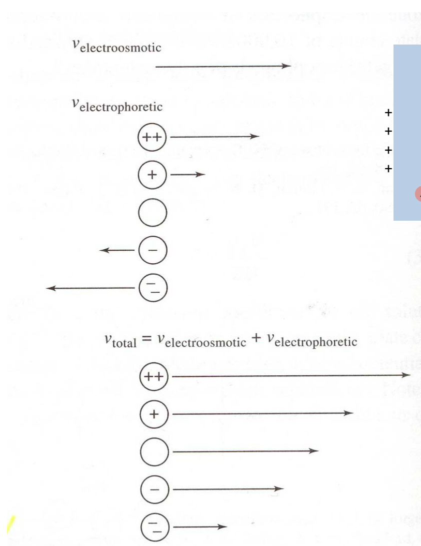
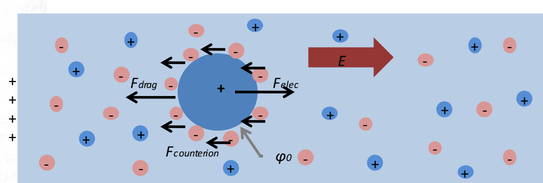
Surface Modification
Self Assembly

Sang-Gook Kim

Capillary Electrophoresis (CE)

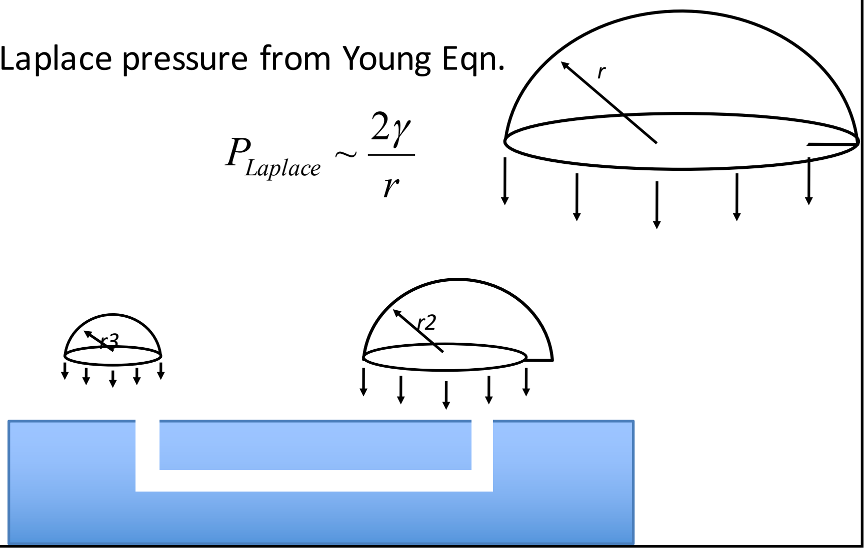




Surface Tension Flow

- Laplace pressure from Young Eqn.

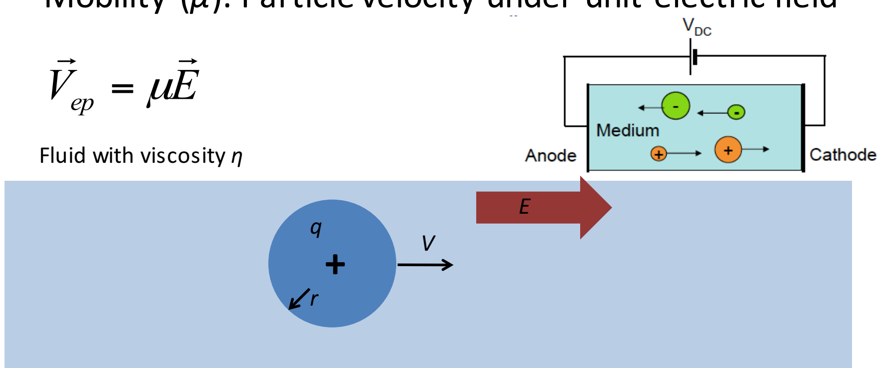
$$P_{Laplace} \sim \frac{2\gamma}{r}$$



Electrophoretic mobility

- Mobility (μ): Particle velocity under unit electric field

$$\vec{V}_{ep} = \mu\vec{E}$$



$$F_{drag} = 6\pi\eta rV$$

$$F_{electric} = qE$$

$$\vec{V}_{ep} = \frac{q\vec{E}}{6\pi\eta r}$$

$$\mu_{EF} = \left(\frac{q}{6\pi\eta r}\right)$$

(Hückel equation)

Dielectrophoresis

- A polarizable particle is attracted to a region of high electric field strength

Voldman, Annu. Rev. Biomed. Eng. (2006)

High Sped Sorting

https://www.youtube.com/watch?v=4zsSET80jpQ
Agresti, PNAS 2010

Dielectrophoresis

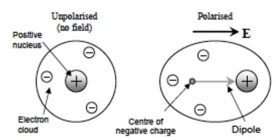
This image has been removed due to copyright restrictions. Please see http://nano.tu-dres den.de/pubs/reprints/covers/2012_Master_Gur.png?id=3679.

