Semiconductor Devices II

Part 2

Chapter 2: Defects in 2D materials

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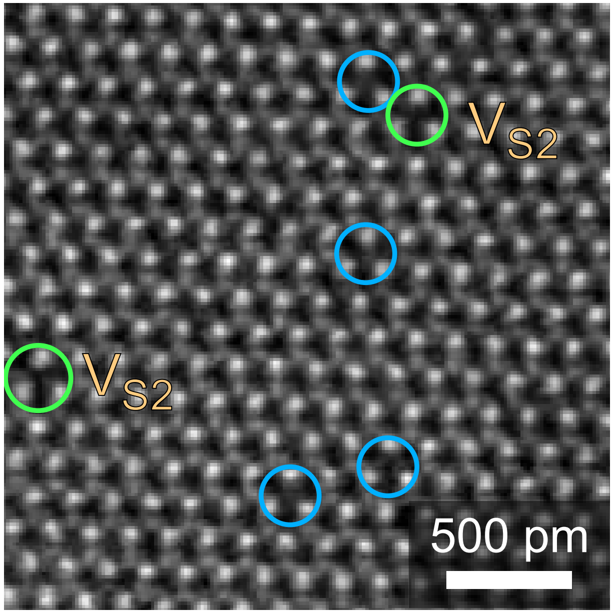
[Outline] Chapter 2: Defects in 2D materials

- Overview of defects in 2D materials
- Point defects
- How to mitigate (some) defects
- Positive applications of defects

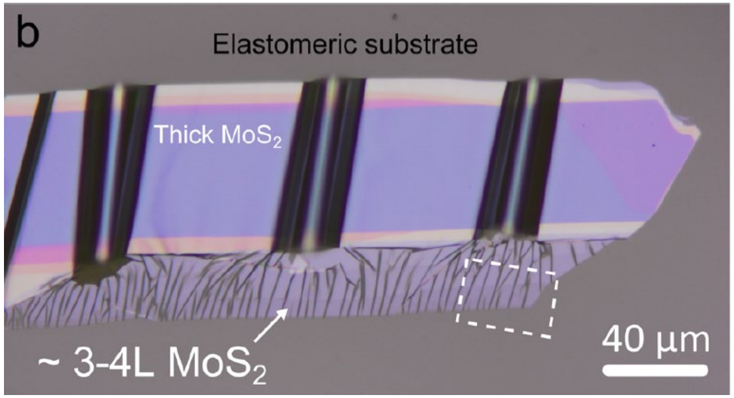
Most common defect types in 2D

- Point defects
  - vacancies
  - substitutions
  - dopants
- Line defects
  - grain boundaries
  - lateral heterostructures
  - vacancy lines
- Two-dimensional defects
  - wrinkles
  - ripples

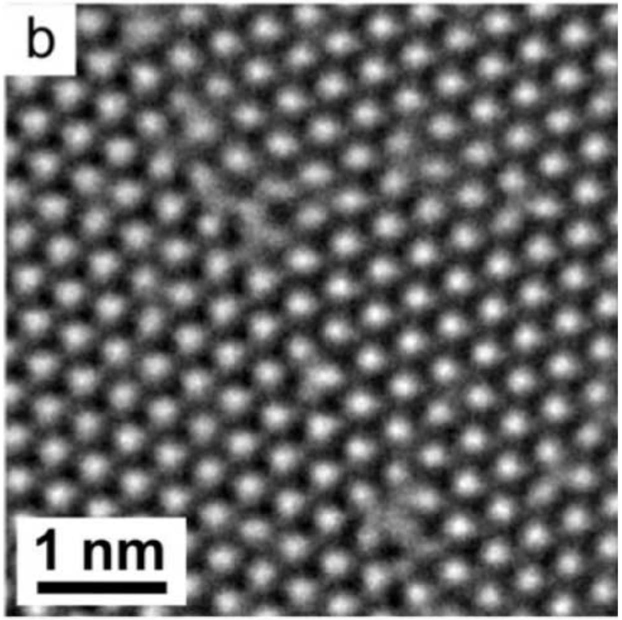
> *Crystals are like people, it is the defects in them which tend to make them interesting!*
>
> \- Sir Colin Humphreys, CBE FRS FREng FIMMM FInstP



Dumcenco et al. 2D Mater. (2015)



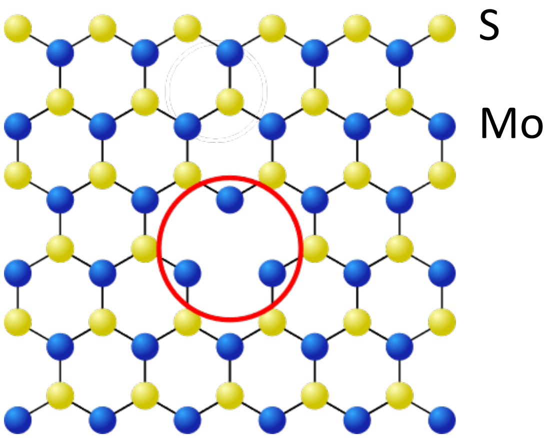
Castellanos-Gomez et al. Nano Letters (2013)



ACS Nano (2015) Lehtinen

Most common defects: point defects

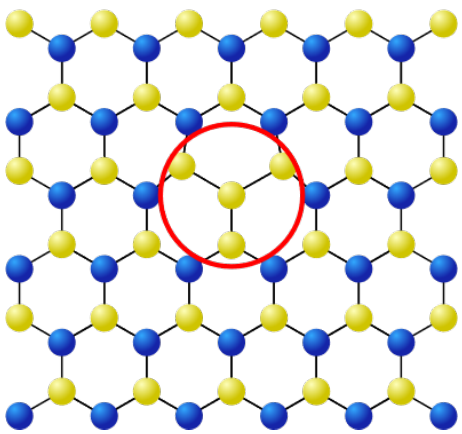
Missing atom



vacancy

V_{S2}

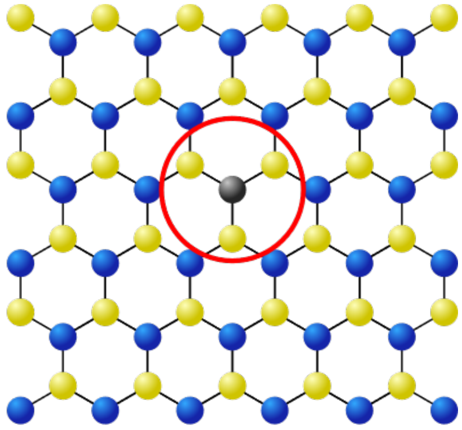
Native atom in the wrong place



antisite defect

$S2_{Mo}$

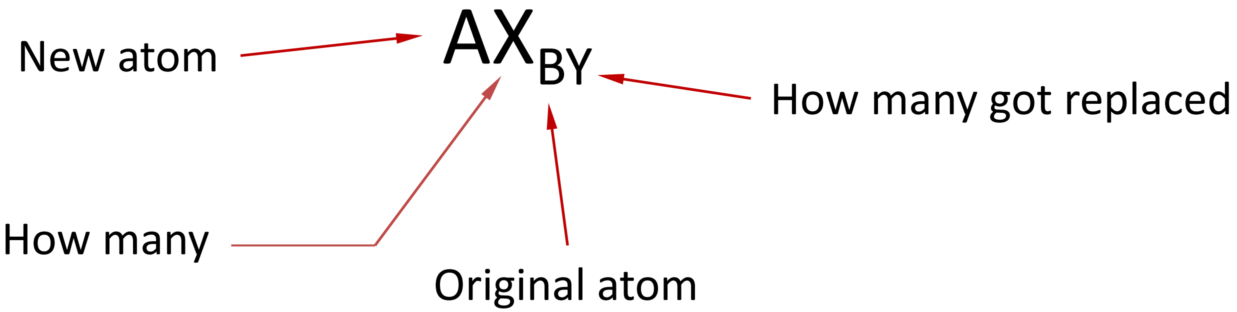
Foreign atom



substitutional doping

Nb_{Mo}

Nomenclature:



AX_{BY}

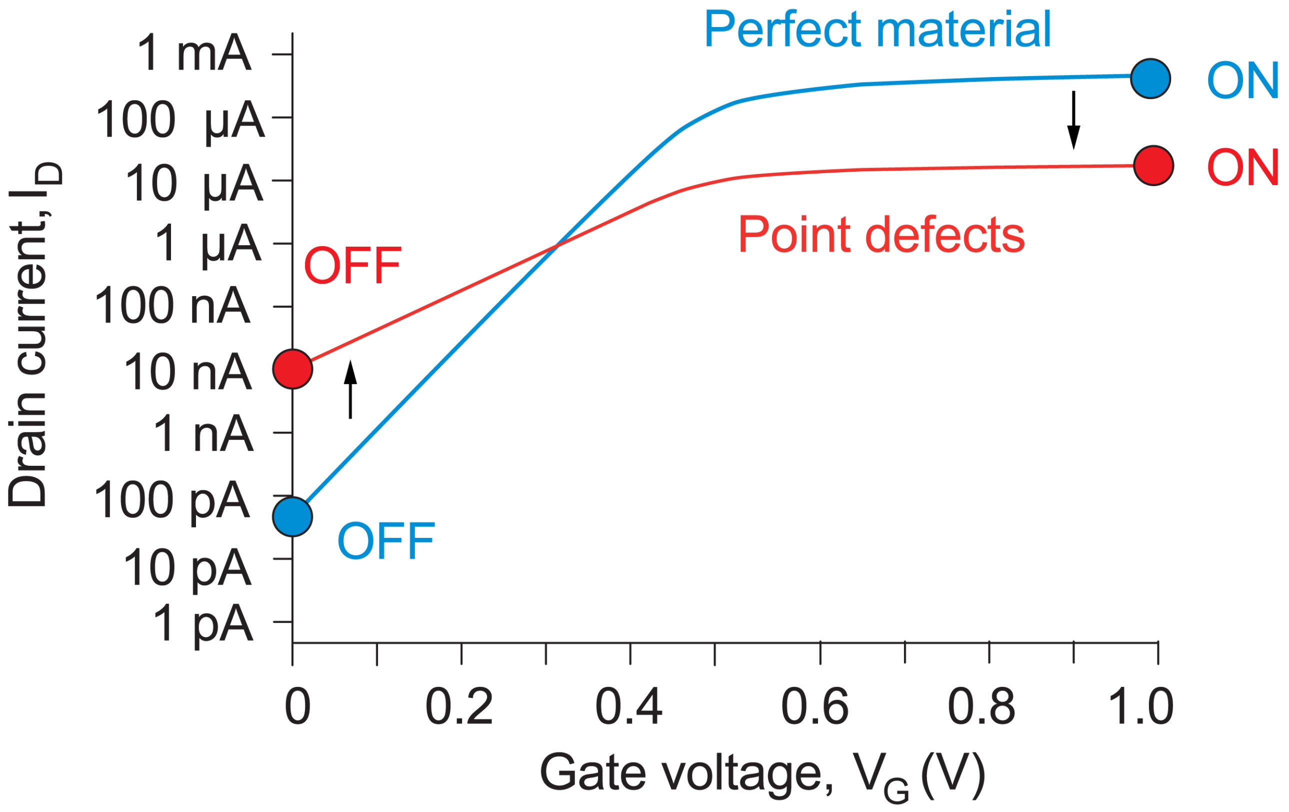
New atom

How many got replaced

How many

Original atom

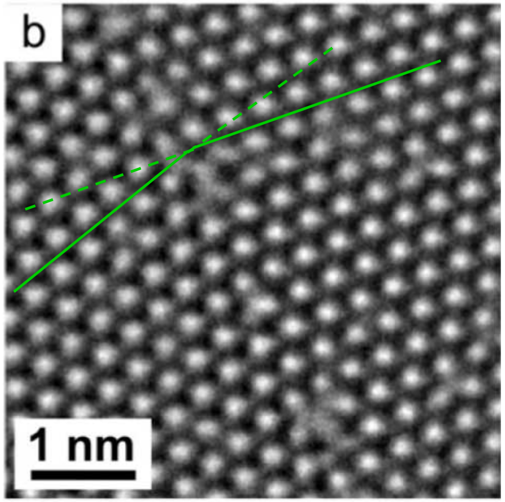
Influence of point defects on FET characteristics



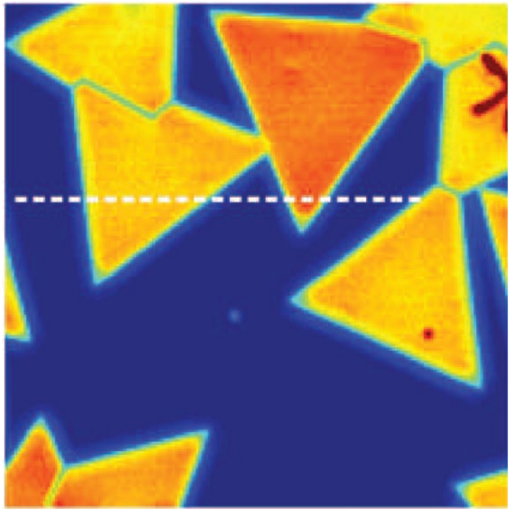
- ON current: decreases
- OFF current: increases
- I_{ON}/I_{OFF}: decreases
- Subthreshold swing: increases

Most common defects: line defects

Grain boundaries

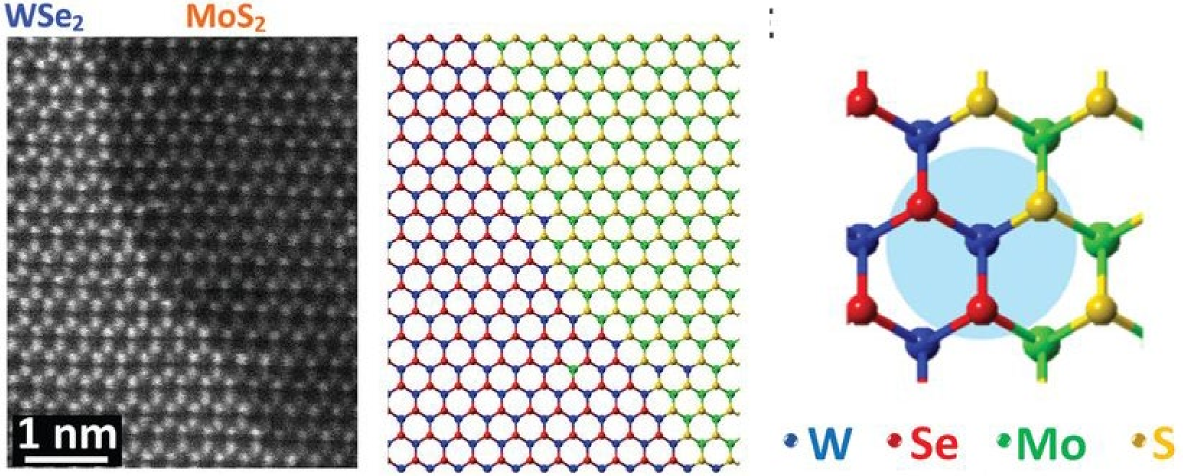


Lehtinen et al. ACS Nano (2015)



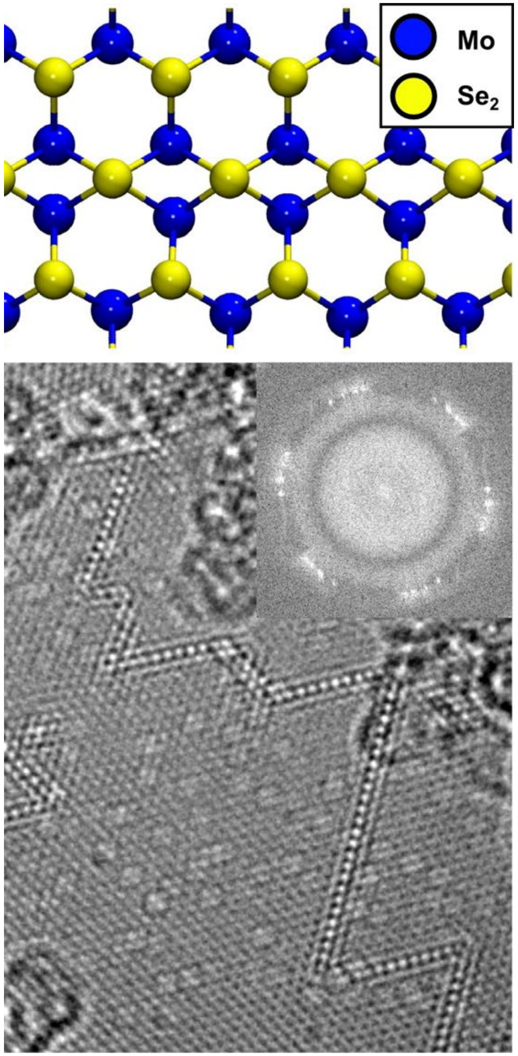
Yin et al. Science (2014)

Lateral heterostructures



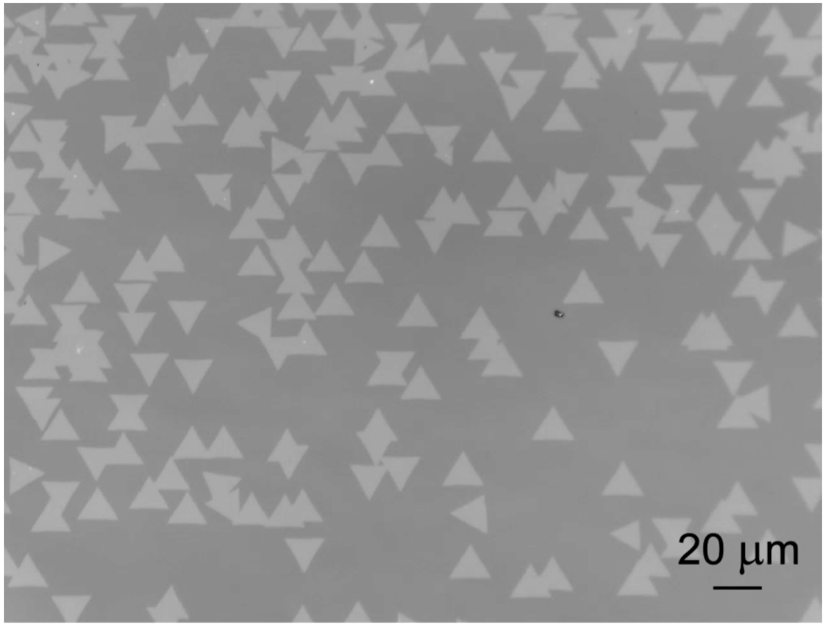
Li et al, Science (2015)

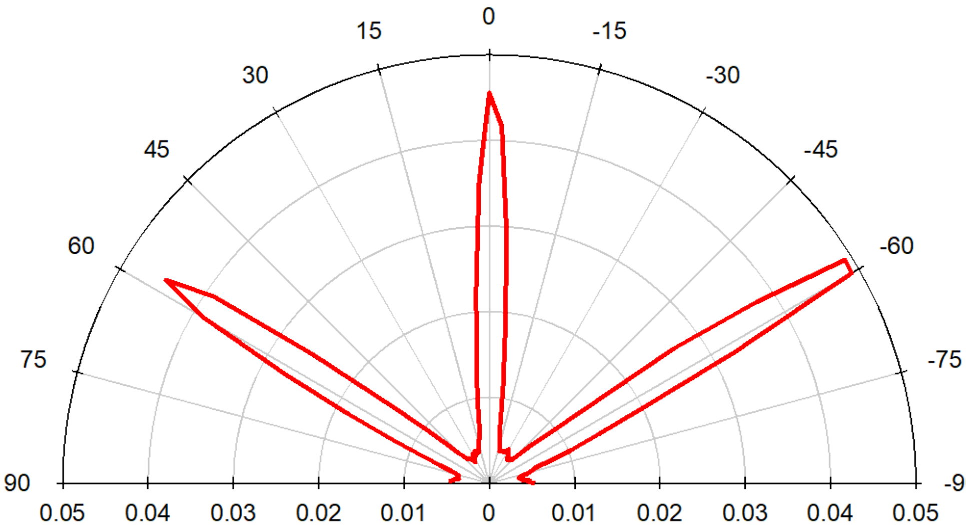
Vacancy lines

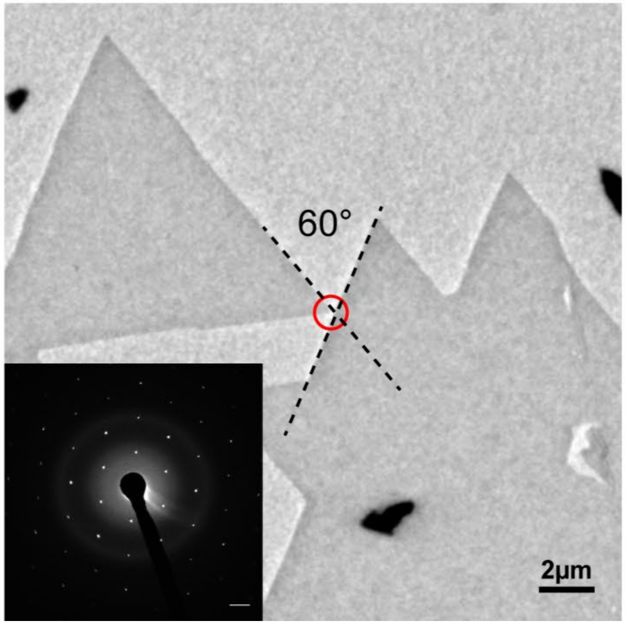


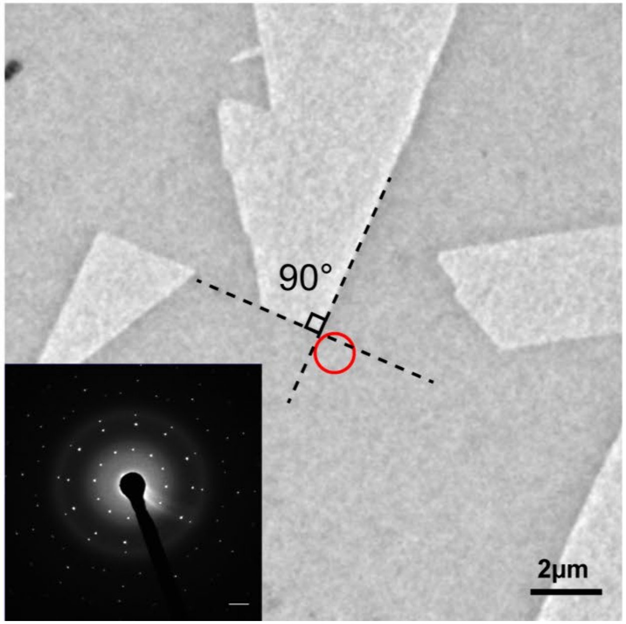
Lehtinen et al. ACS Nano (2015)

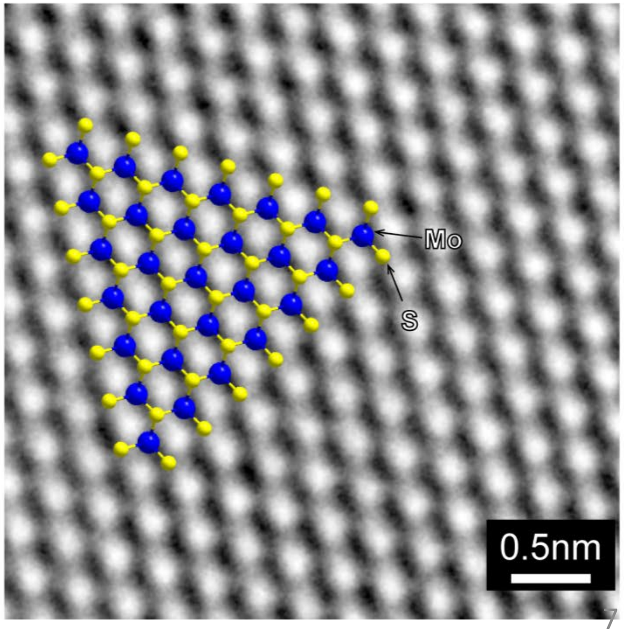
Can we avoid grain boundaries?



