SAND2022-10103C

Sandia National Laboratories

Imaging atomically thin transition metal dichalcogenides using deep ultraviolet photoelectron emission microscopy

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Microscopy and Microanalysis (M&M) Meeting: July-Aug. 2022
A07.1: Science of Metrology with Electrons
Presentation Time: 8:45 AM
Session Location: Oregon Convention Center

U.S. DEPARTMENT OF ENERGY NNSA

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SAND2022 - XXXX

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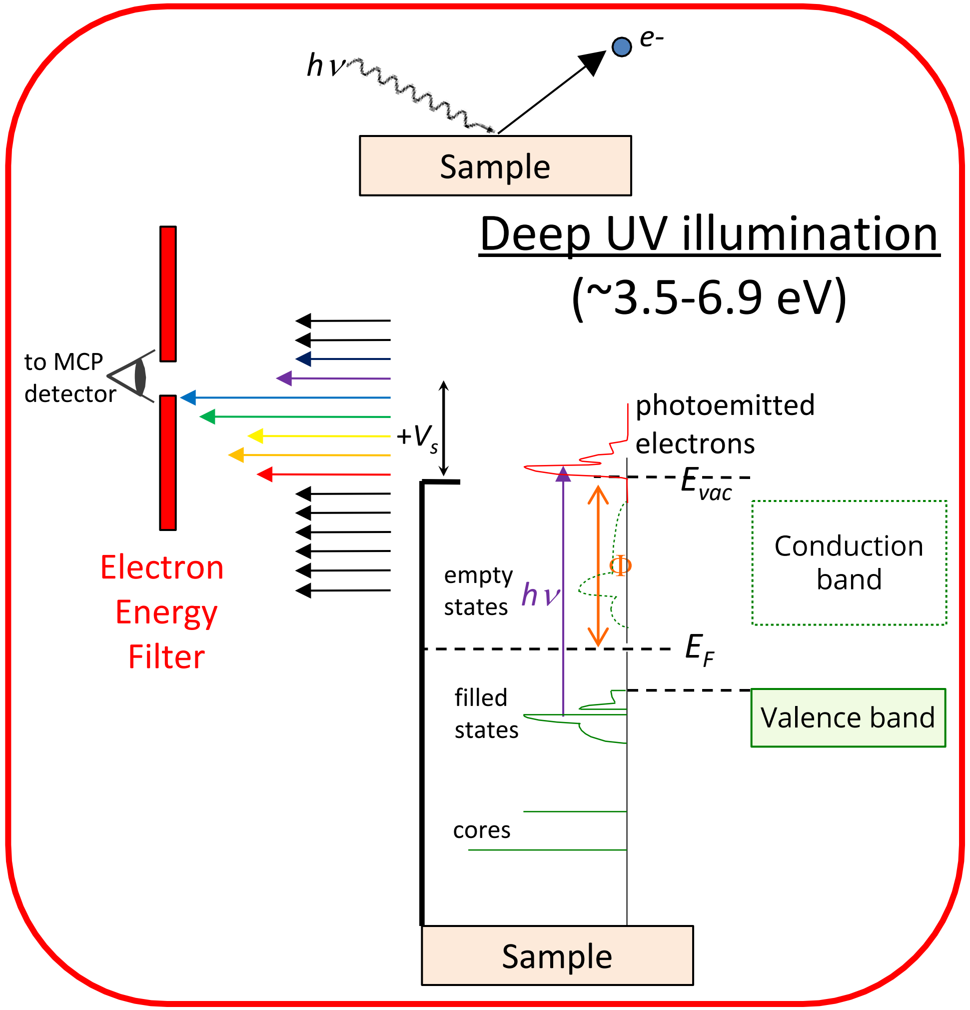
We use photoelectric effect in photoelectron emission microscopy



Photoelectric effect

PEEM (PhotoElectron Emission Microscopy):

An electron microscope, which projects the nanometer scale variations of the photoelectron intensity from the sample

Electromagnetic field

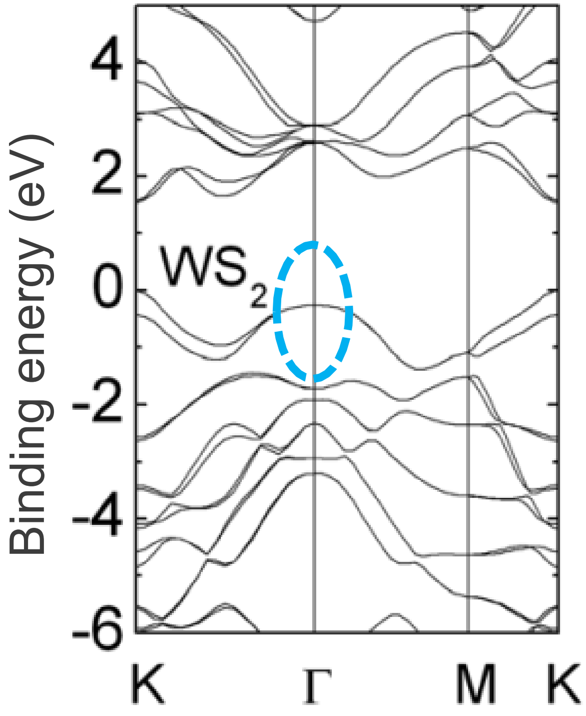
$$\Gamma_{i\to f} \propto |\langle f|\mathbf{A}\cdot \mathrm{p}|i\rangle|^2\,\delta(E_f - E_i - h\nu)$$

Transition probability

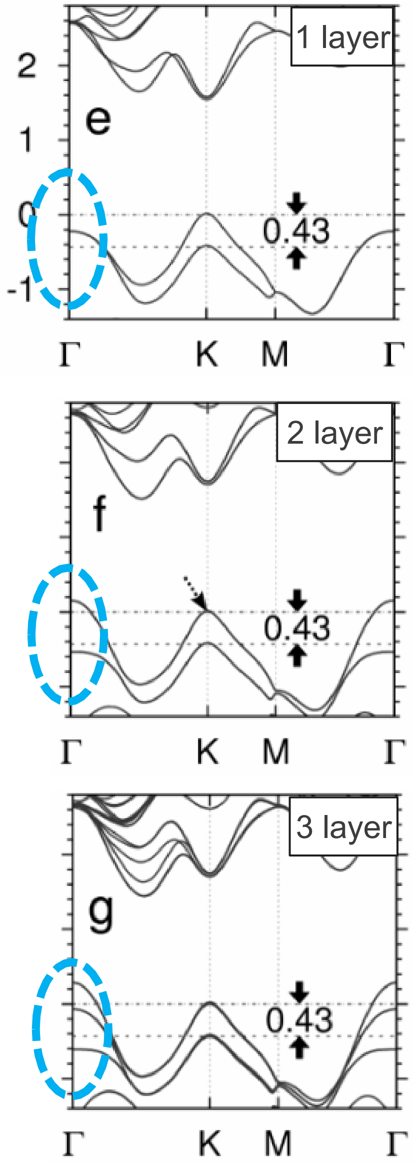
Occupied electronic state

Figure courtesy: M. Berg, C. Chan

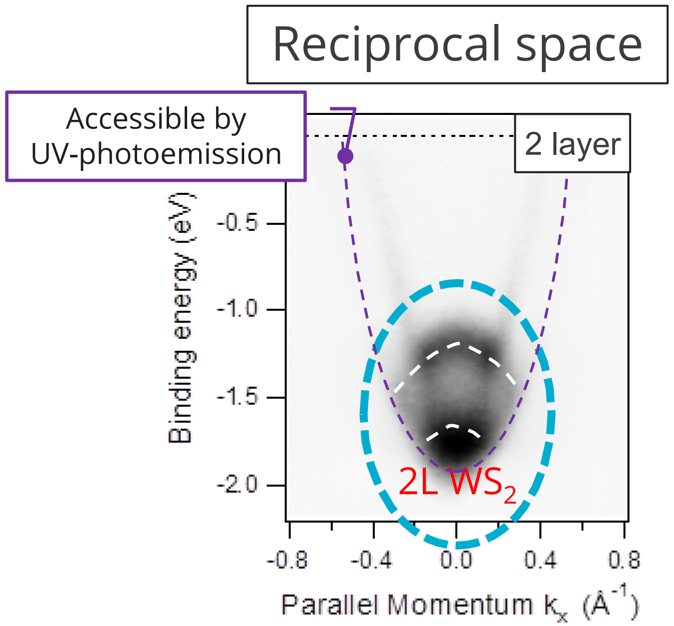
Photoelectron spectrum reflects the electron dispersion of the sample



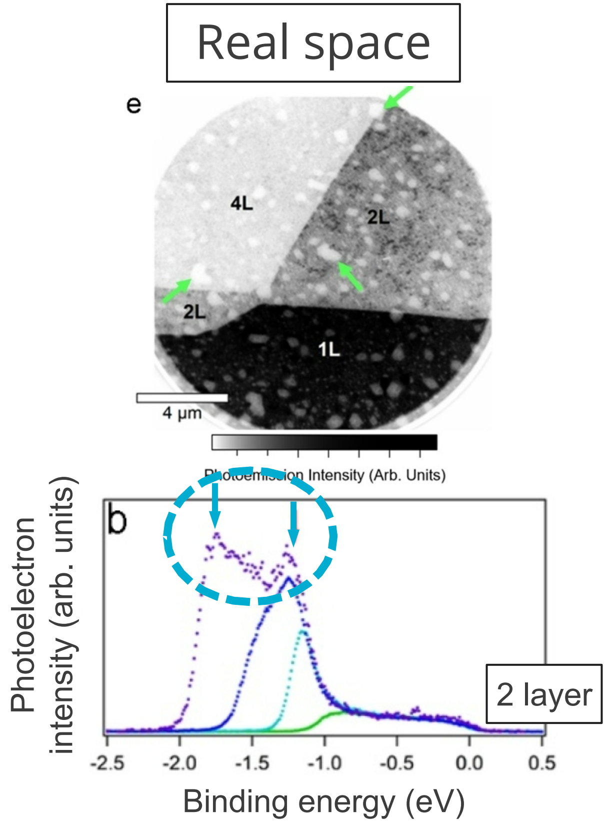
Kang, et al., APL 102, 012111 (2013)