Voldman, Annu. Rev. Biomed. Eng. (2006)

- A polarizable particle is attracted to a region of high electric field strength
- Direction of force is independent of direction of electric field
- Useful for manipulating cells and microscale particles

Polarization

- Atomic polarization
- Ionic, molecular…
- Interfacial polarization



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http://www.nanotech.upenn.edu/nuggets/0032.html

Dielectrophoresis

If a suspended particle has polarizability higher than the medium, the DEP force will push the particle toward regions of higher electric field (positive DEP). If the medium has a higher polarizability than the suspended particle, the particle is driven toward regions of low field strength (negative DEP).

DEP Force

$$F = 2\pi r^3 \varepsilon_m \operatorname{Re}[K] \nabla E^2$$

- r – radius
- E – nonuniform electric field
- ε_m-permittivity of medium
- * - Complex permittivity
- Re[K] – Clasius-Mossotti Factor where

$$K = \frac{\varepsilon_p^* - \varepsilon_m^*}{\varepsilon_p^* + 2\varepsilon_m^*}$$

Clausius-Mossotti Factor

- At low frequencies: $$K \approx \frac{\sigma_p - \sigma_m}{\sigma_p + 2\sigma_m}$$
- At high frequencies: $$K \approx \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_p + 2\varepsilon_m}$$
- Polarization Factor (K) can be switched between positive or negative values

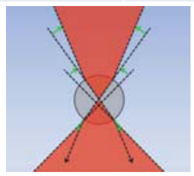
Single Cell Cage

Voldman, MIT

Comparison

Electrophoresis	Dielectrophoresis
Motion of a particle is determined by the net electrical charge of the particle	Determined by the polarity and magnitude of induced charges
DC field, homogeneous	AC field, inhomogeneous

Optical Tweezer
Grier, Nature, 2003



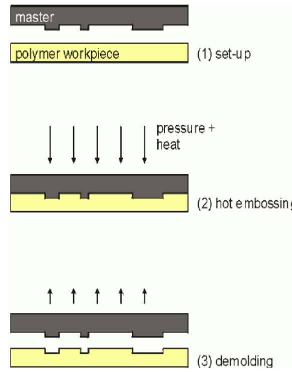
Nagle, MIt

Microcontact printing (μCP)

- Pattern Transfer
- Lithography

$W = k\,\lambda / NA$ (Rayleigh Eqn.)
deep-UV (248-nm) KrF Excimer laser, 193 nm ArF laser, 157nm

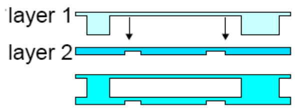
PDMS embossing process

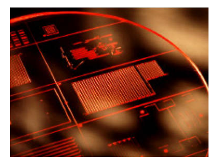


- Master fabrication (MEMS)
- Mold by PDMS casting
- Bond onto a substrate
- Multi-layered PDMS

This image has been removed due to copyright restrictions. Please see http://bdml.stanford.edu/twiki/pub/Rise/PDMSProceSS/pdms01.png.

Prof. Dr. Roland Zengerle / Claudio Cupelli





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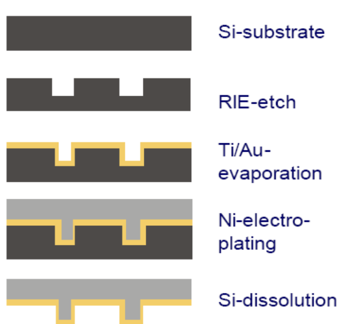
Micro-Injection



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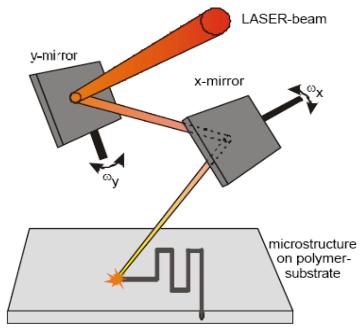
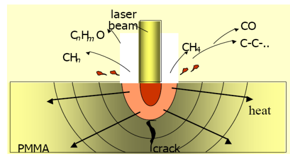
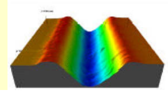
© Telleman / Geschke 2004

