



# Semiconductor Physics and Computational Methods (21PYB102J)

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# **DEPARTMENT OF PHYSICS AND NANOTECHNOLOGY SRM INSTITUTE OF SCIENCE AND TECHNOLOGY**

## **MODULE 5**

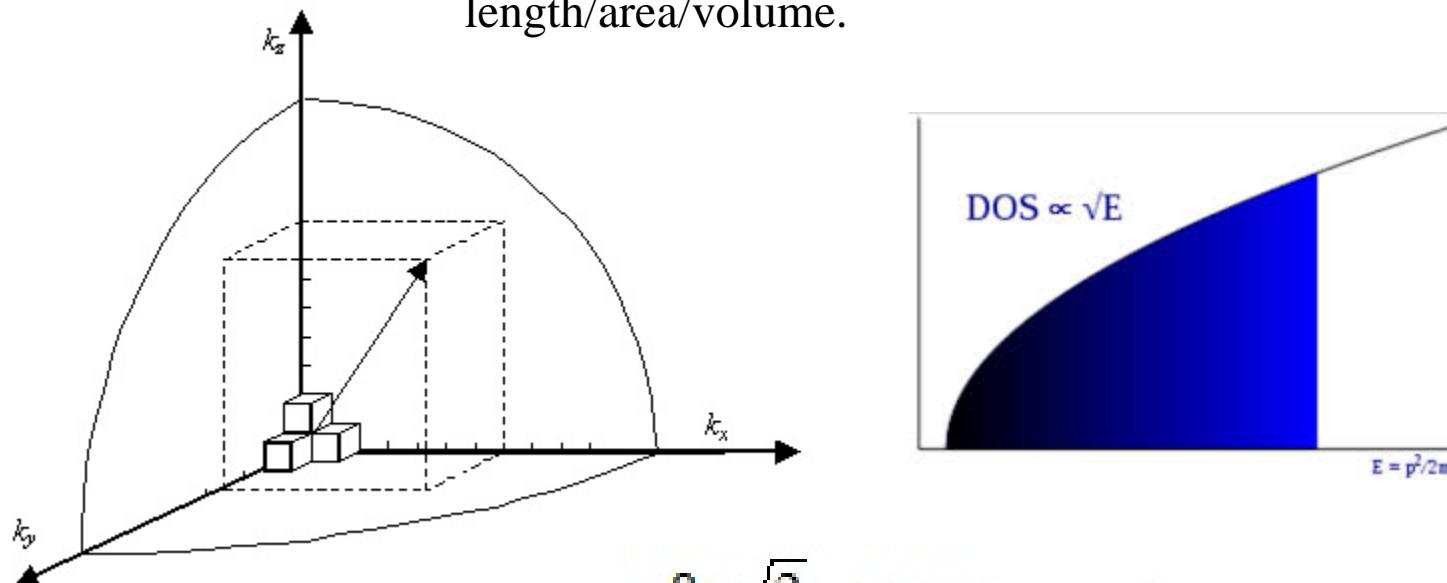
### **Density of states in 2D, 1D and 0D**

# Density Of States

- The density of states function describes the number of energy states that are available in a system and is essential for determining the carrier concentrations and energy distributions of carriers within a semiconductor.
- In semiconductors, the free motion of carriers is limited to two, one and zero spatial dimensions. When applying semiconductor statistics to systems of these dimensions, the density of states in quantum well (2D), quantum wires (1D) and quantum dots (0D) must be known.

# Density of states in 3D

The number of allowed single-particle (electron/ hole) states with energies between  $E$  and  $E+dE$ , in an element of length/area/volume.



$$g_c(E) = \frac{8\pi\sqrt{2}}{h^3} m^{3/2} \sqrt{E - E_c}, \text{ for } E \geq E_c$$

# Density of states in lower-dimensional systems

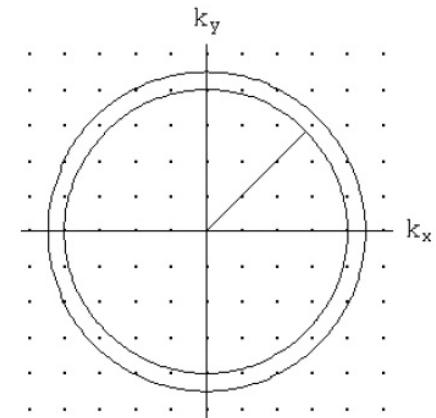
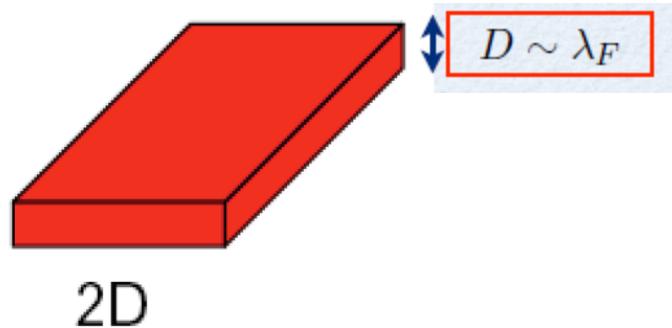
- Three-dimensional electron or hole obtained by doping semiconductors are not ideal for studying quantum effects for two reasons: (i) they are strongly disordered owing to the background of ionized impurities and (ii) the most quantum effects are more pronounced in lower-dimensional systems than those of bulk constituents.
- Therefore, reduction in the dimensionality of a physical system has profound consequences on its profile and new types of electronic and photonic devices can be designed. These devices make use of electron motion through potentials that change rapidly on a length scale comparable to the wavelength associated with the electron and they operate on the rules of quantum mechanics.
- The low dimensional semiconductor systems play a critical role in determining the properties of materials due to the different ways that electrons interact in two-dimensional, one-dimensional and zero-dimensional structures.

# Density of states in lower-dimensional systems

- A low-dimensional system is one where the motion of microscopic degrees-of-freedom, such as electrons, phonons or photons, is restricted from exploring the full three dimensions of the present world.
- In the low dimensional quantum systems such as Quantum well, Quantum wire and Quantum dot, the charge carriers are free to move in two, one and zero dimensions respectively.
- This high confinement brings out new effects of great technological potential applications. Quantum mechanics plays a major role as the semiconductor size approaches the nanoscale.
- The main advantages of these low dimensional semiconductor systems are in the realizations of important devices, like the double heterostructure lasers with low threshold at room temperature, high effective LEDs, bipolar transistors, p-n-p-n switching devices, high electron mobility transistors (HEMT) and many other optoelectronic devices.

# Density of states in 2D

- Quantum effects arise in systems which confine electrons to regions comparable to their de Broglie wavelength. When such confinement occurs in one dimension only (say, by a restriction on the motion of the electron in the z-direction), with free motion in the x- and y-directions, a two-dimensional system is created.
- Consider a slab of material that has macroscopic dimensions in the x- and y directions while the thickness is small (in the nanometer range-Quantum Well).



# Density of states in 2D

$$k = n\pi/L$$

Where  $n=1, 2, 3 \dots$

In k-space diagram, each energy state occurs at  $\pi/L$

$$\text{Then Area} = (\pi/L)^2$$

The number of states  $N$  within a circle with radius  $k$  is then

$$N = ([1/4^{\text{th}} \text{ Area of circle}] \times \text{electron spin}) / \text{Area of energy state}$$

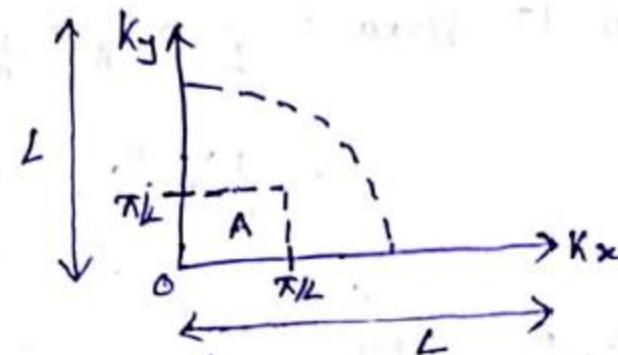
$$N = \frac{1}{4} \pi k^2 \times \left(\frac{L}{\pi}\right)^2 \times 2$$

Differentiating with respect to  $k$

$$\frac{dN}{dk} = \frac{L^2}{\pi} k$$

$$\frac{dN dE}{A} = \frac{1}{A} \cdot \frac{dN}{dk} \cdot \frac{dk}{dE}$$

Then DOS in 2D systems =



# Density of states in 2D

To find  $\frac{dk}{dE}$ , we know that

Therefore,  $\frac{dE}{dk} = \frac{\hbar^2 k}{m} \Rightarrow \frac{dk}{dE} = \frac{m}{\hbar^2 k}$

Then DOS in 2D systems =  $\frac{1}{4\pi} \times \frac{\ell^2 k}{\pi} \times \frac{m}{\hbar^2 k} = \frac{m}{\hbar^2 \pi}$

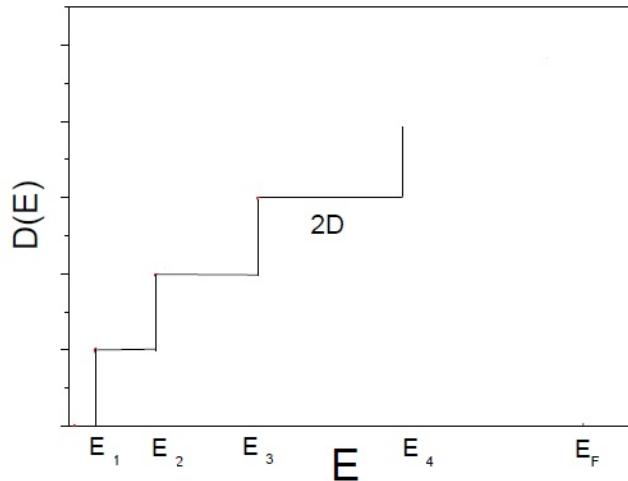
$$= \frac{4\pi^2 m}{h^2 \pi} = \boxed{\frac{4\pi m}{h^2}}$$

where  $\left[ \because \frac{\hbar^2}{k} = \frac{h^2}{4\pi^2} \right]$

DOS in 2D systems =  $\frac{4\pi m}{h^2}$

# Density of states in 2D

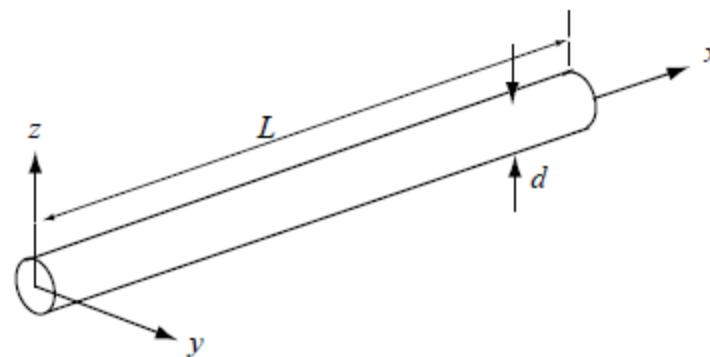
- It is important to notice that the 2D density of states is independent of the energy. However, DOS depends on the number of levels and is thus a sum of the contributions from the discrete levels appearing as a result of the quantization.



Density of states for a 2D system.

# Density of states in 1D

- Quantum effects in systems which confine electrons to regions comparable to their de Broglie wavelength. When such confinement occurs in two dimensions only (say, by two restrictions on the motion of the electron in the z- and y-directions), with free motion in the x-direction, a one-dimensional system is created.

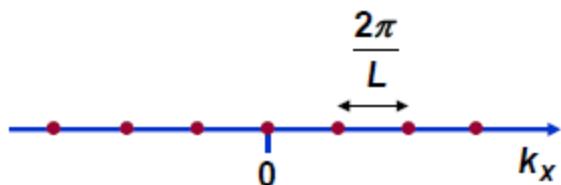


# Density of states in 1D

- Consider a systems where electrons are free to move in one direction and confined in the other two directions (Quantum wire).
- In one dimension two of the  $k$ -components are fixed, therefore the area of  $k$ -space becomes a length and the area of the annulus becomes a line.

# Density of states in 1D

- k-space Visualization: The allowed quantum states can be visualized as a 1D grid of points in the entire “k-space”
- Looking at the figure, in k-space there is only one grid point in every small length of size:  $(2\pi/L)$



$$k_x = n \frac{2\pi}{L}$$

$$n = 0, \pm 1, \pm 2, \pm 3, \dots$$

# Density of states in 1D

- Number of energy states is given by  
 $N=2k(L/\pi)$

on differentiation we get

$$\underline{dN/dk} = 2L/\pi$$

Density of states in 1D systems =

$$\frac{(dN/dE)}{L} = \frac{1}{L} \cdot \frac{dN}{dk} \cdot \frac{dk}{dE}$$

# Density of states in 1D

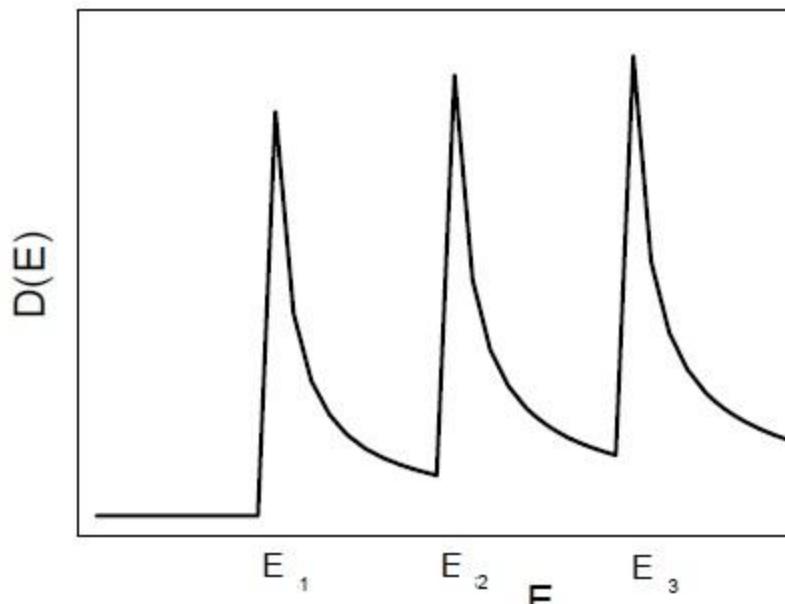
From 2D systems we know  $\frac{dE}{dk} = \frac{m}{\hbar^2 k}$  where  $k = \frac{\sqrt{2mE}}{\hbar}$

Then Density of states in 1D system =  $\frac{1}{L} \times \frac{2L}{\pi} \times \frac{m}{\hbar^2} \left[ \frac{\sqrt{2mE}}{\hbar} \right]$

$$= \frac{1}{4} \times \frac{2k}{\pi} \times \frac{m \times 2\pi}{h \sqrt{2mE}}$$

Density of states in 1D system = 
$$\boxed{\frac{2\sqrt{2}(m)^{1/2}(E)^{-1/2}}{h}}$$

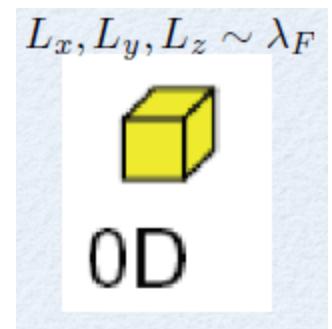
# Density of states in 1D



Density of states of a 1D system.

# Density of states in 0D

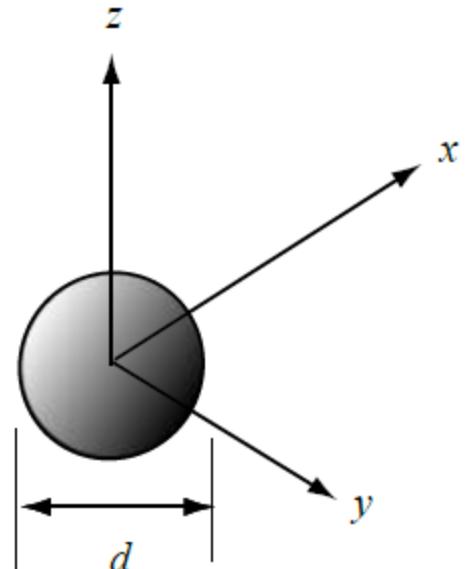
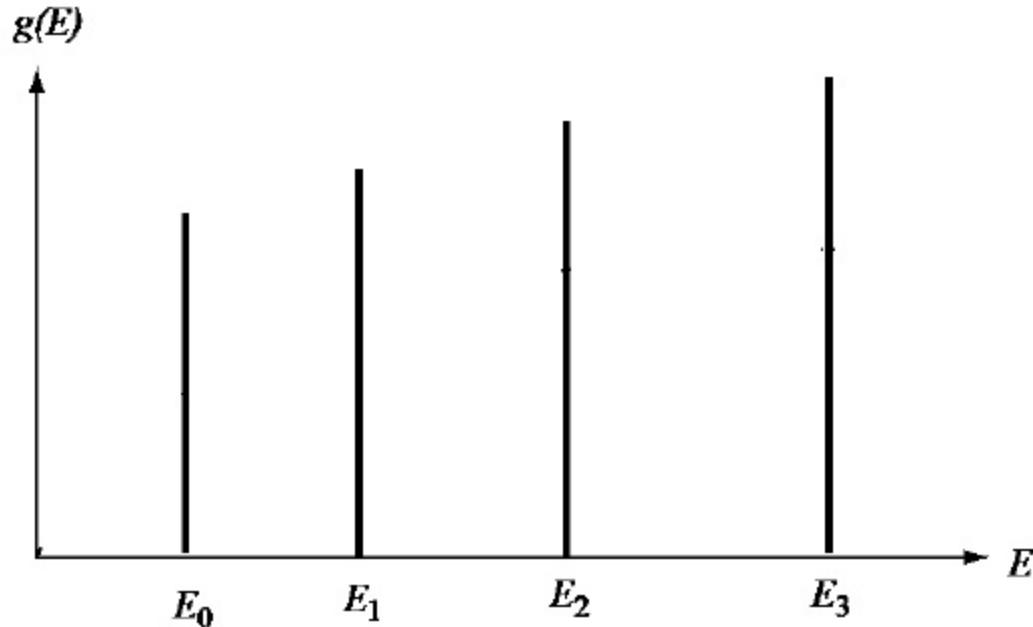
- Electrons can be confined in all three dimensions in a dot. The situation is analogous to that of a hydrogen atom: only discrete energy levels are possible for electrons trapped by such a zero-dimensional potential. The spacing of these levels depends on the precise shape of the potential.
- When considering the density of states for a 0D structure (Quantum dot), no  $k$  – space is available as all dimensions are reduced.



# Density of states in 0D

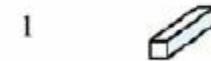
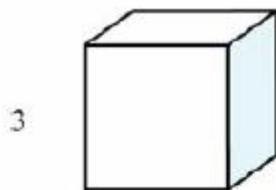
- Therefore DOS of 0D can be expressed as a delta function

$$g(E)_{0D} = 2\delta(E - E_c)$$

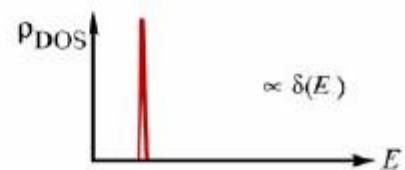
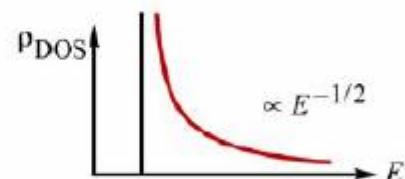
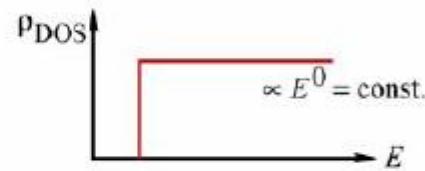
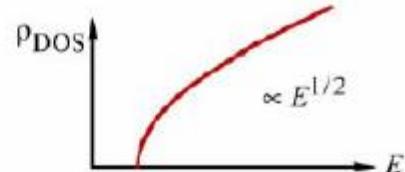


# Conclusion

Degrees of freedom



Density of states



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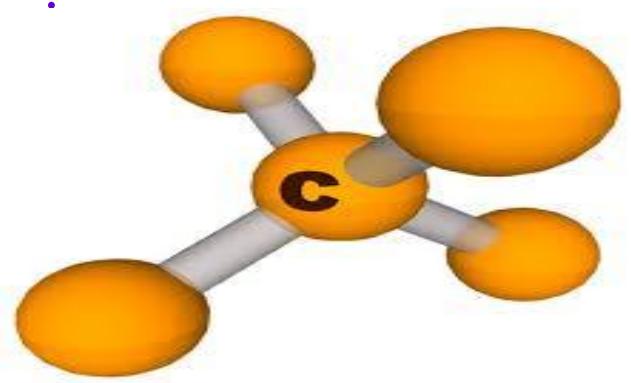
**Introduction to Low dimensional systems**

**Quantum Well, Wire, Dot**

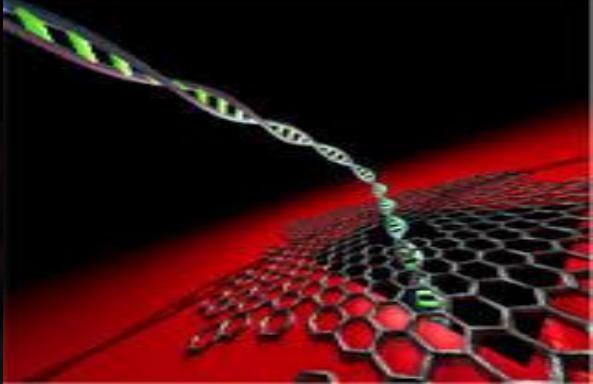
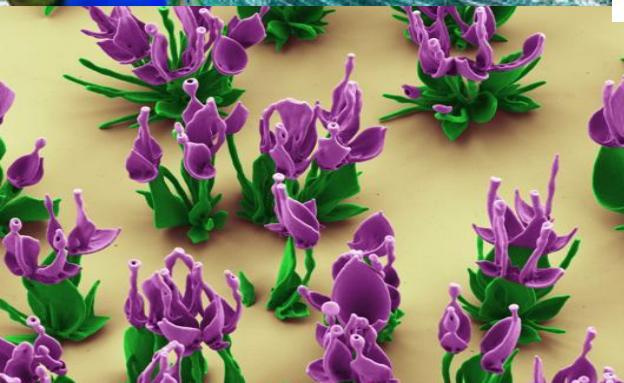


**SRM**  
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# Nanoscience & Nanotechnology



*all length scale?*



# “Nano”: How small is that, really?



Mountain  
1 km  
1000 m

$$0.001 \text{ km} = 1 \text{ m}$$



Child  
1 m



Ant  
1 mm  
0.001 m

$$1,000 \text{ mm} = 1 \text{ m}$$



Bacteria  
1  $\mu\text{m}$   
0.000001 m

$$1,000,000 \mu\text{m} = 1 \text{ m}$$



Sugar Molecule  
1 nm  
0.000000001 m

$$1,000,000,000 \text{ nm} = 1 \text{ m}$$



RICE

# What is Nano ?

- 

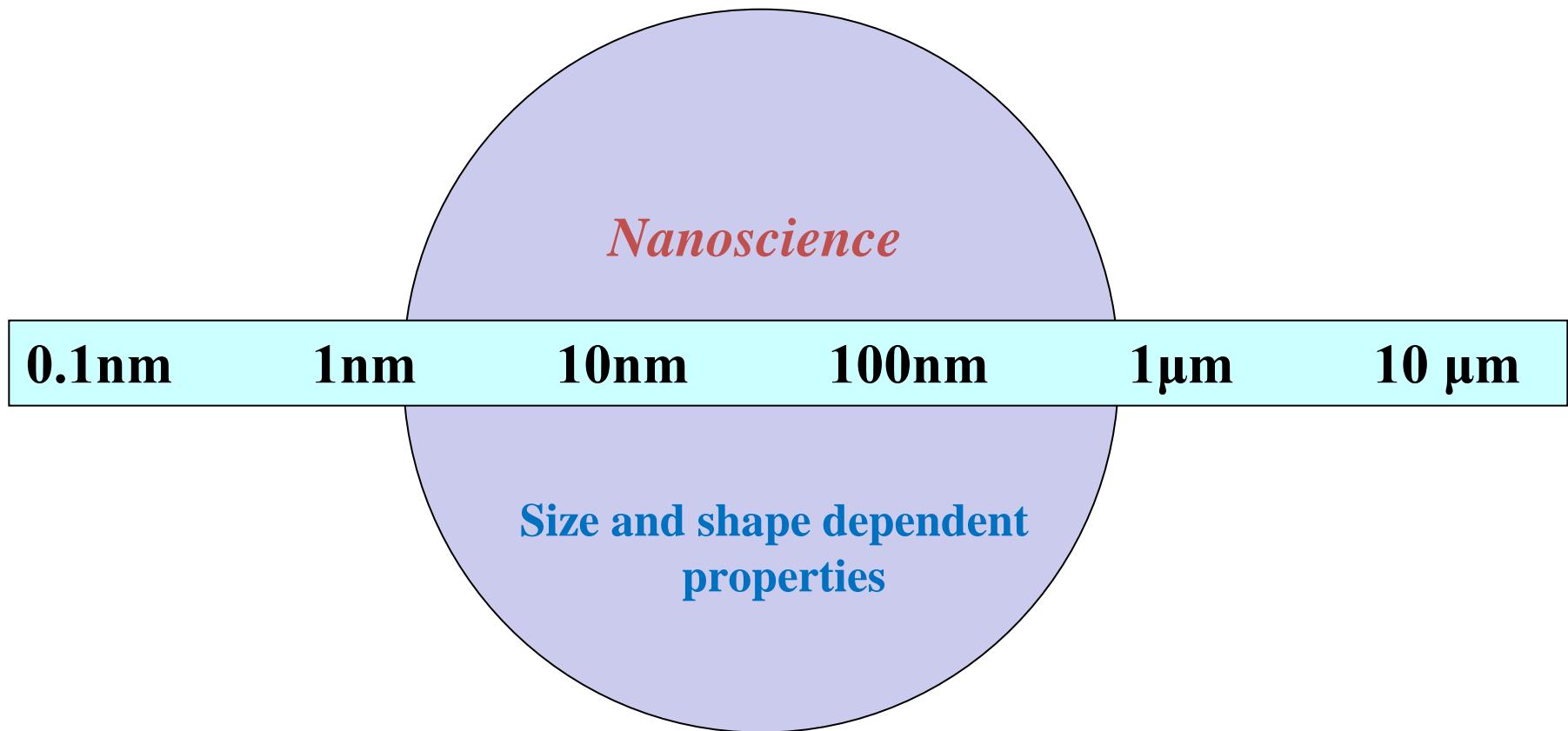
Nano - a prefix that means ***very, very, small*** !

