

Frontiers in Nanosciences

Marina Pivetta

Stefano Rusponi

Laboratory of Nanostructures at Surfaces
IPHYS

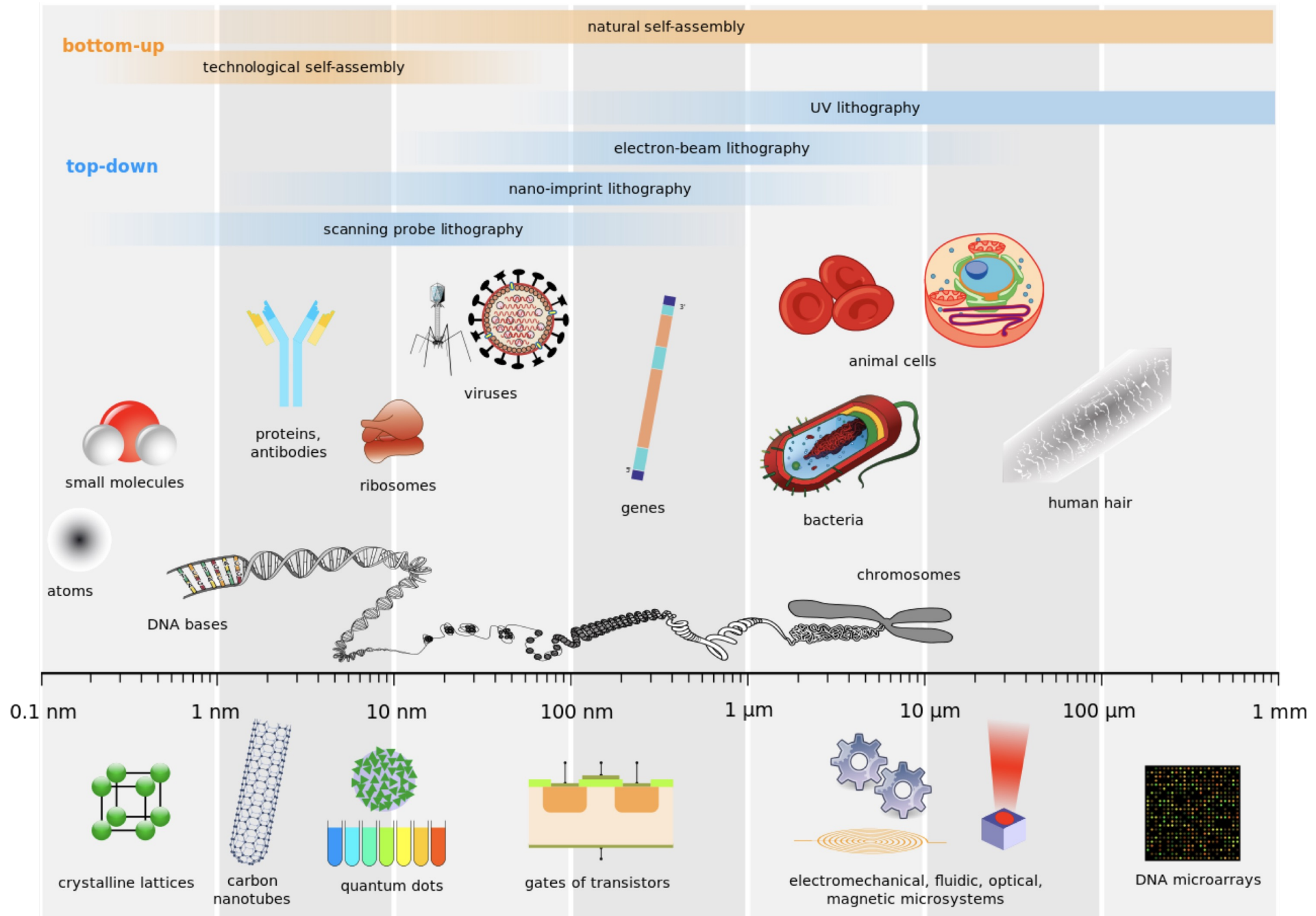
Fall 2024

Frontiers in Nanosciences

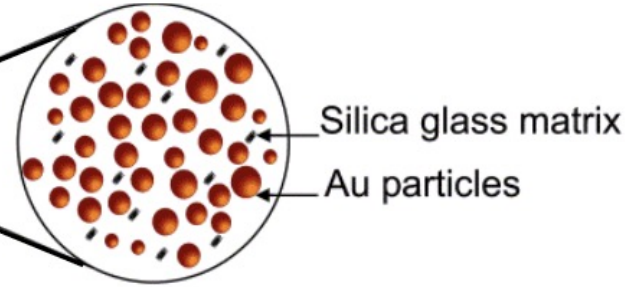
Program

Introduction to the concepts of nanoscale science	week 1	
From atoms to bulk: electronic states	week 2	
Imaging and manipulation at the atomic scale: scanning probe techniques	weeks 3-4	
Magnetism at the nanoscale: magnetic data storage concepts (hard disk drive)	weeks 5-7	Rusponi
Spin transport: spin valve, GMR and TMR effects	week 8	Rusponi
Making the nanostructures: top-down and bottom-up approaches	...	
Electron transport in low-dimensional systems	...	
Characterization of structural and electronic properties, for example by TEM, XPS, XAS	...	
2D materials	...	

Nanoscale



(Quantum) Size Effects



Westminster Abbey,
East-Window

Medieval Nanotechnology



Lycurgus Cup

Au and Ag particles, 70 nm

Au nanoparticles



Michael Faraday discovered in **1851** that the colors of ruby gold were due to its finely divided state



Original Au colloids still on display at the Royal Institution

Au nanoparticles

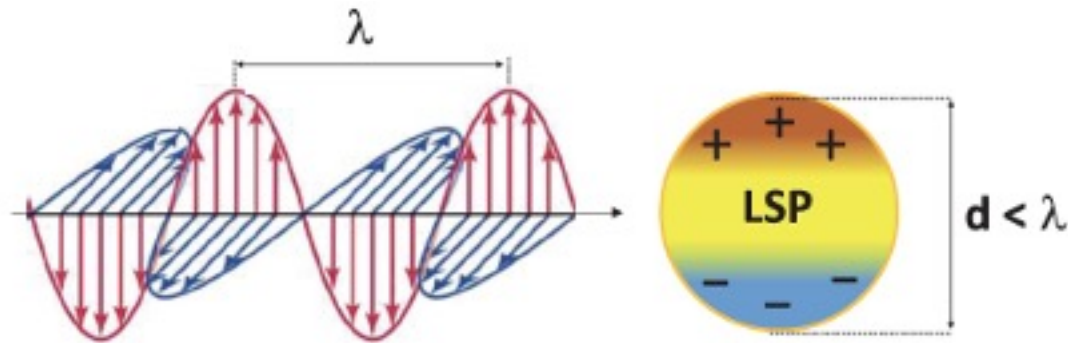
Plasmons: collective oscillations of free electrons in metals

Light: limited penetration depth (skin depth)

→ excitation of Surface Plasmon Resonances

Metallic nanoparticles (size comparable to the metal skin depth)

→ Localized Surface Plasmon Resonances

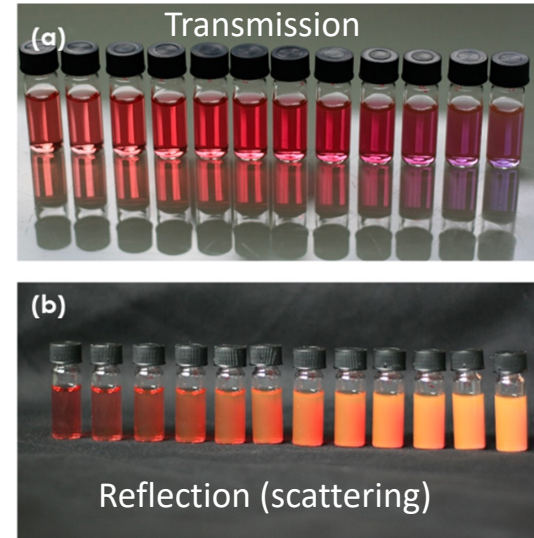


Au nanoparticles, size 20 – 100 nm

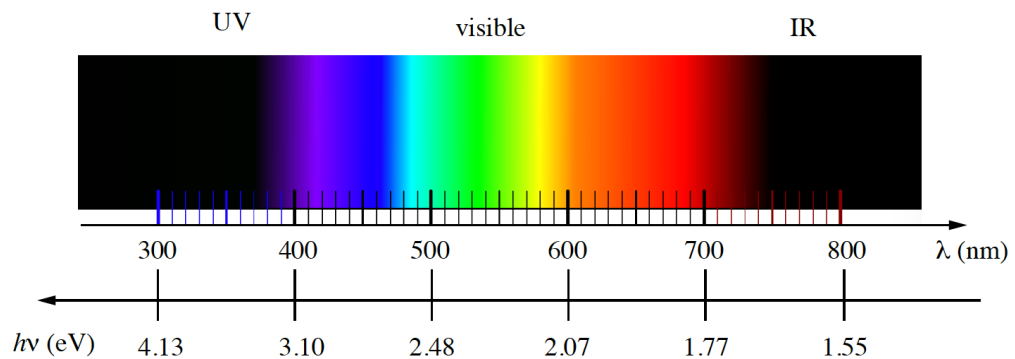
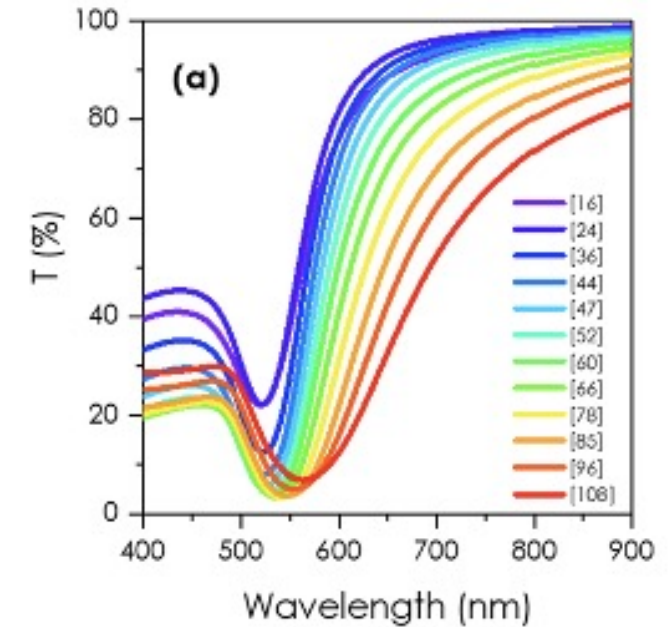
the plasmon resonance is in the 500 - 600 nm range (green) → they appear red / reddish in transmission

Au nanoparticles

A complete explanation of the plasmonic colours of gold nanoparticles and of the bichromatic effect,
J. Mater. Chem. C **11**, 15824 (2023)



Au₁₆ to Au₁₀₈



When scattering dominates the LSP resonance color is observed

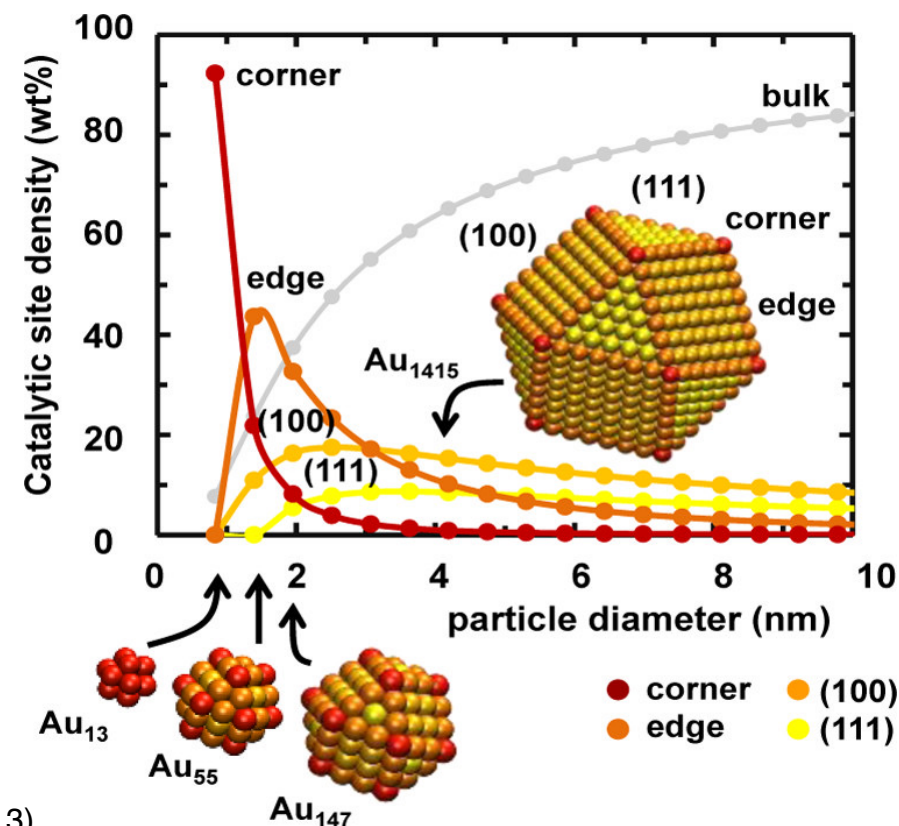
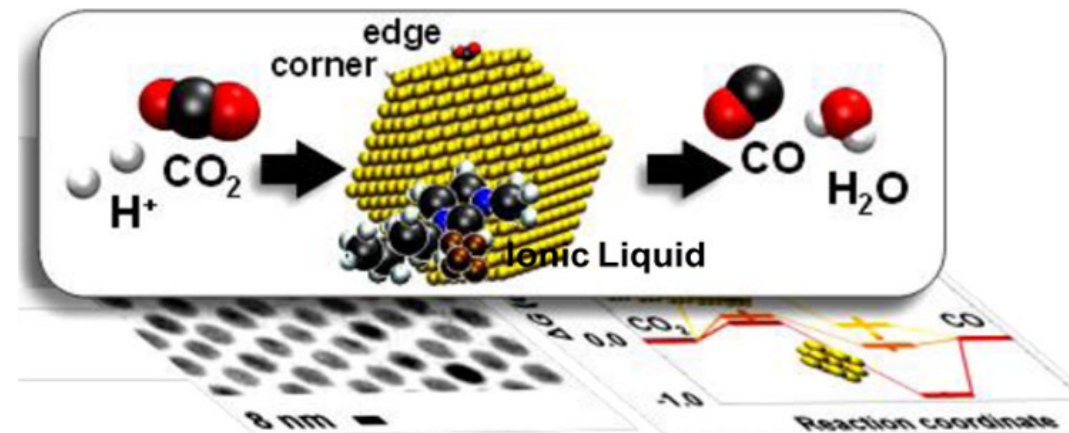
When absorption dominates, the complementary color is seen

Au nanoparticles

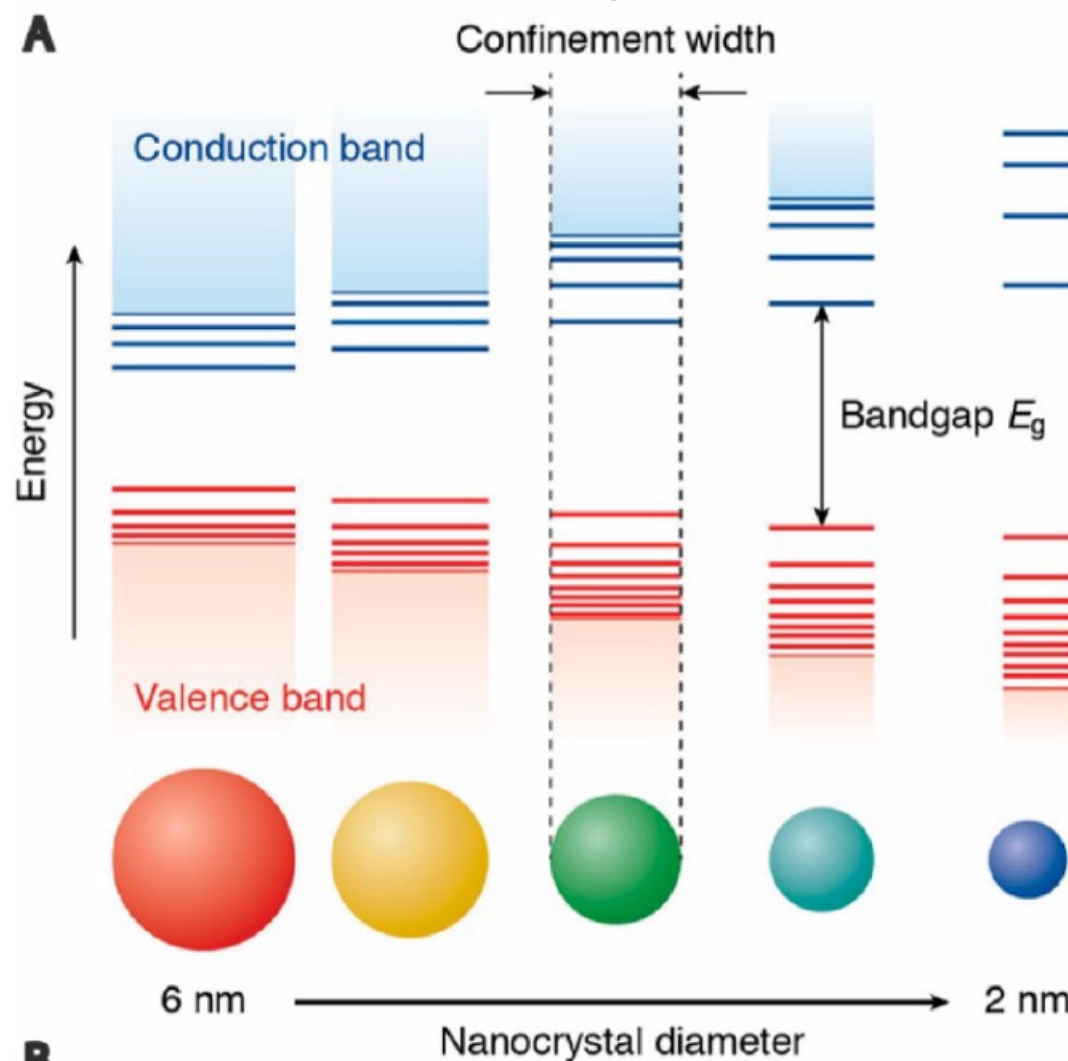
Modern applications:

organic photovoltaics
 sensor probes
 staining
 therapeutic agents
 drug delivery
 electronic conductors
 catalysis
 ...

