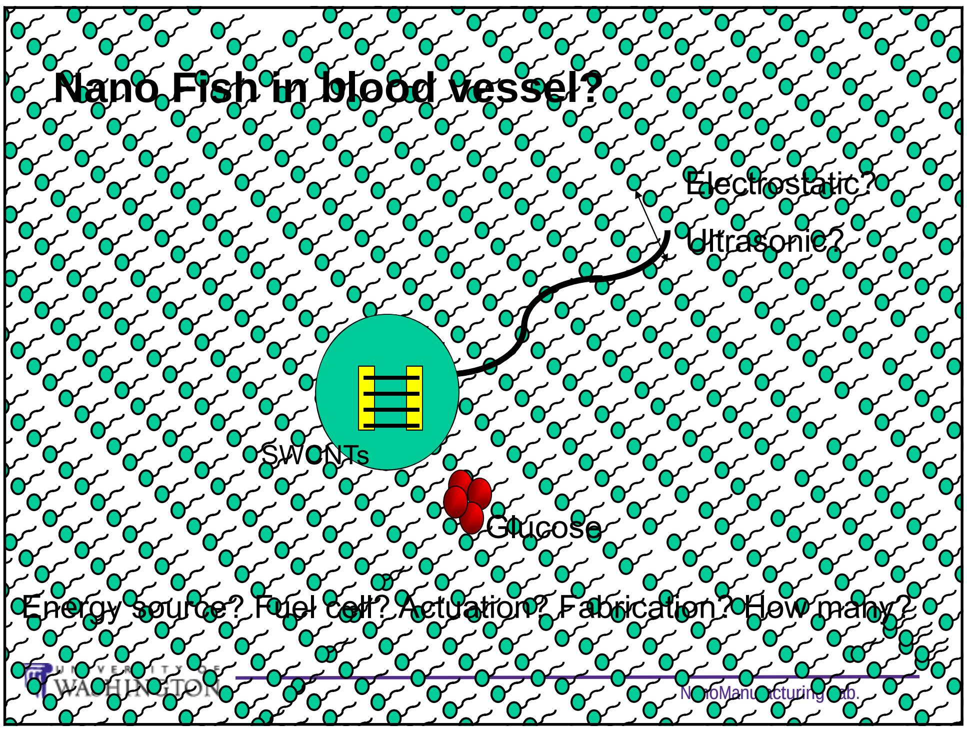
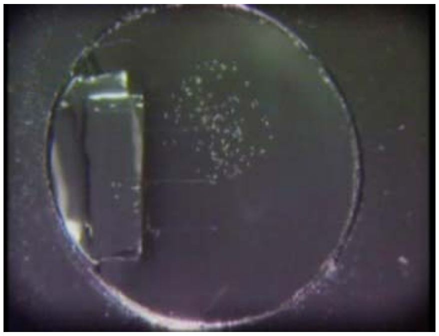
Fundamentals of nanoscale patterning and manipulation

NanoScience and Molecular Engineering
Feb 1, 2010

Chung, Jae-Hyun, Mechanical Engineering, University of Washington



Introduction of Chung's research



Biomimetic cilia mixer
Mixing and reaction enhancement

Tip enrichment system
Molecular enrichment, transport, and detection

Contents

MEMS/Nanotechnology

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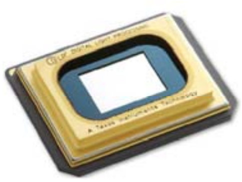
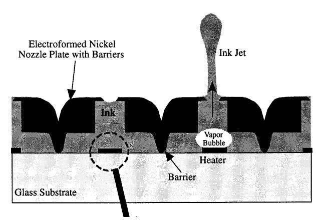
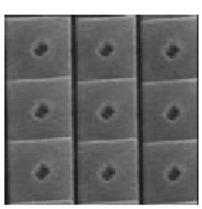
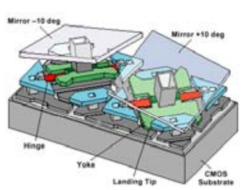
MEMS product









TI mirror array

Ink jet printers

G.T.A. Kovacs, Micromachined Transducers Sourcebook (1998)

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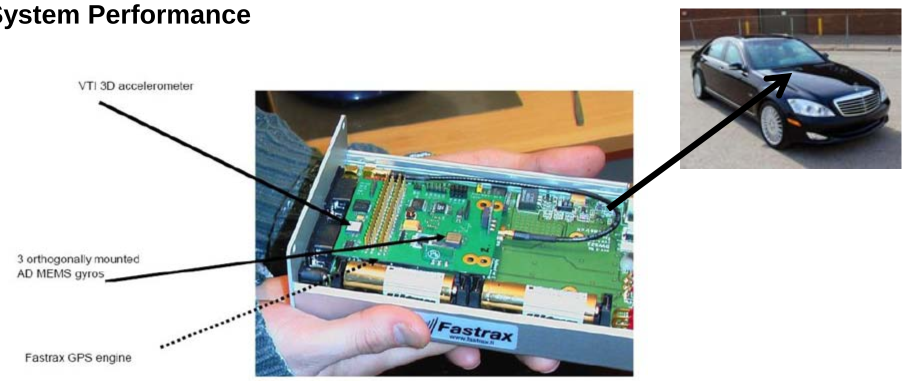
MEMS product (cont'd)

