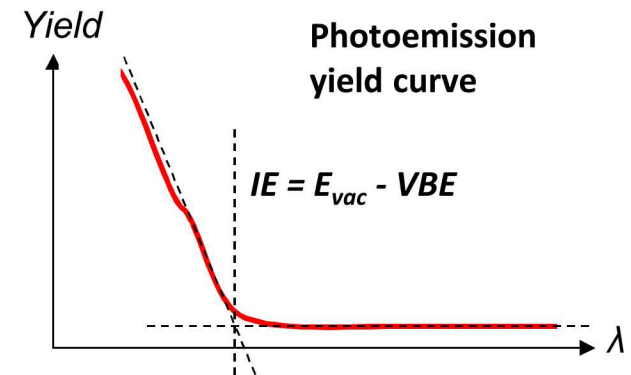
$$BE = KE - h\nu$$



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

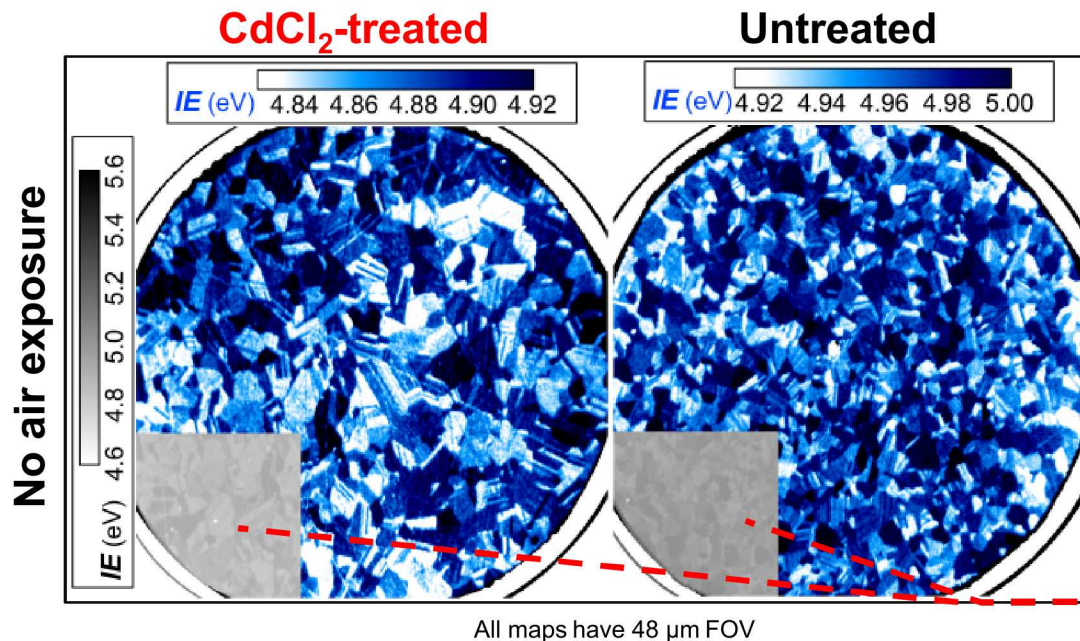


Photoemission yield





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