Zeng, et al., Scientific Reports 3, 1608 (2013)

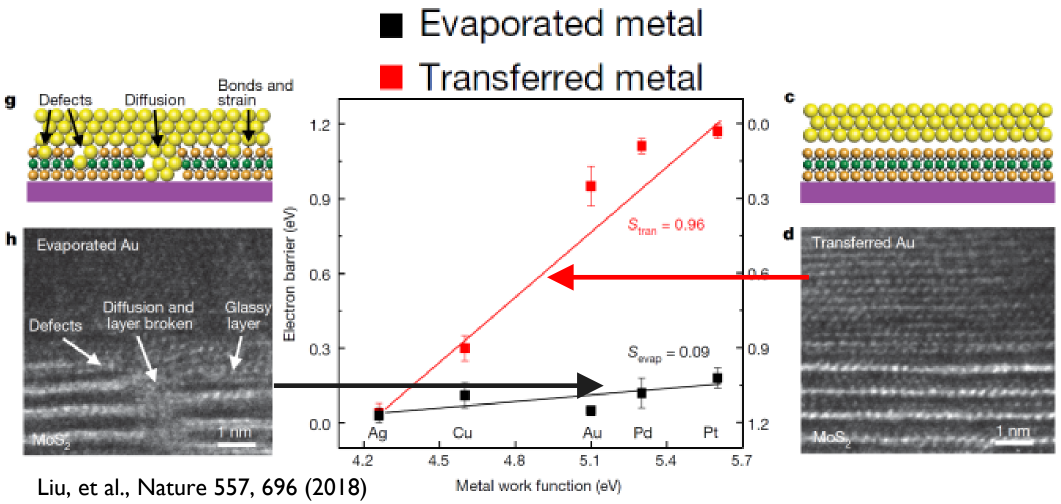


Similar to angle-resolved photoemission spectroscopy



- PEEM probes the occupied electronic states in real space & the reciprocal space
  - Deep UV-photoemission probes the states only near the Brillion zone center (i.e. Γ-point)

TMD-metal contact impacts device performance



Liu, et al., Nature 557, 696 (2018)

TMD: Transition Metal Dichalcogenides

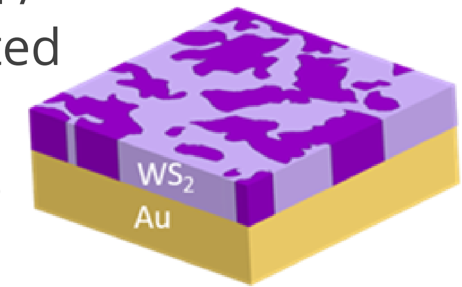
- Inevitable & critical components to incorporate 2D materials in electronic devices
- TMD-metal contacts made via **transfer** approach the Schottky–Mott limit
  - van der Waals-type semiconductor-metal junctions confirmed by cross sectional imaging

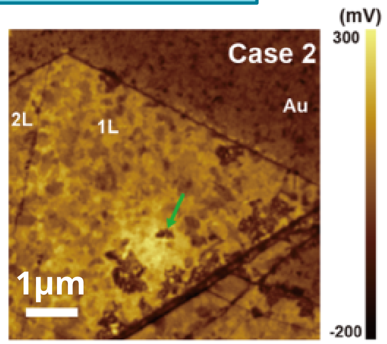
Questions:

- What is the nature of the TMD-metal interfaces when made via transfer process?
- Are there heterogeneities in the electronic structure at the TMD-metal interfaces?

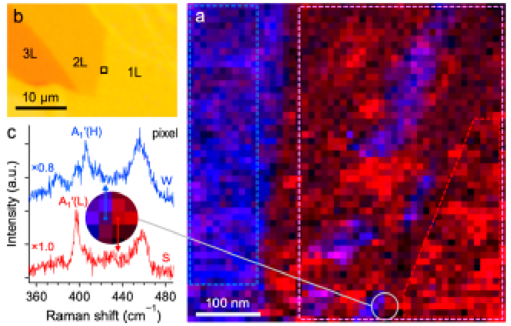
System 1: WS_2 exfoliated on a freshly deposited polycrystalline Au film

- Local variations of the surface potential / conductance & Raman response reported for the similar system: MoS_2 on Au
- Nature of the WS_2-Au interface is yet to be understood



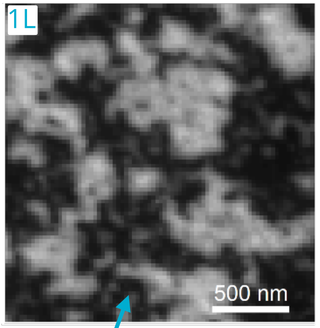


Jo, et al., ACS Nano 2021, 15, 5618

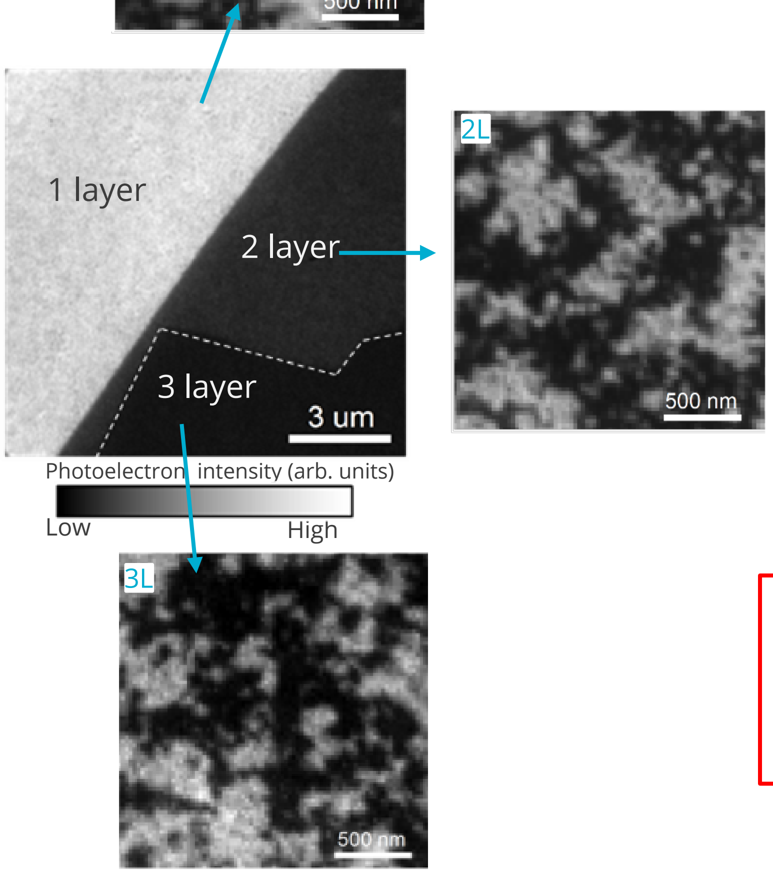


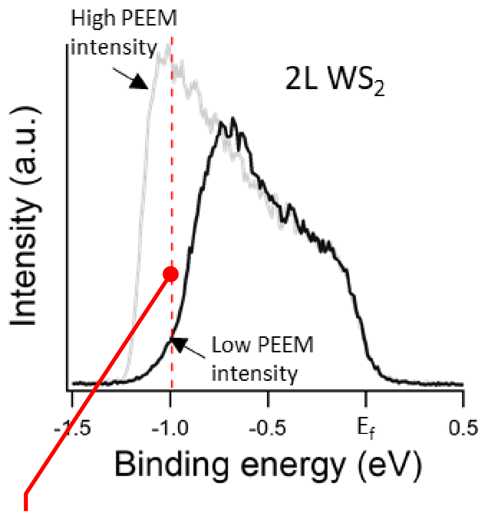
Velickyi, et al., J. Phys. Chem. Lett. 2020, 11, 6112

Submicron-scale work function heterogeneity in freshly-deposited Au-WS_2 interfaces

