

# Promise of 2D Crystals

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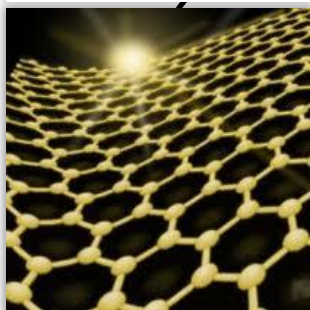
Center for Nanoscale Materials, Nanoscience and Technology Division. High Energy  
Physics Division, Argonne National Laboratory, Lemont, Illinois , USA 60439

- 1. 2D Crystals**
- 2. 2D Electronics**
- 3. 2D Optoelectronics**
- 4. 2D Engineering**

- 1. 2D Crystals**
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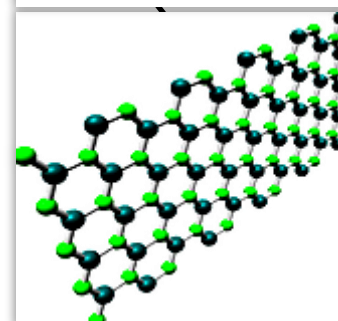
Excellent  
Conductor

Graphene

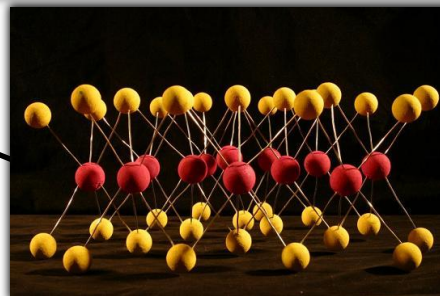


Excellent  
Insulator

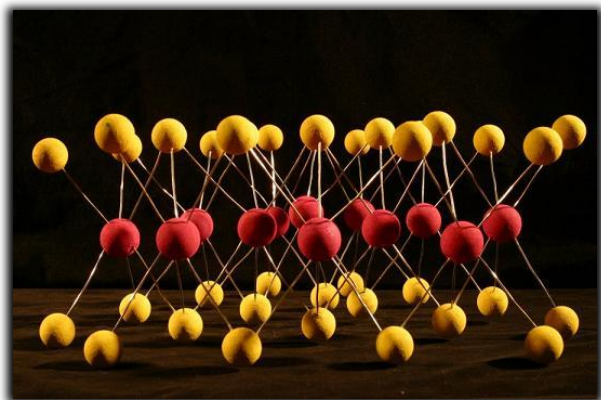
h-BN



Transition Metal Dichalcogenides



## Transition Metal Dichalcogenides



88 TMDs have been explored since 1960s

Metals: **ScTe<sub>2</sub>**, **TaS<sub>2</sub>**, etc.

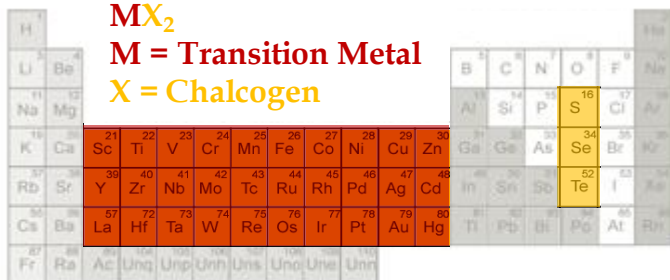
Semiconductors: **WSe<sub>2</sub>**, **MoS<sub>2</sub>**, etc.

Insulators: **PtSe<sub>2</sub>**, **PdS<sub>2</sub>**, etc.

Superconductors: **VS<sub>2</sub>**, **NbSe<sub>2</sub>**, etc.

