Novel Materials for Organic and Thin Film Electronics

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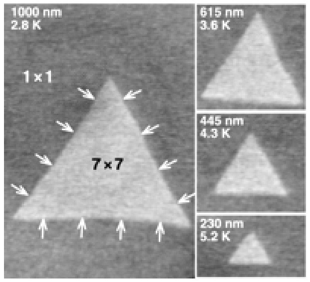
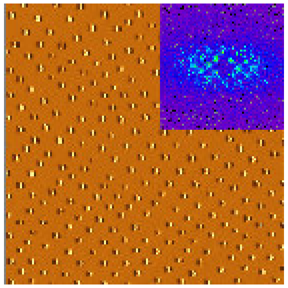
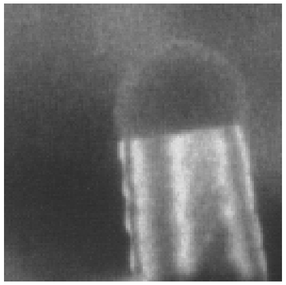
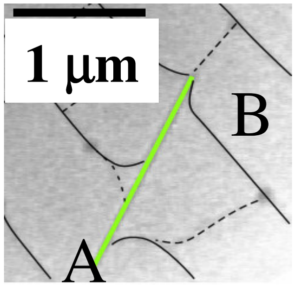
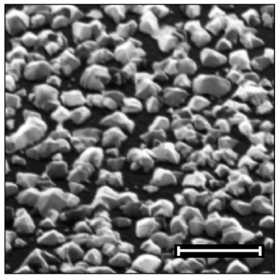
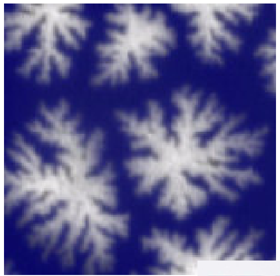










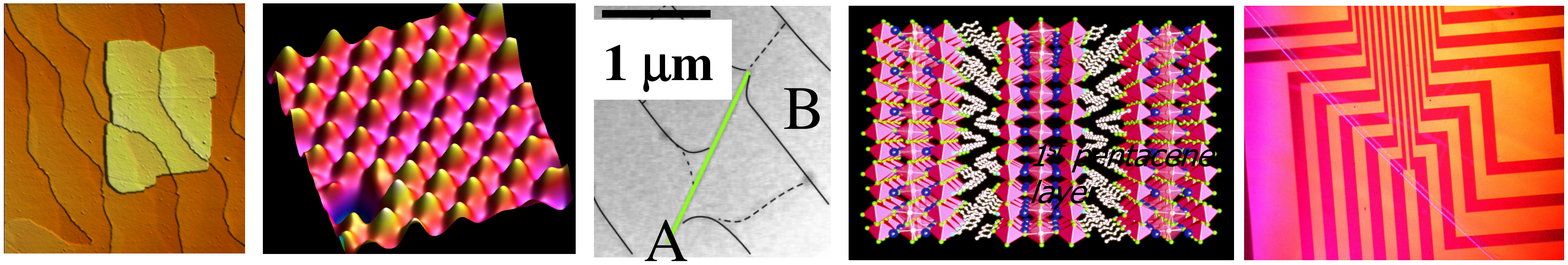


The road beyond CMOS : Nano ?

Nano: things smaller than 100 nm

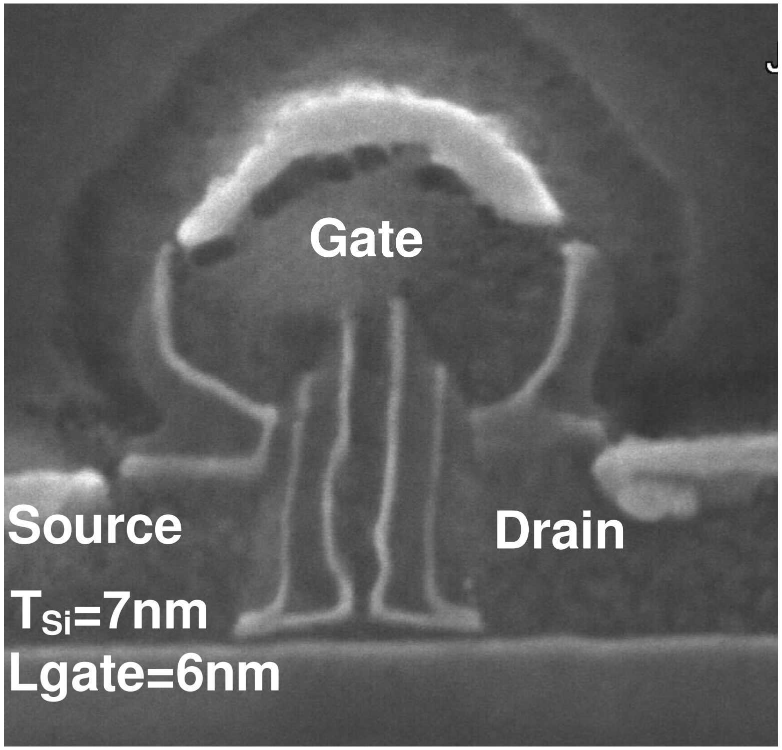
Opportunities for revolutionary new materials, processes, and technologies

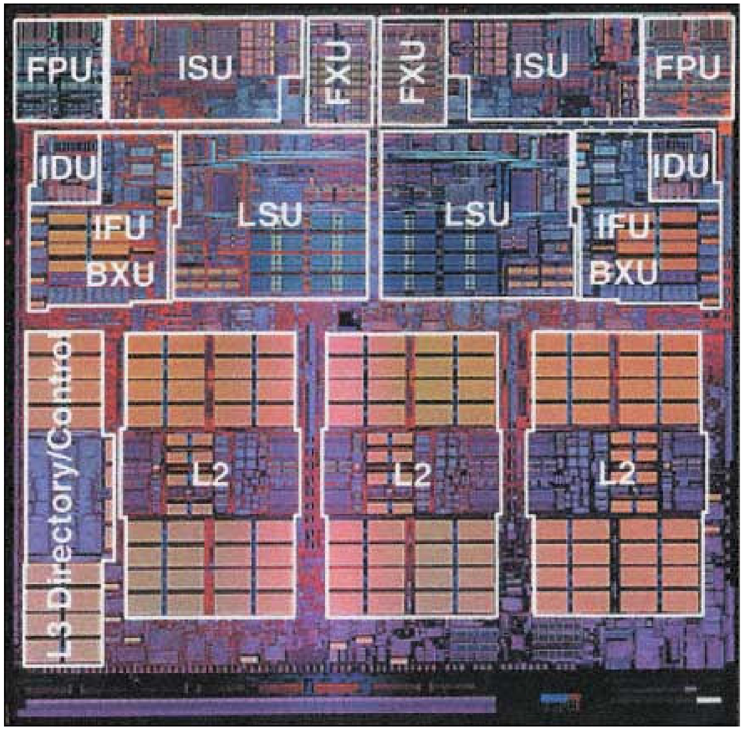
But: also many opportunities to improve, extend, and transform present technologies, including computer hardware technologies



Silicon Logic - Already at the Nanoscale

(That’s what got us into trouble!)





