2.76/2.760 Multiscale Systems Design & Manufacturing

Fall 2004

Carbon Nanotubes

Sang-Gook Kim,
MIT

Moore’s Law

The number of transistors per chip doubles every 18 months.
– Moore’s Law

_ Moor’s Second Law

	Year of introduction	Transistors
4004	1971	2,250
8008	1972	2,500
8080	1974	5,000
8086	1978	29,000
286	1982	120,000
386™	1985	275,000
486™ DX	1989	1,180,000
Pentium®	1993	3,100,000
Pentium II	1997	7,500,000
Pentium III	1999	24,000,000
Pentium 4	2000	42,000,000

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Lithography Tool Cost

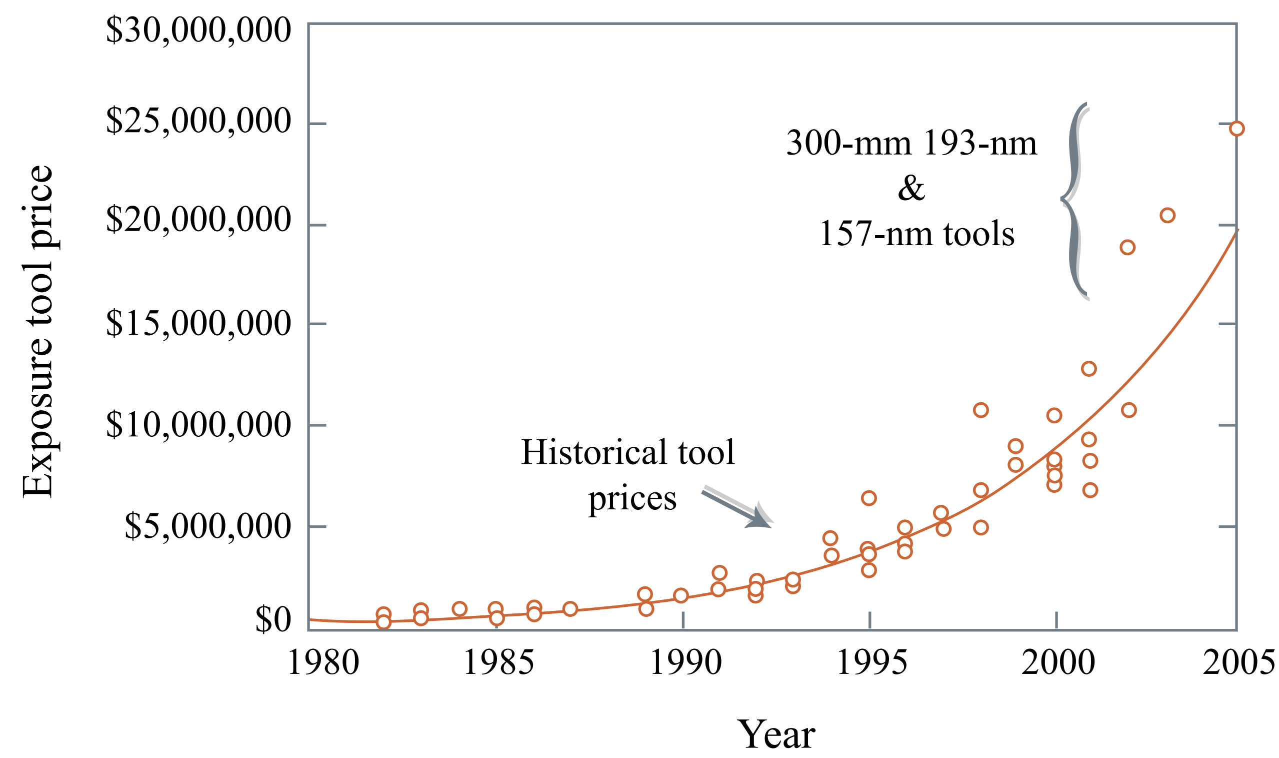

Figure by MIT OCW. After International Sematech.

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Aerial density, hard disk

Graph removed for copyright reasons.

- Superparamagnetic Effect

  "a point where the data bearing particles are so small that random atomic level vibrations present in all materials at room temperature can cause the bits to spontaneously flip their magnetic orientation, effectively erasing the recorded data. "

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Limit of Optical Lithography

- $W = k\,\lambda/NA$ (Rayleigh Eqn.) = $\lambda/(2.\ n.NA)$
- In 1975, 405 nm (Hg H-line) at an NA of 0.32, a linewidth of 1 μm
- deep-UV (248-nm), 193 nm, 157nm

- Nanoimprinting
- Soft Lithography
- Dip Pen Lithography
- SPM-based patterning

Table 1: *Wavelength "Generations"*
Intel Road Map

Year	Node	Lithography
1981	2000nm	i/g-line Steppers
1984	1500nm	i/g-line Steppers
1987	1000nm	i/g-line Steppers
1990	800nm	i/g-line Steppers
1993	500nm	i/g-line Steppers
1995	350nm	i-line -> DUV
1997	250nm	DUV
1999	180nm	DUV
2001	130nm	DUV
2003	90nm	193nm
~~2005~~	~~65nm~~	~~193nm -> 157nm~~
~~2007~~	~~45nm~~	~~157nm -> EUV~~
2009	32nm and below	EUV

193 nm immersion lithography

Nanotechnology

Top-down Method

- nanostructures by shrinking macrostructures

Bottom-up Method

- self assembly of atoms or molecules into nanostructures

Science meets Engineering

Nanomanufacturing

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MIT

Carbon nanotube

- 1959: Richard Feynman's famed talk.
- 1981: Binnig and Rohrer created the STM to image individual atoms.
- 1985: Curl, Kroto, Smalley discovered C_{60}.
- 1993: Iijima, Bethune discovered single wall carbon nanotubes.
- 1998: Cees Dekker's group created a TUBEFET

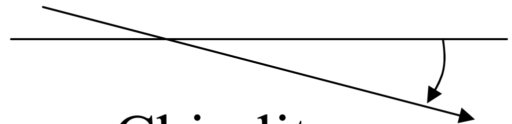
- Discovered by Sumio Ijima (NEC) in his study of arc-discharge products. *Nature*, 354, 56 (1991)
- Giant Fullerene molecules made of sheets of carbon atoms, coaxially arranged in a cylindrical shape.
  - • SWNT, single-walled nanotube (1 < d < 3 nm.)
  - • MWNT, multi-walled nanotube (d > 3 nm)

Properties of Carbon Nanotubes

Diagrams removed for copyright reasons.

Roll up

Graphene sheet



Chirality

Diagrams removed for copyright reasons.

- Size: dimensions of ~1 nm diameter (~20 atoms around the cylinder)
- Electronic Properties: Can be either metallic or semiconducting depending on the diameter or orientation of the hexagons
- Mechanical: Very high strength and modulus. Good properties on compression and extension
- Highest Young's Modulus of all known materials (Y ~ 1.2 TPa).
- Extraordinary mechanical resilience: compression, tension, torsion and buckling without breaking C-C bonds

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***Graphene** is a single planar sheet of sp2 bonded carbon.

Rolling up graphene layer ⇒ Nanotubes

armchair $\theta = 30°$

zigzag $\theta = 0°$

chiral $0 < \theta < 30°$

Diagrams removed for copyright reasons. See source below.

$$Ch = n\bar{a}_1 + m\bar{a}_2$$

$$d_{tube} = \frac{\sqrt{3}a_{cc}}{\pi}\sqrt{n^2 + nm + m^2}$$

$$\theta = \tan^{-1}\left[\sqrt{3}m/(2n+m)\right]$$

1.P. J. F. Harris, Carbon nanotubes and related structures: new materials for the twenty-first century, (Cambridge University Press, Cambridge, UK, 1999).

Possible Chiral Vectors

$$Ch = n\bar{a}_1 + m\bar{a}_2$$

$$|Ch| = \sqrt{3}a_{cc}\sqrt{n^2 + nm + m^2}$$

Diagram removed for copyright reasons.

