UNIT-5

Nano science

Objectives

- At the end of lesson we shall understand about,
    - nano science.
    - Density of states (1D, 2D, 3D)
    - Synthesis (Top-down and bottom-up)
    - Ball milling method.
    - Sol-Gel methods.
    - Carbon nano tube (CNT)- Properties, synthesis)
    - Applications of carbon nano tubes.

Introduction:

Nanotechnology is the science and technology of small things that are less than 100nm in size. One nanometer is 10^{-9} meters or about 3 atoms long. For comparison, a human hair is about 60-80,000 nanometers wide. When the dimensions of the material such as its, length, breadth, thickness fall in the range of 1-100 nm, the resulting structures exhibit characteristics that are specific to their sizes and dimensions. Such materials are called as nanomaterials. Further Nanoparticles are particles between 1 and 100 nanometers in size. Thus confining the dimensions of a bulk can show different physical and chemical properties. The confinement of dimensions of a bulk can result in 2D,1D, 0D.

Density of states (DOS) in 0D, 1D, 2D and 3D:

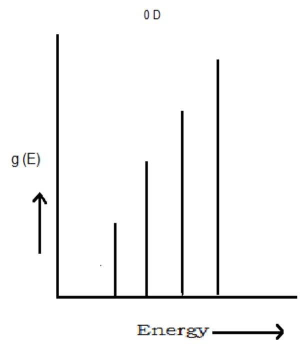
In case solid-state and condensed matter physics, the density of states (DOS) of a system gives the number of states per interval of energy at each energy level that is available to be occupied.

Basically the nanoparticles are classified on the basis of dimensions as zero dimensional (0D), one dimensional (1D), two dimensional (2D) and three dimensional (3D) nano particles.

Zero dimensional (0D): A zero dimensional structures the simplest building block that may be used for nonmaterial design.

Eg: Quantum dots

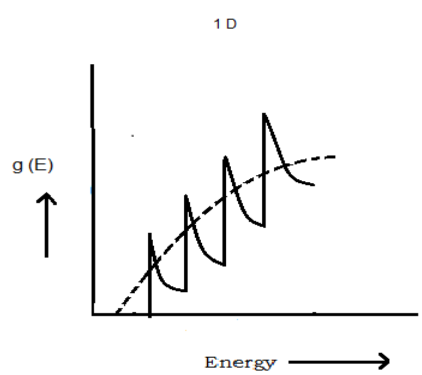
Density of states for 0D is as shown below,



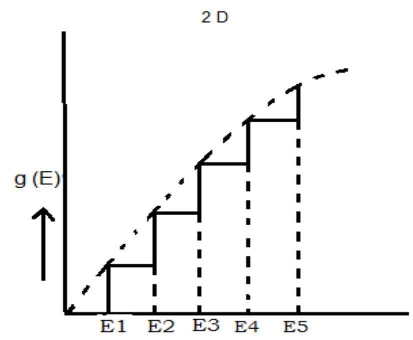
One dimensional (1D): In one dimensional structure only one dimension of the material is reduced to nanometer range and the other dimensions remain large.

Eg: nanorod, nanowire.

Density of states for 1D is as shown below,



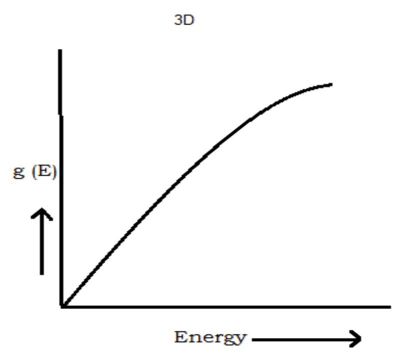
Two dimensional (2D): In 2D structures two of dimensions of the material are reduced to nanometer range and one dimension remains large called quantum wire. Eg: Quantum wire, fibers, plate lets etc. Density of states for 2D is as shown below:



Three dimensional (3D): If bulk material there is no confinement in any of its material dimensions.