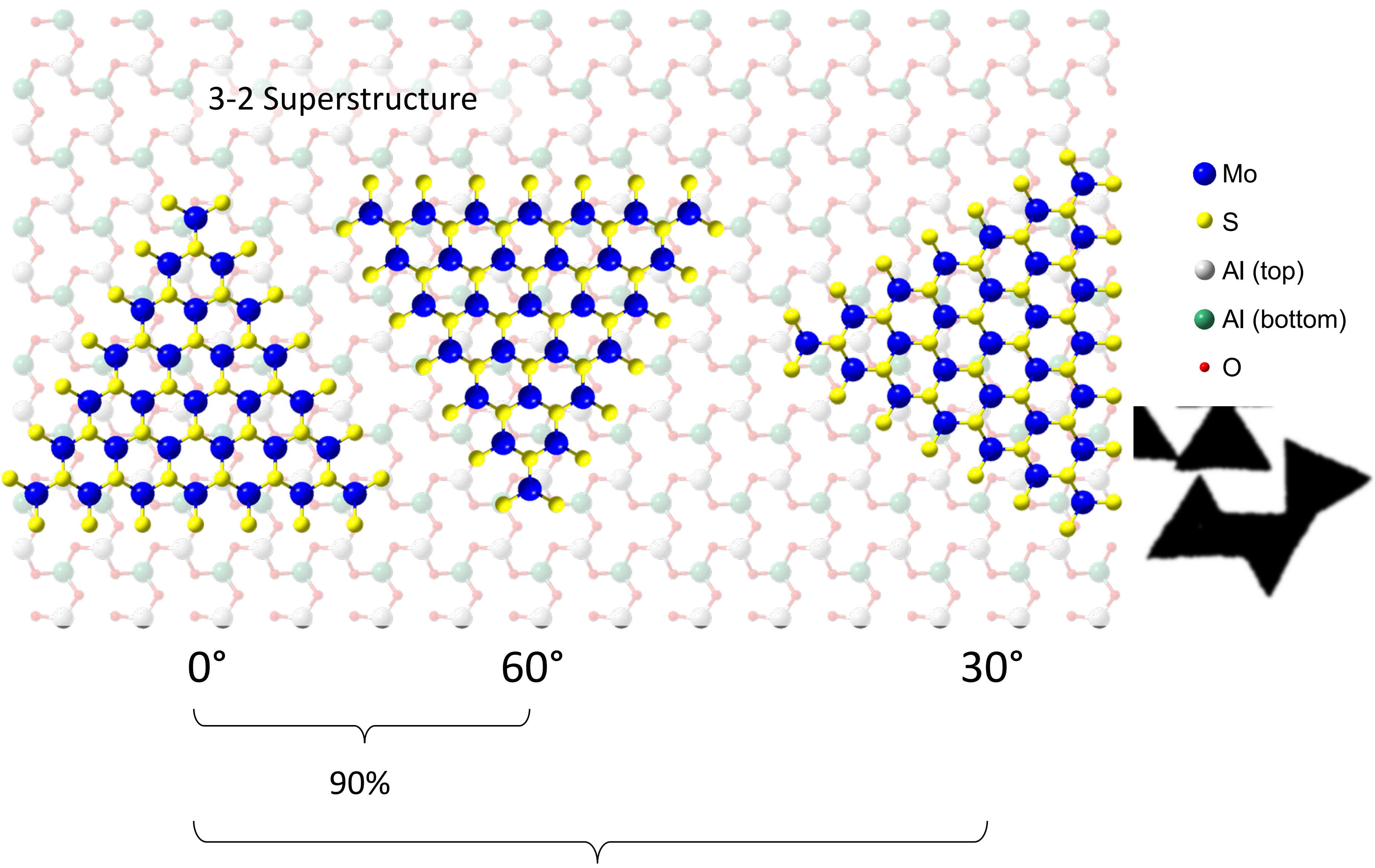








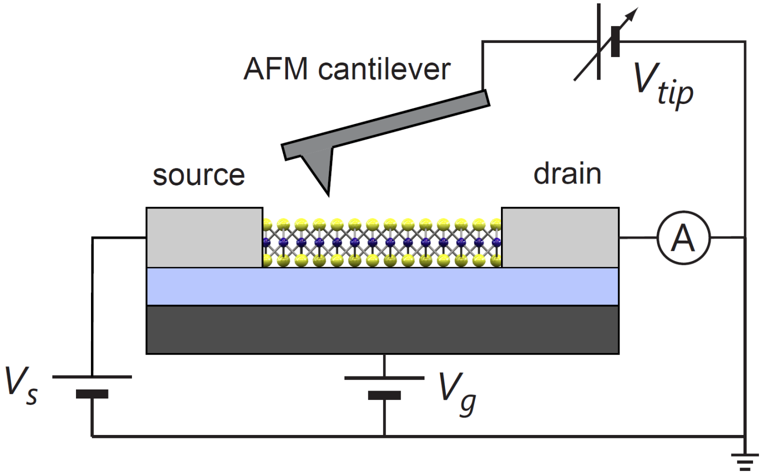
Epitaxial CVD MoS_2: domain orientations

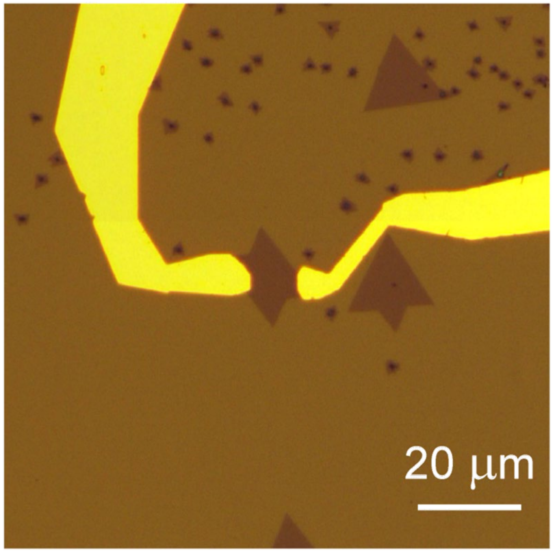


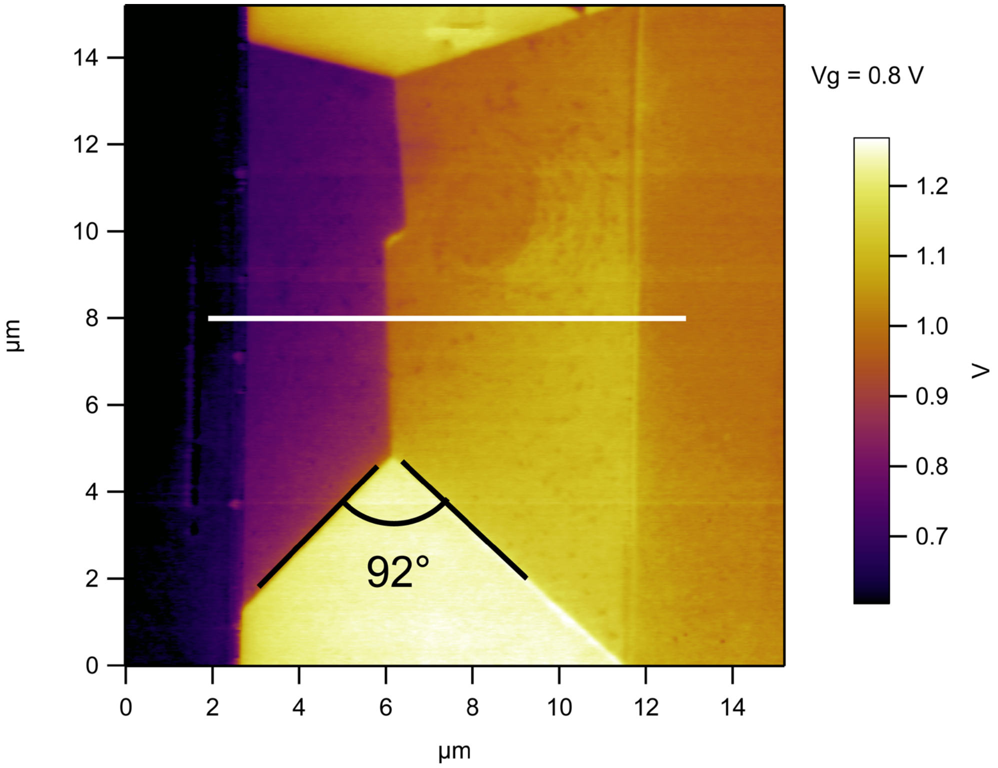
Dumcenco et al. ACS Nano (2015)

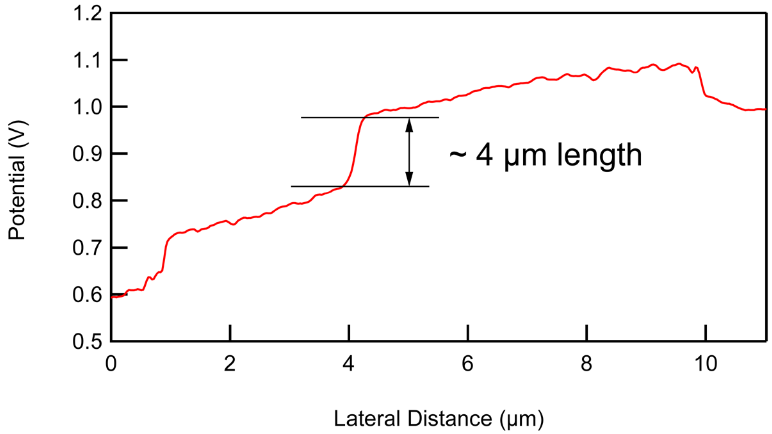
Conductivity and grain boundaries

Scanning Kelvin probe microscopy

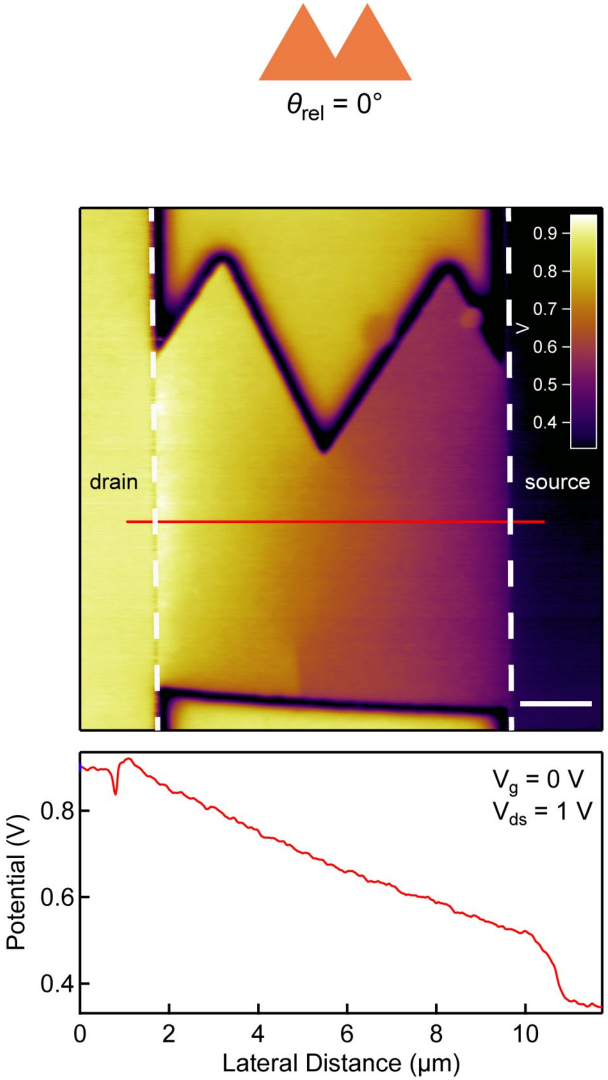


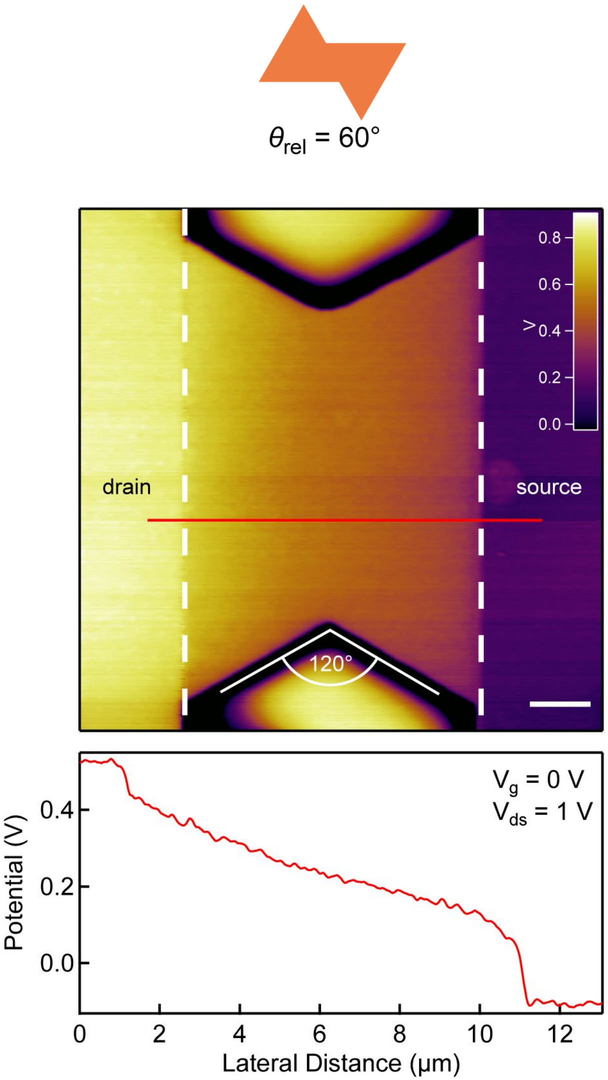


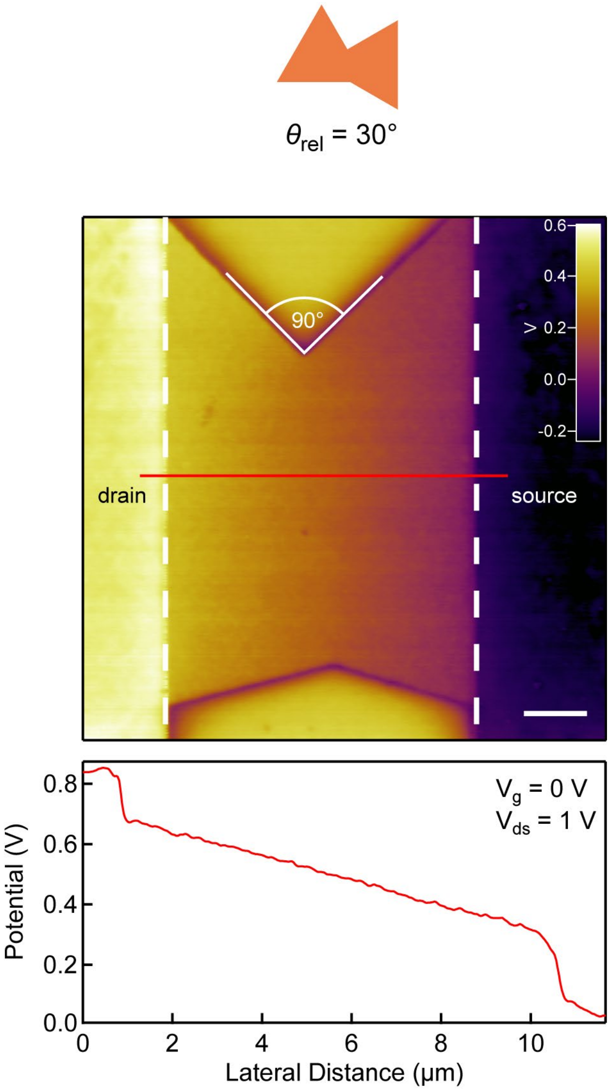




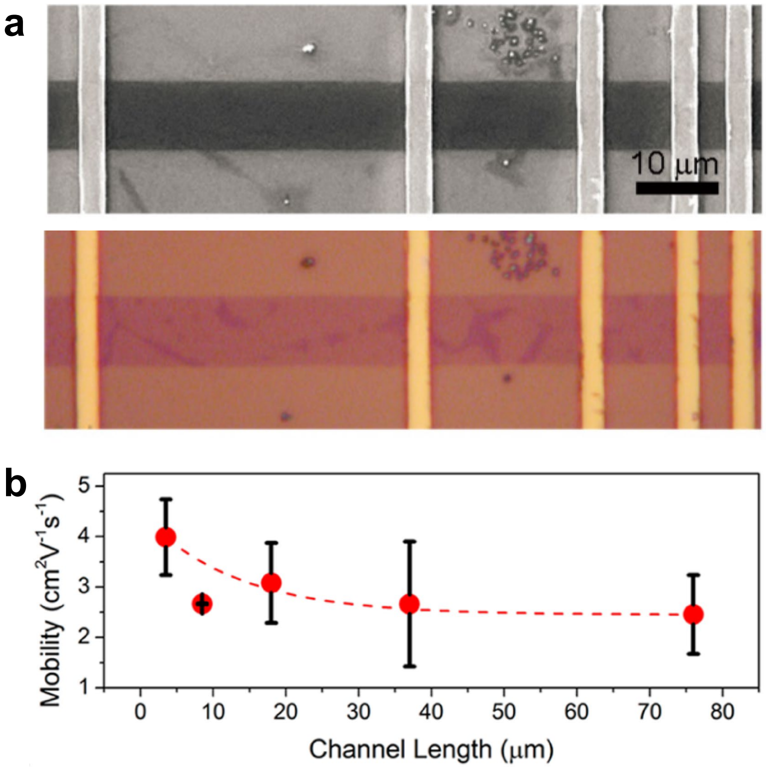
Conductivity and grain boundaries


$\theta_{rel} = 0°$

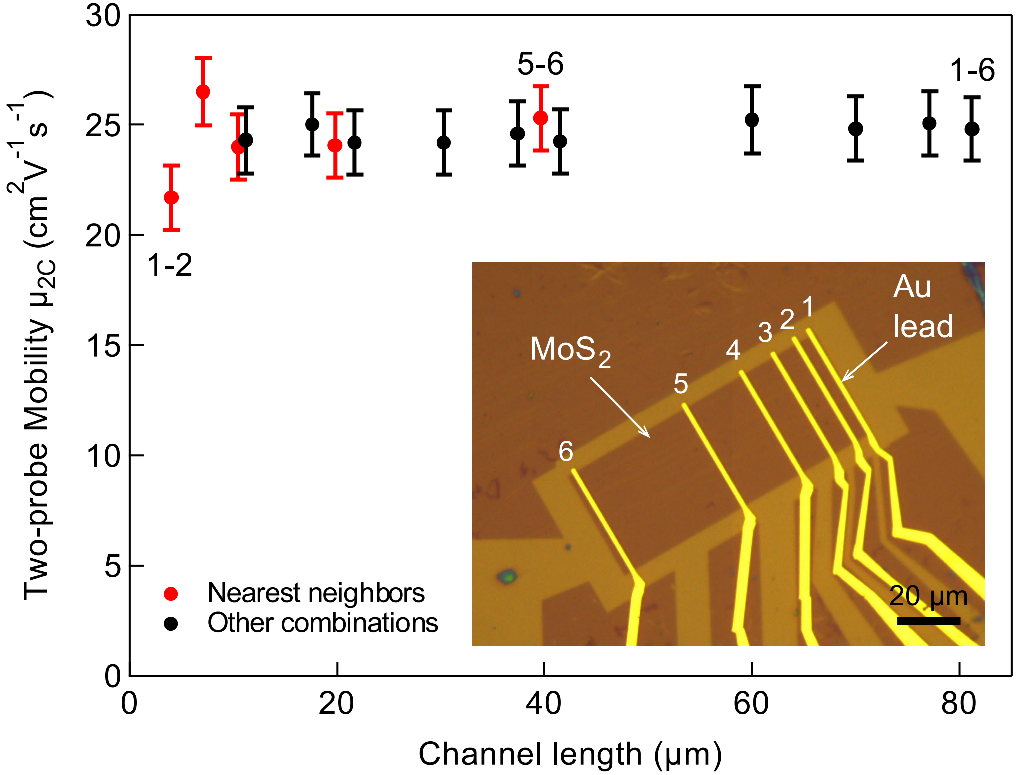

$\theta_{rel} = 60°$


$\theta_{rel} = 30°$

Conductivity and grain boundaries



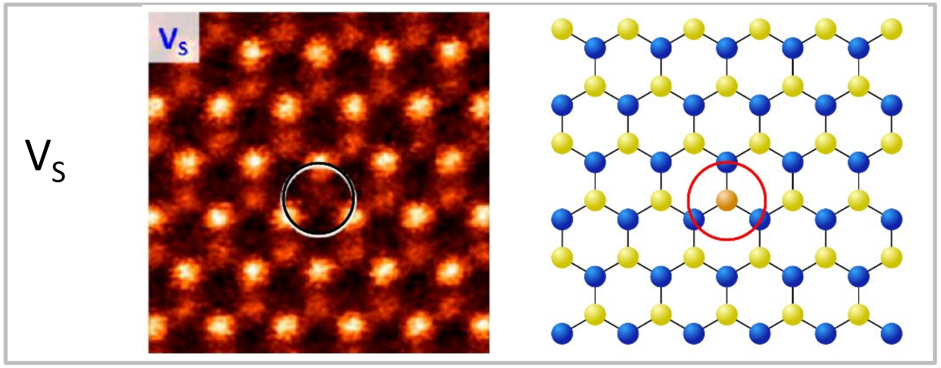
Najmaei, Ajayan et al. ACS Nano 2014



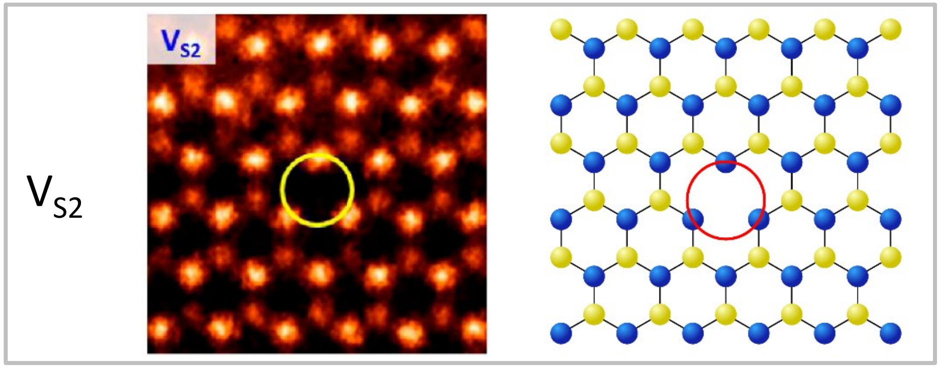
Dumcenco…Kis; ACS Nano (2015)

