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.

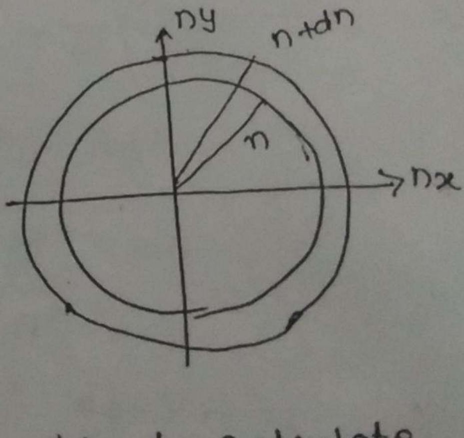
Density of States in 2D :-

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

$$E = \frac{h^2}{8ma^2}(n_x^2 + n_y^2) = \frac{h^2 n^2}{8ma^2} \quad -(1)$$

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

(1) 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.



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

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

$$N = \frac{\pi n^2}{2} \quad -(2)$$

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

$$N(E) = \frac{\pi}{2} \cdot \frac{8ma^2E}{h^2} = \frac{4\pi ma^2E}{h^2} = \frac{ma^2E}{\hbar^2 \cdot \pi} \quad -(3)$$

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

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

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)

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

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

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).

$$\text{So} \quad E = \frac{h^2}{8ma^2} n^2$$

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

So, the effective no. of states will be

$$N = 2n$$

$$\text{or} \quad N(E) = 2 \cdot \sqrt{\frac{8ma^2E}{h^2}}$$

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

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

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

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

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

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

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

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

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

Introduction of low dimensional systems :-

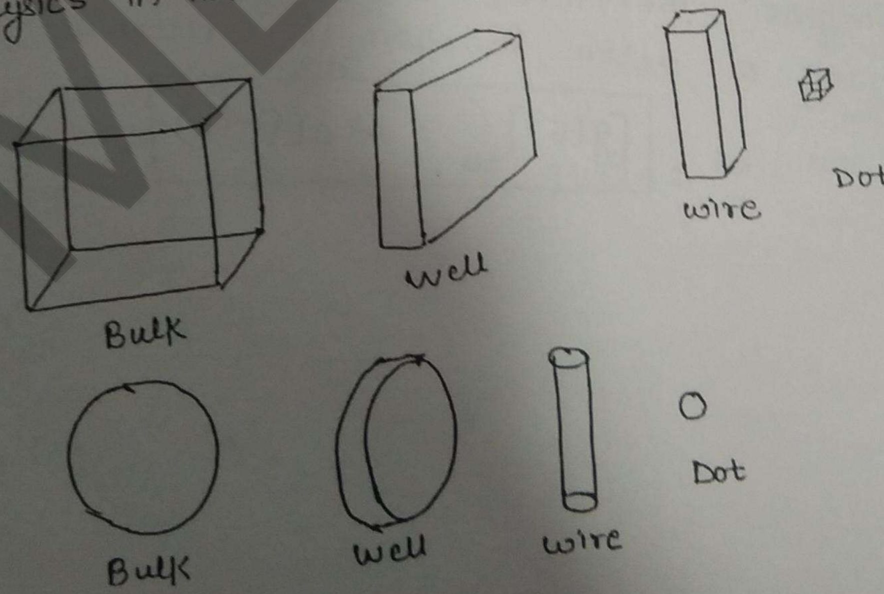
when the size or dimension of a material is continuously reduced from a large or macroscopic size, such as a meter or centimeter, to a very small size, the properties remain the same at first, then small changes begin to occur, until finally when the size drops below 100 nm, dramatic changes in properties 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 becoz the change in properties arise from the quantum-mechanical nature of physics in the domain of ultrasmall.



Introduction of novel low dimensional systems:-

low dimensional systems or materials is the structure of materials with improved properties through controlled synthesis and assembly of the material at nano-scale level. If at least one dimension of a structured component of a material is less than 100 nm, then it is called a nano-materials.

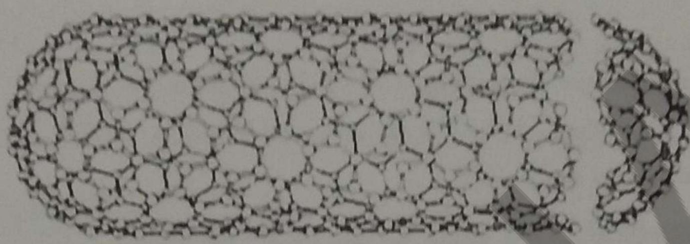
The factors that differentiate nanomaterials from bulk materials is the increase in surface area to volume ratio and quantum confinement effects. These are explained below.

(a) Surface area to volume ratio:- The nano-materials possess large value of surface area to volume ratio as compared to the bulk material. The high surface area can be attained either by fabricating small particles or clusters where the surface to volume ratio of each particle is high. This unique property of surface to volume ratio leads to greater chemical reactivity and effect their strength. The electrical conductivity of nano-materials also enhanced appreciably due to better ordering in microstructure.

(b) Quantum confinement effect:- According to band theory, solid materials have energy bands and isolated atoms possess discrete energy levels. Nanomaterials are in intermediate to the above two cases. for nanomaterials, if the dimensions of potential well or potential boxes are of the order of de-broglie wavelength of electrons or mean free path of electrons, then the energy levels of electrons change, and the electron will remain confined to a small region of the material. This is called quantum confinement. So, The quantum effects are dominant in nanoparticle materials.

CARBON NANOTUBES (CNT):

Carbon nanotubes or CNT in short, are allotropes of carbon with a cylindrical nanostructure. They are the cylindrical rolled up sheet of graphene, which is a single layer of graphite atoms arranged in a hexagonal pattern. These are also known as **tubular fullerenes**. This cylinder can be closed or open at the end.



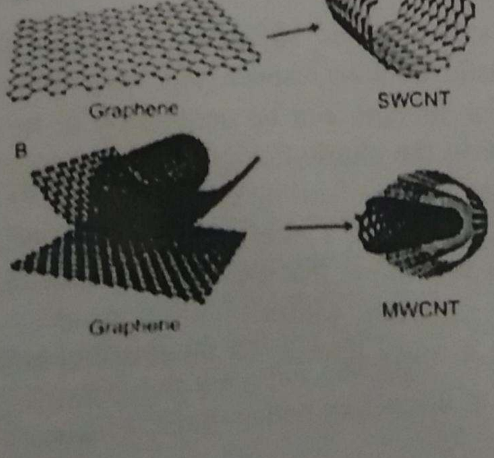
The diameter of a CNT is typically in the nanometer range (1 nm to 20 nm) and length can be several hundred times the width (Fig.a). The longest CNT can have length of the order of micrometers(approx. 100 μm). They have many other unusual properties which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology.

Types of Carbon Nanotube:

The nanotubes may consists of Single wall or multi walls. Depending upon the number of walls, they are classified into single wall carbon nanotube (SWNT) and Multiwall nanotubes (MWNT). Both are shown in Fig. b.

The **single walled nanotube** resembles a pipe that is capped at each end. A single walled nanotube can have a diameter of about 1 to 5 mm and a length of μm, effectively making it one dimensional structure called nanowire.

The**Multiwalled nanotubes** comprise an array of such nanotubes that are concentrically nested-like rings of a tree trunk. The inner diameter of a MWNT varies from 1.5 nm to 5 nm and its outer diameter varies from 2.5 to 30 nm.



