Molecular and carbon-based electronic systems

when	Wednesday, 10h15-12h00
where	seminar room 3.12, Physics Dpt, Klingelbergstrasse 82
credit	2KP
debit	attendance + 1 presentation
VV	lecture Nr. 37839-01
web	**https://www.empa.ch/web/s405/lectures**

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Vorlesung Uni Basel, FS2019

Molecular and carbon-based electronic systems

Goals

- provide background & fundamental aspects to anchor understanding
- discuss hybrid devices/applications combining organic compounds with solid-state systems

Contents

Introduction. Carbon from 0D to 3D.

Condensed matter physics reminder and fundamental properties of electronic systems.

Molecular junctions: formation mechanisms, transport, spectroscopy, data analysis and insights from theory.

Graphene for electronics: electrodes, junctions, nanoribbons, quantum interference effects & thermal transport.

Molecule assemblies: imaging, contacting, from junction to function.

Nanoscale devices for neuromorphic computing.

Nanoscale devices for sensing.

Mini-workshop: Talks by students (15′ talk + 5′ discussion).

Schedule

20.02	L1	Lecture organisation & contents Introduction: Carbon 0D to 3D	mc	
27.02	-	no lecture		
06.03	-	no lecture		
13.03		no lecture		Fasnacht
20.03	L2	Introduction: Carbon 0D to 3D continued Condensed matter reminder and basics	mc	
27.03	L3	Junctions I	mc	
03.04	L4	Junctions II	mc	
08.04	L5	Empa visit, 14h00-16h00, Dübendorf	mc	tbd: FIBs, CC, NEST
10.04	L6	Graphene junctions I: gaps, molecules	mc	
17.04	L7	Graphene junctions II: molecules, GNRs	mc	
24.04	*L8*	*Neuromorphic computing with nanodevices*	*M. Csontos*	
01.05	*L9*	*DFT basics*	*M. Perrin*	
08.05	*L10*	*Molecule assemblies: analysis & contacting*	*P. Nirmalraj*	
15.05	L11	Junction to function	mc	
22.05	L12	Nanoscale devices for sensing	mc	
29.05	L13	Workshop: talks by students		

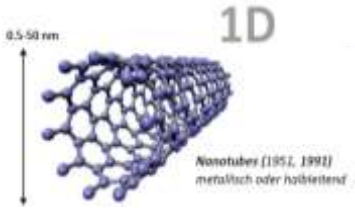
outline

electronics beyond Silicon

- other possible pathways for electronics

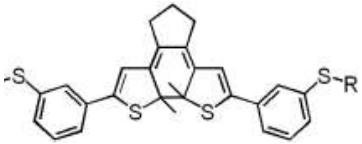
Carbon allotropes

- discovery



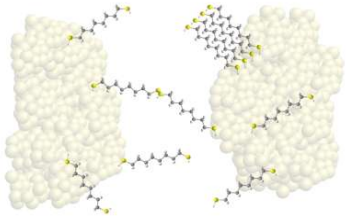
Carbon & molecular electronics

- brief historical account
- why molecules



molecular junctions

- how to contact nm-scale objects



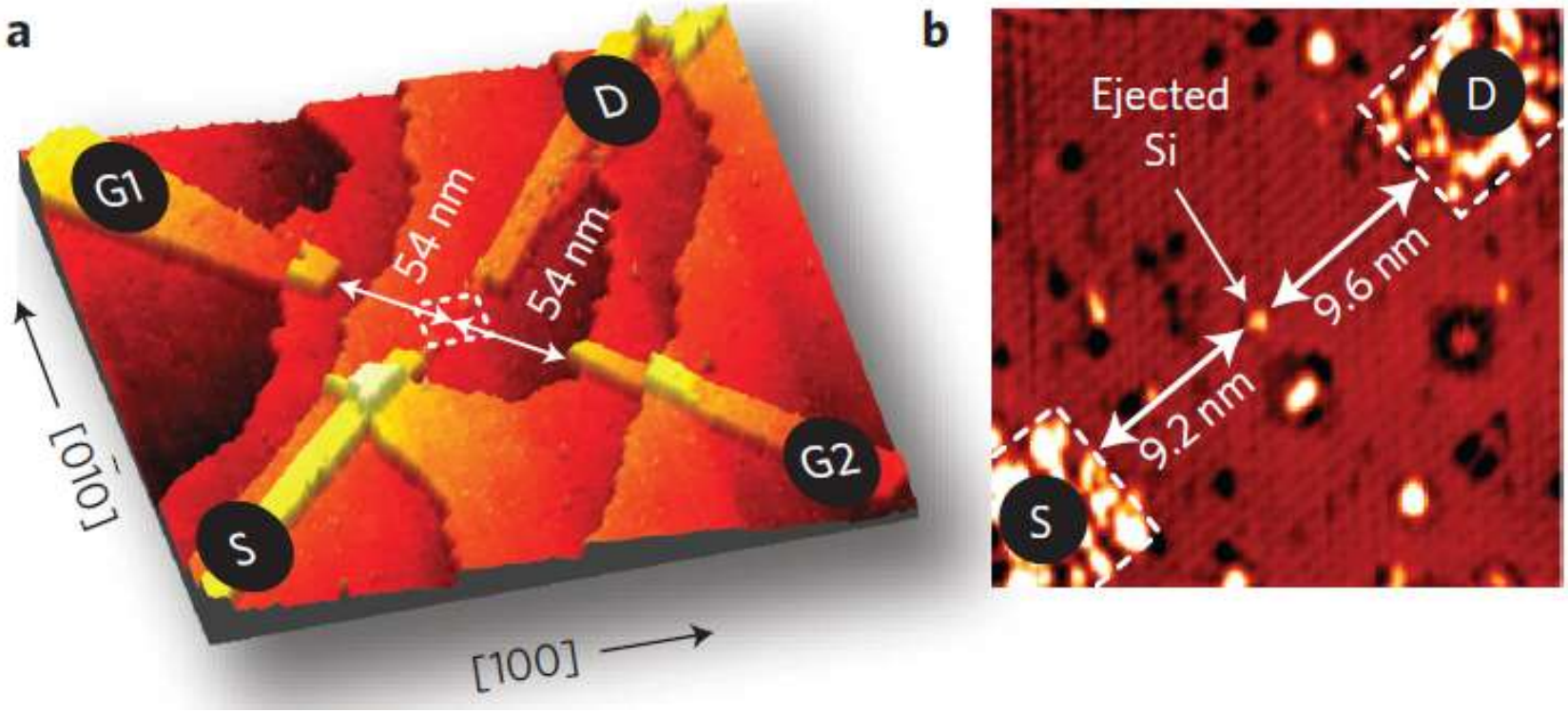
… really small

LETTERS
PUBLISHED ONLINE: 19 FEBRUARY 2012 | DOI: 10.1038/NNANO.2012.21
nature nanotechnology

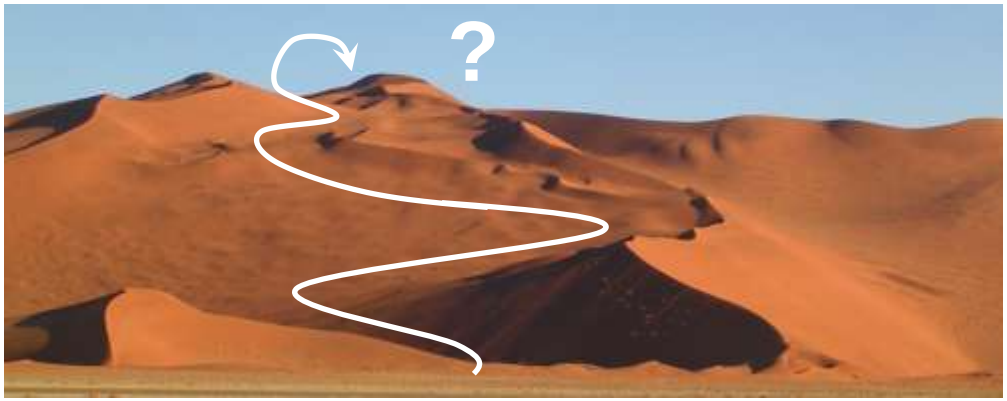
A single-atom transistor

Martin Fuechsle[1], Jill A. Miwa[1], Suddhasatta Mahapatra[1], Hoon Ryu[2], Sunhee Lee[3], Oliver Warschkow[4], Lloyd C. L. Hollenberg[5], Gerhard Klimeck[3] and Michelle Y. Simmons[1]*

STM lithography and phosphine (PH_3) dosing

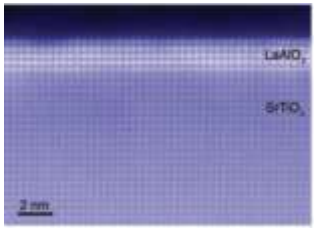


electronics beyond Si



materials

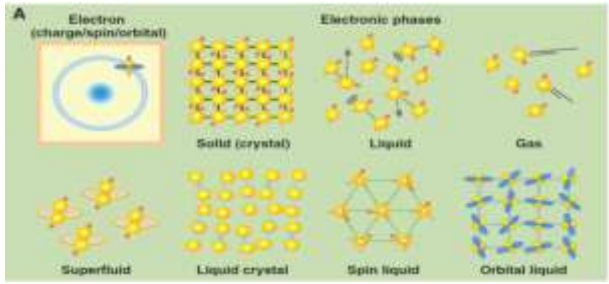
Oxides interfaces



LaAlO3-SrTiO3 heterostructures
Mannhardt et al., Science 2013

Transition metal oxides

charge, spin, orbital degrees of freedom for diversity of phases exploiting e-e correlation

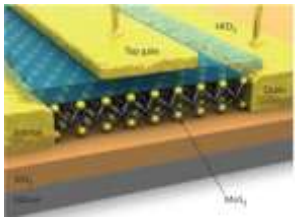


Takagi et al., Science 2013

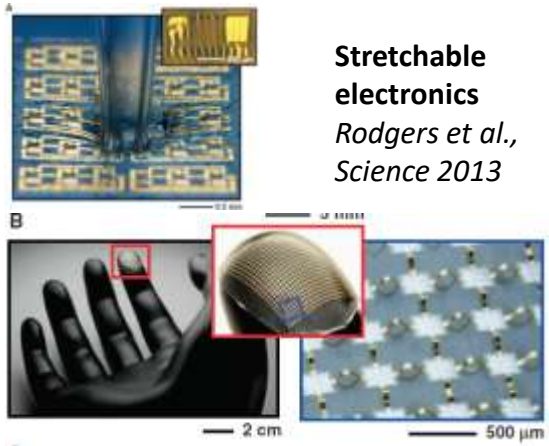
Transition metal dichalcogenides (2D)

MoS_2, WS_2, …

Strano et al., Nat. Nano 2012



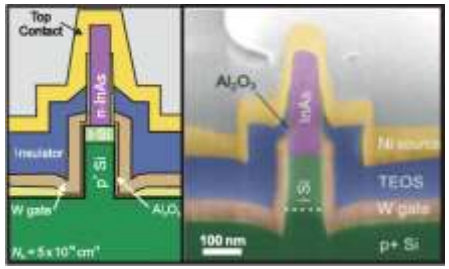
Organic & inorganic materials with elastomeric substrates



Stretchable electronics
Rodgers et al., Science 2013

III–V compound semic. transistors

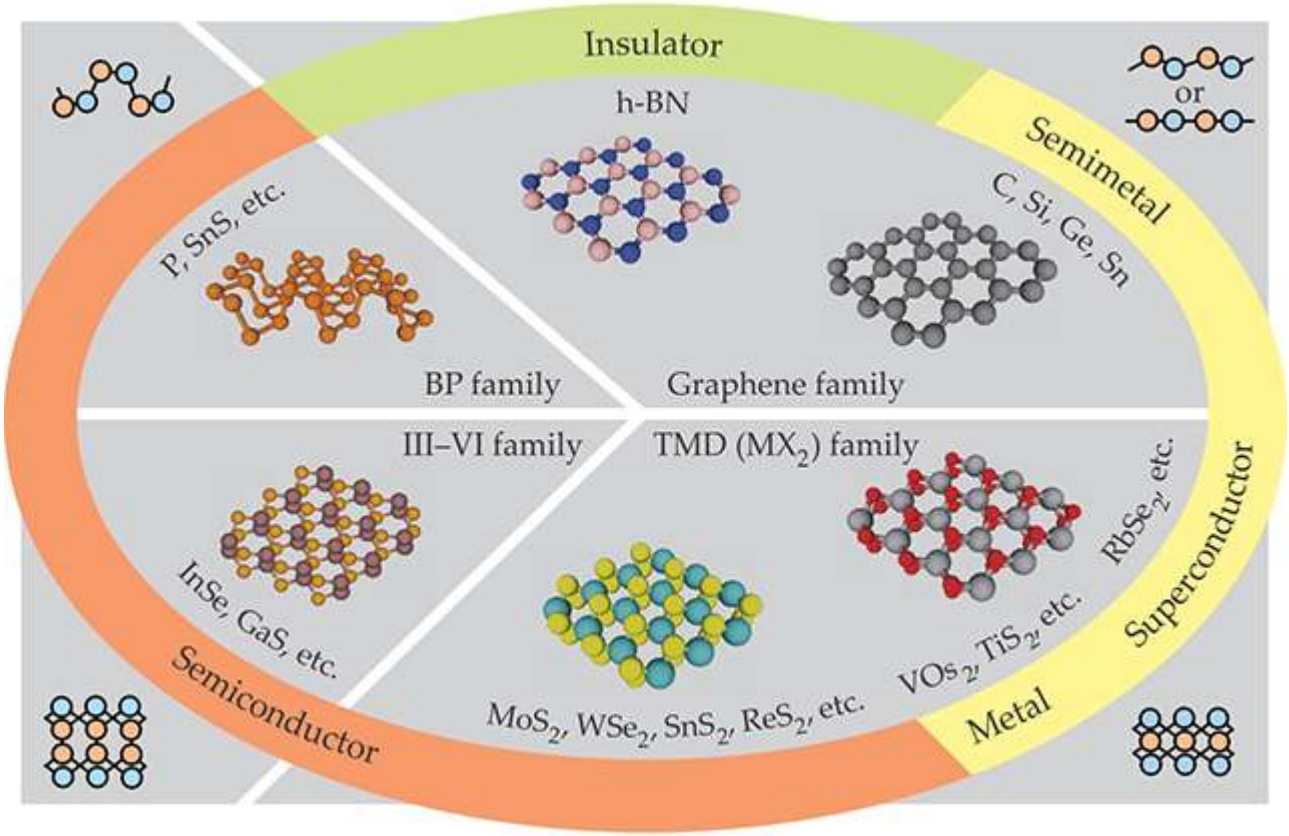
NW tunnel FETs
Riel et al., MRS Bulletin 2014



electronics beyond Si: "hot" materials

graphene, boron nitride (hBN) & analogues

black phosphorus (BP) & analogues

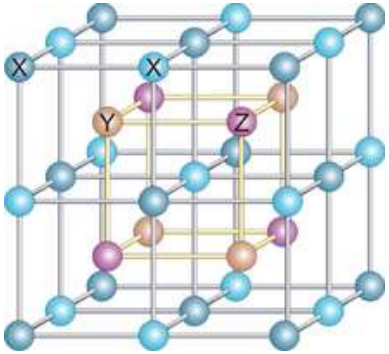


transition-metal dichalcogenides (TMDs)

Ajayan, Kim et al., Phys. Today (2016)

electronics beyond Si: "hot" materials

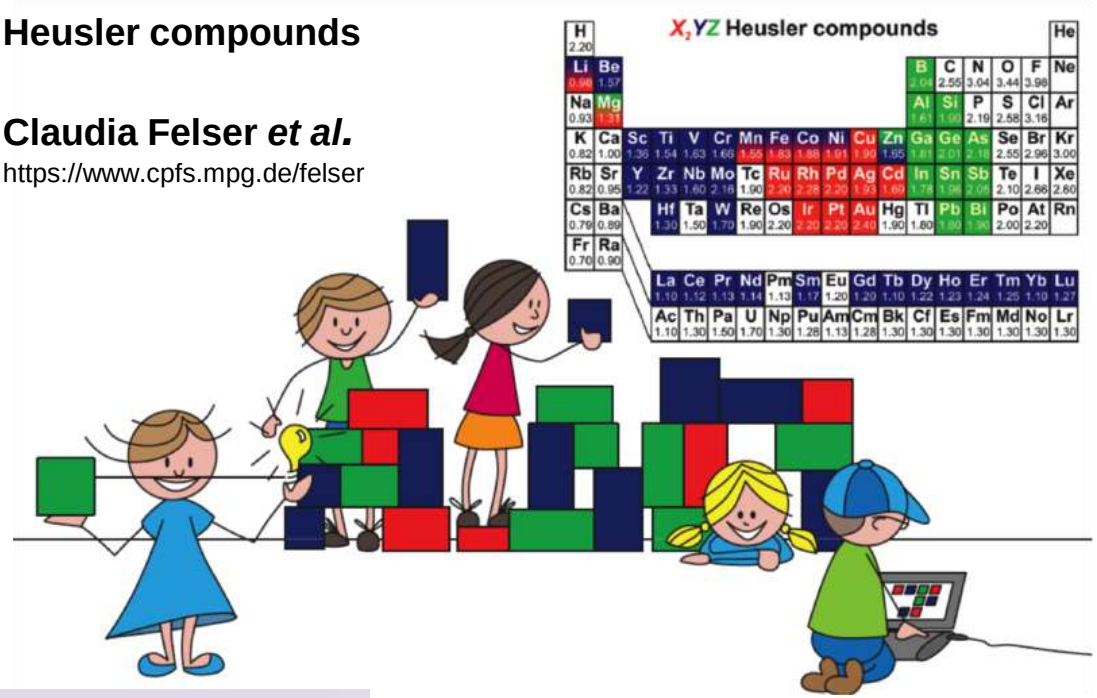
Kavli symposium @ APS
March meeting 2019

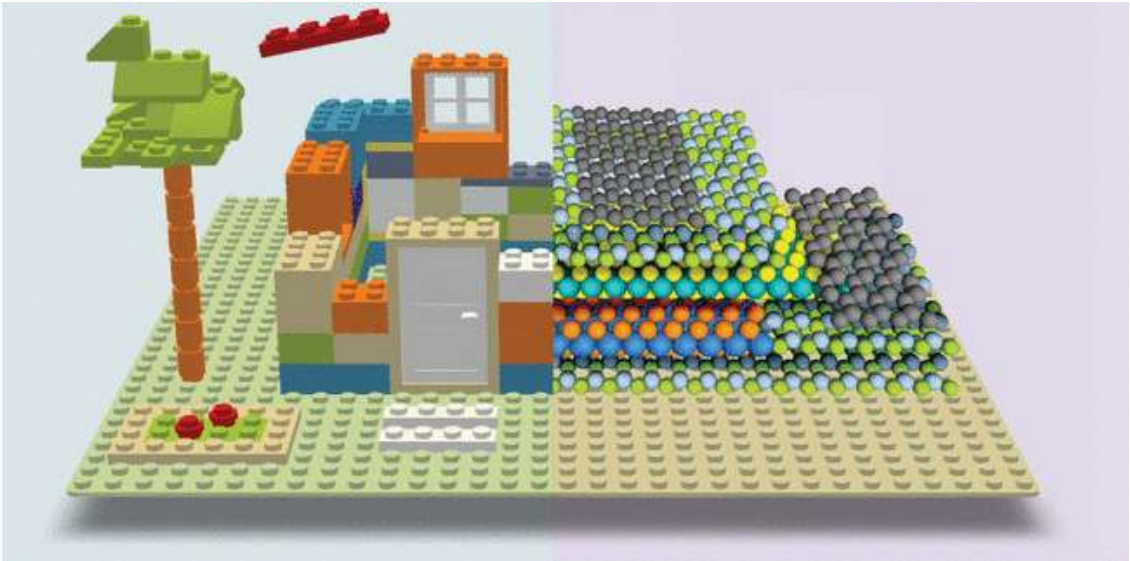


wiki

Heusler compounds

Claudia Felser *et al.*
https://www.cpfs.mpg.de/felser





Mixed van der Waals heterostructures

Philip Kim *et al.*
Phys. Today (2016)
http://kim.physics.harvard.edu/

nanoelectronics roadmap for Europe (NEREID)

Overview on Technology Sectors and their Main Concepts

The NEREID roadmap is structured by the following nanoelectronic technology sectors, which are covered in the following Chapters (II.1 to II.8). Within all these technology sectors the roadmap follows a fixed structure which addresses the technologies' relevance, its competitive value, its vision, its scope and ambition, its synergies with other topics and its main concepts. Finally, each chapter ends with some recommendations for the technology sector.

