Perspectives on Physics: *Organic Electronics and Spintronics*

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New Materials: a simple time line

- Stone, Wood, Copper, Bronze, Paper, Glass, Iron
- Rubber, Steel
- Steel alloys, Light alloys, Cement, Polymers (Nylon, etc)
- Silicon!, Super Alloys
- Conducting Polymers, Liquid Crystals, Electrochromic mat.
  - Optical fibers, Fullerenes, Nanotubes, GMR, etc,
Inorganic Semiconductor Technology

- "Lego-technology"
- Atom layer by atom layer
- Control the electronic and optical properties by:
  - "building blocks" (elements)
  - Position
  - Mixture
  - Crystalline structure
Organic Electronics

**Nature:**

Carbon, Oxygen, Nitrogen, Hydrogen, etc + sun

Imitation is the sincerest form of flattery.
Oscar Wilde

Functional and esthetically pleasing solar cell.
Nobel Prize in Chemistry 2000

"...for the discovery and development of conducting polymers.”

1977

Polyacetylene (PA)

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\]

\[
\text{C} = \text{C} \quad \text{C} = \text{C} \quad \text{C} = \text{C} \quad \text{C} = \text{C} \\
\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H}
\]

\[\sigma = 10^{-9} \text{ S/cm} \quad \xrightarrow{\text{I}_2} \quad \sigma = 38 \text{ S/cm}\]

- Prof. A.J. Heeger
- Prof. A.G. MacDiarmid
- Prof. H. Shirakawa
Polymers: Insulators and Metals

Conjugated polymers

S/cm \(10^{-18}\) \(10^{-14}\) \(10^{-10}\) \(10^{-6}\) \(10^{-2}\) \(10^{2}\) \(10^{6}\)

Quartz Diamond Glass Silicon Germanium Copper

Insulators Semi-Conductors Metals

Mats Fahlman, LiU
10/02/2010
Polymers can exist as:

- Linear chains
- Cross-linked chains
- Networks

Chemically identical polymers can have completely different properties depending on degree of cross-linking.
Organic Electronics

Conducting Polymers in solution = Electronic Ink
The Goal: Organic electronics printed onto paper/plastic

- Cheap!
- Environmentally compatible
  - recycling
- Existing printing techniques:
  - Screen, Off-set, Ink-jet, etc
- Applications:
  - Sensors in food packaging
  - Large area displays
  - RF-ID (Barcodes, Security tags, etc)
  - Photovoltaics
Soft Lithography

Stamp ‘negative’:

Pour polymer into ‘negative’

Cure, Lift off

Stamp!

Cover stamp with Ink

Au

Stamp surface

Au

Substrate

Ink

Substrate

Magnification of surface area

Example: R hydrophobe => Polymer cast from water solution goes to the empty surface areas
Atoms: the electron orbitals

Energy of the orbital (Defined as negative)

Unlike satellites, electrons can only exist in certain orbits with certain energies (quantum mechanics).

Compare with satellite orbiting the earth
Fermions - Bosons

**Fermions**
- Electrons are fermions
- Have spin 1/2
- Can’t have the same quantum state (Pauli principle)
- Only two $e^-$ per energy level (orbital)

**Bosons**
- Photons are bosons
- Have integer spin
- Can have identical quantum states
- “Unlimited” number per energy level (orbital)
Many atoms => fine structure of many split levels with small $\Delta E$ => 'bands'
Wave mechanics of the hydrogen atom

the hydrogen atom is the only system found in our world which we can describe exactly with quantum mechanics.... for all others, approximations.

\[
\frac{i\hbar}{\partial t} \frac{\partial \Psi}{\partial t} = \left( -\frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_p} \nabla_p^2 \right) \Psi + V(\vec{r}_{e,p}) \Psi
\]

- \( \Psi \): the wave function describing the motion of the proton and the electron;
- \( \hbar \): Planck's constant (h) divided by 2\(\pi\);
- \( m_e, m_p \): the electron mass and the proton mass;
- \( V(\vec{r}_{e,p}) \): the Coulomb potential;
- \( \vec{r}_{e,p} \): the position of electron and proton, respectively;
- \( \nabla_e^2, \nabla_p^2 \): Laplace operators (2\textsuperscript{nd} derivative in space coordinates) for the electron and proton.
The hydrogen molecular ion ($\text{H}_2$)

$\Psi_{-} = \{2(1-S)\}^{-1/2}(A - B)$

$\Psi_{+} = \{2(1+S)\}^{-1/2}(A + B)$
From bonds to energy bands in solids

For the total *number* $N$ of atoms in a solid ($10^{23}$ cm$^{-3}$), $N$ energy levels split apart within a width $\Delta E$. Leads to a band of energies for each initial atomic energy level (e.g. $3s$ energy band for $3s$ energy level).

