

Semiconductor Devices II

Chapter 2: Introduction to 2D materials

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ÉCOLE POLYTECHNIQUE
FÉDÉRALE DE LAUSANNE

Introduction

Why semiconducting nanostructures for nanoelectronics

Historic overview

- Graphene
- Transition metal dichalcogenides and 2D materials

Charged impurities

- Point defects
- Screening and its signatures in electrical transport
- Disorder engineering

Material growth

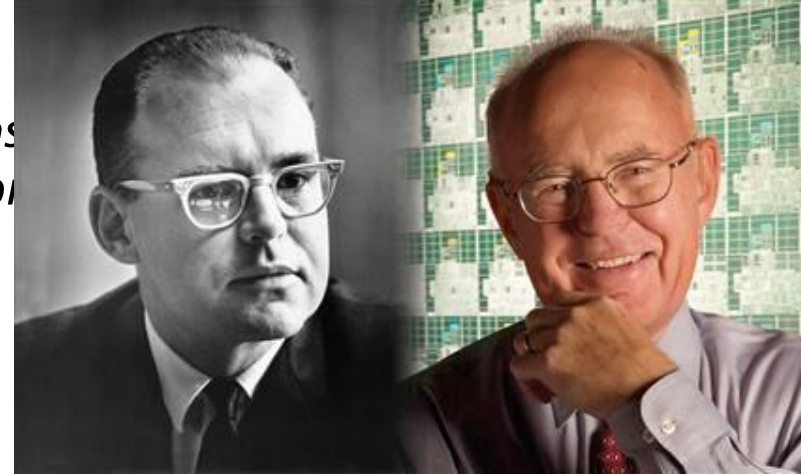
- CVD

Electrical contacts to 2D materials

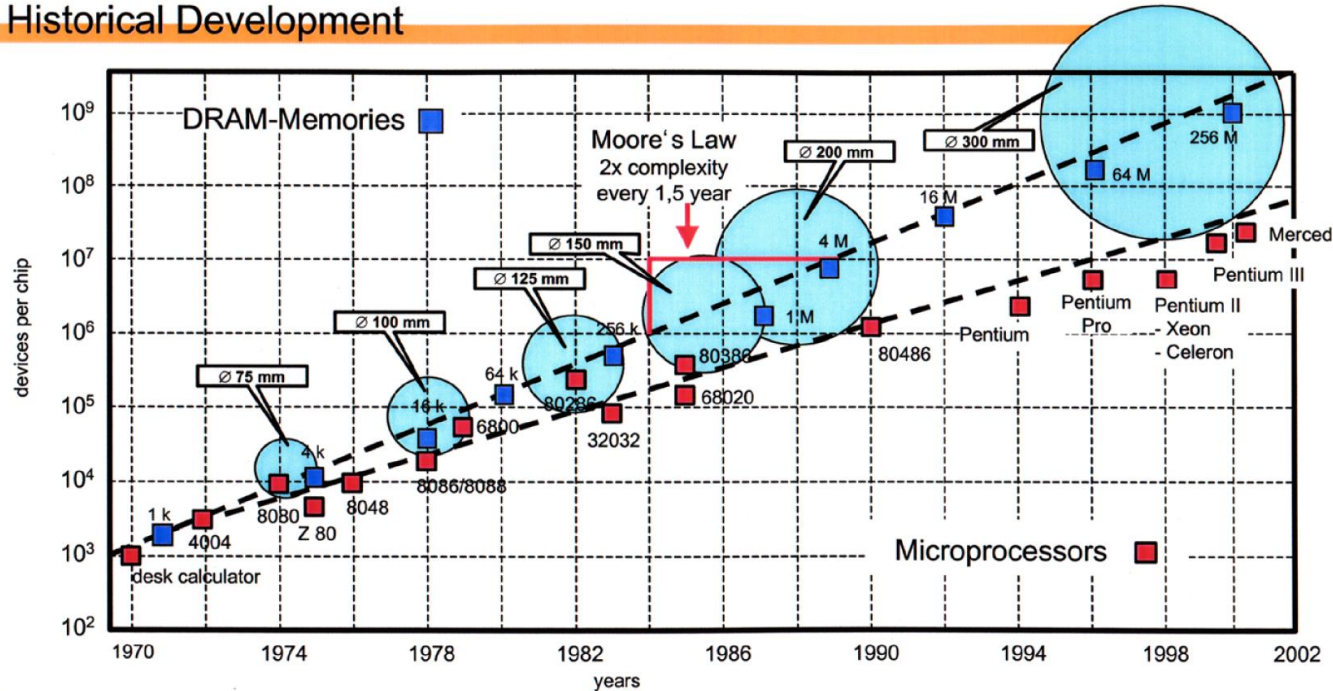
Moore's Law

Gordon Moore, co-founder of Intel stated in 1965:

"The number of transistors that can be inexpensively integrated into a silicon circuit is increasing exponentially, doubling approximately every two years."



Historical Development



Dissipated Heat

Processor coolers 20 years ago and now

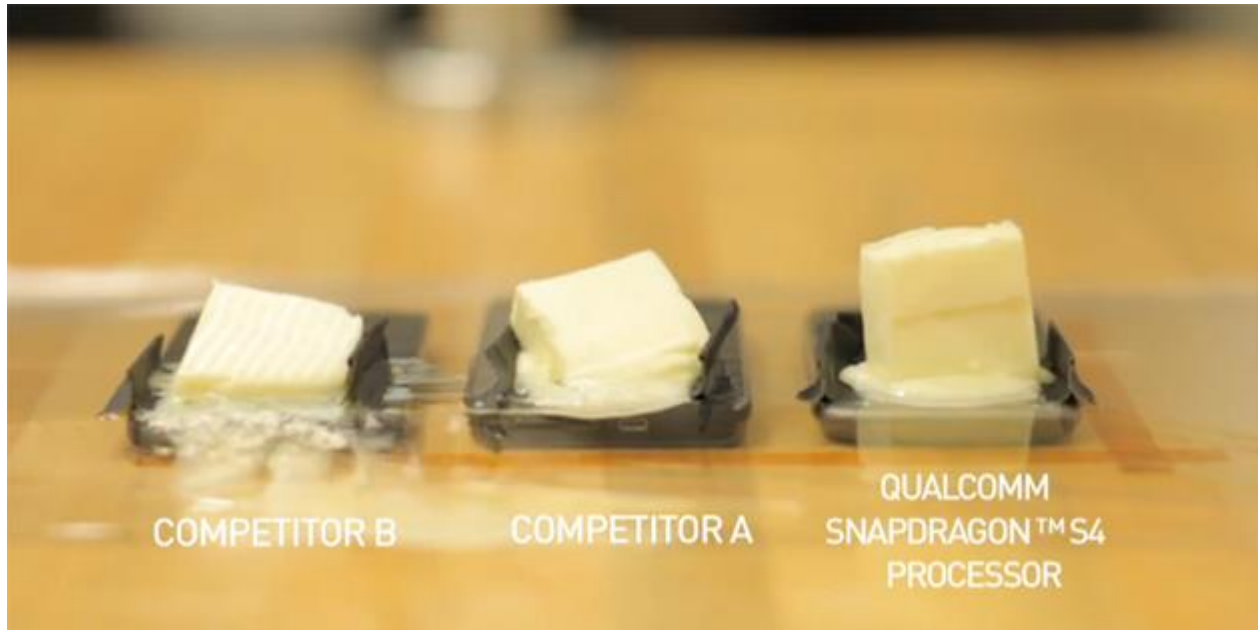


Dissipated Heat

Frying eggs on processors



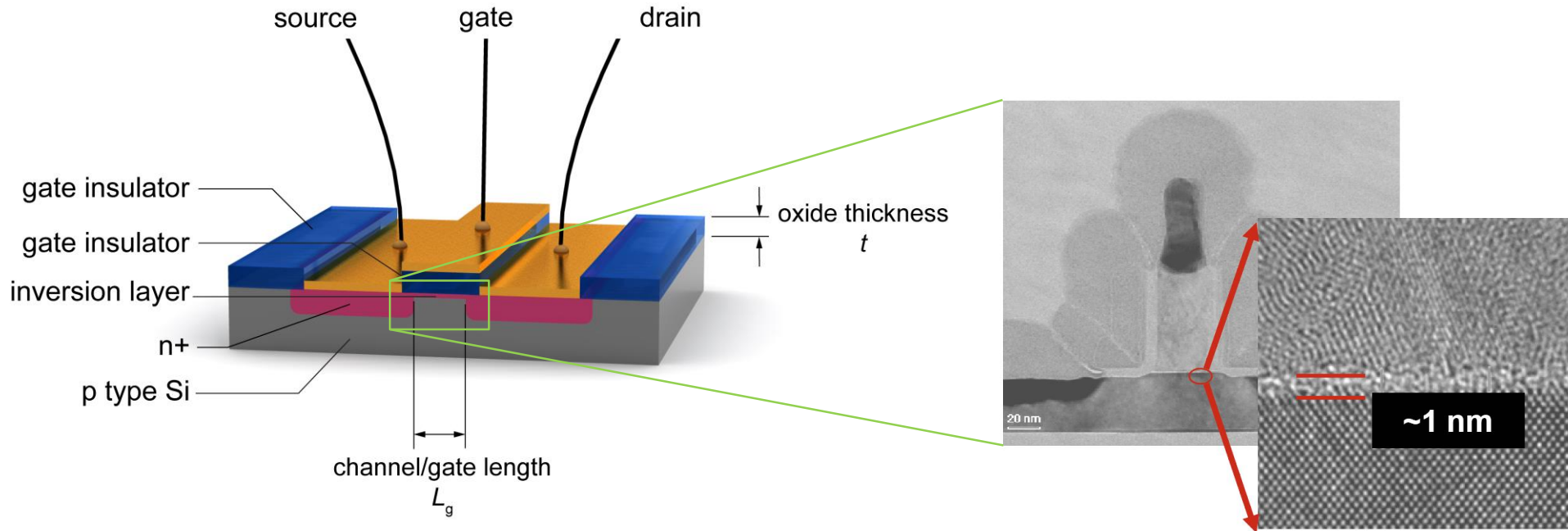
Melting-butter Benchmark



Source: Android andMe.com

MOSFET

Metal–oxide–semiconductor field-effect transistor (MOSFET)



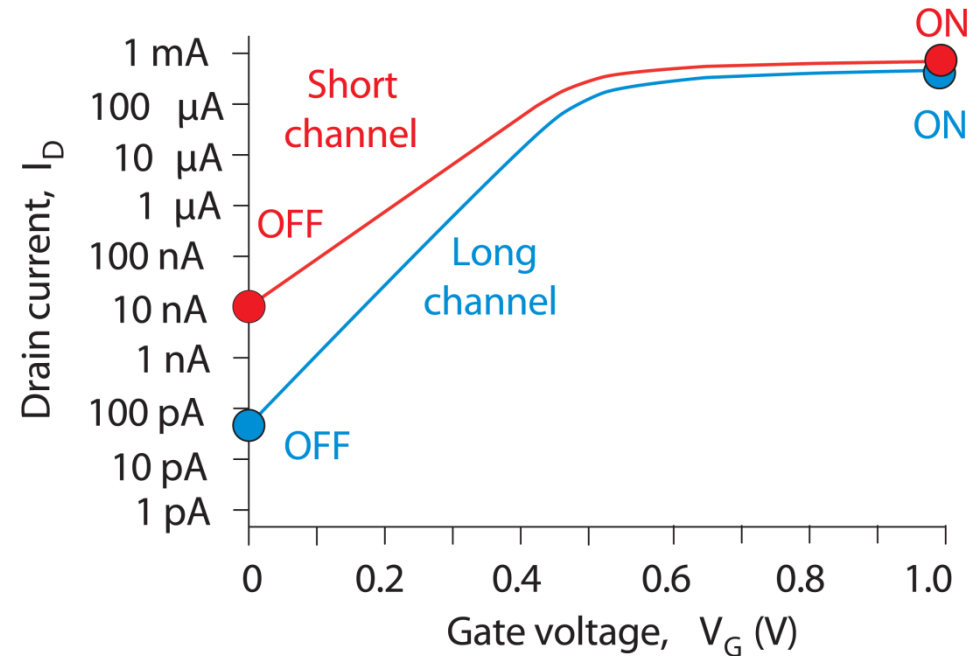
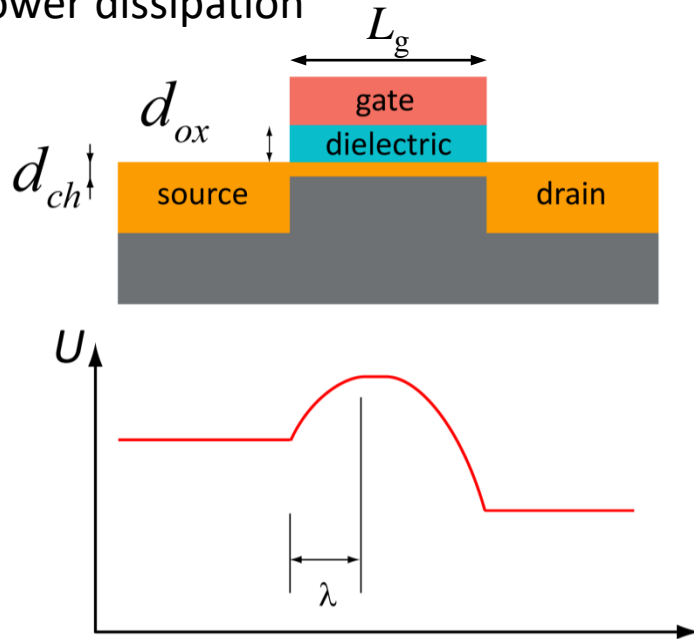
Approaching atomistic limits

Channel length in Intel processors:

14 nm	2014
10 nm	2017
7 nm	2018?

Why Heat Dissipation in Small Transistors?

Planar MOSFET – short channel effects; standby power dissipation



$$\lambda = \sqrt{\frac{\epsilon_{ch}}{\epsilon_{ox}} d_{ox} d_{ch}}$$

$\epsilon(\text{Si})=11.9$

To deplete the channel: L_g at least $3-5 \times \lambda$

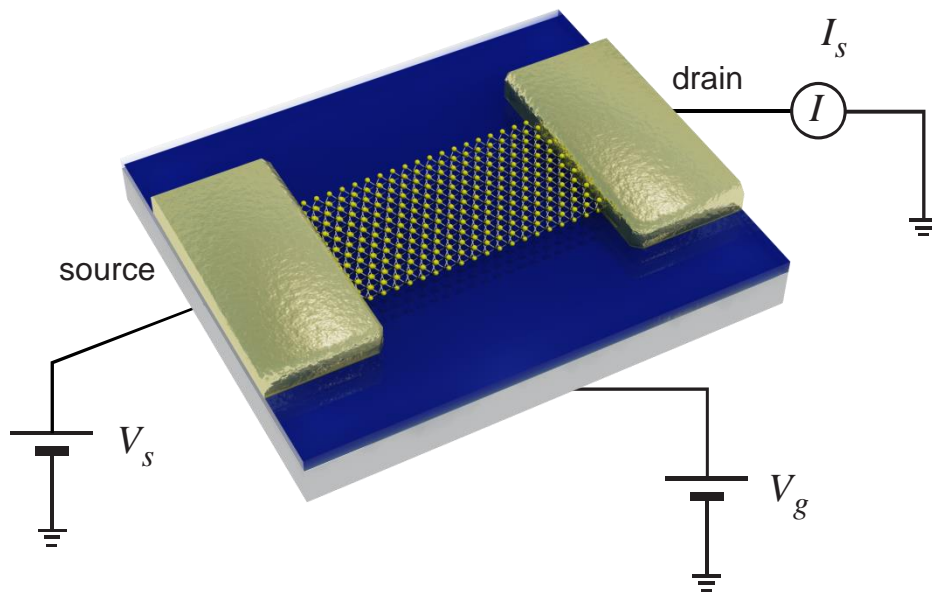
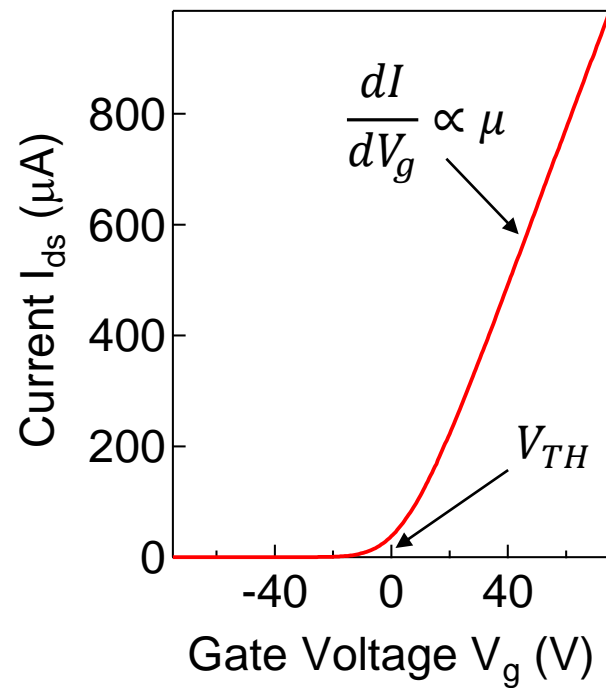
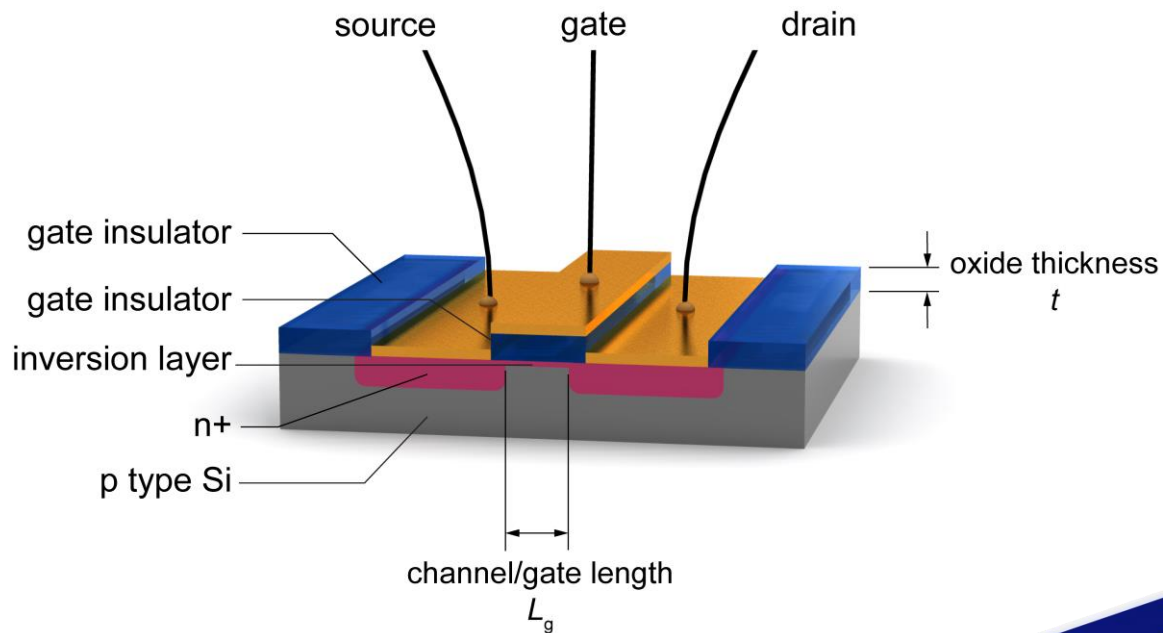
Example:

2nm thin Si, 1nm SiO_2 : $L_g > 10\text{nm}$

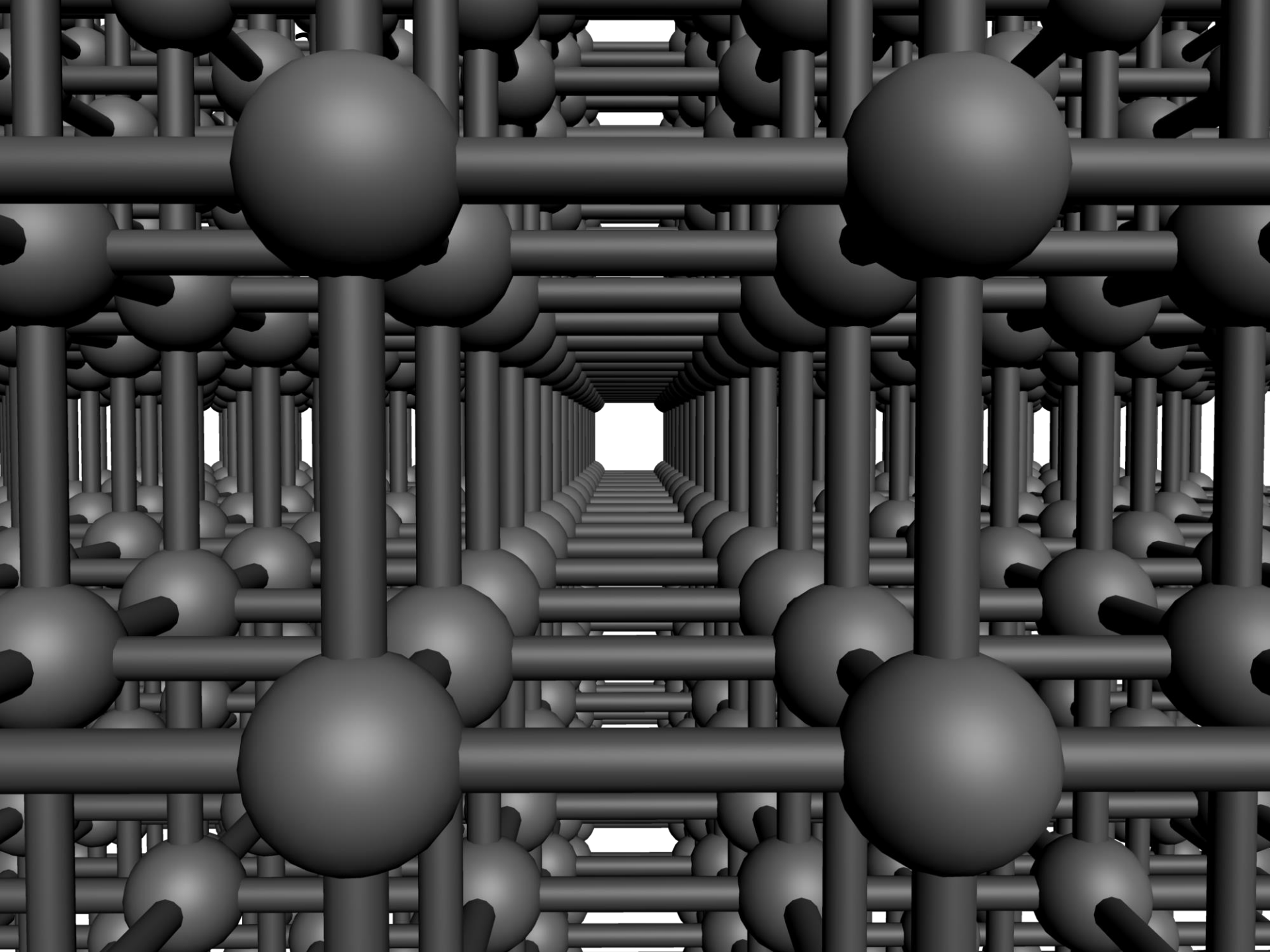
Ferain et al., Nature 479, 310 (2011)

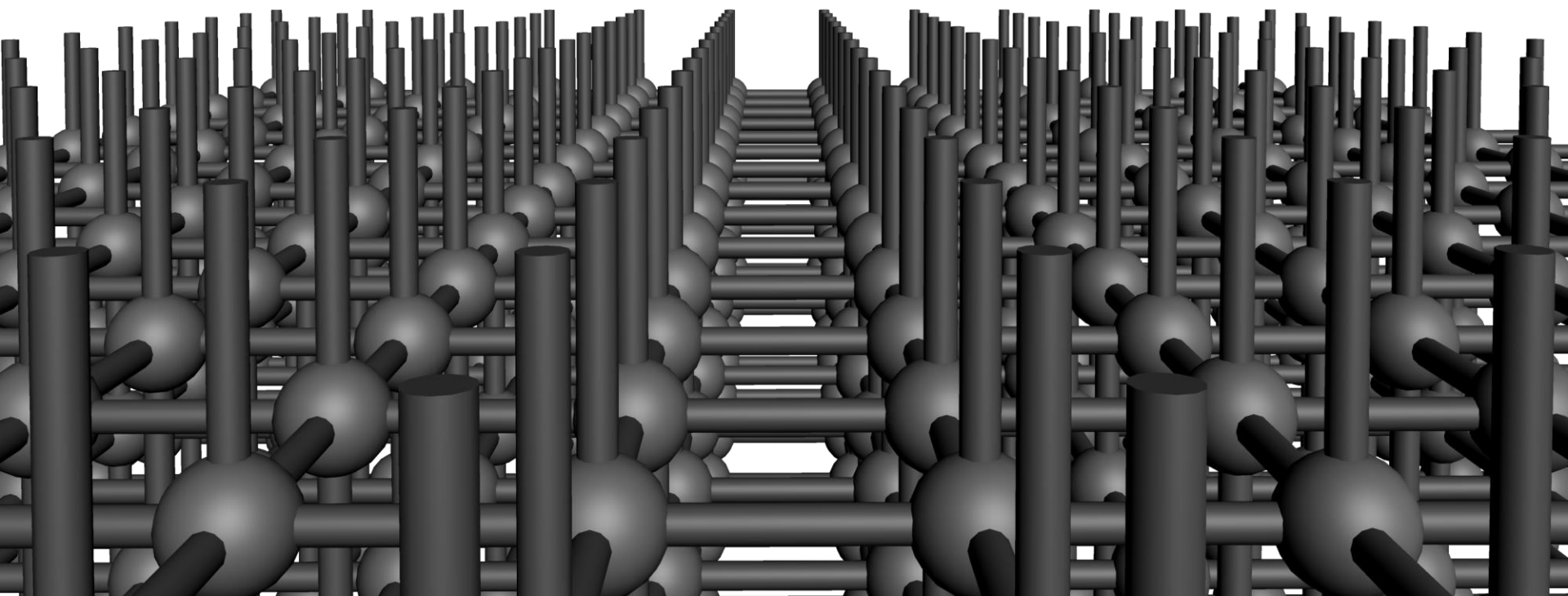
Colinge, Sol. State El. 48, 897 (2004)

