

2D Materials

an introduction starting from the discovery of graphene

Alberto Morpurgo

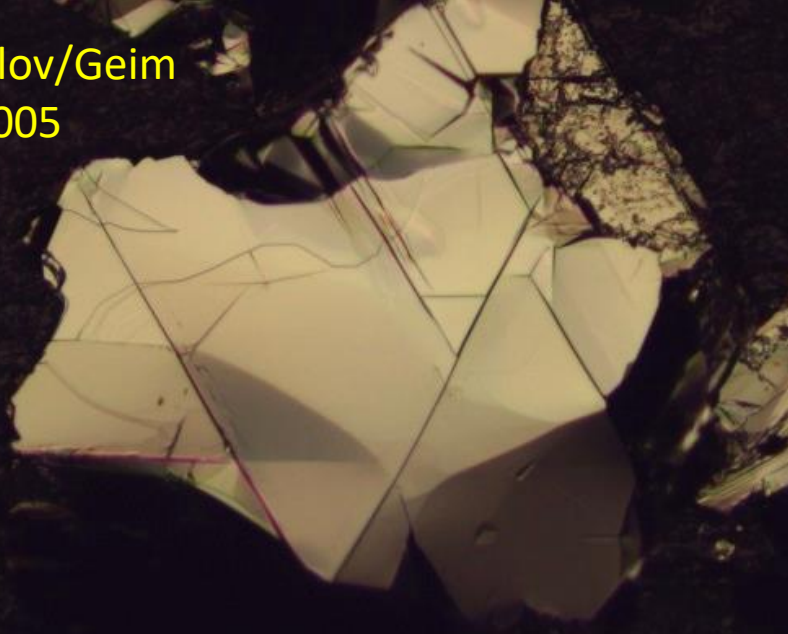


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- Developments in material control now enable *perfect crystals only one or a few atom thick* to be investigated
- The very broad variety of 2D materials available gives access to *unexplored physical phenomena*
- *Realization of artificial materials* with properties engineered by design at the atomic scale

Philosophy: some idea is better than no idea

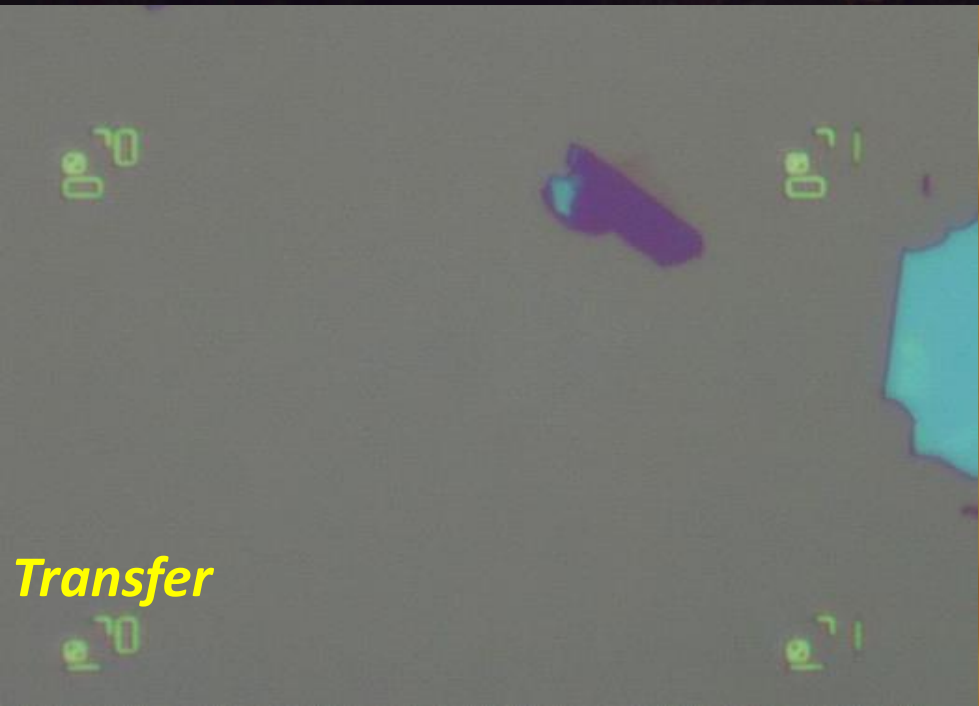
Novoselov/Geim
2004/2005



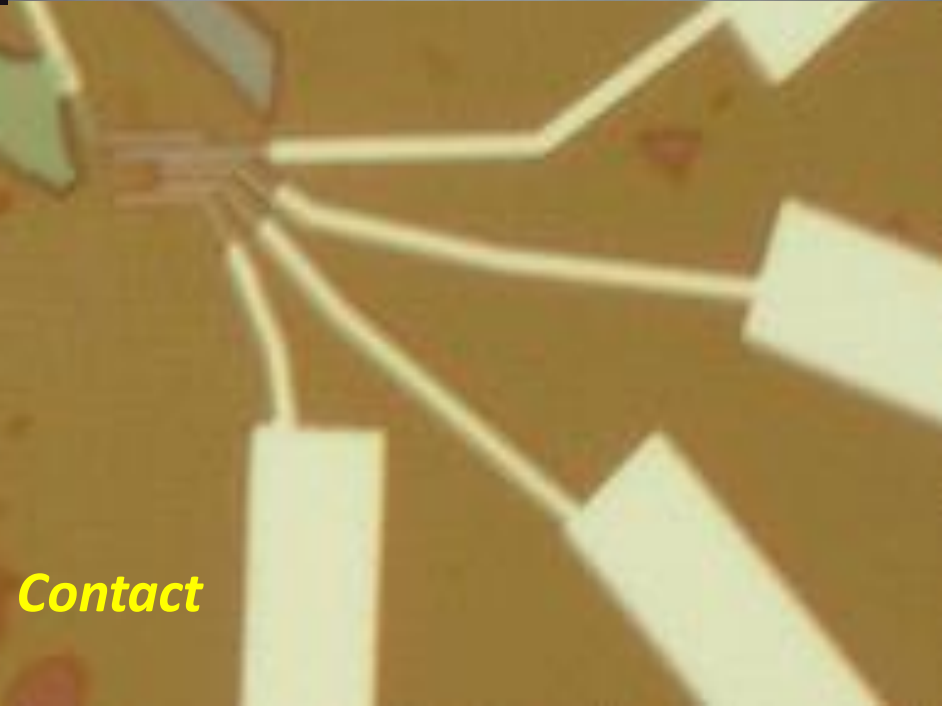
Natural Graphite



Exfoliation

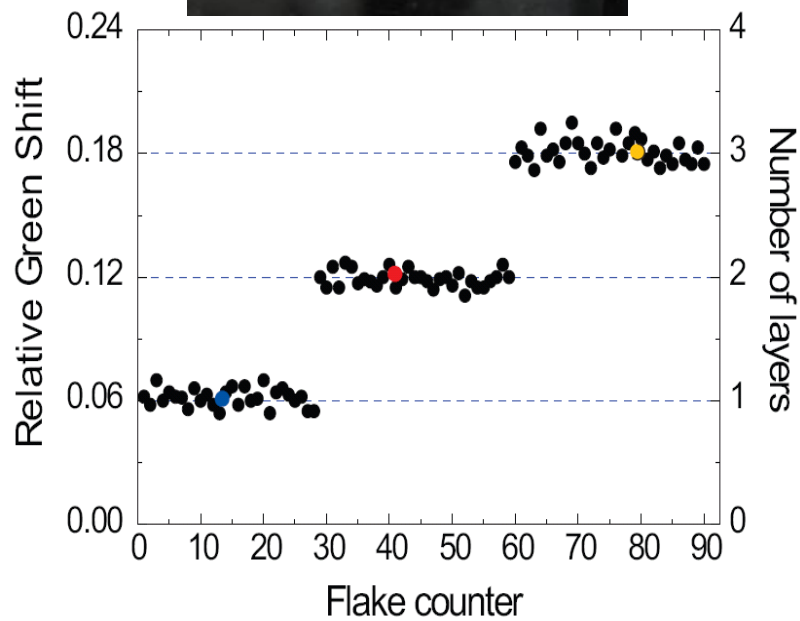
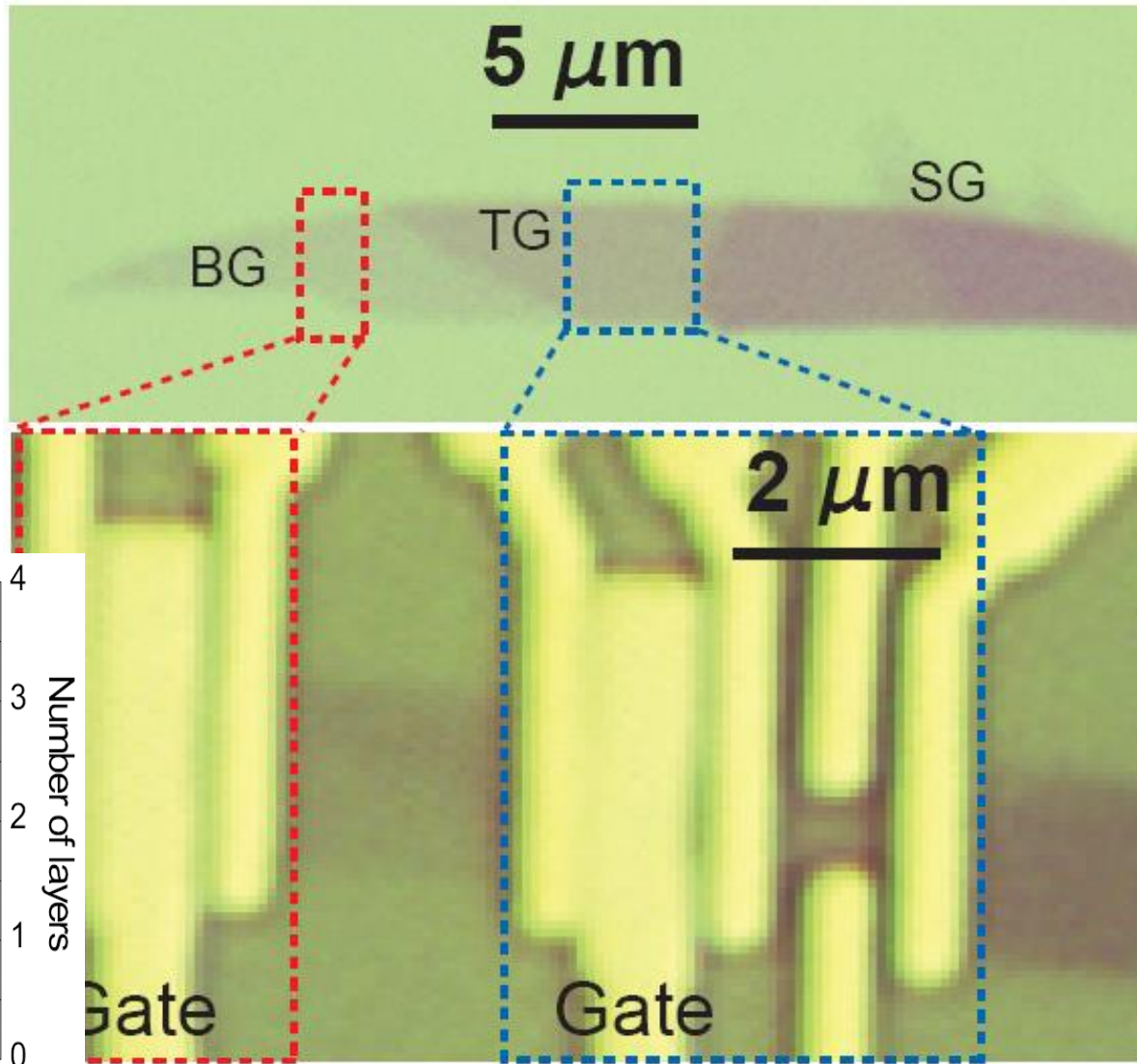


Transfer



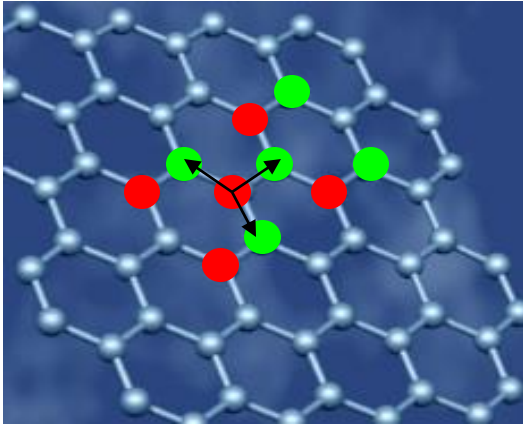
Contact

Seeing one-atom layers one at a time



Relativistic electrons in graphene

Two inequivalent C atoms



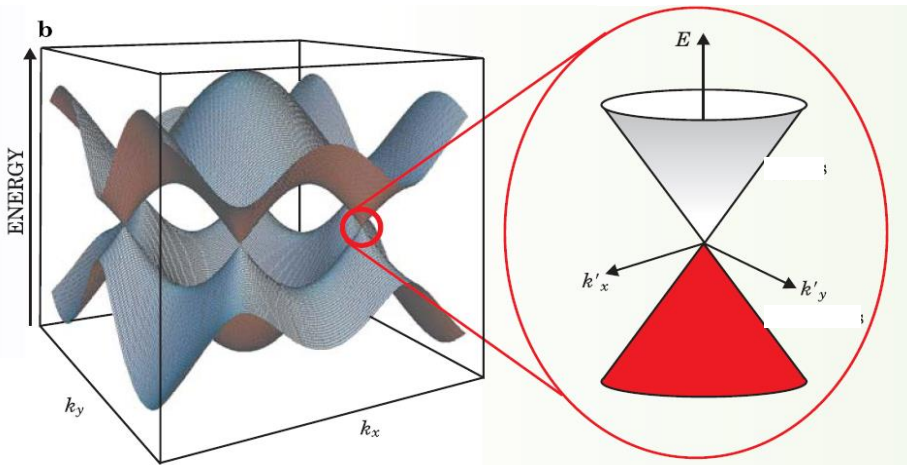
$$H = t \sum_{i,j} A_{\vec{R}_i}^\dagger B_{\vec{R}_i + \vec{\delta}_j} + B_{\vec{R}_i + \vec{\delta}}^\dagger A_{\vec{R}_i}$$

$$|\psi_k\rangle = \left(\alpha_k \sum_i \left(e^{i\vec{k}\vec{R}_i} A_{\vec{R}_i}^\dagger \right) + \beta_k \sum_i \left(e^{i\vec{k}\vec{R}_i} B_{\vec{R}_i}^\dagger \right) \right) |0\rangle$$

