

## What are Nano materials?

- Nano scale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair. Nano materials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields.
- Some Nano materials occur naturally, but of particular interest are engineered Nano materials (EN), which are designed for, and already being used in many commercial products and processes. They can be found in such things as sunscreens, cosmetics, sporting goods, stain-resistant clothing, tires, electronics, as well as many other everyday items, and are used in medicine for purposes of diagnosis, imaging and drug delivery.
- Engineered Nano materials are resources designed at the molecular (nanometre) level to take advantage of their small size and novel properties which are generally not seen in their conventional, bulk counterparts. The two main reasons why materials at the nano scale can have different properties are increased relative surface area and new quantum effects. Nanomaterials have a much greater surface area to volume ratio than their conventional forms, which can lead to greater chemical reactivity and affect their strength.

### 1. Classification is based on the number of dimensions:

#### *1.1. Zero-dimensional nanomaterials:*

- \_ Materials wherein all the dimensions are measured within the nanoscale (no dimensions, or 0-D, are larger than 100 nm).
- \_ The most common representation of zero-dimensional nanomaterials are nanoparticles.

Nanoparticles can:

- \_ Be amorphous or crystalline
- \_ Be single crystalline or polycrystalline
- \_ Be composed of single or multi-chemical elements
- \_ Exhibit various shapes and forms
- \_ Exist individually or incorporated in a matrix
- \_ Be metallic, ceramic, or polymeric

#### *1.2. One-dimensional nanomaterials:*

- \_ One dimension that is outside the nanoscale.
- \_ This leads to needle like-shaped nanomaterials.
- \_ 1-D materials include nanotubes, nanorods, and nanowires.

1-D nanomaterials can be

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- \_ Amorphous or crystalline
- \_ Single crystalline or polycrystalline
- \_ Chemically pure or impure
- \_ Standalone materials or embedded in within another medium
- \_ Metallic, ceramic, or polymeric

## *1.3.Two-dimensional nanomaterials:*

- \_ Two of the dimensions are not confined to the nanoscale.
- \_ 2-D nanomaterials exhibit plate-like shapes.
- \_ Two-dimensional nanomaterials include nanofilms, nanolayers, and nanocoatings.

2-D nanomaterials can be:

- \_ Amorphous or crystalline
- \_ Made up of various chemical compositions
- \_ Used as a single layer or as multilayer structures
- \_ Deposited on a substrate
- \_ Integrated in a surrounding matrix material
- \_ Metallic, ceramic, or polymeric

## *1.4.Three-dimensional nanomaterials:*

- \_ Bulk nanomaterials are materials that are not confined to the nanoscale in any dimension. These materials are thus characterized by having three arbitrarily dimensions above 100 nm.
- \_ Materials possess a nanocrystalline structure or involve the presence of features at the nanoscale.
- \_ In terms of nanocrystalline structure, bulk nanomaterials can be composed of a multiple arrangement of nanosize crystals, most typically in different orientations.
- \_ With respect to the presence of features at the nanoscale, 3-D nanomaterials can contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multilayers.

## **2.Methods for creating nanostructures**

There are many different ways of creating nanostructures: of course, macromolecules or nanoparticles or buckyballs or nanotubes and so on can be synthesized artificially for certain specific materials. They can also be arranged by methods based on equilibrium or near-equilibrium thermodynamics such as methods of self-organization and self-assembly (sometimes also called bio-mimetic processes). Using these methods, synthesized materials can be arranged into useful shapes so that finally the material can be applied to a certain application.

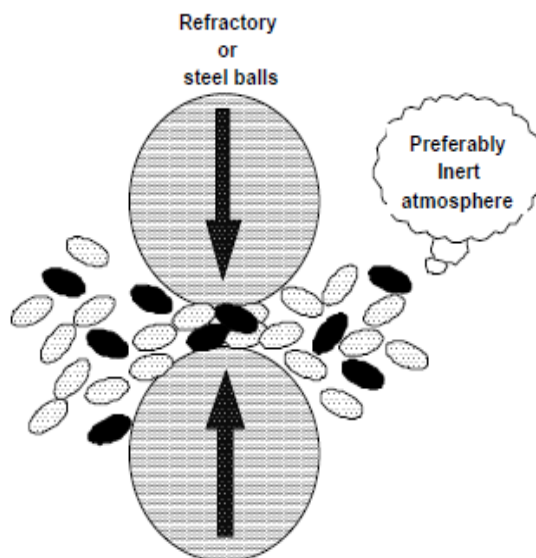
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## 2.1. Mechanical grinding

Mechanical attrition is a typical example of 'top down' method of synthesis of nanomaterials, where the material is prepared not by cluster assembly but by the structural decomposition of coarser-grained structures as the result of severe plastic deformation. This has become a popular method to make nanocrystalline materials because of its simplicity, the relatively inexpensive equipment needed, and the applicability to essentially the synthesis of all classes of materials.

The major advantage often quoted is the possibility for easily scaling up to tonnage quantities of material for various applications. Similarly, the serious problems that are usually cited are;

- contamination from milling media and/or atmosphere, and to consolidate the powder product without coarsening the nanocrystalline microstructure. In fact, the contamination problem is often given as a reason to dismiss the method, at least for some materials. Here we will review the mechanisms presently believed responsible for formation of nanocrystalline structures by mechanical attrition of single phase powders, mechanical alloying of dissimilar powders, and mechanical crystallization of amorphous materials. The two important problems of contamination and powder consolidation will be briefly considered.



*Fig.1. Schematic representation of the principle of mechanical milling*

- Mechanical milling is typically achieved using high energy shaker, planetary ball, or tumbler mills. The energy transferred to the powder from refractory or steel balls depends on the rotational (vibrational) speed, size and number of the balls, ratio of the ball to powder mass, the time of milling and the milling atmosphere. Nanoparticles are produced by the shear action during grinding. Milling in cryogenic liquids can greatly increase the brittleness of the powders influencing the fracture process.

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- As with any process that produces fine particles, an adequate step to prevent oxidation is necessary. Hence this process is very restrictive for the production of non-oxide materials since then it requires that the milling take place in an inert atmosphere and that the powder particles be handled in an appropriate vacuum system or glove box.
- This method of synthesis is suitable for producing amorphous or nanocrystalline alloy particles, elemental or compound powders. If the mechanical milling imparts sufficient energy to the constituent powders a homogeneous alloy can be formed. Based on the energy of the milling process and thermodynamic properties of the constituents the alloy can be rendered amorphous by this processing.

## 2.2. Chemical Synthesis of Nanomaterials

In principle we can classify the wet chemical synthesis of nanomaterials into two broad groups:

1. The top down method: where single crystals are etched in an aqueous solution for producing nanomaterials, For example, the synthesis of porous silicon by electrochemical etching.
2. The bottom up method: consisting of sol-gel method, precipitation etc. where materials containing the desired precursors are mixed in a controlled fashion to form a colloidal solution.

