

UNIT-2
Synthesis of nanomaterials
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MISSION

CHRIST is a nurturing ground for an individual's holistic development to make effective contribution to the society in a dynamic environment

VISION

Excellence and Service

CORE VALUES

Faith in God | Moral Uprightness
Love of Fellow Beings
Social Responsibility | Pursuit of Excellence

UNIT – II Synthesis of nanomaterials

9 hours

Bottom-up approaches for nanostructure fabrication:

Sol-gel method

Top down approaches for nanostructure fabrication:

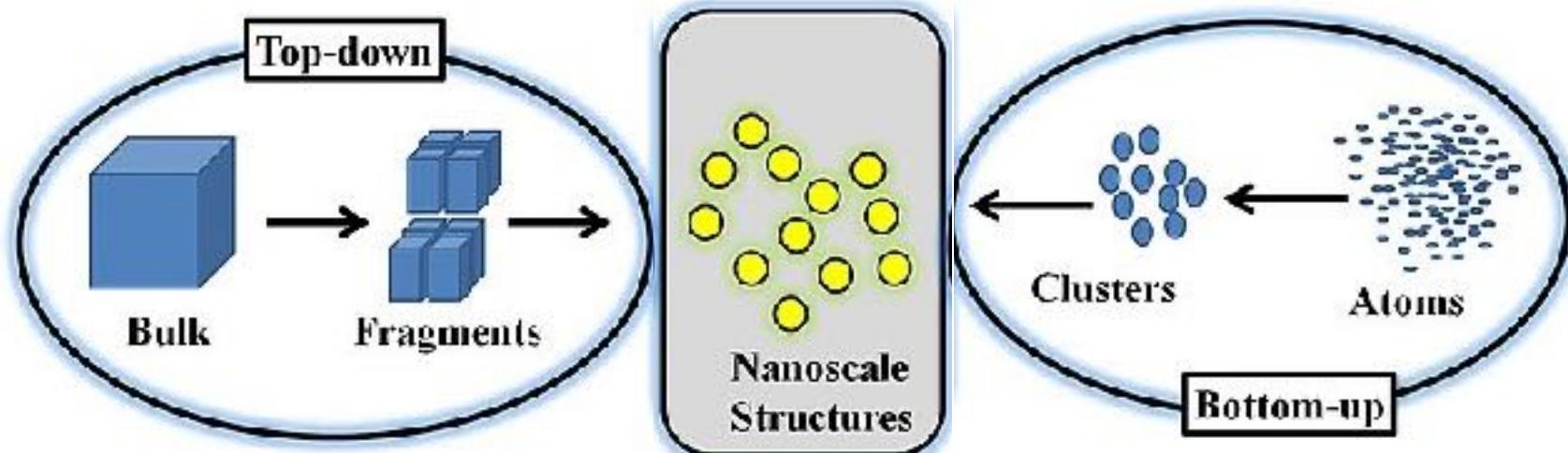
Ball milling, Lithography, melt quenching and annealing.

Self Assembled Monolayers (SAM), Chemical Vapour Deposition (CVD), Spin coating.

Nanoparticle Synthesis

There are two approaches for synthesis of nanomaterials and the fabrication of nano structures.

Top-Down approach Bottom-Up approach

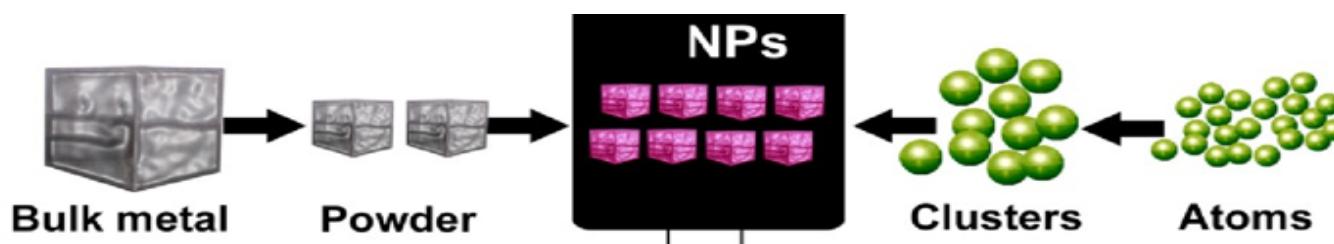


Top Down Approach

- Top down approach refers to slicing or successive cutting of a bulk material to get nano sized particle.

Bottom Up Approach

- Bottom up approach refers to the build up of a material from the bottom: atom by atom, molecule by molecule
- Atom by atom deposition leads to formation of Self- assembly of atoms/molecules and clusters
- These clusters come together to form self-assembled monolayers on the surface of substrate



Techniques of synthesis nano materials-

In top-down techniques, the starting material is solid state

Physical processing methods:

- Mechanical methods :**
 - cutting , etching, grinding
 - ball milling
- Lithographic techniques:**
 - Photo Lithography
 - Electron Beam Lithography

Ion beam Lithography
X-Ray lithography

Techniques of synthesis of nano materials-

Bottom up Approach:

All bottom up approach uses starting material – either gaseous state or liquid state of matter

Chemical techniques

- Chemical vapour deposition:
- PECVD,MPECVD)
- Self-assembled Monolayer :
Electrolytic deposition, Sol-gel method, Microemulsion route & pyrolysis.

Physical techniques

- Physical Vapor Deposition (PVD):
involves condensation of vapor phase species
- Evaporation (Thermal , e-beam)
 - Sputtering
 - Plasma Arcing,
 - Laser ablation,

Top Down

ADVANTAGES

- Large scale production: deposition over a large substrate is possible
- Chemical purification is not required

DISADVANTAGES

- broad size distribution (10-1000 nm)
- varied particle shapes or geometry
- Control over deposition parameters is difficult to achieve
- Impurities: stresses, defects and imperfections get introduced
- Expensive technique

Bottom Up Approach

ADVANTAGES

- Ultra-fine nanoparticles, nanoshells, nanotubes can be prepared
- Deposition parameters can be controlled
- Narrow size distribution is possible (1-20 nm)
- Cheaper technique

DISADVANTAGES

- Large scale production is difficult
- Chemical purification of nanoparticles is required

