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Nanoscale heterogeneities at Transition Metal Dichalcogenide-Au Interfaces

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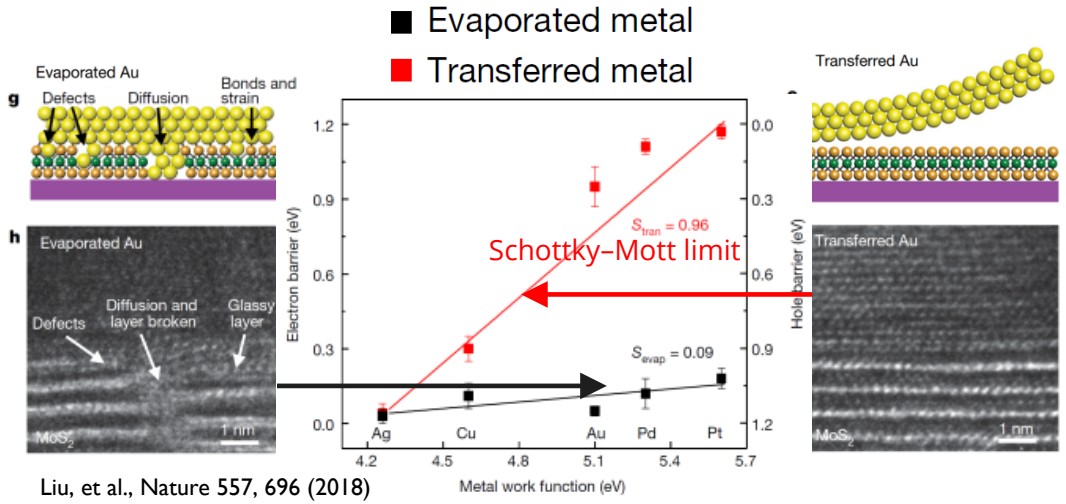
SAND2024-XXXX

TMD-metal contact impacts device performance

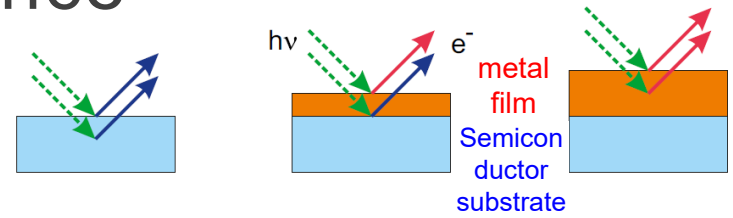
- **Transition metal dichalcogenides (TMD) is a new class of semiconductors** with enormous technological implications
- **TMD-metal contact is a critical component** to incorporate 2D materials in electronic devices

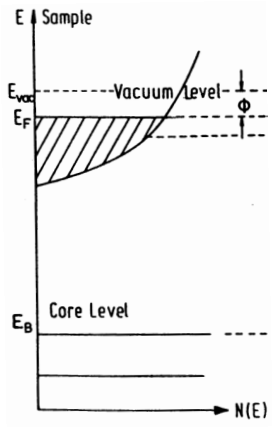
Questions:

- What are the difference of the TMD-metal interfaces fabricated via evaporation vs transfer?
- Are there heterogeneities in the electronic structure at the TMD-metal interfaces?
  - Impacts of the microstructures of Au or TMD?

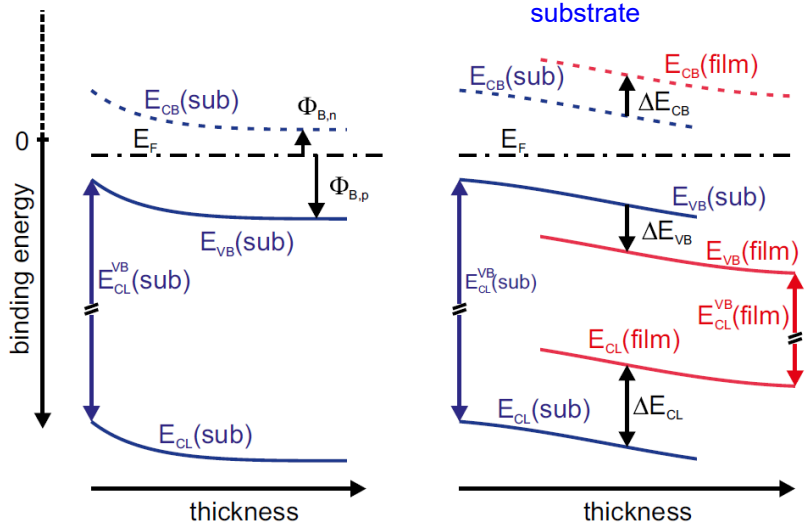


Liu, et al., Nature 557, 696 (2018)





Hufner, Photoelectron Spectroscopy (1995)



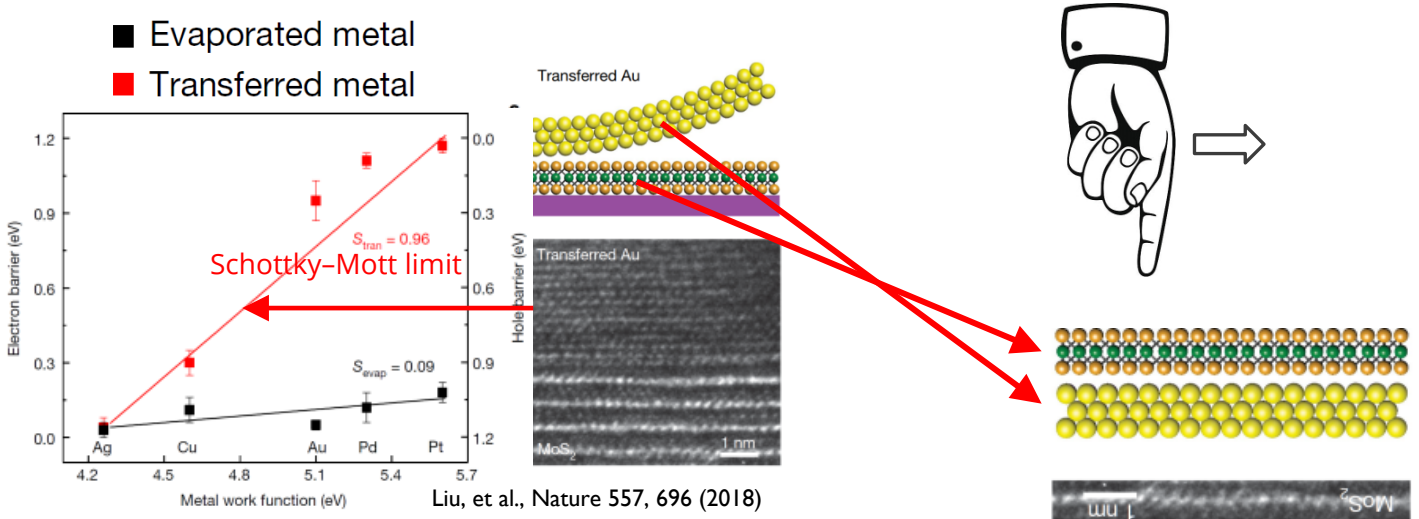
Klein, J. Am. Ceram. Soc., 99 [2] 369–387 (2016)

Challenges in examining TMD-metal contact using photoelectron spectroscopy:

- Object of interest is buried preventing direct access to the valence states
  - Energetics of valence states are inferred from the core level assuming E^{VB}_{CL}(sub) and E^{VB}_{CL}(film) stay unchanged
  - E^{VB}_{CL}(sub), E^{VB}_{CL}(film), & bandgap may not be constant since TMDs are susceptible to screening environment

- **How about upside-down geometry?**

Upside-down geometry enables access to the electronic structure of the TMD & interfaces