### 2.2.1. Sol-gel process

The sol-gel process, involves the evolution of inorganic networks through the formation of a colloidal suspension (**sol**) and gelation of the sol to form a network in a continuous liquid phase (**gel**). The precursors for synthesizing these colloids consist usually of a metal or metalloid element surrounded by various reactive ligands. The starting material is processed to form a dispersible oxide and forms a sol in contact with water or dilute acid. Removal of the liquid from the sol yields the gel, and the sol/gel transition controls the particle size and shape. Calcination of the gel produces the oxide.

Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based precursors such as  $\text{Si}(\text{OEt})_4$  (tetraethyl orthosilicate, or TEOS). The reactions involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides.

$\text{M}(\text{OR})_2$  can be described as follows:

$\text{MOR} + \text{H}_2\text{O} \rightarrow \text{MOH} + \text{ROH}$ (hydrolysis)
$\text{MOH} + \text{ROM} \rightarrow \text{M-O-M} + \text{ROH}$ (condensation)

Sol-gel method of synthesizing nanomaterials is very popular amongst chemists and is widely employed to prepare oxide materials. The sol-gel process can be characterized by a series of distinct steps.

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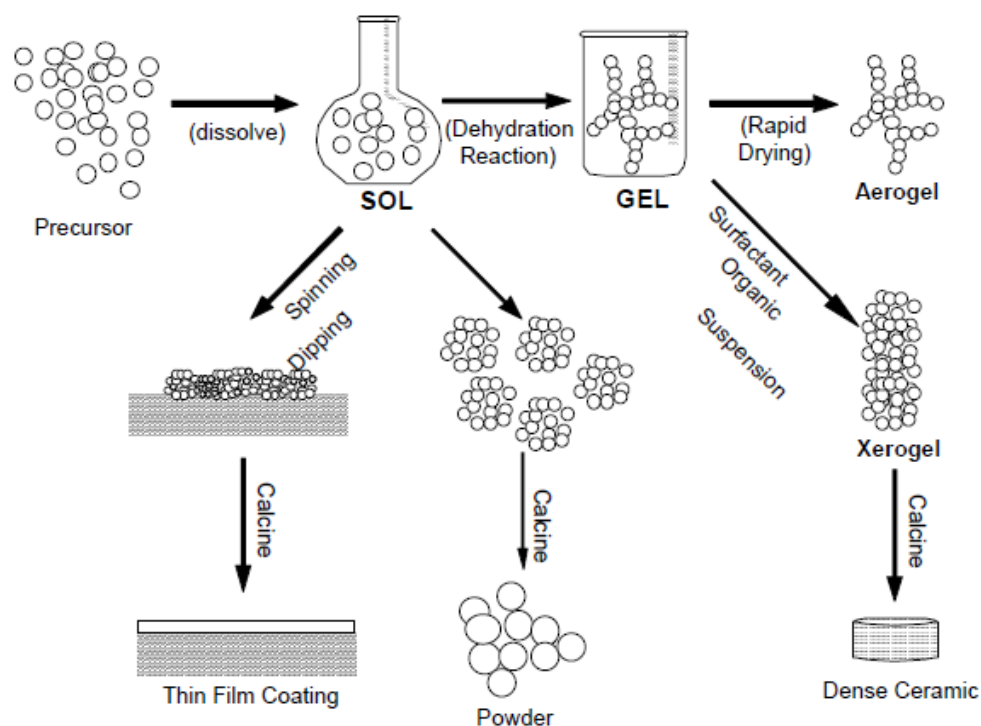


Fig.2.Schematic representation of sol-gel process of synthesis of nanomaterials.

- ✚ Formation of different stable solutions of the alkoxide or solvated metal precursor.
- ✚ Gelation resulting from the formation of an oxide- or alcohol- bridged network (the gel) by a polycondensation reaction that results in a dramatic increase in the viscosity of the solution.
- ✚ Aging of the gel (Syneresis), during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores.
- ✚ Ostwald ripening (also referred to as coarsening, is the phenomenon by which smaller particles are consumed by larger particles during the growth process) and phase transformations may occur concurrently with syneresis. The aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels that have been cast.
- ✚ Drying of the gel, when water and other volatile liquids are removed from the gel network. This process is complicated due to fundamental changes in the structure of the gel. The drying process has itself been broken into four distinct steps:
  - (i) the constant rate period,
  - (ii) the critical point,
  - (iii) the falling rate period,
  - (iv) the second falling rate period.

If isolated by thermal evaporation, the resulting monolith is termed a *xerogel*.

If the solvent (such as water) is extracted under supercritical or near super critical conditions, the product is an *aerogel*.

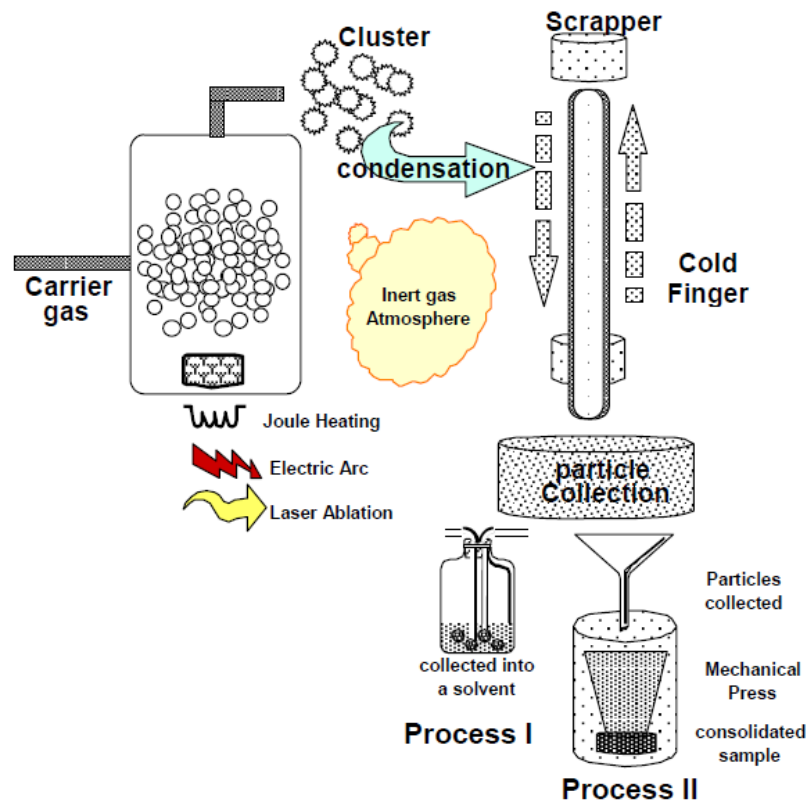
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- ✚ Dehydration, during which surface- bound M-OH groups are removed, there by stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperatures up to 8000C.
- ✚ Densification and decomposition of the gels at high temperatures ( $T > 8000\text{C}$ ). The pores of the gel network are collapsed, and remaining organic species are volatilized. The typical steps that are involved in sol-gel processing are shown in the schematic diagram below.
- ✚ The interest in this synthesis method arises due to the possibility of synthesizing nonmetallic inorganic materials like glasses, glass ceramics or ceramic materials at very low temperatures compared to the high temperature process required by melting glass or firing ceramics.
- ✚ The major difficulties to overcome in developing a successful bottom-up approach is controlling the growth of the particles and then stopping the newly formed particles from agglomerating. Other technical issues are ensuring the reactions are complete so that no unwanted reactant is left on the product and completely removing any growth aids that may have been used in the process. Also production rates of nano powders are very low by this process. The main advantage is one can get monosized nano particles by any bottom up approach.

