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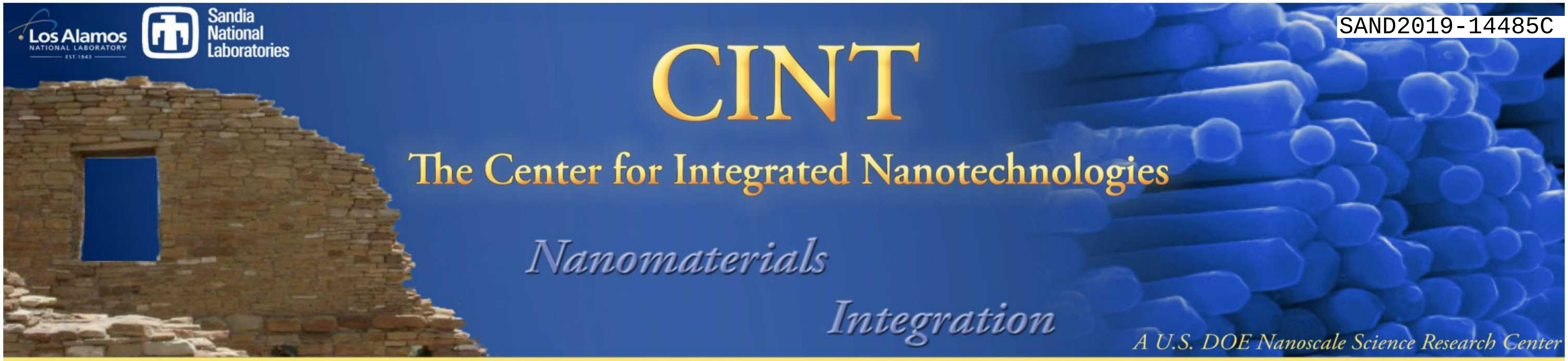

Experimental Determination of the Ionization Energies of $MoSe_2$, WS_2, and MoS_2 Using Photoemission Electron Microscopy

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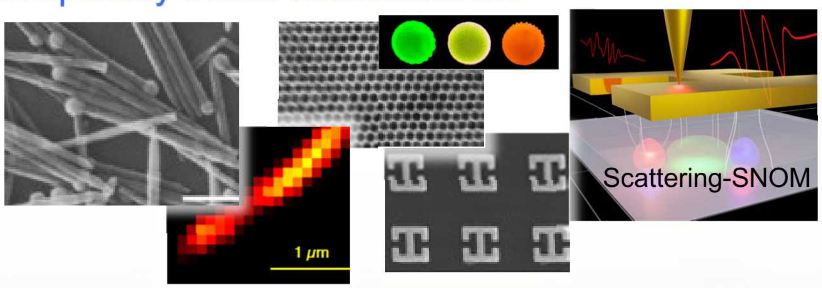
CINT is a DOE user facility with focuses on Nano Science & Nano Integration

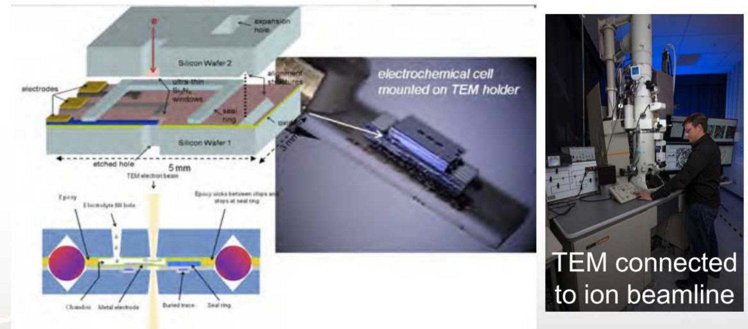
Nanophotonics & Optical Nanomaterials (NPON)

Synthesis, excitation, and energy transformations of optically active nanomaterials



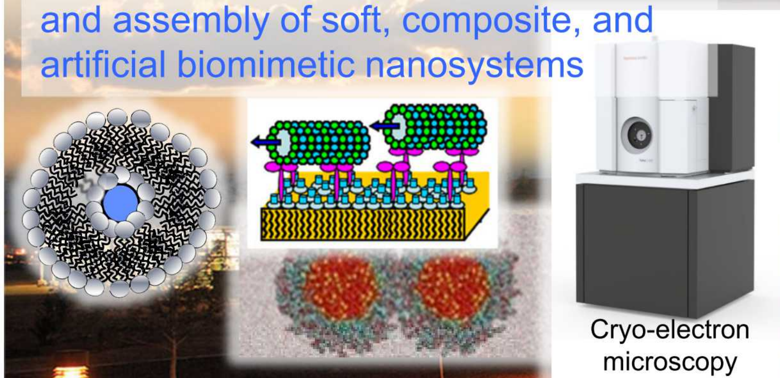
In-situ Characterization and Nanomechanics

Developing capabilities to study the dynamic response of materials and nanosystems to mechanical, electrical, or other stimuli



Soft, Biological, & Composite Nanomaterials (SBCN)

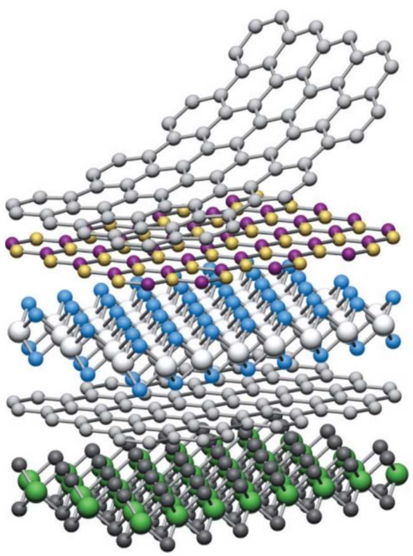
Solution-based nanomaterials synthesis and assembly of soft, composite, and artificial biomimetic nanosystems

