

What could we do with layered structures of materials with just the right layers? -Feynman

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Periodic table: 2D layered materials

What could we do with layered structures of materials with just the right layers? -Feynman

- Metal, insulator, semiconductors (small or large E_g)
- Vertical stacking
- New tunneling vertical devices
- New optoelectronic/magnetic properties
- Flexible, transparent

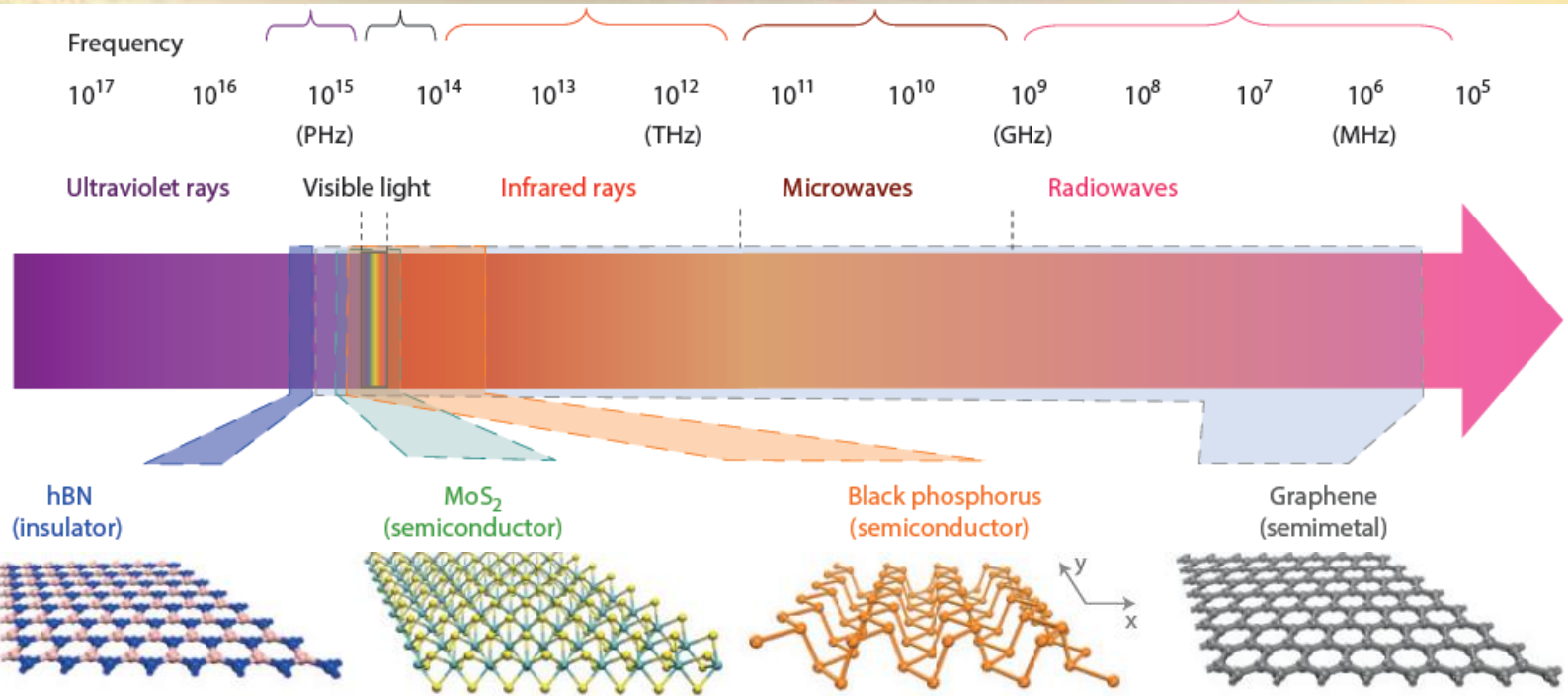
1 IA 11A H Hydrogen 1.008	2 IIA 2A He Helium 4.003																	18 VIIIA 8A
3 Li Lithium 6.941	4 Be Beryllium 9.012																	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A	
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.88	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.933	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.61	33 As Arsenic 74.922	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 84.80	
37 Rb Rubidium 84.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.29	
55 Cs Cesium 132.905	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.967	80 Hg Mercury 200.59	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018	
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Fl Flerovium [289]	115 Uup Ununpentium unknown	116 Lv Livermorium [293]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown	

Lanthanide Series	57 La Lanthanum 138.906	58 Ce Cerium 140.115	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.966	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.50	67 Ho Holmium 164.930	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

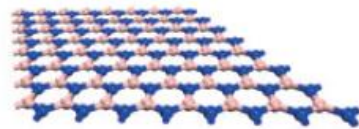
Alkali Metal	Alkaline Earth	Transition Metal	Semimetal	Nonmetal	Basic Metal	Halogen	Noble Gas	Lanthanide	Actinide
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New material and physics world in 2D !!!!

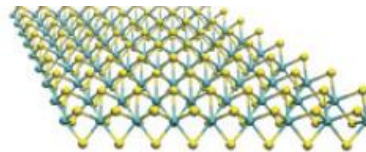
Atomic layered materials



hBN
(insulator)



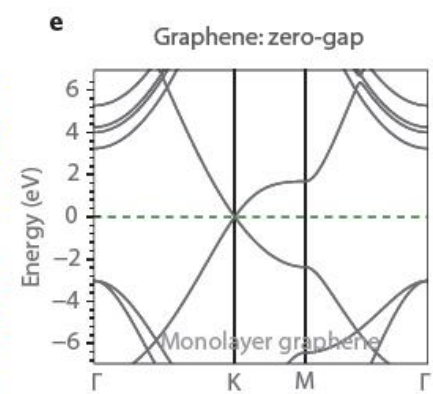
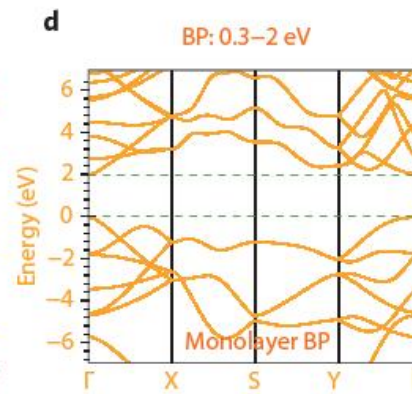
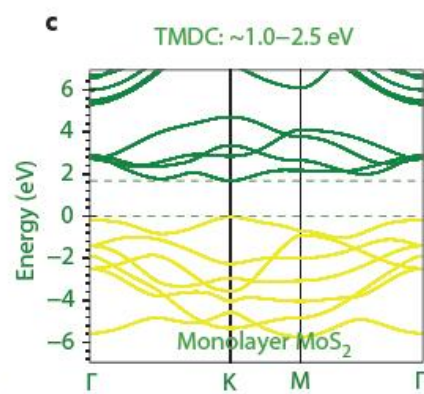
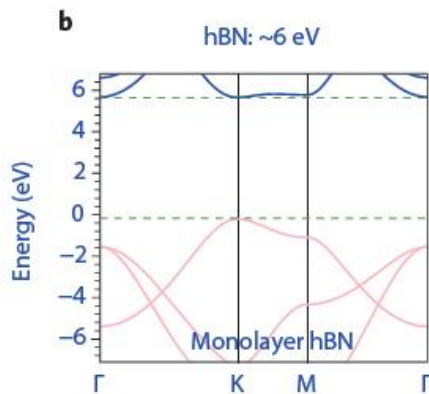
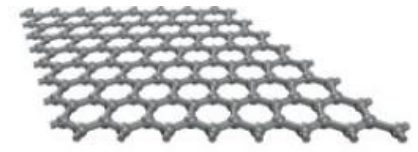
MoS₂
(semiconductor)



Black phosphorus
(semiconductor)

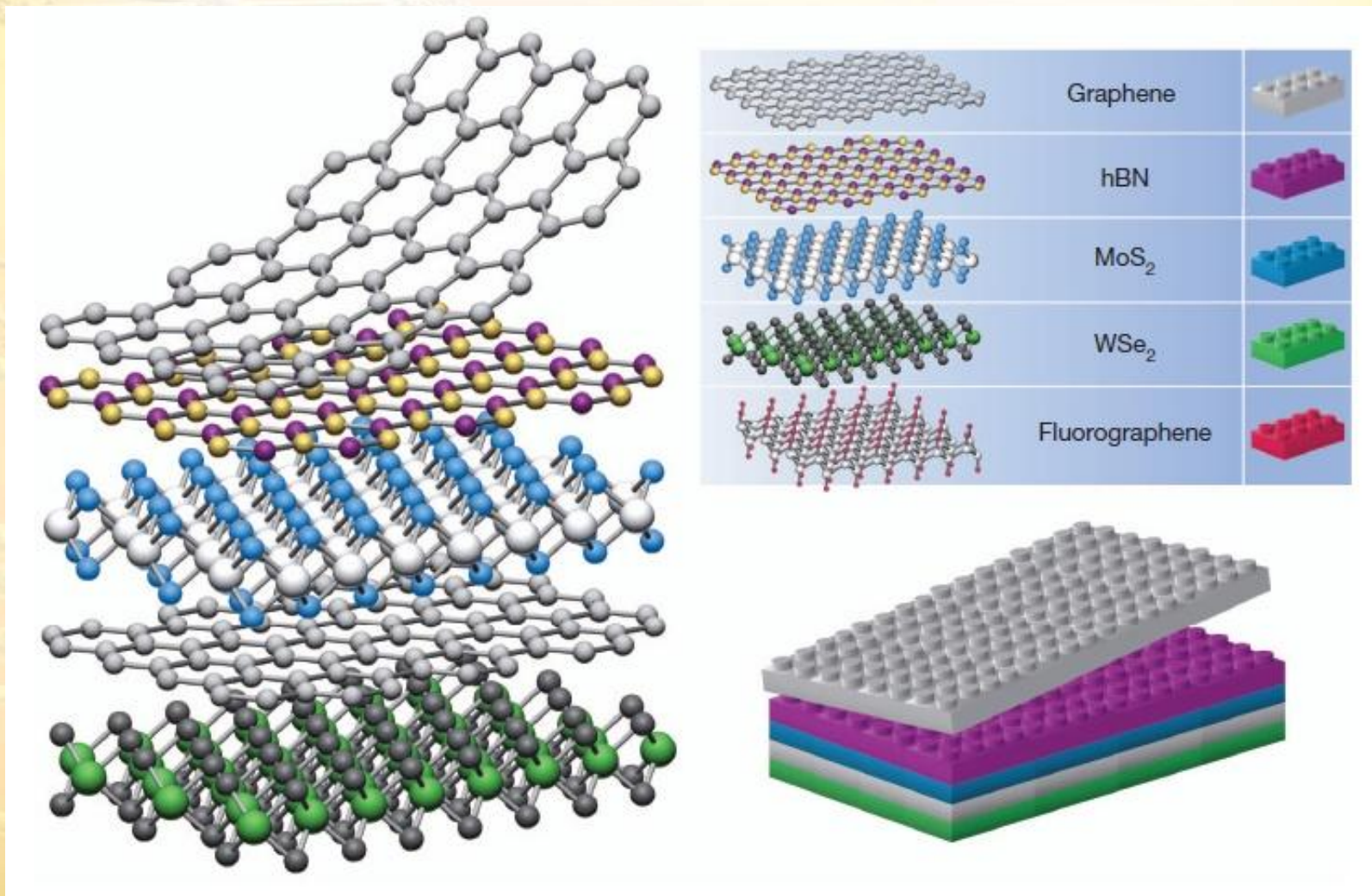


Graphene
(semimetal)



