# Introduction to Nanotechnology and Nanoscience – Class#16

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# Outline

- Small Project
- Nanowire Synthesis
- Nanowire Integration and Assembly
- Paper 6-1

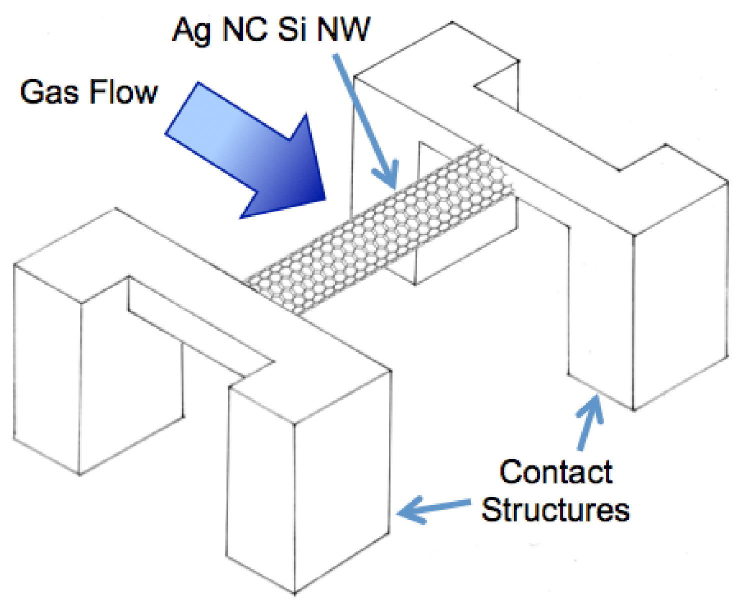
# Six Key Questions Ahead of Biden's State of the Union

# 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

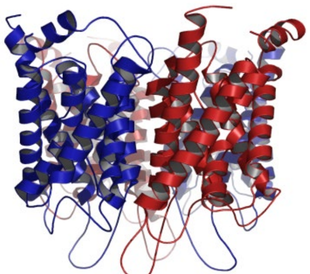


# Process for Synthesizing Protein-Mimicking, End-Linked SWCNT Chains and Measuring their Enthalpy of Folding

**Joshua Price**
**ME 118 Proposal**
**March 23, 2017**

## Motivation:

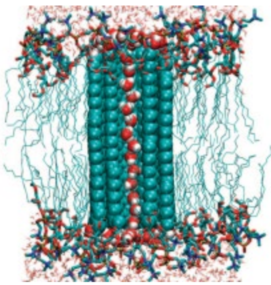
aquaporin protein



From Wikipedia

mimicked function

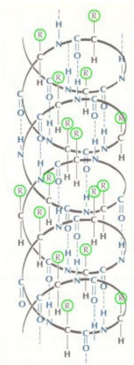
CNT-based artificial aquaporin



Liu et al, 2009

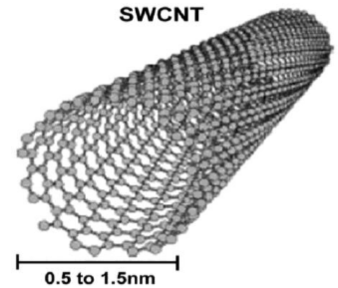
## Goal:

Alpha helix: 1.2 nm dia.



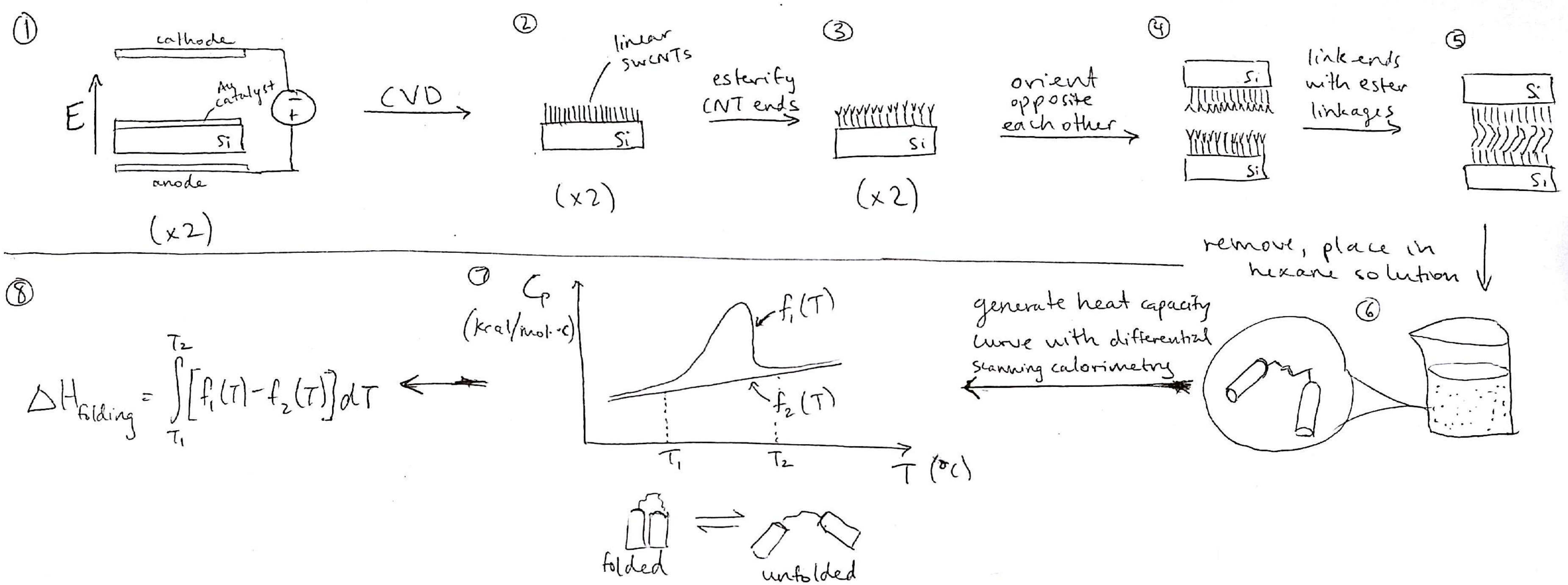
http://www.metafysica.nl/wings/wings_15i.html

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 $10^{-4}\ \frac{\mathrm{nN}}{\mathrm{nm}^2}$
- Artificial nanoscale adhesives with adhesive force of $1.6 \pm 0.5 \times 10^{-2}$ $\frac{\mathrm{nN}}{\mathrm{nm}^2}$ 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

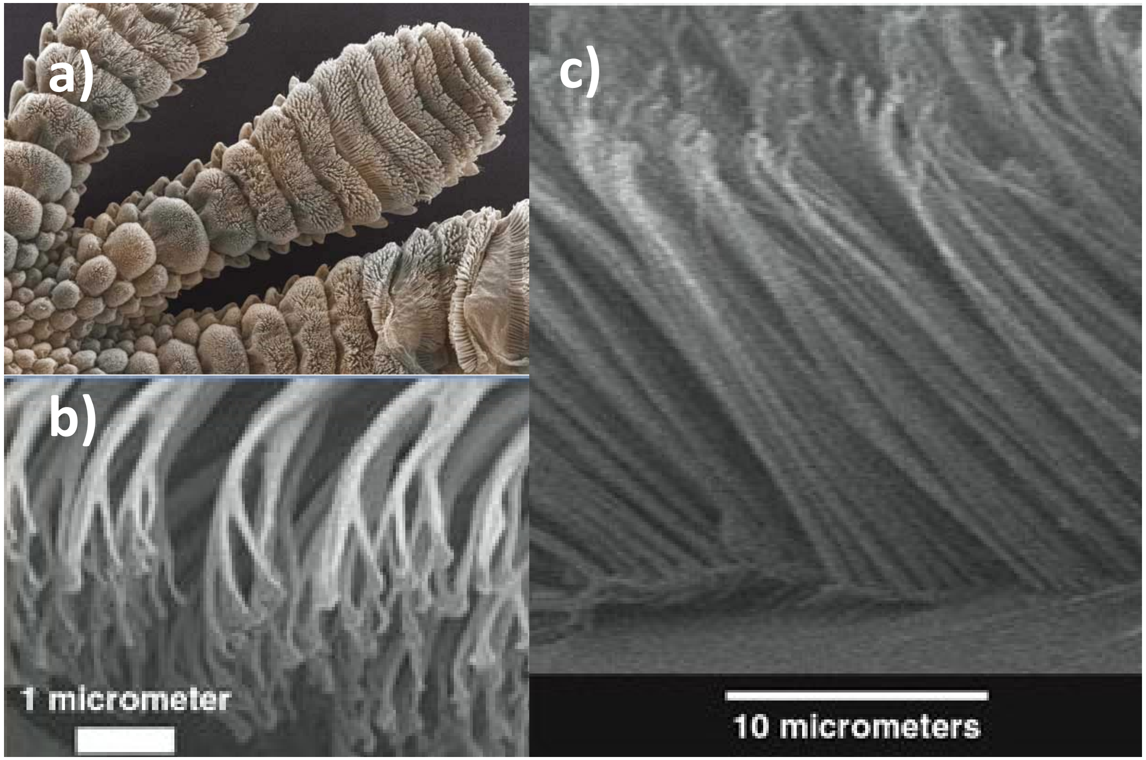
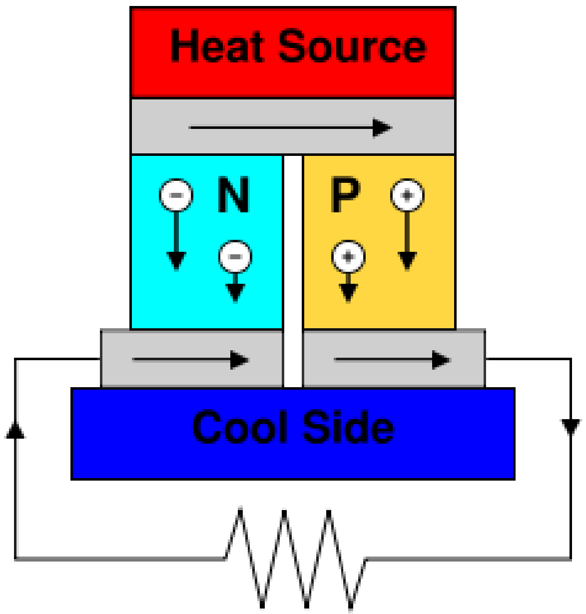



**Figure 1.** Scanning electron micrographs of a) tokay gecko toes, b) higher magnification of tokay gecko toes, and c) artificially made nanoscale adhesives [1].

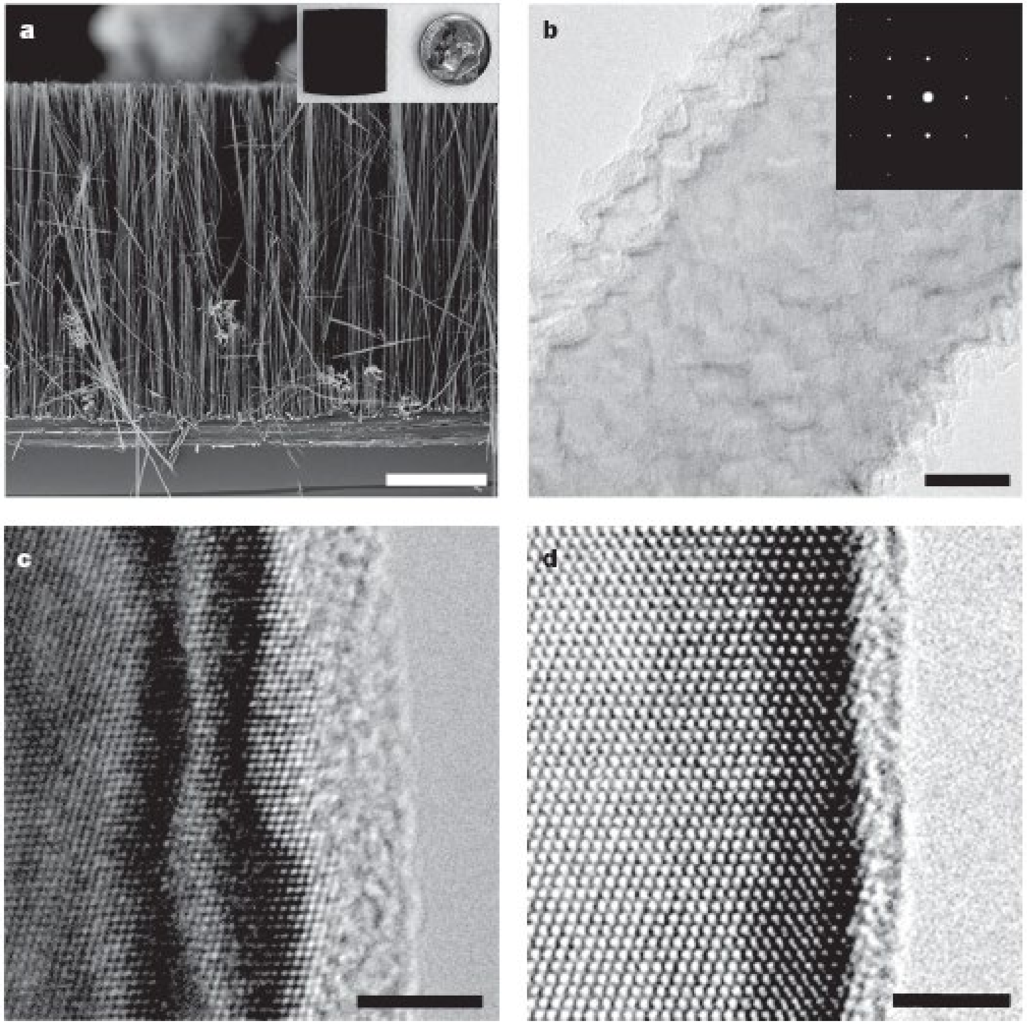

1. Autumn, K., *How gecko toes stick - The powerful, fantastic adhesive used by geckos is made of nanoscale hairs that engage tiny forces, inspiring envy among human imitators.* American Scientist, 2006. **94**(2): p. 124-132.
2. Yurdumakan, B., et al., *Synthetic gecko foot-hairs from multiwalled carbon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

# Rough Silicon Nanowire for Thermoelectric Cooling?



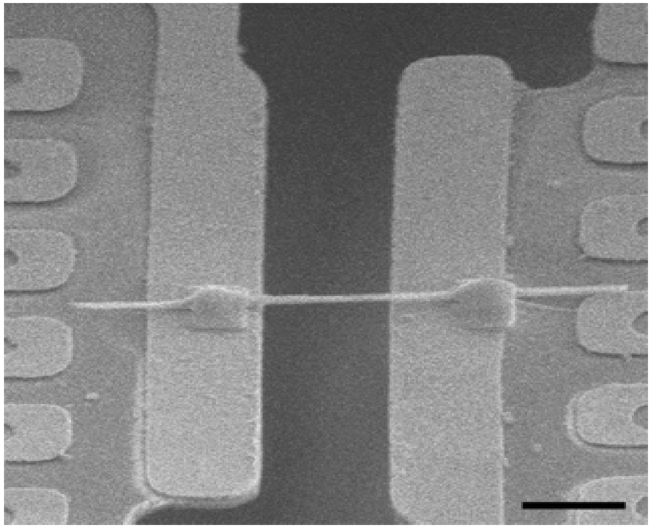

- Thermoelectric effects (my figure)

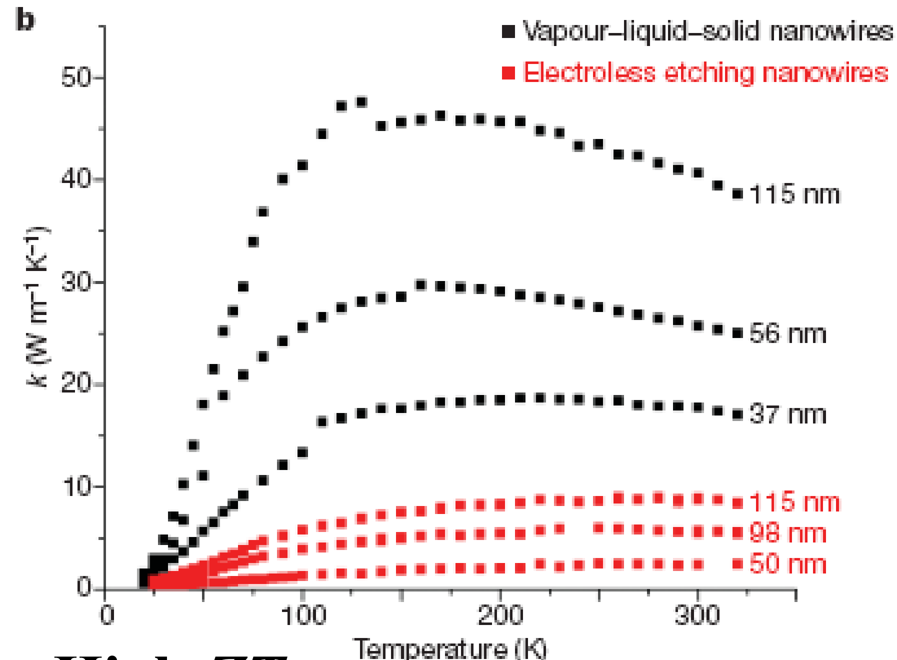
**Issues: Low figure of merit (ZT) such that low energy transfer efficiency**




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

# Why Nanowires?



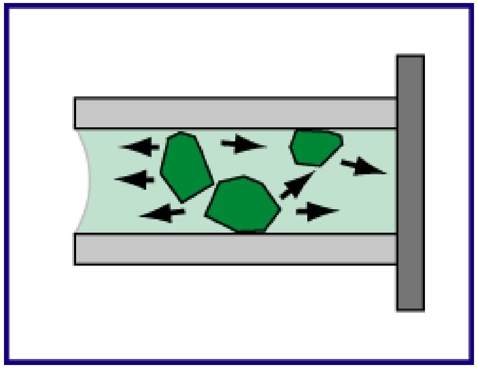



1. **High surface area**
2. **Low thermal conductivity for High $ZT = S^2\sigma T/k$**

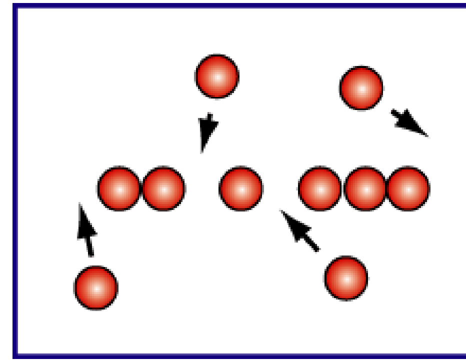
**Issues**

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

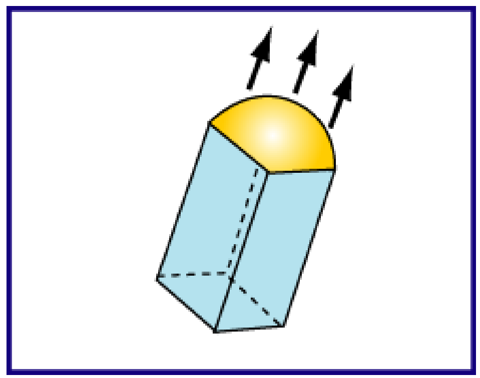
# Nanowire Synthesis - Strategies



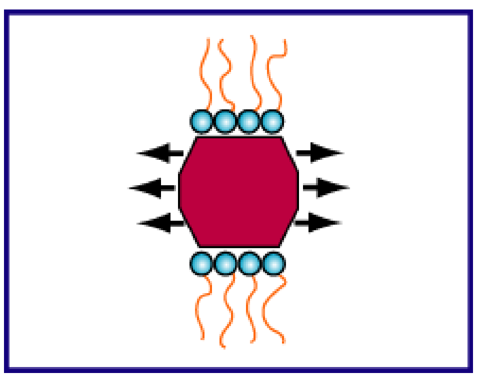
**Template Growth**



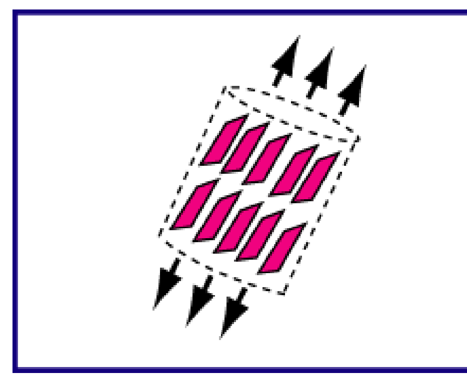
**Self-assembly of 0D**



**VLS (Vapor-Liquid-Solid)**



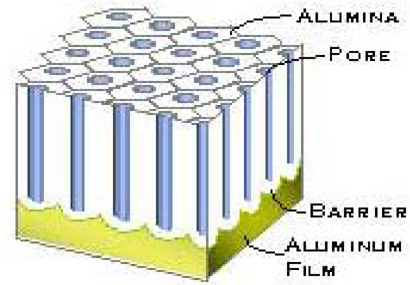
**Capping Control**



**Anisotropic Crystal**

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

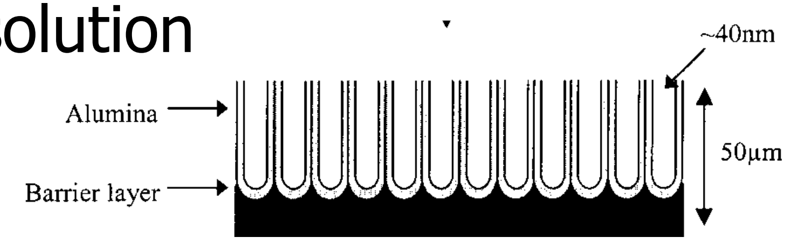
# Template Assisted Growth




- Create a template for nanowires to grow within
- Based on aluminum's unique property of self organized pore arrays as a result of anodization to form alumina ($Al_2O_3$)
- Very high aspect ratios may be achieved
- Pore diameter and pore packing densities are a function of acid strength and voltage in the anodization step
- Pore filling – nanowire formation via various physical and chemical deposition methods

