Introduction to Nanotechnology and Nanoscience – Class#14

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Outline

- Review
- CNT Applications – AFM example
- HW #5
- Nanowires
- Paper 5 & 5-1
- Paper 6

HW#4 Due Date

- New due date – March 5, 2024

ABET Outcomes

- a. An ability to apply knowledge of mathematics, science, and engineering
- b. an ability to design and conduct experiments, as well as to analyze and interpret data
- e. an ability to identify, formulate, and solve engineering problems
- f. an understanding of professional and ethical responsibility
- g. an ability to communicate effectively

ABET Outcomes

- h. the broad education necessary to understand the impact of engineering solutions in a global, economic, environmental, and societal context
- i. a recognition of the need for, and an ability to engage in life-long learning
- j. a knowledge of contemporary issues
- k. an ability to use the techniques, skills, and modern engineering tools necessary for engineering practice.

CNT Structure

Chiral vector for (n_1, n_2) CNT

$$\mathbf{C}_{\mathrm{CNT}} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 = (n_1, n_2)$$

Tube diameter

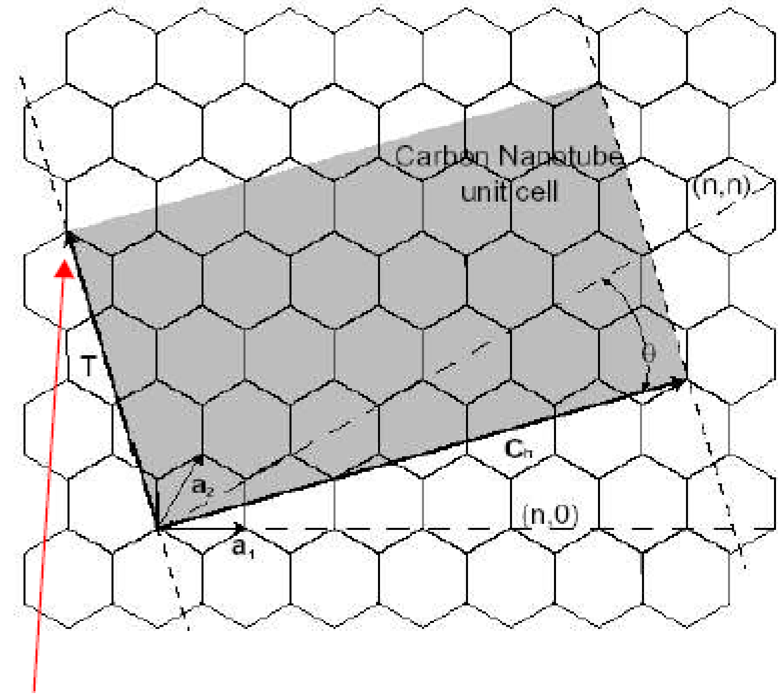
$$d_{\mathrm{CNT}} = \frac{|\mathbf{C}_{\mathrm{CNT}}|}{\pi} = a\sqrt{n_1^2 + n_2^2 + n_1 n_2}$$

CNT "translation" vector

$$\mathbf{T}_{\mathrm{CNT}} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2 = (t_1, t_2)$$

$$t_1 = \frac{2n_2 + n_1}{d_{\mathrm{R}}} \qquad t_2 = -\frac{2n_1 + n_2}{d_{\mathrm{R}}}$$

$d_{\mathrm{R}} =$ Greatest common devisor of $(2n_1 + n_2, n_1 + 2n_2)$



1st lattice point reached!

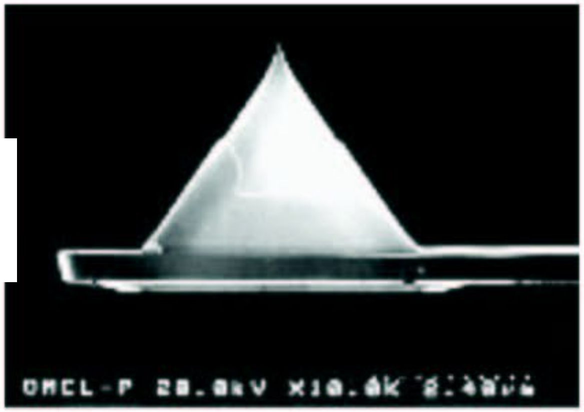
Number of hexagons in **nanotube** unit cell:

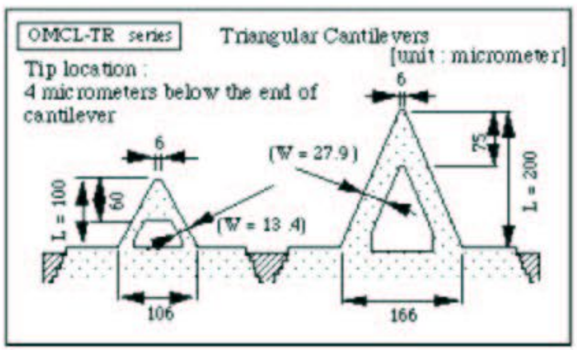
$$N_{\mathrm{CNT}} = \frac{2(n_1^2 + n_2^2 + n_1 n_2)}{d_{\mathrm{R}}}$$

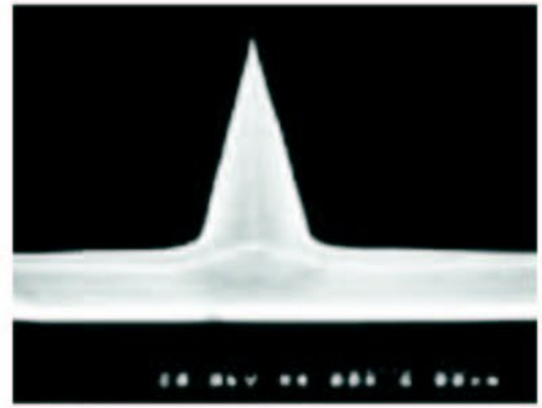
Chiral angle (definition)

$$\cos\theta = \frac{\mathbf{C}_{n_1,n_2} \cdot \mathbf{a}_1}{|\mathbf{C}_{n_1,n_2}||\mathbf{a}_1|} = \frac{2n_1 + n_2}{2\sqrt{n_1^2 + n_2^2 + n_1 n_2}}$$

Cantilevers for the AFM



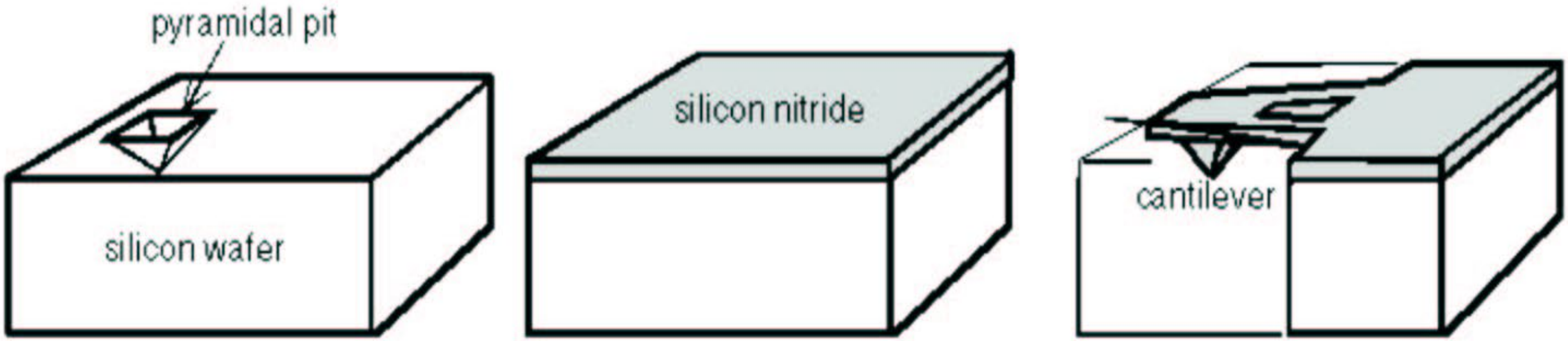




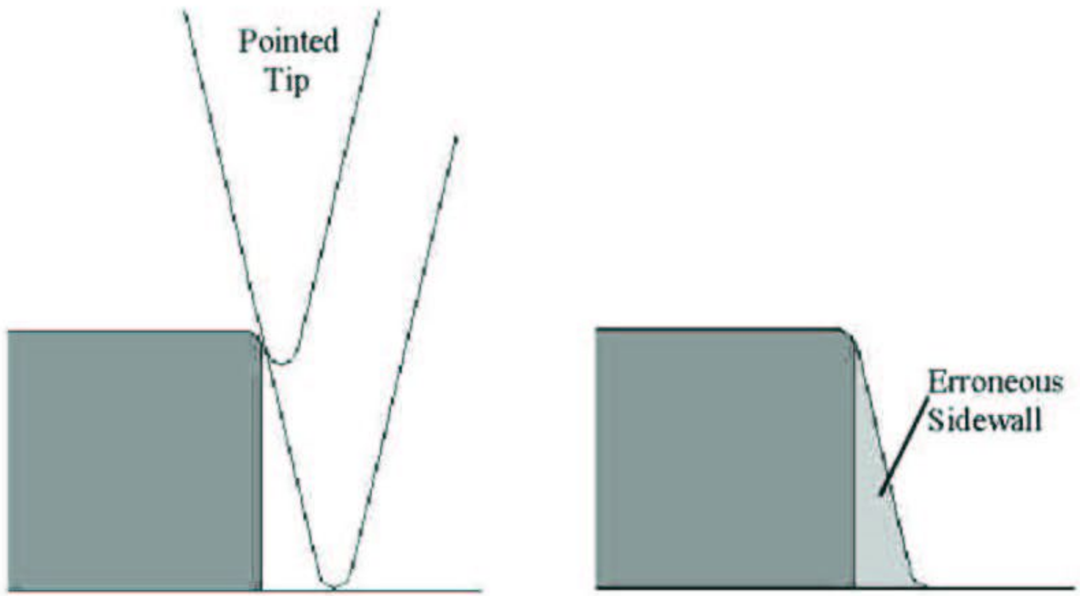
Silicon Nitride Tip

Silicon Tip

Silicon Nitride Cantilevers



How does your tip profile affect your AFM scan?



http://www.photronics.com/templates/techpapers/bacus_manuscript/bacus_manuscript4.pdf

Using CNT as AFM Tips

- If a tip were sharper and at less of an angle
- If a tip didn't get destroyed when crashing
- If a tips didn't show wear

Then we would have the "perfect" tip for AFM

CNT satisfy some of these requirements!