Bottom-up Approach: Synthesis of nanomaterials-Sol-Gel method



Sol

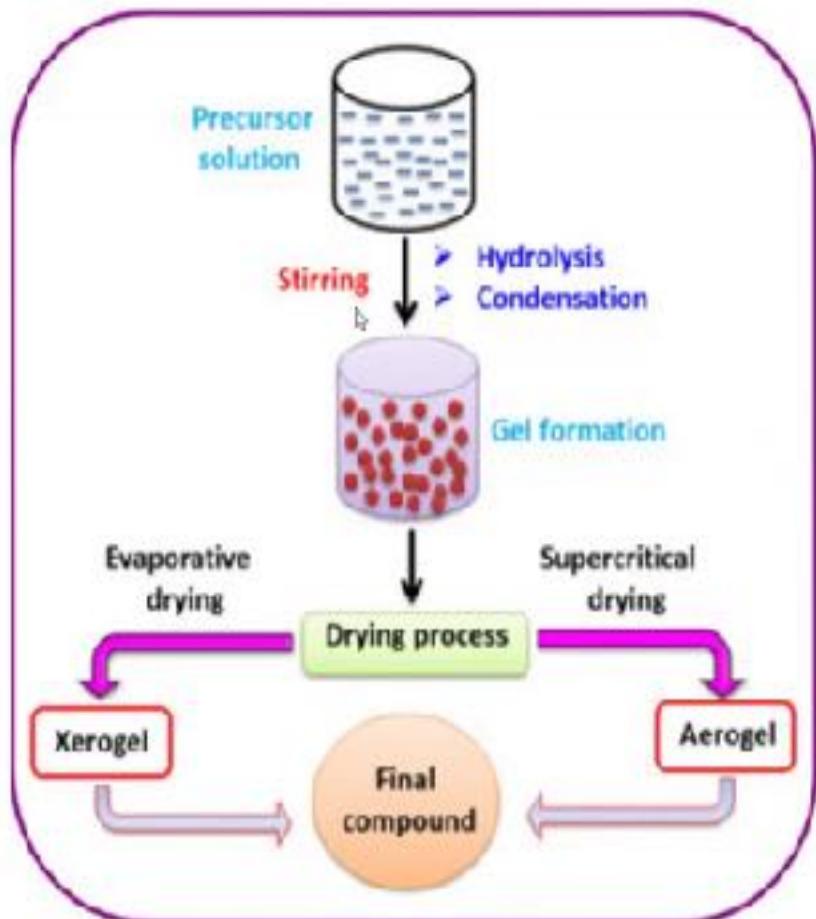


Gel

Sol: Solid particles are suspended in liquid.
The particles are so small that the gravitational force does not exist only Vader-Waals forces are present.

When the solvent from the sol gets evaporated, a semi rigid mass remains.
This semi rigid mass is called gel

Process involved in Sol-Gel synthesis



1. Hydrolysis: Metal Alkoxide react with water to form sol



2. Poly-condensation:

Hydrated sol reacts with the precursor to form gel



3. Syneresis: Transformation of gel in to solid mass

4. Drying of Gel: This is done by either thermal drying or super critical drying

Metal Alkoxide Ex: Tetramethoxy silane & tetraethoxy silane

Sol-Gel synthesis

Advantages

- Process is simple
- can produce high purity products.
- Very high production efficiency
- Can synthesis uniform compounds in the form of composite oxides.
- Can obtain homogeneous composition.

Disadvantages

- Cost of the raw material is high
- There is large volume shrinkage and cracking during drying.
- The process is not very clean, it contains undesired atoms and molecules.
- Difficult to avoid residual porosity and OH groups.

Applications:

- Protective coating
- Lubricants and scratch free paints
- Fire retardant materials
- Ultraviolet protection gels

Self Assembled Monolayer (SAM):

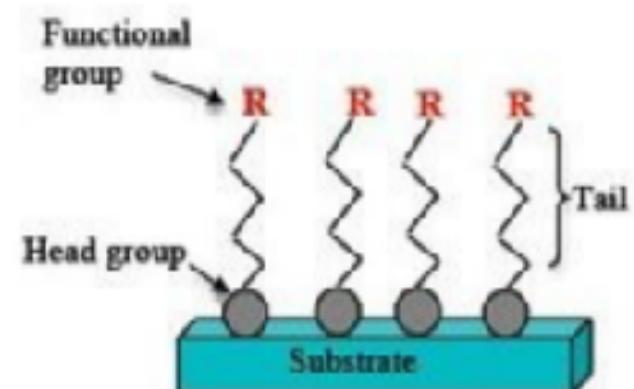
- Monolayer is a single 2D layer of the molecule formed due to the self assembly of molecules.
- It is based on the principle of adsorption of single layer of molecule from a solution on to a surface.

How do we do that?

- A solution is left on the substrate.
- After certain time the molecules are chemisorbed on to the surface, that means they form strong chemical bonds (covalent/ionic bond) on to the substrate.

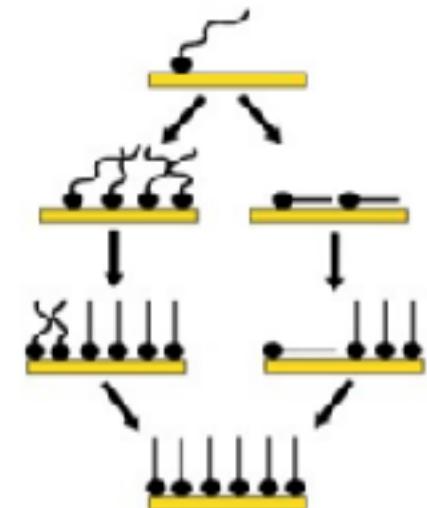
Chemisorptions Means : The molecules from the liquid forms a covalent/ionic bond to the substrate.

A **self assembled monolayer (SAM)** is an organized layer of **amphiphilic** molecules in which one end of the molecule, the "head group" shows a special affinity for a substrate. SAMs also consist of a tail with a functional group at the terminal end as seen in Figure 1.



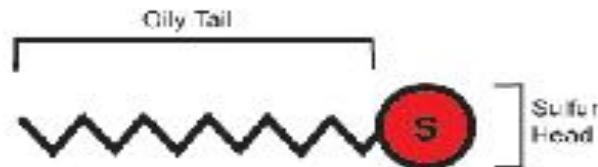
Self Assembled Monolayer (SAM):

- SAMs are created by the chemisorption of "head groups" onto a substrate from either the vapour or liquid phase.
- followed by a slow organization of "tail groups".
- Initially, at small molecular density on the surface,
- Adsorbate molecules form either a disordered mass of molecules or form an ordered two-dimensional "lying down phase"
- The "head groups" assemble together on the substrate, while the tail groups assemble far from the substrate.
- Areas of close-packed molecules nucleate and grow until the surface of the substrate is covered in a single monolayer.
- Adsorbate molecules adsorb readily because they lower the surface free-energy of the substrate and are stable due to the strong chemisorption of the "head groups".

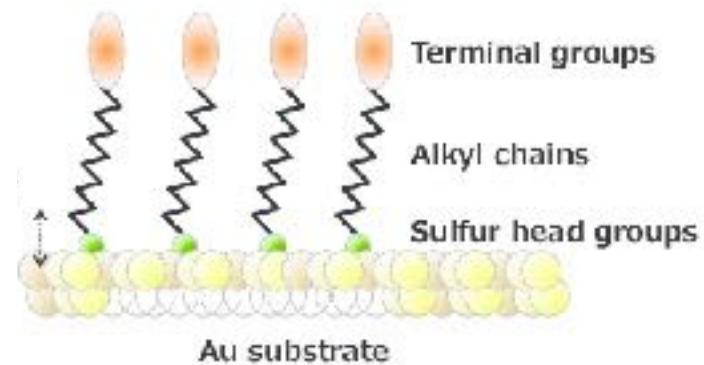
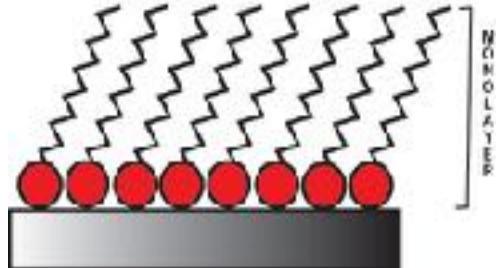


Self Assembled Monolayer (SAM): Alkanethiols

- The most common monolayer's are made from alkanethiols – molecules that have an oil-like chain with a sulfur atom at one end.