Most common point defects in MoS_2

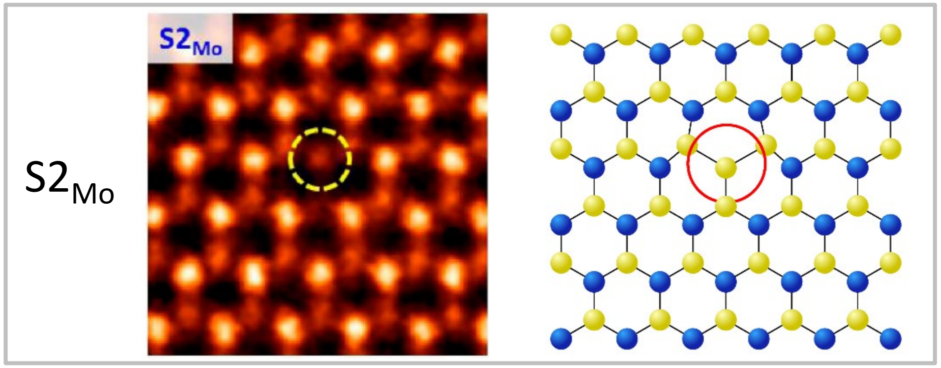
V_S



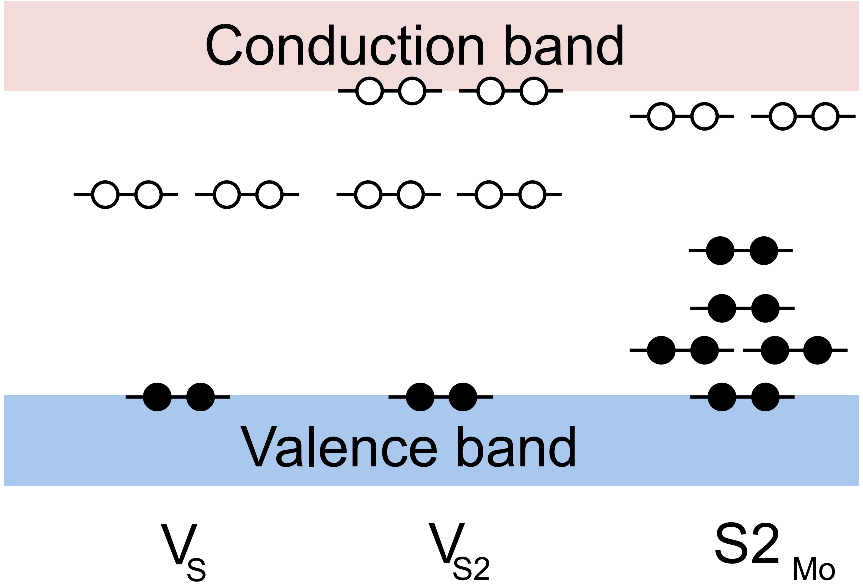
V_{S2}



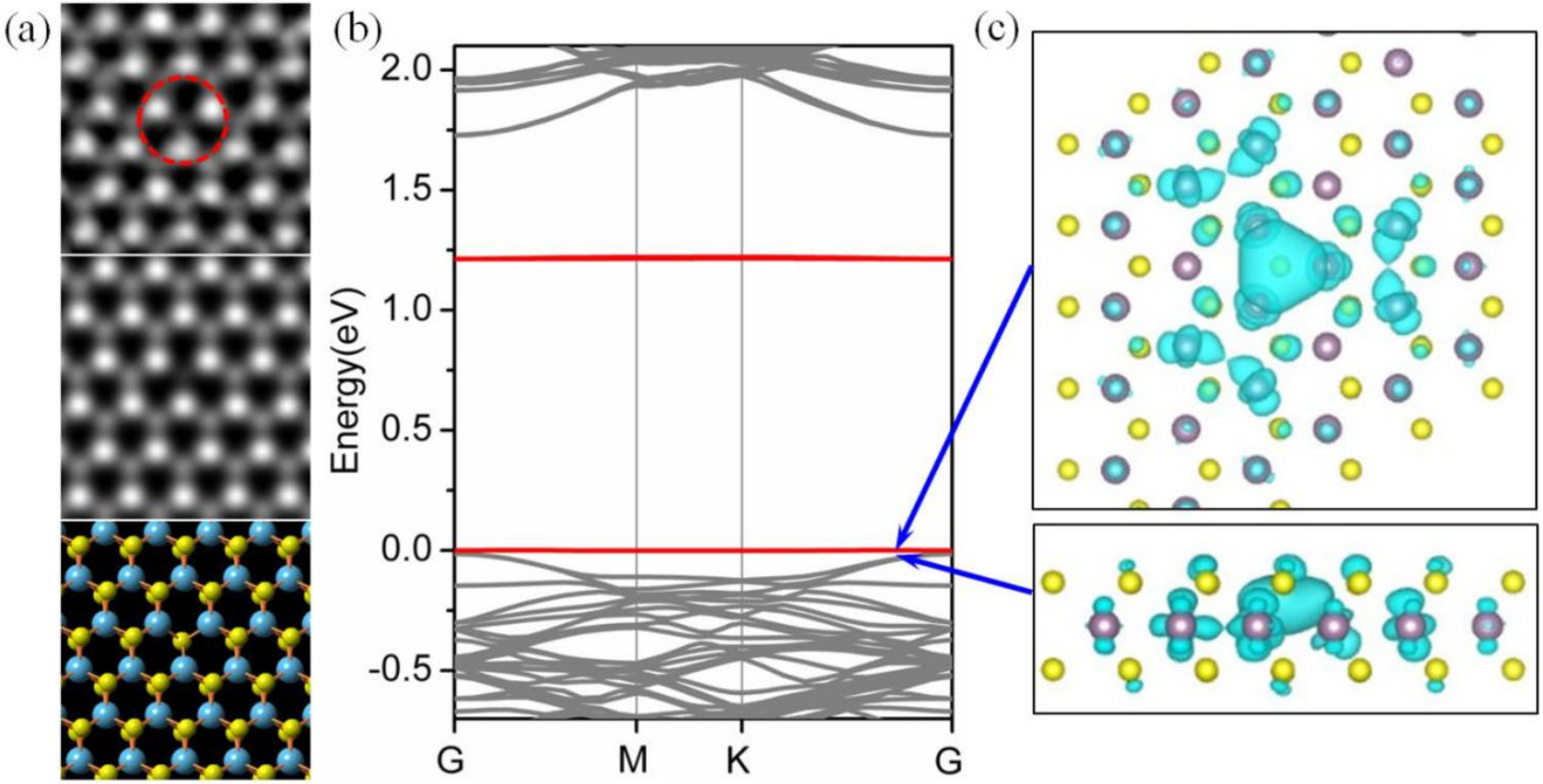
$S2_{Mo}$



Zhou et al. Nano Letters (2013)



Atomic and electronic structure of V_S



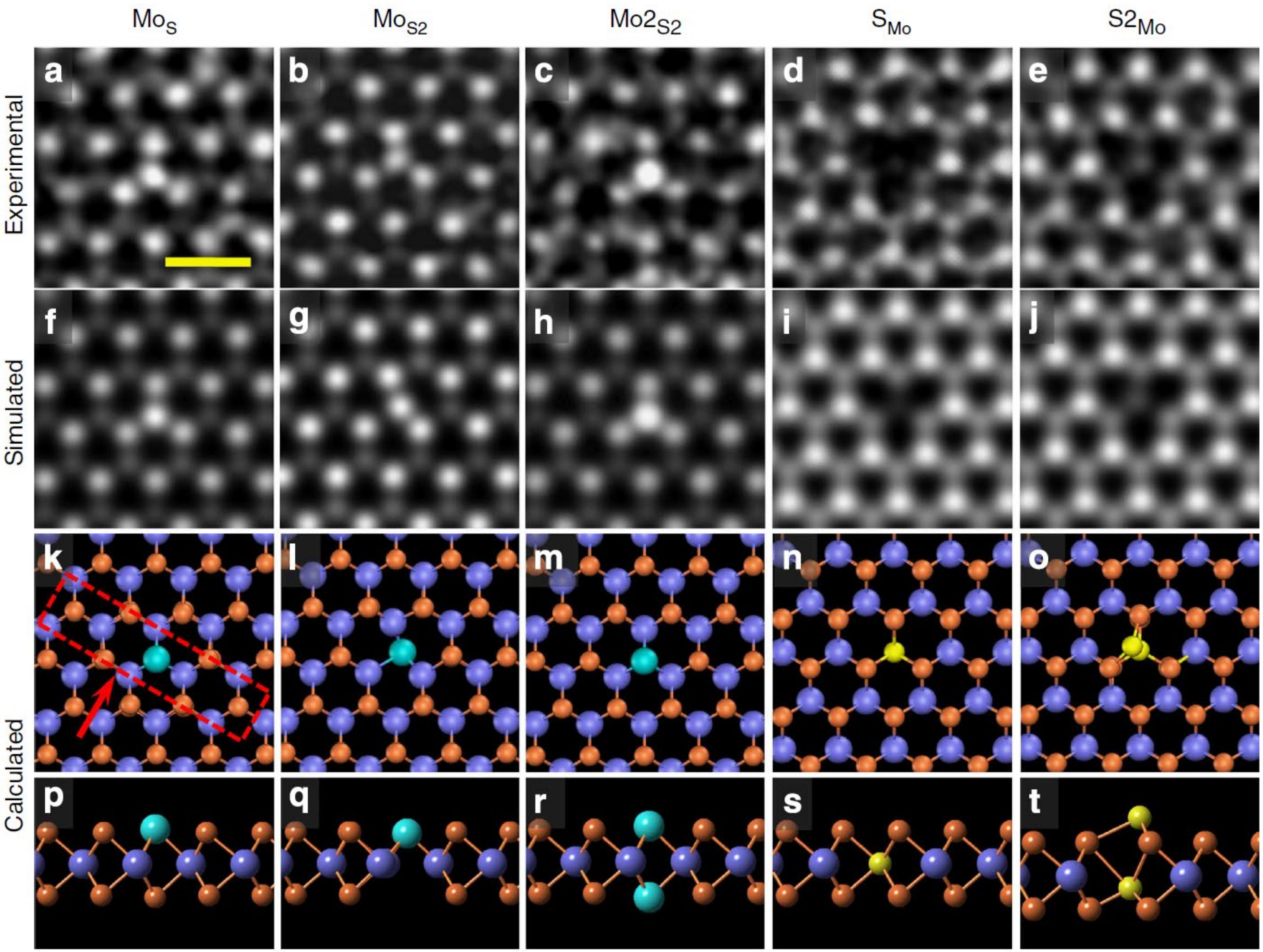
TEM image and structural model

Band structure

Defect state wavefunction

Hong et al, Nature Communications (2015)

Antisite defects in MoS_2



Hong et al, Nature Communications (2015)

Defect formation energy and concentration

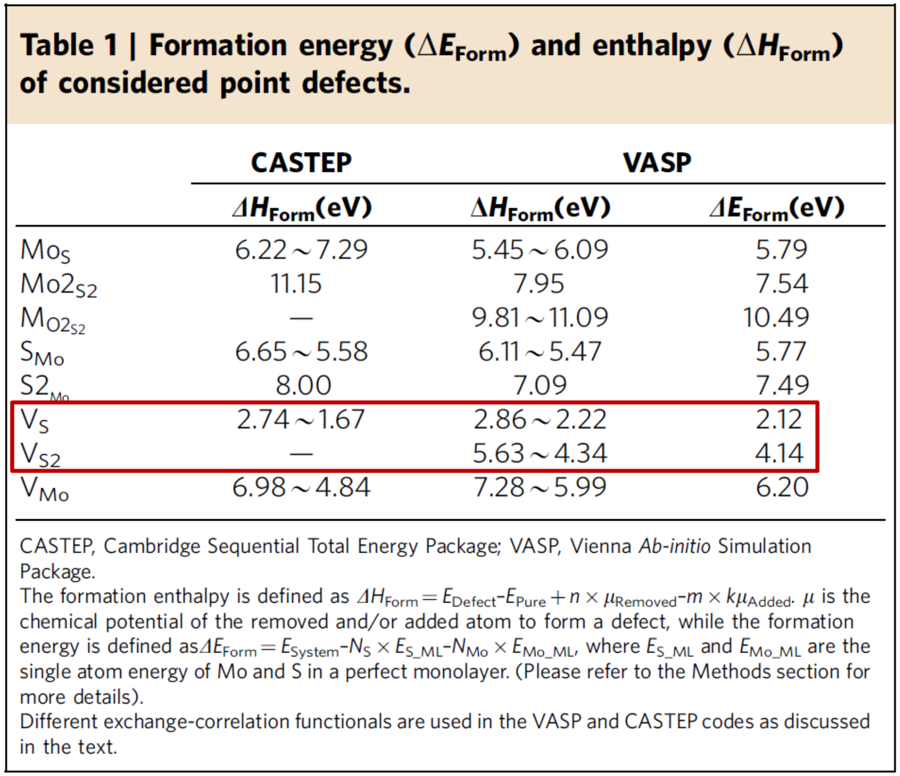
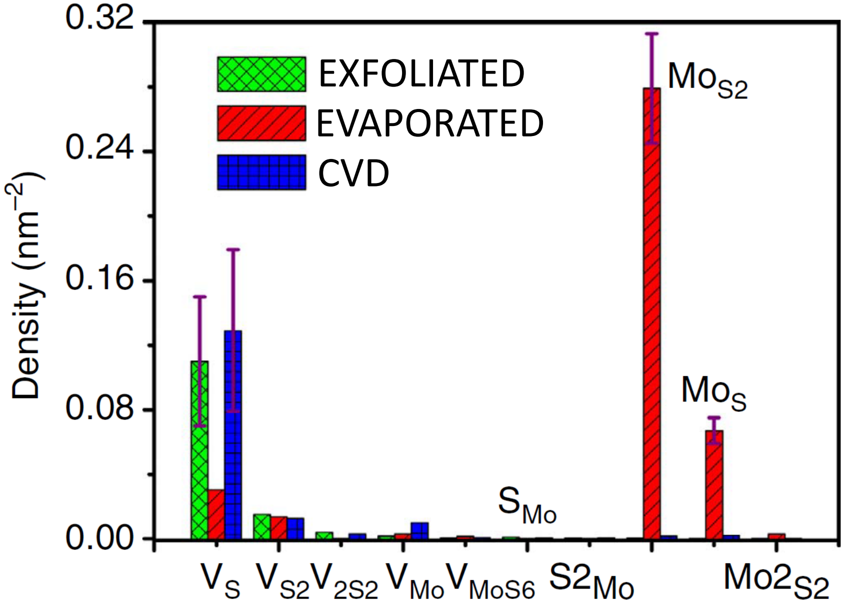


Table 1 | Formation energy (ΔE_{Form}) and enthalpy (ΔH_{Form}) of considered point defects.

	CASTEP	VASP	
	ΔH_{Form}(eV)	ΔH_{Form}(eV)	ΔE_{Form}(eV)
Mo_{S}	6.22 ~ 7.29	5.45 ~ 6.09	5.79
$\mathrm{Mo2}_{\mathrm{S2}}$	11.15	7.95	7.54
$\mathrm{Mo}_{\mathrm{2S2}}$	—	9.81 ~ 11.09	10.49
S_{Mo}	6.65 ~ 5.58	6.11 ~ 5.47	5.77
$\mathrm{S2}_{\mathrm{Mo}}$	8.00	7.09	7.49
V_{S}	2.74 ~ 1.67	2.86 ~ 2.22	2.12
V_{S2}	—	5.63 ~ 4.34	4.14
V_{Mo}	6.98 ~ 4.84	7.28 ~ 5.99	6.20

CASTEP, Cambridge Sequential Total Energy Package; VASP, Vienna *Ab-initio* Simulation Package.
The formation enthalpy is defined as $\Delta H_{\mathrm{Form}} = E_{\mathrm{Defect}} - E_{\mathrm{Pure}} + n \times \mu_{\mathrm{Removed}} - m \times k\mu_{\mathrm{Added}}$. μ is the chemical potential of the removed and/or added atom to form a defect, while the formation energy is defined as $\Delta E_{\mathrm{Form}} = E_{\mathrm{System}} - N_{\mathrm{S}} \times E_{\mathrm{S\_ML}} - N_{\mathrm{Mo}} \times E_{\mathrm{Mo\_ML}}$, where $E_{\mathrm{S\_ML}}$ and $E_{\mathrm{Mo\_ML}}$ are the single atom energy of Mo and S in a perfect monolayer. (Please refer to the Methods section for more details).
Different exchange-correlation functionals are used in the VASP and CASTEP codes as discussed in the text.



Defect concentration ~10^{13} cm^{-2} !