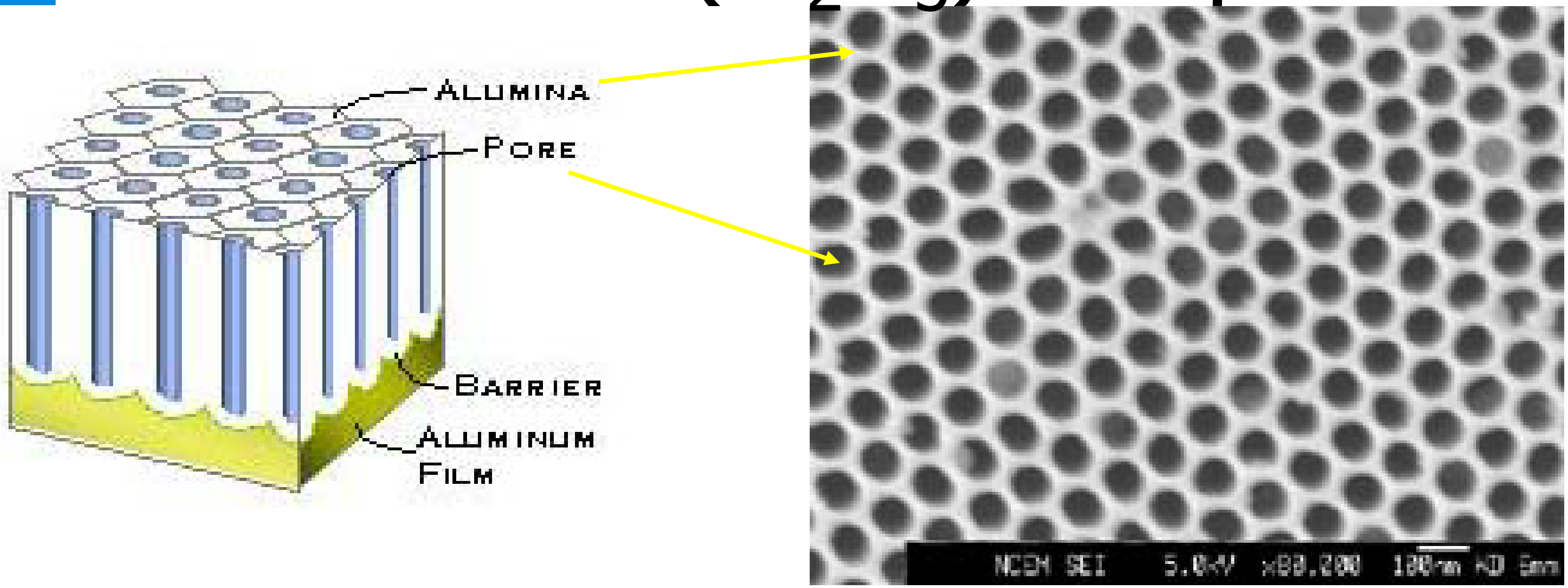
# $Al_2O_3$ Template Preparation

- Anodization of aluminum
- Start with uniform layer of ~1μm Al
- Al serves as the anode, Pt may serve as the cathode, and 0.3M oxalic acid is the electrolytic solution
- Low temperature process (2-5$^0$C)
- 40V is applied




- Anodization time is a function of sample size and distance between anode and cathode
- Key Attributes of the process
  - Pore ordering increases with template thickness – pores are more ordered on bottom of template
  - Process always results in nearly uniform diameter pore, but not always ordered pore arrangement
- Aspect ratios are reduced when process is performed when in contact with substrate (template is ~0.3-3 μm thick)

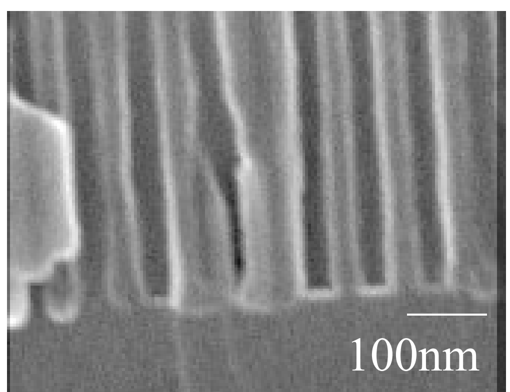
# The Alumina ($Al_2O_3$) Template




(T. Sands/ HEMI group http://www.mse.berkeley.edu/groups/Sands/HEMI/nanoTE.html)

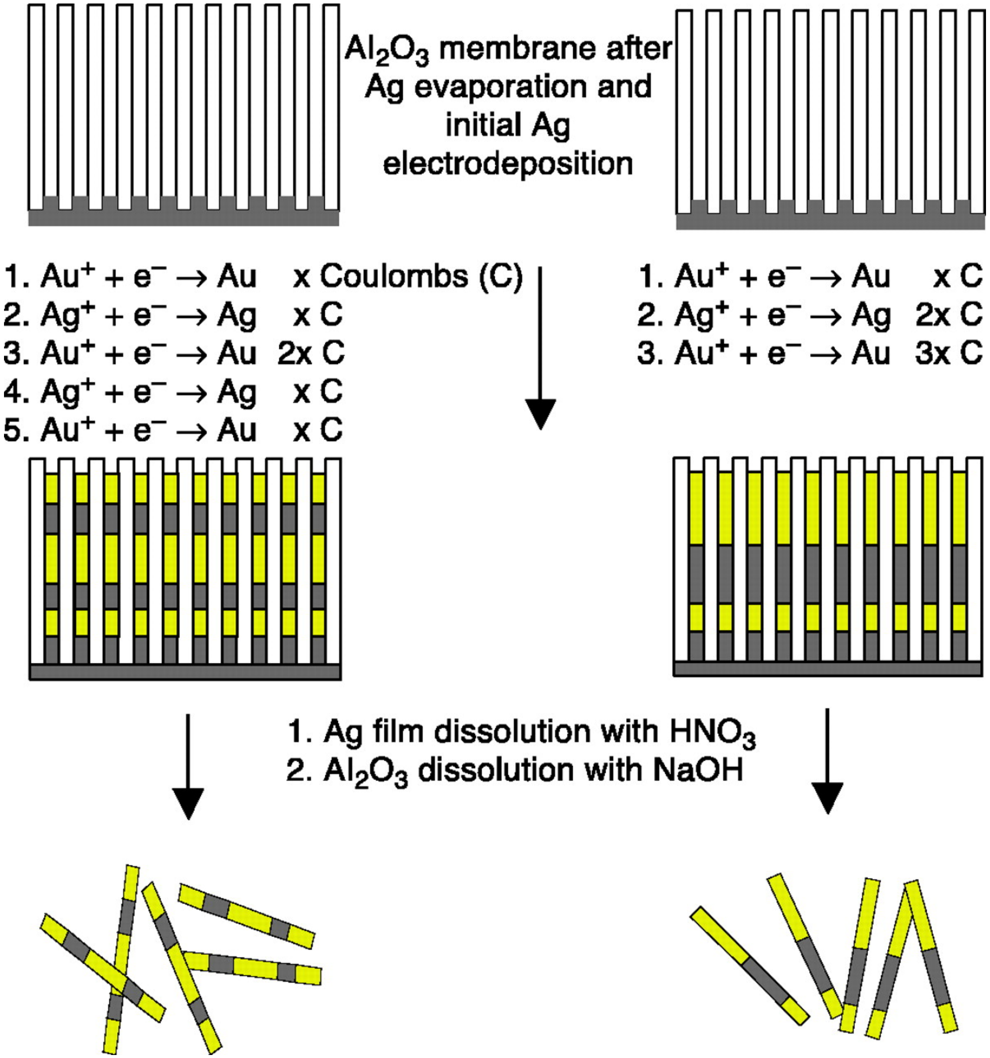
alumina template →

Si substrate →

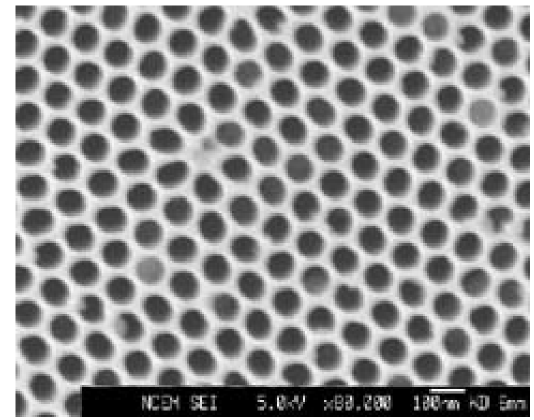


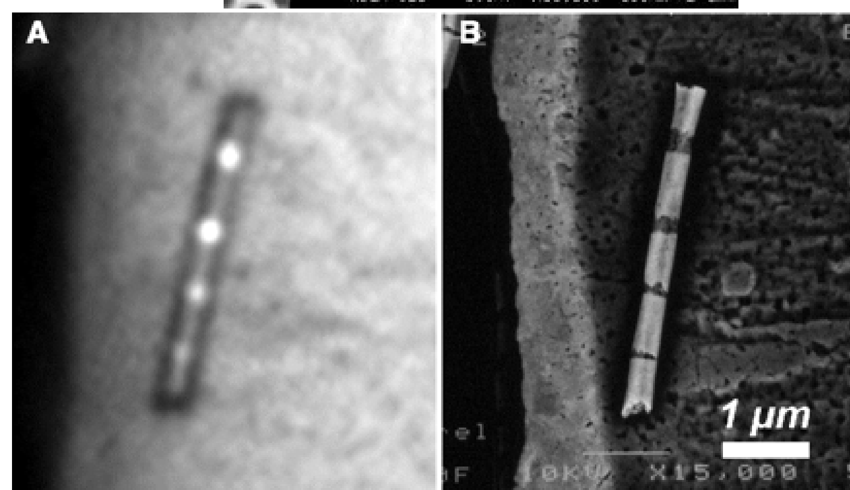

(M. Sander)

# Template - Electrodeposition




- **Alumina, polycarbonate track etched, and silica membranes**
- **5-10 μm thick with pore sizes to 10 nm**

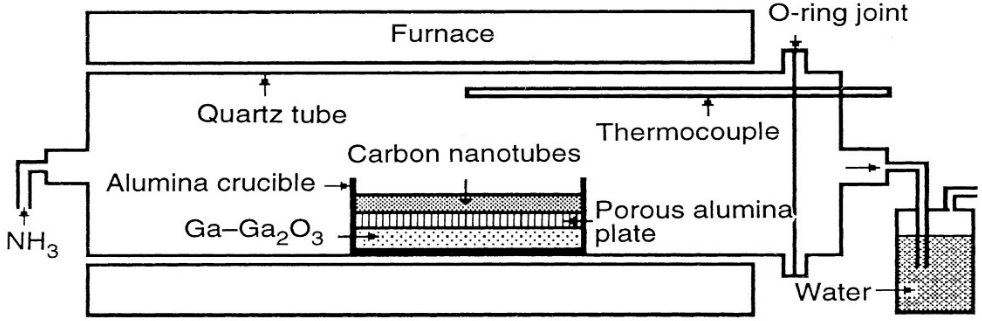


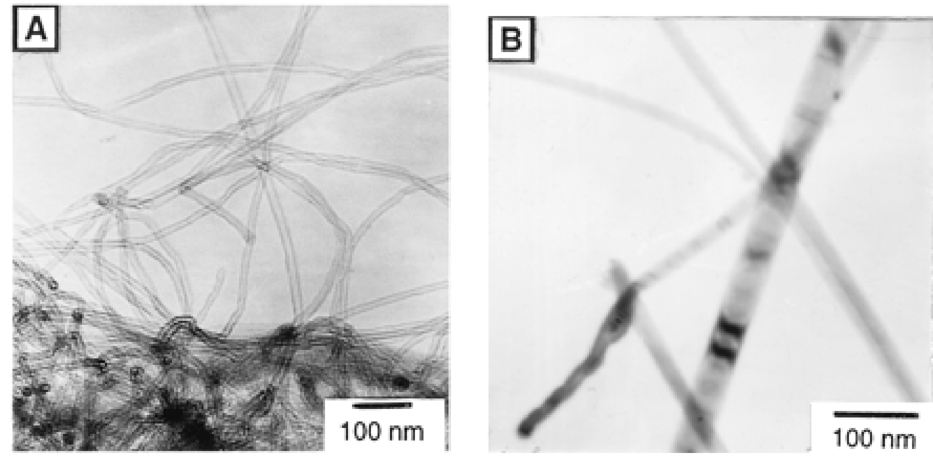



**S. Nicewarner-Peña, et al., *Science* 294, 137 (2001)**

# CNT-Template

## GaN nanorods from MWNTs

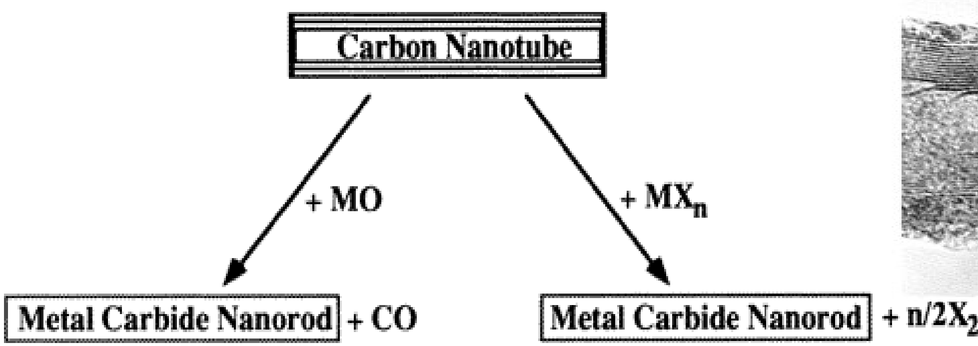


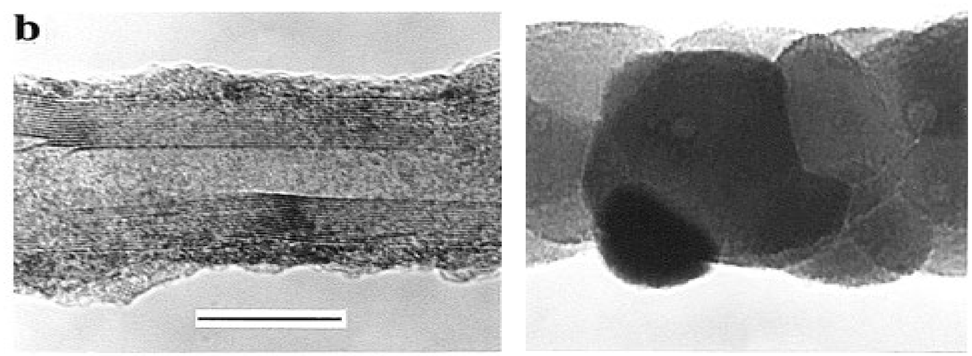




$2Ga_2O$ (g) + nanotube + $NH_3$ → $4GaN + H_20 + 5H_2 + CO$

W. Han, et al., *Science* 277, 1287 (1997)

## TiC nanorods from MWNTs



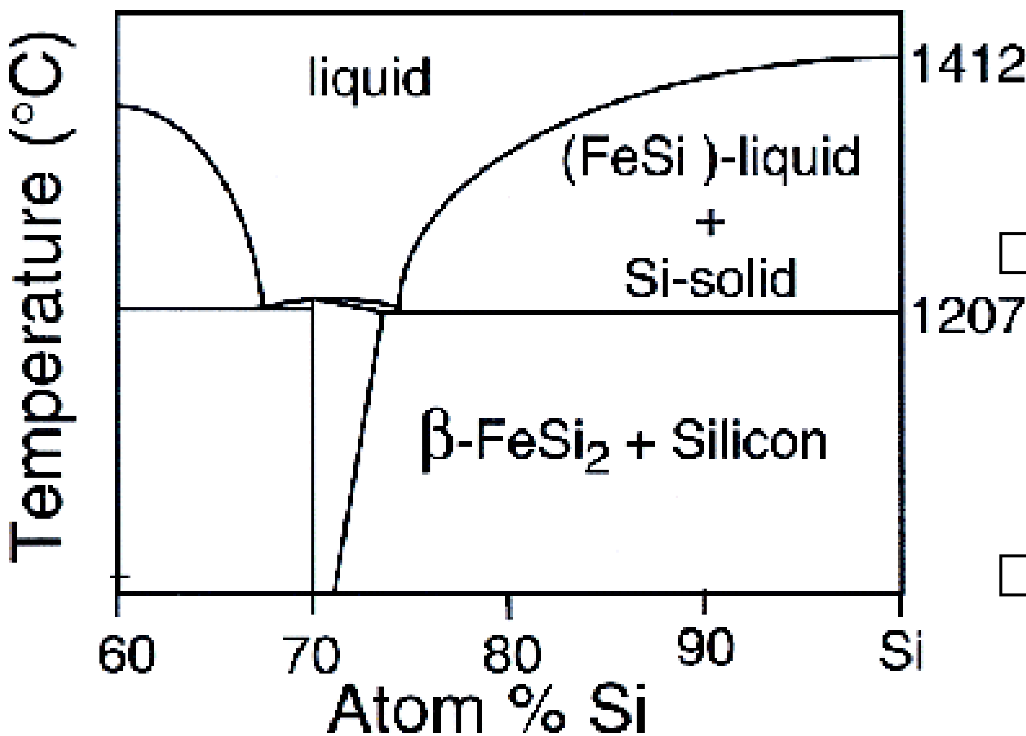

E. Wong, et al., *Chem. Mater.*, 8, 2041 (1996)

# Templating vs. Others

- Nanoscale structures generated by templating methods are typically not crystalline
  - Number of defects is larger
  - Quantum size effects usually not observed
  - Monodispersity is limited by the structure of template
  - Free-standing, 1D structures are difficult to obtain
- What are the requirements for a general, synthetic approach to nanowires?
  - Anisotropic growth
  - Control of catalyst size

# Vapor-liquid-solid (VLS) Growth

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




- $\sigma_{LV}$ 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.