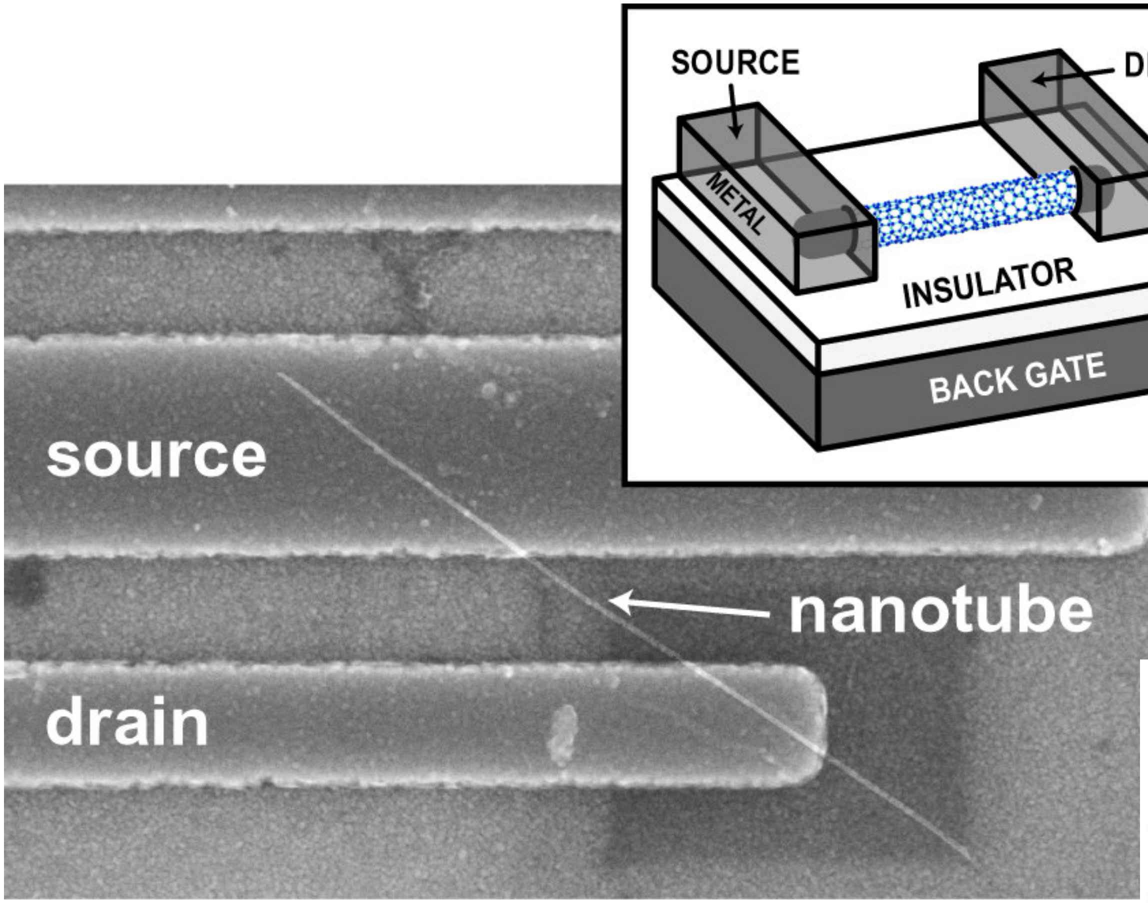
- Power4 Chip
- 174 million transistors

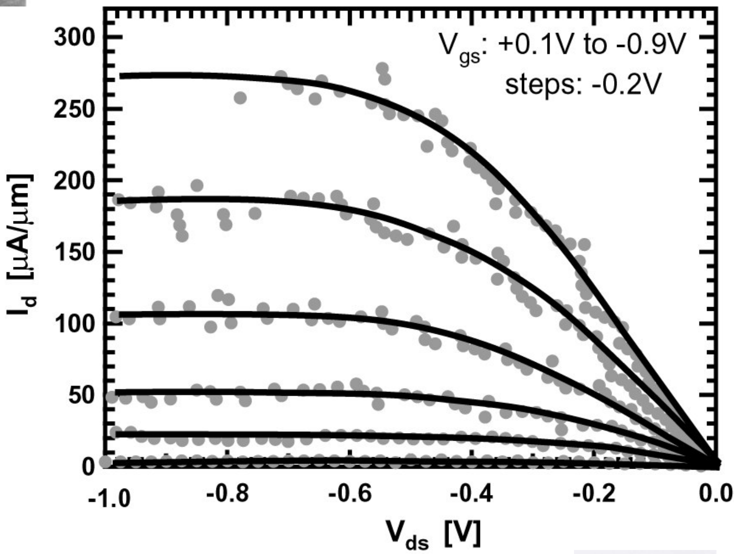
- Gate length = 6 nm

B. Doris et al., *IEDM* , paper 10.6, 2002.

J. Warnock et al., *IBM J. R&D*, p. 27, 2002

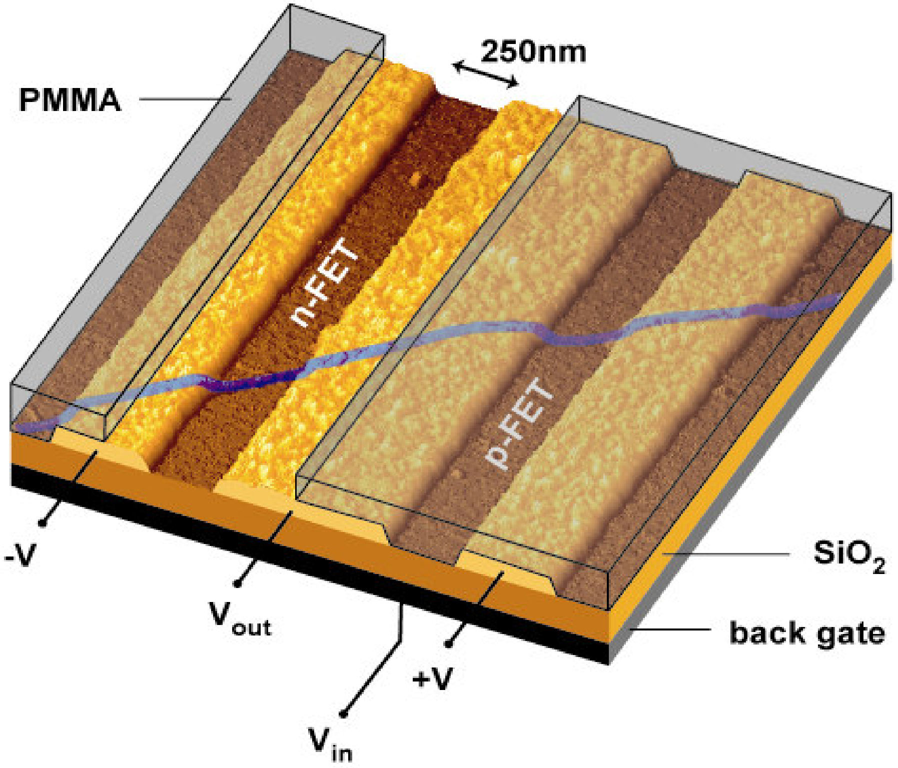
One alternative: Carbon Nanotube FET

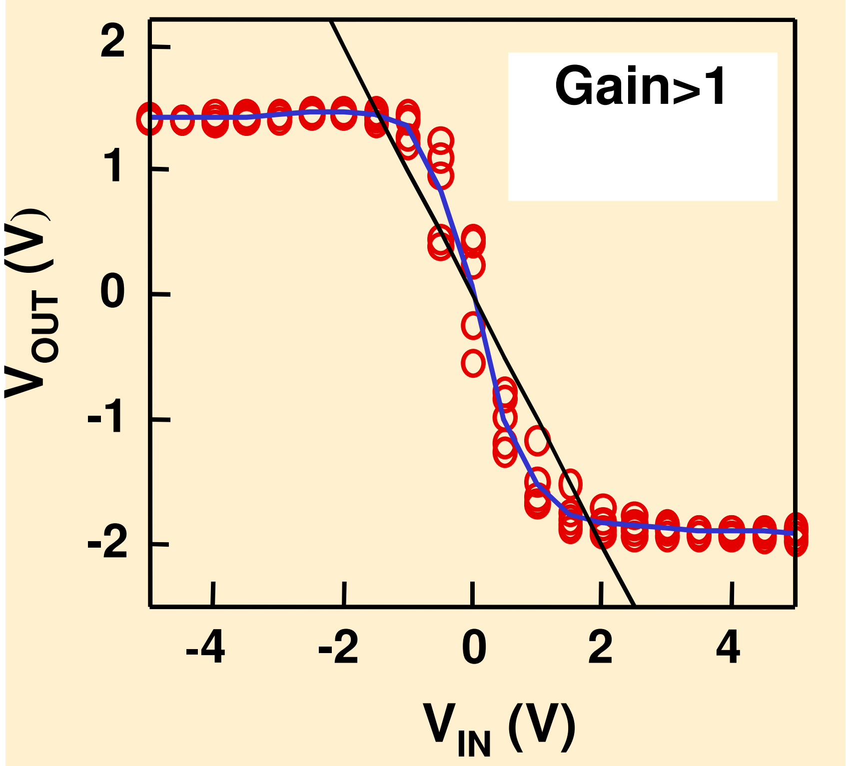




Semiconductor mobilities @ RT (cm^2/V.s)	
InSb	77,000
CdSe	650
c-Si	1,500 – 100
a-Si	1
CNT	100,000
Polymer	10^{-5} – 10^{-2}
Pentacene	0.1 – 5
Chalcogenides (spinc.)	1 -20

Carbon Nanotube Inverter



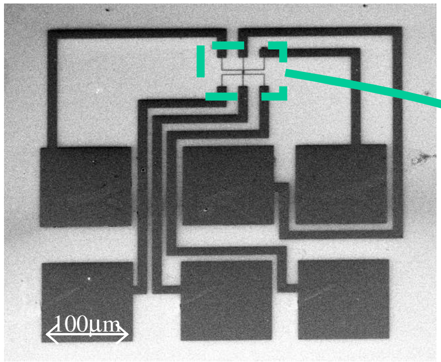


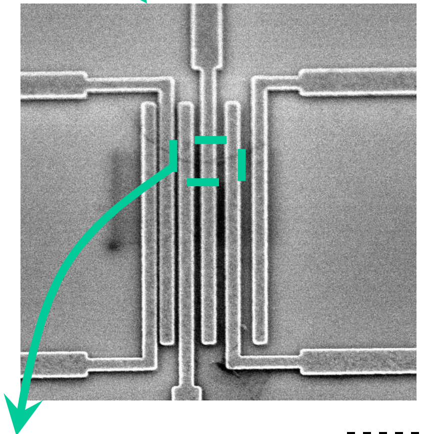
Nanotube *Technology* ?

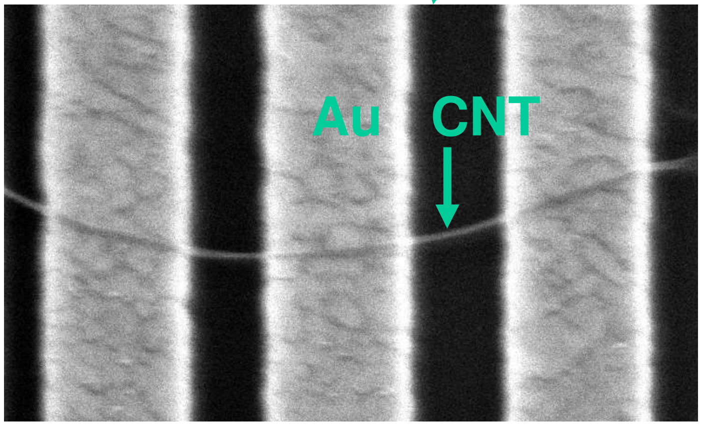
Plenty of room for improvement !

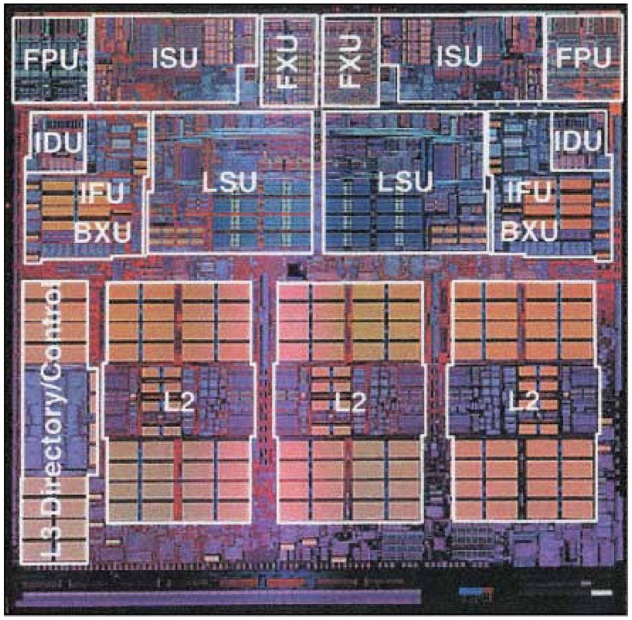
No new architecture !

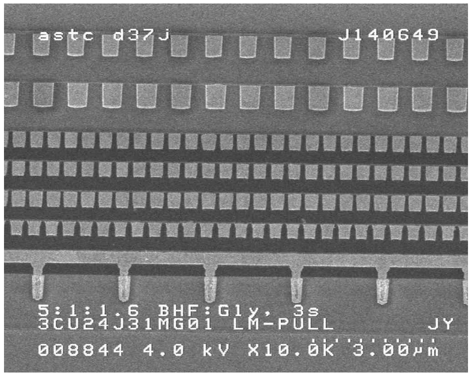
How do you get from here to there?

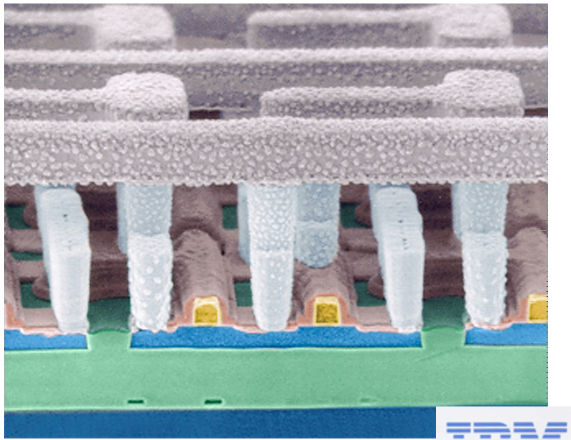






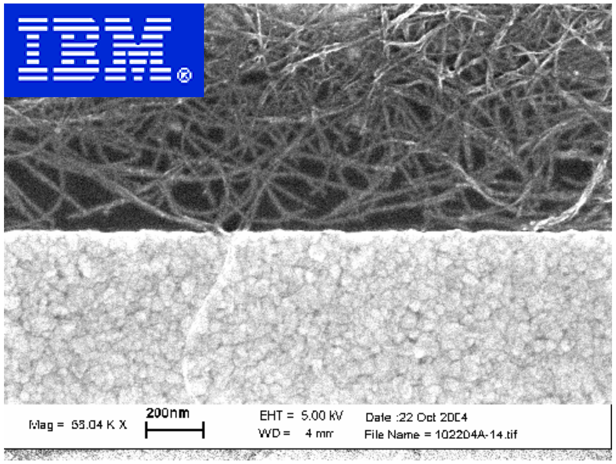


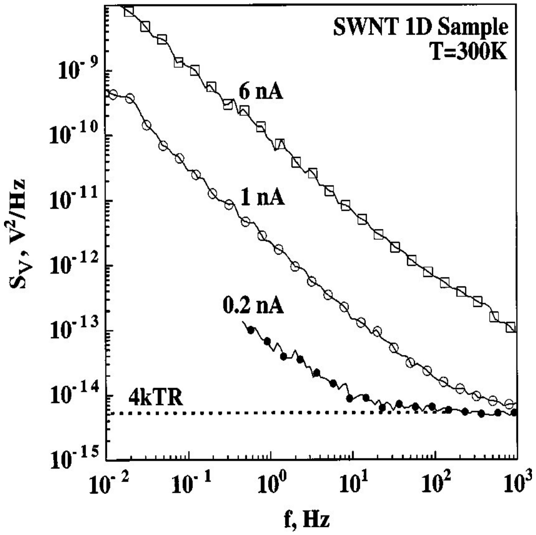




Some of the issues

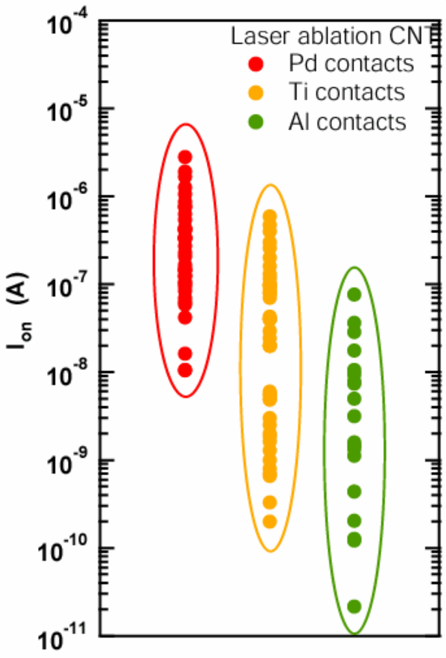
- CNT synthesis and purification; control of diameter and chirality
- CNT placement in integrated circuit hierarchy with nm precision
- Site- and/or area-selective n- and p-type CNT doping on nm scale
- Control over contacts to CNT, injection barrier to n-, p-, i-CNTs
- Elimination of parasitics for 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

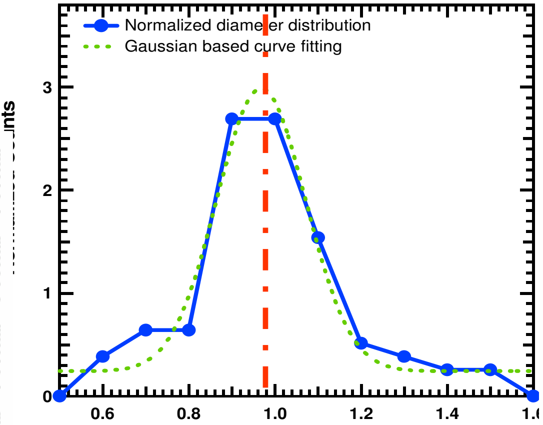


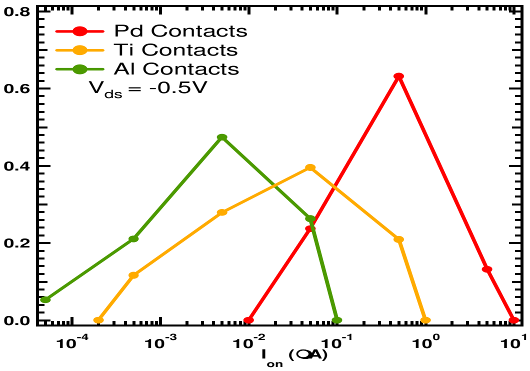


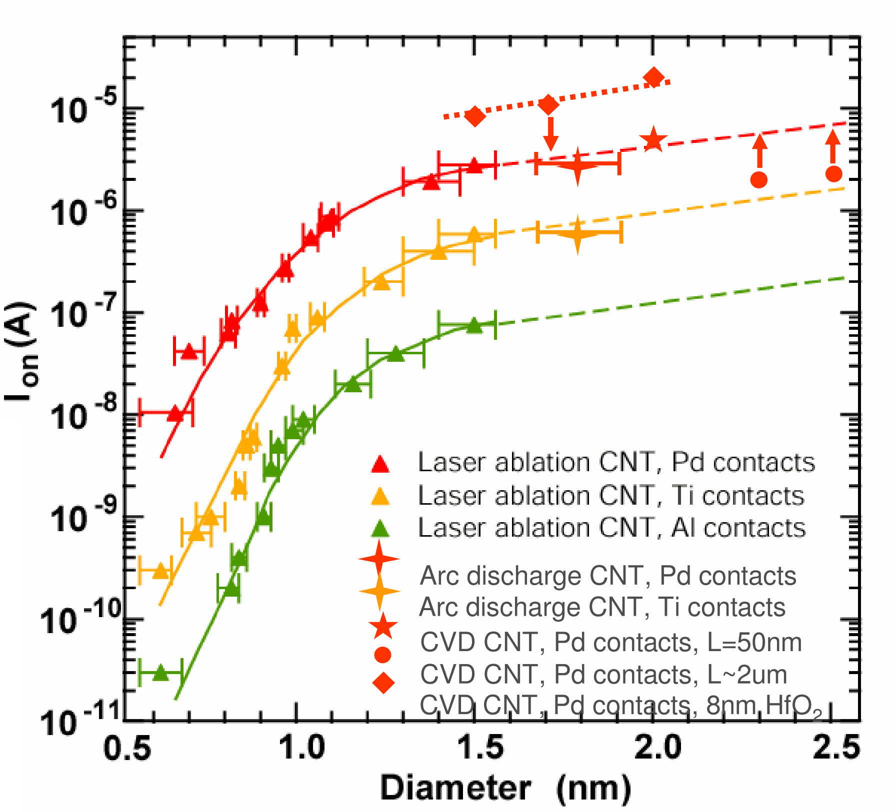
1/f noise in carbon nanotubes
Philip G. Collins, M. S. Fuhrer, and A. Zettl
APL 76, 894 (2000)