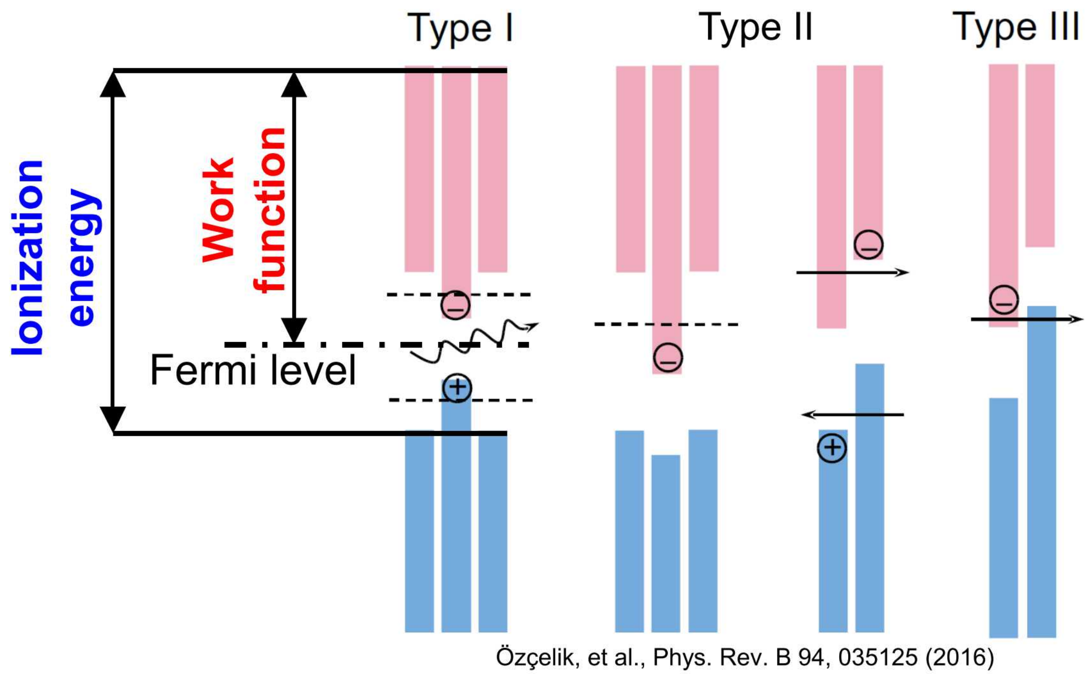


Quantum Materials

Understanding and designing nanomaterials to create new functionalities based on quantum effects that span multiple length scales (from nm to mm)

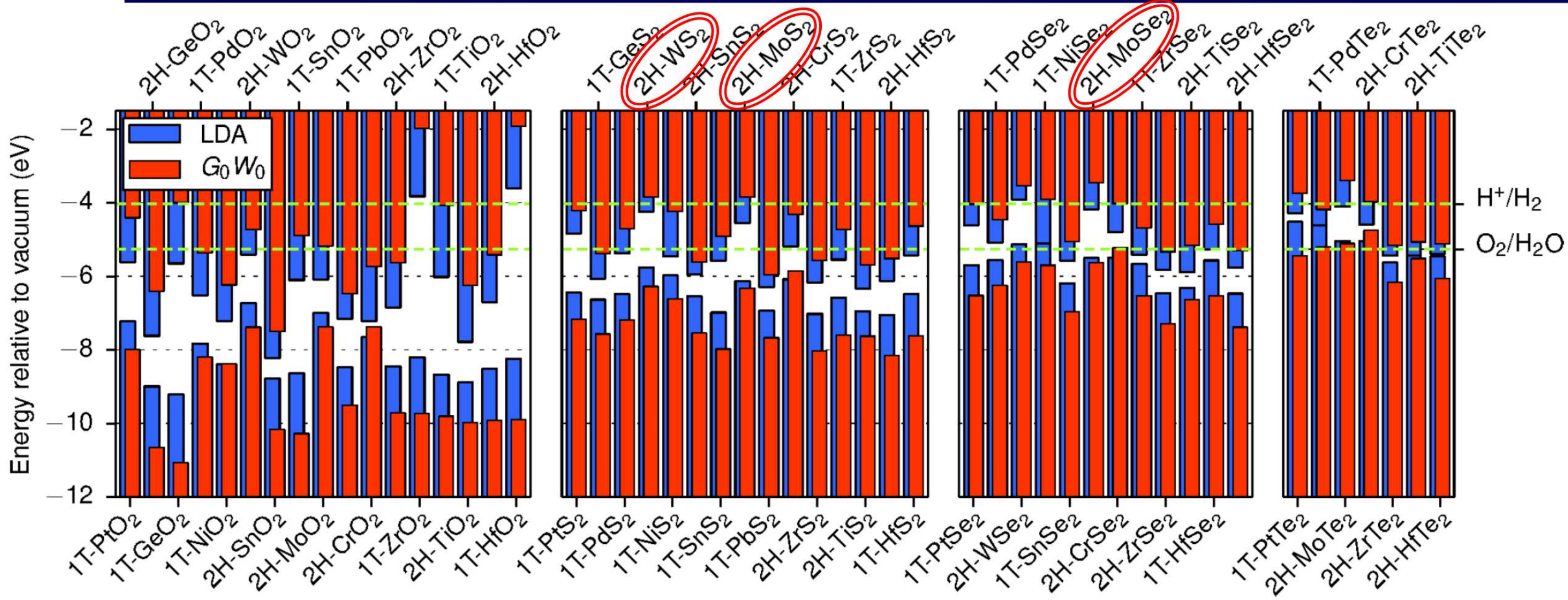
Band alignment of transition metal dichalcogenide dictates the properties of TMD heterostructures





TMDs are ideal platforms to create heterostructures with designed properties

Most studies of the ionization energies are based on modeling



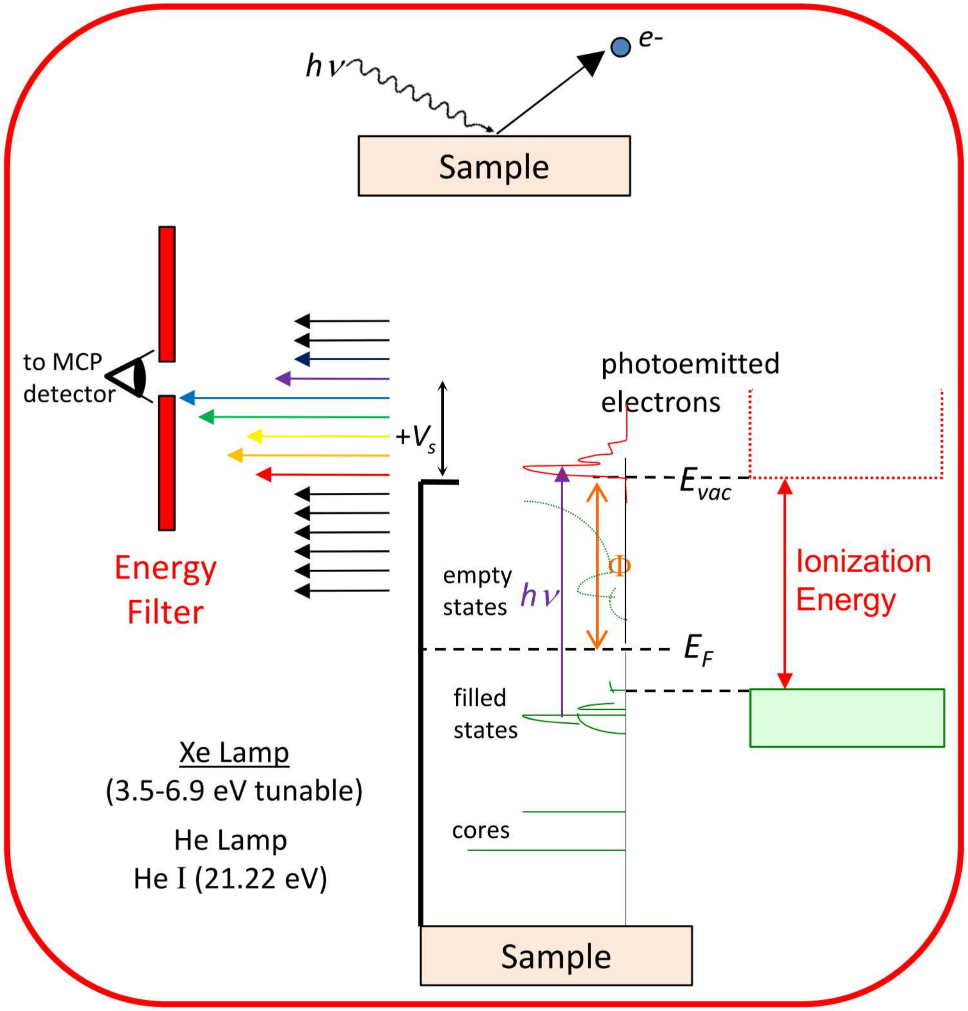
Rasmussen & Thygesen, J. Phys. Chem. C, 2015, 119, 13169