Eg: Any bulk structure

Density of states for 3D is as shown below:



Synthesis of materials:

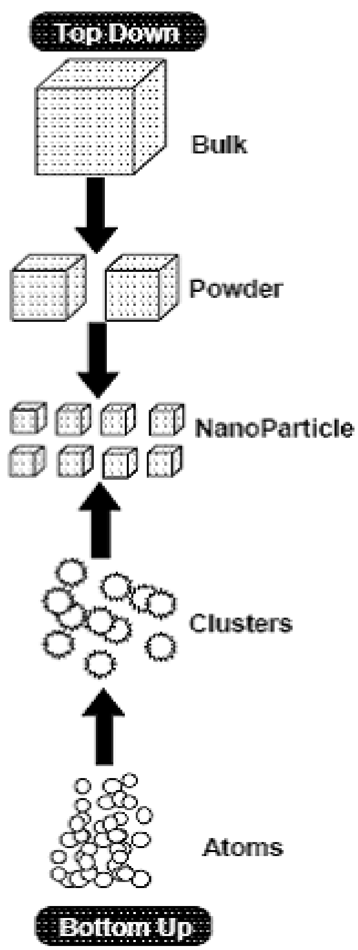
Nanomaterials can be natural or can be synthesized by various processes that can be categorized into two approaches namely,

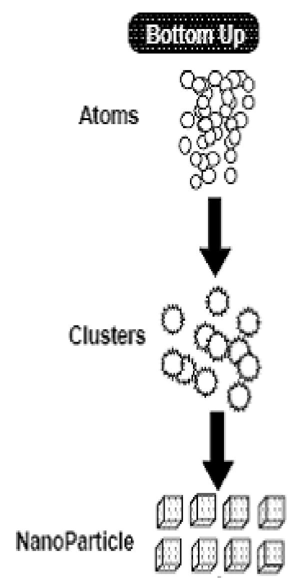
1. Top-down
2. Bottom-up

In case of Top-Down approach the synthesis is initiated with the bulk material and undergoing size reduction becomes powder and then a nano particle and cluster finally yielding atoms. One of the examples of top-down approach is Ball milling method.

Where as in Bottom-up approach the synthesis is initiated with atoms as the starting element and undergoes polymerization giving nano particles as the end product. One of the examples of approach is Ball milling method.

The steps of synthesis of nanoparticles are represented in the diagram given below:

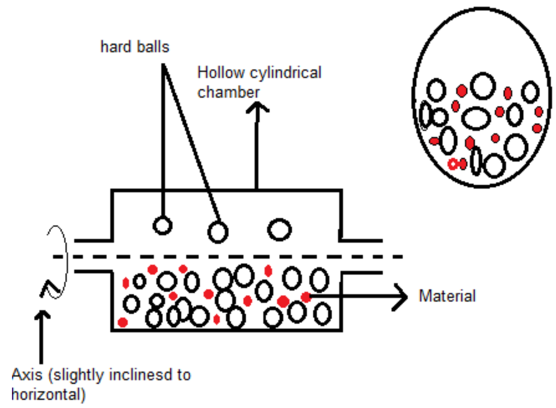




Example of Top-Down method: Ball milling method.

Example for Bottom-up method: sol-gel method.

Ball milling method: (Top-Down method)



The ball mill consists of a hollow cylindrical chamber that can rotate about axis. There are hard and heavy balls made of tungsten/steel inside the chamber. Larger balls are used for milling to produce smaller particle size. The chamber is mounted such that, its axis is slightly inclined to the horizontal to enable the material inside to slide and accumulate around in one region. The given material is crushed into small grain size and fed into the chamber. As the cylindrical chamber is rotated around its own axis, the balls get carried upwards. But under gravity they drop down and hit the sample with high speed. This happens repeatedly and the material will be pounded to get reduce to nano size particles. However the speed of the rotation must be less than a critical speed beyond which the balls instead of falling down will be carried along the periphery of the chamber all along. Then the material size misses the hit and reduction in size stops before attaining the nano particle size.

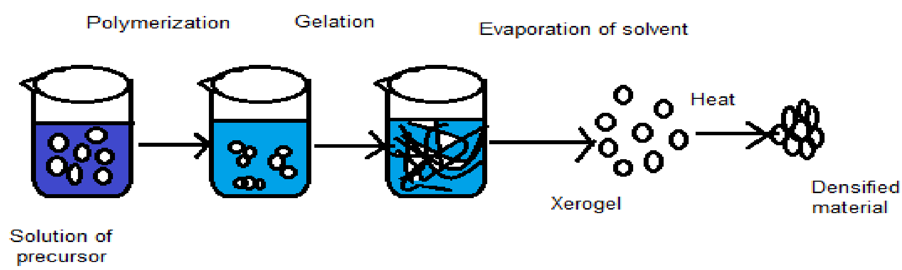
Advantages:

- This method is suitable for large scale production at low cost.
- It can be used to grind material irrespective of hardness

Disadvantages:

- Because of the nature of use, the purity of the material is affected

Sol-gel method: Bottom-up method



Sol-gel is a process in which precipitated tiny solid particles agglomerate to form long networks which spared continuously throughout a liquid in the form of a gel. Sols are solid particles suspended in liquid medium. Gels comprise of long networks of particles like polymers in which the interspaces form pores that contain liquid.

