UNI BASEL

SNI SWISS NANOSCIENCE INSTITUTE
EINE INITIATIVE DER UNIVERSITÄT BASEL UND DES KANTONS AARGAU

Molecular and carbon-based electronic systems

when	Wednesday, 08h15-10h00
where	seminar room 1.22, Physics Dpt, Klingelbergstrasse 82
credit	2KP
debit	attendance + 1 presentation
VV	lecture Nr. 37839-01
web	**http://calame.unibas.ch/teaching**

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Vorlesung Uni Basel, FS2017

Molecular and carbon-based electronic systems

goals

- provide background & fundamental aspects to anchor understanding
- discuss devices/applications where organic compounds are currently used

fundamental aspects

towards applications/ devices

workshop

Tentative program

1.	22.02	**08:30**	Introduction. Carbon from 0D to 3D: fundamental properties (mc)
2	01.03	08:15	Single molecule deposition and properties on surfaces (tg)
3.	*08.03*		*No lectures 6.03-10.03 – Carneval*
4.	15.03	08:15	Molecule assemblies analysis and contacting on surfaces (tg)
5.	22.03	08:15	Template structures for functional molecular junctions: nanoparticle arrays (AV)
6.	29.03		Molecular junctions: formation mechanisms, transport basic (mc)
7.	05.04		Molecular junctions: spectroscopy, light coupling (mc)
8.	12.04		Insights in density functional theory for molecular junctions (MP)

Molecular and carbon-based electronic systems

goals

- provide background & fundamental aspects to anchor understanding
- discuss devices/applications where organic compounds are currently used

fundamental aspects

towards applications/ devices

Tentative program

9 .	19.04		Thermal transport in junctions (BG, tbc)
10.	26.04		Mechanical properties of carbon-based composite materials (CD, tbc)
11.	03.05		Graphene for molecular electronics (mc)
12.	10.05		Sensing (mc)
13.	17.05		Diamond: production, nano-diamond, NV vacancies (tg)
14.	24.05		Graphene oxide and applications (tg)
15.	31.05		**Workshop: talks by students**

workshop & preparing the talk: a few hints

- define topic, your main interest (see list by Anton)

  pre-screening work, basic topic understanding

  email to Anton *by* ***March 22nd*** *anton.vladyka@unibas.ch*

- structure the document

  what do you need / have ? What do you want to learn/convey ?

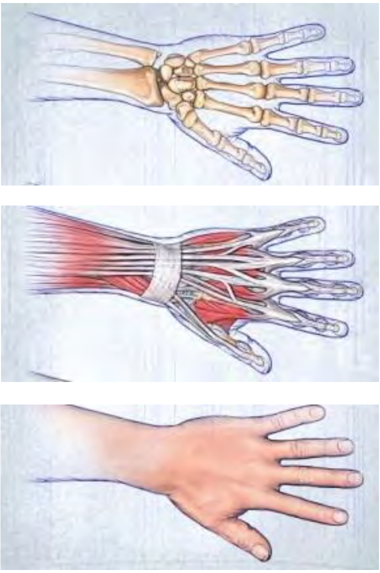
- collect & select contents

  ⇨ main message, refine contents

  key publications & data checked & available

- identify supporting information

  background knowledge, backup information, context, impact



timing - review the above workflow and attribute a given nb of hours to each step
- check back whether your prediction was appropriate

help - ask for feedback/discuss with Anton (topic, key papers, on what shall I focus)

obviously if you are not interested/convinced yourself, neither will your audience/readership be

CONTEXT

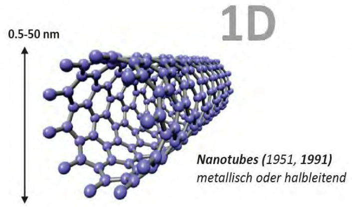
outline

electronics beyond Silicon

- other possible pathways for electronics

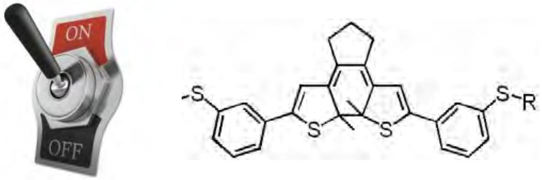
Carbon allotropes

- discovery



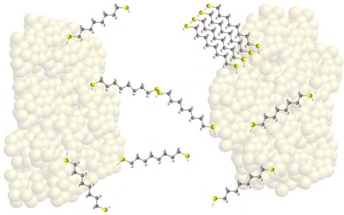
Carbon & molecular electronics

- brief historical account
- why molecules



molecular junctions

- how to contact nm-scale objects



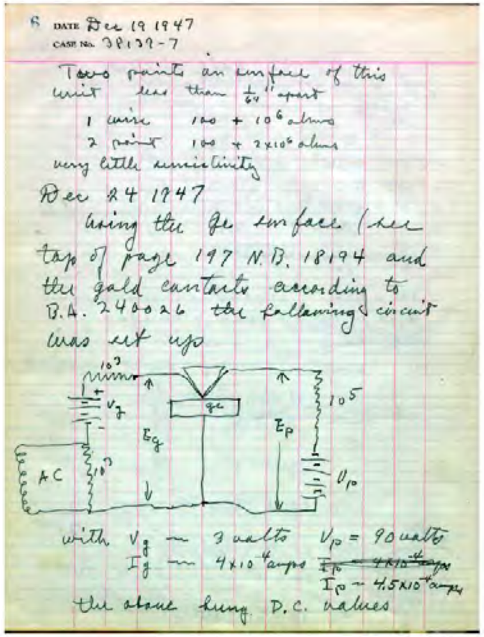
the evolution of electronics

transistor > 60 years old

1947, 24th December
John Bardeen, Walter Brattain, William Schockley

ATT Bell Labs

first point contact transfer resistor
Nobel 1956



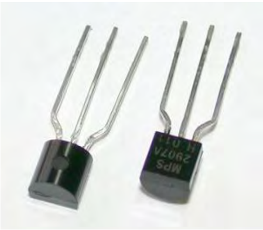
6 DATE Dec 19 1947
CASE No. 38139-7
Two points on surface of this unit less than 1/64" apart
1 wire 100 + 10^6 ohms
2 point 100 + 2×10^6 ohms
very little sensitivity
Dec 24 1947
Using the Ge surface (see top of page 197 N.B. 18194 and the gold contacts according to B.A. 240026 the following circuit was set up
with V_g ~ 3 volts V_p = 90 volts
I_g ~ 4×10^{-4} amps ~~I_p ~ 4×10^{-4} amps~~
I_p ~ 4.5×10^{-4} amps
the above being D.C. values

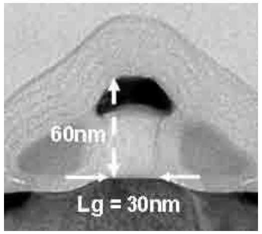
Bell labs

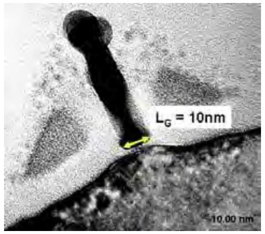
Bell labs

the evolution of electronics

Bardeen,
Brattain,
Shockley





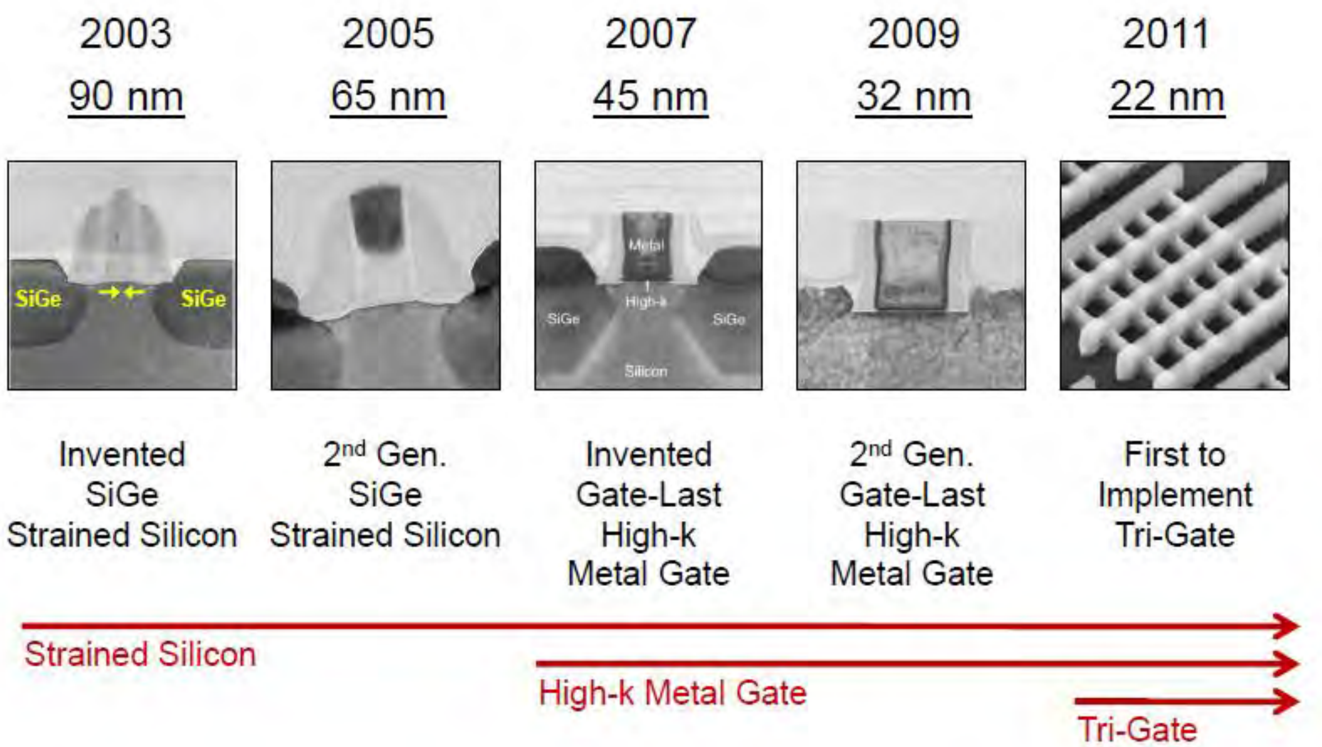


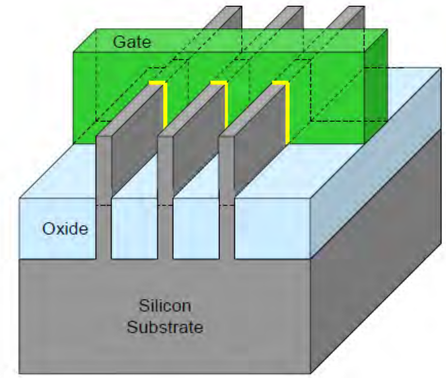
1947 … today

⇨ ***Building blocks (transistors) at nm scale***

Volume reduced by 10^{12}

the evolution of electronics



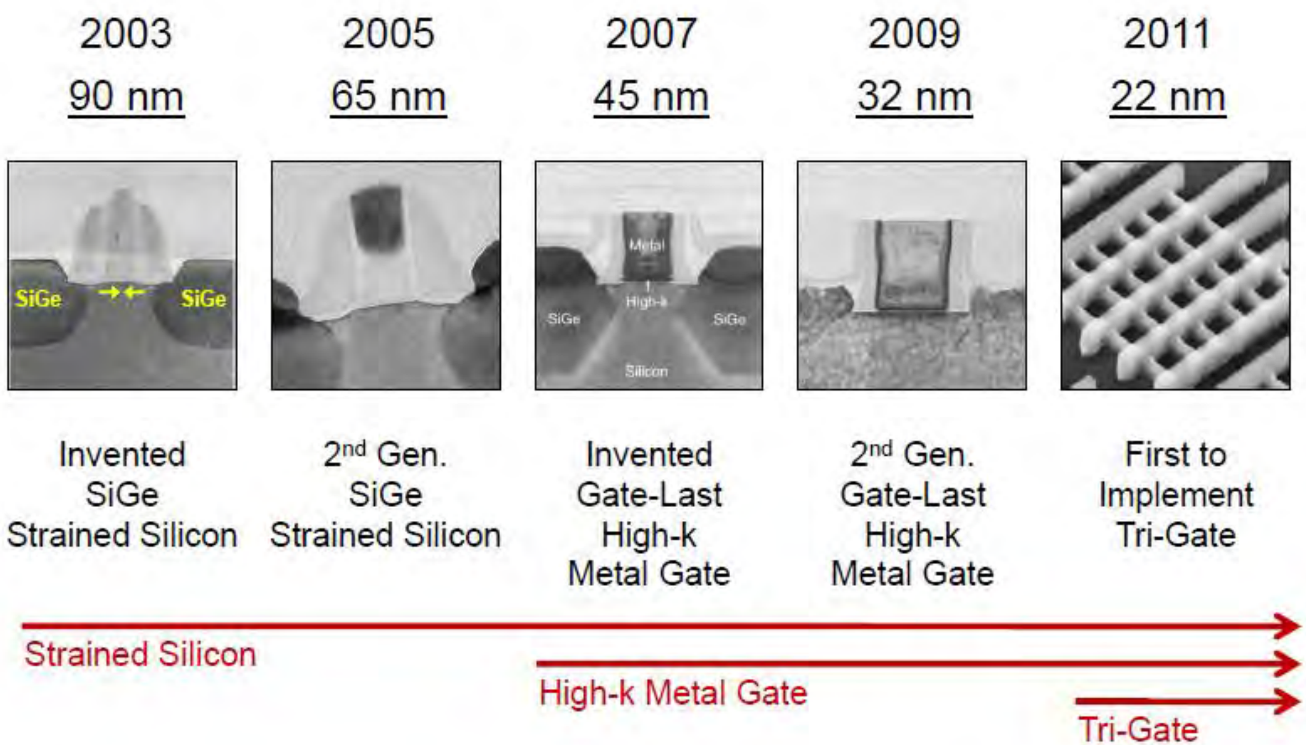


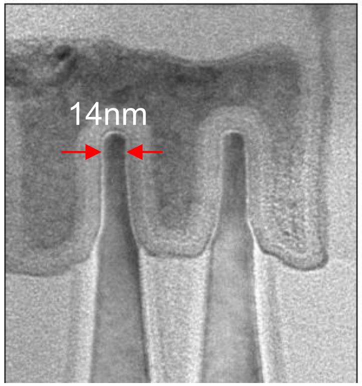
planar geometry to 3D geometry fin-FETs & gate all-around (GAA)

improvement of substreshold swing, higher switching speed, lower operation Voltage

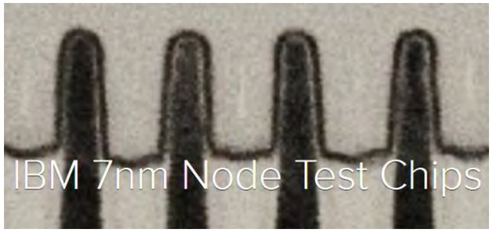
M. Bohr, Intel

the evolution of electronics

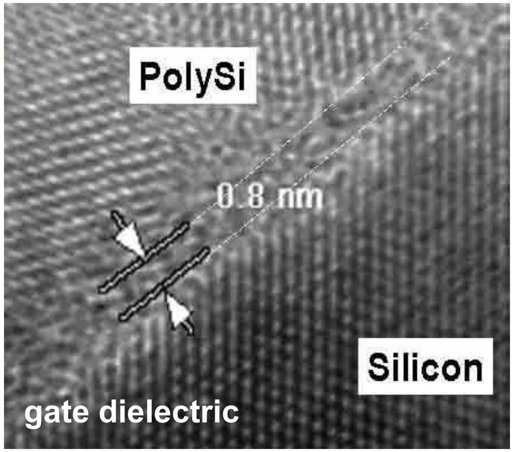




Intel 14nm node



IBM, 2015



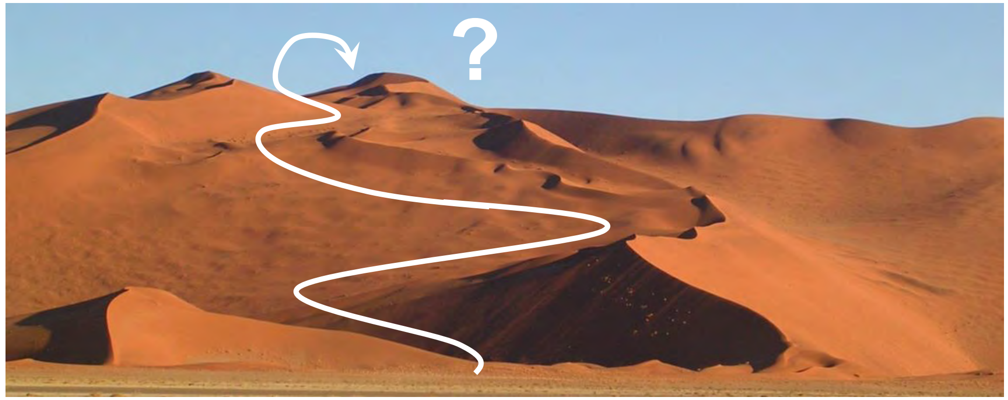
planar geometry to 3D geometry fin-FETs & gate all-around (GAA)

improvement of substreshold swing, higher switching speed, lower operation Voltage

Major issues: power, leakage current, reproducibility

since 2005, speed ⇨

electronics beyond Si



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

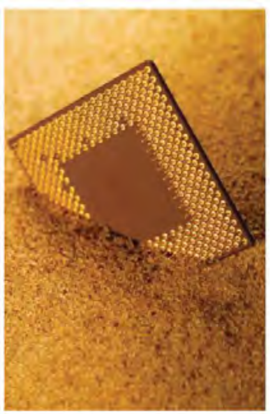
Beyond Silicon: New Materials for 21st Century Electronics

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 Bulleting 2010 special issue



INTRODUCTION

Looking Beyond Silicon

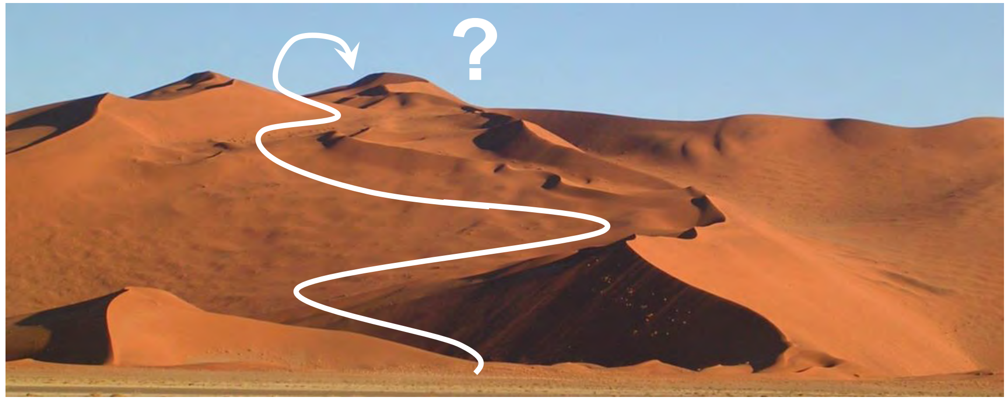
Science 2010 special issue

physicstoday

Industrial Physics Forum 2013: The future of electronics

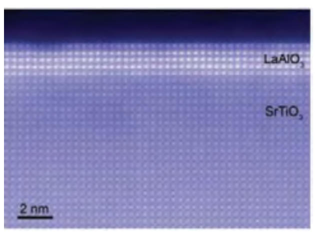
What technologies will extend silicon's reign as the preeminent material for electronics? What materials will ultimately supplant silicon?
Charles Day, December 2013

electronics beyond Si



materials

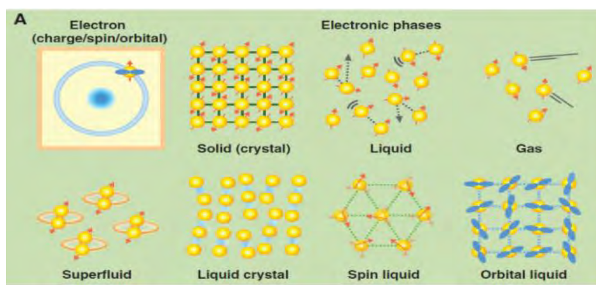
Oxides interfaces



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

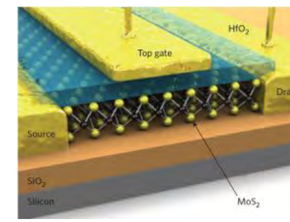


Takagi et al., Science 2013

Transition metal dichalcogenides (2D)

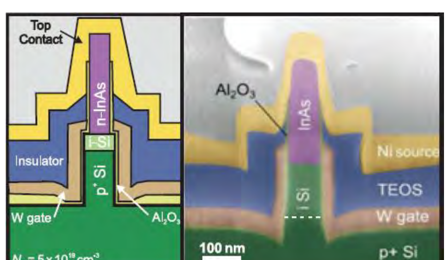
MoS_2, WS_2, …

Strano et al., Nat. Nano 2012

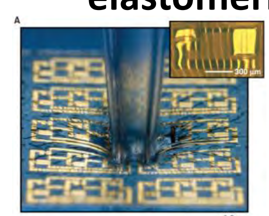


III–V compound semic. transistors

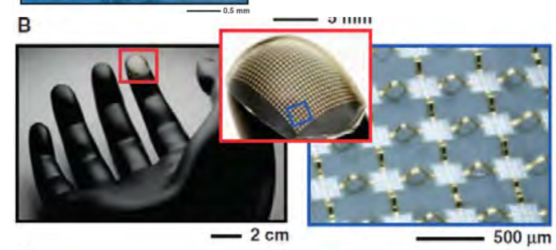
NW tunnel FETs
Riel et al., MRS Bulletin 2014



Organic & inorganic materials with elastomeric substrates



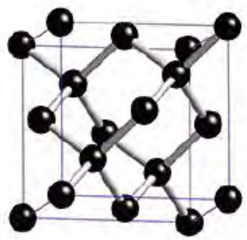
Stretchable electronics
Rodgers et al., Science 2013



carbon-based materials

Diamant (sp^3 Carbon)
- _das härteste Material_
- _sehr guter Isolator, trotzdem aber exzellenter Wärmeleiter_

sp^3 hybridization



3D

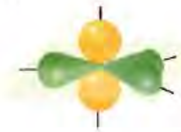
6 Carbon

C

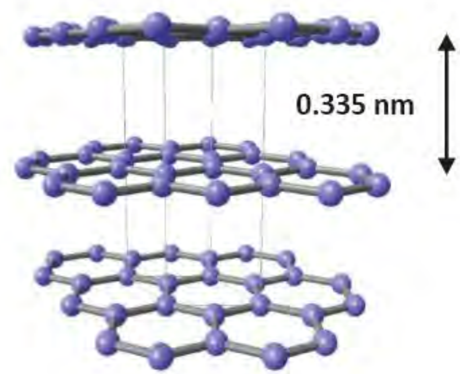
12.011

$1s^2\ 2s^2\ 2p^2$

Graphit (sp^2 Carbon)
- _lässt sich leicht abtragen (Bleistift)_
- _recht guter elektrischer Leiter_

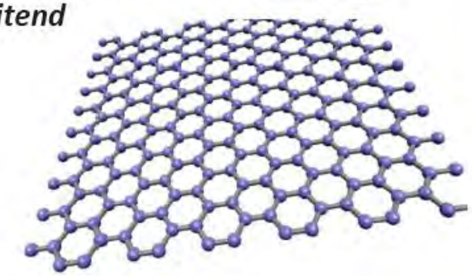


sp^2 hybridization

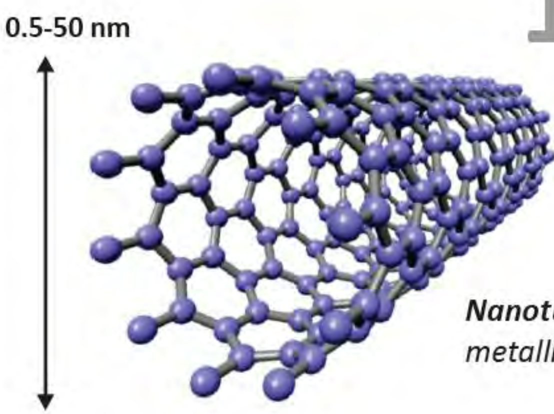


Graphene (2004)
"zwischen" metallisch und halbleitend

2D

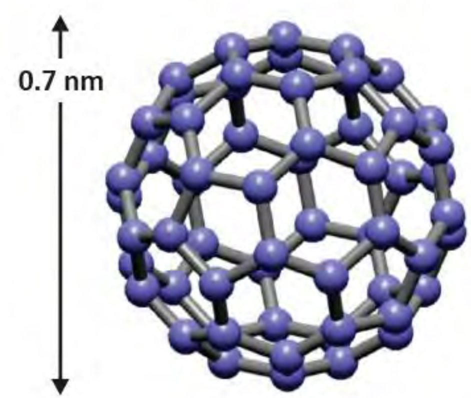


1D



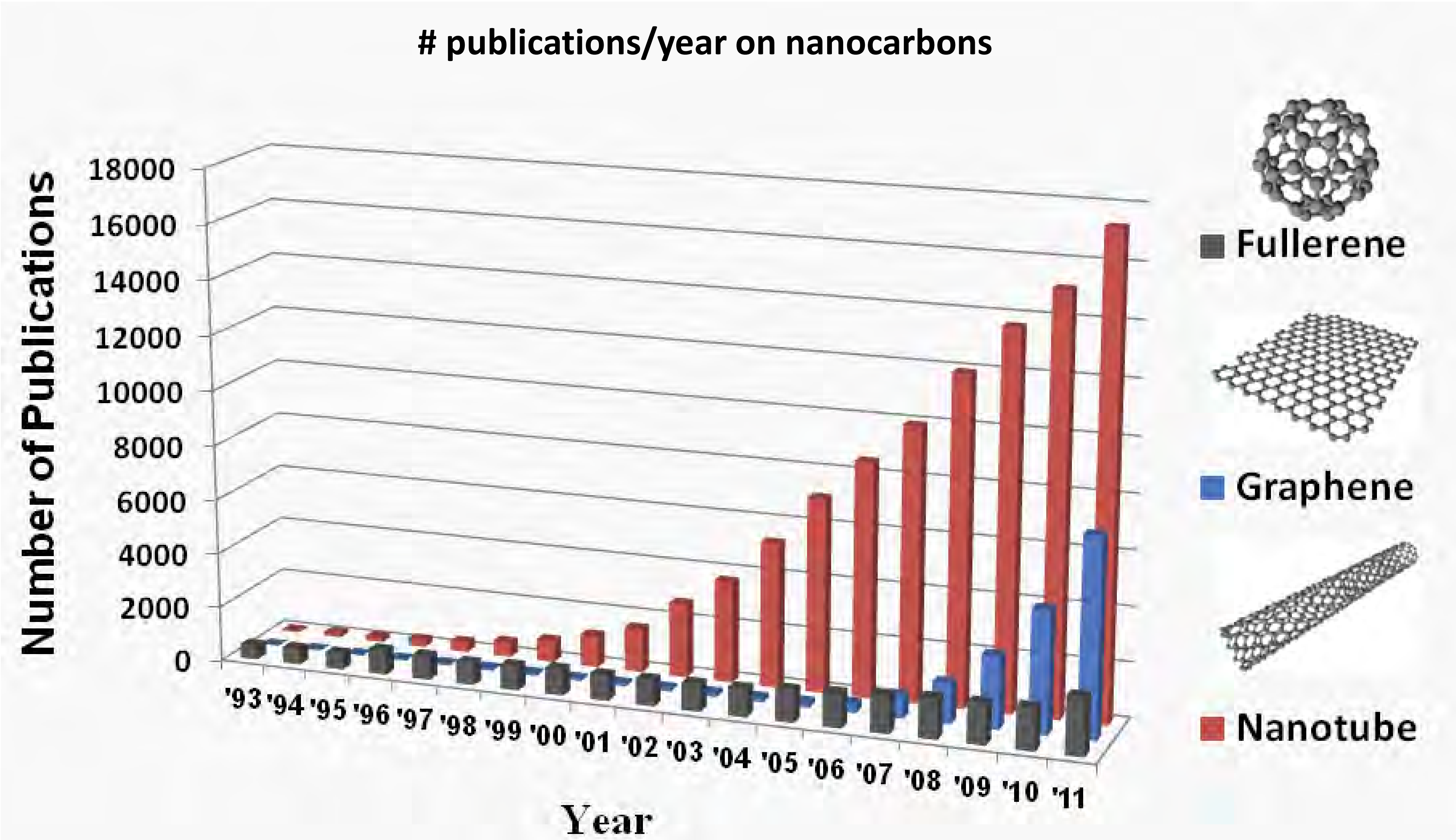
Nanotubes _(1951, 1991)_
metallisch oder halbleitend