Systematic experimental verification is missing

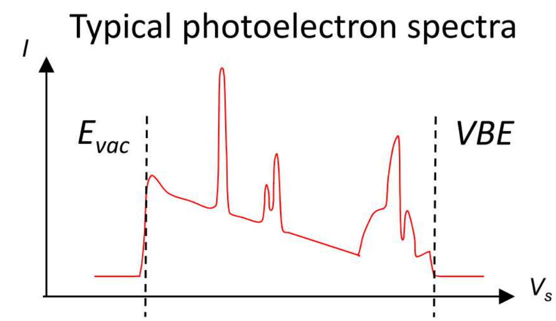
Required (or preferred) characteristics for the experimental approach

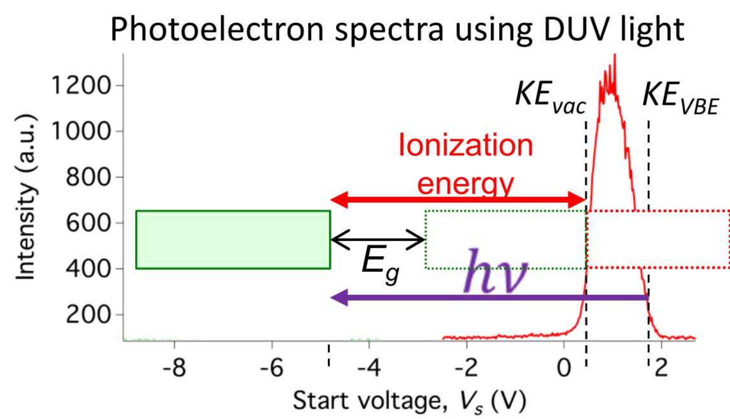
- Microscopy function to locate small specimens (good lateral resolution)
- Environment that has little impact on the sample's electronic properties, i.e. vacuum
- Adequate energy resolution
- No need to add a measurement-specific modification to the sample, i.e. electrical ground

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

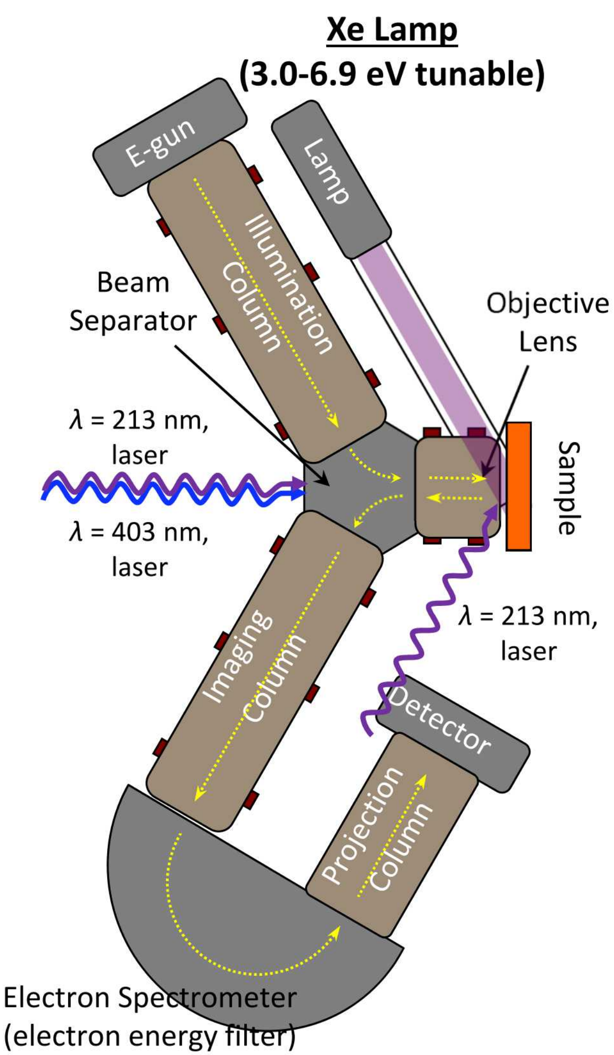
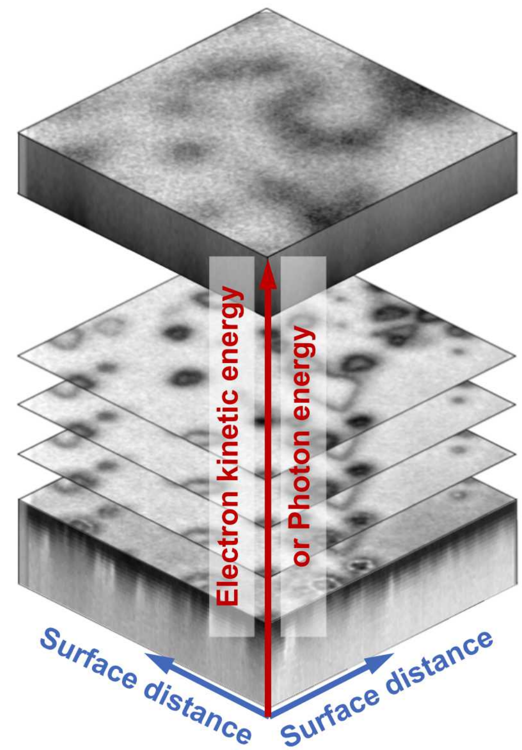
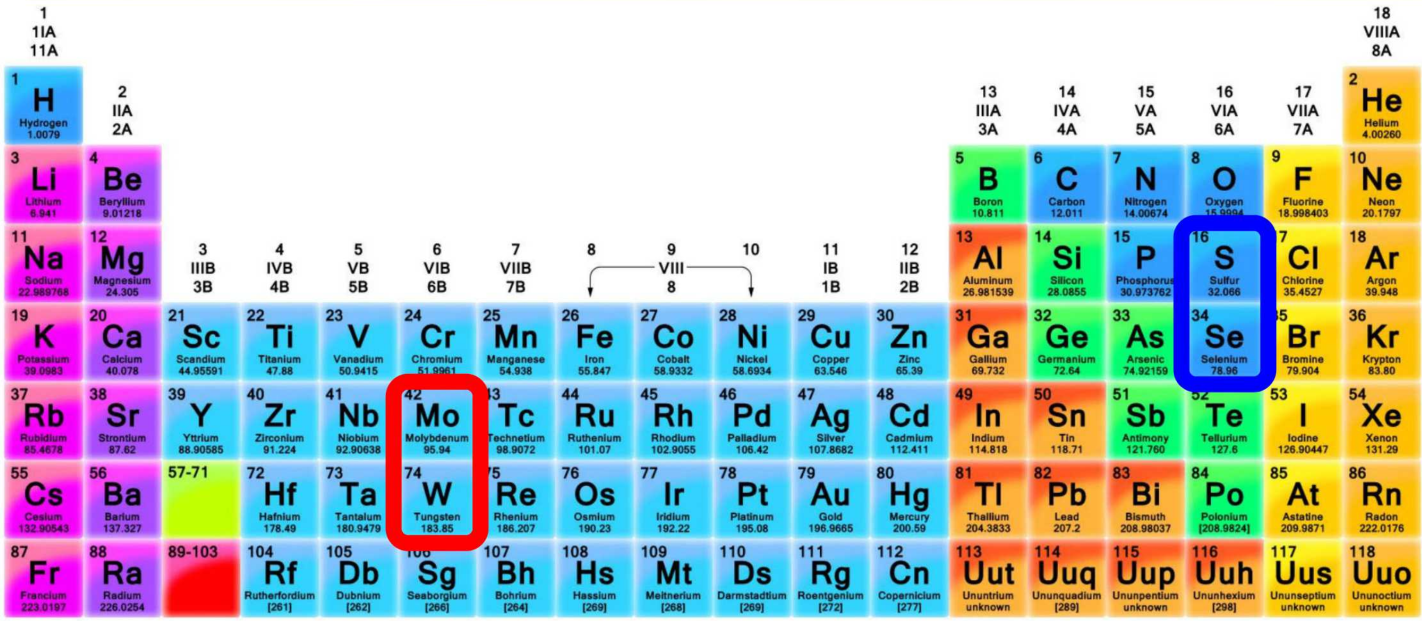


