Introduction to Nanotechnology and Nanoscience – Class#15

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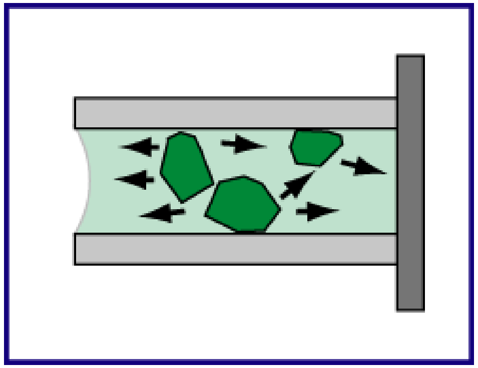
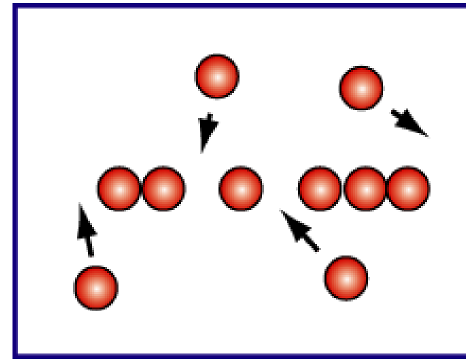
Outline

- Review
- Nanowire Applications – thermoelectric effect
- Small Project Assignments
- Paper 6
- Nanowire Integration and Assembly

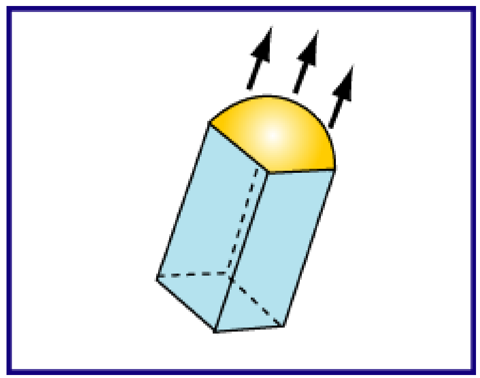
Nanowire Synthesis - Strategies



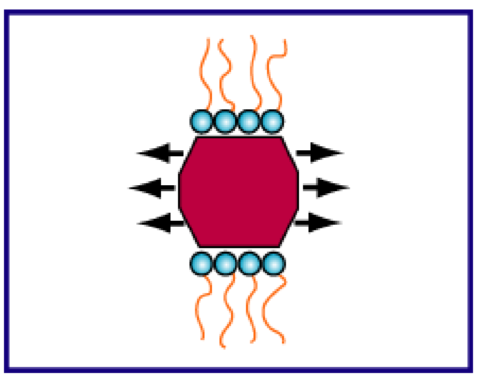
Template Growth



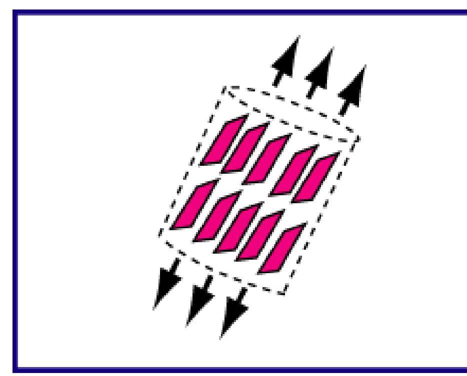
Self-assembly of 0D



VLS (Vapor-Liquid-Solid)



Capping Control

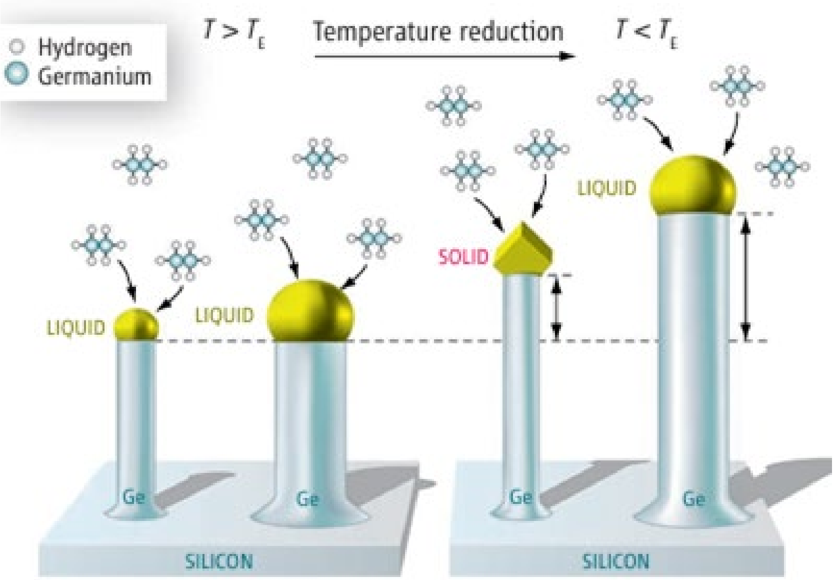


Anisotropic Crystal

Adapted after Y. Xia et al., *Adv. Mat.* 15, 353 (2003)

Solid Catalyst Growth Methode

- Different shape of the gold at the tip of the nanowire.
  - A liquid gold droplet has a smooth, almost half spherical shape
  - solid gold shows planes, edges, and corners that may easily be identified
- Gold nanodroplets remained liquid
  - authors observed this VLS-type growth mostly for nanowires with relatively large diameters.
- Gold droplet became solid as the temperature fell below TE
  - In contrast, for nanowires with relatively small diameters
  - Nanowires continued to grow, but much more slowly than in the case of VLS growth

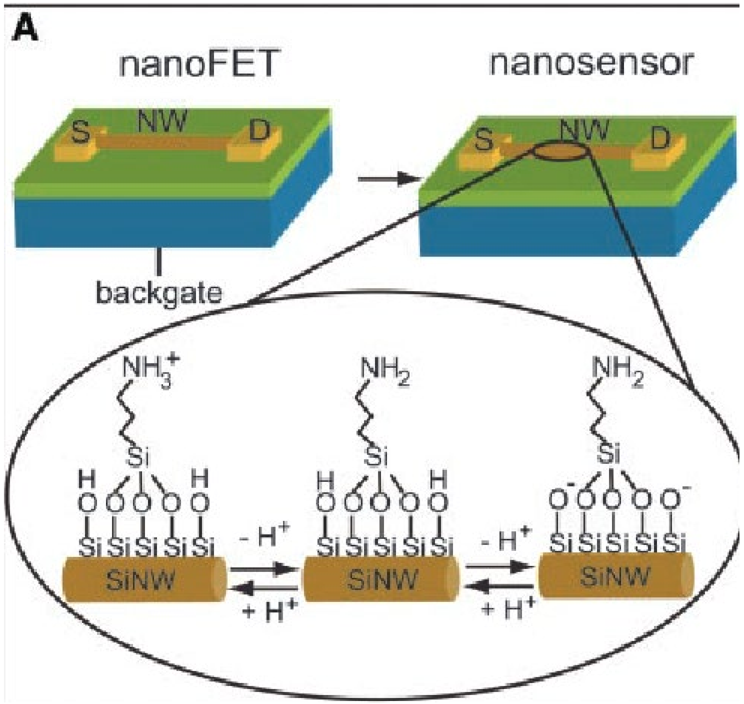


NW FET

Vasileios

- Paper used Si NWs
- Chemically modified to change conductivity based on pH

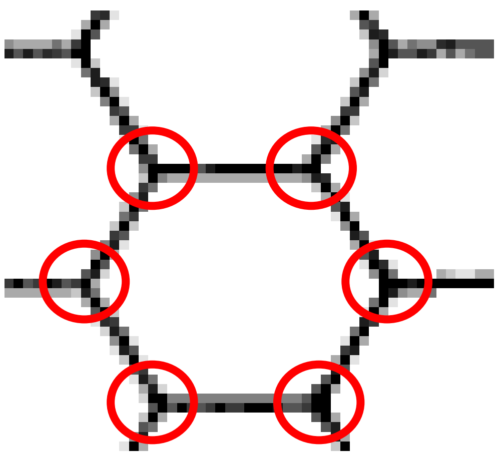
- Same principle can be applied for conductivity based on biochemicals



HW#4 Problem 2

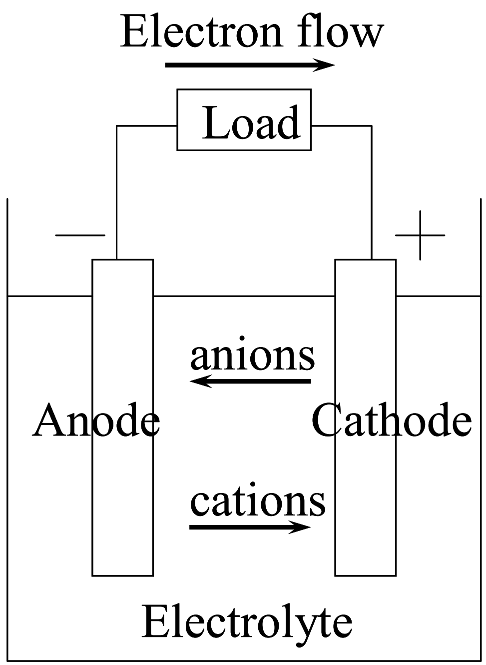
d. Number of carbon atoms per unit cell N.

N number of hexagons per 1D unit cell $N = \frac{2(n^2 + m^2 + nm)}{d_R}$



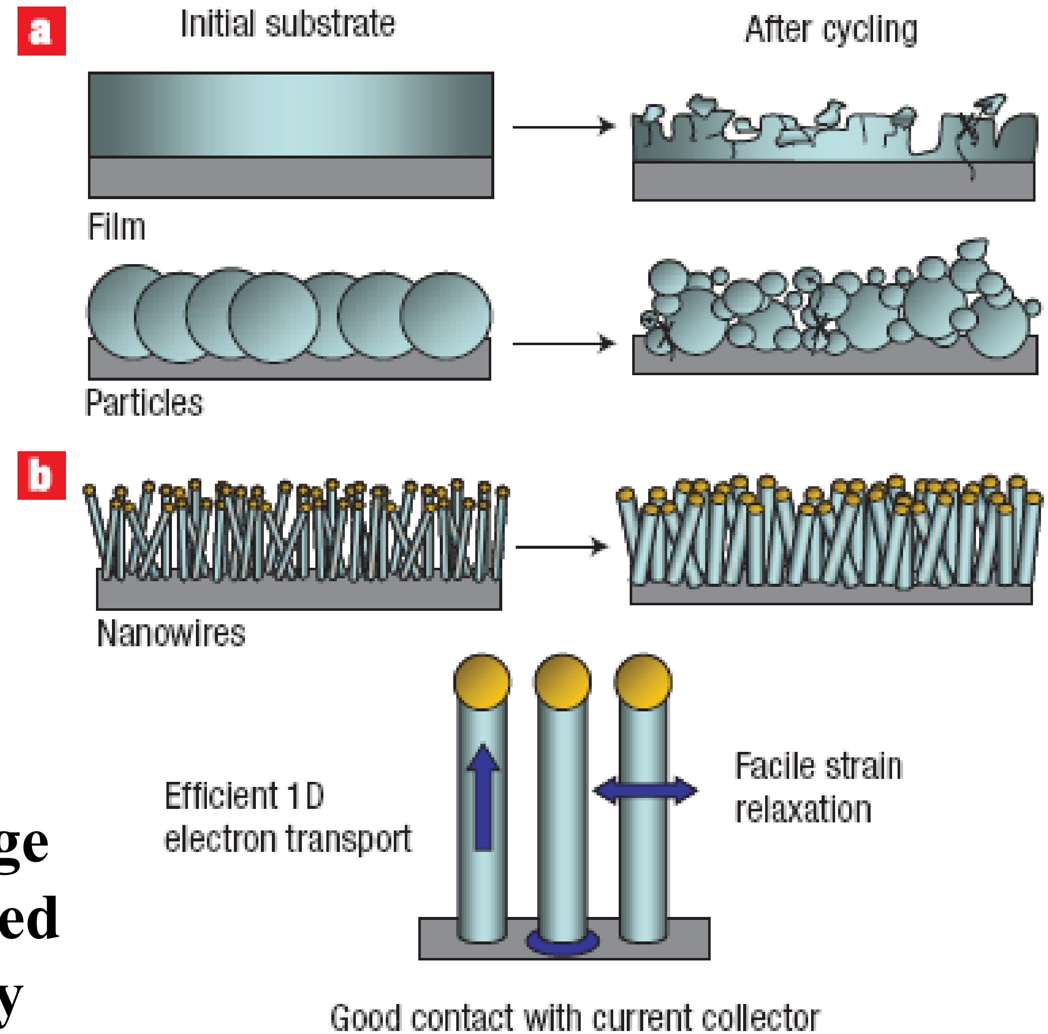
Total carbon atoms per hexagon is 6 * 1/3 = 2

