

Nanomaterials - *Quantum Dots, Nanowires and Nanotubes*

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100 nm

Si/SiGe nanowires grown by the vapor-liquid-solid mechanism - Y. Wu et. al., Nano Lett 2:83 2002

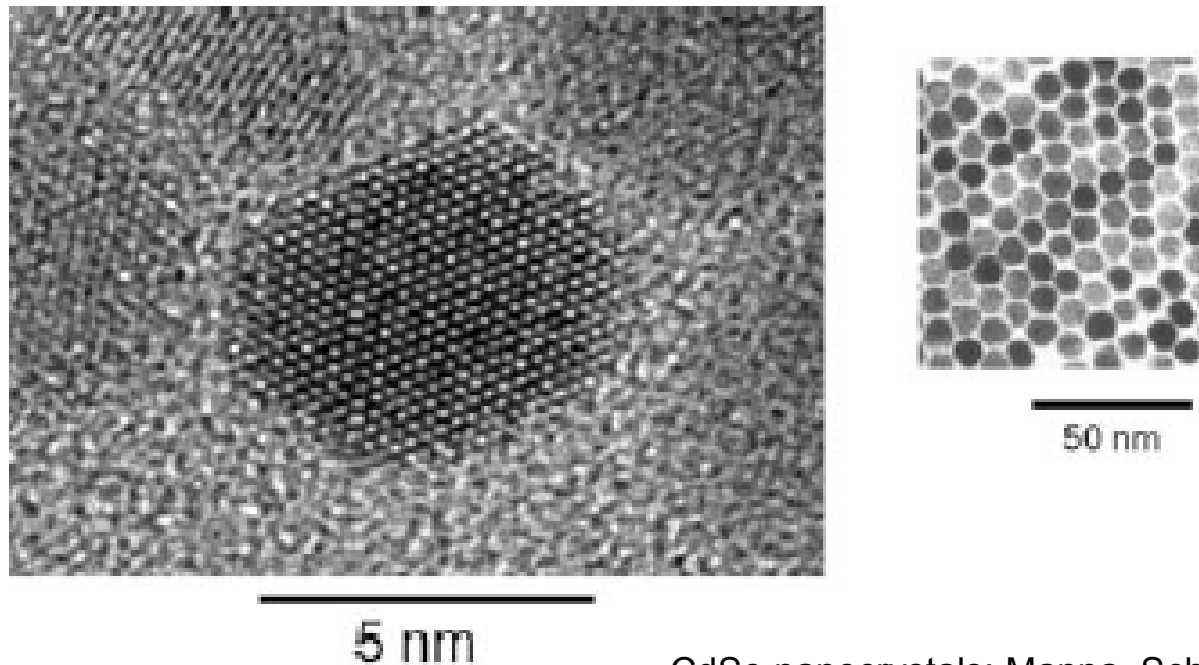
*Note: The diameter of these relatively large nanowires is 1/1,000th the diameter of a human hair!*¹

Questions...

- What is a quantum dot? What is a nanowire?
What is a nanotube?
- Why are they (scientifically) interesting?
- What are their potential applications?
- How are they made?
- ???

Q: What is a quantum dot?

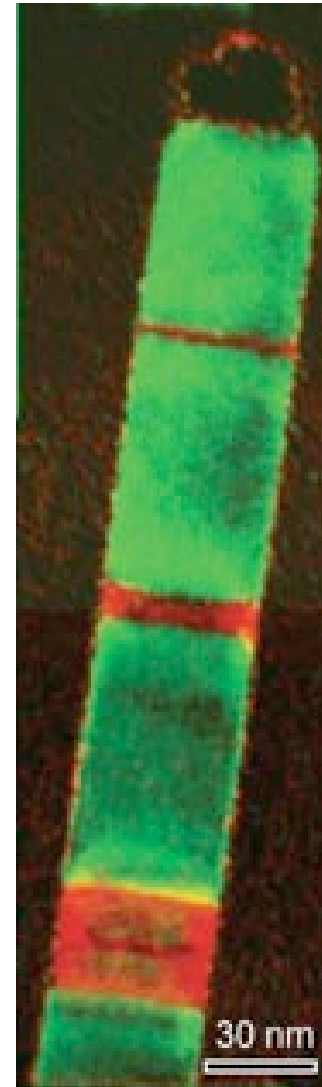
- A: Any solid material in the form of a particle with a diameter comparable to the wavelength of an electron (more later...)



CdSe nanocrystals; Manna, Scher and Alivisatos, J. Cluster Sci. 13 (2002)521

Q: What is a nanowire?

- A: Any solid material in the form of wire with diameter smaller than about 100 nm

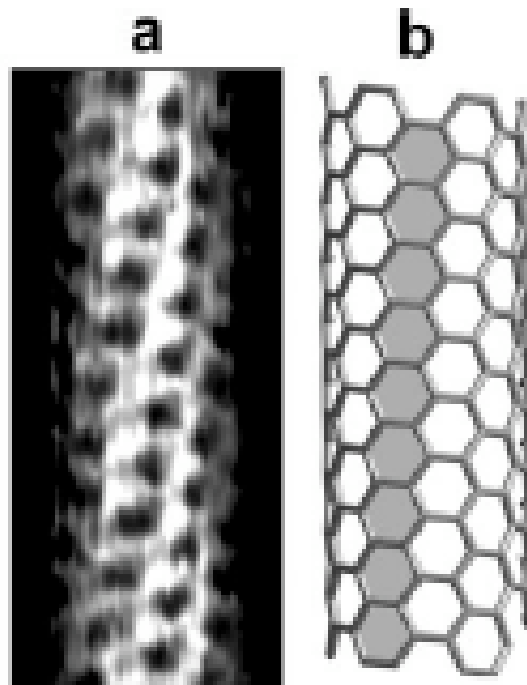


Transmission electron micrograph of an InP/InAs **nanowire**

(M.T. Bjork et. al., Nanoletters, 2:2 2002)

Q: What is a nanotube?

- A: A hollow nanowire, typically with a wall thickness on the order of molecular dimensions
- The smallest (and most interesting) nanotube is the single-walled carbon nanotube (SWNT) consisting of a single graphene sheet rolled up into a tube

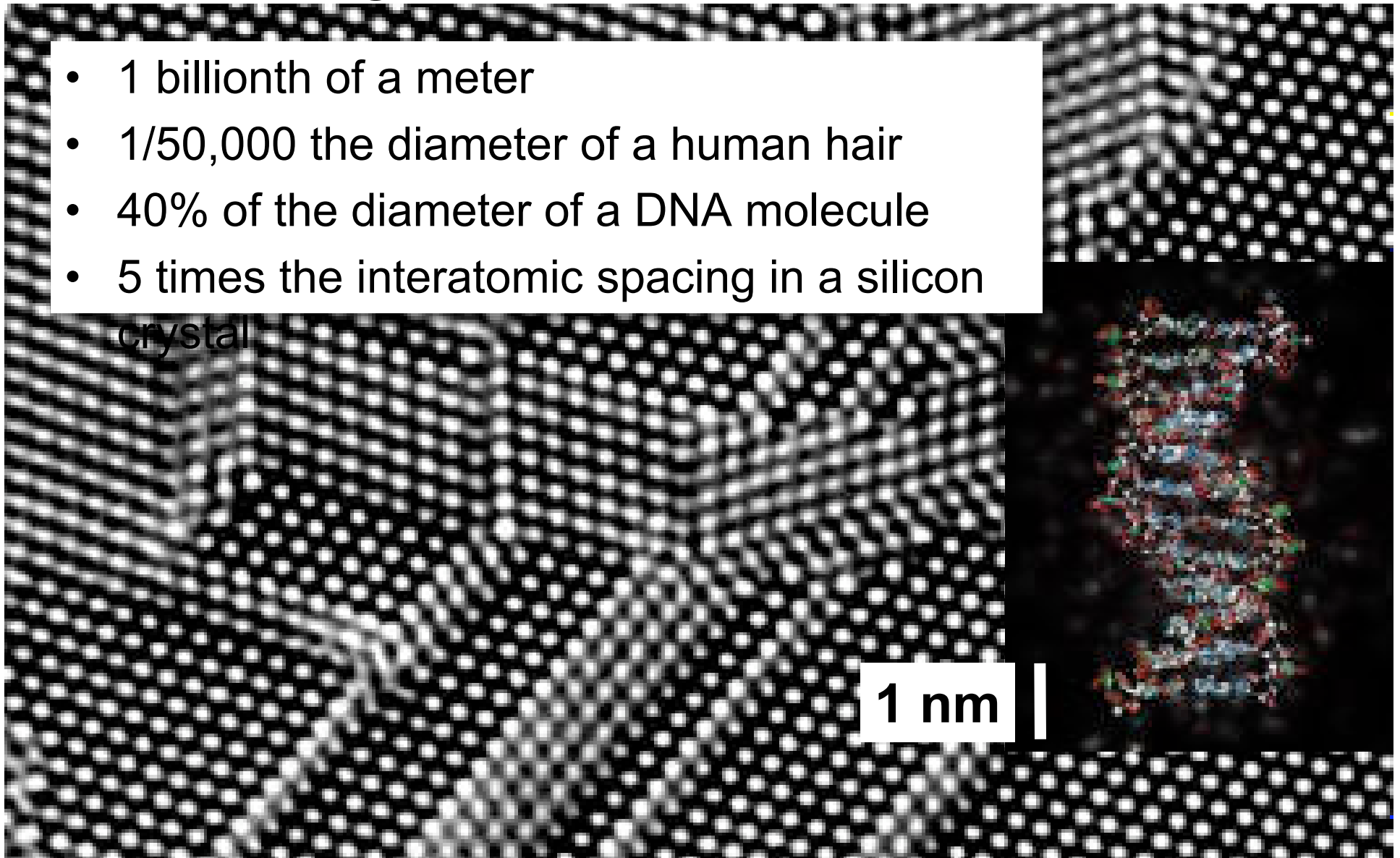


Scanning
Tunneling
Micrograph of a
single-walled
carbon **nanotube**
and
corresponding
model (Dekker)

