

Characterization of 2D Materials : Challenges and Opportunities

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Acknowledgements

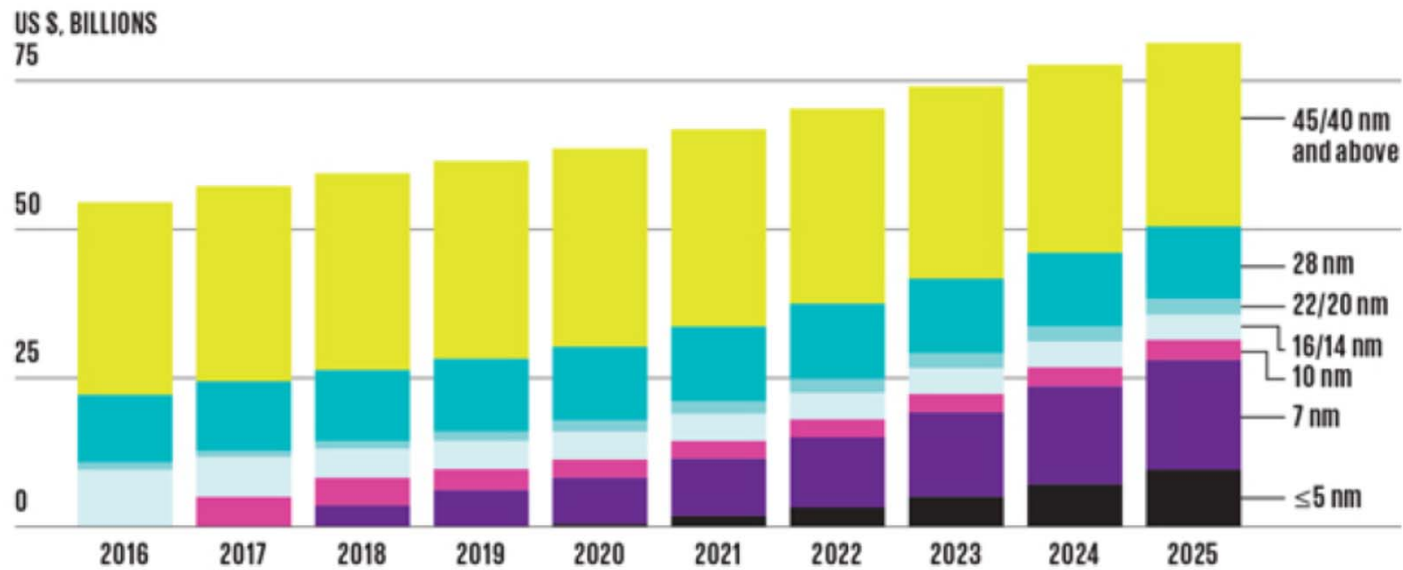
- Students
 - Angie Azcatl, Hui Zhu, Chris Smyth, Qingxiao Wang, C. Zhang
- Research Scientists
 - Rafik Addou, Xiaoye Qin, Stephen McDonnell (Now @ UVa)
- Colleagues
 - K.J.Cho (DFT of interfaces), Chris Hinkle (MBE), Jiyoung Kim (Raman),
 - Moon Kim (HRTEM), Chad Young (Device Measurements)
- Collaborators
 - Joerg Appenzeller (Purdue), Paul Hurley (UCC/Tyndall), Ali Javey (UC Berkeley), Josh Robinson (Penn State)



Center for Low Energy Systems Technology



- **Materials Challenges**
- Tools and Methods
- TMDs
- Summary



Source: IBS

The Evolving Foundry Market: Chips built with 10-nanometer technology will come first. But International Business Strategies projects that Apple and others will be drawn to the next node in line: 7 nm.

IEEE Spectrum, 30 Dec 2016

- CMOS performance requirements point toward alternative...
 - Materials (e.g., Si→Ge→III-V→2D?)
 - Structures (planar → 3D Fin FET → Gate all around)
 - Devices (MOSFET → TFET)

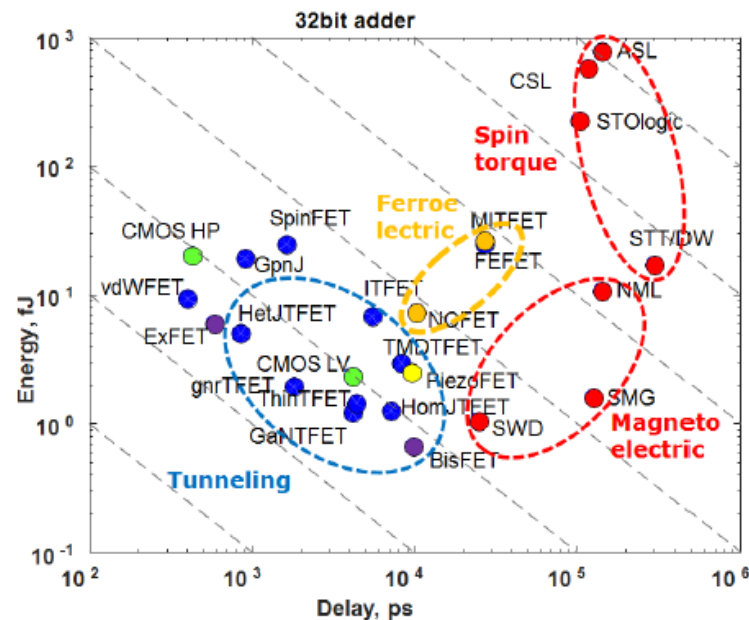


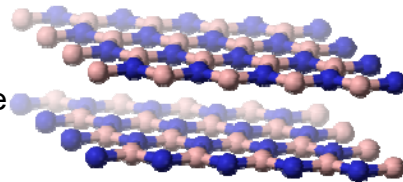
Fig. 5. Switching energy vs. delay of a 32-bit adder.

Beyond CMOS – Some Recent References

Nikinov and Young, JxCDC (2015), Proc. IEEE (2013); Bernstein, et al., Proc. IEEE 98 (2010) 2169; Seabaugh and Zhang, Proc. IEEE 98 (2010) 2095; D. Jena, Proc. IEEE (2013)

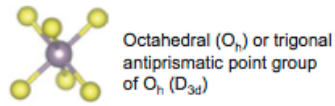
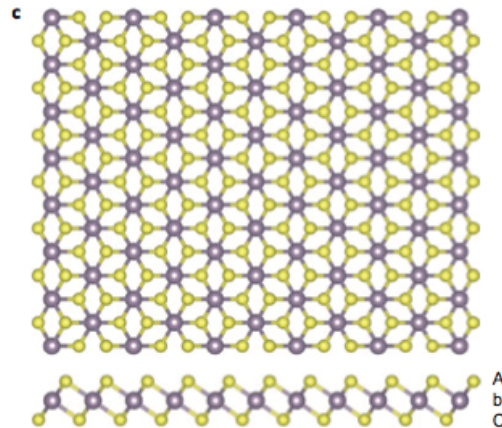
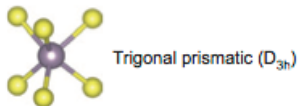
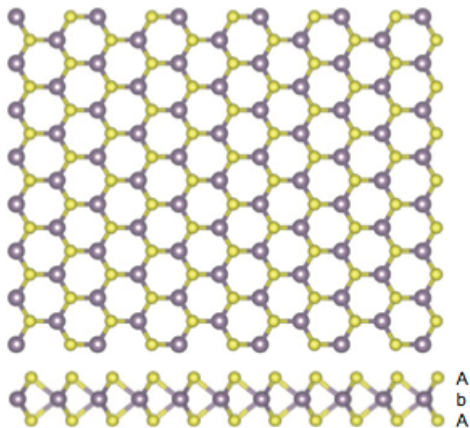
Boron Nitride

http://en.wikipedia.org/wiki/Boron_nitride

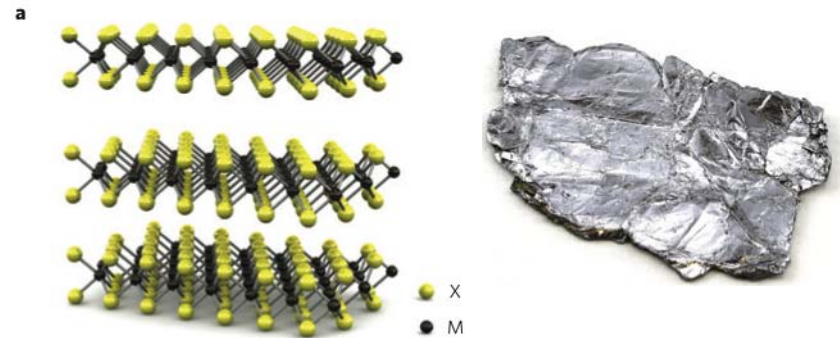


Chhowalla et al. Nature Chemistry 5 (2013) 263

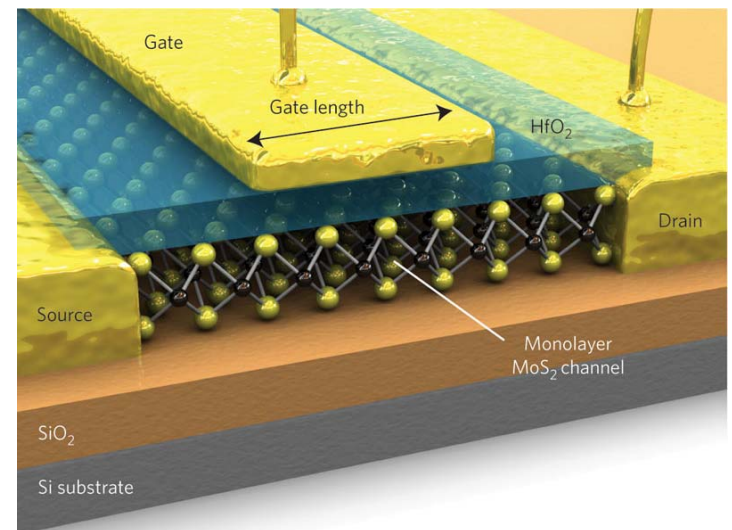
										MX ₂ M = Transition metal X = Chalcogen											
H																	He				
Li	Be											B	C	N	O	F	Ne				
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar				
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo				



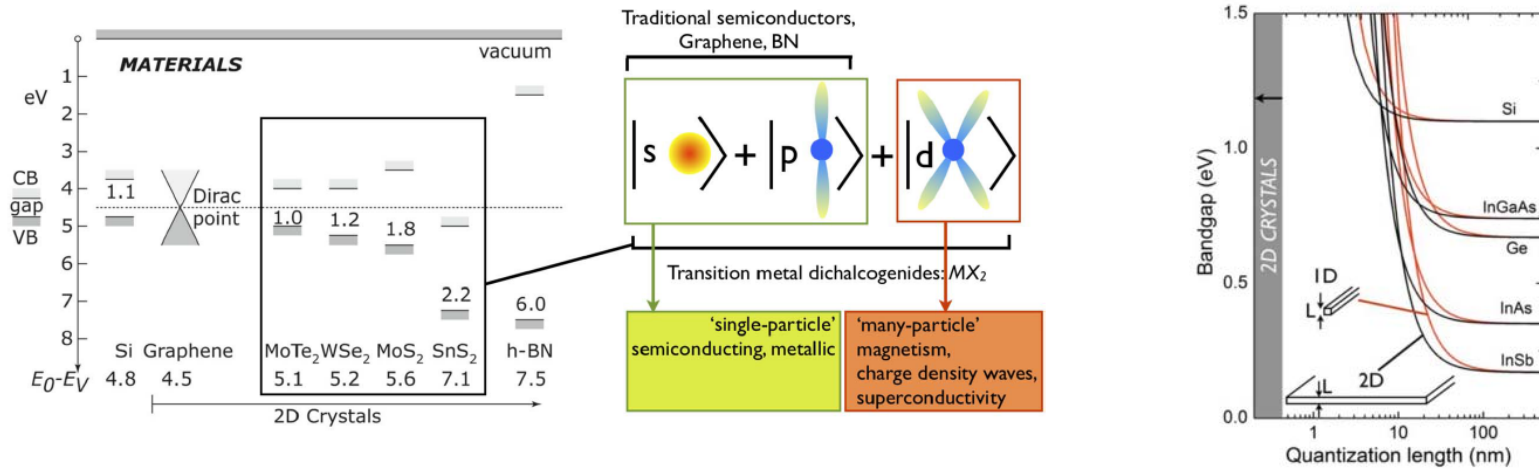
MoS₂



Wang et al. Nature Nanotech. 7 (2012) 699



B. Radisavljevic et al. Nature Nanotech. 6 (2011)



- Limited quantization effects for single layer channels
- Useful effective masses, bandgaps, and band offsets for transistors
- Full penetration of electric field through layer
- Anticipated dearth of defects like dangling bonds anticipated
- TMD Combinations + *d* orbitals anticipated to enable new functionalities

Table 1

Layered materials conference series titles with book chapters covering layered materials research from 1976–2000.

Physics and chemistry of materials with low-dimension structures

(Previously published under the series title: physics and chemistry of materials with layered structures)

1. R.M.A. Lieth (Ed.): *Preparation and Crystal Growth of Materials with Layered Structures*. 1977 ISBN 90-277-0638-7
 2. F. Levy (Ed.): *Crystallography and Crystal Chemistry of Materials with Layered Structures* 1976 ISBN 90-277-0586-0
 3. T.J. Wieting and M. Schluter (eds.): *Electrons and Phonons in Layered Crystal Structures*. 1979 ISBN 90-277-0897-5
 4. P.A. Lee (Ed.): *Optical and Electrical Properties*. 1976 ISBN 90-277-0676-X
 5. F. Hulliger: *Structural Chemistry of Layer-Type Phases*. Ed. by F. Levy. 1976 ISBN 90-277-0714-6
 6. F. Levy (Ed.): *Intercalated Layered Materials*. 1979 ISBN 90-277-0967-X
- Physics and chemistry of materials with low-dimensional structures series a: layered structures**
7. V. Grasso (Ed.): *Electronic Structure and Electronic Transitions in Layered Materials*. 1986 ISBN 90-277-2102-5
 8. K. Motizuki (ed.): *Structural Phase Transitions in Layered Transition Metal Compounds*. 1986 ISBN 90-277-2171-8
 9. L.J. de Jongh (ed.): *Magnetic Properties of Layered Transition Metal Compounds*. 1990 ISBN 0-7923-0238-9
 10. E. Doni, R. Giralanda, G. Pastori Parravicini and A. Quattropani (eds.): *Progress in Electron Properties of Solids*. Festschrift in Honour of Franco Bassani. 1989 ISBN 0-7923-0337-7
 11. C. Schlenker (Ed.): *Low-Dimensional Electronic Properties of Molybdenum Bronzes and Oxides*. 1989 ISBN 0-7923-0085-8
 12. Not published.
 13. H. Aoki, M. Tsukada, M. Schluter and F. Levy (eds.): *New Horizons in Low-Dimensional Electron Systems*. A Festschrift in Honour of Professor H. Kamimura. 1992 ISBN 0-7923-1302-X
 14. A. Aruchamy (Ed.): *Photoelectrochemistry and Photovoltaics of Layered Semiconductors*. 1992 ISBN 0-7923-1556-1
 15. T. Butz (Ed.): *Nuclear Spectroscopy on Charge Density Wave Systems*. 1992 ISBN 0-7923-1779-3
 16. G. Benedek (Ed.): *Surface Properties of Layered Structures*. 1992 ISBN 0-7923-1961-3
 17. W. Muller-Warmuth and R. Schollhorn (eds.): *Progress in Intercalation Research*. 1994 ISBN 0-7923-2357-2
 18. L.J. de Jongh (Ed.): *Physics and Chemistry of Metal Cluster Compounds. Model Systems for Small Metal Particles*. 1994 ISBN 0-7923-2715-2
 19. E.Y. Andrei (Ed.): *Two-Dimensional Electron Systems. On Helium and other Cryogenic Substrates*. 1997 ISBN 0-7923-4738-2
 20. A. Furrer: *Neutron Scattering in Layered Copper-Oxide Superconductors*. 1998 ISBN 0-7923-5226-2
 21. R.B. Heimann, S.E. Evsyukov and L. Kavan (eds.): *Carbyne and Carbynoid Structures*. 1999 ISBN 0-7923-5323-4
 22. F.W. Boswell and J.C. Bennett (eds.): *Advances in the Crystallographic and Microstructural Analysis of Charge Density Wave Modulated Crystals*. 1999 ISBN 0-7923-5604-7
 23. W. Andreoni (Ed.): *The Physics of Fullerene-Based and Fullerene-Related Materials*. 2000 ISBN 0-7923-6234-9
 24. H.P. Hughes and H.I. Stamberg (eds.): *Electron Spectroscopies Applied to Low-Dimensional Structures*. 2000 ISBN 0-7923-6526-7

J. Appl. Physics 37 (1966) 1928

Single Crystals of MoS₂ Several Molecular Layers Thick

R. F. FRINDI*

Physics and Chemistry of Solids, Cavendish Laboratory, Cambridge, England

(Received 24 March 1965; in final form 18 June 1965)

Adv. Physics 18 (1969) 193-335

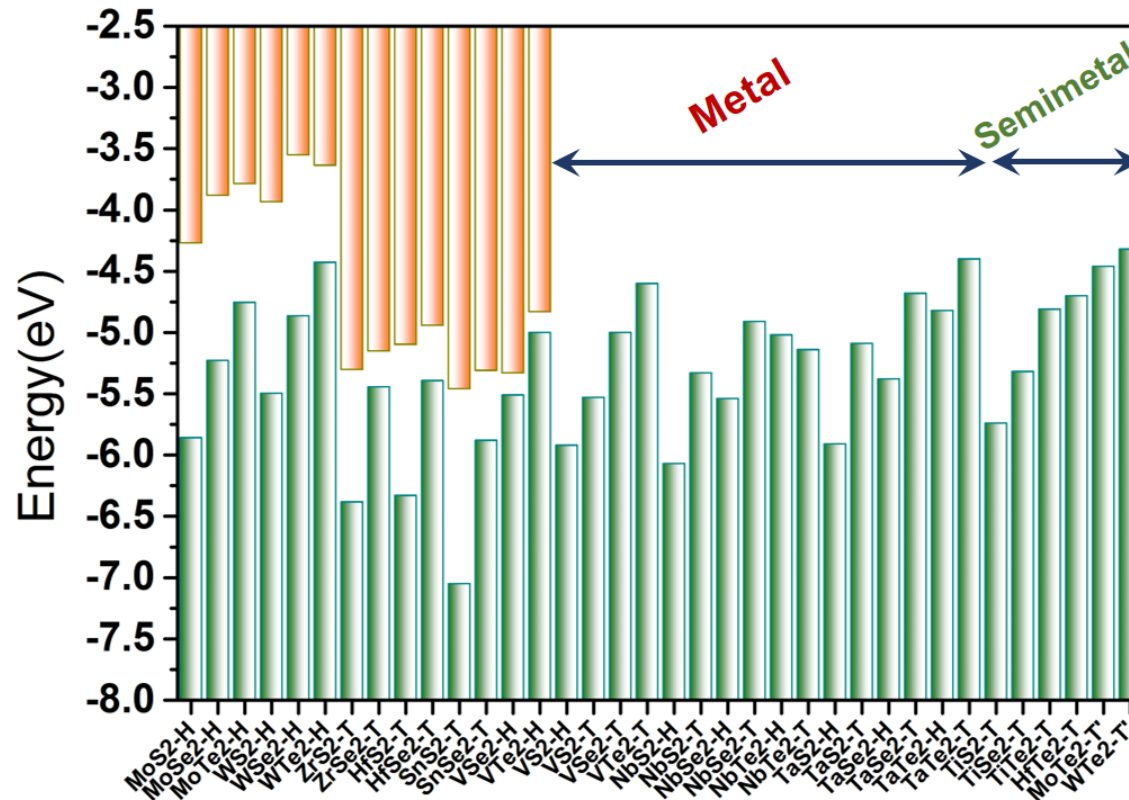
The Transition Metal Dichalcogenides**Discussion and Interpretation of the Observed Optical, Electrical and Structural Properties**By J. A. WILSON and A. D. YOFFE
Cavendish Laboratory, Cambridge

Prog. Surf. Sci. 29 (1988) 1-167

INTERFACIAL PROPERTIES OF SEMICONDUCTING TRANSITION METAL CHALCOGENIDES

W. JAEGERMANN and H. TRIBUTSCH

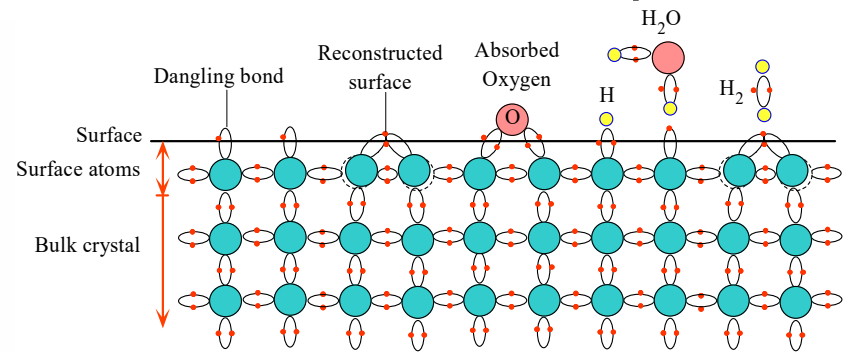
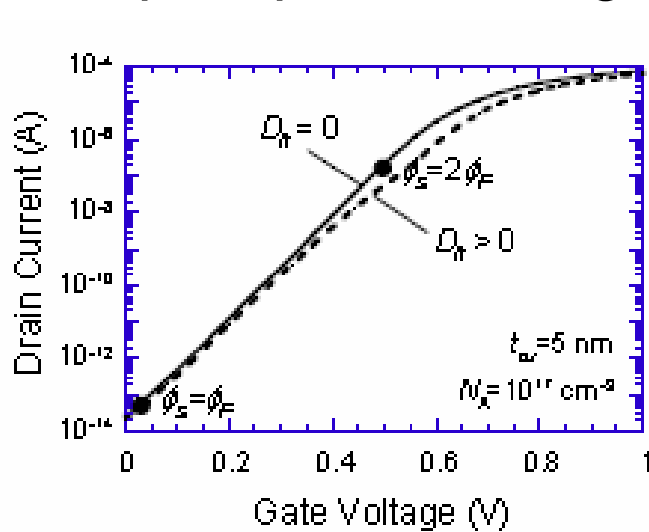
*Hahn-Meitner-Institut, Bereich S
Glienicke Str. 100, D-1000 Berlin 39, Germany*



- Useful band structure for TFET heterostructure transistors
- Metal and semi-metal properties
- Applications in Nanoelectronics, Optoelectronics, Photovoltaics, and Photocatalysis

See also: C. Gong *et al.* APL 103 (5), 053513 (2013); APL 107 (2015) 139904

Steep slope switching: The Effect of Interface Traps



At the surface of a hypothetical two dimensional crystal, the atoms cannot fulfill their bonding requirements and therefore have broken, or dangling, bonds. Some of the surface atoms bond with each other; the surface becomes reconstructed. The surface can have physisorbed and chemisorbed atoms.

Fig. 26 Theoretical I_D - V_G curves for $D_{it}=0$ and $D_{it, min}=2.7 \times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$.