In sol-gel method, precursors which have a tendency to form gel are selected. A solution of the precursor is obtained by dissolving it in a suitable solvent. The precursors are generally inorganic metal salts or alkoxides which undergo hydrolysis. By poly condensation process, nucleation of solid particles starts and sols are formed.

The sols undergo polymerization which turns the solution into a gel. The sol-gel is then centrifuged from which a form of gel called Xerogel which has no traces of the dispersion medium is obtained. The xerogel is then dried by heating it up to a temperature of 800°C during which time, the pores of the gel network collapse. This is called densification after which we obtain the desired nanomaterials. The steps are represented in the diagram above.

Advantages:

- Highly pure and uniform nanostructures can be obtained in sol-gel processing
- It is an inexpensive technique with fine control of the product's chemical composition

➢ With this method powder/fiber/thin film coating can be made.

Disadvantages:

➢ Precursors having a tendency of forming gel can only be selected.

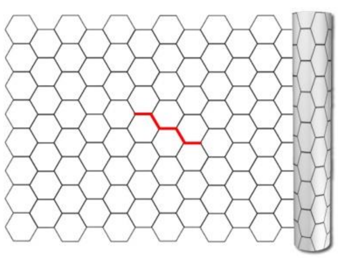
Carbon Nano Tubes (CNTs):

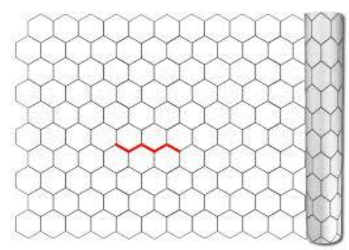
A carbon nanotube is a sheet of carbon (graphite) atoms joined in a pattern of hexagons rolled into a cylinder.

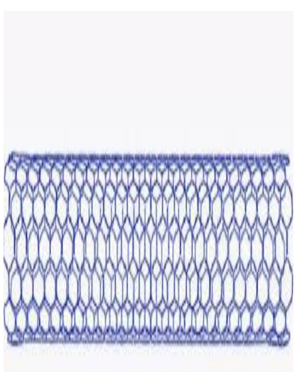
Structure of carbon nano tube:

Carbon nano tubes are appearing in 3 different structures namely

➢ Armchair Zigzag Chiral







CNTs can be single or multi walled depending on the number of graphene layers present in the formation of tube structure.

Properties of CNT's:

Mechanical properties of CNT'S

The tensile strength of CNT'S is 100 times as that of steel. The weight of the CNT'S is about 1/10 as that of steel. They have the highest tensile strength of all known materials so far. They are also highly elastic.

Thermal properties of CNT'S

They possess thermal conductivity which is 2 times that of diamonds. They retain their physical structure in vacuum even up to 2800° C. They are thermally stable.

Electrical properties of CNT'S

They can be metallic or semiconducting depending on their structure and size. Their current carrying is 1000 times that of copper.

Graphene

Graphene is an allotrope of carbon in the form of a two-dimensional, atomic-scale hexagonal lattice. It is the basic structural element of other allotropes, including graphite, charcoal, carbon nanotubes and fullerenes. It can also be considered as an indefinitely large aromatic molecule, the limiting case of the family of flat polycyclic aromatic hydrocarbons. Graphene has many extraordinary properties. It is about 200 times stronger than steel by weight, conducts heat and electricity with great efficiency and is nearly transparent. Researchers have identified the bipolar transistor effect, ballistic transport of charges and large quantum oscillations in the material.

Scientists have theorized about graphene for decades. It is quite likely that graphene was unwittingly produced in small quantities for centuries through the use of pencils and other similar applications of graphite, but it was first measurably produced and isolated in the lab in 2003.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."