MEMS Accelerometer and Gyroscope to Improve Car GPS Navigation System Performance

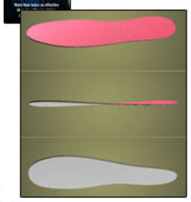


http://datasheetoo.com/datasheet-application/automotive/mems-accelerometer-and-gyroscope-to-improve-car-gps-navigation-system-performance.html

Nanotech product

Footwarmers (Shock Doctor/Aerogel Hotbeds)

Northborough, Mass.-based Aspen Aerogels launched a nanotechnology-based footwarmer in March of 2004, which is now used by the 2004 winner of the North Pole Marathon, the Canadian Ski Team and the U.S. Military's Elite Special Forces. Aspen's Pyrogel AR5401 utilizes highly-insulative nanoporous-aerogel technology, providing 3-to-20 times more thermal performance at a given thickness when compared to existing materials. Plymouth, Minn.-based Shock Doctor has developed a product called Hotbeds, which is being used in military boots for improving the level of comfort in cold weather operations. Since the Pyrogel AR5401 is so efficient, the Hotbeds are only 2.5mm thick.



BASF Superhydrophobic Spray

BASF is now wielding its nanotech muscle in the building-material industry, especially in concrete, brick facings, limestone and plasters. In the near future, your home may be coated with Mincor, an additive that helps to improve the hydrophobic effect of building materials. Its extreme water repellence minimizes contact and adhesion among water drops and surfaces, which means rain water pearls up immediately. The nanoparticles in Mincor reduce the adhesion of water and particulate soiling to a minimum. Dirt particles are simply rinsed away by rain water. BASF is currently looking for distributors.

http://www.forbes.com/investmentnewsletters/2005/01/12/cz_jw_0112soapbox.html

Top Ten Nanotech Products, Josh Wolfe, Forbes/Wolfe Nanotech Report,

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NanoManufacturing Lab.

Nanotech product (cont'd)

Golf Balls And The "Nano" Driver

Tokyo-based Maruman & Co. has adopted fullerenes from Honjo Chemical for use in the top of the line "New Majesty" driver, which went on sale on July 5 of 2004. Compared to conventional titanium, the new driver resists bending 12% better, has a hardness 3.6% better than titanium, a 20% more resilient head and an increased flight distance of 15 yards as compared to their old 360cc class driver.

Buffalo, N.Y.-based NanoDynamics might have a nice accompanying stocking stuffer. NanoDynamics came up with a golf ball that can correct its own flight path. The design of the ball--and the undisclosed nanomaterials it's made of--serve to better channel the energy received from the club head, and thus correct a wobble or slight drift. The ball is expected to hit stores in the spring of 2005.

3M Dental Adhesive

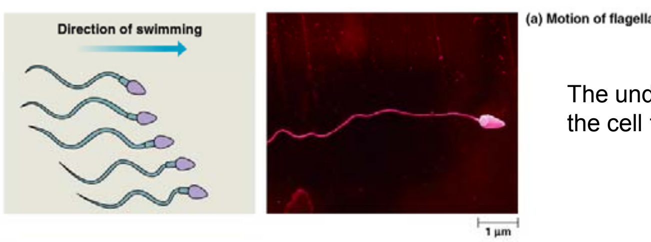
Having a porcelain veneer, tooth restoration or root canal work soon? Your dentist just may put nanoparticles in your mouth to help your new crown stick better. As we featured in our September story, "3M: Practicing Nanotechnology Without the Hype," 3M ESPE, a 3M subsidiary in dental adhesives, announced a new option in total-etch dental adhesives: Adper Single-Bond Plus Adhesive. The new adhesive incorporates a silica nanofiller technology that forms a stronger bond to tooth enamel and does not need to be shaken by dentists prior to using in order to prevent particle clustering, which can decrease performance.

http://www.forbes.com/investmentnewsletters/2005/01/12/cz_jw_0112soapbox.html

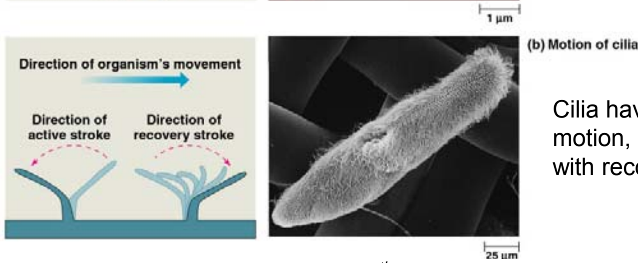
Top Ten Nanotech Products, Josh Wolfe, Forbes/Wolfe Nanotech Report,

Nanodevice?

•Transistors, memory chips, etc.



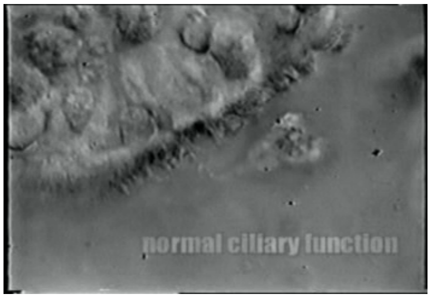
The undulating motion enables the cell to swim.