Structure of CNT:

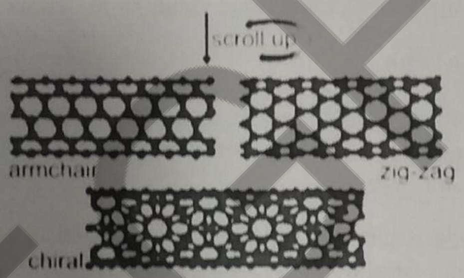
To give a complete description of the nanotube structure, we must examine the way the graphene sheet is rolled up. A carbon nanotube is produced by curling a graphene sheet. Just like a paper, there are infinite ways of folding the graphene sheet, thereby resulting in tubes of different chiral angles or helicities, which specifies the direction in which the sheet is rolled up. All these are different kinds of tubes. Since the extent of helicity varies, various tube structures are possible, which results in both variety and diversity in the properties of the tubes. The electronic structure of the tube also varies as the helicity changes.

Zigzag carbon nanotubes: Zigzag tubes have chiral angle equal to 0°. The graphene layer is rolled up in a way to make the ideal ends of an open tube be a zig - zagged edge.

Armchair carbon nanotubes: In comparison to the zig-zag tubes, the graphene sheet is turned by 30° before rolling up.

Chiral carbon nanotubes: If the angle of turning the graphene layer before rolling up is between 0° and 30° , chiral nanotubes are obtained.

(a)



Properties of CNT:

The properties of the nanotube arise by adapting the properties of graphite to the conditions imposed by rolling up the graphene sheets. This may be classified into electrical conduction properties, mechanical properties, thermal properties and chemical properties.

1. **Mechanical Properties**:
   - CNTs are the strongest and stiffest materials on earth, in terms of tensile strength and elastic modulus respectively. They are very stiff and hard to bend.
   - Their mechanical strength can be understood in terms of Young's modulus, which characterizes the elastic flexibility of a material. The larger the value of Young's modulus, the less flexible is the material. Young's modulus of steel is 0.21 tera-pascal. However, Young's modulus of CNTs ranges from 1.3 to 1.8 tera-pascal. This data shows that a CNT is almost 10 times stronger than steel.
   - The tubes are mechanically robust.
   - CNTs are about 6 times lighter, 10 times stiffer and 20 times stronger than steel.

- Many of the applications of nanotubes such as composite reinforcement or lubrication, are related in one way or other to their mechanical properties.

2. **Electrical Properties**:
   - The tube behaves as a metal and as a semiconductor depending on its structure. As a metal, its electrical conductivity is 1000 times more than that of copper while others behave more like silicon.
   - The differences in conductivity can easily be derived from the graphene sheet properties.
   - The electrical conductivity of nanotubes is a function of diameter. Conductivity in multi-walled nanotubes is quite complex.

3. **Chemical Properties :**
   - Carbon nanotubes are polymers of pure carbon and thus possess all of carbon's versatility, including the ability to form countless combinations and derivatives.
   - Carbon nanotubes can be functionalized in countless ways using a variety of well-understood chemical reactions. In addition, the geometry of a nanotube allows for the formation of novel synthetic structures not possible with other carbon structures. Carbon nanotubes can be derivatized both covalently in which other molecules being bonded to the nanotube share an electron with the tube, and non-covalently, in which theother molecule simply adheres to the carbon nanotube's sidewall, providing a nano-scale coating of the carbon nanotube. When molecules adhere even non-covalently to the carbon nanotube surface they often cause subtle changes in the electronic structure of the tubes. Such changes can be easily detected, making carbon nanotubes exquisitely sensitive chemical sensors.

4. **Thermal Properties**:
   - All nanotubes are expected to be very good thermalconductors along the tube, exhibiting a property known as ballistic conduction, but are good insulators laterally to the tube axis.
   - The thermal conductivity of CNTs is 10 times that of silver.

Synthesis of CNT:

There are a number of methods of making nanotubes:

(i) **Plasma Arching Method:** Carbon nanotubes are prepared by putting an electric current across two carbonaceous electrodes (graphite) as in a helium or argon atmosphere as shown in Fig.This method is called the plasma arching method. In this method, evaporation of one electrode (anode) takes place as cations, and the particles are deposited at the other electrode. The deposition on the cathode are nanotubes. Normally, multi-walled nanotubes are formed from plasma arching.

Single-walled nanotubes are formed if the electrodes are bored out and cobalt or other metals are included.

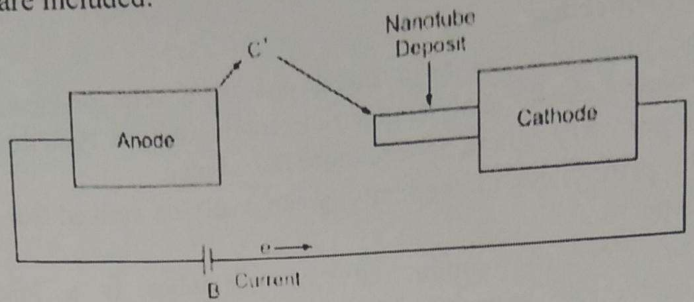


Fig. 7.14. Plasma a Arching Method

ii. Laser Ablation Method:

Large quantities of single-walled nanotubes can be prepared by dual-pulsed laser vaporization method. In this method, the samples can be prepared by laser vaporization of graphite rods with equal amounts of cobalt and nickel powder at 1200°C in flowing argon. After this, heat treatment is carried out at 1000°C in vacuum to remove C_{60} and other fullerenes. The first laser vaporization pulse is followed by a second pulse for more uniform vaporization. The product appears as a mat of ropes having a diameter of 10-20 nm and a length of 100 μm or more. The diameter of tubes can be controlled by varying the parameters such as growing temperature and catalyst composition.The other method include arcing in the presence of cobalt, chemical vapour deposition method, ball milling, diffusion flame synthesis, electrolysis, solar energy pyrolysis at low temperature, heat treatment of a polymer, etc.

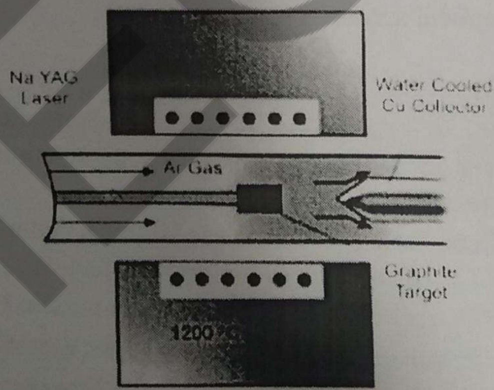


Fig. 7.15. Laser ablation method

Applications of CNTs:

The small dimensions, strength and the remarkable physical properties of these structures make them a very unique material with a whole range of promising applications.

1. Hydrogen Storage: Storing hydrogen in nanotubes is another possible applications, one that it is related to the development of fuel cells as sources of electrical energy for future automobiles. Because of their cylindrical and hollow geometry, and extremely small diameters, carbon nanotubes can store hydrogen in the inner cores through a capillary effect. It is estimated that to be useful in this application, the tubes need to hold 6.5% hydrogen by weight. At present only about 4% hydrogen by weight has been successfully put inside the tubes.

2. In Chip Designing as a Transistor and Interconnect: In present scenario, the main objective in chip designing is to increase the number of switches on a chip. So, smaller switches and small diameter interconnecting wires are used and then packed more tightly on the chip. The carbon nanotubes with diameter of 2 nm have extremely low resistance, and thus can carry large currents without heating, so they can be used as interconnects. Due to their high thermal conductivity, they can serve as a heat sinks, allowing heat to be rapidly transferred away from the chip. Nanotube-based transistors, also known as carbon nanotube field-effect transistors (CNTFETs), have been made that operate at room temperature and that are capable of digital switching using a single electron.