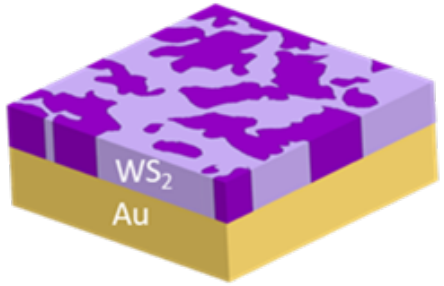
Liu, et al., Nature 557, 696 (2018)

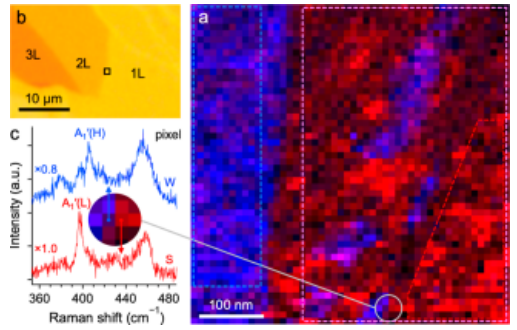
Upside-down geometry enables access to:

- valence band density of states in TMD
- electronic structure of a metal film (when TMD is thin)
- atomic arrangement & microstructures of TMD & metal grains

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

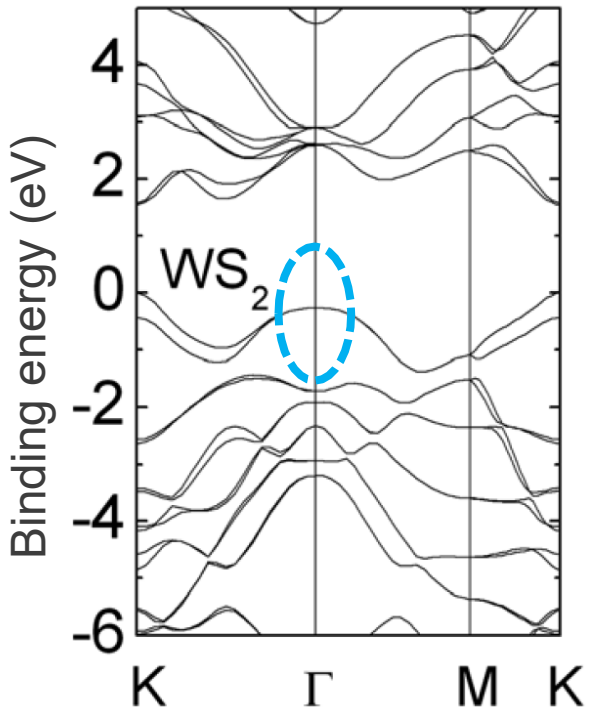
- A similar system (MoS_2 on Au) shows local variations of the surface potential, conductance, & Raman response
- Direct probe the electronic structures is desirable



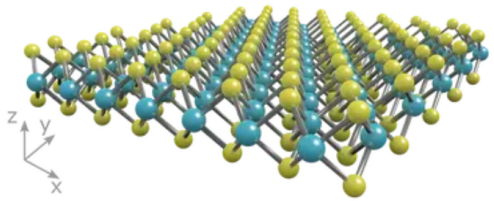


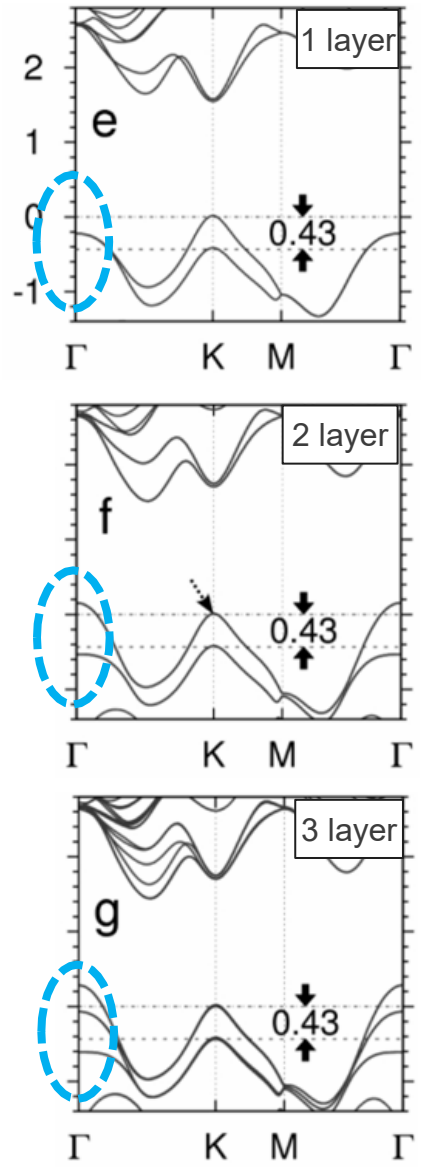
Velickyi, et al., J. Phys. Chem. Lett. 2020, 11, 6112

Photoelectron spectra reflect the electron dispersion of the sample



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

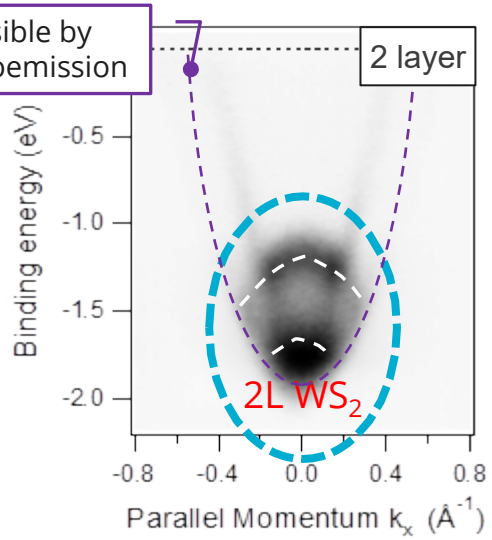




Zeng, et al., Scientific Reports 3, 1608 (2013)