Laser Ablation





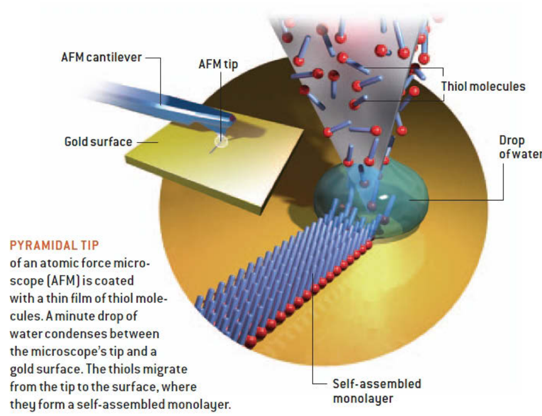


Oliver Gescheke, DTU, 2004

17

Dip-pen nanolithography (DPN)

Mirkin, Northwestern



Whitesides and Love, Scientific American, Sept. 2007

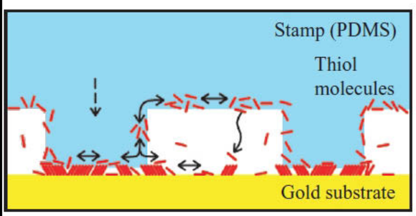
Microcontact printing (μCP)

- Conformal stamp is "inked"
- Stamp is placed in contact with surface(non-planar)
- Molecules transfer to surface where stamp makes contact

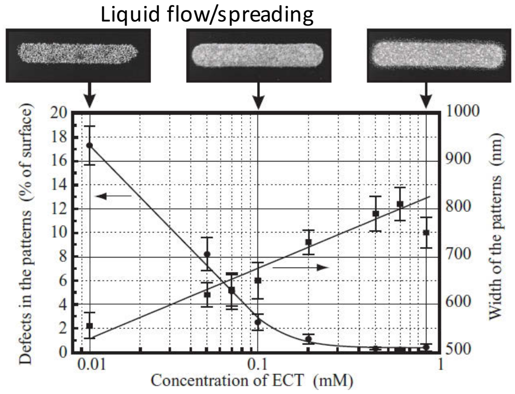
This image has been removed due to copyright restrictions. Please see Figure 1 in http://www.aspe.net/publications/Short%20Abstracts%2013A /3751.pdf.

Michel et al., IBM J. Res. & Dev., 45, 697 (2001)

Transport of molecules in μCP



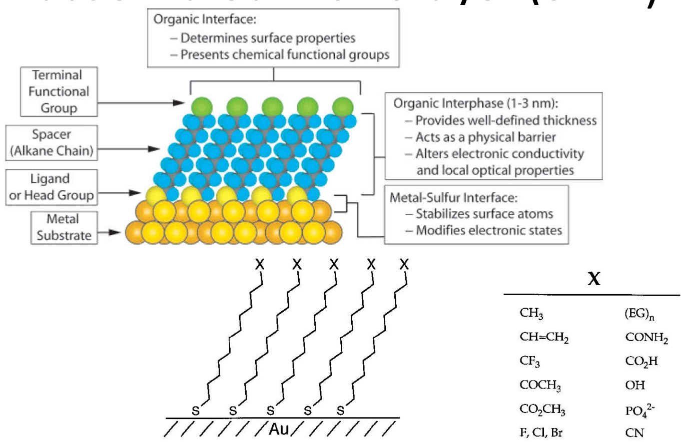
Paths of transport of molecules in μCP
Diffusion within PDMS
Diffusion on surfaces
Evaporation-condensation
Liquid flow/spreading



Effect of thiol concentration examined by SEM
(ECT- eicosanethiol, 20 carbons)
Increasing concentration decreases defects, but increases pattern width

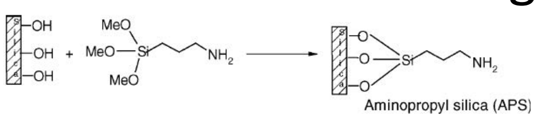
Michel et al., IBM J. Res. & Dev., 45, 697 (2001)

Alkanethiolated self-assembled monolayer (SAM)