$$d_{tube} = \frac{\sqrt{3}a_{cc}}{\pi}\sqrt{n^2 + nm + m^2}$$

$(n\text{-}m) = 3q$ metallic

$(n\text{-}m) = 3q \pm 1$ semiconducting

● metal ○ semiconductor

M. S. Dresselhaus, Electronic Structure of Chiral Graphene Tubules, Appl. Phys. Lett. 60 (18), 1992

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MIT

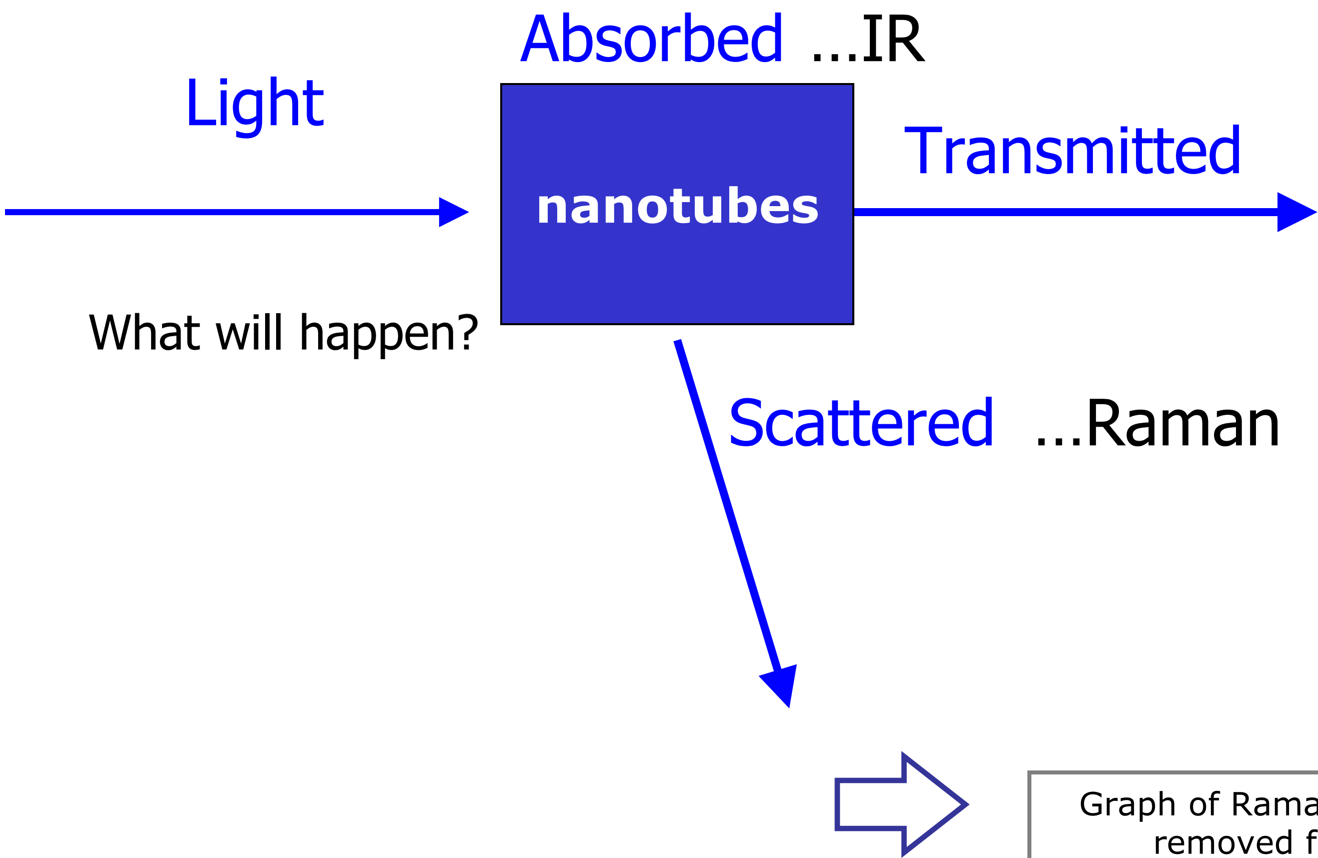
Characterization

- Structural
- Electrical
- Optical

Vibrational modes in nanotubes

Diagrams removed for copyright reasons.

Raman Spectroscopy



Graph of Raman Intensity vs. Frequency removed for copyright reasons.

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Raman Spectroscopy of Carbon Nanotubes

M. S. Dresselhaus and P. C. Eklund, Advances in Physics 49 705 (2000)

- Non-destructive, contactless measurement
  - Room Temperature
  - In Air at Ambient Pressure
  - Quick (1min), Accurate in Energy
- Diameter Selective (Resonant Raman Effect)
- Diameter and Chirality dependent phonons
  - Characterization of *(n,m)*
  - Related to Low Dimensional Physics

Synthesis

- Arc discharge
  - Nanotubes found in soot produced in arc-discharge with catalytic metals such as Fe, Ni and Co (S. Iijima, 1991)
- Laser ablation
  - YAG laser ablation of graphite target in a furnace at 1200 °C. (R. Smalley, 1996)

  The location and alignment of the synthesized nanotubes can not be controlled.
- CVD
  - NT grown from nucleation sites of a catalyst in carbon based gas environments (Ethylene, Methane, etc.) at elevated temperatures (600 - 1000 °C).

  Control of location, alignment, length and diameter, spacing between tubes

Arc Discharge

5-20mm diameter carbon rod

Diagram removed for copyright reasons.

Y. Saito *et al.*
Phys. Rev. 48 1907 (1993)

Laser Ablation

Nd-Yb-Al-garnet Laser, 1200

Diagram removed for copyright reasons.

A. Thess *et al.*
Science 273 483 (1996)

- Yields >70% SWNT if double pulsed
- Ropes 10-20 nm dia, 100 μm length
- How to scale up?

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MIT

Chemical vapour deposition (CVD)

- Acetylene over iron nanoparticles 700^{O}C forms MWNT covered with amorphous C on outer layer
- Ethylene, hydrogen + methane over Co, Ni, Fe nanoparticles at 1000^{O}C forms 70-80% SWNT uncapped
- 2CO -> C + CO_2 also forms NT

Diagram removed for copyright reasons.

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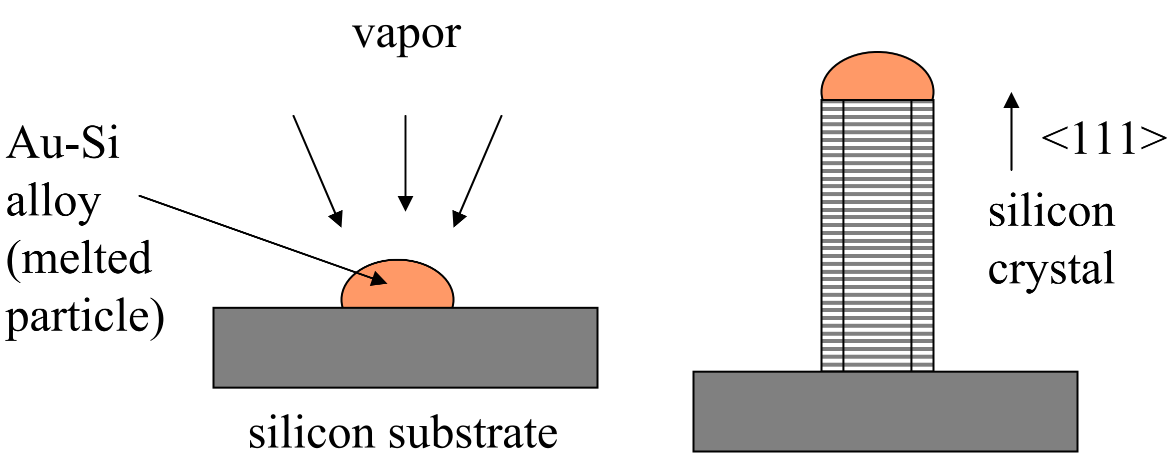
VLS Mechanism



Process diagram removed for copyright reasons.

Si nanowire

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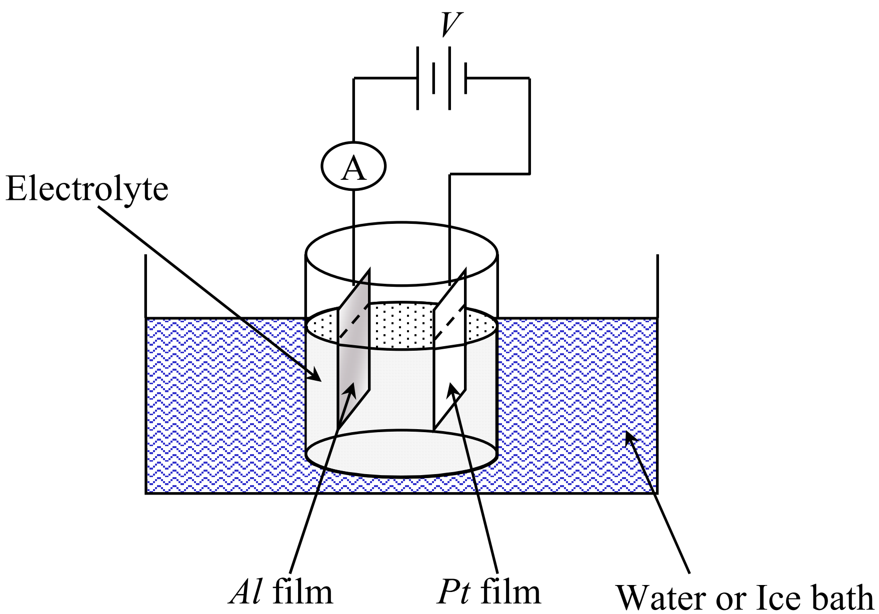
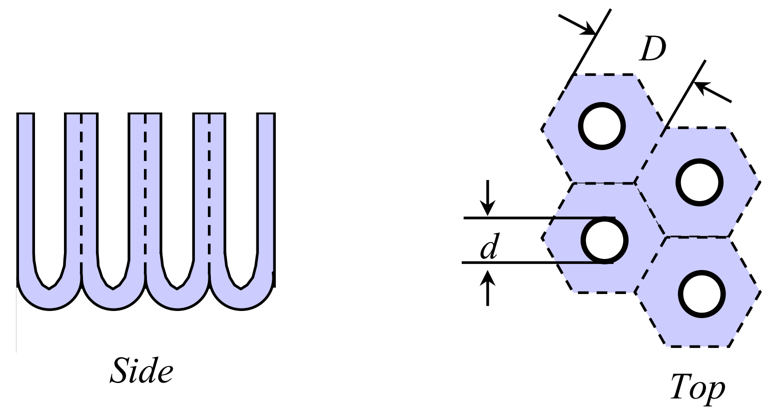
Porous Anodic Alumina Films