Vertical structure

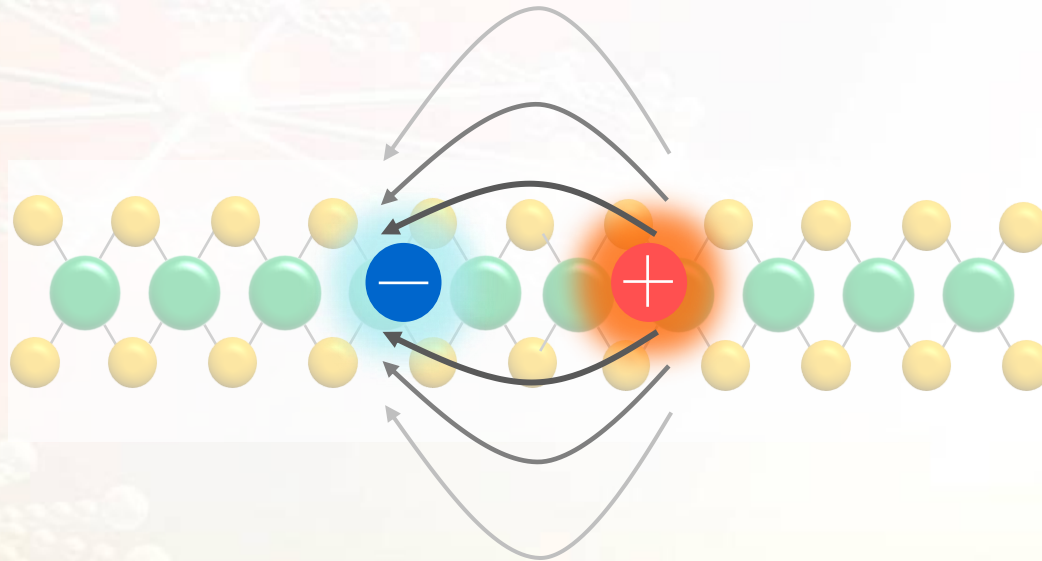
New device structures by van der Waals stacking



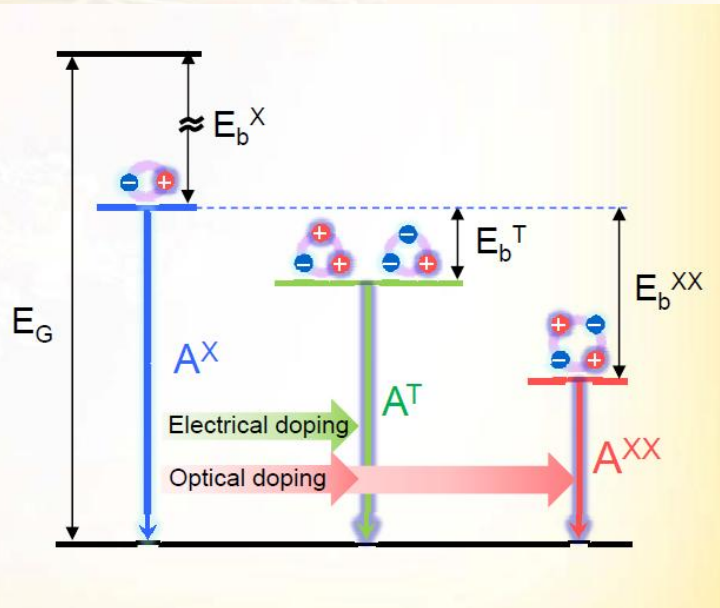
What is new in 2D?

Strong Coulomb interaction or less charge screening

Coulomb interaction

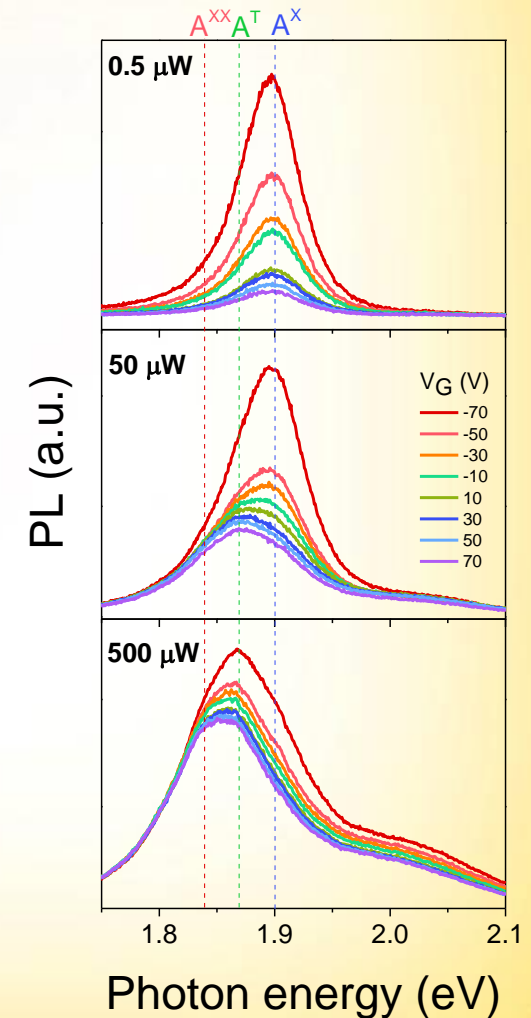


Large exciton binding energy



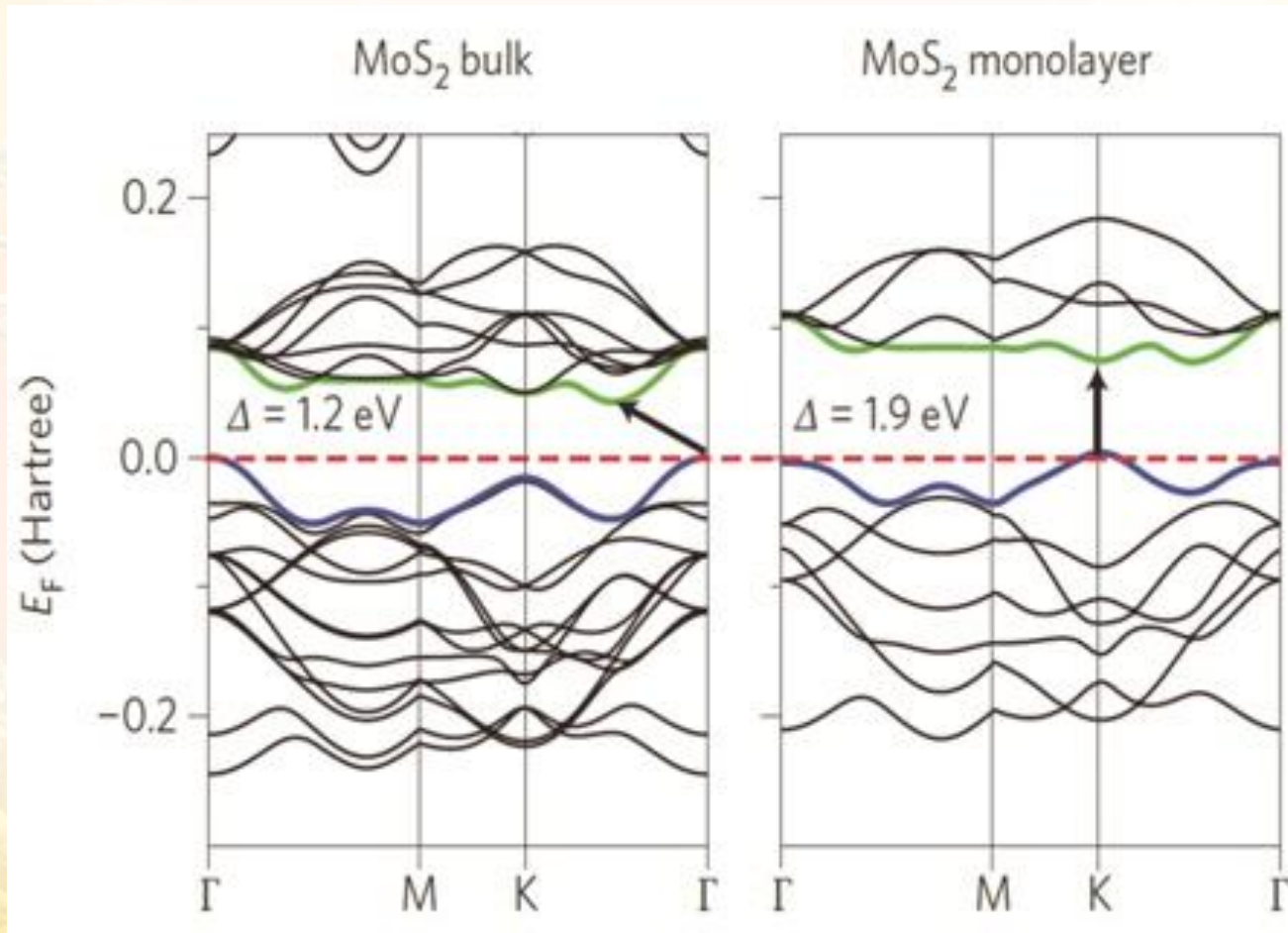
- Emergence of excitons at room temperature
: $E_b^X \sim 1$ eV
- Emergence of multiexcitons at room temperature
: trions, $E_b^{\text{tri}} \sim E_b^X + 30 \sim 40$ meV
: biexcitons, $E_b^{\text{bi}} \sim E_b^{\text{tri}} + 30$ meV

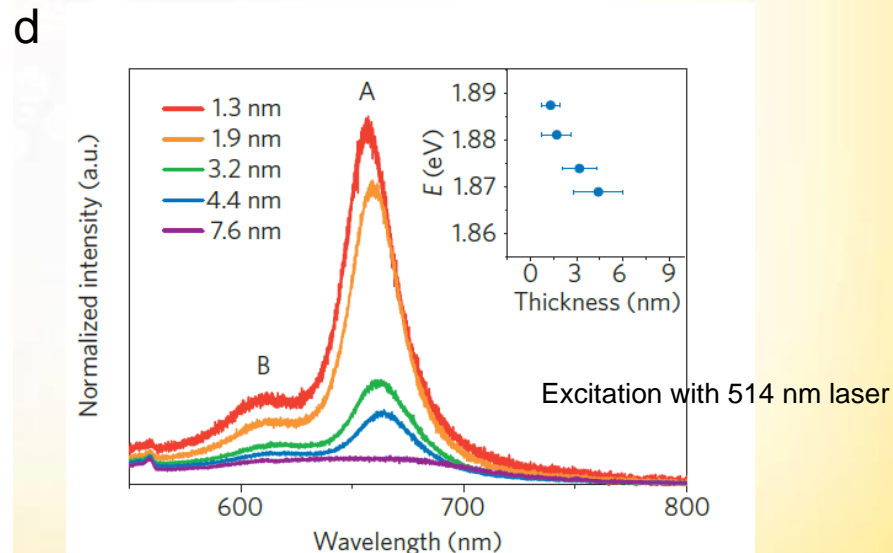
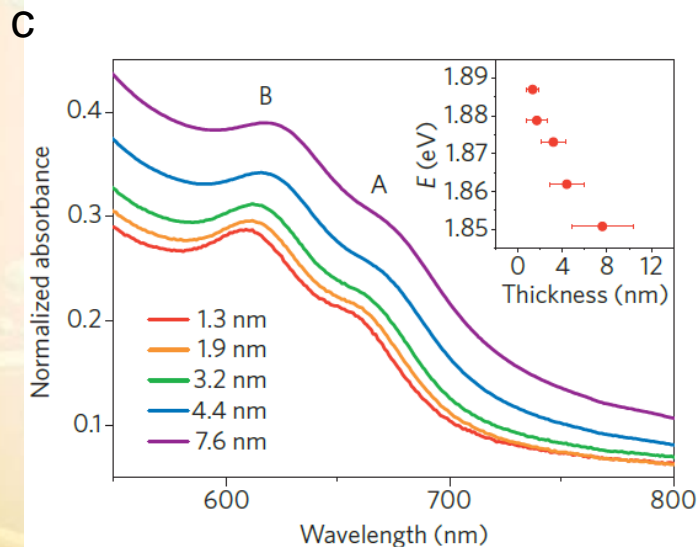
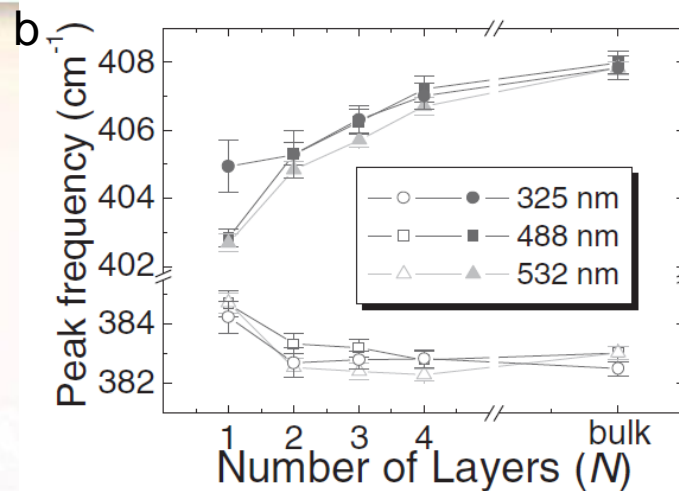
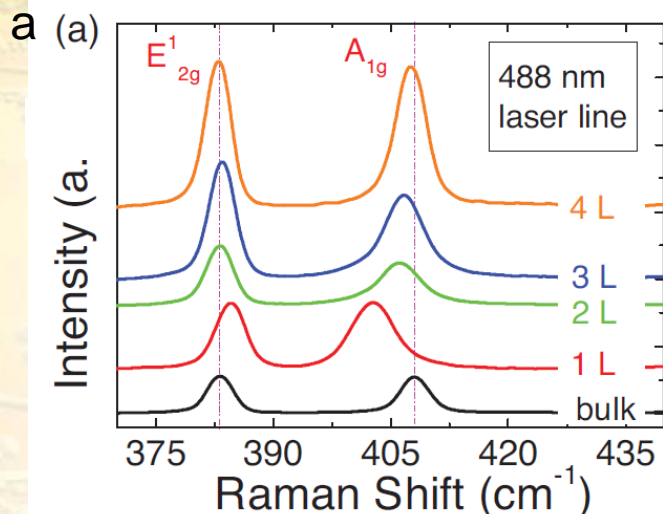
H. S. Lee et al. PRL, ASAP