3. Field Emission and Shielding: If a solid subjected to a high sufficiently high electric field, electrons tunnel through the surface potential barrier of the solid. This is known as field emission. The high aspect ratio of CNT makes it ideal field emission material. Examples of potential applications for nanotubes as field emitting devices are flat panel displays, gas discharge tubes in telecom networks, vacuum tube lamps, electron guns from electron microscopes, atomic force microscope (AFM) tips and microwave amplifiers. Due to high electrical conductivity, carbon nanotubes are poor transmitters of electromagnetic energy. So, a plastic composite of CNTs could provide lightweight shielding material for electromagnetic radiation. This can be very useful in military, which is developing a highly digitized battlefield for command, control and communication. The computers and electronic devices that are a part of this system need to be protected from weapons that emit electromagnetic pulses.

4. Nanoprobes and Sensors: Since MWNT tips are conducting, they can be used in scanning tunnelling microscope (STM) and atomic force microscope (AFM) instruments. The advantage of the nanotube tip is its slenderness and the possibility to image features (such as very small, deep surface cracks), which are almost impossible to probe using the larger, blunter etched Si or metal tips. Biological molecules, such as DNA can also be imaged with higher resolution using nanotube tips, compared to conventional STM tips. Also, being flexible, the probes are not susceptible to frequent crashes, unlike in the case of normal STM tips. Another interesting property of carbon nanotubes is that their electrical resistance changes significantly when exposed to gaseous ambient containing molecules of NO_2, NH_3 and O_2. Companies are using this property to develop sensors that can detect chemical vapors such as carbon monoxide or biological molecules. It was seen that the response times of nanotube sensors are at least an order of magnitude faster than those based on presently available solid-state (metal-oxide and polymers) sensors. In addition, the small dimensions and high surface area offer special advantages for nanotube sensors, which could be operated at room temperature or at higher temperatures for sensing applications.

5. Medical: Medical implants made of porous plastic, coated with carbon nanotubes. Therapeutic drugs, which are attached to the nanotubes can be released into the bloodstream, for example, when a change in the blood chemistry signals a problem. NASA is developing these implants, called a "bio capsule", to protect astronauts from the effects of radiation however the implants may also be useful for releasing insulin for diabetes patients or for delivering chemotherapy drugs directly to tumours.

6. Composites: Nanotube composites can be replacement material for existing materials where properties not as superior to nanotube composites or to create nanocomposites for applications where composites have traditionally not been used before. The high aspect ratio (length to radius ratio) and high conductivity of CNTs makes them excellent for conducting composites. The first use of such composites was by Hyperion for electrostatistically applying paint onto car components. Another use of CNT composites is as antistatic shielding on airplane wings and fugue lages. Researchers are developing materials, such as a carbon nanotube based composite that bends with when a voltage is applied, that will need only an electrical voltage to change the shape (morphing) of aircraft wings and other structures. Also, NASA are combining carbon nanotubes with other materials into composites that can be used to build lightweight spacecraft.

7. Catalysis: Nanotubes act as catalysts when an electric current is passed through them. This enables them to donate electrons to molecules that come in contact with the reaction sites. The reaction is similar to what happens in fuel cells, so further research may help in making better fuel cells. Carbon nanotubes also provide a certain potential for metal-free catalysis of inorganic and organic reactions. For instance, oxygen groups attached to the surface of carbon nanotubes have the potential to catalyze oxidative dehydrogenations or selective oxidations. Researchers have found that Nitrogen and iron doped carbon nanotubes may replace expensive platinum catalysts which most catalysts are based upon, used to reduce oxygen in fuel cells.

8. Energy Storage: Carbon nanotubes are being considered for energy production and storage. Graphite, carbonaceous materials and carbon fibre electrode are commonly used in fuel cells, batteries and other electromechanical applications. The efficiency of fuel cells is determined by the electron transfer rate at the carbon electrodes which is the fastest on nanotubes. The outstanding mechanical properties and the high surface-to-volume ratio make carbon nanotubes potentially useful as anode materials or as additives in lithium-ion battery systems.

Material processing by chemical vapor Deposition :-

Chemical vapor deposition is a chemical process used to produce a solid material from a gaseous phase. Microfabrication processes widely use CVD to deposit materials in various forms. These materials include: silicon, carbon fiber, carbon nanofiber, SiO_2, tungsten etc.

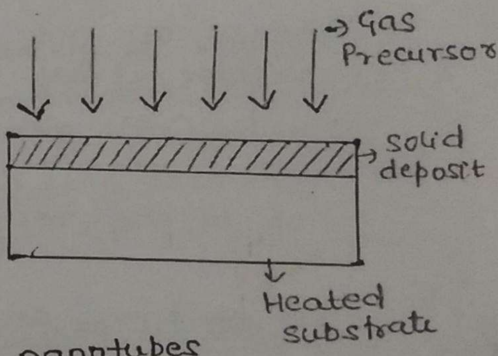
Working concept :- In CVD, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber.

metal deposition :-

metal halide (g) → metal (s) + by products (g).

ceramic deposition :-

metal halide (g) + oxygen/carbon/nitrogen/boron (g) → ceramic (s) + by products (g)



Process :- In a CVD method, a gaseous carbon source, such as acetylene, methane and carbon mono-oxide, is used. An energy source, such as a heating coil, provides energy to the gaseous carbon molecules, cracking them into reactive atomic carbon. The carbon then diffuses towards the substate, on which carbon nanotubes are formed. Usually, the subtrate, is coated with a catalyst, such as Ni, Fe or Co, and in the synthesis procedure. It is heated to 650 - 900°C. Using this method, excellent alignment and positional control at the nanometer scale can be achieved. SWNTs can be synthesized by using an appropriate metal catalyst. This method has a yield of about 30%.

(*) (Precursor → a substance, from which another substance is formed)

15.

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 and process conditions.

CVD reactors can be classified on the basis of operating pressure.

- Atmospheric pressure CVD (APCVD) :- reactors operate at atmospheric pressure.
- low-pressure CVD (LPCVD) :- reactors operate at medium vacuum (30-250 Pa) and higher temp. than APCVD.
- Plasma enhanced CVD (PECVD) :- Also operate at very low pressure (10^{-6} Pa).

CVD reactors can also be classified on the basis of reactor temperature:

- Hot wall reactor :- 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.
- Cold-wall reactor :- Cold wall reactors use heating systems that minimize the heating up of the reactor walls while the wafer is being heated up.

CVD Coatings and their properties :-

CVD coatings containing	On to various substrate	Properties
• Chromium	Solid solution alloy (i) with Fe, Ni, Co ii) on Iron as carbide and nitride	(i) corrosion/oxidation resistance ii) wear/corrosion resistance
• Aluminium	As aluminides with Fe, Co, Ni	High temp. oxidation resistance
• Boron	As borides with Fe, Co, Ni	wear/erosion resistance
• Silicon	As silicides with Fe, W, Mo	High temp. oxidation resistance
• Titanium	As carbides, nitrides and carbonitride on ferrous and non-ferrous alloy	wear resistance
• Manganese	Solid solution alloys on carbon still	wear resistance

Advantages :-

- can be used for a wide range of metals and ceramics
- can be used for coating or free standing structure
- Extreamly high purity deposits (>> 99.995% purity)
- Has controllable thickness and morphology
- Can simultaneousy coat multiple components.

Applications :-

- Photoresist adhesion for semiconductor wafers.
- Anti-corrosive coating
- MEMS coating to reduce stiction.
- copper capping
- Promote biocampatiblity between natural and synthetic materials.