CNTs - Nearly Ideal AFM Tips

- CNTs are **nearly ideal** because they have
  - —small diameters
  - —high aspect ratios ("long and skinny")
- They also **buckle reversibly**

$$F_{EULER} = \pi^2 YI/L^2$$

where Y = Young's Modulus
I = stress moment over the cross-section of the nanotube of radius r
L = length of the nanotube

Euler Buckling Force - CNT

$$F_{EULER} = \pi^2 YI/L^2$$

For a Multi-Walled Carbon Nanotube:

$L = 250$ nm

$r = 2.5$ nm

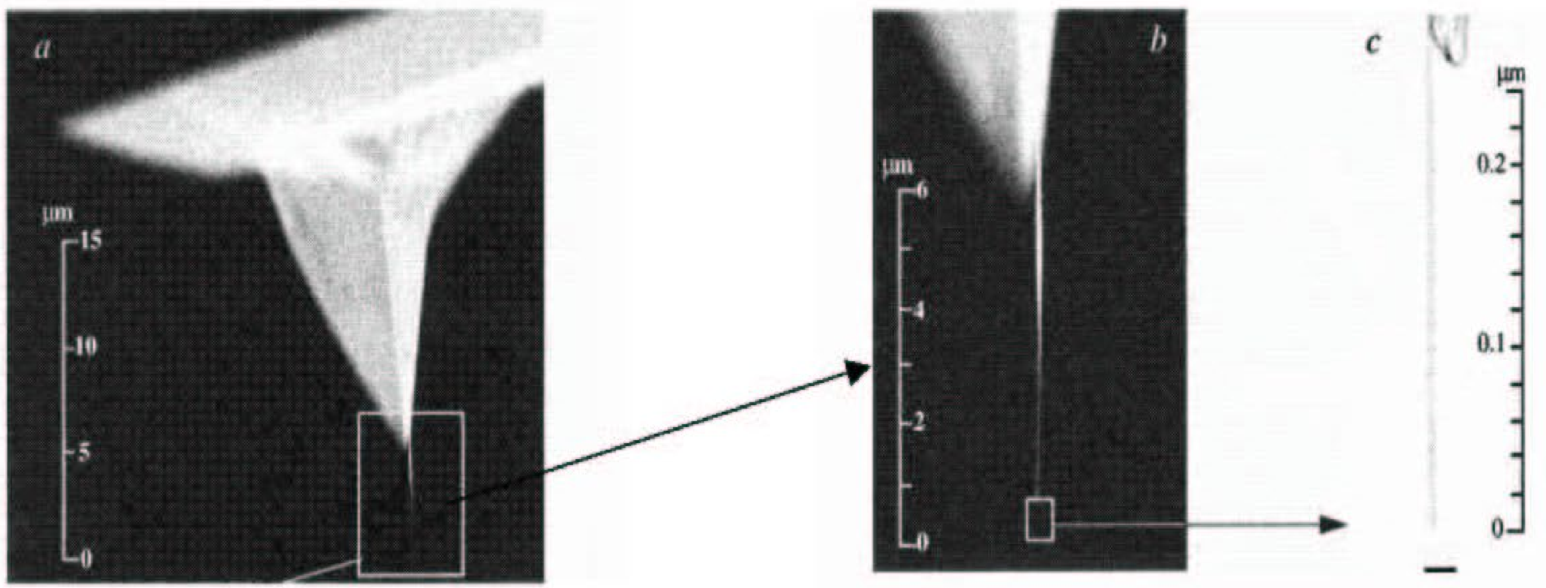
$Y = 1$ Tpa (approximating that Y is similar to in-plane graphite)

$$F_{EULER} = 5 \text{ nN}$$

Once CNT goes beyond 5 nN, it will bend through large amplitudes and buckle reversibly

Two Ways to Make AFM Tips

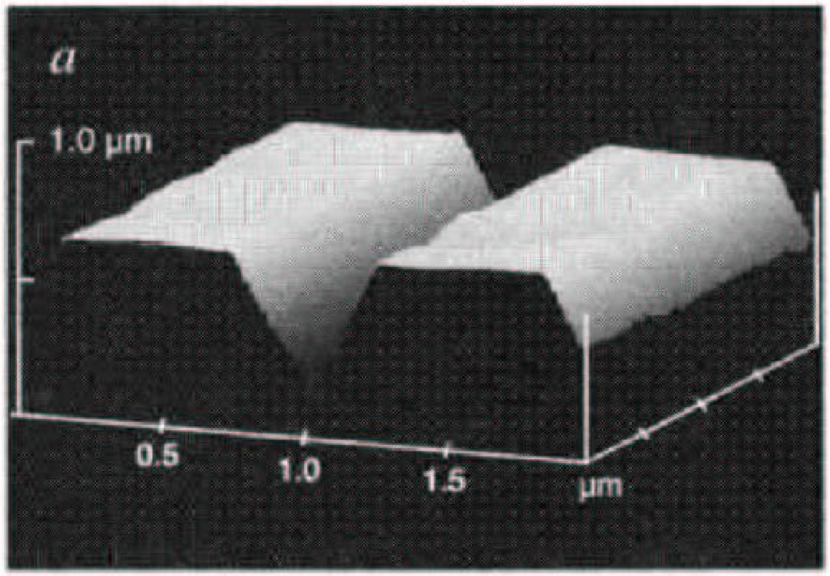
First Way:



- Dai et al. used tape to attach a CNT to a Si cantilever (Dai et al. Nature , 1996)
- Note the length of the nanotube tip and its "verticality"
- Can shorten the tip using an electron microscope

