

UNIT-5

Density of states in 2D, 1D and 0D :-

The density of states function describes the no. of 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 wells (2D), quantum wires (1D) and quantum dot (0D) must be known.

Density of states in 2D :-

The energy of a particle in a 2D potential well is

given by $E = \frac{\hbar^2}{8ma^2} (n_x^2 + n_y^2) = \frac{\hbar^2 n^2}{8ma^2}$ — (1)

where, $n_x^2 + n_y^2 = n^2$

- for a 2D case, n represents the radius of a circle and only the first quadrant can be considered since the quantum number (i.e n_x, n_y) should be positive.

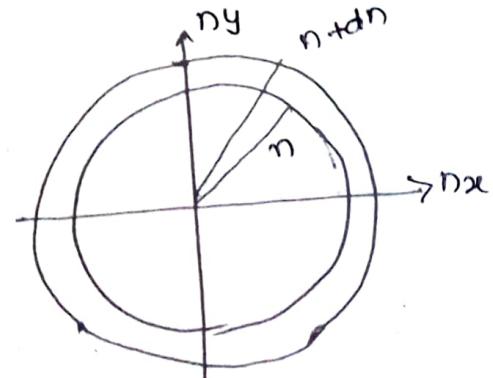
- Each state can accommodate two electrons, so, the effective no. of states will be

$$N = \frac{1}{4} \times 2 \times \pi n^2$$

$$N = \frac{\pi n^2}{2} — (2)$$

By using equ: (1), it is possible to calculate the DOS in terms of energy. So

$$N(E) = \frac{\pi}{2} \cdot \frac{gma^2 E}{\hbar^2} = \frac{g\pi ma^2 E}{h^2} = \frac{m a^2 E}{h^2 \pi} — (3)$$



Thus, density of state per unit energy is then obtained by differentiating equation (3) with respect to E:

$$\Rightarrow \frac{dN(E)}{dE} = \frac{ma^2}{\hbar^2 \pi}$$

The density of state per unit area, per unit energy is found by dividing by a^2 (area of the crystal i.e. a^2)

$$g(E) = \frac{dN(E)}{dE \cdot V} = \frac{ma^2}{\hbar^2 \pi \cdot a^2}$$

$$(g(E))_{2D} = \frac{m}{\pi \hbar^2} \quad (4)$$

Hence, the density of state function is independent of energy.

Density of state in 1D:

The calculation for a 1D solid is similar to the earlier calculations except that there is only one quantum number ($n_x = n$) and it is represented on a line (instead of circle in 2D).

$$\text{so } E = \frac{\hbar^2}{8ma^2} n^2$$

$$\text{or } n^2 = \frac{8ma^2 E}{\hbar^2}$$

So, the effective no. of states will be

$$\begin{aligned} N &= 2n \\ \text{or } N(E) &= 2 \cdot \sqrt{\frac{8ma^2 E}{\hbar^2}} \\ N(E) &= 2a \sqrt{\frac{8m}{\hbar^2} E^{1/2}} \end{aligned}$$

Thus, density of state per unit energy is then obtained by differentiating eqn(1) w.r.t. to E

$$\frac{N(E)}{dE} = \frac{2a}{2} \sqrt{\frac{8m}{h^2}} \cdot E^{-\frac{1}{2}}$$

$$\therefore \frac{N(E)}{dE} = a \sqrt{\frac{8m}{h^2}} \cdot E^{-\frac{1}{2}}$$

The density of state per unit line, per unit energy is found by dividing by 'a'.

$$g(E) = \frac{N(E)}{dE \cdot a} = \sqrt{\frac{8m}{h^2}} E^{-\frac{1}{2}}$$

$$[g(E)]_{1D} = \sqrt{\frac{8m}{h^2}} \cdot \frac{1}{\sqrt{E}} = \frac{1}{\hbar \pi} \cdot \sqrt{\frac{2m}{E}} =$$

So, In a 1D solid, the density of states decreases with energy.

