NANO-MATERIALS
&
NANO-TECHNOLOGY

INTRODUCTION

- Nanomaterials are crystalline materials having grain sizes on the order of a billionth of a meter.
- All crystalline materials are made up of grains which in turn comprised of many atoms.
- Materials normally have grain size varying from micrometer to millimeter.
- A nanometer (nm) is very smaller than even microns which is a billionth (10^{-9}) of a meter.
- A nano crystalline material has grains of the order of 1-100nm.
- 1nm = $10A^0$ and hence in 1nm there may be 3-5 atoms.
- Nanomaterials may be inorganic, organic as well as bio-organic.

NANO TECHNOLOGY DEFINED

- "The development and use of devices that have a size of only a few nanometres." physics.about.com
- "Research and technology development at the atomic, molecular or macromolecular level in the length scale of approximately 1 - 100 nm 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." www.nano.gov
- "Branch of engineering that deals with things smaller than 100 nm (especially with the manipulation of individual molecules)." www.hyperdictionary.com
- "Nanotechnology, or, as it is sometimes called, *molecular manufacturing*, is a branch of engineering that deals with the design and manufacture of extremely small electronic circuits and mechanical devices built at the molecular level of matter." www.whatis.com
- "The art of manipulating materials on an atomic or molecular scale especially to build microscopic devices." *Miriam Webster Dictionary*

PERSPECTIVE OF LENGTH SCALE

Top Down

Bottom Up

1 km

1 m

1 mm

1 μm

1 nm

Aircraft Carrier

Boeing 747

Car

Humans

Laptop

Butterfly

Size of a Microprocessor

Gnat

Resolving power of the eye ~ 0.2 mm

Micromachines

Biological cell

Nucleus of a cell

Wavelength of Visible Light

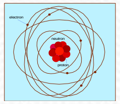
Smallest feature in microelectronic chips

Nanostructures & Quantum Devices

Proteins

Width of DNA

Size of an atom



NANO FABRICATION

Nanofabrication can generally be divided into two categories based on the approach:

“Top-Down”:

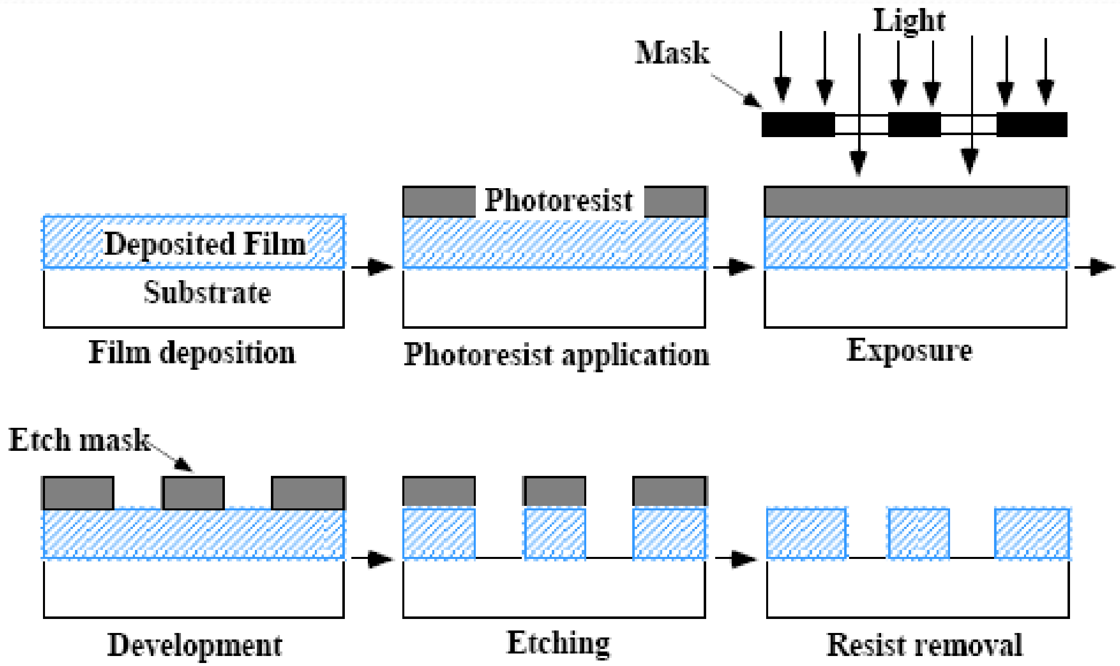
Fabrication of device structures via monolithic processing on the nanoscale.

“Bottom-Up”:

Fabrication of device structures via systematic assembly of atoms, molecules or other basic units of matter.

NANOTECH & MICRO - FABRICATION

- Microfabrication is a top-down technique utilizing the following processes in sequential fashion:
  - Film Deposition
    - CVD, PVD
  - Photolithography
    - Optical exposure, PR
  - Etching
    - Aqueous, plasma



Many of these techniques are useful, directly or indirectly in nanofabrication

MANUFACTURE OF NANOMATERIALS

The following are some of the techniques or methods used for the production of nanomaterials:

1. Sol-Gel Synthesis
2. High Energy Ball-Milling or Mechanical Alloying
3. Plasma Synthesis
4. Electro-deposition
5. Inert Gas Condensation
6. Chemical Vapor Deposition (CVD)

Sol-Gel Synthesis

Sol-gel Process: The sol gel technique is a long-established industrial process for the generation of colloidal nanoparticles from liquid phase, that has been further developed in last years for the production of advanced nanomaterials and coatings. Sol-gel-processes are well adapted for oxide nanoparticles and composites nanopowders synthesis. The main advantages of sol-gel techniques for the preparation of materials are low temperature of processing, versatility, and flexible rheology allowing easy shaping and embedding. They offer unique opportunities for access to organic-inorganic materials. The most commonly used precursors of oxides are alkoxides, due to their commercial availability and to the high liability of the M-OR bond allowing facile tailoring in situ during processing.

- It can produce materials
  - at low temperature
  - in large quantities and
  - in a cost effective manner
- Coat one material over the other.
- Homogeneous alloys can be produced
- Pure materials tailored to the composition can be produced

NANO FILM TECHNOLOGY

- There is a great demand for nanofilm coatings in:
  - Cutting tools
  - Wear resistant materials
  - Tribological Applications
  - Micro Electronic Applications
- Most Popular ones are:
  - CVD (Chemical Vapor Deposition) Process
  - FCVA (Filtered Cathodic Vacuum Arc) Process

Chemical Vapour Deposition (CVD): CVD consists in activating a chemical reaction between the substrate surface and a gaseous precursor. Activation can be achieved either with temperature (Thermal CVD) or with a plasma (PECVD: Plasma Enhanced Chemical Vapour Deposition). The main advantage is the nondirective aspect of this technology. Plasma allows to decrease significantly the process temperature compared to the thermal CVD process. CVD is widely used to produce carbon nanotubes.

FCVA TECHNOLOGY

- Can produce high quality Tetrahedral Amorphous Carbon (TAC) coatings with nanoscale accuracy.
- It involves the micro deposition process using a plasma beam of ions, macro particles and neutral atoms.
- Harder, denser and cleaner nanofilms can be produced
- The deposited films adhere well on substrate and have good chemical, mechanical, electrical and optical properties.
- Substrate temp: $70^{o}C$

FCVA TECHNOLOGY Applications

- Computer Hardware Technology
- Copper Coatings
- Metallization on PCB and Plastic substrates
- Super Thin Protecting Nanofilm (HDD’s etc.,)
- Oxide films such as Al_2O_3, ZnO

CVD DIAMOND TECHNOLOGY

- Most common type of Low Pressure Reactors for nanofilm:
  - Both Film Reactor
  - Microwave Plasma Enhanced Reactor

- All CVD process require activating gas phase using Plasma activation or use of oxy-acelytene flame.