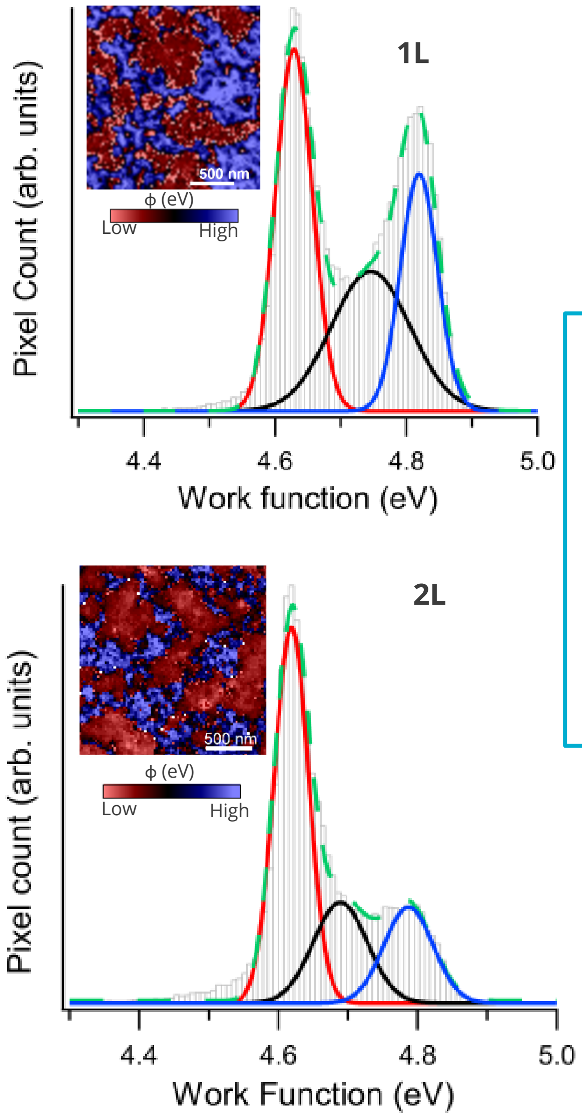


- Contrasting µm sized domains in PEEM intensity
- Present in 1-3L WS_2 thickness



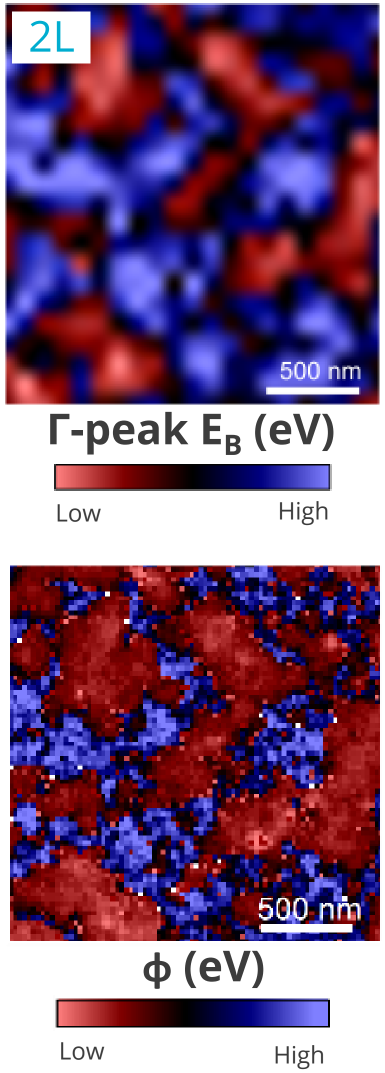


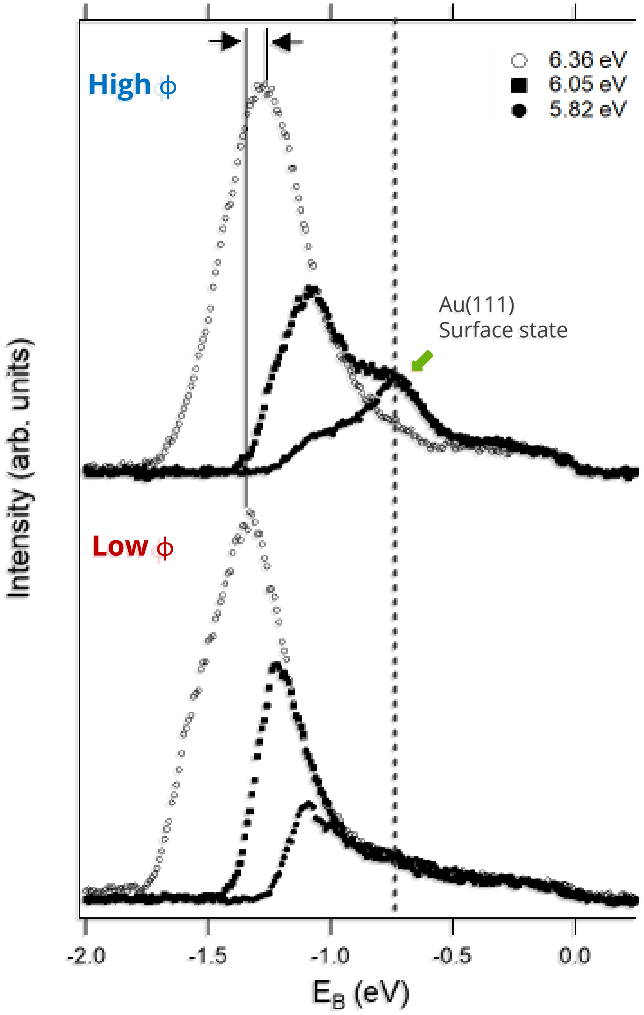
PEEM contrasts arise from difference in work function

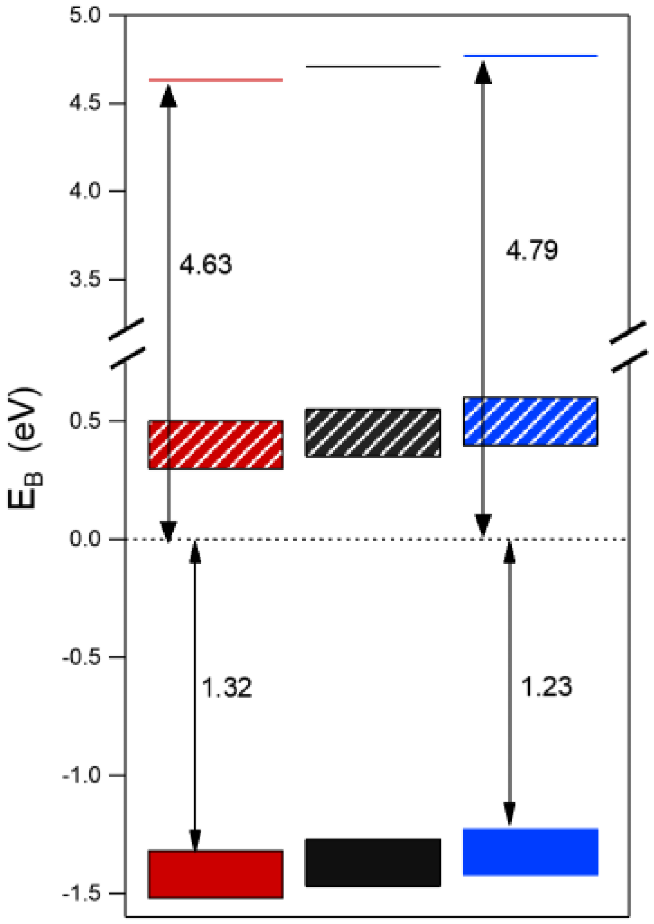


- Large work function variation (>200 meV)
- Varying carrier density within the WS_2 flake

Submicron-scale Γ-point peak position heterogeneity in freshly -deposited Au-WS_2 interfaces

