Nanoscale Quantum Materials

2018 Quantum Science Summer School (NSF/DOE/AFSOR)

Judy J. Cha
Yale University

Overview

- Why Nanoscale Materials
  - Emergent properties (band engineering, surface properties)
  - Examples (quantum dots, carbon nanotubes, …)
- Synthesis of Nanowires
  - Various growth methods
  - Vapor-liquid-solid growth
  - Doping / surface passivation
- Synthesis of 2D Materials
  - Chemical vapor deposition
  - Precursors / additives

Overview

- Case Study of Nanowires: Si Nanowires
  - Thermal transport modulation
  - Si nanowire batteries
- Case Study of Topological Nanomaterials
  - Bi_2Se_3 topological insulator nanoribbons
  - SnTe Topological crystalline insulator nanowires
- Case Study of 2D Materials for Energy
  - MoS_2 for hydrogen evolution reaction (HER)
  - Phase transition via intercalation and consequences for HER

What you will learn from this class

- What are nanomaterials?
- How do we make them?
- How are they different from bulk forms?
- How do we characterize them? - STM / (S)TEM / Diffraction / Raman …
- Are they useful for technology?

What is Nanotechnology (Nanomaterials)?

The National Science Foundation defines nanotechnology as "research and technology development at the atomic, molecular or macromolecular levels, in the length scale of **approximately** ??? range, to provide a fundamental understanding of phenomena and materials at the nanoscale and to create and use structures, devices and systems that have novel properties and functions because of their small and/or intermediate size.

Nanoscience Beginning

Jan. 21, 2000 - President Clinton announced his FY 2001 budget will include a National Nanotechnology Initiative (NNI):

"My budget supports a major new National Nanotechnology Initiative, worth $500 million. ….Imagine the possibilities: materials with ten times the strength of steel---.shrinking all the information housed at the Library of Congress into a device the size of a sugar cube---detecting cancerous tumors when they are only a few cells in size."

NSF response in 2001:
Nanoscale Science and Engineering Research Centers (NSERCs)
Cornell, Columbia, RPI, Northwestern, Rice, Harvard

Since 2001, more than 22 billion research budget (2015)

President Clinton at CalTech

http://assets.kennislink.nl/system/files/000/082/771/large/ClintonNNI.jpg

Announcing the National Nanotechnology Initiative - January 21, 2000

Some of these research goals will take 20 or more years to achieve. But that is why -- precisely why -- ...there is such a critical role for the Federal government.

Is Nanotechnology Something New?

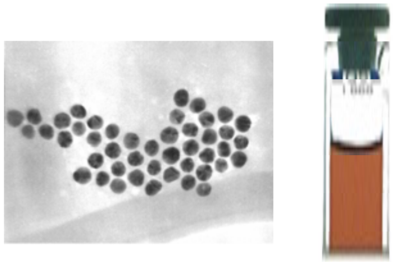
Red gold:

Stained-glass window in Milan Cathedral, Italy, made by Niccolo da Varallo between 1480 and 1486, showing the birth of St. Eligius, patron saint of goldsmiths. The red colors are due to colloidal gold.

C. Murphy. *Science*, 298, 2139 (2002)

10-100nm gold spheres appear red, not gold, when well dispersed

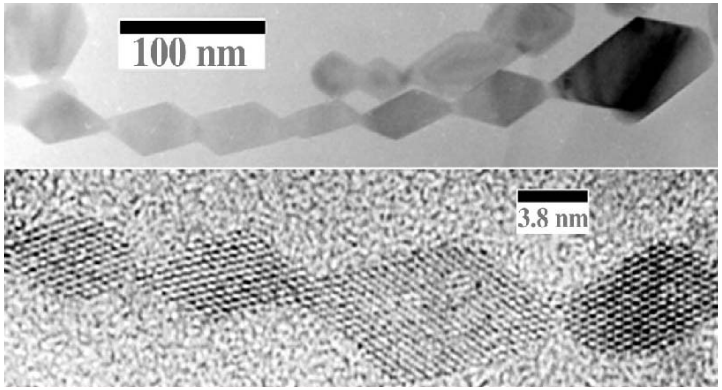
Bulk Gold
Color = gold



10 nm Gold Particles
Color = red

Is Nanotechnology Something New?

Fe_3O_4 magnetite particles as found in certain types of bacteria cells; use these as compasses for navigation



Nanoparticles are widely found in nature, and regularly formed in combustion processes. Extensively used in coatings, composites etc.

Lotus effect: self-cleaning surfaces due to the nanostructure of the surface

SEM image: Barthlott et al., *Planta* 202 (1997) 1-8

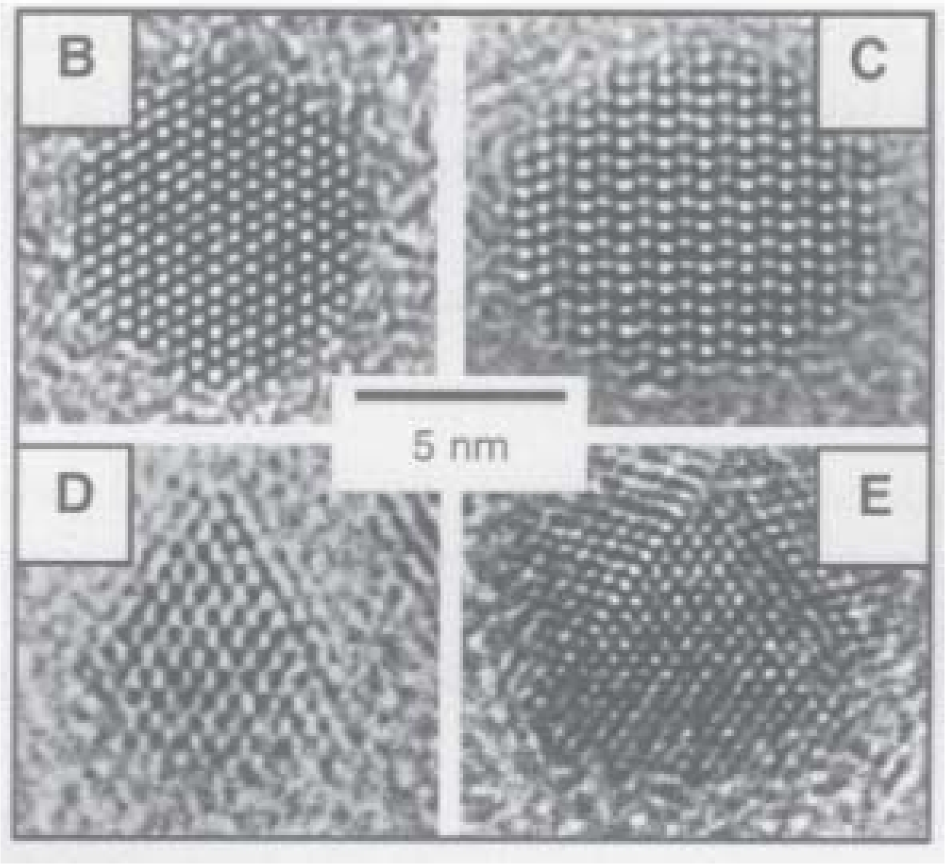
Self-cleaning surfaces can be technically manufactured using available nanostructured coating materials.

Benefits of Nanoscale Materials

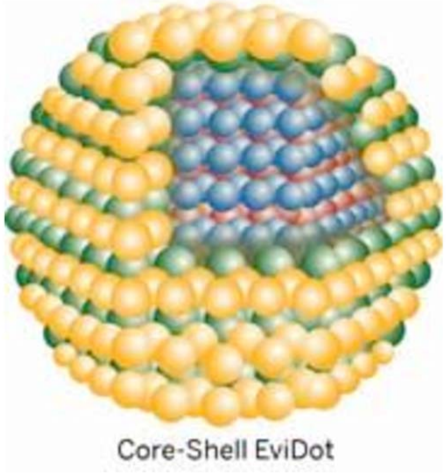
- Band structure engineering via nanoscale confinement
  - Quantum dots
  - Carbon nanotubes
- Enhanced surface properties
  - Catalysts
  - Sensors
- Emergent Properties
  - Dislocation starvation in metallic systems

Nano Highlight 1: Quantum Dots

CdSe Quantum Dots (B, C)



Science 271, p.933 (1996)

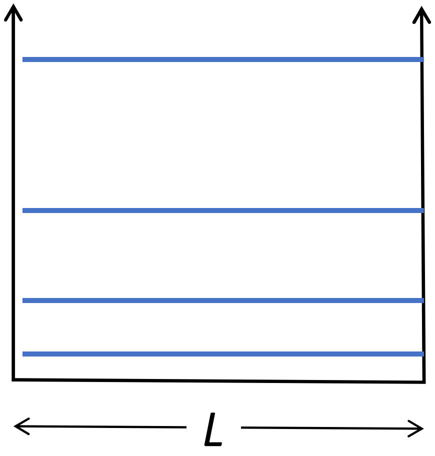


- Nanocrystals
- 2-10 nm diameter
- semiconductors

Benefits: Tunable bandgap with the dot size

Quantum Effects at the Nanoscale

Particle in a Box Problem



V(x) = 0, 0 < x < L
∞, otherwise

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) + V(x)\psi(x)$$

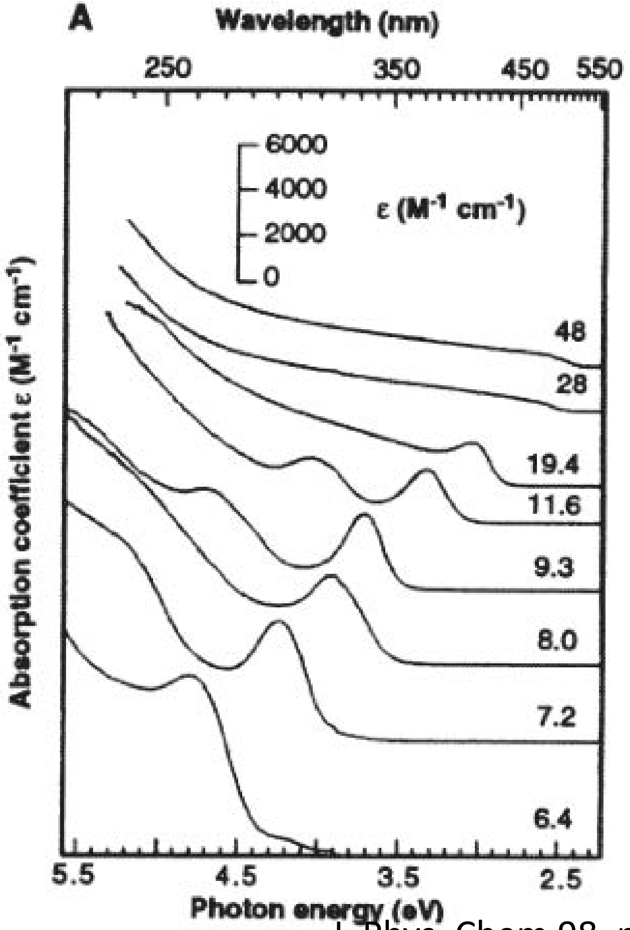
$$\psi(x) \sim \sin(kx)$$

$$k = \frac{n\pi}{L}, E = \frac{\hbar^2 k^2}{2m} \propto \frac{1}{L^2}$$

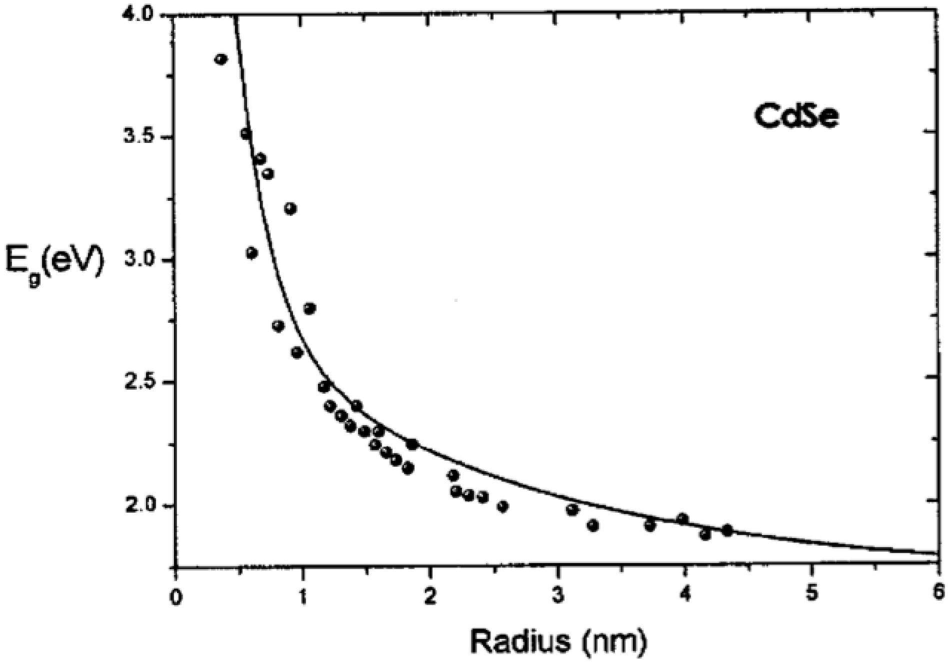
Energy levels inversely proportional to the size of the box!

Nano Highlight 1: Quantum Dots

Band gap increases with decreasing size of quantum dots.

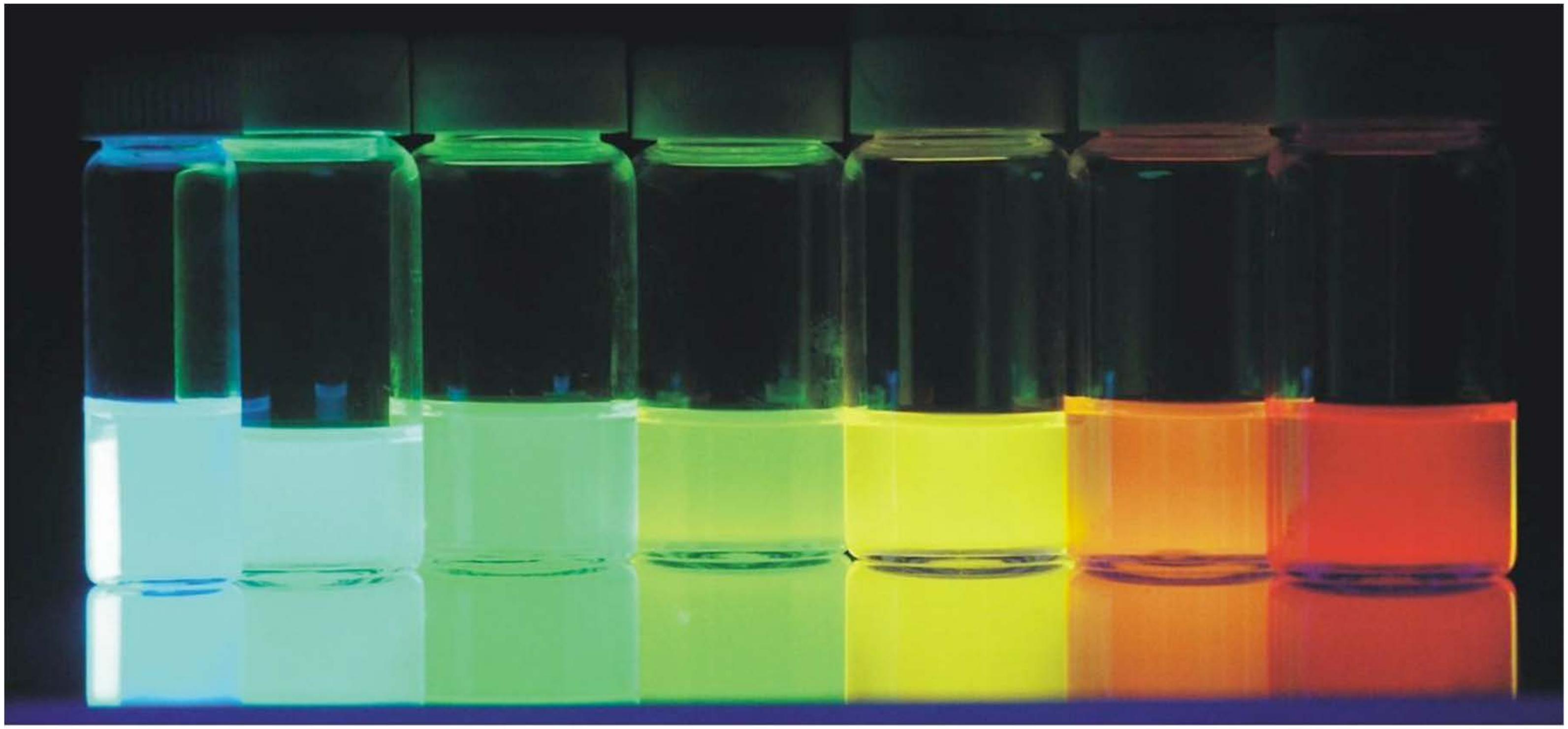


J. Phys. Chem 98, p.7665 (1994)



J. Appl. Phys. 99, 013708 (2006)

CdTe Quantum Dots



???

???

Size (nanometers)

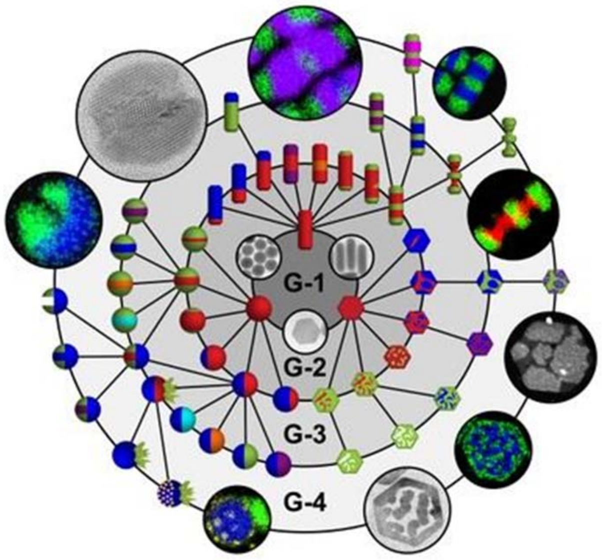
Quantum Dot TV

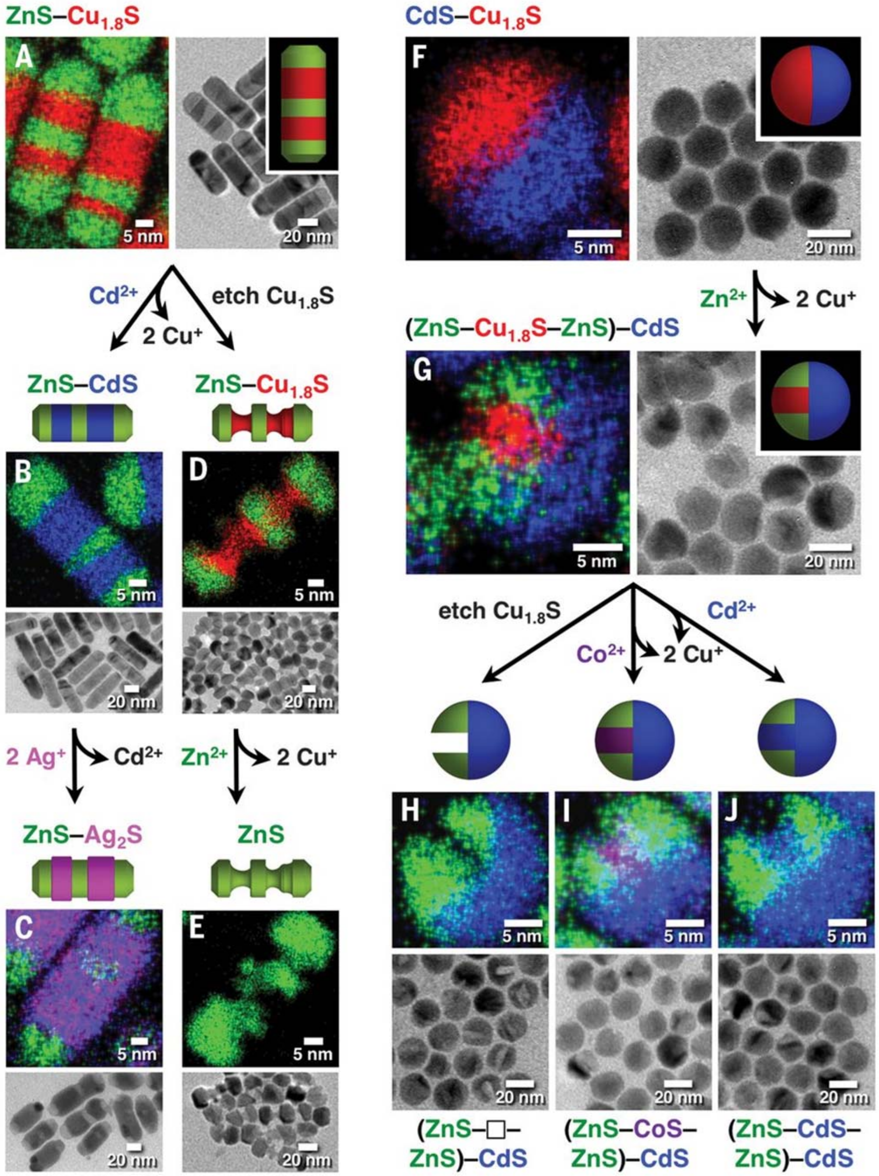
- Higher Contrast Ratios
- Better Brightness
- More Efficient

Complex Quandom Dot Heterostructures

Schaak Group
Penn State

Colloidal Synthesis of
Quantum dots





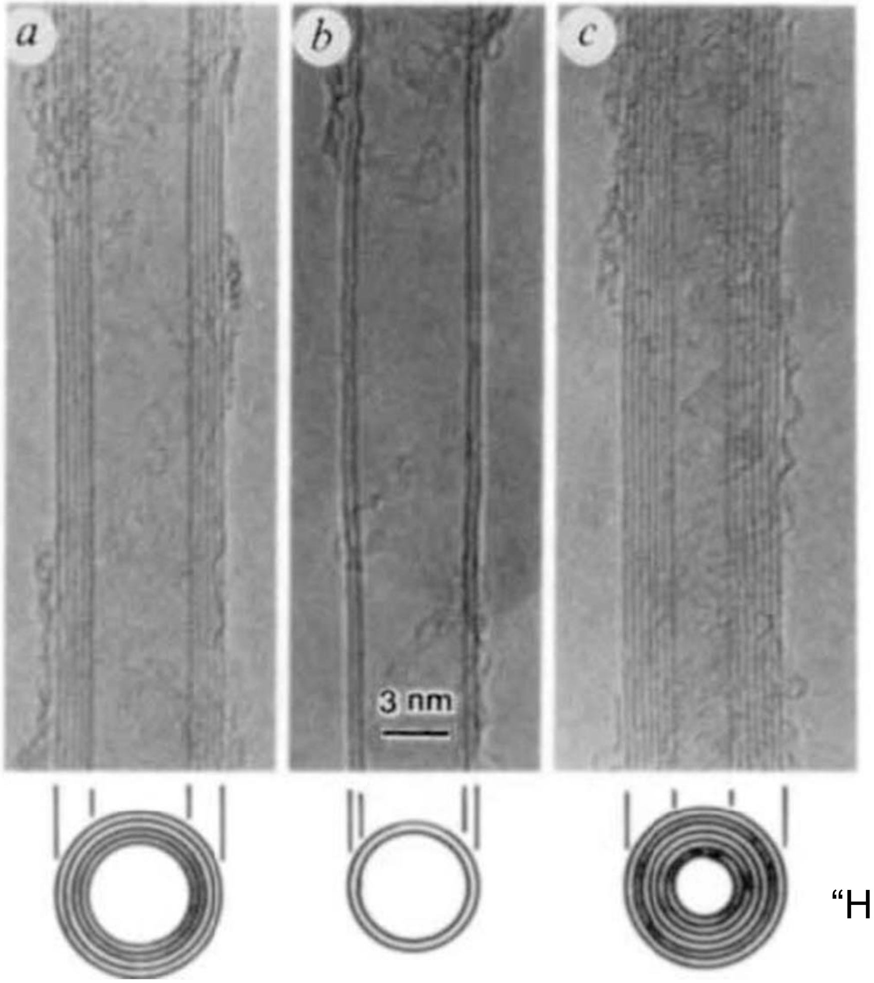
Cation Exchange
Kirkendall Effect

Science 360, p.513-517 (2018)

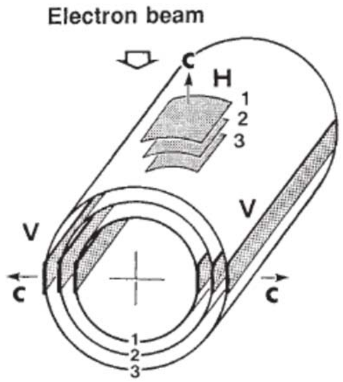
Benefits of Nanoscale Materials

- Band structure engineering via nanoscale confinement
  - Quantum dots
  - Carbon nanotubes
- Enhanced surface properties
  - Catalysts
  - Sensors
- Emergent Properties
  - Dislocation starvation in metallic systems

Carbon Nanotubes Discovered in 1991



Sumio Iijima



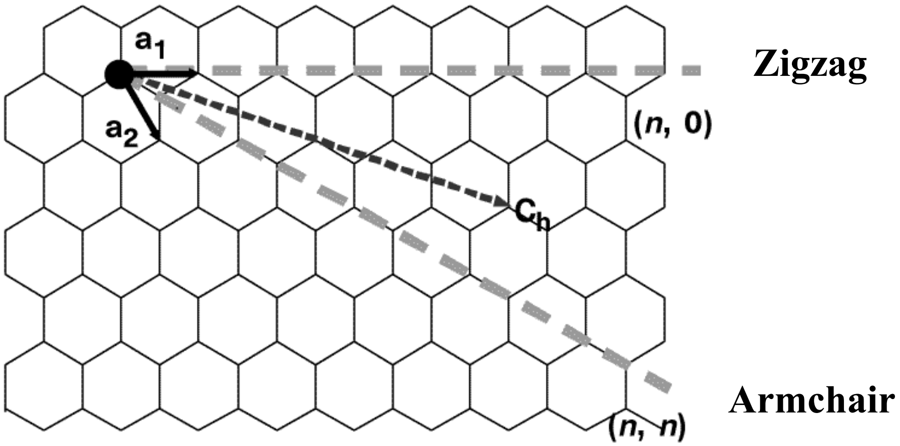
“Helical Microtubules of Graphitic Carbon”

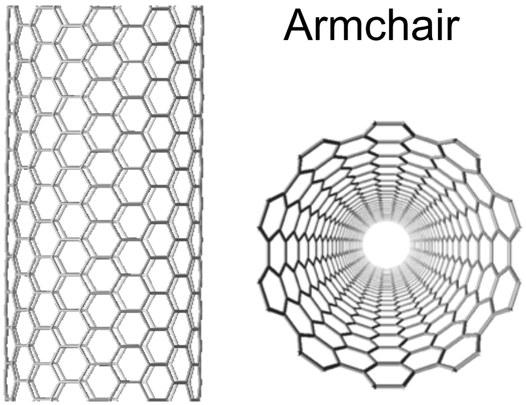
Nature 354, p.7 (1991)

Nano Highlight 2: Carbon Nanotubes

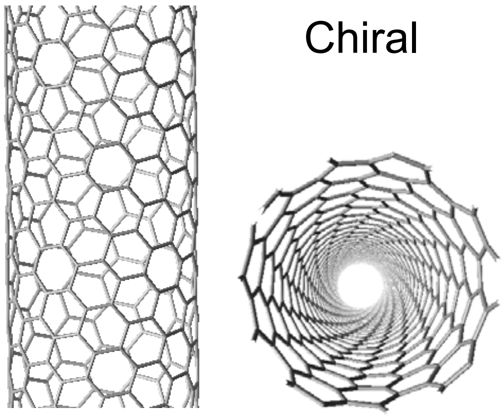
Rolling vector

$$\vec{C}_h = n_1 \vec{a}_1 + n_2 \vec{a}_2$$



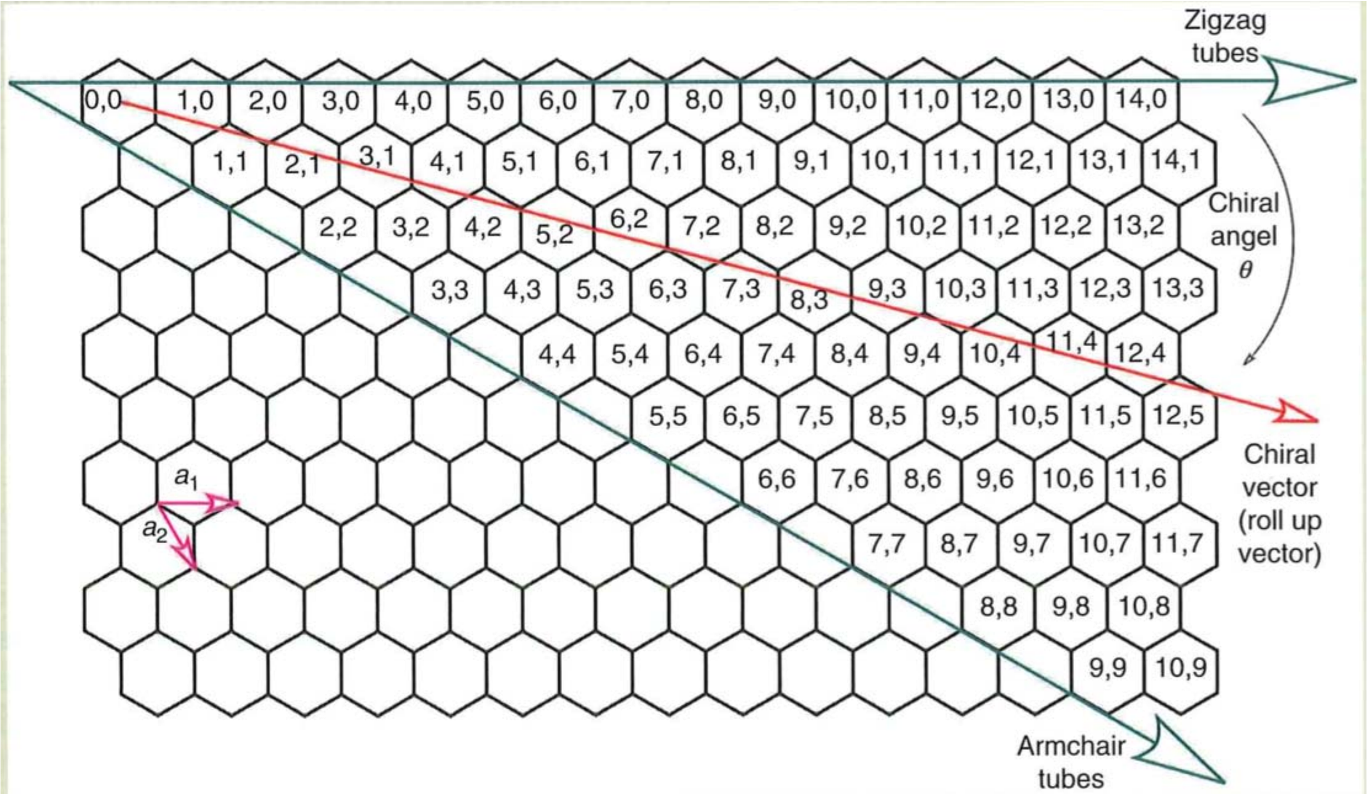


Armchair



Chiral

Indexing Carbon Nanotubes



Electrical properties determined by (n,m) indices.