Nanowire for Battery Electrodes



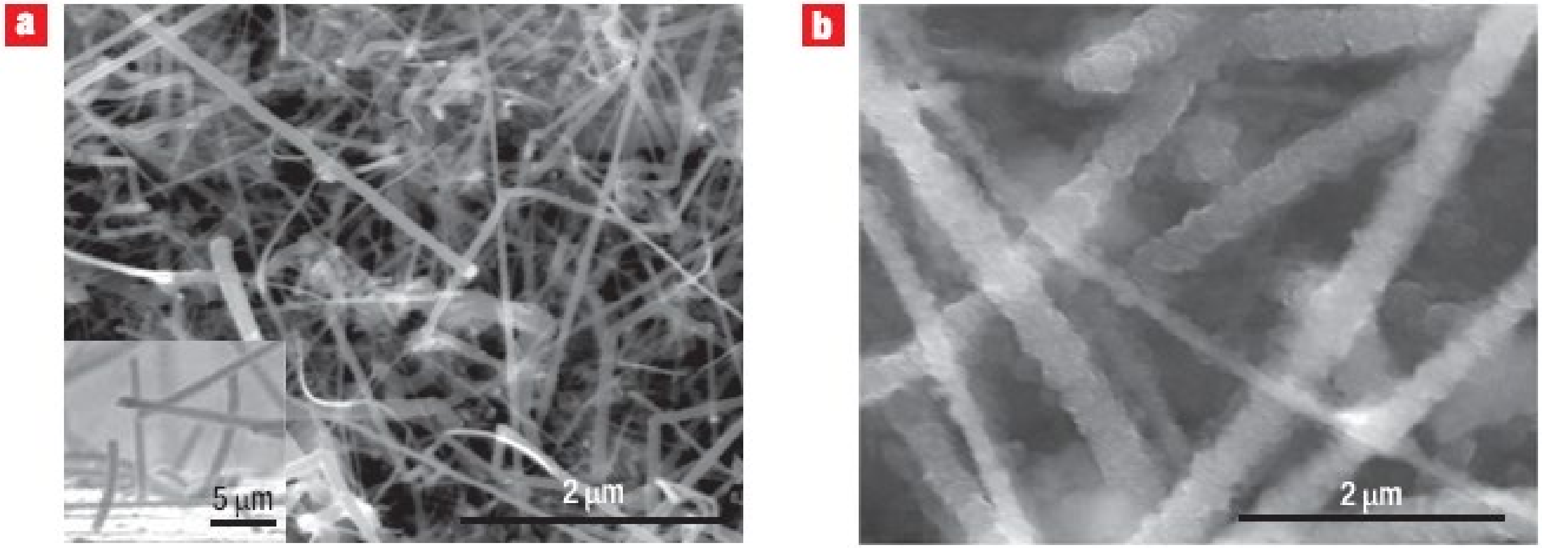
- Typical Battery (my figure)

Issues: after charge/discharge cycles, film and particle-based electrodes have discontinuity and prevent electron/iron transfer

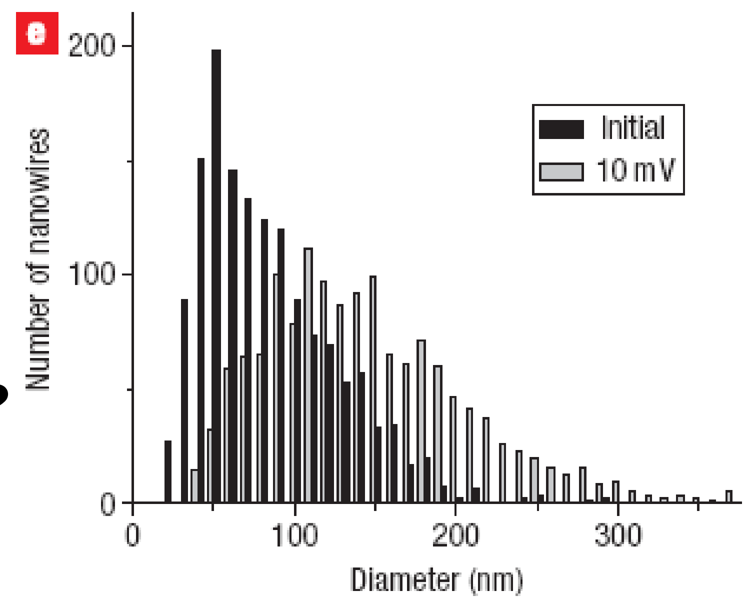


- Nanowires for battery electrode? (Nature Nanotechnology, Vol. 3, pp31-35, 2008)

Why Nanowires?



1. **High surface area**
2. **Direct connection to substrate**
3. **Possible stress relieve**



Issues

1. **Which material is best for this?**
2. **How to grow these nanowires?**
3. **Problems?**

Thermoelectric Figure of Merit (*ZT*)

Coefficient of Performance

$$\mathrm{COP}_{\max} = \frac{T_c}{T_h - T_c} \frac{\sqrt{1 + zT_m} - T_h / T_c}{\sqrt{1 + zT_m} + 1}$$

where

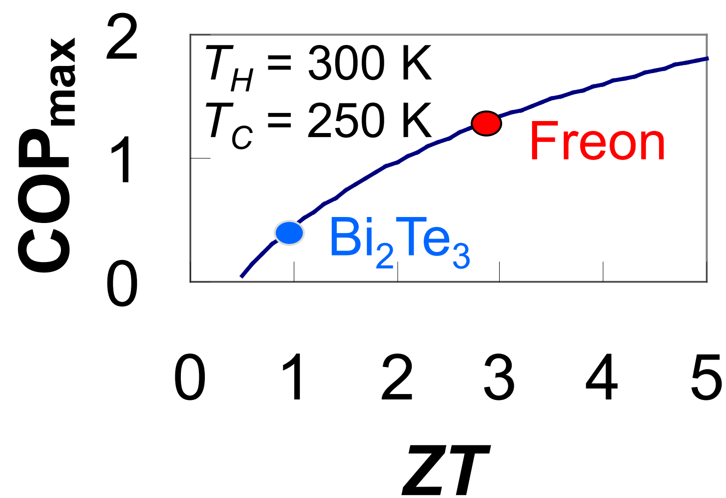
Seebeck coefficient

Electrical conductivity

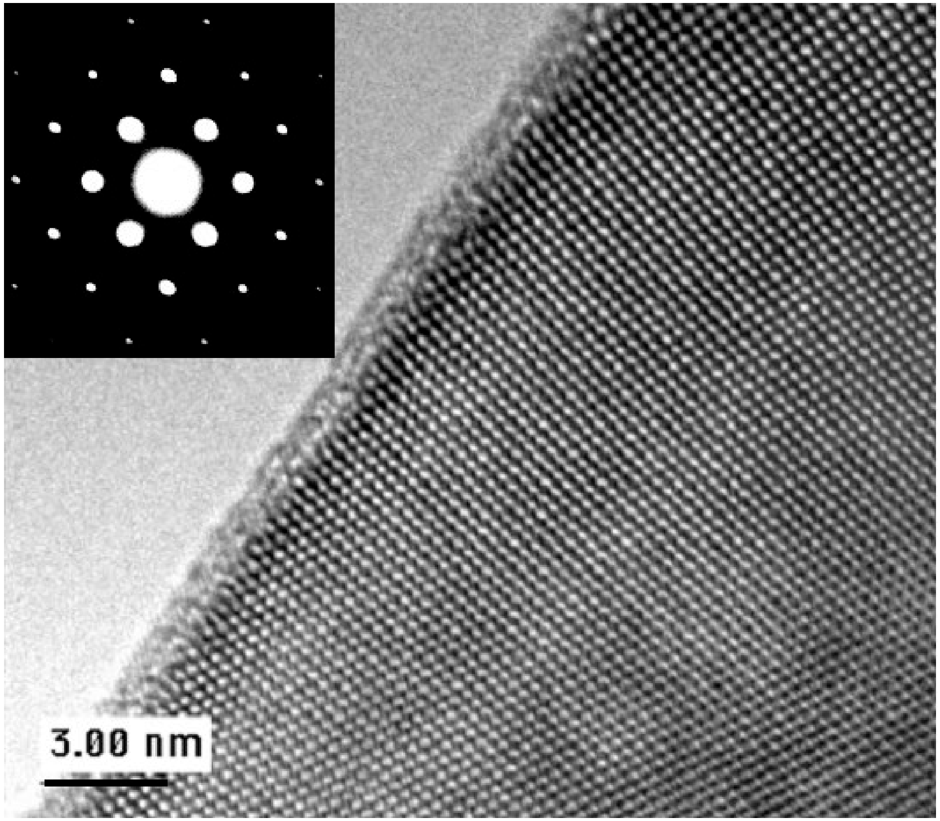
$$ZT \equiv \frac{S^2 \sigma}{\kappa} T$$