Layer dependence

Band structures: Indirect bandgap (ML) => direct bandgap (1L)





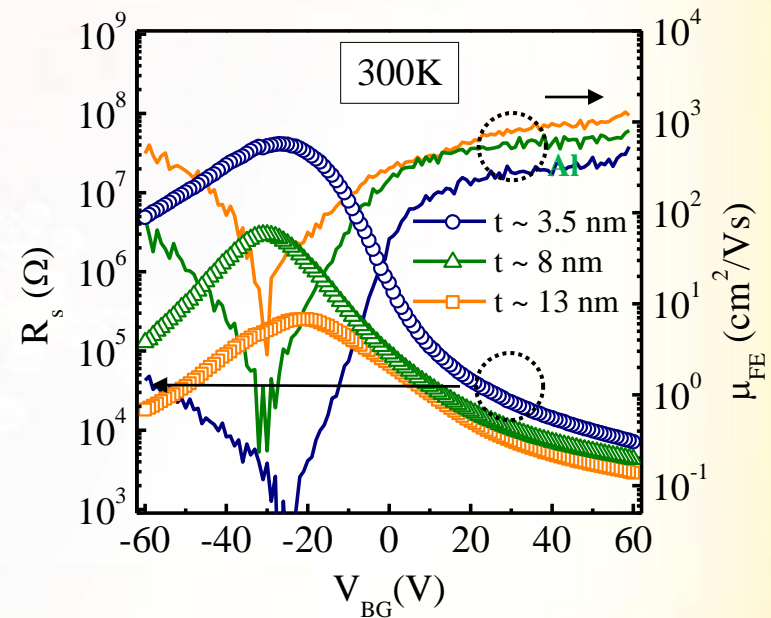
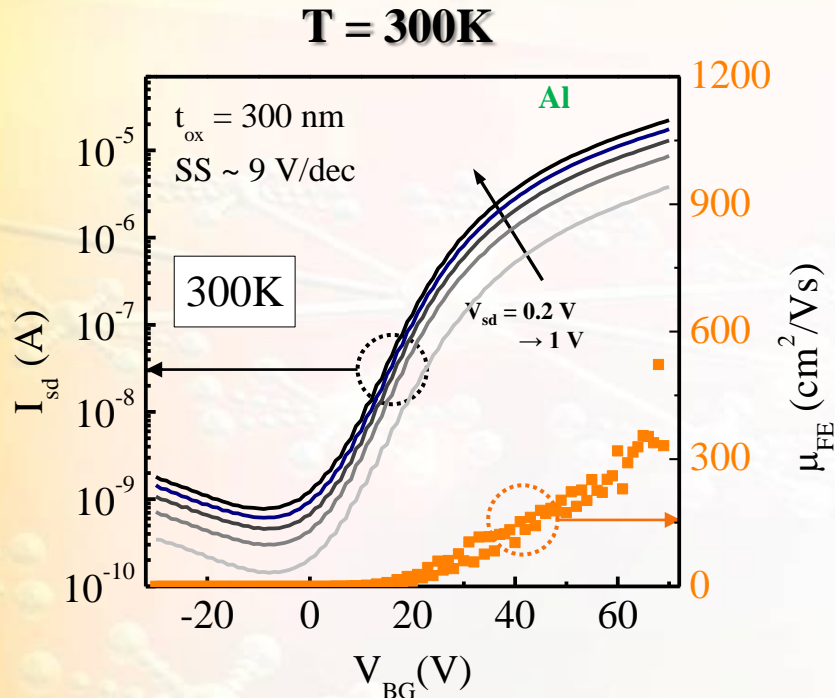
(a,b) Li, H. et al. *Adv. Funct. Mater.* **2012**, 22, 1385–1390
 (c,d) Eda, G. et al. *Nano Lett.* **2011**, 11, 5111–5116

Layer dependence

Transport properties

Al contact for n-type Tr

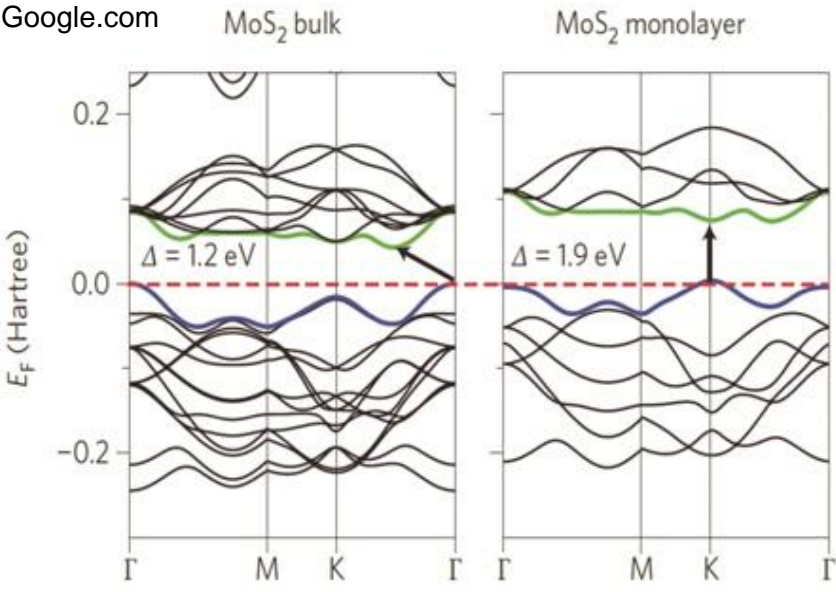
D. Perrelo et al., Nature Comm. 6, 1-8 (2015)



- Type conversion with flake thickness: n-type to ambipolar
 - Graphene-like electron and hole mobilities
- Mobility increases in proportion to film thickness
 - Bandgap shrinkage and surface scattering reduction

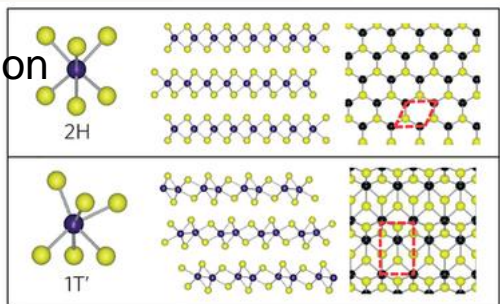
Structural phase transition

Why MoS₂?

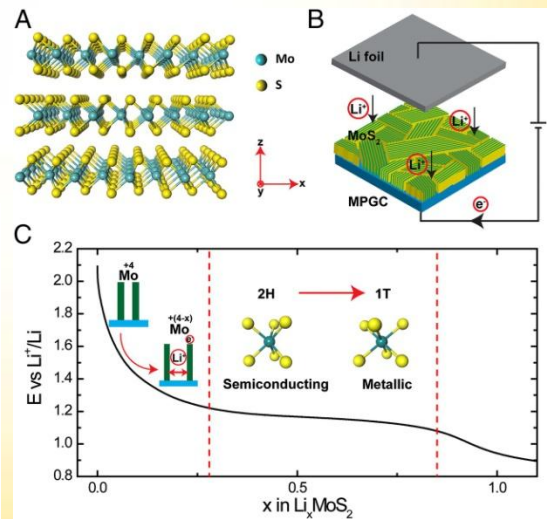


- **Reduced charge screening**
- High mobility $\sim 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (MoS₂)
- Optical properties:
Indirect bandgap (bulk) \Rightarrow direct bandgap (1L)
Wide range of bandgap (1.0 ~ 2.5 eV)

- Various phases exist
- Tailoring such phases is a big challenge
- MoS₂ phase transition:
2H (semicond) \Rightarrow 1T (metal)
by Li intercalation
- Difficult to realize
- Severe lattice distortion
- Local phenomena



H. Wang et al., PNAS 11, 19701 (2013)

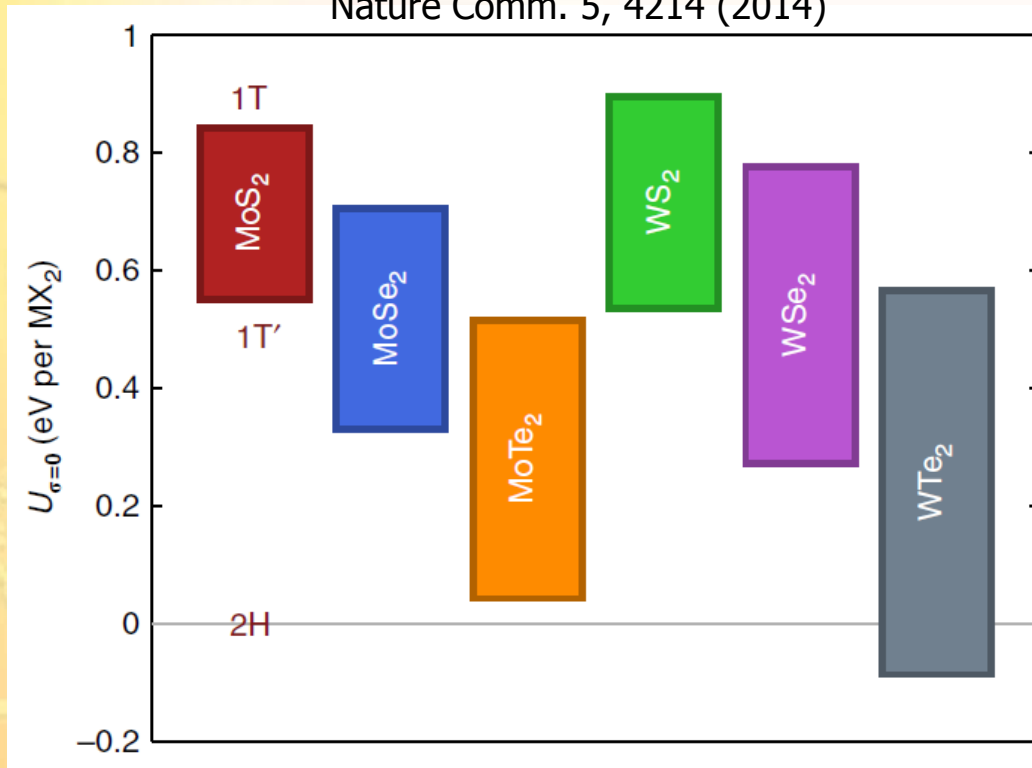


Similar to MoS₂ but.....

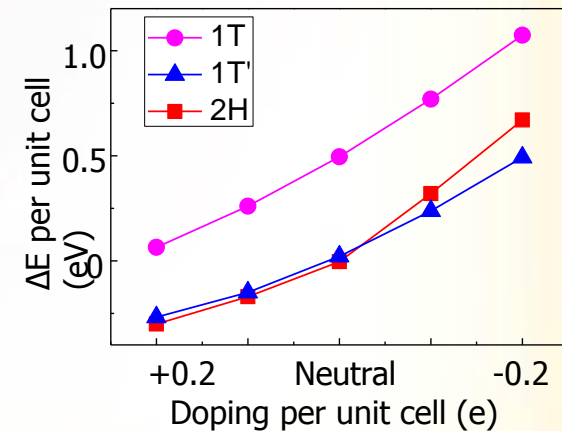
- Bandgap : ~ 1 eV, similar to Si
- good for energy harvesting
- good for TFET
- Cohesive energy difference between 2H and 1T is smaller than that of MoS₂
- Rich physics: CDW, superconductivity...