- *Question : How small is ‘Nano’ ?*

*Answer: “One billionth” of something, or  
0.000000001.*

$$\frac{1}{1000000000} = 10^{-9}$$

# Actual physical dimensions relevant to Nanosystem

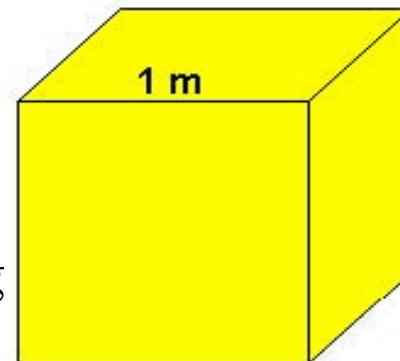


**Nanometer scale :** The length scale where corresponding property is size & shape dependent.

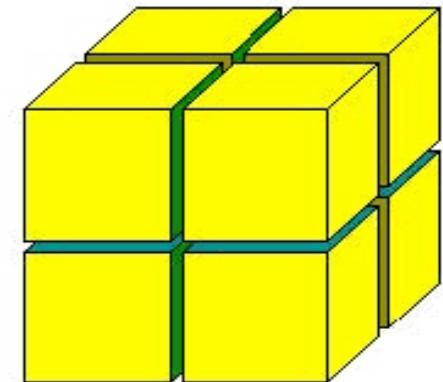
# Surface to Volume Ratio Increases

As surface to volume ratio increases

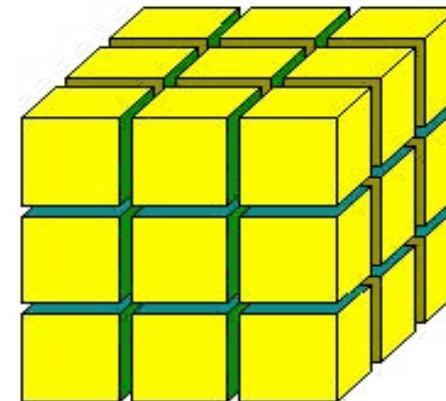
- A greater amount of a substance comes in contact with surrounding material.
- This results in better catalysts, since a greater proportion of the material is exposed for potential reaction.



$$\text{Area} = 6 \times 1\text{m}^2 = 6 \text{ m}^2$$



$$\text{Area} = 6 \times (1/2\text{m})^2 \times 8 = 12 \text{ m}^2$$



$$\text{Area} = 6 \times (1/3\text{m})^2 \times 27 = 18 \text{ m}^2$$

# What's interesting about the nanoscale?

- Nano sized particles exhibit different properties than larger particles of the same substance.
- Nano sized particle exhibit size & shape dependent properties.

**How do properties  
change at the  
Nanoscale ?**

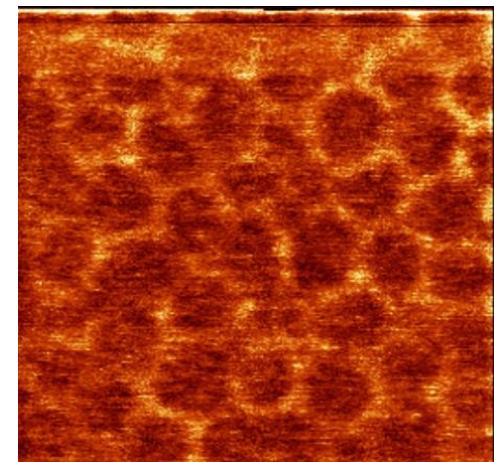
# Optical Properties: Colour of Gold

- **Bulk gold**  
appears **yellow** in colour.



- **Nano sized gold**  
appears **red** in colour.

The particles are so small that electrons are not free to move about as in bulk gold. Because this movement is restricted, the particles react differently with light.



12 nanometer gold clusters of particles look red.

Sources:

<http://www.sharps-jewellers.co.uk/rings/images/bien-hccncsq5.jpg>

<http://www.foresight.org/Conferences/MNT7/Abstracts/Levi/>

# Nanoscience: Nanometer scale science

- A part of science that studies small stuff

So, what is ***Nano science*** ?

- It is not only Biology.
- It is not only Physics .
- It is not only Chemistry.
- It is **all sciences** that work with the very small.

□ ***Nanoscience is not physics, chemistry, engineering or biology. It is all of them.***

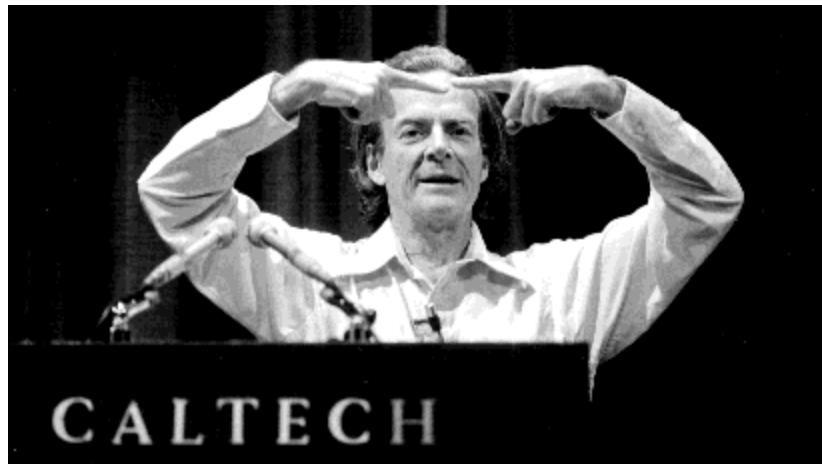
S.M. Lindsay, Introduction to Nanoscience,  
Oxford University Press (2009).

# *Interdisciplinary*

- **Physicists:** physical forces between the individual atoms composing them – quantum effects  
**Chemists :** The interaction of different molecules is governed by chemical forces.  
**Biologists :** creation of small devices (encoding informations in DNA to perform multitasks)  
**Computer Scientists :** *Steady miniaturization* : - Moore's Law and its corollaries, the phenomena whereby the price performance, speed, and capacity of almost every component of the computer.  
**Electrical Engineers :** a steady supply of power. A control of electric signals is also vital to transistor switches and memory storage.  
**Mechanical Engineers:** nanolevel issues such as load bearing, wear, material fatigue, and lubrication

# *What makes the nanoscale special?*

- 1) High density of structures is possible with small size.
- 2) Physical and chemical properties can be different at the nano-scale (e.g. *electronic, optical, mechanical, thermal, chemical*).
- 3) The physical behavior of material can be different in the nano-regime because of the different ways physical properties scale with dimension (e.g. area vs. volume).



***Prof. Richard Feynman***  
***“There’s plenty of room at the bottom”***

Dr. Richard P. Feynman

- *“Why cannot we write the entire 24 volumes of the Encyclopedia Britannica on the head of a pin?”*

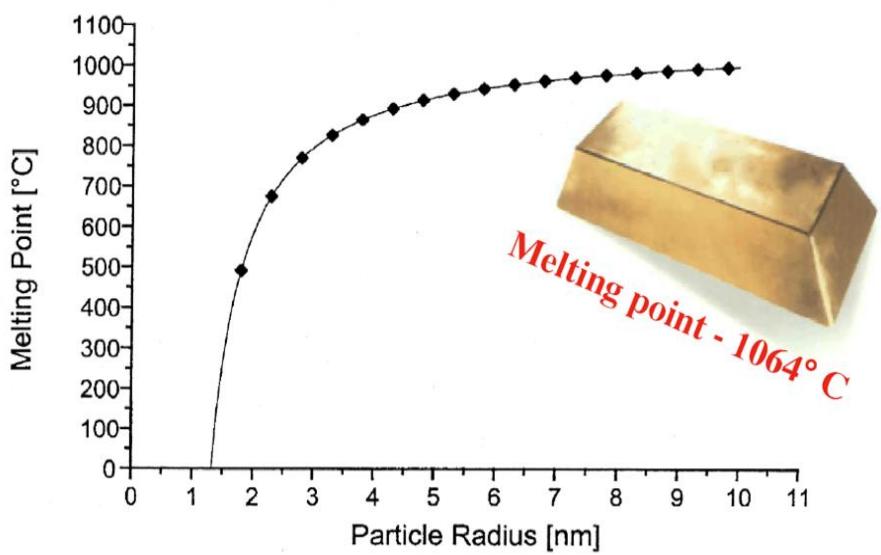
Dr. Richard Feynman, one of America's most notable physicists, 1918-1988.



**Figure 1.11:** Richard Feynman.

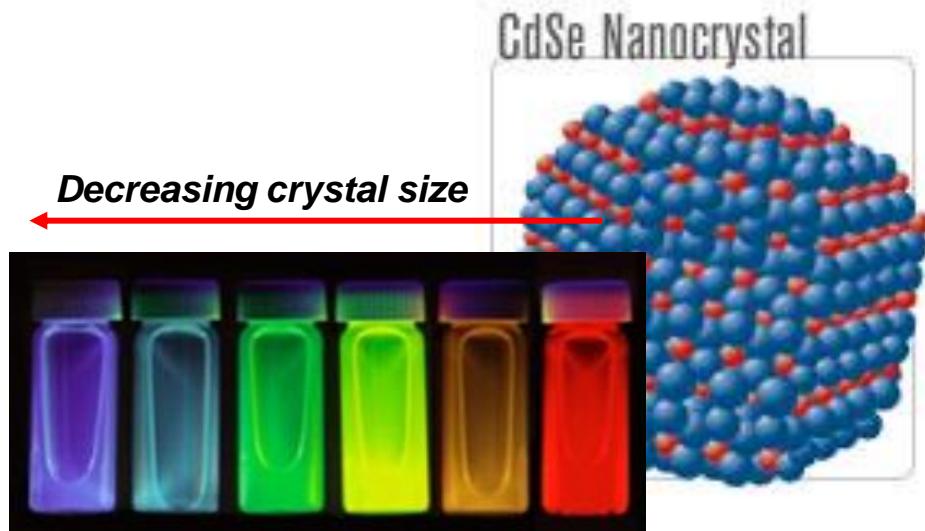
*Physical/chemical properties can change as we approach the nano-scale*

### *Melting point of gold particles*



*K. J. Klabunde, 2001*

### *Fluorescence of semiconductor nanocrystals*



*M. Bawendi, MIT: [web.mit.edu/chemistry/nanocluster](http://web.mit.edu/chemistry/nanocluster)  
Evident, Inc.: [www.evidenttech.com](http://www.evidenttech.com)*

**By controlling nano-scale (1) composition, (2) size, and (3) shape, we can create new materials with new properties**  **New technologies**

# The Lycurgus Cup

## A Roman Nanotechnology

Reflected, transmitted



The Lycurgus Cup represents one of the outstanding achievements of the ancient glass industry. This late Roman cut glass vessel is extraordinary in several respects, firstly in the method of fabrication and the exceptional workmanship involved and secondly in terms of the unusual optical effects displayed by the glass.

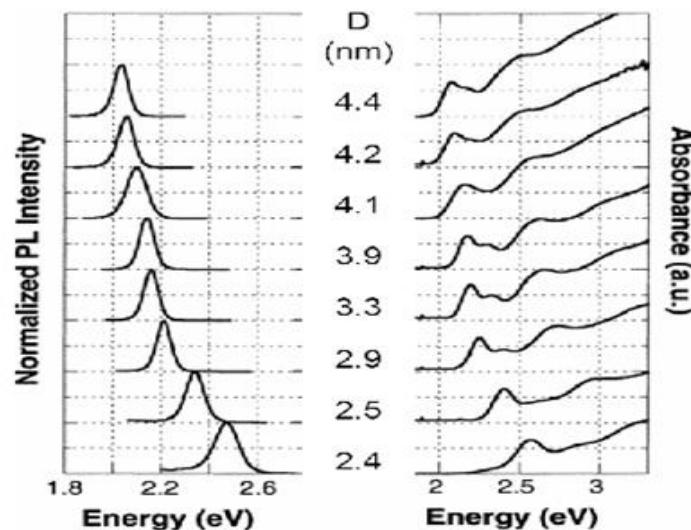
Chemical analysis showed the glass to be of the soda-lime-silica type, similar to most other Roman glass (and to modern window and bottle glass) containing in addition about 0.5% of manganese. In addition, a number of trace elements including silver and gold make up the final 1%. It was further suggested that the unique optical characteristics of the glass might be connected with the presence in the glass of colloidal gold



# Optical properties of semiconductor NP

Since the promoted electron and the VB hole have opposite charges, a strong electrostatic attraction causes them to remain relatively localized within a nanometer-sized region. The exciton volume can be calculated for a given material, and the corresponding radius is known as the Bohr radius.

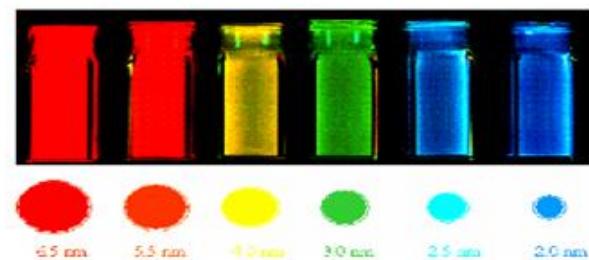
For a semiconductor particle, quantum confinement occurs when the nanocrystal radius becomes comparable to the Bohr radius. For CdSe the Bohr radius amounts to ca. 5.6 nm.



Emission and absorption spectra of CdSe nanocrystals of different sizes. The change in the emission width is due to the decrease in the nanocrystal diameter distribution with increase in diameter.



Vials of CdSe nanocrystals from NN-labs ([www.nn-labs.com](http://www.nn-labs.com))



Size tunable fluorescence emission from CdSe/ZnS core shell nanocrystals synthesized by Quantum Dot Corporation ([www.qdots.com](http://www.qdots.com)). The size of the CdSe core dictates the emission wavelength through quantum confinement.

- The semiconductors like PbS, GaAs, CdS etc., can be synthesized in the nanometer level and they are called as semiconductor quantum dots. Their properties like band gap, luminescence etc., always differs from their bulk counterpart.

The quantum structures are useful in the fabrication of high efficiency solar cells, infrared detectors, quantum dot lasers etc.

## ➤ **Properties of Nanomaterials**

### **Unique properties**

They have very high magneto resistance

They have lower melting point, high solid state phase transition pressure, lower ferroelectric phase transition temperature

Lower Debye temperature and high self diffusion coefficient

They have high catalytic activity

## **Variation of physical properties with size**

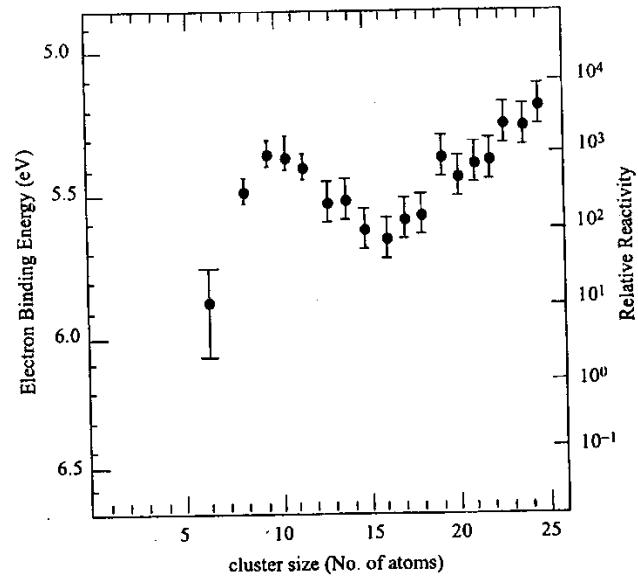
It is well established that mechanical, electrical, optical, chemical, semi conducting and magnetic properties of a material depend strongly upon the size and the arrangement of the constituent clusters or grains.

### **(i) Electron affinities and chemical properties**

Variation in electronic properties with size occurs only when there is a variation in inter particle spacing and geometry. As the size is reduced from the bulk, the electronic bands in metals become narrower and the delocalized electronic states are transformed to more localized molecular bonds.

- Variation in electronic properties with size occurs only when there is a variation in inter particle spacing and geometry. As the size is reduced from the bulk, the electronic bands in metals become narrower and the delocalized electronic states are **transformed** to more localized molecular bonds.

- Fig shows the ionization potential and reactivity of Fen clusters as a function of size.
- The ionization potential are higher at smaller sizes than at the bulk work function .
- The large surface – to – volume ratio and the variation in geometry and electronic structure have a strong effect on catalysis properties.



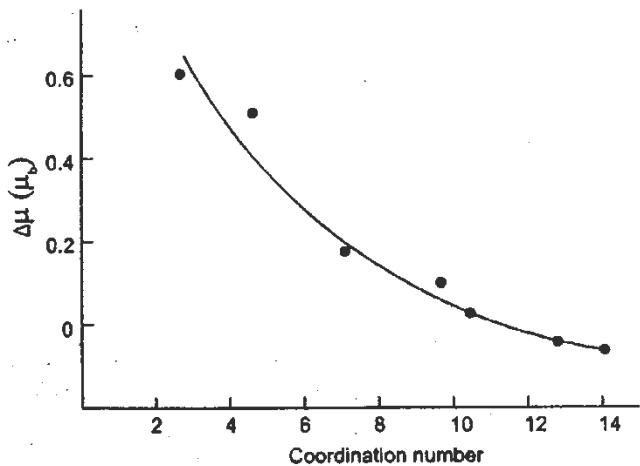
**Ionization potential and reactivity of Fe clusters as a function of size**

## (ii) Magnetic properties

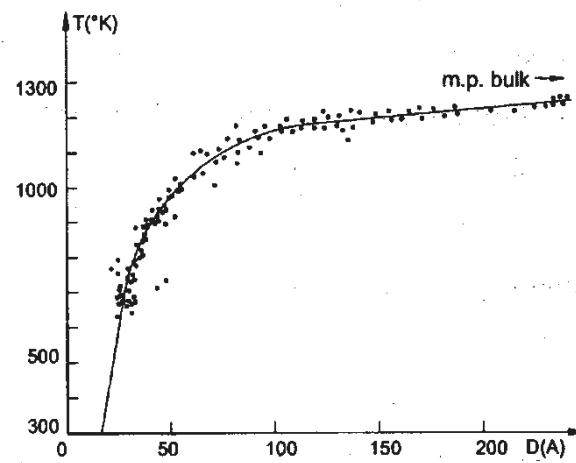
- Nano particles of magnetic and even non magnetic solids exhibit a totally new class of magnetic properties.
- Table gives an account of magnetic behavior of very small particles of various metals.
- Ferro magnetic and anti ferromagnetic multilayers have been found to exhibit *Giant Magneto Resistance (GMR)*.
- Small particles differ from the bulk in that these atoms will have lower co-ordination number.
- From the Fig, it is inferred that the small particles are more magnetic than the bulk material

| Metal      | Bulk           | Cluster            |
|------------|----------------|--------------------|
| Na, K      | Paramagnetic   | Ferromagnetic      |
| Fe, Co, Ni | Ferro magnetic | Super paramagnetic |
| Gd, Tb     | Ferromagnetic  | Super paramagnetic |
| Rh         | Paramagnetic   | Ferromagnetic      |

**Table: Magnetism in bulk and in nanoparticles**



Change in bulk magnetic moment  
versus co-ordination number

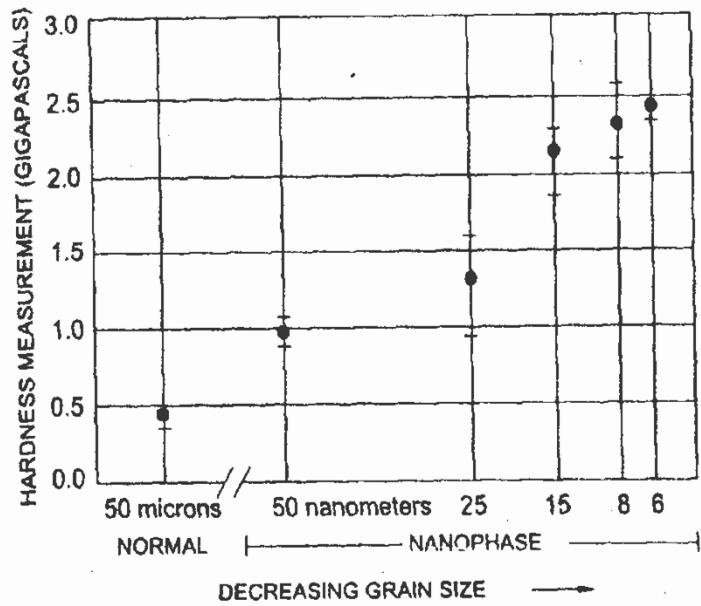


Melting point of gold as a function of  
grain size

### (iii) Mechanical behaviour

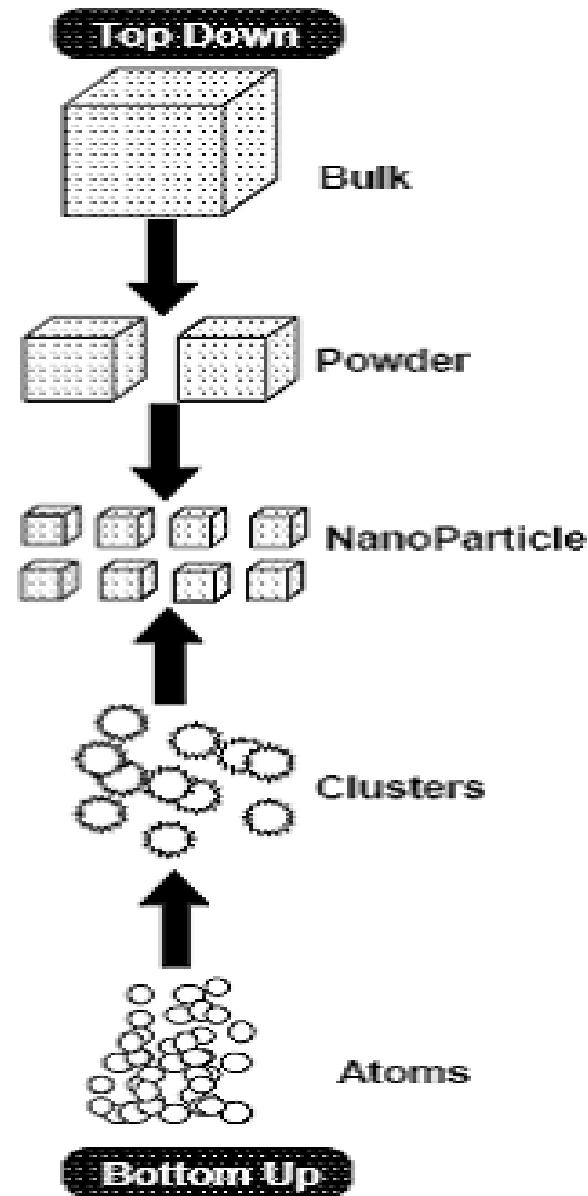
From the Fig. it is evident that the melting point reduction is not really significant until the particle size is less than about 10nm.