From *Principles of Electronic Materials and Devices, Third Edition*, S.O. Kasap (© McGraw-Hill, 2005)

Subthreshold swing “SS”: gate voltage required to change the I_D by one decade

$$SS = \frac{\partial V_g}{\partial (\log I_d)} = \underbrace{\frac{\partial V_g}{\partial \psi_s}}_{\text{Body factor}} \underbrace{\frac{\partial \psi_s}{\partial (\log I_d)}}_{\text{Carrier injection mechanism}} = \frac{\ln(10)kT}{q} \left[1 + \frac{C_{bulk} + C_{it}}{C_{ox}} \right] \approx \frac{60T(K)}{300} \left[1 + \frac{C_{bulk} + C_{it}}{C_{ox}} \right]$$

Steep slope switching: The Effect of Interface Traps

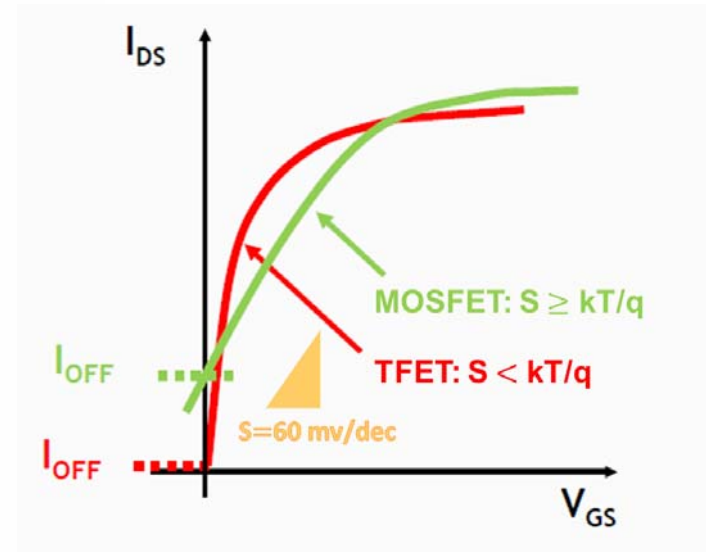
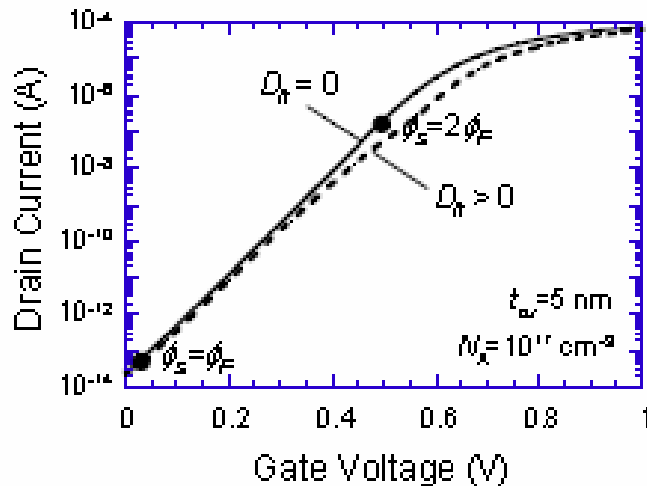


Fig. 26 Theoretical I_D - V_G curves for $D_{it}=0$ and $D_{it,min}=2.7 \times 10^{10} \text{ cm}^{-2} \text{ eV}^{-1}$.

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Orientation and (Intrinsic) Interface State Density

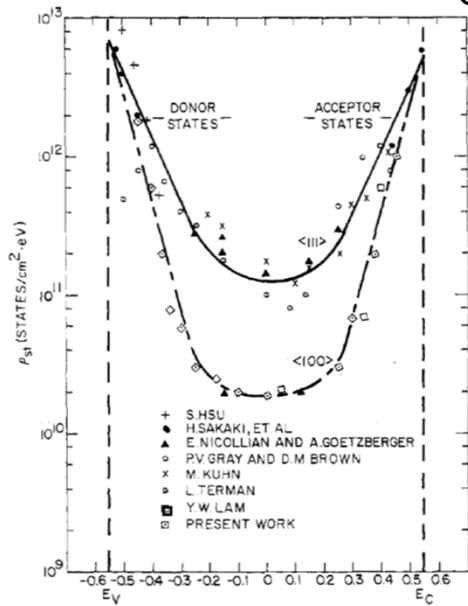


Fig. 3. Interface state density in the Si-SiO₂ system.

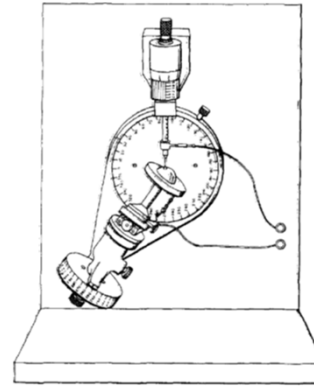
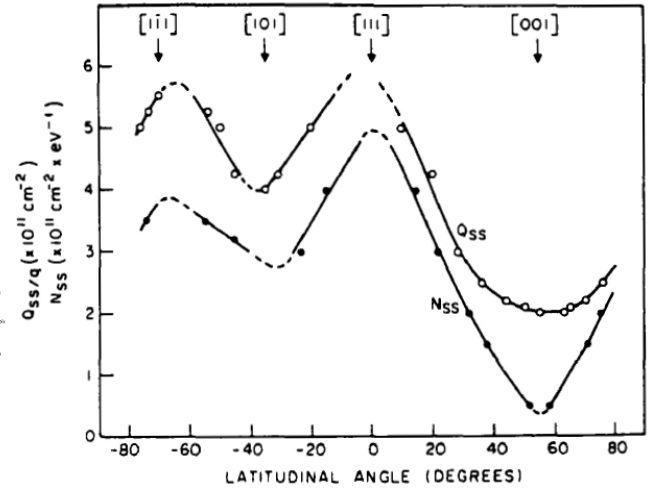
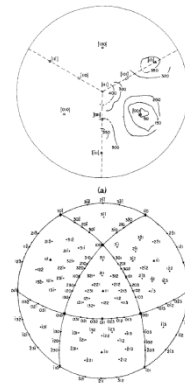


Fig. 1. Goniometer used for measuring the MOS capacitance and ac conductance on the surface of the oxidized silicon hemisphere. The hemisphere can be rotated to place any desired surface orientation under the stationary mercury-drop field electrode.



Arnold, *et al.*, APL 13(12) 413(1968)
Abowitz, *et al.*, PRL 18, 543 (1967)

White and Cricchi, IEEE TED 19(12), 1280 (1972)

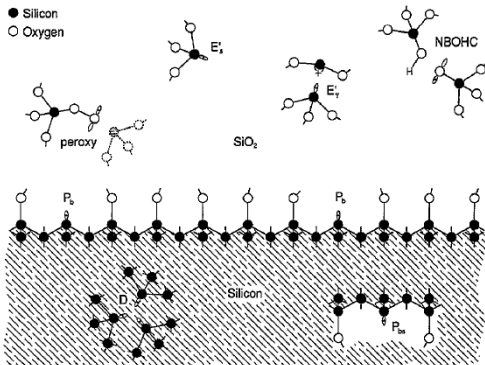


Figure 11. Paramagnetic point defects observed in Si-SiO₂ structures by electron spin resonance.

Helms and Poindexter, Rep.Prog.Phys. 57, 791 (1994)

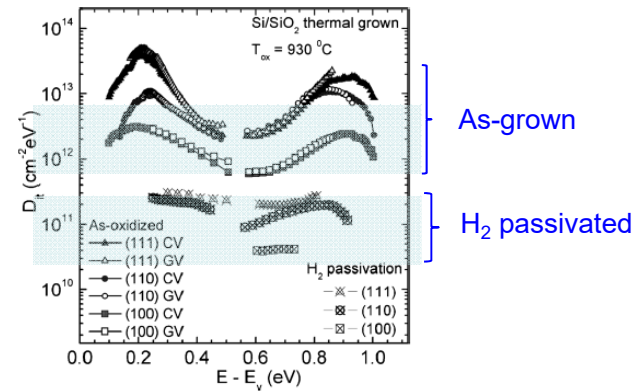


FIG. 3. $D_{it}(E)$ profiles of Si/SiO₂ interfaces derived from the CV (solid symbols) and GV (open symbols) methods in Si/SiO₂ samples fabricated on (100), (110), and (111) faces of Si. Results are shown for both the as-oxidized samples (no H-passivation) and those subjected to H₂ passivation (30 min anneal in 1.1 atm H₂ at 400 °C).

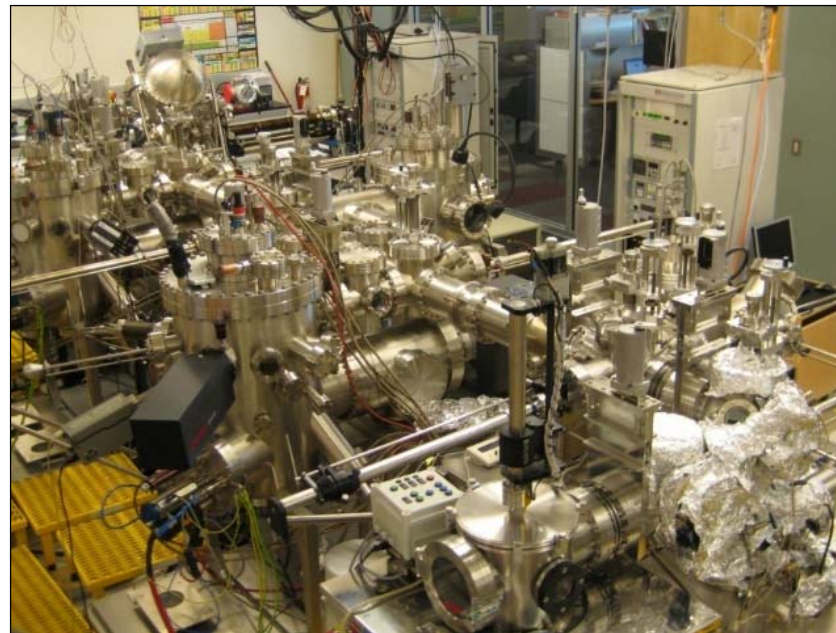
Thoan, *et al.*, J. Appl. Phys. 109, 013710 (2011)

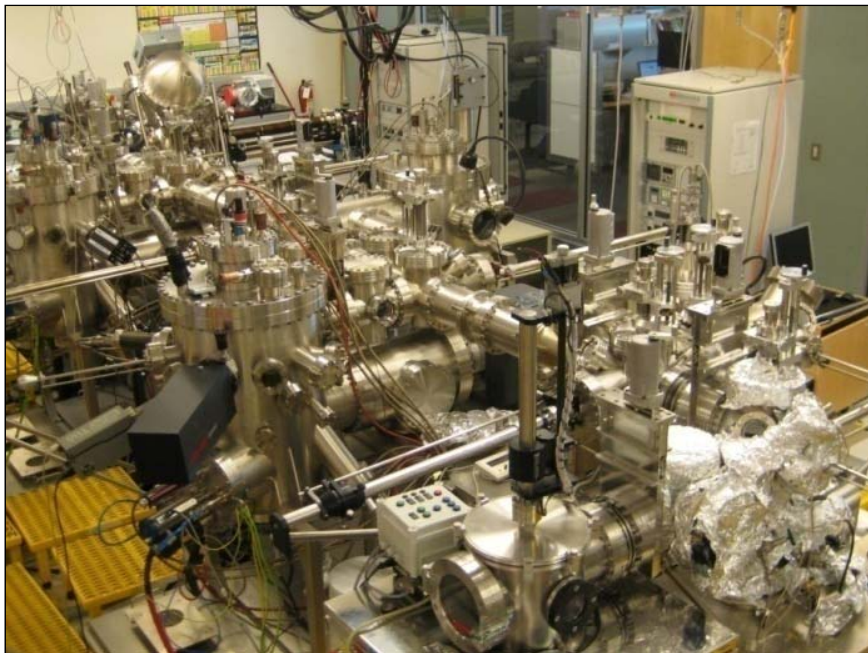
Intrinsic Interface Defects

- Si(100) surface orientation provides the lowest theoretical dangling bond density (reactivity)
 - Density Si(100) = 6.8×10^{14} /cm²
 - Density Si(111) = 11.8×10^{14} /cm²
 - Density Si(110) = 9.6×10^{14} /cm²
- Dangling bonds (“P_b”) provide a dominant defect population
 - As-grown interfaces can have densities $\geq 10^{12}$ /cm²
- Passivation of dangling bonds by hydrogen is effective
 - Density can be reduced to $\sim 5 \times 10^{10}$ /cm²
- Detection by sensitive characterization techniques
 - Surfaces: Thermal Desorption, FTIR, LEED, STS, PES, etc.
 - Devices: Spin Resonance, Capacitance-Voltage, Transistors, etc.
- Detection of defects in SiO₂ bonding as well
 - Strained bonds, dangling bonds (E’), peroxy bonding, hydroxyls, etc.
 - Depends on growth T, stoichiometry, charge injection, radiation, etc.
 - Can be located near interfaces (channel or gate) or within bulk

- **Large areas synthesis**
 - As large as possible or perhaps selective growth and within CMOS thermal constraints
 - “Back End of Line” → $T_{\max} = 500^{\circ}\text{C}$
- **High quality material**
 - Uniform, continuous/coalesced
 - Low defect density
 - Low impurity concentrations
 - High mobility
- **Contacts**
 - Doping control
 - Low contact resistance
- **Etching**
 - Atomic layer etching control

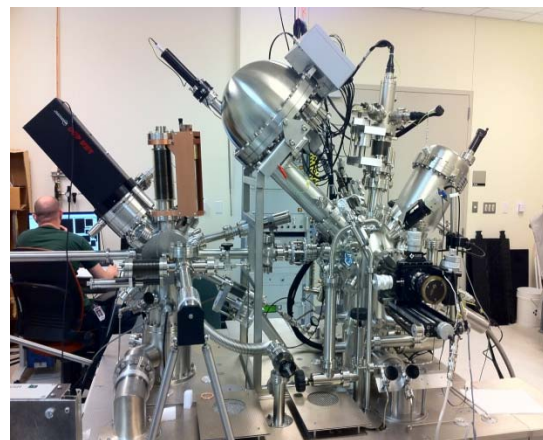
- Materials Challenges
- **Tools and Methods**
- TMDs
- Summary





UHV Cluster System

UHV Surface Science System



Annealing Module

- Custom UHV furnace
- 100mm sample, $T \leq 700^\circ \text{C}$, O_2 , 1atm.
- Ports for UV/ O_3 treatments
- Gas flow control

Sputter Module

- UHV capable
- 4 RF magnetrons
- Pressure/valve control
- Sample $T \leq 1000^\circ \text{C}$ (Pt)

PEALD Module

- Hot wall reactor
- Custom UHV transfer system
- 100mm sample, $T \leq 350^\circ \text{C}$
- Liquid, gas and solid sources
- Gas flow control

Metal MBD Module

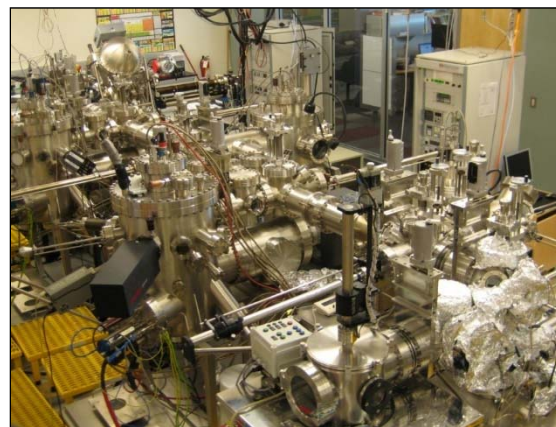
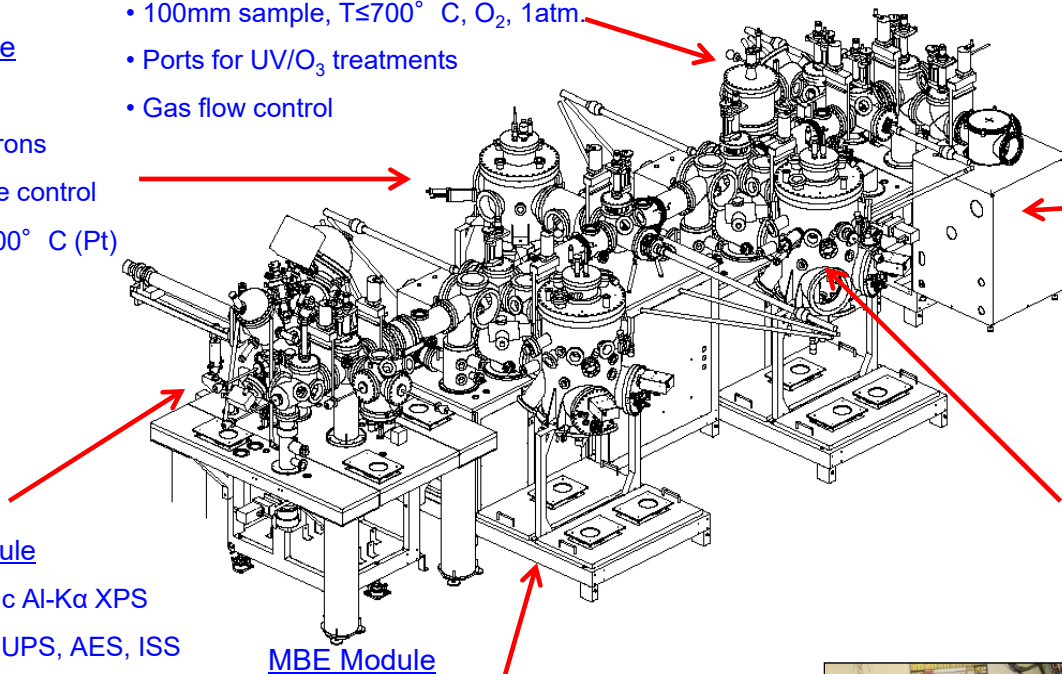
- 4 pocket e-gun hearth
- Sample heater ($T \leq 1000^\circ \text{C}$)
- Effusion cells
- Atomic hydrogen source (H_2 cracker)
- RHEED

Analytical Module

- Monochromatic Al-K α XPS
- High Intensity UPS, AES, ISS
- LEED
- Substrate size flexible
- 1000°C sample heater
- LN_2 sample cooling
- Sample rotation, ARXPS

MBE Module

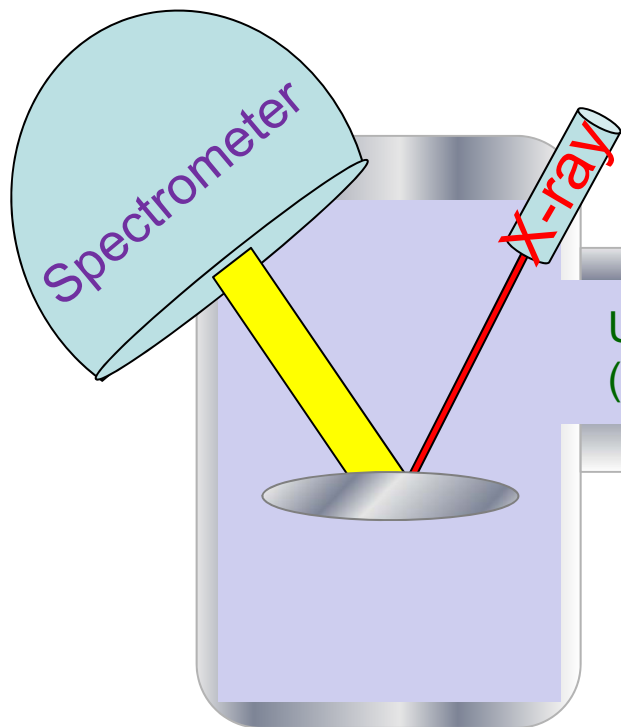
- 2 e-gun hearths (Group IV – Si, Ge)
- P, As, Sb, B effusion cells
- 100mm wafer, $T \leq 1200^\circ \text{C}$, shutter
- QMS (x-beam), quartz microbalance
- RHEED





Remote Plasma-Enhanced R200 ALD Reactor at UT-Dallas

High Resolution Monochromatic XPS



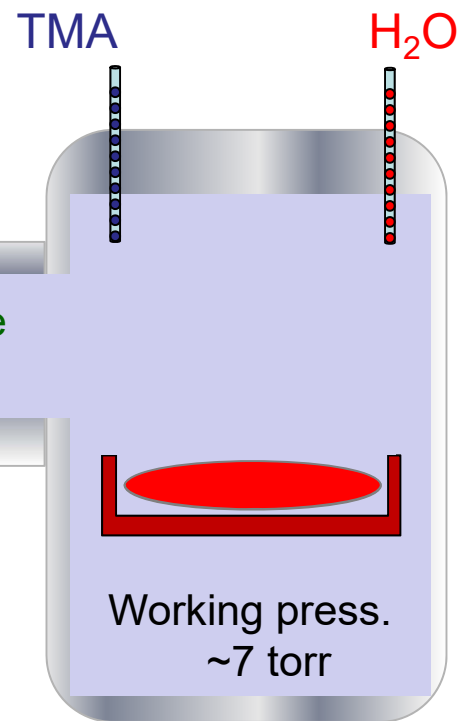
XPS Analysis

Pre-substrate Scan

Analysis after 1st Al pulse

Analysis after 1st H₂O pulse

Picosun PEALD
Hot wall and Shower head type



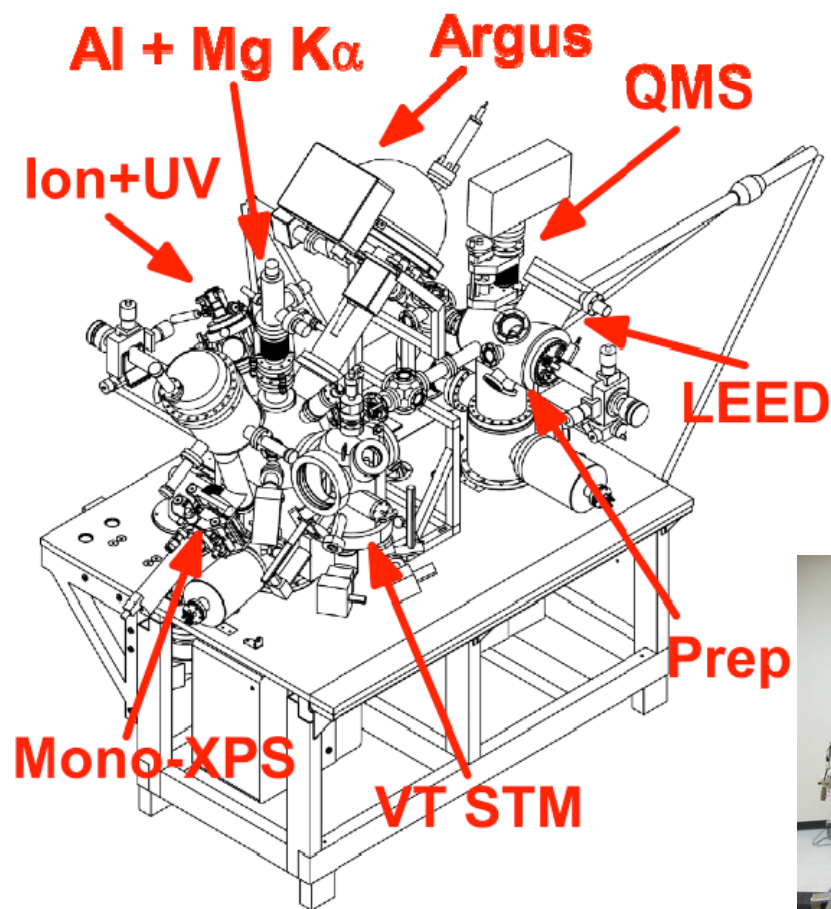
ALD (Al & H₂O)

Al pulse

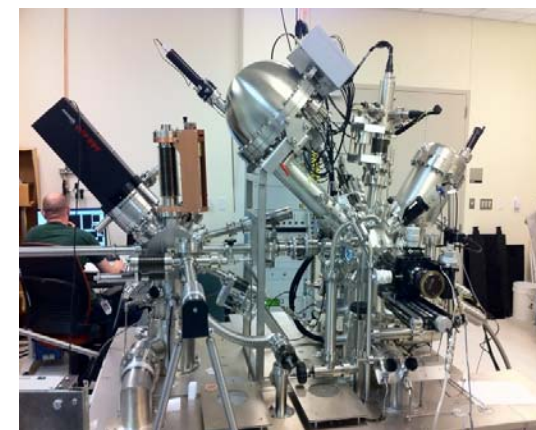
H₂O pulse

UHV chamber & transfer line
($< 2 \times 10^{-11}$ torr)

