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Nanomaterials
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A U.S. DOE Nanoscale Science Research Center
SAND2018-5357PE

How we map potential landscapes using photoemission electron microscopy

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Polycrystalline CdTe: Morgann Berg[1,2], Jason M. Kephart[3], Amit Munshi[3], Walajabad S. Sampath[3], Calvin Chan[1]

Isoelectric transition metal dichalcogenides: Kunttal Keyshar[4,5], Morgann Berg[1,2], Calvin Chan[1], Gautam Gupta[5], Pulickel Ajayan[4], Aditya Mohite[2,4,5]

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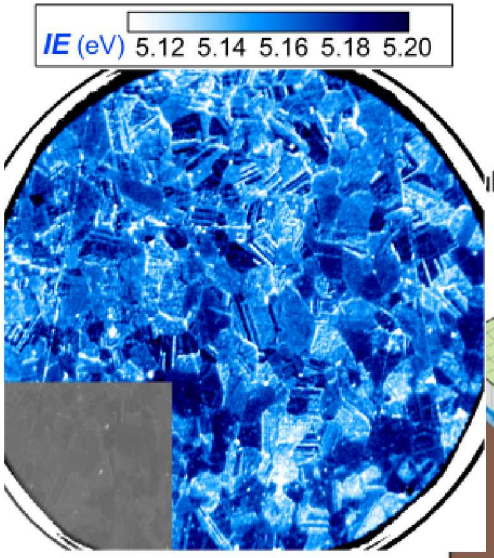
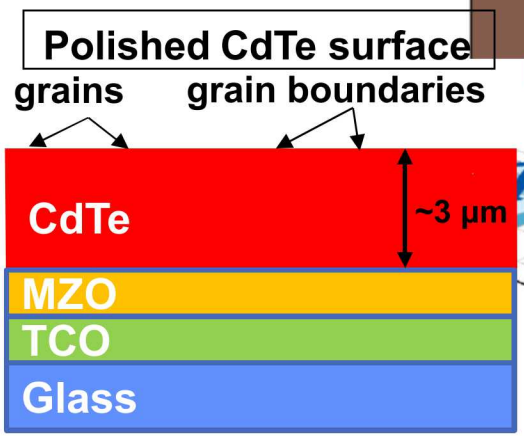
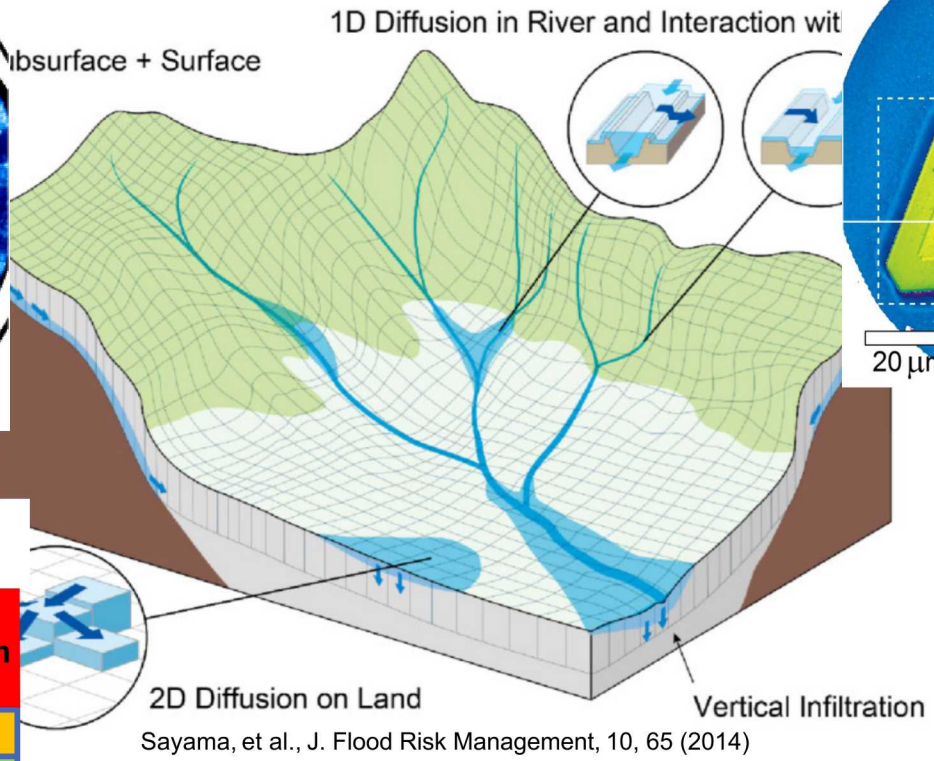
We measure potential landscapes to evaluate the band alignment in electronics materials

- Ionization energy map of polycrystalline CdTe

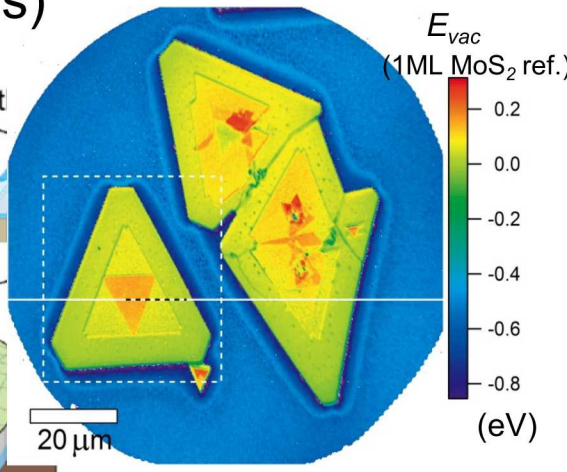


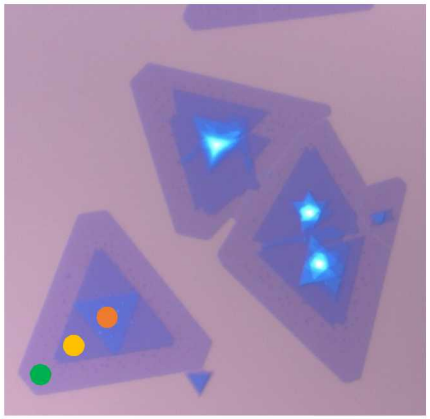




Sayama, et al., J. Flood Risk Management, 10, 65 (2014)

- Vacuum level map of MoS_2 (one, two, & three monolayer islands)