- (n, 0): Metallic if n/3 = integer, Semiconducting otherwise
- (n, m): Metallic if (2n+m)/3=integer, Semiconducting otherwise

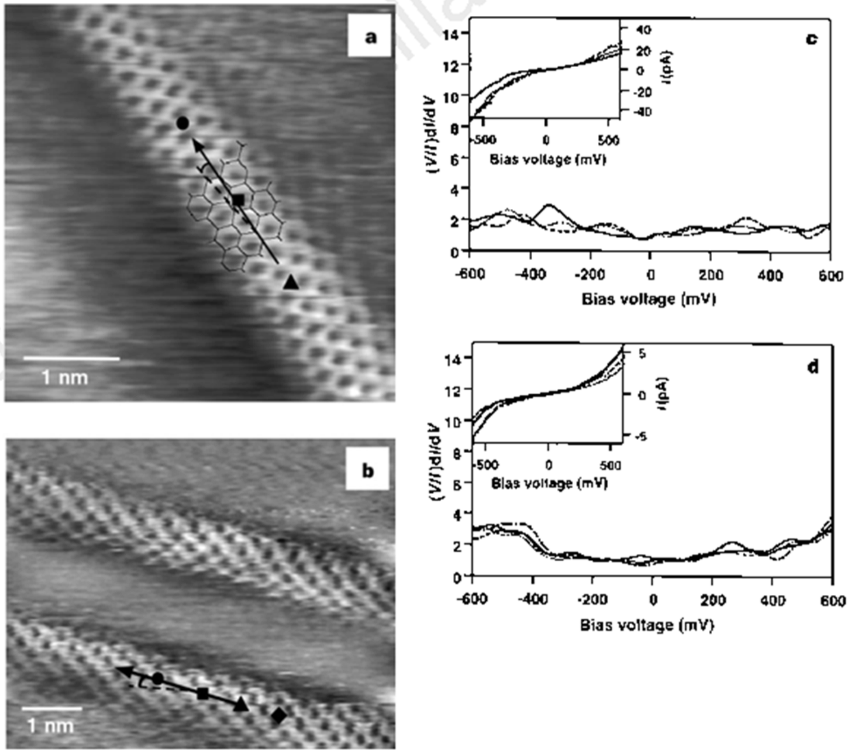
Like quantum dots, bandgap is determined by the diameter

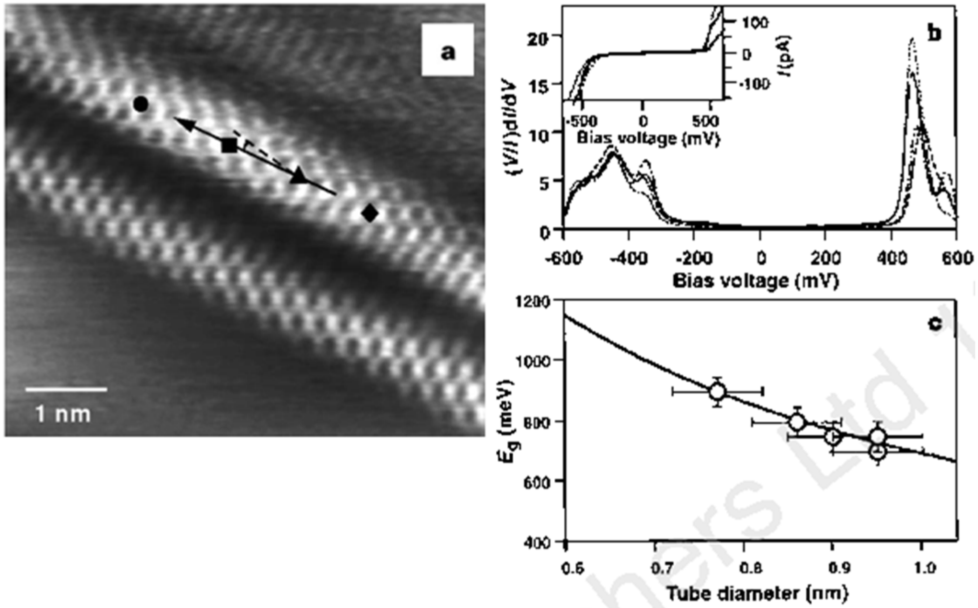
Nature 391, 62-64 (1998)

Metallic and Semiconducting Carbon Nanotubes by STM

???

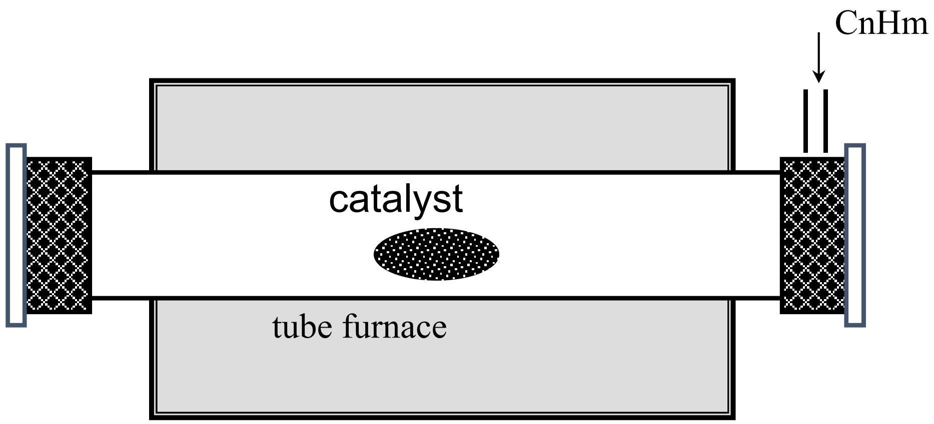
???





Nature 391, 62-64 (1998)

CVD Synthesis of Nanotubes



Gas Source $\xrightarrow[\text{600 to 1000 }^{\circ}\text{C}]{\text{Catalysts}}$ Nanotubes

Carbon sources: methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), alcohols, propylene (C_3H_6), hexane (C_6H_{14}), benzene (C_6H_6), etc..

Catalyst: Ni, Fe, Co, Cu, ...

Phase Diagram of C and Fe

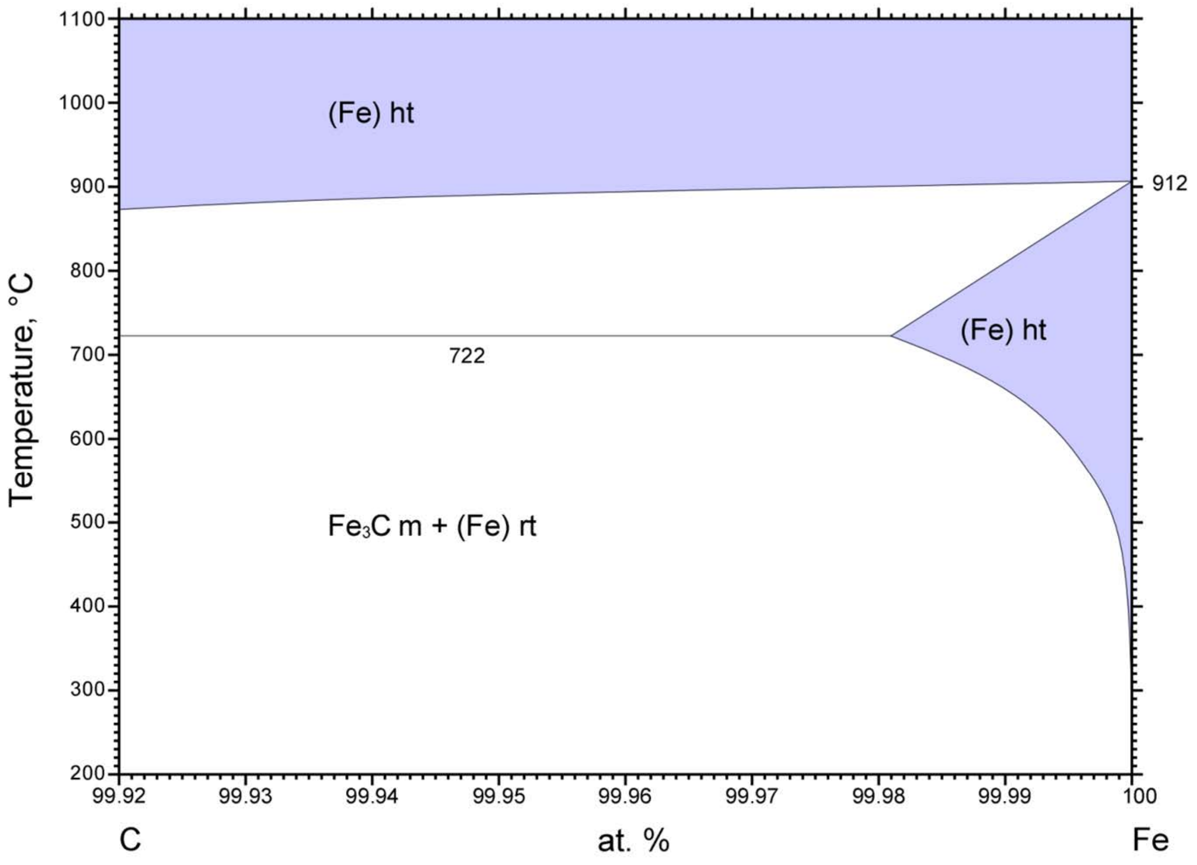
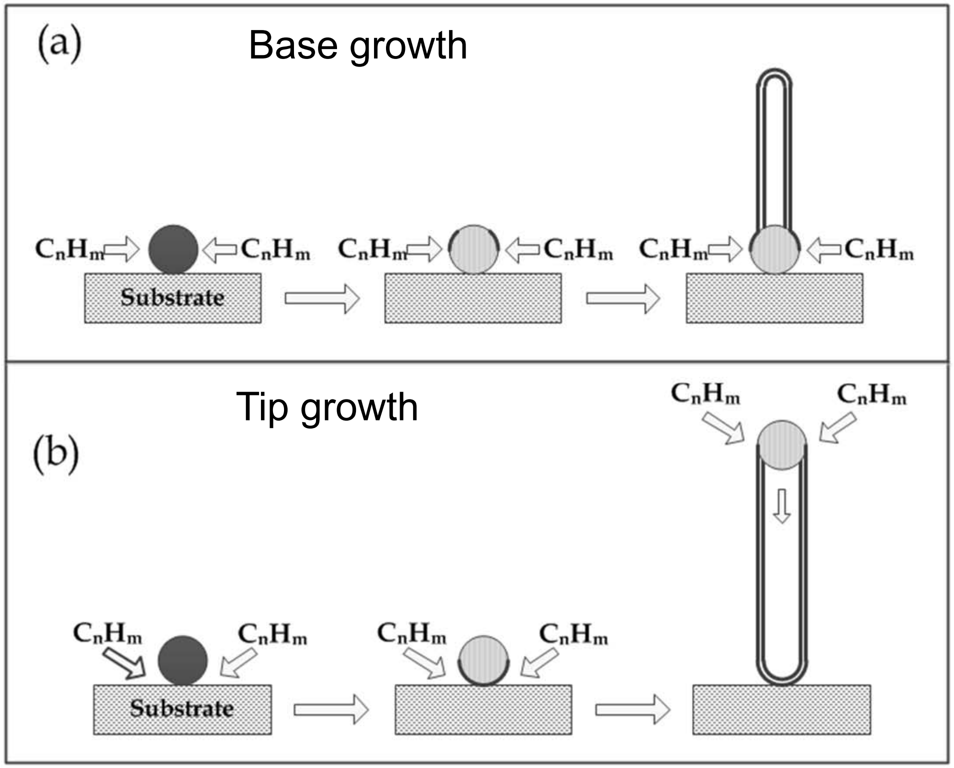
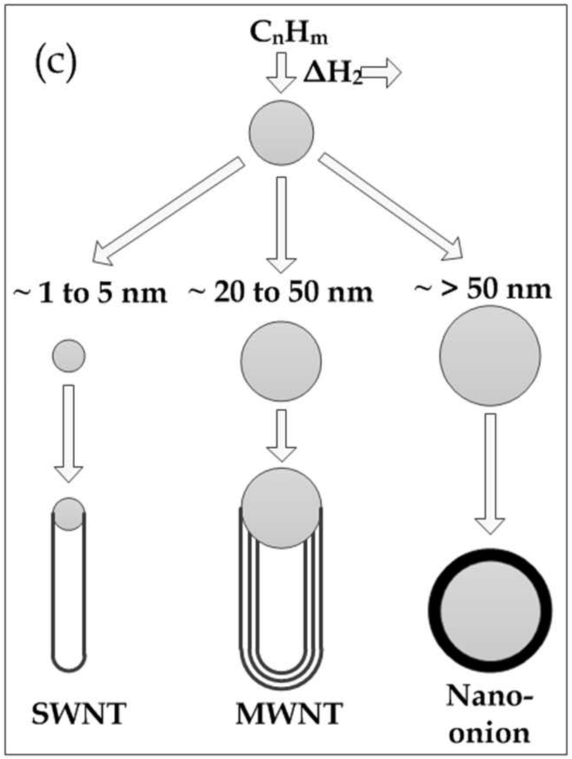


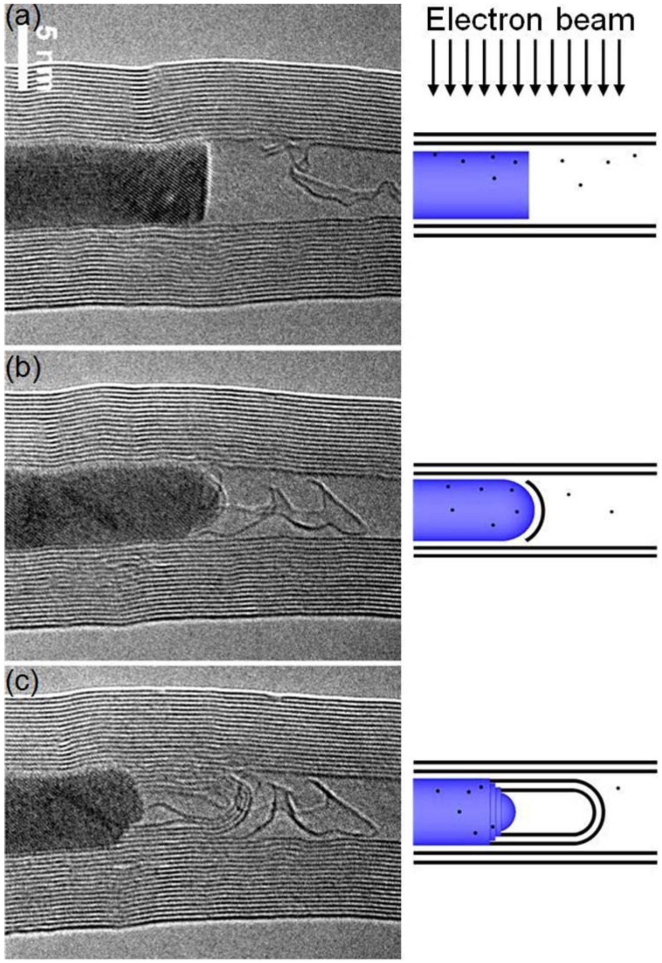
Diagram No. 104069

Nanotube Growth Mechanism





In Situ TEM of Multi-Walled Carbon Nanotube Growth



In-situ observation of CNT growth under HRTEM.

(a) Electron beam knocks some carbon atoms from the MWCNT side walls into the encapsulated metal cluster.

(b) The metal cluster reshapes its flat cross section into a convex dome and a carbon cap appears over the dome.

(c) At the base of the metal dome, atomic steps develop and new MWCNTs emerge coaxial to the original MWCNT.

Nanotechnology and Nanomaterials, Ch. 8
DOI:10.5772/19331

Overview

- Benefits of Nanoscale Materials
  - Emergent properties (band engineering, surface properties)
  - Examples (quantum dots, carbon nanotubes, …)
- Synthesis of nanowires
  - Various growth methods (etching, templating, anisotropic crystal structure, …)
  - Vapor-liquid-solid growth
  - Doping / Surface passivation
- Synthesis of 2D materials
  - Chemical vapor deposition
  - Precursors / additives

Definition of Nanowires

- Critical dimension: Diameter < ???
- Aspect ratio (length to diameter). “nanorods” for small aspect ratio
  The borderline between nanowires and nanorods is very vague.
- Materials: semiconductor, metal, oxides, insulators.

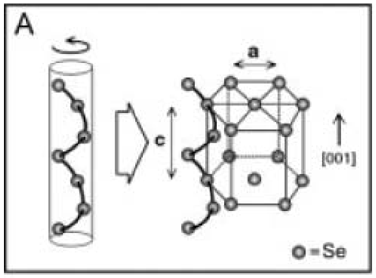
Other names:

Quantum wires: showing quantum properties.

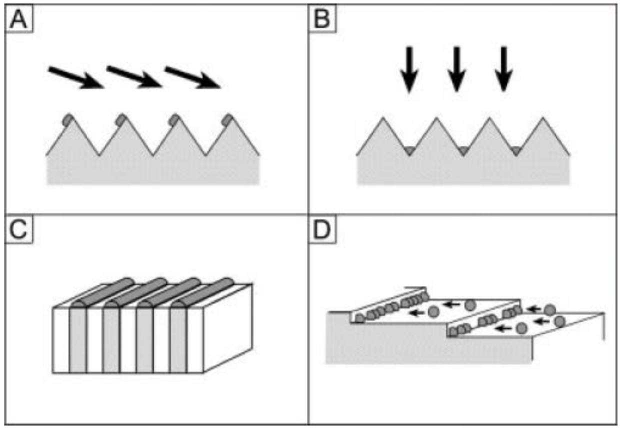
Molecular wires: with well defined molecular diameter dimension.

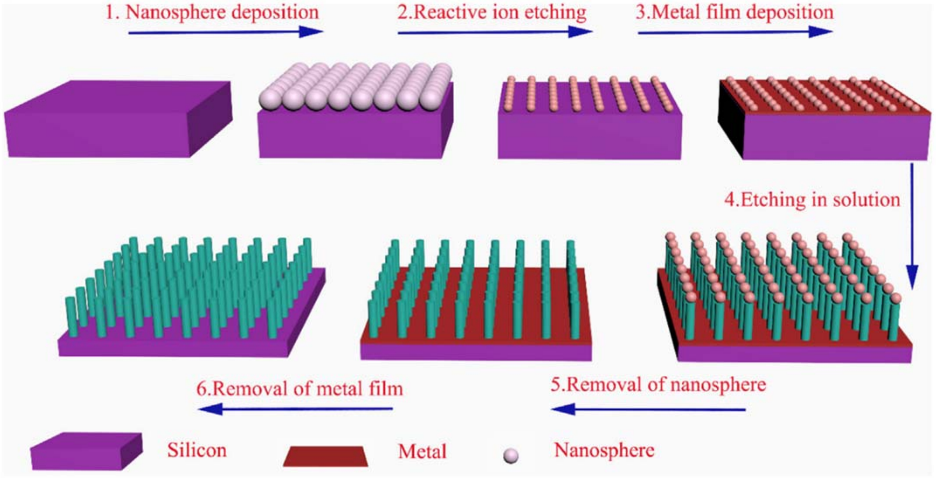
Synthesis Strategies

1) **Anisotropic crystal structures**
2) **Templates**
3) **Vapor-liquid-solid (VLS)**
4) **MOCVD / MBE**
5) **Electrospinning**
5) **Chemical etching from bulk size materials**



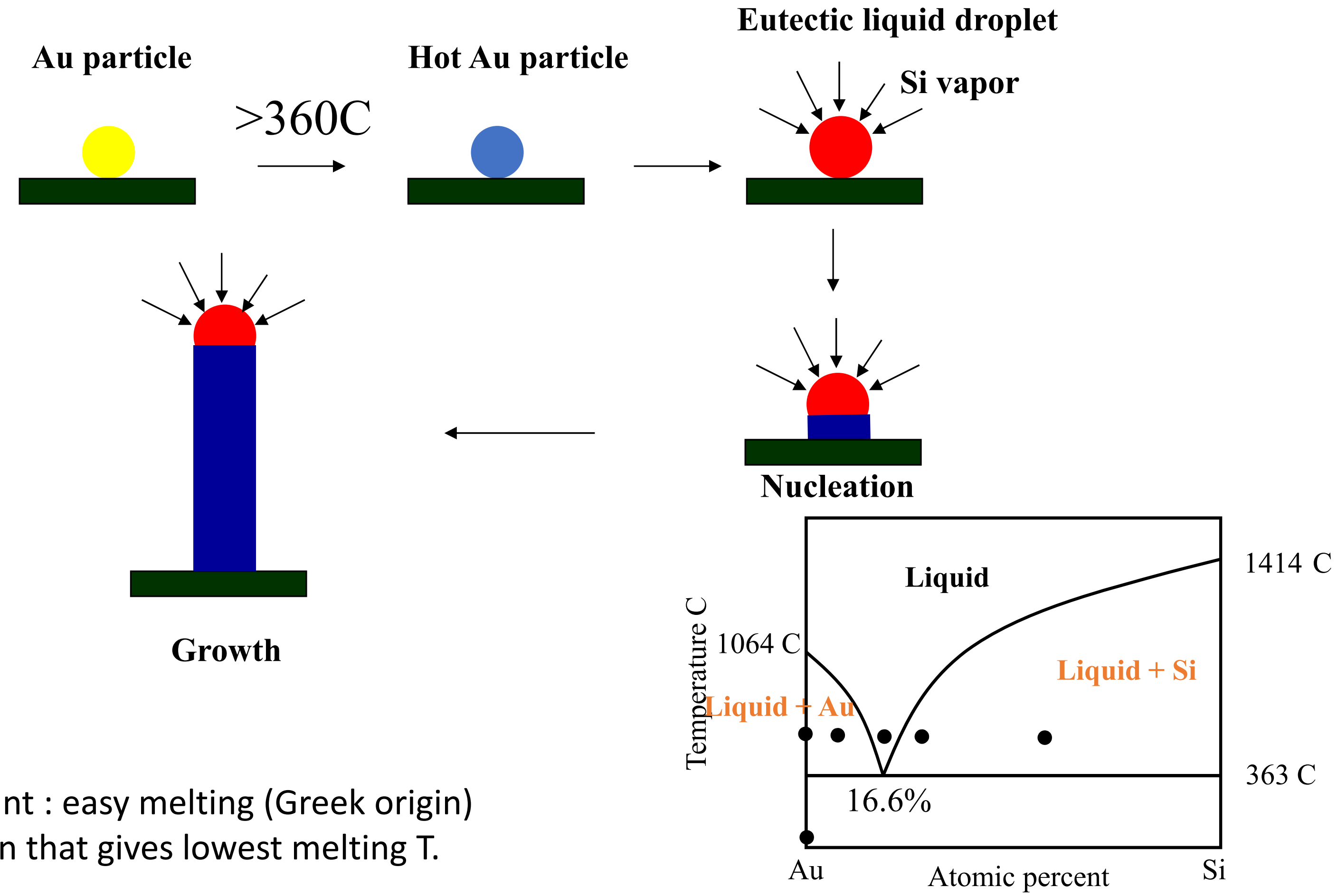
Se nanowires ($4S^24P^4$)
8 electron rule:
1 Se bonds to 2 neighbors





Nano Today 11 (2016) 704-737

Vapor-Liquid-Solid Process



??? point : easy melting (Greek origin)

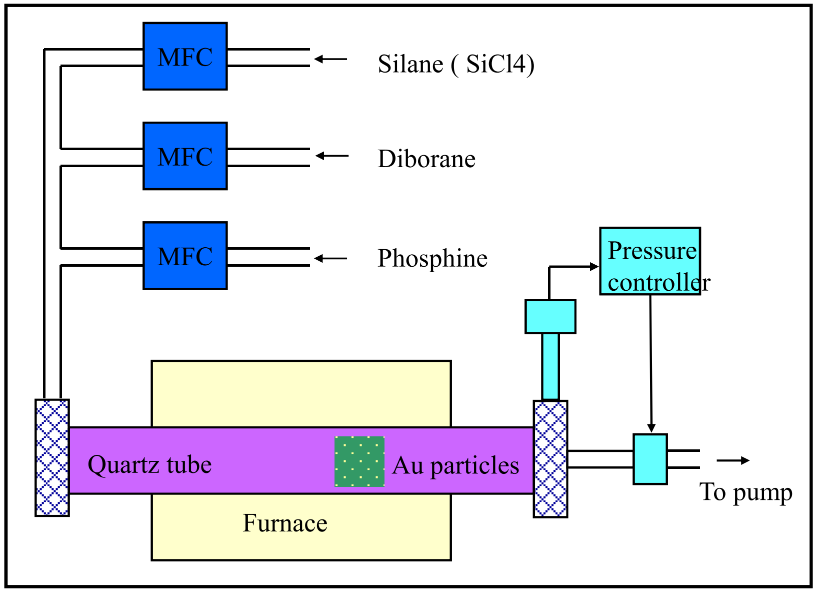
Composition that gives lowest melting T.

Vapor-Liquid-Solid (VLS) Growth Apparatus

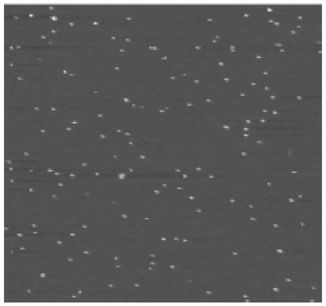
Chemical vapor deposition method

Precise control on different molecular species: doping, heterostructures.

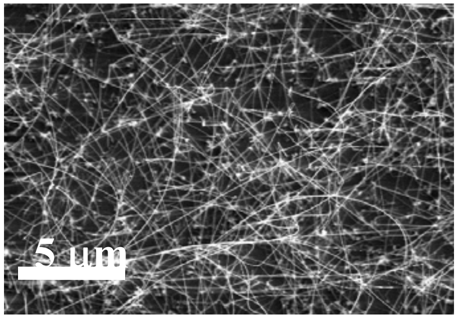
(MFC: Mass Flow Controller)

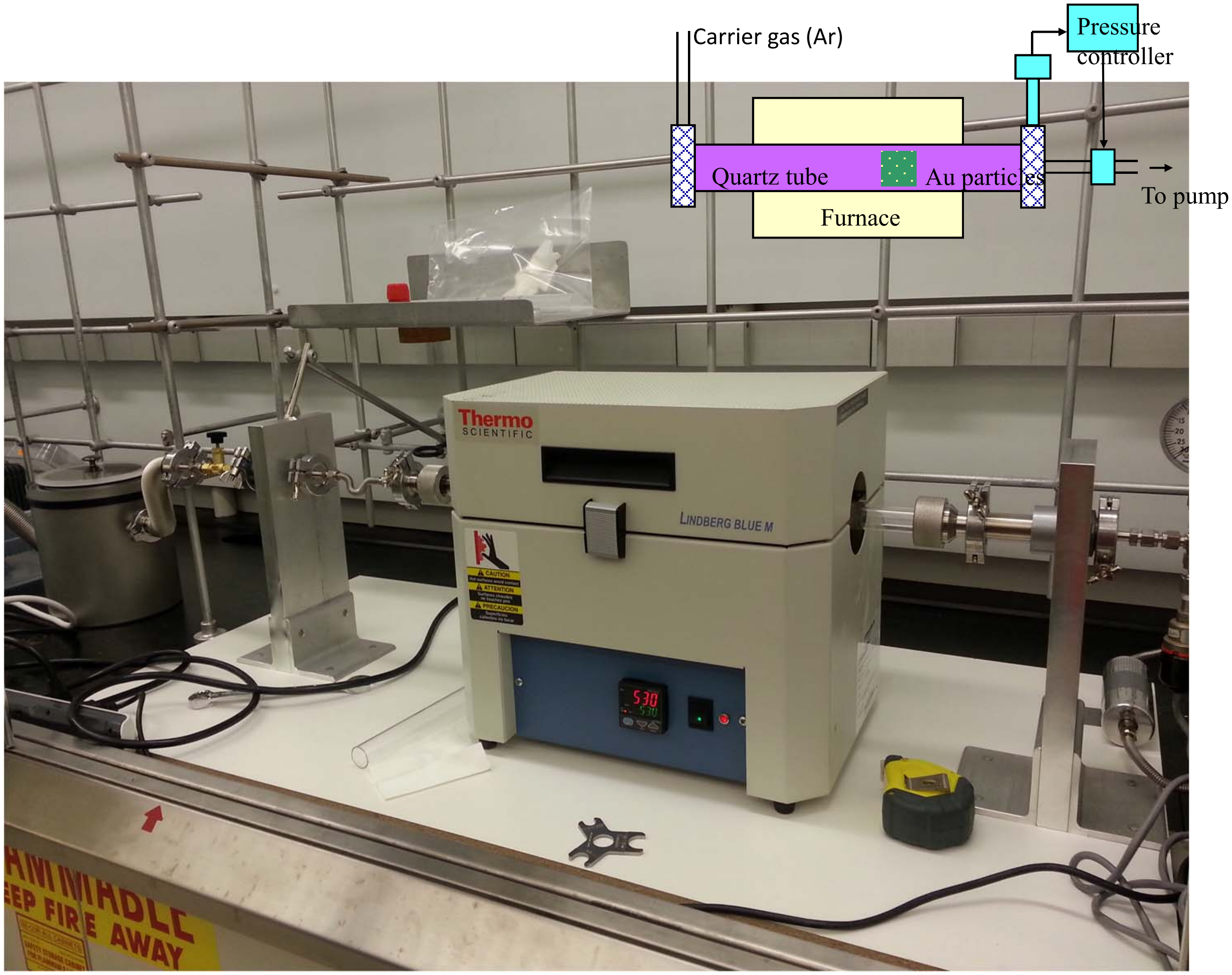


AFM of Au particles



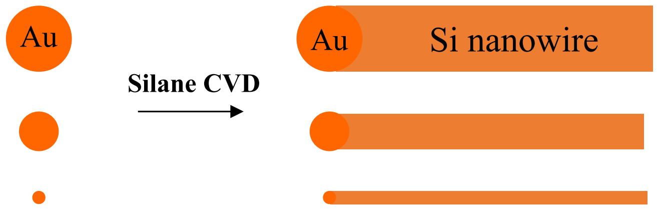
SEM on NWs

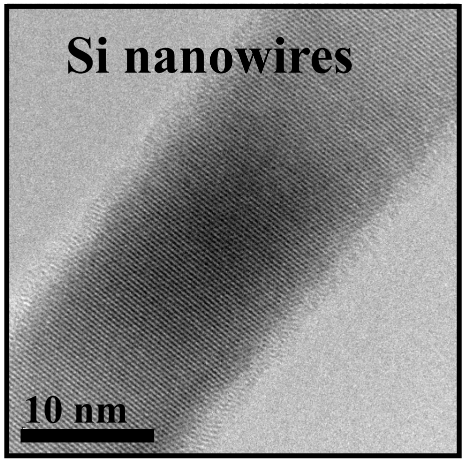



Carrier gas (Ar)
Pressure controller
Quartz tube
Au particles
Furnace
To pump
Thermo SCIENTIFIC
LINDBERG BLUE M

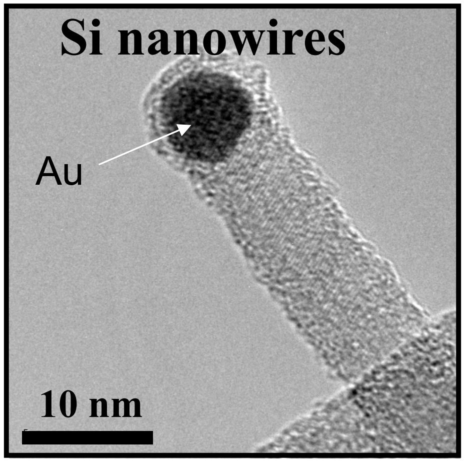
Characteristics of VLS Growth

Diameter control



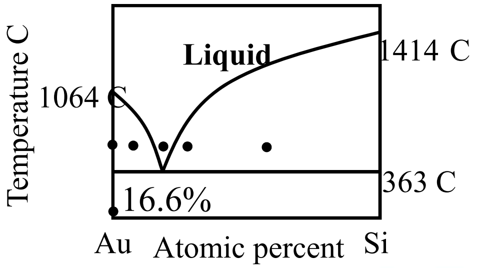


- Nanowire are single crystal
- Nanowire diameters are mainly controlled by the diameter of Au catalyst
- Au nanoparticles can be synthesized with controlled diameters.



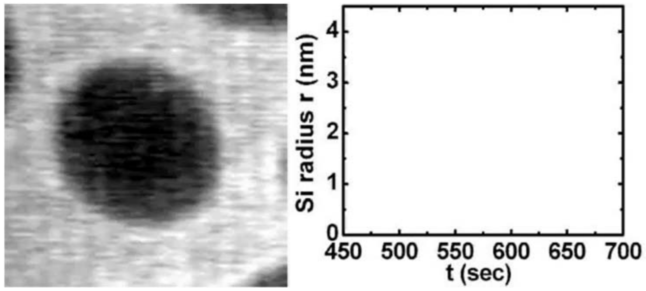
Cui and Lieber, *App. Phys. Lett. 78*, Page 2214-2216 (2001).