Working press.
~7 torr

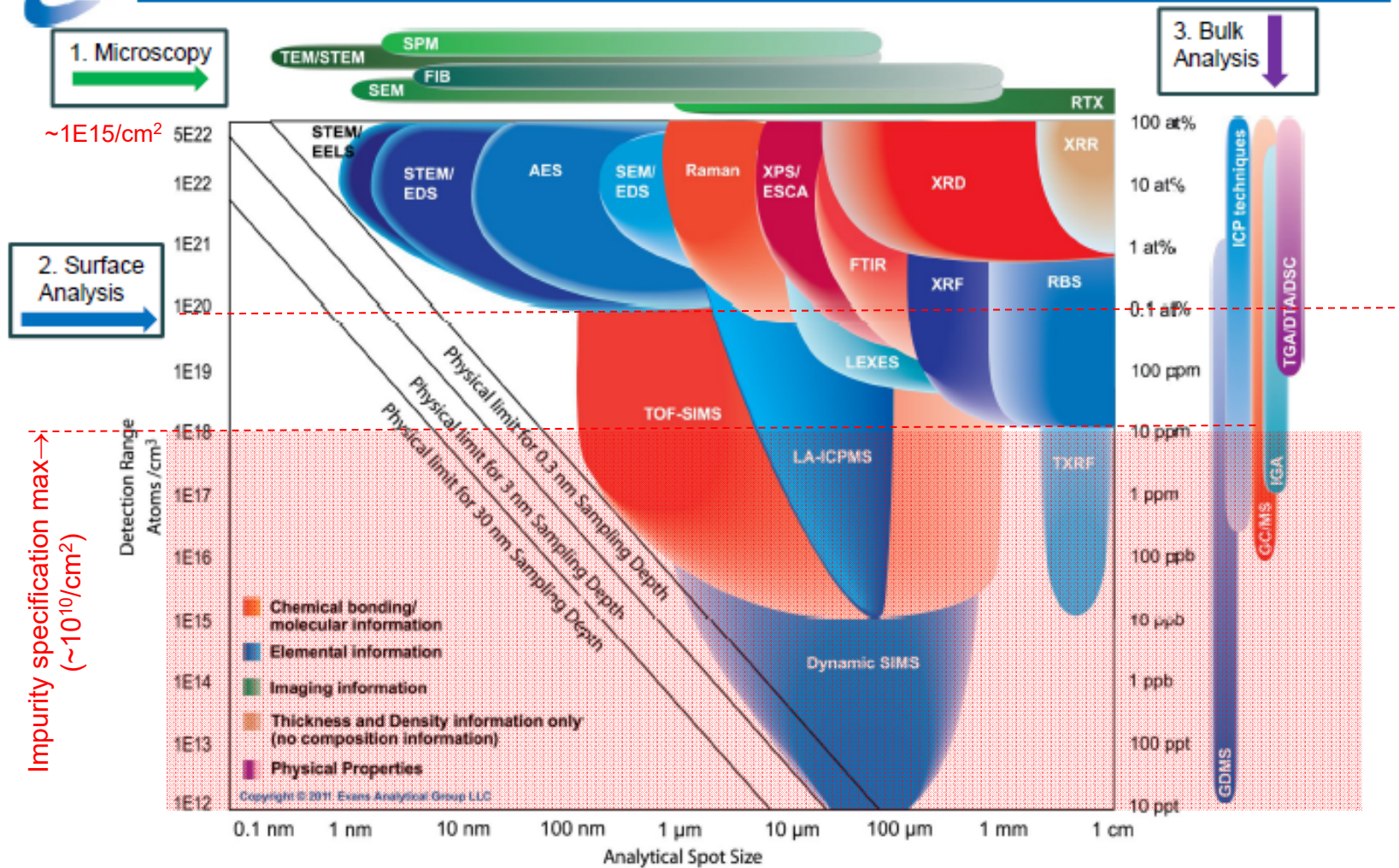


- Variable Temperature STM/AFM
- Monochromatic XPS with Argus 128 channel detection
- Twin Anode X-ray Source
- UPS – valence band studies
- Thermal Desorption Spectroscopy
- Low Energy Electron Diffraction
- Effusion/e-beam deposition





Bubble Chart for Analytical Techniques



- Materials Challenges
- Methods
- TMDs
- Impurities
- Summary

1												3								
H												He								
3	4											5	6	7	8	9	10			
<0.1	<0.1											<0.1	<1.8E10							
-5.4E10	+8.4E10																			
Li		Be												B		C	N	O	F	Ne
11	12													13	14	15	16	17	18	
6.6	0.3													15.7	8.4E11					
8.8E10	8.2E10																			
Na		Mg												Al		Si	P	S	Cl	Ar
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36			
4.2	0.4	27	2.7	45.1	<0.1	<0.1	1.3E12	<0.1	<0.1	5	<0.1	<0.1	0.2	0.3						
4.3E11	6.3E11		1.8E11	<4.4E10	<4.8E10	<4.8E10	<4.8E10	<4.8E10	<4.8E10	6.9E11	<5.2E10	<6.1E11	7.0E10	1.1E11						
K		Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54			
<0.1	2.8		2.8	0.4						7.2	54	0.2	1.1	152						
+8.3E10	6.1E11		6.1E11	1.7E11						1.3E10	4.9E+12	9.9E10	7.3E10	3.7E14						
Rb		Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
55	56		72	73	74	75	76	77	78	79	80	81	82	83	84	85	86			
2	4.4E11		<0.1	2.1E13	0.85	4.4E+11					<0.1	<4.8E10	5.2E12	3.8E14						
Cs		Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
57	58		104	105	106	107	108	109	110	111	112	113	114	115	116	117	118			
			Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo			
Fr		Ra																		
		*Lanthanide Series																		
		87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103		
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
		89	90	91	92	93	94	95	96	97	98	99	100	101	102	103				
		**Actinide Series																		
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

MoS₂ from Australian source 'a-MoS₂'

at. # ppbw at./cm ²		Element			
		>5E10/cm ²	>1E11/cm ²	>1E12/cm ²	Not measured
1	H				
2	He				
3	Li	<0.1 <5.4E10			
4	Be	<0.1 <6.4E10			
5	B	<0.1 <1.6E10			
6	C				
7	N				
8	O				
9	F				
10	Ne				
11	Na	0.6 8.5E10			
12	Mg	0.3 6.2E10			
13	Al	15.7 8.4E11			
14	Si				
15	P				
16	S				
17	Cl				
18	Ar				
19	K	4.2 4.5E11			
20	Ca	0.4 6.3E11			
21	Sc				
22	Ti	0.7 1.5E11			
23	V	<0.1 <4.4E10			
24	Cr	<0.1 <4.5E10			
25	Mn	<0.1 <4.6E10			
26	Fe	15.1 1.3E12			
27	Co	<0.1 <4.9E10			
28	Ni	<0.1 <4.8E10			
29	Cu	5 6.9E11			
30	Zn	<0.1 <5.2E10			
31	Ga	<0.1 <6.1E11			
32	Ge	0.2 7.9E10			
33	As	0.3 1.1E11			
34	Se				
35	Br				
36	Kr				
37	Rb	<0.1 <6.3E10			
38	Sr	2.8 6.1E11			
39	Y				
40	Zr	2.8 6.1E11			
41	Nb	0.4 1.7E11			
42	Mo				
43	Tc				
44	Ru				
45	Rh				
46	Pd				
47	Ag	7.9 1.3E12			
48	Cd	54 4.9E+12			
49	In	0.2 9.9E10			
50	Sn	1.1 7.3E10			
51	Sb	1032 3.7E13			
52	Te				
53	I				
54	Xe				
55	Cs	2 4.4E11			
56	Ba				
57	La				
58	Ce				
59	Pr				
60	Nd				
61	Pm				
62	Sm				
63	Eu				
64	Gd				
65	Tb				
66	Dy				
67	Ho				
68	Er				
69	Tm				
70	Yb				
71	Lu				
72	Hf				
73	Ta	<0.1 <1.0E11			
74	W	408 2.7E13			
75	Re	0.85 4.4E11			
76	Os				
77	Ir				
78	Pt				
79	Au	<0.1 <4.8E10			
80	Hg				
81	Tl				
82	Pb	1252 3.2E12			
83	Bi	20311 3.9E14			
84	Po				
85	At				
86	Rn				
87	Fr				
88	Ra				
89	Ac				
90	Th				
91	Pa				
92	U				
93	Np				
94	Pu				
95	Am				
96	Cm				
97	Bk				
98	Cf				
99	Es				
100	Fm				
101	Md				
102	No				
103	Lr				
104	Rf				
105	Db				
106	Sg				
107	Bh				
108	Hs				
109	Mt				
110	Ds				
111	Rg				
112	Cn				
113	Uut				
114	Fl				
115	Uup				
116	Lv				
117	Uus				
118	Uuo				

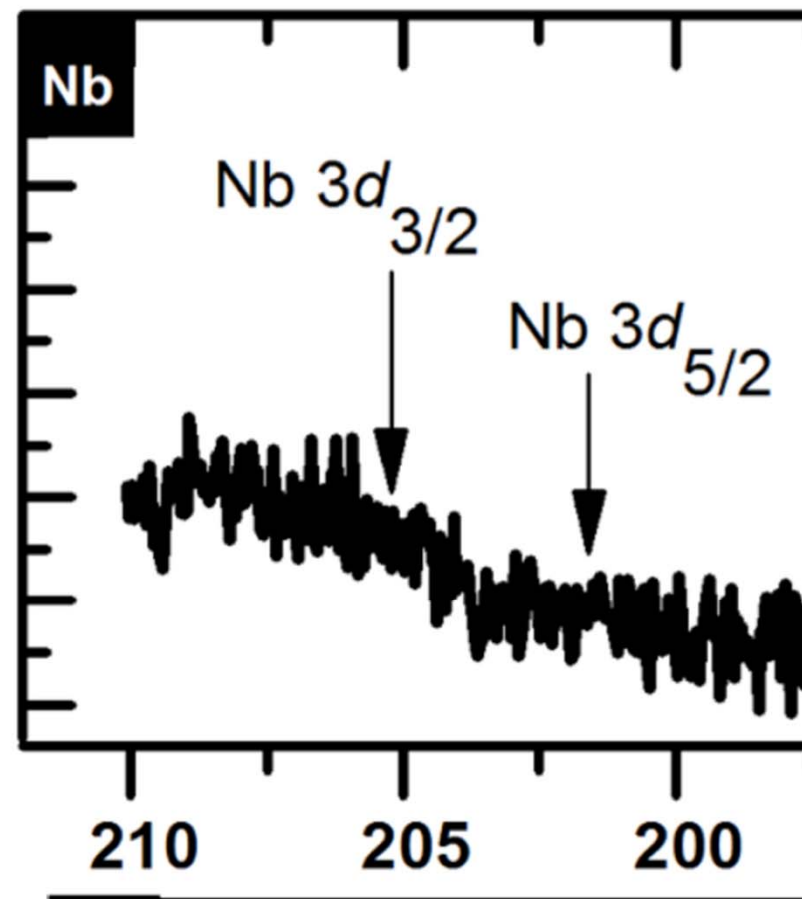
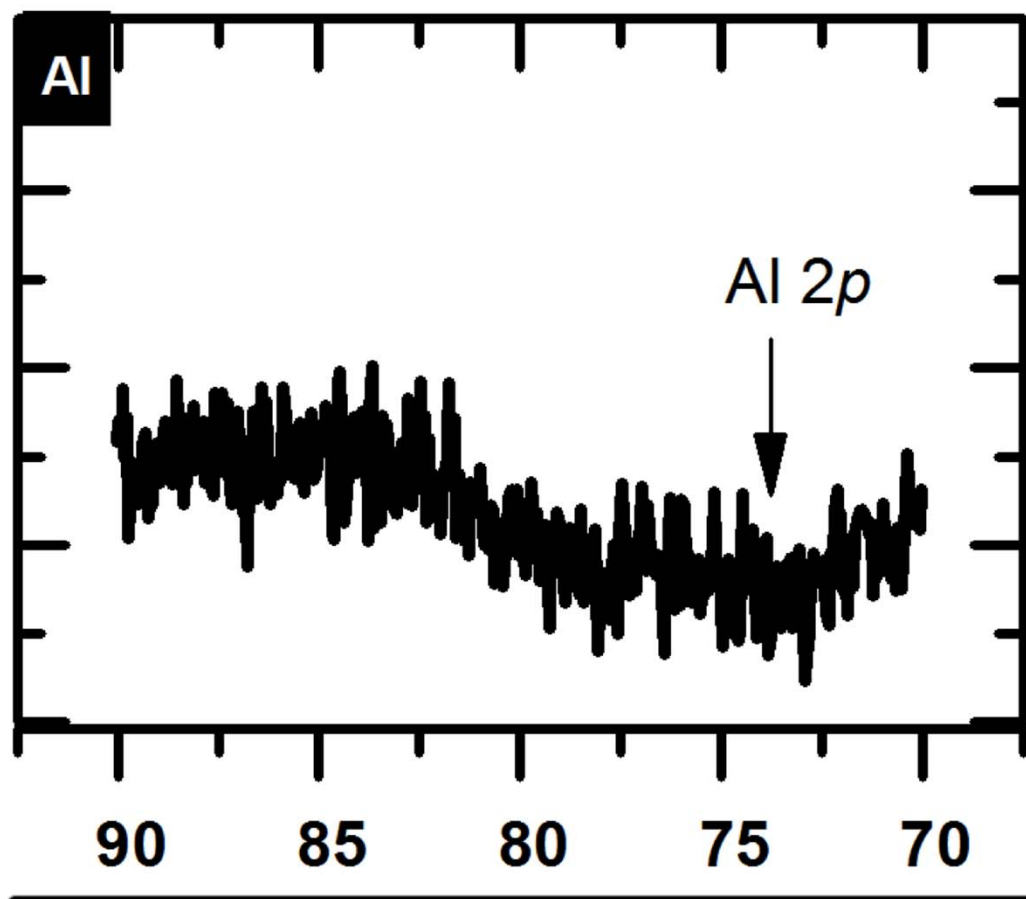
- Vapor ICPMS utilized by commercial laboratory
- “Digestion” here entails only surface region impurities
- Element list mainly based on Si-industry relevant impurity species – i.e. impurities that induce levels in the band gap

Synthetic (VPT) MoS₂, 's-MoS₂'

at. # ppbw at./cm ²																	
Element	>5E10/cm ²	>1E11/cm ²	>1E12/cm ²	NOT measured													
1 H	3 0.1 5.4E10	4 <0.1 <1.6E10	5 <0.1 <1.6E10	6	7	8	9	10 He									
11 0.5 5.5E10	12 0.3 5.0E10	13 2.1 2.2E11	14	15	16	17	18										
19 0.5 4.3E13	20 1.0 1.8E11	21	22 0.5 1.3E11	23 <0.1 <4.4E10	24 <0.1 <4.5E10	25 <0.1 <4.6E10	26 7.4 8.3E11	27 <0.1 <4.9E10	28 <0.1 <4.8E10	29 0.5 1.4E10	30 0.1 5.5E10	31 0.1 6.1E11	32 0.1 5.6E10	33 6.1 8.8E11	34	35	36
37	38 <1.7 <1.0E11	39	40 <0.1 <6.5E10	41 <0.1 <6.6E10	42	43	44	45	46	47 0.3 1.5E11	48 43.5 4.3E12	49 <0.1 <7.6E10	50 0.1 7.3E10	51 8.2 1.5E12	52	53	54
55	56 1.3 4.3E11	57	72	73 <0.1 <1.0E11	74 98.2 1.0E13	75 <0.1 <1.0E11	76	77	78	79 0.1 1.1E11	80	81	82 15.2 3.2E12	83 451.1 3.1E13	84	85	86
87	88	**	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
*Lanthanide Series			57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
**Actinide Series			89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

- Impurity concentration easily exceed $5 \times 10^{10}/\text{cm}^2$.
- Many impurities have energy levels within the bandgap of silicon.
- Presence of ionized impurities is expected to have a high impact in carrier transport measurements

As expected, many below the limit of detection!



- Impurity concentration easily exceed $5 \times 10^{10}/\text{cm}^2$.
- Sensitivity of the characterization method is essential
- Incorrect to state "No Impurities"...

- Theory → Impurities must be kept well below 10¹²/cm²

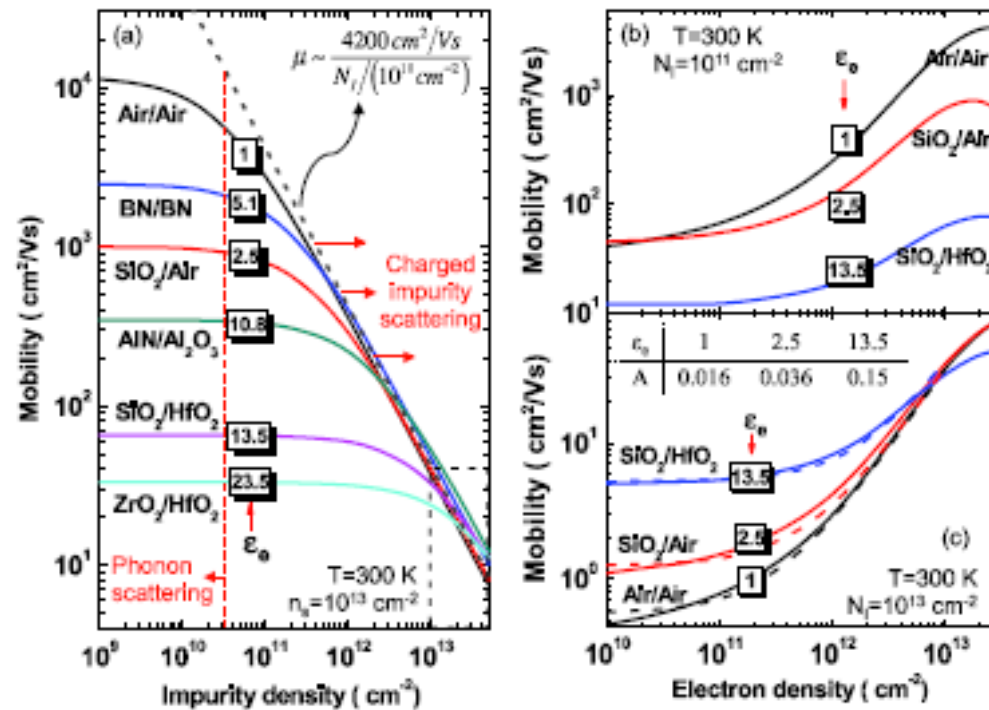


FIG. 7. The room-temperature net electron mobilities in SL MoS₂, considering all kinds of scattering mechanisms as a function of (a) N_I with fixed n_s at 10^{13} cm⁻²; (b) and (c) n_s with N_I fixing at 10^{11} and 10^{13} cm⁻², respectively. The numbers on the curves show the average dielectric constant of the surrounding dielectrics. Dashed lines show the fitted electron mobilities.

1																	2		
H																	He		
3 <0.1	4 <0.1													5 <0.1	6	7	8	9	10
Li	Be													B	C	N	O	F	Ne
11 0.19 4.0×10 ⁸	12 <0.1													13 <0.1	14	15	16	17	18
Na	Mg													Al	Si	P	S	Cl	Ar
19 0.22 6.2×10 ⁸	20 0.31 8.0×10 ⁸	21 <0.1	22 0.17 6.0×10 ⁸	23 <0.1	24 <0.1	25 <0.1	26 0.3 9.7×10 ⁸	27 <0.1	28 <0.1	29 <0.1	30 <0.1	31 <0.1	32 <0.1	33 <0.1	34 <0.1	35	36		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
37	38 <0.1	39	40 <0.1	41 0.11 7.0×10 ⁸	42 1.73 4.5×10 ⁹	43	44 <0.1	45	46	47 <0.1	48 <0.1	49 <0.1	50 0.99 3.6×10 ⁹	51 <0.1	52 10.79 1.8×10 ¹⁰	53	54		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
55	56 <0.1	*	72	73 <0.1	74	75 0.42 2.7×10 ⁹	76	77	78	79 1.21 5.7×10 ⁹	80	81	82 <0.1	83 <0.1	84	85	86		
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
87	88	**	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118		
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo		

at. # ppbw at./cm ²	<1×10 ¹⁰ /cm ²	>1×10 ¹⁰ /cm ²	Below detection limit	Not measured
Element				

- Impurity concentration kept below 5×10¹⁰/cm².
- Better control of growth process and environment

at. # ppbw at./cm ²		Element															
		<1×10/cm ²	>1×10/cm ²	Below detection limit	Not measured												
1 H																	
2 He																	
3 <0.1 Li	4 <0.1 Be																
5 <0.1 B	6 C	7 N	8 O	9 F	10 Ne												
11 0.5 7.6×10 ⁸ Na	12 0.18 4×10 ⁸ Mg																
13 3.85 2.1×10 ⁹ Al	14 Si	15 P	16 <50.00 S	17 Cl	18 Ar												
19 0.69 1.3×10 ⁹ K	20 1.66 2.4×10 ⁹ Ca	21 <0.1 Sc	22 1.25 2.3×10 ⁹ Ti	23 <0.1 V	24 0.36 1.1×10 ⁹ Cr	25 <0.1 Mn	26 1.55 2.9×10 ⁹ Fe	27 <0.1 Co	28 0.32 1.1×10 ⁹ Ni	29 0.12 5.8×10 ⁸ Cu	30 <0.1 Zn	31 <0.1 Ga	32 60.78 4.0×10 ¹⁰ Ge	33 <0.1 As	34 Se	35 Br	36 Kr
37 Rb	38 <0.1 Sr	39 Y	40 <0.1 Zr	41 <0.1 Nb	42 28.32 2.9×10 ¹⁰ Mo	43 Tc	44 <0.1 Ru	45 Rh	46 Pd	47 <0.1 Ag	48 <0.1 Cd	49 0.14 9.5×10 ⁸ In	50 0.84 3.2×10 ⁹ Sn	51 <0.1 Sb	52 0.32 1.8×10 ⁹ Te	53 I	54 Xe
55 Cs	56 <0.1 Ba	*	72 Hf	73 <0.1 Ta	74 W	75 <0.1 Re	76 Os	77 Ir	78 Pt	79 0.26 2.1×10 ⁹ Au	80 Hg	81 Tl	82 <0.1 Pb	83 <0.1 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo

- Impurity concentration kept below 5×10¹⁰/cm².
- Better control of growth process and environment

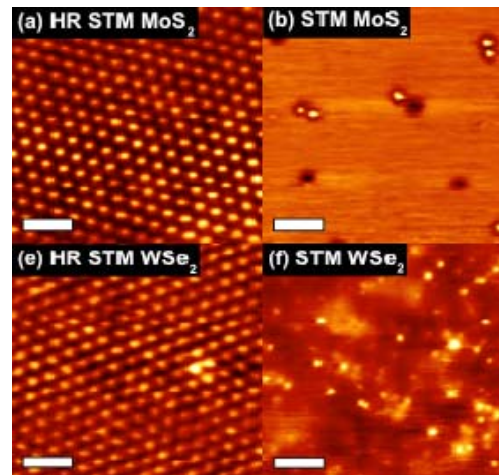
at. # ppbw at./cm ²		Element															
		<1×10 ¹⁰ /cm ²	>1×10 ¹⁰ /cm ²	Below detection limit	Not measured												
1	2																
H	He																
3 0.47 3.3×10 ⁸	4 <0.1																
Li	Be																
11 3.45 2.8×10 ⁹	12 0.54 8.3×10 ⁸																
Na	Mg																
19 0.68 1.3×10 ⁹	20 4.69 4.9×10 ⁹	21 <0.1	22 <0.1	23 0.15 5.8×10 ¹⁰	24 6.1 6.9×10 ⁹	25 0.18 6.9×10 ⁸	26 21.28 1.7×10 ¹⁰	27 2.78 4.5×10 ⁹	28 2.58 4.2×10 ⁹	29 5.42 7.3×10 ⁹	30 <0.1	31 0.11 5.8×10 ⁸	32 <0.1	33 <0.1	34 <0.1	35	36
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38 <0.1	39	40 <0.1	41 0.15 8.6×10 ⁸	42 1.73 3.7×10 ⁹	43	44 <0.1	45	46	47 0.37 1.7×10 ⁹	48 <0.1	49 <0.1	50 0.14 9.7×10 ⁸	51 <0.1	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
55	56 4.55 1.1×10 ¹⁰	*	72	73 <0.1	74	75 1.31 5.8×10 ⁹	76	77	78	79 4.26 1.3×10 ¹⁰	80	81	82 12.38 2.8×10 ¹⁰	83 <0.1	84	85	86
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
87	88	**	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

- Impurity concentration kept below $5 \times 10^{10}/\text{cm}^2$.
- Better control of growth process and environment

Metrology Opportunities?