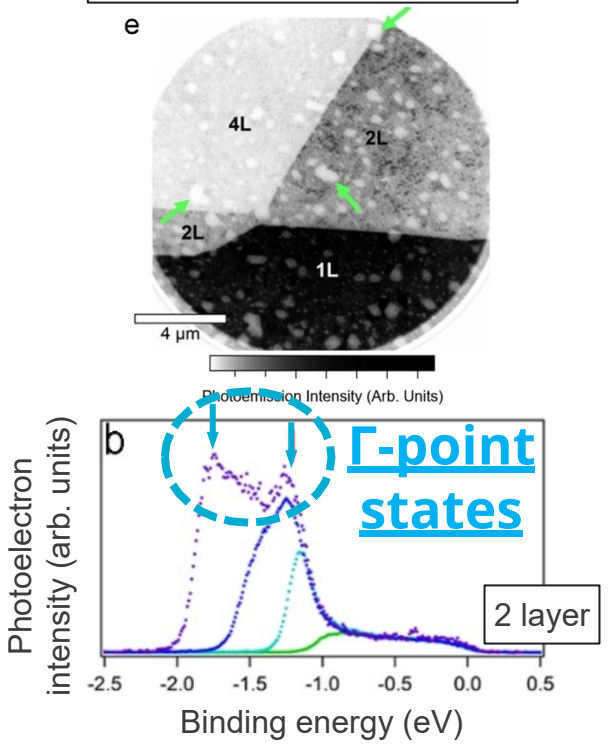
Reciprocal space PEEM

Accessible by UV-photoemission



Similar to angle-resolved photoemission spectroscopy

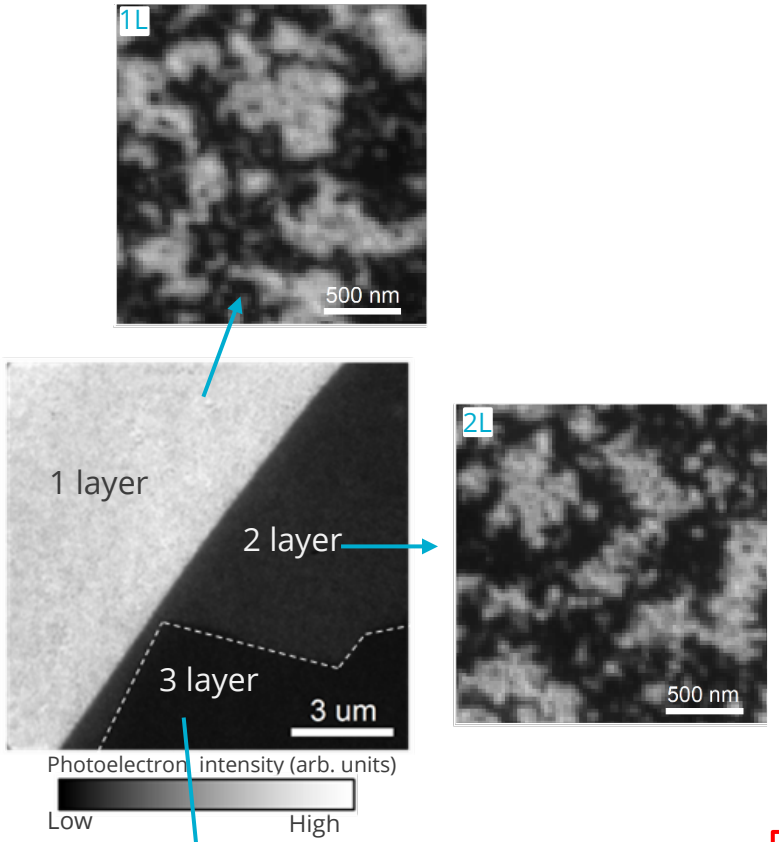
Real space PEEM

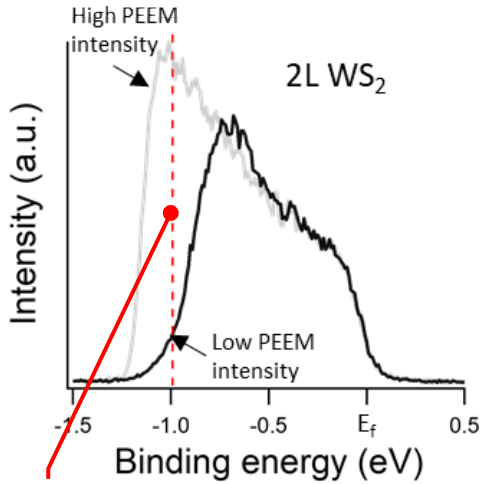


- PEEM probes the occupied electronic states in real space & reciprocal space

  - Deep UV-photoemission probes the states only near the Brillion zone center (i.e., Γ-point)

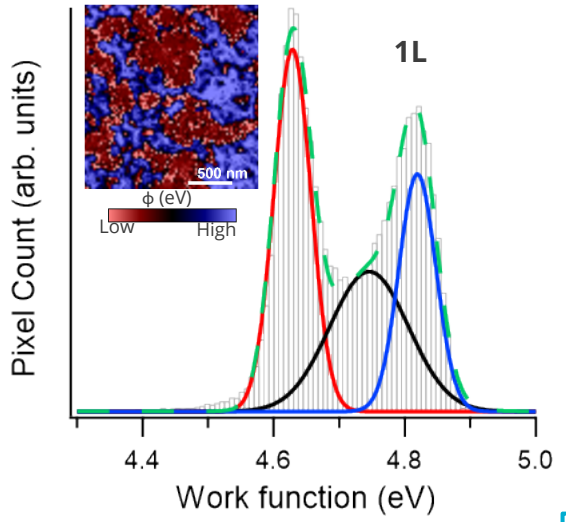
We observe submicron-scale work function heterogeneity in WS_2 exfoliated on freshly-deposited Au