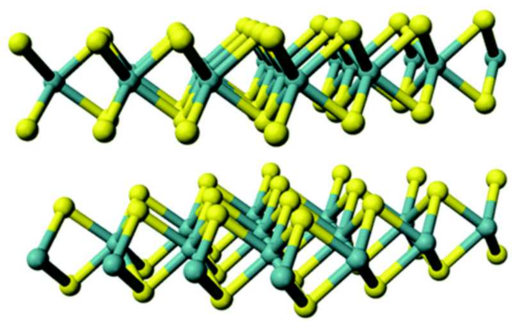
Figure courtesy: M. Berg

- 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

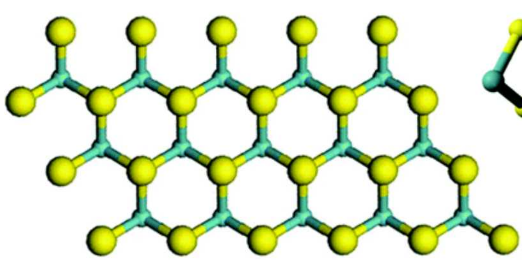


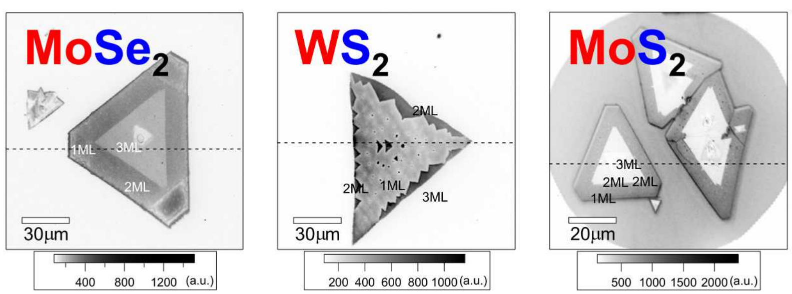
How band alignment changes for isoelectric TMDs