## 2.2.2. Gas Condensation Processing (GPC)

- In this technique, a metallic or inorganic material, e.g. a suboxide, is vaporized using thermal evaporation sources such as crucibles, electron beam evaporation devices or sputtering sources in an atmosphere of 1-50 mbar He (or another inert gas like Ar, Ne, Kr). Cluster form in the vicinity of the source by homogenous nucleation in the gas phase and grow by coalescence and incorporation of atoms from the gas phase.
- The cluster or particle size depends critically on the residence time of the particles in the growth system and can be influenced by the gas pressure, the kind of inert gas, i.e. He, Ar or Kr, and on the evaporation rate/vapor pressure of the evaporating material. With increasing gas pressure, vapor pressure and mass of the inert gas used the average particle size of the nanoparticles increases.
- Lognormal size distributions have been found experimentally and have been explained theoretically by the growth mechanisms of the particles. Even in more complex processes such as the low pressure combustion flame synthesis where a number of chemical reactions are involved the size distributions are determined to be lognormal.

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*Fig.3. Schematic representation of typical set-up for gas condensation synthesis of nanomaterials followed by consolidation in a mechanical press or collection in an appropriate solvent media.*

- Originally, a rotating cylindrical device cooled with liquid nitrogen was employed for the particle collection: the nanoparticles in the size range from 2-50 nm are extracted from the gas flow by thermophoretic forces and deposited loosely on the surface of the collection device as a powder of low density and no agglomeration.
- Subsequently, the nanoparticles are removed from the surface of the cylinder by means of a scraper in the form of a metallic plate. In addition to this cold finger device several techniques known from aerosol science have now been implemented for the use in gas condensation systems such as corona discharge, etc.
- These methods allow for the continuous operation of the collection device and are better suited for larger scale synthesis of nano powders. However, these methods can only be used in a system designed for gas flow, i.e. a dynamic vacuum is generated by means of both continuous pumping and gas inlet via mass flow controller.
- A major advantage over convectional gas flow is the improved control of the particle sizes. It has been found that the particle size distributions in gas flow systems, which are also lognormal, are shifted towards smaller average values with an appreciable reduction



of the standard deviation of the distribution. Depending on the flow rate of the He-gas, particle sizes are reduced by 80% and standard deviations by 18%.

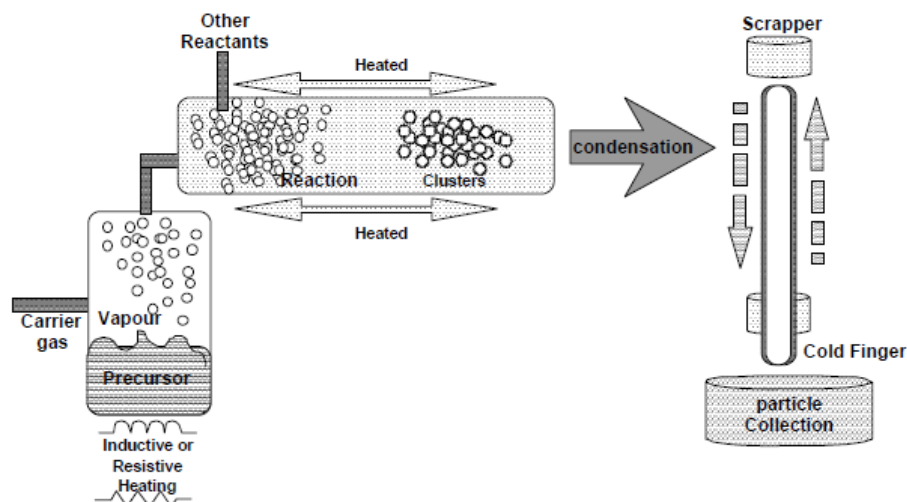
- The synthesis of nanocrystalline pure metals is relatively straightforward as long as evaporation can be done from refractory metal crucibles (W, Ta or Mo). If metals with high melting points or metals which react with the crucibles, are to be prepared, sputtering, i.e. for W and Zr, or laser or electron beam evaporation has to be used. Synthesis of alloys or intermetallic compounds by thermal evaporation can only be done in the exceptional cases that the vapor pressures of the elements are similar. As an alternative, sputtering from an alloy or mixed target can be employed.

## 2.2.3. Chemical Vapor Condensation (CVC)

As shown schematically in Figure, the evaporative source used in GPC is replaced by a hot wall reactor in the Chemical Vapor Condensation or the CVC process. Depending on the processing parameters nucleation of nanoparticles is observed during chemical vapour deposition (CVC) of thin films and poses a major problem in obtaining good film qualities.

- The original idea of the novel CVC process which is schematically shown below where, it was intended to adjust the parameter field during the synthesis in order to suppress film formation and enhance homogeneous nucleation of particles in the gas flow. It is readily found that the residence time of the precursor in the reactor determines if films or particles are formed. In a certain range of residence time both particle and film formation can be obtained.
- Adjusting the residence time of the precursor molecules by changing the gas flow rate, the pressure difference between the precursor delivery system and the main chamber occurs. Then the temperature of the hot wall reactor results in the fertile production of nanosized particles of metals and ceramics instead of thin films as in CVD processing. In the simplest form a metal organic precursor is introduced into the hot zone of the reactor using mass flow controller.
- Besides the increased quantities in this continuous process compared to GPC has been demonstrated that a wider range of ceramics including nitrides and carbides can be synthesized. Additionally, more complex oxides such as BaTiO<sub>3</sub> or composite structures can be formed as well. Appropriate precursor compounds can be readily found in the CVD literature.
- The extension to production of nanoparticles requires the determination of a modified parameter field in order to promote particle formation instead of film formation.
- In addition to the formation of single phase nanoparticles by CVC of a single precursor the reactor allows the synthesis of mixtures of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of the reactor, and coated nanoparticles, i.e., n-ZrO<sub>2</sub> coated with n-Al<sub>2</sub>O<sub>3</sub> or vice versa, by supplying a second precursor at a second stage of the reactor. In this case nanoparticles which have been formed by homogeneous nucleation are coated by heterogeneous nucleation in a second stage of the reactor.





*Fig.4.A schematic of a typical CVC reactor*

- Because CVC processing is continuous, the production capabilities are much larger than in GPC processing. Quantities in excess of 20 g/hr have been readily produced with a small scale laboratory reactor. A further expansion can be envisaged by simply enlarging the diameter of the hot wall reactor and the mass flow through the reactor.