# VLS Fabrication

- Vapor-liquid-solid(VLS)
  - Wagner and Ellic
- Semiconductor gas blown over liquid catalyst
- Vertical growth due to saturation and condensation of semiconductor material
- Temperature greater than eutectic temperature

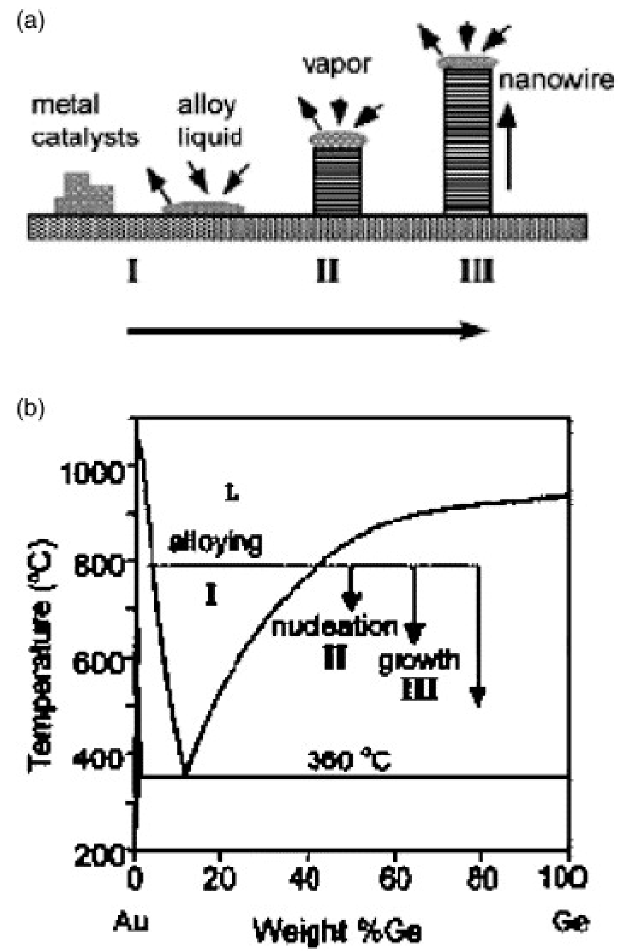
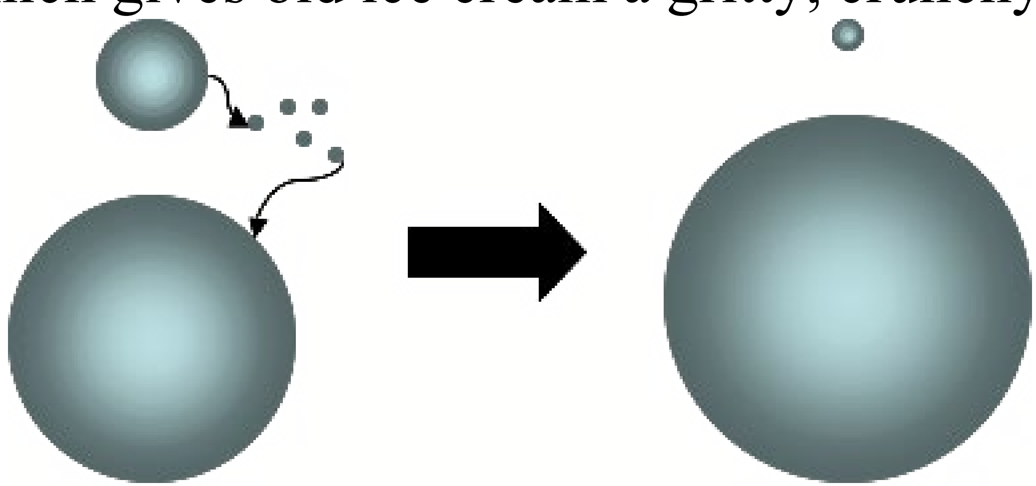



Image: C.N.R. Rao, F.L Deepak, Gautam Gundiah, A. Govindarah. "Inorganic Nanowires." *Progress in Solid State Chemistry*

# Ostwald Ripening

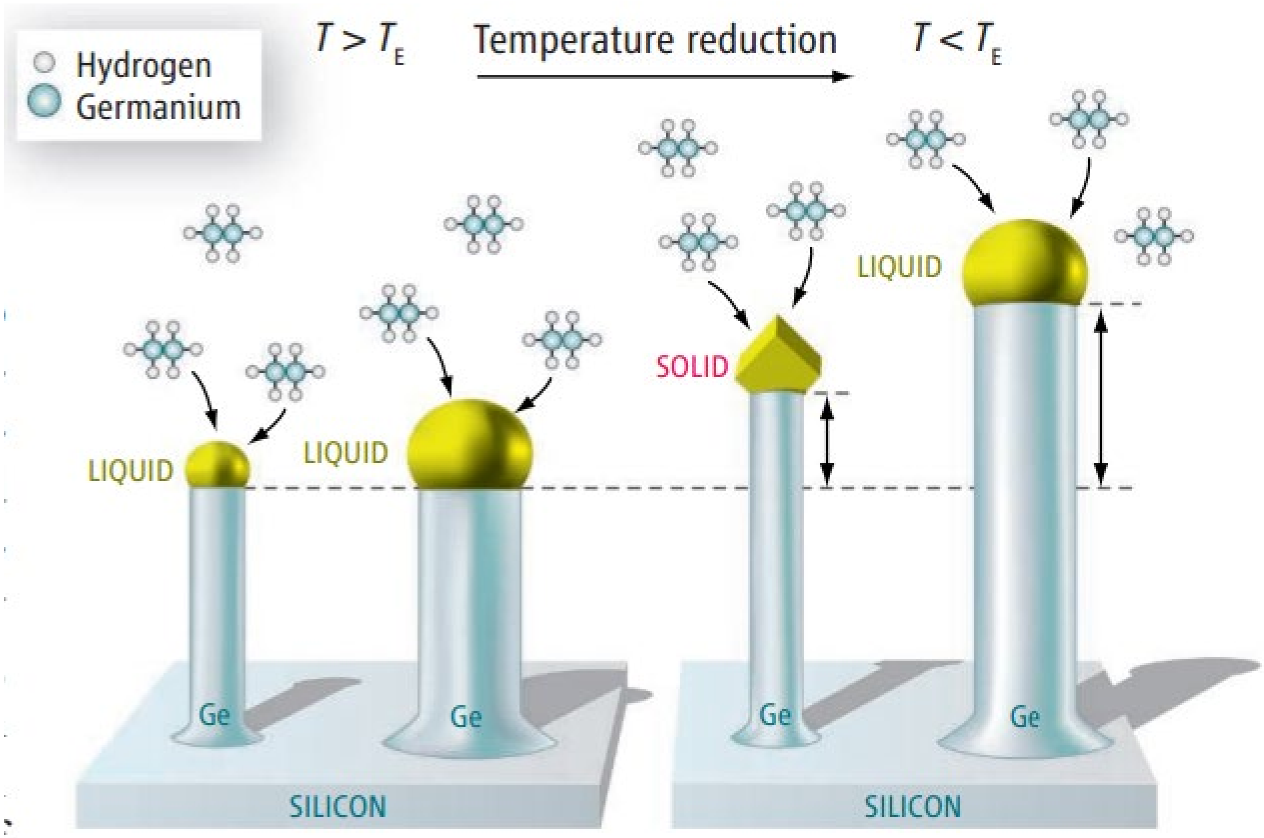
- First observed by Wilhelm Ostwald in 1896
  - When a phase precipitates out of a solid (or liquid) causing large precipitates to grow, drawing material from the smaller precipitates, which shrink. Larger particles are more energetically favored than smaller particles as their greater volume to surface area ratio, represent a lower energy state.
  - An everyday example is the re-crystallization of water within ice cream which gives old ice cream a gritty, crunchy texture.



# Germanium Nanowires

(Temperature above eutectic temperature of 361C)

(Temperature below eutectic temperature of 361C)




*Schmidt et al, 2007*

# Sub-Eutectic Growth

- Euctectic Point
  - Temp: 361°C
  - Ge:Au Ratio: 7:18
- It is possible to grow nanowires below eutectic point
- Growth via Vapor-Solid-Solid and Vapor-Liquid-Solid processes
- Solid and liquid catalysts tips

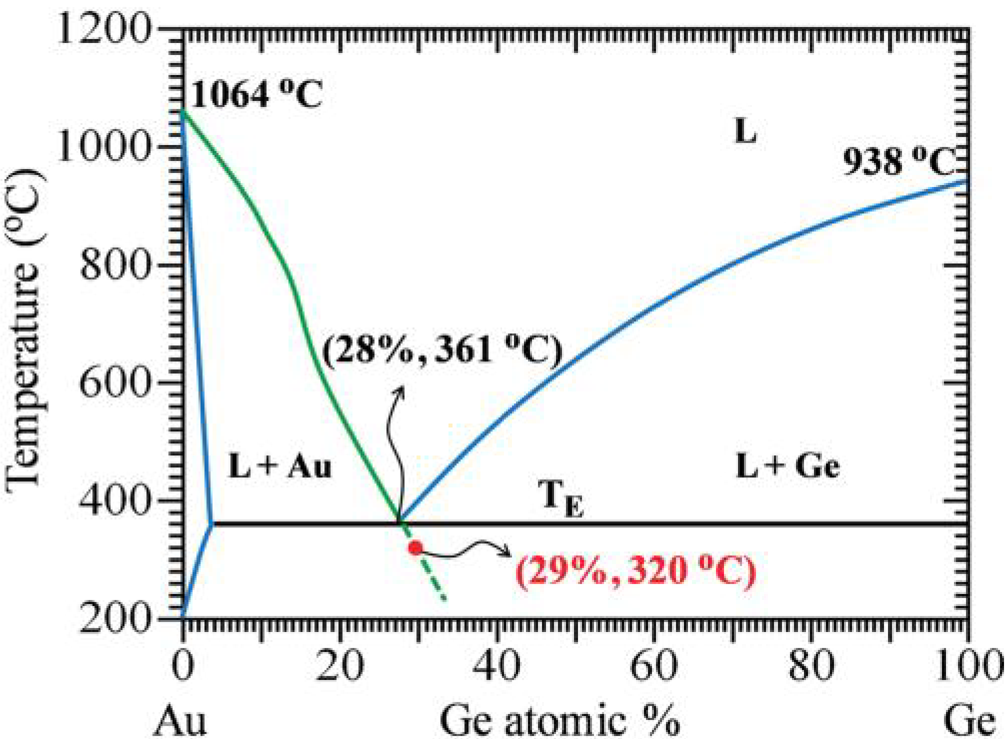



Image: S. Kodambaka et al. "Germanium Nanowire Growth Below the Eutectic Temperature"

# VLS Growth: Nanowire fabrication process

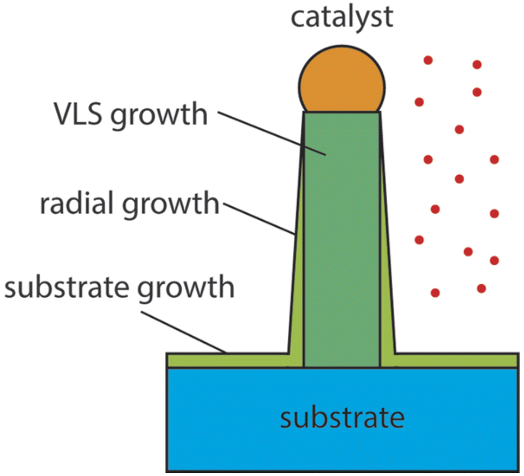
- Vapor-Liquid-Solid Process

- Usually: Semiconductor material as a gas is absorbed by **liquid** catalyst nanodroplet

e.g. Germanium absorbs onto Gold catalyst

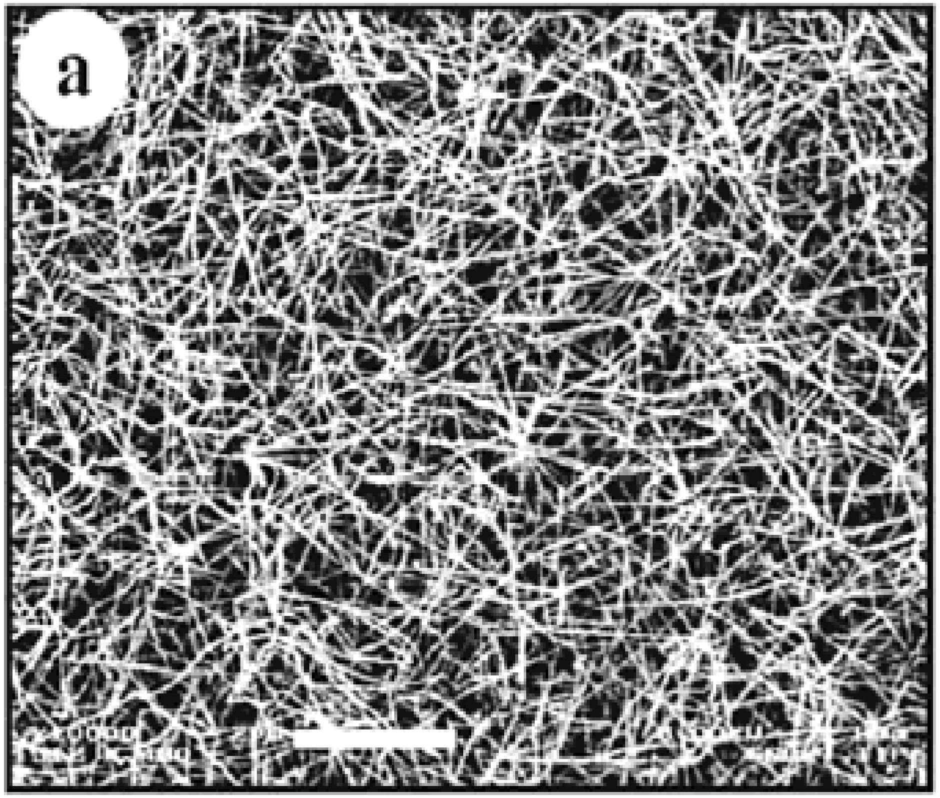
- Catalyst nanodroplets serve as 'seeds' for nanowire growth and their size also determines nanowire diameter

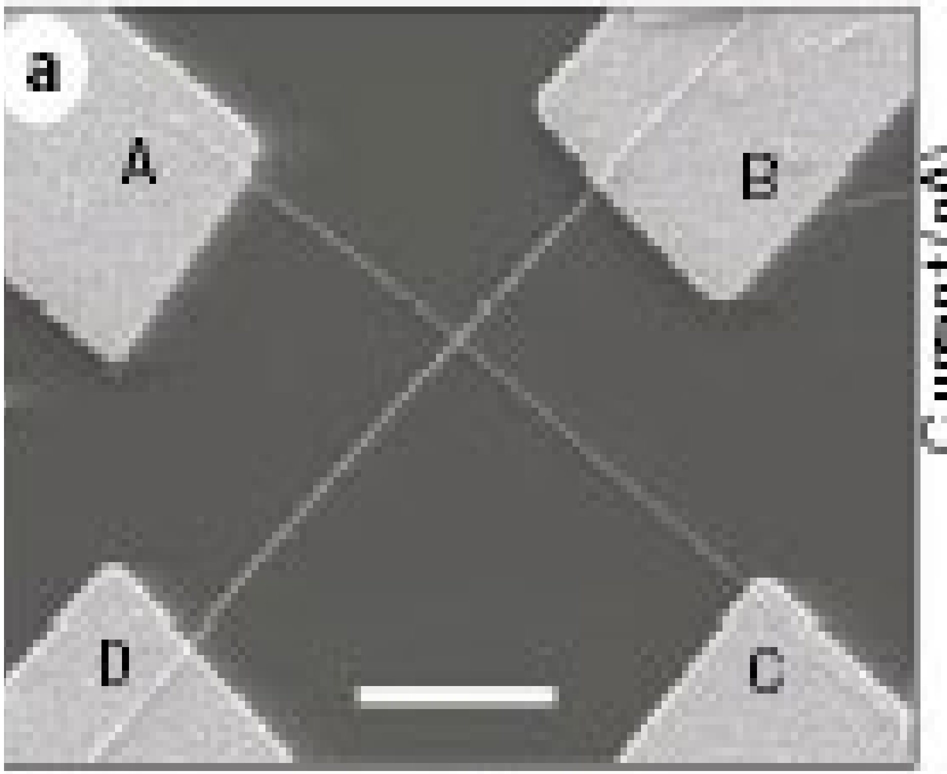
- "The semiconductor material condenses at the interface between the droplet and the nanowire, thereby extending the length of the nanowire."




http://pubs.rsc.org/en/content/chapterhtml/2014/bk9781849738156-00001?isbn=978-1-84973-815-6

# Nanoscale Assembly




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

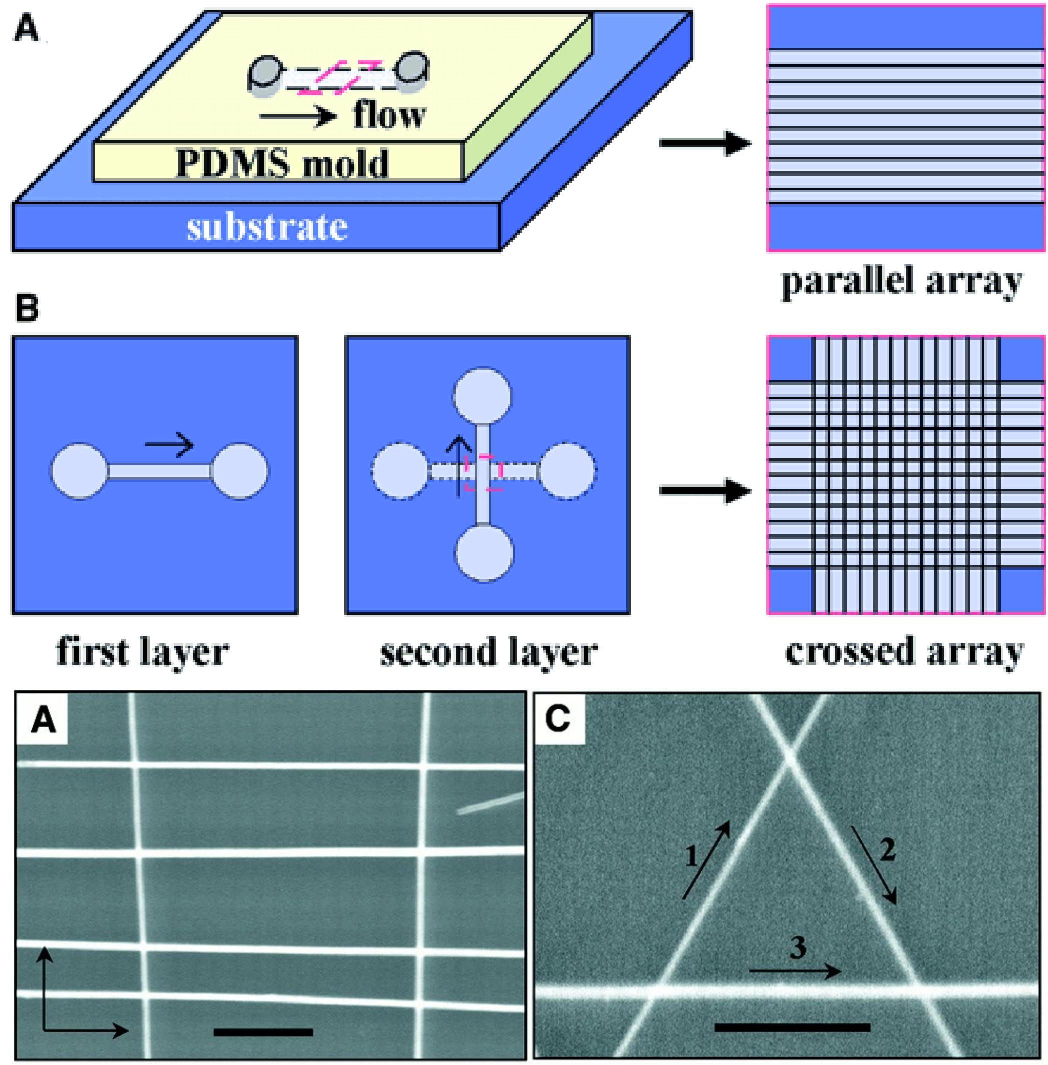
BSAC

# *X*-based assembly vs. self-assembly

- Non-equilibrium compared to equilibrium
- Non-reversible
- Assembly of components on a template rather than individual components forming aggregates
- Takes advantage of other intrinsic properties (magnetic, electrostatic, etc.)
- Can position nanostructures in specific locations
- *Examples*: Energy of interaction and distance-dependence
  - Electrostatic energy: $1/r$ (long range)
  - Van der Waals: $1/r^6$ (short range)
  - Dipole-dipole: $1/r^3$
  - Ion-dipole: $1/r^2$

# Fluidic Directed Assembly

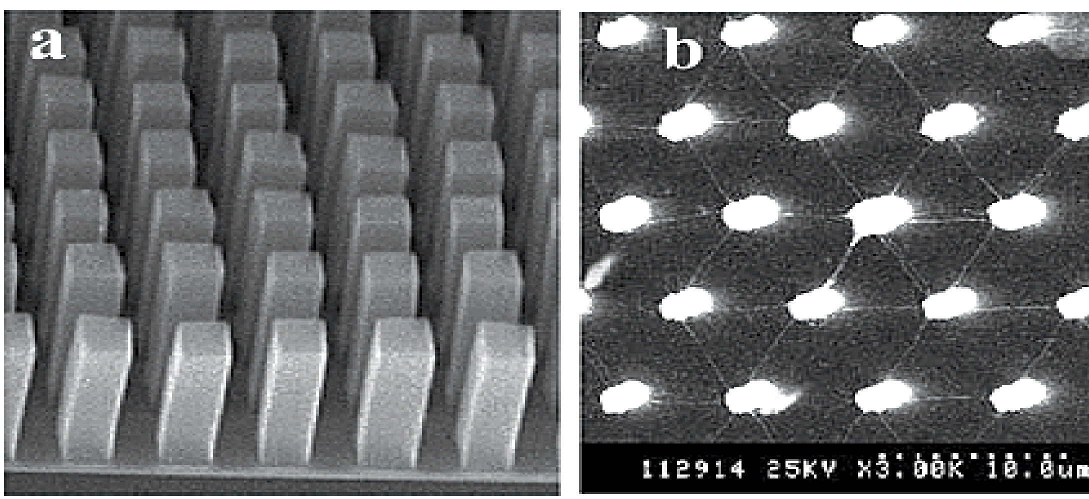
- Use PDMS channels to align nanowires
  - Suspend nanowires in ethanol and inject in inlet
  - Control flow rate and duration
- Chemically functionalize substrate to enhance deposition
- Rotate the orientation of the channel to achieve 2D assembly



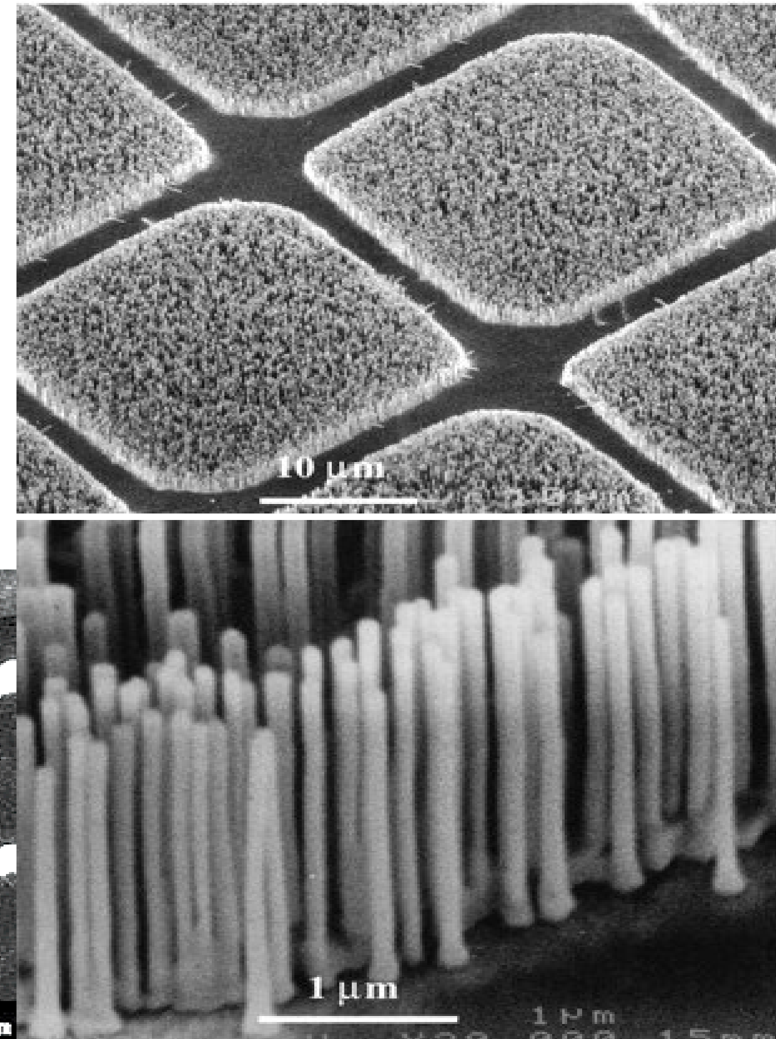

Y. Huang, et al., *Science* 291, 630 (2001)

# Direct Assembly of Nanostructures

- Pattern catalyst on surface
  - Microcontact printing
  - Photolithography
  - Electron beam lithography
- Grow nanotubes and nanowires