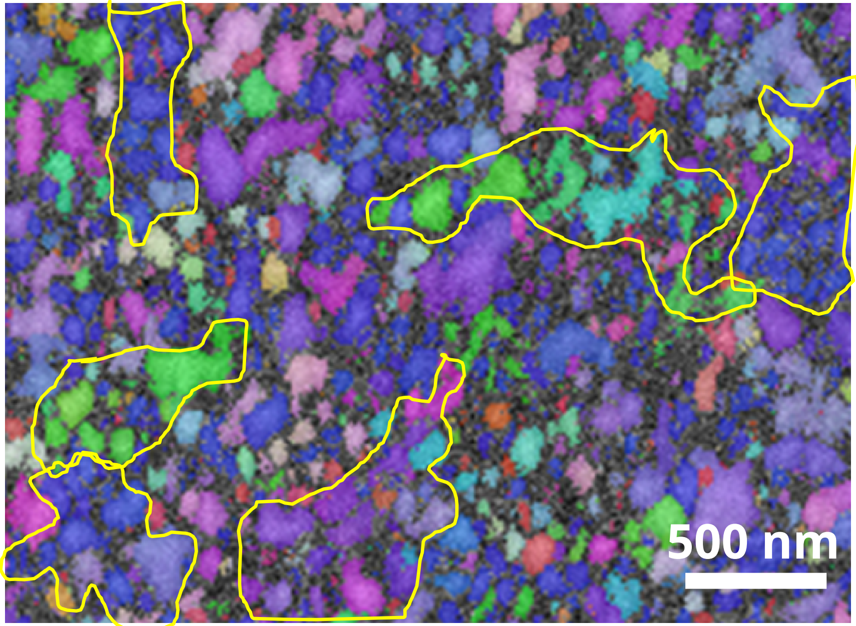


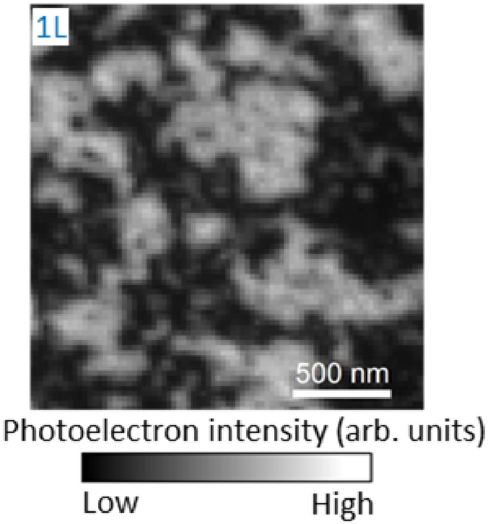


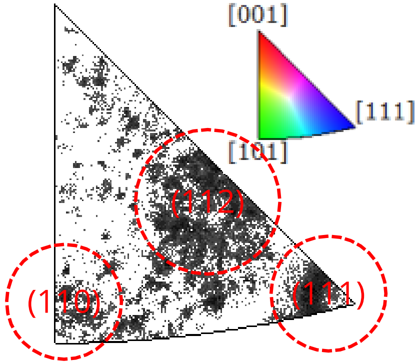


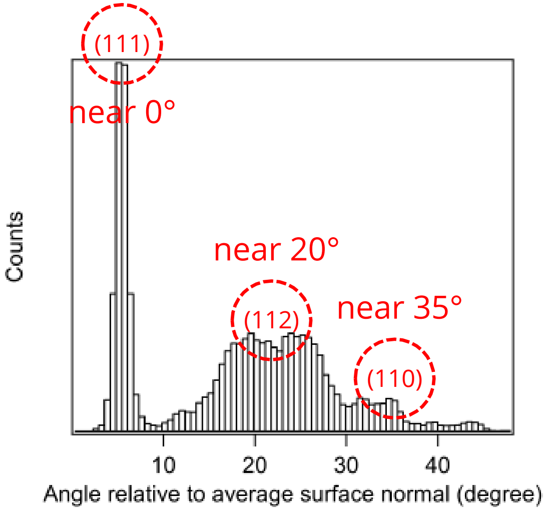
- Same micron-sized domains from photoelectron intensity and ϕ maps
- Higher work function regions show corresponding upshift in VBM
- Low BE peak (-0.7eV) observed near fermi level only in high work function areas
  - Au (111) surface state
- More n-type
- More p-type
- **Schottky barrier height appears to vary by ~0.1eV across the metal contact**

EBSD elucidated three predominant crystallographic orientations of the Au grains







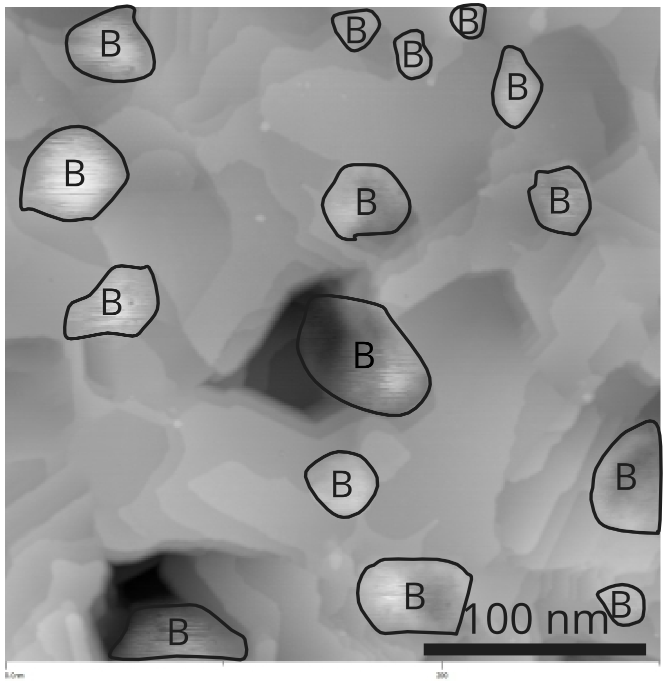


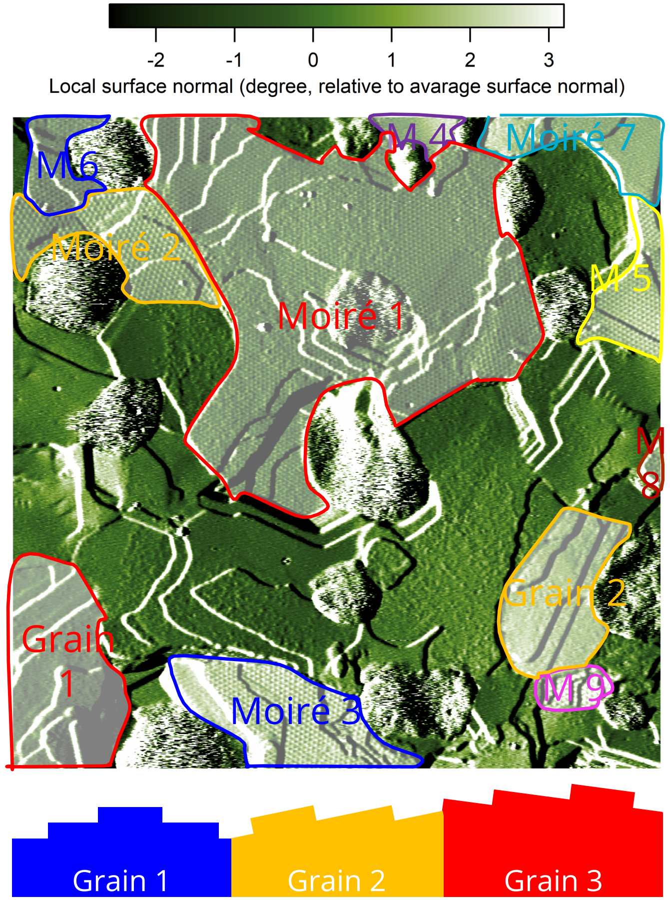
EBSD: Electron BackScatter Diffraction

- Majority of the grains have (111), (112), or (110) facets aligned close to the substrate normal
- Clusters with the similar crystallographic orientations resemble the heterogenous domains of WS_2 probed using PEEM
- Work function variations of Au surfaces are similar in magnitude to those of Au-WS_2 interfaces determined using PEEM

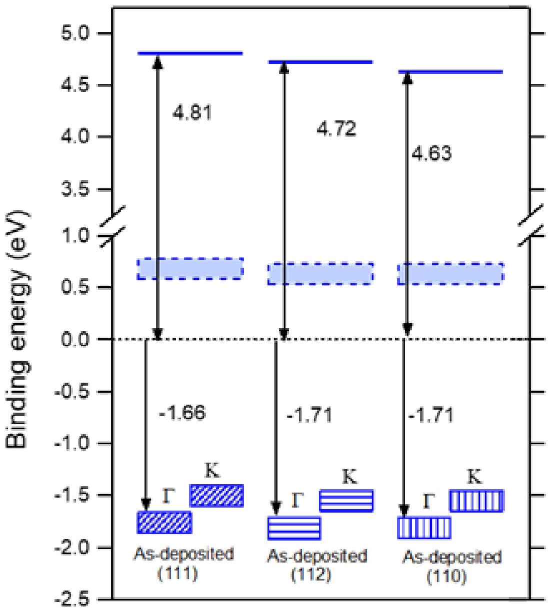
	J. Vac. Sci. Technol., A 33 060801 (2015)	Electrochimica Acta, 35, 1383 (1990)	Our DFT work
Au(111), (1x1) structure	5.33eV	5.30eV	5.20eV
Au(311), (1x1) structure		5.16eV	
Au(211)			5.08eV
Au(110), (1x1) structure	5.16eV	5.12eV	5.00eV

STM further supports the notion of the WS_2's electronic properties impacted by the Au grains





- We found Au atomic terraces & blisters using STM
  - Molecules physisorbed prior to the exfoliation are likely captured by the blisters
- Moiré patterns with varying superlattice periodicities found on some Au terraces
  - Moiré results from overlapping WS_2 & Au(111) 1x1 lattices w/ azimuthal misalignment
- Shapes of Au grains resemble the heterogenous domains of WS_2 probed using PEEM



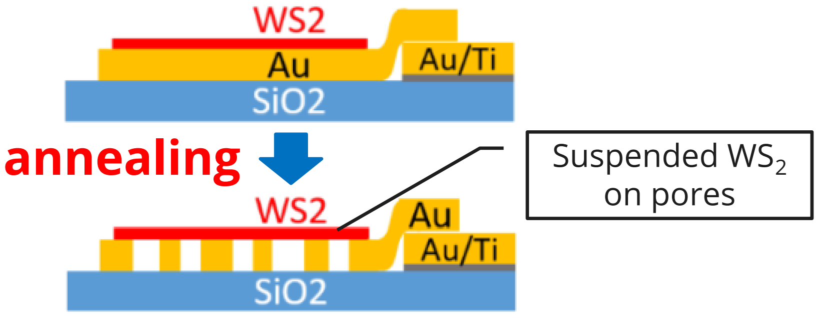
High work function, less n-type WS_2 on Au(111) (ϕ = 5.20eV)

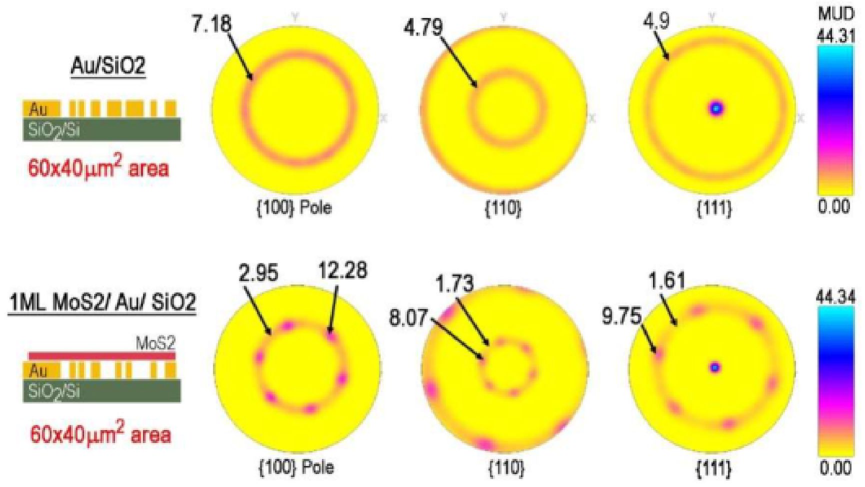
Low work function, more n-type WS_2 on Au(110) (ϕ = 5.00eV)