Temperature

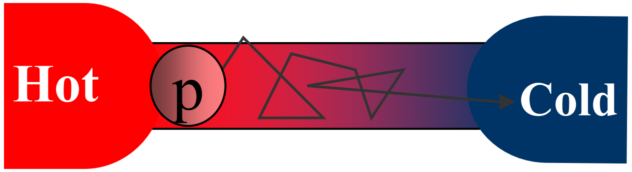
Thermal conductivity



Nanowires



22 nm diameter Si nanowire, P. Yang, Berkeley

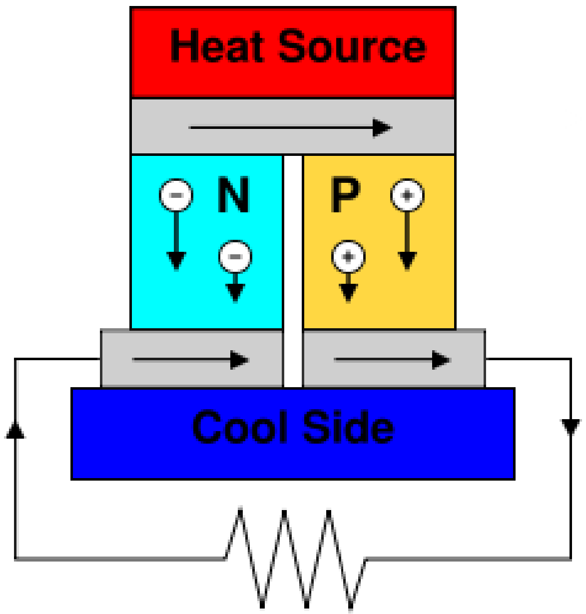


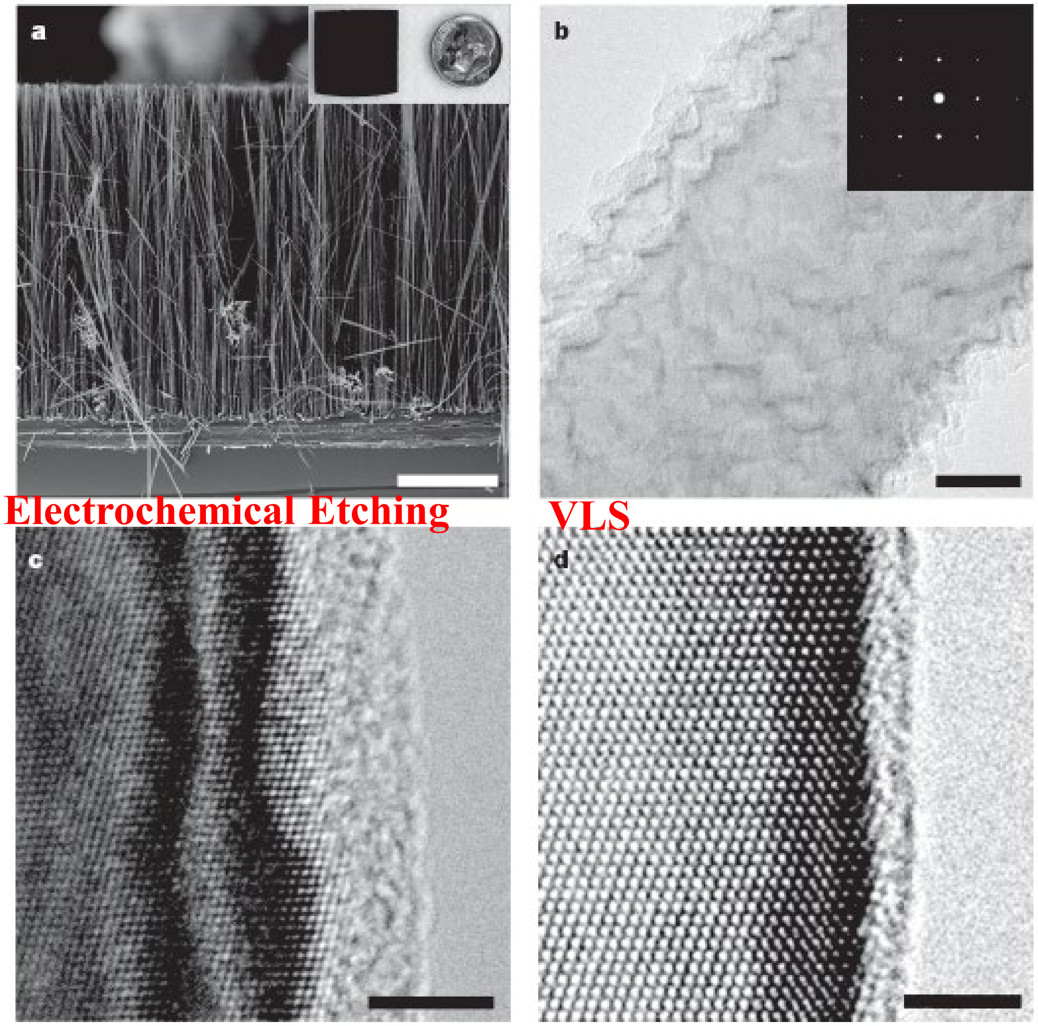
- Increased phonon-boundary scattering
- Modified phonon dispersion

→ Suppressed thermal conductivity

Ref: Chen and Shakouri, *J. Heat Transfer* **124**, 242

Rough Silicon Nanowire for Thermoelectric Cooling?



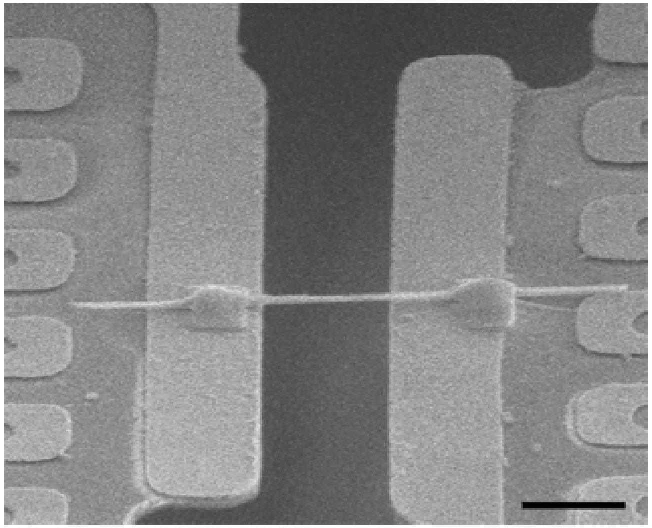


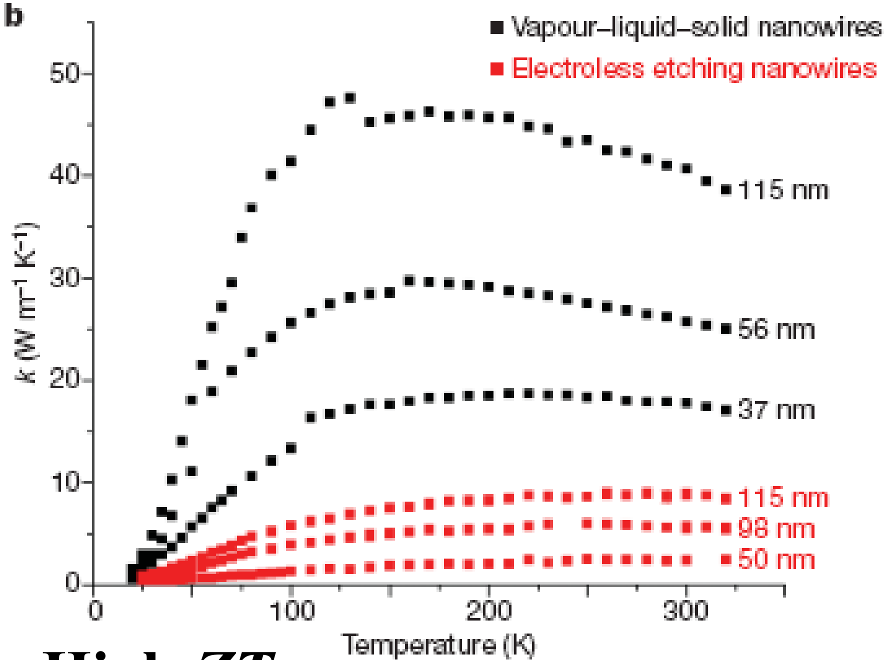
- Thermoelectric effects

Issues: Low figure of merit (ZT) such that low energy transfer efficiency

- Rough silicon nanowires for thermoelectric cooling? (Nature, Vol. 451, pp163-165, 2008)

Why Nanowires?





1. **High surface area**
2. **Low thermal conductivity for High *ZT* = *S*² σ*T*/*k***

Issues

1. **Which material is best for this?**
2. **How to grow these nanowires?**
3. **Problems?**

Plans & Discussions

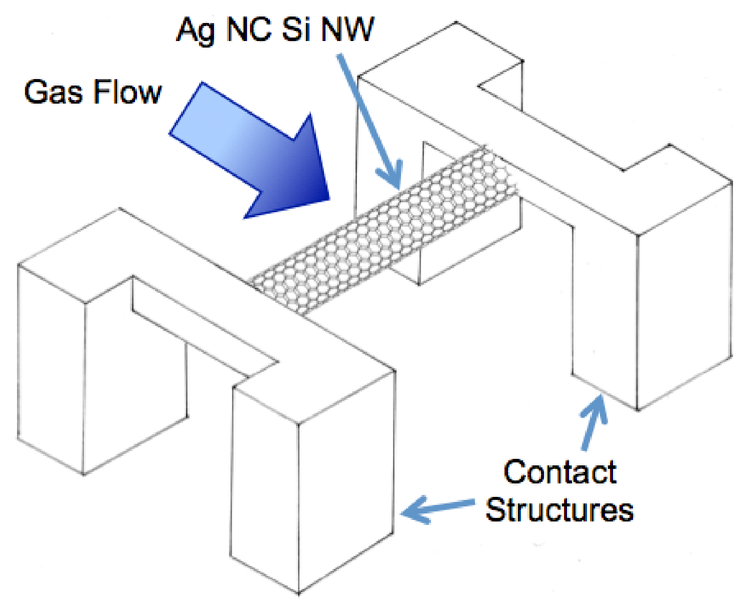
- Small Project – due 3/21/2023 (before the Spring Break) – one-page ppt slide due at bcourse. You will present you project during the lectures of 3/14 & 3/19

Example for 1-page Slides

Silver Nanocrystal functionalized Silicon Nanowire Hot Wire Ammonia Detector

(AgNcSiNWHW NH3 Detector)

- A portable, non-invasive, near-instantaneous measure of kidney function
- NH3 is filtered out of blood by kidneys
  - concentration of NH3 in exhaled by patient can indicate kidney function
- Cui et al. *Fast and Selective Room-Temperature Ammonia Sensors* (2012)
  - Functionalized CNTs
  - Alignment via E-field
- Propose:
  - Functionalized silicon nanowires for increased sensitivity
  - Localized heating growth method for ease of fabrication
  - Packaged as a hand-held device

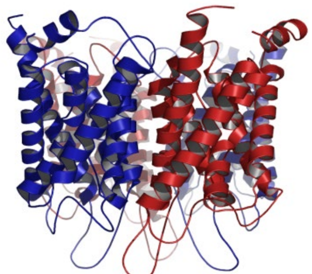


Process for Synthesizing Protein-Mimicking, End-Linked SWCNT Chains and Measuring their Enthalpy of Folding

Joshua Price
ME 118 Proposal
March 23, 2017

Motivation:

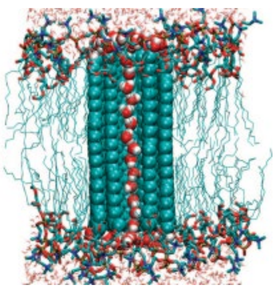
aquaporin protein



From Wikipedia

mimicked function

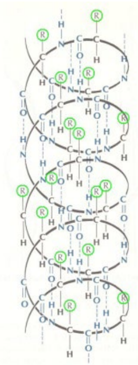
CNT-based artificial aquaporin



Liu et al, 2009

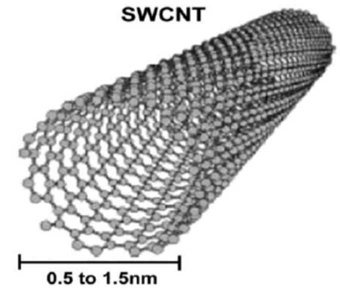
Goal:

Alpha helix: 1.2 nm dia.



