



Molecular and carbon-based electronic systems

when	Wednesday, 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/mces
Contact	Michel Calame <i>Empa & Physics Dpt., Uni Basel</i> <i>michel.calame@empa.ch, michel.calame@unibas.ch</i>

Topics & Presentations

Timeline

- 19.03.2025 **Papers selection**
 - AC Fullerene-Based Single Molecule Diodes with Huge Rectification Ratios (2025)
<https://doi.org/10.1039/D4TC04233F>
 - TLA Robust chemical analysis with graphene chemosensors and machine learning (2024)
<https://doi.org/10.1038/s41586-024-08003-w>
 - AYY Biosensor Chip for Point-of-Care Diagnostics: Carbon Nanotube Sensing Platform for Bacterial Detection and Identification (2024)
<https://doi.org/10.1109/TNANO.2024.3380997>

Topics & Presentations

Timeline

- 19.03.2025 Papers selection
- **16.04.2025 V1 Presentation to MC**
feedback on 23.04
- **21.05.2025 Final presentation to MC**
- 28.05.2025 Presentations by students

Presentation

Presentation (15-20 min)

Q&A, discussion with Audience (5-10 min)

- Encourage questions and critical thinking
- Discuss potential implications (understanding) or applications

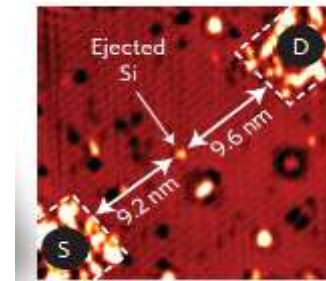
- Introduction (1 min)
 - Title/authors/journal/date
 - Brief overview of the topic and its importance; your motivation for choosing this topic
- Background and Context (2 min)
 - Brief literature review / timeline of related research & Goal of research
- Methods (1 min)
 - Study design (what is studied) and key experimental techniques
- **Results (6-8 min)**
 - Present main findings using figures and tables from the paper; explain the figures and the graphs
 - Highlight key data and significance
- **Discussion and Critical Analysis (3-6 min)**
 - Interpretation of results
 - Strengths and limitations of the study
- Conclusion (2 min)
 - Summary of main points; take home message
 - Outlook: open questions, future directions

Summary

- On the importance of electronic chips
- Basic building block : the transistor
- The transistor is 75
Science, Special section, 18 Nov. 2022
- How small can it get ?



STM lithography and phosphine (PH_3) dosing



LETTERS

PUBLISHED ONLINE: 19 FEBRUARY 2022 | DOI: 10.1038/NANNANO.2022.21

nature
nanotechnology

A single-atom transistor

Martin Fuechsle¹, Jill A. Miwa¹, Suddhasatta Mahapatra¹, Hoon Ryu², Sunhee Lee¹,
Oliver Warschkow¹, Lloyd C. L. Hollenberg², Gerhard Klimeck³ and Michelle Y. Simmons^{1*}

Outline

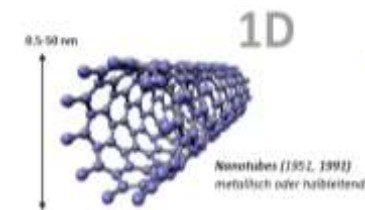
Electronics beyond Silicon

- other possible pathways for electronics
power consumption, sustainability & life cycle, energy conversion



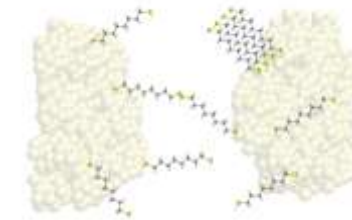
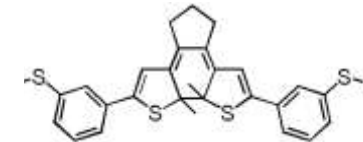
Carbon allotropes

- discovery



Carbon & molecular electronics

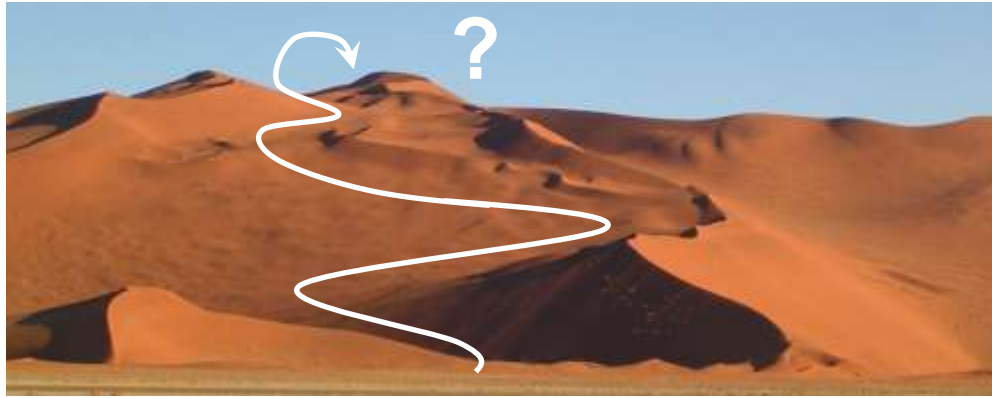
- brief historical account
- a word about computing
- why molecules



Nanoscale junctions

- how to contact nm-scale objects

electronics beyond Si

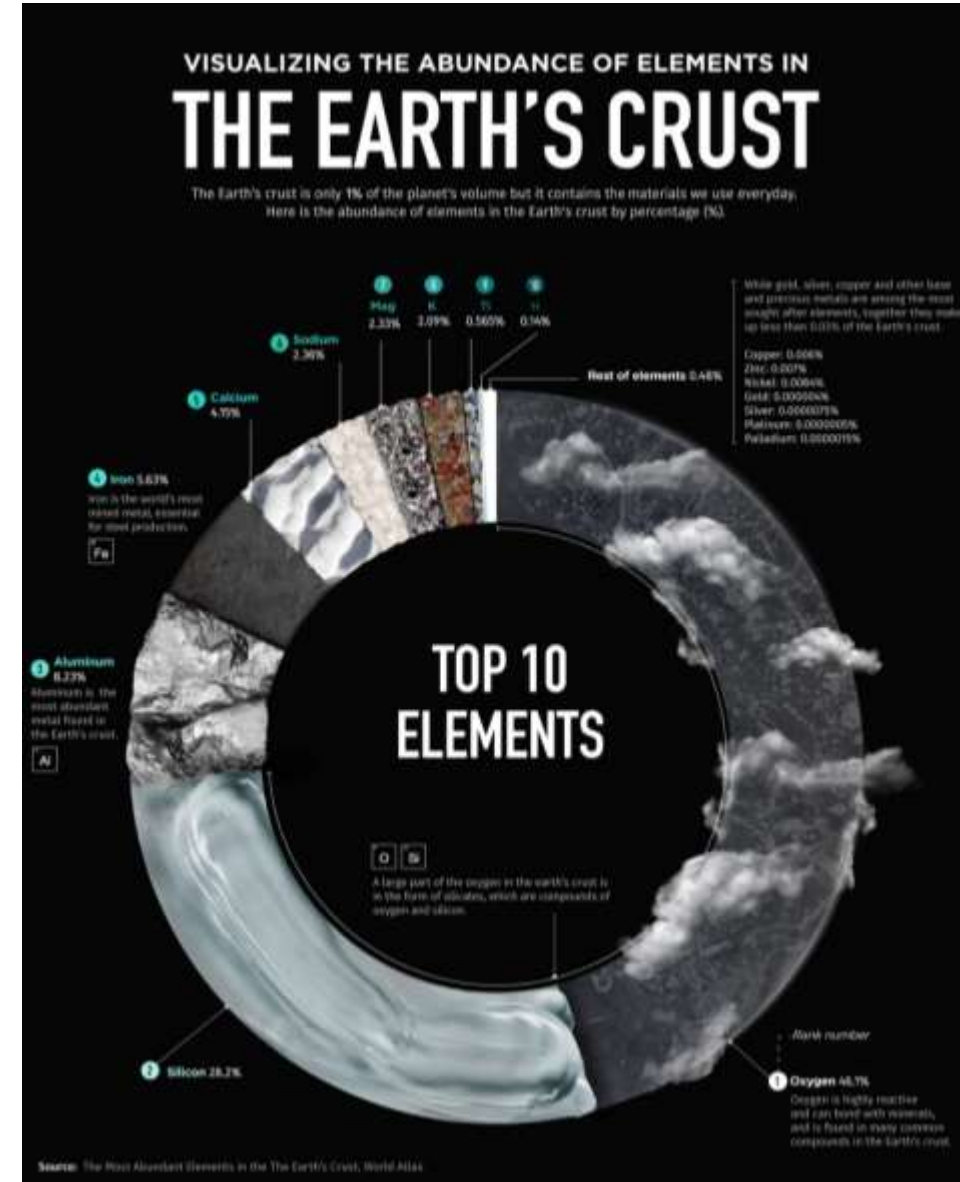
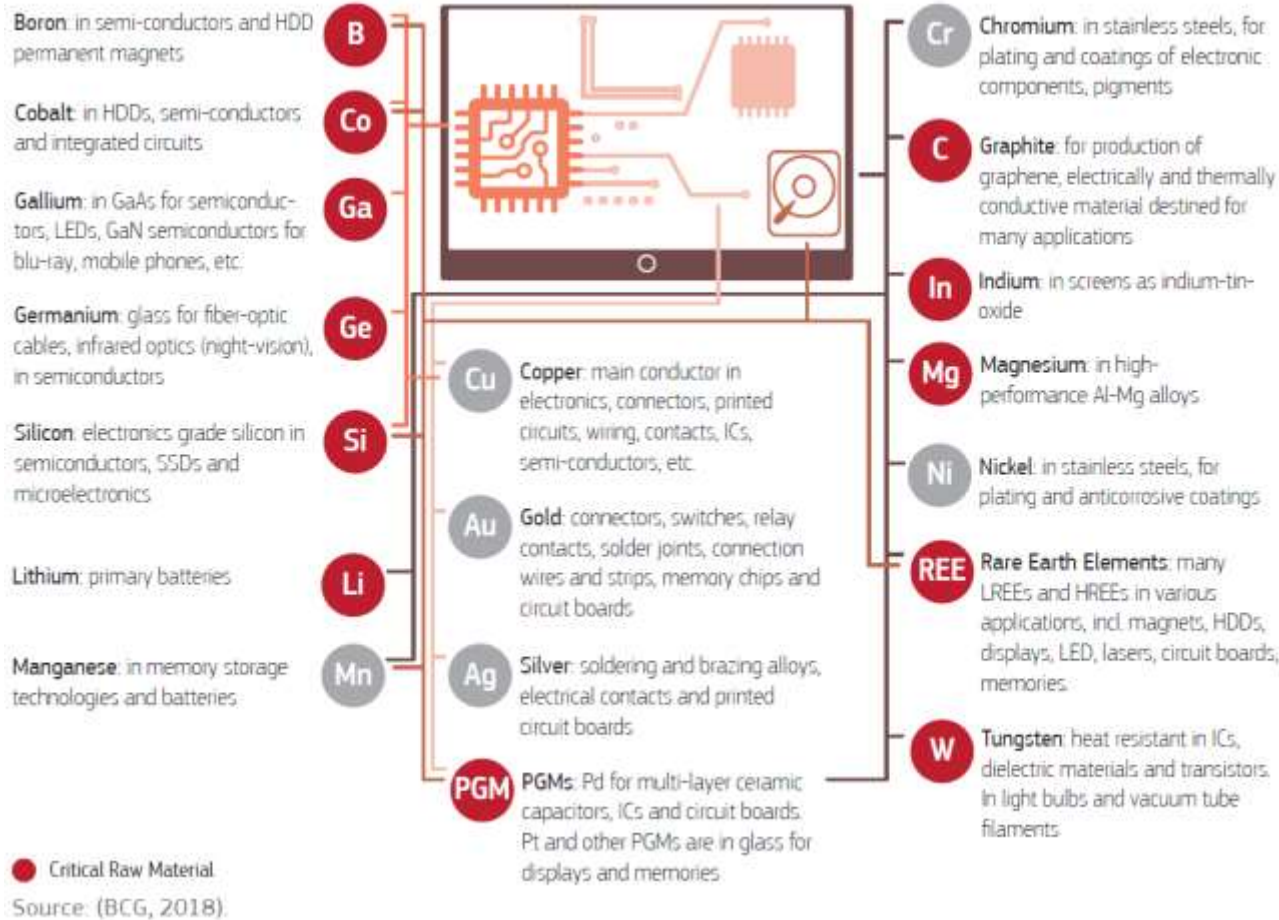


Other materials ?

