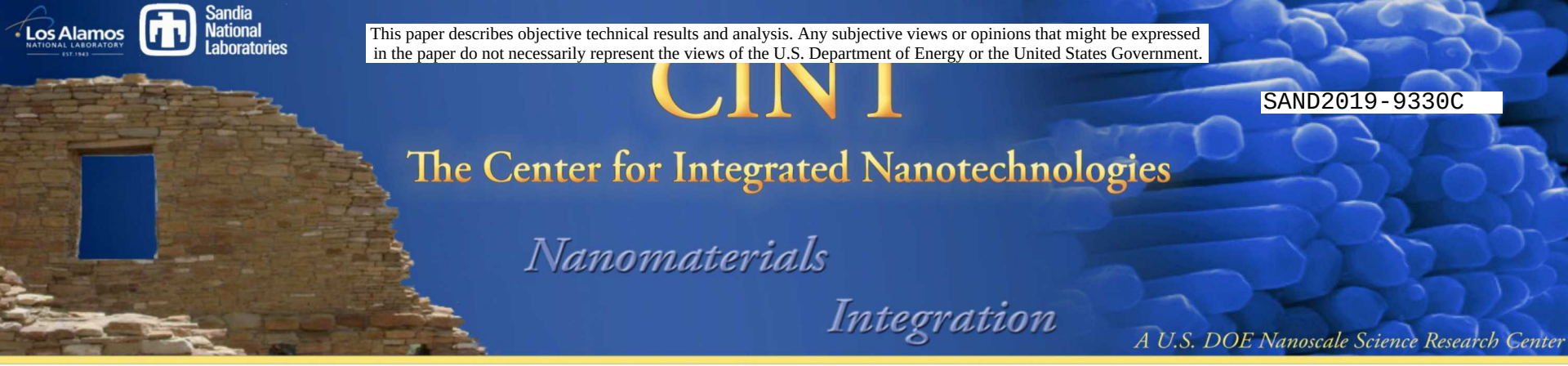
SAND2019-9330C



PEEM as a new Metrology Tool to Examine the Electronic Structures of 2D Crystals on Silicon Oxide

Taisuke Ohta

Center for Integrated Technology, Sandia National Laboratories, Albuquerque, New Mexico, United States

In collaboration with:

Morgann Berg[1], Thomas E. Beechem[1], Calvin Chan[1]

[1] Sandia National Laboratories, Albuquerque, New Mexico, United States

Kunttal Keyshar[2,3], Xiang Zhang[2], Robert Vajtai[2], Gautam Gupta[3], Pulickel Ajayan[2], Aditya Mohite[2]

[2] Rice University, Houston, Texas, United States

[3] Los Alamos National Laboratory, Los Alamos, New Mexico, United States

Jason M. Kephart[4], Amit Munshi[4], Walajabad S. Sampath[4]

[4] Department of Mechanical Engineering, Colorado State University, Fort Collins, Colorado, United States

2019 August 12

11085-23 SPIE Conference: Low-Dimensional Materials and Devices 2019

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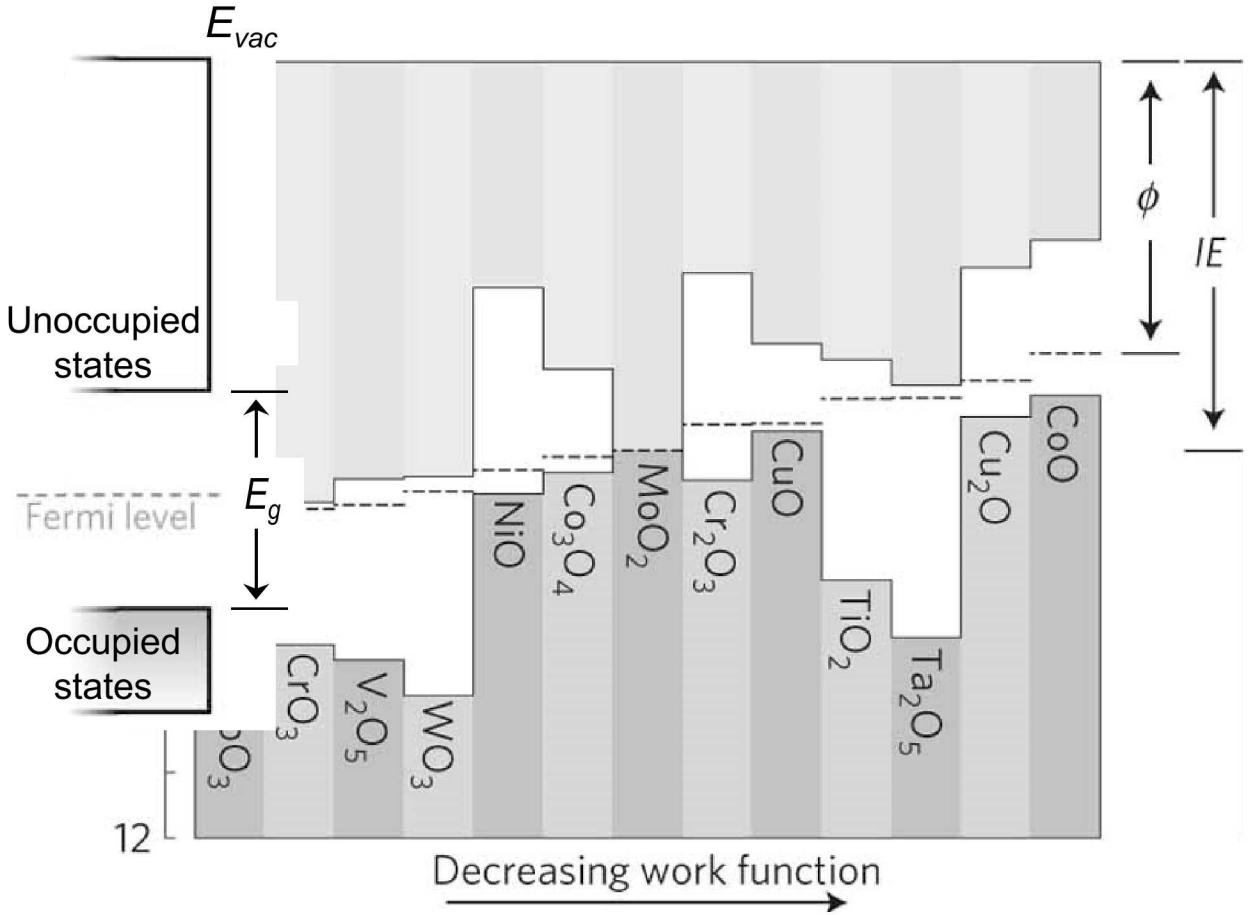
How to evaluate the band alignment?

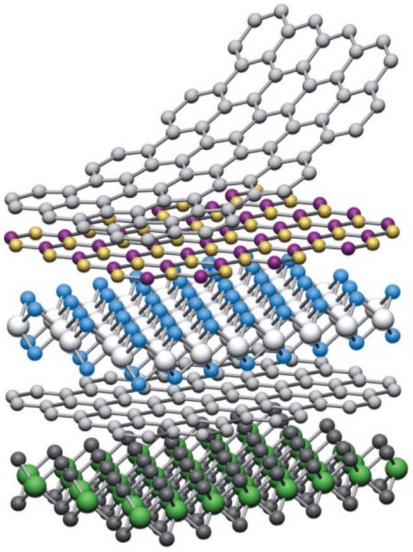


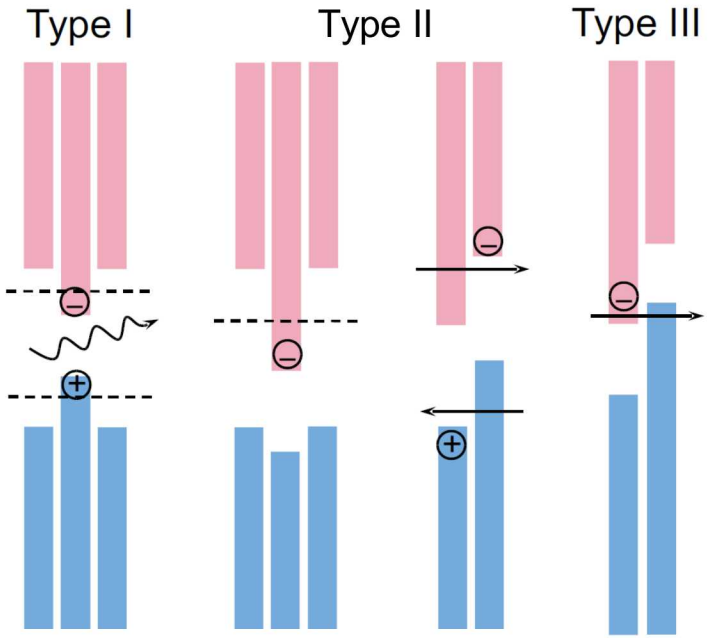
Semiconductor Devices or heterostructure

Band structure *Band alignment*

Nature Materials 11, 76 (2012)

Band alignment of transition metal dichalcogenide dictates the properties of TMD heterostructures