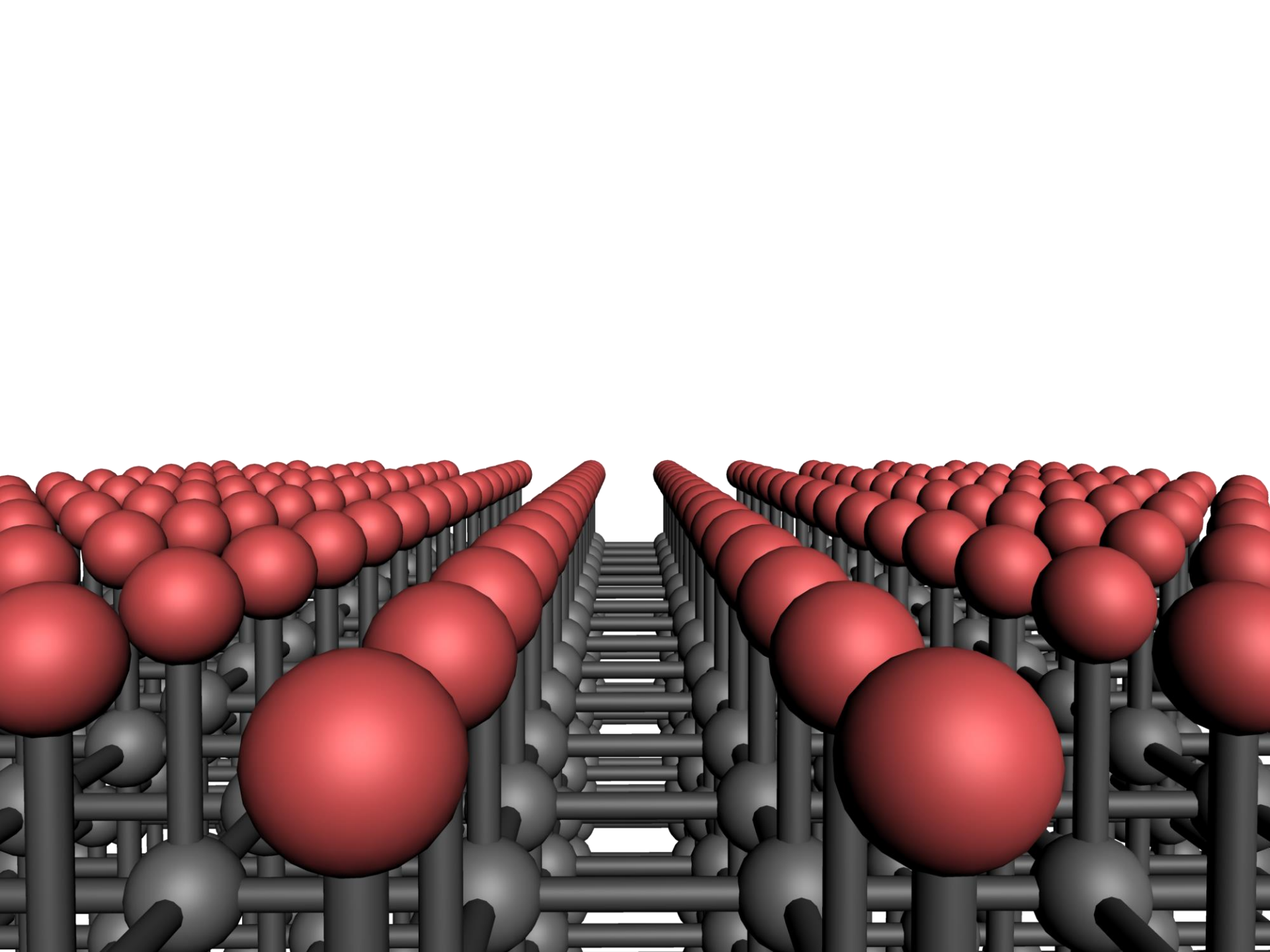
FETs Based on Nanomaterials



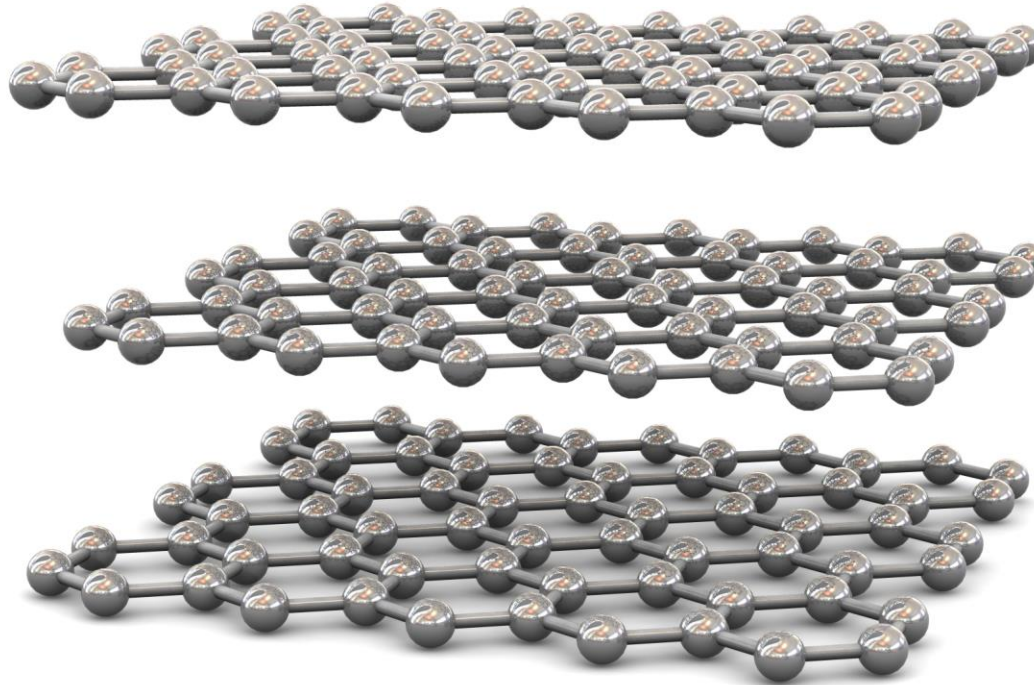
FET with a nanomaterial channel



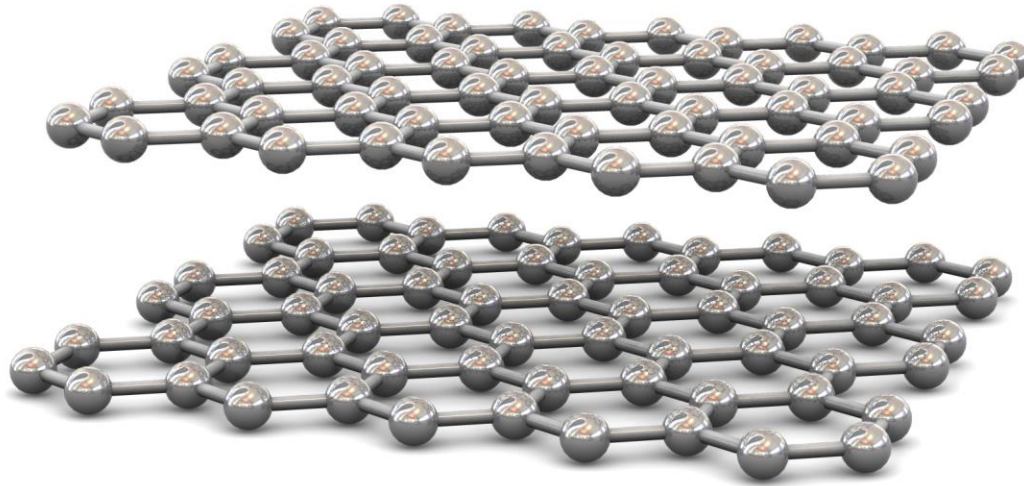




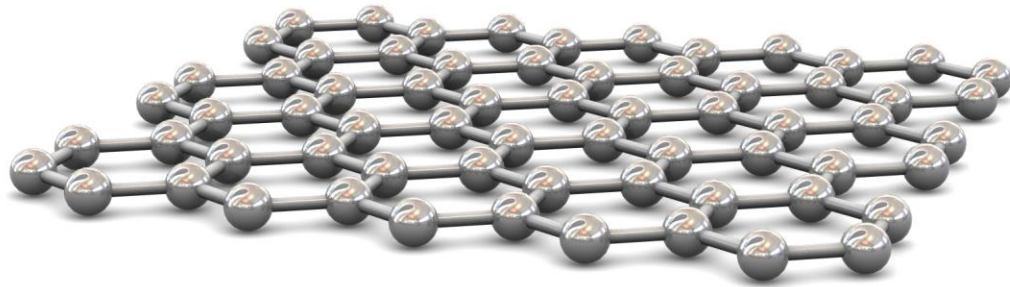
Graphite and Graphene



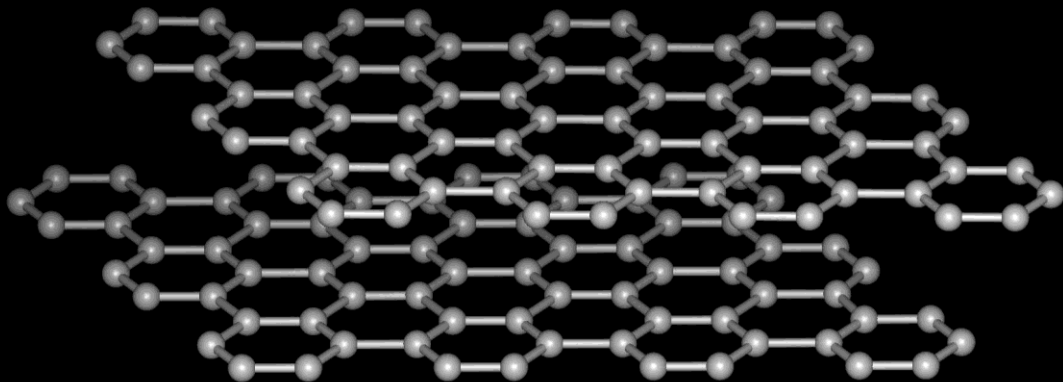
Graphite and Graphene



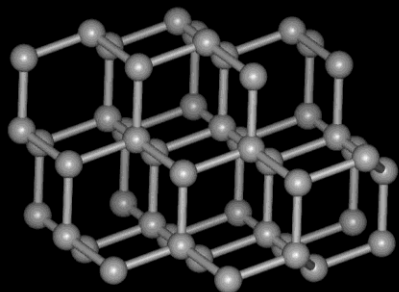
Graphite and Graphene



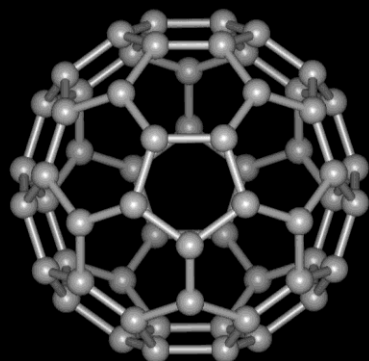
(Some) Carbon Nanostructures



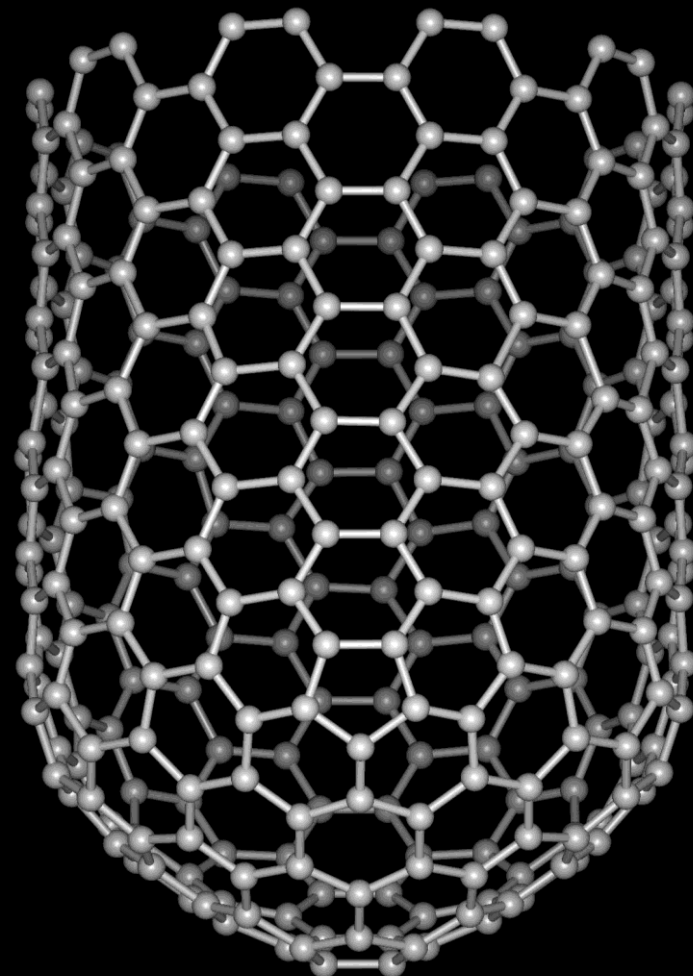
graphite



diamond



C_{60}
"buckyball"



nanotubes

Dimensions in Geometry and Semiconductor Physics

Geometry

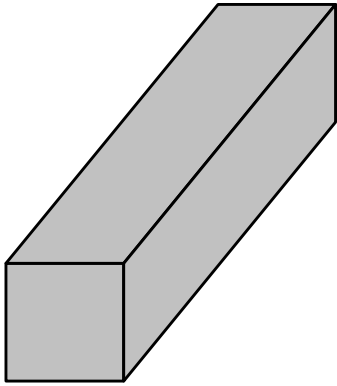
- Refers to the system size
- Planes (2D), lines (1D), dots (0D)

Semiconductor Physics

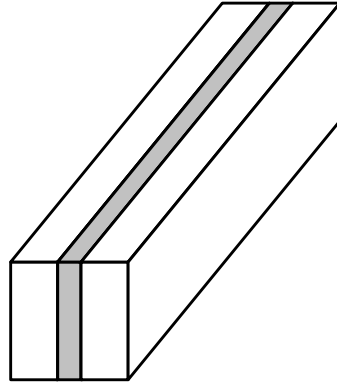
- Refers to the free motion of charge carriers
- Can be constrained due to quantum confinement
- Quantum wells (2D), quantum wires (1D), quantum dots (0D)

Dimensions in Semiconductor Physics

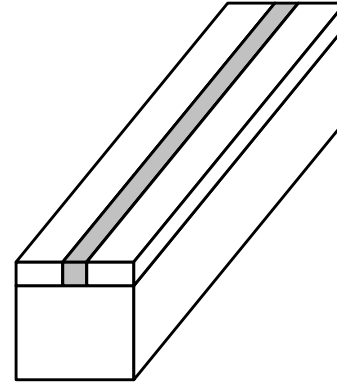
3D



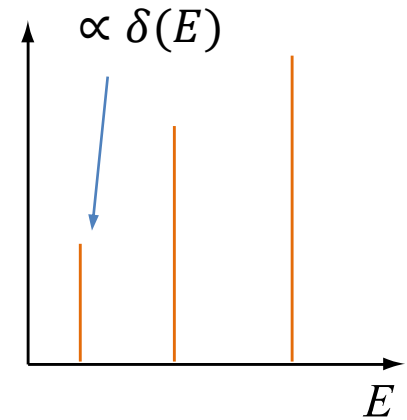
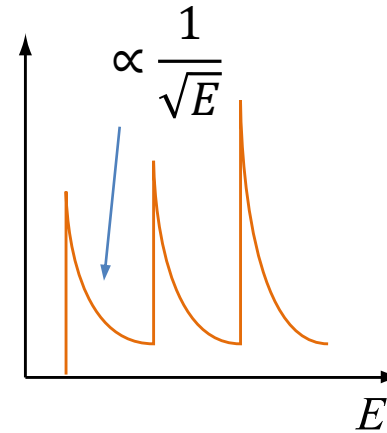
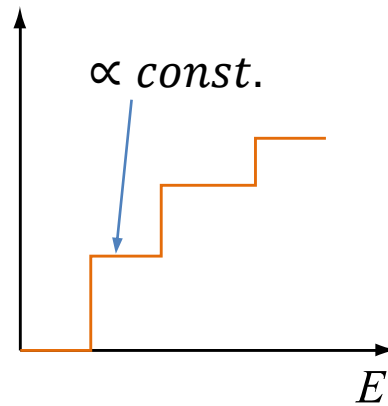
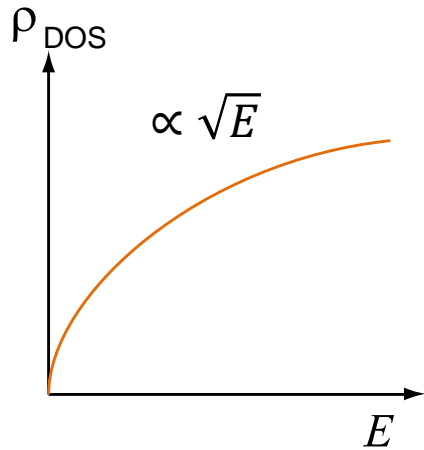
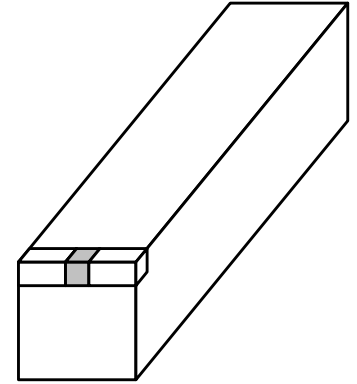
2D



1D



0D



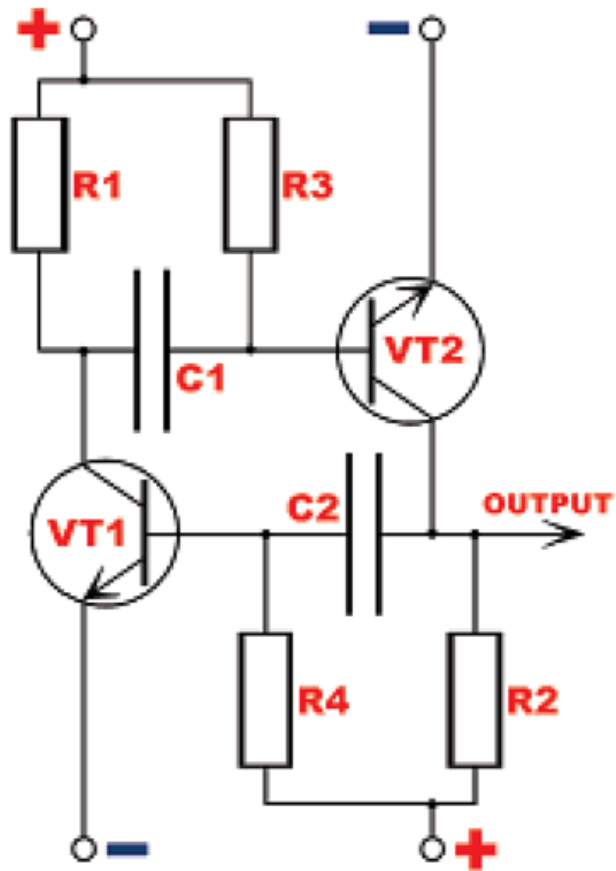
assuming $E = \frac{\hbar^2 k^2}{2m}$

→ Exercise session today

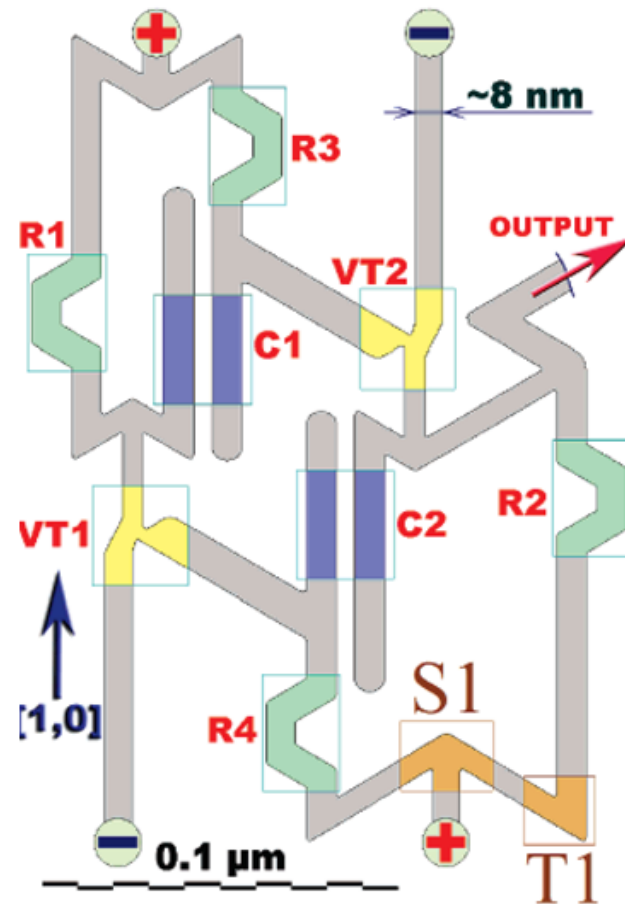
2D Circuits

Example: Flip-flop circuit

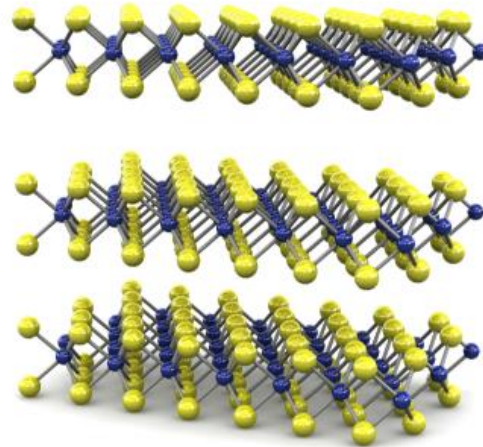
Circuit diagram



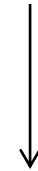
Graphene circuit



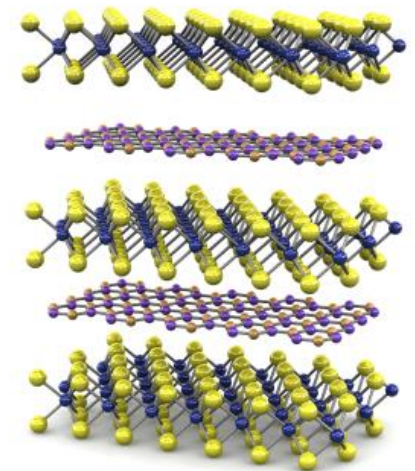
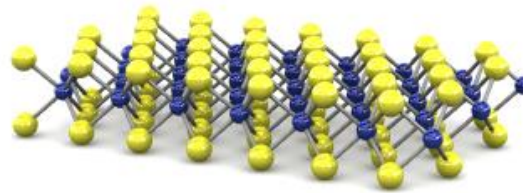
2D Materials: Wide Range of Geometries



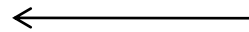
3D
Crystal



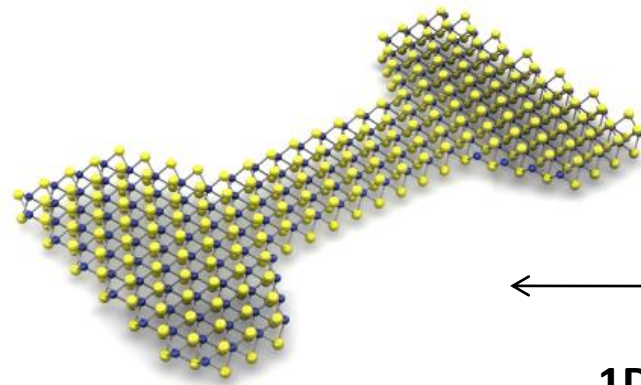
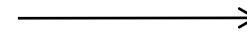
2D
Nanolayer



3D version 2.0
Heterostructure

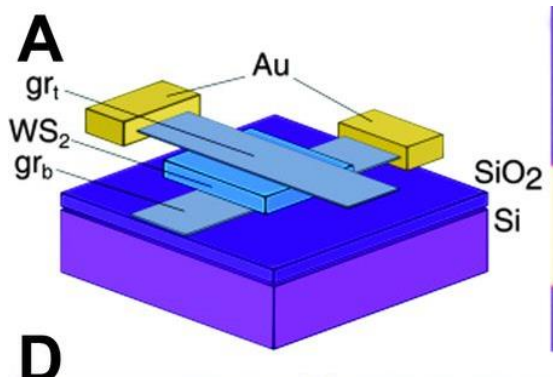
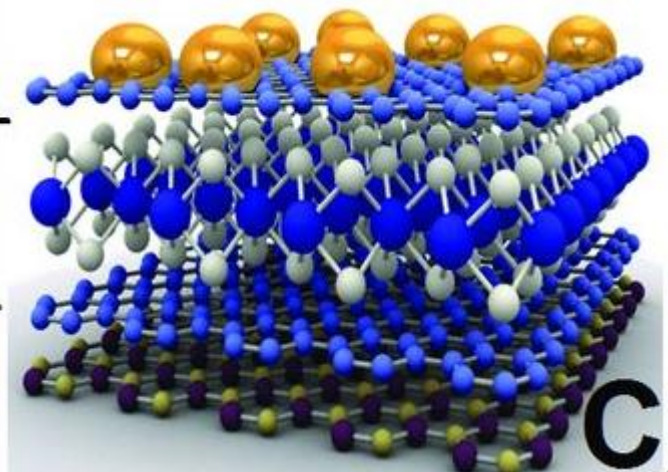


1D
Nanoribbon



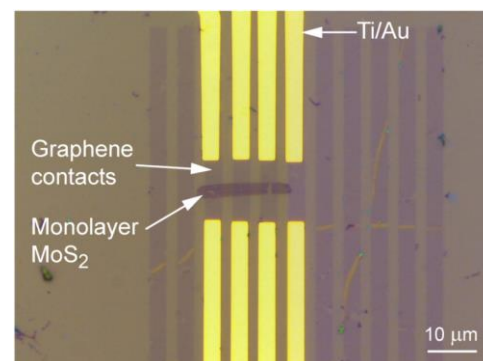
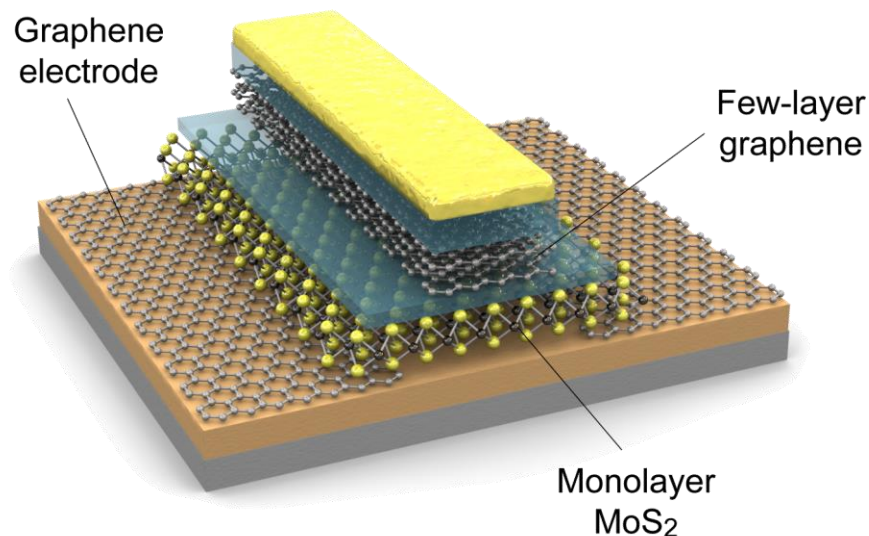
Heterostructures Based on 2D Materials

Vertical: FETs, solar cells



Britnell, Novoselov et al.
Science 340, 1311 (2013)

Lateral/vertical: Flash memory



Bertolazzi, Krasnozhan, Kis
ACS Nano (2013)

Early Attempts

Graphene in 3-Dimensions: Towards Graphite Origami

By Thomas W. Ebbesen* and Hidefumi Hiura

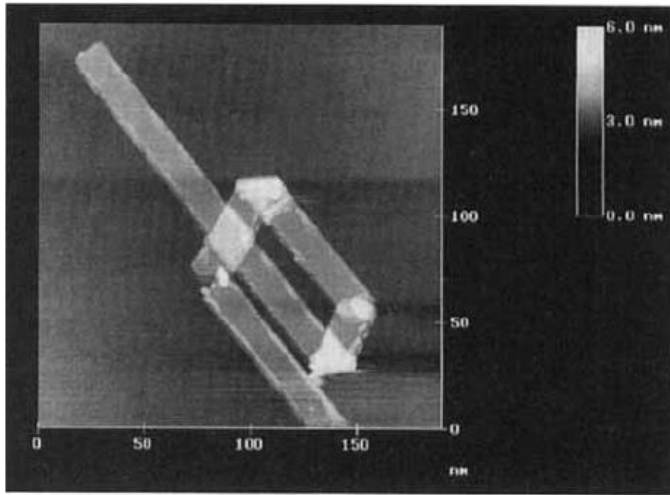


Fig. 1. AFM picture of a graphitic ribbon folded 4 times on the surface of HOPG reminiscent of origami.