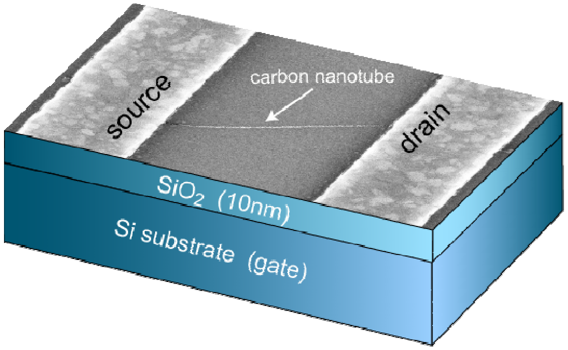
Contacts





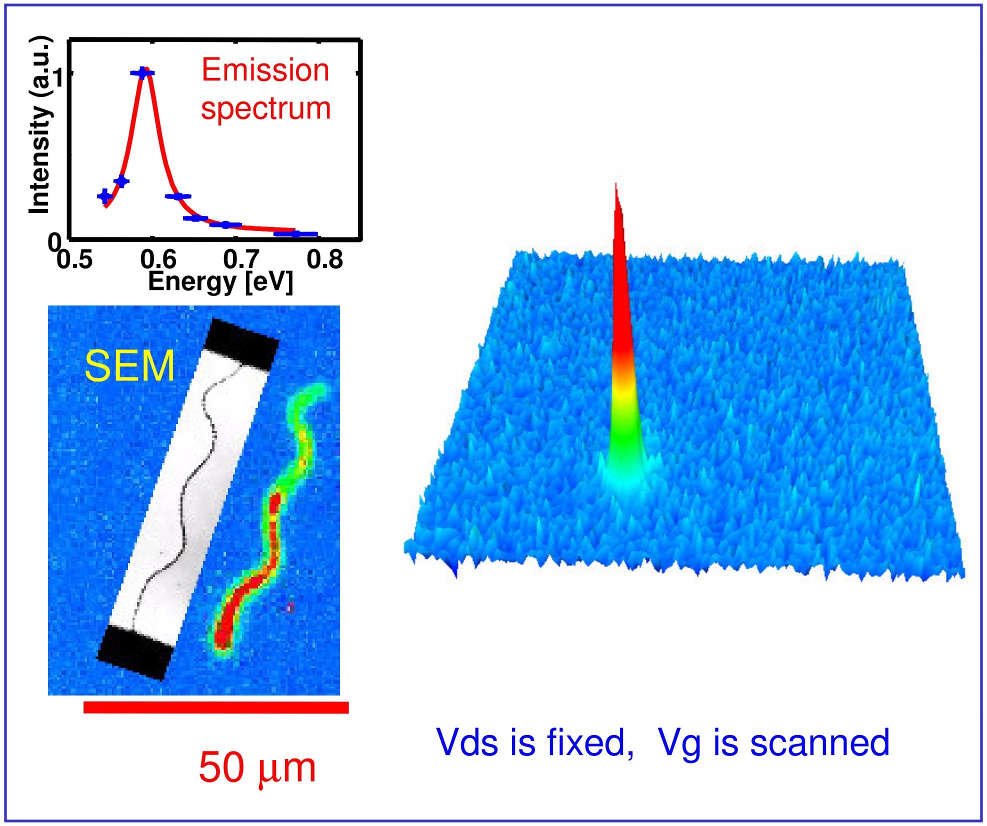






Zhihong Chen, Joerg Appenzeller, Joachim Knoch,
Yu-Ming Lin, Phaedon Avouris
A26-5

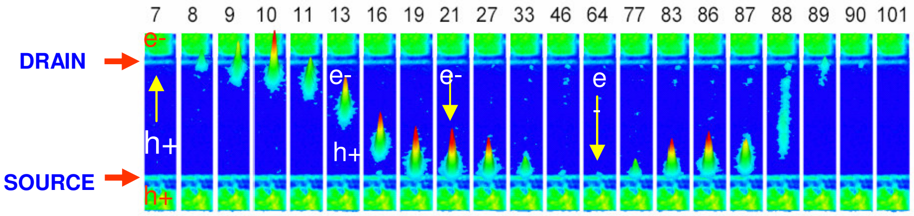
CNT Optoelectronics

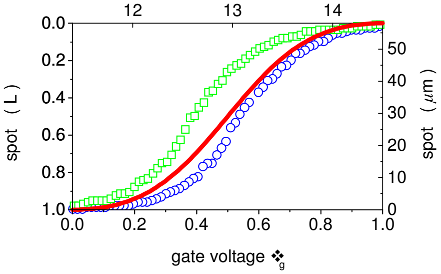


CNT optoelectronic properties are key in understanding basic transport properties, effects of defects, CNT electronic structure, excited states, etcetera.
There is room for much experimental work, as well as more advanced theoretical understanding.

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





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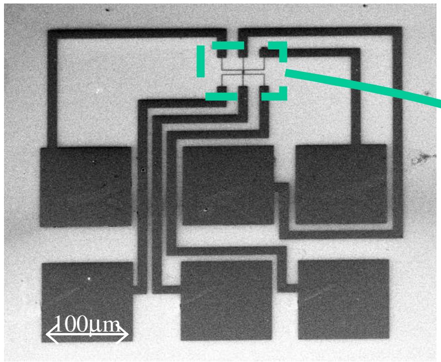
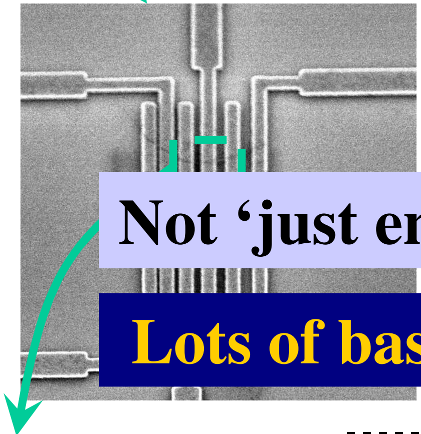
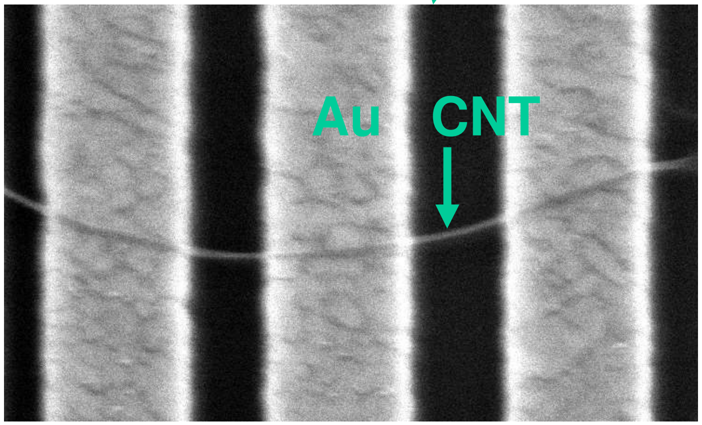
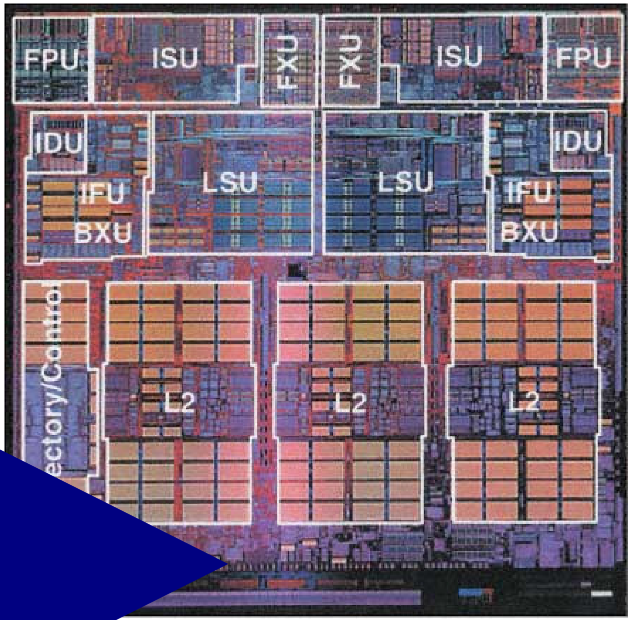


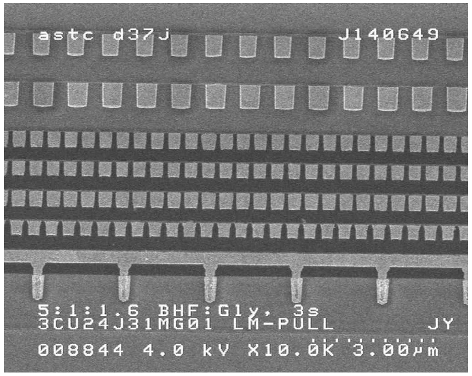


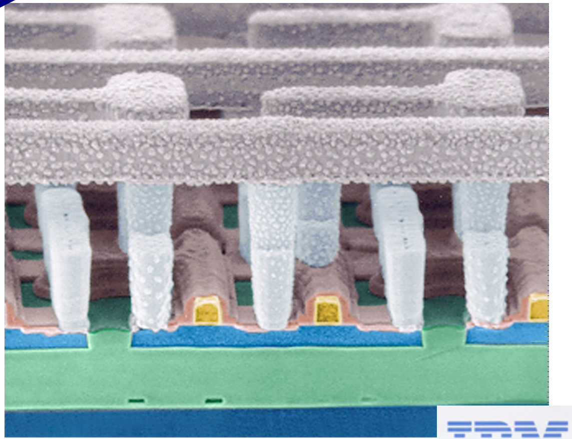
Not ‘just engineering’

Lots of basic science !

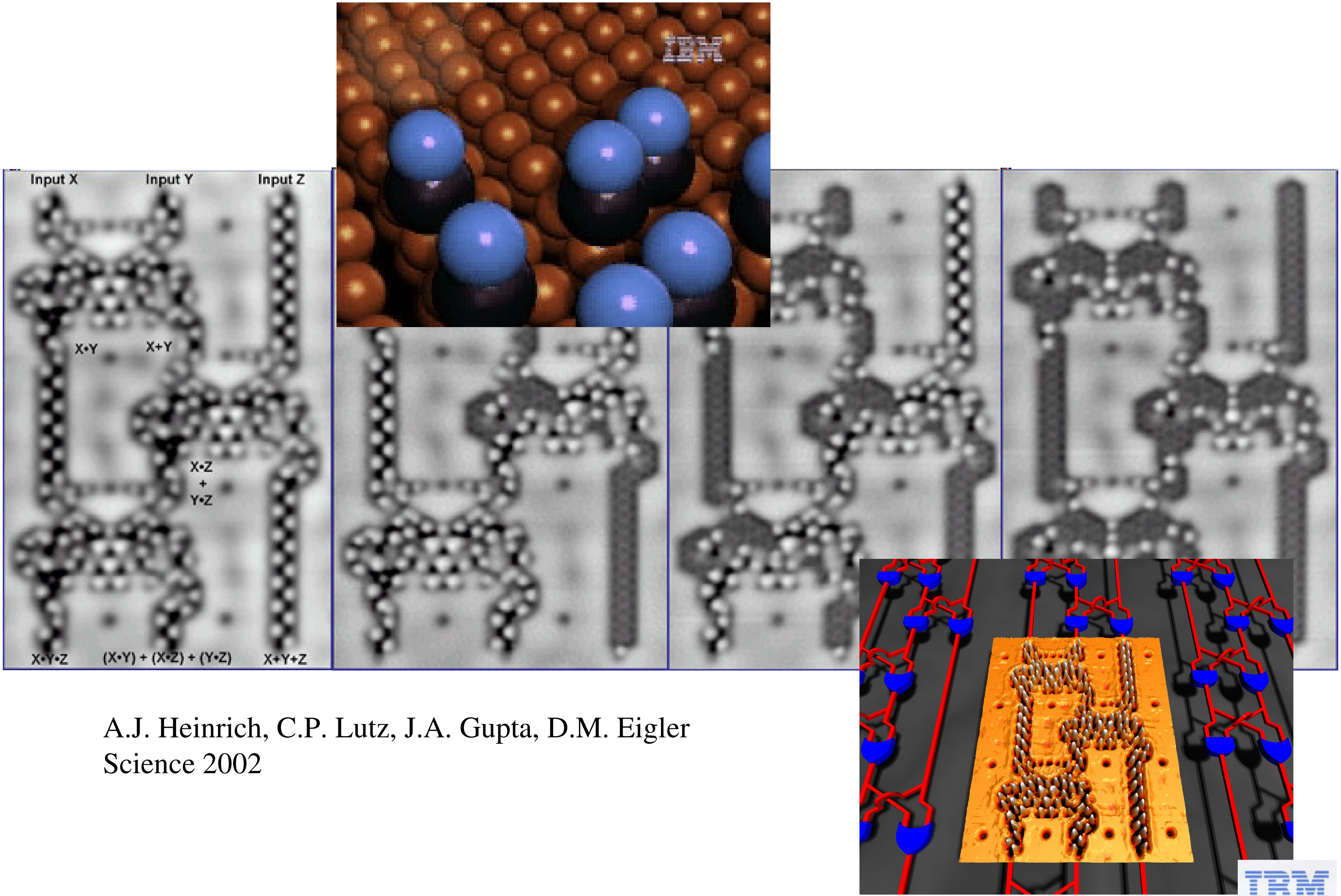








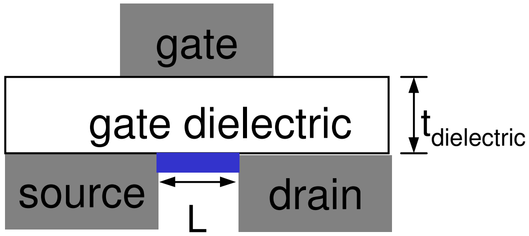
A Molecular Computer – Slow but it works (once)