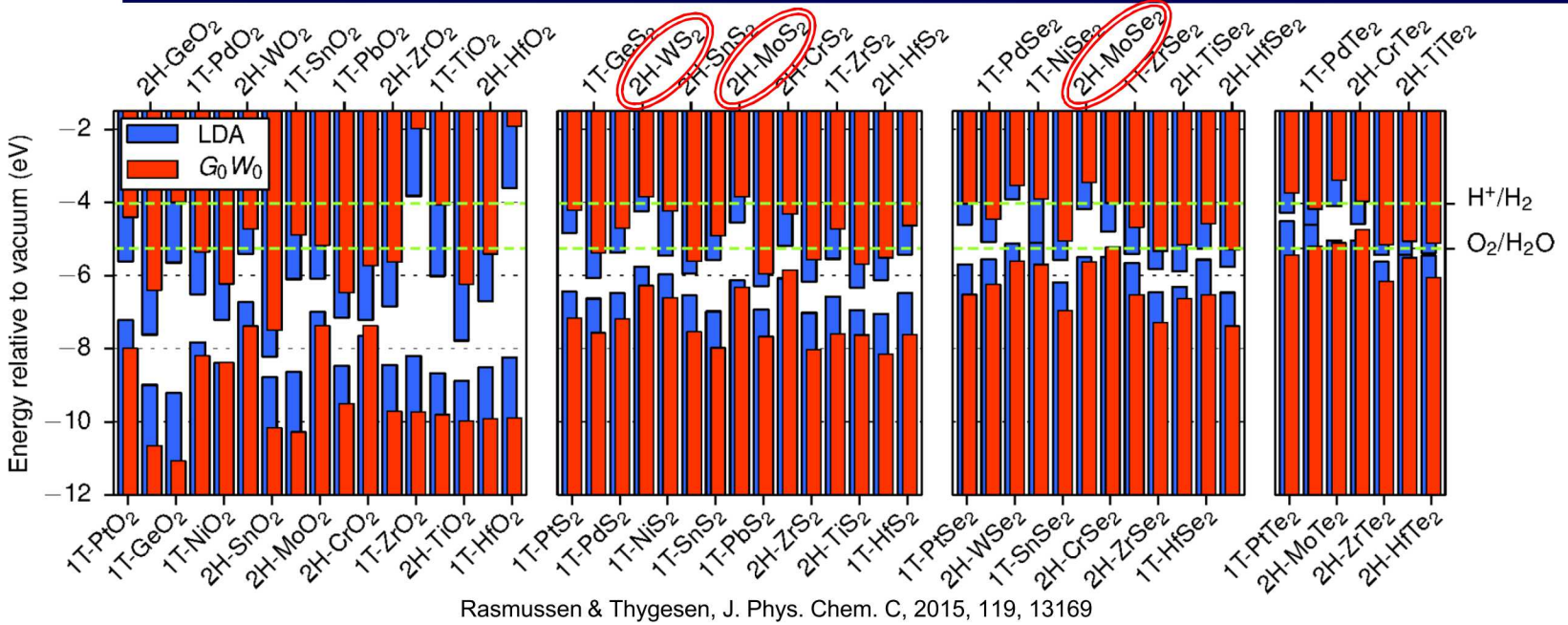




Özçelik, et al., Phys. Rev. B 94, 035125 (2016)

Heterostructures with designed properties can be created using TMDs

Most studies of the ionization energies are based on modeling



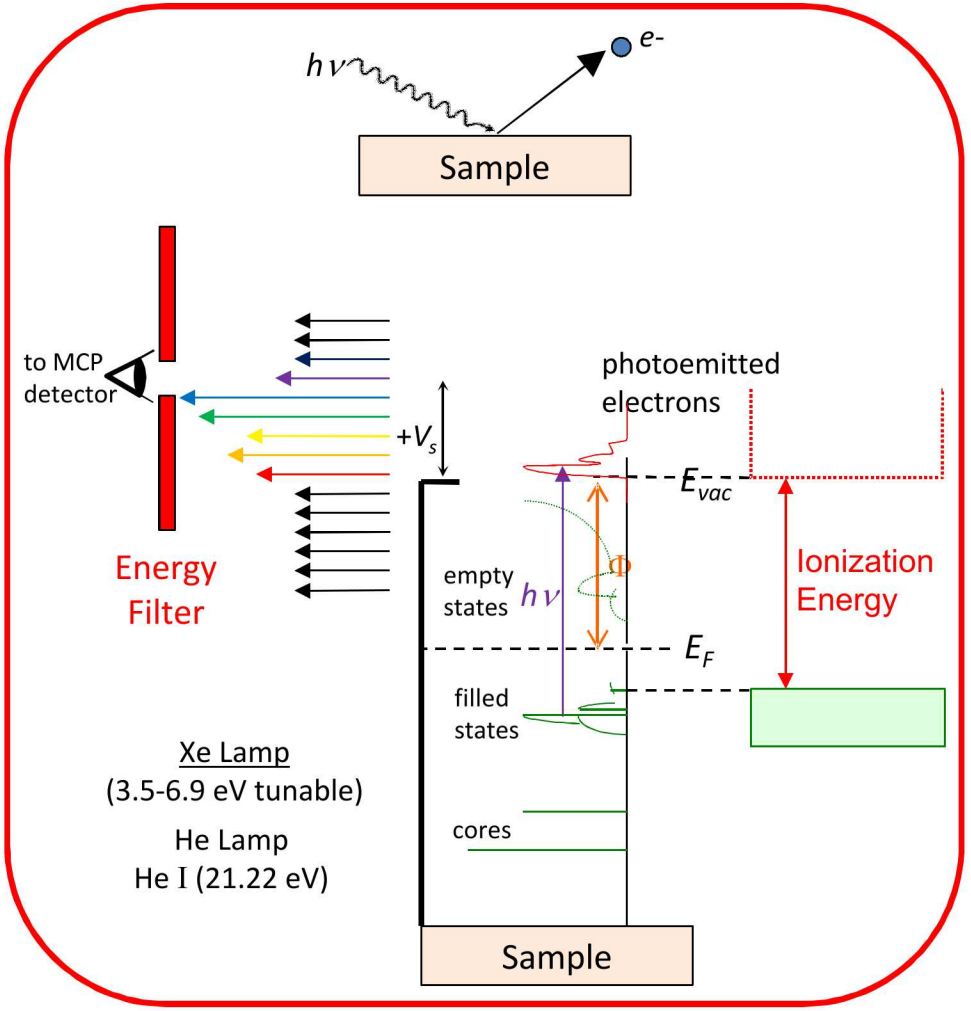
Rasmussen & Thygesen, J. Phys. Chem. C, 2015, 119, 13169

Systematic experimental verification is missing

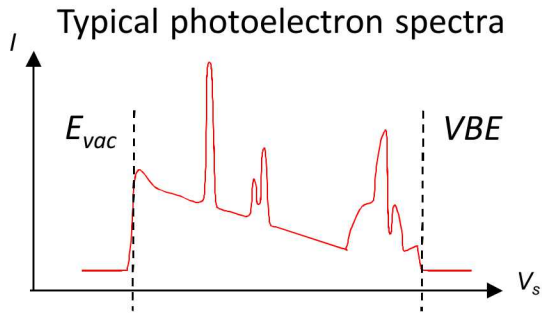
Required (or preferred) characteristics for the experimental approach

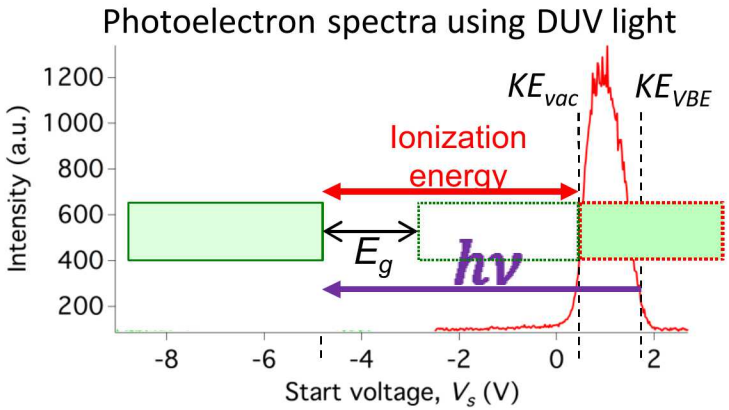
- Microscopy function to locate small specimens (good lateral resolution)
- Environment that has little impact on the sample's electronic properties, i.e. vacuum
- Adequate energy resolution
- No need to add a measurement-specific modification to the sample, i.e. electrical ground

We extract E_{vac} & valence band edge at Brillouin zone center from photoelectron (or photoemission) spectra



Photoemission process





$$BE = KE - h\nu$$

Figure courtesy: M. Berg, C. Chan

We use photoemission microscopy & spectroscopy to evaluate the band alignment

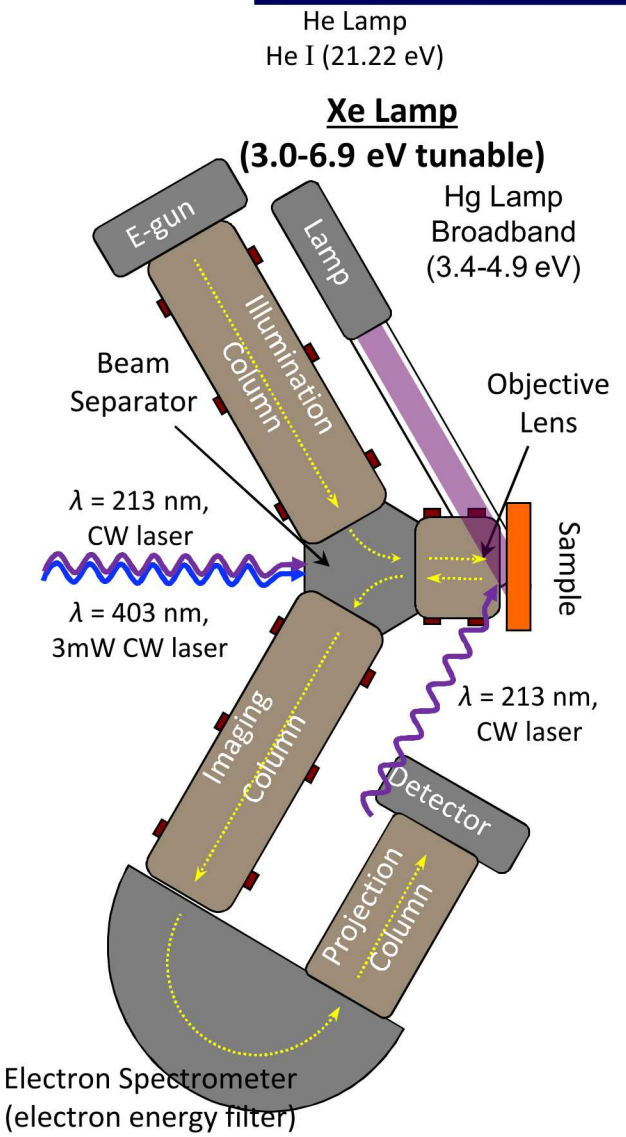
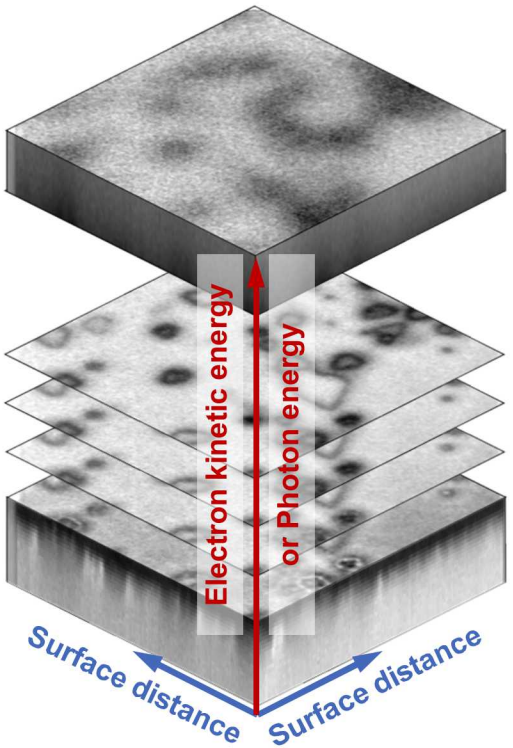
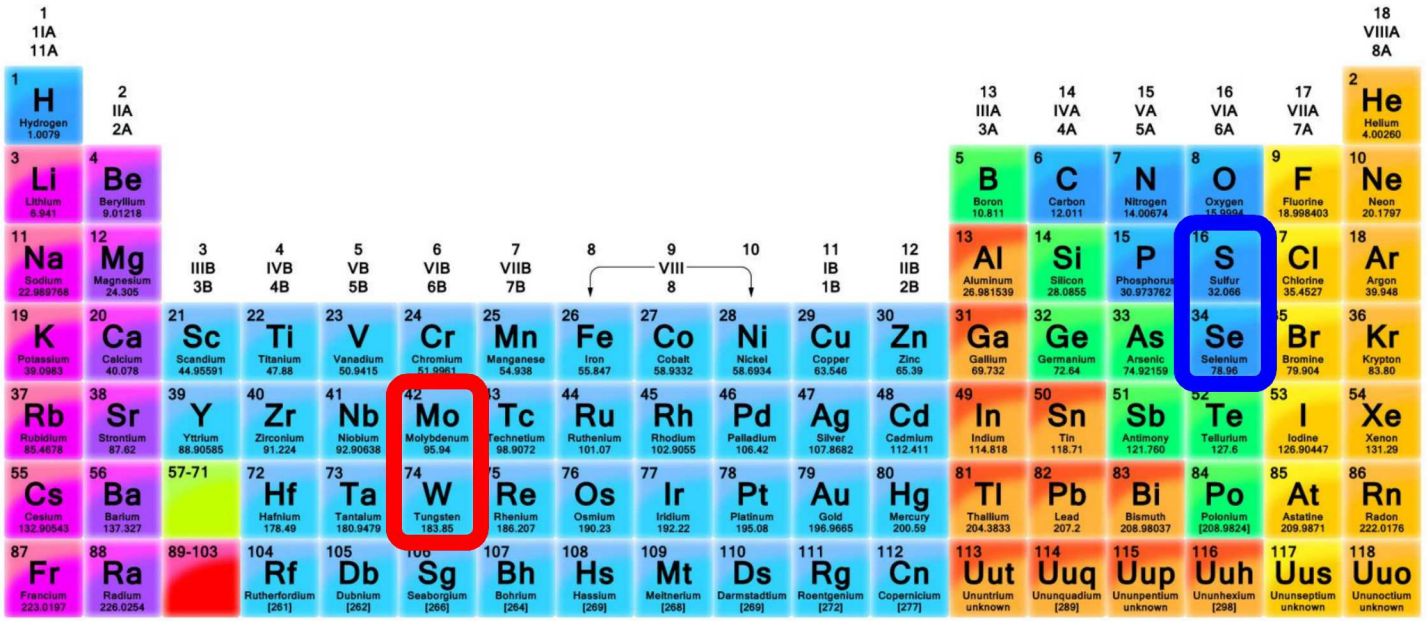