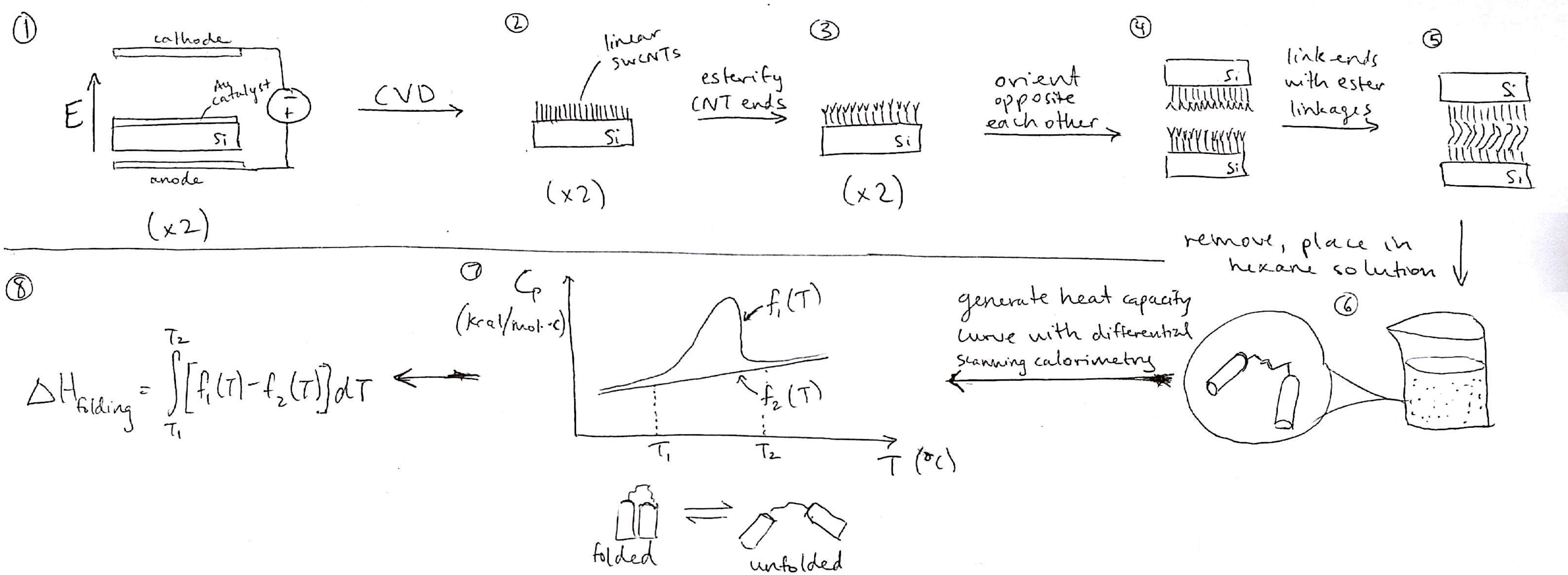
http://www.metafysica.nl/wings/wings_15i.html

Compare linked folding energetics



Malhotra et al, 2015

Process Flow:



Grappling Gecko Gloves

Jason Becker

- Geckos' feet are covered in small hair like structures call *setae*
- Gecko fingertips have a total surface area of 227 mm^3 and have been measured to withstand a maximum force of 20.1 N [1]
- Corresponds to an adhesive force of $10^{-4}\ \frac{nN}{nm^2}$
- Artificial nanoscale adhesives with adhesive force of $1.6 \pm 0.5 \times 10^{-2}\ \frac{nN}{nm^2}$ have been developed [2]
- Amounts to over 2000 times required adhesion to support human weight
- CVD used to grow nanotubes, which are subsequently embedded and stabilized in PMMA matrix

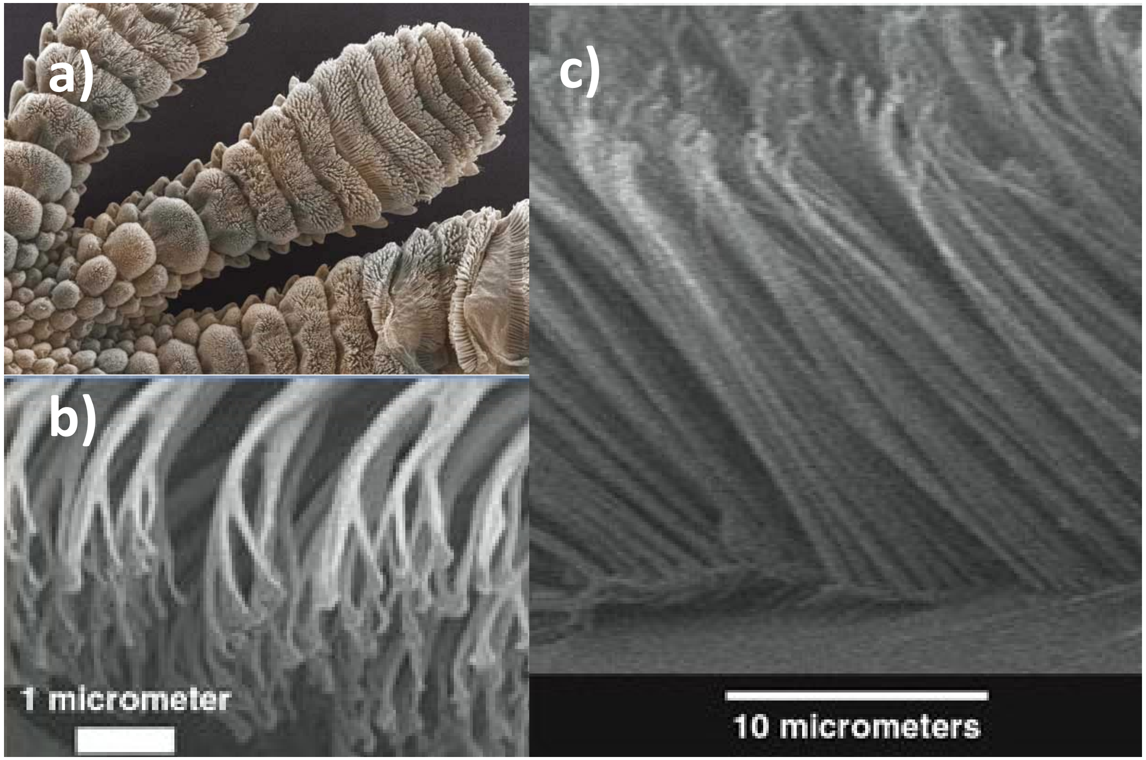


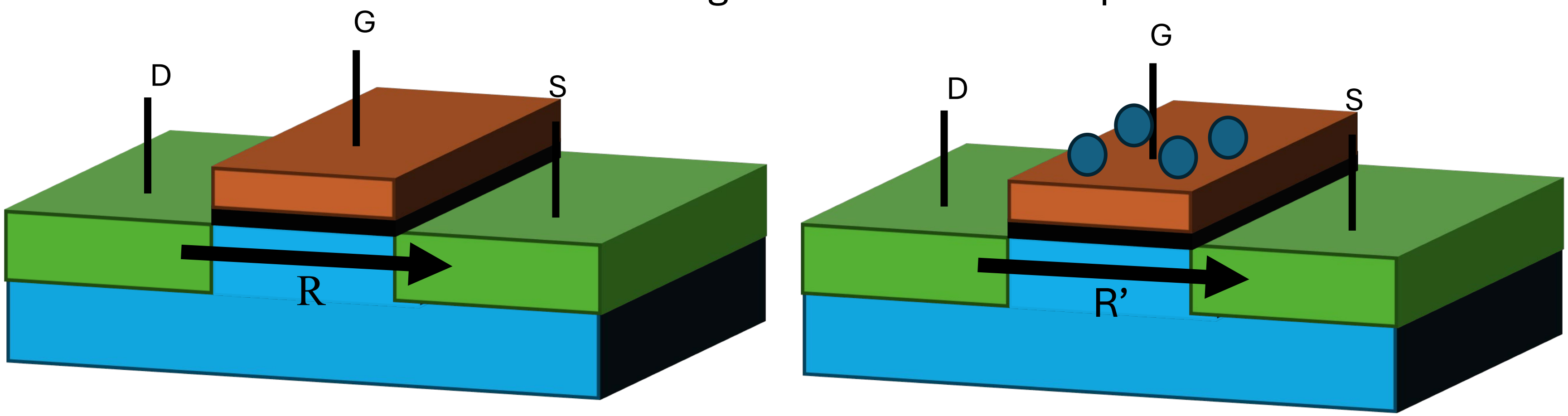
Figure 1. Scanning electron micrographs of a) tokay gecko toes, b) higher magnification of tokay gecko toes, and c) artificially made nanoscale adhesives [1].

1. Autumn, K., *How gecko toes stick - The powerful, fantastic adhesive used by geckos is made of nanoscale hairs that engage tiny forces, inspiring envy among human imitators.* American Scientist, 2006. **94**(2): p. 124-132.
2. Yurdumakan, B., et al., *Synthetic gecko foot-hairs from multiwalled carbon nanotubes.* Chemical Communications, 2005(30): p. 3799-3801.

Paper 6

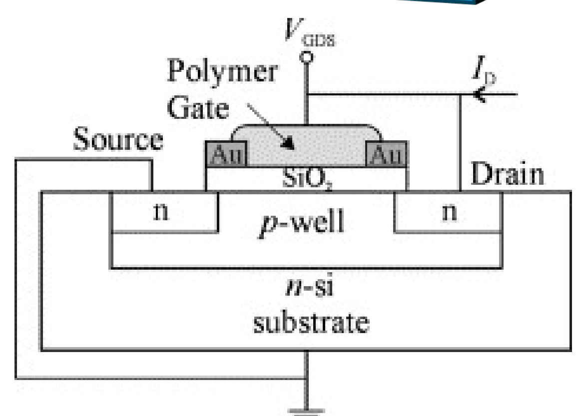
Nanowire Nanosensors for Highly Sensitive and Selective Detection of Biological and Chemical Species

Vasileios



Change in R due to:

- Solubility of species into gate changes geometry
- Partial charge transfer from species to gate
- both



A polymer gate FET sensor array for detecting organic vapours, J.A Covington et Al
FET-type gas sensors: A review, Seongbin Hong

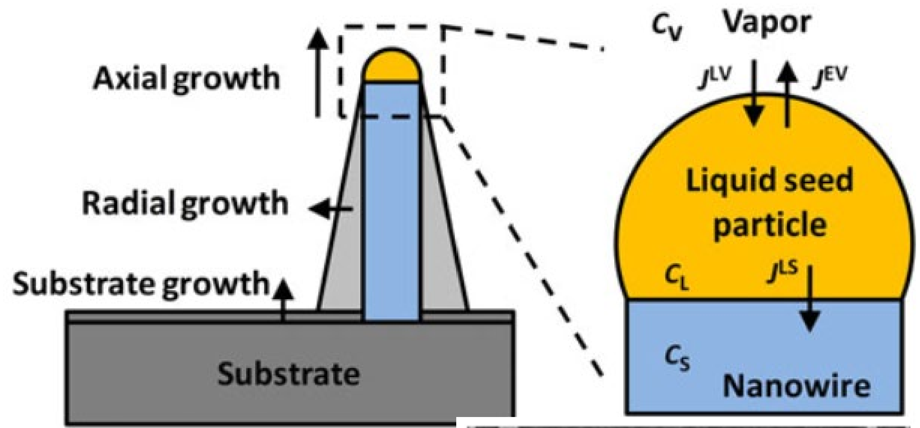
NW FET

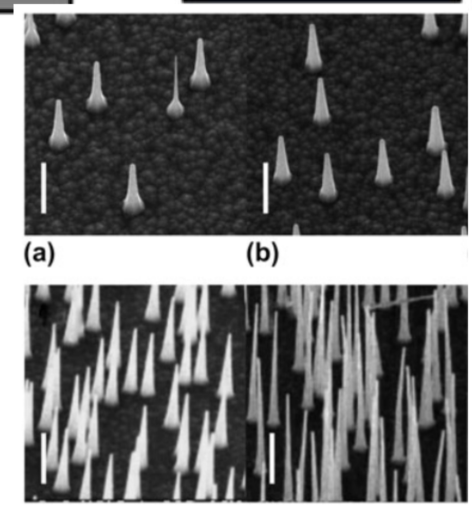
Vasileios

1. Easy to control diameter
2. Easy to dope
3. Easy to functionalize

4. Si based NW benefit from semiconductor knowledge base

Robust manufacturing





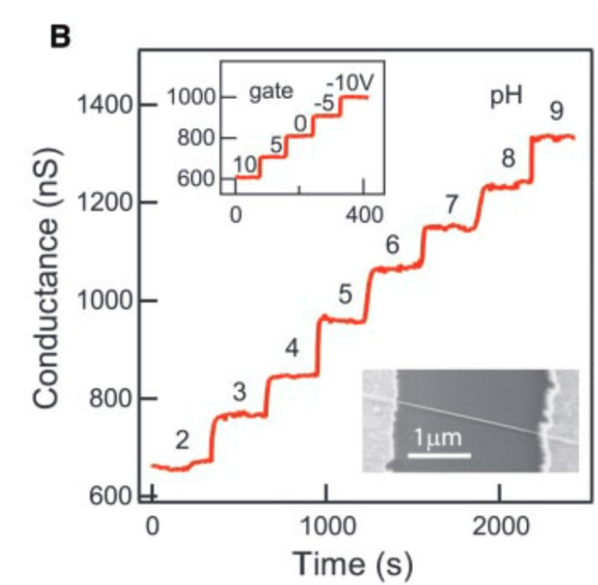
Doping of semiconductor nanowires, Jesper Wallentin et al.