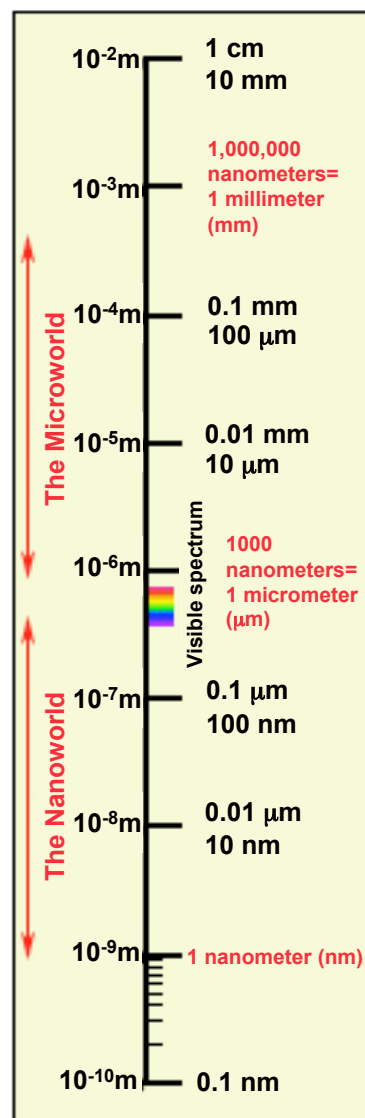
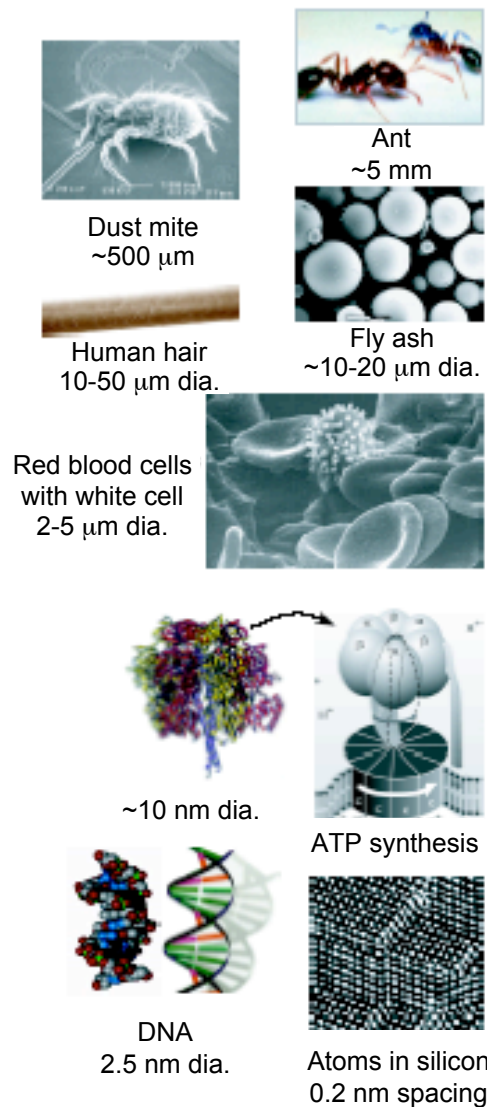
Q: How big is a nanometer?

PolySi image: C. Song, NCEM

- 1 billionth of a meter
- 1/50,000 the diameter of a human hair
- 40% of the diameter of a DNA molecule
- 5 times the interatomic spacing in a silicon crystal



Things Natural



Things Man-made

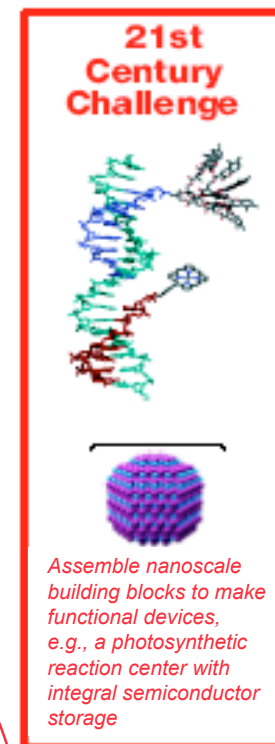
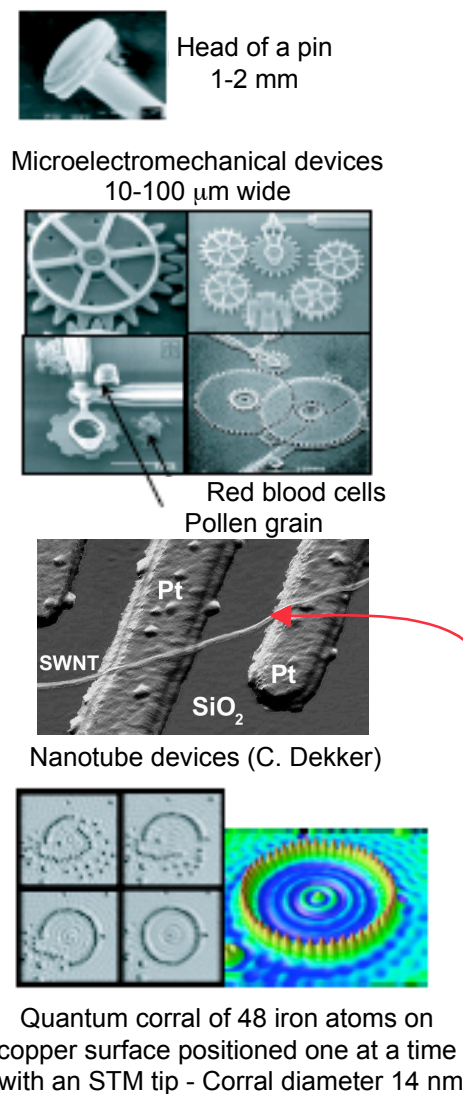


FIGURE 1.1 The size of nanoscale objects and phenomena compared with the size of small everyday objects. Courtesy of Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy.

Adapted from: NRC Report: Small Wonders, Endless Frontiers: Review of the National Nanotechnology Initiative (National Research Council, July 2002)

Q: What makes nanostructured materials (scientifically) interesting?

- **Electronic & optical properties**
 - Nanowires and nanotubes are the most confining electrical conductors - puts the squeeze on electrons
 - Can be defect free - electrons move “ballistically”
 - Quantum confinement - tunable optical properties
- **Mechanical properties**
 - Small enough to be defect-free, thus exhibiting ideal strength
- **Thermal properties**
 - Can be designed to conduct heat substantially better (or much worse) than nearly every bulk material
- **Chemical properties**
 - Dominated by large surface-to-volume ratio

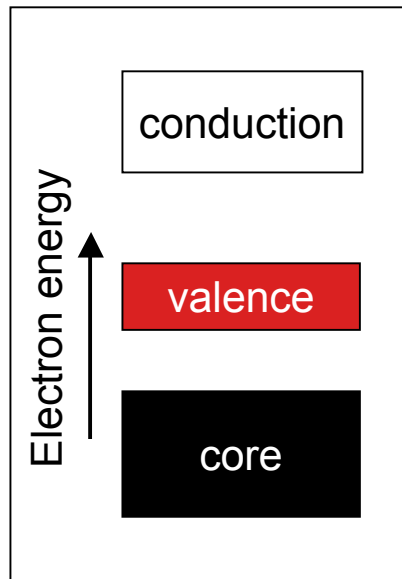
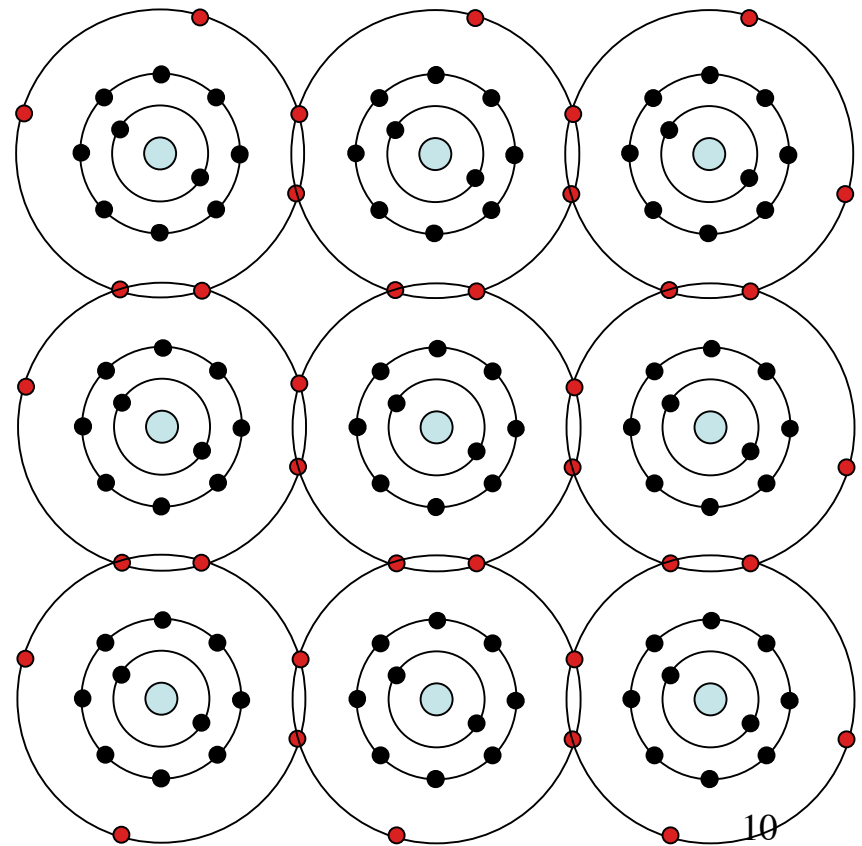
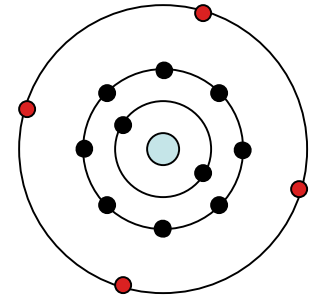
Nanowires and Nanotubes are New Materials!