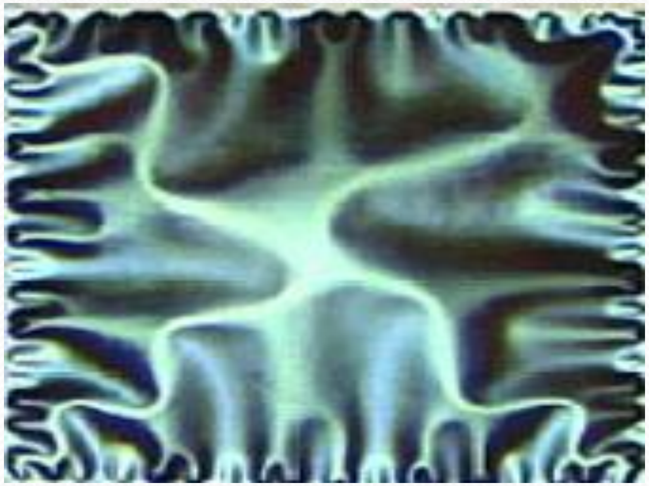
- Temp: 1000-1400k

- The surface morphology of the nanofilms by CVD depends critically upon the gas mixing ration and the substrate temperature.

- Various substrates are: Si, Mo, W etc

THIN FILM APPLICATIONS

Solid Fuel Cells: (nanostructured) thin film solid electrolytes and electrodes with high conductance

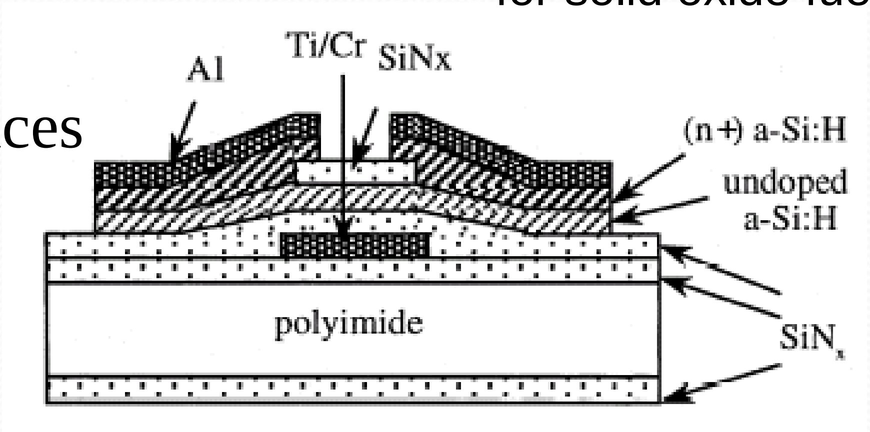


100 nm sputtered YSZ film for solid oxide fuel cells

Thin Film Transistors for liquid crystal displays: requires high mobility and flexible substrates

Gas sensing applications

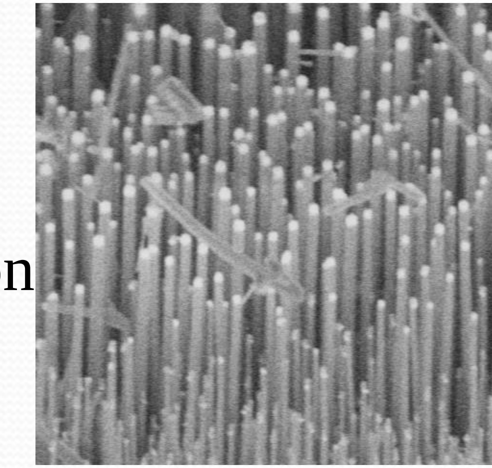
Thin layers in electronic devices



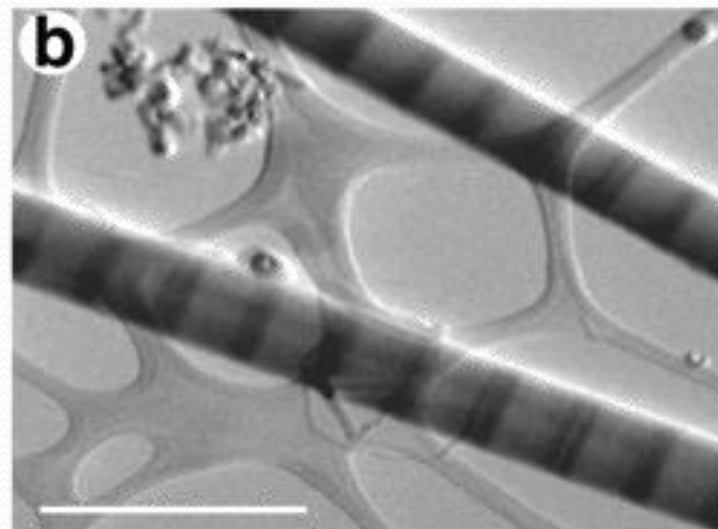
Amorphous Si TFT on a SiN_x passivated polyimide foil

NANOWIRES

- Solid, “one dimensional”
- Can be conducting, semiconducting, insulating
- Can be crystalline, low defects
- Can exhibit quantum confinement effects (electron phonon)
- Narrowing wire diameter results in increase in band gap
- Narrowing wire diameter can result in decrease in thermal conductivity
- New forms include core-shell and superlattice nanowires