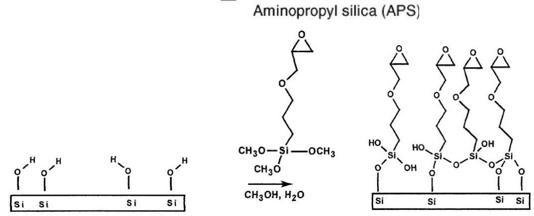


Love et al, Chem. Rev. 105, 1103 (2005) Mrksich et al, Expt. Cell Res. 235, 305 (1997)

Silanization of glass



Amino Silane



Possible end groups:
NH_2, SH, OEG/PEG, epoxy, CF_3, $CH=CH_2$, COOH, CHO, …

- More variety than alkanethiols
- Less robust
- Less easily ordered

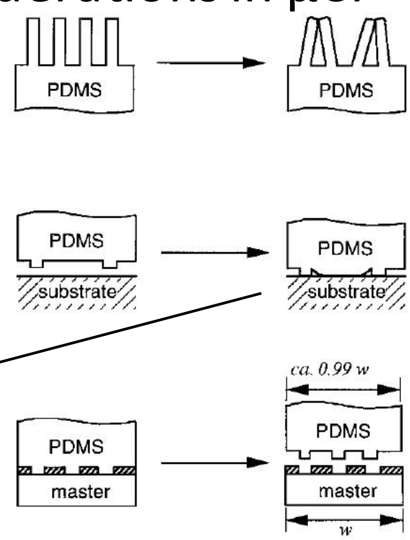
Jal et al., Talanta 62, 1005 (2004), Macanovic et al, Nucleic Acids Res. 32 (2004)

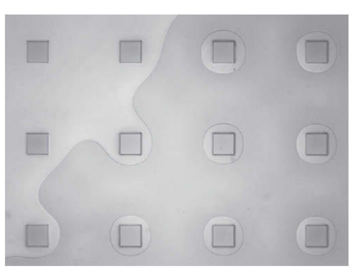
Modification of surfaces

- Alkane-thiols or silanes enable functionalization of gold and glass with different end groups
- A variety of reagents are available to join these end groups with
  - Groups present on other surfaces
  - Groups (NH_2, COOH, SH) present on biomolecules
  - Other molecules (dyes, biotin, etc.)

Mechanical considerations in μCP

- Conformal contact requires stamp flexibility
- Large aspect ratio stamps can collapse or distort
- Large gaps can collapse.
- Smudging during placing and lifting off stamp

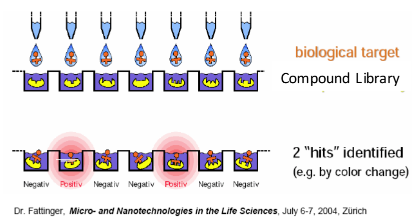


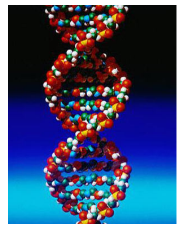


Xia and Whitesides, Ang. Chem. Int. Ed., 37, 550 (1998)
Michel et al., IBM J. Res. & Dev., 45, 697 (2001)

Drug Screening

- “Key” and “Lock”
- Chemical compounds to biological targets
- High Throughputs Screening, 100K/day





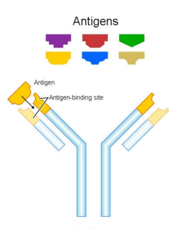
DNA strand hybridization

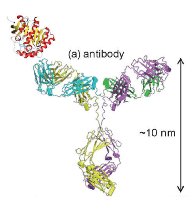
faculty.washington.edu/stenkamp http://en.wikipedia.org/wiki/Antibody pbs.org, Lee et al., Lab Chip 9, 2267 (2009).

25

Bio molecular recognition

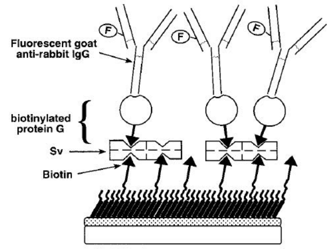
- Biomolecules can “recognize” other molecules and specifically bind to them
  - Enzymes and their substrates
  - Antibodies and antigens
  - Avidins and biotin

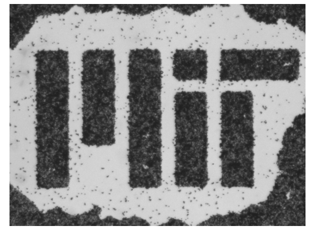


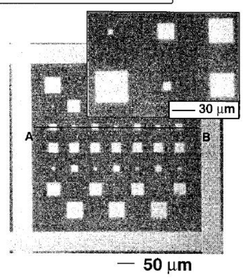


Antibody-antigen interaction

Patterning of antibodies using streptavidin-biotin interactions







Nanowire sensors: Surface modification

Patolsky et al, Nat. Protocols, 4, 1711 (2006)