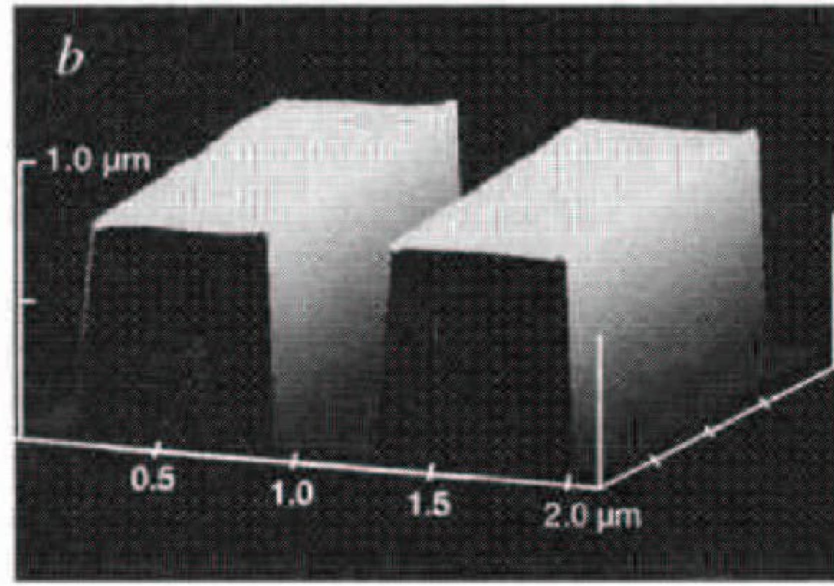
Improvement on Imaging

0.4 μm wide x 0.8 μm deep trench



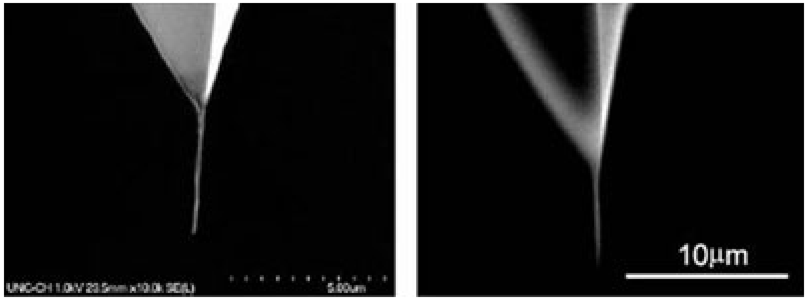
Si_3N_4 Tip

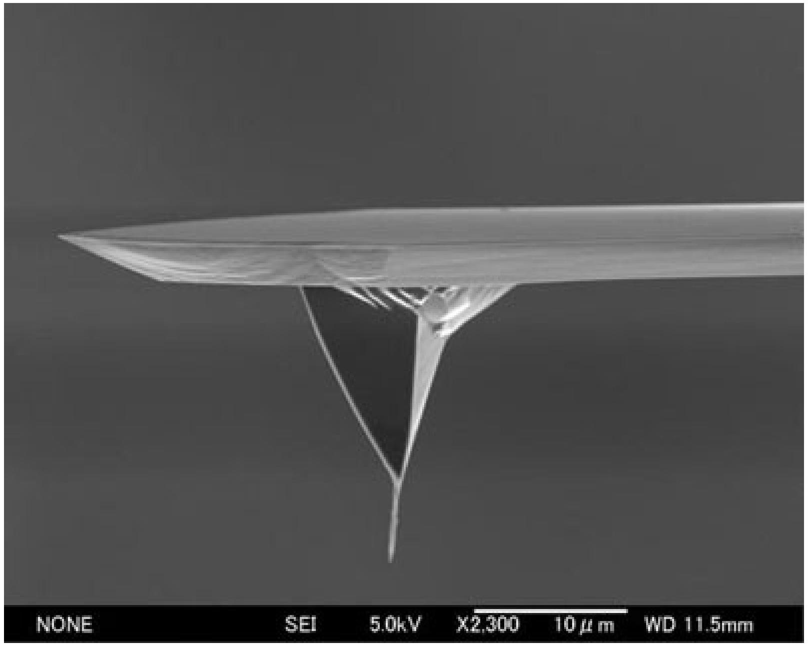
0.4 μm wide x 0.8 μm deep trench

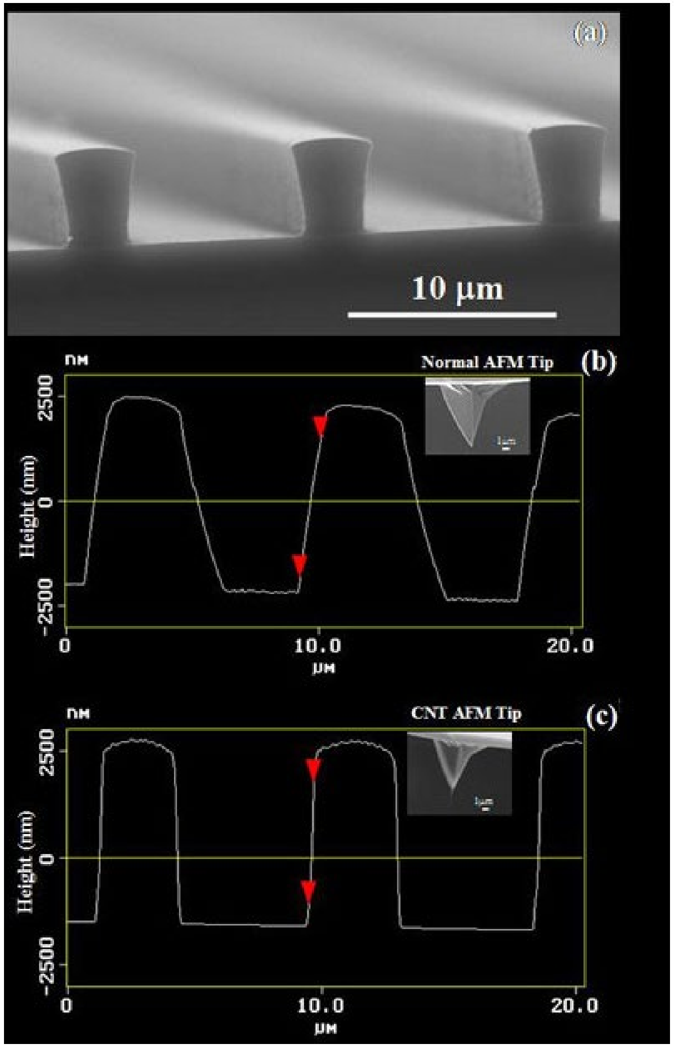


CNT Tip

From Dai et al., Nature 1996







http://www.xintek.com/products/afm/index.htm

Second Method – AFM-CNT Tip

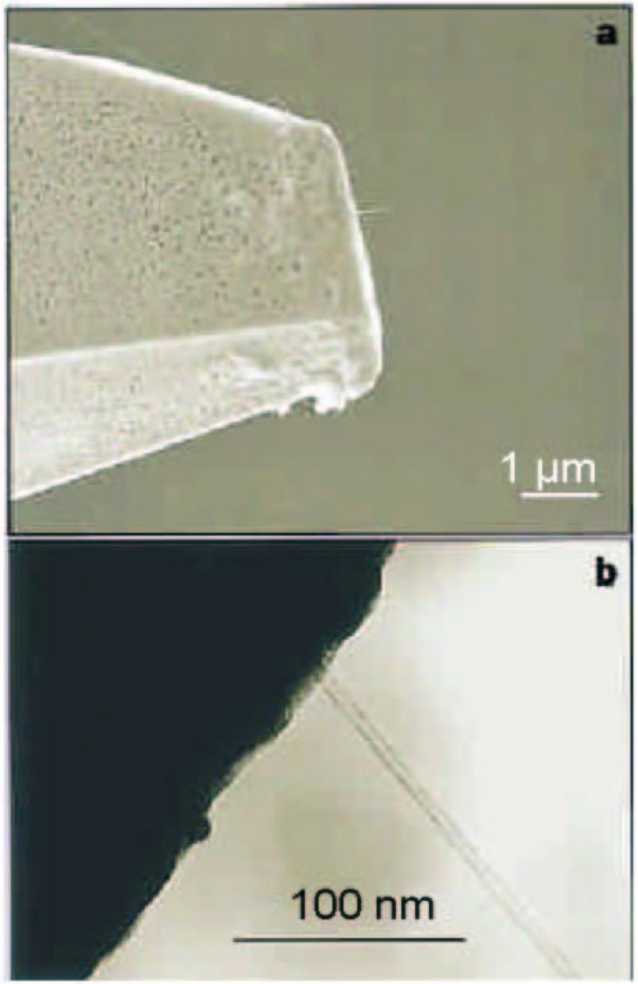
•As great as the previous method was to making AFM tips with CNTs, there are **problems**:

—**time-consuming** process
—selects only **large nanotubes**
—**limits the quality** of the tips

•A **second way** of making tips with CNTs overcomes some of these hurdles

CVD CNTs directly onto the AFM tips!

CVD Fabrication of CNT Tips



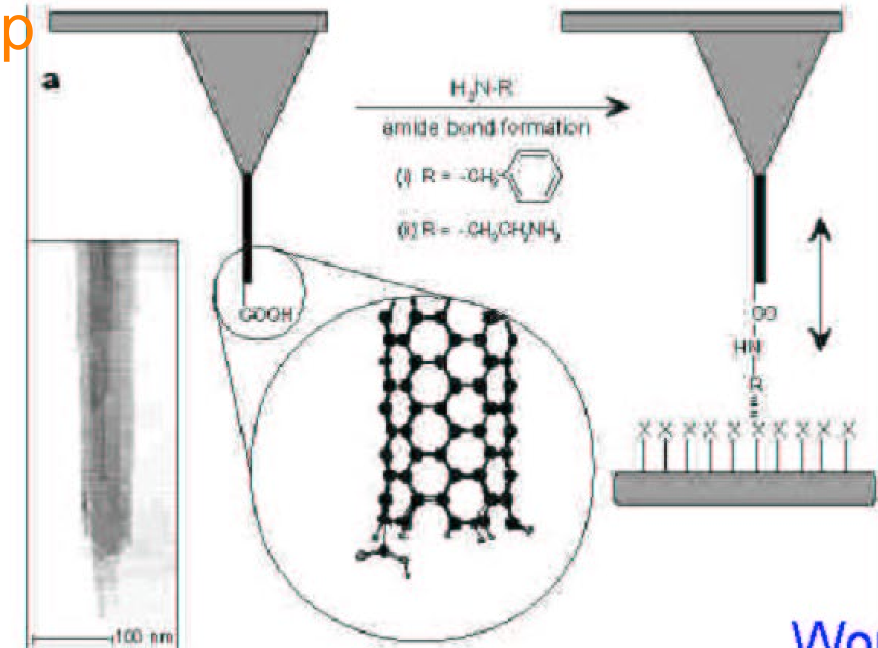
Hafner et al., Nature 1999

- "Shave" off the tip end of cantilever
- Annodize in HF to create nanopores of size 50-100 nm at tip
- Iron catalyst deposited in nanopore
- CVD growth of nanotube with ethylene and hydrogen at 750 C
- Tip often too long, so can shorten with electron gun
- CNTs are multiwalled and 10 nm diam
- Flexible and can buckle but not break
- If tip is bad, the CNT can be removed with oxidation and regrown

Functionalized CNT AFM Tips

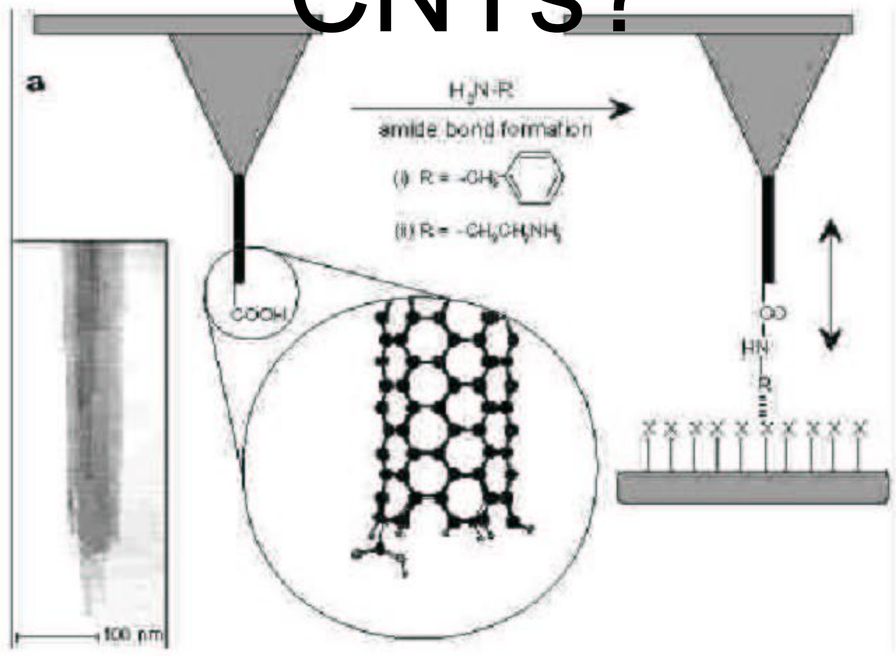
•Because CNT tips have a small effective radius (i.e. high lateral resolution), and because they can buckle elastically, they can be used to probe organic or biological molecules

•The way to scan organic/biological molecules is to functionalize the CNT AFM tip



Wong et al, Nature 1998

How Do We Functionalize CNTs?



- CNT exposed to O_2 plasma opens up the end of the nanotube
- Carboxy group (-COOH) forms at the end of the tube
- Add an amine group (H_2NR)
- Check to see you have the amine group by performing

Chemical Force Microscopy

University of California at Berkeley
College of Engineering
Mechanical Engineering Department

ME118/218N, Spring 2024 **Liwei Lin**

Problem Set #5
Due March 12 (Tuesday)

Problem 1 (AFM)

You are performing an AFM measurement of CNTs on a surface.

a) What is the "apparent" or "measured" radius (width) **ρ** of a CNT of radius **r** if the radius of the AFM tip is **R**? Derive an algebraic expression for **ρ**, showing all relevant steps.

b) Can a carbon nanotube of diameter 1 nm lying on a flat surface be "detected" by your AFM with a Si_3N_4 tip radius of 10 nm? Can it be "resolved"? Discuss qualitatively the difference between resolution and detection.

Problem 2 (CNT Properties for AFM)

The Euler buckling force for a carbon nanotube is given by:

$$F_{EULER} = \pi^2 YI/L^2$$

where Y is the Young's modulus of the nanotube, I is the moment of the cross-sectional area of the carbon nanotube about the "neutral axis", and L is the length of the carbon nanotube. Please calculate F_{EULER} for a nanotube 3 micron long, and 3 nm in diameter.

Why Nanowires?