Electronic and Optical Properties

Quantum Confinement

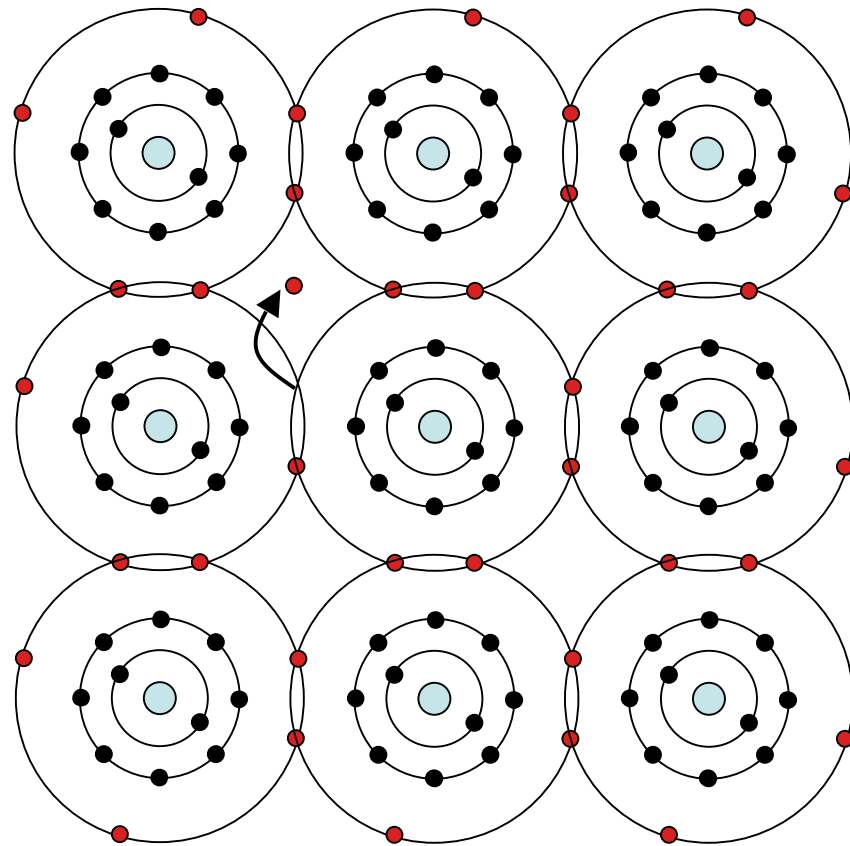
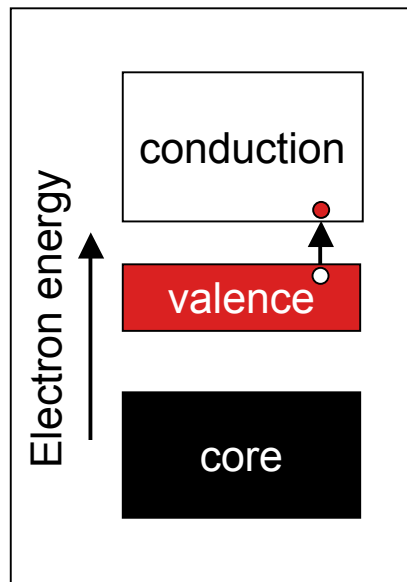
Electrons in solids

- Core shell electrons are tightly bound to atoms, and do not interact strongly with electrons in other atoms
- Valence shell electrons are the outer electrons that contribute to bonds between atoms
- If all of the bonds are “satisfied” by valence electrons, and if these bonds are strong, then the material does not conduct electricity - an **insulator**



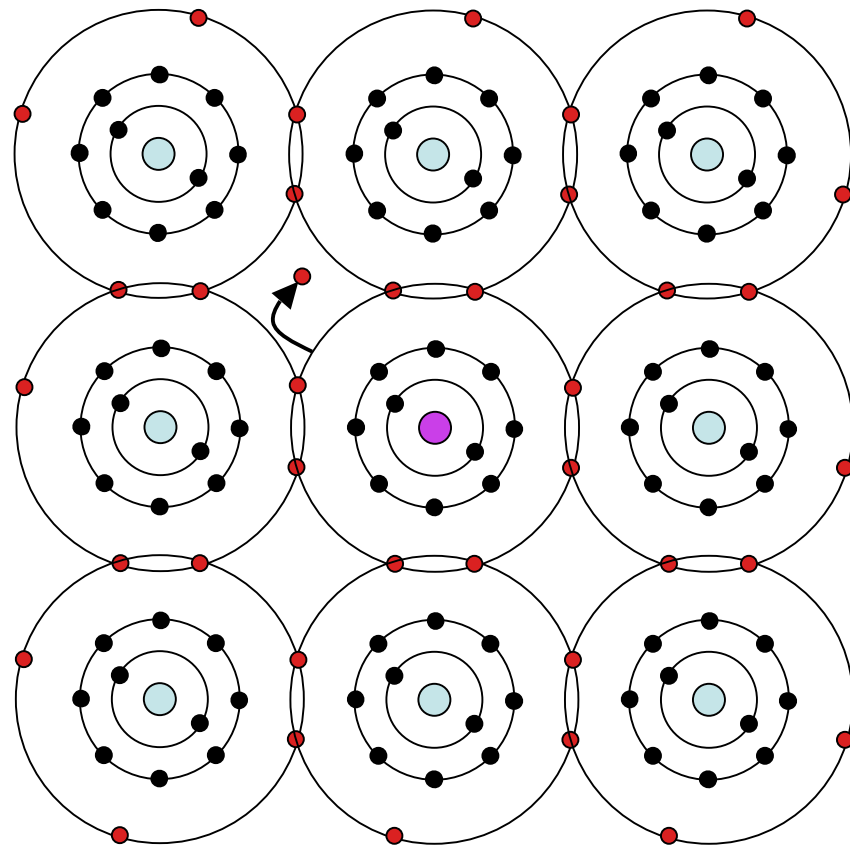
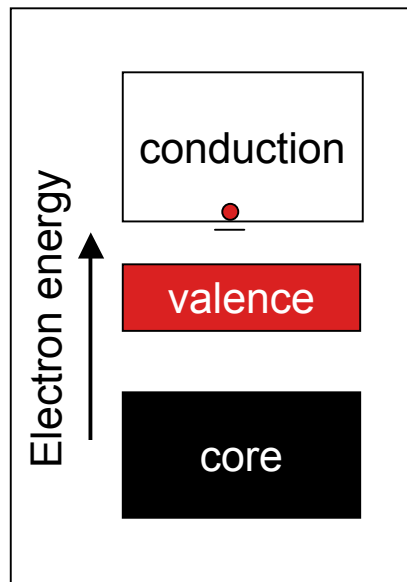
Electrons in solids

- If all the bonds are “satisfied”, but the bonds are relatively weak, then the material is an **intrinsic semiconductor**, and thermal energy can break a small number of bonds, releasing the electrons to conduct electricity



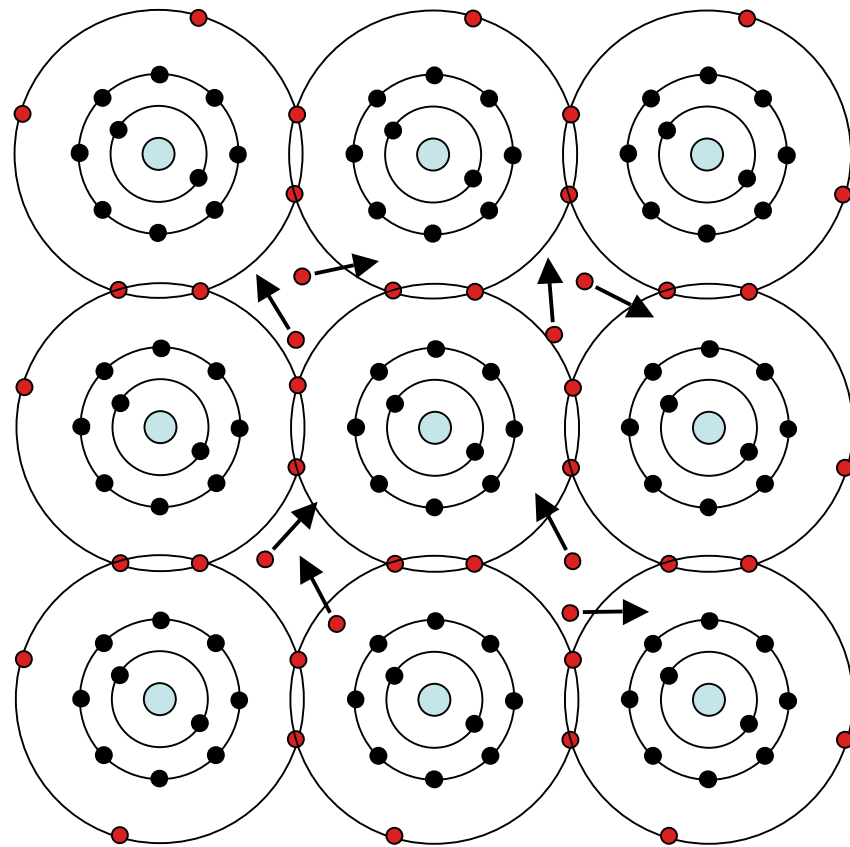
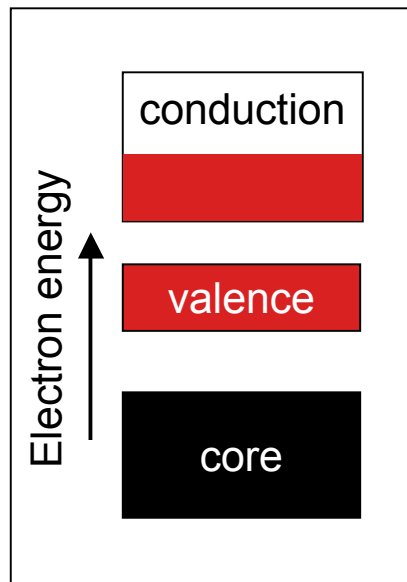
Electrons in solids