Si Nanowire Array



Si/SiGe Nanowires

Nanotube defined – a long cylinder with inner and outer nm-sized diameters

Nanowire defined – a long, solid wire with nm diameter

NANOWIRE APPLICATIONS

Field effect transistors

Thermoelectric materials

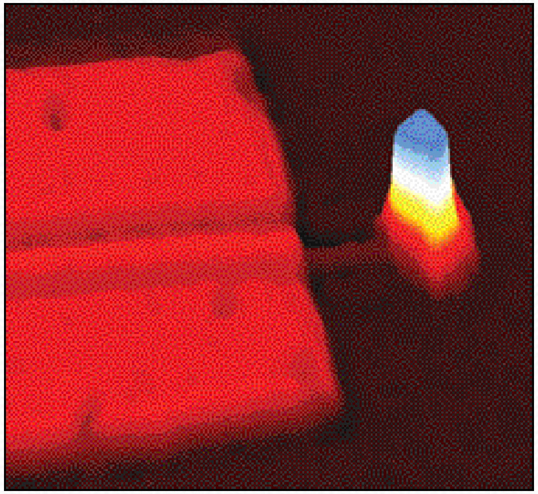
Light emitting diodes

Detectors

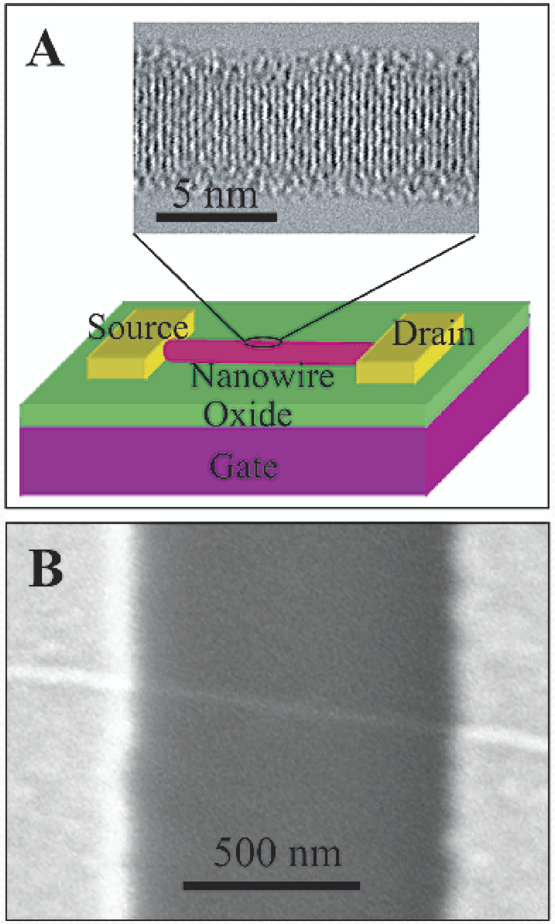
Sensors

Nanolasers

Superlattice nanowires applications requiring



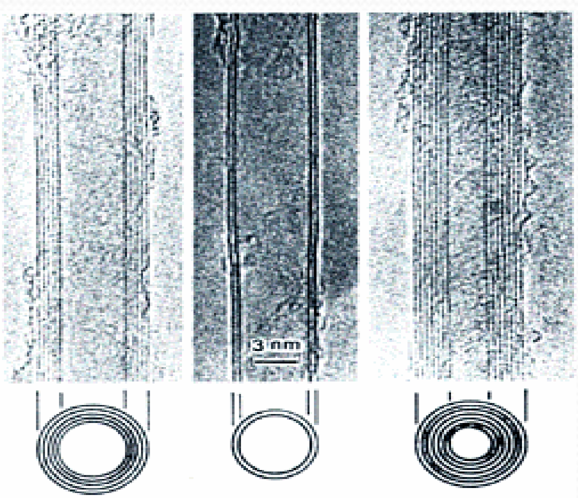
Nanolaser from 100 nm CdSe nanowire



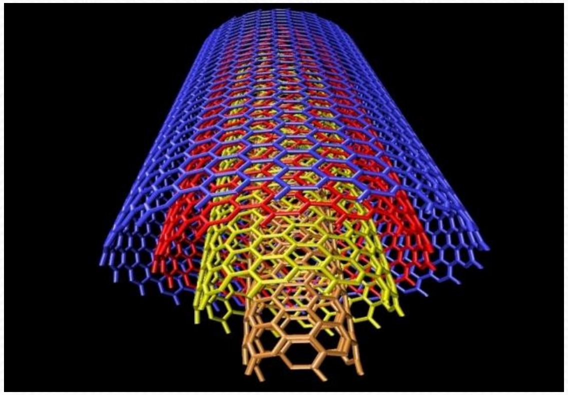
5 nm Si nanowire FET

NANOTUBES

- Single-wall carbon nanotubes are a new form of carbon made by rolling up a single graphite sheet to a narrow but long tube closed at both sides by fullerene-like end caps.
- However, their attraction lies not only in the beauty of their molecular structures: through intentional alteration of their physical and chemical properties fullerenes exhibit an extremely wide range of interesting and potentially useful properties.



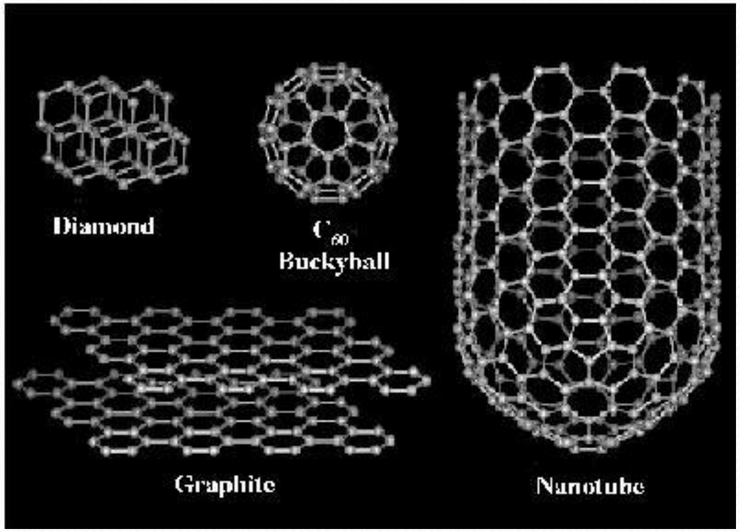
(From Iijima, Nature 1991)



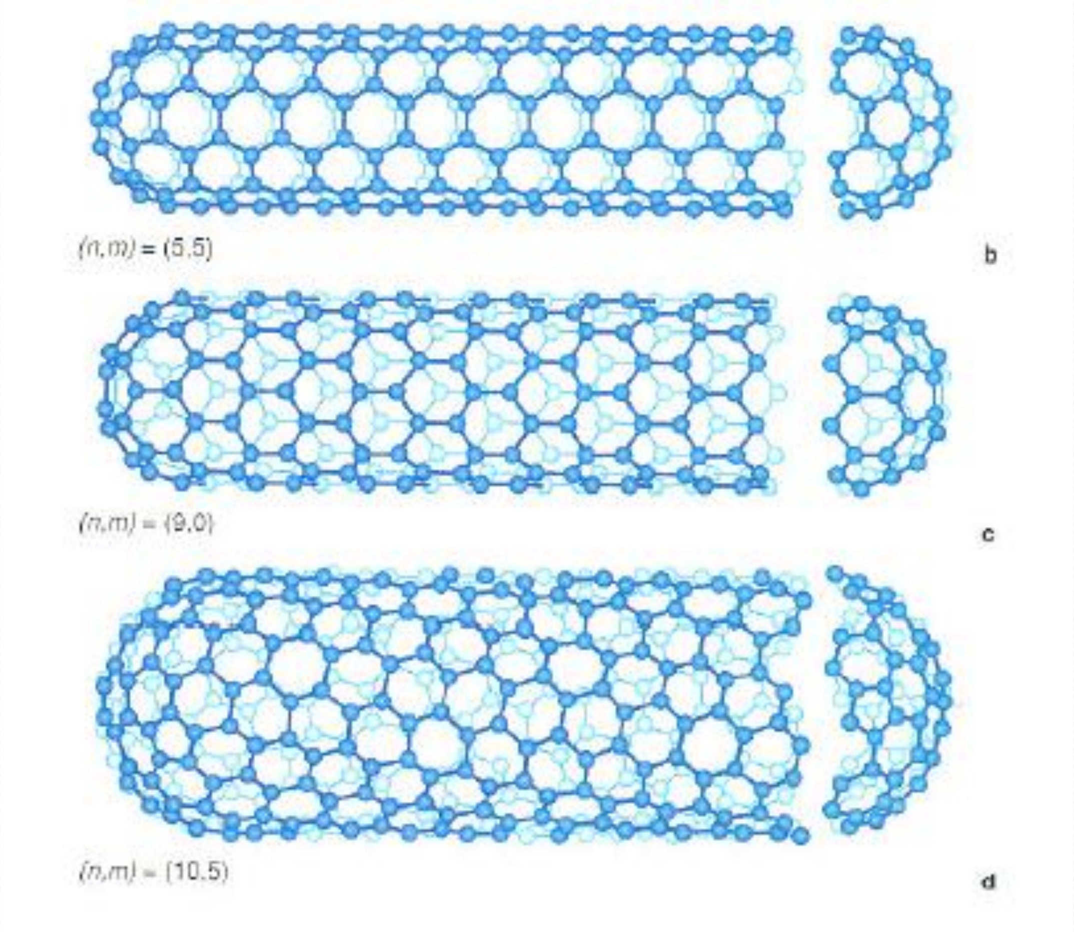
(Copyright: A. Rochefort, Nano-CERCA, Univ. Montreal)