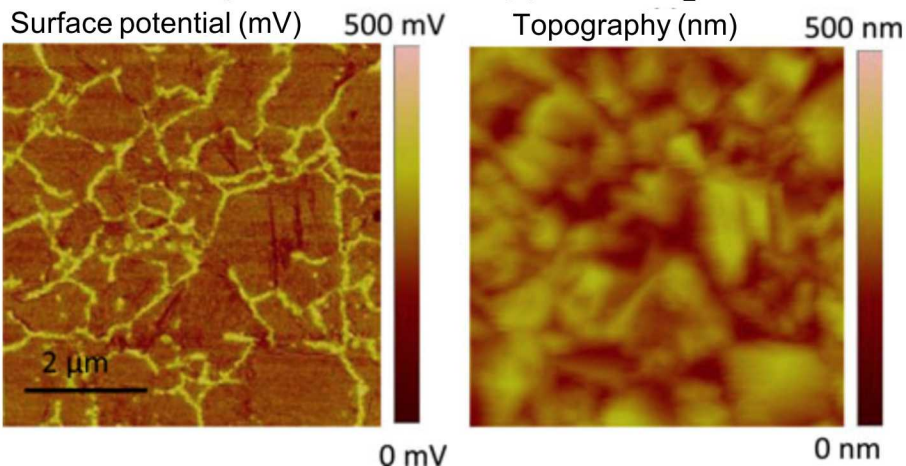
Grain-to-grain variation

Anticipated for polycrystalline films

CdCl₂ treatment decreases ionization energy

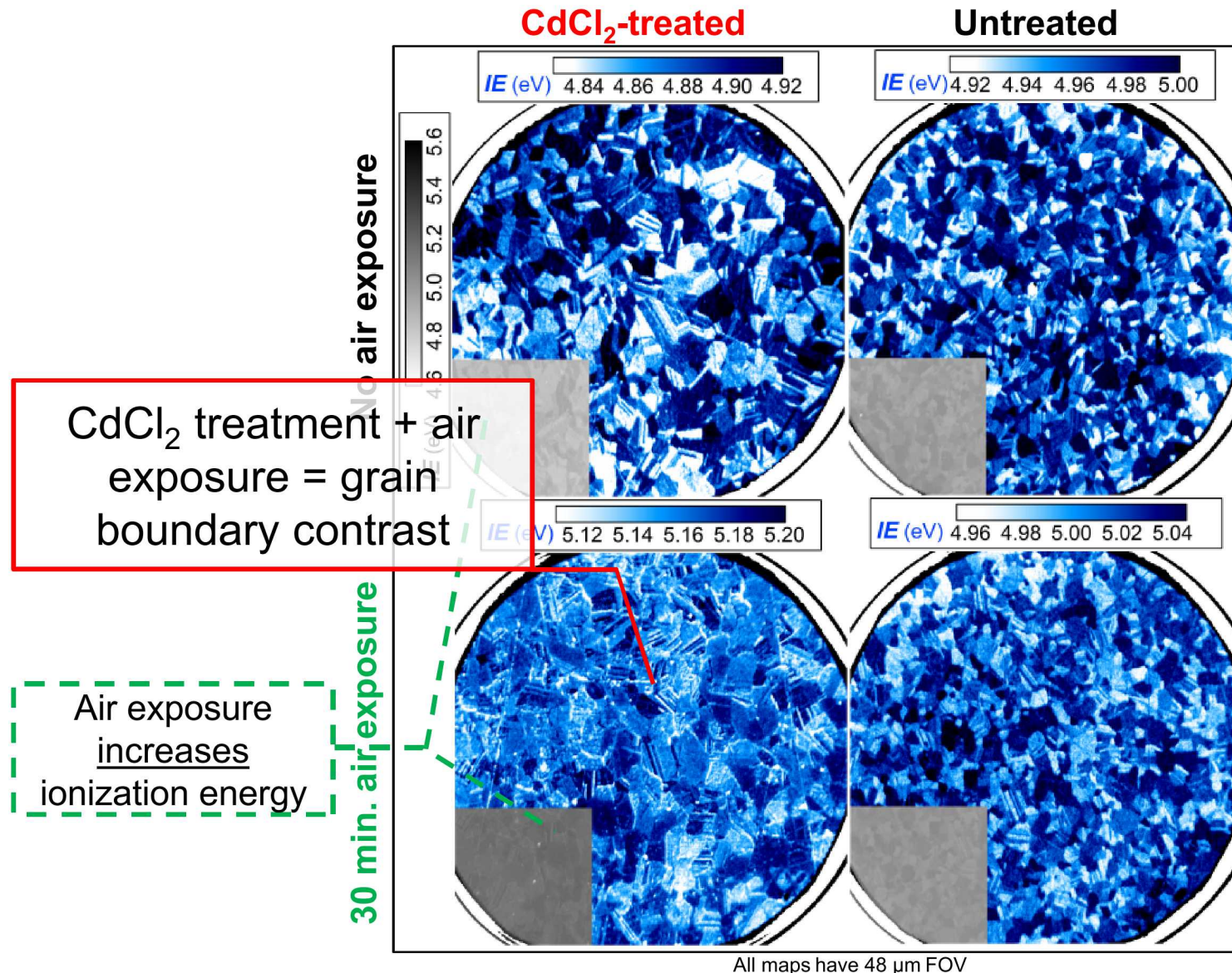
Consistent w/ the idea of electron doping by Cl through CdCl₂ activation