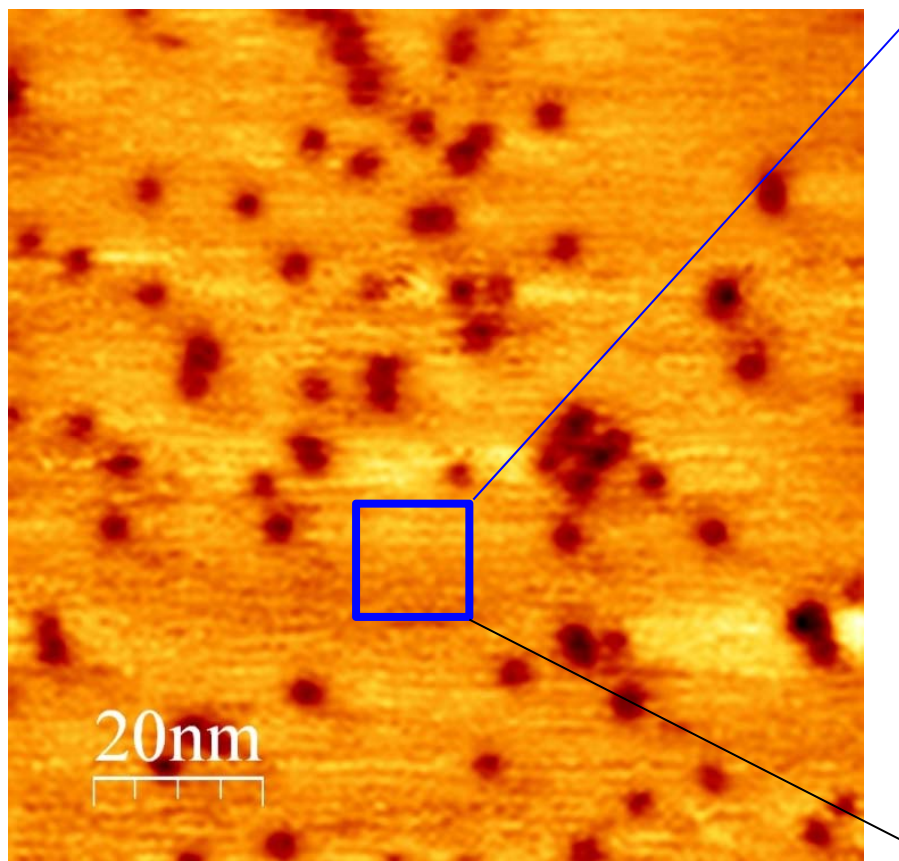
- Develop protocol for 2D materials impurity analysis
- Establish correlations with electronic/photonic device response

- Materials Challenges
- Methods
- TMDs
 - Defects
- Summary



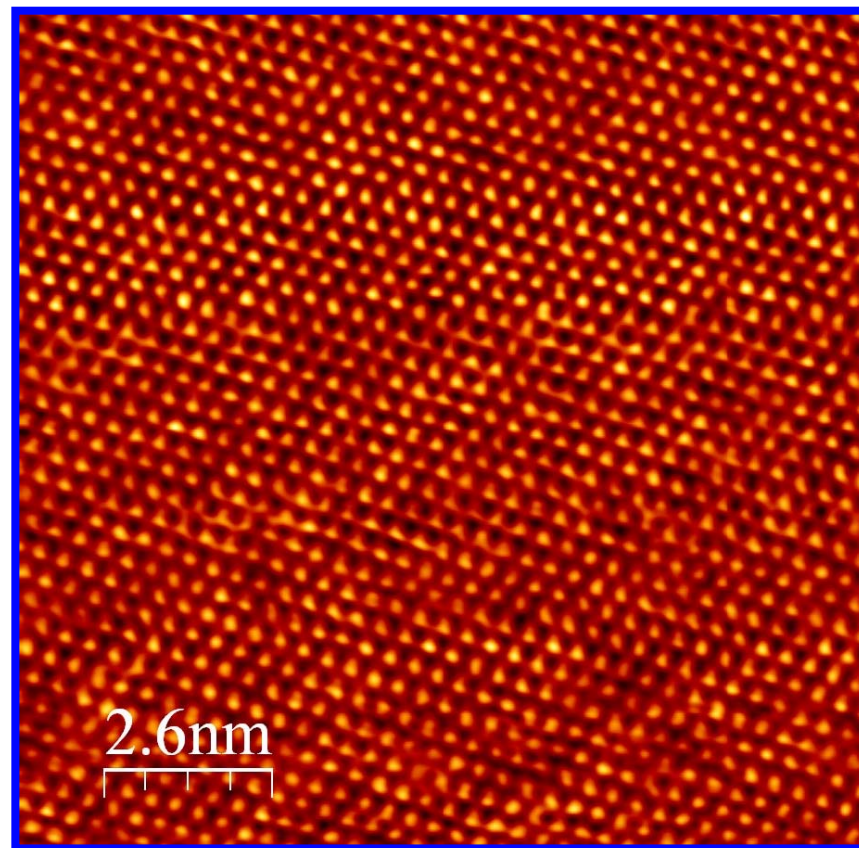
Reality!

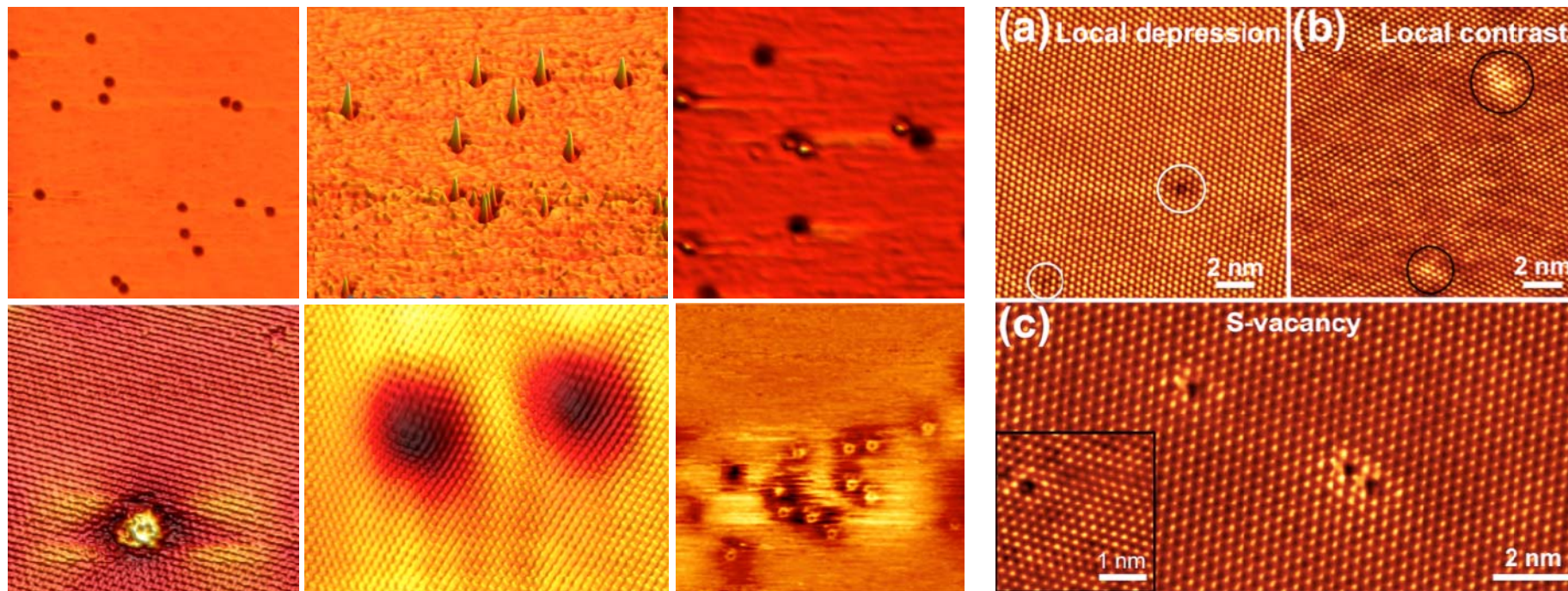
- 100 nm × 100 nm



Pleasant to the “eye”!

- 13 nm × 13 nm



Defects observed on exfoliated, geological MoS₂

- Defect density up to 8 %.
- Various imperfections: metallic defects, donor and acceptor atoms, S-vacancy, structural defects...
- Impact on electronic and physical properties?

Exfoliated TMDs

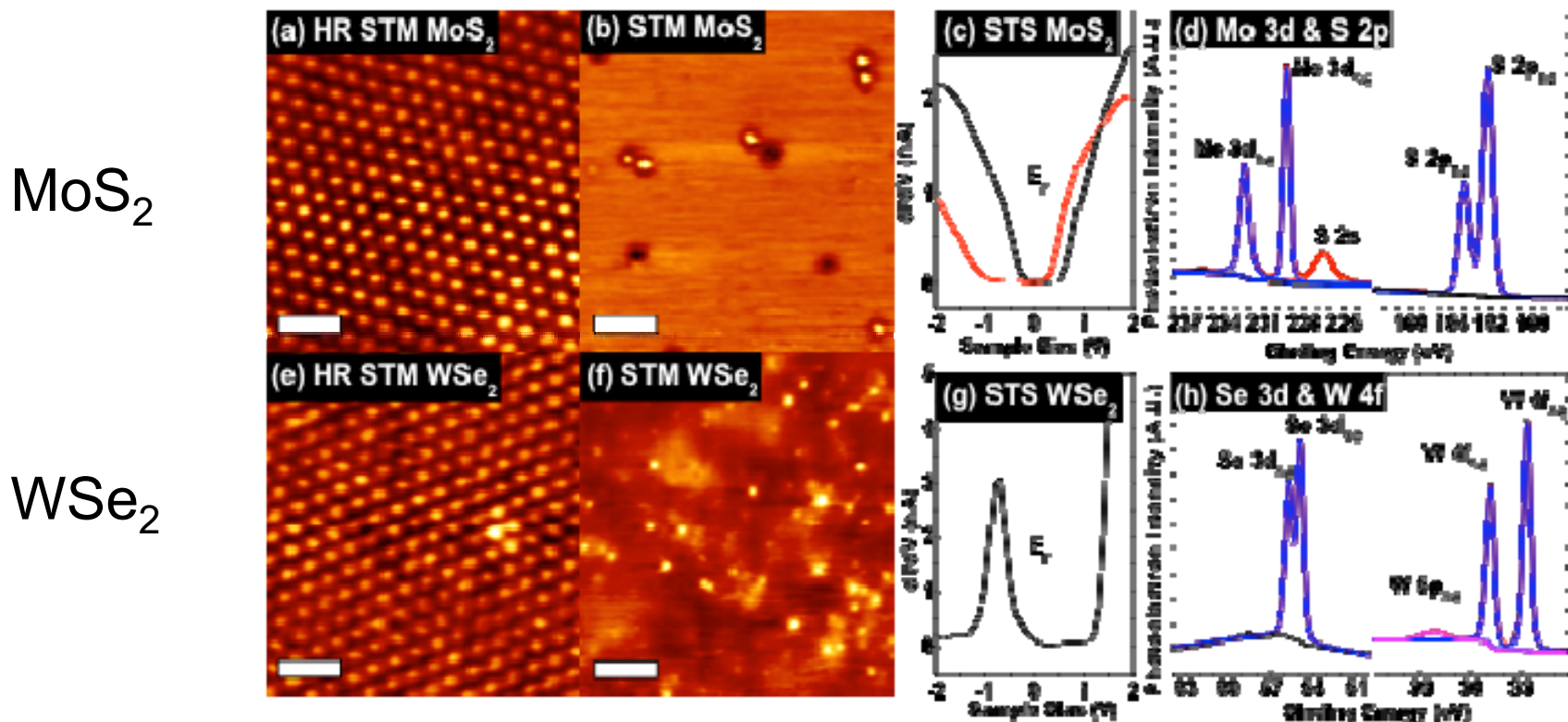


Figure 1. Initial MoS₂ (a–d) and WSe₂ (e–h) characterization. (a and e) High-resolution STM showing the atomic structure, scale bar 1 nm, imaging conditions (a) 0.7 V, 1 nA, and (e) 1.5 V, 1.5 nA. (b and f) 60 nm × 60 nm image showing that both surfaces are defective, scale bar 12 nm, imaging conditions (b) –0.3 V, 0.1 nA, and (f) 0.5 V, 1.3 nA. (c and g) STS spectra showing typical n- and p-type variability of MoS₂, and typically p-type behavior of WSe₂. (d and h) XPS of the initial surfaces showing the expected MoS₂ and WSe₂ chemical states.

- Defects evident at the atomic scale
- STS shows defect impact on doping

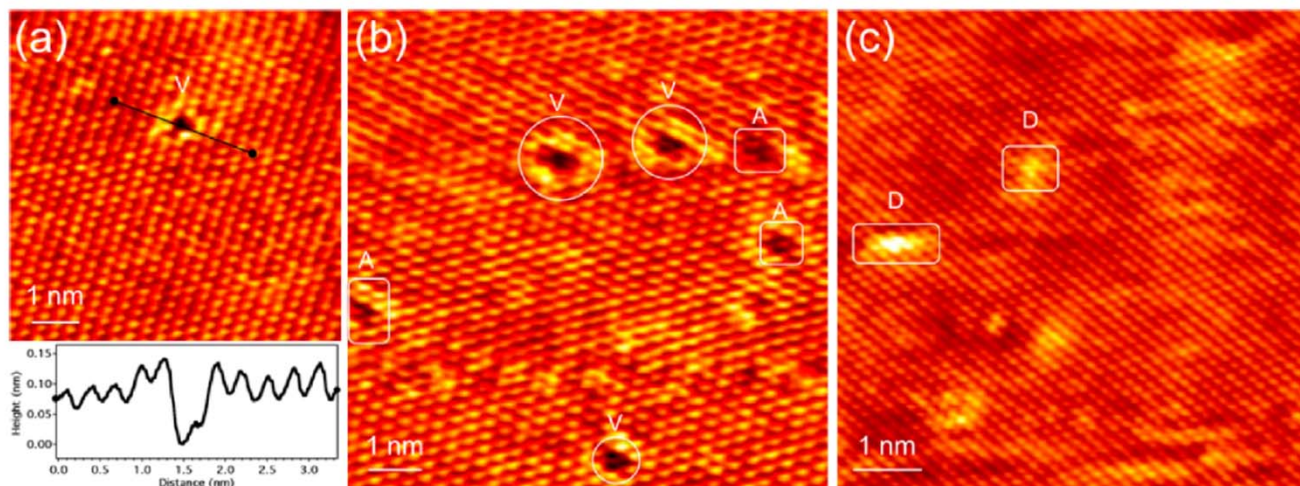


Figure 2. Imaging of atomic size imperfections on WSe₂ (sample A). (a) STM image ($V_b = 1.5$ V, $I_t = 1.5$ nA) shows a single Se vacancy with the corresponding line profile. (b) STM image ($V_b = 1.5$ V, $I_t = 1.5$ nA) showing two types of point defects: single vacancy (noted as “V”) and local depression (noted as “A”) caused by the presence of an acceptor at this area. (c) STM image ($V_b = 1.5$ V, $I_t = 0.5$ nA) shows an atomic bright spot (noted as “D”) induced by the presence of donor atom at the vicinity of the surface.

- Defects evident at the atomic scale
 - “V” type density: $\sim 0.7 \times 10^{12}/\text{cm}^2$
 - “D” type density: $\sim 1.7 \times 10^{12}/\text{cm}^2$
 - “A” type density: $\sim 1.2 \times 10^{12}/\text{cm}^2$

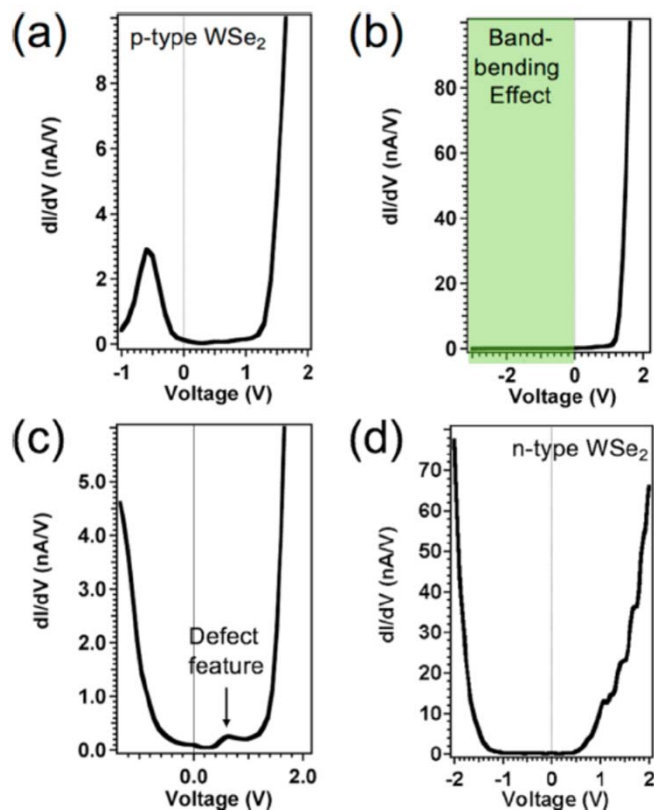
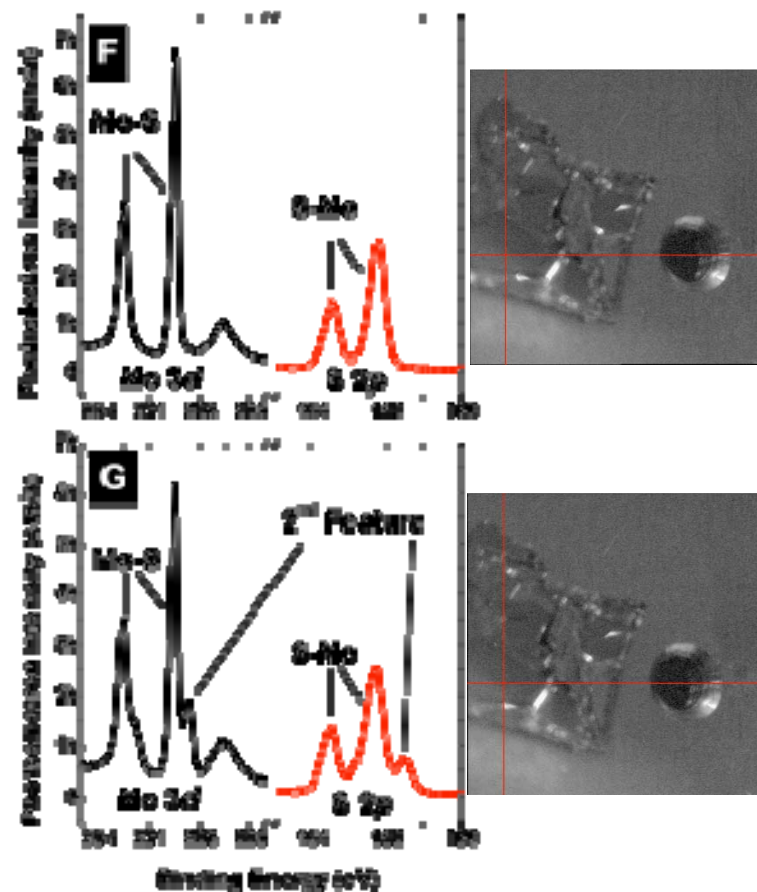


Figure 3. dI/dV vs V spectra recorded on two different freshly exfoliated WSe₂ samples (A, B) showing different behaviors: (a) p-type conductivity, (b) band bending effect ($I_t \sim 0$ when $V_b = 0$), (c) defect state in the gap, and n-type conductivity. The STS in (a–c) was recorded on sample “A”, and the STS in (d) was recorded on sample “B”.

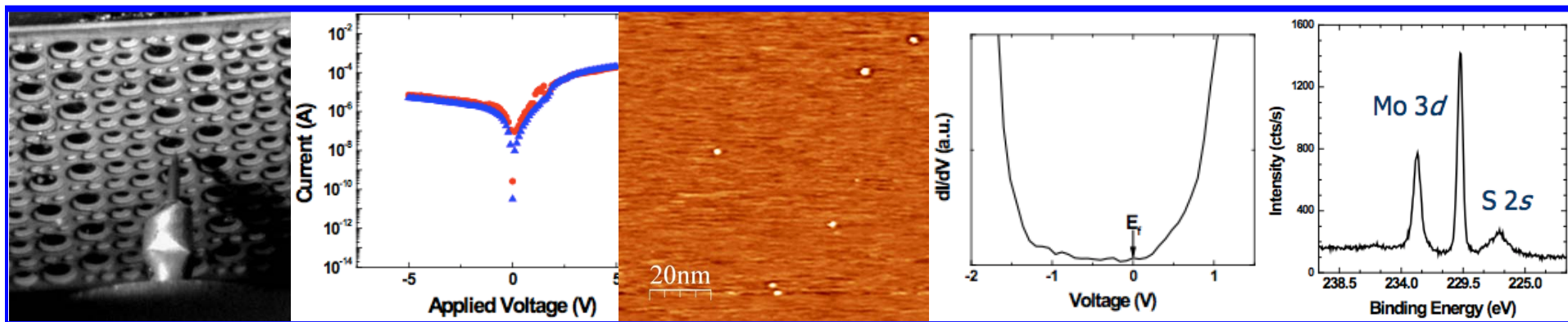
- Electronic structure variation
 - P-type
 - N-type
 - Gap states
 - Tip/Band bending effects?