Fullerene C_{60} (1985)



0D

"nano-carbons"



M.S. Dresselhaus
Data extracted from Science Citation Index searching for the words fullerene, nanotube, and graphene

NB: nanoribbons

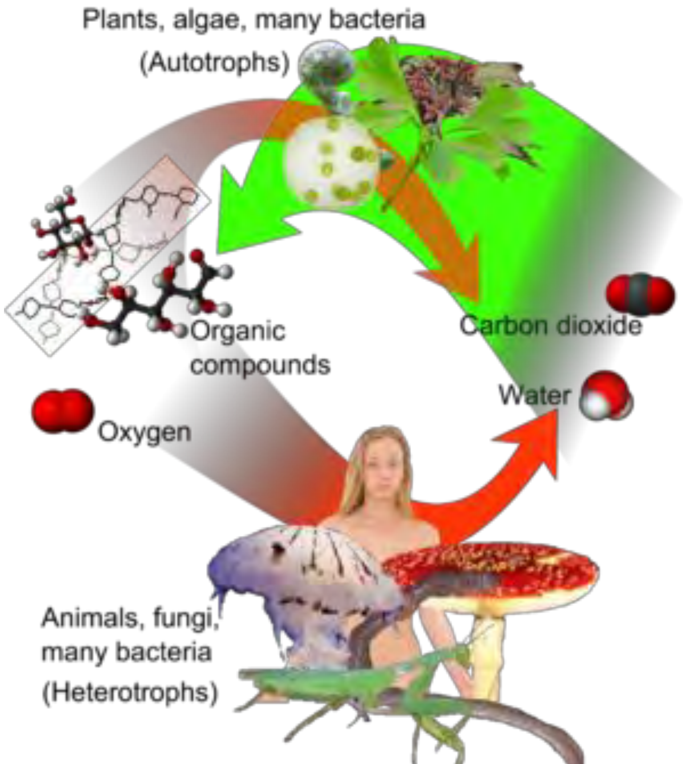
carbon

6 Carbon

C

12.011

$1s^2\ 2s^2\ 2p^2$

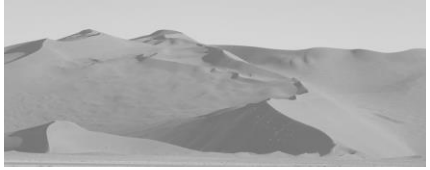


wiki

outline

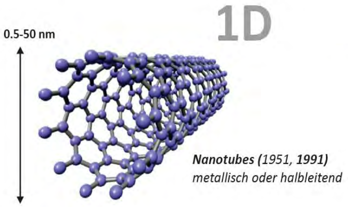
electronics beyond Silicon

- other possible pathways for electronics



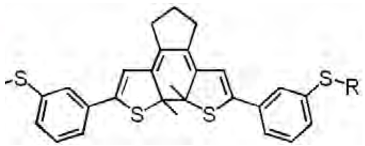
Carbon allotropes

- discovery



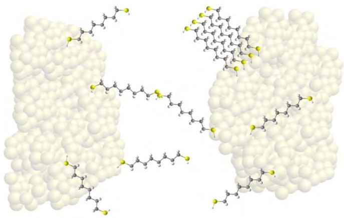
Carbon & molecular electronics

- brief historical account
- why molecules



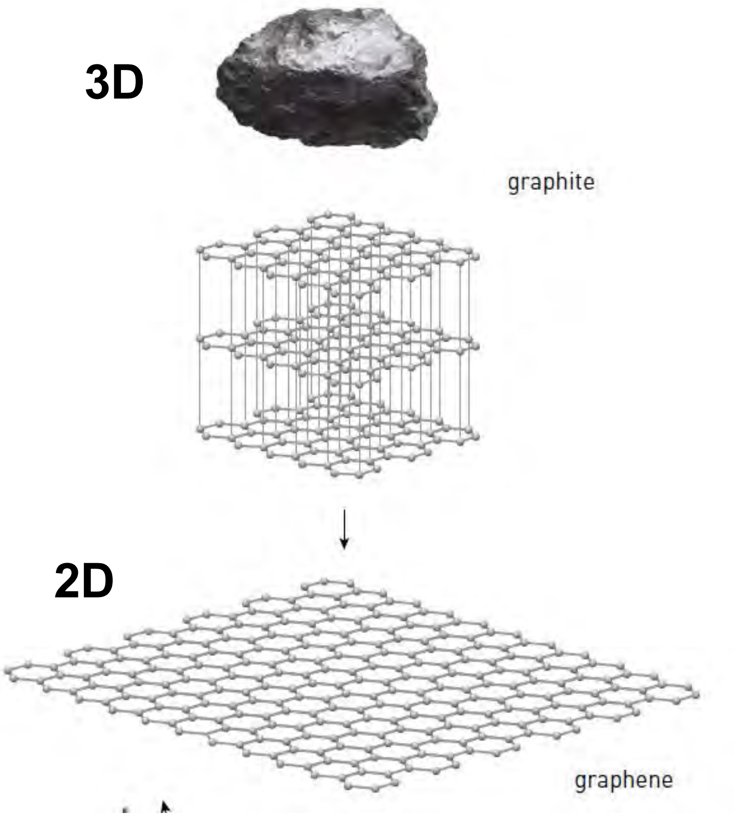
molecular junctions

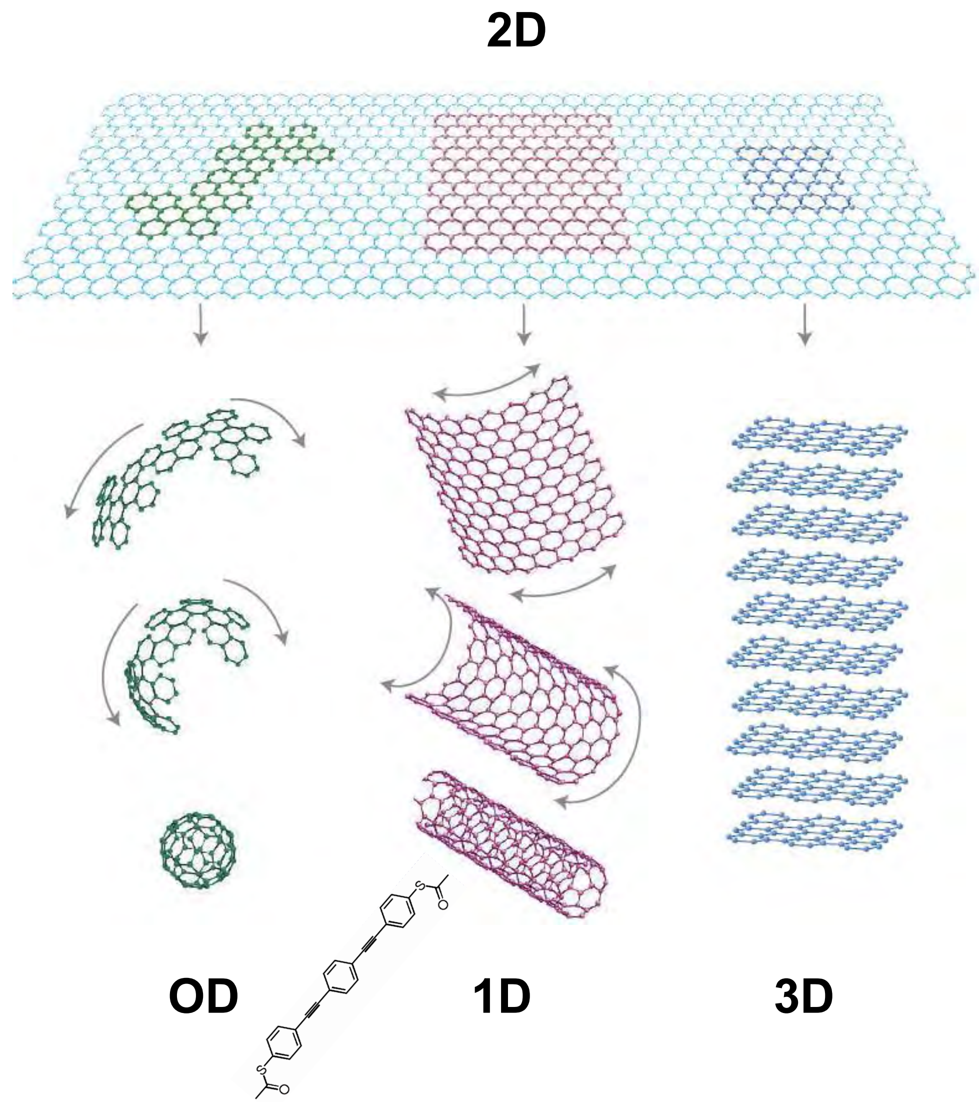
- how to contact nm-scale objects



carbon-based materials

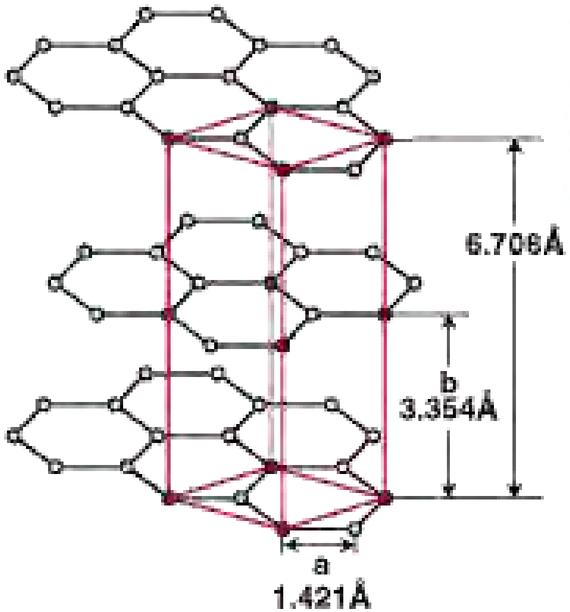
sp^2 allotropes of carbon

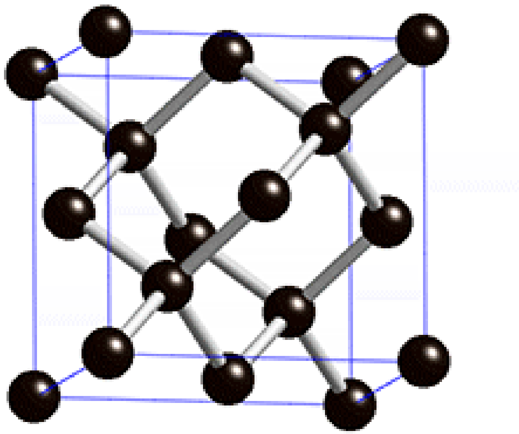


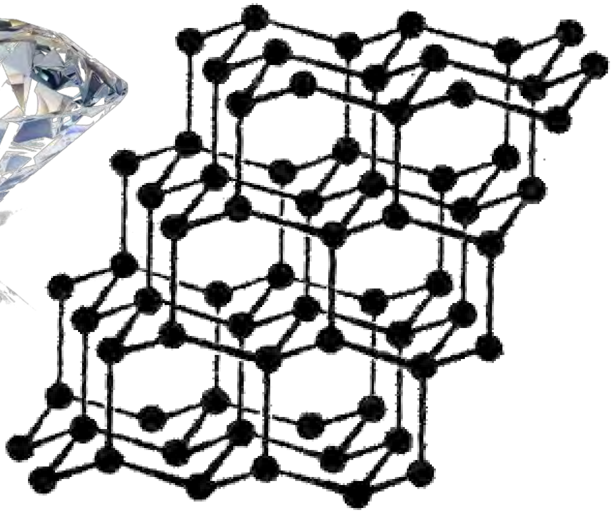


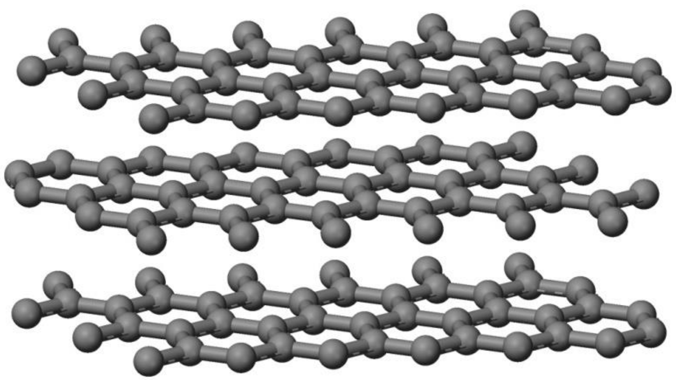
Nobel lectures, Geim & Novoselov, 2010

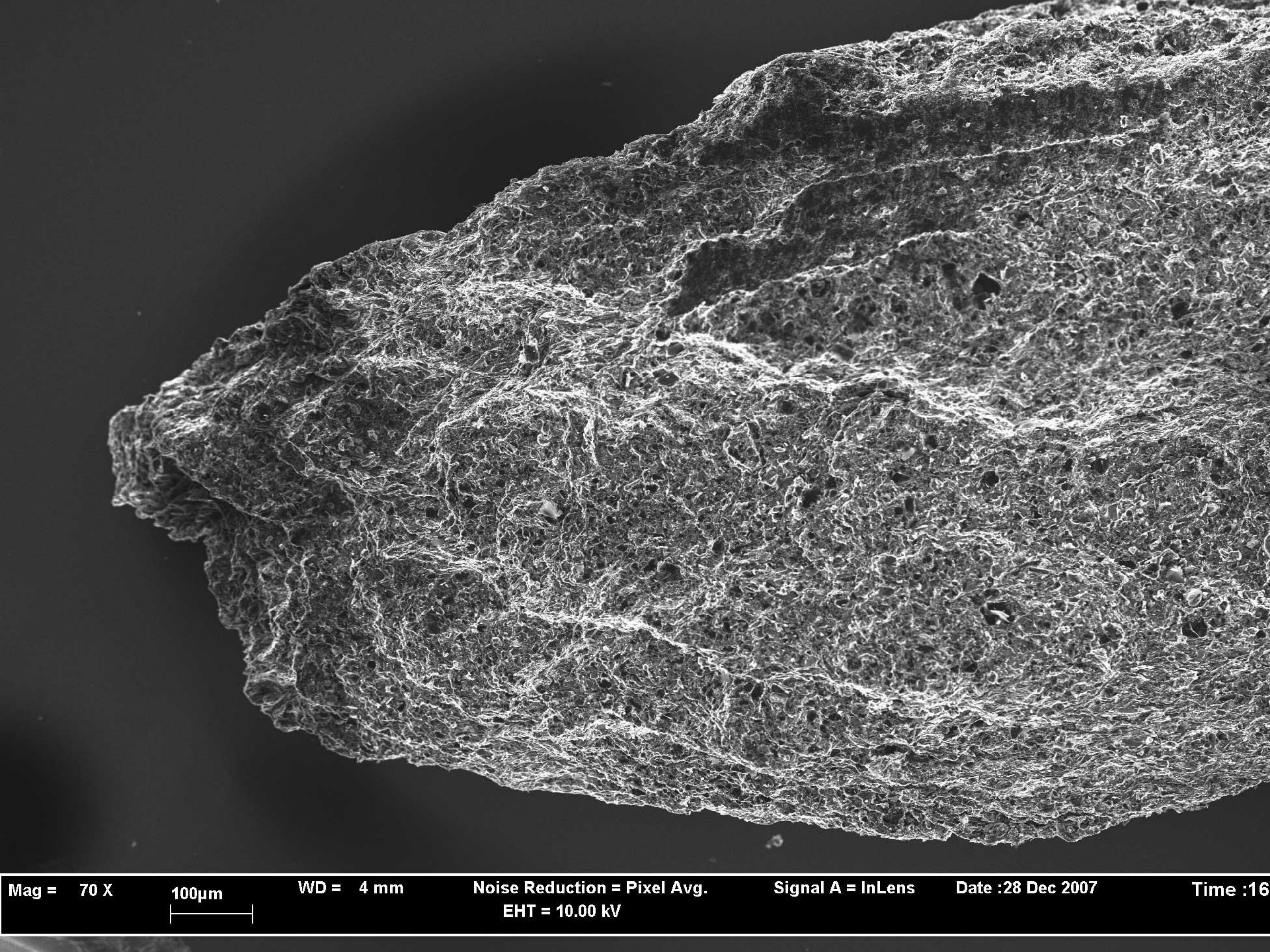
carbon allotropes discovery







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100µm
WD = 4 mm
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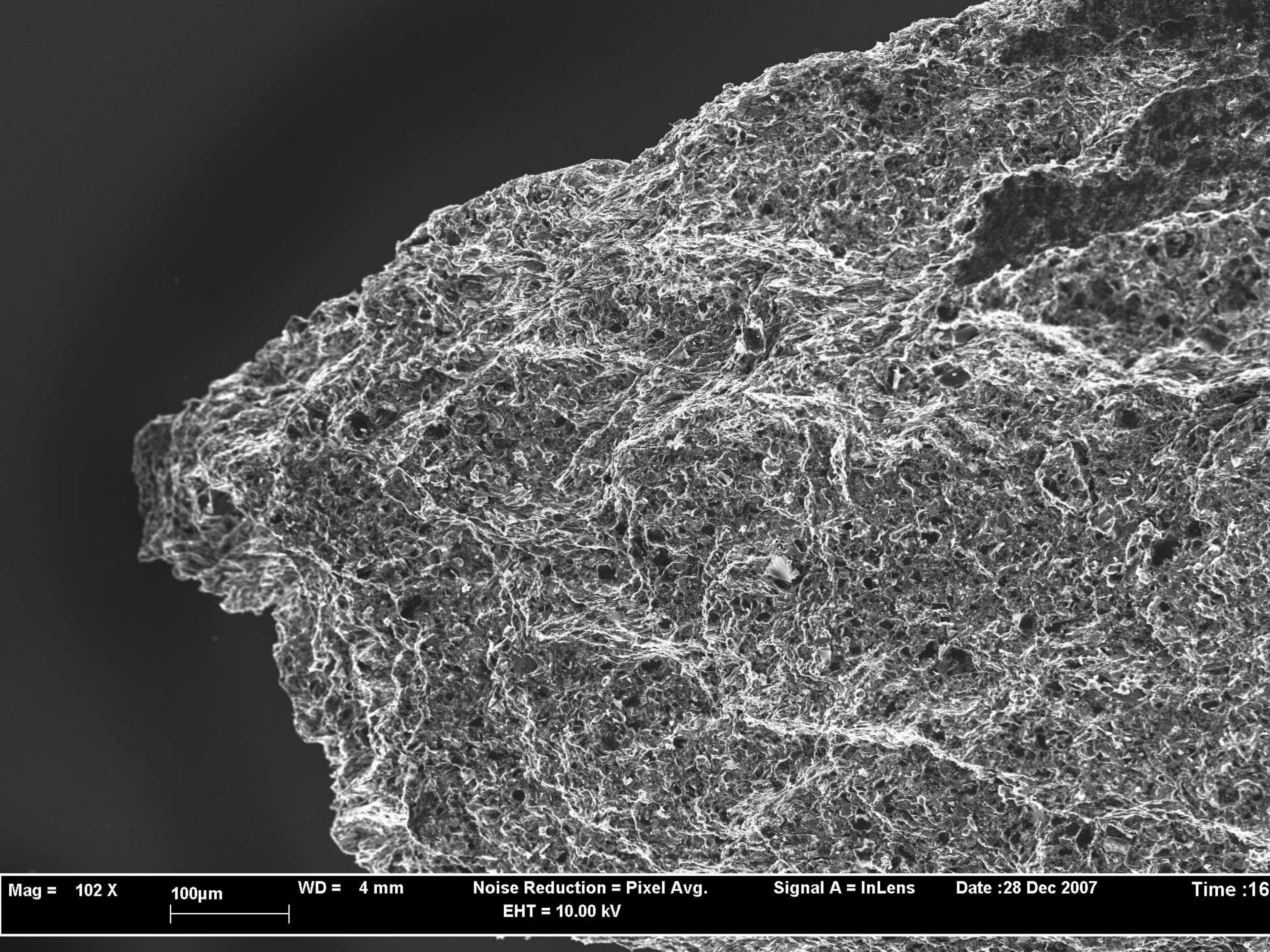
EHT = 10.00 kV
Signal A = InLens
Date :28 Dec 2007
Time :16