Density of state in 0D :-

In 0D material, no free motion is possible. Becoz there is no space to be filled with electrons and all available states exist only in discrete energies. Therefore, the density of states for 0D using a delta function is written as

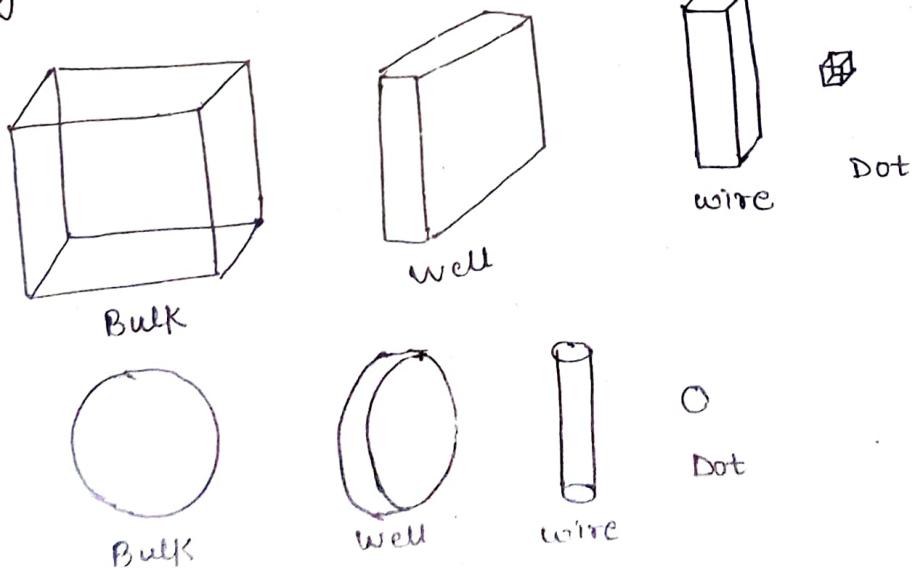
$$[g(E)]_{0D} = 2\delta(E - E_c)$$

Introduction of low dimensional systems :-

When the size or dimension of a material is continuously reduced from a large or macroscopic size, such as a meter or centimeter, 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 nanorange, while the other two dimensions remain large, then we obtain a structure known as a quantum well.
- If two dimensions are so reduced and one remain 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 these three types of ^{nano}structure bcz the change in properties arise from the quantum-mechanical nature of physics in the domain of ultrasmall.



Nano Materials & Nano Technology

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UNIT - II

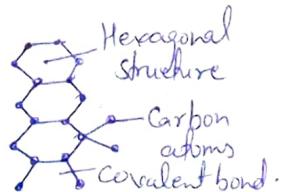
Carbon Nanotubes - [CNT].

- Nanotubes are about 100 times stronger than steel but just a sixth of the weight.
- They have unusual heat and conductive characteristic.

Carbon Nanotube can be a single walled or multiple walled. A single walled is just a single cylinder of graphite while a multiwalled carbon nanotube is an assembly of concentric circles of single walled carbon nanotubes one with another.

Single Walled Nanotubes : - [SWNT's] -

This is formed by rolling a single layer of graphite (hexagonal lattice of carbon), called layer into a cylinder.



A graphene sheet can be rolled into a more than one way producing different types of Carbon Nanotubes.

Main types are - (i) Arm chair (ii) Zig-zag
(iii) Chiral.

Graphene sheet wrapped is represented by a pair of indices (n, m) - called chiral vector. The unit vectors n & m represent the no. of unit

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unit vector \hat{n} along two directions in honey comb crystal lattice of graphite. If $m=0$, the nanotubes are called zig-zag.

If $n=m$, — Armchair nanotubes otherwise chiral. The length and the diameter of a single walled nanotubes varies but a typical tube would be about 1nm in diameter & the few hundred nm's in length. The production of SWCNT's are quite expensive.

Mult-walled Nanotube (MWNTs) —

It consists of multiple concentric nanotubes cylinder. The interlayer distance b/w the concentric b/w graphene layer in the graphite. It is approximately 3.3 \AA° .

Synthesis of Carbon Nanotubes — Carbon

nanotubes can be synthesized in a sizeable quantities by no. of methods including arc discharge, laser Ablation, High pressure carbon monoxide deposition & chemical vapor deposition techniques etc. Most of these techniques takes place in vacuum. Large CNT's can be synthesized by CVD growth techniques.