We use photoemission microscopy & spectroscopy

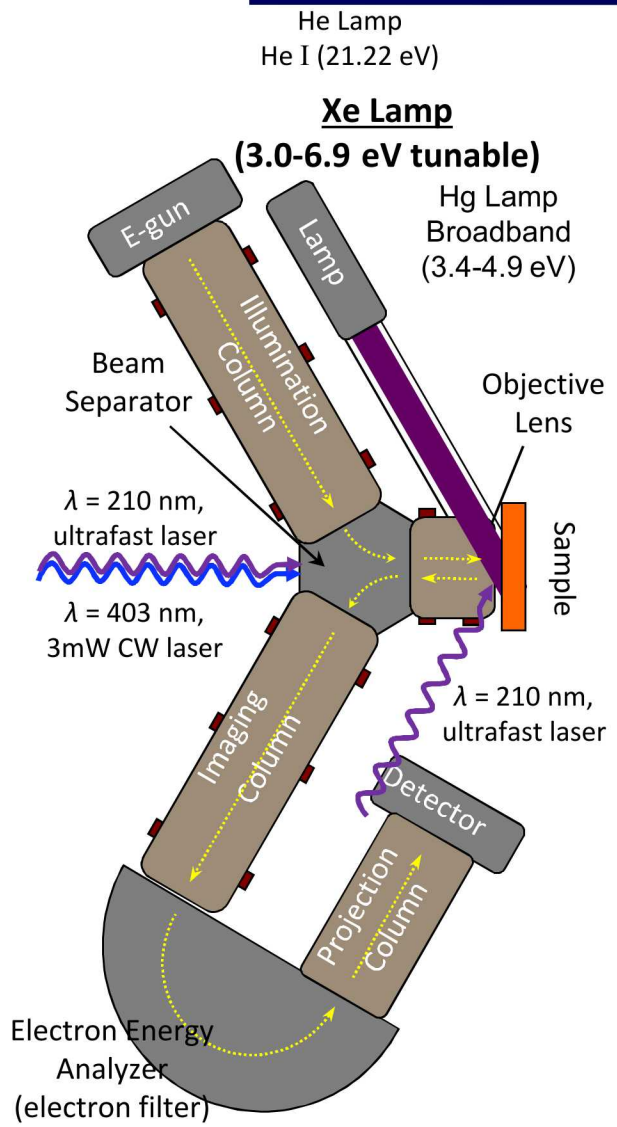
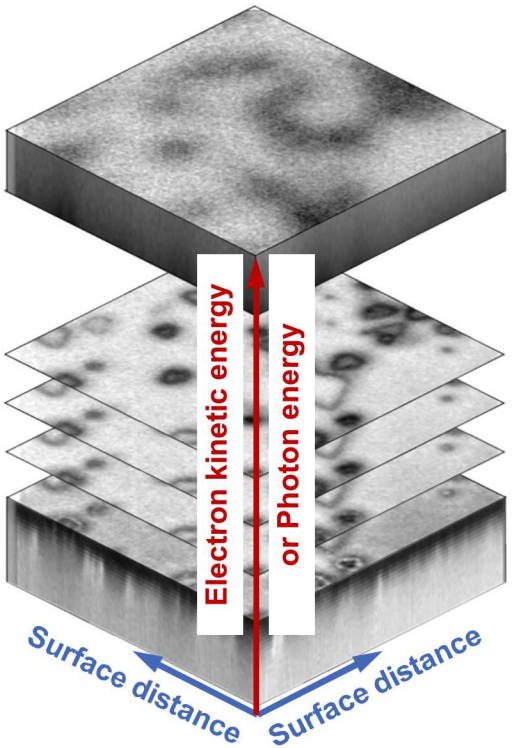
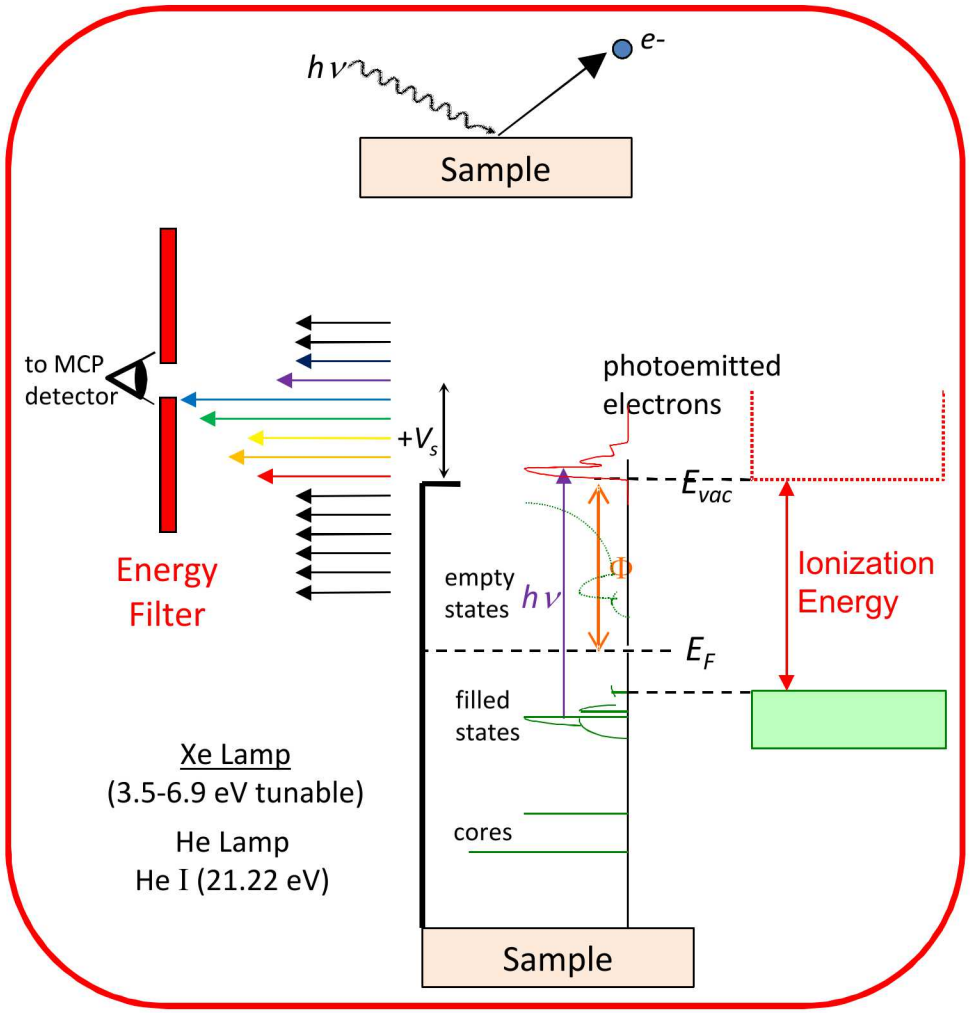


Figure courtesy: M. Berg

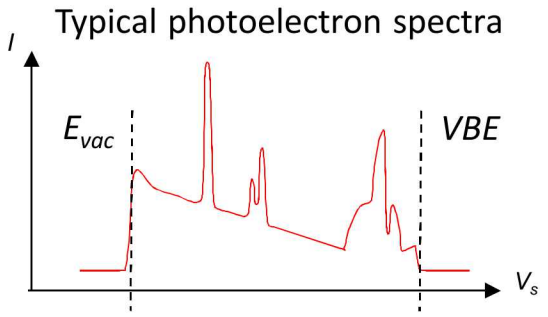
- Monochromatic light sources combined with an electron energy filter in photoemission electron microscopy (PEEM) to acquire electron spectra
  - Spatial resolution ~50 – 200nm
  - Energy resolution ~0.2 – 0.5eV
- Spectrum is extracted from each pixel in the image stack or data cube, and fitted to create maps
- 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