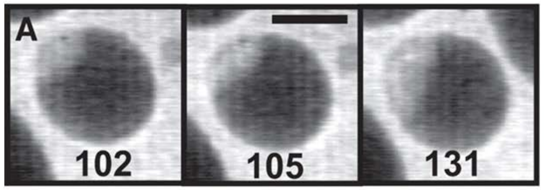
In-situ TEM Observation of VLS Process

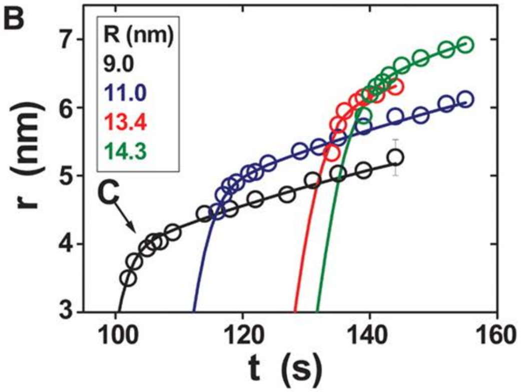


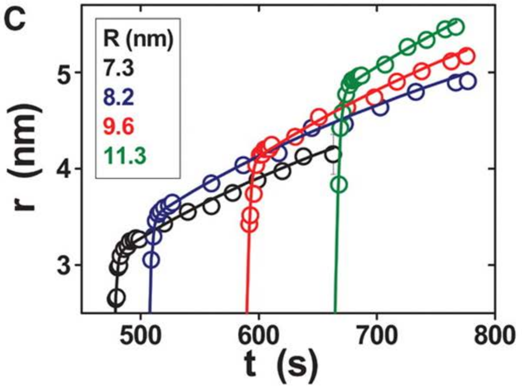
Science 2008, V.322, P.1070

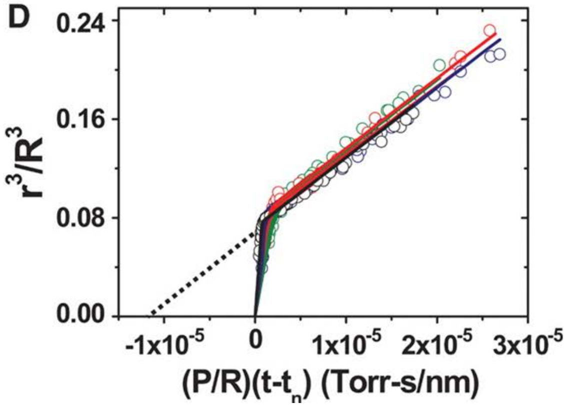
Si NW using Au Catalyst (F. M. Ross at IBM)









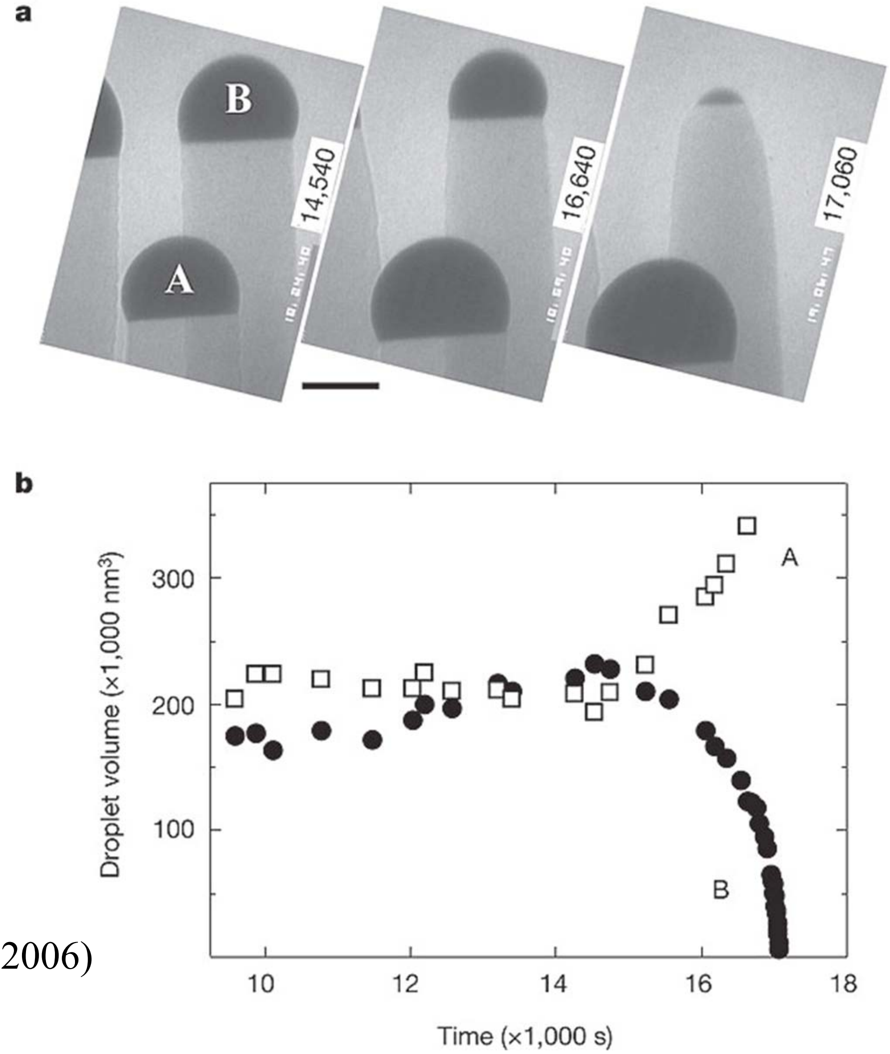


UHV: Si_2H_6 (disilane) gas precursor
Au droplets on SiNx membrane.

A: Si nucleation out of Au. 525 C, 4×10^{-6} torr.
B: Si nucleus, r, versus time.
C: Si nucleus, r, versus time. 525 C, 8×10^{-7} torr.
D: 525C, 4 different pressures, showing the same turn-over behavior

Kink: kinetic model.
Initial nucleation: nucleation out of supersaturated Si in Au.
Later growth: growth rate determined by the Si supply rate.

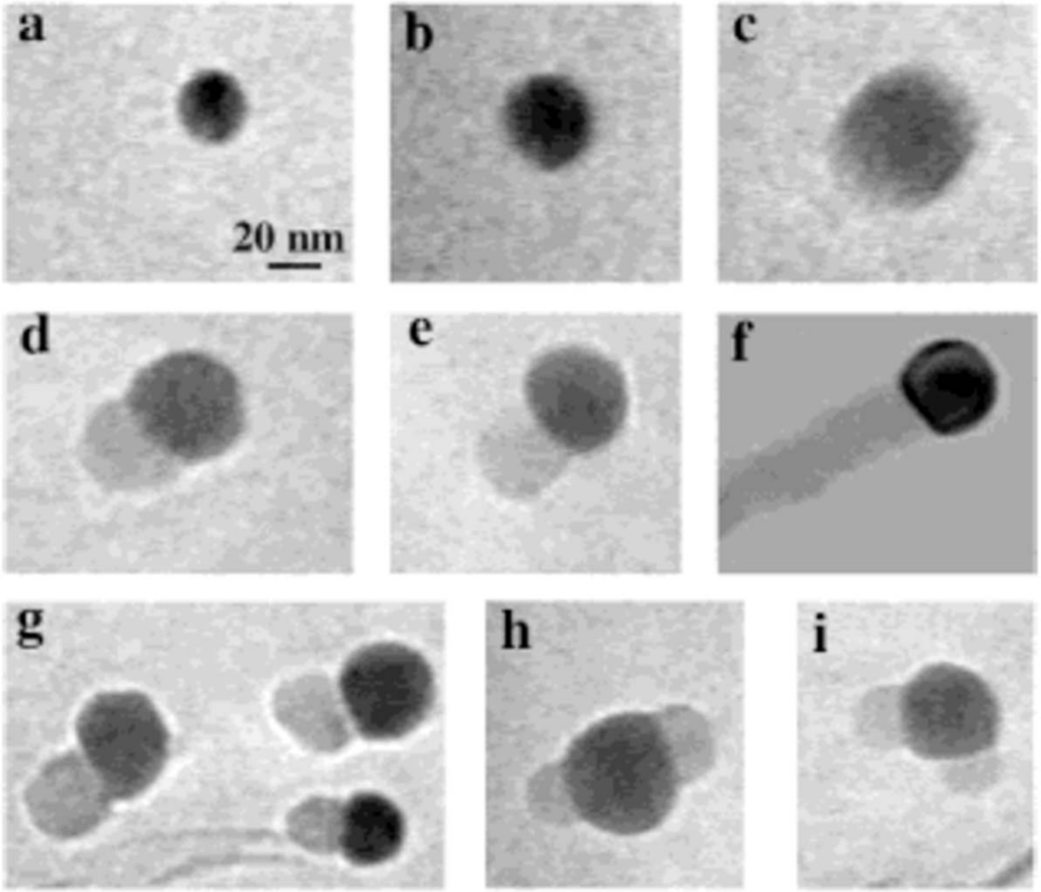
Au diffuses at elevated temperature, terminating growth



Nature 440, 69-71 (2006)

In-situ TEM Observation of VLS Process

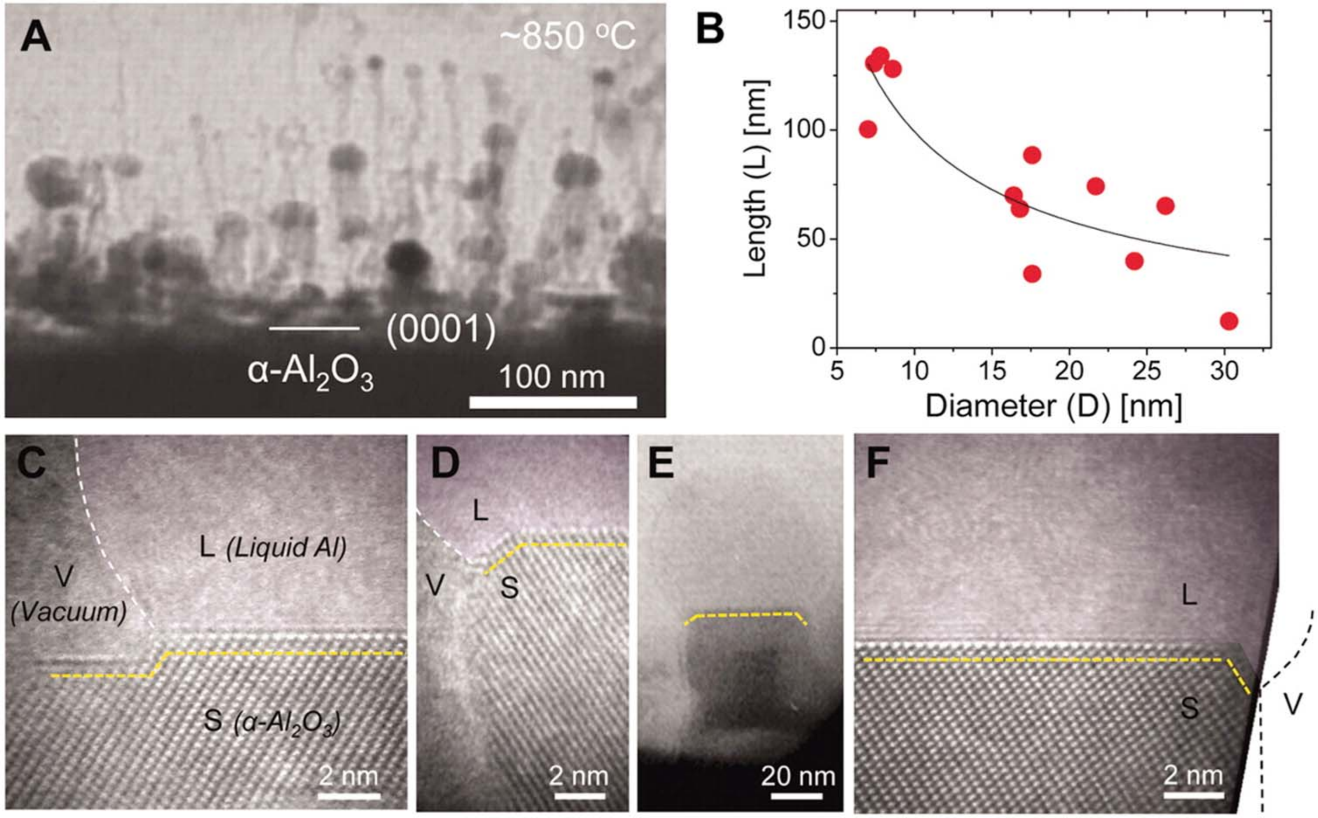
Ge NW
Using Au
Catalysts



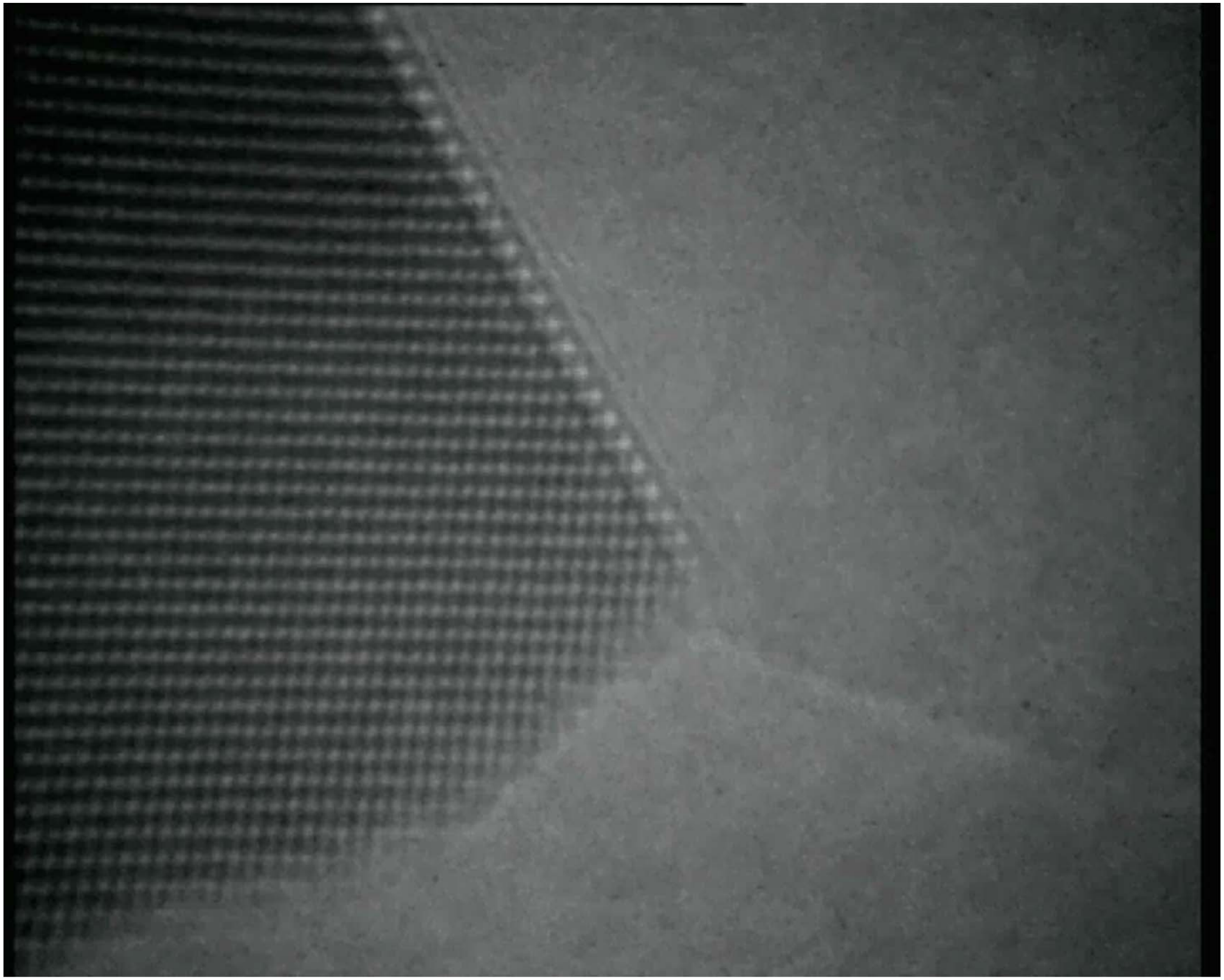
Journal of the American Chemical Society 2001, V123, P3165

VLS growth of Sapphire NWs

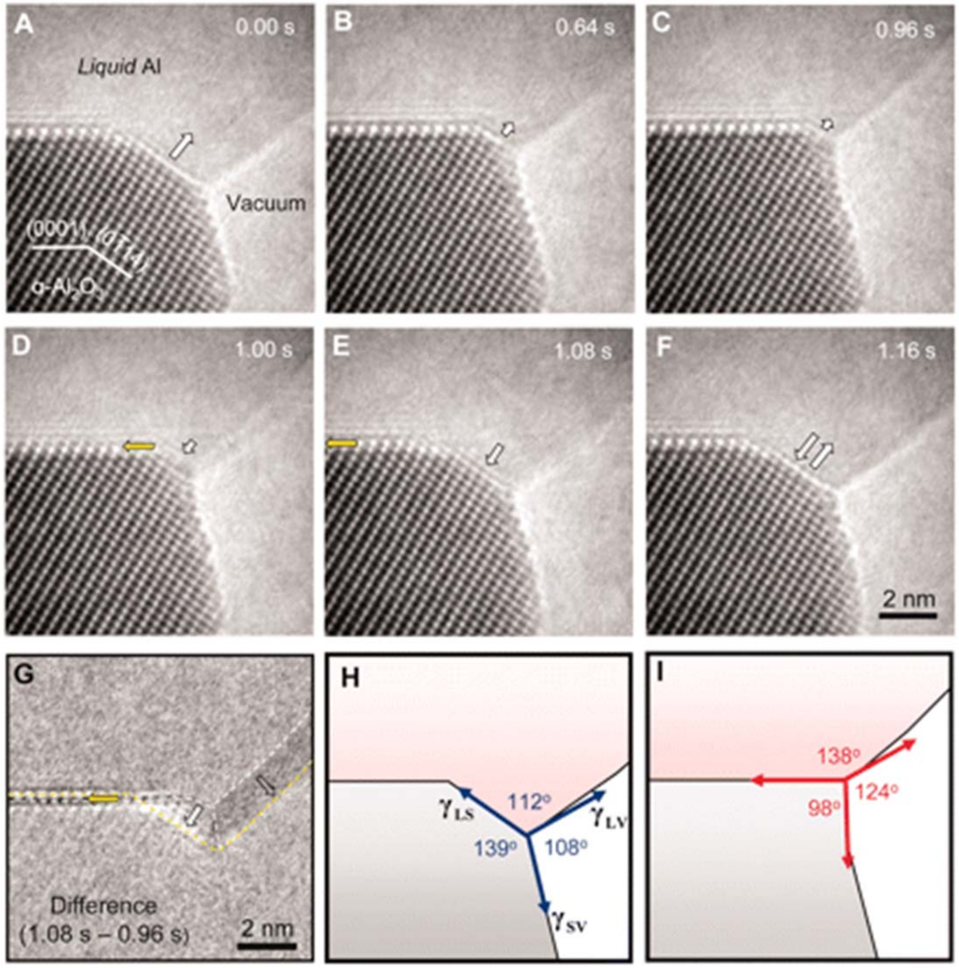
Al droplets formed on alpha- Al_2O_3 single crystal by heating above 660 C, while irradiating it with the e-beam. The liquid Al droplet oxidizes (with residual O in the chamber) to form Al_2O_3 nanowires.



Science 330, p.489 (2010)



VLS growth of Sapphire NWs



Layer by layer growth:
Oscillatory growth and dissolution reactions

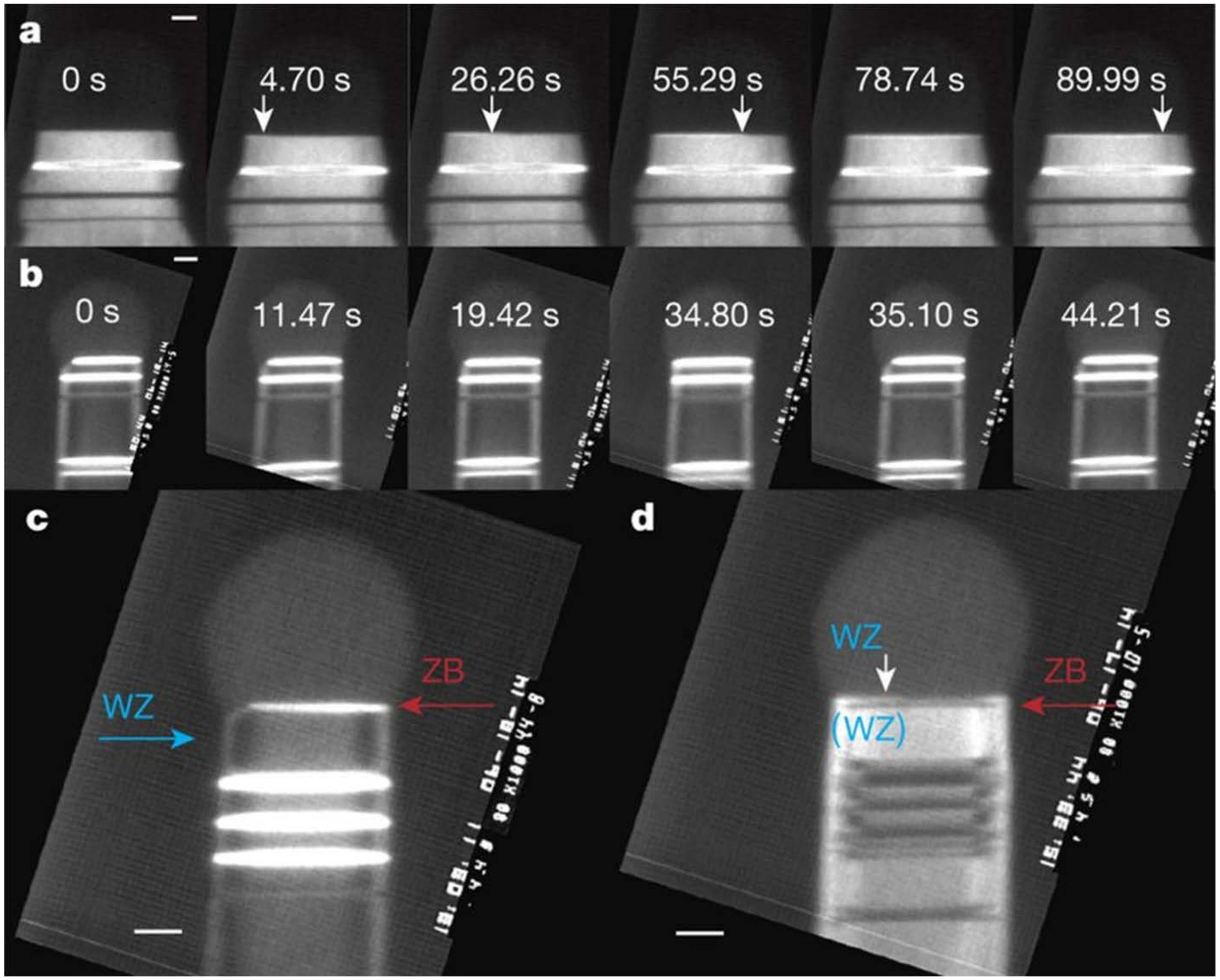
A – C : At the triple junction (V-L-S),
Mass diffusion from the LV surface to (0-114) Al_2O_3 facet

After C: the LS (0001) interface in direct contact with the LV interface.

D – F: Dissolution of the previously grown part to supply oxygen and complete a (0006) layer.

Role of triple junction in controlling growth

In situ TEM study of GaAs nanowire growth (Wurtzite versus Zinc-blend)

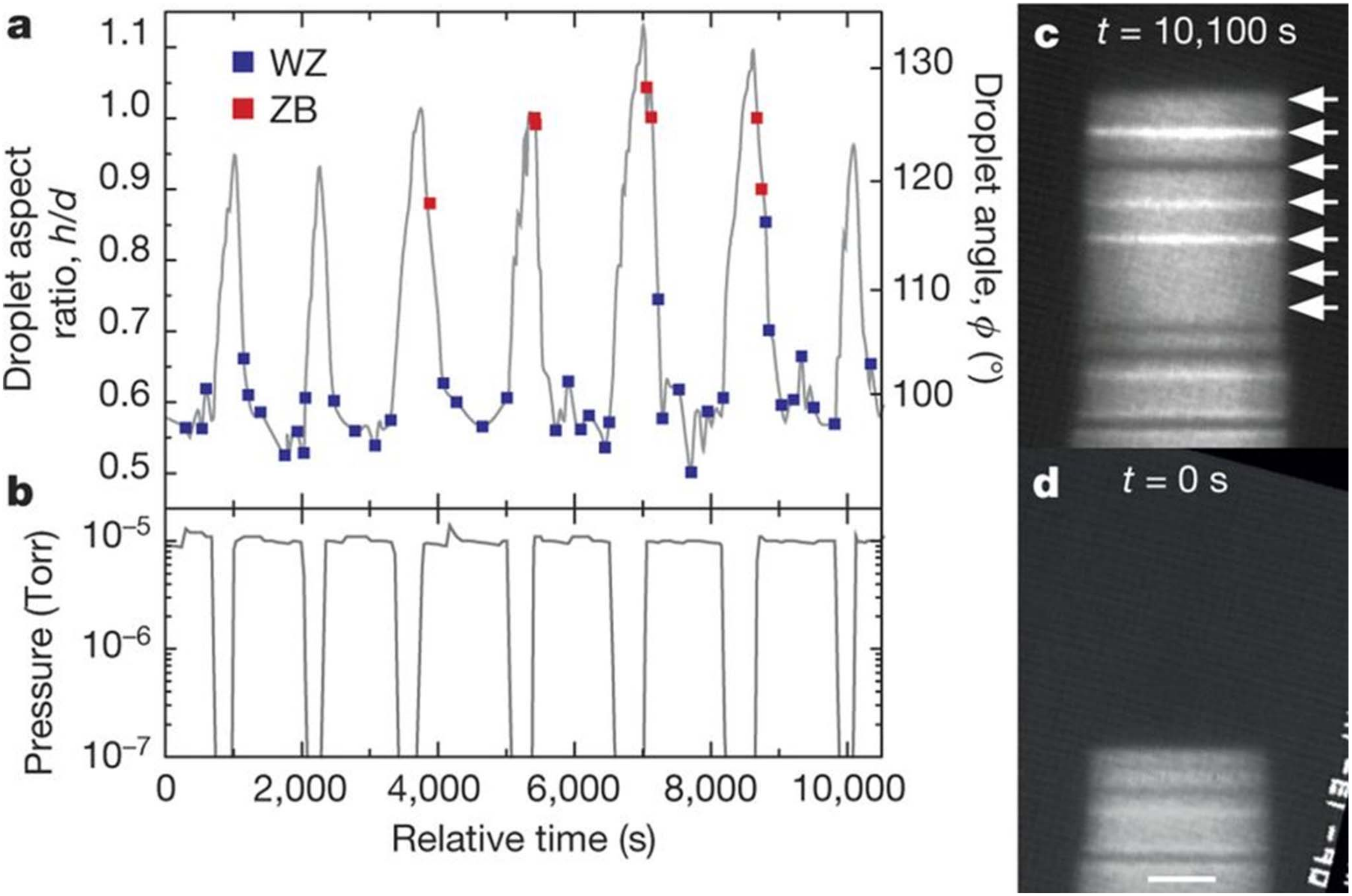


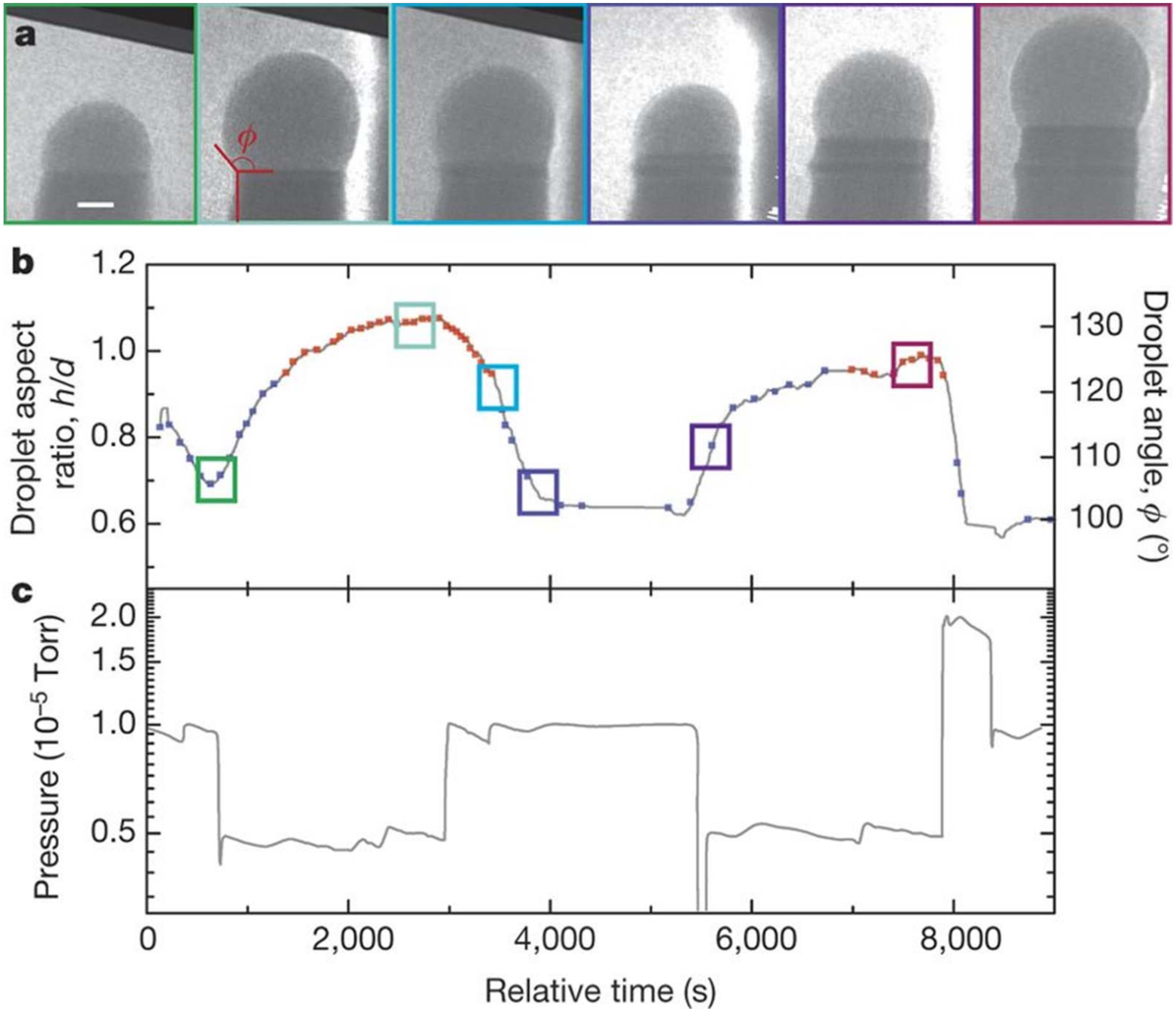
A: WZ segment
Growth conditions:
550 C, AsH_3 (arsine) pressure of $1x10^{-5}$ torr
TMGa (trimethylgallium) pressure of $3.5x10^{-8}$ Torr

B: ZB segment
550 C, AsH_3 pressure from 10^{-7} to $1.5x10^{-5}$ torr
TMGa pressure of $2x10^{-8}$ Torr

So, the As/Ga ration controls the structure.