PHYSICAL VAPOUR DEPOSITION (PVD) :-

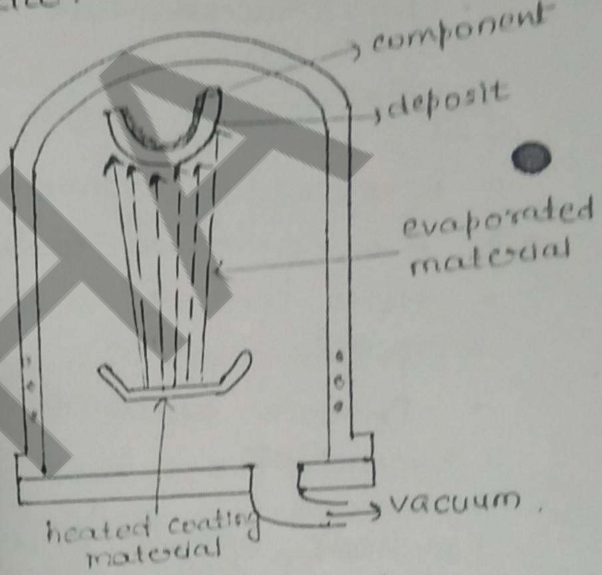
Physical vapor deposition describes a variety of vacuum deposition method which can be used to produce thin films. PVD uses physical process (such as heating or sputtering) to produce a vapour of material, which is then deposited on the object which requires coating.

working concept :- PVD techniques consists of four fundamental steps.

1. Vapourization or Evaporation :- vaporization of the material from a solid source assisted by high temp. vaccum (thermal evaporation) or gaseous plasma (sputtering).
2. Transportation :- This process simply consists of the movement of vaporised atoms from the target to the substrate to be coated.

3. Reaction :- In some cases coatings will consists of metal oxides, nitrides, carbides and other such materials. In these cases, the target will consi of the metal. The atom of metal will then react with the appropriate gas (oxygen, nitrogen and methane) during the transport stage.

4. Deposition :- This is the process of coating build up on the substrate surface.



Construction :- The component that is to be coated is placed in a vacuum chamber. The coating material is evaporated by intense heat. The coating is then formed by atoms of the coating material being deposited onto the surface of the component being treated.

Variants of PVD:-

1. Evaporative Deposition:- material to be deposited is heated to a high vapour pressure by electrically resistive heating in high vacuum.

2. Electron beam physical vapor deposition :- material to be deposited is heated to a high vapor pressure by electron bombardment in high vacuum.

3. Sputter deposition :- A glow plasma discharge bombards the material sputtering some away as a vapor.

4. Cathode arc deposition:- high power arc directed at the target material blasts away some into a vapor.

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

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 shorten 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.

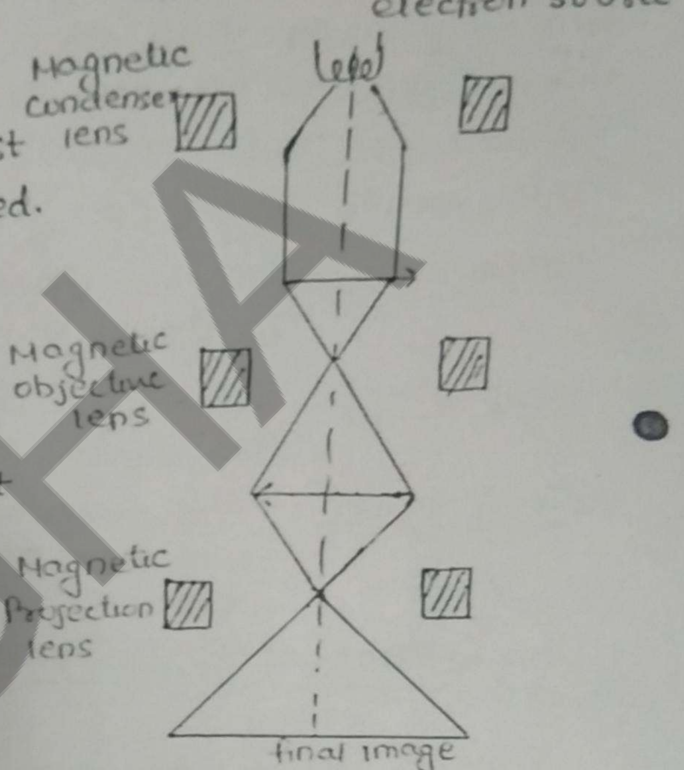
Types :- There are two main electron microscopy techniques:

- 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 ~~th~~ technique wherby 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.



<u>Nature of the specimen</u> :-

The object to be investigated must be specially prepared and mounted. It must be <u>transparent</u> 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 cellulase or a similar material and dried before being mounted on special holders.

<u>Magnification</u> :- 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.

<u>Limitations</u> :-

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.

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

Projector/ lens or eye lens increases/ the magnification.
The lens is adjusted to give a sharp image./

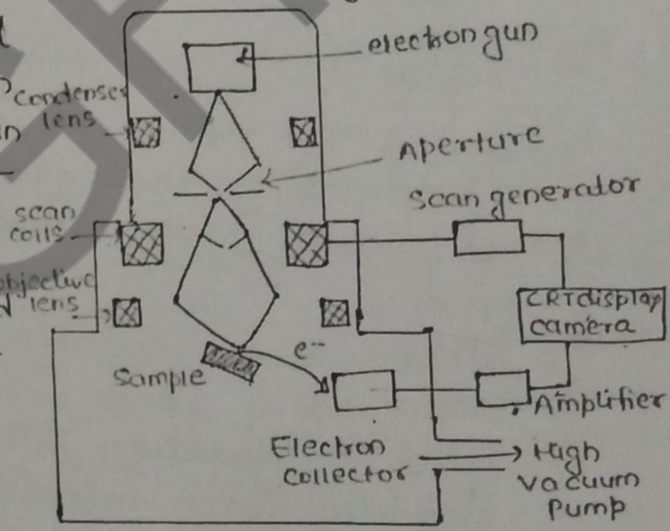
ii) It is used heavily in materials, metallurgy and biological sciences.

iii) 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 anode that is held at a positive potential with respect to the specimen. 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,~~

22.

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 :-

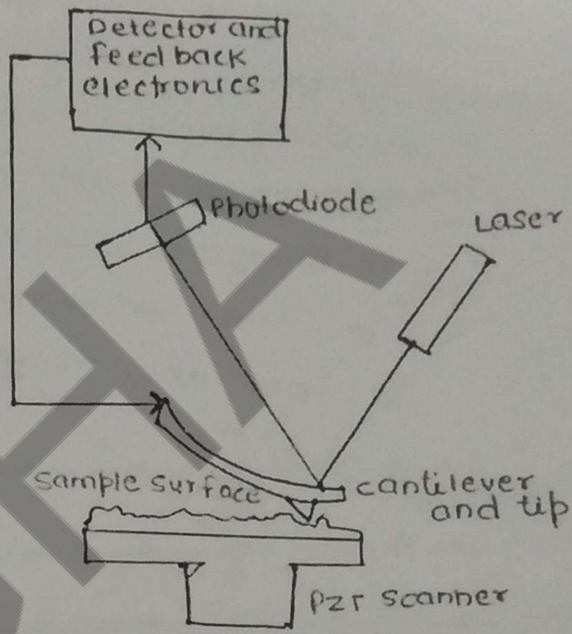
Scanning probe microscopy is a new branch of spectroscopy that forms images of surfaces using a physical probe that scans the specimen.

Types :-

- Atomic force microscopy (AFM)
- electrostatic force microscope (EFM)
- force modulation microscopy (FMM)
- Magnetic force microscopy (MFM)
- 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.

28.

Applications :-

The AFM is useful for obtaining three-dimensional topographic information of insulating and conducting structures with lateral resolution down to 1.5 nm and vertical resolution down to 0.05 nm.

A concise applications listing is given below.

- Metals : tooling studies, roughness, measurements, corrosion
- Solid powder catalyst : aggregate structural determination
- Polymers : determination of morphology and surface properties.
- Biological samples, biomaterials : macromolecules association and conformation studies.
- Nano and microparticle structures.