Scanning Probe Microscopy of CdCl₂-CdTe

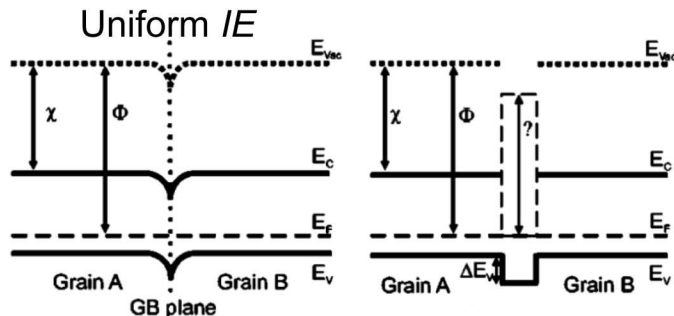
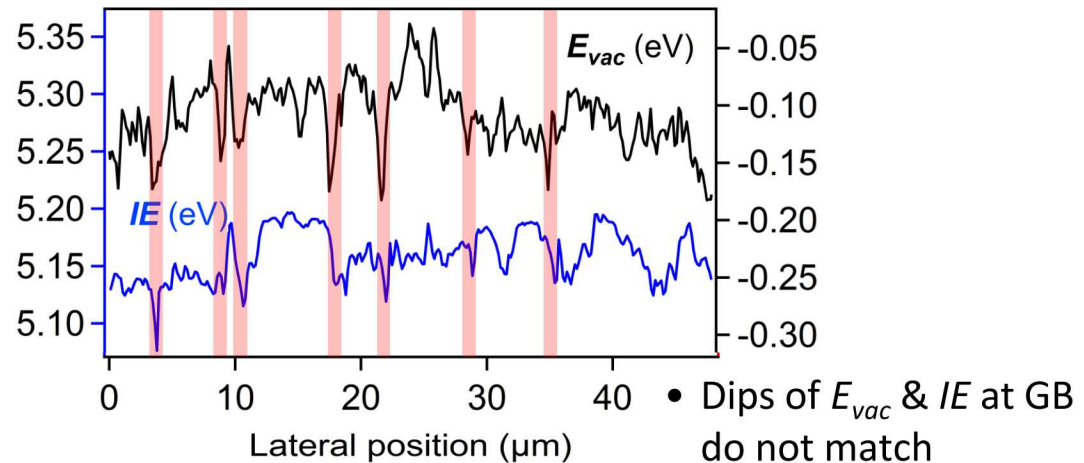
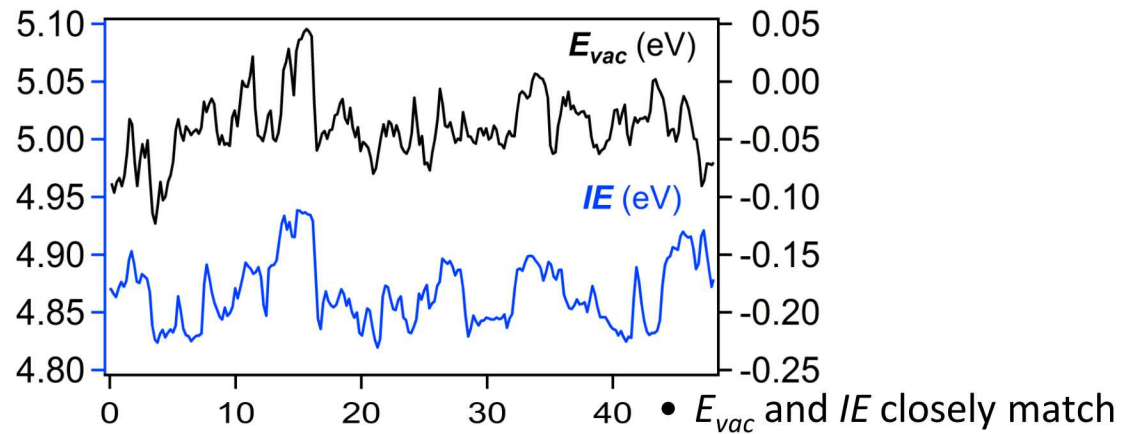
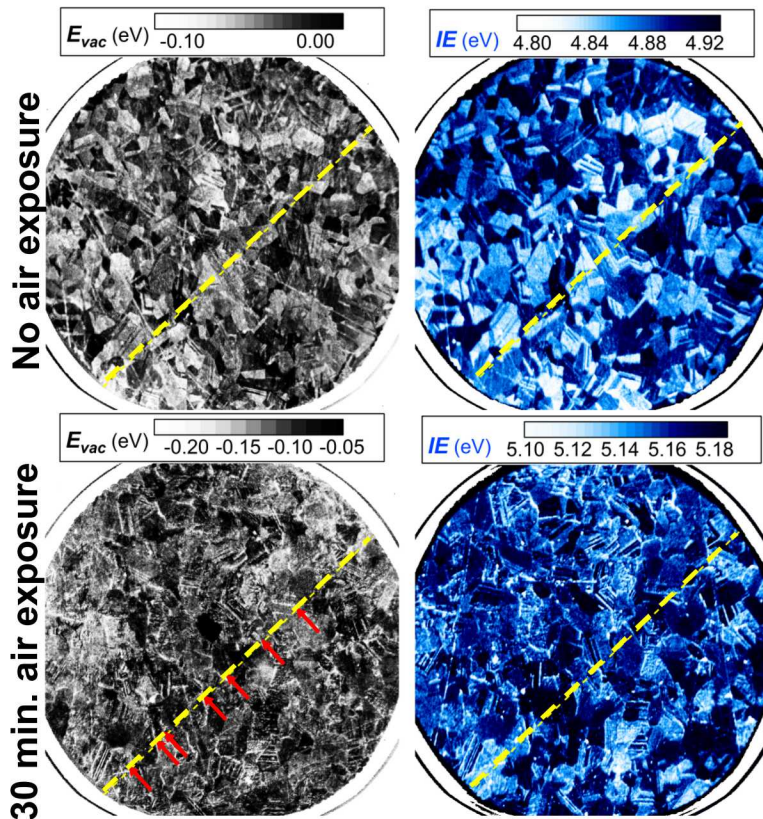