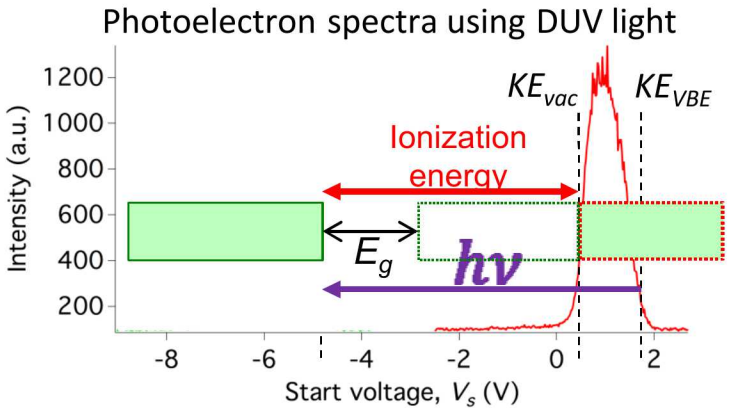


We extract E_{vac} and E_{VB} from photoelectron (photoemission) spectra



Photoemission process

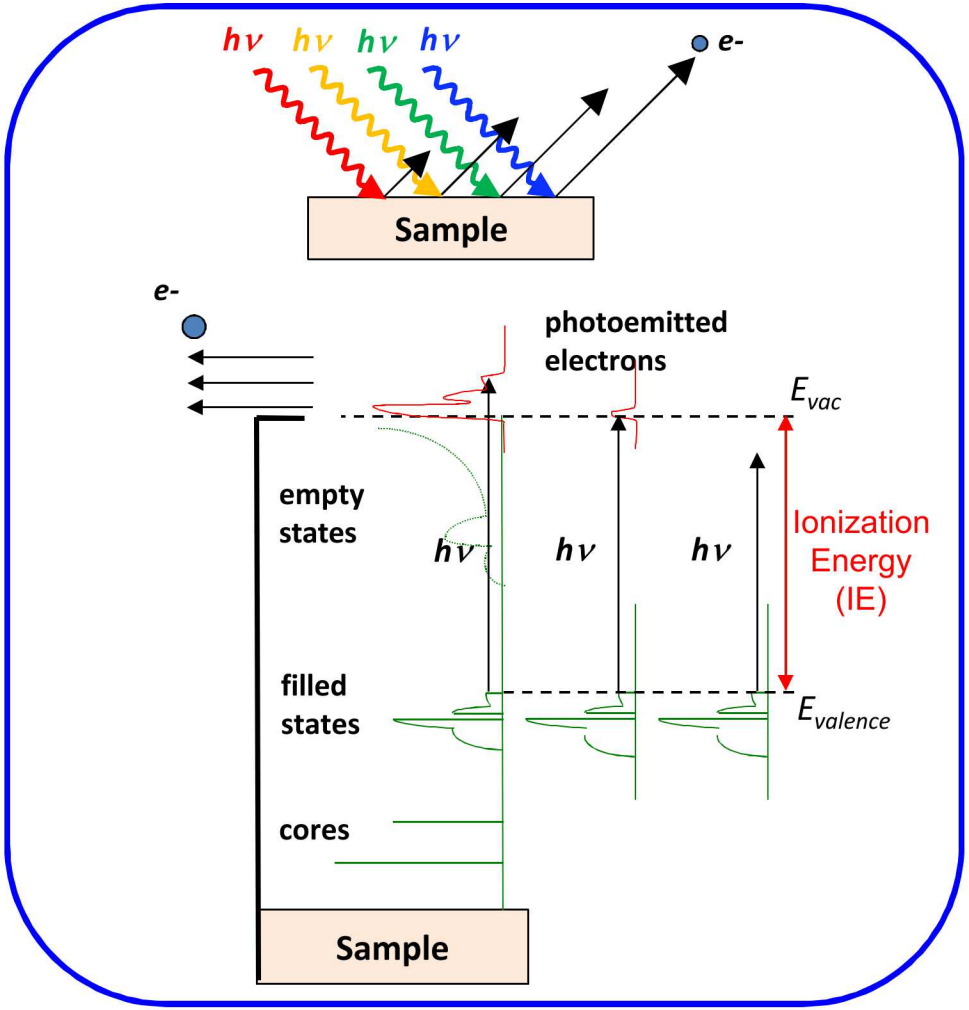




$$BE = KE - h\nu$$

Figure courtesy: M. Berg, C. Chan

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



Photoemission yield

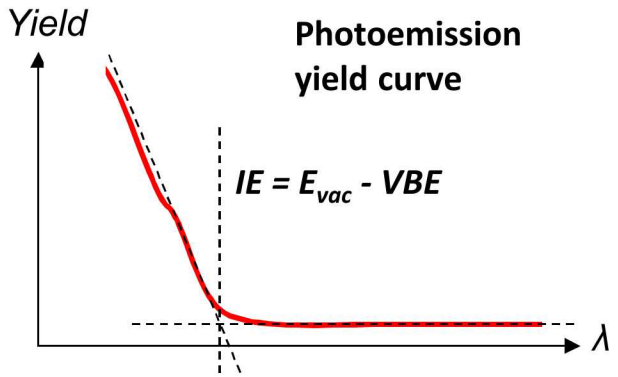
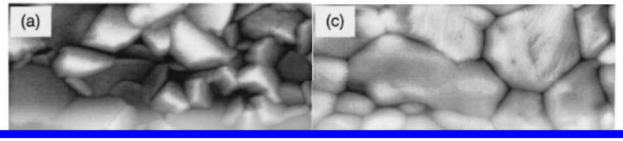
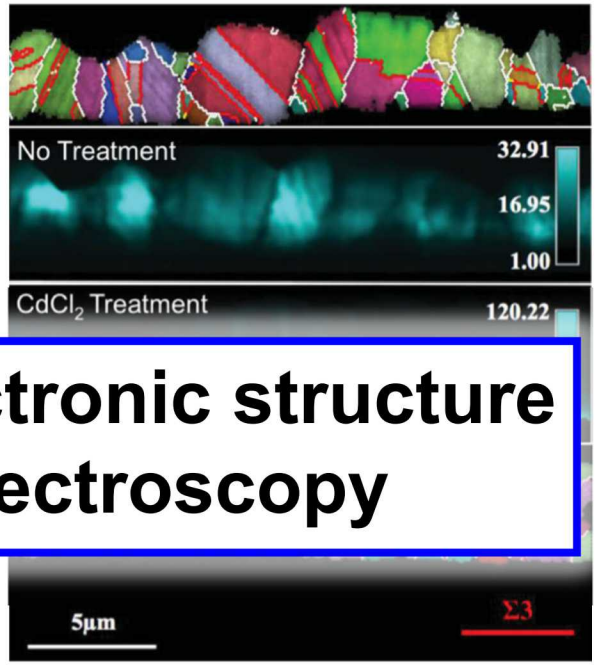


Figure courtesy: M. Berg, C. Chan

A key processing step to improve the grain size & PV efficiency of CdTe is $CdCl_2$ "activation"

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

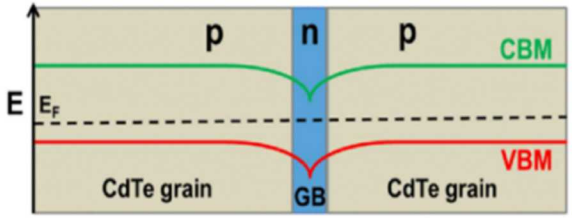


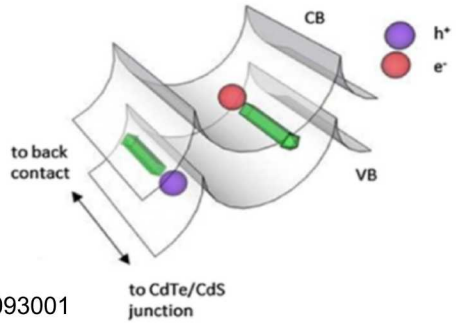


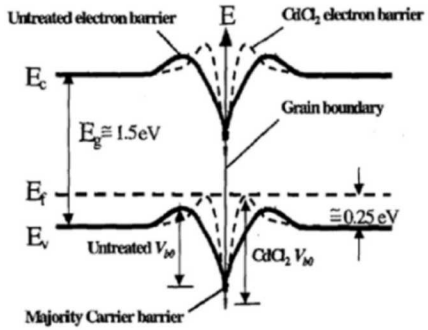
Poplawsky et al., Adv. Energy Mater. 4 1400454 (2014)

Our approach: probing local electronic structure based on photoemission spectroscopy

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



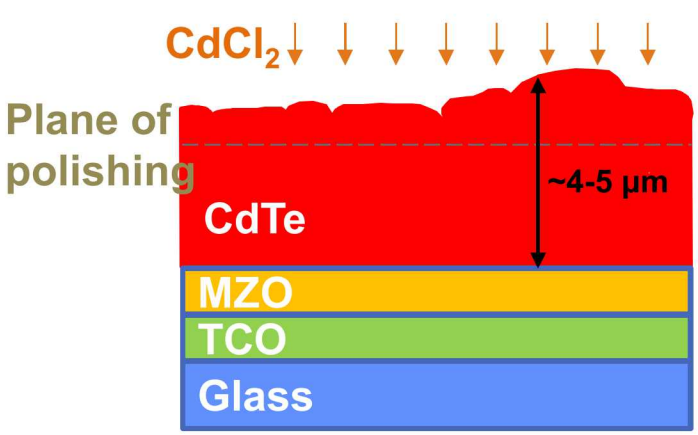




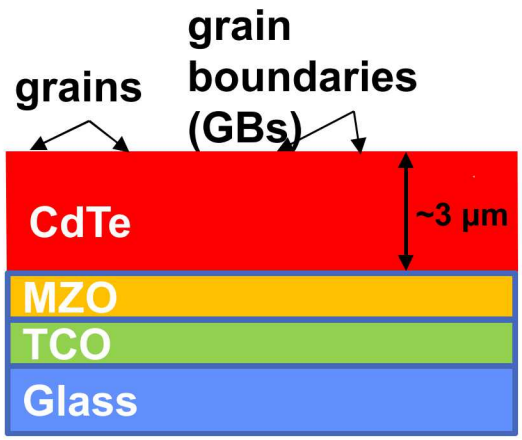
Major, Semicond. Sci. Technol. 31 (2016) 093001