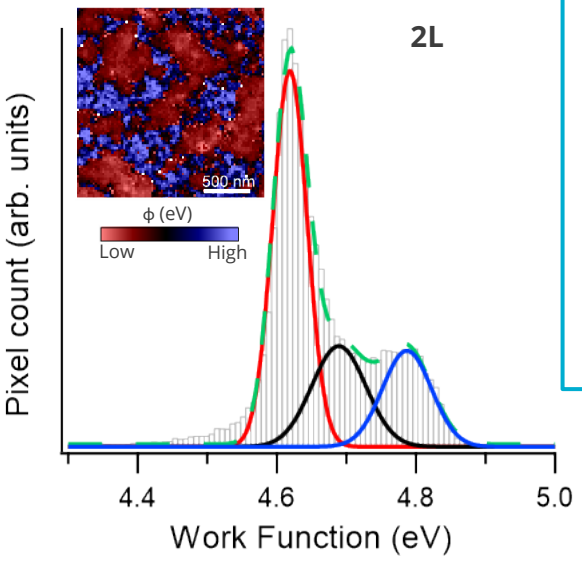


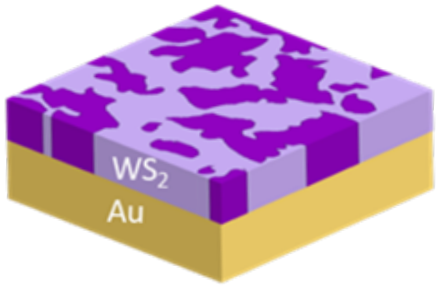


PEEM contrasts arise from difference in work function

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



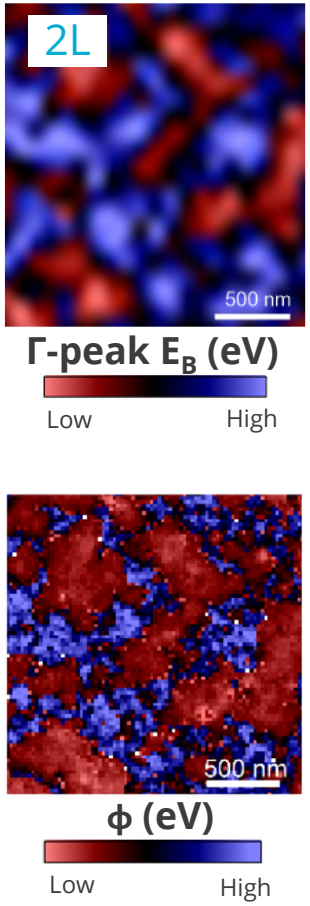


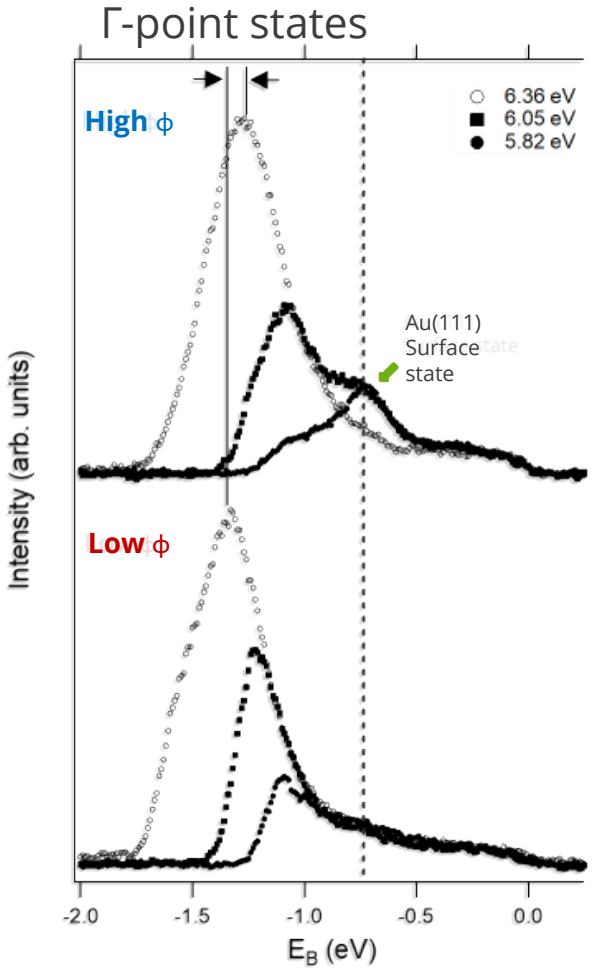


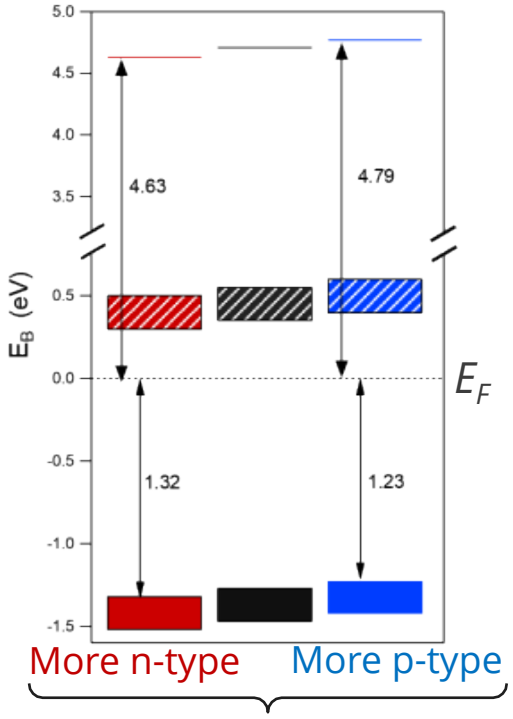
- Large work function variation (>200 meV)
- Varying carrier density within the WS_2 flake

Boehm et al., Nano Lett., 23, 2792-2799, 2023

We determine submicron-scale carrier density variations in freshly-deposited Au-WS_2 interfaces







within the single-crystalline flake

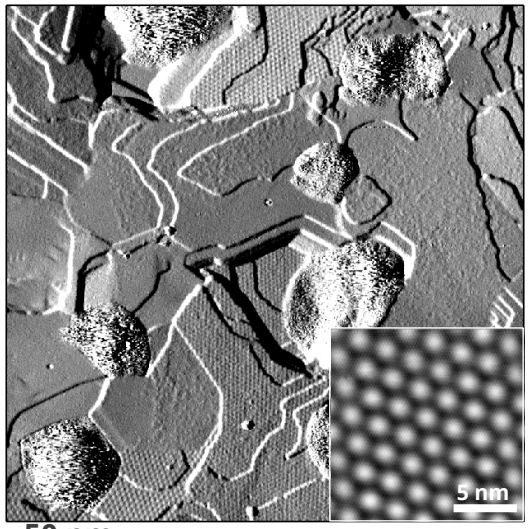
- Same micron-sized domains from photoelectron intensity & work function (ϕ) maps
- Higher work function regions show corresponding upshift in VBM
- Low BE peak (-0.7eV) observed near fermi level only in high work function areas
  - **Au (111) surface state:** impact of substrate?
- **Schottky barrier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

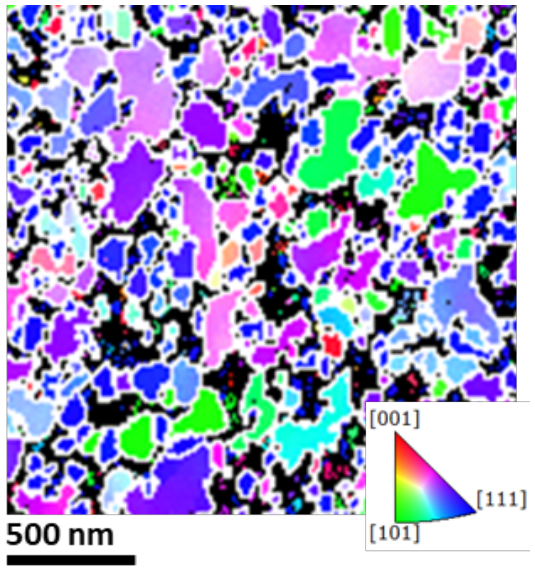
Low work function, more n-type	Medium work function	High work function, less n-type

Boehm et al., Nano Lett., 23, 2792-2799, 2023

Three predominant crystallographic orientations of the Au grains elucidated via EBSD

WS_2 covered as-deposited Au





Scanning tunneling microscopy:

- Atomic terraces of Au & trapped blisters
- Hexagonal Moiré patterns indicate closely adhered WS_2 to Au & van der Waals interface

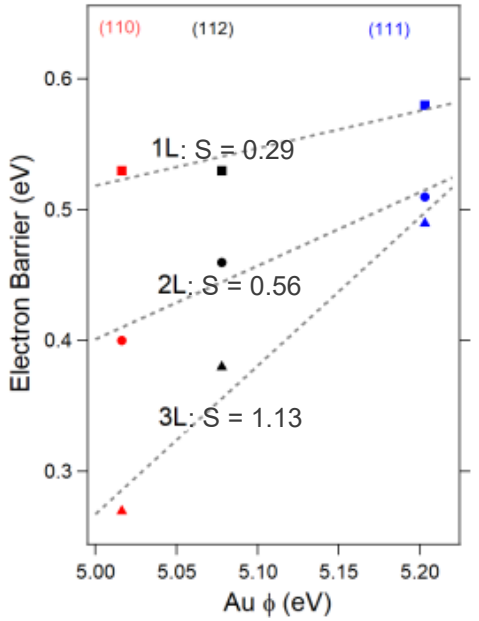
EBSD: Electron Backscatter Diffraction

- Majority of Au grains have (111), (112), or (110) facets according to inverse pole figure
- Consistent with localization of Moiré patterns in STM and Au(111) surface state in PEEM
- Same length scale as heterogenous electronic structure domains

Au	(110)	(112)	(111)	$\Delta\phi_{Au}$ (eV)
ϕ_{Au} (eV)	5.02	5.08	5.2	0.18

WS_2	1L	2L	3L
$\Delta\phi_{WS2}$ (eV)	0.18	0.16	0.13

$\Delta\phi_{Au} \approx \Delta\phi_{WS_2}$



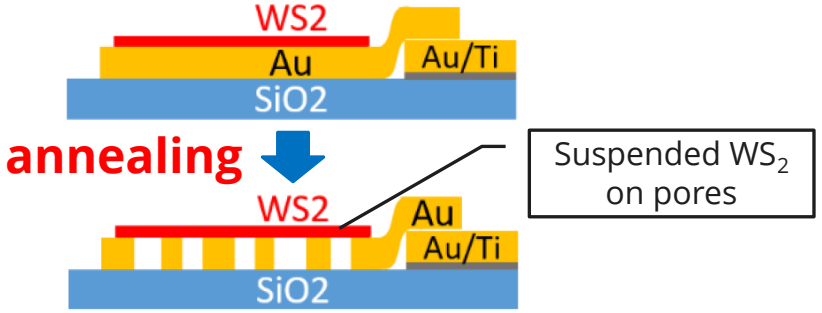
Take-home messages:

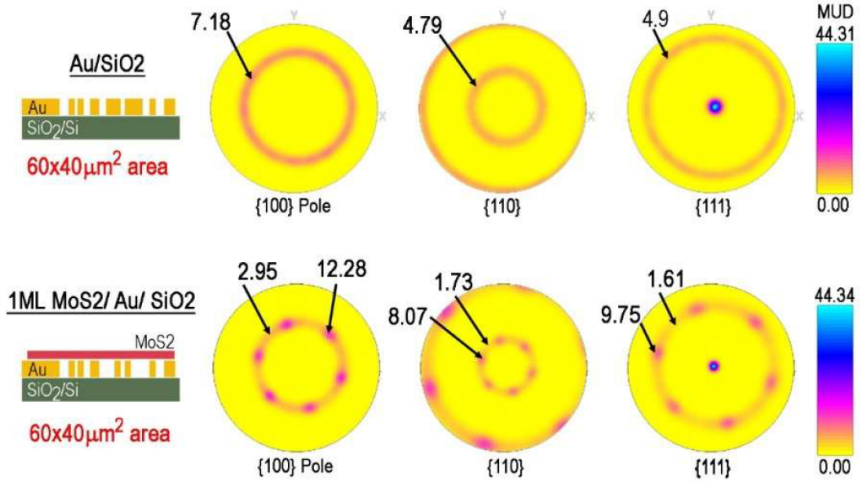
- **3 different Schottky barriers** within a single junction
- **Crystal facets of Au grains** govern the **Schottky barrier height** between Au & WS_2
- Relatively high S (pinning factor or interface parameter) expected for van der Waals bonding

Boehm et al., Nano Lett., 23, 2792-2799, 2023

What happens if there are WS_2-Au(111) interfaces only?