- Sulfur likes to bond to gold and silver surfaces so when the alkane thiol comes in contact with a gold surface, the molecules self assemble to form the monolayer.



head groups are connected to a molecular chain in which the terminal end can be functionalized (i.e. adding $-OH$, $-NH_2$, $-COOH$, or $-SH$ groups) to vary the wetting and interfacial properties.

Applications of Self Assembled Monolayer (SAM):

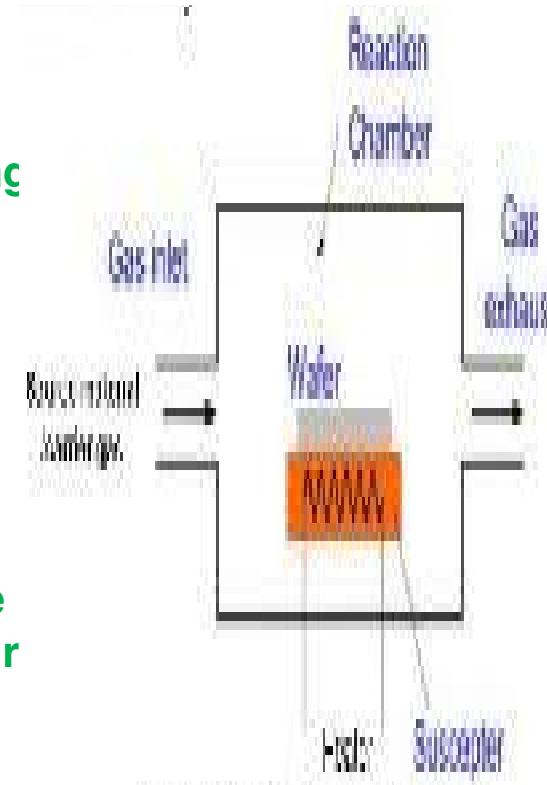
- surface coating applications: control of wetting and adhesion
chemical
Resistance & Bio compatibility
Molecular recognition for sensors and nano fabrication
- **Areas of application for SAMs also include**
nanoelectromechanical systems (NEMS)
and microelectromechanical systems (MEMS).
- **It can serve as models for studying membrane properties of**
cells and organelles and cell attachment on surfaces.
- **It can also be used to modify the surface properties of**
electrodes for electrochemistry, general electronics.

Chemical vapour deposition :

- **Chemical vapour deposition (CVD) is a deposition process where chemical precursors are transported in the vapour phase to decompose on a heated substrate to form a film.**
- **The films may be polycrystalline or amorphous depending on the materials and reactor conditions.**
- **CVD is one of the important method of film deposition for the semiconductor industry due to its high purity and low cost of operation.**
- **CVD is also commonly used in optoelectronics applications, optical coatings, and coatings of wear resistant parts.**

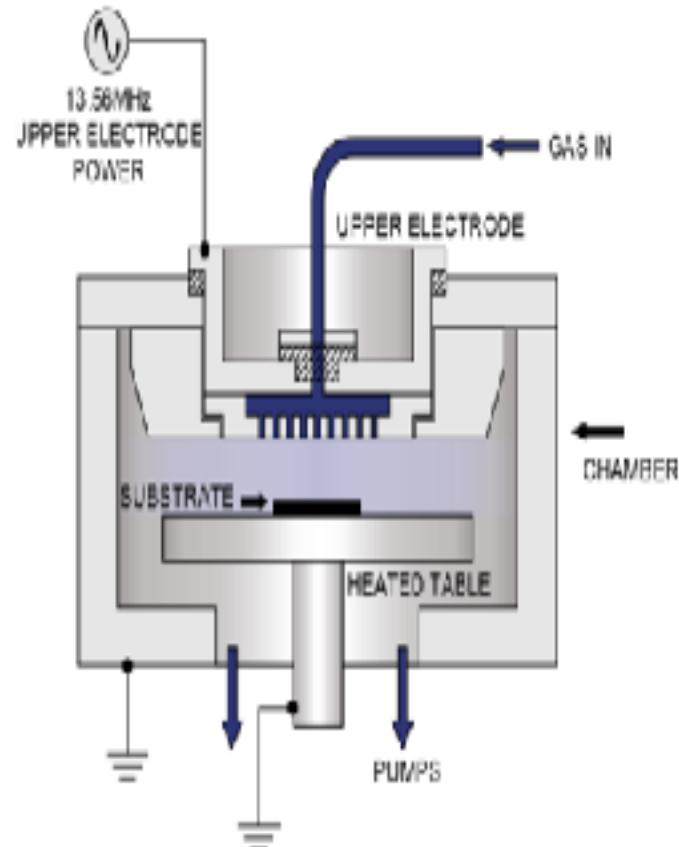
Components of CVD Techniques:

- **Gas delivery system:** For the supply of precursors to the reactor chamber.
- **Reactor chamber:** Chamber within which deposition takes place.
- **Substrate loading mechanism:** A system for introducing and removing substrates.
- **Energy source:** energy/heat that is required to get the precursors to react/decompose.
- **Vacuum system:** to removal all other gaseous species other than those required for the reaction/deposition..
- **Exhaust system:** for removal of volatile by-products from the reaction chamber.
- **Exhaust treatment systems:** exhaust gases may not be suitable for release into the atmosphere and may require treatment or conversion to safe/harmless compounds.
- **Process control equipment:** Gauges, controls etc to monitor process parameters such as pressure, temperature and time.