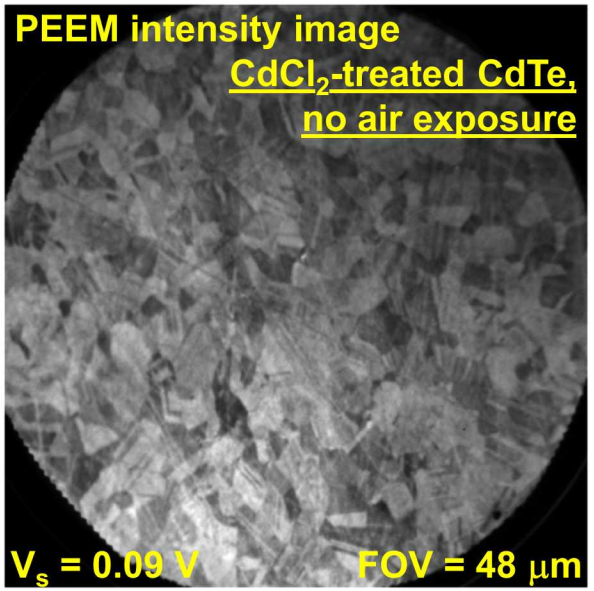
We polished the sample surface to expose the grain interiors and grain boundaries

CdTe, superstrate configuration



Polished CdTe surface



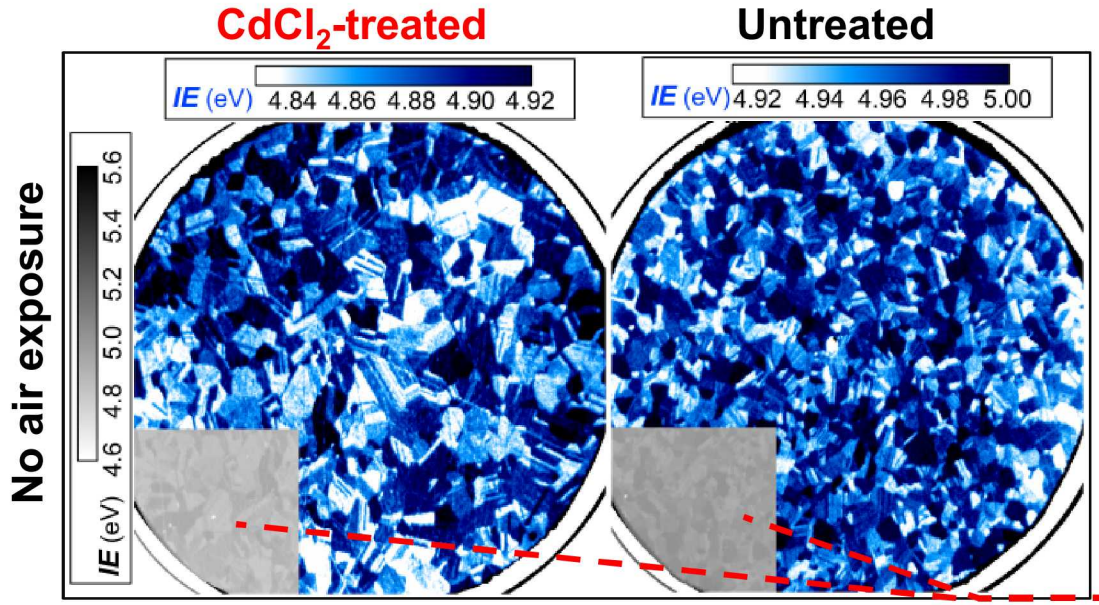


Grain size ~3 μm

- 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: important!**
  - 30 min air exposure step

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

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



All maps have 48 μm FOV

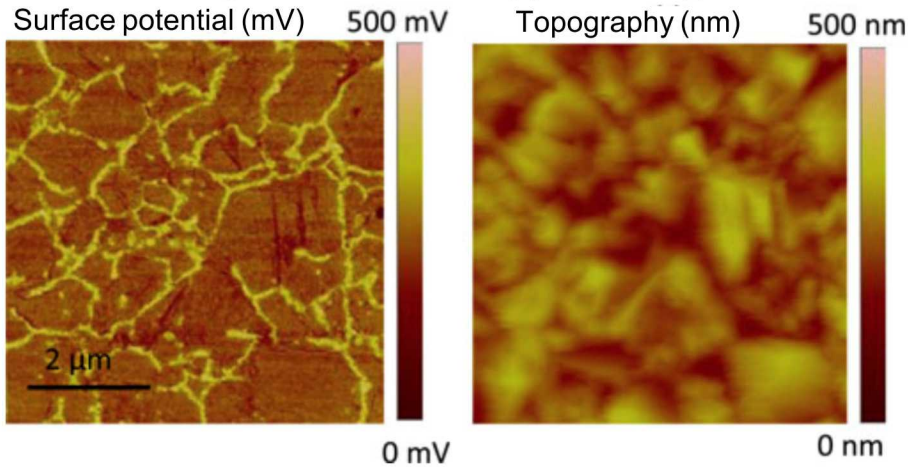
Grain-to-grain variation

Anticipated for polycrystalline films

$CdCl_2$ treatment decreases ionization energy

Consistent w/ the idea of electron doping by Cl through $CdCl_2$ activation

Scanning Probe Microscopy of $CdCl_2$-CdTe

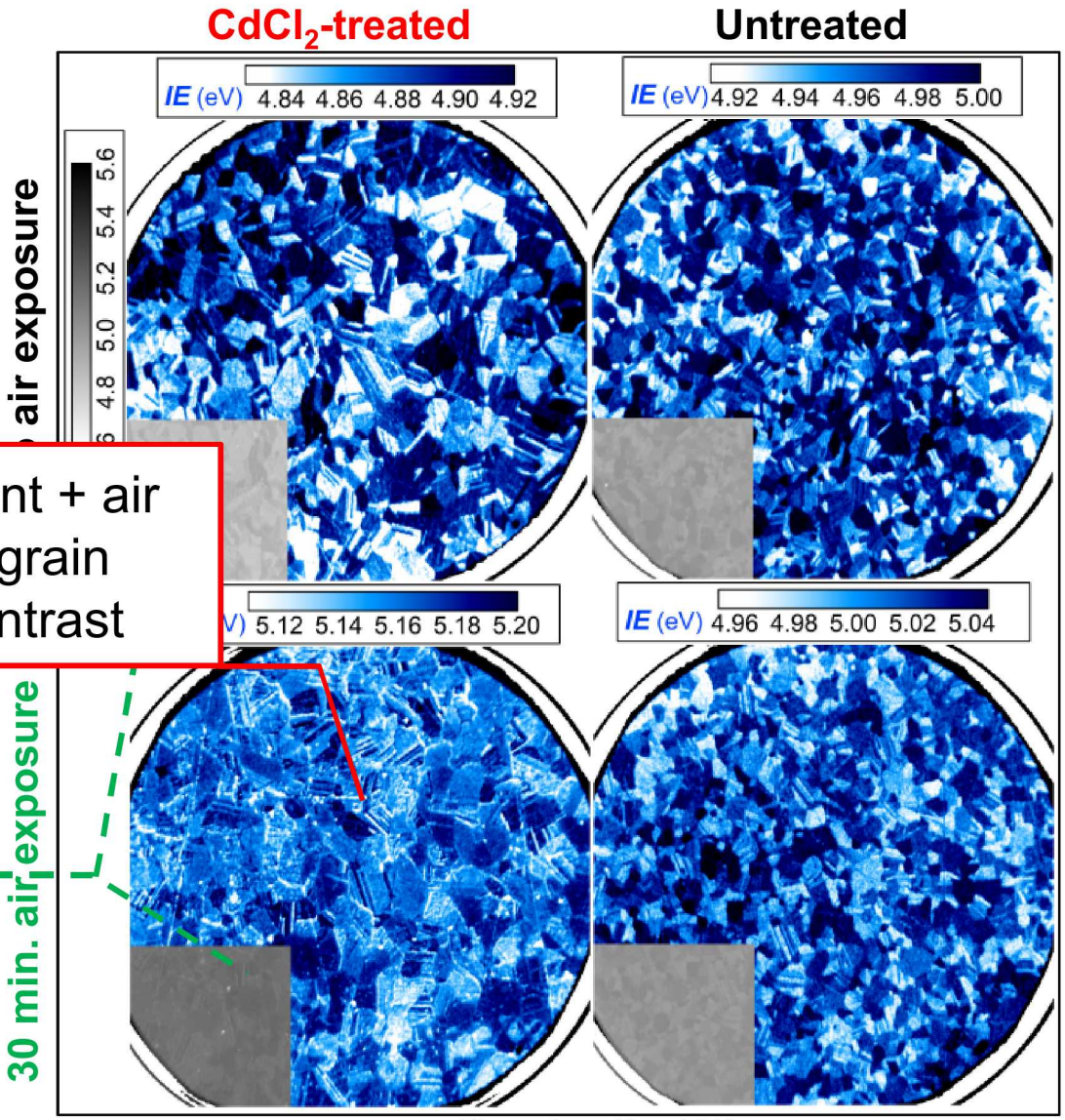


- No potential variation at grain boundaries?