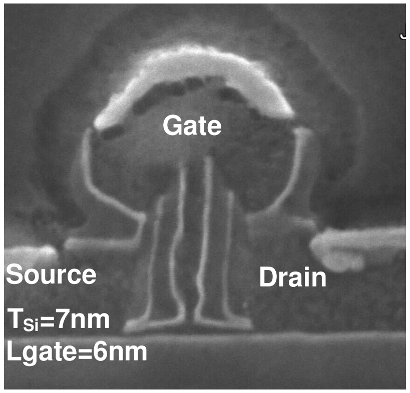


A.J. Heinrich, C.P. Lutz, J.A. Gupta, D.M. Eigler
Science 2002

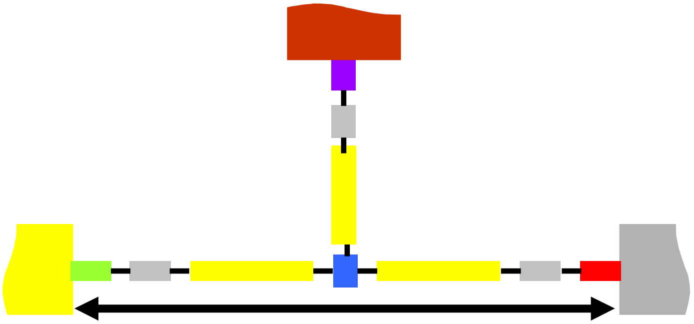
Molecular Transistors

Electrostatics of Molecular Transistors

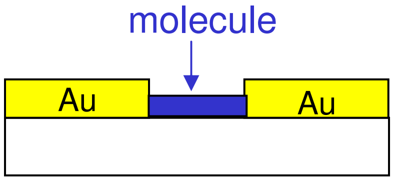




Is Si really that much bigger?

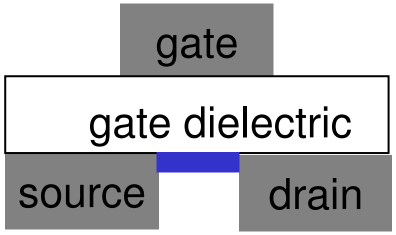


① OFF state: Limited by Tunneling



Barrier lowered by
Energy level offset
Hybridization
and Charge transfer
between metal-molecule

② Gate Modulation: Electrostatics



$\underline{t_{dielectric} \lesssim L}$

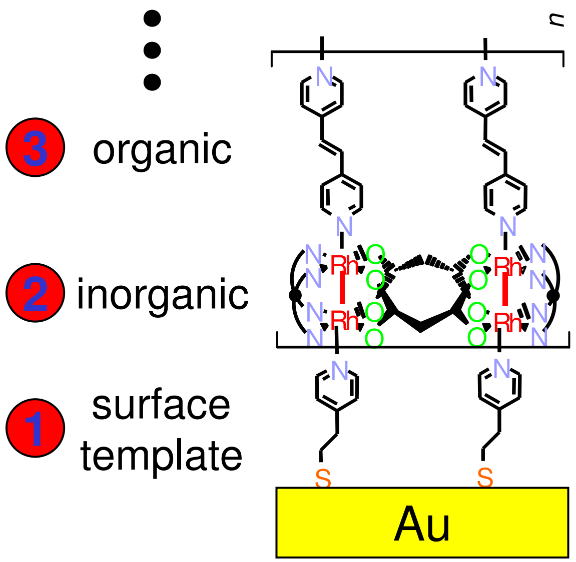
to attain gate field
not dominated by
drain field
Yet
dielectric not leaky

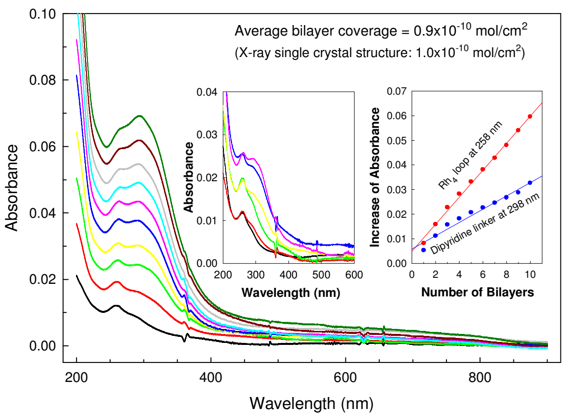
Design molecules with L>2.5-3 nm
Tailor tunnel barriers through chemistry