(i) Arc Discharge — During this process, the carbon contained in the -ve electrode sublimates due to high temperature generated during the discharge.

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With this arc discharge method both single walled and multi walled nanotubes with length upto 50μm can be synthesized.

③ Laser Ablation— In this technique, a pulse laser vaporizes a graphite target in high temperature reactor while an inert gas is bled into the chamber. The nanotubes develop as the vaporized carbon condenses on the cooler surface of the reactor. A water cooled surface is provided in the system to collect the carbon nanotubes. This method is used to produce single walled CNT's and is more expensive than either Arc Discharge or CVD.

③ Chemical Vapour Deposition— It is the common method for commercial production of CNT's.

In this a substrate is prepared with a layer of metal catalyst particles (such as Nickel, Cobalt, iron etc.). Substrate is heated to approximately 700°C. To initiate the growth of nanotubes two gases are bled into the reactor, a process gas (Nitrogen, hydrogen etc.) and a carbon containing gas (like ethylene, ethanol etc.). The temperature is high enough to break the bond between the carbon atoms & hydrogen atoms of the carbon containing gas at the surface of the catalyst particle and the carbon atom is transported to the edge of the particle where it forms the nanotubes.

Special properties of CNT's -

nanotubes possess many unique properties and have a very broad range of electronic, kinetic, electrical, thermal, structural properties.

i) Electrical — They are greatly affected by the symmetric & unique electronic structure of the graphene with which it is manufactured
eg- If $n-m$ is a multiple of 3, then it is metallic.
If $n-m$, it is armchair.

Electric current density of metallic CNT is more than ~~to~~ 100 times greater than of metal such as Ag, Cu.

ii) Kinetic — Multivalled nanotubes is a combination of multiple concentric single walled nanotubes. MWNT's exhibits a striking telescope properties whereby inner nanotube core may slide without friction. Thus creating perfect linear or rotational bearing.

iii) Thermal — Nanotubes are good thermal conductors along the tube but good insulators. The temperature stability of carbon nanotubes is expected to be upto 2800°C in vacuum & approximately 750°C in air.

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Mechanical Strength — CNT's have a very large Young's Modulus and these compounds are particularly potentially suitable for applications in composite materials.

Optical Activity — Studies revealed that optical activity of chiral nanotubes disappears if the nanotubes becomes layer.

Potential Application of CNT's —

Pg. no - 4.14 & 4.15 (on your own).

Chemical Vapor Deposition — (CVD) :-

It is a generic name for a group of processes that involve depositing a solid material from a gaseous phase.

This process is often used in the semiconductor industry to produce thin films. Microfabrication processes widely use CVD to deposit materials like — monocrystalline, polycrystalline, amorphous etc. This is also used to produce synthetic diamonds.

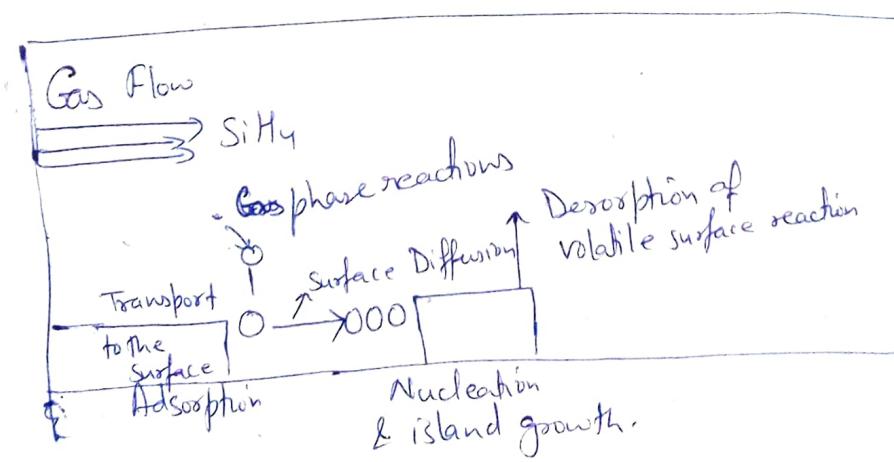
Working — Precursor gases (often diluted in carrier gases) are delivered into the reaction chamber at approximately ambient temperatures. As they pass over or come in