The optical and electronic properties of gold nanoparticles are tunable by changing the size, shape, surface chemistry, or aggregation state.

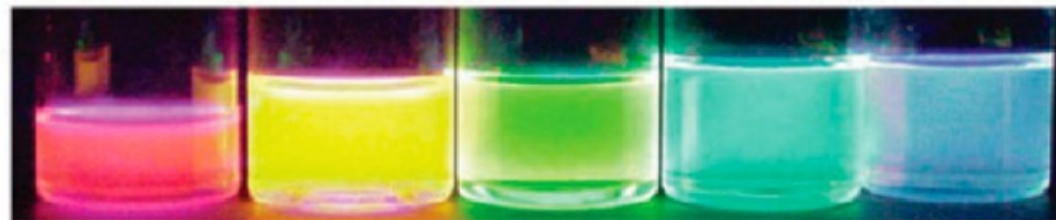


Semiconductor quantum dots



CdSe Nanocrystals

B



[10.1021/acs.jpclett.7b01640](https://doi.org/10.1021/acs.jpclett.7b01640)

J. Phys. Chem. Lett. **8**, 4077 (2017)

*Nothing tends so much
to the advancement of
knowledge as the
application of a
new instrument*

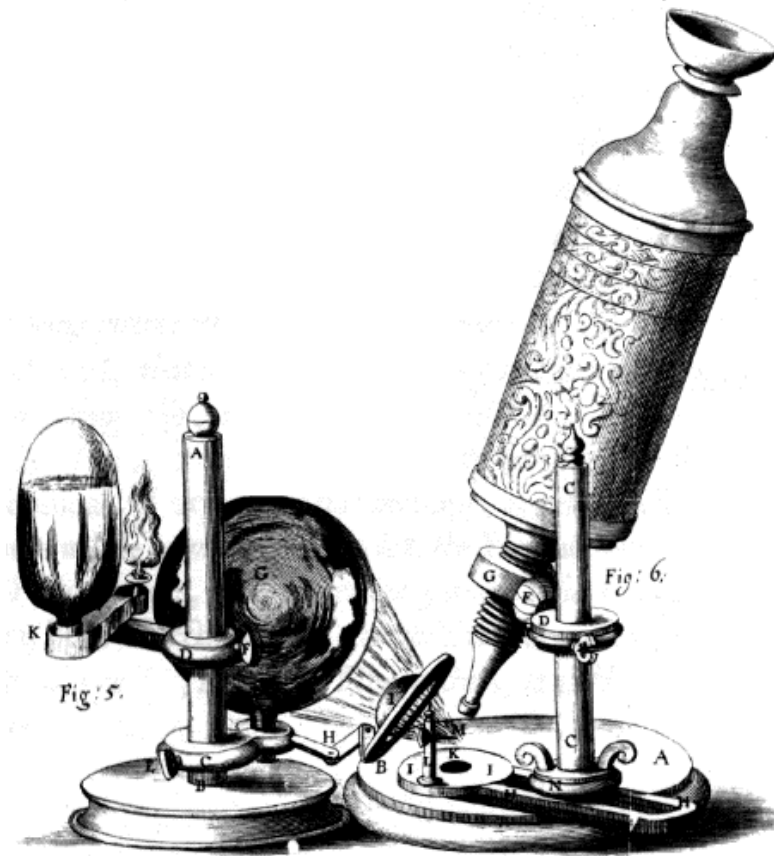
Sir Humphry Davy
(1778 – 1829)



THEPALMER / Getty Images

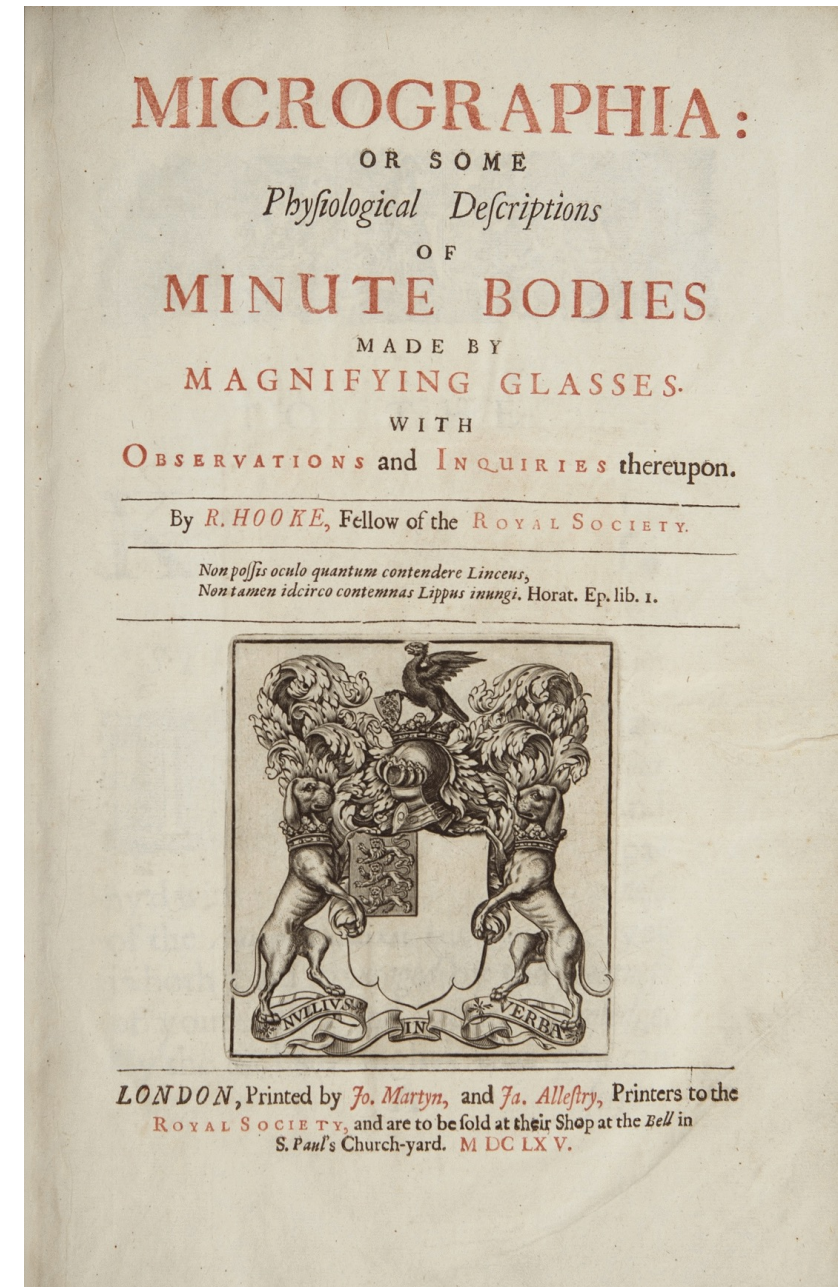
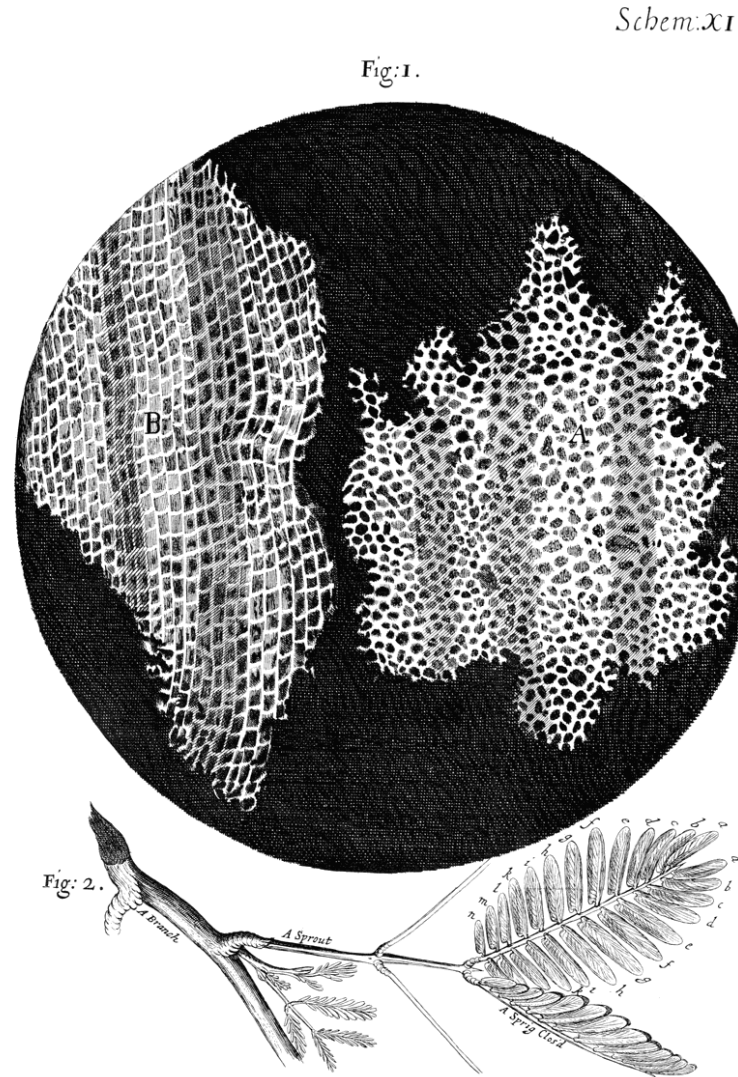
A Very Short History of Microscopy

Optical microscopes



discovery of cells
discovery of microorganisms

Robert Hooke (1635-1703) – compound microscopes, 30x
Antoni van Leeuwenhoek (1632-1723) – single-lens microscopes, 250x

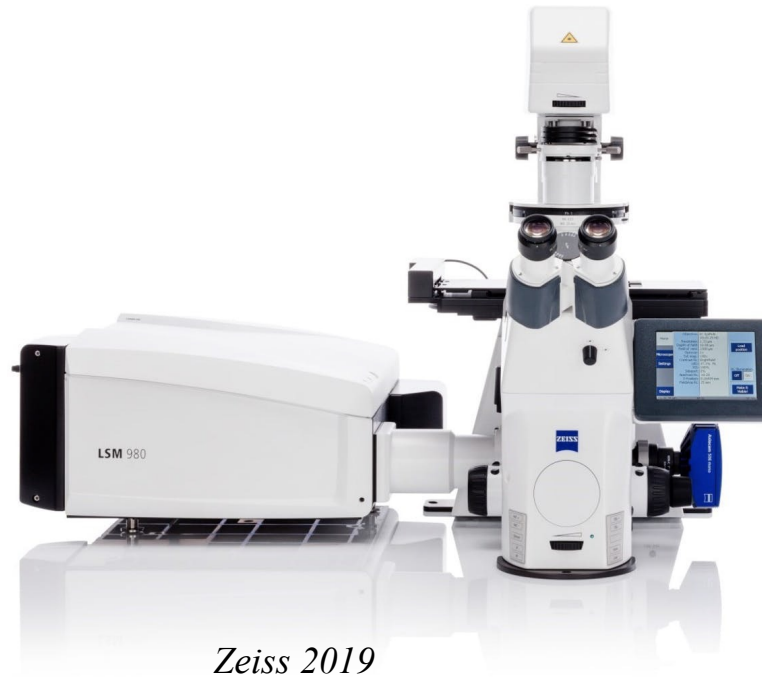


Optical microscope



Zeiss 1914

Confocal microscope



Zeiss 2019

Confocal and Widefield Fluorescence Microscopy

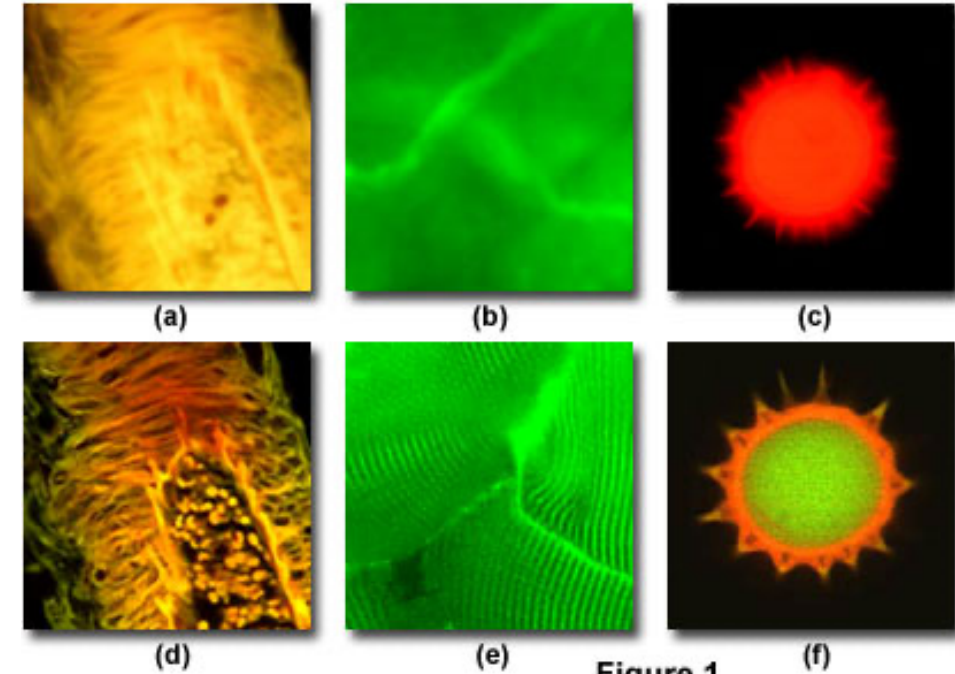


Figure 1

Excitation source: laser

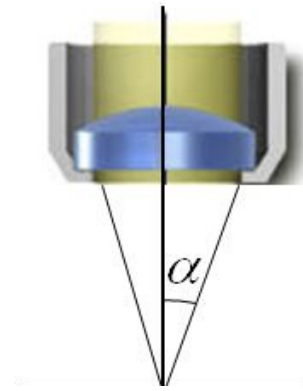
Advanced optical system that selects only the part of the sample that is on focus (field depth) + successive images (optical sections)