AFM image of a folded
graphitic ribbon

Ebbesen et al., Adv. Mater. 7, 582 (1995)

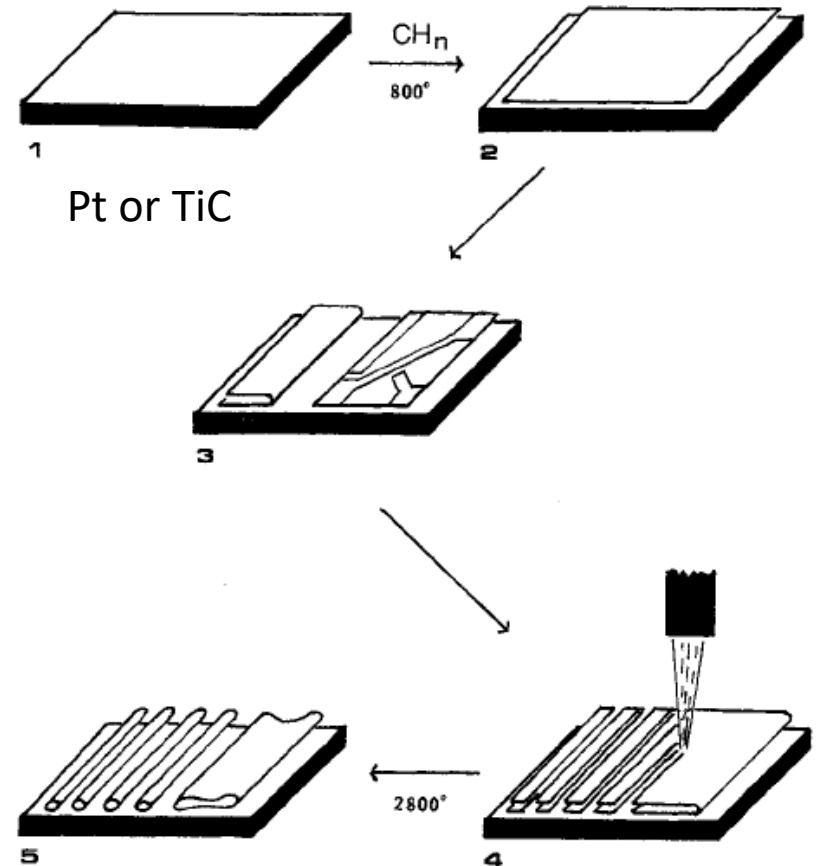


Fig. 6. Schematic diagram of possible approaches for fabricating carbon structures by design (see text).

Proposed device fabrication
procedure

Patterning of highly oriented pyrolytic graphite by oxygen plasma etching

Xuekun Lu,^{a)} Hui Huang, Nikolay Nemchuk, and Rodney S. Ruoff^{b)}
Department of Physics, Washington University, CB1105, St. Louis, Missouri 63130

(Received 18 January 1999; accepted for publication 18 May 1999)

We were motivated to pattern HOPG because of our interest in the mechanical strength of graphite in the basal plane, which has not been determined to date. Mechanical strengths as high as ~ 300 GPa for defect-free regions are theoretically predicted from local-density approximation cal-

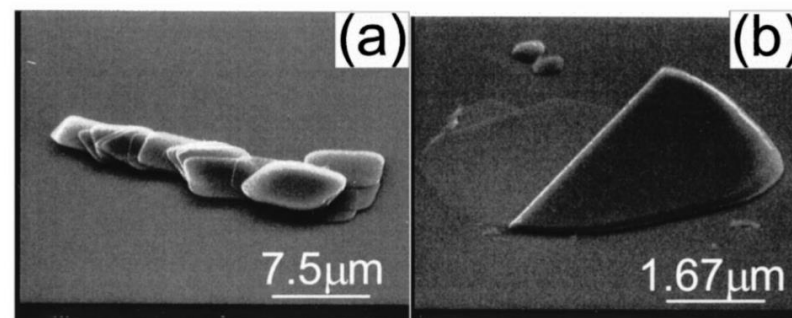
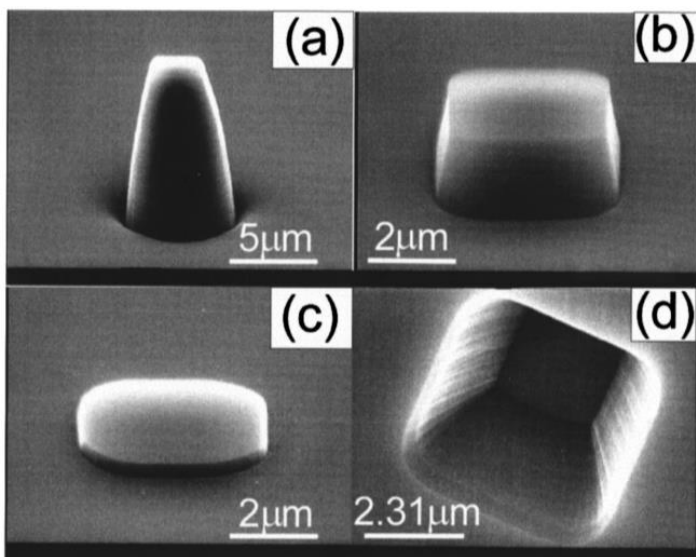
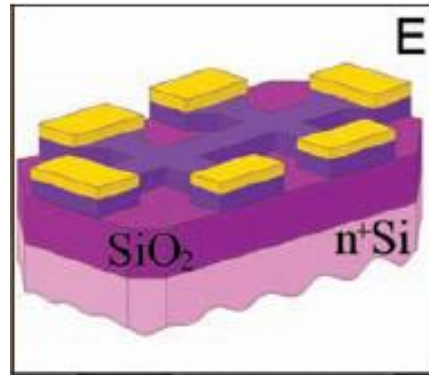
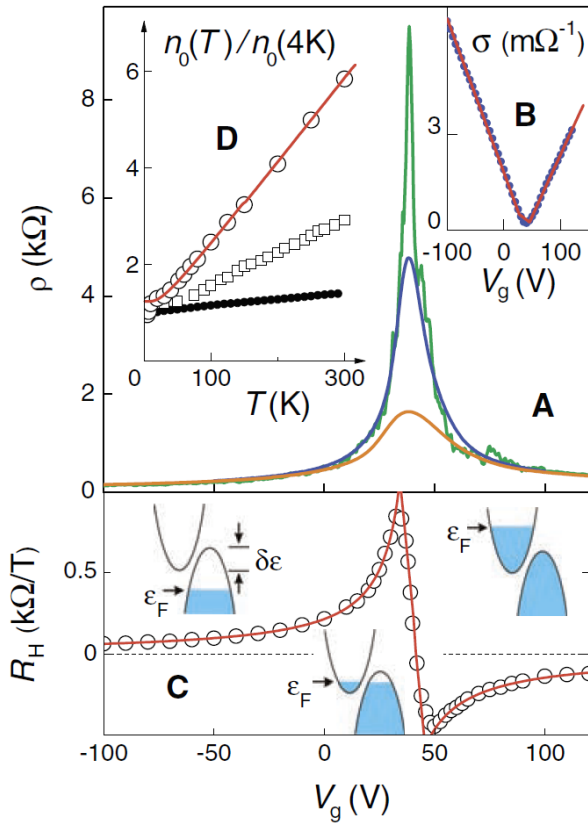


FIG. 5. SEM images of HOPG islands smeared on a Si(001) substrate. (a) Stacked thin platelets. (b) Example of a very thin layer left on the substrate while the platelet folds over.

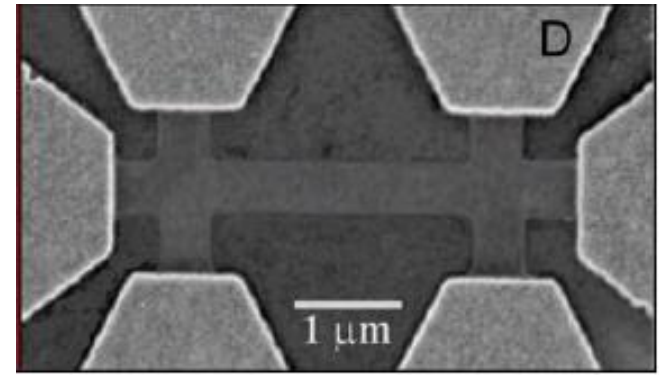
First Devices: Geim and Novoselov

Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,¹ A. K. Geim,^{1*} S. V. Morozov,² D. Jiang,¹
Y. Zhang,¹ S. V. Dubonos,² I. V. Grigorieva,¹ A. A. Firsov²



Schematic of the Hall bar device



SEM image of the graphene Hall bar device

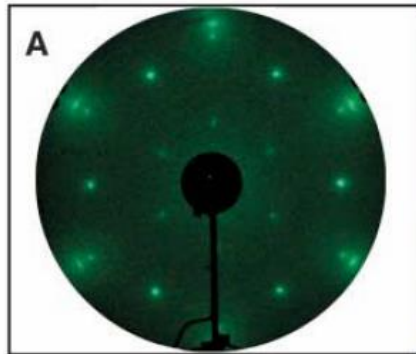
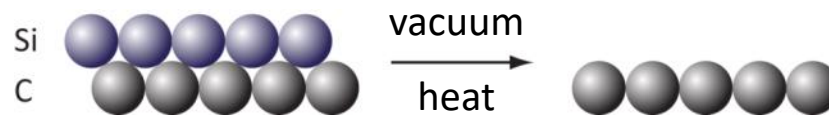
De Heer Group: Epitaxial Graphene

Ultrathin Epitaxial Graphite: 2D Electron Gas Properties and a Route toward Graphene-based Nanoelectronics

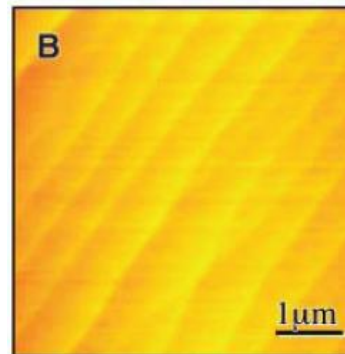
Claire Berger,[†] Zhimin Song, Tianbo Li, Xuebin Li, Asmerom Y. Ogbazghi, Rui Feng, Zhenting Dai, Alexei N. Marchenkov, Edward H. Conrad, Phillip N. First, and Walt A. de Heer*

School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332-0430

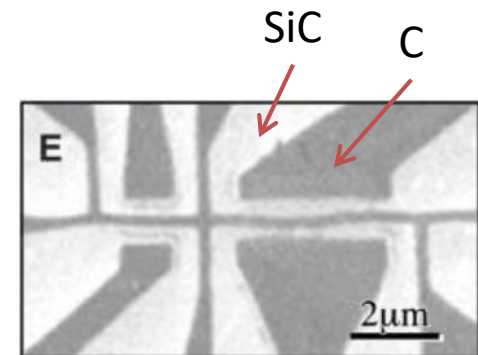
Received: October 7, 2004



Diffraction pattern



AFM image
of the surface



Device

Berger et al., J. Phys. Chem. B 108, 19912 (2004)

Berger et al., Science 312, 1191 (2006)

Berger et al., J. Phys. Chem. B 108, 19912 (2004)

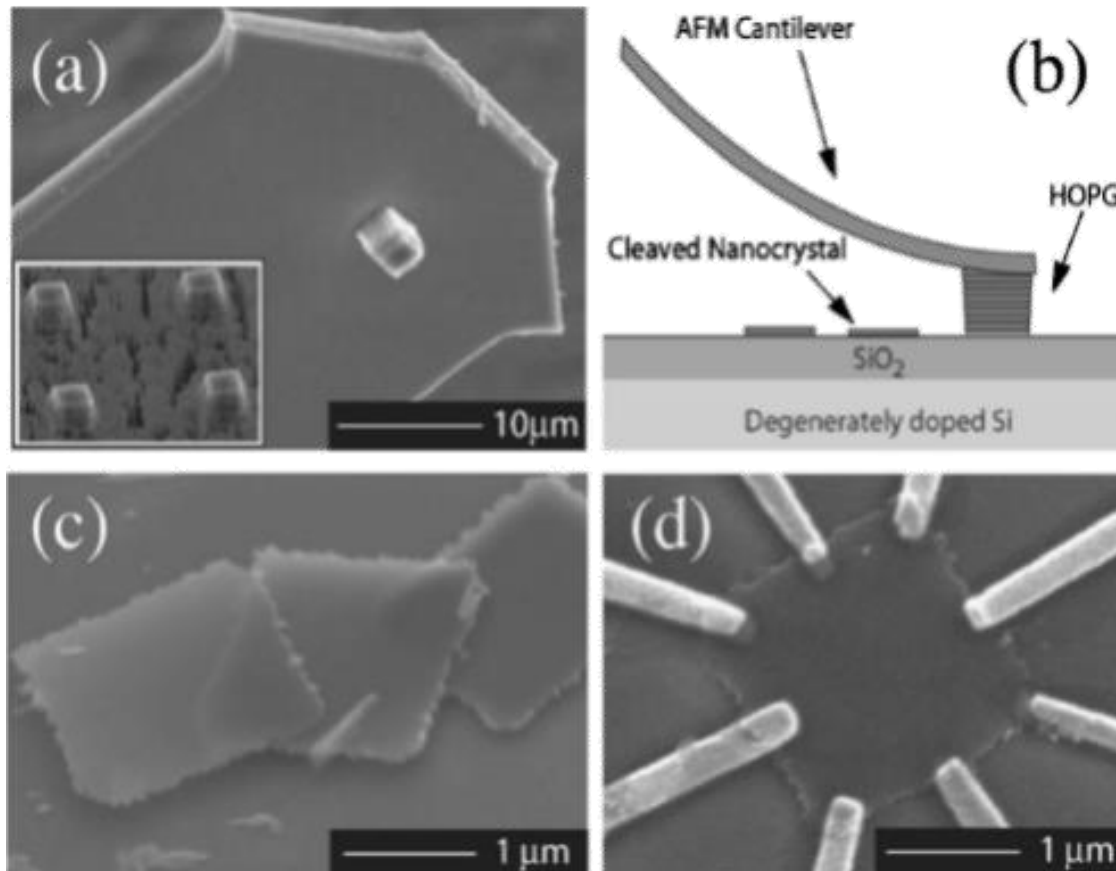
Berger et al., Science 312, 1191 (2006)

Kim Group: Mechanical Exfoliation

Fabrication and electric-field-dependent transport measurements of mesoscopic graphite devices

Yuanbo Zhang, Joshua P. Small, William V. Pontius, and Philip Kim^{a)}
*Department of Physics and the Columbia Nanoscale Science and Engineering Center, Columbia University,
New York, New York 10027*

(Received 31 August 2004; accepted 11 December 2004; published online 7 February 2005)



Zhang et al., Phys. Rev. Lett. 94, 176803 (2005)

Zhang et al., App. Phys. Lett. 86, 073104 (2005)

First Actual Measurements on Graphene

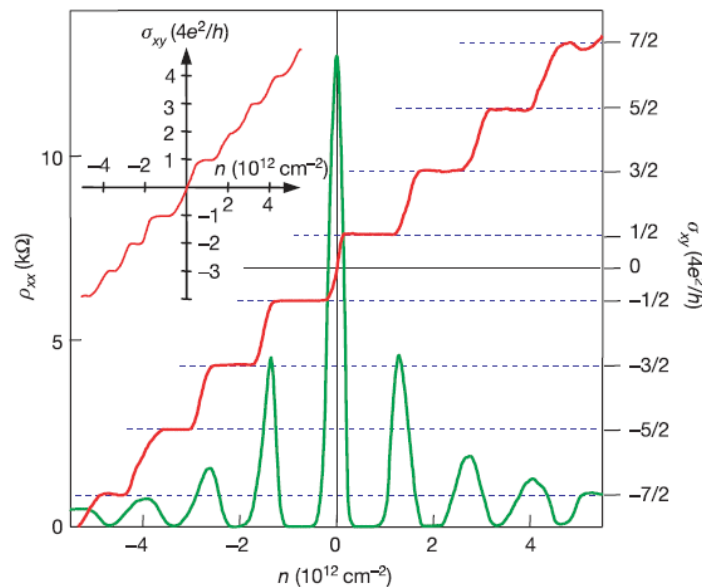
Vol 438|10 November 2005|doi:10.1038/nature04233

nature

LETTERS

Two-dimensional gas of massless Dirac fermions in graphene

K. S. Novoselov¹, A. K. Geim¹, S. V. Morozov², D. Jiang¹, M. I. Katsnelson³, I. V. Grigorieva¹, S. V. Dubonos² & A. A. Firsov²



Vol 438|10 November 2005|doi:10.1038/nature04235

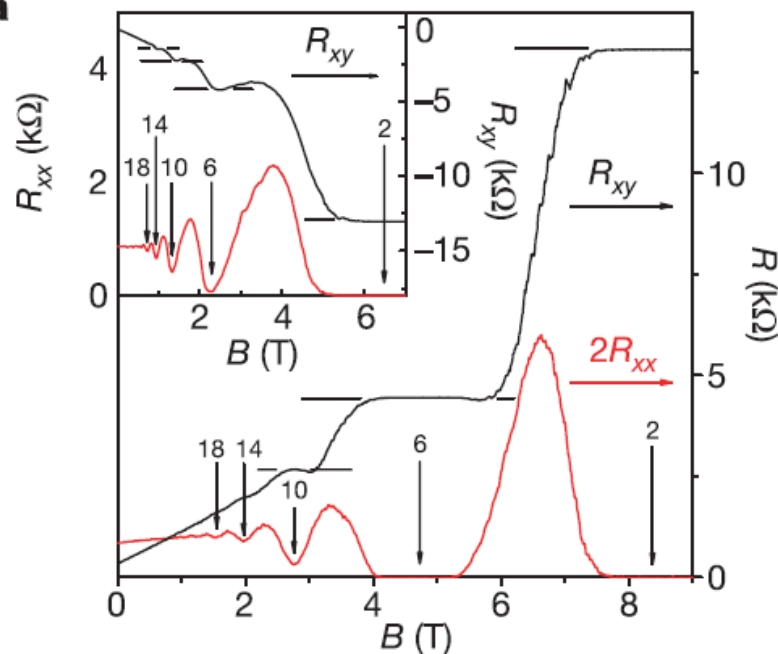
nature

LETTER

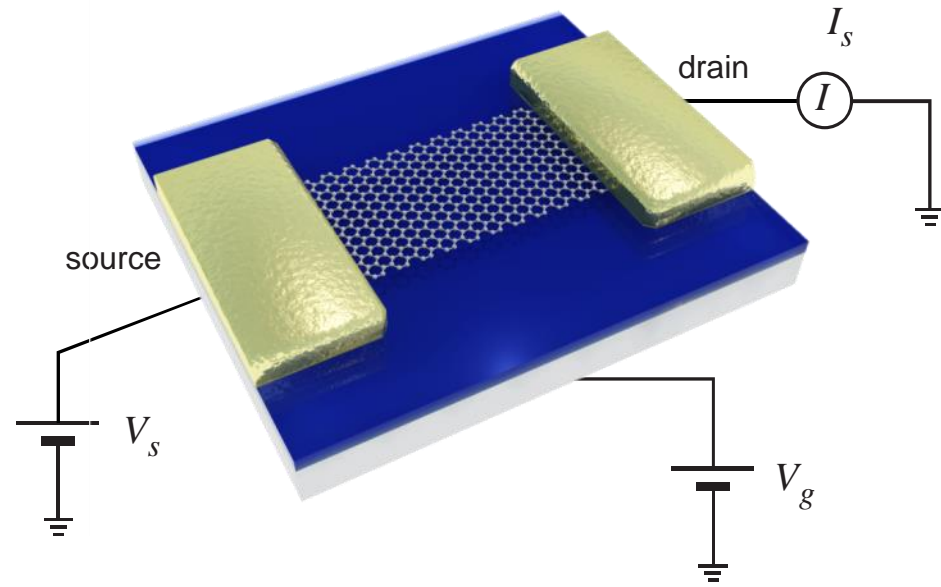
Experimental observation of the quantum Hall effect and Berry's phase in graphene

Yuanbo Zhang¹, Yan-Wen Tan¹, Horst L. Stormer^{1,2} & Philip Kim¹

a



Graphene FET Characteristics



Ambipolar behavior

Large current density – 10^8 A/cm²

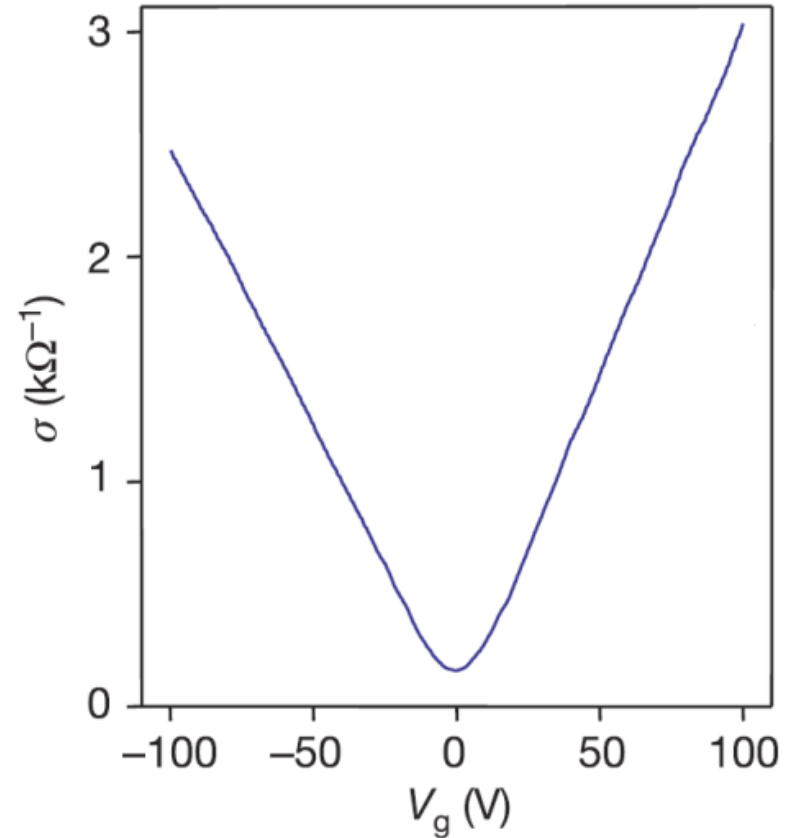
- Moser et al.; APL 91, 163513 (2007)

High mobility – 200 000 cm²/Vs

- Bolotin et al.; Sol. St. Comm. 146, 351 (2008)

Suppression of noise in double layers

- Lin and Avouris; Nano Letters 8, 2119 (2008)

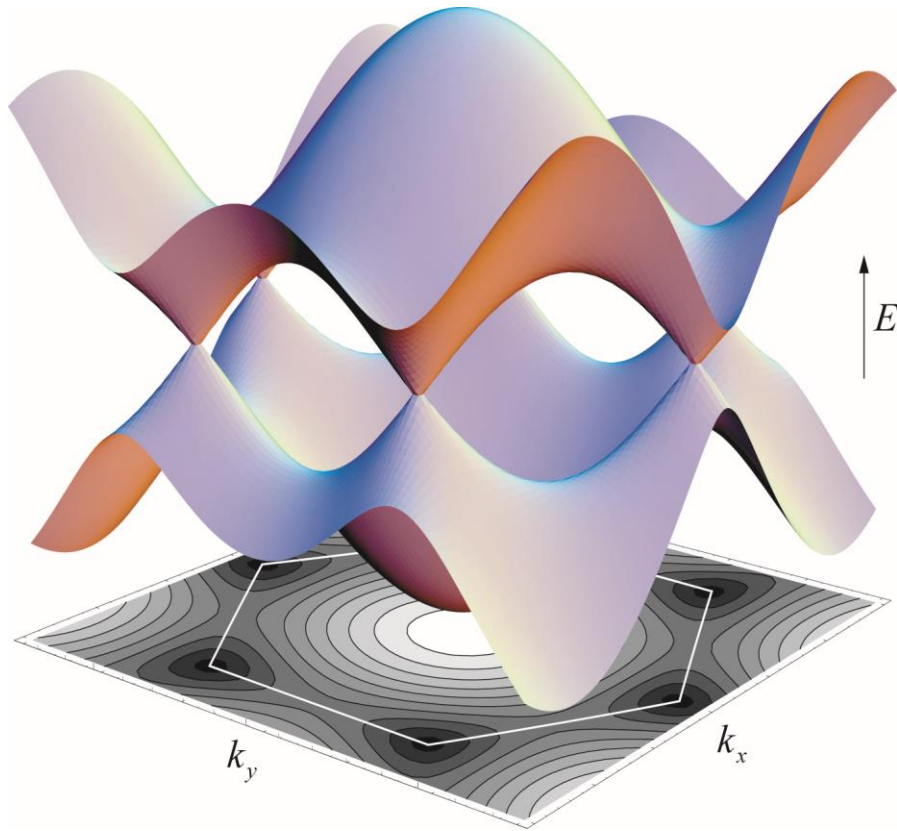


Novoselov et al., Nature 438, 197 (2005)

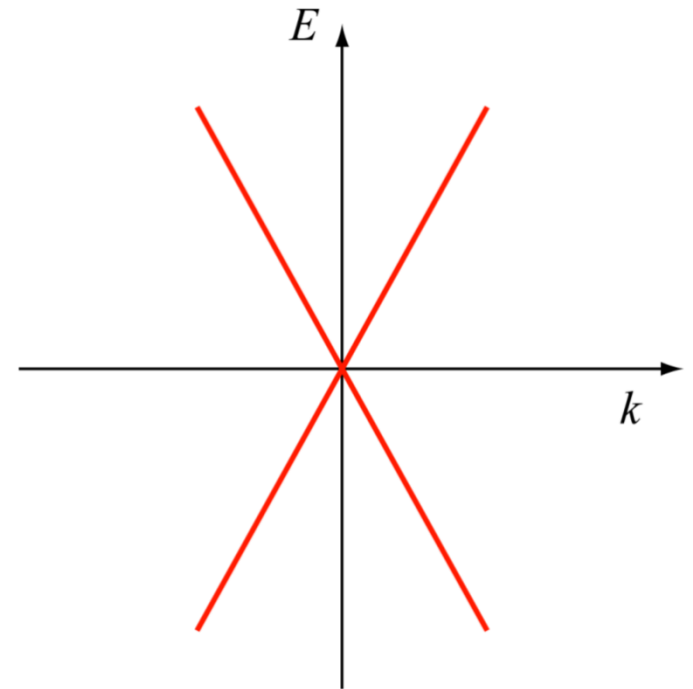
Graphene Band Structure

Dispersion relation:

$$E(k) = \pm t \left[1 + 4 \cos\left(\frac{\sqrt{3}k_x a}{2}\right) \cos\left(\frac{k_y a}{2}\right) + 4 \cos^2\left(\frac{k_y a}{2}\right) \right]^{1/2}$$



No band gap!