- If impurities with one more or one fewer electrons than a host atom are substituted for host atoms in a semiconductor, then the material becomes conductive - an **extrinsic semiconductor**



Electrons in solids

- If only a fraction of the bonds are satisfied (or alternatively, if there are many more electrons than are needed for bonding) then there is a high density of electrons that contribute to conduction, and the solid is a **metal**

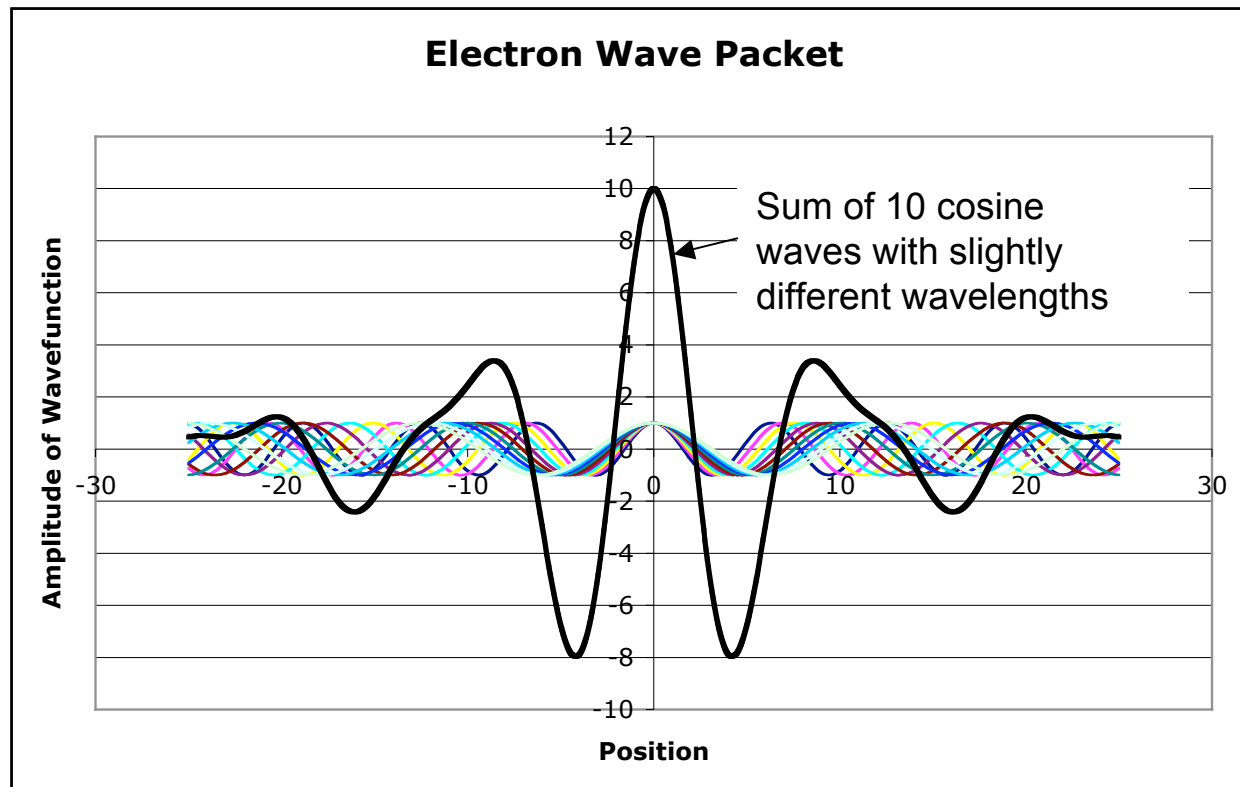


Electrons in nanostructured materials

- Electrons can be considered to be both waves and particles
- **Particle:** momentum = mass x velocity ($p = mv$)
- **Wave:** momentum = Planck's constant/wavelength ($p = h/\lambda$)
- **Particle or wave:** kinetic energy = $p^2/2m$

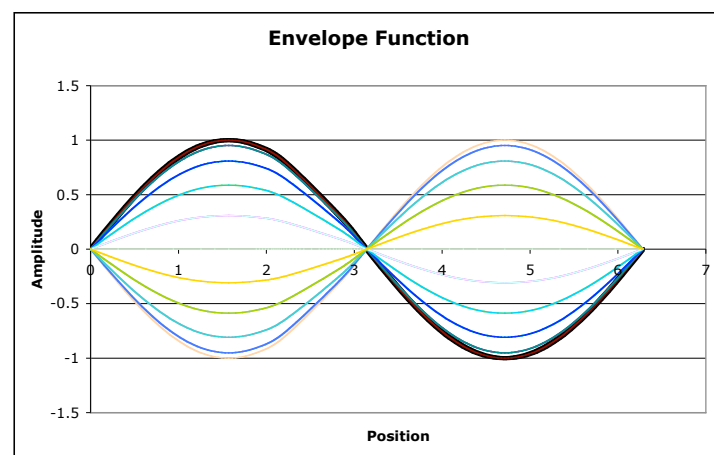
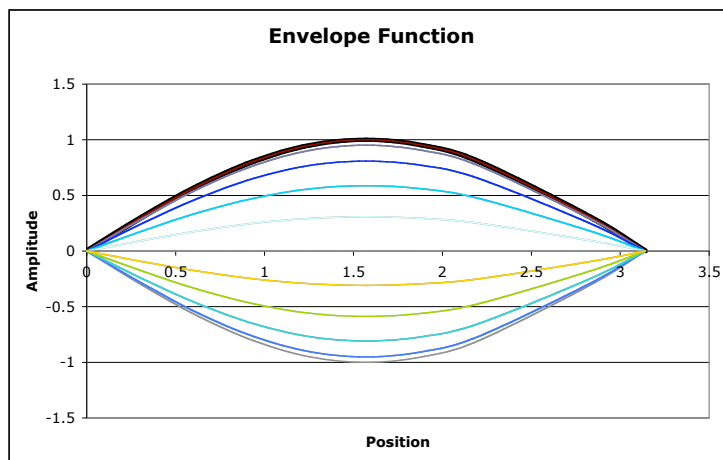
Electrons in nanostructured materials

- An electron (particle) can be described as a wave packet, i.e. the sum of sinusoidal waves, each with a slightly different wavelength



Electrons in nanostructured materials

- Each wave (“wavefunction”) is analogous to the shape of a vibrating string (or jump rope).
- If we hold two ends of the string, we constrain the string to vibrate within an “envelope” that contains an integer number of half wavelengths...a “standing wave”.
- Each half-wavelength exists between two “nodes” - points that do not move
- The shorter the wavelength (shorter string or more nodes), the more energy it takes to vibrate the string



From vibrating strings to electrons

- An electron's wavefunction is just like the vibrating string
- If we move the nodes closer together, the electron's energy increases.
- If we put an electron in a “box”, the walls of the box become nodes - so the smaller the box, the higher the energy of the electron

Confining the electrons fundamentally changes their electronic structure...

Quantum confining materials are *NEW* materials with properties that are tunable with size

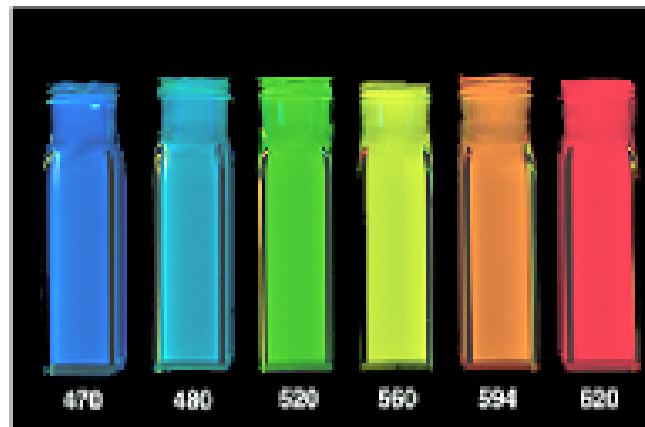
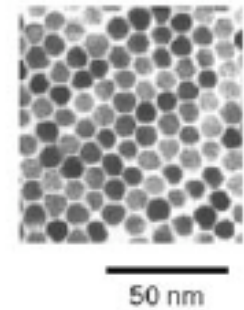
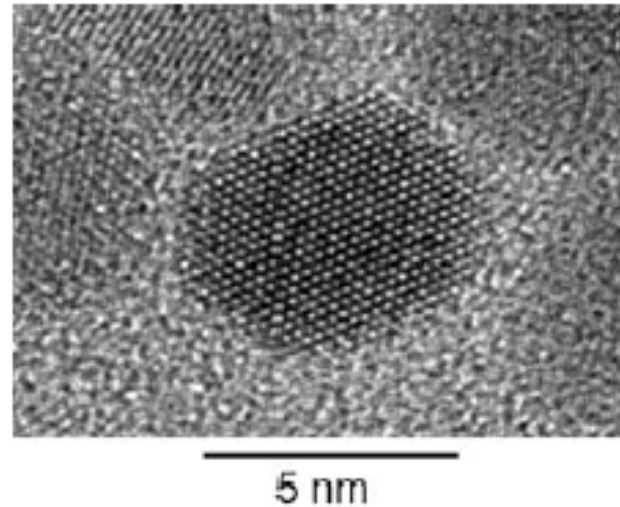
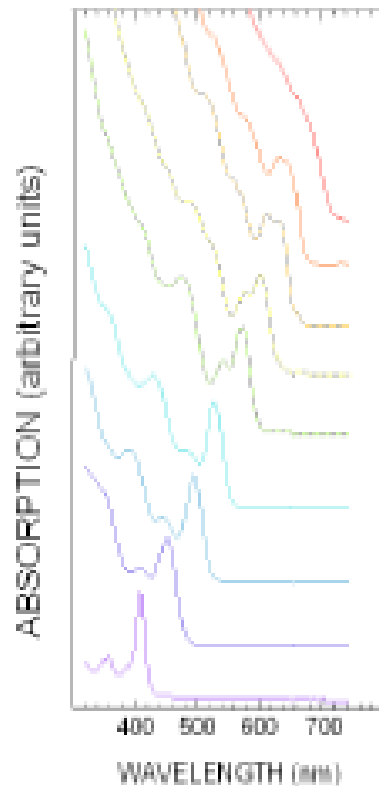
Optical properties