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

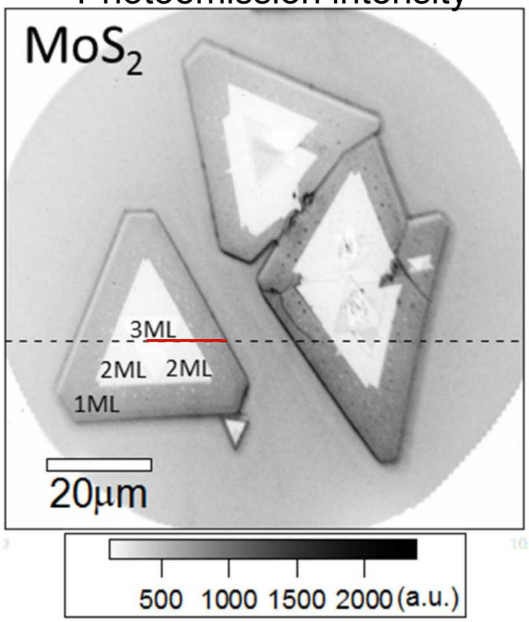


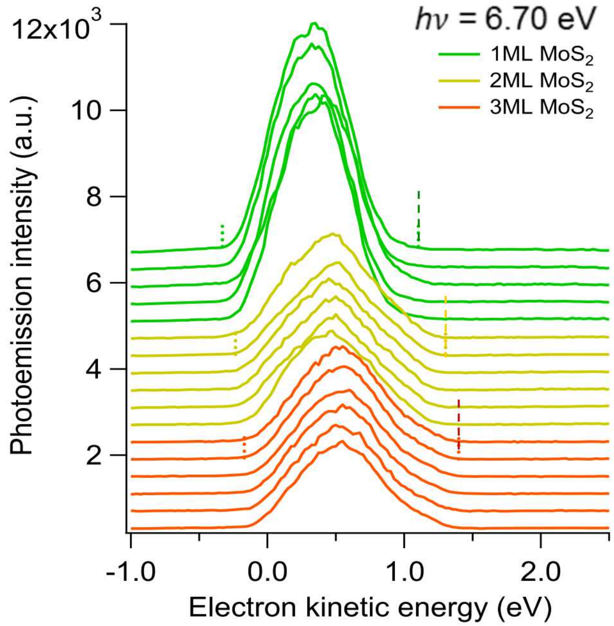


$\mathbf{MX_2}$ M = Mo, W X = S, Se

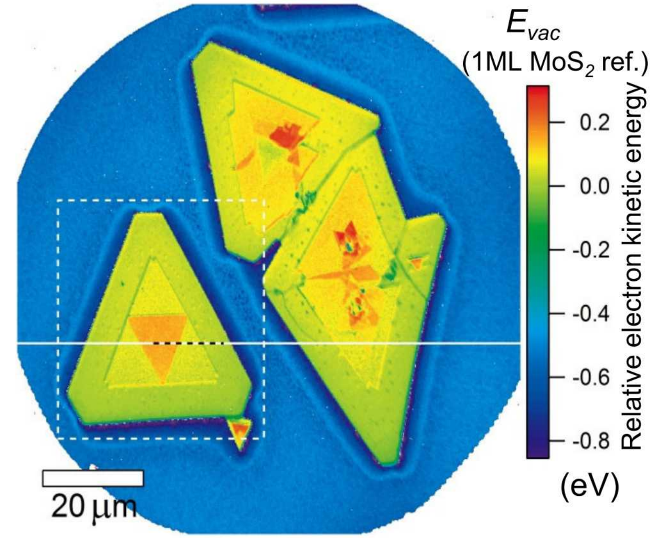
We determine E_{vac} & valence band edge on MoS_2 multi layers

