Molecular and carbon-based electronic systems

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

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Vorlesung Uni Basel, FS2019
Goals
- provide background & fundamental aspects to anchor understanding
- discuss hybrid devices/applications combining organic compounds with solid-state systems

Contents
Introduction. Carbon from 0D to 3D.

Condensed matter physics reminder and fundamental properties of electronic systems.

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

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

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

Nanoscale devices for neuromorphic computing.

Nanoscale devices for sensing.

Mini-workshop: Talks by students (15’ talk + 5’ discussion).
<table>
<thead>
<tr>
<th>Date</th>
<th>Lecture</th>
<th>Topic</th>
<th>Instructor(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.02</td>
<td>L1</td>
<td>Lecture organisation &amp; contents Introduction: Carbon 0D to 3D</td>
<td>mc</td>
</tr>
<tr>
<td>27.02</td>
<td>-</td>
<td>No lecture</td>
<td></td>
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<tr>
<td>06.03</td>
<td>-</td>
<td>No lecture</td>
<td></td>
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<tr>
<td>13.03</td>
<td>-</td>
<td>No lecture</td>
<td>Fasnacht</td>
</tr>
<tr>
<td>20.03</td>
<td>L2</td>
<td>Introduction: Carbon 0D to 3D continued Condensed matter reminder and basics</td>
<td>mc</td>
</tr>
<tr>
<td>27.03</td>
<td>L3</td>
<td>Junctions I</td>
<td>mc</td>
</tr>
<tr>
<td>03.04</td>
<td>L4</td>
<td>Junctions II</td>
<td>mc</td>
</tr>
<tr>
<td>08.04</td>
<td>L5</td>
<td>Empa visit, 14h00-16h00, Dübendorf</td>
<td>mc</td>
</tr>
<tr>
<td>10.04</td>
<td>L6</td>
<td>Graphene junctions I: gaps, molecules</td>
<td>mc</td>
</tr>
<tr>
<td>17.04</td>
<td>L7</td>
<td>Graphene junctions II: molecules, GNRs</td>
<td>mc</td>
</tr>
<tr>
<td>24.04</td>
<td>L8</td>
<td><em>Neuromorphic computing with nanodevices</em></td>
<td>M. Csontos</td>
</tr>
<tr>
<td>01.05</td>
<td>L9</td>
<td><em>DFT basics</em></td>
<td>M. Perrin</td>
</tr>
<tr>
<td>08.05</td>
<td>L10</td>
<td><em>Molecule assemblies: analysis &amp; contacting</em></td>
<td>P. Nirmalraj</td>
</tr>
<tr>
<td>15.05</td>
<td>L11</td>
<td>Junction to function</td>
<td>mc</td>
</tr>
<tr>
<td>22.05</td>
<td>L12</td>
<td>Nanoscale devices for sensing</td>
<td>mc</td>
</tr>
<tr>
<td>29.05</td>
<td>L13</td>
<td>Workshop: talks by students</td>
<td></td>
</tr>
</tbody>
</table>
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
A single-atom transistor

STM lithography and phosphine (PH$_3$) dosing

... really small
electronics beyond Si

materials

Oxides interfaces
LaAlO$_3$-SrTiO$_3$ heterostructures
Mannhardt et al., Science 2013

Transition metal oxides
charge, spin, orbital degrees of freedom for diversity of phases exploiting e-e correlation
Takagi et al., Science 2013

Transition metal dichalcogenides (2D)
MoS$_2$, WS$_2$, ...
Strano et al., Nat. Nano 2012

Organic & inorganic materials with elastomeric substrates

III–V compound semic. transistors
NW tunnel FETs
Riel et al., MRS Bulletin 2014

Stretchable electronics
Rodgers et al., Science 2013
electronics beyond Si: "hot" materials

- graphene, boron nitride (hBN) & analogues
- black phosphorus (BP) & analogues
- transition-metal dichalcogenides (TMDs)

electronics beyond Si: "hot" materials

Kavli symposium @ APS
March meeting 2019

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

Mixed van der Waals heterostructures
Philip Kim et al.
http://kim.physics.harvard.edu/
Overview on Technology Sectors and their Main Concepts

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

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

II.1 Advanced Logic and Memories (NEREID TASK 3.1)
- Nanowires
- FinFET
- FD-SOI
- Negative Capacitance FET (NCFET)
- Carbon Nanotubes (CNTFET)
- Memories, Concept 1 - OxRAM
- Memories, Concept 2 - CBRAM
- Memories, Concept 3 - PCM
- Memories, Concept 4 - MRAM
- 3D sequential Integration
- Reliability