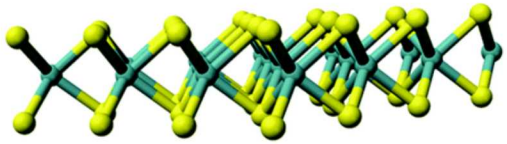
Figure courtesy: M. Berg

- Specifications of the photoemission electron microscope (PEEM)
  - Spatial resolution ~15 – 200nm
  - Energy resolution ~0.2 – 0.5eV
- Deep UV monochromatic light sources are used for the work presented here
  - λ = 180 – 350nm (hv = 3.54 – 6.89eV): tunable-energy photon source based on a Xe-lamp
- Spectrum is extracted from each pixel in the image stack or data cube, and fitted to create maps
- Meet the four required (or preferred) characteristics for systematic measurements

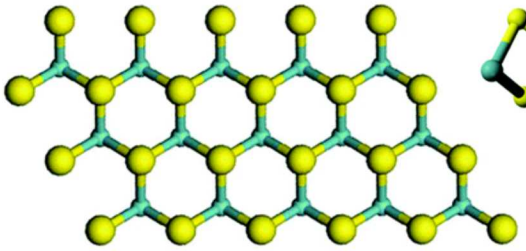


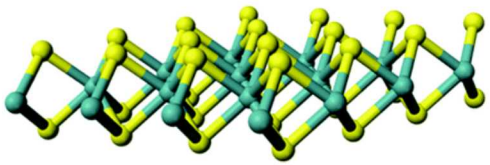
How band alignment changes for isoelectric TMDs

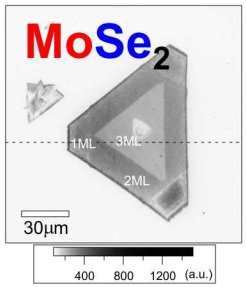


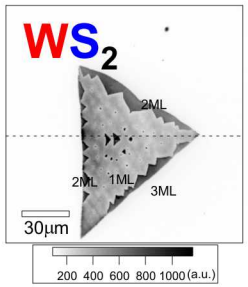


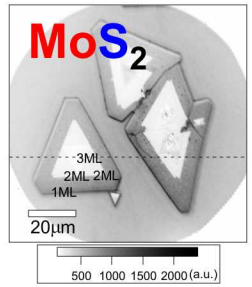
Kang, et al., Appl. Phys. Lett. 102, 012111 (2013)





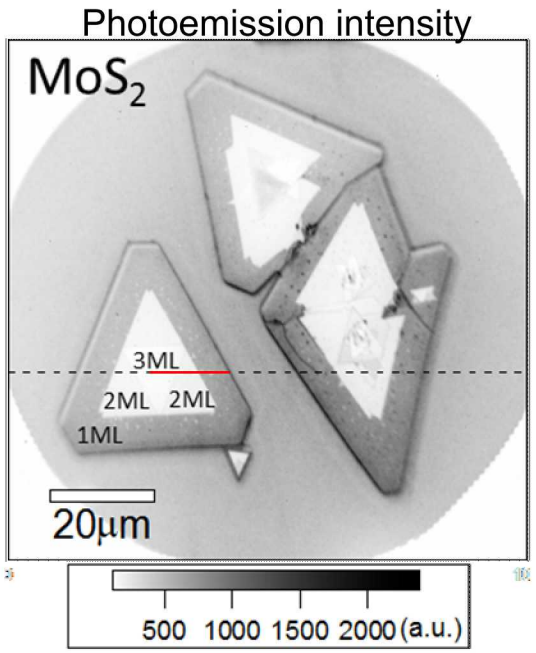


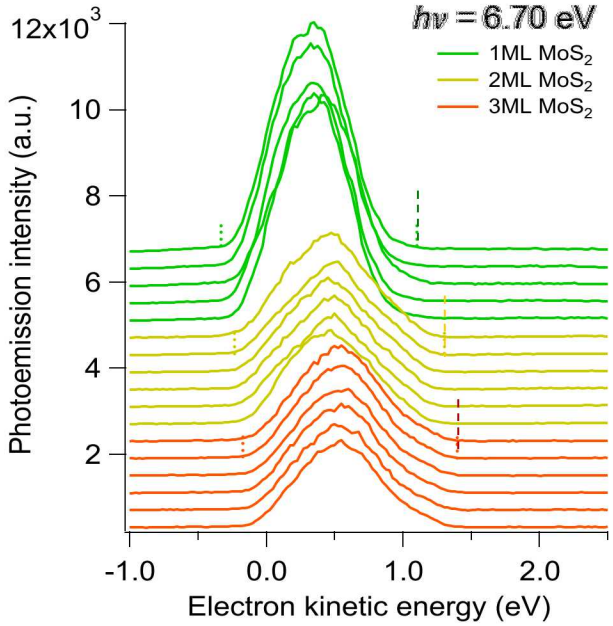


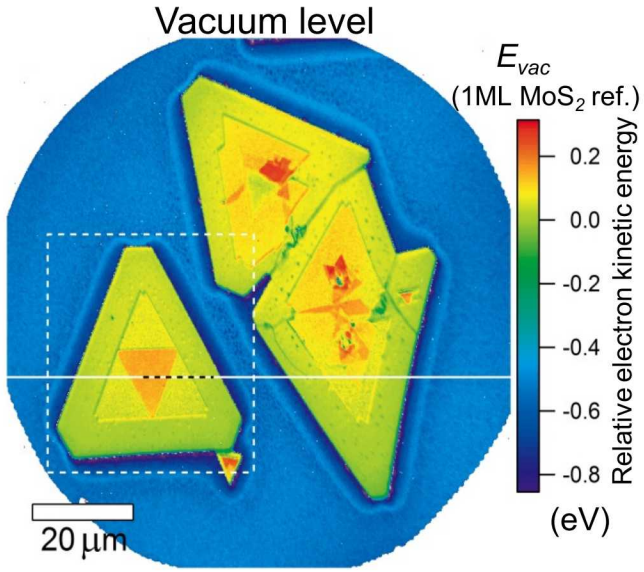


MX_2 M = Mo, W X = S, Se

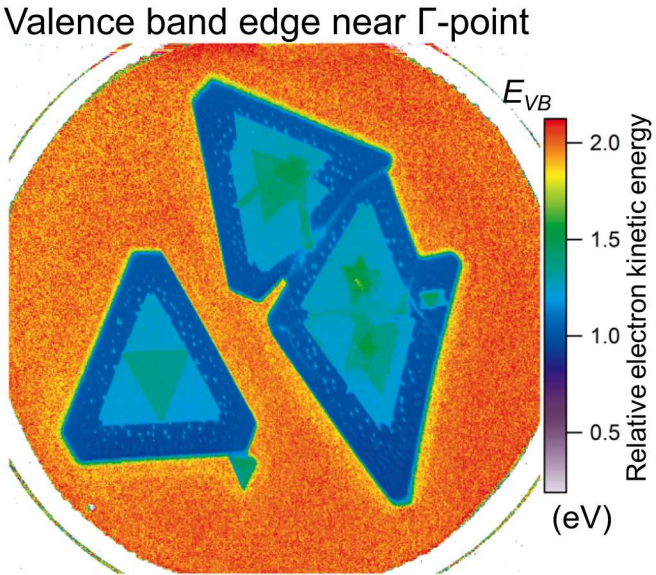
We determine E_{vac} & valence band edge on MoS_2 multi layers