## 2.2.4.Sputtered Plasma Processing:

In this method is yet again a variation of the gas-condensation method excepting the fact that the source material is a sputtering target and this target is sputtered using rare gases and the constituents are allowed to agglomerate to produce nanomaterial. Both dc (direct current) and rf (radio-frequency) sputtering has been used to synthesize nanoparticles. Again reactive sputtering or multi target sputtering has been used to make alloys and/or oxides, carbides, nitrides of materials. This method is specifically suitable for the preparation of ultrapure and non-agglomerated nanoparticles of metal.

## 2.2.5.Microwave Plasma Processing

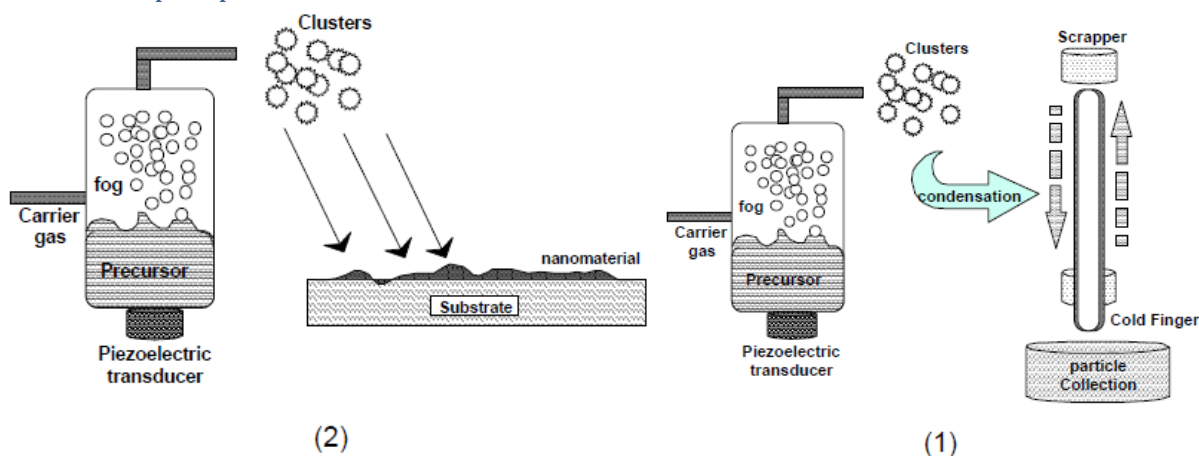
This technique is similar to the previously discussed CVC method but employs plasma instead of high temperature for decomposition of the metal organic precursors. The method uses microwave plasma in a 50 mm diameter reaction vessel made of quartz placed in a cavity connected to a microwave generator. A precursor such as a chloride compound is introduced into the front end of the reactor. The major advantage of the plasma assisted pyrolysis in contrast to the thermal activation is the low temperature reaction which reduces the tendency for agglomeration of the primary particles. This is also true in the case of plasma-CVD processes.

Additionally, it has been shown that by introducing another precursor into a second reaction zone of the tubular reactor, e.g. by splitting the microwave guide tubes, the primary particles can be coated with a second phase. While the formation of the primary particles occurs by homogeneous nucleation, it can be easily estimated using gas reaction kinetics that the

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coating on the primary particles grows heterogeneously and that homogeneous nucleation of nanoparticles originating from the second compound has a very low probability. A schematic representation of the particle growth in plasma's is given below:

## 2.2.6. Particle precipitation aided CVD:



*Fig.5. Schematic representation of (1) nanoparticle, and (2) particulate film formation*

In another variation of this process, colloidal clusters of materials are used to prepare nanoparticles. The CVD reaction conditions are so set that particles form by condensation in the gas phase and collect onto a substrate, which is kept under a different condition that allows heterogeneous nucleation. By this method both nanoparticles and particulate films can be prepared. An example of this method has been used to form nanomaterials eg.  $\text{SnO}_2$ , by a method called pyrosol deposition process, where clusters of tin hydroxide are transformed into small aerosol droplets, following which they are reacted onto a heated glass substrate.

## 3. Properties of Nanomaterials

Nanomaterials have the structural features in between of those of atoms and the bulk materials. While most micro structured materials have similar properties to the corresponding bulk materials, the properties of materials with nanometer dimensions are significantly different from those of atoms and bulks materials. This is mainly due to the nanometer size of the materials which render them:

- (i) large fraction of surface atoms;
- (ii) high surface energy;
- (iii) spatial confinement;
- (iv) reduced imperfections, which do not exist in the corresponding bulk materials.

Due to their small dimensions, nanomaterials have extremely large surface area to volume ratio, which makes a large to be the surface or interfacial atoms, resulting in more “surface” dependent material properties. Especially when the sizes of nanomaterials are comparable to

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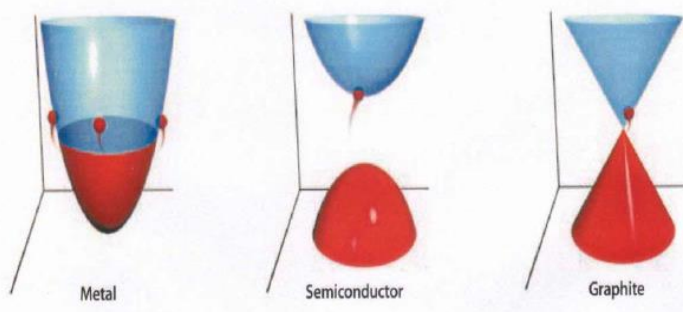
length, the entire material will be affected by the surface properties of nanomaterials. This in turn may enhance or modify the properties of the bulk materials.

## 3.1. Optical properties

- 1) One of the most fascinating and useful aspects of nanomaterials is their optical properties. Applications based on optical properties of nanomaterials include optical detector, laser, sensor, imaging, phosphor, display, solar cell, photo catalysis, photo electrochemistry and biomedicine.
- 2) The optical properties of nanomaterials depend on parameters such as feature size, shape, surface characteristics, and other variables including doping and interaction with the surrounding environment or other nanostructures. Likewise, shape can have dramatic influence on optical properties of metal nanostructures.

## 3.2. Electrical properties

- 1) Electrical Properties of Nanoparticles” discuss about fundamentals of electrical conductivity in nanotubes and nanorods, carbon nanotubes, photoconductivity of nanorods, electrical conductivity of Nano composites.
- 2) One interesting method which can be used to demonstrate the steps in conductance is the mechanical thinning of a nanowire and measurement of the electrical current at a constant applied voltage. The important point here is that, with decreasing diameter of the wire, the number of electron wave modes contributing to the electrical conductivity is becoming increasingly smaller by well-defined quantized steps.
- 3) In electrically conducting carbon nanotubes, only one electron wave mode is observed which transport the electrical current. As the lengths and orientations of the carbon nanotubes are different, they touch the surface of the mercury at different times, which provides two sets of information:
  - (i) the influence of carbon nanotube length on the resistance; and
  - (ii) the resistances of the different nanotubes.