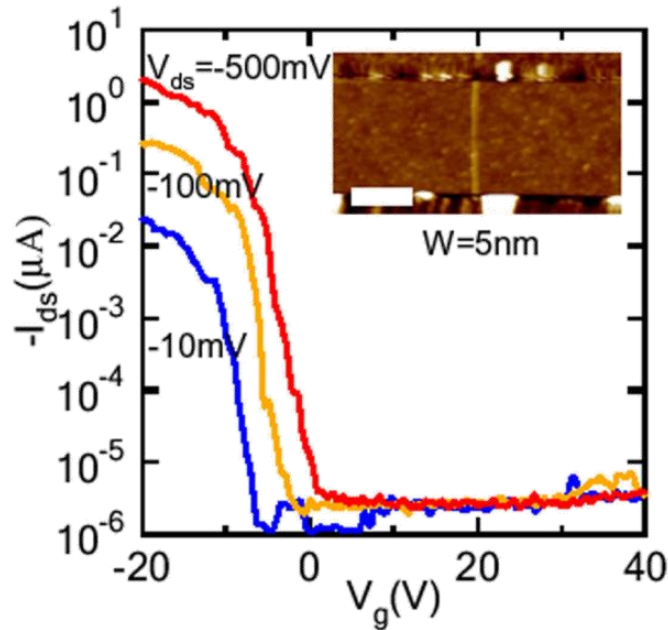


~~$E = \frac{\hbar^2 k^2}{2m}$~~ $E = \hbar k v_F, \quad v_F = c / 300$

Graphene Has No Band Gap

Possible solutions

Nanoribbons



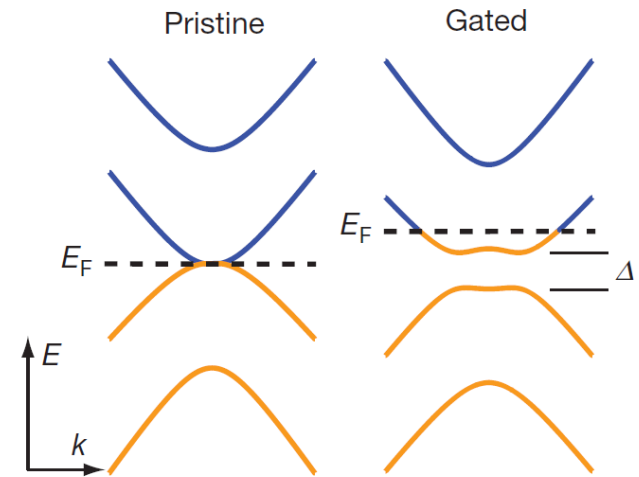
Hongjie Dai group: Science 319 1229 (2008)

Kim group: PRL 98, 206805 (2007)

Avouris group: Physica E 40, 228 (2007)

Max band gap: 400 meV for 5 nm

Bilayer Graphene



Zettl, Crommie, Wang: Nature 459, 820 (2009)

Avouris group: NanoLet 10, 715 (2010)

Max band gap: 250 meV for 120 V

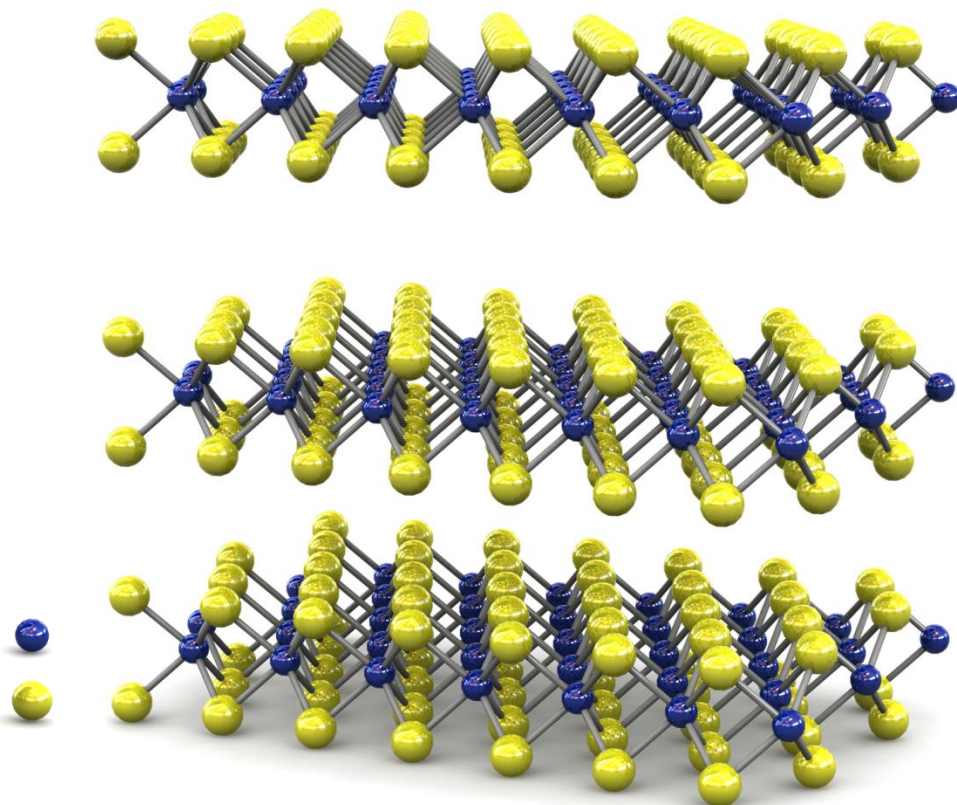
2D Transition Metal Dichalcogenides (TMDCs)

Common formula: MX_2

Electrical property	Material
semiconducting	MoS_2 MoSe_2 WS_2 WSe_2 MoTe_2 WTe_2
semimetallic	TiS_2 TiSe_2
metallic, CDW, superconducting	NbSe_2 NbS_2 NbTe_2 TaS_2 TaSe_2 TaTe_2

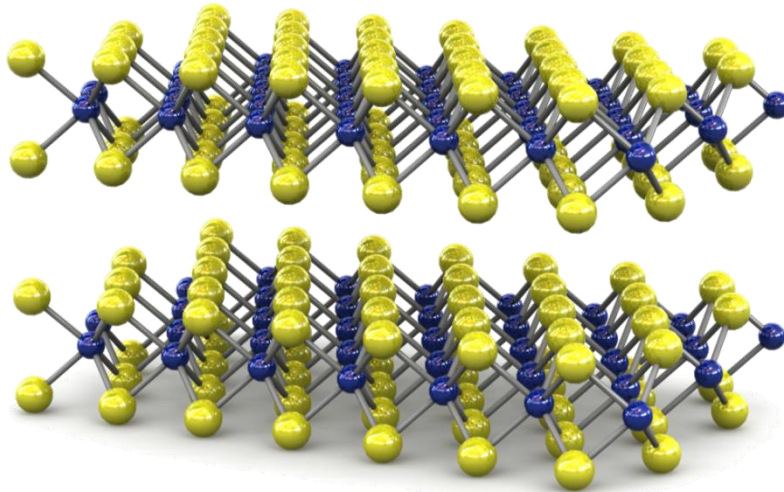
Metal M = Ta, Nb, Mo, W, Ti, Re

Chalcogenide X = S, Se, Te



MoS₂

0.65nm



MoS₂ crystal

- Band gap:** 1.2 eV (bulk); 1.8 eV direct (optical) gap (single layer)
- Stability:** > 1000 °C in inert atmosphere
no dangling bonds
- Max J:** 5×10⁷ A/cm² (copper: 10⁵, graphene: 10⁸)
- Stiffness:** 280 GPa (slightly higher than stainless steel)
- Mech. failure:** 6-11% strain (30x stronger than steel)

Kam et al., J. Phys. Chem. 86, 463 (1982)

Splendiani et al., Nano Lett. 10, 1271 (2010)

Mak et al., PRL 105, 136805 (2010)

Bertolazzi et al., ACS Nano 5, 9703 (2011)

Lembke et al., ACS Nano 6, 10070 (2012)

Review papers:

Wang et al., Nature Nanotech. (2012)

Allain...Kis; Nature Mater. (2015)



SONA
Das Original

Mos2

- Rostlöser
- Schmiermittel
- Reiniger
- Korrosionsschutz
- Kontaktspray
- Kriechöl



- Kunststoffverträglich
- Verharzt nicht
- Silikonfrei

Physical properties of layer structures : optical properties
and photoconductivity of thin crystals
of molybdenum disulphide

BY R. F. FRINDT AND A. D. YOFFE

*Physics and Chemistry of Solids, Cavendish Laboratory,
University of Cambridge*

(Communicated by F. P. Bowden, F.R.S.—Received 16 August 1962—
Revised 23 November 1962)

[Plates 1 and 2]

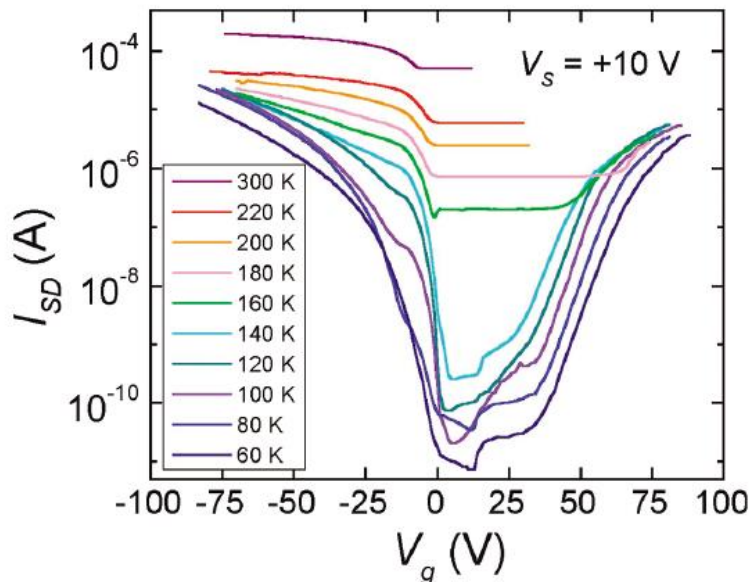
Very thin crystals of molybdenum disulphide, less than 100 Å thick, have been prepared by cleavage. The optical absorption spectra in the thickness range several micrometres to less than 100 Å are similar. Absorption coefficients have been measured to values close to 10^6 cm^{-1} . The absorption bands observed with thin crystals are associated with bulk rather than surface properties.

SINGLE-LAYER MoS₂

Per Joensen, R.F. Frindt, and S. Roy Morrison
Energy Research Institute
Department of Physics
Simon Fraser University
Burnaby, B.C., Canada V5A 1S6

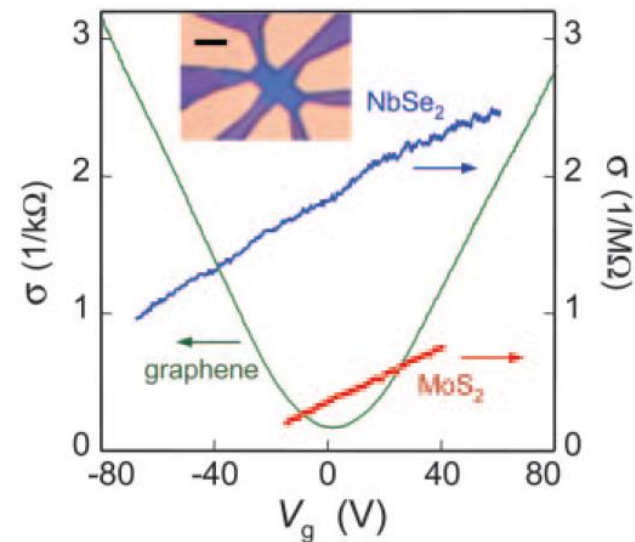
(Received January 27, 1986; Communicated by A. Wold)

Frindt and Yoffe, Proc. Roy. Soc. A (1963)



Podzorov et al. APL (2004)

Joensen et al., Mat. Res. Bull. 21, 457 (1986)



Novoselov et al., PNAS (2005)

Prevailing Opinion at the Time

Perspectives on the 2010 Nobel Prize in Physics for Graphene

Mildred S. Dresselhaus* and Paulo T. Araujo

ACS Nano 4, 6297 (2010)

In 2005, Novoselov and Geim performed comparative studies in other atomically layered 2D systems like boron nitride (BN), MoS₂, NbSe₂, and Bi₂Sr₂CaCu₂O_x.³¹ All of the materials were exfoliated in the same way as had been done for graphene and were shown to be morphologically stable, although with electrical and mechanical properties much inferior to those of 2D graphene. Later, the production of monolayer graphene suspended over microfabricated trenches exhibited striking stability and opened a new channel for technological devices.^{32,33}

Was the Mobility Really Supposed to Be low?

PHYSICAL REVIEW

VOLUME 163, NUMBER 3

15 NOVEMBER 1967

Mobility of Charge Carriers in Semiconducting Layer Structures

R. FIVAZ* AND E. MOOSER

Cyanamid European Research Institute, Coligny, Geneva, Switzerland

(Received 26 May 1967)

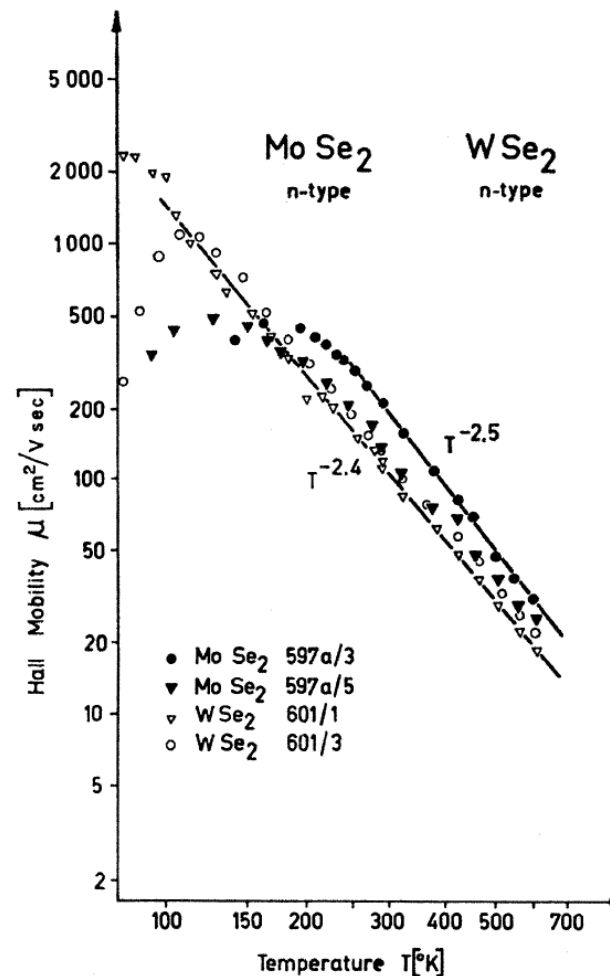
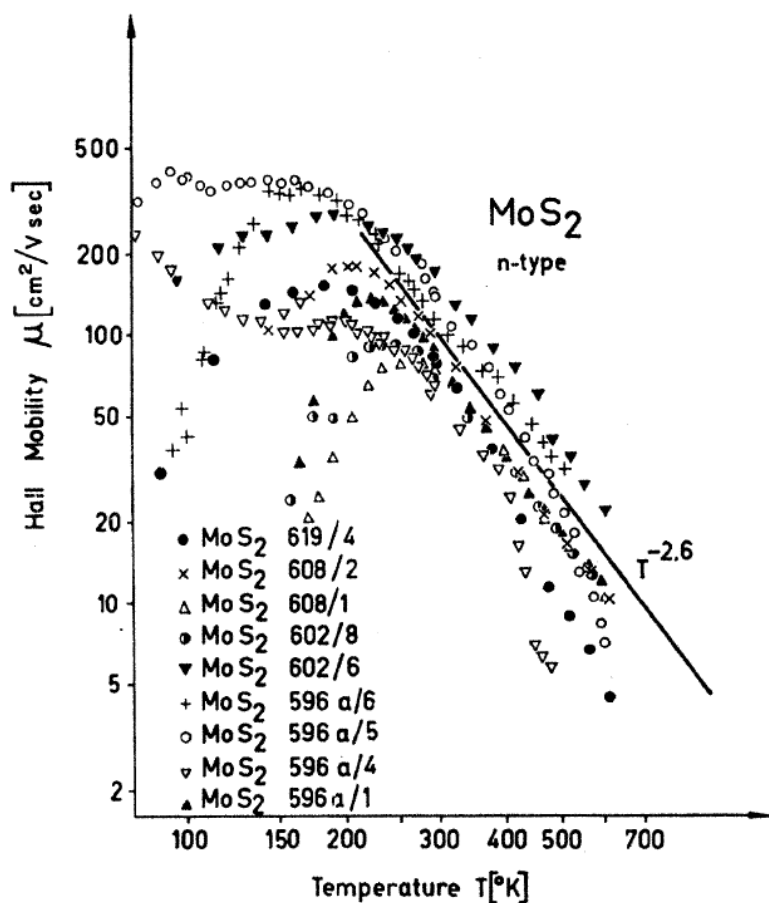
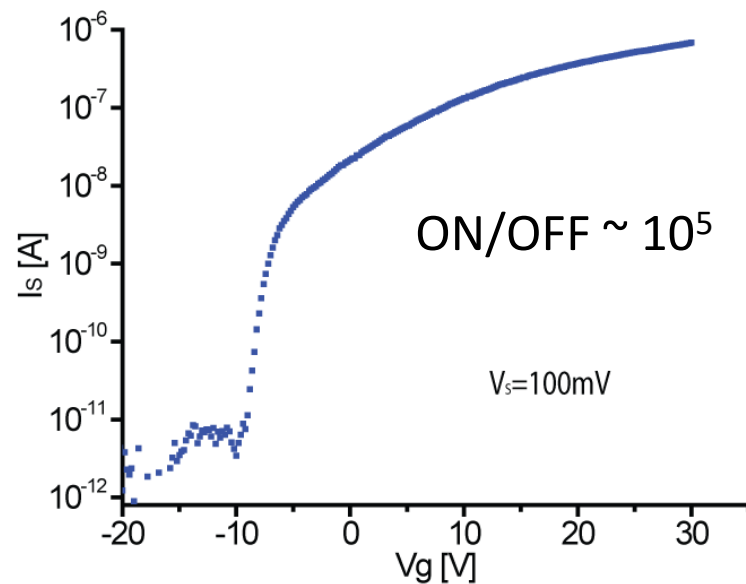
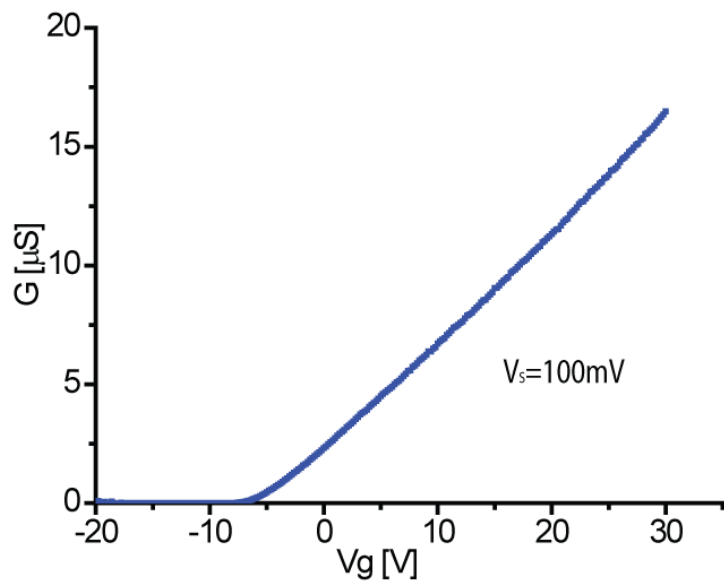
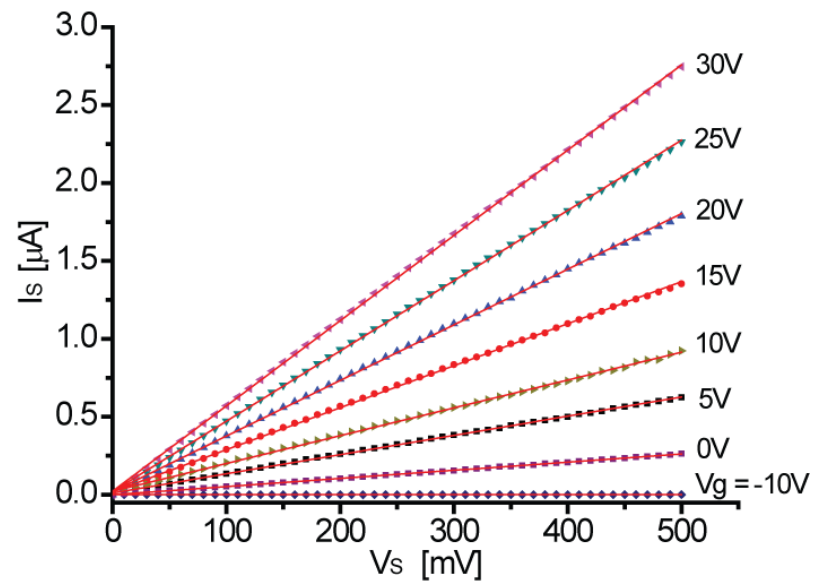
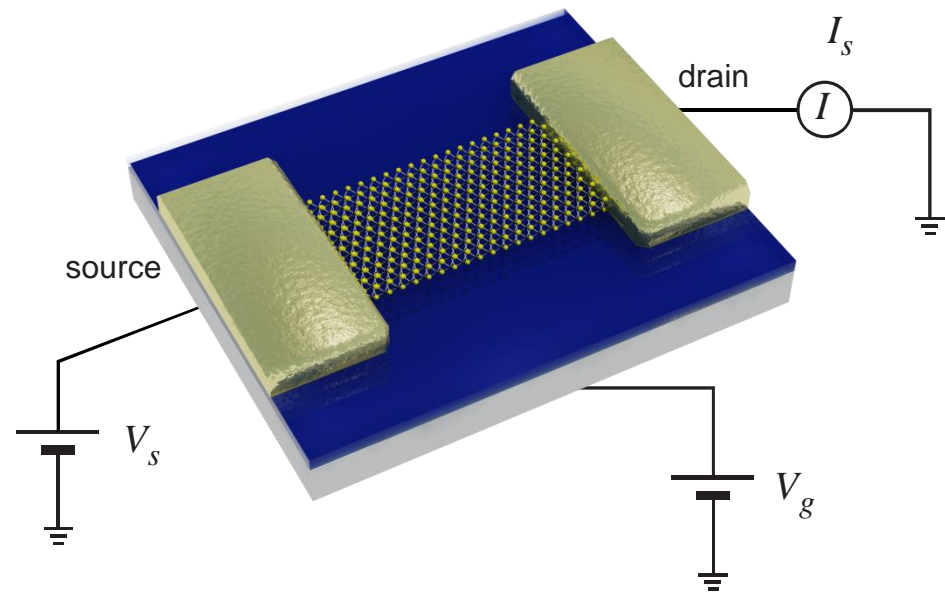
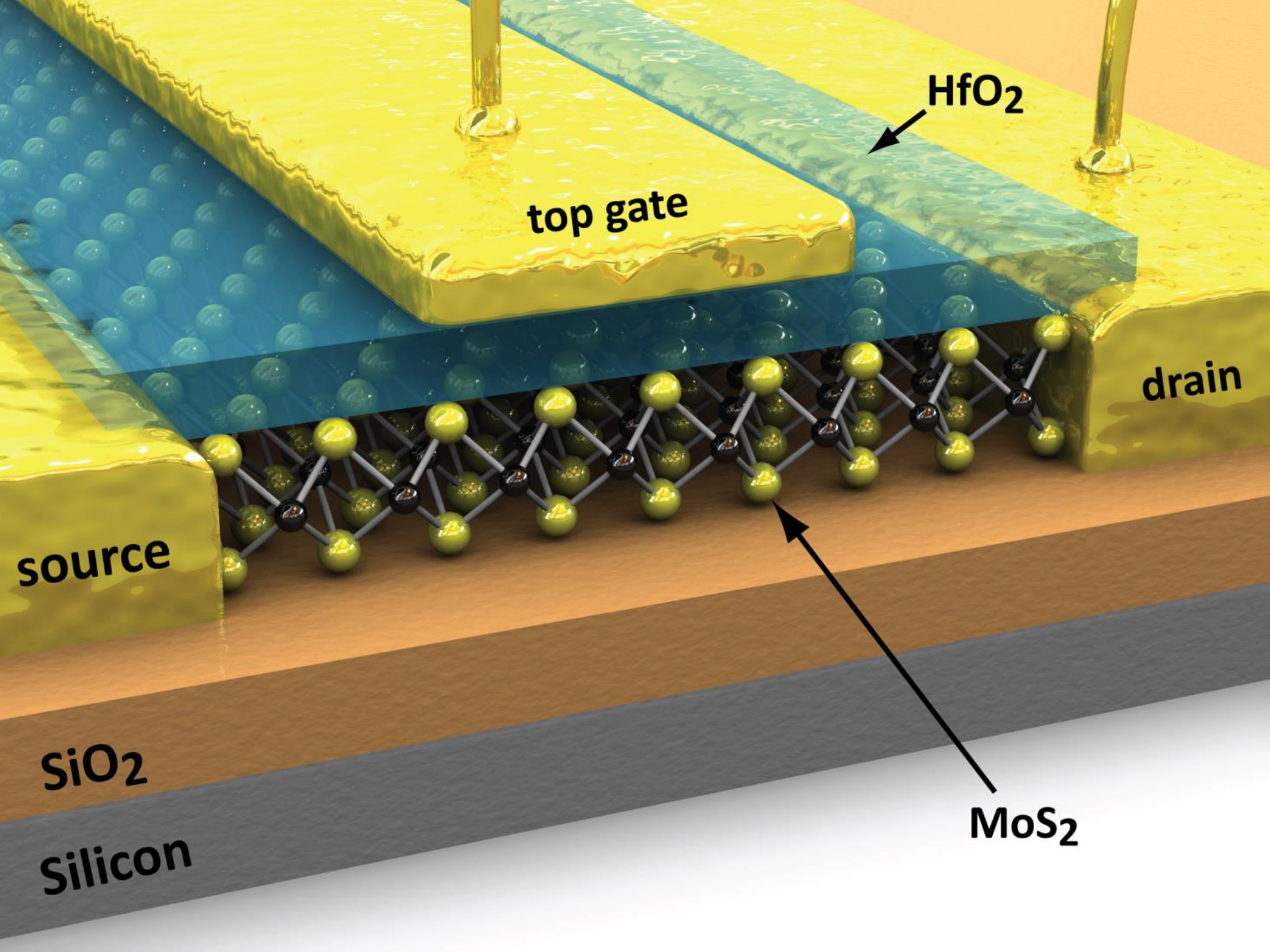


FIG. 7. Mobility of the electrons in MoS_2 .