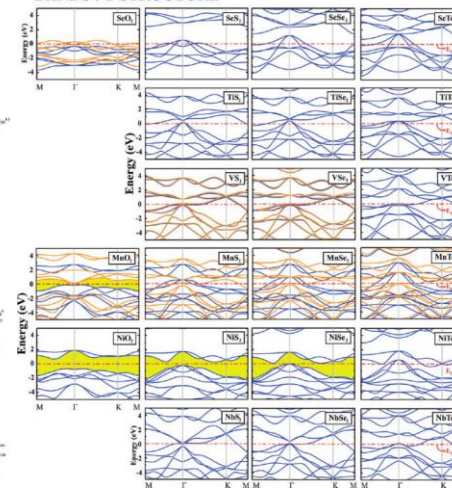
## Periodic Table of Elements

**MX<sub>2</sub>**  
**M = Transition Metal**  
**X = Chalcogen**

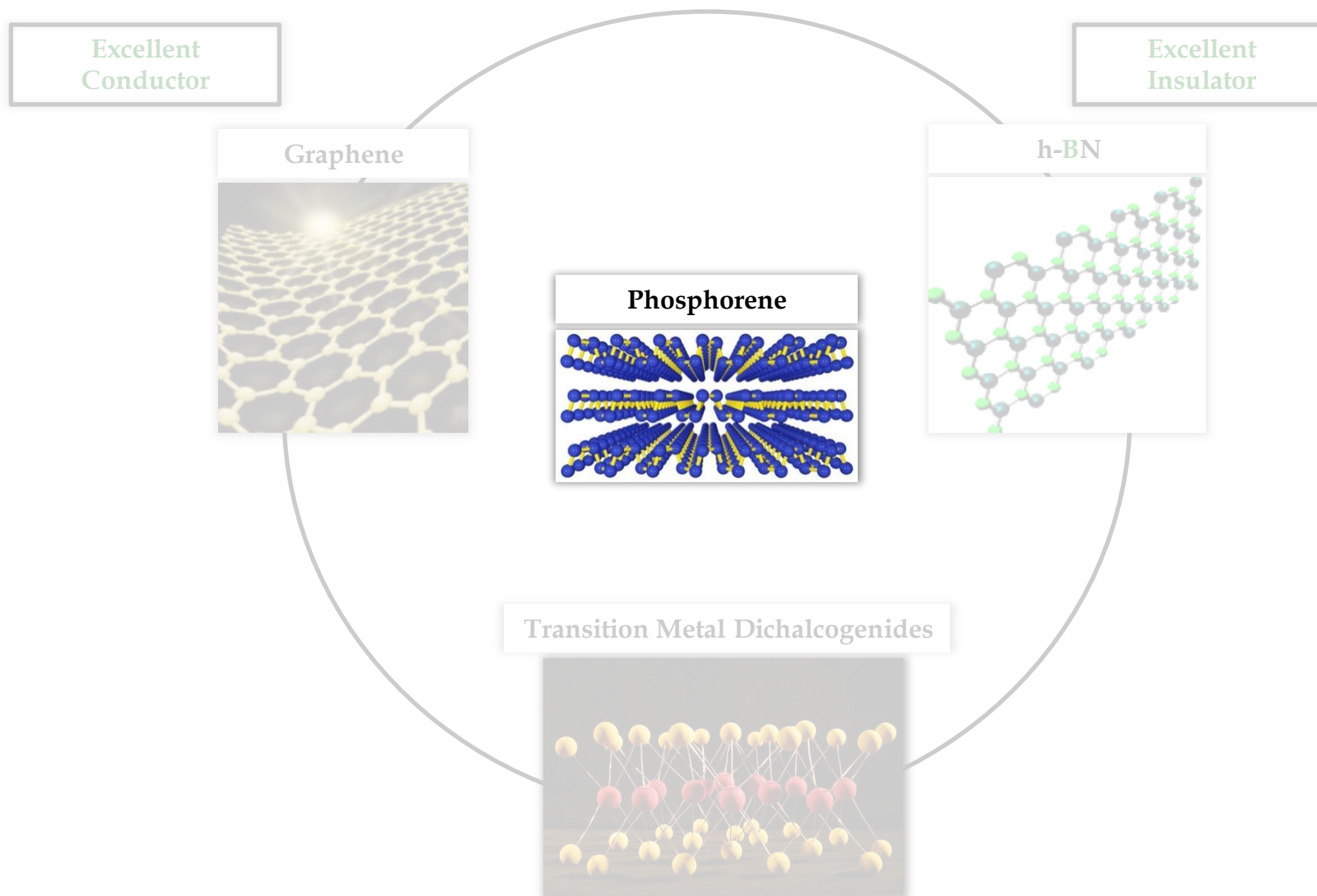



Symbol	Z	$r_0$ (Å)	$r_0^*$ (Å)	$r_0^{**}$ (Å)	$E_0$ (eV)	$E_0^*$ (eV)	$E_0^{**}$ (eV)	$\rho$ (g/cm <sup>3</sup> )	$\rho_0$ (atoms/cm <sup>3</sup> )	$\rho_0^*$ (atoms/cm <sup>3</sup> )	$\rho_0^{**}$ (atoms/cm <sup>3</sup> )	$\chi$ (eV)	SO band structure
ScS <sub>2</sub>	21	1.69	2.08	18.39	20.55	75.11(12.2)	1.05	—	1.00	1.00	-0.05	76.33	—
Ti	22	2.07	2.61	70.01	20.55	80.11(14.5)	—	—	1.00	1.00	-0.06	14.07	—
V	23	2.52	2.99	64.82	18.31	134.6(7.7)	0.44	—	1.00	1.04	-0.02	44.61	—
Cr	24	2.96	3.44	67.05	16.48	171.0(8.0)	—	—	1.00	1.02	-0.01	28.29	—
Mn	25	2.65	2.90	46.39	15.12	133.0(8.30)	0.17	—	1.00	1.06	-0.79	30.09	—
Fe	26	2.64	2.98	66.82	15.82	134.6(8.0)	—	—	1.04	1.04	-0.12	18.47	—
Cobalt	27	2.89	3.08	67.17	15.07	125.0(8.30)	—	—	1.04	1.14	-0.07	38.28	—
Ni	28	2.85	4.33	68.58	14.05	145.0(13.77)	—	—	1.04	1.13	-0.07	13.49	—
Cu	29	2.39	3.42	61.73	18.36	107.0(8.3)	—	—	1.04	1.00	-0.40	76.33	1T <sup>10</sup>
Zn	30	2.51	3.08	60.04	16.02	142.0(7.5)	—	—	1.04	1.10	-0.70	43.02	1T <sup>10</sup>
Ga	31	2.73	3.57	61.09	14.76	172.0(5.5)	—	—	1.04	1.16	-0.38	9.10	1T <sup>10</sup>
Ge	32	3.73	4.08	66.30	15.10	120.0(8.37)	—	—	1.04	1.18	-0.39	41.61	—
As	33	1.93	2.24	71.34	21.64	120.0(11.13)	—	—	0.52	1.79	-0.80	17.94	Pt <sup>100</sup> /M <sup>100</sup>
Se	34	2.31	2.95	70.14	17.47	129.0(6.4)	—	—	0.10	1.18	-0.49	104.03	1T <sup>10</sup> /M <sup>100</sup>
Br	35	2.43	3.17	60.49	15.97	137.0(7.5)	—	—	0.66	1.06	-0.51	82.00	1T <sup>10</sup>
Kr	36	2.44	3.60	67.04	15.09	120.0(8.30)	—	—	0.15	1.08	-0.54	80.24	—
Rb	37	2.66	3.48	61.80	14.17	103.0(4.40)	—	—	0.85	0.80	-0.40	49.64	1T <sup>10</sup>
Sr	38	2.64	4.00	69.33	14.54	109.0(4.53)	—	—	1.04	0.85	-0.42	14.43	—
Y	39	1.88	2.29	73.21	19.55	625.0(18.2)	0.58	1.00	1.04	1.04	-0.77	220.94	2T <sup>10</sup>
Zr	40	2.07	2.52	60.06	15.89	133.0(8.0)	1.07	1.04	1.04	0.92	-0.40	120.00	1T <sup>10</sup> /M <sup>100</sup>
Nb	41	2.38	3.11	61.54	14.32	145.0(8.30)	0.86	1.01	1.04	0.77	-0.38	104.14	1T <sup>10</sup> /M <sup>100</sup>
Mo	42	2.58	3.38	61.56	12.52	632.0(14.6)	0.60	1.12	1.04	0.66	-0.23	77.57	—
Tc	43	1.87	2.22	72.70	17.71	637.0(9.8)	—	—	0.60	1.11	-0.45	134.07	R <sup>10</sup>
Ru	44	1.88	2.40	63.07	14.83	128.0(10.0)	0.24	—	1.00	1.04	-0.02	127.12	—
Rh	45	2.27	3.29	63.08	14.82	143.0(8.30)	—	—	1.28	0.92	-0.40	66.87	Pt <sup>10</sup> -M <sup>100</sup>
Pd	46	2.39	3.49	63.78	13.61	133.0(7.7)	—	—	1.26	0.76	-0.37	56.61	Pt <sup>10</sup> /M <sup>100</sup>
Ag	47	2.58	3.77	63.56	12.27	622.0(4.97)	—	—	2.39	0.41	-0.20	44.77	—
Cd	48	1.88	2.24	73.08	17.37	325.0(7.80)	—	—	1.43	1.38	-0.40	133.99	M <sup>100</sup>
In	49	2.22	2.68	74.20	15.50	114.0(5.52)	—	—	1.12	0.57	-0.29	95.20	Pt <sup>10</sup> /M <sup>100</sup>
Sn	50	2.58	2.87	75.88	14.80	145.0(8.30)	—	—	1.10	0.42	-0.21	49.89	Pt <sup>10</sup> /M <sup>100</sup>
Sb	51	2.34	3.08	74.08	13.21	619.0(5.5)	—	—	1.08	0.60	-0.01	37.71	M <sup>100</sup>
Te	52	2.51	2.98	72.16	13.44	629.0(4.67)	—	—	1.07	-0.19	0.30	56.13	M <sup>100</sup> /M <sup>100</sup>
I	53	2.74	2.84	62.53	16.76	110.0(7.23)	1.38	—	1.04	1.04	-0.07	104.64	1T <sup>10</sup> /M <sup>100</sup>
Xe	54	2.24	2.14	27.16	14.35	85.0(4.21)	—	—	1.04	0.42	-0.21	38.51	Pt <sup>10</sup>
Ba	56	2.12	2.97	64.46	14.91	100.0(7.7)	0.51	—	1.04	0.89	-0.24	86.23	—
La	57	2.35	2.71	70.29	13.69	647.0(4.5)	—	—	1.04	0.52	-0.12	34.82	—
Ce	58	2.34	3.15	64.59	13.97	695.0(4.6)	0.38	—	1.04	0.27	-0.13	65.73	—
Pr	59	2.54	2.85	70.55	12.80	640.0(4.49)	—	—	1.04	0.42	0.00	41.60	—
Nd	60	2.52	3.47	67.33	13.19	603.0(4.97)	—	—	1.04	-0.12	0.00	43.65	1T <sup>10</sup>
Pm	61	2.30	2.43	62.55	19.64	317.0(6.7)	—	—	1.04	1.52	-0.76	96.60	1T <sup>10</sup> /Pt <sup>100</sup>
Sm	62	2.57	3.87	67.58	18.13	136.0(4.6)	—	—	1.04	1.27	-0.44	78.47	2T <sup>10</sup> /Pt <sup>100</sup>
Eu	63	2.57	3.30	68.03	18.33	145.0(5.7)	—	—	1.04	1.23	-0.62	87.24	1T <sup>10</sup>
Gd	64	2.77	4.24	60.03	16.38	136.0(4.6)	—	—	1.04	0.80	-0.41	44.08	1T <sup>10</sup>
Tb	65	2.78	2.60	2.42	15.92	22.65	679.0(16.6)	0.47	1.04	1.84	-0.42	233.83	R <sup>100</sup> /M <sup>100</sup>

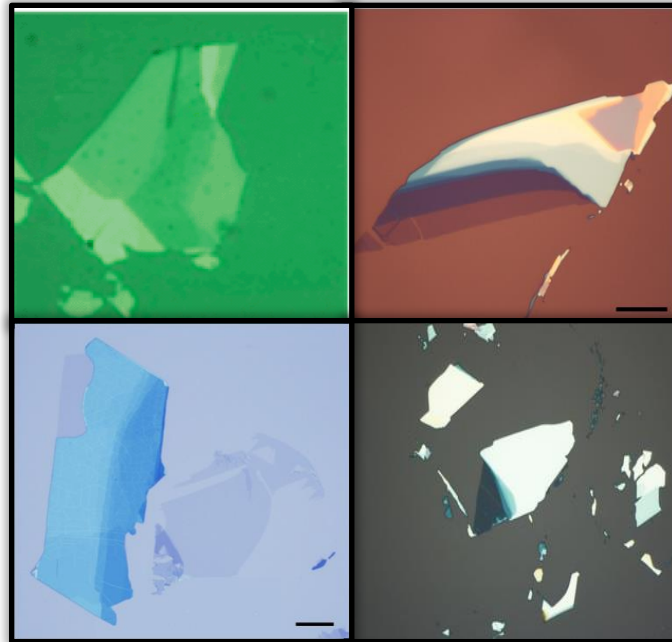
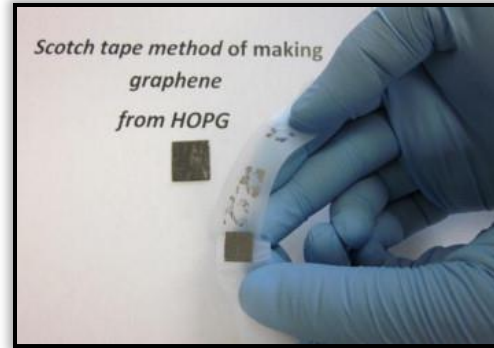
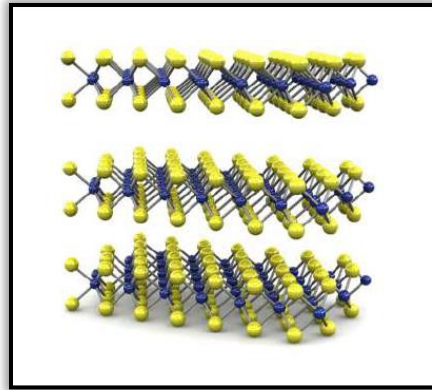
## BANDS: T-STRUCTURE