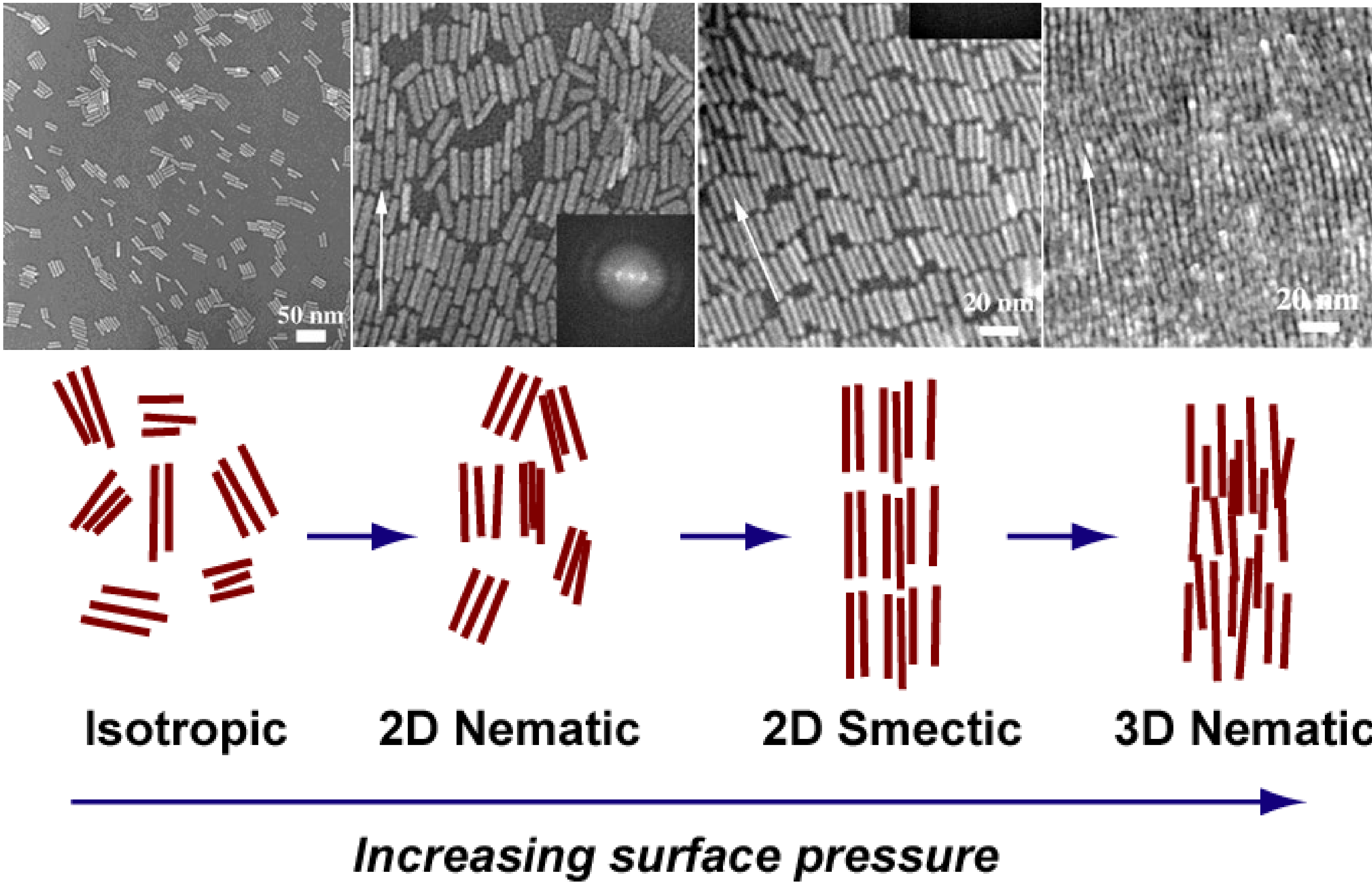



**H. Dai, *Acc. Chem. Res.* 35, 1035 (2002)**



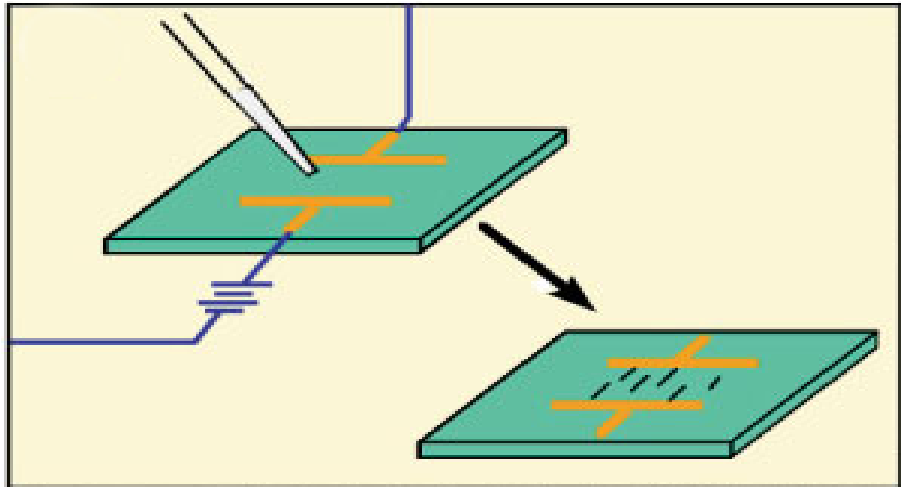

**M. Huang, et al., *Science* 292, 1897 (2001)**

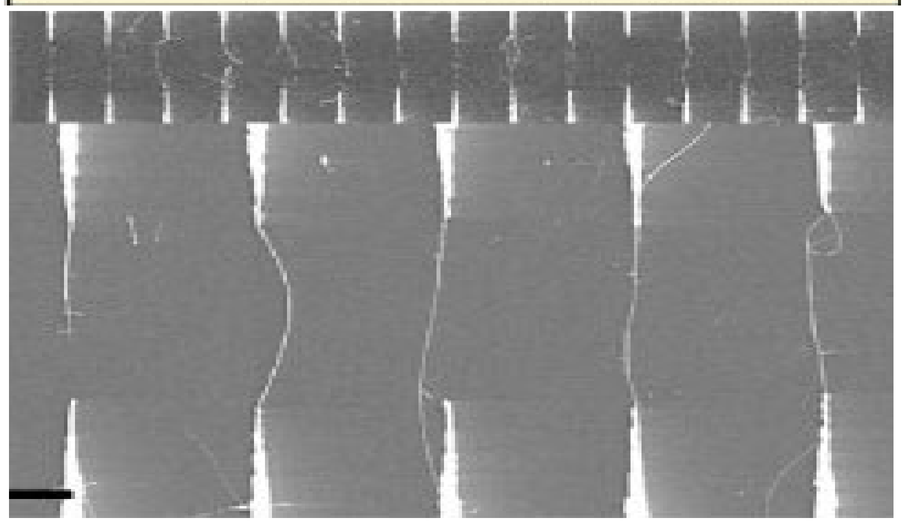
# Langmuir-Blodgett Assembly

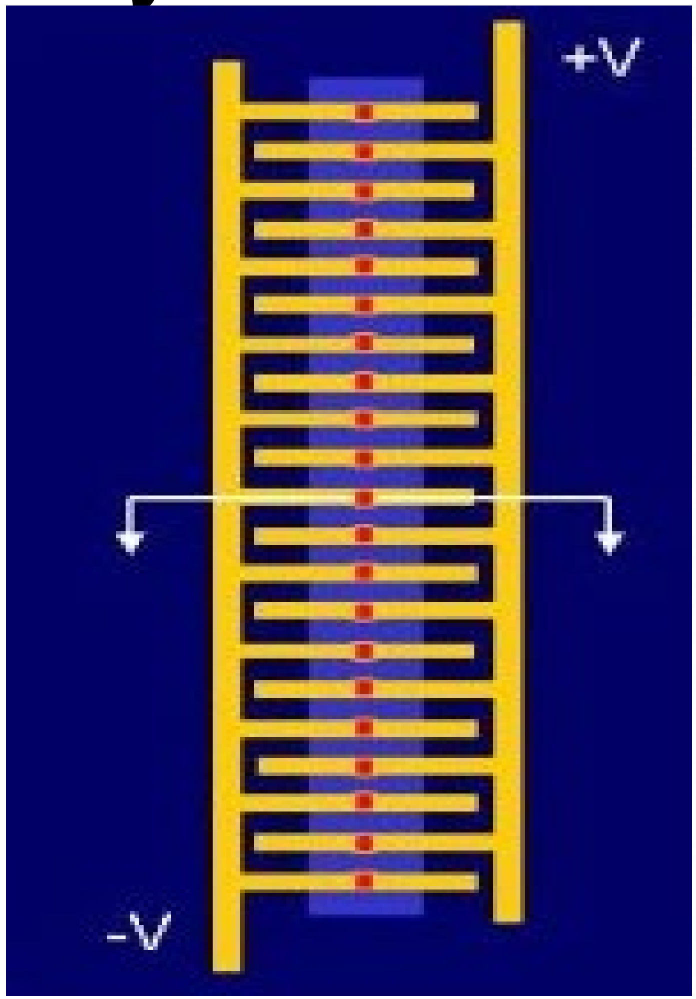


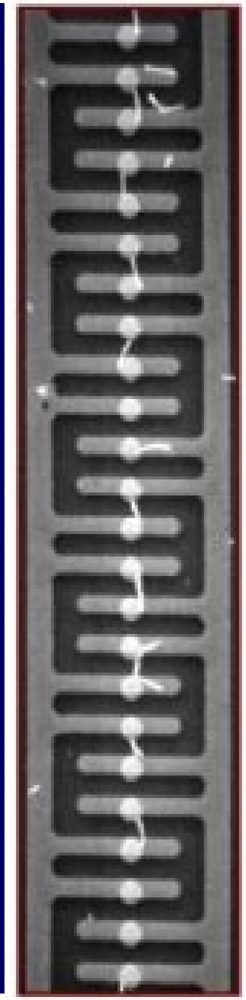

F. Kim, et al., *JACS* 123, 4386 (2001)

# Electric Field Directed Assembly







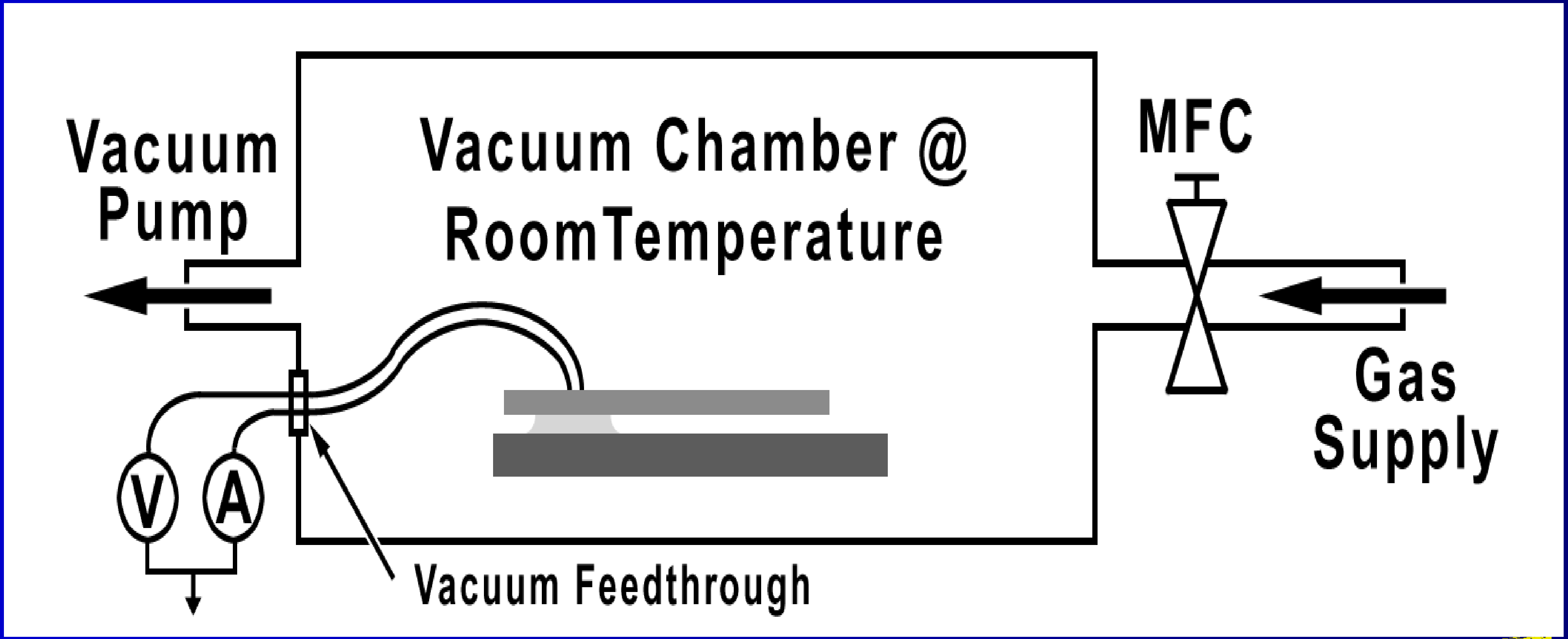



**Nanowires (15-50 nm), 80-100 VDC**
**Y. Huang, et al., *Nature* 409, 66 (2001)**

**Nanorods (200 - 350 nm), 5-70 VAC**
**P.A. Smith, et al., *App. Phy. Lett.* 77, 1399 (2000)**

# Room Temperature Chamber

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

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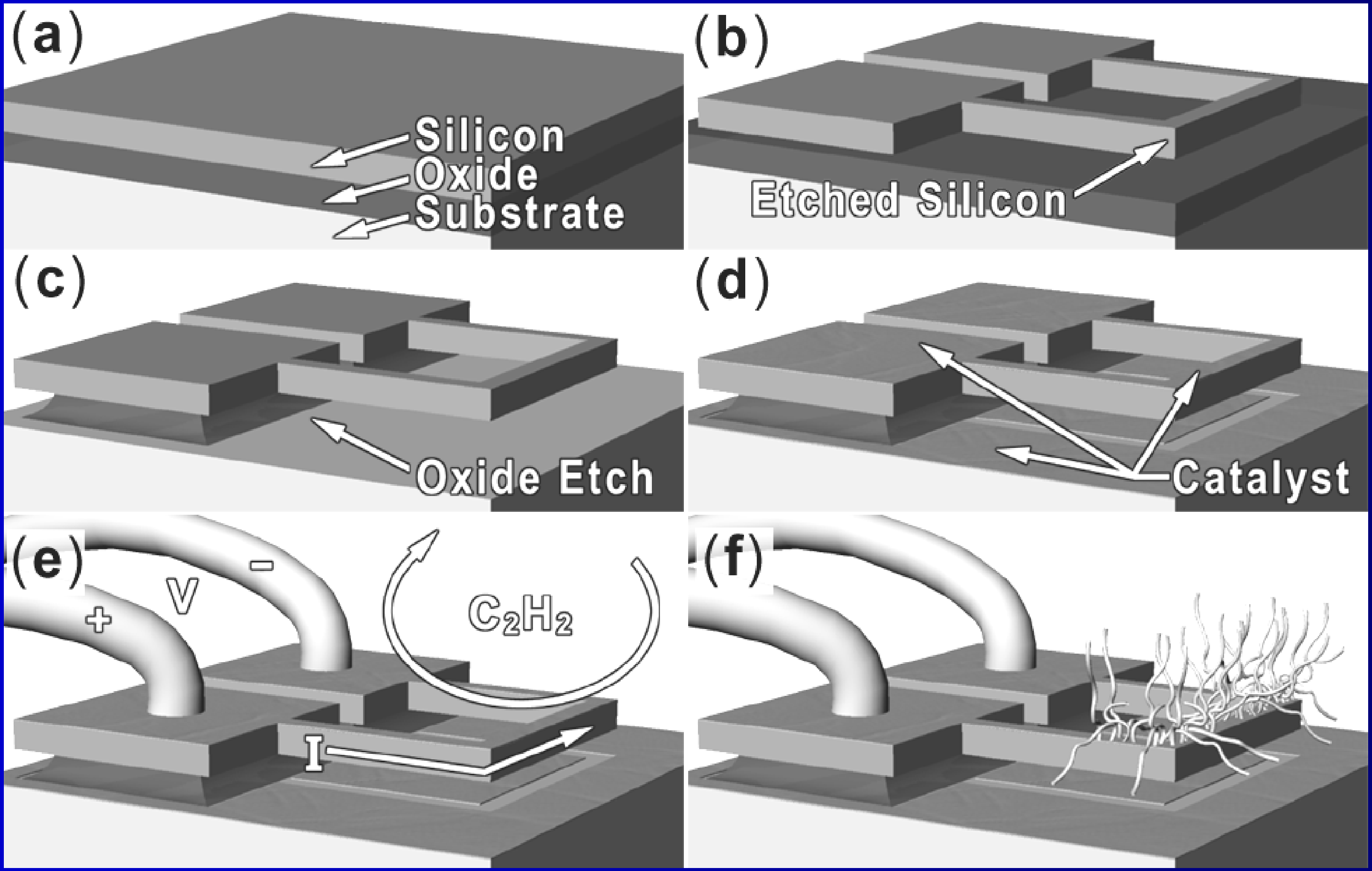
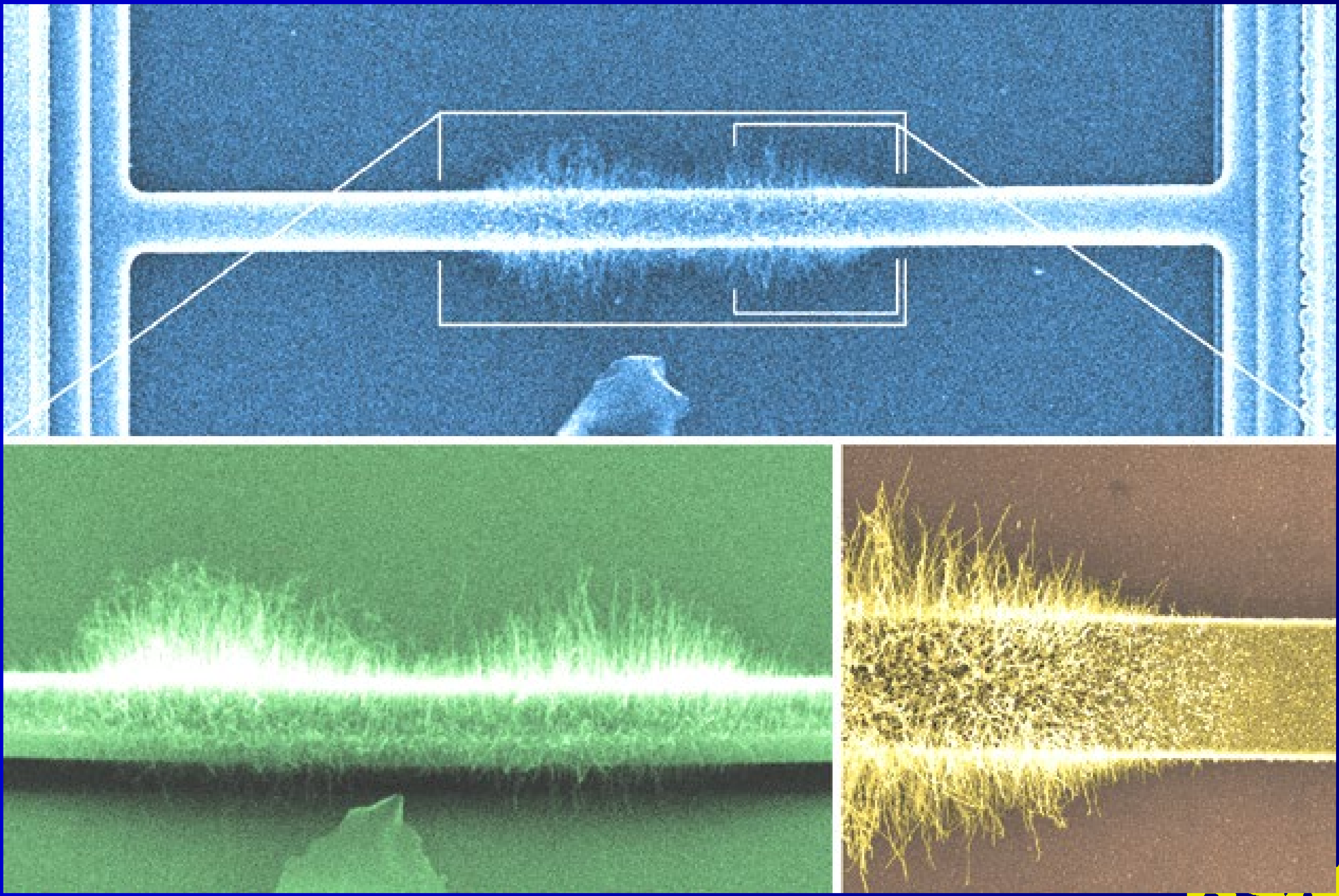
# One-Mask Process