Our First MoS₂ Transistor (5 layers, 2009)





HfO₂

top gate

drain

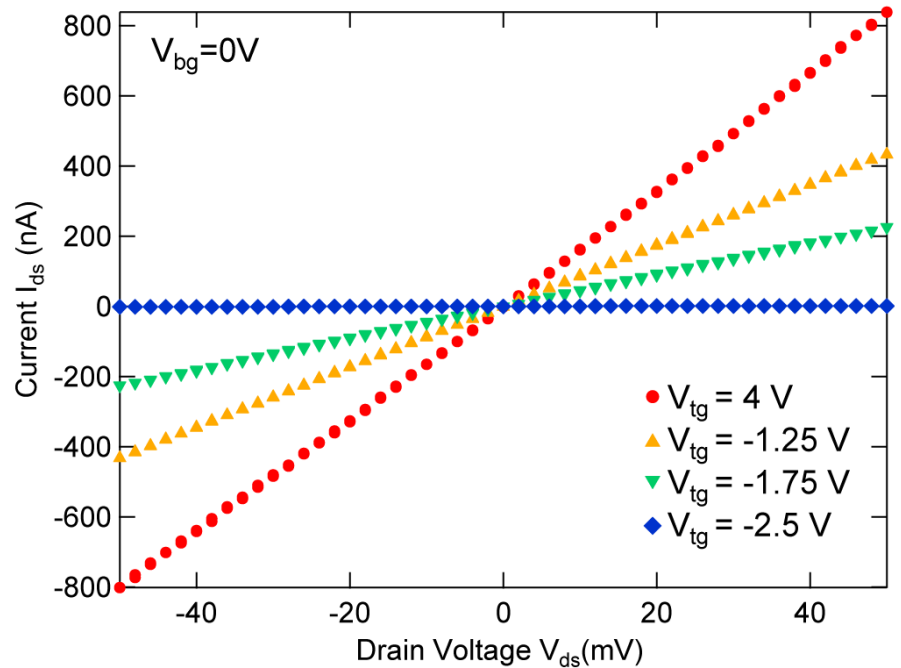
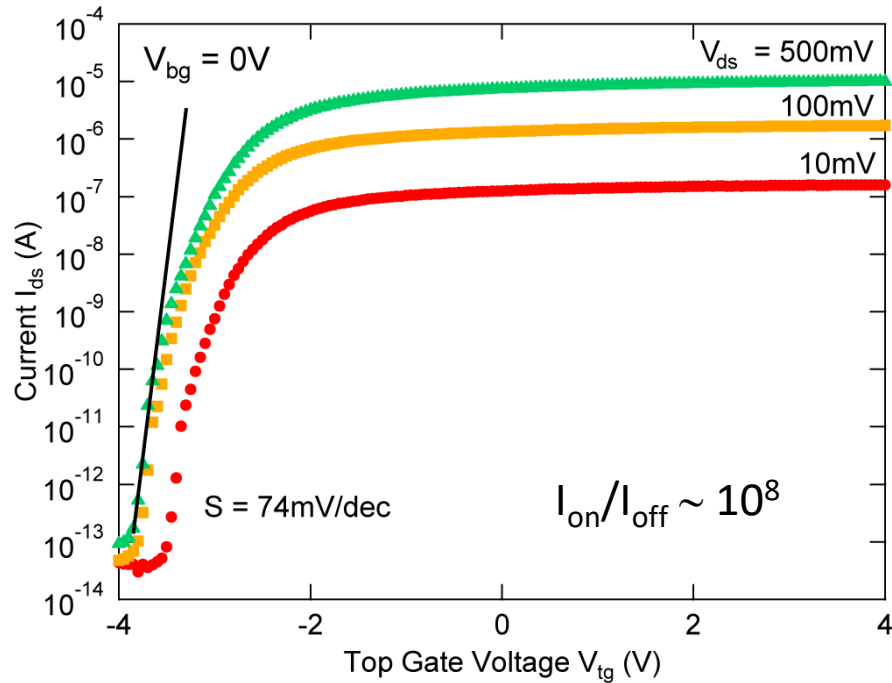
source

SiO₂

Silicon

MoS₂

Monolayer MoS₂ Transistor

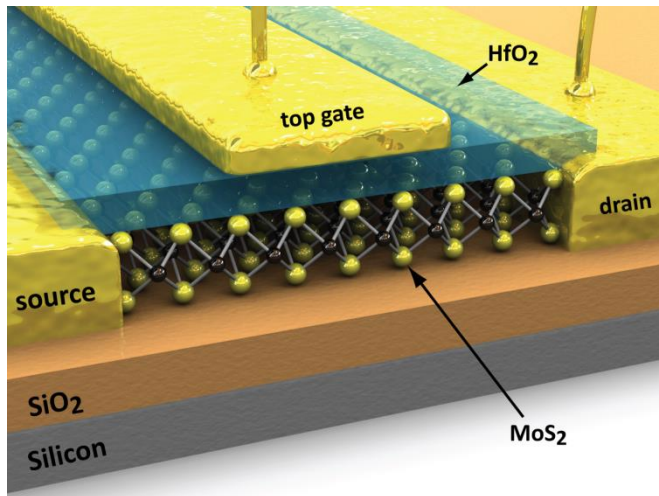


Radisavljevic...Kis,
 Nature Nanotechnology (2011)

Gate length:	500 nm
Channel width:	4 μm
On/Off:	10^8
ON current:	2.5 $\mu A/\mu m$
OFF current:	25 fA/ μm
Transconductance:	1 $\mu S/\mu m$

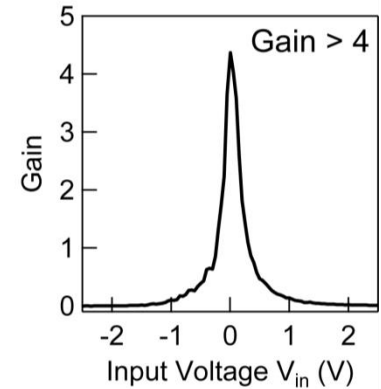
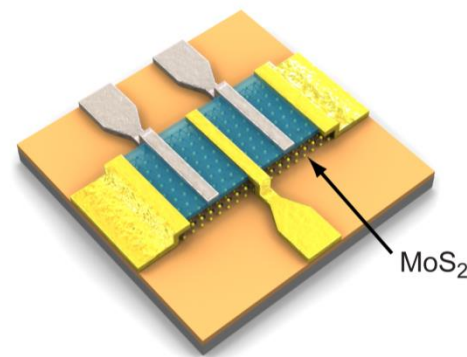
Devices Based on Monolayer MoS₂

MoS₂ Transistor



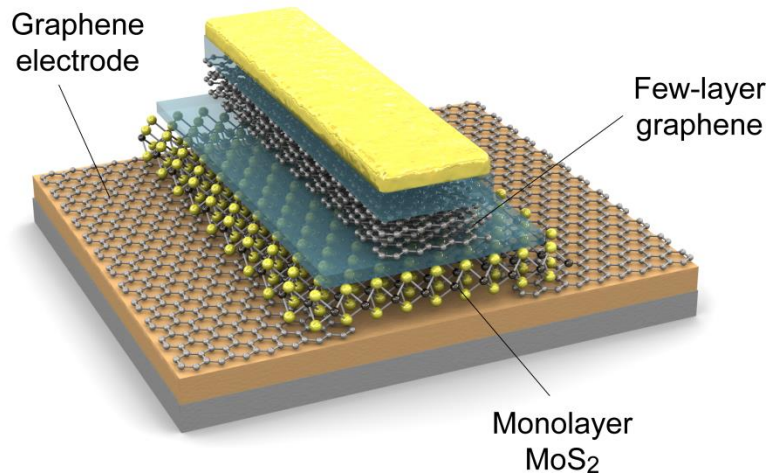
Radisavljevic...Kis; Nature Nanotech. (2011)

MoS₂ Inverter



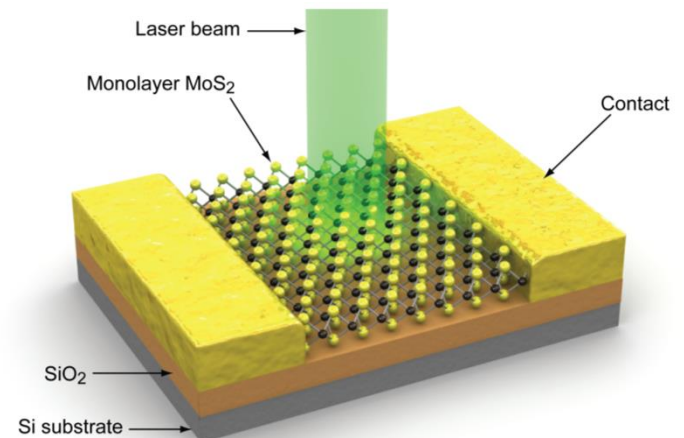
Radisavljevic...Kis; ACS Nano (2011)

MoS₂/graphene Memory Cell



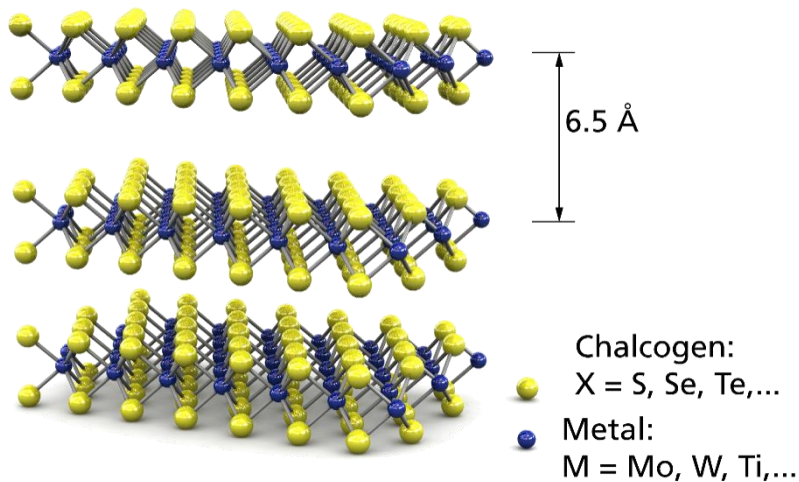
Bertolazzi...Kis; ACS Nano (2013)

Ultrasensitive Photodetector



Lopez-Sanchez...Kis; Nature Nanotech. (2013)

Structure



Radisavljevic...Kis; Nature Nanotech. (2011)

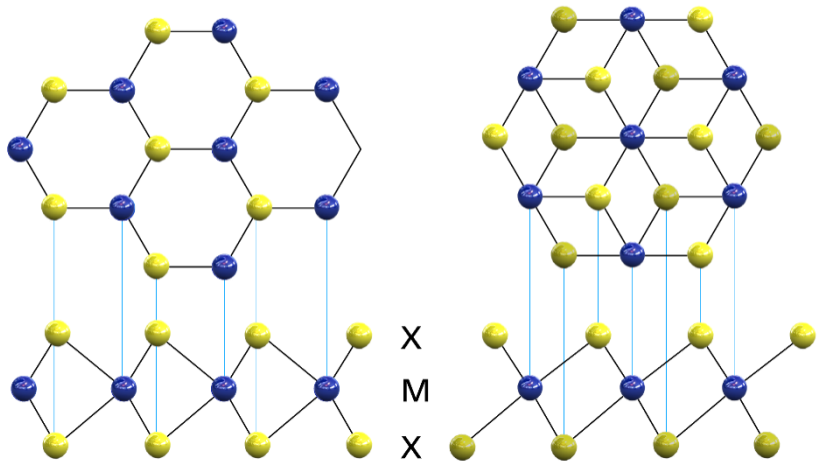
MX_2
M = transition metal
X = Chalcogen

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

Chhowalla...Zhang; Nature Chemistry (2013)

2H (trigonal prismatic)

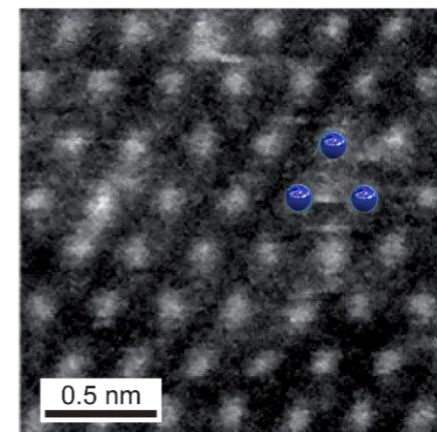
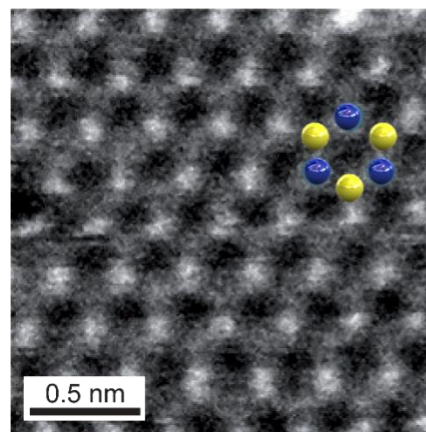
1T (octahedral)



Kuc...Kis; MRS Bull. (2015)

2H

1T



Eda...Chhowalla; ACS Nano (2012)

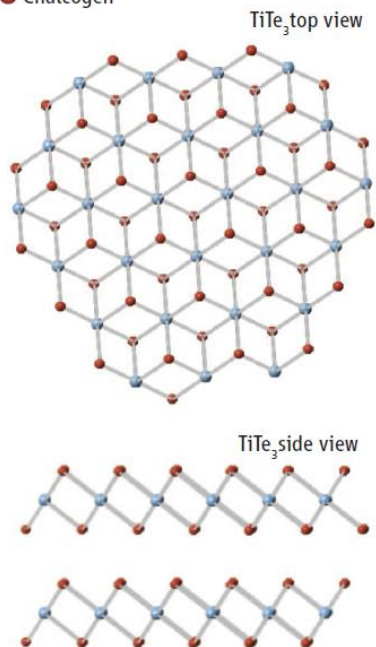
Tip of the Iceberg

>500 potentially interesting 2D materials

Transition metal trichalcogenides

AMo_3X_3 , NbX_3 , TiX_3 , and TaX_3 (X = S, Se, or Te)

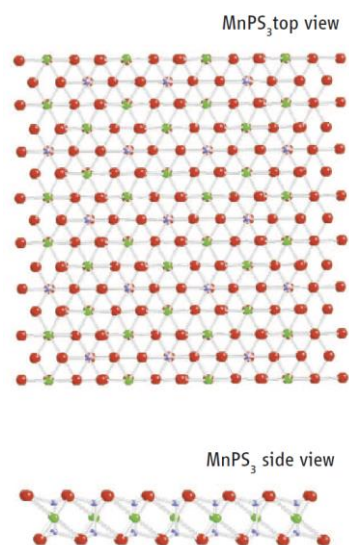
- Transition metal
- Chalcogen



Metal phosphorous trichalcogenides (MPX₃)

Metal phosphorous trichalcogenides (MPX₃), such as MnPS₃, CdPS₃, NiPS₃, ZnPS₃, and Mn_{0.5}Fe_{0.5}PS₃

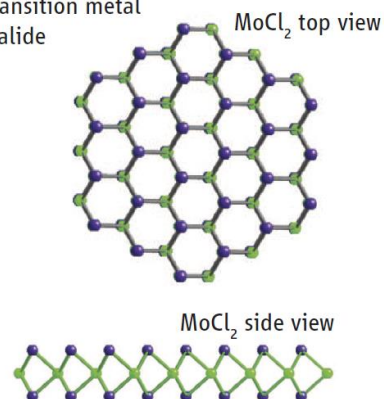
- Transition metal
- Chalcogen
- Phosphorus



Transition metal dihalides

Transition-metal dihalides*

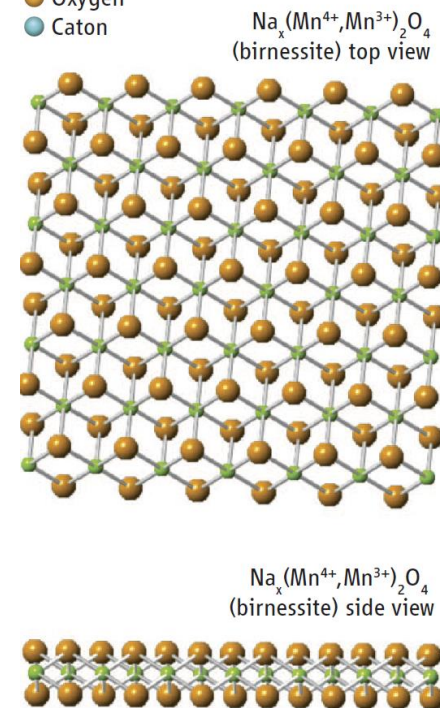
- Transition metal
- Halide



Transition metal oxides

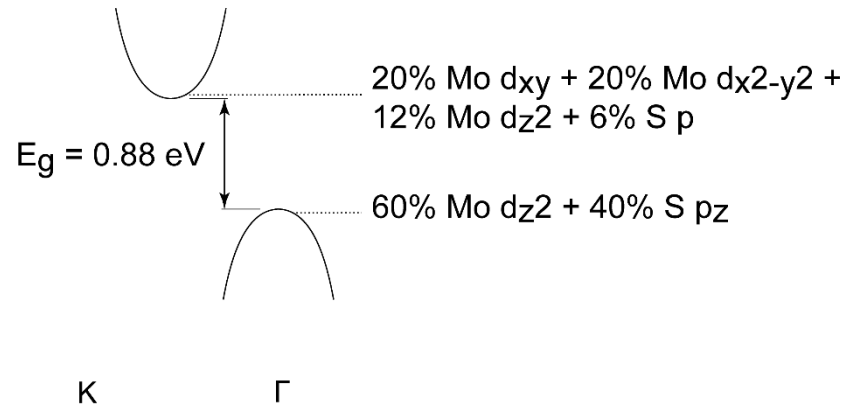
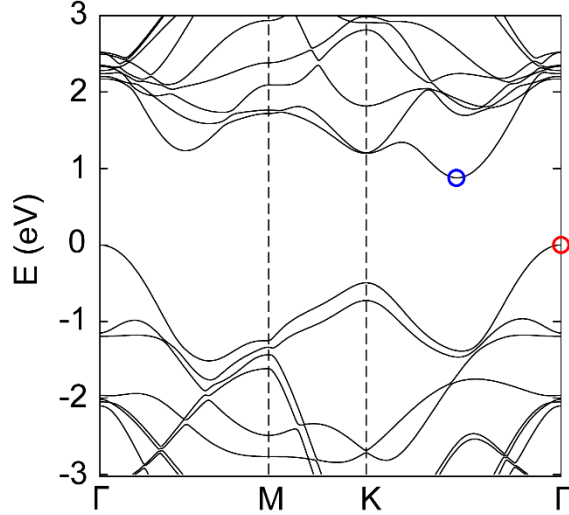
Transition metal oxides : Ti oxides, Ti_{0.91}O₂, Ti_{0.87}O₂, Ti₃O₇, Ti₄O₇, Ti₅O₁₁; Nb oxides, Nb₃O₈, Nb₆O₁₇, HNb₃O₈; Mn oxides, MnO₂, Ti₃O₇, Na_x(Mn⁴⁺, Mn³⁺)₂O₄

- Transition metal
- Oxygen
- Cation

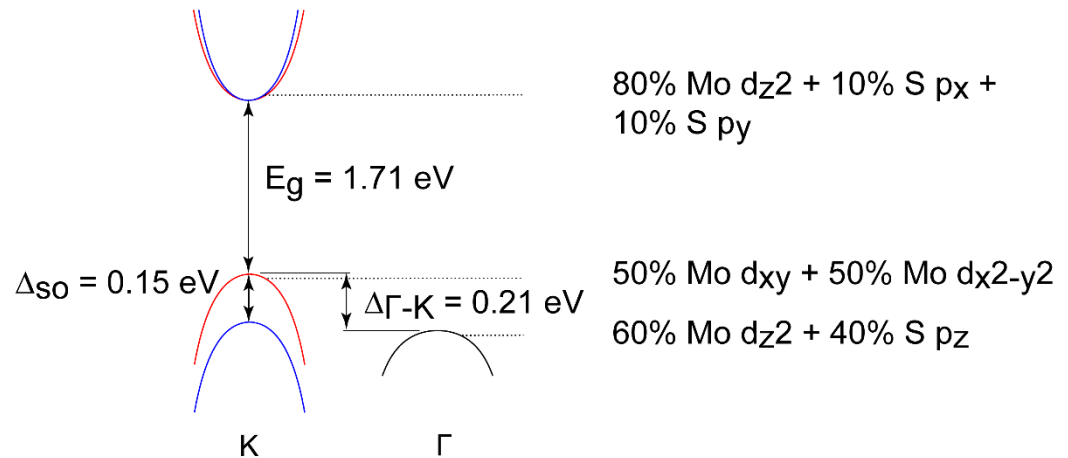
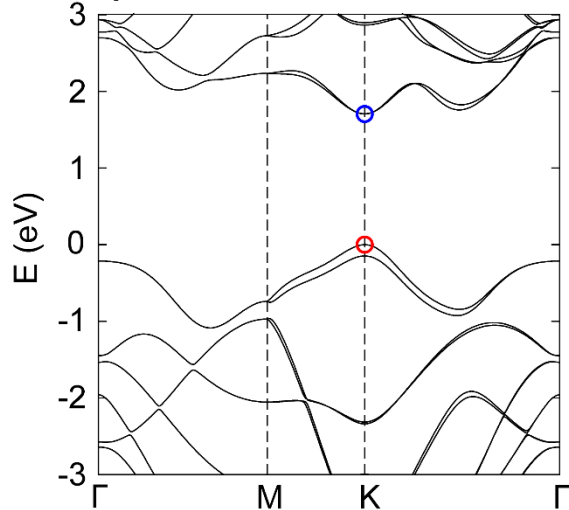


Band Structure of 2H MoS₂

Bulk MoS₂



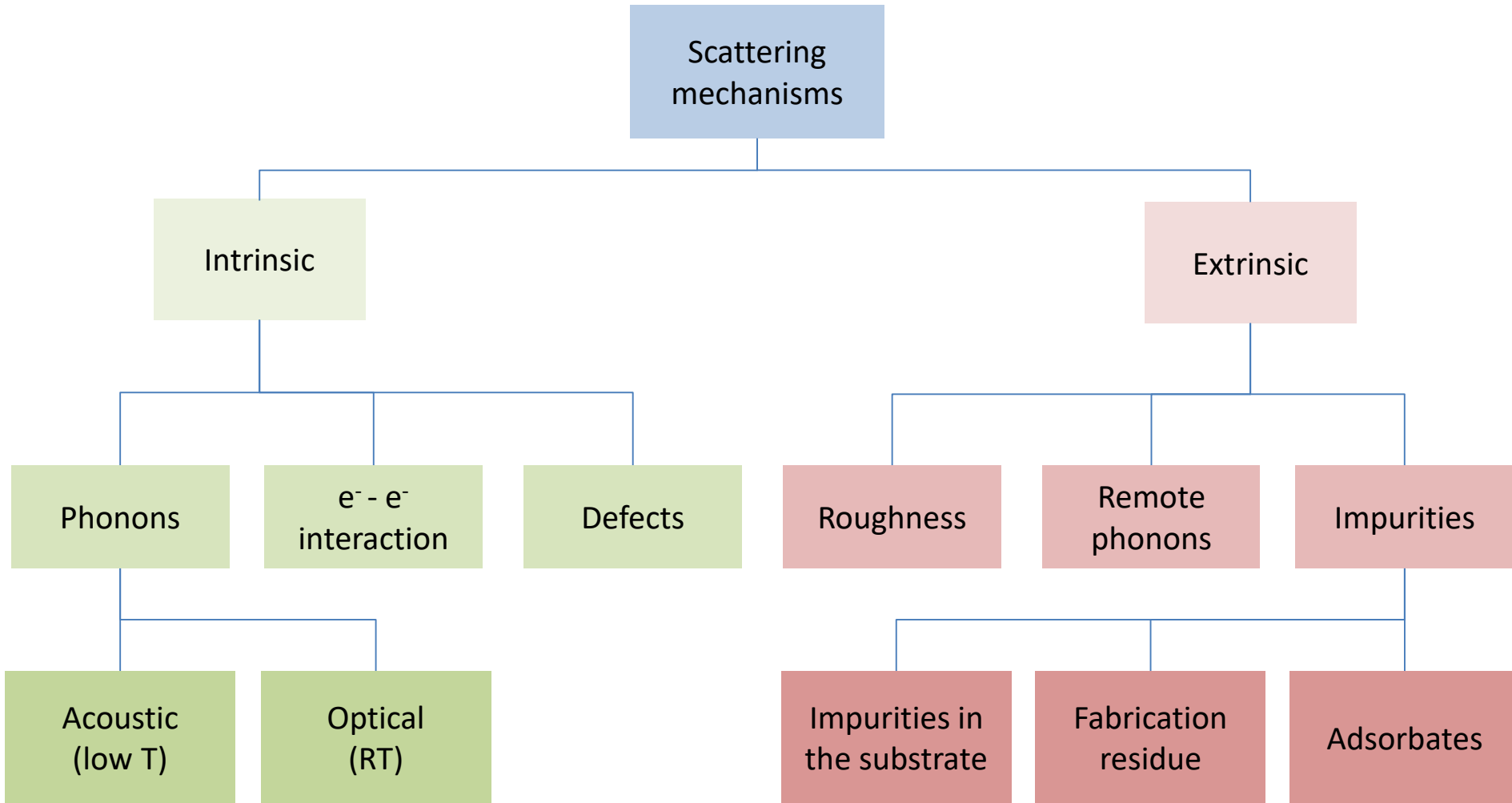
Monolayer MoS₂



Kuc...Heine; Physical Review B (2011)

Yazyev and Kis; Materials Today (2014)