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

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

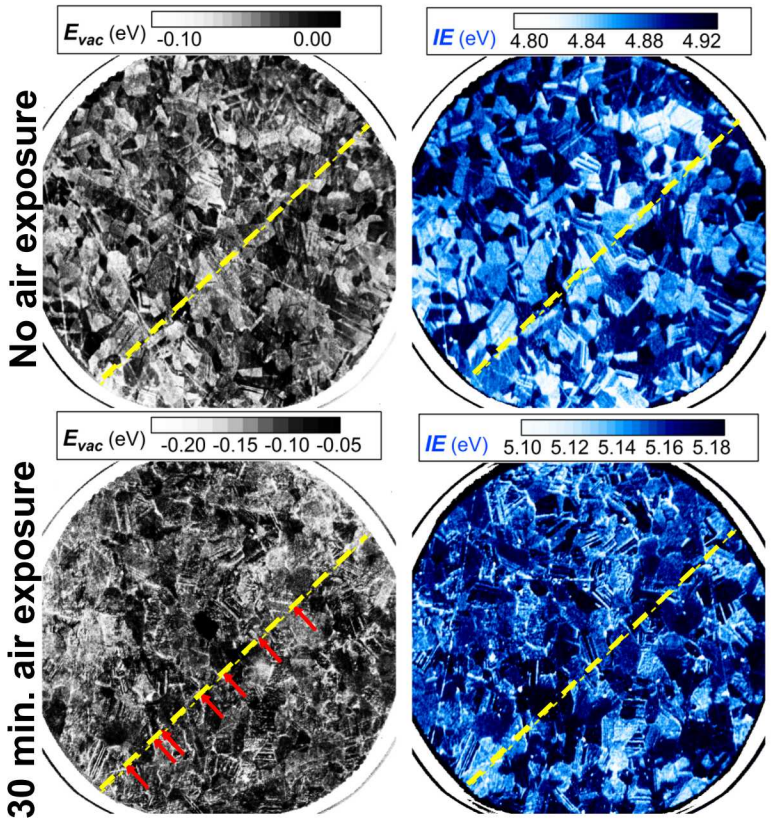


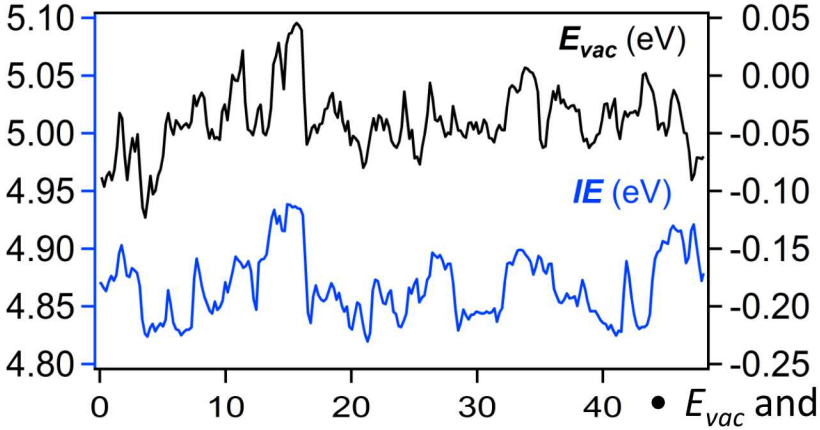
$CdCl_2$ treatment + air exposure = grain boundary contrast

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

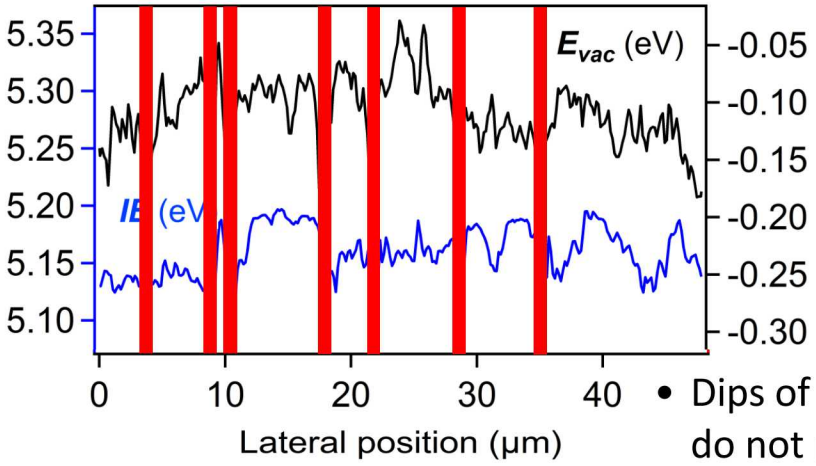
All maps have 48 μm FOV

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

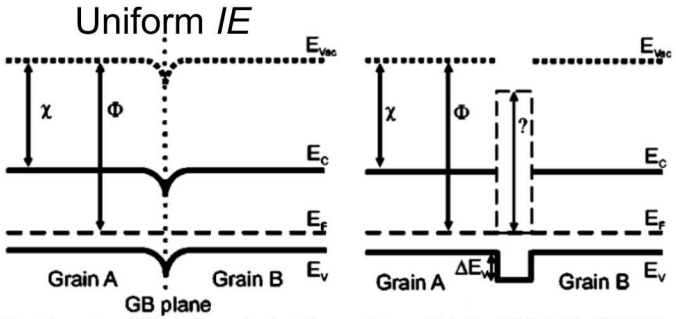




- E_{vac} and *IE* closely match



- Dips of E_{vac} & *IE* at GB do not match

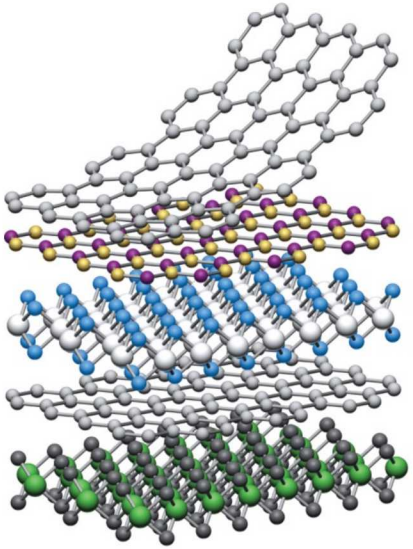


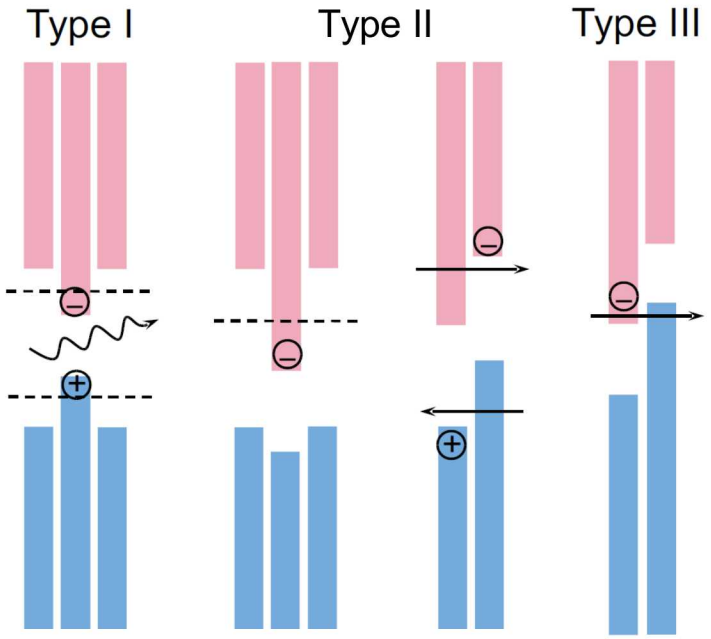
D. Fuertes Marrón et al. *Phys. Rev. B* 71, 033306 (2005).