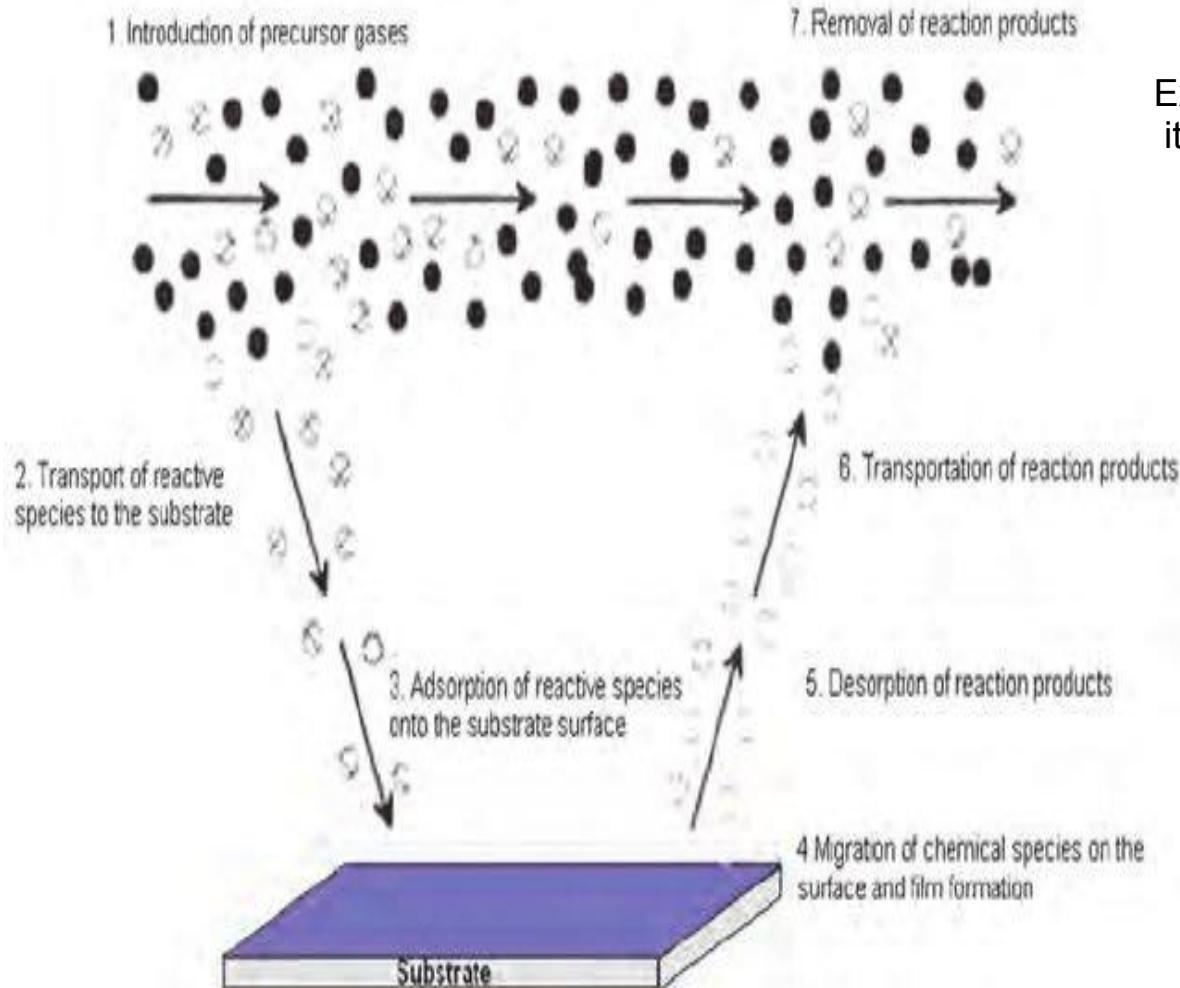


Chemical vapour deposition :

- Precursor (halides and metal organic compounds) gases are delivered into the reaction chamber at approximately ambient temperatures.
- As they pass over or come into contact with a heated substrate, they react or decompose forming a solid phase which are deposited onto the substrate.
- The substrate temperature is critical and can influence what reactions will take place.



CVD Techniques :



Example : TiCl₄ is the precursor gas & it is mixed with carrier gas

Types of CVD Techniques

- APCVD
- LPCVD
- PECVD
- HDPCVD

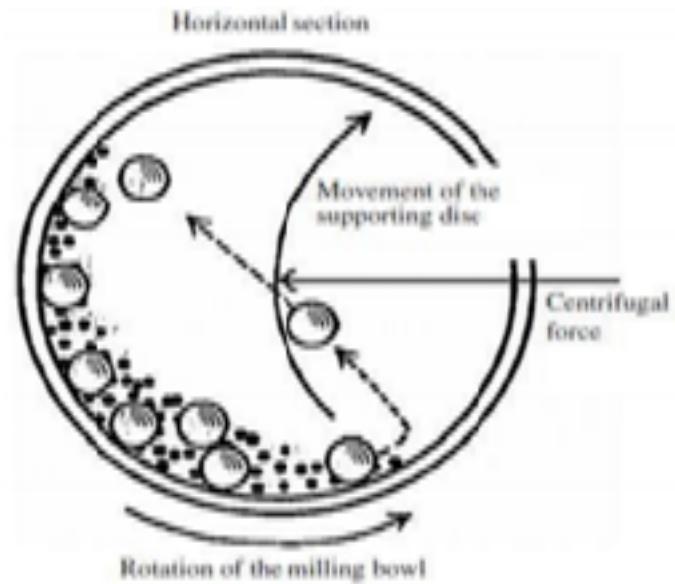
Applications of CVD

- In semiconductor and microelectronic industries
- In metallurgical coating industries
- Optical fibers for telecommunications
- Wear resistant coatings, corrosion resistant coatings, heat-resistant coatings etc.
- Preparation of high temperature materials

Top down approaches for nanostructure fabrication

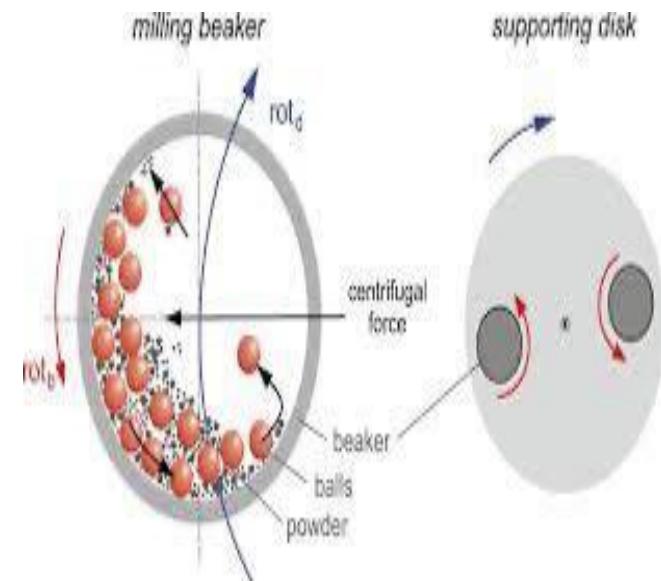
Ball milling method:

- ✓ It's a top-down approach
- ✓ It works on the principle of impact & attrition
- ✓ The structural &chemical changes in the material is obtained by mechanical energy
- ✓ The ball milling method consists of balls and a mill chamber.
- ✓ Ball mill contains a stainless steel container and many small iron, hardened steel, silicon carbide, or tungsten carbide balls are made to rotate inside a mill (drum).
- ✓ Rotating container is called mill, when the mill rotates the balls also will move
- ✓ The powder of a material is taken inside the steel container.



Top down approaches – Ball mill

- ✓ This powder will be made into nano size using the ball milling technique.
- ✓ A magnet is placed outside the container to provide the pulling force to the material and this magnetic force increases the milling energy when milling container or chamber rotates the metal balls.
- ✓ The ball to material mass ratio is normally maintained at 2 :1.
- ✓ silicon carbide balls provide large amount of energy to the material powder and the powder then get crushed.
- ✓ The process of ball milling is done approximately 100 to 150 hrs to get uniform fine powder.