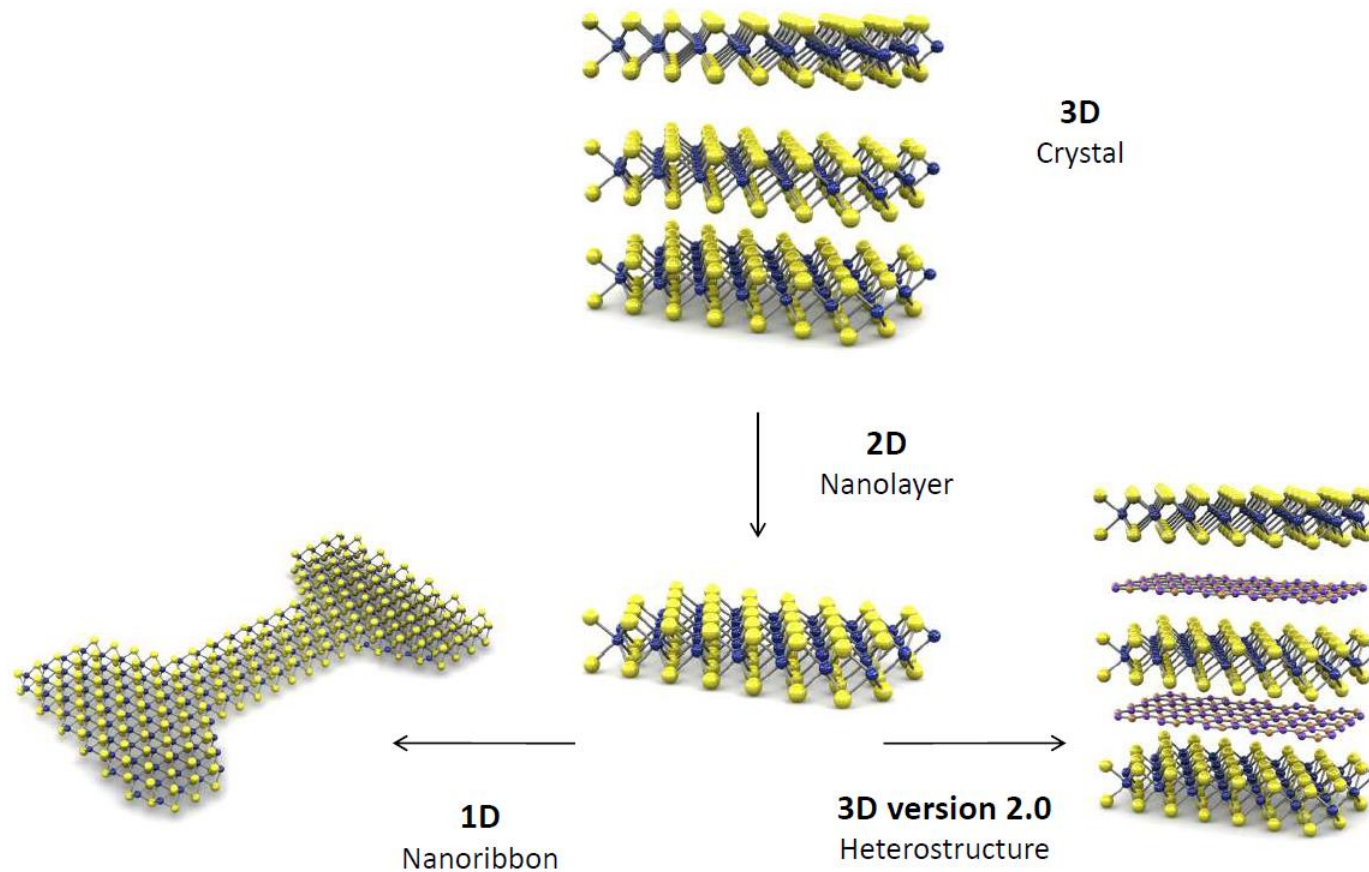
# Natural 2D Crystals



# Exfoliation



# Layered Compounds

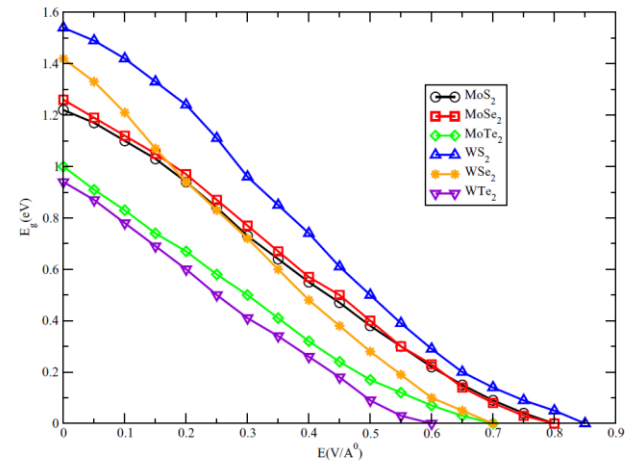






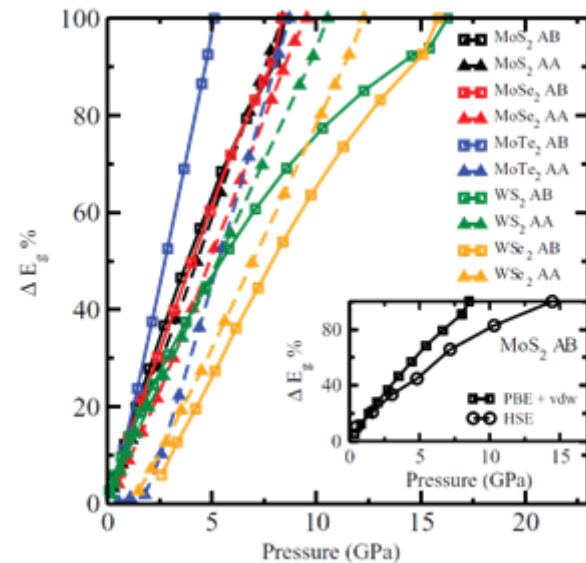
## Electric Field Induced

Swastibrata Bhattacharyya, *et al.*  
Physical Review B, 86, 2012



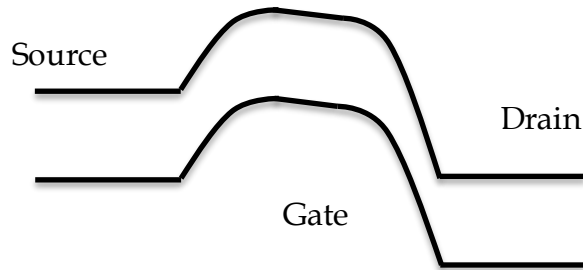
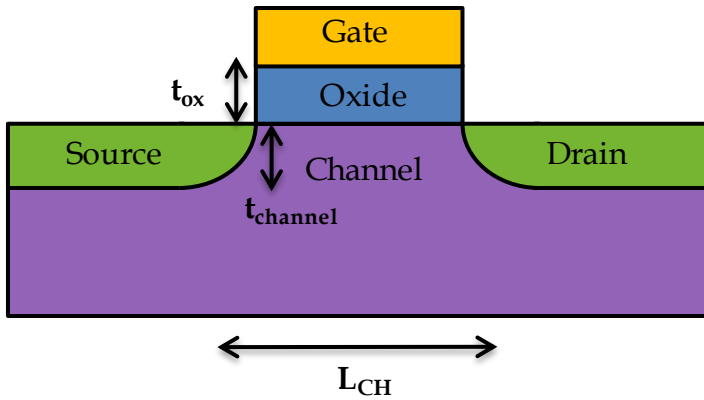
## Mechanical Force Induced

Ashok Kumar, *et al.* Modeling and Simulation in  
Material Science and Engineering, 21, 2012

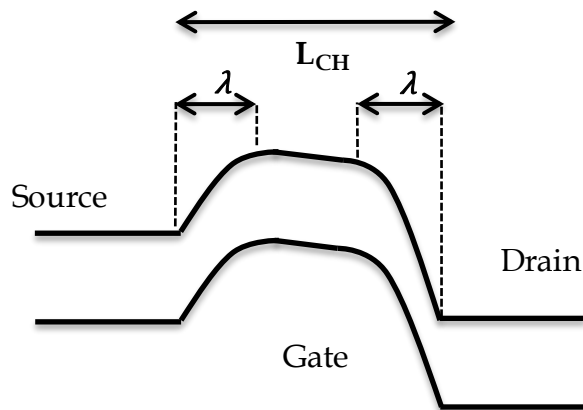
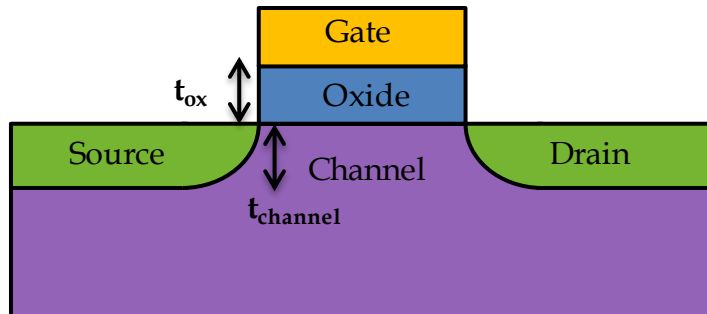


1. 2D Crystals
- 2. 2D Electronics**
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4. 2D Engineering

## Field Effect Transistor



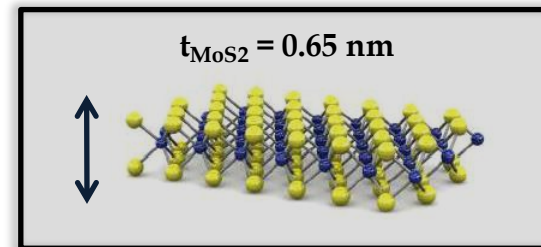
## Field Effect Transistor



$$\lambda = \sqrt{t_{channel} t_{ox}}$$
$$L_{CH} > 3\lambda$$

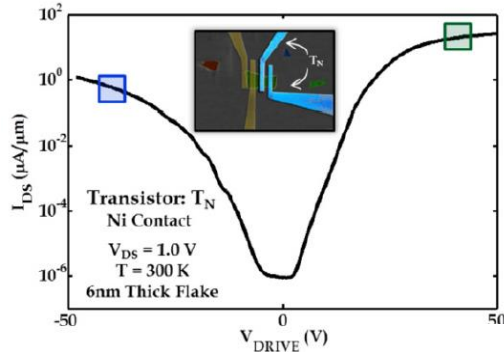
Gate Leakage Current does not allow thinning down of gate Oxide

Quantum Confinement does not allow thinning down of Si channel



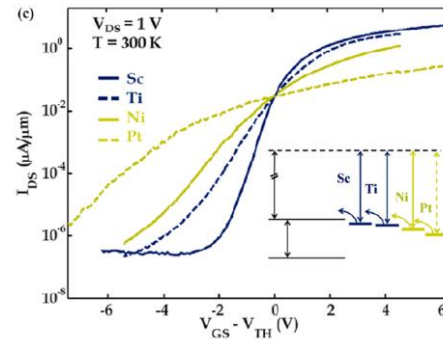
## WSe<sub>2</sub> FET

Saptarshi. *et al.* Applied Physics Letters, 103, 2013.