Or

$$|\psi_k\rangle = \sum_i e^{i\vec{k}\vec{R}_i} \begin{pmatrix} \alpha_k A_{\vec{R}_i}^\dagger \\ \beta_k B_{\vec{R}_i}^\dagger \end{pmatrix} |0\rangle \quad \text{pseudo spin}$$

$$H |\psi_k\rangle = E(k) |\psi_k\rangle$$



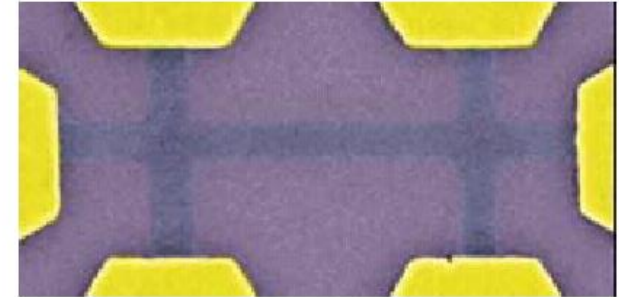
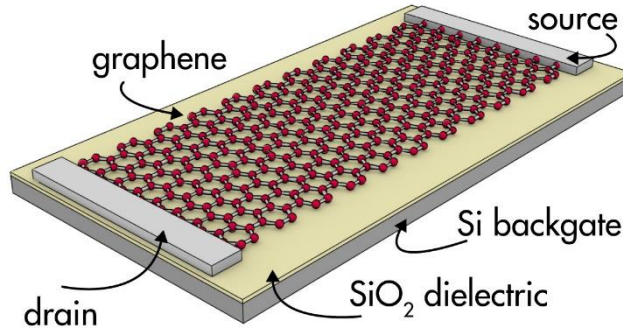
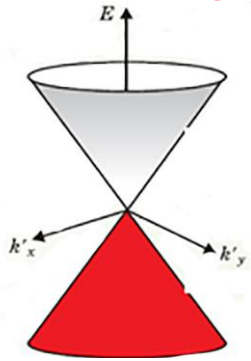
Dirac Equation

$$v_F (-i\hbar \vec{\nabla}) \cdot \vec{\sigma} \begin{pmatrix} \alpha_k e^{i\vec{k}\cdot\vec{r}} \\ \beta_k e^{i\vec{k}\cdot\vec{r}} \end{pmatrix} = E(k) \begin{pmatrix} \alpha_k e^{i\vec{k}\cdot\vec{r}} \\ \beta_k e^{i\vec{k}\cdot\vec{r}} \end{pmatrix}$$

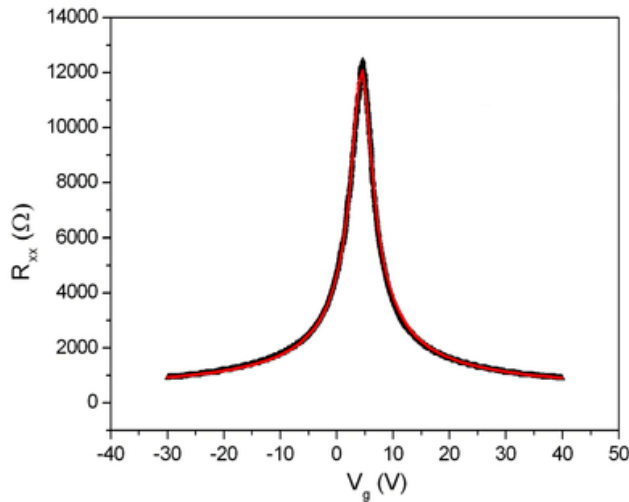
Direct Experimental manifestations

Graphene field-effect transistor

Novoselov/Geim/Kim2005

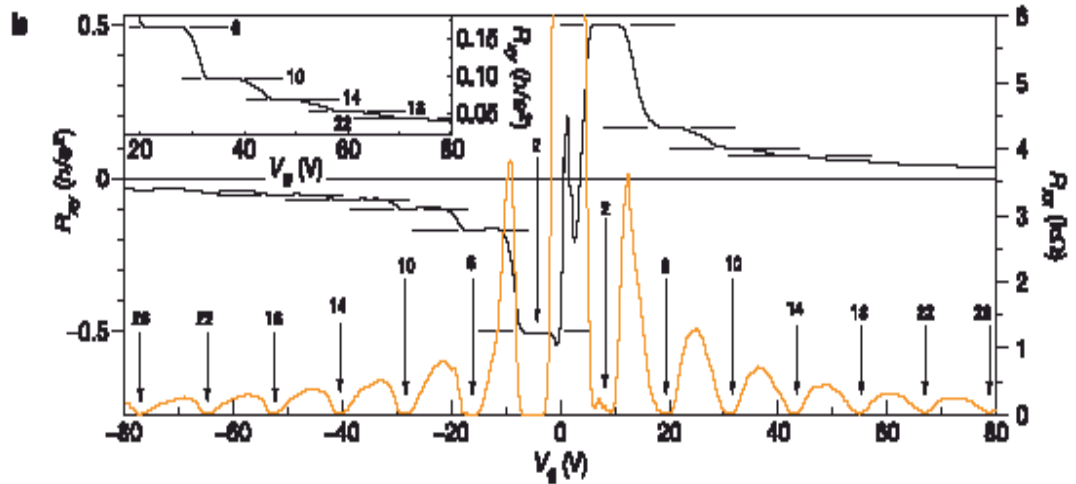


Resistivity



Dirac "peak"

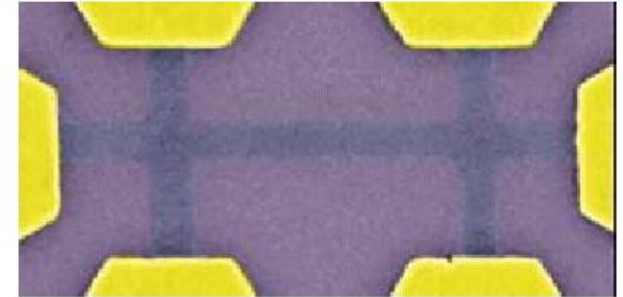
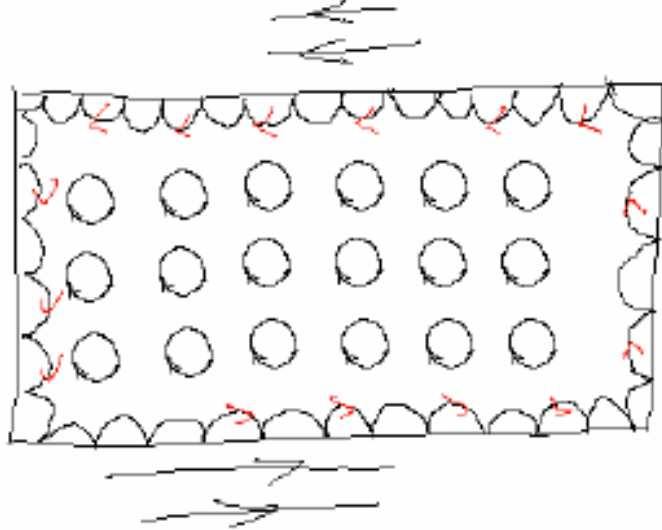
Quantum Hall effect



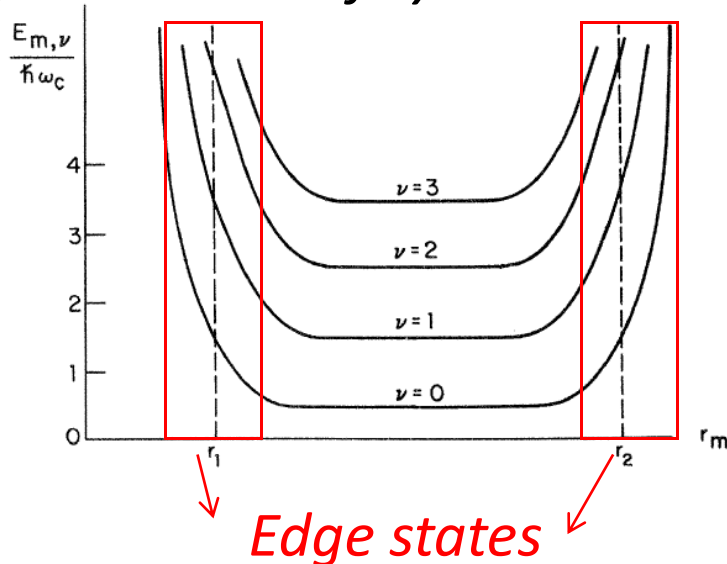
$$G_{Hall} = 4 \frac{e^2}{h} \left(N + \frac{1}{2} \right)$$

Quantum Hall effect for dummies

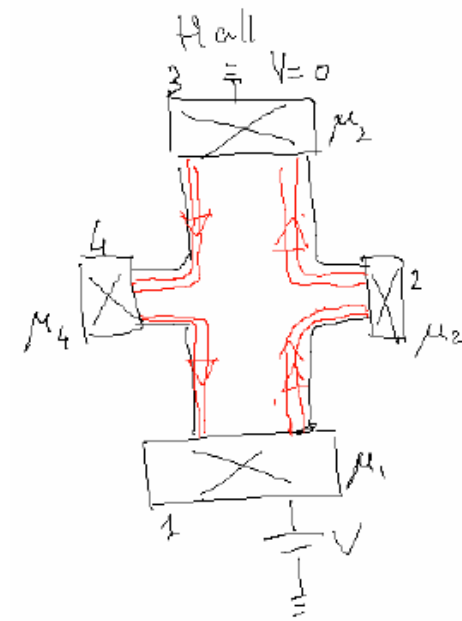
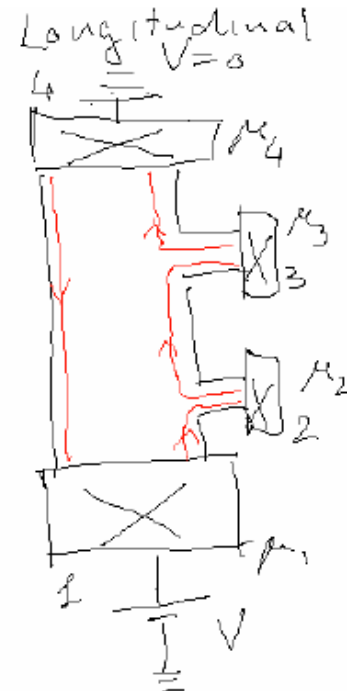
Quasiclassical orbits



Landau levels =
quantization of cyclotron motion



Transport through edge channels



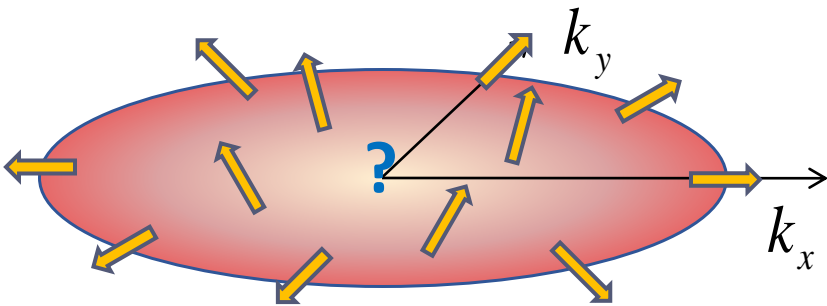
Band structure topology: basic idea

Think of Hamiltonian as a k -dependent magnetic field

Graphene $H = v_F (-i\hbar\vec{\nabla}) \cdot \vec{\sigma} = \hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix}$

$$H = \alpha \vec{B}(\vec{k}) \cdot \vec{\sigma}$$

$$\vec{B}(\vec{k}) = (k_x, k_y, 0)$$

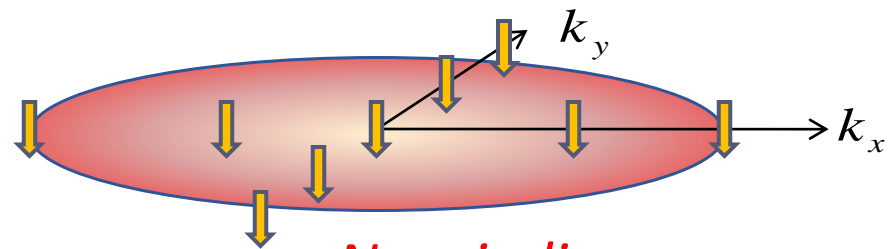


Bloch functions wind around in the Brillouin zone =
topologically non-trivial

Trivial insulator

$$H = A \begin{pmatrix} \Delta/2 + bk^2 & 0 \\ 0 & -\frac{\Delta}{2} - bk^2 \end{pmatrix} = A B_z \sigma_z$$

$$\vec{B}(\vec{k}) = (0, 0, \Delta/2 + bk^2)$$

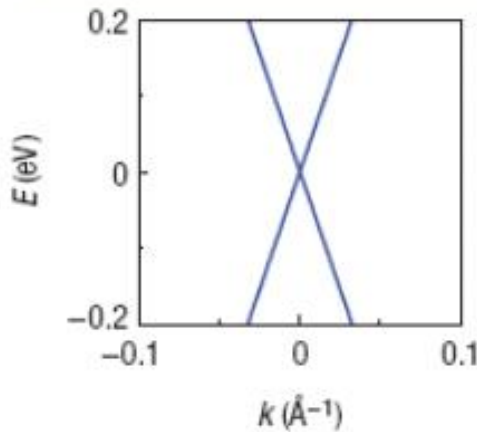
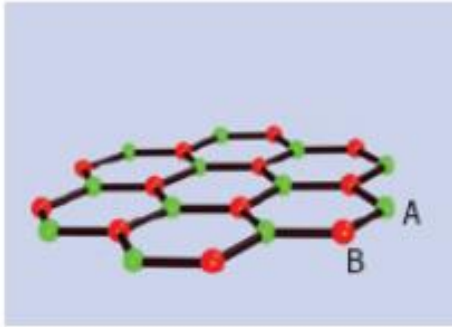


No winding

Non-trivial topology leads to states at the edges

Different thickness = different electronic systems

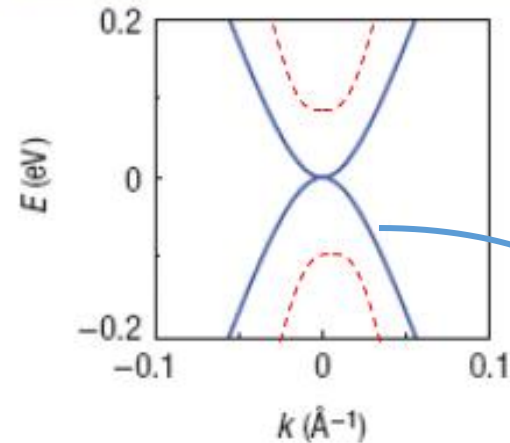
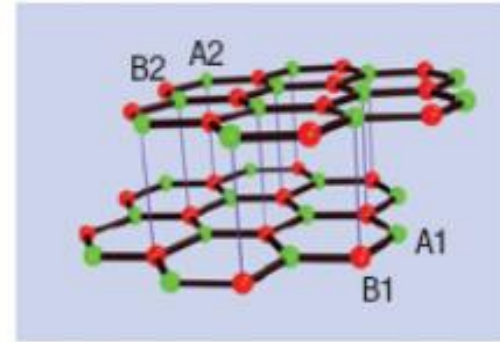
Monolayer



$$H_{1L} \propto \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix}$$

$$\psi = \begin{pmatrix} \psi_A \\ \psi_B \end{pmatrix} \quad E(k) \propto k$$

Bilayer

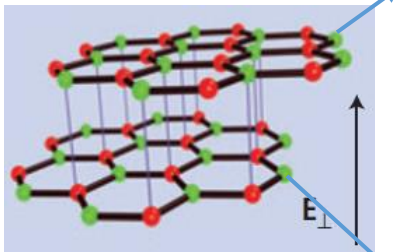


$$H_{2L} \propto \begin{pmatrix} 0 & (k_x - ik_y)^2 \\ (k_x + ik_y)^2 & 0 \end{pmatrix}$$

$$\psi = \begin{pmatrix} \psi_{A1} \\ \psi_{B2} \end{pmatrix} \quad E(k) \propto k^2$$