Mag = 102 X
100µm
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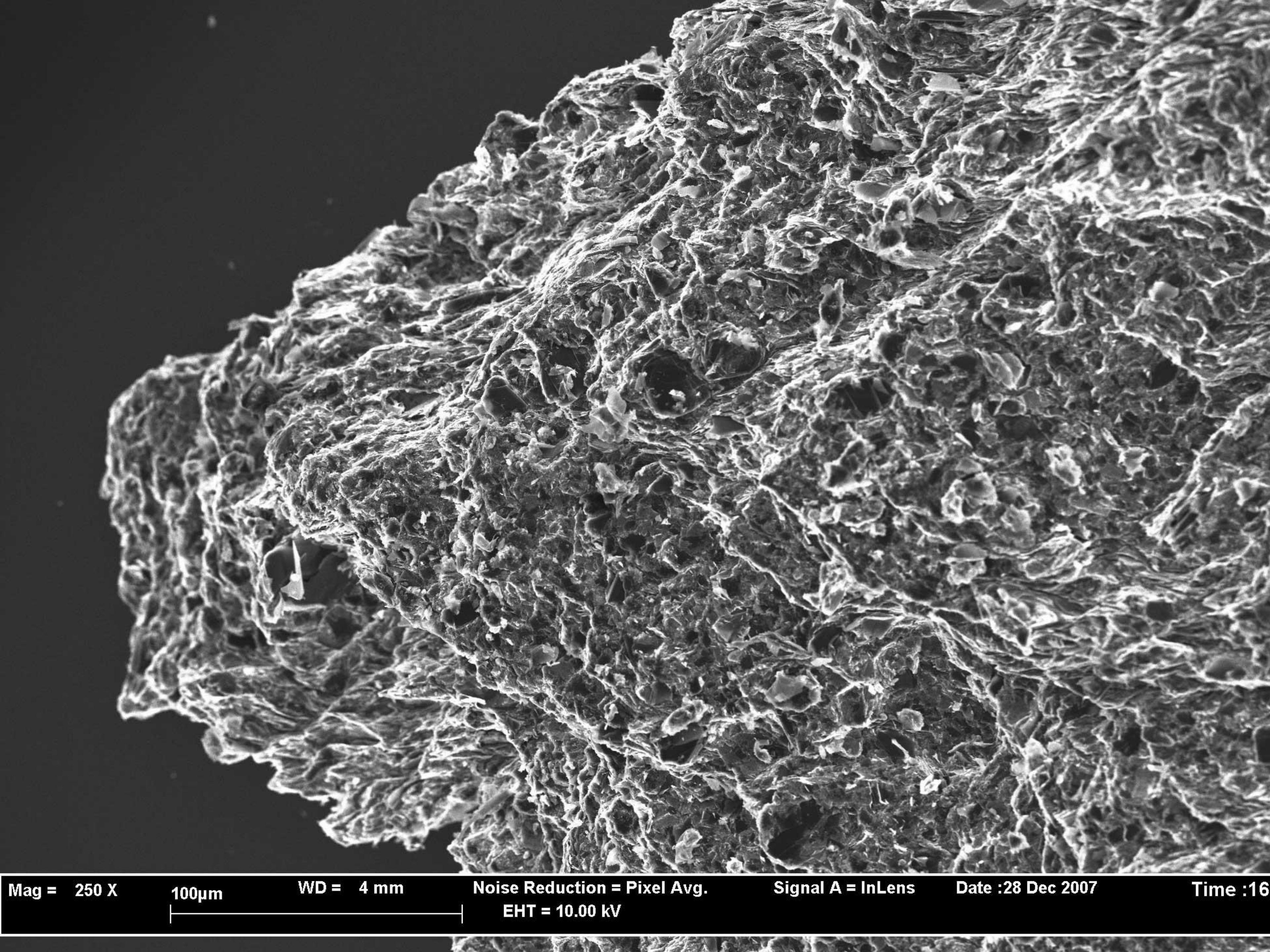
Time :16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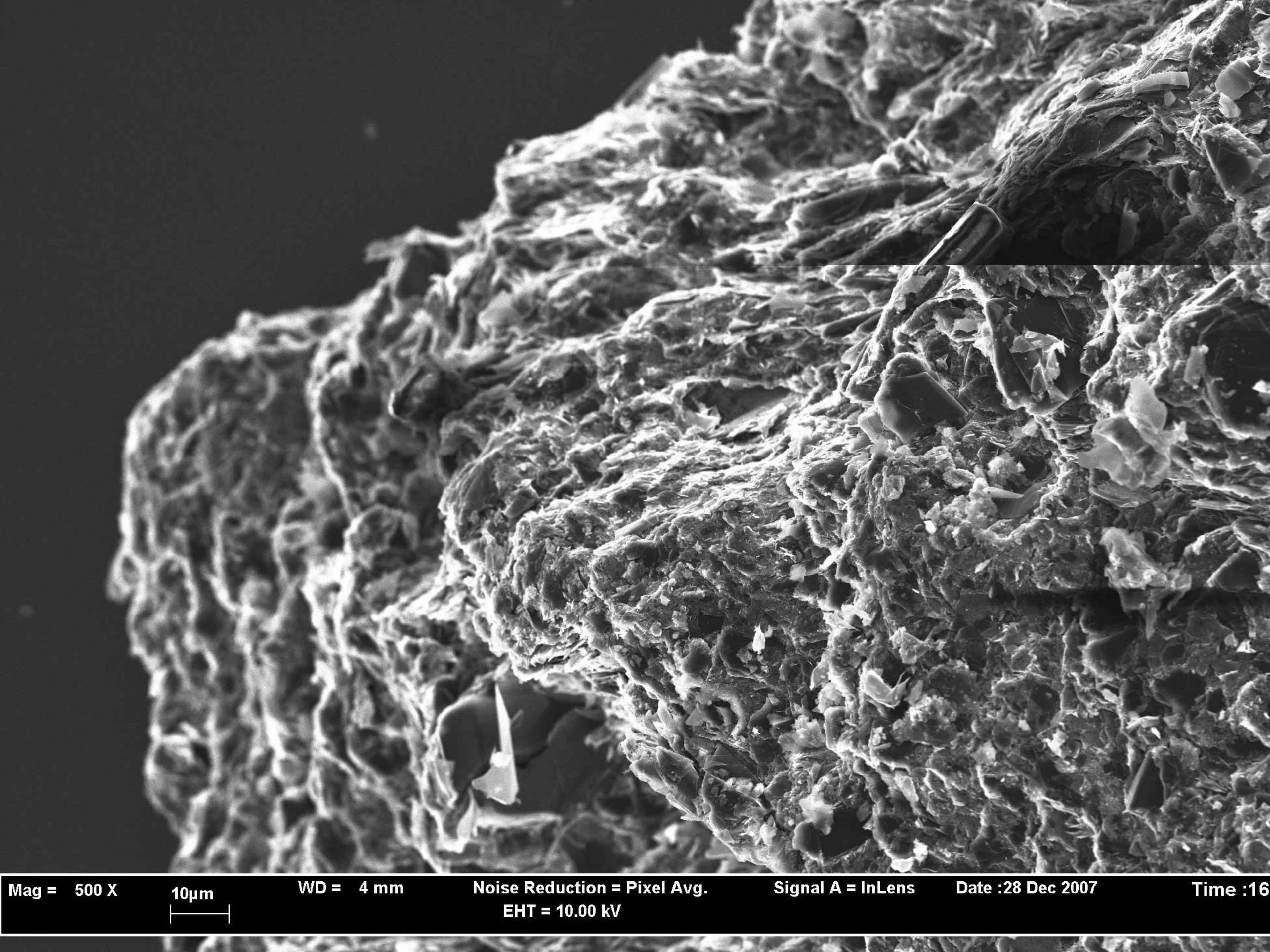
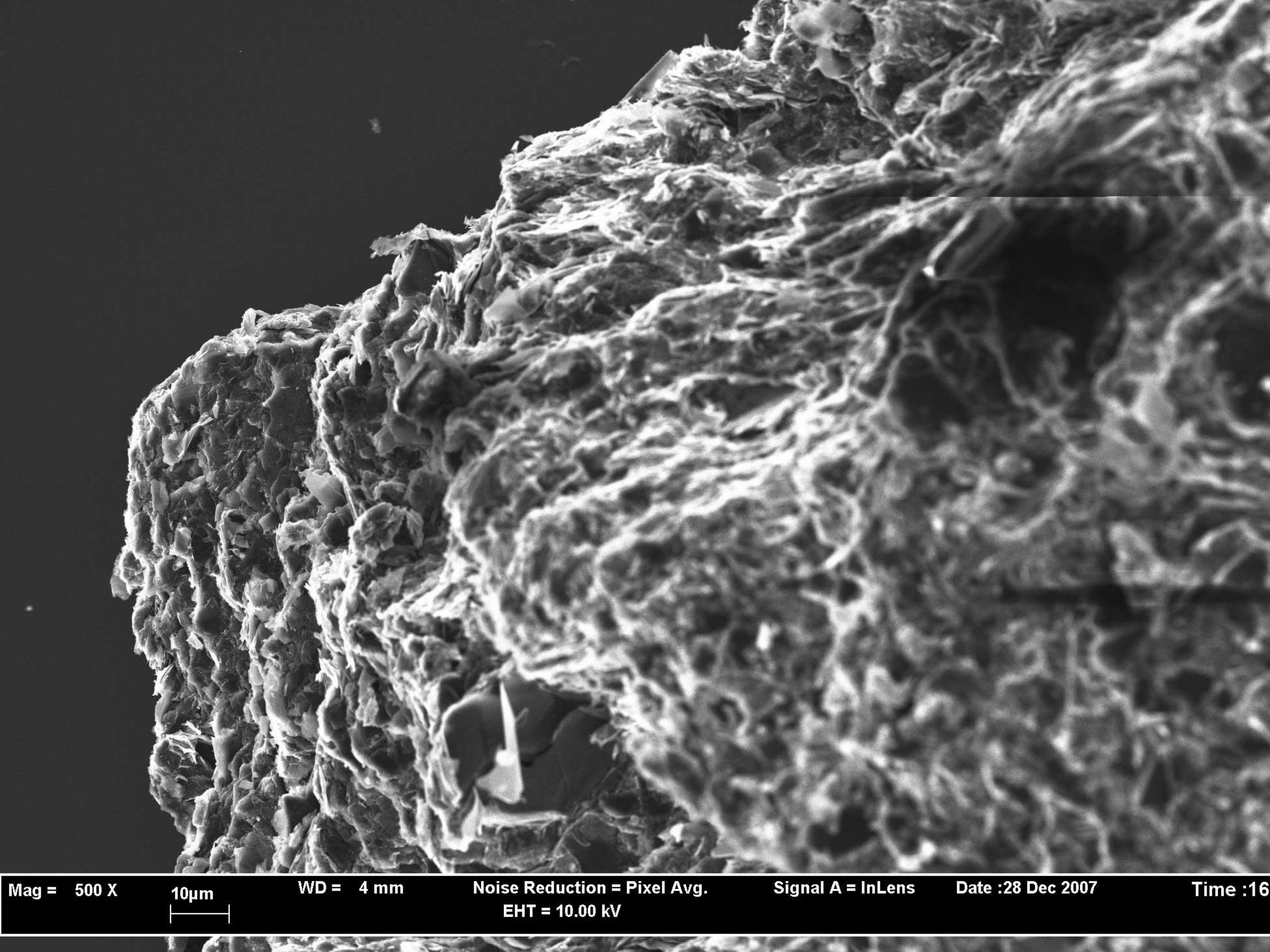
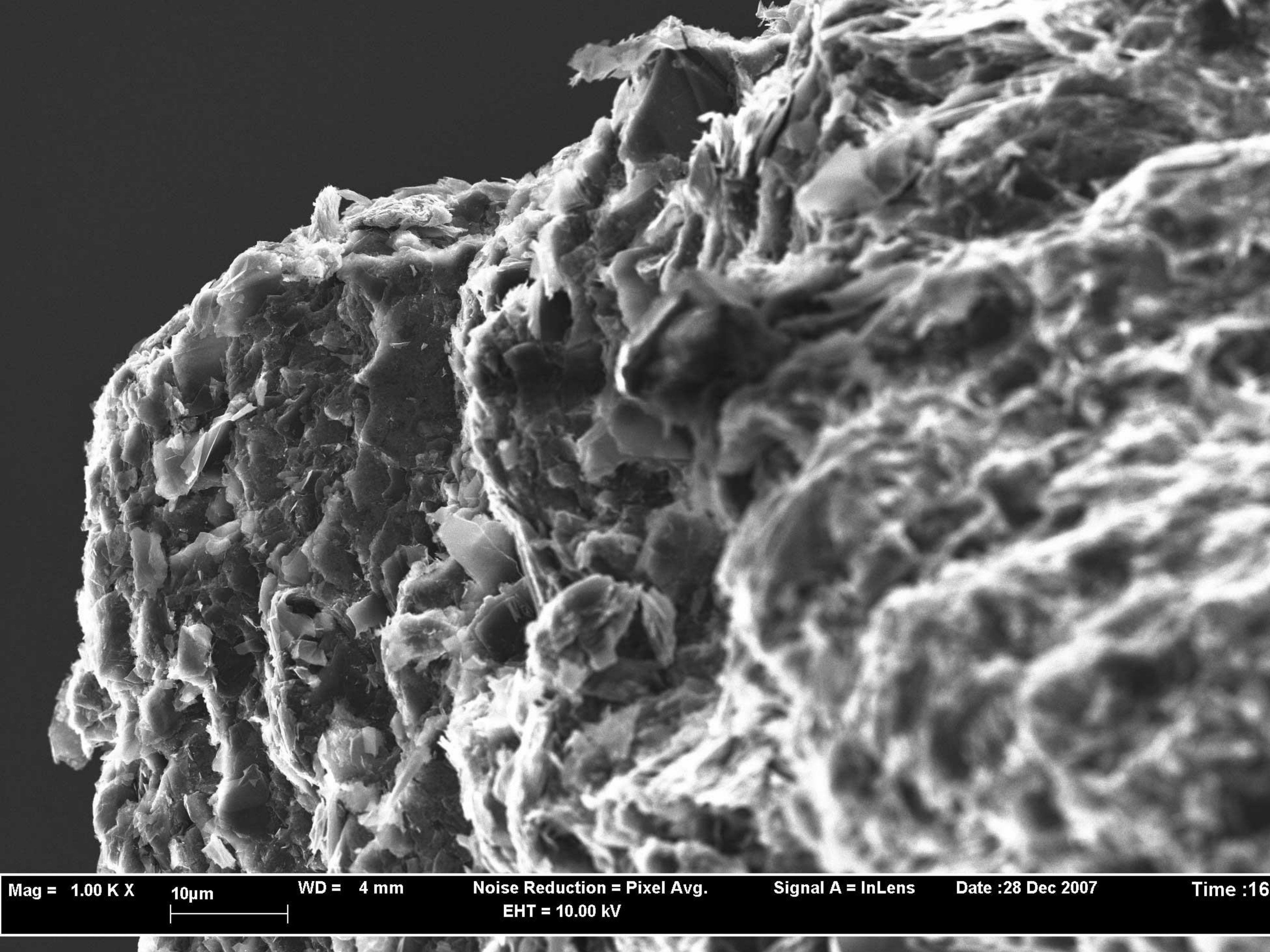
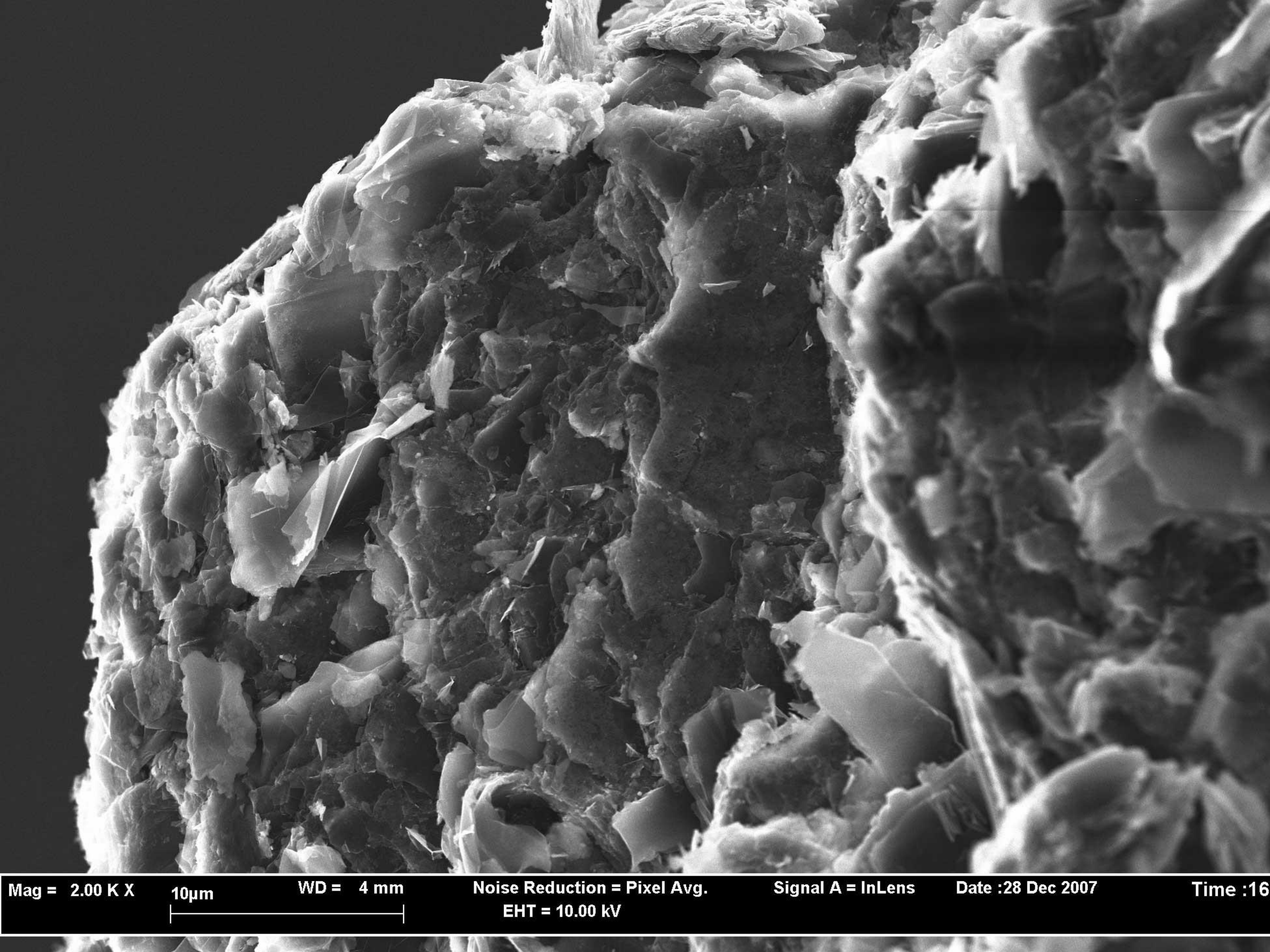
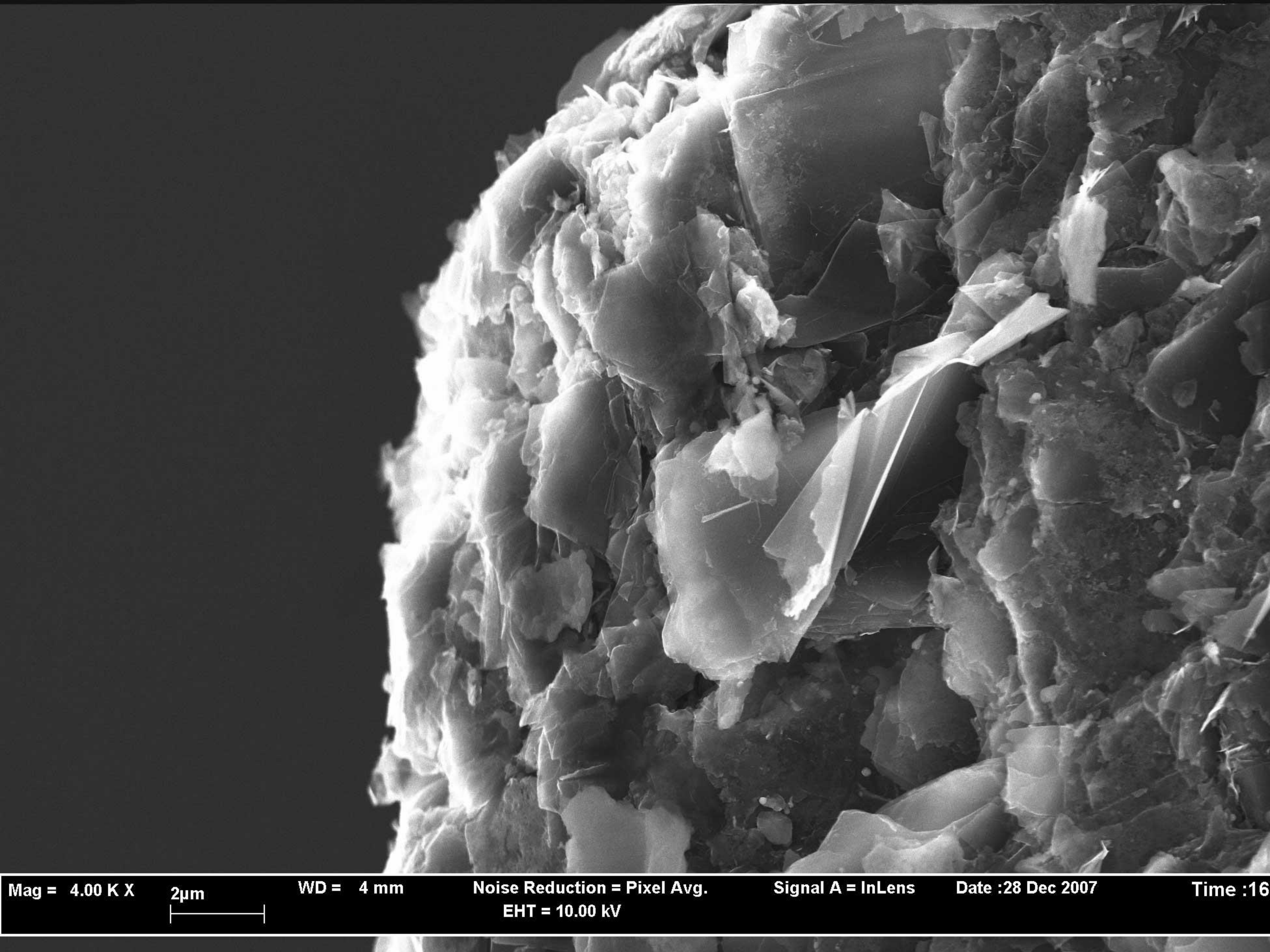
Time :16

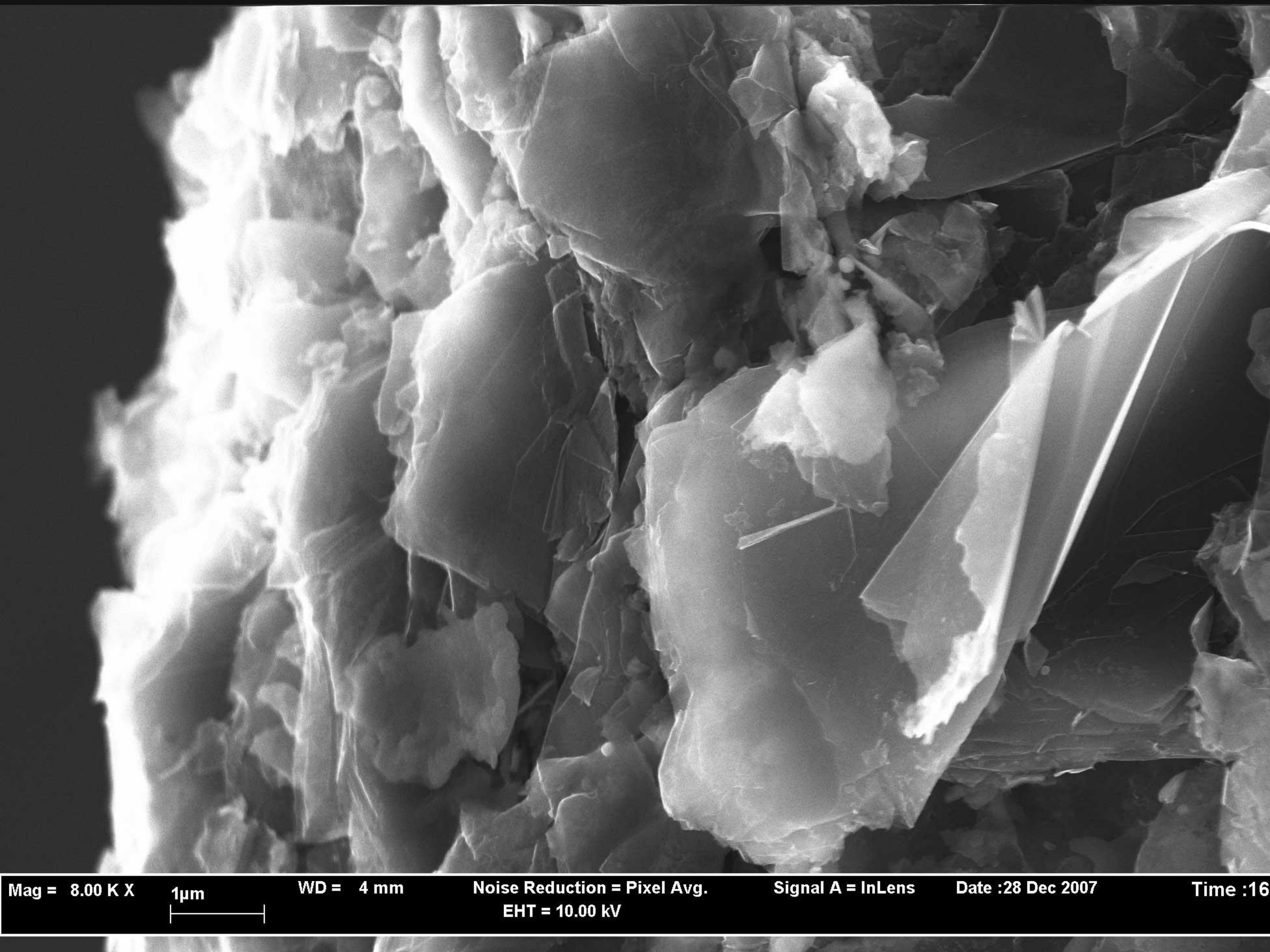

Mag = 500 X
10µm
WD = 4 mm
Noise Reduction = Pixel Avg.
EHT = 10.00 kV
Signal A = InLens
Date :28 Dec 2007
Time :16


Mag = 500 X
10µm
WD = 4 mm
Noise Reduction = Pixel Avg.
EHT = 10.00 kV
Signal A = InLens
Date :28 Dec 2007
Time :16

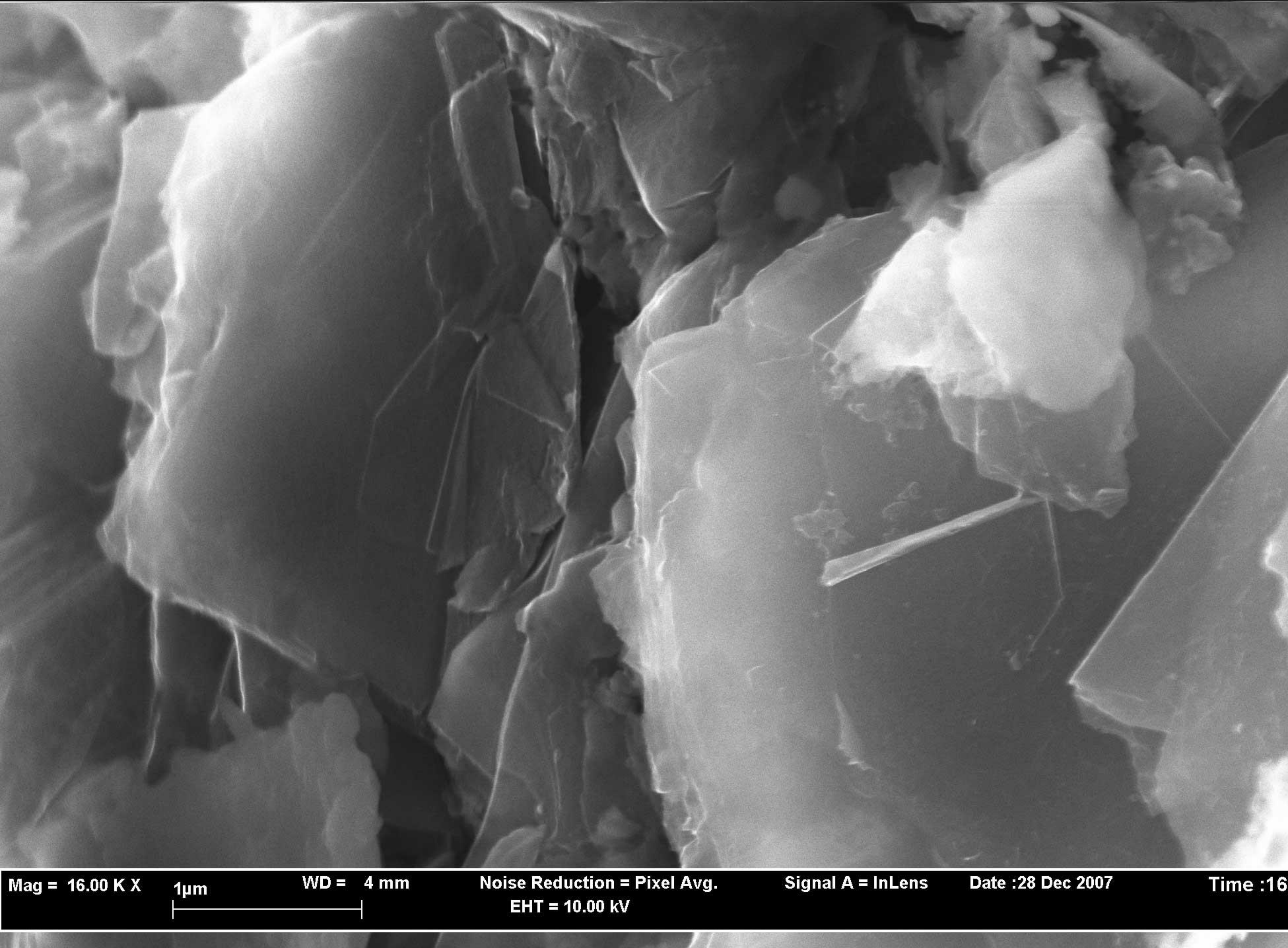

Mag = 1.00 K X
10μm
WD = 4 mm
Noise Reduction = Pixel Avg.
EHT = 10.00 kV
Signal A = InLens
Date :28 Dec 2007
Time :16


Mag = 2.00 K X
10μm
WD = 4 mm
Noise Reduction = Pixel Avg.
EHT = 10.00 kV
Signal A = InLens
Date :28 Dec 2007
Time :16


Mag = 4.00 K X
2µm
WD = 4 mm
Noise Reduction = Pixel Avg.
EHT = 10.00 kV
Signal A = InLens
Date :28 Dec 2007
Time :16



Mag = 8.00 K X
1μm
WD = 4 mm
Noise Reduction = Pixel Avg.
EHT = 10.00 kV
Signal A = InLens
Date :28 Dec 2007
Time :16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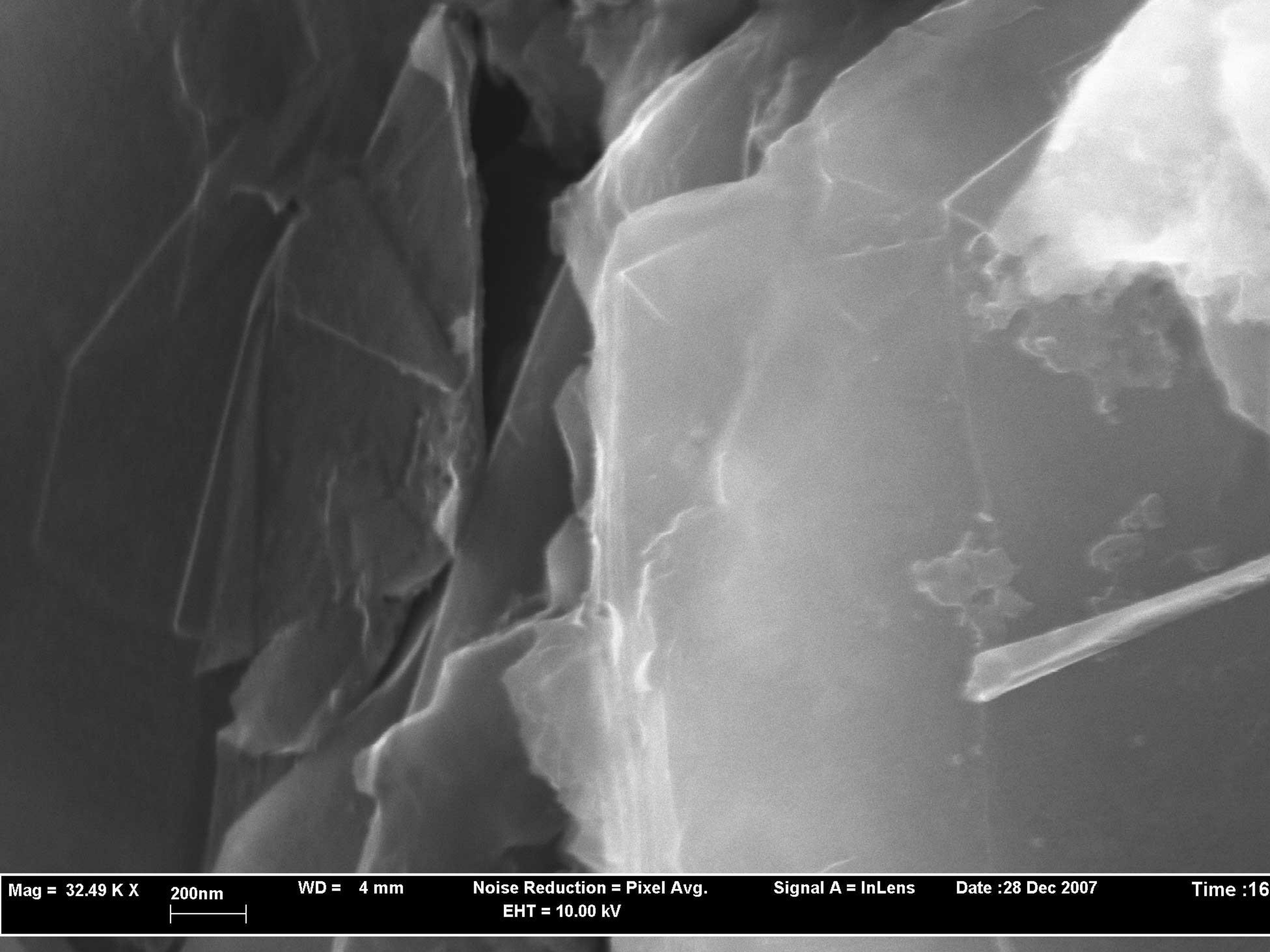
WD = 4 mm
Noise Reduction = Pixel Avg.
EHT = 10.00 kV
Signal A = InLens
Date :28 Dec 2007
Time :16