Anodization Reaction :

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6e^- + 6\,H^+$$

Experiment Setup :

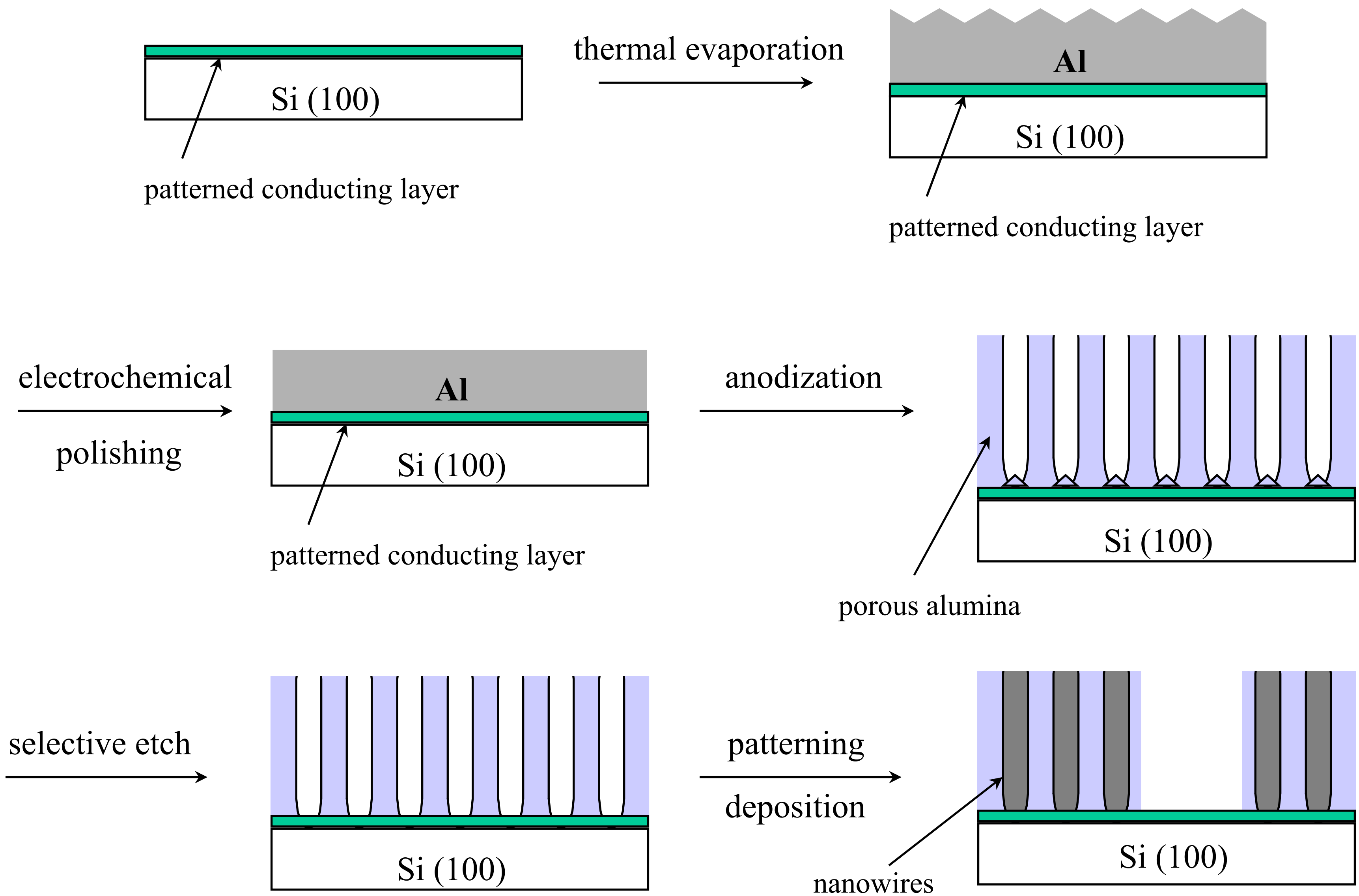




- Controlling parameters:
  - Voltage, Electrolyte, Temperature, Time
- Cell size D ~ 2.5 × *V* (nm)
- Pore size d ~ *V* (nm)
- Pore size can be enlarged in acids

* *Al* film is electrochemically polished before anodization

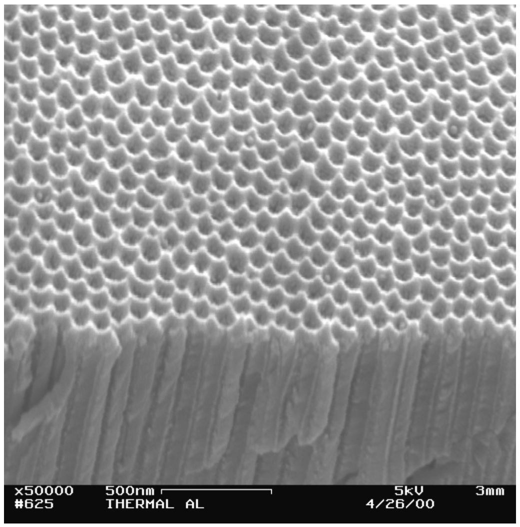
Alumina Templates on Silicon Wafers



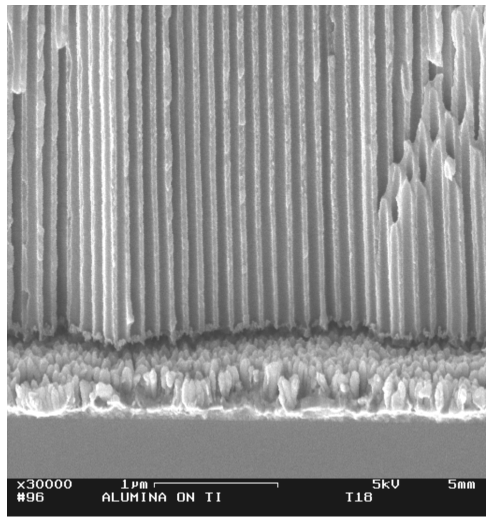
M. Dresselhaus, MIT

Nanowire by Alumina Template

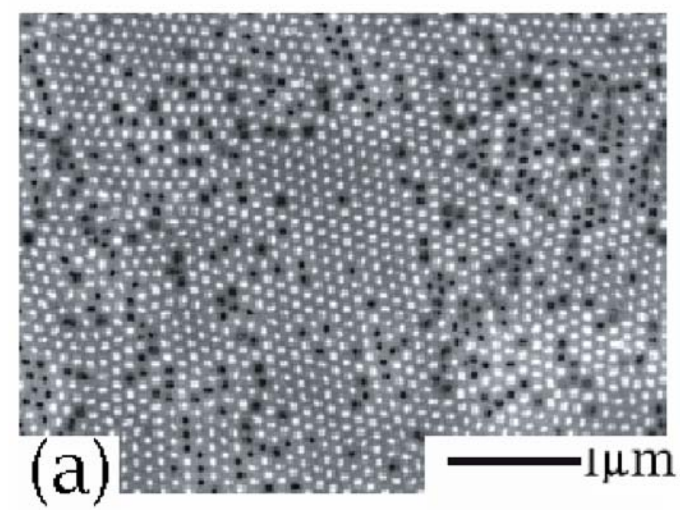
Oblique View



Cross Section



Filled



The new Al_2O_3/Si structure conserves the dense uniform porous morphology with long channels, but consists of a thinner barrier layer.

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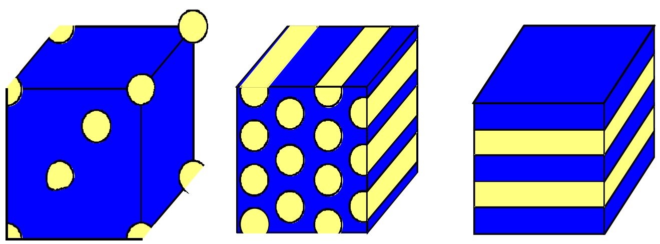
MIT

Block Copolymer Template

PS+PMMA copolymers



PMMA
<10%

PMMA
<30%

PMMA
50%

Diagram removed for copyright reasons.