Photoemission intensity

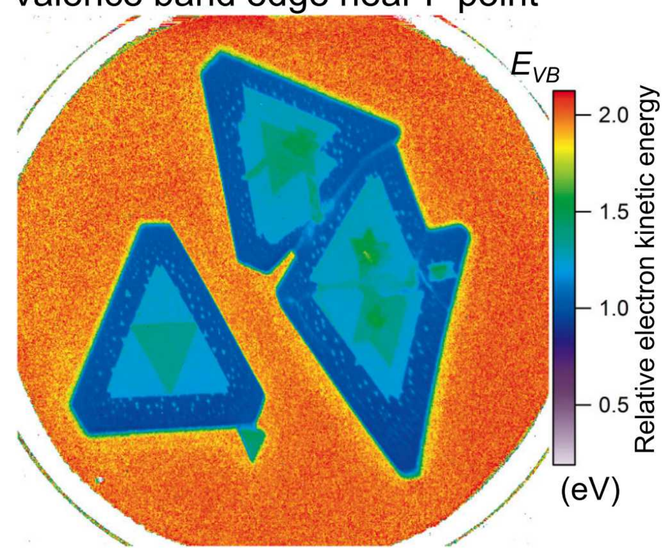




Vacuum level



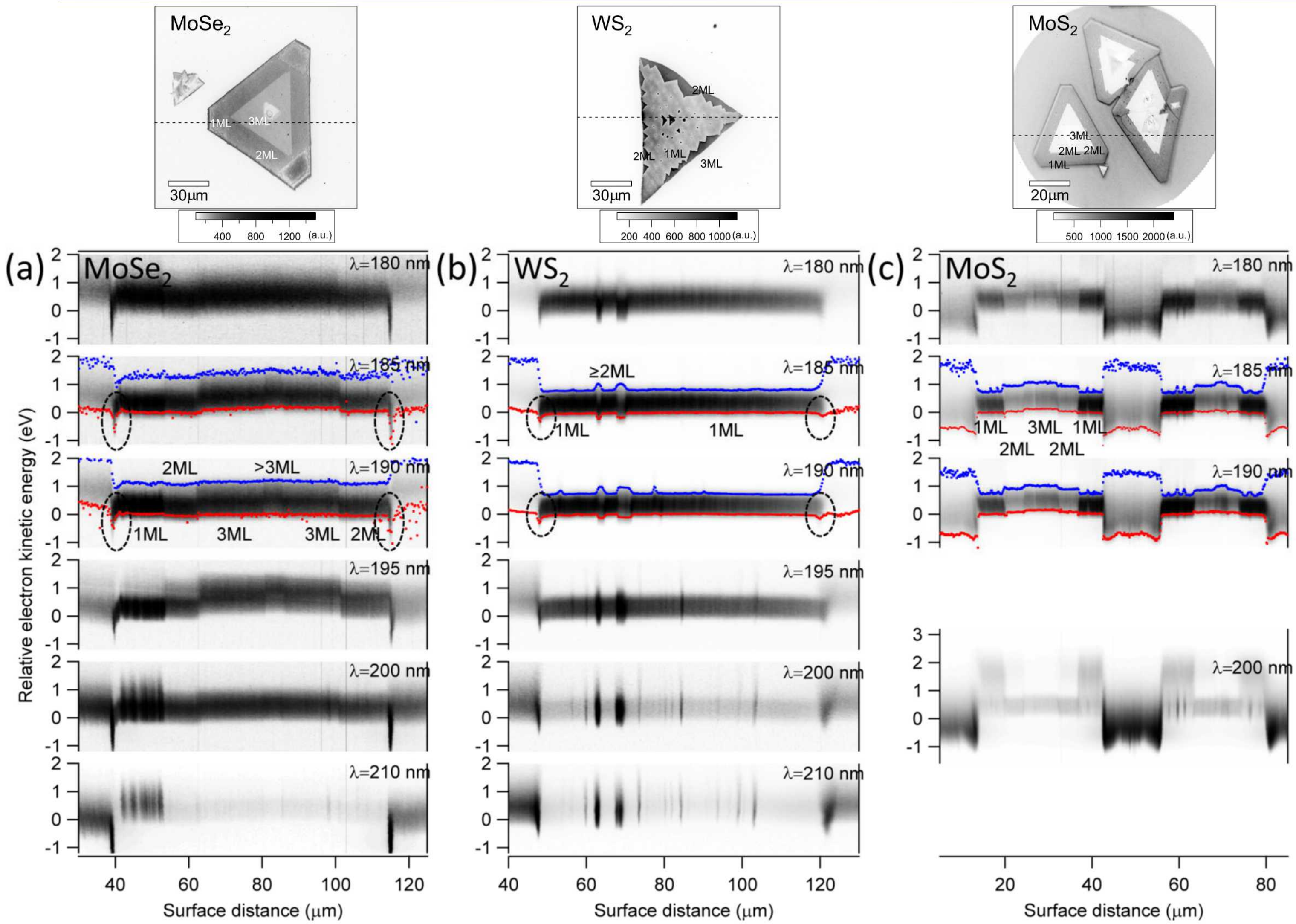
Valence band edge near Γ-point



- **Concurrent imaging and spectroscopy**

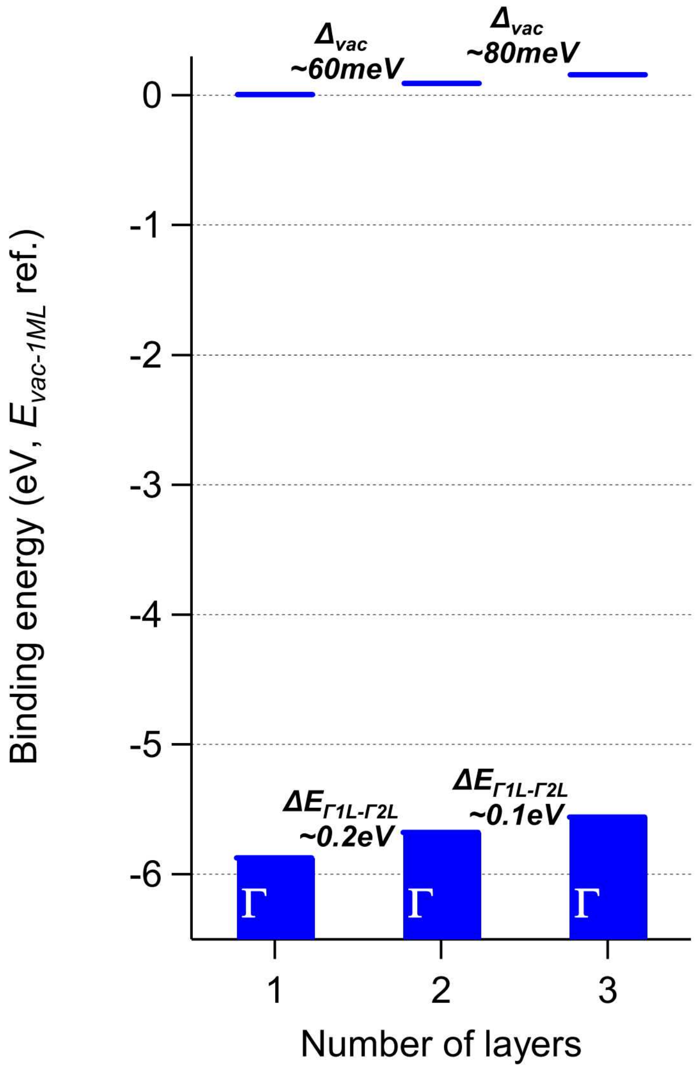
Berg, et al., Layer-Dependence of the Electronic Band Alignment of Few-Layer MoS_2 on SiO_2 Measured Using Photoemission Electron Microscopy, Phys. Rev. B, 95, 235406 (2017)

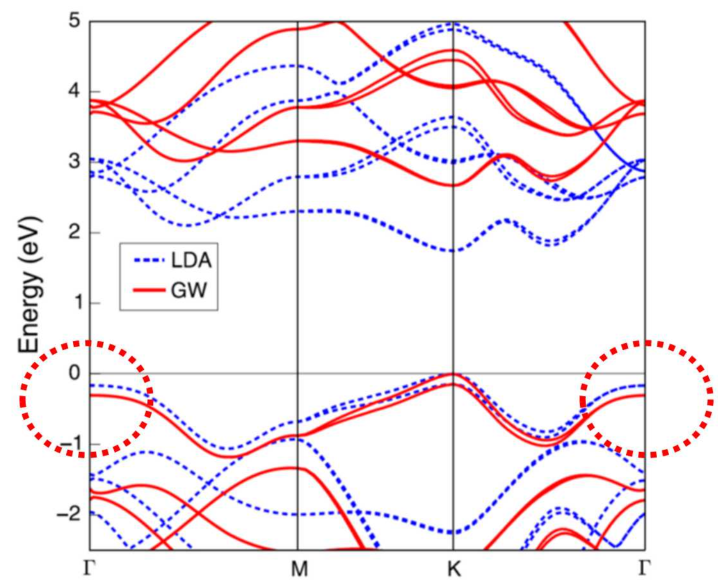
We measure photoemission spectra from $MoSe_2$, WS_2, and MoS_2