Gate control of electronic bands

Layer potential



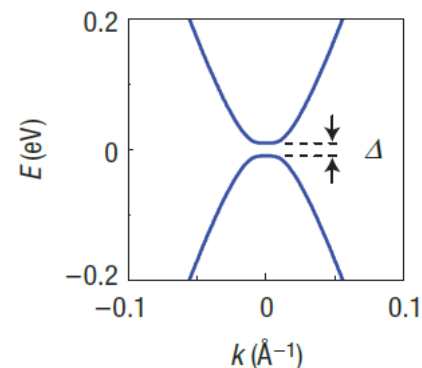
$$V = \Delta/2$$

$$V = -\Delta/2$$

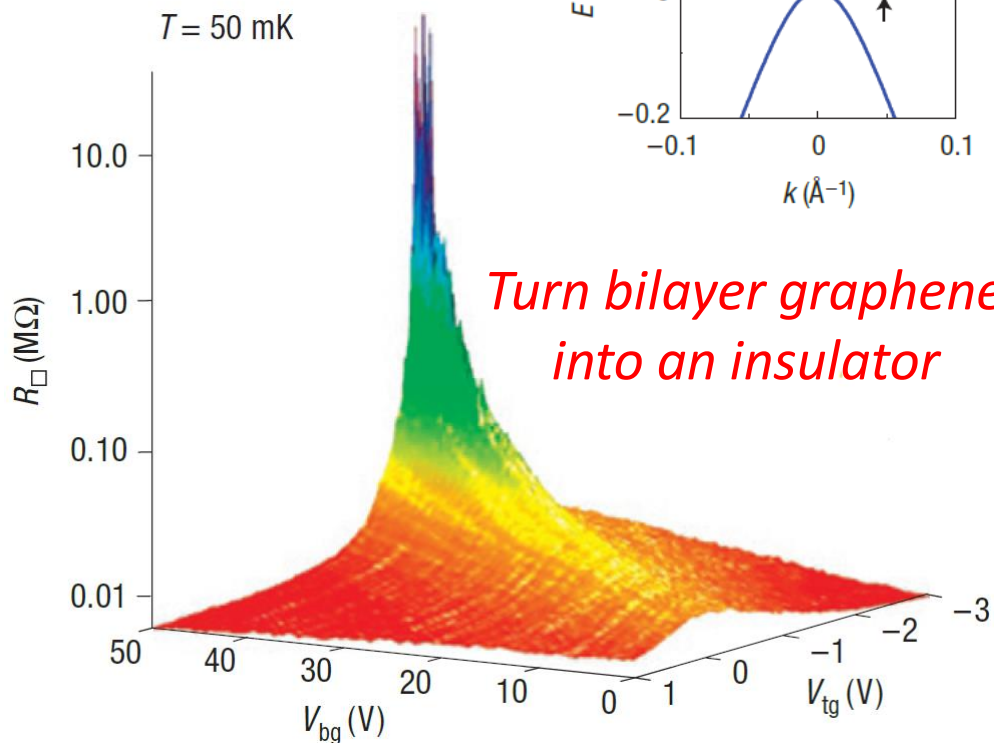
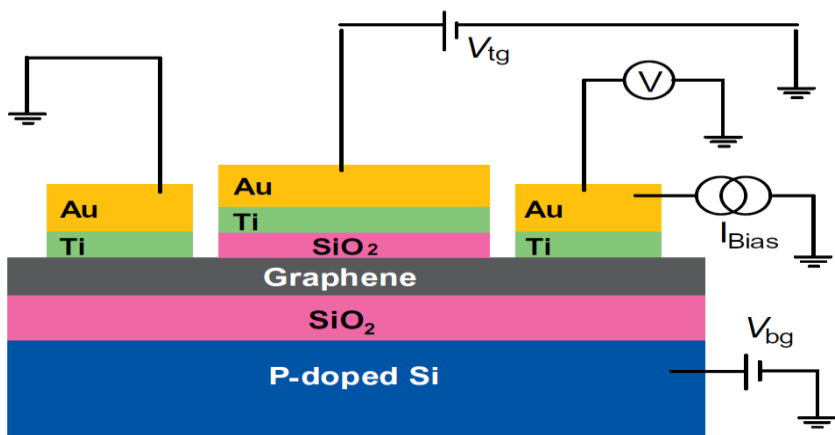
$$H_{2L} \propto \begin{pmatrix} \frac{\Delta}{2} & (k_x - ik_y)^2 \\ (k_x + ik_y)^2 & -\frac{\Delta}{2} \end{pmatrix}$$

$$E(k) \propto \sqrt{\Delta + ak^2}$$

Open band-gap

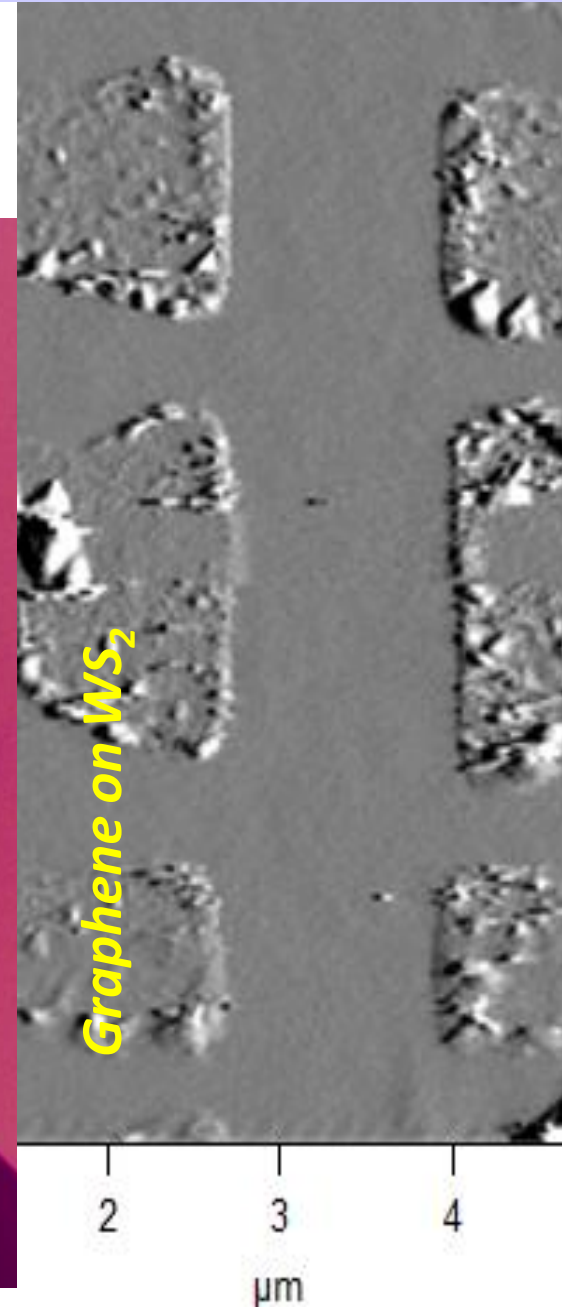
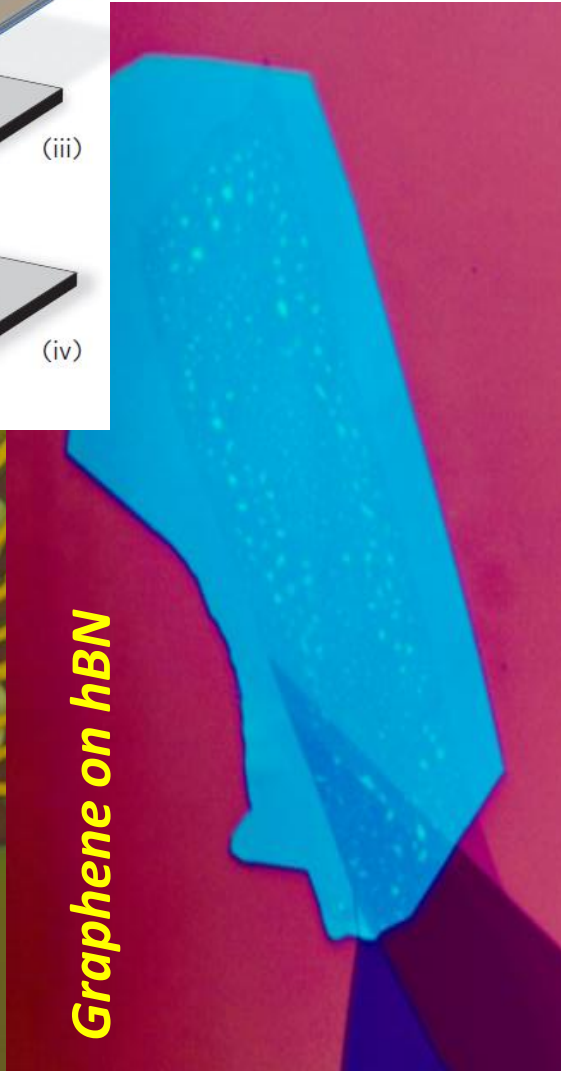
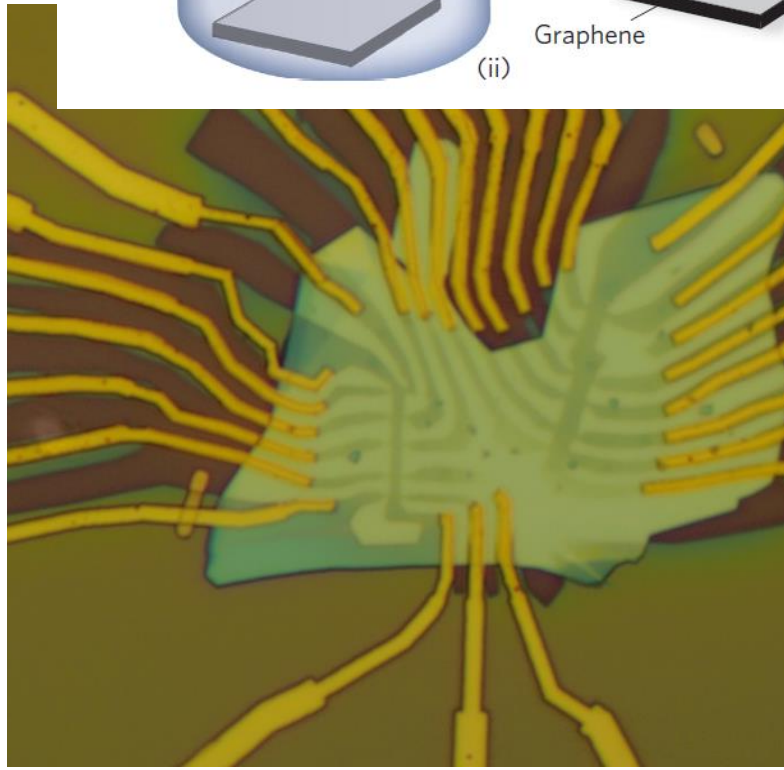
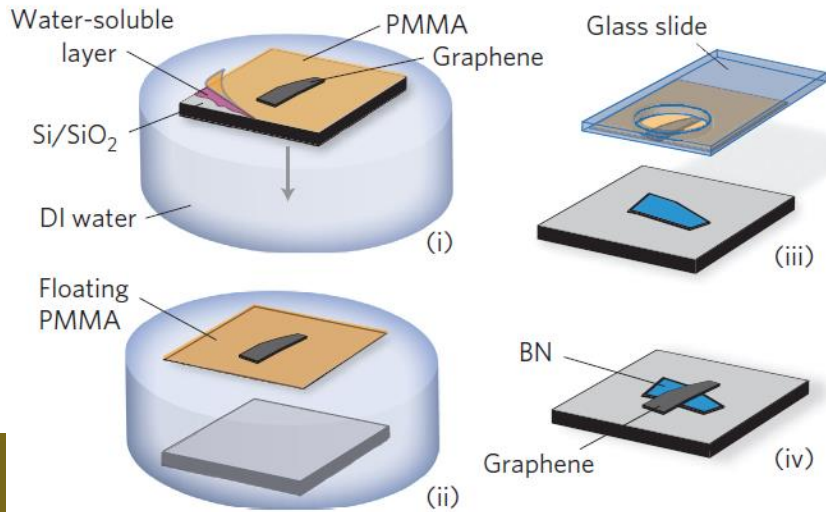


Double-gated devices



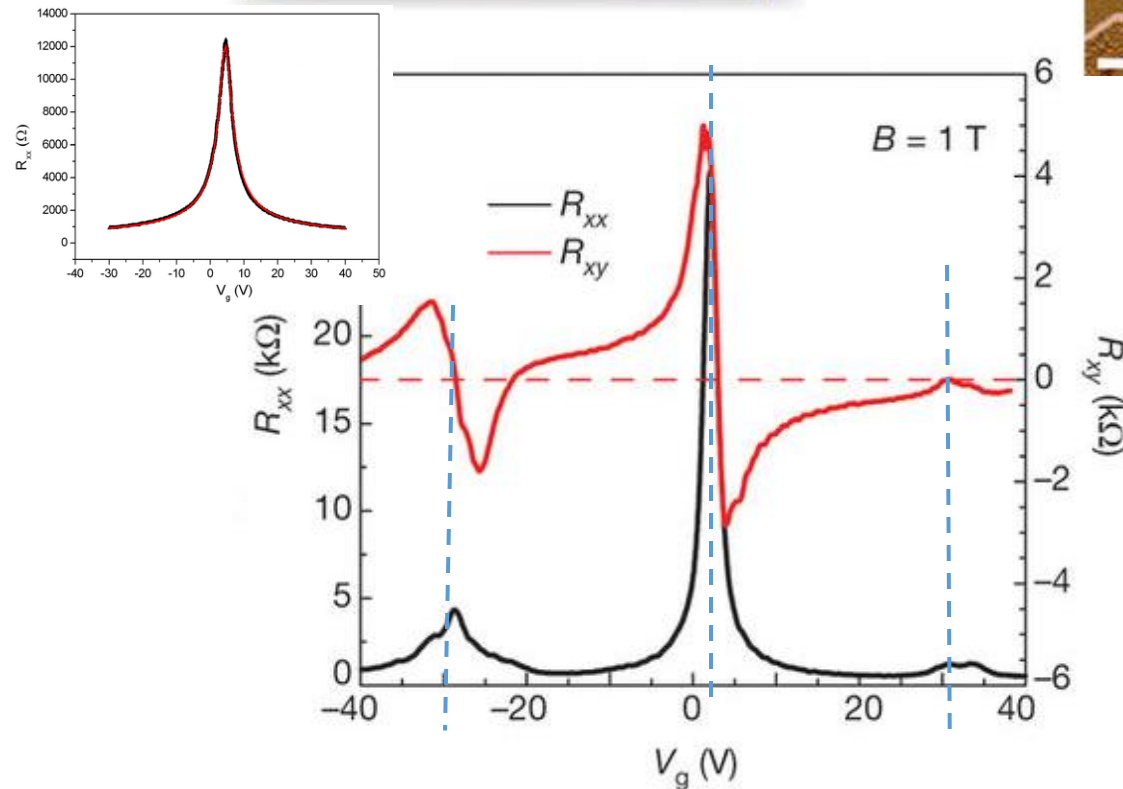
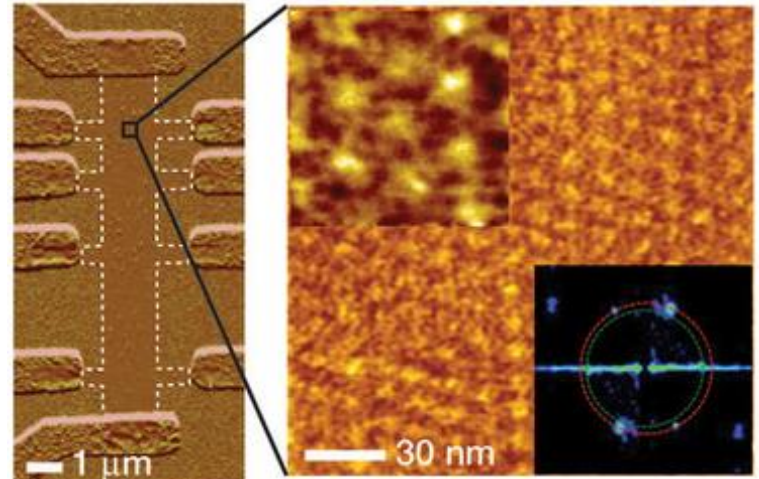
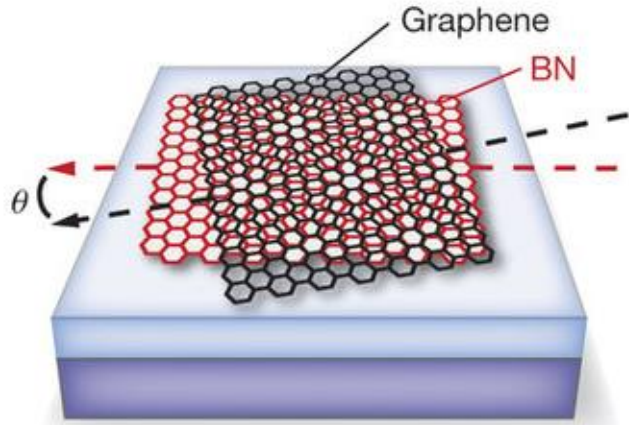
Manipulating atomic crystals