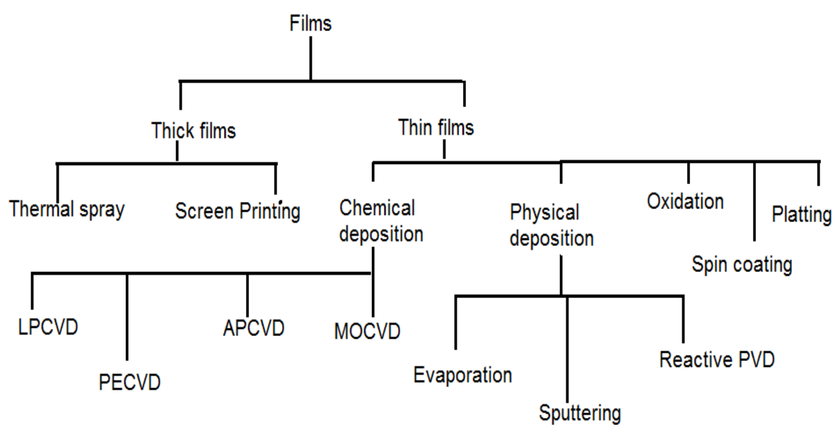
Applications of carbon nanotubes:

- Using semiconducting nano tubes it is possible to make electronic components such as transistors logic gates and nano capacitors, energy storage, super capacitors, field emission transistors, high-performance catalysis, photovoltaic, and biomedical devices and implants.
- Carbon nano tubes are used in medical field for delivering complex natured drugs.
- As these materials are strong as well as light weight, they are being used in building aircrafts and making of Micro Electro Mechanical Systems (MEMS).

Thin films

Introduction

Films can be divided into two categories depending on the thickness of the film and the process of deposition. They are thick films and thin films as explained in the following sections.



Thick films

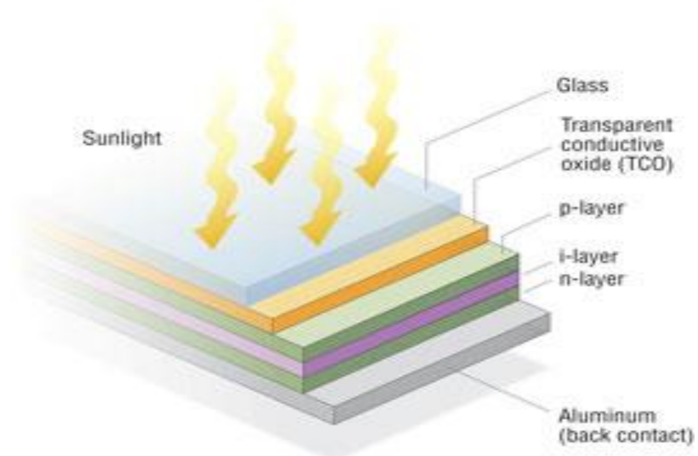
A thick film is the one whose film thickness falls in the range of micrometers (µm) to few millimeters (mm). Major applications of thick films are in the field of electronics as surface mount devices, sensors and hybrid integrated circuits. Some of the methods used to coat thick films are thermal spray technique, screen printing and so on.

Thin films

Basically a thin film is considered to be a layer deposited of any material whose thickness ranges from a few nanometers (nm) to some micrometers (µm).

Applications: Thin film solar cells

Major applications of thin films are in the field of electronics as semiconductor devices and sensors. In polycrystalline solar cells, layers of n and p type semiconductors are deposited as thin films.



Application Fields	Examples
Electronics	Semiconductor devices, solar cells and sensors
Optics	Antireflection coating; on lenses or solar cells, Reflection coatings for mirrors. Coatings to produce decorations (color, luster), Interference filters, **CD's**, **DVD's** and Waveguides.
Chemistry	Diffusion barriers, Protection against corrosion / oxidation. Sensors for liquid / gaseous chemicals.
Mechanical Engineering	"Hard" layers (e.g. on drill bits). Adhesion providers, Friction reduction.