NANOTUBES

- Carbon-60 "Buckyball" (1 nm)
- Rolled sheets of graphite (graphene)
- Three conformations
  - armchair (top-to-bottom)
  - zigzag (side-to-side)
  - chiral (corner-to-corner)
- Single, Multi-walled (SWNT, MWNT)



TYPES OF NANOTUBES



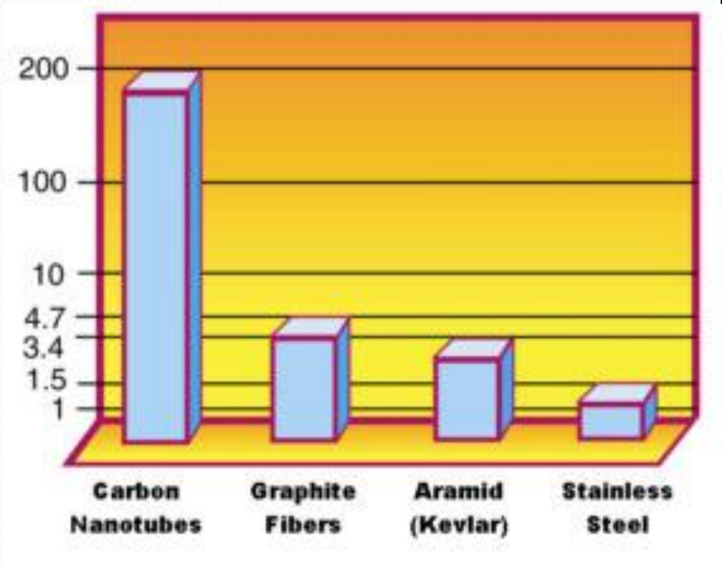
Armchair (n,m) = (5,5)
$\theta = 30^\circ$

Zig Zag (n,m) = (9,0)
$\theta = 0^\circ$

Chiral (n,m) = (10,5)
$0^\circ < \theta < 30^\circ$

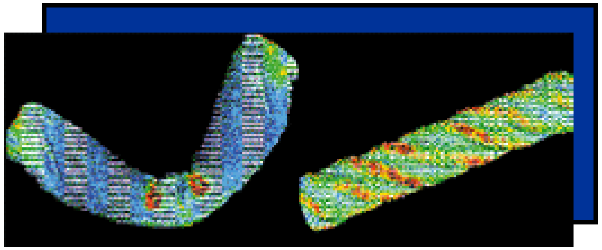
PROPERTIES OF NANOTUBES

- The chart compares the tensile strength of SWNT's to some common high-strength materials.
- Nanotubes can be either electrically conductive or semiconductive, depending on their helicity.
- These one-dimensional fibers exhibit electrical conductivity as high as copper, thermal conductivity as high as diamond,
- Strength 100 times greater than steel at one sixth the weight, and high strain to failure.
- Current length limits are about one millimeter.

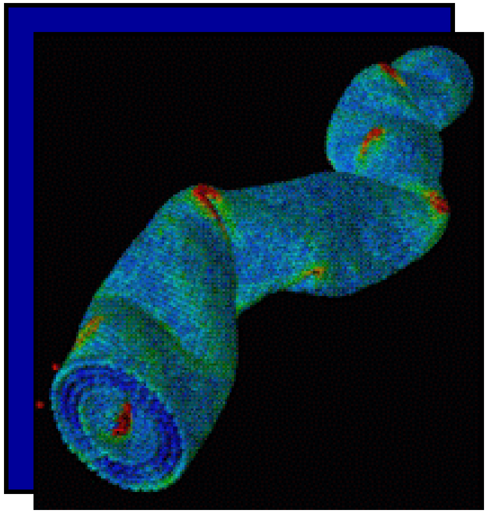


PROPERTIES OF NANOTUBES

- The strongest and most flexible molecular material because of C-C covalent bonding and seamless hexagonal network architecture



- Young's modulus of over 1 TPa vs 70 GPa for Aluminum, 700 GPA for C-fiber
  - strength to weight ratio 500 time > for Al; similar improvements over steel and titanium; one order of magnitude improvement over graphite/epoxy



- Maximum strain ~10% much higher than any material

- Thermal conductivity ~ 3000 W/mK in the axial direction with small values in the radial direction

PROPERTIES OF NANOTUBES (Contd)

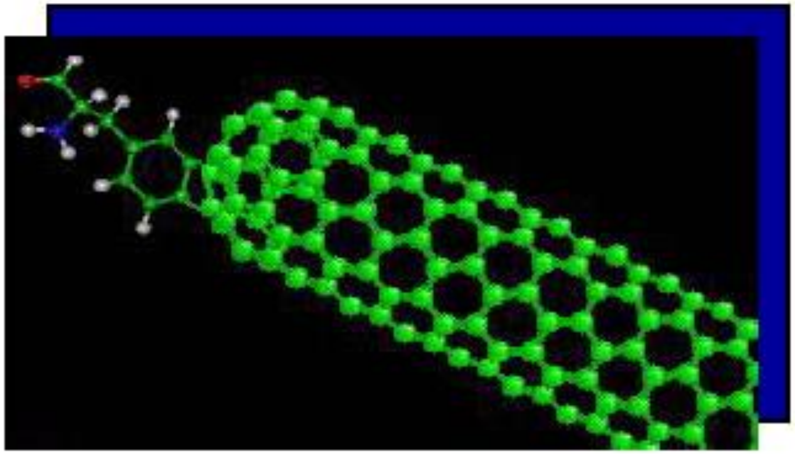
- Electrical conductivity six orders of magnitude higher than copper

- Can be metallic or semiconducting depending on chirality
    - 'tunable' bandgap
    - electronic properties can be tailored through application of external magnetic field, application of mechanical deformation…