- Noticeable variations in the core-level spectra are observed across an MoS₂ sample
- Low binding energy shoulder on the Mo 3d
- Degree of variability is vendor material specific
- Highest quality vendor materials can still result in ~20% of the surface exhibiting regions with shoulder features

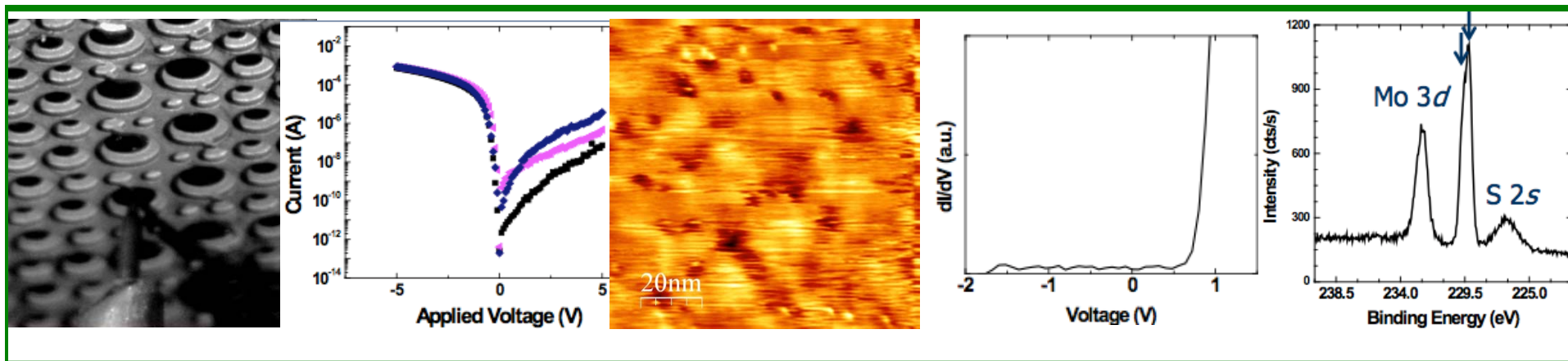


XPS variability

- All the measurements are performed on the identical spot
- Reproducible regardless of the order of measurements



At ~1.25 mm far away:

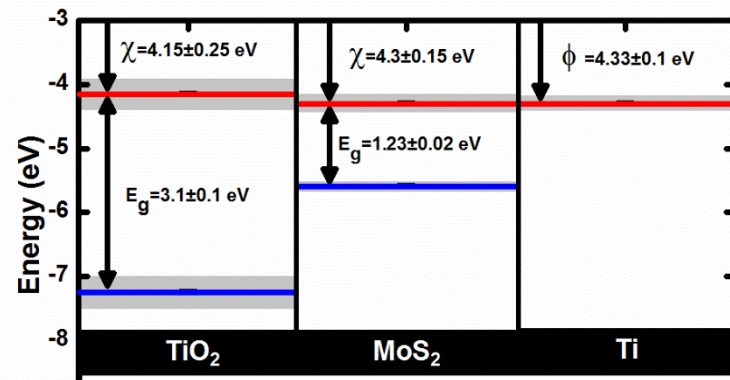
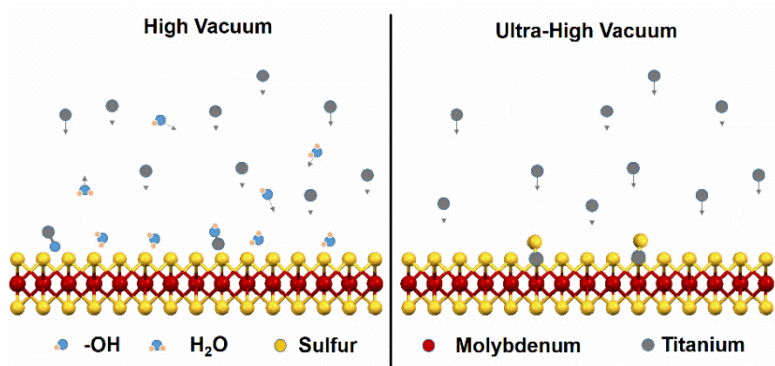


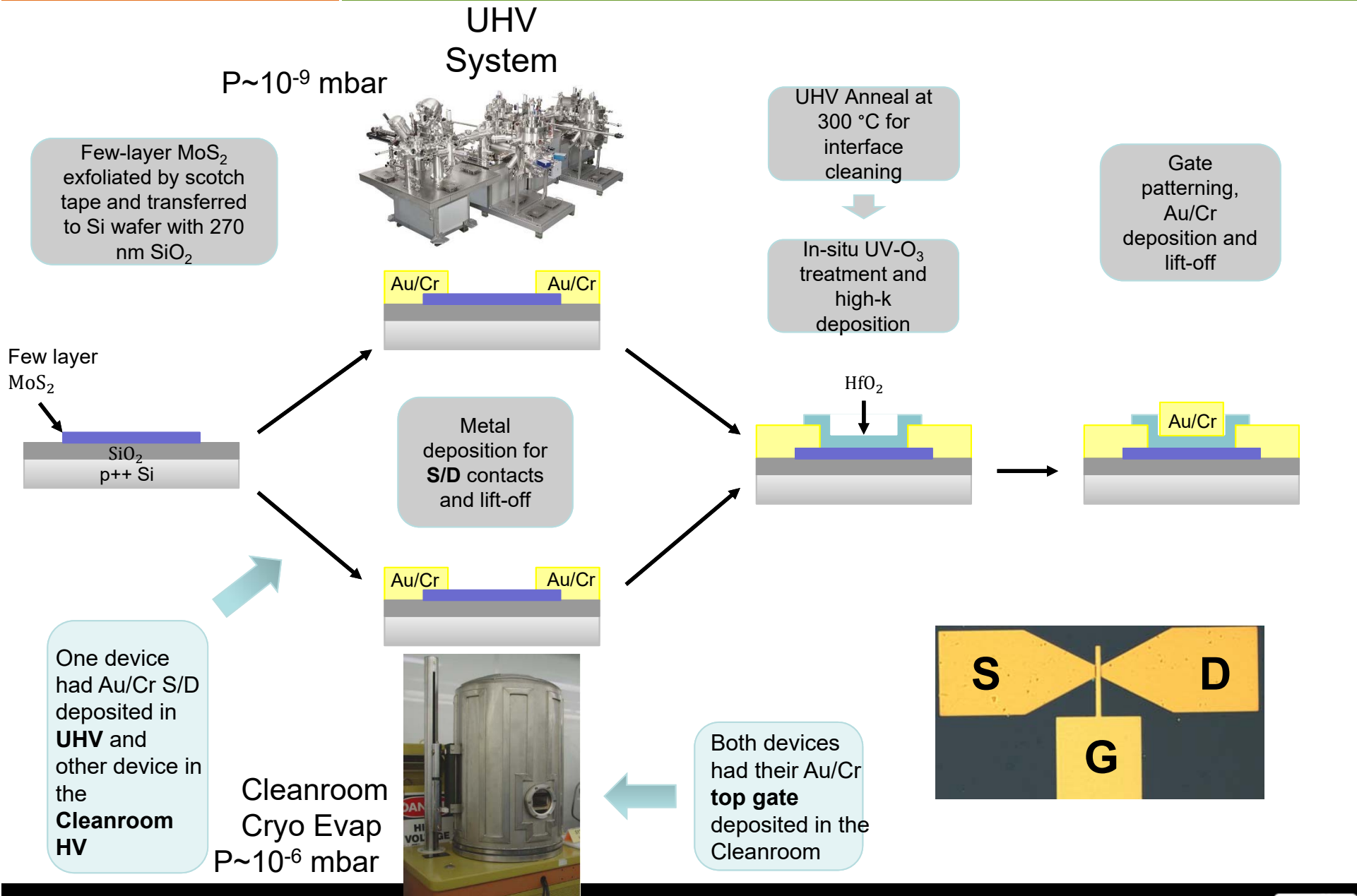
- Correlation founded between defects and the level of variability
 - Regions with low defect density – n-type MoS₂ (S:Mo = 1.8:1)
 - Regions with high defect density – p-type MoS₂ (S:Mo = 2.3:1)

Metrology Opportunities?

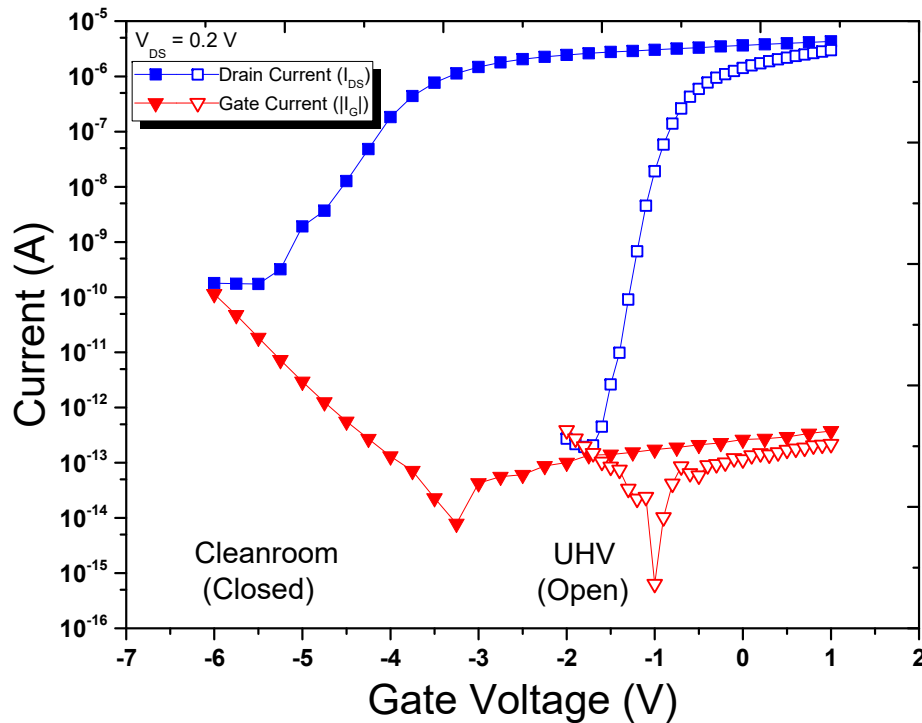
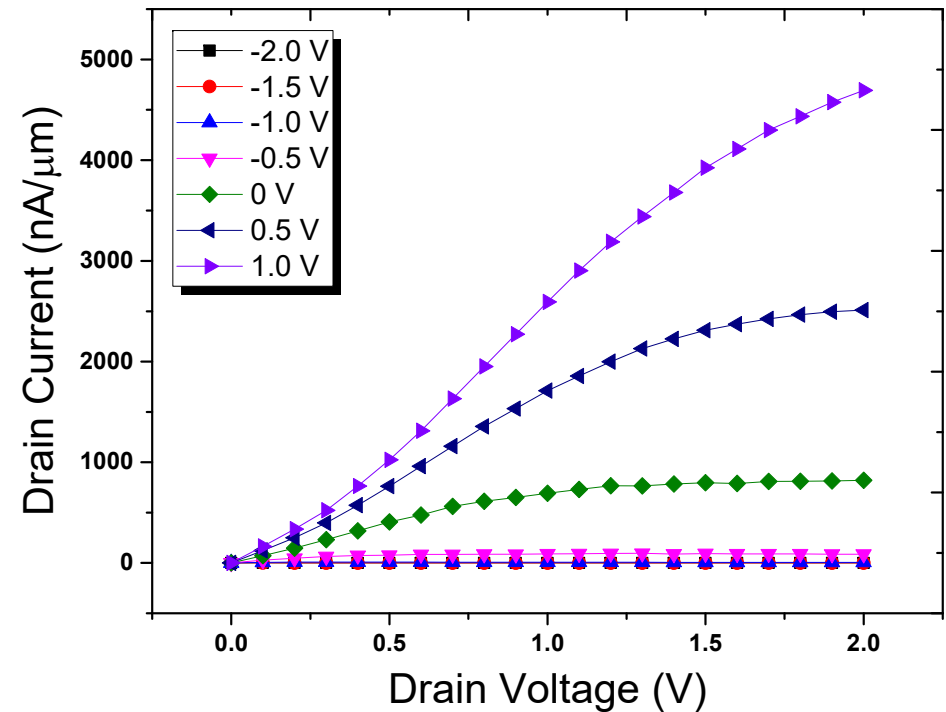
- Develop protocol for 2D materials defect analysis and densities
- Establish correlations with electronic/photonics device response (D_{it} , lifetime, etc)

- Materials Challenges
- Methods
- TMDs
 - Contacts
- Summary

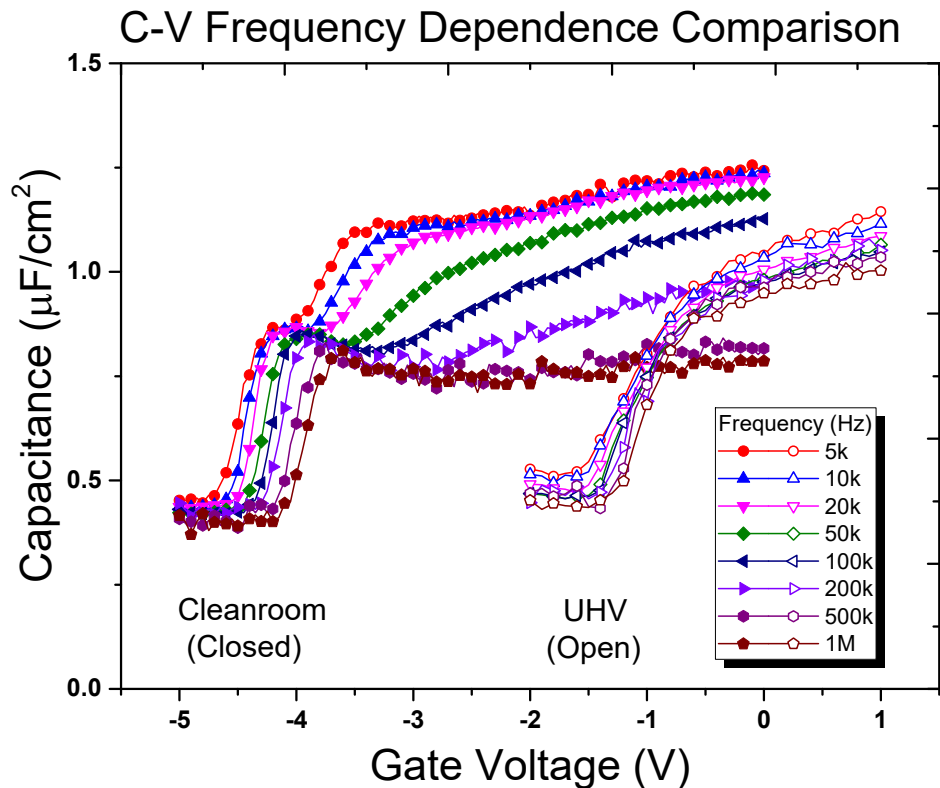




HV (Cleanroom) & UHV Comparison

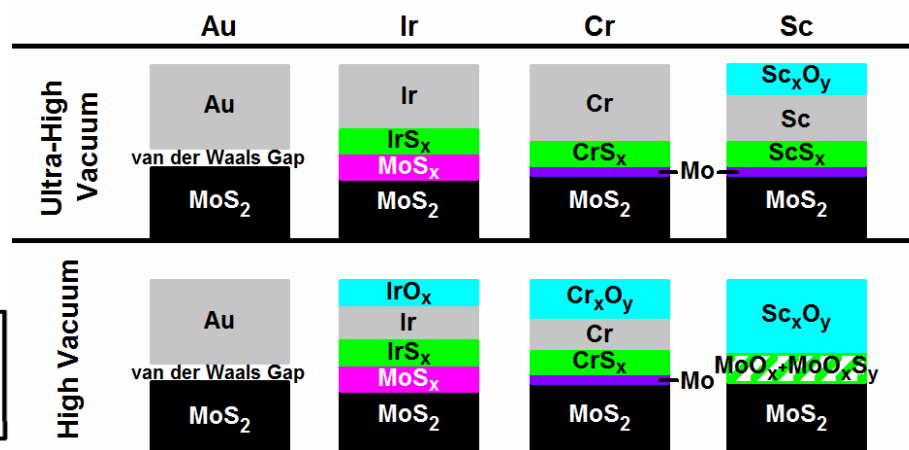
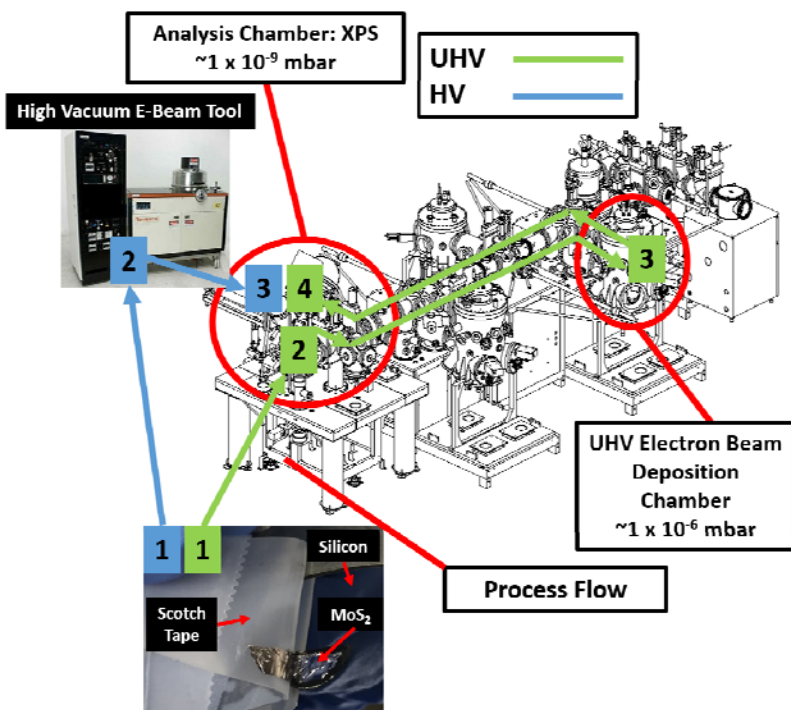
UHV I_D - V_D 

- Lower threshold voltage
- Increase in on/off ratio
- Reduction in contact resistance



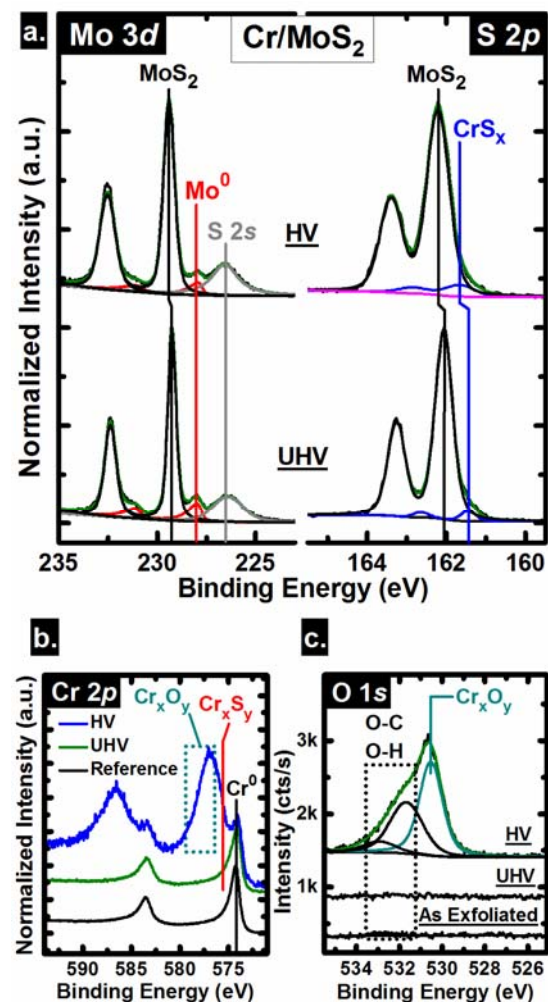
- Less dispersion over a large frequency range is due to lower series resistance
- Lack of “humps” in the depletion of UHV sample suggests a smaller number of interface traps

- Comparison of cleanroom tool (HV) and UHV deposition ambient reveals significant differences in contact interfacial chemistry for MoS₂...

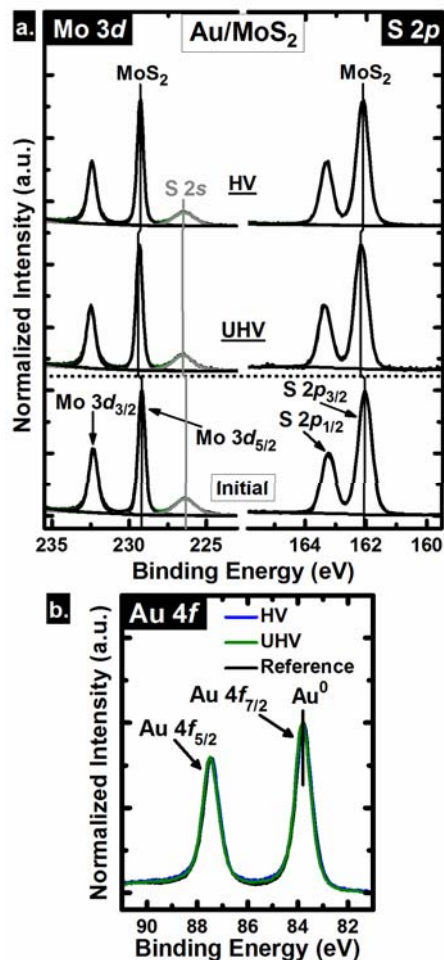


Ti/MoS₂: See ACS Applied Materials and Interfaces, 8 (12), 8289–8294 (2016)

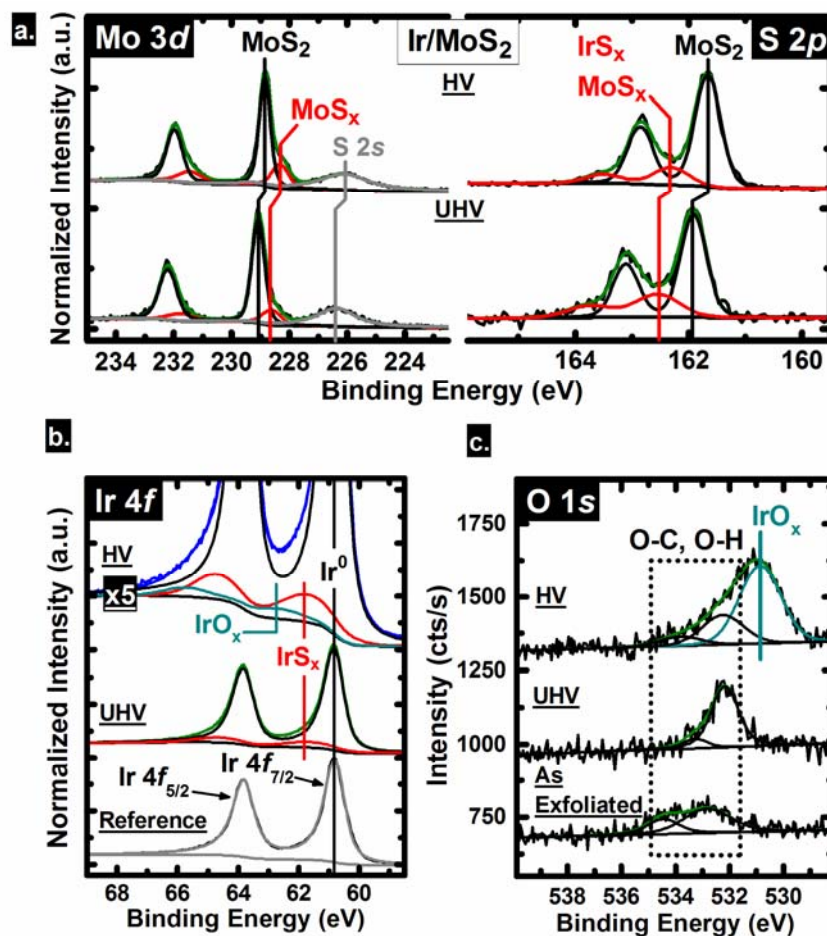
- Deposition by cleanroom tool (HV)
 - CrO_x formation detected
 - Some CrS_x reaction products also detected
- UHV deposition ambient reveals
 - CrO_x formation below limit of detection
 - More CrS_x formation detected
- Interfacial chemistry very different depending upon deposition process ambient
- UHV ambient appears to correlate with improved device behavior