Phase stability

Nature Comm. 5, 4214 (2014)



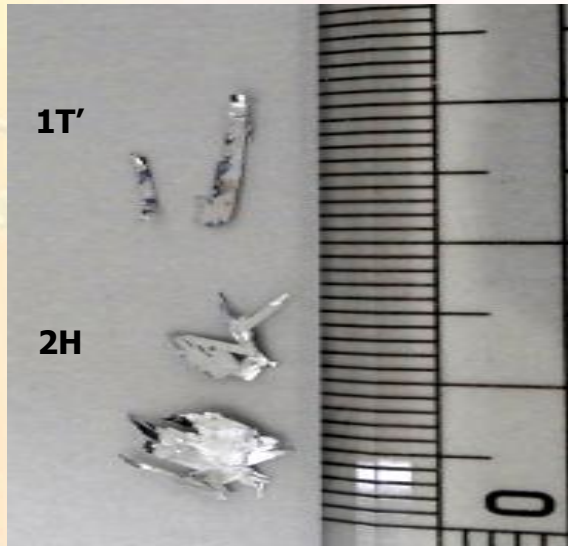
Cohesive energy of MOTE₂



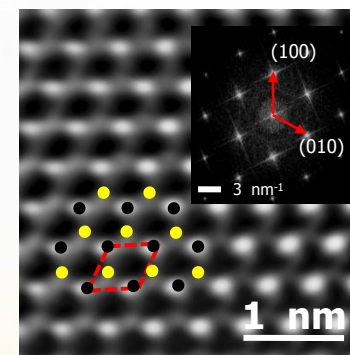
-> Polymorph engineering is easier in MoTe₂

Single crystal MoTe_2 by flux method

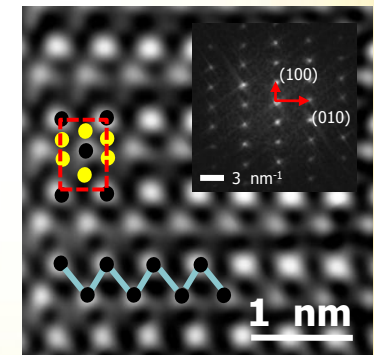
Single crystal growth (flux method): mix Mo and Te powder with sodium flux & sintering



TEM comparison



2H-MoTe₂



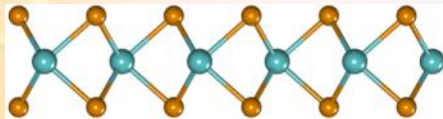
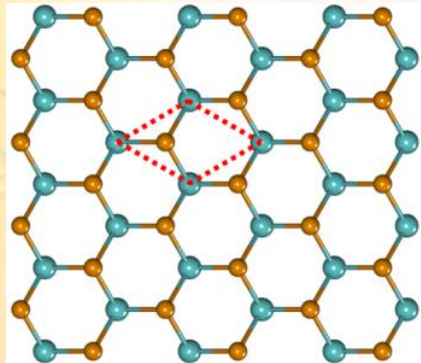
1T'-MoTe₂

Structures of MoTe₂

D. H. Keum & S. Y. Cho et al., Nature Phys. 11, 482 (2015)

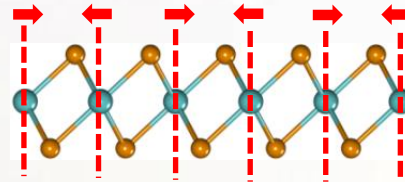
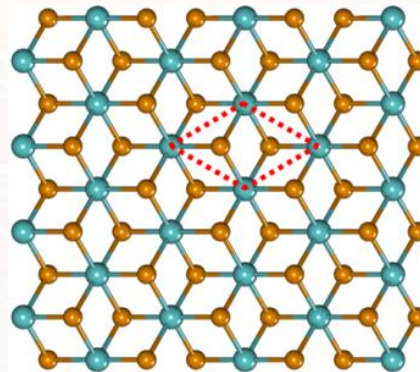
Semiconductor 2H

Hexagonal



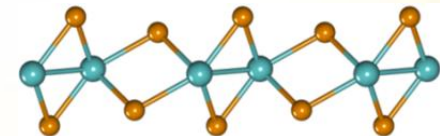
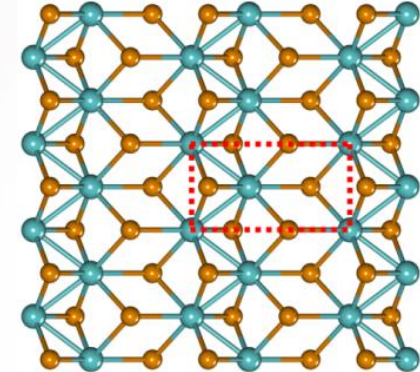
Metal 1T

Octahedral



Small bandgap metal 1T'

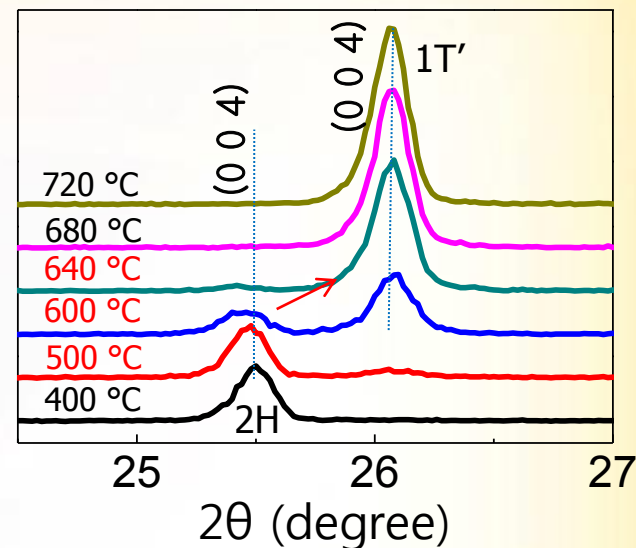
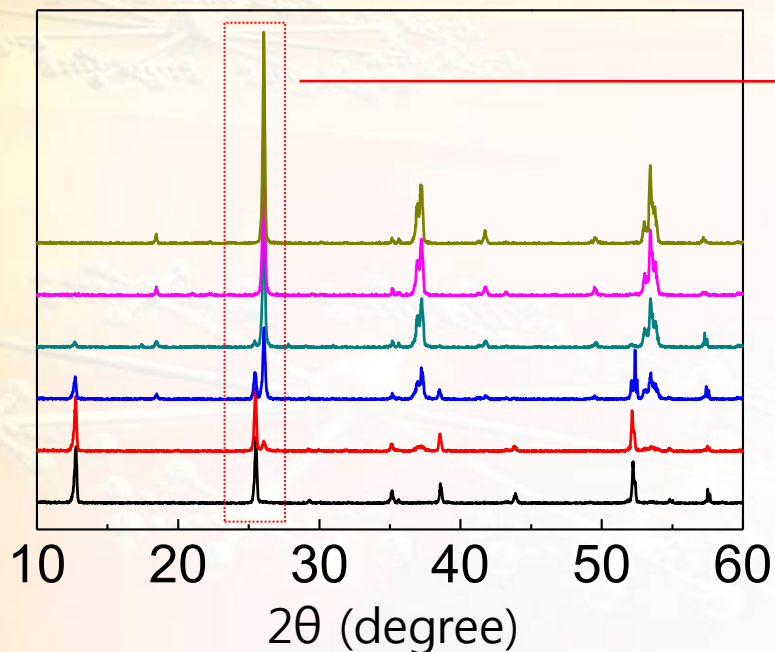
Distorted octahedral



Peierls distortion
-> Band inversion

1T' phase is more stable than 1T phase!

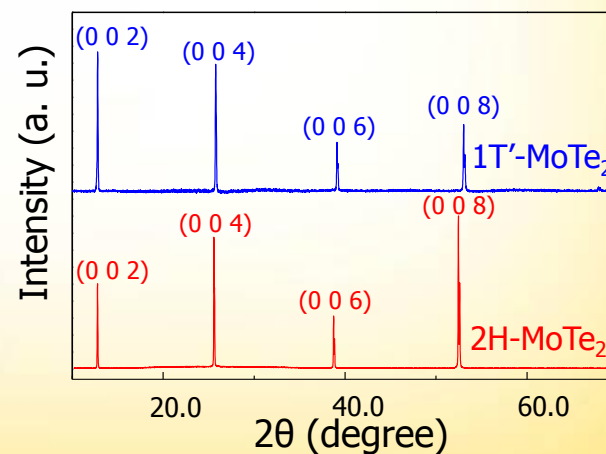
Temperature-dependent XRD



Structural phase transition by temperature

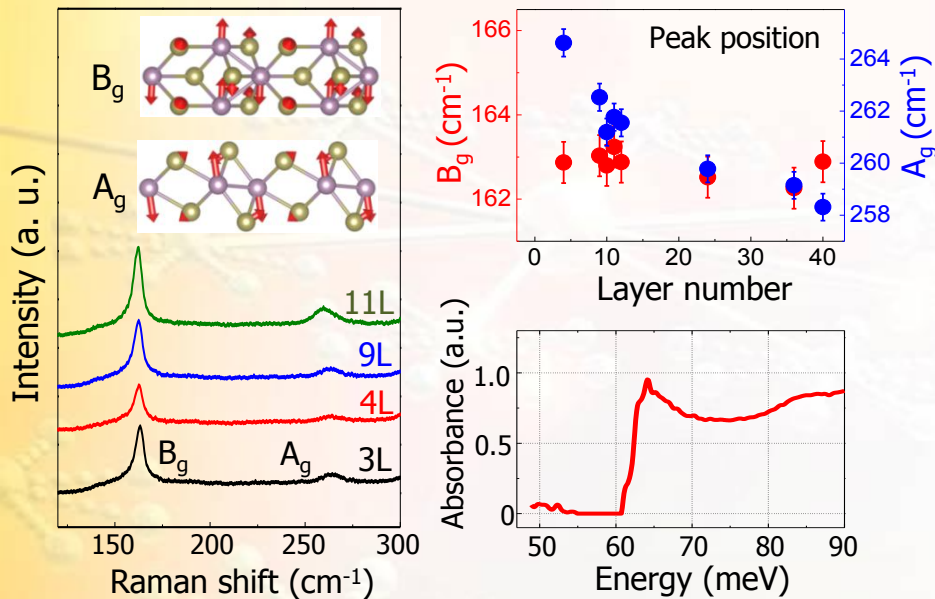
-> absence of Te deficiency

-> reversible phase transition



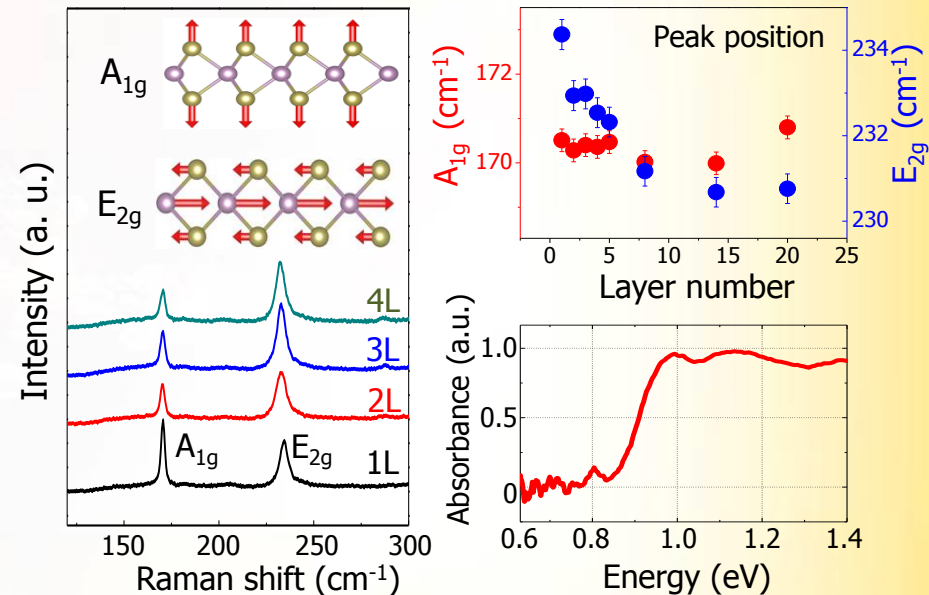
D. H. Keum & S. Y. Cho et al., Nature Phys. 11, 482 (2015)