Conclusion: **Crystal facets** of Au appear to govern the electronic properties of WS_2 and TMD-metal junction barrier heights across the metal contact

Probing the pseudo-epitaxial interface between WS_2 & Au(111)

- Reflow & recrystallization create WS_2-Au(111) interface with pseudo -epitaxial relation: System 2

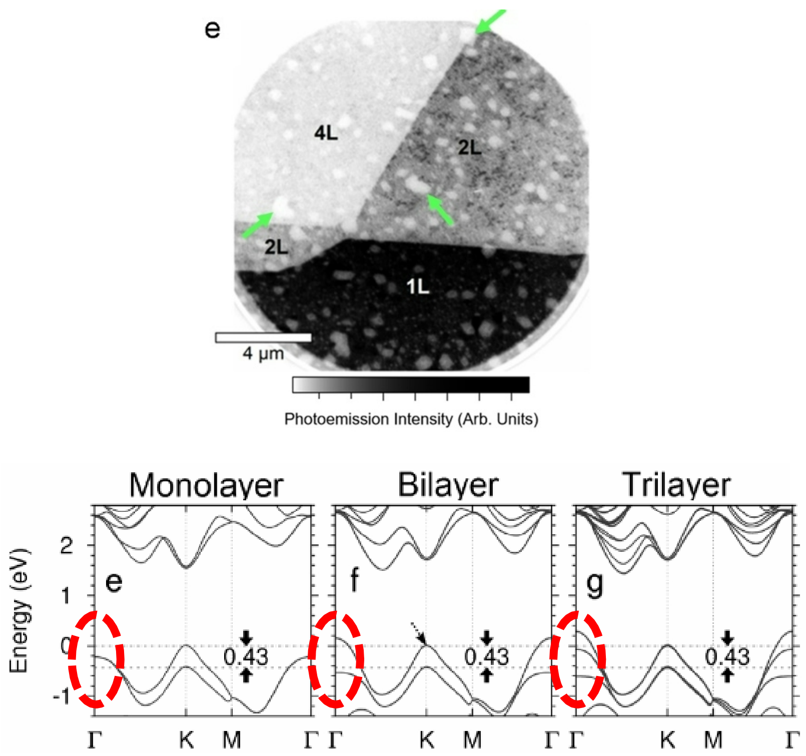




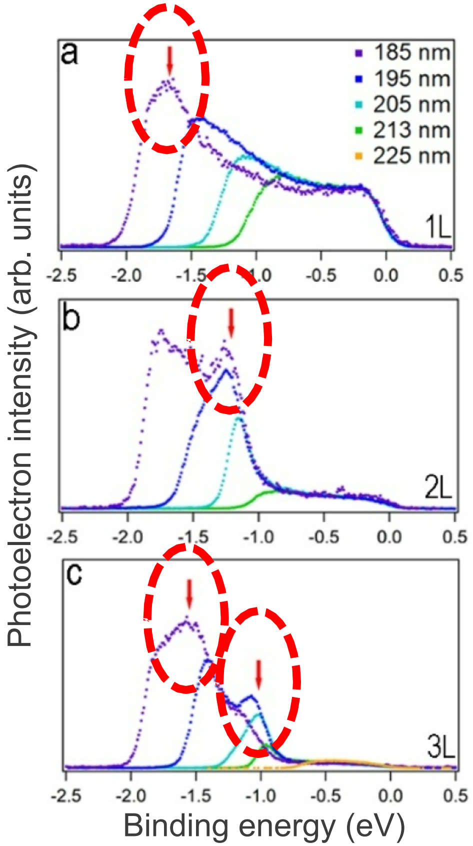
EBSD confirmed pseudo-epitaxial interface

Fonseca, et al., Nature Communications 11, 5 (2020)

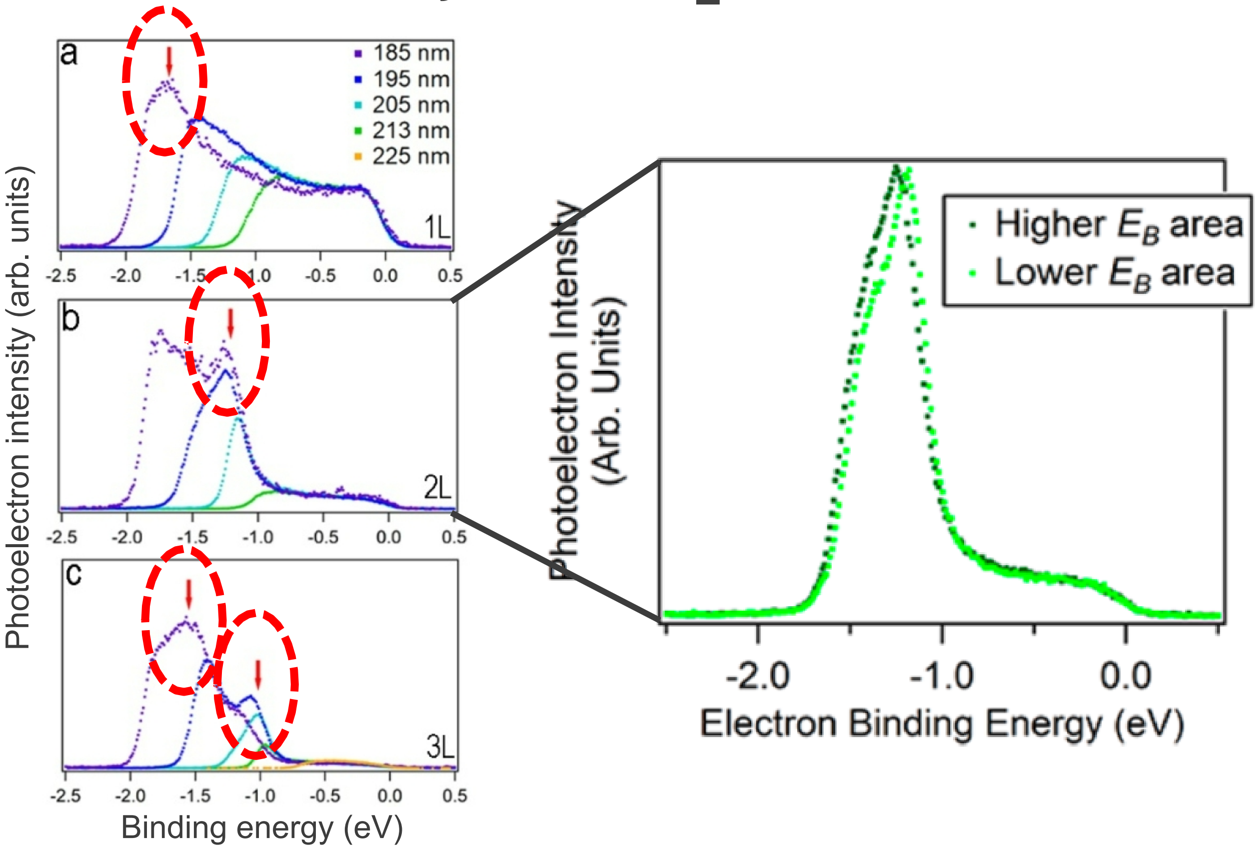
- Photoelectron spectra show characteristic splitting of the highest occupied states at Γ-point

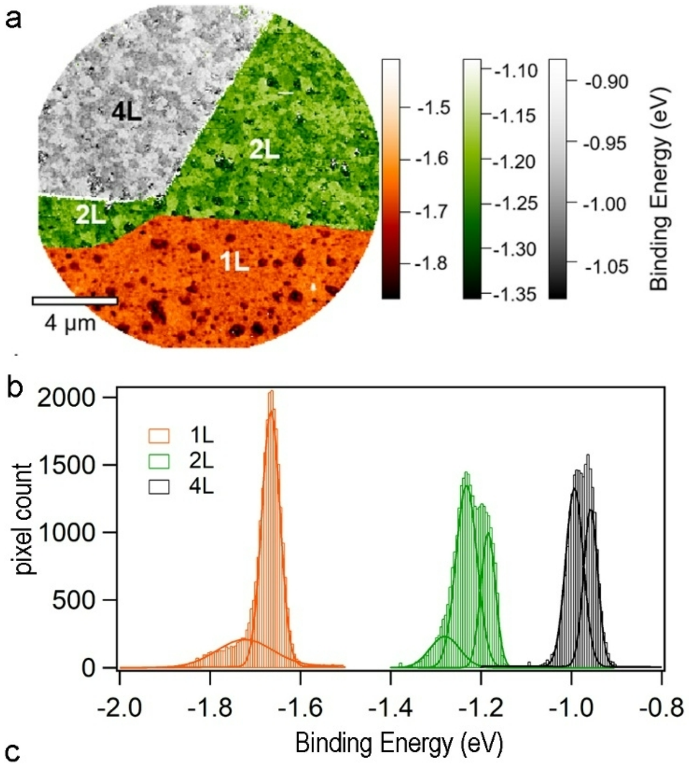


Zeng, et al., Scientific Reports 3, 1608 (2013)