II.2 Connectivity (Wireline and Wireless) (NEREID TASK 3.2)
- The Outdoor Wireless Applications
- The Outdoor Wireline Applications
- The Indoor Wireless Applications
- The Indoor Wireline Applications
- The Device to Device Wireless Applications
- The In Package/Device Photonics Wireline Applications

II.3 Smart Sensors (NEREID TASK 4.1)
- Sensors for car internal system performance
- Motion and Pressure sensors
- Advance Driver Assistance System (ADAS)
  - Image Sensors, Radar LiDAR, and Infrared sensors
- Environmental monitoring:
  - Gas and Particulate Matter sensors
  - Sensors for medical and healthcare
  - Physiological signal monitoring
  - Implantable sensors
  - Molecular diagnostics

II.4 Smart Energy (NEREID TASK 4.2)
- Si based power devices
- GaN-devices and substrates
- SiC-based substrates
- Alternative Wide Bandgap Semiconductors

II.5 Energy for Autonomous Systems (NEREID SubTASK 4.2.11)
- Mechanical EH: Electrostatic transduction
- Mechanical EH: Piezoelectric transduction
- Mechanical EH: Electromagnetic transduction
- Thermal energy harvesting
- Photovoltaic Energy Harvesting
- RF energy harvesting/wireless power transfer
- Energy storage - Microbatteries
- Energy storage - Microcapacitors
- Micro-Power Management

II.6 System Design and Heterogeneous Integration (NEREID Workpackage 5, WP5)
In this chapter, the main concepts are classified by connecting the three applications
- Automated Driving:
- Implantable Devices:
- Environmental Monitoring and Wearable Systems, with different elements of Application-Aware Hardware-Software-Co-Design. These Elements comprise Functionalities, Implementation Qualities and Criticalities and Needs.

II.7 Equipment and Manufacturing Science (NEREID Workpackage 6, WP6)
- More Moore
- More-than-Moore
- Manufacturing Science

II.8 Beyond-CMOS – Emerging devices and Computing Paradigms (NEREID Workpackage 2, WP2)
- Steep slope switches: Tunnel FETS
- Neuromorphic circuits and computing
- Spintronics
- Quantum Photonics
- Phonon, Brownian and nano-opto-mechanical computing

electronics beyond Silicon
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Carbon allotropes
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Carbon & molecular electronics
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molecular junctions
- how to contact nm-scale objects
**carbon-based materials**

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

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

**Graphene (2004)**
"zwischen" metallisch und halbleitend

**Nanotubes (1951, 1991)**
metallisch oder halbleitend

**Fullerene C\(_{60}\) (1985)**
- 0.335 nm
- 0.7 nm

**3D**

**2D**

**1D**

**0D**

sp\(^3\) hybridization
The Nobel Prize in Physics 2010

Andre Geim
Prize share: 1/2

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".
Graphene: scotch tape

Mechanical exfoliation
*scotch tape technique*

Chemical Vapor Deposition (CVD) and transfer

*Nature's top ten, 2018 (PhD comics)*

*Novoselov, Castro-Neto, Phys. Scripta (2012)*
**Flexible conductor**
may replace ITO

**Mechanically strong**: composite materials
A 1m² "hamac" weighting 0.77mg
could support a 4kg load

**High charge mobility**: electrical applications
Energy gaps

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

NB: kT (RT) ~ 25 meV

Reminder: energy bands

Semimetals: small overlap between valence and conduction bands
C: $1s^22s^22p^2$

Carbon: $Z=6$ ; 4 valence electrons

1 extra electron / p orbital $\Rightarrow$ half-filled $\pi$ band
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
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

\[ E = h\nu = \hbar ck \]

Graphene:

\[ E = \hbar v_F k \]

where \( v_F \), Fermi velocity is \( \approx c/300 \)

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

graphene roadmap

Materials & processing

- Mobility > 2 m²/Vs on large area
- R2R Transparent (>90%) conductive (Rₛ < 100 Ω/□) films
- Transparent (>90%) Conductive (Rₛ < 1000 Ω/□) films
- Conductive inks
- Flexible electronics and optoelectronics

System Integration

- Printed RF tags
- Foldable OLED
- Rollable E-paper
- Touch screen and displays

Fiber-optical communication system

- Optical modulation (0.05-10GHz)
- Ultrafast optical response (<5fs)
- Mode-locked solid state laser
- Photodetectors
- Printed RF tags

Distributed sensor networks

- Young modulus > 100 GPa composites
- High surface area (> 2000 m²/g)
- Wafer scale doping control
- Large area inorganic 2d crystals
- Hybrid superstructures

Self-powered flexible mobile devices

- Ultrafast low-power electronics
- Medical repair kits
- THz oscillators
- RF AD converters