- Decreasing the size of a nanostructured material increases the energy difference, ΔE , between allowed electron energy levels
- When an electron drops from a higher energy state to a lower energy state, a quantum of light (“photon”) with wavelength, $\lambda = hc/\Delta E$ may be emitted
- Larger ΔE implies shorter wavelength (“blue shifted”)

h is Planck’s constant; c is the speed of light

Example: Quantum Dots

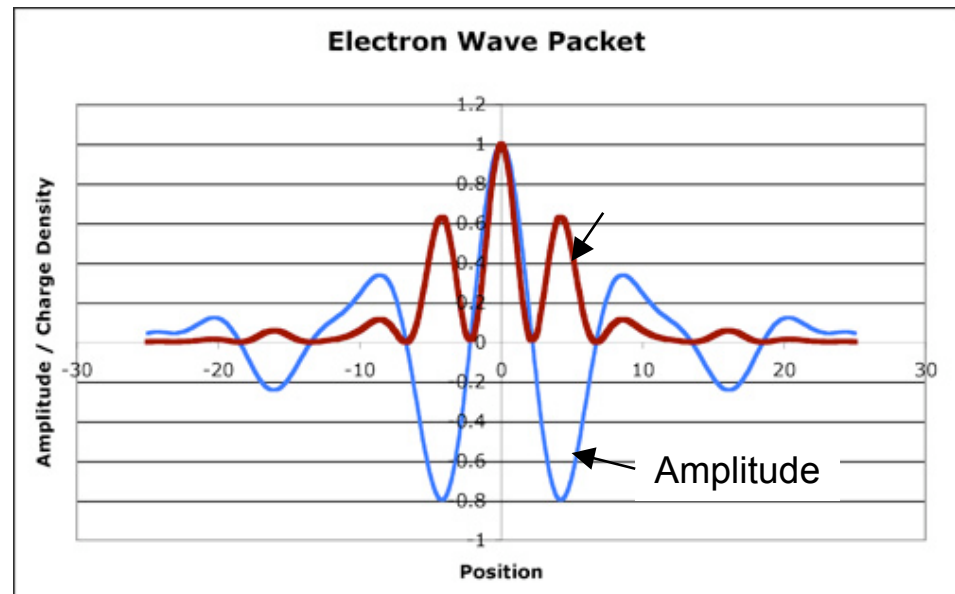
CdSe nanocrystals; Manna, Scher and Alivisatos, J. Cluster Sci. 13 (2002)521



Left- absorption spectra of semiconductor nanoparticles of different diameter (Murray, MIT). *Right-* nanoparticles suspended in solution (Frankel, MIT) - National Science Foundation Report, "Societal Implications of Nanotechnology" March 2001

...but what is the wavefunction?

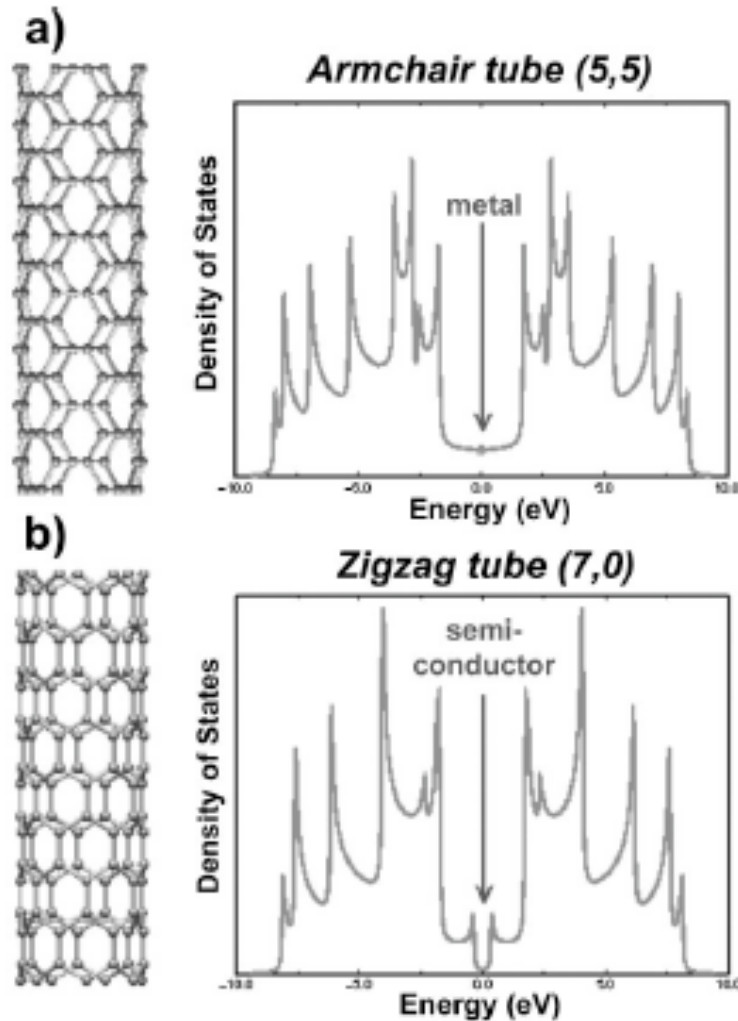
- Unlike the case of the vibrating string (or jump rope), the electron's wavefunction is a mathematical abstraction that is not tangible
- The square of the wavefunction, however, represents the probability distribution describing the likelihood of finding the electron at a particular location
- Multiplying the square of the wavefunction by the charge on an electron, we have the charge distribution



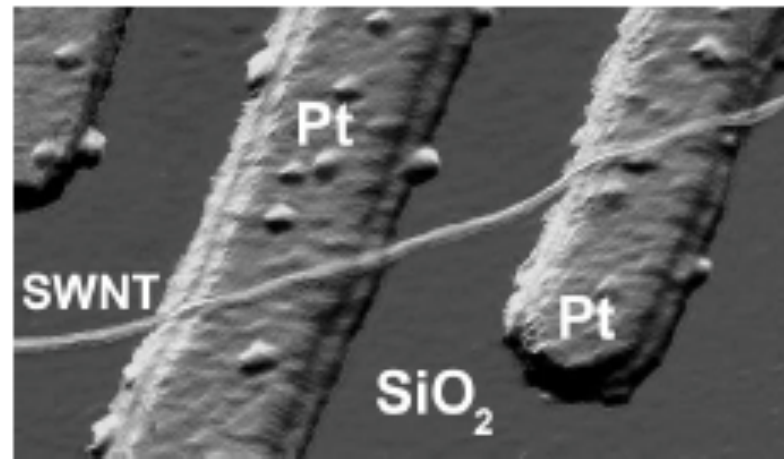
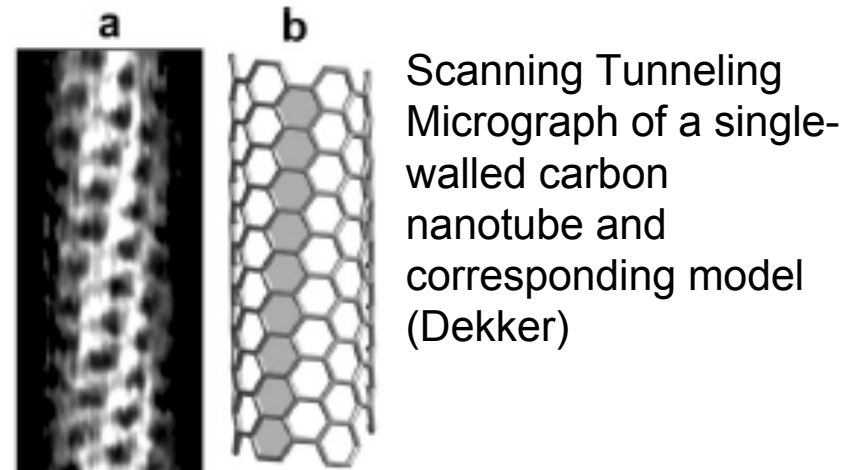
How does quantum confinement work in a nanowire?

- If a nanowire's diameter is comparable to the typical wavelength of a conduction electron in the bulk material, then the nanowire becomes a “quantum wire”, and the electrons are squeezed in two dimensions, but can move freely in the third

The carbon nanotubeneither diamond nor graphite



Nanotubes of different flavors (Charlier)



1.4 nm diameter single-walled carbon nanotube across two electrodes (Dekker)

Applications of nanostructured materials

- Quantum dots as fluorescent markers for biomedicine
- Nanotubes as structural reinforcement in composite materials
- Nanowires and nanotubes as conducting channels for future electronics
- Nanowires for tunable lasers and light-emitting diodes
- Quantum dots, nanotubes and nanowires for high-surface area sensors
-

Don't forget Nanopants...



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Free Babolat Tee Shirt AND a \$20 Instant rebate on any Nanotechnology racket for a limited time only!