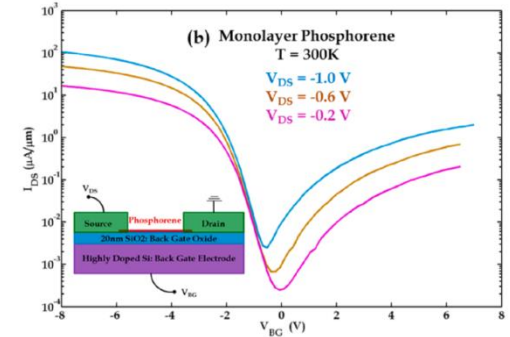
## MoS<sub>2</sub> FET

Saptarshi. *et al.* Nano Letters, 13(1), 2013.



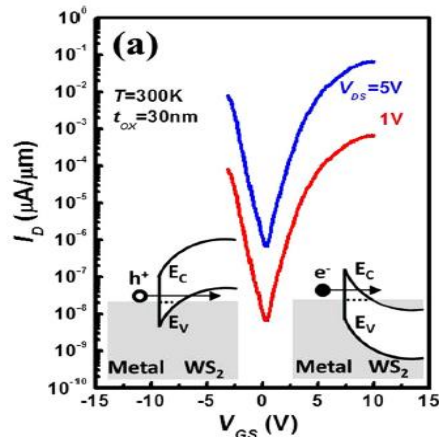
## Phosphorene FET

Saptarshi. *et al.* Nano Letters, 14(10), 2014.



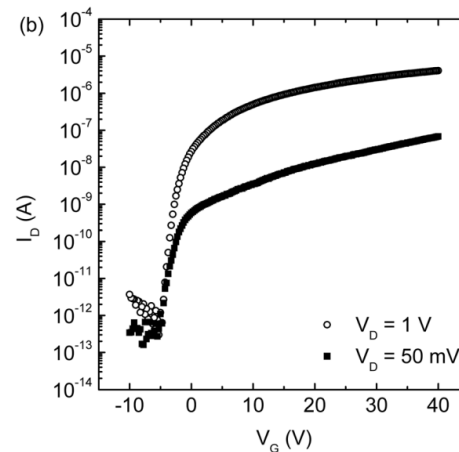
## WS<sub>2</sub> FET

Hwang. *et al.* Applied Physics Letters, 101, 2012.



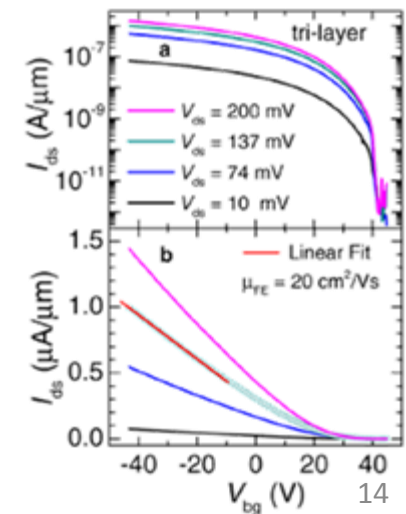
## MoSe<sub>2</sub> FET

Pradhan. *et al.* ACS Nano, 8(6), 2014.

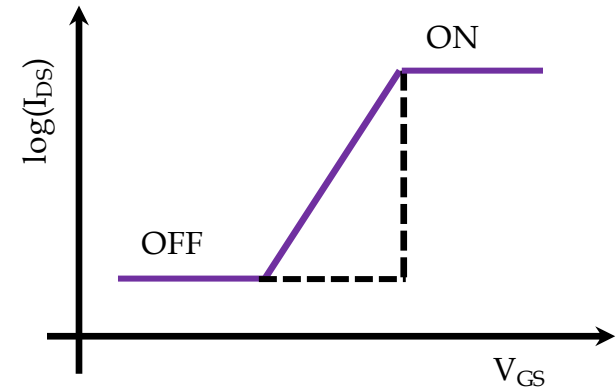
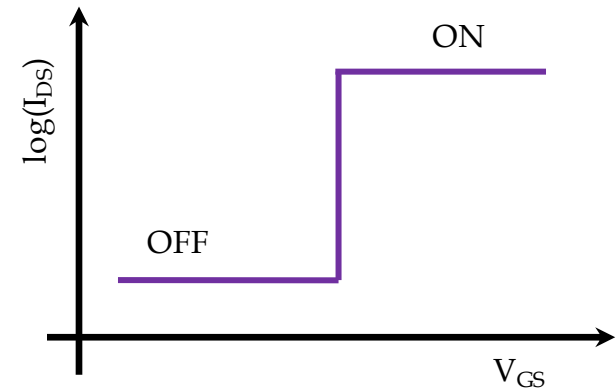
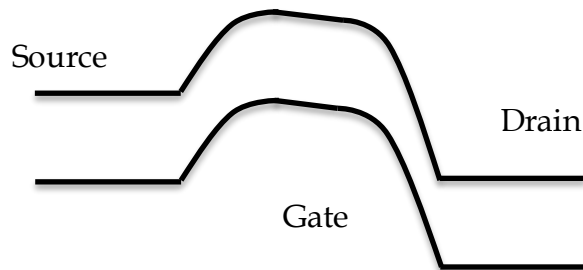
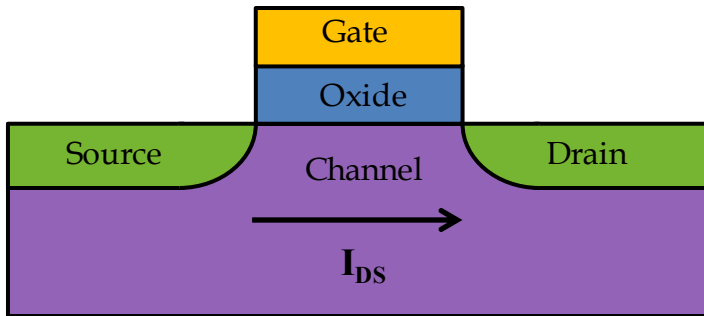


## MoTe<sub>2</sub> FET

Pradhan. *et al.* ACS Nano, 8(8), 2014.

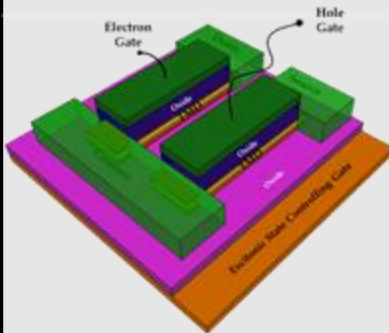


## Field Effect Transistor



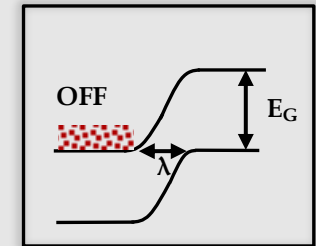
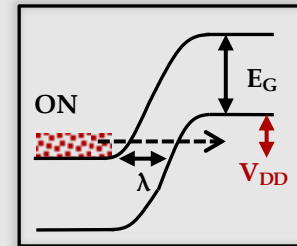
Boltzmann Statistics limits power dissipation

## Excitonic Transistors



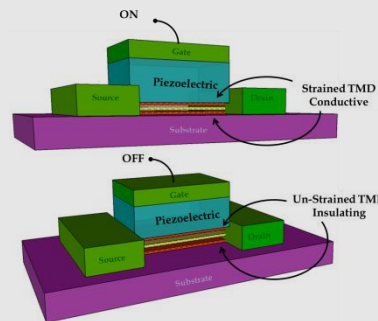
- ✓ Columbic Interaction between Electrons and Holes Resulting in Phase Transition
- ✓ Possibility of Room Temperature Superconductivity

## Tunneling Transistors



$$T_{WKB} = \exp\left(-\frac{4}{3\hbar}\sqrt{2m_e E_G d_{OX} d_{BODY}}\right)$$

## Mott Transition Transistors



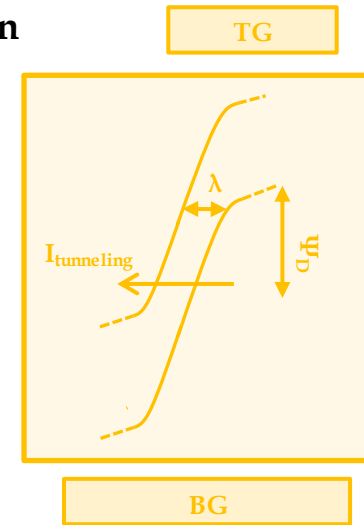
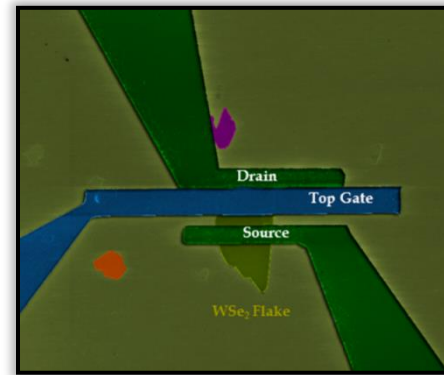
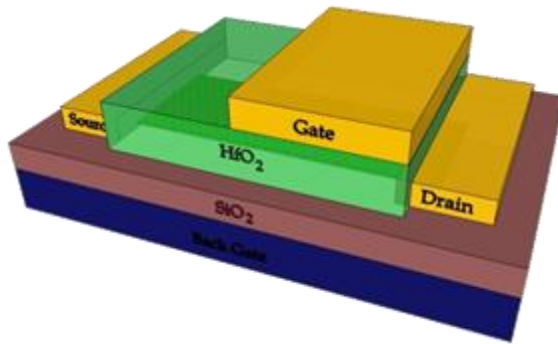
### Gate Tunable

- ✓ Electronic Properties
- ✓ Photonic Properties
- ✓ Thermal Properties
- ✓ Mechanical Properties



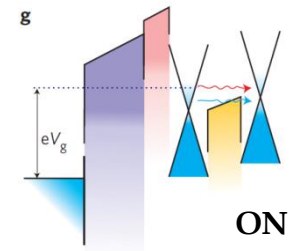
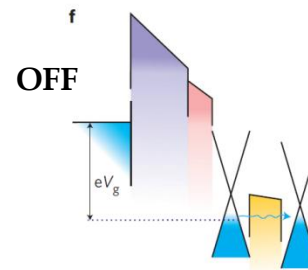
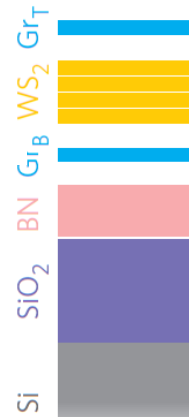
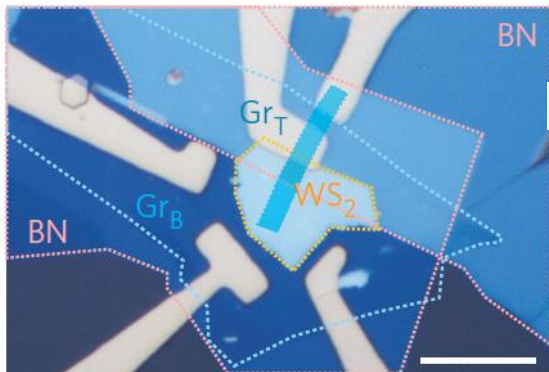
## Electrostatically doped WSe<sub>2</sub> Lateral tunnel junction

Saptarshi Das. *et al.* ACS Nano, 8(2), 2014.