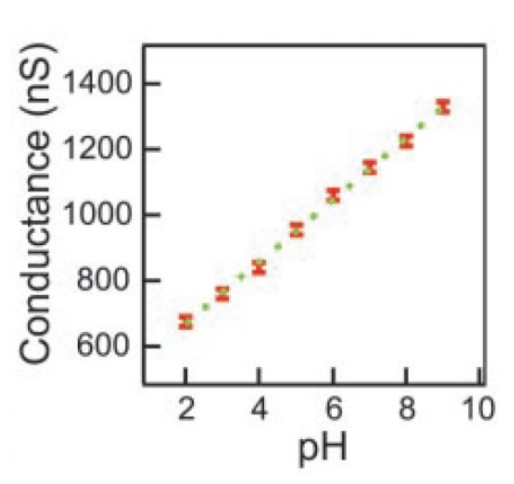
Experimental set-up

- Nanosensor formed by modifying the silcon oxide surface of a silicon nanowire (SiNW) solid state FET with 3-aminopropyltri-ethoxysilane (APTES)
- Changes in surface charge undergoing protonization or deprotonization will chemically gate the SiNW
- SiNWs are prepared by a nanocluster-mediated vapor-liquid-solid growth method
- Devices are fashioned by flow aligning SiNWs on oxidized silicon substrates
- Ohmic electrical contacts to the NW ends by using electron-beam lithography
- The Conductance (dI/dV) versus gate voltage is nearly linear

The response of the conductance to changes in solution pH

- Evaluated by the use of a cell comprised of a microfluidic channel established between a poly(dimethylsiloxane) (PDMS) mold and the SiNW/substrate
- Nanowire conductance is linear over the pH range from 2 to 9

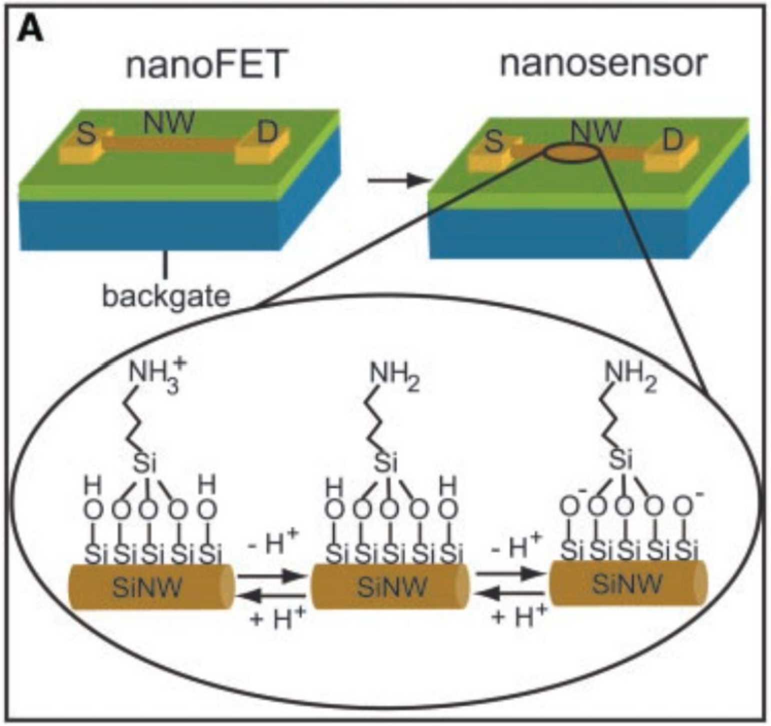




Interpretation

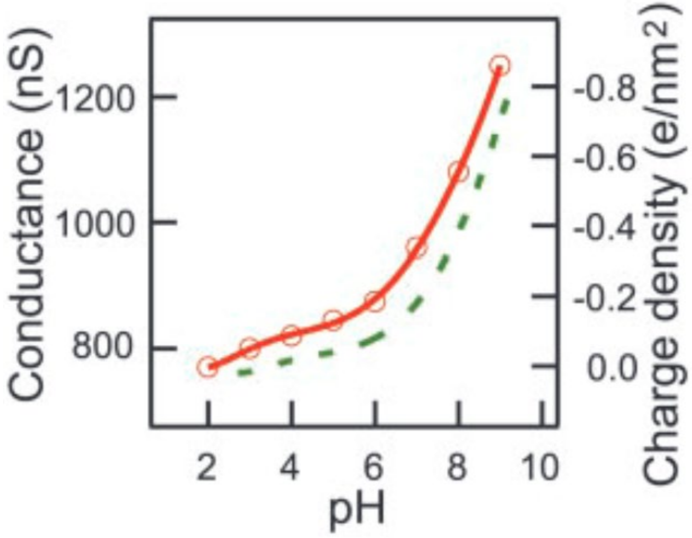
- Termination of $-NH_2$ and $-SiOH$ groups (due to the linking of APTES to the SiNW oxide surface)
- Low pH:
  - -NH_2protonates to NH_3^+
  - Acts as a positive gate
  - Deplets hole carriers in the p-type SiNW
  - Decreases the conductance
- High pH:
  - -$SiOH$ deprotonates to SiO^-
  - Increases the conductance

- Linear response due to an approximately linear change in the total surface charge density



Also supported by measurements on unmodifed SiNWs

- Here the conductance shows a nonlinear pH dependence.
- In agreement with previous measurements of the pH-dependent surface charge density derived from silica

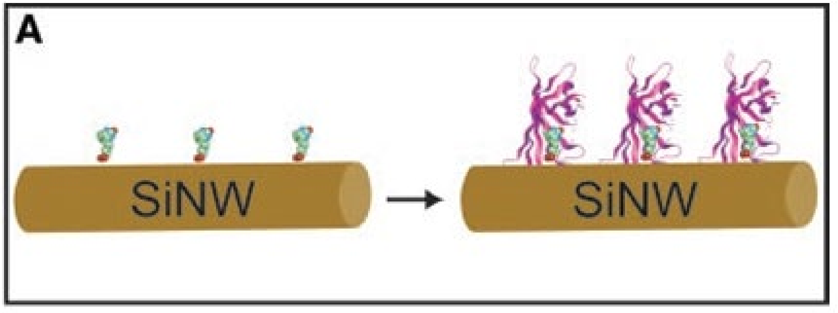


Functionalization of SiNWs with biotin

- Functionalized SiNWs with biotin-streptavidin and studied the well-characterized ligand-receptor binding of biotin-streptavidin
- Condunctance increases rapdily upon addition of a 250 nM streptavidin solution to a constant value (binding of the negatively charged streptavidin species to the p-type SiNW surface)
- Conductance maintained after the addition of pure buffer solution (small dissociation rate for biotin-streptavidin)

Control Experiments

- If changes in conductance for biotin-modified SiNWs were only because of interactions between biotin and streptavidin



Control Tests

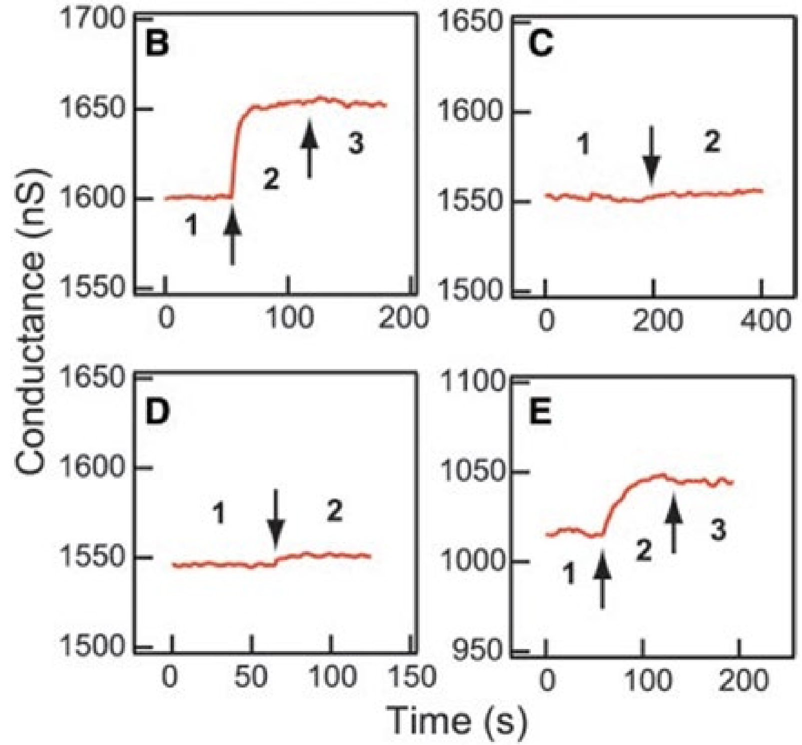
B) BiotinSiNW > 250 nM Streptavidin > Pure Buffer

C) Just SiNW > 250 nM Streptavidin > Pure Buffer

D) Biotin SiNW > Streptavidin that's already

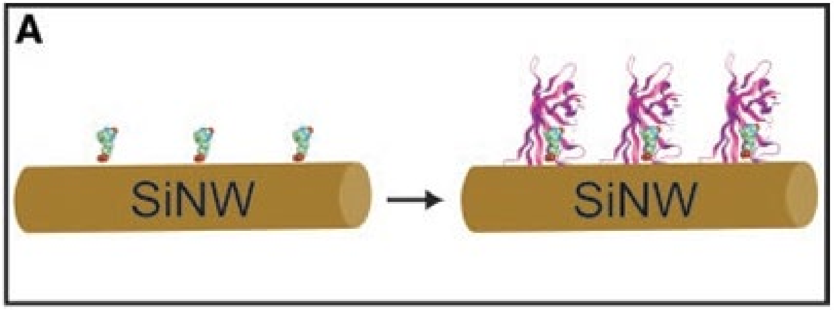
binded to biotion > Pure Buffer

E) BiotinSiNW > 25 pM Streptavidin > Pure Buffer



Problems

- If biotin-modified nanowire is binded before the experiment, then there will be no change in conductance
- Reversible binding of monoclonal antibiotin (m-antibiotin) with biotin