DNA microarrays

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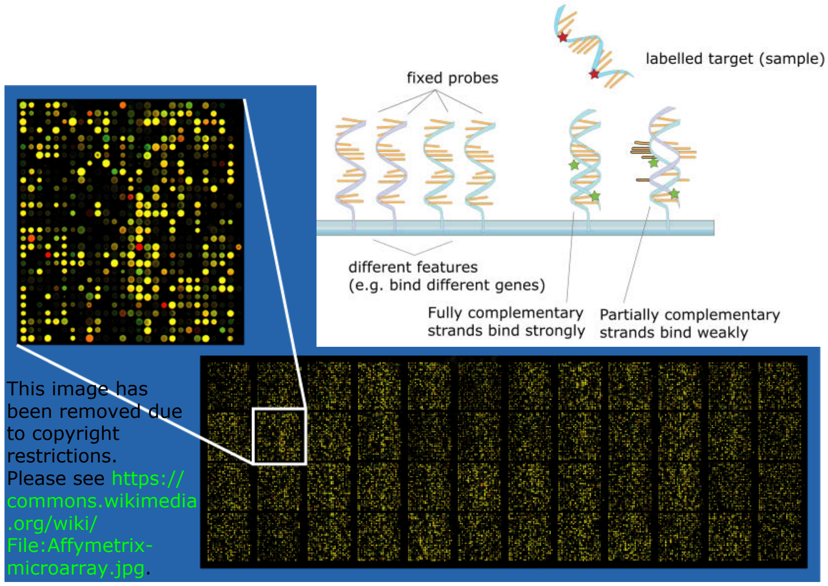

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en.wikipedia.org/wiki/DNA_microarray

Self-Assembly

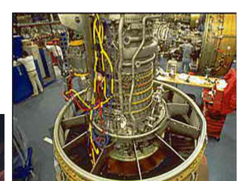
as·sem·bly

n. pl. **as·sem·blies**

a..

b.The putting together of manufactured parts to make a completed product, such as a machine or electronic circuit.

Source: The American Heritage® Dictionary of the English Language, Fourth Edition



~$2 trillion

Complexity of microchip assembly

- Old assembly technology for microstructures

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- **Tyranny of numbers**

Monolithic Design

J. Kirby of TI (1958)
R. Noyce, Intel (1959)

- Design for assembly at small scales?
- Design tools for small scale products?
- How to achieve commercial success of MEMS products?

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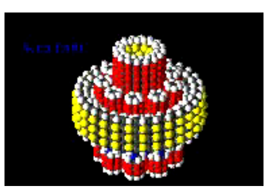
S.G. Kim, CIRP 2006, STCA

Assembly of Molecular Machines ?

32

On Dec. 9, 2003 *The New York Times* carried a story on the debate: "Yes, They Can! No, They Can't: Charges Fly in Nanobot Debate". A week later, the *Times* published the following (edited) letter from Dr. Drexler.



E. Drexler, Proc. Natl. Acad. Sci. USA
Vol. 78, No. 9, pp. 5275-5278, September 1981

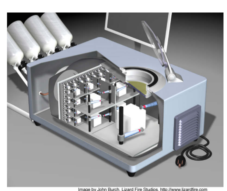


Image by John Burch, Lizard Fire Studios, http://www.lizardfire.com

Proposed desktop-scale molecular manufacturing appliance. Tiny machines join molecules, then larger and larger parts, in a convergent assembly process that makes products such as computers with a billion processors. (Parts shown as white cubes.)

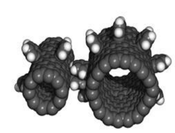
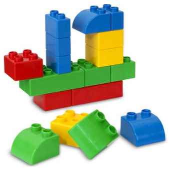


Image courtesy NASA Advanced Supercomputing Division

Gulliver, 6ft tall, 160 lb weight
Lilliputian, 6 in tall, 1.5 ounce.



Size of lego?

9.6 mm by 8 mm
800 μm by 660 μm

Self-assembly?
Gulliver in Broadingnag?
Assemby by Bacteria?