1T'-MoTe₂



Few-layer MoTe₂

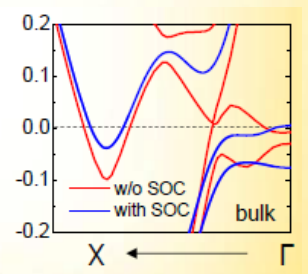
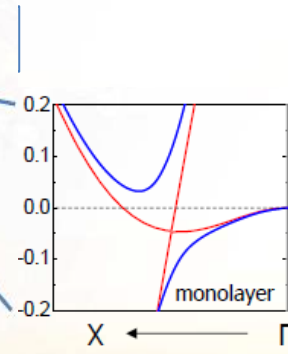
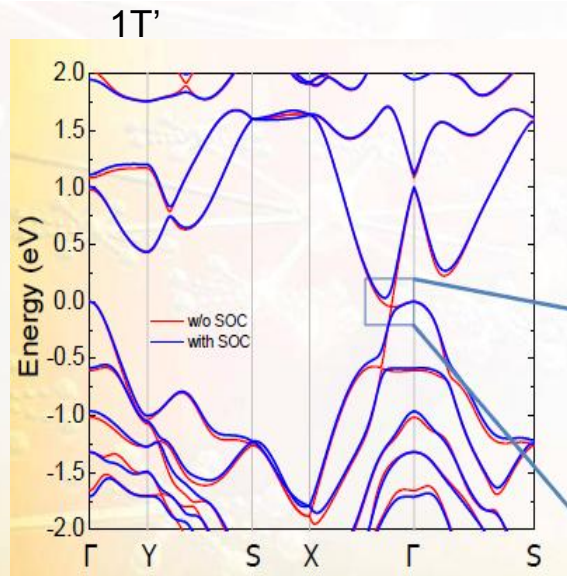
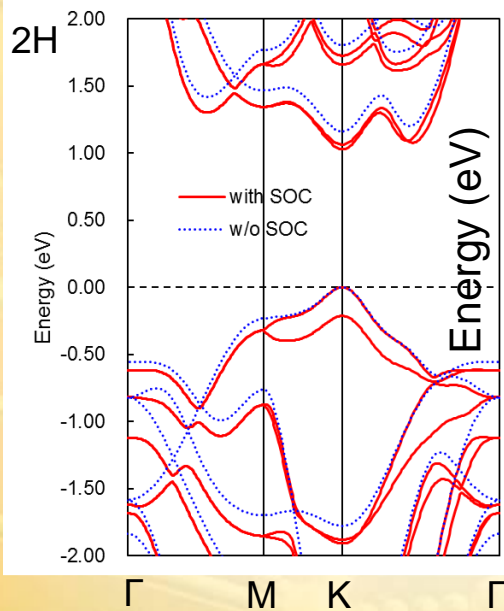
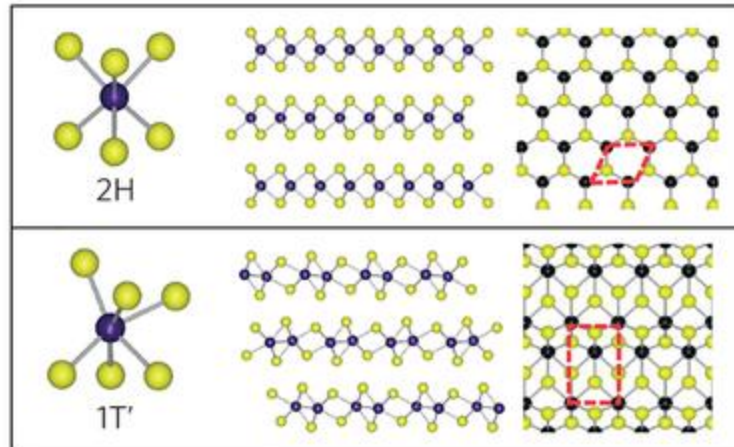
2H-MoTe₂



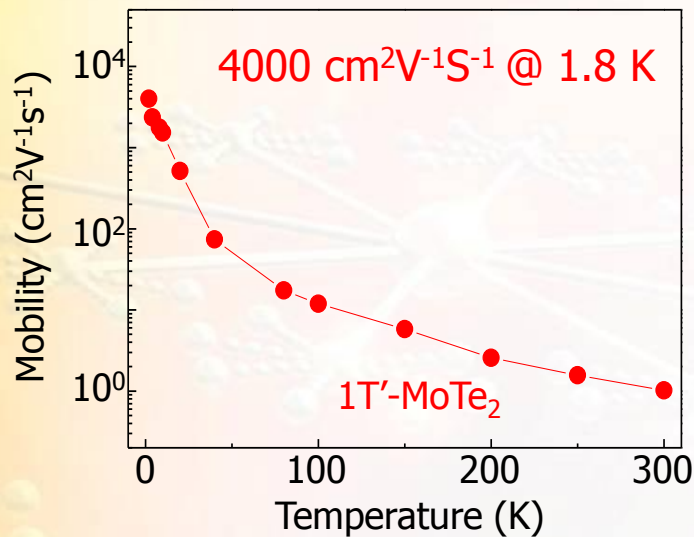
- > Sign of small bandgap in monoclinic TMDs
- > New results on Raman and absorption spectroscopy in 1T'-MoTe₂

Large spin-orbit coupling

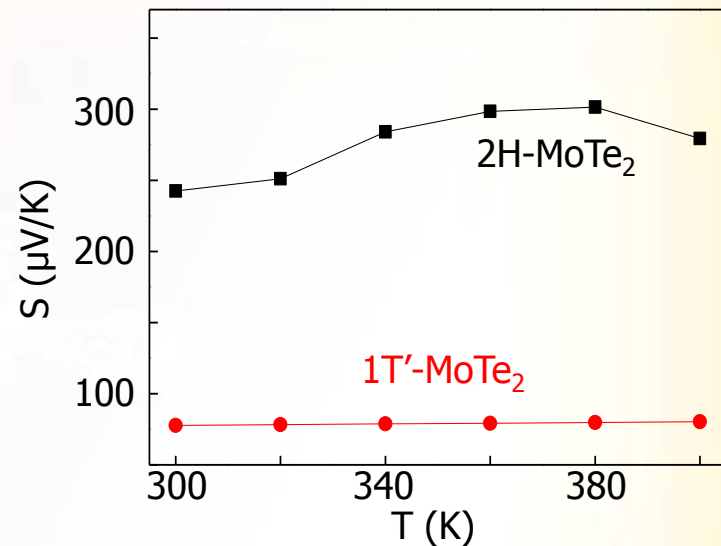
band splitting in VBM at K
- SOC effect



Carrier mobility of 1T'-MoTe₂



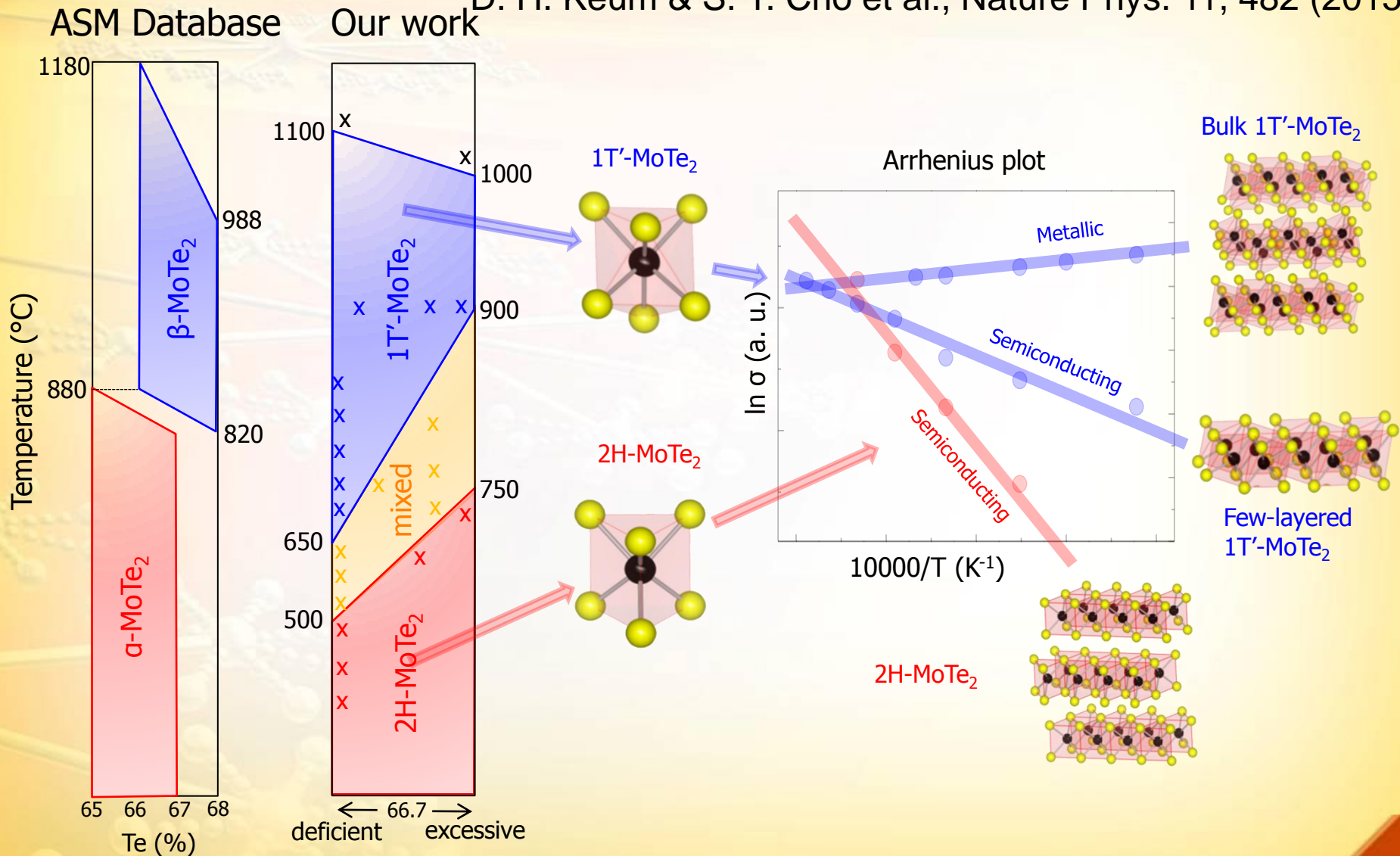
Seebeck constants of MoTe₂



- > High carrier mobility at low temperature
- > High power factor : 0.04 ~ 11 mW/mK²
(4 mW/mK² : state-of-the-art thermoelectric materials)

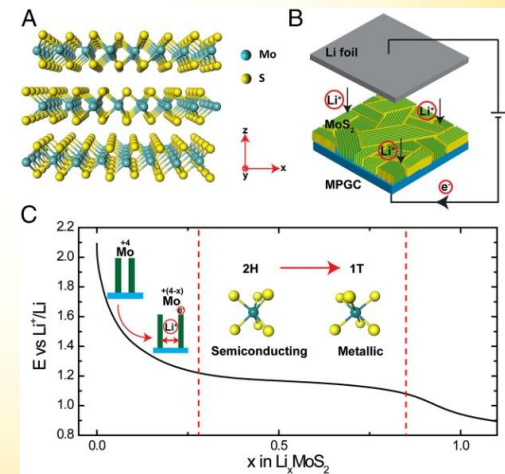
Electronic phase transition in MoTe₂

D. H. Keum & S. Y. Cho et al., Nature Phys. 11, 482 (2015)



- Ohmic contact in Si: Ion implantation
- Ohmic contact in 2D?
 - ion implantation damages 2D layer
 - metal/2D: weak van der Waals interface
 - => side contact to provoke covalent bonds?
 - phase transition from 2H to 1T by Li intercalation in MoS₂
 - phase transition by light irradiation
 - BN to modulate Schottky barrier??