Ball milling Process:

Advantages

1. Nano powders of 2 to 20 nm in size can be produced.
2. The size of nano powder also depends upon the speed of the rotation of the balls.
3. It is an inexpensive and easy process.

Disadvantages

1. Shape of the nanomaterials is irregular.
2. There may be contaminants inserted from ball and milling additives.
3. This method produces crystal defects.

This method can be used to prepare

- ceramic and metal nano particles
- closed or curved shell carbon nanostructure by ball milling of graphite
- Nanoporous carbon
- Carbon nanotubes

Lithography:

- Lithography comes from the Greek word, lithos, means "stone" and graphein, means "to write".
- First introduced by German author Alois Senefelder at 1771-1834.

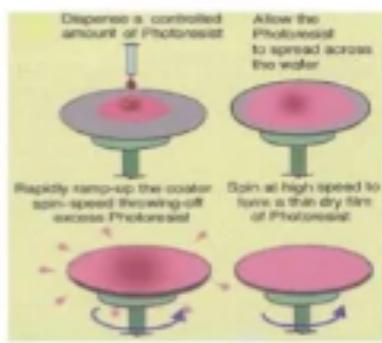
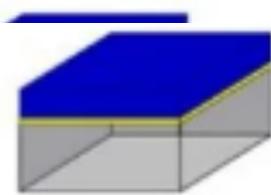
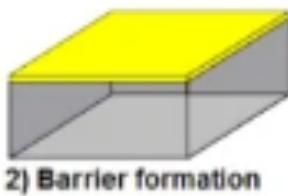
It is a process of transferring geometric shapes on a mask to a thin layer of radiation sensitive material (photo resist) covering the surface of a semiconducting wafer.

Types of Lithography

- Photolithography (Optical and UV)
- Electron beam and Ion beam lithography
- X-ray lithography
- Interference lithography
- Scanning probe lithography
- Charged particle lithography

Photolithography is a process of transferring geometric shapes on a mask to the surface of silicon wafer .

Photolithography – Steps Involved



1) Wafer Cleaning:

In the first step, the wafers are chemically cleaned to remove organic, ionic, and metallic impurities.

2) Barrier Layer Formation:

After cleaning, silicon dioxide, which serves as a barrier layer, is deposited on the surface of the wafer.

3) Photoresist Application:

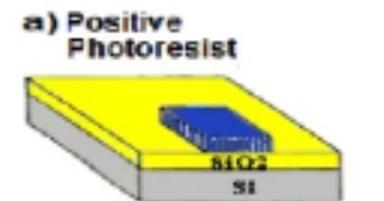
Photoresist is applied to the surface of the wafer by high-speed centrifugal spinning. This technique, known as "Spin Coating," produces a thin uniform layer of photoresist on the wafer surface. In this process a liquid solution of photoresist is given out from the wafer by rapid spin and produce uniform thin layer ($0.5\mu\text{m}$ to $2.5\mu\text{m}$). Spin coating/ spinner typically runs at 1200rpm to 4800rpm for 30sec to 60sec. Chemicals commonly used as photoresist are;

- Poly methyl methacrylate (PMMA)
- Poly methyl glutarimide (PMGI)
- Phenol formaldehyde resin (DNO/Novolac)

Photolithography – Steps Involved

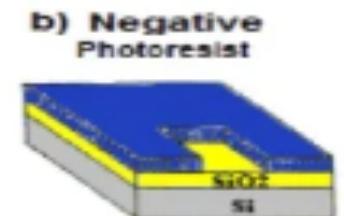
a) Positive Photoresist:

Positive photoresists are exposed to UV light, the underlying material is to be removed. In these resists, exposure to the UV light changes the chemical structure of the resist so that it becomes more soluble in the developer. The exposed resist is then washed away by the developer solution. In other words, "whatever shows, goes."



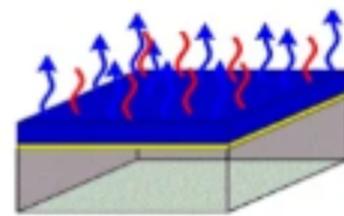
b) Negative Photoresist:

Negative photoresists behave in just the opposite manner. Exposure to the UV light causes the negative resist to become polymerized, and more difficult to dissolve. Therefore, the negative resist remains on the surface wherever it is exposed, and the developer solution removes only the unexposed portions.



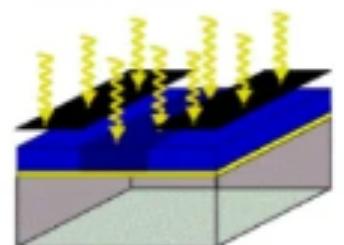
4) Prebaking:

Prebaking is the step during which almost all of the solvents are removed from the photoresist. The photoresist becomes photosensitive after prebaking. Photoresist is prebaked at 90°C to 100°C for 5min to 30min.



5) Mask Alignment and Exposure:

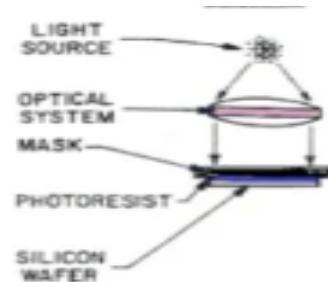
A mask or "photo mask" is a square glass plate with a patterned combination of metal film on one side transferred onto the wafer surface. There are three primary exposure methods: contact, proximity, and projection. They are shown in the figure below.



Photolithography :Steps Involved

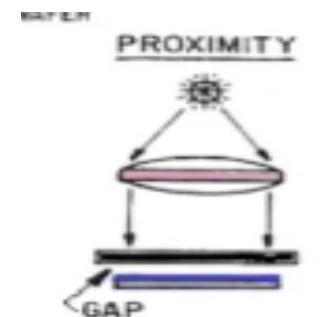
Contact Printing:

In contact printing wafer is brought into physical contact with photo mask. Because of the contact between the resist and mask, very high resolution is possible. The problem with contact printing is that fragments trapped between the resist and the mask, can damage the mask and cause defects in the pattern.



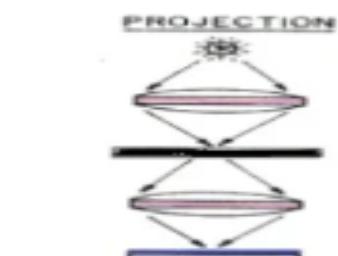
Proximity Printing:

The proximity exposure method is similar to contact printing except that a small gap, 10 to 25 microns wide is maintained between the wafer and the mask. This gap minimizes (but may not eliminate) mask damage. Approximately 2 to 4 micron resolution is possible with proximity printing.