Electronics beyond Si

Materials resources are not infinite

Figure 44. Raw materials in digital technologies

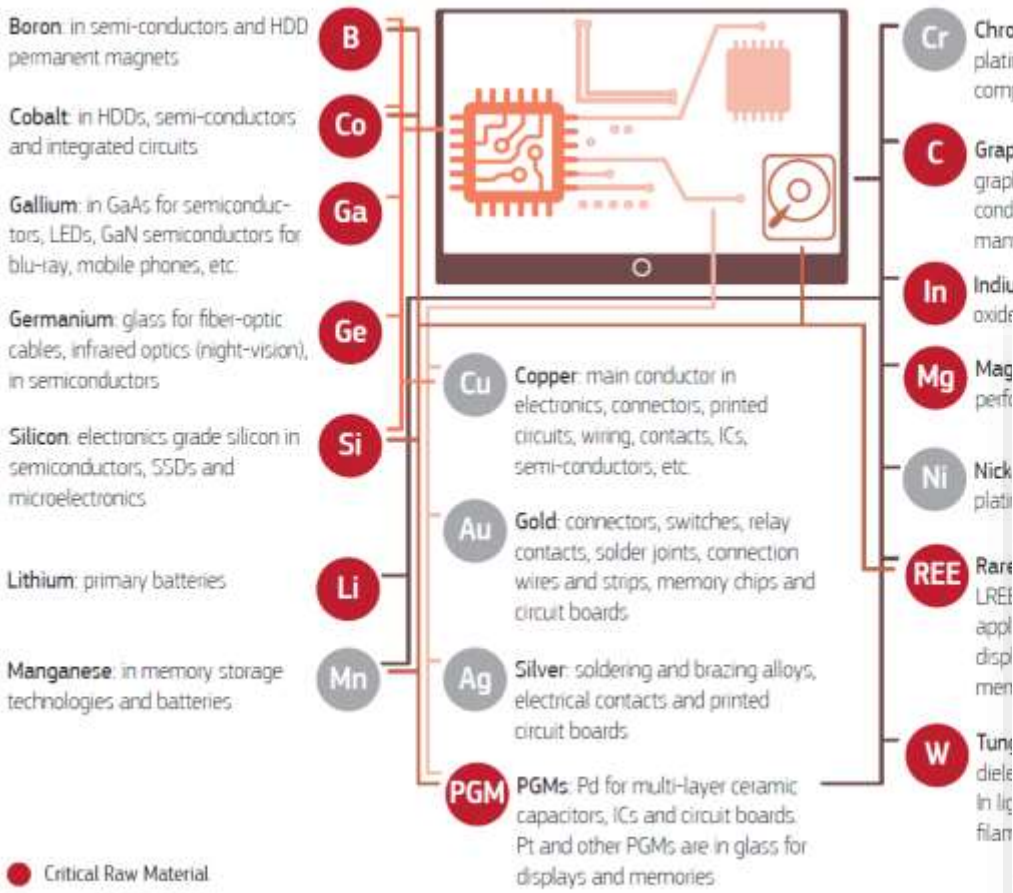


<https://www.visualcapitalist.com/visualizing-the-abundance-of-elements-in-the-earths-crust/>

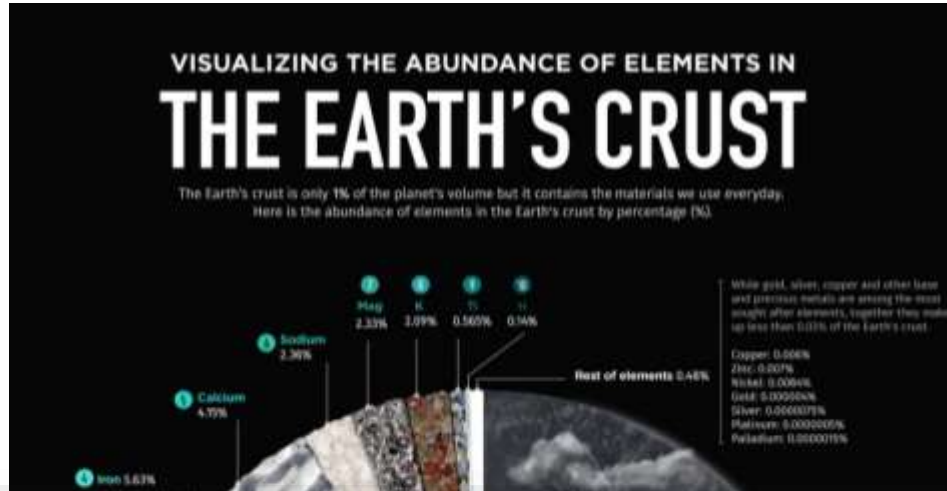
Electronics beyond Si

Materials resources are not infinite

Figure 44. Raw materials in digital technologies



● Critical Raw Material
Source: (BCG, 2018).



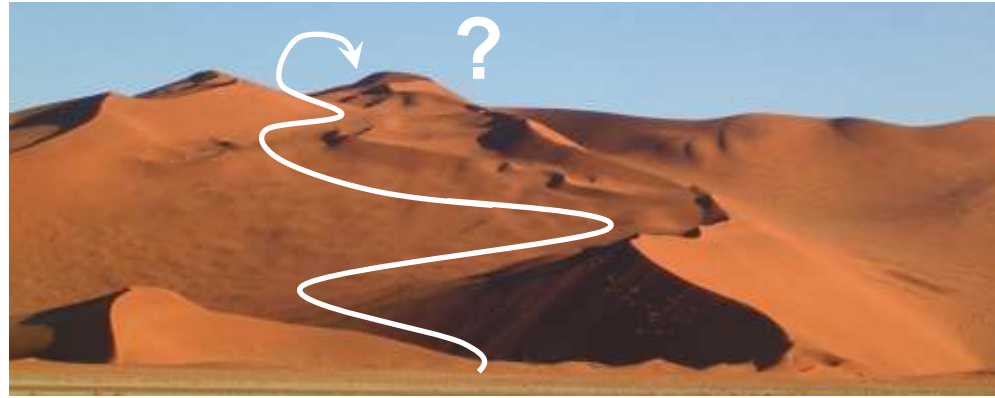
Rank	Element	% of Earth's Crust
1	Oxygen (O)	46.1%
2	Silicon (Si)	28.2%
3	Aluminum (Al)	8.2%
4	Iron (Fe)	5.6%
5	Calcium (Ca)	4.1%
6	Sodium (Na)	2.3%
7	Magnesium (Mg)	2.3%
8	Potassium (K)	2.0%
9	Titanium (Ti)	0.5%
10	Hydrogen (H)	0.1%
	Other elements	0.5%
	Total	100.0%

Oxygen, silicon, aluminum, and iron account for **88.1%** of Earth's mass.

90 elements make up the remaining **11.9%**.

gold, silver, copper and other base and precious metals: **<0.03%** (by mass)

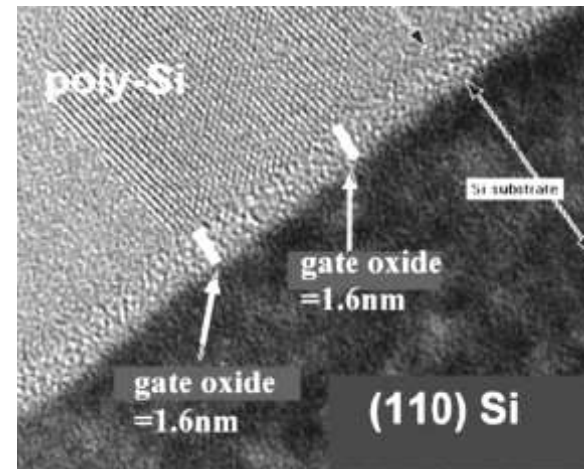
electronics beyond Si



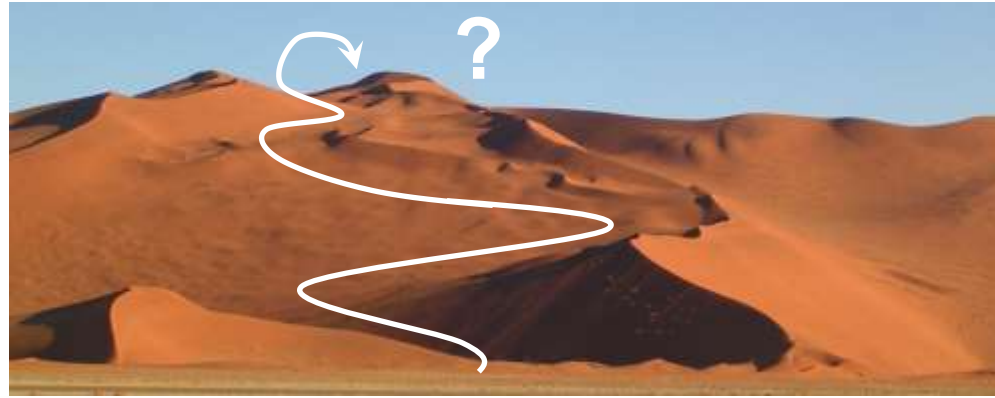
What is the Problem with Silicon ?

Transistors "carved" out of bulk materials (Si)
⇒ surface roughness impacts mobility, band gap & leads to device to device variability
(each atom matters!)

High density
⇒ thermal issues



electronics beyond Si



Other materials

Other architectures ?

electronics beyond Si

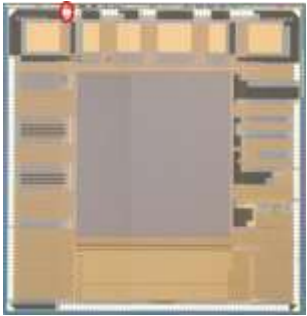
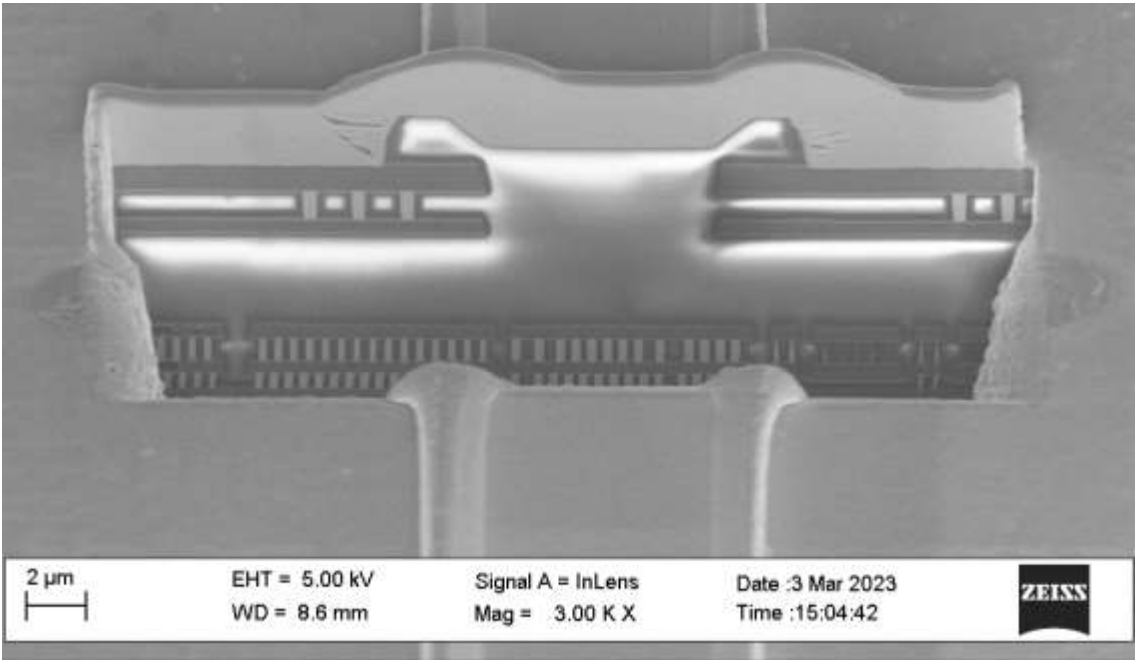
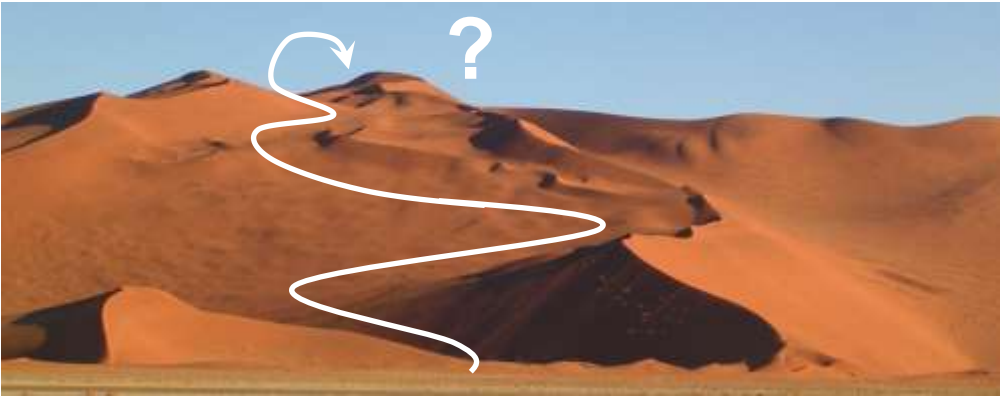