*Fig.6. Electrical behavior of nanotubes*

## 3.3. Mechanical properties

“Mechanical Properties of Nanoparticles” deals with bulk metallic and ceramic materials, influence of porosity, influence of grain size, super plasticity, filled polymer composites, particle-filled polymers, polymer-based Nano composites filled with platelets, carbon nanotube-based composites.

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These materials are polymers which contain nanoparticles or nanotubes to improve their mechanical behaviors, and severely plastic-deformed metals, which exhibit astonishing properties. However, because of their larger grain size, the latter are generally not accepted as nanomaterials. Experimental studies on the mechanical properties of bulk nanomaterials are generally impaired by major experimental problems in producing specimens with exactly defined grain sizes and porosities. Therefore, model calculations and molecular dynamic studies are of major importance for an understanding of the mechanical properties of these materials.

Filling polymers with nanoparticles or nanorods and nanotubes, respectively, leads to significant improvements in their mechanical properties. Such improvements depend heavily on the type of the filler and the way in which the filling is conducted. The latter point is of special importance, as any specific advantages of a Nano particulate filler may be lost if the filler forms aggregates, thereby mimicking the large particles.

- 1) Particulate filled polymer-based Nano composites exhibit a broad range of failure strengths and strains. This depends on the shape of the filler, particles or platelets, and on the degree of agglomeration.
- 2) In this class of material, polymers filled with silicate platelets exhibit the best mechanical properties and are of the greatest economic relevance. The larger the particles of the filler or agglomerates, the poorer are the properties obtained.
- 3) Although, potentially, the best composites are those filled with Nano fibers or nanotubes, experience teaches that sometimes such composites have the least ductility. On the other hand, by using carbon nanotubes it is possible to produce composite fibers with extremely high strength and strain at rupture.
- 4) Among the most exciting Nano composites are the polymer ceramic Nano composites, where the ceramic phase is platelet-shaped. This type of composite is preferred in nature, and is found in the structure of bones, where it consists of crystallized mineral platelets of a few nanometers thickness that are bound together with collagen as the matrix. Composites consisting of a polymer matrix and defoliated phyllosilicates exhibit excellent mechanical and thermal properties.

## 3.4.Magnetic properties

Bulk gold and Pt are non-magnetic, but at the nano size they are magnetic. Surface atoms are not only different to bulk atoms, but they can also be modified by interaction with other chemical species, that is, by capping the nanoparticles

One can obtain magnetic nanoparticles of Pd, Pt and the surprising case of Au (that is diamagnetic in bulk) from non-magnetic bulk materials. In the case of Pt and Pd, the ferromagnetism arises from the structural changes associated with size effects.

However, gold nanoparticles become ferromagnetic when they are capped with appropriate molecules, the charge localized at the particle surface gives rise to ferromagnetic-like behavior.

- 1) Surface and the core of Au nanoparticles with 2 nm in diameter show ferromagnetic and paramagnetic character, respectively. The large spin-orbit coupling of these noble metals can yield to a large anisotropy and therefore exhibit high ordering temperatures.

- 2) More surprisingly, permanent magnetism was observed up to room temperature for thiol-capped Au nanoparticles. For nanoparticles with sizes below 2 nm the localized carriers are in the 5d band.
- 3) Bulk Au has an extremely low density of states and becomes diamagnetic, as is also the case for bare Au nanoparticles. This observation suggested that modification of the band structure by chemical bonding can induce ferromagnetic like character in metallic clusters.

## 4. Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is a powerful and frequently used instrument, in both academia and industry for imaging the surfaces of almost any material with a resolution down to about 1 nm. Most scanning electron microscope has magnification ranges from X20 to X100000. SEM images have a characteristic three-dimensional appearance and are useful for adjudging the surface structure of the sample.

**Principle:** In the scanning electron microscope (SEM) electrons are made to fall on the sample and the scattered or generated electrons are detected. The SEM is usually operated with an acceleration voltage of 1K V to 40 K V for the electrons. The incoming electrons interact with the sample on a depth of  $\sim 1\mu\text{m}$ . This electron beam generates a number of different types of signals, which are emitted from the area of the specimen where the electron beam is impinging. The induced signals are detected and the intensity of one of the signals (at a time) is amplified and used to as the intensity of a pixel on the image on the computer screen. The electron beam then moves to next position on the sample and the detected intensity gives the intensity in the second pixel and so on. This produces an image with depth-of-field which is usually 300-600 times better than that of an optical microscope, and also enables a three-dimensional image to be obtained.

**Construction:** A schematic of typical SEM is shown in the above figure. Electrons thermionically emitted from a tungsten filament (cathode) are drawn to an anode and focused by two successive magnetic lenses into a beam with a very fine spot size that is typically  $10\text{\AA}$  in diameter. Pairs of scanning coils located at the objective (magnetic) lens deflect the beam either linearly or in raster fashion over a rectangular area of the specimen surface. Upon impinging on the specimen, the primary electrons decelerate and several processes such as elastic scattering *viz.*, forward scattering and backscattering of the incoming electrons and inelastic scattering *viz.*, generation of secondary electrons, Auger electrons, bremsstrahlung, characteristic x-rays, electron-hole pairs (in insulators and semiconductors), long-wavelength electromagnetic radiation. A number of different types of signals, which are emitted from the area of the specimen where the electron beam is impinging, is as shown in fig.