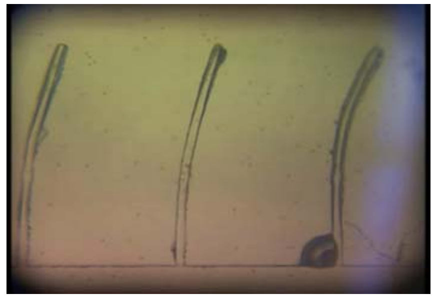
Cilia have a back-and-forth motion, alternating active strokes with recovery strokes.

Biology 5th edition, 1999, Neil A. Campbell et. al, p121

Nanodevice? (cont'd)



Biological cilia



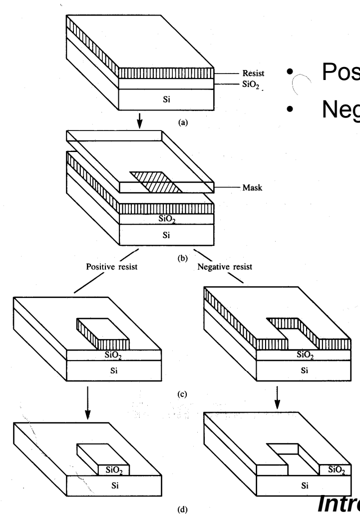
Biomimetic cilia

1) http://pcdprese.tripod.com/index.html

2) PDMS cilia (from NSF supported project)

Fundamentals for micromachining

MEMS: 1. Lithography



- Positive photoresist
- Negative photoresist

- Mask aligner : MA6

Introduction to Microelectronic Fabrication

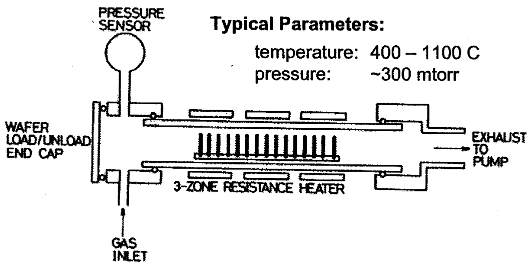
(by Richard Jaeger)

2. Thermal oxidation

- Oxide layer growing process
- Si (solid) + O_2 (vapor) --> SiO_2 (solid)
- Operating temperature 800~1100ºC

3. Chemical Vapor Deposition (CVD)

- SiN, Oxide, poly Si, etc
- Lower temp. than thermal oxide
- Structural layer



4. Metal deposition

- Electrical connection
- Mask layer
- Sacrificial layer
- Structural layer

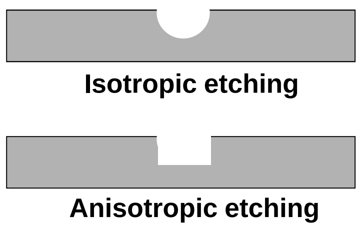
- High vacuum operation (10^{-6}~10^{-7} torr)
- Cryo-pump or turbo pump

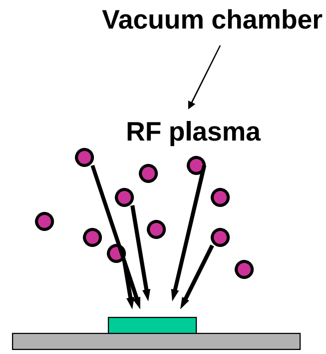
Electron beam evaporator
Washington technology center

5. Etching

- **Wet etching**

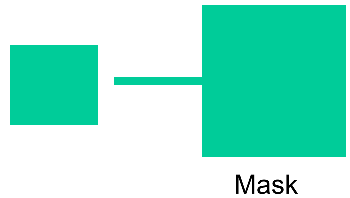
  Anisotropic etching and Isotropic etching
- **Gas phase etching**
  - **Reactive ion etching**
  - **Deep RIE**
  - **No surface tension**