Image: E. Wu et al., Empa

FIB cross-section and SEM image of a bonding pad in a Readout Integrated Circuit (ROIC) chip

electronics beyond Si

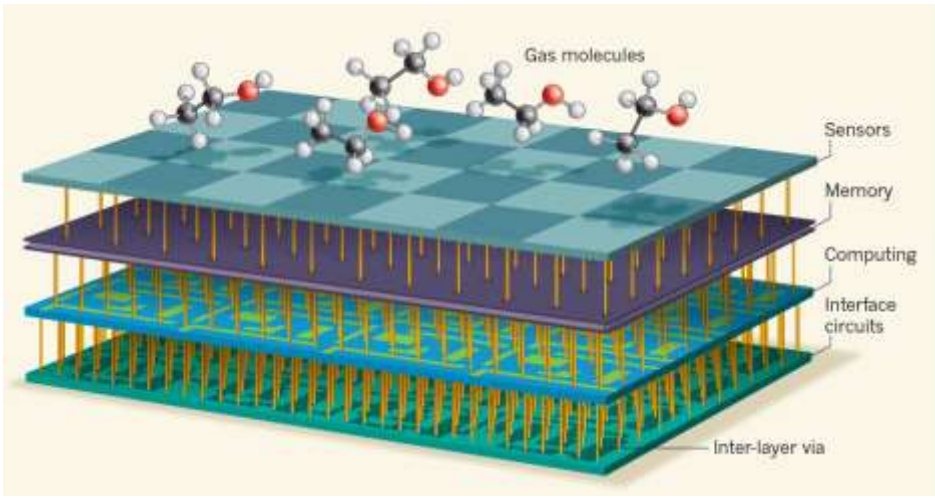


Architectures : 3D integration, new nanosystems

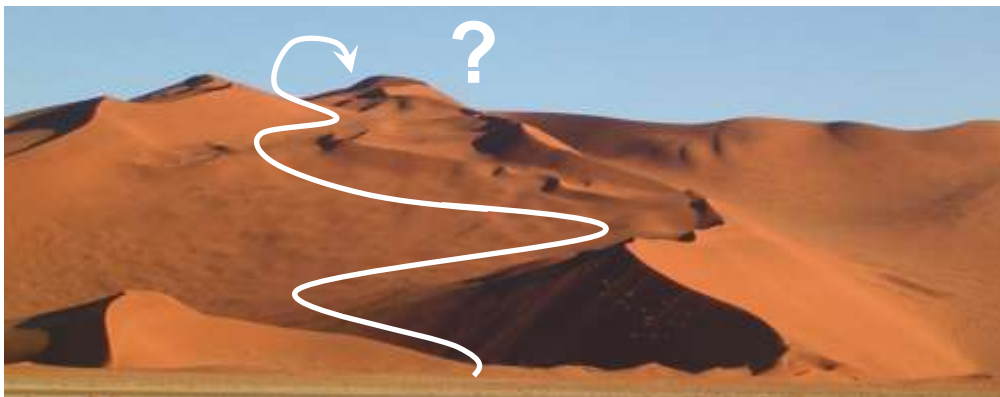
LETTER *Shulaker, Wong, Mitra et al. Nature 2017*
doi:10.1038/nature22994

Three-dimensional integration of nanotechnologies for computing and data storage on a single chip

Max M. Shulaker^{1,2}, Gagr Hillis¹, Rebecca S. Park¹, Roger T. Howe¹, Krishna Saramwar¹, H.-S. Philip Wong¹ & Subhasis Mitra^{1,3}

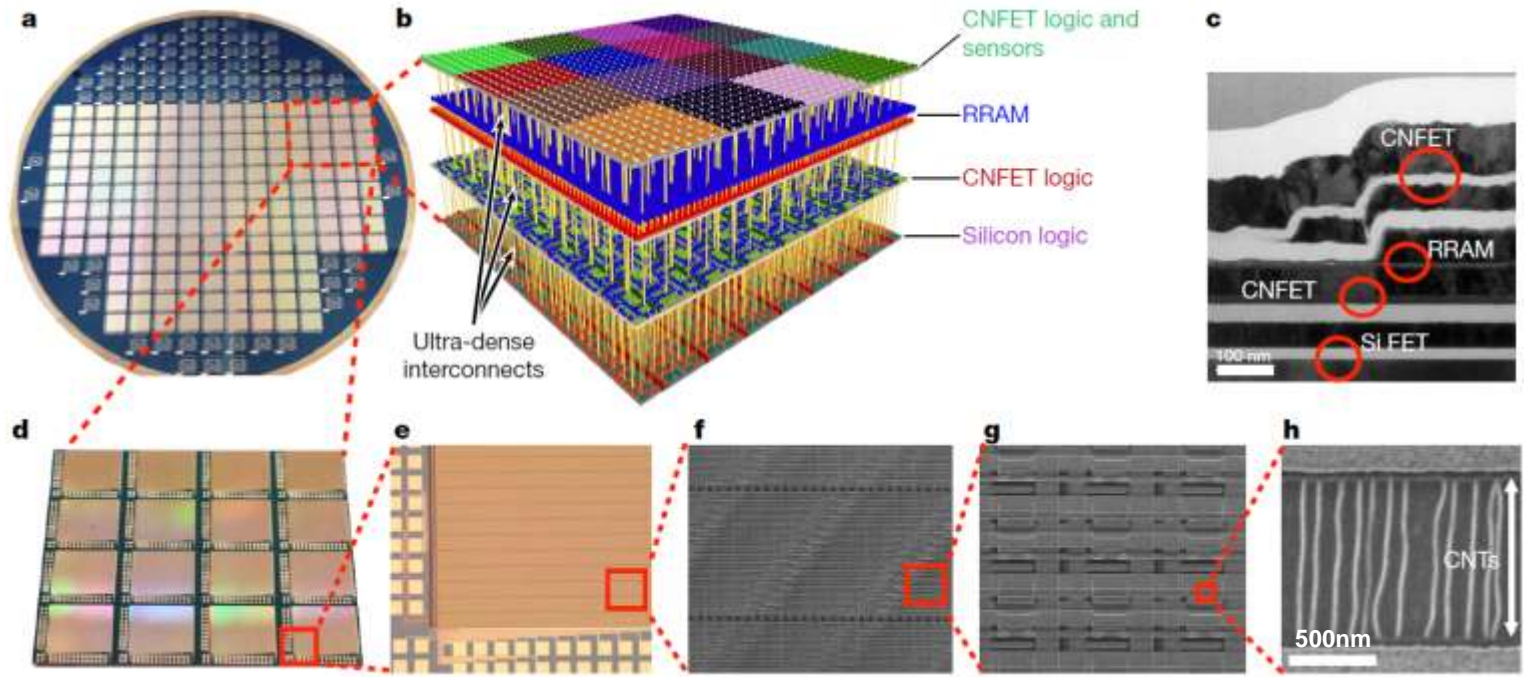


electronics beyond Si



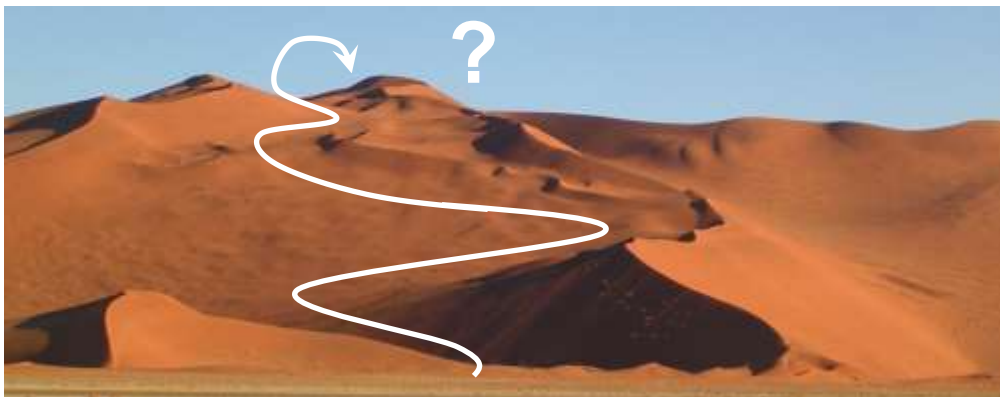
3D integration, novel nanosystem

Shulaker, Wong, Mitra et al. Nature 2017

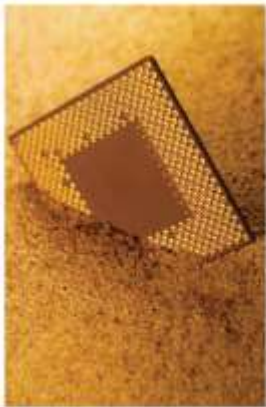


Full chip dimensions,
1.7 cm × 2.2 cm;
scale bar, 500 nm

electronics beyond Si



Other materials



INTRODUCTION
**Looking
Beyond Silicon**

Science 2010 special issue

AAAS 2015 ANNUAL MEETING
INNOVATIONS, INFORMATION, AND IMAGING
SAN JOSE, CA

Beyond Silicon: New Materials for 21st Century Electronics

Saturday, 14 February 2015: 8:00 AM-9:30 AM

**Beyond Silicon:
Carbon-Based
Nanotechnology**

Nathan P. Guisinger and Michael S. Arnold,
Guest Editors

MRS Bulletin 2010 special issue

physicstoday

Industrial Physics Forum 2013: The future of electronics

What technologies will extend silicon's reign as the preeminent material for electronics? What materials will ultimately supplant silicon?

Charles Day, December 2013

a quiz about best materials

Mechanical

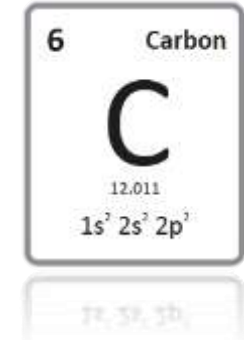
- Highest Young's modulus? → Diamond
- Highest tensile strength? → Graphene
- Hardest? → Diamond

Thermal

- Best heat conductor? → Diamond, graphene
- Highest melting point? → Tantalum hafnium carbide, graphene

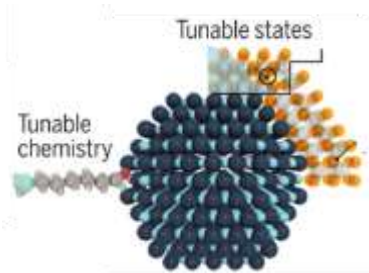
Best electric conductor?