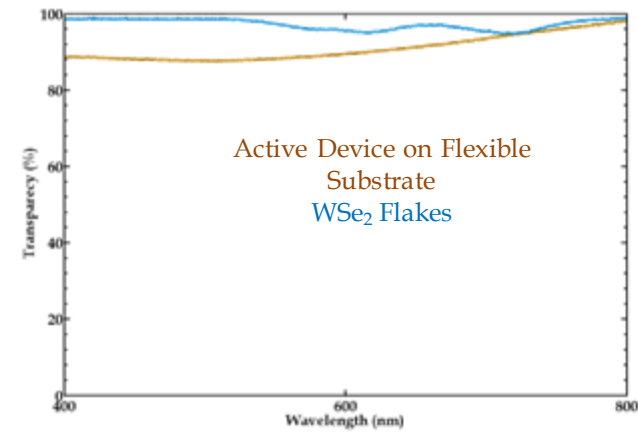
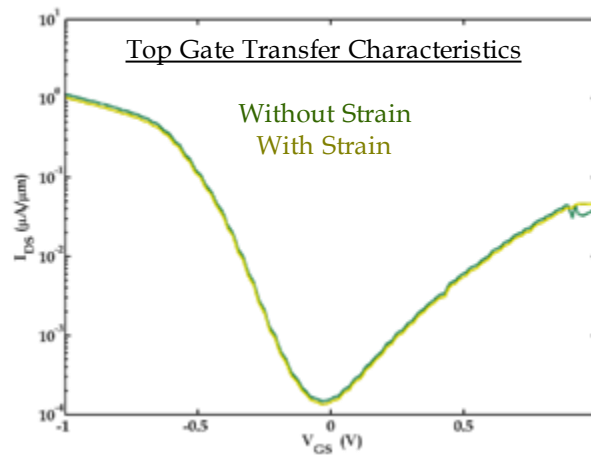
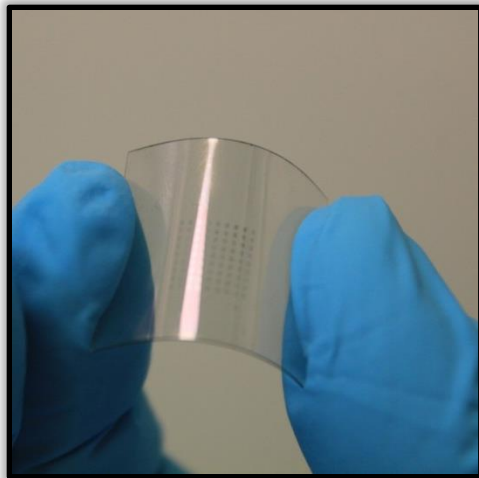
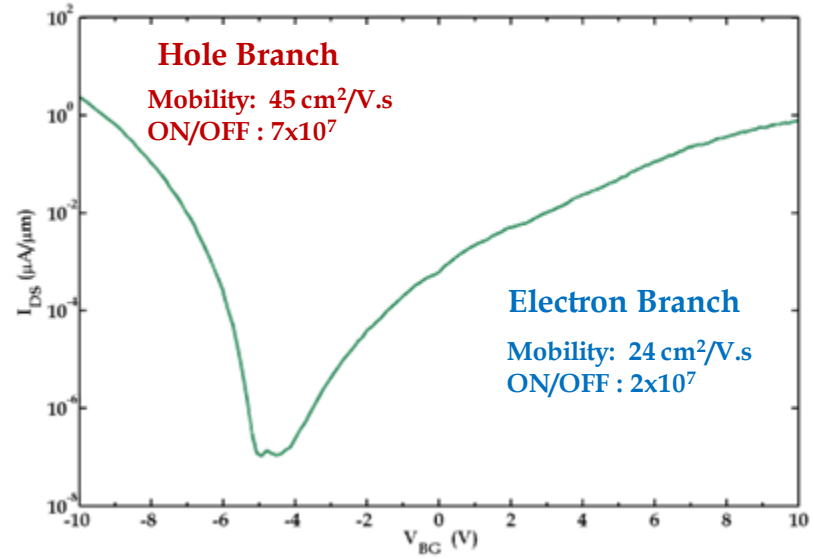
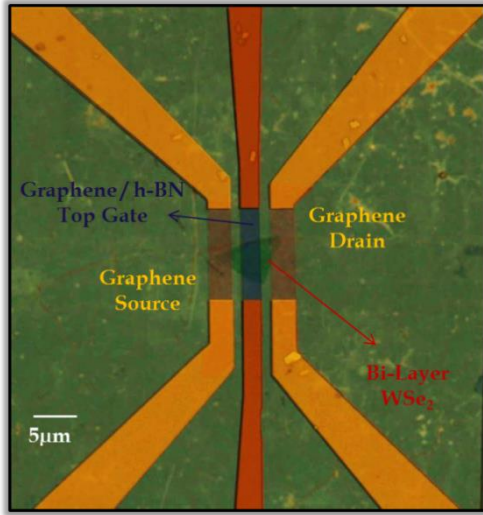
## Graphene-WS<sub>2</sub>-Graphene Vertical tunnel junction

Georgiou. *et al.* Nature Nanotechnology, 8, 2013.



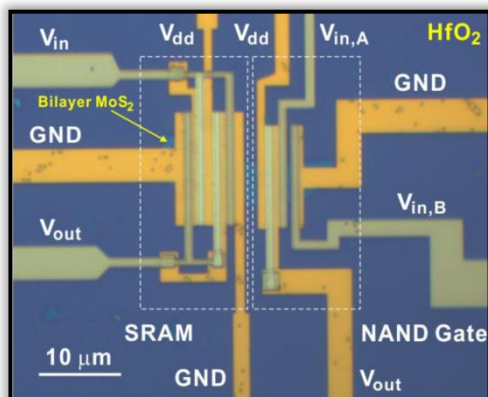
# Integration: All 2D Transistor

Saptarshi, *et al.*  
Nano Letters 14 (5), 2014.



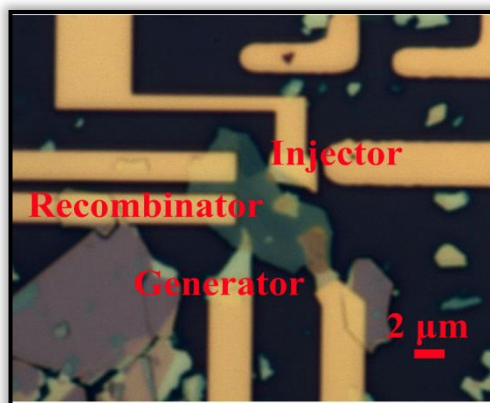
## Integrated circuit based on MoS<sub>2</sub>

Wang. *et al.* Nano Letters, 12(9), 2012.



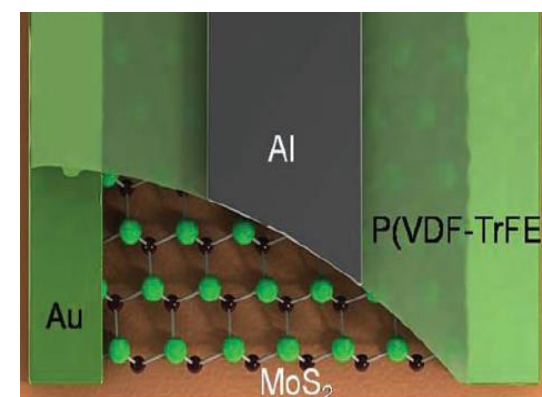
## Analog small signal generator

Tan. *et al.* Applied Physics Letters, 103, 2013.



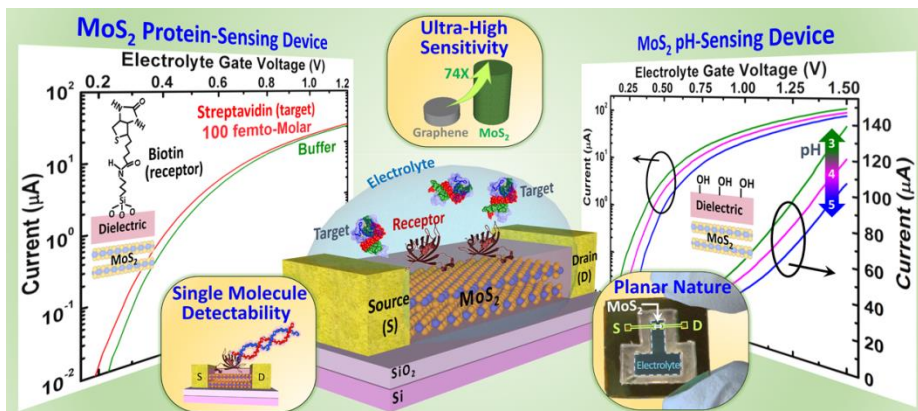
## Memory transistor with MoS<sub>2</sub>

Lee. *et al.* Small, 8(20), 2012.