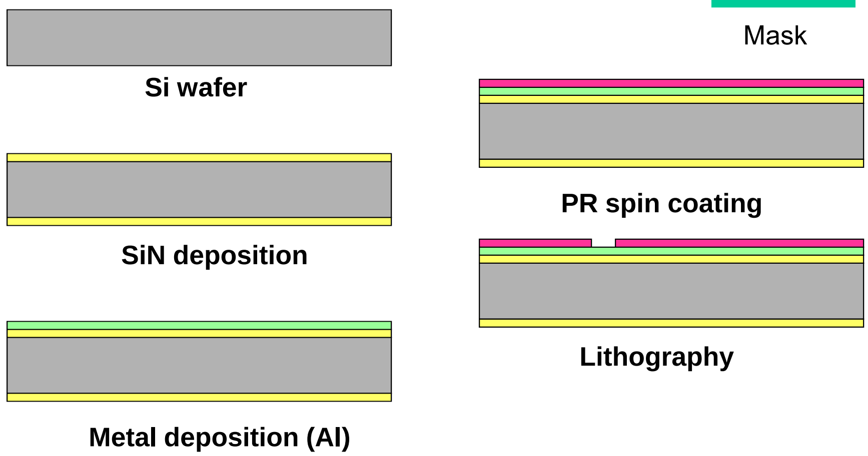




Beam fabrication
Top-down vs. Bottom-up

Top-down Approach





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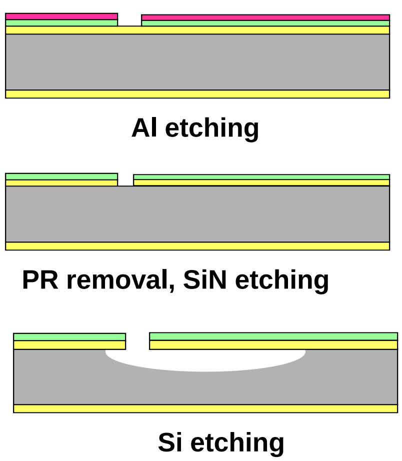
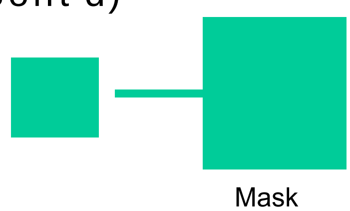
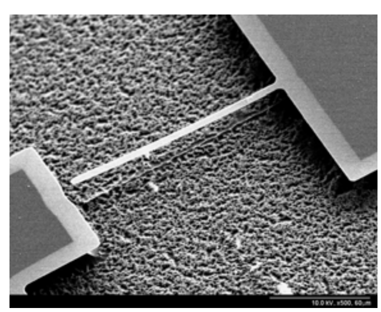
Top-down Approach (cont'd)







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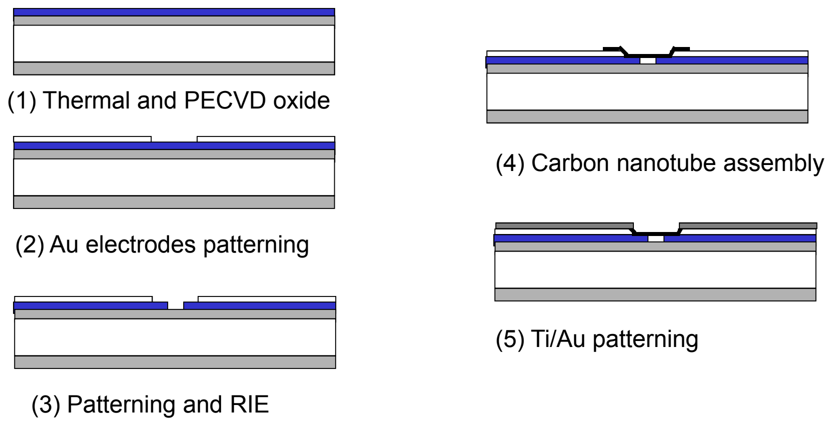
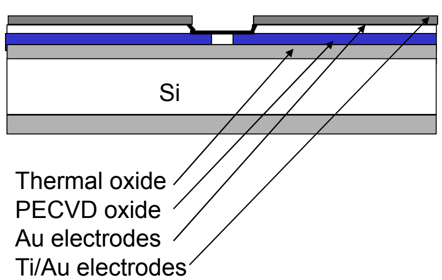
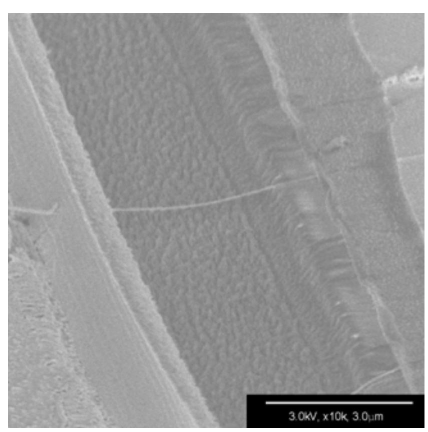
Bottom-up Approach



Bottom-up Approach





MWCNTs assembled across a trench

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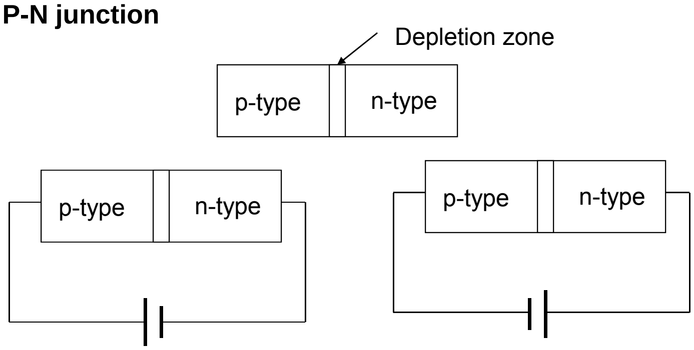
Nanodevice; Inverter
Top-down vs. Bottom-up

Inverter: Fundamentals

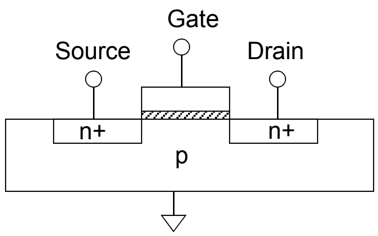
- **P-N junction**



1) Repel holes and electrons	1) Pull holes and electrons
2) Decrease depletion zone	2) Increase depletion zone
3) Electric current Flow	***3) No current***