On this page, all technology sectors are listed with all the main concepts that have been considered in the NEREID roadmap.

II.1 Advanced Logic and Memories (NEREID TASK 3.1)

- Nanowires
- FinFET
- FD-SOI
- Negative Capacitance FET (NCFET)
- Carbon Nanotubes (CNTFET)
- Memories, Concept 1 - OxRAM:
- Memories, Concept 2 - CBRAM
- Memories, Concept 3 - PCM
- Memories, Concept 4 - MRAM
- 3D sequential integration
- Reliability

II.2 Connectivity (Wireline and Wireless) (NEREID TASK 3.2)

- The Outdoor Wireless Applications
- The Outdoor Wireline Applications
- The Indoor Wireless Applications
- The Indoor Wireline Applications
- The Device to Device Wireless Applications
- The In Package/Device Photonics Wireline Applications

II.3 Smart Sensors (NEREID TASK 4.1)

- Sensor's for car internal system performance
  - Motion and Pressure sensors
  - Advance Driver Assistance System (ADAS)
    - Image Sensors-, Radar LiDAR- and Infrared sensors
- Environmental monitoring:
  - Gas and Particulate Matter sensors
  - Sensors for medical and healthcare
  - Physiological signal monitoring
  - Implantable sensors
  - Molecular diagnostics

II.4 Smart Energy (NEREID TASK 4.2)

- Si based power devices
- GaN-devices and substrates
- SiC-based substrates
- Alternative Wide Bandgap Semiconductors

II.5 Energy for Autonomous Systems (NEREID SubTASK 4.2.11)

- Mechanical EH: Electrostatic transduction
- Mechanical EH: Piezoelectric transduction
- Mechanical EH: Electromagnetic transduction
- Thermal energy harvesting
- Photovoltaic Energy Harvesting
- RF energy harvesting/wireless power transfer
- Energy storage - Microbatteries
- Energy storage - Microcapacitors
- Micro-Power Management

II.6 System Design and Heterogeneous Integration (NEREID Workpackage 5, WP5)

In this chapter, the main concepts are classified by connecting the three applications

- Automated Driving;
- Implantable Devices;
- Environmental Monitoring and Wearable Systems,

with different elements of Application-Aware Hardware-Software-Co-Design. These Elements comprise Functionalities, Implementation Qualities and Criticalities and Needs.

II.7 Equipment and Manufacturing Science (NEREID Workpackage 6, WP6)

- More Moore
- More-than-Moore
- Manufacturing Science

II.8 Beyond-CMOS – Emerging devices and Computing Paradigms (NEREID Workpackage 2, WP2)

- Steep slope switches: Tunnel FETs
- Neuromorphic circuits and computing
- Spintronics
- Quantum Photonics
- Phonon, Brownian and nano-opto-mechanical computing

Dec. 2018 - https://www.nereid-h2020.eu/roadmap

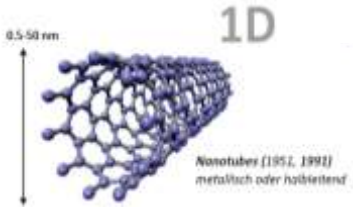
outline

electronics beyond Silicon

- other possible pathways for electronics

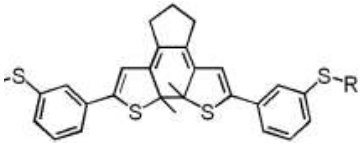
Carbon allotropes

- discovery



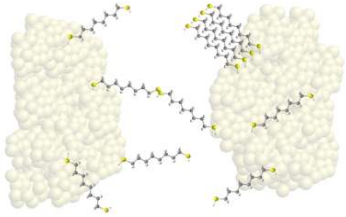
Carbon & molecular electronics

- brief historical account
- why molecules



molecular junctions

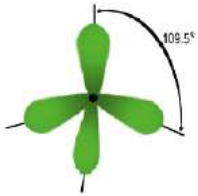
- how to contact nm-scale objects



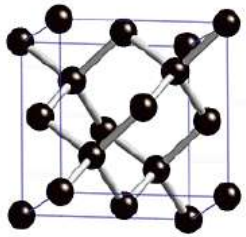
carbon-based materials

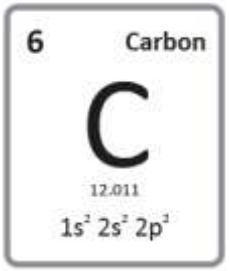
3D

Diamant (sp³ Carbon)
- *das härteste Material*
- *sehr guter Isolator, trotzdem aber exzellenter Wärmeleiter*



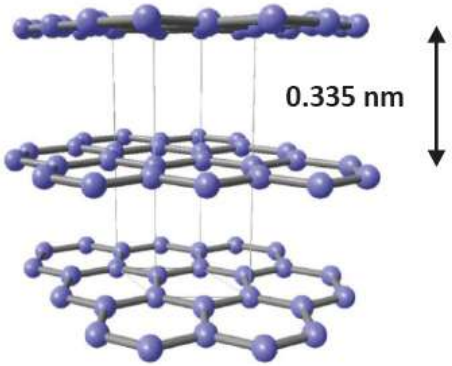
sp³ hybridization





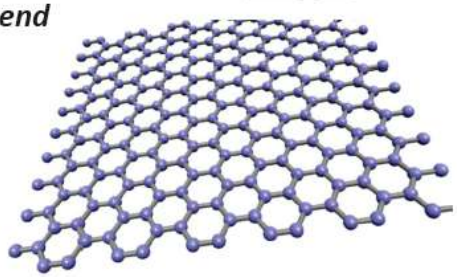
Graphit (sp² Carbon)
- *lässt sich leicht abtragen (Bleistift)*
- *recht guter elektrischer Leiter*

sp² hybridization



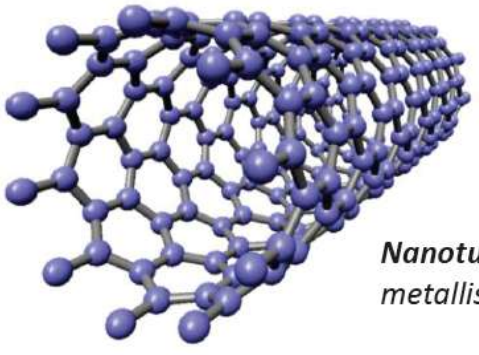
2D

Graphene (2004)
"zwischen" metallisch und halbleitend



1D

0.5-50 nm

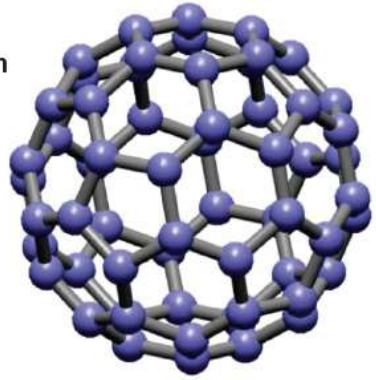


Nanotubes (1951, 1991)
metallisch oder halbleitend

0D

Fullerene C_{60} (1985)

0.7 nm



carbon allotropes discovery

The Nobel Prize in Physics 2010

Photo: U. Montan

Andre Geim

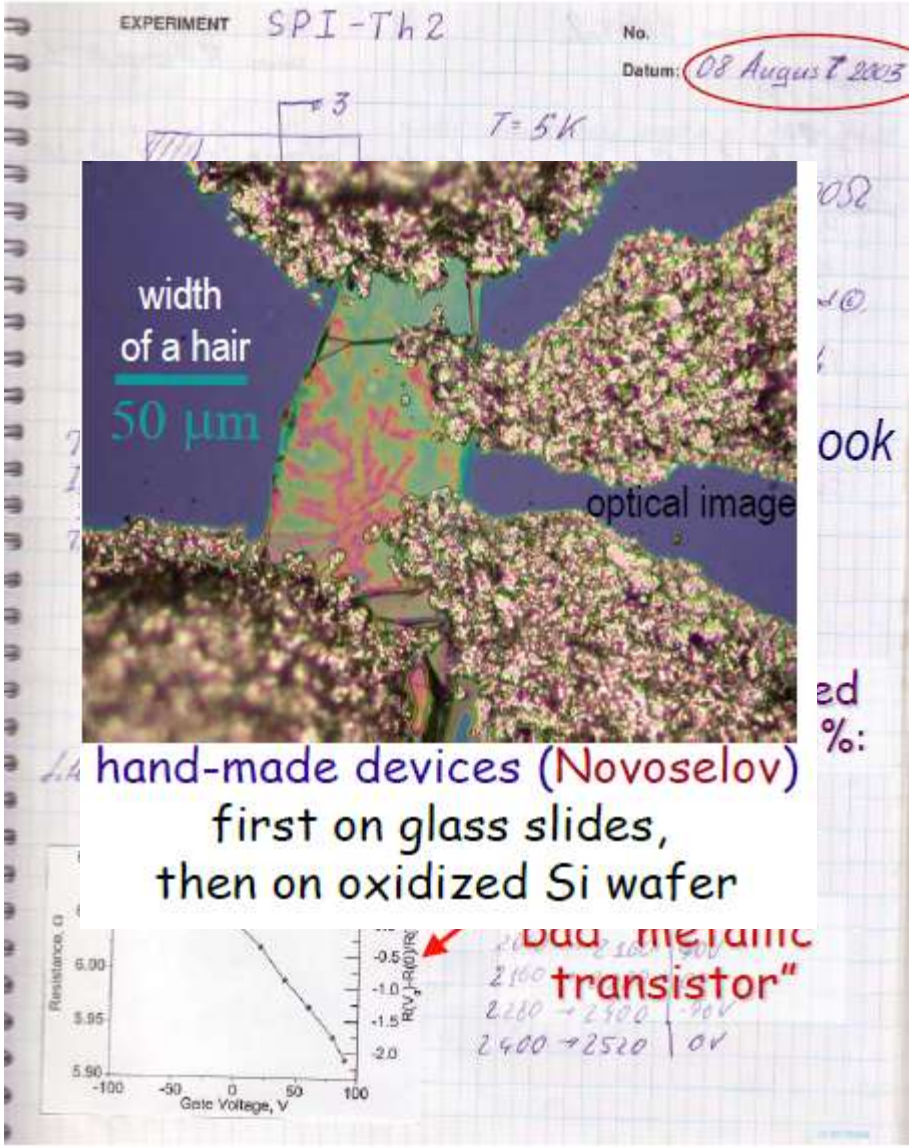
Prize share: 1/2

Photo: U. Montan

Konstantin Novoselov

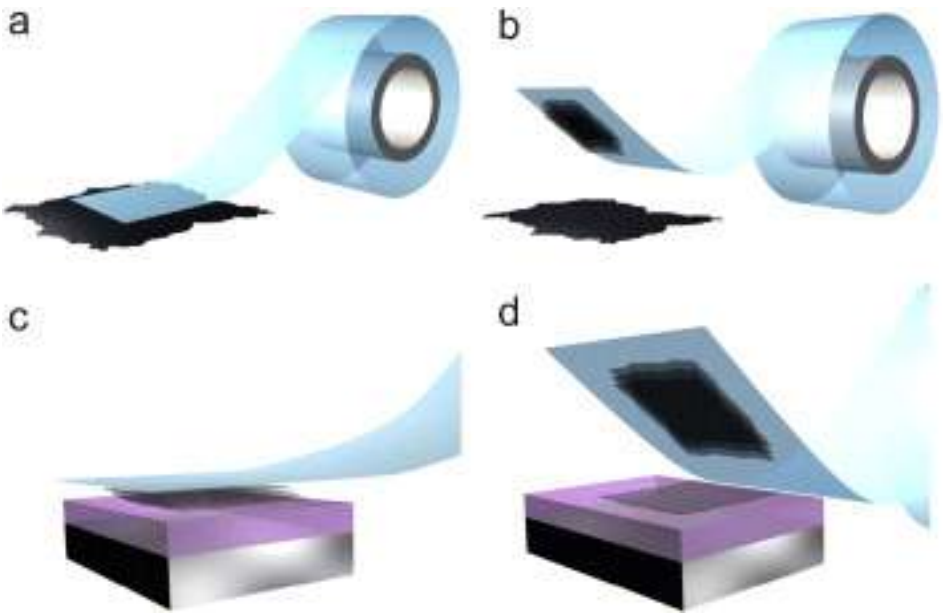
Prize share: 1/2

The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov *"for groundbreaking experiments regarding the two-dimensional material graphene"*

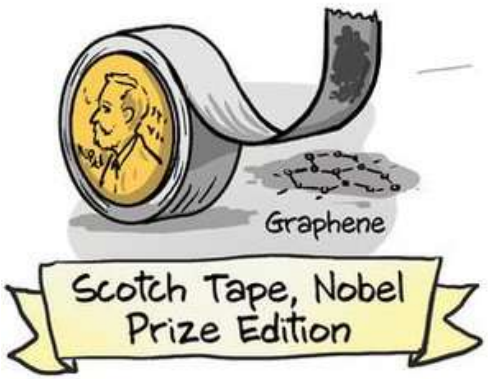


Nobel.se

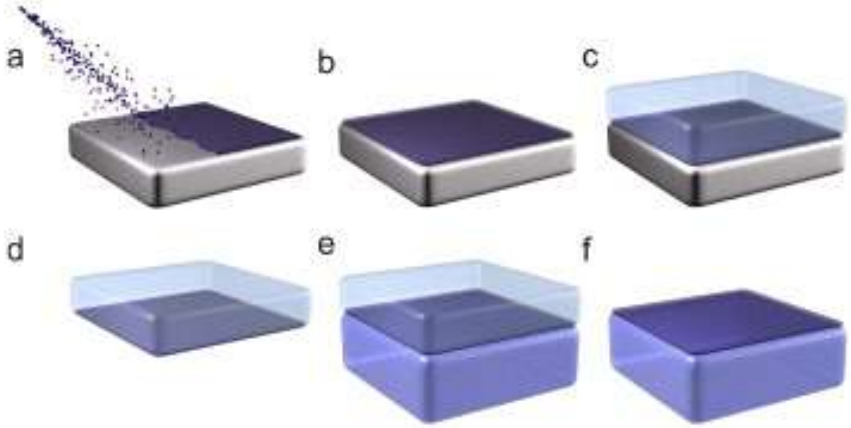
Graphene: scotch tape



Mechanical exfoliation
scotch tape technique



Nature's top ten, 2018 (PhD comics)



Chemical Vapor Deposition
(CVD) and transfer

Novoselov, Castro-Neto, Phys. Scripta (2012)

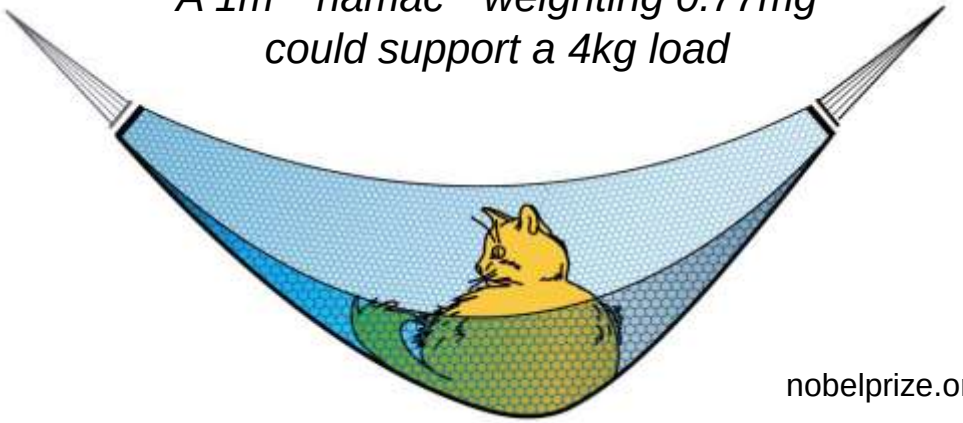
graphene

0.14nm

0.12nm

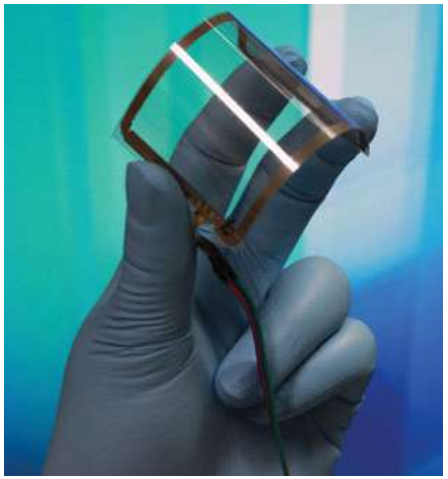
Mechanically strong: composite materials

A 1m² "hamac" weighting 0.77mg could support a 4kg load

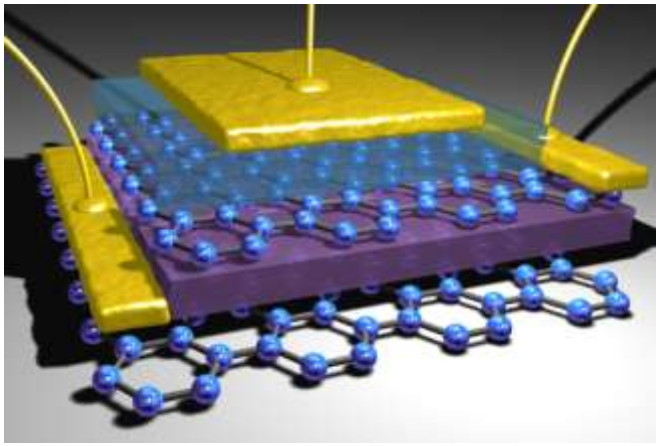


nobelprize.org

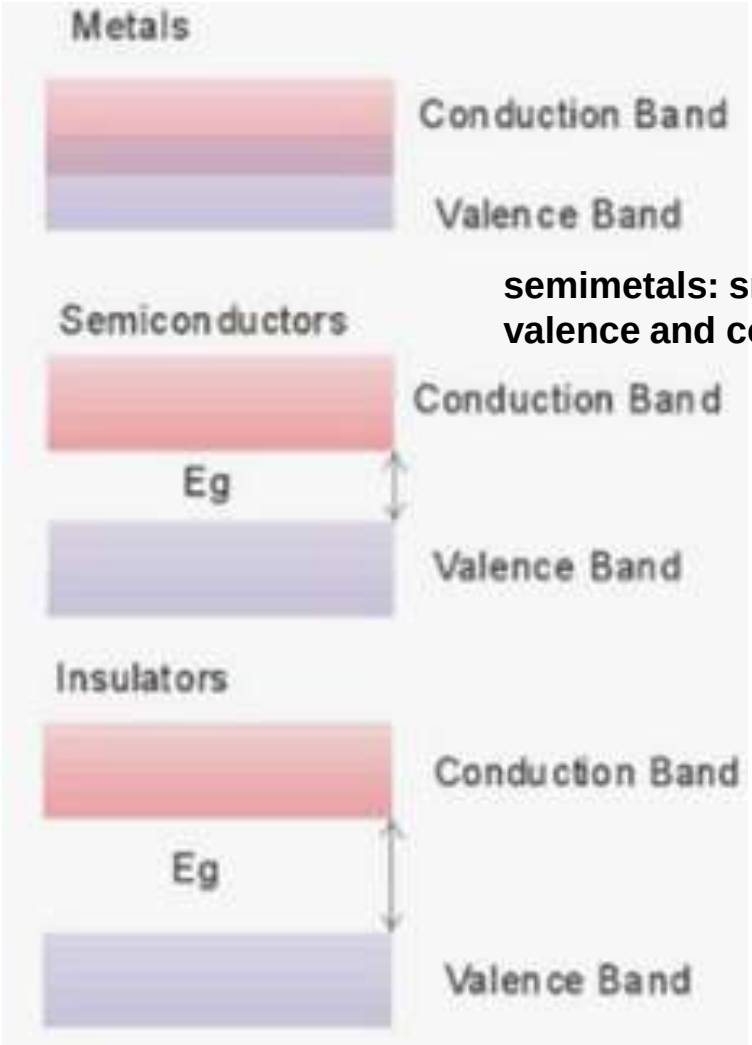
Flexible conductor
may replace ITO



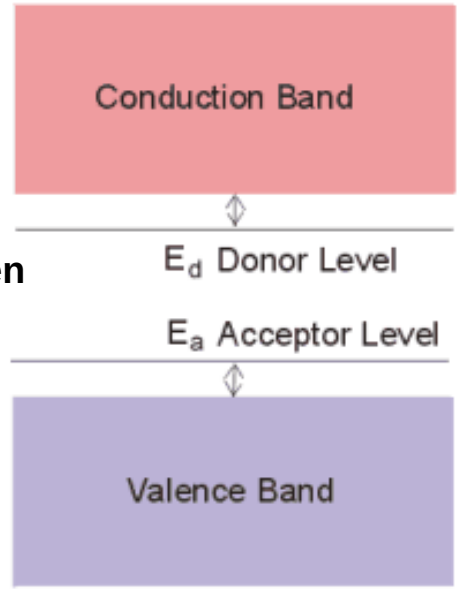
High charge mobility:
electrical applications