Electrons must occupy different levels due to Pauli Exclusion principle.

Each level contains $2(2l+1)$ electrons, so each band contains $2(2l+1)N$ electrons.
Electrons are fermions: limited number per band!
Metal
Semiconductor & Insulator

Under construction
Under construction
Photocurrent generation: Organic Solar Cells

S.R. Forrest, MRS bulletin, January 2005
Polymer solar cells: Donor and acceptor materials

- Soluble in same solvents
- Phase segregates into networks
- Band offsets facilitate charge transfer

Donors

Acceptors
Bulk heterojunction solar cells
Market Opportunity

Area of opportunity for organic solar cells

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Field effect transistors: a short review

- n-type source and drain + p-type substrate or p-type source and drain and n-type substrate
- $V_{GS}$ creates inversion layer (attracts $h^+$ or $e^-$ at the insulator depending on bias)
- Charge is transported between source and drain in the inversion layer under $V_{DS}$ bias.
Organic transistors: molecular film

Single crystals (vacuum deposited):
Pentacene: $\mu \sim 1 \text{ cm}^2/\text{Vs}$
Sexithiényl: $\mu \sim 0.1 \text{ cm}^2/\text{Vs}$

If amorphous, $\mu \sim 0.01 \text{ cm}^2/\text{Vs}$

Pentacene

Sexithiényl
Polymer transistors

Ordered films (solution deposited):
Polyhexyltiophene: $\mu \sim 0.1 \text{ cm}^2/\text{Vs}$

Disordered films (solution deposited):
Polyhexyltiophene: $\mu \sim 10^{-4} \text{ cm}^2/\text{Vs}$
Poly(p-penylenevinylene): $\mu \sim 10^{-4} \text{ cm}^2/\text{Vs}$
Polyfluorene: $\mu \sim 10^{-3}-10^{-4} \text{ cm}^2/\text{Vs}$

etc

\[
\begin{array}{c}
\text{Polythiophene, PT} \\
\text{Polyfluorene, PFO}
\end{array}
\]
Field effect transistors: a short review

Linear region:

\[ I_D = -\frac{Q_{\text{inv}} WL}{t_r} \quad \Rightarrow \quad t_r = \frac{L}{v} \quad \text{and} \quad v = \mu E = \mu \frac{V_{DS}}{L} \quad \Rightarrow \quad I_D = -\mu Q_{\text{inv}} \frac{W}{L} V_{DS} \]

\[ Q_{\text{inv}} = -C_{ox} (V_{GS} - V_T) \quad \Rightarrow \quad I_D = \mu C_{ox} \frac{W}{L} (V_{GS} - V_T) V_{DS} \]

- \( Q_{\text{inv}} \) = Charge per unit area in inversion layer
- \( t_r \) = Transit time for charge between source and drain
- \( V_T \) = Threshold Voltage (\( Q_{\text{inv}} = 0 \) if \( V_{GS} < V_T \))
- \( C_{ox} \) = Gate oxide capacitance per unit area

Saturated region:

\[ I_{D,\text{sat}} = \mu C_{ox} \frac{W}{L} \frac{(V_{GS} - V_T)^2}{2} (1 + \lambda V_{DS}) \]

Empirically derived
Polyelectrolyte gate dielectric

Nothing new under the sun: Helmholtz Double Layer (~1850):

Capacitor:

The surface charge is neutralized by ions at the respective interface.

The surface charge potential decreases linearly from the surface to the center of the ions situated at $d$ nm from the surface.