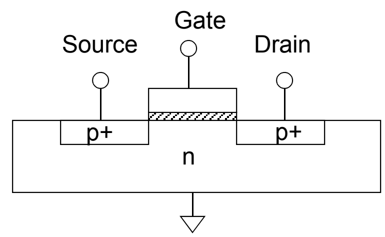
Inverter: Fundamentals

- **nMOS transistor**

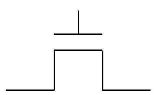


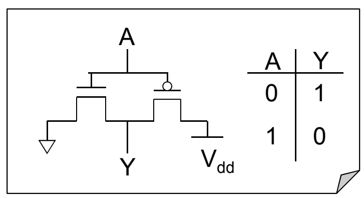
Gate-low : no current – transistor off
Gate-high: current - transistor on

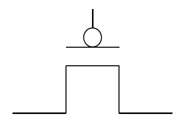
- **pMOS transistor**



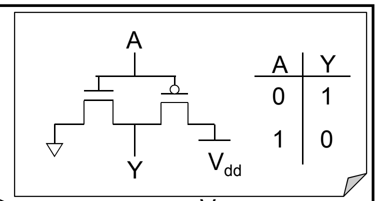
Gate-high : no current – transistor off
Gate-low : current –transistor on

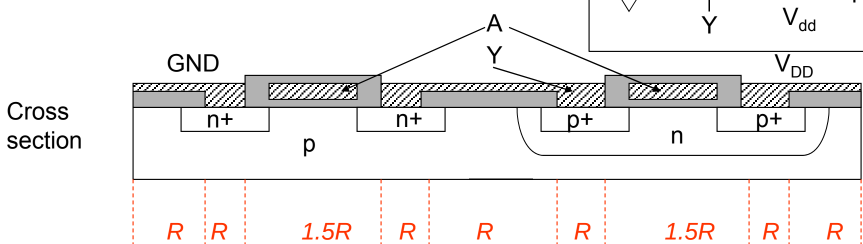






Inverter: by top-down





•Rough approximation of the inverter size

10R x 6R is required for the area; pattern resolution: R ≅ 4λ (wavelength)

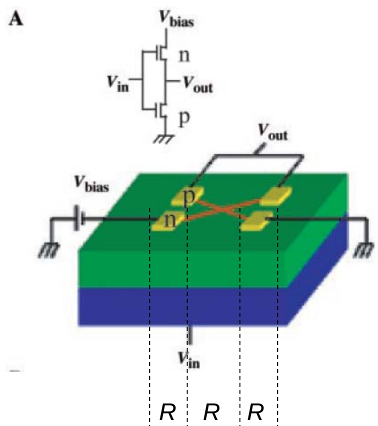
•6 Mask steps for fabrication

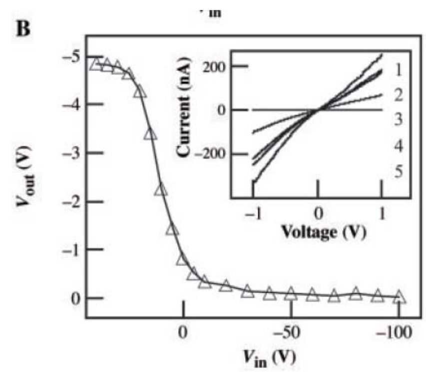
VLSI design techniques for analog and digital circuits, by Randall L. Geiger, et al., McGraw-Hill publishing company.

Intuitive CMOS electronics by Thomas M. Frederiksen, McGraw-Hill series

Inverter: by bottom-up

Inverter using Si nanowires



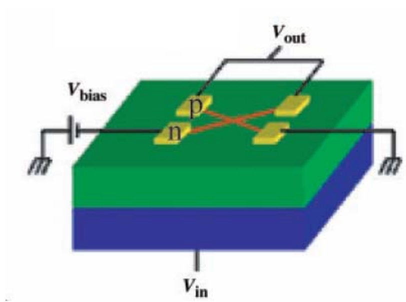


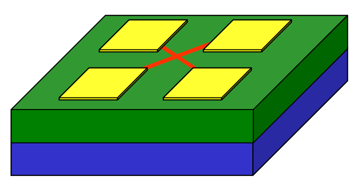
3R x 3R is required.

Cui Y and Lieber CM, SCIENCE, 2001.

Inverter: by bottom-up

Inverter Fabrication using Si nanowires



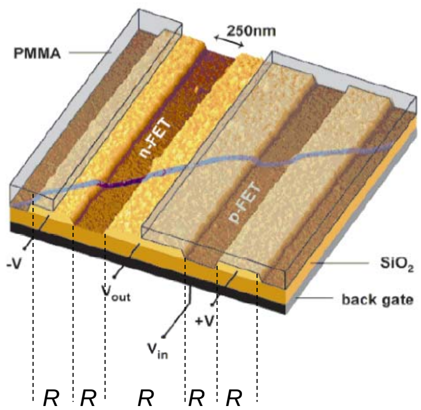


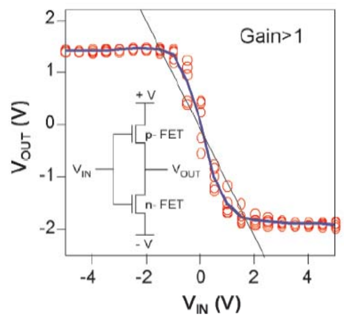
Fabrication process:

Si wafer - oxidation - *1st Si nanowire assembly* - *2nd Si nanowire* - electrode patterning

Inverter: by bottom-up

Inverter using carbon nanotubes





5R x 1R is required.