reminder: energy bands



semimetals: small overlap between valence and conduction bands



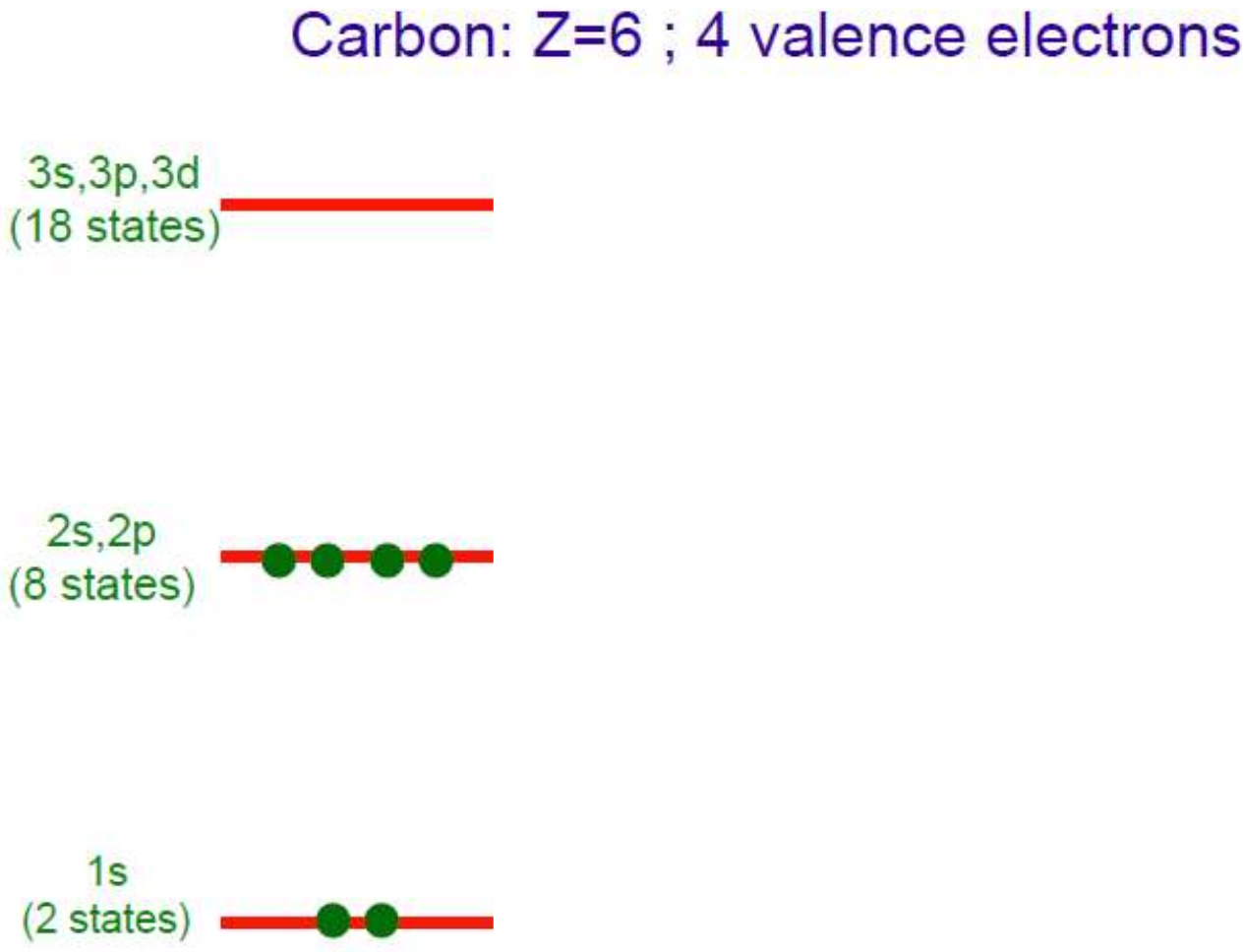
Energy gaps

Si ~ 1.12 eV
Ge ~ 0.66 eV
GaAs ~ 1.43 eV

NB: kT (RT) ~25meV

graphene electronic structure

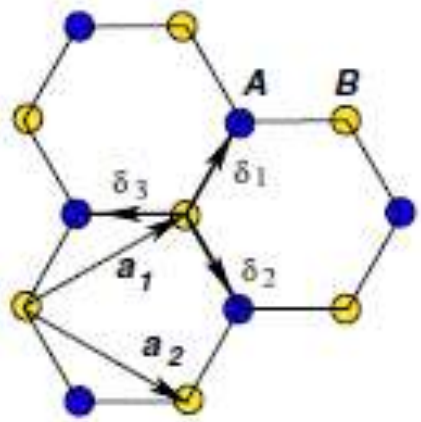
C: $1s^2 2s^2 2p^2$

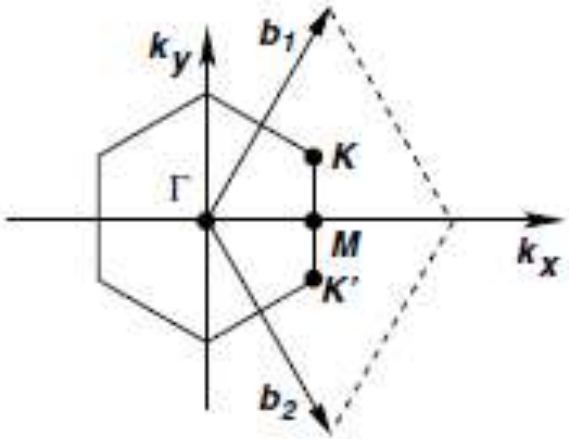


1 extra electron / p orbital ⇨ half-filled π band

Kane, Princeton

graphene electronic structure

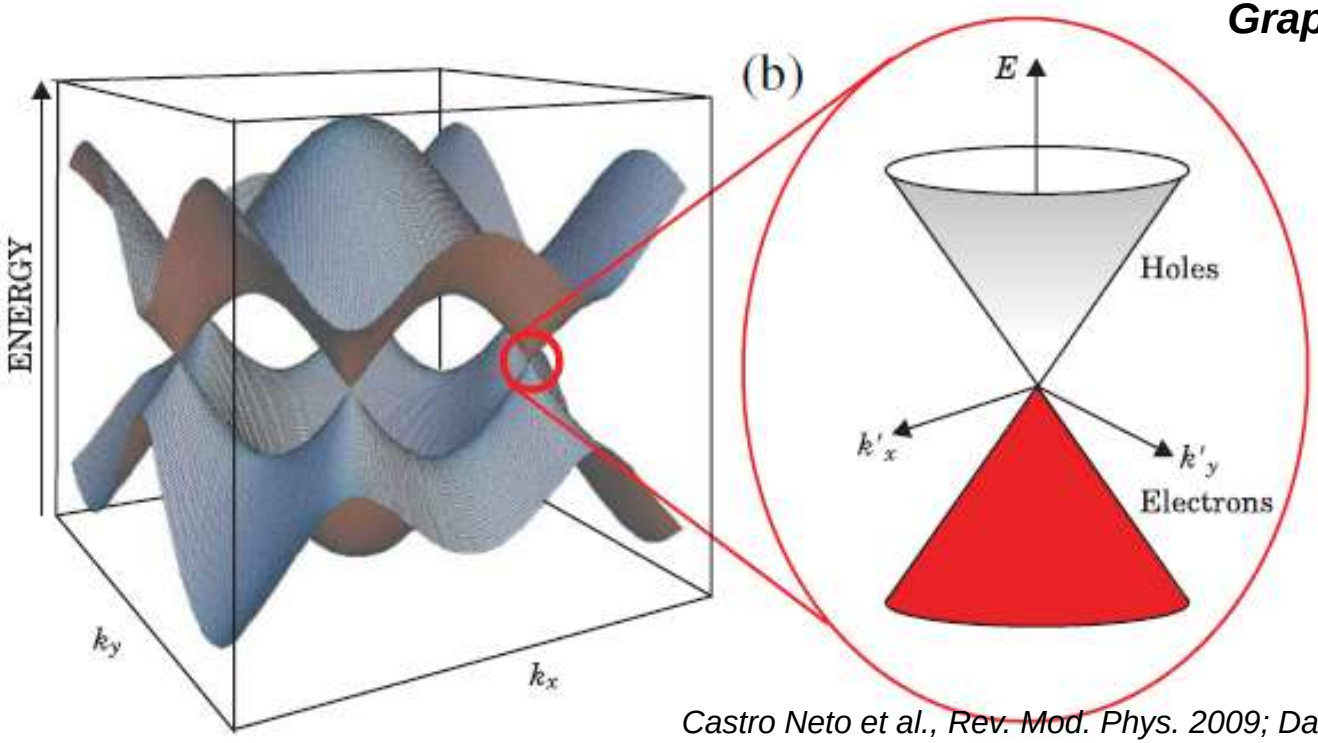




Graphene honeycomb lattice with the two triangular sublattices
blue – sublattice A
yellow – sublattice B

Graphene Brillouin zone in momentum space

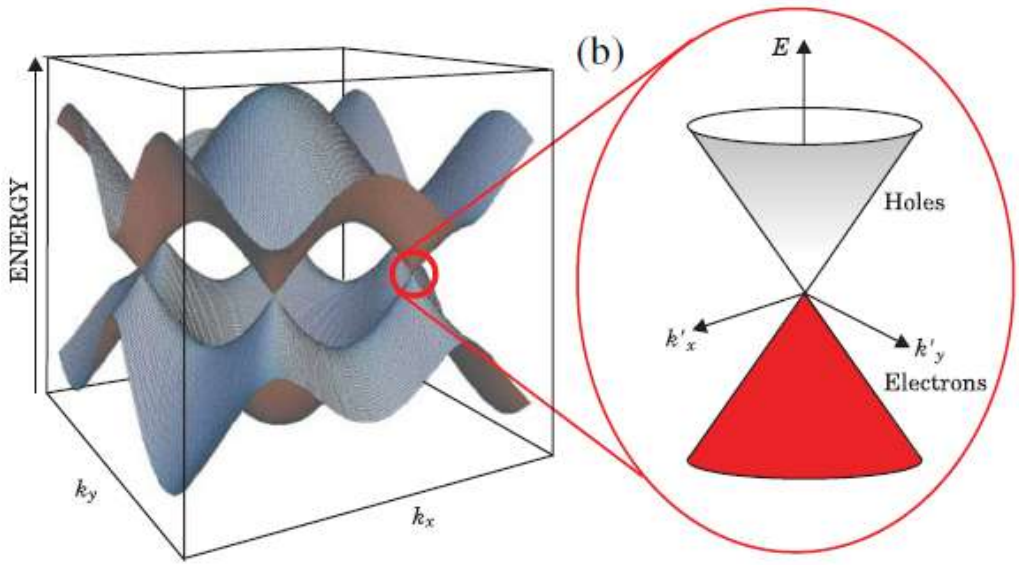
Graphene bandstructure



- Valence band filled, fermi energy at E=0
  for neutral graphene
- Zero band-gap semiconductor
- Two non-equivalent 'valleys', K and K'
  pseudo-spin

Castro Neto et al., Rev. Mod. Phys. 2009; Das Sarma et al., Rev. Mod. Phys 2011

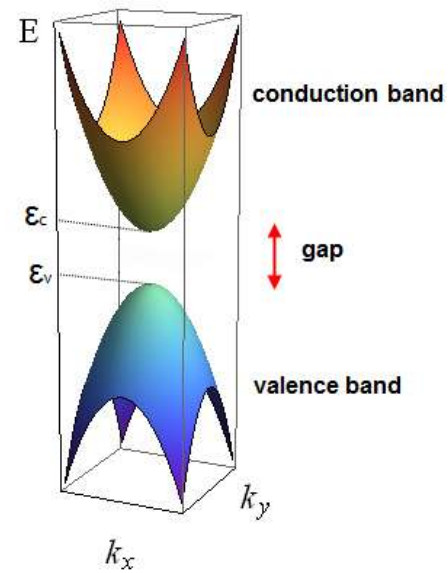
graphene electronic structure



Low-energy excitations:
massless, chiral Dirac Fermions

At the Fermi energy the spectra are linear, hence the electrons are here massless.

”Normal” materials



Normal (free electrons), particles with mass:

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

Massless particles, photons

$$E = h\nu = \hbar c k$$

Graphene:

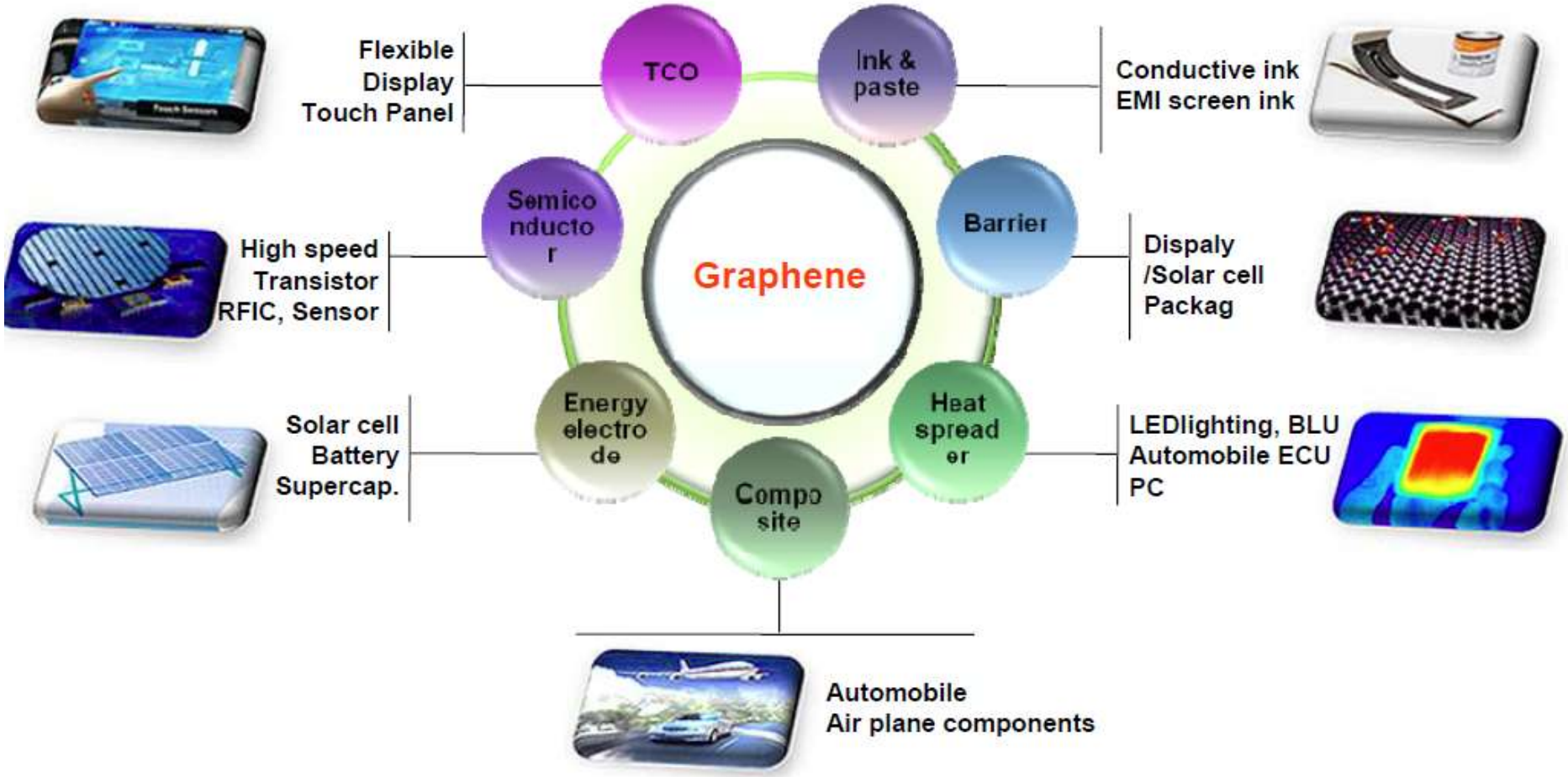
$$E = \hbar v_F k$$

where v_F, Fermi velocity is ≈ c/300

Dirac electrons in graphene mimic the physics of quant. electrodynamics for massless Fermions
Relativistic effects can be seen in graphene

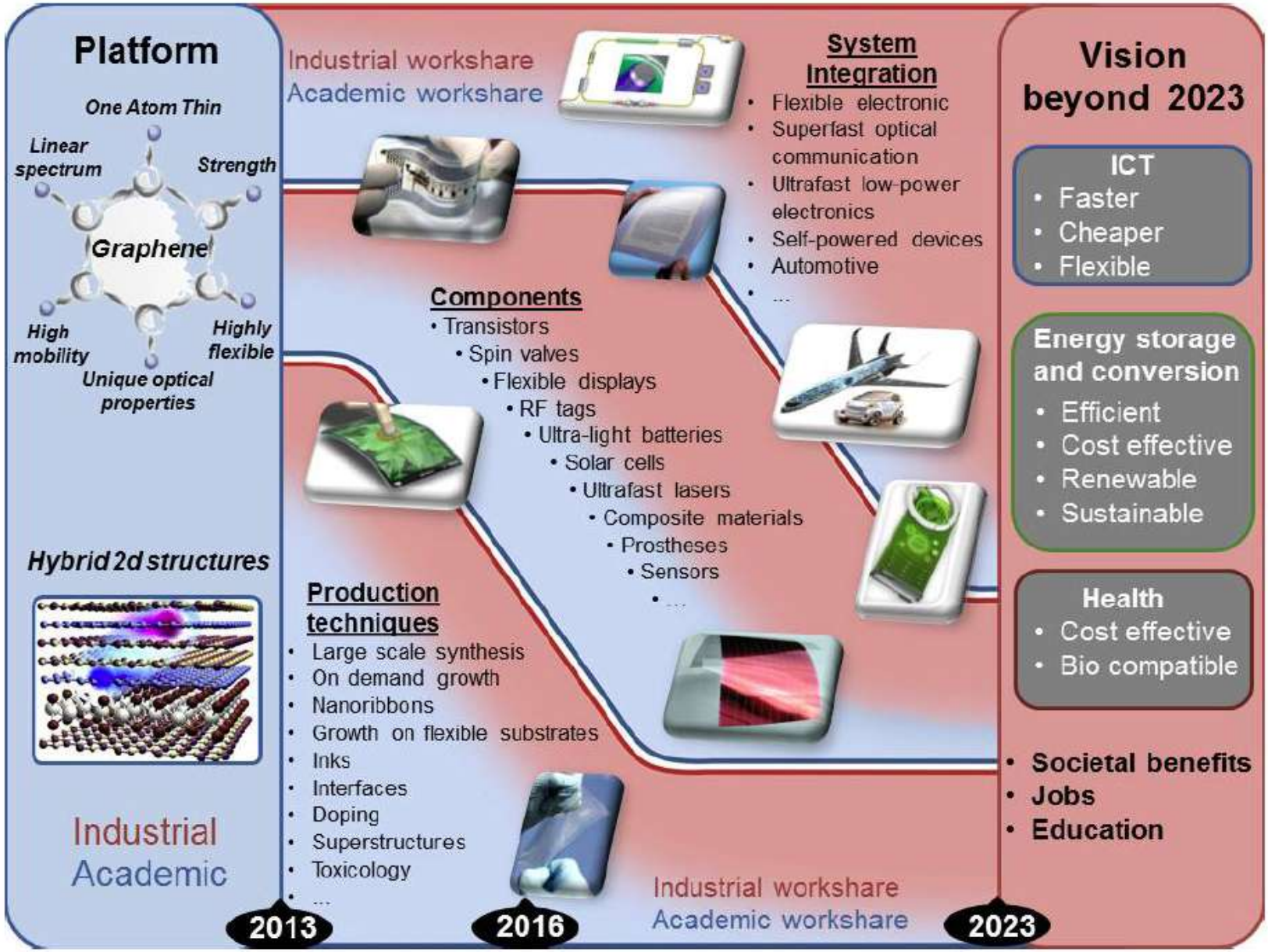
Castro Neto et al., Rev. Mod. Phys. 2009; Das Sarma et al., Rev. Mod. Phys 2011