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

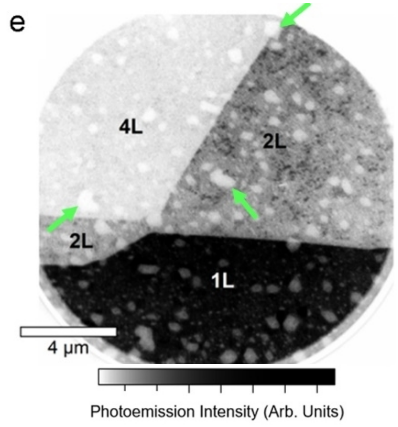


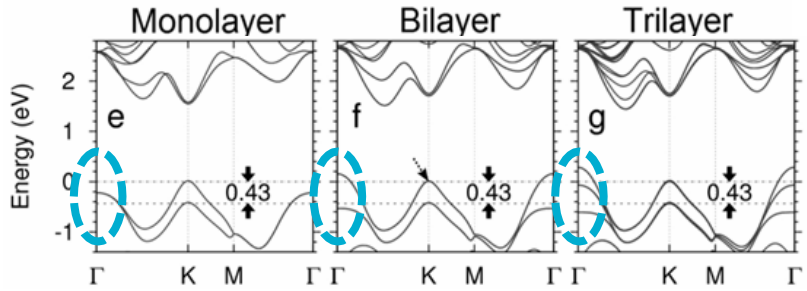


EBSD confirmed pseudo-epitaxial interface

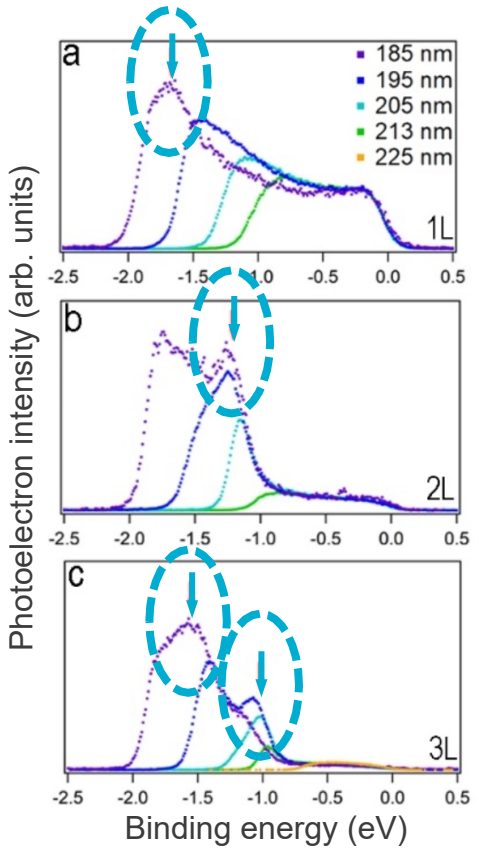
Fonseca, et al., Nature Communications 11, 5 (2020)

- Photoelectron spectra show characteristic splitting of the highest occupied states at Γ-point in this pseudo-epitaxial WS_2-Au system