Mag = 32.49 K X
200nm
WD = 4 mm
Noise Reduction = Pixel Avg.
EHT = 10.00 kV
Signal A = InLens
Date :28 Dec 2007
Time :16

fullerenes

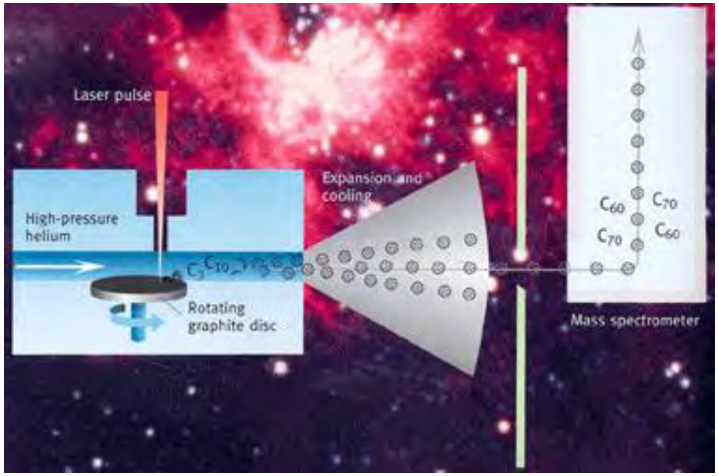
The Nobel Prize in Chemistry 1996

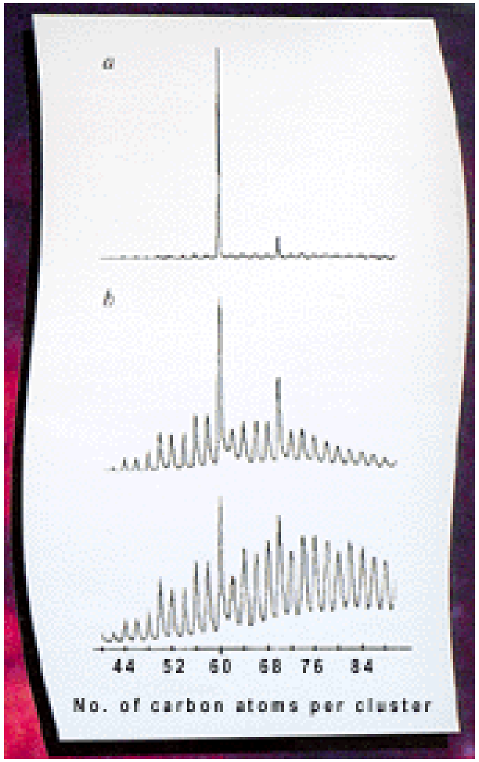
Robert F. Curl Jr.
Prize share: 1/3

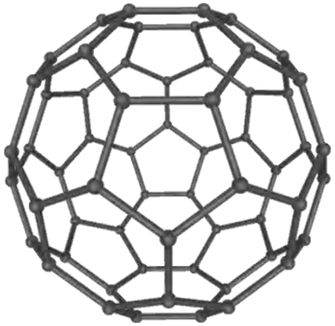
Sir Harold W. Kroto
Prize share: 1/3

Richard E. Smalley
Prize share: 1/3

The Nobel Prize in Chemistry 1996 was awarded jointly to Robert F. Curl Jr., Sir Harold W. Kroto and Richard E. Smalley *"for their discovery of fullerenes"*.







fullerenes
C60, C70, ...

Buckminster Fuller dome, Montreal, 1967

Nobel.se

carbon allotropes discovery

SWISS NANOSCIENCE INSTITUTE

EINE INITIATIVE DER UNIVERSITÄT BASEL UND DES KANTONS AARGAU

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- Teaching – bachelor & master
- Tech. transfer
- Public outreach

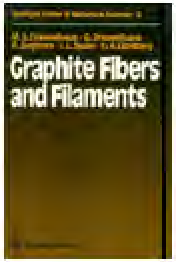
www. nanoscience.ch

H.G. Güntherodt (✝ 2014)
& Harry W. Kroto (✝ 2016)
in Basel for the 10th Anniversary celebration of the NCCR Nanoscale Science

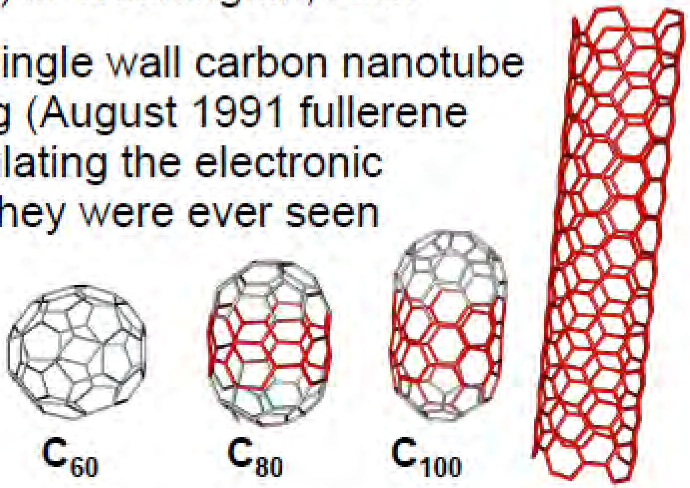
Sir Harold W. Kroto

Forerunners of carbon nanotubes

- My studies on carbon fibers started in 1980 through a collaboration with Morinobu Endo in Japan: M. S. Dresselhaus, G. Dresselhaus, K. Sugihara, I. L. Spain, H. A. Goldberg, *Graphite Fibers and Filaments*, Springer (1988)



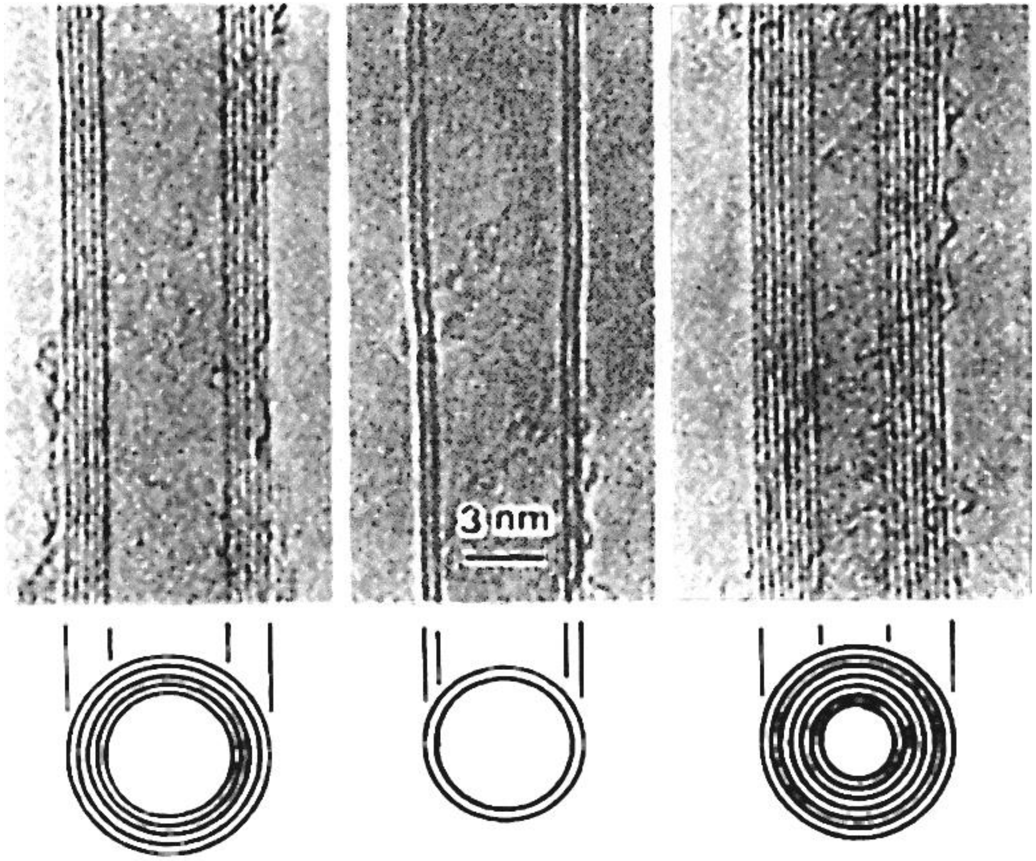
- The nanotube-fullerene connection was made by going from $C_{60} \rightarrow C_{70} \rightarrow C_{80} \rightarrow$CNT in a public discussion with Richard Smalley (Dec. 1990) in Washington, D.C.
- This idea suggested that a single wall carbon nanotube (SWNT) would be interesting (August 1991 fullerene conference) and led to calculating the electronic structure of SWNTs before they were ever seen



R. Saito, M. Fujita, G. Dresselhaus, M. S. Dresselhaus, *APL* 60:2204 (1992)

2012 Kavli Prize in Nanoscience
M. Dresselhaus
"for her pioneering contributions to the study of phonons, electron-phonon interactions, and thermal transport in nanostructures"

carbon nanotubes

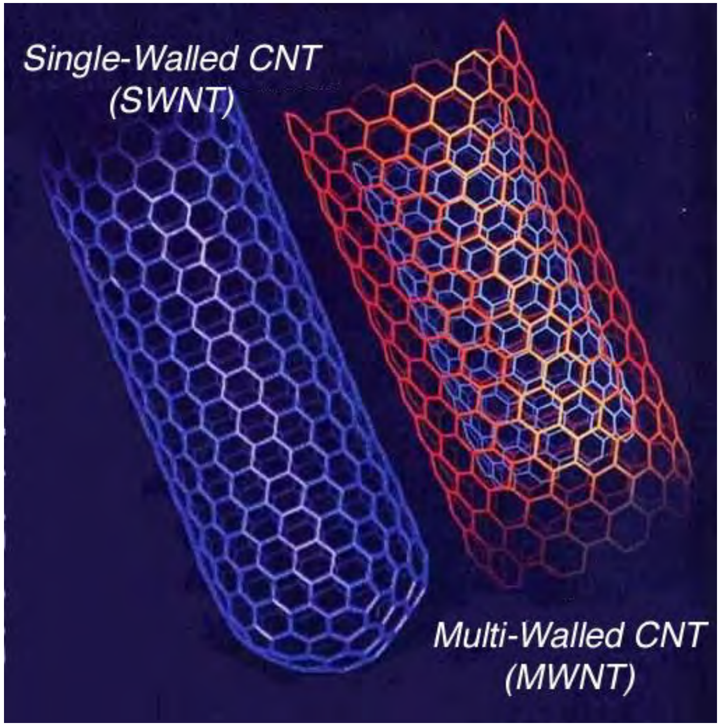


S. Iijima, 1991, 1993

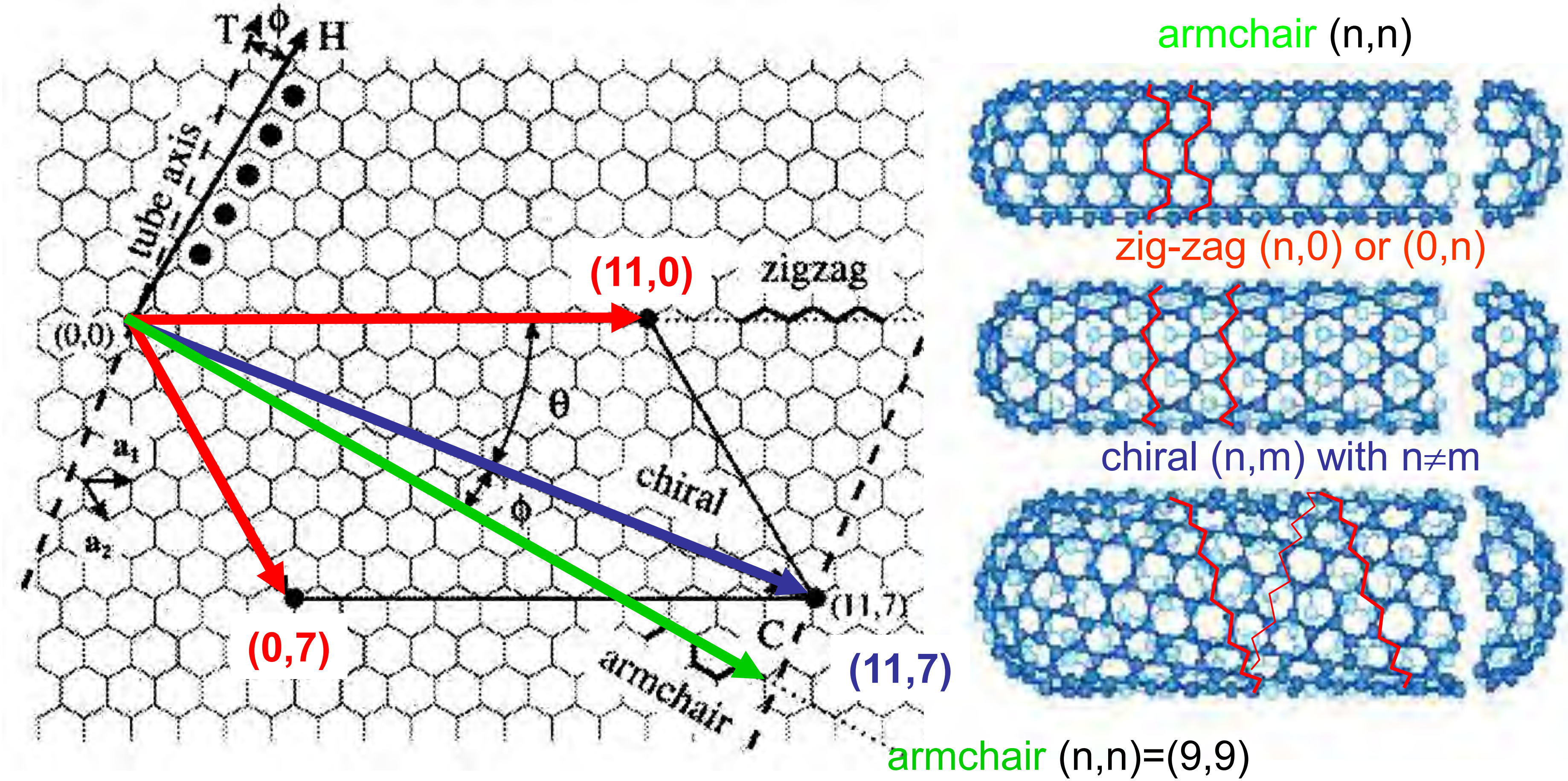
Single-wall or multi-wall

Metallic or semiconducting

Diameter: 0.5 - 50 nm
Length: < 100 mm



carbon nanotubes structure (wrapping vector)



n-m = 3*i: metallic

n-m <> 3*i: semiconducting

carbon allotropes discovery

The Nobel Prize in Physics 2010

Photo: U. Montan

Andre Geim

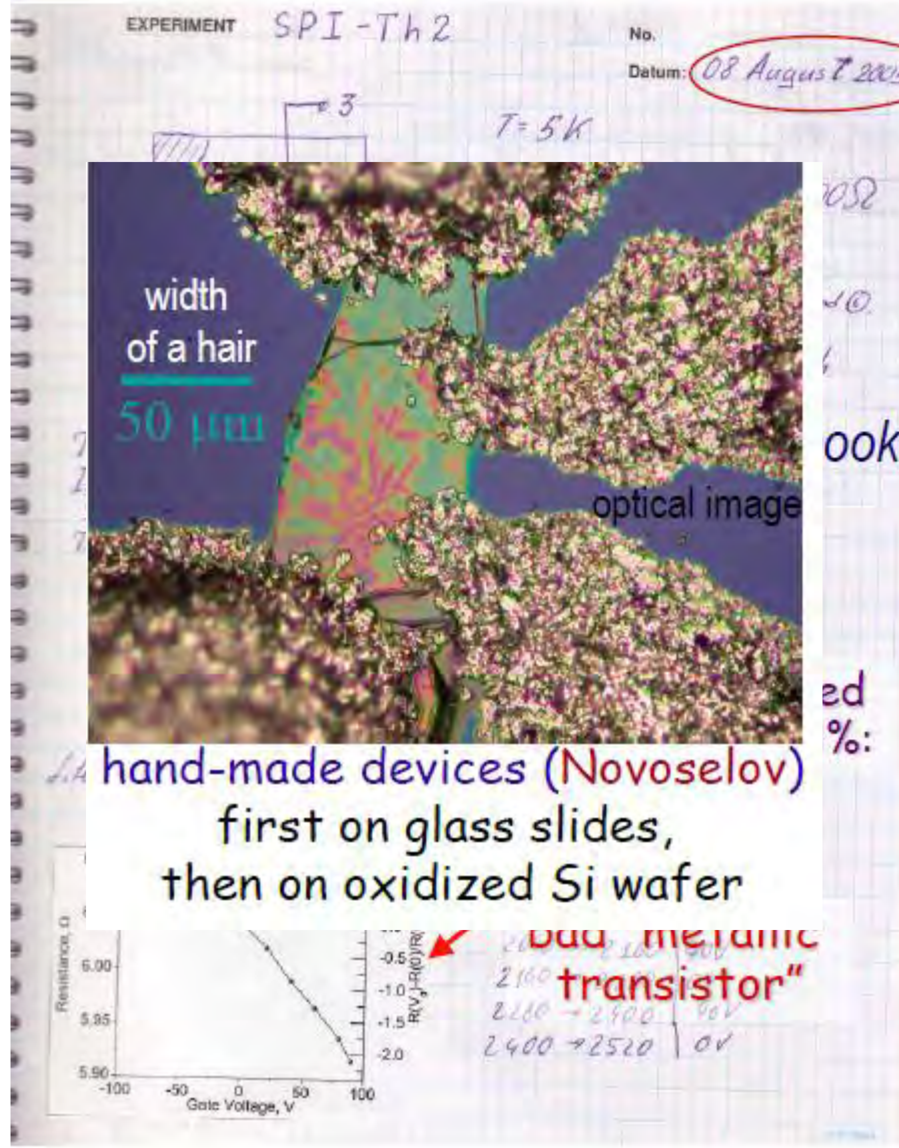
Prize share: 1/2

Photo: U. Montan

Konstantin Novoselov

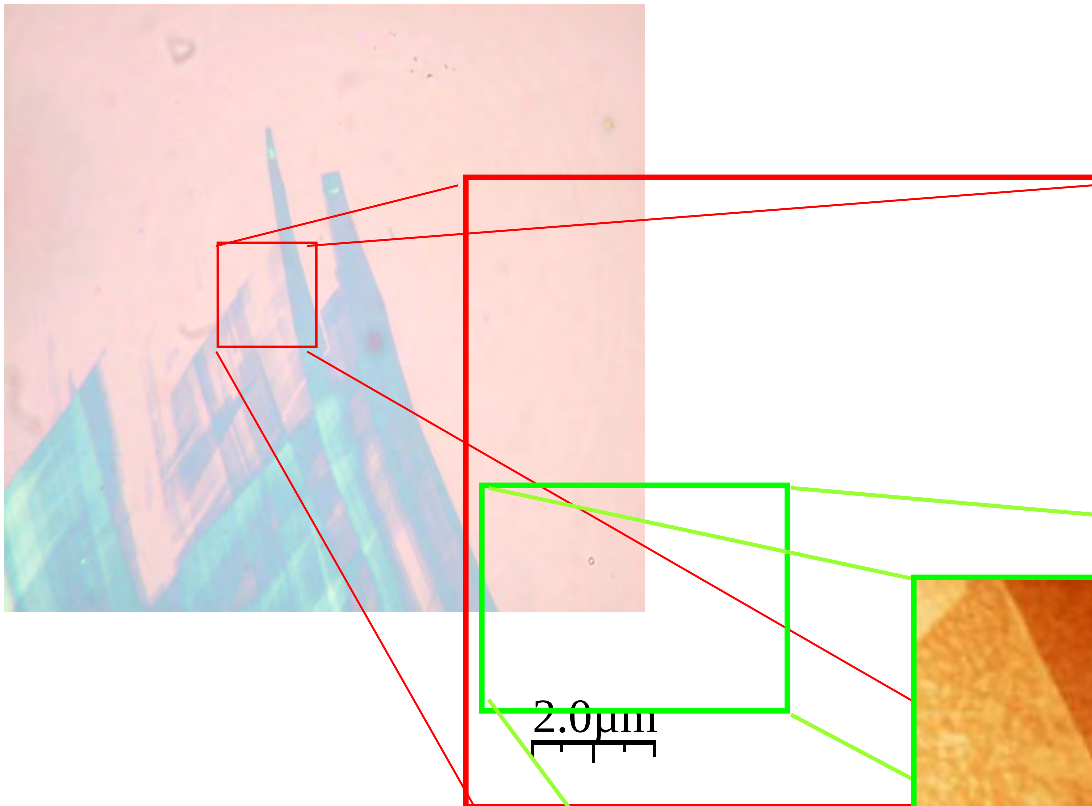
Prize share: 1/2

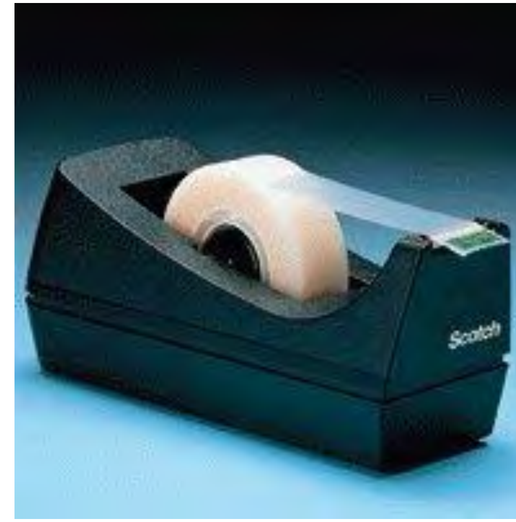
The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov *"for groundbreaking experiments regarding the two-dimensional material graphene"*

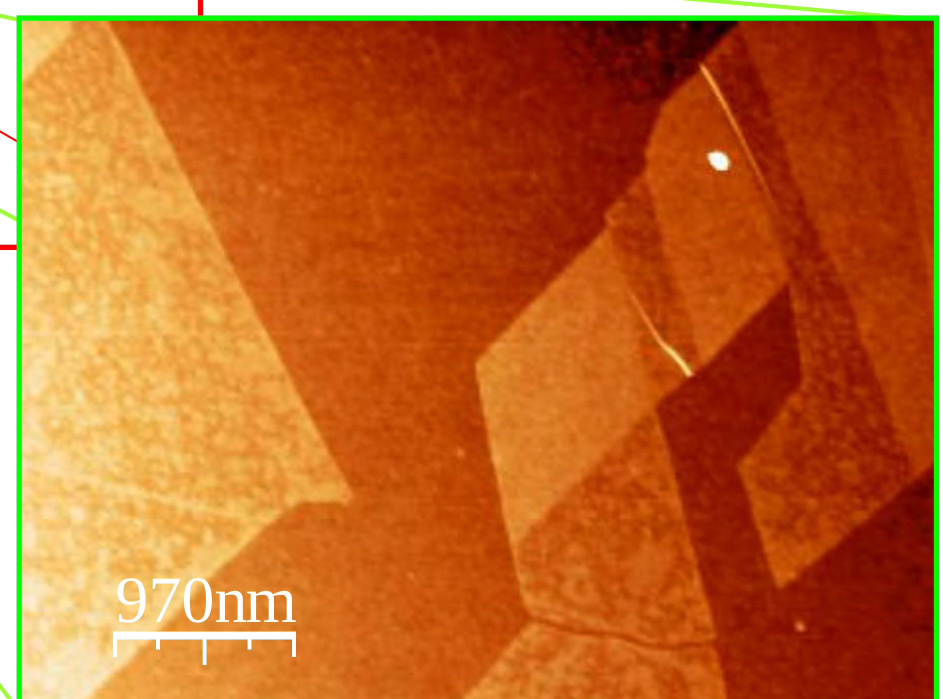


Nobel.se

Graphene: scotch tape







J. Trbovic and H. Aurich

graphene discovery

graphene : the missing 2D system in carbon allotropes

1947	Graphene first studied as a limiting case for theoretical work on graphite by Phillip **Wallace**
1966	First attempts to grow multilayer graphite Hess W M and Ban L L also Karu A E and Beer M
1984	Massless charge carriers in graphene pointed out theoretically by Gordon Walter **Semenoff**, David P. **DeVincenzo** and Eugene J. **Mele**
1987	Name “graphene” first mentioned by S. Mouras and co-workers
2004	Graphene isolated in free form by Andre **Geim** and Kostya **Novoselov**
2004	Observation of graphene’s **ambipolar field effect** by Geim & Novoselov
2005	**Anomalous quantum hall effect** detected showing massless nature of charge carriers in graphene Geim, Novoselov and **Kim**, Zhang
2006	**Quantum Hall effect seen at room temperature** by Novoselov et. al.
2007	first detection of a single molecule adsorption event by Schedin et. al.
2008	Measurements of extremely high carrier mobility by Bolotin et. al.
2010	Nobel prize in physics to Geim & Novoselov

from http://www.graphene.manchester.ac.uk

graphene: why it may have taken so long…

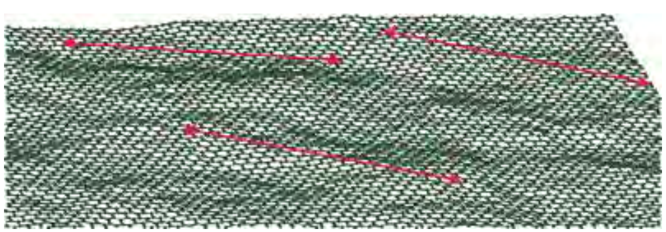
Here, however, the following reservation is necessary. The result obtained, strictly speaking, means only that the fluctuational displacement becomes infinite when the size (area) of the two-dimensional system increases without limit (so that the wave number may be arbitrarily small). But, because of the slow (logarithmic) divergence of the integral, the size of the film for which the fluctuations are still small may be very great.†

fluctuations "kill" a 2D crystal

Let us note first of all that, when $T = 0$, a two-dimensional lattice of *any* size could exist: the divergence of the integral (137.11) is due to the thermal fluctuations ($T \neq 0$).

Landau & Lifschitz, Statistical Physics,
3rd ed.,1980, Part I, §137 & 138, pp435-436

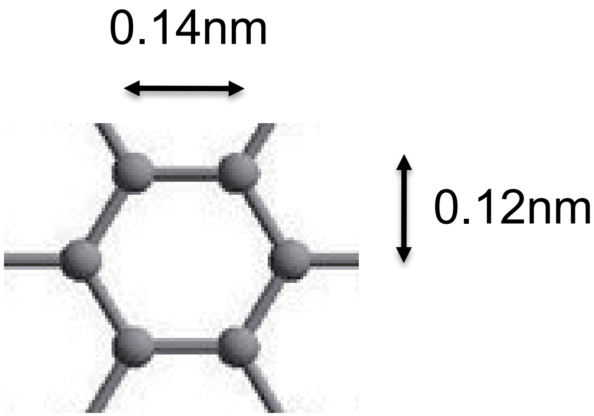
the ripples of graphene



"According to the so-called Mermin–Wagner theorem[1], long-wavelength fluctuations destroy the long-range order of 2D crystals. Similarly, 2D membranes embedded in a 3D space have a tendency to be crumpled[2]. These fluctuations can, however, be suppressed by anharmonic coupling between bending and stretching modes meaning that a 2D membrane can exist but will exhibit strong height fluctuations."

