

Semiconductor Devices II

Part 2

Chapter 1: Introduction to 2D materials

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Electrical Engineering Institute



Subjects and goals

2D materials – introduction and materials aspects

FETs with 2D materials – switching, contact resistance, trap states, applications in sensing and memories

Optoelectronics with 2D materials

Emerging, post-CMOS concepts: valleytronics, spintronics, excitonic devices

Implementation:

- Lectures

- Exercises

- Lab demonstrations

Introduction

Why semiconducting nanostructures for nanoelectronics

Historic overview

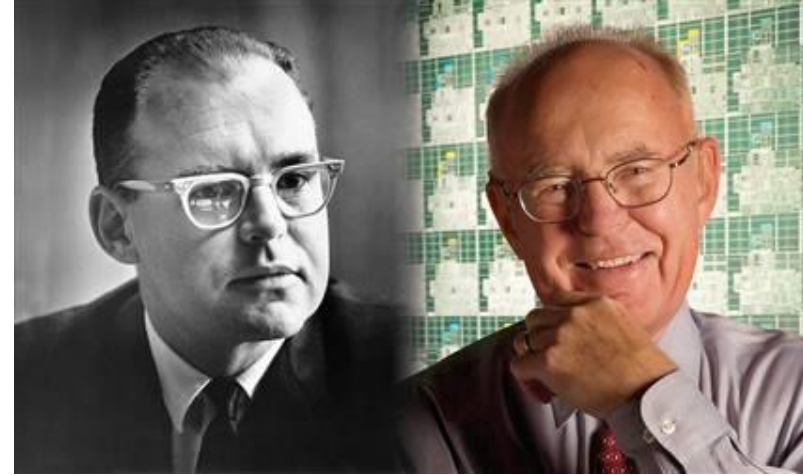
- Graphene
- Transition metal dichalcogenides and 2D materials

Material growth

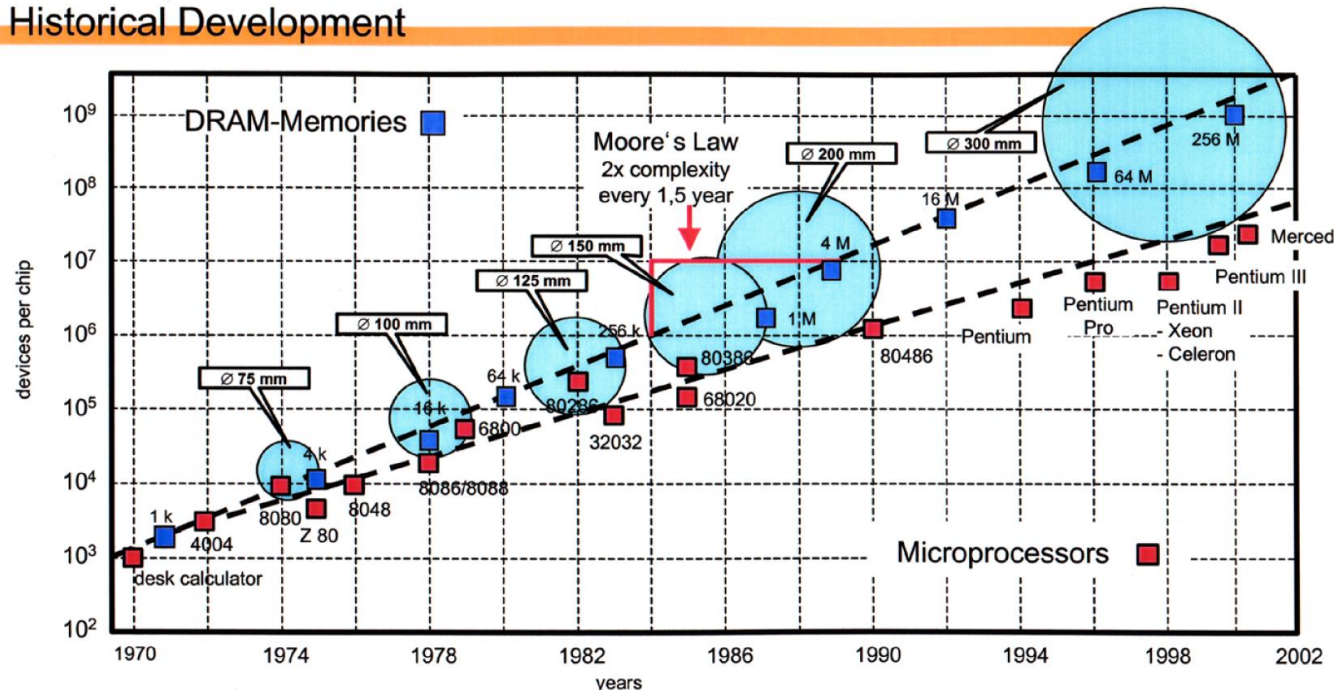
- CVD

Moore's Law

Gordon Moore, co-founder of Intel stated in 1965:
"The number of transistors that can be inexpensively placed on an integrated circuit is increasing exponentially, doubling approximately every two years"



Historical Development



http://nobelprize.org/nobel_prizes/physics/laureates/2000/phyadv.pdf

Moore's Law

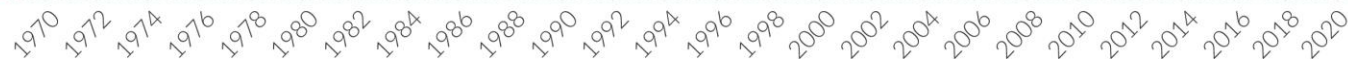
Moore's Law: The number of transistors on microchips doubles every two years

Moore's law describes the empirical regularity that the number of transistors on integrated circuits doubles approximately every two years.

This advancement is important for other aspects of technological progress in computing – such as processing speed or the price of computers.

Our World
in Data

Transistor count



Data source: Wikipedia (wikipedia.org/wiki/Transistor_count)

Year in which the microchip was first introduced

OurWorldinData.org – Research and data to make progress against the world's largest problems.

Licensed under CC-BY by the authors Hannah Ritchie and Max Roser.

Source: Wikipedia ([Wikipedia.org/wiki/Transistor_count](https://en.wikipedia.org/wiki/Transistor_count))

Dissipated Heat

Processor coolers 20 years ago and now



Source: [bequiet.com](https://www.bequiet.com)
Dark Rock Elite

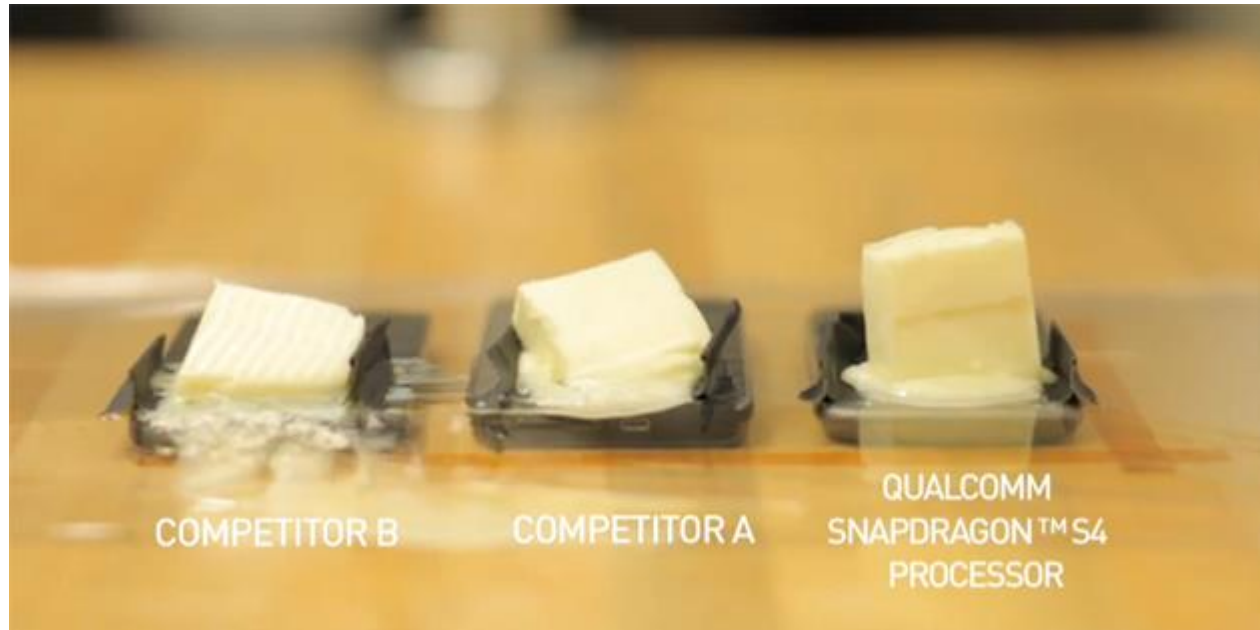
Dissipated Heat

Frying eggs on processors



http://www.phys.ncku.edu.tw/~htsu/humor/fry_egg.html

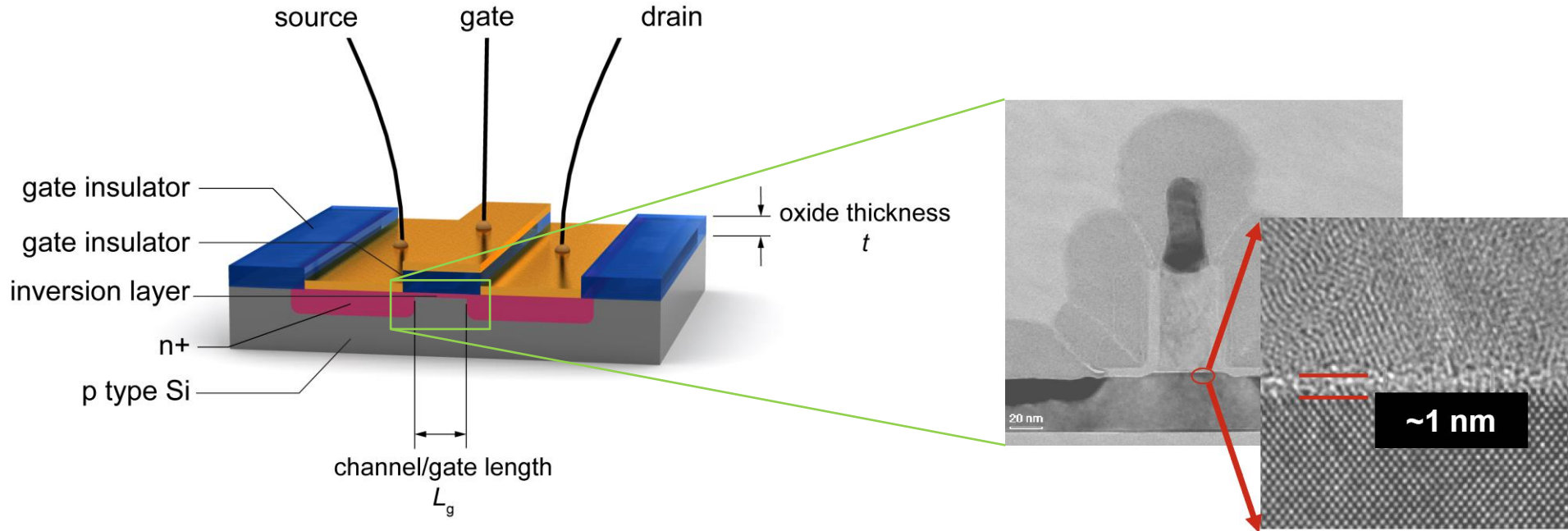
Melting-butter Benchmark



Source: Android andMe.com

MOSFET

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



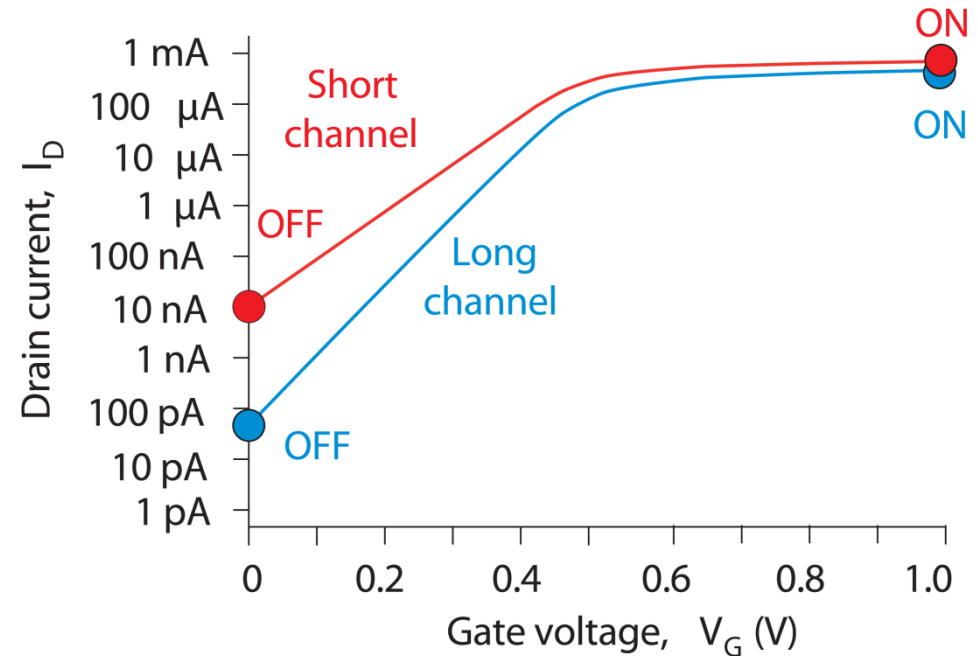
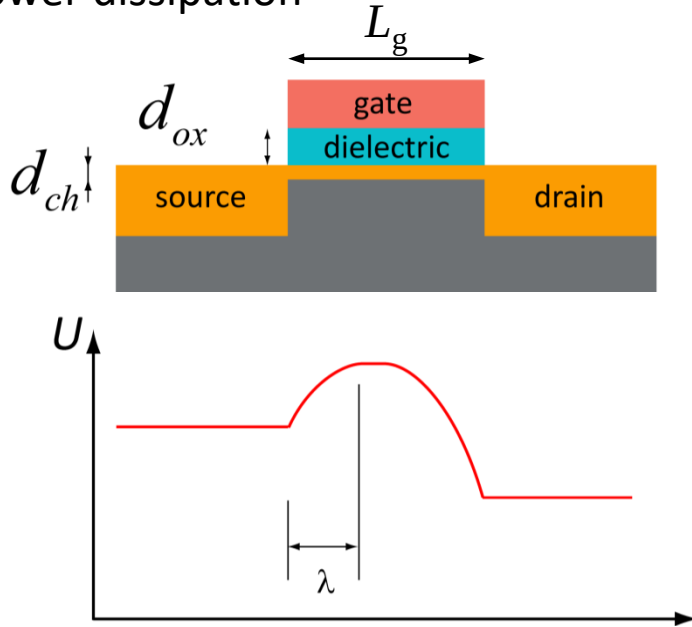
Approaching atomistic limits

Channel length in Intel processors:

14 nm	2014
10 nm	2017
7 nm	2018? 2022!

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 $3-5 \times \lambda$

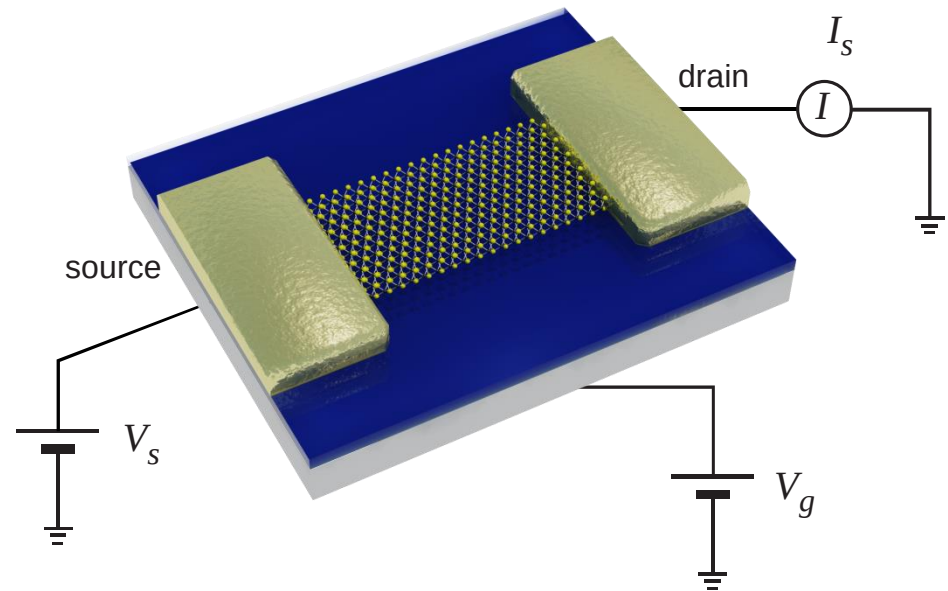
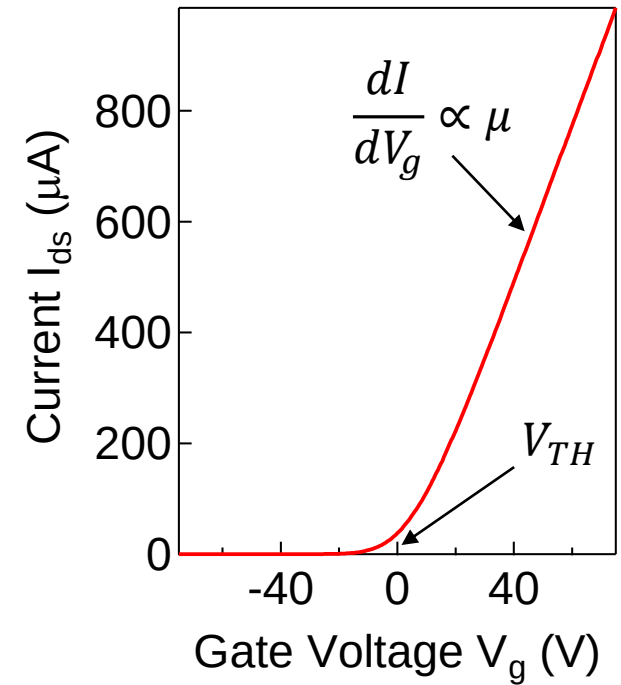
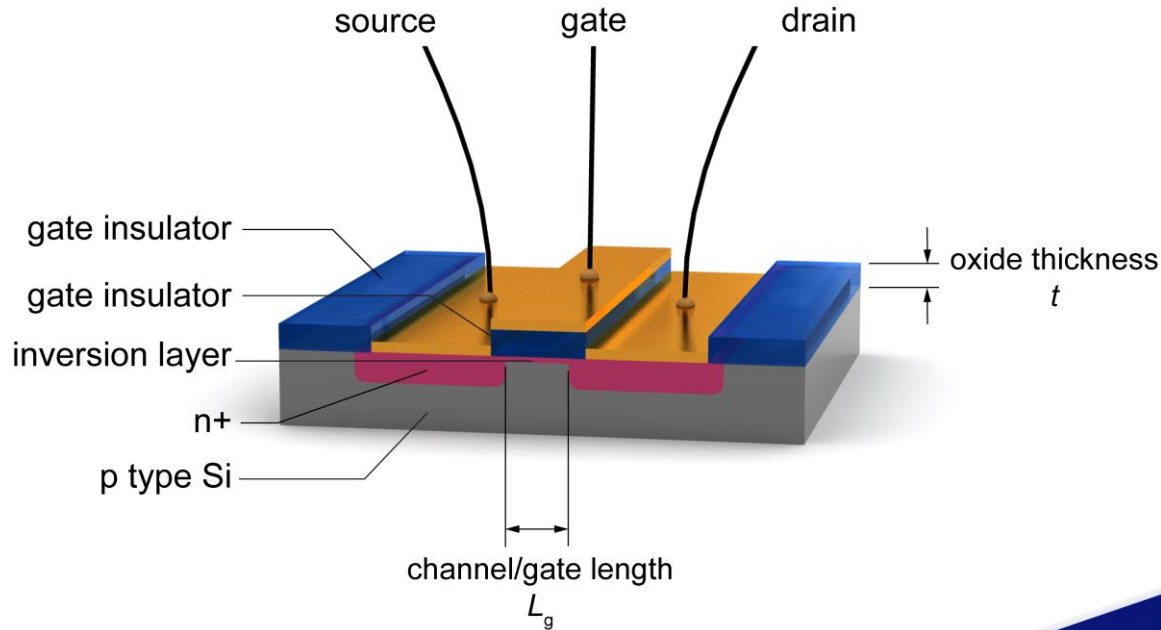
Example:

2 nm thin Si, 1 nm SiO_2 : $L_g > 10$ nm

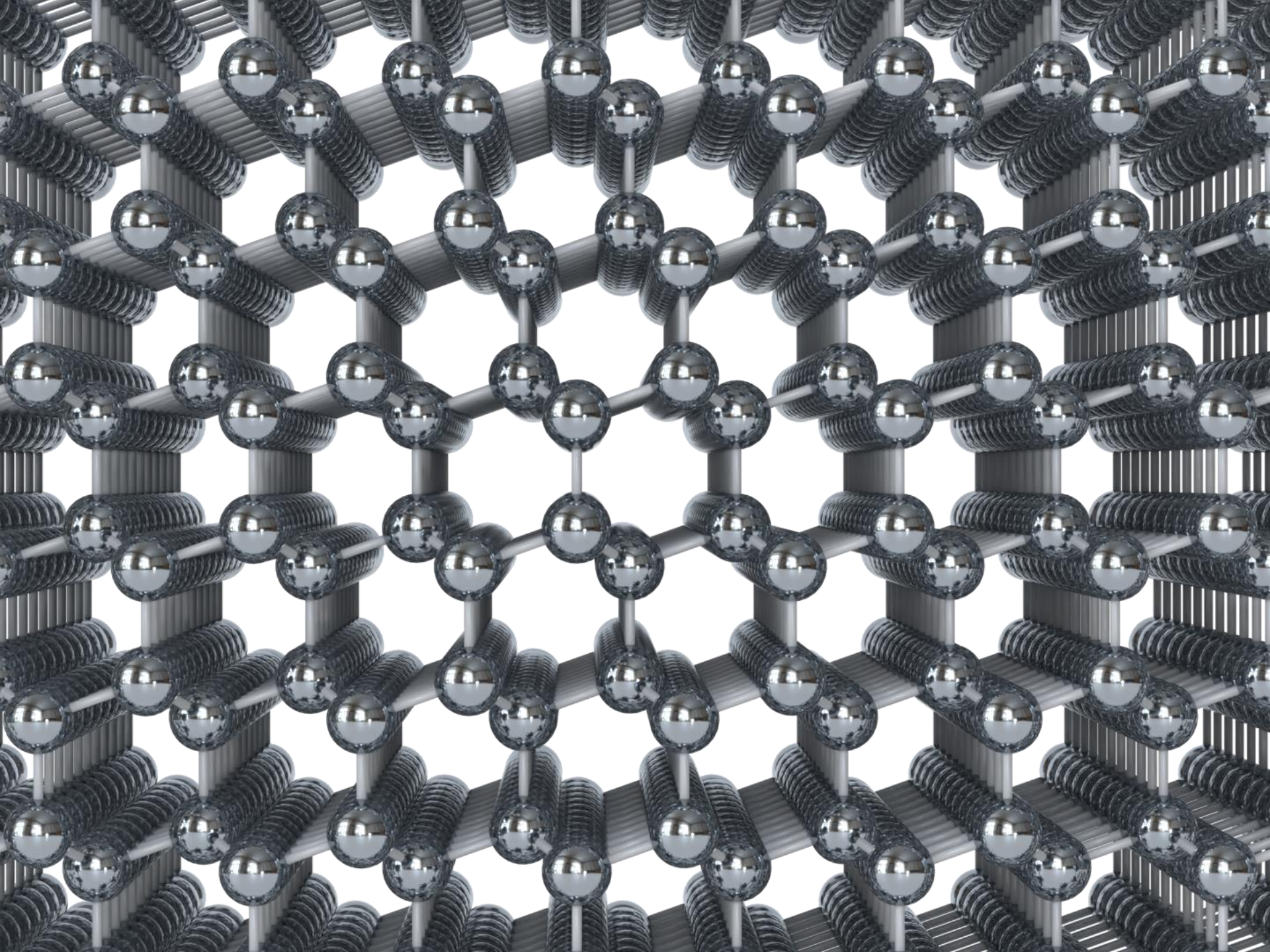
Ferain et al., Nature 479, 310 (2011)