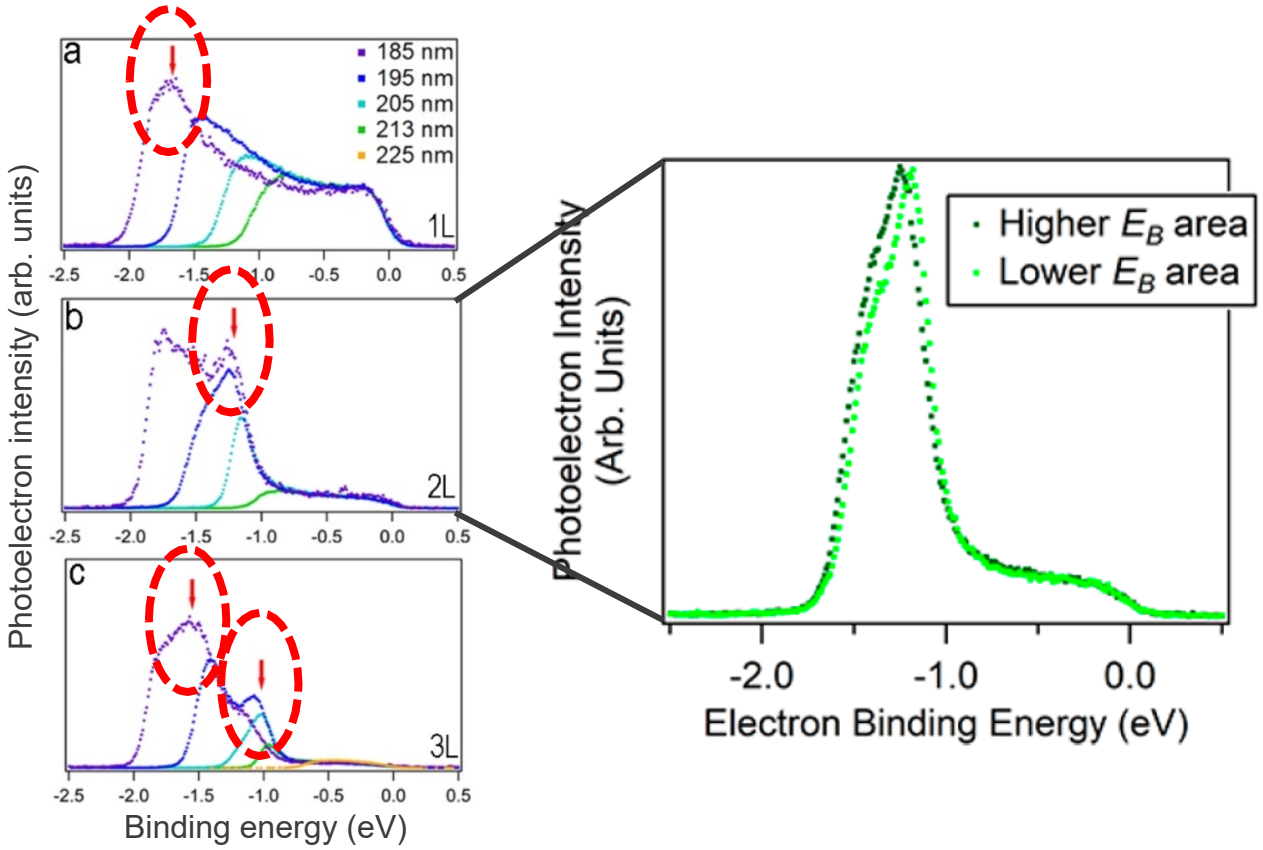


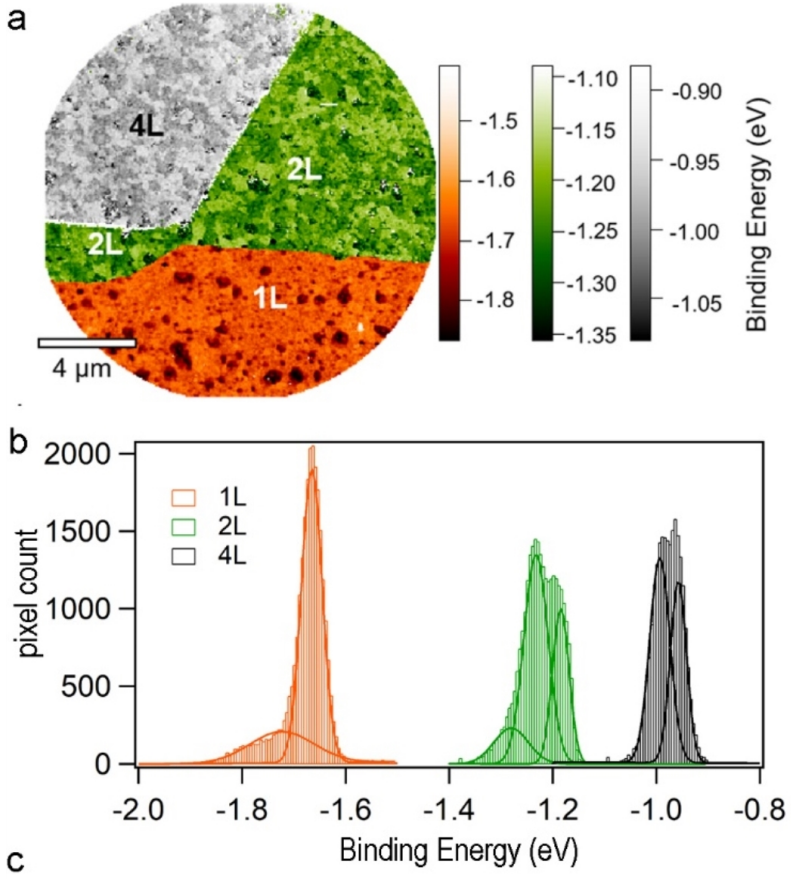
Zeng, et al., Scientific Reports 3, 1608 (2013)



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

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



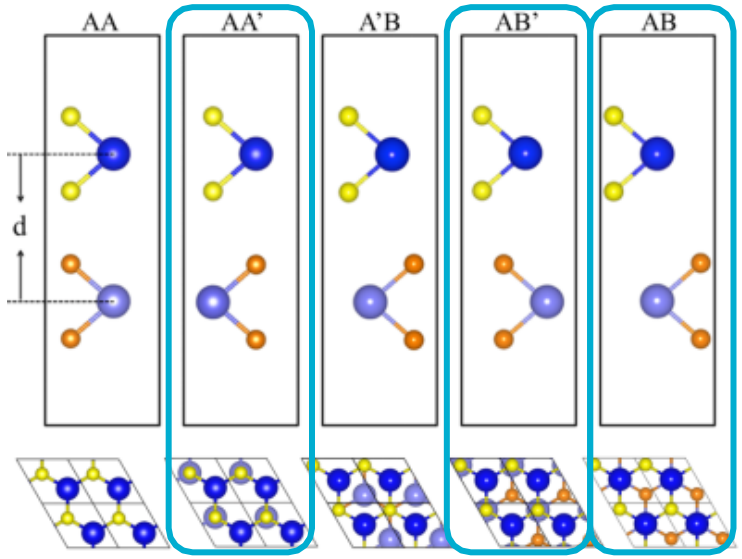


- The variations of the Γ-point peak position are 30-50meV
- Shape & size of the variations match the crystal grains in the Au-film
- The variations found in multilayer, but absent in single layer

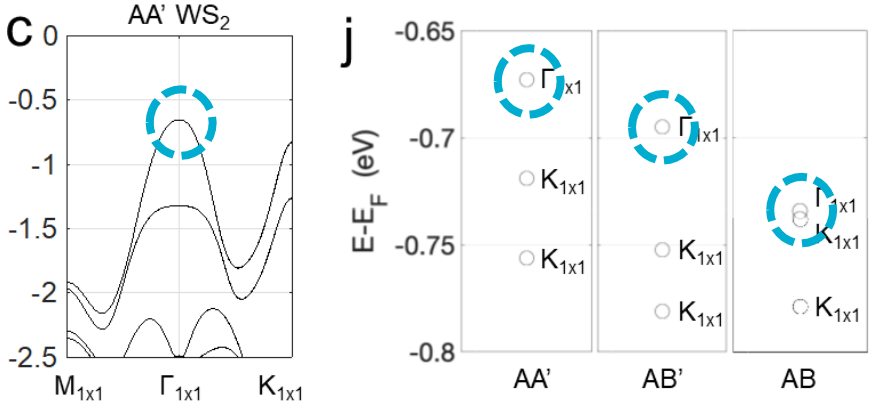
Hypothesis: layer slippage due to the strong adhesion between WS_2 & Au?

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

DFT modeling supports the layer slippage model

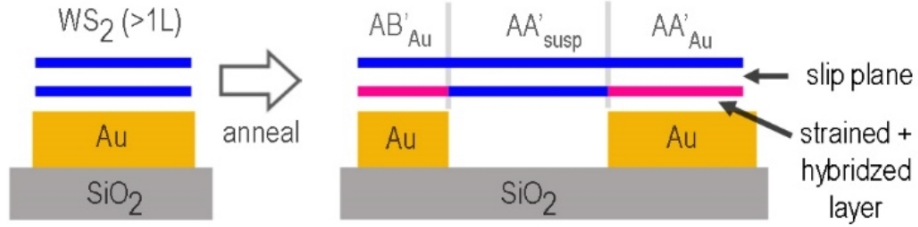


He, et al., PRB 89, 075409 (2014)



- 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



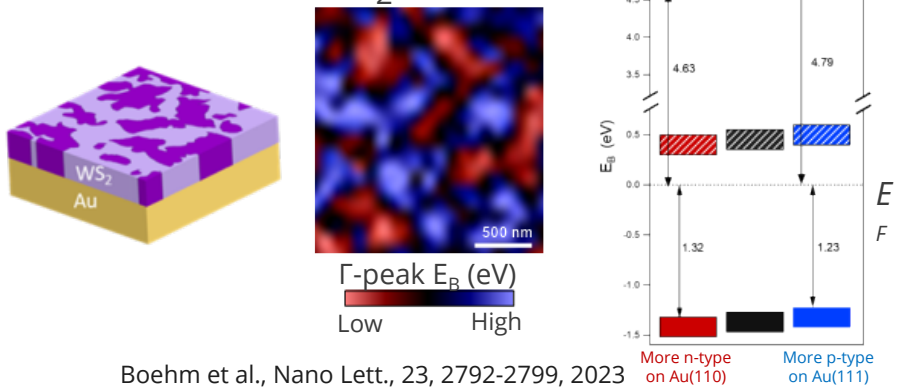
Take-home message:

- Microstructures of Au films plays important role in the electronic properties of the WS_2-Au contacts

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

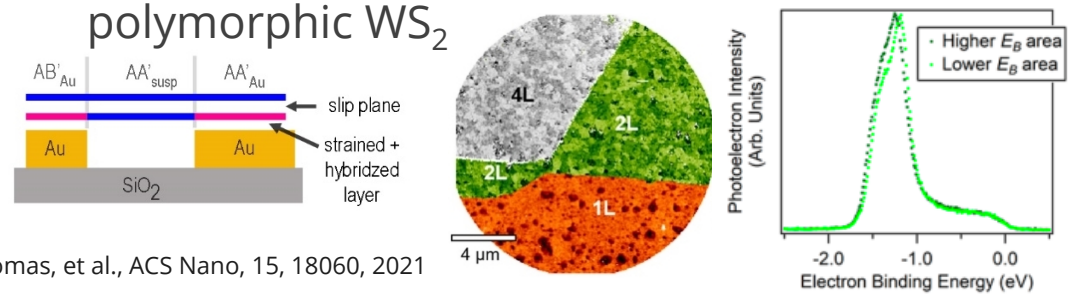
Concluding remarks

- Upside-down geometry allows direct access to semiconductor electronic properties & help us understand the metal contacts
- Microstructures of Au films plays important role at WS_2-Au contacts
  - Au grains' facet govern the local electronic structures of WS_2