- Highest current density → Carbon nanotubes
- Low resistivity? → Graphene
- Highest electron mobility → Two-dimensional electron gas in semiconductor heterostructure at cryogenic temperature, graphene at room temperature



low D(imensional) Materials

Small Molecules & Synthetic Quantum Dots



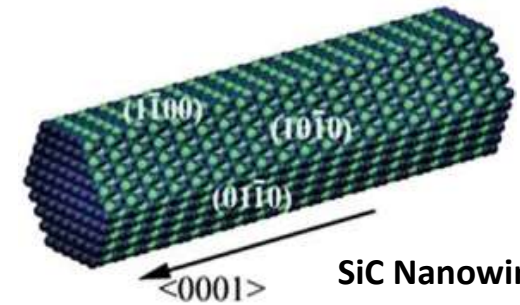
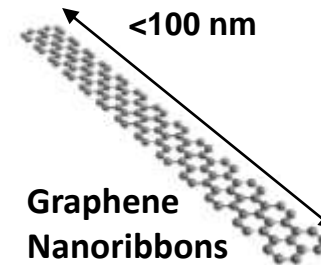
de Arquer *et al.* Science (2021)

0D



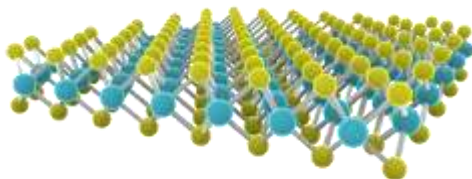
1D

Nanowires, Nanoribbons

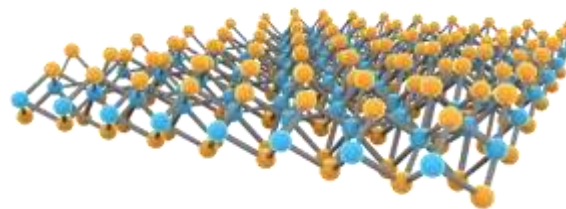


2D

E.g.: Transition Metal Dicalchogenides

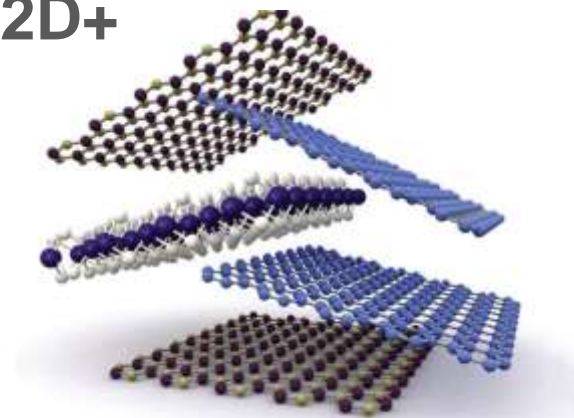


Molybdenum disulphide (MoS₂)



Tungsten ditelluride (WTe₂)

2D+



Novoselov *et al.* Science (2016)

Heterogeneous Integration
with/without lattice mismatch

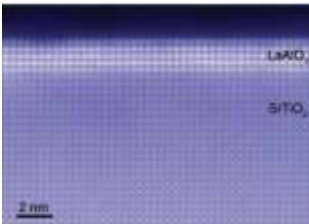
electronics beyond Si

Materials...



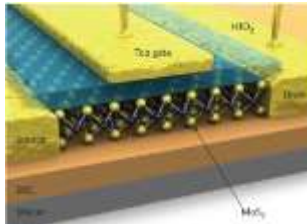
Transition metal oxides
 charge, spin, orbital degrees of freedom
 for diversity of phases exploiting e-e
 correlation (e.g.: TiO_2 , perovskites ABO_3)

Oxides interfaces
 LaAlO_3 - SrTiO_3
 heterostructures

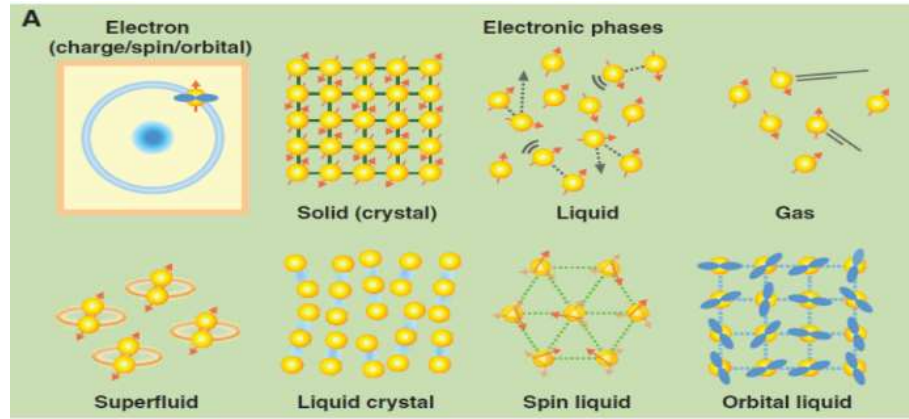


Mannhardt et al., Science 2013

Transition metal dichalcogenides ("Native" 2D)
 MoS_2 , WS_2 , ...



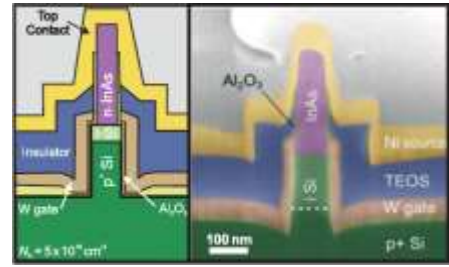
Strano et al., Nat. Nano 2012



Takagi et al., Science 2013

III-V compound semic. transistors

NW tunnel FETs
Riel et al., MRS Bulletin 2014



... and transport regimes

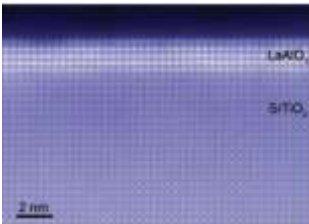
diffusive, ballistic, tunneling, hydrodynamic
 control of e-e, e-ph, e-defect interactions

electronics beyond Si

Materials...

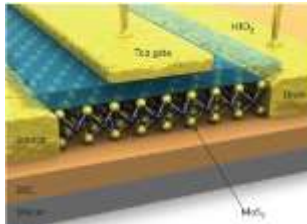


Oxides interfaces
LaAlO₃-SrTiO₃
heterostructures



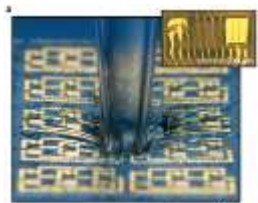
Mannhardt et al., Science 2013

Transition metal dichalcogenides ("Native" 2D)
MoS₂, WS₂, ...

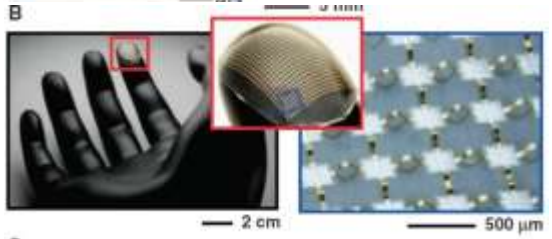


Strano et al., Nat. Nano 2012

Organic & inorganic materials with elastomeric substrates

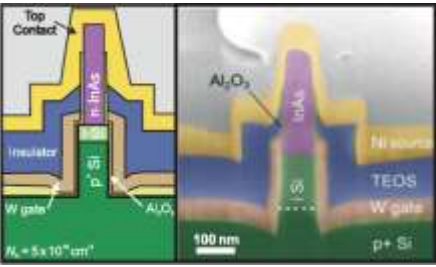


Stretchable electronics
Rodgers et al.,
Science 2013



III-V compound semic. transistors

NW tunnel FETs
Riel et al., MRS Bulletin 2014



Thousands (?) of 2D Materials

Structural and Chemical Diversity beyond graphene

2D

E.g.: Transition Metal Dicalchogenides

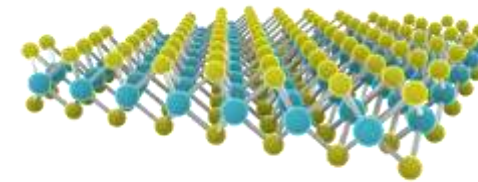
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl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

MX_2
M = Transition metal
X = Chalcogen

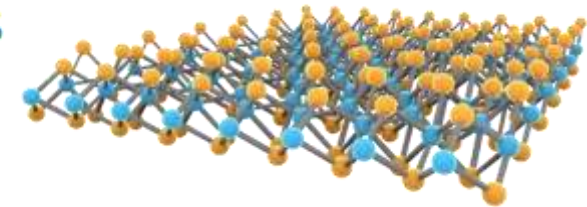
Transition metal

chalcogen

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



Molybdenum disulphide (MoS_2)



Tungsten ditelluride (WTe_2)

- **Structure** first determined by **Linus Pauling in 1923**
- By the late **1960s**, around **60 TMDCs** were known, at **least 40 of them with a layered structure**.
- First reports on the use of **adhesive tapes** for **producing ultrathin MoS_2 layers**, by **Robert Frindt in 1963**
- Production of **monolayer MoS_2 suspensions** was first achieved in **1986**.

See e.g. A. Kis et al., *Nat. Rev. Materials* (2017)

Thousands (?) of 2D Materials

Structural and Chemical Diversity

2D and 2D+

E.g.: Transition Metal Dicalchogenides

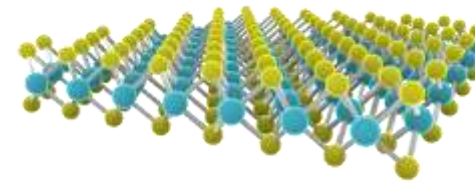
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl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

MX_2
M = Transition metal
X = Chalcogen

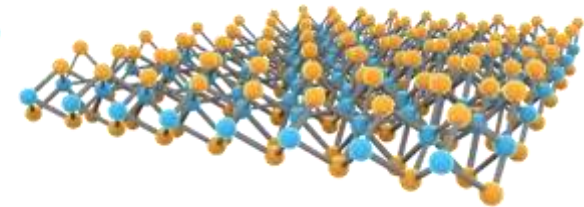
Transition metal

chalcogen

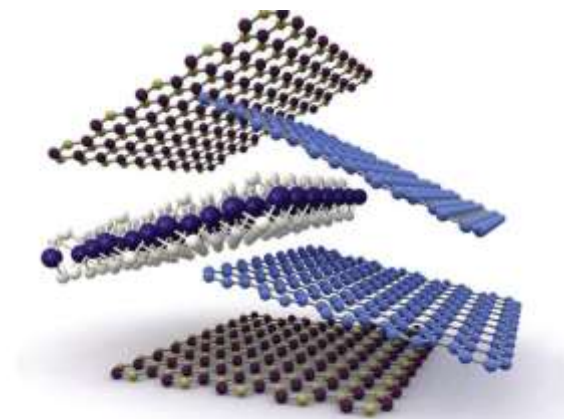
Chowalla et al., Nat. Chem. (2013)
Dresselhaus, Cargèse, 2014



Molybdenum disulphide (MoS_2)



Tungsten ditelluride (WTe_2)

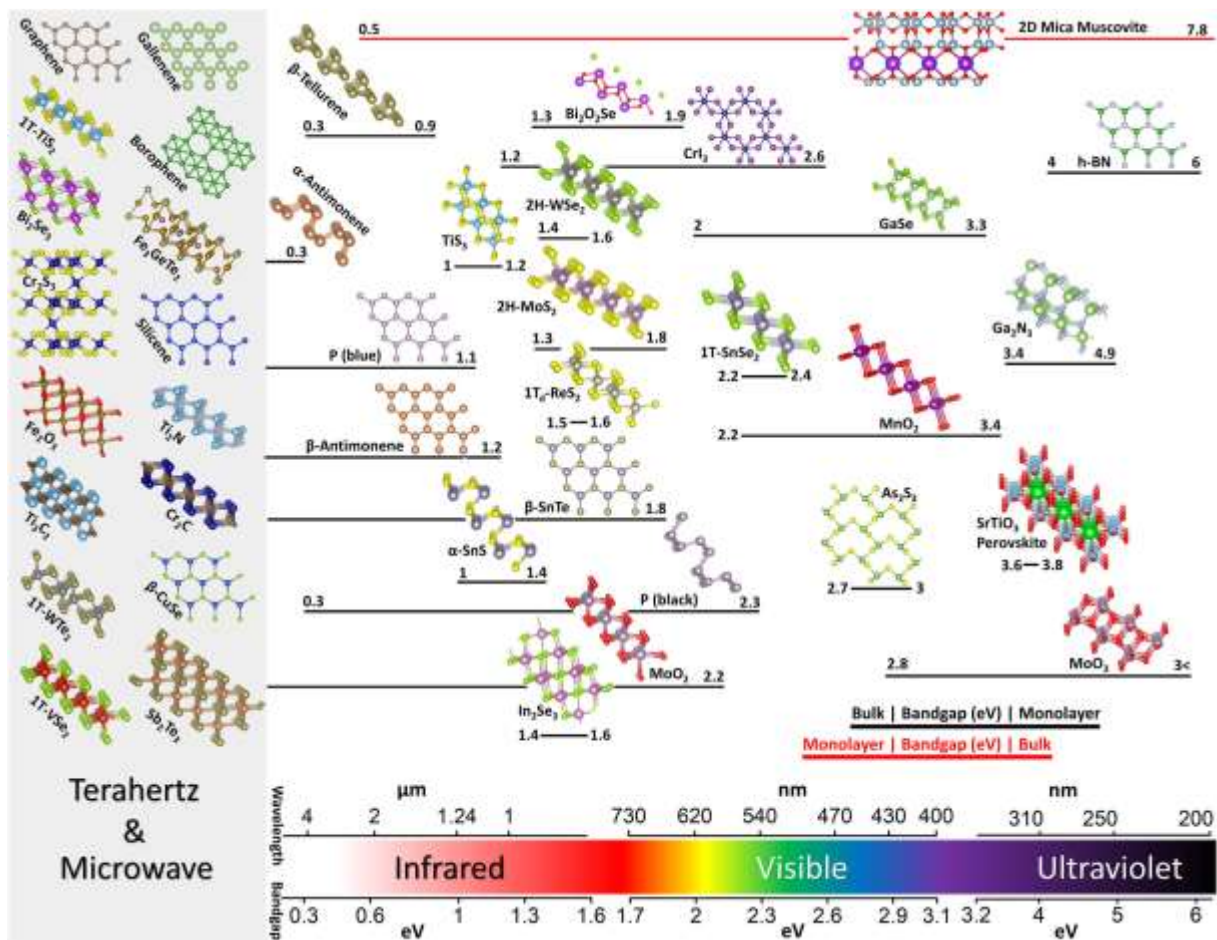


Heterogeneous Integration
with/without
lattice mismatch

Novoselov et al. Science (2016)