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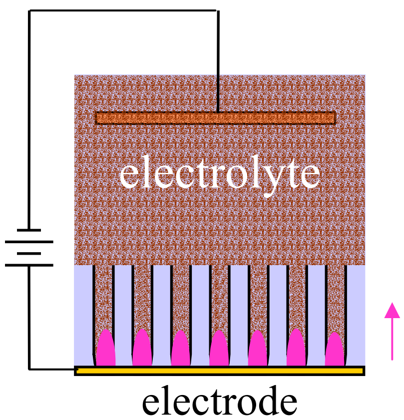
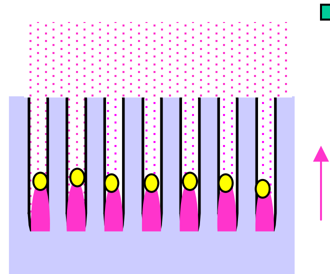
MIT

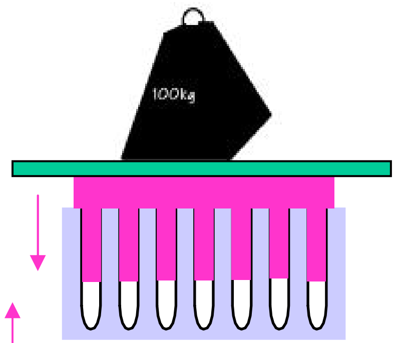
Filling methods



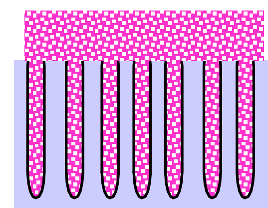
- Electrochemical deposition



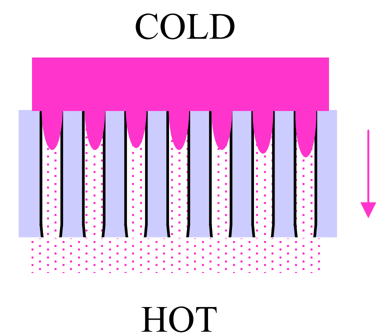
- Chemical vapor deposition



- Pressure injection of melt



- Vapor condensation



- Sol-Gel

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Vertical growth with controlled density

Photos removed for copyright reasons.

- Aligned growth through PECVD
- Control nanotube density through controlling catalyst site density

Sang-Gook Kim, MIT

Aligned Carbon Nanotube Growth

Catalytic CVD process: thermal or PE CVD

<u>Carbon Source Gas</u>

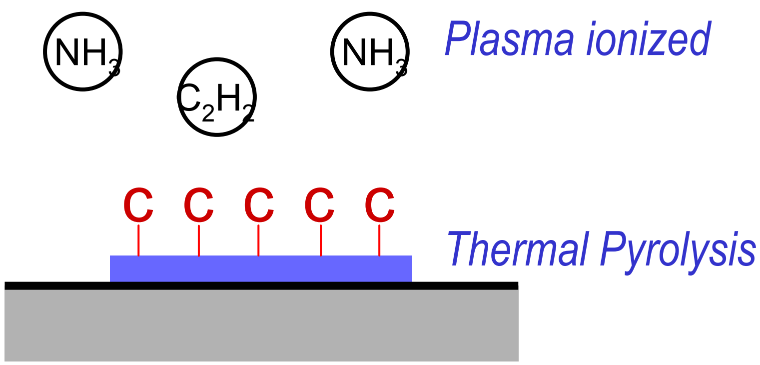
C_2H_2: relatively low temp.
CH_4: high temp.

<u>Dilution Gas</u>

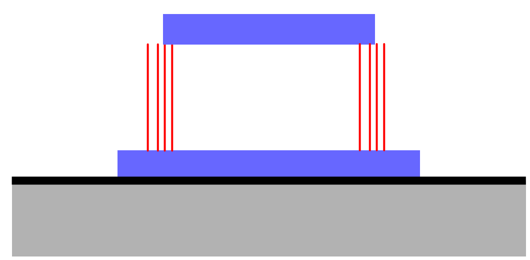
NH_3, N_2, H_2

→ Thermal Decomposition on <u>Catalysts (Co, Ni, Fe)</u>

finite solubility with carbon



Carbon Nanotube growth



Z. Ren, BC

MIT CNT PECVD

Electrode Connector I
(steel) E

Electrode Connector II
(steel) F

Electrode
(steel) G

Support for electrode
and thermocouple
(steel) D

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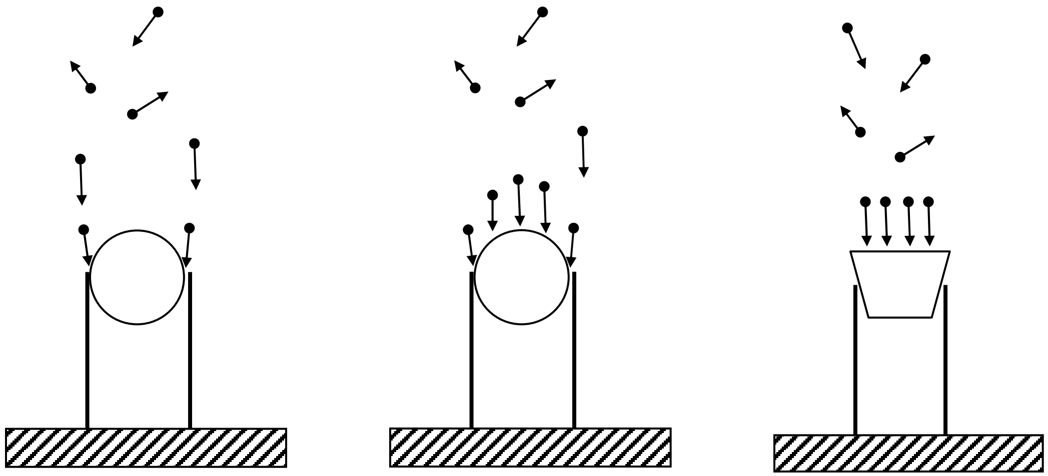
MIT

Vertically grown CNTs

- Growth modes



- PECVD parameters
  - ✓Diameter
  - ✓Length

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MIT

The Debye Length

- At some distance from the perturbing charge the electric potential energy will be equal to the thermal (kinetic) energy
- The quantity

$$\lambda_{De} = \sqrt{\frac{\varepsilon_0 k_B T}{n q_e^2}}$$

is called the (electron) Debye length of the plasma

- The Debye length is a measure of the effective shielding length beyond which the electron motions are shielding charge density fluctuations in the plasma

Carbon-nano tube Growth using Methane

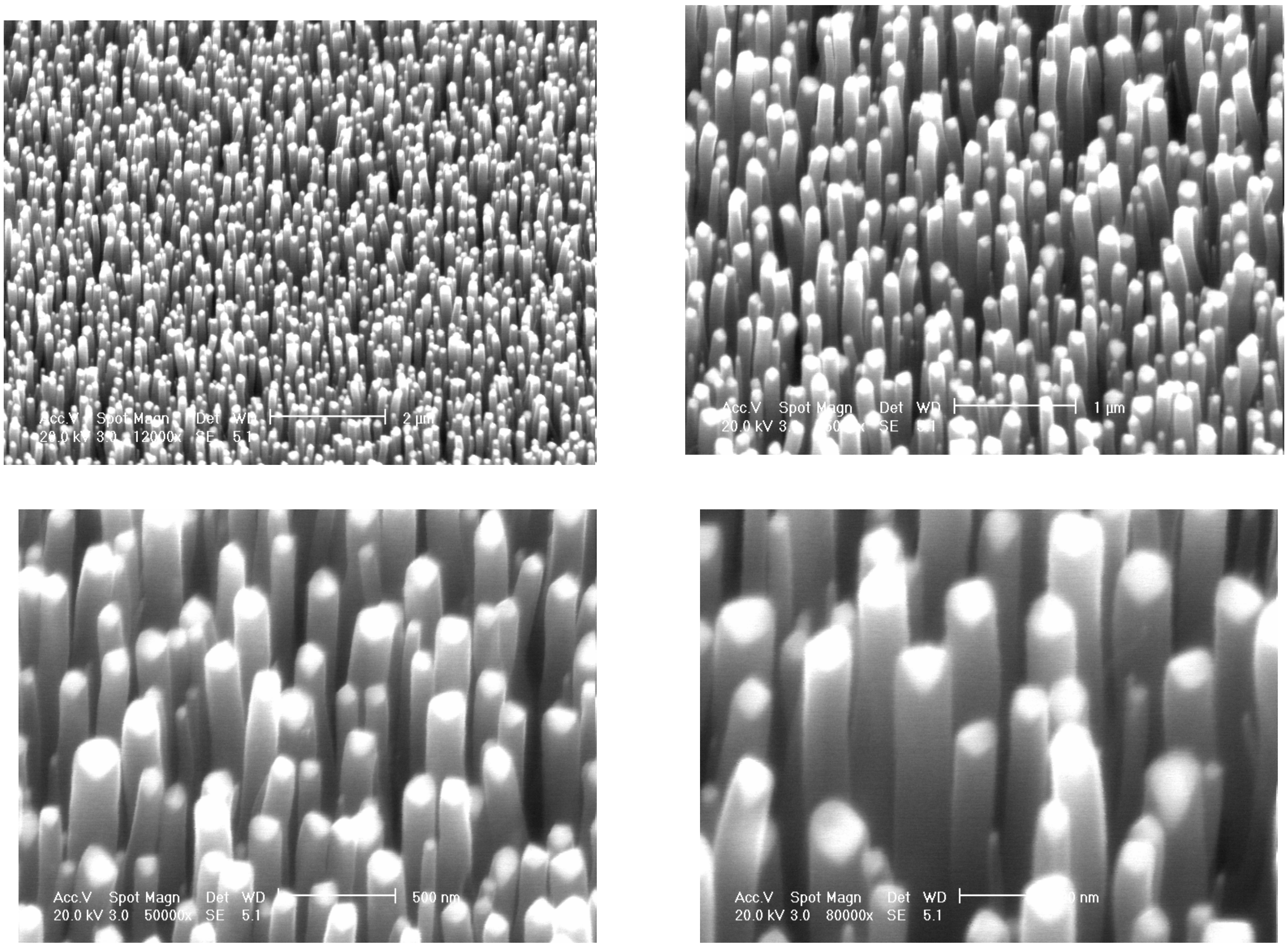
Growth Conditions:

- Growth Time: 25 minutes
- Methane flow rate: 200sccm; Ammonia flow rate: 100sccm
- Pressure: 8 Torr
- Temperature: 600 C
- Plasma Voltage: 500V; Power: 165-215 Watts

Results:

- Length of tubes: 1-1.5 micro meters
- Diameter of tubes: 100-150 nm
- Perpendicularity: Vertical (Straight)

CNTs with methane PECVD



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MIT

SWCN directly grown on silicon tip

Photos removed for copyright reasons.