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



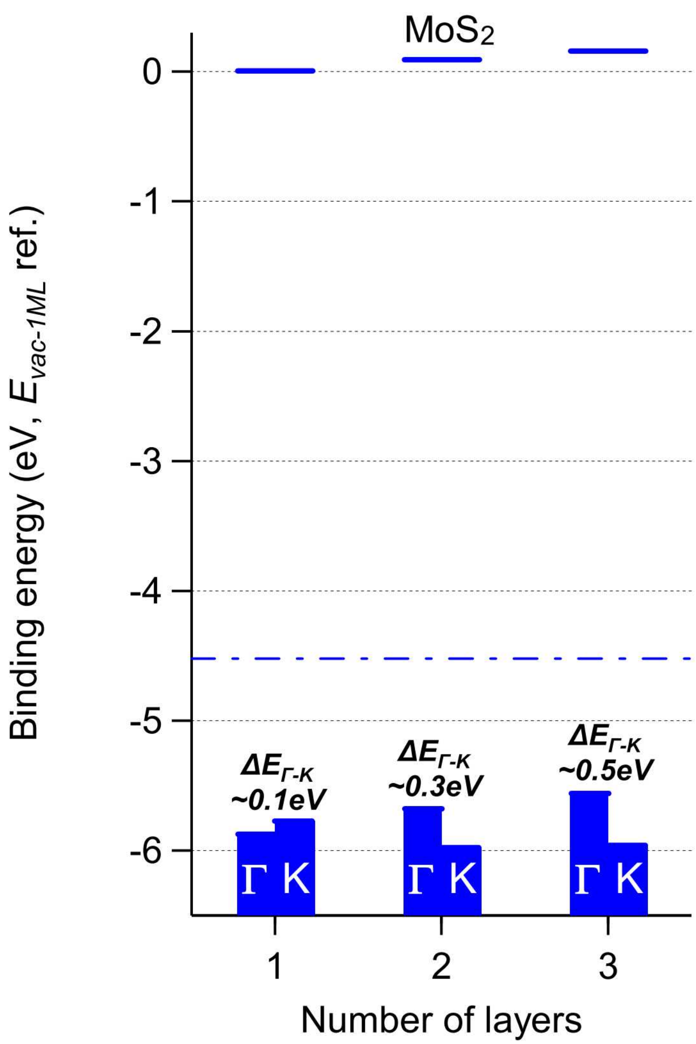


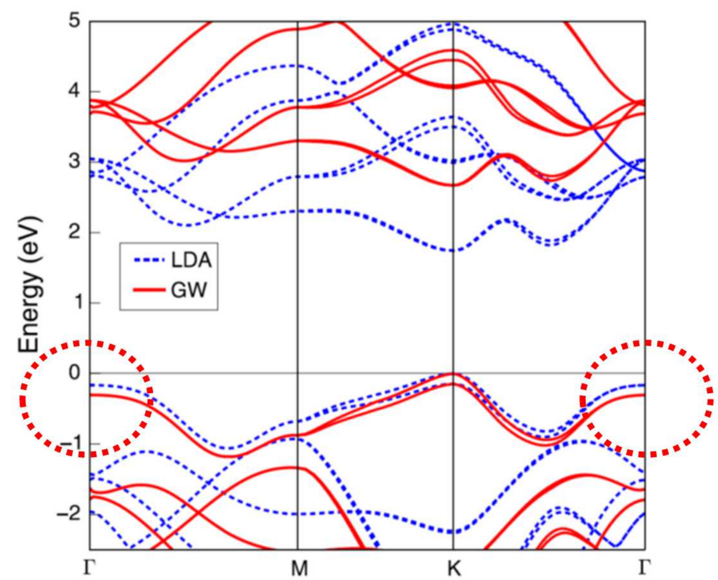
Qiu, et al., Phys. Rev. B 93, 235435 (2016)

- 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

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)

Hetero-junctions are formed between MoS_2 with different thicknesses





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

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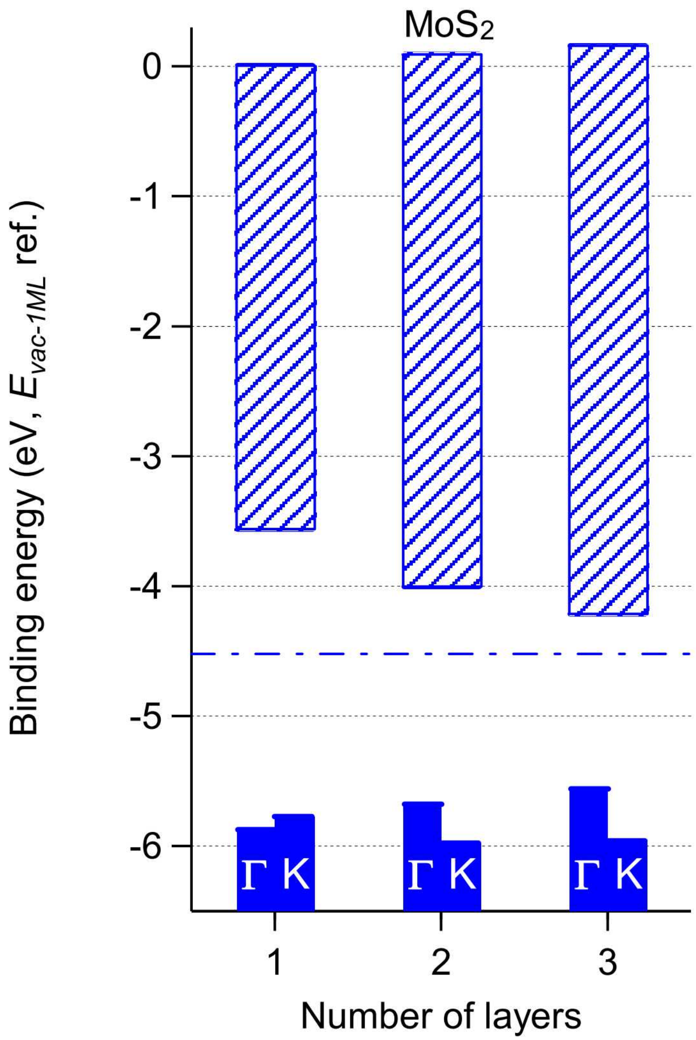
Berg, et al., Layer-Dependence of the Electronic Band Alignment of Few-Layer MoS_2 on SiO_2 Measured Using Photoemission Electron Microscopy, Phys. Rev. B, 95, 235406 (2017)

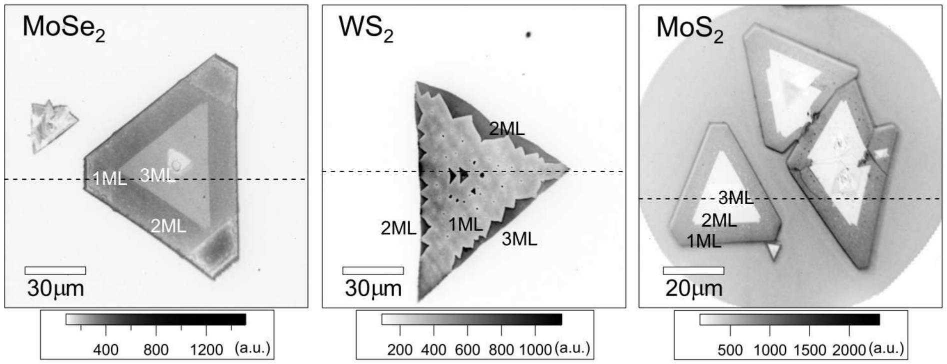
MoS_2 with different thicknesses forms type-I hetero-junctions