C. R. Kagan, A. Afzali, R. Martel, L. M. Gignac, P. M. Solomon, A. G. Schrott, B. Ek, *Nano Letters*, **3**, 119 (2003).

Directed Assembly of Molecular Devices

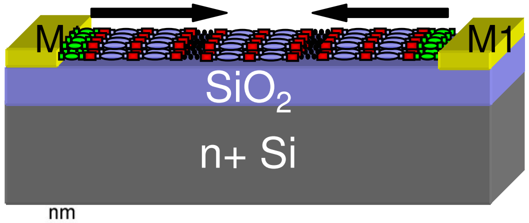
Layer-by-Layer Assembly

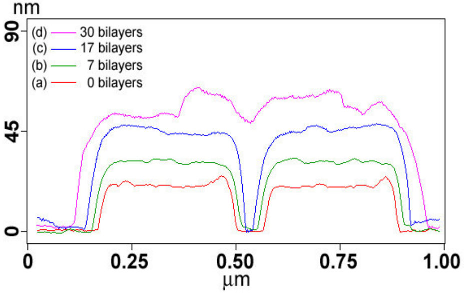


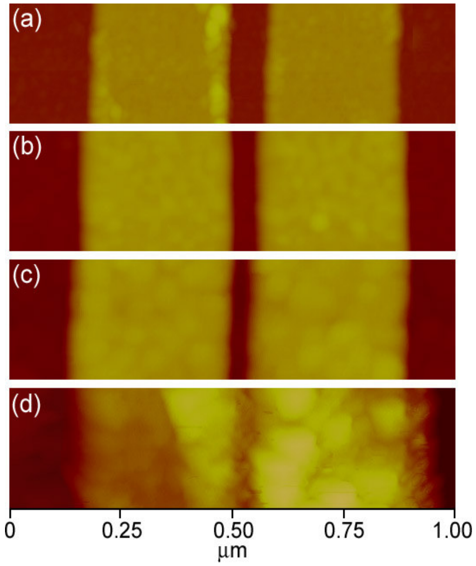


Manipulate chemistry of template, organic, and inorganic

Device Assembly

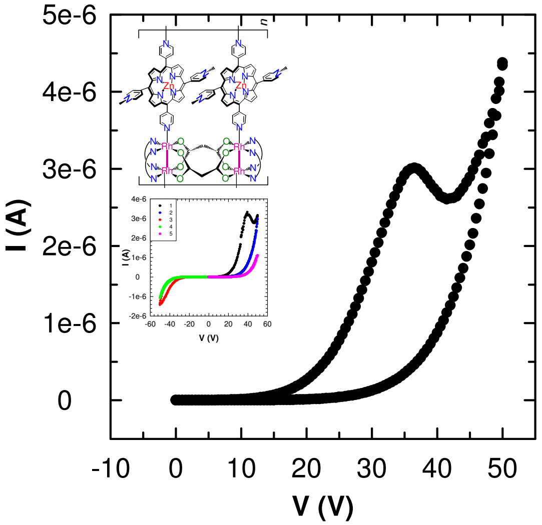


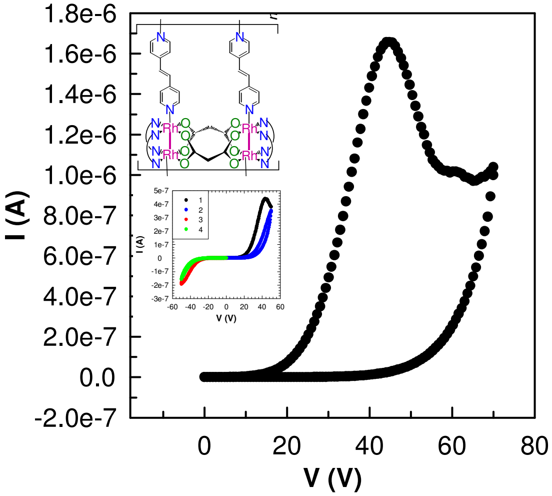




Manipulate device geometry and molecular assembly

Device Characteristics

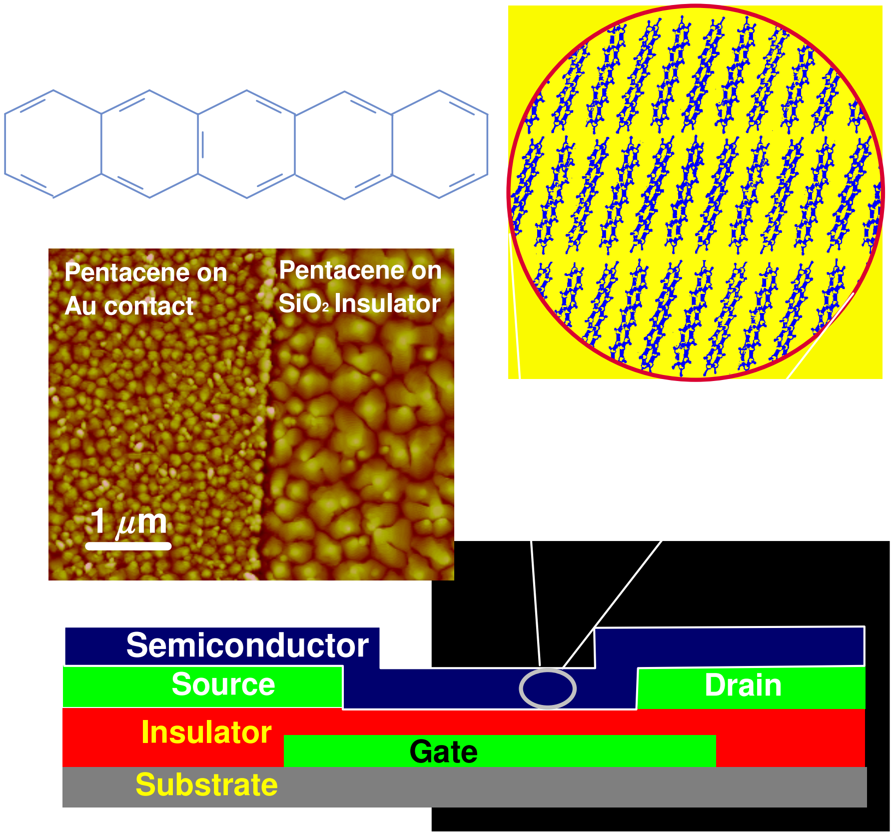


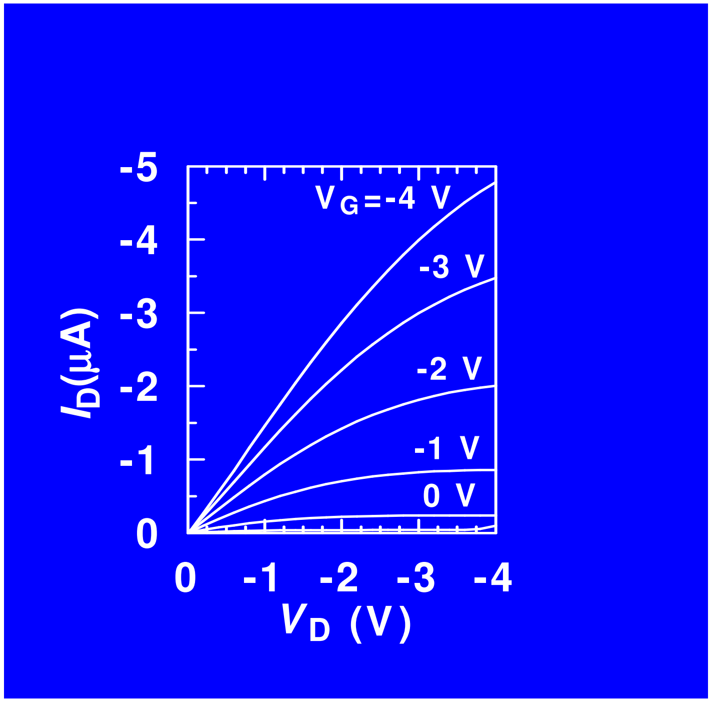


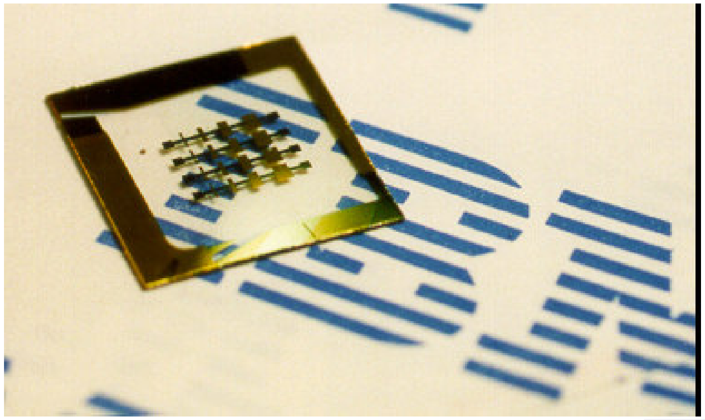
Study low and high bias characteristics

C. Lin, C. R. Kagan *JACS*, **125**, 336 (2003)

Pentacene: the world's best organic semiconductor



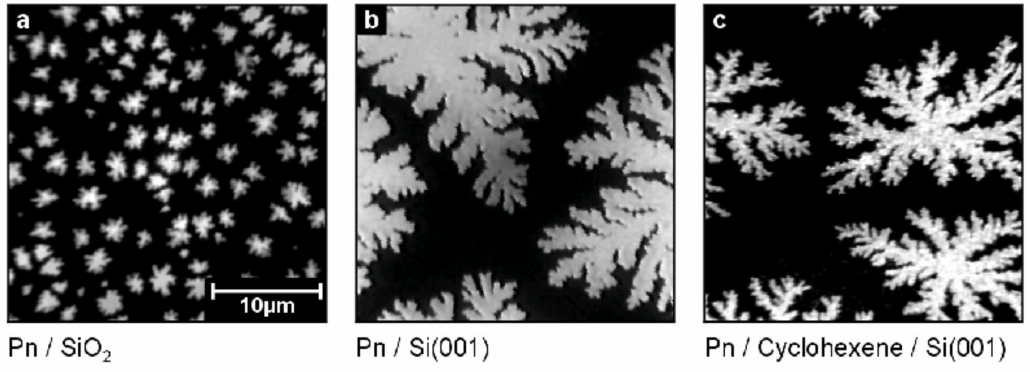




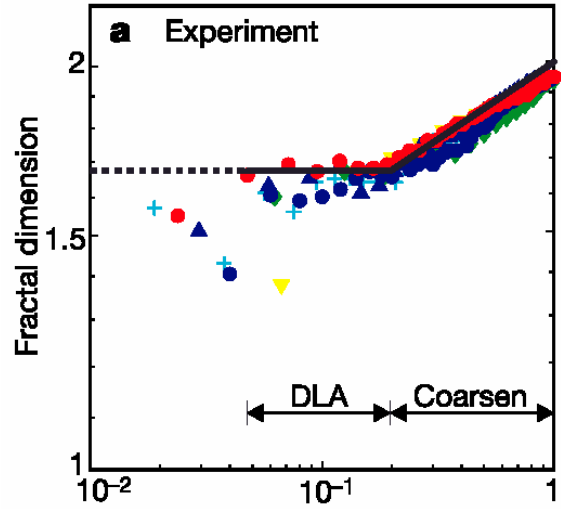
Mobilities up to 5 cm^2/Volt.sec reported (a-Si: 1 cm^2/Volt.sec)

Vacuum deposition

Key Question: How do Molecules interact with Contacts?



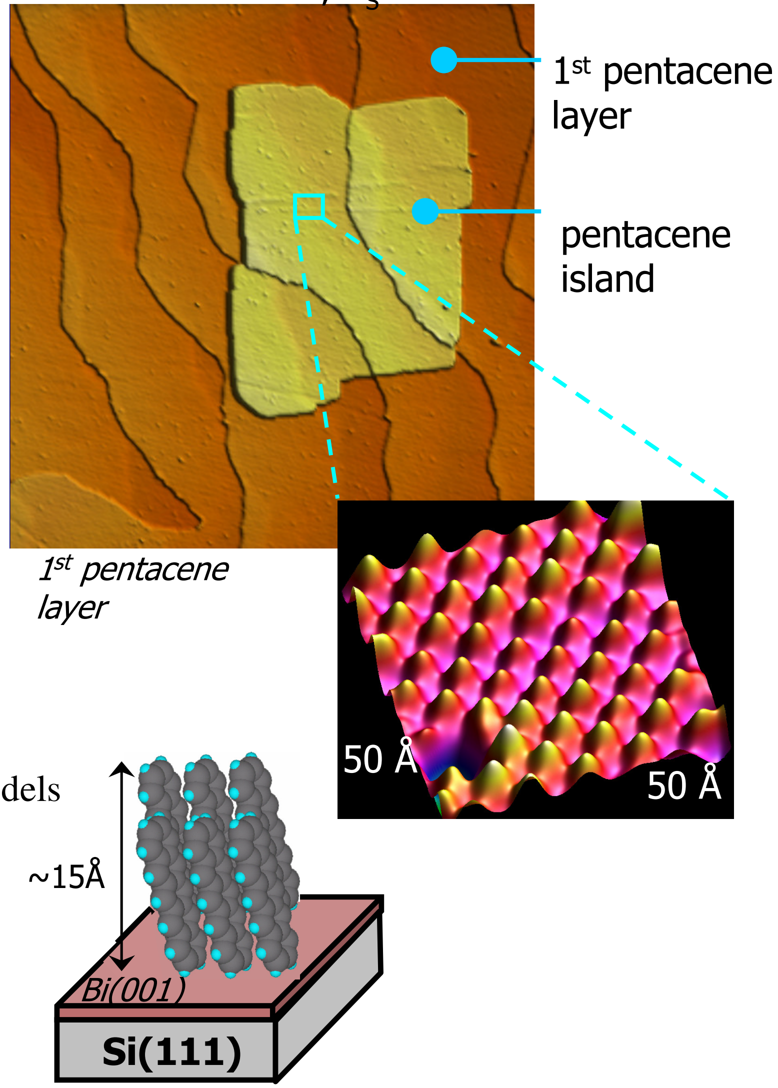
Pn / SiO_2 Pn / Si(001) Pn / Cyclohexene / Si(001)



Pn stands up on non-metallic surfaces, such as oxides, semiconductors or semimetals, but lies down flat on metals.

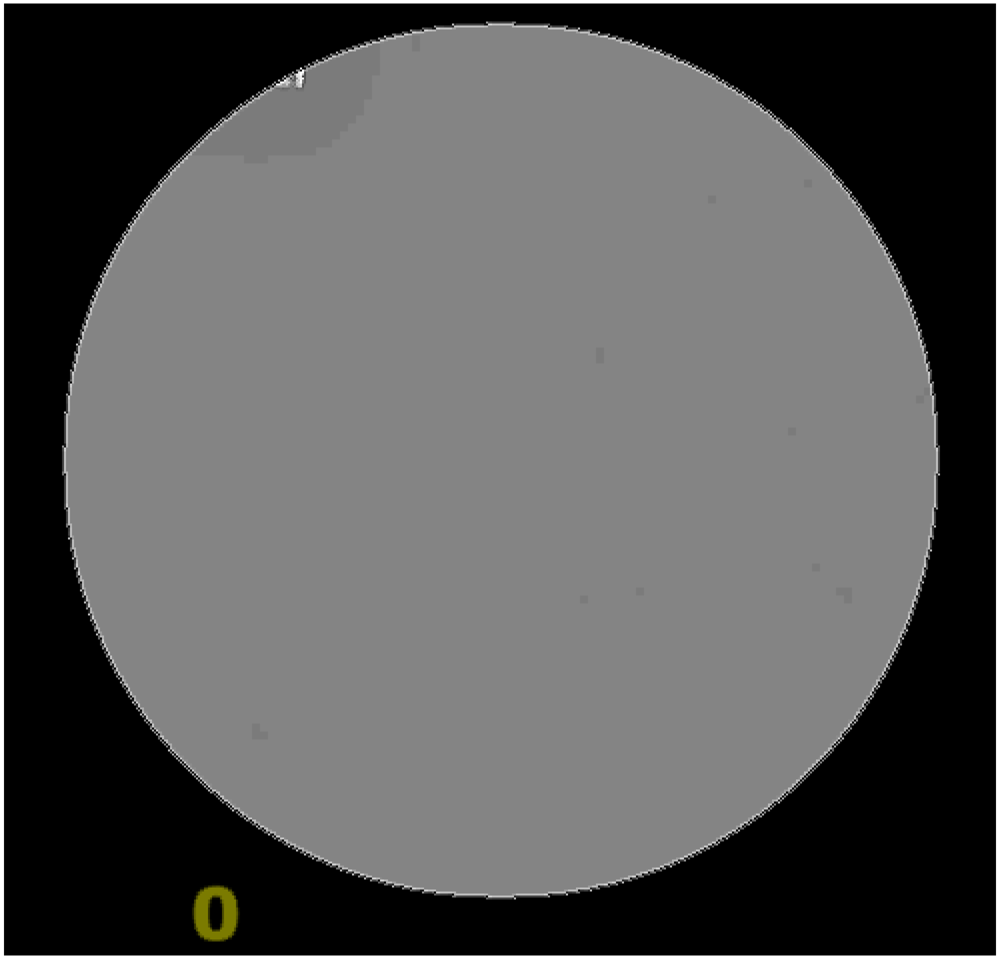
Fractal growth and scaling is consistent with classical growth models developed for inorganic materials

500 nm × 500 nm, V_S = -2.0V

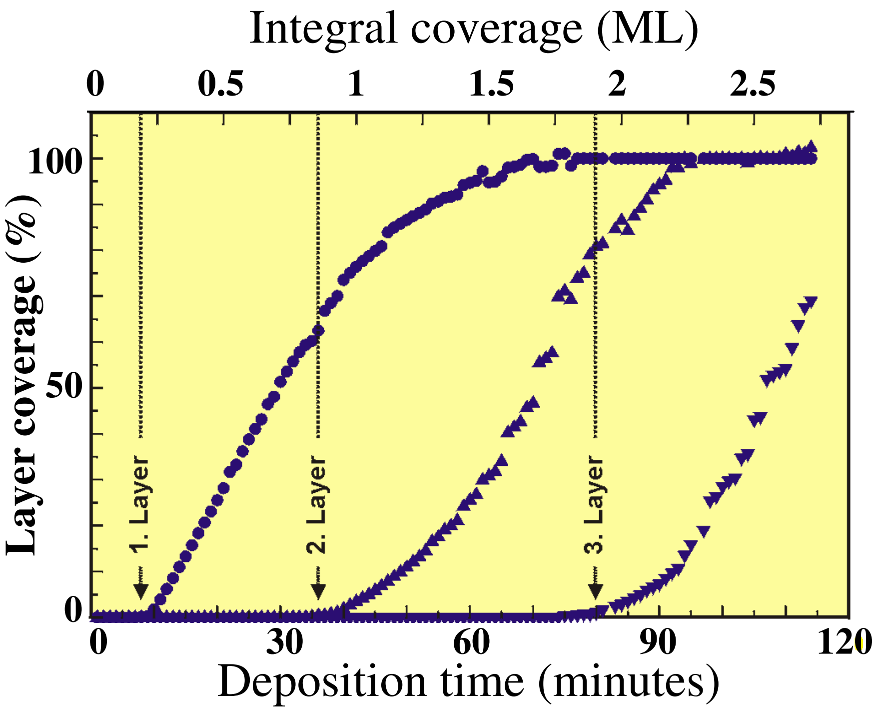


J. Sadowski, G. Thayer, F. Meyer zu Heringdorf, R. Tromp

Growth on clean Si

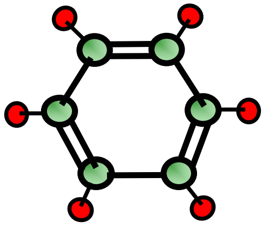


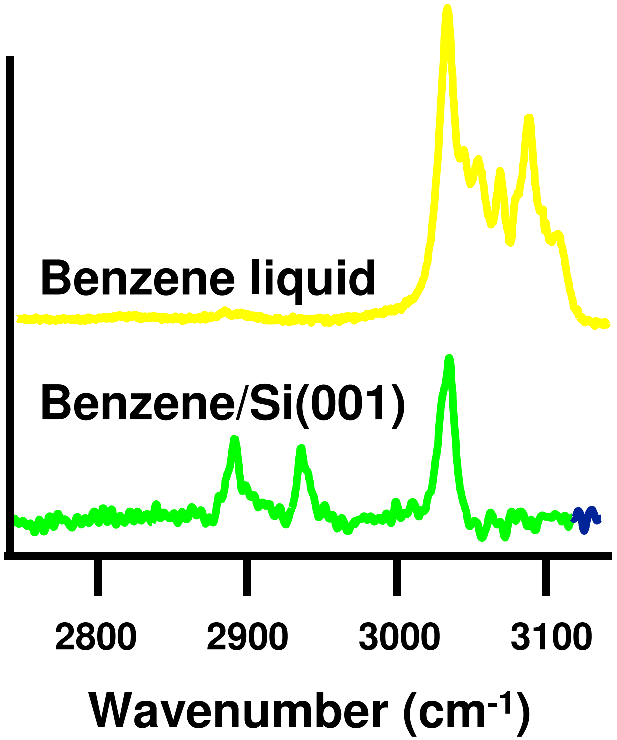
Field of view 65 µm
Room temperature
1 image/minute

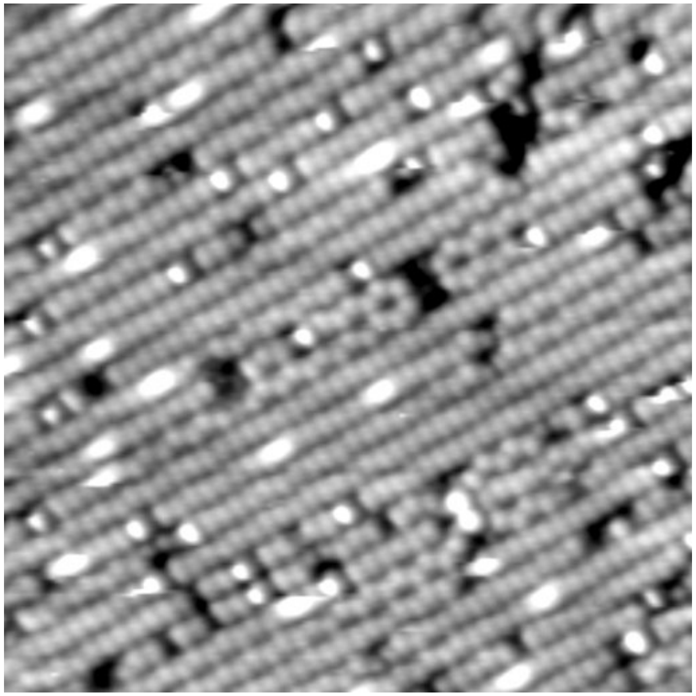


Meyer zu Heringdorf, F.-J.; Reuter, M.C.; Tromp, R.M. *Nature* **2001**, *412*, 517-520