Nature 531, p.317 (2016)

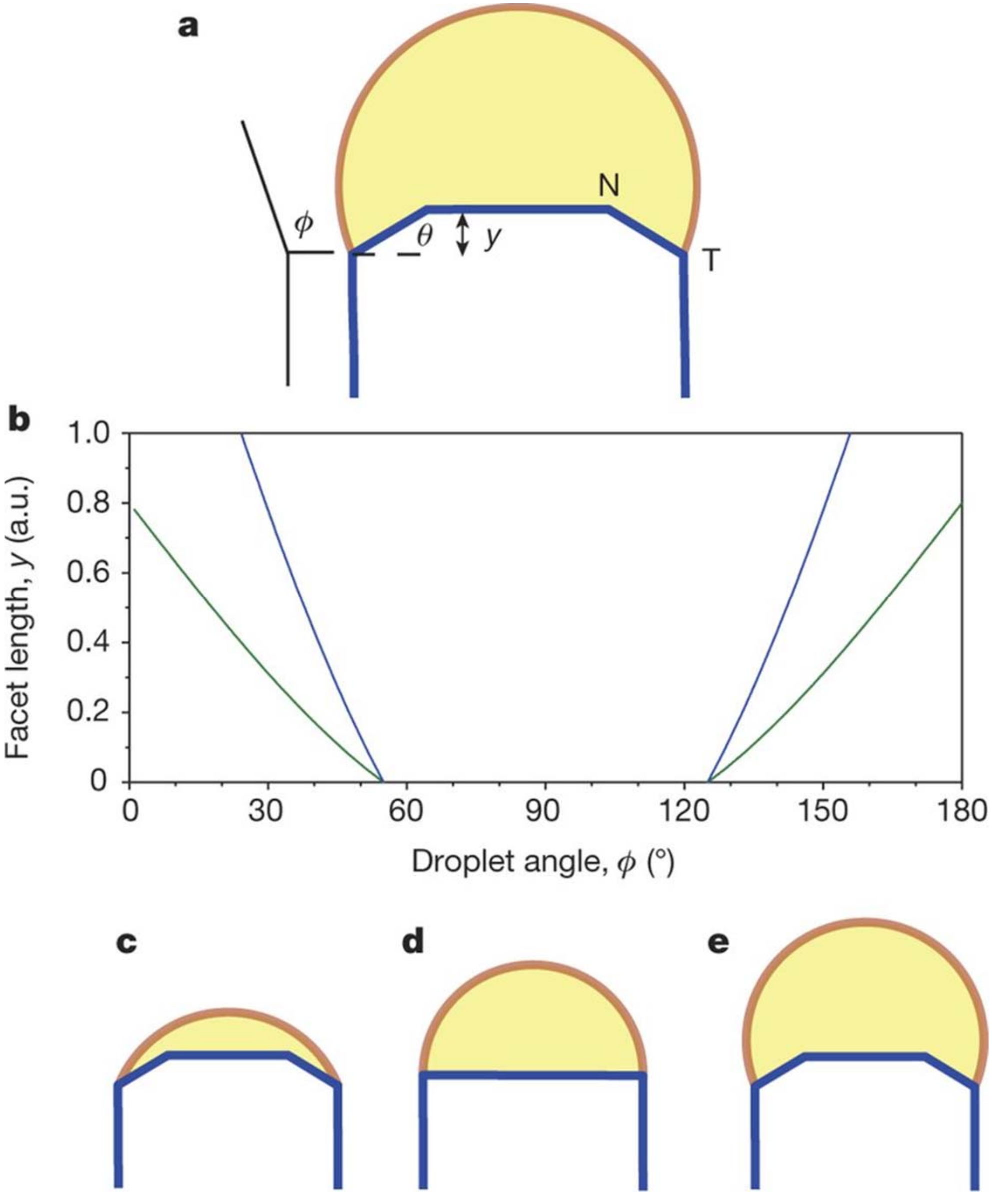

a
b
c
d
Droplet aspect ratio, h/d
Droplet angle, ϕ (°)
Pressure (Torr)
Relative time (s)
WZ
ZB
1.1
1.0
0.9
0.8
0.7
0.6
0.5
130
120
110
100
10−5
10−6
10−7
0
2,000
4,000
6,000
8,000
10,000
t = 10,100 s
t = 0 s



Constant T (550 C)
Constant TMGa pressure
Varying AH_3 pressure

With varying AH_3, the droplet changes its shape along with the contact angle at the triple (VLS) point.

Blue : WZ
Red: ZB



Nucleation / Growt :
Controlled by the balance of interfacial energies at the triple point.

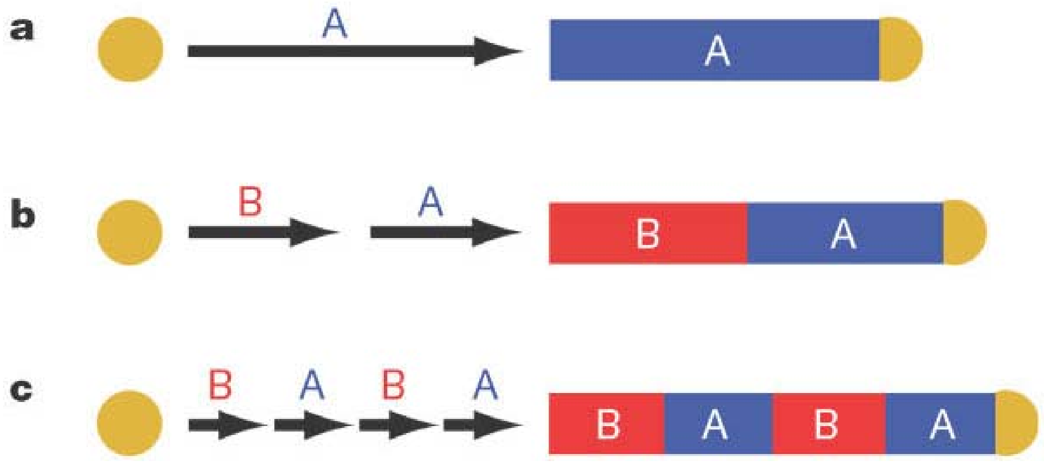
Influenced by local vapor pressures, temperatures, …

Overview

- Benefits of Nanoscale Materials
  - Emergent properties (band engineering, surface properties)
  - Examples (quantum dots, carbon nanotubes, mechanical properties)
- Synthesis of nanowires
  - Various growth methods (etching, templating, anisotropic crystal structure, …)
  - Vapor-liquid-solid growth (heterostructures)
  - Doping / surface passivation
- Synthesis of 2D materials
  - Chemical vapor deposition
  - Precursors / additives

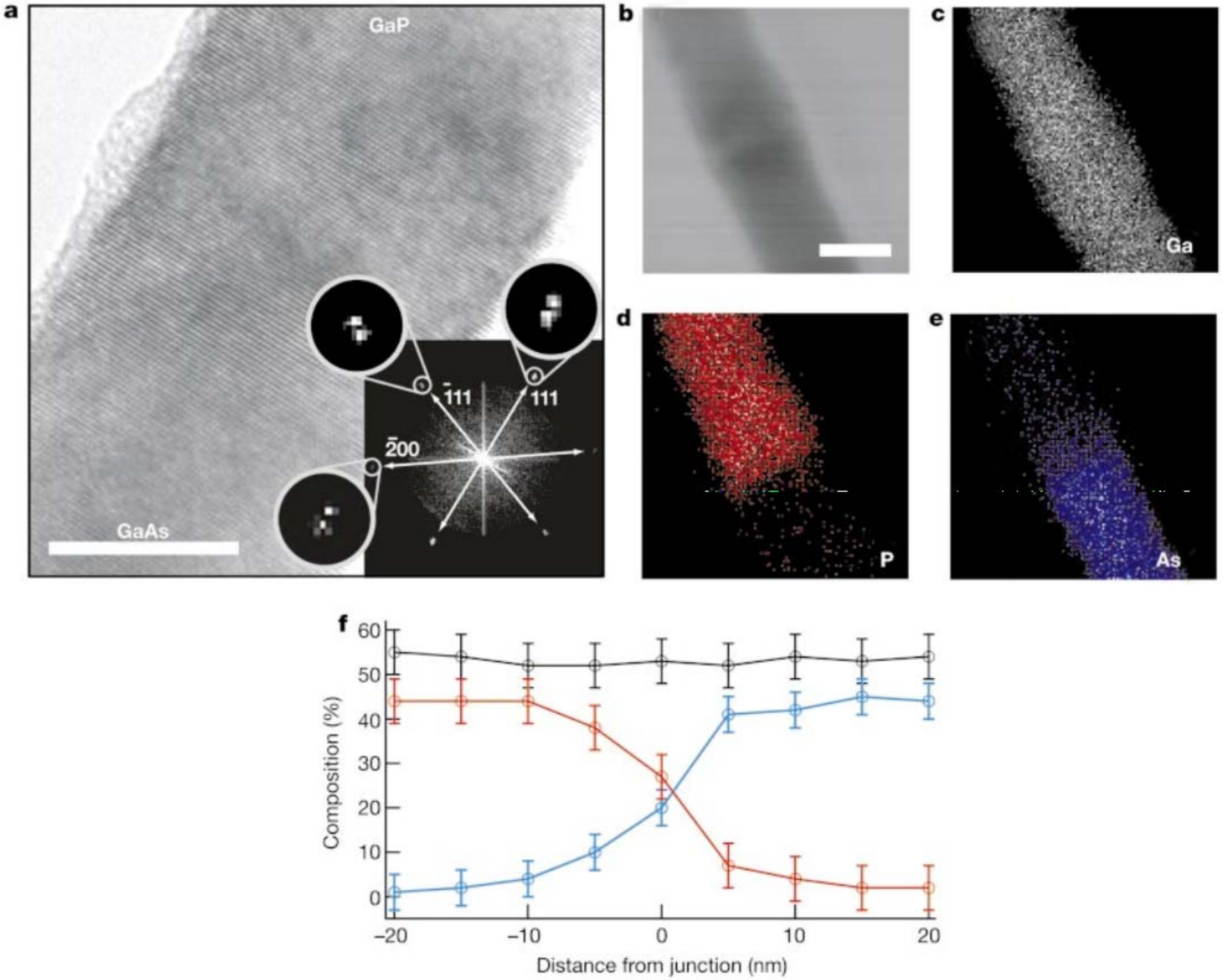
Characteristics of VLS Growth

Linear Heterostructure



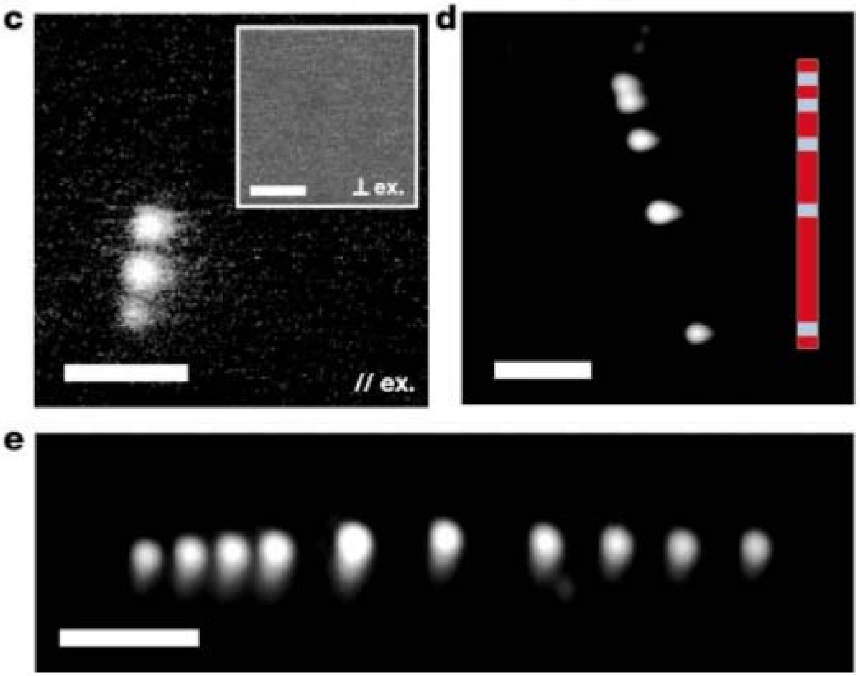
- Au nanoparticles serve as common catalysts for Materials A and B.
- Switch the gas vapor during growth.

GaP/GaAs linear heterostructure



C. M. Lieber *Nature 415*, 617-620 (2002)

Optical Property Tuning via Heterostructure



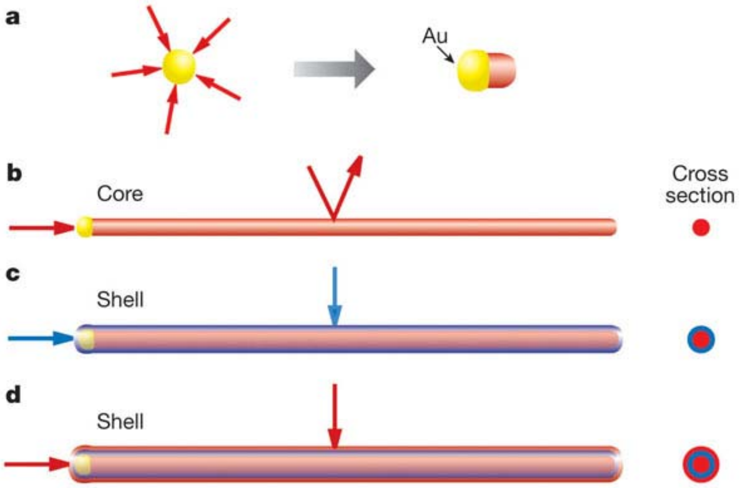
- GaP/GaAs heterostructures
- GaP is an indirect bandgap semiconductor
- GaAs is a direct bandgap semiconductor

- Photoluminescence images
- Bright regions are GaAs segments.

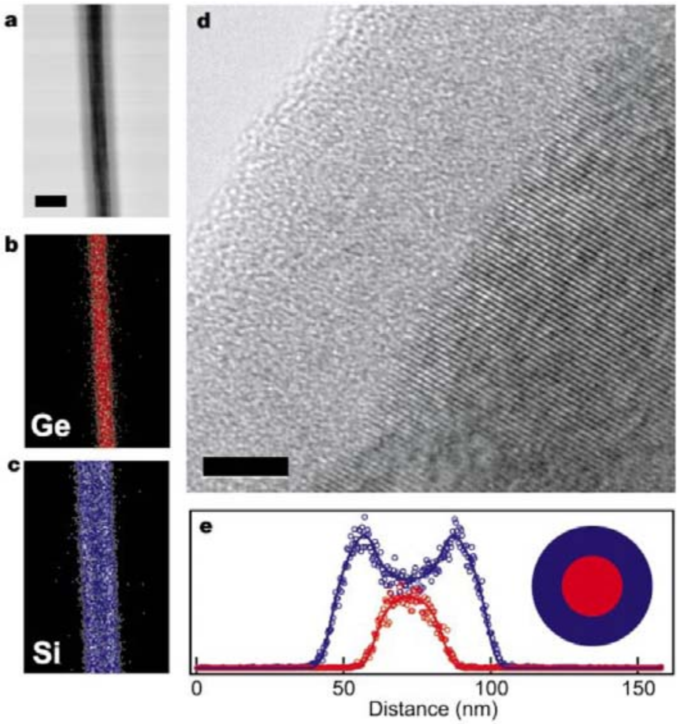
C. M. Lieber *Nature 415*, 617-620 (2002)

Characteristics of VLS Growth

Core-shell Nanowires



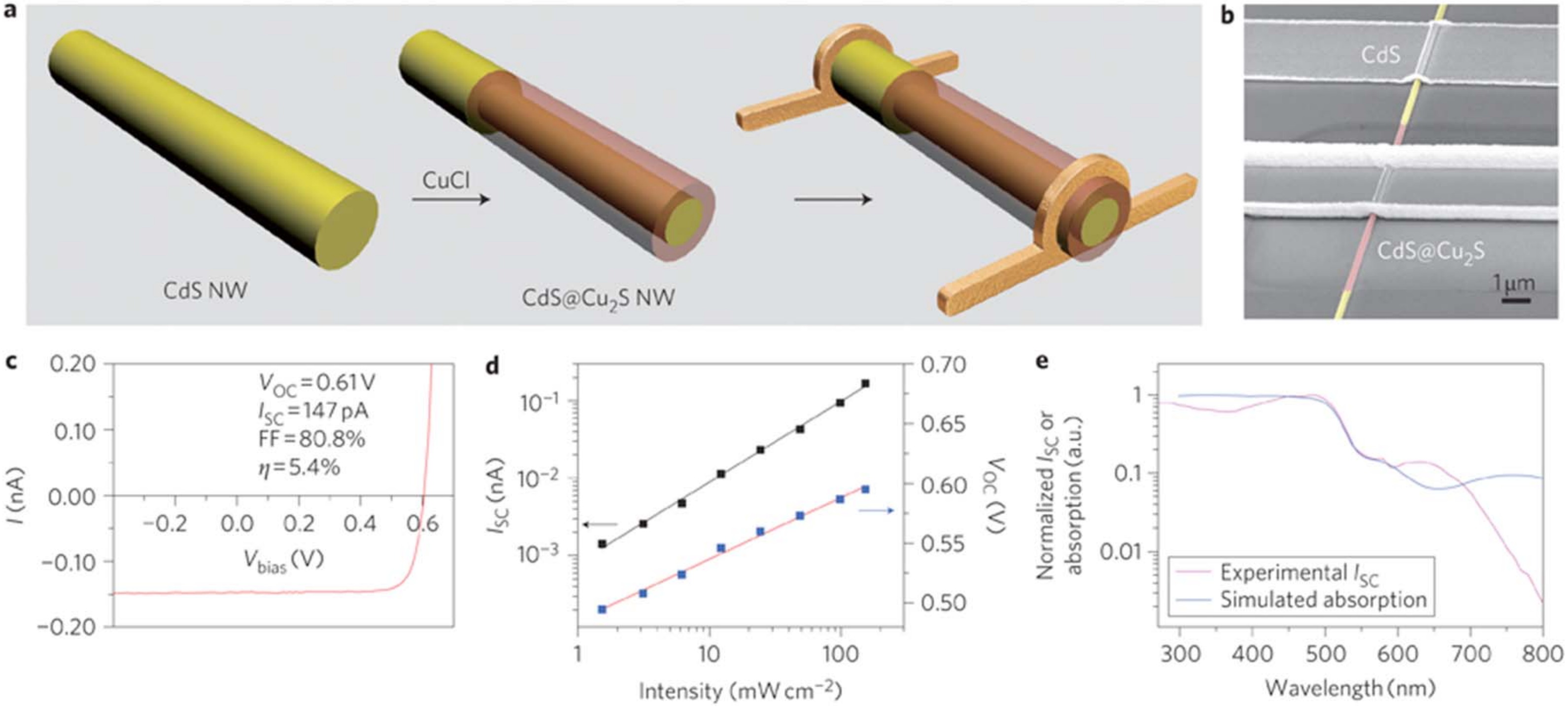
Ge-Si core-shell nanowires



- Use the growth conditions that suppress linear growth.

C. M. Lieber *Nature 420*, 57 (2002)

Radial PN Junction for Core/Shell NW (Solar Cell)



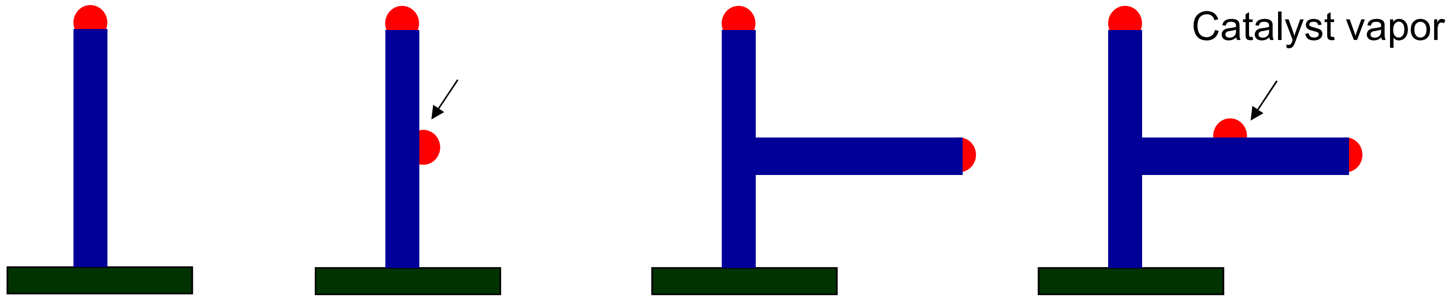
Cation Exchange

The as-grown CdS nanowire was dipped into a 0.5 M CuCl solution at 50 °C for 5–10 s to convert the surface CdS to a Cu_2S shell.

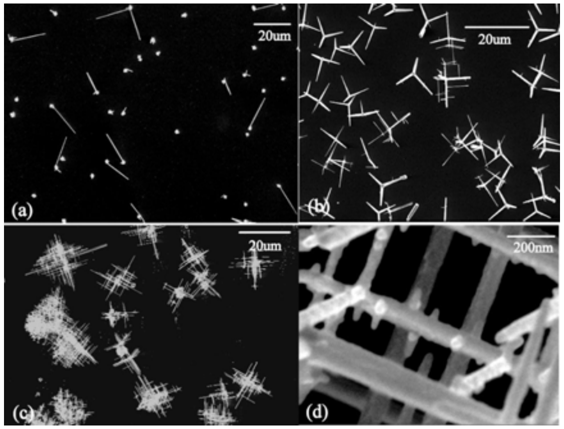
Nature Nanotech 6, 568 – 572 (2011)

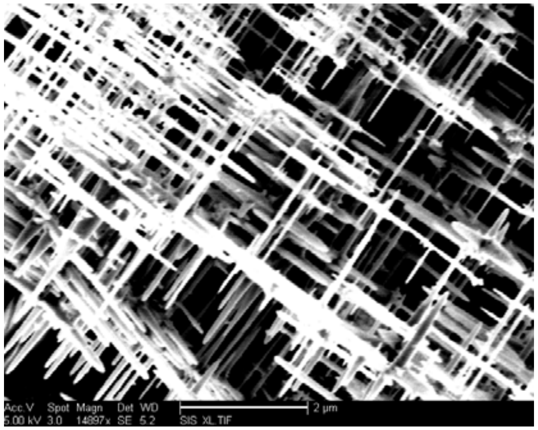
Characteristics of VLS Growth

Hyperbranched nanowires

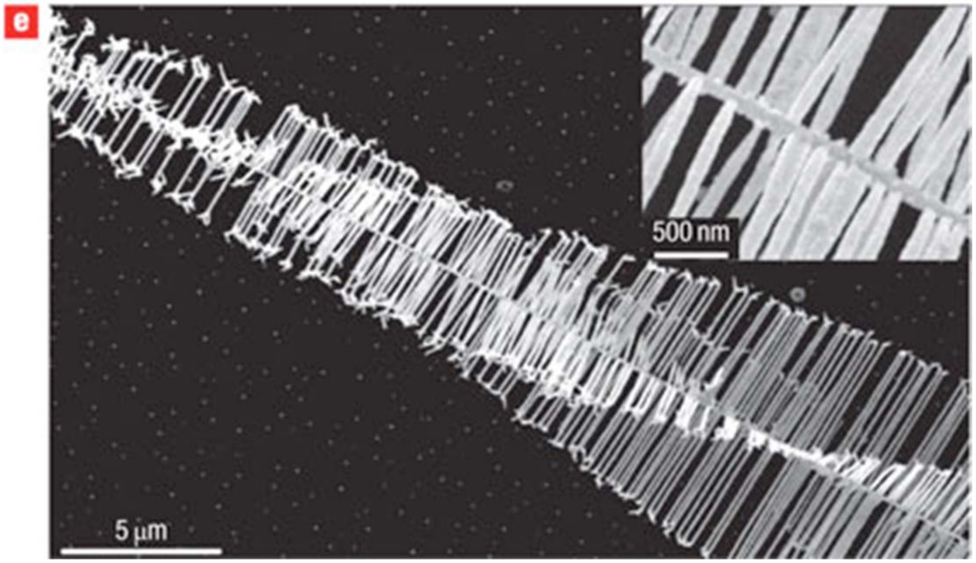


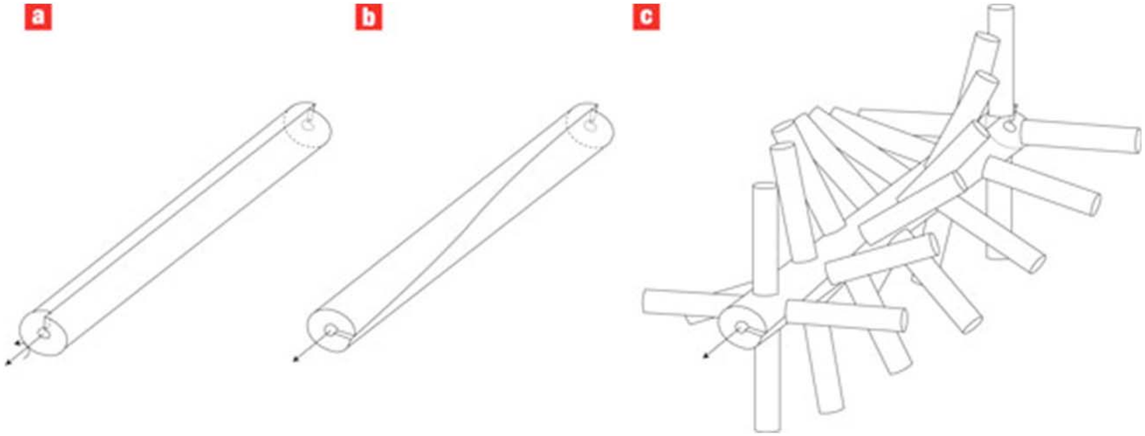
PbSe hyperbranched nanowires





Jia Zhu and Yi Cui, ***Nano Lett.*** *7*, 1095-1099 (2007)





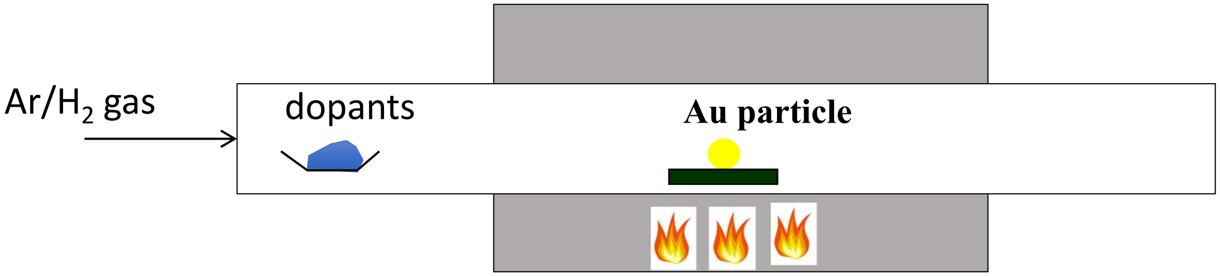
Nature Nanotech 3, 477 – 481 (2008)

Overview

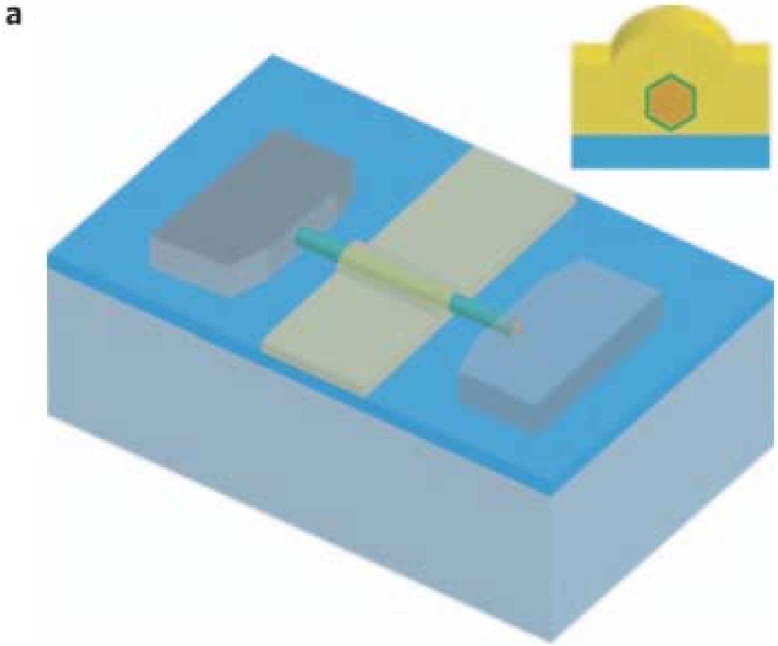
- Benefits of Nanoscale Materials
  - Emergent Properties (band engineering, surface properties)
  - Examples (quantum dots, carbon nanotubes, mechanical properties)
- Synthesis of nanowires
  - Various growth methods (etching, templating, anisotropic crystal structure, …)
  - Vapor-liquid-solid growth
  - Doping / Surface passivation
- Synthesis of 2D materials
  - Chemical vapor deposition
  - Precursors / additives

How do you dope nanowires?

- Growth happens in an open system
- Kinetics more / equally important to thermodynamics
  - Co-vaporization (wire material and dopants)
  - Post-growth doping
  - Using the metal catalyst



Post-growth doping: b-doped Si NWs



Radial p-n junction

1. VLS-grown Si NWs (n-type)
2. Post doping using BCl_3 gas source
   (Vapor source, diffusion into Si NWs)
   p-doping

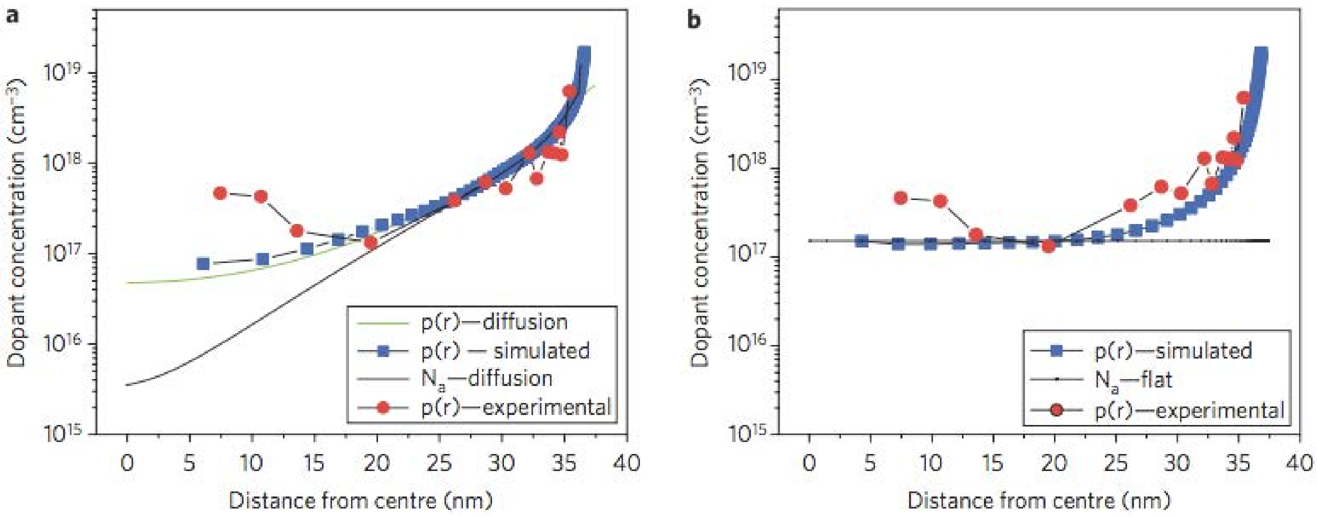
How does the doping profile look like?

A. Uniform across the NW?
B. Uneven inside the NW?

Nature Nanotechnology 4, 311-314 (2009)

Dopant profile measured from capacitance measurements

Post doping: diffusion limited process. Dopants are more concentrated near surface of the wires



Majority carrier concentration for the case of
A: Radially distributed dopant profile. (Concentration higher at the outer edge of NW)
B: Homogeneously distributed dopant profile.

Red: Extracted from CV measurements
Black: Calculated assuming radially dependent dopant profile (A) or flat dopant profile (B)

B: The black curve does not match red dots.

Nature Nanotechnology 4, 311-314 (2009)

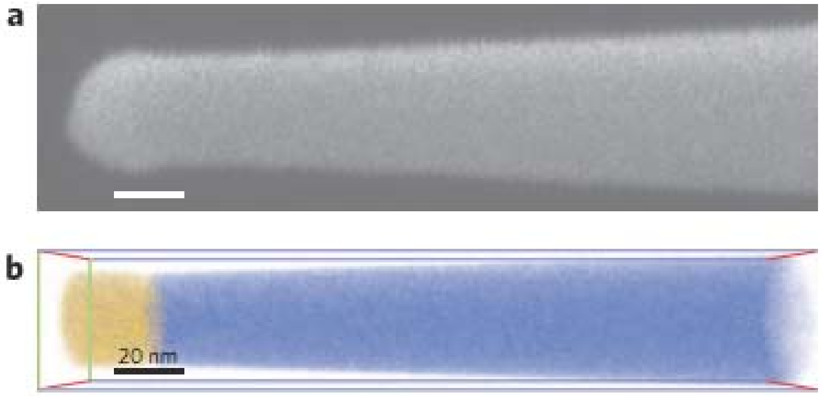
Co-doping during growth: Ge wire with P-doping

- VLS grown P-doped Ge NWs
- Used GeH_4 (germanium hydride) and PH_3 (phosphine) gases as precursors with hydrogen and helium co-flows (50 torr)
- Au nanoparticles as metal catalyst

Used Atom Probe Tomography (APT) to reconstruct the sample.

How does the doping profile look like?