- Nanophase metals with their exceptionally small grain size are found to be exceptionally strong.
- It is because clusters and grains in nanophase material are mostly free from dislocations.
- The variation of hardness with diameter of copper nano crystals is shown in Fig.
- From the Fig. it is revealed that when the grains size was **50nm** in diameter, the copper was twice as hard as usual.
- Thus the material in **nano phase** has very high strength and super hardness.



**Fig. Strength of nanophase copper as a function of grain size**

- The general synthetic pathways to synthesize nanomaterials are **top-down** and **bottom-up** approach
- In the later method, chemistry plays a unique role in assembling and building up nanometric units from smaller ones.



# Low-Dimensional Systems

A low-dimensional system, also called confined system, is any quantum system in which the carriers are free to move in two, one, or zero dimensions. In these systems, the spatial dimensions are of the order of the De Broglie wavelength of the carriers and therefore the carrier energy states and density of states become quantized. As a result the electronic, electrical, and optical behavior of the carriers are governed by quantum mechanical principles or mechanisms.

# Classification

- Classification is based on the number of dimensions, which are not confined to the nanoscale range (<100 nm).
  1. Zero-dimensional (0-D) (spherical)
  2. One-dimensional (1-D) (nanorods, nanowires, nanofibers, nanotubes)
  3. Two-dimensional (2-D) (flat membranes, nanosheets, nanodisc)
  4. Three-dimensional (3-D) (nanodots)

# Low-Dimensional Systems Classifications

The most universal classification scheme of low-dimensional system is by considering the number of spatial directions where the particles in the system could move freely. This approach leads.

**Quantum-Well Systems.** *In these systems the particles are confined in one direction and are free to move in two directions.*

**Quantum-Wire Systems.** *In these systems the particles are confined in two directions and are free to move in one direction.*

**Quantum-Dot Systems.** *In these systems the particles are confined in all three directions and can not move freely in any spatial direction.*

## **Quantum well, Quantum wire and Quantum dots**

- When the size or dimension of a material is continuously reduced from a large or macroscopic size, such a metre or centimetre, to a very small size, the properties remain the same at first, then small changes begin to occur, until finally when the size drops below 100 nm, dramatic changes in properties can occur.
- If one dimension is reduced to the nanorange while the other dimensions remain large, them we obtain a structure known as **quantum well**.
- If two dimensions are so reduced and one remains large, the resulting structure is referred to as a **quantum wire**.
- The extreme case of this process of size reduction in which all three dimensions reach the low nanometer range is called a **quantum dot**.

The word **quantum** is associated with the above three types of nanostructures because the changes in properties arise from the quantum mechanical nature of physics in the domain of the ultra small geometry.

The conduction electrons are confined in a narrow dimension and such a configuration is referred as *quantum well*.

A *quantum wire* is a structure such as a copper wire that is long in one dimension, but has a nanometer size as its diameter. In this case, the electrons move freely along the wire but are confined in the transverse directions.

The *quantum dot* may have the shape of a tiny cube, a short cylinder or a sphere with low nanometre dimensions.

## **TECHNOLOGICAL ADVANTAGES OF NANOTECHNOLOGY AND NANOMATERIALS**

### **1. IMPROVED TRANSPORTATION**

- Today, most airplanes are made from metal despite the fact that diamond has a strength-to-weight ratio over 50 times that of aerospace aluminum.
- Diamond is expensive, it is not possible to make it in the required shapes, and it shatters. Nanotechnology will let us inexpensively make shatterproof diamond in exactly the shapes we want.
- Nanotechnology will dramatically reduce the costs and increase the capabilities of space ships and space flight.
- The strength-to-weight ratio and the cost of components are absolutely critical to the performance and economy of space ships: with nanotechnology, both of these parameters will be improved.
- Nanotechnology will also provide extremely powerful computers with which to guide both those ships and a wide range of other activities in space.

## 2. ATOM COMPUTERS

- Today, computer chips are made using lithography -- literally, "stone writing."
- If the computer hardware revolution is to continue at its current pace, in a decade or so we'll have to move beyond lithography to some new post lithographic manufacturing technology. Ultimately, each logic element will be made from just a few atoms.
- Designs for computer gates with less than 1,000 atoms have already been proposed -- but each atom in such a small device has to be in exactly the right place.
- To economically build and interconnect trillions upon trillions of such small and precise devices in a complex three dimensional pattern we'll need a manufacturing technology well beyond today's lithography: we'll need nanotechnology.
- With it, we should be able to build mass storage devices that can store more than a hundred billion billion bytes in a volume the size of a sugar cube;
- **RAM** that can store a mere billion billion bytes in such a volume; and massively parallel computers of the same size that can deliver a billion billion instructions per second.

### **3. MILITARY APPLICATIONS:**

- Today, "smart" weapons are fairly big -- we have the "smart bomb" but not the "smart bullet."
- In the future, even weapons as small as a single bullet could pack more computer power than the largest supercomputer in existence today, allowing them to perform real time image analysis of their surroundings and communicate with weapons tracking systems to acquire and navigate to targets with greater precision and control.
- We'll also be able to build weapons both inexpensively and much more rapidly, at the same time taking full advantage of the remarkable materials properties of diamond.
- Rapid and inexpensive manufacture of great quantities of stronger more precise weapons guided by massively increased computational power will alter the way we fight wars.
- Changes of this magnitude could destabilize existing power structures in unpredictable ways.
- Military applications of **nanotechnology** raise a number of concerns that prudence suggests we begin to investigate before, rather than after, we develop this new technology.

## **4. SOLAR ENERGY**

Nanotechnology will cut costs both of the solar cells and the equipment needed to deploy them, making solar power economical.

In this application we need not make new or technically superior solar cells: making inexpensively what we already know how to make expensively would move solar power into the mainstream.

## **5. MEDICAL USES**

- It is not modern medicine that does the healing, but the cells themselves: we are but onlookers.
- If we had surgical tools that were molecular both in their size and precision, we could develop a medical technology that for the first time would let us directly heal the injuries at the molecular and cellular level that are the root causes of disease and ill health.
- With the precision of drugs combined with the intelligent guidance of the surgeon's scalpel, we can expect a quantum leap in our medical capabilities.

## **6. Other Advantages**

### *Less Pollution*

The problem with past technologies is that they pollute the environment in cases where we humans would die in years.

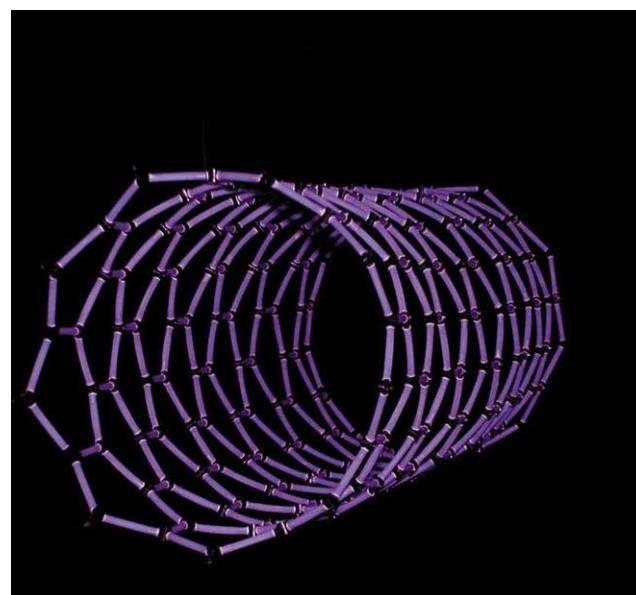
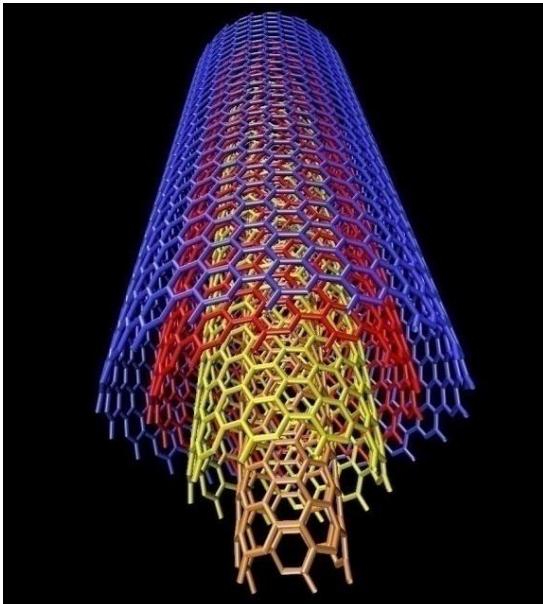
A good example of a bad polluting invention would be the automobile. The automobile ran on gas and the gas fumes destroyed the ozone layer.

**DEPARTMENT OF PHYSICS AND NANOTECHNOLOGY  
SRM INSTITUTE OF SCIENCE AND TECHNOLOGY**

**Carbon Nano Tubes-Properties, Synthesis and Applications**

# Carbon Nanotubes

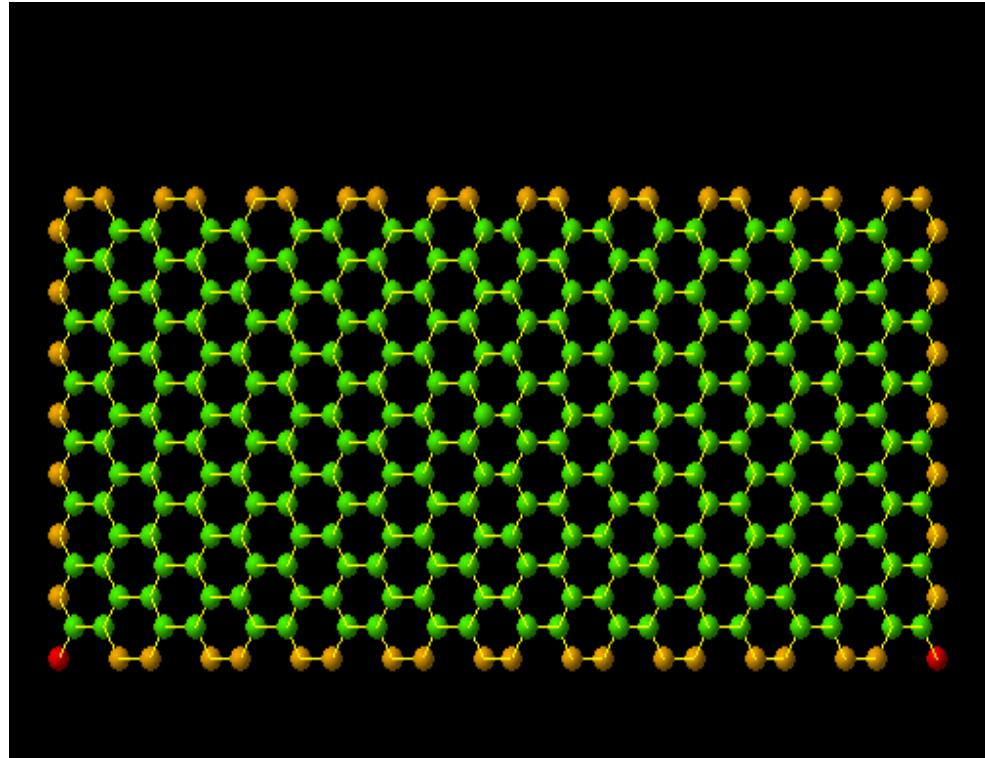
- **Carbon nanotubes (CNTs)** are allotropes of carbon.
- These cylindrical carbon molecules have interesting properties that make them potentially useful in many applications in nanotechnology, electronics, optics and other fields of materials science, as well as potential uses in architectural fields.
- They exhibit extraordinary strength and unique electrical properties, and are efficient conductors of heat. Their final usage, however, may be limited by their potential toxicity.





# What Are Carbon Nanotubes?

- CNT can be described as a sheet of graphite rolled into a cylinder
- Constructed from hexagonal rings of carbon
- Can have one layer or multiple layers
- Can have caps at the ends making them look like pills



# Discovery

## Nano-tubes

They were discovered in 1991 by the Japanese electron microscopist **Sumio Iijima** who was studying the material deposited on the cathode during the arc-evaporation synthesis of fullerenes. He found that the central core of the cathodic deposit contained a variety of closed graphitic structures including nanoparticles and nanotubes, of a type which had never previously been observed



Carbon Nanotube can be classified into Two type

1. Single wall carbon Nanotube (SWNT)
2. Multiwall Carbon Nanotube (MWNT)

Single-wall carbon Nanotubes (SWCNTs) can be considered to be formed by the **rolling of a single layer of graphite** into a seamless cylinder.

A **Multiwall** carbon Nanotube (MWCNT) can similarly be considered to be a **coaxial assembly of cylinders of SWCNTs**, one within another.

The separation between tubes is about equal to that between the layers in natural graphite. Hence, Nanotubes are one-dimensional objects.

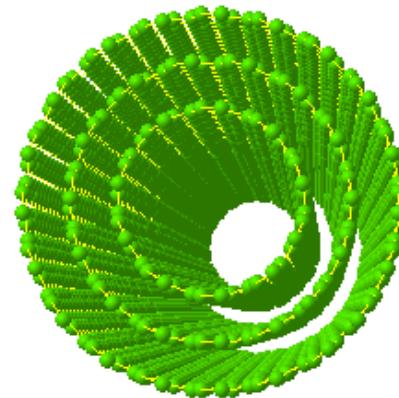


## • MWNT

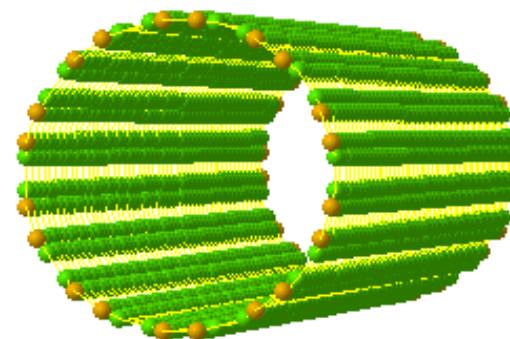
- Consist of 2 or more layers of carbon
- Tend to form unordered clumps

## • SWNT

- Consist of just one layer of carbon
- Greater tendency to align into ordered bundles
- Used to test theory of nanotube properties



Multi wall CNT



Single wall CNT



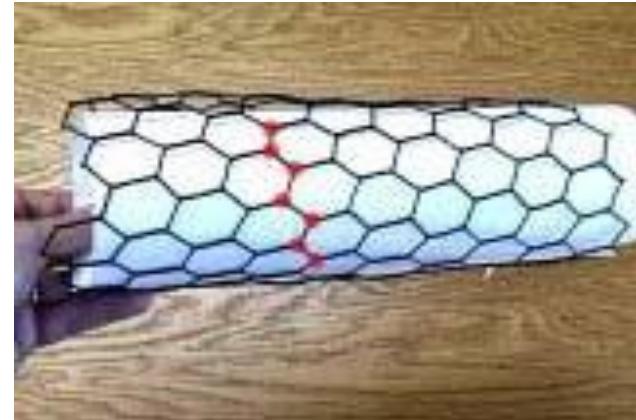
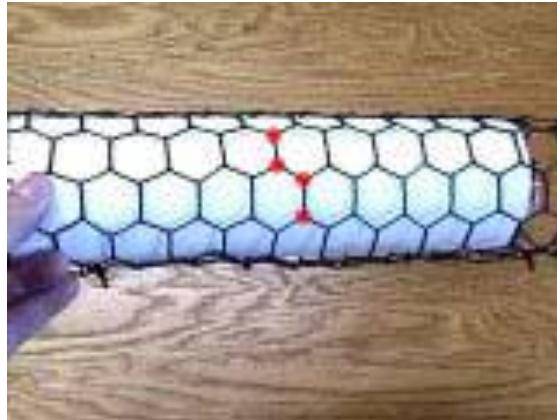
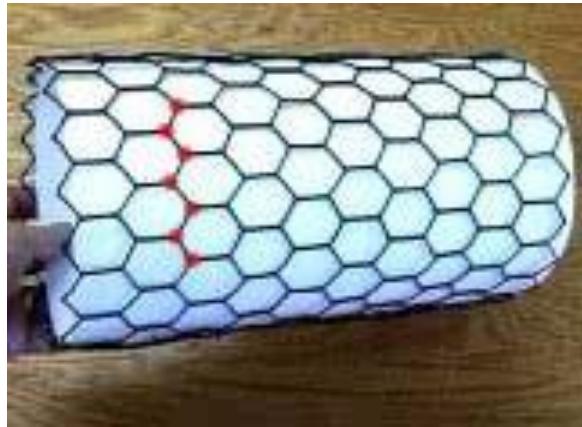
## *Nanotube's characteristic*

- Seemless cylindrical molecules
- Diameter as small as 1 nm.
- Length: a few nm. to several micron
- As a monoelemental polymer: Carbon atoms only
- As hexagonal network of carbon atoms
- CNTs are single molecules comprised of rolled up graphene sheets capped at each end.



## NANOTUBE GEOMETRY:

- There are three unique geometries of carbon nanotubes.
- The three different geometries are also referred to as flavors.
- The three flavors are **zig-zag**, **armchair**, and **chiral** [e.g. zig-zag ( $n, 0$ ); armchair ( $n, n$ ); and chiral ( $n, m$ )].
- These flavors can be classified by how the carbon sheet is wrapped into a tube

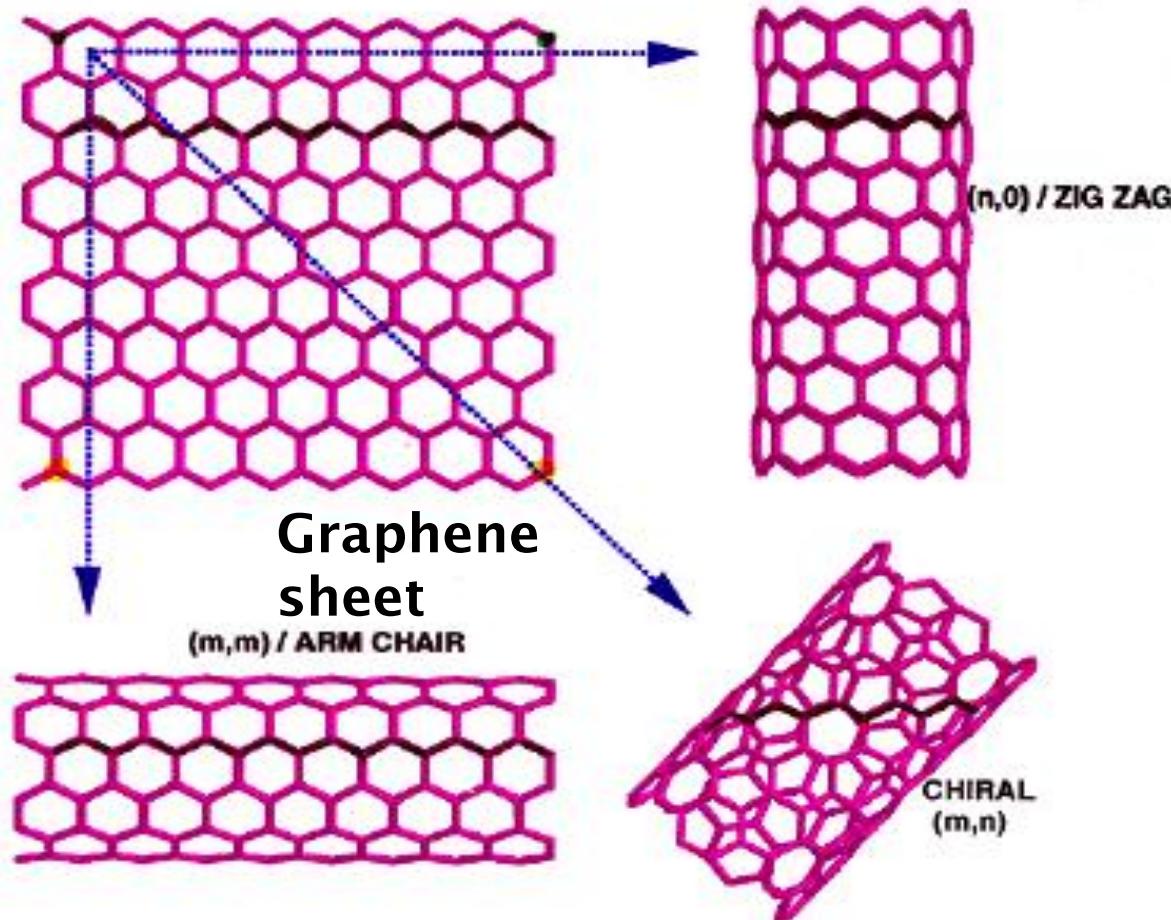


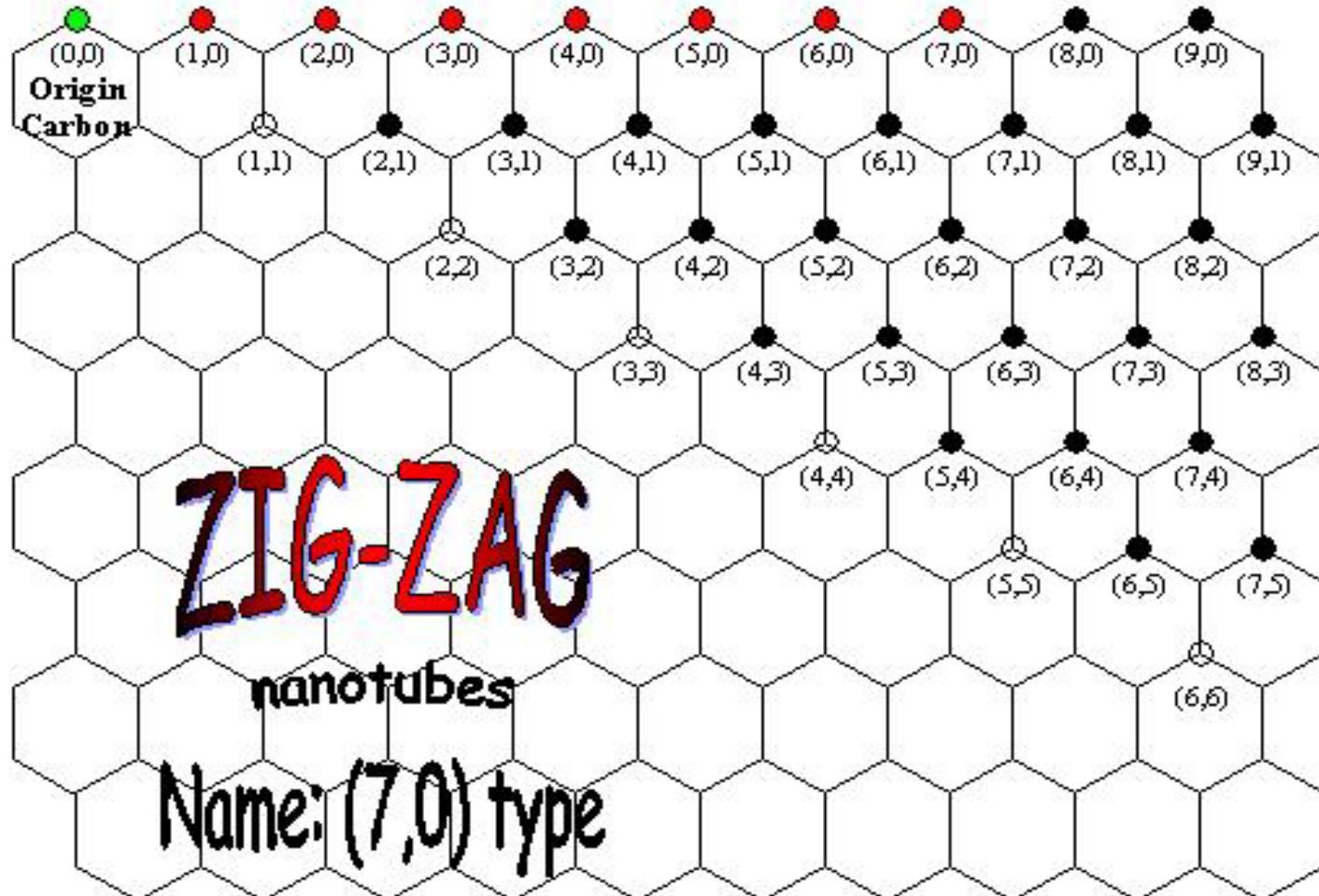
- If the Chiral vector passes through mid point of atomic bonding, it called "zig-zag line" Nanotube
- If the Chiral vector passes through the atoms of six fold axis, it armchair line" Nanotube
- If the Chiral vector line is not along a mirror line then it is called chiral Nanotube