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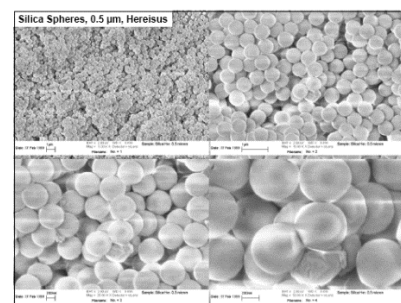
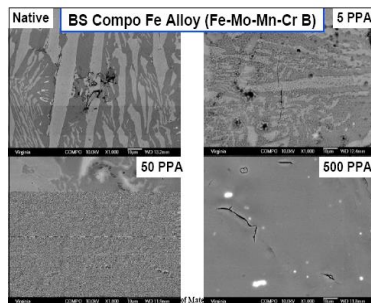
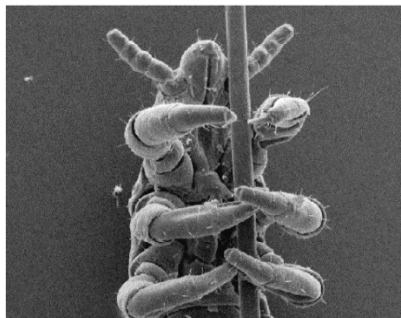
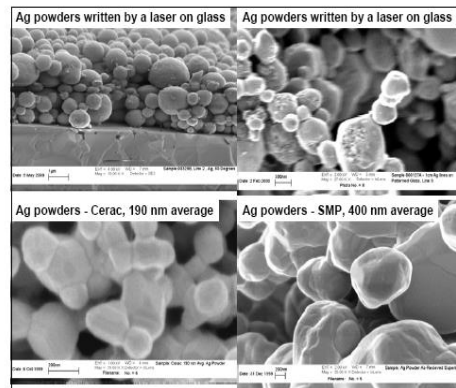
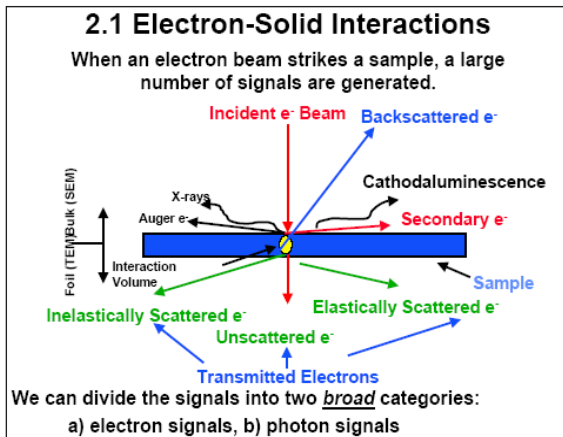
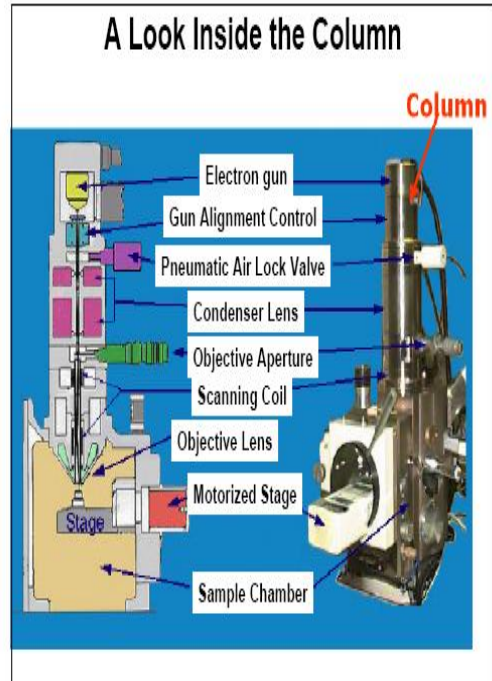
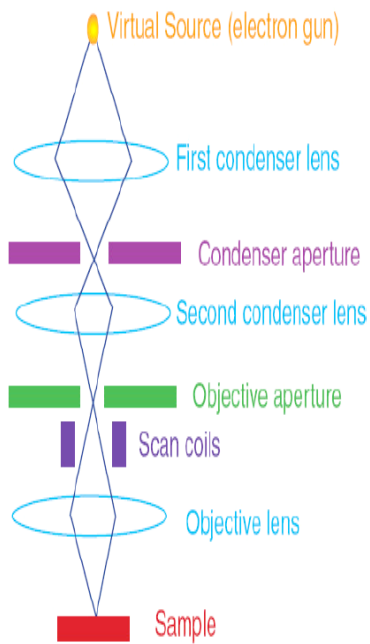


Fig.7.scanning electron microscope and images

Various **SEM** techniques are differentiated on the basis of what is subsequently detected and imaged, and the principle images produced in the **SEM** are of three types:

- Secondary electron images,
- Backscattered electron images and
- Elemental X-ray maps.

The secondary electrons are the electrons which are generated from the surface of the specimen when it is bombarded by high energy primary electrons. These electrons are collected by detector which creates a pattern of light and dark areas in CRT corresponding to the emission of secondary electrons from the specimen. As the number of electrons produced at any given point can be related directly to the topography of the specimen with respect to the detector, the patterns created on the viewing screen represent the surface topography of the specimen.

Backscattered electrons are the high energy electrons that are elastically scattered and essentially possess the same energy as the incident or primary electrons. The probability of backscattering increases with the atomic number of the sample material. Therefore the primary electrons arriving at a given detector position can be used to yield images containing information on both topology and atomic composition.

An additional electron interaction in the SEM is that the primary electron collides with and ejects a core electron from an atom in the sample. The excited atom will decay to its ground state by emitting either a characteristic X-ray photon or an Auger electron. By analyzing energies of characteristic of the x-ray photon the atoms can be identified. Further the concentration of atoms in the specimen can be determined by counting the number of X-rays emitted.

## 5. TEM : Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is a technique where an electron beam interacts and passes through a specimen. The electrons are emitted by a source and are focused and magnified by a system of magnetic lenses. The geometry of TEM is shown in figure . The electron beam is confined by the two condenser lenses which also control the brightness of the beam, passes the condenser aperture and “hits” the sample surface. The electrons that are elastically scattered consist the transmitted beams, which pass through the objective lens. The objective lens forms the image display and the following apertures, the objective and selected area aperture are used to choose of the elastically scattered electrons that will form the image of the microscope. Finally, the beam goes to the magnifying system that is consisted of three lenses, the first and second intermediate lenses which control the magnification of the image and the projector lens. The formed image is shown either on a fluorescent screen or in monitor or both and is printed on a photographic film.



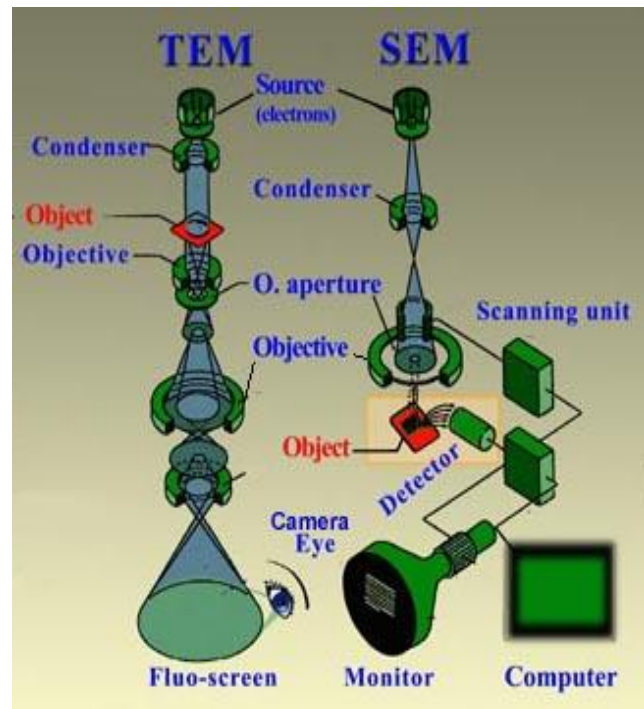
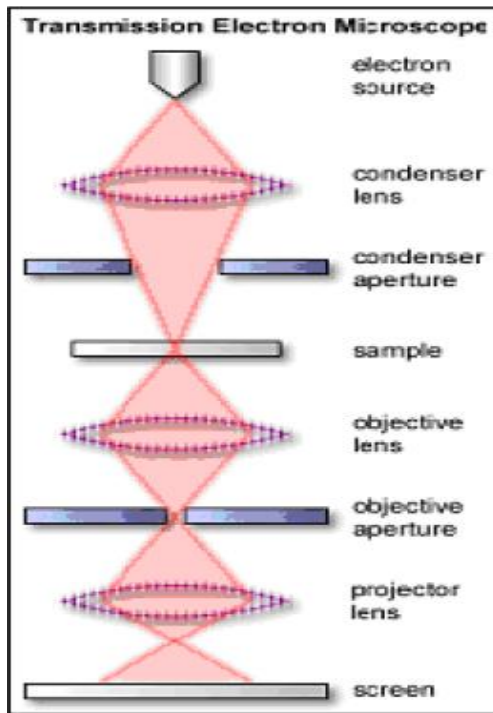