Fluorescence version (staining with fluorescent dyes)

Abbe's Diffraction Limit:

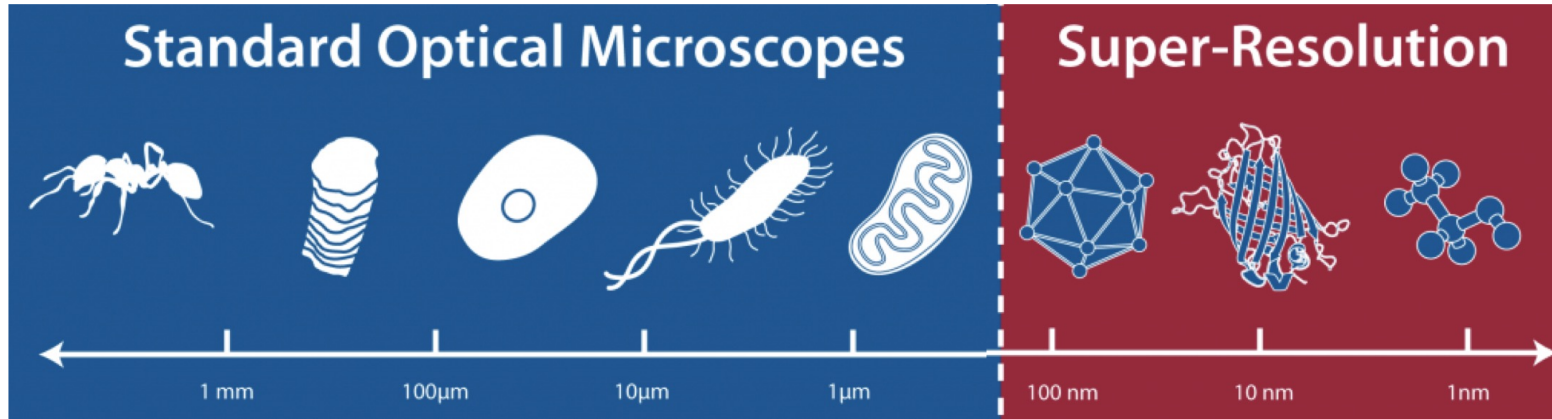
→ resolution limit

$$\Delta x \cong \frac{\lambda}{2n \sin \alpha}$$



Stefan Hell
STED

Eric Betzig
William E. Moerner
PALM

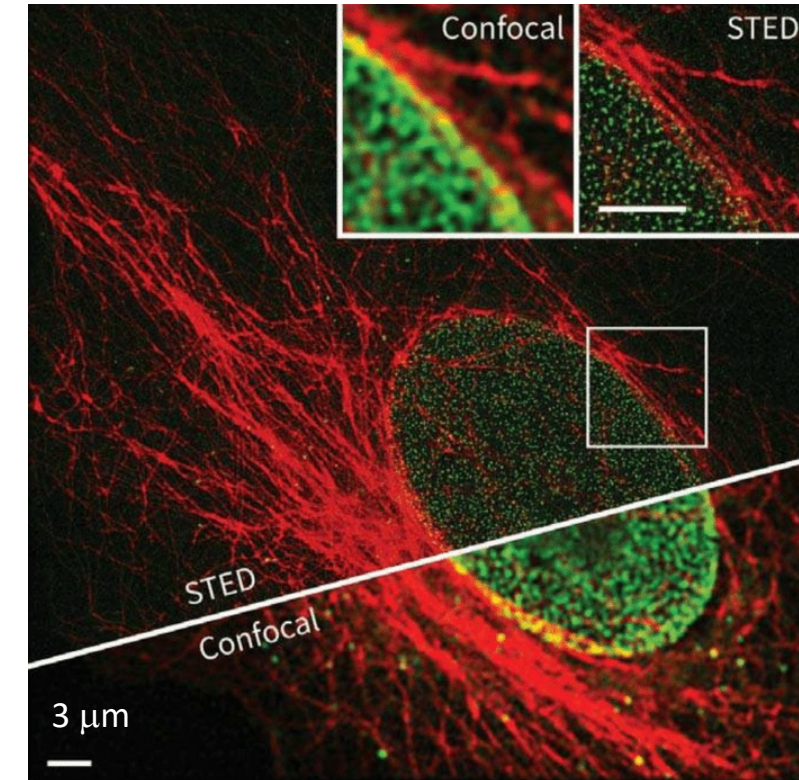


Abbe's Equation Modified for Fluorescence:

$$\Delta x \cong \frac{\lambda}{2n \sin \alpha \sqrt{1 + \zeta}}$$

$\zeta \rightarrow 0$	Abbe Limit
$\zeta \rightarrow \infty$	$\Delta x \rightarrow 0$

Saturation Factor $\zeta = I(x) / I_{sat}$



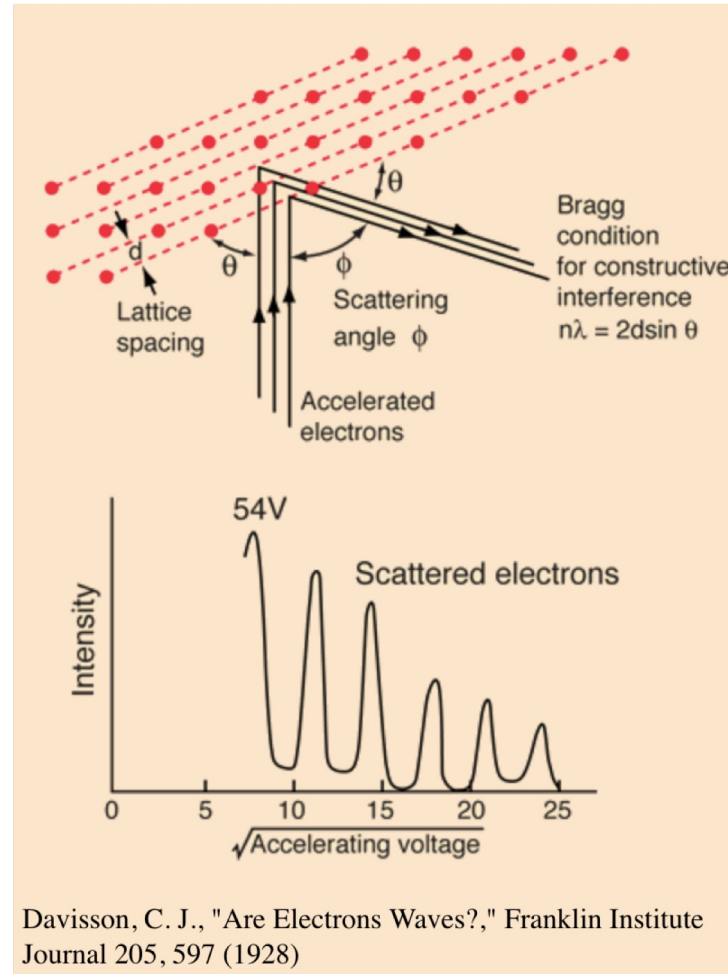
Wave nature of electrons

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}$$

wave-particle duality
de Broglie wavelength
(1924)

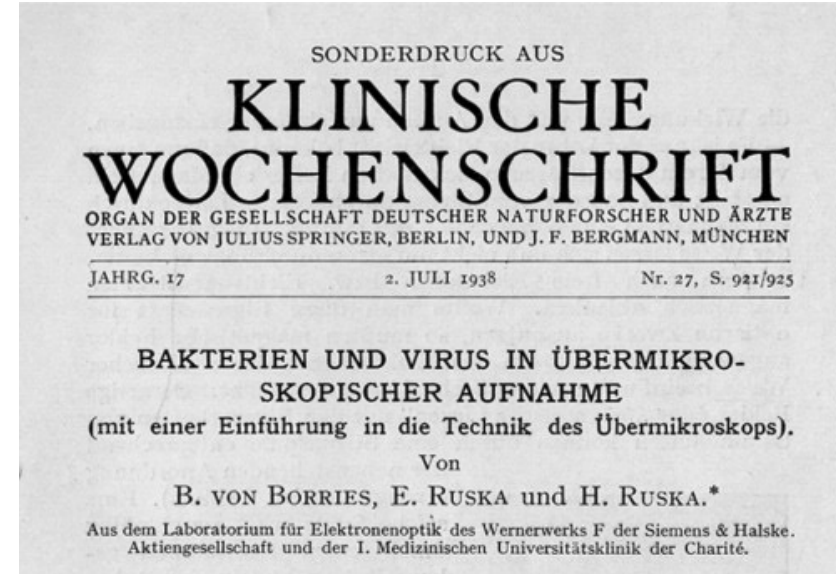
diffraction peaks observed

$$E = 54 \text{ eV}$$
$$\lambda = 0.17 \text{ nm}$$

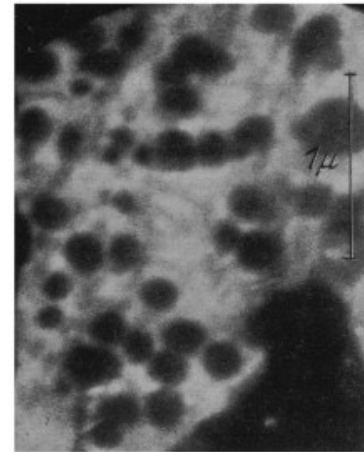


LEED (low energy electron diffraction), surface science tool

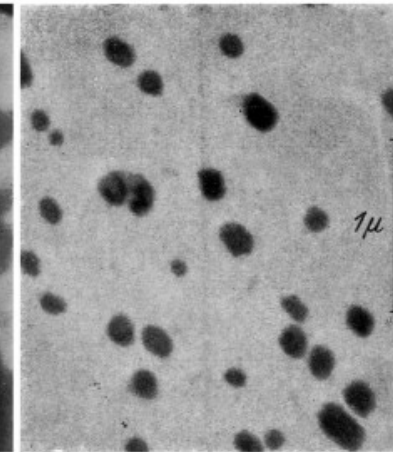
Transmission Electron Microscope (TEM)



(a)



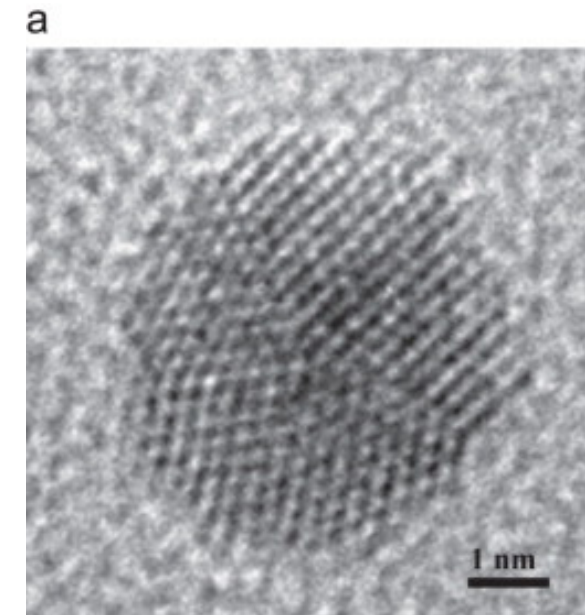
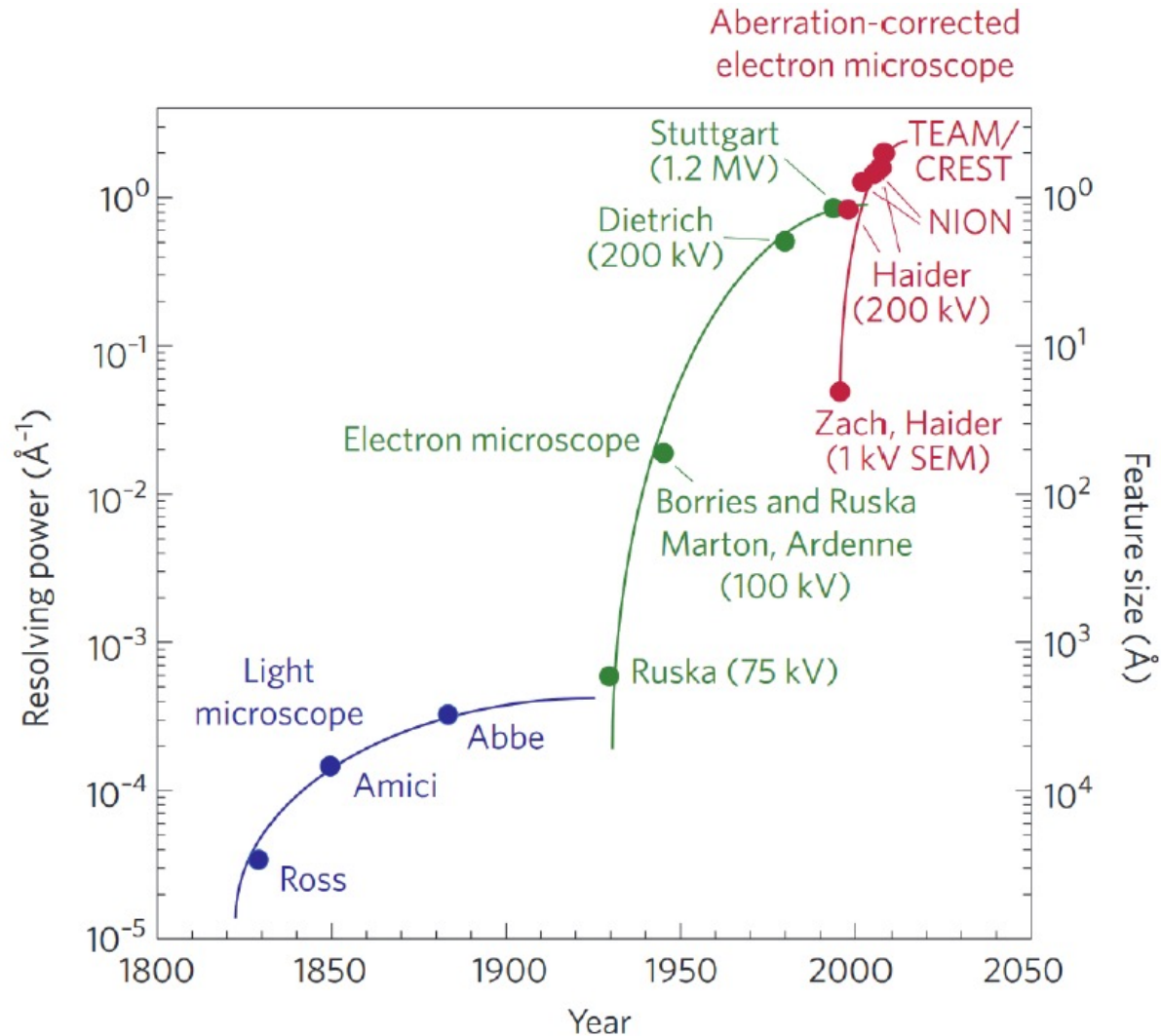
(b)