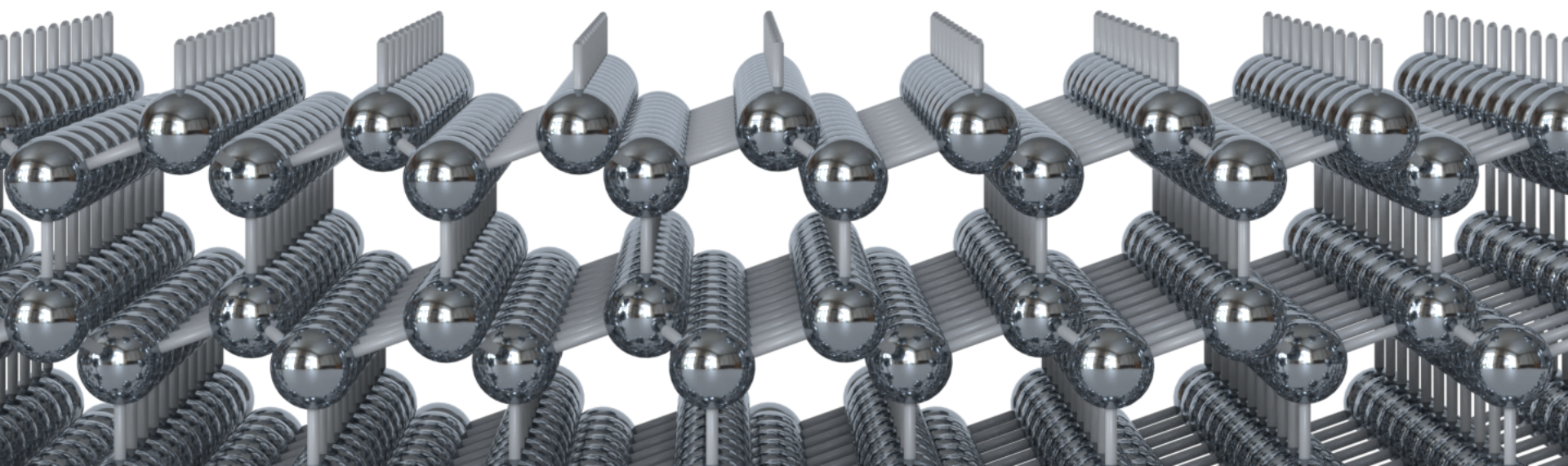
Colinge, Sol. State El. 48, 897 (2004)

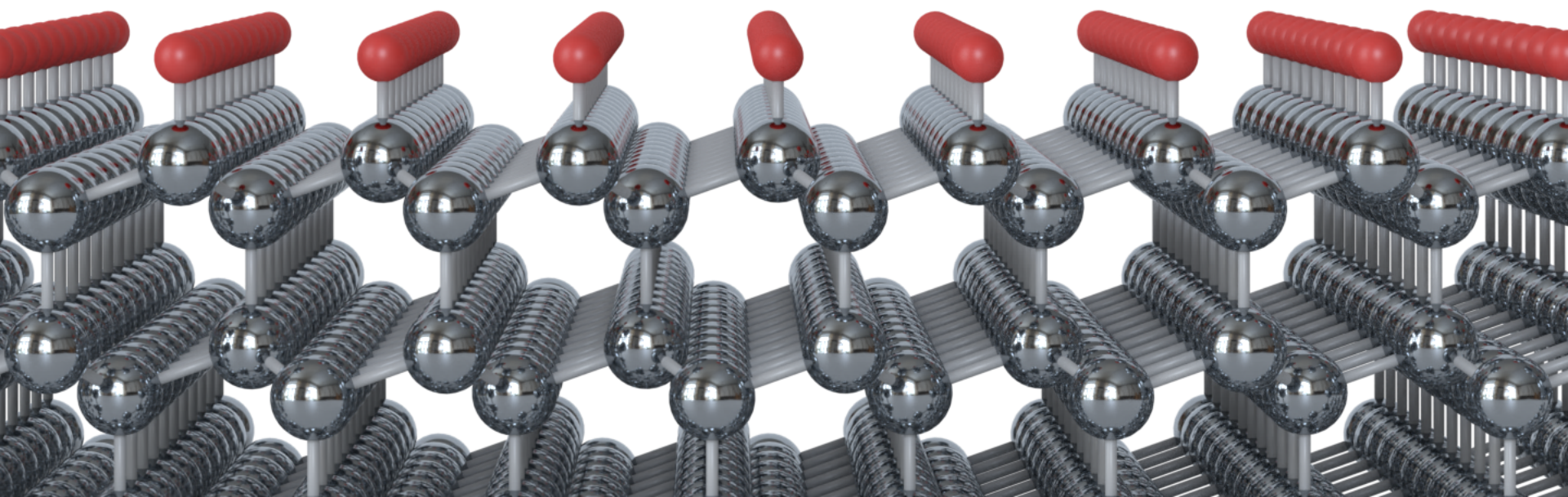
FETs Based on Nanomaterials



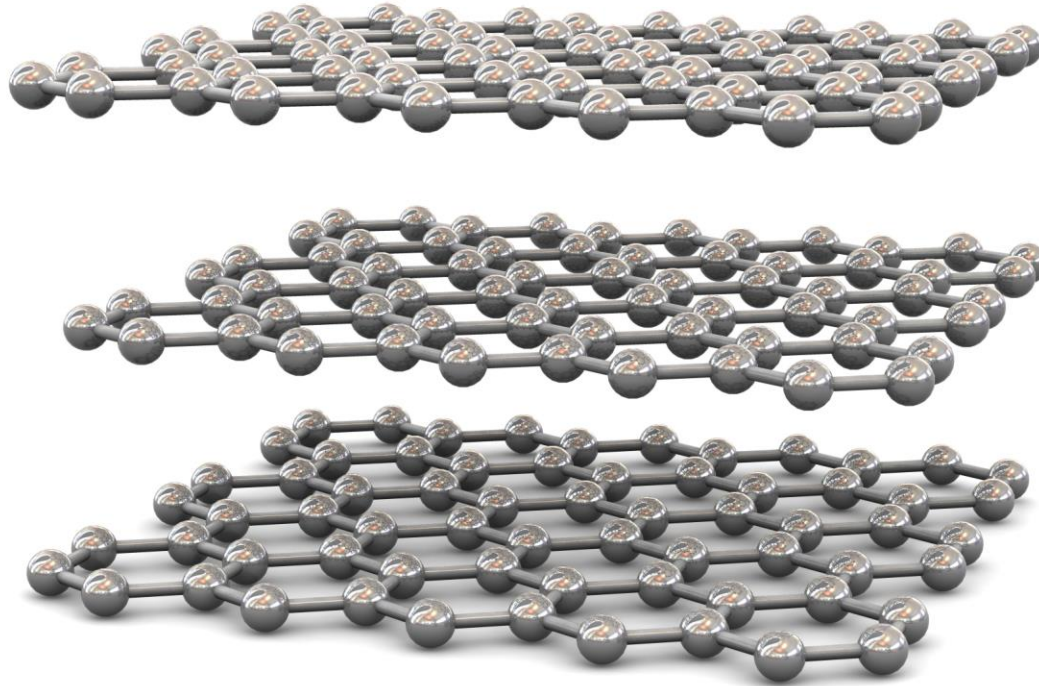
FET with a nanomaterial channel



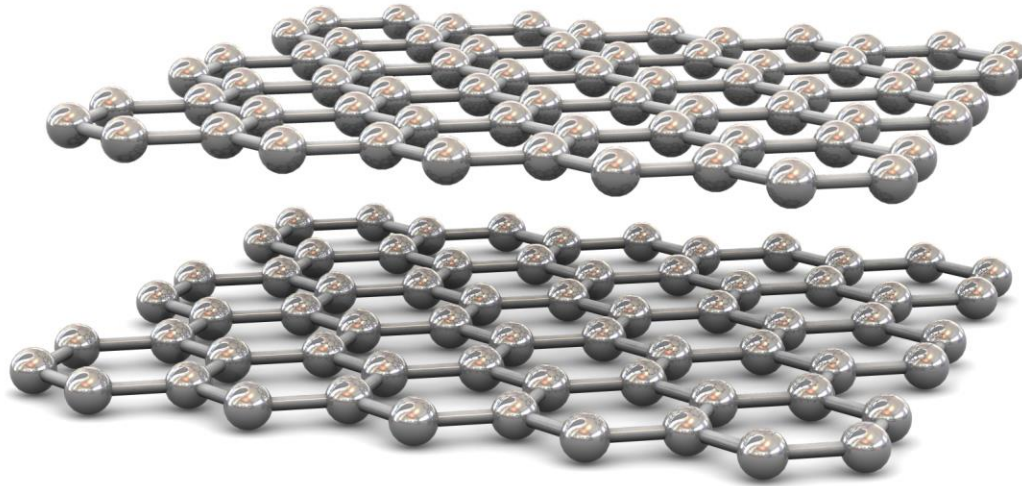




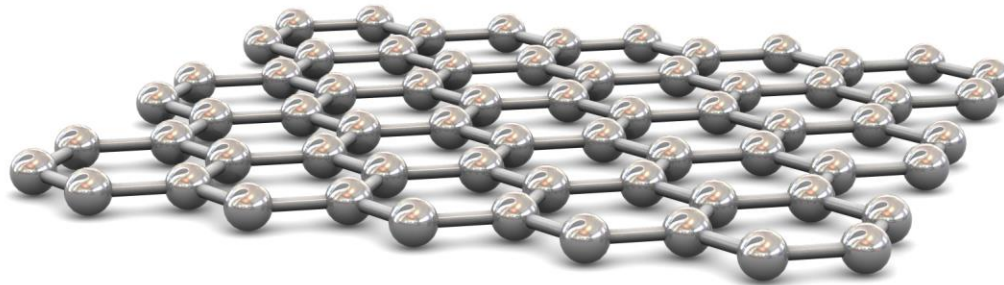
Graphite and Graphene



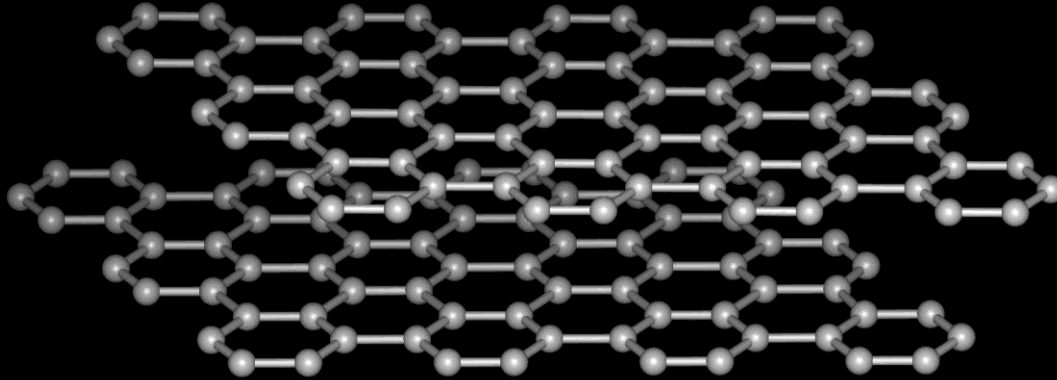
Graphite and Graphene



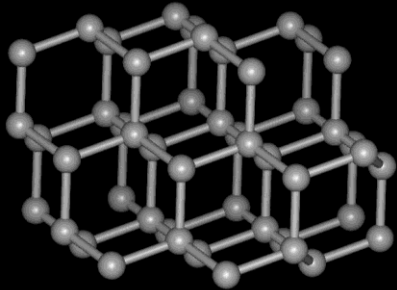
Graphite and Graphene



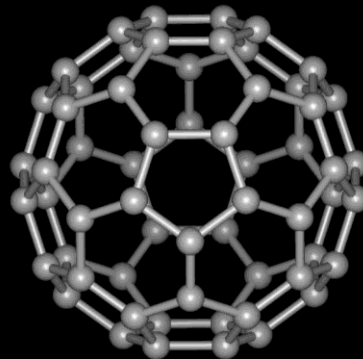
(Some) Carbon Nanostructures



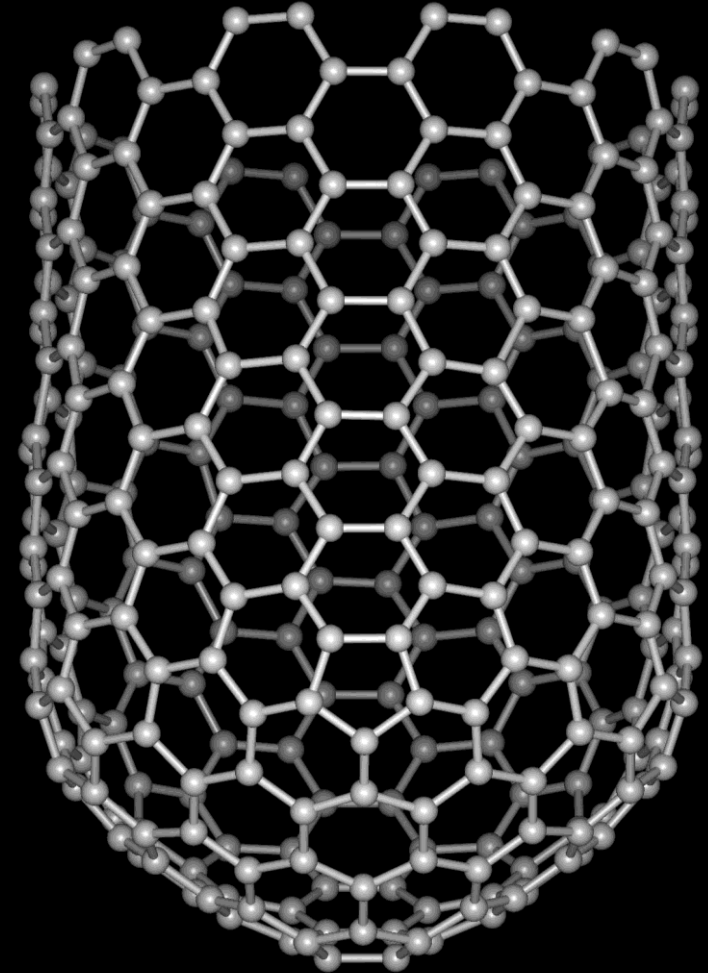
graphite



diamond



C_{60}
"buckyball"



nanotubes

Dimensions in Geometry and Semiconductor Physics

Geometry

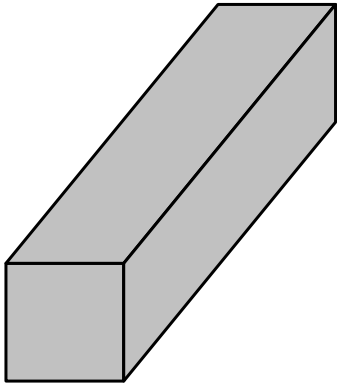
- Refers to the system size
- Planes (2D), lines (1D), dots (0D)

Semiconductor Physics

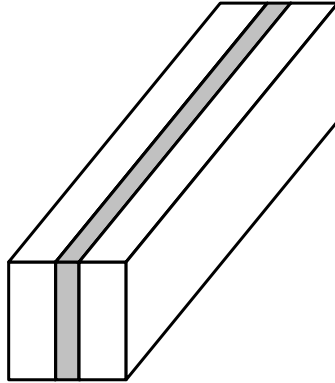
- Refers to the free motion of charge carriers
- Can be constrained due to quantum confinement
- Quantum wells (2D), quantum wires (1D), quantum dots (0D)

Dimensions in Semiconductor Physics

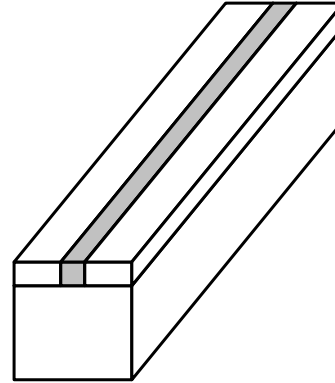
3D



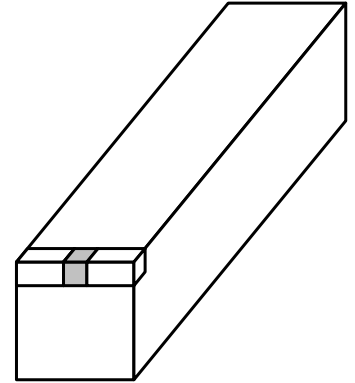
2D



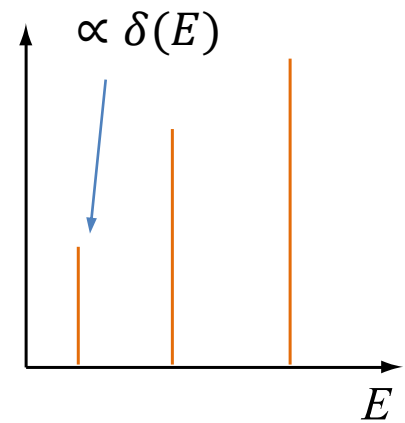
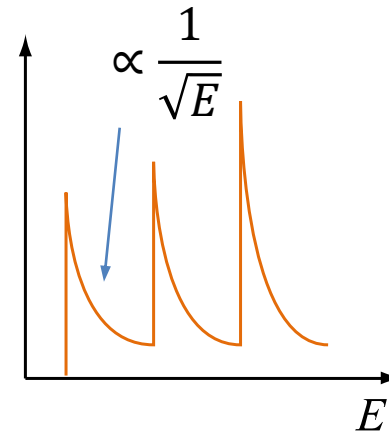
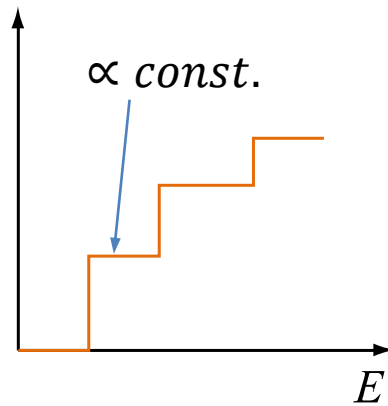
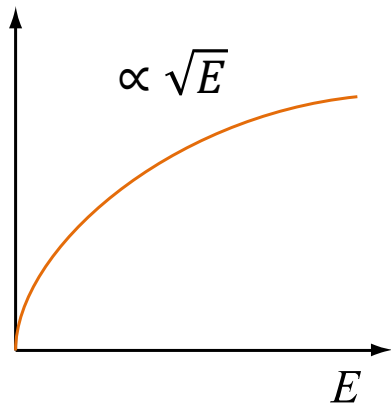
1D