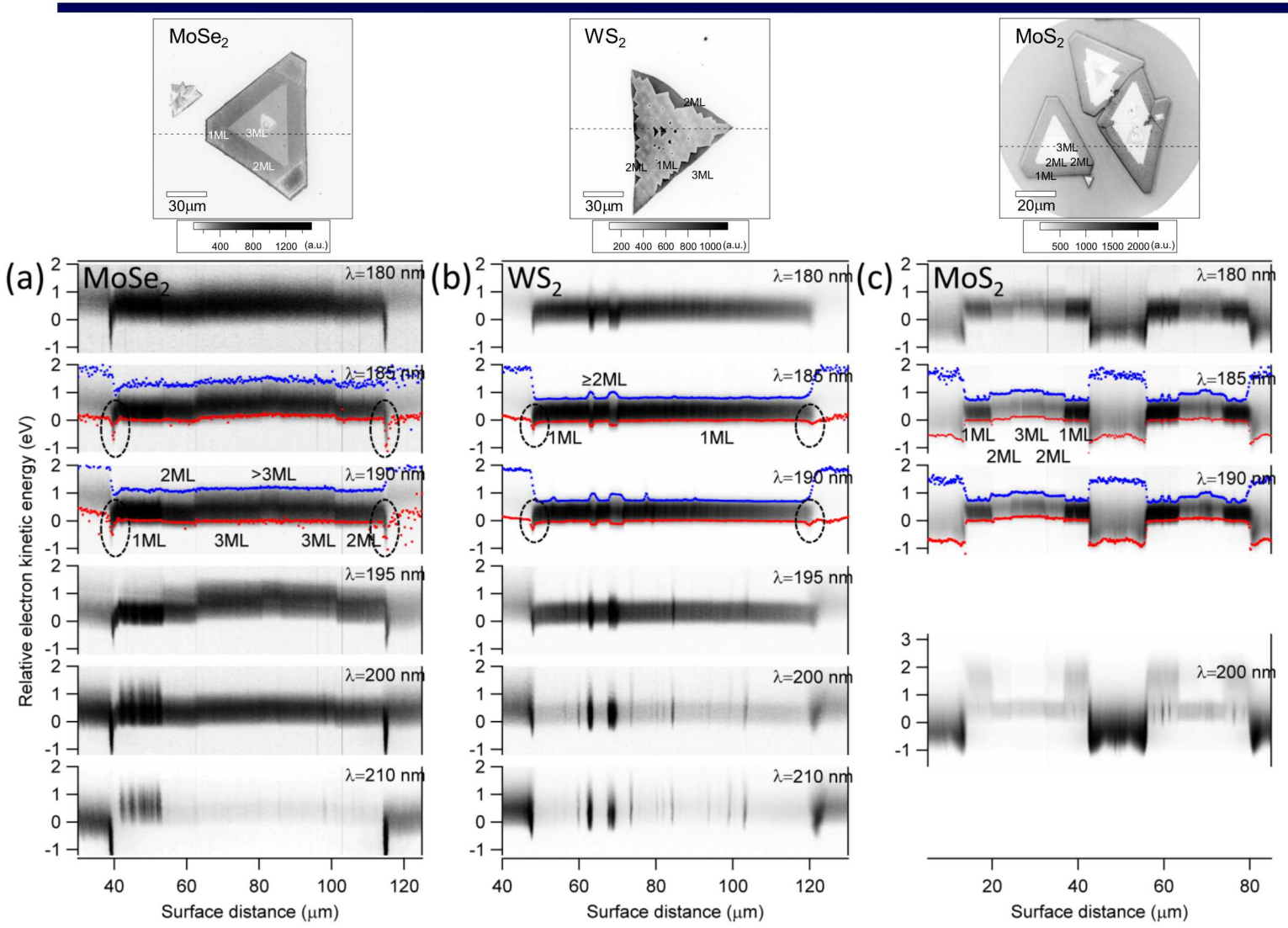


- **Concurrent imaging and spectroscopy**



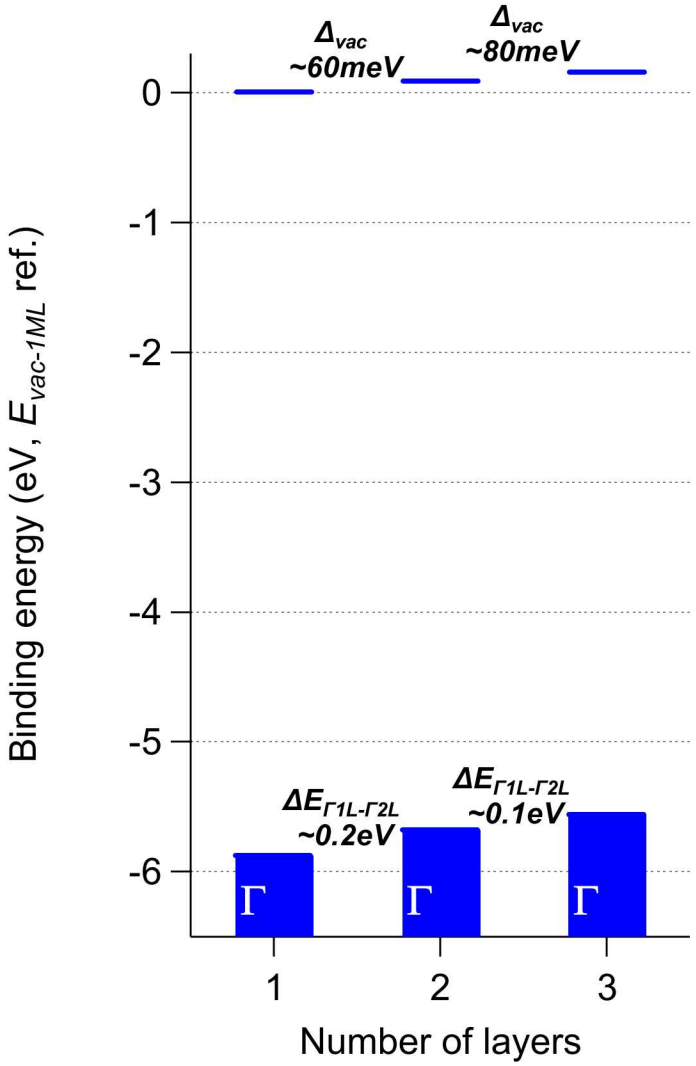
Berg, et al., Layer-Dependence of the Electronic Band Alignment of Few-Layer MoS_2 on SiO_2 Measured Using Photoemission Electron Microscopy, Phys. Rev. B, 95, 235406 (2017)

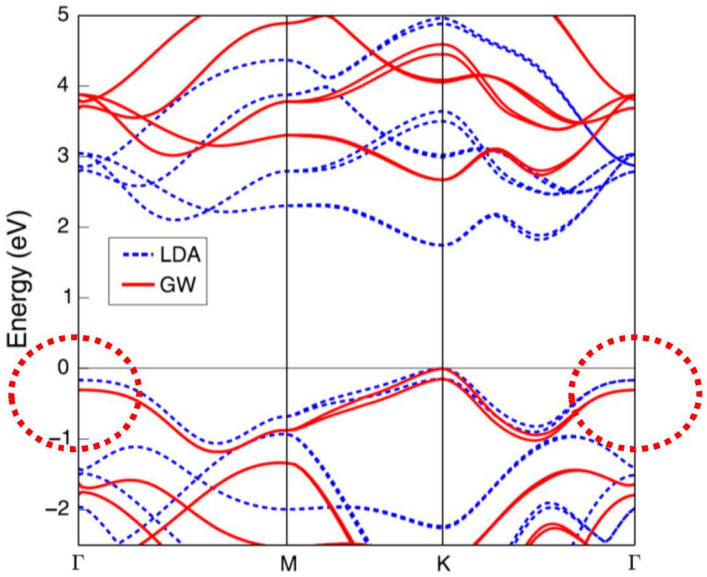
We measure photoemission spectra from $MoSe_2$, WS_2, and MoS_2



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

Hetero-junctions are formed between MoS_2 with different thicknesses





Qiu, et al., Phys. Rev. B 93, 235435 (2016)

- Valence band edge signal comes from near Γ-point due to the limited momentum range accessible by DUV photon-photoemission
- $\Delta E_{\Gamma\text{-}K}$ based on DFT calculation

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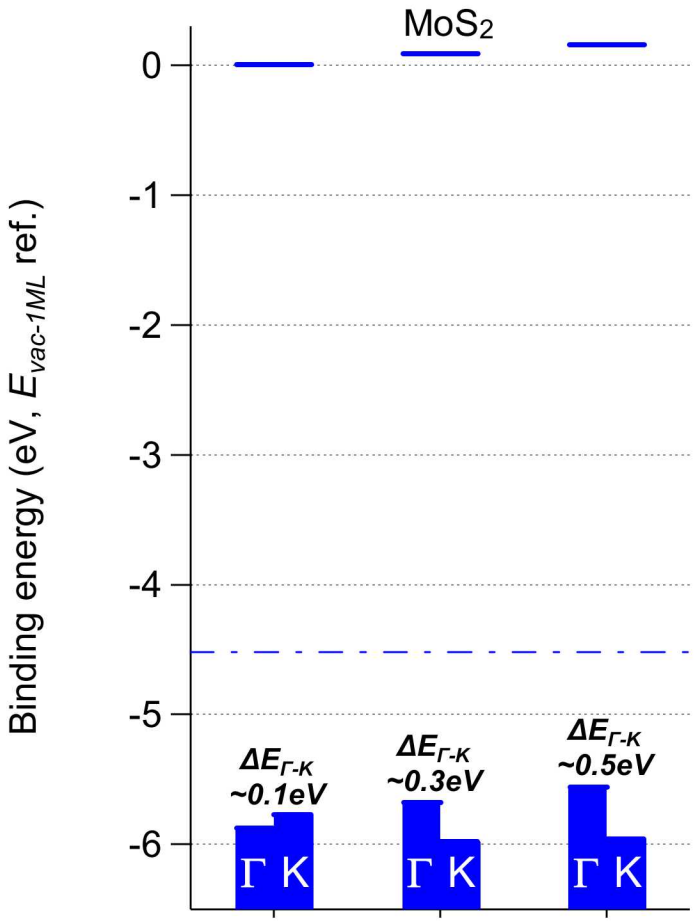