1933 Ernst Ruska

Transmission Electron Microscope (TEM)

energies in the range 50 keV to 400 keV



Au nanoparticle

DUBOCHET'S VITRIFICATION METHOD

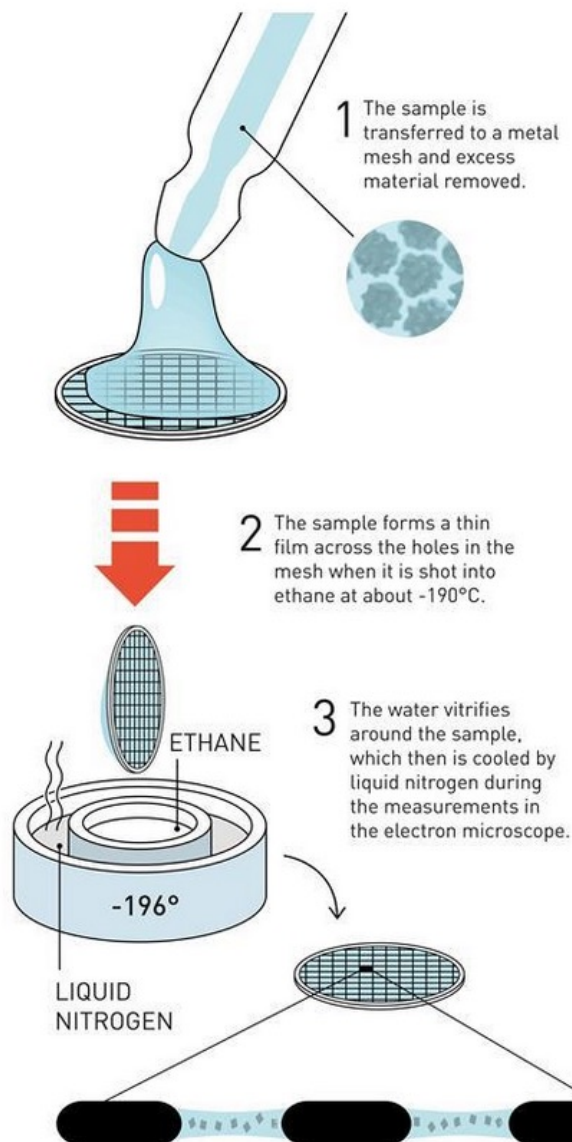


Illustration: ©Johan Jarnestad/The Royal Swedish Academy of Sciences

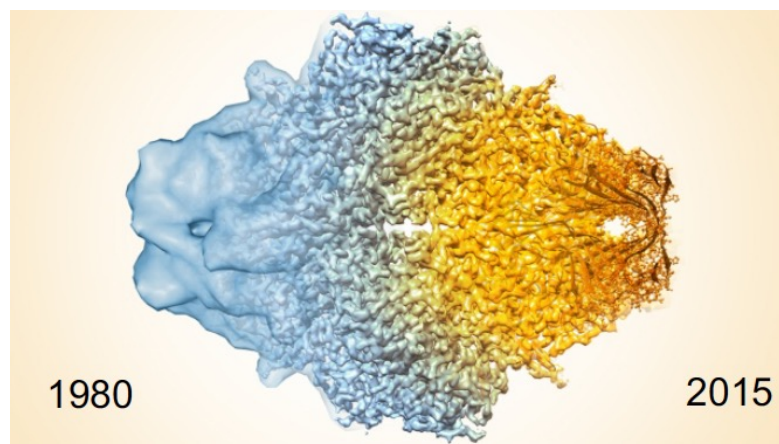
Cryo TEM



Jacques Dubochet
Joachim Frank
Richard Henderson

biological samples are not compatible with UHV:
water desorbs and the sample is destroyed by the
TEM e-beam

vitrification: rapid cooling of the sample, no water
crystallization, but vitreous matrix that protects the
biological samples



1986



Helv. Phys. Acta **55**, 726 (1982)



Scanning Tunneling Microscope (STM)

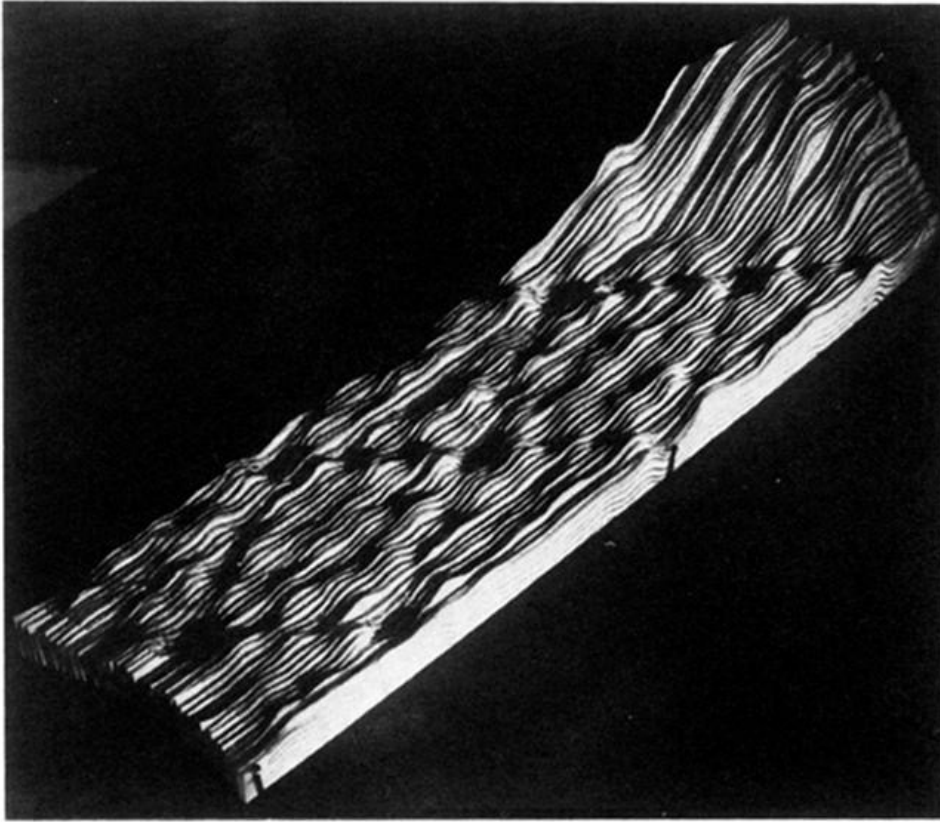
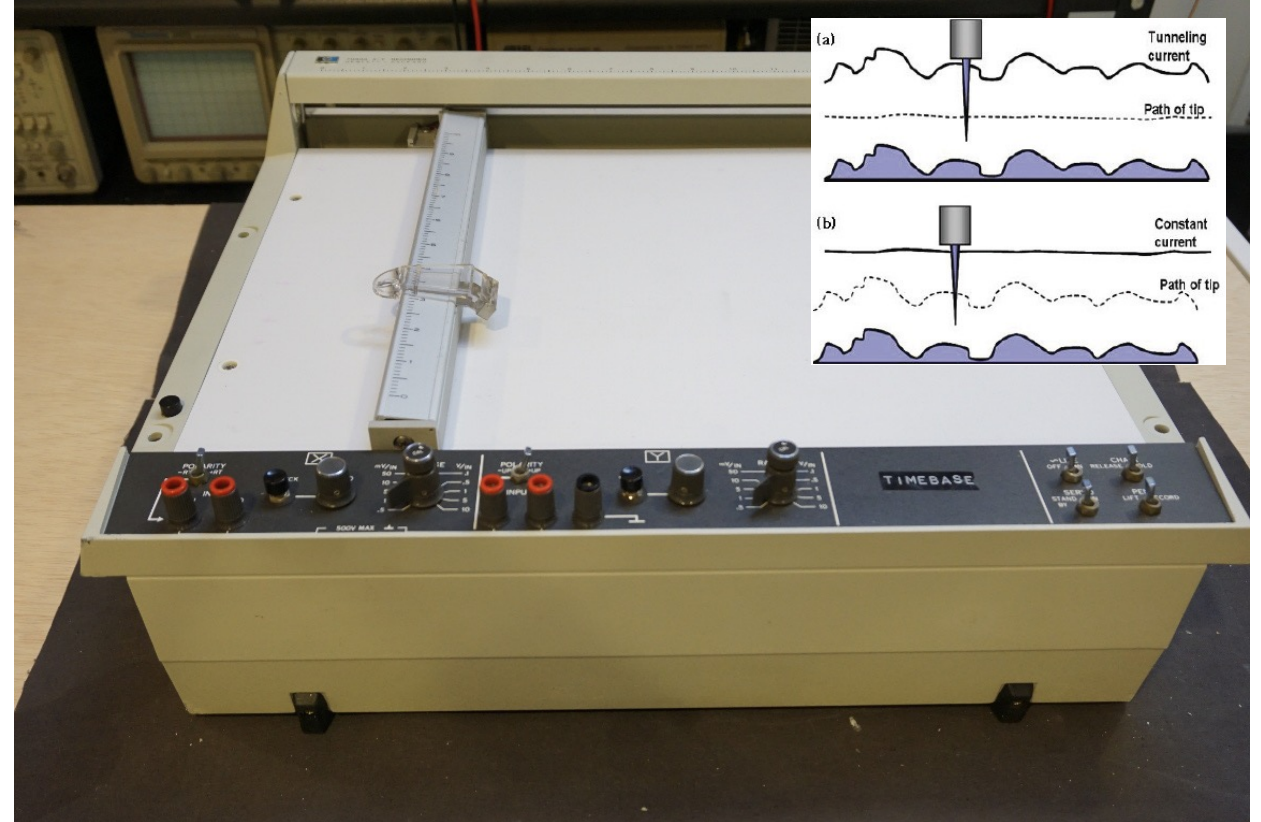
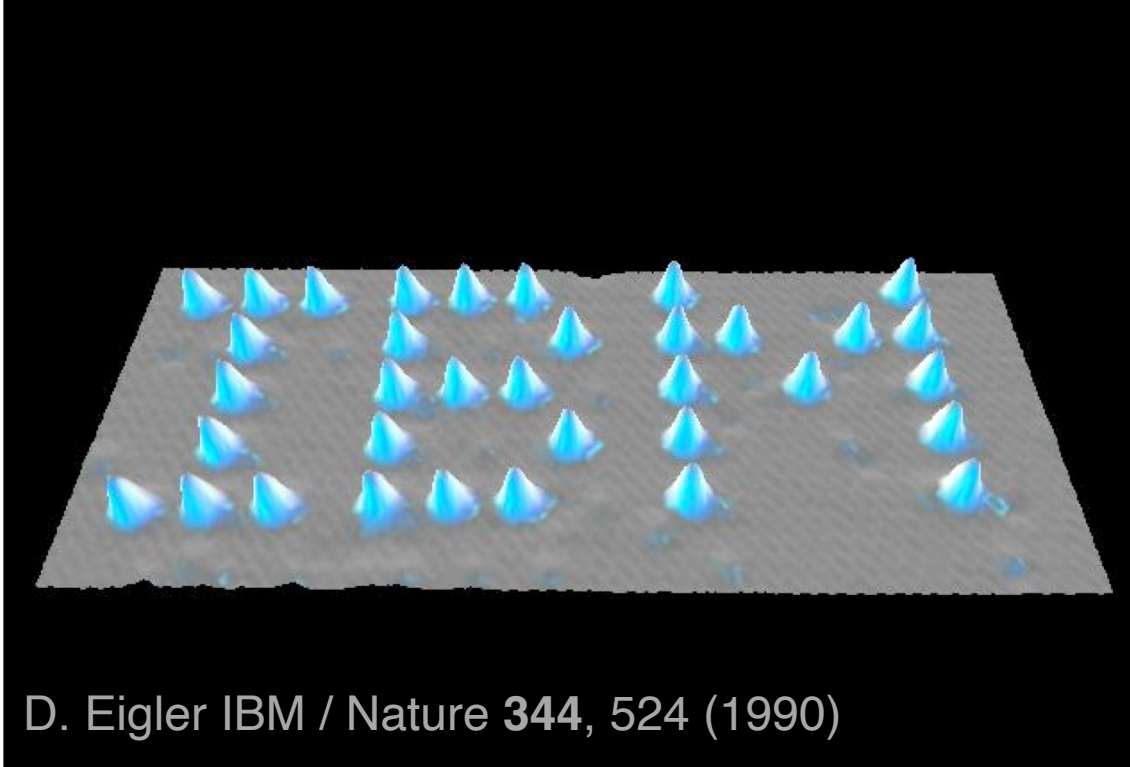


FIG. 1. Relief of two complete 7×7 unit cells, with nine minima and twelve maxima each, taken at 300°C . Heights are enhanced by 55%; the hill at the right grows to a maximal height of $15 \text{ \AA}$. The $[\bar{2}11]$ direction points from right to left, along the long diagonal.



Scanning Tunneling Microscope (STM)



D. Eigler IBM / Nature **344**, 524 (1990)

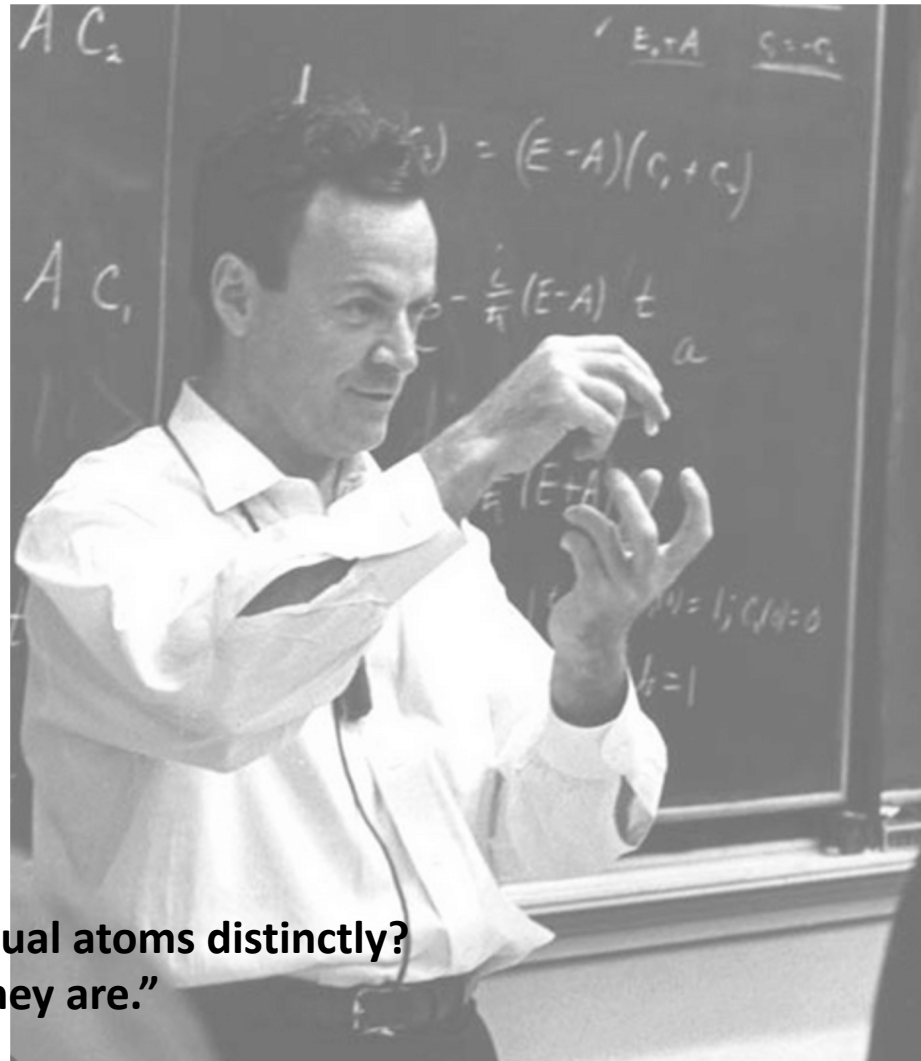
a powerful tool:

- imaging of surfaces and supported nanostructures
- manipulation at atomic level
- spectroscopy

for high-end applications, requirements:

- UHV
- low noise
- low vibrations
- low temperature

There's plenty of room at the bottom (1959)