0D



DOS



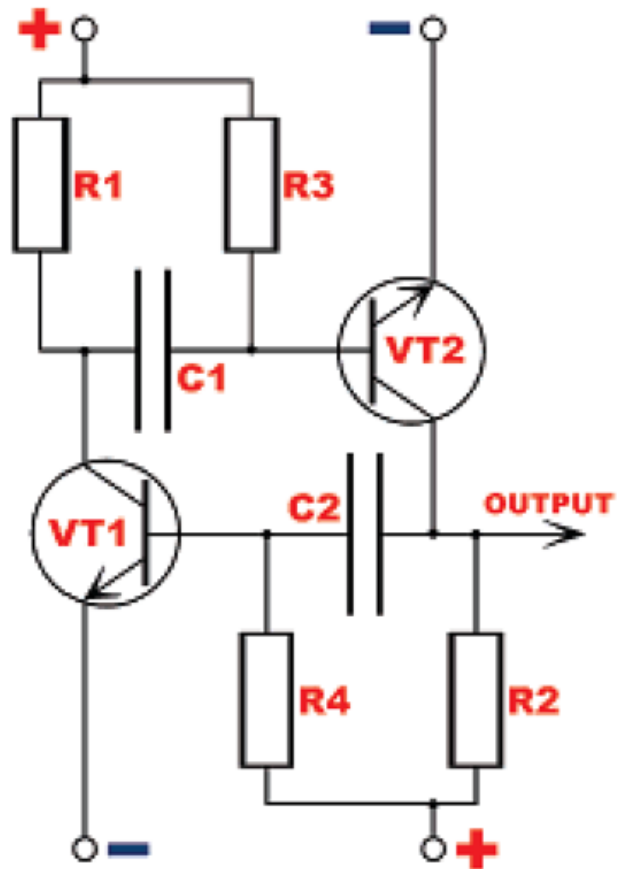
assuming $E = \frac{\hbar^2 k^2}{2m}$

→ Exercise session 1

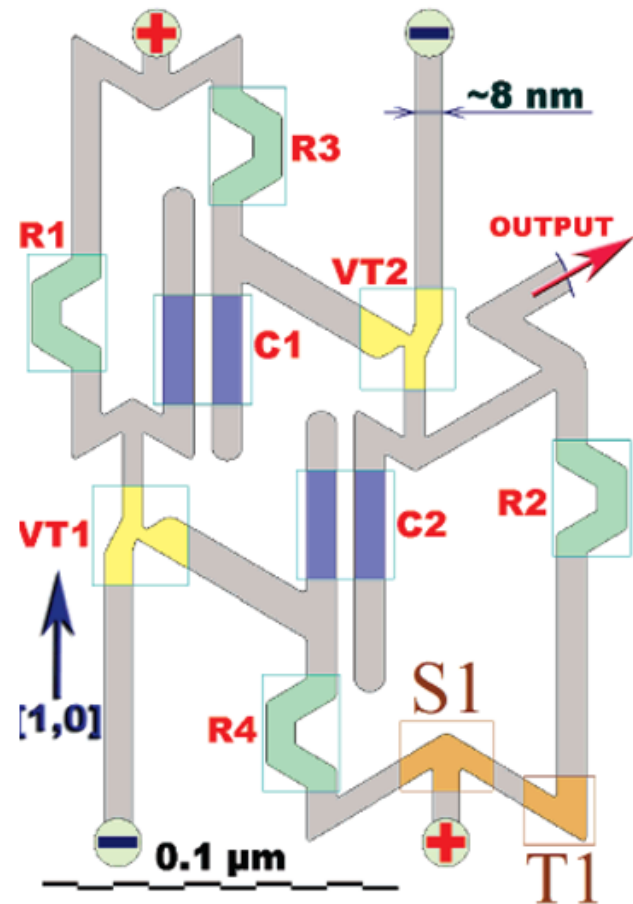
2D Circuits

Example: Flip-flop circuit

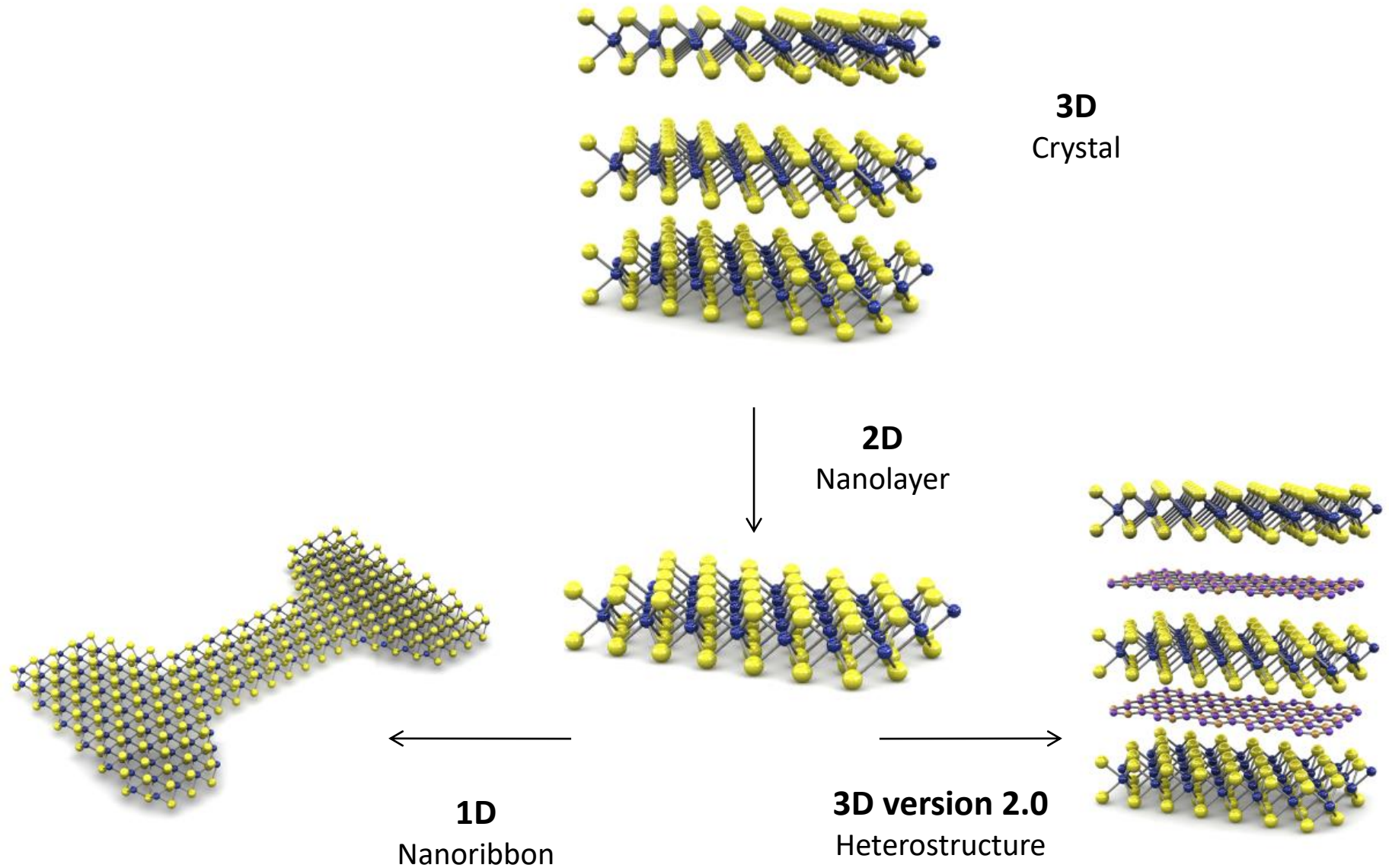
Circuit diagram



Graphene circuit

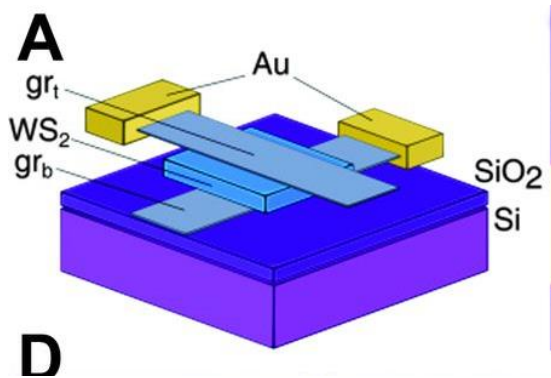
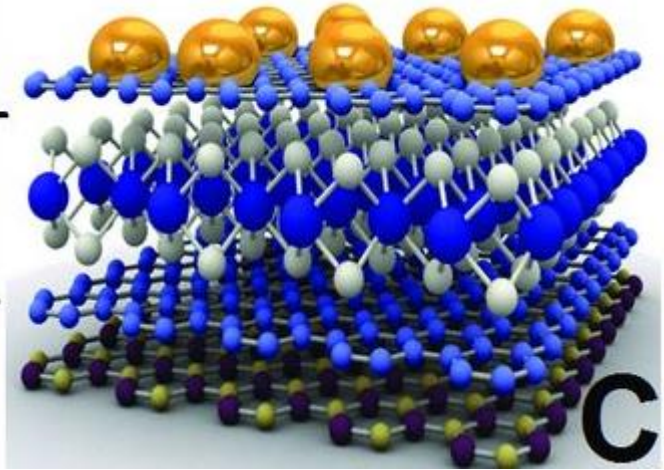


2D Materials: Wide Range of Geometries



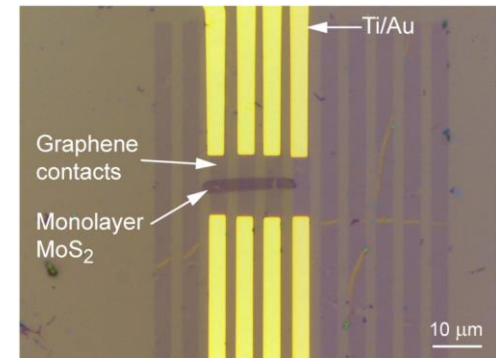
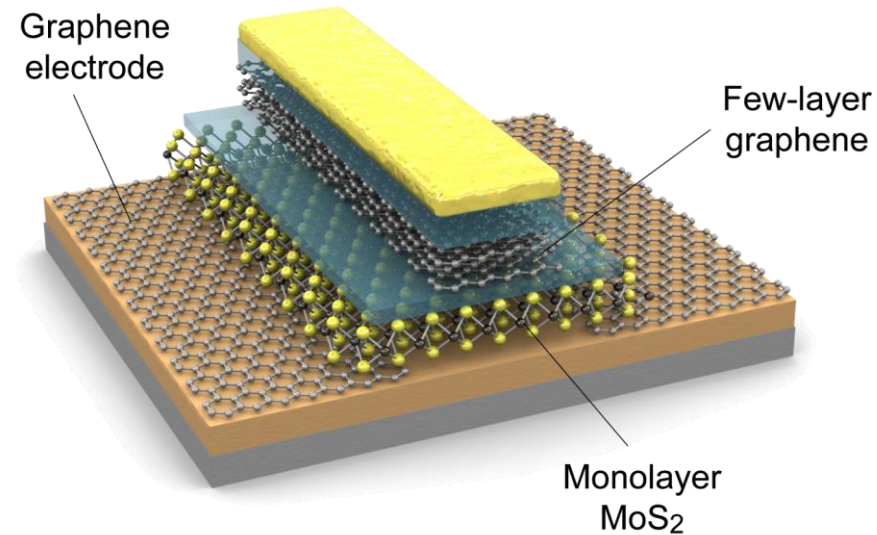
Heterostructures Based on 2D Materials

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

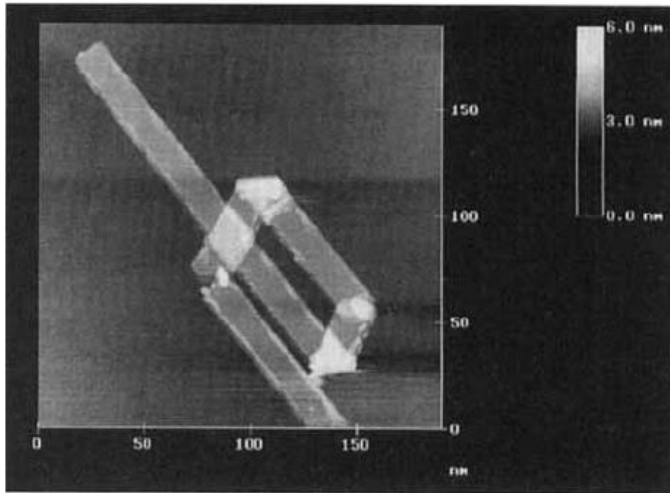


Fig. 1. AFM picture of a graphitic ribbon folded 4 times on the surface of HOPG reminiscent of origami.

AFM image of a folded
graphitic ribbon

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

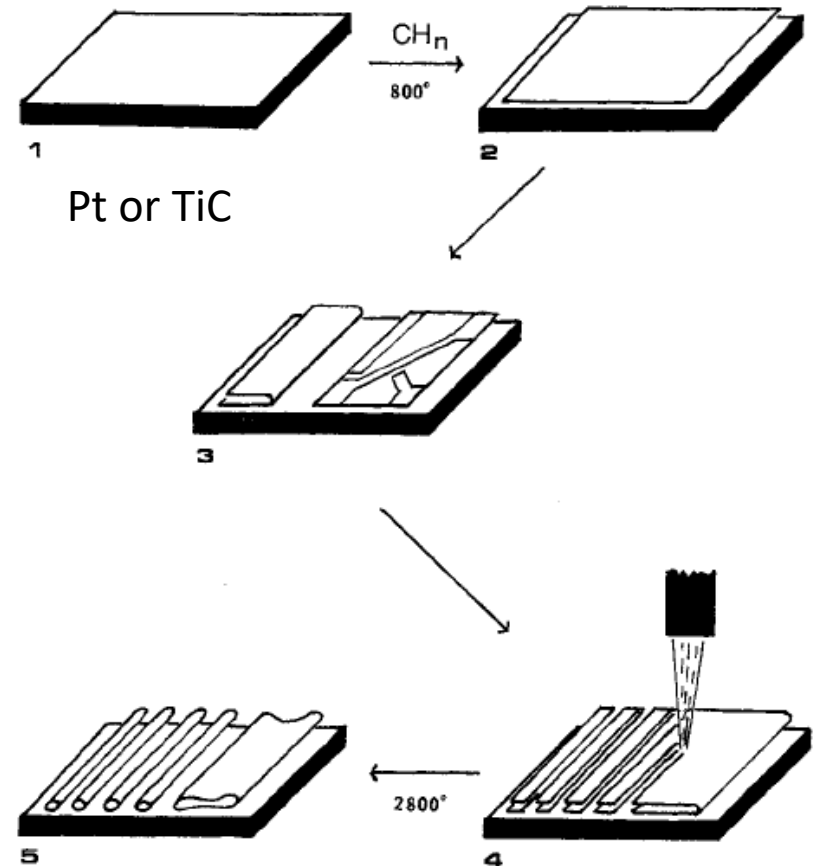


Fig. 6. Schematic diagram of possible approaches for fabricating carbon structures by design (see text).

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-

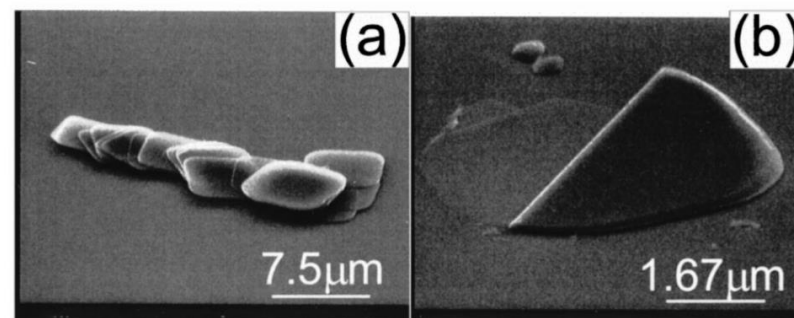
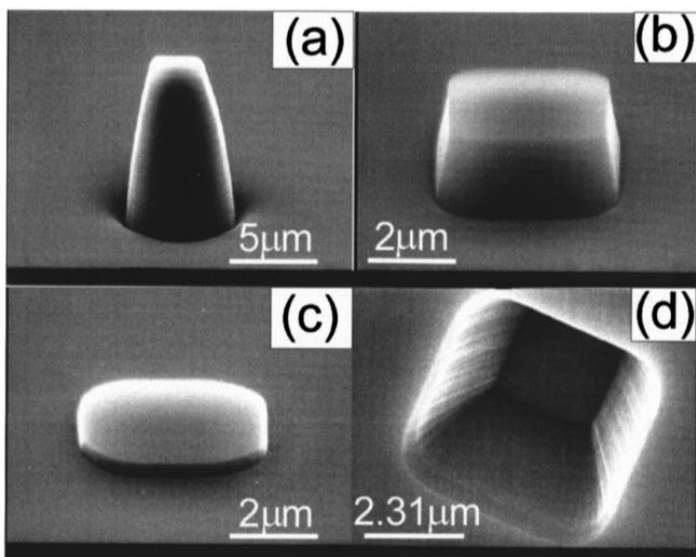
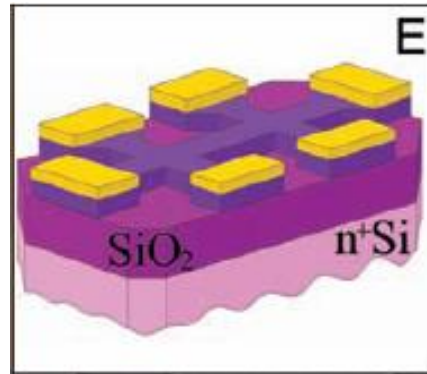
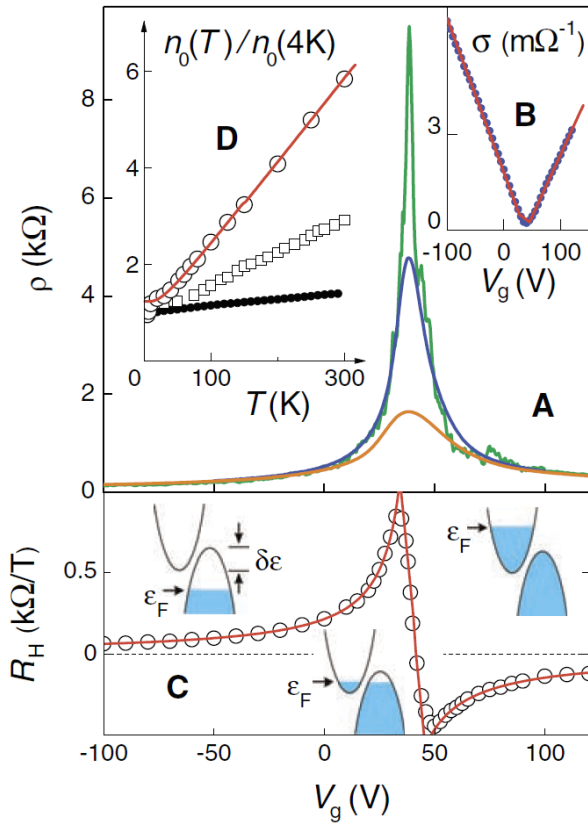


FIG. 5. SEM images of HOPG islands smeared on a Si(001) substrate. (a) Stacked thin platelets. (b) Example of a very thin layer left on the substrate while the platelet folds over.

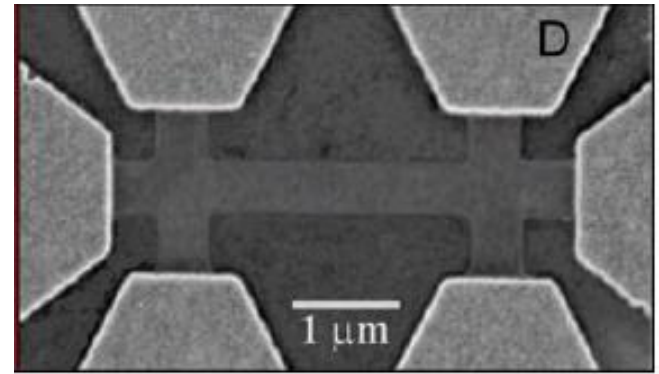
First Devices: Geim and Novoselov

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

Novoselov et al., Science 306, 666 (2004)

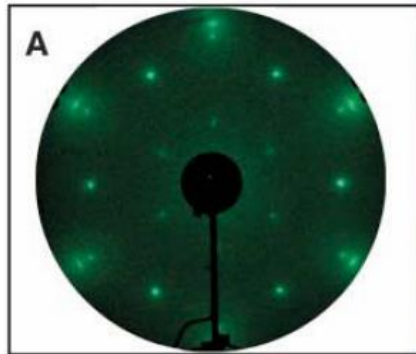
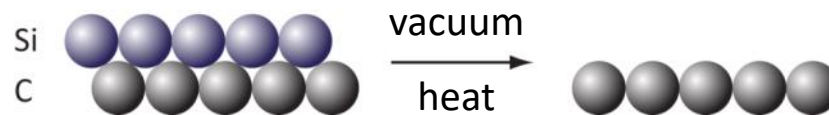
De Heer Group: Epitaxial Graphene

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

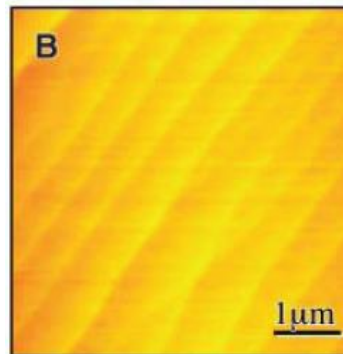
Claire Berger,[†] Zhimin Song, Tianbo Li, Xuebin Li, Asmerom Y. Ogbazghi, Rui Feng, Zhenting Dai, Alexei N. Marchenkov, Edward H. Conrad, Phillip N. First, and Walt A. de Heer*

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

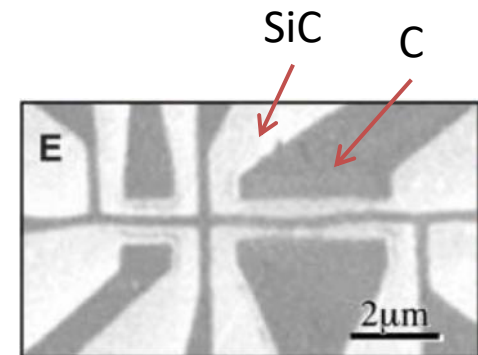
Received: October 7, 2004



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)

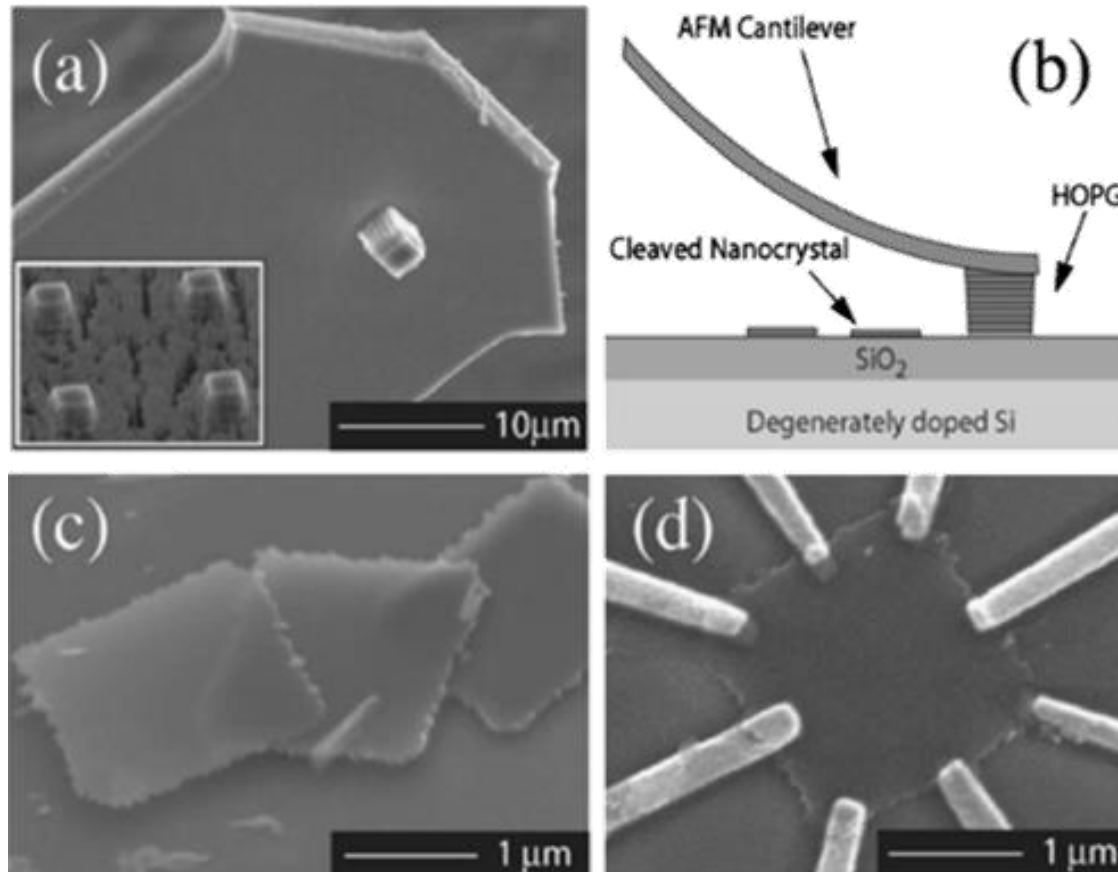
Kim Group: Mechanical Exfoliation

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

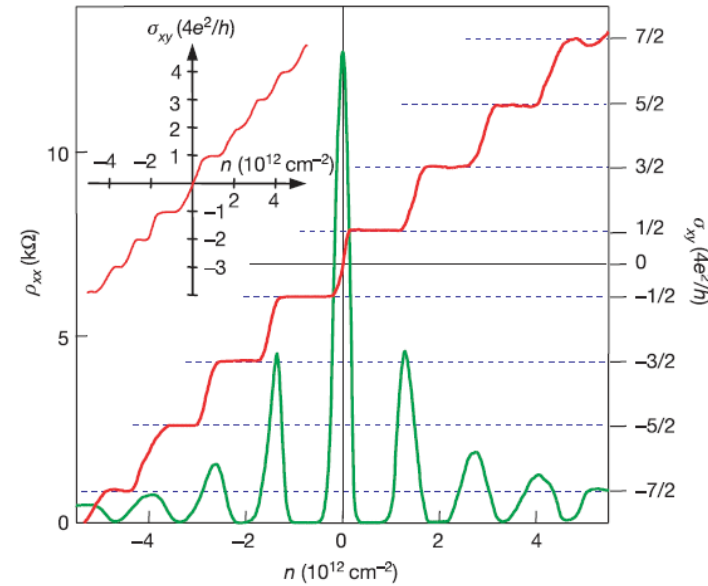
Vol 438|10 November 2005|doi:10.1038/nature04233