New high Modulus Carbon Graphite Carbon Nanotube

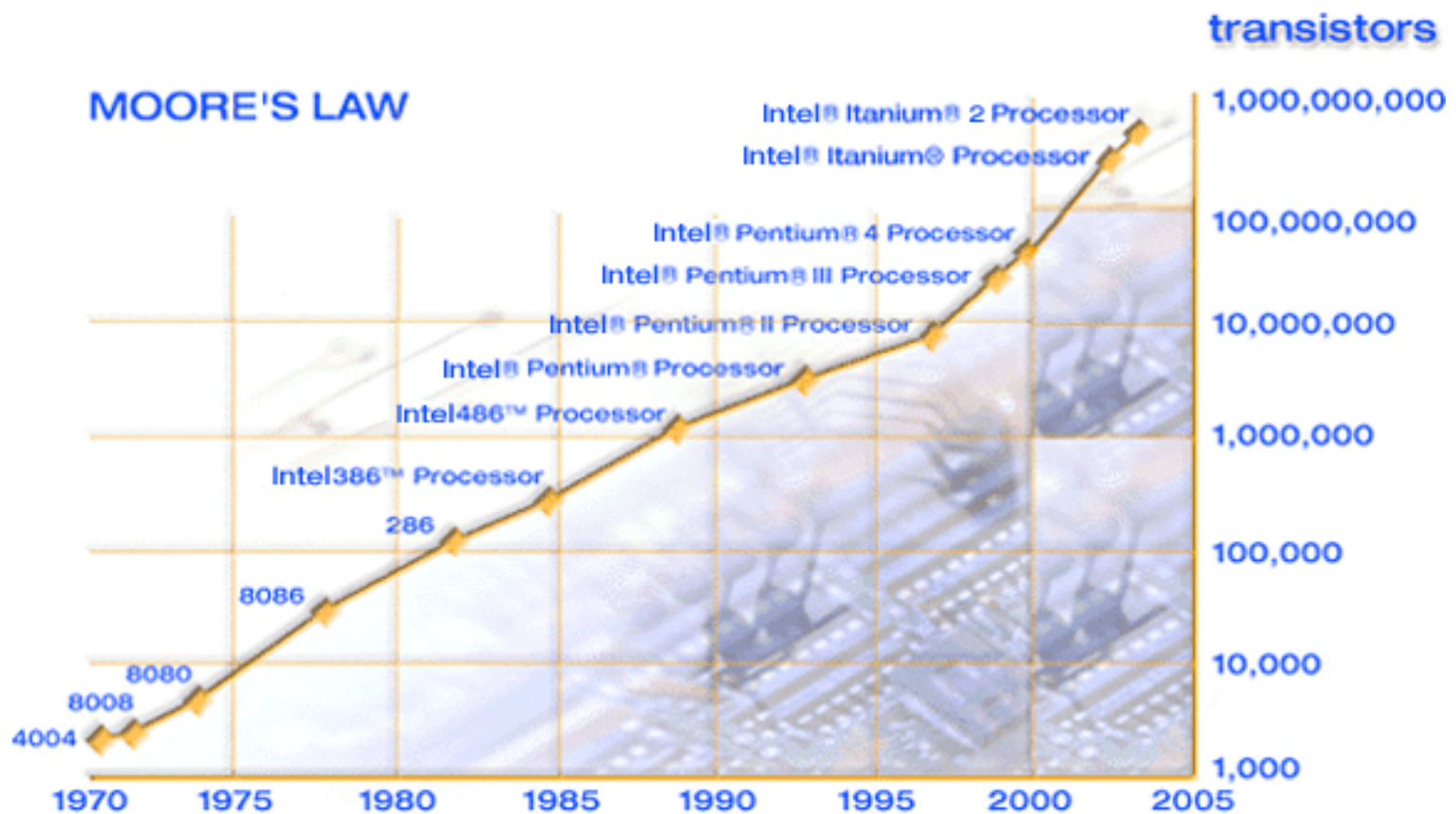
Headsizes:118 sq. in. * Length:28 in. * Weight (strung):9.3 oz.
* Stiffness (Babolat RDC):73 * Balance:14.63 in. Head Heavy *
Cross Section: 28mm Head/26mm Throat * Swingweight: 326
kg*sq. cm * "This year, Babolat introduced two Nano Carbon
Technology, or NCT, racquets, the Tour and the Power. The Tour,
above is geared toward high-level intermediates while the Power
(below) is for those with short strokes. Both models are **reinforced
in the throat and the bottom half of the head with carbon nanotubes,
strings of carbon molecules constructed at the nano level, which
are five times stiffer than graphite**. Net result: Babolat is able to
increase the stiffness and power of the racquets without adding
weight."—Racquet Sports Industry.



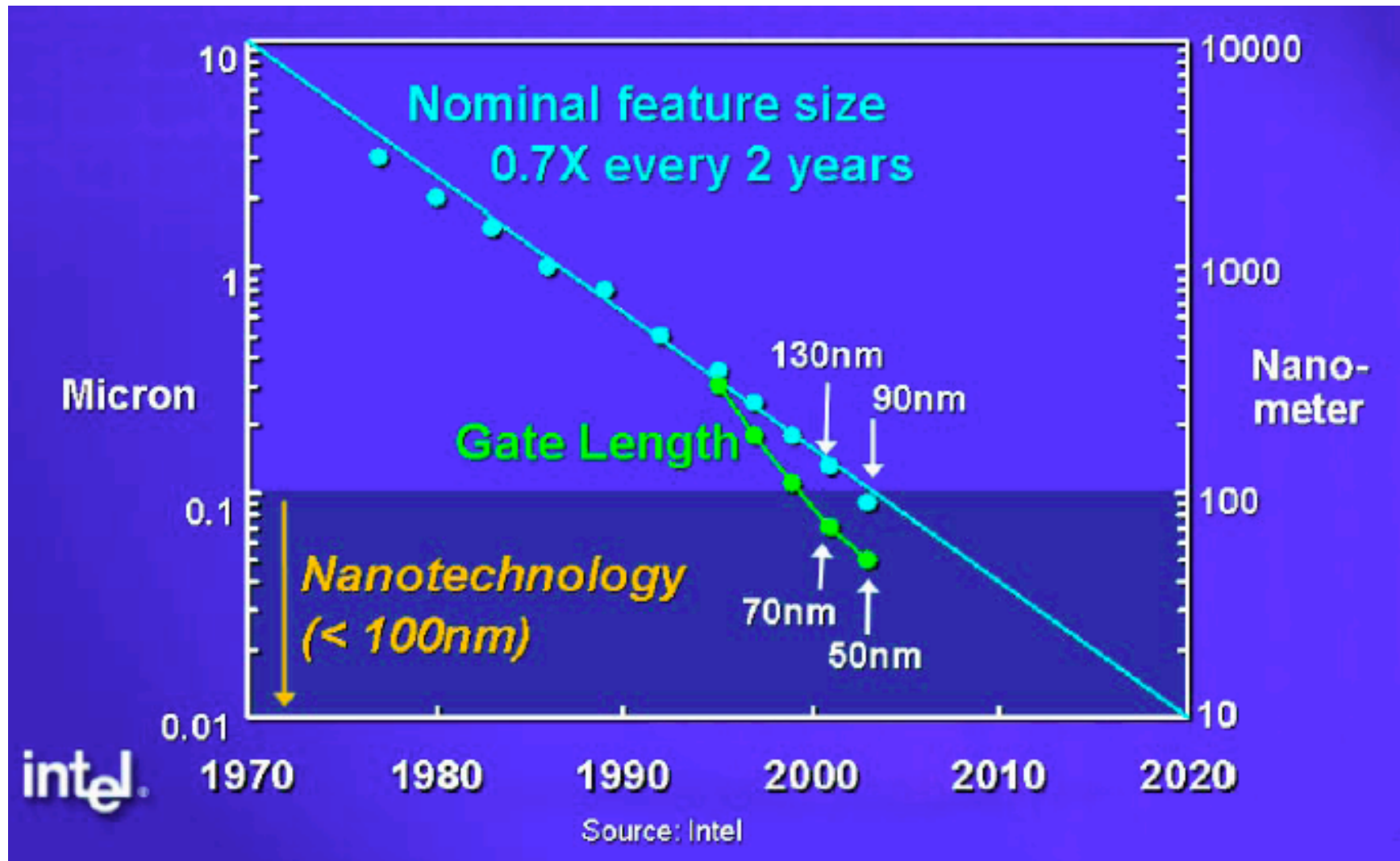
Application to nanoelectronics

Four decades of Moore's Law

- Increase in number of transistors/chip by 100,000X since 1974
- Decrease in cost/transistor by >100,000X since 1974
- 1 billion transistors per chip in 2005, < 100 nano\$/transistor!

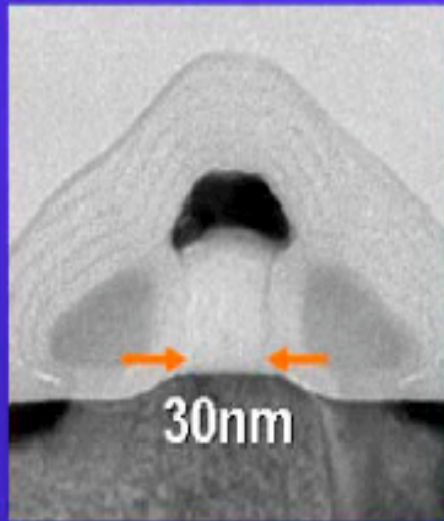


Si is already in the “nano” realm

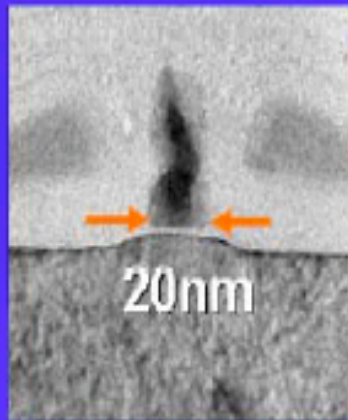


How far can we go with silicon?