- No potential variation at grain boundaries?

Expected grain boundary (GB) contrast appeared only after exposing CdCl_2 activated CdTe to air



Maps of E_{vac} & IE elucidate complex electronic structures at grain boundaries (GB)



Electrostatic rigid band shift or something else at GB?

Not a simple rigid band shift



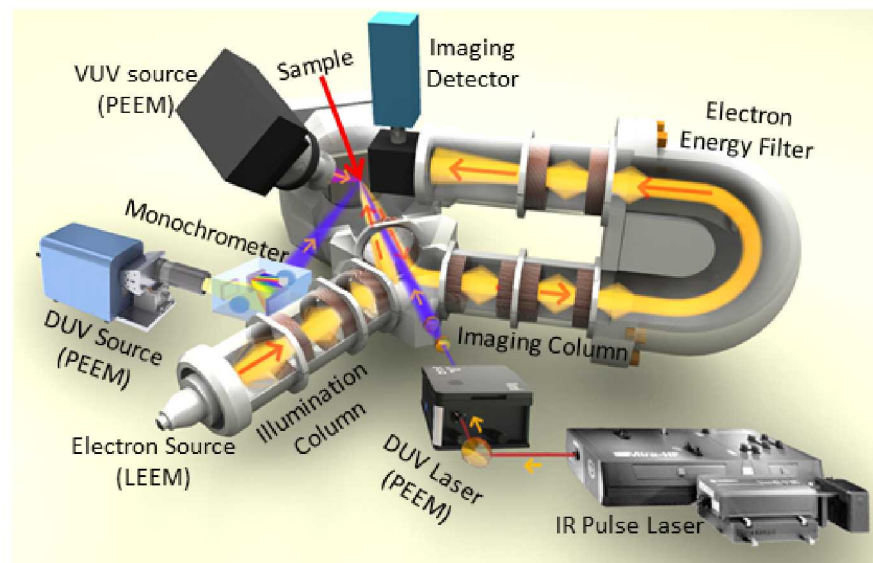
Summary

- 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



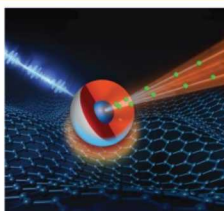
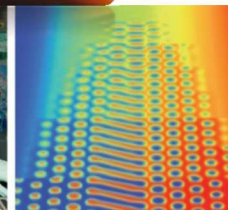
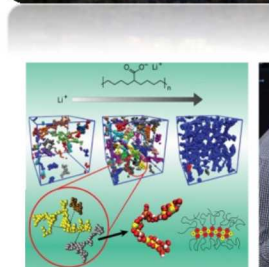
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LEEM-PEEM contact:

Taisuke Ohta (tohta@sandia.gov)