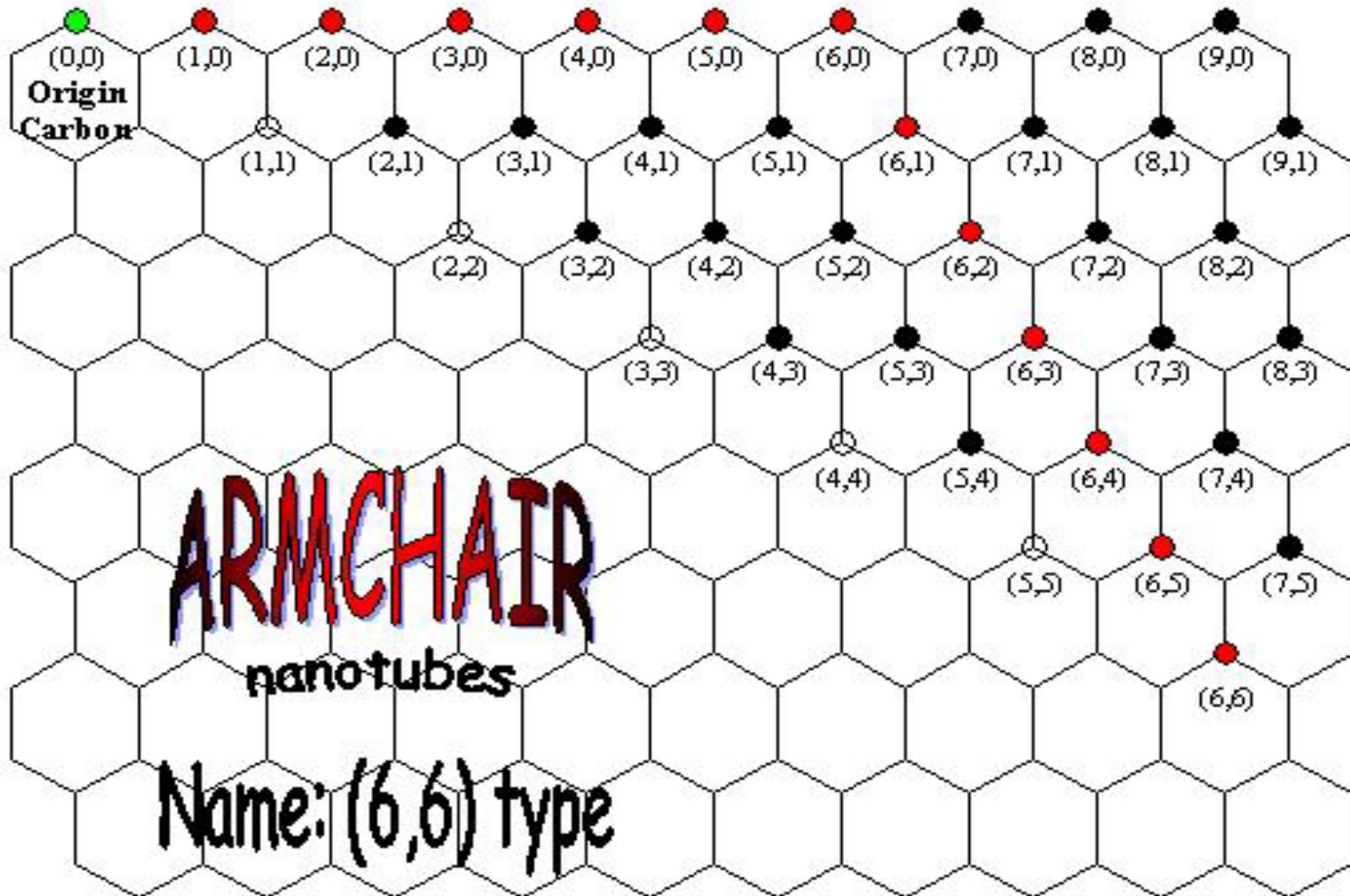
- The Chiral angle and Chiral vector ( $C_h$ ) of zigzag Nanotubes is  $0^\circ$  and  $(n,0)$
- The Chiral angle is  $30^\circ$  and Chiral vector ( $C_h$ ) is  $(n,n)$  for armchair Nanotubes
- The Chiral angle is  $0 \leq \theta \leq 30^\circ$   
The Chiral vector  $n \neq m$  for Chiral Nanotube

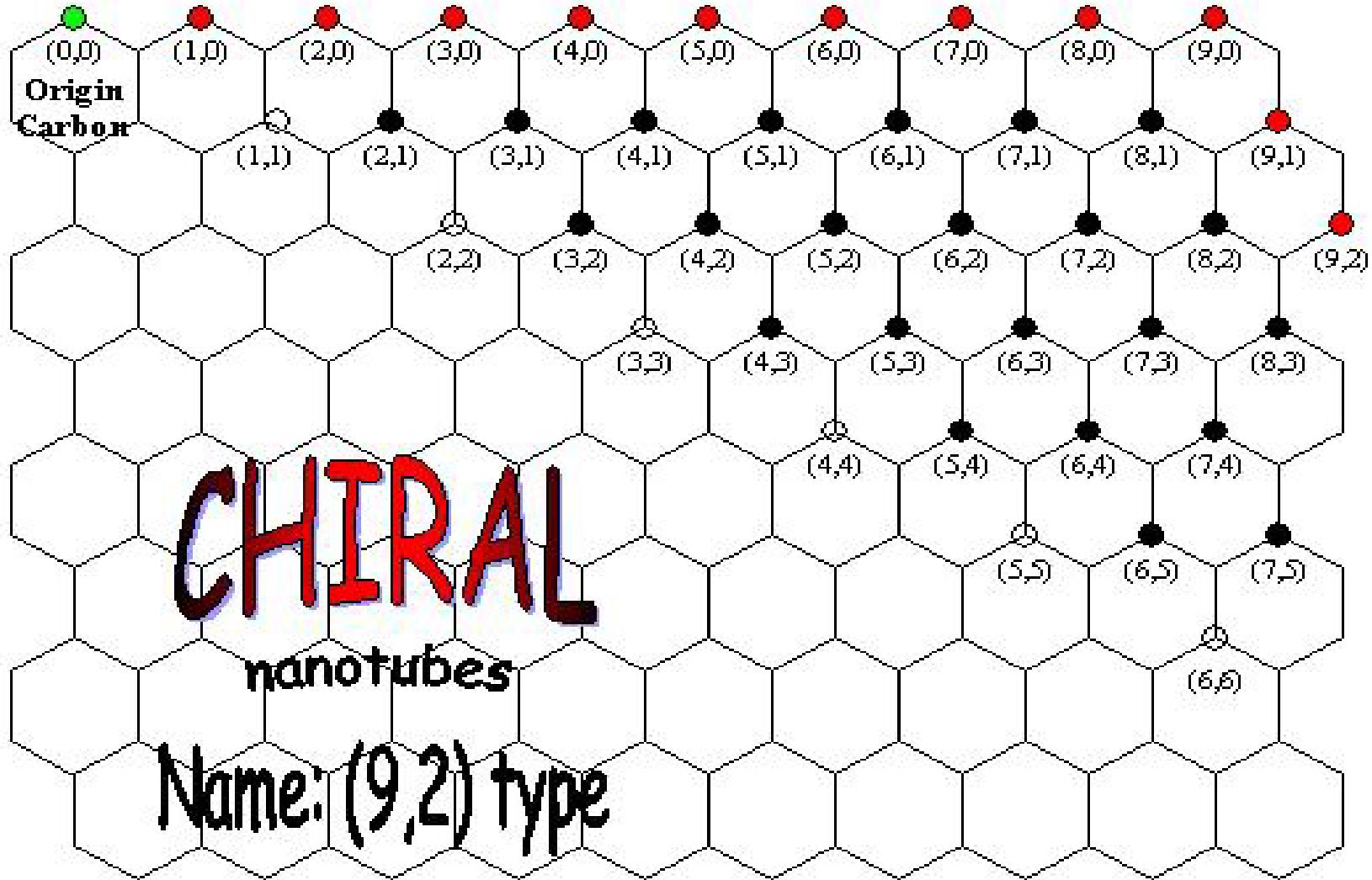


- STRIP OF A GRAPHENE SHEET ROLLED INTO A TUBE









## CNT exhibits extraordinary mechanical properties:

- The Young's modulus is over 1 Tera Pascal. It is stiff as diamond.
- The estimated tensile strength is 200 GPa. These properties are ideal for reinforced composites, Nano electromechanical systems (NEMS)

- The dimensions of CNT are variable (down to 0.4 nm in diameter)
- Apart from remarkable tensile strength, CNT nanotubes exhibit varying electrical properties (depending on the way the graphite structure spirals around the tube, and other factors, such as doping), and can be superconducting, insulating, semiconducting or conducting (metallic)

□ CNT Nanotubes can be either electrically conductive or semi conductive, depending on their helicity (shape), leading to nanoscale wires and electrical components.

□ These one-dimensional CNT 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

□ **Chemical reactivity.**

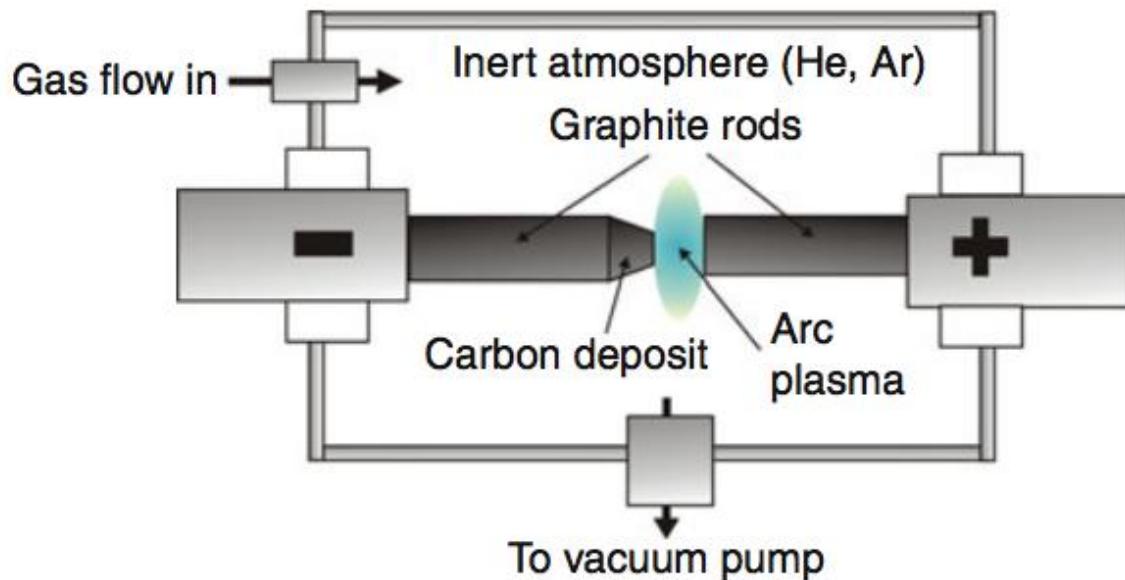
□ The chemical reactivity of a CNT is very high as compared with a graphene sheet because of its curved surface.

□ A Nanotube with smaller diameter results in increased reactivity.



## Synthesis of CNTs- Arc Discharge Method

- A direct current creates a high temperature discharge between two electrodes (carbon is vapourized)
- Atmosphere is composed of inert gas at a low pressure
- Originally used to make  $C_{60}$  fullerenes
- Cobalt is a popular catalyst
- Typical yield is 30-90%



## Arc Discharge Method

### Advantages

- Simple procedure
- High quality product
- Inexpensive

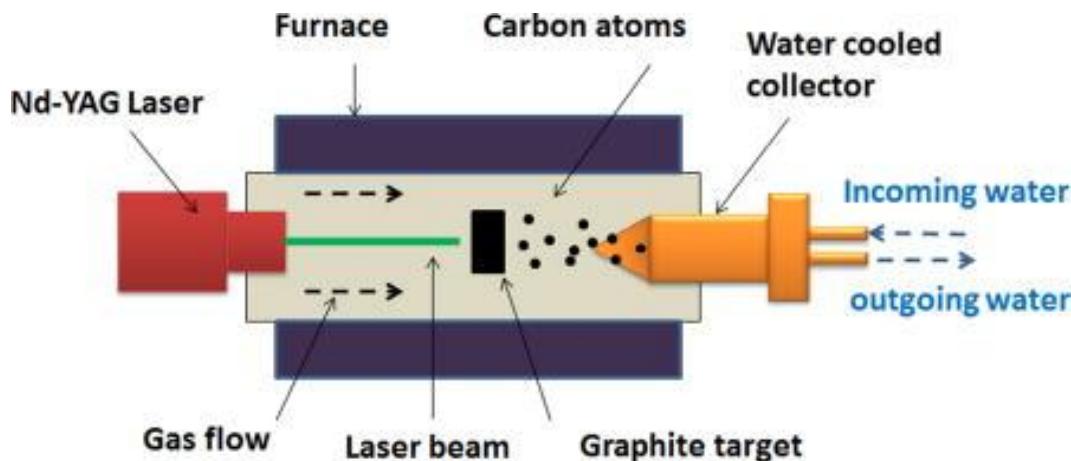
### Disadvantages

- Requires further purification
- Tubes tend to be short with random sizes



## Laser Ablation Method

- Discovered in 1995 at Rice University
- Vaporizes graphite at 1200 °C
- Helium or argon gas
- A hot vapor plume forms and expands and cools rapidly
- Carbon molecules condense to form large clusters
- Similar to arc discharge
- Yield of up to 70%



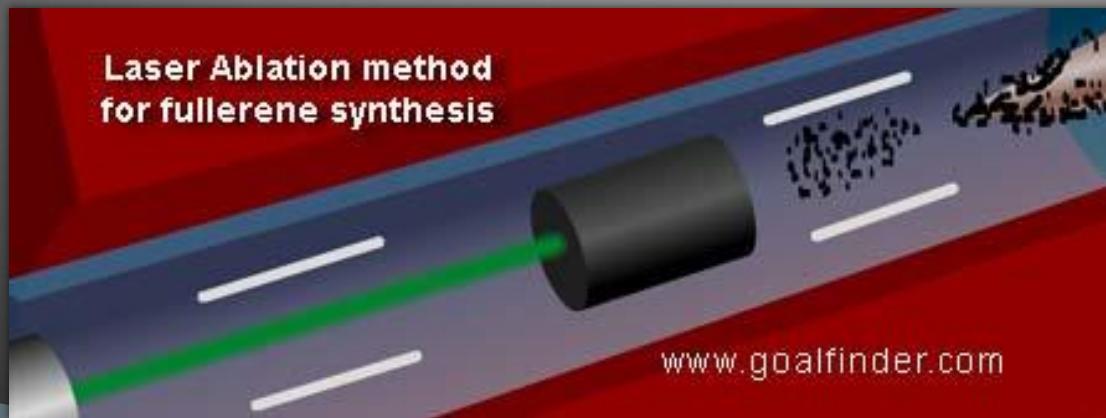
# Types of Laser Ablation

- Pulsed

- Much higher light intensity ( $100 \text{ kW/cm}^2$ )

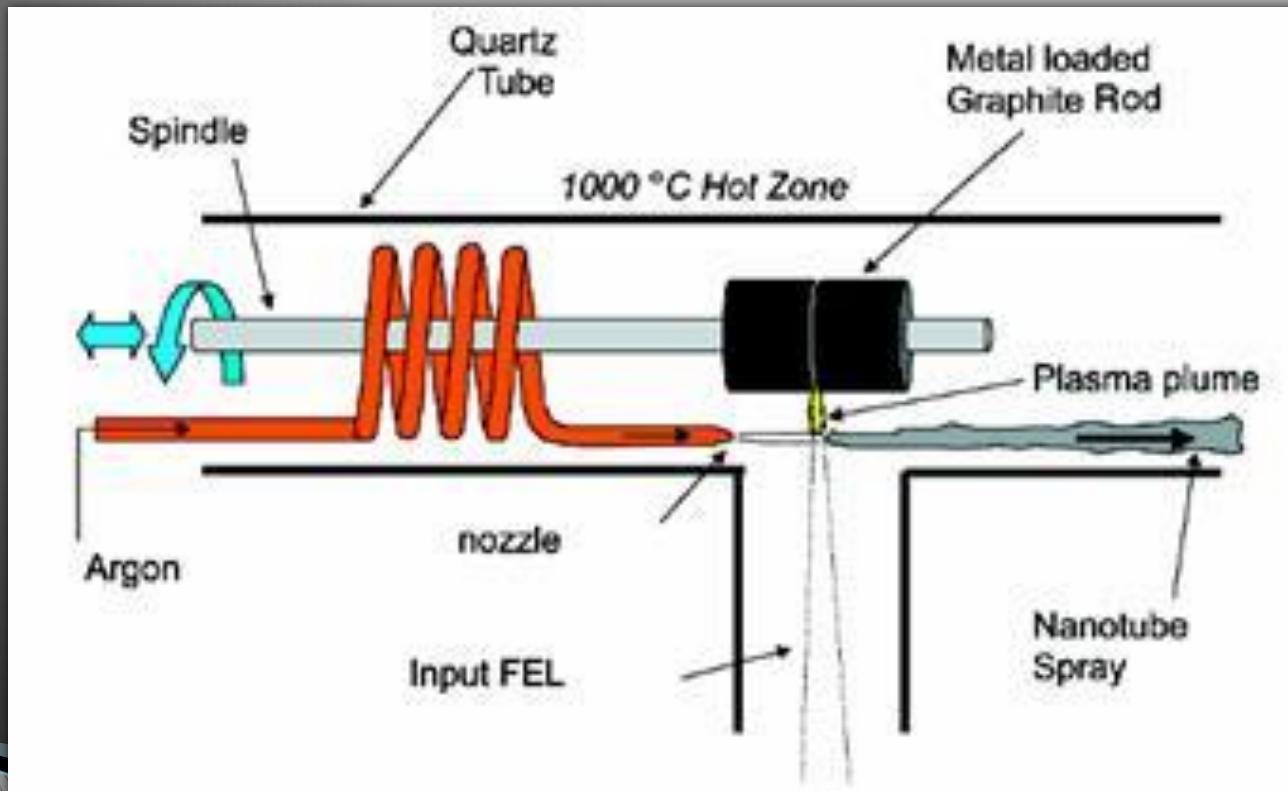
- Continuous

- Much lower light intensity ( $12 \text{ kW/cm}^2$ )





# Ultra Fast-pulsed Laser Ablation





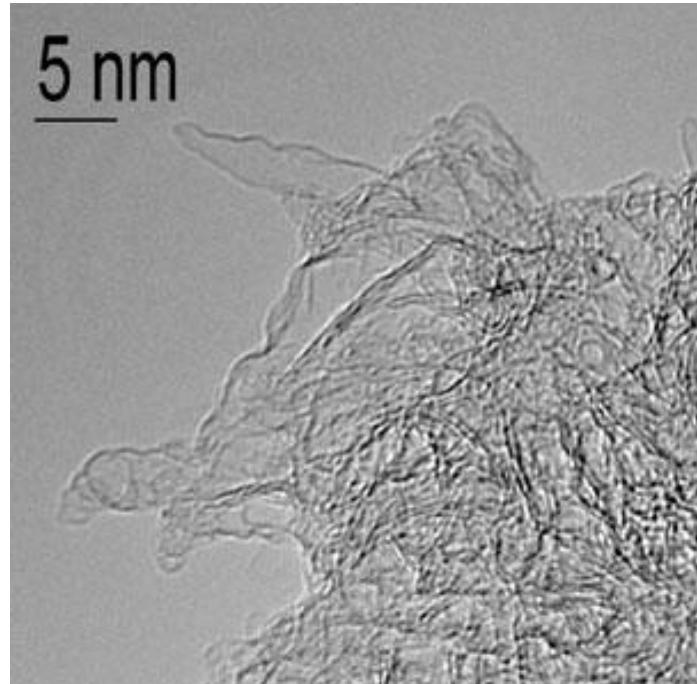
## Laser Ablation

### Advantages

- Good diameter control
- Few defects
- Pure product

### Disadvantages

- Expensive because of lasers and high powered equipment



# Chemical Vapor Deposition

- Carbon is in the gas phase
- Energy source transfers energy to carbon molecule
- Common Carbon Gases
  - Methane
  - Carbon monoxide
  - Acetylene

# Chemical Vapour Deposition (CVD)

- CVD is a process whereby a solid material is deposited from a vapor by a chemical reaction occurring on or in the vicinity of a normally heated substrate surface
- Chemical vapor deposition (CVD) is a commonly used process to deposit thin films on a desired substrate
- It involves using volatile precursors that can react or decompose onto a surface, yielding the desired material