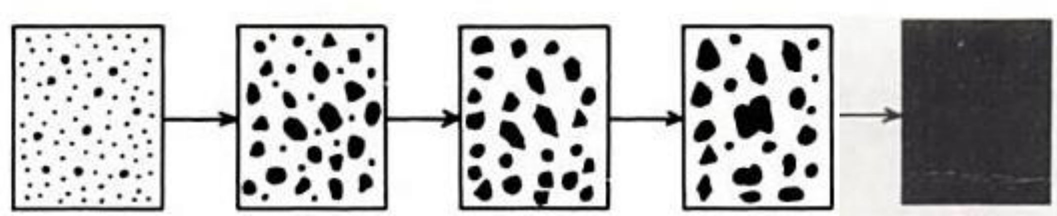
Vacuum ranges

Various degrees of vacuum are mainly classified as follows:

1. Low vacuum - 760 - 25 Torr
2. Medium vacuum - 25 - 10^{-3} Torr
3. High vacuum - 10^{-3} - 10^{-6} Torr

Stages of thin film growth

There are several stages in the growth process of thin film, from the initial nucleation stage to final continuous three dimensional film formation state. These stages of growth were observed by the scientists using microscopic studies. Nucleation includes condensation of vapours, adsorption of atoms, migration of atoms, formation of critical nuclei and and stable clusters. Nucleation is the first step in the formation of a new structure. Nucleation is often found to be very sensitive to impurities in the system. Because of this, it is often important to distinguish between heterogeneous nucleation and homogeneous nucleation.



a b c d

a: nucleation on glass, b: growth, c: coalescence or agglomeration with island formation d: continuous film.

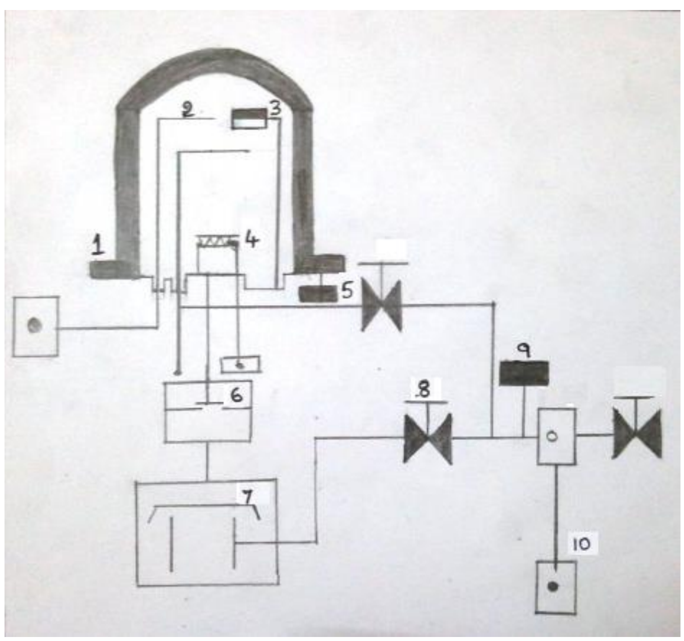
Coalescence and agglomeration is the action or process of collecting in mass or cluster of materials. Larger islands grow together, leaving channels and holes of uncovered substrate. These islands consist of comparatively larger nuclei with size more than 10 Å generally with three dimensional nature. The process of formation of these islands takes place either by the addition of atoms from the vapor phase or by diffusion of atoms on the substrate. A nucleus of 5 Å size is made up of 20 atoms or so and the will be made up of around 100 to 150 atoms. During coalescence many small islands disappear rapidly leading to some definite shapes of larger islands. The time of coalescence is less say about 0.6 sec. As the deposition continues, the gaps disappear to form a continuous film by filling up of the channels and holes in the aggregate mass.

Block diagram of a thin film coating unit

A standard vacuum coating unit consists of a pumping system which comprises of a rotary vacuum pump, a diffusion pump and additional fully integrated and wired parts like valves, baffles, and gauges.

Photograph of a vacuum coating unit (Courtesy: Hind Hivac, Bangalore)

Photograph of the vacuum coating unit is shown in the figure above. A schematic diagram of a vacuum coating unit is shown in the figure below. A rotary pump (Pirani gauge to measure vacuum till 10^{-3} Torr) along with a diffusion pump (a penning gauge to measure vacuum above 10^{-3} Torr) is used to ensure clean and better vacuum of the range of 10^{-6} Torr. Thus coating unit is fitted with a Pirani gauge used to measure the roughing vacuum and a Penning gauge to measure very high vacuum.



Schematic diagram of vacuum coating unit.