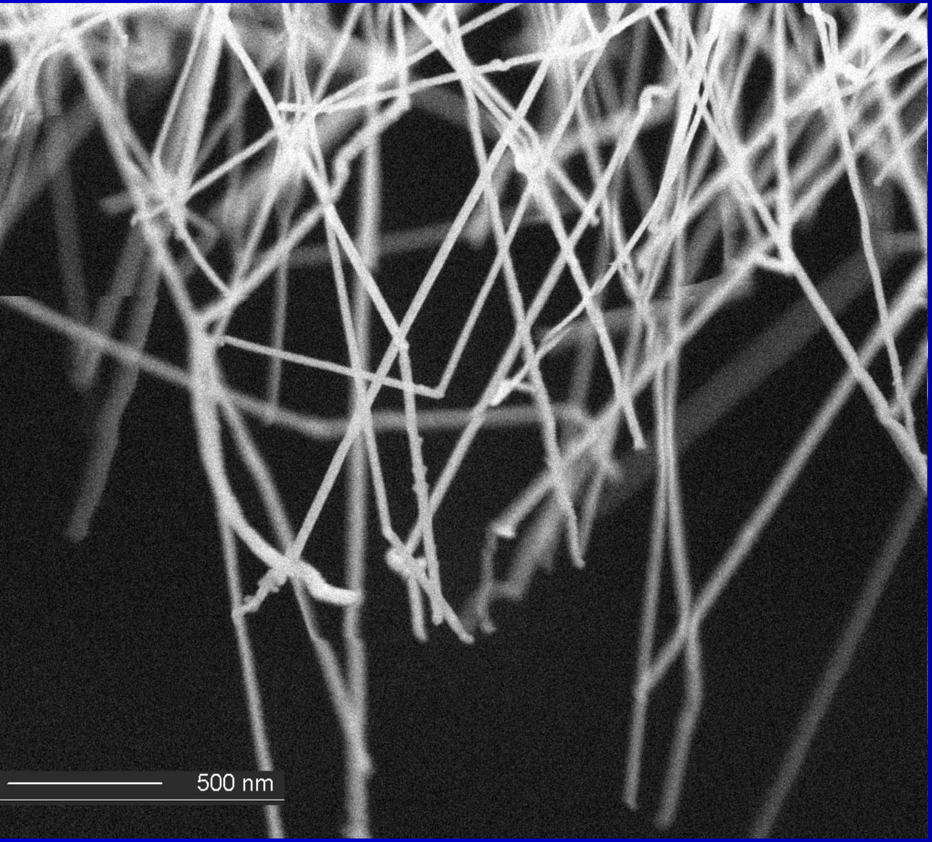


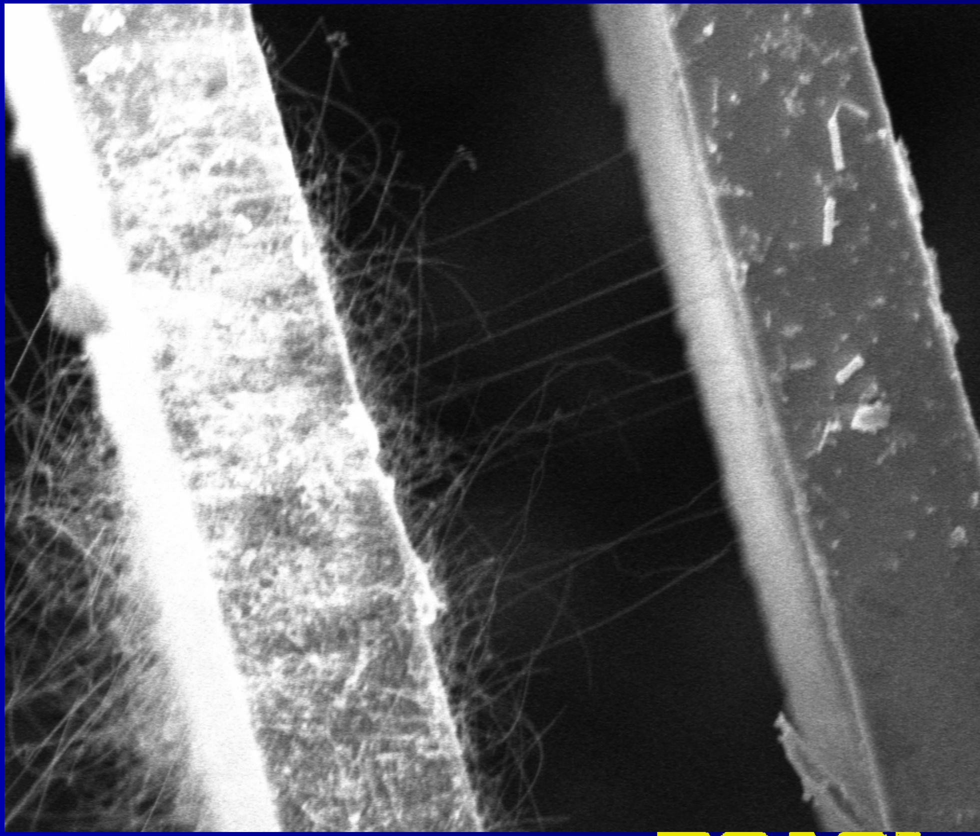
# Silicon Nanowires – 1st Demo



# Silicon Nanowires

- Single crystal silicon of < 30nm with 1μm/min growth rate
- Applications: chemical/biological sensors; nanoelectronics for advanced military systems



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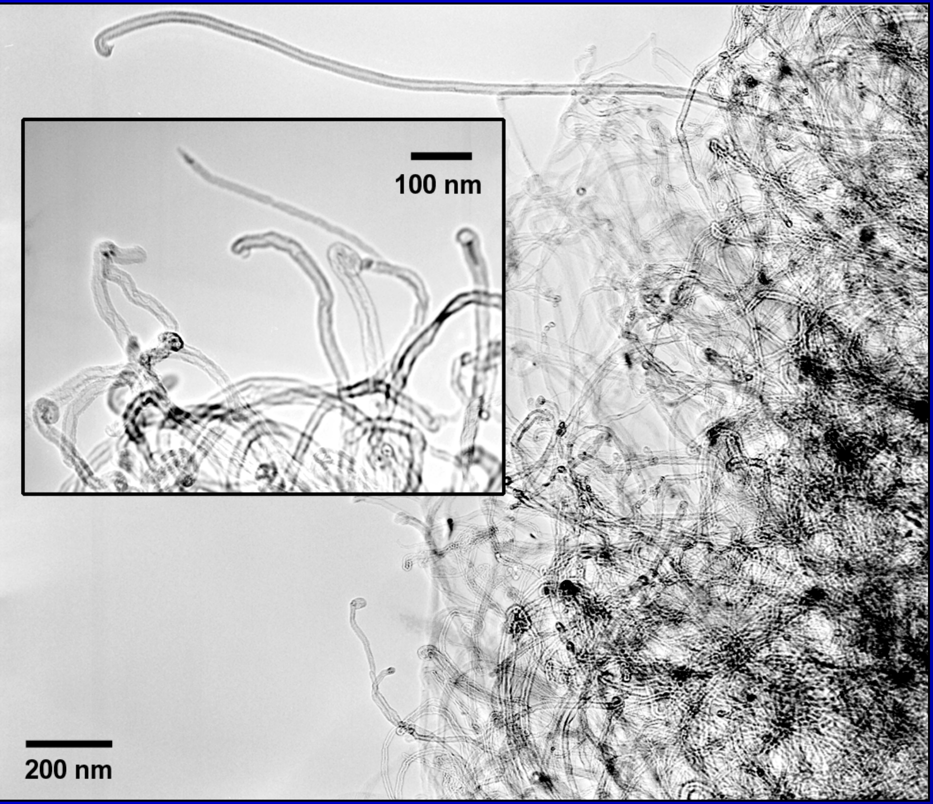
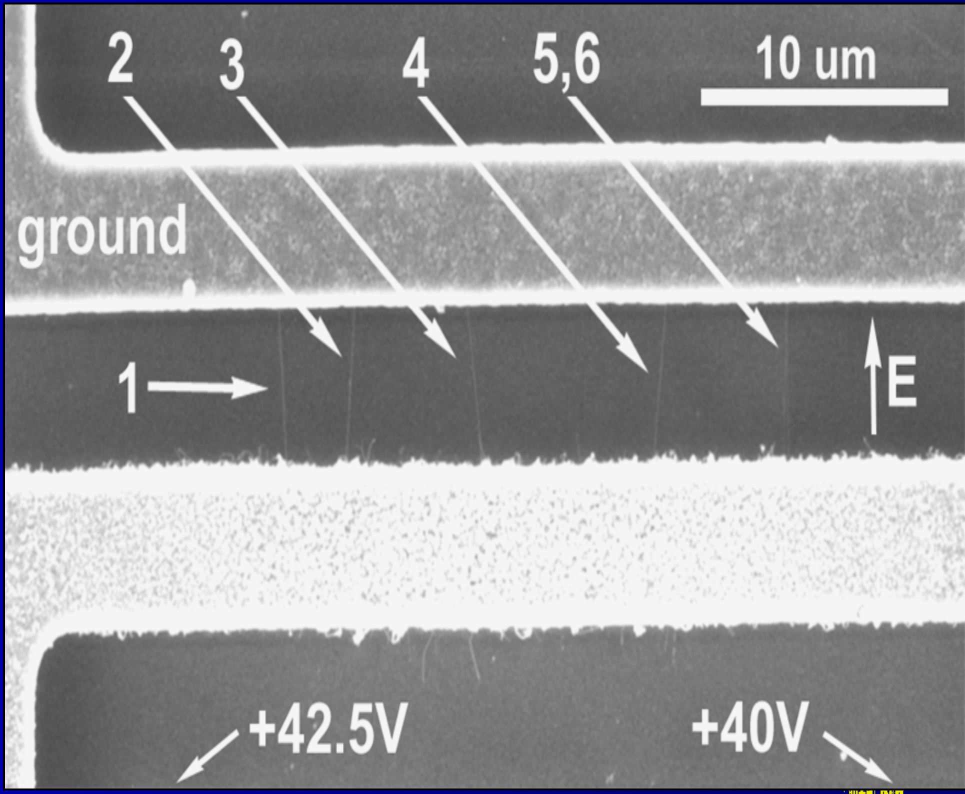
# Carbon Nanotubes

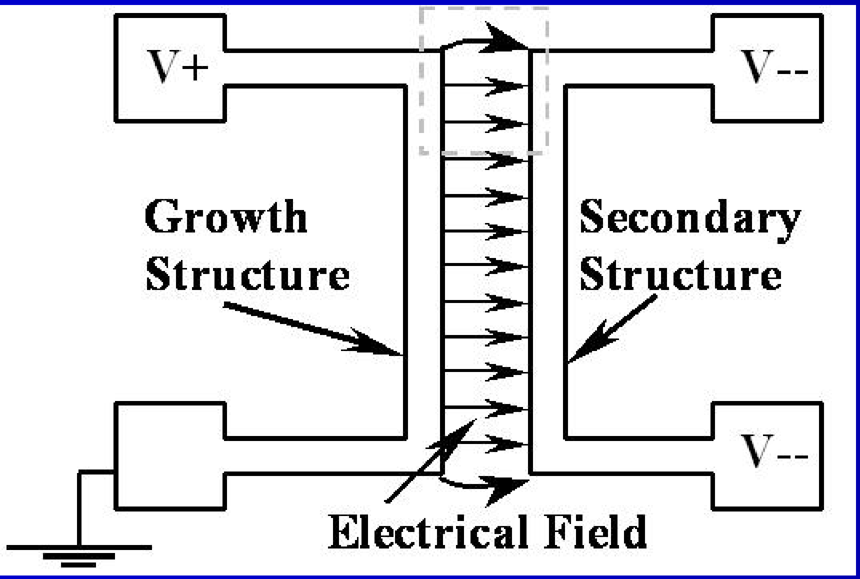
- Carbon nanotubes of 5 ~ 20nm with 0.5μm/min growth rate
- Applications: nanoelectronis (transistors, switches) and bio/chemical sensors

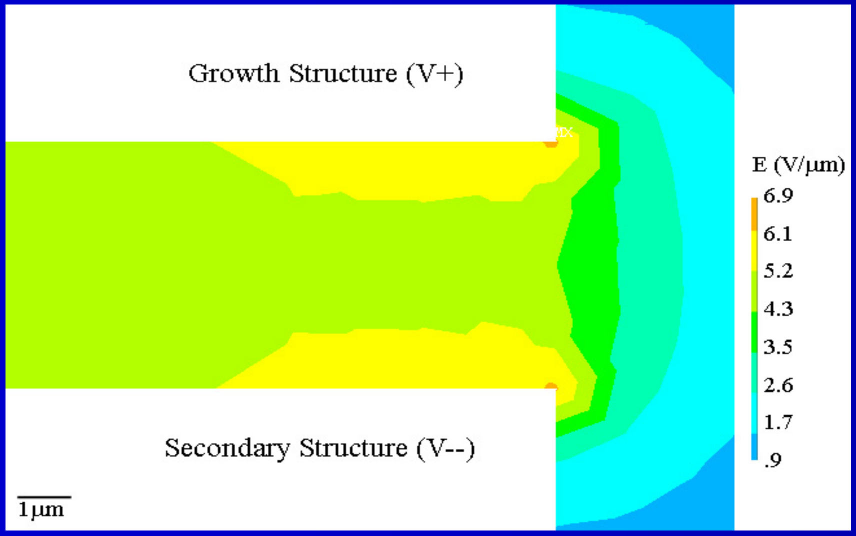


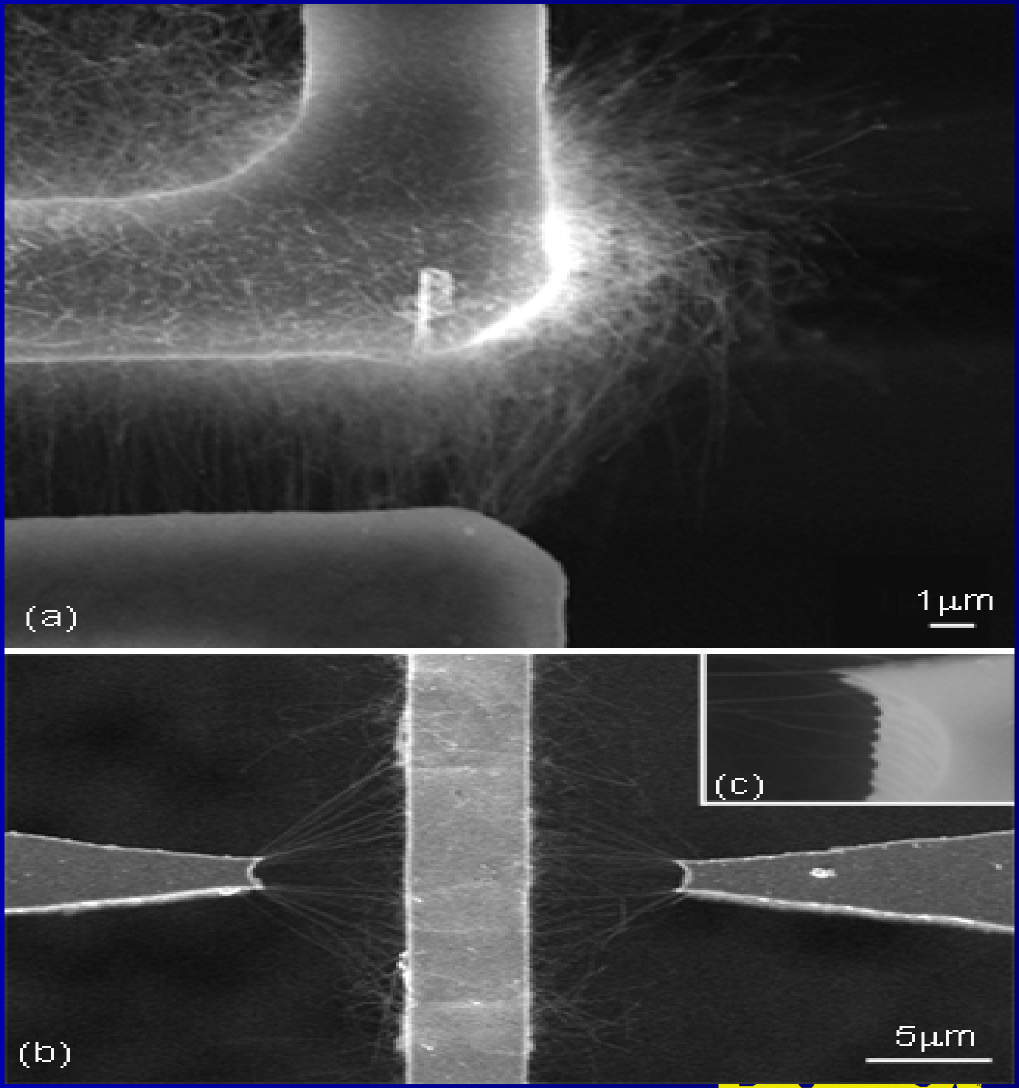



# Self-Assembly of Silicon Nanowires

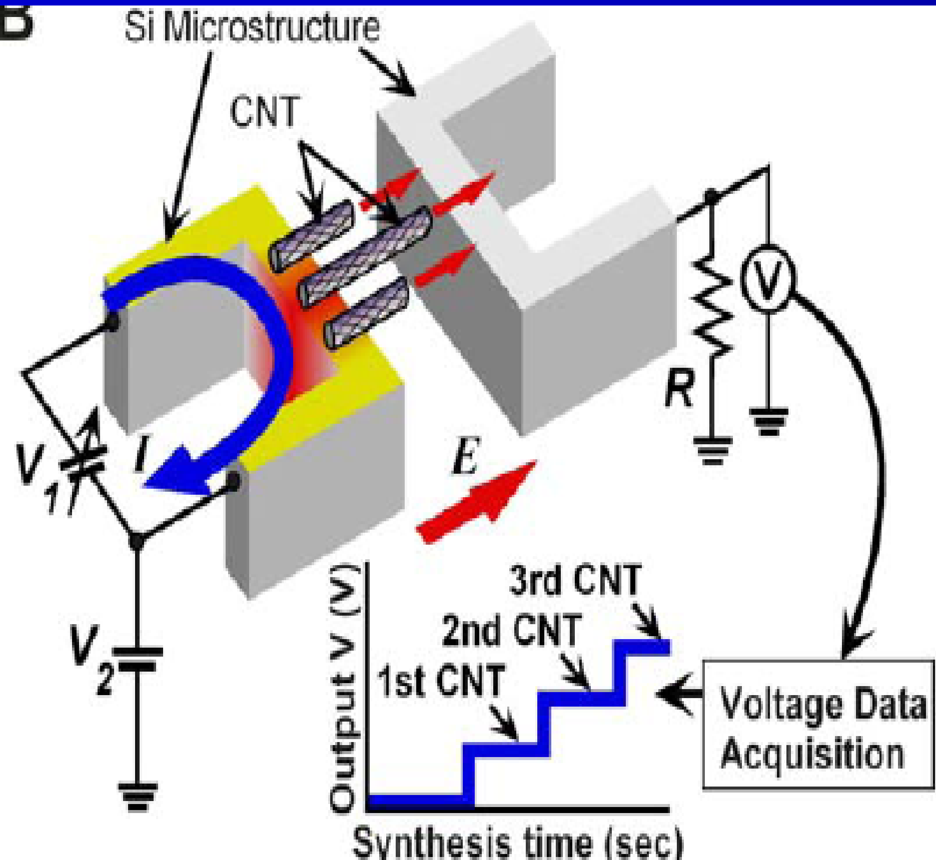
Englander, Christensen, Kim, Lin, and Morris, Nanoletters, Vol. 5, pp. 705-708, 2005