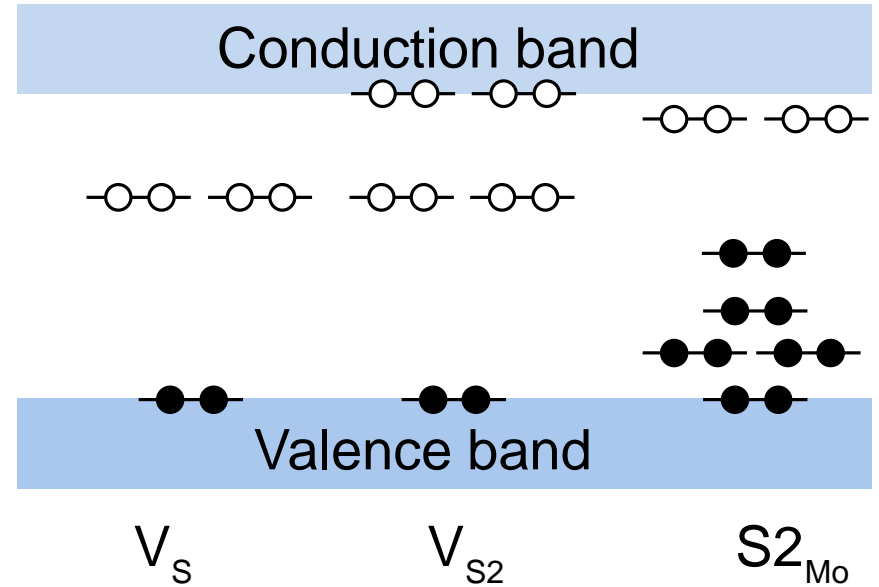
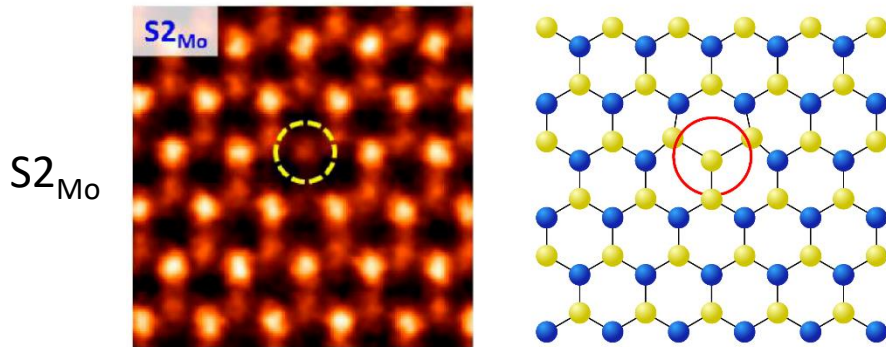
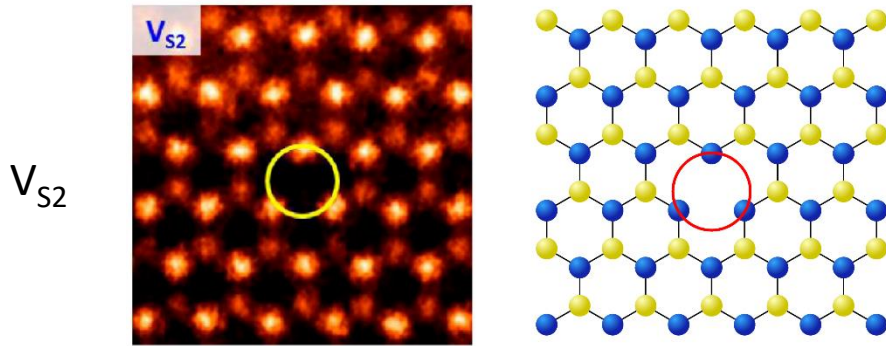
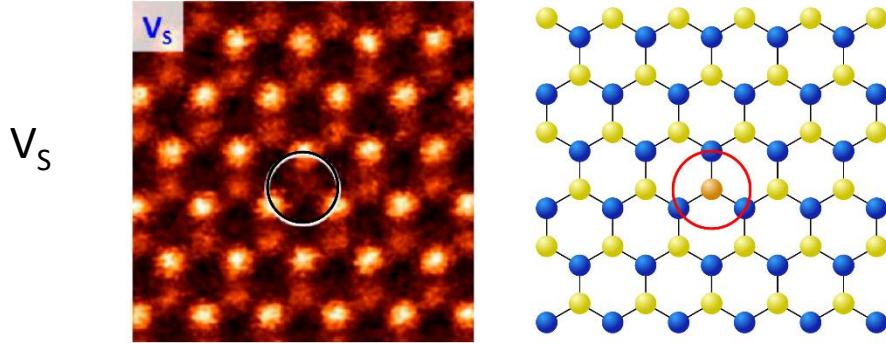
Charge Scattering Mechanisms



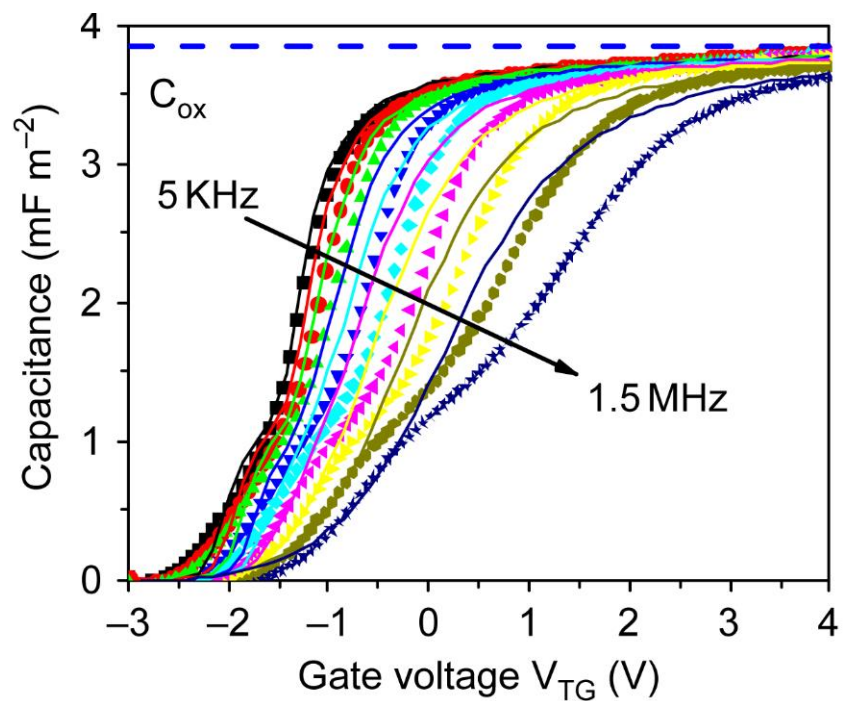
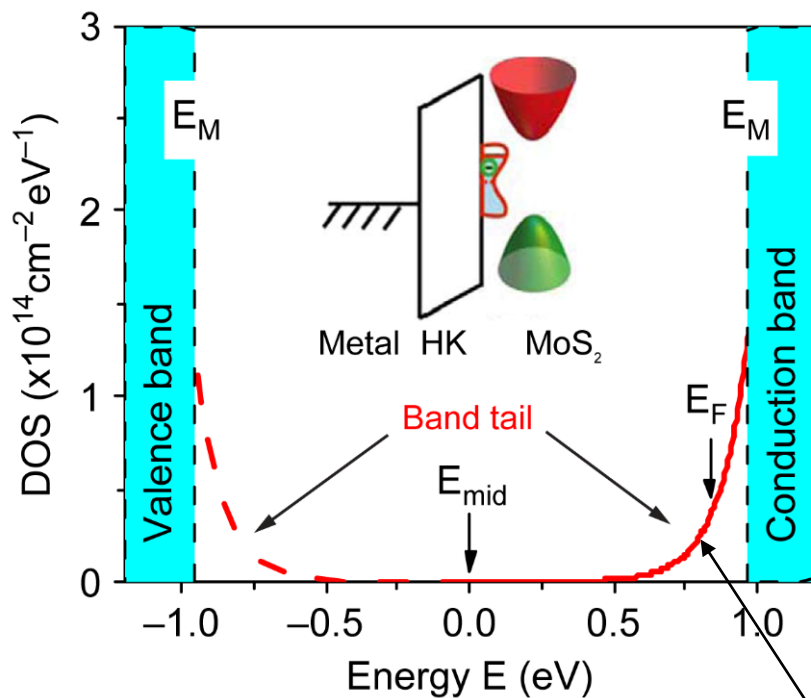
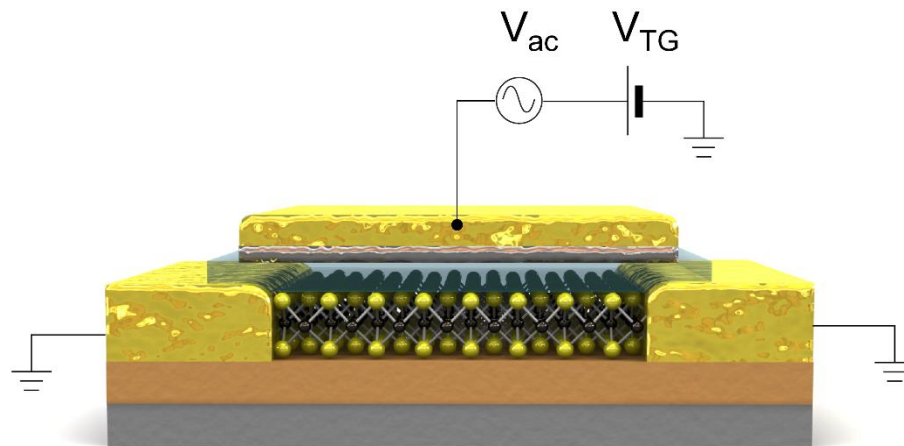
Mobility follows Mathiessen's rule:

$$\frac{1}{\mu} = \frac{1}{\mu_{defects}} + \frac{1}{\mu_{phonons}} + \frac{1}{\mu_{remote\ phonons}} + \dots$$

Most Common Point Defects in MoS₂



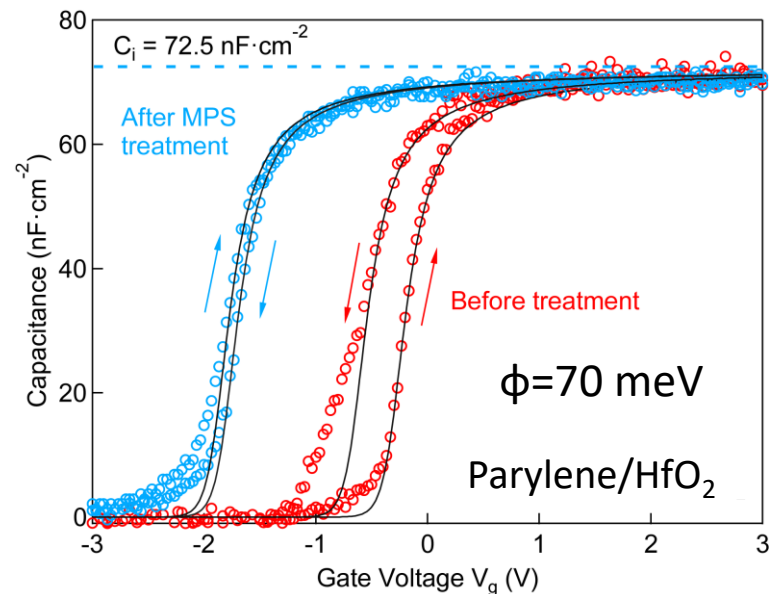
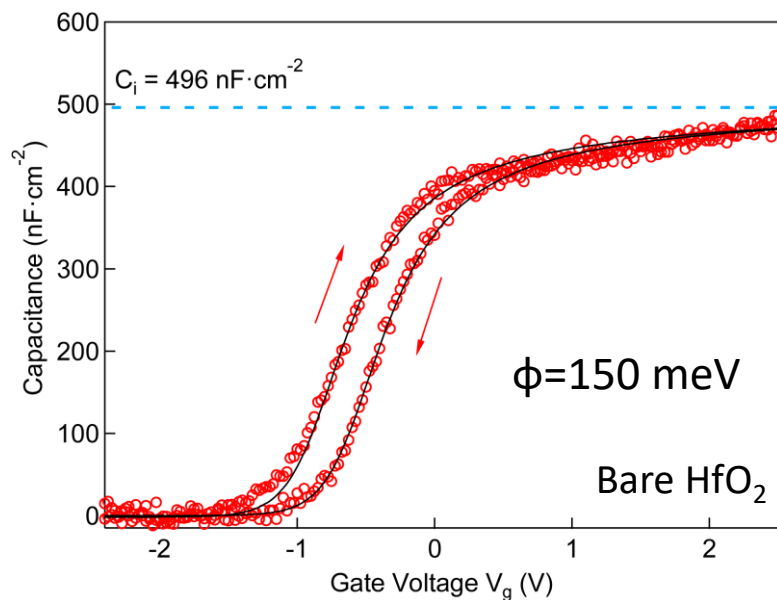
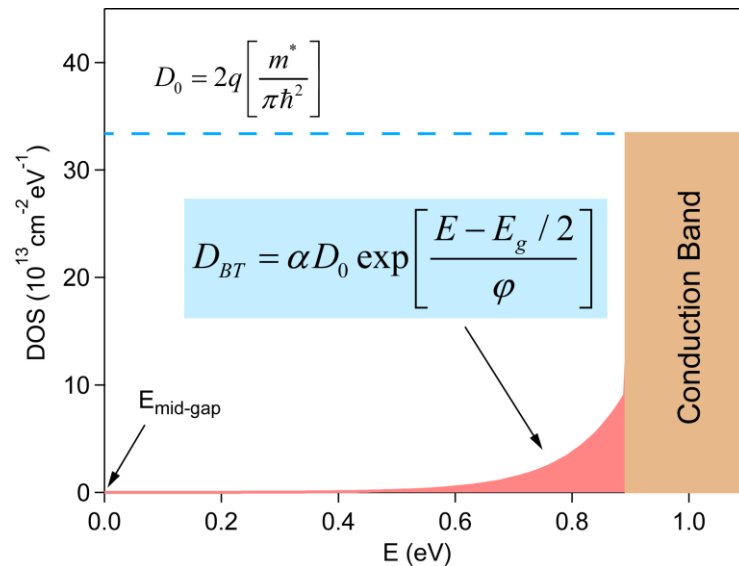
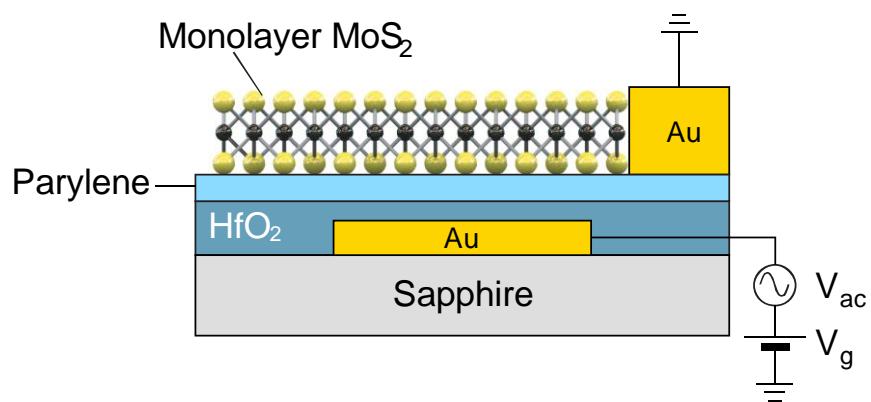
Band Tail



Zhu...Avouris; Nature Communications (2014)

$$D_{BT} = \alpha D_0 \exp \left[\frac{E - E_g/2}{\varphi} \right] \quad \varphi = 100 \text{ meV}$$

CV Measurements



Screening of Charged Impurities by the Environment

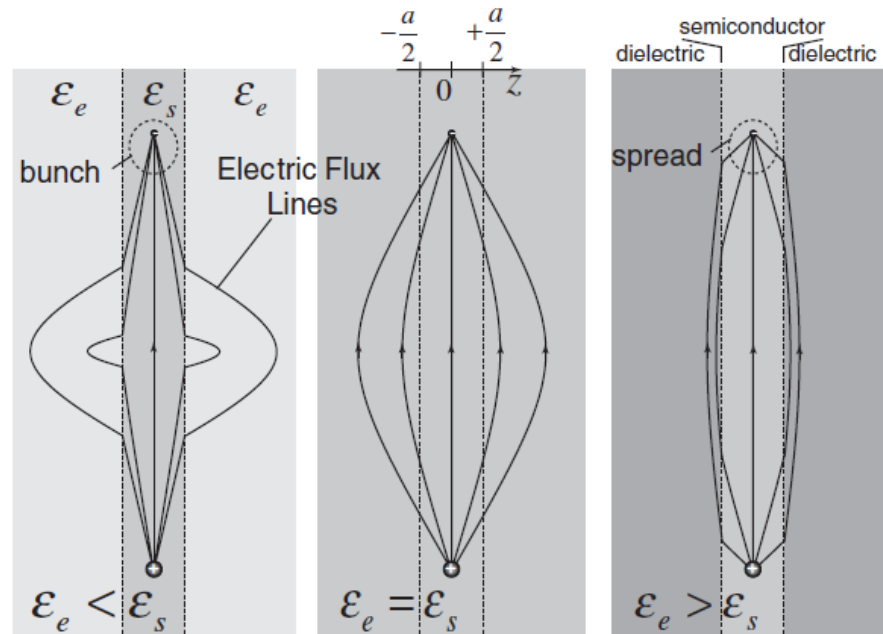
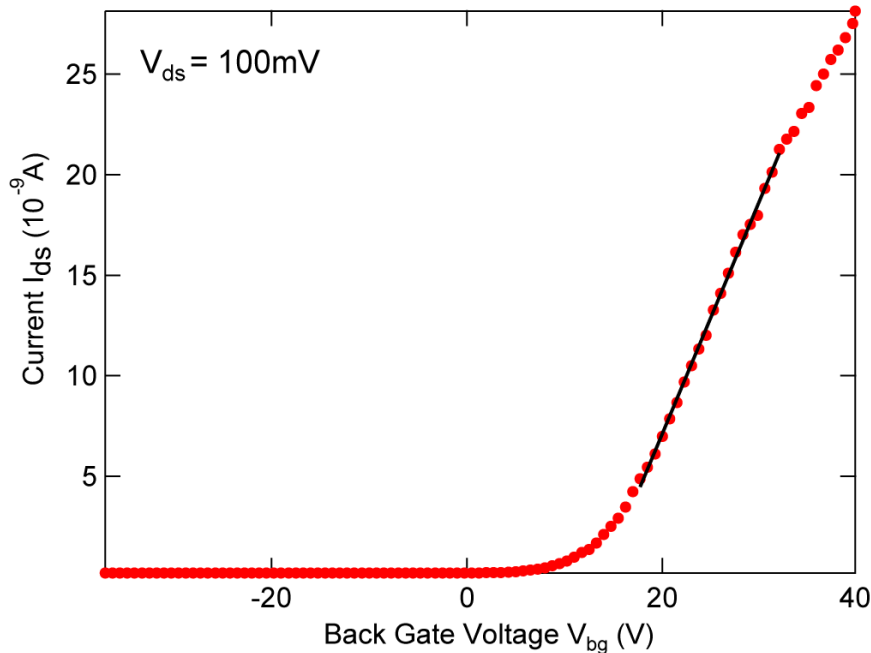


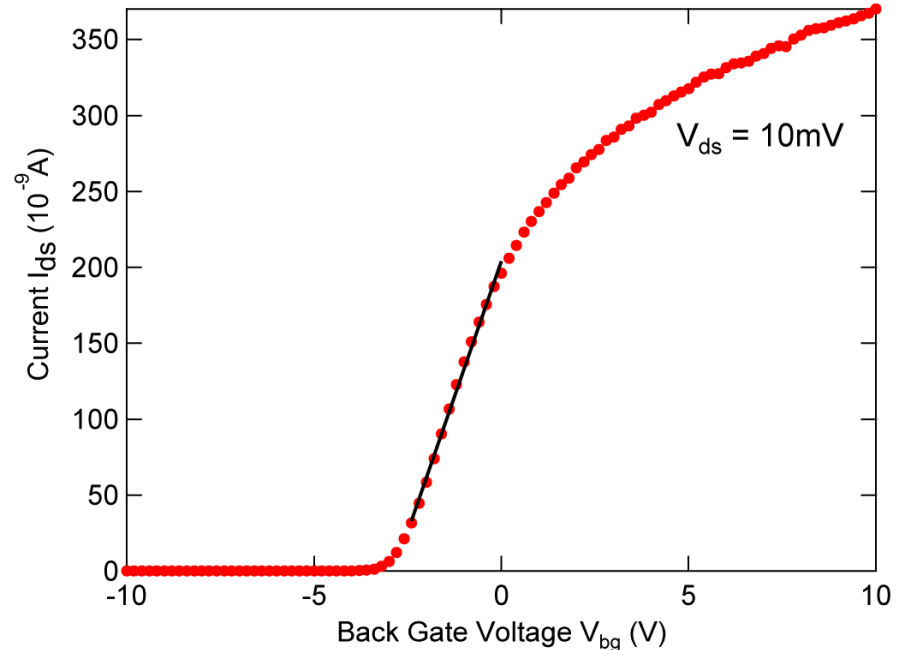
FIG. 1. Electric flux lines originating from a fixed ionized impurity and terminating on a mobile electron, and the effect of the dielectric environment. The flux lines bunch closer inside the semiconductor layer if $\epsilon_e < \epsilon_s$, and spread farther apart if $\epsilon_e > \epsilon_s$, thus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

Screening of Charged Impurities by the Environment

No dielectric coating



With 30nm ALD HfO₂



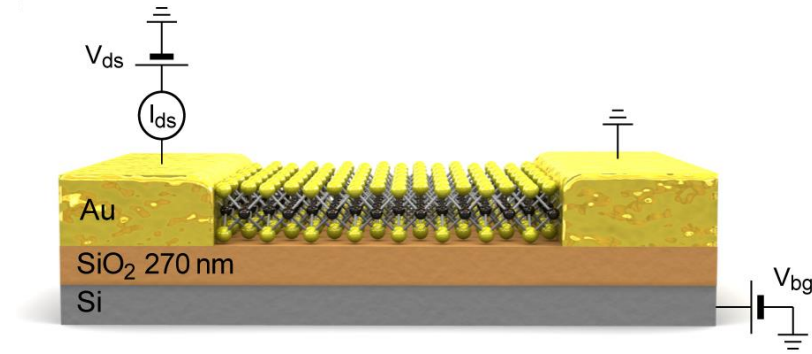
$$\mu = \frac{L}{WC_i V_{ds}} \frac{dI_{ds}}{dV_{bg}}$$

Screening of charged impurities

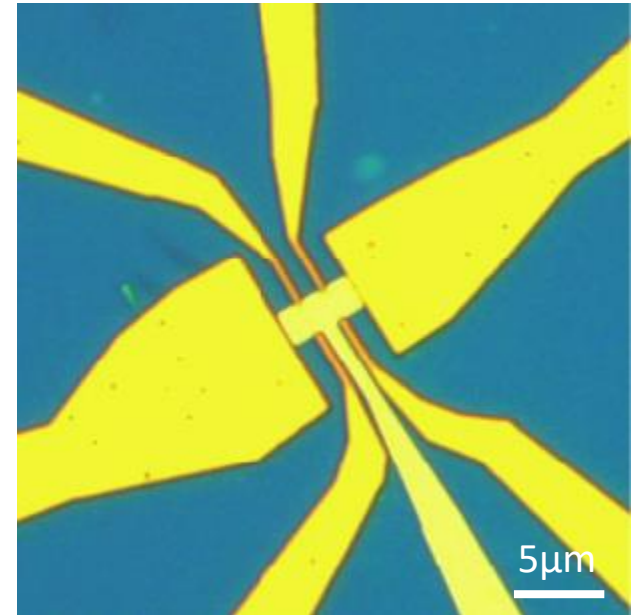
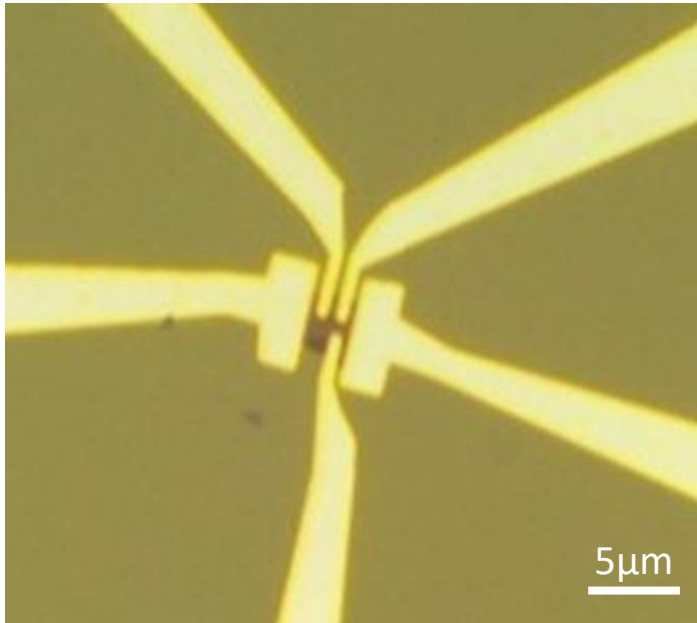
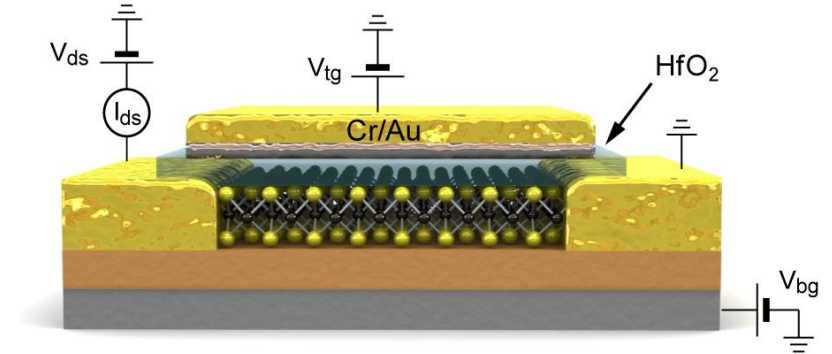
Modification of the MoS₂ phonon spectrum