4.4 Graphene

Andre Geim and Konstantin Novoselov at the University of Manchester won the Nobel Prize in Physics in 2010 for groundbreaking experiments regarding the two-dimensional material graphene. They isolated a graphene layer from a pencil lead… by simply using a roll of adhesive tape to extract ever thinner graphite layers one by one – until they formed but one single layer of atoms.

Carbon is an extremely versatile element, not only in the form of organic compounds, but also in inorganic (nano)materials. The two well-known allotropes of crystalline carbon, graphite with sp2 hybridization (black, good electric conductor, soft) and diamond with sp3 hybridization (transparent, insulator, hard), have very different physical properties.

The International Union of Pure and Applied Chemistry (IUPAC) defines graphene as a single carbon layer of the graphite structure, describing its nature by analogy to a polycyclic aromatic hydrocarbon of quasi infinite size.Thus, the term graphene should be used only when the reactions, structural relations, or other properties of a single layer are discussed.

Graphene is an atomic-scale honeycomb lattice made of carbon atoms with many superlatives to its name. It is the thinnest known material in the universe and the strongest ever measured.

Due to its many extraordinary properties,graphene, single-atom thick material,a honeycomb network of sp^2 carbon atoms, is the wonder material of the 21st century.

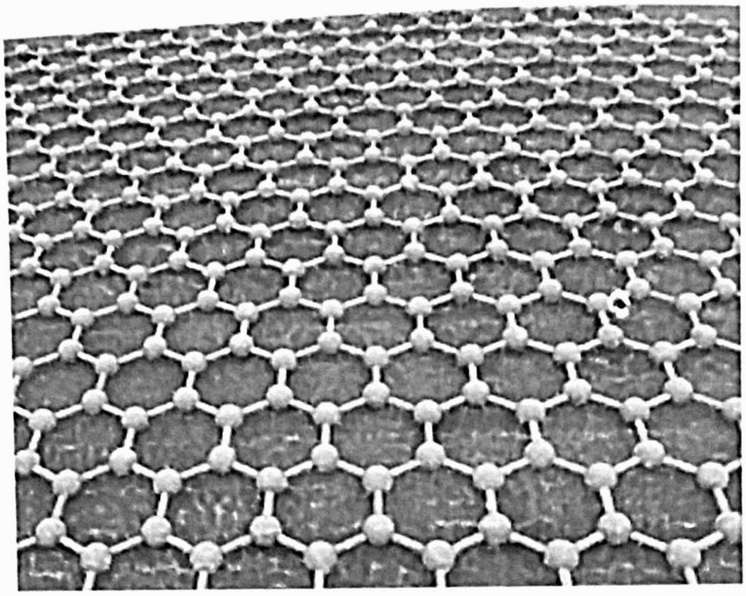


Fig.4.5 Graphene is a 2D building block for carbon-based materials

Properties

a)Electronic Properties: Graphene is great conductor; electrons are able to flow through graphene more easily than through even copper. The electrons travel through the graphene sheet as if they carry no mass, as fast as just one hundredth that of the speed of light. Graphene is a semi-metal and is a zero-gap semiconductor .

b)Thermal Properties: Graphene is a perfect thermal conductor.Its thermal conductivity is much higher than the value observed in all the other carbon structures as carbon nanotubes, graphite and diamond (> 5000 W/m/K).

The ballistic thermal conductance of graphene is isotropic, i.e. same in all directions. The study of thermal conductivity in graphene may have important implications in graphene-based electronic devices. As devices continue to shrink and circuit density increases, high thermal conductivity, which is essential for dissipating heat efficiently to keep electronics cool, plays an increasingly larger role in device reliability.

c)Mechanical Properties: It was found that graphene is harder than **diamond** and about 300 times harder than **steel**. The tensile strength of graphene exceeds 1 TPa.

Even though graphene is so robust, it is also very stretchable. It is expected that graphene's mechanical properties will find applications into making a new generation of super strong composite materials and along combined with its optical properties, making flexible displays.

d)**Optical Properties:** Graphene is almost completely transparent, yet so dense that even the smallest atom helium cannot pass through it.

e)**Chemical Properties:** Similar to the surface of graphite, graphene can adsorb and desorb various atoms and molecules (for example, NO2, NH3, K, and OH).Weakly attached adsorbates often act as donors or acceptors and lead to changes in the carrier concentration, so graphene remains highly conductive. This can be exploited for applications as sensors for chemicals.

Other than weakly attached adsobates, graphene can be functionalized by several chemical groups (for instances OH-, F-) forming graphene oxide and fluorinated graphene. It has also been revealed that single-layer graphene is much more reactive than 2, 3 or higher numbers or layers.

Also, the edge of graphene has been shown to be more reactive than the surface. Unless exposed to reasonably harsh reaction conditions, graphene is a fairly inert material, and does not react readily despite every atom being exposed and vulnerable to it's surroundings.

Graphene synthesis

Graphene has been synthesized in various ways and on different substrates.

i) Mechanical Exfoliation (Scotch-tape method) : Repeated peeling of graphite to get an atom-thick layer of graphite, which is called grapheme. This simple, low-budget technique has been widely credited for the explosive growth of interest in graphene. Graphene flakes have been invaluable to the study and elucidation of graphene properties. Unfortunately, however, they are usually available at a size of several-microns (or tens of microns at best), have irregular shapes, and their azimuthal orientation is not deterministically controlled.

ii) Chemical Vapor Deposition : Graphene and few-layer graphene (FLG) have been grown by chemical vapor deposition (CVD) from C-containing gases on catalytic metal surfaces and/or by surface segregation of C dissolved in the bulk of such metals. Depending on the solubility of C in the metal, the former or the latter can be the dominant growth process, or they can coexist.The electrical properties of CVD graphene cannot be tested *in situ* on the conductive metal substrates. Thus, processes to transfer graphene on an appropriate insulating substrate have been developed. The ability to select the host substrate independently of the sacrificial growth substrate is a major advantage for graphene grown on metals. At the same time, the transfer process often affects negatively graphene's integrity, properties, and performance. Wrinkle formation, impurities, graphene tearing, and other structural defects, can occur during transfer

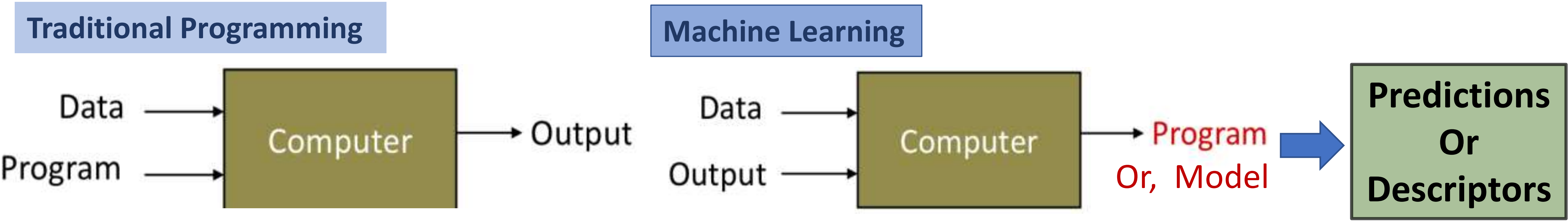
Applications

A cross-section of applications, that leverage specific graphene properties, is given below:

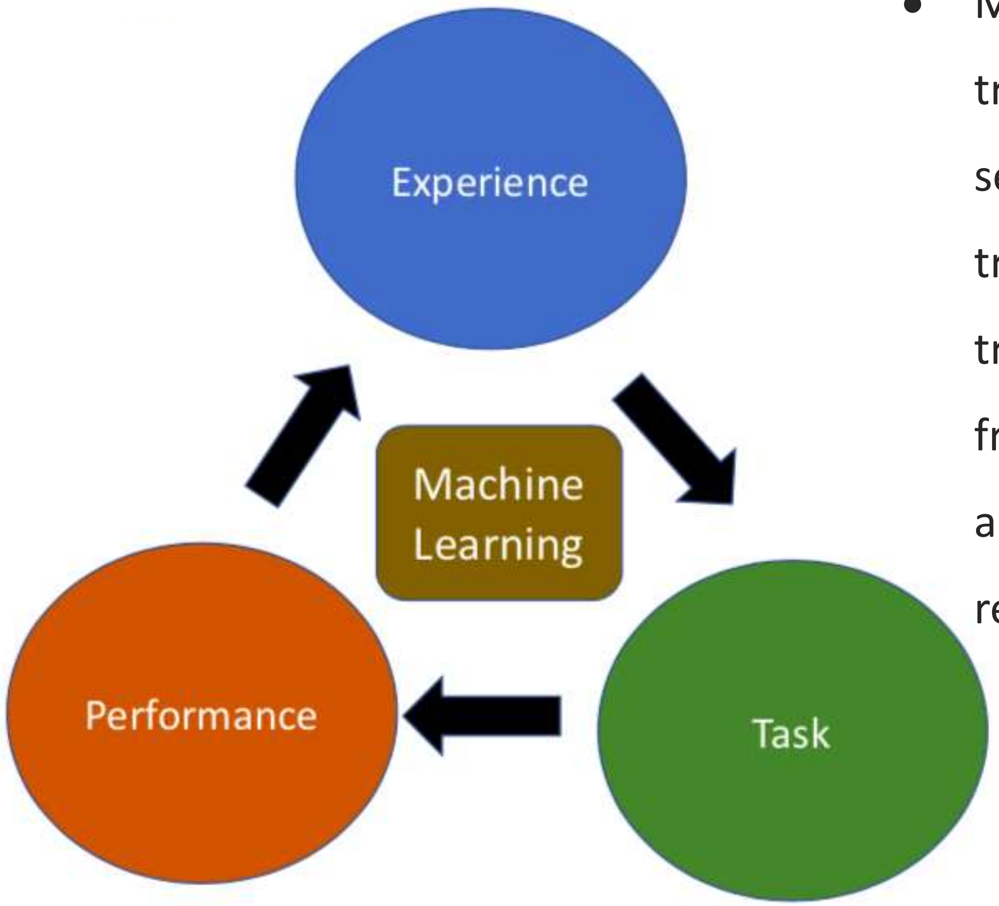
- The high mobility even at highest E-field-induced concentrations makes the carriers go ballistic giving rise to a ballistic FET device at 300 K.
- Due to its e-h symmetry and linear dispersion it is suitable for RF and high frequency applications such THz detectors and lasers.
- Graphene could also be used to improve solar cells and to enhance the service life of batteries.

Current computational and machine learning approach for as an electron microscopy image processing using Graphene

What is machine learning? (Ref: https://mitsloan.mit.edu/ideas-made-to-matter/machine-learning-explained)



- Machine learning (ML) is a subfield of artificial intelligence, which is broadly defined as the capability of a machine to imitate intelligent human behavior. Artificial intelligence (AI) systems are used to perform complex tasks in a way that is similar to how humans solve problems.
- The goal of AI is to create computer models that exhibit “intelligent behaviors” like humans, according to Boris Katz, a principal research scientist and head of the InfoLab Group at CSAIL. This means machines that can recognize a visual scene, understand a text written in natural language, or perform an action in the physical world.
- Machine learning is one way to use AI. It was defined in the 1950s by AI pioneer Arthur Samuel as “the field of study that gives computers the ability to learn without explicitly being programmed.”



- Machine learning starts with data — numbers, photos, or text, like bank transactions, pictures of people, repair records, time series data from sensors, or sales reports. The data is gathered and prepared to be used as training data, or the information the machine learning model will be trained on. The more data, the better the program. Some data is held out from the training data to be used as evaluation data, which tests how accurate the machine learning model is when it is shown new data. The result is a model that can be used in the future with different sets of data.

Machine learning working principle has been shown. The algorithms are design to work in three steps.

1. The computer has been asked to perform a task
2. The task performance will be evaluated, and a reward will be given
3. With the reward the computer will gain experience and finally with the experience gain it will perform the task again

This cycle will go on a training data and computer will build a model. Finally, the model will be tested in a training set for prediction and validation.

Machine Learning in Materials Science

- **Supervised learning**
  - Prediction
  - Classification (discrete labels), Regression (real values)
- **Unsupervised learning**
  - Clustering
  - Probability distribution estimation
  - Finding association (in features)
  - Dimension reduction
- **Reinforcement learning**
  - Decision making (robot, chess machine)

Unsupervised Learning

Dataset: Only the inputs are known

Objective: Train a model to find existing patterns in the data to learn more about it.

Association

We want to discover rules that describes our data

e.g. material which is soluble in water, also soluble in kerosene.

Clustering

We want to discover the inherent categories in the data.

e.g. grouping of materials by their solubility.

Supervised Learning

Dataset: Has example inputs and outputs

Objective: Train a model to predict outputs from feature inputs.

Classification

The output variable is a category. e.g.

[spin up/spin down] or

[ferromagnetic/paramagnetic /diamagnetic]

Regression

Attempts to determine the relationship between one dependent variable and a series of independent variables.

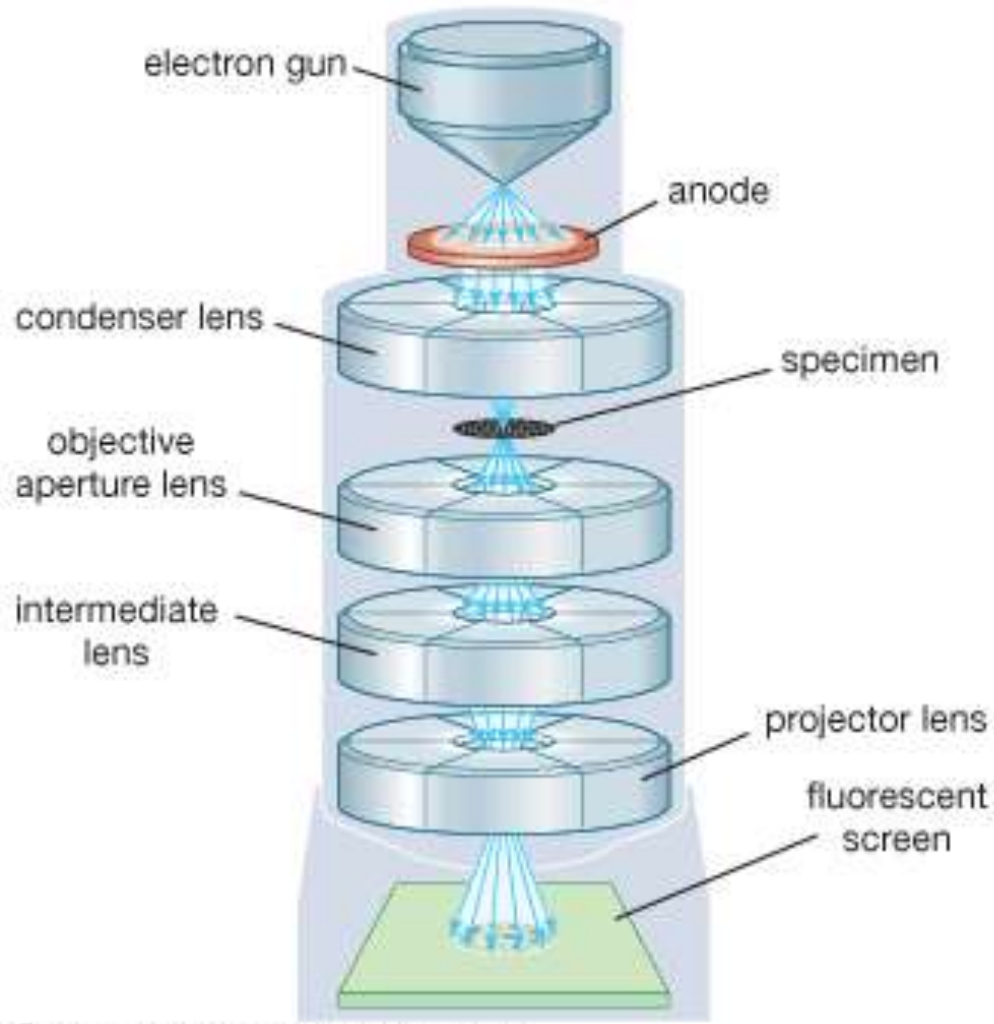
Ref: [1] Bishop CM. Pattern recognition and machine learning. New York: Springer; 2007.