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



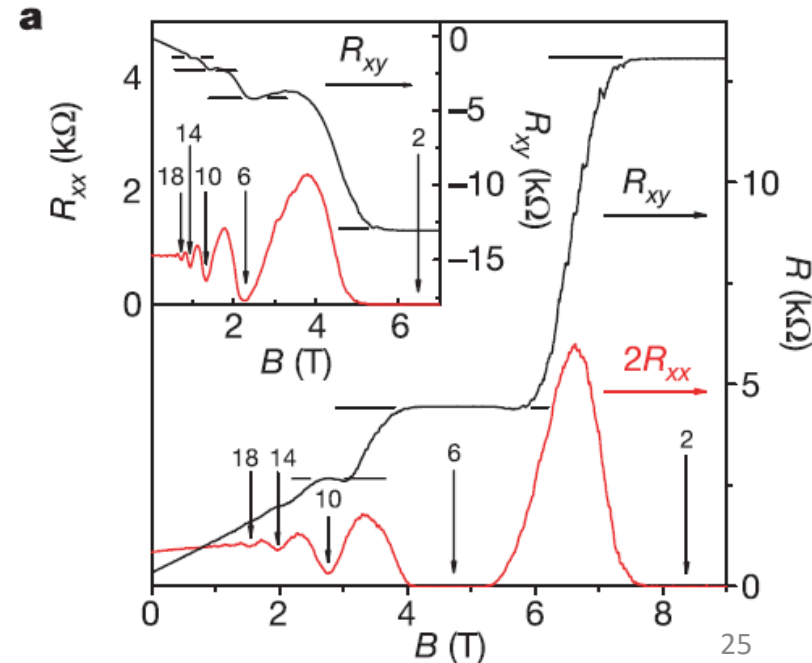
Vol 438|10 November 2005|doi:10.1038/nature04235

nature

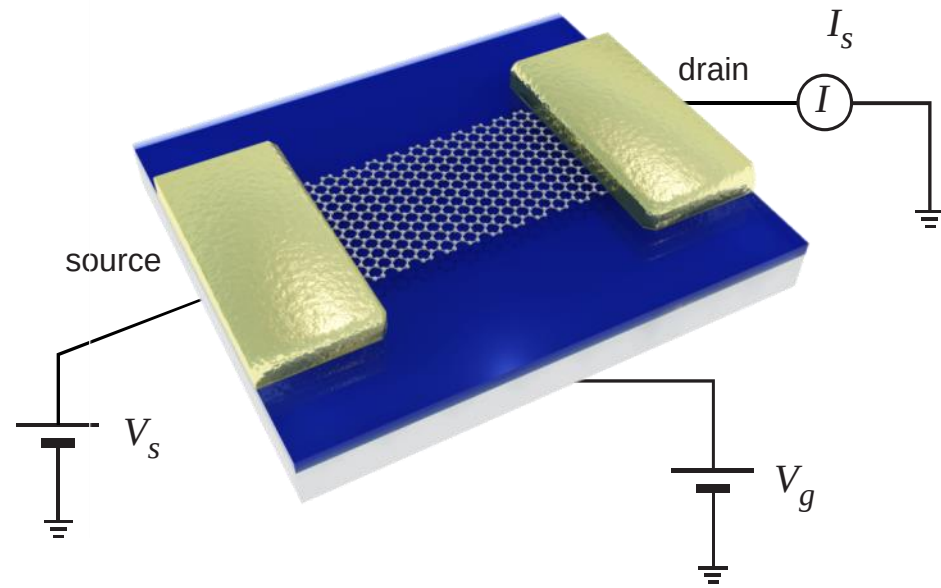
LETTER

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



Graphene FET Characteristics



Ambipolar behavior

Large current density – 10^8 A/cm^2

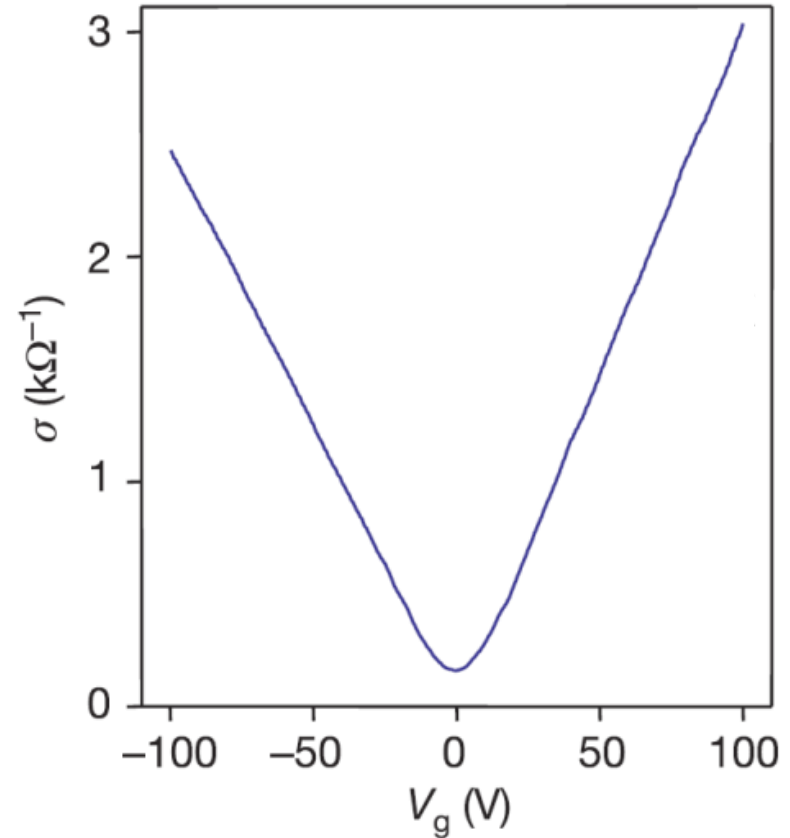
- Moser et al.; APL 91, 163513 (2007)

High mobility – $200\,000 \text{ cm}^2/\text{Vs}$

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

Suppression of noise in double layers

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

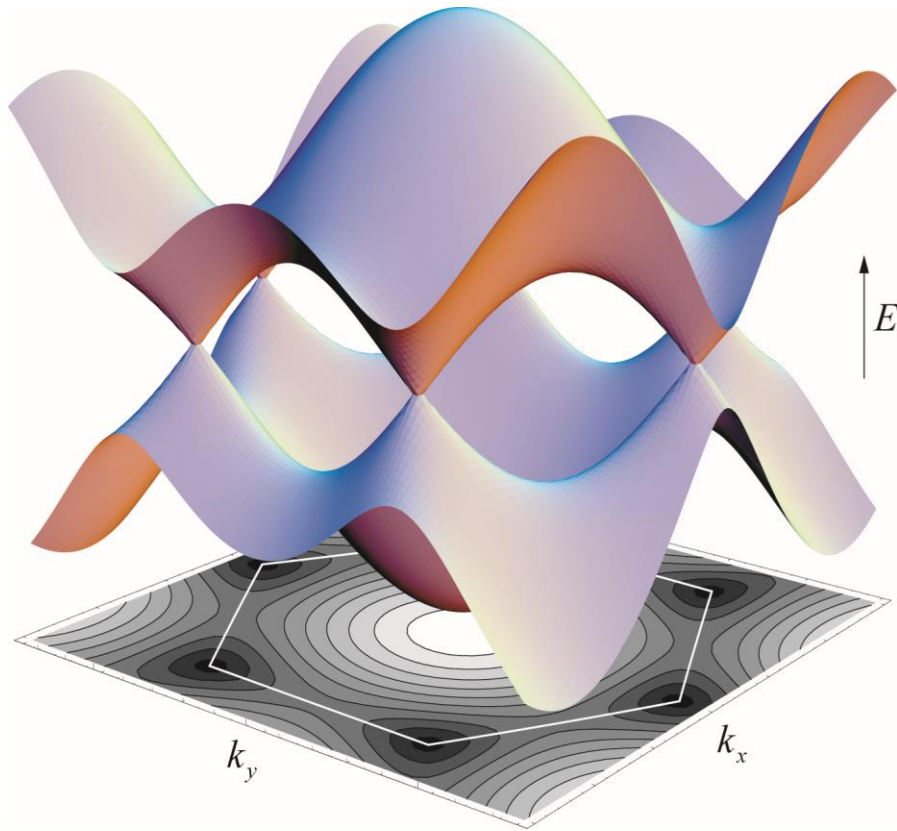


Novoselov et al., Nature 438, 197 (2005)

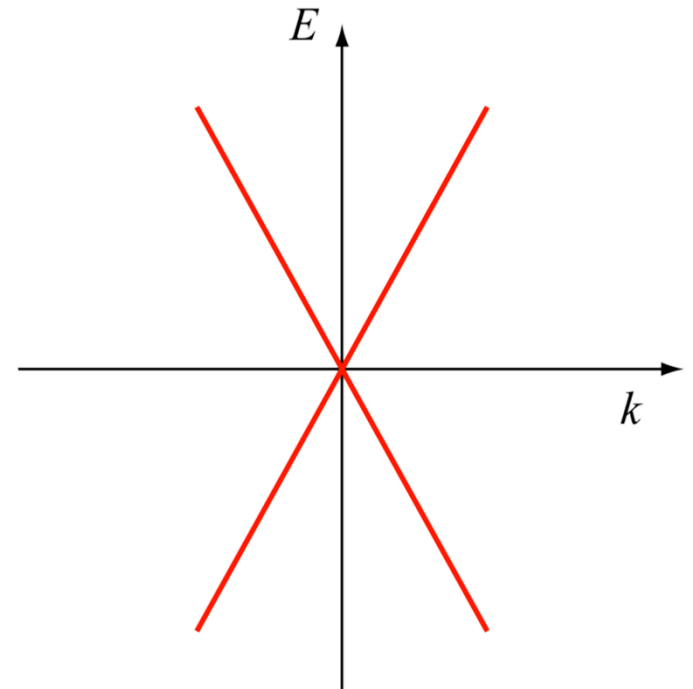
Graphene Band Structure

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!



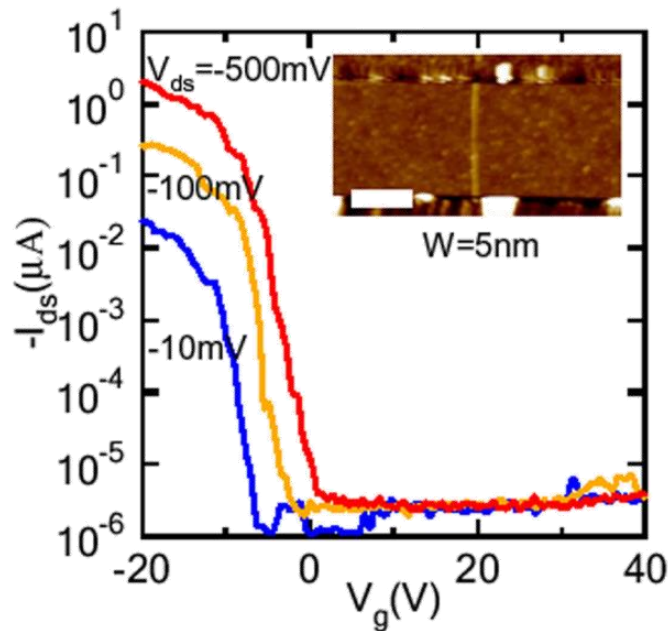
~~$$E = \frac{\hbar^2 k^2}{2m}$$~~

$$E = \hbar k v_F, \quad v_F = c / 300$$

Graphene Has No Band Gap

Possible solutions

Nanoribbons



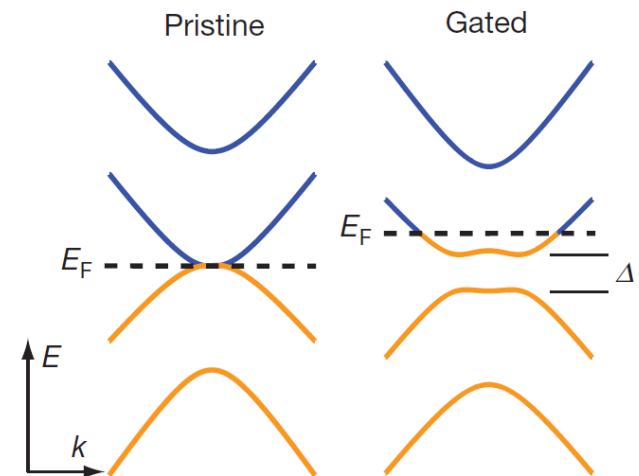
Hongjie Dai group: Science 319 1229 (2008)

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

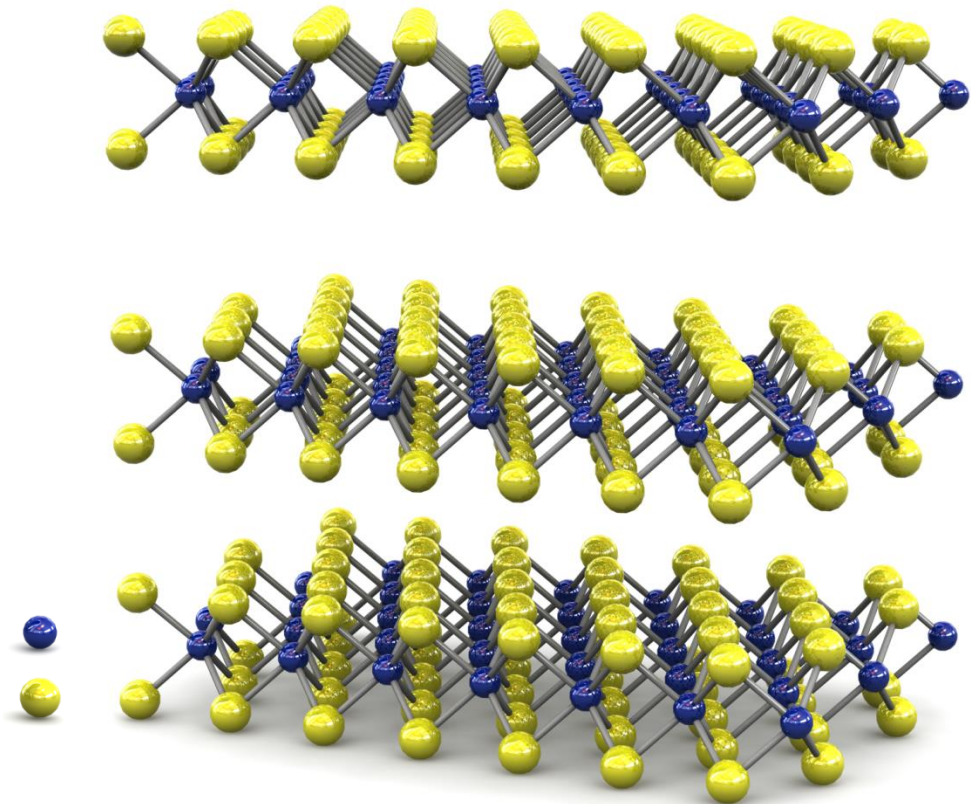
2D Transition Metal Dichalcogenides (TMDCs)

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

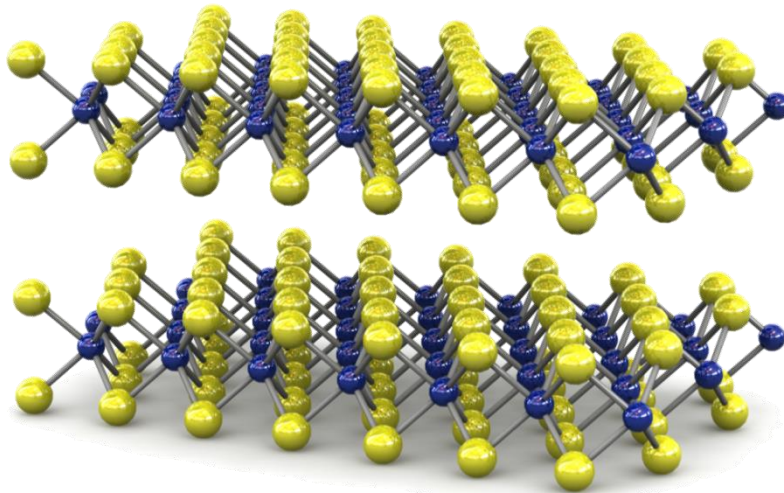
Chalcogenide X = S, Se, Te



MoS₂

0.65nm

Mo 
S 



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: 5×10^7 A/cm² (copper: 10^5 , graphene: 10^8)

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)



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

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

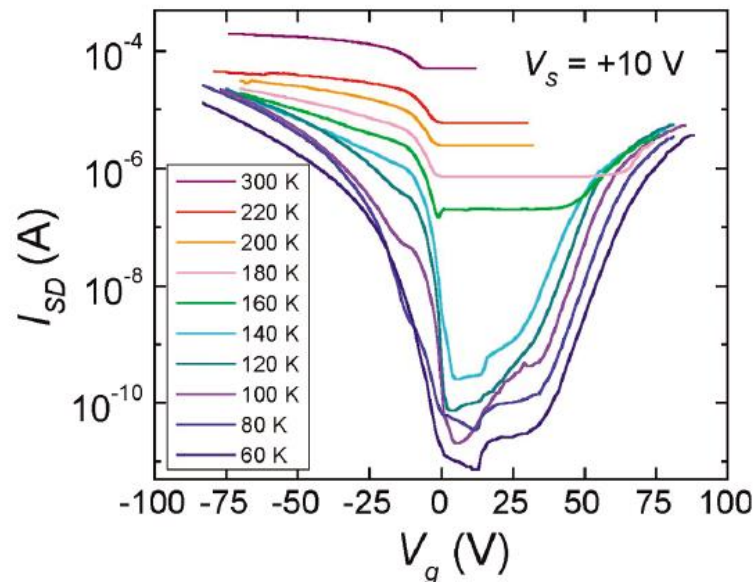
*Physics and Chemistry of Solids, Cavendish Laboratory,
University of Cambridge*

(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.