Au

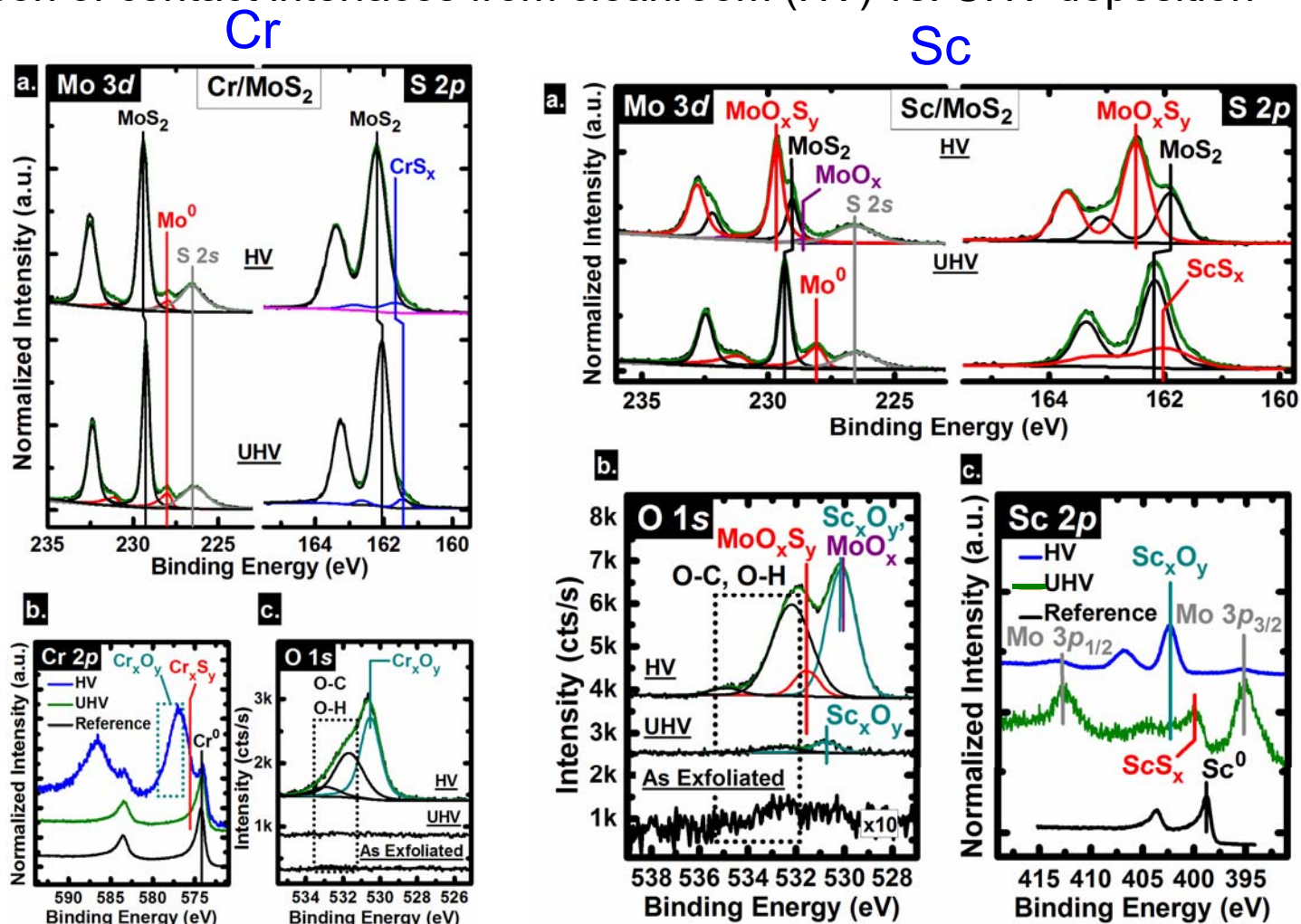


Ir



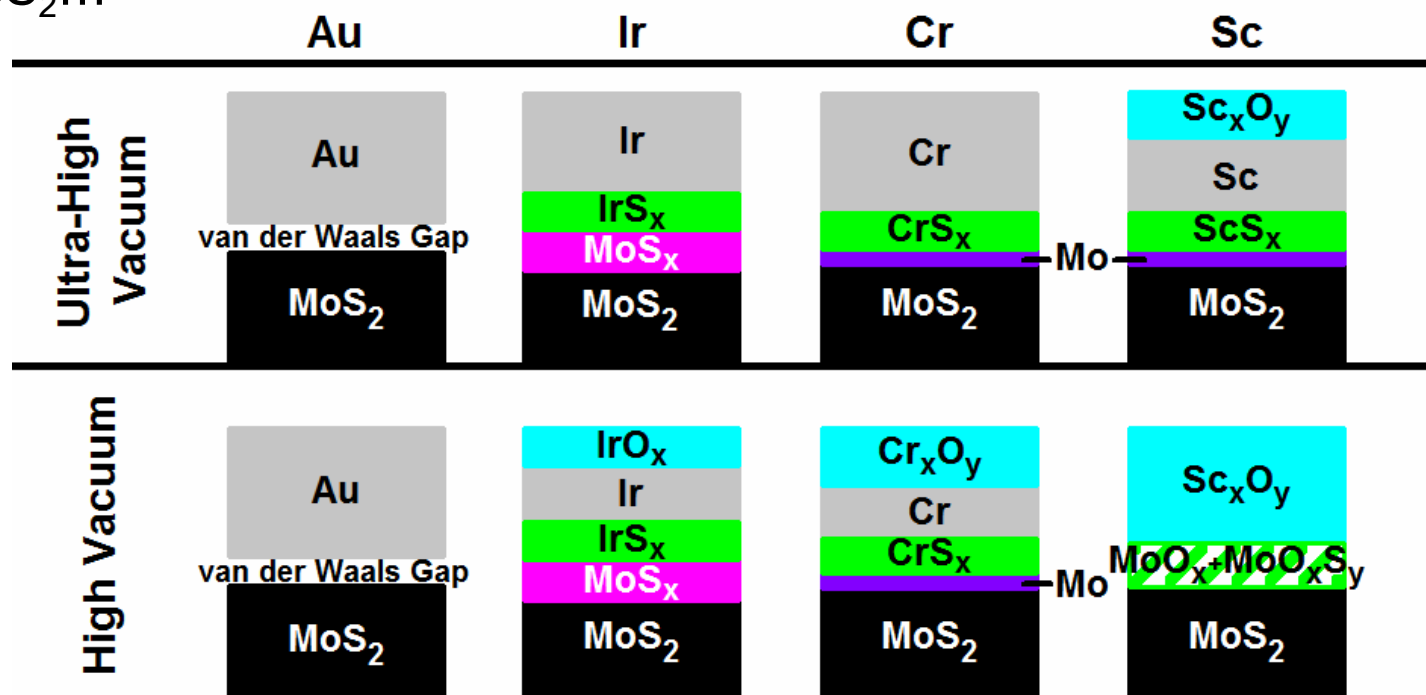
- No reaction of Au with the MoS₂ substrate detected
- Oxygen species (HV) can partially mitigate the reaction with Ir

Comparison of contact interfaces from cleanroom (HV) vs. UHV deposition



- Both Cr and Sc react with the MoS₂ substrate
- Oxygen species (HV) can Partially mitigate the reaction

- Comparison of cleanroom tool (HV) and UHV deposition ambient reveals significant differences in contact interfacial chemistry for MoS_2 ...



Ti/ MoS_2 : See also *ACS Applied Materials and Interfaces*, **8** (12), 8289–8294 (2016)

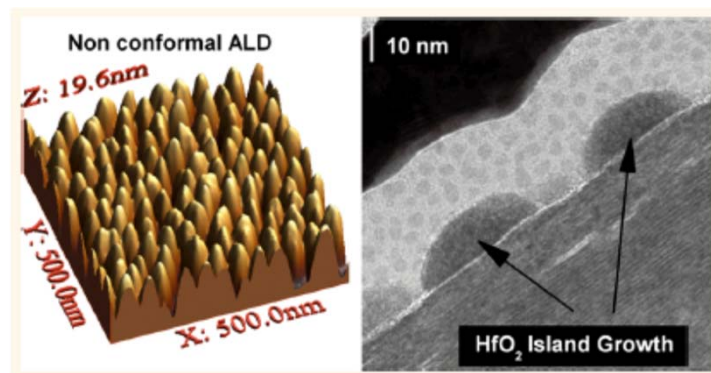
Pop group recent work, *Nanoletters* (2016)

<http://dx.doi.org/10.1021/acs.nanolett.6b01309>

Metrology Opportunities?

- Develop protocol for 2D materials contact characterization (physical and electrical)
- Establish correlations with electronic/photonic device response

- Materials Challenges
- Methods
- TMDs
 - Functionalization
- Summary



- Transition metal dichalcogenides (TMDs) based transistor has drawn significant attention because of the two dimensional structure and moderate bandgap value (1.8 – 1.2eV).

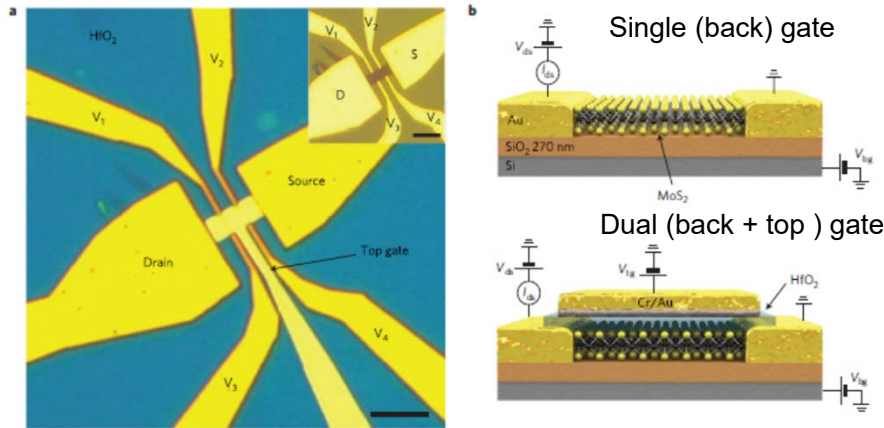
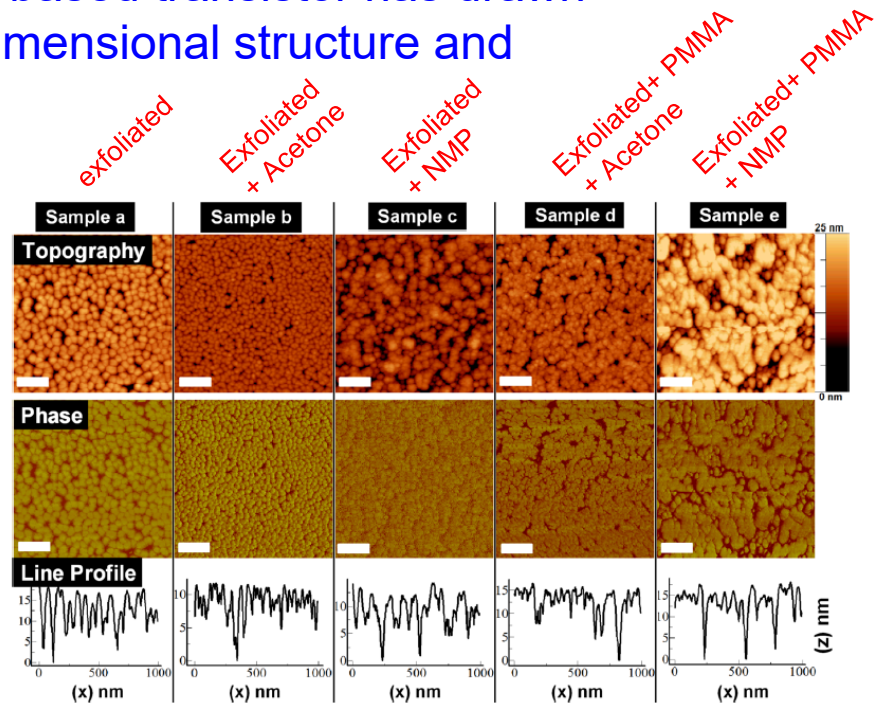


Figure 1 | Fabrication of single-gated and dual-gated MoS₂ devices. **a**, Optical image of the MoS₂ dual-gated device used in our measurements. The inset shows the single-gate version of the same device before ALD deposition of HfO₂ and top-gate electrode fabrication. Scale bars, 5 μm. **b**, Cross-sectional views of devices based on single-layer MoS₂ in a single-gate (top) and dual-gate (bottom) configuration. Gold leads are used for the source, drain and voltage probes (V₁, V₂, V₃ and V₄). Voltage probes have been omitted from the drawing. The silicon substrate, covered with a 270-nm-thick SiO₂ layer was used as the back gate. The top-gate dielectric is a 30-nm-thick HfO₂ layer.

Radisavljevic and Kis, Nat. Mat. 12 (2013) 815

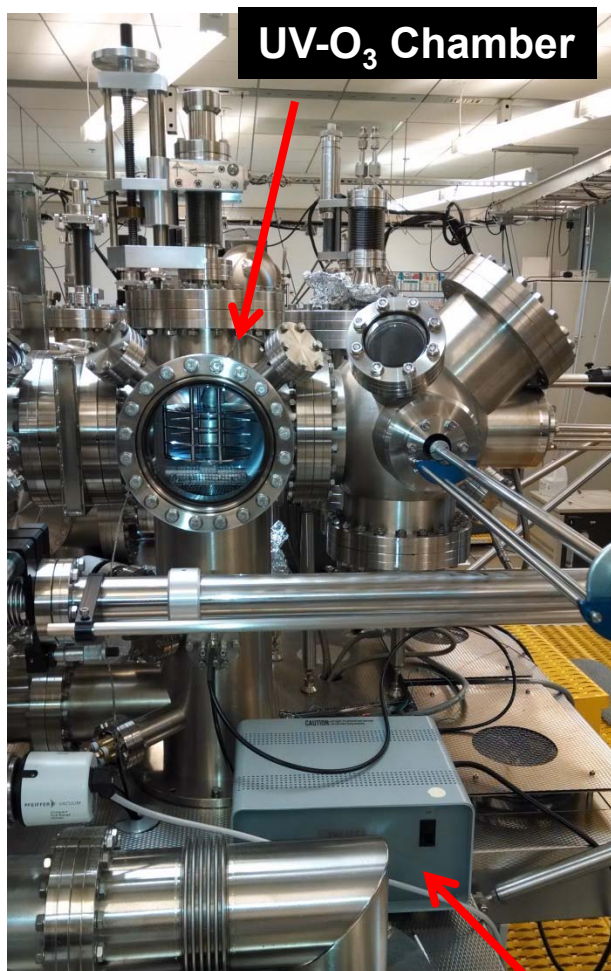


AFM images of ALD HfO₂ on MoS₂ without surface functionalization (only residues!)

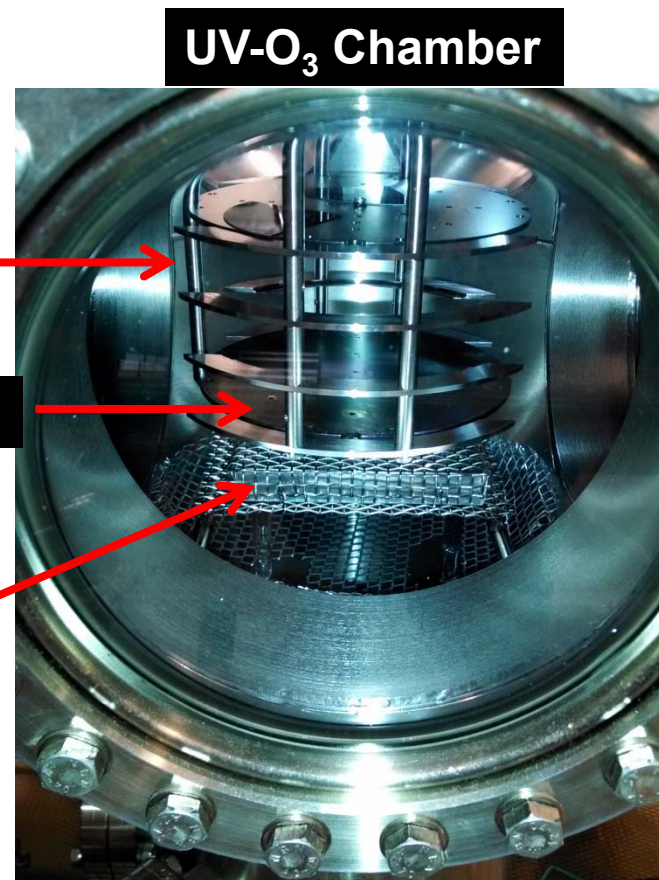
- Due to the relatively inert surface of sulfide-based TMDs, deposition of high-k dielectrics and surface functionalization on TMDs have been investigated.

S. McDonnell, et al., *ACS Nano*. **7** (2013) 10354; A. Azcatl, et al., *Appl. Phys. Lett.* **104** (2014) 11160; A. Azcatl, et al., *2D Materials* **2** (2015) 014004; P. Zhao, et al., *Microelectron Eng.* **147** (2015) 154

Sample surface (facing down) is <3mm from lamp



UV-O₃ Chamber



UV-O₃ Chamber

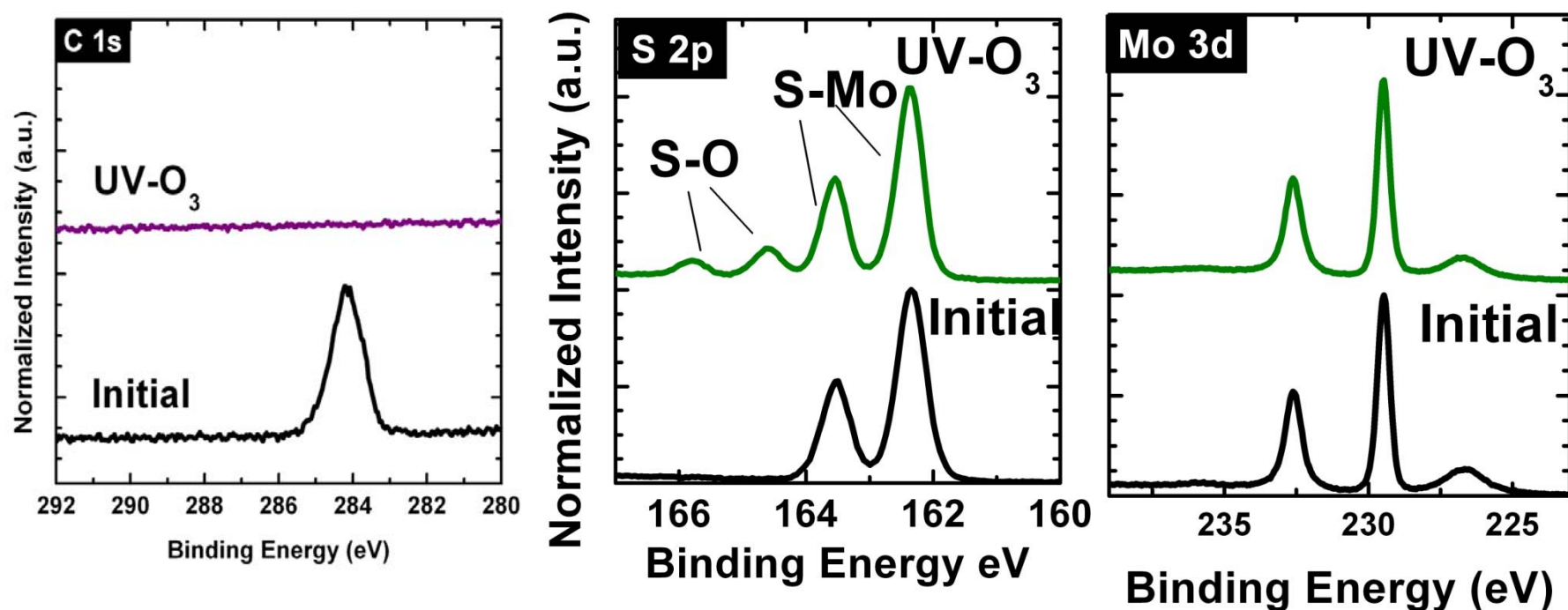
Carousel

Sample Plate

UV-Lamp
with
protective
mesh

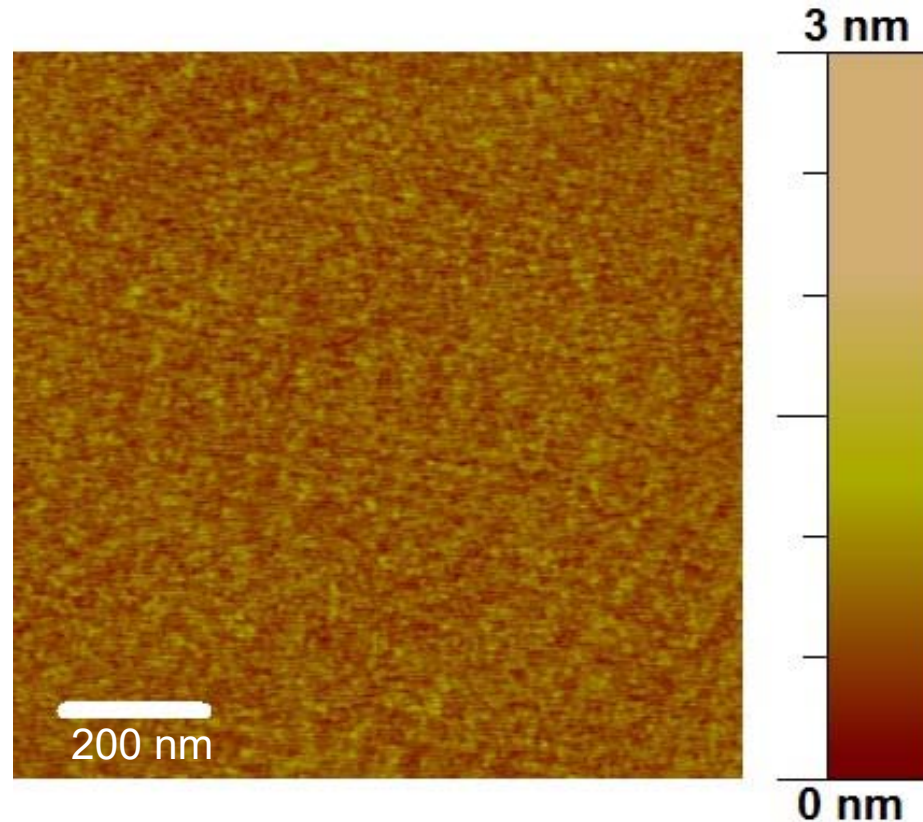
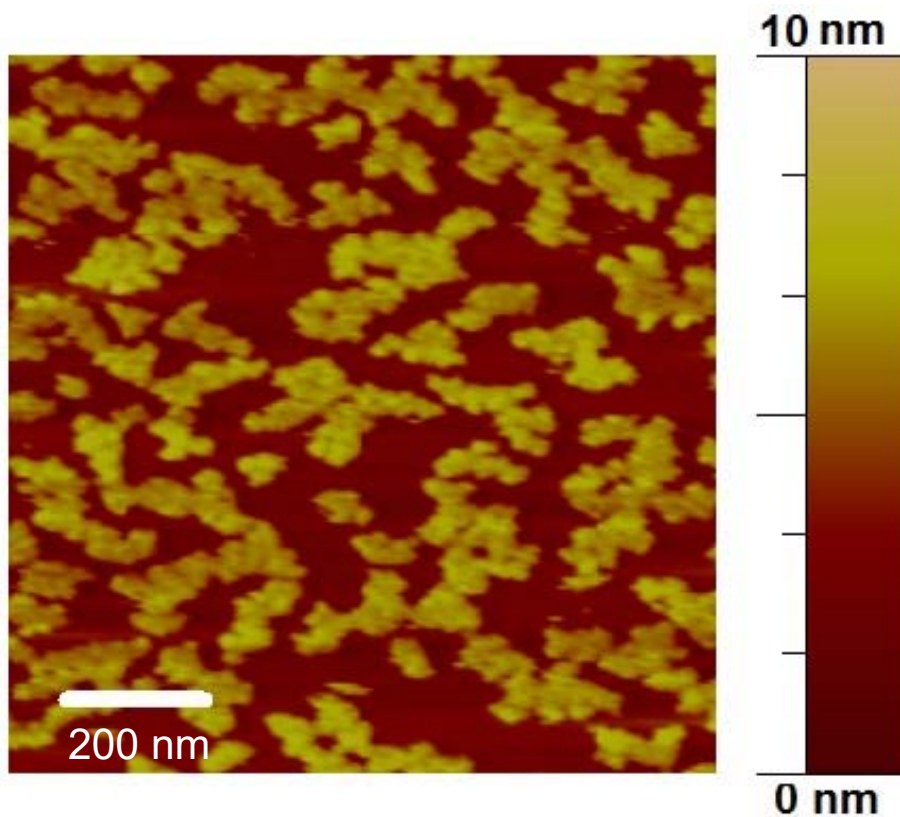
UV-Lamp Power Supply