graphene roadmap



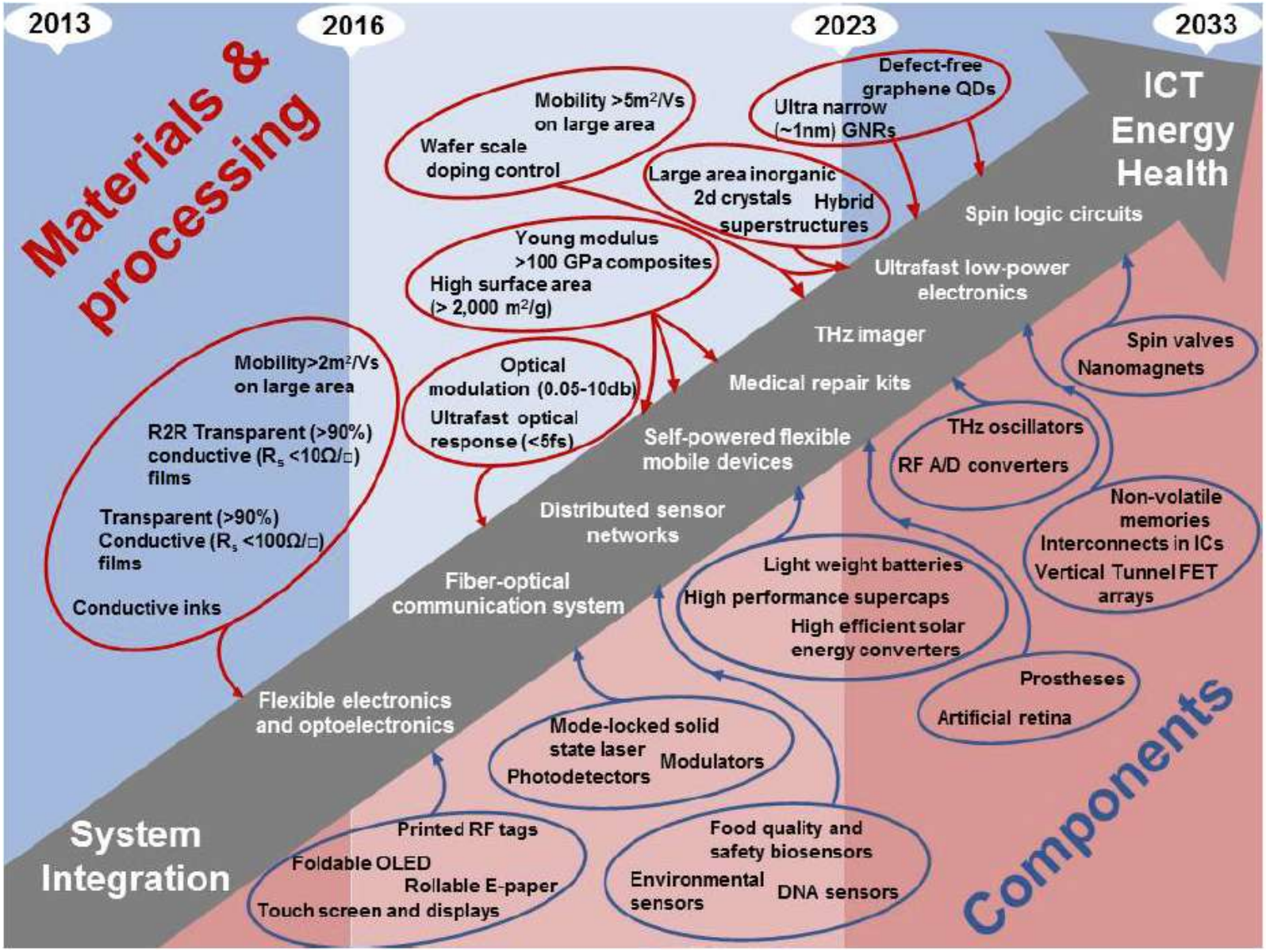
A. Ferrari, et al. 2011, 2015

graphene roadmap



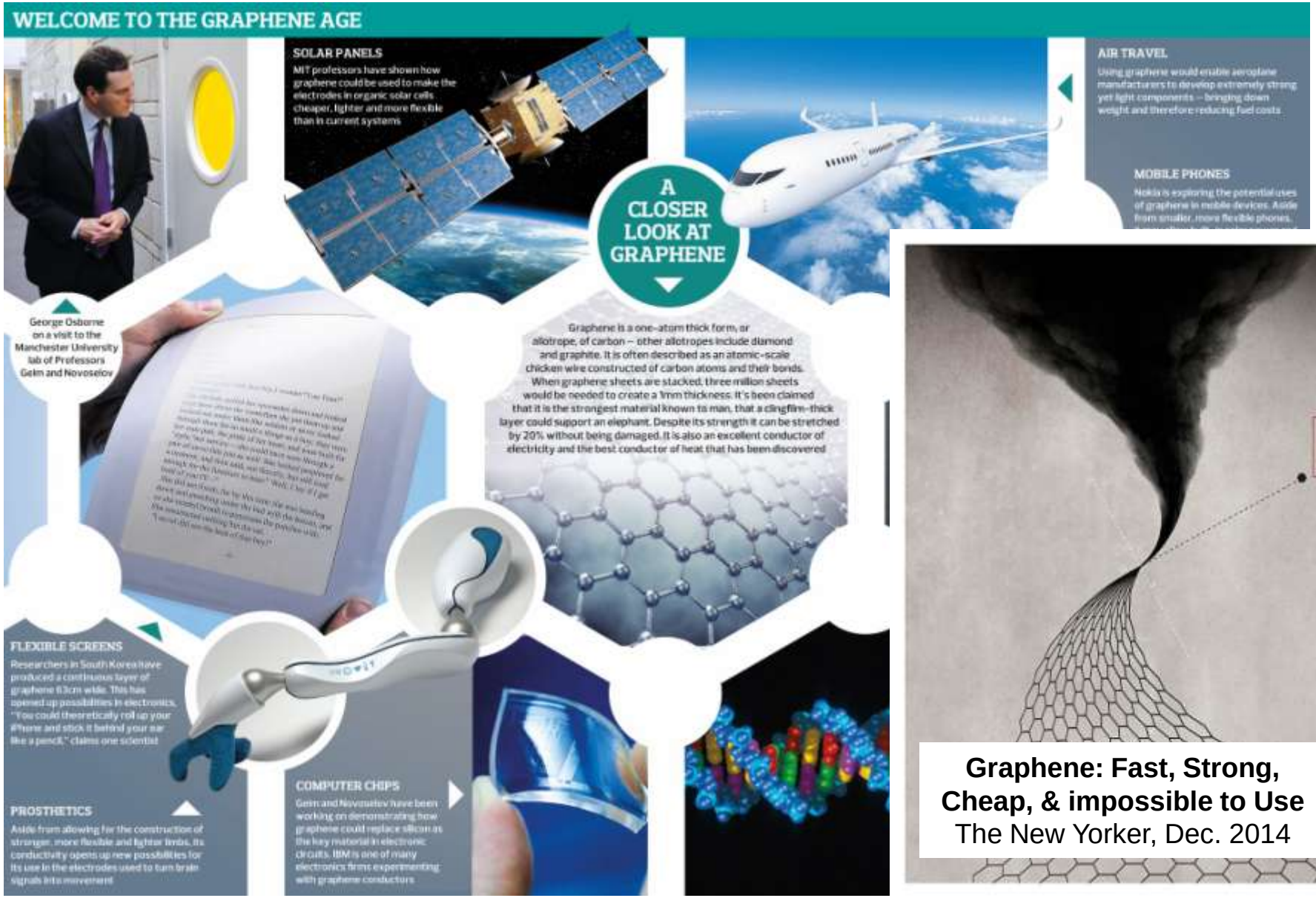
graphene-flagship.eu/

graphene roadmap



graphene-flagship.eu/

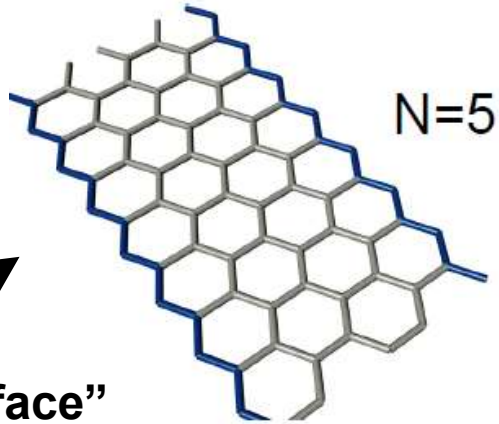
graphene age ...?



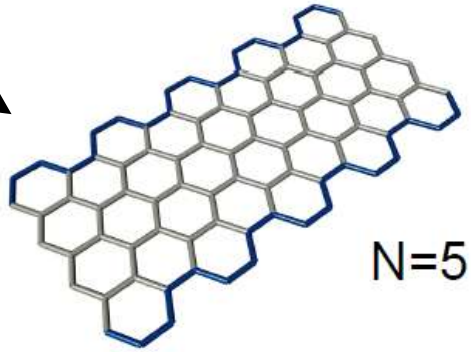
The Guardian, The New-Yorker (2014)

adding a gap: graphene ribbons structure

Zigzag edges

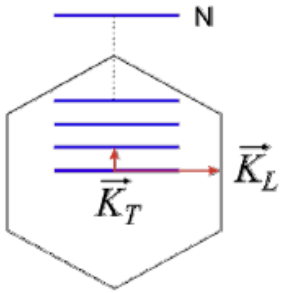


graphene "surface" (edges) states: two types of edges



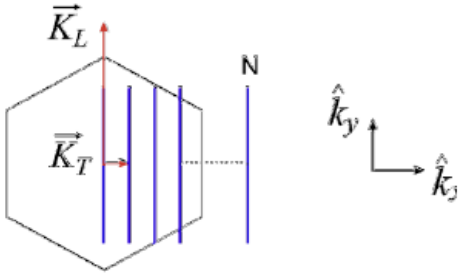
Armchair edges

- **Always metallic**
- **Presence of localized edge states at the Fermi level**



Nakada et al., *PRB* 54:17954 (1996)

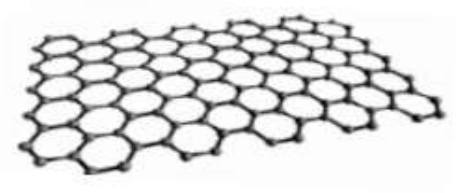
Metallic for N=3M-1 (M integer)
Semiconducting for N=3M and 3M-2
Examples: ***Metallic for N=5 and Semiconducting for N=4, 6***



Dresselhaus, Cargèse, 2014

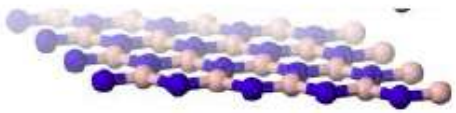
other 2D systems for electronics

Metallic:
graphene



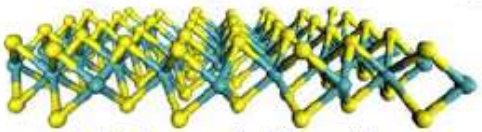
High mobility

Insulating:
h-BN (5.9 eV)



Inert blocking layer

Semiconducting:
Transition metal dichalcogenides
(MoS_2 (1.8～2.7eV))

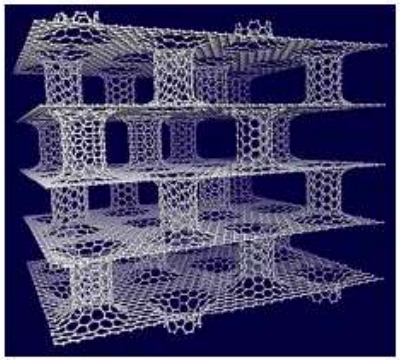


High on/off ratio
Photosensetive

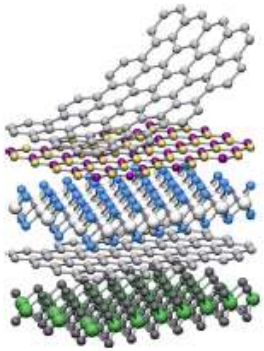
1991 **2004** **2010** **2012**

Various hybrid structure

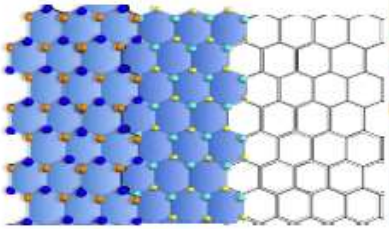
Network architecture



Stacked heterostructure



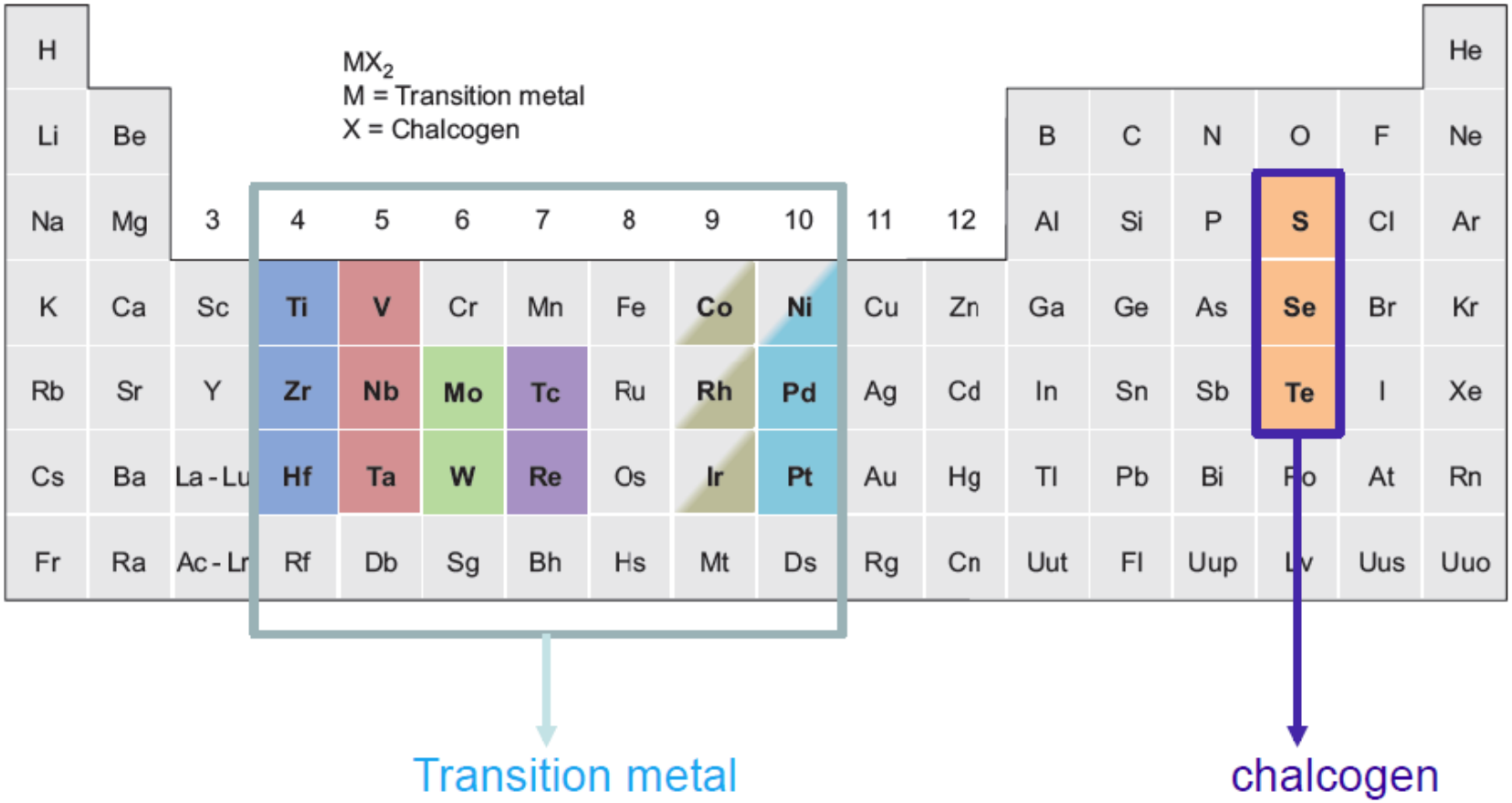
Lateral heterostructure



Dresselhaus, Cargèse, 2014

other 2D systems

Transition Metal Dichalcogenides (TMDs)



Chhowalla et al., Nat. Chem. (2013); Dresselhaus, Cargèse, 2014

other 2D systems

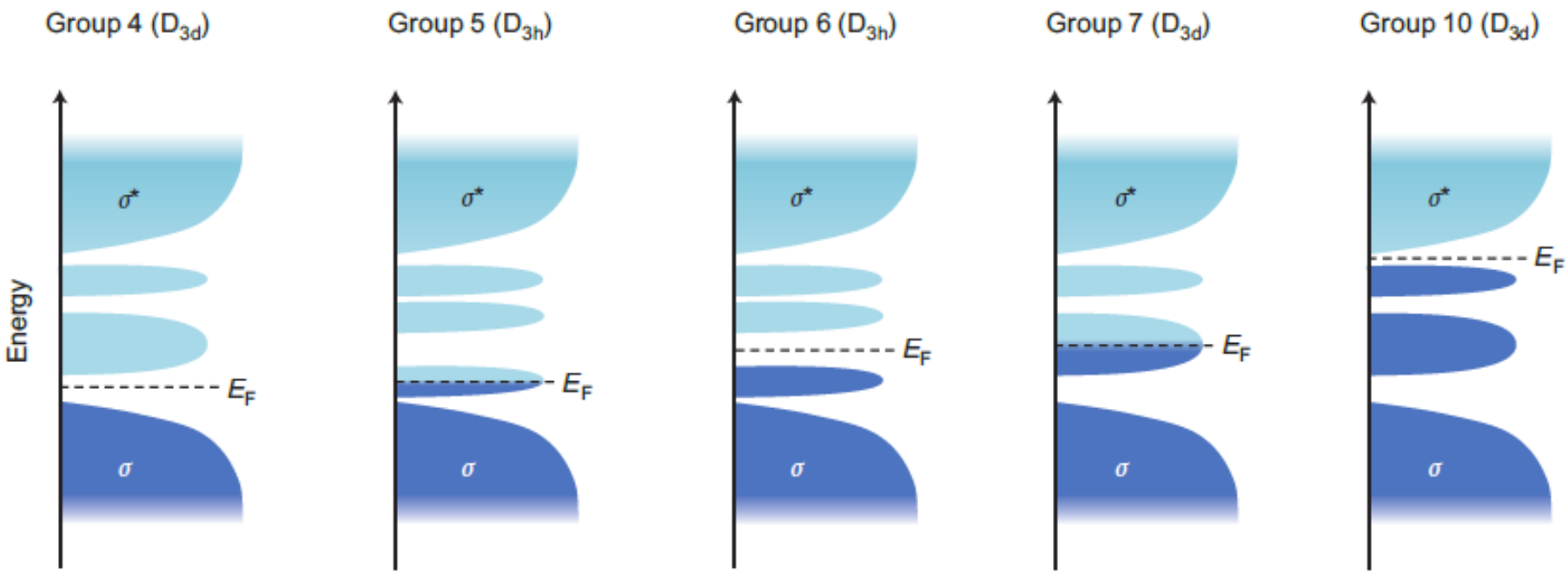
Table 1 | Electronic character of different layered TMDs[25].