Projection Printing:

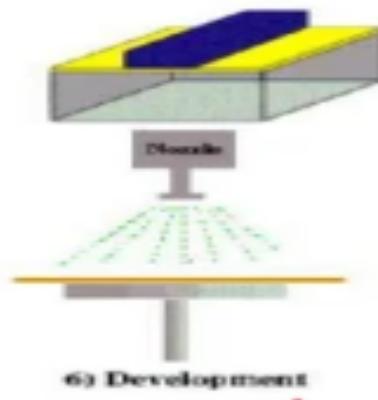
Projection printing avoids mask damage entirely. An image of the patterns on the mask is projected onto the wafer, which is many centimetres away. To achieve high resolution, only a small portion of the mask is imaged it has about 1-micron resolution.



Photolithography: Steps Involved

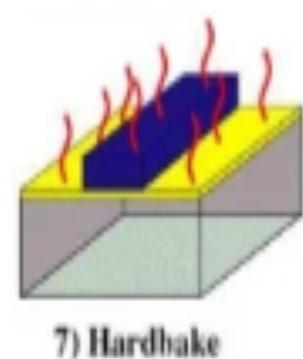
6) Development:

Development is a process in which exposed/non-exposed area is dissolved by developer. Most commonly used developer is tetra methyl ammonium hydroxide is used in concentrations of 0.2 - 0.26. Developer is important in controlling the development uniformity. Therefore two methods are mainly used i.e. spin development and spray development. During spin development wafers are spun and developer is poured onto the rotating wafer. In spray development, the developer is sprayed rather than poured, on the wafer by using a nozzle that produces a fine spray over the wafer.



7) Hard-Baking:

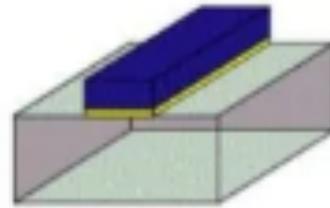
The hard bake is used to harden the final resist image at the temperature (120°C - 150°C), so that it will hold out the harsh environments of etching.



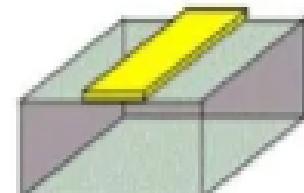
Photolithography: Steps Involved

8) Etching:

Etching is performed either using wet chemicals such as acids, or more commonly in a dry etching (*by exposing the material to a bombardment of ions*) . The photoresist will "resists" the etching and protects the material covered by the resist. When the etching is complete, the resist is stripped leaving the desired pattern.



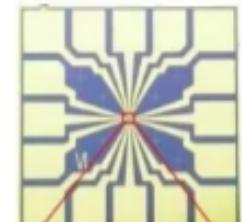
8) Etching



9) Stripping

9. Stripping:

After the imaged wafer has been etched the remaining photoresist must be removed. There are two classes of stripping techniques; wet stripping and dry stripping. A simple example of stripper is acetone. Acetone tends to leave residues on the wafer. Most commercial organic strippers are phenol-based.



Sample fabricated
by photolithography

Applications of Photolithography

□ Main application:

IC designing process

□ Other applications:

Printed electronic board, nameplate and printer plate.

X-ray Lithography

➤ **X-ray radiation** : Transfers the image on the mask to the substrate.

➤ **Mask** is kept little away from the substrate.
Mask alignment is done using the visible light and alignment optics.

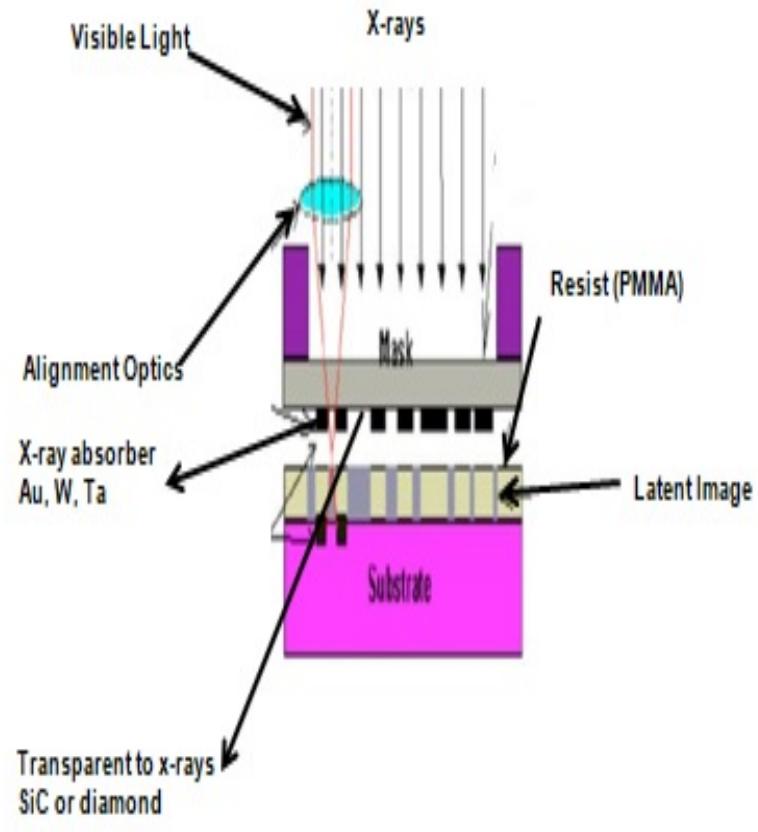
Mask has two parts:

X-ray absorber and X-ray transparent region

X-ray absorber : Absorbs the X-ray radiation and **Transparent region** allows the X-rays to fall on the photo resist.

➤ **Photo Resist:** Is a polymer (PMMA) film on the substrate on to which image is formed.
The design on the mask is recreated on the film and it is called latent image.

The gap seen on the film is removed by x-rays and where ever there is x-ray absorber, that part of the film is intact.



X-ray Lithography:

Advantages

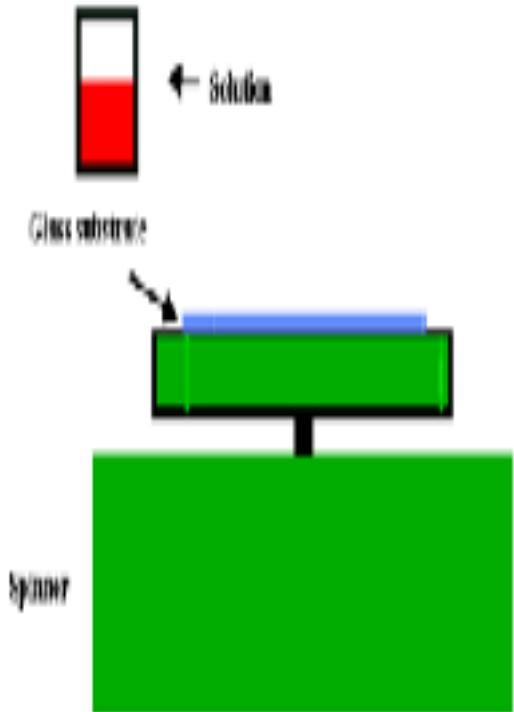
- Shorter wavelength of 0.4 to 4 nm.
- No diffraction effect.
- Faster than EBL.
- Simple to use.