Thousands (?) of 2D Materials & Opportunities

Structural and Chemical Diversity



Zero or near-zero bandgap, metallic, or semimetallic

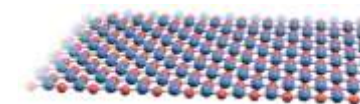
Selected family of 2D materials and their bandgaps
Chaves et al., npj 2D Materials (2022)

Richness of Properties

Sometimes no bulk analogue

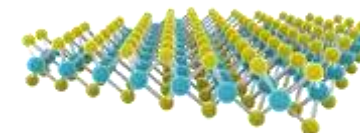
Insulating

hexagonal Boron Nitride (~5.9eV)



Semiconducting

Molybdenum Disulfide (1.8-2.7eV)



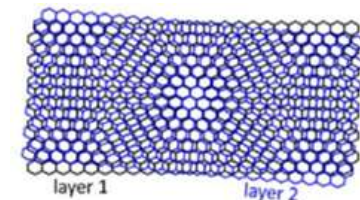
Metallic

Graphene



Superconducting

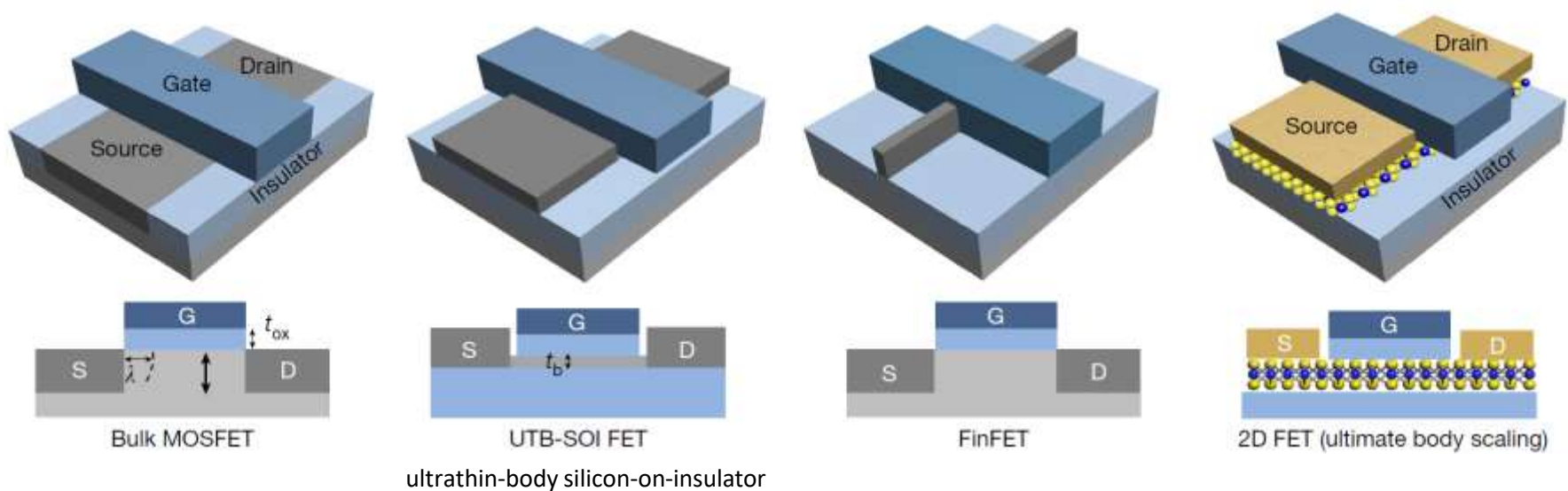
Twisted bilayer Graphene "Magic Angle"



Electronics beyond Si: emergence of 2D transistors, selected properties

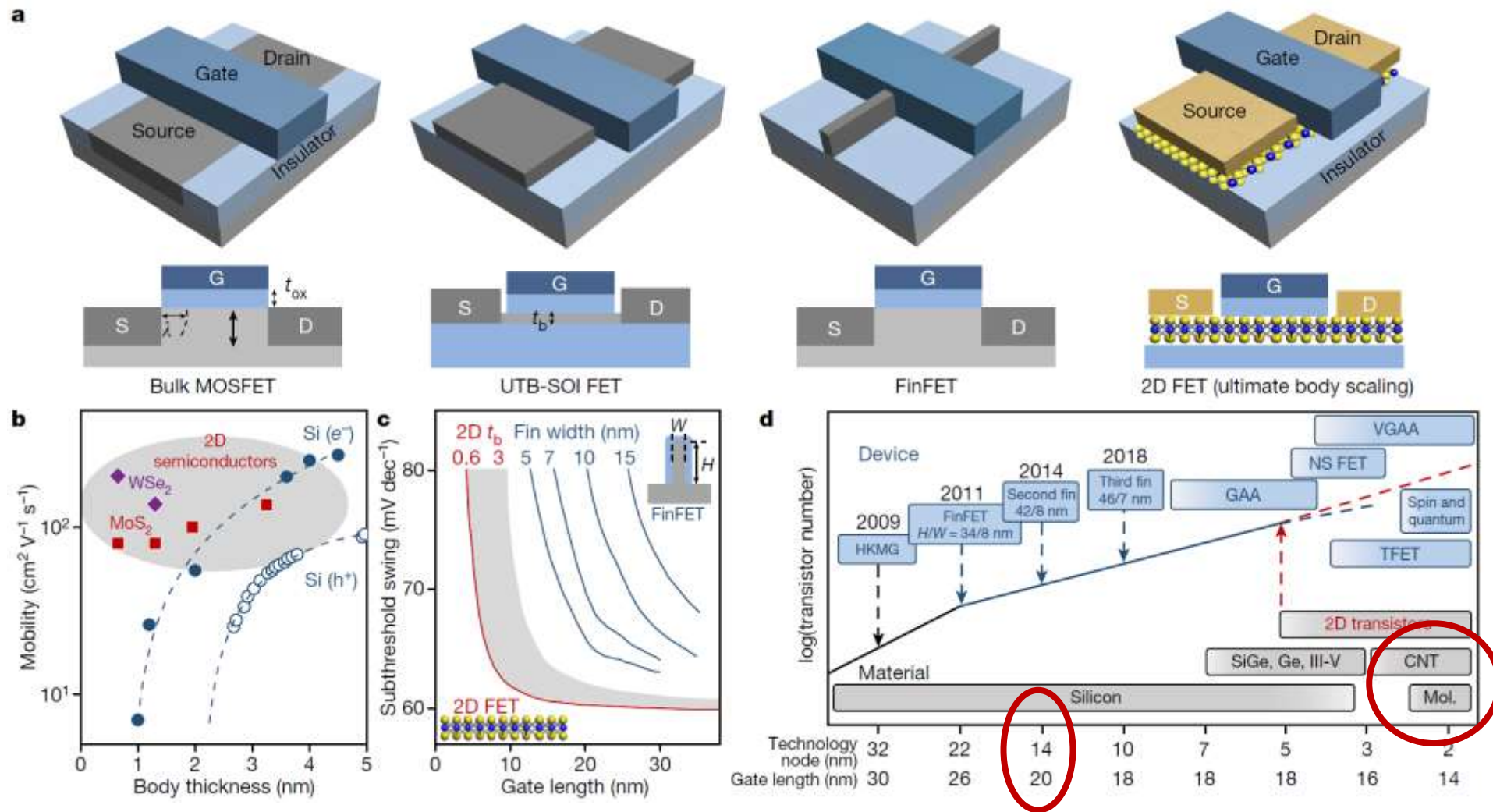
Body thickness scaling in FETs

a



Light grey, dark grey, light blue and dark blue represent the bulk semiconductor, doped contact region, oxide and gate electrode, respectively. S, source; D, drain; G, gate

Electronics beyond Si: emergence of 2D transistors, selected properties



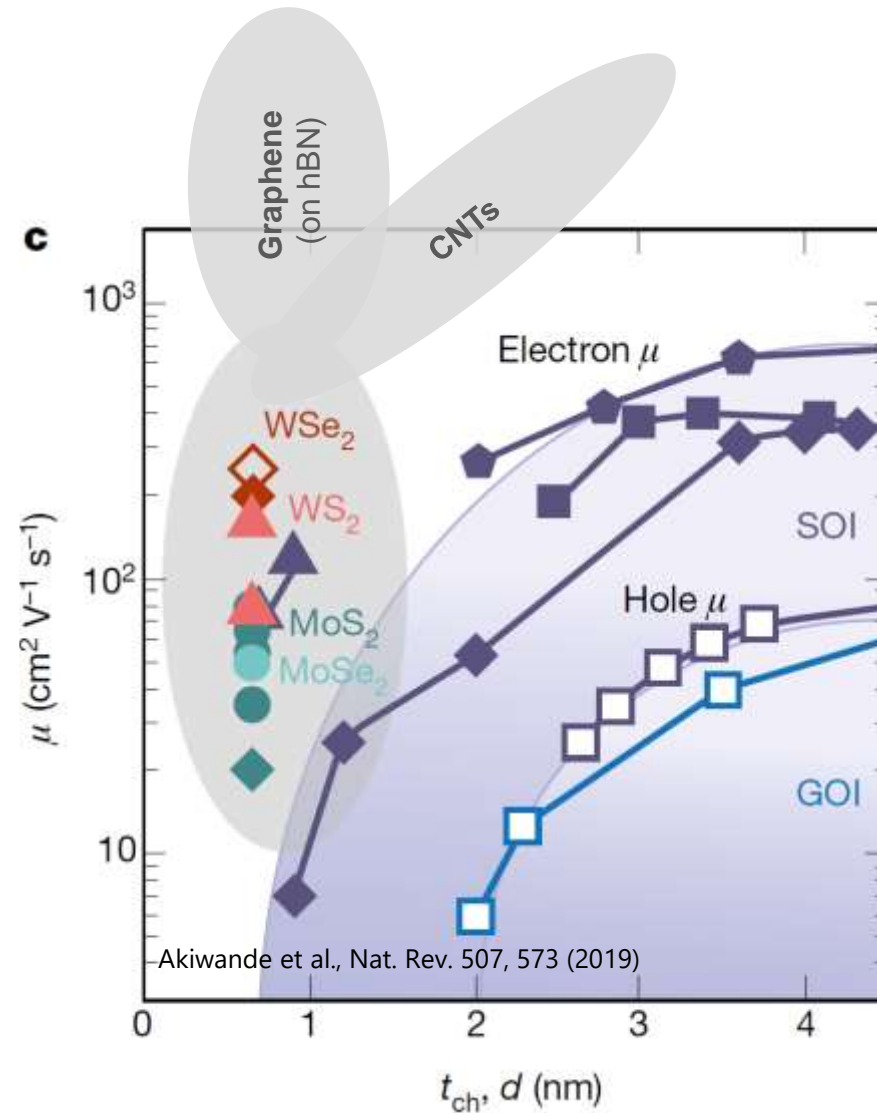
Light grey, dark grey, light blue and dark blue represent the bulk semiconductor, doped contact region, oxide and gate electrode, respectively. S, source; D, drain; G, gate