Hong et al., Nature Communications (2015)

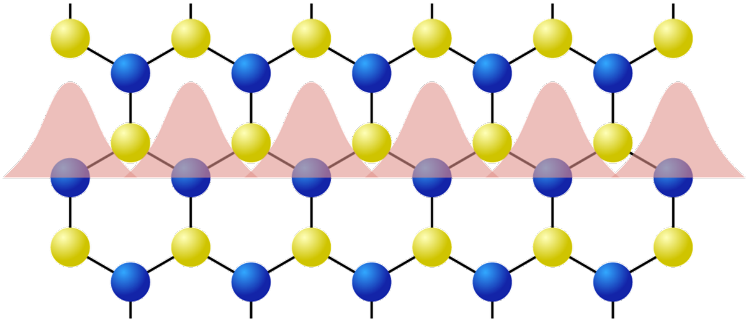
$$N_V = N_S e^{-(\Delta E_{Form}/k_B T)}$$

N_V	vacancy concentration
N_S	number of lattice sites
T	temperature
k_B	Boltzmann constant
ΔE_{Form}	defect formation energy

Transport in a disordered semiconductor

Perfect semiconductor:

- Delocalized charge carriers
- Band transport

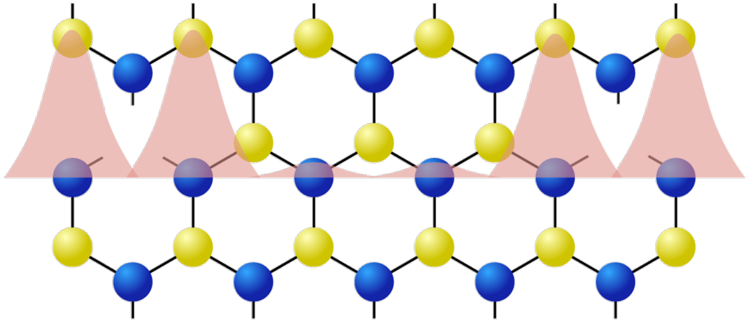


Electrical conductivity:

$$\sigma = \sigma_0 e^{-(E_A/k_B T)}$$

Disordered semiconductor:

- Trapped charges
- Localisation
- Hopping transport



$$\sigma = \sigma_0 e^{-(T_0/T)^{\beta}}$$

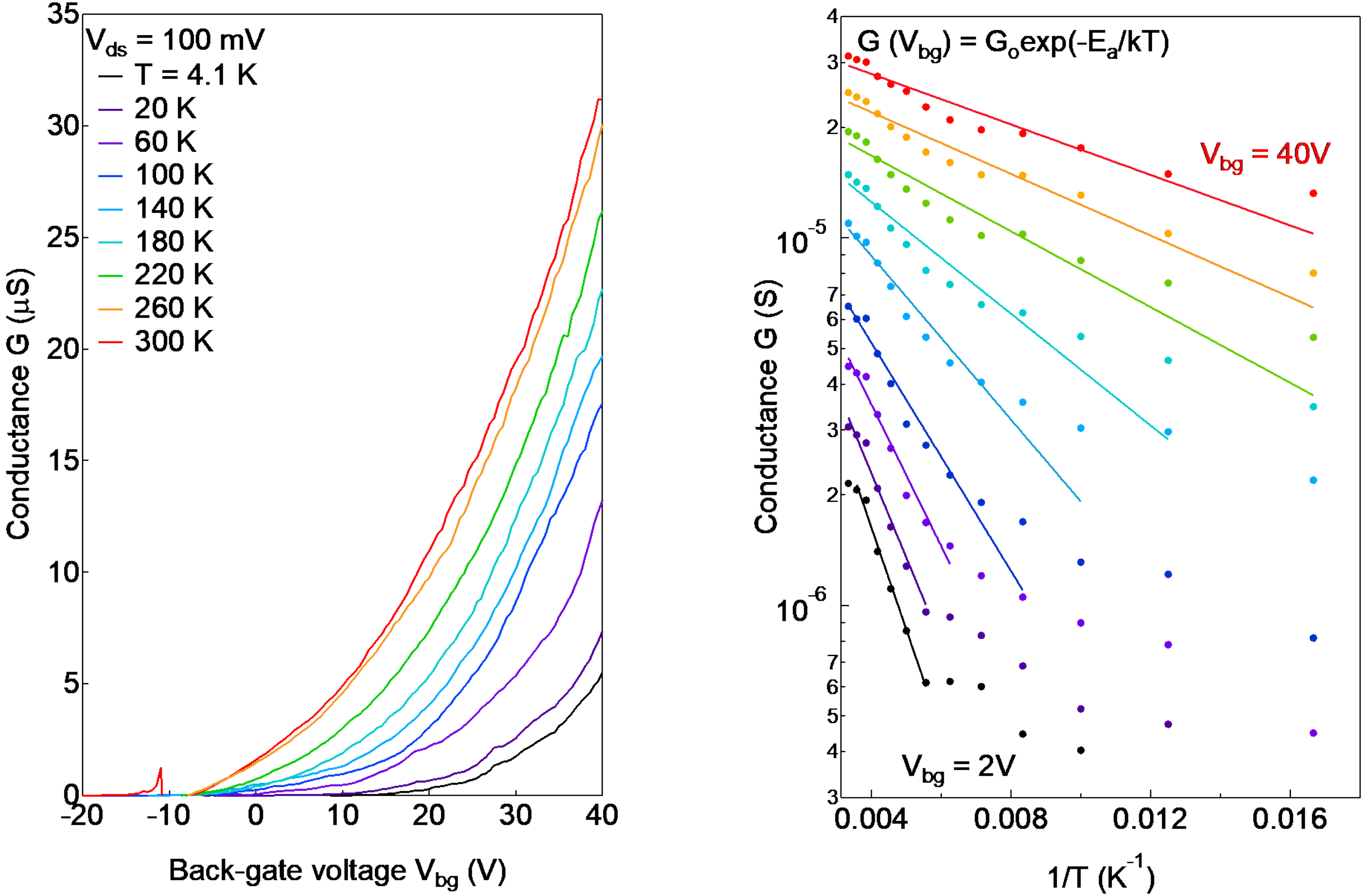
With four parameters I can fit an elephant, and with five I can make him wiggle his trunk.

- John von Neumann

σ	electrical conductivity
T	temperature
k_B	Boltzmann constant
E_A	activation energy
T_0, β	fitting parameters

Temperature-dependent electrical transport in MoS_2

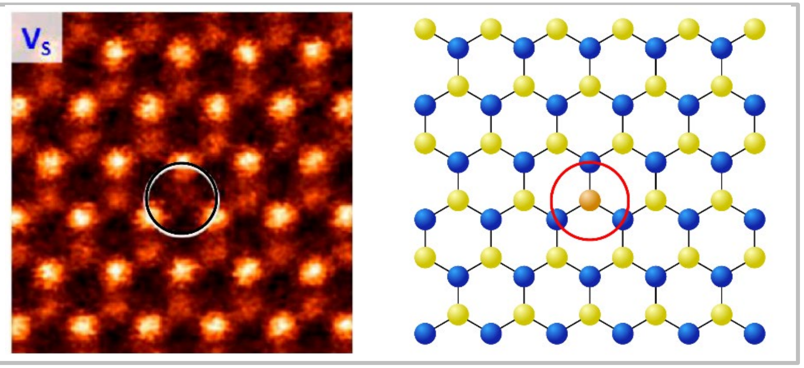
No top-gate dielectric



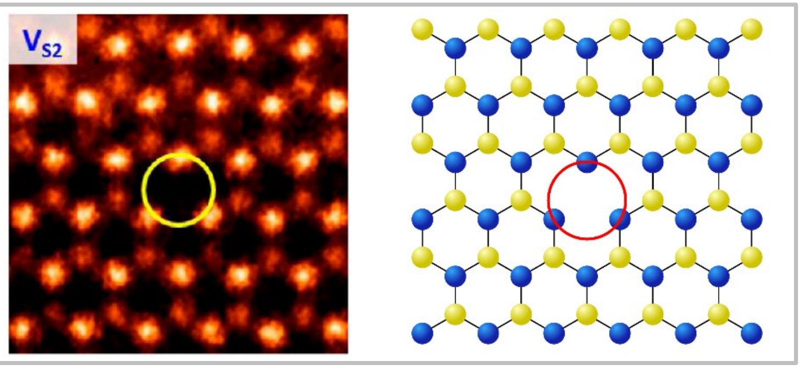
Radisavljevic and Kis; Nature Materials (2013)

Most common point defects in MoS_2

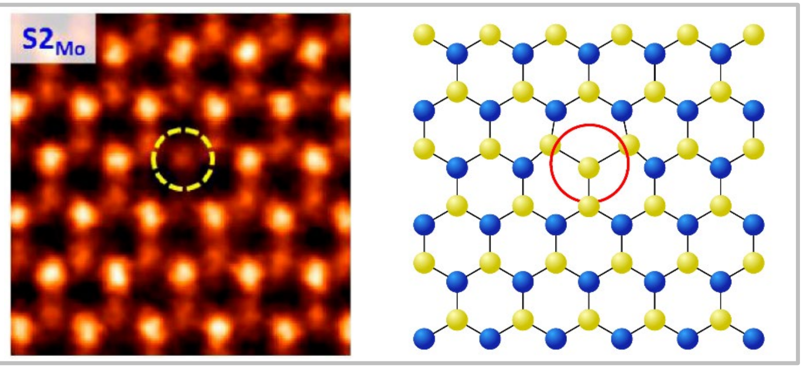
V_S



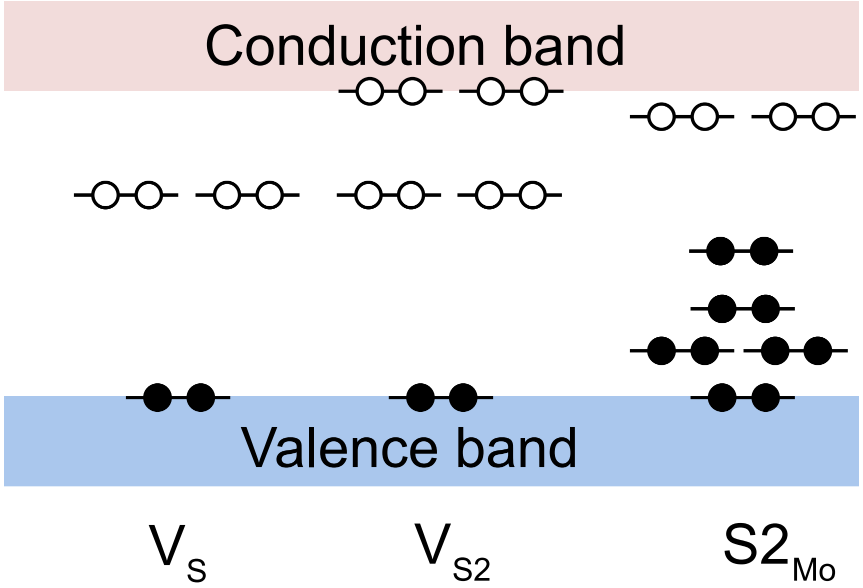
V_{S2}



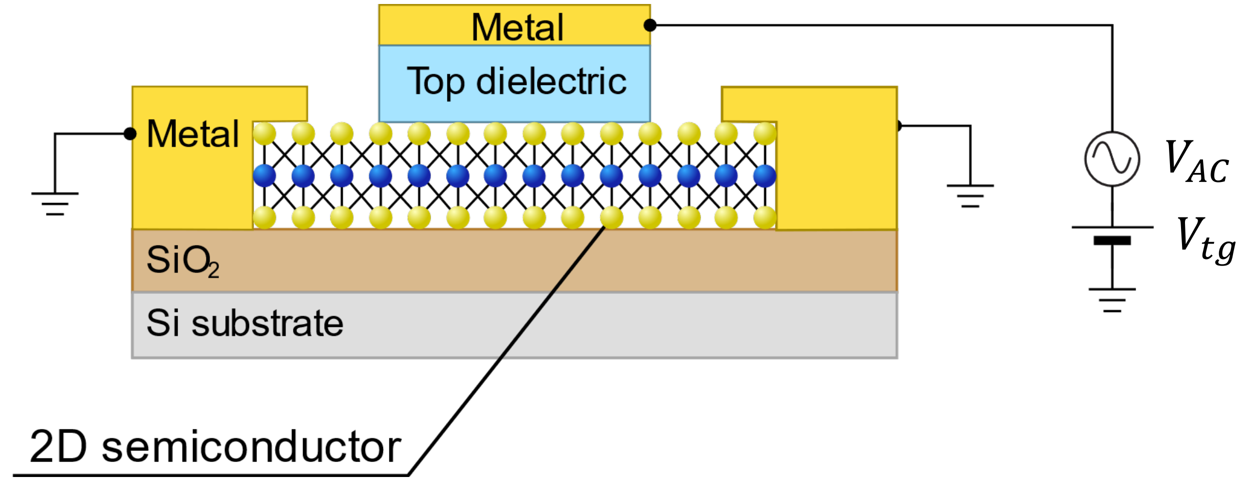
$S2_{Mo}$



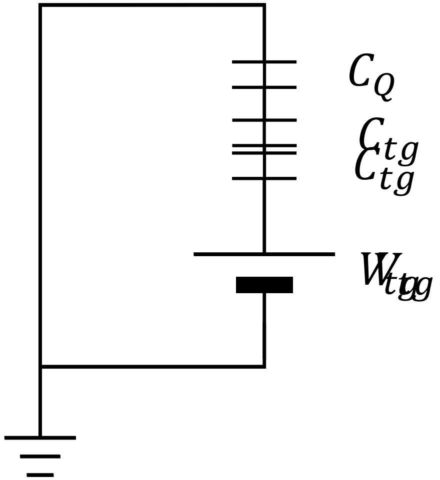
Zhou et al. Nano Letters (2013)



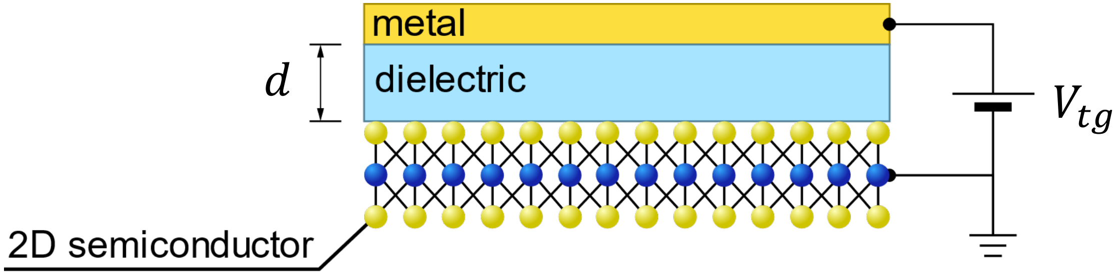
Quantum capacitance



Equivalent circuit



Equivalent device: capacitor with the 2D material as one of the electrodes



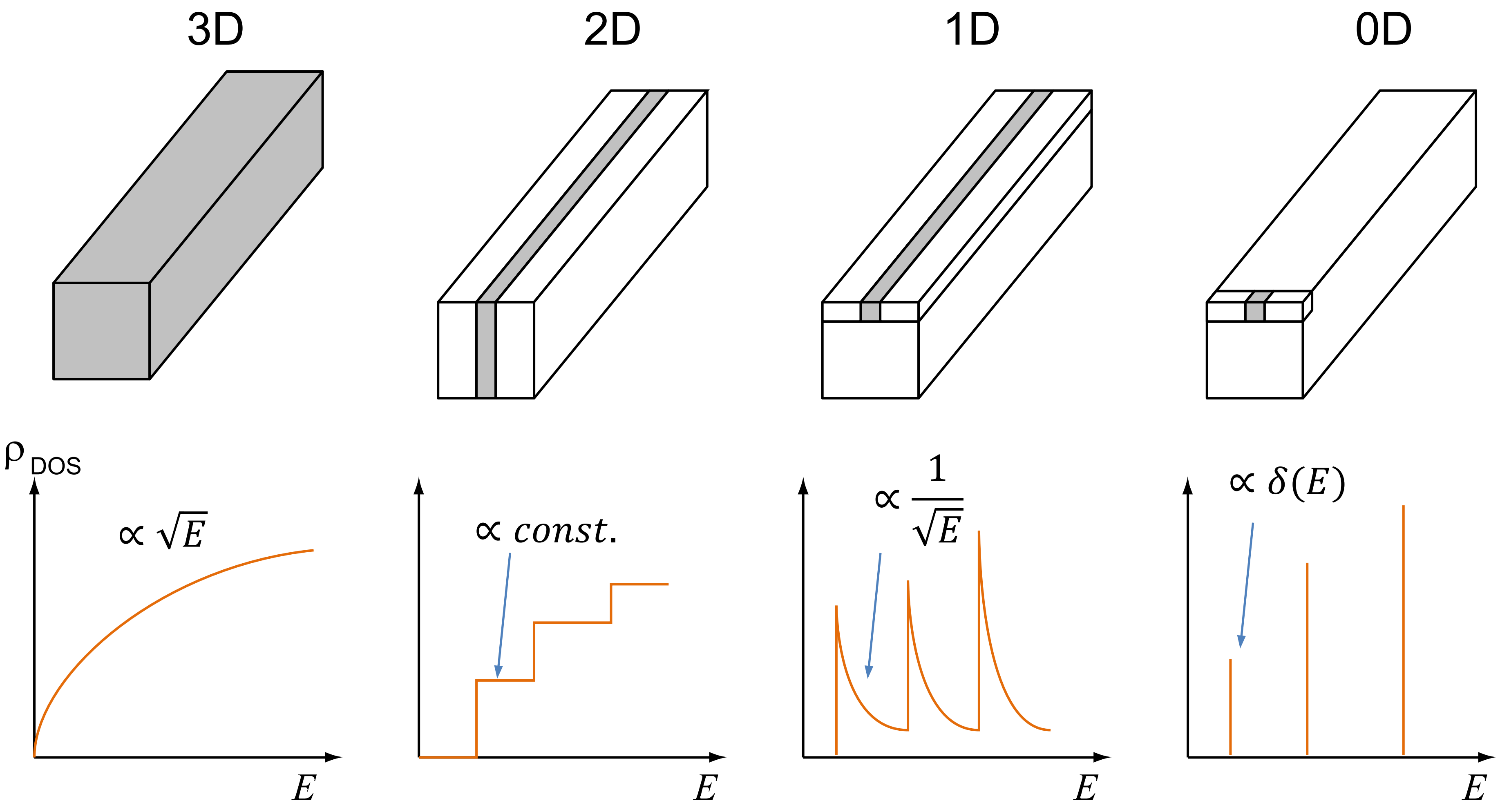
$C_{tg} = \frac{S\varepsilon}{d}$ Geometric capacitance

$C_Q = e^2 \cdot DOS$ quantum capacitance

For $C_{tg} \gg C_Q, C_Q$ dominates

$C_Q = \frac{2em^*}{\pi\hbar^2}$ for 2D inside the 1st subband

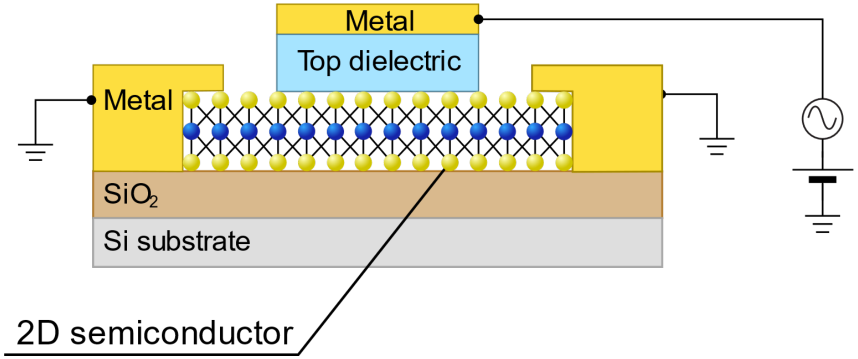
Repeated from 2.1: Dimensions in Semiconductor Physics

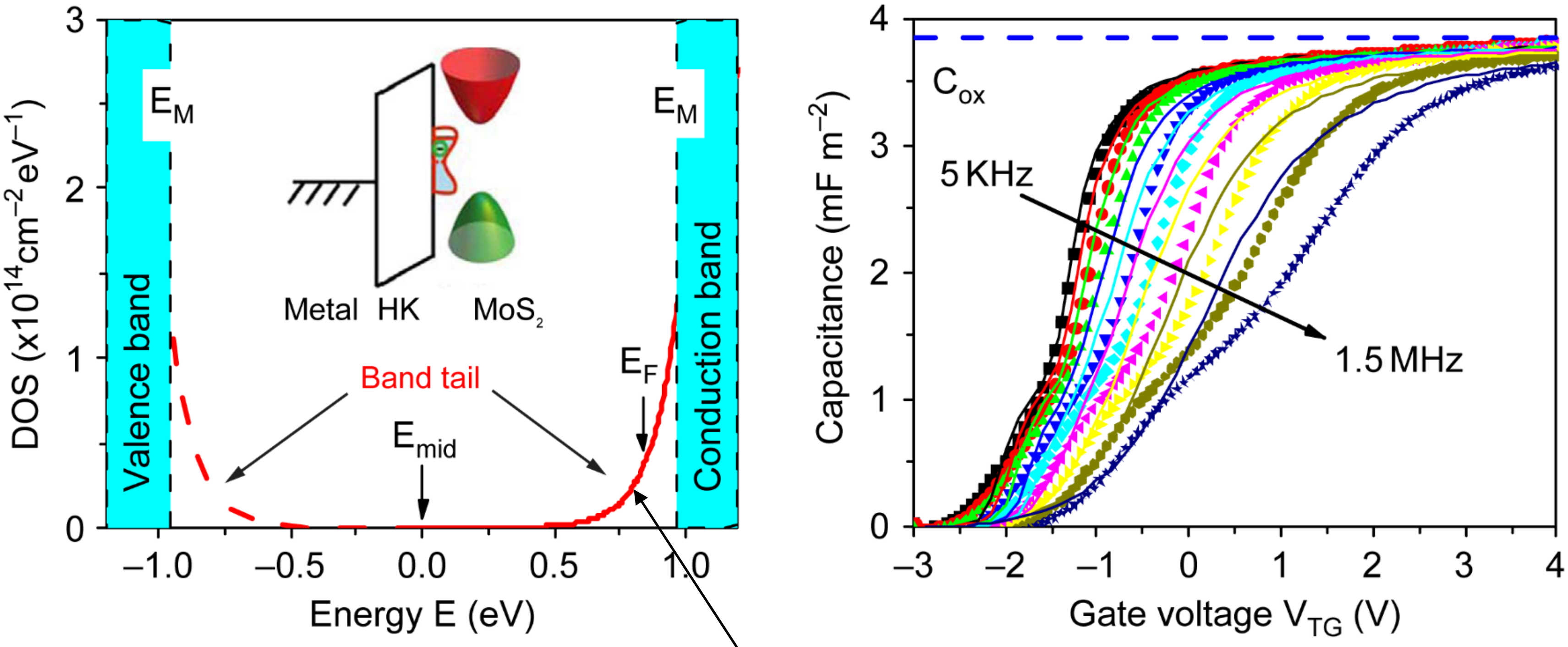


assuming $E = \frac{\hbar^2 k^2}{2m}$

→ **Exercise session today**

Capacitance - voltage measurements



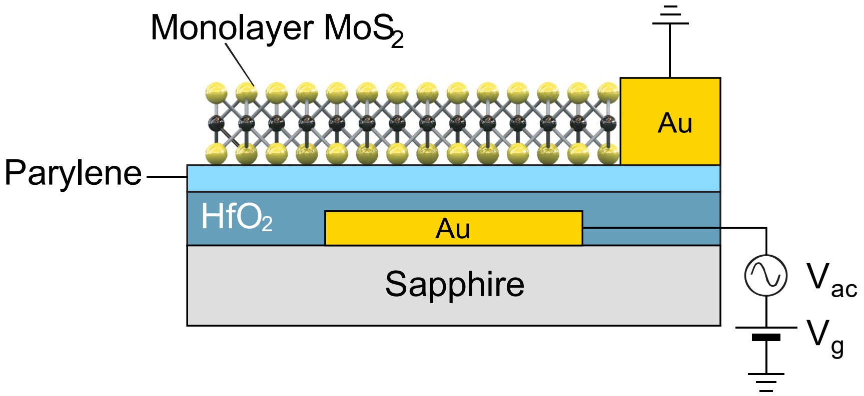


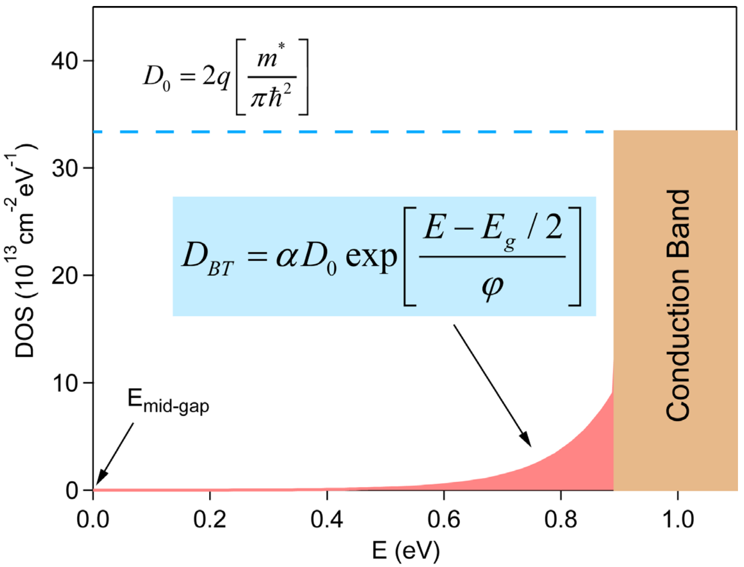
Zhu et al., Nature Communications (2014)