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

Not a simple rigid band shift

Ionization energies govern the band alignment of designers TMD heterostructures

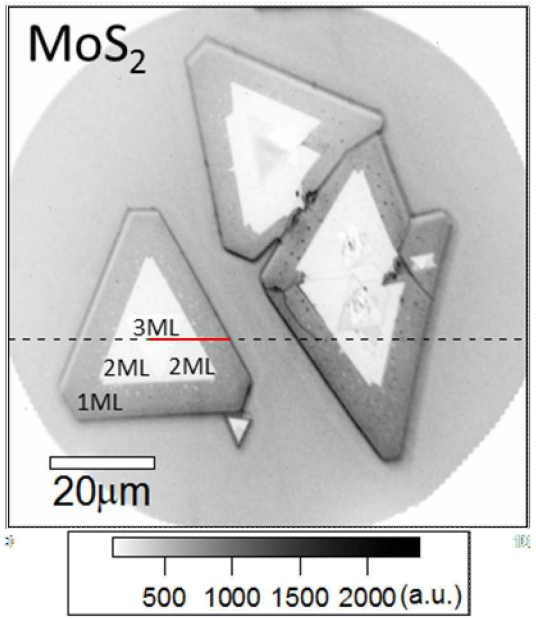


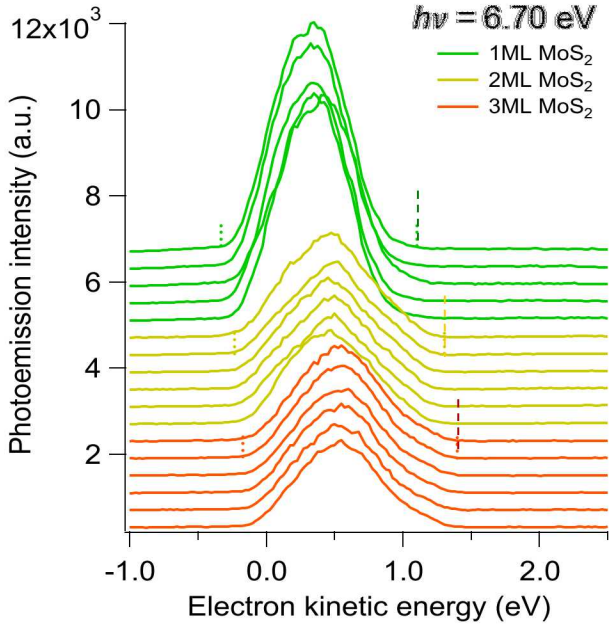


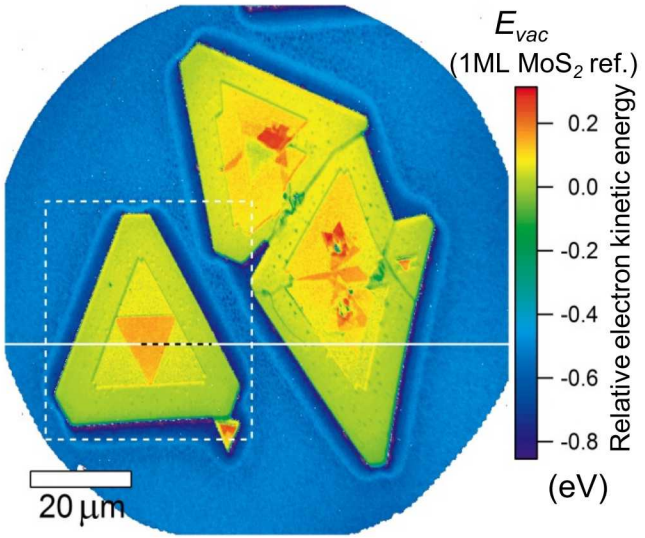
Özçelik, et al., Phys. Rev. B 94, 035125 (2016)

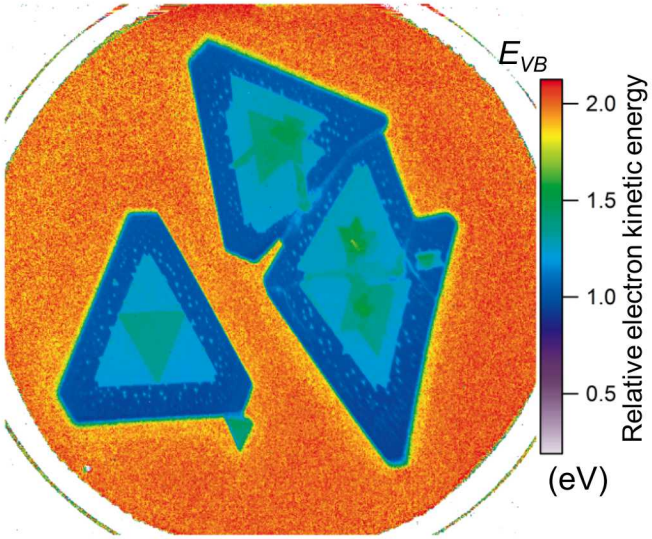
Heterostructures with designed properties can be created using TMDs

We determine E_{vac} & valence band edge on MoS_2 multi layers





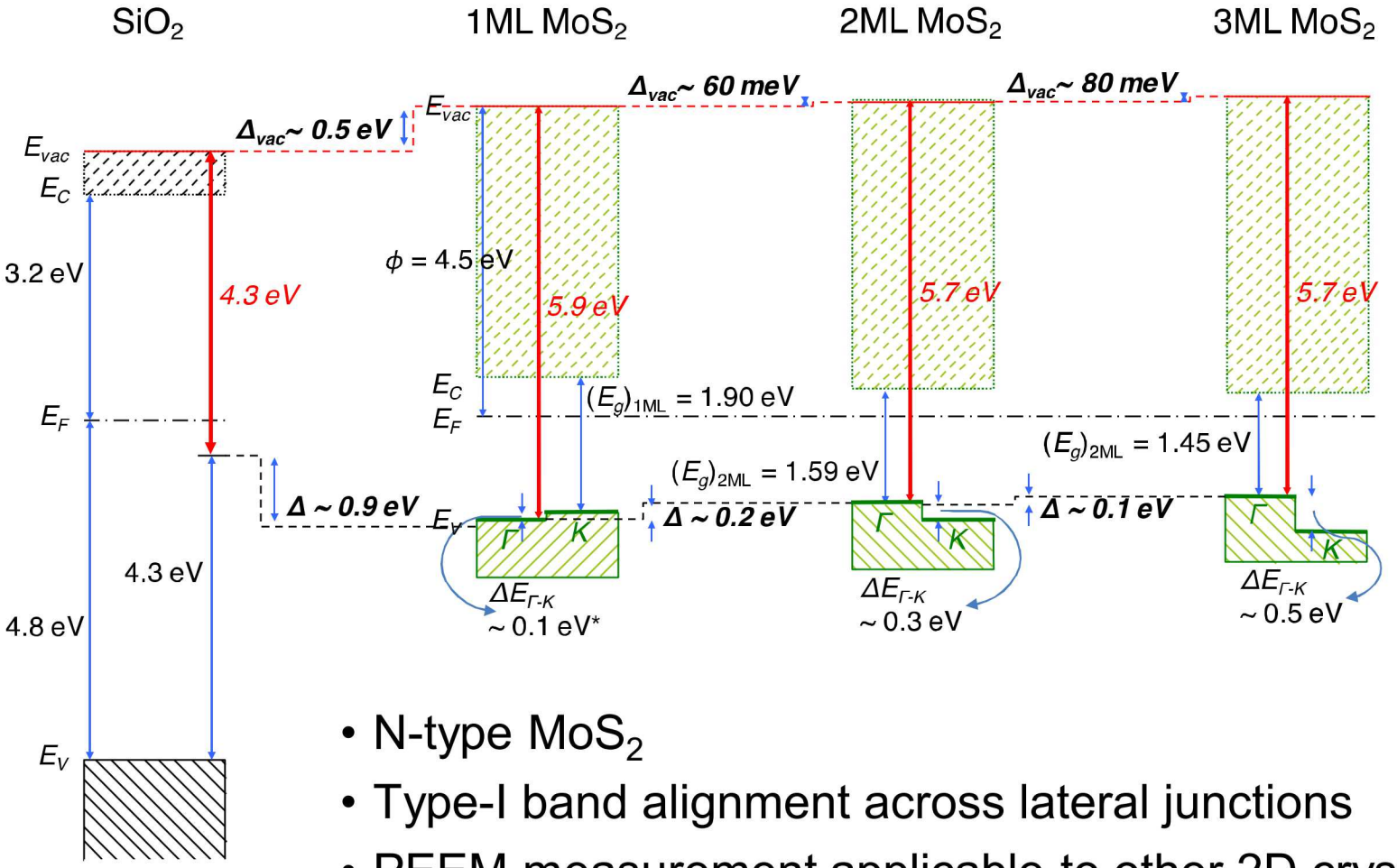




- **Concurrent imaging and spectroscopy**

Berg, et al., Layer-Dependence of the Electronic Band Alignment of Few-Layer MoS_2 on SiO_2 Measured Using Photoemission Electron Microscopy, Phys. Rev. B, 95, 235406 (2017)