Note: Helmholtz double layer assumes rigid layers of opposite charges at the interfaces which is highly unlikely to occur in “real” situations…
Organic Electronics: Solar cells and RF-ID tags

- [www.konarka.com](http://www.konarka.com) – solar cells
- [www.polyic.com](http://www.polyic.com) – printed RF-ID tags, etc.
Liquid crystal display pixel

- Diffusive reflector
- Liquid Crystal film
- Glass filter
- Glass filter
- Cover Glass
- Polarizing film
- Positive electrode
- Negative electrode
- Polarizing film (90° angle to first film)

- Liquid crystal film filters light if aligned
- Orientation can be affected by e.g. electric current
- Active matrix display: thin film transistors of amorphous silicon
- Backlighting provided by cold cathode fluorescent lamp
Organic electronics: e-paper

Example: QUE proReader
- 21.6 x 28 cm² display
- Driving circuitry – printed polymer transistors
- Pixels – E-ink

‘Looks white’

Dye
Micro-capsule

Electrode

http://www.que.com/
The active part is very thin (< 1 mm)

Cathode: Metal (0.1–0.5 mm) [Ca, Mg/Al]

Glass or PET (10 mm–5 mm)

Anode: Indium-Tin Oxide (0.1–0.3 mm) transparent, e.g., in LCDs

Polymer Light Emitting Diode

Curtesy: R. H. Friend

Polymer (~ 0.1 mm)
Polymer Light Emitting Diode

Polymer LED

Color through synthesis!

Nature 372 (1994) 444

M. Andersson, Chalmers
PLEXDs: example of an active-matrix display

Circuits made by ink-jet printing (a disruptive technology)
Organic Electronics: flat screen TVs

- Sony, Samsung, etc
- [http://www.youtube.com/watch?v=FAk4bjdbtCI](http://www.youtube.com/watch?v=FAk4bjdbtCI)
Spintronics

what is it?

Electronics

"1" "0"

read/write information by charge pulses

Spintronics

"1" "0"

process information by selecting spin up/down

manipulate spin, measure a property that depends on spin

use spin directly, as in quantum computation
Magnetoresistance

- Magnetoresistance: change in resistance under an applied magnetic field
- Can be positive or negative effect
- Typically defined as $\Delta R = (R(B) - R(0))/R(0)$
- Using “normal” mechanisms for magnetoresistance in materials, the $\pi$-conjugated molecules should have $|\Delta R|<10^{-6}$ at low magnetic fields
- However…
Magnetoresistance in $\pi$-conjugated organic semiconductors (OMAR)

- Organic Magnetoresistance (OMAR) effect
- Simple diode structure
- Insensitive to magnetic field (B) direction
- Non-magnetic electrodes
- Non-magnetic organic semiconductor
- $|\Delta R| \sim 5-15\%$ at RT!
Magnetoresistance in $\pi$-conjugated organic semiconductors (OMAR)

Some more peculiarities...

- OMAR-effect changes sign depending on voltage
- OMAR also affects light emission: control light output by magnetic field

Ö. Mermer, et al, PHYSICAL REVIEW B 72, 205202 2005
Spin valve

$n$: spin density at distance $x$ from the ferromagnet/paramagnet interface

$n_0$: spin density at distance $x=0$

Ferromagnetic half metal

Paramagnetic (semi)conductor

Change Magnetization

"Valve" on/off!
M(TCNE)$_x$ molecule-based magnets

Molecule-based magnets vs. Atom-based magnets
Organic or hybrid organic/inorganic compounds
• Active organic component (net spin in p-orbitals)
• Passive organic component (no net spin)

“Designer magnets”, properties can be tuned by organic chemistry

Advantages:
• Flexible
• Low density
• Potential low cost, low temperature synthesis
• Variable electrical conductivity
• Compatible with polymers and composites
• Magneto-optic effects
• …

Applications: SPIN elecTRONICS
“Ingredients” for magnetic ordering

1. existence of a magnetic moment (a net spin)

2. existence of magnetic interactions between spins

3. collective behavior
   ordering effect of interaction > disordering effect of thermal agitation

Below $T_c$  \hspace{2cm} $T_c$ \hspace{2cm} Above $T_c$

Ferromagnet \hspace{2cm} Paramagnet

10/02/2010 Mats Fahlman, LiU
M(TCNE)$_x$ molecule-based magnets

$M(\text{TCNE})_x$, $x\sim 2$, $M=V, Mn, Fe...$

![Tetracyanoethylene (TCNE)](image)