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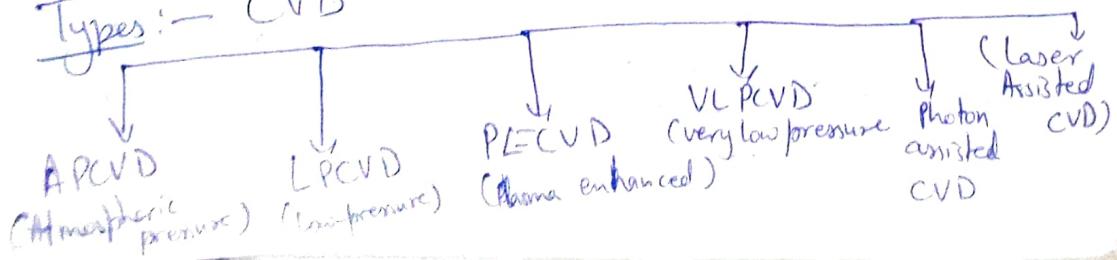
contact with a heated substrate, they react or decompose forming a solid phase and are deposited onto the substrate. The substrate temperature is critical & can influence the reactions.

CVD Reaction Mechanism —

- Mass transport of the reactions in bulk.
- ~~gas~~ gas-phase reactions (homogeneous)
- Mass-transport to the surface.
- Adsorption on the surface.
- Surface reactions ~~heterogeneous~~ (heterogeneous)
- Surface migration.
- Incorporation of film constituents, island formation.
- Deposition of by products.
- Mass transport of by products in bulk.



Types: — CVD



Comparison of AP, LP of PE CVD techniques.

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APCVD

Advantage

- (i) Simple
- (ii) Fast deposition
- (iii) Low temperature.

Disadvantage

- (i) Poor step coverage
- (ii) Contamination.

Application → low temperature oxide.

LPCVD

Advantage → Purity, uniformity, step coverage,
large wafer capacity.

Disadv. High temperature, slow deposition

Application → high temp. oxides.

PECVD

Adv. Good step coverage, low temperature.

Disadv. Contamination of chemicals + particle.

Application → low temp. insulators over metals.

Physical Vapor Deposition →

This technique is based on the formation of vapour of the material to be deposited as a thin film. This is similar to CVD except that the raw materials which are to be deposited are in solid form whereas in CVD this is

introduced in the form of gases.

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Working — steps are —

① Evaporation — In this process the target material to be deposit is bombarded by a high energy source ie electrons or ions. These high energy e⁻ or ions vaporise the atom from the surface of the material.
fig - on your own.

② Transport — In this process the vaporized atoms move directly to the substrate on which the material is to be deposited.

③ Reaction — This step is involved in case of metal oxide in which the target material (metal) will react with the gas. Gases used in this stage are oxygen, nitrogen + methane.

④ Deposition — Its the last step during evaporated material gets deposited on the substrate. The process of PVD is done in vacuum chamber.

There are other methods of PVD as follows —

- (i) Evaporation Deposition (ii) Electron beam PVD
- (iii) Sputter Deposition (iv) Cathode Arc Deposition
- (v) Pulsed Laser Deposition

Comparative study of e-beam, sputter & filament evaporation

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	<u>Merits</u>	<u>Demerits</u>
Electron Beam —	high temp mat. high purity.	poor step coverage. Alloys Alloys difficult.
Filament Evaporation —	Simple implementation	Poor step coverage Alloys difficult.
Sputter Deposition —	High temp material good step coverage less radiation damage.	Porous films Plasma damage or contamination.

Importance of PVD Coating —

- ① Improved hardness ② Reduced friction
- ③ Improved Oxidation Resistance

Advantages + Disadvantages & Applications —

On your own (3 to 6 pts each).

Electron Microscopy Techniques :-

An electron microscope is a microscope that uses a beam of accelerated electrons as a source of illumination. Because the wavelength of an electron can be upto 100,000 times shorter than that of visible light photons. The electron microscope has a higher resolving power than a light microscope and can reveal the structure of smaller objects. This examination can yield the following information.

Topography :- The surface features of an object like texture, hardness, reflectivity etc.