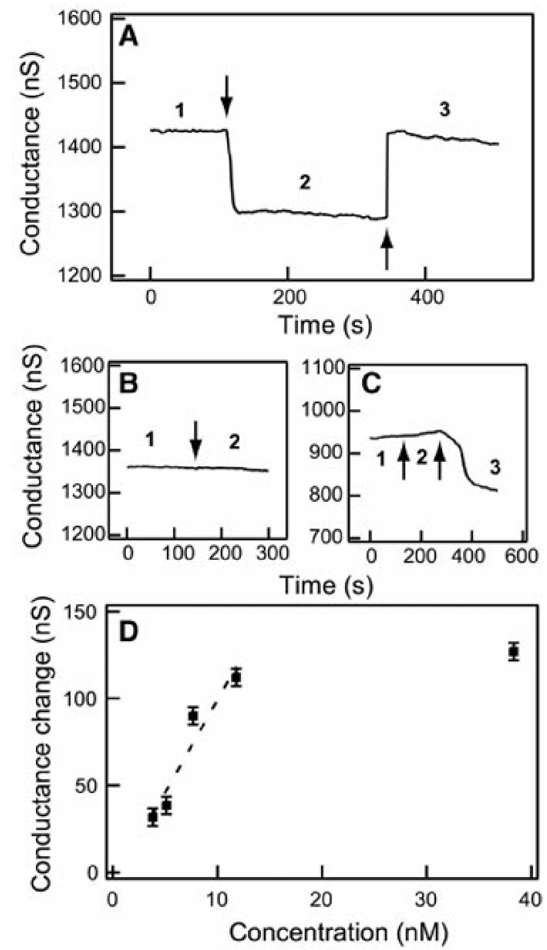
m-Antibiotin Test

A) BiotinSiNW > 3 μM m-antibiotin > Pure Buffer

B) Just SiNW > 3 μM m-antibiotin > Pure Buffer

C) Biotin SiNW > bovine IgG > 3 μM m-antibiotin

D) BiotinSiNW > Different m-antibiotin concentrations

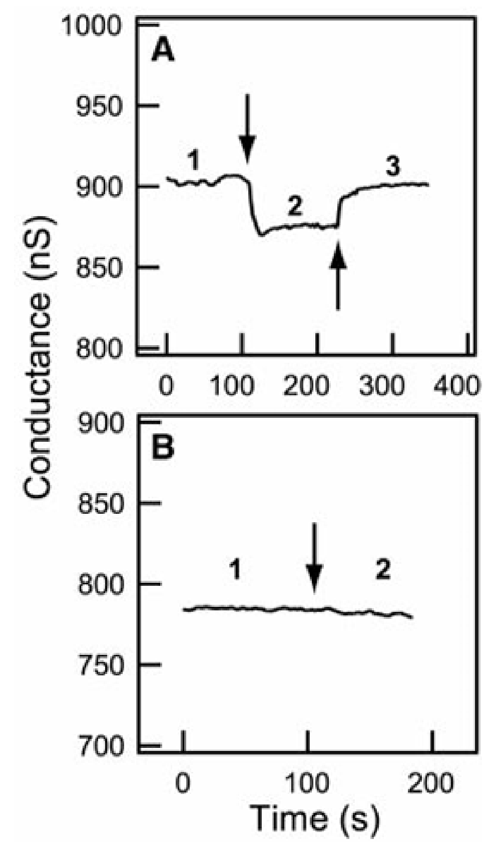


Ca^{2+} Test

A) Calmodulin-Terminated SiNW > 25 μM Ca^{2+} > Pure Buffer

B) Just SiNW > 25 μM Ca^{2+} > Pure Buffer

Conclusion: Nanowire sensors can also calcium ions



Nanowire Nanolasers

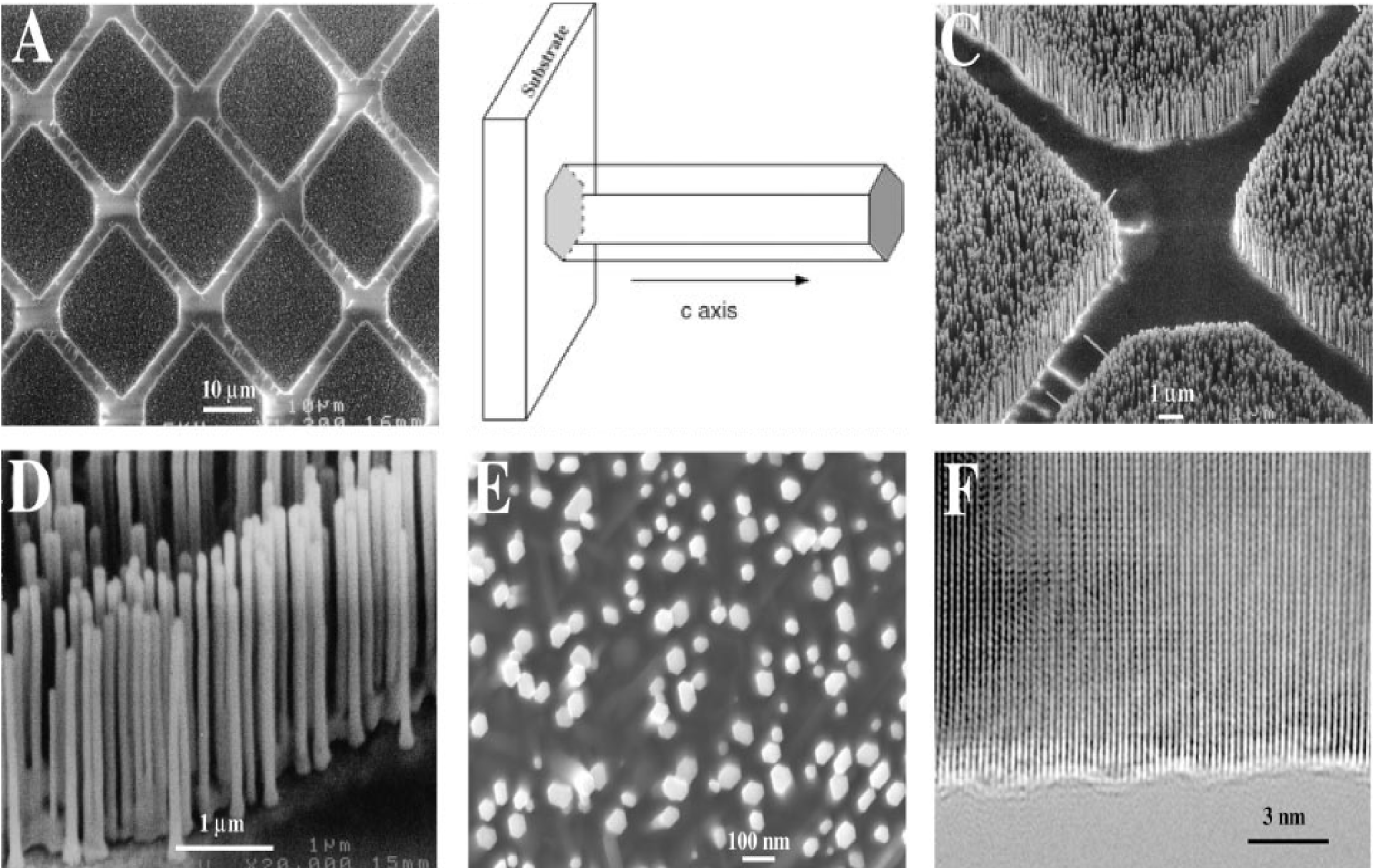
REPORTS

Room-Temperature Ultraviolet Nanowire Nanolasers

Michael H. Huang,[1] Samuel Mao,[2] Henning Feick,[3] Haoquan Yan,[1] Yiying Wu,[1] Hannes Kind,[1] Eicke Weber,[3] Richard Russo,[2] Peidong Yang[1,3]*

www.sciencemag.org SCIENCE VOL 292 8 JUNE 2001

“Vertically Aligned”



Nanostructure Synthesis

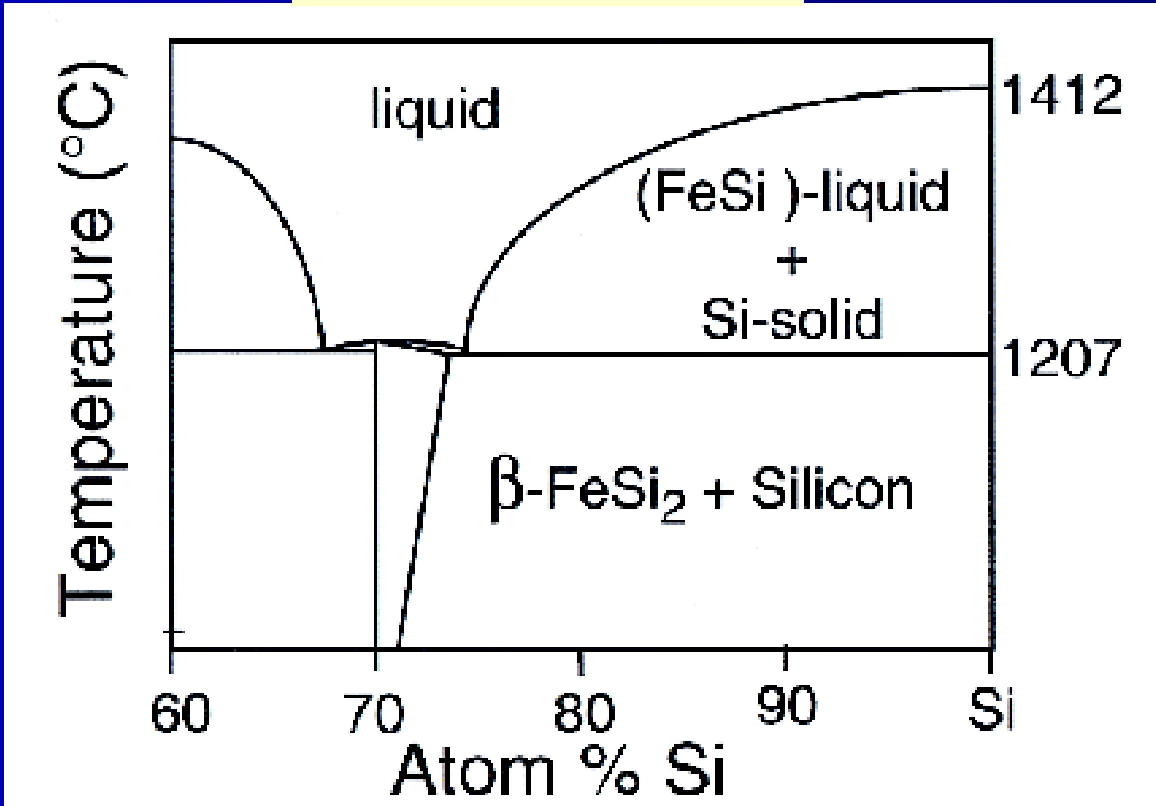
- CVD (Chemical Vapor Deposition) with VLS (Vapor-Liquid-Solid) growth
- Silane (SiH_4) - *vapor* phase reactant
- Gold-Palladium (AuPd) - *solid* phase, metal catalyst
- Silicon from the thermal decomposition of silane and AuPd form a *liquid* alloy at the eutectic temperature of AuPd-Si (high temperature)