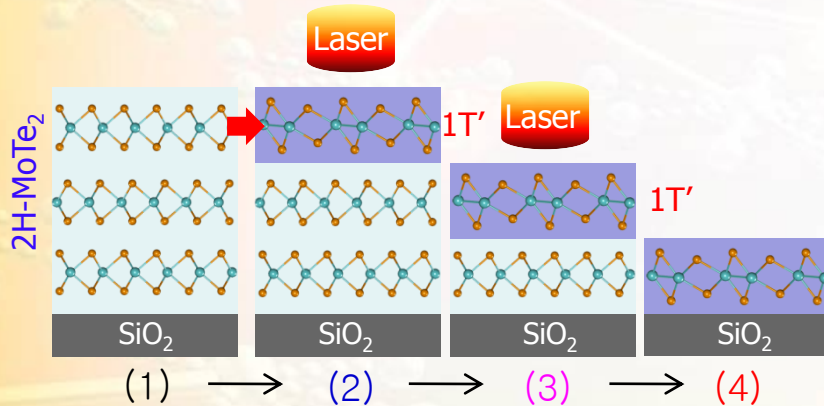
H. Wang et al., PNAS 11, 19701 (2013)



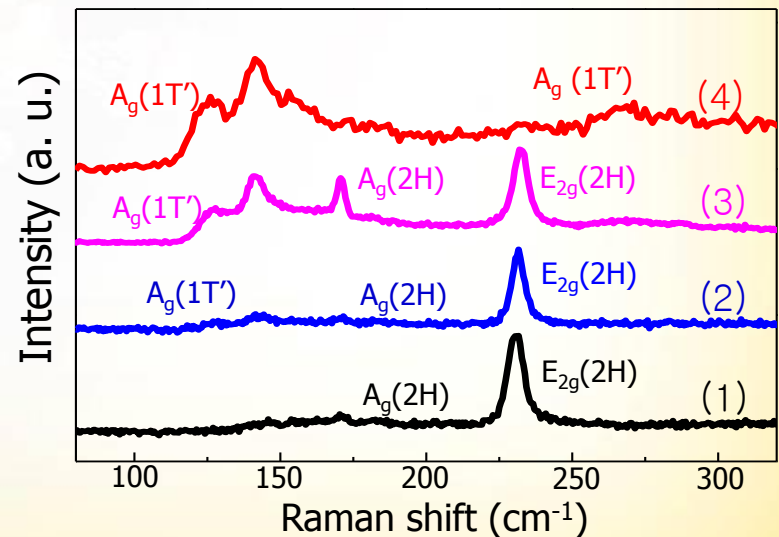
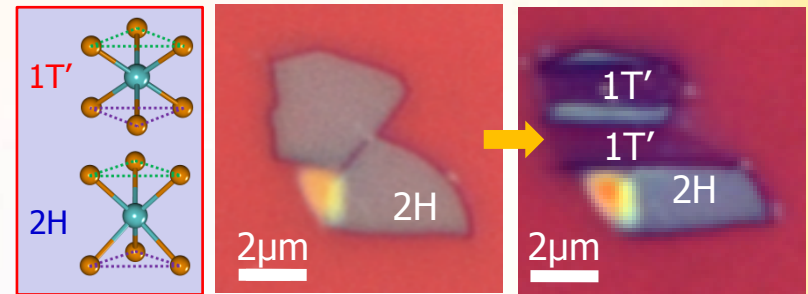
S. Cho et al., Science 349, 625 (2015)

Light illumination!!

Laser irradiation at a chosen local area
 => Phase control with 1 μm spatial resolution



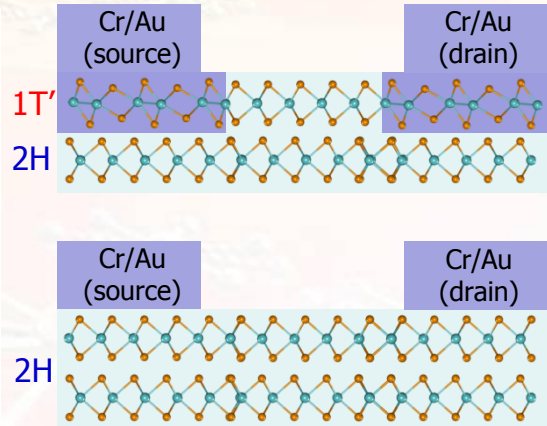
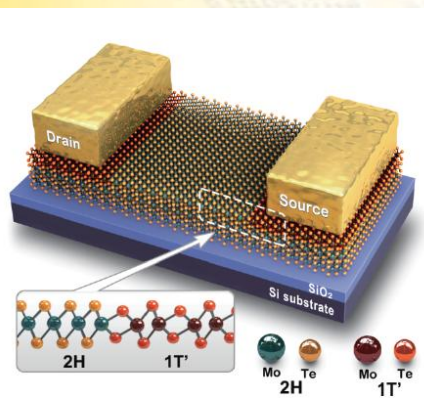
- Laser thinning
- Phase conversion to 1T'



Laser-patterned Ohmic junction in MoTe₂

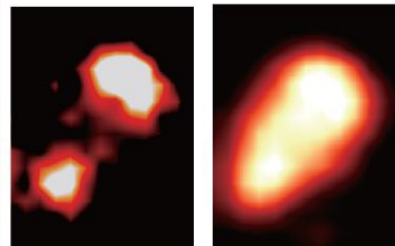
Center for Integrated Nanoscale Physics

Laser patterning on transistor
(only at source/drain area)

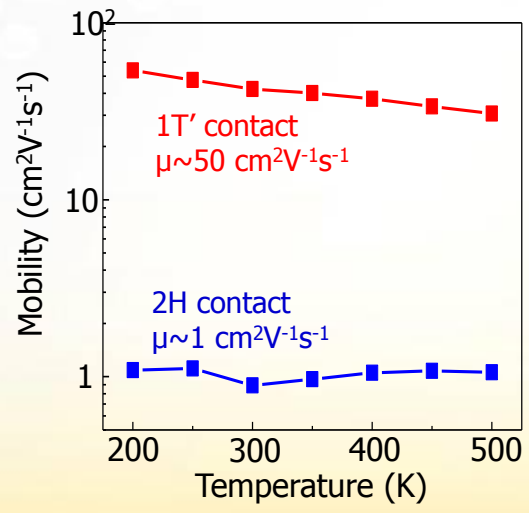
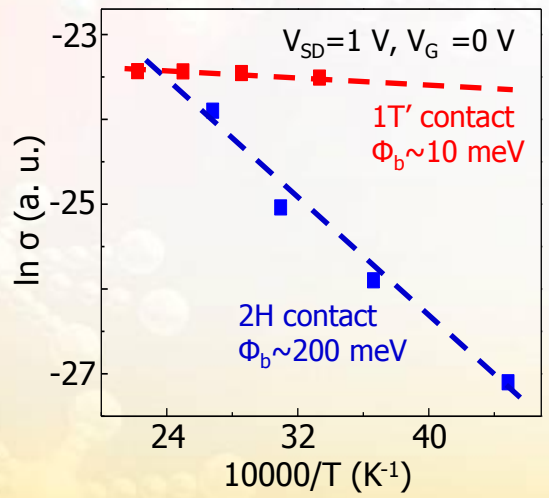
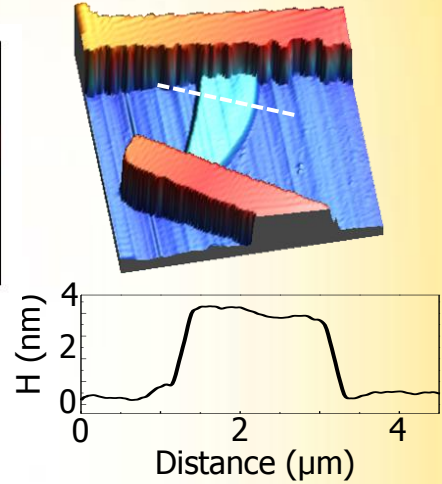


S. Cho et al., Science 349, 625 (2015)

Local 1T' at S & D



Laser thinning



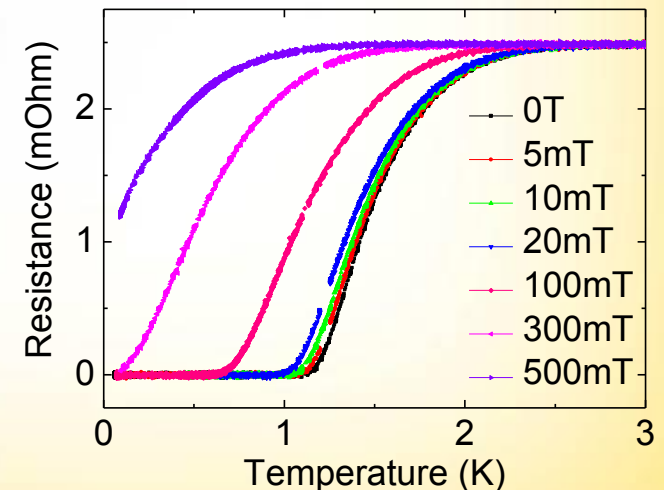
-> New ohmic contact formed at the junction

Key findings

- Reversible Structural Phase Transition
- Bandgap Opening in $1T'$ - MoTe_2 by 'Spin-Orbit Coupling'
- Local Phase Transition \rightarrow Ohmic contact in 2D
- Room-Temperature Phase Transition by Small Strain

Future projects

- Superconductivity in MoTe_2
- Bandgap ~ 1 eV
 \Rightarrow Photovoltaic, Optoelectronic devices
- Vertical tunneling device