A. Uniform across the NW?
B. Uneven inside the NW?

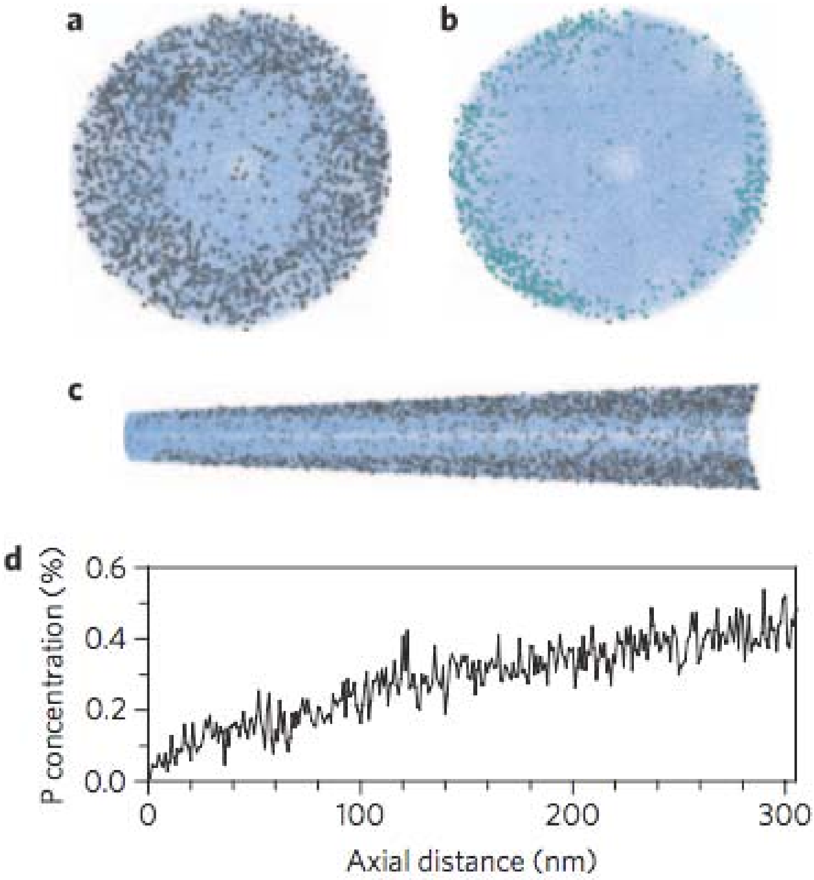


SEM Image

ATP 3D Reconstruction
Yellow: Gold atoms
Blue: Ge atoms

Nature Nanotech. 4, p.315 (2009)

Directly Imaging the Dopant Profile



Grey: Phosphorus
Light blue: Germanium
Blue: Oxygen

Phosphorus dopants are concentrated near the outer part of the Ge NWs.

Nature Nanotech. 4, p.315 (2009)

Directly Imaging the Dopant Profile

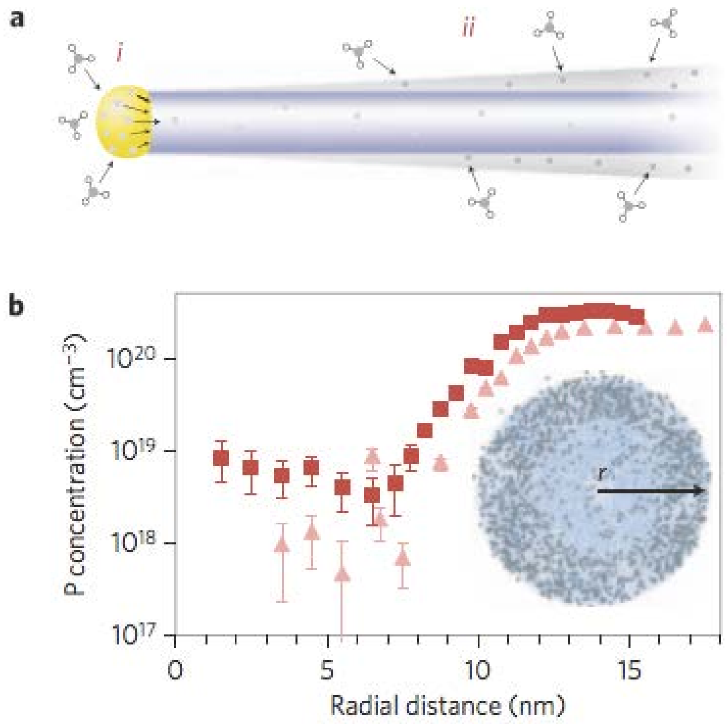
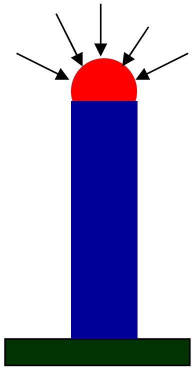


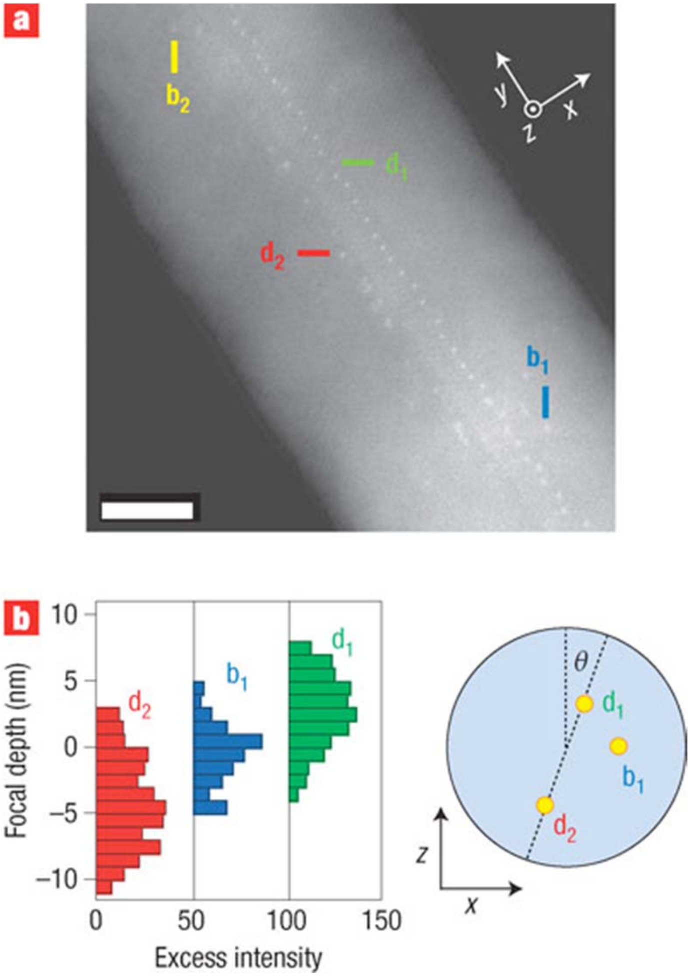
Figure 3 | Dopant incorporation pathways and distribution. a, Schematic representation of dopant incorporation pathways via the catalyst (*i*) and surface decomposition (*ii*). **b**, Radial plot of phosphorus concentration for germanium nanowires grown at 380 °C and PH_3 : GeH_4 ratios of 1 : 1,000 (triangles) and 1 : 500 (squares). The inset shows the path along which the concentration was measured.

Nanotech. 4, p.315 (2009)

Au atoms in Si NWs!!!

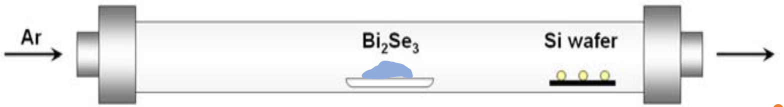


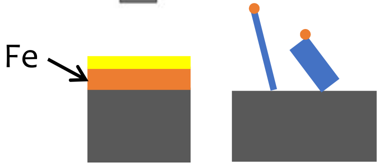
Growth



Nature 440, 69-71 (2006)

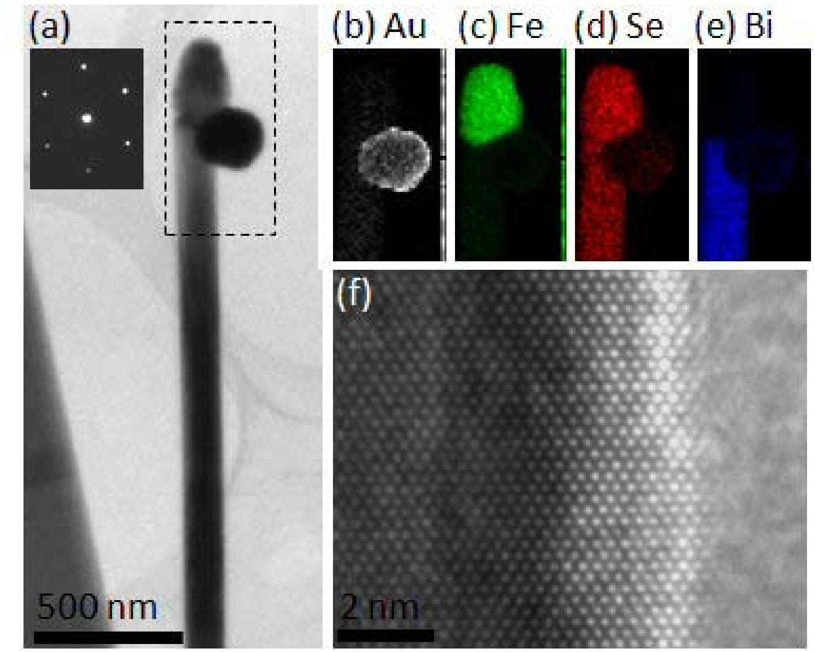
Doping Through Catalyst: Kondo Effect by Fe Impurities





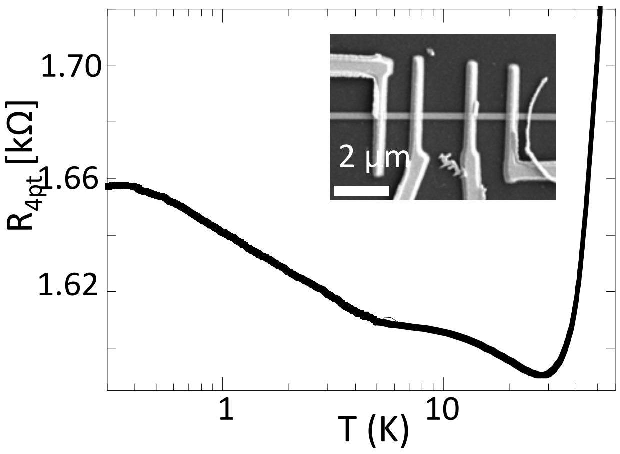
Some of metal catalyst diffuse into Bi_2Se_3 as dopants.

Fe doping



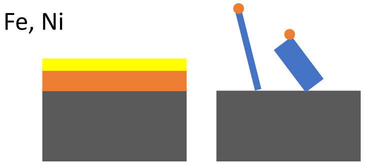
Cha, et al. Nano Lett. 10, 1076 (2010)

Kondo behavior

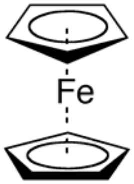


Ferrocene as Dopant Source

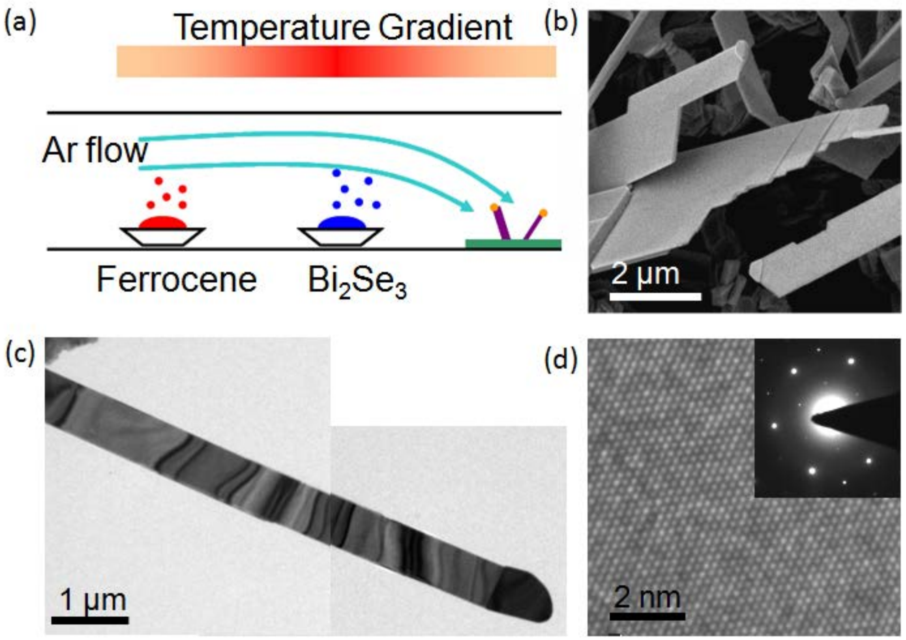
Before



Now

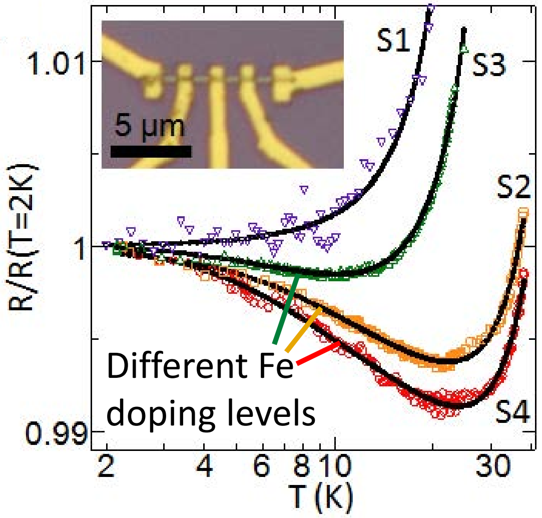


$Fe(C_5H_5)_2$

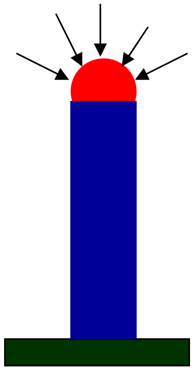


<u>Cha</u>, et al. Nano Lett. 12, 4355 (2012)

Kondo behavior



VLS must go though the catalyst

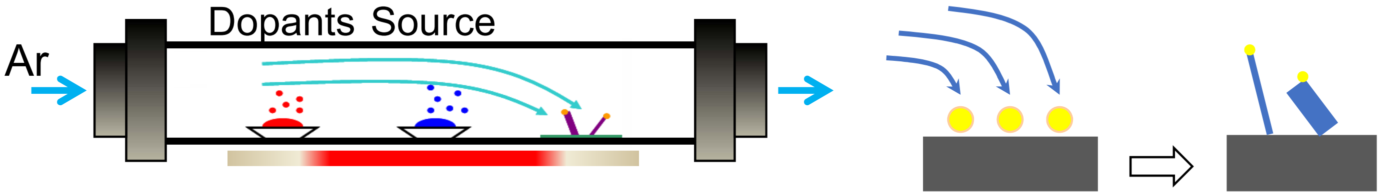


Growth

Often times, side growth occurs at the same time.
→ Vapor-solid deposition at the side
→ Makes nanoribbons with widths wider than the catalyst size

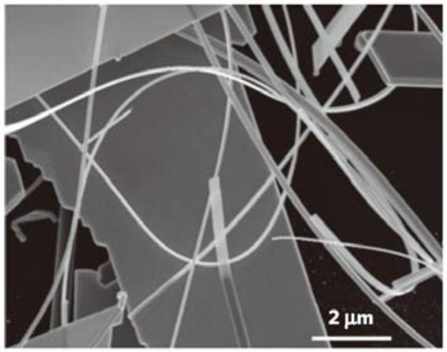
Chemical Vapor Deposition:
Precursors in the vapor form, react / decompose on the substrate, then deposit on the substrate.

Synthesis of Topological Insulators



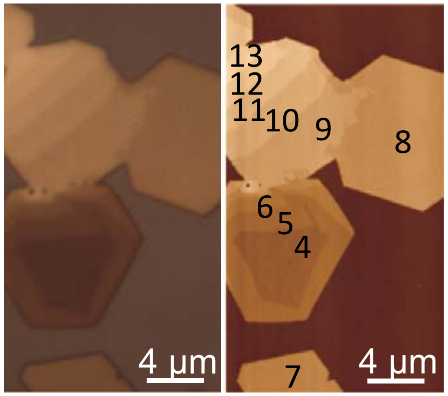
Source : Bi_2Se_3, Bi_2Te_3, Sb_2Te_3, Sb_2Se_3, …
Dopants : Sb, Cu, Ferrocene, …

Bi_2Se_3 Nanoribbons



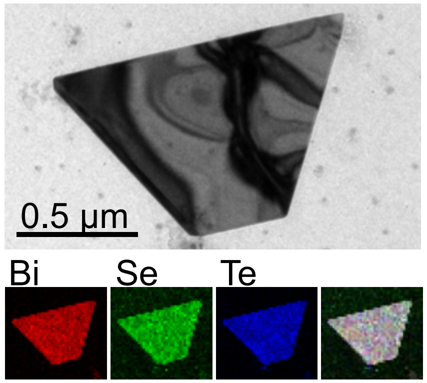
Cha, et al. Nano Lett. 10, 1076 (2010)

Bi_2Te_3 Nanoplates



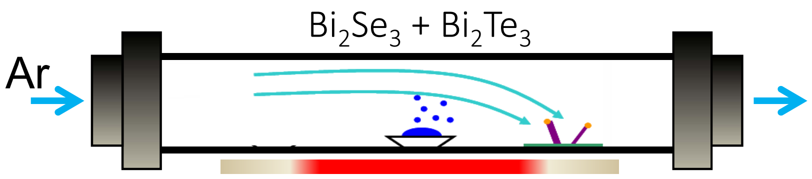
Kong, Dang, **Cha**, et al.
Nano Lett. 10, 2245 (2010)

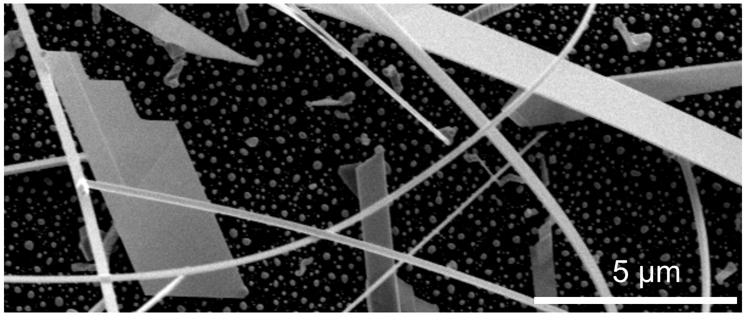
$Bi_2(Se_xTe_{1-x})_3$

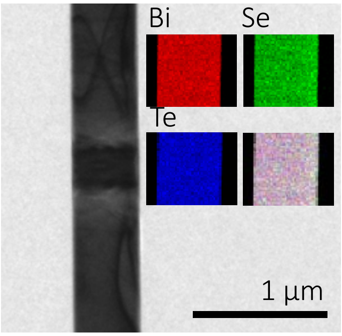


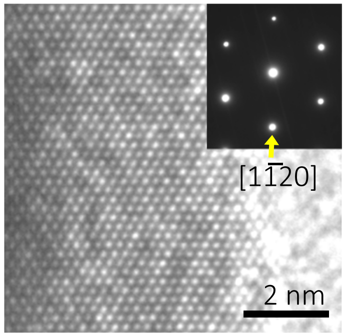
Cha, et al. Nano Lett. 12, 1107 (2012)

$Bi_2(Se_xTe_{1-x})_3$ Nanoribbons

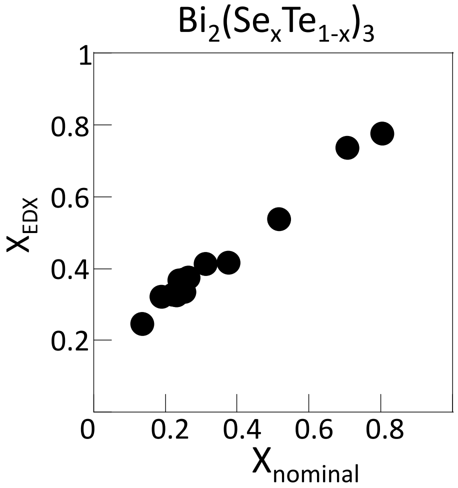


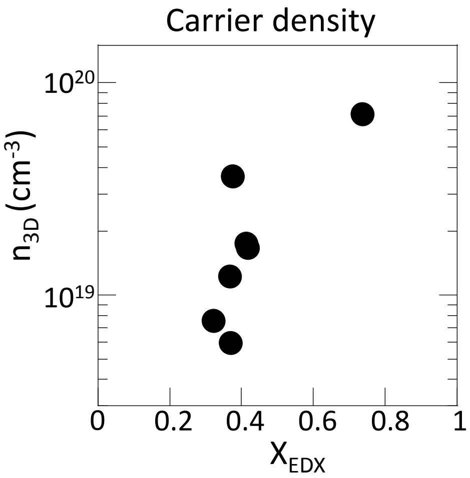






Cha, et al. Nano Lett. 12, 1107 (2012)

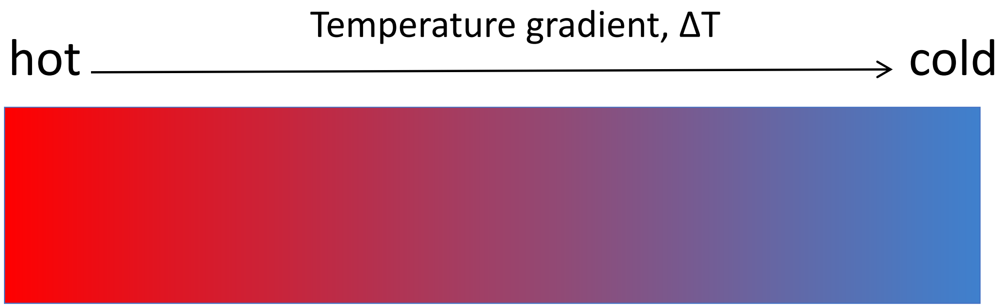




Overview

- Case Study of Nanowires: Si Nanowires
  - Thermal transport modulation
  - Si nanowire batteries
- Case study of topological nanomaterials
  - Bi_2Se_3 topological insulator nanoribbons
  - SnTe Topological crystalline insulator nanowires
- Case study of 2D materials for energy
  - MoS_2 for hydrogen evolution reaction (HER)
  - Phase transition via intercalation and consequences for HER

Thermoelectricity



Temperature gradient, ΔT

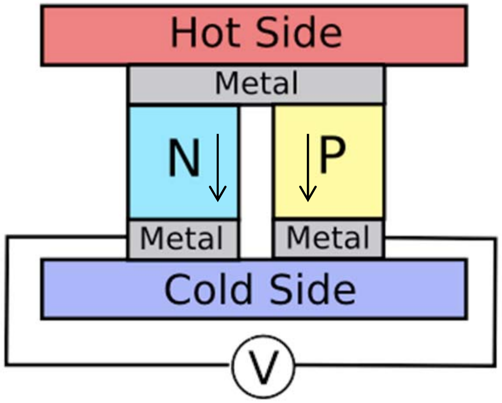
hot → cold

Electrons in the hot side want to diffuse to the cold side to reach thermal equilibrium.
Electrons carry charge.
So as they diffuse, current is generated.

→ Temperature gradient generates voltage.

Thermoelectric effect: Conversion of temperature difference to electric voltage

Thermoelectric Device



- ZT: Figure of merit, dimensionless number.
- ZT indicates how efficiently a material produces thermoelectric power.
- The higher ZT, the better thermoelectric device.

- State-of-the-art ZT: ~ 1.5 (Bi_2Te_3 based)

- If ZT is ~ 3, we will have a refrigerator that is cooled by a thermoelectric device.

$$ZT = \frac{\sigma S^2 T}{k}$$

σ: Electrical conductivity
S: Seeback cofficient
k: Thermal conductivity

- σ and S are usually fixed materials properties at the nanoscale.
- k can be tuned by nanostructuring

- This is because phonon wavelengths (collective modes of lattice vibration) are at the nanoscale.
- Electron wavelengths are at the angstrom scale.

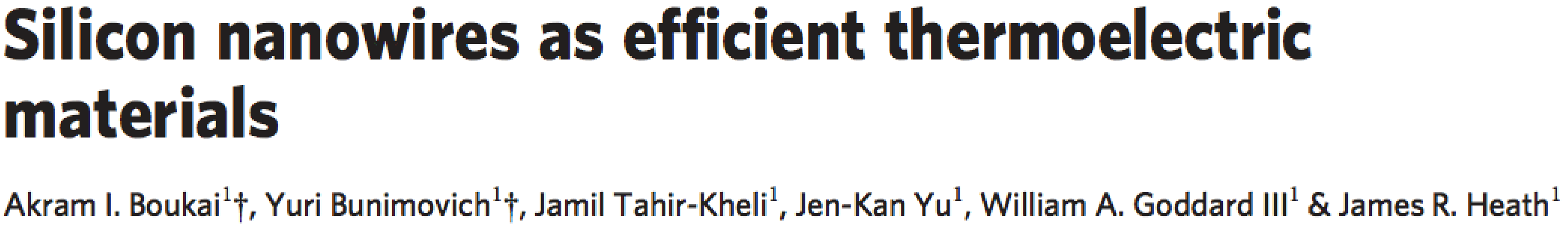
Enhance thermoelectric property of Si by using Si NWs.

$$ZT = \frac{\sigma S^2 T}{k}$$

Electrical conductivity: propagation of electrons
Thermal conductivity: propagation of phonons (collective vibration modes of lattice atoms)

Mean free path: an average path length for a particle (electron or phonon) to travel inside a material without being scattered.

Make nanostructures to control the mean free path of phonons
→ This can potentially reduce k, the thermal conductivity, increasing ZT.



Silicon nanowires as efficient thermoelectric materials

Akram I. Boukai[1]†, Yuri Bunimovich[1]†, Jamil Tahir-Kheli[1], Jen-Kan Yu[1], William A. Goddard III[1] & James R. Heath[1]

- Varied the Si NW size and impurity doping levels.
- ZT enhancement of ~ 100 times compared to bulk Si at 200 K.

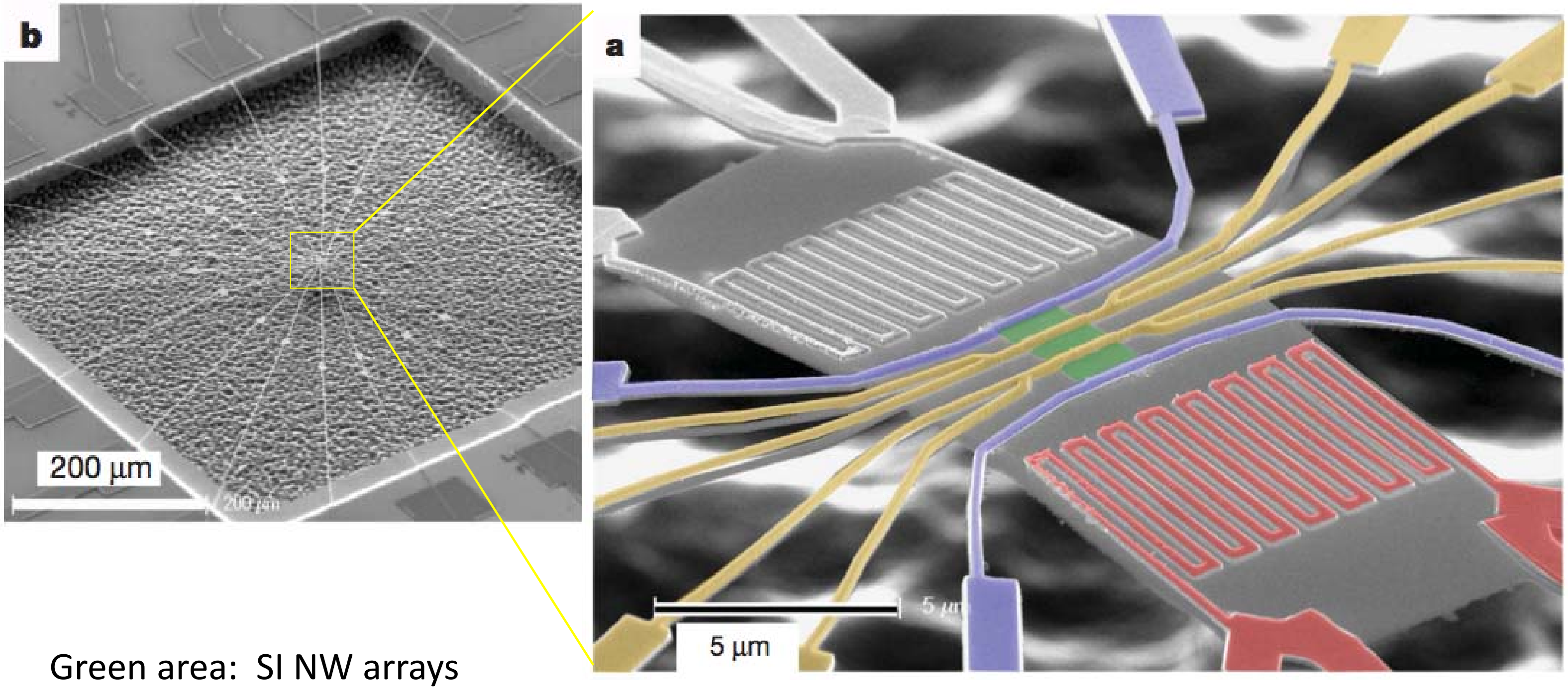
Nature 451, p.168 (2008)

Enhanced thermoelectrical property in Si NWs

- Si bulk ZT value is very low (~0.01)
- Phonon engineering to suppress heat flow
- Reduce the dimension of the sample so that the phonon wavelength is comparable to the sample size.

Nature 451, 163 (2008)
Nature 451, 168 (2008)

Si NW thermoelectric device



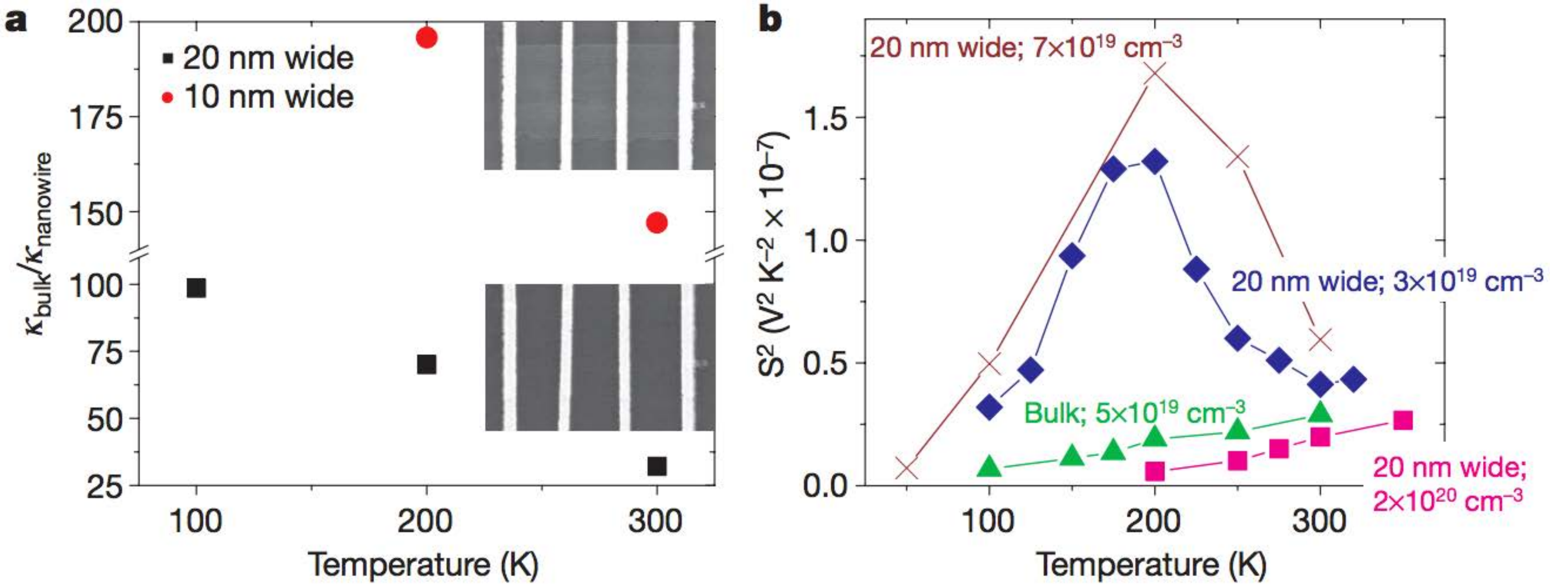
Green area: SI NW arrays
Yellow: thermometry electrodes to measure the temperature difference across the NWs
Red: Joule heaters (two total, only one is colored)
Yellow + Blue: four point electrical conductivity measurements

Suspending the NWs are key to create thermal isolation from the Si wafer.