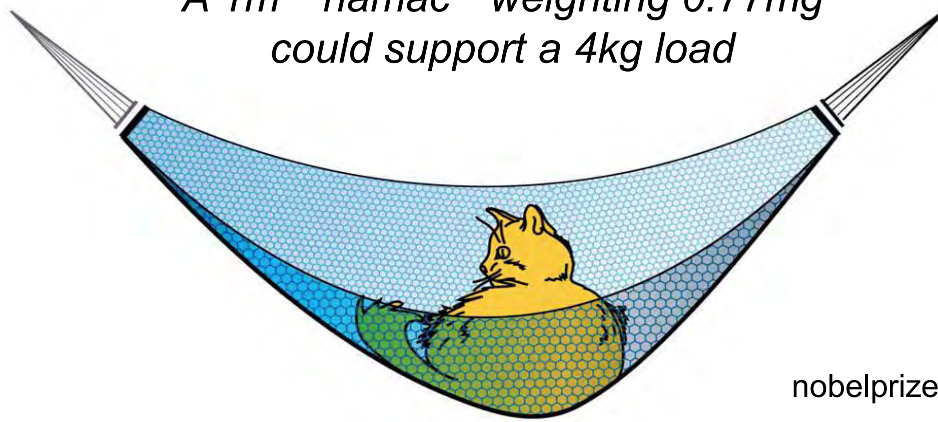
Katsnelson et al., Nature Mat. (2007)

graphene



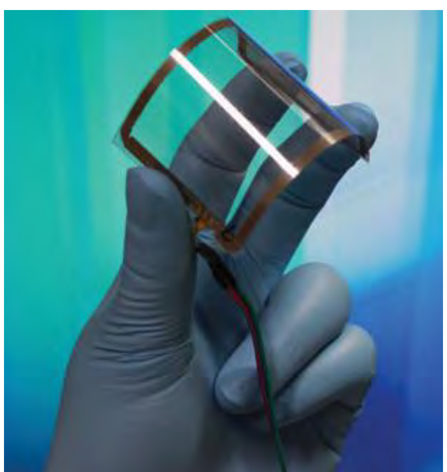
Mechanically strong: composite materials

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

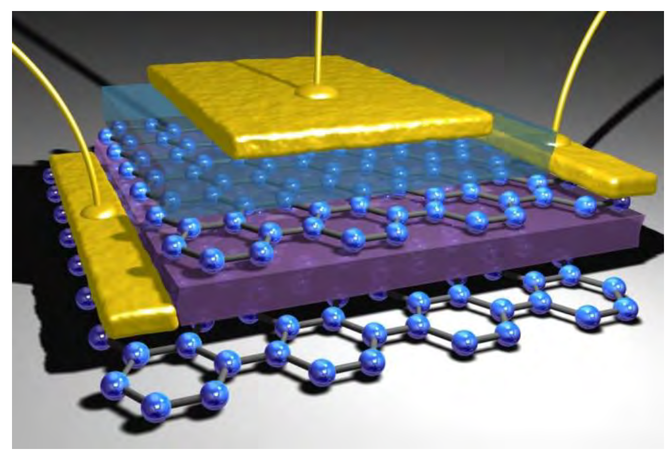


nobelprize.org

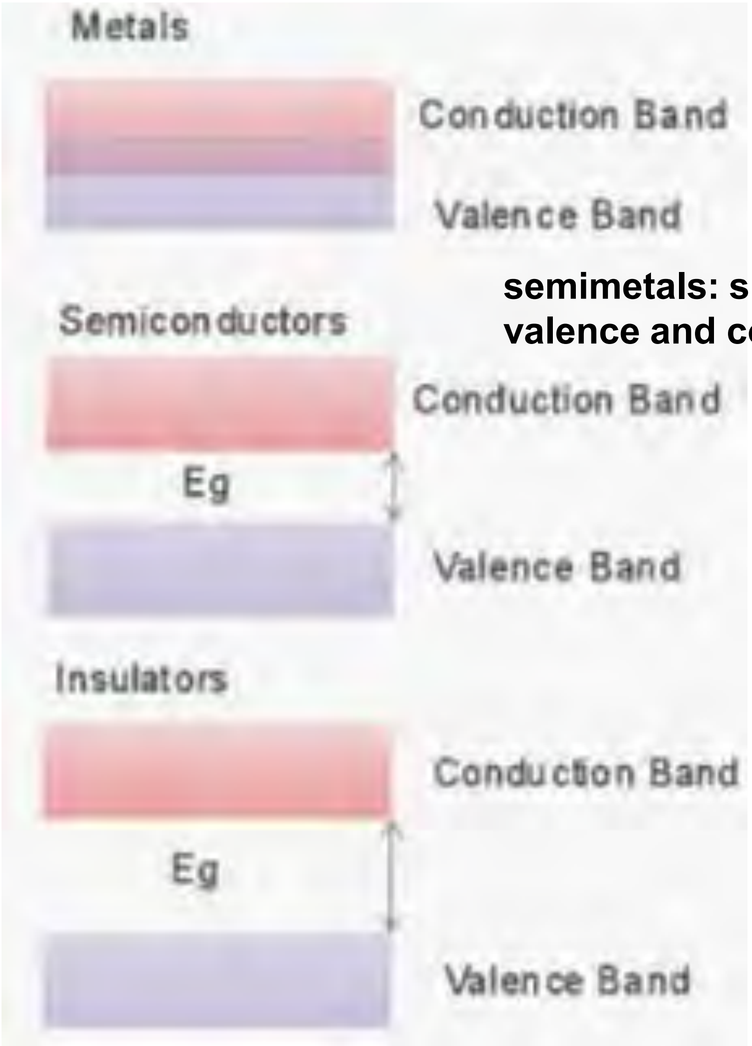
Flexible conductor
may replace ITO



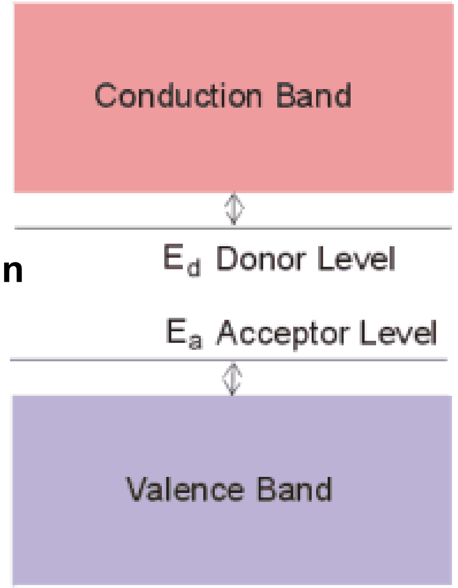
High charge mobility:
electrical applications



reminder: energy bands



semimetals: small overlap between valence and conduction bands



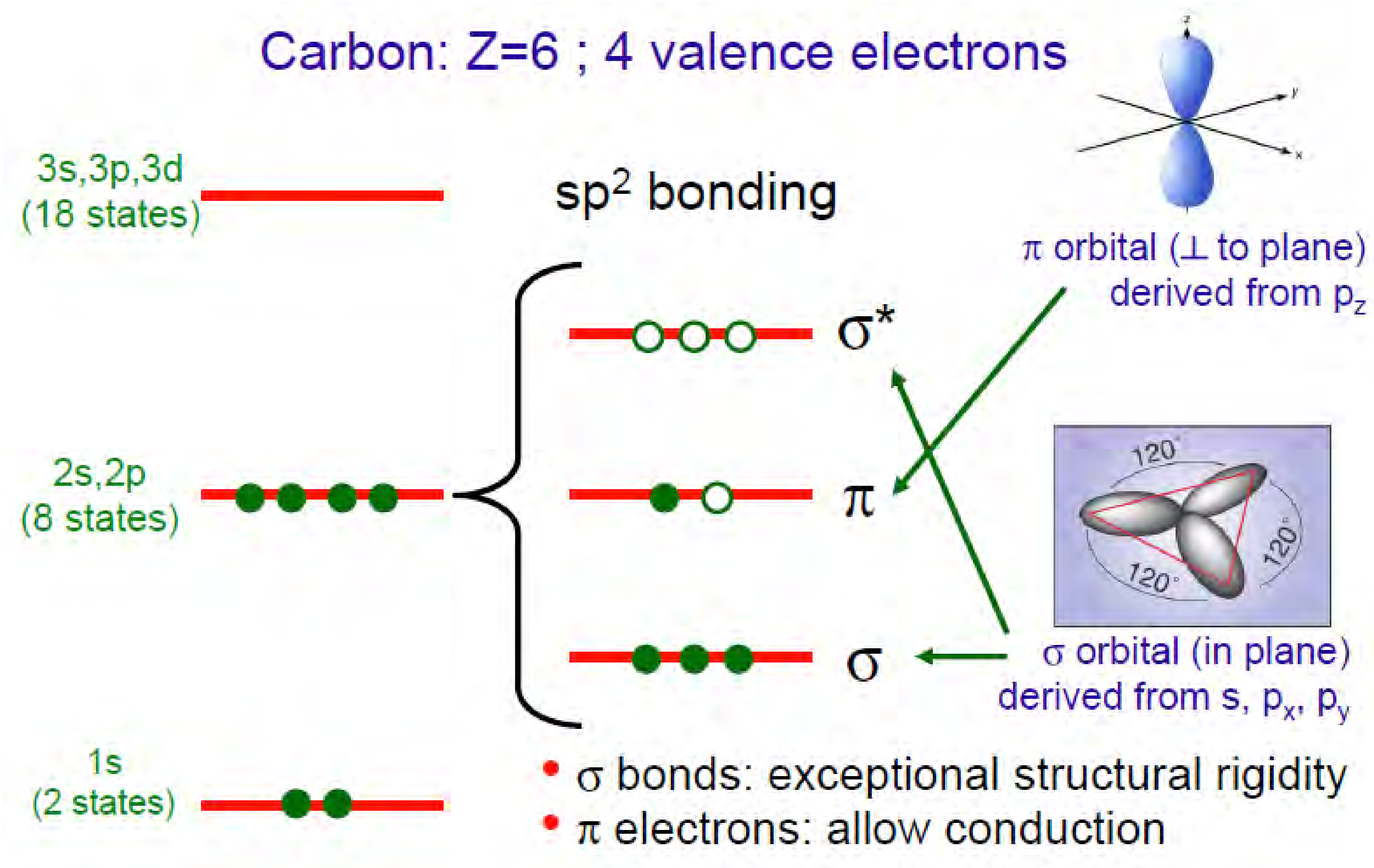
Energy gaps

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

NB: kT (RT) ~25meV

graphene electronic structure

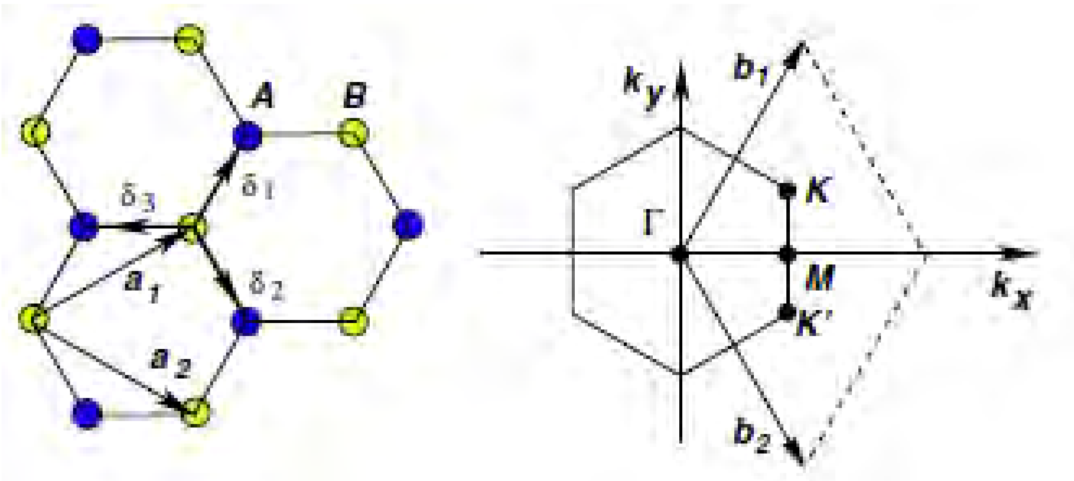
C: $1s^2 2s^2 2p^2$



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

Kane, Princeton

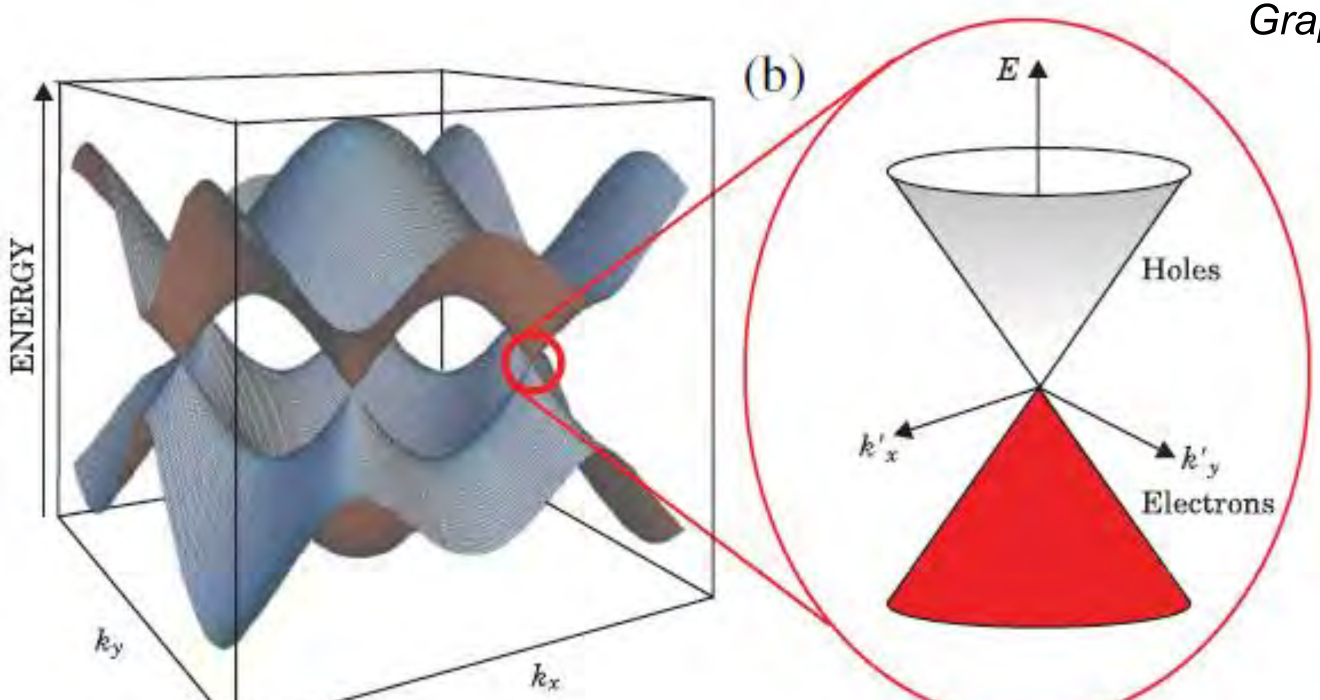
graphene electronic structure



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

Graphene Brillouin zone in momentum space

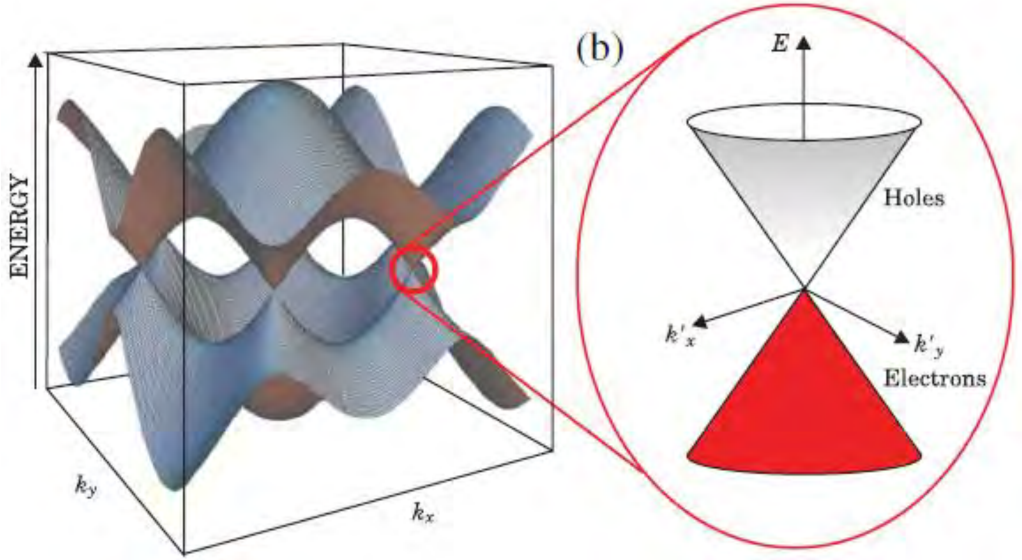
Graphene bandstructure



- 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

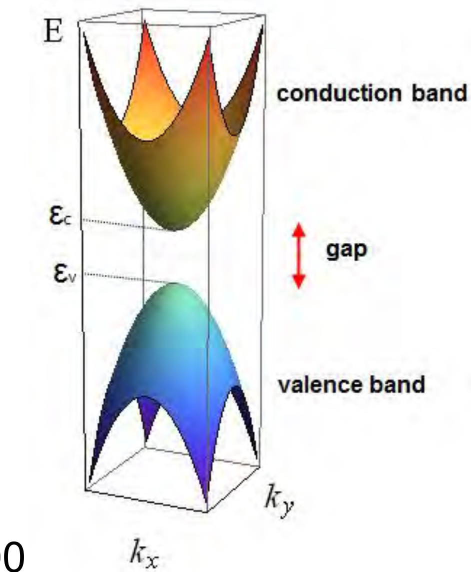
graphene electronic structure



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

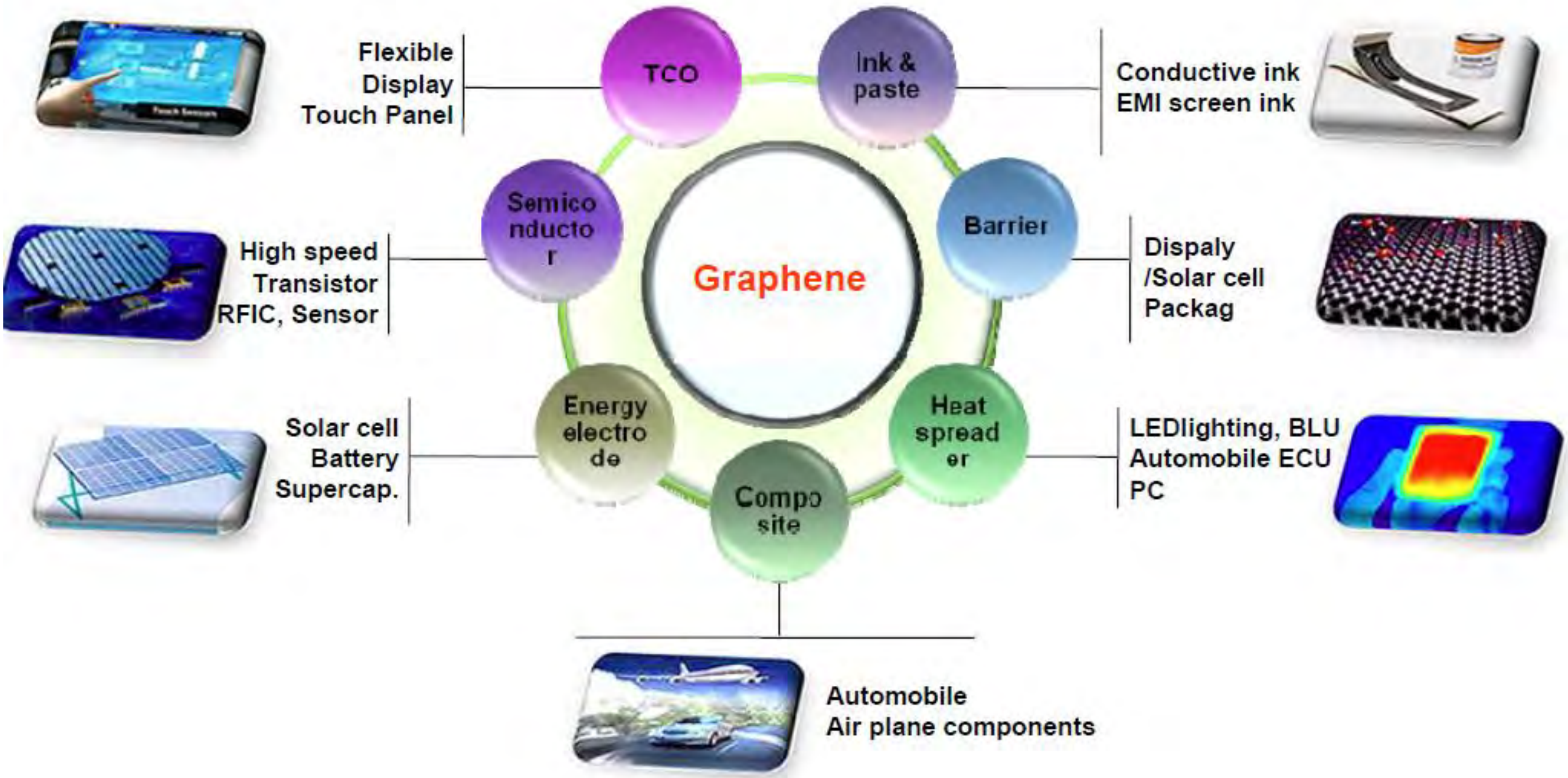
Graphene: $$E = \hbar v_F k$$

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

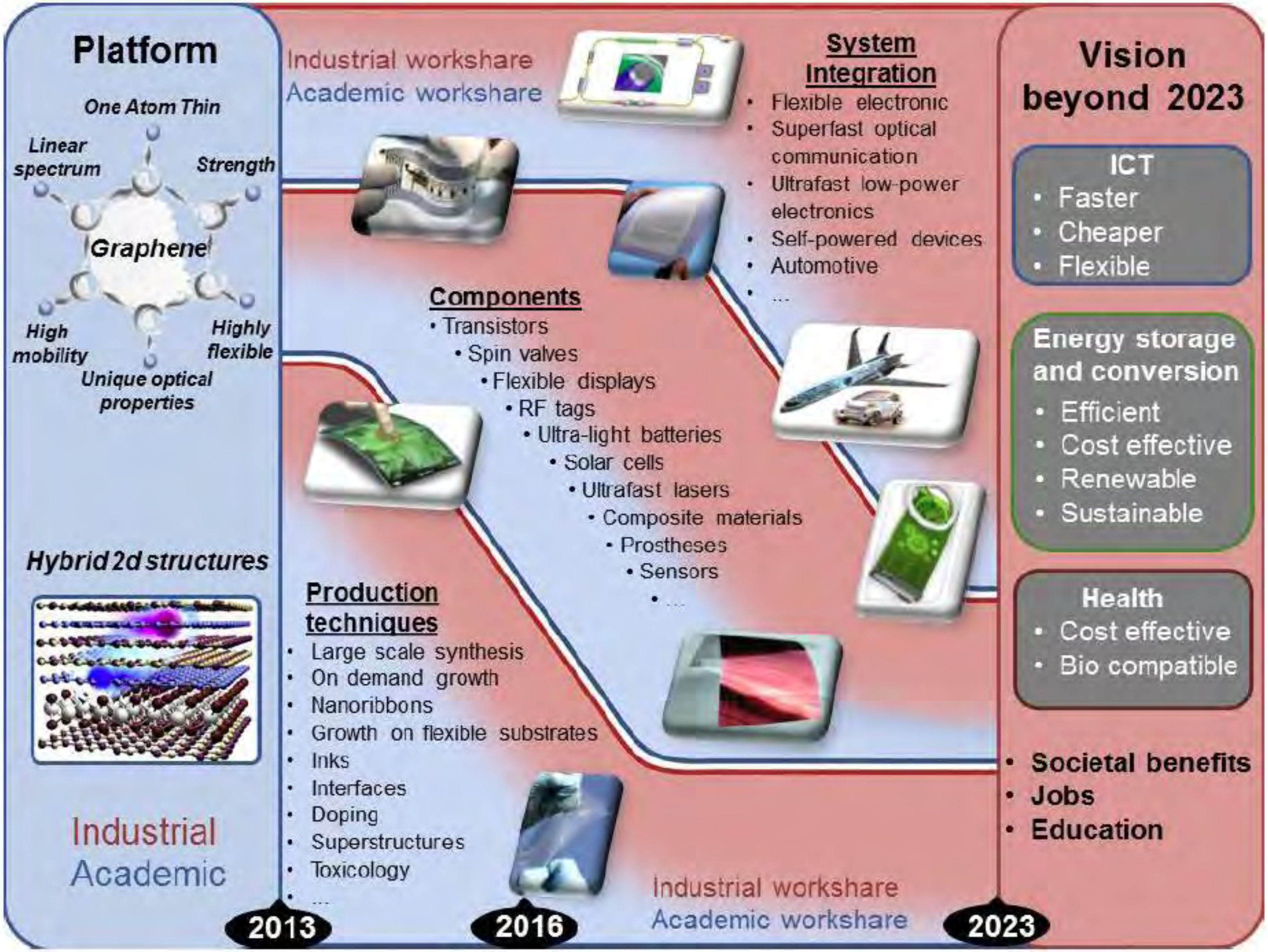
Castro Neto et al., Rev. Mod. Phys. 2009; Das Sarma et al., Rev. Mod. Phys 2011