- ☐ CNTs and semiconducting nanowires promising for use in nano-scale electronic devices
- ☐ Issues with CNTs
  - Semiconducting or Metallic
  - Difficult to select form
- ☐ Pros of Nanowires
  - Properties of semiconducting nanowires set by material choice
  - Wide range of possible materials means a wide range of properties

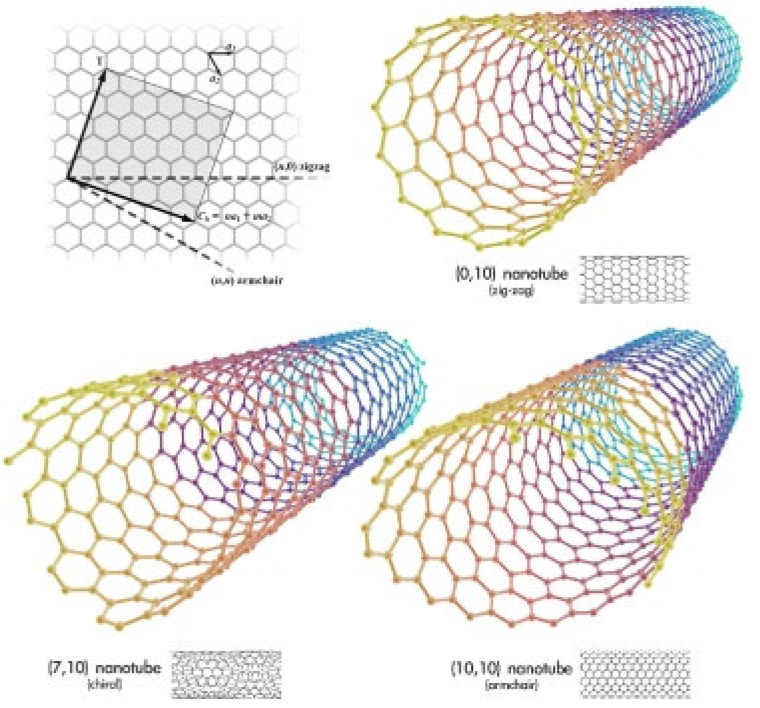


Image courtesy of www.grin.com

Why nanowires?

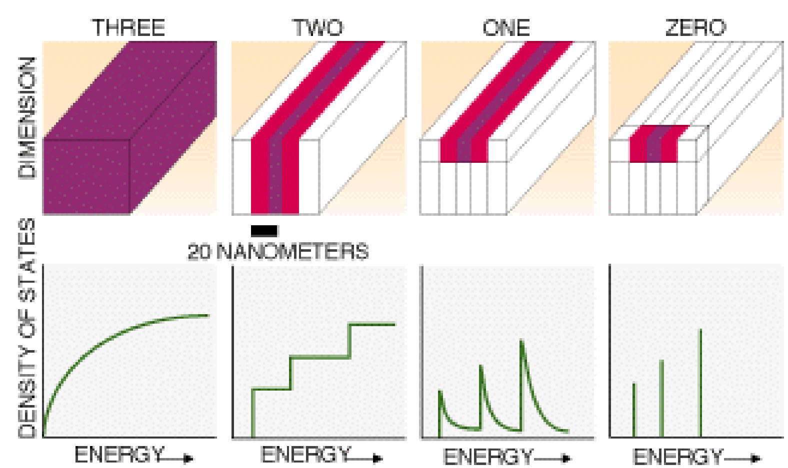
"They represent the smallest dimension for efficient transport of electrons and excitons, and thus will be used as interconnects and critical devices in nanoelectronics and nano-optoelectronics." (CM Lieber, Harvard)

General attributes & desired properties

- Diameter – 10s of nanometers
- Single crystal formation -- common crystallographic orientation along the nanowire axis
- Minimal defects within wire
- Minimal irregularities within nanowire arrays

Why Nanowires? Quantum confinement

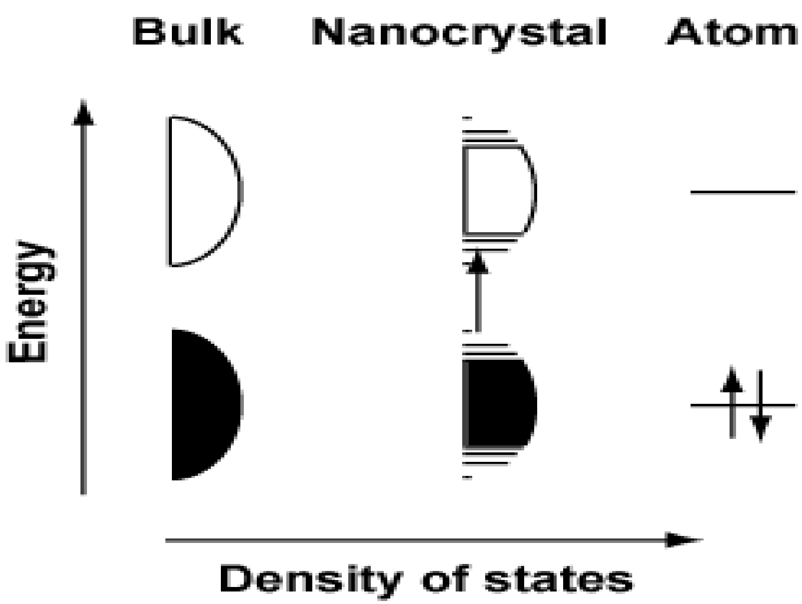
- Trap particles and restrict their motion
- Quantum confinement produces new material behavior/phenomena
- "Engineer confinement"- control for specific applications
- Structures
  - Quantum dots (0-D) only confined states, and no freely moving ones
  - Nanowires (1-D) particles travel only along the wire
  - Quantum wells (2-D) confines particles within a thin layer



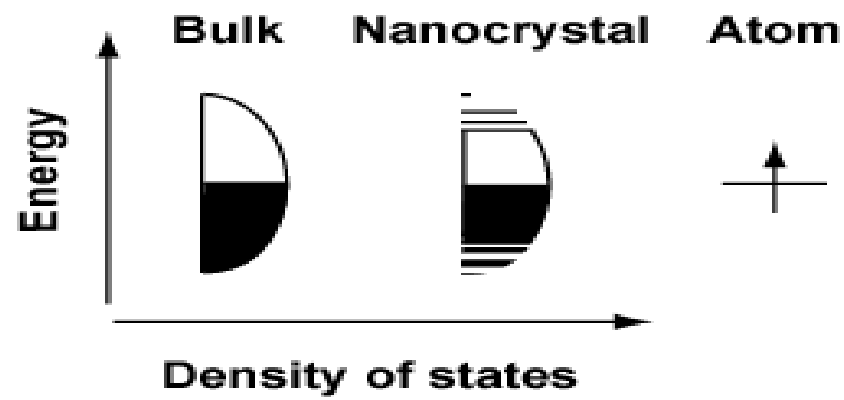
(Scientific American)

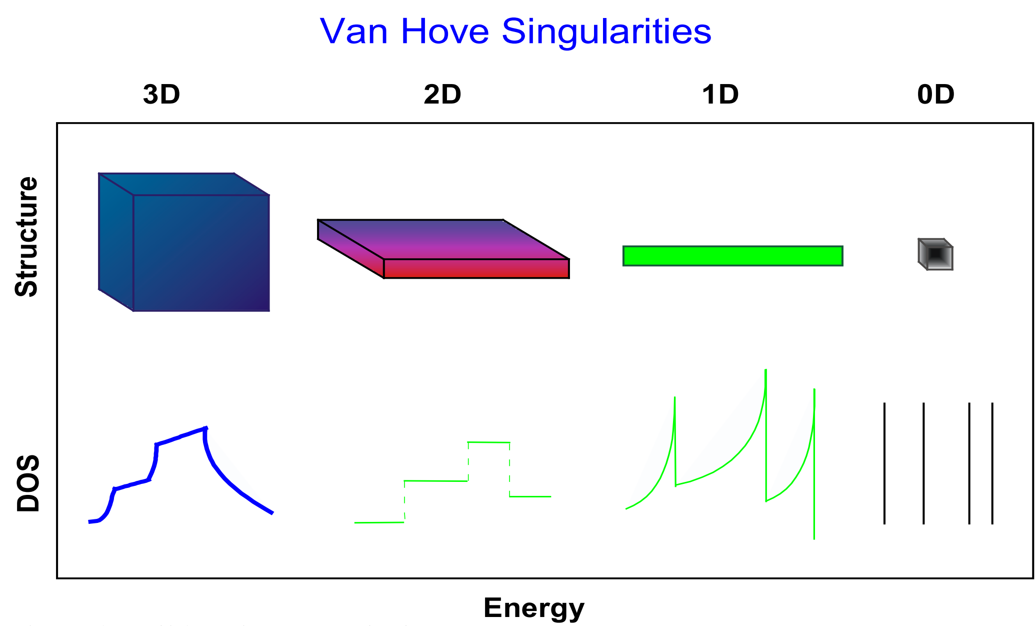
Fundamental Science

Semiconductor



Metal





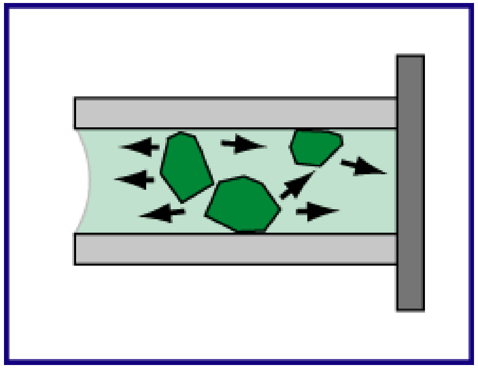
Density of States in d-dimensions :

$$DOS(E) = \left(\frac{L}{2\pi}\right)^d \int dk^d \frac{\delta(k(E)-k)}{|\vec{\nabla}_k E|}$$

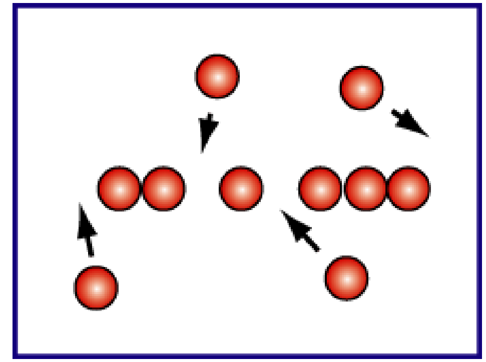
At a band edge, as $\vec{\nabla}_k E \rightarrow 0$

DOS(E) has a singularity at E.