Boehm et al., Nano Lett., 23, 2792-2799, 2023

  - Layer slippage induces stacking variation & polymorphic WS_2



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

Special thanks:

- WS_2-Au interface interactions

N. Bartelt, C. Smyth, F. Leonard, C. J. Thomas, T.-M. Lu, R. G. Copeland, P. Mantos

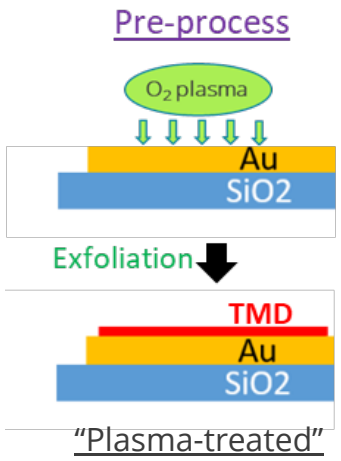
Announcement:

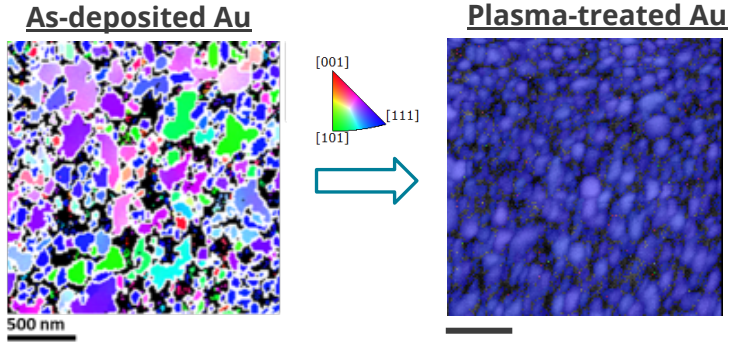
Looking for postdoc candidate: investigating the optical resonances in TMD disk structures

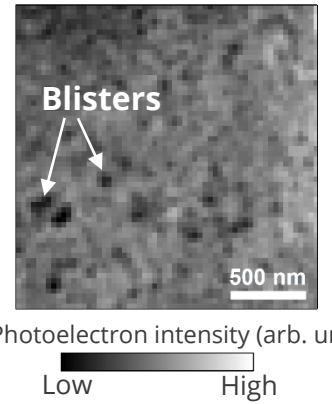
Thank you for your attention!

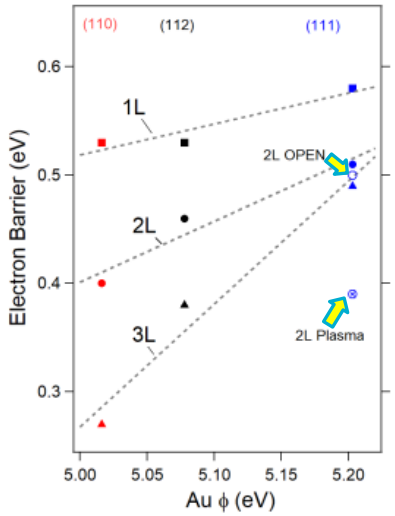
Supplemental info

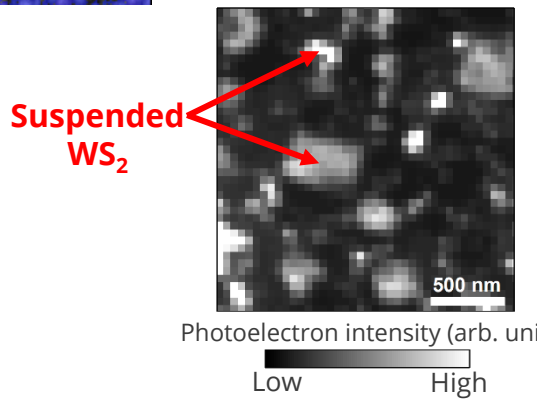
TMD on OPEN and Plasma-treated Au yield more uniform electronic structures