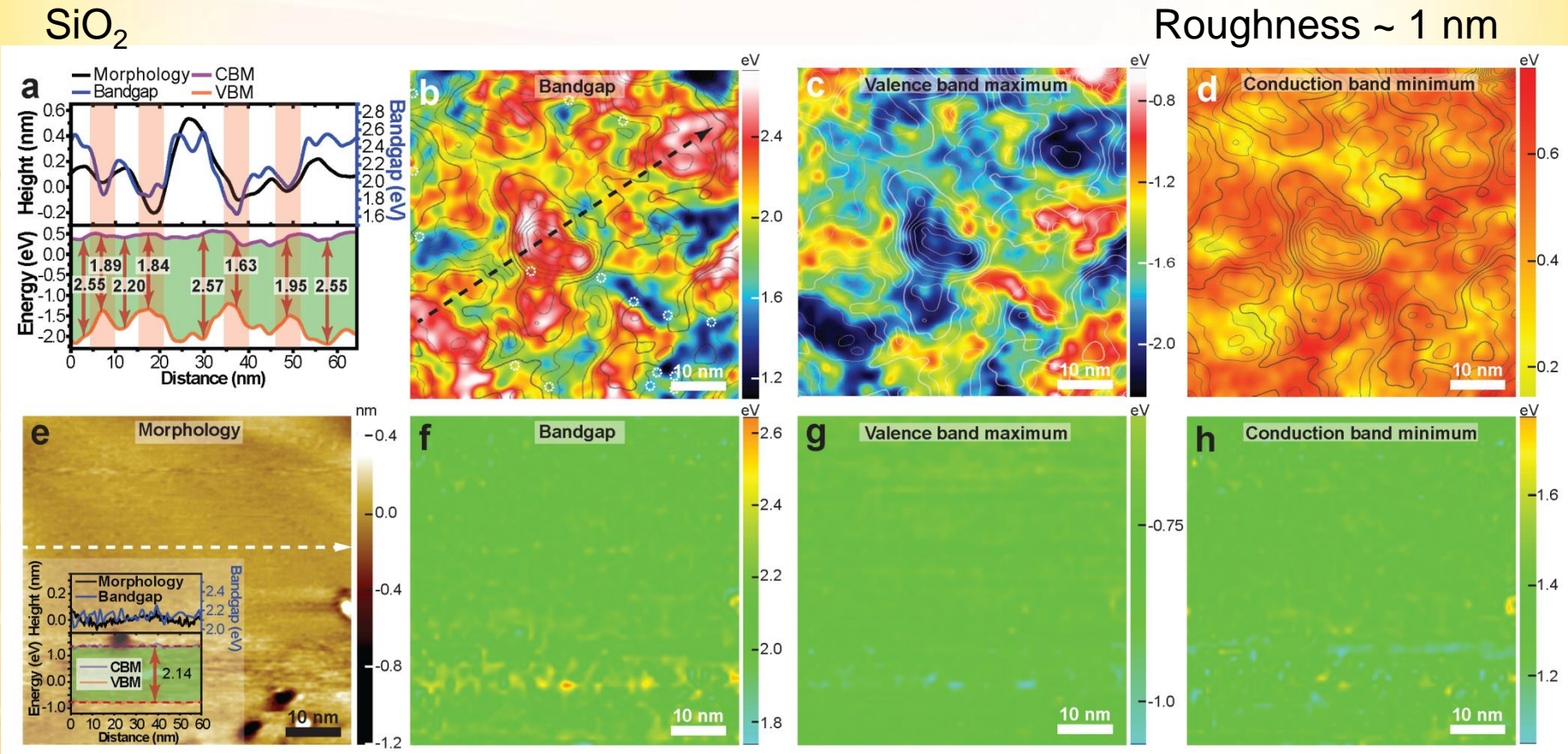


Physical and chemical properties can be easily modulated by environment

Strain effect

B. G. Shin et al., submitted!

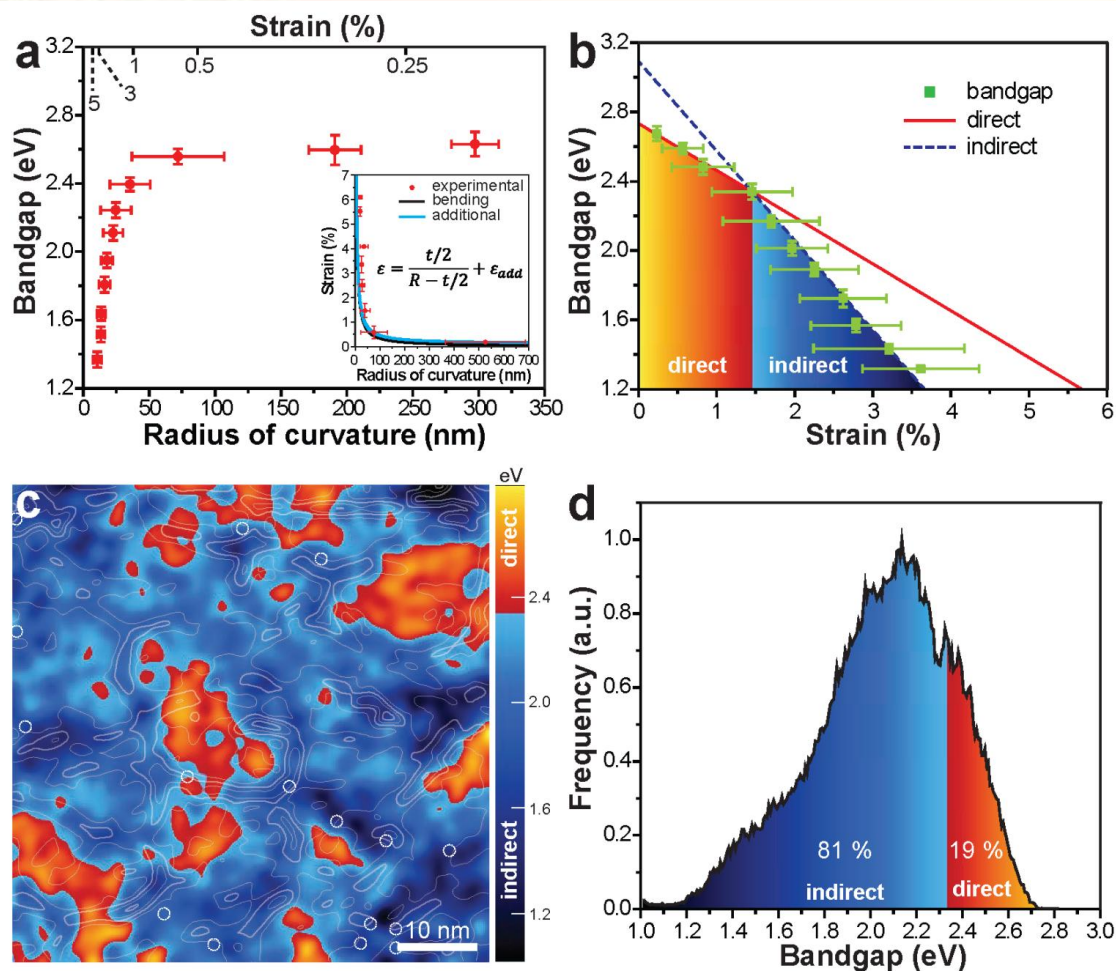
Bandgap is strongly modulated with local strain in MoS₂!



HOPG

B. G. Shin et al., submitted!

80% area is converted to indirect bandgap from direct bandgap!

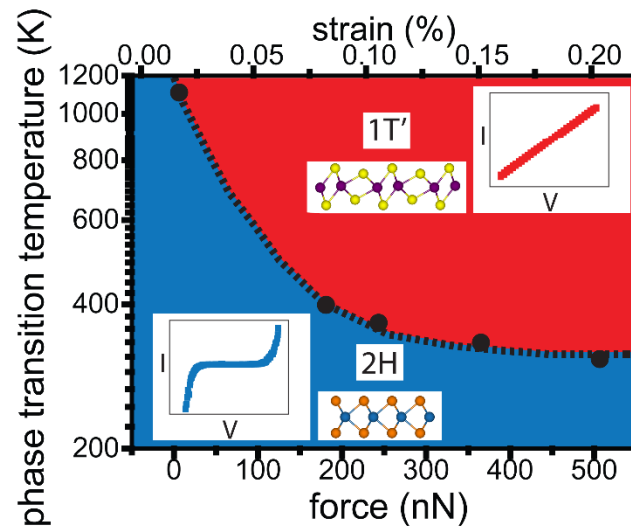
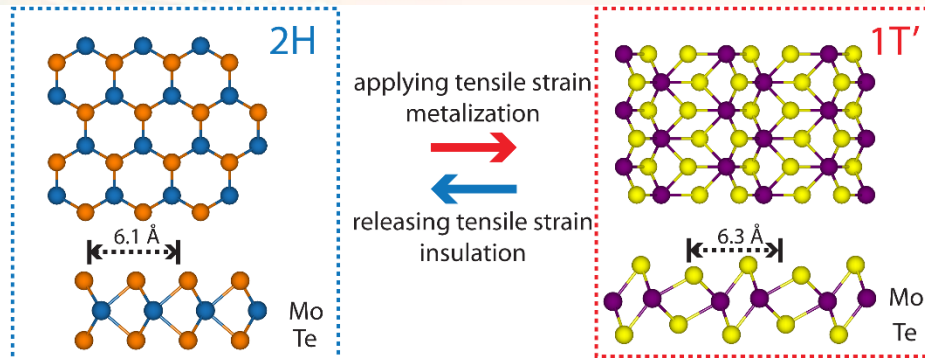


Room-temperature phase transition

High phase transition T to low phase transition T ???

S. H. Song *et al.*, submitted

Tensile strain



Fully reversible upon release

1100 K at zero strain
=> 300 K at 0.2% tensile strain

First-order M-I transition at RT can be induced by small tensile strain (0.2%)

Dielectric constant modulation

Lin et al., NanoLett. 14, 5569 (2014)

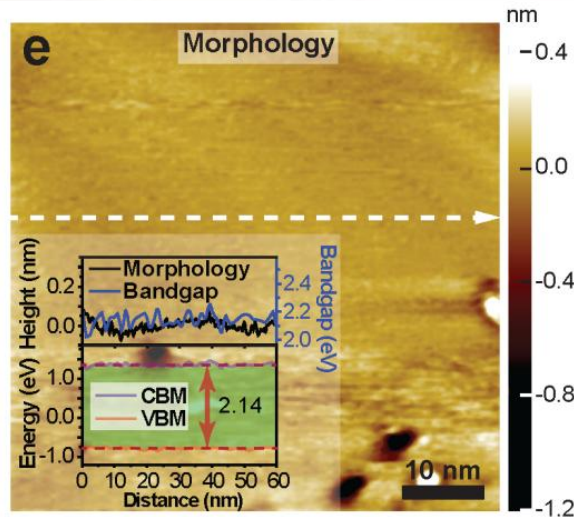
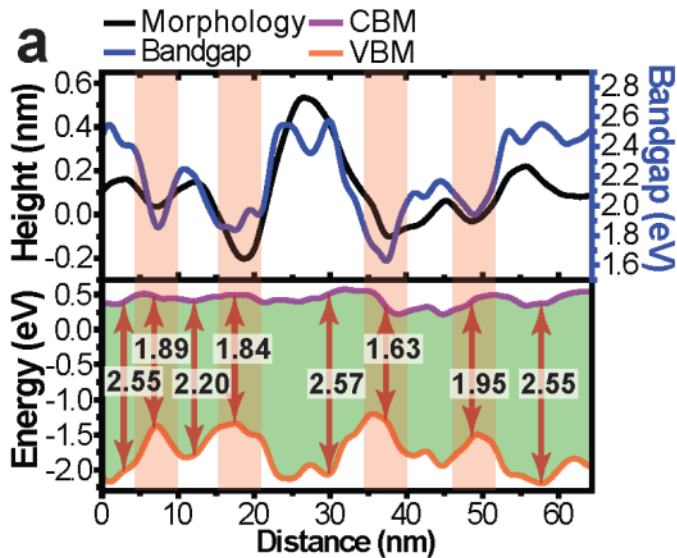
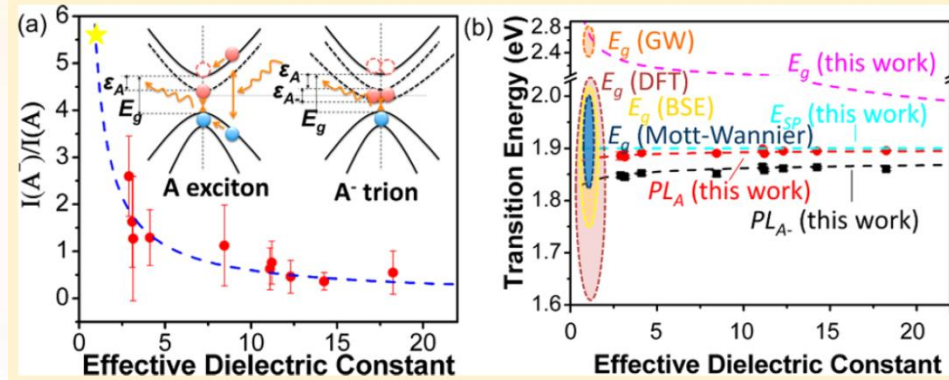
Elias et al., Nature Physics 2011