HKMG, high- κ dielectric and metal gate; NS FET, nano-sheet FET; CNT, carbon nanotube; Mol., molecules

electronics beyond Si: emergence of 2D transistors

Atomically-thin and -
precise materials

Charge carrier mobility



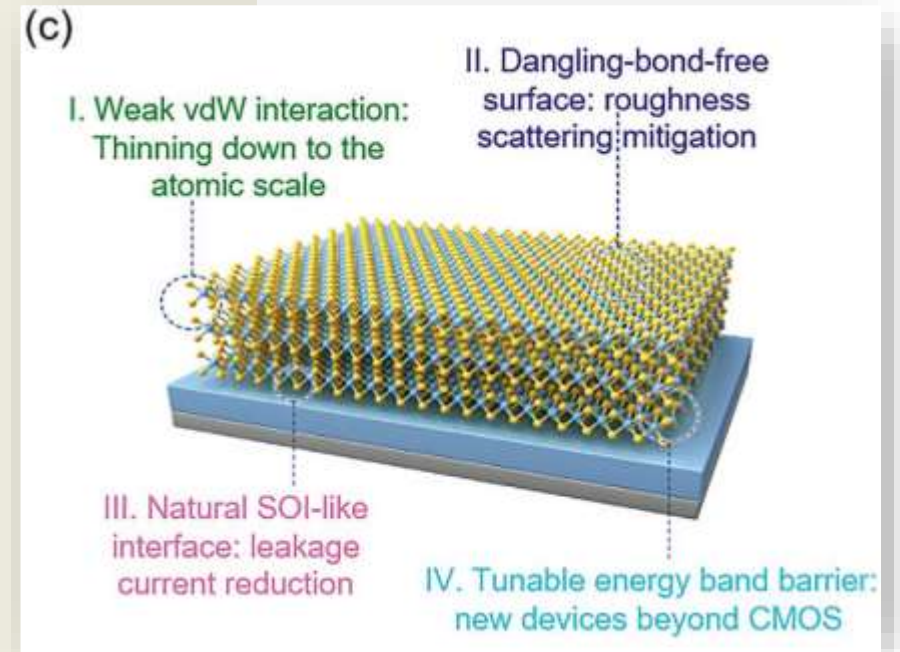
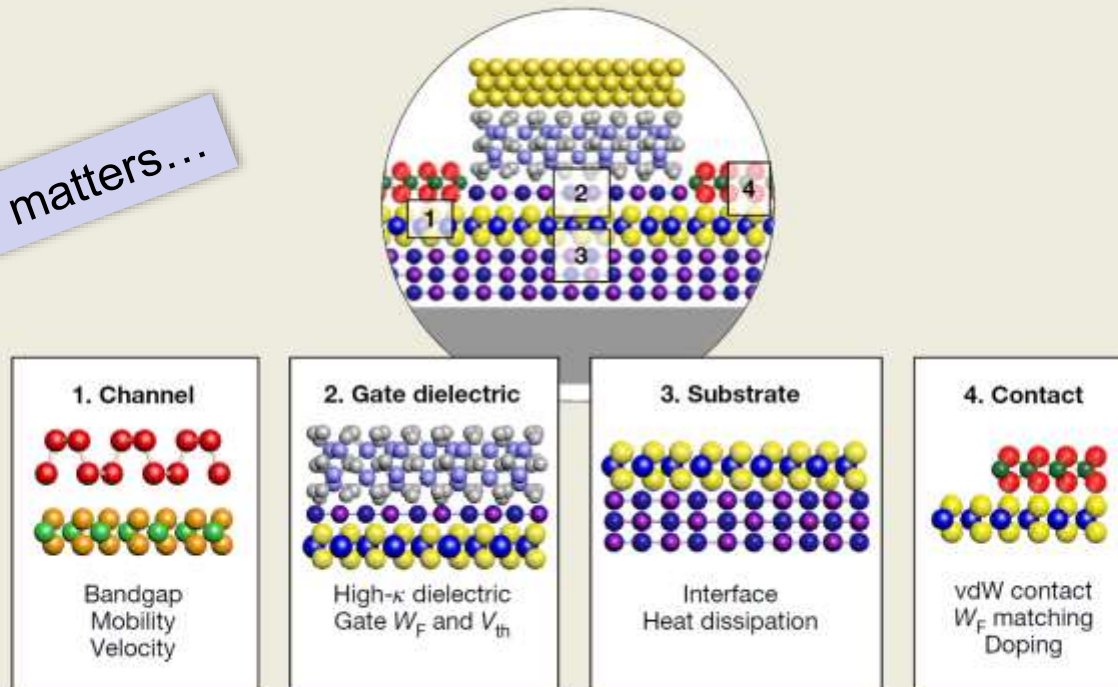
electronics beyond Si: emergence of 2D transistors

Pathway for pushing the performance limit of 2D transistors

In an idealized 2D transistor, a high-mobility 2D semiconductor (monolayer or bilayer) with a desired bandgap and high ν_{sat} is used as the channel material with low channel resistance; an ultrathin 2D metal with the appropriate work function is used as a pinning-free vdW contact with minimized R_c ; a high- κ dielectric with ultrasmall equivalent oxide thickness is used as the dielectric layer to maximize the transconductance; a metal gate with designed work function is used to control the threshold voltage; and an ultrasmooth, high-thermal-conductance substrate (for example,

BN) may be used for effective heat dissipation. Additionally, a monolayer BN may be used as a protection layer and interfacial layer for high- κ dielectric integration to reduce the integration-induced structural damage and the associated interface states, and provide an additional heat-releasing pathway. The atomically clean 2D/BN vdW heterojunction at the dielectric-2D semiconductor and substrate/2D semiconductor interfaces could also minimize the interfacial trapping states and prevent undesired substrate scattering effects, thus further boosting I_{on} .

Each atom matters...



Wang et al., Adv. Mat. (2022)

Box 1 Figure | Schematic of an idealized 2D transistor showing the ultimate potential of 2D semiconductors. W_F , work function; V_{th} , threshold voltage.

Duan et al., Nature (2021)

outline

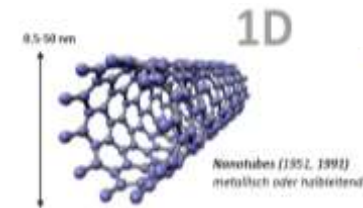
Electronics beyond Silicon

- other possible pathways for electronics



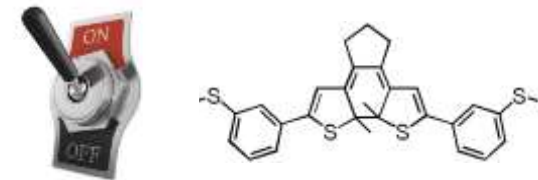
Carbon allotropes

- discovery



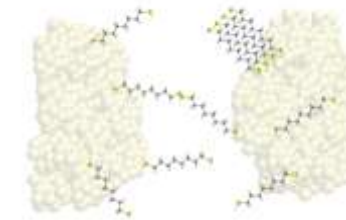
Carbon & molecular electronics

- brief historical account
- a word about computing
- why molecules



Molecular junctions

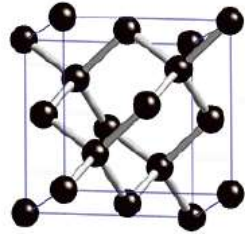
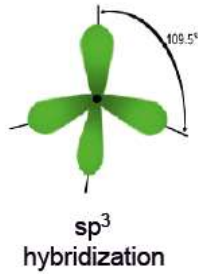
- how to contact nm-scale objects



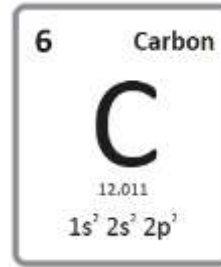
Carbon and its allotropes



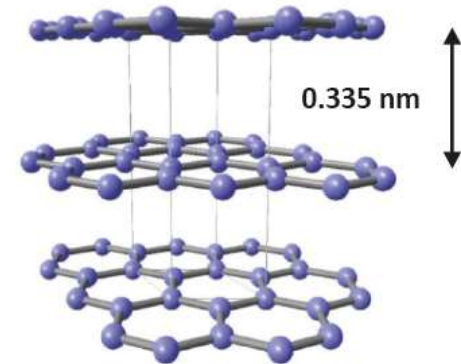
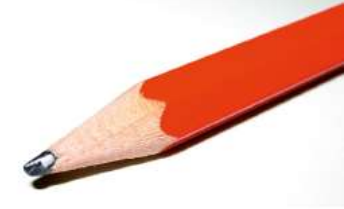
Diamant (sp^3 Carbon)
- das härteste Material
- sehr guter Isolator, trotzdem aber exzellenter Wärmeleiter



3D

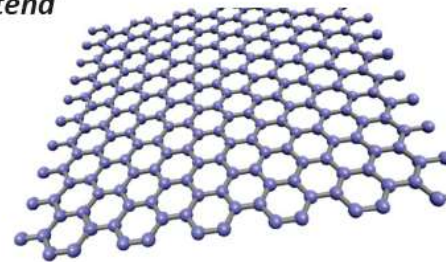


Graphit (sp^2 Carbon)
- lässt sich leicht abtragen (Bleistift)
- recht guter elektrischer Leiter

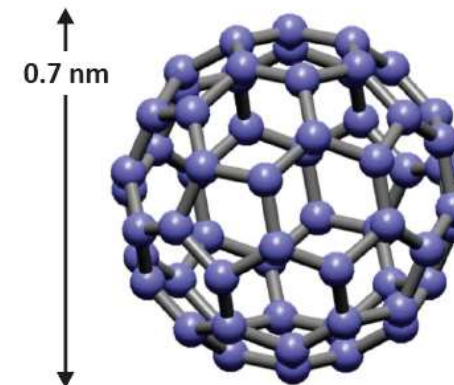


Graphene (2004)
"zwischen" metallisch und halbleitend

2D

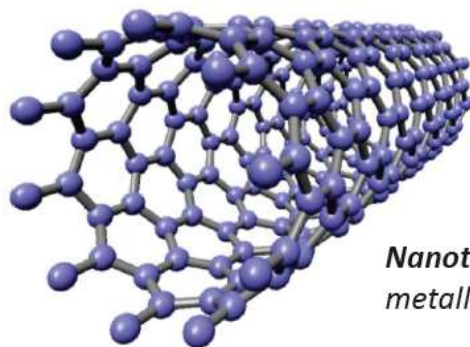


Fullerene C_{60} (1985)



1D

0.5-50 nm



Nanotubes (1951, 1991)
metallisch oder halbleitend

0D

outline

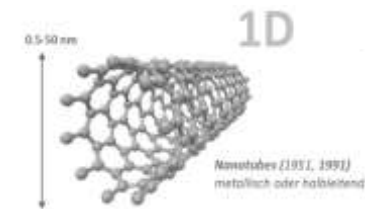
Electronics beyond Silicon

- other possible pathways for electronics



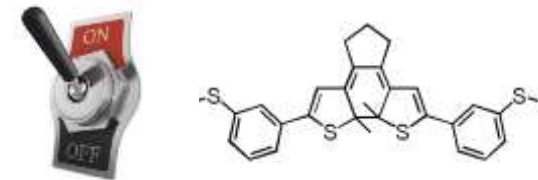
Carbon allotropes

- discovery



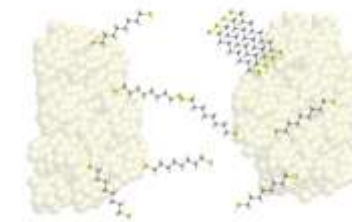
Carbon & molecular electronics

- brief historical account
- a word about computing
- why molecules



Molecular junctions

- how to contact nm-scale objects



carbon-based electronics

materials

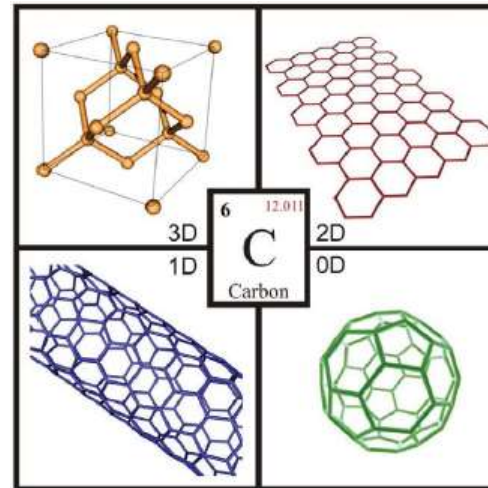


Table I. Electronic Properties of Carbon-Based Materials Compared with Other Common Semiconductors.