- C contamination reduced below detection limit
- S-O bonding formation: functionalization
- Mo-O bonding not detected



ALD: 200°C, TMA- H_2O

ALD only

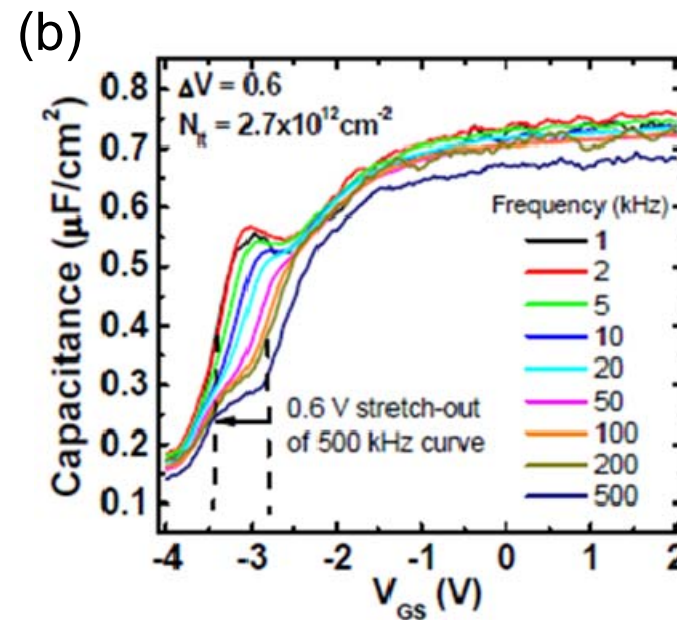
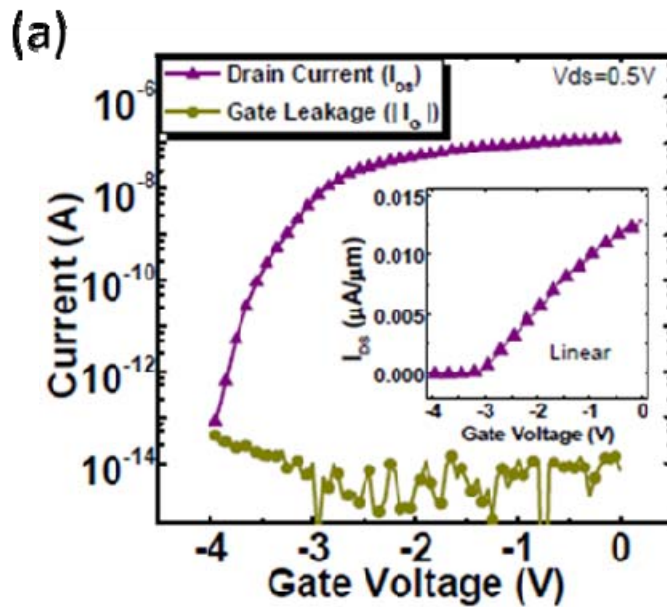
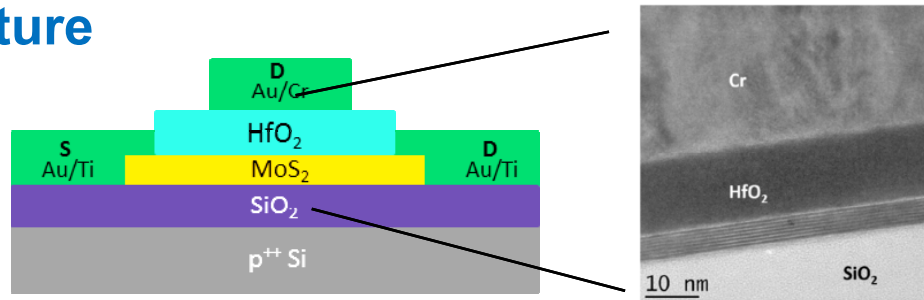
UV- O_3 + ALD

Surface Preparation: Exfoliation

900 mbar O_2 , 15 minutes, room temperature

In collaboration with Prof. Chadwin Young, Prof. Paul Hurley, and Mr. Peng Zhao

Device Structure



- High I_{ON}/I_{OFF} ratio ~10⁶
- Low leakage current level ~10⁻¹⁴ A → Good insulating properties of HfO₂

- Hump → Interface trap charge response
- D_{it} ≈ 2.7 × 10¹² cm⁻²

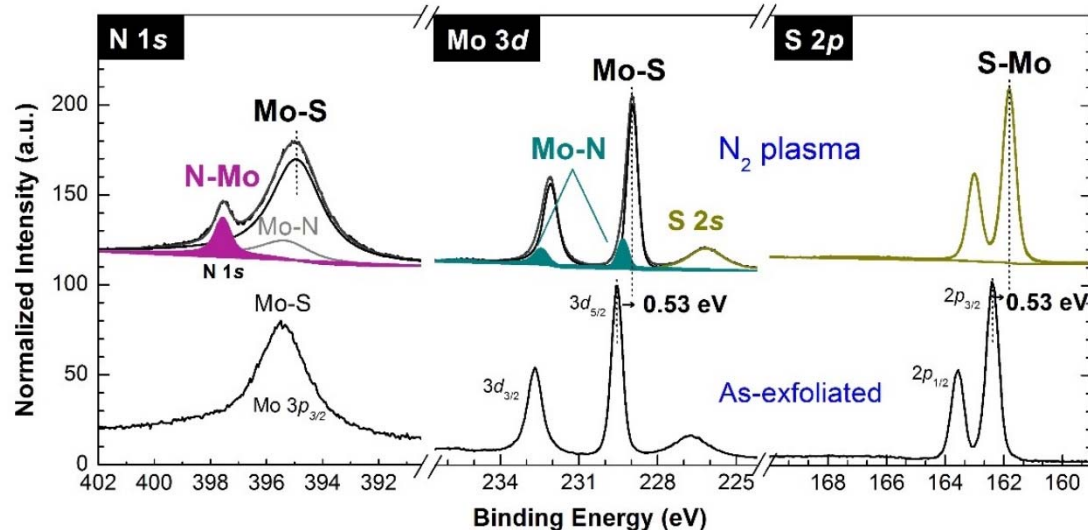
Metrology Opportunities?

- Develop protocol for 2D materials cleaning, controlled functionalization, characterization (physical and electrical)
- Establish correlations with electronic/photonic device response

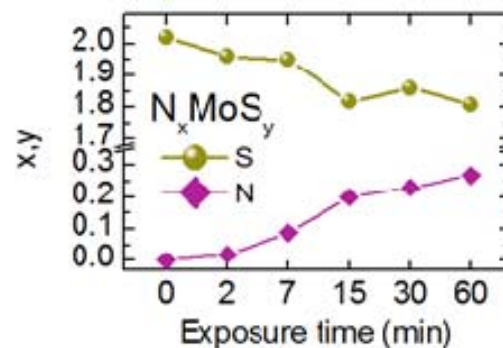
- Materials Challenges
- Methods
- TMDs
 - Doping
- Summary

*In-situ XPS

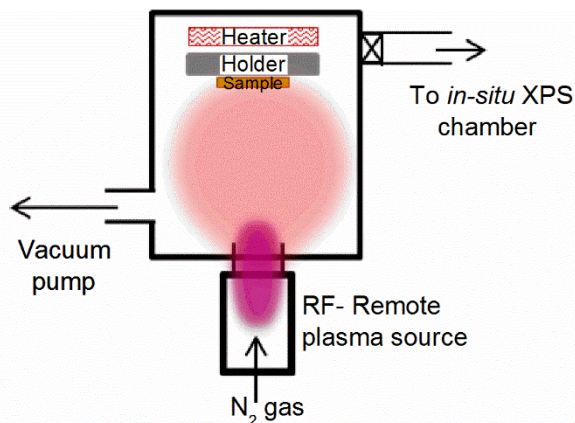
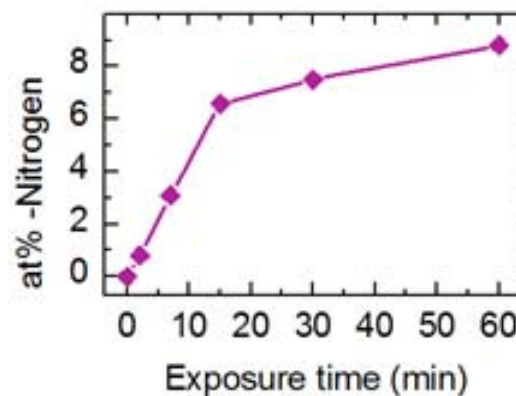
Covalent Nitrogen doping of MoS₂



Sulfur substitution by Nitrogen

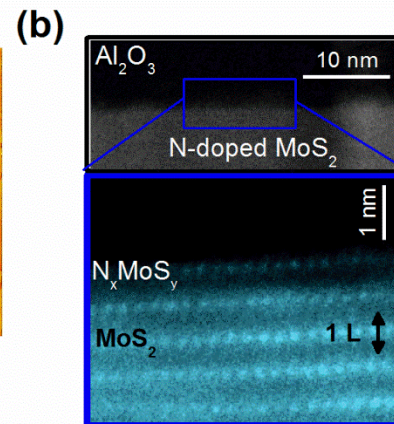
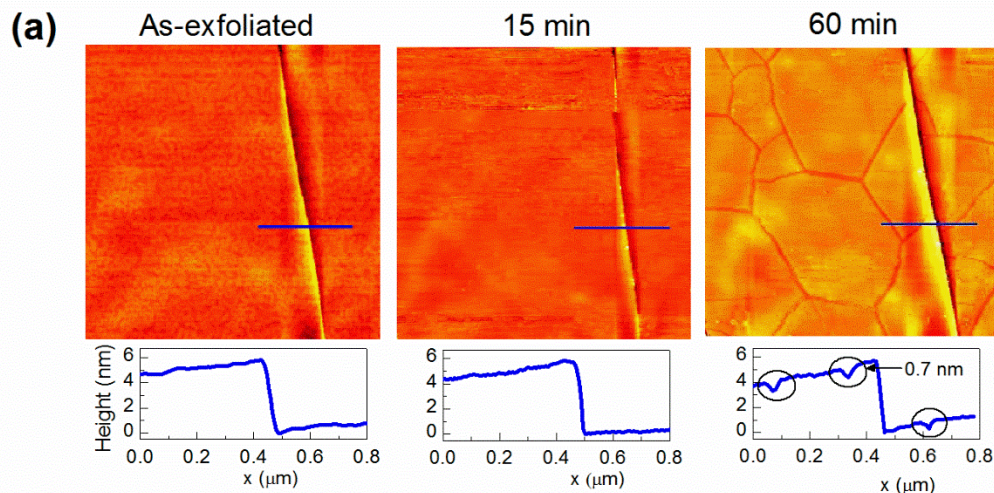


Controllable at% Nitrogen

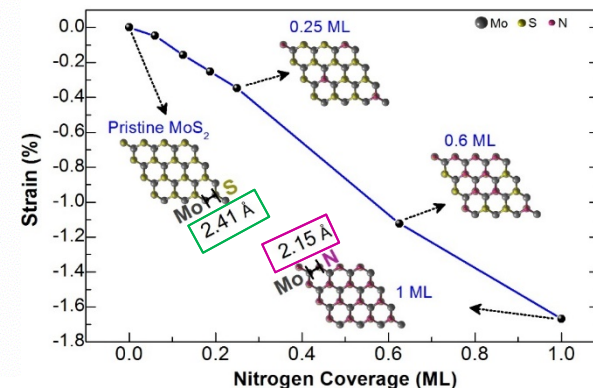
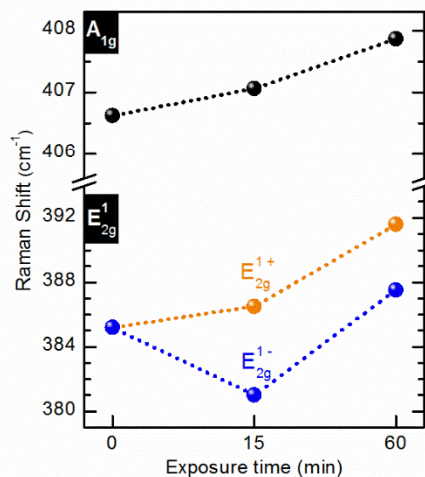
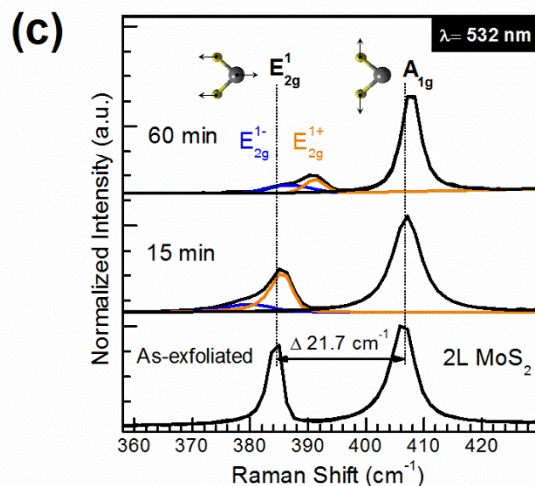


- Nitrogen concentration controlled with N₂ plasma exposure time

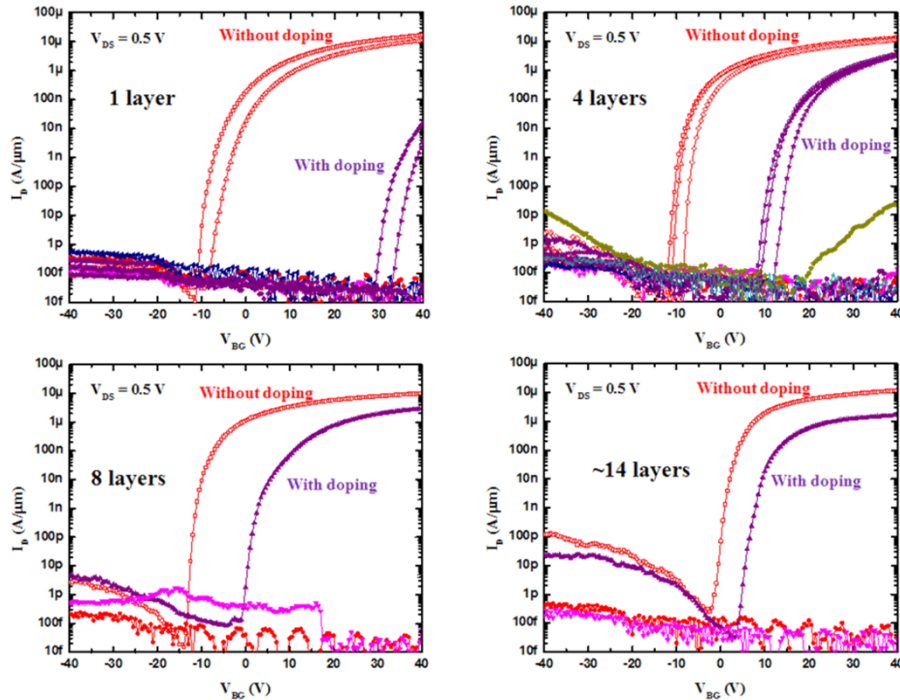
Strain induced by Nitrogen doping in MoS₂



- Compressive strain was identified in MoS₂ - Blue shift of both E_{2g}¹ and A_{1g} Raman modes¹
- Compressive strain can be tuned with nitrogen coverage up to 1.7% at 1 ML



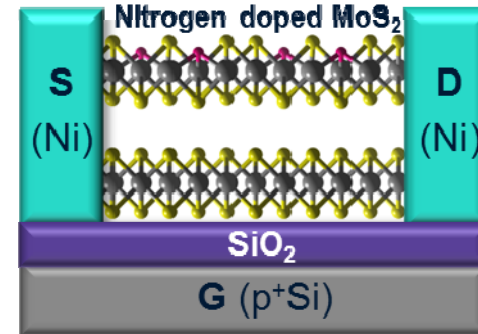
Electrical Characterization of Nitrogen Doped MoS_2



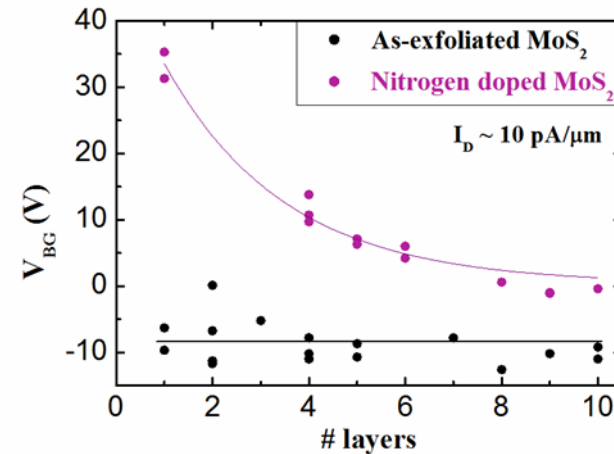
Nitrogen doped MoS_2 Stoichiometry: $\text{N}_{0.2}\text{MoS}_{0.8}$

- ✓ Threshold voltage shift consistent with the claim of p-doping
- ✓ ON current levels are preserved

Device Structure



Channel Thickness Dependent Shift

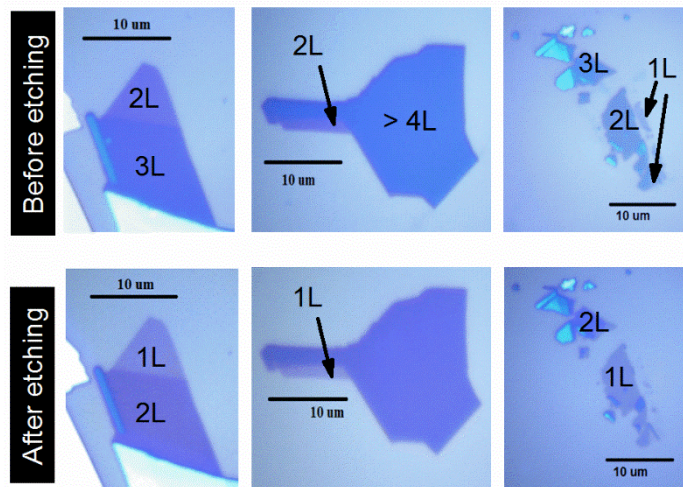


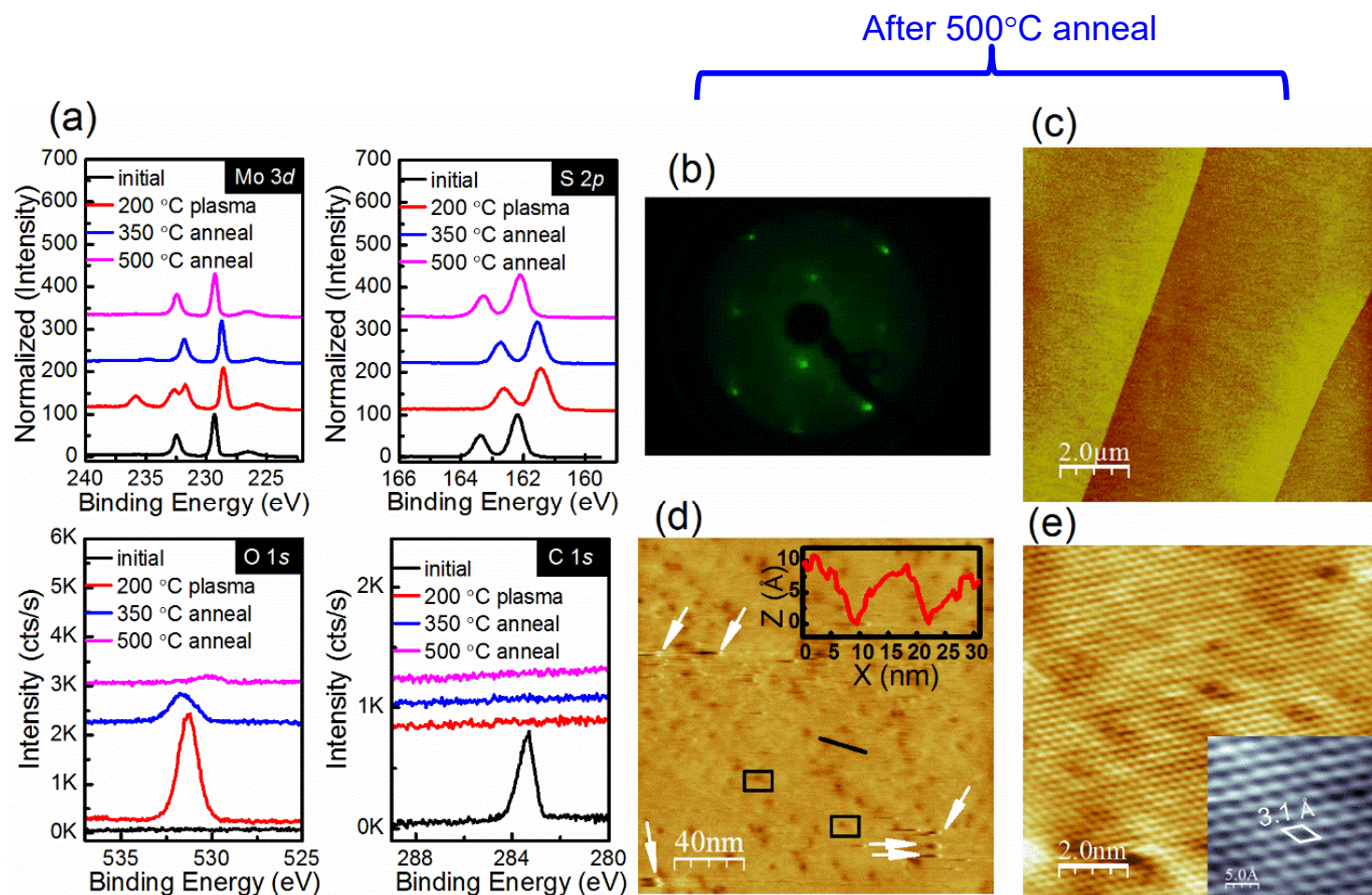
- ✓ The donor doping level in Nitrogen doped MoS_2 was found to be in the range of $\sim 2.5 \times 10^{18} \text{ cm}^{-3} - 1.5 \times 10^{19} \text{ cm}^{-3}$, having a reference doping level of $1.55 \times 10^{18} \text{ cm}^{-3}$ for undoped MoS_2

Metrology Opportunities?