From the renormalization group theory:

$$\frac{k}{v_F} \frac{\partial v_F}{\partial k} = -\frac{e^2}{4\epsilon \hbar v_F}$$

where $\epsilon = (1 + \epsilon_s)/2$

$$\alpha = e^2 / \epsilon \hbar v_F$$

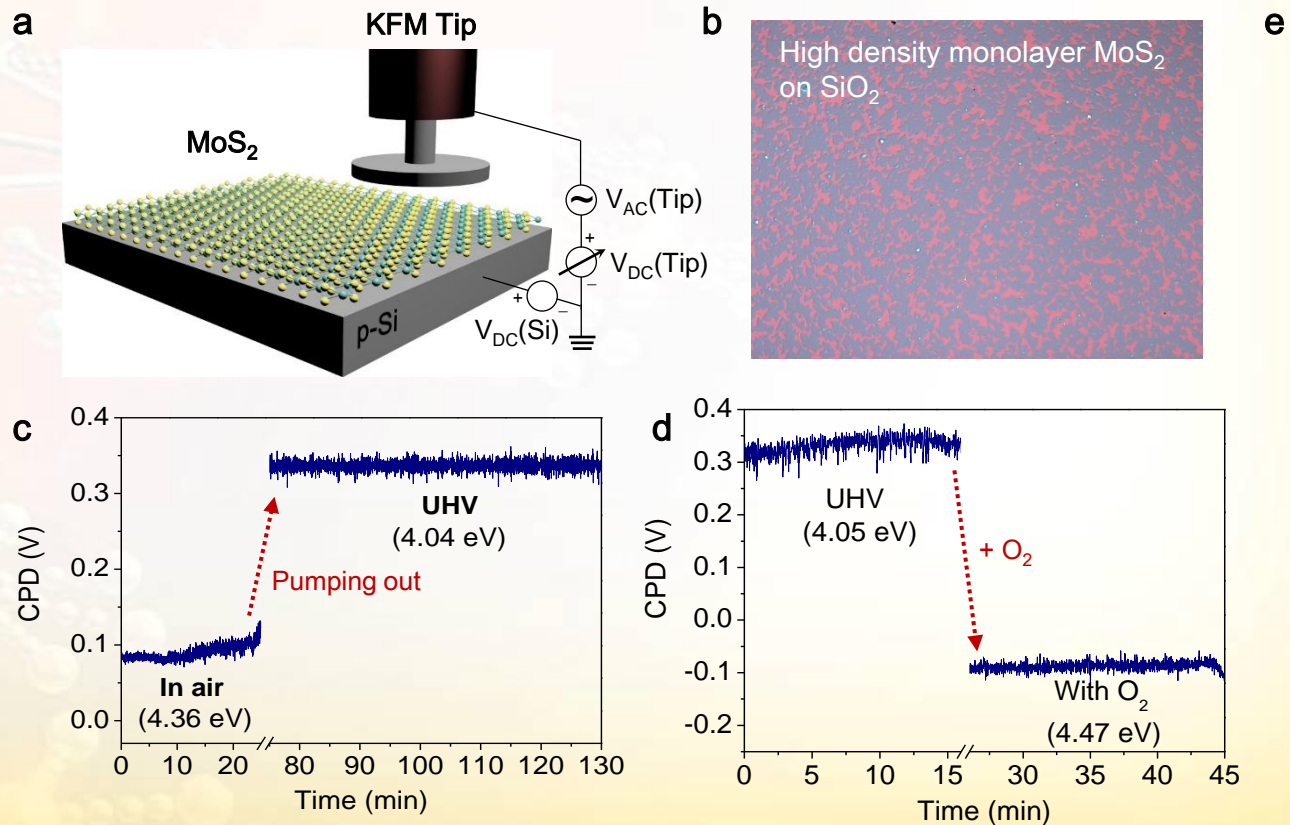


Work function modulation

S. Y. Lee et al., submitted

Work function of MoS₂ is modulated by O₂ adsorption/desorption!

: 0.4 eV, similar to graphene



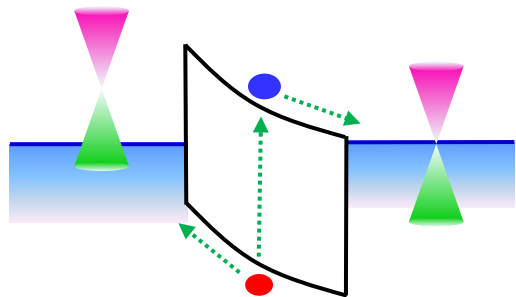
Quantum mechanical phenomena

1L-MoS₂ vs 6L-MoS₂

W. J. Yu et al., submitted

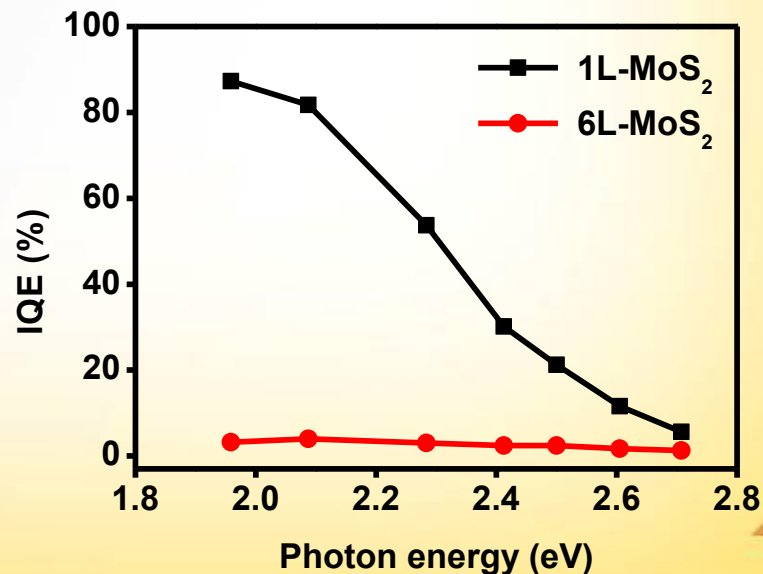
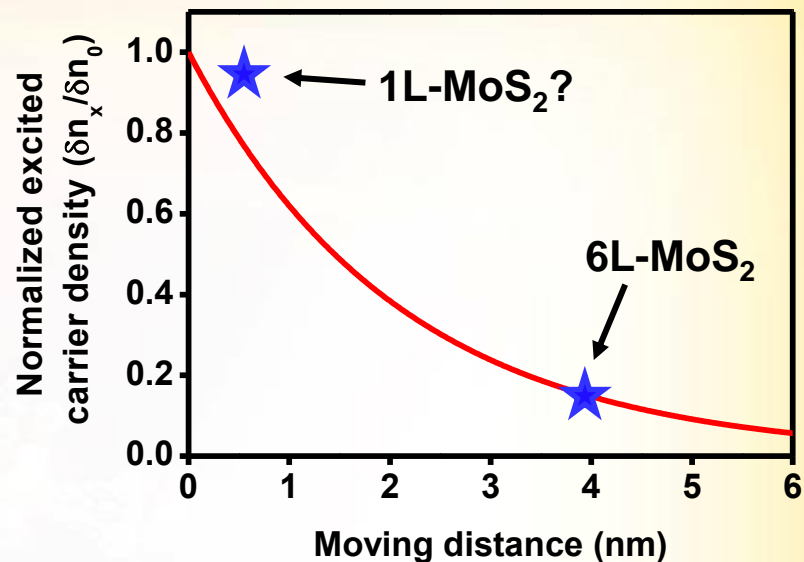
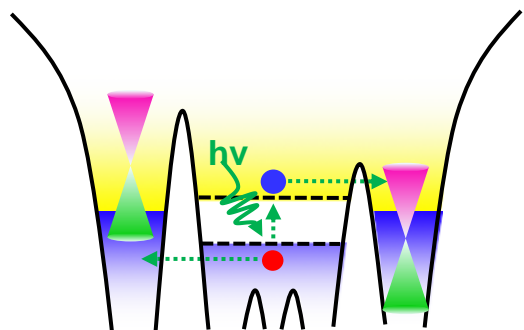
Multi-layer charge transport

Continuity equation
$$\frac{d}{dt} \delta n = D \frac{d^2}{dx^2} \delta n + \mu \xi \frac{d}{dx} \delta n - \frac{\delta n}{\tau} + g$$



Monolayer charge transport

Tunneling probability
$$\bar{\Psi} \cdot \Psi = \bar{A} \cdot A e^{-2\alpha x}$$



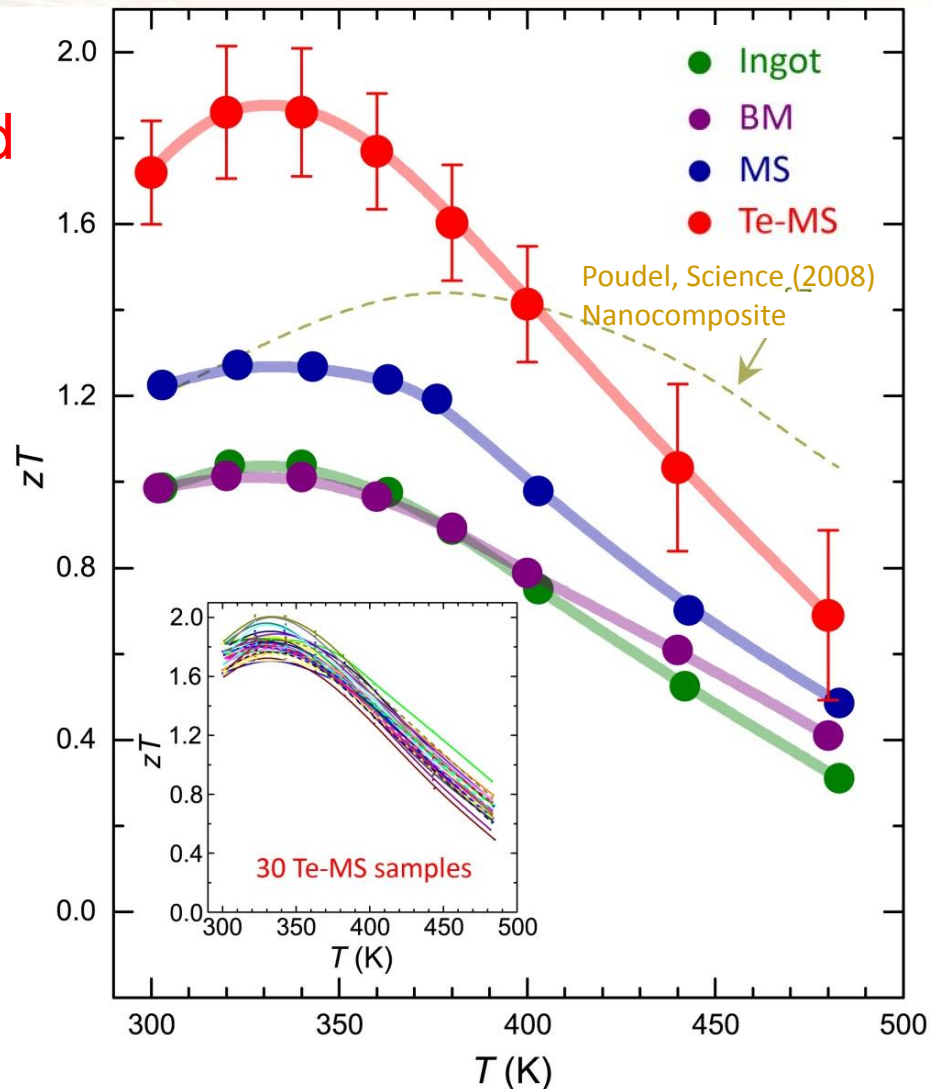
Thermoelectric Properties ($\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$)

Dimensionless Figure of Merit, zT

S. I. Kim et al., Science 348, 109-114 (2015)

World-best record
for RT TE!

$$zT = S^2 \sigma / \kappa T$$

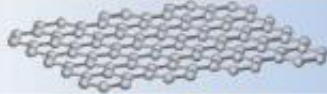

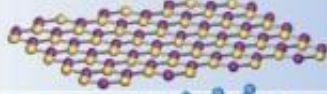





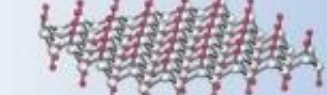



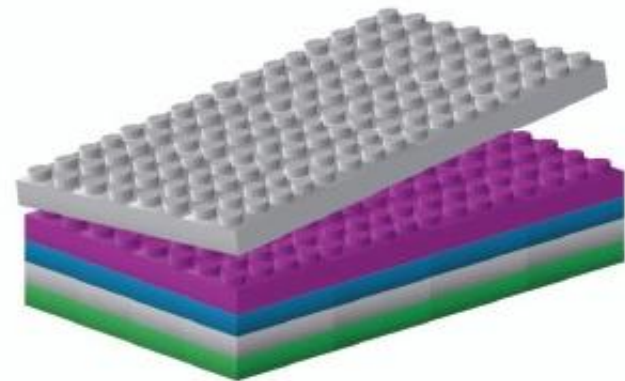
Synthesis of 2D materials

- Large-area, monolayer monocrystalline graphene
(Adv. Mat. 27, 1376 (2015))
- Large-area, AB stacking bilayer graphene (unpublished)
- Large-area, monolayer MoS₂, seed growth by CVD
(Nature Comm. (2015))
- Large-area monolayer WSe₂ on Au substrate by CVD
(ACS Nano 9, 5510 (2015))
- Seed growth for MX₂ (M: Mo, W, X: S, Se) (unpublished)
- Thin MoTe₂ film from Mo metal
(ACS Nano 9, 6548 (2015))
- Multilayer hBN is also available
 - => on SiO₂/Si, unpublished
 - => on Fe : Nature Comm., ASAP
- on Pt: Large area monolayer hBN, ACS NANO 8, 8520 (2014)
- on Au: mm-size monolayer singlecrystalline hBN, unpublished

Summary

van der Waals engineering!

	Graphene	
	hBN	
	MoS ₂	
	WSe ₂	
	Fluorographene	



There is a plenty of room
for new phenomena in
2D materials!