P. Kim's group 2010



Moire superlattice for graphene on hBN

Kim's group



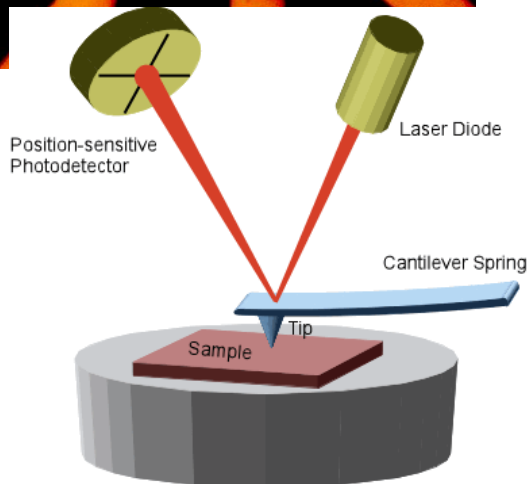
Contact with hBN generates periodic potential:

Graphene band structure modified

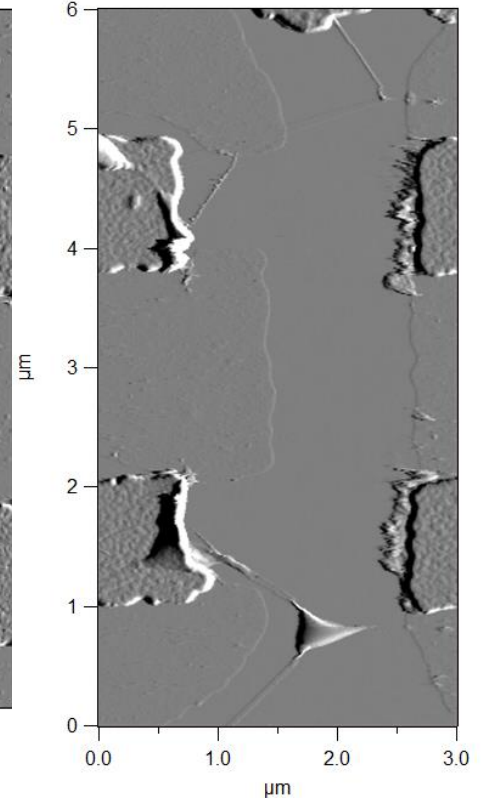
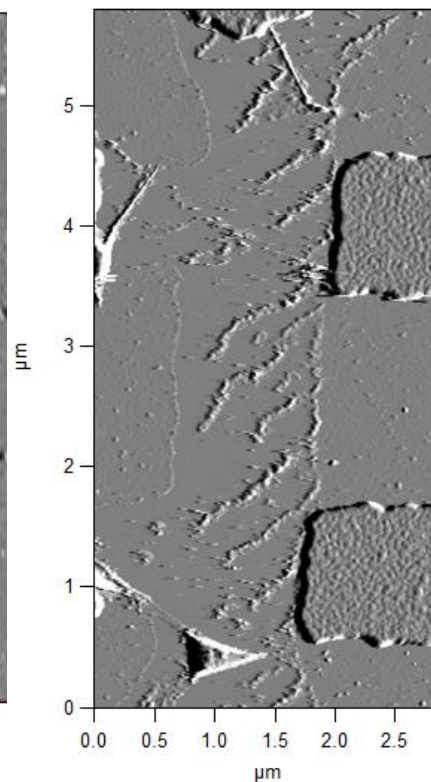
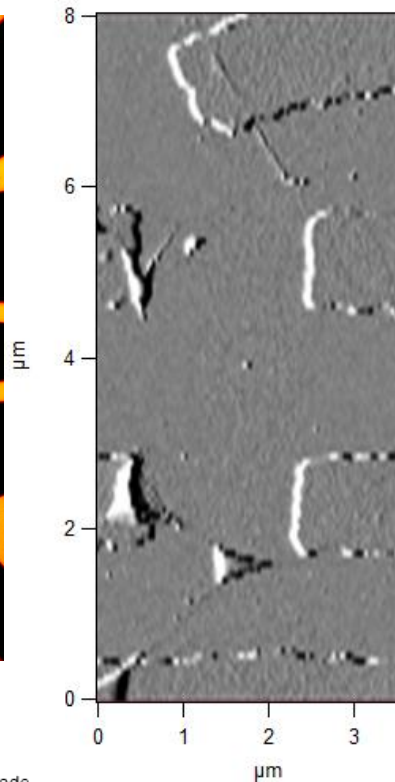
Satellite Dirac points

Cleaning 2D materials

Optical image



Before cleaning → During cleaning → After cleaning



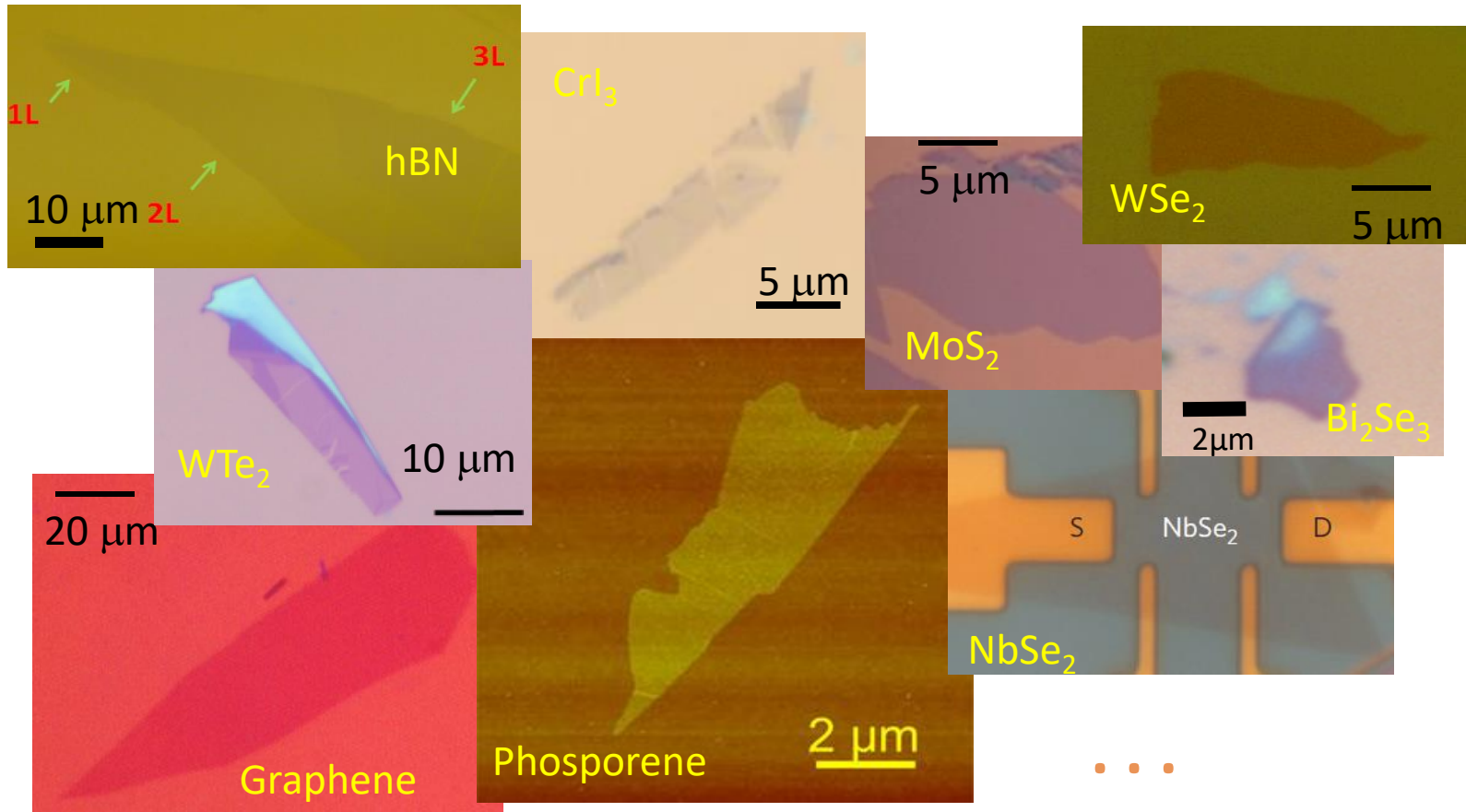
Contact mode AFM

removes residues of

nano-fabrication processes

A virtually infinite variety of systems

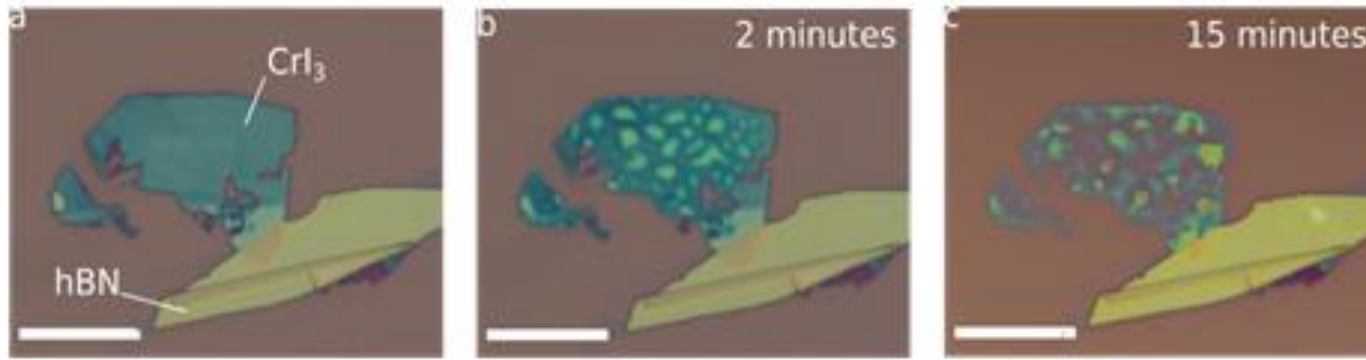
More than 50 monolayers demonstrated, including: Insulators, semiconductors, semi-metals, topological insulators, superconductors, charge density waves, ferromagnets, antiferromagnets...



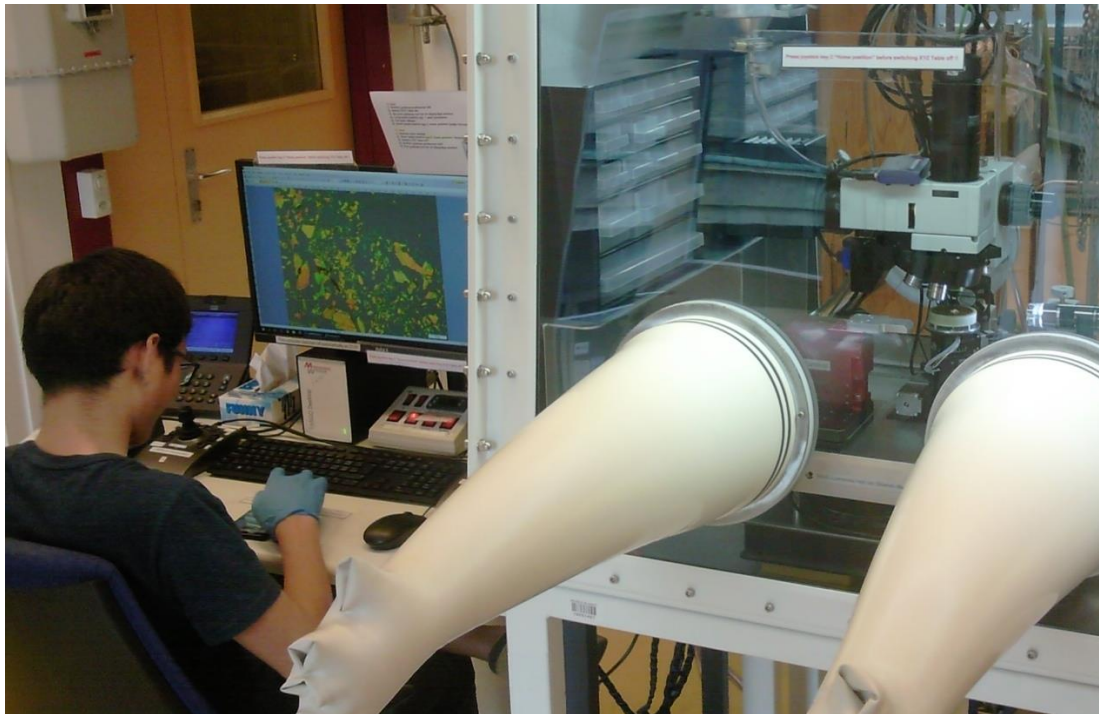
Theory predicts that ~ 1000 different atomic crystals can be produced using similar techniques