Derycke V, et al., NANO LETTERS, 2001.

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Inverter: by top-down vs. bottom-up

Inverter	Top-down	Bottom-up (Si nanowire)	Bottom-up (CNT)
Area	10R x 6R	3R x 3R	5R x 1R
Limited by	Wavelength	Assembly process	
Mask steps	6 mask process	1 mask process	2 mask process
Pros	Well established	Simple structures and fabrication	
Cons	Complicated fabrication	Low yield for assembly processes	
Future	Resolution can be 30 nm.	? (may be dominant under 10nm)	

Nanowire assembly is key to the future!

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Nanowire (nanotube) assembly

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Assembly Methods

❑**Growth methods** : Chemical vapor deposition (CVD), Plasma enhanced vapor deposition (PECVD), Vapor-liquid-solid growth, etc.

❑**Chemical patterning**: assembly using an electrostatic attraction of nanowires (nanotubes) suspended in solution.

❑**Electric field guided assembly**: dielectrophoresis and electrophoresis.

❑Other methods:

- Manipulation using either a micromanipulator or an atomic force microscope (AFM)
- Magnetic and optical fields
- Shear force in viscous solution (ex: spin coating and fluid flow)

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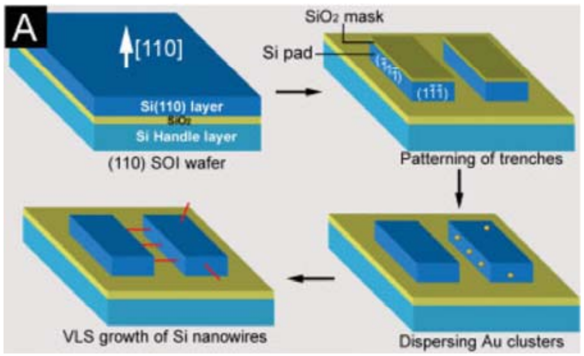
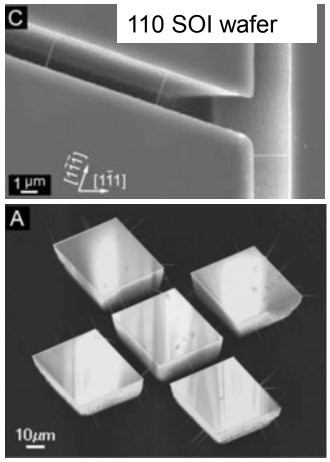
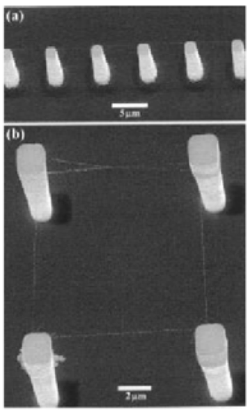
Growth (Si nanowires; VLS CVD)



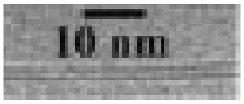


He RR et al., ADVANCED MATERIALS, 2005

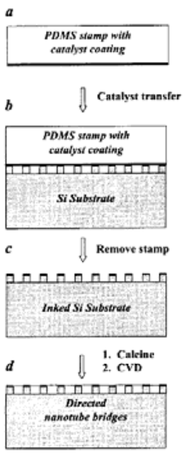
Growth (SWCNT; Chemical vapor deposition)



•*SEM image*



•*TEM image*



•*Procedure for CVD growth*

• *Cassell AM, et al. JACS 1999*

Growth (MWCNT; Chemical vapor deposition)

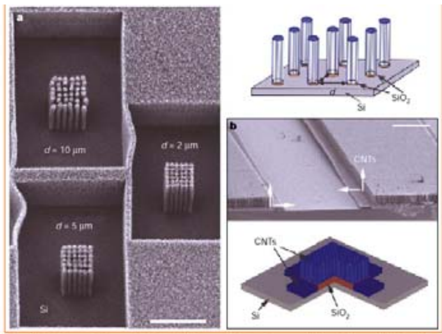


Figure 1 Directed assembly of organized, multiwalled carbon-nanotube structures grown by chemical-vapour deposition. **a,** Image obtained by scanning electron microscopy of three blocks of cylindrical pillars (about 10 μm in diameter) of aligned carbon-nanotube arrays. Each pillar consists of several tens of nanotubes grown in vertical alignment and in a normal direction to SiO_2 patterns on the Si/SiO_2 template. No growth occurs on the Si parts of the template. The separation (*d* in diagram, top right) between pillars in the three blocks is indicated. **b,** Vertical and horizontal growth of aligned nanotubes (CNTs), viewed in a cross-section of a patterned Si/SiO_2 wafer. Scale bars, 100 μm.

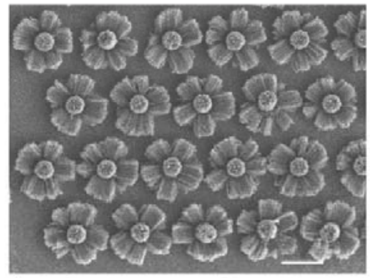


Figure 2 Repeating patterns containing mutually orthogonal nanotube arrays produced on deep (about 5 μm) silica features (circular cross-section) machined on silicon substrates. Growth in the vertical direction occurs from the top silica surface (seen as arrays emanating from the centre of each pattern); growth on the sides occurs as horizontal arrays (sideways growth seen on each pattern). Scale bar, 50 μm.