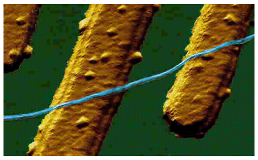
33

Carbon Nanotube

34

- Discovered during the study of arc-discharge products. *Nature*, 354, 56 (1991)
- Rolled graphene sheets of carbon atoms, coaxially arranged in a cylindrical shape.
  - SWNT, single-walled nanotube (1 < d < 3 nm.)
  - MWNT, multi-walled nanotube

How to assemble?



Dekker group, Nature, **393**, 49 (1998)

Complexity

A system is complex when;

- A design is coupled.
- Coupling propagates through combinatorial manner
- The scale order is very high. (over 10^9)
- System ranges vary with time. The outcome is uncertain. (low probability of success)

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Micro/Nano Assembly

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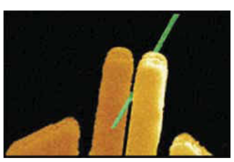
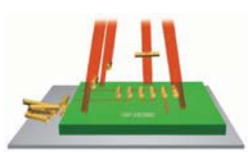
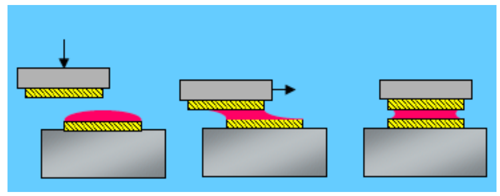
- Parallel assembly
  - *Deterministic*: pre-determined destination for parts
  - *Stochastic*: random process determines part destinations
- Serial assembly
  - "Pick and place"





Pattern matching



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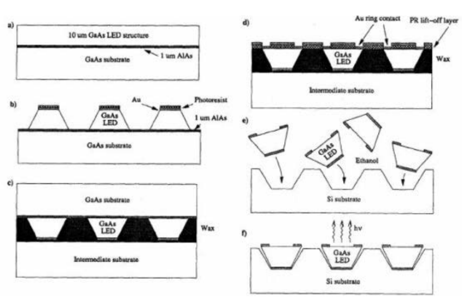
Fluidic Self Assembly



Fluidic self-assembly of GaAs LEDs on a templated Si substrate.

Fluidic self assembly

Alien Technology

38

Fluidic Self-Assembly

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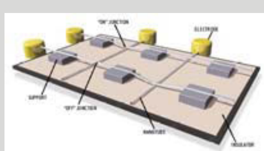
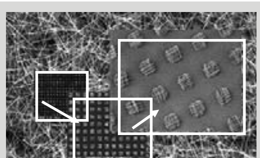
Self Assembly: Physical, Chemical, Biological pattern matching



Lieber Group



Langmuir-Blodgett approach (raft)

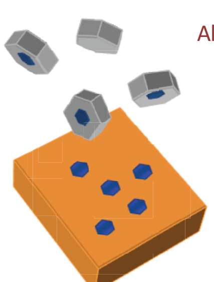
G. Whiteside Group, 3D Self-assembly

Alignment by Fields

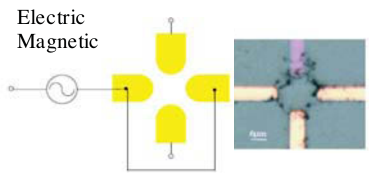
Capillary
Shear
Electric
Magnetic

SEM Photograph of 185 Micron NanoBlocks

S. Smith and Alien Co.



Howe group



R.H.M. Chan et al, Nanotechnology 15, 672-677, 2004

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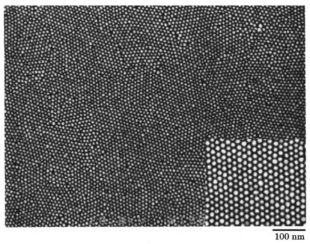
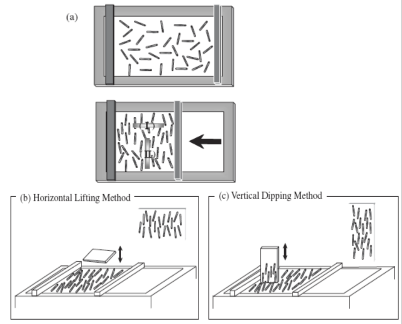
LB Assembly



SEM image of a LB monolayer of dodecanethiol-encapsulated gold particles 8.3 nm in diameter. The inset shows a high-magnification SEM image. Reprinted with permission from Ref. 24 S. Huang et al., J. Vac. Sci. Technol. B **19**, 2045, 2001,