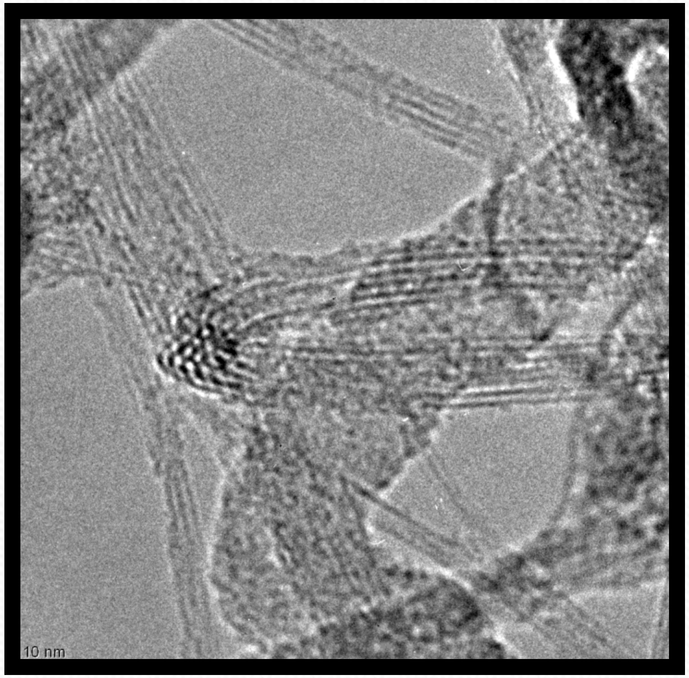
- Very high current carrying capacity

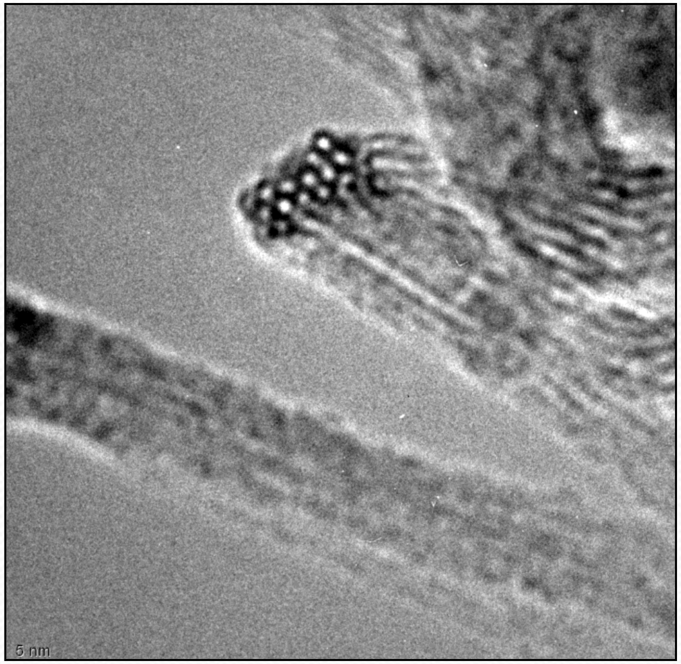
- Excellent field emitter; high aspect ratio and small tip radius of curvature are ideal for field emission

- Can be functionalized



NANOTUBES



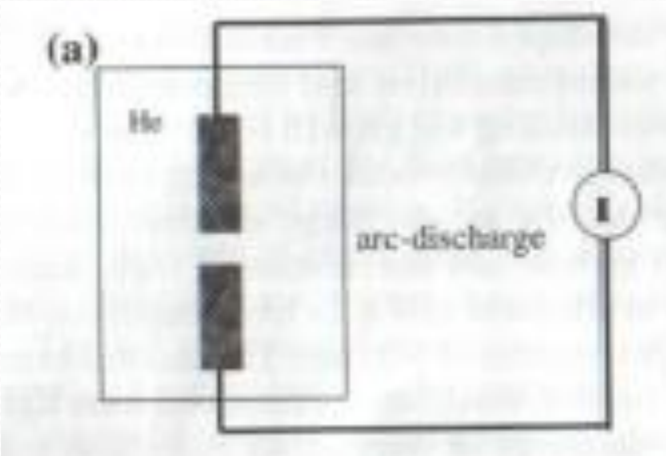


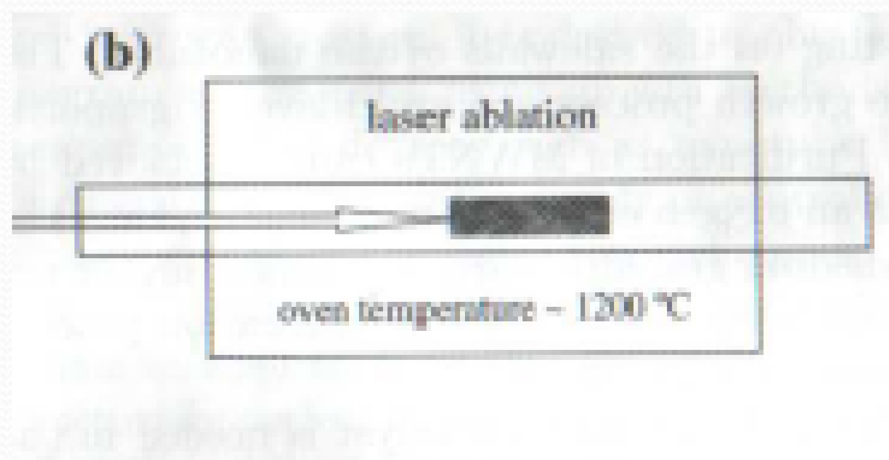
SEM of Multi-walled Carbon Nanotubes (MWNT)

Nanotubes Growth Method

a) Arc Discharge   b) Laser Abalation

- Involve condensation of C-atoms generated from evaporation of solid carbon sources. Temperature ~ 3000-4000K, close to melting point of graphite.
- Both produce high-quality SWNTs and MWNTs.
- MWNT: 10's of μm long, very straight & have 5-30nm diameter.
- SWNT: needs metal catalyst (Ni,Co etc.).
- Produced in form of ropes consisting of 10's of individual nanotubes close packed in hexagonal crystals.

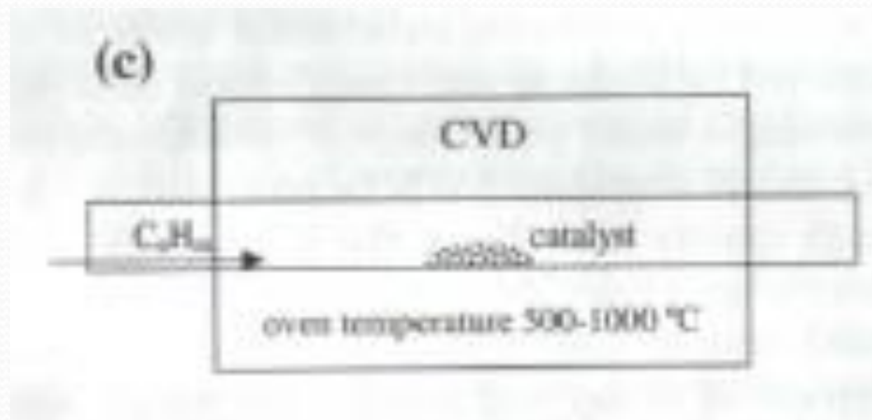




Nanotubes Growth Method

c) Chemical Vapor Deposition:

Hydrocarbon + Fe/Co/Ni catalyst $\xrightarrow{550\text{-}750^{\circ}C}$ CNT



Steps:

- Dissociation of hydrocarbon.
- Dissolution and saturation of C atoms in metal nanoparticle.
- Precipitation of Carbon.

Choice of catalyst material?