- Wide usage:
  - high resolution imaging
  - chemical biological sensor
- Fabrication:
  - manual assembly(mounting)
  - CVD growth

*Kazuhiko et al. APL, **78**, 539, 2001*

Nanotube AFM tip

Y. Nakayama *et al, J. Vac. Sci. Tech*., **B18** (2000) 661.

- Merits of NT AFM tip
  - High aspect ratio
  - Small diameter
  - Flexible
  - Conductive

Photos and diagram removed for copyright reasons.

Challenges for Carbon Nanotube Research

- Process control to produce nanotubes with same diameter and chirality
  - metallic or semiconducting
- Develop large-scale, high productivity synthesis methods
- Develop large-scale, long range order assembly processes

Nanowire Array (Charles Lieber)

Image removed due to copyright reasons.

Source: Prof. Charles Lieber, Harvard University.

How to make horizontal wiring networks?

Directed Assembly

- One-dimensional assembly into functional networks
  - Lieber group, Science (291, 2001)

Figures removed for copyright reasons.

Sang-Gook Kim, MIT

Aligned NT

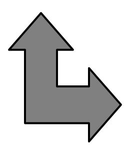
- Large arrays of well-aligned Carbon on glass
  - Ren, *Science* (282, 1999), SUNY

Photos removed for copyright reasons.

Nanotubes for manufacturing

- Growing and controlling nanotube is a coupled process.
- Decoupling them as we do sodding?

Seeding



Sodding

Carbon Nanotube Assembly

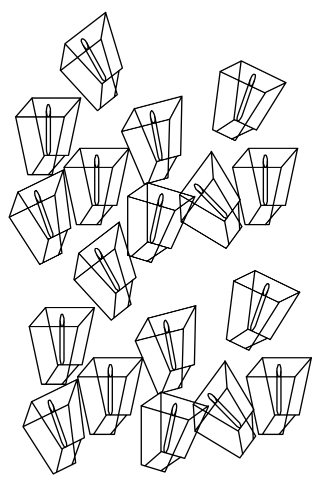
Photos removed for copyright reasons.

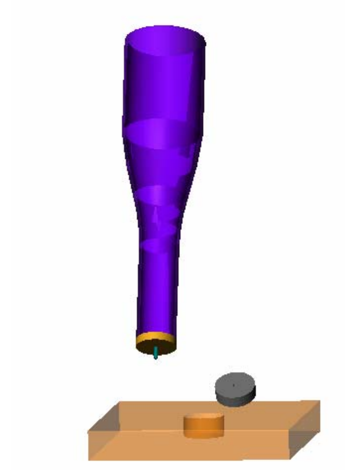
Vertically grown MWNTs
Ren, *J. Mater. Res.16* (2001)

Nanostructures by growing only?