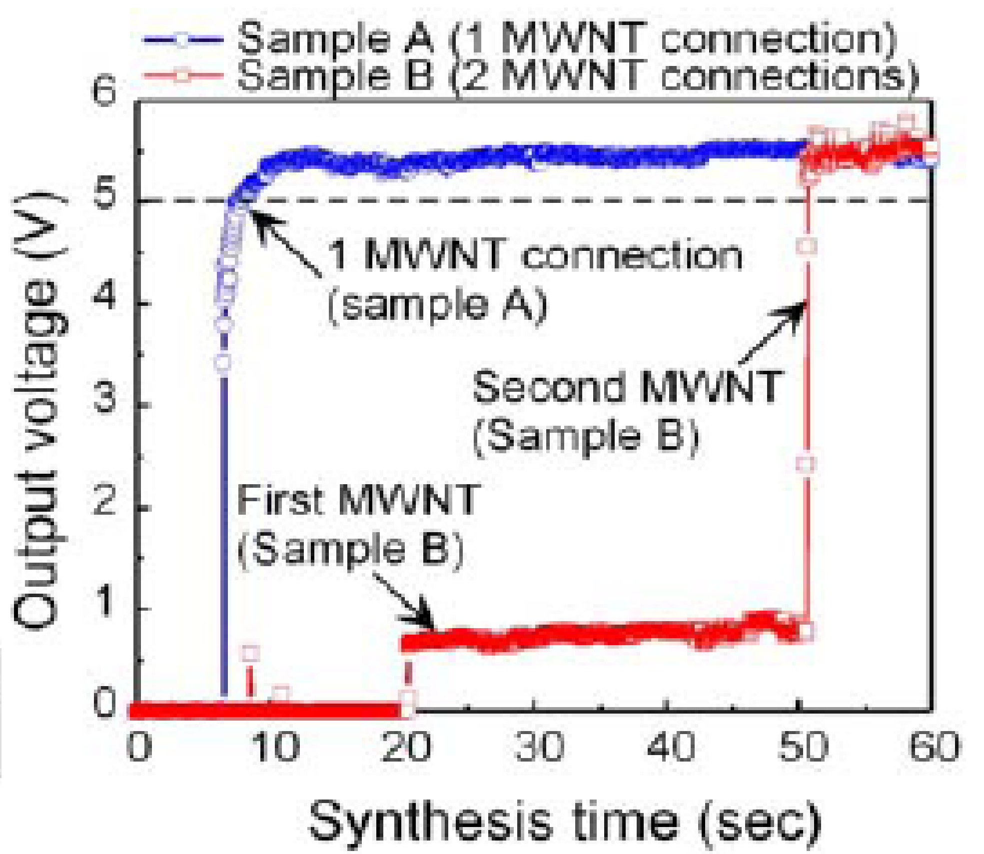


# Electric Field Assisted in-situ Synthesis & Assembly

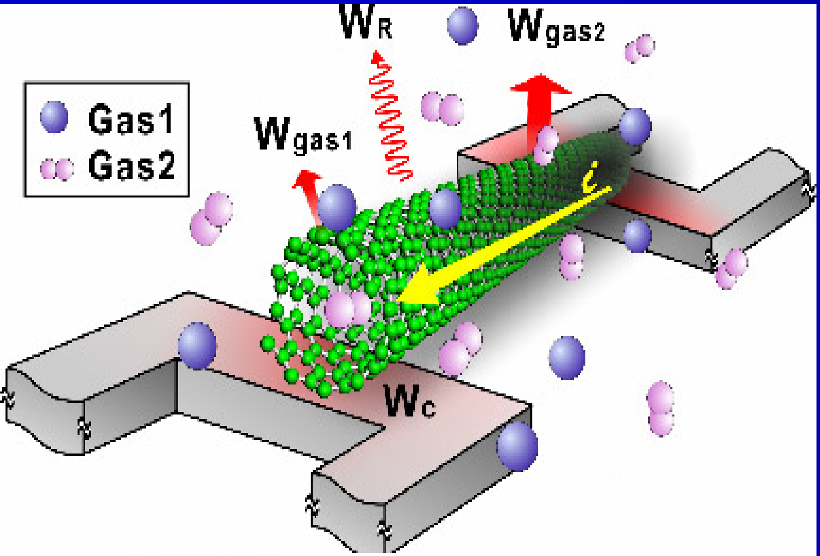


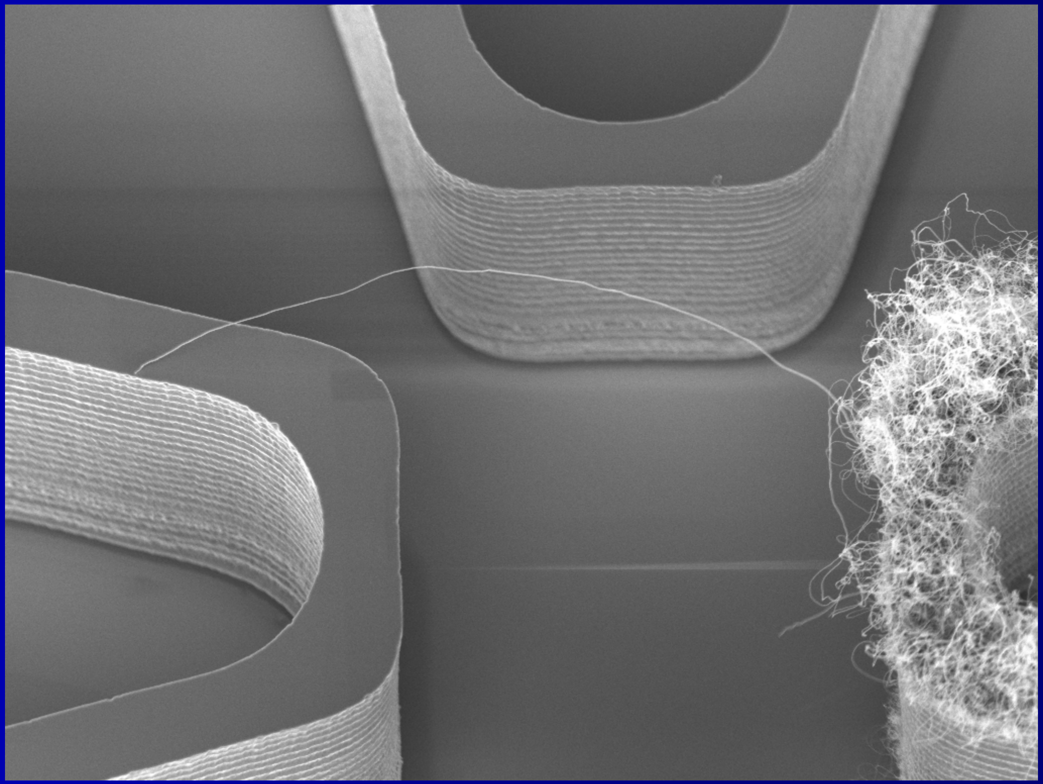

| | | | |
|---|---|---|---|
| Temperature | 850 – 900°C | Gaps between Si structures | 5 – 10 μm |
| $C_2H_2$ gas flow | 50 sccm | Bias between Si ($V_2$) | 2 – 5 V |
| Synthesis pressure | 50 – 250 Torr | Electric field ($V_2$ / gaps) | 0.2 – 1 V/μm |

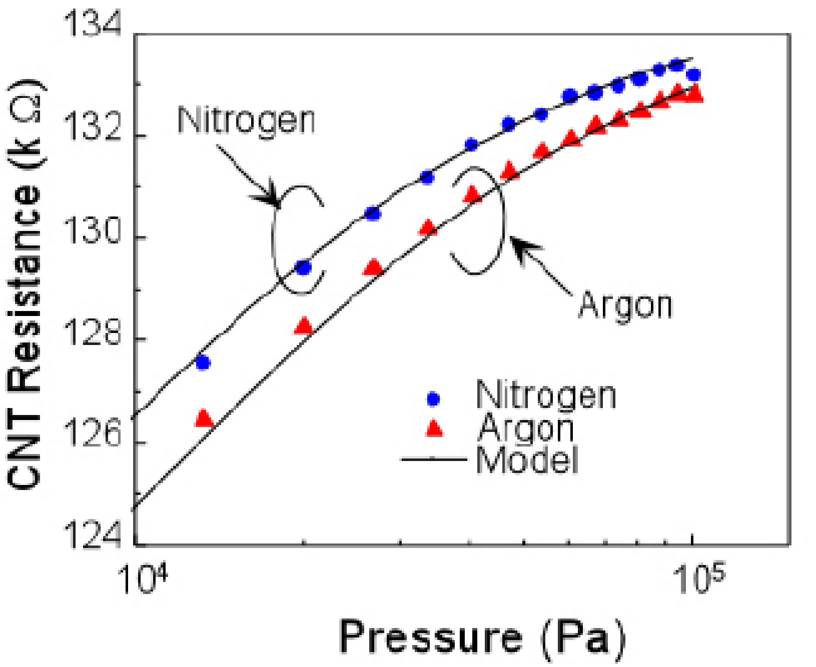
BSAC

# Electrothermal CNT Gas Sensor




Kawano, Chiamori, Suter, Zhou, Sosnowchik, and Lin, *Nanoletters,* Vol. 7, pp. 3686-3690, 2007.






$$\frac{1}{2}W_C = k_{CNT} A \frac{dT_{CNT}}{dl}\Big|_{l=0}$$

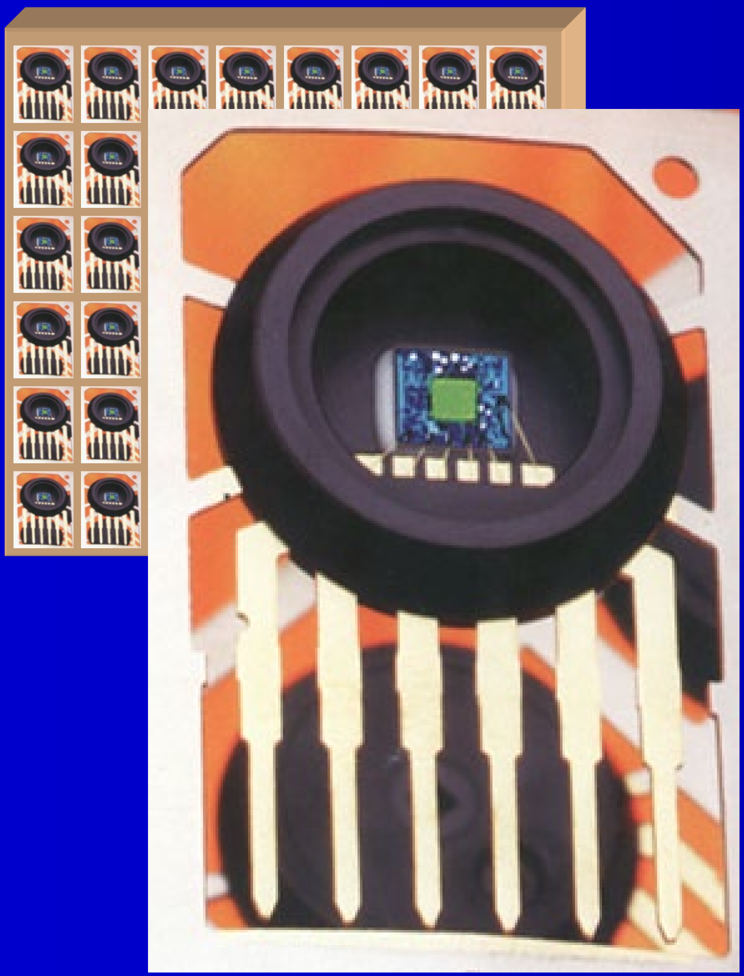
BSAC

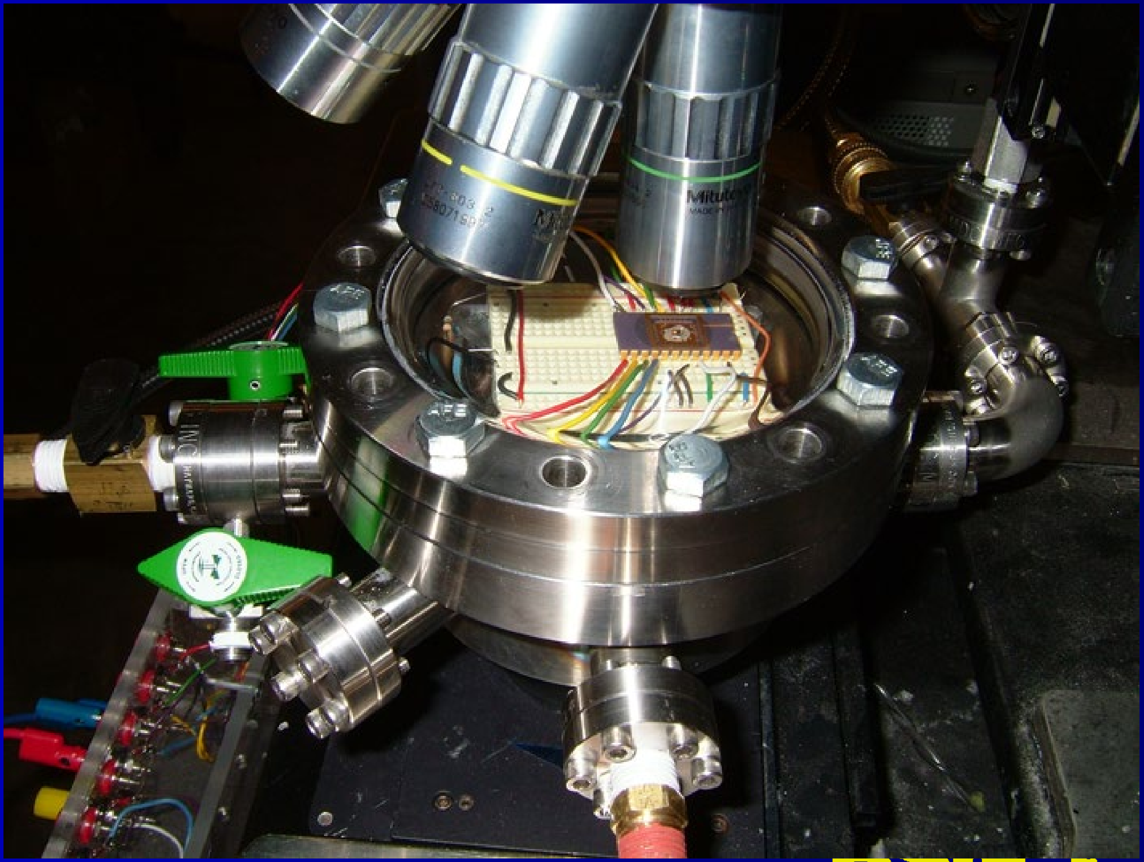


35

# Massively and Parallel Assembly

- **Packaging-level synthesis, assembly and bonding of structures with self-diagnosis and calibration circuits**



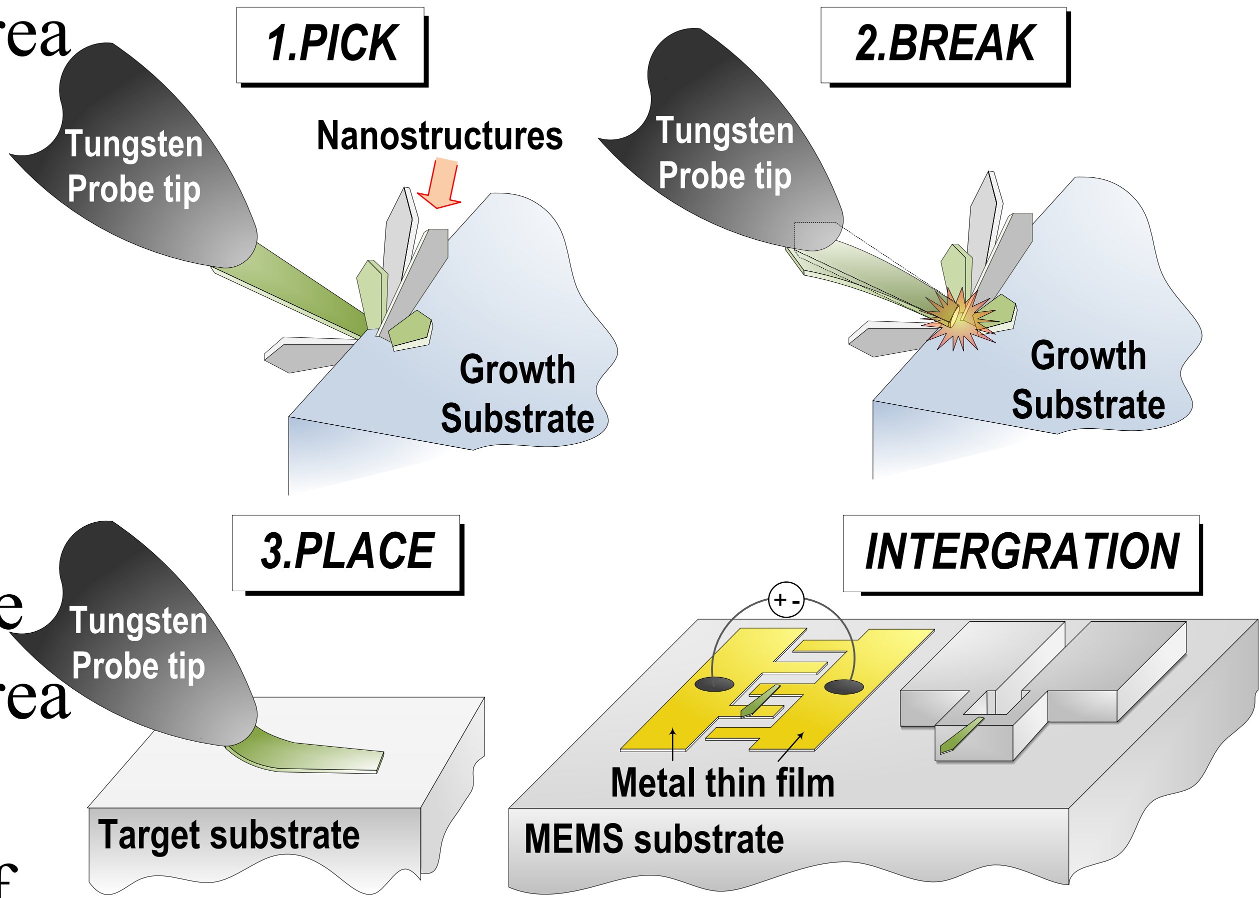


# Process Advantages

- **Fast** – with 0.5~1μm/min growth rate, a two-terminal device between a 5μm gap is accomplished in 10 minutes
- **Site-specific** synthesis –by localized heating
- **Self-assembly** - no need for manually manipulation of nanostructures into place
- **Self-bonding** – no post-assembly bonding such as using E-beam or Focus-Ion-Beam
- **CMOS-compatible** – room temperature chamber
- **Massively and parallel** - multiple synthesis sites/devices with automatic on-chip or off-chip control circuitry

# Pick, Break and Place of Nanostructures

- Pick: Need to have adequate contact area for strong enough attraction force
- Break: Need to sustain the shock force
- Place: Need to have adequate contact area with the substrate
- Integration: Lots of applications