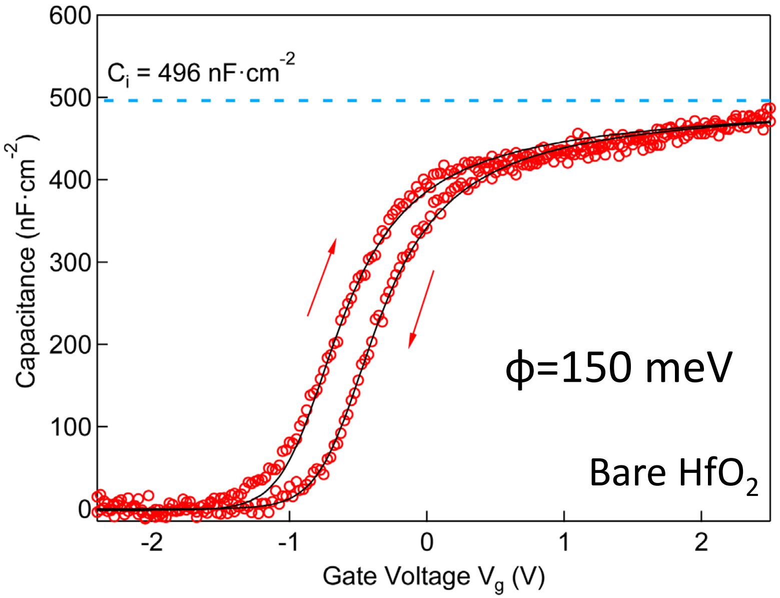
$$D_{BT} = \alpha D_0 \exp\left[\frac{E - E_g/2}{\varphi}\right]$$

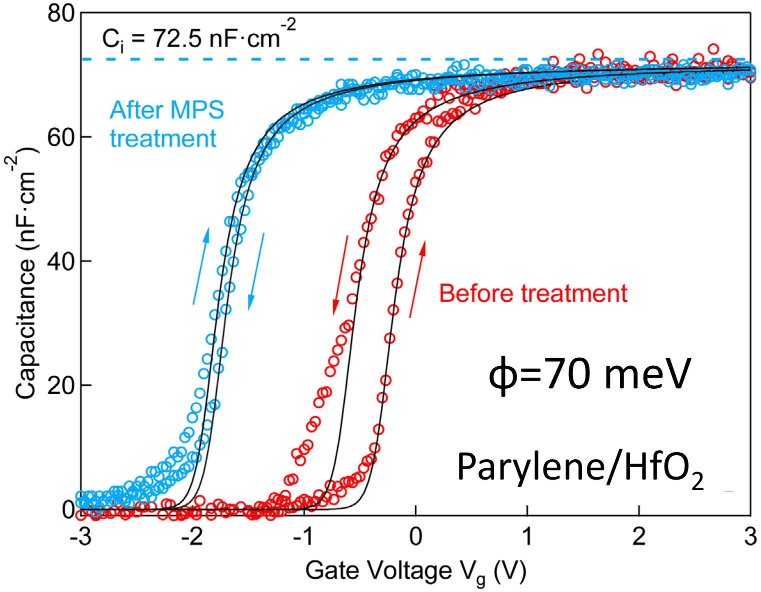
$$\boxed{\varphi \approx 100 \text{ meV}}$$

CV measurements



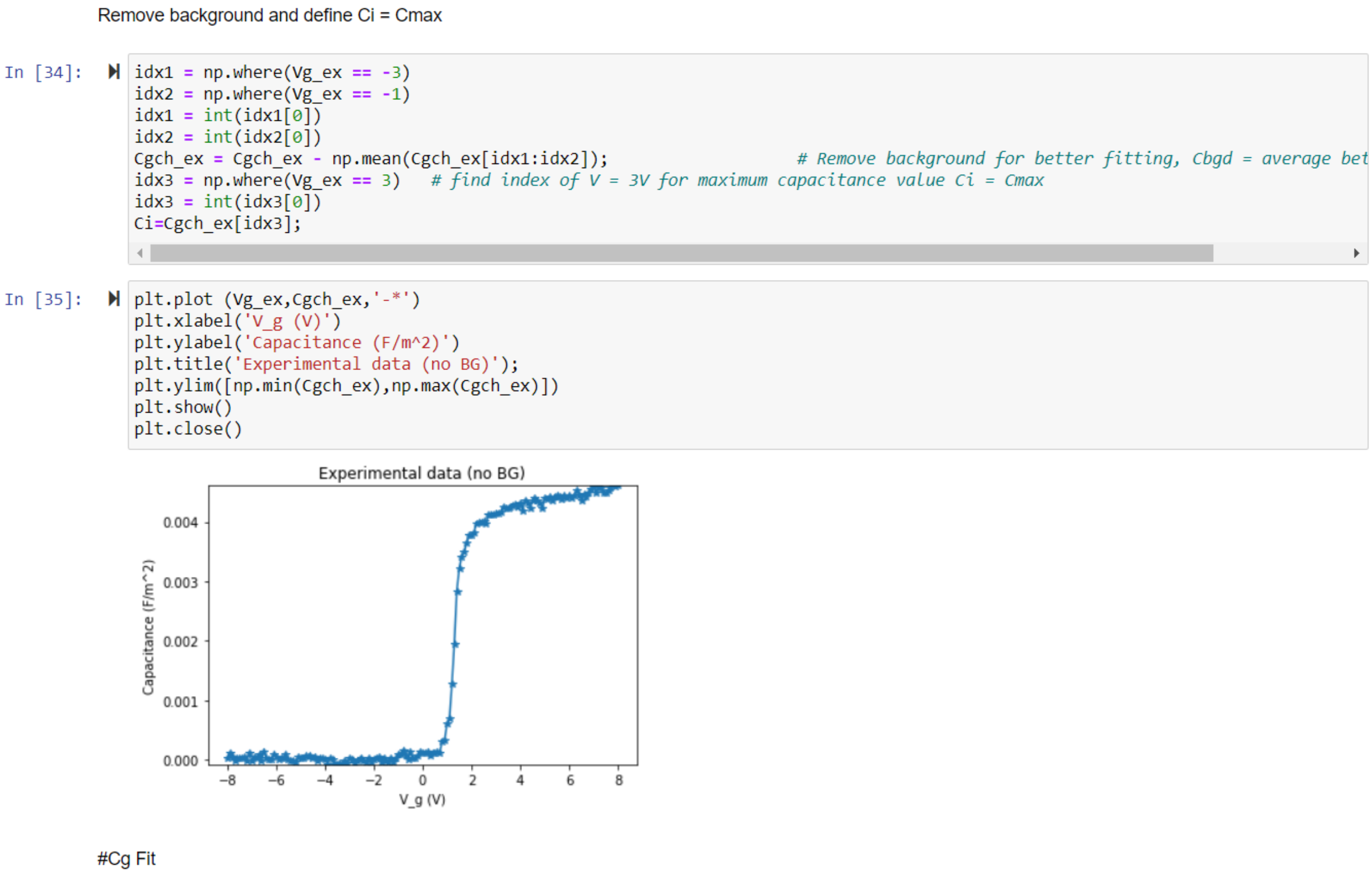






CV measurements – parameter extraction

→ Exercise session later today



Remove background and define Ci = Cmax

In [34]:

```
idx1 = np.where(Vg_ex == -3)
idx2 = np.where(Vg_ex == -1)
idx1 = int(idx1[0])
idx2 = int(idx2[0])
Cgch_ex = Cgch_ex - np.mean(Cgch_ex[idx1:idx2]);                    # Remove background for better fitting, Cbgd = average bet
idx3 = np.where(Vg_ex == 3)    # find index of V = 3V for maximum capacitance value Ci = Cmax
idx3 = int(idx3[0])
Ci=Cgch_ex[idx3];
```

In [35]:

```
plt.plot (Vg_ex,Cgch_ex,'-*')
plt.xlabel('V_g (V)')
plt.ylabel('Capacitance (F/m^2)')
plt.title('Experimental data (no BG)');
plt.ylim([np.min(Cgch_ex),np.max(Cgch_ex)])
plt.show()
plt.close()
```

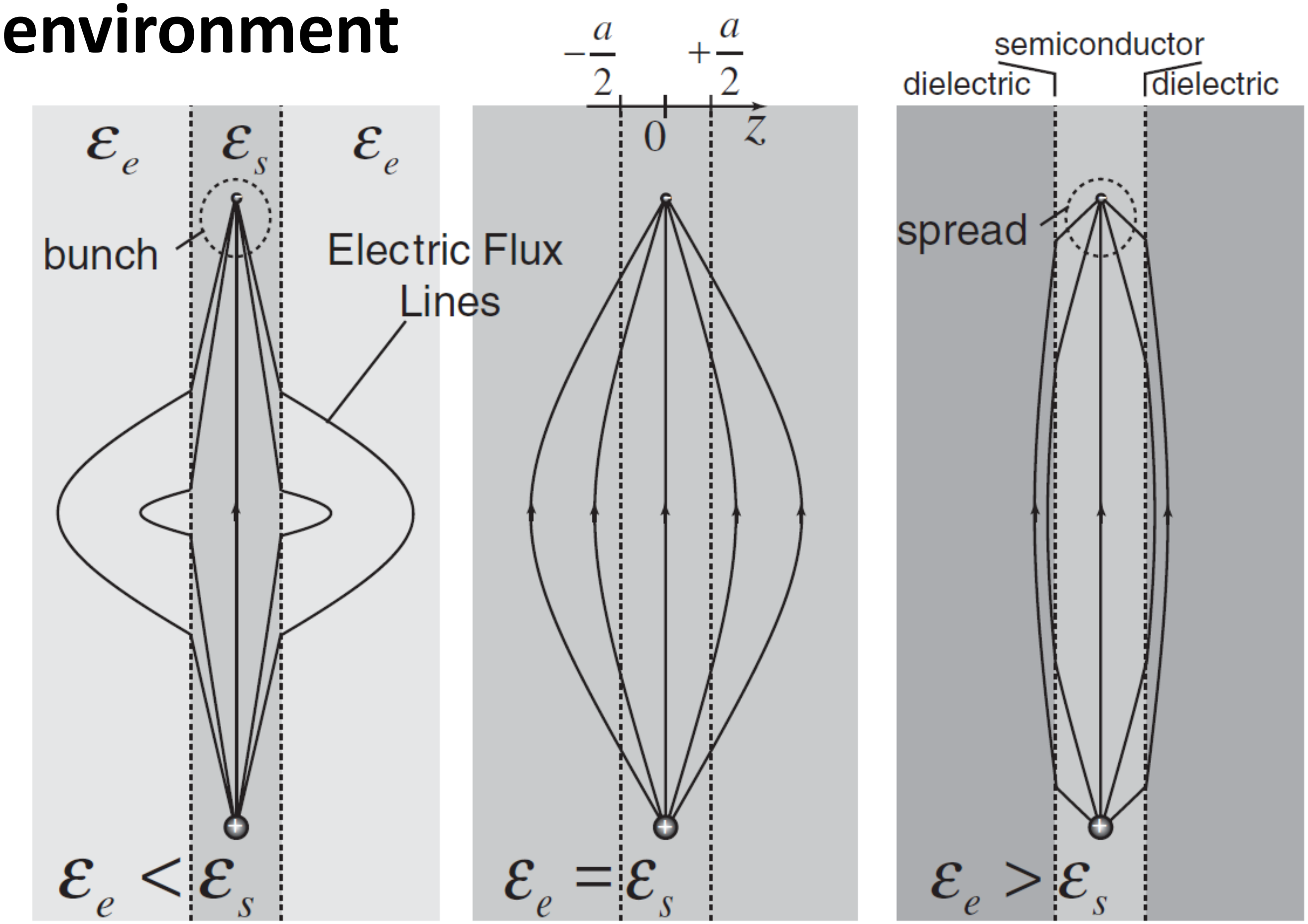
#Cg Fit

Mitigation strategies - overview

Various strategies for reducing the impact of point defects:

- Dielectric environment (encapsulation)
- Chemical treatment

Dielectric environment



Enhanced Coulomb interaction

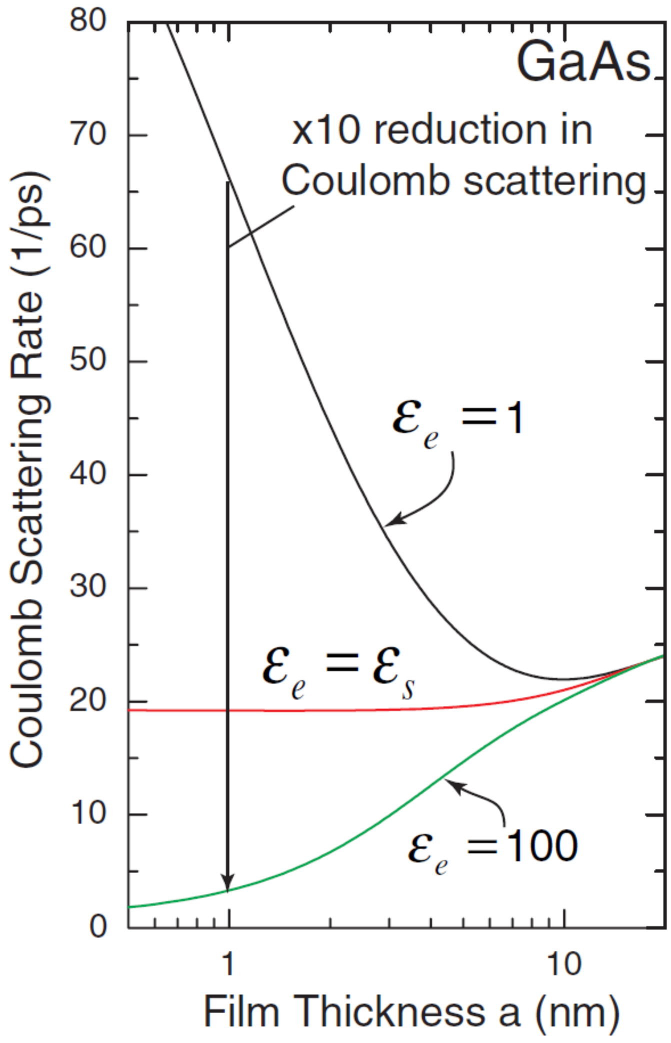
initial

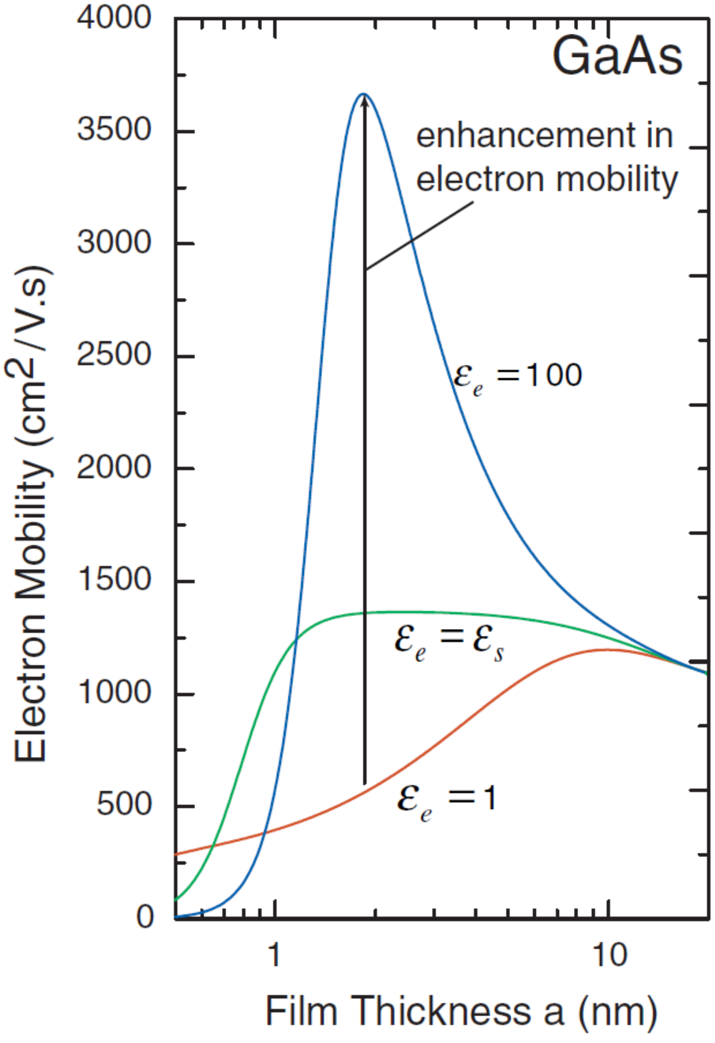
Dampened Coulomb interaction

FIG. 1. Electric flux lines originating from a fixed ionized impurity and terminating on a mobile electron, and the effect of the dielectric environment. The flux lines bunch closer inside the semiconductor layer if $\epsilon_e < \epsilon_s$, and spread farther apart if $\epsilon_e < \epsilon_s$, thus enhancing Coulomb interaction in the former case and damping it in the latter.

Jena and Konar, PRL 98, 136805 (2007)

Dielectric environment

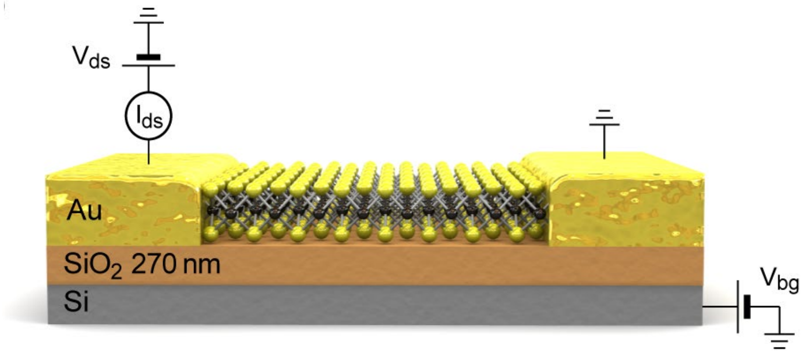


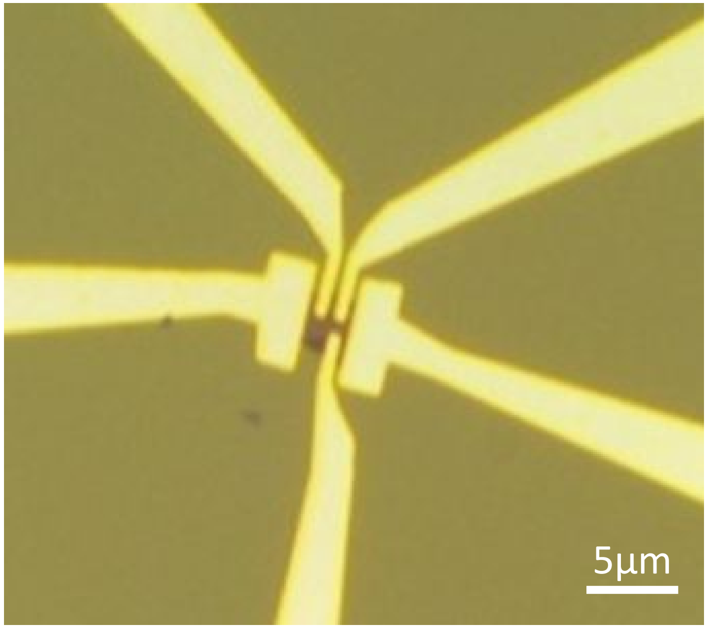


Jena and Konar, PRL 98, 136805 (2007)

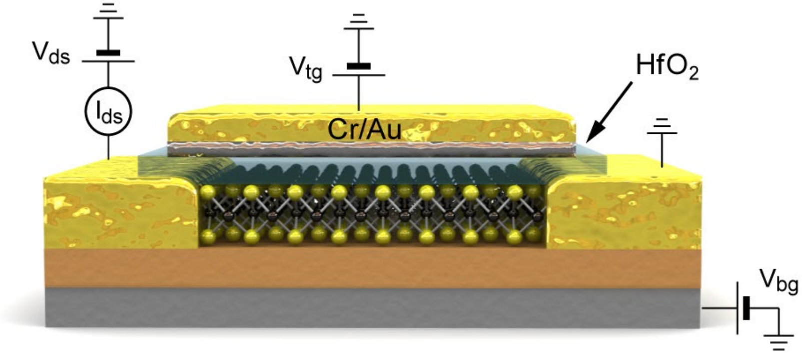
Temperature-dependent electrical transport