Morphology :- The shape and size of the particles making up the object.

Composition :- The elements and compounds that the object is composed of and the relative amount of them.

Crystallographic Information :- How the atoms are arranged in the object.

Types :- There are two main electron microscopy techniques:

- Transmission electron microscopy (TEM)
- Scanning electron microscopy (SEM)

Transmission Electron Microscope (TEM) :- The modern TEMs are used to produce the images in the scanning range of 0.1nm with a magnification of 50 million times.

TEM is a microscopy technique whereby a beam of electrons is produced from an electron gun and transmitted through an ultra thin specimen interacting with the specimen, magnified and focused by an objective electromagnetic lens. The final image may appear on an imaging screen or a photographic film or a CCD camera.

Electrons are generally produced by thermionic emission, then accelerated by an electric potential and focused by electromagnetic lenses on to the sample. The transmitted beam contains information about electron density, phase and periodicity that are used to form an image.

electron source

Nature of the specimen :-

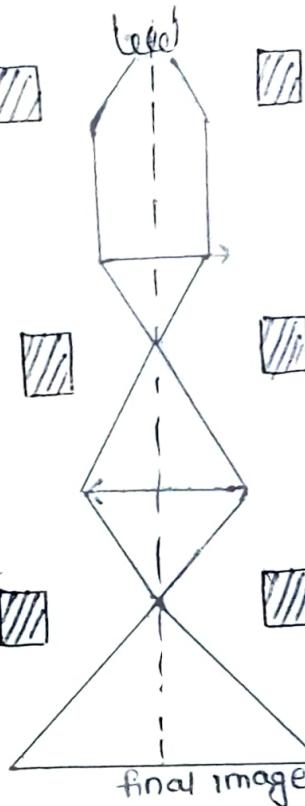
The object to be investigated must be specially prepared and mounted.

It must be transparent to the electron beam and its thickness must be less than 50nm. further, the specimen should be able to withstand the high vacuum present inside the instrument. The object is generally deposited on a thin cellulose or a similar material and dried before being mounted on special holders.

Magnetic condenser lens

Magnetic objective lens

Magnetic projection lens



Magnification :- TEM gives a magnification of the order of 10,000 to 20,000 times and the smallest distance that can be resolved is about 10nm.

Limitations :-

1. Many materials require extensive sample preparation to produce a thin sample and hence it is time consuming.
2. The structure of the sample may change during the sampling process.
3. The field of view is relatively small.
4. Biological samples may be damaged due to bombardment of electrons.

Uses :- 1. One can obtain the imaging of individual molecules or macromolecular assemblies.

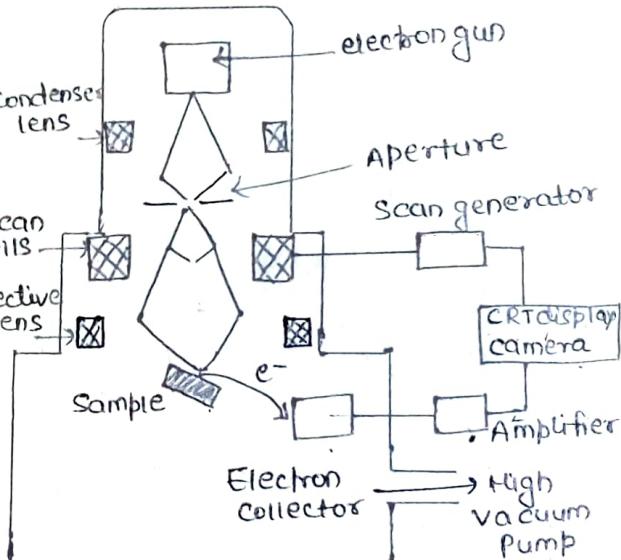
- iv) It is used heavily in materials, metallurgy and biological sciences.
- v) Computer modeling of the images is an added advantage in TEM characterisation.

Scanning electron microscope (SEM):

A scanning electron microscope is used to produce a three dimensional image of a specimen of any size and thickness.

A schematic diagram of the SEM is shown in figure.