graphene roadmap



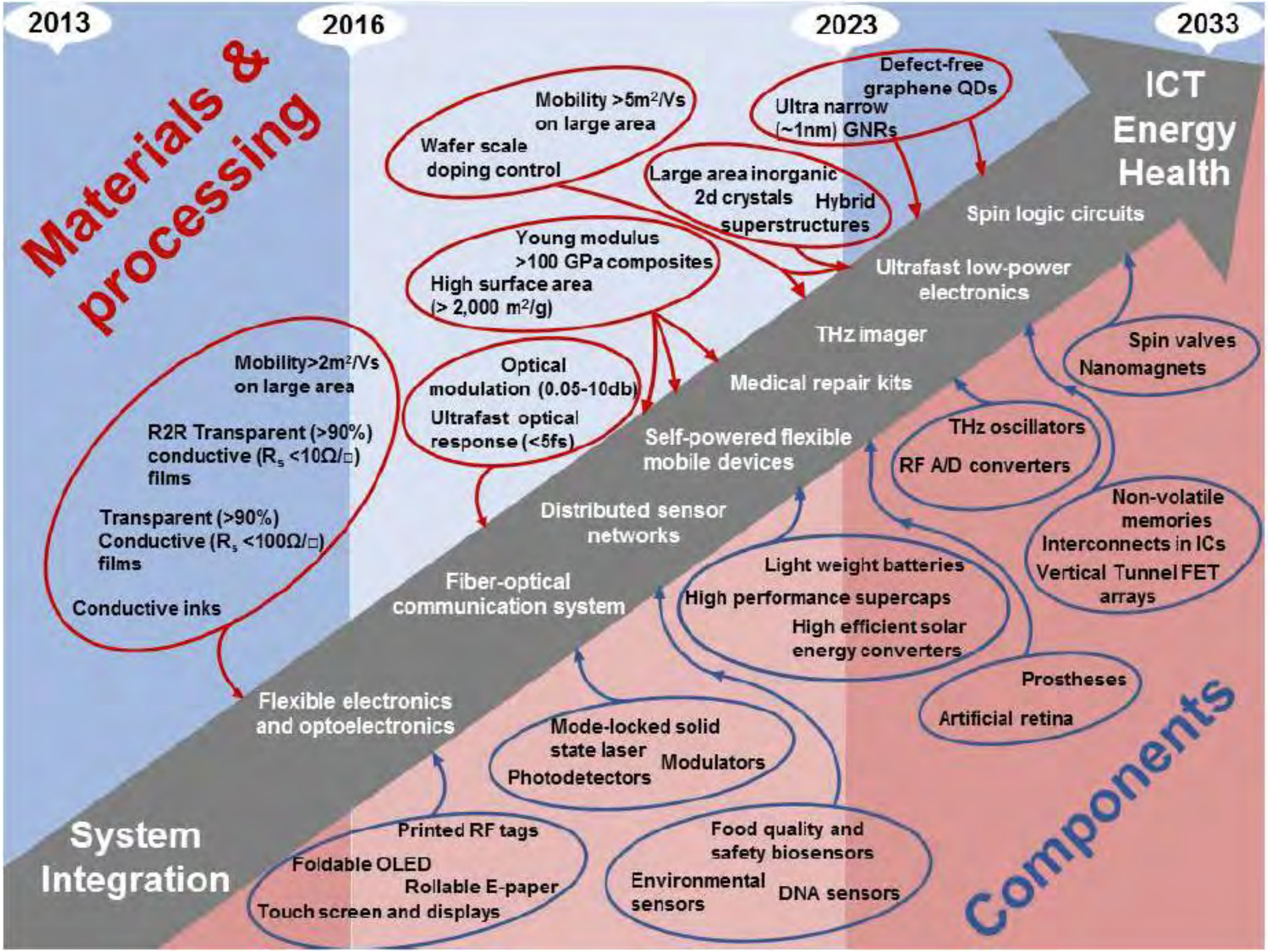
A. Ferrari, et al. 2011, 2015

graphene roadmap



graphene-flagship.eu/

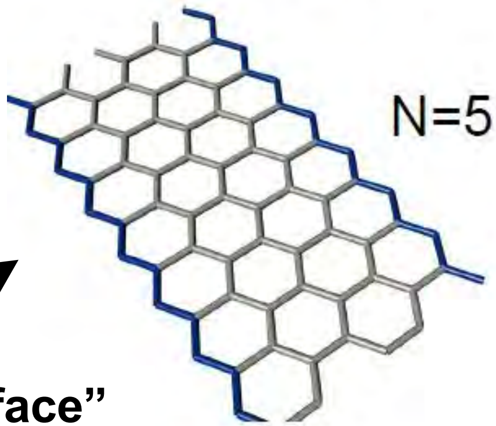
graphene roadmap



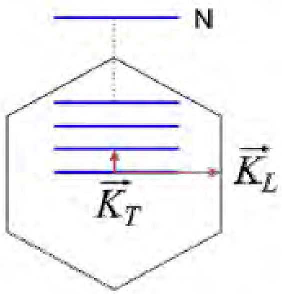
graphene-flagship.eu/

adding a gap: graphene ribbons structure

Zigzag edges

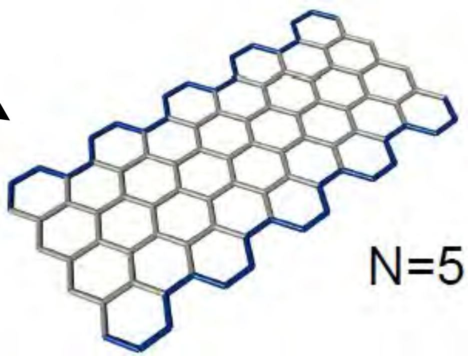


- **Always metallic**
- **Presence of localized edge states at the Fermi level**



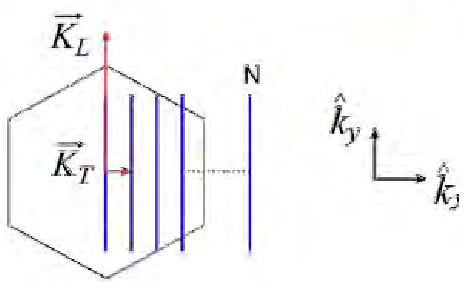
Nakada et al., *PRB* 54:17954 (1996)

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



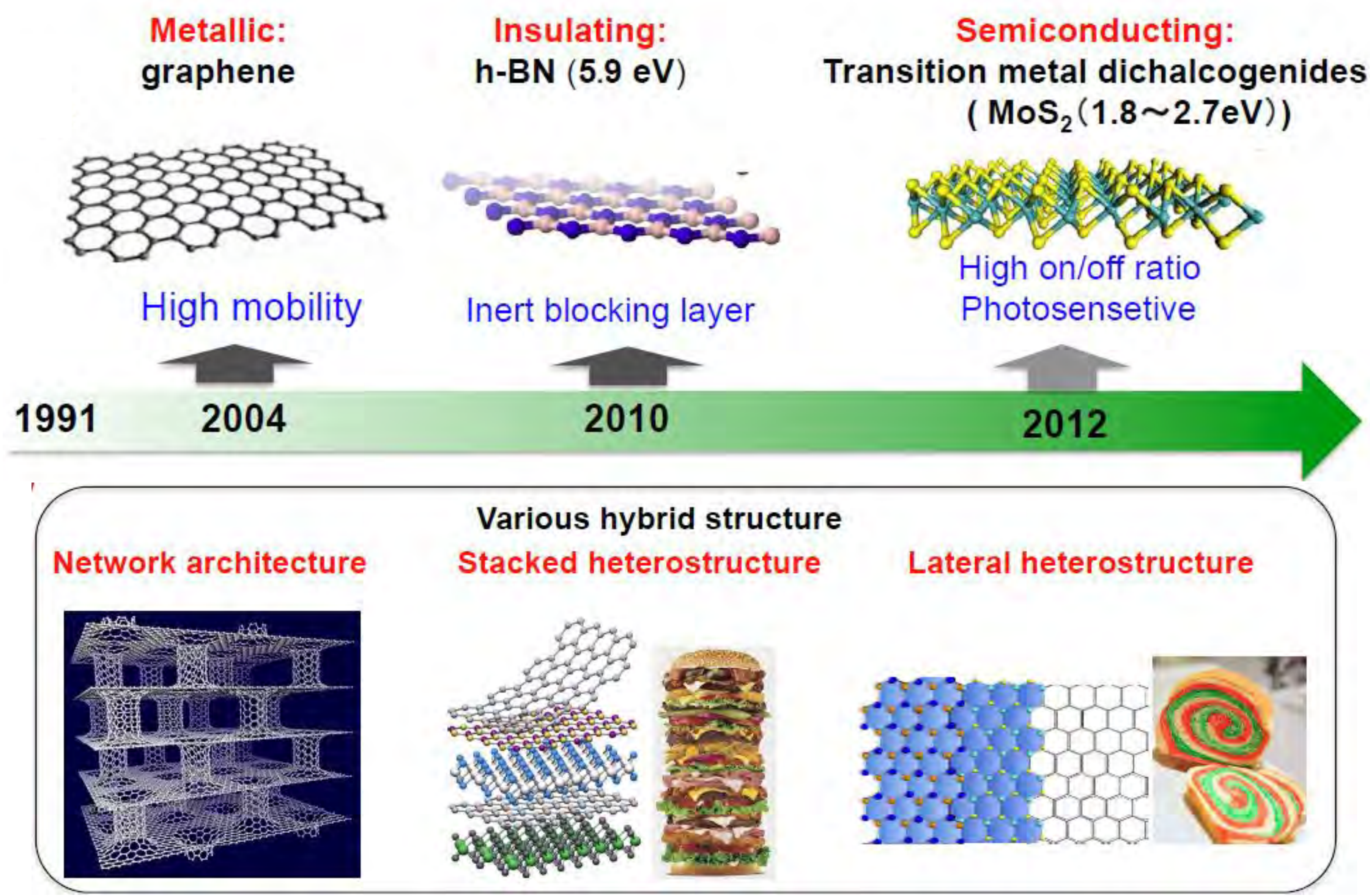
Armchair edges

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

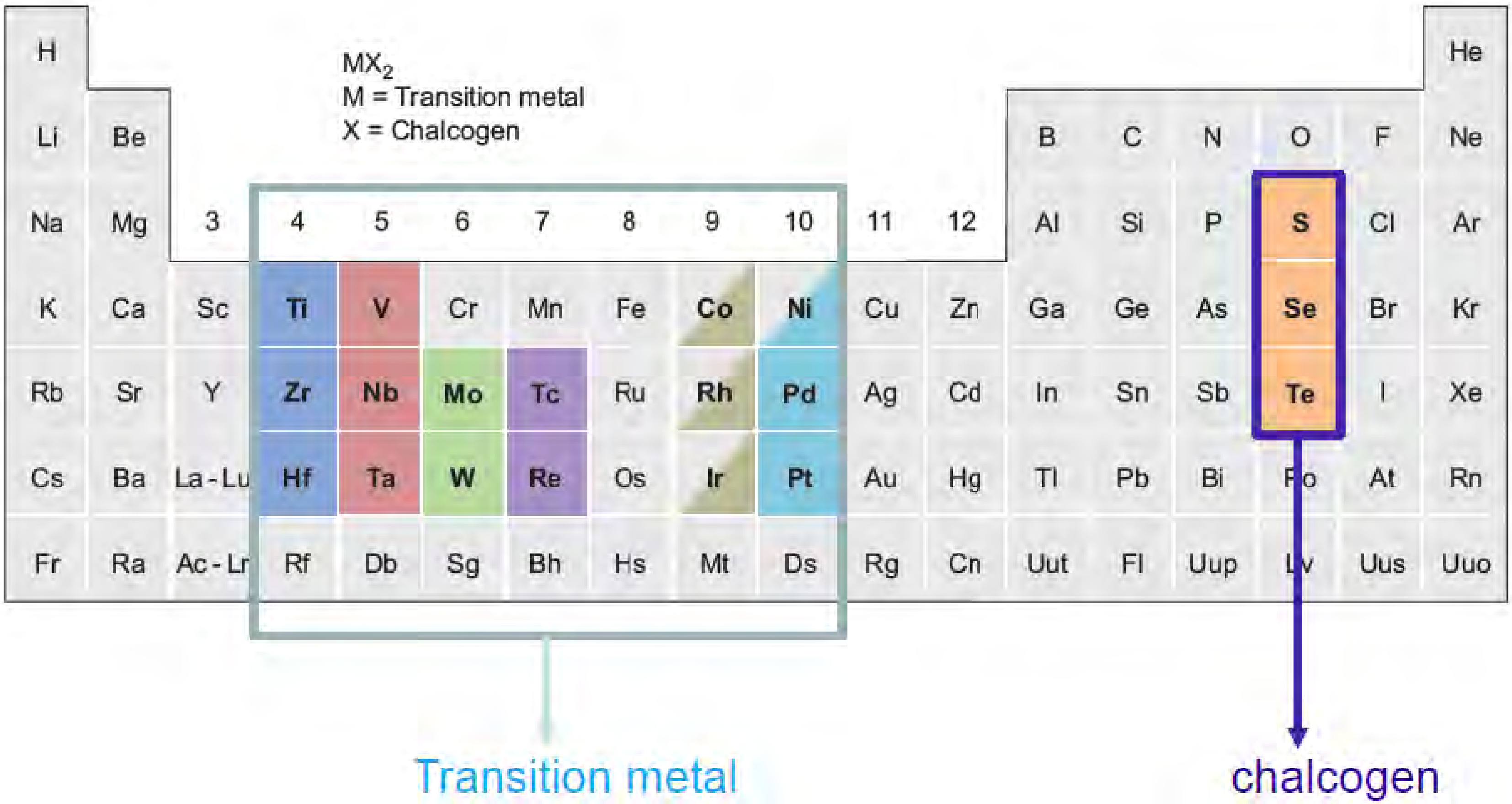
other 2D systems for electronics



Dresselhaus, Cargèse, 2014

other 2D systems

Transition Metal Dichalcogenides (TMDs)



Many possibilities for this materials system

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

other 2D systems

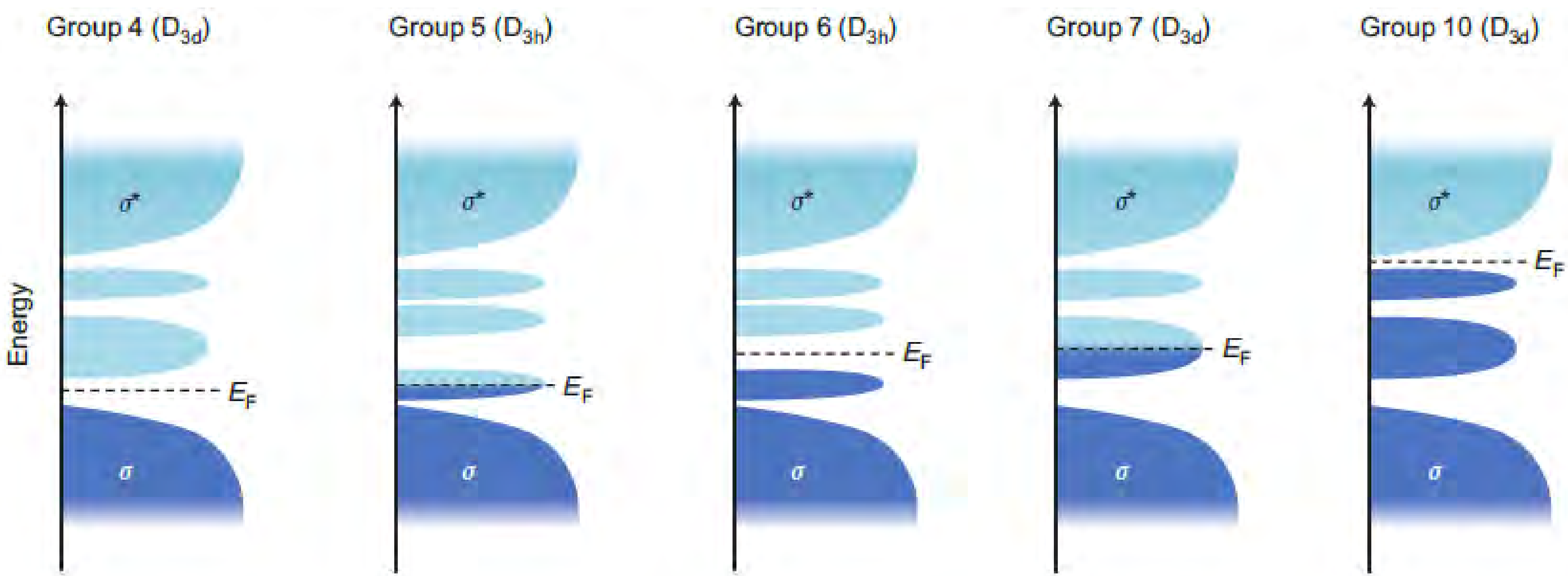
Table 1 | Electronic character of different layered TMDs[25].

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 ($\rho \sim 10^{-4}$ Ω.cm) or semimetals. Superconducting. Charge density wave (CDW). Paramagnetic, antiferromagnetic, or diamagnetic.
6	Mo, W	S, Se, Te	Sulfides and selenides are semiconducting ($E_g \sim 1$ eV). Tellurides are semimetallic ($\rho \sim 10^{-3}$ 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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4	Ti, Hf, Zr	S, Se, Te	Semiconducting (E_g = 0.2–2 eV). Diamagnetic.
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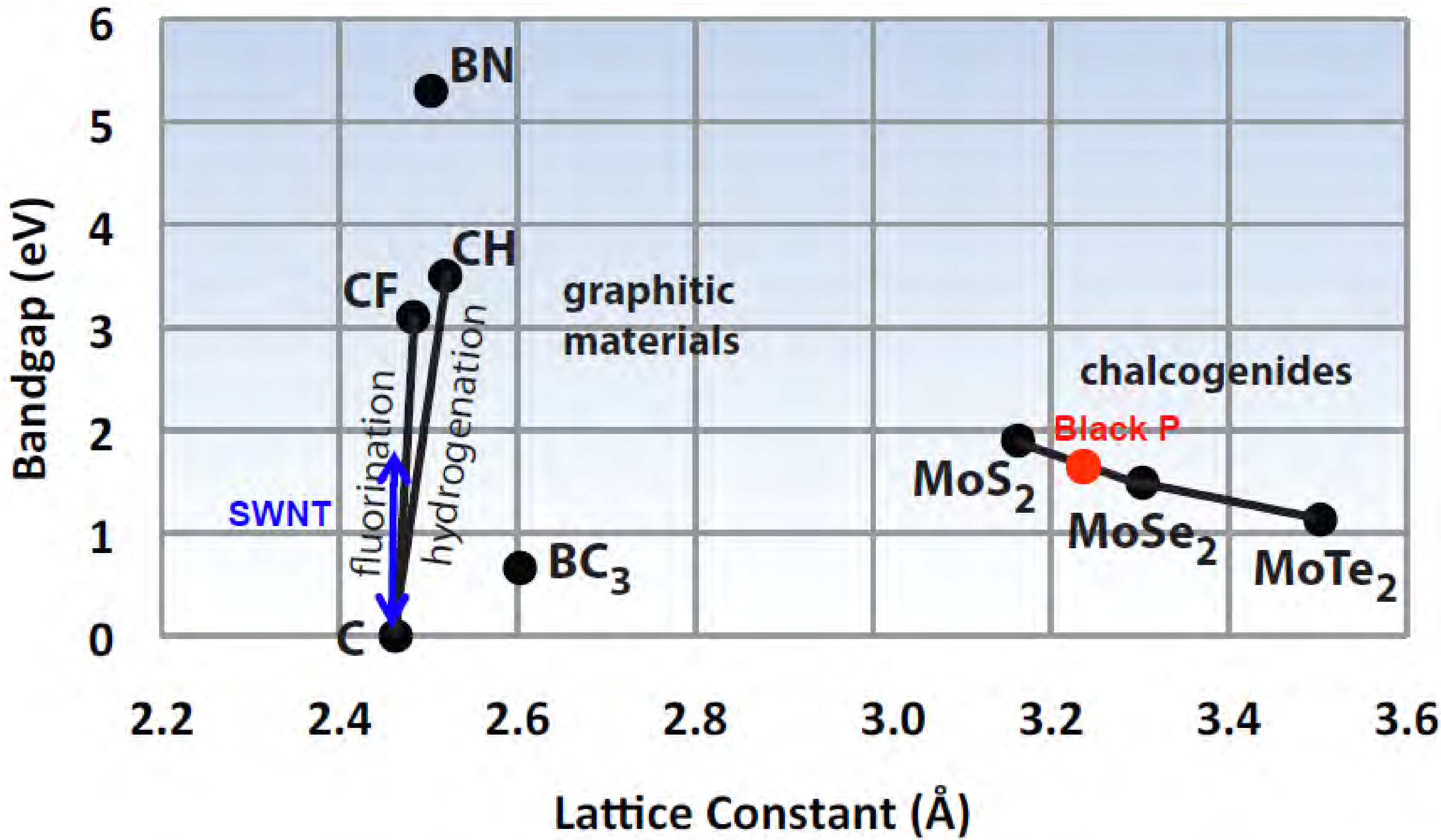
Chhowalla et al., Nat. Chem. (2013)

other 2D systems

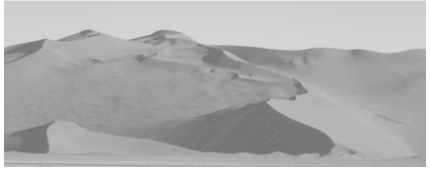


Martel, Szkopek, Cargèse, 2014

outline

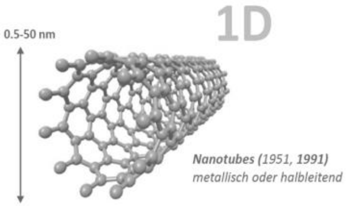
electronics beyond Silicon

- other possible pathways for electronics



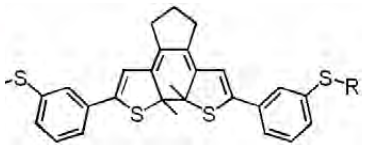
Carbon allotropes

- discovery



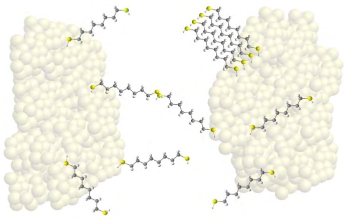
Carbon & molecular electronics

- brief historical account
- why molecules



molecular junctions

- how to contact nm-scale objects



carbon-based electronics

materials

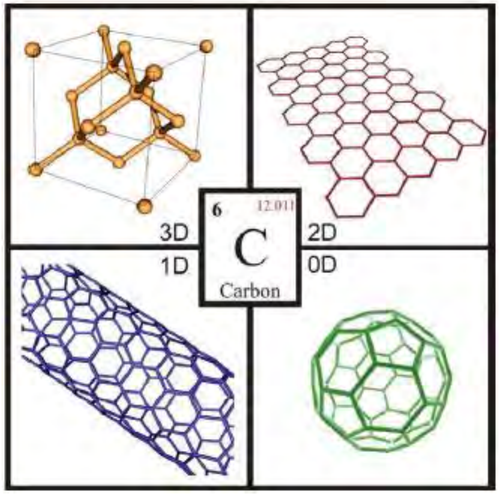


Table I. Electronic Properties of Carbon-Based Materials Compared with Other Common Semiconductors.

	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

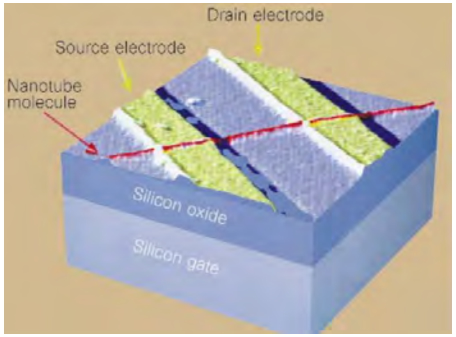
Overview Carbon-based electronics: see e.g. . Avouris et al. Nat. Nano 2007, McCreery, Faraday Disc. 2014

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)

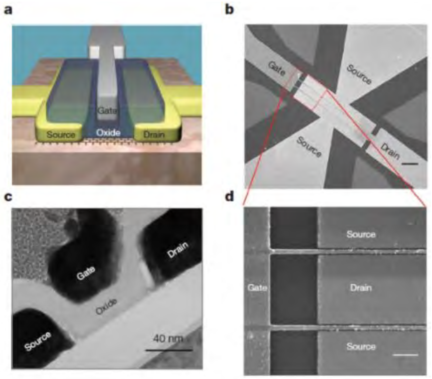
Paul McEuen, professor of physics at Cornell University and director of the Kavli Institute at Cornell for Nanoscale Science.

LETTER

doi:10.1038/nature09979

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

Yanqing Wu[1], Yu-ming Lin[1], Ageeth A. Bol[1], Keith A. Jenkins[1], Fengnian Xia[1], Damon B. Farmer[1], Yu Zhu[1] & Phaedon Avouris[1]



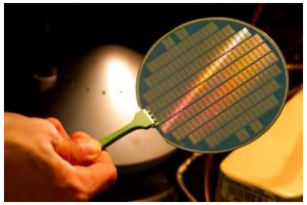
Nature 2011

LETTER

doi:10.1038/nature12502

Carbon nanotube computer

Max M. Shulaker[1], Gage Hills[2], Nishant Patil[3], Hai Wei[4], Hong-Yu Chen[5], H.-S. Philip Wong[6] & Subhasish Mitra[7]



Nature 2013

LETTER

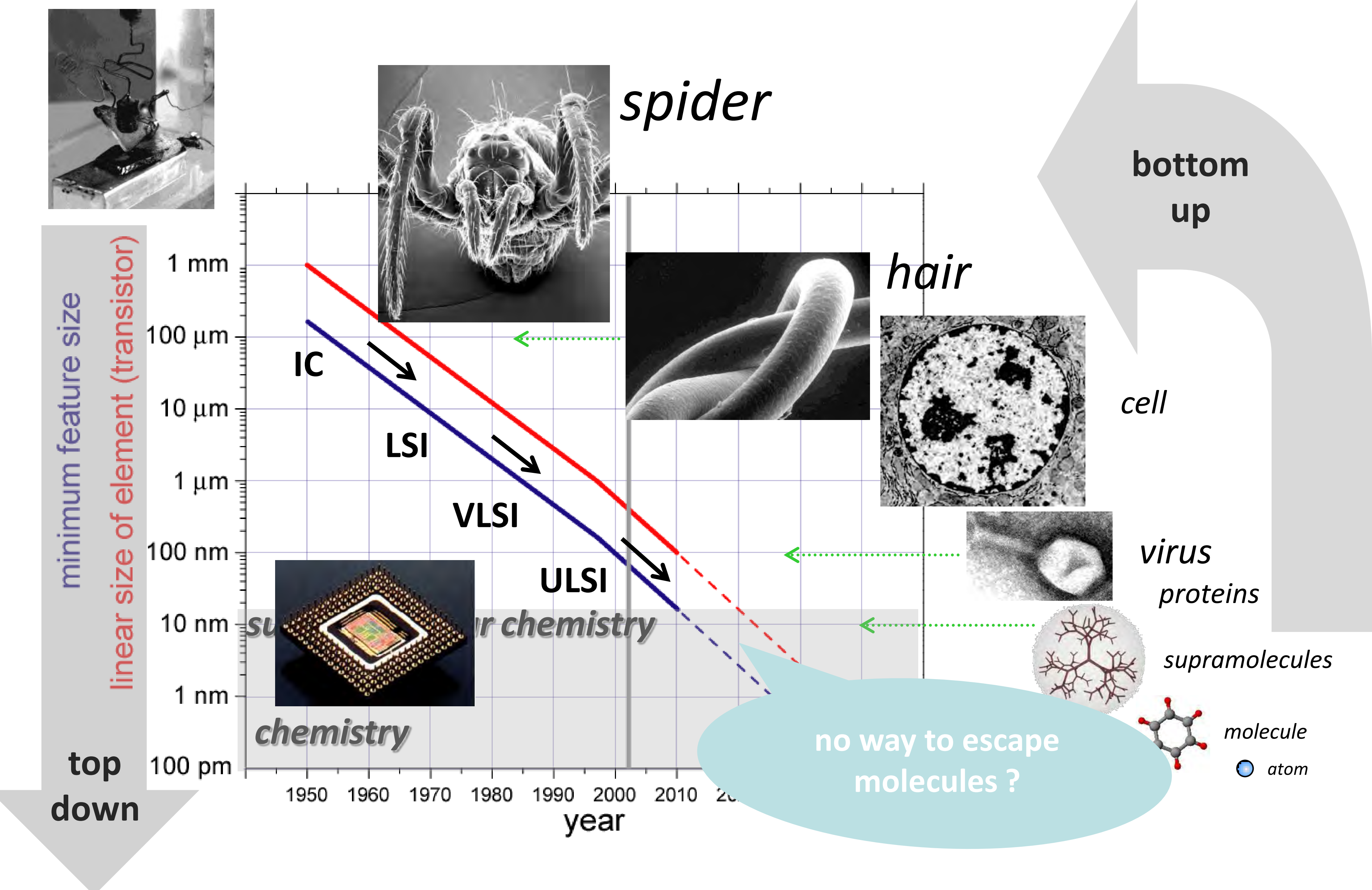
doi:10.1038/nature12952

Exceptional ballistic transport in epitaxial graphene nanoribbons

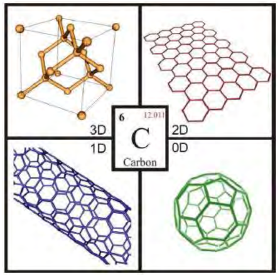
Jens Baringhaus[1]*, Ming Ruan[2]*, Frederik Edler[1], Antonio Tejeda[3,4], Muriel Sicot[3], Amina Taleb-Ibrahimi[4], An-Ping Li[5], Zhigang Jiang[2], Edward H. Conrad[2], Claire Berger[2,6], Christoph Tegenkamp[1] & Walt A. de Heer[2]