Group	M	X	Properties
4	Ti, Hf, Zr	S, Se, Te	Semiconducting (E_g = 0.2~2 eV). Diamagnetic.
5	V, Nb, Ta	S, Se, Te	Narrow band metals (ρ ~10^{-4} Ω.cm) or semimetals. Superconducting. Charge density wave (CDW). Paramagnetic, antiferromagnetic, or diamagnetic.
6	Mo, W	S, Se, Te	Sulfides and selenides are semiconducting (E_g ~1 eV). Tellurides are semimetallic (ρ ~10^{-3} Ω cm). Diamagnetic.
7	Tc, Re	S, Se, Te	Small-gap semiconductors. Diamagnetic.
10	Pd, Pt	S, Se, Te	Sulfides and selenides are semiconducting (E_g = 0.4 eV) and diamagnetic. Tellurides are metallic and paramagnetic. $PdTe_2$ is superconducting.

ρ, in-plane electrical resistivity.

Chhowalla et al., Nat. Chem. (2013)

other 2D systems



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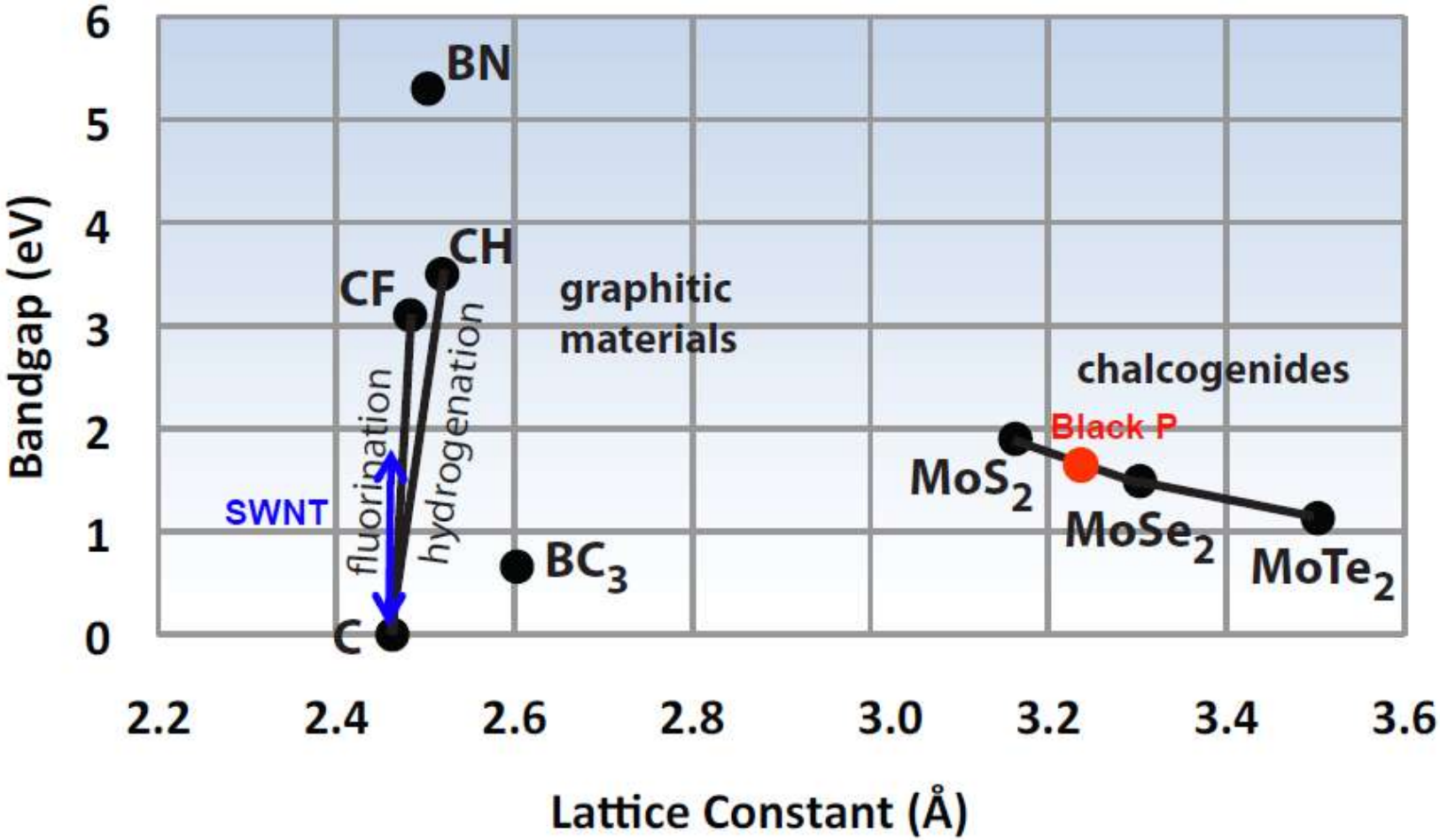
"band engineering"

Chhowalla et al., Nat. Chem. (2013)

other 2D systems



Martel, Szkopek, Cargèse, 2014

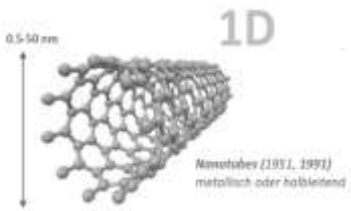
outline

electronics beyond Silicon

- other possible pathways for electronics

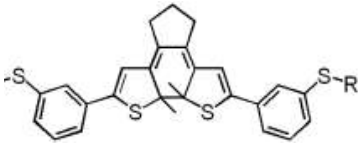
Carbon allotropes

- discovery



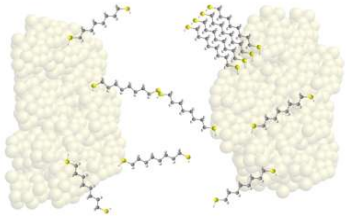
Carbon & molecular electronics

- brief historical account
- why molecules



molecular junctions

- how to contact nm-scale objects



carbon-based electronics

materials

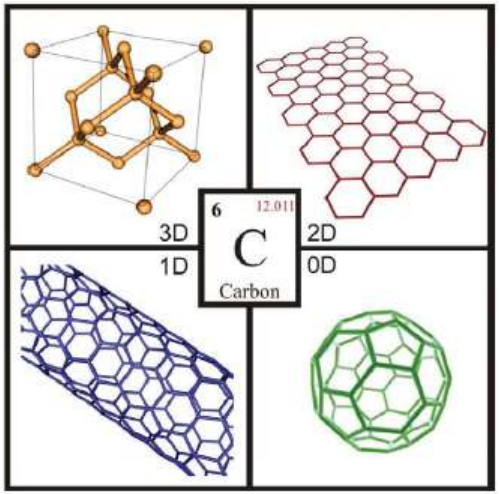


Table I. Electronic Properties of Carbon-Based Materials Compared with Other Common Semiconductors.

	Electron Mobility ($cm^2 V^{-1} s^{-1}$)	Bandgap (eV)	Thermal Conductivity ($W cm^{-1} K^{-1}$)
Si	1600	1.12	1.5
Ge	3900	0.66	0.6
GaAs	9200	1.42	0.46
InAs	4×10^4	1.34	0.27
Diamond	2200	5.45	22
Carbon Nanotubes	1×10^5	(0 to 1)	30
Graphene	1×10^4 to 2×10^5	(0 to 0.5)	40

MRS Bulleting 2010 special issue

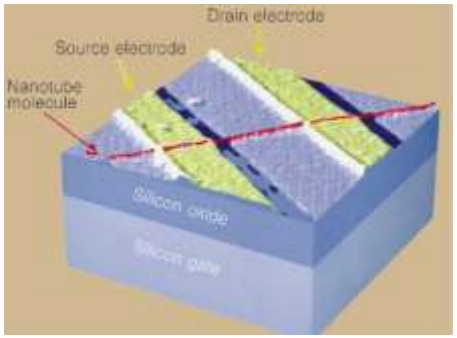
Overview Carbon-based electronics: see e.g. . Avouris et al. Nat. Nano 2007, McCreery, Faraday Disc. 2014

carbon-based electronics

Nanotechnology

Carbon-based electronics

Paul L. McEuen



Nature 1998, news&views

FROM THE JULY/AUGUST 2013 ISSUE

Graphene and Nanotubes Will Replace Silicon in Tomorrow's Nano-Machines

Physicist and novelist Paul McEuen says one day nanobots will carry medicine through your bloodstream and rebuild your brain's circuitry.

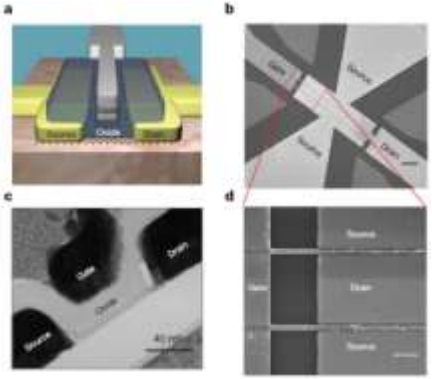
By Doug Stewart | Wednesday, December 11, 2013

Discovery magazine 2013

NB: novel (Spiral)

LETTER

High-frequency, scaled graphene transistors on diamond-like carbon



Nature 2011

LETTER

Carbon nanotube computer

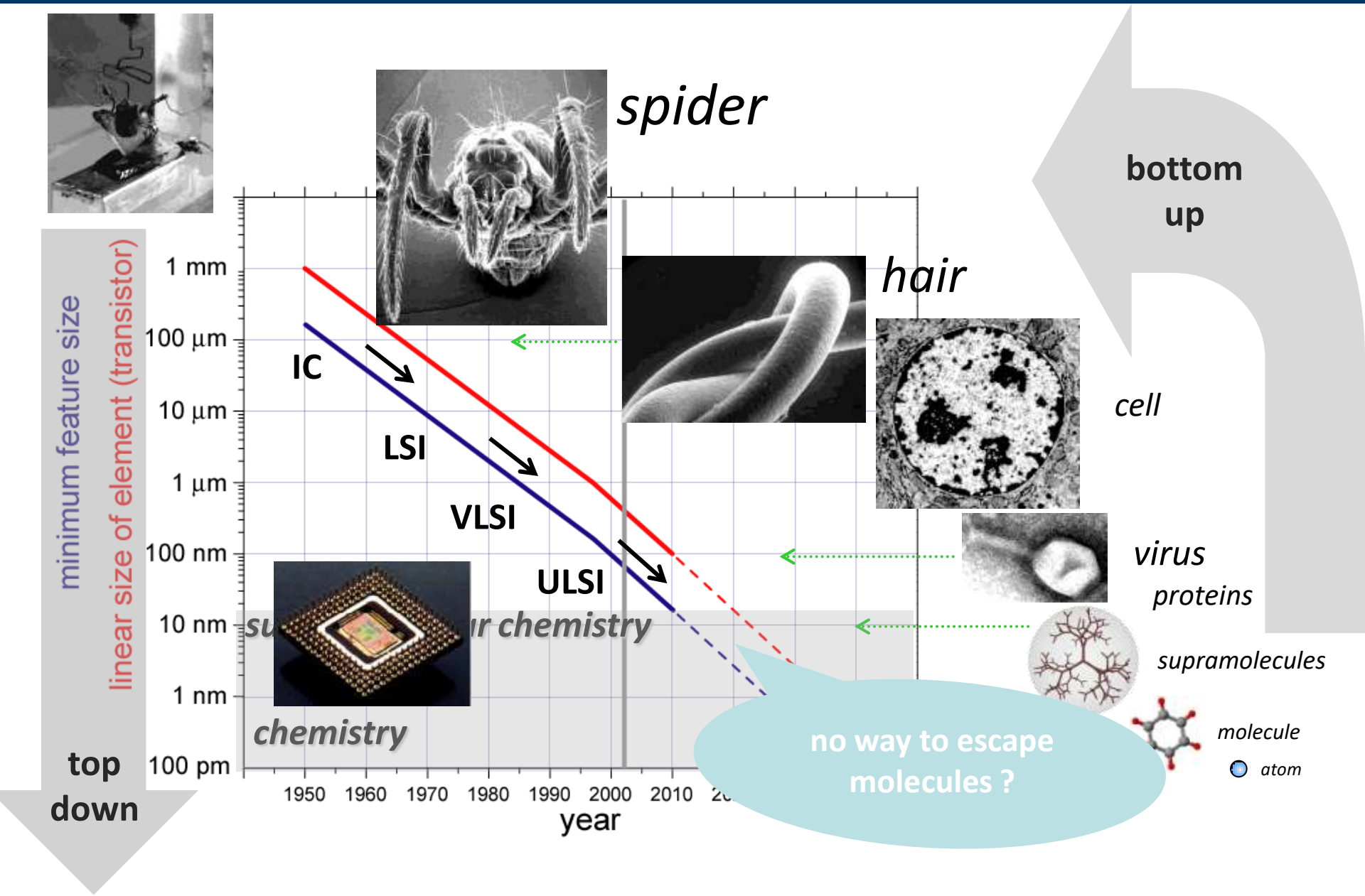
Nature 2013

LETTER

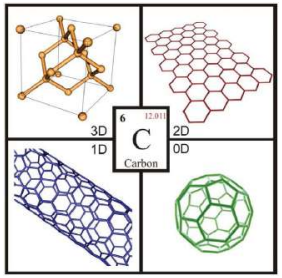
Exceptional ballistic transport in epitaxial graphene nanoribbons

Nature 2014

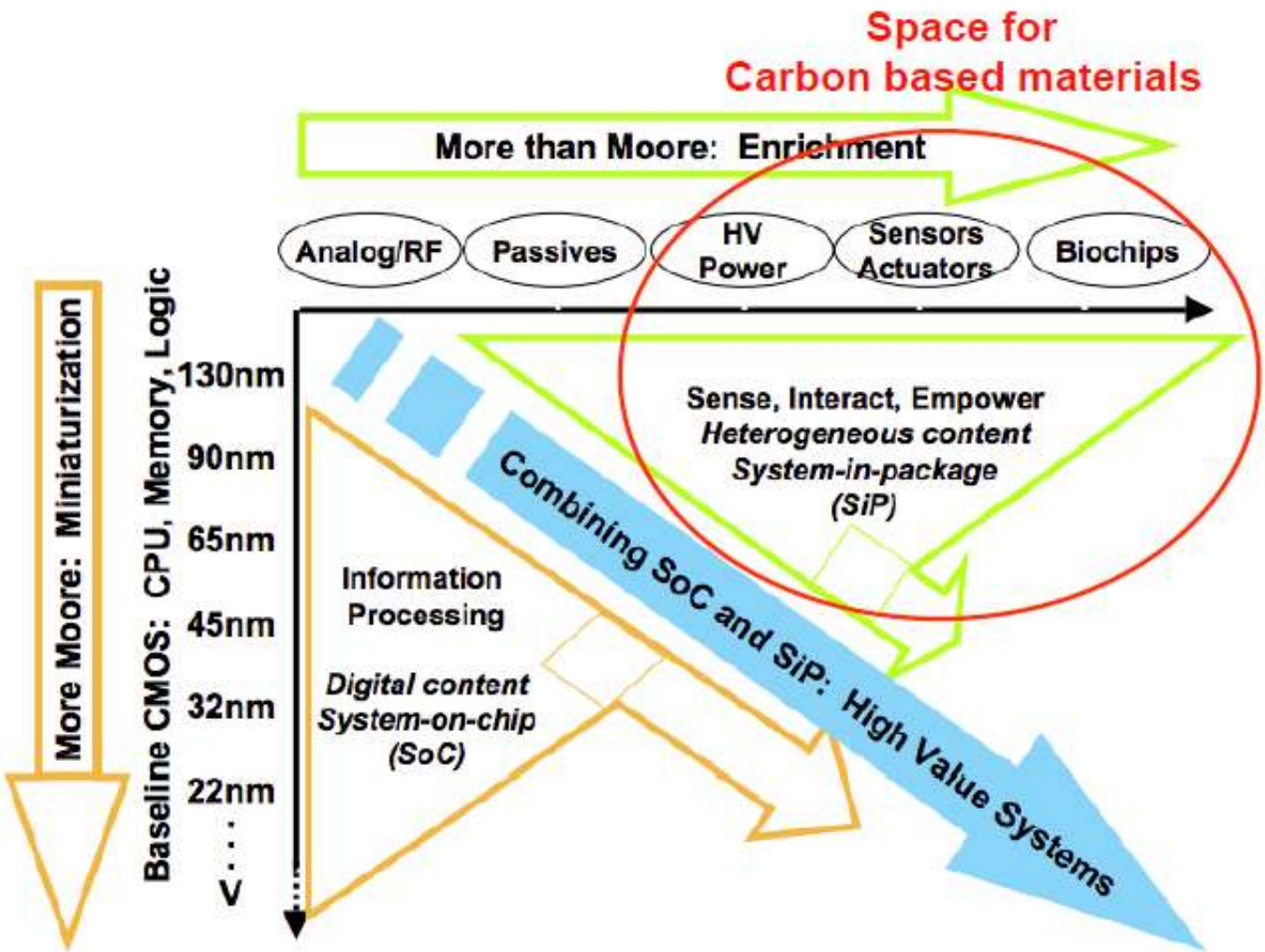
when macro meets nano: molecules



carbon-based electronics



materials



ITRS 2013, 2015; Martel, Cargèse, 2014

electronics with molecules ?

editorial

Nature Nanotech. 2013

Does molecular electronics compute?

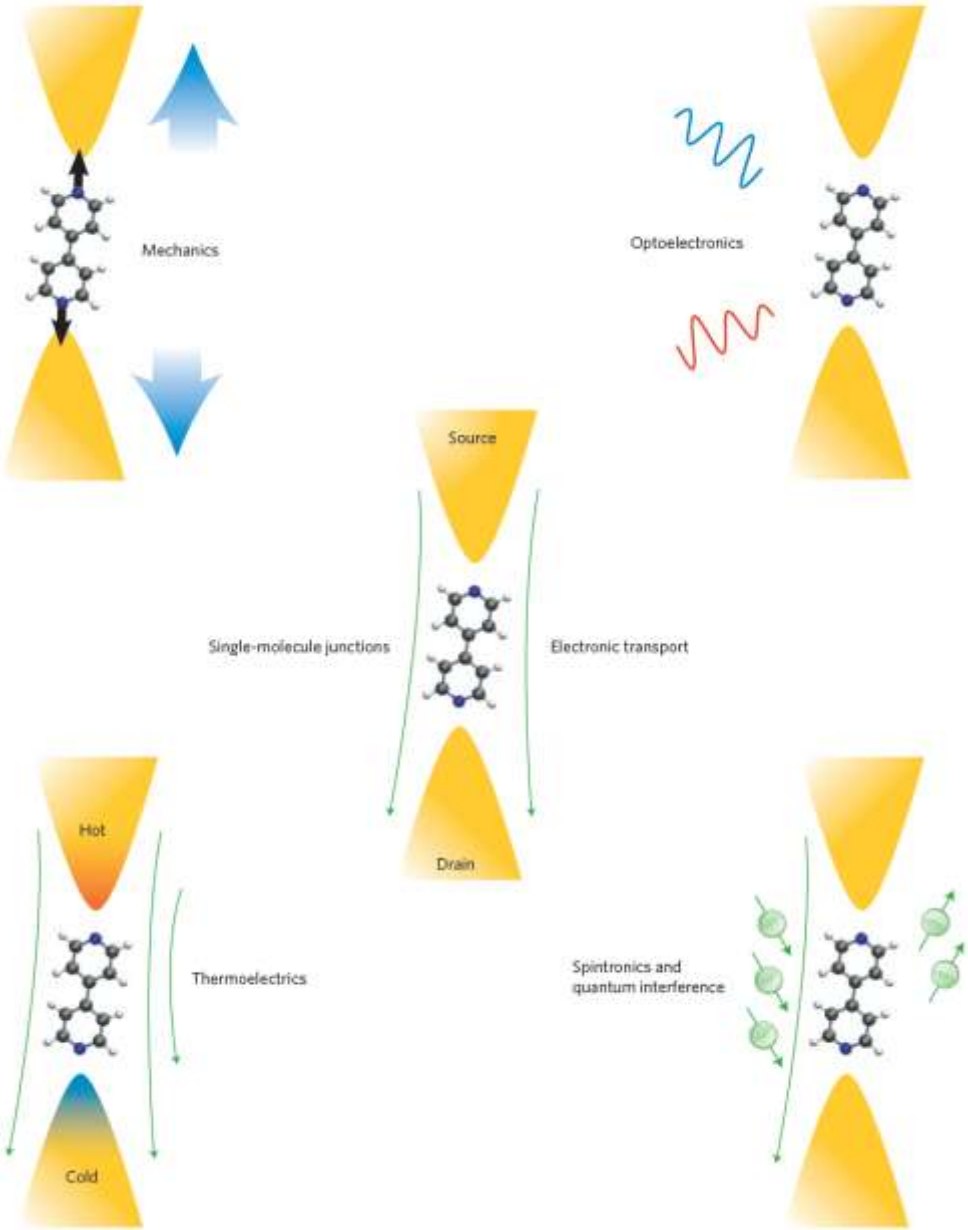
The field of molecular electronics originally set out to build computers, but silicon-based technology is unlikely to be replaced anytime soon. Nevertheless, the field has developed into a highly interdisciplinary endeavour, which could have a variety of ramifications that extend beyond computing.