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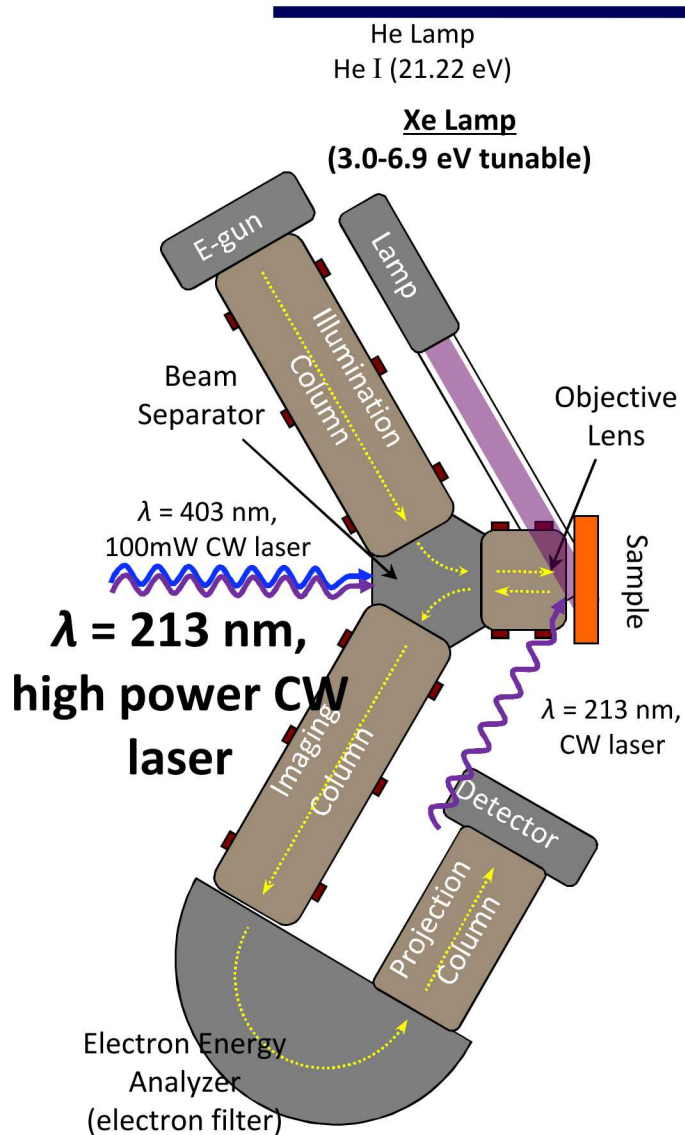
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We have opportunities for higher resolution imaging



- (Goal) ~ 10 nm lateral resolution using $\lambda = 213$ nm, high power CW laser (installed last week)
- Postdoc opportunities (pending)
 - Subsurface imaging of dielectrics/insulators and buried defects using photoemission microscopy
 - Starting date: Summer/Autumn 2019