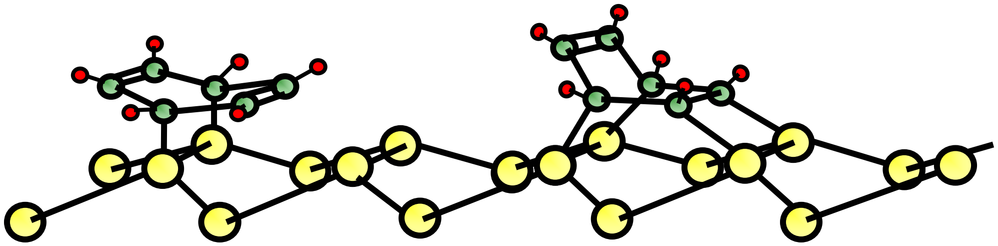
Aromatic and Pi-conjugated systems:







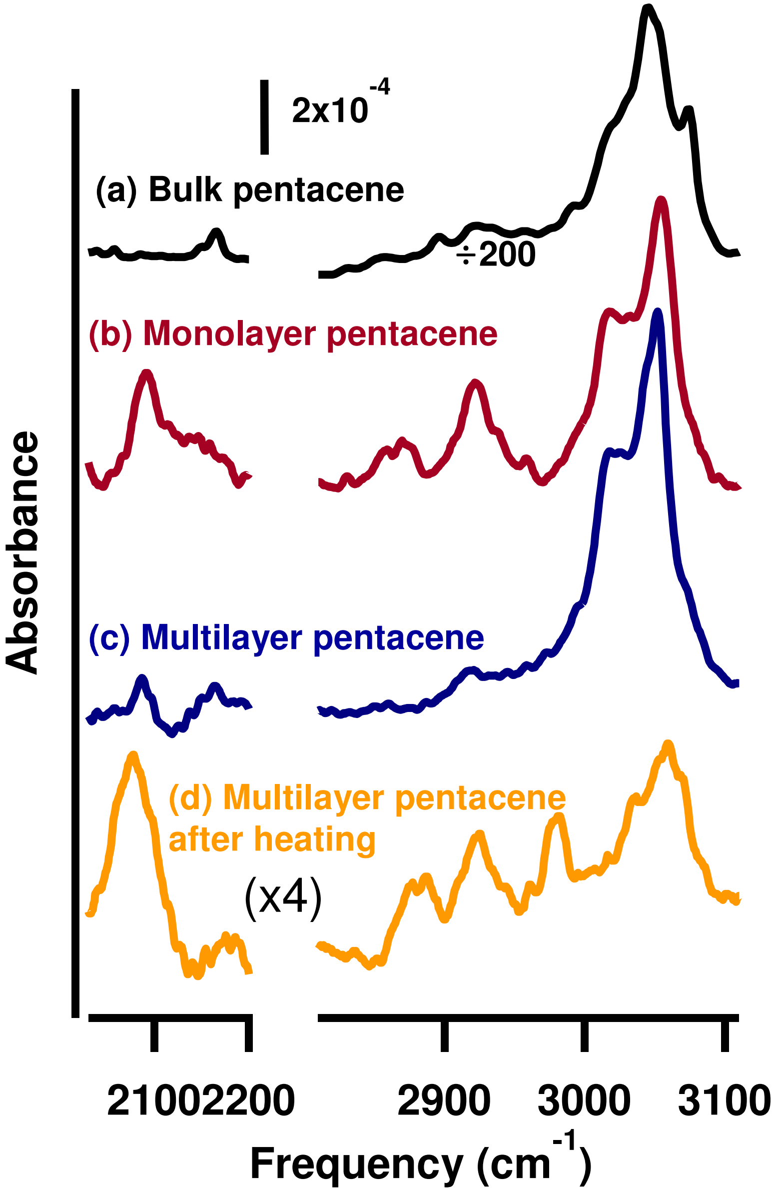
Multiple binding configurations



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

K.P. Weidkamp, C.A. Hacker, M.P. Schwartz, X. Cao, R.M. Tromp and R.J. Hamers,

Pentacene on Si(001): Infrared Spectra

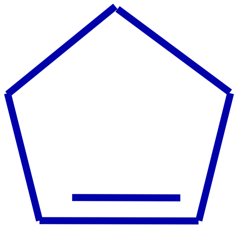


- Pentacene (bulk) shows no *sp*^{3} hybridized C-H stretching vibrations
- Monolayer coverage – peaks at 2091, 2870, 2922 cm^{-1} indicate Si-H and *sp*^{3} hybridized C-H bonds, also thermally stable
- Multilayer coverage – small Si-H peak, peaks above 3000 cm^{-1} are much larger than any below 3000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

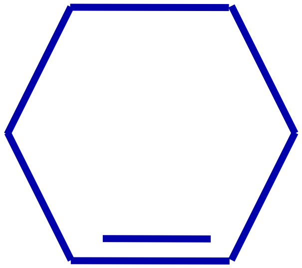
Interfacial layer involves transition of some C atoms to sp3 hybridization and some dissocation. Layer appears to be thermally stable and *irreversibly* bound.

K.P. Weidkamp, C.A. Hacker, M.P. Schwartz, X. Cao, R.M. Tromp and R.J. Hamers,

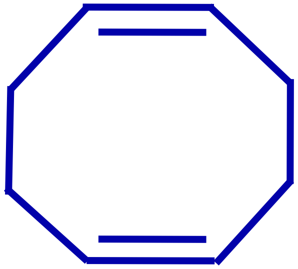
Cyclo-addition reaction on Si



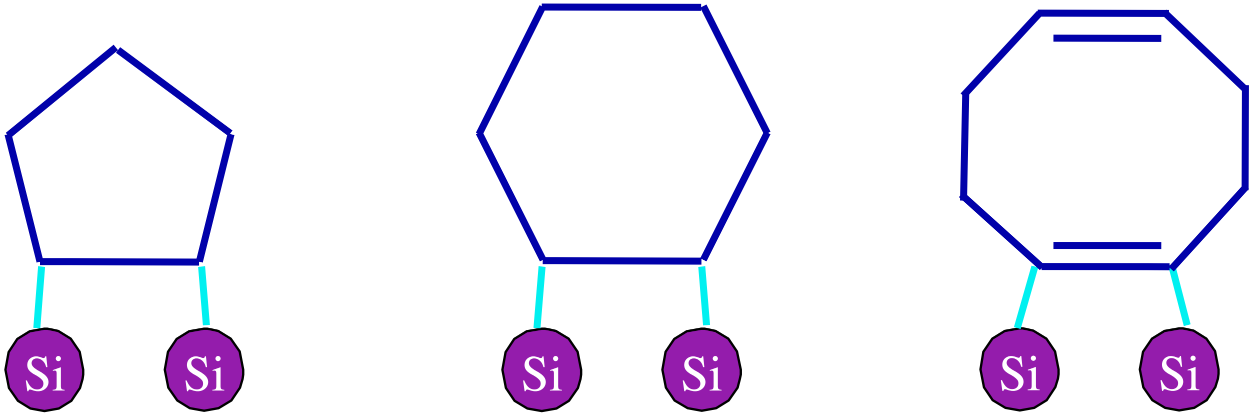
cyclopentene



cyclohexene

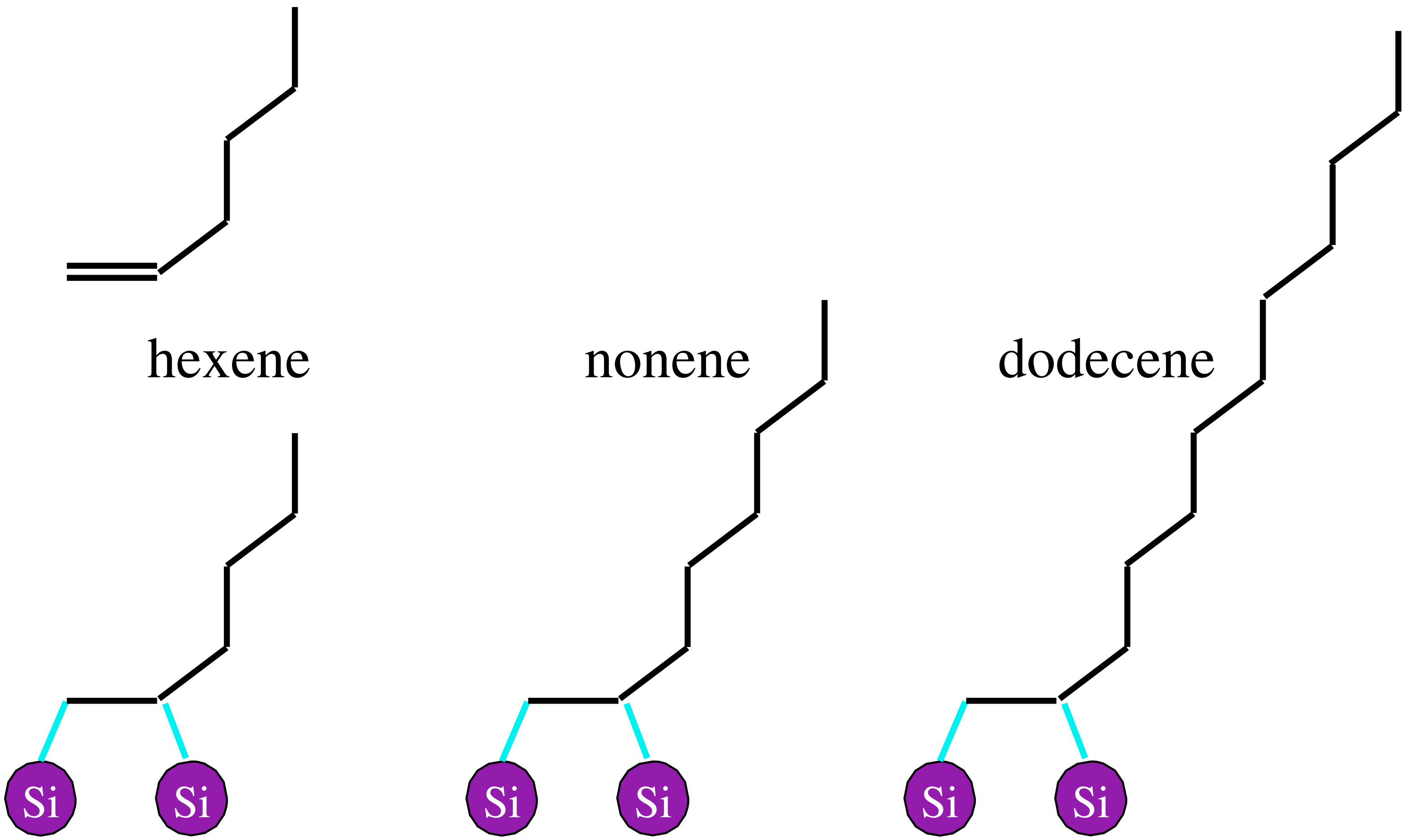


cyclo-octadiene



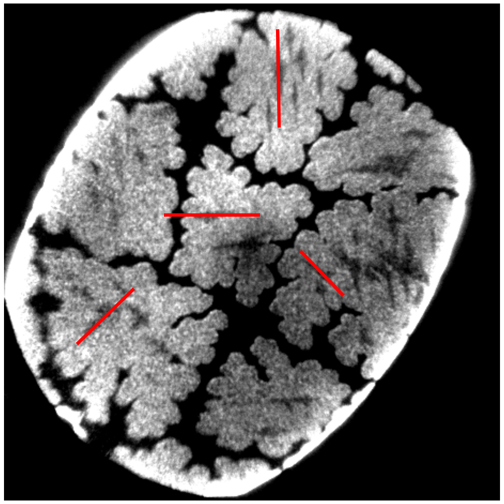
Organic surface termination renders Si surface inert, providing an ideal substrate for subsequent pentacene growth

From cyclical molecules to chains

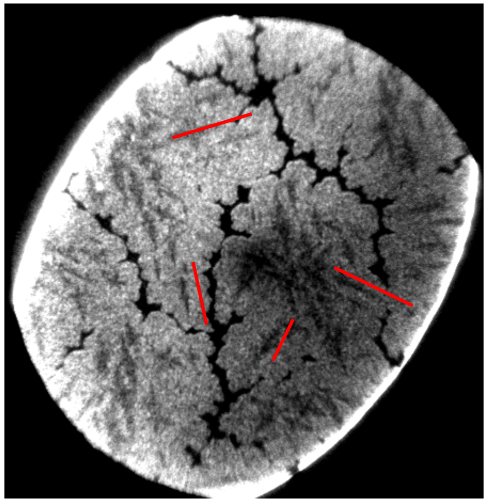


Chainlike molecules render Si surface inert, but affect diffusion and aggregation during pentacene growth