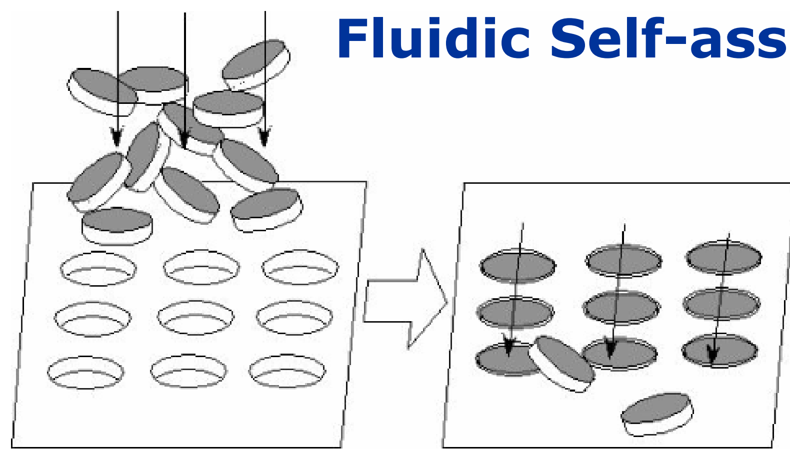
Sang-Gook Kim,
MIT

Nanopellets



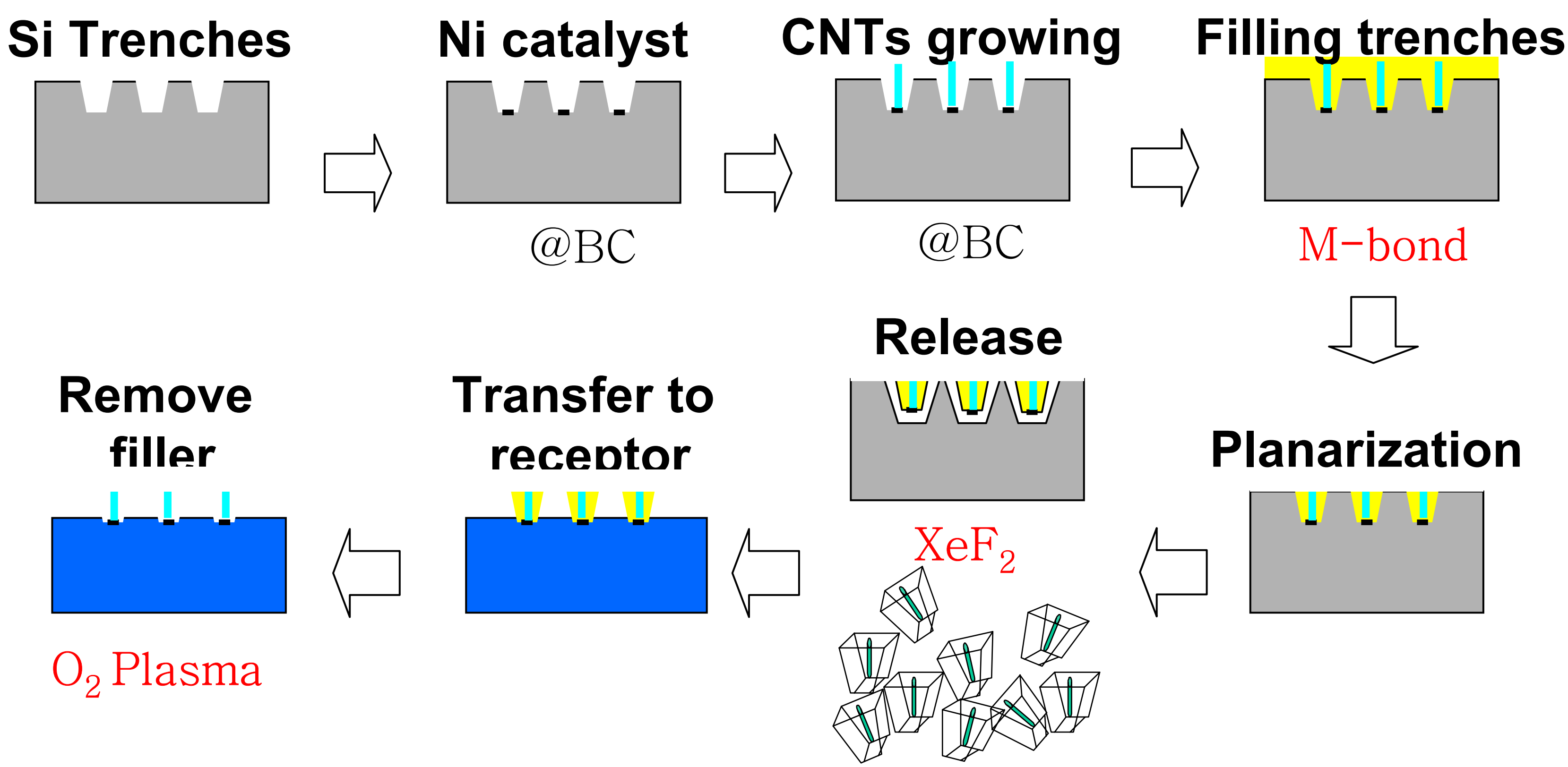


Guided Assembly



Fluidic Self-assembly

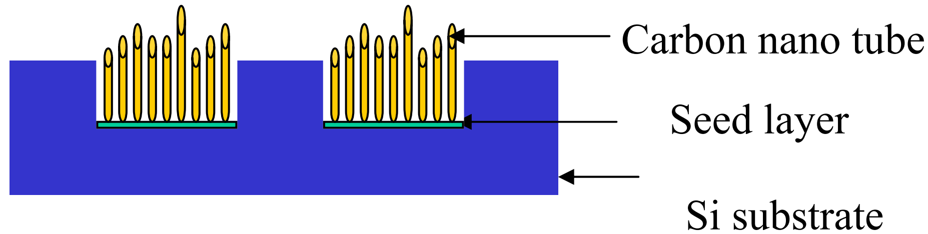
Nanopelleting



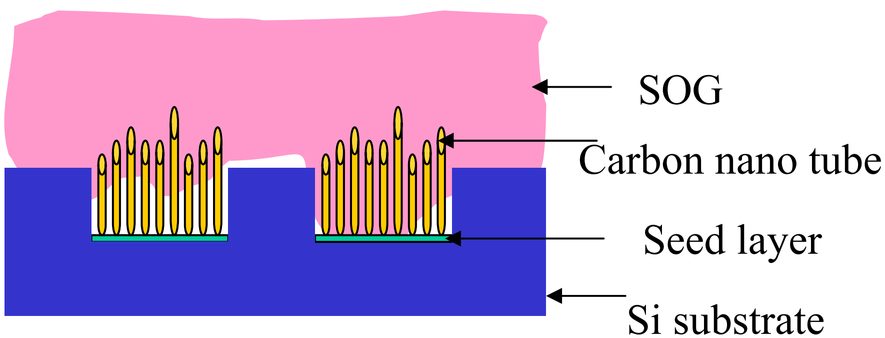
S. Kim, US patent application No 60/417,959

1) RIE patterning

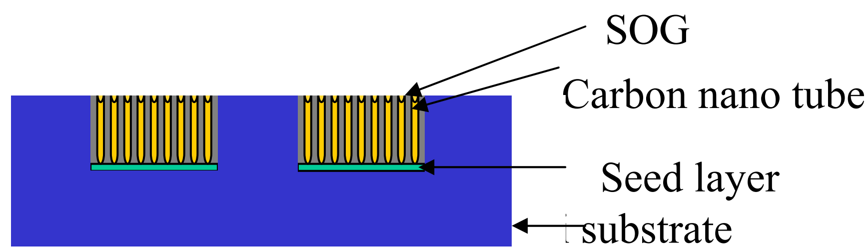
2) Deposition seed layer
Carbon nano tube growing



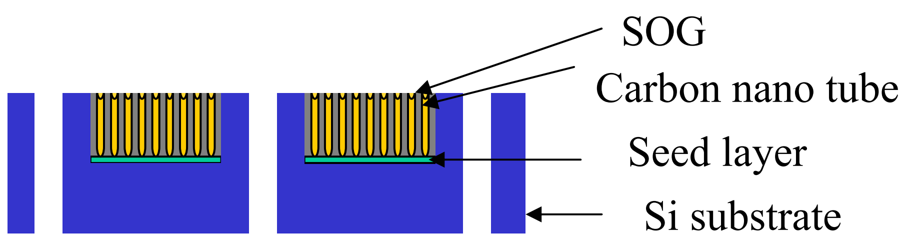
3) SOG deposition/Dry/Cure



4) CMP



5) Pelletizing



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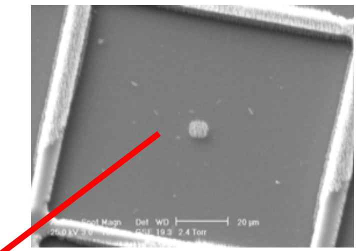
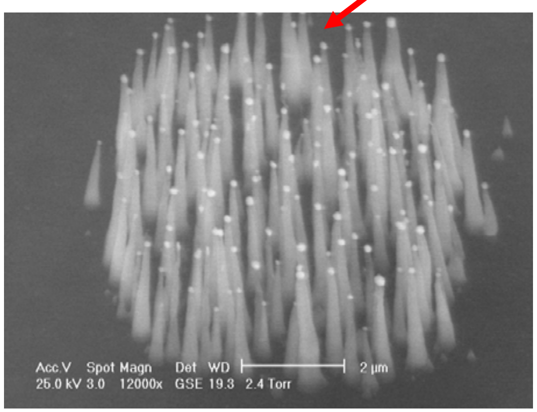
MIT

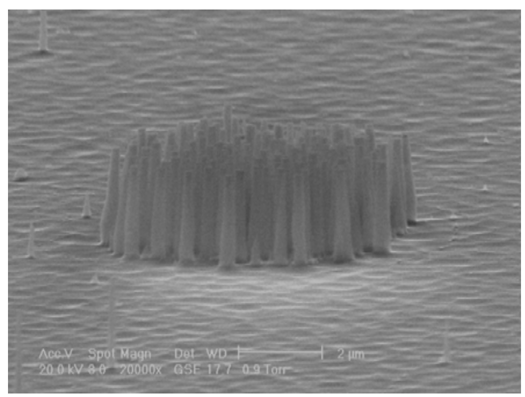
Bundle CNT nanopellet CMPed and Transplanted

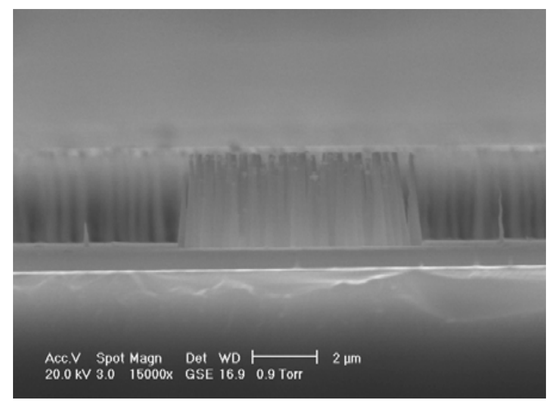
Ni(MTL,15nm)/SiO_2/Si





After CMP and then O_2 ashing





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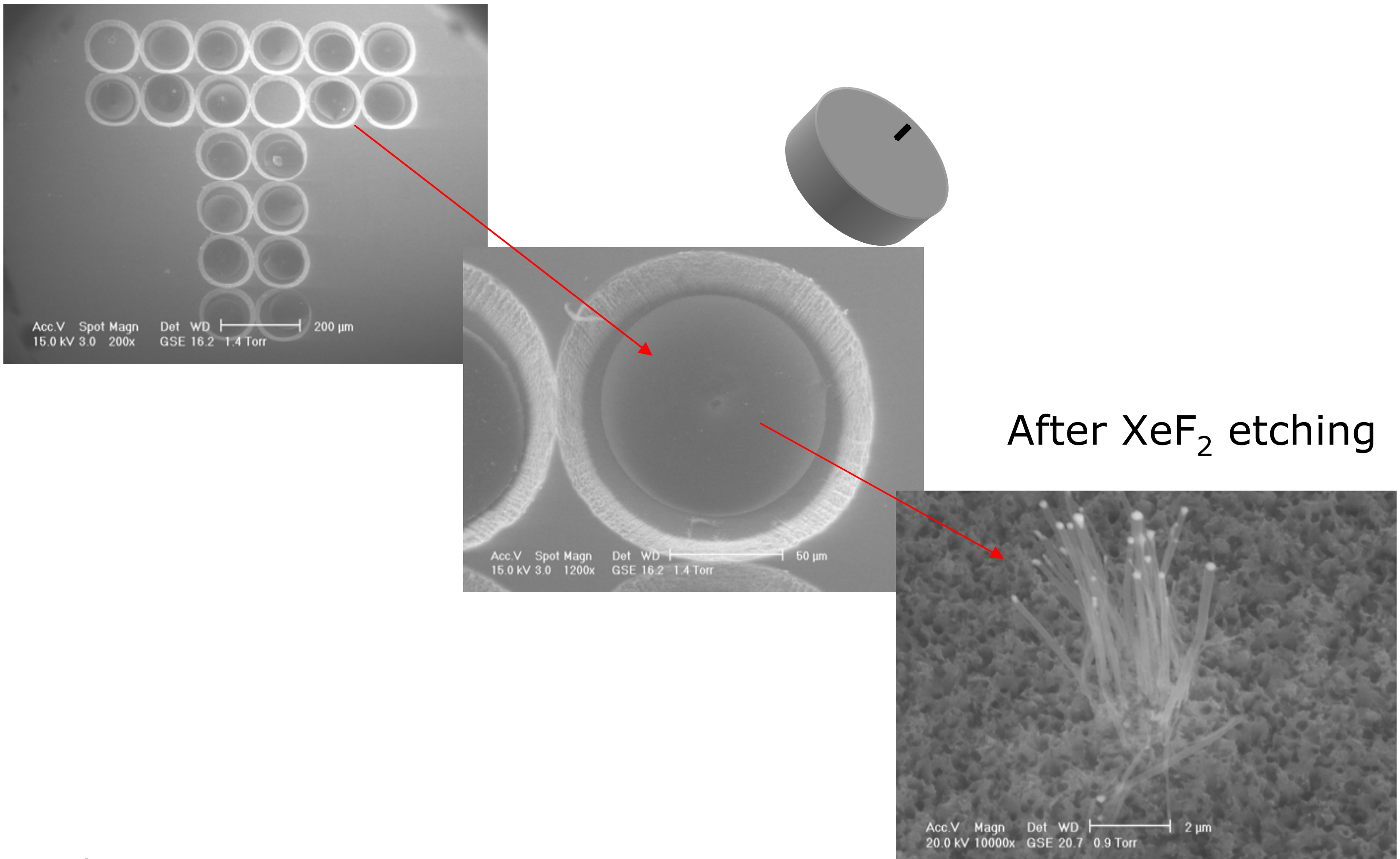
Pelletizing & Transplanting



