Novel Materials for Organic and Thin Film Electronics

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The road beyond CMOS: Nano?

Nano: things smaller than 100 nm

Opportunities for revolutionary new materials, processes, and technologies

But: also many opportunities to improve, extend, and transform present technologies, including computer hardware technologies.
Silicon Logic - Already at the Nanoscale

(That’s what got us into trouble!)

- Gate length = 6 nm

- Power4 Chip
- 174 million transistors


J. Warnock et al., *IBM J. R&D*, p. 27, 2002
One alternative: Carbon Nanotube FET

Semiconductor mobilities @ RT (cm²/V.s)
- InSb: 77,000
- CdSe: 650
- c-Si: 1,500 – 100
- a-Si: 1
- CNT: 100,000
- Polymer: $10^{-5} – 10^{-2}$
- Pentacene: 0.1 – 5
- Chalcogenides (spinc.): 1 - 20
Carbon Nanotube Inverter

Gain > 1
Nanotube Technology?

How do you get from here to there?

Plenty of room for improvement!
No new architecture!
Some of the issues

• CNT synthesis and purification; control of diameter and chirality
• CNT placement in integrated circuit hierarchy with nm precision
• Site- and/or area-selective n- and p-type CNT doping on nm scale
• Control over contacts to CNT, injection barrier to n-, p-, i-CNTs
• Elimination of parasitics for high performance
• Elimination of 1/f noise in CNFET devices
• Theoretical modeling of CNT physics, chemistry, and devices
• CNT and device physical characterization
• Optoelectronic properties

1/f noise in carbon nanotubes
Philip G. Collins, M. S. Fuhrer, and A. Zettl
APL 76, 894 (2000)
Contacts

Zihong Chen, Joerg Appenzeller, Joachim Knoch, Yu-Ming Lin, Phaedon Avouris
A26-5
CNT optoelectronic properties are key in understanding basic transport properties, effects of defects, CNT electronic structure, excited states, etcetera. There is room for much experimental work, as well as more advanced theoretical understanding.

Exciton binding energy is CNTs (0.1-0.5 eV) much larger than in III-V’s (10’s of meV). CNT exciton bonding energy depends on environment.

Ph. Avouris, A26-4
Nanotube Technology?

How do you get from here to there?

Not ‘just engineering’
Lots of basic science!

Plenty of room for improvement!
No new architecture!
A Molecular Computer – Slow but it works (once)

A.J. Heinrich, C.P. Lutz, J.A. Gupta, D.M. Eigler
Science 2002
Molecular Transistors

Electrostatics of Molecular Transistors

OFF state: Limited by Tunneling

Gate Modulation: Electrostatics

Is Si really that much bigger?

Design molecules with $L > 2.5 - 3$ nm
Tailor tunnel barriers through chemistry

Directed Assembly of Molecular Devices

**Layer-by-Layer Assembly**

1. **Surface template**
2. **Inorganic**
3. **Organic**

**Device Assembly**

- **SiO₂**
- **n+ Si**
- **M1**

**Device Characteristics**

**Study low and high bias characteristics**


**Manipulate chemistry of template, organic, and inorganic**

**Manipulate device geometry and molecular assembly**

- **Absorbance**
- **Wavelength (nm)**
- **Average bilayer coverage**
  - 0.9x10⁻¹⁰ mol/cm²
  - X-ray single crystal structure: 1.0x10⁻¹⁰ mol/cm²

- **Number of Bilayers**
- **Increase of Absorbance**
- **Rh loop at 258 nm**
- **Dipyridine linker at 298 nm**

- **Layer Assembly**
- **V (V)**
- **I (A)**
  - 1e⁻⁶
  - 2e⁻⁶
  - 3e⁻⁶
  - 4e⁻⁶
  - 5e⁻⁶
  - 10⁻⁶
Pentacene: the world’s best organic semiconductor

Mobilities up to 5 cm²/Volt.sec reported (a-Si: 1 cm²/Volt.sec)

Vacuum deposition
Key Question: How do Molecules interact with Contacts?

Pn stands up on non-metallic surfaces, such as oxides, semiconductors or semimetals, but lies down flat on metals. Fractal growth and scaling is consistent with classical growth models developed for inorganic materials.

J. Sadowski, G. Thayer, F. Meyer zu Heringdorf, R. Tromp
Growth on clean Si

Field of view 65 µm
Room temperature
1 image/minute

Deposition time (minutes)

Integral coverage (ML)

Layer coverage (%) 0                 30                60                90                120

0 0.5 1 1.5 2 2.5

0 50 100

Meyer zu Heringdorf, F.-J.; Reuter, M.C.; Tromp, R.M. Nature 2001, 412, 517-520
Aromatic and Pi-conjugated systems:

Benzene/Si(001) also undergoes transition from sp2 to sp3 hybridization
Reversibly adsorbs, desorbs

Benzene liquid
Benzene/Si(001)

Multiple binding configurations

K.P. Weidkamp, C.A. Hacker, M.P. Schwartz, X. Cao, R.M. Tromp and R.J. Hamers,
Pentacene on Si(001): Infrared Spectra

- Pentacene (bulk) shows no $sp^3$ hybridized C-H stretching vibrations
- Monolayer coverage – peaks at 2091, 2870, 2922 cm$^{-1}$ indicate Si-H and $sp^3$ hybridized C-H bonds, also thermally stable
- Multilayer coverage – small Si-H peak, peaks above 3000 cm$^{-1}$ are much larger than any below 3000 cm$^{-1}$
- Heating multilayer – broader Si-H peak, peaks almost identical to those of monolayer

Interfacial layer involves transition of some C atoms to $sp^3$ hybridization and some dissociation. Layer appears to be thermally stable and irreversibly bound.