**Gaseous reactants → Solid material + Gaseous products**

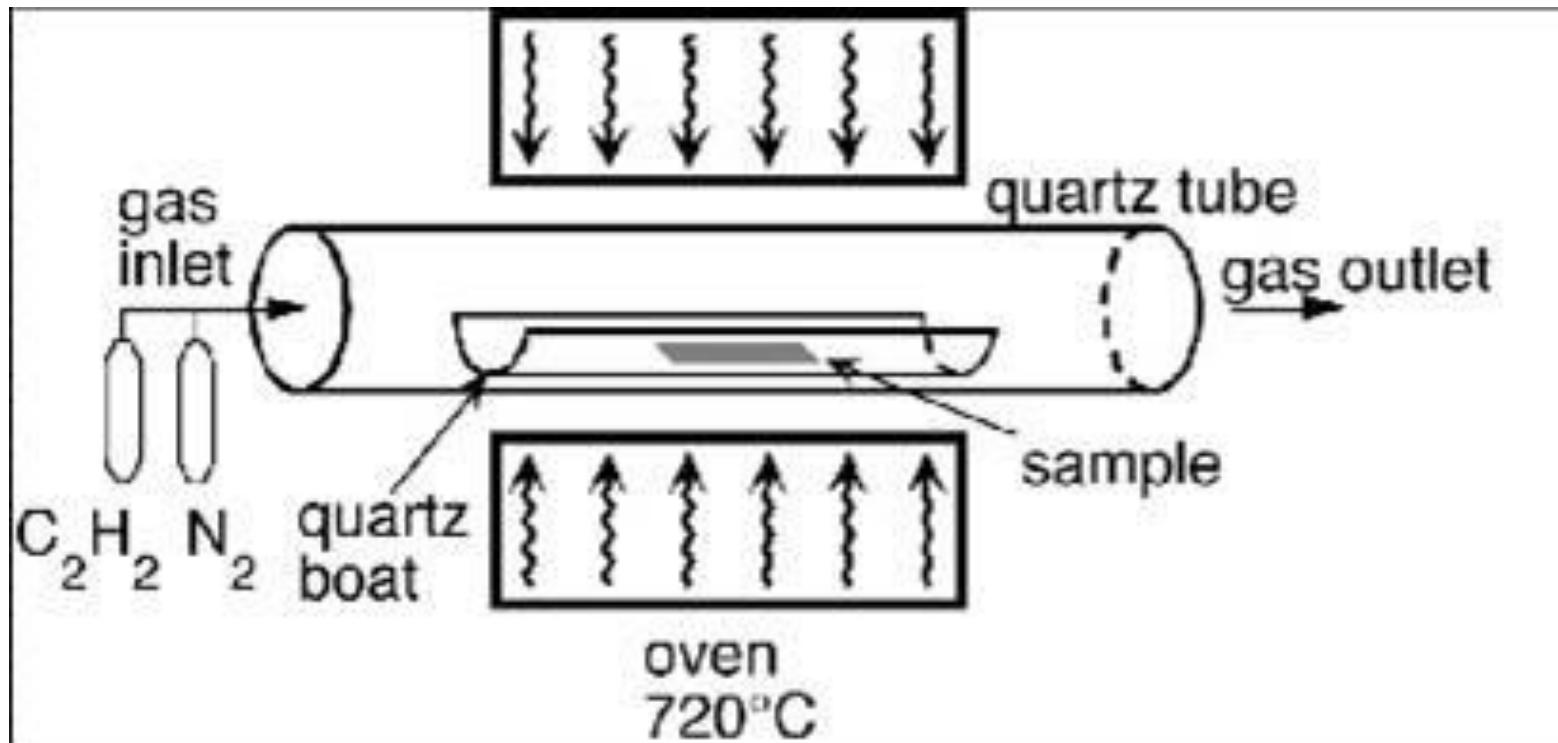
- Bottom-up approach
- Deposited films range from metals to semiconductors to insulators
- High temperatures and low pressures are the most common process conditions, but are not necessary
- CVD involves energy source to break reactant gases into reactive species for deposition

# Chemical Vapour Deposition (CVD)

- The process can sometimes be epitaxial where the desired material is deposited on a substrate that is nearly lattice-matched
- The deposition can also occur on amorphous substrates
- The precursors have to be volatile (gaseous) at room temperature
  - Ex:  $\text{SiH}_4$  (Silane) is a popular precursor to deposit Silicon
- The chemical reactions need to be thermodynamically predicted to result in a solid film
  - There should be an energy advantage for the desired reaction to occur, meaning the Gibbs Free Energy has to decrease
  - T and P can be adjusted for  $\Delta G < 0$
- The by-products need to be volatile (gaseous)

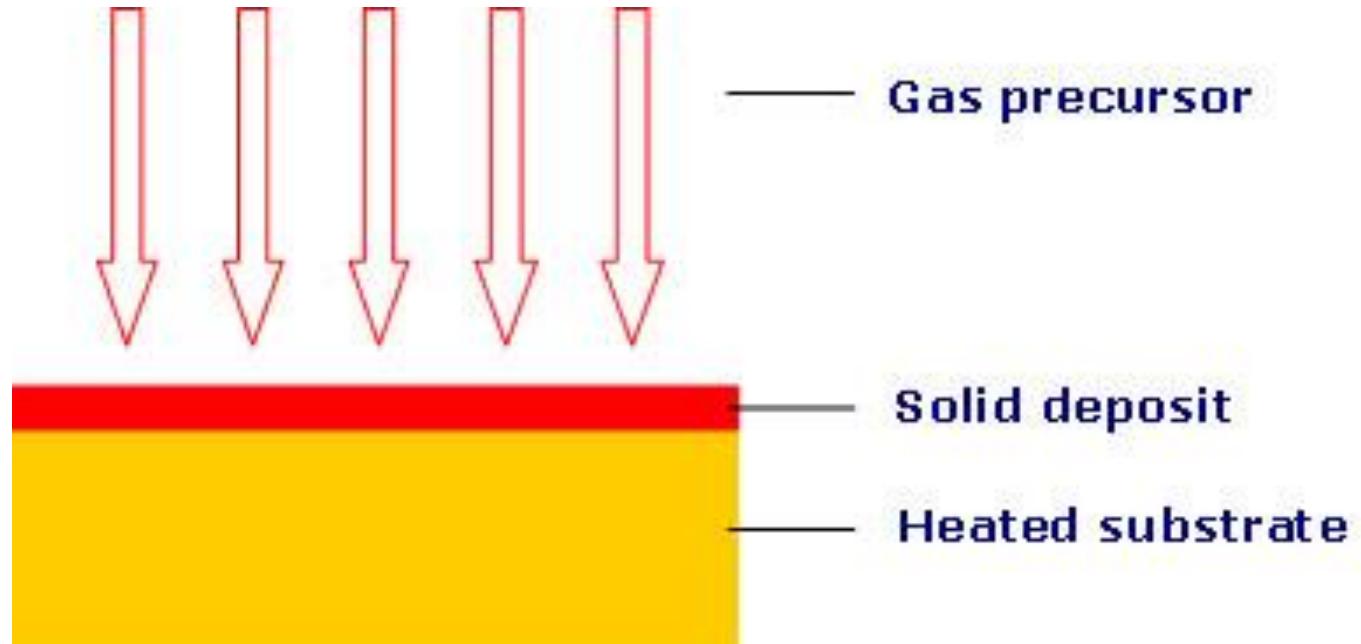


## Chemical vapour Deposition



## A typical CVD system consists of the following parts:

- sources of and feed lines for gases;
- mass flow controllers for metering the gases into the system;
- a reaction chamber or reactor;
- a system for heating up the wafer on which the film is to be deposited; and
- temperature sensors.

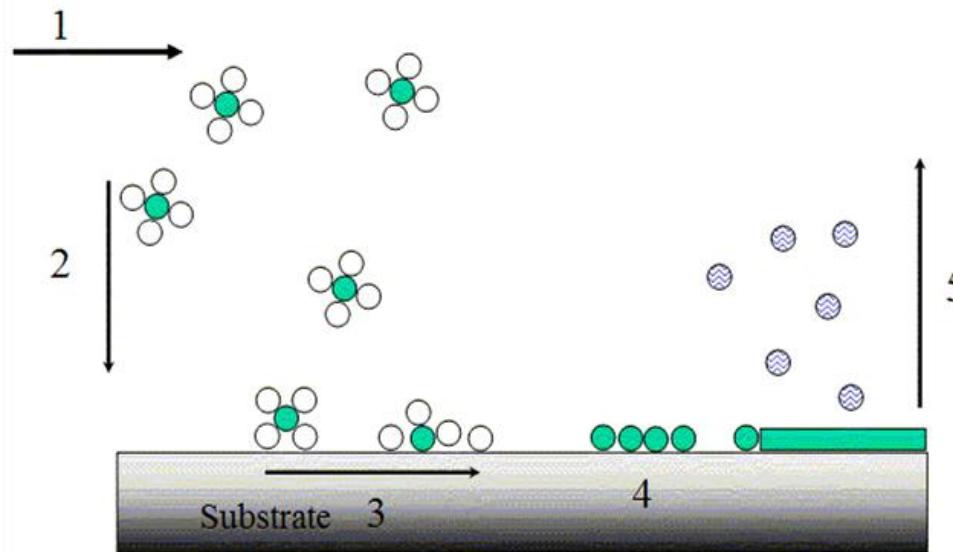


CVD REACTION

# CVD Steps

## ✓ Five steps occur

1. Reactants pumped through the reactor
2. Reactants diffuse across boundary layer to surface of the substrate
3. Reactants adsorb on surface (chemical or physical)
4. Surface reactions leading to film formation
5. Diffusion of by-products away from surface



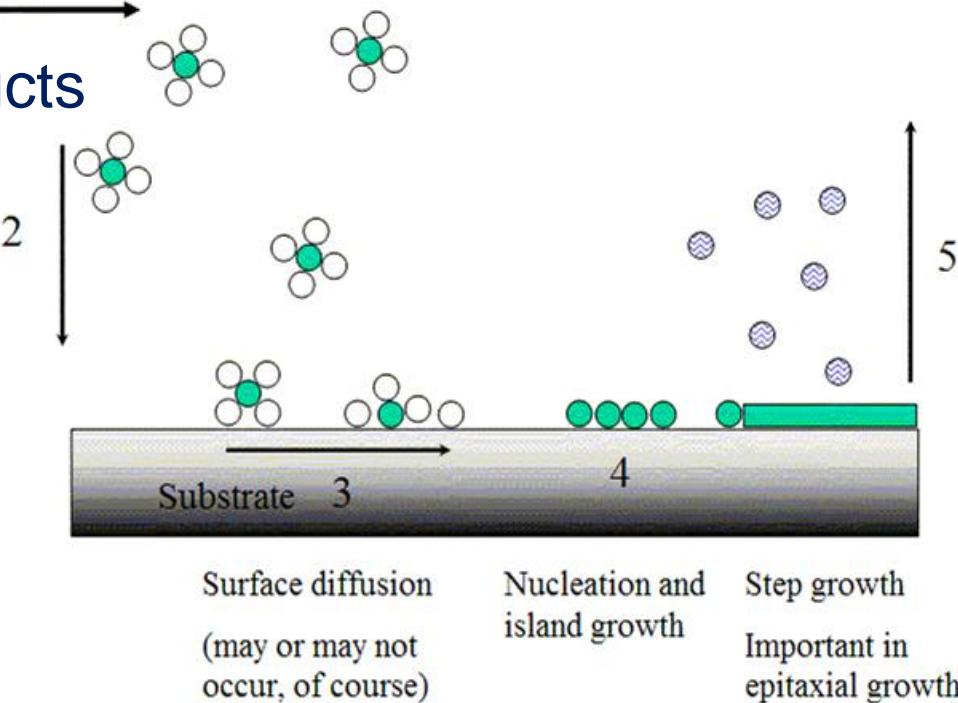
Surface diffusion  
(may or may not  
occur, of course)

Nucleation and  
island growth

Step growth  
Important in  
epitaxial growth

# Processes on surface of the substrate

- Adsorption
- Decomposition
- Surface migration
- Chemical reaction  $\xrightarrow{1}$
- Desorption of products



## A basic CVD process consists of the following steps:

- A predefined mix of reactant gases and diluent inert gases are introduced at a specified flow rate into the reaction chamber;
- The gas species move to the substrate;
- The reactants get adsorbed on the surface of the substrate;
- The reactants undergo chemical reactions with the substrate to form the film; and
- The gaseous by-products of the reactions are desorbed and evacuated from the reaction chamber.

- During the process of chemical vapor deposition, the reactant gases not only react with the substrate material at the wafer surface (or very close to it), but also in gas phase in the reactor's atmosphere.
- Reactions that take place at the substrate surface are known as heterogeneous reactions, and are selectively occurring on the heated surface of the wafer where they create good-quality films.
- Reactions that take place in the gas phase are known as homogeneous reactions.
- Homogeneous reactions form gas phase aggregates of the depositing material, which adhere to the surface poorly and at the same time form low-density films with lots of defects.
- In short, heterogeneous reactions are much more desirable than homogeneous reactions during chemical vapor deposition.

## Types of chemical vapor deposition

- A number of forms of CVD are in wide use.
- These processes differ in the means by which chemical reactions are initiated (e.g., activation process) and process conditions.
- For instance, a reactor is said to be '**hot-wall**' if it uses a heating system that heats up not only the wafer, but the walls of the reactor itself, an example of which is radiant heating from resistance-heated coils.
- '**Cold-wall**' reactors use heating systems that minimize the heating up of the reactor walls while the wafer is being heated up, an example of which is heating via IR lamps inside the reactor.
- In hot-wall reactors, films are deposited on the walls in much the same way as they are deposited on wafers.
- so this type of reactor requires frequent wall cleaning.

- Another way of classifying CVD reactors is by basing it on the range of their operating pressure.
- Atmospheric pressure CVD (APCVD) reactors operate at atmospheric pressure, and are therefore the simplest in design.
- Low-pressure CVD (LPCVD) reactors operate at medium vacuum (30-250 Pa) and higher temperature than APCVD reactors.
- Plasma Enhanced CVD (PECVD) reactors also operate under low pressure, but do not depend completely on thermal energy to accelerate the reaction processes.
- They also transfer energy to the reactant gases by using an RF-induced glow discharge.

- The glow discharge used by a PECVD reactor is created by applying an RF field to a low-pressure gas, creating free electrons within the discharge region.
- The electrons are sufficiently energized by the electric field that gas-phase dissociation and ionization of the reactant gases occur when the free electrons collide with them.
- Energetic species are then adsorbed on the film surface, where they are subjected to ion and electron bombardment, rearrangements, reactions with other species, new bond formation, and film formation and growth.
- Table compares the characteristics of typical APCVD, LPCVD, and PECVD reactors.

## APCVD, LPCVD, and PECVD Comparison

| CVD Process  | Advantages  | Disadvantages                          | Applications  |
|--------------|---|--|---|
| <b>APCVD</b> | Simple,<br>Fast Deposition,<br>Low Temperature  | Poor Step Coverage,<br>Contamination   | Low-temperature Oxides  |
| <b>LPCVD</b> | Excellent Purity,<br>Excellent Uniformity,<br>Good Step Coverage,<br>Large Wafer Capacity | High Temperature,<br>Slow Deposition   | High-temperature Oxides, Silicon<br>Nitride, Poly-Si, W, WSi <sub>2</sub> |
| <b>PECVD</b> | Low Temperature,<br>Good Step Coverage  | Chemical and Particle<br>Contamination | Low-temperature Insulators over<br>Metals, Nitride Passivation            |

## Advantages of CVD

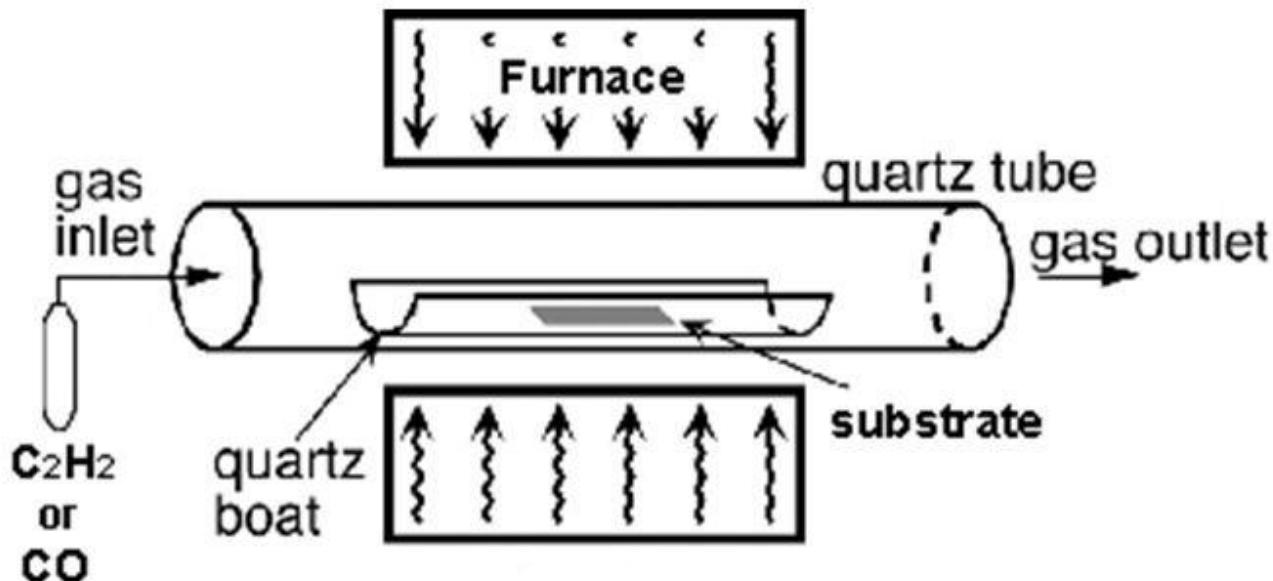
- Can be used for a wide range of metals and ceramics
- Can be used for coatings or freestanding structures
- Fabricates net or near-net complex shapes
- Is self-cleaning—extremely high purity deposits (>99.995% purity)
- Conforms homogeneously to contours of substrate surface
- Has near-theoretical as-deposited density
- Has controllable thickness and morphology
- Forms alloys
- Infiltrates fiber preforms and foam structures
- Coats internal passages with high length-to-diameter ratios
- Can simultaneously coat multiple components
- Coats powders

## Applications

- CVD processes are used on a surprisingly wide range of industrial components, from aircraft and land gas turbine blades, timing chain pins for the automotive industry, radiant grills for gas cookers and items of chemical plant, to resist various attacks by carbon, oxygen and sulphur.
- Some important applications are listed below.
- Surface modification to prevent or promote adhesion
- Photoresist adhesion for semiconductor wafers Silane/substrate adhesion for microarrays (DNA, gene, protein, antibody, tissue)
- MEMS coating to reduce stiction
- BioMEMS and biosensor coating to reduce "drift" in device performance
- Promote biocompatibility between natural and synthetic materials  
Copper capping Anti-corrosive coating

# Synthesis Method of CNT

## III. Chemical Vapor Deposition (CVD)



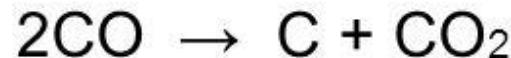
MWCNT

600-800 °



SWCNT

900-1000 °





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## Physical Vapour Deposition(PVD)

### Introduction

1. Physical vapour deposition (PVD) is fundamentally a vaporisation coating technique, involving transfer of material on an atomic level. It is an alternative process to electroplating
2. The process is similar to chemical vapour deposition (CVD) except that the raw materials/precursors, i.e. the material that is going to be deposited starts out in solid form, whereas in CVD, the precursors are introduced to the reaction chamber in the gaseous state.

### Working Concept

PVD processes are carried out under vacuum conditions. The process involved four steps:

1. Evaporation
2. Transportation
3. Reaction
4. Deposition



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## Evaporation

During this stage, a target, consisting of the material to be deposited is bombarded by a high energy source such as a beam of electrons or ions. This dislodges atoms from the surface of the target, ‘vaporising’ them.

## Transport

This process simply consists of the movement of ‘vaporised’ atoms from the target to the substrate to be coated and will generally be a straight line affair.

## Reaction

- In some cases coatings will consist of metal oxides, nitrides, carbides and other such materials.
  - In these cases, the target will consist of the metal.
  - The atoms of metal will then react with the appropriate gas during the transport stage.
  - For the above examples, the reactive gases may be oxygen, nitrogen and methane.
- In instances where the coating consists of the target material alone, this step would not be part of the process.

## Deposition

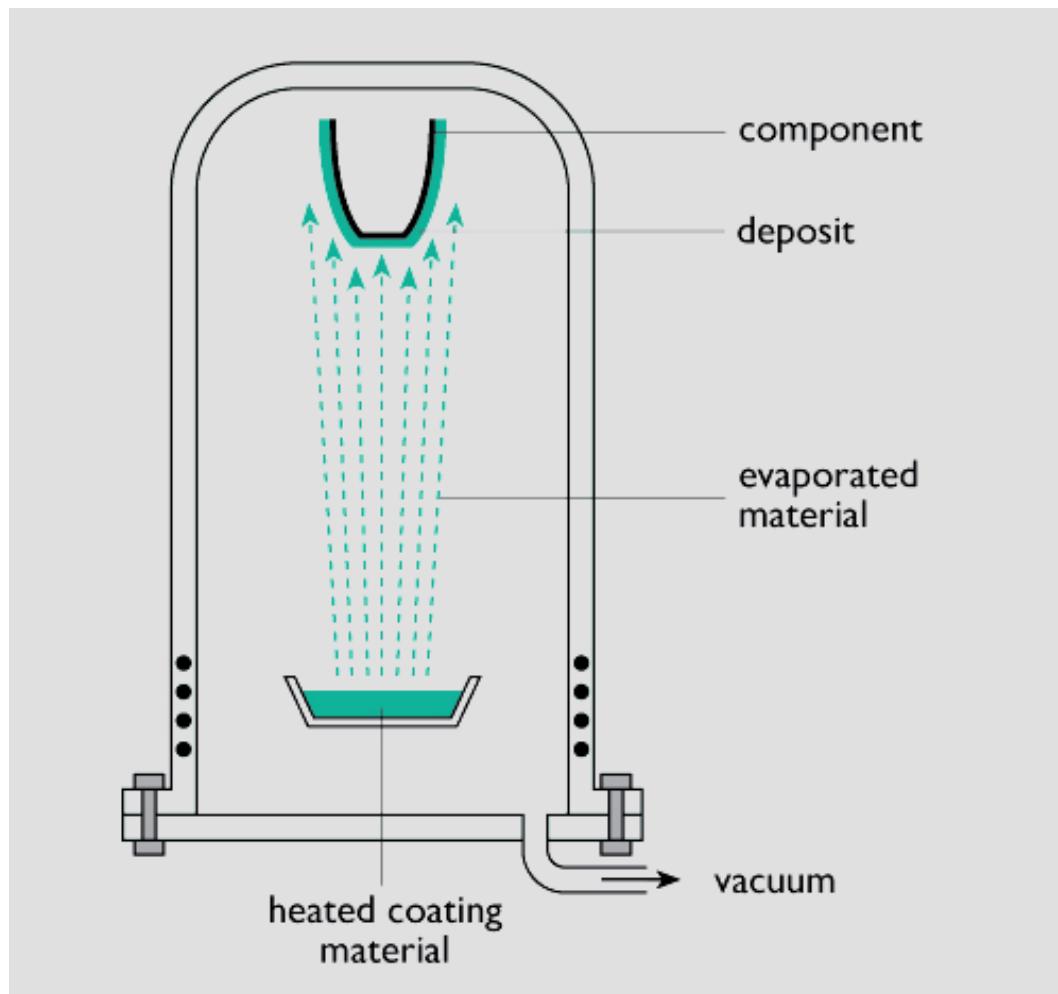
This is the process of coating build up on the substrate surface. Depending on the actual process, some reactions between target materials and the reactive gases may also take place at the substrate surface simultaneously with the deposition process.

Fig. shows a schematic diagram of the principles behind one common PVD method.

The component that is to be coated is placed in a vacuum chamber. The coating material is evaporated by intense heat from, for example, a tungsten filament.

An alternative method is to evaporate the coating material by a complex ion bombardment technique.

The coating is then formed by atoms of the coating material being deposited onto the surface of the component being treated.