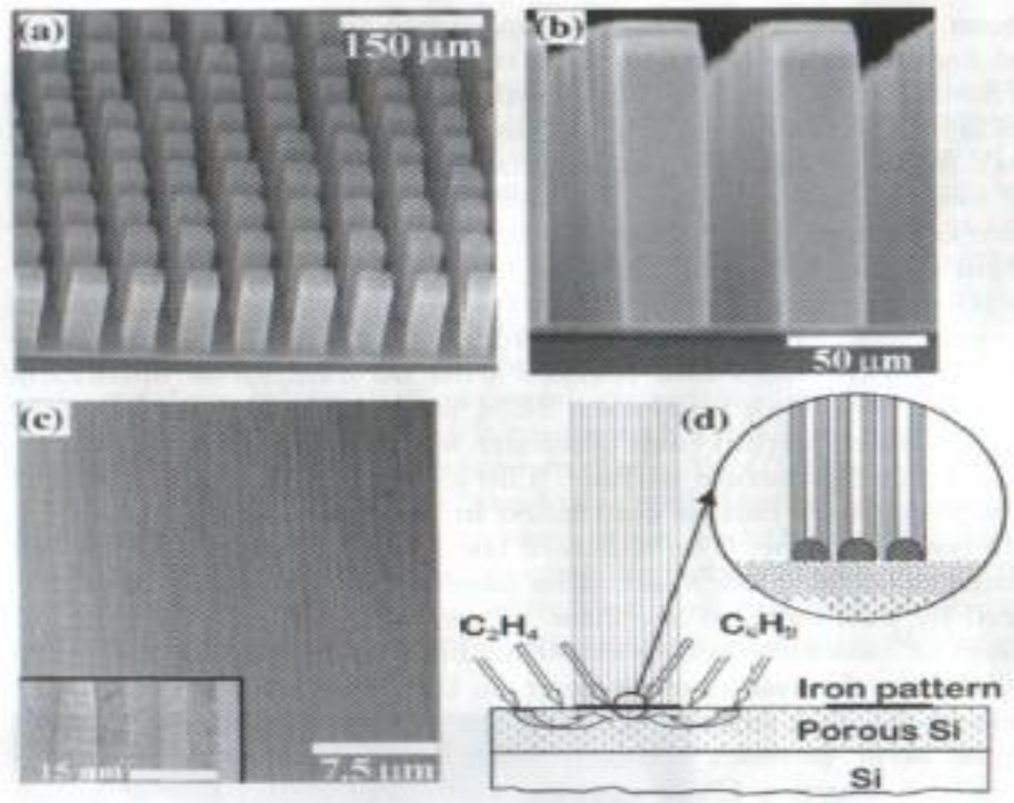
Base Growth Mode or Tip Growth Mode?

- Metal support interactions

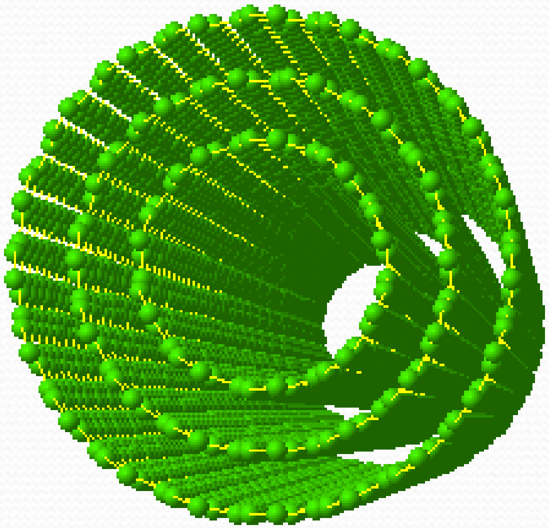
Controlled Growth by CVD

Methane + Porous Si + Fe pattern $\xrightarrow{\text{CVD}}$ Aligned MWNTs

a) SEM image of aligned nanotubes.
a) SEM image of side view of towers. Self-alignment due to Van der Walls interaction.
a) High magnification SEM image showing aligned nanotubes.
d) Growth Process: Base growth mode.

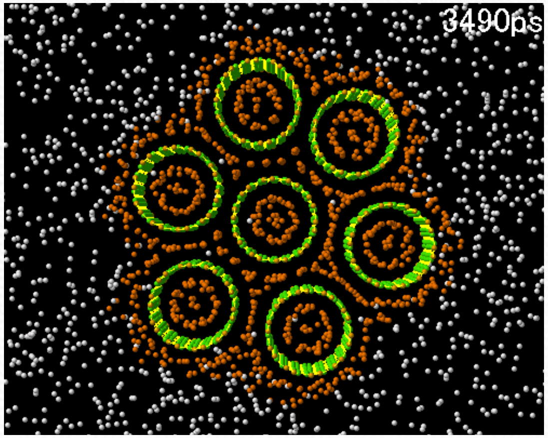


Uses of Carbon Nanotubes: Present and Future



- Light-weight, high-strength materials
  - tennis rackets (“nanotube nylon”)
  - bullet-proof vests
  - space elevator
- Conductive materials
  - “quantum wires”
  - fuel cell application (using Pt electrode)
- Biosensors and Biomedical materials
  - soluble nanotubes (more applications)

Carbon Nanotubes - Applications

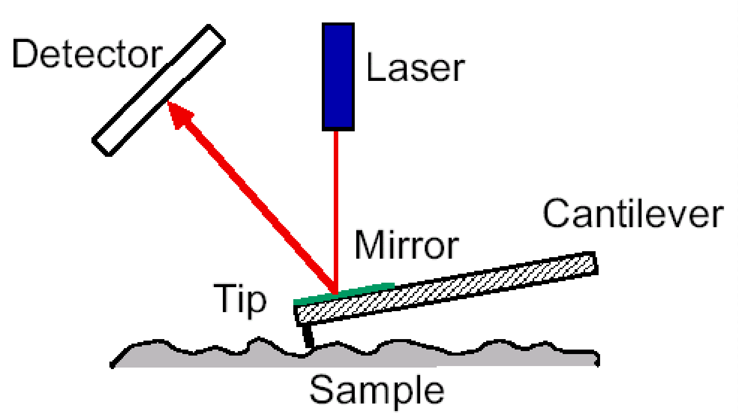


- Molecular transistors.
- Field emitters.
- Building blocks for bottom-up electronics.
- Smaller, lighter weight components for next generation spacecraft.
- Enable large quantities of hydrogen to be stored in small low pressure tanks.
- Space elevator, Instead of blasting off for the heavens astronauts could reach the ISS as easily as they would a department store !!

Atomic Force Microscope (AFM)

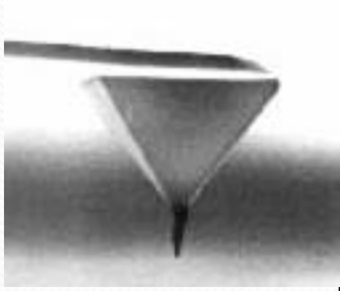
The optical microscope – cannot see features smaller than ~half the wavelength of light

Can we use something other than light and lenses?



AFM basic components:

- Tip (<~10 nm diameter) on a cantilever
- Detector (generally position)
- Raster-scan (to drag tip)
- Force/height control
- Image processing software



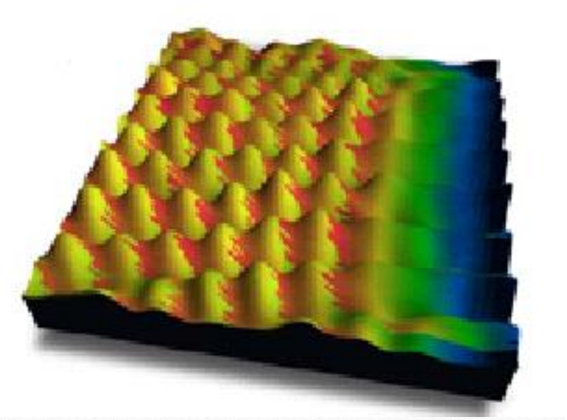


Image of graphite using an AFM

Lateral resolution 0.1 nm Vertical resolution 0.02 nm

Scanning Electron Microscope (SEM)

Instead of light, the SEM uses electrons to see 3-D images

SEM operation:

• Air pumped out (vacuum)