Nature 451, p.168 (2008)

Si NW thermoelectric device

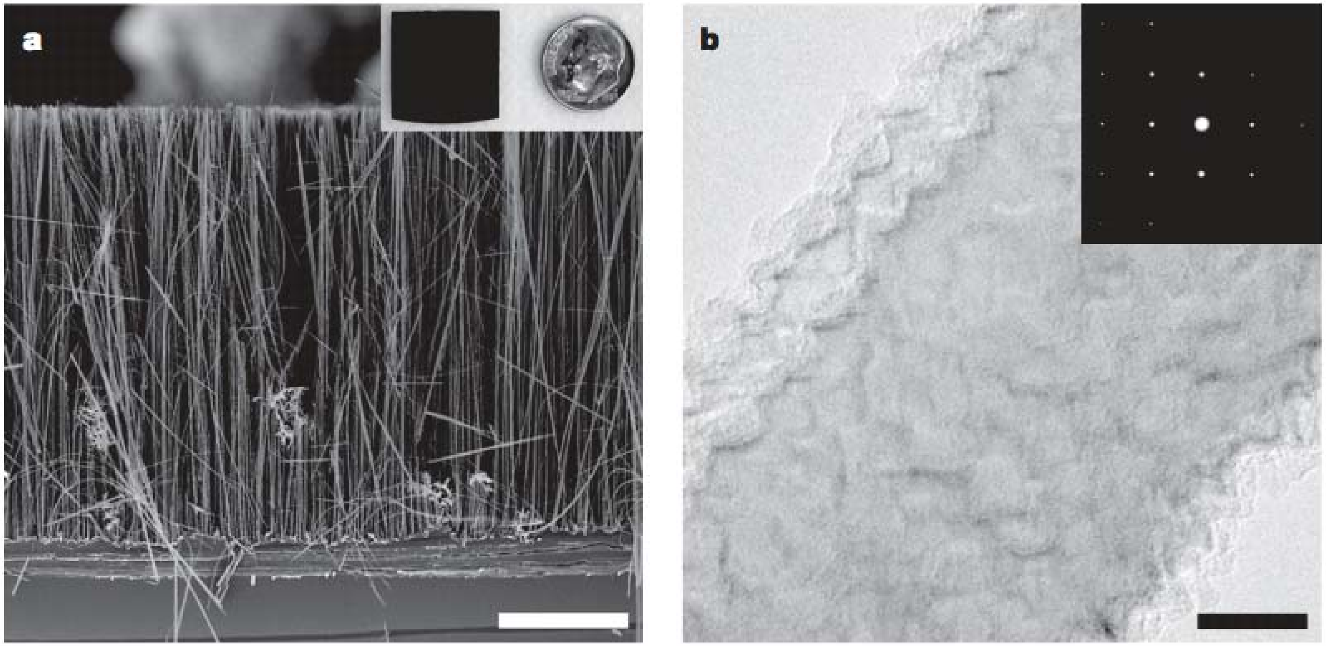
$$ZT = \frac{\sigma S^2 T}{k}$$



ZT of silicon: ~ 0.01

Nature 451, p.168 (2008)

Decreased thermal conductivity in rough Si NWs

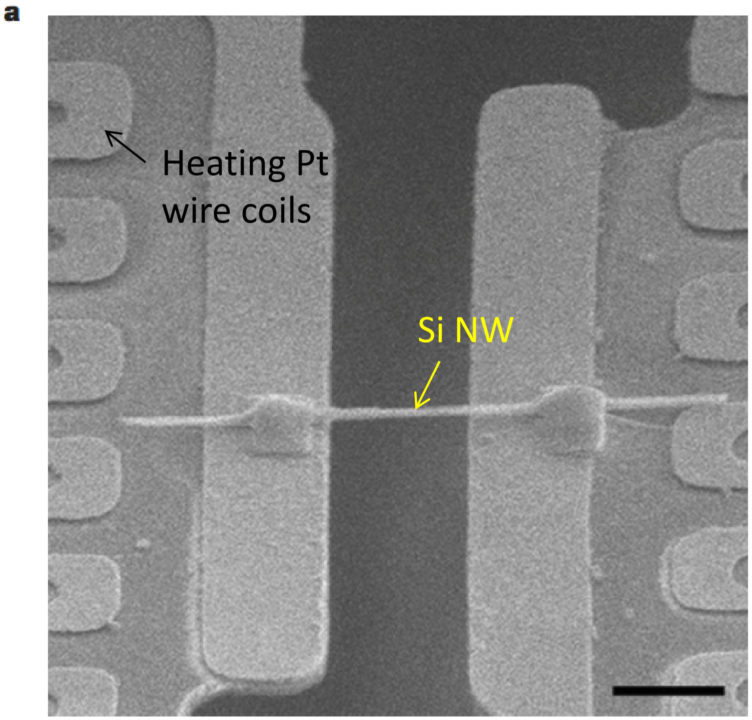


a. Si NW arrays were synthesized by a top-down electroless etching method.
   - Galvanic displacement of Si by $Ag^+ \rightarrow Ag^0$. The oxidized Si gets etched by HF

b. The surface of Si NWs is rough.
   - Generally bottom-up, CVD grown Si NWs have smooth surface
   - Here, due to HF etching and corrosive aqueous solution these Si NWs were subjected to, the surface is rough.

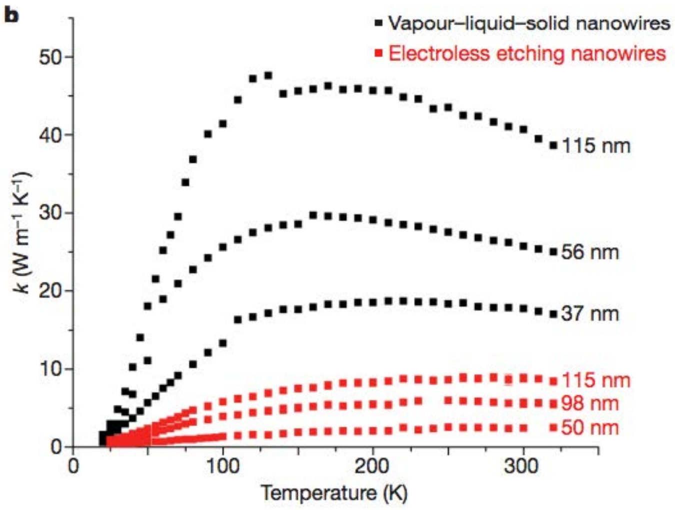
Nature 451, p.163 (2008)

Decreased thermal conductivity in rough Si NWs



To create temperature gradient within the single NW, the NW needs to be suspended! If it was sitting on the substrate, then the temperature of the NW will be that of the substrate. No ΔT.

Thermal conductivity measurement



$$ZT = \frac{\sigma S^2 T}{k}$$

Nature 451, p.163 (2008)

Overview

- Case Study of Nanowires: Si Nanowires
  - Thermal transport modulation
  - Si nanowire batteries
- Case study of topological nanomaterials
  - Bi_2Se_3 topological insulator nanoribbons
  - SnTe Topological crystalline insulator nanowires
- Case study of 2D materials for energy
  - MoS_2 for hydrogen evolution reaction (HER)
  - Phase transition via intercalation and consequences for HER

Topological Materials: Pick Your Favorite!

http://www.issp.ac.ru/lpcbc/DANDP/Bi-Ch.html

Explosion of Topological Materials

2007: CdTe/HgTe/CdTe quantum wells to show topological edge states (Science, Molenkamp)

2009: $Bi_{1-x}Sb_x$ alloy (Science, Princeton)

2009: Bi_2Se_3, Bi_2Te_3, Sb_2Te_3 Topological Insulators (Nature Phys, Nature, Science, Stanford)

2010: Half Heusler compounds: LnPtSb, LnPtBi, LnPdBi, (Nat. Mater, Max Planck)

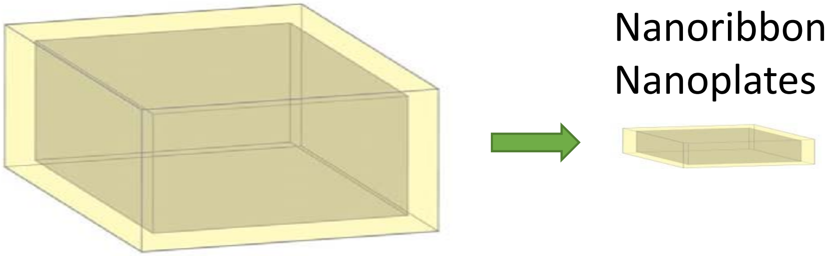
2011: SnTe Topological Crystalline Insulators (Nat. Phys, Experimental Verification 2012, MIT)

2011: Weyl Semimetals (PRL, Experimental Verification 2015 Science): WTe_2, TaAs, …

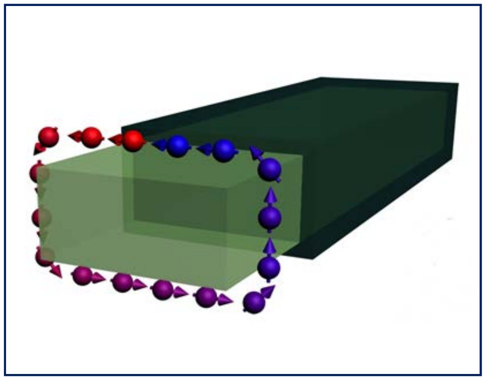
2014: Monolayer transition metal dichalcogenides (2014 Science theory): 1T'-MoS_2, …

Nanostructure Approach to Study Topological Insulators

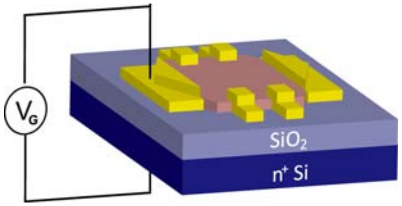
Increase Surface-to-Volume Ratio

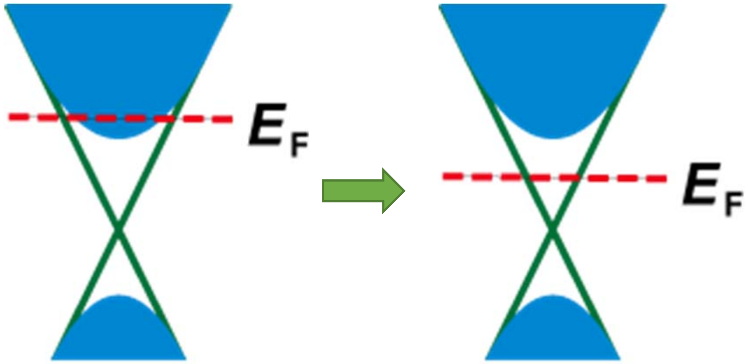


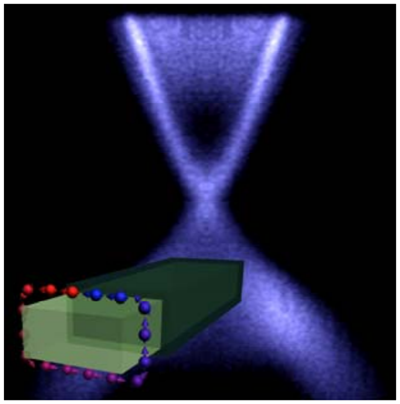
Nanoribbons,
Nanoplates



Manipulate Fermi Energy by Gating



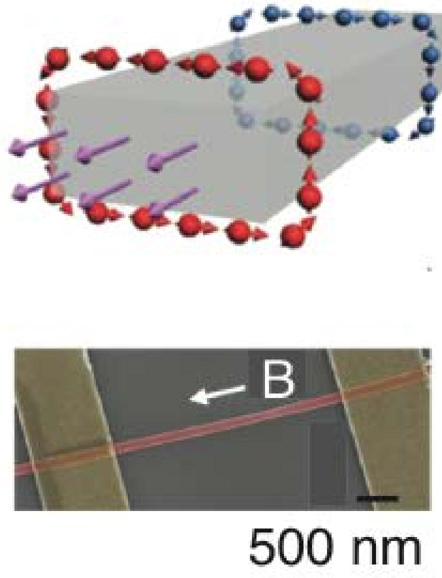


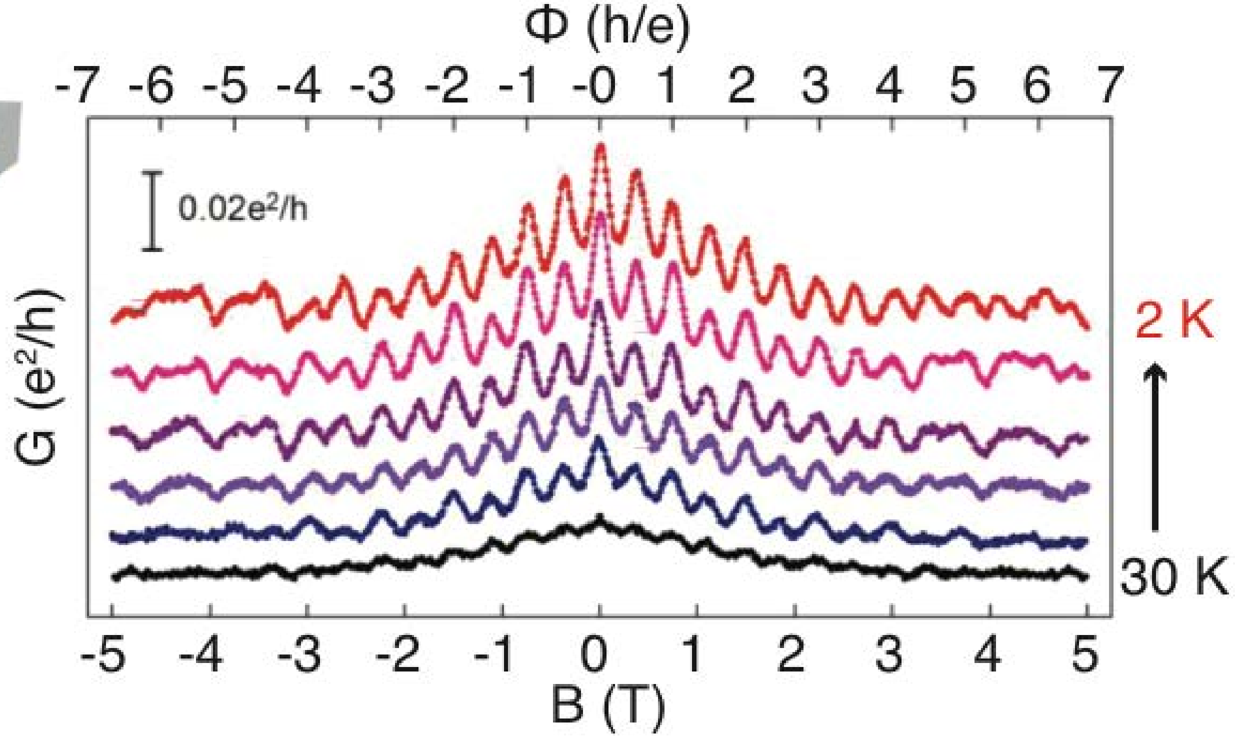


Nature Nanotech. 6, 705 (2011); Nano Lett. 14 2815 (2014)

1D Nanowire Interferometer

Aharonov Bohm oscillations in Bi_2Se_3 nanoribbons

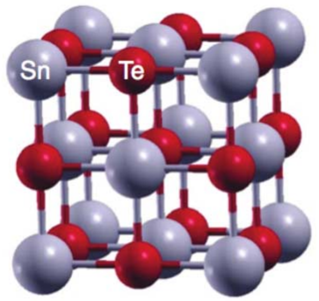




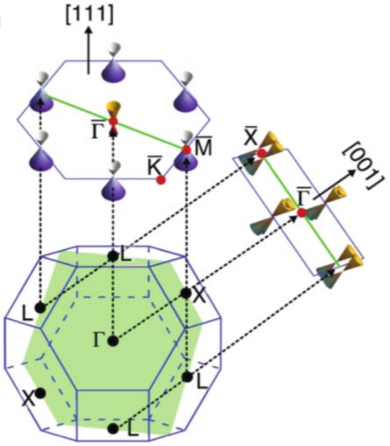
Nano Lett. 14, 2815 (2014)

SnTe: Topological Crystalline Insulator

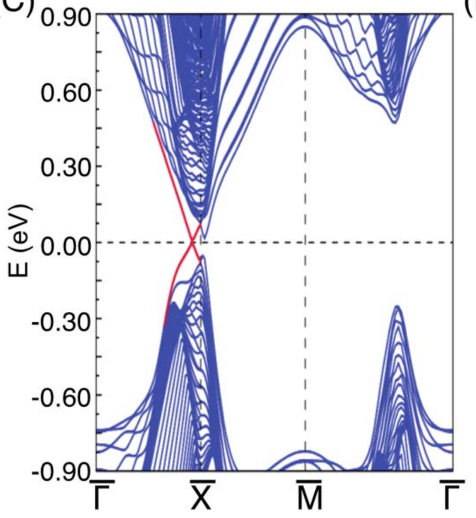
(A)



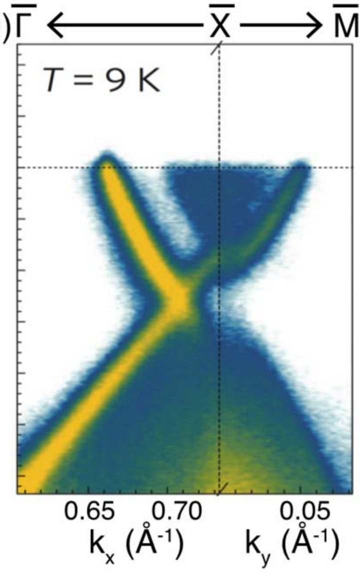
(B)



(C)

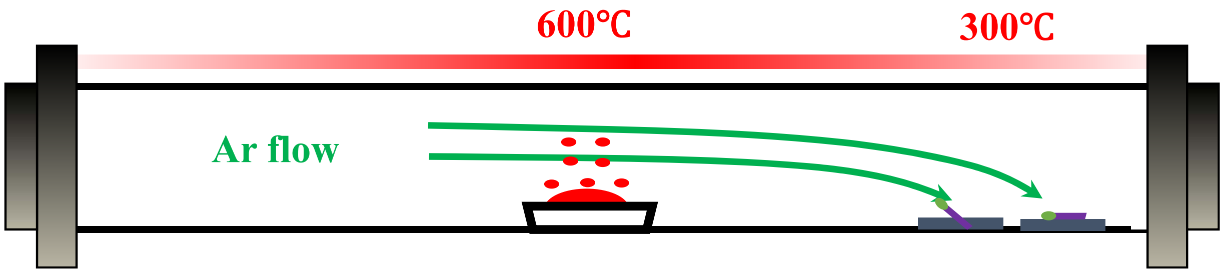


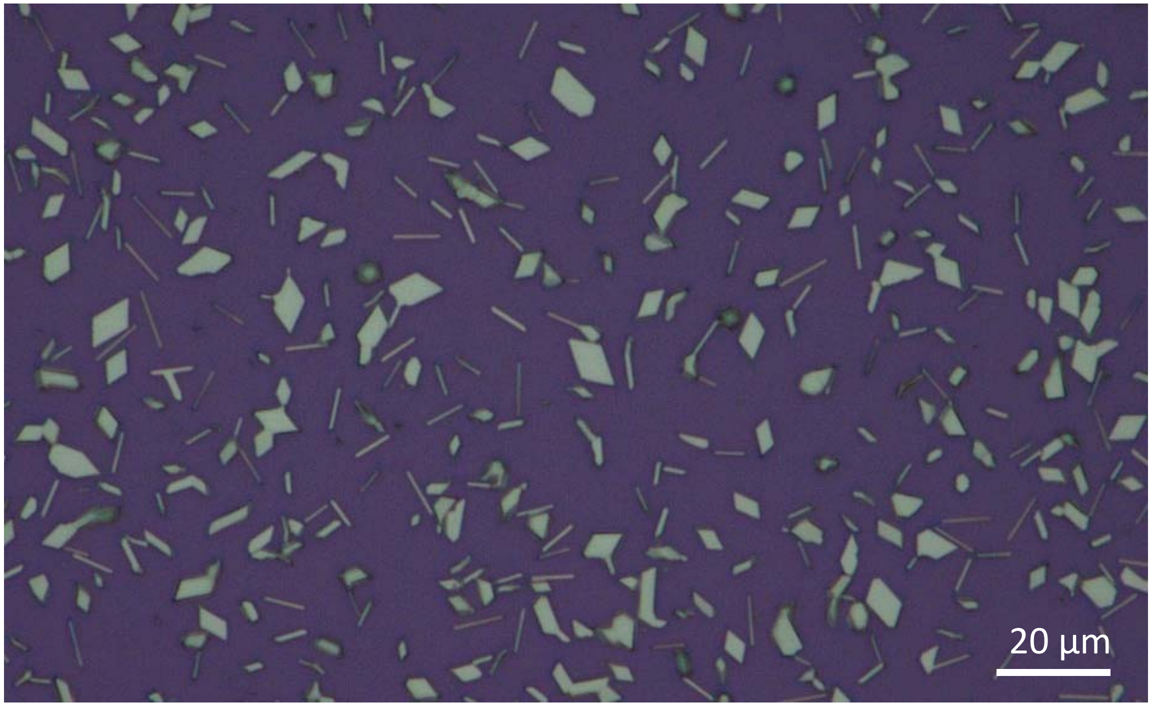
(D)



References:
Nat. Commun. 3:982 (2012)
Nat. Mater. 11, 1023 (2012)

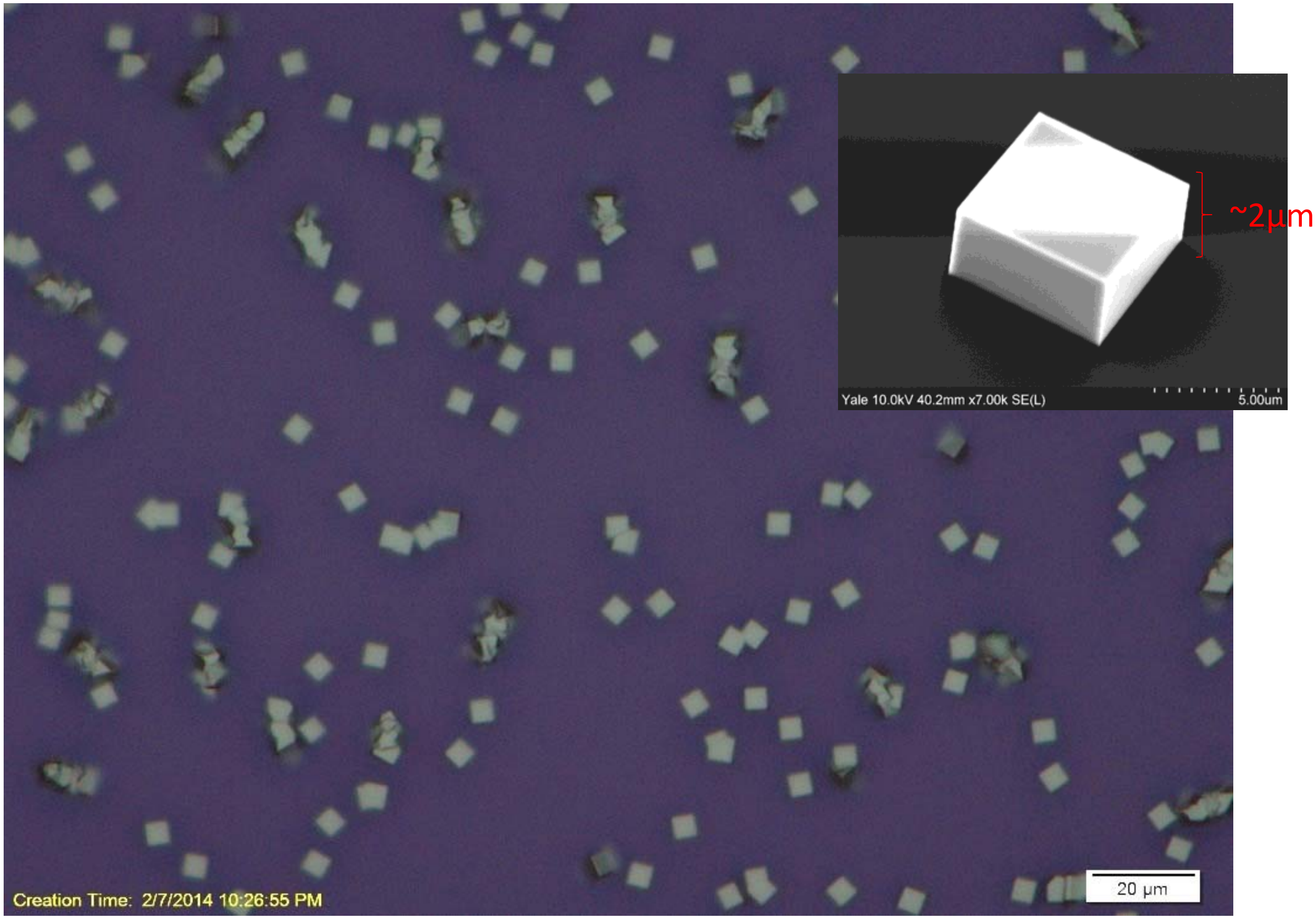
SnTe Nanostructure Growth



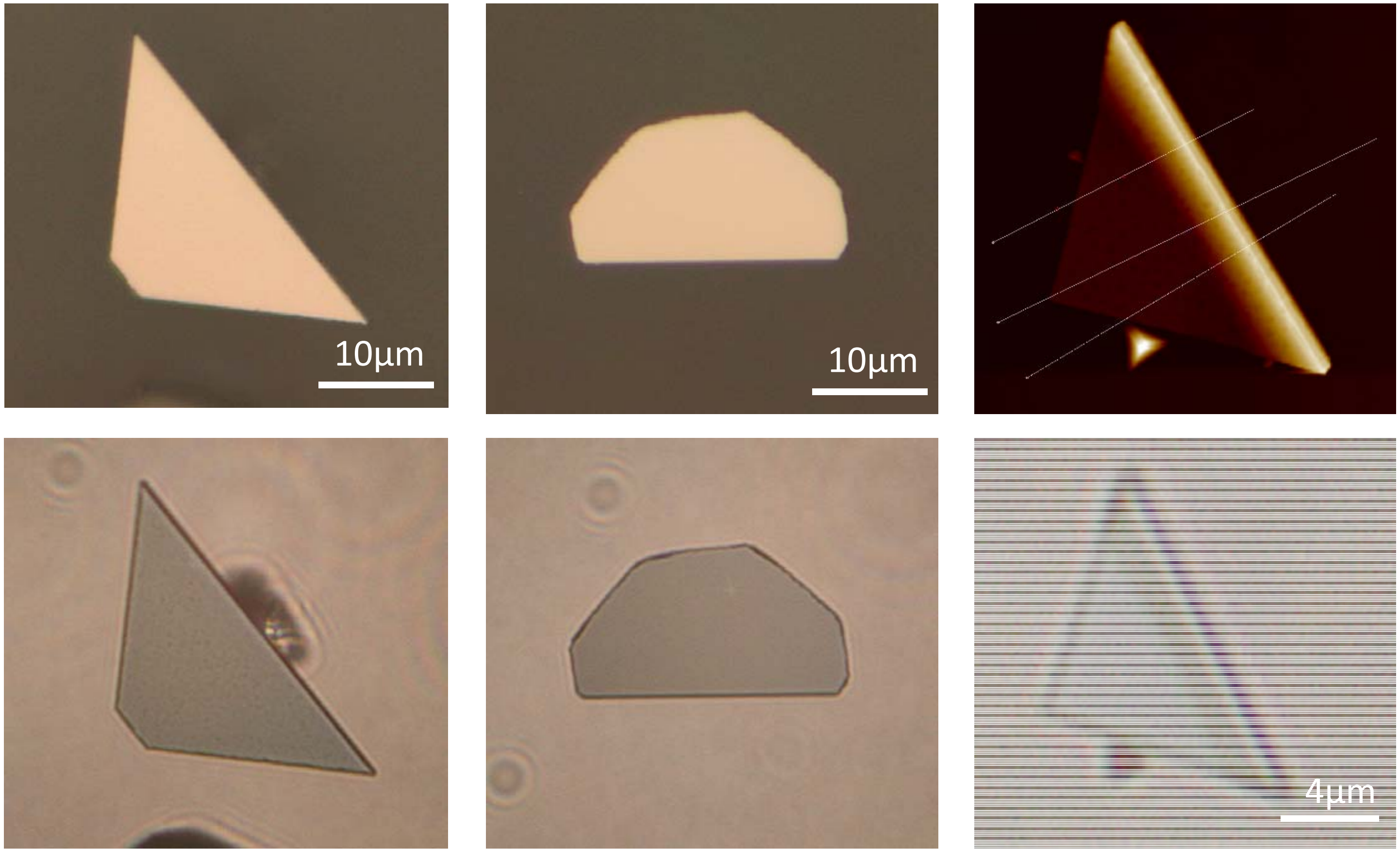


Nano Lett. 14 p.4183 (2014)

SnTe Nanoblocks on SiO_2 without Au Catalyst



Substrate Effects: SnTe grown on Mica


Thickness ~ 40 nm

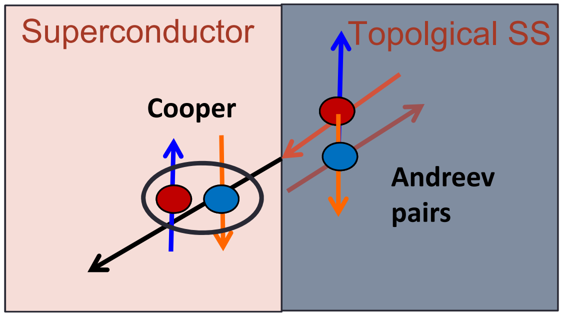
Topological Superconductors (TSCs)

Topological surface states + Superconductor correlations

⬇

Potential base system for a quantum information processor

Approach 1: Proximity-induced superconductivity
(Contacting TIs to superconducting metals to induce superconductivity to SS)

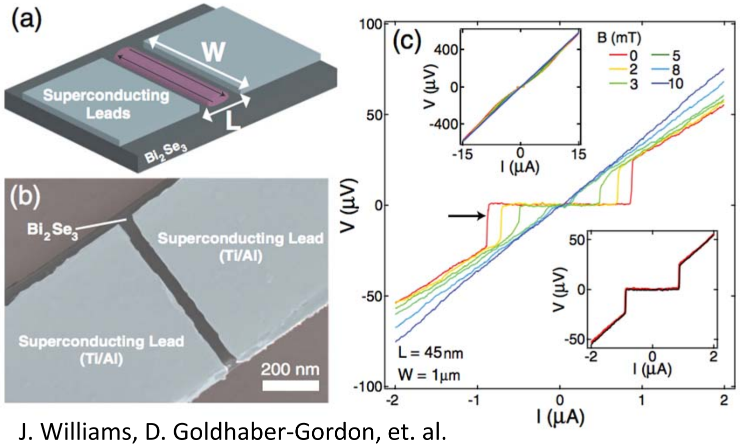


Superconducting proximity effect via Andreev refelction

Approach 2: Directly synthesize a bulk TSC

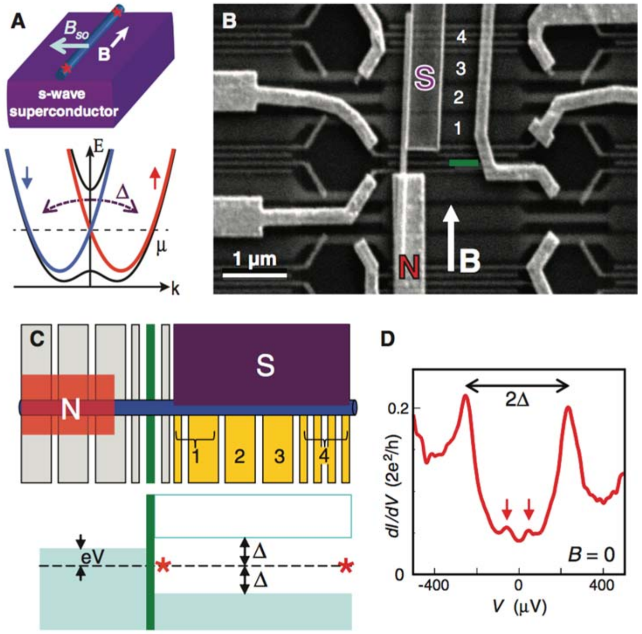
Examples based on Approach 1

TI - SC Josephson junctions



J. Williams, D. Goldhaber-Gordon, et. al.
PRL 109, 056803 (2012)

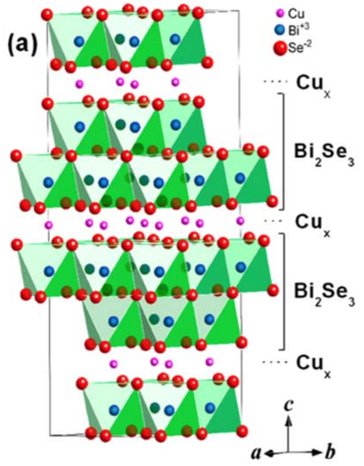
Semiconducting NW + SC contacts

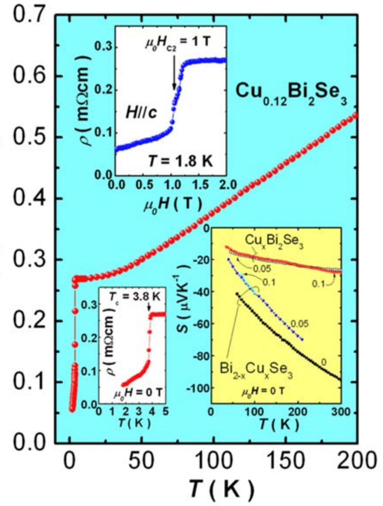


Kouwenhoven et. al., Science 336 p.1003 (2012)
Yazdani et. al., Science 346, p.6209 (2014)
Markus et. al., Nat. Nanotech 10, p.232 (2015)