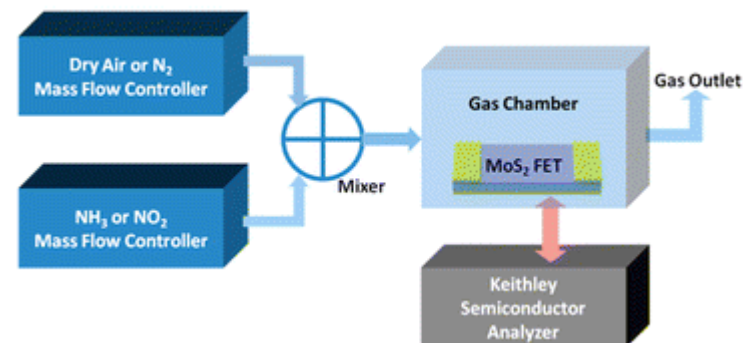
## MoS<sub>2</sub> FET based bio-sensor

Late. *et al.* ACS Nano, 7(6), 2013.

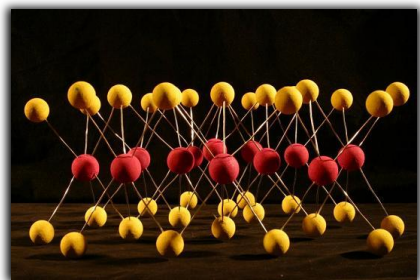


## MoS<sub>2</sub> FET based gas-sensor

Sarkar. *et al.* ACS Nano, 8(4), 2014.

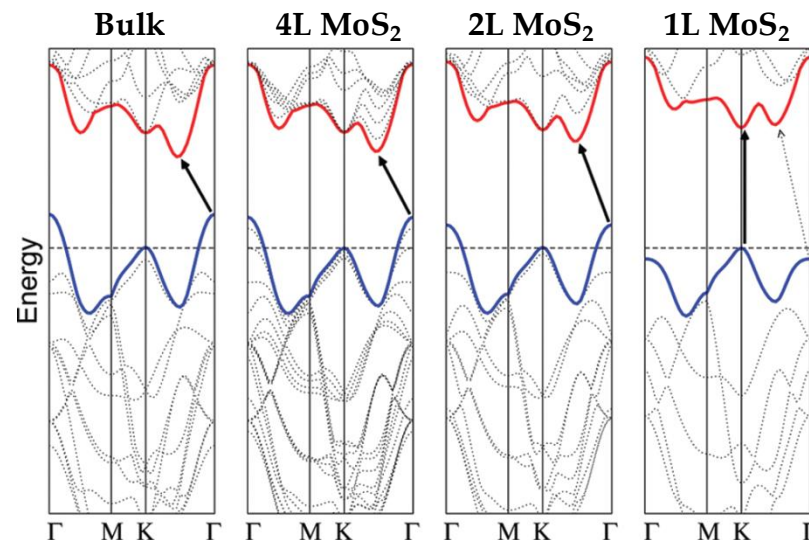


1. 2D Crystals
2. 2D Electronics
- 3. 2D Optoelectronics**
4. 2D Engineering



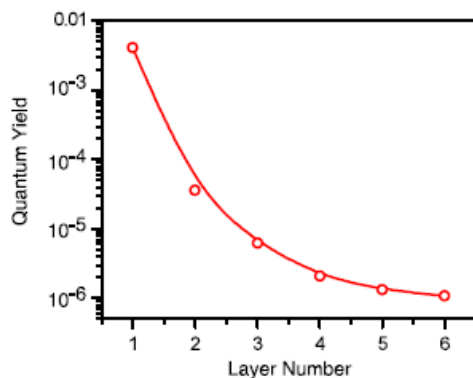
**K point:** localized d orbitals at the Mo atom

**$\Gamma$  point:** linear combination of d orbitals on the Mo atoms and anti-bonding  $p_z$  orbitals on the S atoms

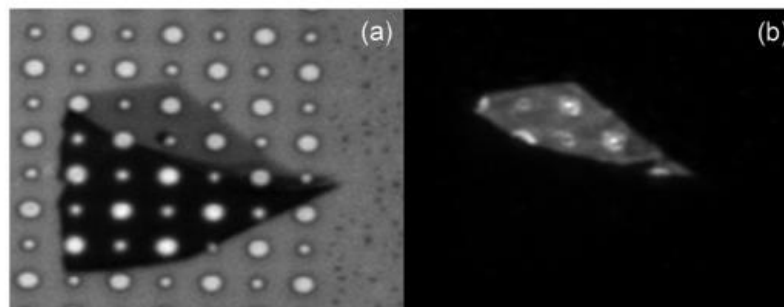


## Photoluminescence in MoS<sub>2</sub>

Splendiani. *et al.* Nano Letters, 10(4), 2010.

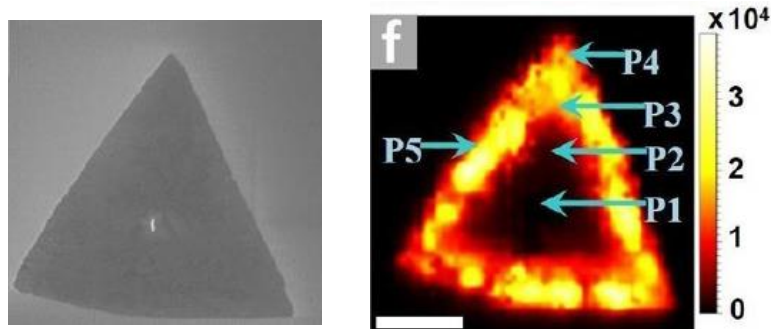


## Photoluminescence from suspended flakes

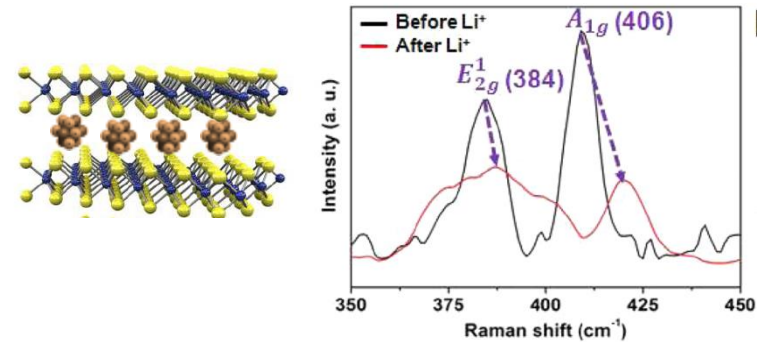


## Enhanced photoluminescence from **edges** of WS<sub>2</sub>      Photoluminescence modulation through **intercalation**

Gutierrez. *et al.* Nano Letters, 13(12), 2013.

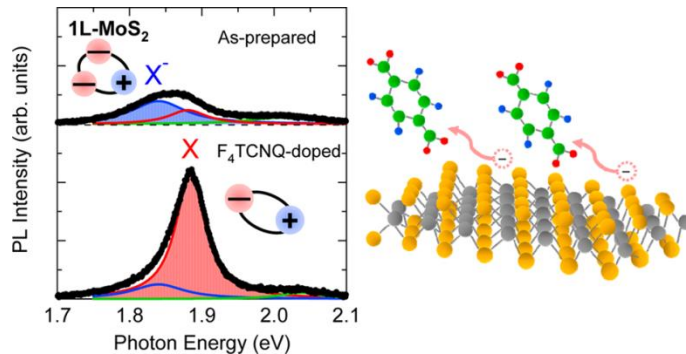


Wang. *et al.* ACS Nano, 7(11), 2013.

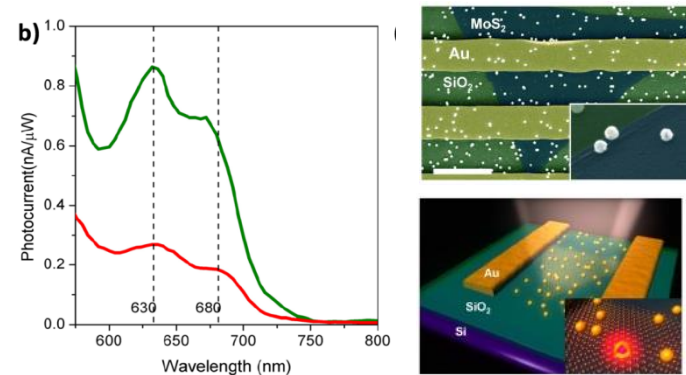


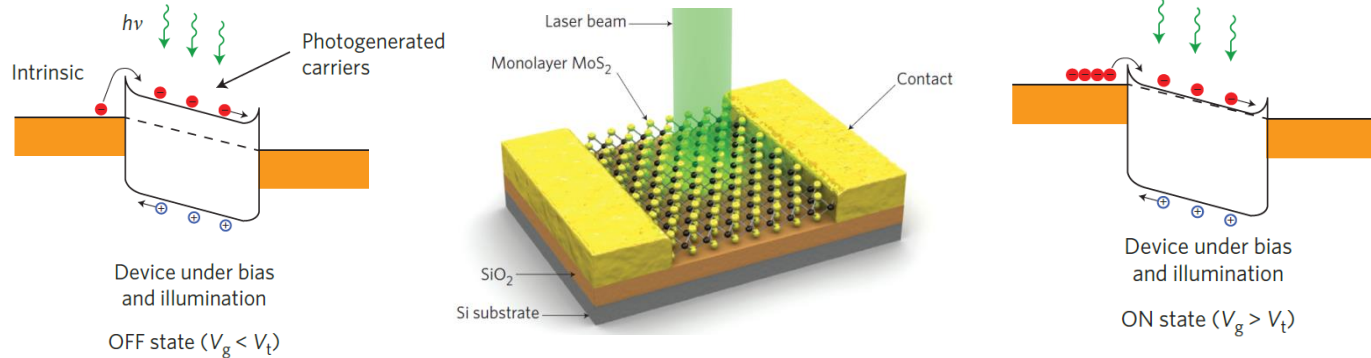
## Photoluminescence modulation through **doping**      Photoluminescence modulation through **plasmon**

Mouri. *et al.* Nano Letters, 13(12), 2013.