Disadvantages

- Very thin lens
- Distortion in absorber.
- Masks are expensive to produce.
- Vibration and time consuming.

Spin coating :

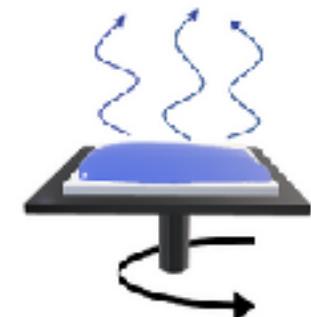
- Spin coating is a procedure used to deposit uniform thin films onto flat substrates.
- Usually a small amount of coating material is applied on the centre of the substrate, which is either spinning at low speed or not spinning at all.
- The substrate is then rotated at speed up to 10,000 rpm to spread the coating material by centrifugal force.
- The rotation of the substrate at high speed, means the centripetal force combined with the surface tension of the solution pulls the liquid coating into an even covering.



A machine used for spin coating is called a spin coater.

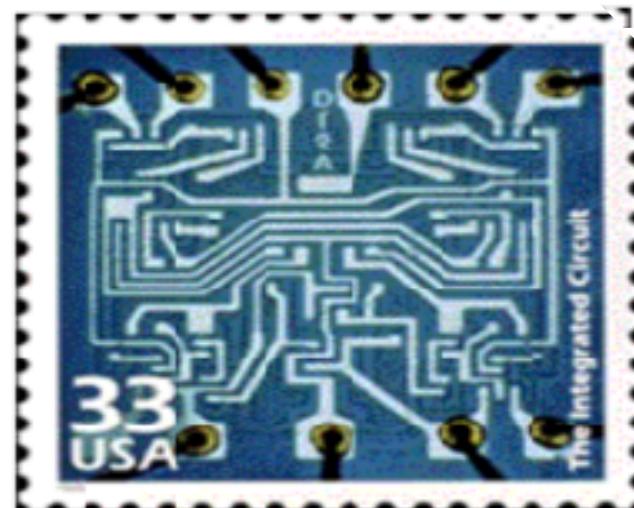
Spin coating :

- Rotation is continued while the fluid spins off the edges of the substrate, until the desired thickness of the film is achieved.
- The applied solvent is usually volatile, and simultaneously evaporates.
- The higher the angular speed of spinning, the thinner the film.
- The thickness of the film also depends on the viscosity and concentration of the solution, and the solvent.



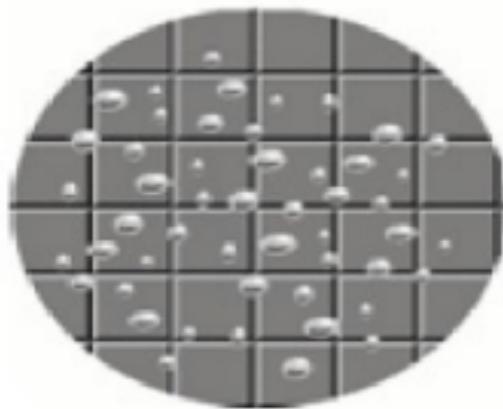
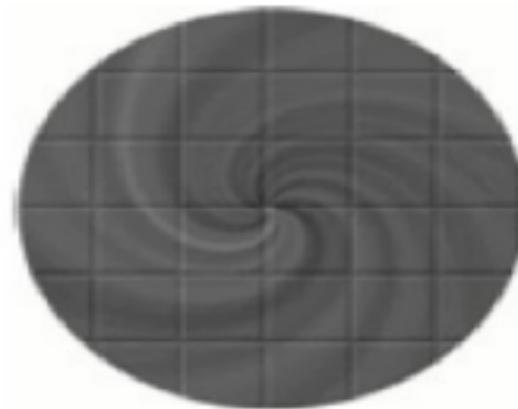
Uses of Spin coating

- **Photoresist for patterning wafers in microcircuit production.**
- **Insulating layers for microcircuit fabrication such as polymers.**
- **Flat screen display coatings.
Antireflection coatings and conductive oxide.**
- **DVD and CD ROM**
- **Television tube antireflection coatings.**



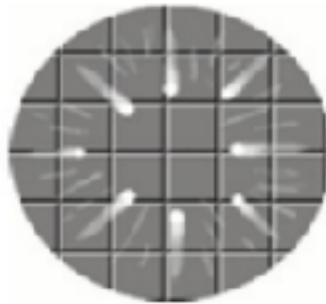
Common Spin Coating Defects

- A swirling pattern may be observed.
- Causes:
 - Fluid deposited off center
 - Acceleration too high
 - Spin time too short
 - Exhaust rate too high

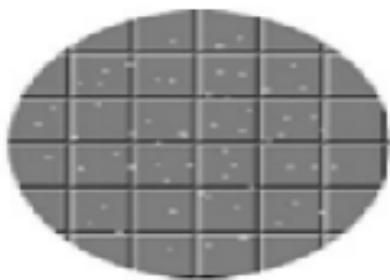


- Bubbles on the surface of the coated wafer.
- This occurs when fluid is deposited as the wafer is spinning, and may be caused by a faulty dispense tip.

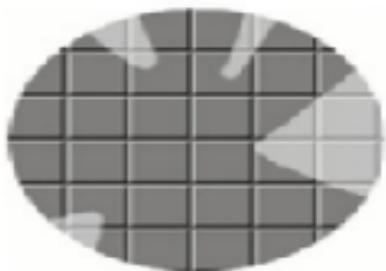
Common Spin Coating Defects



- Streaks can occur on the wafer for a number of reasons including:
 - Acceleration too high
 - Fluid deposited off center
 - Particles on surface prior to spin



- Pinhole defects can be caused by:
 - Air bubbles
 - Particles in fluid
 - Particles on substrate.



- Uncoated areas on wafer occur when too little fluid is deposited on the wafer.

Introduction

. Heat Treatment

- *Heat Treatment process is a series of operations involving the **Heating and Cooling** of metals in the solid state.*
- *Its purpose is to change a mechanical property or combination of mechanical properties so that the metal will be more useful, serviceable, and safe for definite purpose.*
- *By heat treating, a metal can be made harder, stronger, and more resistant to impact, heat treatment can also make a metal softer and more ductile.*

Types of Heat Treatment

1. Annealing
2. Normalizing
3. Quenching or Hardening
4. Tempering
5. Surface Hardening
6. Case Hardening
7. Austempering
8. Marquenching



- *No one heat-treating operation can produce all of these characteristics. In fact, some properties are often improved at the expense of others. In being hardened, for example, a metal may become brittle.*

Annealing :

Annealing is a heat treatment process used mostly to increase ductility and reduce the hardness of a material.

The change in hardness and ductility is a result of the reduction of dislocations in the crystal structure of the material being annealed

Why annealing is Important?

Changing the mechanical properties through annealing is important for many reasons:

- It improves the formability of a material. Hard, brittle materials can be difficult to bend or press without breaking the material. Annealing eliminates this risk.
- It can also improve machinability. A material that is extremely brittle can cause excessive tool wear. By reducing the hardness of a material by annealing, the wear and tear of the tool can be reduced.
- It removes residual stresses. Residual stresses can cause cracks and other mechanical complications.