The vacuum evaporation PVD process

Variants of PVD include, in order of increasing novelty:

Evaporative Deposition: In which the material to be deposited is heated to a high vapor pressure by electrically resistive heating in "high" vacuum.

Electron Beam Physical Vapor Deposition: In which the material to be deposited is heated to a high vapor pressure by electron bombardment in "high" vacuum.

Sputter Deposition: In which a glow plasma discharge (usually localized around the "target" by a magnet) bombards the material sputtering some away as a vapor.

Cathodic Arc Deposition: In which a high power arc directed at the target material blasts away some into a vapor.

Pulsed Laser Deposition: In which a high power laser ablates material from the target into a vapor.

## Merits and Demerits of evaporation methods

| Method                      | Merits   | Demerits  |
|-----------------------------|--|---|
| <b>E-Beam Evaporation</b>   | <ul style="list-style-type: none"> <li>1. high temp materials</li> <li>2. good for liftoff</li> <li>3. highest purity</li> </ul>                               | <ul style="list-style-type: none"> <li>1. some CMOS processes sensitive to radiation</li> <li>2. alloys difficult</li> <li>3. poor step coverage</li> </ul> |
| <b>Filament Evaporation</b> | <ul style="list-style-type: none"> <li>1. simple to implement</li> <li>2. good for liftoff</li> </ul>  | <ul style="list-style-type: none"> <li>1. limited source material (no high temp)</li> <li>2. alloys difficult</li> <li>3. poor step coverage</li> </ul>     |
| <b>Sputter Deposition</b>   | <ul style="list-style-type: none"> <li>1. better step coverage</li> <li>2. alloys</li> <li>3. high temp materials</li> <li>4. less radiation damage</li> </ul> | <ul style="list-style-type: none"> <li>1. possible grainy films</li> <li>2. porous films</li> <li>3. plasma damage/contamination</li> </ul>                 |

## Importance of PVD Coatings

- PVD coatings are deposited for numerous reasons. Some of the main ones are:
- Improved hardness and wear resistance
- Reduced friction
- Improved oxidation resistance
- The use of such coatings is aimed at improving efficiency through improved performance and longer component life.
- They may also allow coated components to operate in environments that the uncoated component would not otherwise have been able to perform.

## Advantages

- Materials can be deposited with improved properties compared to the substrate material
- Almost any type of inorganic material can be used as well as some kinds of organic materials
- The process is more environmentally friendly than processes such as electroplating

## Disadvantages

- It is a line of sight technique meaning that it is extremely difficult to coat undercuts and similar surface features
- High capital cost
- Some processes operate at high vacuums and temperatures requiring skilled operators
- Processes requiring large amounts of heat require appropriate cooling systems
- The rate of coating deposition is usually quite slow

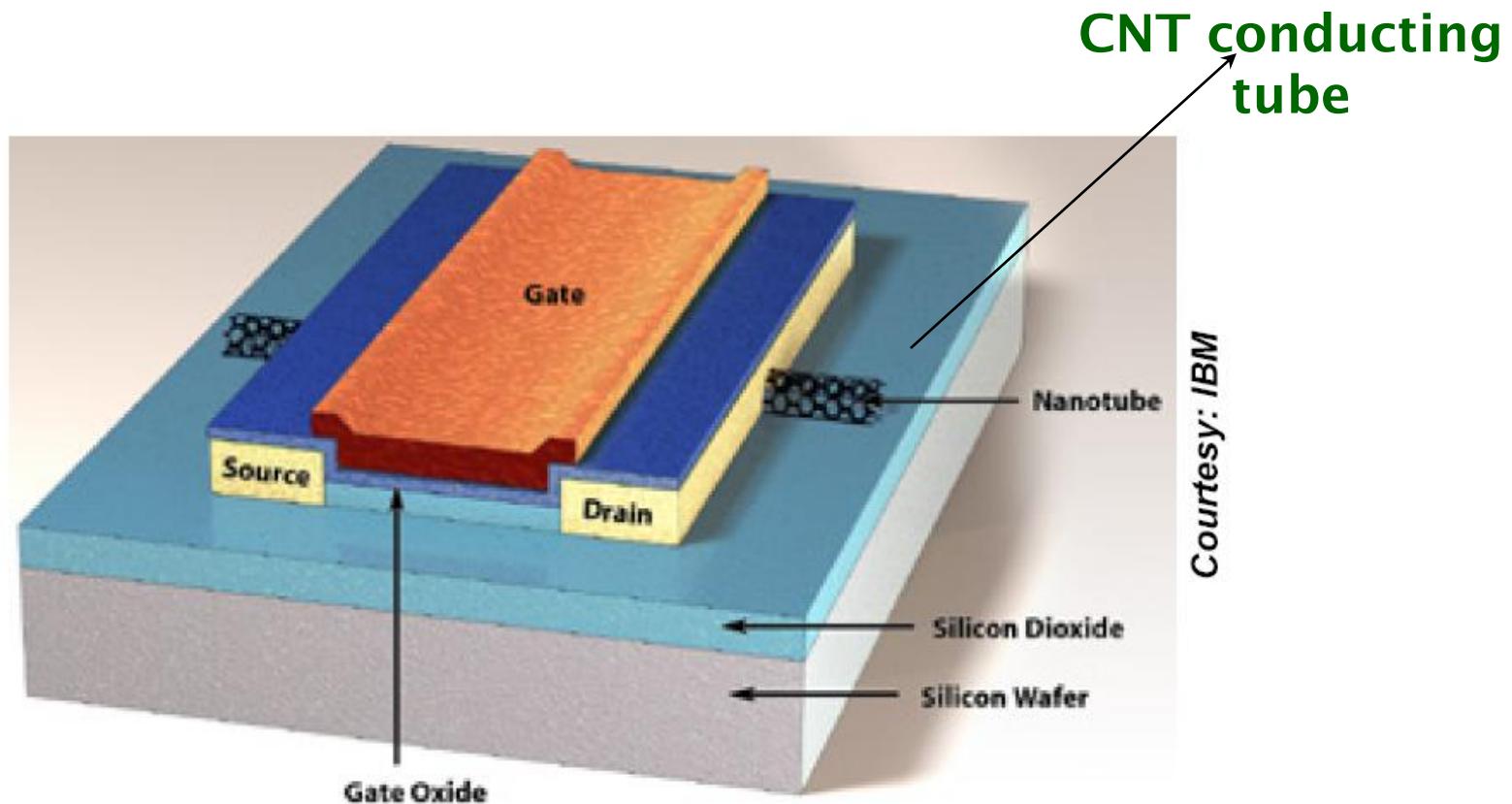
## Applications

- PVD coatings are generally used to improve hardness, wear resistance and oxidation resistance.
- Thus, such coatings use in a wide range of applications such as:
- Aerospace
- Automotive
- Surgical/Medical
- Dies and moulds for all manner of material processing
- Cutting tools

# **Applications of carbon Nanotubes**



- Carbon Nanotube can be used as a **conducting channel** in Field emission Transistor
- CNT conducting channel result the device with low power consumption



## Nanoprobes and sensors

- Because of their flexibility, nanotubes can also be used in scanning probe instruments.
- Since MWNT tips are conducting, they can be used in STM and AFM instruments.
- Advantages are the improved resolution in comparison with conventional Si or metal tips and the tips do not suffer from crashes with the surfaces because of their high elasticity.
- However, Nanotube vibration, due to their large length, will remain an important issue until shorter nanotubes can be grown controllably.
- Nanotube tips can be modified chemically by attachment of functional groups.

## 1. Electronic Devices

Nanotube TV's

Nano-wiring

## 2. High Strength Composites

100 times as strong as steel and 1/6 the weight

## 3. Conductive Composites

## 4. Medical Applications

Encase drug into nanotube capsule for more predictable time release

## Composite materials

- Because of the stiffness of carbon nanotubes, they are ideal candidates for structural applications.
- For example, they may be used as reinforcements in high strength, low weight, and high performance composites.
- Theoretically, SWNTs could have a Young's Modulus of 1 TPa.
- MWNTs are weaker because the individual cylinders slide with respect to each other.
- Ropes of SWNTs are also less strong.
- The individual tubes can pull out by shearing and at last the whole rope will break.

## Templates

- Because of the small channels, strong capillary forces exist in nanotubes.
- These forces are strong enough to hold gases and fluids in nanotubes.
- In this way, it may be possible to fill the cavities of the nanotubes to create nanowires.

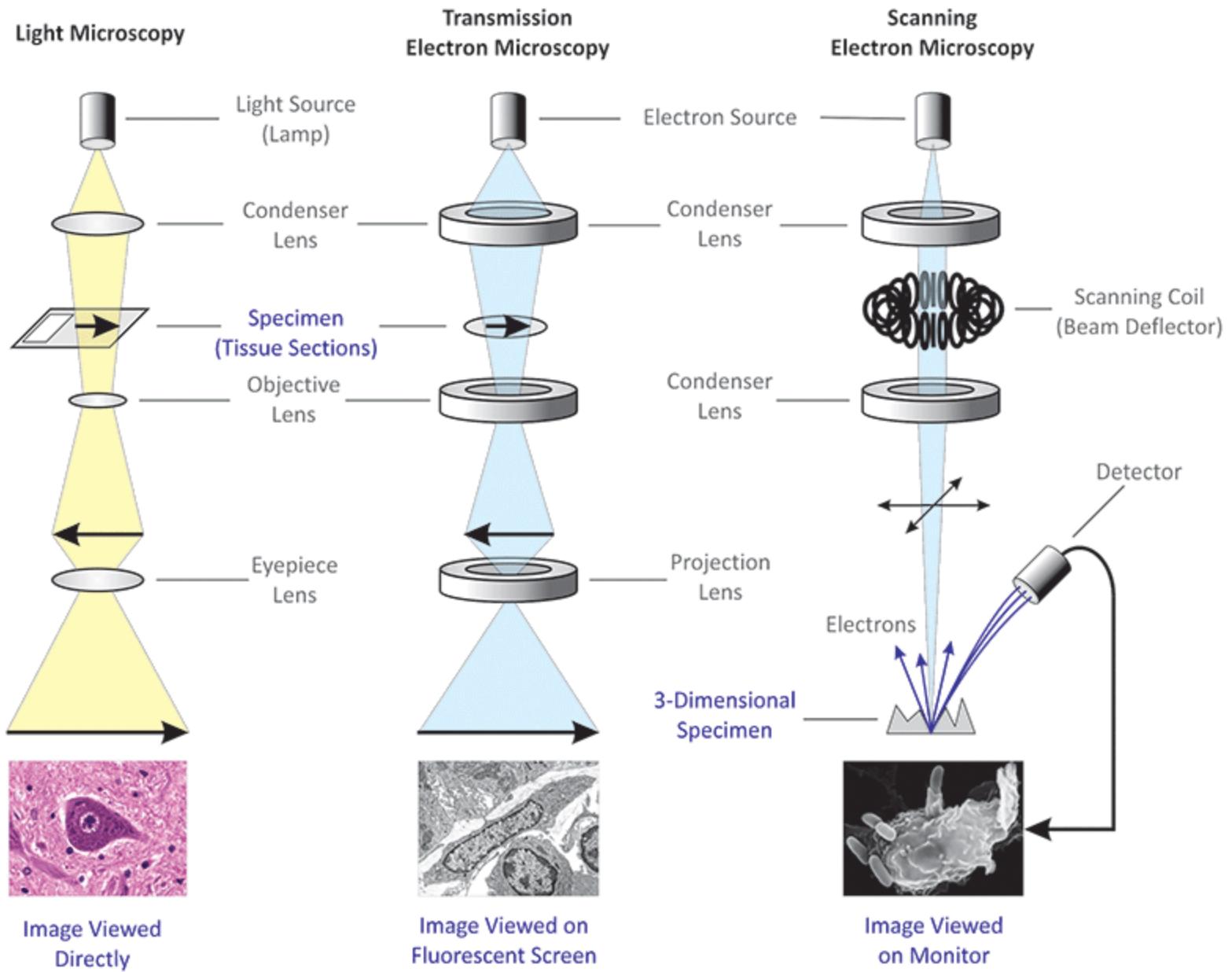


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# **Scanning Electron Microscope (SEM)**

# Basic Electron Optics

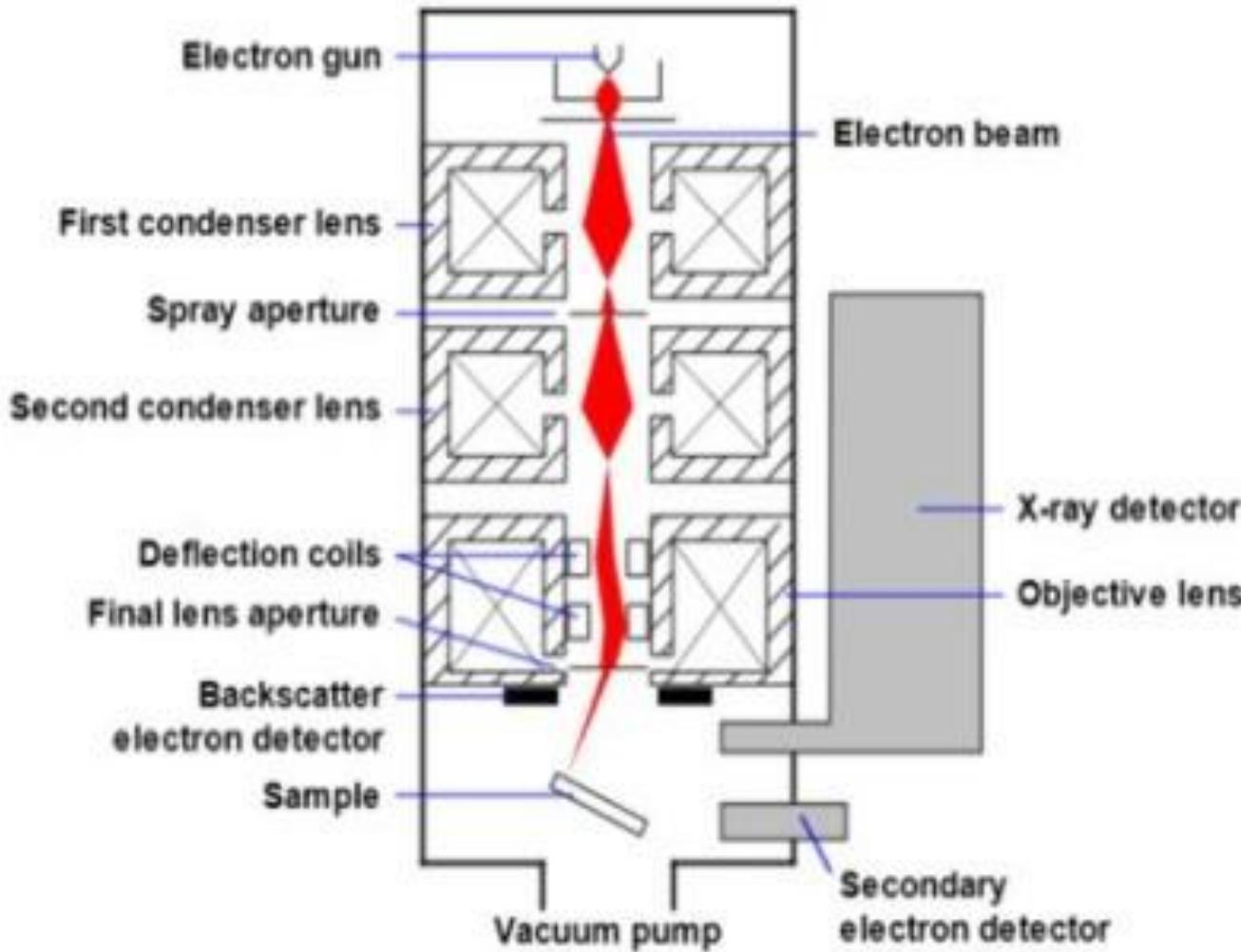
- Electrons and ions are charged particles; they can be accelerated in an electric field
- The trajectory of an accelerated charged particle can be changed (deflected) by E and/ or B field.
- The accelerated particles also behave like waves (de Broglie)



## Scanning Electron Microscope (SEM)

### Working Concept

- **SEM** allows surfaces of objects to be seen in their natural state without staining.
- The specimen is put into the vacuum chamber and covered with a thin coating of gold to increase electrical conductivity and thus forms a less blurred image.
- The electron beam then sweeps across the object building an image line by line as in a TV Camera.
- As electrons strike the object, they knock loose showers of electrons that are captured by a detector to form the image.

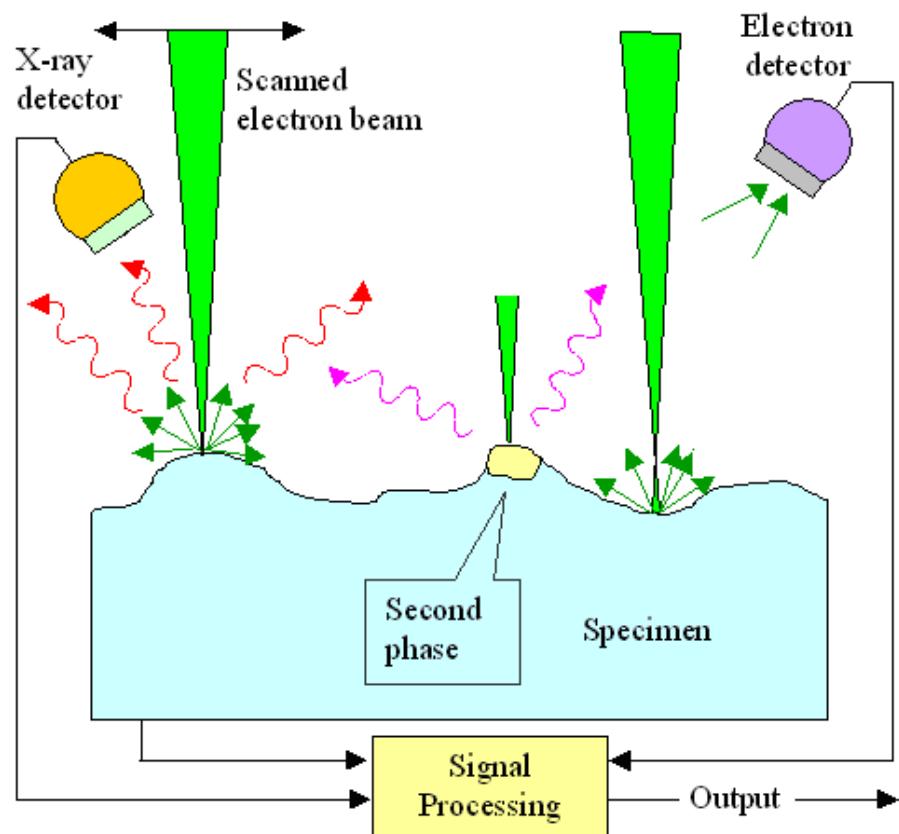
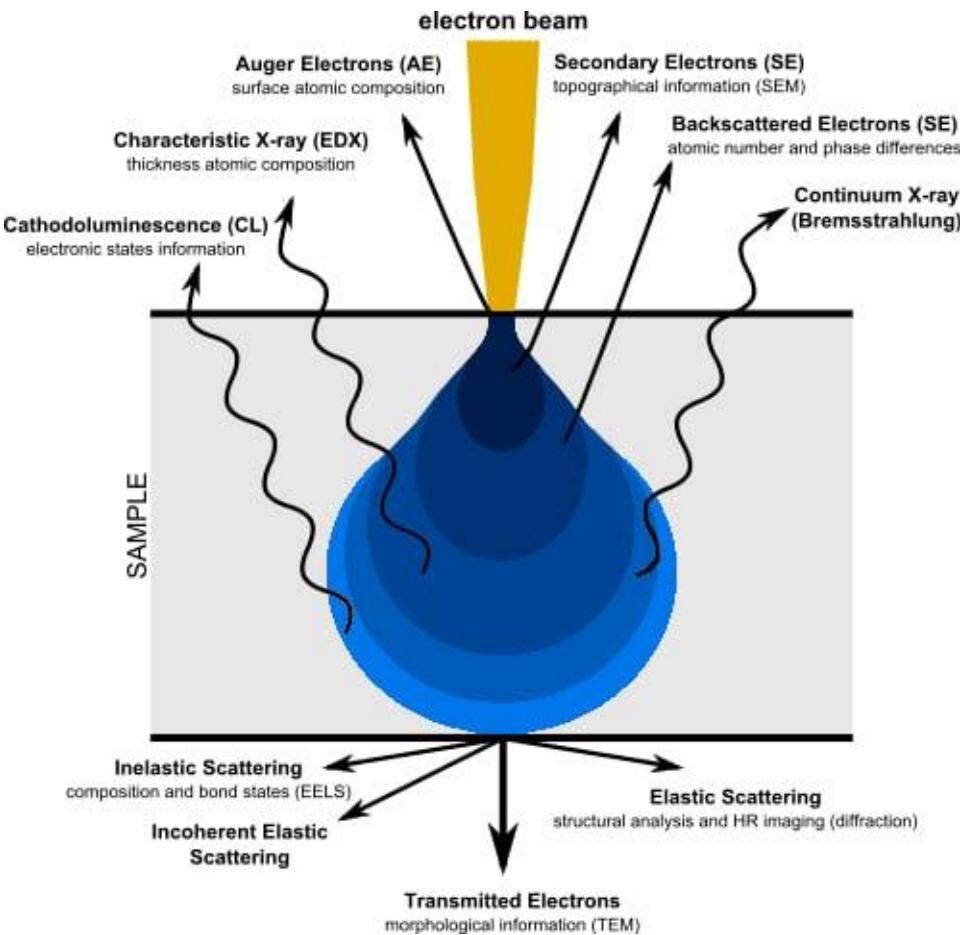


Schematic of SEM

- The "Virtual Source" at the top represents the electron gun, producing a stream of monochromatic electrons.
- The stream is condensed by the first condenser lens (usually controlled by the "coarse probe current knob").
- This lens is used to both form the beam and limit the amount of current in the beam.
- It works in conjunction with the condenser aperture to eliminate the high-angle electrons from the beam
- The beam is then constricted by the condenser aperture, eliminating some high-angle electrons
- The second condenser lens forms the electrons into a thin, tight, coherent beam and is usually controlled by the "fine probe current knob"

- A set of coils then "scan" or "sweep" the beam in a grid fashion (like a television), dwelling on points for a period of time determined by the scan speed (usually in the microsecond range)
- The final lens, the Objective, focuses the scanning beam onto the part of the specimen desired.
- When the beam strikes the sample (and dwells for a few microseconds) interactions occur inside the sample and are detected with various instruments
- Before the beam moves to its next dwell point these instruments count the number of interactions and display a pixel on a CRT whose intensity is determined by this number (the more reactions the brighter the pixel).
- This process is repeated until the grid scan is finished and then repeated, the entire pattern can be scanned 30 times per second.

# Scanning Electron Microscope (SEM)



## Specimen Interactions and utilization: Backscattered Electrons

### *Formation*

- Caused by an incident electron colliding with an atom in the specimen which is nearly normal to the incident's path.
- The incident electron is then scattered "backward" 180 degrees.

### *Utilization*

- The production of backscattered electrons varies directly with the specimen's atomic number.
- This differing production rates causes higher atomic number elements to appear brighter than lower atomic number elements.
- This interaction is utilized to differentiate parts of the specimen that have different average atomic number.