We found local variations of the Γ-point peak positions in multilayer WS_2

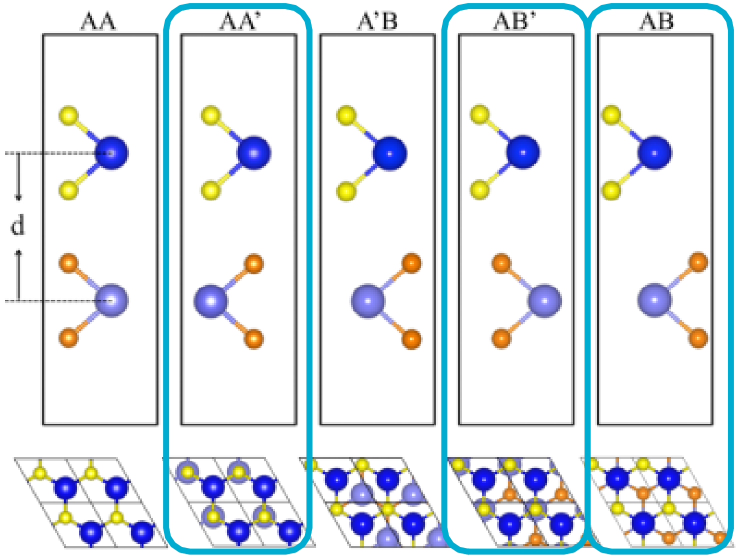




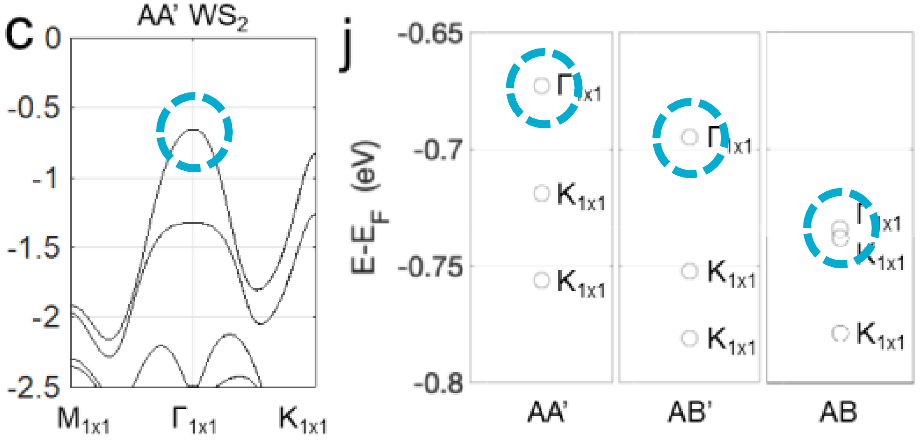
- The variations of the Γ-point peak position are 30-50meV
- Shape & size of the variations match the crystal grains in the Au-film
- The variations found in multilayer, but absent in single layer

Layer slippage due to the strong adhesion between WS_2 & Au?

DFT modeling supports the layer slippage model

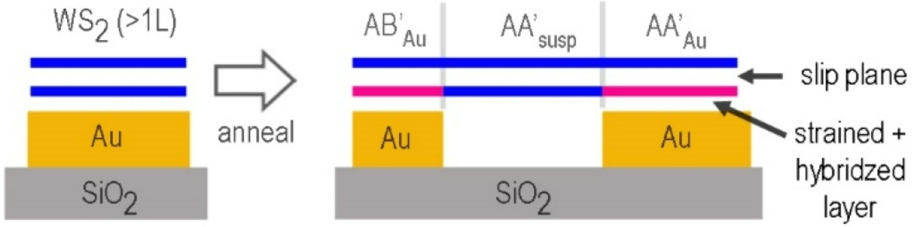


He, et al., PRB 89, 075409 (2014)



- Compared stacking sequences for 2L: AA′, AB′, and AB
  - AA′ common for bulk WS_2
  - Alignment of one layer is slightly shifted with respect to another
- 20-50meV variations of Γ-point state depending on the stacking sequence
  - Similar to the PEEM result of 30-50meV variations
- Support the metal adhesion-induced layer slippage model resulting in the WS_2's local electronic structure variations

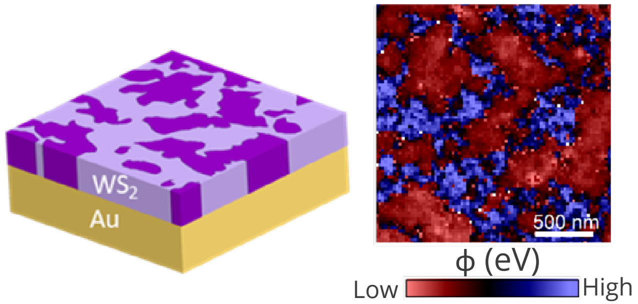
Conclusion: electronic properties of TMD is **altered mechanically** by the metal



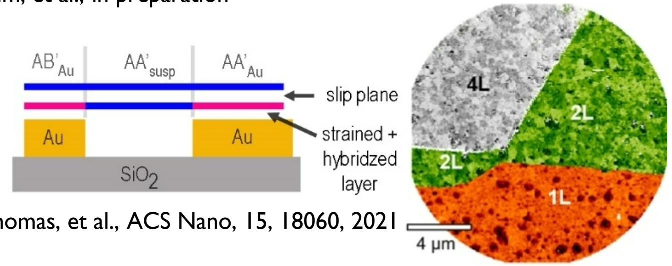
Concluding remarks

Take-home messages:

- Microstructures of Au films plays important role in the WS_2-Au contacts
  - **Crystal facets** of Au grains appear to govern local variations of the WS_2 electronic structures
  - **Stacking variation** is induced by the layer slippage due to strong interaction between WS_2 & Au
- Photoelectron is an effective probe to study electronic structures in microscopes



Boehm, et al., in preparation



Thomas, et al., ACS Nano, 15, 18060, 2021

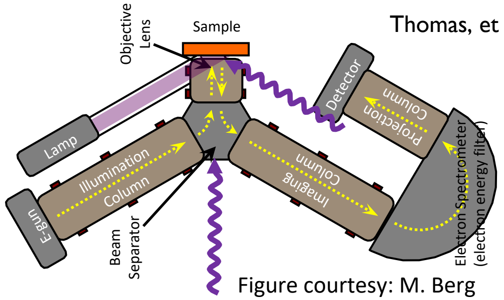


Figure courtesy: M. Berg

Financial support:

- Sandia LDRD program

Special thanks:

- N. Bartelt, F. Leonard, S. Kumar, C. Smyth, T.-M. Lu, R. G. Copeland, Sandia National Laboratories

Postdoc opportunity at Sandia National Laboratories

We seek to hire a qualified postdoctoral research associate to conduct PEEM research focusing on nanostructured optical materials. If you are interested in, please contact: tohta@sandia.gov

Supporting slides follow:

Imaging with photoelectron microscopy (PEEM)

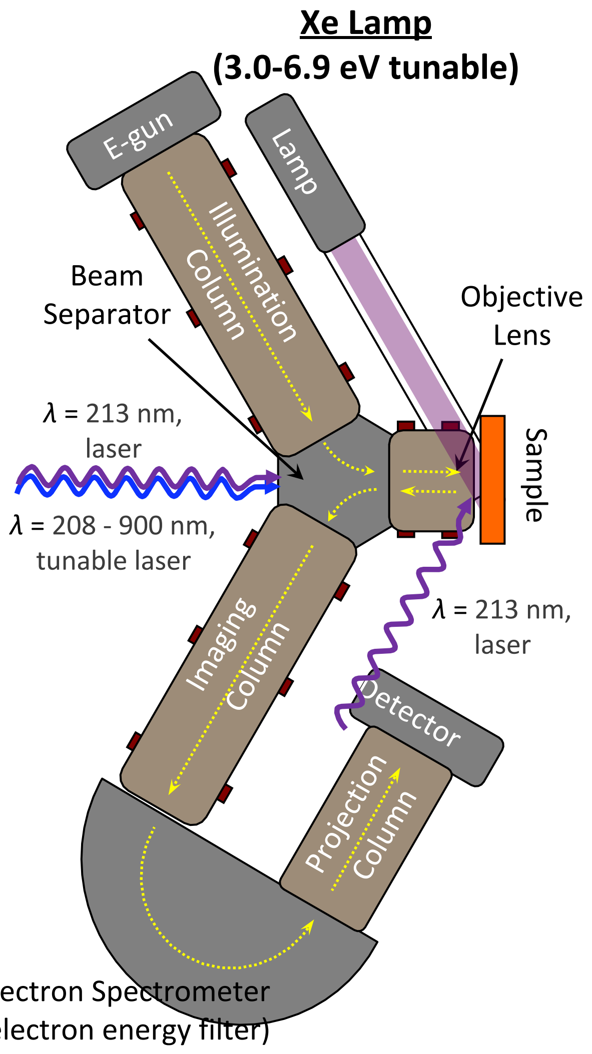


Figure courtesy: M. Berg

Conducted in low energy electron microscopy instrument

Two specifications of the photoemission electron microscope

- Spatial resolution ~15 – 200nm
- Energy resolution ~0.2 – 0.5eV

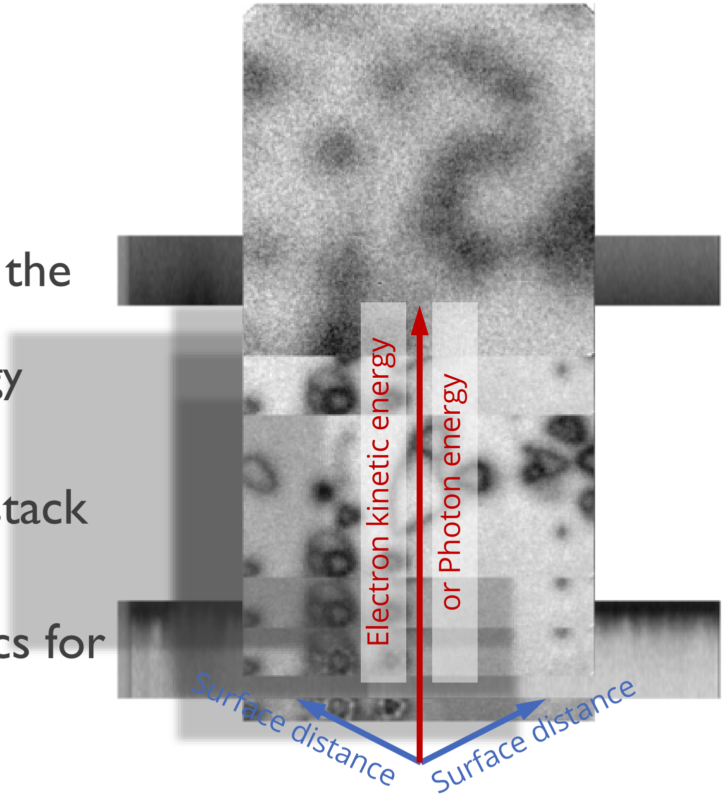
Deep UV monochromatic light sources are used for the work presented here