Remember that …?

from chemical supply houses. Imagine what the impact could be. Essentially, every technology you have ever heard of where electrons move from here to there, has the potential to be revolutionized by the availability of molecular wires made up of carbon. Organic chemists will start building devices. Molecular electronics could become reality.

R.S. Smalley, Nobel lecture, 1996

electronics with molecules



editorial

Does molecular electronics compute?

The field of molecular electronics originally set out to build computers, but silicon-based technology is unlikely to be replaced anytime soon. Nevertheless, the field has developed into a highly interdisciplinary endeavour, which could have a variety of ramifications that extend beyond computing.

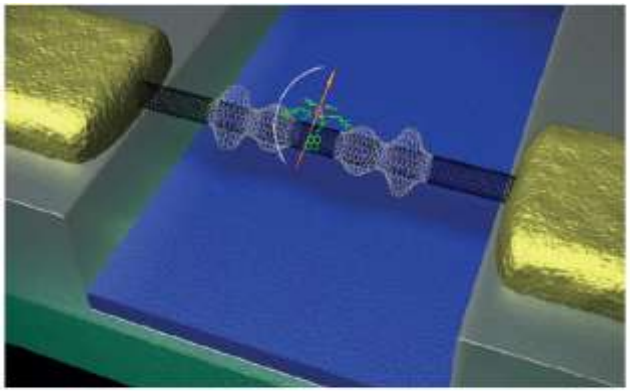
electronics with molecules

FOCUS | FEATURE

Visions for a molecular future

Leading researchers in molecular electronics discuss the motivation behind their work and what they consider to be the grand challenges for the field.

Molecular electronics has been around for more than 40 years, but scientists have only recently really begun to explore the properties and opportunities of single molecules. This collection of 12 features from researchers from a variety of backgrounds provides an overview of the different directions the field is going in.



The phonon modes of a carbon nanotube set between two electrodes can control the spin states of a molecule. Image reproduced with permission from C. Grupe/KIT.

electronics with molecules

devices. Hopefully, this technical limitation will be overcome with enough focus, innovation and resources.

Mark Reed is at the School of Engineering and Applied Science, Yale University, New Haven, Connecticut 06520, USA.
email: mark.reed@yale.edu

Molecular junctions are a formidable test bed for investigating structure–function correlations in charge-transport phenomena at the nanometre scale. Various aspects of electron–electron and electron–phonon interactions are currently being explored including spin-mediated charge transport, molecular ferroelectricity, and light-coupled interactions in metal–molecule–metal junctions.

Making electronic devices that use molecules as the active element, however, requires atomic-scale precision fabrication and long-term stability. Also, the complexity of such systems still limits our predictive understanding of charge and energy transport at the interface of hybrid organic–inorganic systems. Despite these difficulties, it is striking to notice that organic electronic devices are nowadays finding their way into consumer electronics. At the industrial level, molecular fabrication processes are progressing fast and reaching an unprecedented accuracy.

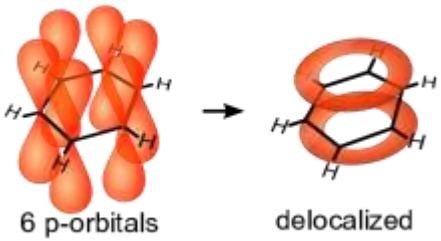
Remarkably, we haven't yet really made the most out of the molecules' potential and specificity. Molecules are not simply quantum dots that can be fabricated at a large scale; they can undergo conformational changes and interact with neighbouring molecules. These aspects however do not easily translate into conventional electronics paradigms and the intrinsic functionality of molecules have been barely explored so far. But exploiting molecular properties may result in alternative ways to process information. Here, hybrid devices integrating molecular functionalities for massively parallel *in vivo* information processing together with more conventional electronic circuits for signal post-processing could open fascinating perspectives, for instance in the development of neuroprosthetic devices. It is time to put molecules to work, so they can do what they do best.

Michel Calame is at the Department of Physics and Swiss Nanoscience Institute, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland.
email: michel.calame@unibas.ch

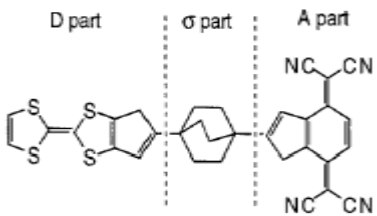
Nature Nanotech. 2013

electrically contacting molecules …?

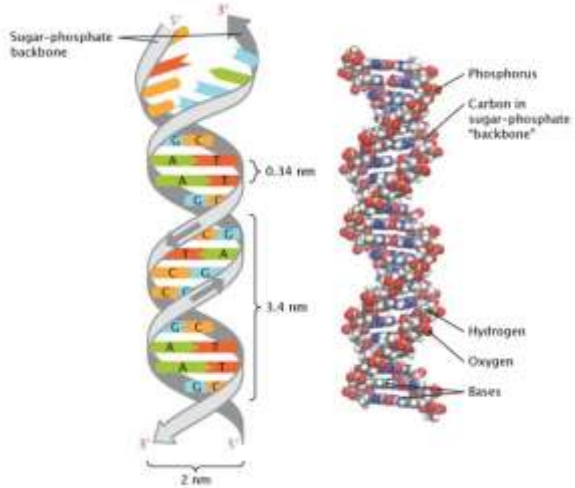
a brief (personal) historical perspective



Robert S. Mulliken
concept of donor-acceptor charge transfer complexes



Albert Szent-Gyorgi
proteins *"might not be insulators"*



Eley and Spivey
Trans. Faraday Soc., 1962
"It seemed therefore reasonable to suppose that a DNA molecule might behave as a 1D aromatic crystal and show a p-electron conductivity down the axis."
*"...**if it should prove possible to measure a single fiber…"***

Feynman *There's Plenty of Room at the Bottom*, 1959

B. Mann and H. Kuhn
J. Appl. Phys. 1971
1st reproducible transport meas. through organic layers

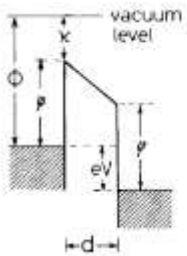


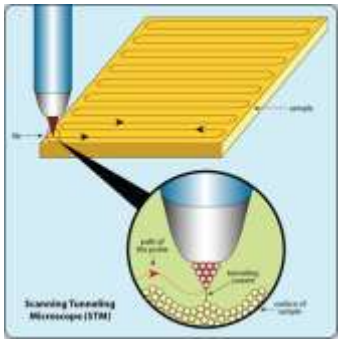
FIG. 1. Idealized potential barrier between similar electrodes separated by a fatty acid monolayer with a biased voltage.

A. Aviram, M. A. Ratner
molecular rectifier, 1974
(theory)
from molecular conduction to molecular electronics

1940 1950 1960 1970

a brief (personal) historical perspective

1981 STM
1982 Atomic resolution
1985 AFM
1987 Atomic resolution
1986 Nobel
with E. Ruska (SEM)



Gerd Binnig Heinrich Rohrer

Kavli prize in nanoscience 2016: AFM

Gerd Binnig, Christoph Gerber, Calvin Quate

1980 **1990** **2000**

a brief (personal) historical perspective

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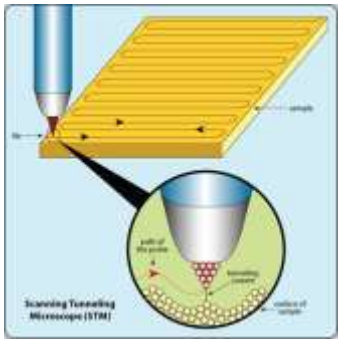
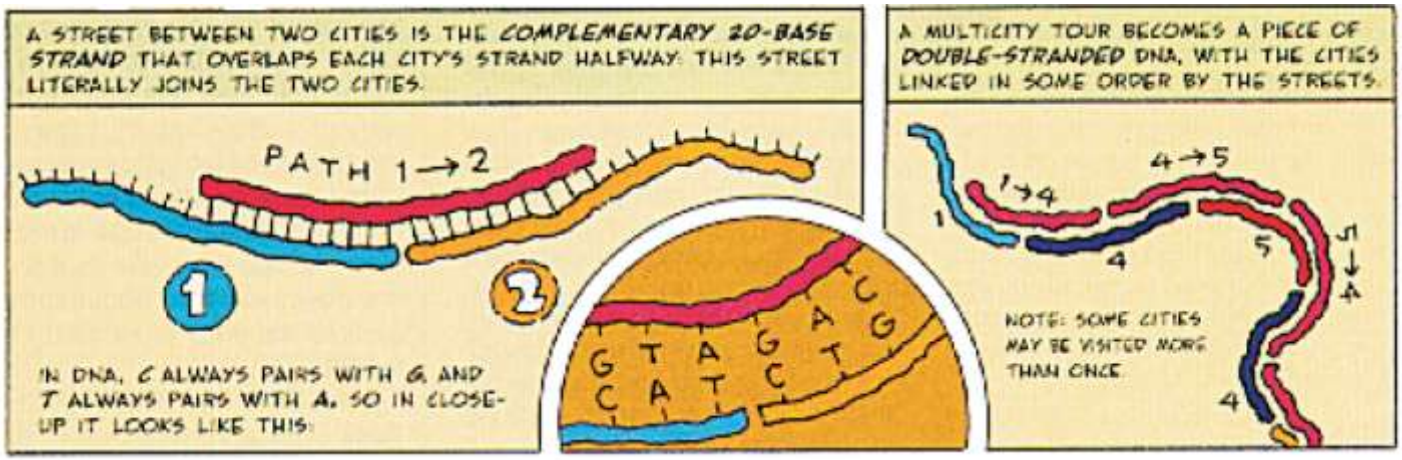


Gerd Binnig Heinrich Rohrer

Long-Range Photoinduced Electron Transfer Through a DNA Helix

C. J. Murphy, M. R. Arkin, Y. Jenkins, N. D. Ghatlia, S. H. Bossmann, N. J. Turro, J. K. Barton*

Molecular computation of solutions to combinatorial problems
L. Adleman, Science (1994)



BY LARRY GONICK

molecular recognition
computing with molecules – in solution - is highly parallel

different aspects to molecular computing:
electronic, chemical and biochemical
e.g. Libermann, Cell as a molecular computer, 1972

Recent: *Fan, Simmel et al., Nat. Mat., 2019 (DNA maze)*
Willsey et al., Proc IEEE, 2019 (DNA data storage)

1980 **1990** **2000**

a brief (personal) historical perspective

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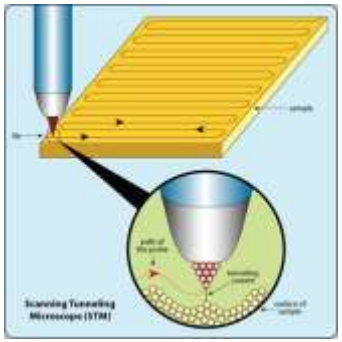


Gerd Binnig Heinrich Rohrer

Long-Range Photoinduced Electron Transfer Through a DNA Helix

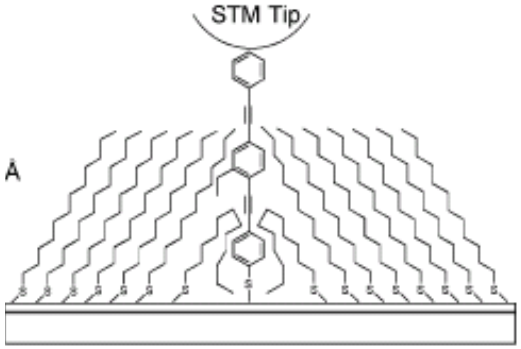
C. J. Murphy, M. R. Arkin, Y. Jenkins, N. D. Ghatlia, S. H. Bossmann, N. J. Turro, J. K. Barton*

Science (1993)

Are Single Molecular Wires Conducting?

L. A. Bumm, J. J. Arnold, M. T. Cygan, T. D. Dunbar, T. P. Burgin, L. Jones II, D. L. Allara,* J. M. Tour,* P. S. Weiss*

Science (1996)

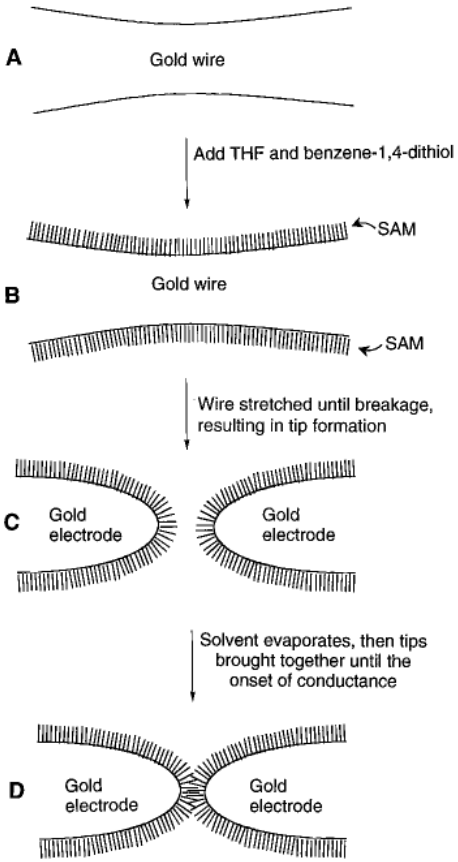


Addressing molecular wire with the STM tip

Conductance of a Molecular Junction

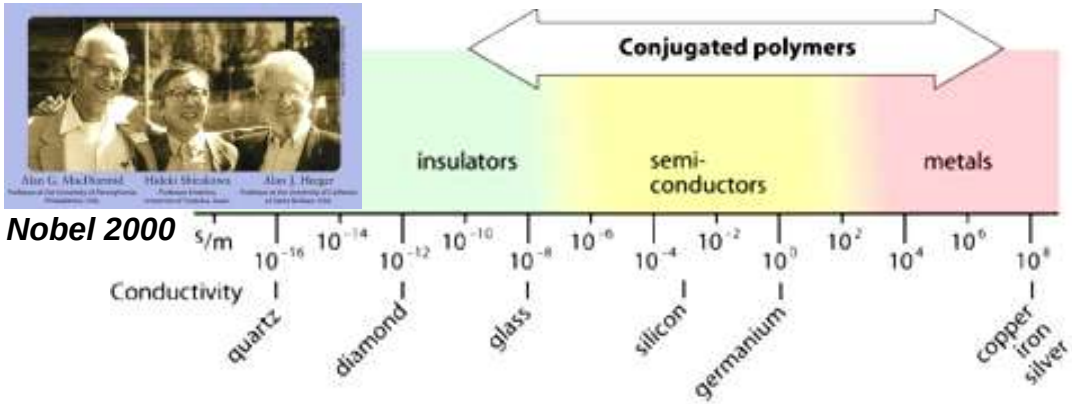
M. A. Reed,* C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour*

Science (1997)



1980 **1990** **2000**

perspective



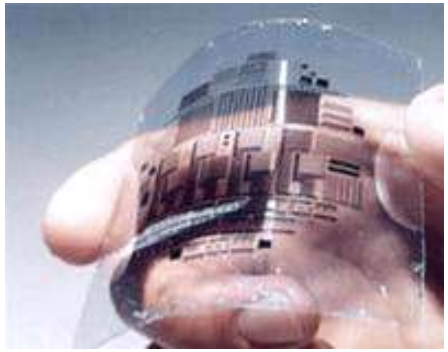
Nobel 2000

press release, Nobel prize 2000

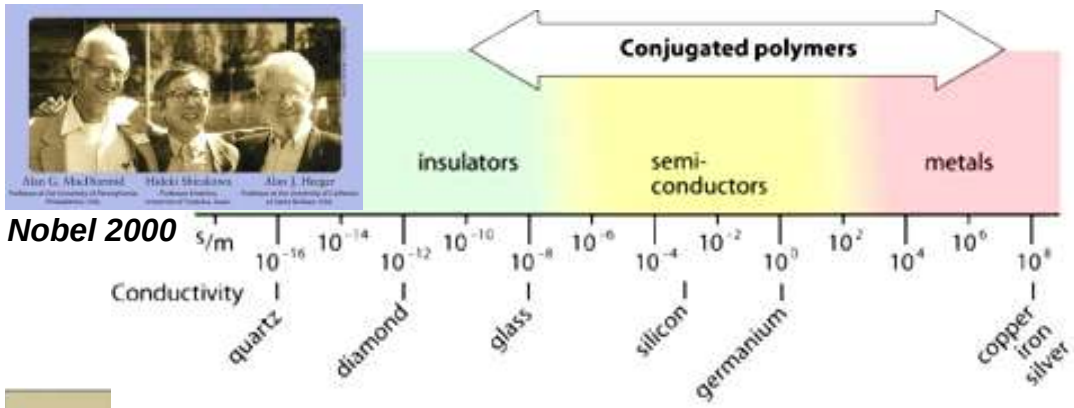
(…) In the future we will be able to produce transistors and other ***electronic components consisting of individual molecules*** - which will dramatically increase the speed and reduce the size of our computers. A computer corresponding to what we now carry around in our bags would suddenly fit inside a watch ...