	Electron Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Bandgap (eV)	Thermal Conductivity ($\text{W cm}^{-1} \text{K}^{-1}$)
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

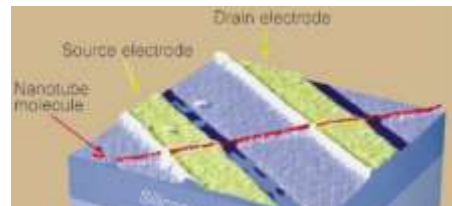
MRS Bulletin 2010 special issue

Carbon-based Electronics ?

Nanotechnology

Carbon-based electronics

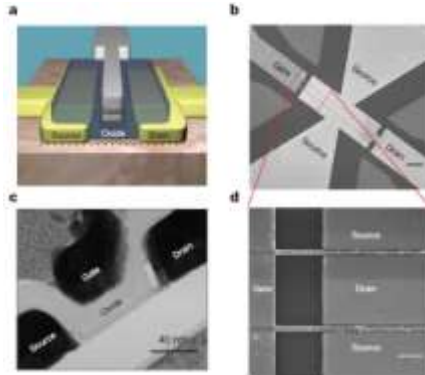
Paul L. McEuen



LETTER

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

Yanming Wu¹, Yu-ming Liu¹, Ajayth A. Suli¹, Keith A. Jenkins¹, Fengnian Xia¹, Damien E. Farmer¹, Yu Zha¹ & Phaedon Avouris¹



Nature 2011

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)



Paul McEuen, professor of physics at Cornell University and director of the Kavli Institute at Cornell for Nanoscale Science.

LETTER

Carbon nanotube computer

Max M. Shulkin¹, Gopi Iyer¹, Nitin Prasad¹, Hai Wu¹, Hong-Yu Chen¹, Li-Q. Peng¹ & Subhashis Maiti¹



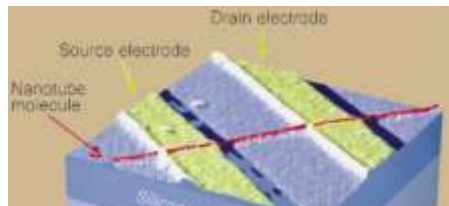
Nature 2013

Carbon-based Electronics ?

Nanotechnology

Carbon-based electronics

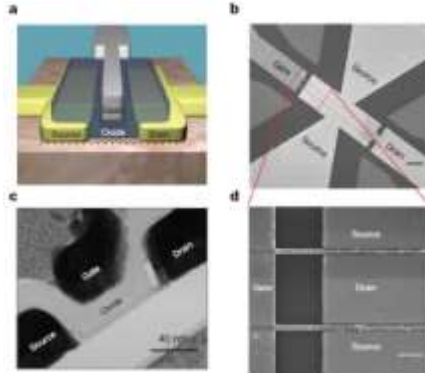
Paul L. McEuen



LETTER

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

Yanrong Wu¹, Yu-ting Lai¹, Ajayth A. Suli¹, Keith A. Jenkins¹, Fengnian Xia¹, Darren E. Farmer¹, Yu Zha¹ & Phaedon Avouris¹



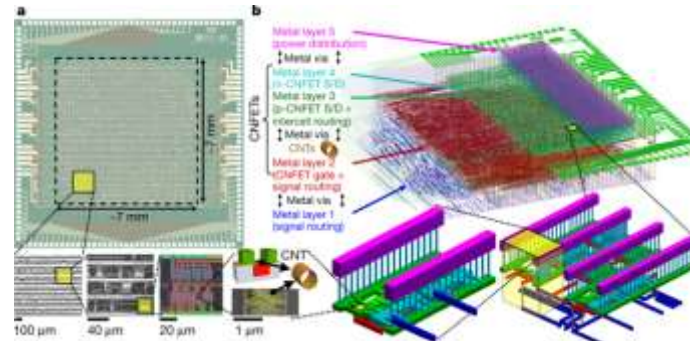
Nature 2011

ARTICLE

<https://doi.org/10.1038/n41586-019-1400-8>

Modern microprocessor built from complementary carbon nanotube transistors

Gage Hills^{1,2}, Christian Lau^{1,2}, Andrew Wright², Samuel Fuller², Mindy D. Bishop², Tarbagata Sriram¹, Prityal Kambhaya¹, Rebecca Ho², Aya Amer², Yosi Stein², Denis Murphy², Arvind¹, Anantha Chandrakasan¹ & Max M. Shulaker^{2*}



Nature 2019

LETTER

[doi:10.1038/s41586-019-1400-8](https://doi.org/10.1038/s41586-019-1400-8)

Carbon nanotube computer

Max M. Shulaker¹, Gage Hills², Nathan Fall², Hai Wu², Hong-Yu Chen², H.-S. Philip Wong² & Siddhant Misra²



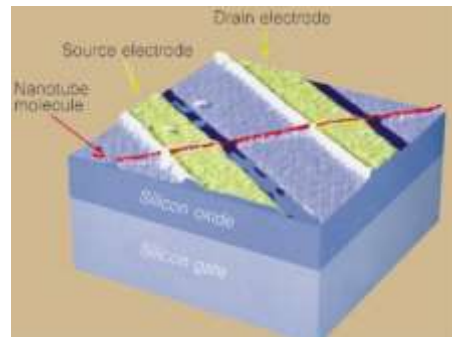
Nature 2013

Carbon-based Electronics ?

Nanotechnology

Carbon-based electronics

Paul L. McEuen



Nature 1998, news&views

1998 – Research Devices,
CNT Transistor

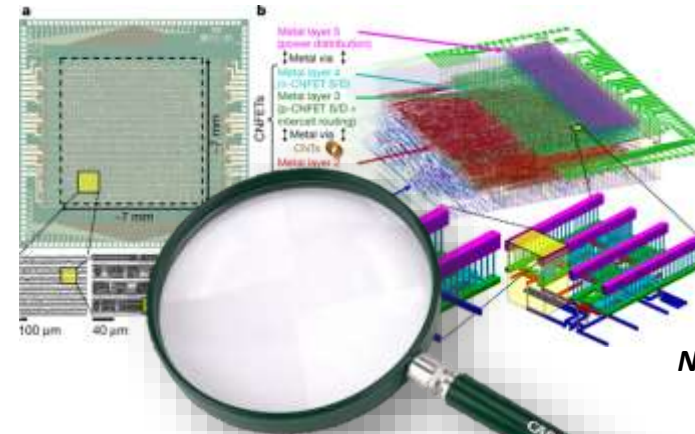


ARTICLE

<https://doi.org/10.1038/41586-019-1003-8>

Modern microprocessor built from complementary carbon nanotube transistors

Gage Hills^{1,2}, Christian Lau^{1,2}, Andrew Wright², Samuel Fuller², Mindy D. Bishop², Tarbagata Srinani¹, Prityal Kambhaya¹, Rebecca Ho², Aya Amer², Yosi Stein², Denis Murphy², Arvind¹, Anantha Chandrakasan¹ & Max M. Shulaker^{2*}

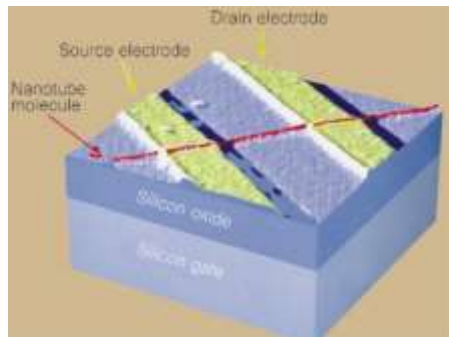


Nature 2019

2019 – CNT 16 bit
Processor

Carbon-based Electronics ?

Nanotechnology Carbon-based electronics Paul L. McEuen



Nature 1998, news&views

1998 – Research Devices,
CNT Transistor

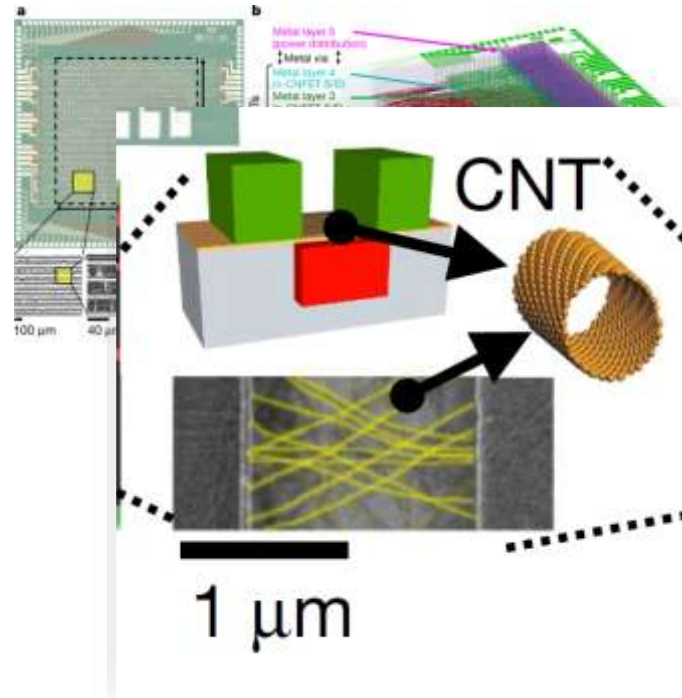


ARTICLE

<https://doi.org/10.1038/s41586-019-1403-8>

Modern microprocessor built from complementary carbon nanotube transistors

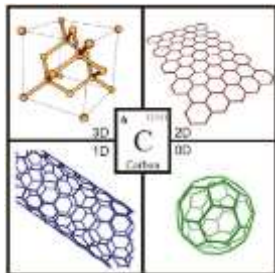
Gage Hills^{1,2}, Christian Lau^{1,2}, Andrew Wright², Samuel Fuller², Mindy D. Bishop², Tarbagata Srivastava¹, Prityal Kantaiya¹, Rebecca Ho², Aya Amer², Yosi Stein², Denis Murphy², Arvind¹, Anantha Chandrakasan¹ & Max M. Shulaker^{2*}



Nature 2019

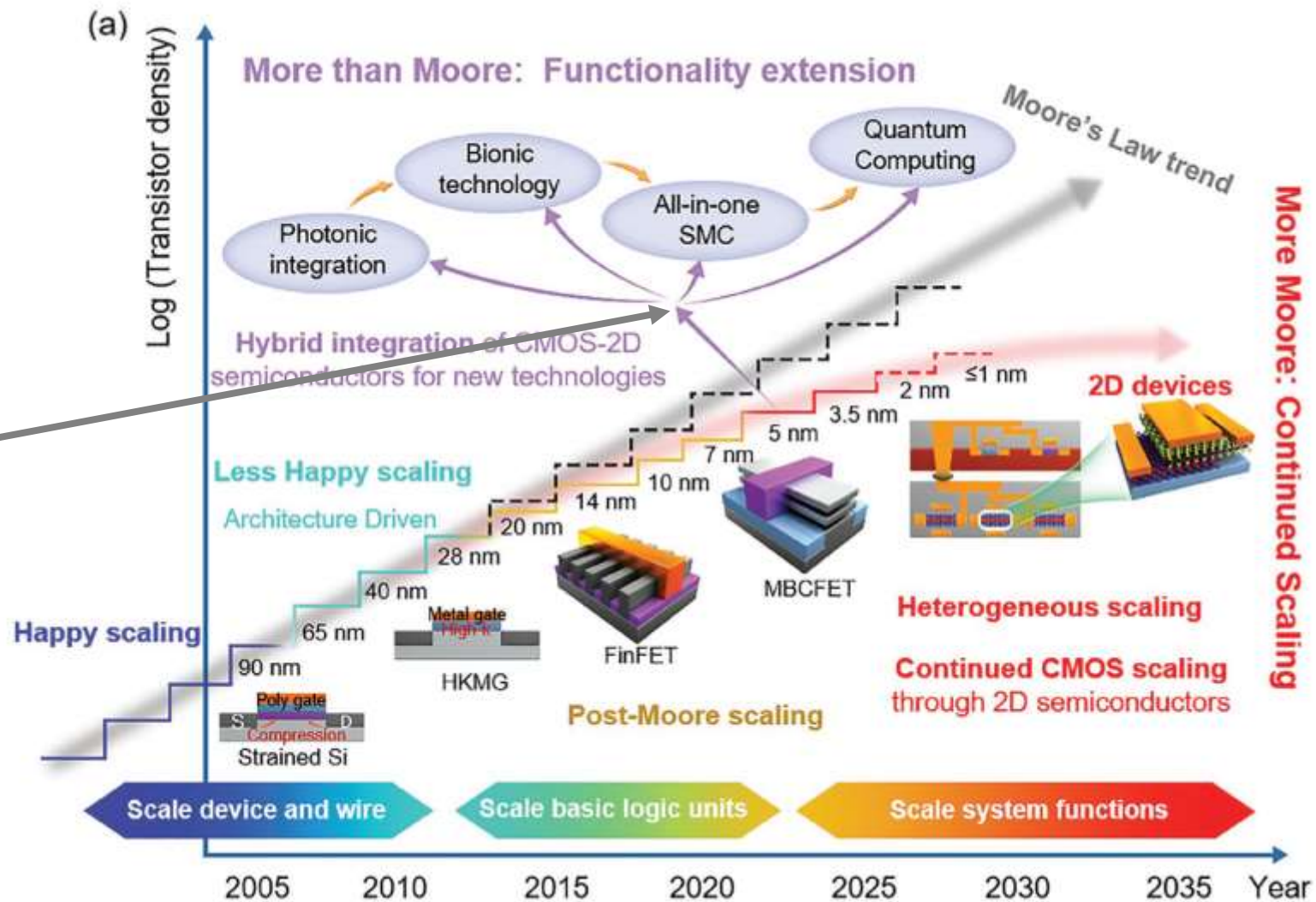
Still, not individual Carbon Nanotubes ...

carbon-based electronics



materials

C-based materials



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.