[TCNE]$^-$ spin density distribution

$V(\text{TCNE})_x$: semiconductor, $T_C$ above room temperature


<table>
<thead>
<tr>
<th>M</th>
<th>$T_C$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>370</td>
</tr>
<tr>
<td>Fe</td>
<td>95</td>
</tr>
<tr>
<td>Mn</td>
<td>75</td>
</tr>
<tr>
<td>Co</td>
<td>40</td>
</tr>
<tr>
<td>Ni</td>
<td>40</td>
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</table>

Material physics: a Matreshka

X-ray diffraction
Photoelectron spectroscopy

Atoms, bonds (~Å)

Cluster, tubes (~nm)

“Substrate” (m)

Surface structure (<mm)

“Grain” (~μm)

Nuclei, electrons (~<Å)

SEM

Microscope
Overview of spectroscopic techniques

neutral spectroscopy:
- NEXAFS
- EELs
- XES

ionizing spectroscopy:
- XPS
- UPS
- Auger
- IPES

transport spectroscopy:
- Scanning Tunneling Spectroscopy
- TSC

- UV-Vis absorption
- fluorescence
- ellipsometry
- EELs
- IR
- Raman
- HREELS
- FTIR
- ESR
- NMR
- neutron scattering
- positron annihilation

- core electron excitations
- electronic excitation
- phonons, magnons,
- spin-excitations,
Photoelectron Spectroscopy

Maps out occupied electronic structure:
- Energy Bands
- Chemical Bonds
- Elements
- Work function

X-rays, UV light

sample

photoelectrons

kinetic energy spectrum

analyzer

www.lasurface.com
Photoelectron spectroscopy

$E_B = h\nu - E_K$

Core levels: $C_1, C_2$

Valence levels: $V_1, V_2, V_3$

Vacuum level

Kinetic energy measured

XPS

Intramolecular relaxation

Intermolecular relaxation
X-ray absorption techniques

- X-ray absorption (NEXAFS) probes the unoccupied states in the presence of a core hole
- Element and site specific method
- It’s possible to obtain magnetic information using circular polarized light (XMCD)
- X-ray absorption can be used to perform resonant PES...

X-ray absorption event

Excitation part

- Unoccupied levels
- Occupied valence levels
- Core levels
- Ground-state
- Photo-excitation

Emission part

- Spectator-decay
- Participator-decay
Through-hole plating in Printed Circuit Boards

- Selectively deposits highly conductive polymer on dielectric resin and glass without the use of electroless copper.
- Formaldehyde-free, environmentally sound technology.
- Fast and uniform coverage of the plated through-hole.
- Costly waste treatment and microetch post-treatments are not required.
Capacitors

• Capacitors make up 90-99% of all components in most electronic devices
• “Super” capacitors: Tantalum (Ta₂O₅) based (10-100 µF)
• Traditional technology: use MnO₂ as negative contact
  • Problem – catches fire at high voltages!
• Use Conducting polymer (PEDOT, Polyaniline) as cathode
  • No fire risk
  • Significantly lower equivalent series resistance (ESR)
Conductive textiles

Textile fibers can be individually coated with conducting polymers

• Surface resistivity controllable between 10 and 106 ohm/sq
• Volume conductivity ranges from 0.0001 to 5 S/cm
• Can absorb up to ~90% of impinging microwave radiation
• Dissipates static charge instantaneously regardless of humidity

Uses:
EDS protection (clothes, carpets, etc)
Microwave/radar absorption
Resistive and microwave heating (clothes, blankets, etc)
Corrosion protection

- Conducting and semiconducting polymer films can anodically protect metals

- Can also act as on demand releasers of corrosion inhibitors

- Polyaniline typically used for steel and aluminum in construction, navy and aircrafts
Organic Electronics Research at LiU

- Prof. Magnus Berggren, ITN, http://orgel.itn.liu.se/
- Prof. Mats Fahlman, IFM, http://www.liu.se/ifm/surfphys/
- Prof. Robert Forchheimer, ISY, http://www.bk.isy.liu.se/
- Prof. Olle Inganäs, IFM, http://www2.ifm.liu.se/biorgel/
- Prof. Sven Stafström, IFM, http://cms.ifm.liu.se/theomod/compphys/