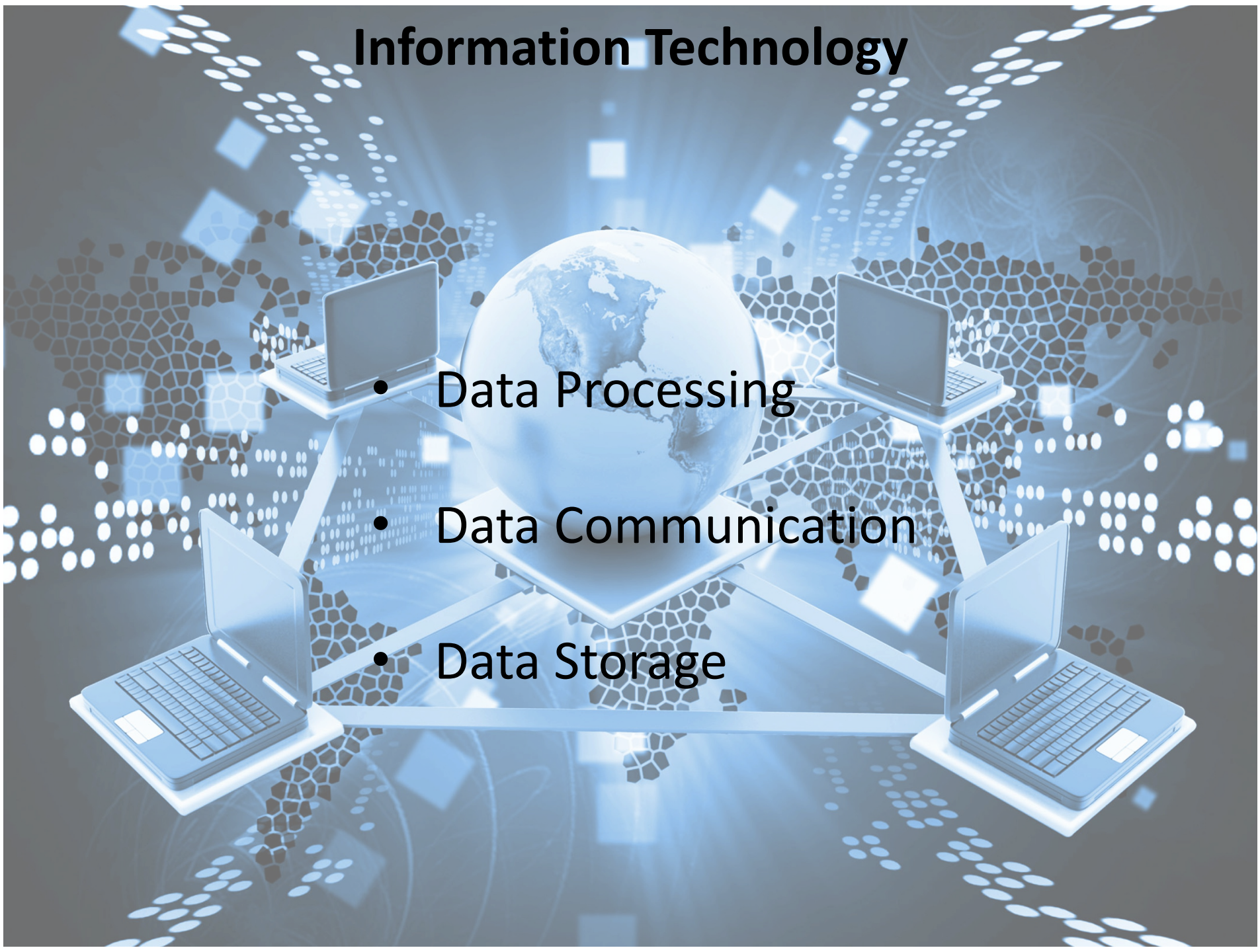


**“What good would it be to see individual atoms distinctly?
.... look at the atoms and see where they are.”**

**“But I am not afraid to consider the final question as to whether, ultimately
– in the great future – we can arrange the atoms the way we want; the very
atoms, all the way down!”**

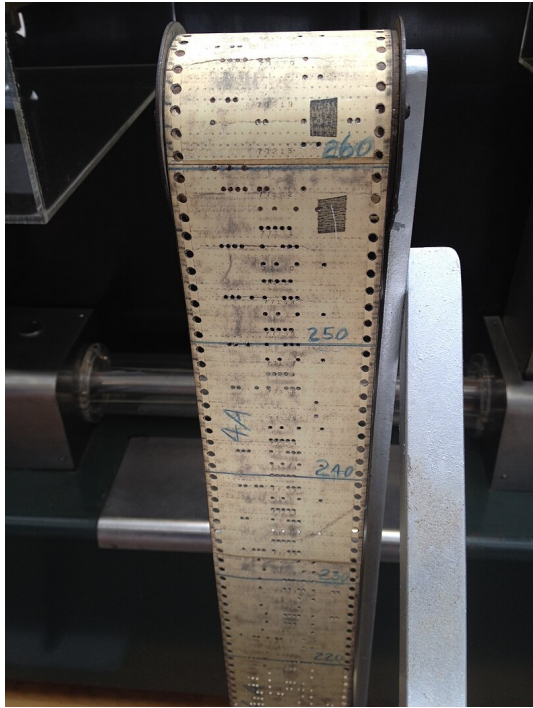
Richard Feynman

Information Technology



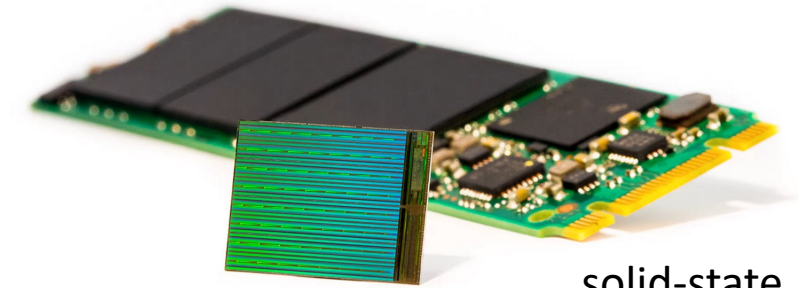
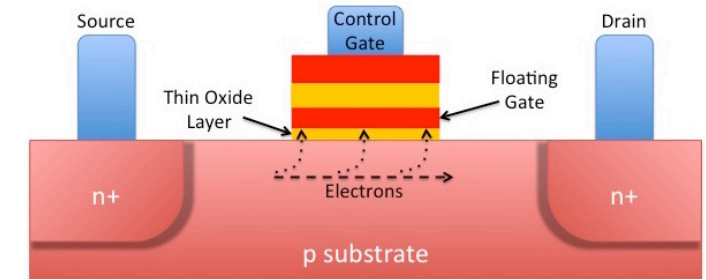
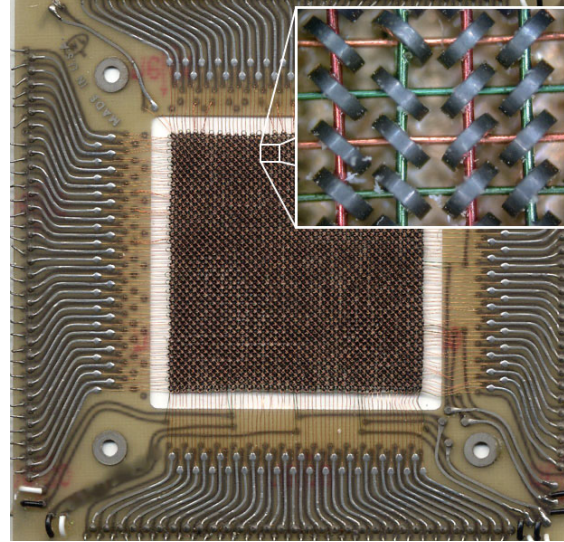
- Data Processing
- Data Communication
- Data Storage

Data storage (historical, not exhaustive)



punched tapes
punched cards

magnetic-core memory



solid-state
drive (SSD)



magnetic
hard-disk drive
(HDD)



digital data binary system

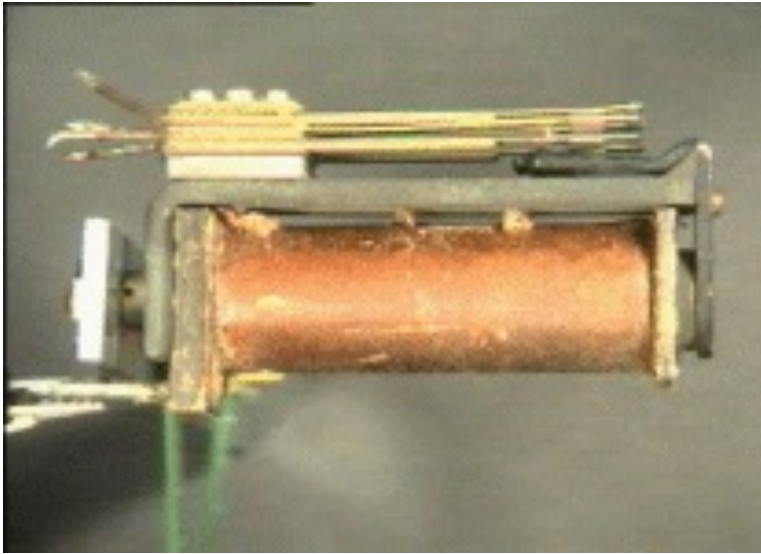
any number (or instruction)
can be represented
by a sequence of bits (binary digits)
which are in turn represented
by any mechanism capable of being
in two mutually exclusive states (1 and 0)

Data processing

binary systems - switches

Boolean algebra

(logical operators, variables: true = 1, false = 0)

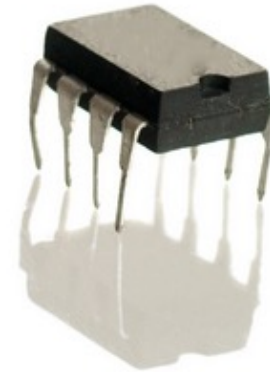


<http://zuse.zib.de/relay>

electromechanical relays
1930-1950



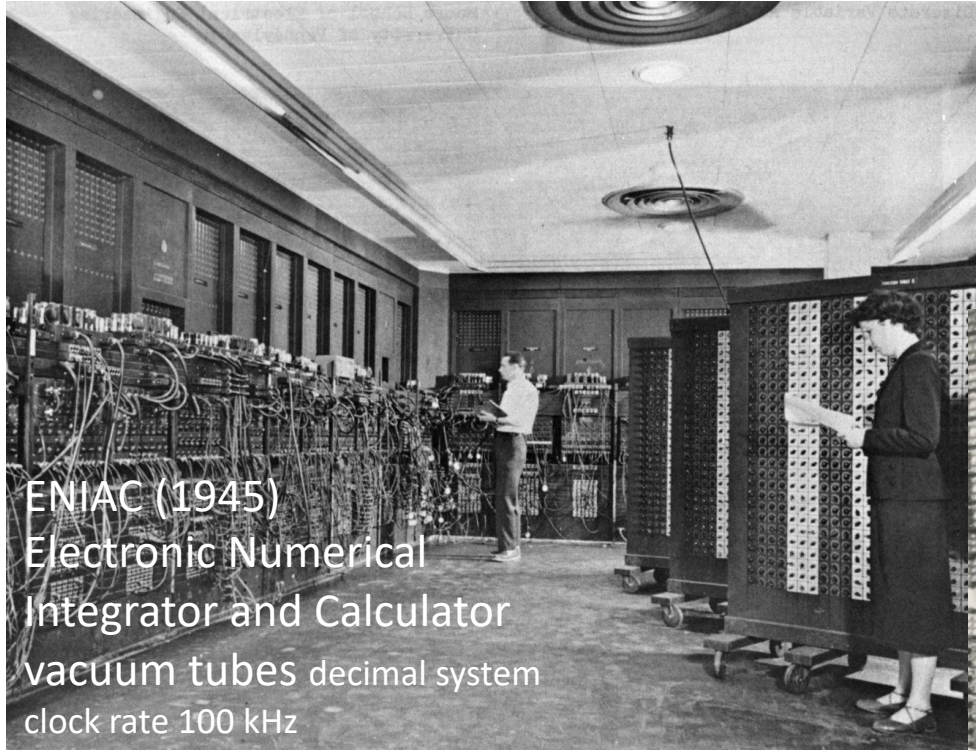
vacuum tubes – triodes
1940-1965



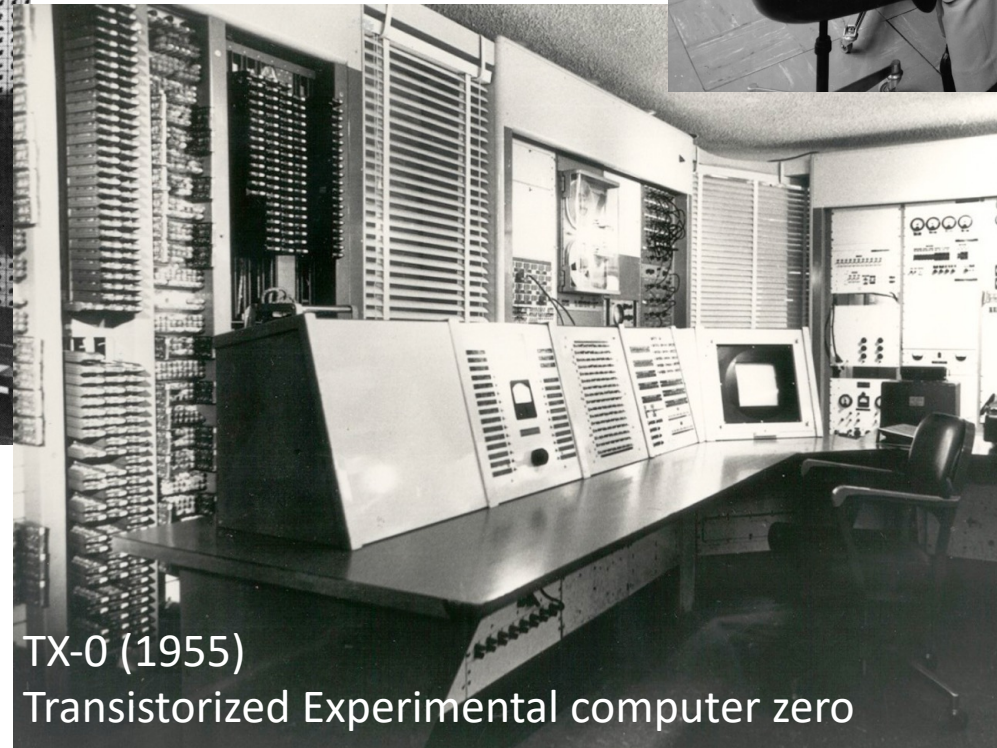
transistors
from 1960

Computers

Zuse Z3 (1941)
electromechanical relays
binary system



EDVAC (1949)
vacuum tubes binary



Smartphones: a Supercomputer in your Pocket



1984

10^7 \$

105 MHz

CPU clock rate

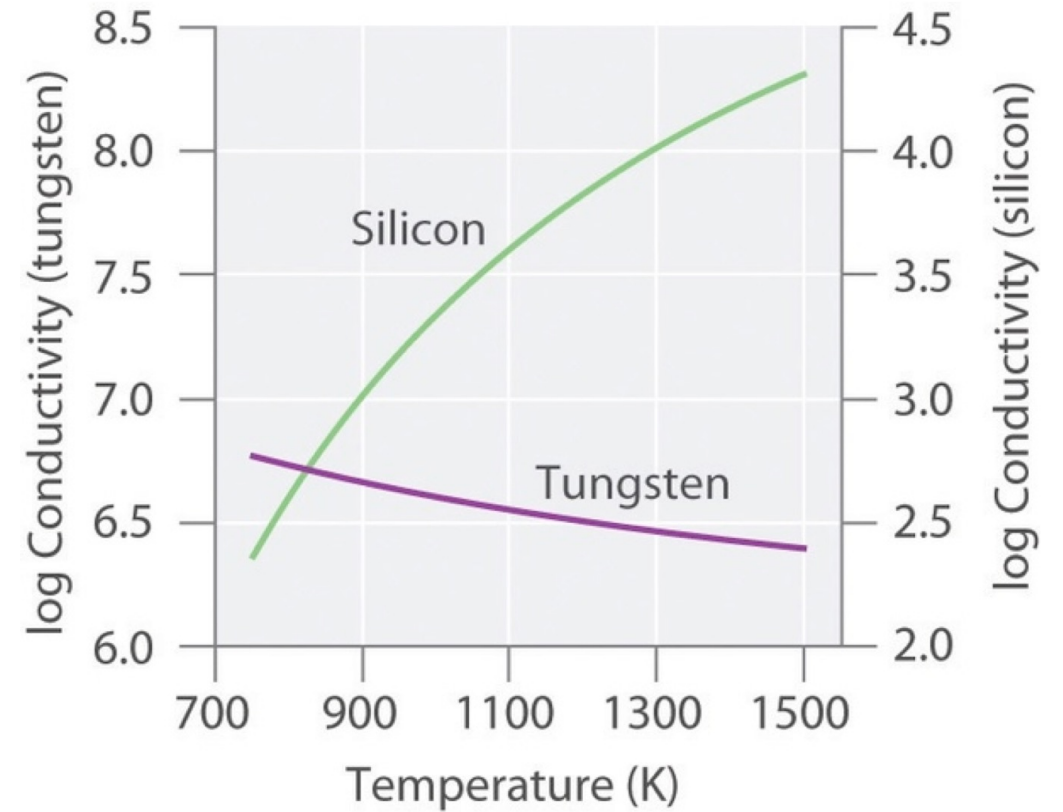
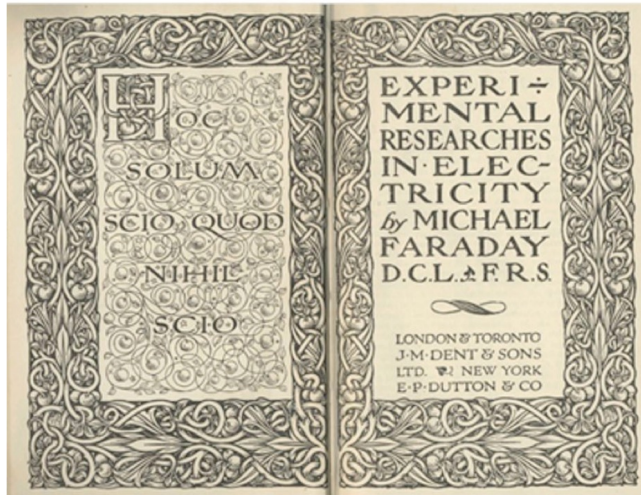
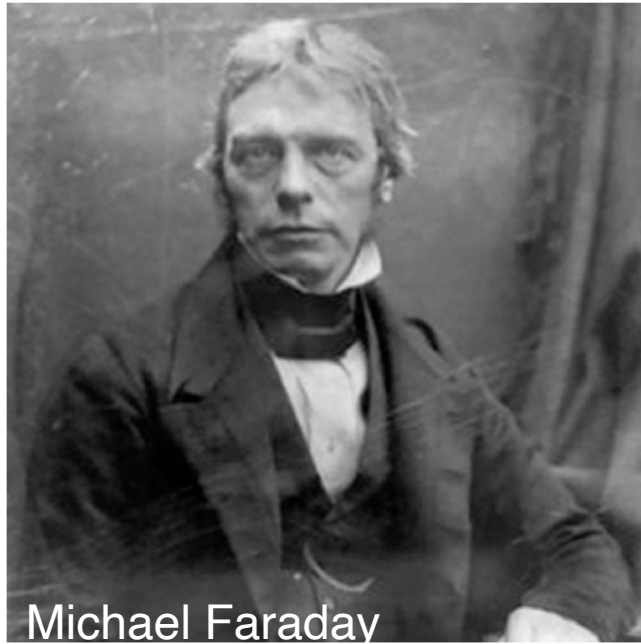