Nature 2014

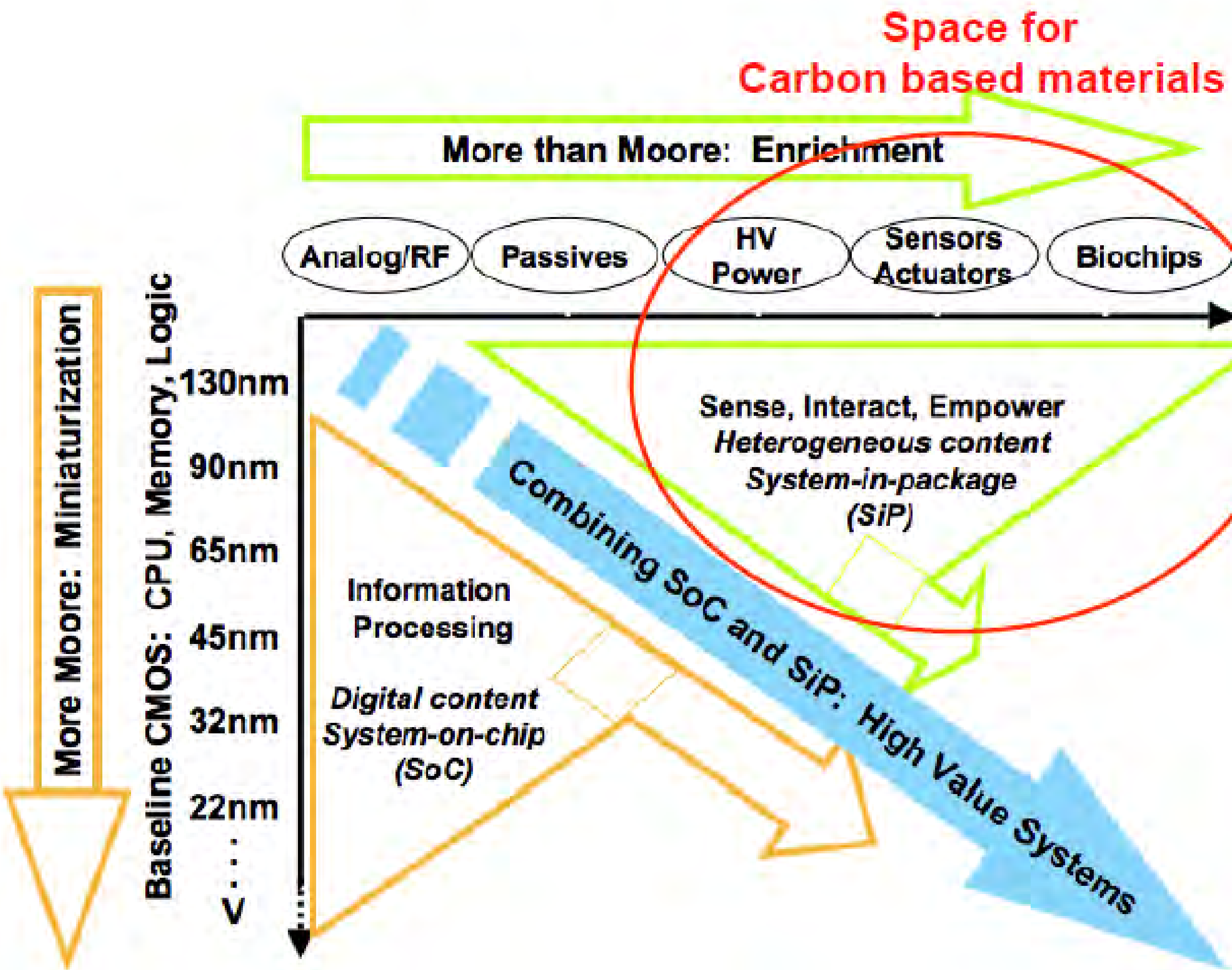
when macro meets nano: molecules



carbon-based electronics



materials



ITRS 2013, 2015; Martel, Cargèse, 2014

electronics with molecules ?

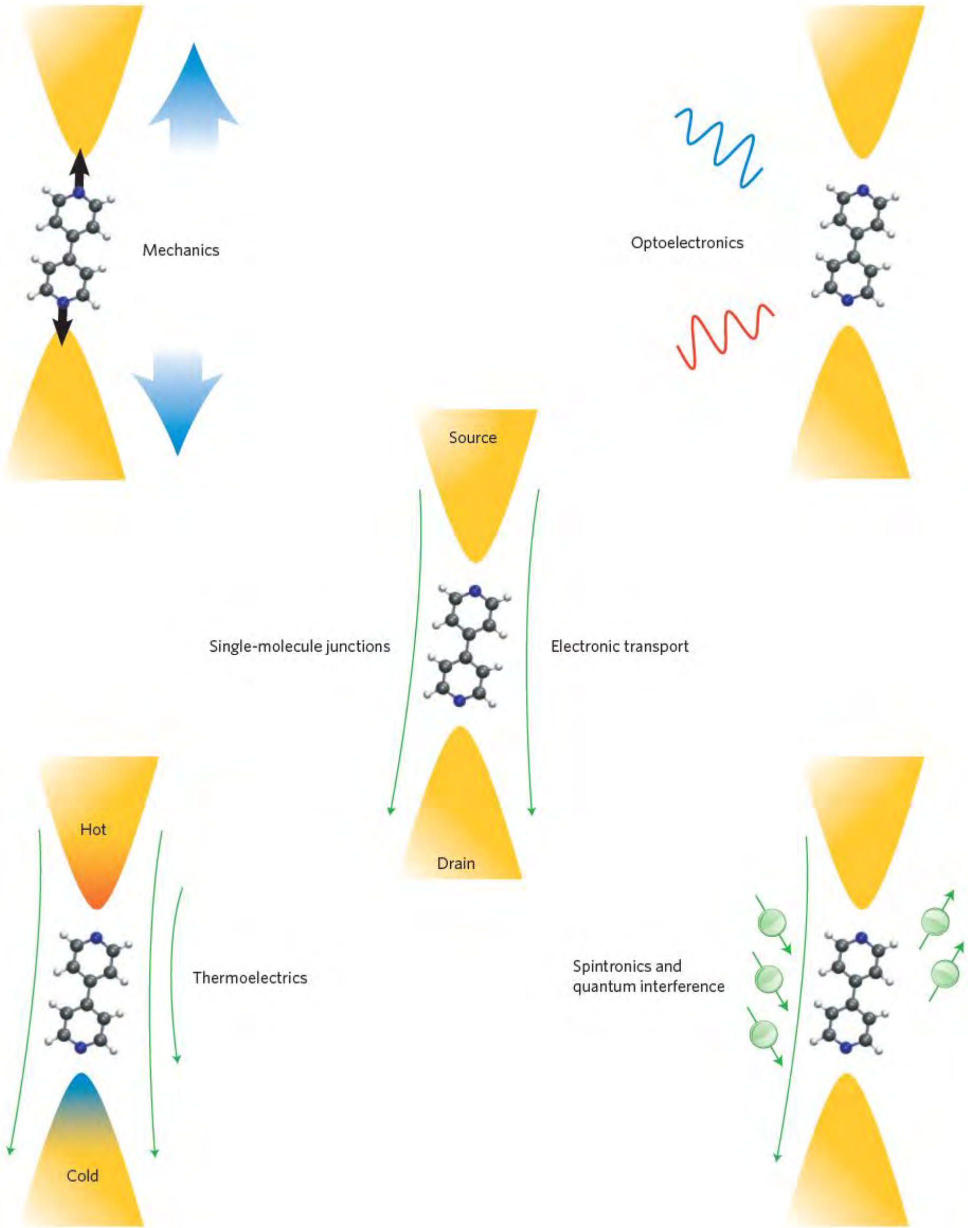
editorial

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.

electronics with molecules



Does molecular electronics compute?

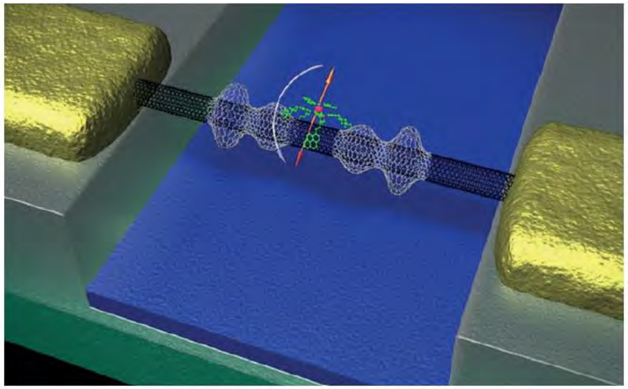
The field of molecular electronics originally set out to build computers, but silicon-based technology is unlikely to be replaced anytime soon. Nevertheless, the field has developed into a highly interdisciplinary endeavour, which could have a variety of ramifications that extend beyond computing.

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.

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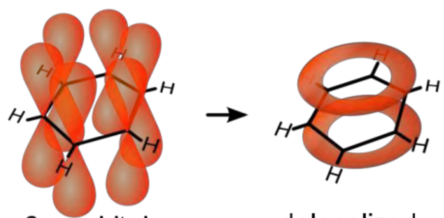
email: michel.calame@unibas.ch

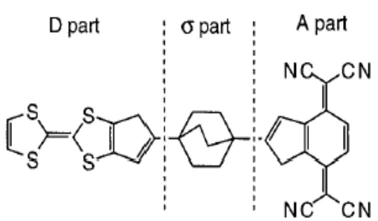
Nature Nanotech. 2013

electrically contacting molecules ...?

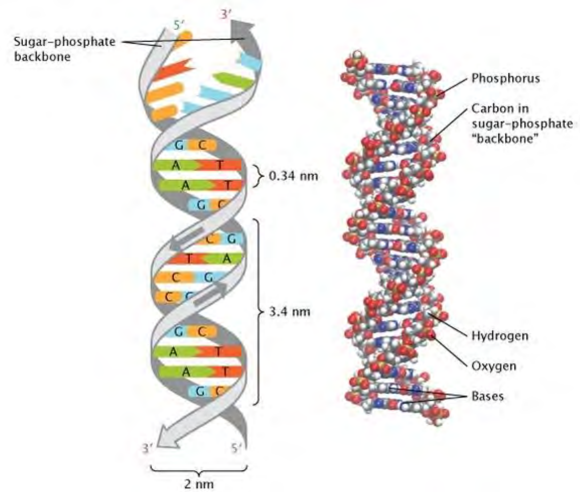
a brief (personal) historical perspective



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

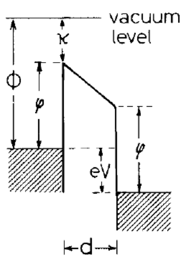


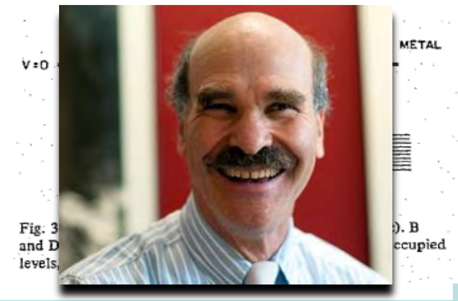
FIG. 1. Idealized potential barrier between similar electrodes separated by a fatty acid monolayer with a biased voltage.

A. Aviram, M. A. Ratner

molecular rectifier, 1974

(theory)

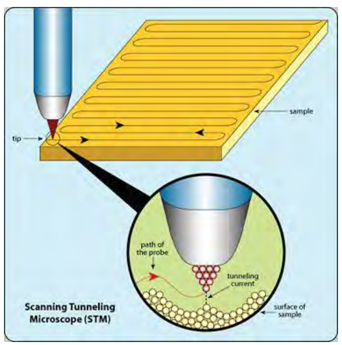
from molecular conduction to molecular electronics



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)



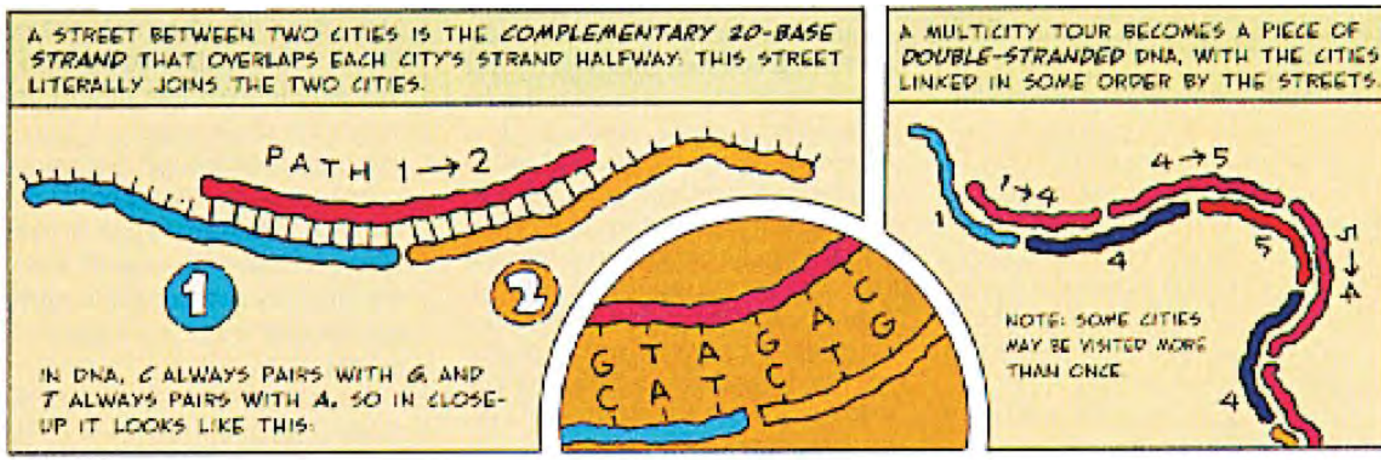
Gerd Binnig

Heinrich Rohrer

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

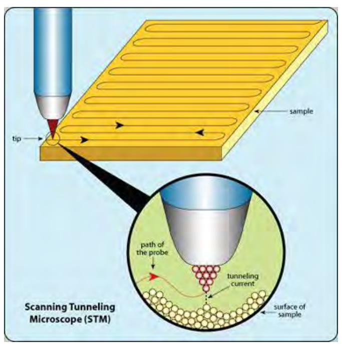
molecular recognition
computing with molecules – in solution - is highly parallel

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

1980 **1990** **2000**

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


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*

light

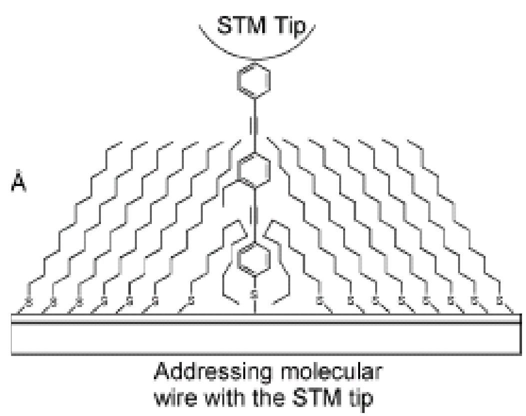
Ru cplx as donor   **Rh cplx as acceptor**

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*

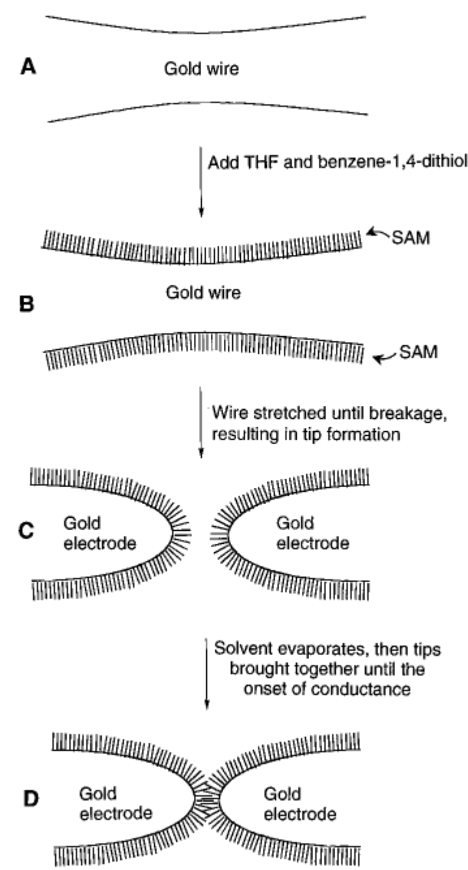
Science (1996)



Conductance of a Molecular Junction

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

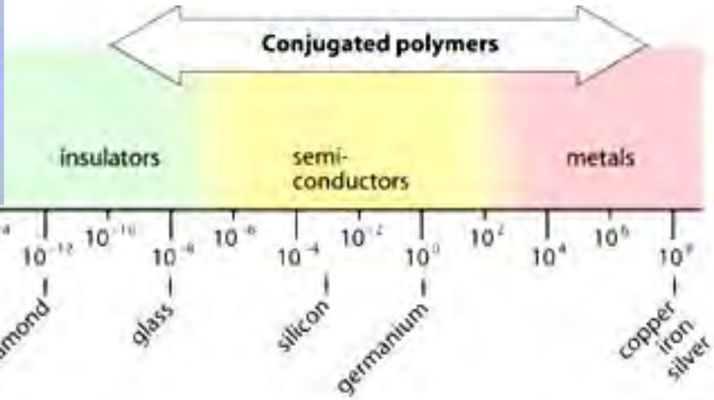
Science (1997)



1980   **1990**   **2000**

perspective

Nobel 2000



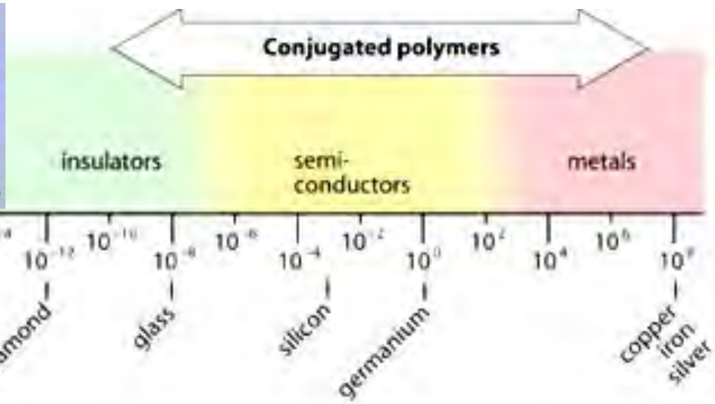
TV display
40” OLED
(EPSON, 2004)

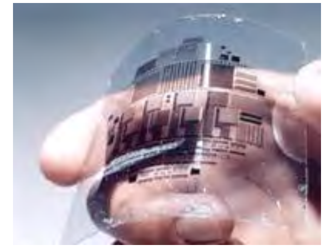
press release, Nobel prize 2000
(…) In the future we will be able to produce transistors and other ***electronic components consisting of individual molecules*** - which will dramatically increase the speed and reduce the size of our computers. A computer corresponding to what we now carry around in our bags would suddenly fit inside a watch ...

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

context

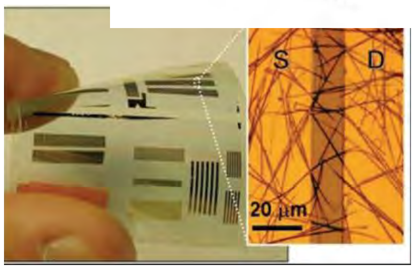
Nobel 2000





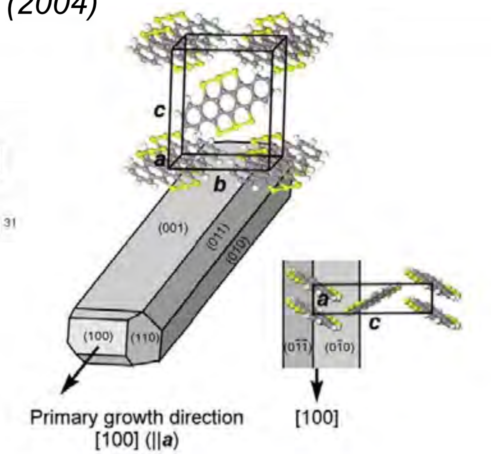
Low-cost organic electronics on plastic
Forrest, Nature (2004)

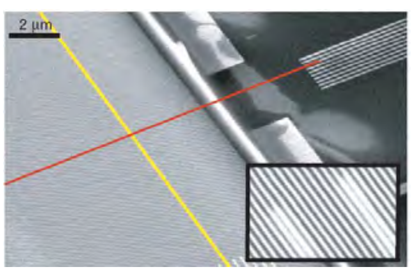
TV display, 40" OLED
(EPSON, 2004)



Organic nanowire transistors
Mat. Today (2008)

molecular crystals
(π-stacking)

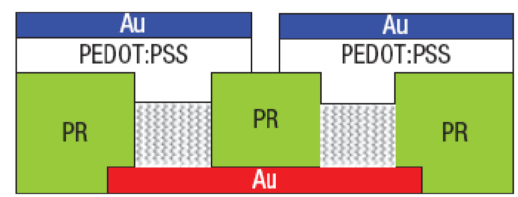




160kb crossed-wire memory
Heat et al., Nature (2007)

molecular mono-layers
(self-assembly)

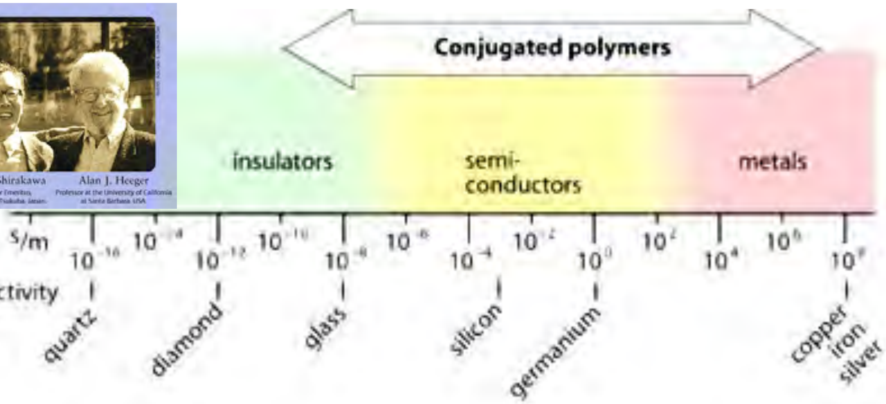
Organic ICs based on self-assembly (SAMFETs)
de Boer et al., Nature (2008)

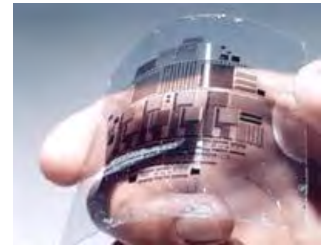


Large scale integr. of molecular junctions
de Leeuw et al., Nature Nano (2008)

perspective

Nobel 2000



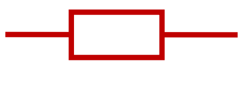


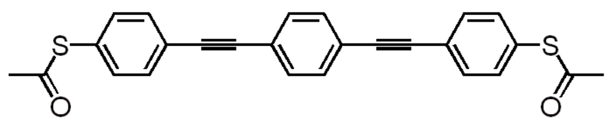
Low-cost organic electronics on plastic
Forrest, Nature (2004)

TV display, 40” OLED
(EPSON, 2004)

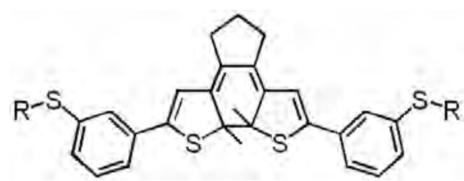
⇨ at the level of a few or even a single molecule ?

resistor
wire

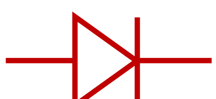


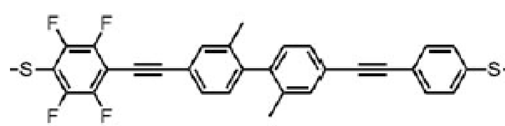


switch



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)

-

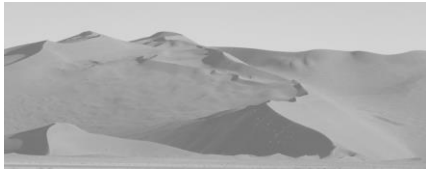
- reliable **connection** to the micro/macro-scopic world (**contacts**) and **characterisation of a single molecule** ?
- limited thermal and electrical **stability**
- what about the **reproducibility** of molecular devices ?
- how to fabricate/integrate **many devices** (upscaling) ?

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

outline

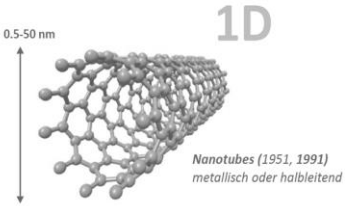
electronics beyond Silicon

- other possible pathways for electronics



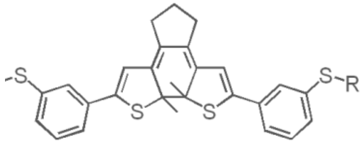
Carbon allotropes

- discovery



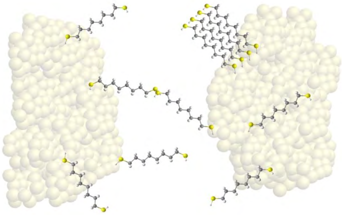
Carbon & molecular electronics

- brief historical account
- why molecules

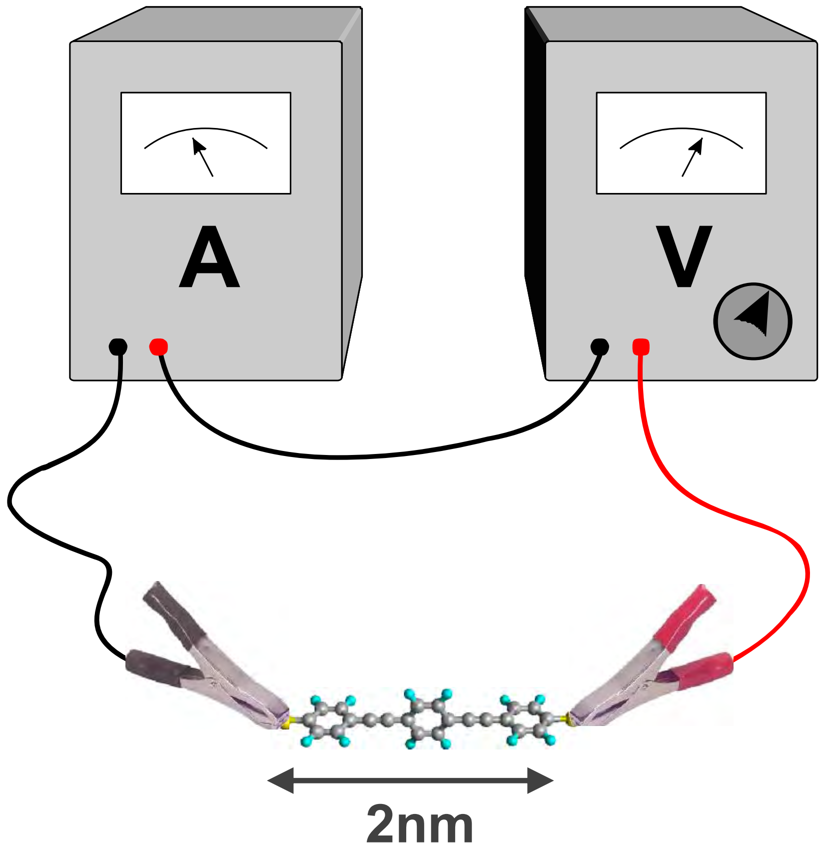


molecular junctions

- how to contact nm-scale objects

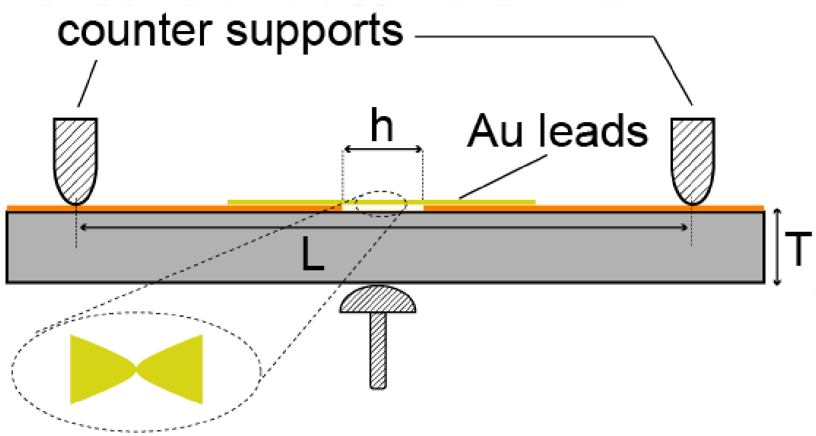


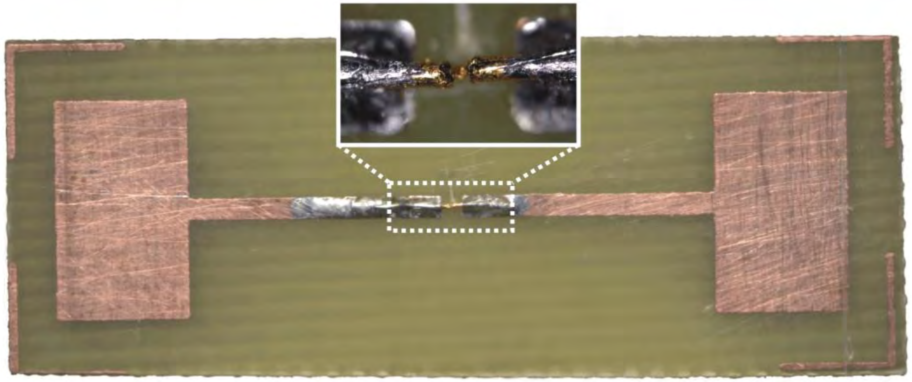
How to hook up crocodile clips to a 10^{-9}m object?