In this a beam of electrons is generated in the electron gun, located at the top of the column. This beam is attracted through the anode, condensed by a condenser lens and focused as a very fine point on the sample by the objective lens. The scan coils are energized and create a magnetic field which deflects the beam back and forth in a controlled pattern. The varying voltage is also applied to the coils around the neck of the CRT which produces a pattern of light deflected back and forth on the surface of the CRT.



The pattern of deflection of the electron beam is the same as the pattern of deflection of the spot of light on the CRT. These electrons are collected by a collecting grid that is held at a positive potential with respect to the anode that is held at a negative potential. The current in the electron collector is converted to a voltage and amplified. The amplified voltage is applied to the grid of the CRT and causes the intensity of the spot of light to change. The image consists of thousands of spots of varying intensity on the face of a CRT that correspond to the topography of the sample.

Comparison between TEM and SEM:— TEM resolution is about an order of magnitude greater than SEM resolution. However,

2. SEM is based on scattered electrons while TEM is based on transmitted electrons.
3. SEM focuses on the sample's surface and its composition whereas TEM provides the details about internal composition.
4. The sample in TEM has to be cut thinner whereas there is no such need with SEM sample.
5. SEM provides a 3D image while TEM provides a 2D picture.
6. SEM is used for surfaces, powders, polished and etched microstructures, IC chips whereas TEM is used for imaging of dislocations, tiny precipitates, grain boundaries and other defect structures in solids.

Scanning Probe Microscopy :-

Scanning Probe microscopy is a new branch of spectroscopy that forms images of surfaces using a physical probe that scans the specimen.

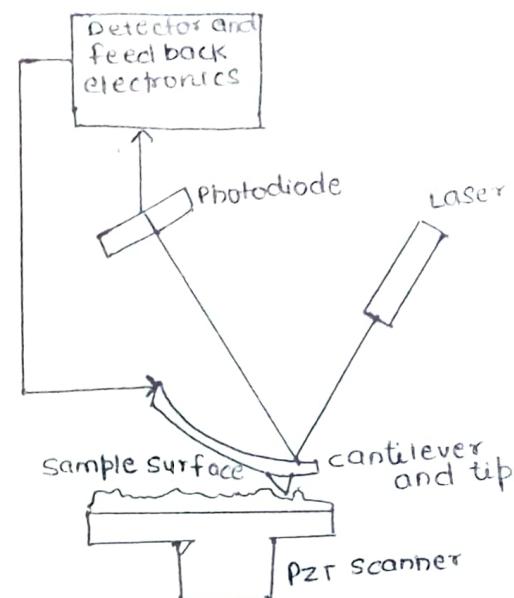
Types :-

- Atomic force microscopy (AFM)
- electrostatic force microscope (EFM)
- force modulation microscopy (FMM)
- magnetic force microscopy (NFM)
- Scanning tunneling microscopy (STM)
- Scanning voltage microscopy (SVM)
- Scanning Hall probe microscopy (SHPM).

Atomic force Microscope :- The AFM has the advantage of imaging almost any type of surface, including polymers, ceramics, composites, glass and biological samples.

The AFM consists of a microscale cantilever shaped much like a diving board with the sharp tip (probe) at its end which is used to scan the sample surface. The

Cantilever is typically made of silicon or silicon nitride. The radius of curvature of the tip is of the order of nanometers. A laser is positioned such that its light strikes at an oblique angle at the very end of the cantilever. When the tip is brought into proximity of a sample surface, the tip is repelled by or attracted to the surface. These forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. As the cantilever bends the light from the laser is reflected onto an array of photodiode. A plot of the laser reflection versus tip position on the sample surface provides the resolution of the hills and valleys that constitute the topography of the surface.



Advantages over SEM:-

1. Unlike the SEM which provides a 2D image of a sample, the AFM provides a 3D surface profile.
2. Sample viewed by AFM do not require any special treatment.
3. SEM needs an vacuum environment for proper operation, most while AFM can work perfectly well in ambient air or even a liquid environment.
4. AFM can provide higher resolution than SEM.

Disadvantages :-

1. The AFM can only image a maximum height on the order of micrometers and a maximum scanning area of around 150 by 150 micrometers.
2. 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.
3. AFM could not scan images as fast as an SEM.
4. AFM images can be affected by hysteresis of the piezo-electric material.