2023

10^3 \$

3.46 GHz

Semiconductors



discovery of semiconductors (1833)
(silver sulfide)



Semiconductors



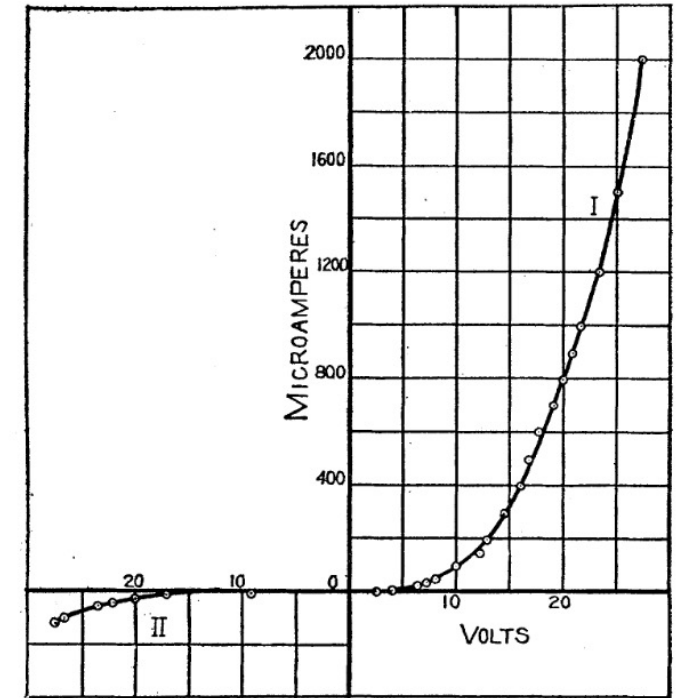
Karl Ferdinand Braun

Ann. der Physik und Chemie (1874)
"Ueber die Stromleitung durch
Schwefelmetalle"



lead sulfide (galena)
wire contact (cat whisker)

unilateral conduction →
crystal detector
point-contact diode



G.W. Pierce
Phys. Rev. 5, 31 (1907)

carborundum

Transistor discovery (1947)



Transistor discovery (1947)

Phys. Rev. **74**, 230 (1948)

The Transistor, A Semi-Conductor Triode

J. BARDEEN AND W. H. BRATTAIN

Bell Telephone Laboratories, Murray Hill, New Jersey

June 25, 1948

A THREE-ELEMENT electronic device which utilizes a newly discovered principle involving a semiconductor as the basic element is described. It may be employed as an amplifier, oscillator, and for other purposes for which vacuum tubes are ordinarily used. The device consists of three electrodes placed on a block of germanium¹ as shown schematically in Fig. 1. Two, called the emitter and collector, are of the point-contact rectifier type and are placed in close proximity (separation $\sim .005$ to $.025$ cm) on the upper surface. The third is a large area low resistance contact on the base.

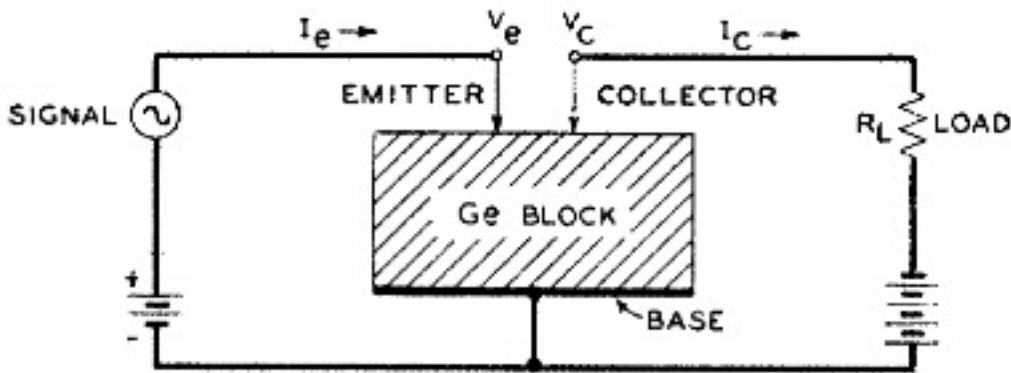
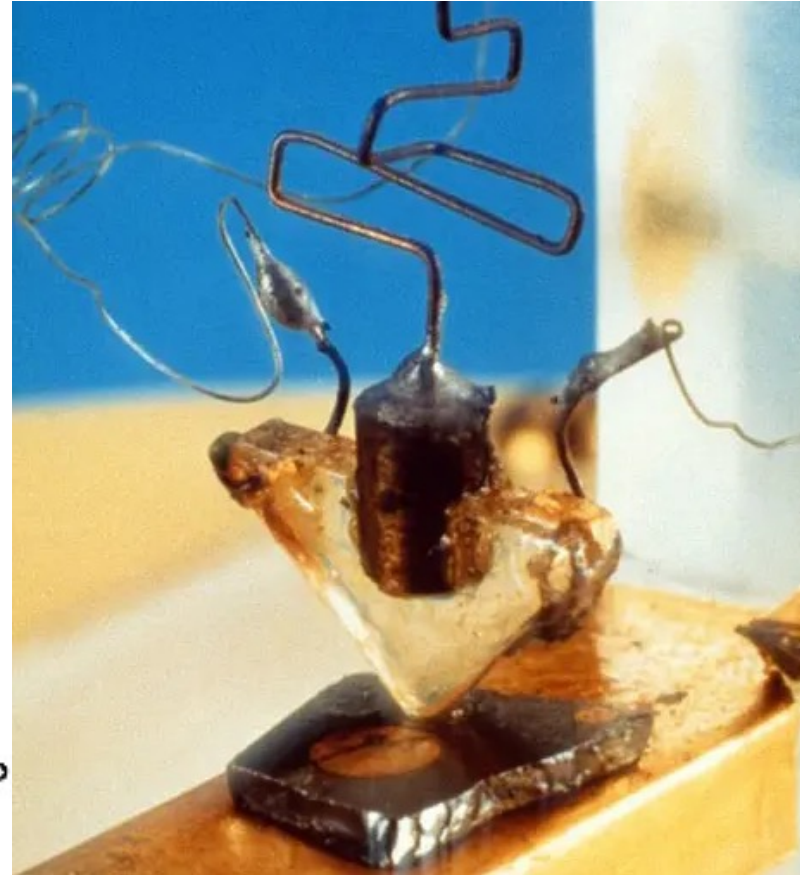
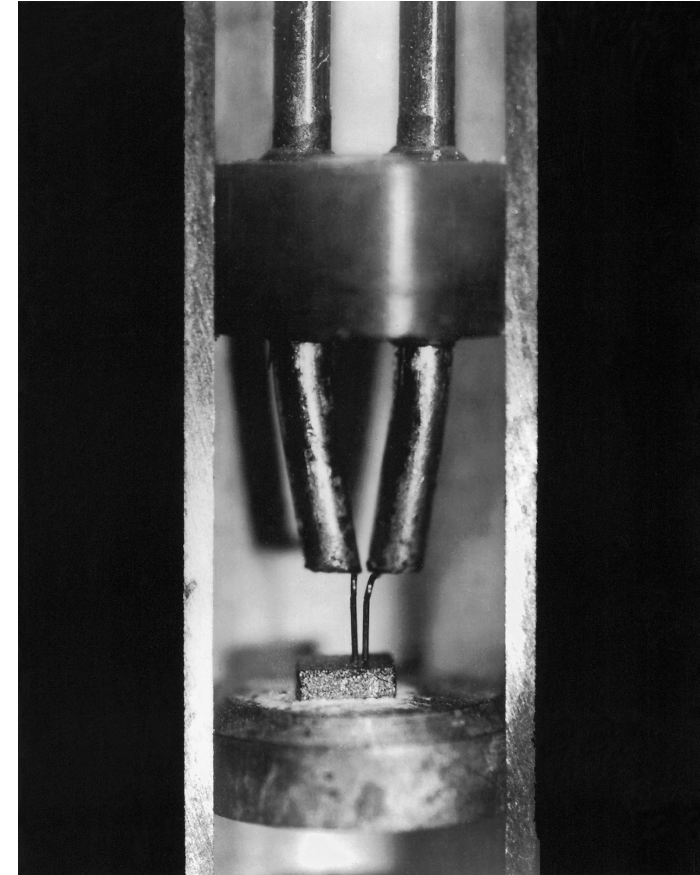


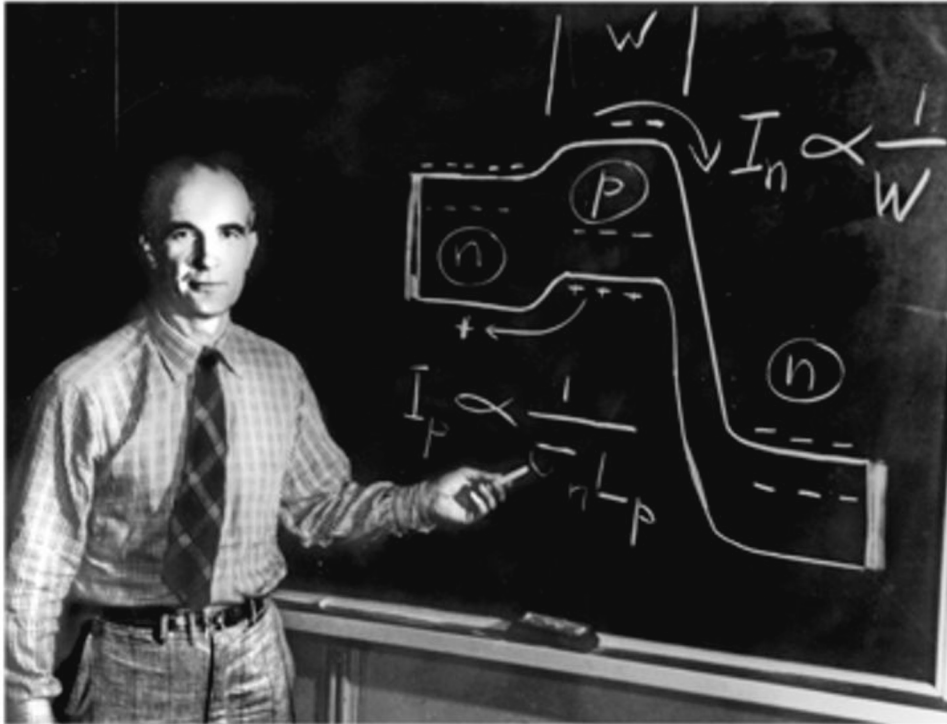
FIG. 1. Schematic of semi-conductor triode.



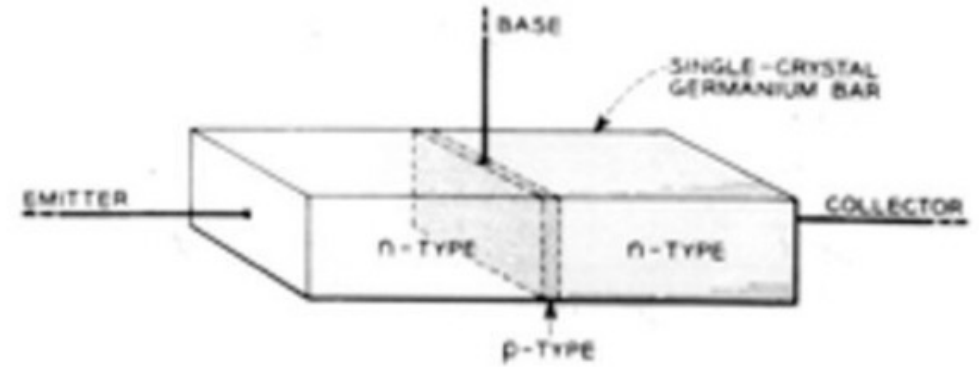
point contact transistor



Bipolar Junction Transistor (1948)



Bill Shockley



From germanium to silicon (mid 1950's)

**silicon transistors
now in production!**

silicon transistors — long awaited by the electronics industry — are finally out of the laboratory and on the market ... brought to you first by Texas Instruments, a leading transistor manufacturer. A new and unrivalled degree of design freedom is created by the TI n-p-n grown junction silicon transistor, now available in production units with glass-to-metal hermetic sealing. silicon transistors radically improve temperature stability and power handling while retaining the best amplification and frequency characteristics of previous semiconductor devices.

write today for detailed information on the silicon transistor!