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



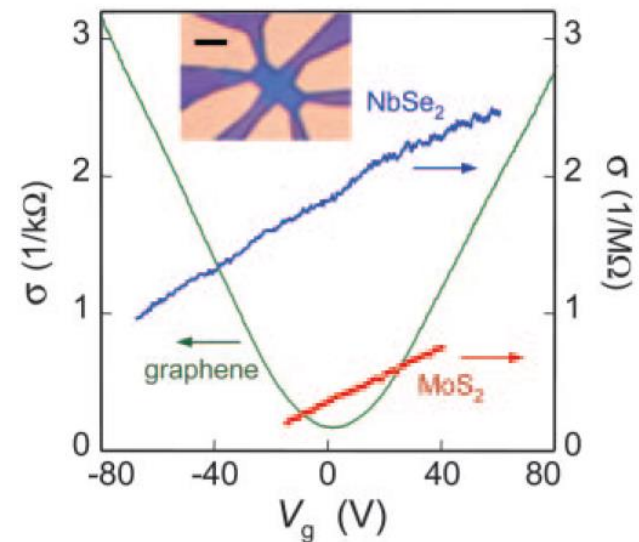
Podzorov et al. APL (2004)

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)

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)

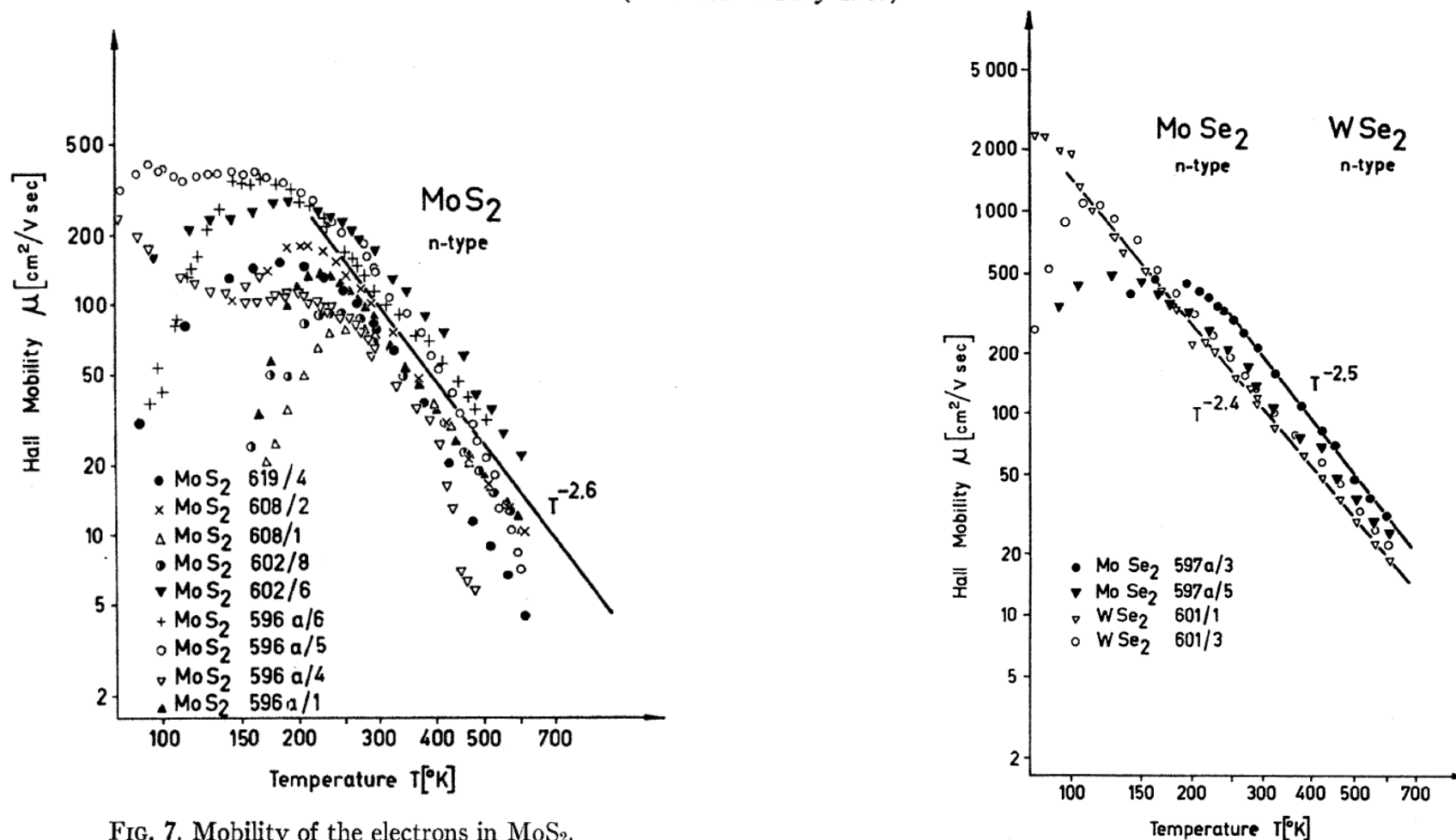
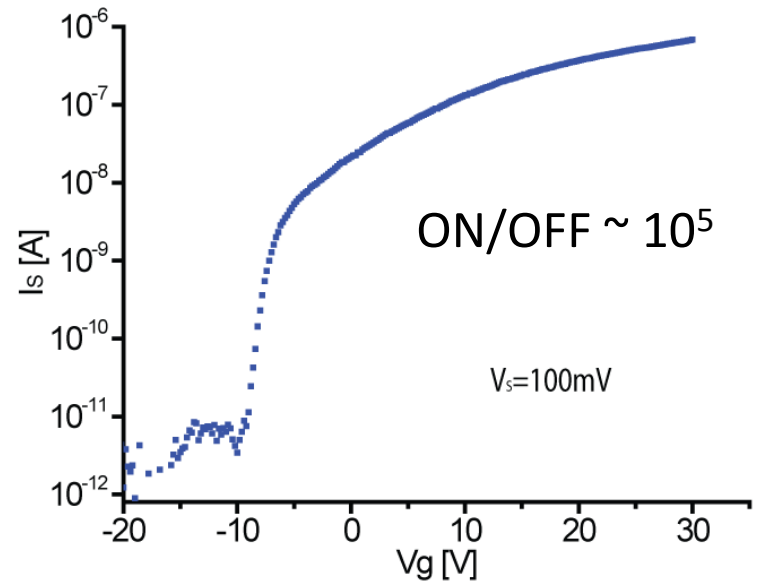
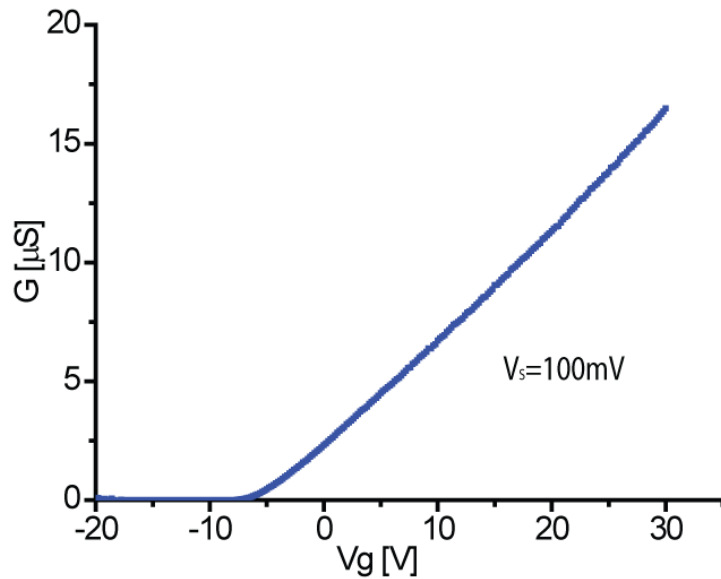
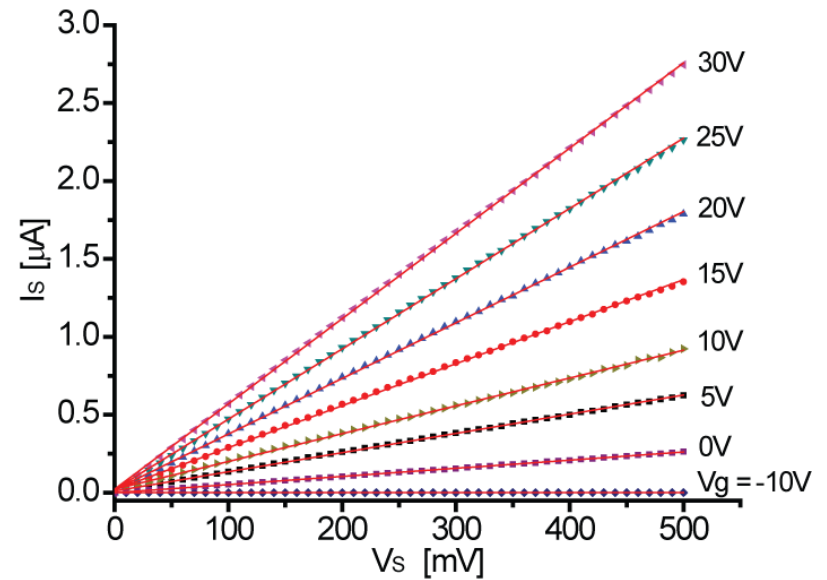
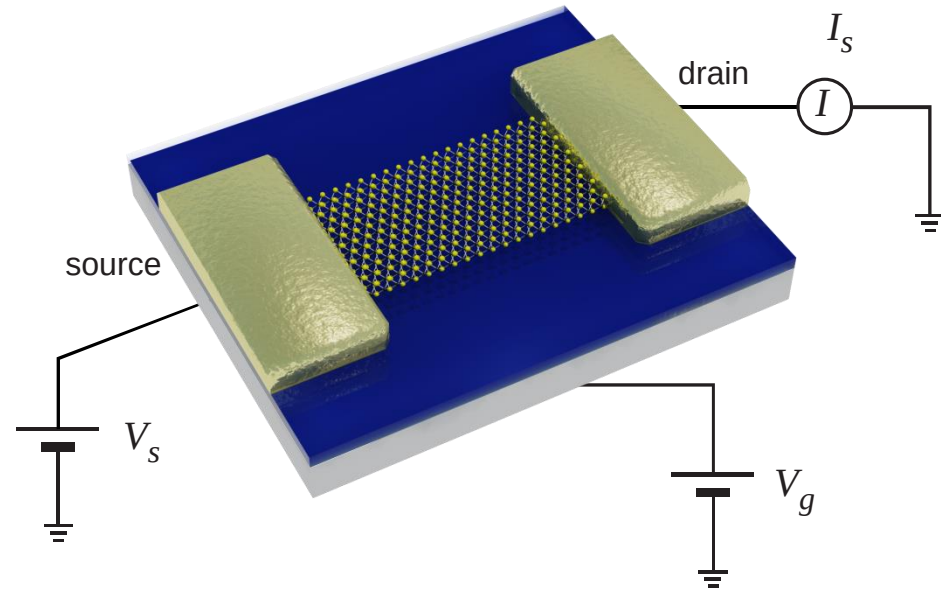
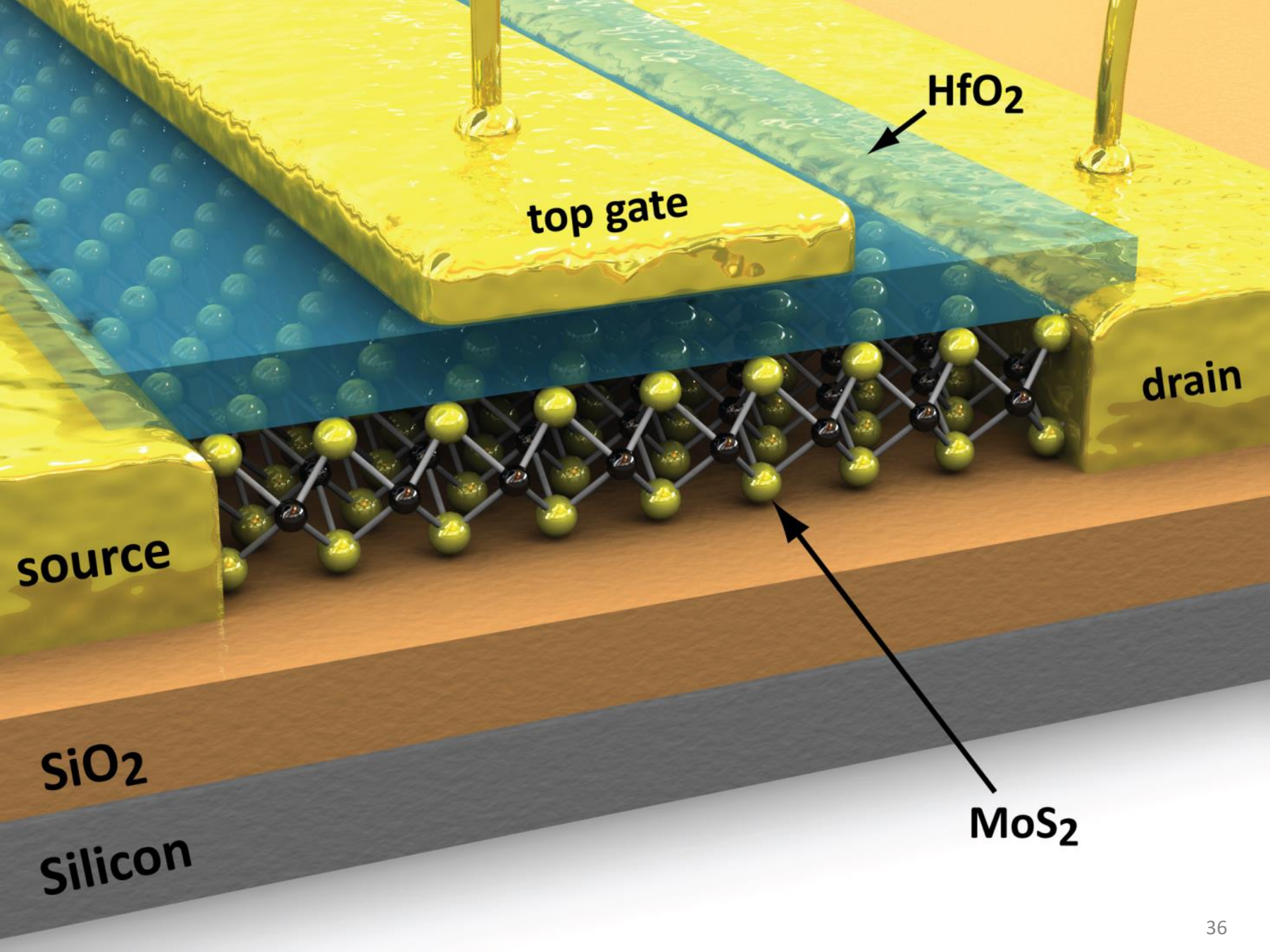


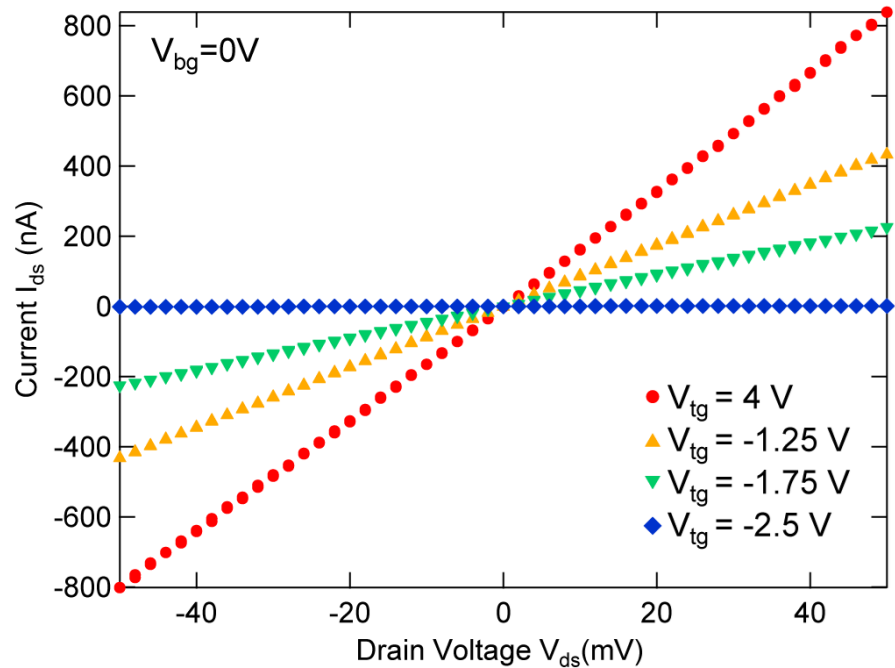
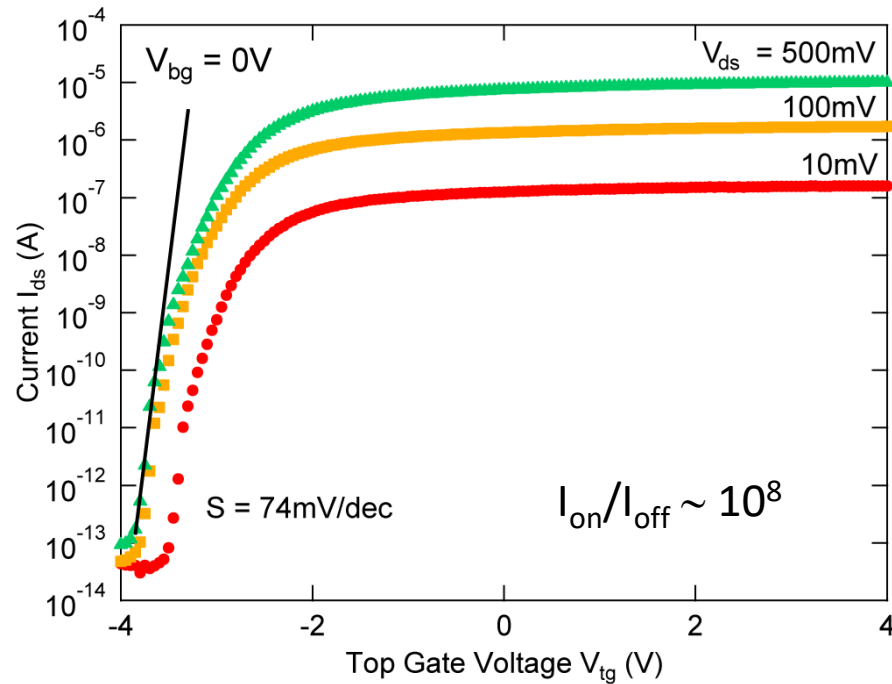
FIG. 7. Mobility of the electrons in MoS₂.

Our First MoS₂ Transistor (5 layers, 2009)





Monolayer MoS₂ Transistor

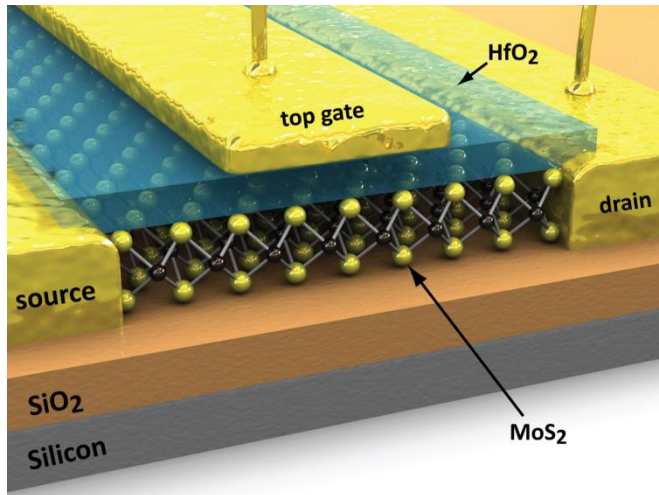


Radisavljevic...Kis,
Nature Nanotechnology (2011)

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

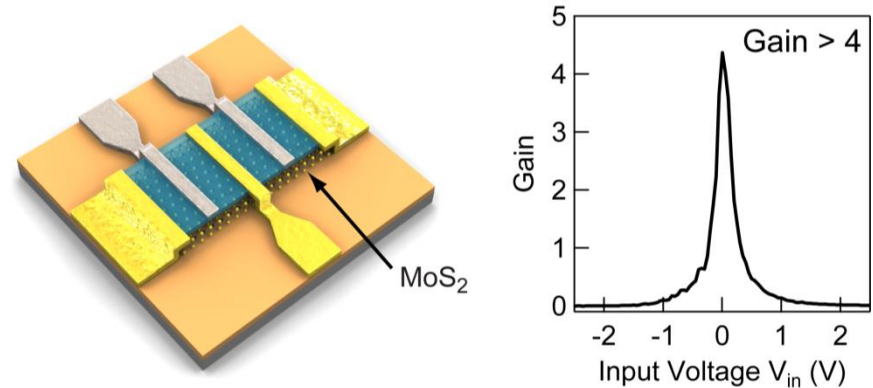
Devices Based on Monolayer MoS₂

MoS₂ Transistor



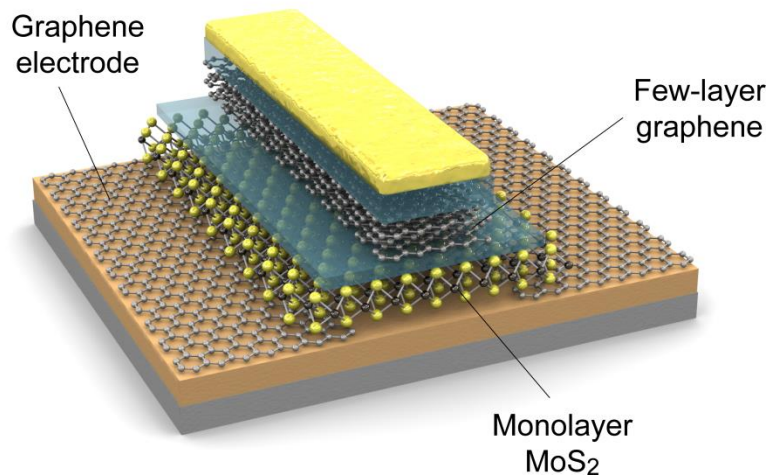
Radisavljevic...Kis; Nature Nanotech. (2011)

MoS₂ Inverter



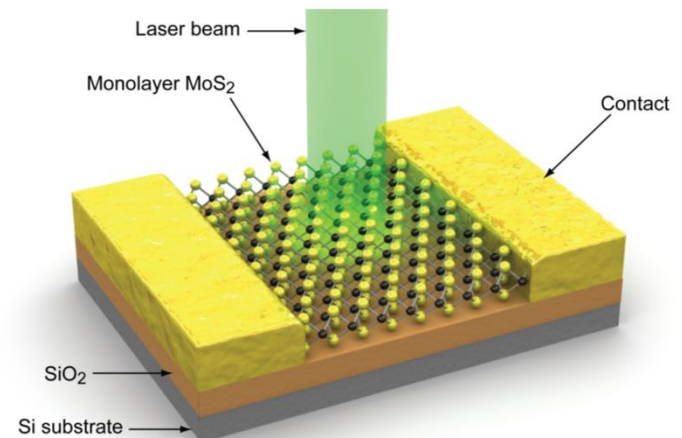
Radisavljevic...Kis; ACS Nano (2011)

MoS₂/graphene Memory Cell



Bertolazzi...Kis; ACS Nano (2013)

Ultrasensitive Photodetector



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

IRDS - International Roadmap for Devices and Systems

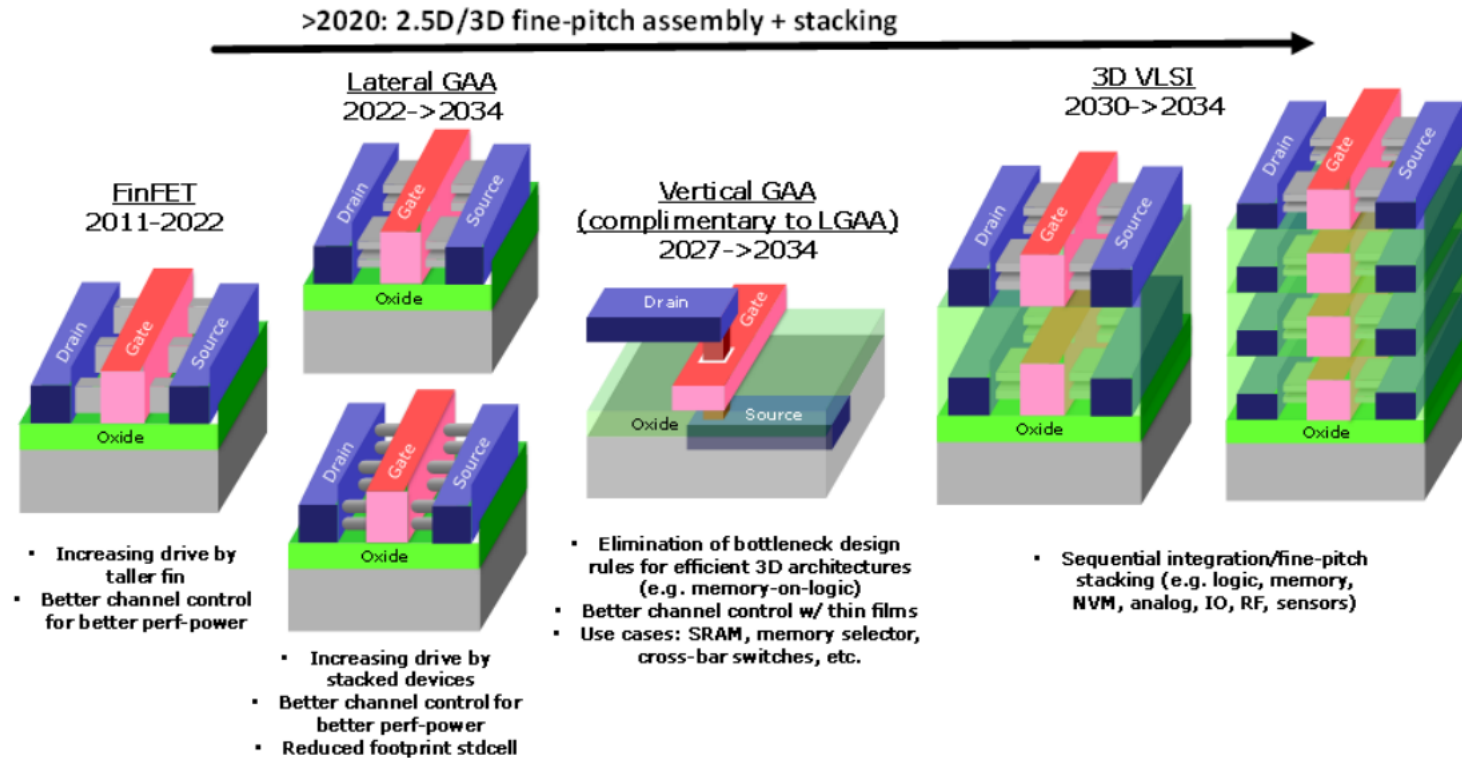


Figure ES48

Change in the MOSFET device architecture from the 2D planar through 2.5D FinFets to 3D monolithic VLSI with GAA