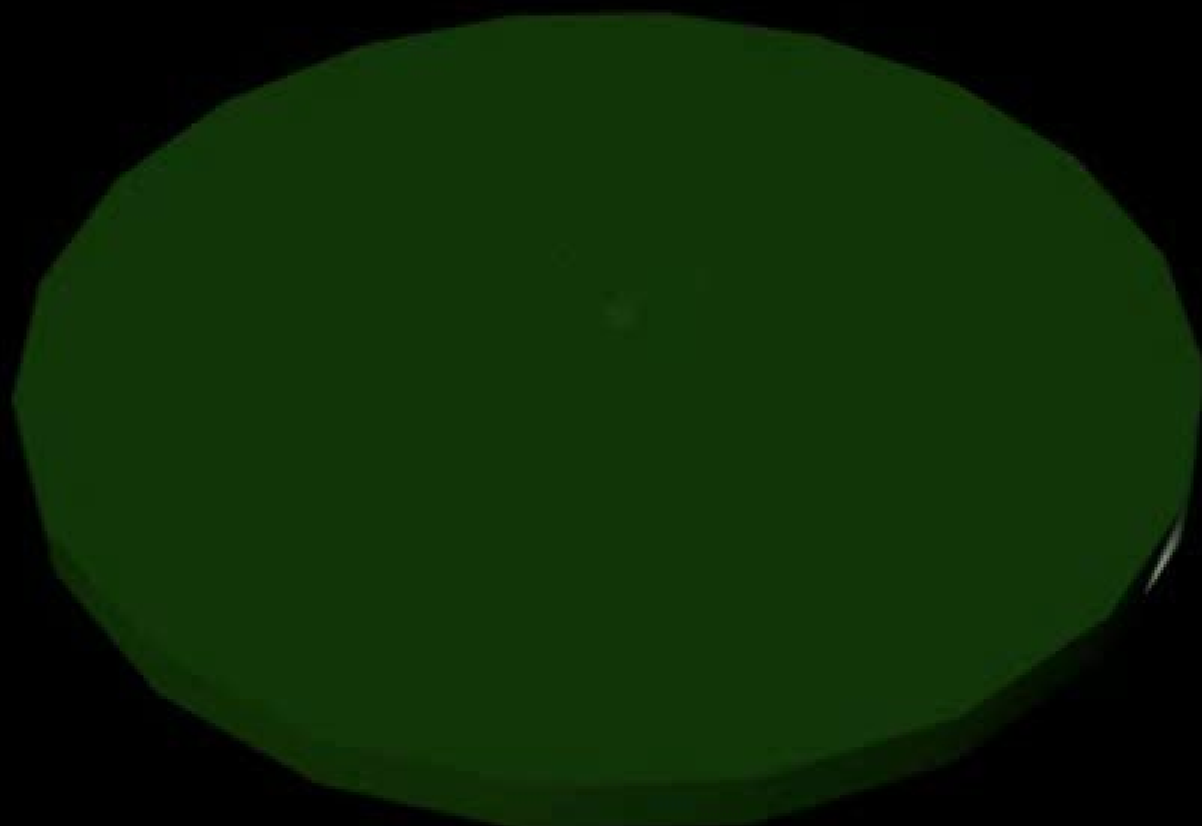
BSAC

Vapor-Liquid-Solid Growth

- σ_{LV} is the liquid-vapor interface free energy, V_L is the molar volume of the liquid, σ is the vapor phase of super-saturation, R is the gas constant and T is the temperature
- Competing conditions: energy gain of condensation and the energy cost in the interfacial energy
- Equilibrium conditions results in nanowires of order 100 nm or larger

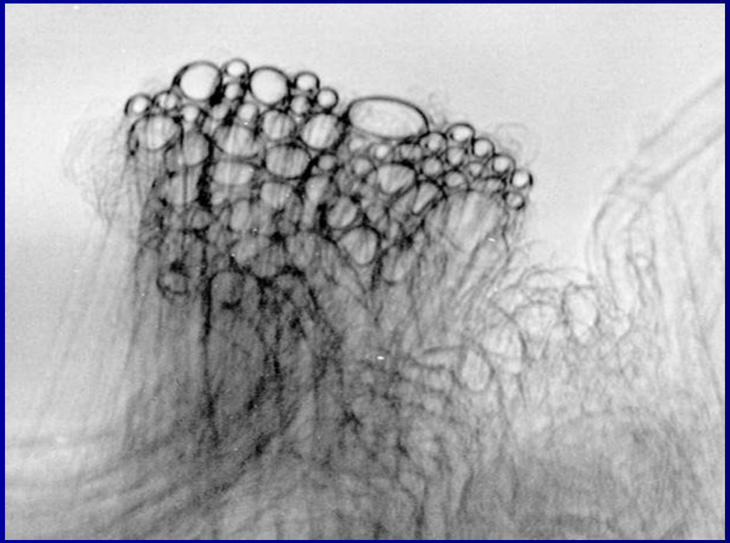
$$r_{\min} = \frac{2\sigma_{LV} V_L}{RT \ln \sigma}$$

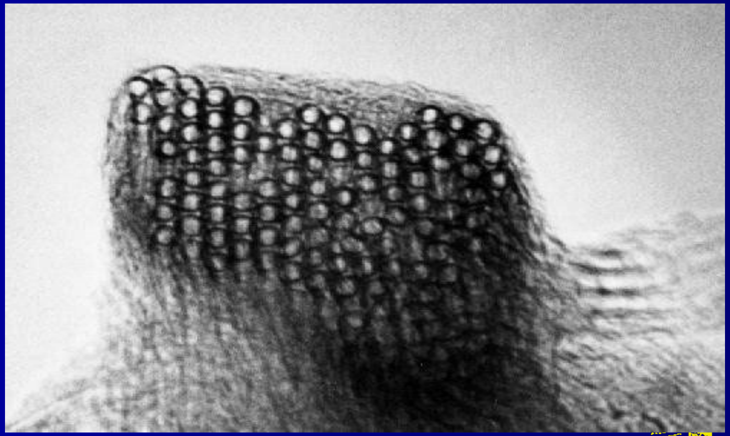




CNTs Synthesis Methods

- Arc Discharge Method
  - Uniform Diameters
  - Fewest Defects
  - SW or MWNTs
  - Highest quality
- Gaseous, Laser-Vaporization, Pyrolysis, other CVD
- Require **high temperature** chamber

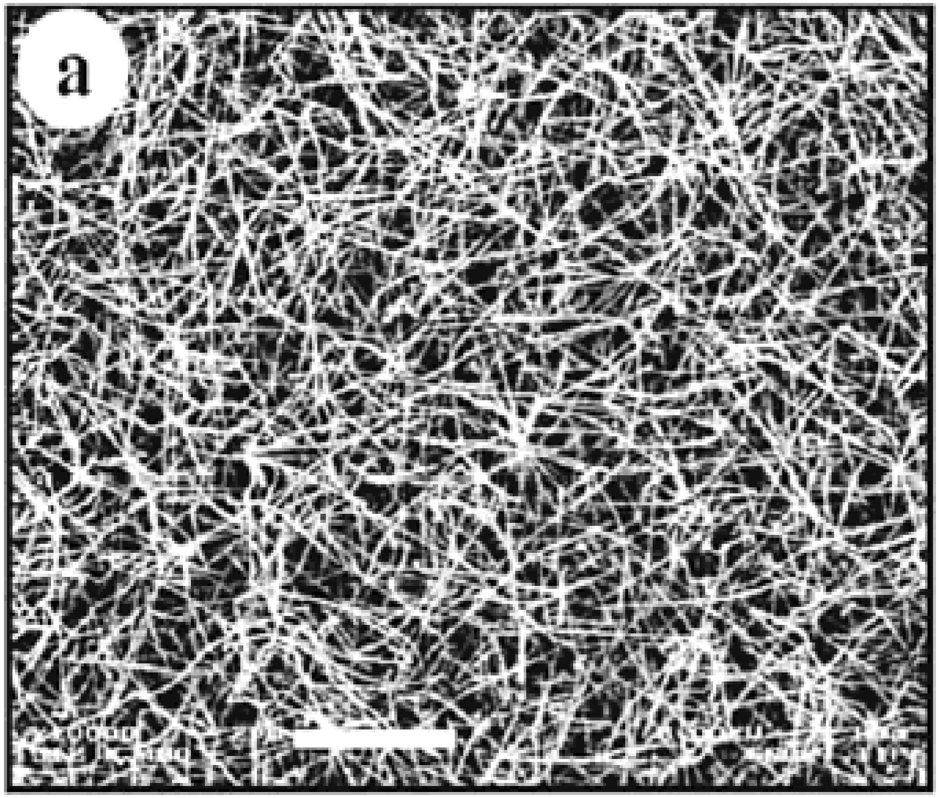


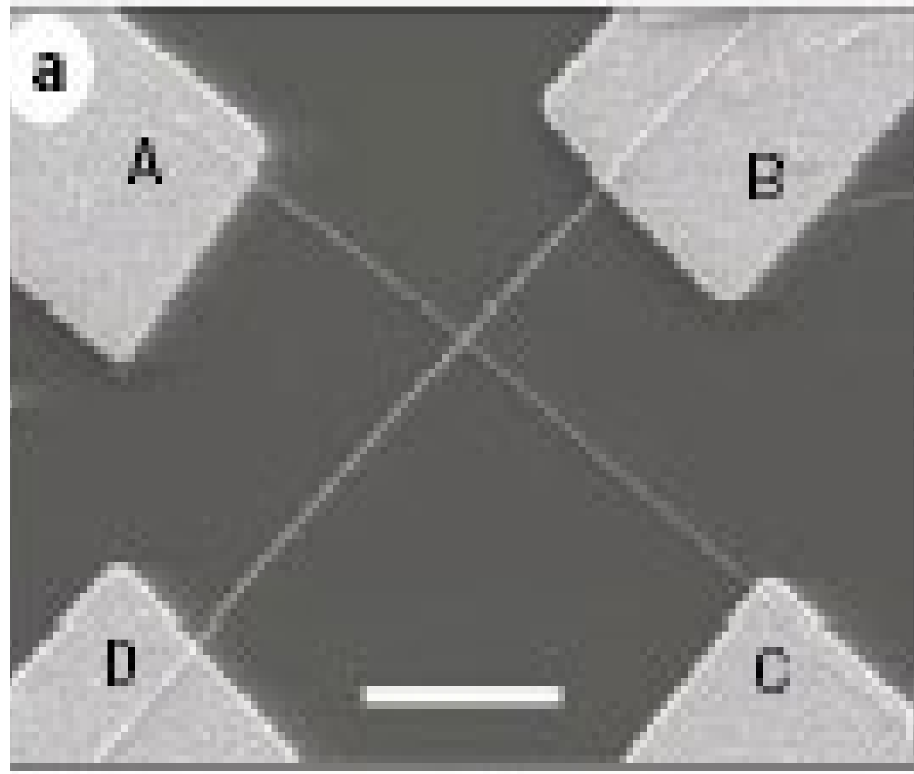


(Smalley Image Gallery)

BSAC

Nanoscale Assembly

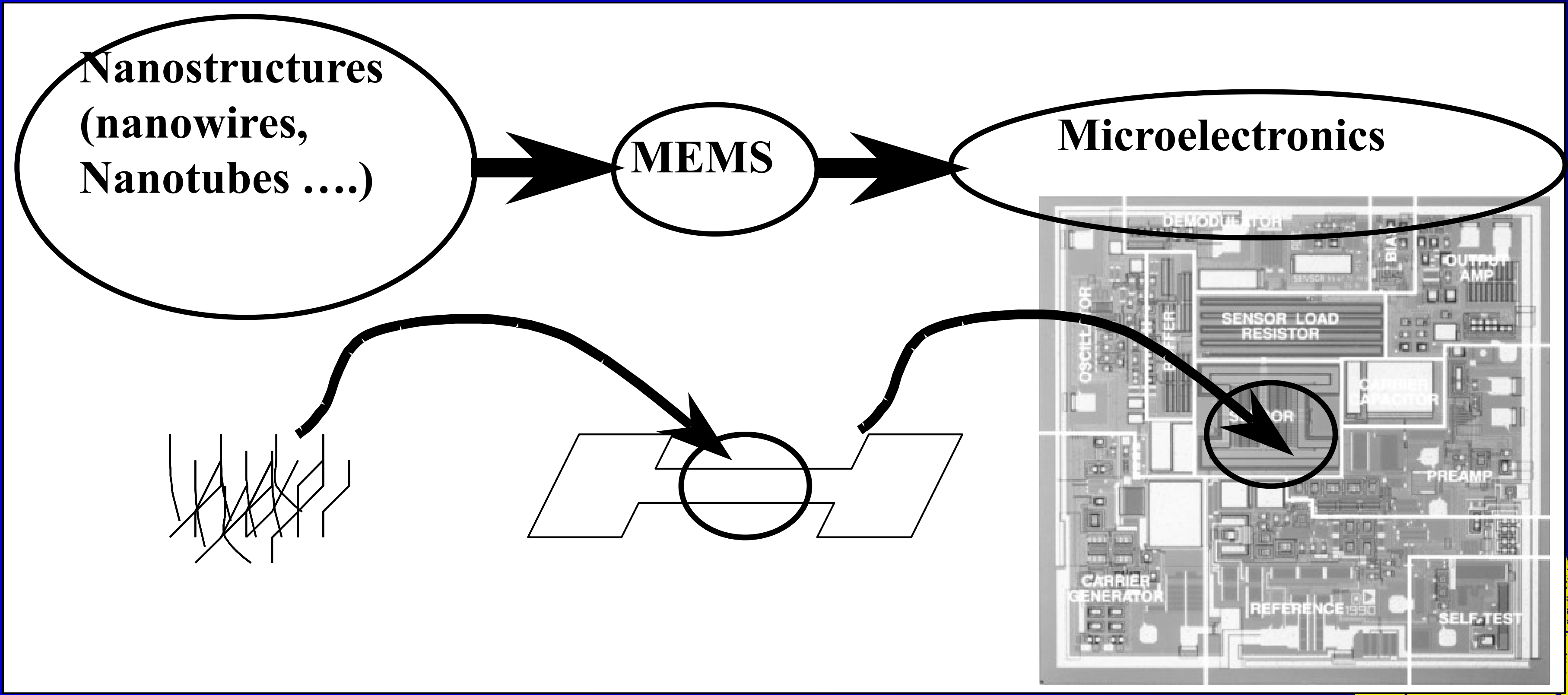




- **Synthesis** in **high temperature** tubes
- **Fluidic** self-**assembly**
- **Focus-Ion-Beam or E-beam for serial bonding**