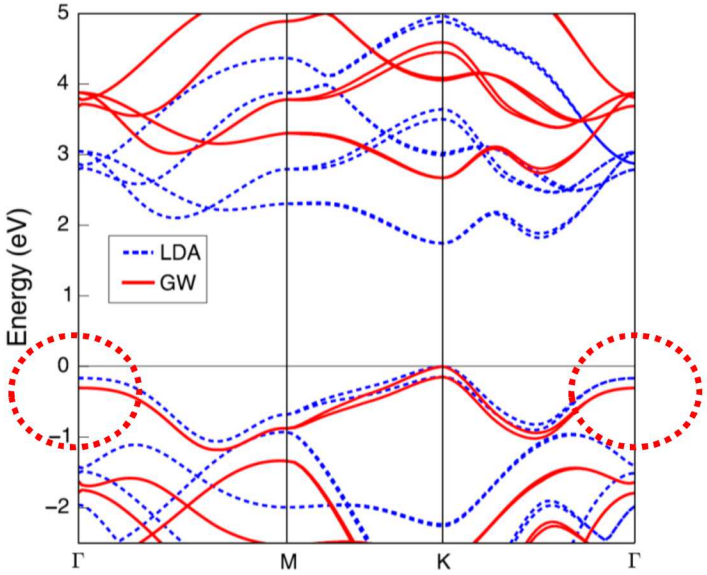

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We compare quasiparticle band gaps of TMDs calculated using GW & determined experimentally

	MoS2 1L	1L w/ doping	1L on SiO2	2L	3L	WS2 1L	1L on SiO2	MoSe2 1L	Exp. Approach
Liang, et al., PRL 114, 063001, 2015	2.66eV	2.18eV							
Ryou et al., Sci Rep, 6, 29184, 2016	2.80eV		2.30eV						
Cheiwchanchamnangij et al., PRB 85, 205302, 2012	2.76eV			1.89eV					
Naik et al., PRB 95, 165125, 2017	2.74eV			2.14eV	1.70eV				
Ramasubramaniam, PRB 86, 115409, 2012	2.82eV					2.88eV		2.41eV	
Qiu et al., PRB 93, 235435, 2016	2.54eV								
Ye et al., Nature 513, 214, 2014						2.70eV			
Liu, et al., PRL, 122, 246803, 2019			2.2eV						TR-ARPES
Rigosi et al., PRB 94, 075440, 2016			2.17eV				2.38eV		STS

- Significant discrepancy between GW and experimental values
- Doped TMD and TMD on dielectrics coincide well

We compare quasiparticle band gaps of TMDs calculated using GW & determined experimentally

	MoS2 1L	1L w/ doping	1L on SiO2	2L	3L	WS2 1L	1L on SiO2	MoSe2 1L	Exp. Approach
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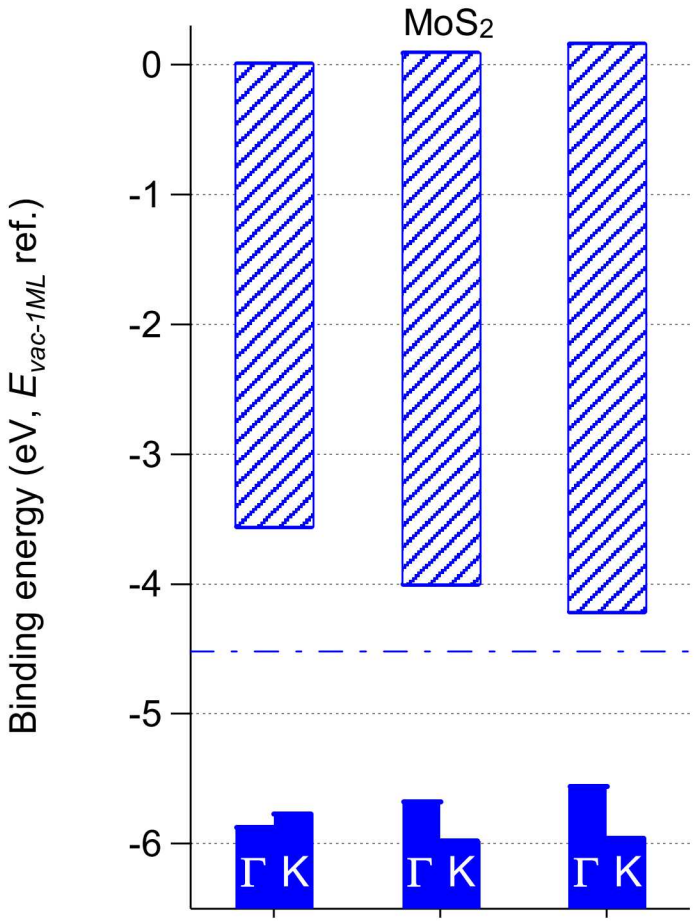
Cheiwchanchamnangij et al., PRB 85, 205302, 2012	2.76eV (2.17)			1.89eV (1.49)					
Naik et al., PRB 95, 165125, 2017	2.74eV (2.17)			2.14eV (1.70)	1.70eV (1.35)				
Ramasubramaniam, PRB 86, 115409, 2012	2.82eV (2.25)					2.88eV (2.30)		2.41eV (1.92)	
Qiu et al., PRB 93, 235435, 2016	2.54eV (2.20)								
Ye et al., Nature 513, 214, 2014						2.70eV (2.34)			
Liu, et al., PRL, 122, 246803, 2019			2.2eV						TR-ARPES
Rigosi et al., PRB 94, 075440, 2016			2.17eV				2.38eV		STS

- Scaling procedure shows better agreement with the experimental result

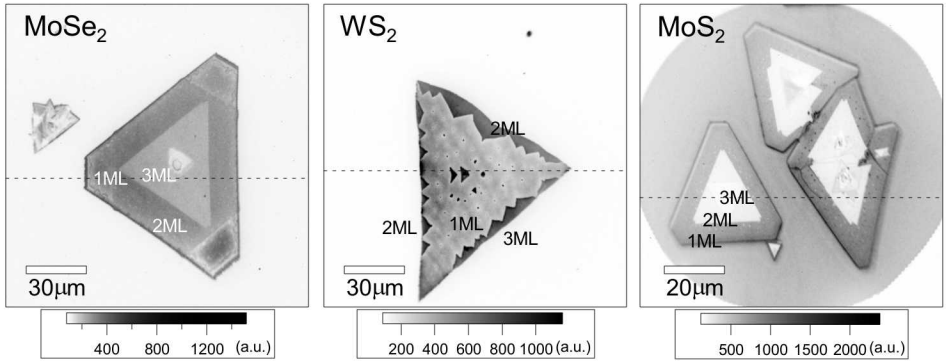
MoS_2 with different thicknesses forms type-I hetero-junctions



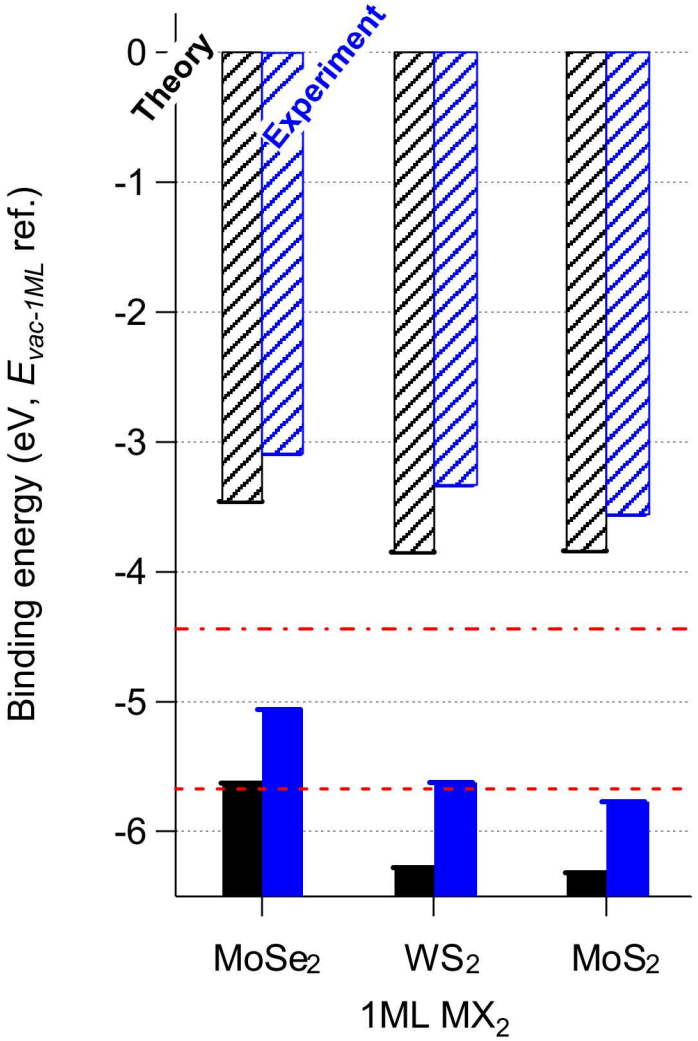
- Type-I band alignments at the junctions between monolayer and bilayer and bilayer and trilayer

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)

Experimentally determined ionization energies match well with those from DFT calculations



- Ionization energy decreases from MoS_2, WS_2, to $MoSe_2$, anticipated from the electronegativities of the constituent atoms
- Good agreement with GW calculation
- Heterostructures containing MoS_2, WS_2, to $MoSe_2$ are likely to display type II alignment

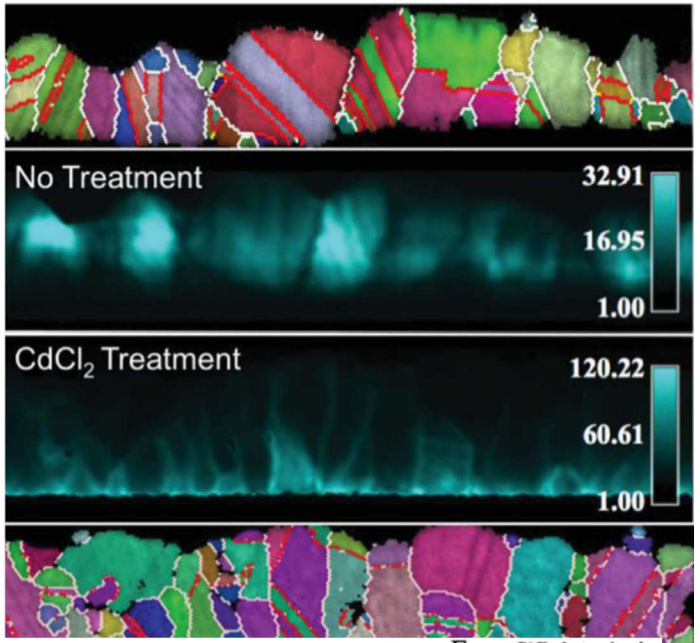


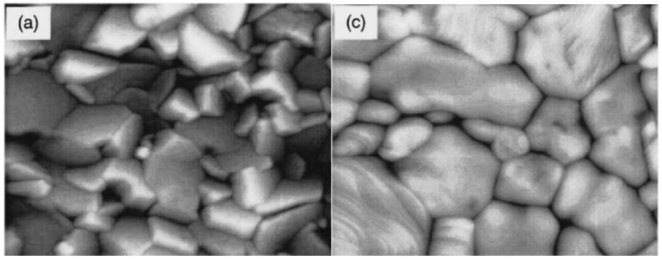
GW Theory: Rasmussen & Thygesen, J. of Phys Chem., 119, 13169, 2015