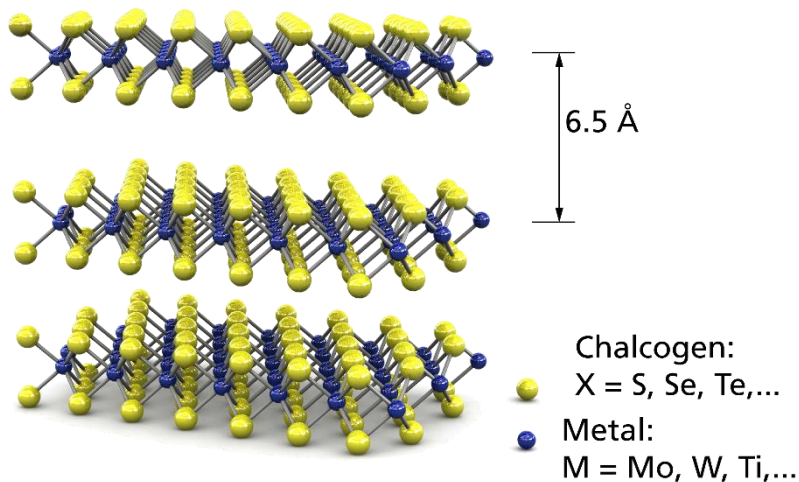
IRDS - International Roadmap for Devices and Systems

YEAR OF PRODUCTION	2021	2022	2025	2028	2031	2034
	G51M30	G48M24	G45M20	G42M16	G40M16/T2	G38M16/T4
Logic industry "Node Range" Labeling (nm)	"5"	"3"	"2.1"	"1.5"	"1.0 eq"	"0.7 eq"
IDM-Foundry node labeling	i7-f5	i5-f3	i3-f2.1	i2.1-f1.5	i1.5e-f1.0e	i1.0e-f0.7e
Logic device structure options	FinFET	finFET LGAA	LGAA	LGAA	LGAA-3D	LGAA-3D
Platform device for logic	finFET	finFET	LGAA	LGAA	LGAA-3D	LGAA-3D
Frequency scaling - node-to-node	-	0.02	0.16	0.09	-0.08	-0.01
CPU frequency at constant power density (GHz)	3.13	2.83	3.53	2.50	1.48	0.86
Power at iso frequency - node-to-node	-	-0.16	-0.27	-0.05	-0.06	-0.08
Power density - relative	1.00	1.12	1.04	1.59	2.51	4.27
LOGIC TECHNOLOGY ANCHORS						
Patterning technology inflection for Mx interconnect	193i, EUV DP	193i, EUV DP	193i, EUV DP	193i, High-NA EUV	193i, High-NA EUV	193i, High-NA EUV
Beyond-CMOS as complimentary to platform CMOS	-	-	-	2D Device, FeFET	2D Device, FeFET	2D Device, FeFET
Channel material technology inflection	SiGe25%	SiGe50%	SiGe50%	Ge, 2D Mat	Ge, 2D Mat	Ge, 2D Mat
Process technology inflection	Conformal Doping, Contact	Channel, RMG	Lateral/Atomic Etch	Non-Cu Mx	3DVLSI	3DVLSI
Stacking generation inflection	2D	3D-stacking: W2W, D2W Mem-on-Logic	3D-stacking: W2W, D2W Mem-on-Logic	3D-stacking, Fine-pitch stacking, P-over-N, Mem-on-Logic	3D-stacking, 3DVLSI: Mem-on-Logic with Interconnect	3D-stacking, 3DVLSI: Logic-on-Logic

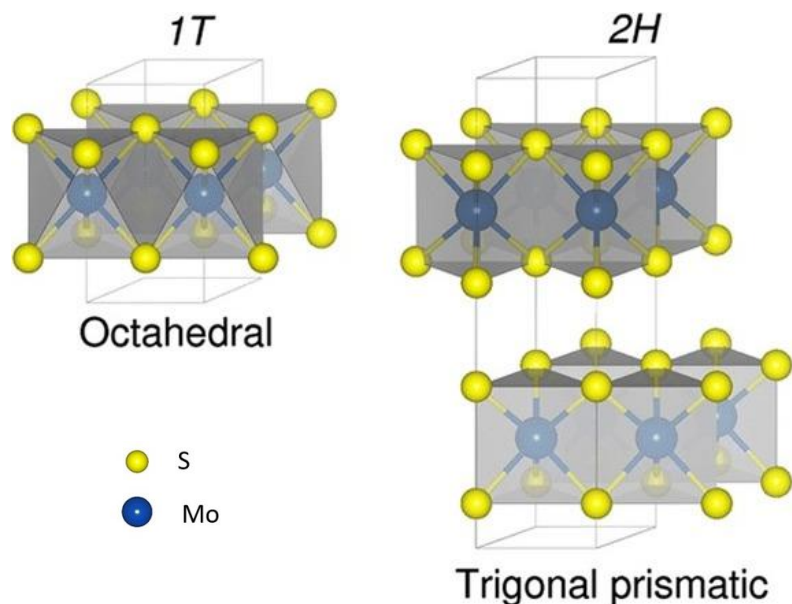
Figure ES9

Devices will continue to aggressively scale in the next 5 years

Structure



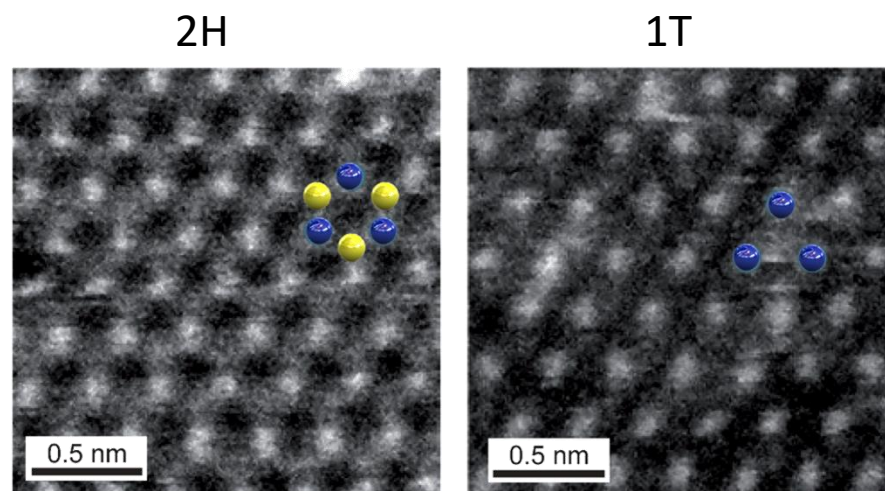
Radisavljevic...Kis; Nature Nanotech. (2011)



Kuc, A. 2015. Pp. 1–29 in
M. Springborg, and J. Joswig, ed. Chemical modelling: volume 11

H	MX ₂ M = Transition metal X = Chalcogen																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)



Eda...Chhowalla; ACS Nano (2012)

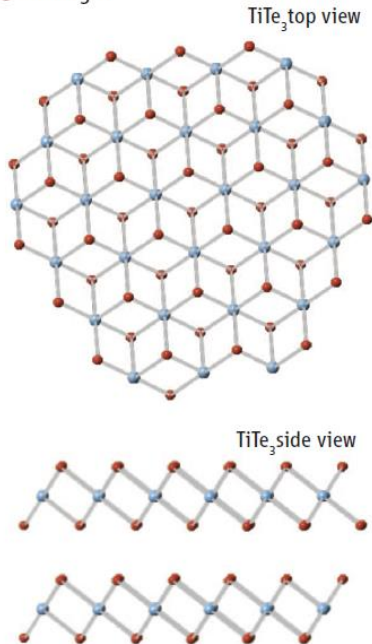
Tip of the Iceberg

>500 potentially interesting 2D materials

Transition metal trichalcogenides

AMo_3X_3 , NbX_3 , TiX_3 , and TaX_3 ($X = S, Se, \text{ or } Te$)

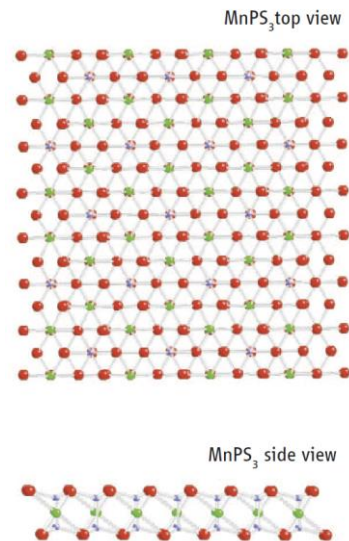
● Transition metal
● Chalcogen



Metal phosphorous trichalcogenides (MPX₃)

Metal phosphorous trichalcogenides (MPX₃), such as $MnPS_3$, $CdPS_3$, $NiPS_3$, $ZnPS_3$, and $Mn_{0.5}Fe_{0.5}PS_3$

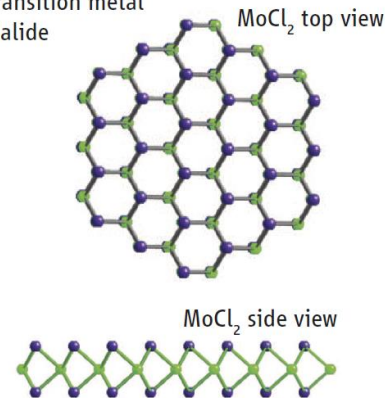
● Transition metal
● Chalcogen
● Phosphorus



Transition metal dihalides

Transition-metal dihalides*

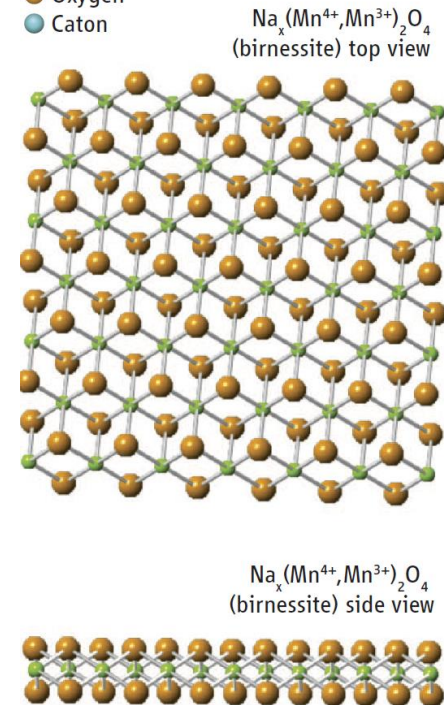
● Transition metal
● Halide



Transition metal oxides

Transition metal oxides : Ti oxides, $Ti_{0.91}O_2$, $Ti_{0.87}O_2$, Ti_3O_7 , Ti_4O_9 , Ti_5O_{11} ; Nb oxides, Nb_3O_8 , Nb_6O_{17} , HNb_3O_8 ; Mn oxides, MnO_2 , Ti_3O_7 , $Na_x(Mn^{4+}, Mn^{3+})_2O_4$

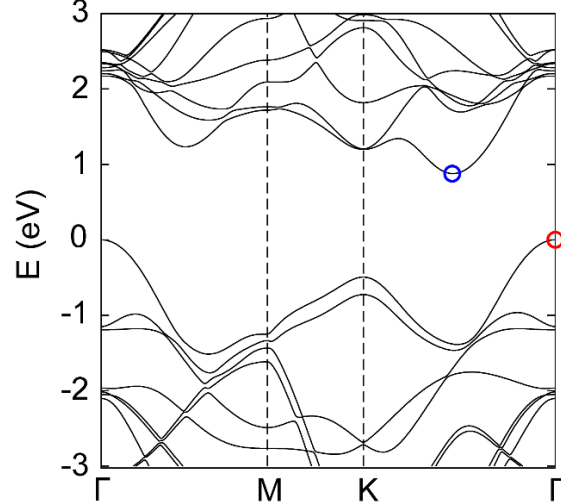
● Transition metal
● Oxygen
● Cation



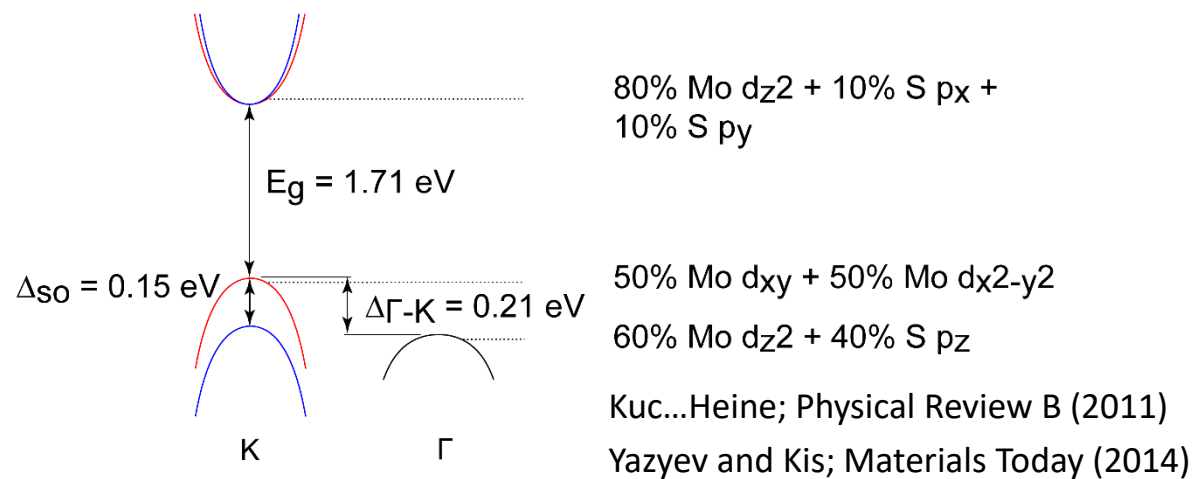
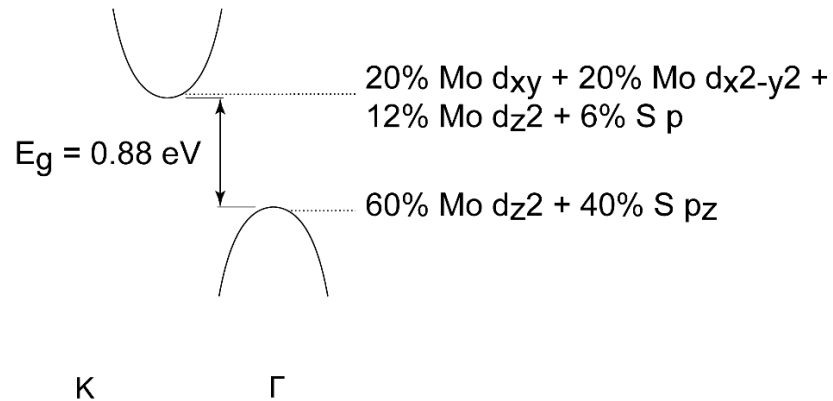
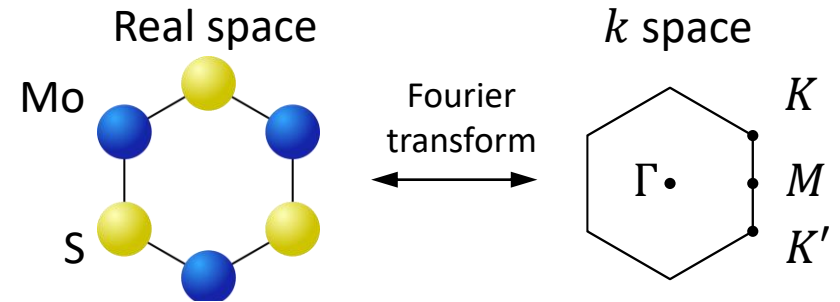
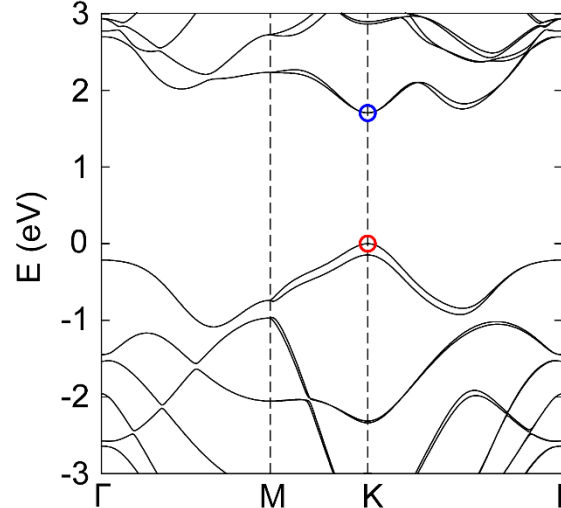
Nicolosi...Coleman; Science (2013)

Band Structure of 2H MoS₂

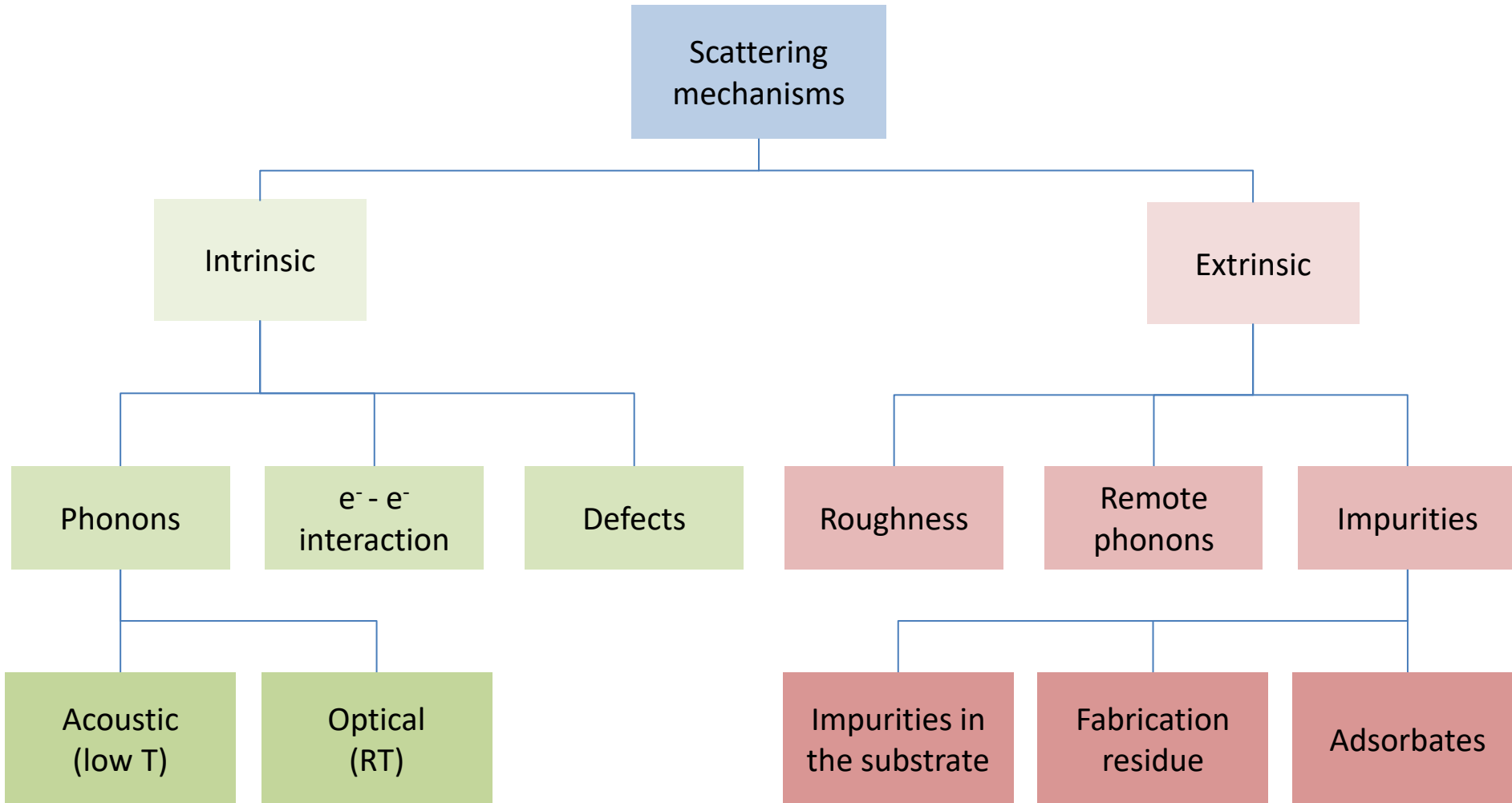
Bulk MoS₂



Monolayer MoS₂



Charge Scattering Mechanisms



Mobility follows Mathiessen's rule:
$$\frac{1}{\mu} = \frac{1}{\mu_{defects}} + \frac{1}{\mu_{phonons}} + \frac{1}{\mu_{remote\ phonons}} + \dots$$

Material Preparation



Quartz (SiO_2)