Shovani. *et al.* Applied Physics Letters, 104, 2014.





$$\text{Photoresponsivity } (\gamma = I_{\text{photo}}/P_{\text{laser}})$$

## Mobility

Exfoliated monolayer MoS<sub>2</sub>: 7.5mA/W

Exfoliated few-layer MoS<sub>2</sub>: 120mA/W

## Ambience

CVD monolayer MoS<sub>2</sub>: 780mA/W (air)

CVD monolayer MoS<sub>2</sub>: 2200mA/W (high vacuum)

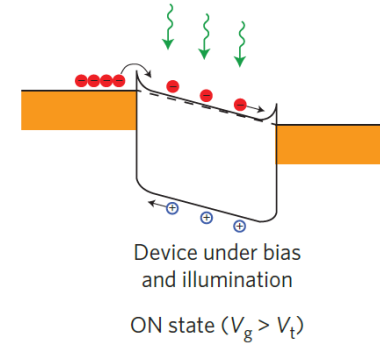
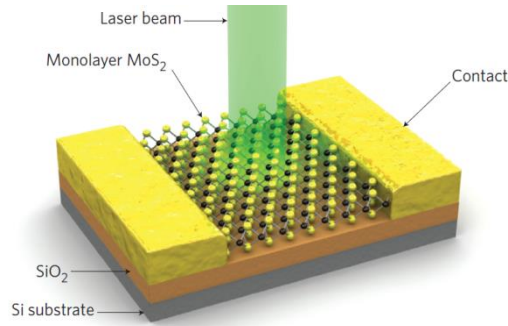
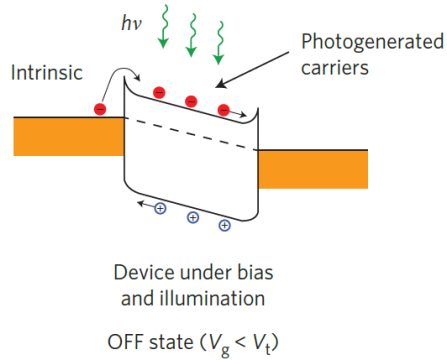
## Contact Resistance

Ohmic contacted monolayer WSe<sub>2</sub>:  $\sim 1.8 \times 10^5$  A/W

Lopez. *et al.* Nature Nanotechnology, 8, 2013.

Zhang. *et al.* Advanced Materials, 25, 2013.

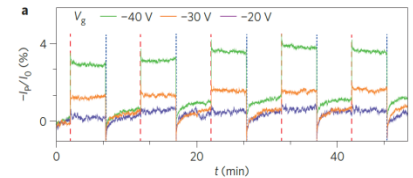
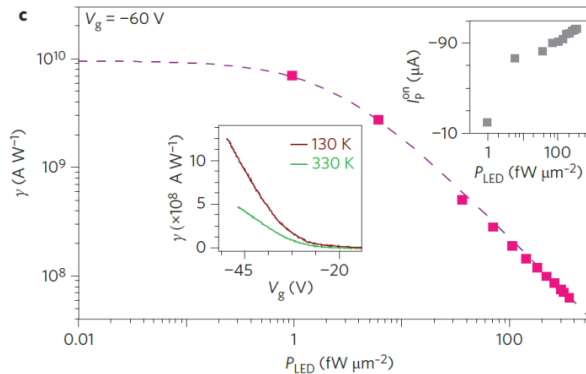
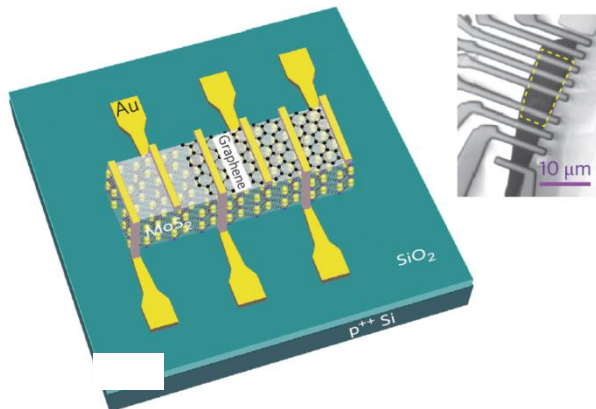
Zhang. *et al.* ACS Nano, 8(8), 2014.



**Photoresponsivity ( $\gamma = 5 \times 10^8 \text{ A/W}$ )**

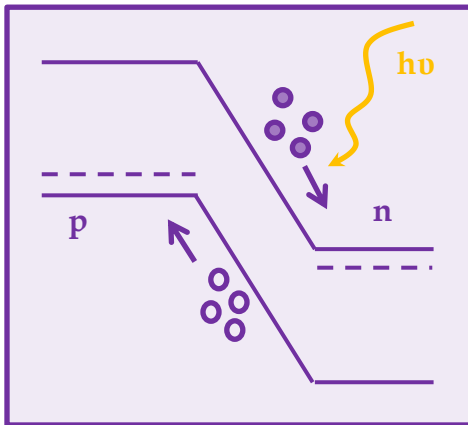
## Graphene - MoS<sub>2</sub> heterojunction phototransistor

Roy. *et al.* Nature Nanotechnology, 8, 2013.

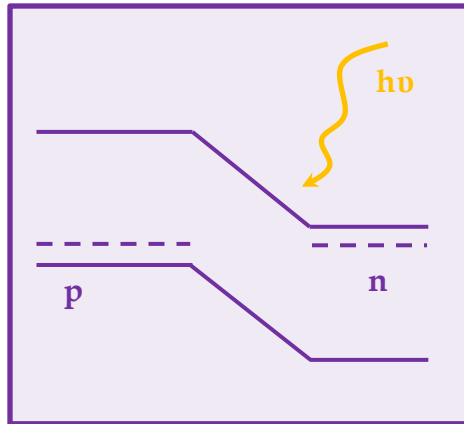




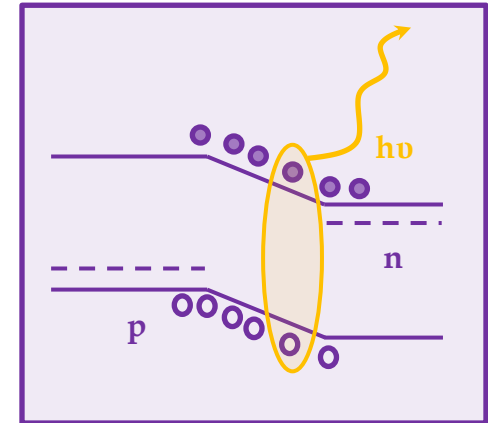
Photodetector:  $I_{ph}$



Photovoltaic (solar cells):  $I_{sc}, V_{oc}$



Electroluminescence (LEDs) :  $h\nu$

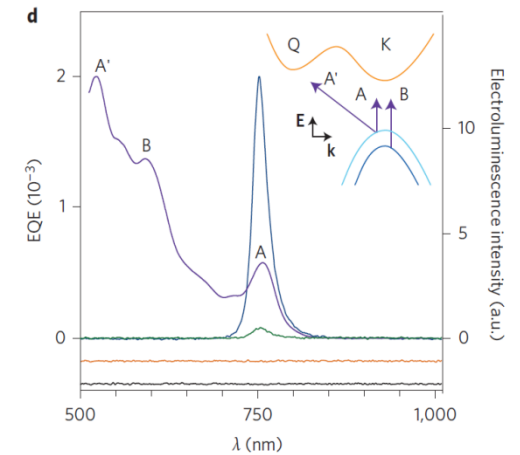
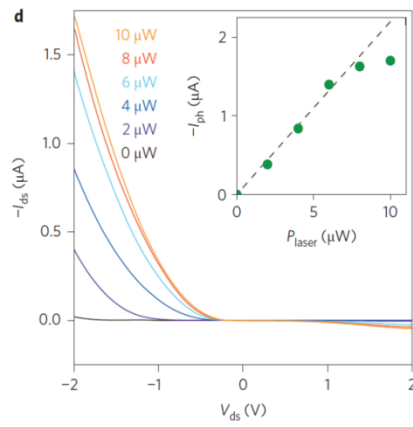
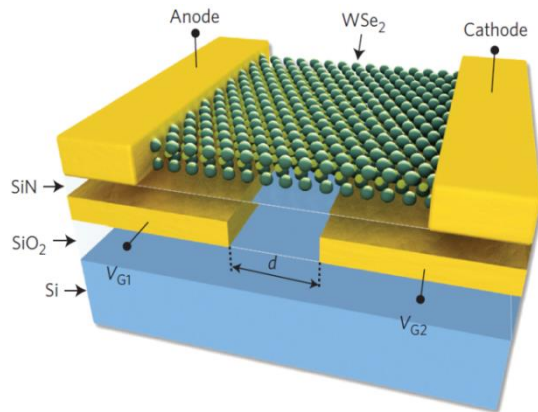


## Electrostatically doped WSe<sub>2</sub> p-n diodes

Baughner. *et al.* Nature Nanotechnology, 9, 2014.