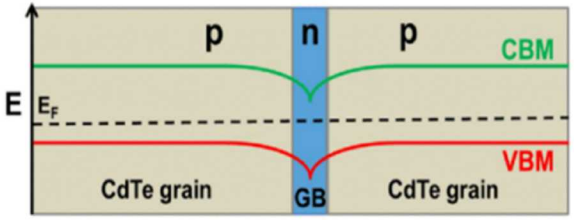
Keyshar, et al., Experimental determination of the ionization energies of MoS_2, WS_2, and $MoSe_2$ on SiO_2 using photoemission electron microscopy, ACS Nano, 11, 8223, 2017

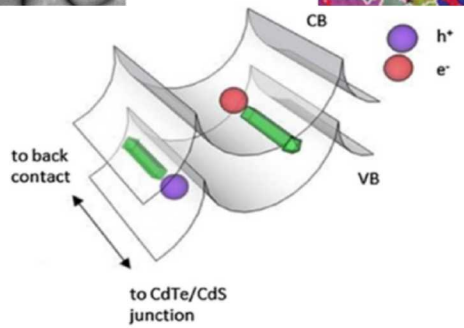
$CdCl_2$ treatment is known to improve the grain size and photovoltaic efficiency of CdTe

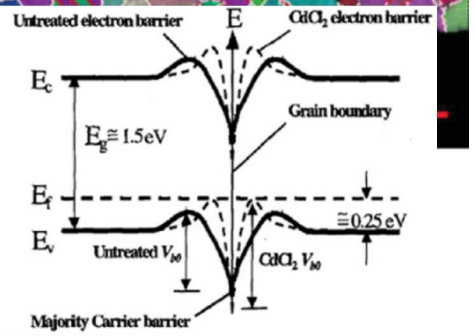
- Polycrystalline cadmium-telluride (CdTe) photovoltaics reaching 21.5% efficiency
  - Serious alternative to silicon-based photovoltaics







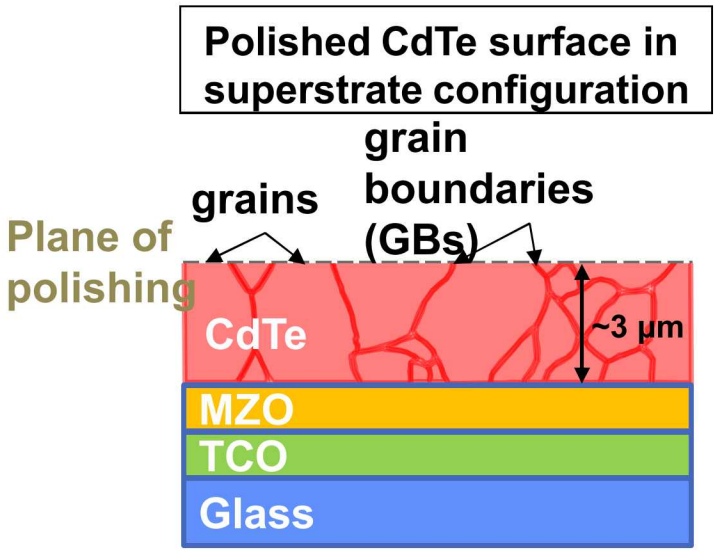




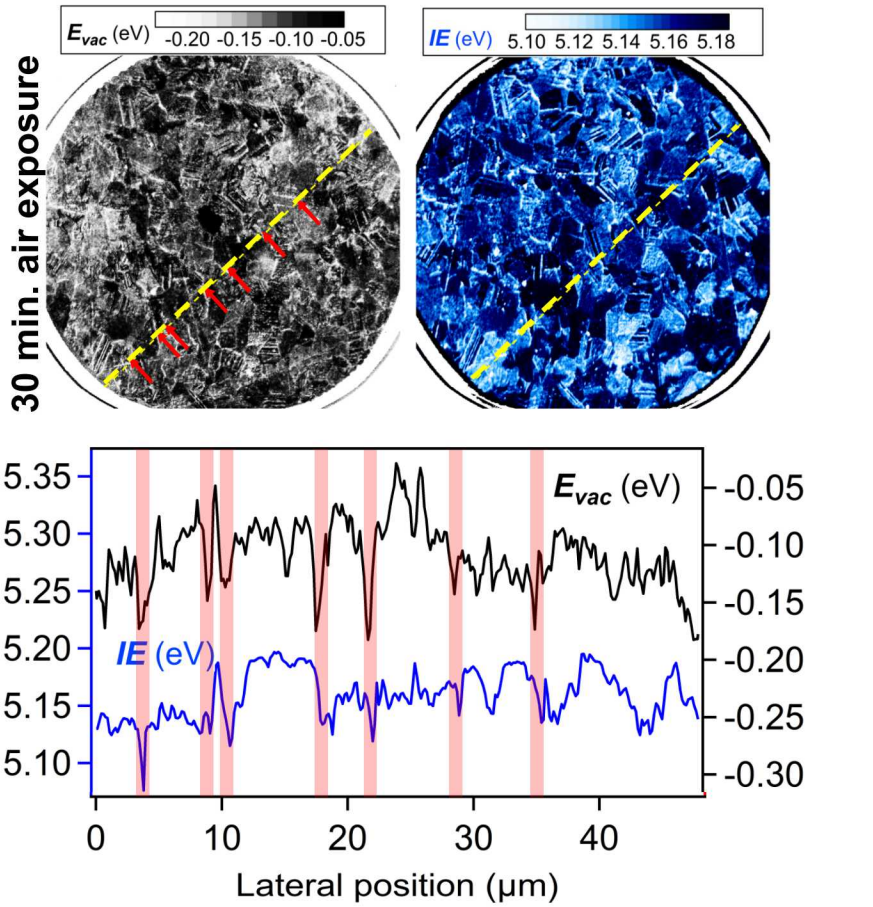
No direct evaluation of the electronic structure of grain interior vs grain boundaries

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

Maps of E_{vac} & *IE* elucidate complex band alignment between grain boundaries (GB) & grain interiors



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



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

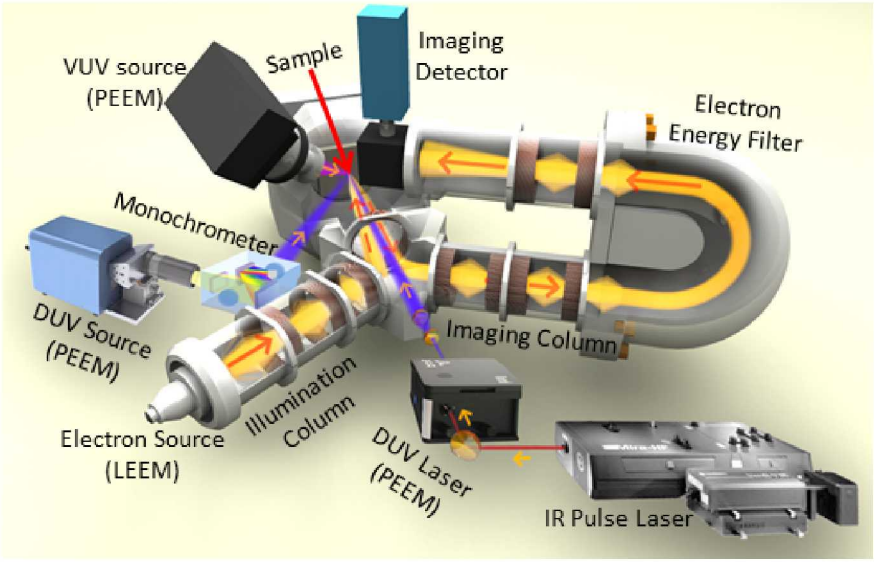
Berg, et al., ACS Applied Materials & Interfaces, 10, 9817 (2018)

Mixture of **electrostatic rigid band shift** & **something else** at GB

Not a simple picture

Summary

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



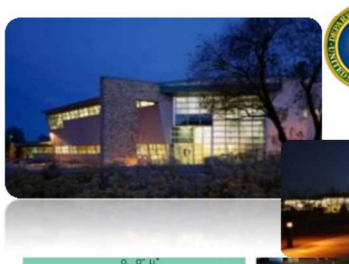
  - Other examples:
    - Graphene multilayers: Robinson, et al., Scientific Reports 8, 2006 (2018)
    - Polycrystalline metal films: Berg, Bussmann, et al., in preparation

Acknowledgements

- TMDs: Kunttal Keyshar
  - Mohite group, Los Alamos National Lab.
  - Ajayan group, Rice Univ.
  - Berg, Beechem, Chan, Sandia National Labs.
- CdTe: Morgann Berg
  - Berg & Chan, Sandia National Labs.
  - Kephart & Sampath, Colorado State Univ.
- Financial support:
  - CINT, US DOE Office of Science (DE-AC04-94AL85000)
  - US DOE EERE SunShot Initiative (BRIDGE, DE-FOA-0000654 CPS25859)
  - Sandia LDRD