MoS_2

Molybdenite Mining



Los Bronces, Chile

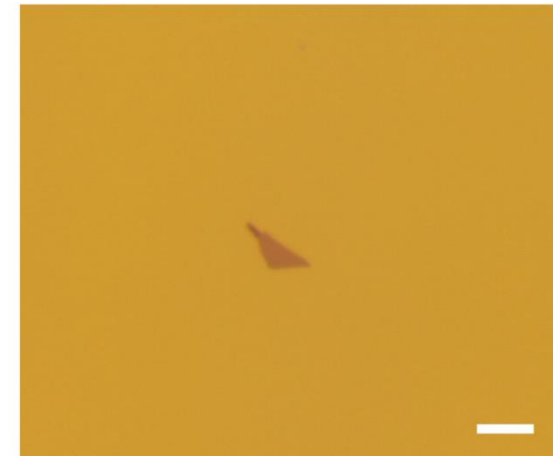
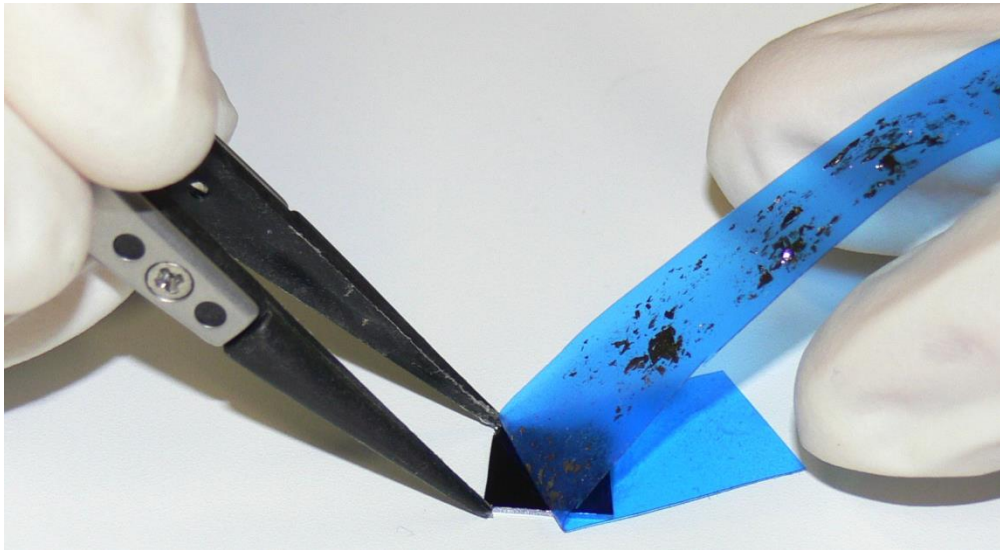
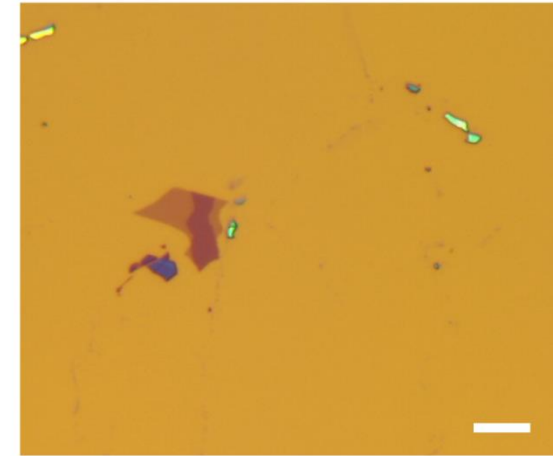
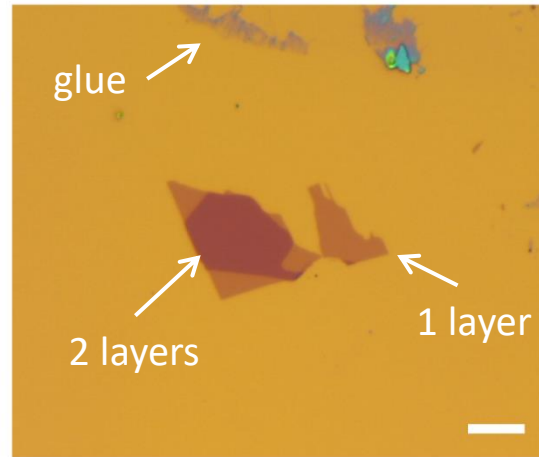
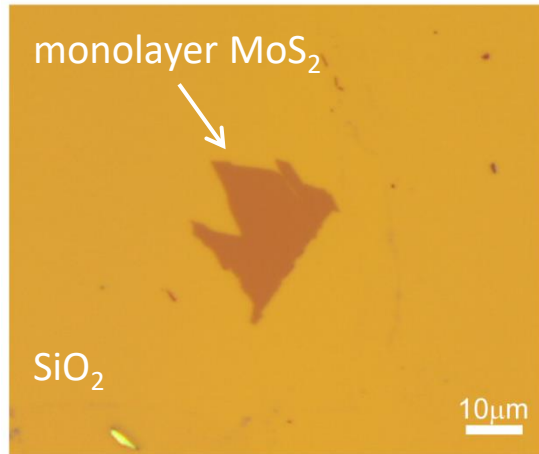


Pinto Valley, Arizona, USA

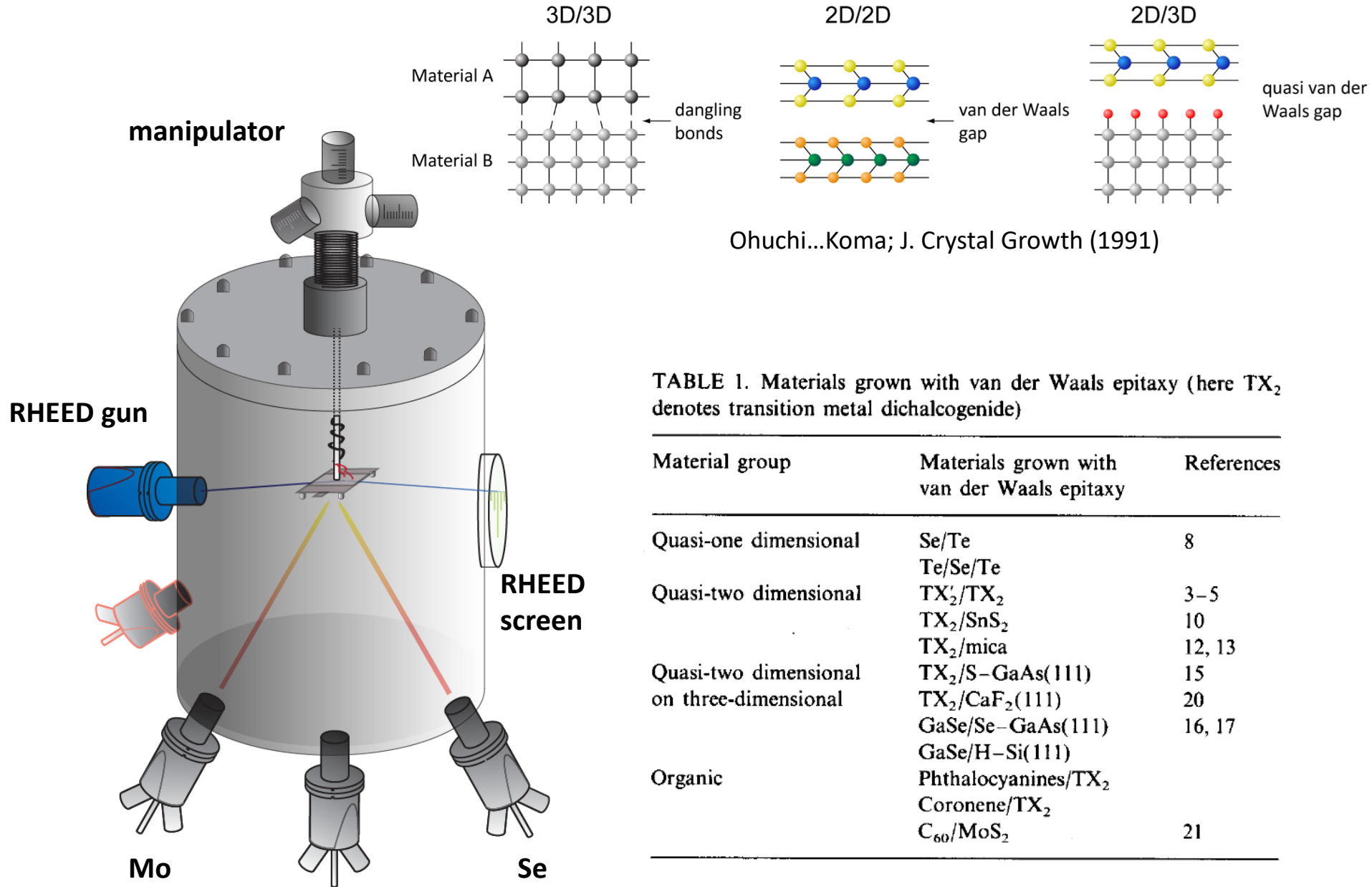


Climax mine, Colorado, USA

Scotch Tape Exfoliation

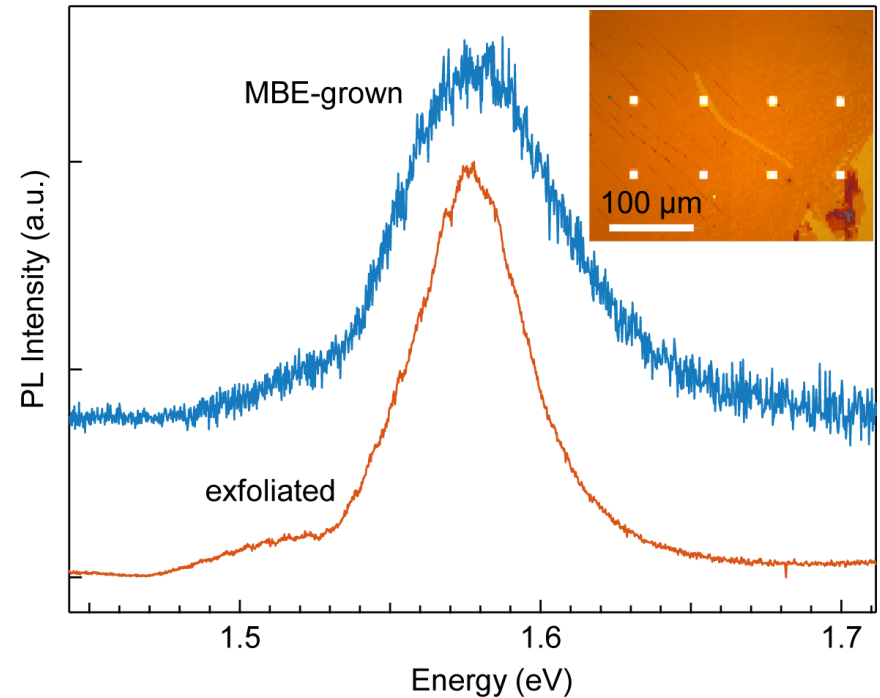
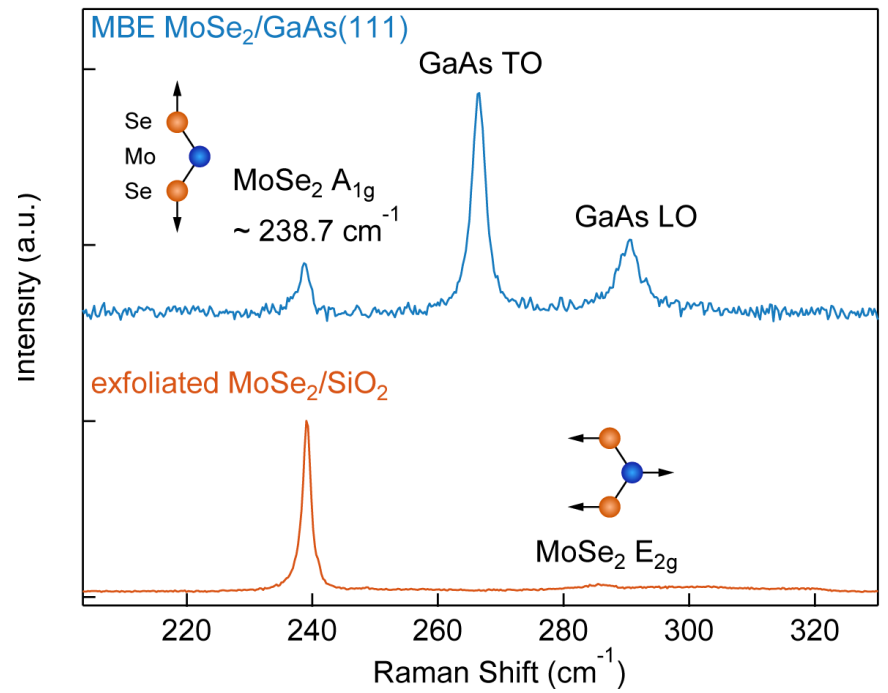
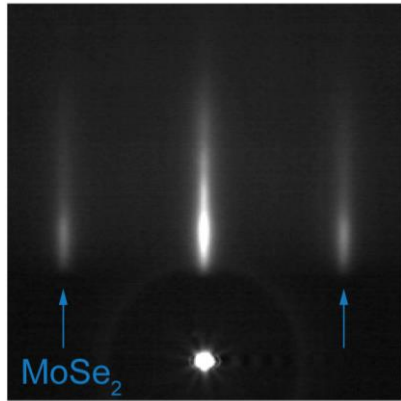
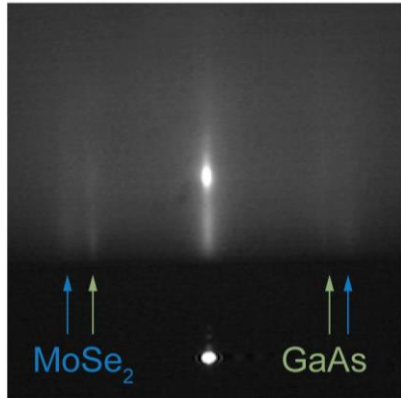
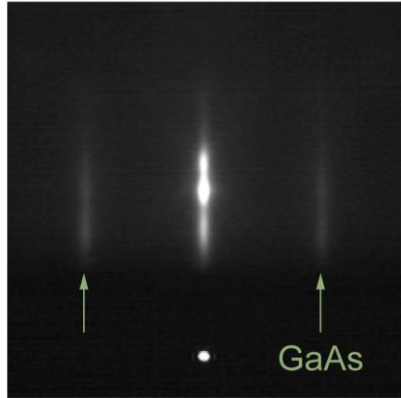


Van der Waals Epitaxy Using an MBE

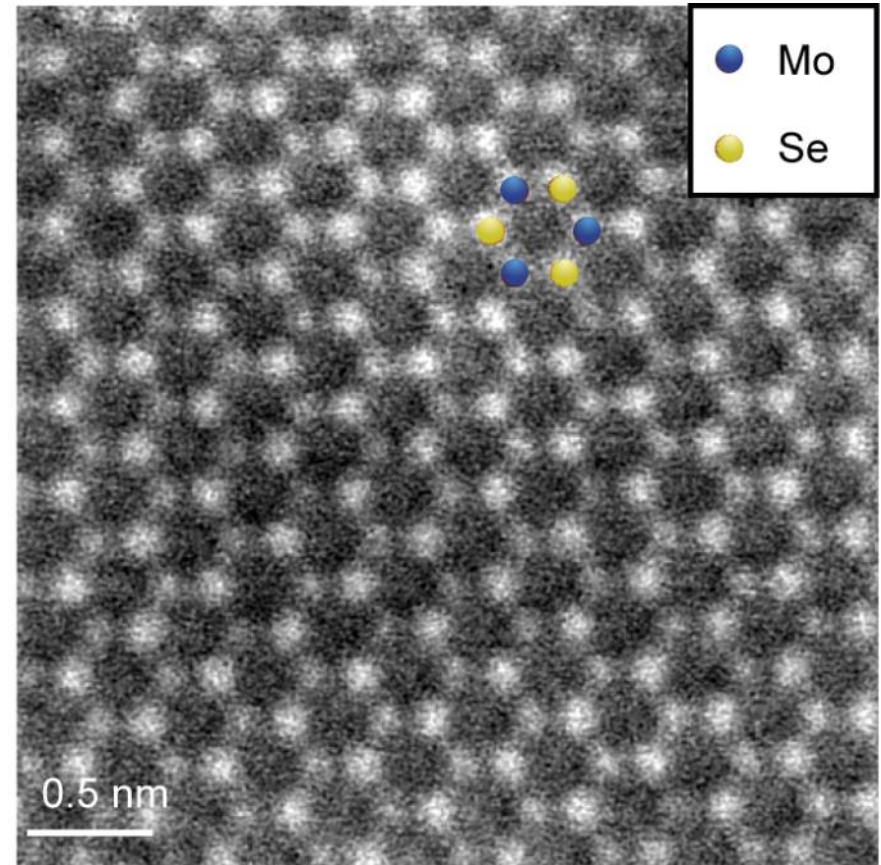
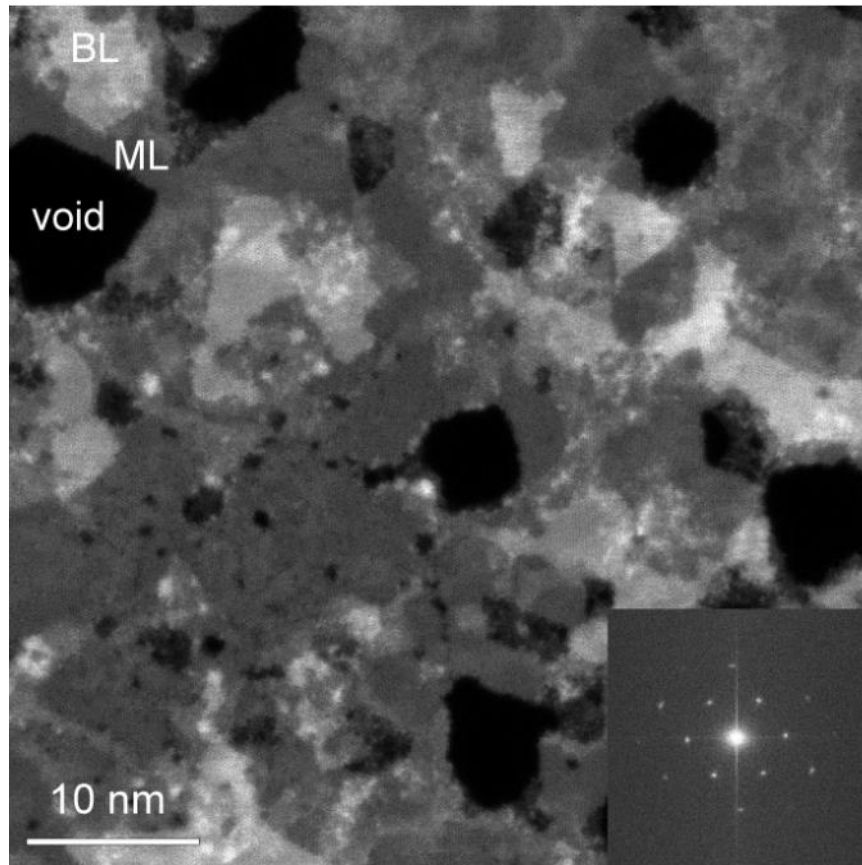


Koma; Thin Solid Films (1992)