- Develop protocol for 2D materials doping, characterization (physical and electrical)
- Establish correlations with electronic/photonic device response

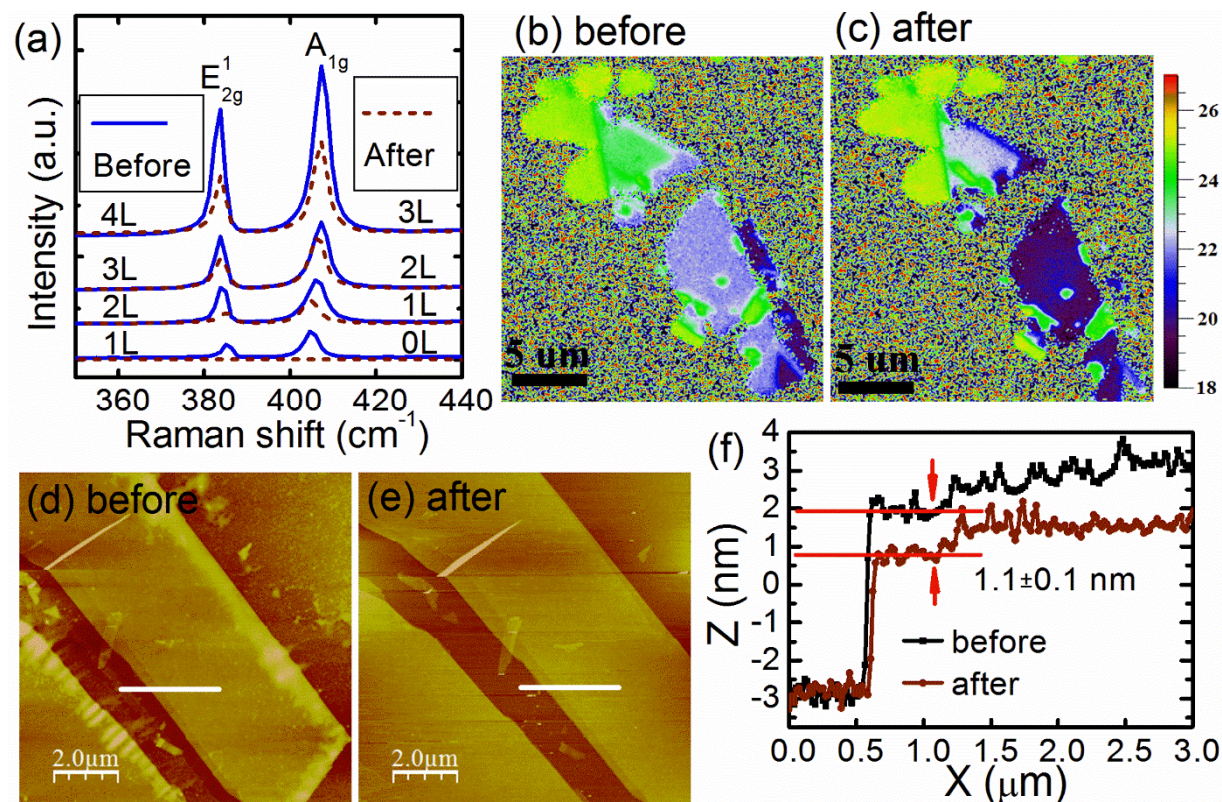
- Materials Challenges
- Methods
- TMDs
 - Etching
- Summary





- Controlled oxidation of MoS₂ surface with a remote O₂ plasma
- Subsequently anneal O/MoS₂ to 500 °C
- Removes layer of MoS₂ without underlying crystal disruption

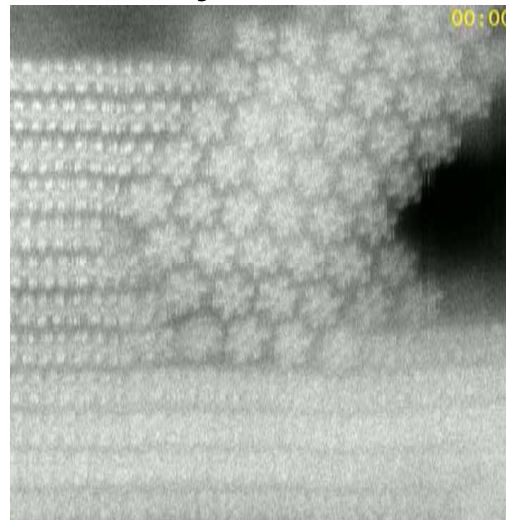
- Controlled oxidation of MoS₂ surface with a remote O₂ plasma
- Subsequently anneal O/MoS₂ to 500°C
- Removes layer of MoS₂ without underlying crystal disruption

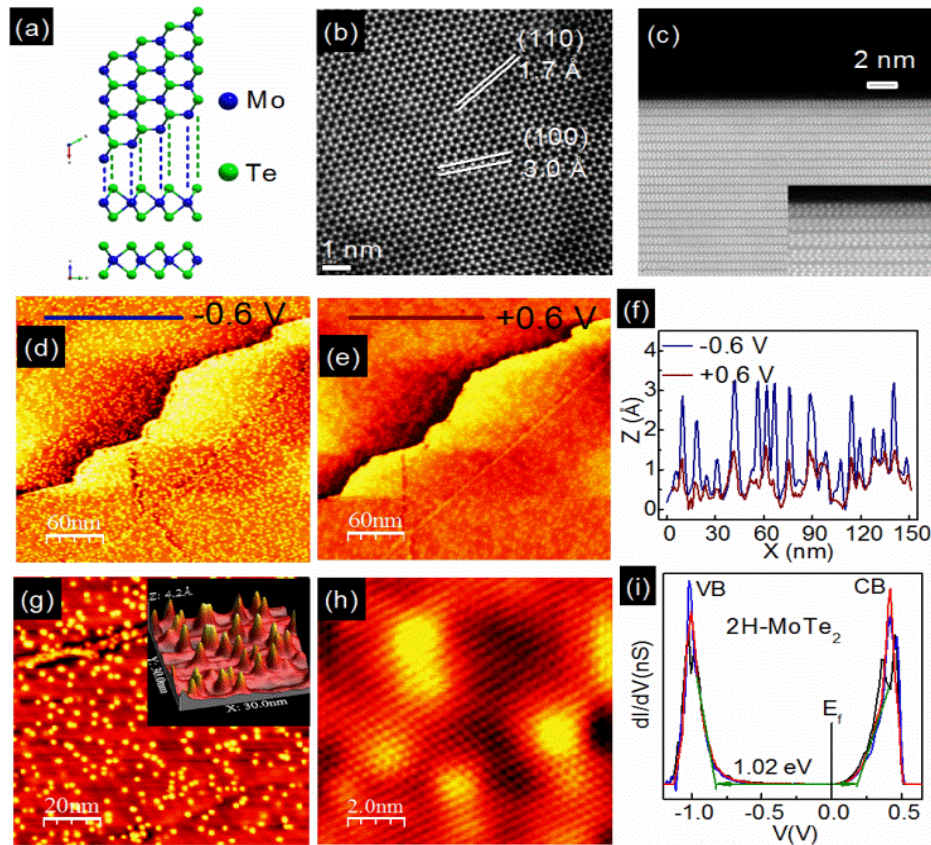


Metrology Opportunities?

- Develop protocol for 2D materials etch rate measurements, characterization (physical and electrical)
- Establish correlations with electronic/photonics device response

- Materials Challenges
- Methods
- TMDs
 - New Phases
- Summary



Surface imperfections characterization of exfoliated CVT MoTe₂ crystals with STM, STS and STEM

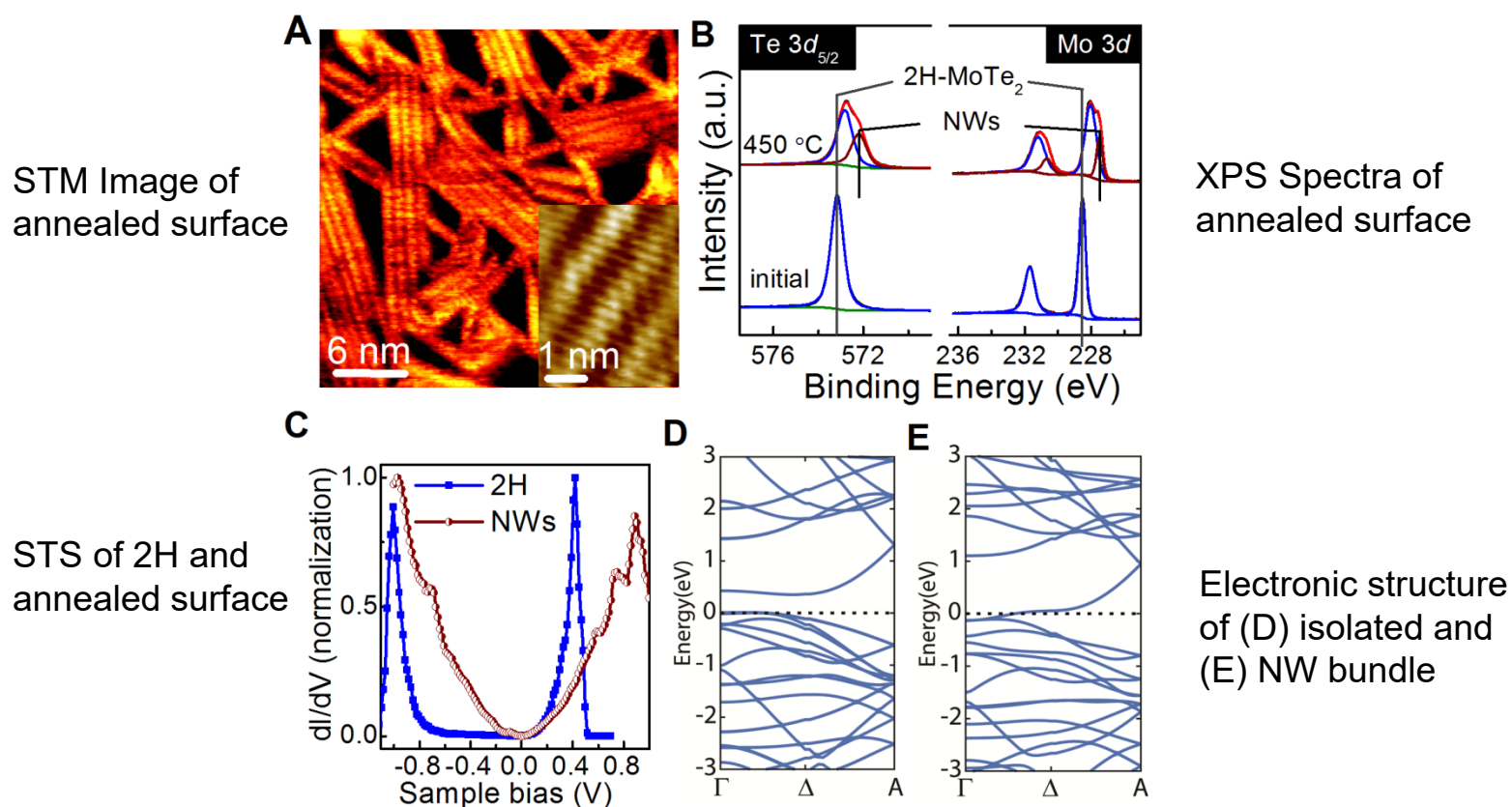
(a) Atomic structure of 2H-MoTe₂. (b) plan-view and (c) cross-section view [11-20] of high resolution STEM images with HAADF Z-contrast mode.

(d, e) Large-scale STM images (300×300 nm²) of the same MoTe₂ surface region taken at a sample bias of -0.6 and +0.6 V, respectively, with a tunneling current of 0.6 nA. The step-edge in the figures is ~ 7 Å, corresponding to one layer of MoTe₂. (f) Line profiles crossing over the same region in d and e.

(g) A STM topographic image (100× 100 nm²) shows the uniform circular shape of bumps/protrusions (bright spots). A 3D zoom-in image is shown in the inset of (g), indicate the average height of protrusions is 3±0.5 Å depending on sample biases and tunneling current. (h) High-resolution STM image of the represented 2H-MoTe₂ lattice decorated with protrusions. The image (g, h) are taken with V_b = -0.6 V, 0.4 V, respectively, and I_t = 1.5 nA. (i) STS measurements from multiple surface regions.

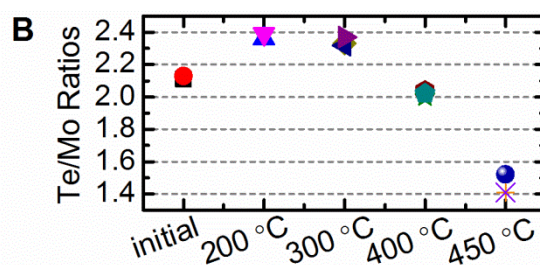
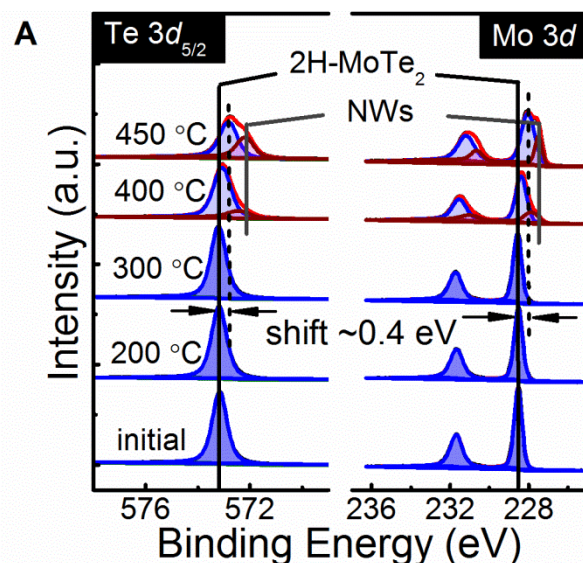
- 2H, 1T' and T_d phases typically noted in the literature
- Variations in electronic nature of the surface
- Sensitivity of TEM vs. STM to defects

Annealing MoTe₂ results in Te loss → phase changes → **Nanowire** formation

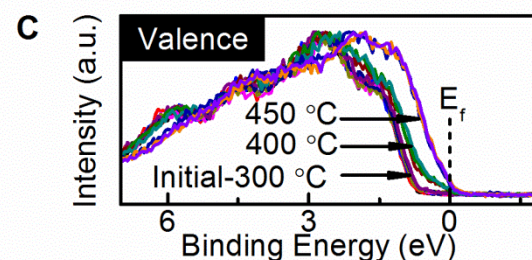


- Te/Mo ratio on the initial surface is around 2.12 ± 0.02 , indicating a homogeneous Te rich environment.
- Subsequent thermal treatment reveals that the Te/Mo ratio is extremely temperature sensitive.

XPS spectra of the Te $3d_{5/2}$ and Mo $3d$ core levels.

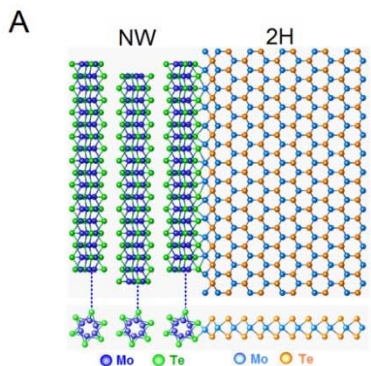


Derived Te/Mo ratios from the Te $3d_{5/2}$ and Mo $3d$ spectra and measured on multiple surface regions.

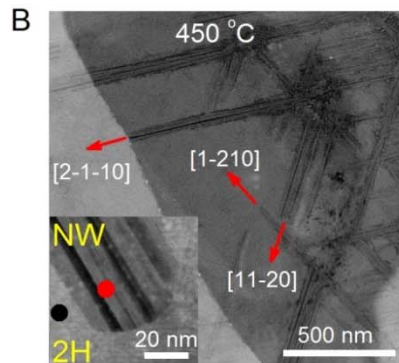


Valence band regions measured on multiple surface regions.

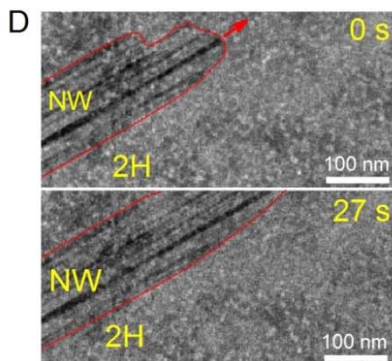
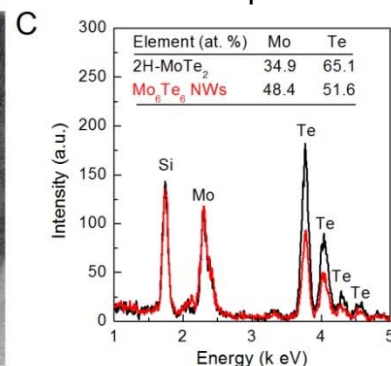
Schematic of the transition from 2H-MoTe₂ to Mo₆Te₆ NWs.



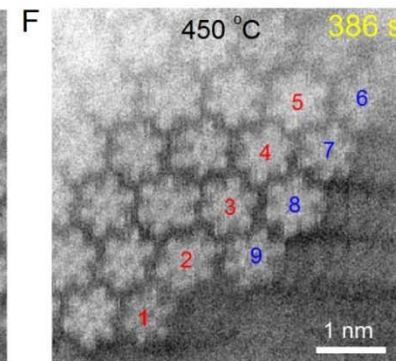
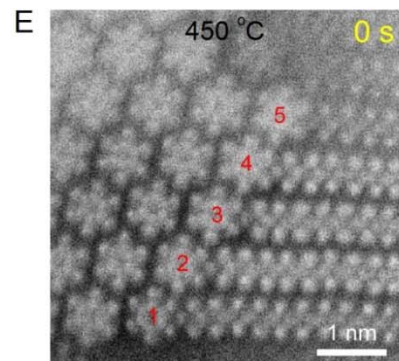
Plan-view image of Mo₆Te₆ NW bundles grown on 2H-MoTe₂ (0001) surface



EDS analysis on top of Mo₆Te₆ NW bundles (red dot) and the nearby 2H-MoTe₂ region (black dot in the inset panel of B)



Time sequence images of 2H-MoTe₂ (0001) show a fast growth of Mo₆Te₆ NWs along the 2H-MoTe₂ <11-20> directions

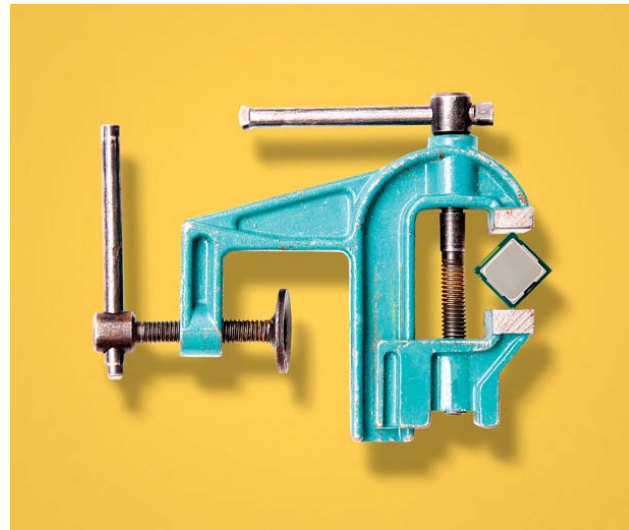


Time sequence images viewed along the 2H-MoTe₂ [11-20] direction (or Mo₆Te₆ [001])

Metrology Opportunities?

- Develop database for 2D materials phases, characterization (physical and electrical)
- Establish correlations with electronic/photonics device response

- Materials Challenges
- Tools and Methods
- TMDs
- **Summary**



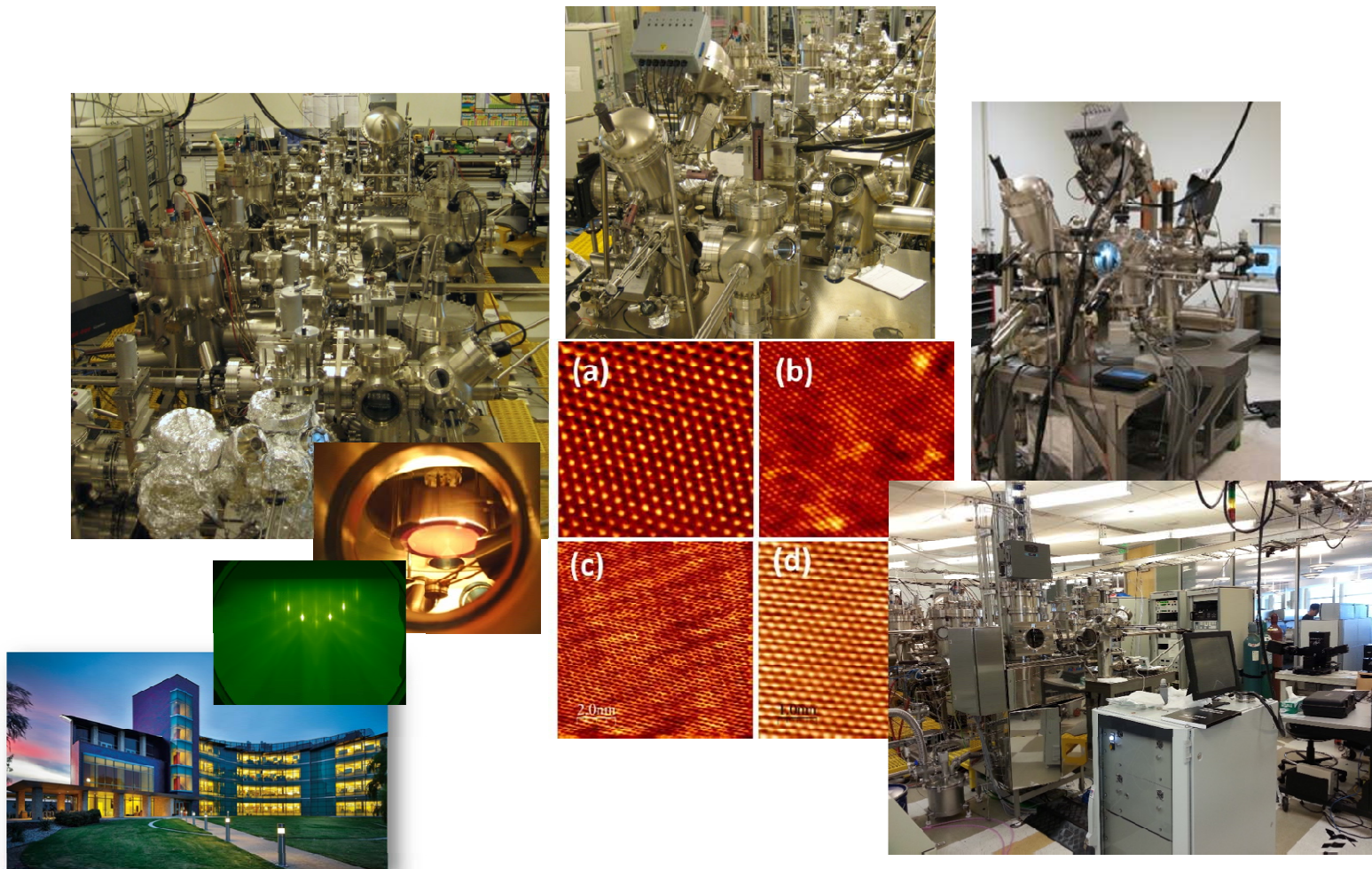
IEEE Spectrum

- ❑ 2D TMD Materials may offer the ultimate scaling: a monolayer transistor channel
- ❑ Steep slope TFETs with useful “on” currents are under research now
- ❑ Cleaning process residues essential for reproducible properties
- ❑ Functionalization without substrate disruption possible, enables efficient ALD
- ❑ Surfaces can be far from perfect: defect density can be significant (several %)
- ❑ Contacts can be dominated by defects and reactions – deposition ambient details are important in interpretation of contact behavior
- ❑ Super acid wet passivation demonstrated on TM-sulfides, but not on selenides
- ❑ Substitutional *chalcogen* doping is possible
- ❑ Atomic layer etching routes are possible
- ❑ Impurities on geological and synthetic crystal surfaces can be substantial, progress has been made recently
- ❑ Large area, high quality (low defect/impurity) films needed for device progress

There appear to be **MANY** opportunities to establish metrology protocols, benchmarks and standards for the device community

- Relative to Si, TMDs exhibit relatively high intrinsic and extrinsic defects/impurities
 - Geological TMDs are far more inferior at this time.
 - Improvements in growth methods and purity have been noted
- Defects and interfacial chemistry, within the detection limit of in-situ surface analysis techniques, provide useful information to guide process development, tool/material requirements
 - Correlation to device behavior is possible and useful!
 - Opportunity to establish what constraints must be addressed
 - Details of process ambient are important!
- All researchers must be cognizant of their materials properties when drawing conclusions
 - Physical characterization has limited sensitivity
 - Electrical characterization is very sensitive, but interpretation can be ambiguous

Thanks!



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<https://sites.google.com/site/robertmwallace01/>