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Text

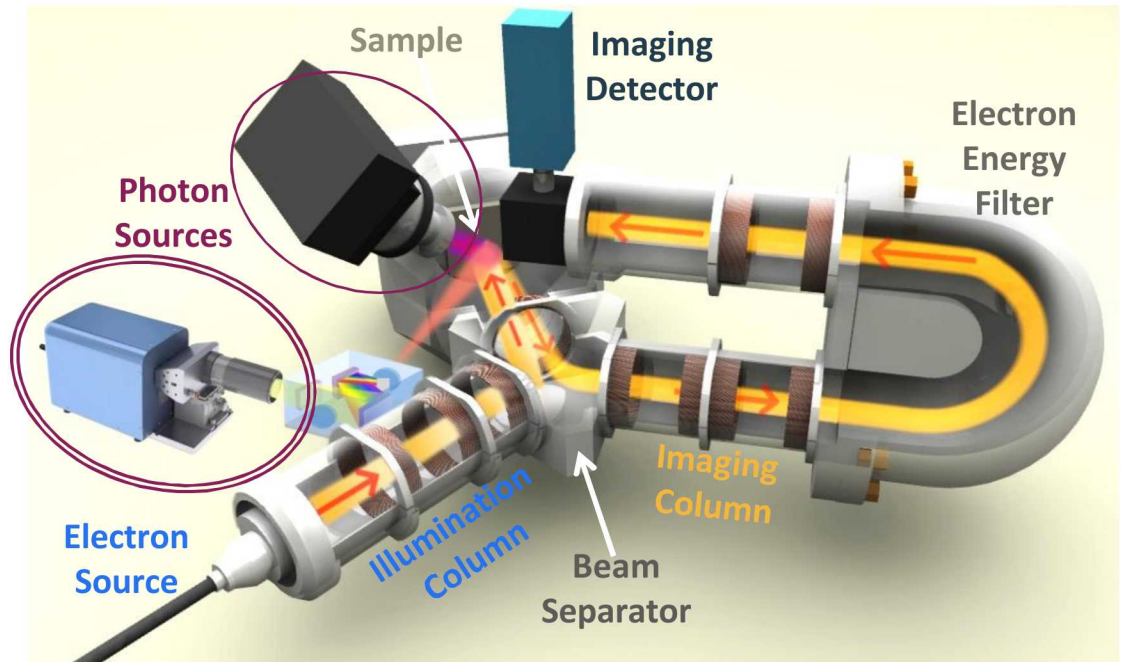
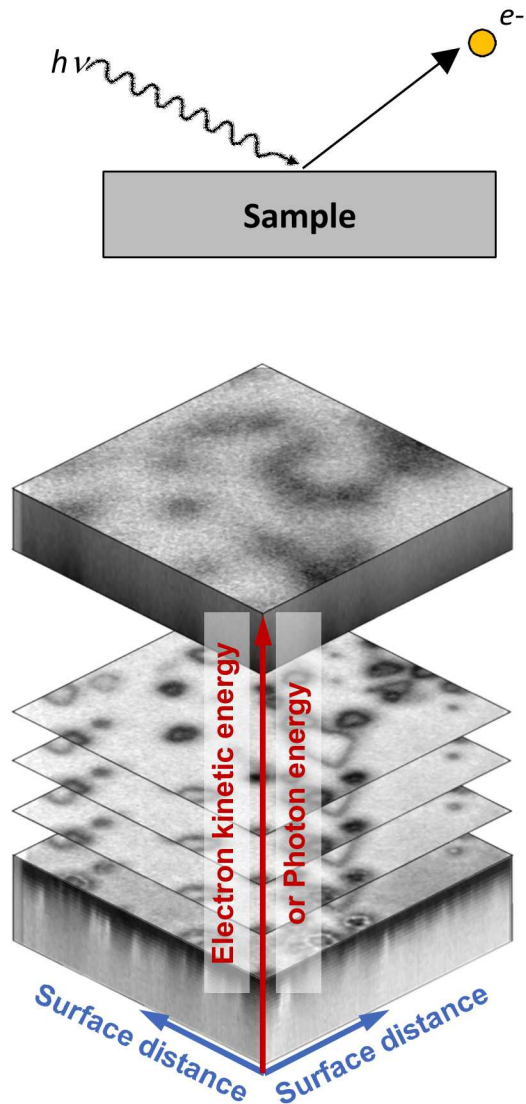


Text





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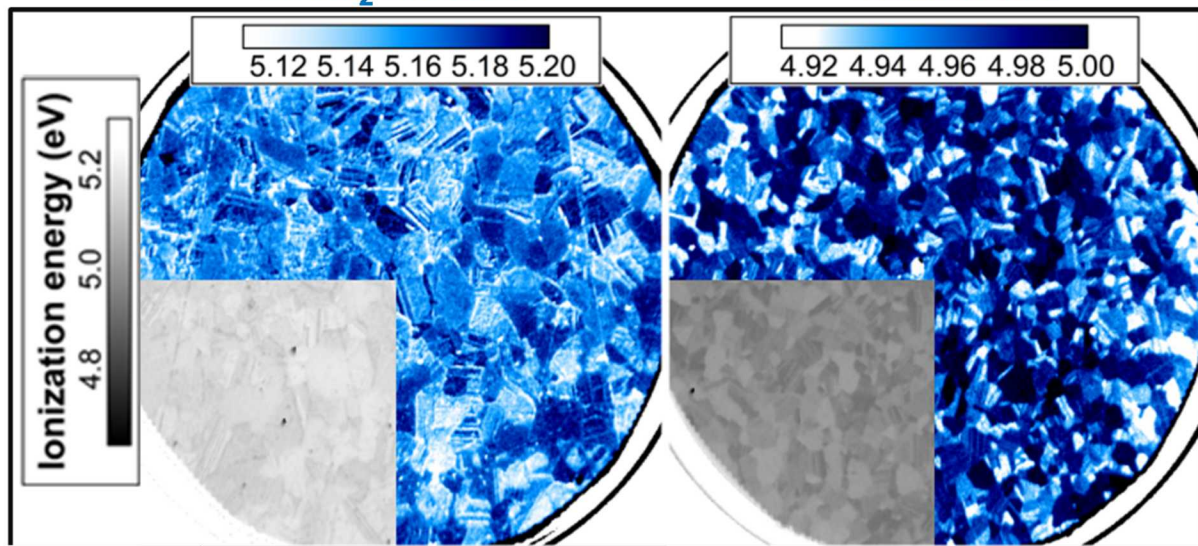
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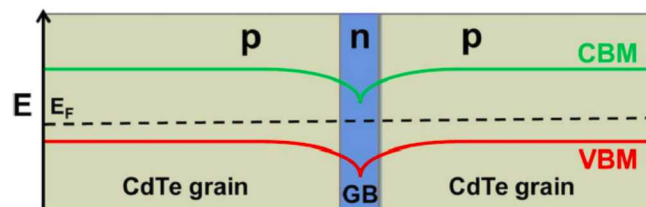
We observe the change of grain boundary energetics by CdCl_2 in polycrystalline CdTe