Can work with materials not stable in air

Example: CrI₃ --- the first ferromagnetic monolayer



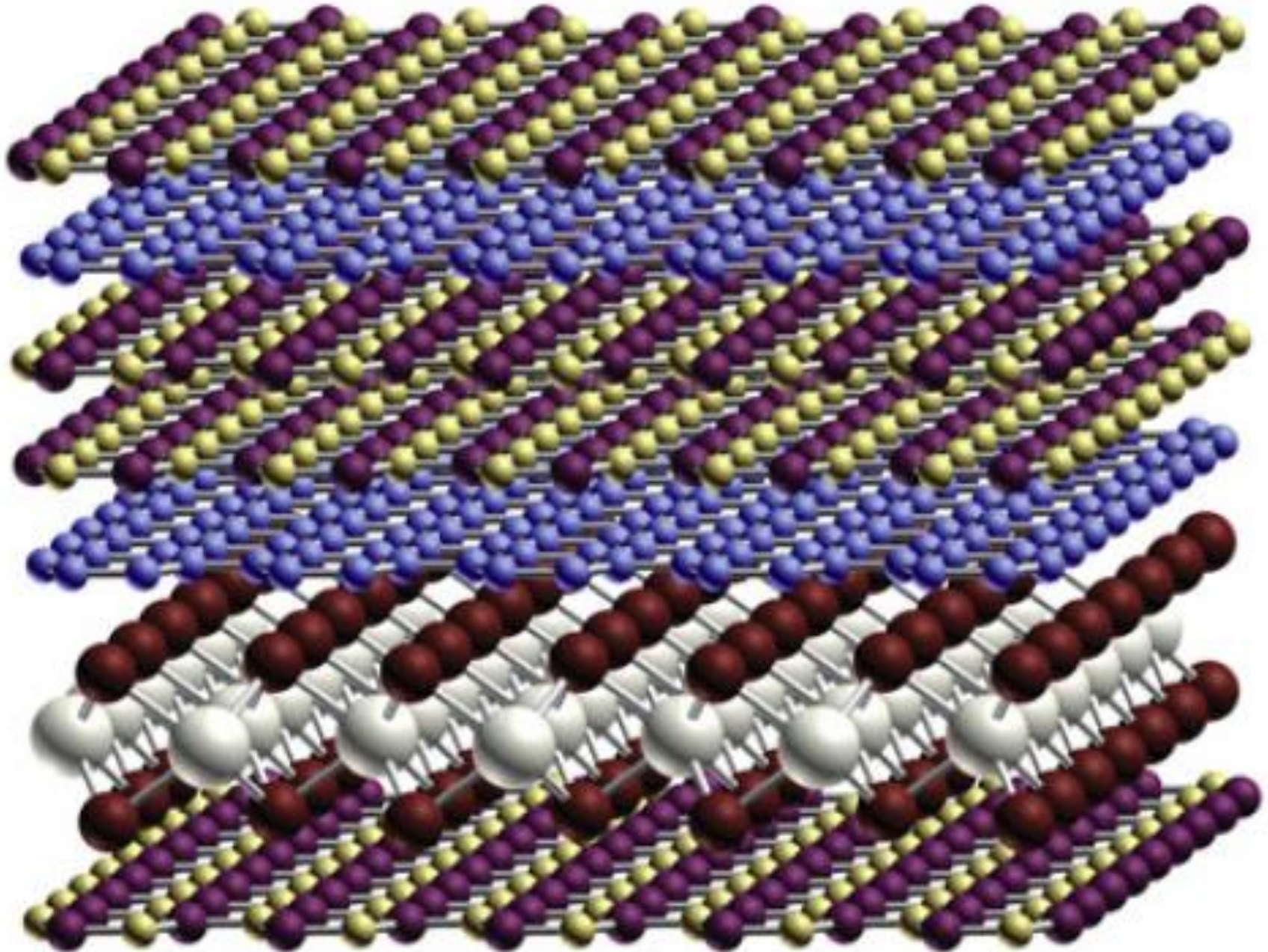
Thin crystals (even 50 nm) dissolve in a few minutes



Exfoliate/transfer/encapsulate in glove box with controlled atmosphere

The Grand Vision – already becoming reality

Novoselov 2011



Examples of interesting physics in 2D materials

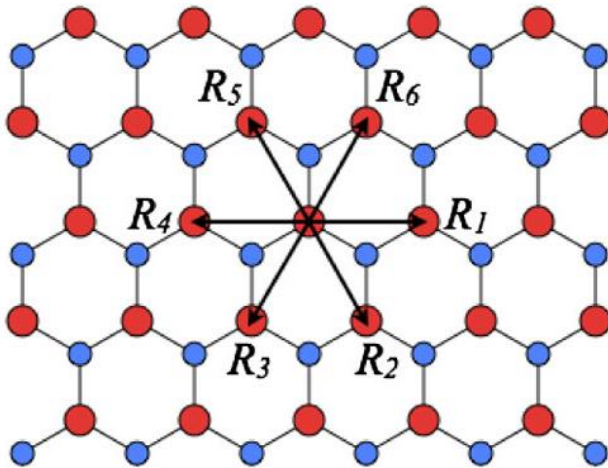
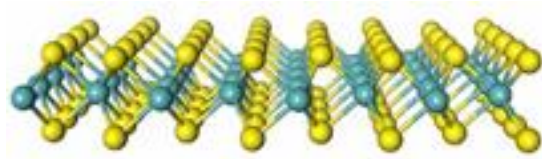
Goal: to illustrate the breadth of scope --- no details

- *Gate-induced superconductivity* in semiconducting transition metal dichalcogenides (TMDs)
- *Giant tunneling magnetoresistance* through 2D magnetic semiconductor tunnel barriers
- *Edge conduction* in monolayer WTe_2 (2D topological insulator)

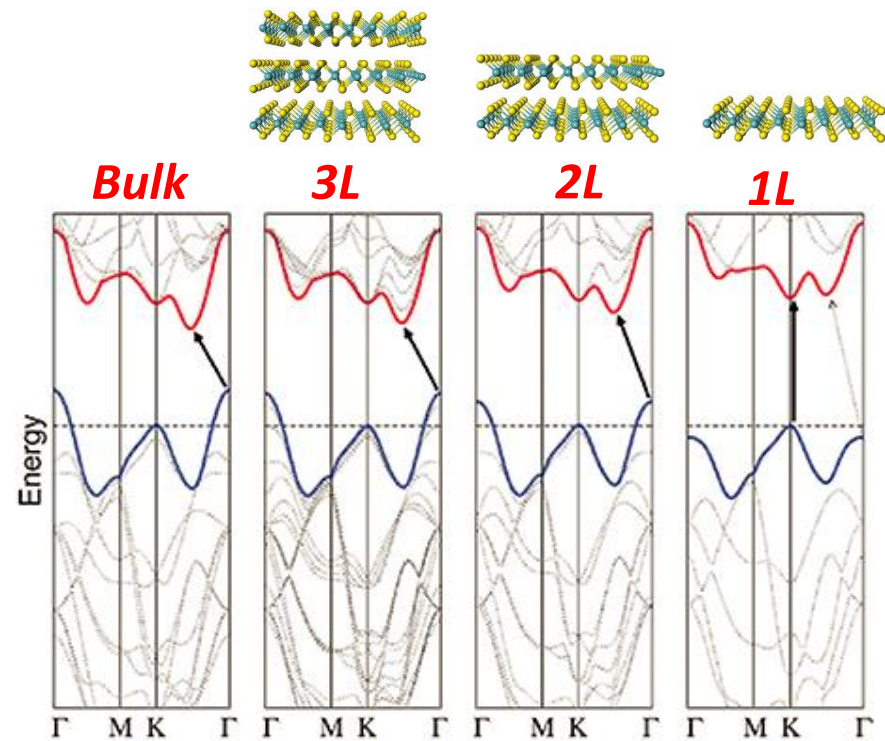
Semiconducting transition metal dichalcogenides

MoS₂, WS₂, MoSe₂, WSe₂, ...

- Honeycomb (= graphene),
- A/B atom different (=gapped),
- very strong SOI



A. Splendiani et al. NL 10, 1271 (2010)

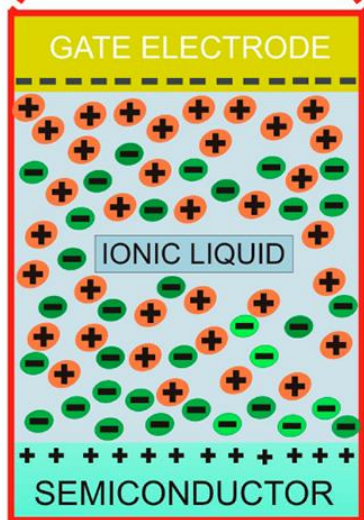
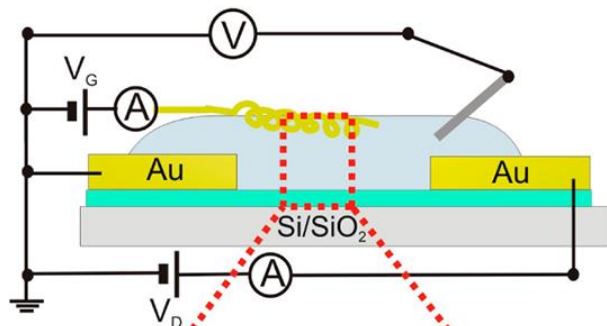


Ionic liquid gating

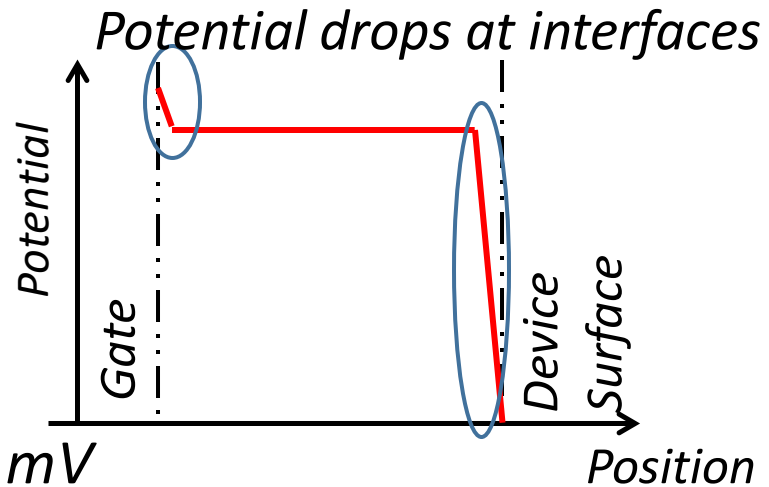
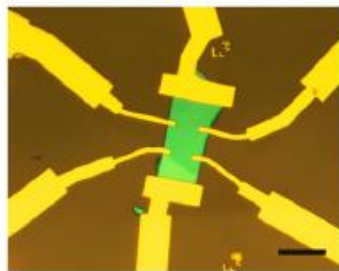
Electrostatics of ionic liquids

similar to metals =

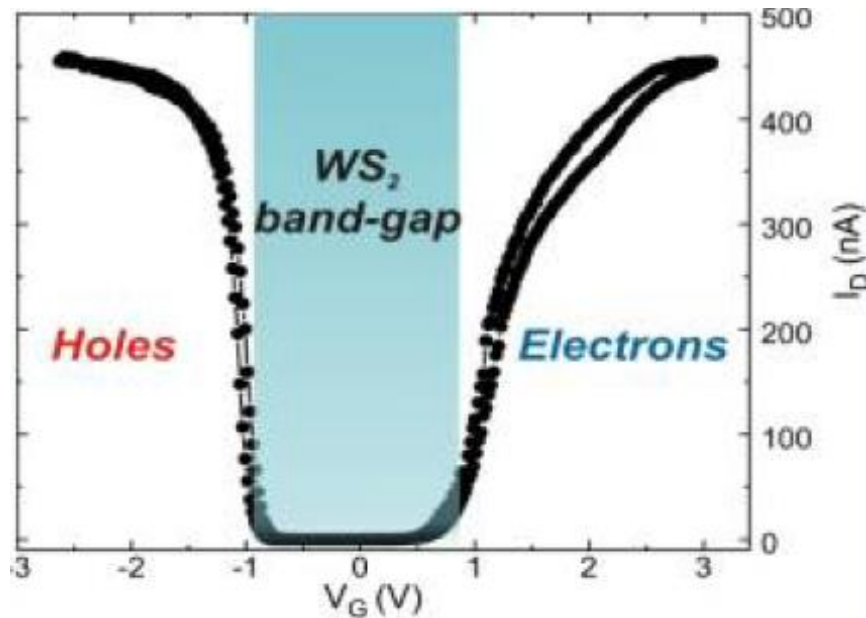
atomic-scale screening length



Ex: WS_2



$V_{sd} = 100 \text{ mV}$



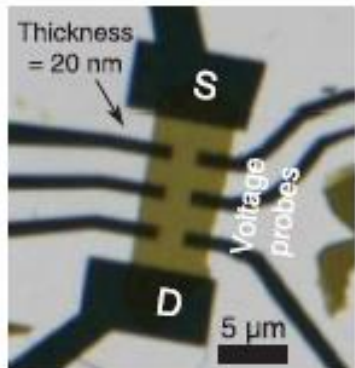
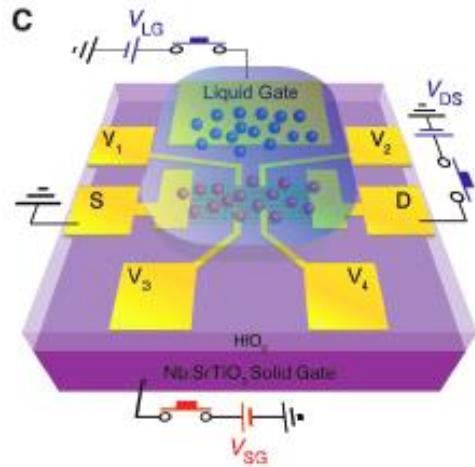
$$e\Delta V_G = \Delta E_F + e\Delta\phi = \Delta E_F + \frac{e^2 n}{C_G}$$

Gate-induced superconductivity in MoS₂ ionic-liquid FETs

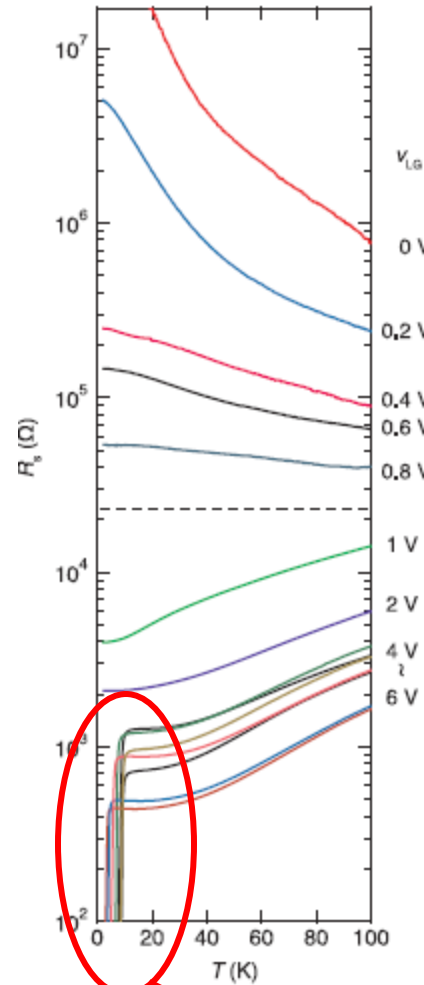
Superconducting Dome in a Gate-Tuned Band Insulator