ICT

- THz imager
- Medical repair kits
- Spin valves
- Nanomagnets
- Non-volatile memories
- Interconnects in ICs

Energy Health

- Light weight batteries
- High performance supercaps
- High efficient solar energy converters
- Artificial retina
- Prostheses

Components

- Defect-free graphene QDs
- Ultra narrow (~1nm) GNRs
- Spin logic circuits
- Prostheses
- Artificial retina
- Food quality and safety biosensors
- DNA sensors
- Environmental sensors
- DNA sensors

Graphene: Fast, Strong, Cheap, & impossible to Use
The New Yorker, Dec. 2014
adding a gap: graphene ribbons structure

Zigzag edges

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

Armchair edges

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

graphene “surface” (edges) states: two types of edges

Nakada et al., PRB 54:17954 (1996)
other 2D systems for electronics

Metallic: graphene
- High mobility

Insulating: h-BN (5.9 eV)
- Inert blocking layer

Semiconducting: Transition metal dichalcogenides (MoS$_2$ (1.8~2.7 eV))
- High on/off ratio
- Photosensitive


Various hybrid structure
- Network architecture
- Stacked heterostructure
- Lateral heterostructure

Dresselhaus, Cargèse, 2014
other 2D systems

Transition Metal Dichalcogenides (TMDs)

\[
\text{MX}_2  \\
M = \text{Transition metal}  \\
X = \text{Chalcogen}
\]

Transition metal

Chhowalla et al., Nat. Chem. (2013); Dresselhaus, Cargèse, 2014
### Table 1 | Electronic character of different layered TMDs

<table>
<thead>
<tr>
<th>Group</th>
<th>M</th>
<th>X</th>
<th>Properties</th>
</tr>
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<tbody>
<tr>
<td>4</td>
<td>Ti, Hf, Zr</td>
<td>S, Se, Te</td>
<td>Semiconducting ($E_g = 0.2$-$2$ eV). Diamagnetic.</td>
</tr>
<tr>
<td>5</td>
<td>V, Nb, Ta</td>
<td>S, Se, Te</td>
<td>Narrow band metals ($\rho \sim 10^{-4} \Omega \cdot \text{cm}$) or semimetals. Superconducting. Charge density wave (CDW). Paramagnetic, antiferromagnetic, or diamagnetic.</td>
</tr>
<tr>
<td>6</td>
<td>Mo, W</td>
<td>S, Se, Te</td>
<td>Sulfides and selenides are semiconducting ($E_g \sim 1$ eV). Tellurides are semimetallic ($\rho \sim 10^{-3} \Omega \cdot \text{cm}$). Diamagnetic.</td>
</tr>
<tr>
<td>7</td>
<td>Tc, Re</td>
<td>S, Se, Te</td>
<td>Small-gap semiconductors. Diamagnetic.</td>
</tr>
<tr>
<td>10</td>
<td>Pd, Pt</td>
<td>S, Se, Te</td>
<td>Sulfides and selenides are semiconducting ($E_g = 0.4$ eV) and diamagnetic. Tellurides are metallic and paramagnetic. PdTe$_2$ is superconducting.</td>
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$\rho$, in-plane electrical resistivity.

*Chhowalla et al., Nat. Chem. (2013)*
other 2D systems

Table 1 | Electronic character of different layered TMDs\textsuperscript{36}.

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$\rho$, in-plane electrical resistivity.

"band engineering"

Chhowalla et al., Nat. Chem. (2013)
other 2D systems

![Graph showing bandgap vs. lattice constant for various 2D materials including BN, CH, CF, CH, BC3, MoS2, MoSe2, MoTe2, and SWNT fluorination and hydrogenation processes.]

Martel, Szkopek, Cargèse, 2014
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.

<table>
<thead>
<tr>
<th></th>
<th>Electron Mobility (cm² V⁻¹ s⁻¹)</th>
<th>Bandgap (eV)</th>
<th>Thermal Conductivity (W cm⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1600</td>
<td>1.12</td>
<td>1.5</td>
</tr>
<tr>
<td>Ge</td>
<td>3900</td>
<td>0.66</td>
<td>0.6</td>
</tr>
<tr>
<td>GaAs</td>
<td>9200</td>
<td>1.42</td>
<td>0.46</td>
</tr>
<tr>
<td>InAs</td>
<td>4 × 10⁴</td>
<td>1.34</td>
<td>0.27</td>
</tr>
<tr>
<td>Diamond</td>
<td>2200</td>
<td>5.45</td>
<td>22</td>
</tr>
<tr>
<td>Carbon Nanotubes</td>
<td>1 × 10⁵</td>
<td>(0 to 1)</td>
<td>30</td>
</tr>
<tr>
<td>Graphene</td>
<td>1 × 10⁴ to 2 × 10⁵</td>
<td>(0 to 0.5)</td>
<td>40</td>
</tr>
</tbody>
</table>

MRS Bulletin 2010 special issue

carbon-based electronics

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)

Nature 1998, news&views

Nature 2011

Nature 2013

Nature 2014

Nature 2014
when macro meets nano: molecules

no way to escape molecules?
carbon-based electronics

materials

ITRS 2013, 2015; Martel, Cargèse, 2014
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
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.
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.
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.
a brief (personal) historical perspective

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

Eley and Spivey
“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...”