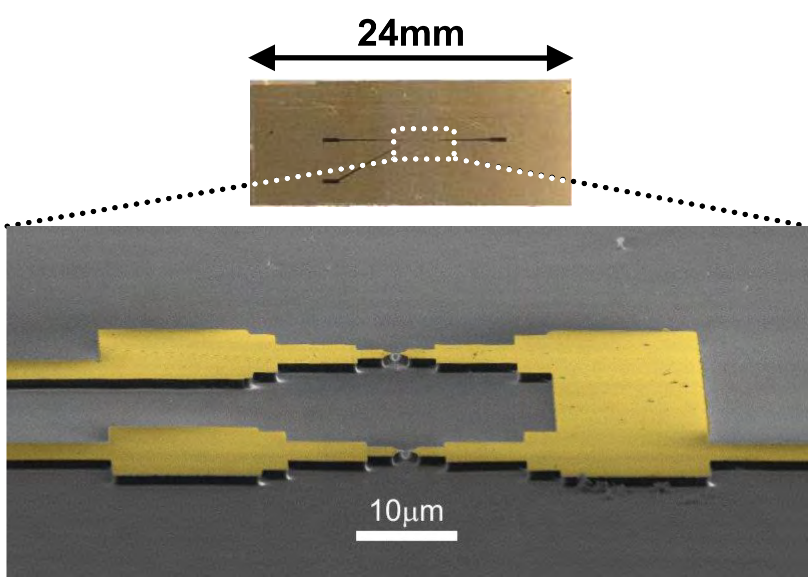
break junctions: a draw bridge at the atomic scale

break junctions: forming atomic contacts

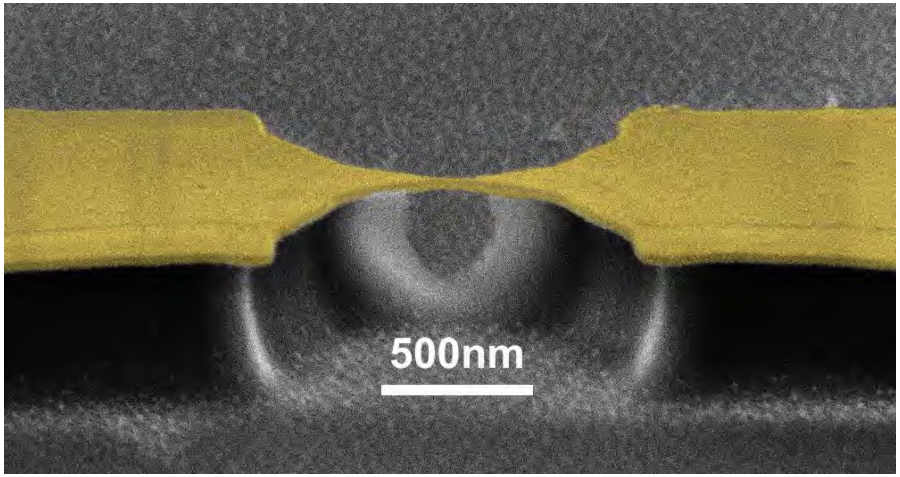




hand-made notched Au wire

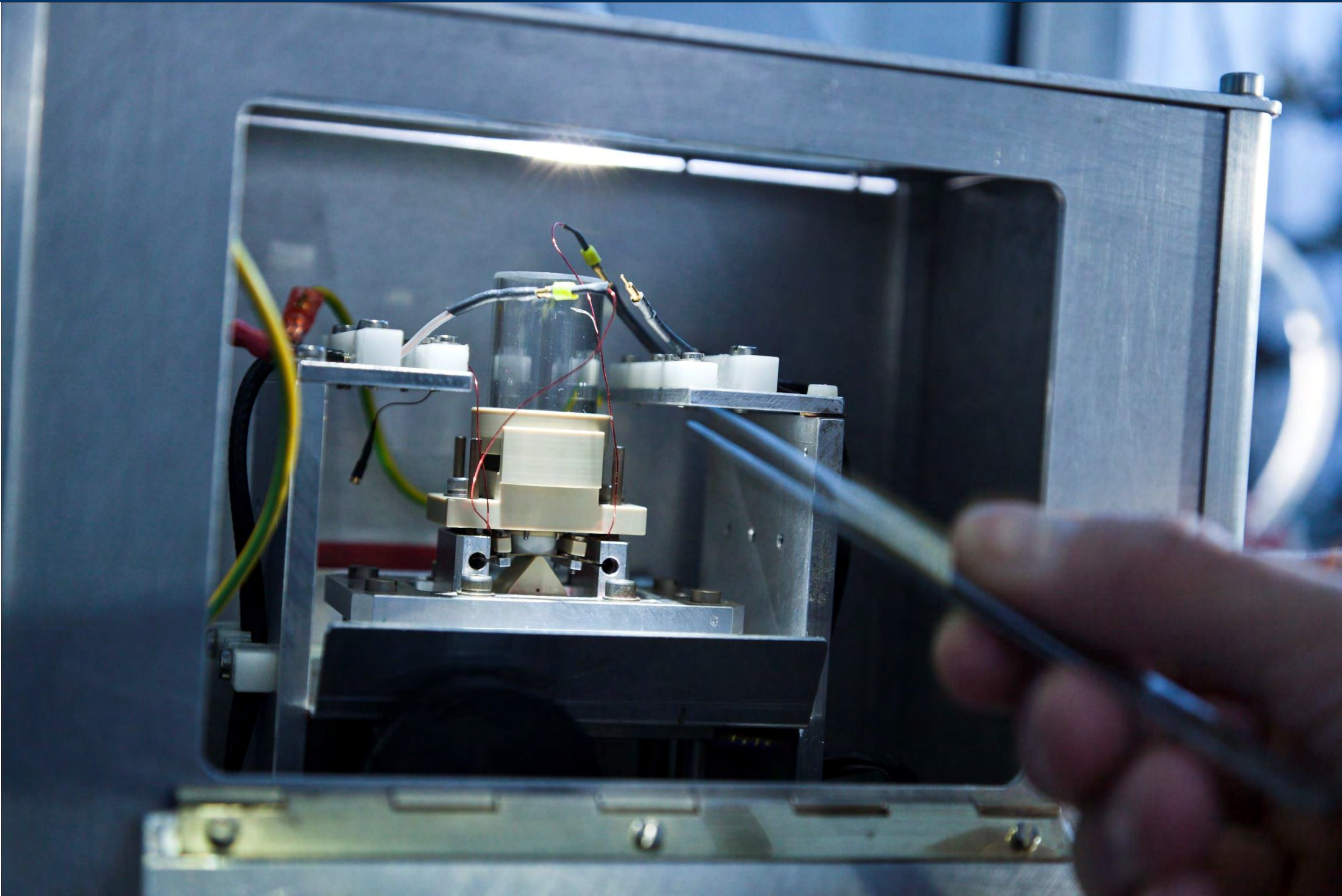


e-beam fabricated Au bridges

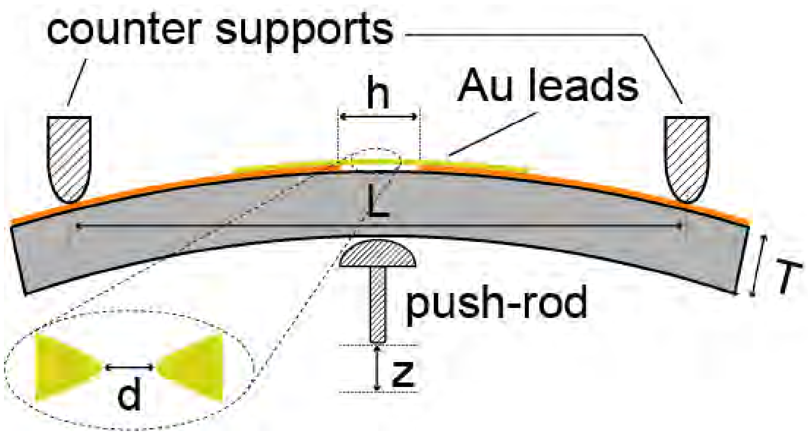


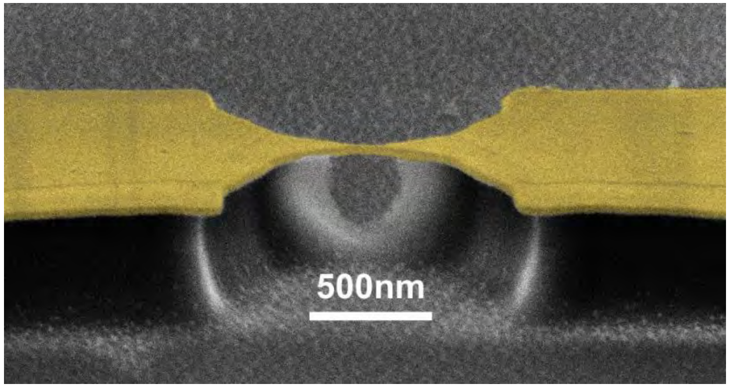
Moreland & Ekin, J. Appl. Phys, (1985); Ruitenbeek et al., Phys. C (1992); Reed et al., APL (1995)

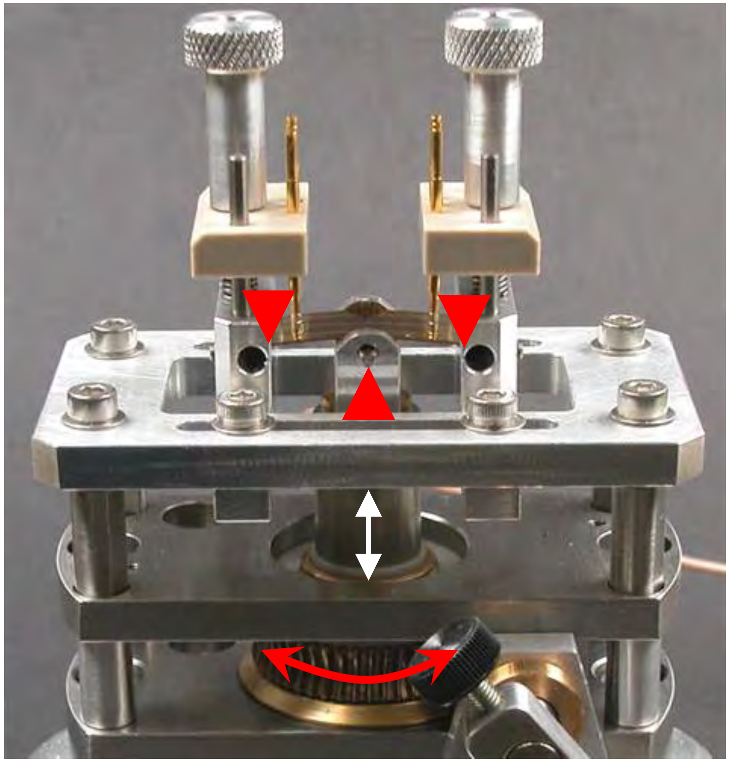
break junctions



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: $v_z = 30\mu m/s$

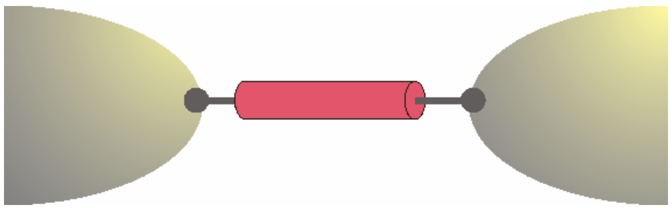
⇨ **0.5 - 1.2 nm/s**

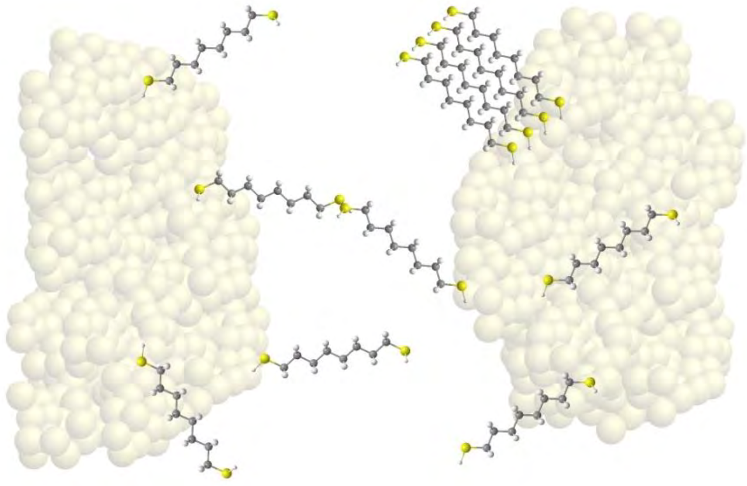
electrodes separation speed

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

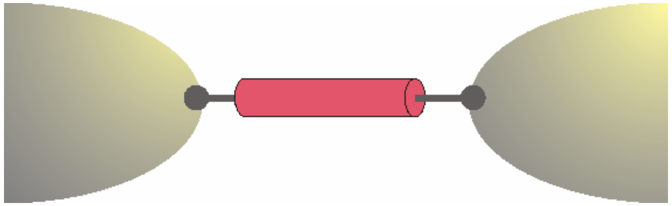


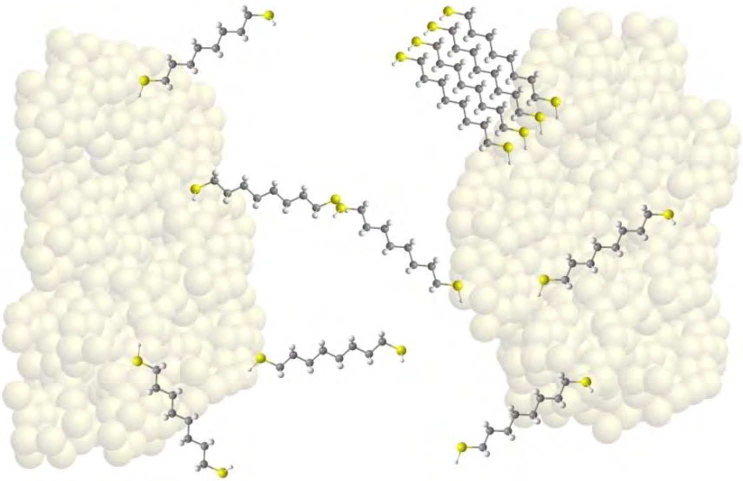


nanometer and molecular-scale junctions

- 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

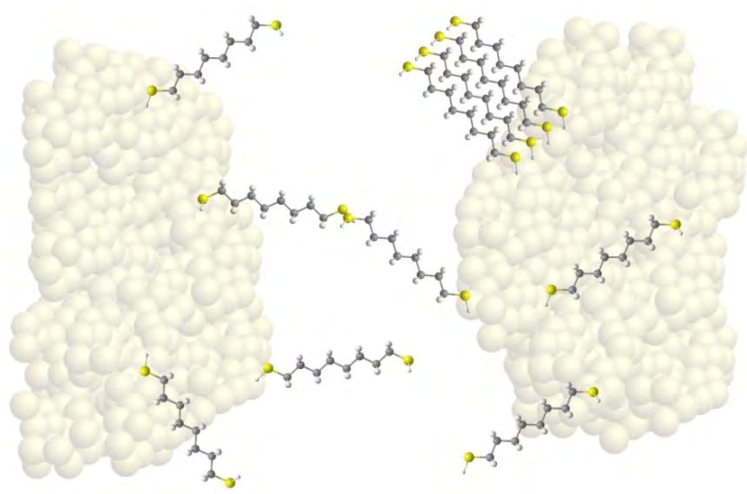
- structural disorder	*electrodes and junction geometry*
- interactions	*anchoring, self-assembly, polymerization*
- fluctuations	*mobility of (surface) atoms, molecular distortions, multiple local energy minima*

⇨ **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

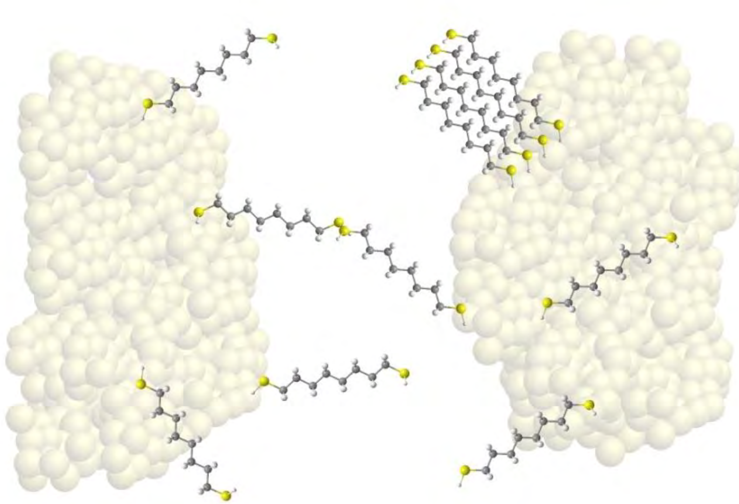
controlling junction formation



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

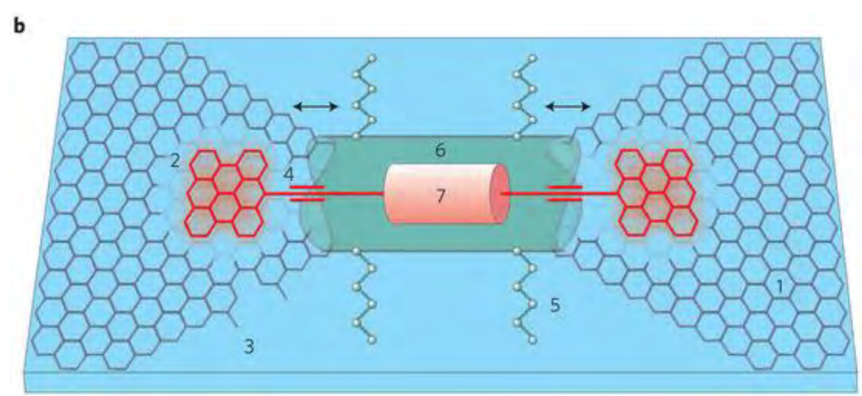
⇨ **variability, low-yield and lack of control in key electrical parameters**

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 ...?

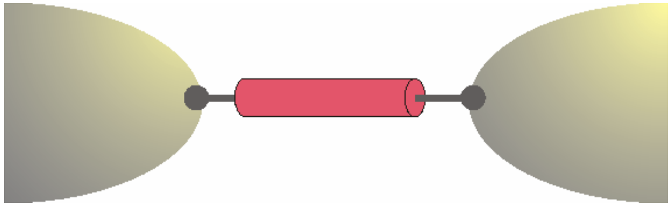
paradigm shift for molecular electronics



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.

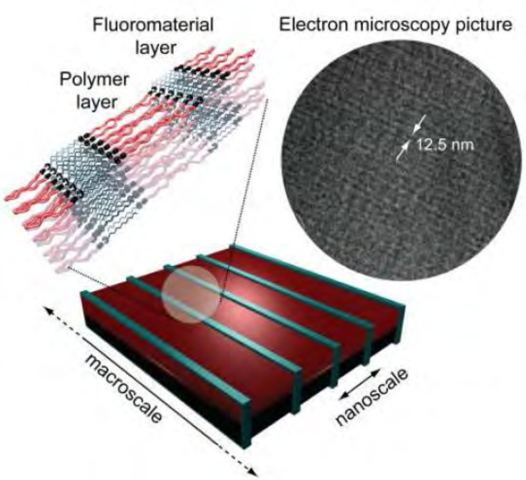
Molecular and carbon-based electronic systems

context

assembly of nanoscale objects?

upscalability
450mm fab / 10^{10} US$
300mm fab / 10^{9} US$

self-assembly

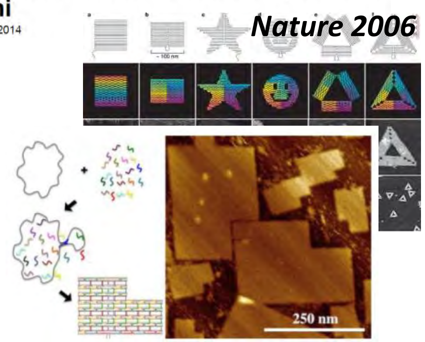


Self-assembled nanostructure keeps aligned up to millimeters

Nature Comm. 2014

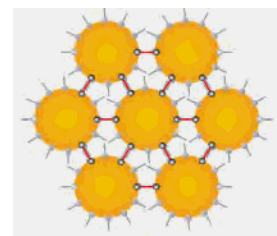
Researchers create world's largest DNA origami
11 September 2014

Nature 2006

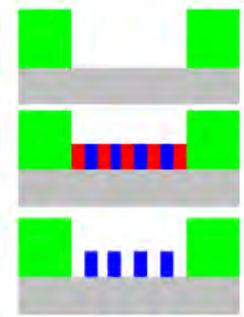


Nano Lett. 2014

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

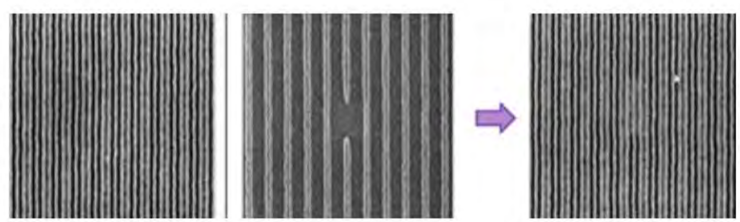


directed self-assembly



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

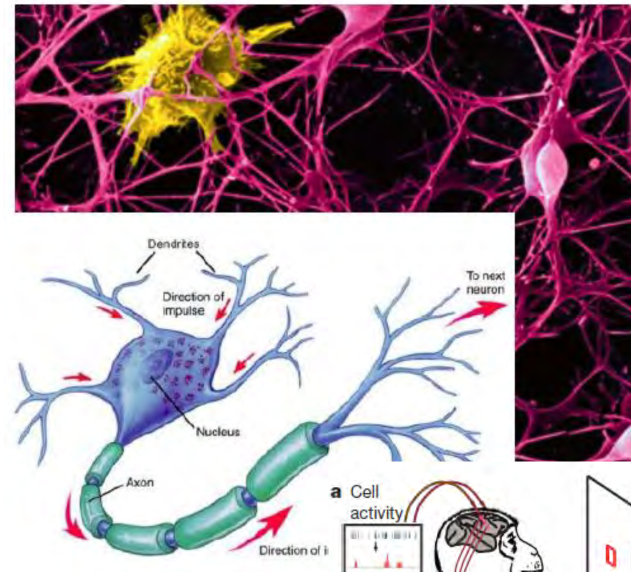
IMEC center, Belgium, 2012
2015: 15nm pitch

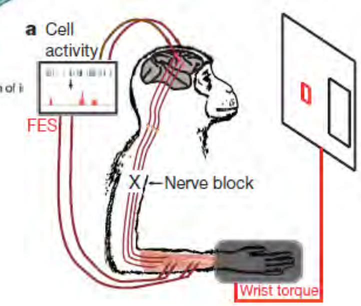


Caption: 14nm polystyrene lines on 28nm pitch after PMMA removal fabricated by DSA using 193nm immersion based 84nm pitch pre-pattern (left) and demonstration of the ability to repair a 200nm gap in the pre-pattern (right).

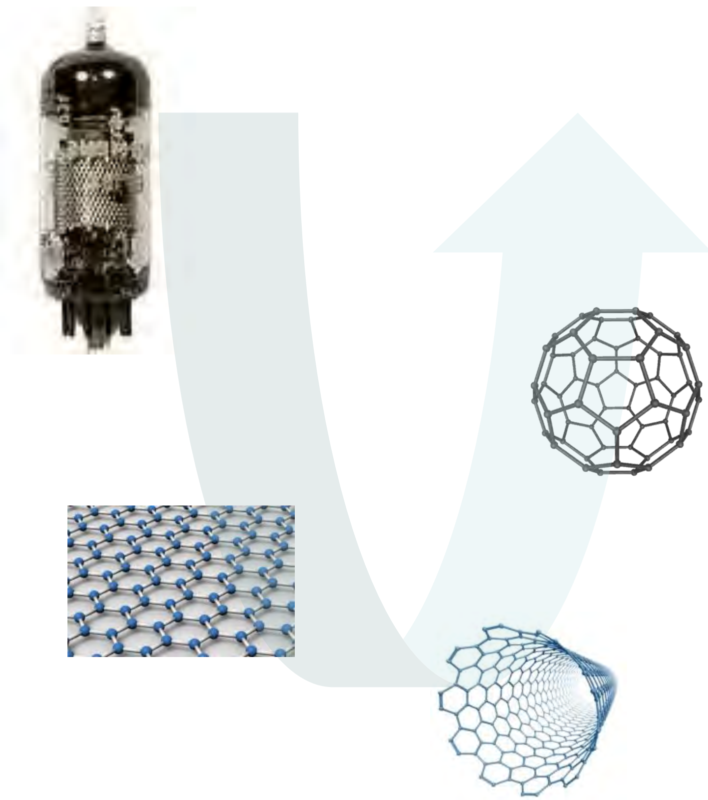
Molecular and carbon-based electronic systems

going 3D...?
- *artificial neural networks*
- *connectivity*
- *non-von Neumann architectures*





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



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)

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