J. T. Ye,^{1*} Y. J. Zhang,¹ R. Akashi,¹ M. S. Bahramy,² R. Arita,^{1,2} Y. Iwasa^{1,2*}

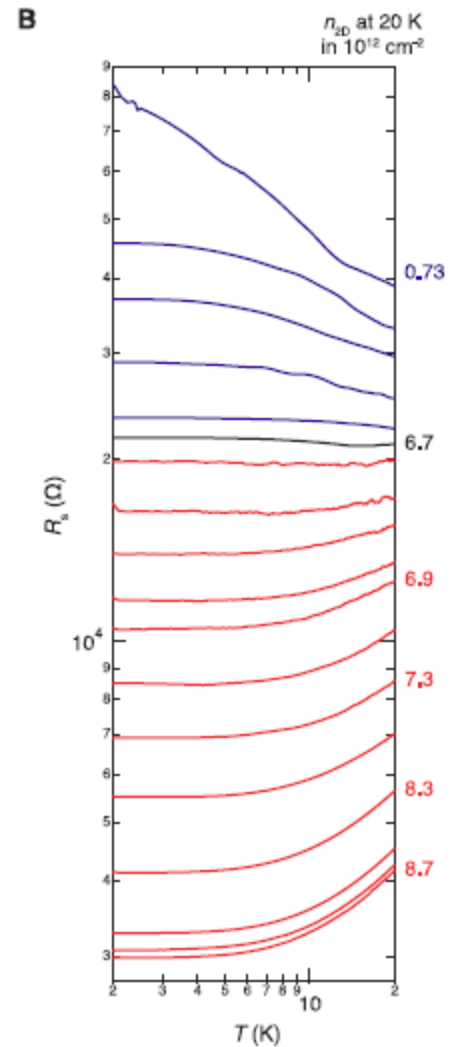
SCIENCE VOL 338 30 NOVEMBER 2012 1193



Evolution of the resistance with gate voltage
(ionic liquid gate and backgate)

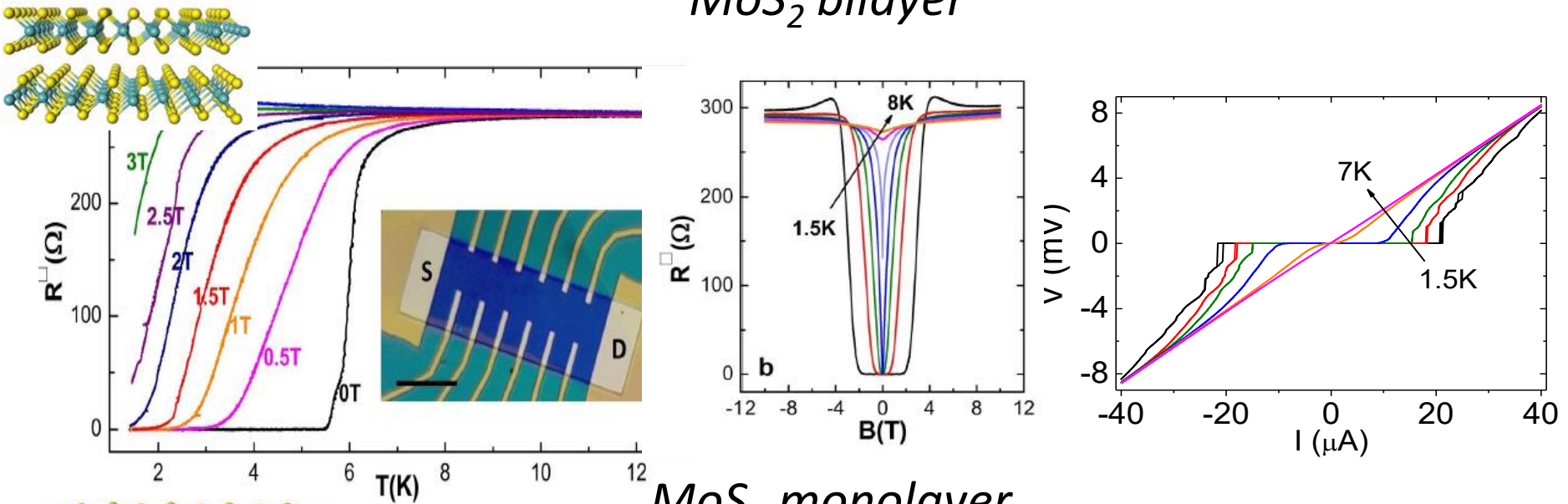


Zero resistance state

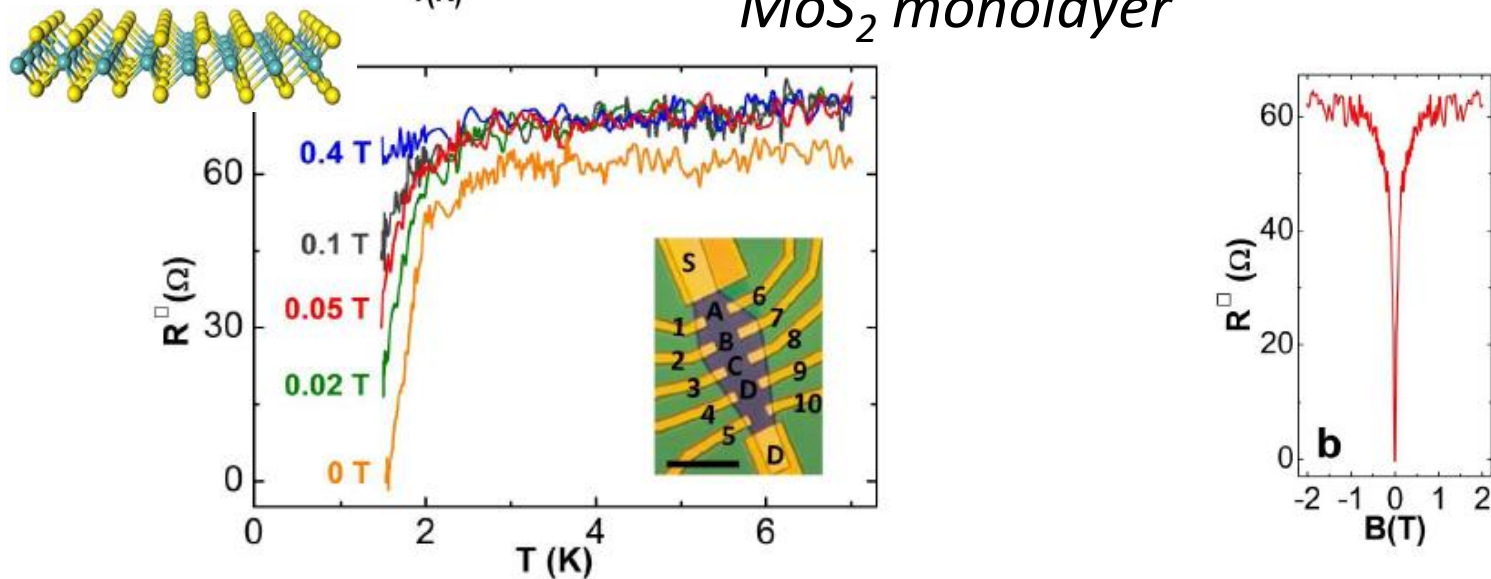


Persists in monolayers

MoS₂ bilayer



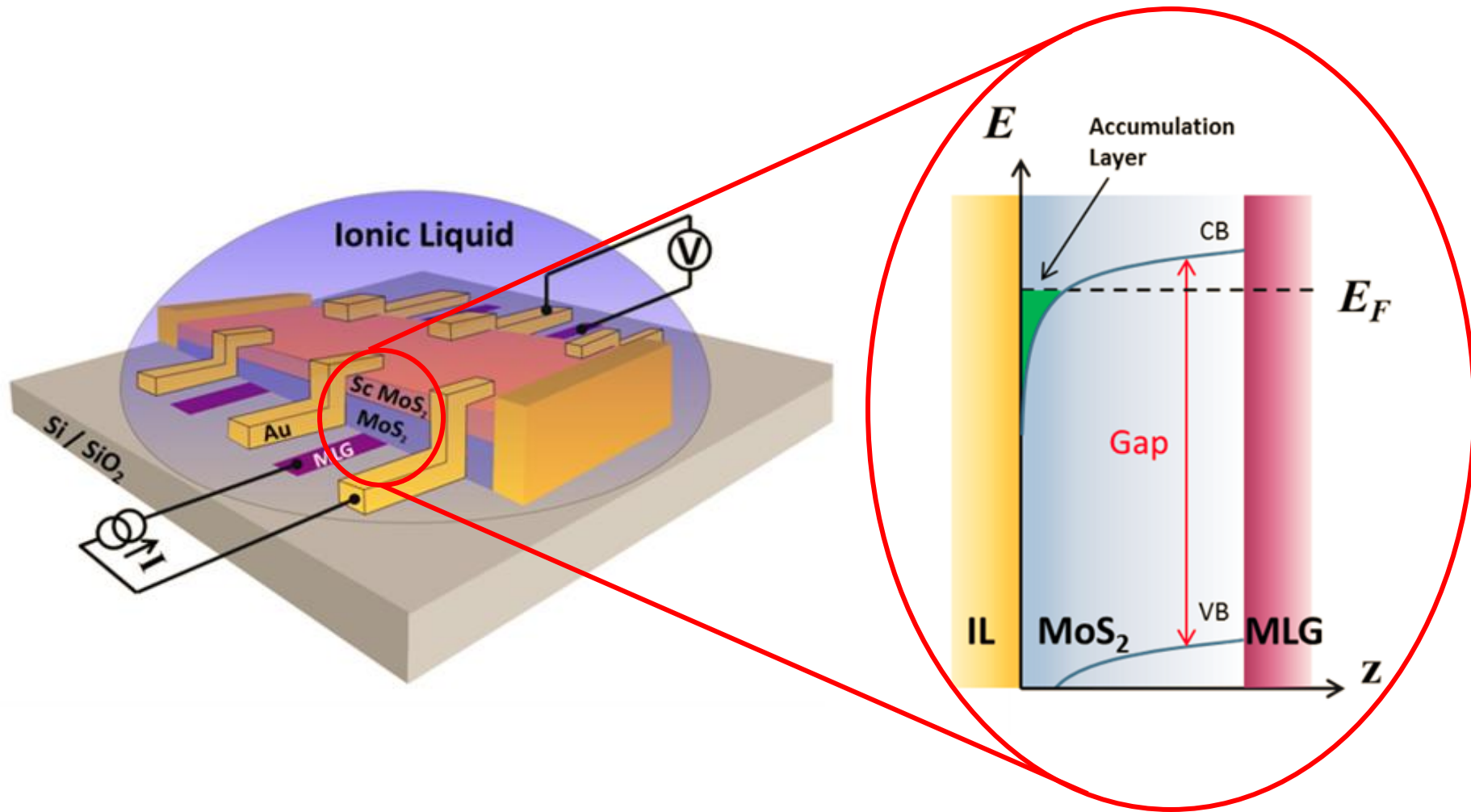
MoS₂ monolayer



Gate-induced superconductivity in 1L MoS₂ with reduced T_c and H_c

Tunneling spectroscopy

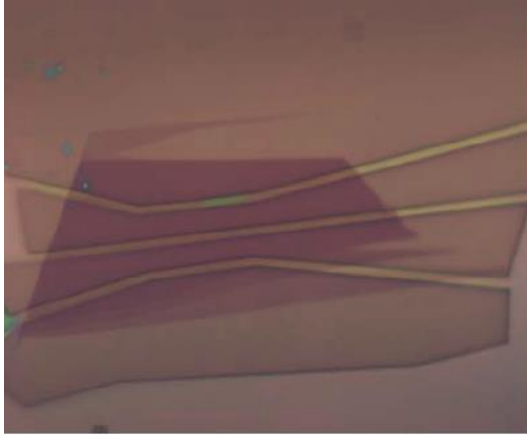
Tunneling into the gate-induced electron accumulation layer



Multilayer graphene as tunneling electrode; MoS₂ as tunnel barrier

An idea of fabrication steps

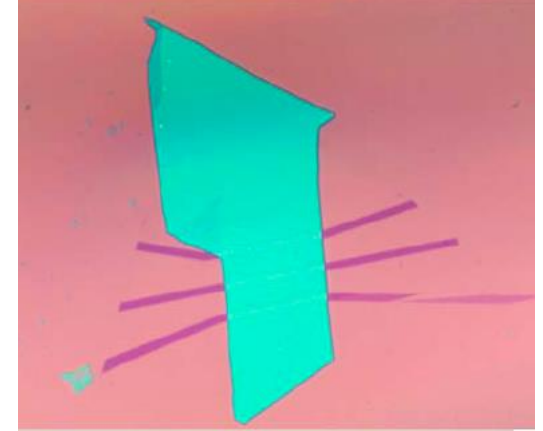
Bottom G multilayer



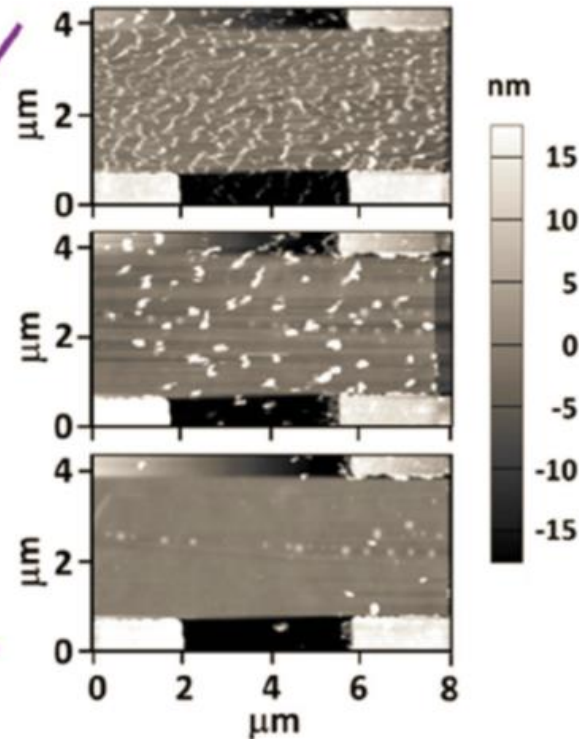
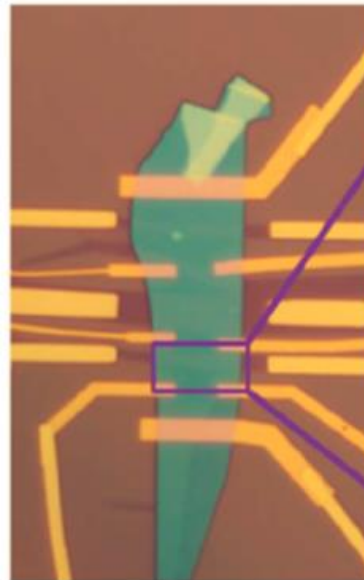
Define tunneling contacts