TV display
40" OLED
(EPSON, 2004)

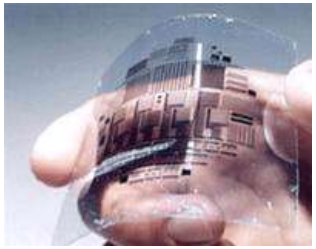
Low-cost organic electronics on plastic
Forrest, Nature (2004)



context



Nobel 2000

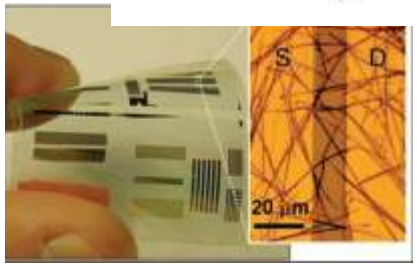


Low-cost organic electronics on plastic

Forrest, Nature (2004)

TV display, 40" OLED

(EPSON, 2004)

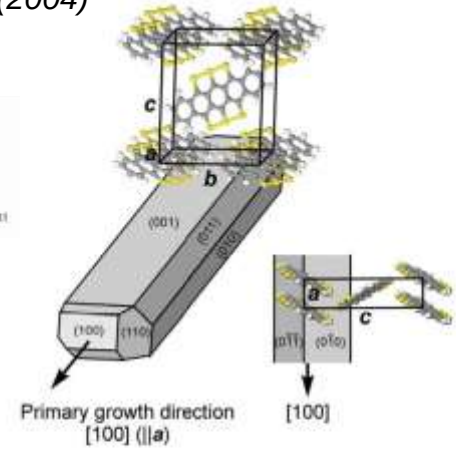


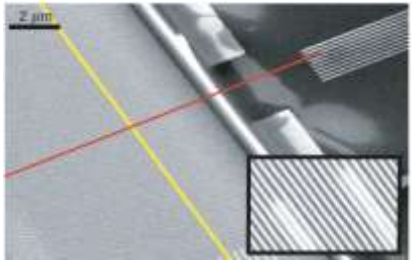
Organic nanowire transistors

Mat. Today (2008)

molecular crystals

(π-stacking)





molecular mono-layers

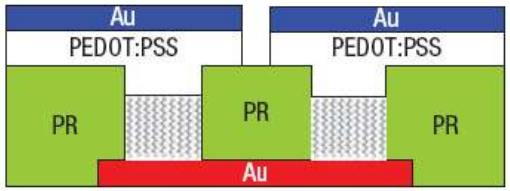
(self-assembly)

160kb crossed-wire memory

Heat et al., Nature (2007)

Organic ICs based on self-assembly (SAMFETs)

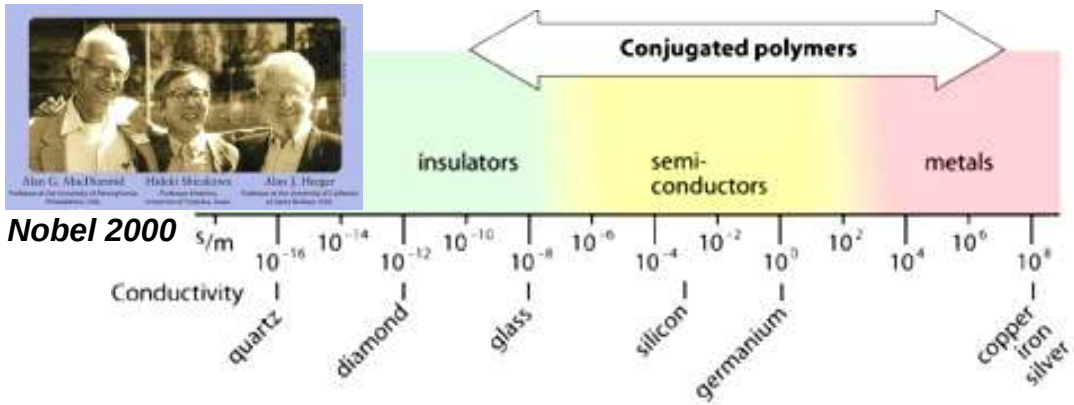
de Boer et al., Nature (2008)

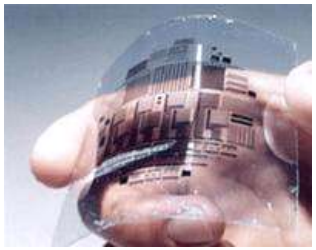


Large scale integr. of molecular junctions

de Leeuw et al., Nature Nano (2008)

perspective



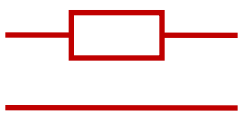


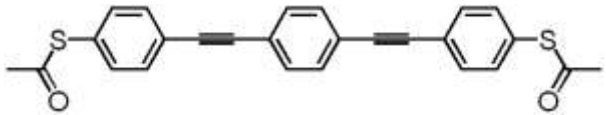
Low-cost organic electronics on plastic
Forrest, Nature (2004)

TV display, 40" OLED
(EPSON, 2004)

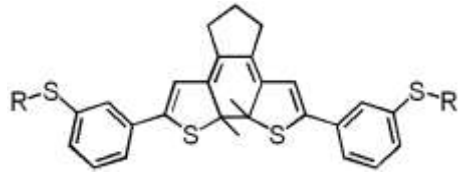
⇨ at the level of a few or even a single molecule ?

resistor
wire

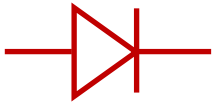


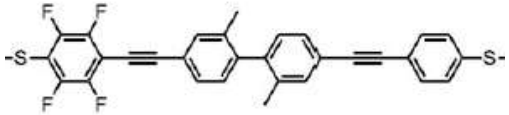


switch



diode





questions…
- *contacts*
- *stability*
-*(self-) assembly*
- *scalability*
- *…*

reviews, e.g.: Liljeroth (2010), de Boer et al., (2008); Ratner et al; (2008); Cahen et al., (2008)

molecules: pros & cons

+

- molecules are **small**: typ. 1-100 nm
- molecules have **extended pi systems**

  provides thermodynamically favorable electron conduit: molecules as "wires"
- molecules have **discrete energy levels**

  better confinement of the charges as in Si devices
- molecules can be **designed/tailored**

  by choice of composition and geometry, the transport, optical and geometrical properties can be adjusted
- molecules are **identical**

  chemists synthesize 1mmol of (identical) molecule at a time, not one device
- molecules can be **active** and provide novel **functions**

  stereochemistry (distinct stable geometric structures – isomers), **mechanical flexibility** (rotation axis), **photochemistry** (photochromism), **electrochemistry** (redox reactions)
  (self-)assembly (building of structures) and **molecular recognition** (switching, sensing)

–

- reliable **connection** to the micro/macro-scopic world (**contacts**) and **characterisation of a single molecule** ?
- limited thermal and electrical **stability**
- what about the **reproducibility** of molecular devices ?
- how to fabricate/integrate **many devices** (upscaling) ?

see e.g.: Nitzan, Ratner, Science 2003; Heath, Ratner, Phys. Today, 2003

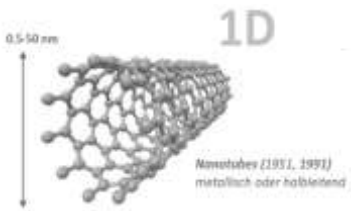
outline

electronics beyond Silicon

- other possible pathways for electronics

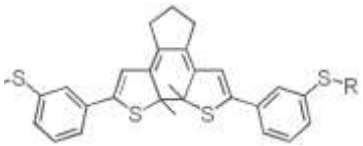
Carbon allotropes

- discovery



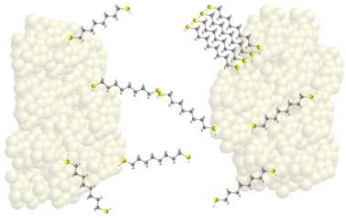
Carbon & molecular electronics

- brief historical account
- why molecules

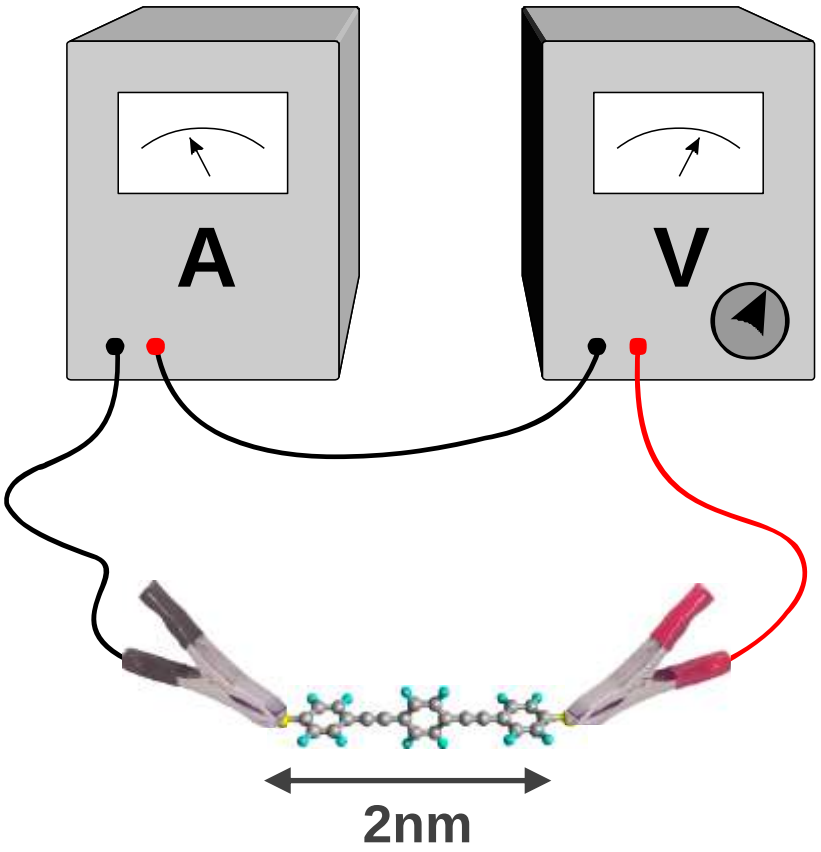


molecular junctions

- how to contact nm-scale objects

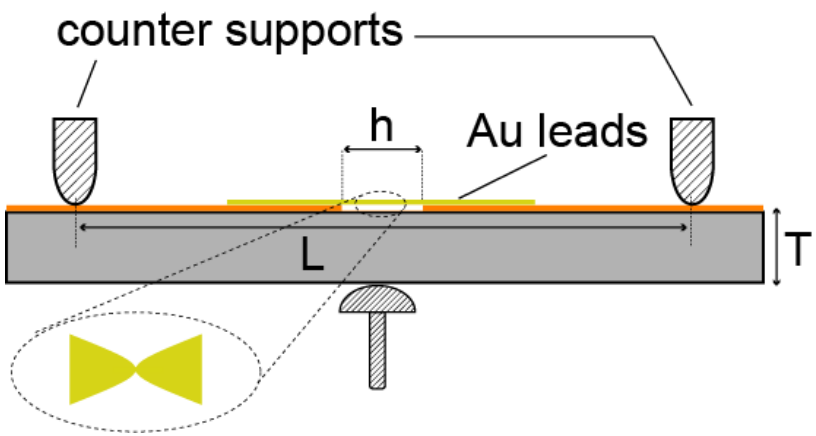


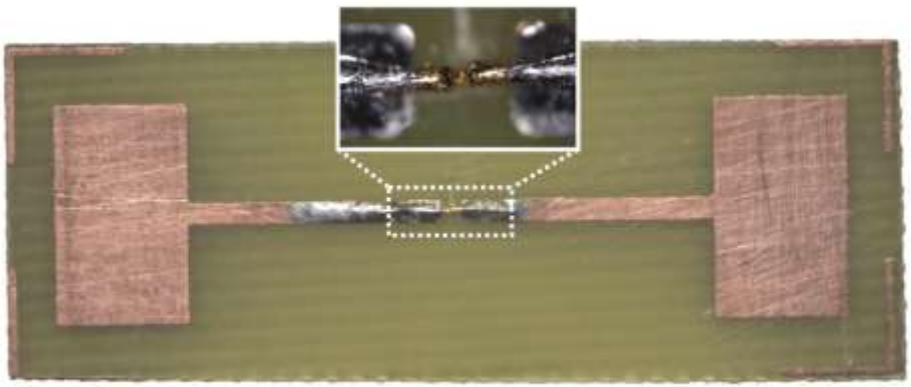
How to hook up crocodile clips to a 10^{-9}m object?



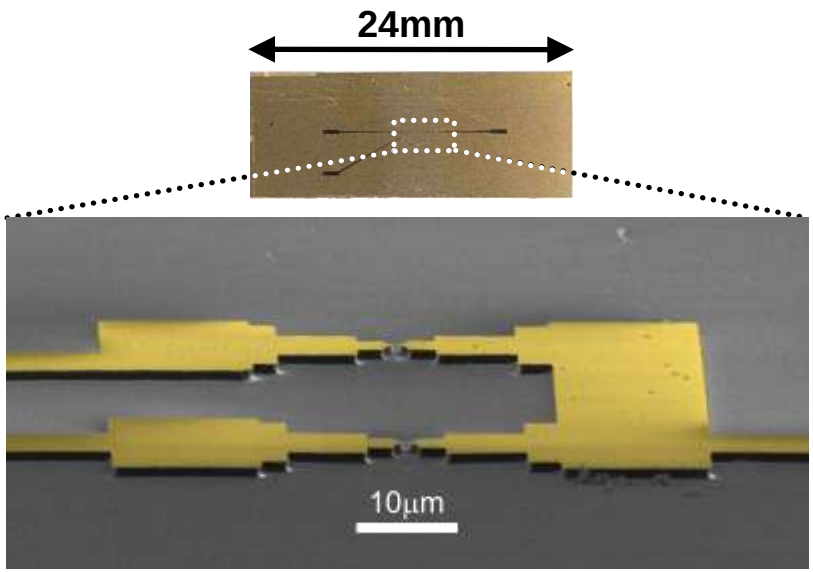
break junctions: a draw bridge at the atomic scale

break junctions: forming atomic contacts

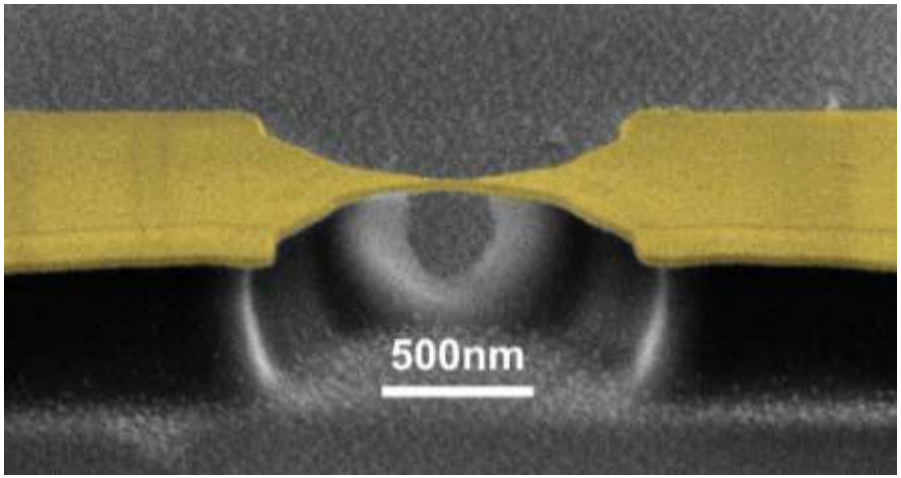




hand-made notched Au wire

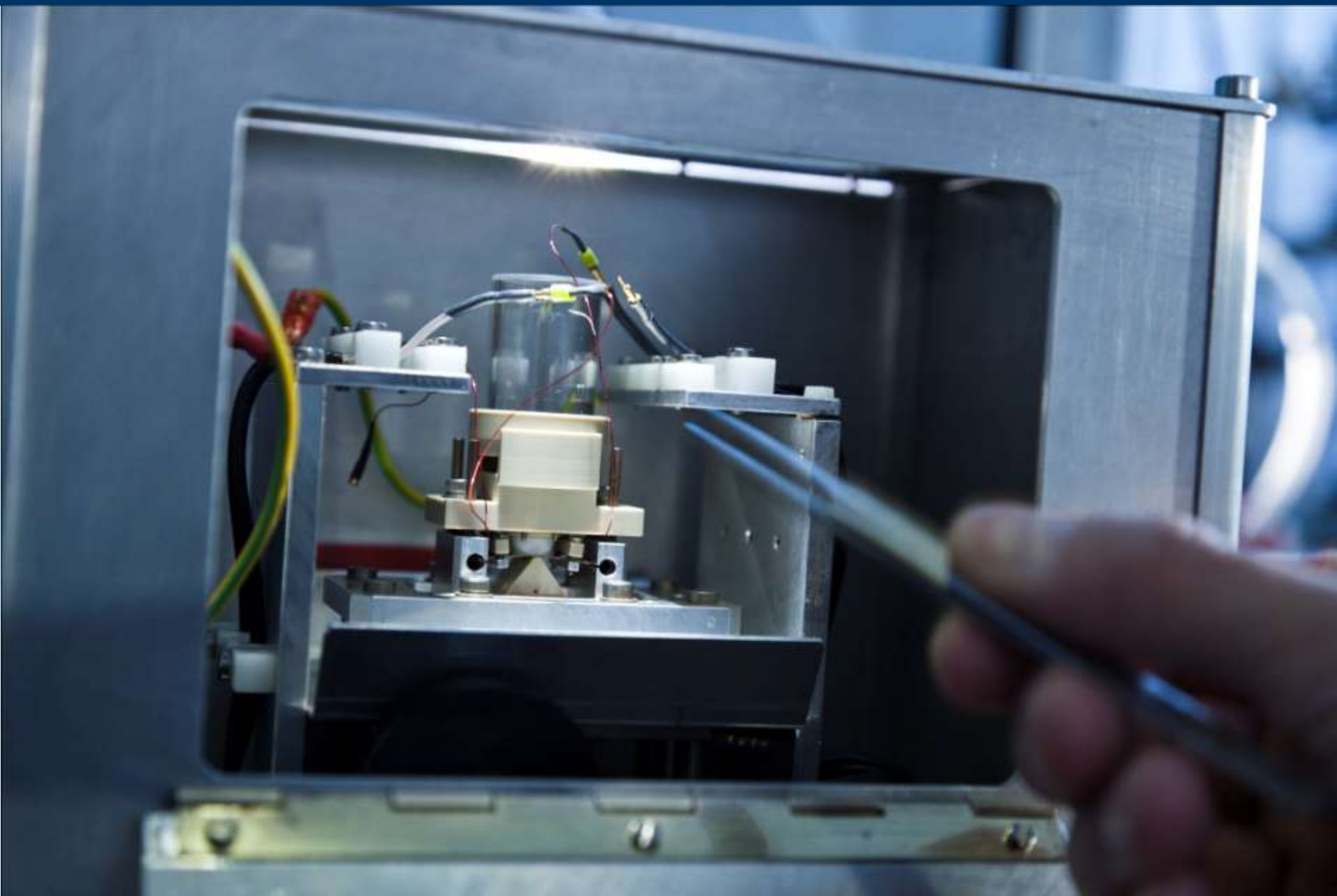


e-beam fabricated Au bridges

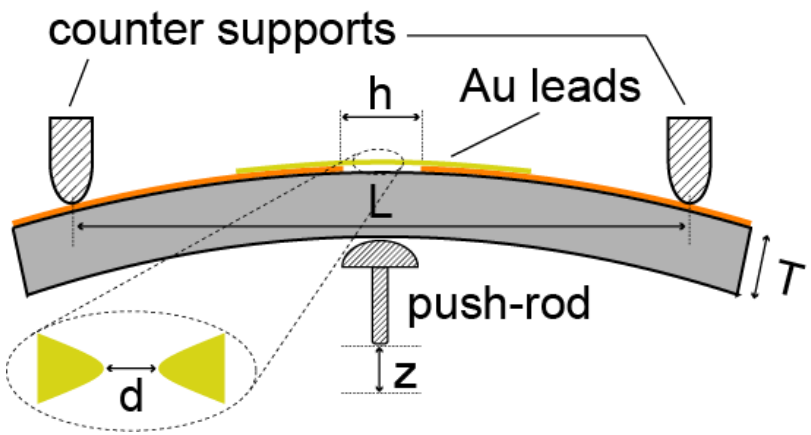


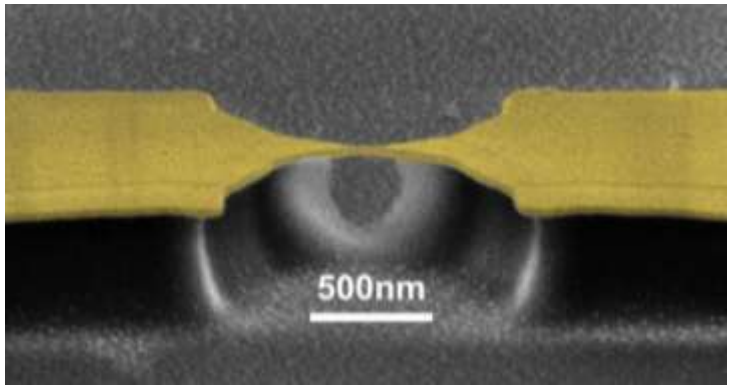
Moreland & Ekin, J. Appl. Phys, (1985); Ruitenbeek et al., Phys. C (1992); Reed et al., APL (1995)