Center for Integrated Nanotechnologies

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



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

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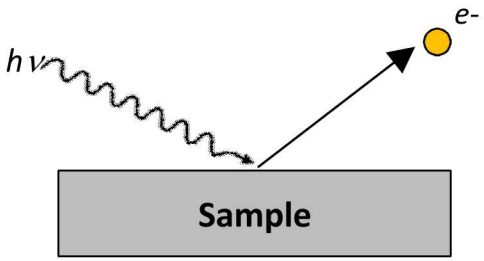
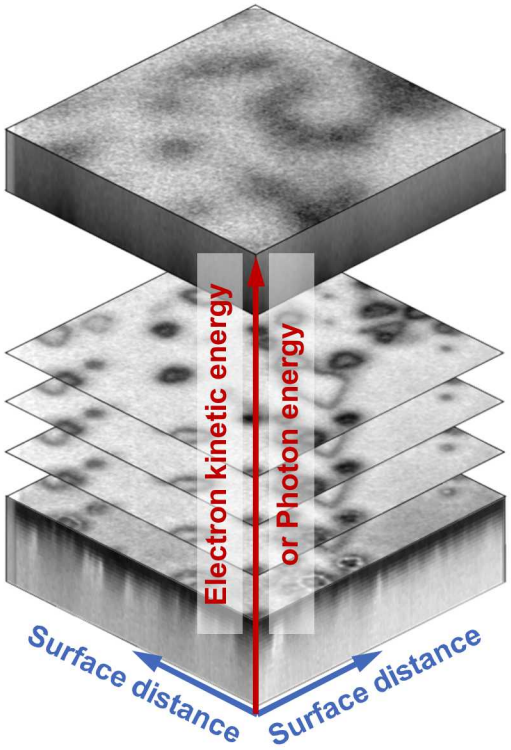
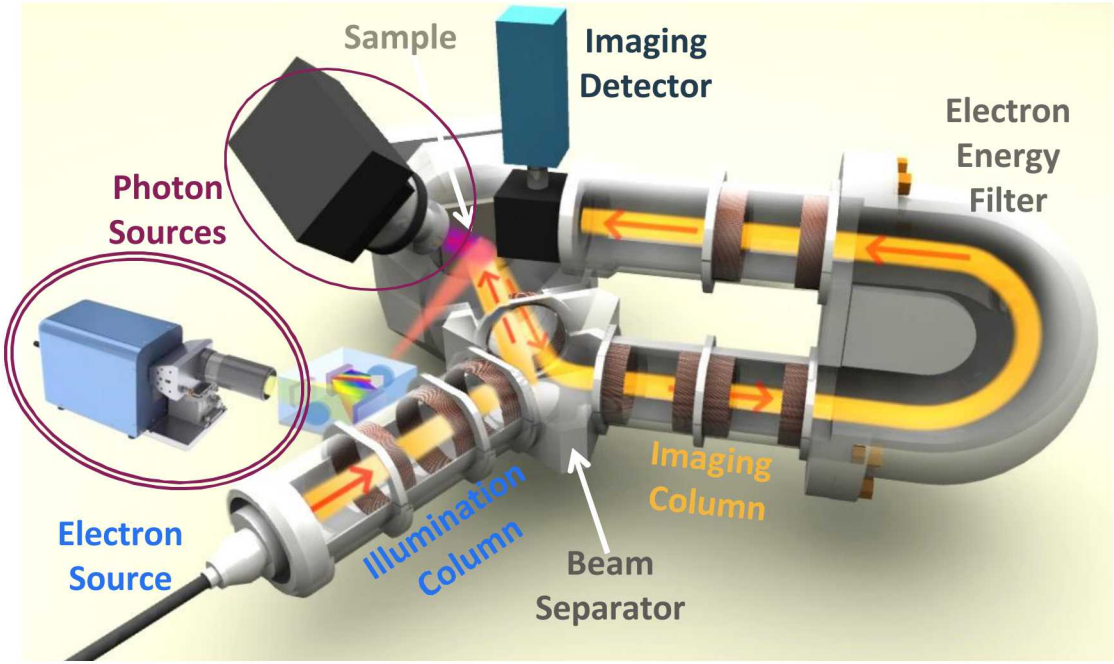
Text

Text

We use photoemission microscopy to map the band alignment



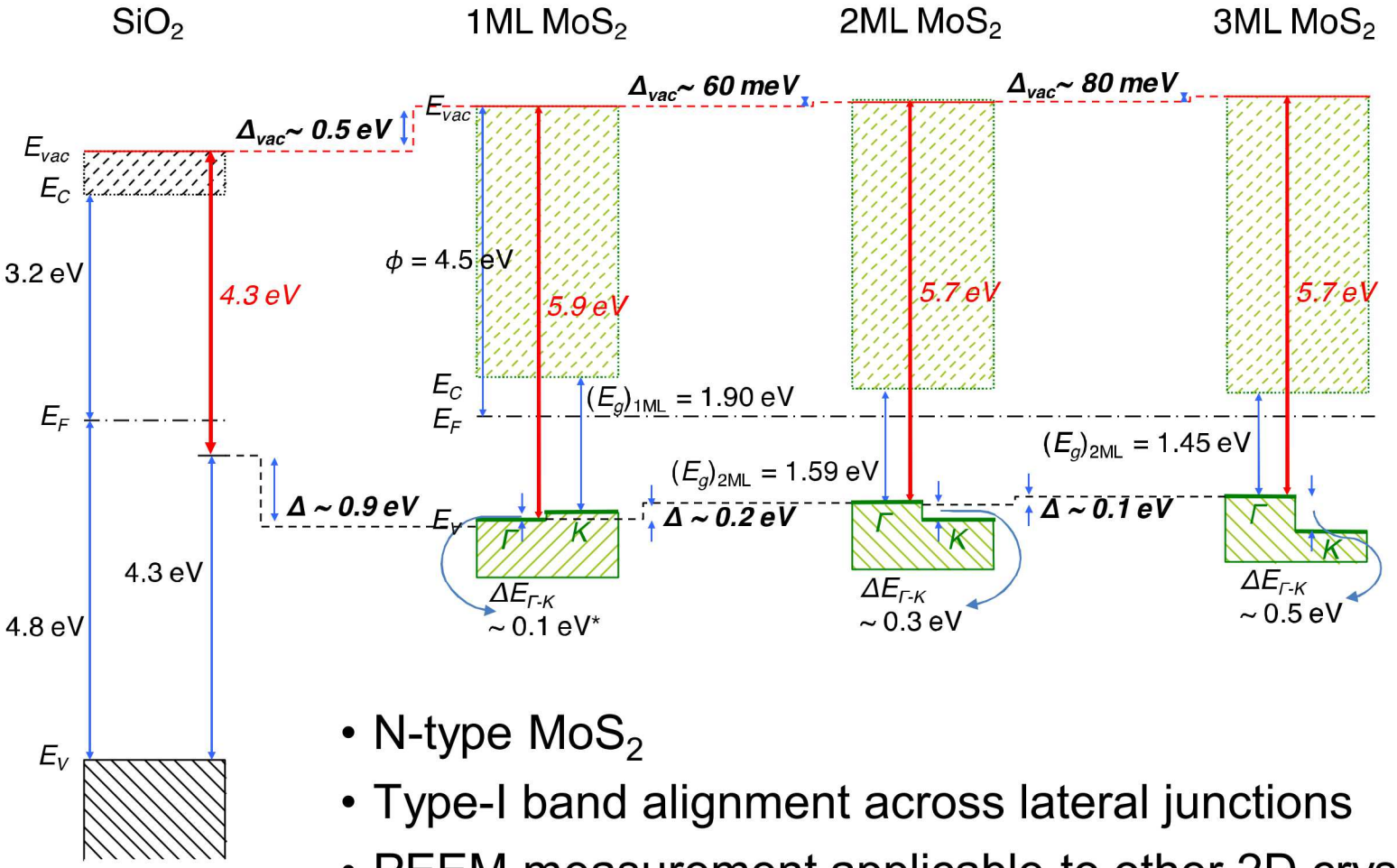




- Monochromatic light sources combined with an electron energy filter in photoemission electron microscopy (PEEM) to acquire electron spectra
  - Spatial resolution ~50 – 200nm
  - Energy resolution ~0.2 – 0.5eV
- Deep UV CW source is used for the work presented here
  - λ = 180 – 350nm (hv = 3.54 –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

Figure courtesy: C. Chan

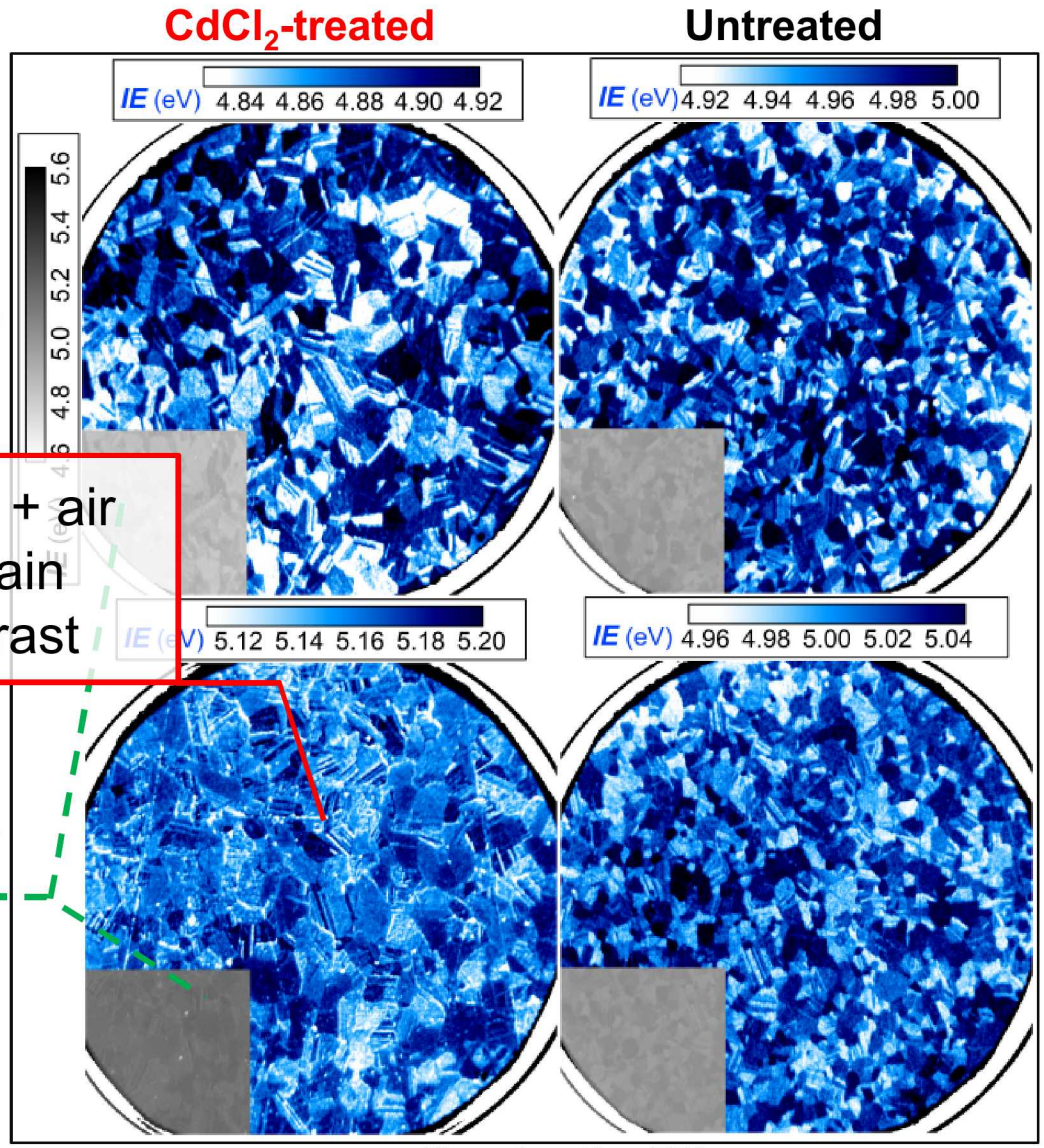
Type I junctions forms between MoS_2 with different thicknesses