1. Bell jar 2. Crystal thickness monitor 3. Substrate holder 4. Filament with source material 5. Penning gauge 6. High vacuum valve 7. Diffusion pump 8. Backing valve 9. Pirani gauge

Besides, inside the coating unit, substrates can be cleaned by an ion bombardment facility in partial vacuum. A low tension transformer of 10V-100A is used to heat the filament for resistive evaporation. Most of the evaporations are processed in a vacuum of about 1-8 x10^{-6} Torr. Once the high vacuum is reached, resistive heating is done by heating the source (semiconductor or metallic) material with a resistively heated filament or boat (fill the boat or filament with the material to be coated), generally made of refractory metals such as W (tungsten) or Mo (molybdenum). Vapor sources of various types, geometrics and sizes can be easily constructed or obtained commercially. Some forms of these sources are basket, spiral, crucible heater dimple boat, etc. if a material has sufficiently high vapor pressure before melting occurs, it will sublime and the condensed vapors form a film.

a. Boat

b. coils or filament

On heating the source material in vacuum, it gets deposited onto the substrate (usually glass) for the required thickness, say 1000 Å and the film is kept in vacuum for few hours for settling. Later the bell jar can be opened and the films can be used for various studies and characterizations.

Pirani gauge

Pirani gauge is used to measure the vacuum inside the vacuum chamber (Bell Jar) till a vacuum of 10^{-3} Torr. Above this vacuum we have to use Penning gauge for the measurement of vacuum inside the chamber.

Hence the pirani gauge may be used to measure vacuum between 0.5 Torr to 10^{-4} Torr.

Penning gauge

It is a cold cathode ionization gauge head and has two electrodes. This gauge is used to measure high vacuum of around 10^{-6} Torr. This high vacuum of 10^{-6} Torr is required inside the chamber so as to proceed with the evaporation of the material. Therefore once this vacuum is reached (by using rotary pump and diffusion pump), the evaporation process can be started and coating continued until desired thickness is reached.

Rotary pump

This is considered as the commonly used mechanical pump so as to attain the necessary initial vacuum of 10^{-3} Torr. This pump comprises of a rotor that is eccentrically mounted within a stator.

Diffusion pump

Gaede was the first person to describe the thought of draining a vessel. This process is performed by means of molecular momentum transfer. Oils are used by the diffusion pumps for the purpose of pushing out the gas molecules. The range of vacuum for diffusion pump is about a value of 10^{-4} to 10^{-8} Torr. Usually, the diffusion pump used in the coating unit has a withdrawal speed of about 500 liters/s.

Quartz crystal thickness monitor

A commonly used thickness monitor is the quartz crystal thickness monitor which is employed to measure the thickness of the deposited thin films. It is a digital thickness monitor with a crystal holder cum feed-through and an oscillation box. It has a 3 digit LED auto-ranging display for rate of deposition and 4 digit LED auto-ranging display for thickness deposition.

Process of thermal evaporation

Thin film deposition techniques can be broadly classified into two categories which depend on the process being mainly physical or chemical.

In physical deposition technique, methods include mainly resistive evaporation and electron beam evaporation techniques. In this method mechanical, electromechanical or thermodynamic techniques are used to deposit a thin film of any solid. Starting solid substance that is deposited has to be taken in a vacuum chamber and the source material is heated in vacuum chamber using tungsten coils or baskets so that the particles of the solid substance escape from the surface. Thus the complete unit is placed in the vacuum deposition chamber, so that the particles can move freely. These moving particles when reaches a surface (usually on glass substrate) which is cooler takes away the energy from these particles thereby letting them to shape into a solid thin layer. Examples of physical deposition include vacuum (thermal) evaporation (or resistive heating) and electron beam evaporation.

A thermal evaporation technique uses an electric resistance (tungsten/ molybdenum) coil or a basket so as to liquefy the starting matter and to increase its vapor pressure up to a required level. The process happens in a considerably high vacuum so that the vapor comes in contact with the substrate and does not interact or does not spread with other gas molecules present inside the vacuum chamber. This also reduces the merging of impurities from the remaining gas. Hence, only the materials which are having a vapor pressure much higher than the heating element gets deposited with minimum contamination of the film.

An electron beam evaporation technique also called as EBG evaporation is as same as the thermal evaporation but uses an electron beam to melt and vaporize the source material. When a beam of electron falls on the source material, the atoms of the source material moves to the substrate and settles. Here the temperature of the source material is made above its boiling/sublimation temperature so as to deposit a film on the required surfaces. E-beam evaporation has a major advantage over thermal evaporation that this method yields a higher density film with a better adhesion to the substrate. As the electron beam heats only the source material and does not heat the entire crucible, the level of contamination due to the crucible is relatively less as in the case of thermal evaporation.