Approach 2: Make TIs Superconducting

Cu-intercalated Bi_2Se_3



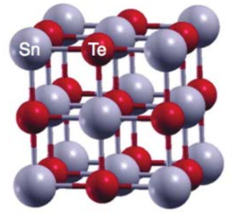


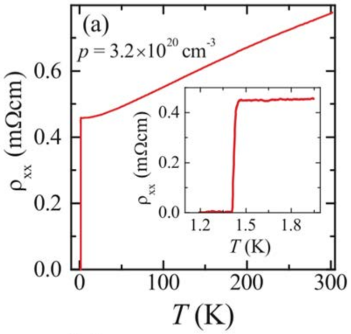
Intercalation: Sr, Tl, …

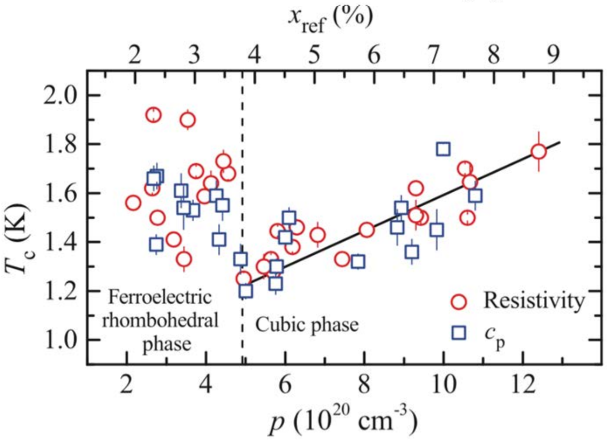
PRB 104, 057001 (2010), PRL 107, 217001 (2011)
JACS 137, 10512 (2015), …

JACS (2012), Nano Lett (2013), Nat. Commun. (2014)

In-doped SnTe

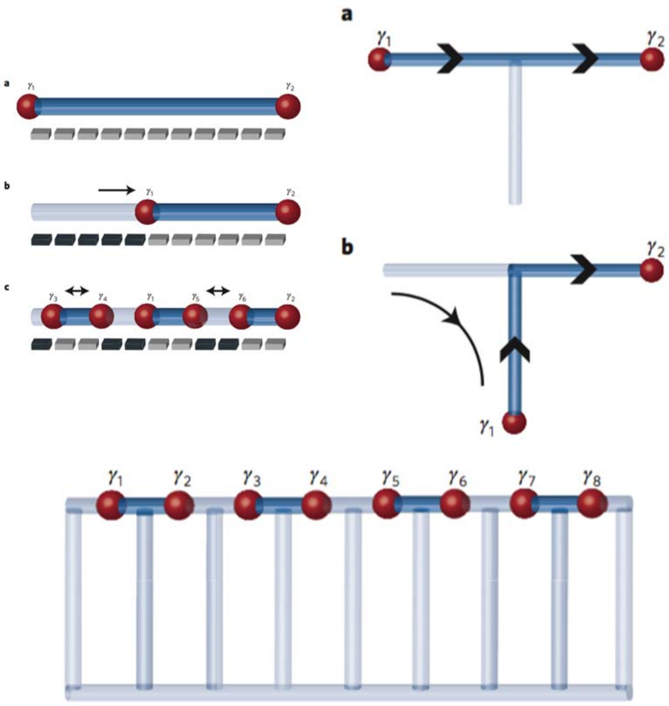


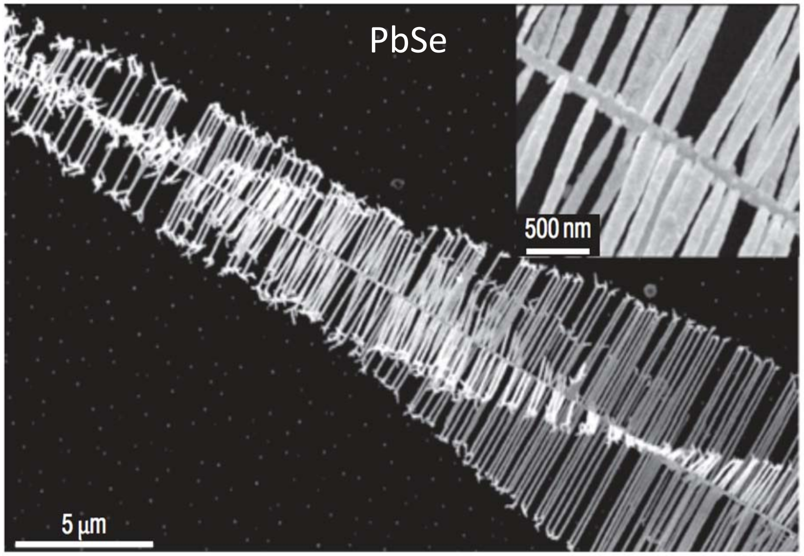




PRB 88, 140502 (2013), PRL 109, 217004 (2012),
PRL 110, 206804 (2013), PRB 93, 024520 (2016), …

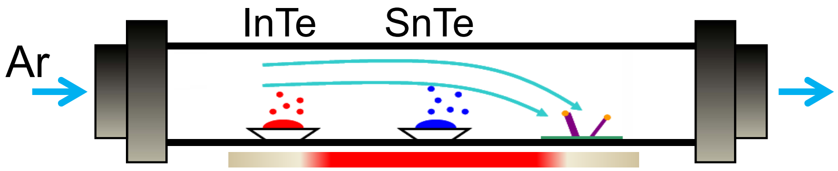
Quantum Processing in 1D Wire Networks



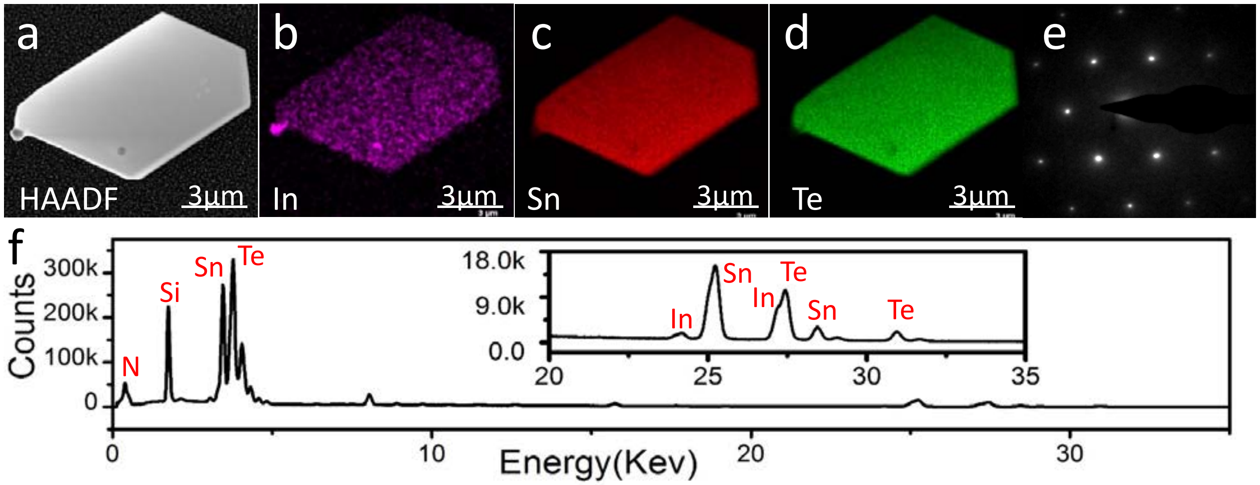


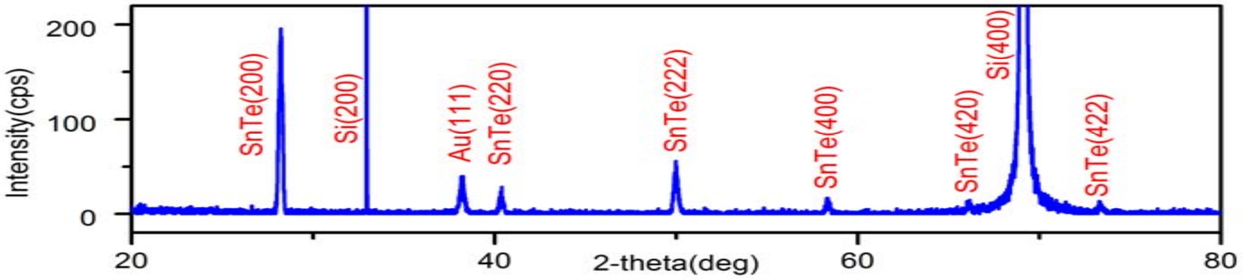
J. Alicea, P. A. Fisher, et. al, Nature Physics 7, 412 (2011)
J. Zhu, Y. Cui, et. al. , Nature Nanotech 3, 477 (2008)

In doping into SnTe Nanoplates

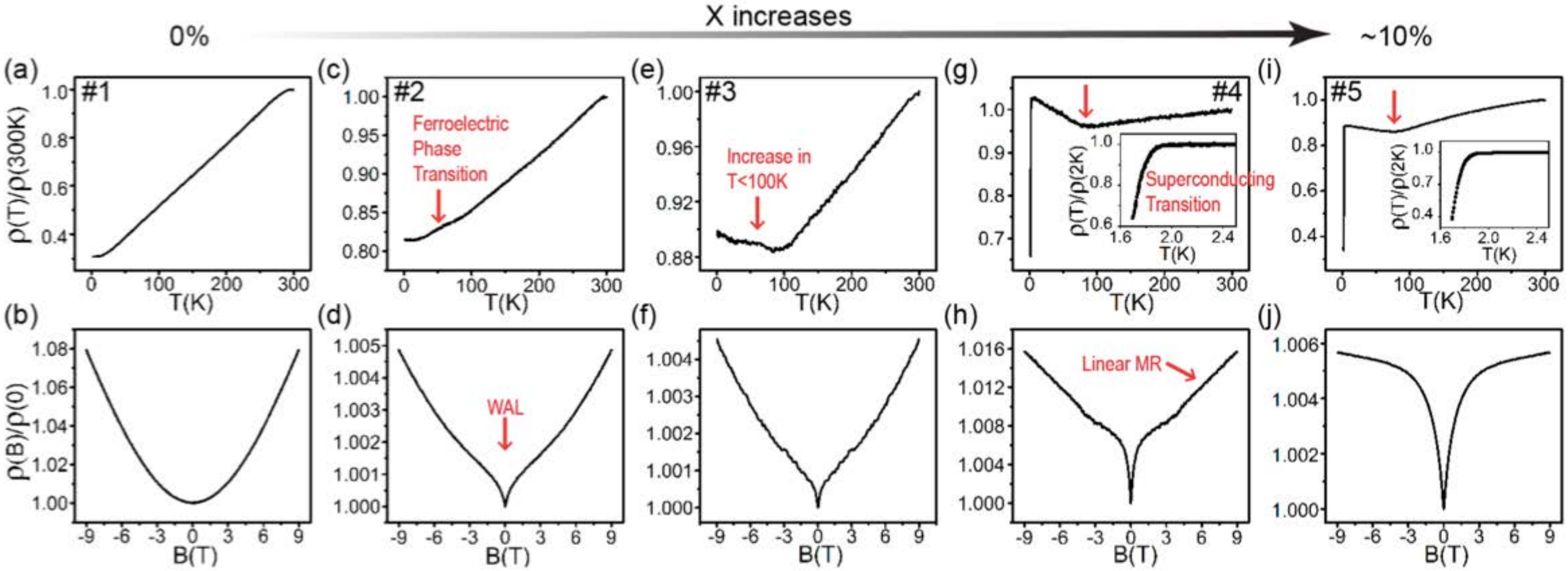


(111) In-doped SnTe Nanoplate



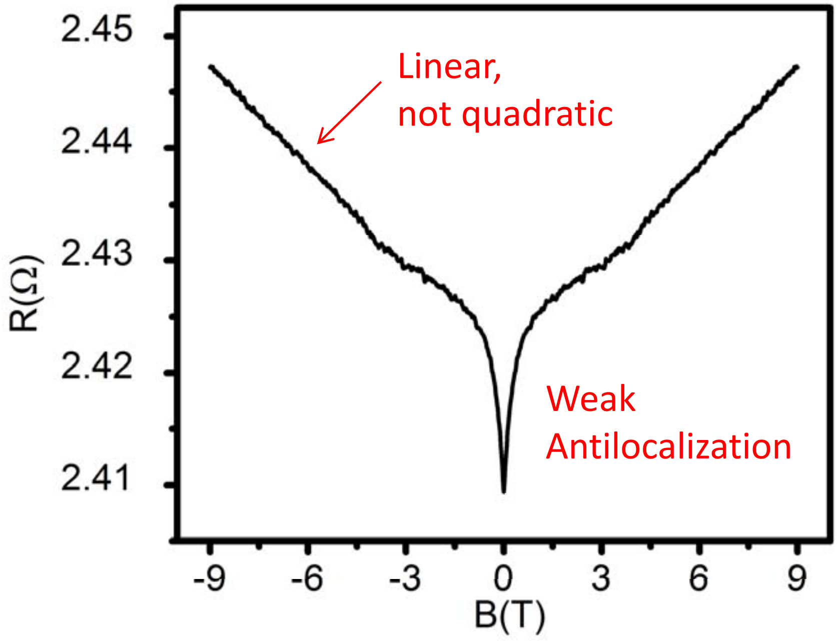


Transport Properties in $In_xSn_{1-x}Te$



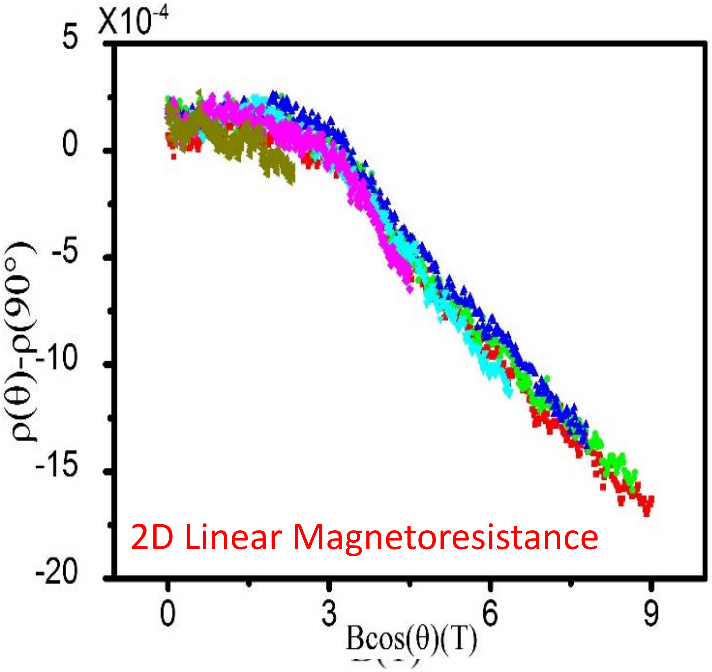
Nano Lett. 15 p.3827 – 3832 (2015)

Linear Magnetoresistance: Surface State?



Linear,
not quadratic

Weak
Antilocalization

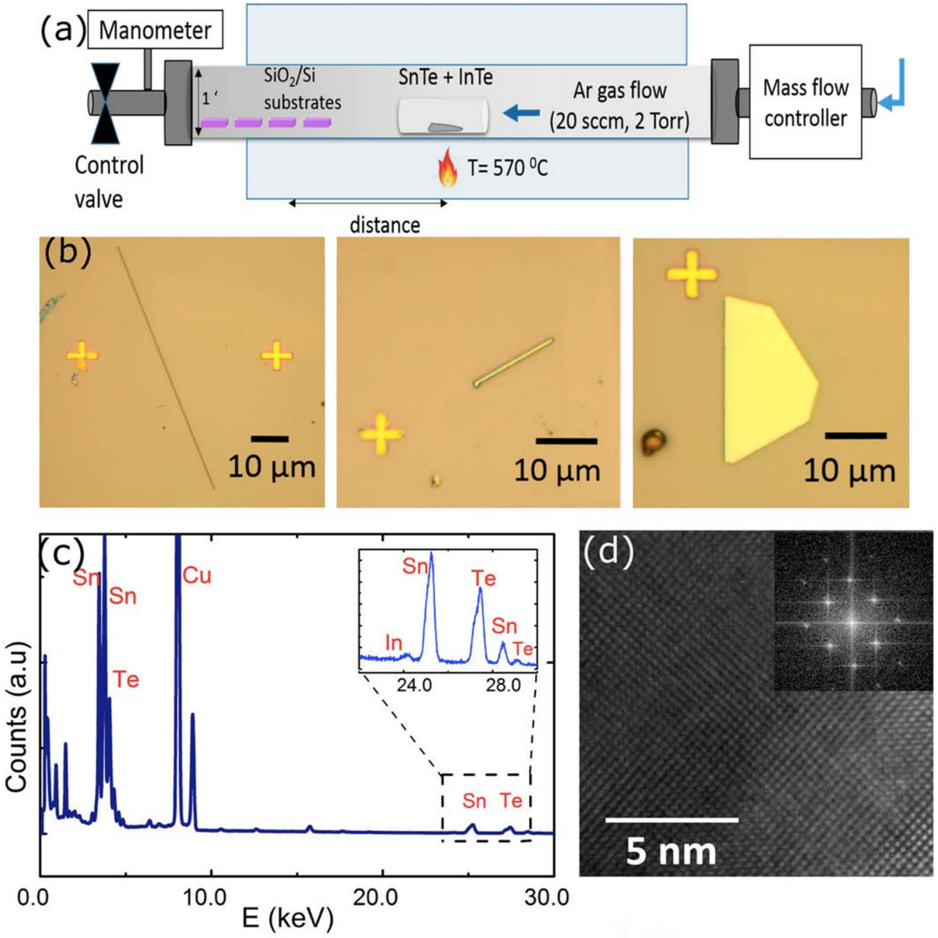


2D Linear Magnetoresistance

Weak antilocalization in SnTe is a bulk effect.

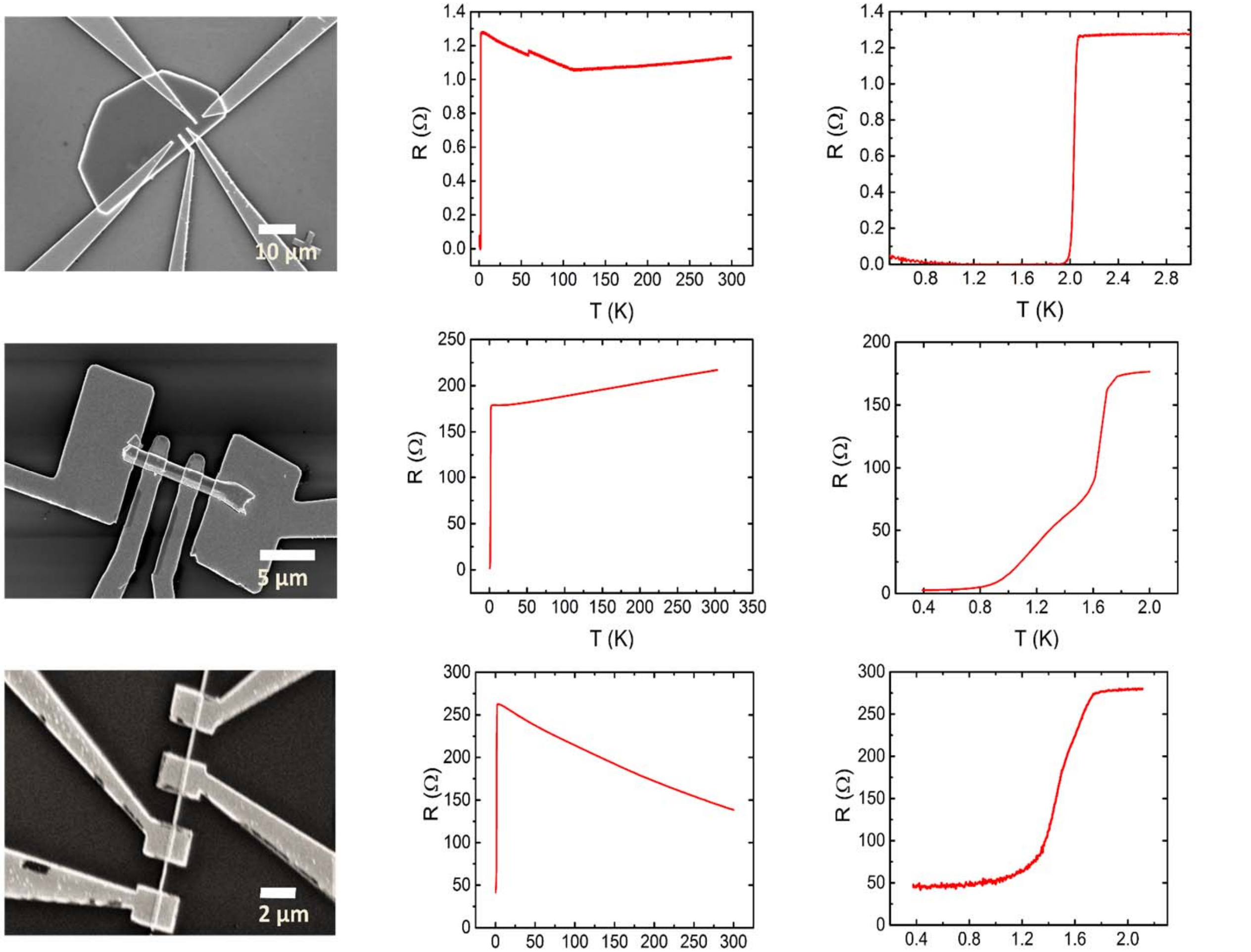
Nano Lett. 15 p.3827 – 3832 (2015)

In-doped SnTe Nanowires



APL Materials 5, 076110 (2017)

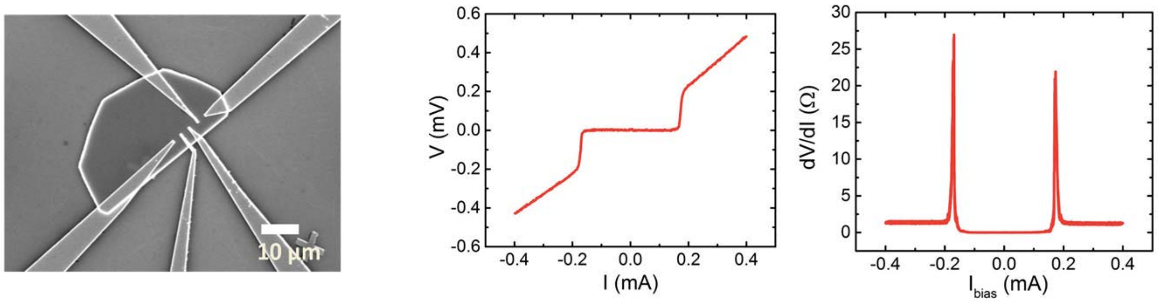
Morphology-dependent Superconducting Behavior



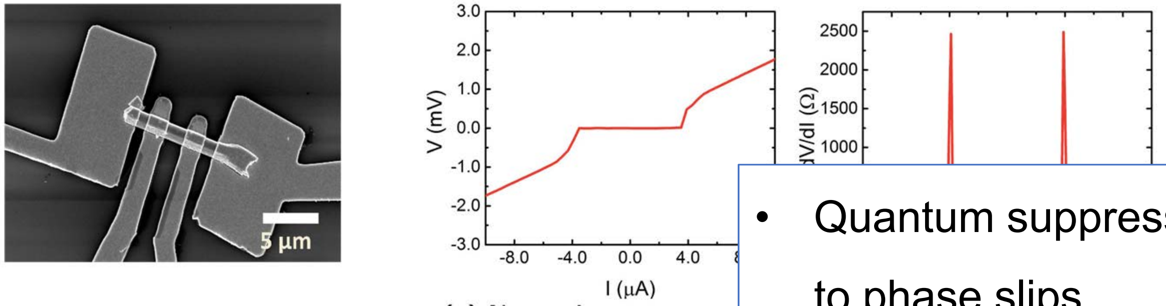
APL Materials 5, 076110 (2017)

Morphology-dependent Superconducting Behavior

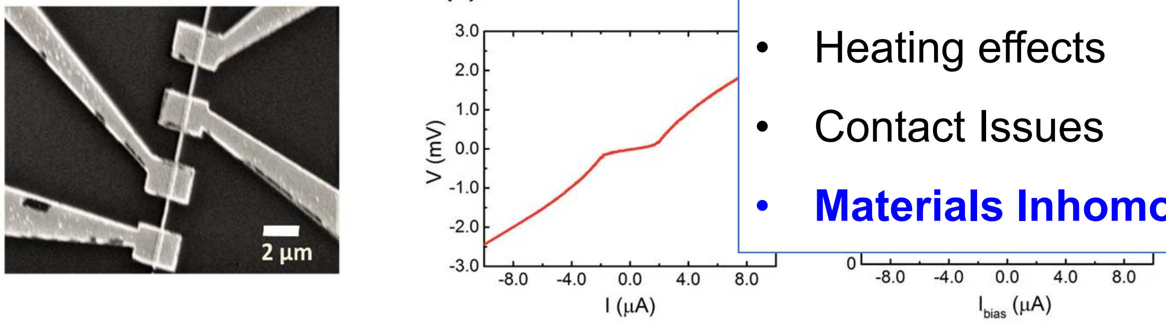
(a) Nanoplate



(b) Nanoribbon

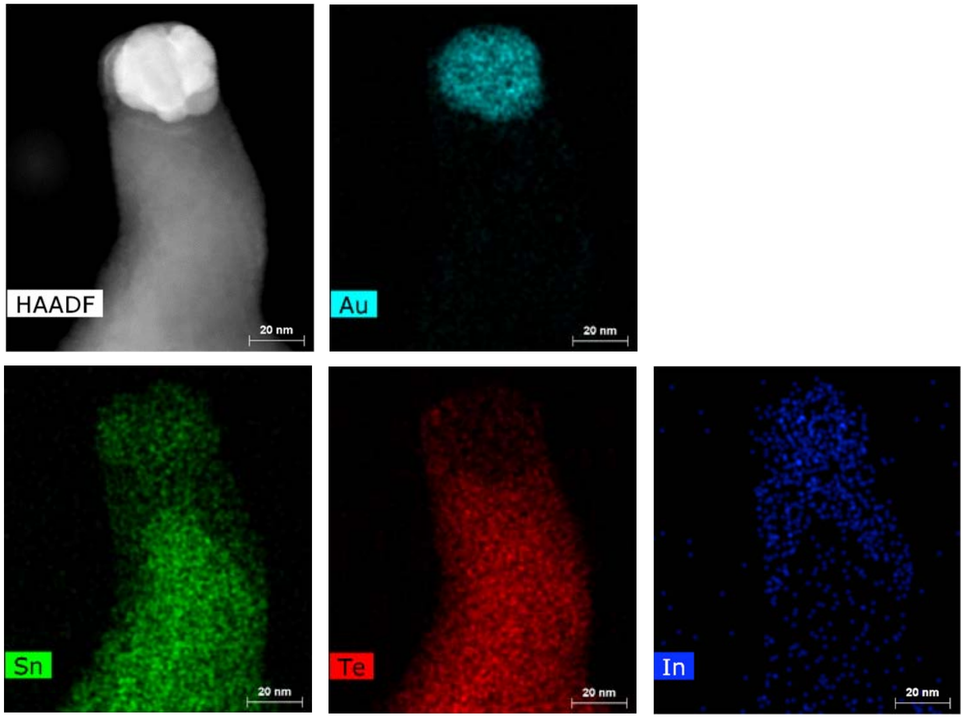


(c) Nanowire

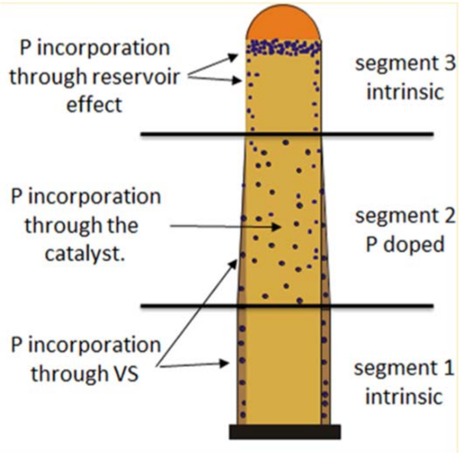


- Quantum suppression due to phase slips
- Heating effects
- Contact Issues
- **Materials Inhomogeneity**

Material Inhomogeneity: In Doping



P-doped Si Nanowires

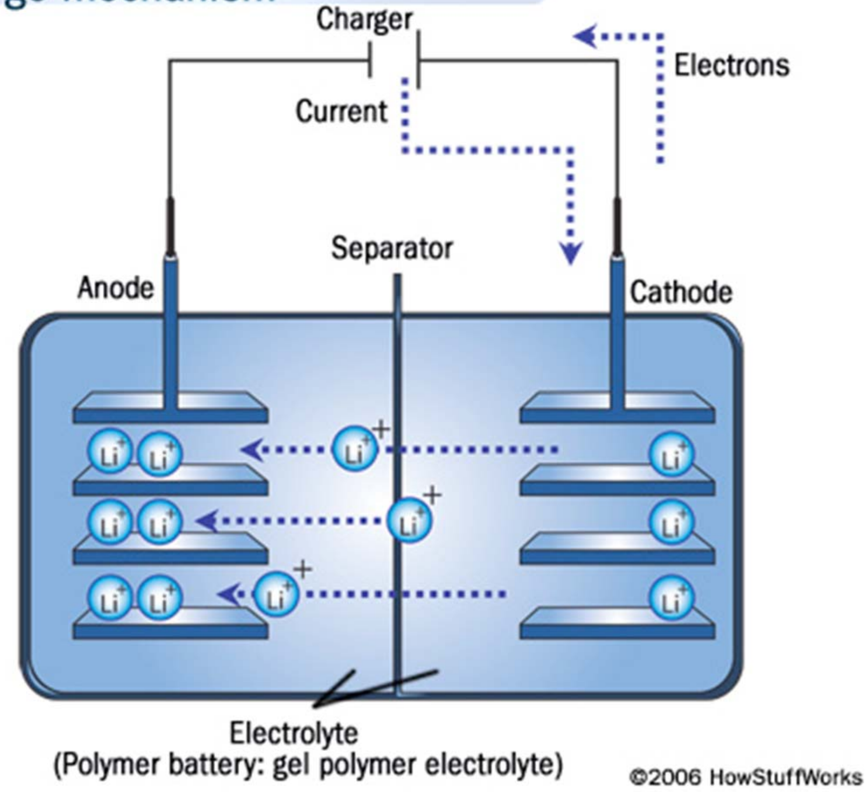


Nano Lett. 13, 2598 (2013)