TEXAS INSTRUMENTS
INCORPORATED
6000 LEMMON AVE. DALLAS 5, TEXAS

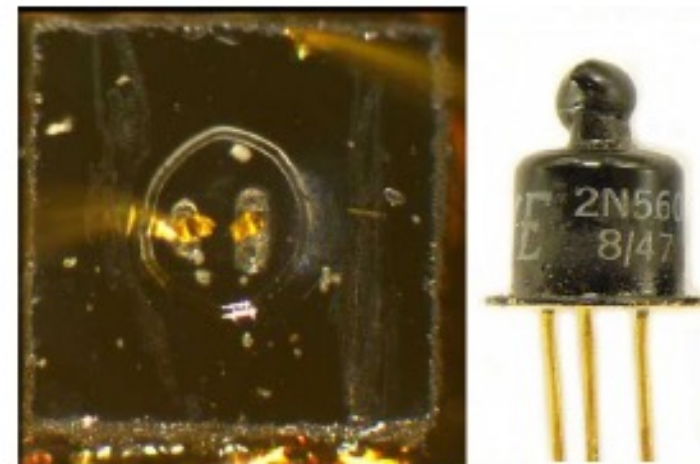
900
900
25
100
50
25
10
5
2
1

ACTUAL SIZE

ELECTRONICS — June, 1954 345



Morris Tanenbaum, Bell Labs, 1954/55



Shockley Semiconductor Lab (1955)



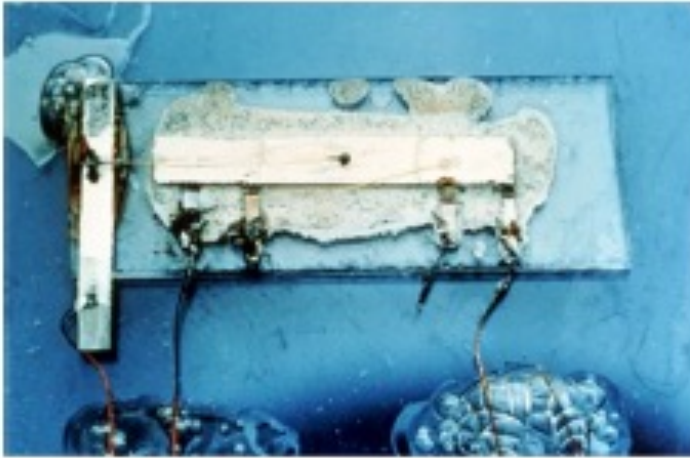
Fairchild Semiconductors (1957)





2000

Going 2D



Jack Kilby

TI

first all
semiconductor
solid circuit

(1958)

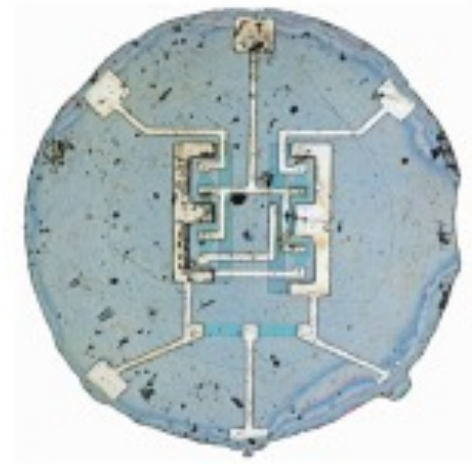


Jean Hoerni

Fairchild

first planar
process

(1960)



Robert Noyce

Fairchild

first planar
IC

(1960)

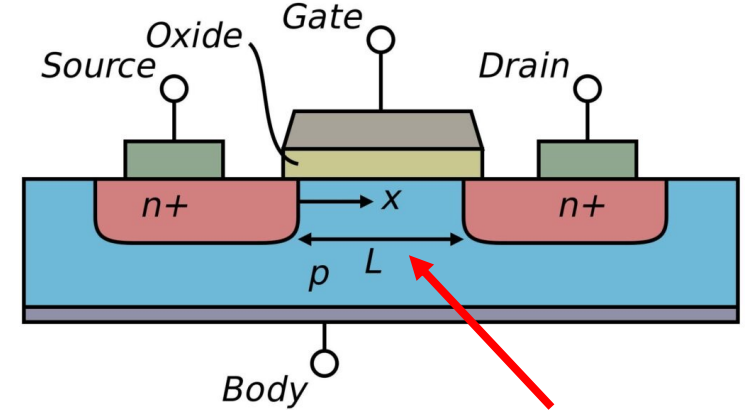
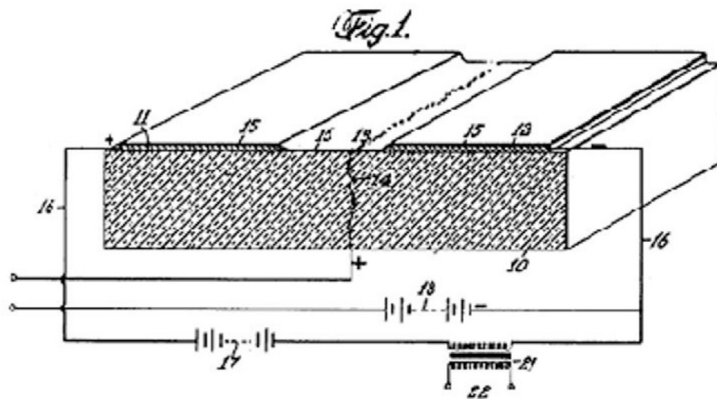
Field Effect Transistor

MOSFET (Metal-Oxide - Semiconductor FET)
Bell Labs (1959)



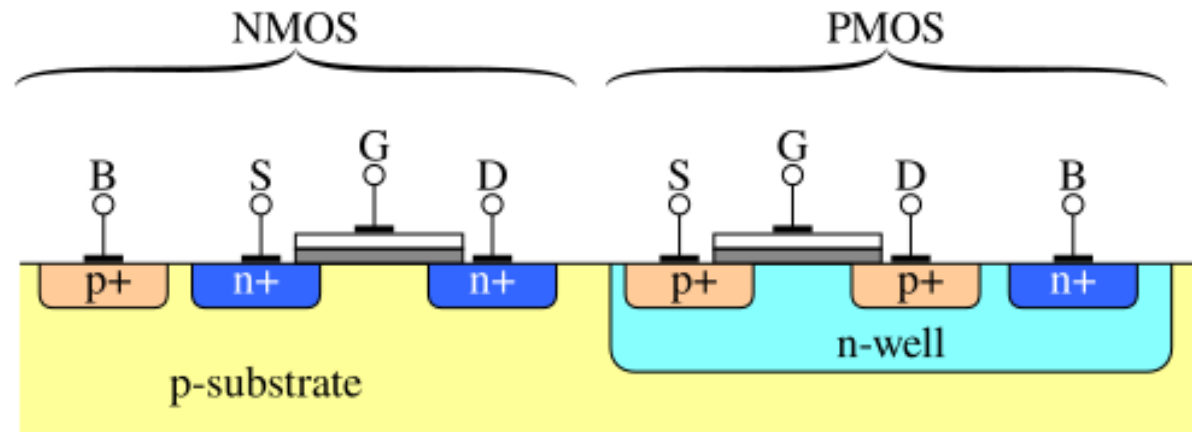
J.E. Lilienfeld, Bell Labs
US Patent (1926)
Semiconductor Field Effect Device

Jan. 28, 1930. J. E. LILIENFELD 1,745,175
METHOD AND APPARATUS FOR CONTROLLING ELECTRIC CURRENTS
Filed Oct. 8, 1926



gate length =
channel length

CMOS (Complementary Metal-Oxide – Semiconductor)
combining p-type and n-type MOSFETs for logic functions
Fairchild Semiconductors (1963)



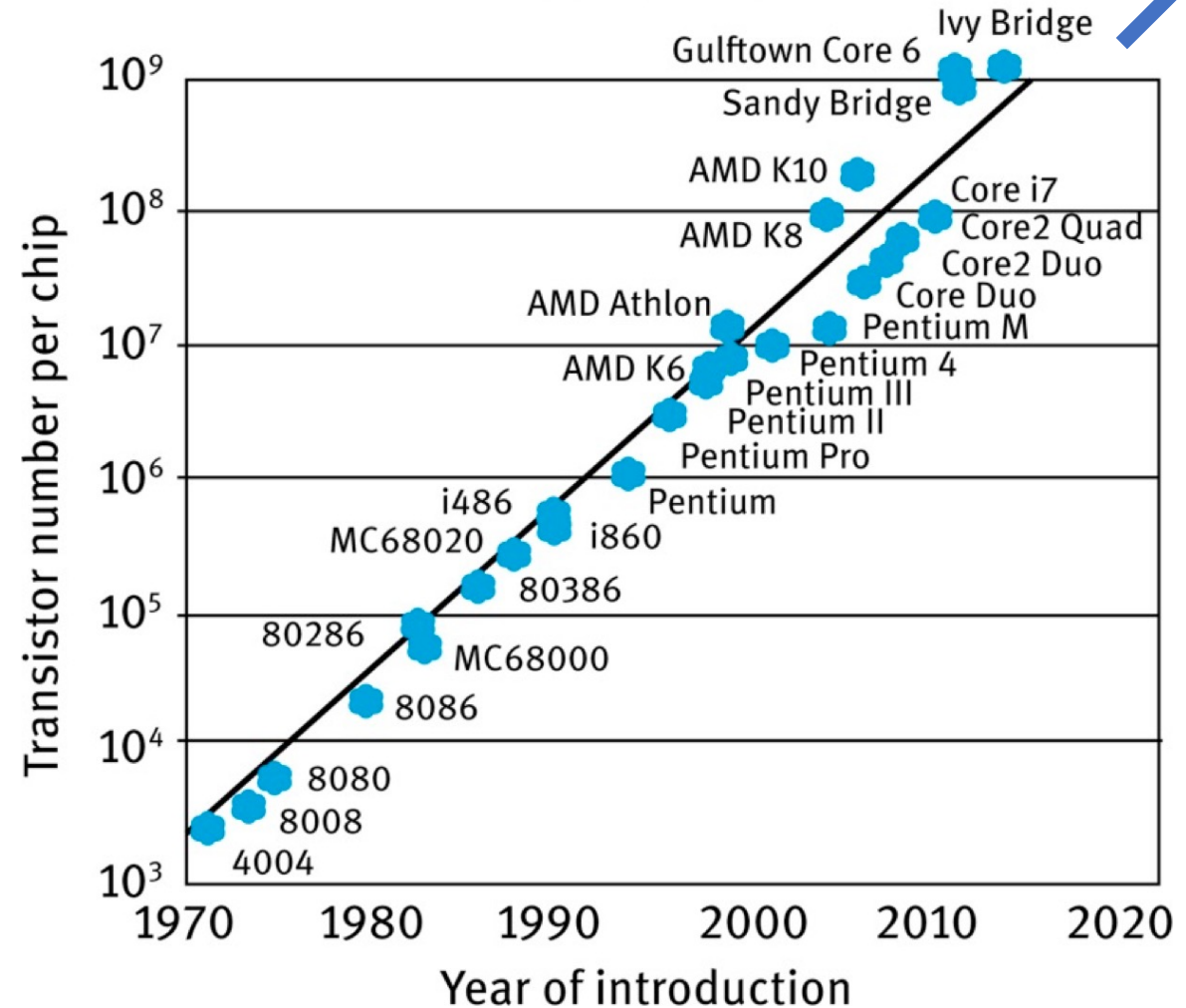
Miniaturization - Moore's law

Gordon E. Moore
Co-founder, Intel Corporation.

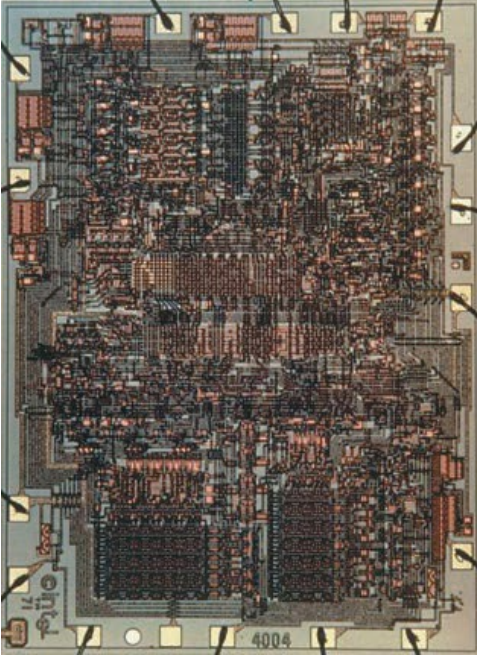
Electronics, Volume 38, Number 8 (1965)

“With unit cost falling as the number of components per circuit rises, by 1975 economics may dictate squeezing as many as 65,000 components on a single silicon chip.”

“The number of transistors on a piece of silicon will double every couple of years.”