Temperature-dependent El. Transport

No top-gate dielectric



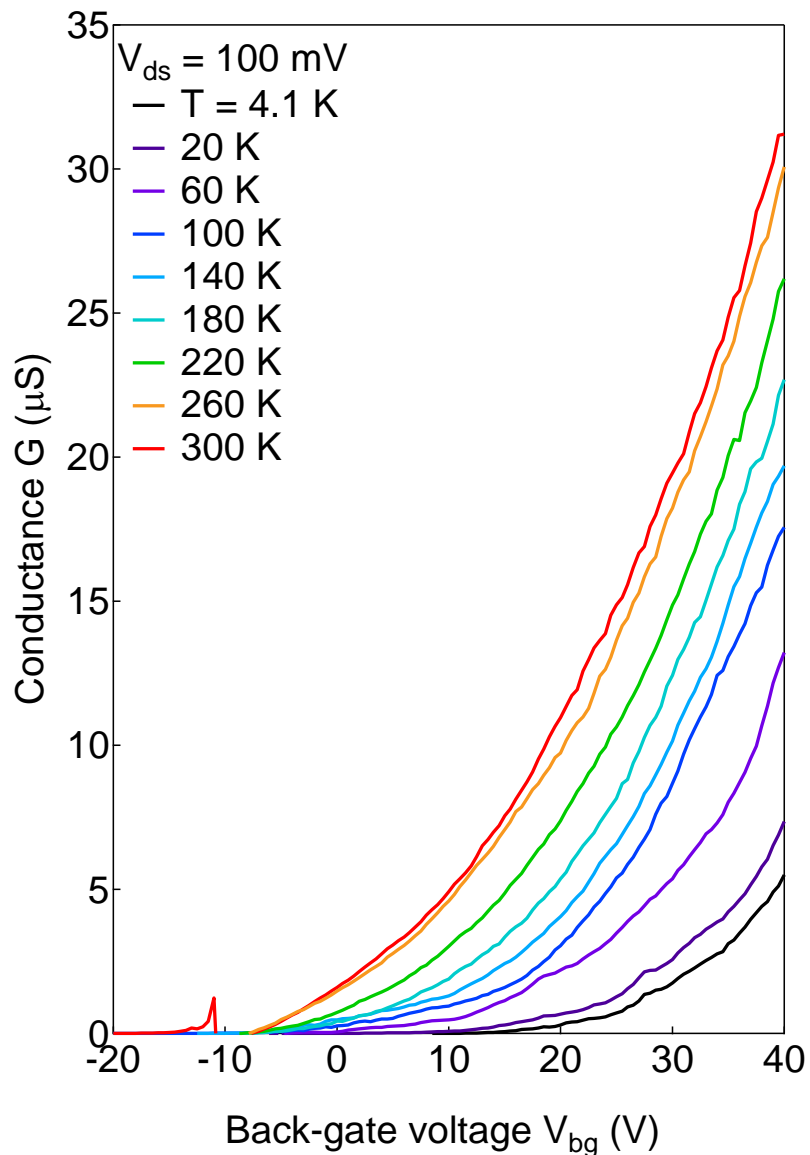
With top-gate dielectric



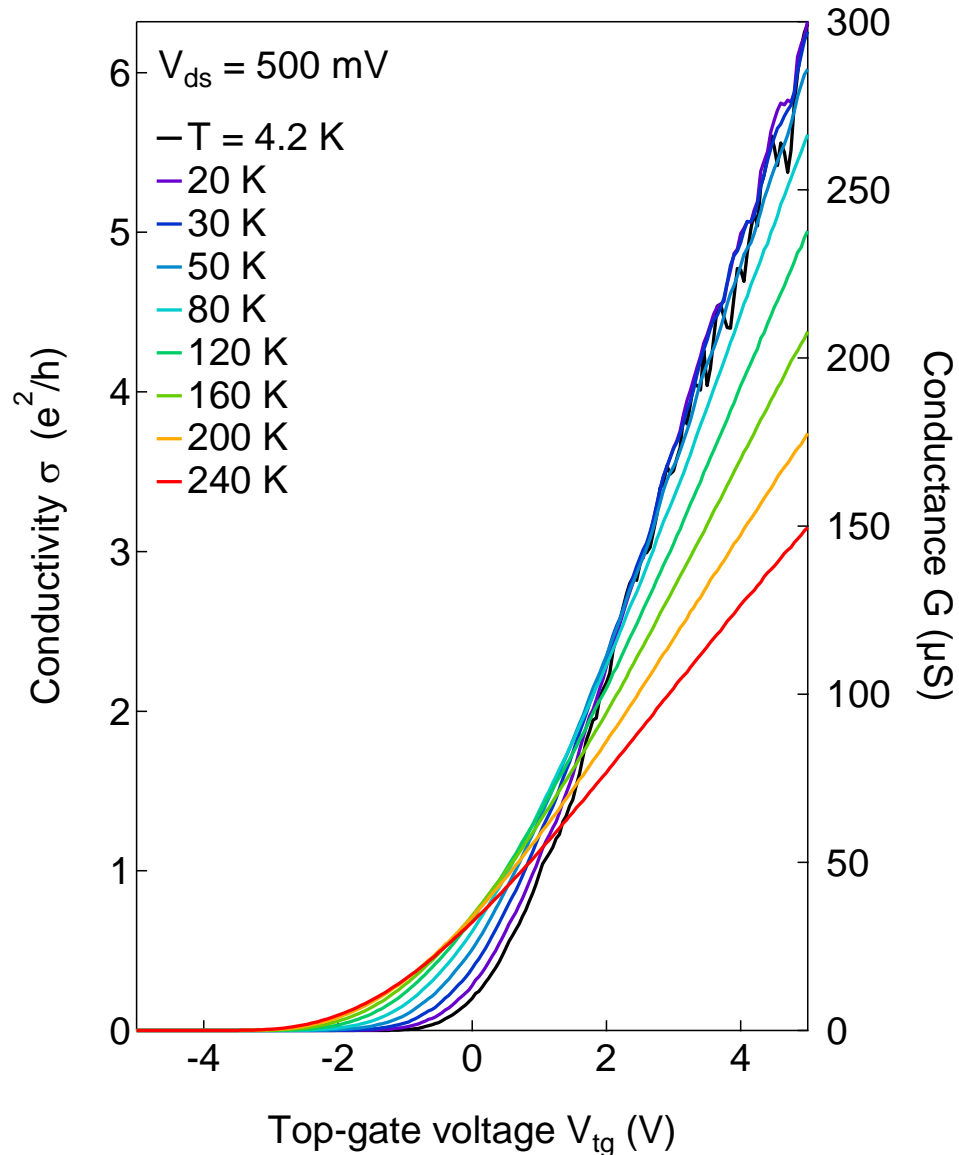
Radisavljevic and Kis; Nature Materials (2013)

Temperature-dependent El. Transport

No top-gate dielectric



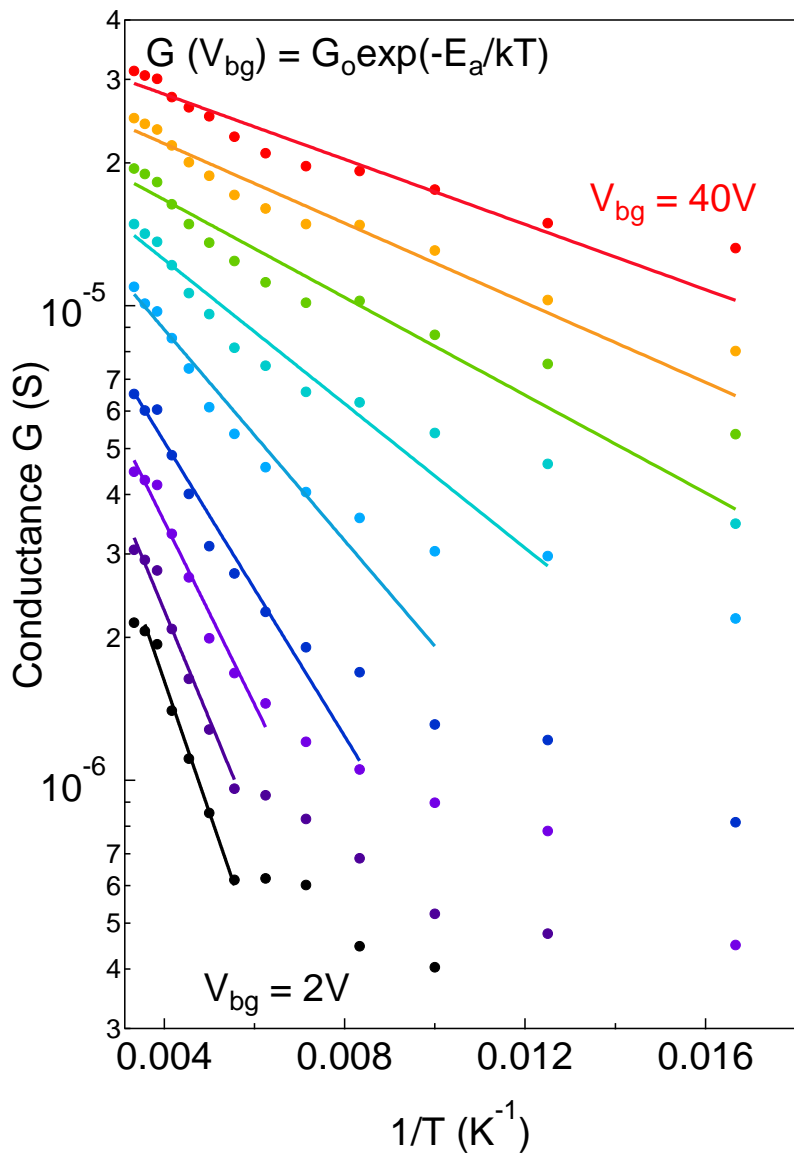
With top-gate dielectric



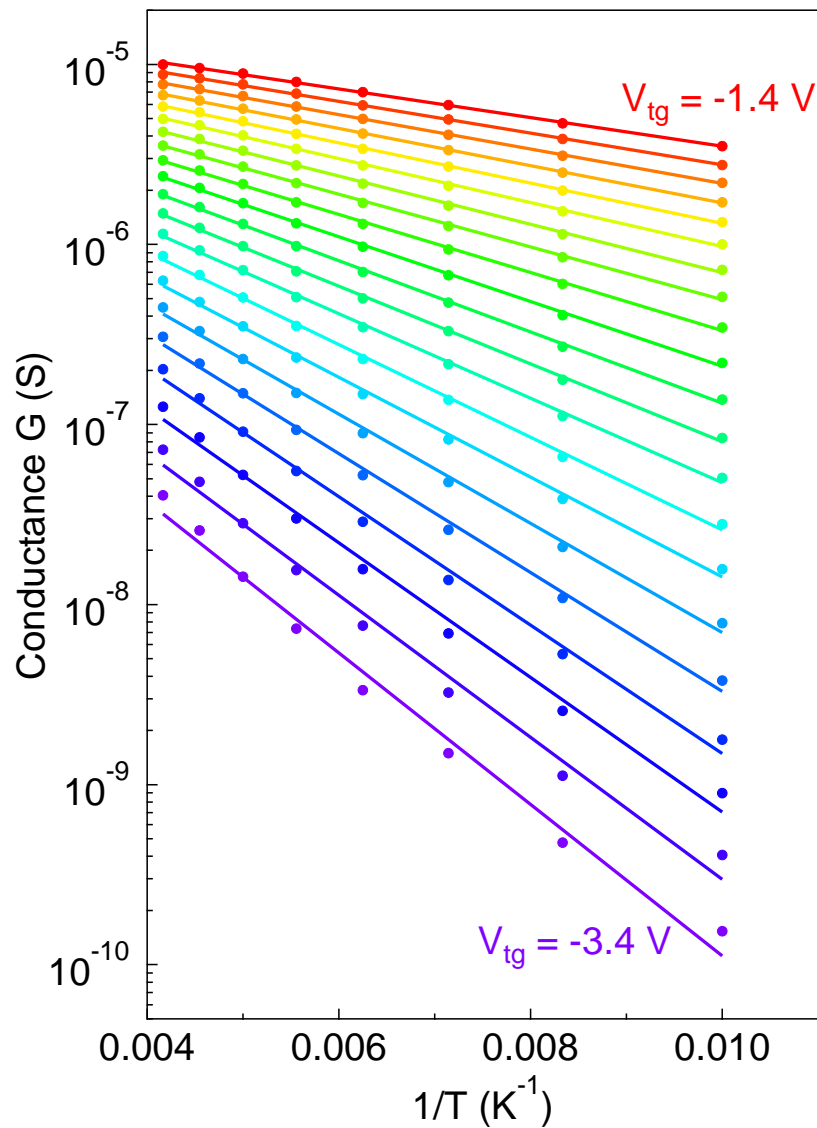
Radisavljevic and Kis; Nature Materials (2013)

Temperature-dependent El. Transport

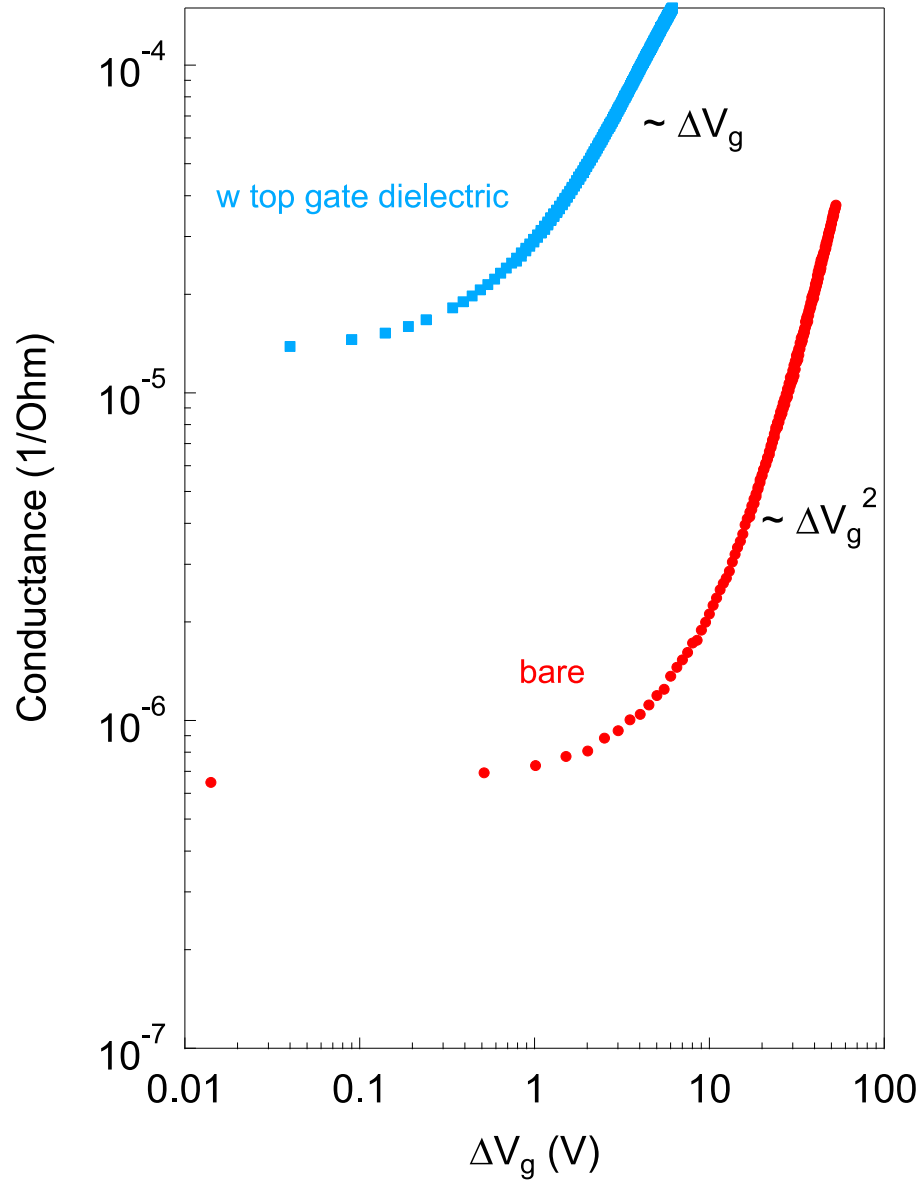
No top-gate dielectric



With top-gate dielectric



Screened vs. Unscreened Disorder Potential



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

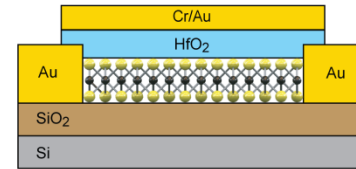
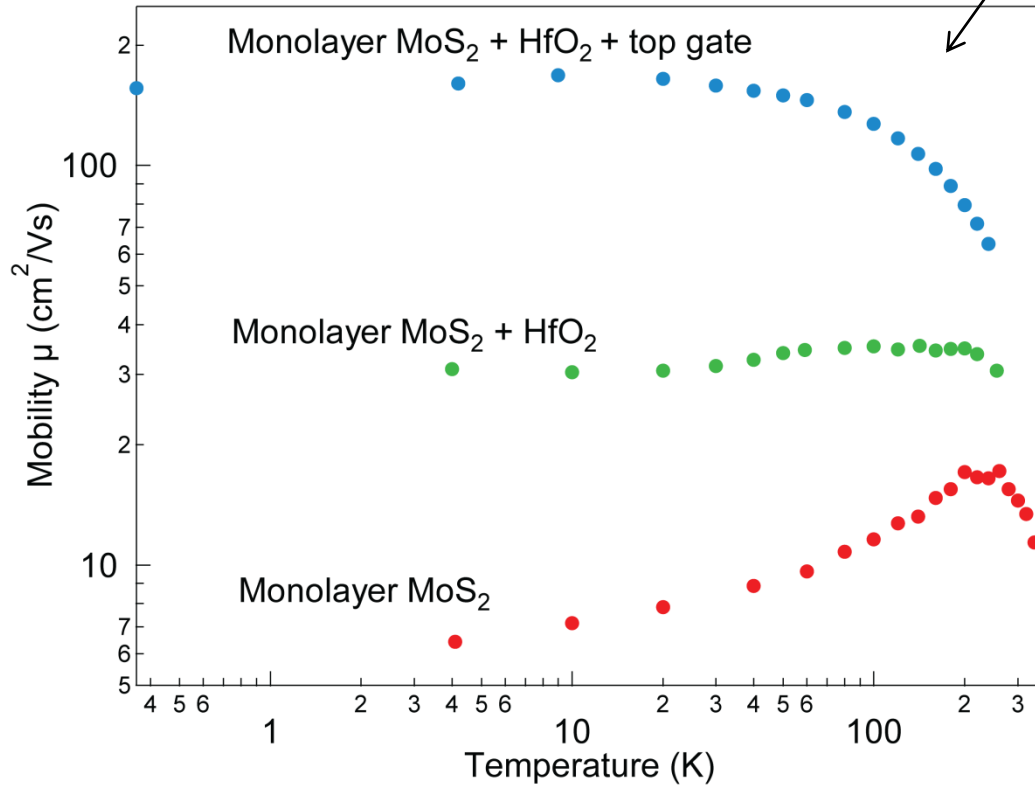
$\sigma \sim n$ screened ch. impurities

$\sigma \sim n^2$ unscreened

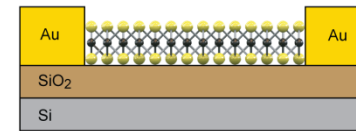
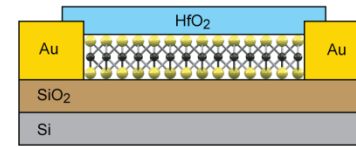
Mobility vs. Temperature

Radisavljevic and Kis; Nature Materials (2013)

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



$$\gamma = 0.73$$



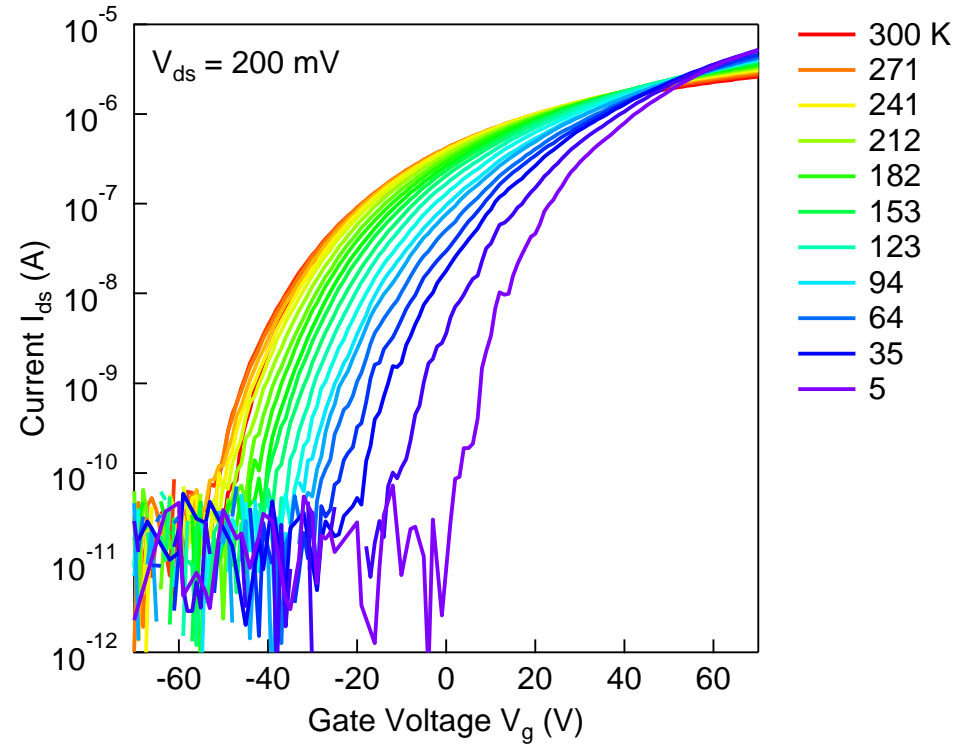
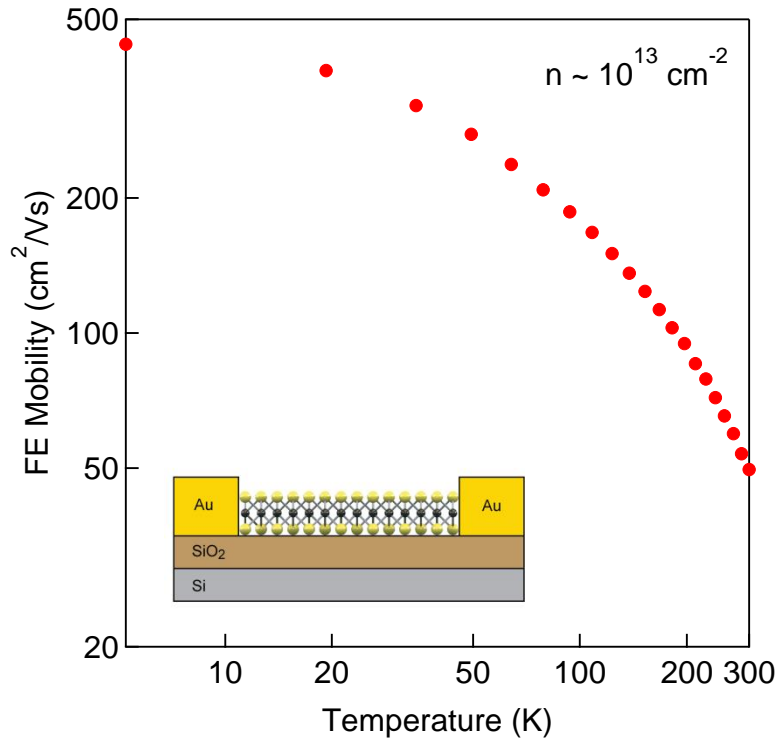
$$\gamma = 1.4$$

$$\text{Bulk } \gamma = 2.6$$

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

High-quality Devices With No Encapsulation

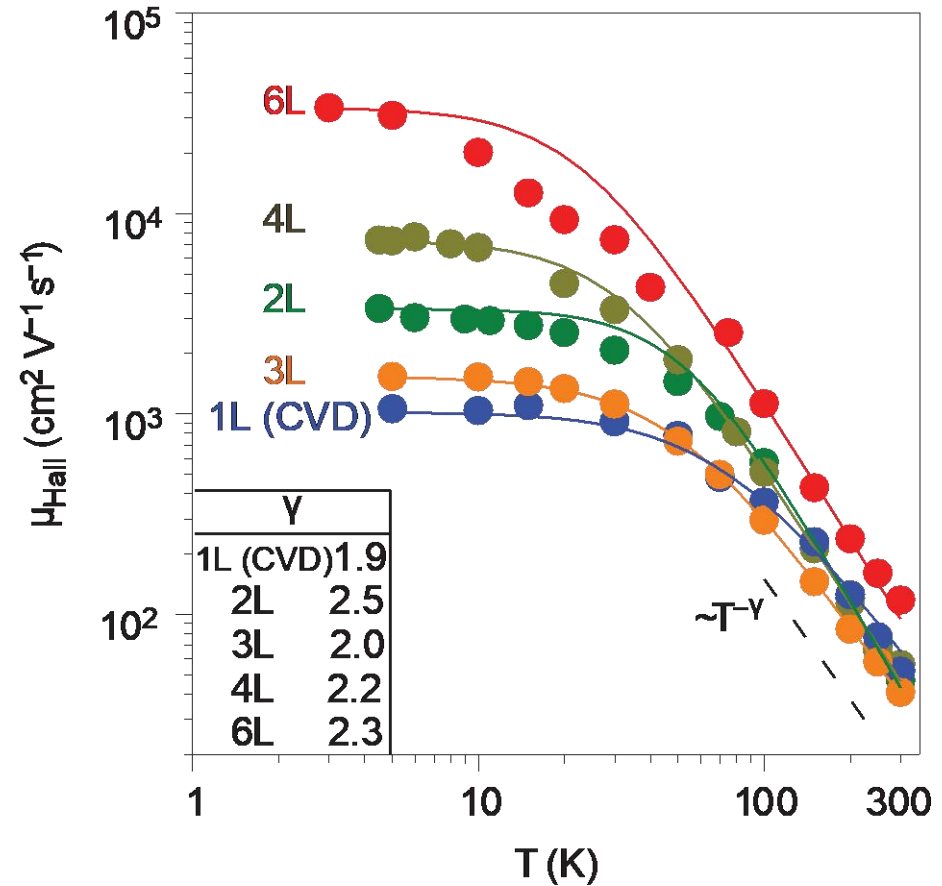
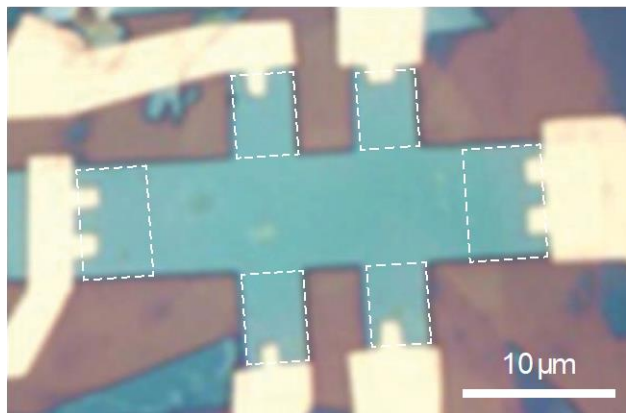
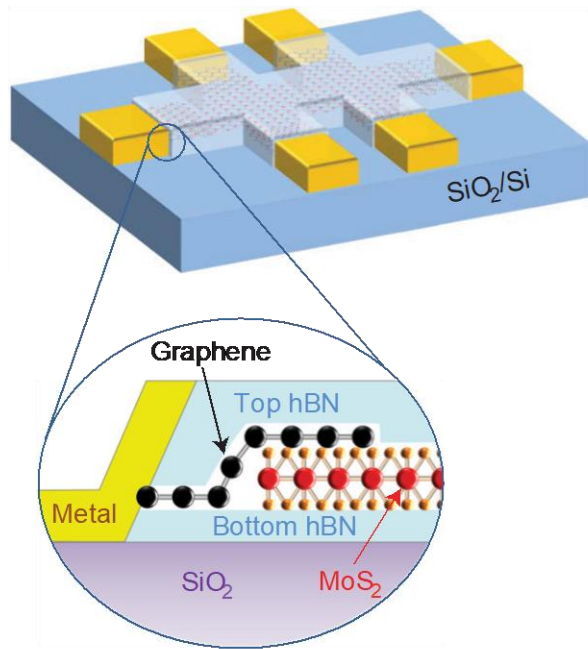


$$\gamma = 1.7 \text{ at RT}$$

See also: Baugher, Herrero et al., Nano Lett. (2013)