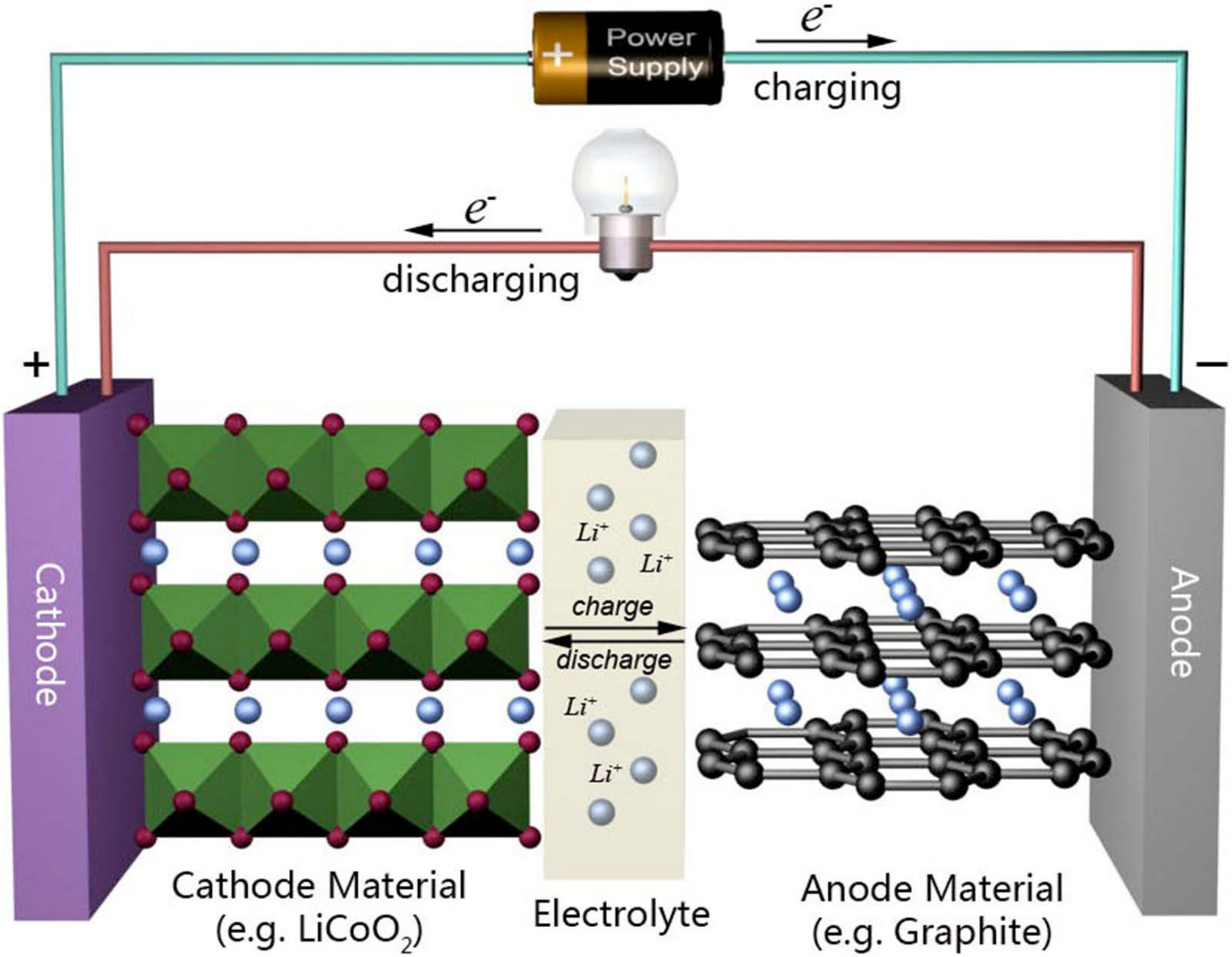
Overview

- Case Study of Nanowires: Si Nanowires
  - Thermal transport modulation
  - Si nanowire batteries
- Case study of topological nanomaterials
  - Bi_2Se_3 topological insulator nanoribbons
  - SnTe Topological crystalline insulator nanowires
- Case study of 2D materials for energy
  - MoS_2 for hydrogen evolution reaction (HER)
  - Phase transition via intercalation and consequences for HER

Lithium-ion rechargeable battery
Charge mechanism



©2006 HowStuffWorks


Power Supply
+
e^-
charging
e^-
discharging
+
−
Cathode
Li^+
Li^+
charge
discharge
Li^+
Li^+
Anode
Cathode Material
(e.g. $LiCoO_2$)
Electrolyte
Anode Material
(e.g. Graphite)

Electrode Materials in Existing Li Ion Batteries

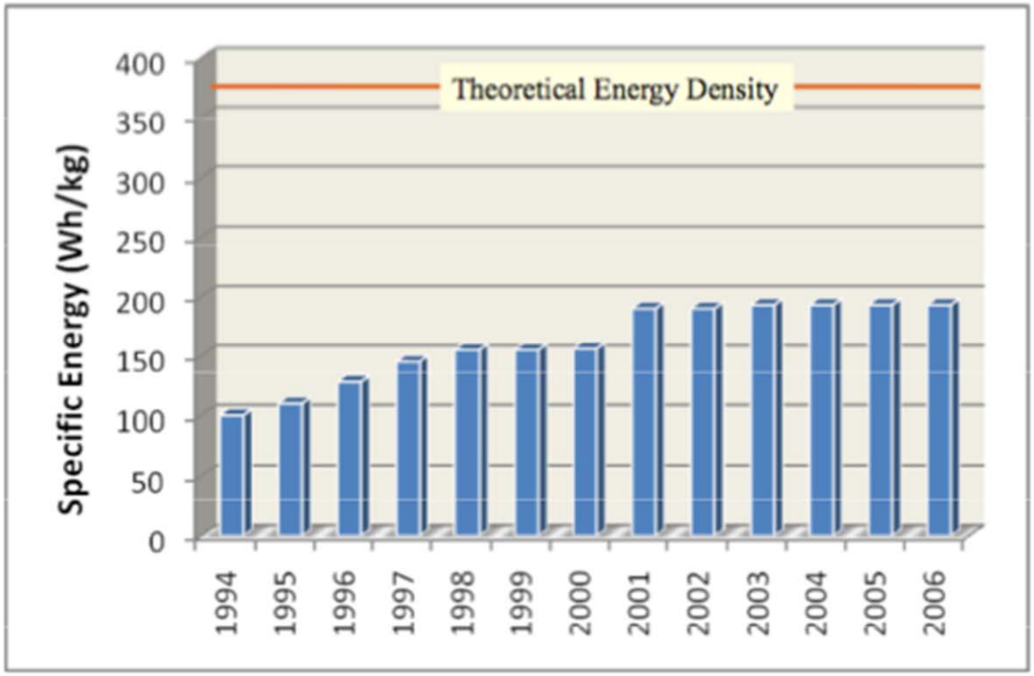
Electrode materials determine the energy density.

Anode materials

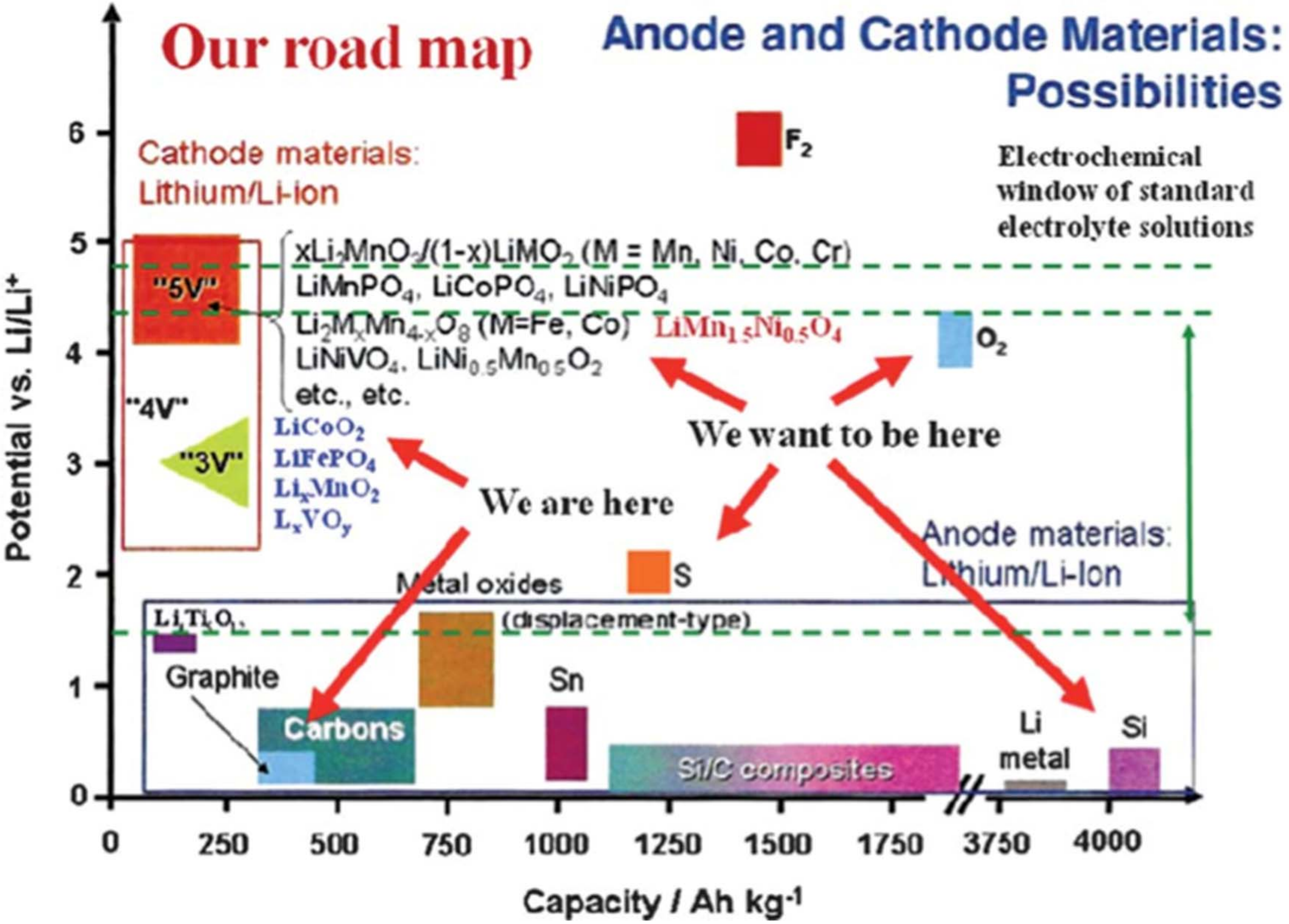
Graphite: 370 mAh/g

Cathode Materials

$LiCoO_2$	150 mAh/g, 3.7V
$LiMn_2O_4$	140 mAh/g, 3.9V
$LiFePO_4$	170 mAh/g, 3.4V



Source: TIAX, LLC


Our road map
Anode and Cathode Materials: Possibilities
Cathode materials: Lithium/Li-ion
F_2
Electrochemical window of standard electrolyte solutions
"5V"
"4V"
"3V"
$xLi_2MnO_3/(1-x)LiMO_2$ (M = Mn, Ni, Co, Cr)
$LiMnPO_4$, $LiCoPO_4$, $LiNiPO_4$
$Li_2M_xMn_{4-x}O_8$ (M=Fe, Co)
$LiNiVO_4$, $LiNi_{0.5}Mn_{0.5}O_2$
etc., etc.
$LiMn_{1.5}Ni_{0.5}O_4$
O_2
$LiCoO_2$
$LiFePO_4$
Li_xMnO_2
L_xVO_y
We want to be here
We are here
Anode materials: Lithium/Li-Ion
S
Metal oxides (displacement-type)
$Li_4Ti_5O_{12}$
Graphite
Carbons
Sn
Si/C composites
Li metal
Si
Potential vs. Li/Li$^+$
0
1
2
3
4
5
6
Capacity / Ah kg^{-1}
0
250
500
750
1000
1250
1500
1750
3750
4000

Next Generation of Anode Materials: Alloy Anode

Li metal: 3830 mAh/g of Li, 1915 mAh/cc of Li

$Li_{4.4}Si$: 4200 mAh/g of Si, 2000mAh/g of $Li_{4.4}Si$, 1925 mAh/cc of $Li_{4.4}Si$.

$Li_{4.4}Ge$: 1600 mAh/g of Ge

$Li_{4.4}Sn$: 990 mAh/g of Sn

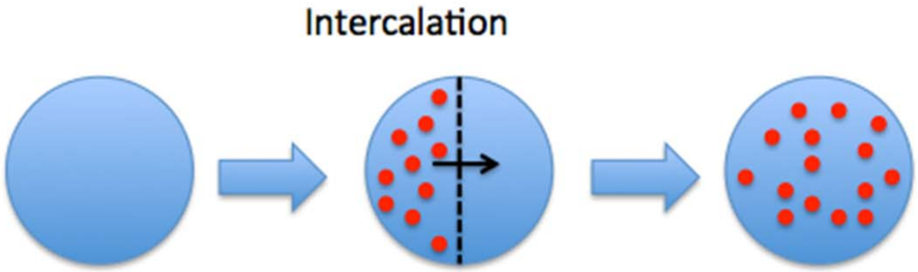
LiAl: 990 mAh/g of Al

$Li_{1.5}Zn$: 615 mAh/g of Zn

Challenges of Alloy Anodes

Existing aodematerials
Graphite: 370 mAh/g

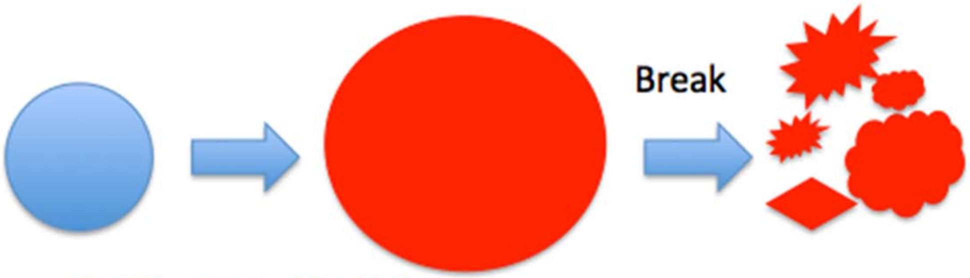
$C_6 \longleftrightarrow LiC_6$



Little structure change, <10% volume change.

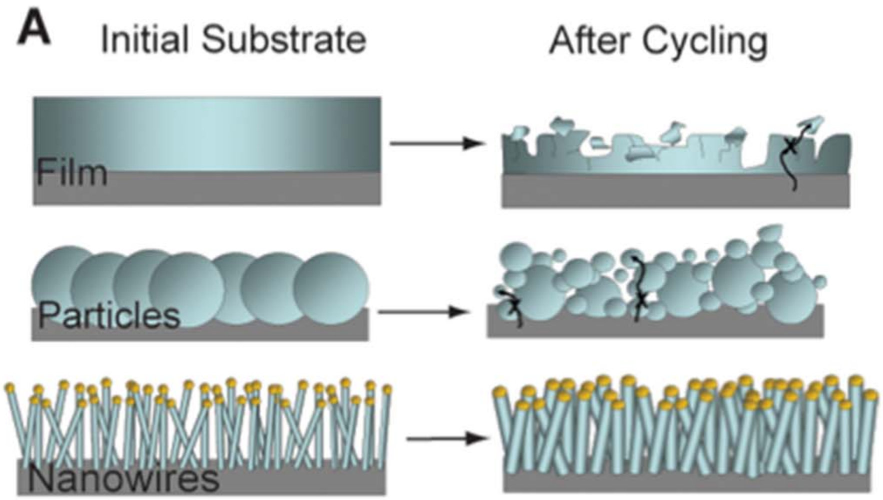
New anode materials (0-0.6V)
Si: 4200 mAh/g, 10X higher

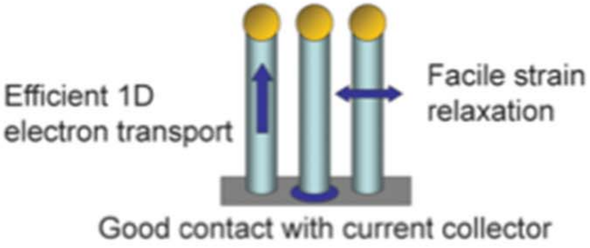
$Si \longleftrightarrow Li_{4.4}Si$



For Si: expand by 4 times.

Nanowires of New Materials For Future Batteries



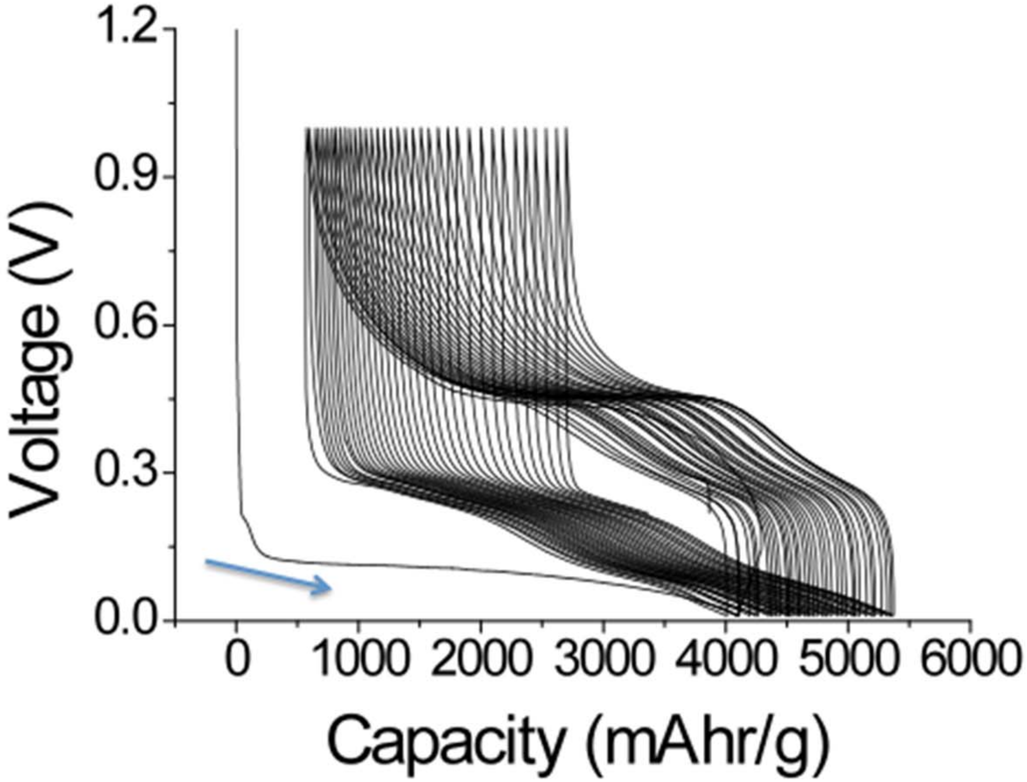


What nanowire can offer:
- Shorter distance for Li diffusion (high power).
- Good strain release and interface control (better cycle life
- Continuous electron transport pathway (high power).

C. K. Chan and Y. Cui, Nature Nanotechnology 3, 31 (2008).

Ultrahigh Capacity Si Nanowire Anodes: Half Cells

Galvanostatic Charge/discharge:
Apply constant current while measuring voltage versus time.



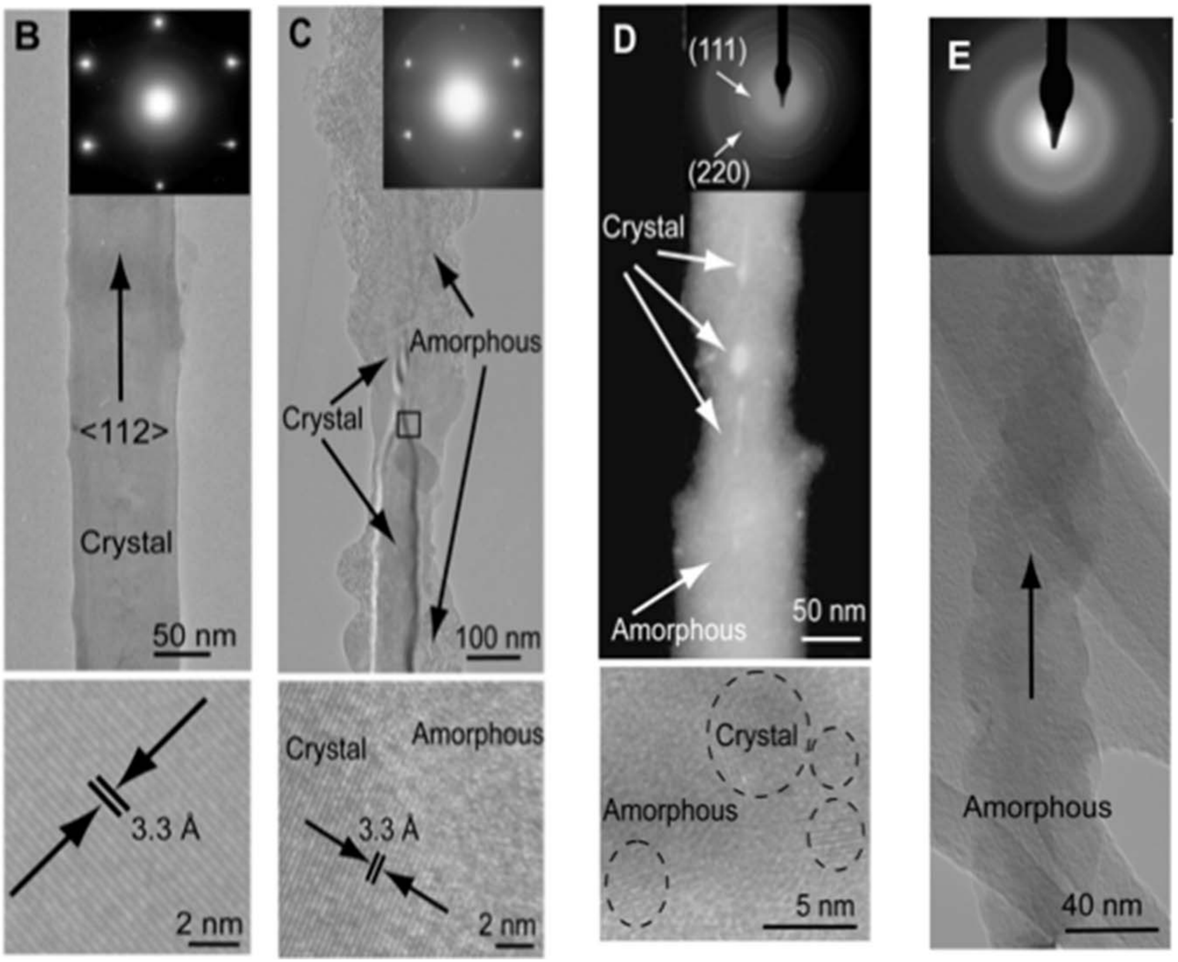
Li insertion progression (crystal-amorphous transition)

Pristine

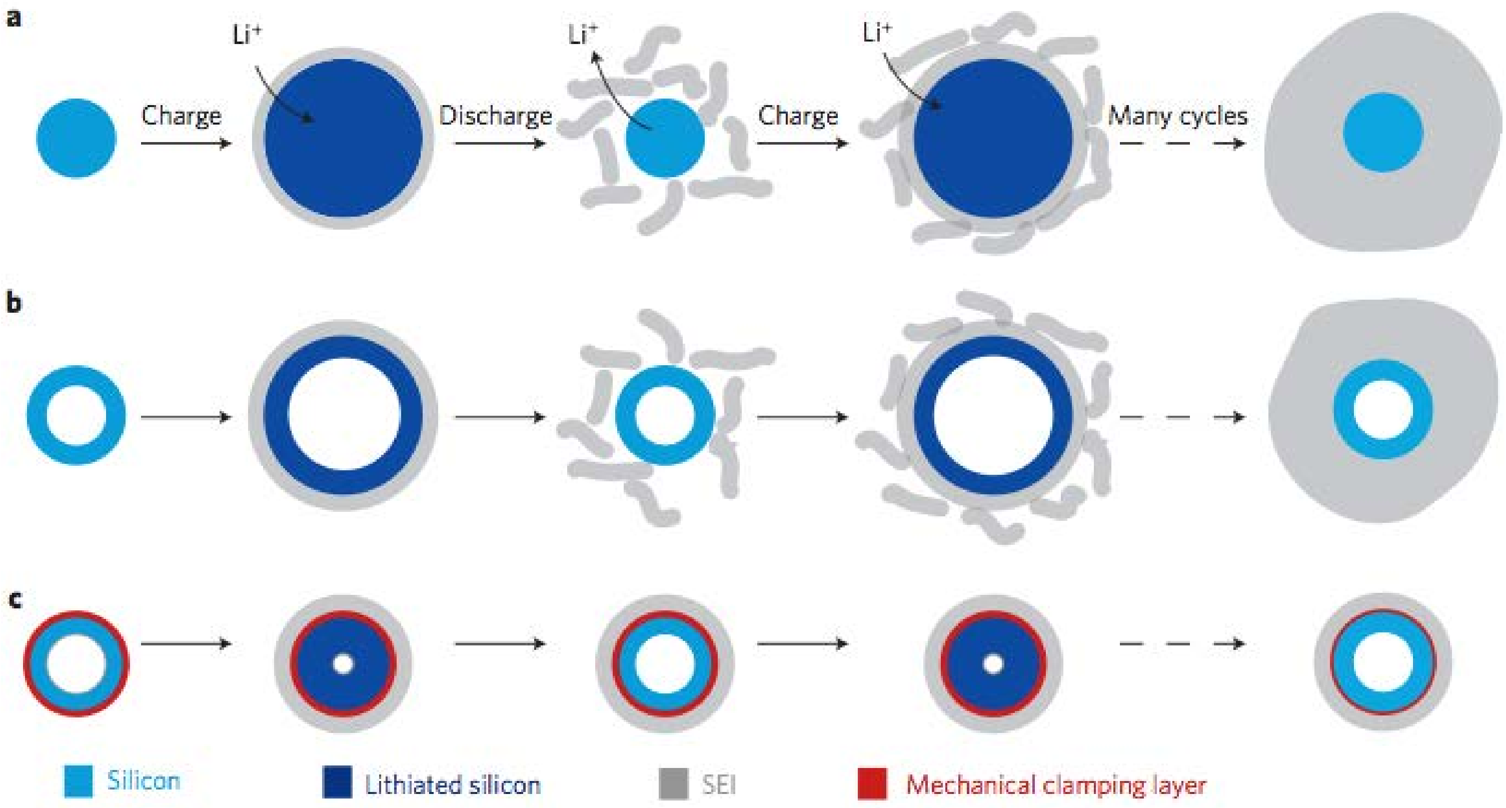
100 mV

50 mV

10 mV

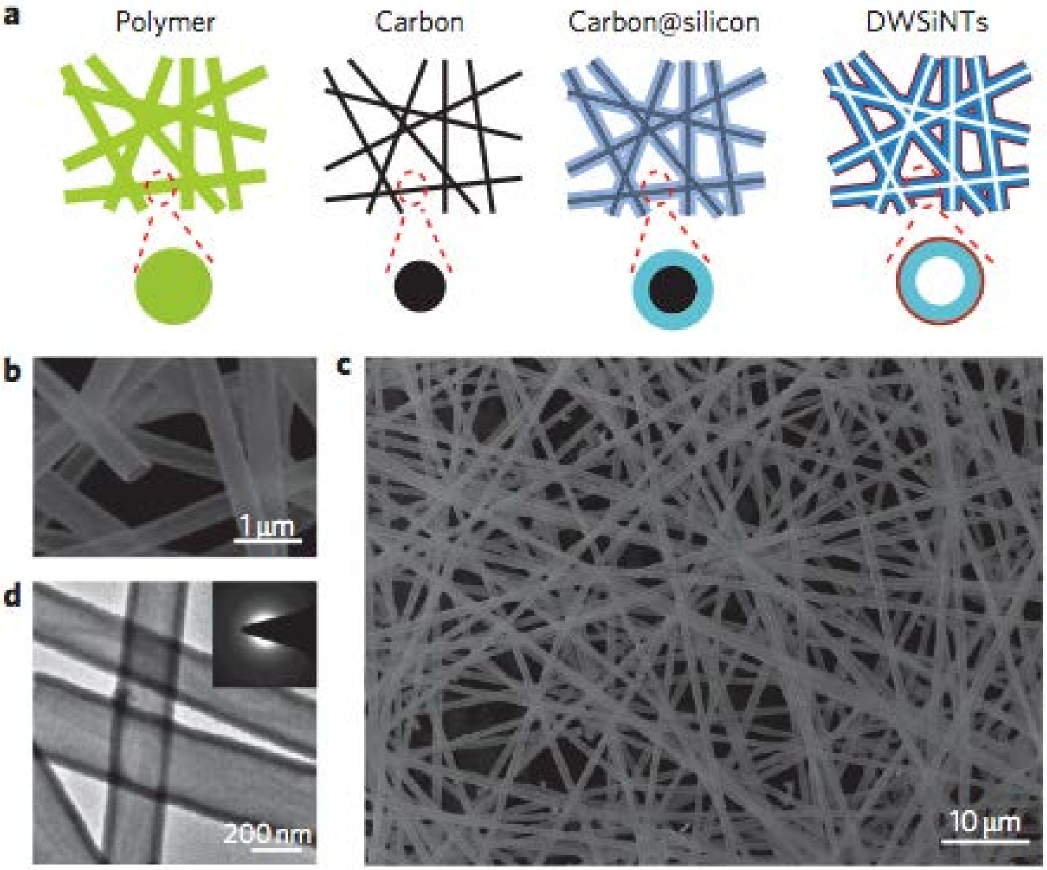


Engineering solutions to solve mechanical expansion problem



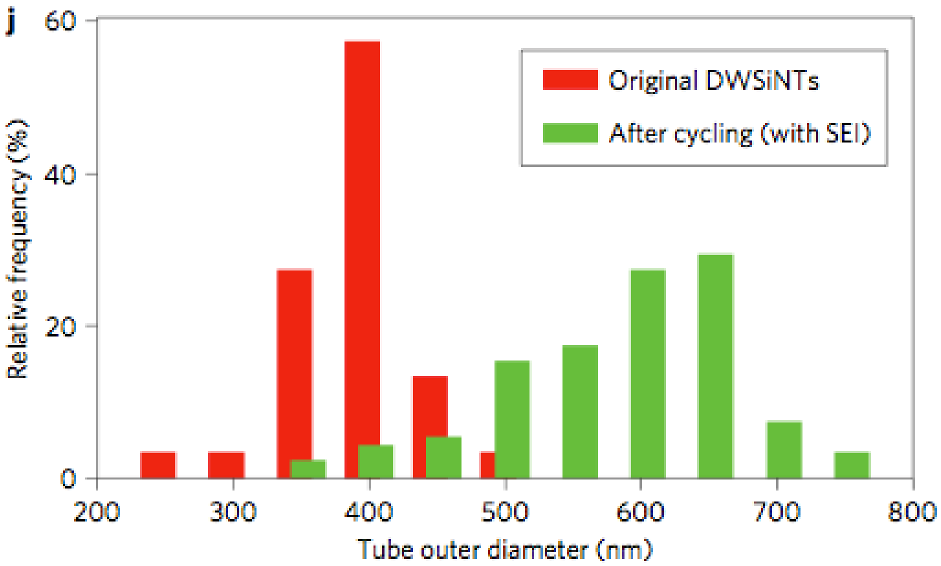
Nature Nanotech. DOI:10.1038/Nnano.2012.35

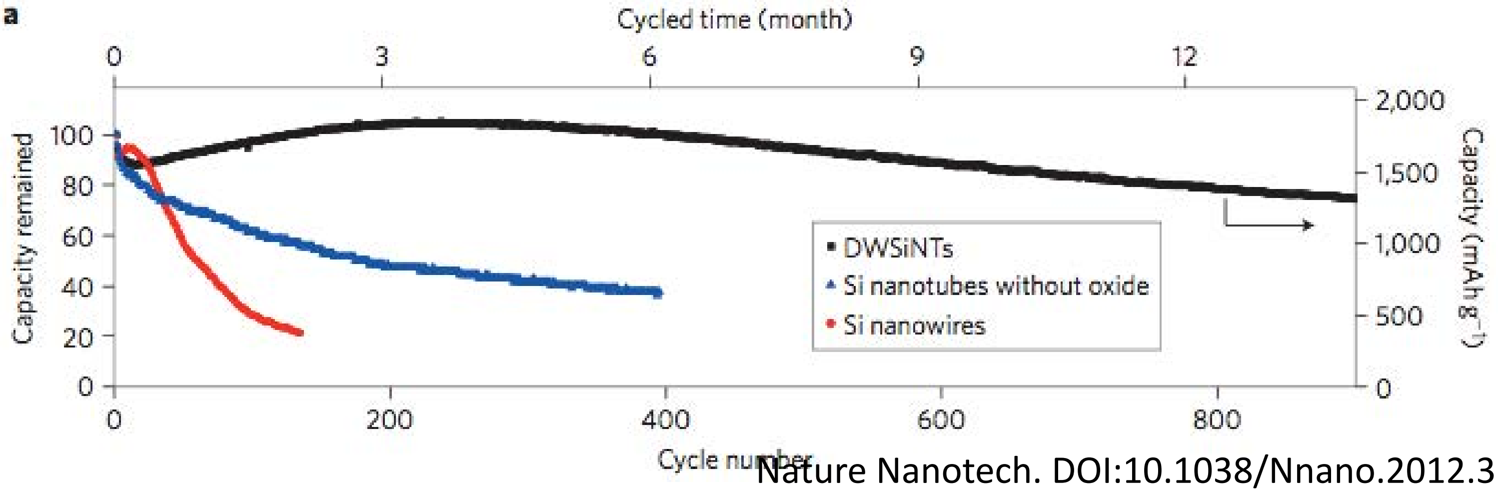
How do we make Si Double-Wall Nanotubes?



Nature Nanotech. DOI:10.1038/Nnano.2012.35

Stable SEI Formation → Longer Cycle Life





Nature Nanotech. DOI:10.1038/Nnano.2012.35