Selection of azimuthal angles: Role of molecular species

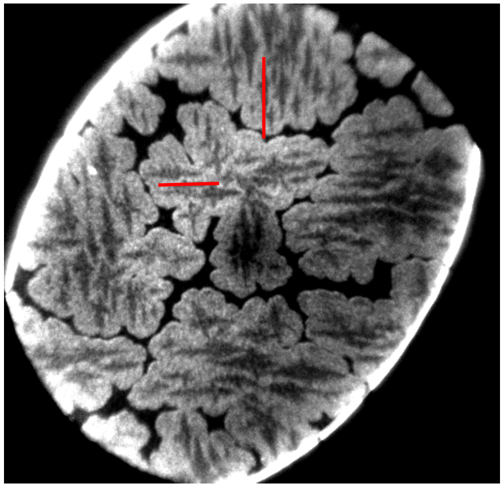


Cyclooctadiene

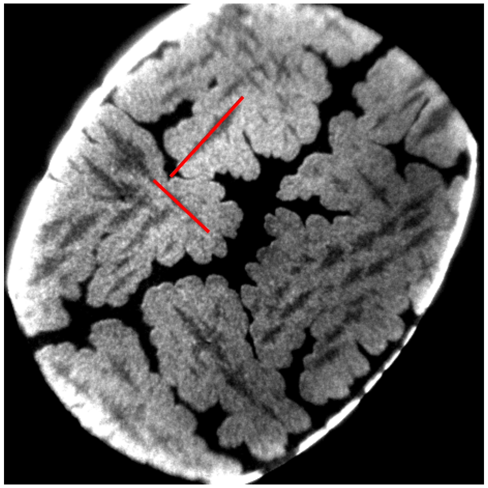


Hexene

Crystals at 45 degrees increments



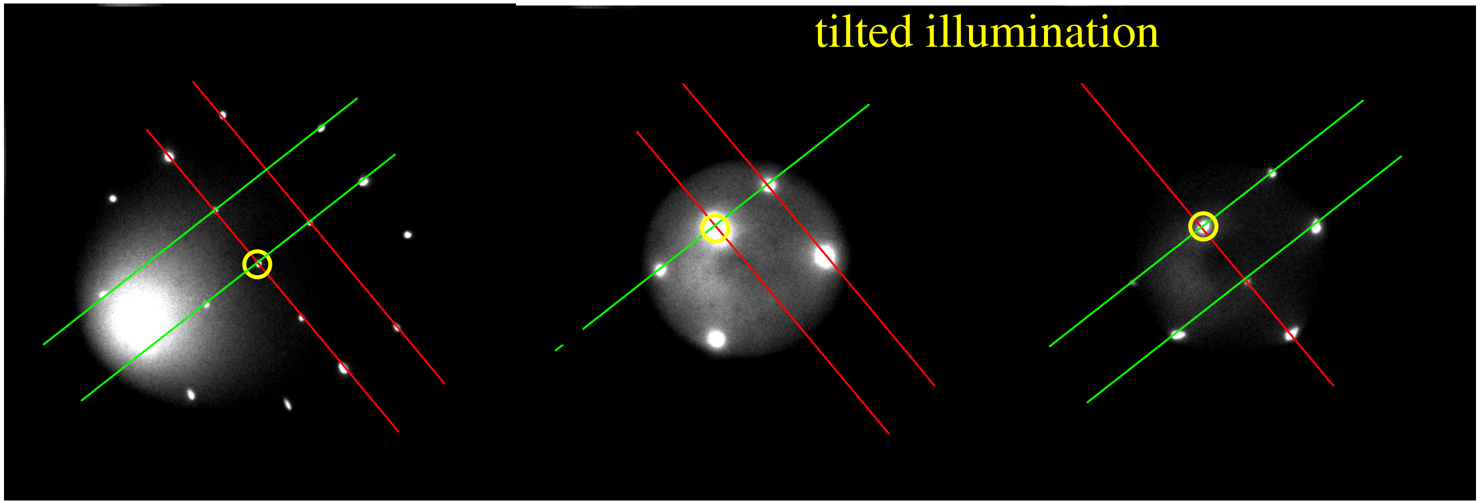
Dodecene on axis



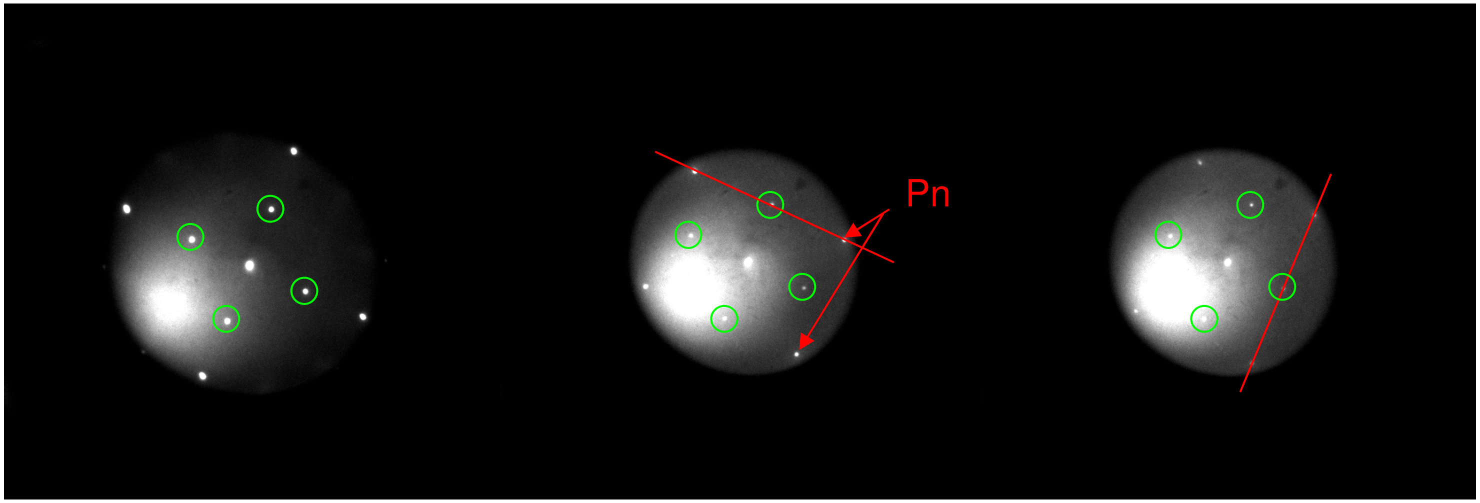
Dodecene off axis

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 nm
b = 0.777 nm
$\gamma = 84.7^{o}$

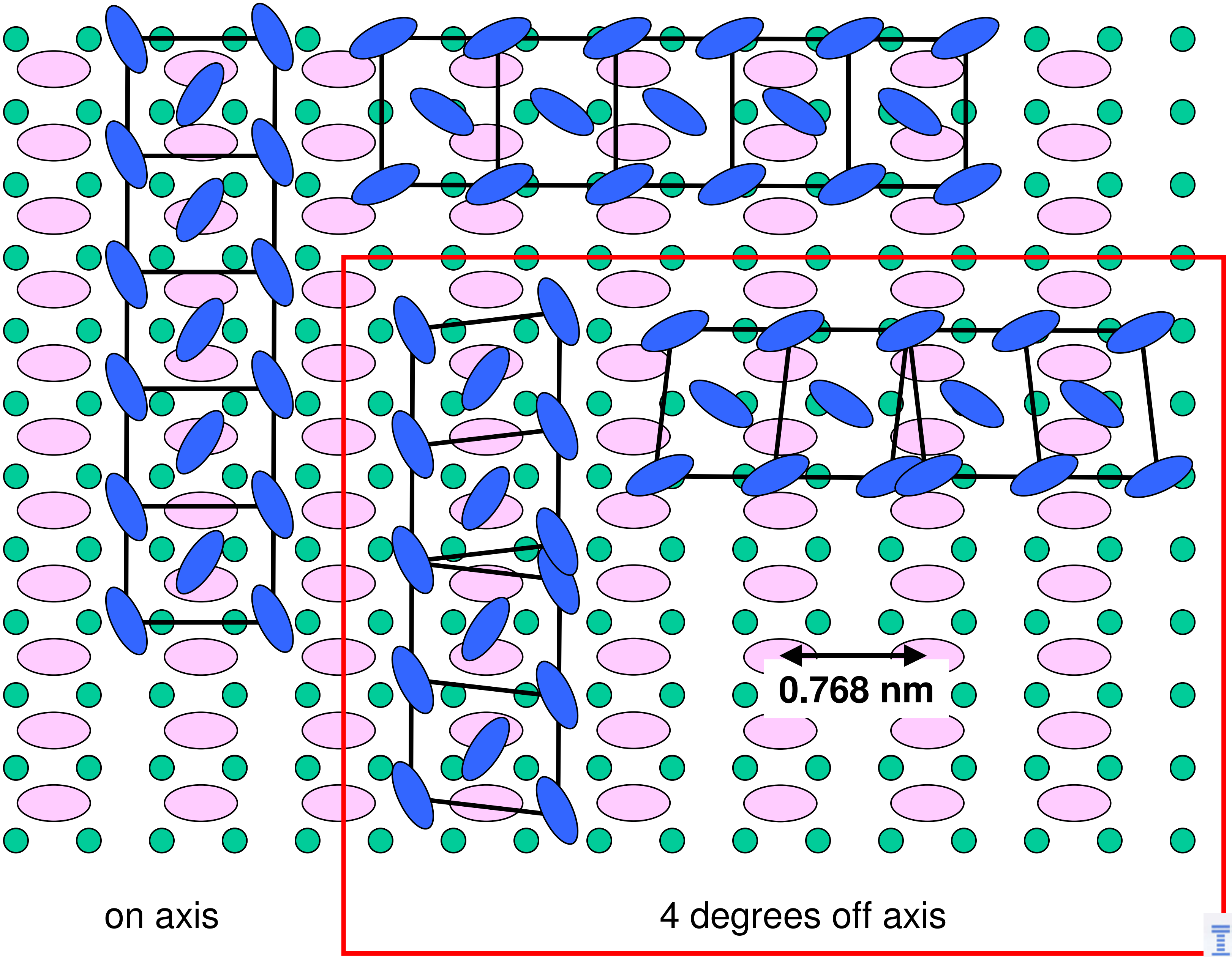
Si(001):
dimer-dimer: 0.384
row-row: 0.768

Mismatch ~ 1%

LEED 6/11 COD Si(001) on axis

Epitaxial growth, rectangular unit cell

PENTACENE /Si(001) EPITAXY



Pentacene MD on IBM BlueGene

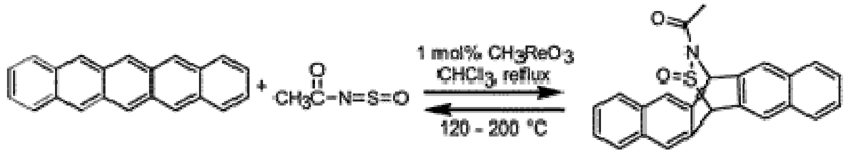
classical diffusion

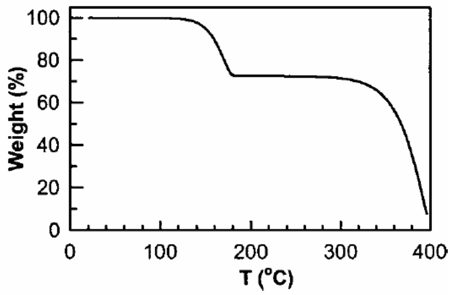
non - classical diffusion

pentacene diffusion on dodecene

Soluble pentacene precursors

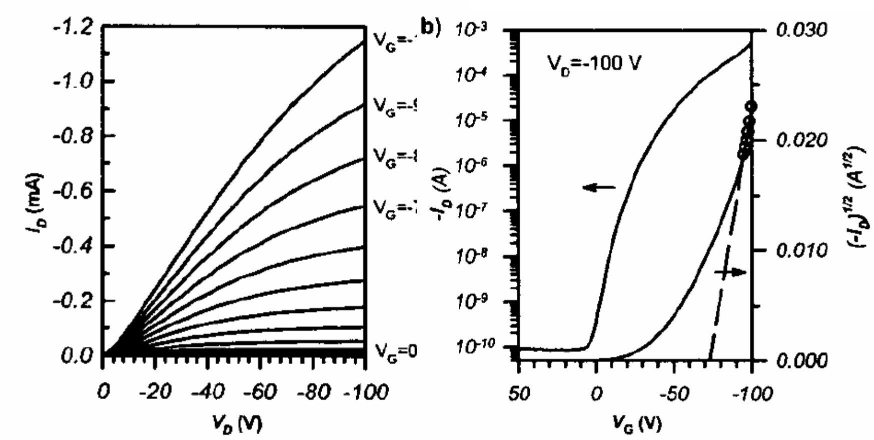
Soluble pentacene for spincoated TFTs



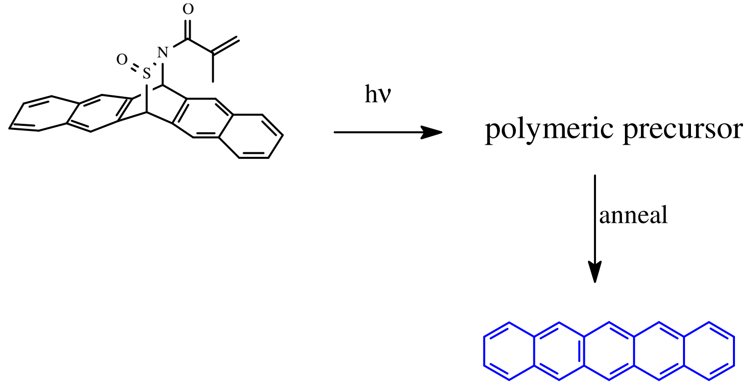


μ_{lin} = 0.4
μ_{sat} = 0.8
on/off > 10^6

Highest performance from solution processed organic TFT



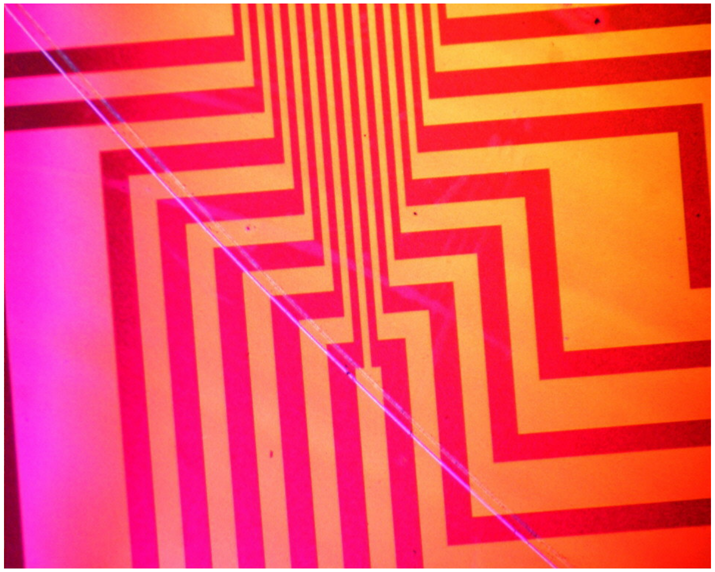
Photosensitive version for patterning



hν

polymeric precursor

anneal



Chalcogenides: a new look at some old materials

	E_g (eV)	μ_n (cm_2/V-sec)	μ_p (cm_2/V-sec)
SnS_2	2.6	18	
$SnSe_2$	1.6	27	
ZnSe	2.7	600	
ZnTe	2.25		100
CdS	2.42	250	
CdSe	1.73	650	