Transfer MoS₂ multilayer

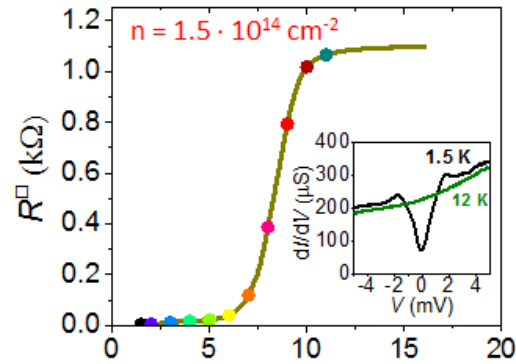


Attach metallic contacts

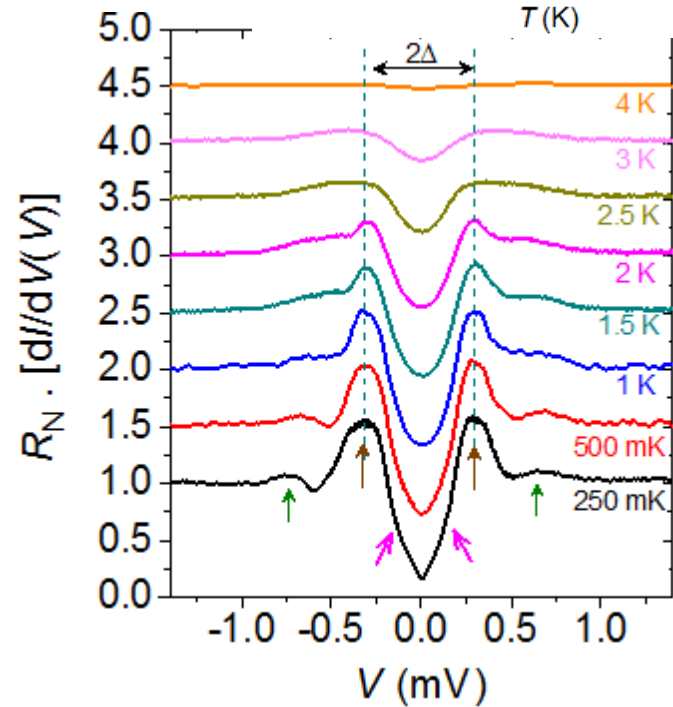
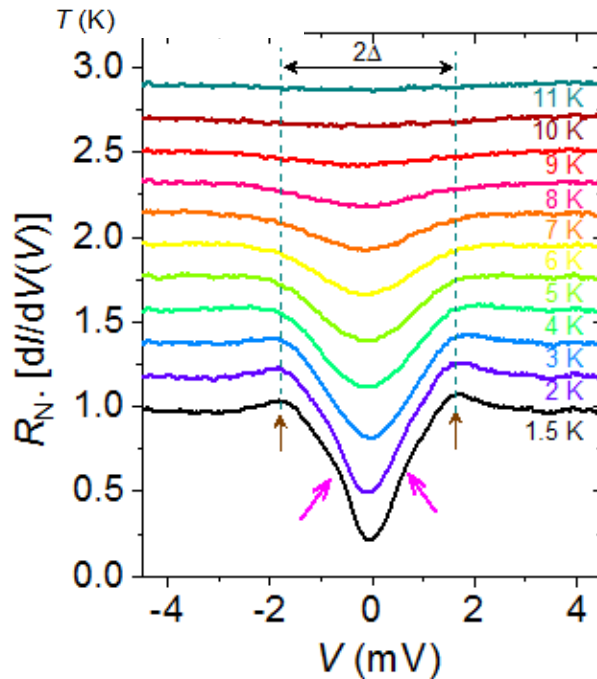
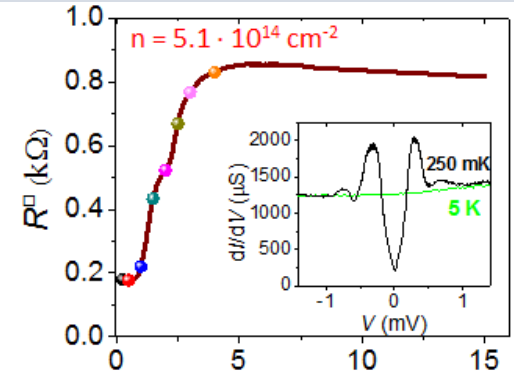


& clean the MoS₂ surface

Tunneling spectroscopy of gate-induced superconductivity



Tunneling spectroscopy
for
 $10^{14} \text{ cm}^{-2} < n < 5 \cdot 10^{14} \text{ cm}^{-2}$



Incomplete DOS suppression & “V-shaped” low-energy DOS
Unconventional superconductivity

2D magnetic materials

Examples

		Interlayer	
		Antiferromagnetic	Ferromagnetic
		$J < 0; J_L > 0$	$J > 0; J_L > 0$
Intralayer	Ferromagnetic	<p>CoPS₃ Ref¹ MnPS₃ Ref²⁻⁵ NiPS₃ Ref⁶⁻⁸</p>	<p>CrI₃ (bulk) Ref^{9,10} CrBr₃ (bulk, few layers) Ref^{11,12} Cr₂Ge₂Te₆ Ref^{13,14}</p>
	Antiferromagnetic	<p>FePS₃ Ref^{20,21} MnPSe₃ Ref³⁵</p>	<p>CrI₃ (few layers) Ref²² CrCl₃ (bulk) Ref³⁷</p>

Green – semiconductor materials; orange - metallic

Does magnetism persists in 2D magnetic materials?

How can we probe it? Is there new physics?

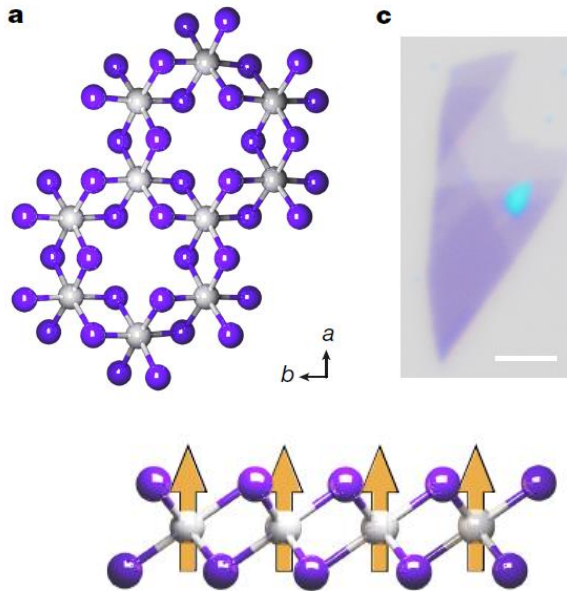
We will discuss experiments on one compound: CrI₃

Magneto-optical Kerr effect

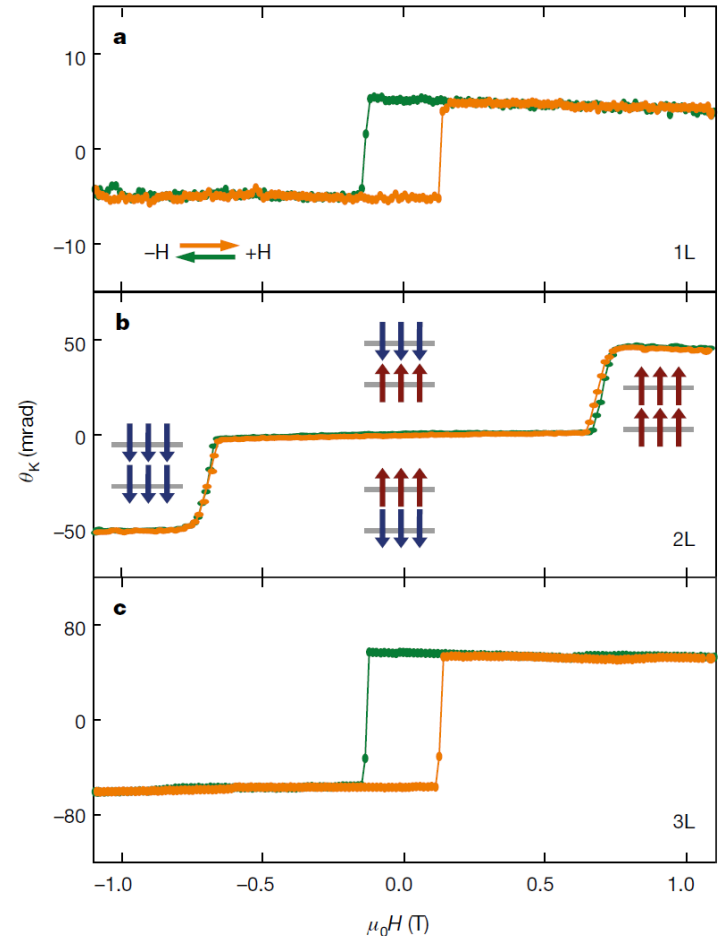
Layer-dependent ferromagnetism in a van der Waals crystal down to the monolayer limit

Bevin Huang^{1*}, Genevieve Clark^{2*}, Efrén Navarro-Moratalla^{3*}, Dahlia R. Klein³, Ran Cheng⁴, Kyle L. Seyler¹, Ding Zhong¹, Emma Schmidgall¹, Michael A. McGuire⁵, David H. Cobden¹, Wang Yao⁶, Di Xiao⁴, Pablo Jarillo-Herrero³ & Xiaodong Xu^{1,2}

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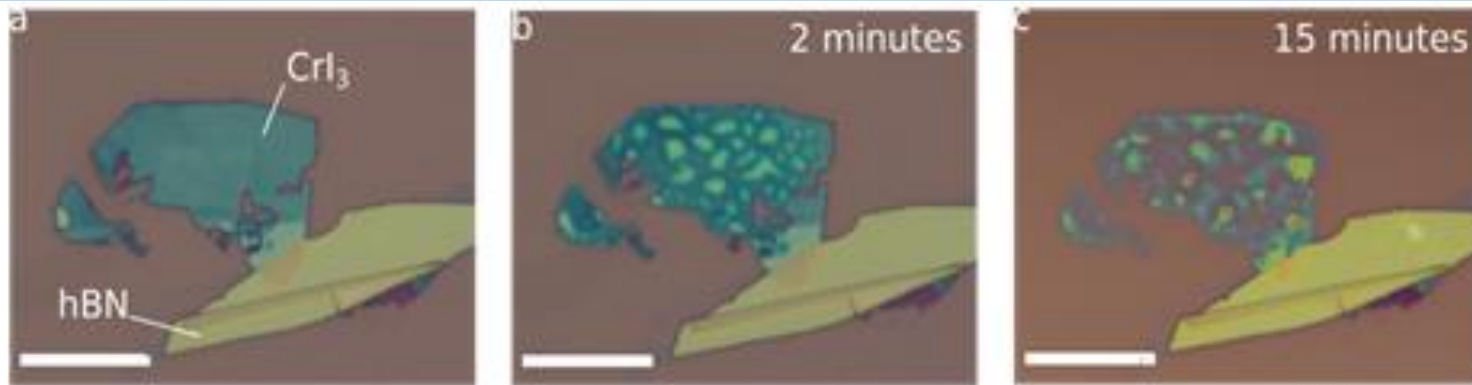


Hysteretic Kerr rotation angle as expected for ferromagnets



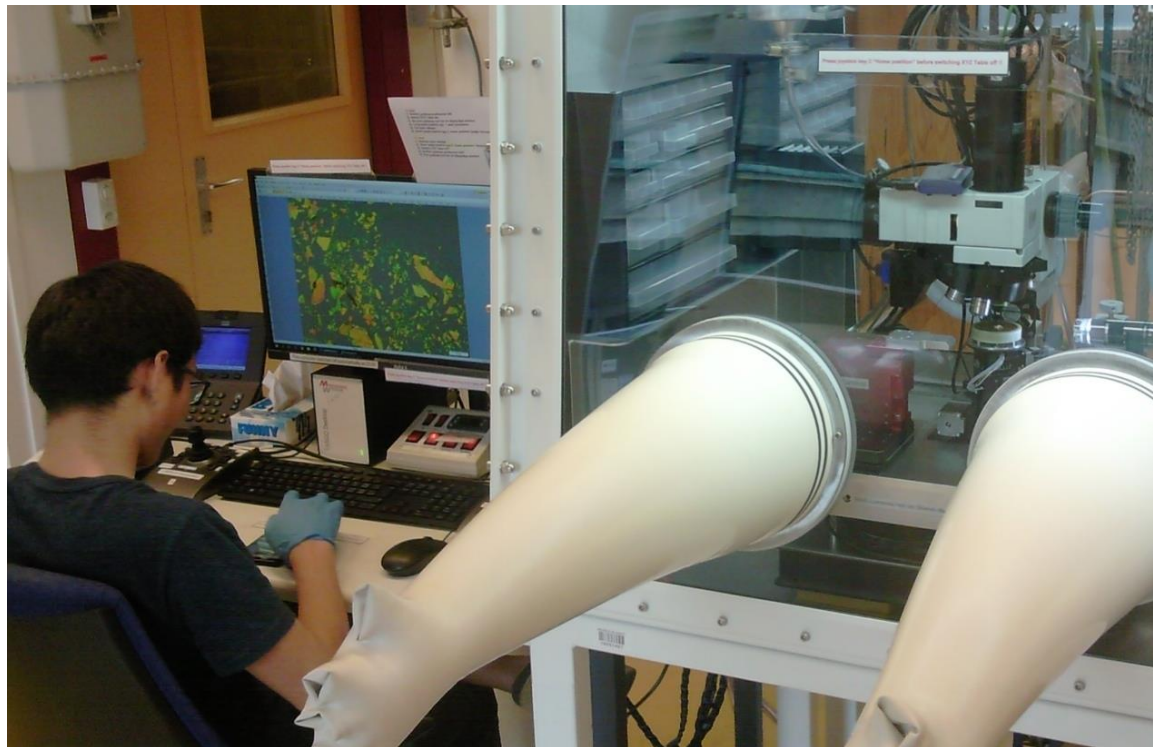
But note: Kerr effect probes broken symmetries not magnetization

Exfoliating/processing/encapsulating in Glove box

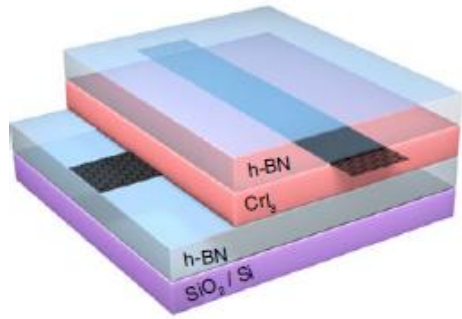


Extremely unstable in air:

Thin crystals (even 50 nm) dissolve in a few minutes

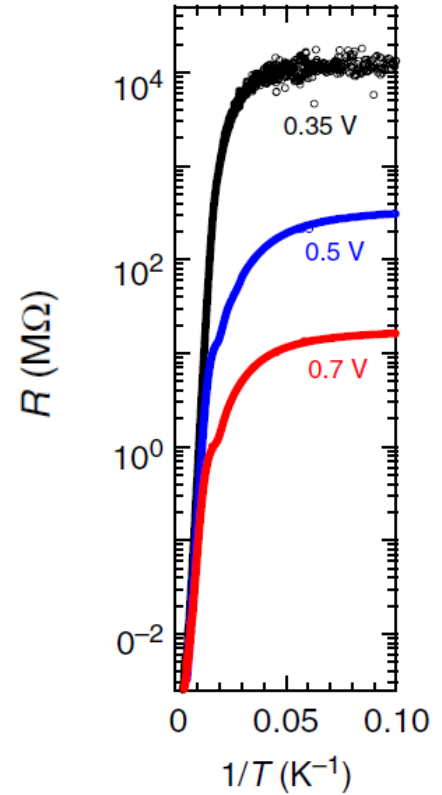
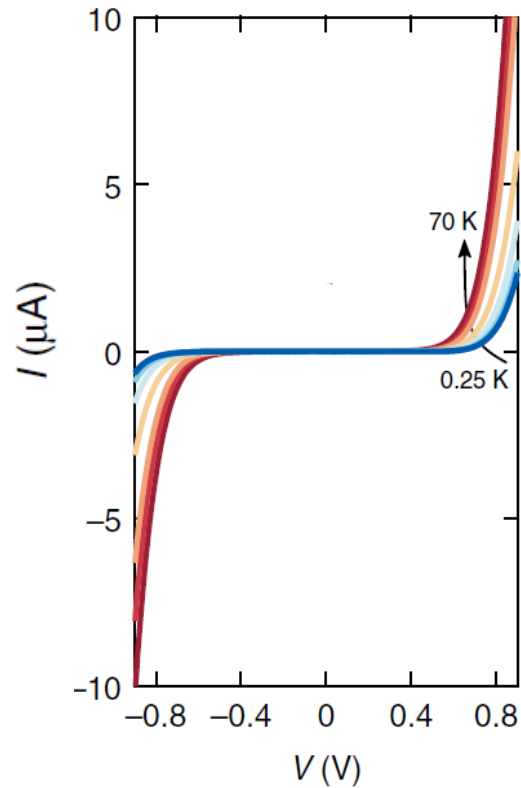
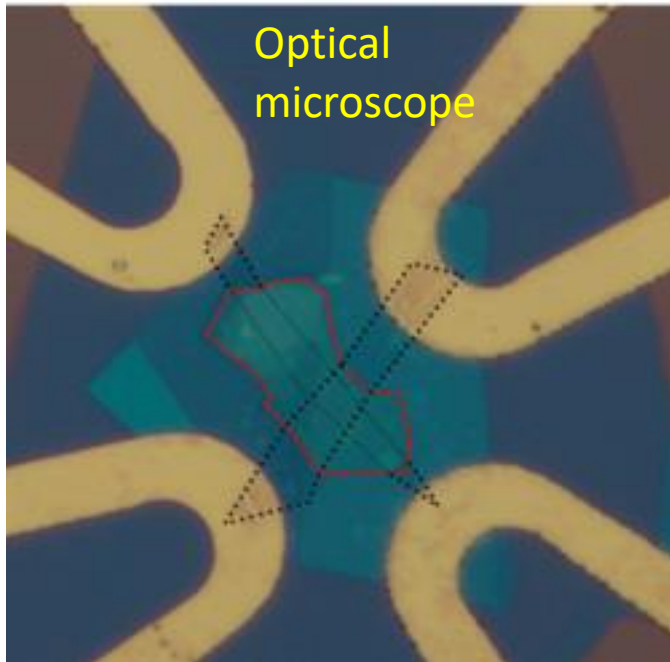


CrI₃ tunnel barriers



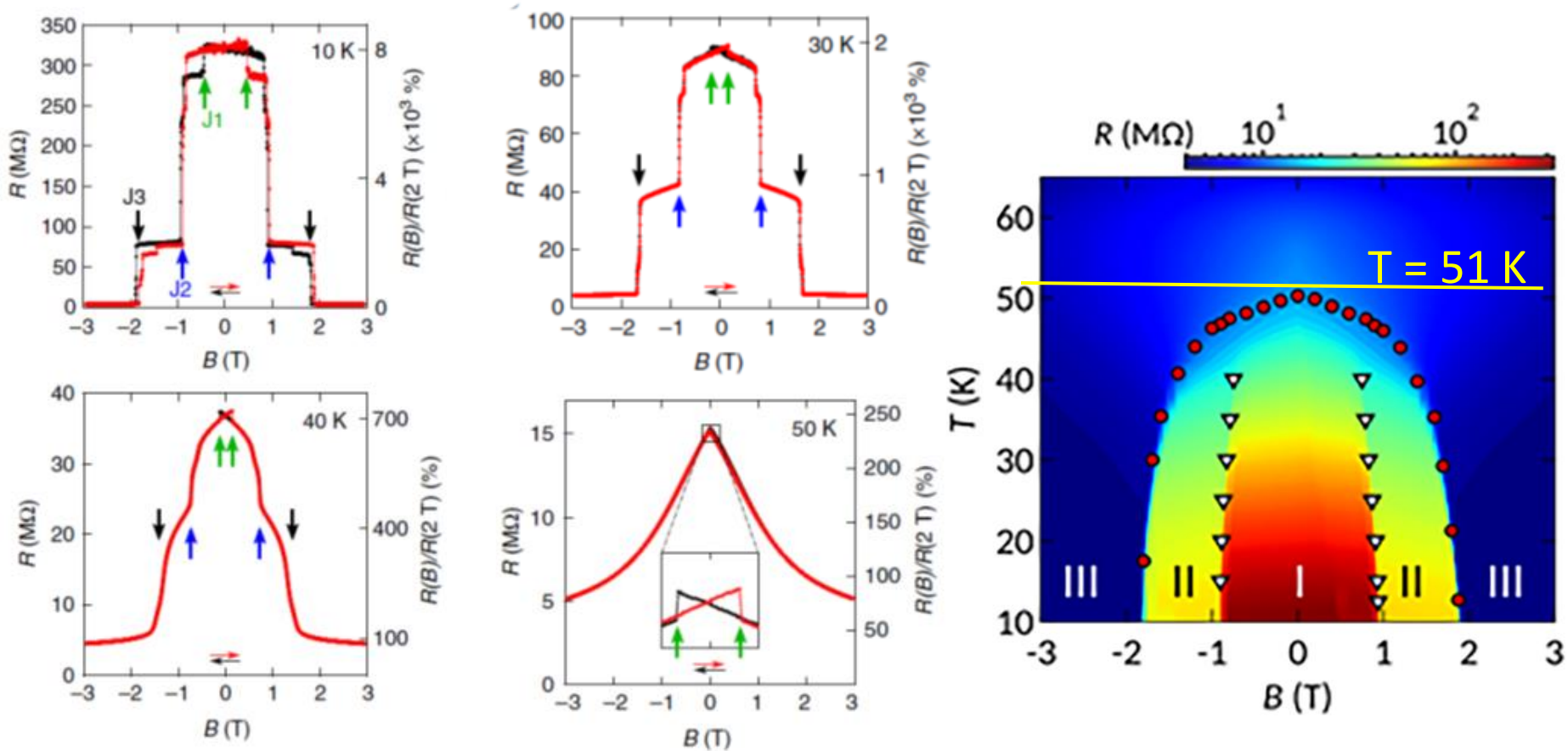
*Thin CrI₃ as tunnel barrier
between graphene contacts*

Tunneling



Tunneling Magnetoresistance

Giant tunneling magneto-resistance: 100 x at $B = 2T$

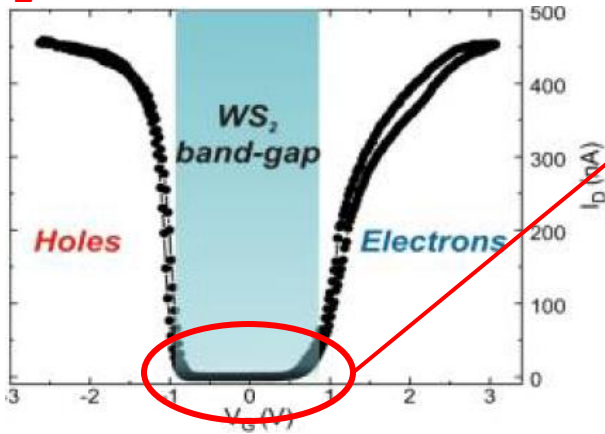


For comparison:
common tunneling spin-valves = 2 x

Extracting magnetic
phase diagram from
tunneling magnetoresistance

Monolayer WTe_2 : topological insulator with edge transport

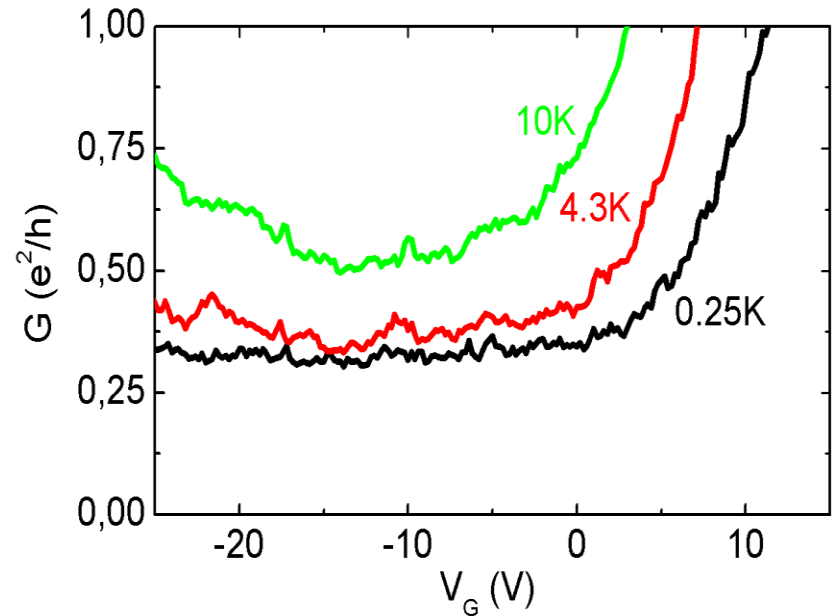
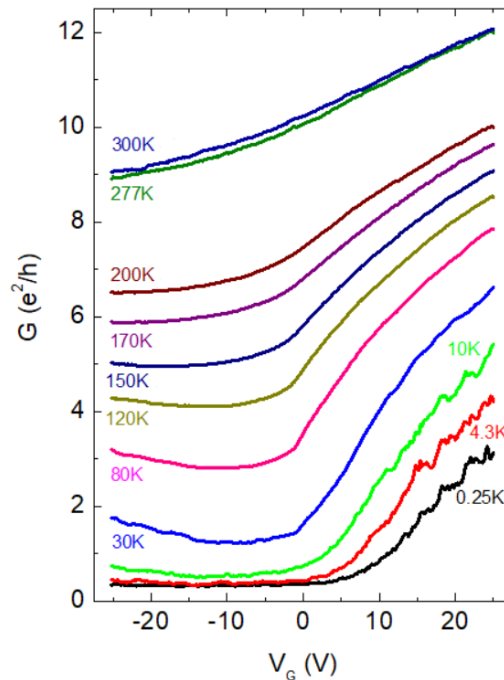
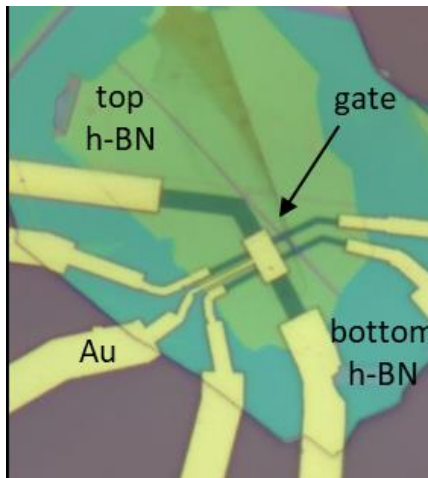
WS_2 = Semiconductor = trivial insulator



Conductance vanishes

(exponentially small $\propto e^{-\frac{\Delta}{2kT}}$)

WTe_2 = topological insulator

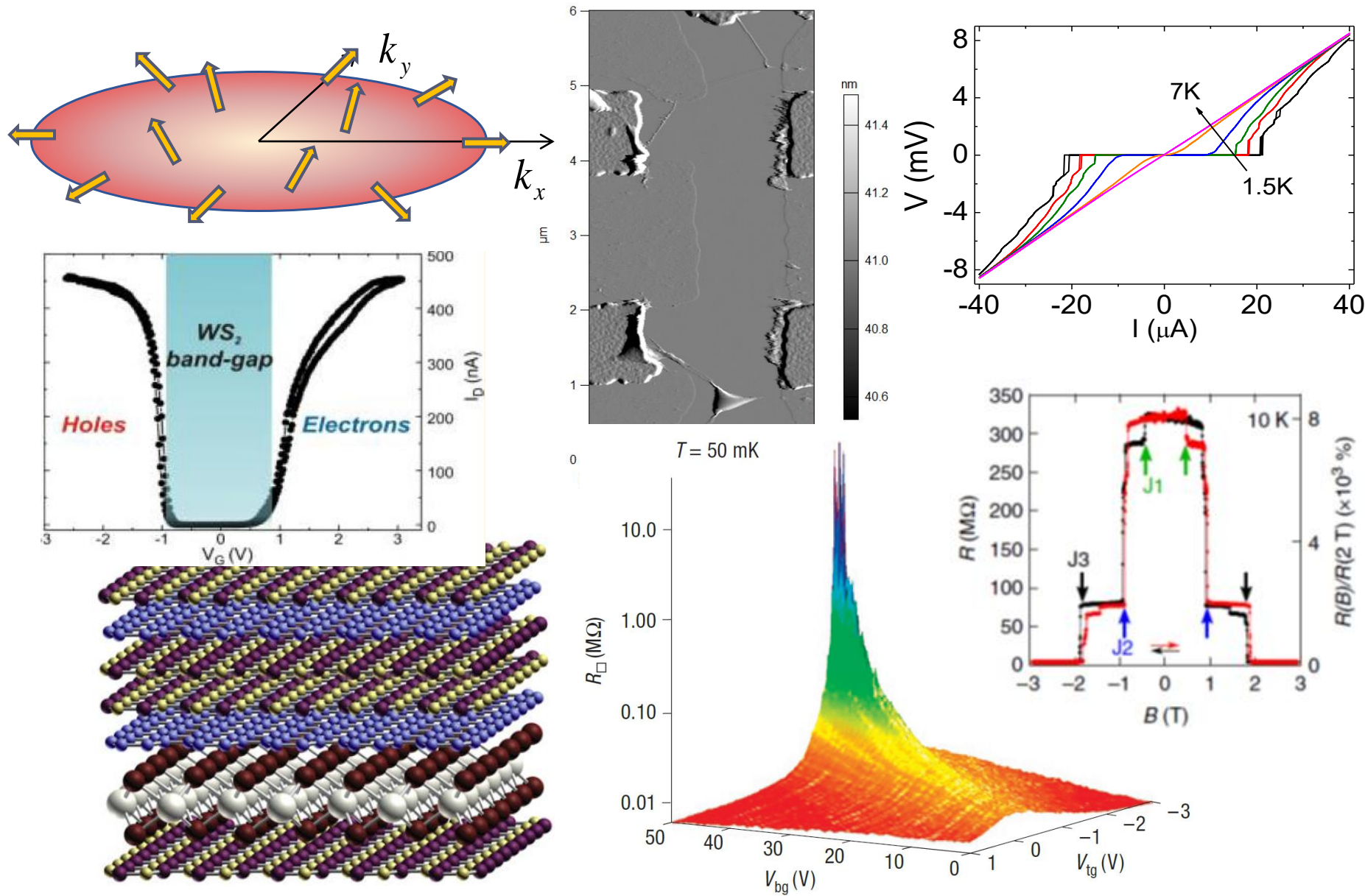


Conductance at low T :

$$G \sim \frac{e^2}{h}$$

Topological insulator = Edge conductance

The exploration of atomically thin crystals has only just started



This is a vast and largely unexplored field of research