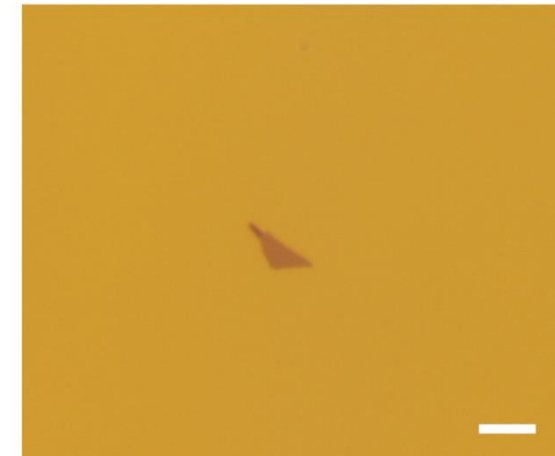
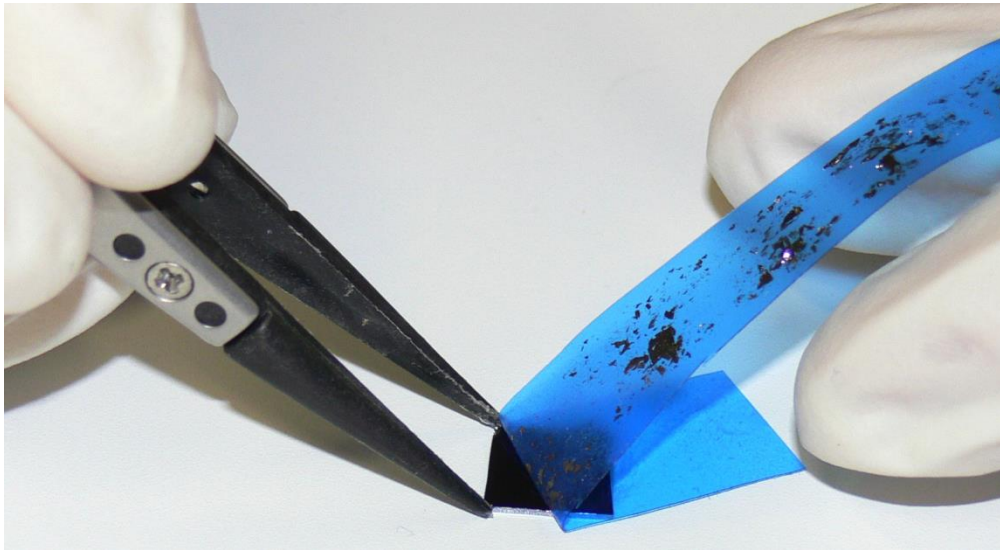
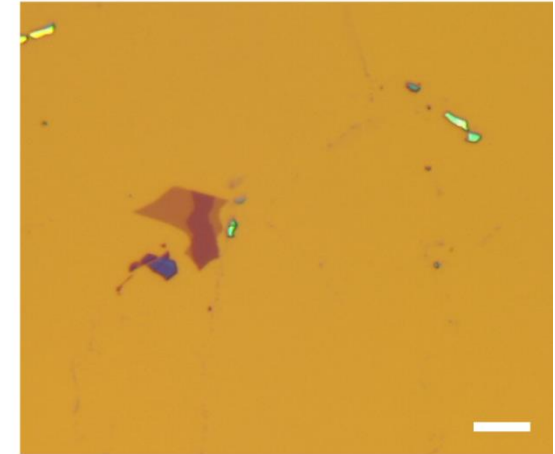
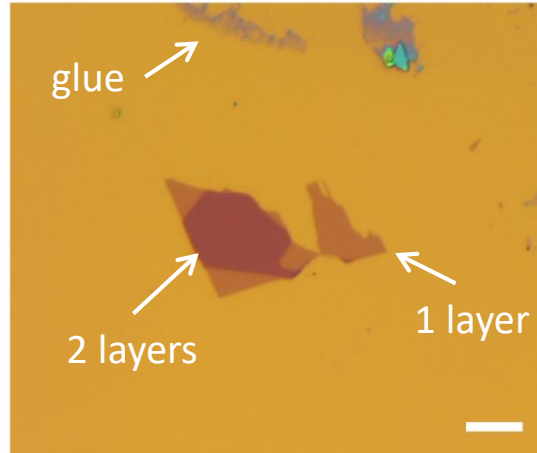
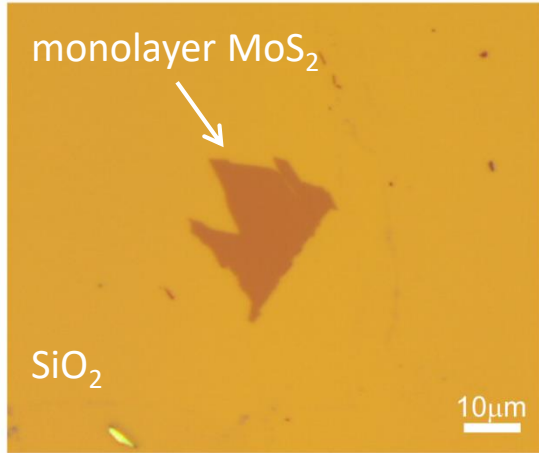
Jariwala, Hersam et al., Appl. Phys. Lett. 102, 173107 (2013)

Encapsulation in Boron Nitride

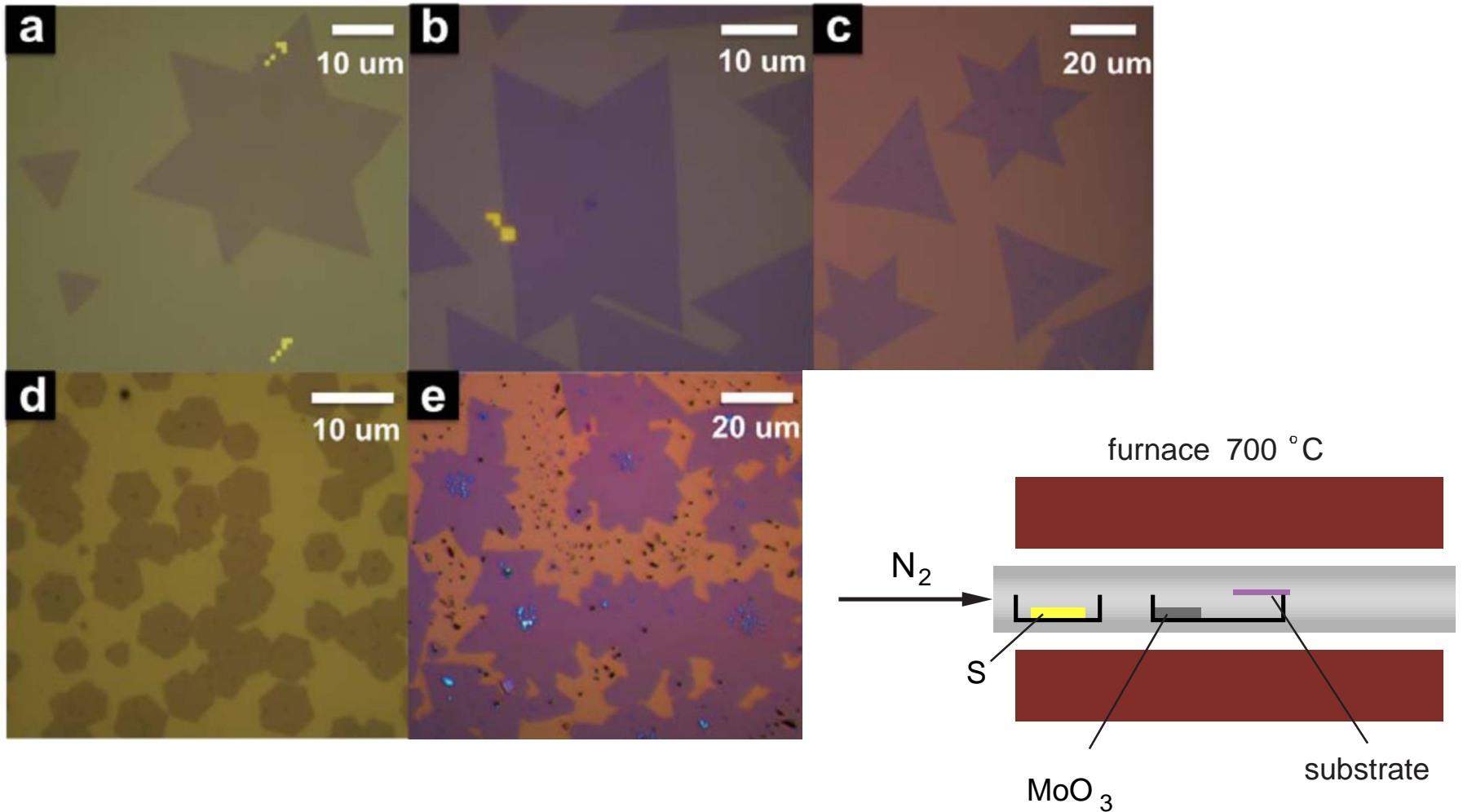


Material Preparation

Scotch Tape Exfoliation

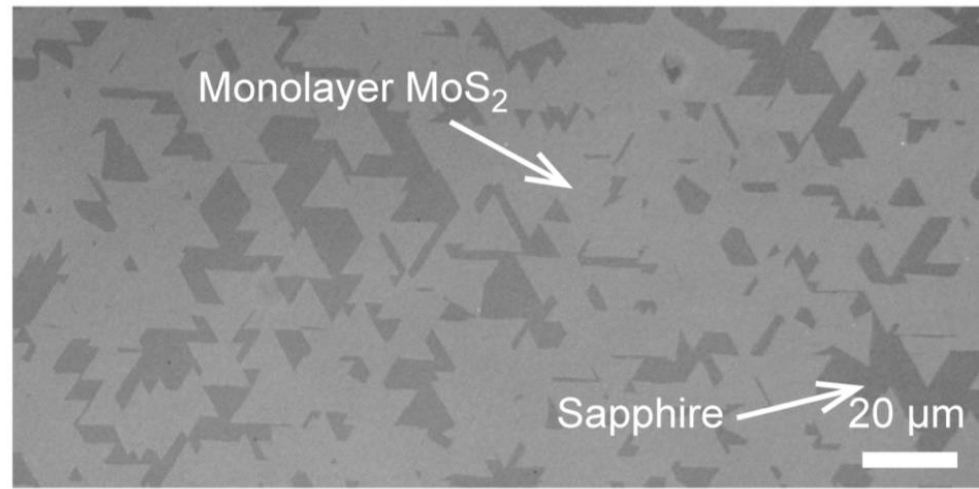
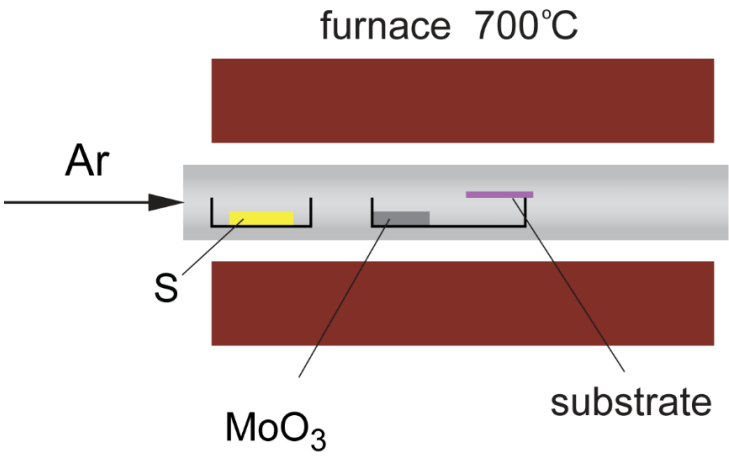


MoS₂: CVD Growth

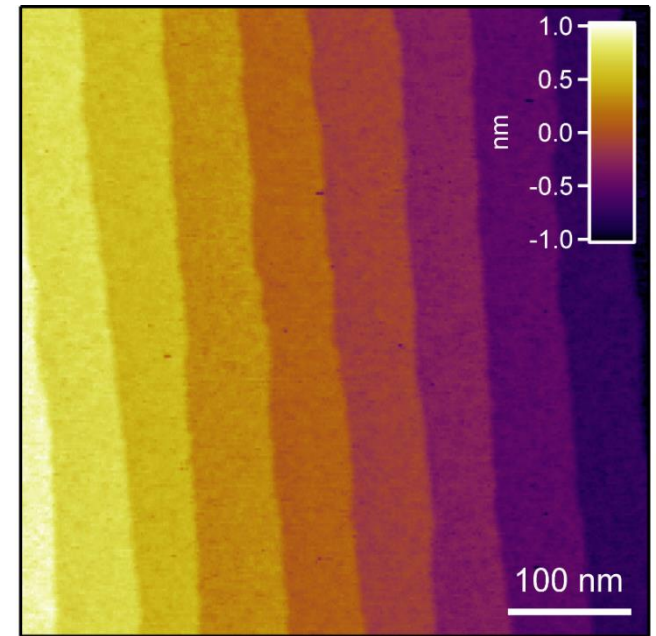


Van der Zande et al. Nature Materials (2013)
Najmaei et al. Nature Materials (2013)

CVD Growth



Dumcenco, Kis et al. ACS Nano 9, 4611 (2015)



AFM image of a sapphire surface

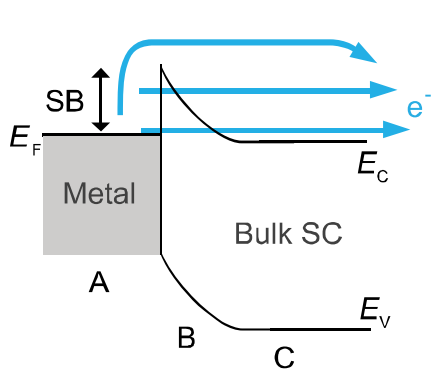
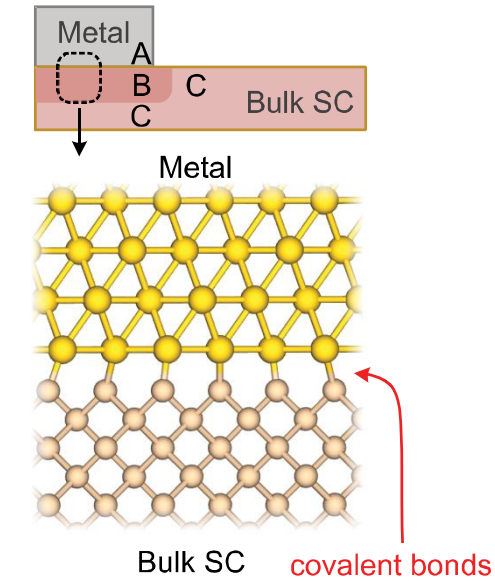
Being commissioned at EPFL: MOCVD – BM 2D NOVO



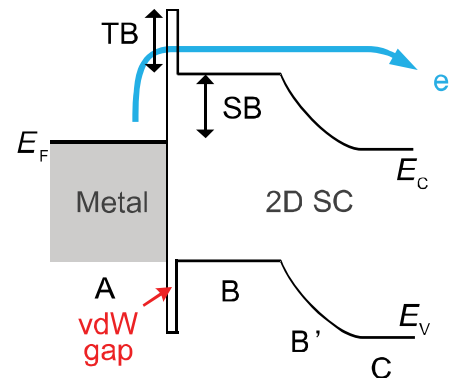
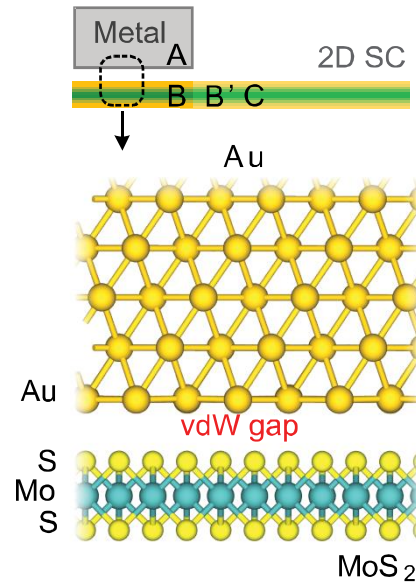
The Contacts

Electrical Contacts to 2D Materials

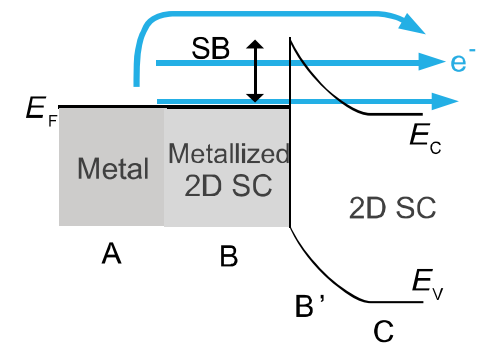
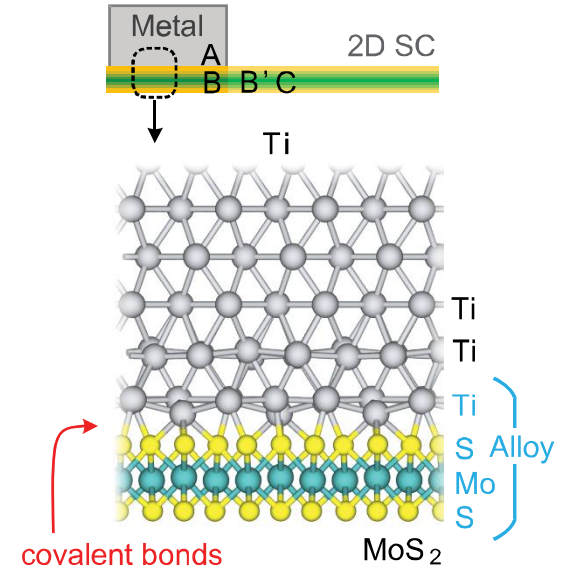
Metal – Bulk SC Contact



Metal - 2D SC Contact (with vdW Gap)

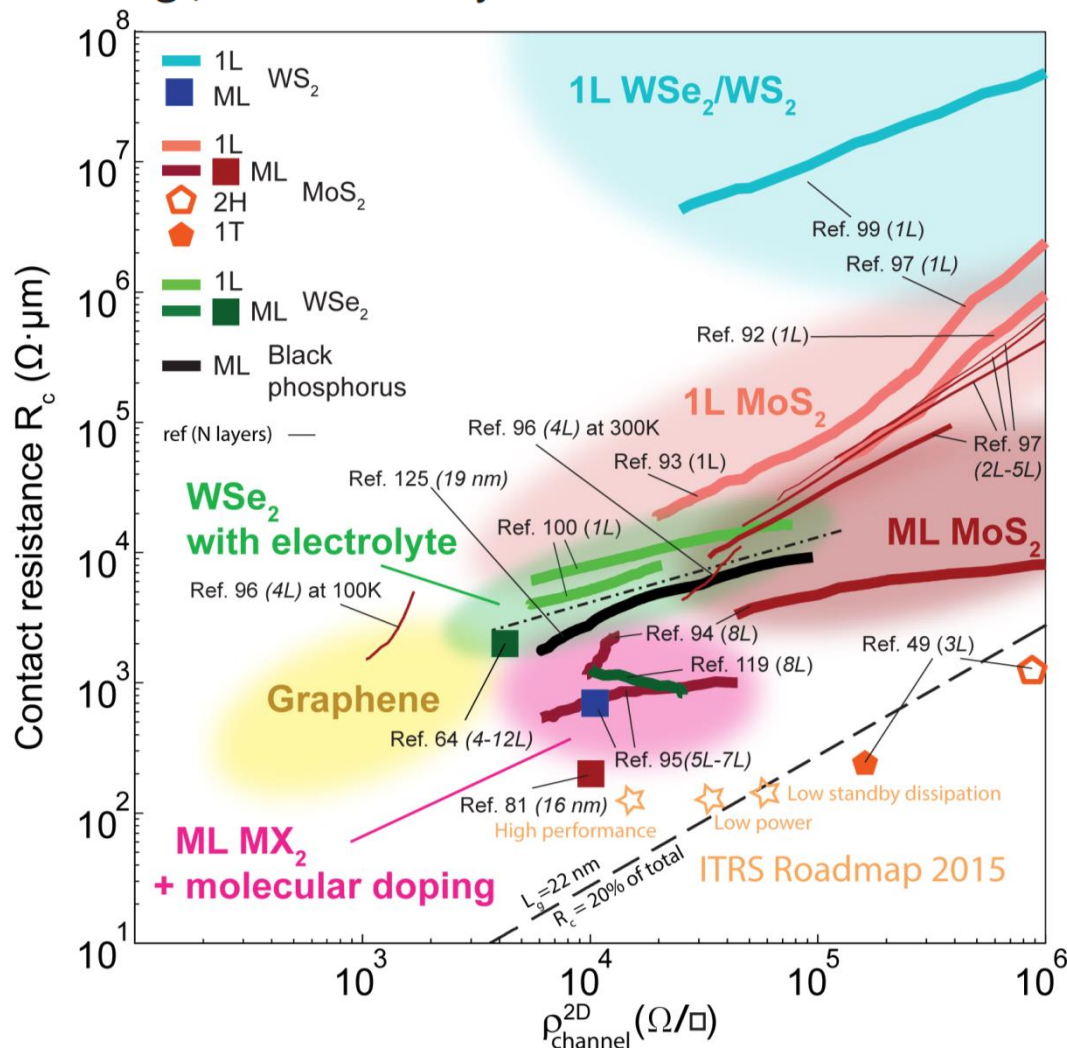


Metal - 2D SC Contact (with Hybridization)

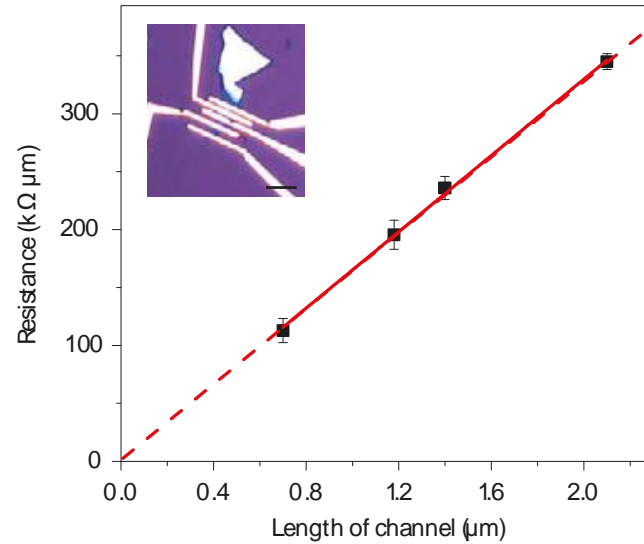
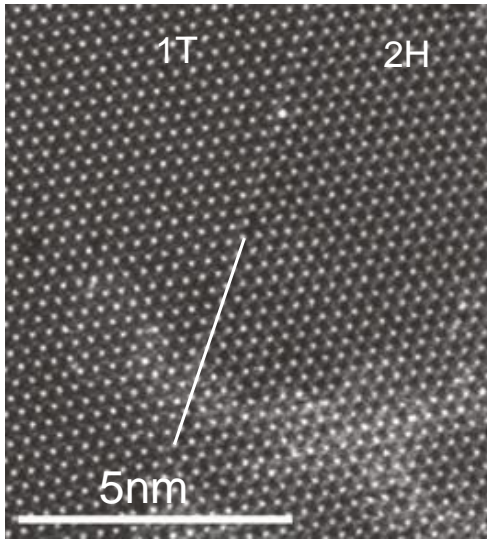


Electrical contacts to two-dimensional semiconductors

Adrien Allain¹, Jiahao Kang², Kaustav Banerjee^{2*} and Andras Kis^{1*}

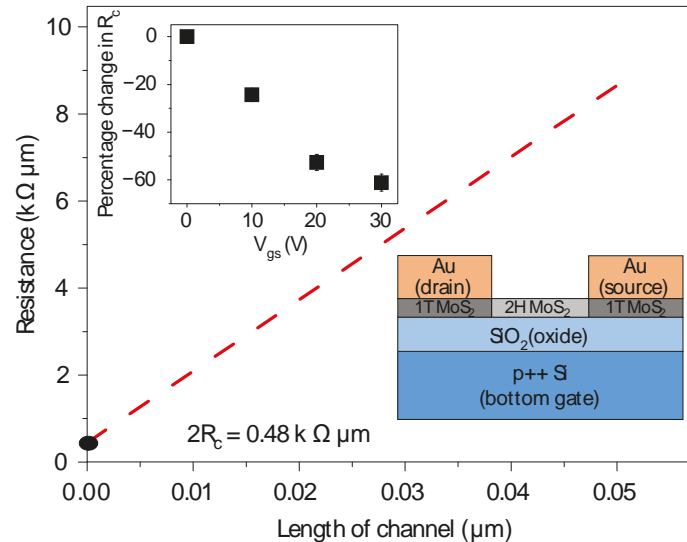
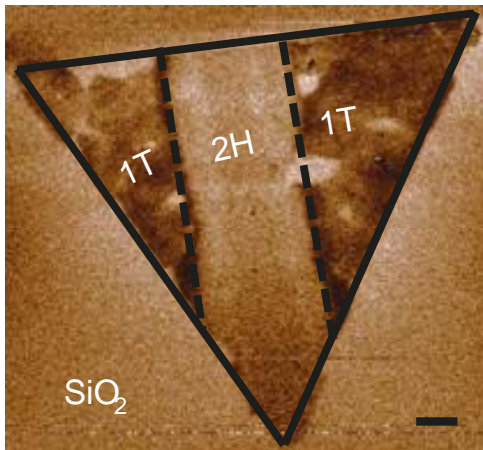


Lowest Reported Contact Resistance



State of the art
 $R_c = 200 - 300 \Omega \mu\text{m}$

Theoretical limit
 $R_c = 30 \Omega \mu\text{m}$ for
 $n_{2D} = 10^{13} \text{ cm}^{-2}$



Recapitulation

Why semiconducting nanostructures for nanoelectronics

Historic overview

- Graphene
- Transition metal dichalcogenides and 2D materials

Charged impurities

- Point defects
- Screening and its signatures in electrical transport
- Disorder engineering

Material growth

- CVD

Electrical contacts to 2D materials