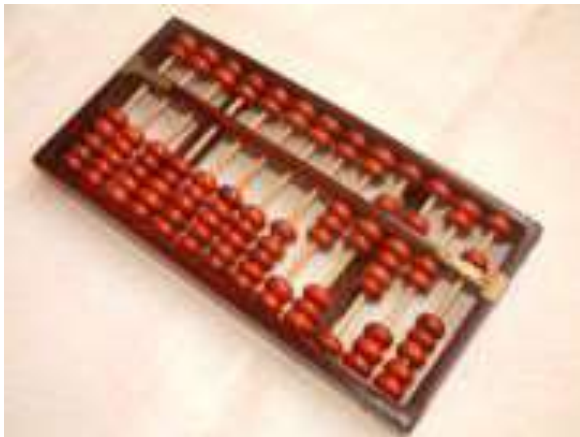
Remember that ...?

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

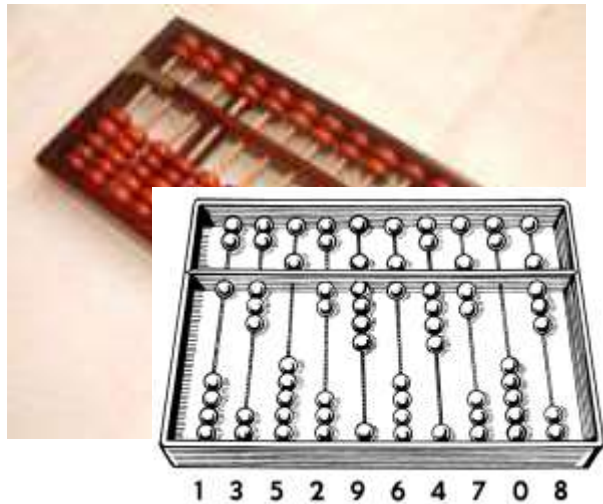
Wait... what is computing actually ?

Computing

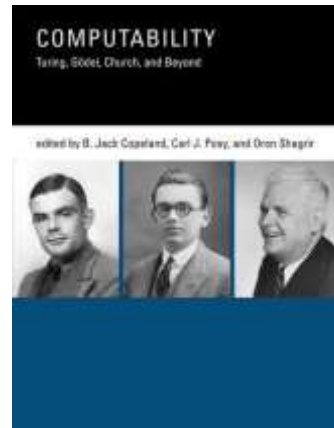


Wait... what is computing actually ?

Computing



Denning, 2010; Horswill, 2008; wikipedia



Computability:
Turing, Gödel, Church, and Beyond
Edited by B.J. Copeland, C.J. Posy,
O. Shagrir, MIT Press,

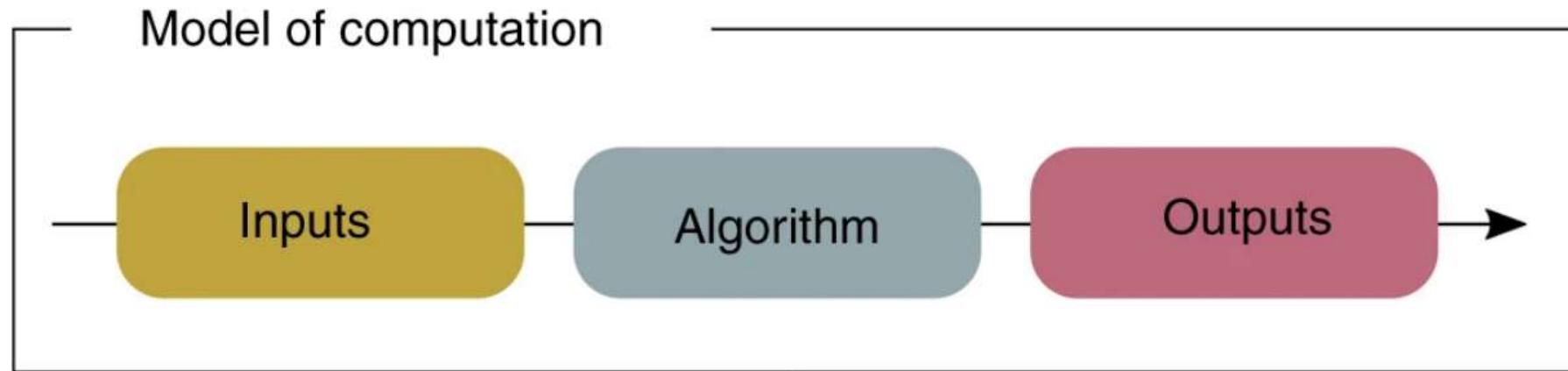


The first IBM system to
include Intel's 80386 chip
Computerhistory.org

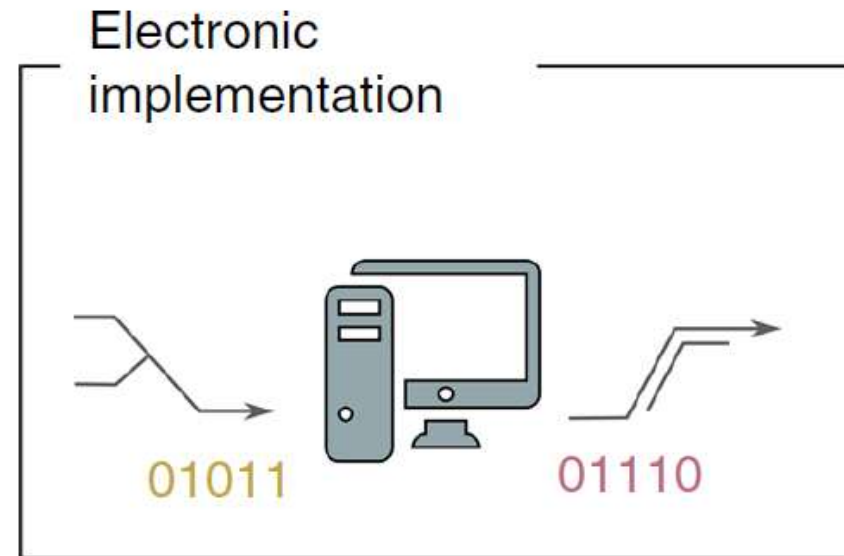
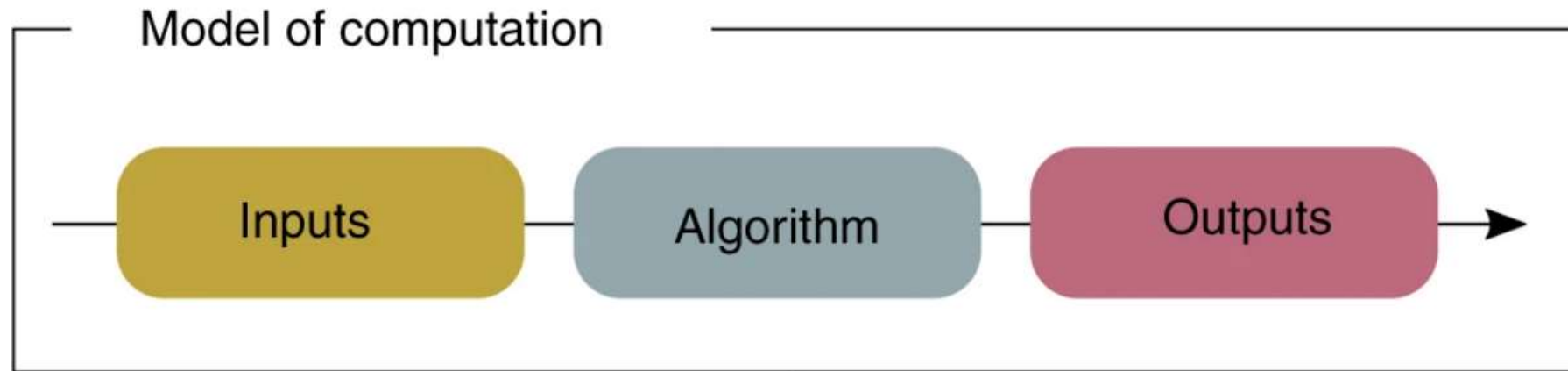


Mary Jackson,
Credit: [NASA](https://www.nasa.gov)

Computation: Model and Implementation



Computation: Model and Implementation



Binary nb **0 1 0 1 1** = 0 + 8 + 0 + 2 + 1 = 11

Weight $2^4 \ 2^3 \ 2^2 \ 2^1 \ 2^0$
 16 8 4 2 1

Operations
 Logic gates
 AND

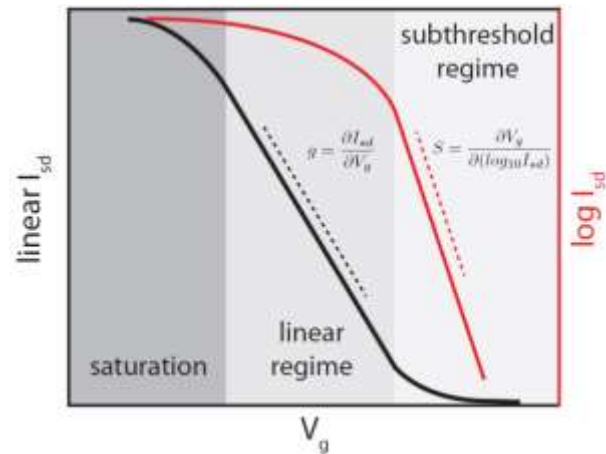
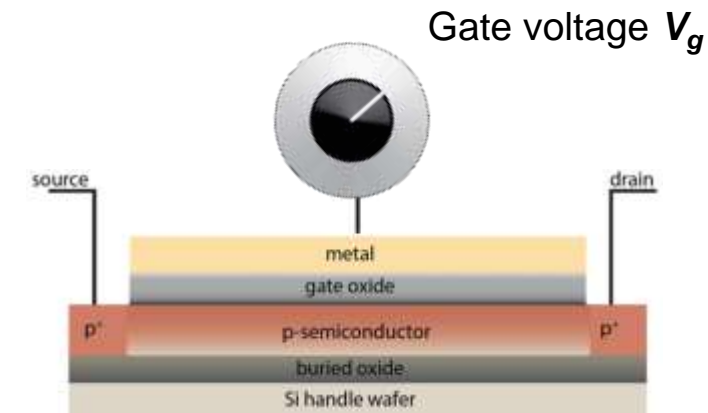


Input		Output
A	B	Q
0	0	0
0	1	0
1	0	0
1	1	1

Electronic Computation: Physical Implementation

Electronic Switch (0, 1)

Field-Effect Transistor (MOSFET)



$$I_{sd} = \mu C_{ox} \frac{W}{L} (V_g - V_{fb}) V_{sd}$$