- There are four types of machine learning that are commonly used in scientific fields
  - Unsupervised learning: In unsupervised learning, the agent learns patterns in the input, even when no explicit feedback is supplied. Clustering is a common example of an unsupervised task, which detects meaningful clusters among input data. For example, a regular office goer, Mr. Neogy, traveling from one area to the other in New York City, will develop a concept or percept of "good traffic days" and "bad traffic days" based on day to day experiences, without ever consulting motor vehicles department or traffic controllers for labelled examples of each.
- Supervised learning: In this mode, the agent learns from a function that maps the input output pairs from some observed instances present in the data. In Mr. Neogy's case, inputs are percepts about traffic conditions that he has developed over time and outputs are provided by him, where he gives directions to the cab-driver. Besides the inputs provided by Mr. Neogy, here the cab-driver can also alter the outcome based on let's say if he passes a bus or a car or a pedestrian on the road and decides to take a different route or more time. Now, Mr. Neogy's final outcome of reaching office on time or late is a function of states such as his own perceptions as well as the cab driver's actions like braking, accelerating or stopping distance. The output is directly available from the agent's percepts, the cab-driver is the environment and the final outcome can be changed if either the percept or environment changes.

- Semi-supervised learning: In this mode, we are given a few labelled instances and a large set of unlabeled ones. Let's assume, we are given a task of creating a model to predict what type of coffee a person drinks on a regular basis. We can gather some data (labelled examples) by interviewing people and / or by visiting multiple coffee shops, which would be identical to supervised learning. However, in reality, some of the people interviewed may not be truthful in their responses. Furthermore, the collected data may be inaccurate for other reasons, e.g., people not knowing specific coffee types and naming different coffee brands instead. Therefore, there is not only random noise in the data, but there are systematic inaccuracies present that can only be identified by utilizing unsupervised learning techniques. In other words, noise and lack of labelled instances create a continuum between supervised and unsupervised learning modes, which constitutes the domain of applicability of semi-supervised approaches.

- Reinforcement learning: This is another hybrid mode in which the agent learns from a series of past events or reinforcements (success or failure). Here, the model gets either rewards or penalties for the actions it performs, such as searches or trials, with a goal to maximize the total reward. For example, if Mr. Neogy reaches his office on time, that gives him an indication that he did something right along the way. It then falls on the agent to decide which of the actions prior to reinforcement had the most pronounced impact on the outcome.

What is electron microscopy? (Ref: https://www.thermofisher.com/us/en/home/materials-science/learning-center/applications/sem-tem-difference.html)



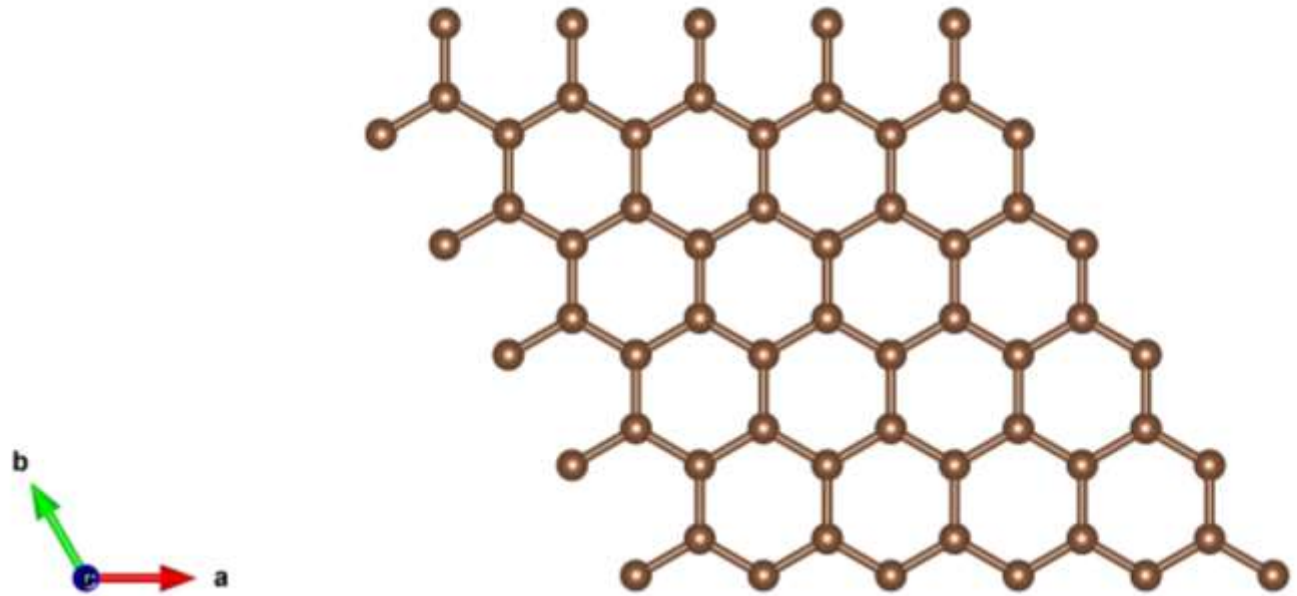
- Electron microscopes were developed in the 1930s to enable us to look more closely at objects than is possible with a light microscope. Scientists correctly predicted that a microscope that used electrons instead of visible light as the illumination source could view objects at far higher resolution than a light microscope. This is because the wavelength of visible light is what limits the resolution of light microscopes, and the wavelength of electrons is far smaller.

- Electron microscopes use a beam of electrons rather than visible light to illuminate the sample.

- Some electron microscopes can detect objects that are approximately one-twentieth of a nanometer (10-9 m) in size – they can be used to visualize objects as small as viruses, molecules or even individual atoms.
- Electron microscopes have emerged as a powerful tool for the characterization of a wide range of materials. Their versatility and extremely high spatial resolution render them a very valuable tool for many applications. The two main types of electron microscopes are the transmission electron microscope (TEM) and the scanning electron microscope (SEM).
- The main difference between SEM and TEM is that SEM creates an image by detecting reflected or knocked-off electrons, while TEM uses transmitted electrons (electrons that are passing through the sample) to create an image. As a result, TEM offers valuable information on the inner structure of the sample, such as crystal structure, morphology and stress state information, while SEM provides information on the sample's surface and its composition.
- For both techniques, electrons are used to acquire images of samples. Their main components are the same:
  - An electron source
  - A series of electromagnetic and electrostatic lenses to control the shape and trajectory of the electron beam
  - Electron apertures
- All of these components are housed inside a chamber that is under high vacuum.