Schematic illustration of the mechanism for the in-plane orientation of s-SWNT: (a) compression-induced orientation in the Langmuir film by barrier compression; (b) in-plane tube orientation for films prepared by horizontal lifting; (c) flow orientation of tubes induced by the vertical motion of the substrate. Reprinted permission from Ref. 25 Y. Kim, N. Minami, W. Zhu, S. Kazaoui, R. Azumi and M. Matsumoto, Jpn. J. Appl. Phys. **42**, 7629, 2003,

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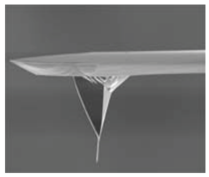
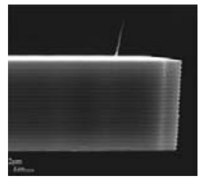
Directed Nano Assembly

Case: CNT tipped AFM cantilever

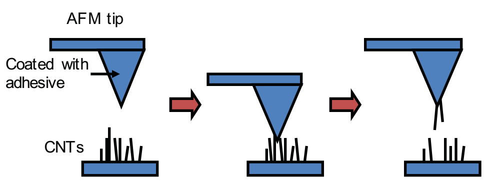


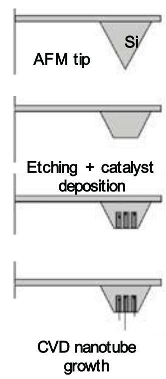
By Picking



By Growing

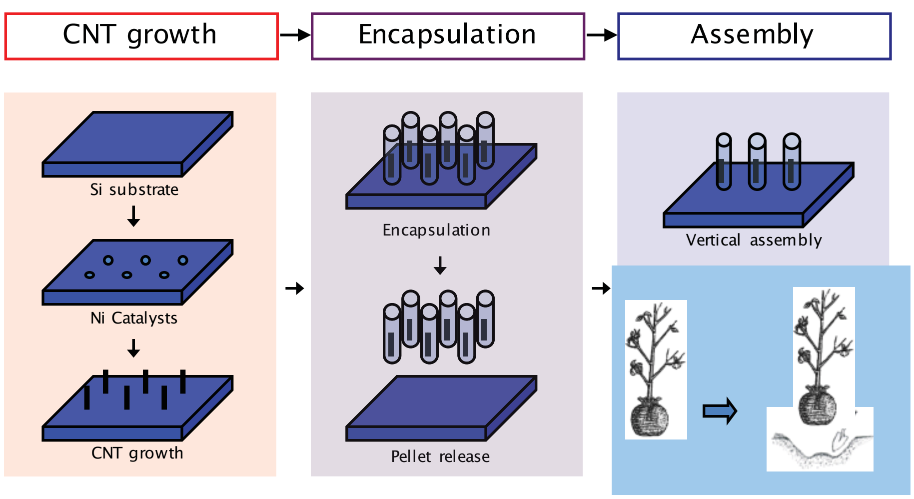
Direct attachment





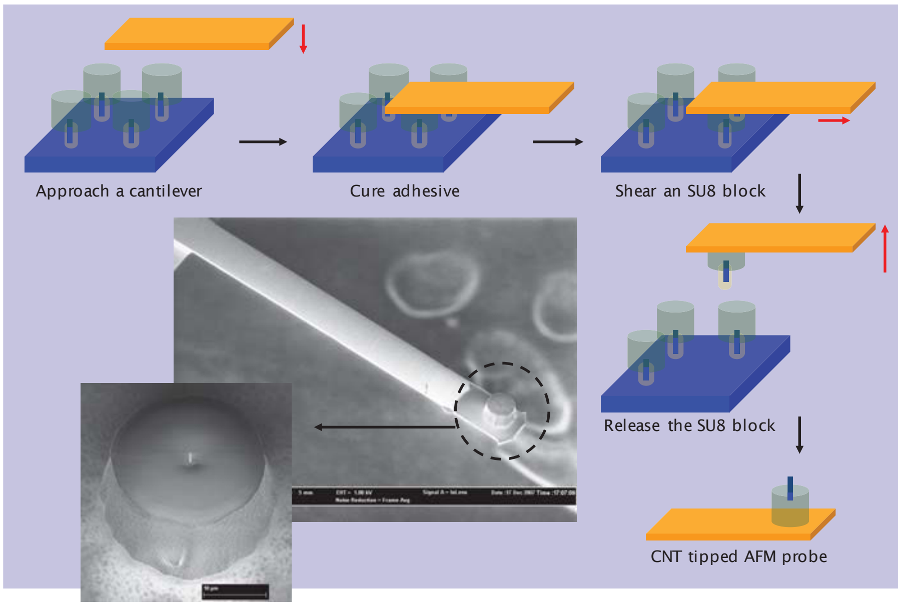
(H. Dai et al, Nature 384, 1996)