Type I junctions forms between MoS_2 with different thicknesses

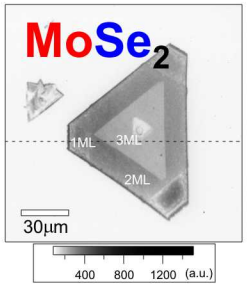


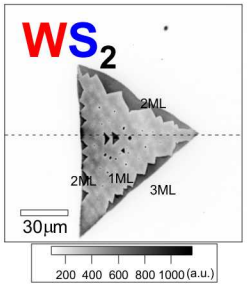
- N-type MoS_2
- Type-I band alignment across lateral junctions
- PEEM measurement applicable to other 2D crystals on 300nm thick SiO_2 on Si

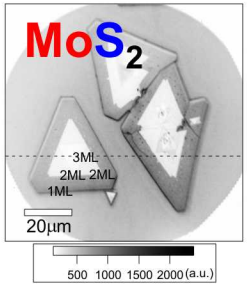
Berg, et al., Layer-Dependence of the Electronic Band Alignment of Few-Layer MoS_2 on SiO_2 Measured Using Photoemission Electron Microscopy, Phys. Rev. B, 95, 235406 (2017)

How band alignment changes for isoelectric TMDs

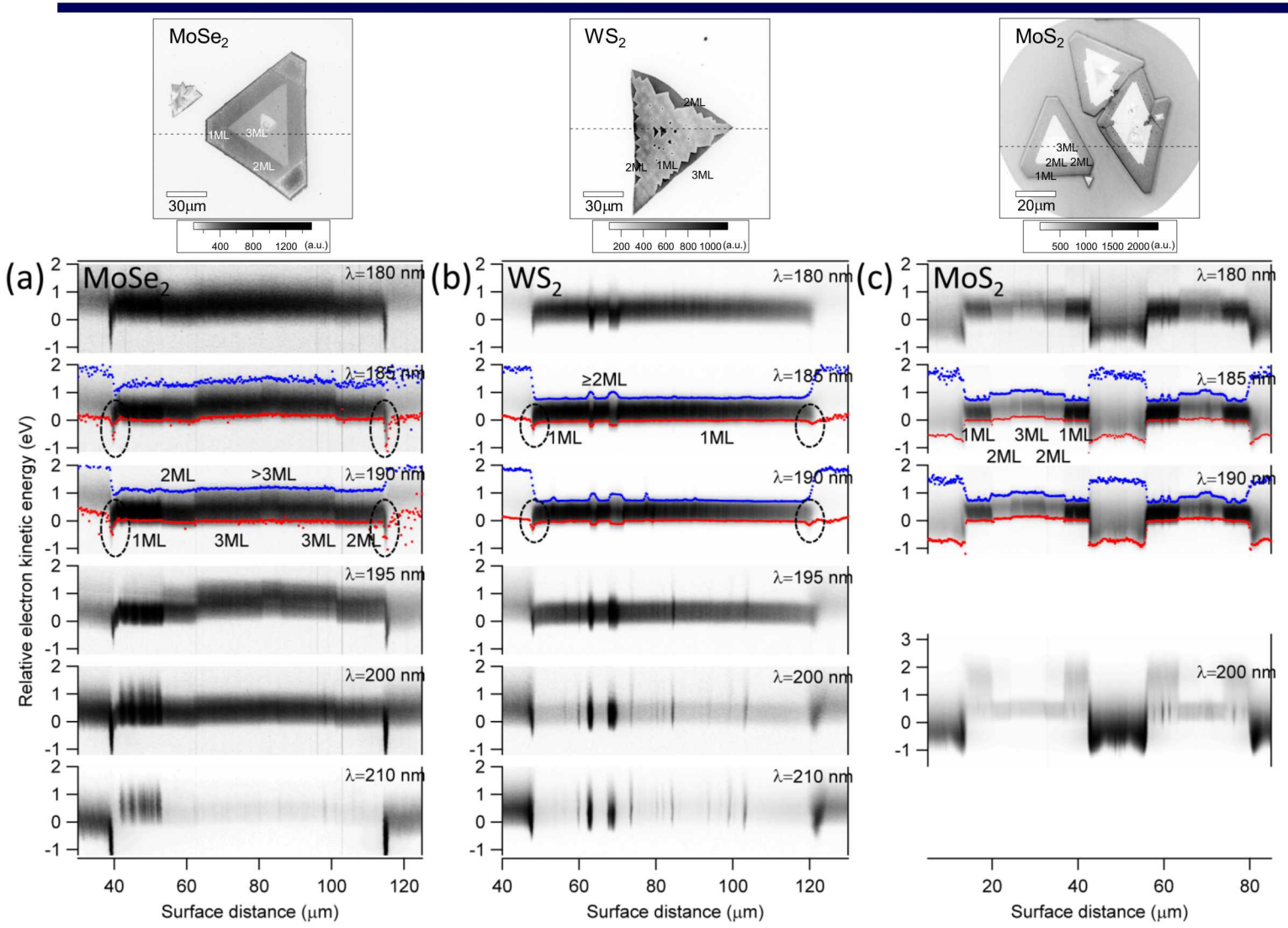
1 1IA 11A																	18 VIIIA 8A
1 H Hydrogen 1.0079	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	2 He Helium 4.00260
3 Li Lithium 6.941	4 Be Beryllium 9.01218											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.998403	10 Ne Neon 20.1797
11 Na Sodium 22.989768	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.981539	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.95591	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938	26 Fe Iron 55.847	27 Co Cobalt 58.9332	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.64	33 As Arsenic 74.92159	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium 98.9072	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.90447	54 Xe Xenon 131.29
55 Cs Cesium 132.90543	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.9665	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98037	84 Po Polonium [208.9824]	85 At Astatine 209.9871	86 Rn Radon 222.0176
87 Fr Francium 223.0197	88 Ra Radium 226.0254	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Uuq Ununquadium [289]	115 Uup Ununpentium unknown	116 Uuh Ununhexium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown





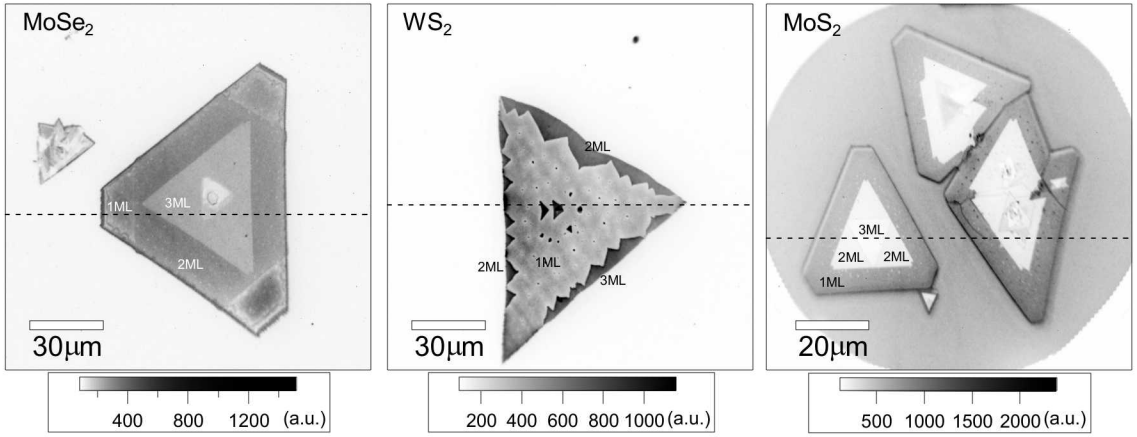


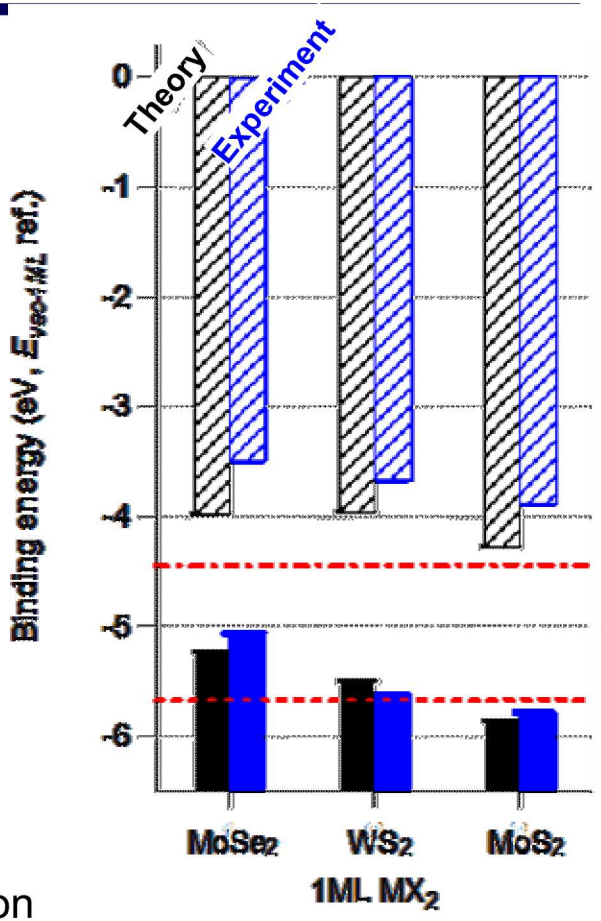
We measure photoemission spectra from $MoSe_2$, WS_2, and MoS_2



K. Keyshar, et al., Experimental determination of the ionization energies of MoS_2, WS_2, and $MoSe_2$ on SiO_2 using photoemission electron microscopy, ACS Nano, 11, 8223, 2017

Experimentally determined ionization energies match well with those from DFT calculations





- **Knowledge of the band alignment enables us to predict the properties of heterostructures**
  - Decrease from MoS_2, WS_2, to $MoSe_2$, anticipated from the electronegativities of the constituent atoms
  - Very good agreement with DFT with GW approximation
  - Heterostructures containing MoS_2, WS_2, to $MoSe_2$ are likely to display type II alignment

K. Keyshar, et al., Experimental determination of the ionization energies of MoS_2, WS_2, and $MoSe_2$ on SiO_2 using photoemission electron microscopy, ACS Nano, 11, 8223, 2017

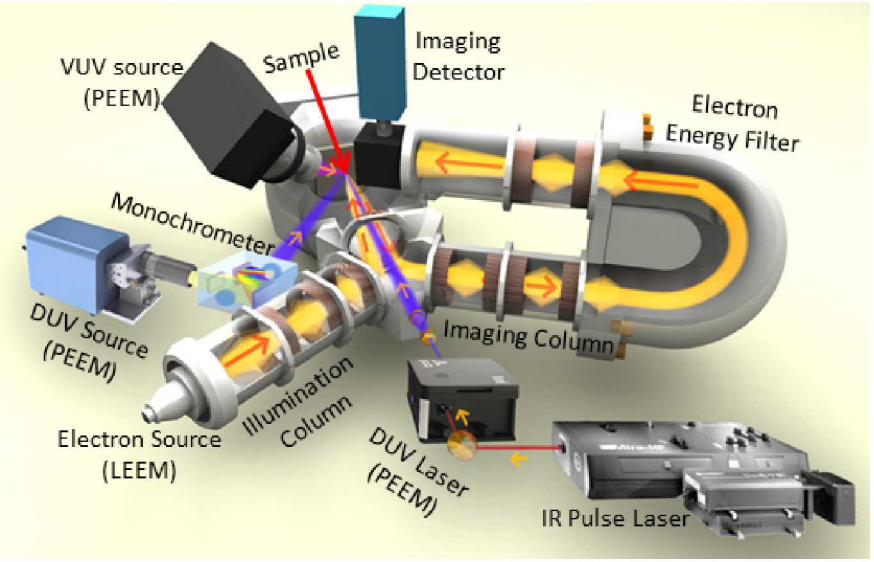
Conclusions

- PEEM coupled to deep ultraviolet (DUV) light sources is an emerging analytical capability to explore the electronic properties of spatially inhomogeneous materials
  - We determined ionization energies of atomically-thin transition metal dichalcogenides and deduced their anticipated heterointerface band alignments

Knowledge of the band alignment enables us to predict the properties of heterostructures

  - We elucidated the electronic properties of grain and grain boundaries in polycrystalline CdTe

Visualization of the electronic structure variation in inhomogeneous semiconductor



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  - Sandia LDRD

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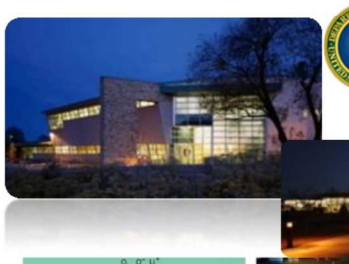
- **<u>Open</u> access for the research community via a proposal process!**



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We have opportunities for higher resolution imaging and postdoc hiring

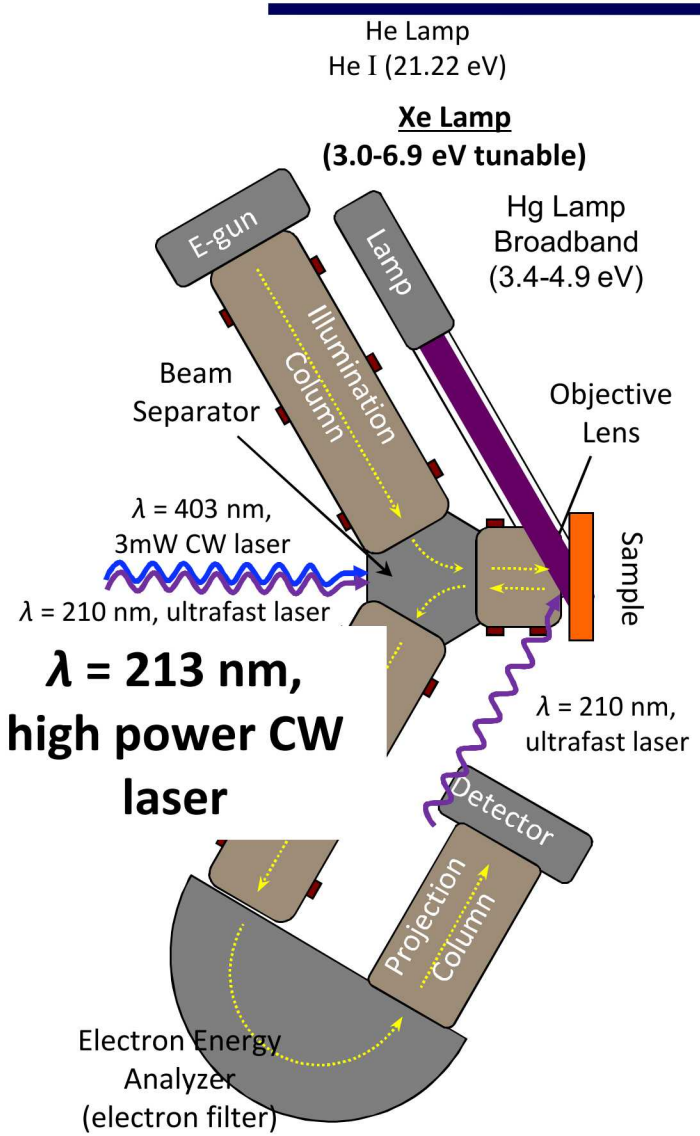
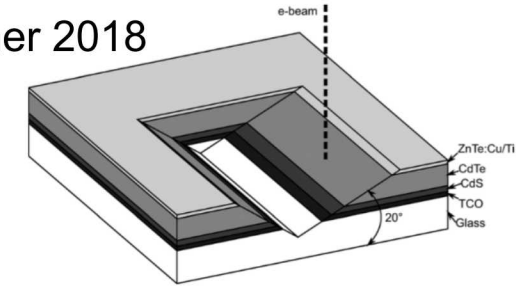


Figure courtesy: M. Berg

- ~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



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