Albert Szent-Gyorgi
proteins "might not be insulators"

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

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

Feynman  There's Plenty of Room at the Bottom, 1959
a brief (personal) historical perspective

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

Kavli prize in nanoscience 2016: AFM
Gerd Binnig, Christoph Gerber, Calvin Quate

Gerd Binnig  Heinrich Rohrer
a brief (personal) historical perspective

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

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

molecular recognition
computing with molecules – in solution - is highly parallel
different aspects to molecular computing:
electronic, chemical and biochemical
e.g. Libermann, Cell as a molecular computer, 1972

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

Gerd Binnig  Heinrich Rohrer

1980  1990  2000
a brief (personal) historical perspective

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

Light
Ru cplx as donor
Rh cplx as acceptor

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)

1980
1990
2000
press release, Nobel prize 2000
(…) In the future we will be able to produce transistors and other electronic components consisting of individual molecules - which will dramatically increase the speed and reduce the size of our computers. A computer corresponding to what we now carry around in our bags would suddenly fit inside a watch …
Organic nanowire transistors
Mat. Today (2008)

molecular crystals
(\pi\text{-stacking})

Low-cost organic electronics on plastic

TV display, 40” OLED
(EPSON, 2004)

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

Large scale integr. of molecular junctions

molecular mono-layers
(self-assembly)

160kb crossed-wire memory

Nobel 2000

context
perspective

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)

Nobel 2000

Low-cost organic electronics on plastic

TV display, 40” OLED
(EPSON, 2004)
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** (upscaleing)?

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

break junctions
break junctions

counter supports

Au leads

push-rod

d

elongation: \( d = \frac{6thz}{L^2} \)

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

\( \Rightarrow \Delta Z = 10 \mu m \Leftrightarrow \Delta d \approx 3 \text{ Å} \)

vertical speed: \( v_z = 30 \mu m/s \)

\( \Rightarrow 0.5 - 1.2 \text{ nm/s} \)

electrodes separation speed

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

nanometer and molecular-scale junctions
- structural disorder
- interactions
- fluctuations

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

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⇒ 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

\[ \text{drifting molecules,}\]
\[ \text{stochastic anchoring,}\]
\[ \text{clustering} \Rightarrow \text{undefined junction}\]
\[ \text{geometry &}\]
\[ \text{conductance}\]

\[ \text{drifting surface}\]
\[ \text{atoms, metal}\]
\[ \text{protrusions} \Rightarrow \text{undefined}\]
\[ \text{electrostatic}\]
\[ \text{landscape}\]

\[ \Rightarrow \text{variability, low-yield and lack of control in}\]
\[ \text{key electrical parameters}\]

\textbf{Carbon-based contact materials as electrodes:}

- FLG \hspace{1cm} \text{vd Zandt et al., Nano Lett. 2011}
- SWNT \hspace{1cm} \text{Krupke et al., Nat. Nanotech. 2010}
- C-fiber tips \hspace{1cm} \text{Agrait et al., Nanoscale Res. Lett. 2012}

\[ \Rightarrow \text{monolayer graphene ...?}\]
\[ \text{paradigm shift for molecular electronics}\]

\textit{FP7 ITN MOLESCO}; see also Focus issue \textit{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

self-assembly

Researchers create world’s largest DNA origami

Nature 2006

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

Nano Lett. 2014

directed self-assembly

IMEC center,
Belgium, 2012
2015: 15nm pitch

self-assembly

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

Pick and place, e.g.: CNTs (Ch. Hierold et al.), nanowires (V. Zwiller et al.)
Molecular and carbon-based electronic systems

context

assembly of nanoscale objects

Hersam et al., Nat. Materials, 2017

0D

1D

2D

2D-0D

2D-1D

Mixed D heterostructures

Loh et al., Nano Today (2015)
Molecular and carbon-based electronic systems

going 3D...?
- artificial neural networks
- connectivity
- non-von Neumann architectures, neuromorphic computing

hybrid interfaces
sensing (chemical, biochemical) and beyond
  e.g.: ion sensitive interfaces for cells, prosthetic interfaces at single molecule level


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

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