Q. Ye et al, Nano Lett, Vol. 4, No. 7, 2004



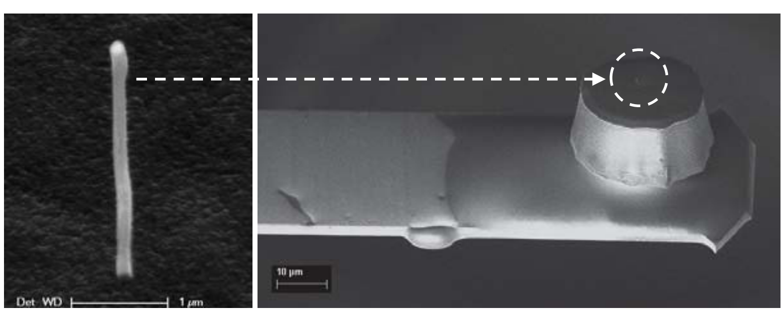
- Decoupling of CNT growth and assembly
- Periodicity – Reduction of Scale Order

* US patent 7507987, Kim et al.



Nanoassembly by manual work…

First demonstration of a deterministic assembly of individual nanostructures (carbon nanotubes)

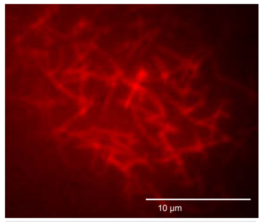


A single strand CNT A CNT-tipped AFM probe

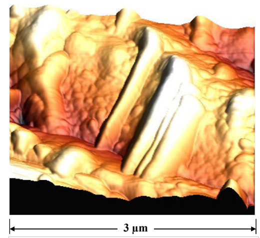
* Kim et al., APL, 2009

AFM Scanning Results : F-actin

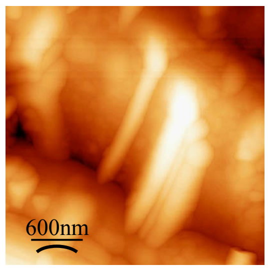
Filament actin (64µl/2..3µM)
In 50ml buffer solution



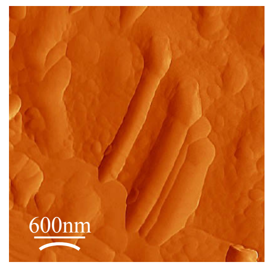
Fluorescent Imaging



3D (height mode)

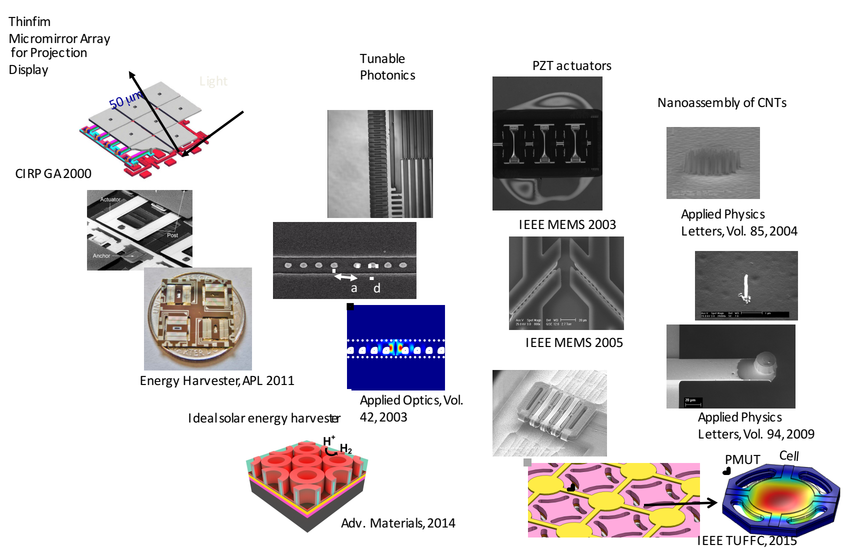


Height mode



Deflection mode

Good design is important at small scales. –Kim Lab



Summary

- Surfaces become more important at smaller length scales
- Surfaces with specific functionalities are desirable in many micro/nano applications
- Integration of 1) patterning techniques, 2) chemistry, and 3) biomolecular interactions provides us with versatile tools to engineer surfaces with specific properties
- We will explore these aspects in lab #6

2.674 / 2.675 Micro/Nano Engineering Laboratory
Spring 2016