MBE MoSe₂ on GaAs(111)B

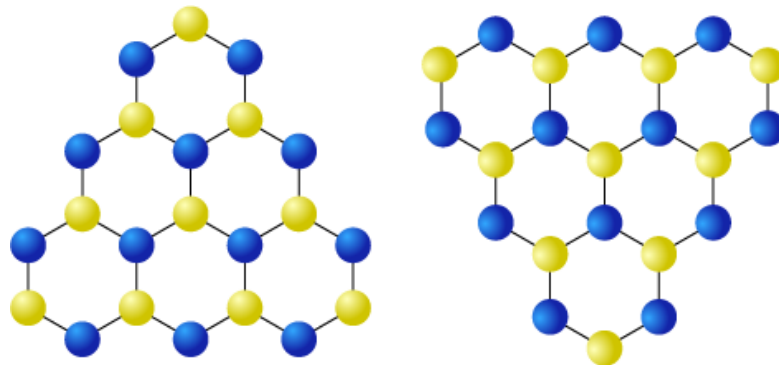


Highly Aligned MoSe₂ on GaAs by MBE

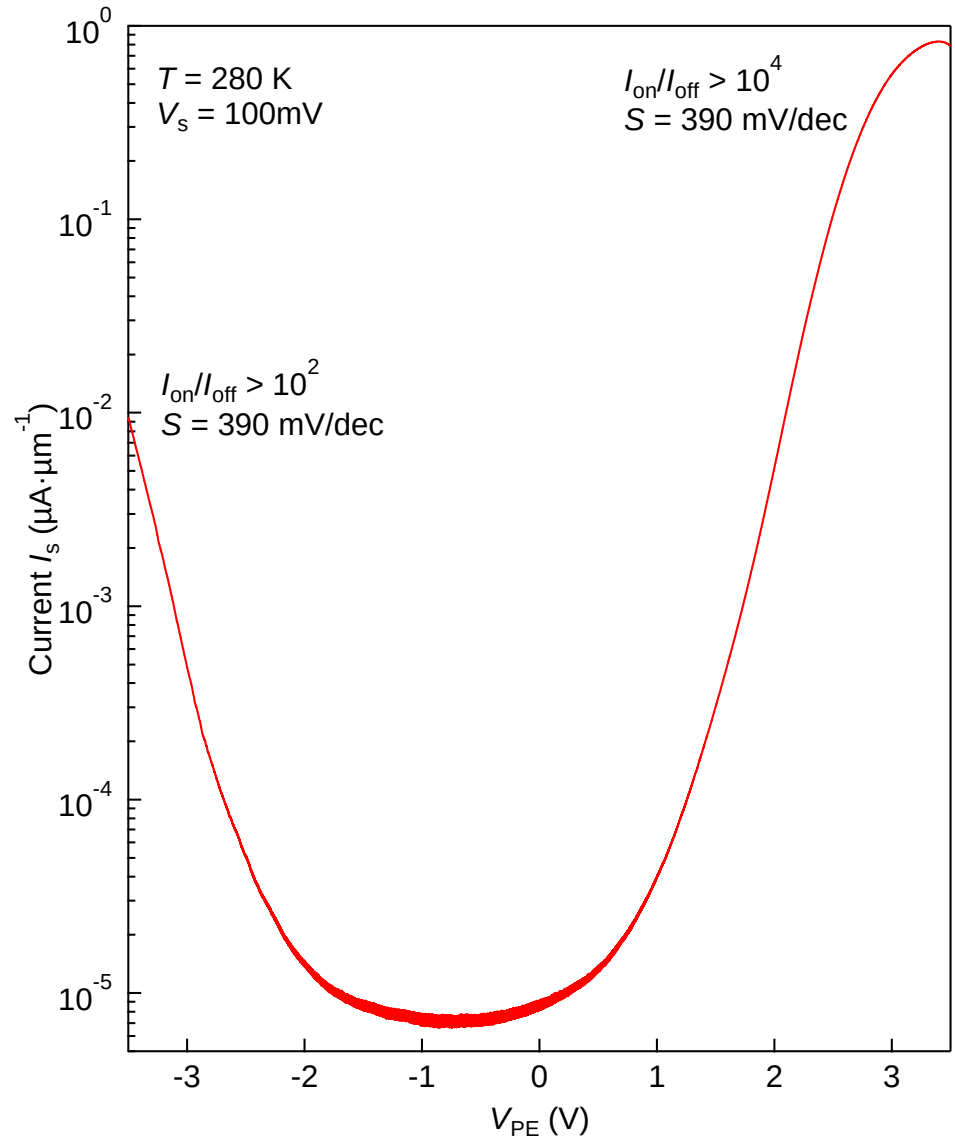
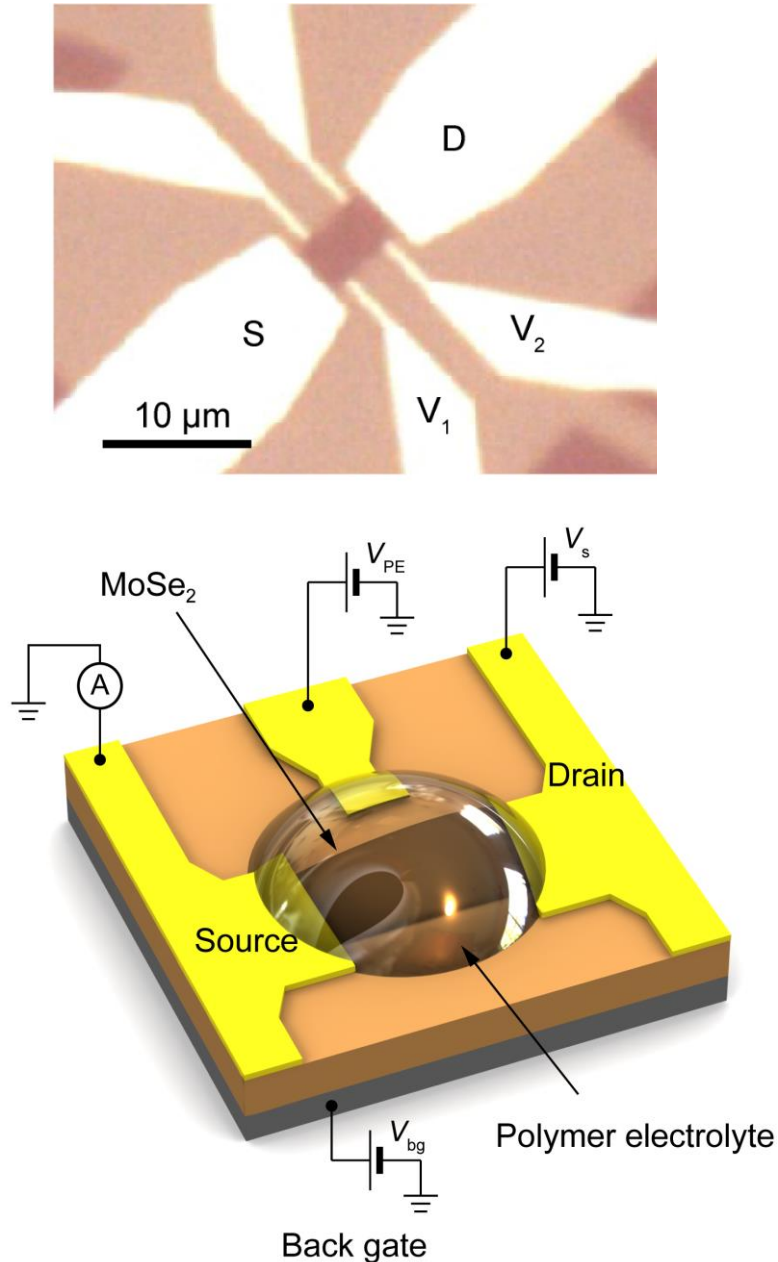


Chen...Kis; ACS Nano (2017)

Possible orientations:

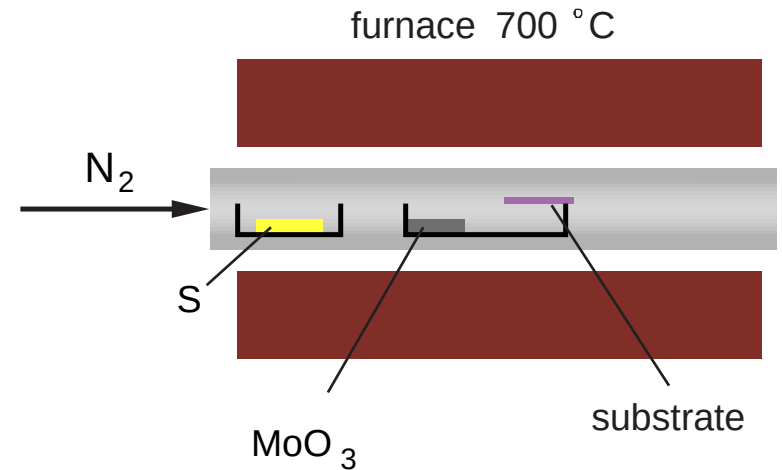
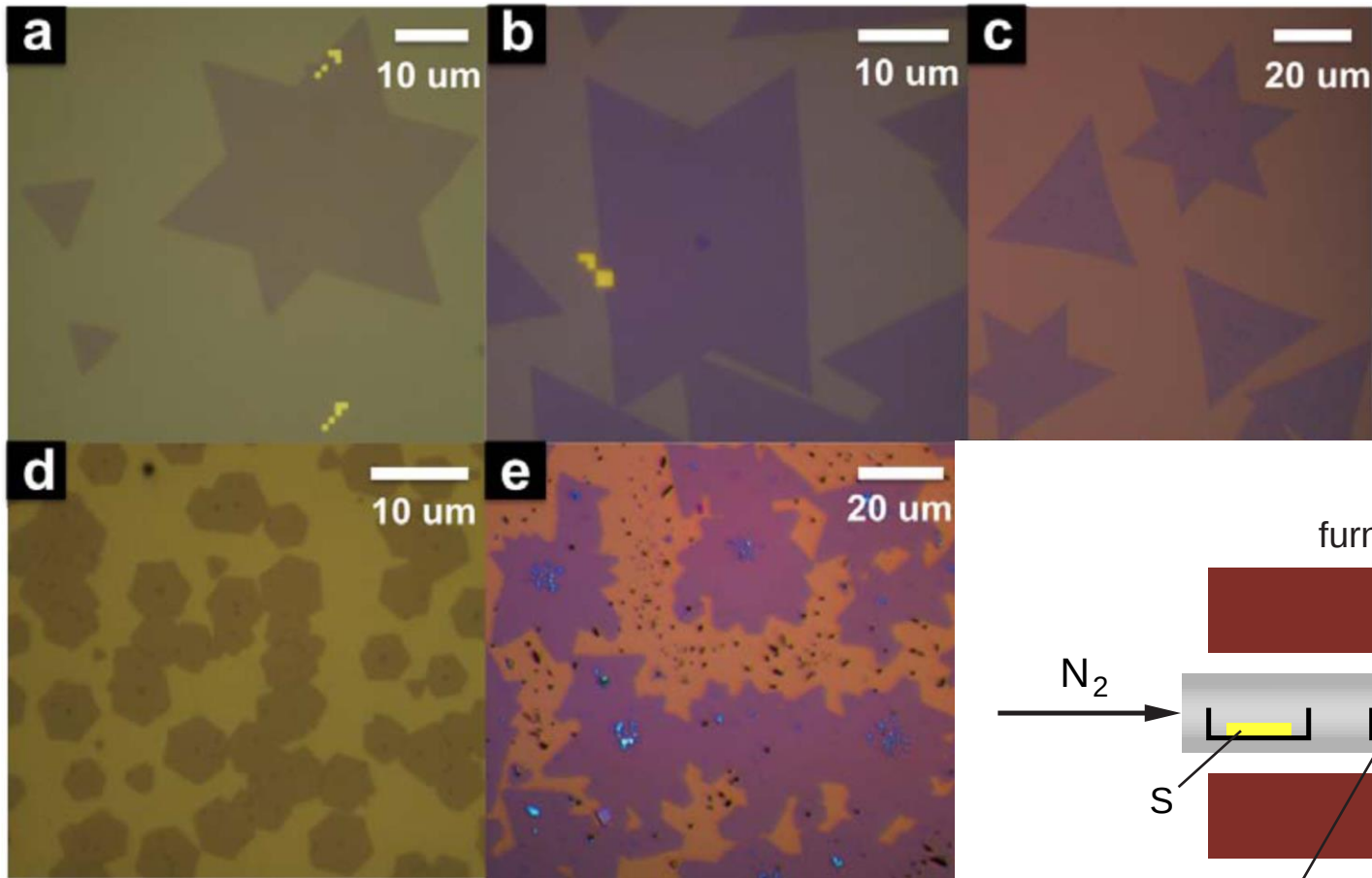


Ambipolar Transport in MBE-grown MoSe₂ EDLTs



Chen...Kis; ACS Nano (2017)

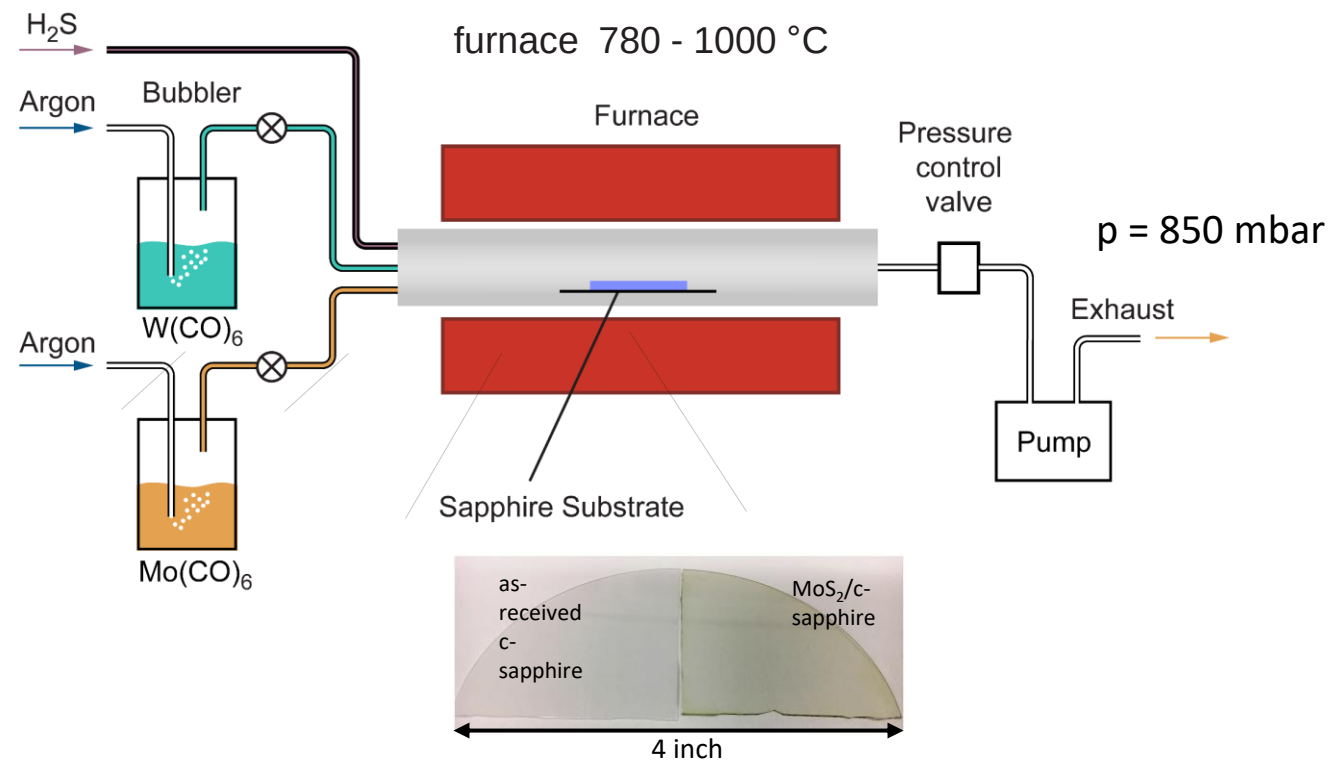
MoS₂: CVD Growth



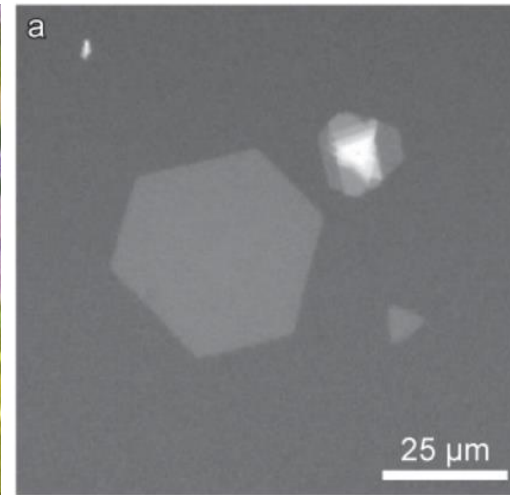
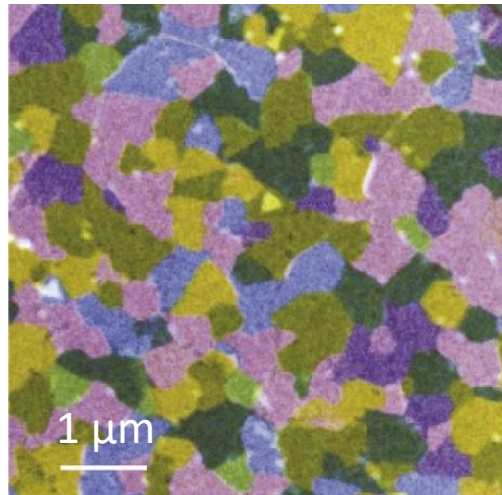
Van der Zande et al. Nature Materials (2013)
Najmaei et al. Nature Materials (2013)

MOCVD Growth

Metalorganic chemical
vapour deposition

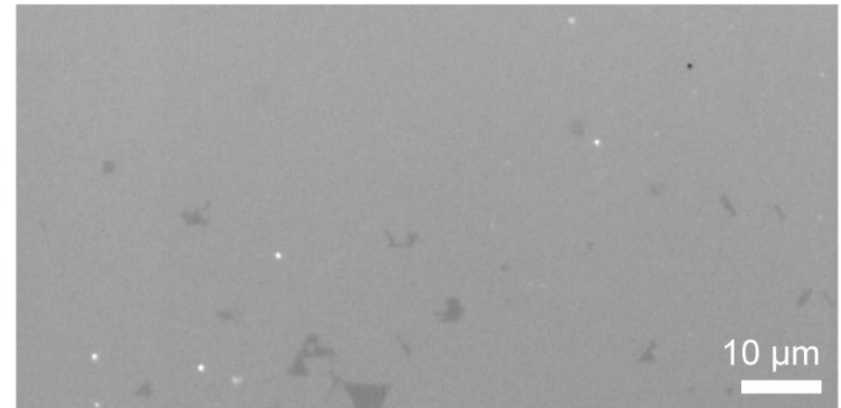
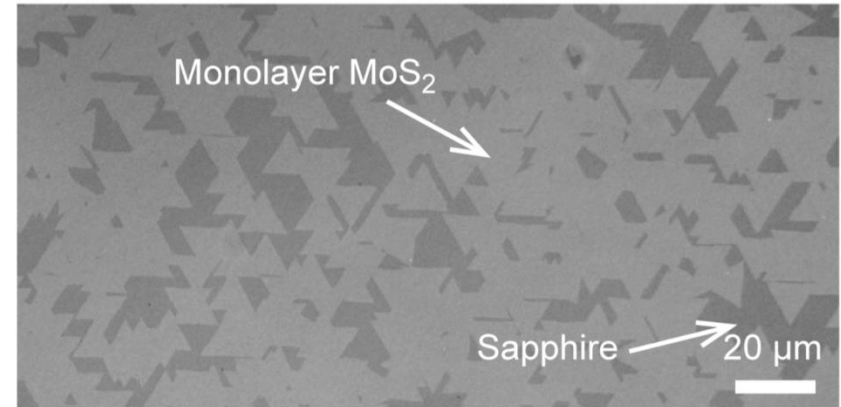
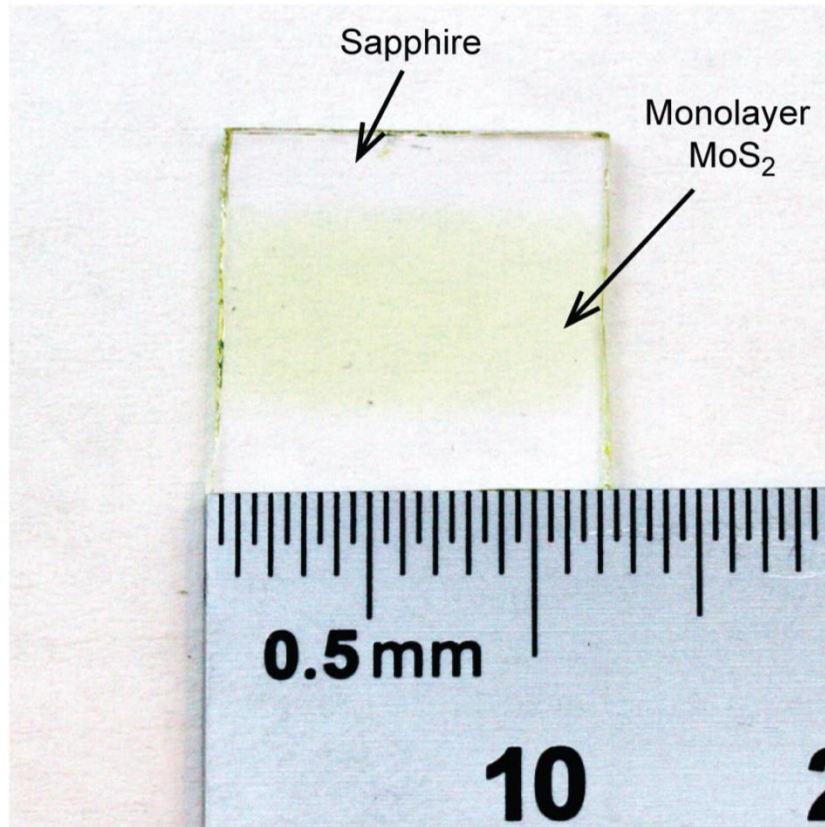


Polycrystalline MoS_2
Sub- $1\mu\text{m}$ grain size
Cornell, Nature (2015)



Large single crystals
EPFL, Kim et al,
Nano Lett (2017)

CVD MoS₂

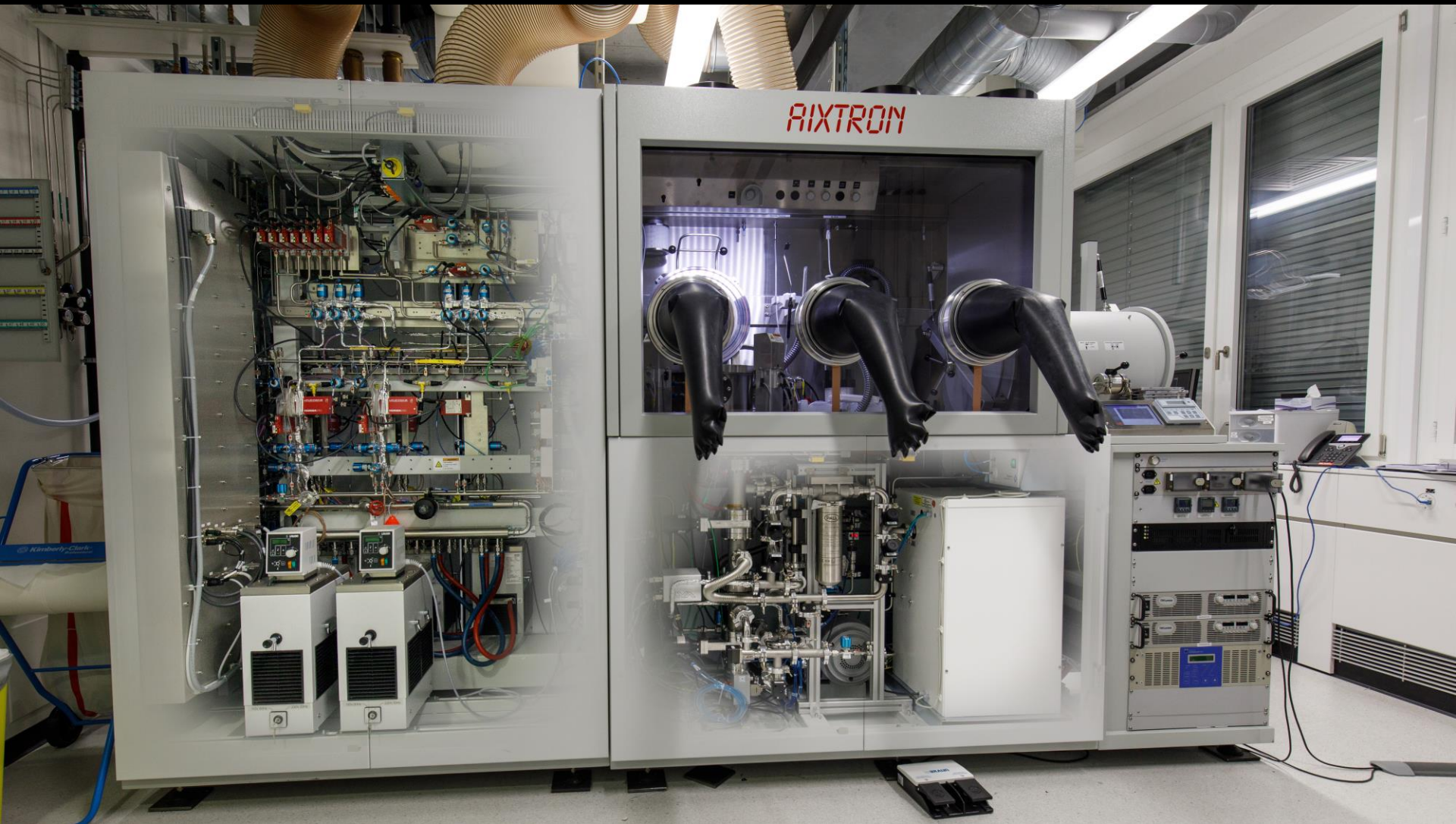


Dumcenco...Kis; ACS Nano (2015)

New at EPFL: MOCVD – BM 2D NOVO



New at EPFL: MOCVD – BM 2D NOVO



Recapitulation

Why semiconducting nanostructures for nanoelectronics

Historic overview

- Graphene
- Transition metal dichalcogenides and 2D materials

Material Growth

- Exfoliation, MBE, CVD, MOCVD