• e^- gun emits beam of high energy electrons

• e^- beam focused via lenses

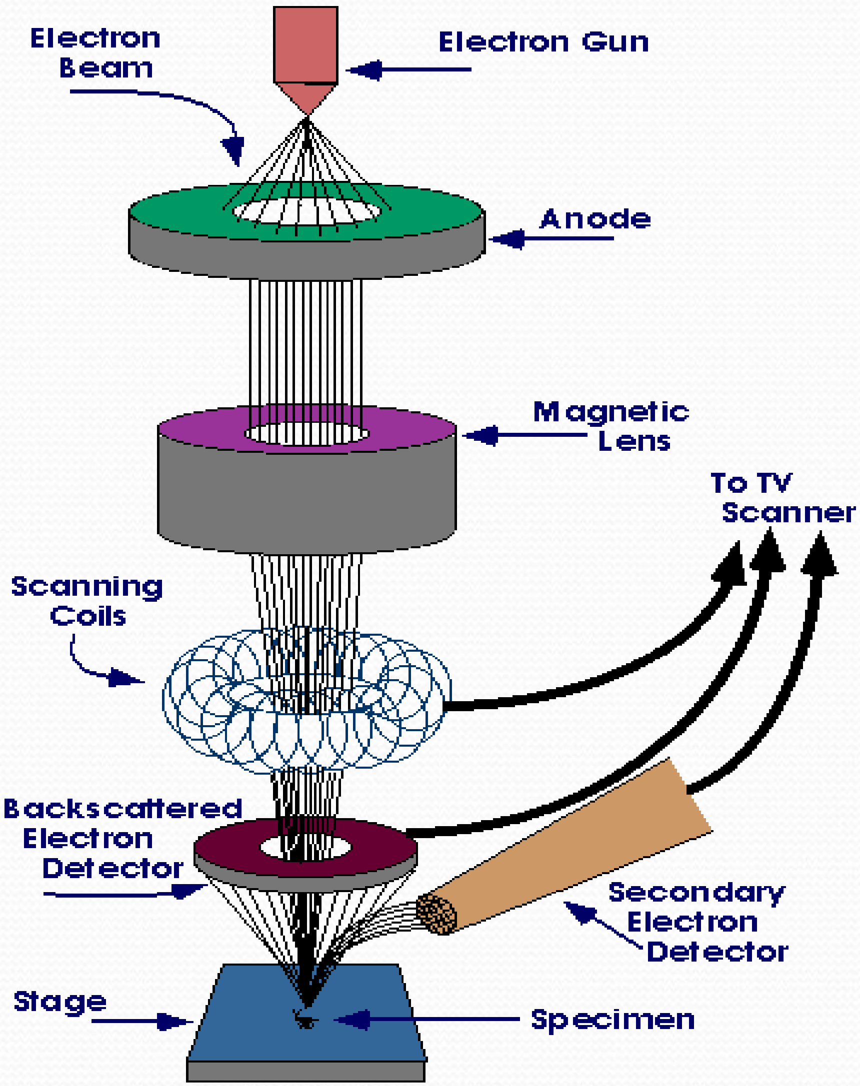
• Scanning coils move beam across sample