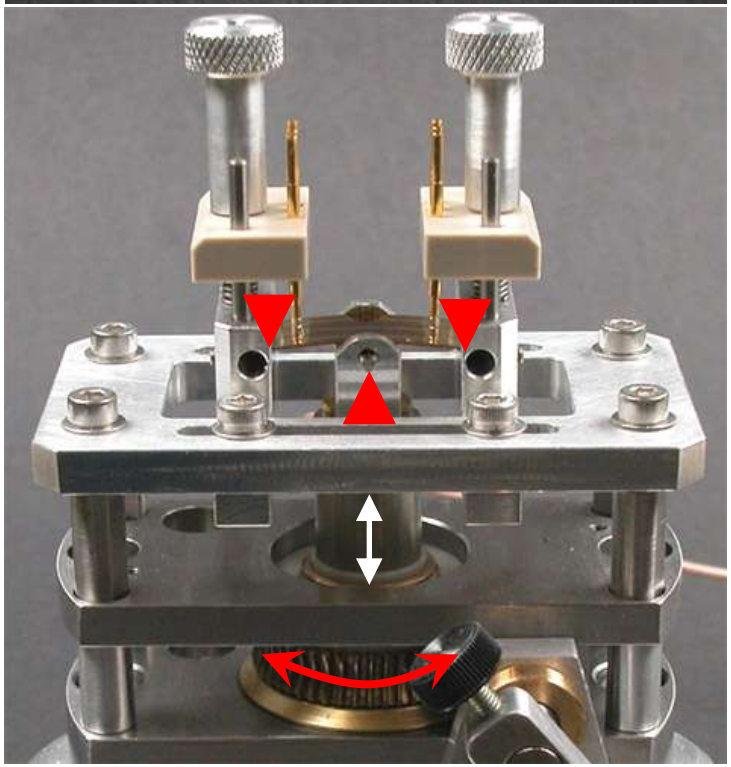
break junctions



break junctions







elongation: $d = 6thz/L^2$

reduction factor: $r = \Delta d/\Delta z \approx (1.6 - 4)\cdot 10^{-5}$

⇨ **$\Delta Z = 10\mu m$ ⇔ $\Delta d \sim 3$ Å**

vertical speed: $v_z = 30\mu m/s$

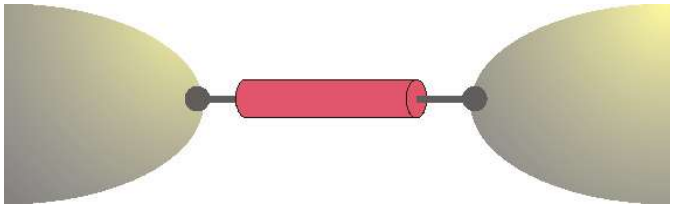
⇨ **0.5 - 1.2 nm/s**

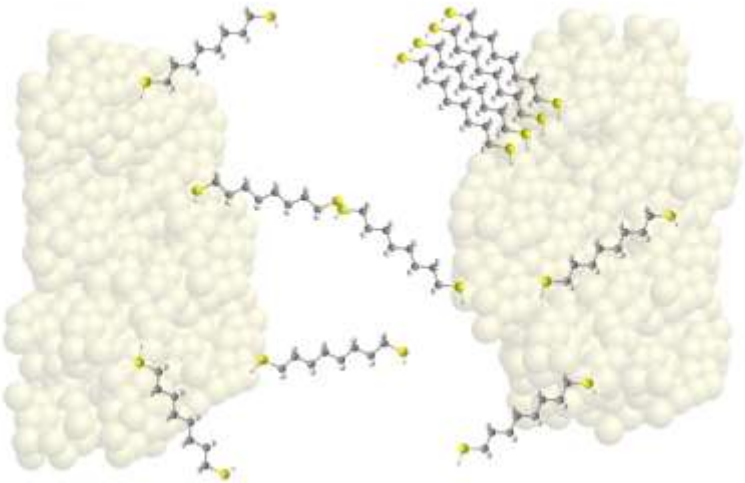
electrodes separation speed

atomic-scale metallic contacts with well controlled sub-nm gap in liquid

Moreland & Ekin, J. Appl. Phys, (1985); Ruitenbeek et al., Phys. C (1992); Reed et al., APL (1995)

molecular junction

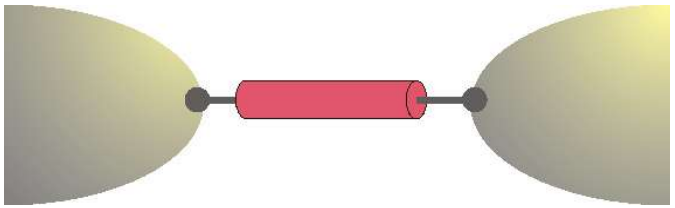


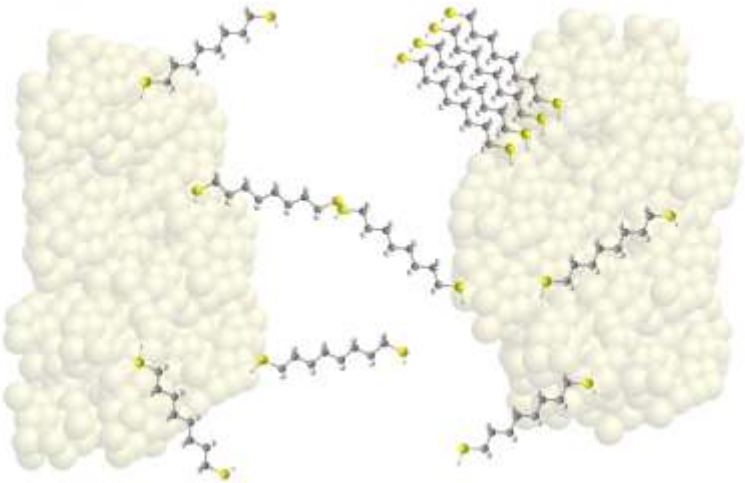


nanometer and molecular-scale junctions

- structural disorder	*electrodes and junction geometry*
- interactions	*anchoring, self-assembly, polymerization*
- fluctuations	*mobility of (surface) atoms, molecular distortions, multiple local energy minima*

molecular junction





nanometer and molecular-scale junctions

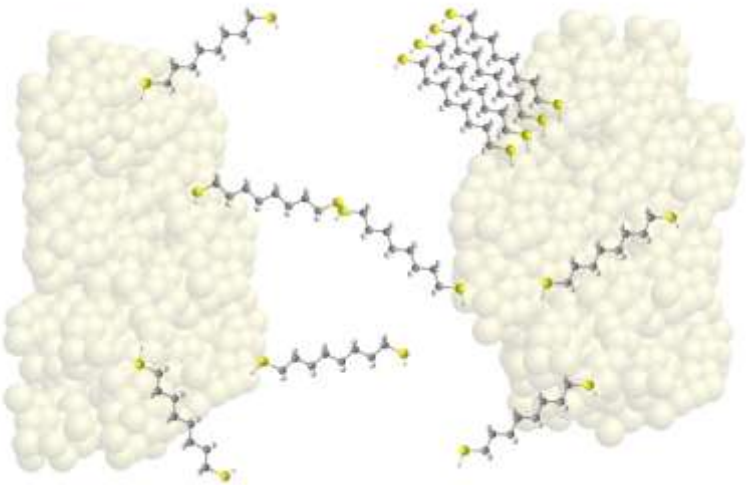
- structural disorder	*electrodes and junction geometry*
- interactions	*anchoring, self-assembly, polymerization*
- fluctuations	*mobility of (surface) atoms, molecular distortions, multiple local energy minima*

⇨ **junction formation** (and breaking up)**: dynamic process, variability**

- ***time scale(s)***
- ***local environment effect***
- ***local geometry and structure effect***

} **G(t), force, current, optical spectroscopy**

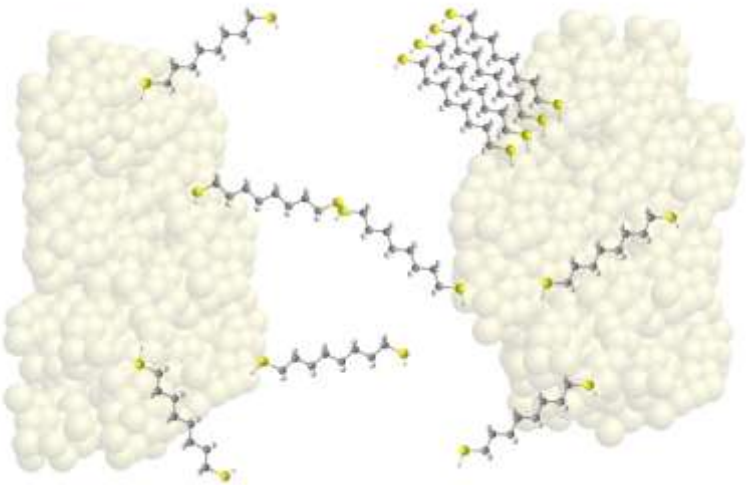
controlling junction formation



drifting molecules, stochastic anchoring, clustering	⇨	***undefined junction geometry & conductance***
drifting surface atoms, metal protrusions	⇨	**undefined electrostatic landscape**

⇨ **variability, low-yield and lack of control in key electrical parameters**

controlling junction formation



drifting molecules, stochastic anchoring, clustering ⇨ ***undefined junction geometry & conductance***

drifting surface atoms, metal protrusions ⇨ **undefined electrostatic landscape**

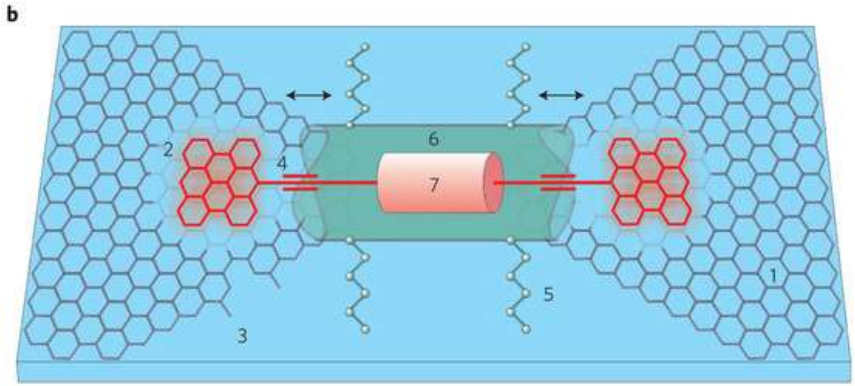
⇨ **variability, low-yield and lack of control in key electrical parameters**

Carbon-based contact materials as electrodes:

FLG	vd Zandt et al., Nano Lett. 2011
SWNT	Krupke et al., Nat. Nanotech. 2010
C-fiber tips	Agrait et al., Nanoscale Res. Lett. 2012

⇨ monolayer graphene ...?

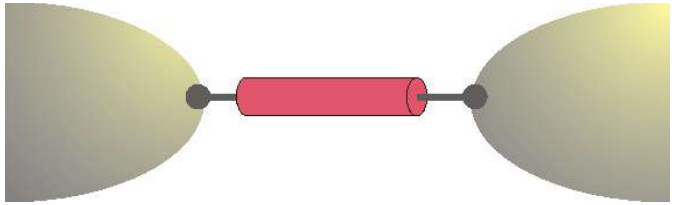
paradigm shift for molecular electronics



Lörtscher, Nat. Nano 2013

*FP7 ITN **MOLESCO**; see also Focus issue **Nat. Nanotech 2013***

nanometer and molecular-scale junctions



"playground " for

fundamental aspects

- electro-mechanical properties
  (e.g.: atomic, molecular switch)
- transport at μs, ns, ps, ...
- e-e and e-ph interactions
- heat flow (atomic & molecular level)
- spin dependent transport & selectivity
- exciton generation, separation
- interaction with EM field (plasmonics)
- coherence aspects
  only indirect evidence to date

device aspects

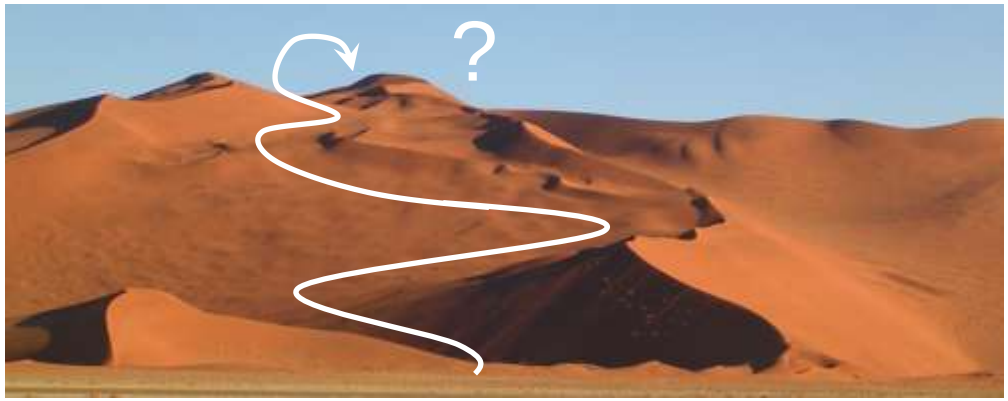
- control of molecule-electrode interface
- reliable 2-terminal switches (V-driven)
  conformational change, interference
- few molecules devices and monolayers, pores & crossbars *(Sony, HP, NIST, IBM)*
- carbon-based electronics
- upscaling, programmability

  NB: variability, tunneling, power dissipation, cost, are current issues in CMOS tech.

Molecular and carbon-based electronic systems

context

assembly of nanoscale objects

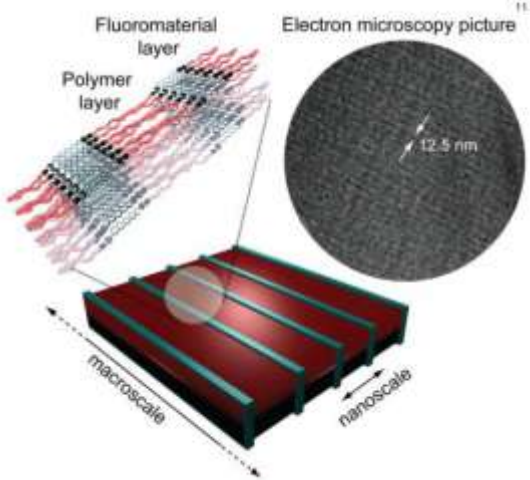


upscalability

450mm fab / 10^{10} US$

300mm fab / 10^{9} US$

self-assembly

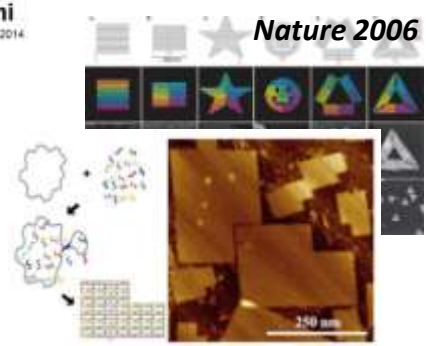


Self-assembled nanostructure keeps aligned up to millimeters

Nature Comm. 2014

Researchers create world's largest DNA origami

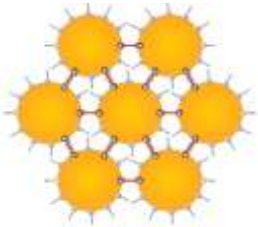
11 September 2014



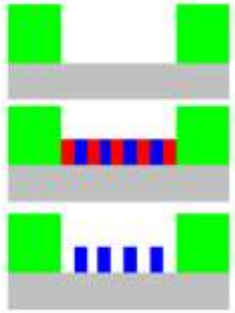
Nature 2006

Nano Lett. 2014

Template architectures, Liao et al. Adv. Mat. 2006, CSR 2015

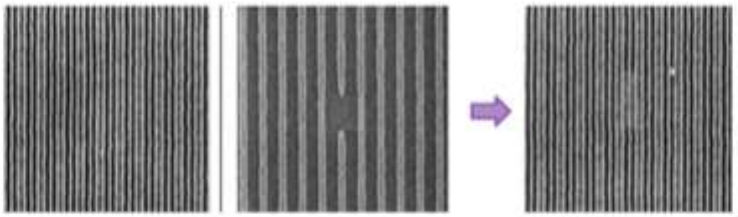


directed self-assembly



Directed self-assembly involves three steps: writing a pattern, depositing the two block copolymers, and removing

IMEC center, Belgium, 2012
2015: 15nm pitch



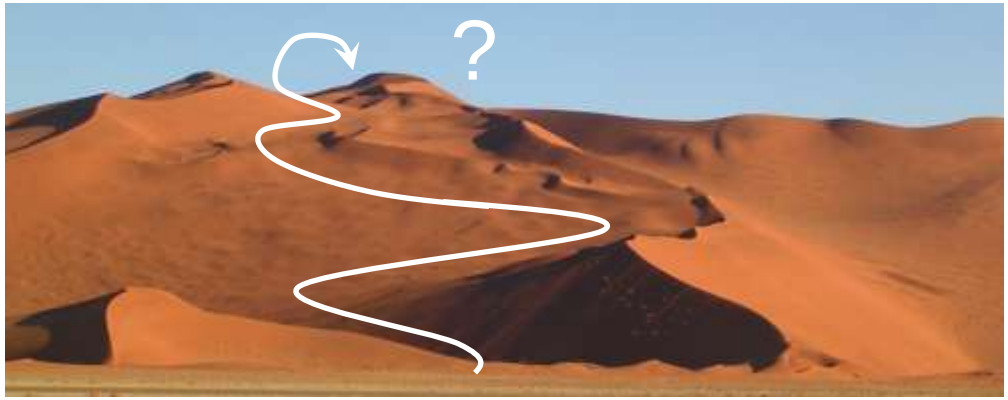
Caption: 14nm polystyrene lines on 28nm pitch after PMMA removal fabricated by DSA using 193nm immersion based 84nm pitch pre-pattern (left) and demonstration of the ability to repair a 200nm gap in the pre-pattern (right).

Pick and place, e.g.: CNTs (Ch. Hierold et al.), nanowires (V. Zwiller et al.)

Molecular and carbon-based electronic systems

context

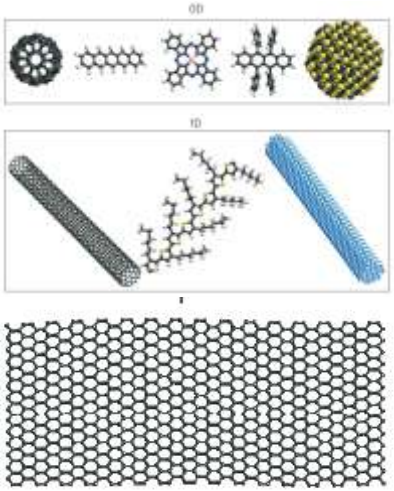
assembly of nanoscale objects



0D

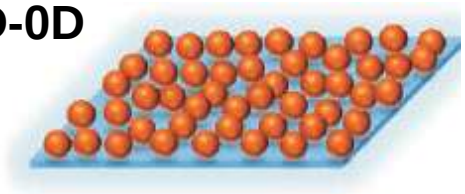
1D

2D



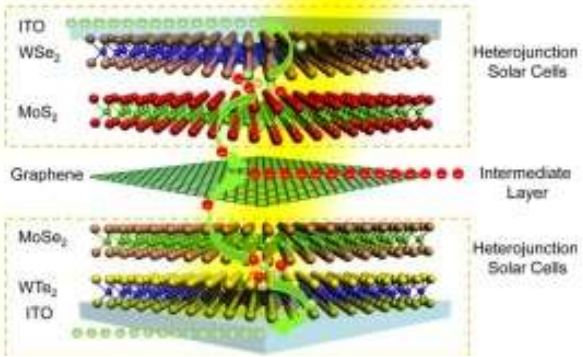
Hersam et al., Nat. Materials, 2017

2D-0D



2D-1D

Mixed D heterostructures

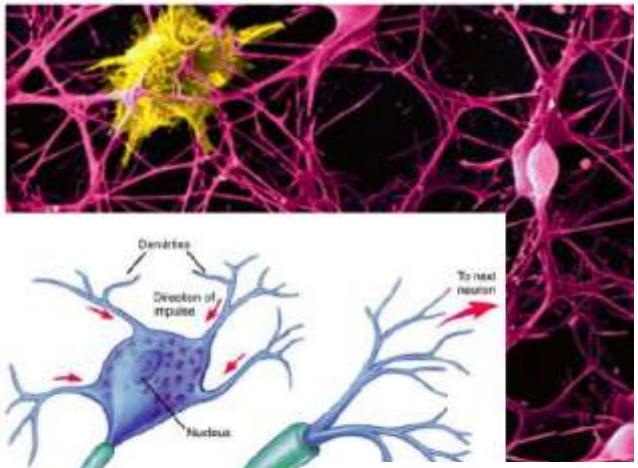


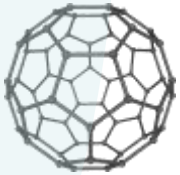
Loh et al., Nano Today (2015)

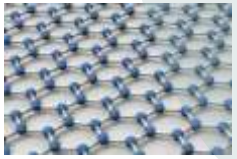
Molecular and carbon-based electronic systems

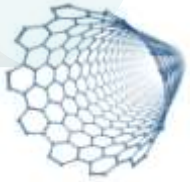
going 3D...?

- *artificial neural networks*
- *connectivity*
- *non-von Neumann architectures,* ***neuromorphic*** *computing*







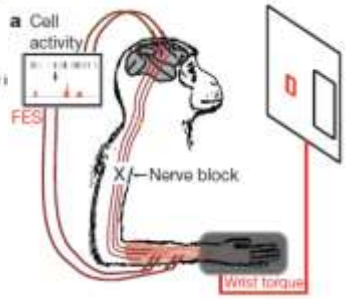


hybrid interfaces

sensing (chemical, biochemical) and beyond

e.g.: ion sensitive interfaces for cells, prosthetic interfaces at single molecule level

Viewpoint in "Visions for a molecular future"
mc , Nat.Nano (2013)



Moritz et al., Direct control of paralysed muscles by cortical neurons , Nature (2008)

Zrenner, McLaren et al., Retinal implants to restore sight in blind people (2013)