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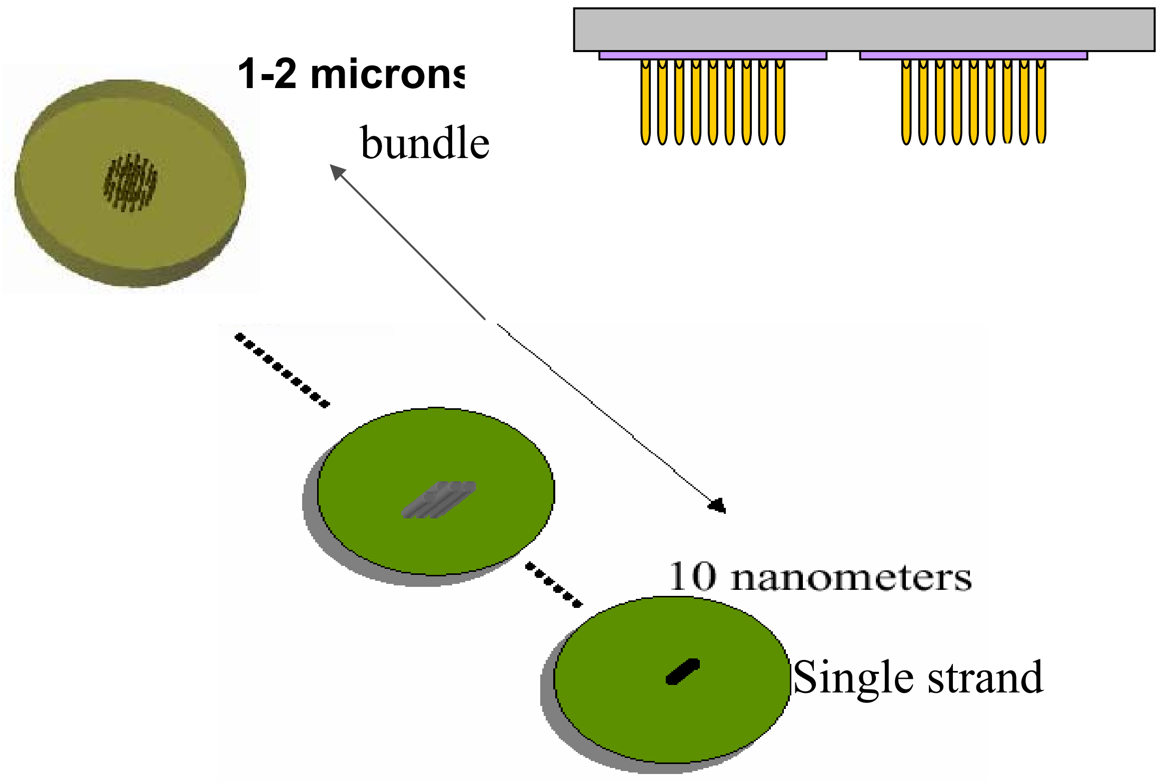
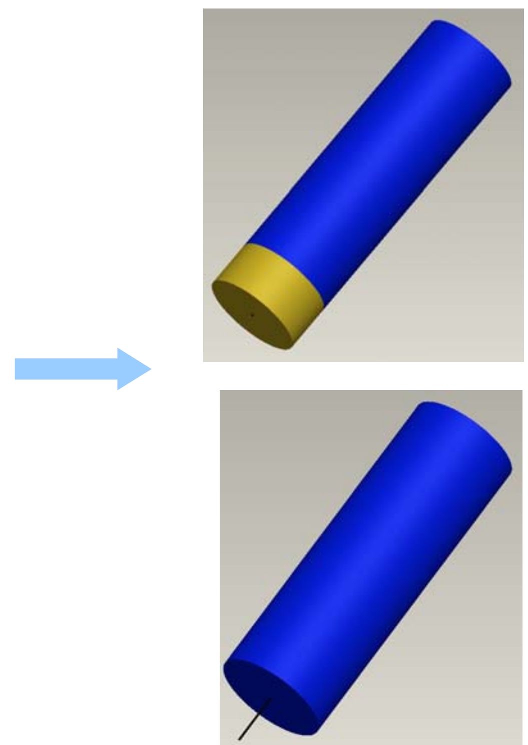
High aspect ratio nanopellets

Cold cathode array,
FED, Data storage,
Multi-E-beam array for NGL



Nanocandles



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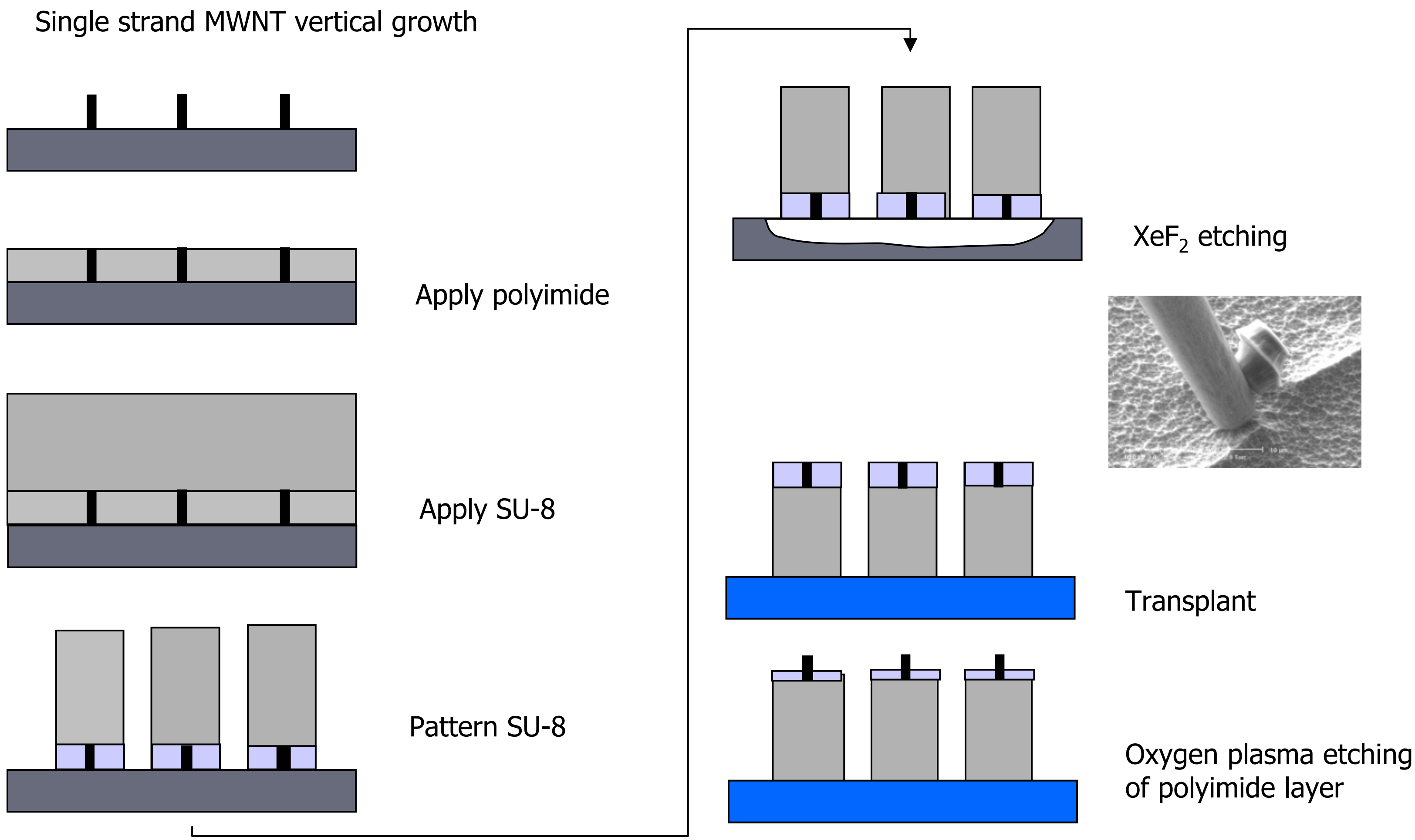
New Nanopelleting process