• Secondary electrons are “knocked off” surface

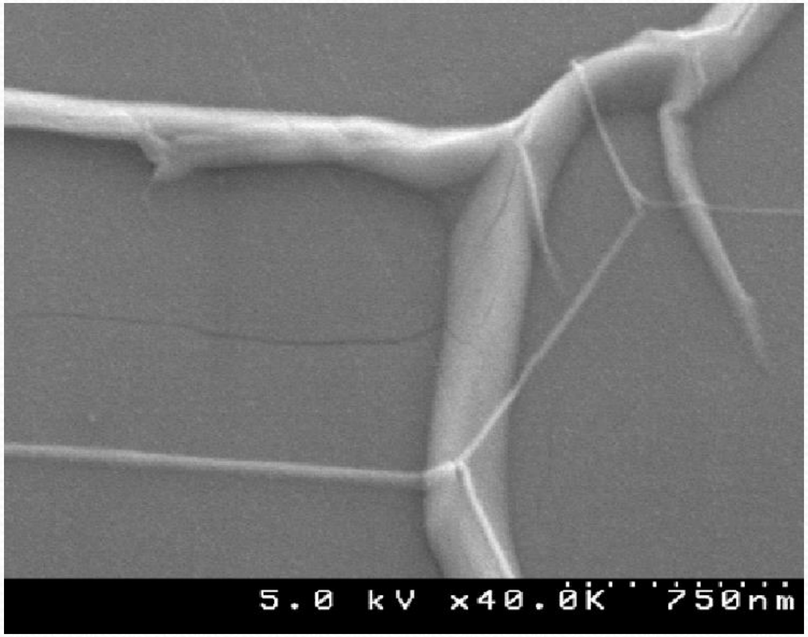
• Detector counts electrons

• Image given by # e^-

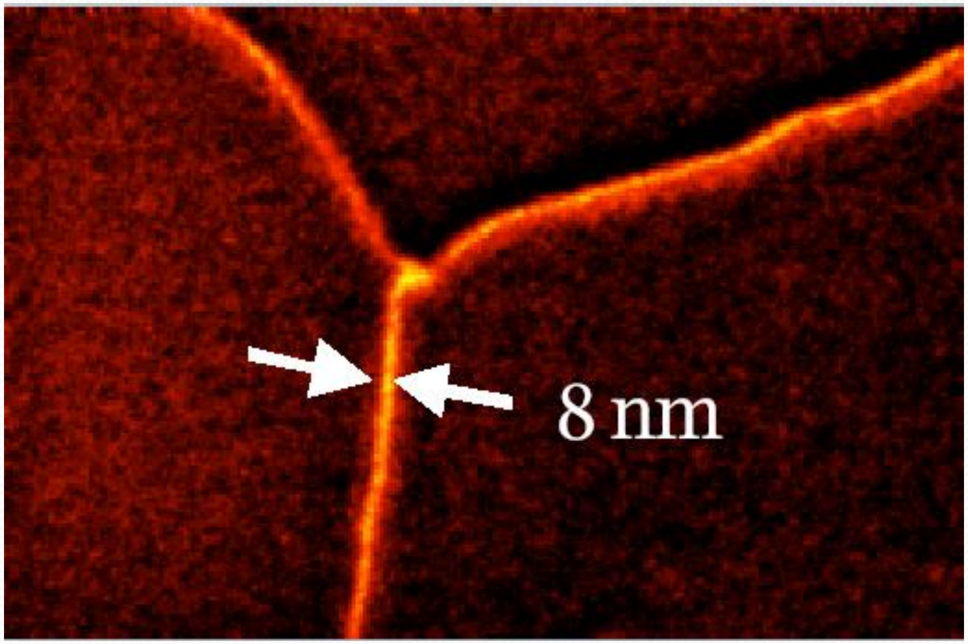
Resolution ~5 nm



SEM & AFM Images



SEM: Cu Nanowires



AFM: Cu Nanowires

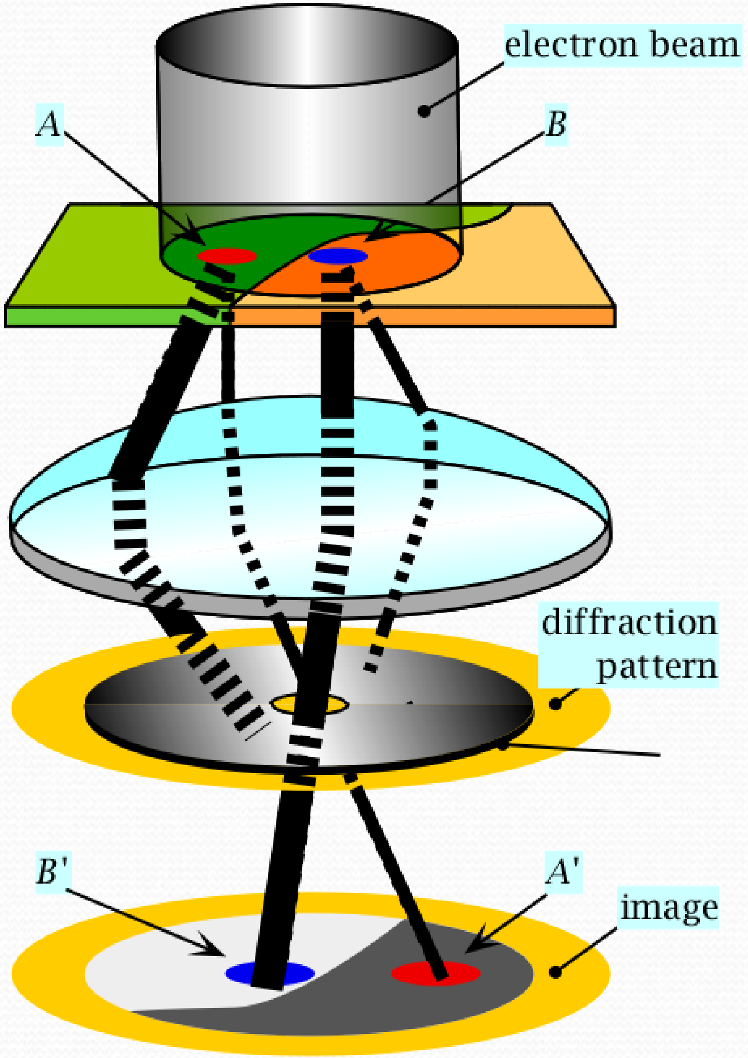
Transmission Electron Microscope (TEM)

A TEM works like a slide projector but with e$^-$ instead of light

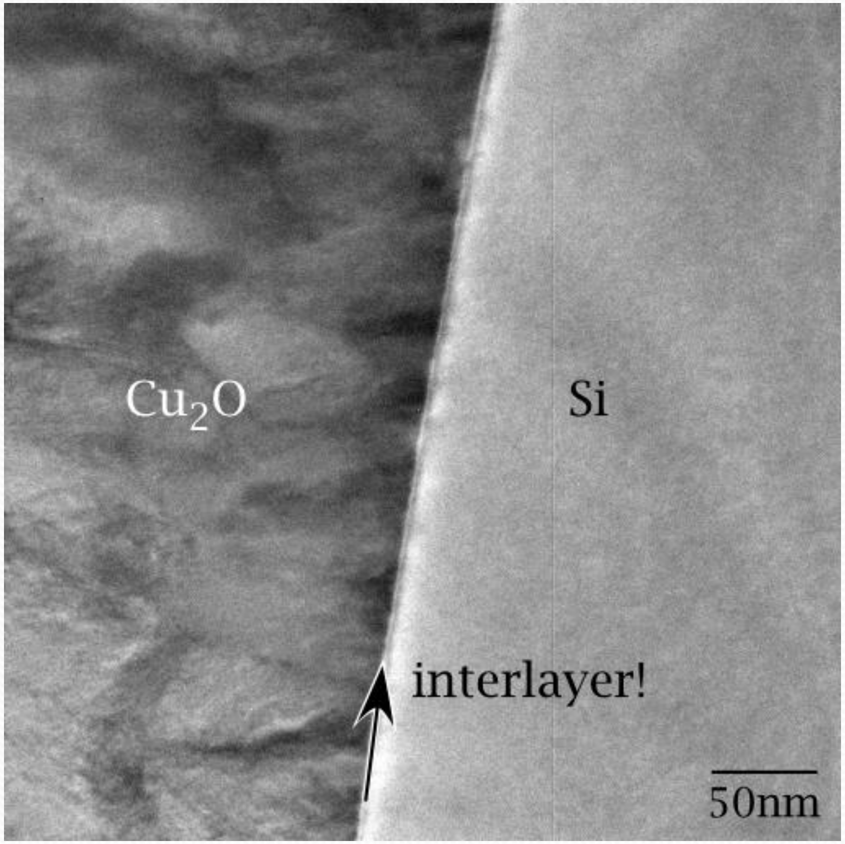
TEM operation:

- Air pumped out (vacuum)
- e$^-$ gun emits beam of high energy e$^-$
- e$^-$ beam focused via lenses
- Beam strikes sample and some e$^-$ are transmitted
- Transmitted e$^-$ are focused, amplified
- Image contrast enhanced by blocking out high-angle diffracted e$^-$
- Image passed through lenses and enlarged
- When image hits phosphor screen, light is generated

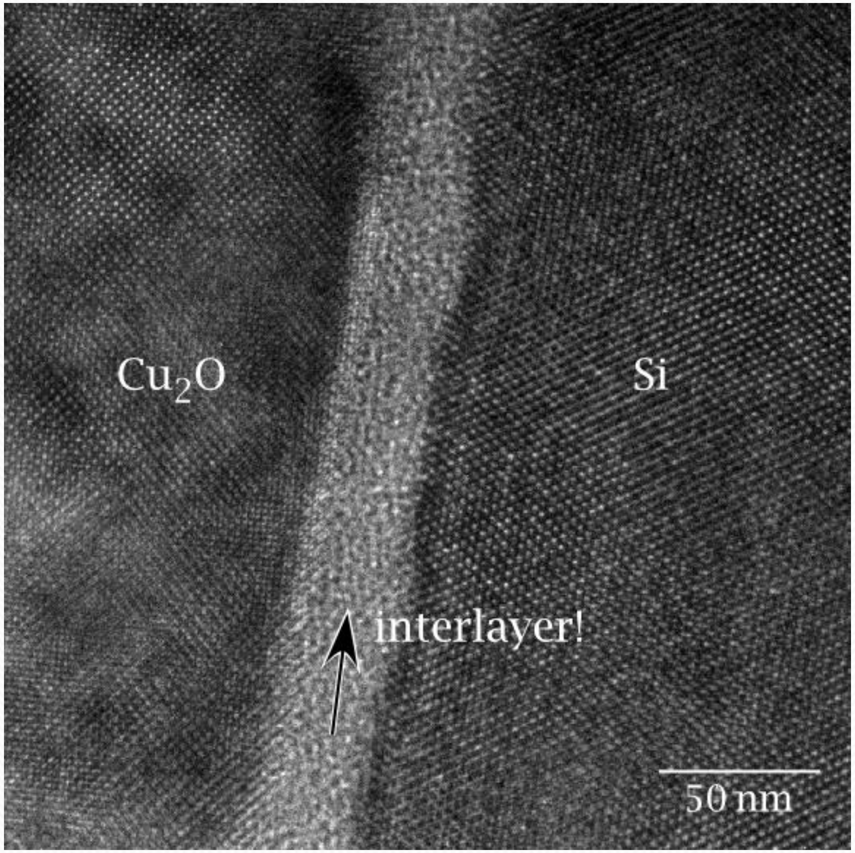
Resolution ~<1 nm



TEM Images



Standard TEM



High resolution TEM

APPLICATIONS OF NANOMATERIALS

- Tougher & Harder cutting Tools
- Machinable Ceramics
- Good Insulation Materials
- High Energy Batteries
- High Energy Magnets
- Catalysts
- Aerospace Materials
- High Sensitivity Sensors
- Weapon Platforms
- Potential Penetrators
- Automobiles
- Propellant Fuels

THANK YOU