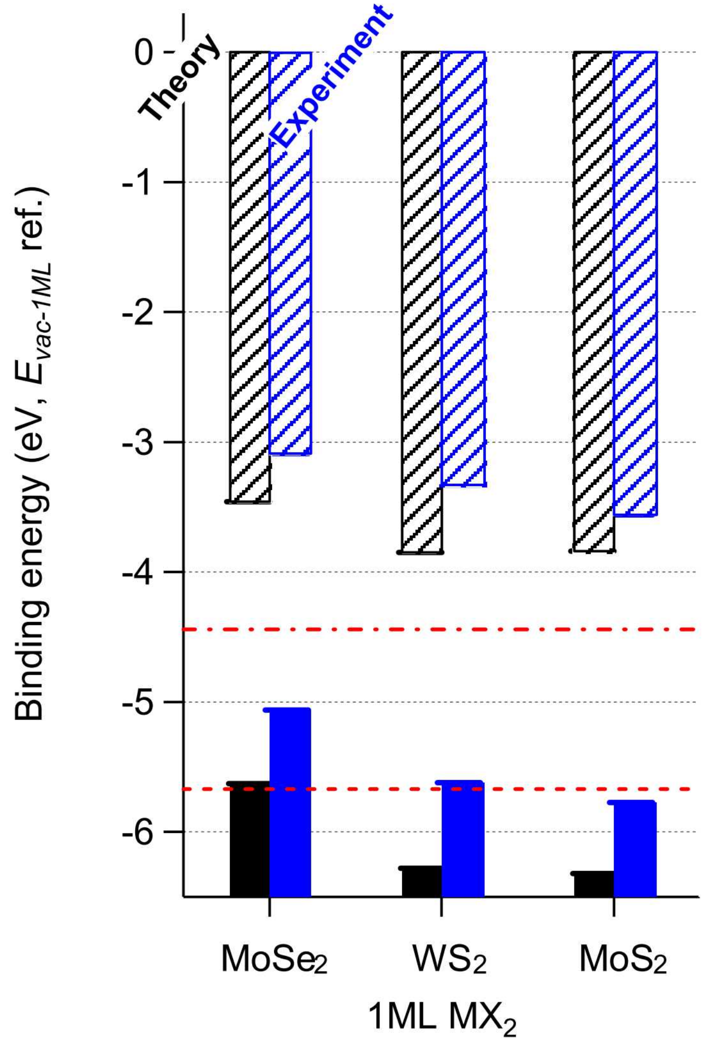
- Experimentally-determined quasi-particle band gap for 1L
  - Liu, et al., PRL, 122, 246803, 2019
  - Rigosi et al., PRB 94, 075440, 2016
- GW-calculated quasi-particle band gap for multilayers
  - Scaled to account for substrate's dielectric environment
- Type-I band alignments at the junctions between 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



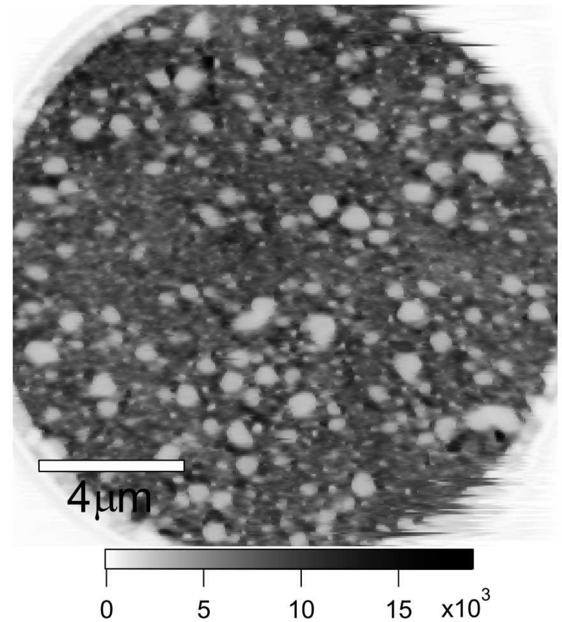
- Ionization energy decreases from MoS_2, WS_2, to $MoSe_2$, anticipated from the electronegativities of the constituent atoms
- Good agreement with GW calculation
- Heterostructures containing MoS_2, WS_2, to $MoSe_2$ are likely to display type II alignment



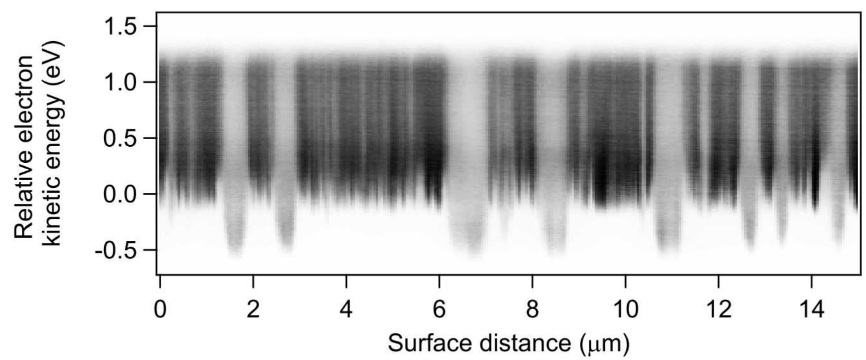
GW Theory: Rasmussen & Thygesen, J. of Phys Chem., 119, 13169, 2015

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

We compare the electronic structures of free-standing and Au-supported WS_2



- Work function of the Au-supported areas is significantly larger than that of free-standing areas reflecting the higher work function of Au

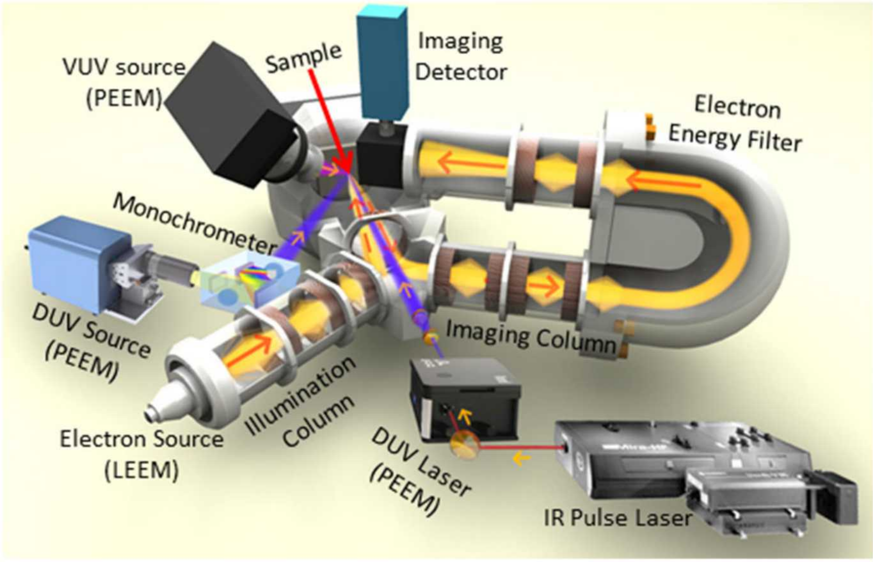


In collaboration with J. Fonseca, J. T. Robinson, Naval Research Laboratory

10:15 AM - FF01.08.01, Jose Fonseca, et al., Non-Local Quantum Emission in 2D Semiconductors via Oriented Pore Enabled Network (OPEN) Films

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



  - Other examples:
    - Graphene multilayers: Robinson, et al., Scientific Reports 8, 2006 (2018)
    - Polycrystalline CdTe: Berg, et al., ACS Appl. Mater. Interfaces, 10, 9817 (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

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