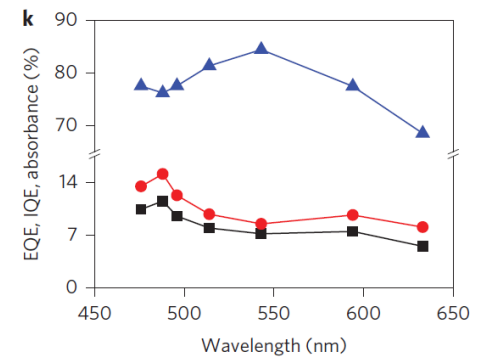
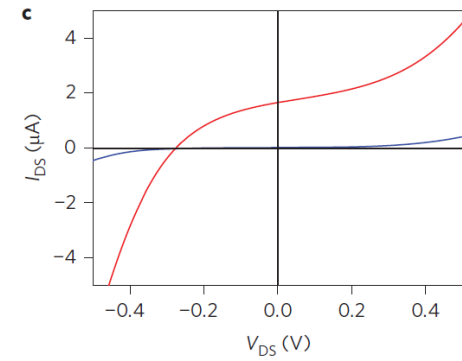
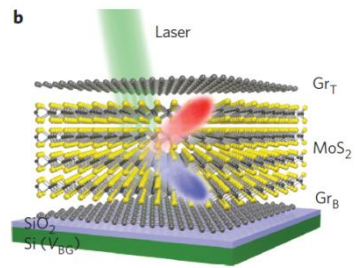
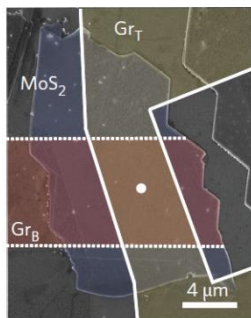
Ross. *et al.* Nature Nanotechnology, 9, 2014.

Pospischil. *et al.* Nature Nanotechnology, 9, 2014.



## Graphene - MoS<sub>2</sub> - Graphene heterojunction photodiode

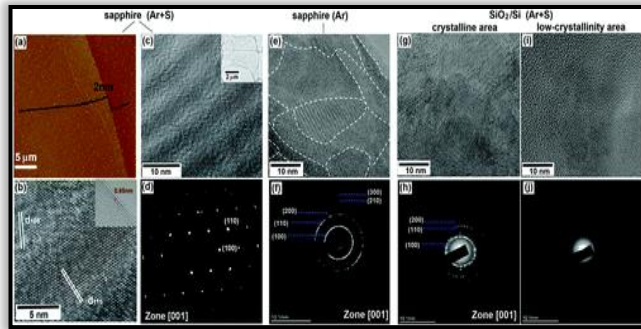
Yu. *et al.* Nature Nanotechnology, 8, 2013.



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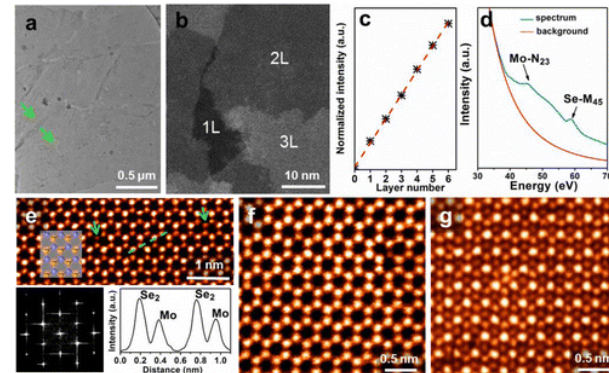
## Physical Vapor Transport

Liu, *et al.* Nano Letters, 12(3), 2012



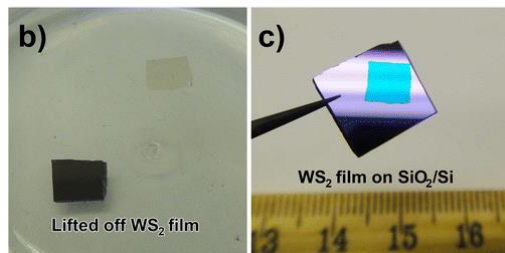
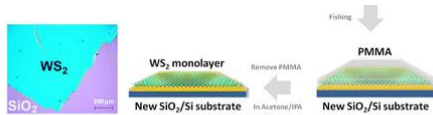
## Chemical Vapor Deposition

Lu, *et al.* Nano Letters, 14(5), 2014



## Thermal Reduction

Elias, *et al.* ACS Nano, 7(6), 2013

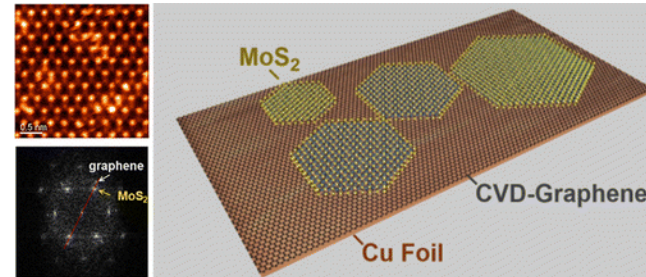


## Atomic Layer Deposition

## Molecular Beam Epitaxy

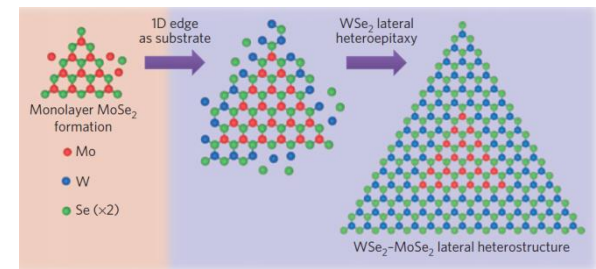
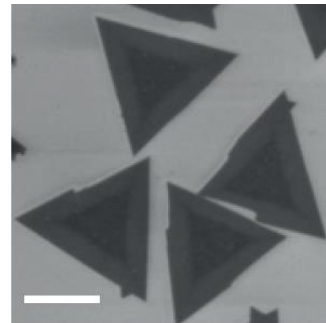
## Vertical Heterostructure: MoS<sub>2</sub> on Graphene

Shi, *et al* Nano Letters, 12(6), 2012



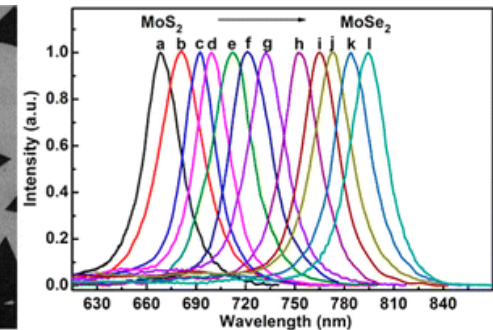
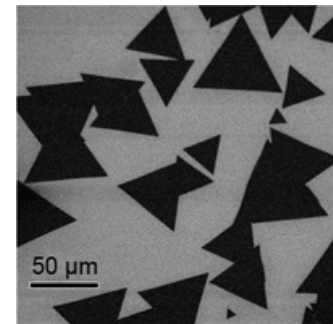
## Lateral Heterostructure: MoSe<sub>2</sub> - WSe<sub>2</sub>

Huang, *et al.* Nature Material, 2014.

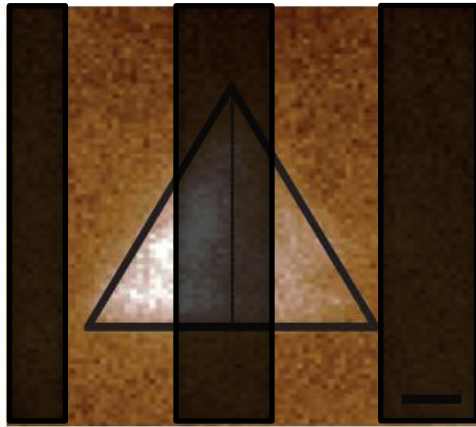


## Stoichiometric Heterostructure: MoS<sub>2x</sub>Se<sub>2(1-x)</sub>

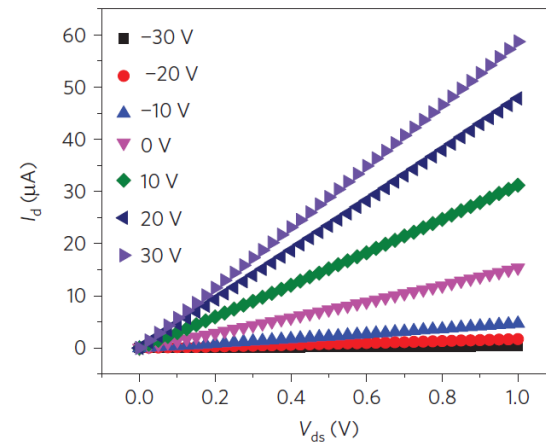
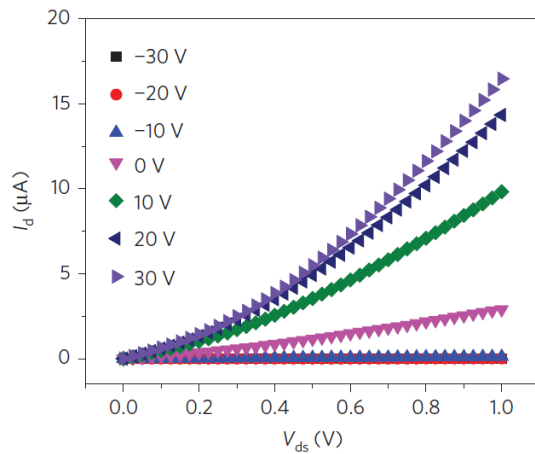
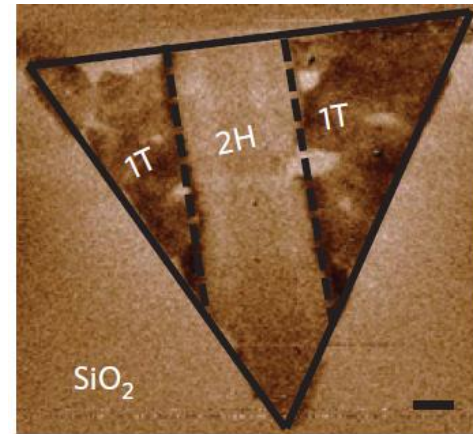
Shi, *et al* Journal of American Chemical Society, 136(10), 2014



Koppera. *et al.* Nature Materials, 2014.



→  
**n-butyl lithium**



## Conclusion

**2D Crystals show a lot of promises and a lot of scope for innovative scientific thinking**



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**Thank You**