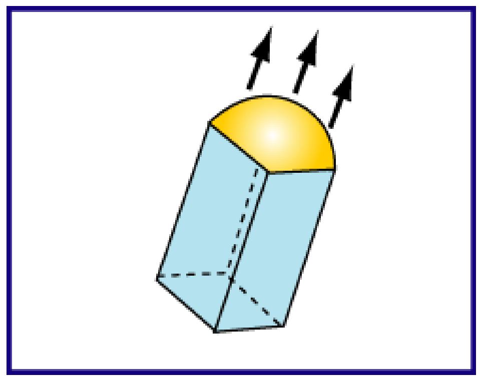
Nanowire Synthesis - Strategies



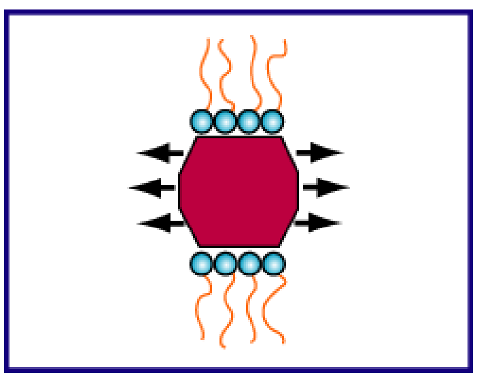
Template Growth



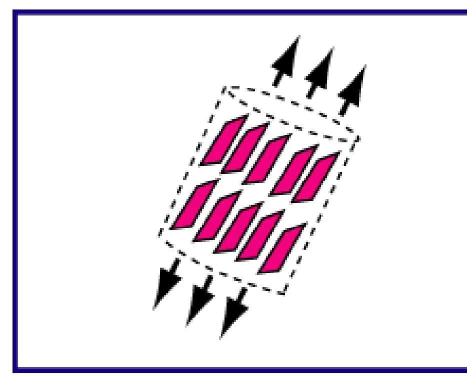
Self-assembly of 0D



VLS (Vapor-Liquid-Solid)



Capping Control

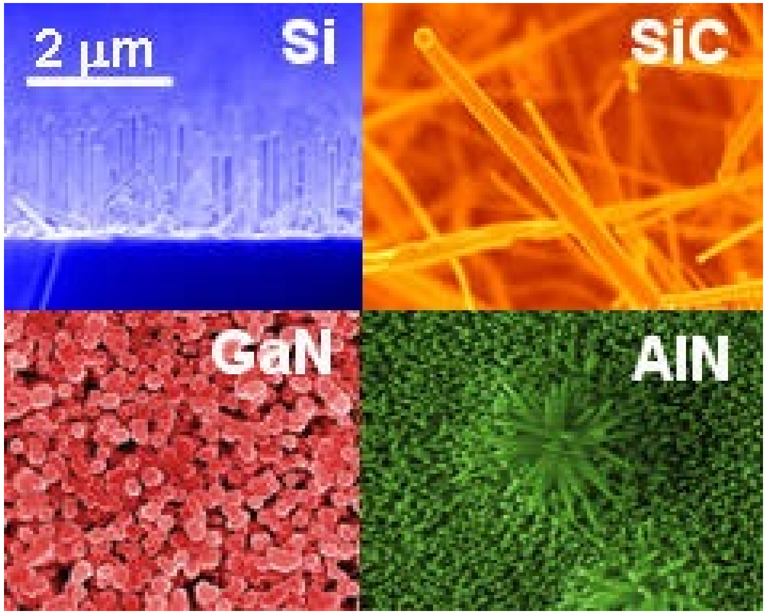


Anisotropic Crystal

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

ME118 Paper 5: Semiconductor Nanowire Growth

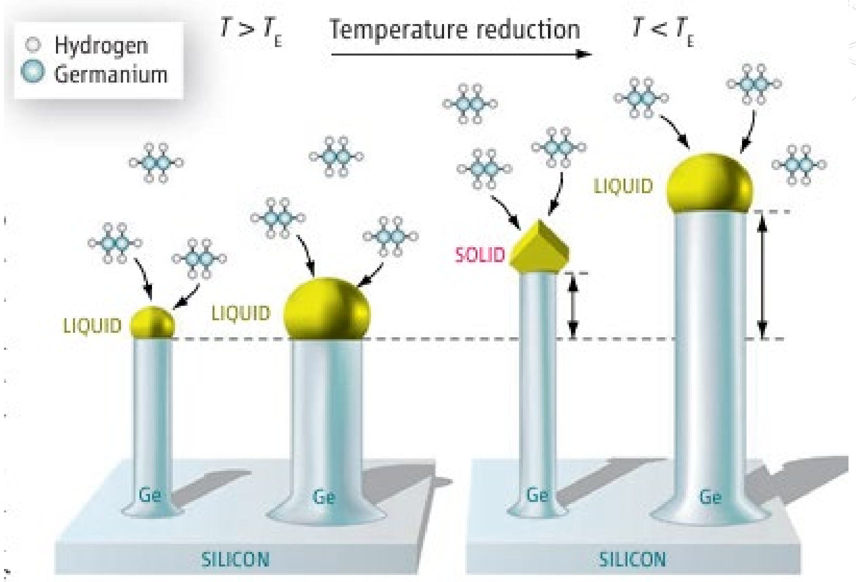
By: Michael Jia and Dawood Junaid



National Institute of Standards and Technology (NIST)

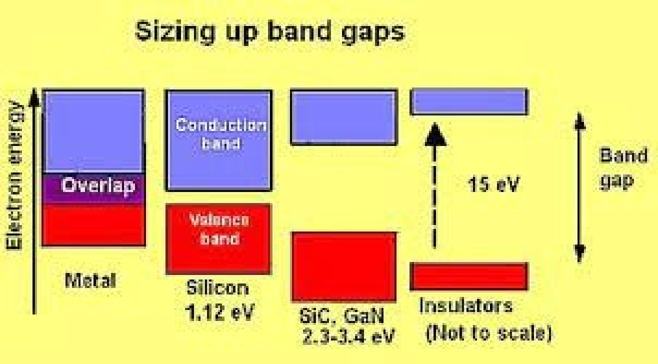
Nanowire Growth Method

- 2 main controversies as to the growth method of semiconductor nanowires
  - liquid catalyst droplet growth method
  - solid catalyst growth method
- Kodambaka in a later paper in the same issue found that both can be true under the same experimental conditions



Why Grow Semiconductor Nanowires

- Semiconductor nanowires can be a potential building block for future nanometer-scale electronic devices.
- Properties of semiconductor nanowires are always determined by the properties of the semiconductor material they are made of.
- Large variety of semiconductor materials:
  - silicon (Si)
  - germanium (Ge)
  - gallium arsenide (GaAs)
  - gallium nitride (GaN)
- Different electronic and optical properties may be fabricated and tuned.



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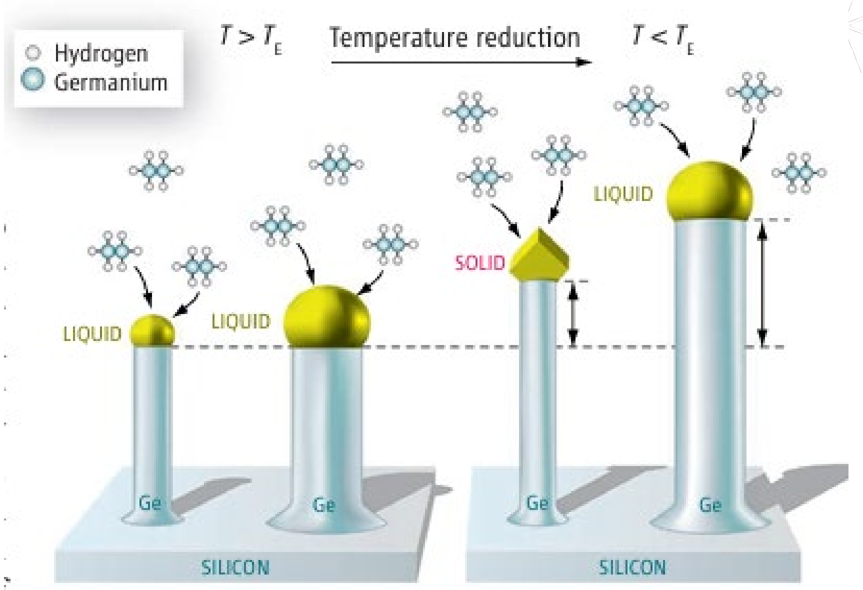
Liquid Droplet Catalyst Growth Method

- Semiconductor nanowires fabricated by the vapor-liquid-solid (VLS) process
  - investigated 40 years ago by Wagner and Ellis.
- Semiconductor material (usually a gas) is absorbed by liquid nanodroplets
  - appropriate catalytic material such as gold.
- These nanodroplets, located at the nanowire tips
  - serve as seeds for nanowire growth and also determine the nanowire diameters.
- The semiconductor material condenses at the interface between the droplet and the nanowire, causing growth
- In VLS growth, the liquid droplet consists not only of the catalytic material but also of a certain amount of the semiconductor material in question.



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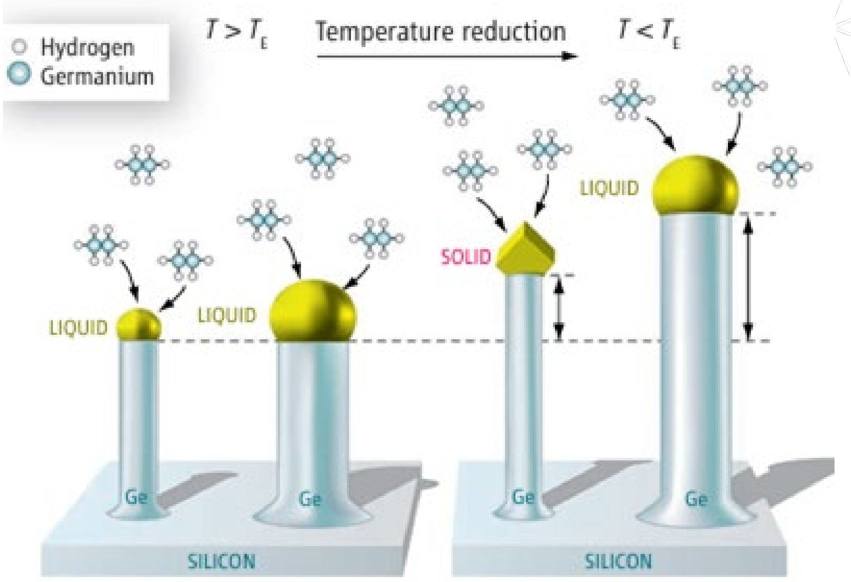
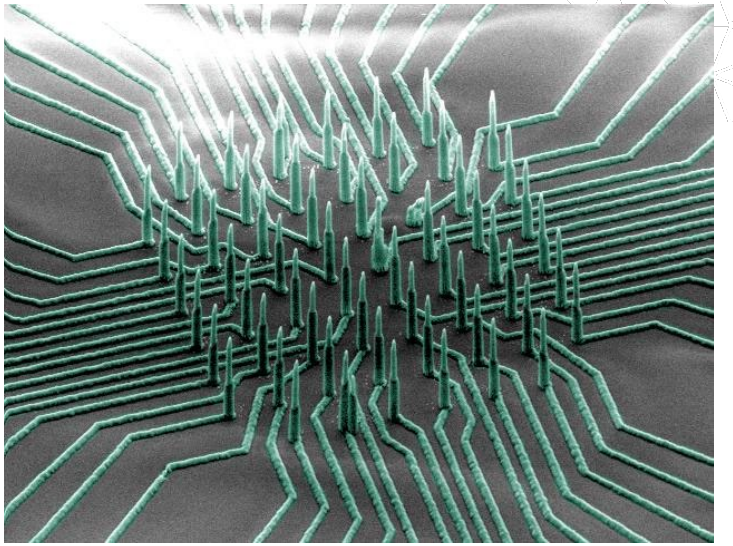
Solid Catalyst Growth Methode

- 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



Future Exploration

- Allows for variation of process and different control methodology of the growth of other semiconducting nanowires
- One step closer to which will bring nanowires one step closer to real applications.
- Possibility to optimize process for ease of manufacturing and cost reduction



Nanowires Array by Integrated Electronics and Biointerfaces Laboratory, UC San Diego

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Problems with Earlier Investigations & its Solution

- With techniques such as Electron Diffraction, additional uncertainties come into play due to the fact that analyses can only be done once growth terminates.