Fig.8. Transmission electron microscope with all of its components

## Operation

The operation of TEM requires an ultrahigh vacuum and a high voltage. The first step is to find the electron beam, so the lights of the room must be turned off. Through a sequence of buttons and adjustments of focus and brightness of the beam, we can adjust the settings of the microscope so that by shifting the sample holder find the thin area of the sample. Then tilting of the sample begins by rotating the holder. This is a way to observe as much areas as we can, so we can obtain as much information. Different types of images are obtained in TEM, using the apertures properly and the different types of electrons. As a result, diffraction patterns are shown due to the scattered electrons. If the unscattered beam is selected, we obtain the Bright Field Image. Dark Field Images are attained if diffracted beams are selected by the objective aperture. In transmission microscopy, we can actually see the specimen's structure and its atomic columns, thus compositional and crystallographic information is attained. However, is a very expensive technique, expertise is needed and the sample preparation phase is too difficult so that very thin samples are achieved.

## Main difficulties in the exploitation of TEM

Transmission Microscopy provides several types of images, as reported above. The diffraction patterns show dots, regions or circles originating from the sample area illuminated by the electron beam that depend on the material's structure. Monocrystals show distinguished dots in diffraction patterns, polycrystalline materials common centered circles and amorphous materials diffused circles. Distortions and defects are visible in bright and dark field images, but expertise is needed

in order to interpret whether they are defects or artifacts. Electron or ion beam damages must be considered in TEM analysis, because of the sensibility of the sample and its really low thickness.

Additionally, there's always the problem of calibration and alignment of the instrument. Both of them require experience and skills so the resulting images and data that emerge are reliable and free of objective astigmatism. These works have to be done in order to keep the instrument in excellent working condition.

## 6. Atomic Force Microscope

The Atomic Force Microscope (AFM) is being used to solve processing and materials problems in a wide range of technologies affecting the electronics, telecommunications, biological, chemical, automotive, aerospace, and energy industries. The materials being investigated include thin and thick film coatings, ceramics, composites, glasses, synthetic and biological membranes, metals, polymers, and semiconductors. The AFM is being applied to studies of phenomena such as abrasion, adhesion, cleaning, corrosion, etching, friction, lubrication, plating, and polishing. By using AFM one can not only image the surface in atomic resolution but also measure the force at nano-newton scale.

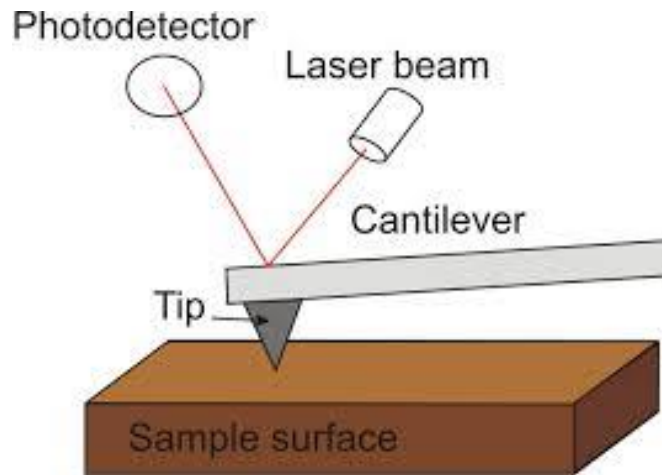
The force between the tip and the sample surface is very small, usually less than  $10^{-9}$  N. How to monitor such small forces is another story. The detection system does not measure force directly. It senses the deflection of the micro cantilever. This is a sensitive system where a change in spacing of 1 Å between tip and cantilever changes the tunneling current by an order of magnitude. It is straightforward to measure deflections smaller than 0.01 Å. Subsequent systems were based on the optical techniques. In this system an optical beam is reflected from the mirrored surface on the back side of the cantilever onto a position-sensitive photo detector. In this arrangement a small deflection of the cantilever will tilt the reflected beam and change the position of beam on the photo detector.

### Operation

The principles on how the AFM works are very simple. An atomically sharp tip is scanned over a surface with feedback mechanisms that enable the piezo-electric scanners to maintain the tip at a constant force (to obtain height information), or height (to obtain force information) above the sample surface. Tips are typically made from  $\text{Si}_3\text{N}_4$  or Si, and extended down from the end of a cantilever. The Nano scope AFM head employs an optical detection system in which the tip is attached to the underside of a reflective cantilever. A diode laser is focused onto the back of a reflective cantilever. As the tip scans the surface of the sample, moving up and down with the contour of the surface, the laser beam is deflected off the attached cantilever into a dual element photodiode. The photo detector measures the difference in light intensities between the upper and lower photo detectors, and then converts to voltage. Feedback from the photodiode difference signal, through software control from the computer, enables the tip to maintain either a constant force or constant height above the sample. In the constant force mode the piezo-electric transducer monitors real time height deviation. In the constant height mode the deflection force on the sample

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is recorded. The latter mode of operation requires calibration parameters of the scanning tip to be inserted in the sensitivity of the AFM head during force calibration of the microscope.



Some AFM's can accept full 200 mm wafers. The primary purpose of these instruments is to quantitatively measure surface roughness with a nominal 5 nm lateral and 0.01nm vertical resolution on all types of samples. Depending on the AFM design, scanners are used to translate either the sample under the cantilever or the cantilever over the sample. By scanning in either way, the local height of the sample is measured. Three dimensional topographical maps of the surface are then constructed by plotting the local sample height versus horizontal probe tip position.

## 7. X-Ray Diffraction

Waves of wavelength comparable to the crystal lattice spacing are strongly scattered (diffracted). Analysis of the diffraction pattern allows to obtain information such as lattice parameter, crystal structure, sample orientation, and particle size. We will only mention that lattice parameters are obtained from the Bragg formula:

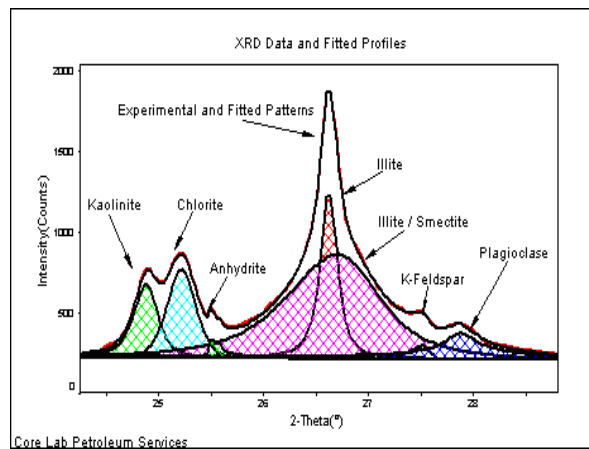
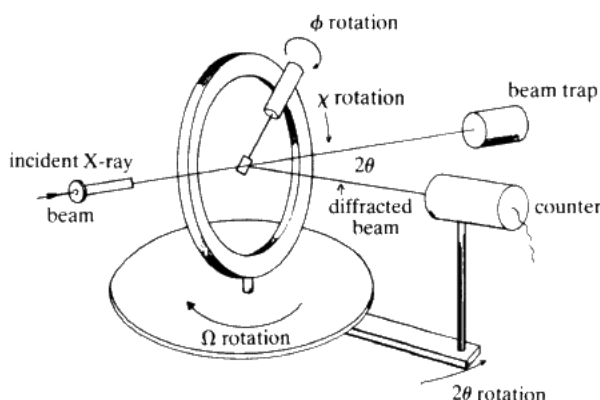


Fig.9. XRD based analysis of crystal

$$2d \sin\theta = n\lambda$$



where  $d$  is the lattice spacing

$\theta$  is the angle b/w reflected ray & normal

$\lambda$  is the wavelength of light

In a typical set-up, a collimated beam of X-rays is incident on the sample. The intensity of the diffracted X-rays is measured as a function of the diffraction angle  $2\theta$ . The intensities of the spots provide information about the atomic basis. The sharpness and shape of the spots are related to the perfection of the crystal. The two basic procedures involve either a single crystal or a powder. With single crystals, a lot of info about the structure can be obtained. On the other hand, single crystals might not be readily available and orientation of the crystal is not straightforward.

- X-ray diffraction (XRD) is a powerful method for the study of nanomaterials. The wavelength of X-rays is on the atomic scale, so X-ray diffraction (XRD) is a primary tool for probing structure of nano-materials. XRD offers unparalleled accuracy in the measurement of atomic spacing and is the technique of choice for determining strain states in thin films. The intensities measured with XRD can provide quantitative, accurate information on the atomic arrangements at interfaces. With lab-based equipment, surface sensitivities down to a thickness of  $\sim 5\text{nm}$  are achievable, but synchrotron radiation allows the characterization of much thinner films and for many materials, monoatomic layers can be analyzed.
- XRD is non-contact and non-destructive. Nanomaterials have a characteristic microstructure length comparable with the critical length scales of physical phenomena, giving them unique mechanical, optical and electronic properties. X-ray diffractograms of nanomaterials provide a wealth of information - from phase composition to crystallite size, from lattice strain to crystallographic orientation. The main use of powder diffraction is to identify components in a sample by a search/match procedure. Furthermore, the areas under the peak are related to the amount of each phase present in the sample
- A typical powder XRD instrumentation consist of four main components such as X-ray source, specimen stage, receiving optics and X-ray detector. The source and detector with its associated optics lie on the circumference of focusing circle and the sample stage at the center of the circle. Bragg's law is the basis of XRD analysis. With this law it is possible to make accurate quantifications of experimental results in the determination of

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crystal structures. The angle between the plane of the specimen and the X-ray source is  $\theta$ , known as Bragg's angle and the angle between the projection of X-ray and the detector is  $2\theta$ . For the XRD analysis, fine powder samples were mounted on the sample holder and the powder was assumed to consist of randomly oriented crystallites.

- When a beam of X-ray is incident on the sample, X-rays are scattered by each atom in the intensity maximum at that particular angle. The atomic planes from where the X-rays are scattered are referred to as 'reflecting planes'.

ADVANTAGES	LIMITATIONS
<ul style="list-style-type: none"><li>• Powerful and rapid (&lt; 20 min) technique for identification of an unknown mineral.</li><li>• In most cases, it provides an unambiguous mineral determination.</li><li>• Minimal sample preparation is required.</li><li>• XRD units are widely available</li><li>• Data interpretation is relatively straight forward</li><li>• It is a non- destructive method of testing</li></ul>	<ul style="list-style-type: none"><li>• Homogeneous and single phase material is best for identification of an unknown</li><li>• Must have access to a standard reference file of inorganic compounds</li><li>• Requires tenths of a gram of material which must be ground into a powder</li><li>• For mixed materials, detection limit is ~ 2% of sample</li><li>• For unit cell determinations, indexing of patterns for non-isometric crystal systems is complicated</li><li>• Peak overlay may occur and worsens for high angle 'reflections'</li></ul>

## \*Applications

- Identification of unknown crystalline materials (e.g. minerals, inorganic compounds).
- Identification of fine-grained minerals such as clays and mixed layer clays that are difficult to determine optically
- determination of unit cell dimensions
- measurement of sample purity
- make textural measurements, such as the orientation of grains, in a polycrystalline sample
- determine crystal structures

## 8. Particle size analysis

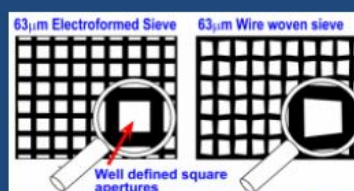
In a pharmaceutical application the particle size of the medicine is to be analyzed as it determines the flow ability, handling and processability on target. Different types of methods are employed in order to analyze the particle in various respects. One of the major methods used is sieving method, in which the sieves are stacked together to perform the sieving operation.



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## Sieving

- **Weight distribution**
- Sieve analysis is performed using a **nest** or **stack** of sieves where each lower sieve has a smaller aperture size than that of the sieve above it.
- Sieves can be referred to either by their **aperture size** = **mesh size** = **sieve number** (BP, PhEur)
- US: The mesh size is the number of wires per linear inch.
  - 250  $\mu\text{m}$  = No. 60
  - 125  $\mu\text{m}$  = No. 120
- Approx. size range : 5 $\mu\text{m}$  - ~3mm
  - Standard woven wire sieves
  - Electroformed micromesh sieves at the lower end or range (< 20 $\mu\text{m}$ )
  - Punch plate sieves at the upper range



Many other methods like electron microscopy, photon correlation spectroscopy and pipette method are used to determine various parameters of the particle like number of particles, diameter of particles and volume of particles etc.

## Different types of analysis give different types of distributions !

Particle size (microns)	Actual number of particles (n)	Percentage by number	Volume of particles ( $V=4/3\pi r^3$ )	Total volume of particles of each size (nV)	Percentage by volume
2	2000	50.92	4	8000	0.06
4	1000	25.46	34	34000	0.3
8	500	12.73	268	134000	1.0
16	250	6.36	2145	5326250	4.1
32	125	3.18	17157	2144625	15.6
64	50	1.27	137259	6862950	52.7
128	3	0.08	1098069	3294207	25.3
	$\Sigma n=3928$			$\Sigma nV=13014032$	

Based on the analysis the particles of the powder are arranged as follows.

Classification of Powder	$d_{50}$ Sieve Opening ( $\mu\text{m}$ )
Very Coarse	> 1000
Coarse	355–1000
Moderately Fine	180–355
Fine	125–180
Very Fine	90–125