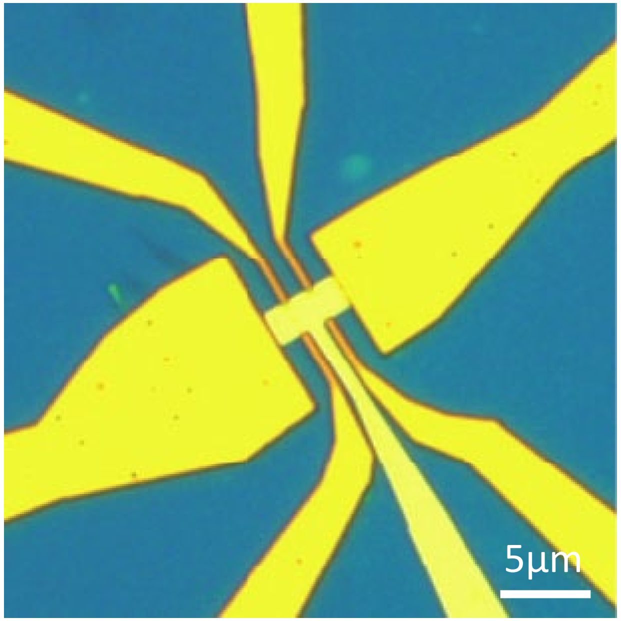
No top-gate dielectric





With top-gate dielectric

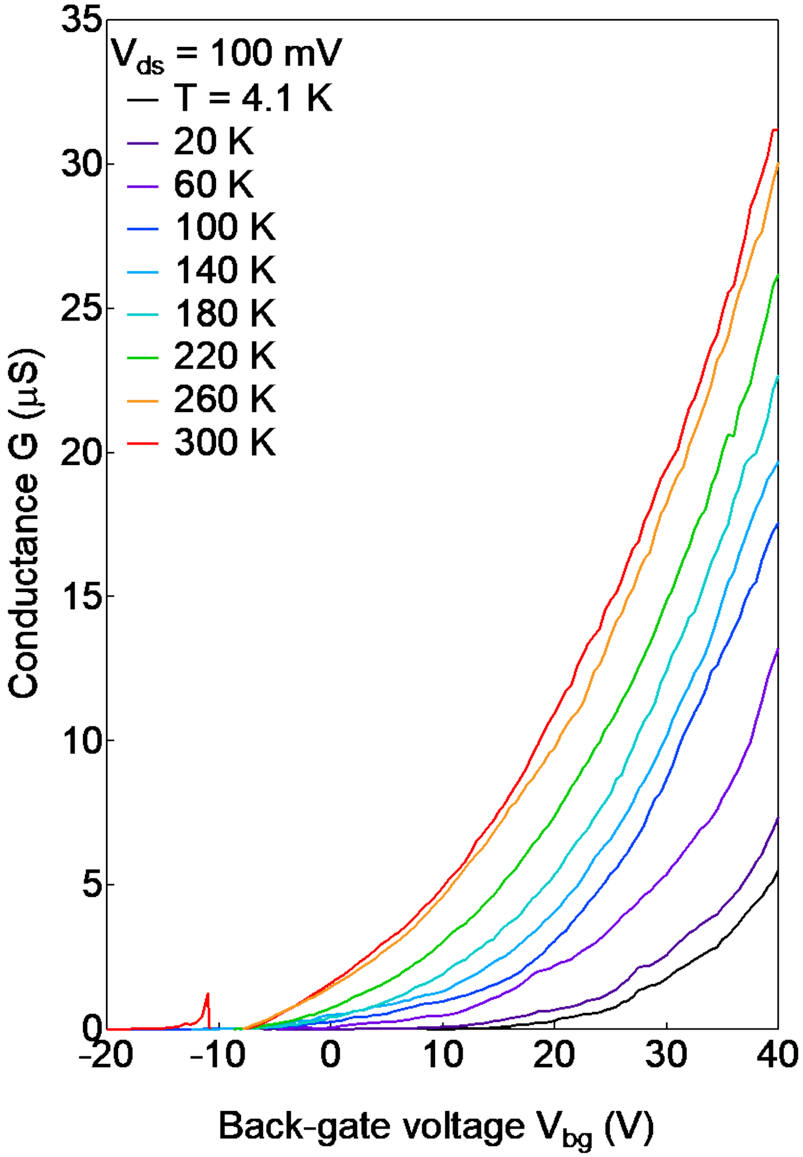




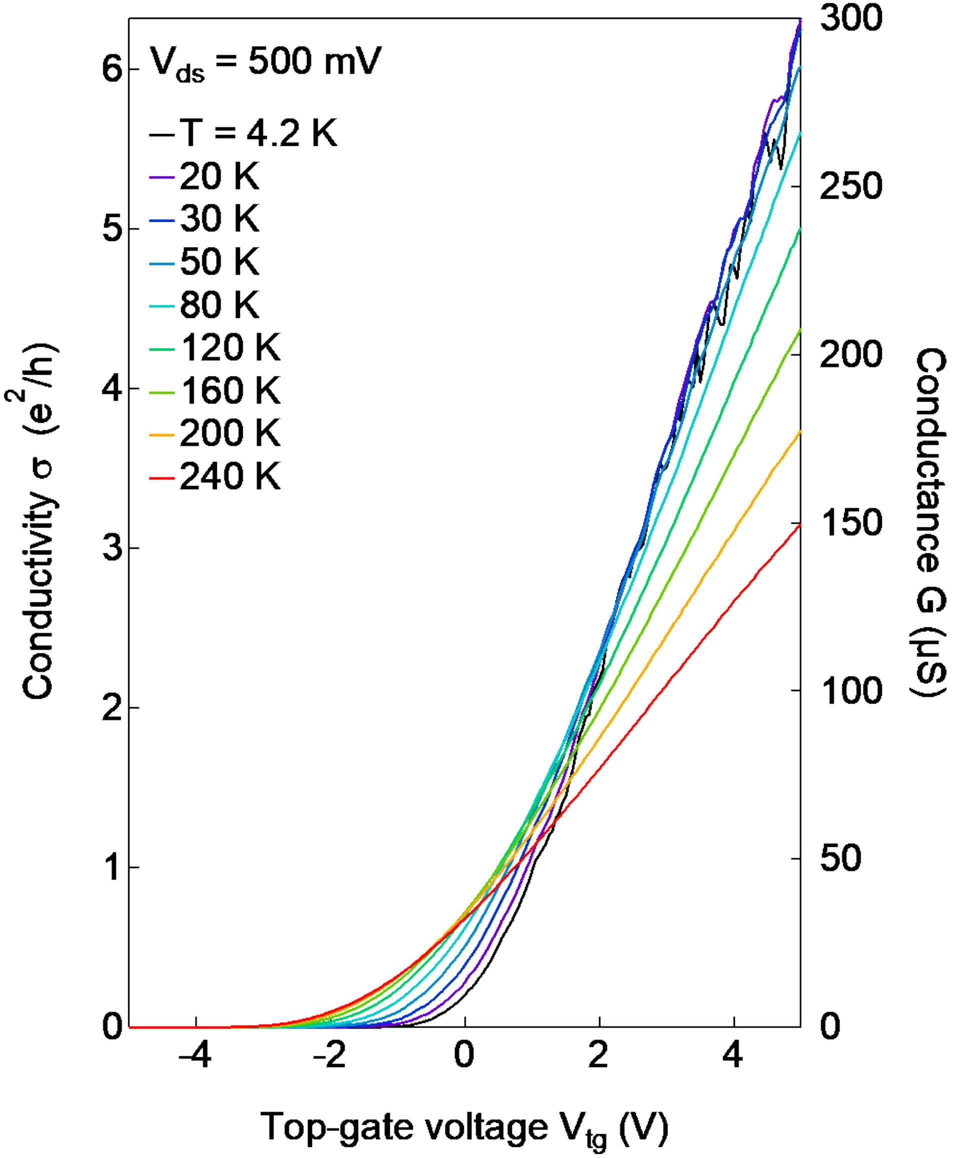
Radisavljevic and Kis; Nature Materials (2013)

Temperature-dependent electrical transport

No top-gate dielectric



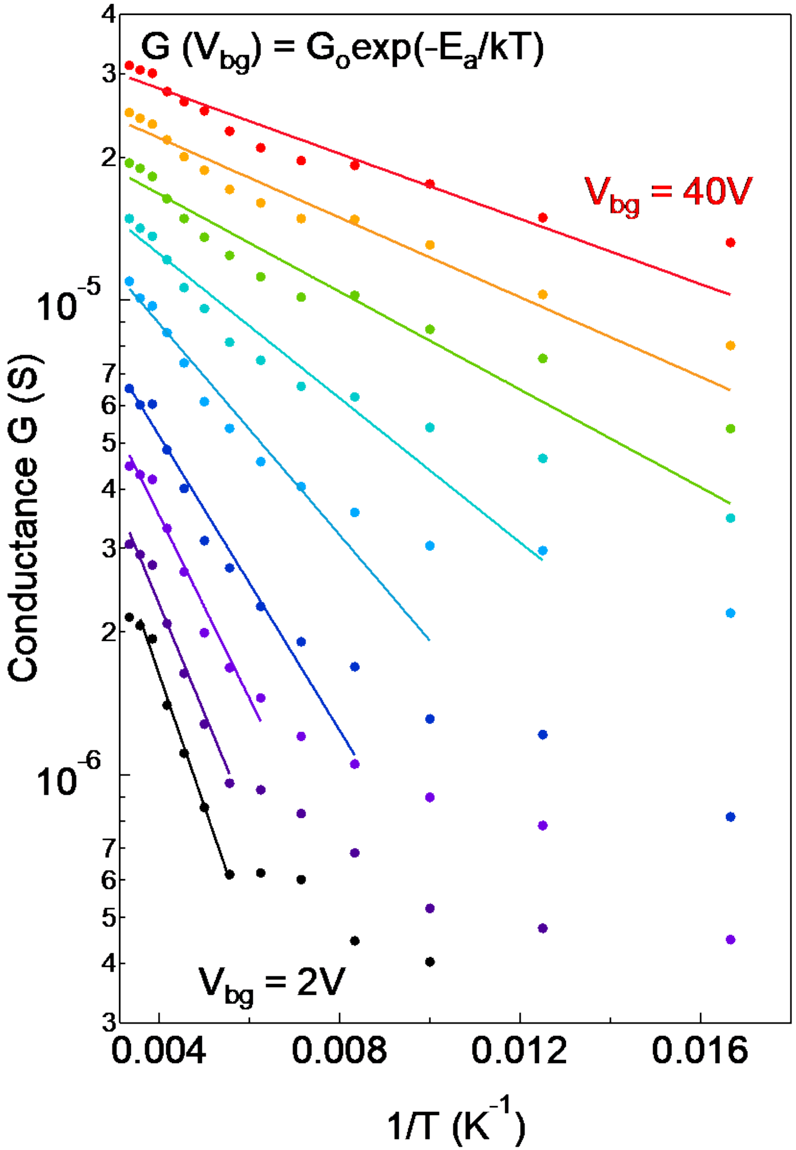
With top-gate dielectric



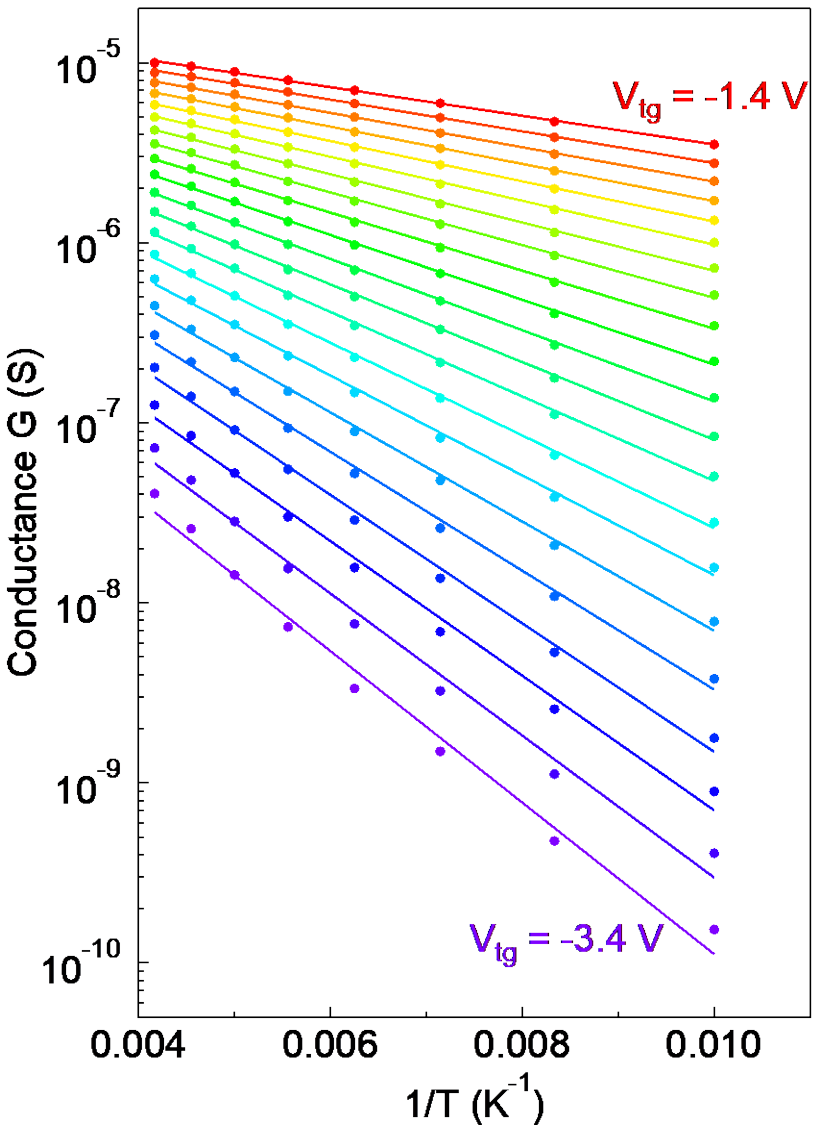
Radisavljevic and Kis; Nature Materials (2013)

Temperature-dependent electrical transport

No top-gate dielectric

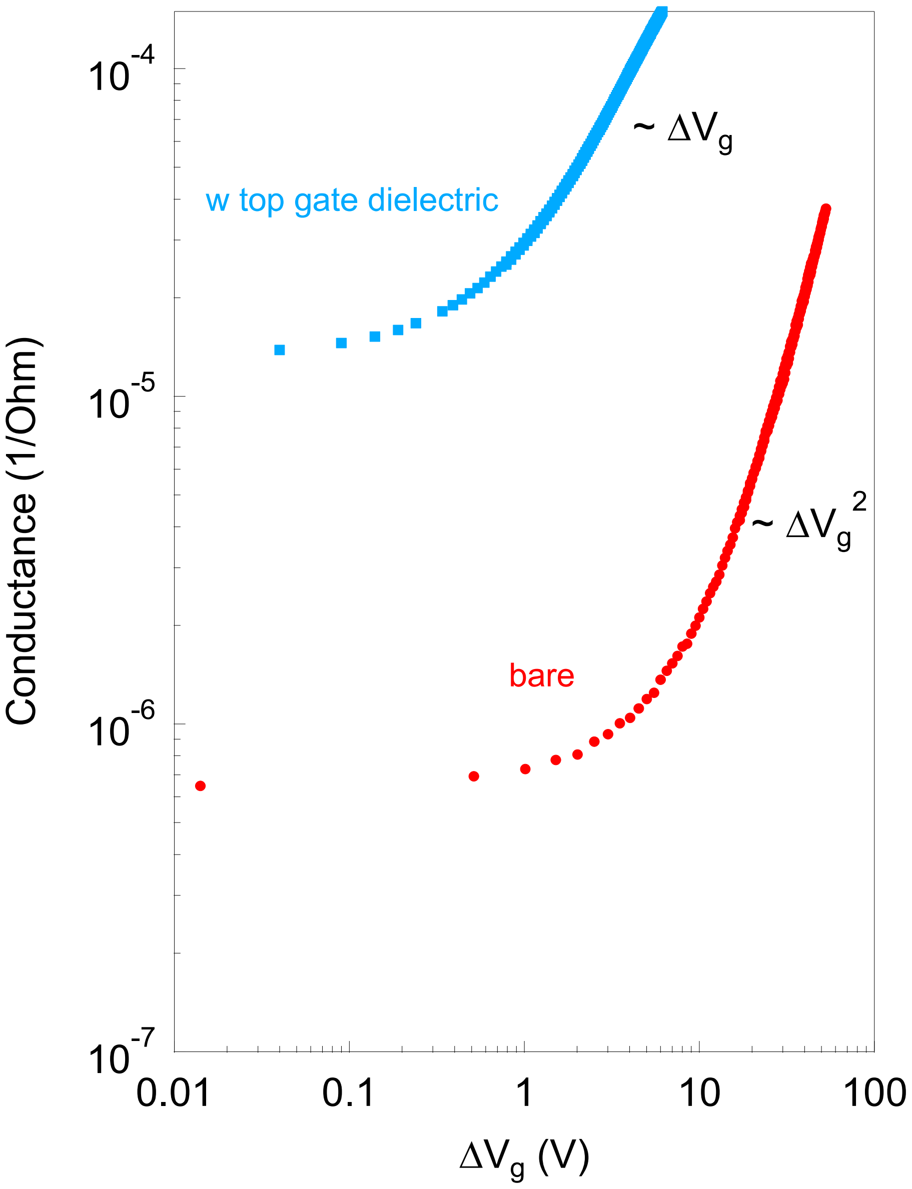


With top-gate dielectric



Radisavljevic and Kis; Nature Materials (2013)

Screened vs. unscreened disorder potential



S. Adam and D. Sarma., PRB (2008):

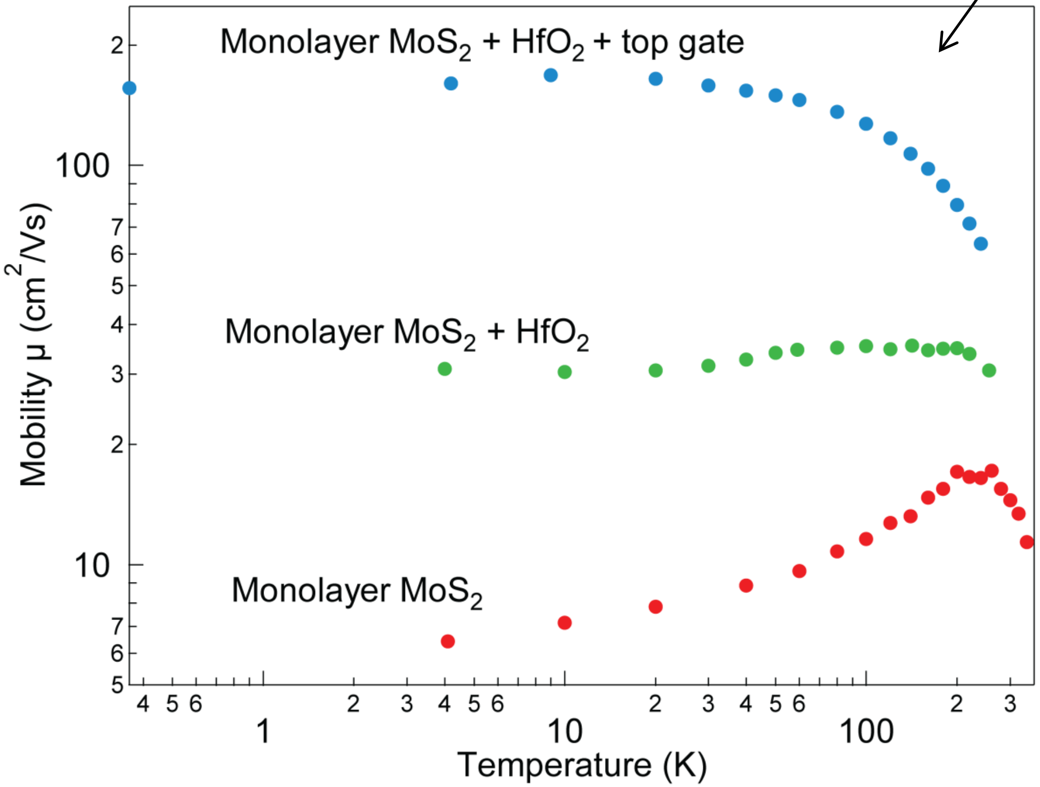
$\sigma \sim n$ screened ch. impurities

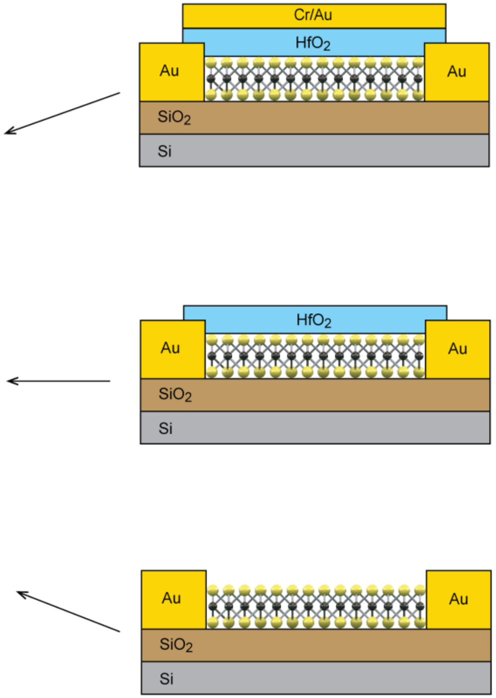
$\sigma \sim n^2$ unscreened

Mobility vs. temperature

Radisavljevic and Kis; Nature Materials (2013)

$\mu \sim T^{-\gamma}$





$\gamma = 0.73$

$\gamma = 1.4$

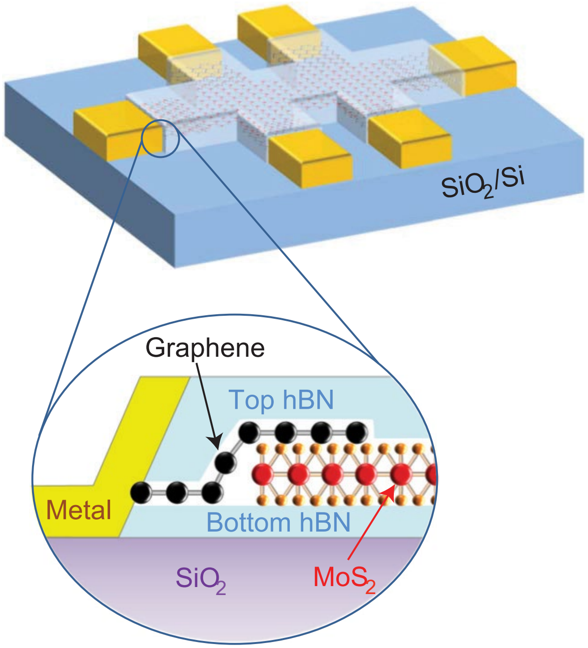
Bulk $\gamma = 2.6$

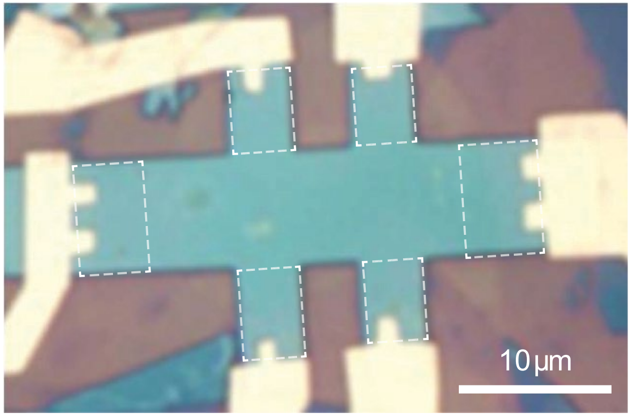
Calculations:

HP mode quenching	$\gamma = 1.5$	Kaasbjerg et al., PRB (2012)
HP mode quenching	$\gamma = 1$	Kaasbjerg et al., PRB (2013)
HP mode quenching	$\gamma = 0.5$	Ong and Fischetti, PRB (2013)

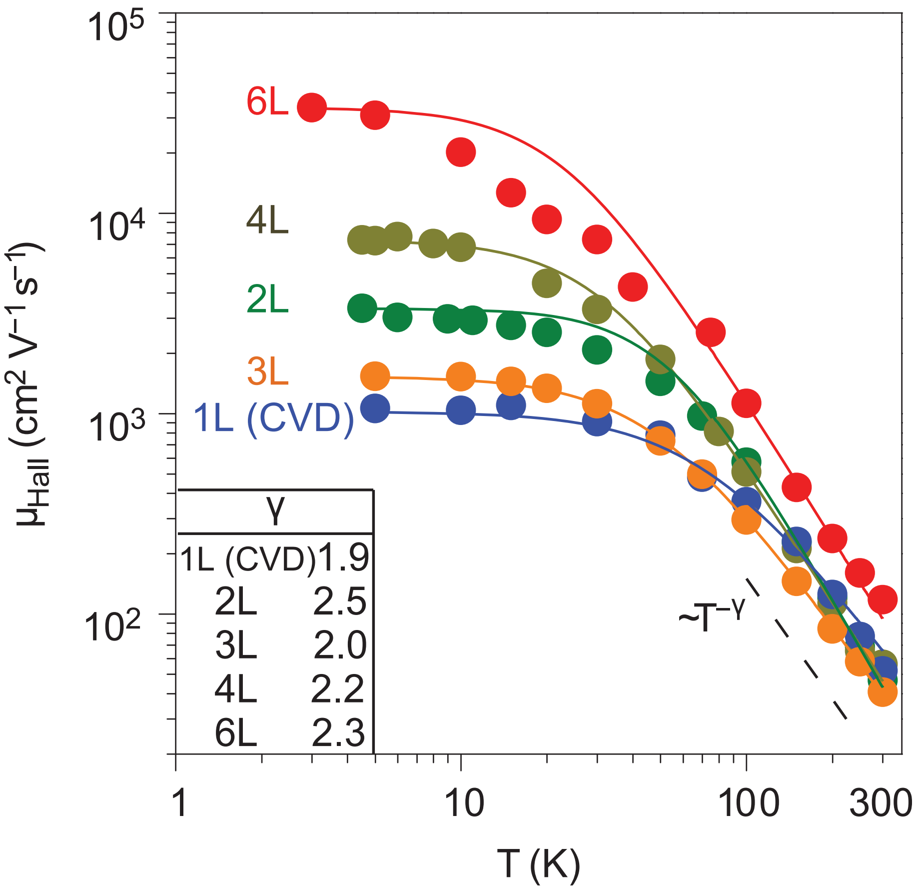
T dep. of screening and CI scattering, TG screening

Encapsulation in Boron Nitride



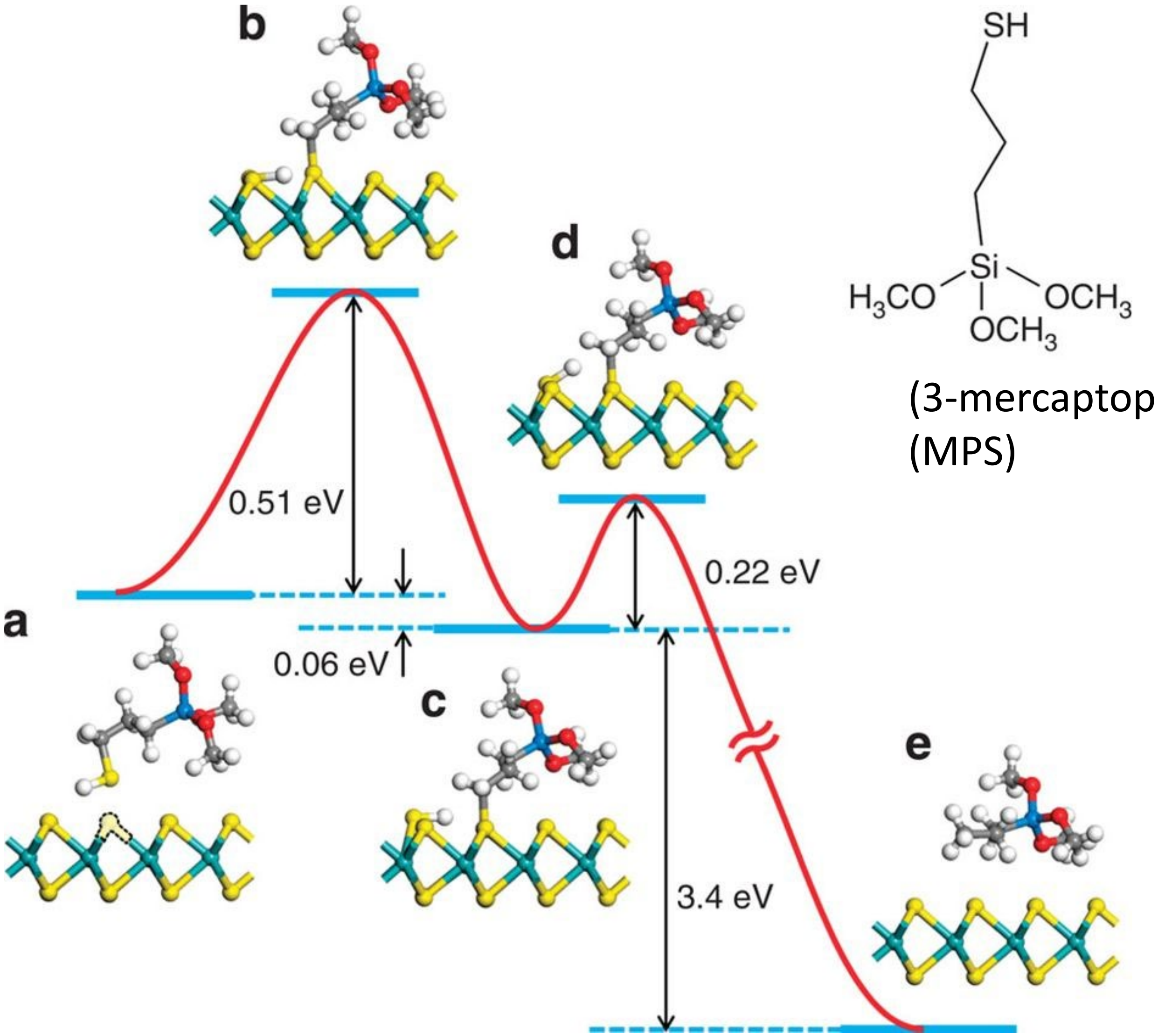


Cui…Hone; Nat. Nano (2015)



	γ
1L (CVD)	1.9
2L	2.5
3L	2.0
4L	2.2
6L	2.3

Defect healing by chemical treatment: thiols



(3-mercaptopropyl)trimethoxysilane
(MPS)

Yu et al, Nature Communications (2014)

Defect healing by chemical treatment: thiols

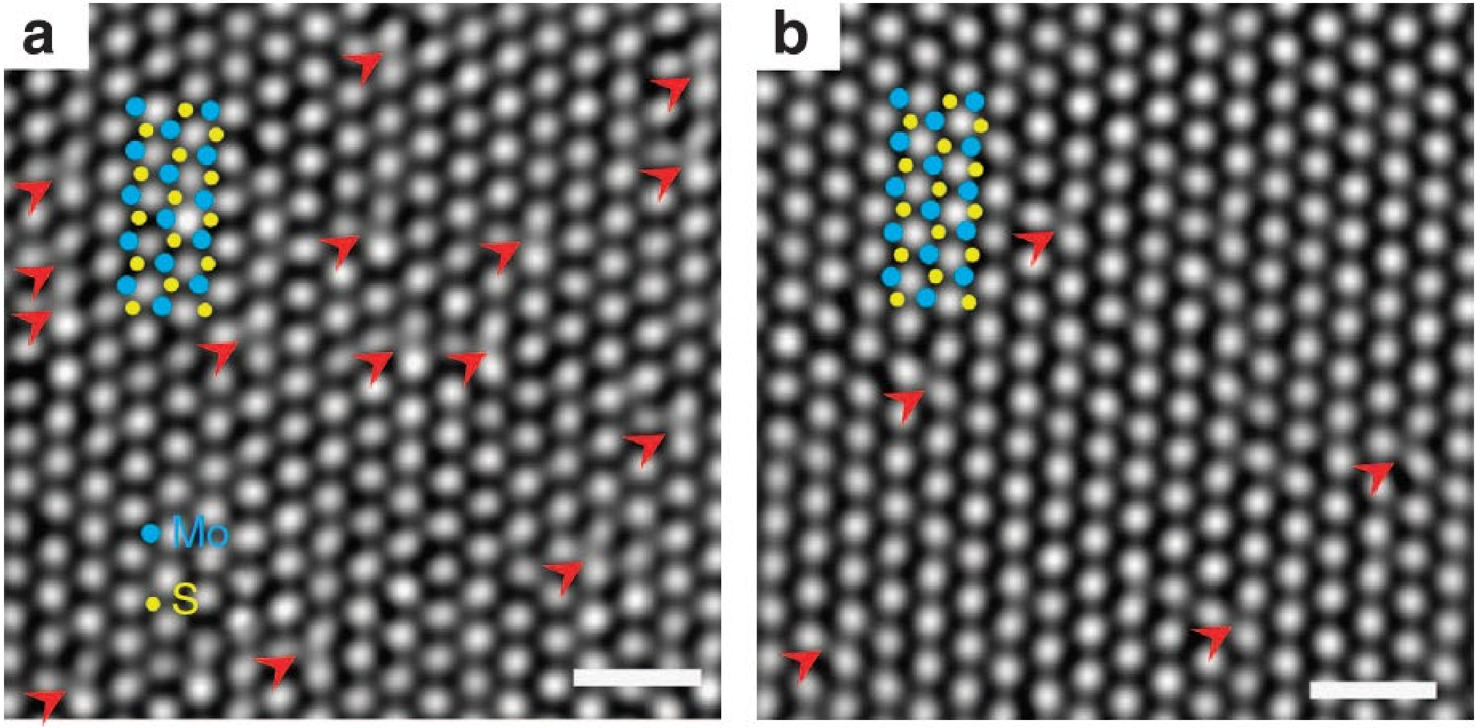
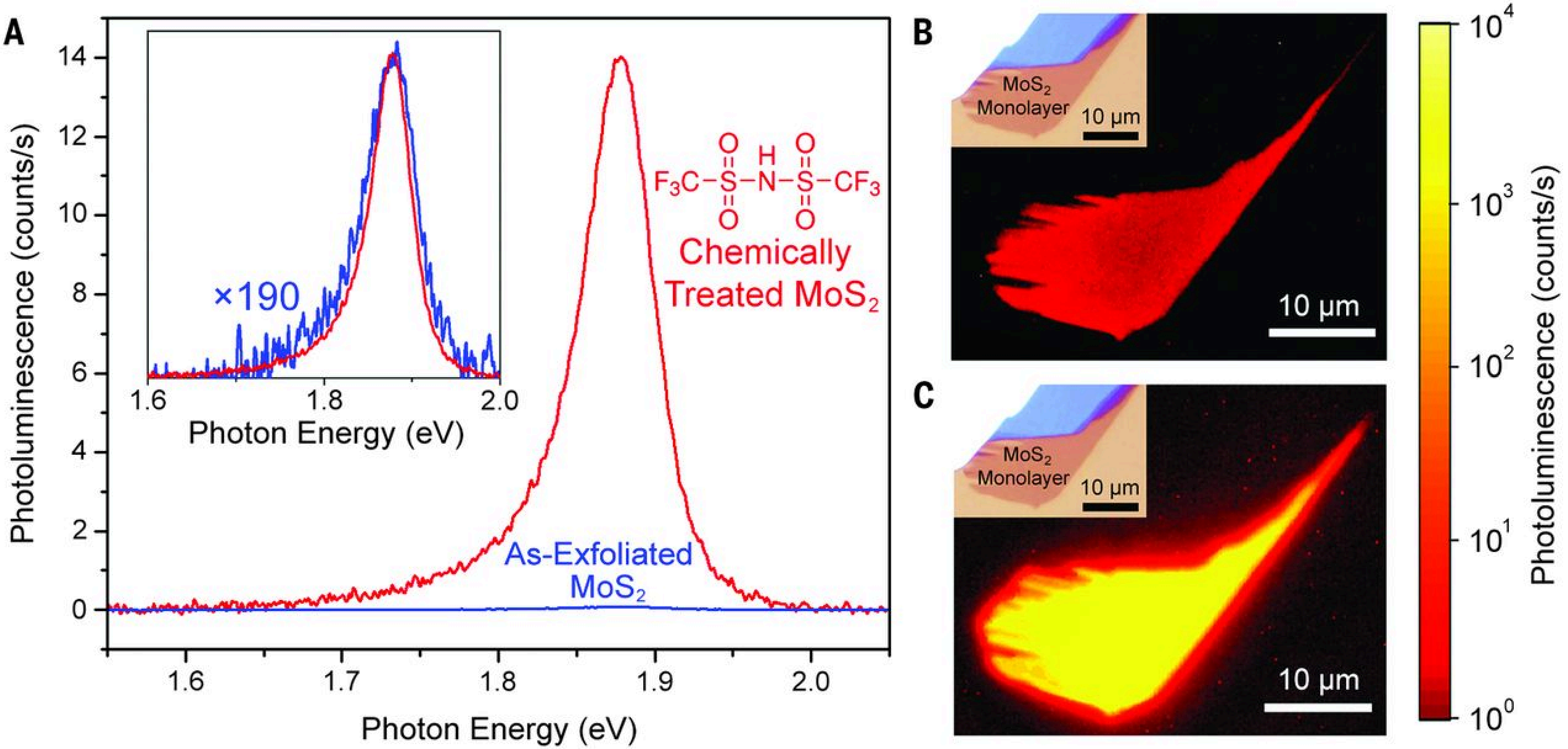


Figure 2 | High-resolution aberration-corrected TEM images.
(**a**) As-exfoliated and (**b**) TS-treated monolayer MoS_2 sample, showing the significant reduction of SV by MPS treatment. The SVs are highlighted by red arrows. The overlaid blue and yellow symbols mark the position of Mo and S atoms, respectively. Scale bar, 1 nm. Detailed intensity profile analysis and histogram of SV density are shown in Supplementary Fig. 9.

Yu et al, Nature Communications (2014)

Defect healing by chemical treatment: TFSI superacid

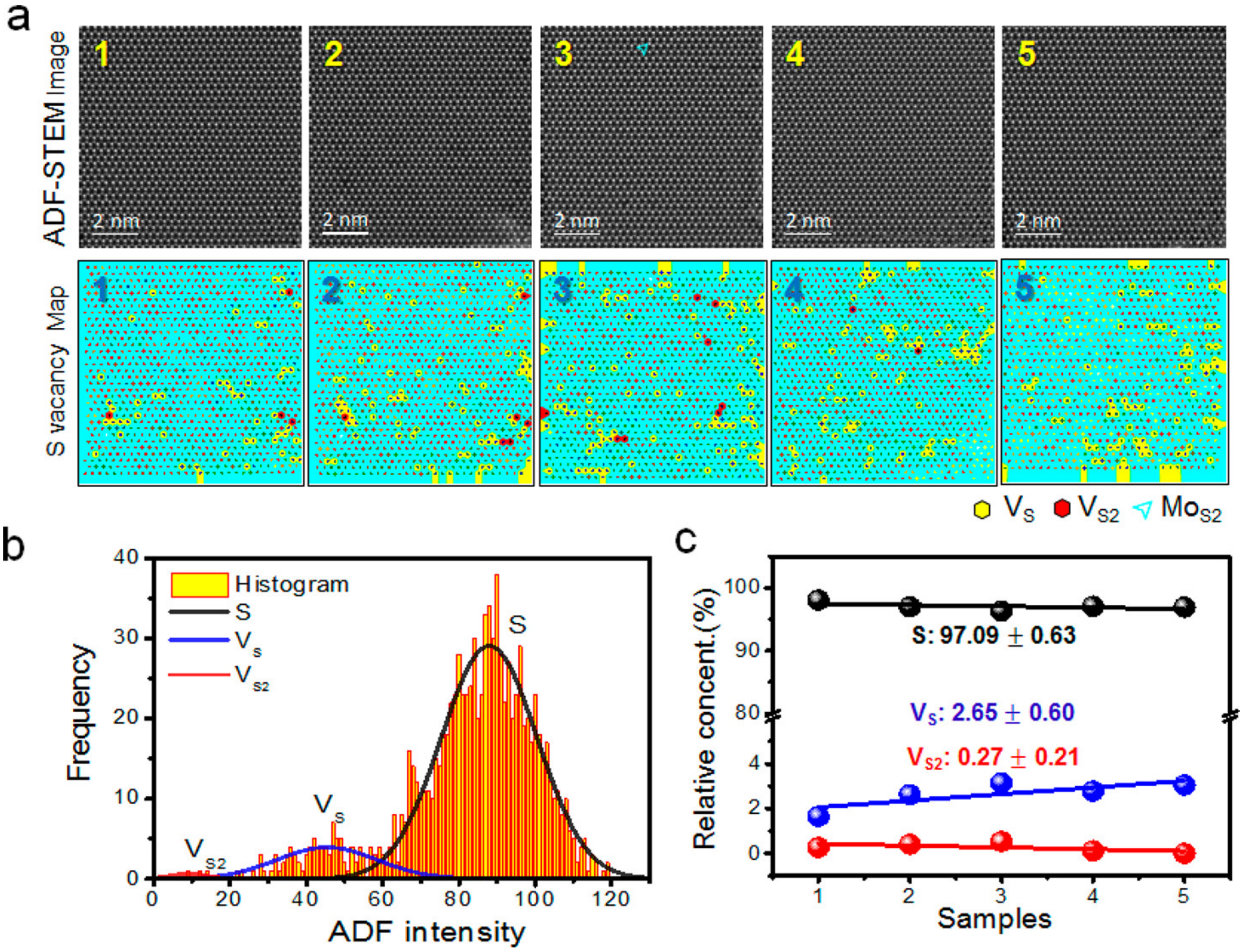
bis(trifluoromethane) sulfonimide (TFSI); stronger acidity than H_2SO_4



Amani et al., Science (2015)

Defect healing by chemical treatment: TFSI superacid

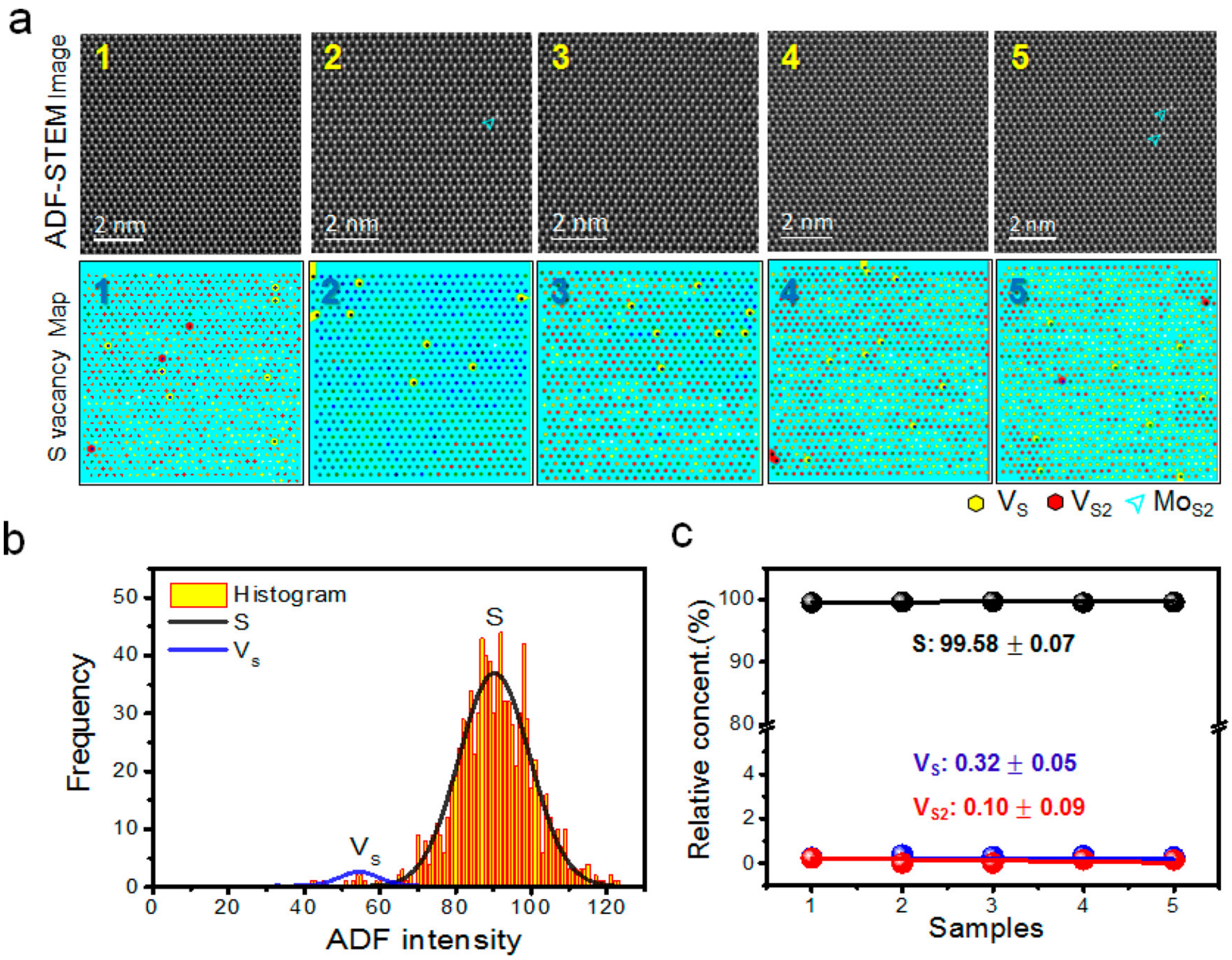
Before:



Roy et al., Nano Lett. (2018)

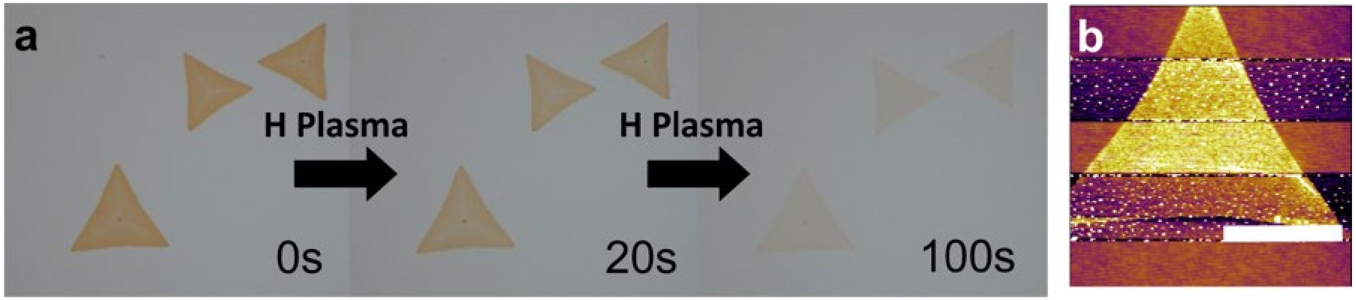
Defect healing by chemical treatment: TFSI superacid

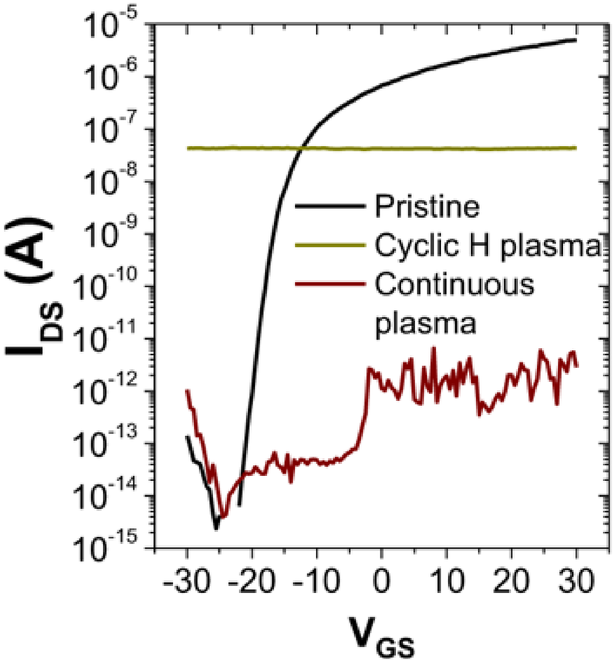
After:

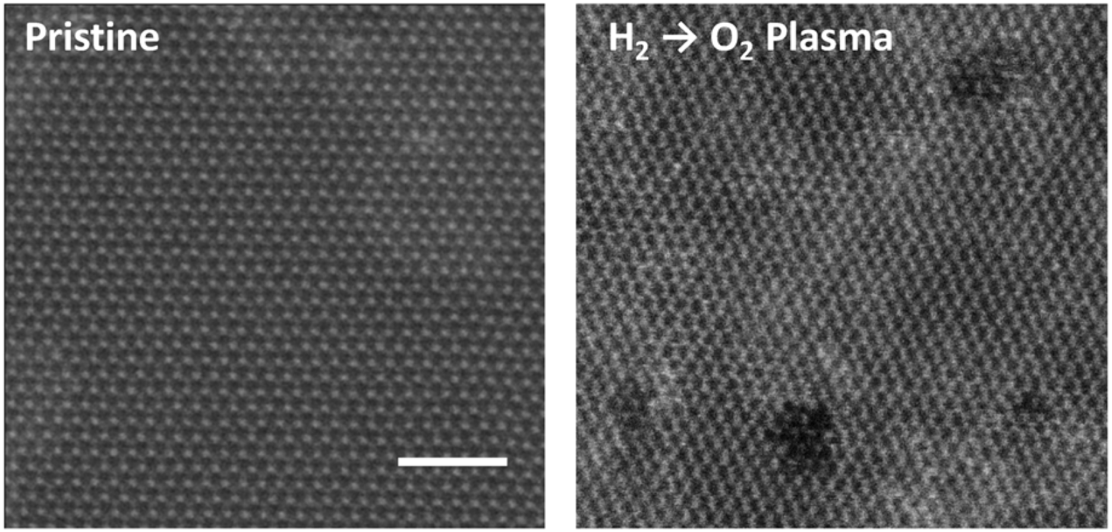


Roy et al., Nano Lett. (2018)

Positive aspects: reduction of contact resistance



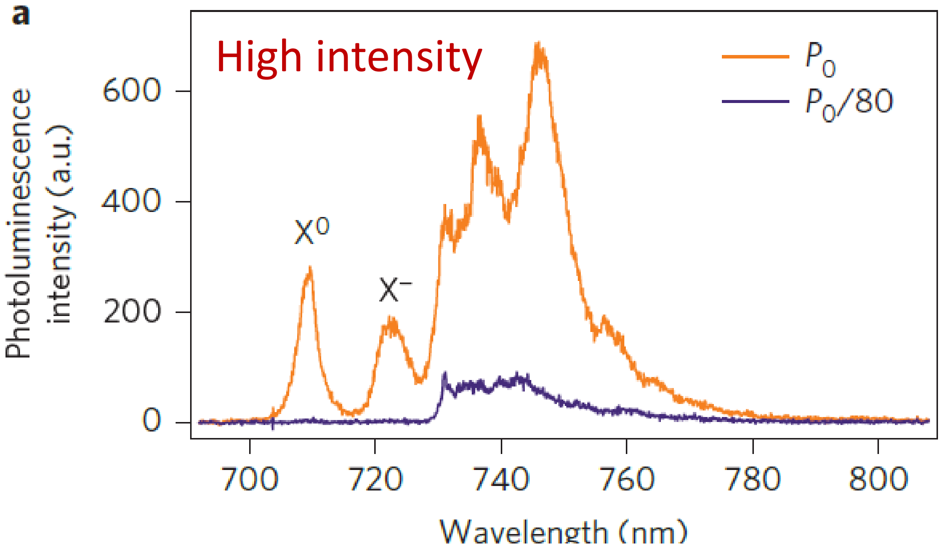




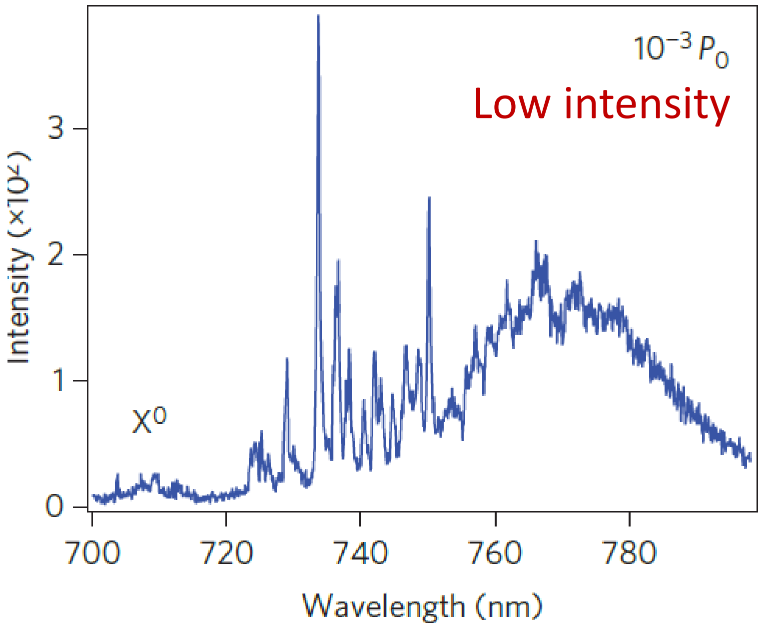
Stanford et al., npj 2D Materials and Applications (2019)

Positive aspects: single-photon sources

Point defects in WSe_2 emit photons one by one

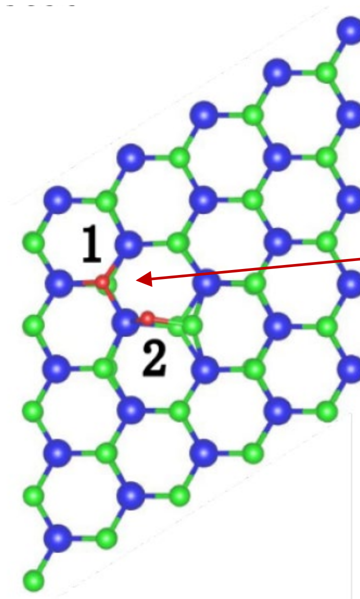


High intensity



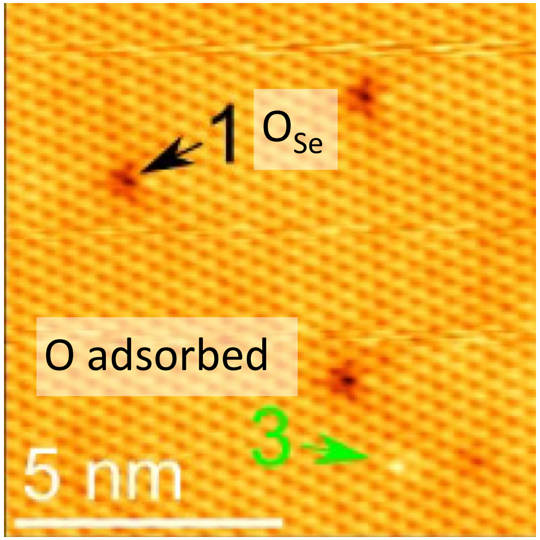
Low intensity

Srivastava et al., Nature Nanotech. (2015)



O_2 dissociated at a Se vacancy

Zheng et al., arXiv:1811.00221

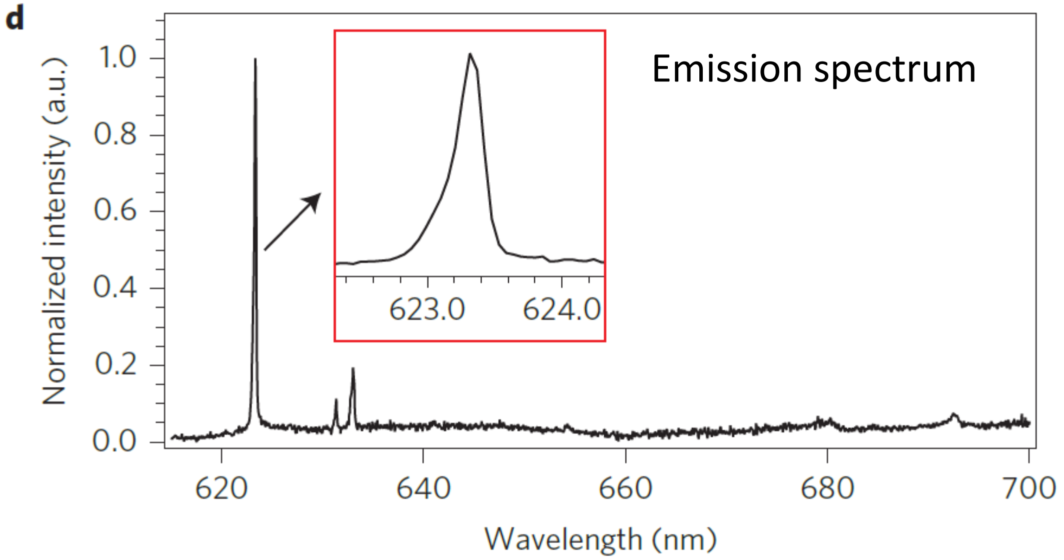


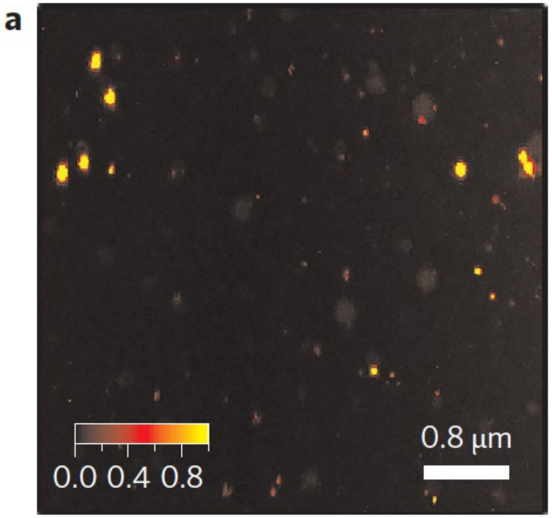
O_{Se}

O adsorbed

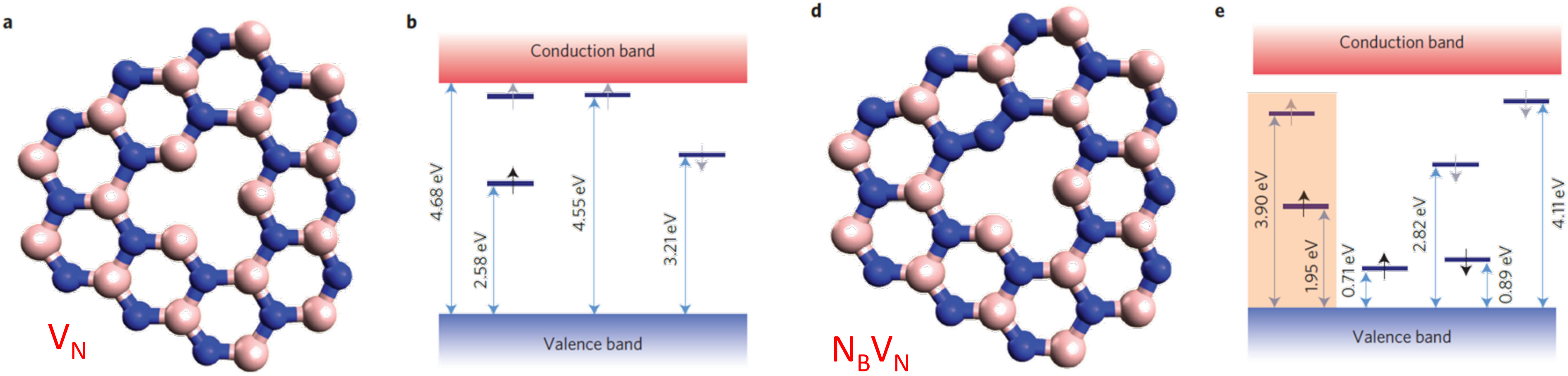
Positive aspects: single-photon sources

Point defects in BN emit photons one by one



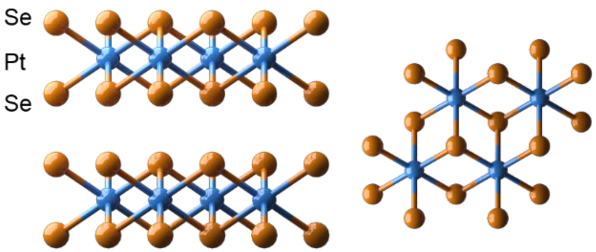


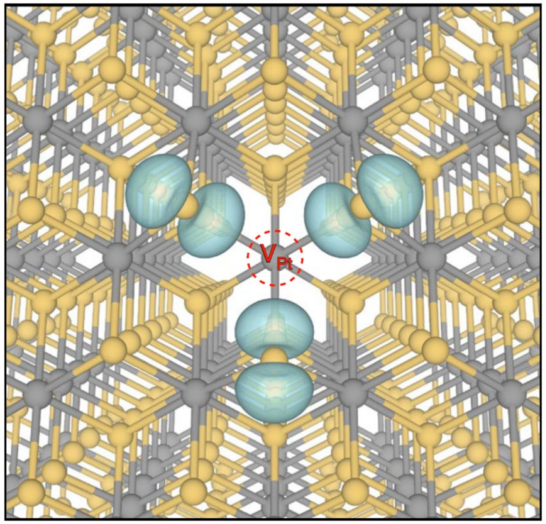
Pholuminescence map

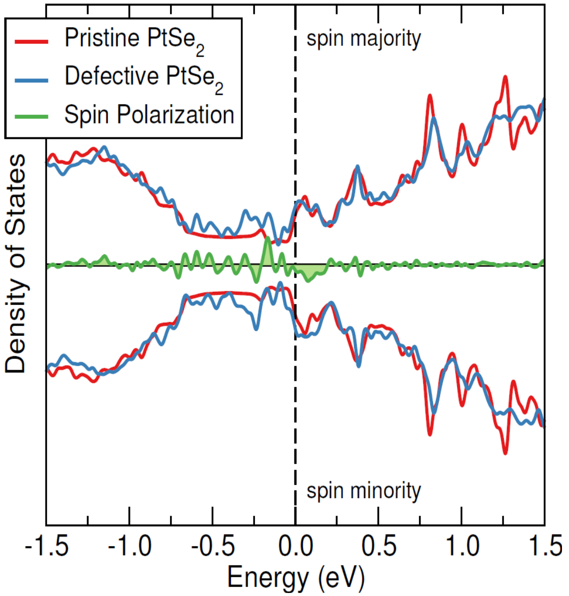


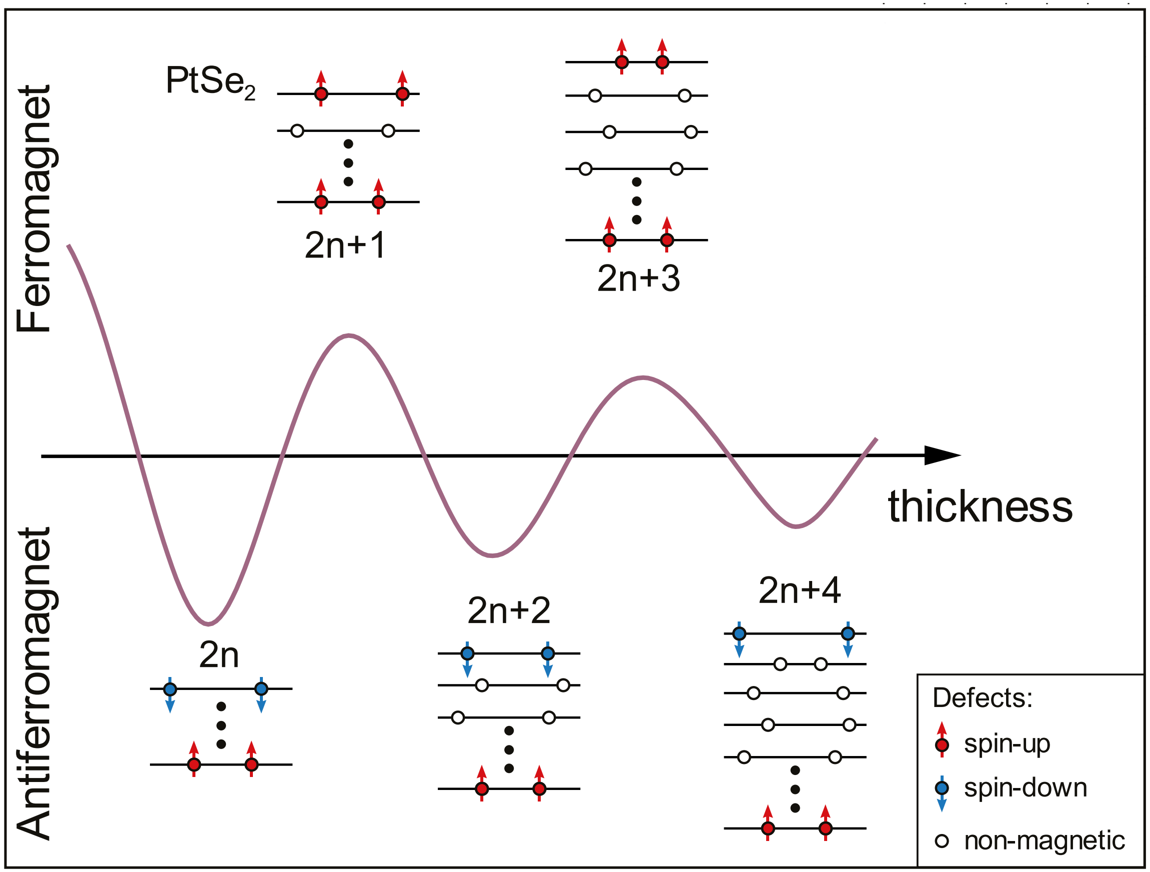
Tran et at., Nature Nanotechnology (2015)

Positive aspects: induced magnetism in $PtSe_2$









Avsar et al. Nature Nanotechnology (2019)

Recapitulation

Defect types

- Two-dimensional defects (wrinkles, ripples)
- Line defects
- Point defects

Impact of point defects

- Reduced device performance due to disorder and charge trapping
- Quantifying their impact on electrical performance (transport and CV measurements)

Point defect mitigation

- Dielectric environment
- Chemical treatment

Positive applications of defects

- Doping, reduced contact resistance
- Single-photon sources
- Defect-induced magnetism