Semiconductor mobilities @ RT (cm^2/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

Organic-derivatized CdSe nanocrystals -- n-type 1.0 cm^2/V-s

[Ridley et. al., Science 286, 746 (1999)]

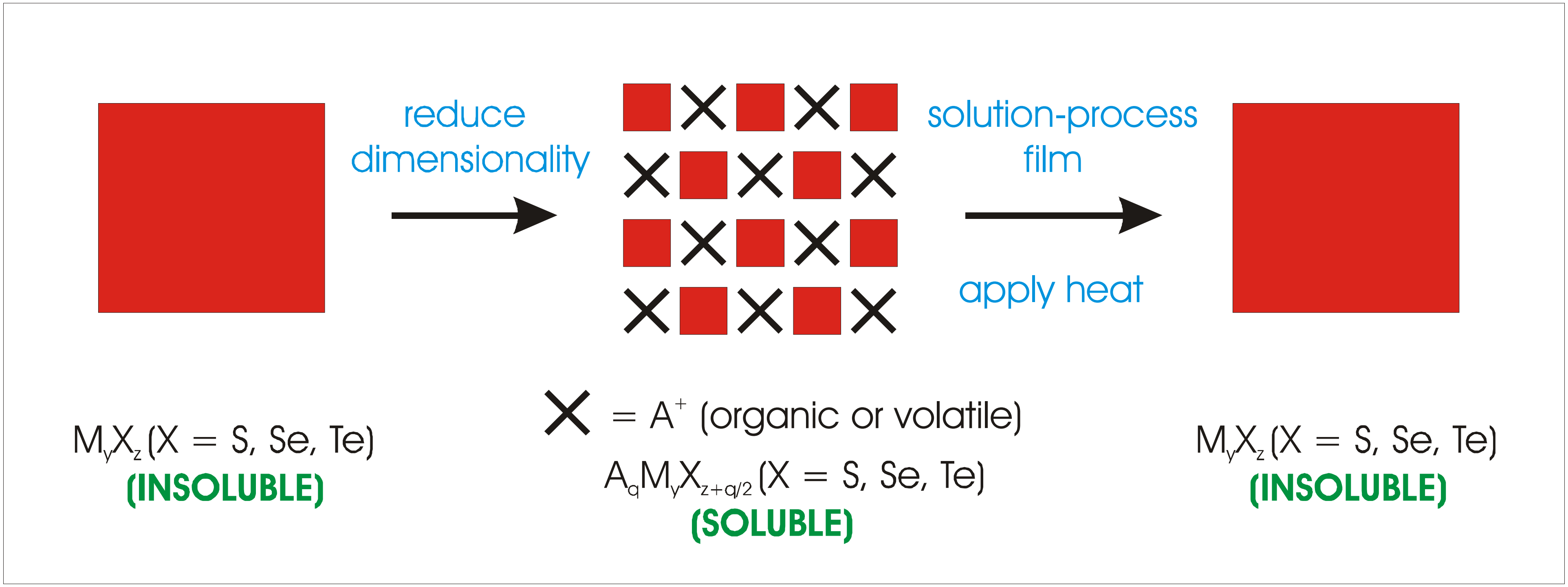
Chemical Bath Technique CdSe -- n-type 15 cm^2/V-s

[Gan et. al., IEEE Trans. Electr. Devices 49, 15 (2002)]

Assembled Nanorod / Nanoribbon -- n-, p-type <300 cm^2/V-s

[Duan et. al., Nature 425, 274 (2003)]

Solution Processable Chalcogenides



M_yX_z (X = S, Se, Te)

(INSOLUBLE)

reduce dimensionality

✕ = A^+ (organic or volatile)

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

(SOLUBLE)

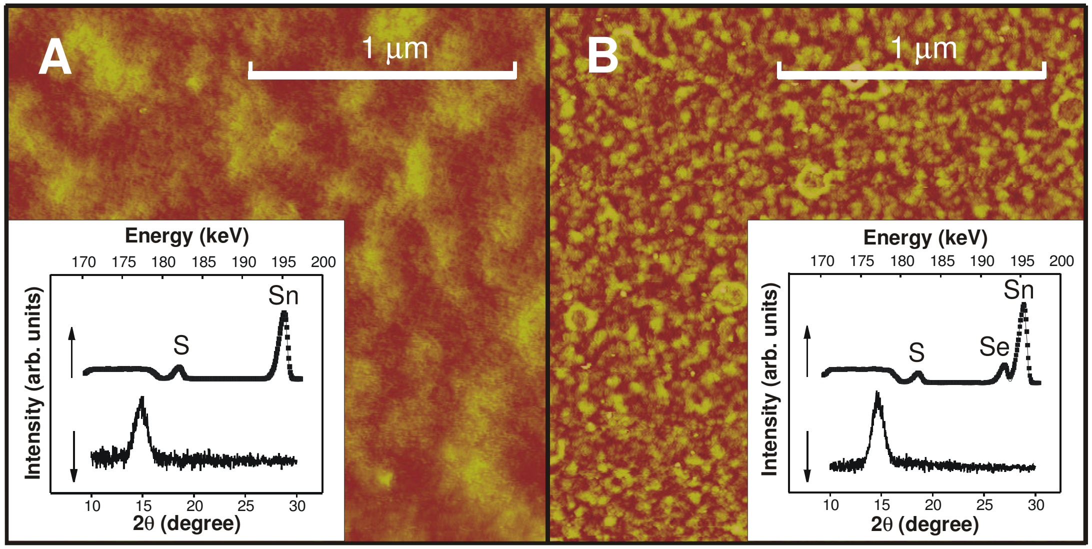
solution-process film

apply heat

M_yX_z (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 $SnS_{1.4}Se_{0.5}$

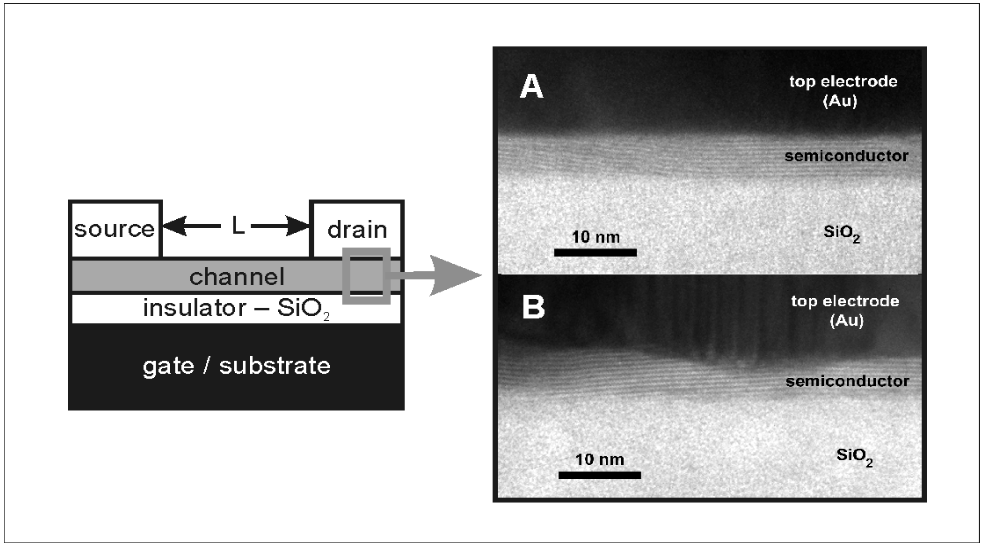
μ_{sat} = 12.0 cm^2/V-s

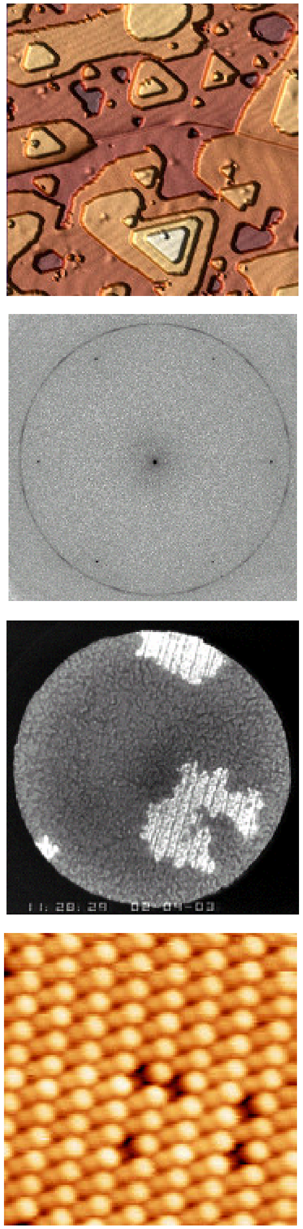
μ_{lin} = 2.4 cm^2/V-s

$I_{on}/I_{off} > 10^6$

L = 14 µm; W = 250 µm

Highest spin-coated channel mobility by ~ 10X

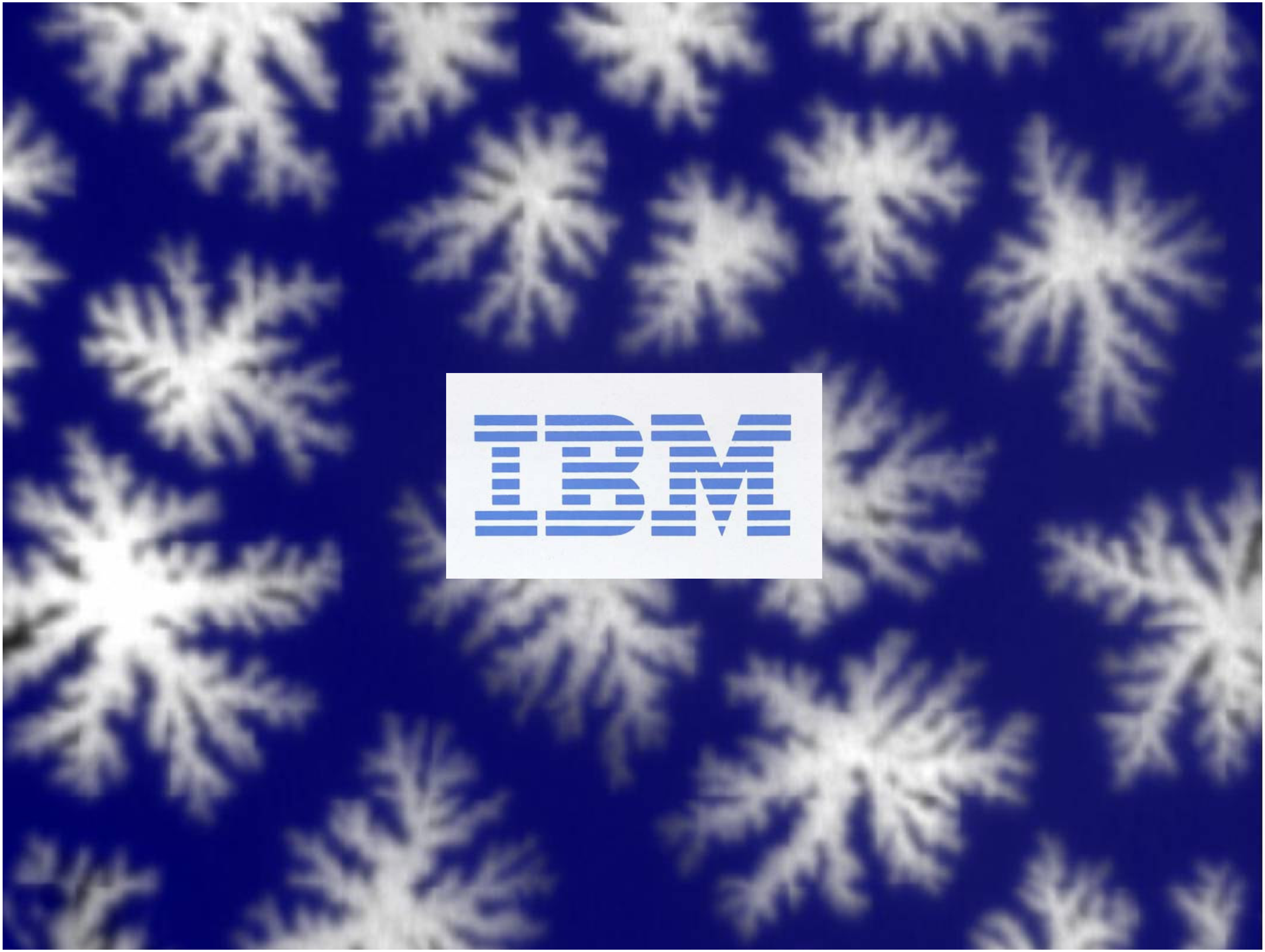




Nanoscience may give rise to future revolutionary technologies relevant to Information Technology: Nanotube or molecular logic; Novel, dense crosspoint memories; New high performance spin-coatable semi-conductors; etcetera.

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.



IBM