- λ = 180 – 350nm (hν = 3.54 – 6.89eV): tunable-energy photon source based on a Xe-lamp

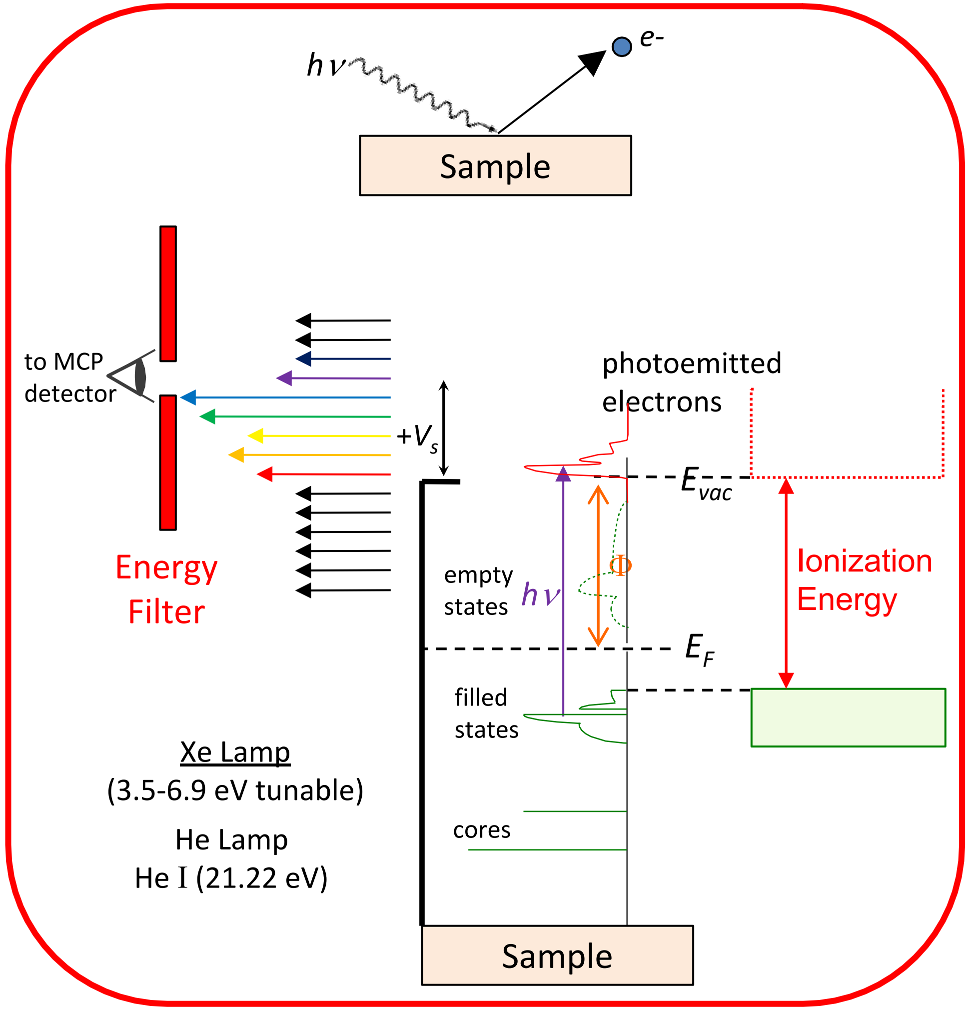
Spectrum is extracted from each pixel in the image stack or data cube, and fitted to create maps

Meets the four required (or preferred) characteristics for systematic measurements:

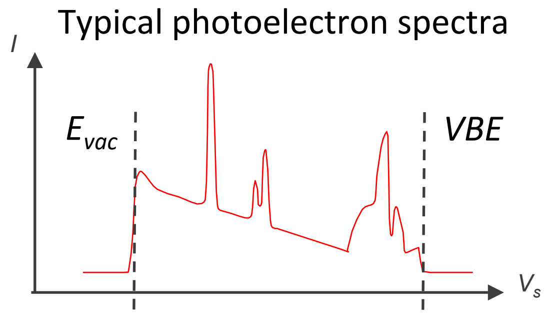
- Microscopy function
- Inert environment, i.e. vacuum
- Adequate energy resolution
- No need for additional sample processing



Photoemission process



Photoemission process



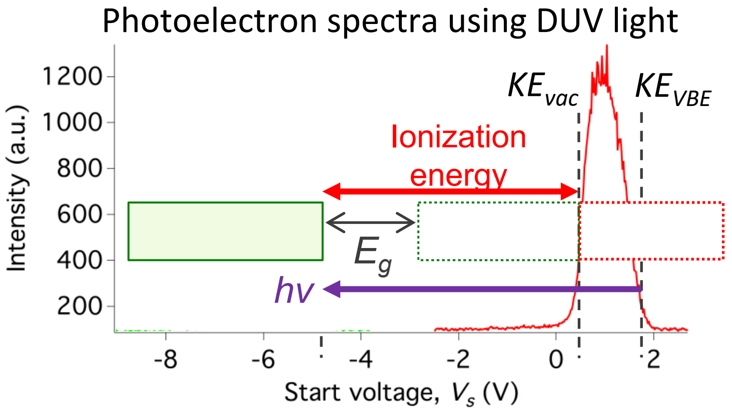
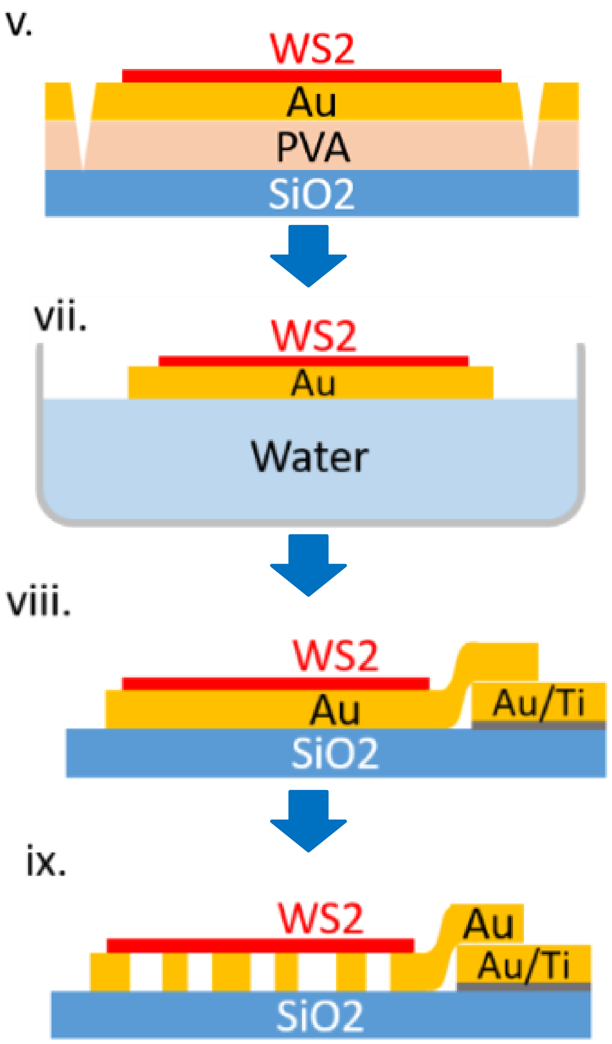