- 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)

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

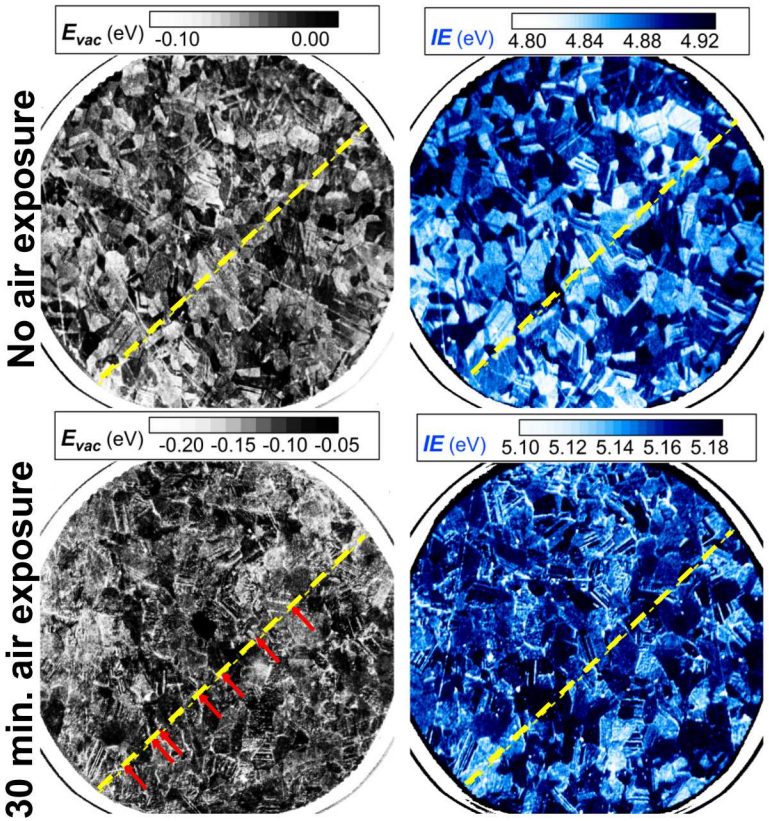


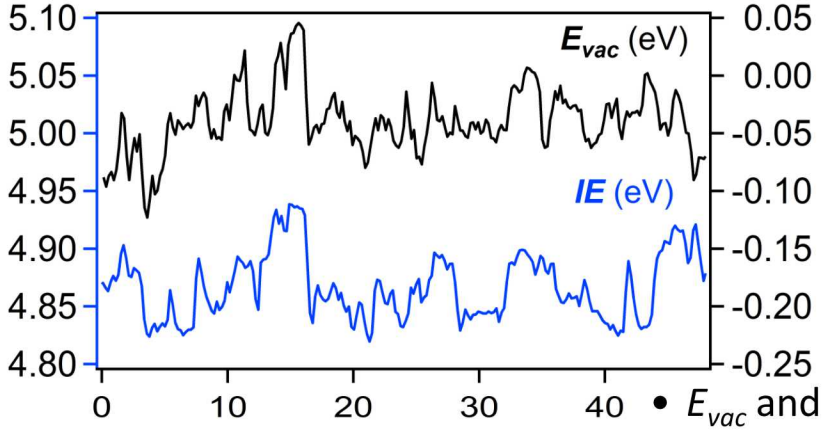
$CdCl_2$ treatment + air exposure = grain boundary contrast

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

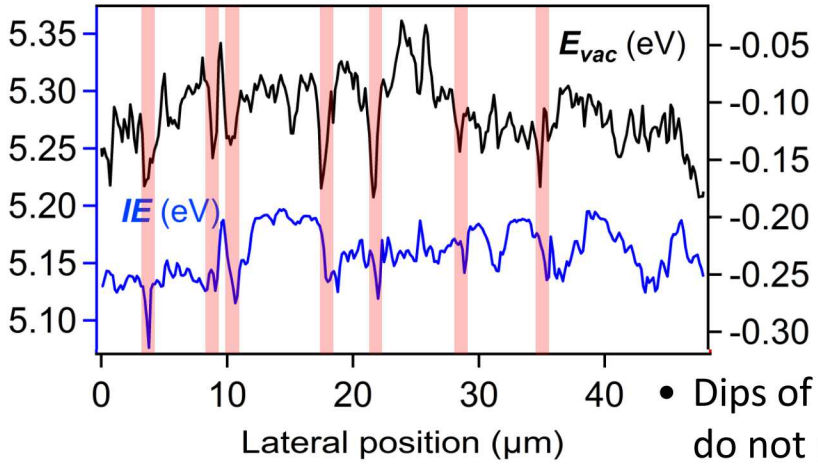
All maps have 48 μm FOV

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



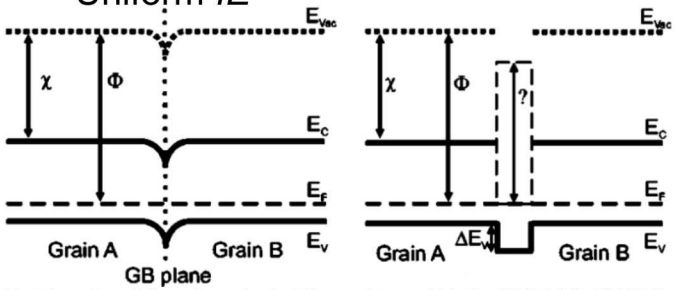


- E_{vac} and *IE* closely match



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

Uniform *IE*



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

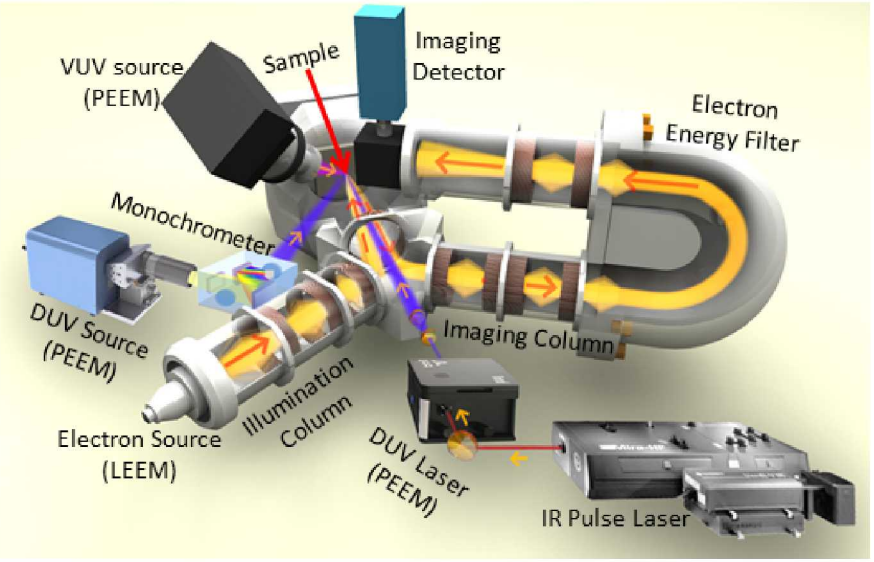
Conclusions

- 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

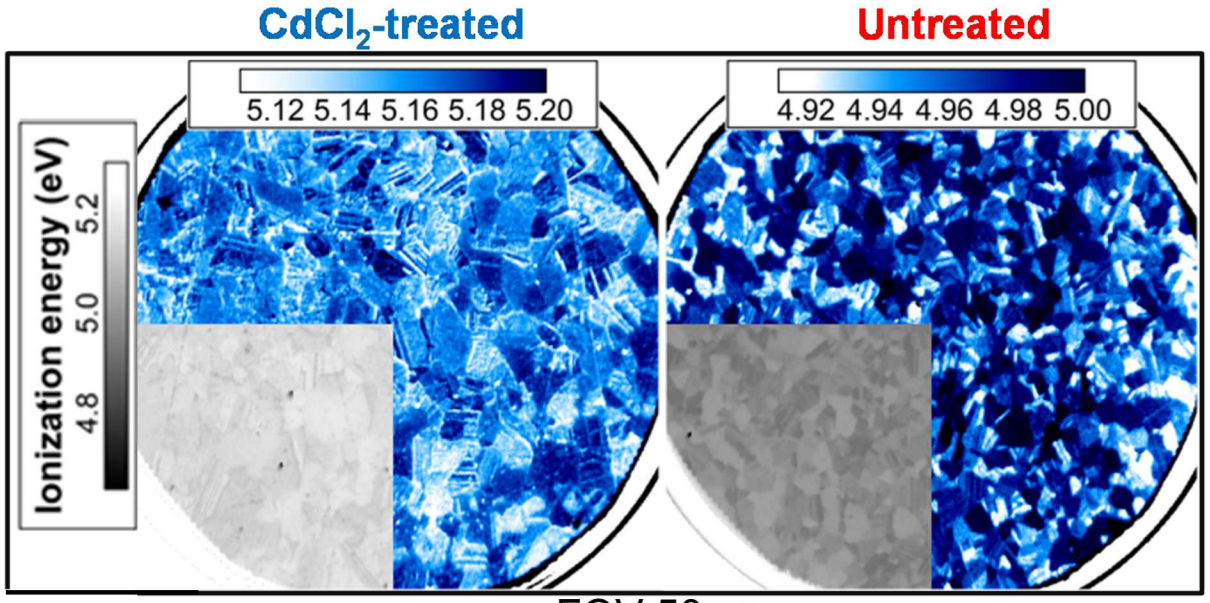
Knowledge of the band alignment enables us to predict the properties of heterostructures

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

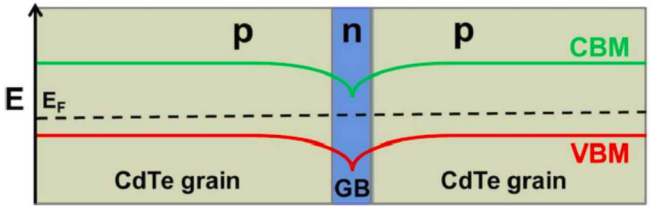
Visualization of the electronic structure variation in inhomogeneous semiconductor



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., in preparation (2017)