## Secondary Electrons

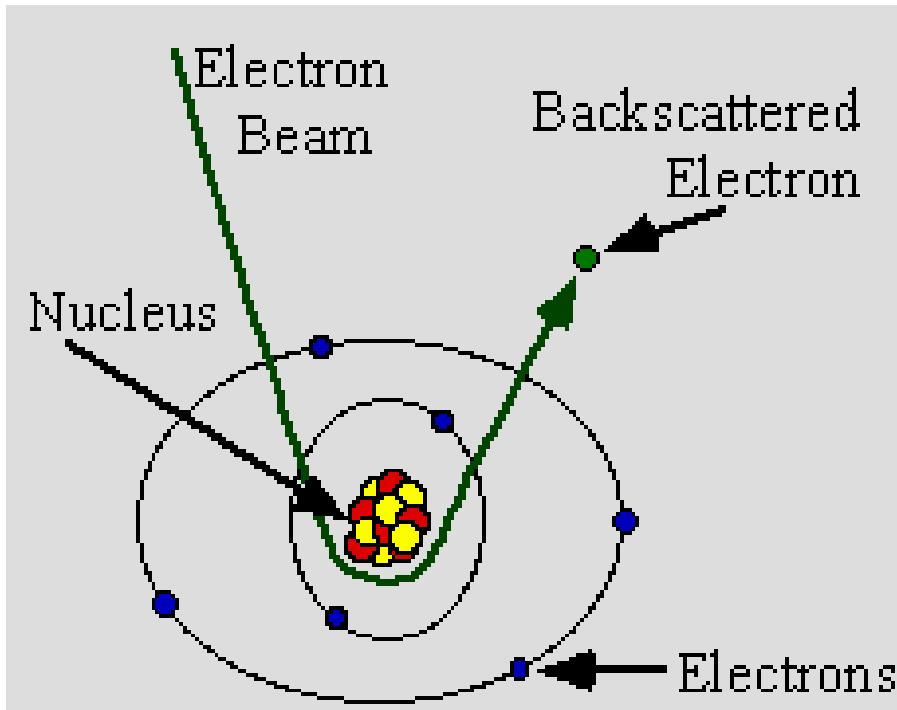
### *Source*

- Caused by an incident electron passing "near" an atom in the specimen, near enough to impart some of its energy to a lower energy electron (usually in the K-shell).
- This causes a slight energy loss and path change in the incident electron and the ionization of the electron in the specimen atom.
- This ionized electron then leaves the atom with a very small kinetic energy (5eV) and is then termed a "secondary electron".
- Each incident electron can produce several secondary electrons.

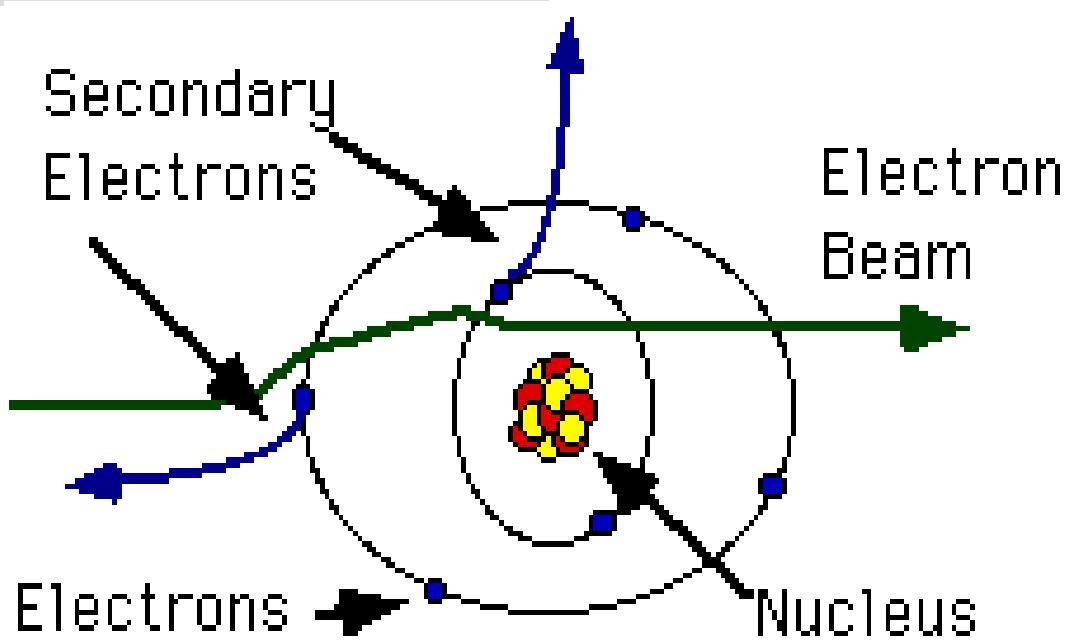


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**BSE**



**SE**



## Utilization

- Production of secondary electrons is very topography related.
- Due to their low energy, 5eV, only secondaries that are very near the surface ( $<10\text{nm}$ ) can exit the sample and be examined.
- Any changes in topography in the sample that are larger than this sampling depth will change the yield of secondaries due to collection efficiencies.
- Collection of these electrons is aided by using a "collector" in conjunction with the secondary electron detector.
- The collector is a grid or mesh with a +100V potential applied to it which is placed in front of the detector, attracting the negatively charged secondary electrons to it which then pass through the grid-holes and into the detector to be counted.

## Auger Electrons

### *Source*

- Caused by the de-energization of the specimen atom after a secondary electron is produced.
- Since a lower (usually K-shell) electron was emitted from the atom during the secondary electron process an inner (lower energy) shell now has a vacancy.
- A higher energy electron from the same atom can "fall" to a lower energy, filling the vacancy.
- This creates an energy surplus in the atom which can be corrected by emitting an outer (lower energy) electron; an Auger Electron.

## *Utilization*

- Auger Electrons have a characteristic energy, unique to each element from which it was emitted from.
- These electrons are collected and sorted according to energy to give compositional information about the specimen

## X-rays

### *Source*

- Caused by the de-energization of the specimen atom after a secondary electron is produced.
- Since a lower (usually K-shell) electron was emitted from the atom during the secondary electron process an inner (lower energy) shell now has a vacancy.
- A higher energy electron can "fall" into the lower energy shell, filling the vacancy.
- As the electron "falls" it emits energy, usually X-rays to balance the total energy of the atom so it .
- X-rays or Light emitted from the atom will have a characteristic energy which is unique to the element from which it originated.

# Modern SEM Instrument





# **DEPARTMENT OF PHYSICS AND NANOTECHNOLOGY**

## **SRM INSTITUTE OF SCIENCE AND TECHNOLOGY**

**Electron Microscopy-Transmission Electron Microscope (TEM)**



## □ **Transmission Electron Microscope (TEM)**

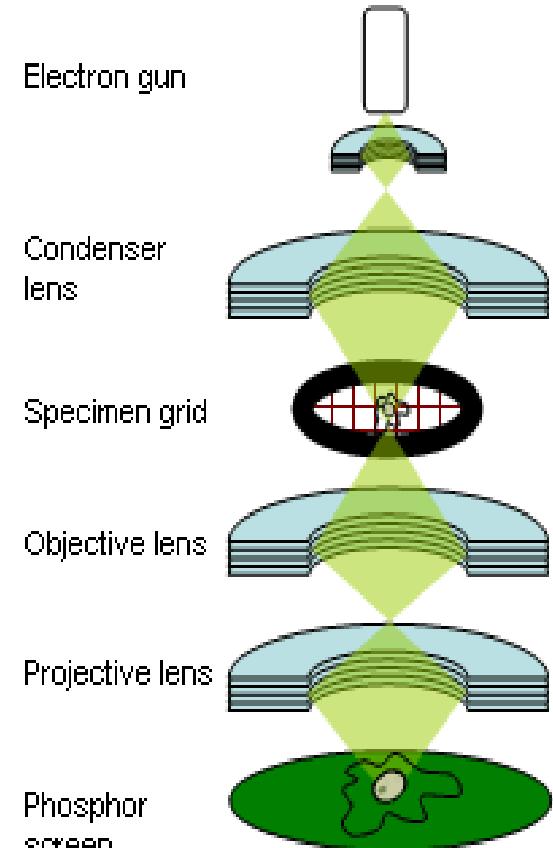
### **Working Concept**

- TEM works much like a slide projector.
- A projector shines a beam of light through (transmits) the slide, as the light passes through it is affected by the structures and objects on the slide.
- These effects result in only certain parts of the light beam being transmitted through certain parts of the slide.
- This transmitted beam is then projected onto the viewing screen, forming an enlarged image of the slide.
- TEMs work the same way except that they shine a beam of electrons (like the light) through the specimen (like the slide).
- Whatever part is transmitted is projected onto a phosphor screen for the user to see.

# Common Modes of Operation of TEM

- **Bright Field (BF) Microscopy**
- **Dark Field (DF)**
- **Selected Area Diffraction**

- The "Virtual Source" - the electron gun, produces a stream of monochromatic electrons.
- This stream is focused to a small, thin, coherent beam by the use of condenser lenses 1 and 2. The first **lens** (usually controlled by the "spot size knob") largely determines the "**spot size**"; the general size range of the final spot that strikes the sample.
- The second lens (usually controlled by the "intensity or brightness knob" actually changes the size of the spot on the sample; changing it from a wide dispersed spot to a pinpoint beam.
- The beam is restricted by the condenser **aperture** (usually user selectable), knocking out high angle electrons (those far from the optic axis, the dotted line down the center)
- The beam strikes the specimen and parts of it are transmitted



### ***Unscattered electrons:***

*Incident electrons which gets transmitted through the specimen without interacting with the sample*

#### ***Utilization:***

*Thicker sample- fewer transmitted electrons-appear darker*

*Thinner sample- more transmission- appear brighter*

### ***Elastically scattered electrons:***

*Incident electrons which gets scattered by the atoms in the sample elastically (no loss of energy). Then they are transmitted*

#### ***Utilization:***

*All electrons follow Braggs condition for scattering*

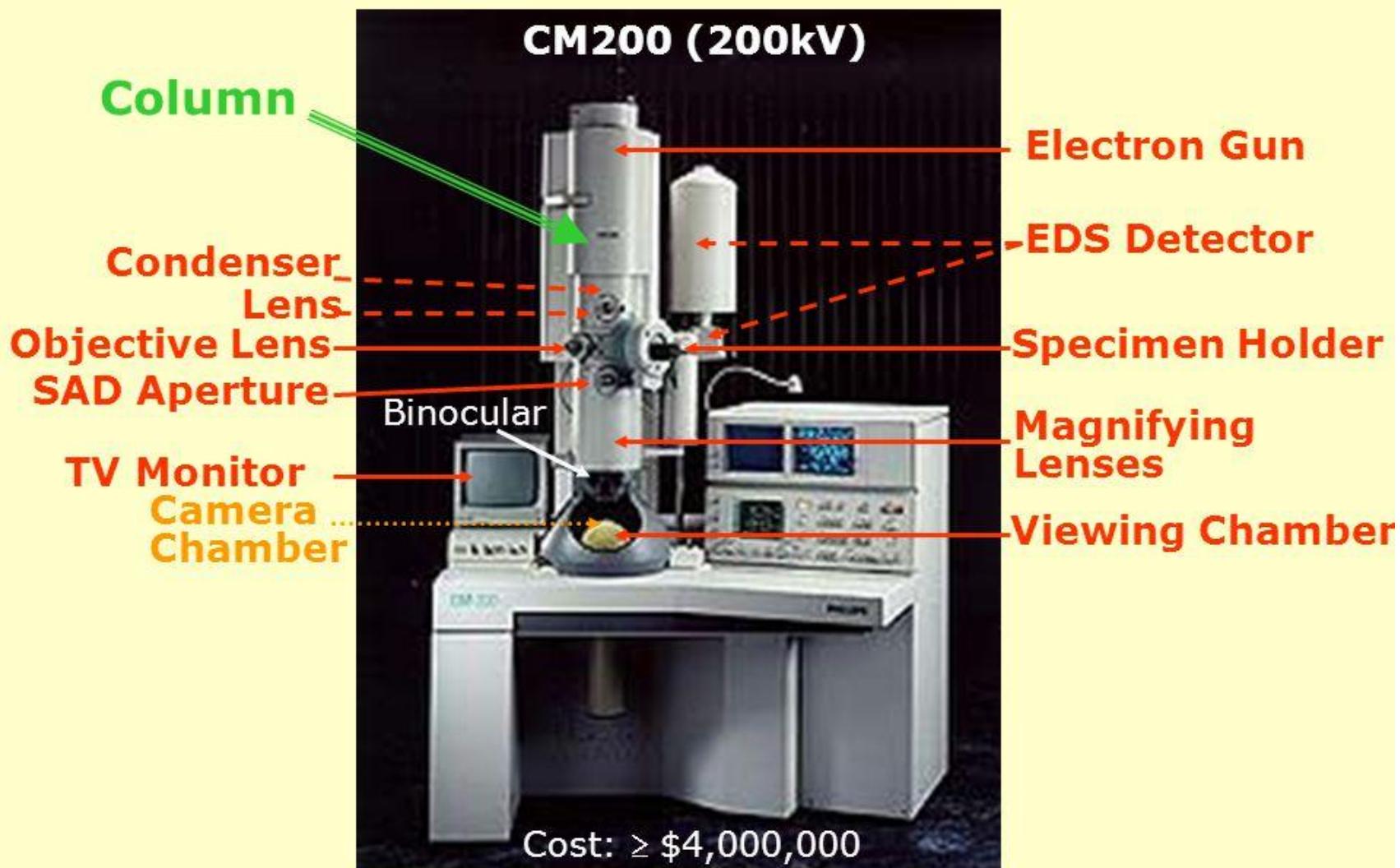
### ***Inelastically Scattered Electrons :***

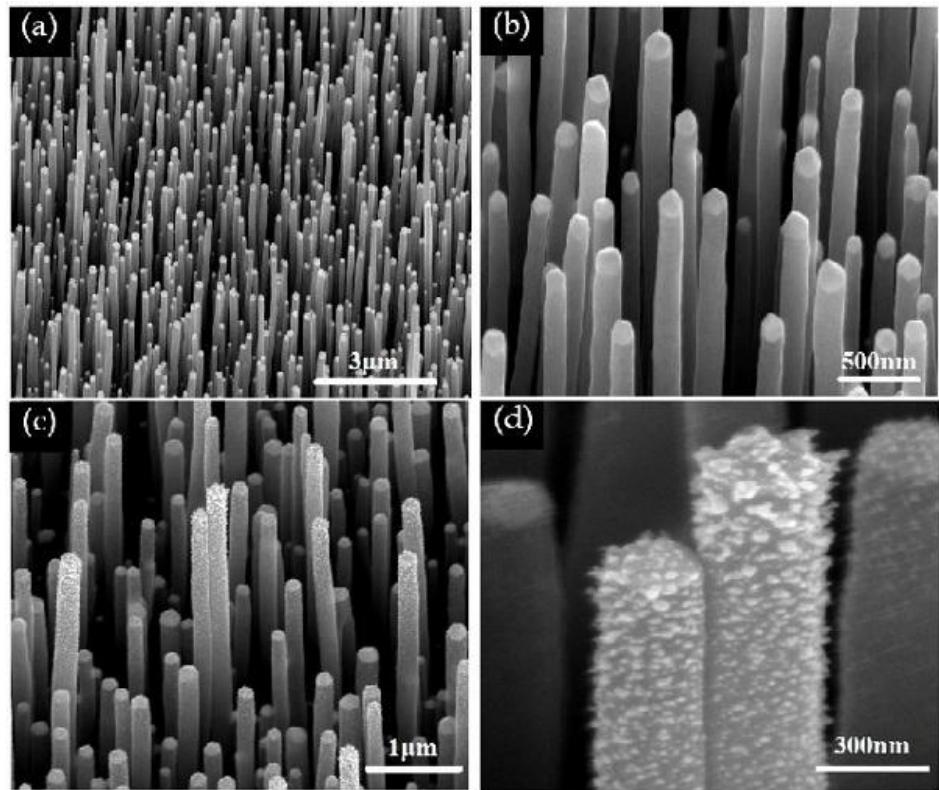
*Incident electrons interact with the sample inelastically (loss of energy) and gets transmitted into the specimen*

*Kakuchi Bands: - Bands of alternating light and dark lines that are formed by inelastic scattering interactions that are related to atomic spacing in the specimen*

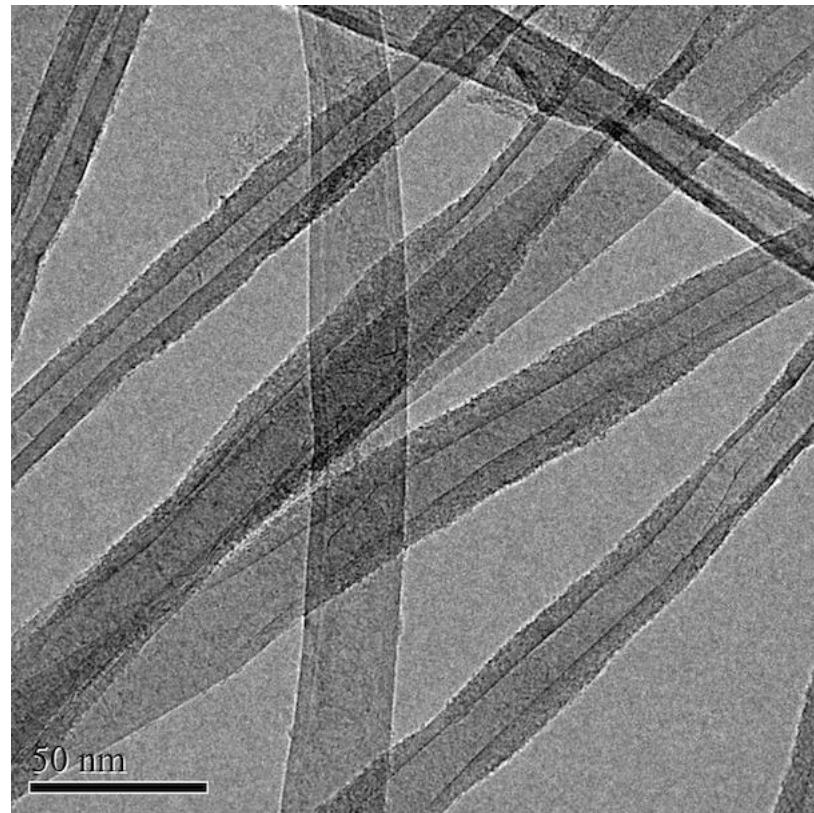
# Modern SEM Instrument

## Basic features of A Modern TEM





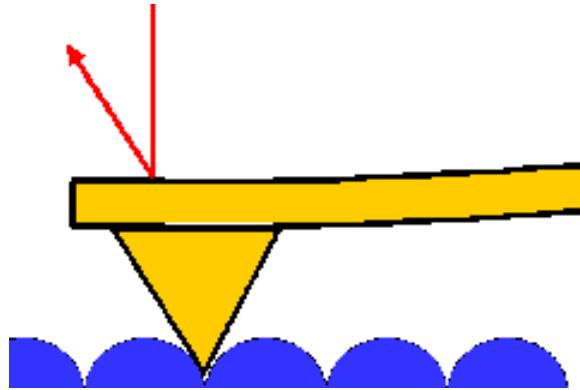
**SEM Images of CNTs**



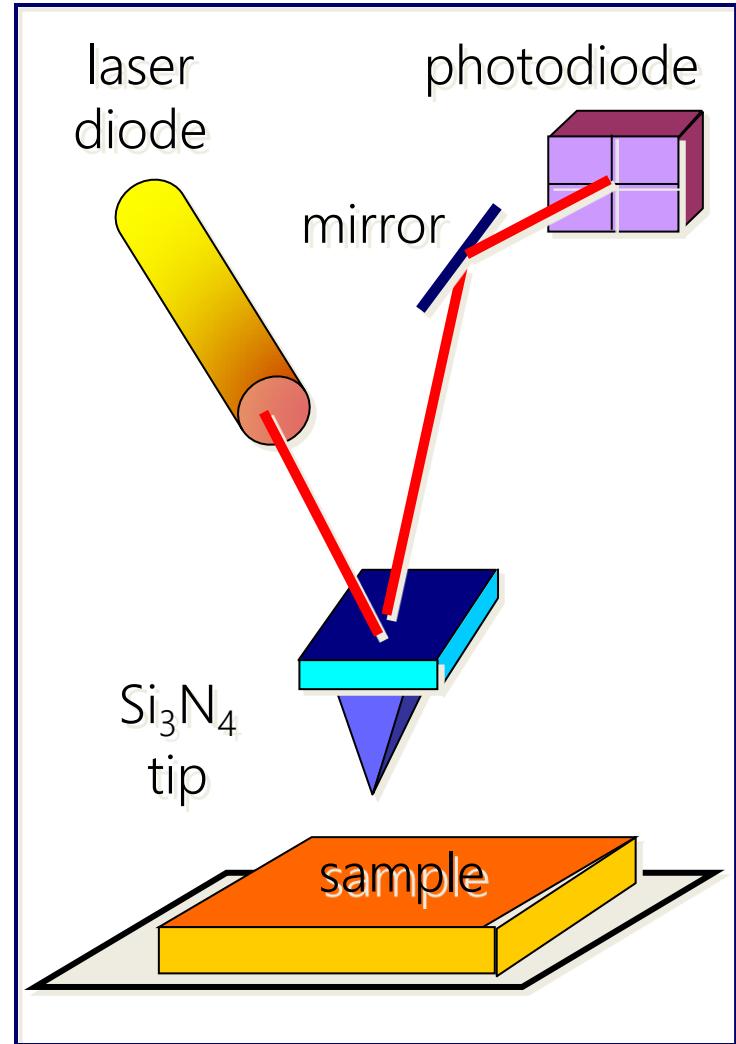
**TEM Image of CNTs**

# AFM - Atomic Force Microscopy

How does the AFM work?