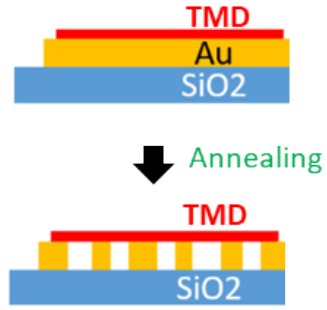


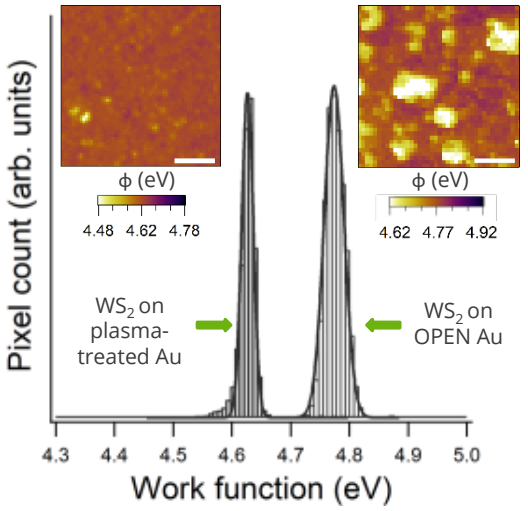


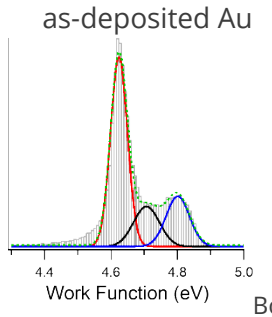




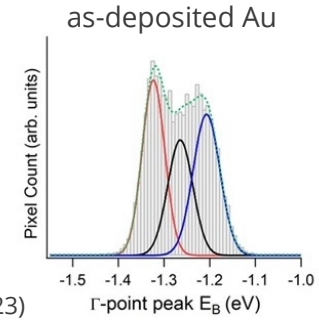


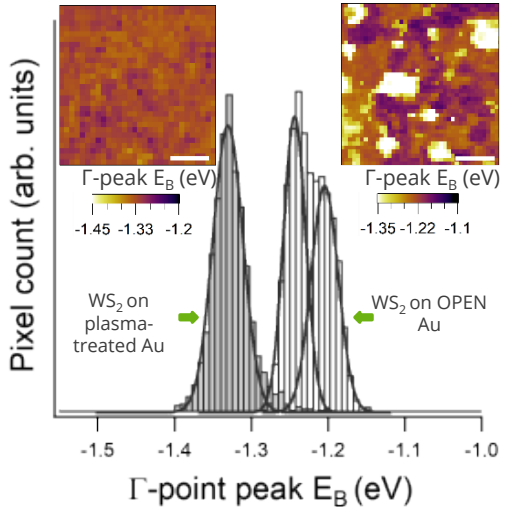






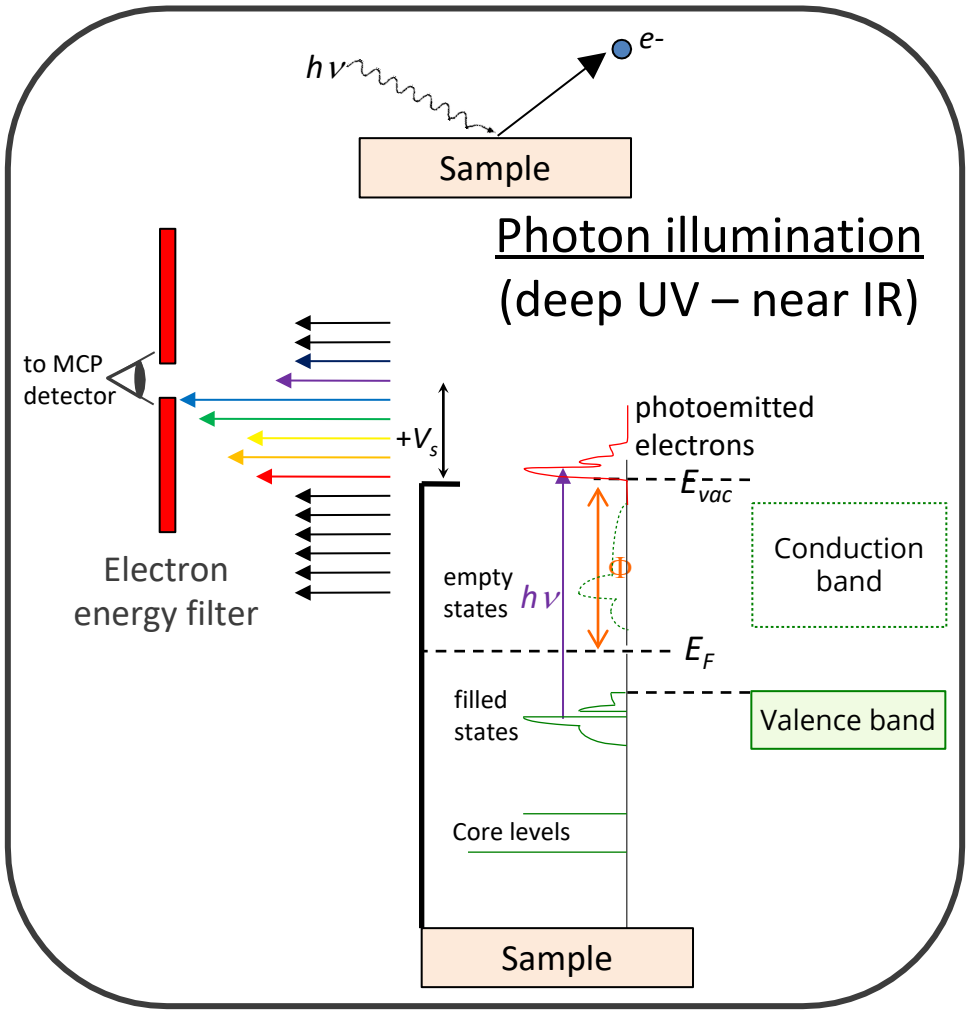
1 SBH for each WS_2–Au junction





Boehm, et al., Nano Letters, 23(7), 2792–2799. (2023)

Reimagining what we can do with photoelectron imaging



Photoelectric effect

Occupied electronic density of state

Transition probability

Final state — Initial state — Energy conservation

$$w_{i\to f} \propto \left|\langle f|H^{int}|i\rangle\right|^2 \delta(E_f - E_i - h\nu)$$

$$H^{int} = \frac{1}{2mc}\left(A \cdot p_{op} + p_{op} \cdot A\right)$$

Hamiltonian for the interaction

Vector potential of the electromagnetic radiation

Momentum operator of the electron

Electromagnetic field

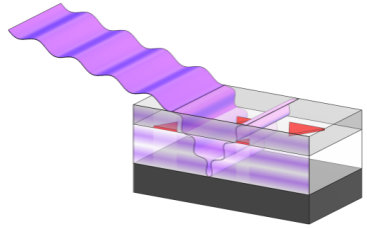
Photoelectron yield varies strongly due to electromagnetic field distribution & occupied electron density of states

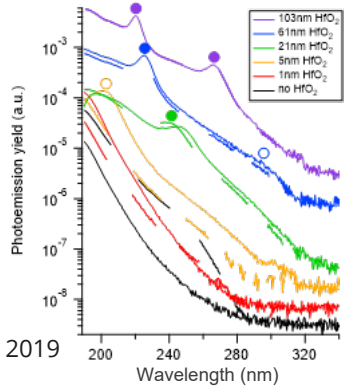
Light-matter interactions & electronic properties are probed based on the photoelectron intensity from the nanoscale materials

Figure courtesy: M. Berg, C. Chan

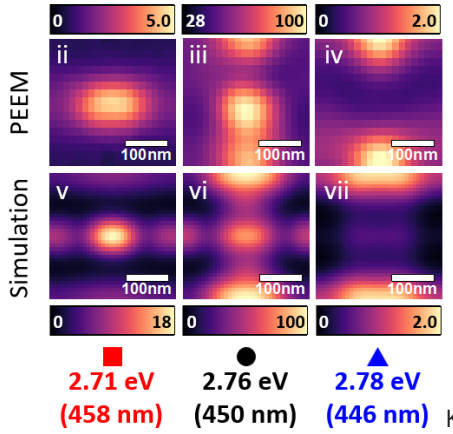
We examine electronic & optical properties using PEEM

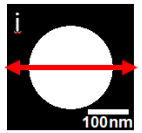
- **Electromagnetic field imaging**
  - Probing Fabry–Pérot resonance of dielectric cavities in **UV**





Berg et al., Phys. Rev. Applied, 12, 064064, 2019

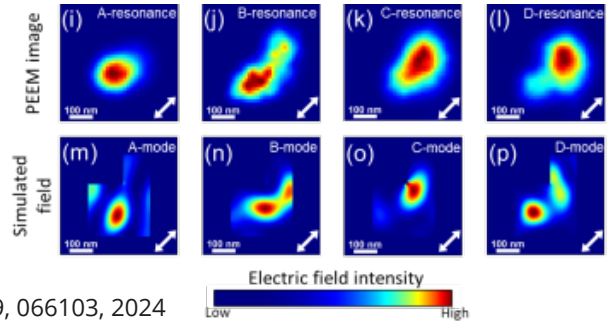


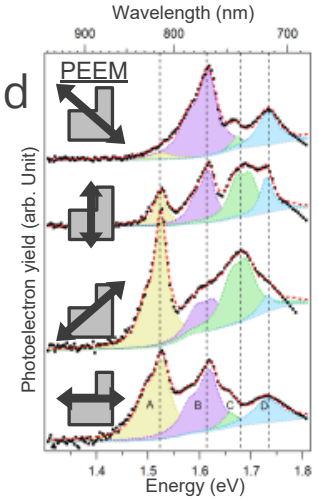


- Evaluating light-matter interaction & inelastic mean-free path (~35 nm) in Mie metasurface in **UV-visible** range

Kim et al., in preparation

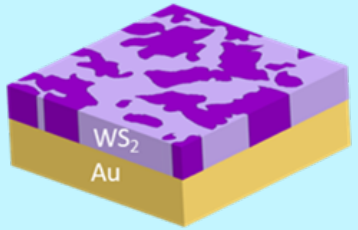
- Imaging **visible-near IR** resonances in Bound states in the continuum metasurfaces

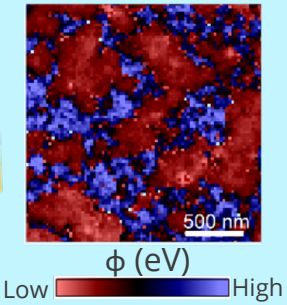




Boehm, A. et al., APL Photonics, 9, 066103, 2024

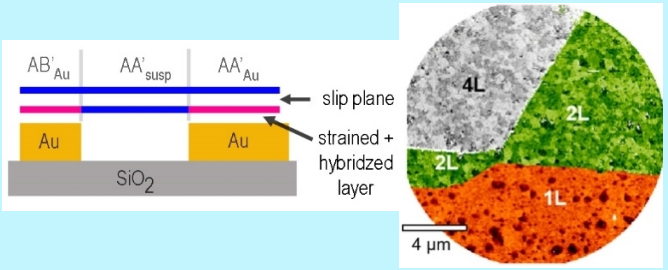
- **Electronic structures of interfaces between WS_2 & gold**
  - Crystal facets of Au grains govern the local electronic structures of WS_2





Boehm et al., Nano Lett., 23, 2792-2799, 2023

- Strong interaction induced layer slippage between WS_2 & Au grains resulting in stacking variation



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