- Kodambaka et al. investigated the growth of gold-catalyzed germanium nanowires in a transmission electron microscope to solve this.

Experiment Setup and Scope

- Germanium vapor in the form of digermane gas was supplied to facilitate controlled growth.
- Previous reports suggested nanowire growth below the eutectic temperature in the gold–germanium system.
- Hence Kodambaka attempted to observe the tip propagation

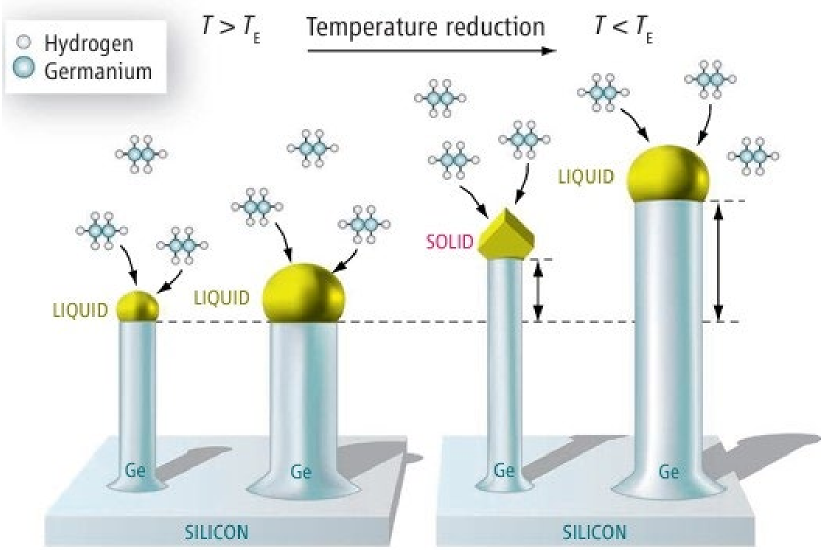
Observations

- Two distinct phenomena were observed for temperatures below the eutectic point.
- Some gold nanodroplets remained liquid even at temperatures significantly below the eutectic temperature, indicating VLS-type growth.
- For nanowires with smaller diameters, gold droplets solidified as temperature decreased, resulting in slower growth compared to VLS growth.

Further Findings

- The transformation of gold from liquid to solid could be delayed for tens of minutes at temperatures below the eutectic point.

- Hence the various parameters such as vapor pressure, temperature, and nanowire diameter influenced the delay in gold solidification.



Conclusion

- These findings offer new avenues for controlling the growth of germanium and other semiconducting nanowires, advancing their potential applications in electronic and photonic devices.

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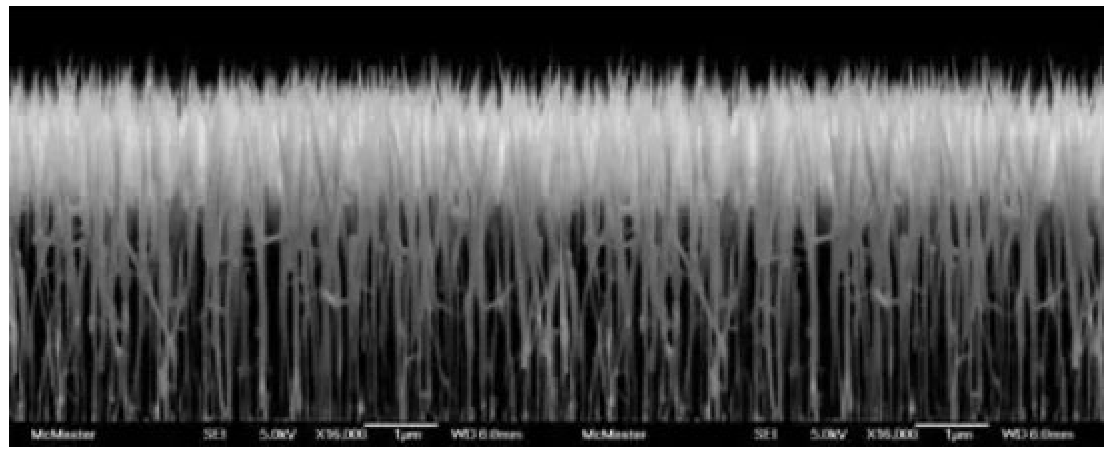
How Nanowires Grow - What is a Nanowire?

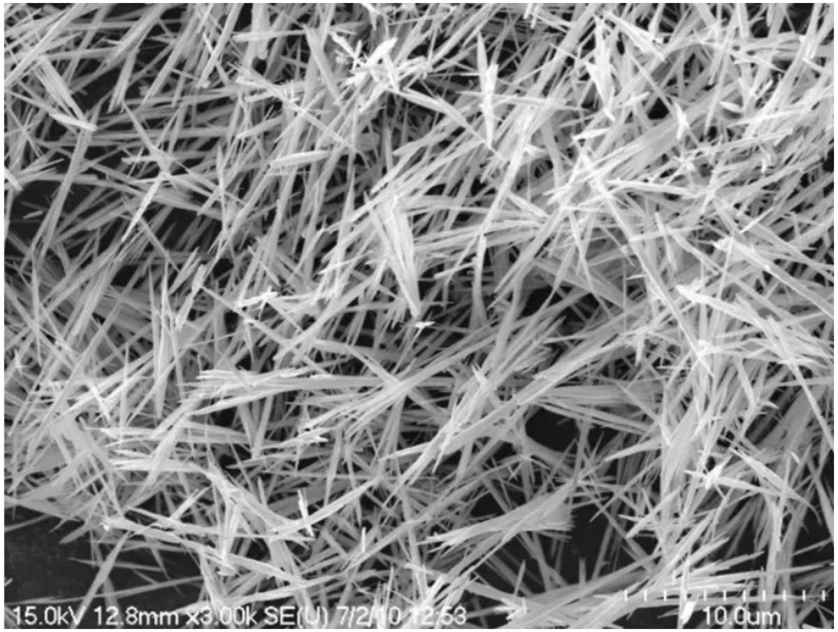
- Solid, 1D nanostructures
- high aspect ratios of up to 1000
- Made of many materials:
  - semiconductors (like silicon or germanium)
  - metals (like gold or silver)
  - insulators (like silicon dioxide)
- Variable crystalline structure and electrical conductivity based on materials instead of chirality.
- Highly customizable to various applications



Quora. (2008). *Nanowires Solar Panel*. How can we differentiate between nanotubes, nanorods, nanowires, and nanoparticles? Retrieved February 2, 2024, from Quora. (2014). Nano wires. How can we differentiate between nanotubes, nanorods, nanowires, and nanoparticles? Retrieved February 2, 2024, from https://www.quora.com/How-can-we-differentiate-between-nanotubes-nanorods-nanowires-and-nanoparticles. .

How Nanowires Grow - Vapor-Liquid-Solid (VLS) pt. 1

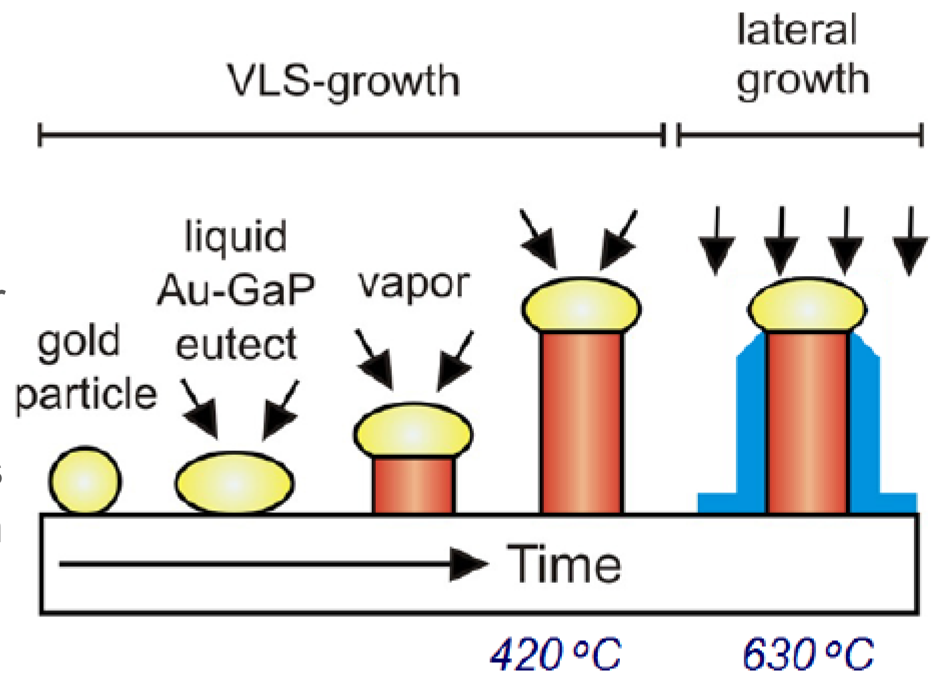
- Like CVD for CNTs, a nanowire undergoes VLS synthesis via a substrate with a catalyst, causing the binding of gaseous materials.
- Substrate: Silicon
- Catalyst: Gold
- Gas: Germanium or gallium



Quora. (2014). *Nano wires*. How can we differentiate between nanotubes, nanorods, nanowires, and nanoparticles? Retrieved February 2, 2024, from https://www.quora.com/How-can-we-differentiate-between-nanotubes-nanorods-nanowires-and-nanoparticles.