CdCl_2 -treated

Untreated



FOV 50 μm

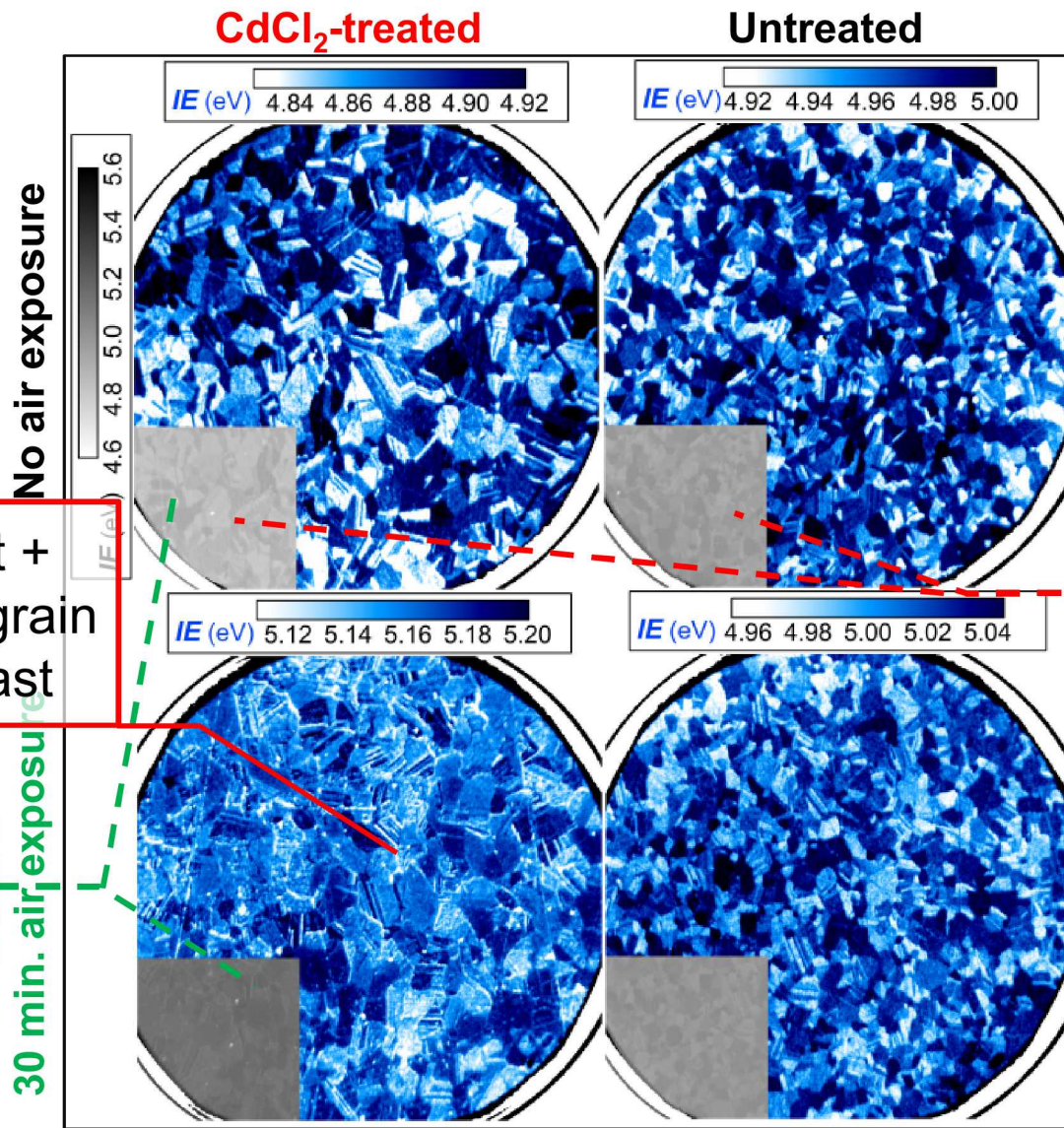


Li, et al., Phys. Rev. Lett. 112, 156103 (2014)