Annealing Process:

There are three main stages to an annealing process:

Recovery stage:

During the recovery stage, a furnace or other type of heating device is used to raise the temperature at which its internal stresses in the material are relieved.

Recrystallization stage:

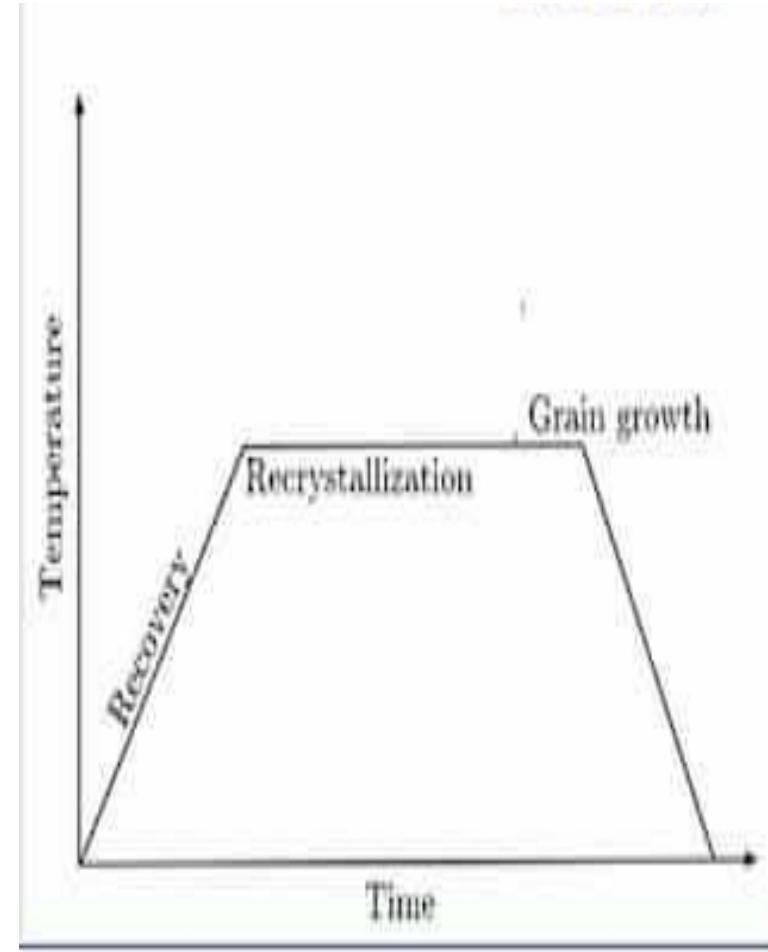
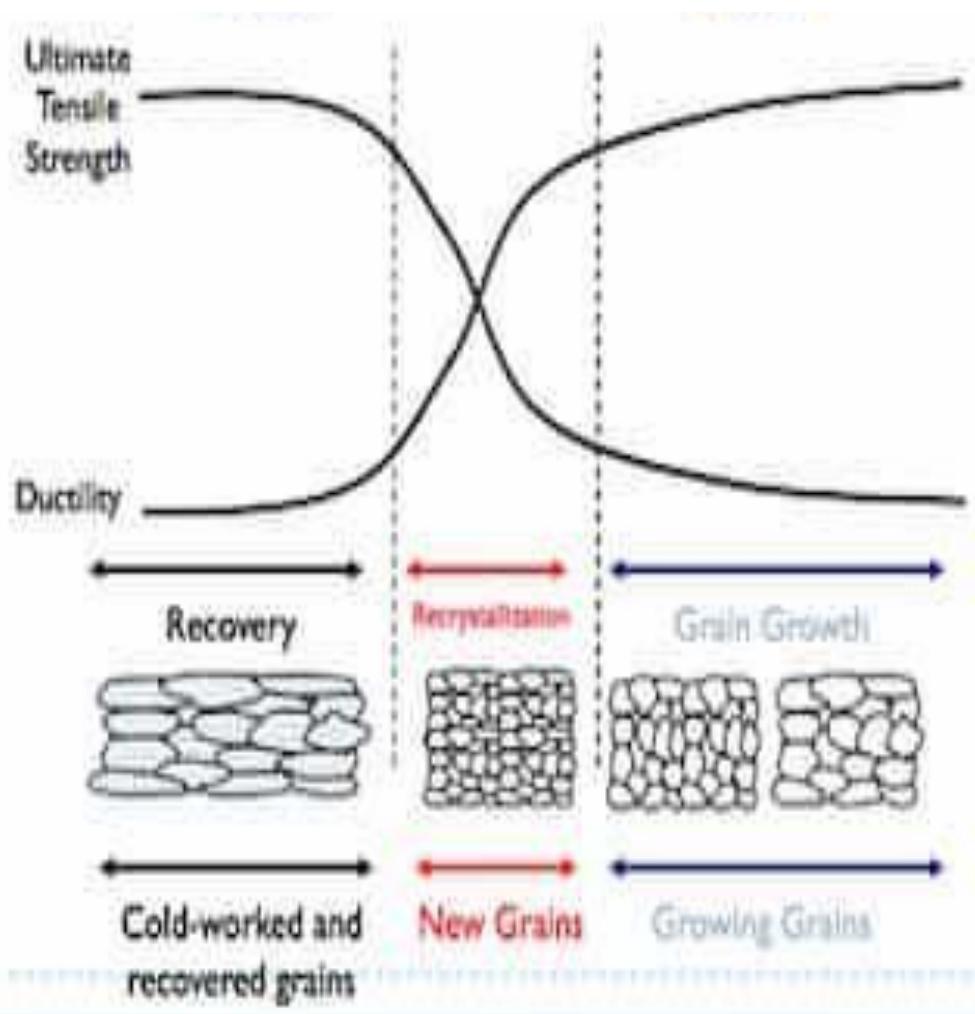
During the recrystallization stage the material is heated above its recrystallization temperature, but below its melting temperature. This causes new grains to form without any pre-existing tension.

Grain growth stage:

As the grain grows, the new grains develop fully. This growth is controlled by letting the material cool down at a certain rate.

The result of completing these three stages is a material with more ductility and reduced hardness. Subsequent processes, which can further change the mechanical properties, are sometimes carried out after the annealing process.

Annealing Process:



Hardening and Quenching

➤ Hardening is a process in which steel is heated to a temperature above the critical point, held at this temperature and Quenched (rapidly cooled) in water, oil or molten baths.

What happens when we do this?

- Suppose If a piece of steel is heated above its upper critical temperature and plunged into water to cool, it become extremely hard, needle-shaped structure known as martensite. In other words, sudden quenching of steel greatly increases its hardness.
- Martensite structures formed by direct quenching of high carbon steel are hard and strong, but unfortunately are also brittle.
- Some of the hardness and strength must be sacrificed to obtain suitable ductility and toughness. This is done by tempering the martensitic steel.
- Tempering : Increase toughness, Decrease hardness, Stabilise structure and Relieve stresses