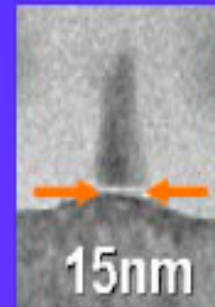
Experimental transistors for future process generations



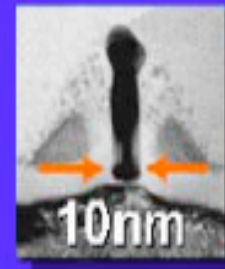
65nm process
2005 production



45nm process
2007 production

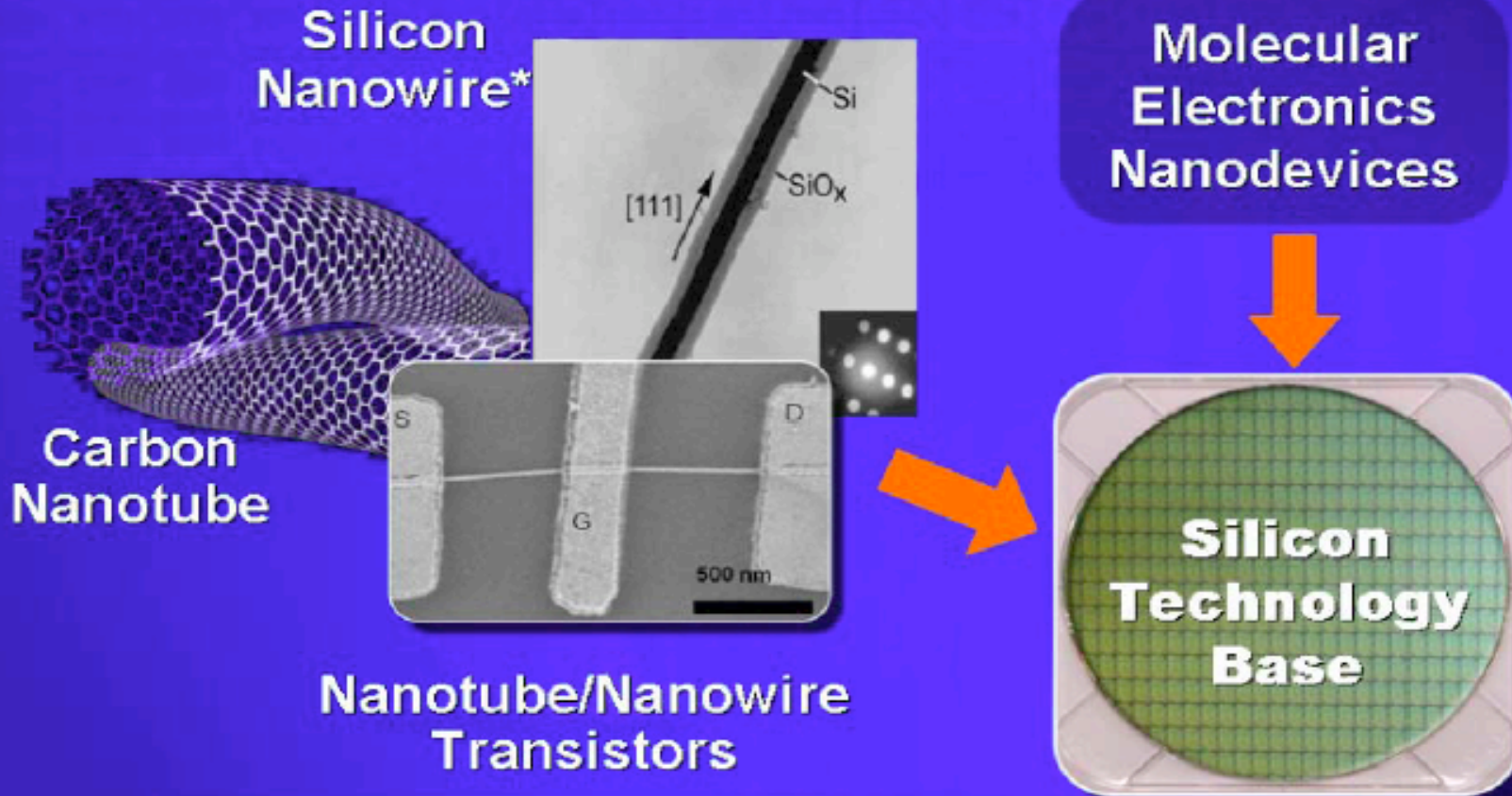


32nm process
2009 production



22nm process
2011 production

Future Nanotechnology will Ride on Silicon Technology Base



intel.

Innovations will extend silicon technology

*Source: Morales & Lieber, Harvard Univ

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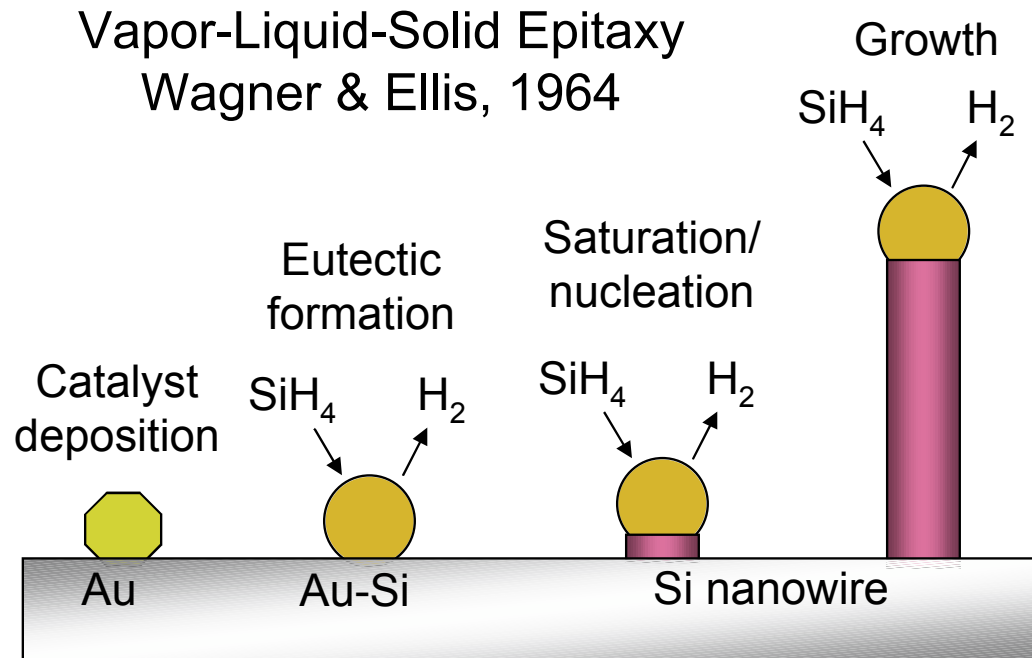
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From "Extending Moore's Law in the Nanotechnology Era" by Sunlin Chou (www.intel.com)

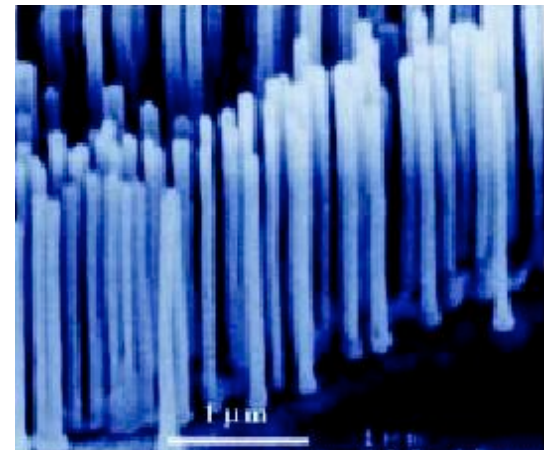
How are nanostructured materials made?

- **Key challenge:** high surface-to-volume ratio
- Surface contributes excess surface free energy per unit area
- Lowest free energy state for a material with a cubic crystal structure is a single faceted spheroid
- Must exploit kinetics (rates of reactions at surfaces) to make small structures and/or structures with very large aspect ratios

One approach: catalysis



ZnO nanowires by VLS

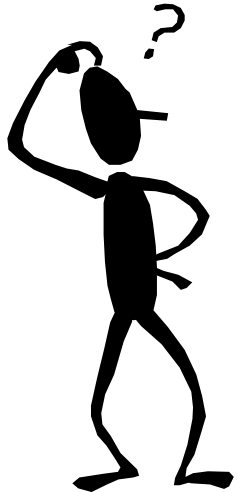


Yang, P. et al., *Chem. Eur. J.* **8**:6 (2002)

A similar catalytic approach is used to make carbon nanotubes

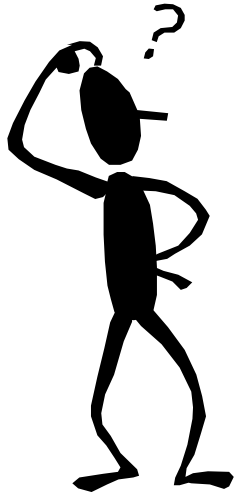
Questions and Answers

- Societal impact of Nanotechnology (question is not audible because the videotape was changed)
- Carbon dispersed when making bucky balls
- What is the protocol in the labs at Purdue when carbon is extracted?
- How is the carbon nanotube/wire made?



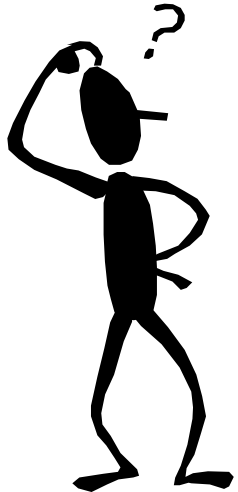
Questions and Answers

- Safety Issues
- If DNA is used to relay information, what keeps it from degrading along the way?
- Mutations of DNA because of stray engery
- Bases and backbones
- Strength of carbon nanotubes



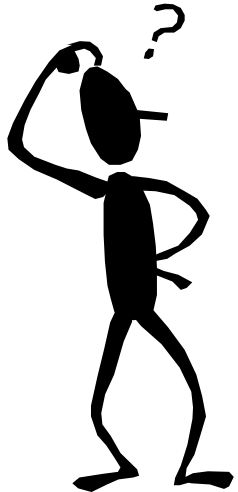
Questions and Answers

- Differences in tinsel strength
- Emphasis of Tim Sands' work
- Electrons: Particle or wave behavior?
- Increasing efficiency of devices
- What is electricity?