*Applied Physics Letters*, Vol. 96, 153101, 2010

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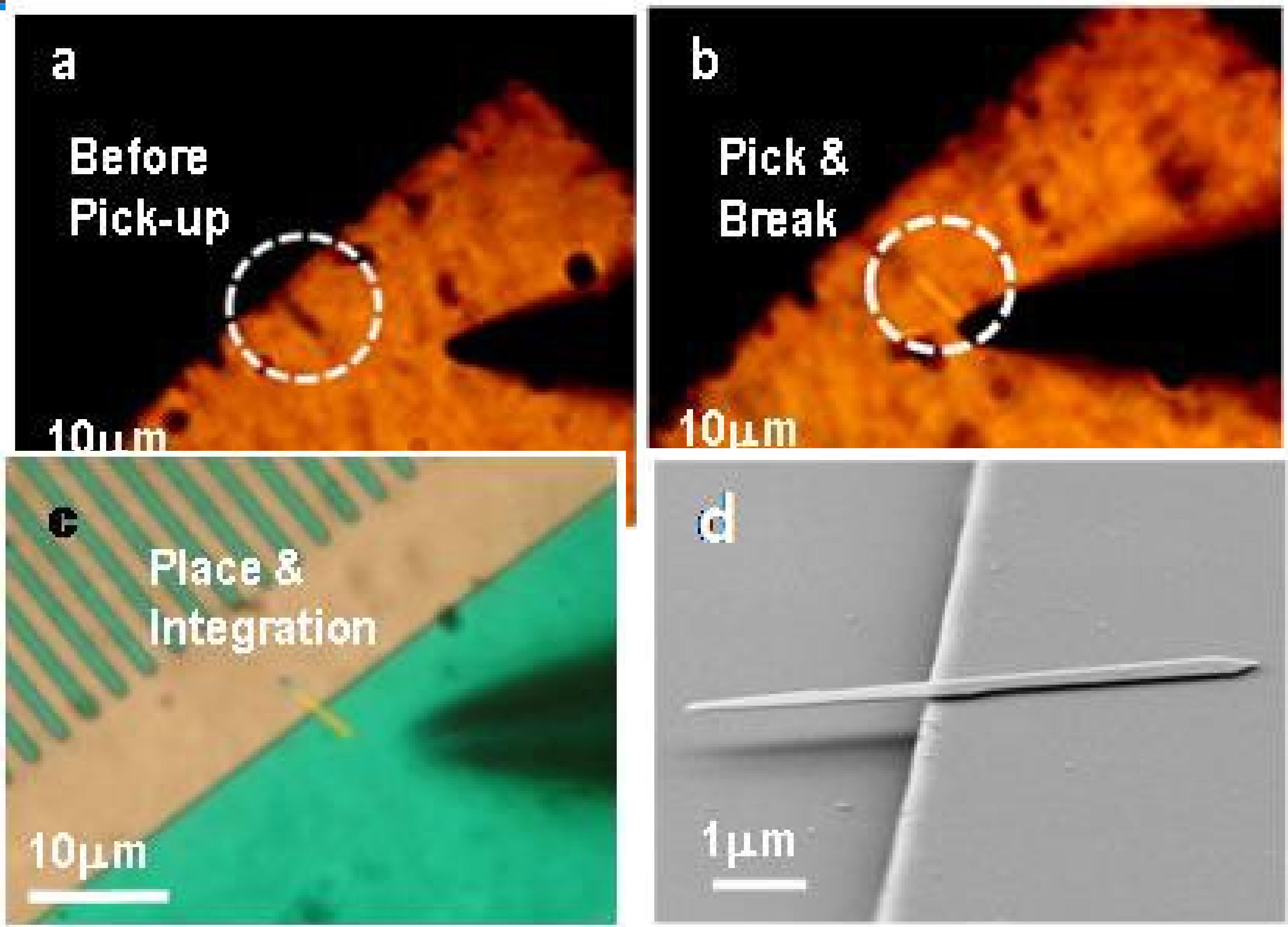
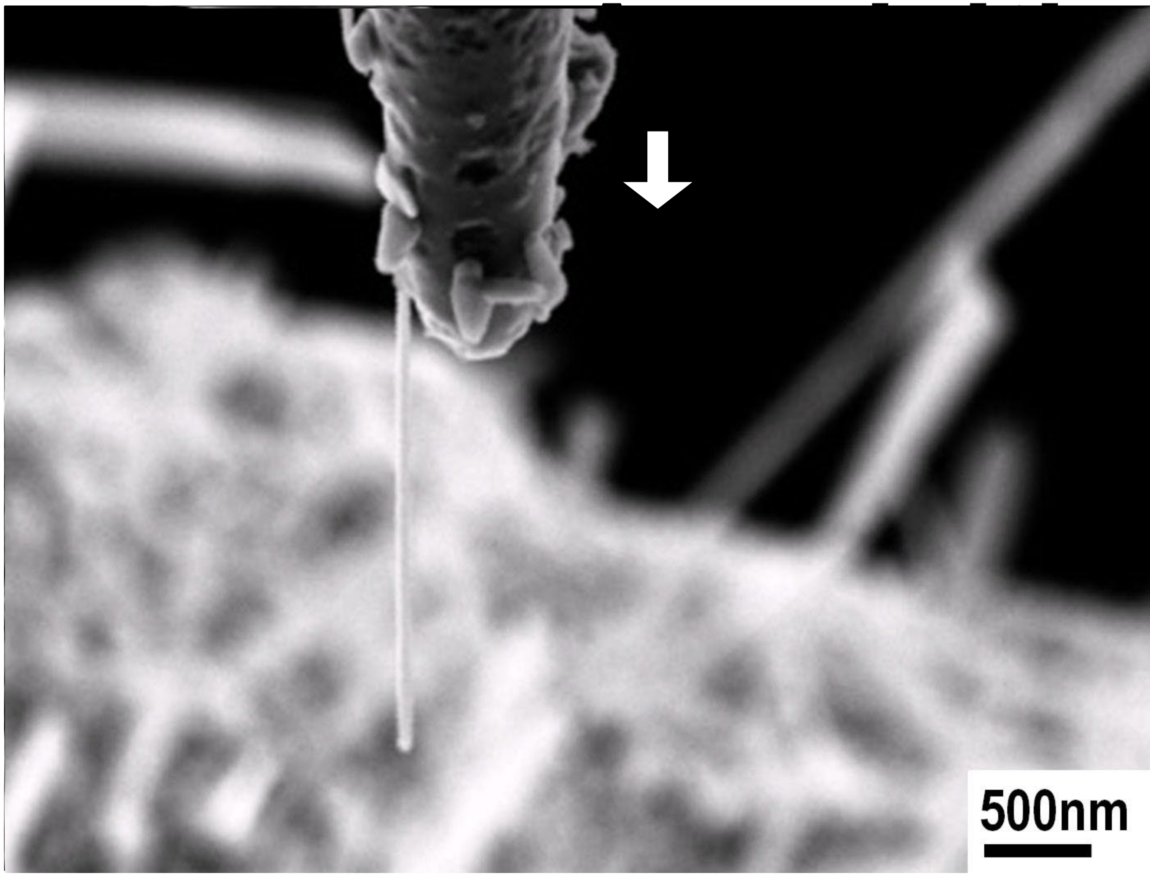
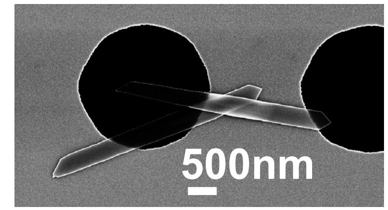
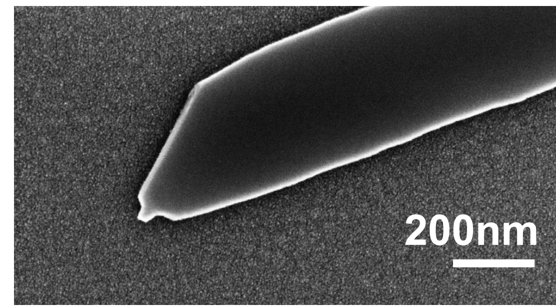
# Operation Sequences

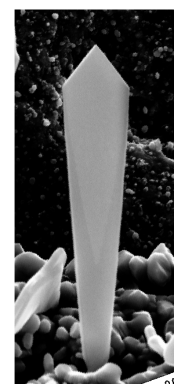


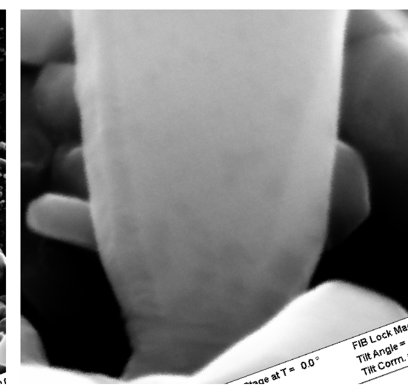
# In-Situ SEM Analysis of





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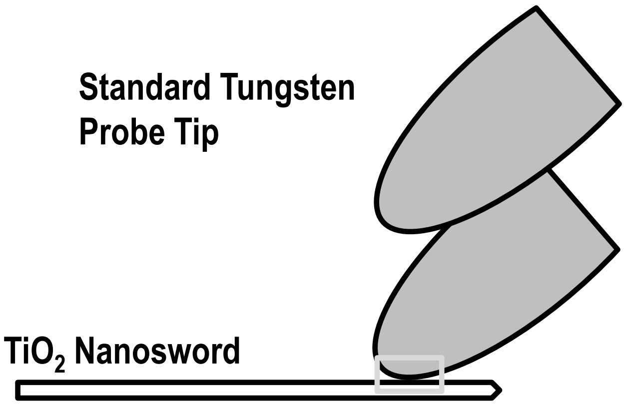
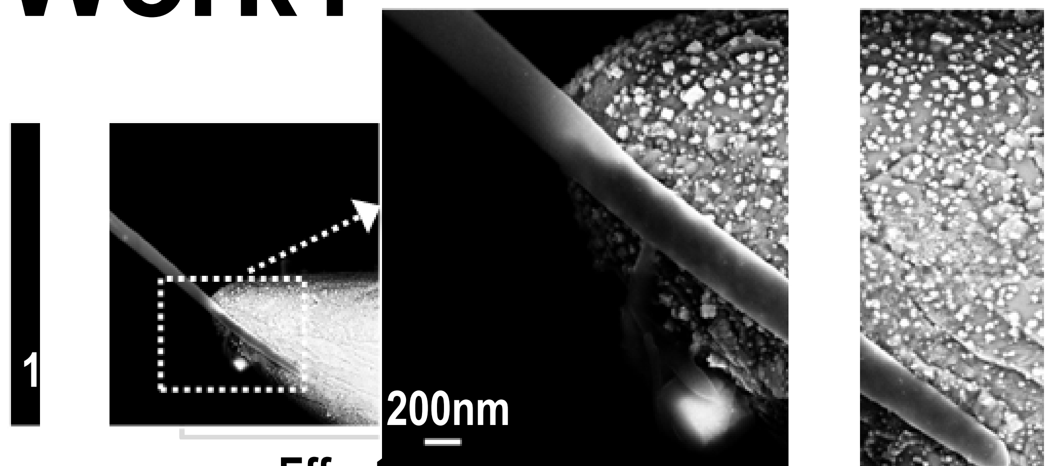
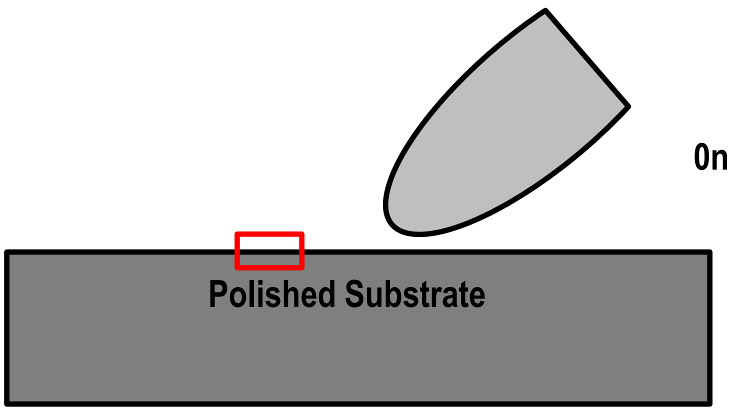
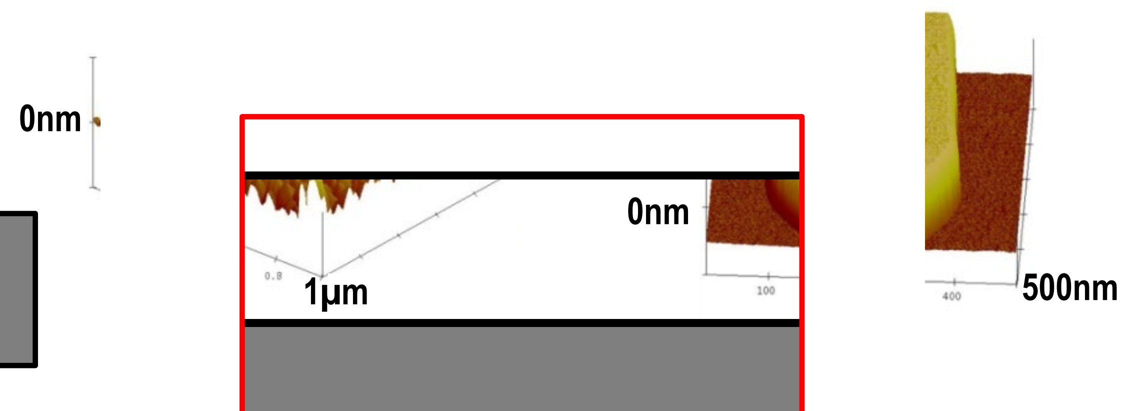
# Why Pick, Break and Place Work?




Effective Contact is Reduced at Interface




Effective Contact is Much Larger

Yeiji Lee, Athena G. Lewis, Jacky Li

# Direct-Current Nanogenerator Driven by Ultrasonic Waves:

Paper 6.1

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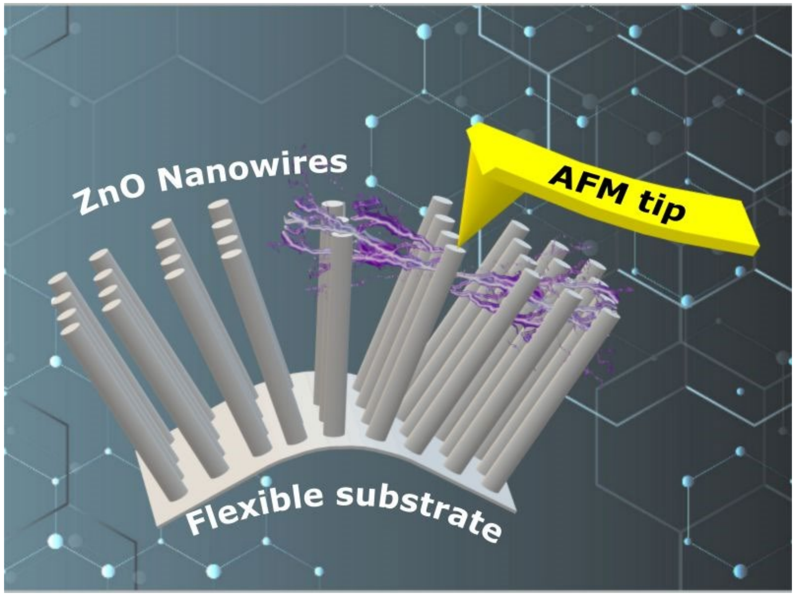
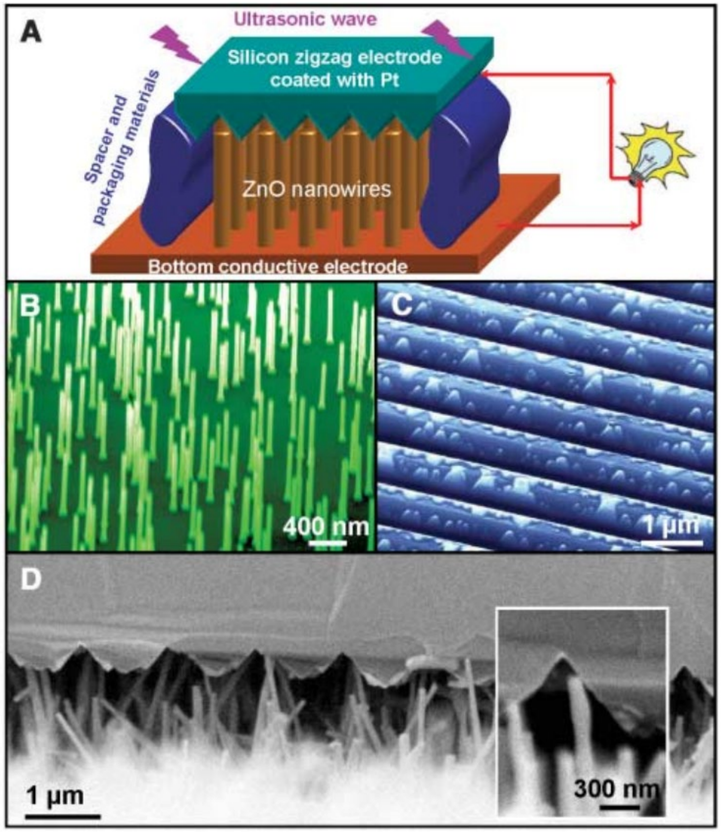
# Background

- Nanodevice fabrication requires an external power source
  - Limitation
- Innovative Approaches
  - Ex. Piezoelectric zinc oxide nanowire (ZnO NW) with AFM deflection
    - Deflection force = converted into electricity
    - Need simpler mechanical energy source with continuous actuation



# Ultrasonic Waves

- Used to produce a continuous direct current output
- Experimental Setup
  - ZnO Nanowires with silicon zigzag electrode coated with Pt
  - Pt Coating = Schottky Contact at ZnO Interface
  - Nanowires grown on GaN substrates (Figure B)
  - Electrode composed of parallel zigzag trenches on Si wafer with a coating of Pt (Figure C)
  - Lip/Teeth relationship between nanowires + electrode
    - Direct and no contact between the two
- Supported by a metal plate that's in direct contact with water of ultrasonic generator

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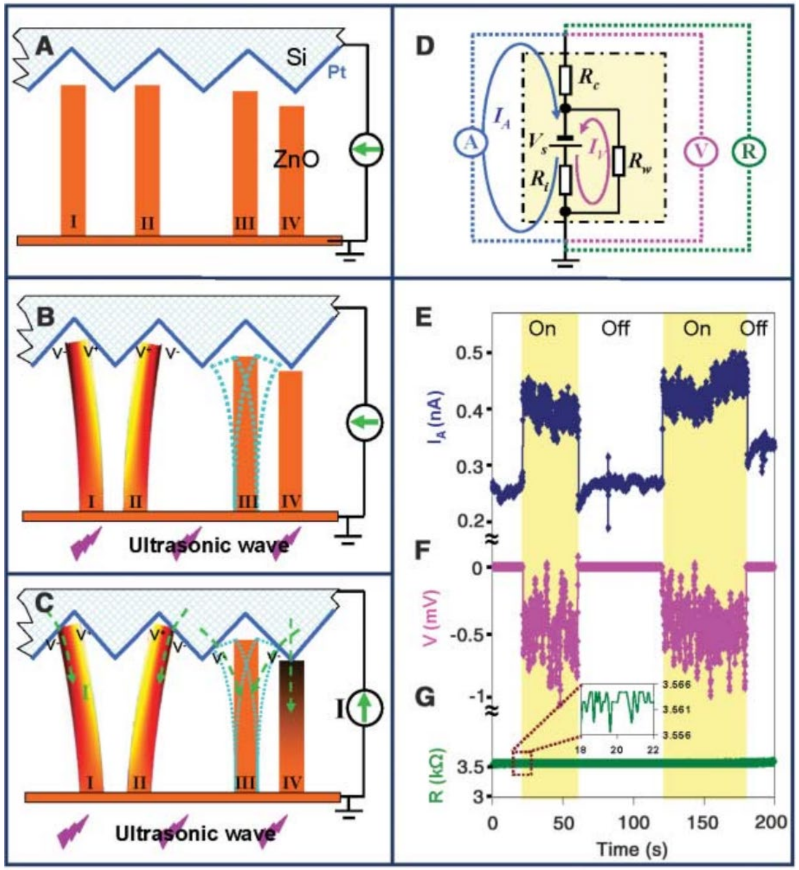
# Ultrasonic Waves cont.

- 2 processes for creating, separating, preserving accumulating, and outputting charges
  - Asymmetric piezoelectric potential
  - Schottky contact
- Top electrode replaces the role of AFM tip
  - Zig zag trenches = array of aligned AFM tips
- **Discharge Process**
  1. Ultrasonic wave excitation
  2. Electrode moves down and pushes NW
  3. Lateral deflection of NW1
  4. Strain field created across width of NW1
  5. Inversion of piezoelectric field (V- to V+)
  6. Electrode contacts NW surface = little current across interface
  7. More pushing = NW reaches other side of adjacent tooth
  8. If electrode is in contact with compressed side of NW = sudden increase in output electric current

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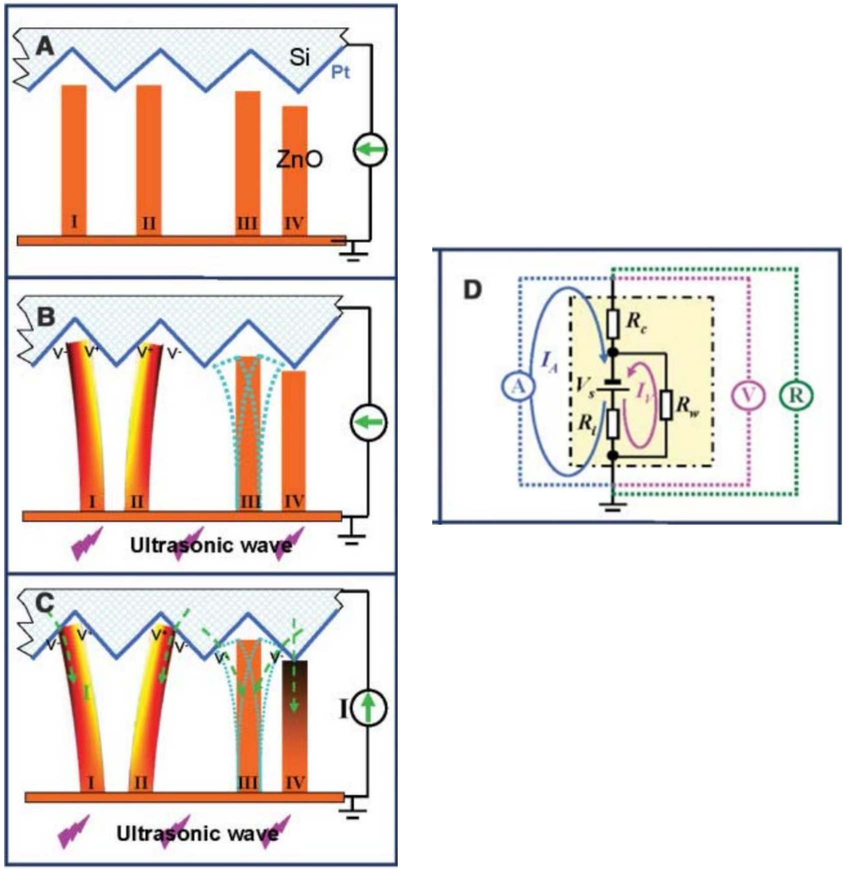
# Configurations of Contact

- 4 different configurations of contact between NW and zigzag electrode (Figures A-D)
  - NWIII elaborates on vibration/resonance by the ultrasonic wave
  - NWIV is forced into compressive strain at tip of zig zag trench
  - All currents add up to same phase
- Figure D: electric circuit to get measurements of nanogenerator outputs
  - NWs produce current
  - Vs = voltage current
  - Ri = inner resistance
  - Many NWs cannot be bent or move freely
    - Do not actively participate in current generation, but make a path for conducting current
  - Rw = resistance parallel to portion that generates power
  - Rc = contact resistance between electrode and external measurement circuit

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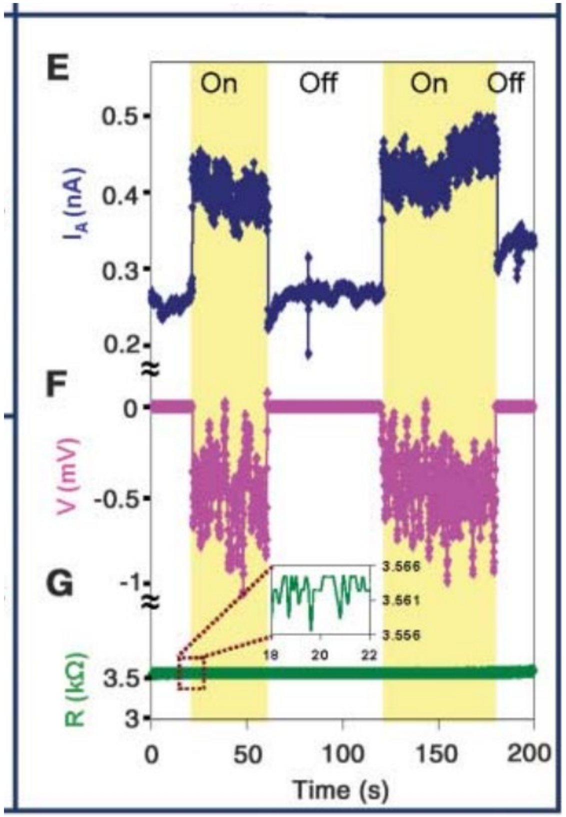
# Current + Voltage Outputs

- Signal-to-noise ratio is better than output voltage because:
  - Resistance of current meter plus Rc =~ 1/1000 Rw
  - Current generated by nanogenerator was bypassing Rw
  - Measured Current: $I_A = V_S/(R_C + R_i)$
- Since Rw is much smaller than inner resistance, a loop was formed between power generating portion and Rw
  - V= $-V_S R_W/(R_W + R_i)$
- V has about 2 times the noise level of $I_A$
  - However, it is relatively unstable with a larger noise level than $I_A$

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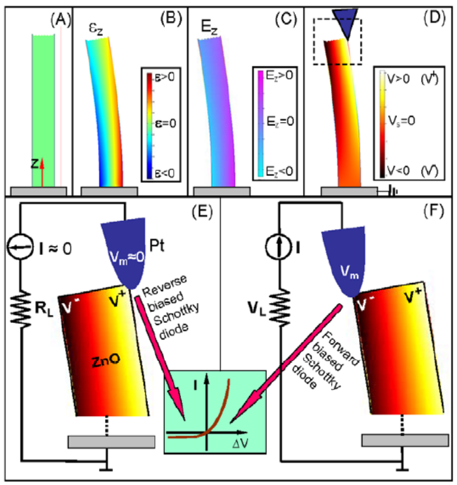
# Schottky Contact

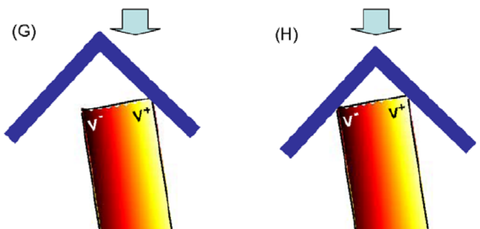
Schottky barriers have rectifying characteristics, suitable for use as a diode.