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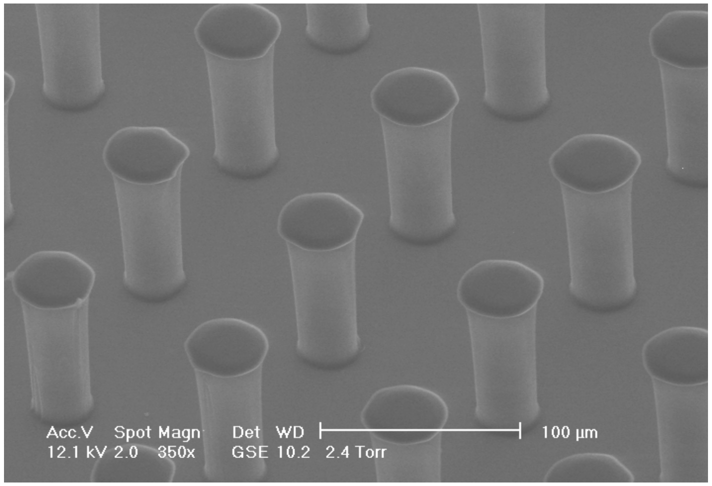
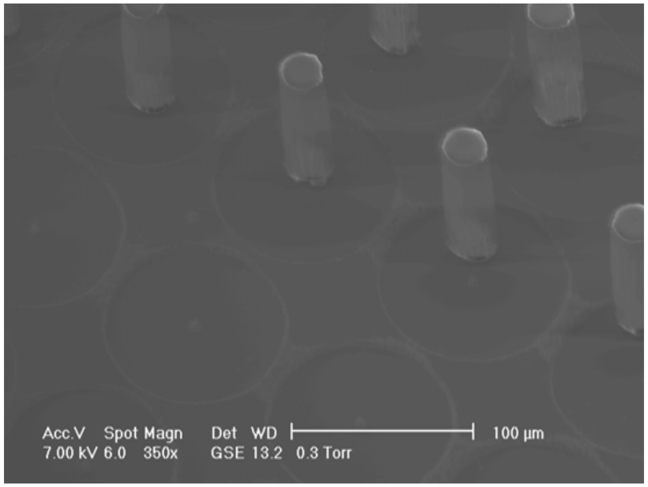
Processing Result

- High-aspect-ratio nanocandles with 20 μm in diameter and 110 μm in height achieved
- Single strand CNTs under progress

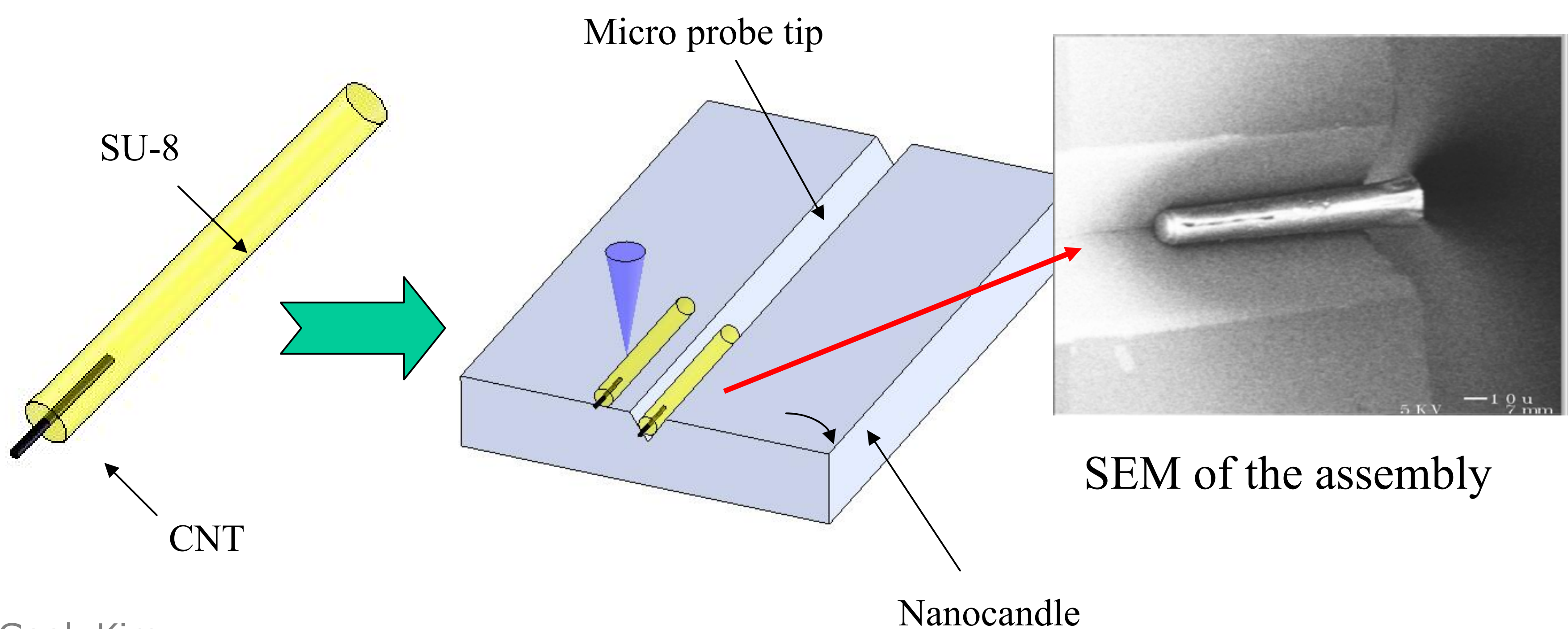




Material: SU-8 2075

In-Plane Assembly of High-Aspect Ratio Nanocandle

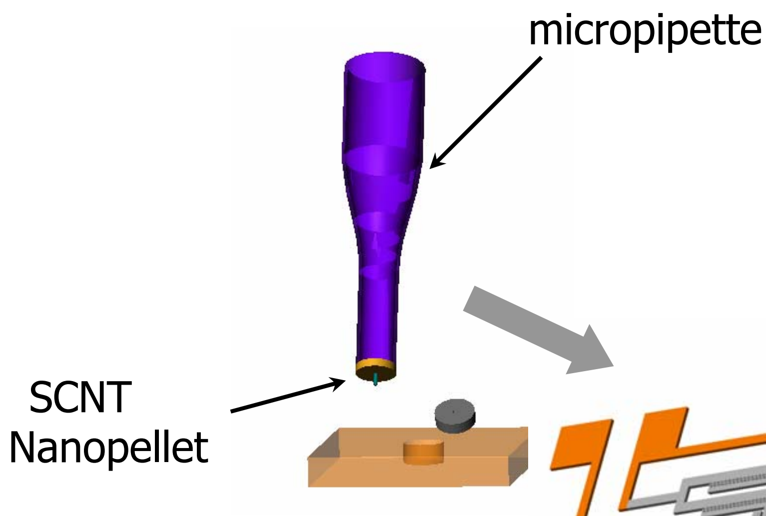
- Mechanical in-plane assembly of nanocandle in the V-groove with a micro probe tip
- Bonding of nanocandle in the V-groove with a drop of epoxy



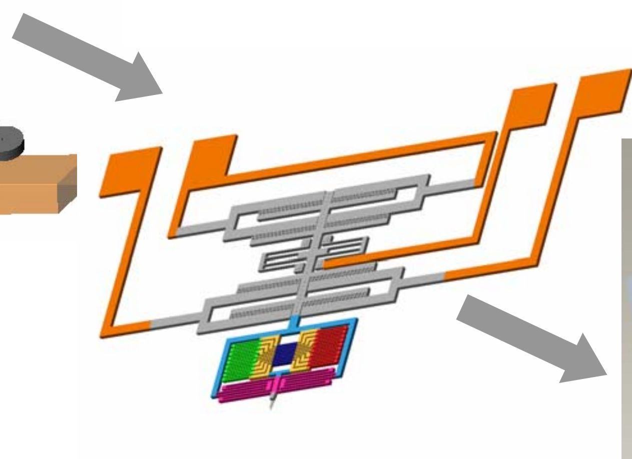
SEM of the assembly

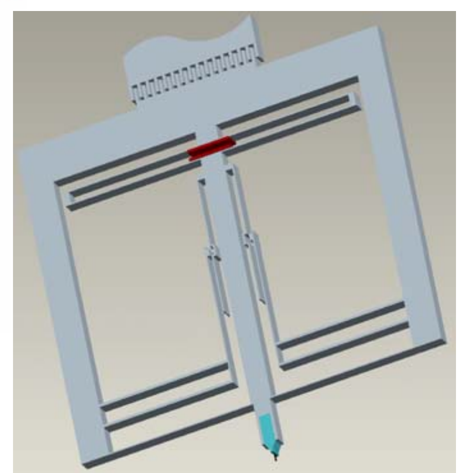
MIT Nanopipette

- Nanotube assembly to the tip of a micropipette



- Nanotube assembly to the tip of an in-plane AFM
  - Parallel Imaging and Pipetting
  - Multi-energy probing
  - Manufacturable
  - Arrayable





Sang-Gook Kim, MIT

Potential applications

- Massive Parallel Nanoprobe Array
- Nanojet Printing
- Nanotip Cell Manipulation
- 3D CNT structures