- 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



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

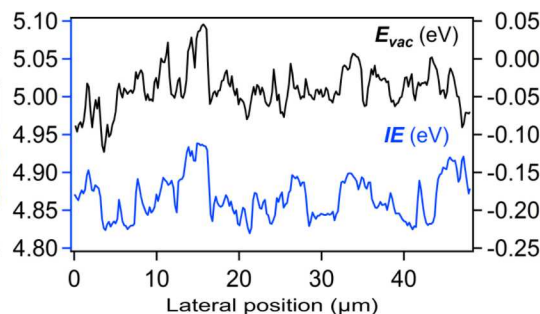
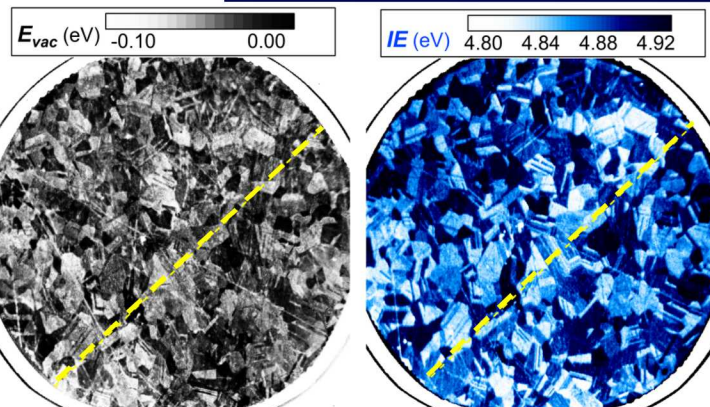
CdCl_2 treatment decreases ionization energy

Air exposure increases ionization energy



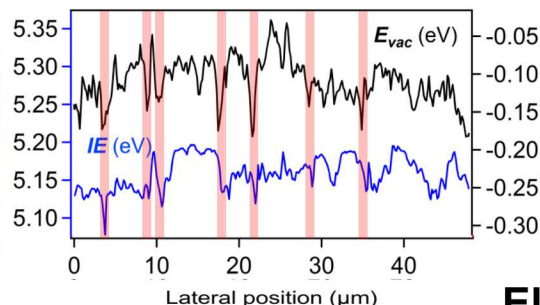
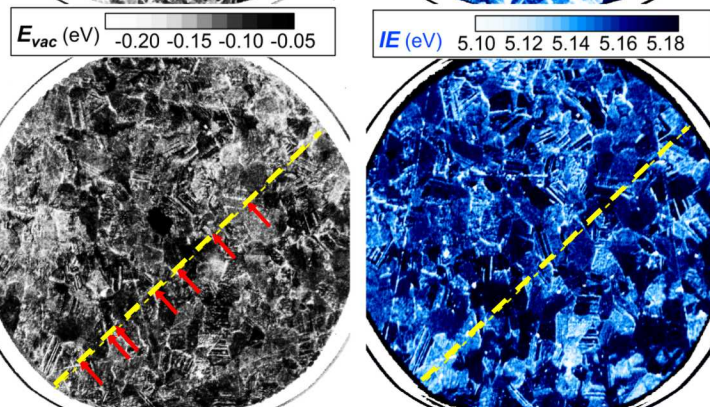
E_{vac} and IE maps elucidate grain boundaries with different electronic structures

No air exposure



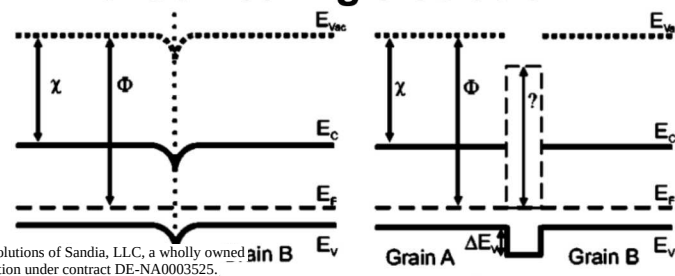
- E_{vac} and IE closely match and vary in step-like fashion along with the grain

30 min. air exposure



- 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 $\sim 10^{15} \text{cm}^{-3}$ and GB trap density of $\sim 10^{11} \text{cm}^{-2}$ expected for undoped CdTe and the admittance spectroscopy measurement

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