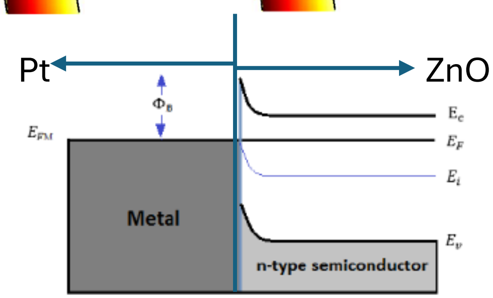
Not all metal–semiconductor junctions form a rectifying Schottky barrier; a metal–semiconductor junction that conducts current in both directions without rectification, perhaps due to its Schottky barrier being too low, is called an ohmic contact.

Schottky contact happens both when the semiconductor is n-type and its work function is smaller than the work function of the metal, and when the semiconductor is p-type and the opposite relation between work functions holds

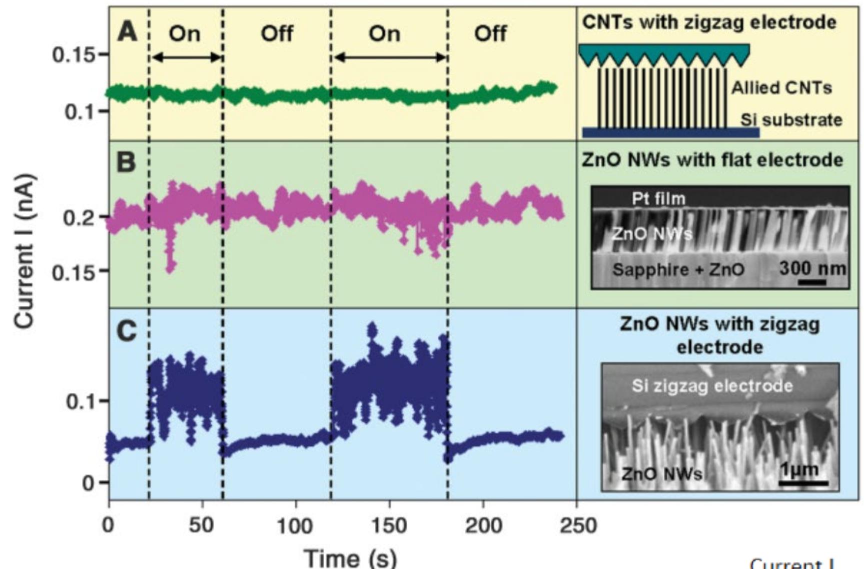
# Mechanism of ZnO Generator and Control study (Page 4)

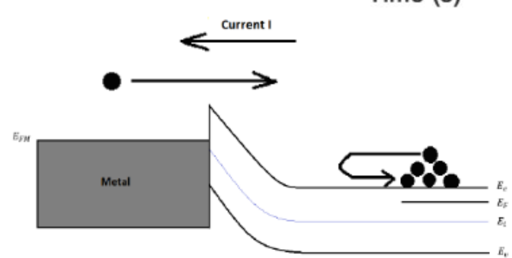


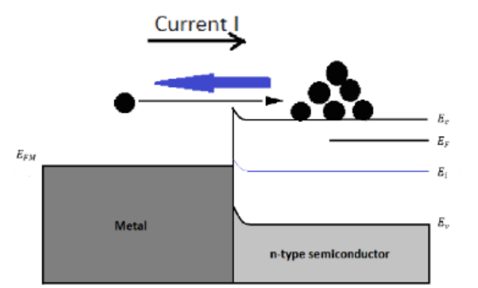




No strain in ZnO NW



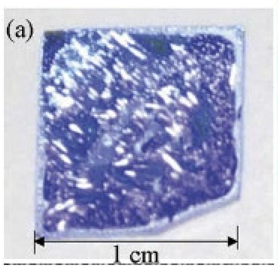

Corresponding to (G) Reverse Bias



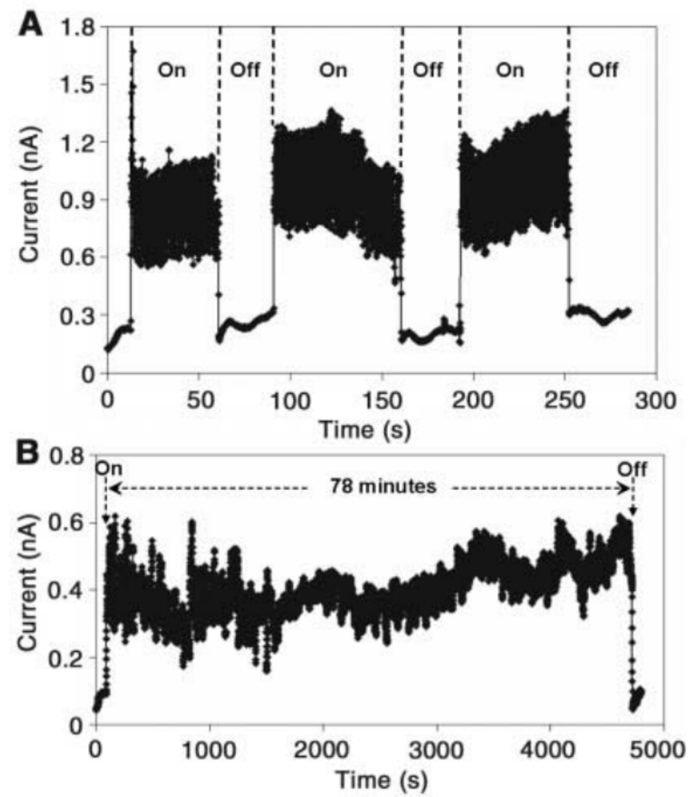

Corresponding to (H) Forward Bias

# Experimental Results

- Excitation frequency ~ 41 kHz
- 80 times smaller than resonance frequency (~3 MHz)

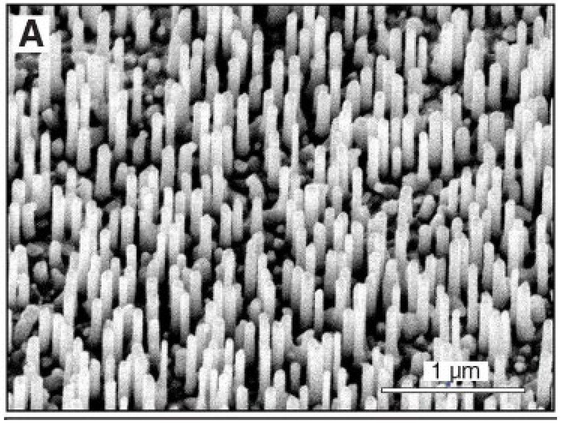



Large-Scale Hexagonal-Patterned Growth of Aligned ZnO Nanorods for Nano-optoelectronics and Nanosensor Arrays. Xudong Wang et al. Nano Letters



# Metrics and Comparison With Previous Work

- ΔE_afm ~ 0.01 fJ, Δt = 1 ms → ΔW = ΔE_afm/Δt = 0.1 pW
- However, since this paper uses ultrasonic excitation instead of AFM (their last paper), so strain magnitude is 5 times less, leading to a smaller voltage, which correspond to a smaller power output of 1 to 4 fW
- The output-power volume density **per NW** is ~1 to 4 W/cm^3
  - Two orders of magnitude higher than vibrational microgenerator
- Measured total power is W = I*V = 1 pW, with a substrate area 2 mm^2, the calculated number of functional nanowire is 250 to 1000.
  - Performance limited by uniformity in height




Zhong Lin Wang,Jinhui Song, Piezoelectric Nanogenerators Based on Zinc Oxide Nanowire Arrays.*Science***312**,242-246(2006).DOI:10.1126/science.1124005

# Optimizing Power per Area and Performance (Future work)

Patterned tip arrays, uniform growth and designed zigzag electrode accordingly

A_tip = 0.5 x 0.5 micron

ρ_nw = 1e9 /cm^2

W = 10 fW

U = 10 microW/cm^2

Power used to operate a device with 1 NW or nanotube is 10 nW, so a 1 cm^2 OPTIMIZED nanogenerator can power 1000 such devices.

The performance can be boosted 2~3 orders of magnitude with improved design.

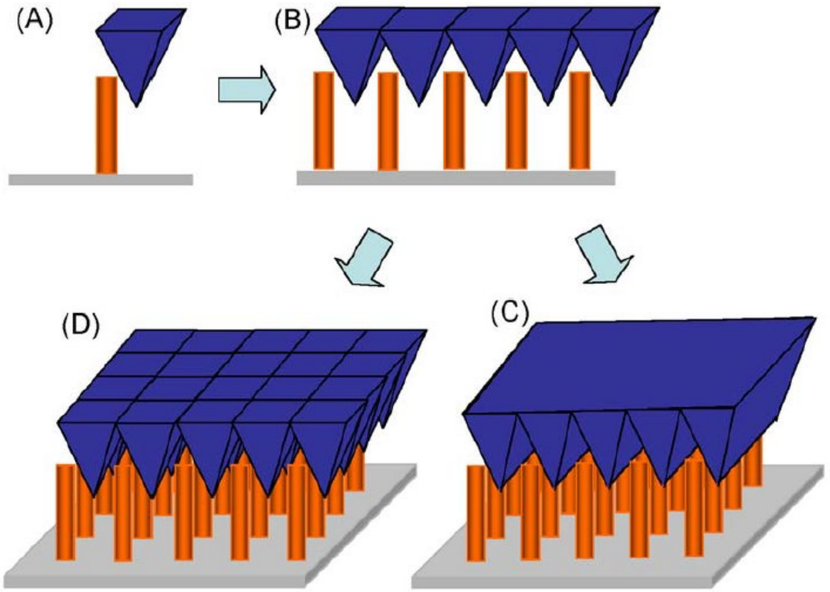
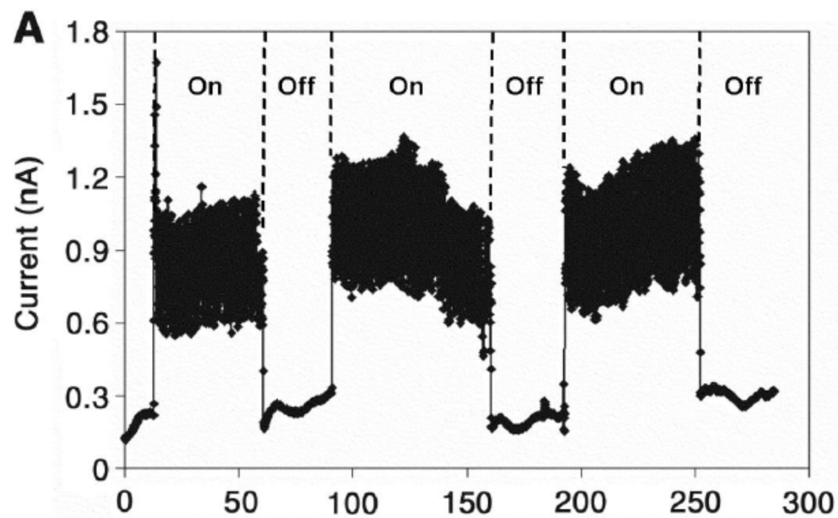



Fig. S2. The design of zigzag electrode according to the mechanism presented in Fig. S1.

# Output Electricity of the Nanogenerator

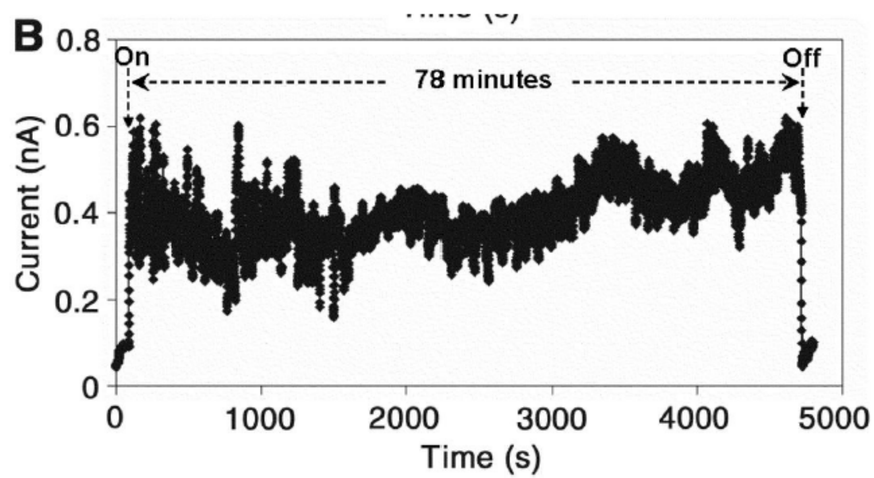
- Continuous current is generated when the ultrasonic wave is turned on and disappears when turned off (Fig A)
  - No direct coupling between the current signal and frequency of ultrasonic wave, because the wave frequency is 80x smaller than the resonance frequency of the NWs (3MHz)




Z. L. Wang et. al, *Science* **312**, 242 (2007).

# Output Electricity of the Nanogenerator

- Figure B shows the nanogenerator continuously working for 78 minutes
  - Nanogenerator is ~2 mm^2 in surface area
  - 250-1000 NWs contributed to the output current observed in the figure

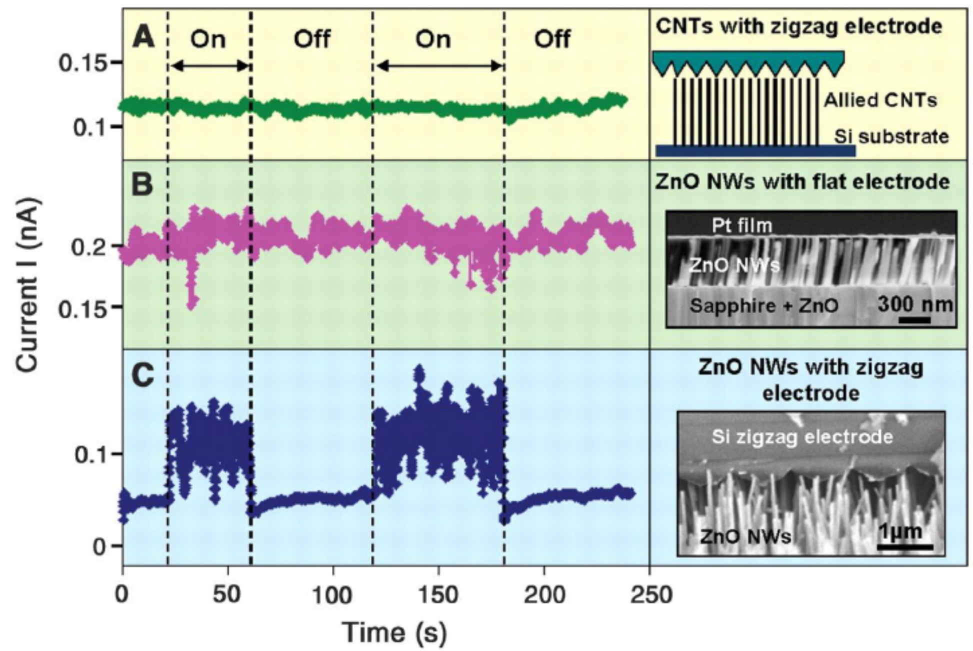



Z. L. Wang et. al, *Science* **312**, 242 (2007).

# Different Materials/Configurations

- CNT with zigzag electrode (A)
  - No jump in current
  - CNTs are not piezoelectric
- Thin PT film (flat electrode) covering tips of NW (B)
  - No jump
  - Design does not follow mechanism of the nanogenerator
- ZnO NWs with zigzag (C)
  - Jump

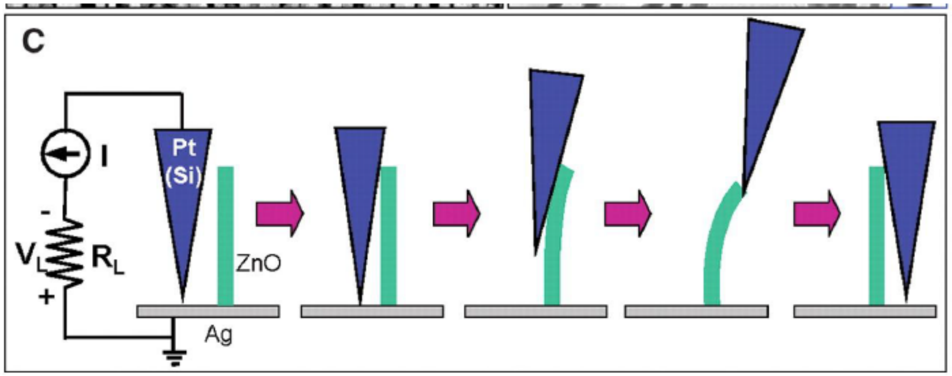
Supports the process proposed for piezoelectric NWs



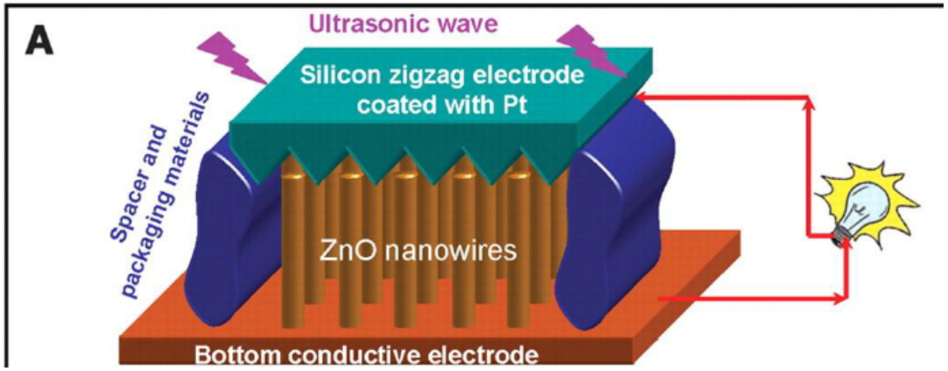

Z. L. Wang et. al, *Science* **312**, 242 (2007).

# 3 Achieved Objectives

- Replaced ADM tip (C) with ultrasonic waves (A) to induce deformation and vibration in NWs which helped to cut down costs for fabricating the nanogenerator




Z. L. Wang, J. Song, *Science* **312**, 242 (2006).




Z. L. Wang et. al, *Science* **312**, 242 (2007).

# 3 Achieved Objectives

- Raised the output power by integrating an array of tips into a zigzag electrode
    - NWs created, collected, and outputed electricity
- Continuous and stable dc output with the system discussed. This sets a stage for powering vivo biosensors, wireless and remote sensors, nanorobots, etc. with energy from the environment