- *Wei BQ, et al., NATURE, 2002*

Chemical patterning (MWCNT)

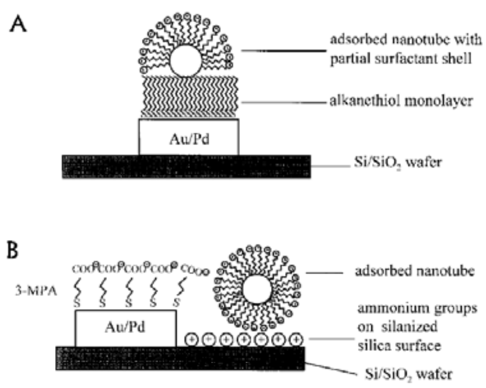


Fig. 1. Schematic representation of the expected attachment of a nanotube surrounded by a negatively charged surfactant shell on two differently modified surfaces prepared by: A) formation of a self-assembled octadecanethiol monolayer on the electrodes, and B) amino-silanization of the SiO_2 surface and adsorption of 3-mercaptopropionic acid (3-MPA) on the gold/palladium

Burghard M, et al. Advanced Materials, 1998.

Chemical patterning (MWCNT)

Experimental procedure

1) CNT

Growth

Dispersion in surfactant by sonication

2) Au lines

Si wafer

Oxidation

Au patterning

Alkanethiol growth (SAM) in solution or with evaporation

3) CNT assembly by self-assembly

Single drop of CNT suspension

Dry

4) Imaging

Case A

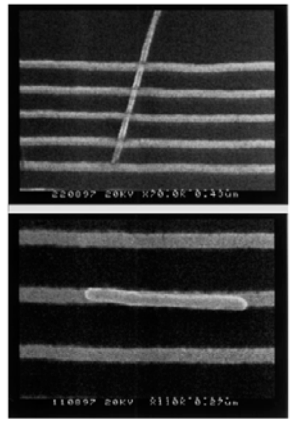


Fig. 2. Electron micrographs of the nanotube arrangement on octadecanethiol-modified electrode surfaces: a tube bridging over five electrodes (top), and a tube deposited on top of one electrode line (bottom).

Burghard M, et al. Advanced Materials, 1998.

Chemical patterning (MWCNT)

Experimental procedure

1) CNT

Growth

Dispersion in surfactant by sonication

2) Au lines

Si wafer

Oxidation

Au patterning

Amino-silanization on oxide layer

3mercaptopropionic acid (3-MPA) on electrodes

3) CNT assembly by self-assembly

Single drop of CNT suspension

Dry

4) Imaging

Case B

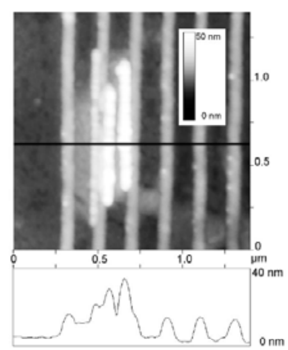


Fig. 3. AFM image of nanotubes located on an amino-silanized silicon wafer with 3-MPA modified electrodes. Shown are three nanotubes adsorbed in a parallel orientation between electrode lines (top) as a representative example and the corresponding section analysis (bottom).

Burghard M, et al. Advanced Materials, 1998.

Chemical patterning (SWCNTs)

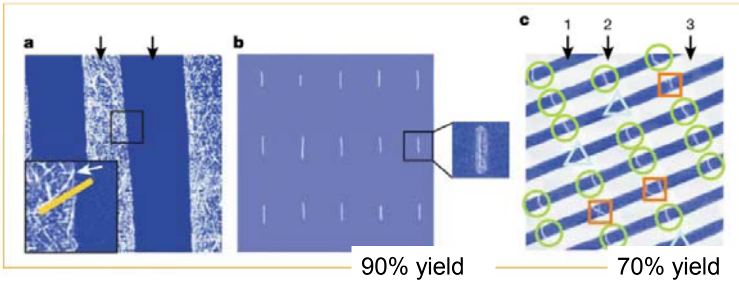


Figure 1 Atomic-force micrographs showing large-scale self-assembly of single-walled carbon nanotubes (swCNTs). **a,** Image ($12 \times 12\ \mu m^2$) showing the topography of swCNTs near the boundary (white arrow, inset) between polar (cysteamine; left arrow) and non-polar (1-octadecanethiol (ODT); right arrow) molecular patterns on gold. No swCNTs are evident in ODT regions. Yellow bar represents a tangent to a bent swCNT, showing the extent of bending due to lateral–directional force. **b,** Topography ($30 \times 30\ \mu m^2$) of an array of individual swCNTs covering about 1 cm^2 of gold surface. The friction-force image (inset) shows a single swCNT (dark line), and the regions containing 2-mercaptoimidazole (bright area) and ODT (dark area). **c,** Topography ($20 \times 20\ \mu m^2$) of an array of junctions with no swCNTs (triangles), one swCNT (circles) or two swCNTs (squares), covering an area of about 1 cm^2. Arrows 1, 2 and 3 indicate octadecyltrichlorosilane (used to passivate the SiO_2 surface), 2-mercaptoimidazole on gold, and ODT on gold, respectively.