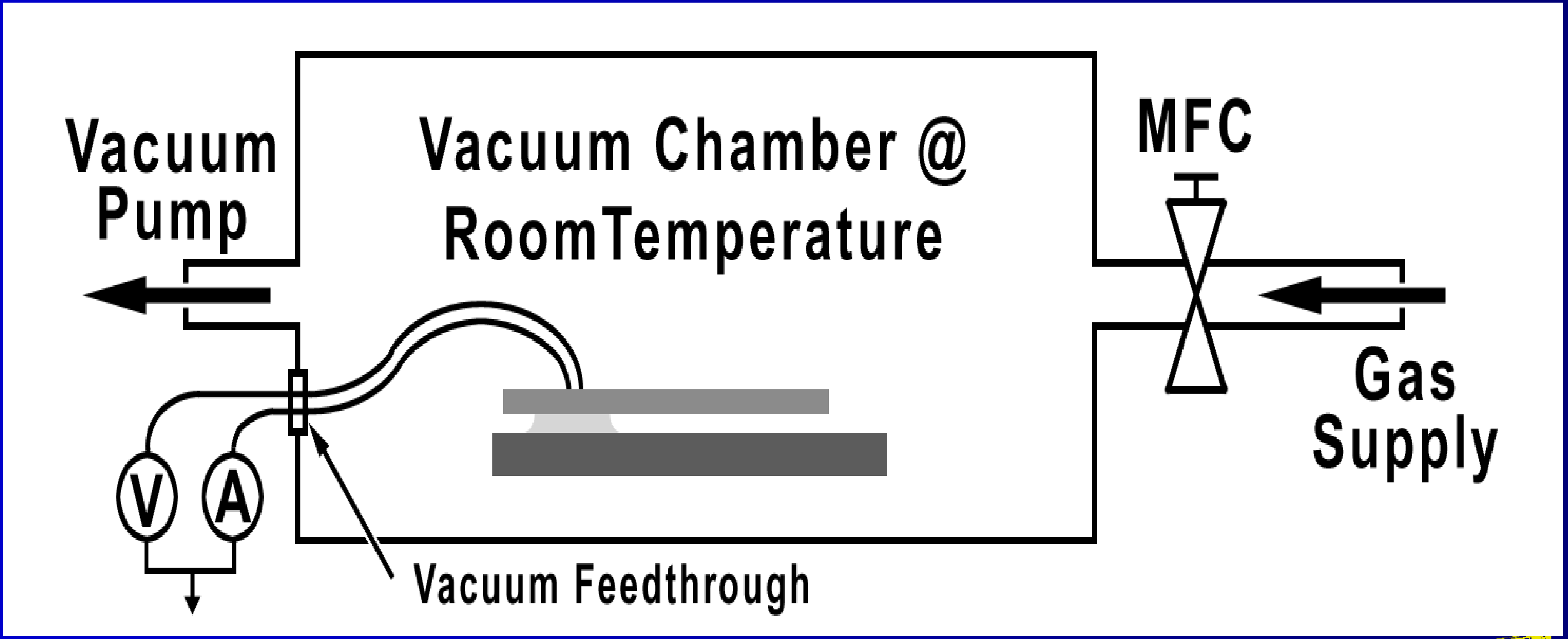
Our Approach

- **Post-CMOS**, **site-specific** **synthesis**, **assembly** and **bonding** using **MEMS** as the "**bridge**"
- **Nano + MEMS + Microelectronics** with on-chip process control and sensing microelectronics



Room Temperature Chamber

- CMOS-compatible nanostructures
- Site-specific CVD activated by resistive heating



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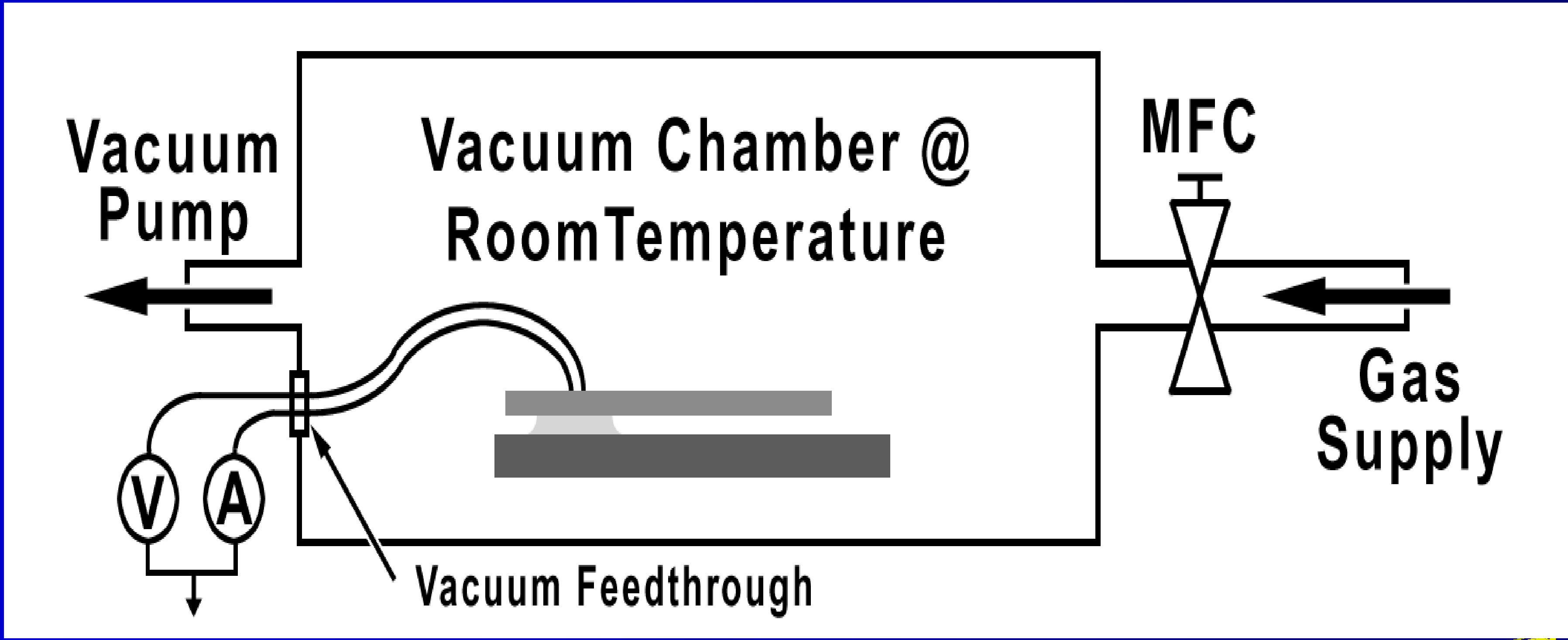
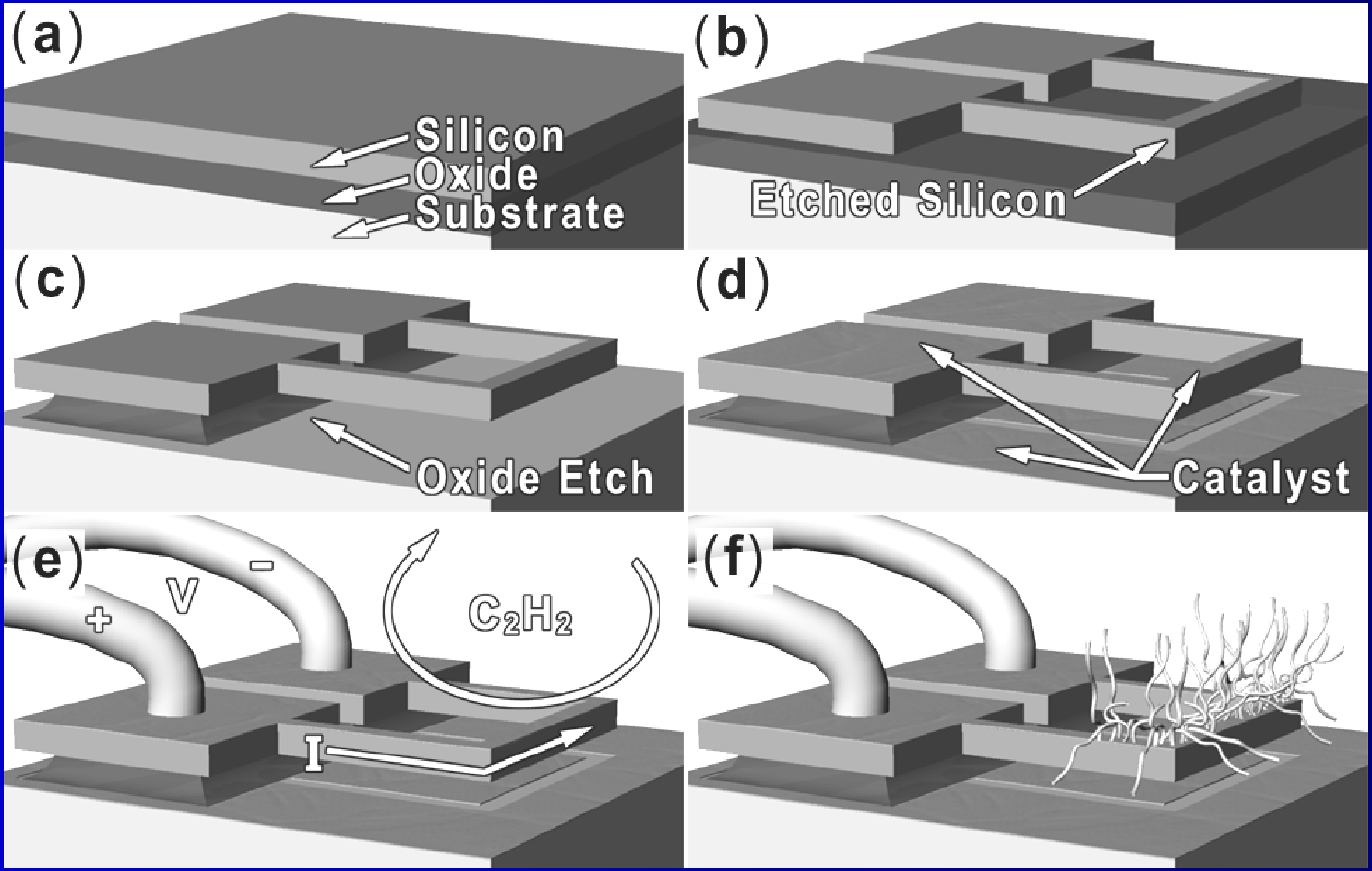
Room Temperature Chamber

- CMOS-compatible nanostructures
- Site-specific CVD activated by resistive heating



One-Mask Process



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Silicon Nanowires – 1st Demo