How Nanowires Grow - Vapor-Liquid-Solid (VLS) pt. 2

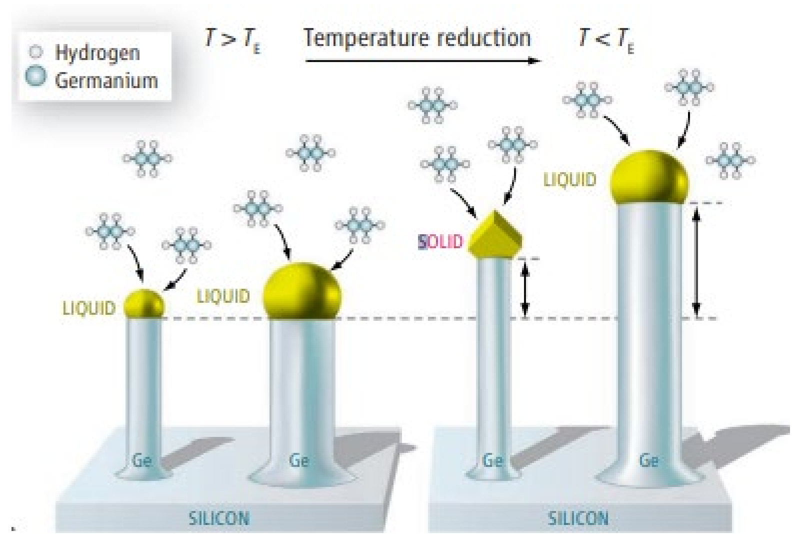
1. Environment is heated to several hundred degrees celsius
2. Gold particle is placed on a silicon substrate to seed growth
   a. Nanodroplet size determines diameter
3. Digermane or Gallium Phosphide vapor deposits onto the catalyst, growing upward
4. Growth continues until desired length is reached, stopping by material depletion or reduction of the temperature below the threshold



Ultrafast active control of optical transmission pseudomodes in a multiple scattering nanowire layer - Scientific Figure on ResearchGate. Available from: https://www.researchgate.net/figure/Scheme-showing-epitaxial-Vapor-liquid-solid-VLS-growth-of-GaP-nanowires-using-gold_fig3_252857733 [accessed 21 Feb, 2024]

How Nanowires Grow - Eutectic Temperature

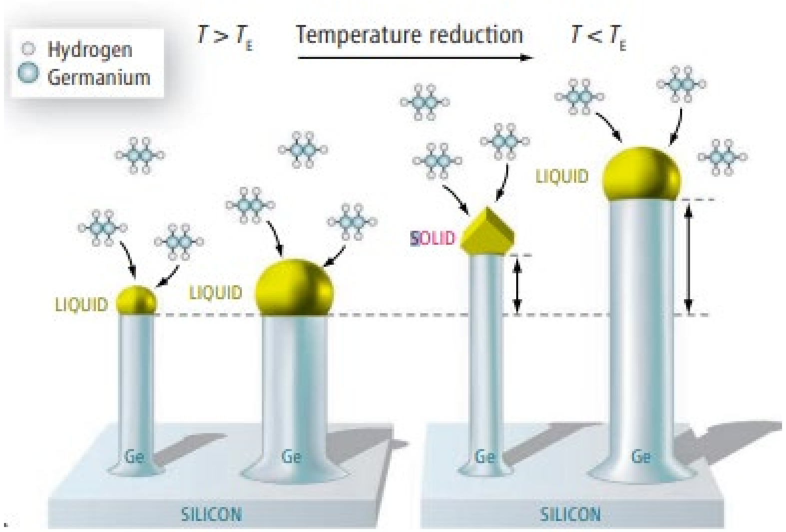
- The liquid droplets contain both catalytic material and semiconductor metals
- The latter exists due to the lowered melting point of the combined metal called the Eutectic Temperature (TE)
- Example: Gold-Germanium ratio of 7:18 yields a lower melting point of 361°C
  - Gold is 1064°C, Germanium is 937°C
- Growth will occur above this temperature and may sometimes occur below this temperature in special cases



Gösele, U., & Schmidt , V. (2007). *Germanium Nanowires*. How Nanowires Grow . Science. Retrieved February 20, 2024, from https://lwlin.me.berkeley.edu/me118/papers/paper5.pdf.

How Nanowires Grow - Solid or Liquid Controversy

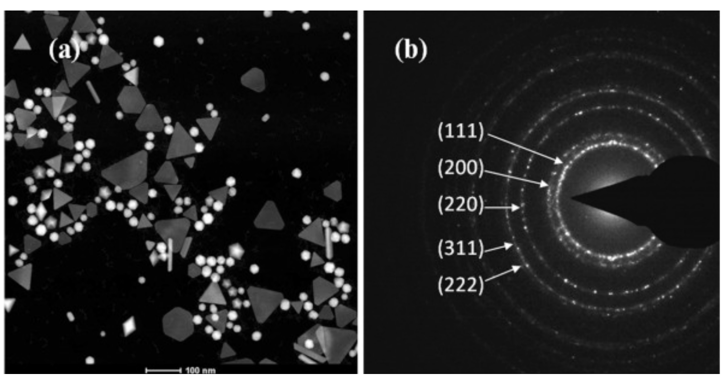
- Controversy existed regarding the state of matter of low-temperature semi-conducting nanowire catalytic particles
  - Solid particle or liquid droplet?
- Both are true
- Below the Eutectic Temperature, wire thickness determine the state of matter of the tips, thin yields solid, thick yields liquid



Gösele, U., & Schmidt , V. (2007). *Germanium Nanowires*. How Nanowires Grow . Science. Retrieved February 20, 2024, from https://lwlin.me.berkeley.edu/me118/papers/paper5.pdf.

Is the gold catalyst a Solid particle or Liquid droplet?

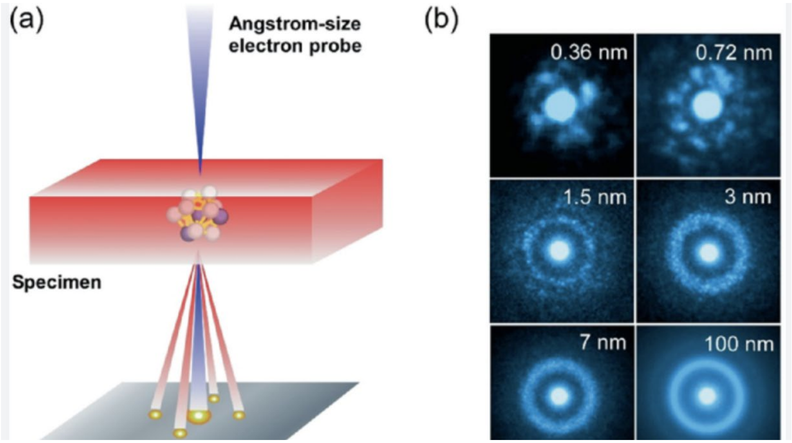
- Initial Studies relied on Electron Diffraction Methods
  - Can only be performed after growth termination
- Transmission Electron Microscopy was favored
  - Allows for structural analysis during growth process
- Shift to in situ microscopy methods to expand scope of studies on nanomaterial synthesis and growth mechanisms



Tunability and stability of gold nanoparticles obtained from chloroauric Acid and sodium thiosulfate reaction - Scientific Figure on ResearchGate. Available from: https://www.researchgate.net/figure/TEM-image-and-electron-diffraction-pattern-of-the-purified-gold-nanoparticles-a-TEM_fig6_228060851 [accessed 21 Feb, 2024]

Electron Diffraction Methods (EDM)

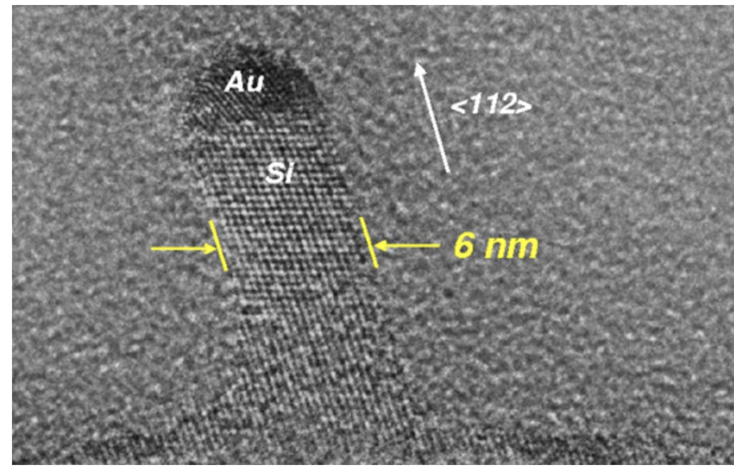
- Electron diffraction relies on the wave nature of electrons.
  - When a rotating beam of electrons is directed at a sample, it diffracts, producing a pattern that can be captured and analyzed.
- By examining the diffraction pattern produced, researchers can infer the atomic structure of the sample
- Method requires the sample to be stationary, which means analysis can only occur after the growth process has completed.
  - Thus, it provides a snapshot of the final structure.



Local Structure Analysis of Amorphous Materials by Angstrom-Beam Electron Diffraction - Scientific Figure on ResearchGate. Available from: https://www.researchgate.net/figure/a-Schematic-diagram-of-the-angstrom-beam-electron-diffraction-mapping-b-Diffraction_fig2_347625056 [accessed 21 Feb, 2024]Zr-Ni alloy with different beam sizes

Transmission Electron Microscopy (TEM)

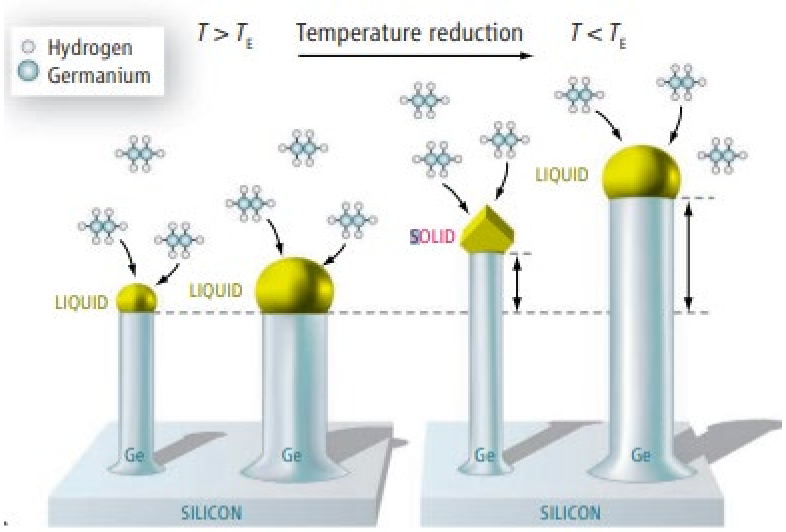
- Transmitting a focused beam of electrons through a thin specimen.
  - As the electrons pass through the sample, they interact with its atoms, undergoing scattering, diffraction, and absorption
- Allows for real-time observation of the sample during growth
  - Achieved by continuously imaging the specimen as it undergoes changes
- Allows for the supply of gases during growth process
  - Schmidt and Gösele used Germanium vapor in the form of Digermane gas (GE_2H_6)
- Can clearly distinguish half spherical liquid state from solid state with planes,edges and corners



Gösele, U., & Schmidt , V. (2007) http://www-old.mpi-halle.mpg.de/department2/index.php?id=573&type=98&no_cache=1

Results

- As expected, above the Eutectic Temperature, nanowire growth involves a liquid droplet on top of the Germanium nanowires
- But liquid Droplets exist below T_E of 361C
  - Up to 100C below!
- Below T_E the state of the Gold is actually dependent on the nanowire diameter
  - Unexpected result!