K.P. Weidkamp, C.A. Hacker, M.P. Schwartz, X. Cao, R.M. Tromp and R.J. Hamers,
Cyclo-addition reaction on Si

Organic surface termination renders Si surface inert, providing an ideal substrate for subsequent pentacene growth
From cyclical molecules to chains

Chainlike molecules render Si surface inert, but affect diffusion and aggregation during pentacene growth
Selection of azimuthal angles: Role of molecular species

Cyclooctadiene

Hexene

Dodecene on axis

Dodecene off axis

Crystals at 45 degrees increments

Crystals at 90 degrees increments
Epitaxial growth of pentacene on Si: diffraction analysis

LEED 8/20 dodecene Si(001) on axis

Pentacene:
- $a = 0.627 \text{ nm}$
- $b = 0.777 \text{ nm}$
- $\gamma = 84.7^\circ$

Si(001):
- Dimer-dimer: 0.384 nm
- Row-row: 0.768 nm

Mismatch $\sim 1\%$

LEED 6/11 COD Si(001) on axis

Epitaxial growth, rectangular unit cell
PENTACENE /Si(001) EPITAXY

on axis

4 degrees off axis

0.768 nm
Pentacene MD on IBM BlueGene

classical diffusion

non-classical diffusion

pentacene diffusion on dodecane
Soluble pentacene precursors

Soluble pentacene for spincoated TFTs

![Diagram of solubility and performance metrics for spincoated TFTs.]

- Linear mobility ($\mu_{\text{lin}}$) = 0.4
- Saturation mobility ($\mu_{\text{sat}}$) = 0.8
- On/off ratio > $10^6$

Highest performance from solution processed organic TFT

Photosensitive version for patterning

![Diagram of photosensitive process with UV light exposure and annealing.]

- UV light exposure
- Annealing
- Polymeric precursor

Image credit: IBM
Chalcogenides: a new look at some old materials

<table>
<thead>
<tr>
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<th>$E_g$ (eV)</th>
<th>$\mu_n$ (cm²/V·sec)</th>
<th>$\mu_p$ (cm²/V·sec)</th>
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<tbody>
<tr>
<td>SnS₂</td>
<td>2.6</td>
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<tr>
<td>SnSe₂</td>
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<tr>
<td>CdSe</td>
<td>1.73</td>
<td>650</td>
<td></td>
</tr>
</tbody>
</table>

Organic-derivatized CdSe nanocrystals -- n-type 1.0 cm²/V·s
[ Ridley et. al., Science 286, 746 (1999)]

Chemical Bath Technique CdSe -- n-type 15 cm²/V·s

Assembled Nanorod / Nanoribbon -- n-, p-type <300 cm²/V·s
[ Duan et. al., Nature 425, 274 (2003)]

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Solution Processable Chalcogenides

$M_1X_2 \ (X = S, \ Se, \ Te)$

**INSOLUBLE**

$\times = A^+$ (organic or volatile)

$A_qM_1X_{z+q/2} \ (X = S, \ Se, \ Te)$

**SOLUBLE**

$M_1X_2 \ (X = S, \ Se, \ Te)$

**INSOLUBLE**
Chalcogenides – a new low-T spin-on semiconductor with high mobility

Developed new chemistries to spin on thin chalcogenide films with low processing temperatures < 300 C

RMS Roughness: 6 Å (A) and 14 Å (B)
Film thickness: only 7-9 unit cells thick!
Composition: SnS$_{1.8}$ and SnS$_{1.4}$Se$_{0.5}$

$\mu_{\text{sat}} = 12.0$ cm$^2$/V-s
$\mu_{\text{lin}} = 2.4$ cm$^2$/V-s
$I_{\text{on}}/I_{\text{off}} > 10^6$
$L = 14$ µm; $W = 250$ µm

Highest spin-coated channel mobility by ~ 10X
Nanoscience may give rise to future revolutionary technologies relevant to Information Technology: Nanotube or molecular logic; Novel, dense crosspoint memories; New high performance spin-coatable semiconductors; etcetera.

Also, Si technology itself is a rapidly changing revolutionary technology that provides a ‘ready’ platform for nanotechnology integration: Materials; Processes; Devices; Lithography; etcetera.

Development of new technologies to replace an existing technology takes decades, not months – but we can utilize nanotechnology on shorter timescales by insertion in existing technologies, and in niche application.