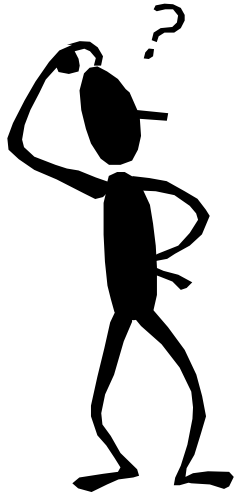
Questions and Answers

- Covalent bonds
- Bond differences
- Deformation mechanisms
- Electricity and crystal deformation



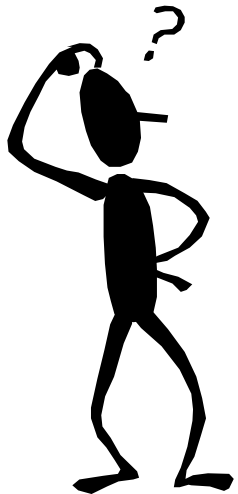
Questions and Answers

- Materials science and engineering
- Teaching materials science
- What's the big hold-up on the white LED?
- What goes bad in a crystal to make it “die out?”
- The continuous spectrum of the Sun



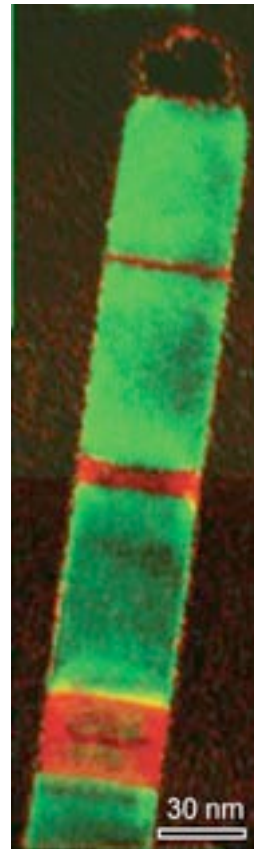
Questions and Answers

- Black-body spectrum & radiation
- What is a fundamental way to explain the origin of black-body radiation?



Nanostructuring in the 3rd dimension

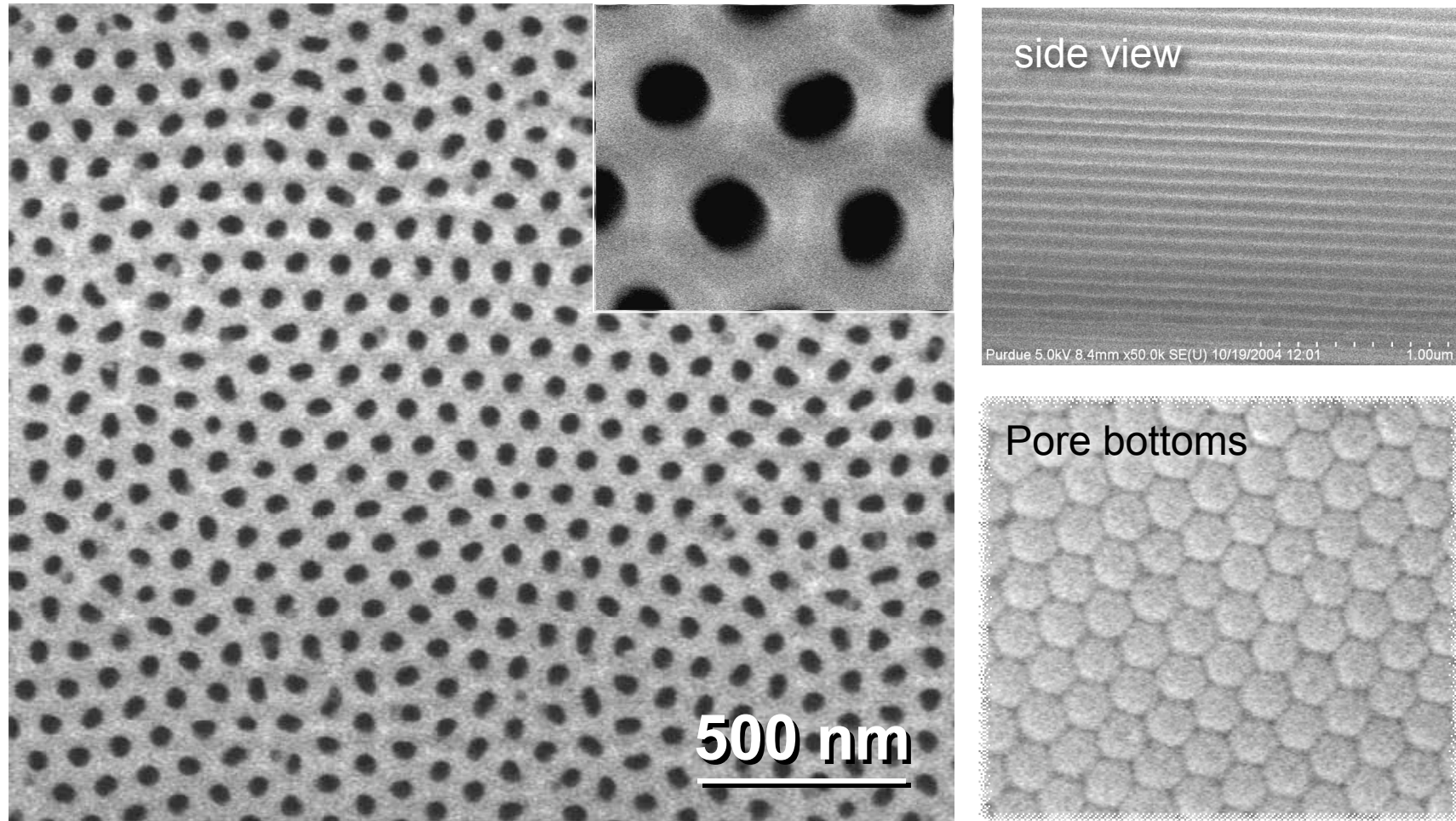
- By changing the vapor precursors during VLS growth, single crystal nanowire heterostructures can be grown



InAs/InP nanowire (false colors correspond to different crystal lattice spacings)

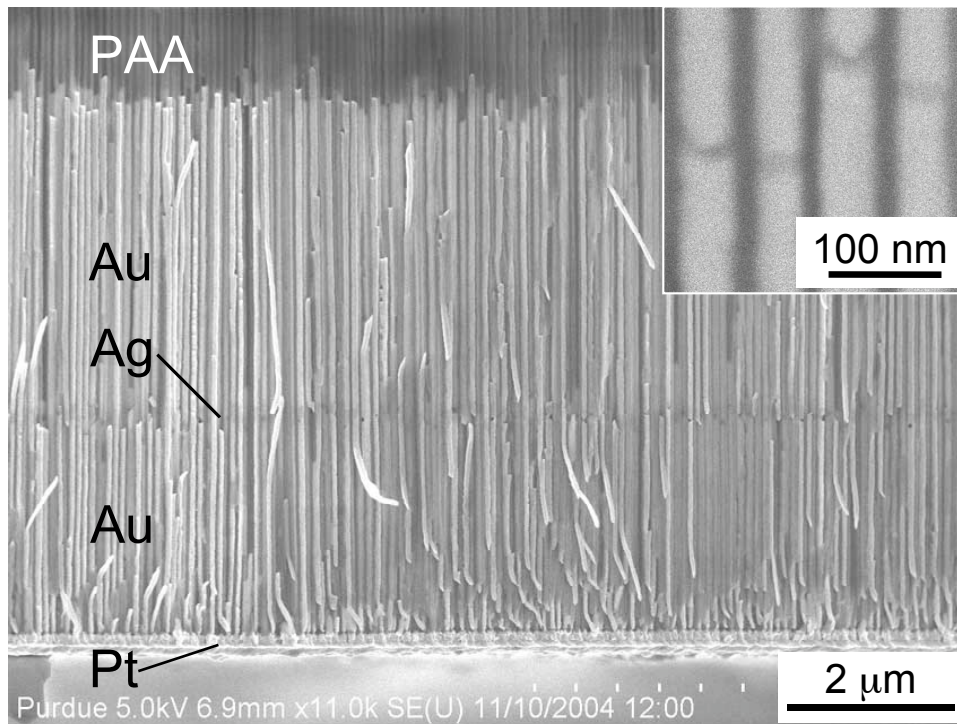
M.T. Bjork et. al., Nanoletters, 2:2 2002

Another approach: nanoporous templates

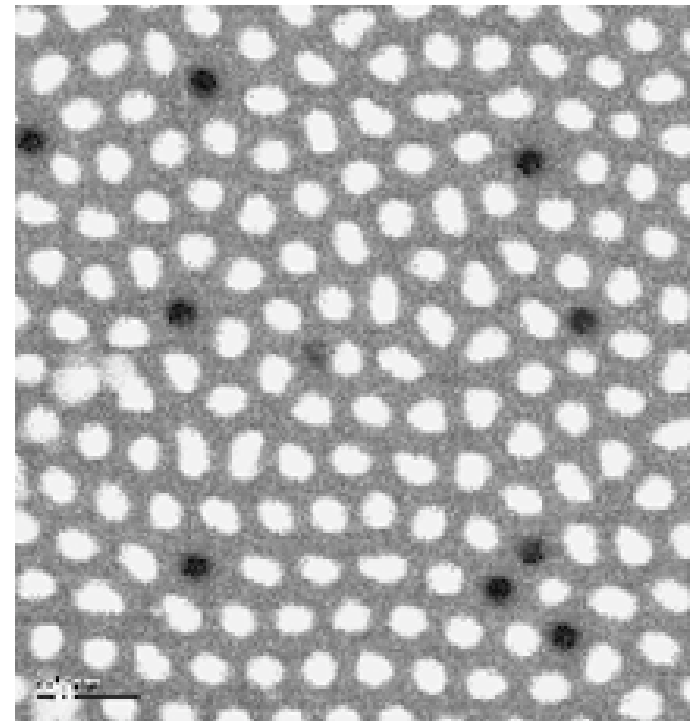


Porous anodic alumina (PAA) with 50 nm diameter pores on 100 nm centers produced by anodizing Al foil at 40V at 4°C in oxalic acid

Pores can be filled by electrodeposition



Au/Ag/Au nanowires produced by electrodeposition into porous anodic alumina [Manuel DaSilva, unpublished]



Crystalline single-phase $\text{Bi}_2\text{Te}_{2.6}\text{Se}_{0.4}$ nanowires electrodeposited into 50 nm pores in anodic alumina [Martín-González et al. Nanoletters 3 (2003) 973]

Conclusions

- Quantum dots, nanowires and nanotubes are new materials with properties that can be markedly different than those of bulk materials or thin films
- ...A new frontier for materials science and materials engineering!