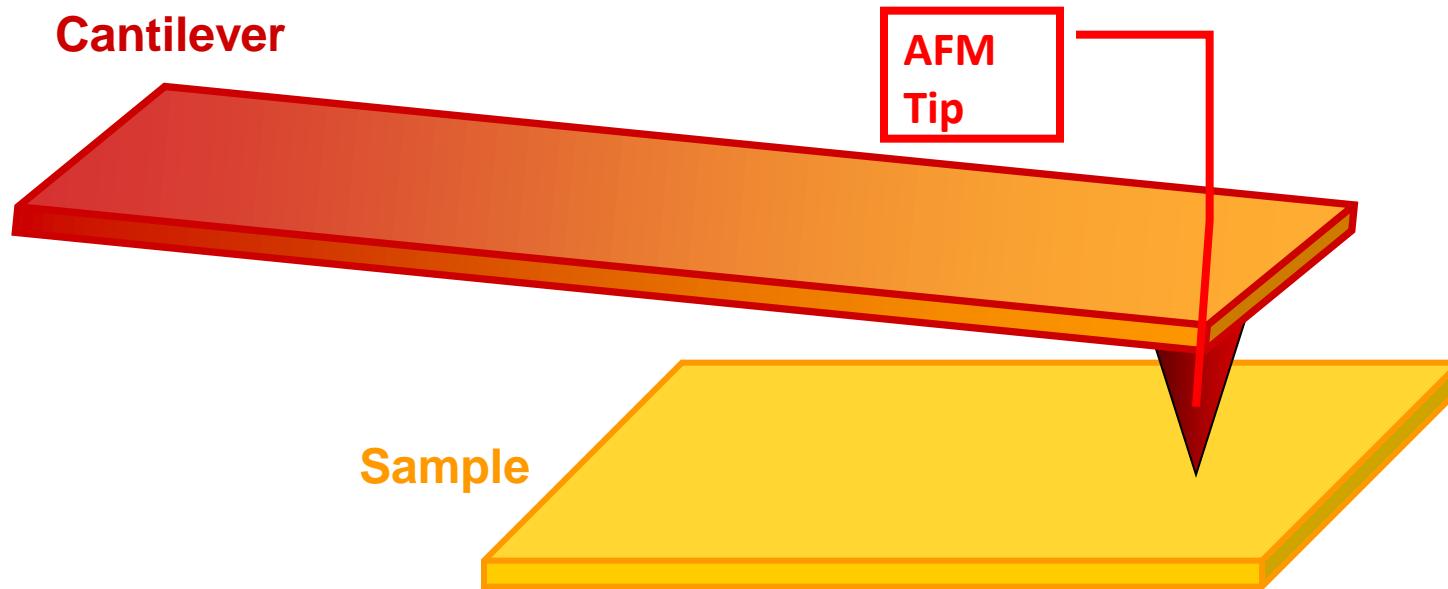


Tip Scans Sample  
Up & down movement of the tip  
is recorded by position sensing  
photodiode



## Scanning Probe Microscopy—the Atomic Force Microscope (AFM)

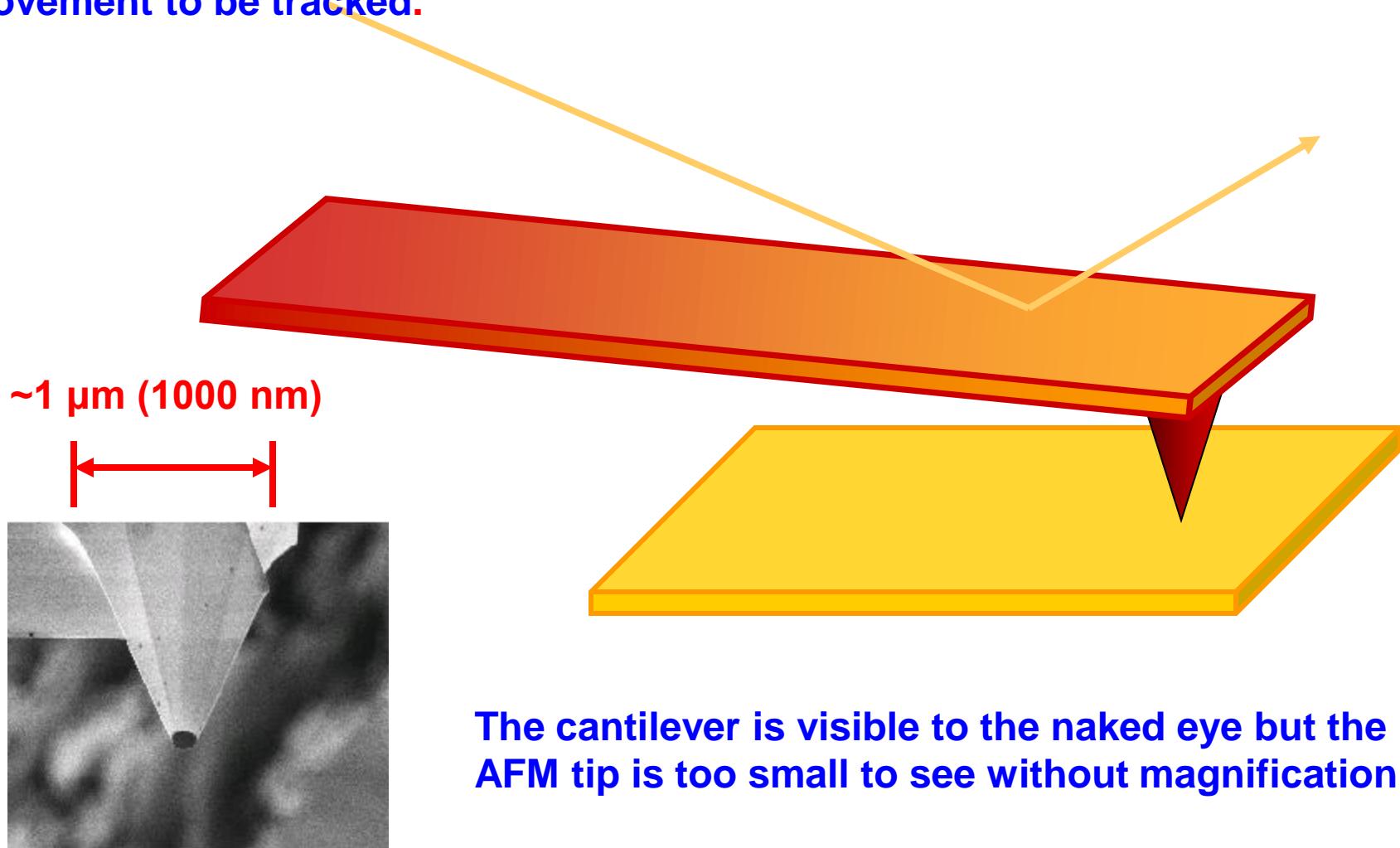
The AFM like the scanning tunneling microscope (STM) is a scanning microscope, but the mechanism depends on the force of attraction between molecules



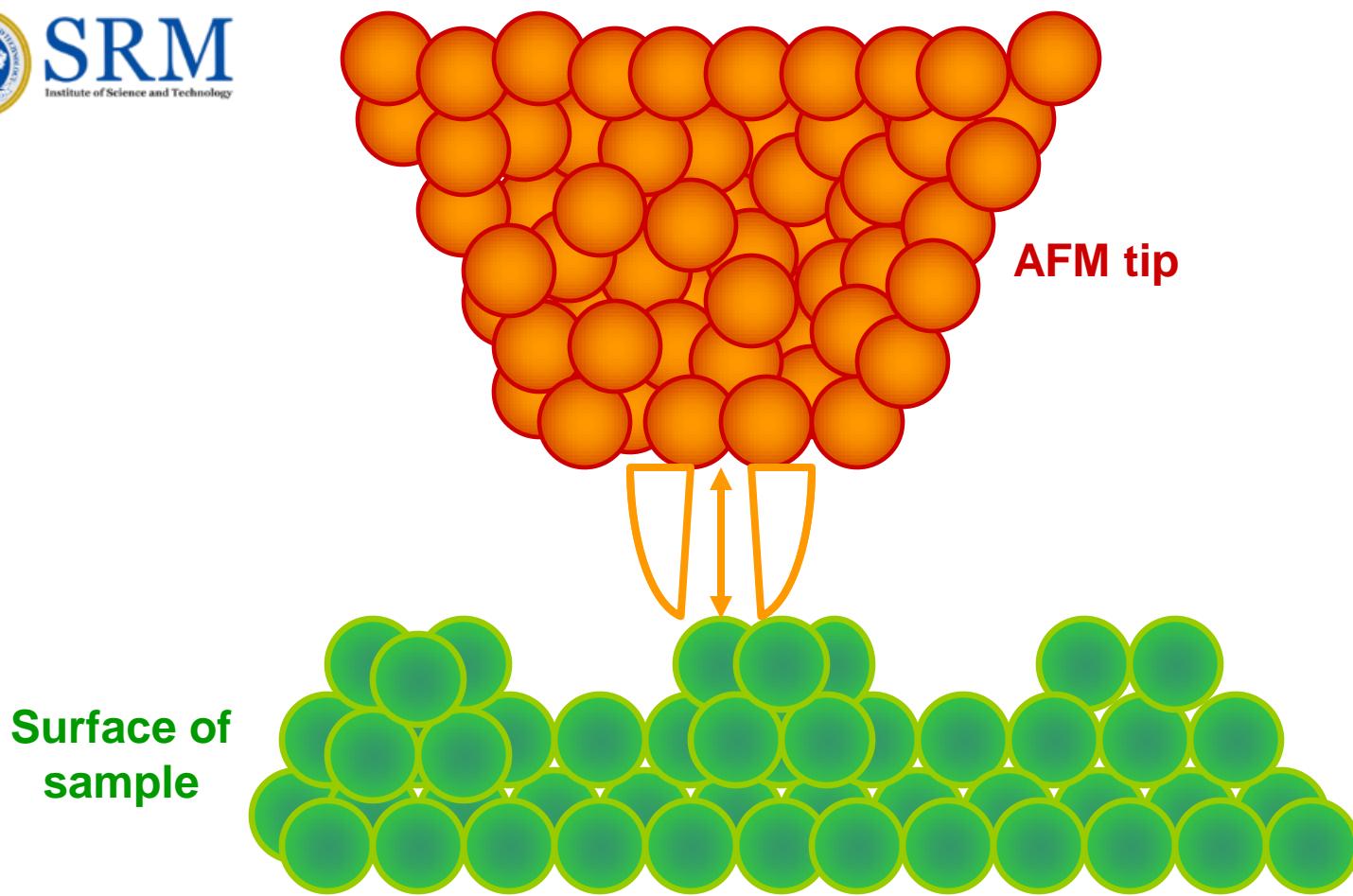
No current flows between the AFM Tip and sample, so the sample need not be conducting [a requirement for the STM].

The atoms of the tip are attracted to the atoms of the sample by the van der Waals interaction.

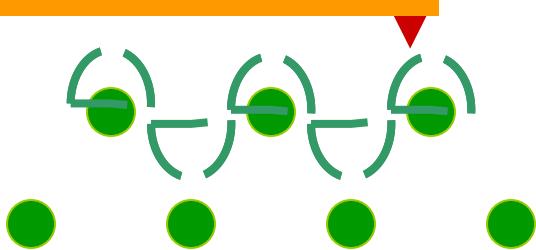
As the AFM tip is attracted to the surface (causing the cantilever to bend), a laser beam bounces off the end of the cantilever—allowing the tip's movement to be tracked.



The cantilever is visible to the naked eye but the AFM tip is too small to see without magnification.



The attractive van der Waals interaction acts at a molecular and atomic level, between the AFM tip and the local atoms at the sample's surface.

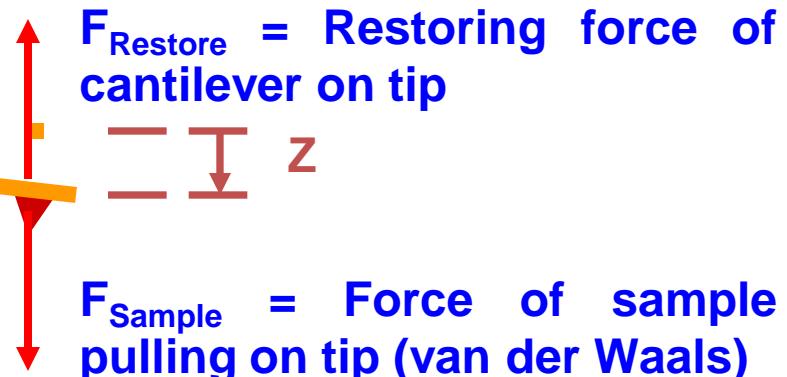


As the AFM tip scans the surface, its up and down motions map the contour of the sample—scanned line by line.

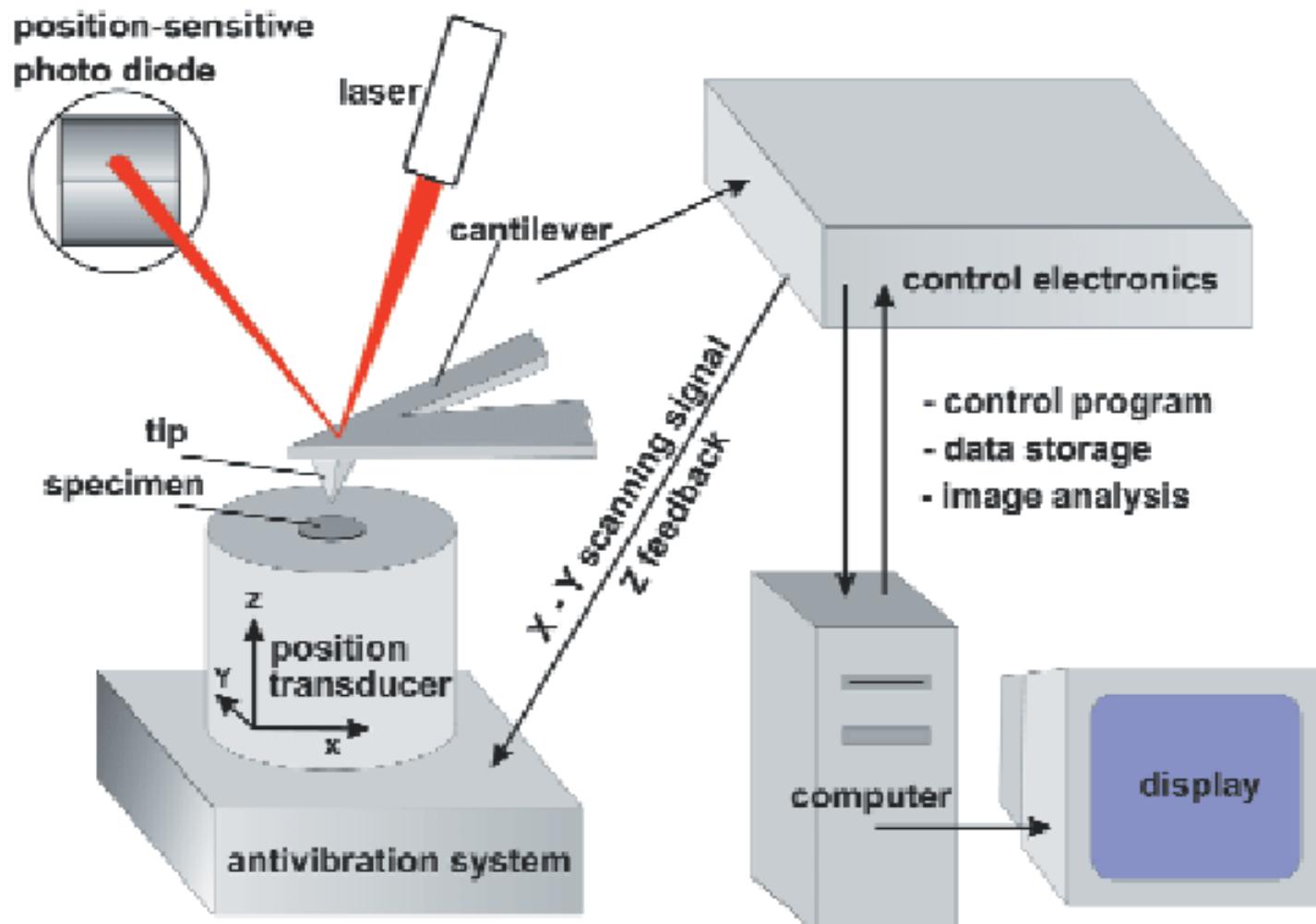
The force on the AFM tip is harmonic (spring like): the tip is displaced toward the surface a distance ( $Z$ ) proportional to the van der Waals force.

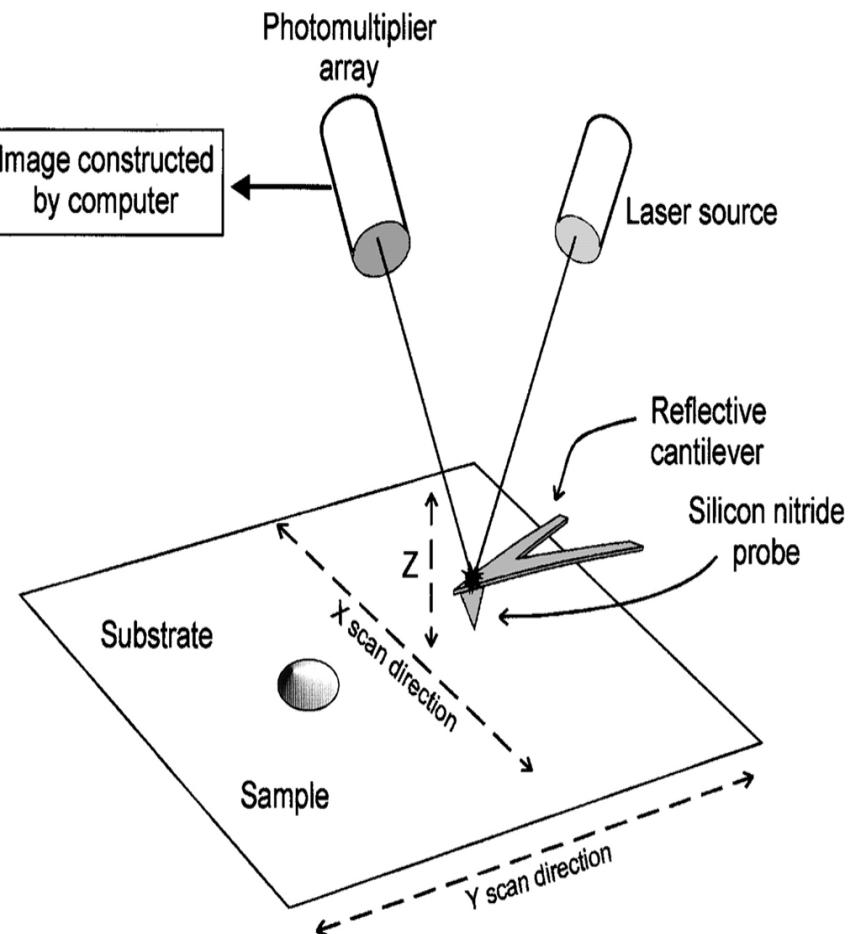
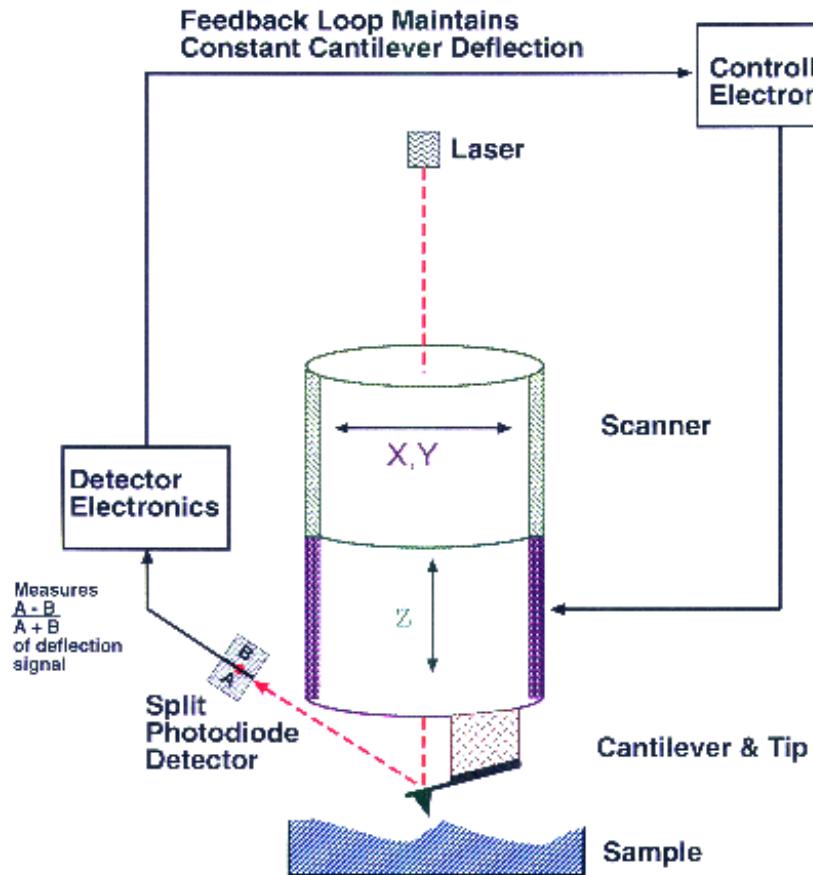
$$F_{\text{Restore}} = -kZ$$

$k \sim 1 \text{ N/m} \Rightarrow$  An AFM can measure forces of pN ( $10^{-12}$  Newton) & even fN ( $10^{-15}$  N) size!



## Principle of an atomic force microscope (AFM)







# IMAGING METHODS

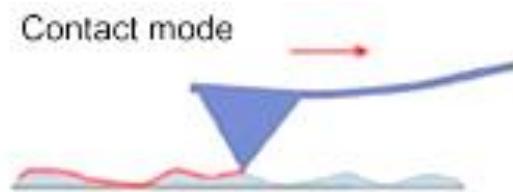
What types of forces are measured ?

## Modes of operation

1. Contact
2. Noncontact
3. Tapping

Contact mode

Contact mode



Noncontact mode

Noncontact mode



Tapping mode

Tapping mode

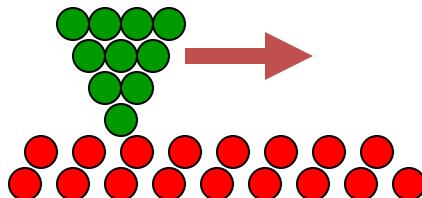




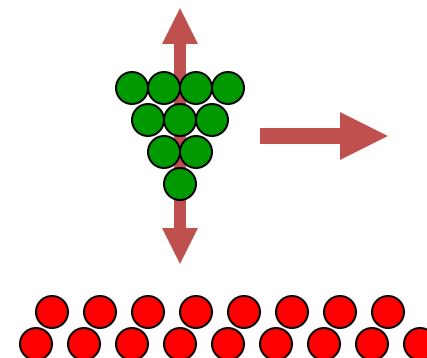
## The AFM can operate in three different ways

1. **Contact Mode**—the tip is dragged along a sample's surface; the cantilever deflection is measured and translated into surface shapes. This mode can damage the surface.
2. **Non-contact mode**—the cantilever oscillates above the sample's surface and is affected by surface/tip forces (van der Waals) as it does so.
3. **Tapping Mode**—The AFM tip taps the sample surface during the closest point of approach of an oscillation cycle.

Contact



Intermittent/Tapping



# ADVANTAGES AND DISADVANTAGES

## **CONTACT MODE:**

- Fast scanning, good for rough samples
- But deforms soft samples

## **TAPPING MODE:**

- good for biological samples
- Slow scan speed and challenging in liquids

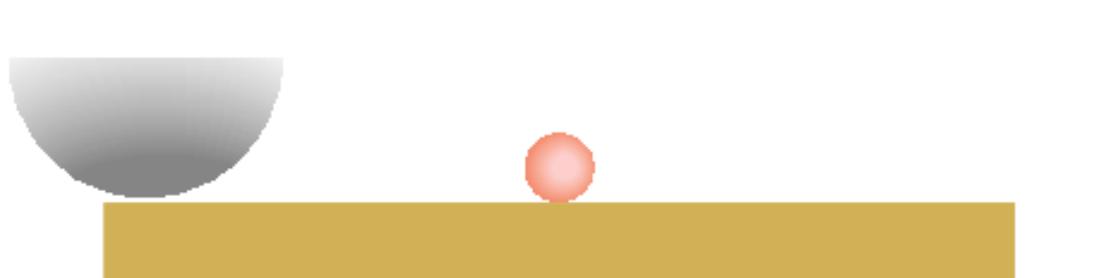
## **NON-CONTACT MODE:**

- low force exerted on the sample
- Low resolution contaminant layer can interfere usually need UHV system for good imaging



# Advantages and Limitations of AFM

- Used to study variety of samples
- Does not require a conducting sample
- Does not reflect the true sample topography but represents the interaction between the tip and the surface called TIP CONVOLUTION



\*Tip broadening – radius of curvature of the tip >size of the feature to be imaged

\*As the tip scans, if the sides of the tip make contact before the apex and the microscope begins to respond to the feature

- **Advantages**

- The AFM has several advantages over the scanning electron microscope (SEM).
- Unlike the electron microscope which provides a two-dimensional projection or a two-dimensional image of a sample, the AFM provides a **true three-dimensional surface profile**.
- Additionally, samples viewed by AFM **do not** require any special treatments (such as metal/carbon coatings) that would irreversibly change or damage the sample.
- While an electron microscope needs an expensive **vacuum** environment for proper operation, most AFM modes can work perfectly **well** in ambient air or even a liquid environment.
- This makes it possible to study biological macromolecules and even living organisms.
- In principle, AFM can provide higher resolution than SEM. It has been shown to give true atomic resolution in ultra-high vacuum (UHV).

- **Disadvantages**

- A disadvantage of AFM compared with the **scanning electron microscope (SEM)** is the image size.
- The SEM can image an area on the order of **millimeters** by millimeters with a **depth of field** on the order of millimeters.
- The AFM can only image a maximum height on the order of micrometers and a maximum scanning area of around 150 by 150 micrometers.
- Another inconvenience is that at high resolution, the **quality of an image** is limited by the **radius of curvature** of the probe tip, and an incorrect choice of tip for the required resolution can lead to image artifacts.
- Slow scan and less scanner area
- Artefacts/Hysteresis effects or cross-talk influences the image

# AFM Images