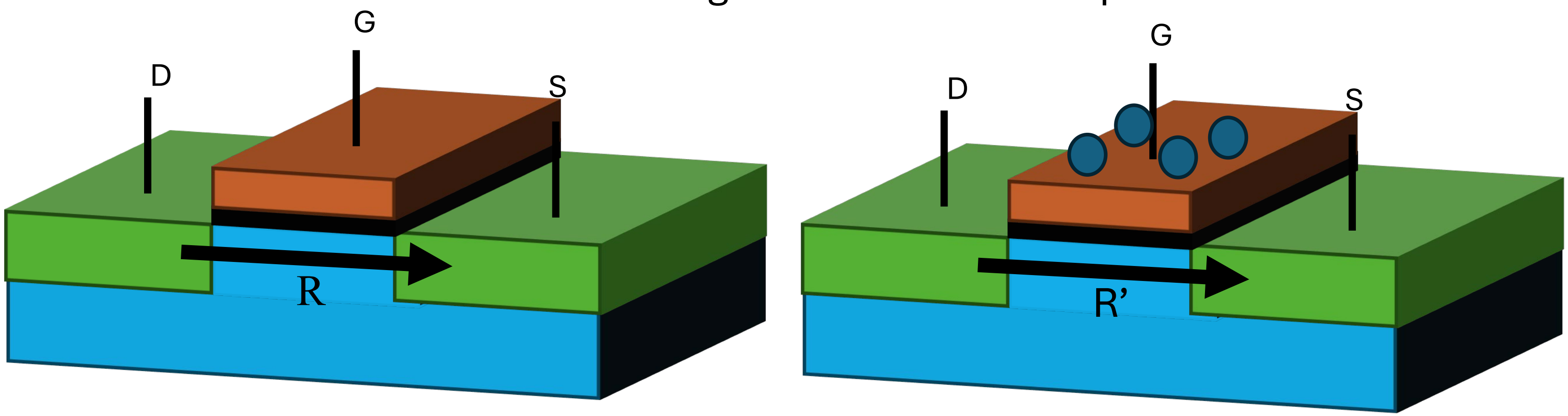
Gösele, U., & Schmidt , V. (2007). *Germanium Nanowires*. How Nanowires Grow . Science. Retrieved February 20, 2024, from https://lwlin.me.berkeley.edu/me118/papers/paper5.pdf.

Further Implications

- Further experiments showed that the transition of the Gold caps from liquid to solid at temperatures below the T_E could be delayed up to tens of minutes
- Kodambakkam (Author on Scimag issue) did further research into this
  - Delay depends on various parameters including vapor pressure, temperature and nanowire diameter
- Whether the gold catalyst is solid or liquid depends on specific parameters, including the sample's thermal history
- New opportunities to control growth of Germanium and other semiconducting nanowires!

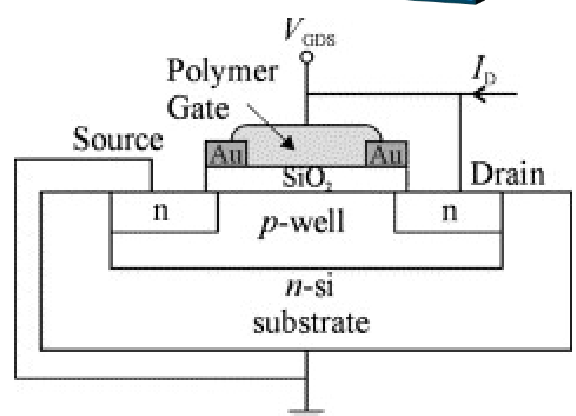
Nanowire Nanosensors for Highly Sensitive and Selective Detection of Biological and Chemical Species

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

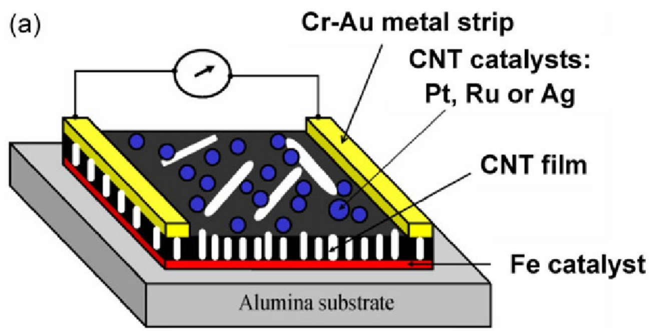
FET Limitations

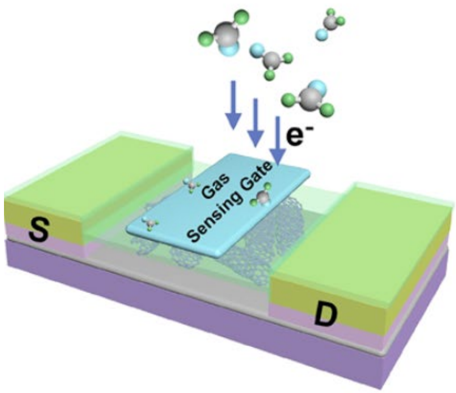
Vasileios

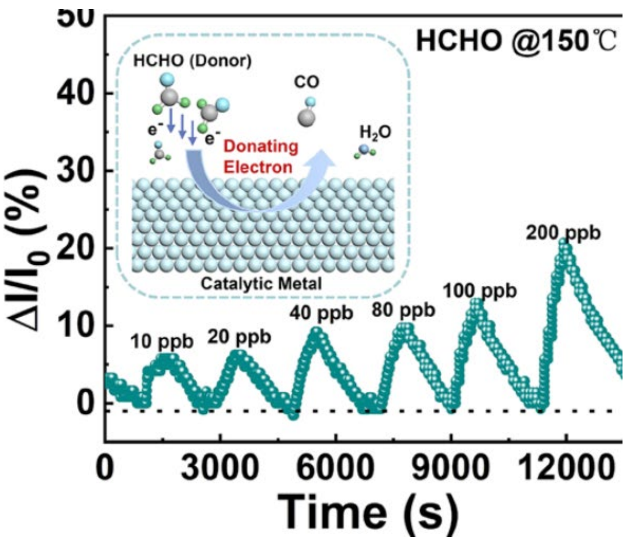
1. Planar Geometry Limits Total Area m^2
2. Sensitivity of the order of ppm

Use CNTs as Gates

- High aspect ratio
- Band gap depends on species







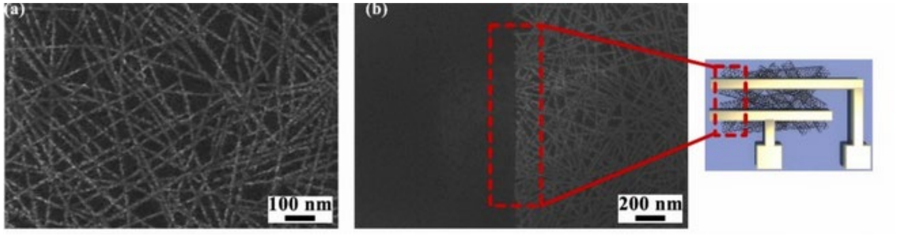
Carbon Nanotube-Based Field-Effect Transistor-Type Sensor with a Sensing Gate for Ppb-Level Formaldehyde Detection, Can Liu et al.
Metal-modified and vertically aligned carbon nanotube sensors array for landfill gas monitoring applications, M Penza et al.

NT FET Limitations

Vasileios

1. Hard to control NT type, needs semi-conducting
2. Hard to control diameter
3. Hard to functionalize

Not a robust sensor



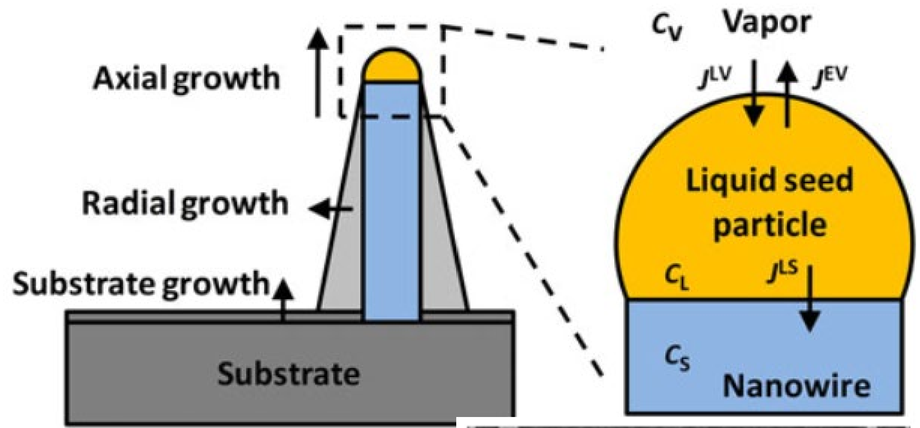
NW FET

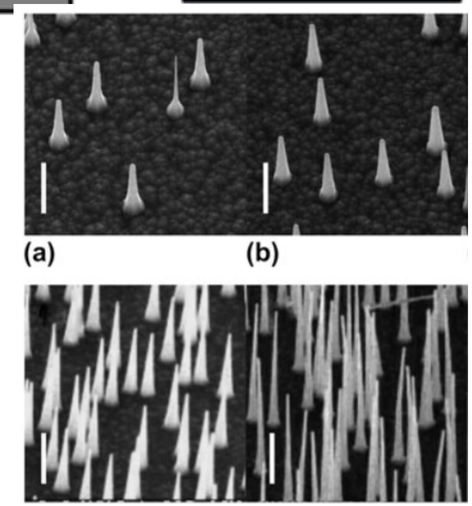
Vasileios

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.

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