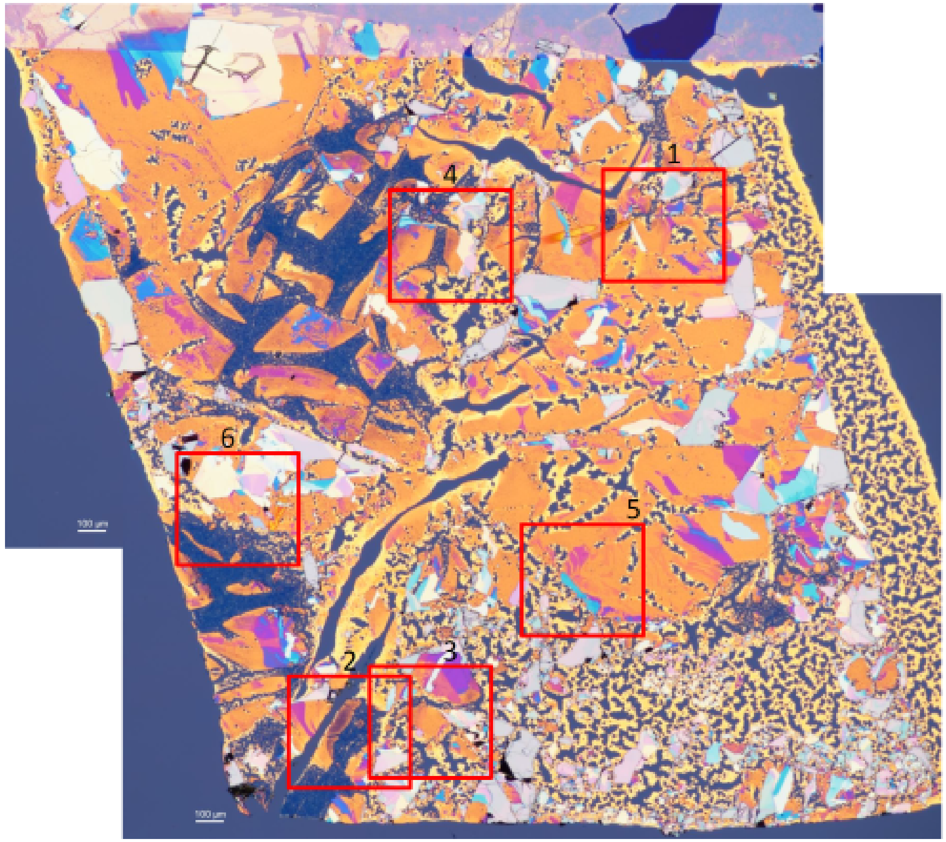
Figure courtesy: M. Berg, C. Chan

How OPEN sample look like & what we know about them



Fabrication:

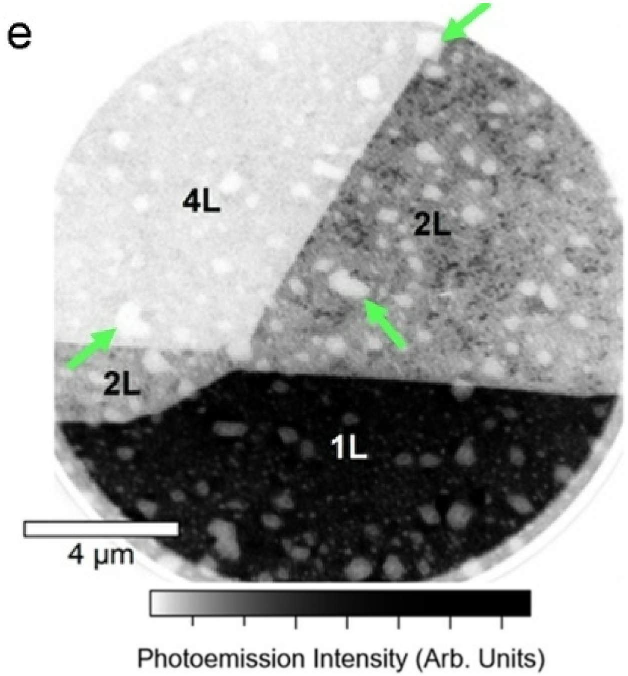
- Water-based transfer of WS_2 exfoliated on Au film
- Reflow and recrystallization in the confined geometry create pseudo-epitaxial relation between WS_2 flake and Au grains
- Au-supported and suspended WS_2 coexist

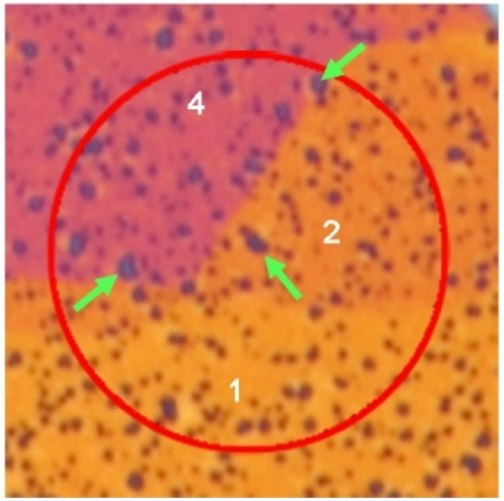


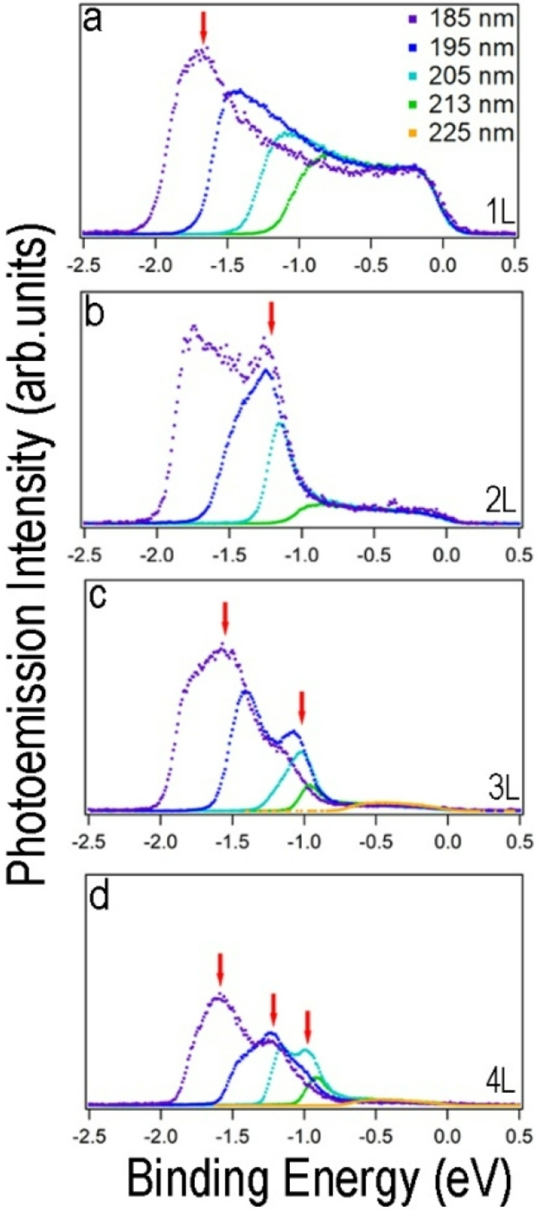
Sample navigation:

- Large-scale optical micrographs to locate WS_2 flakes, followed by PEEM, STM, etc.

We confirm the WS_2 thickness using PEEM & acquire electron DOS spectrum from each thickness

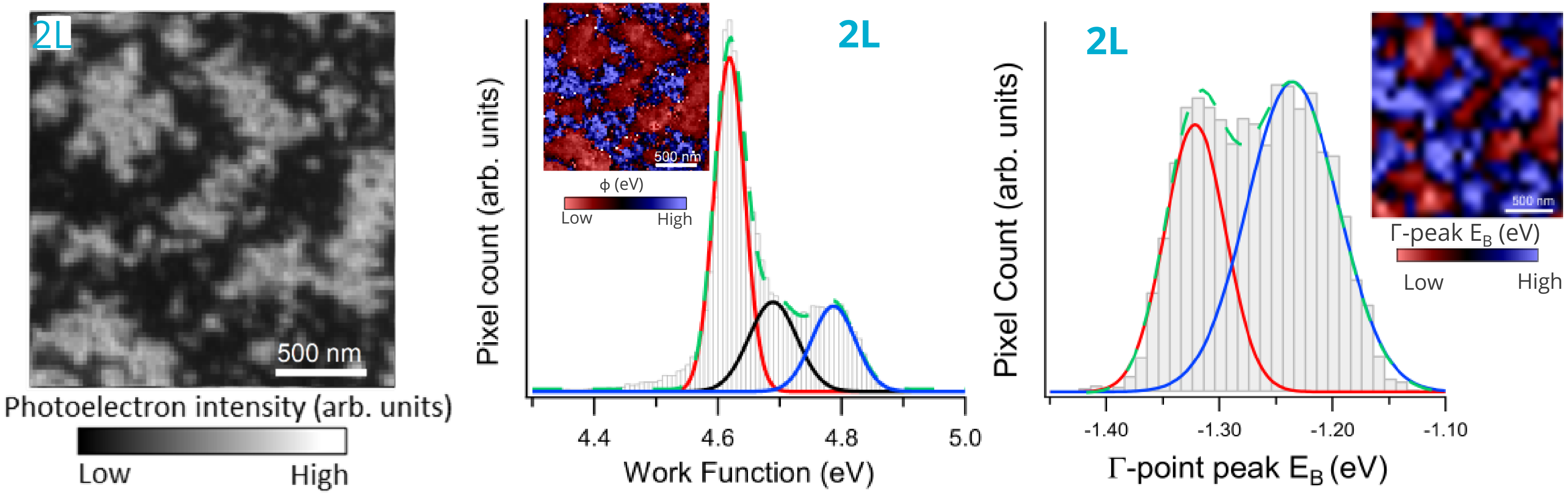






- PEEM intensity contrast match the optical contrast perfectly
- Peaks in the photoelectron spectra (occupied electron DOS spectra) correspond to the highest occupied states at Γ-point

We see significant variation of the work function & the Γ-point peak position in simply exfoliated WS_2 (cont'd)



- Large work function & Γ-point peak variations (>100 meV) with the length scale similar to the layer slippage
  - Shape & electronic structure variations are different from the layer slippage in OPEN samples (30-50 meV)
  - Present in any WS_2 thickness (1L to 3L checked)

Suggesting that the carrier density varies significantly (>100 meV) in a WS_2 flake so as the Schottky barrier height across the metal contact

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