Patterning organic molecules by dip-pen nanolithography and microcontact printing followed by CNT patterning

Rao SG, et al., Nature, 2003.

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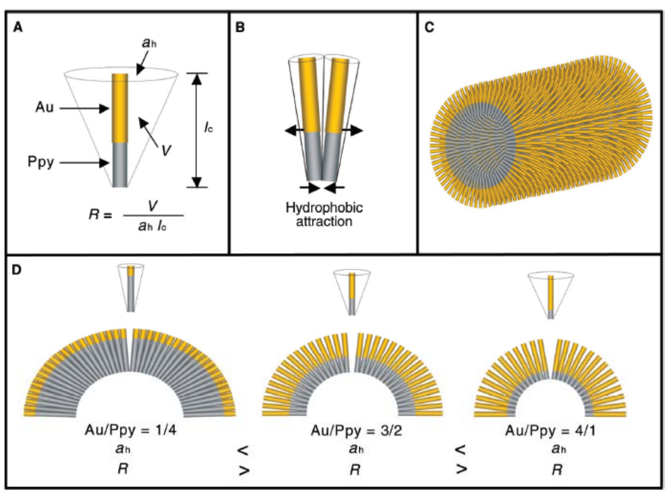
Chemical patterning (3-d structures) Metal-Polymer Amphiphiles

Fig. 2. Schematic representations of the corresponding Au-Ppy rod assemblies described in Fig. 1, B to D. **(A)** Geometric packing parameters (where *V* is the volume of rods, a_h is the average rod head area, and l_c is the rod length), calculated by assuming a truncated cone. **(B)** The estimated a_h can be acquired from a first-order approximation of the average area occupied by the gold end of each rod in the microtubular structure, which is defined by the perimeter area of the tube divided by the total number of rods that make up the superstructure. **(C)** A three-dimensional tubular structure composed of rod-like building blocks. **(D)** Cross-sectional views of tubes of various diameters formed from specific rod compositions with well-defined block-length ratios.



Park S, et al., SCIENCE, 2004

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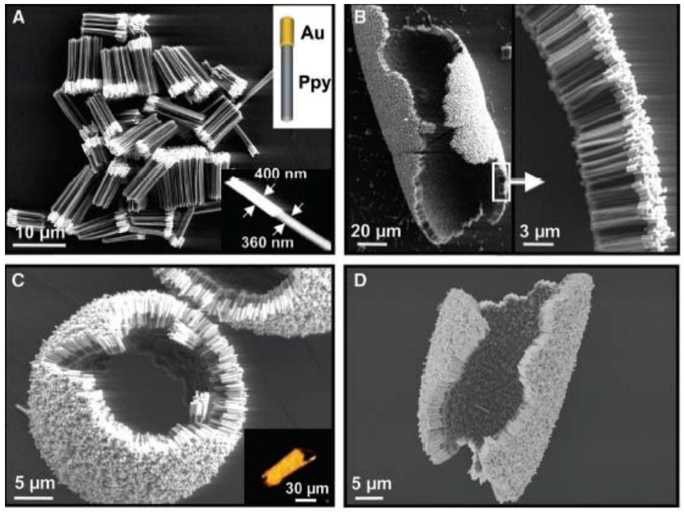
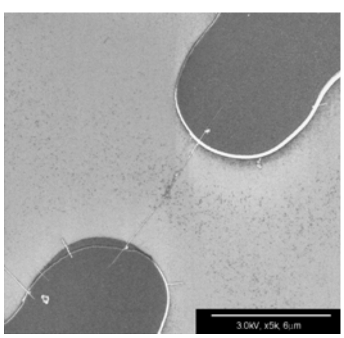
Chemical patterning (3-d structures) Metal-Polymer Amphiphiles



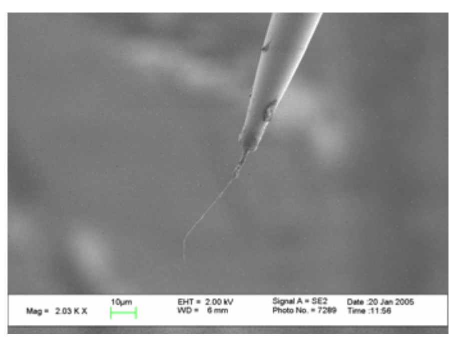
Park S, et al., SCIENCE, 2004

Electric Field Guided Assembly

Parallel Assembly



One dimensional assembly



- Electrodes are required for assembly.
- Electric fields (AC, DC, and composite fields).
- Electrophoresis, Dielectrophoresis, Electrokinetic flow, etc.

We will more discuss electric field guided methods in this lecture.

Comparison for assembly methods

	Growth	Chemical patterning	E-field
Purity demand	High	High	Low
Patterning	Catalyst	Deposition area	Electrodes
Temp./ time	>500°C/ ~hrs.	room temp./ 1min	room temp./ 1min
Sorting	Yes	No	Yes (electrical property & physical size)
Potential for Waferscale fab.	Yes	Yes	Yes

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