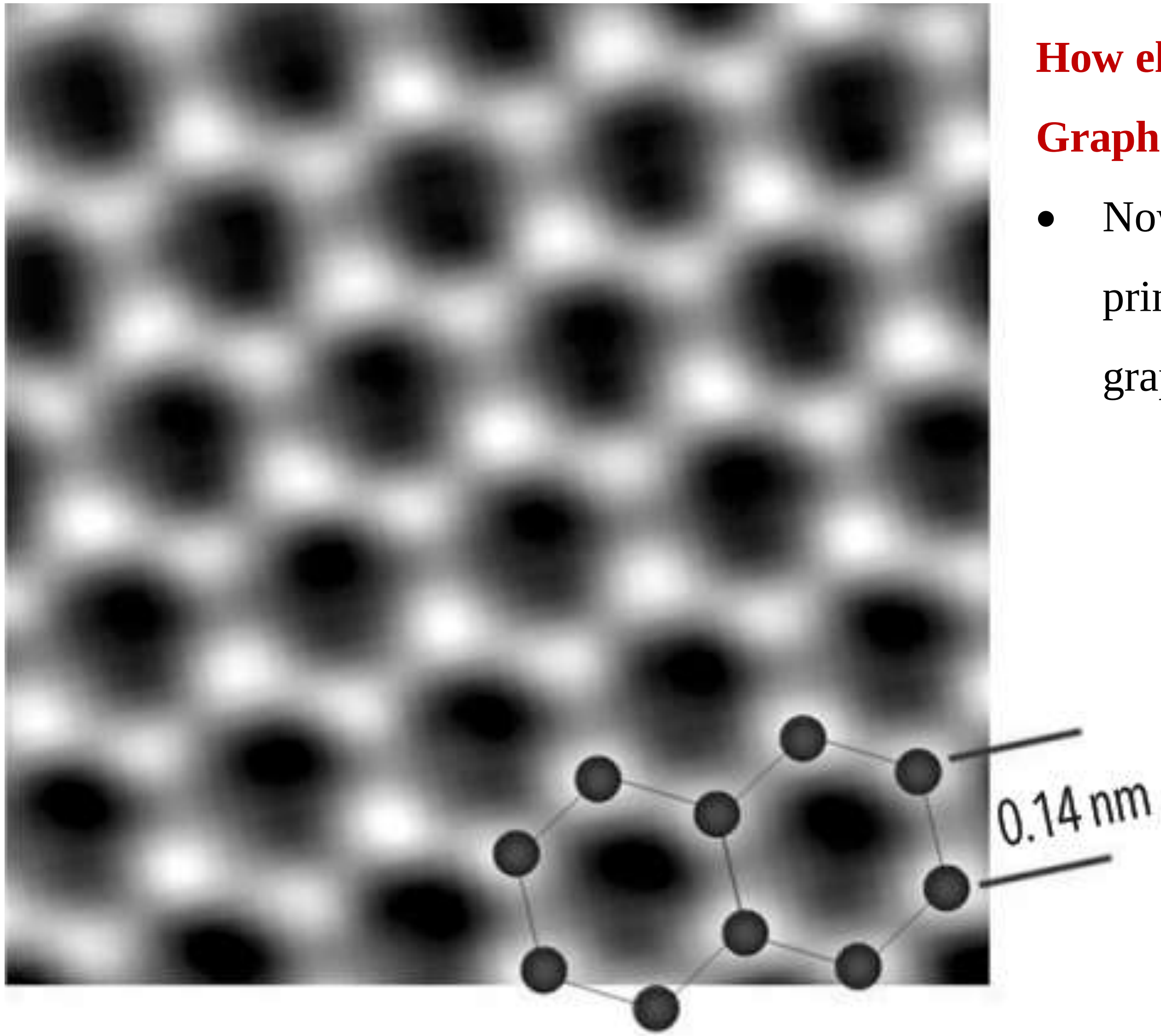
What is a 2D material for example Graphene ?

Graphene is a single atomic layer of carbon atoms tightly packed in a two-dimensional honeycomb lattice. This novel material is atomically thin, chemically inert, consists of light atoms, and possesses a highly ordered structure. Graphene is electrically and thermally conductive, and is the strongest material ever measured. These remarkable properties make graphene the ideal support film for electron microscopy.



How electron microscopy can be used to take images of a 2D Graphene

- Now that we know about SEM, TEM and STEM, their working principles, we can use either of the techniques to image a 2D graphene

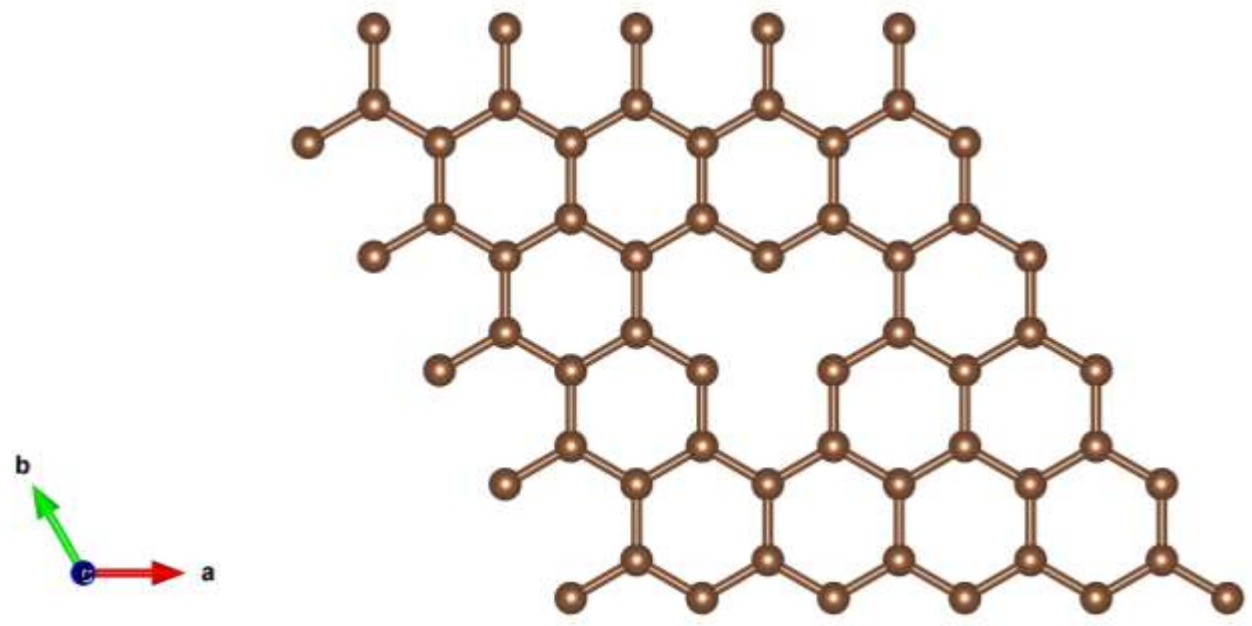


Electron Microscope Image of a 2D material Graphene

What is the main challenge in electron microscopy of 2D Graphene?

Although the general structure of hexagonal rings of carbon can be seen by high-resolution microscopes, imaging the individual atoms and measuring their positions is not as straightforward.

The electron tip must scan the surface of the Graphene to take an electron microscope image. This way if the graphene surface is exposed to the electron beam for longer time, then defects will be formed in the Graphene.



How can machine learning help?

The machine learning models build from a previous large data set (taken from previous experiments) can help to guide on the (key points but not limited to)

(a) Explore time of the beam to reduce defect formation
(b) Where is focus for a clean high-resolution image
(c) Improving signal-to-noise ratio, meaning increasing detections limits
(d) Finite control over the experimental procedure to reduce the human error during performance of the experiment.

References

- Scanning Transmission Electron Microscopy Imaging and Analysis by Stephen J. Pennycook, Peter D. Nellist