Miniaturization

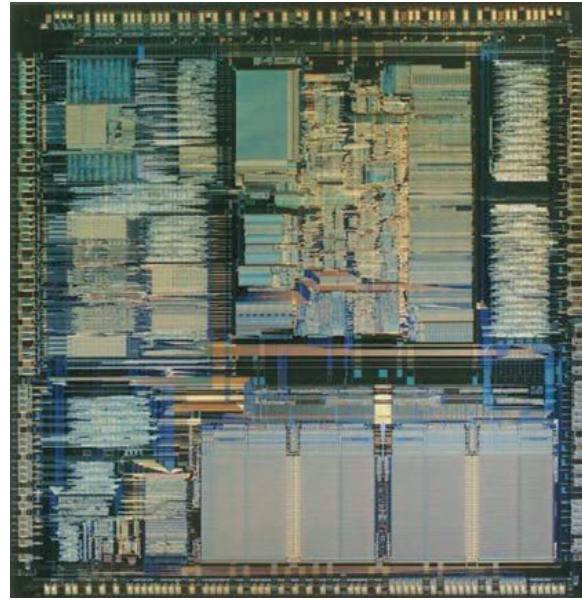


1971
Intel® 4004
processor

Initial clock speed:
108KHz

Transistors:
2,300

Manufacturing technology:
10 micron

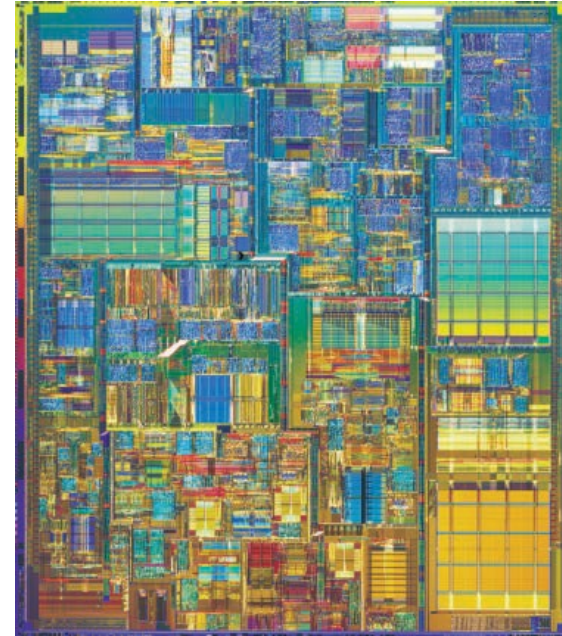


1985
Intel386™
processor

Initial clock speed:
16MHz

Transistors:
275,000

Manufacturing technology:
1.5 micron

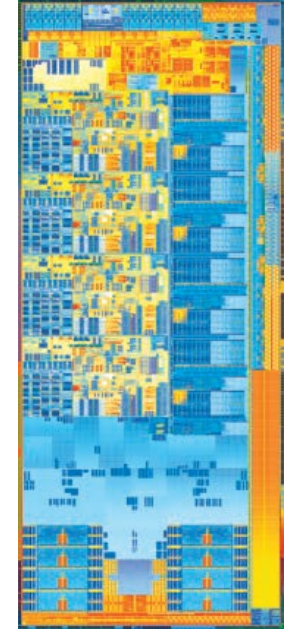


2000
Intel® Pentium® 4
processor

Initial clock speed:
1.5GHz

Transistors:
42 million

Manufacturing technology:
0.18 micron



2012
3rd generation Intel®
Core™ processor

Initial clock speed:
2.9GHz

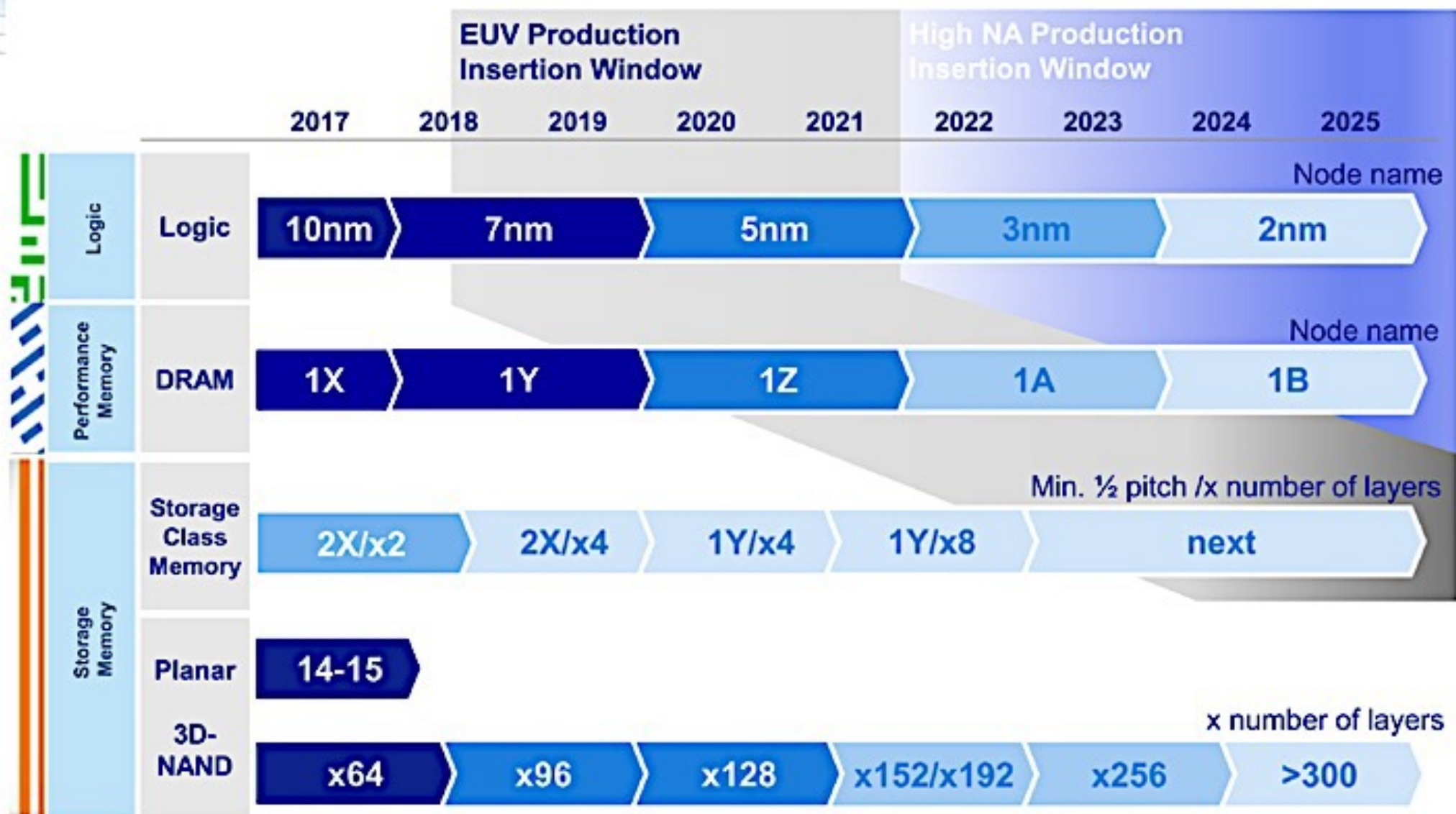
Transistors:
1.4 billion

Manufacturing technology:
22nm

Customers' scaling roadmaps continue

ASML

Public
Slide 9
8 November 2018



Source: ¹ Customers public statements, IC Knowledge LLC; ² ASML extrapolations

FET fabrication technology roadmaps - Nodes

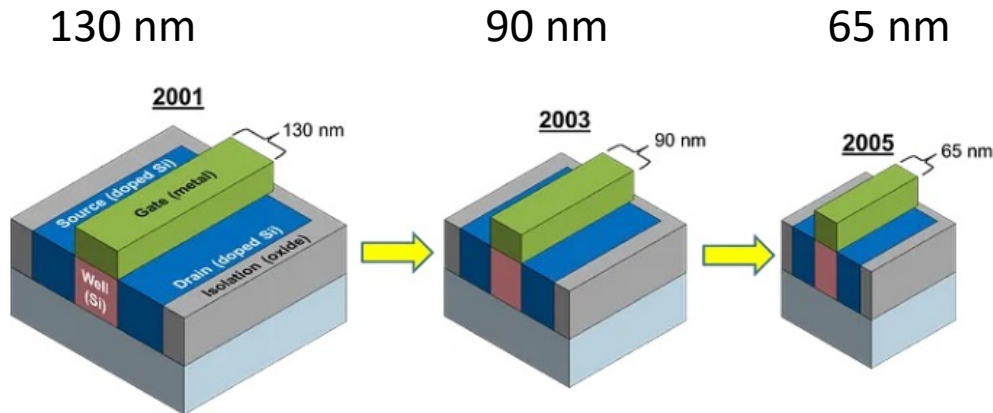
in early days until 2008

MOSFETs were purely planar, the node name (technology or process node) corresponds the size of the smallest feature on a processor, usually the **gate length**

50 μm mid 1960's

1 μm late 1960's

350 nm late 1990's

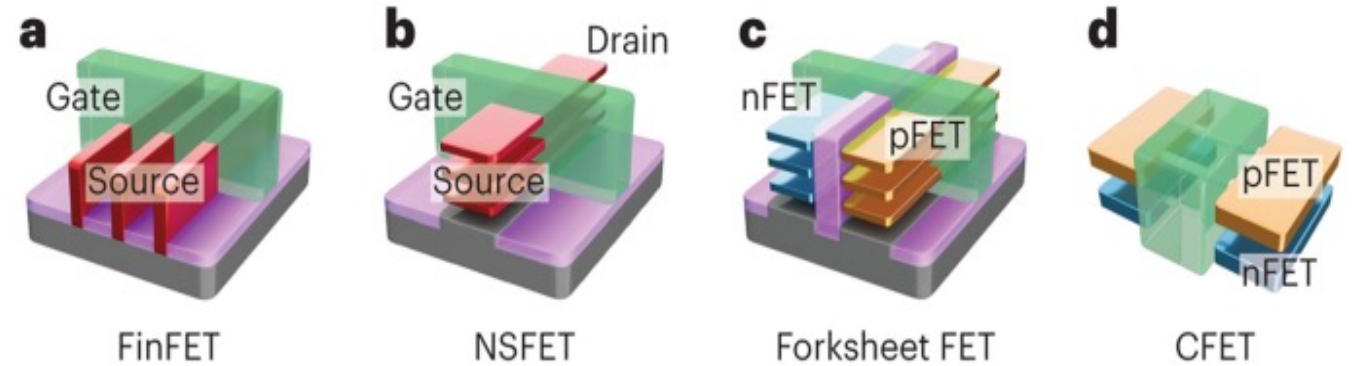


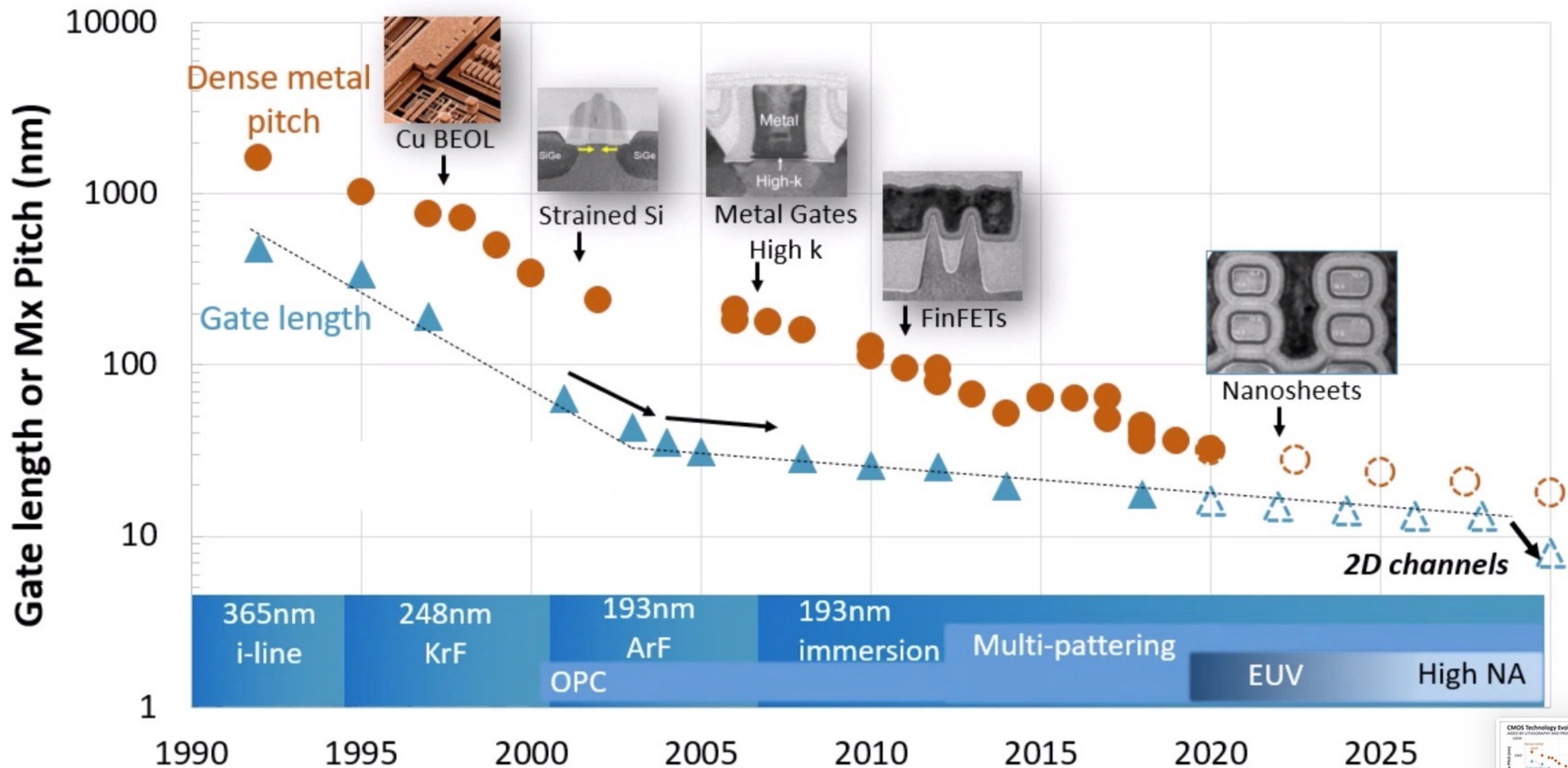
after 2008

transistors go in the third dimension;

the node name is not anymore related to feature sizes; it rather indicates the **transistor density**

other ways to optimize the density (packing, stacking in third dimension...)





Integrated Circuit Fabrication

thin film deposition
CVD, PVD, ALD

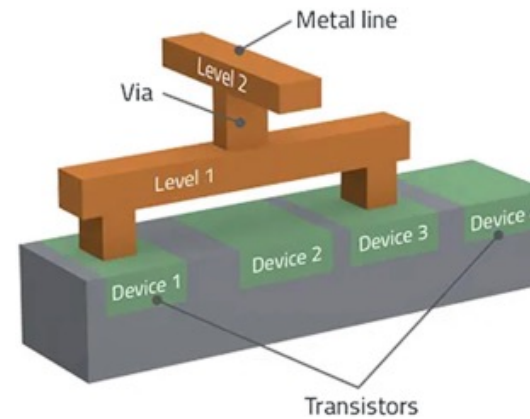
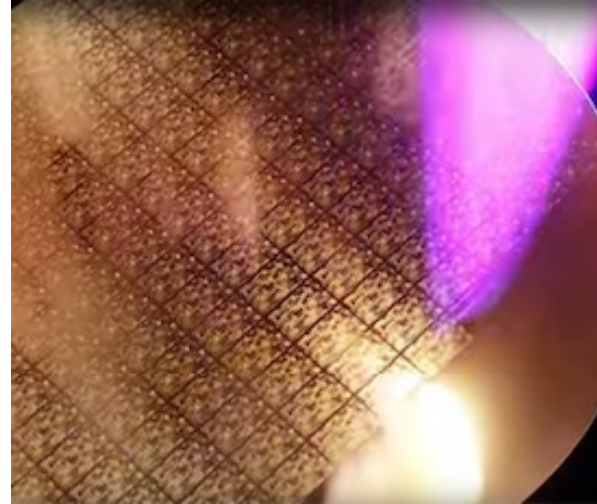
lithography
(today 13.5 nm Extreme UV litography)

etching

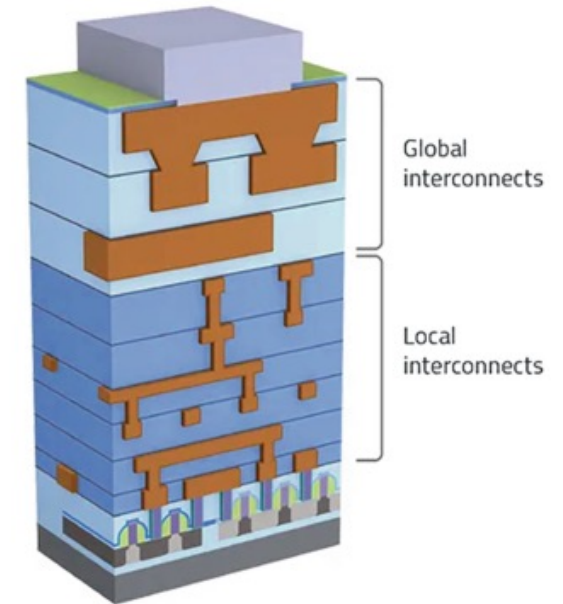
doping

cleaning

requires tens or even hundreds of
successive steps



(a)

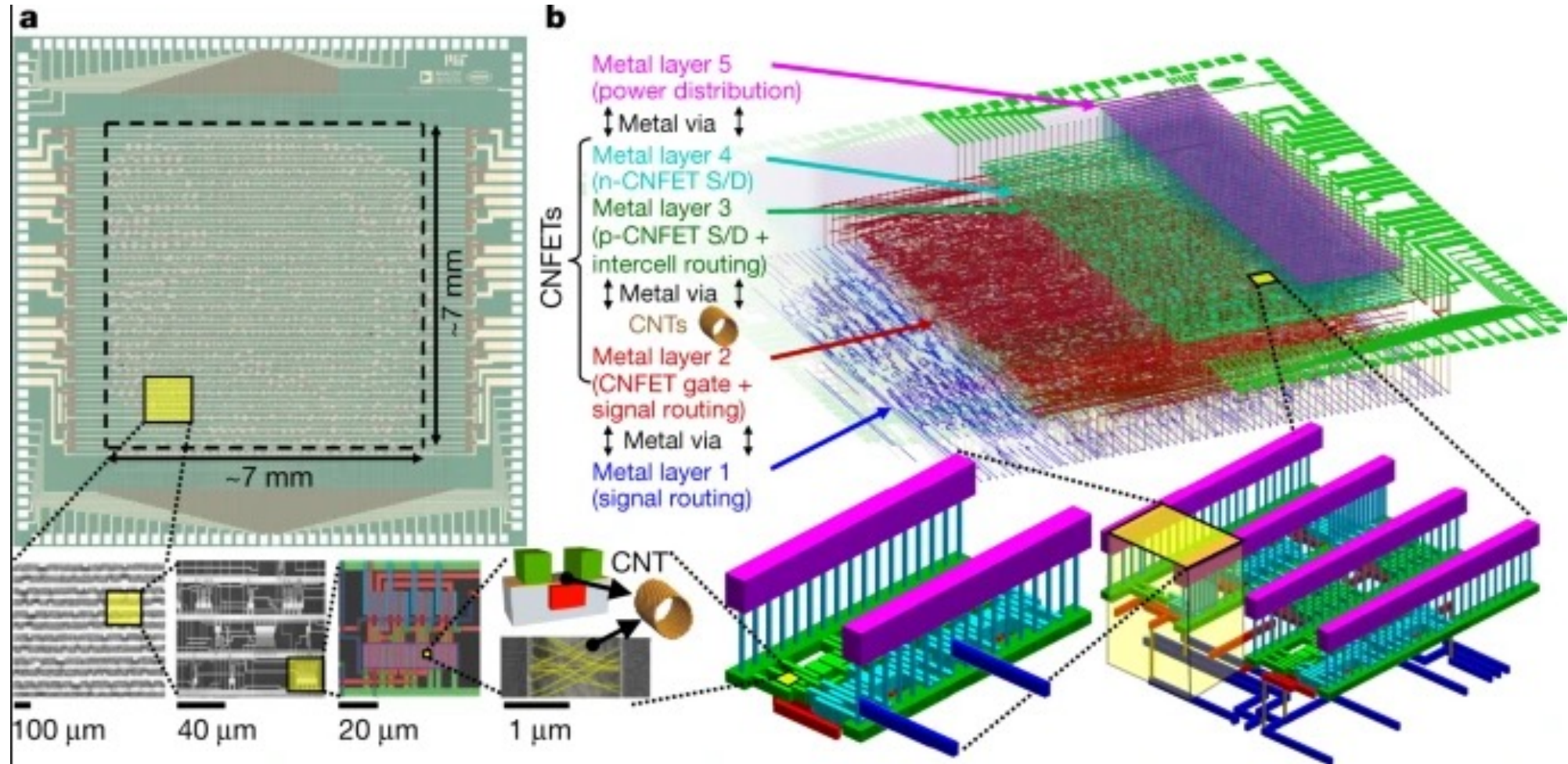


(b)

Carbon-based digital electronics

graphene or
carbon
nanotubes as
channel
materials

other 2D
materials
(MoS_2 , ...)



Modern microprocessor built from complementary carbon nanotube transistors,
Nature **572**, 595 (2019)

14'000 transistor computer – Turing complete