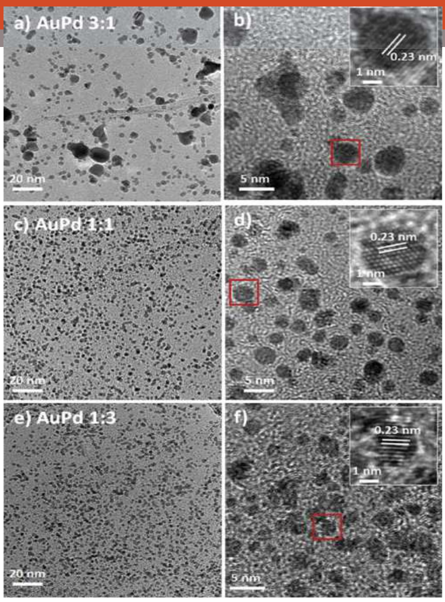
NANOMATERIALS



Dr.SANAA TAREQ SARHAN

Lecture (1)

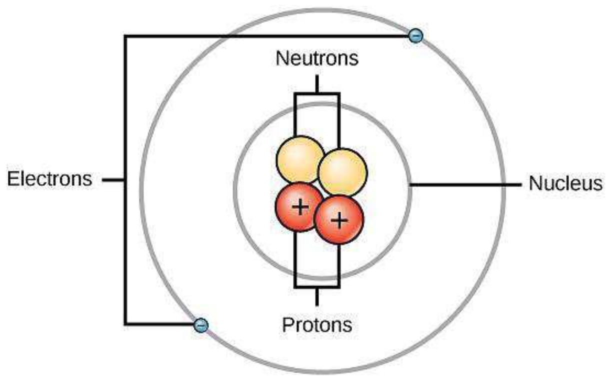
Overview of Atomic Structure

An atom is the smallest unit of matter that retains all of the chemical properties of an element. Atoms combine to form molecules, which then interact to form solids, gases, or liquids. For example, water is composed of hydrogen and oxygen atoms that have combined to form water molecules.

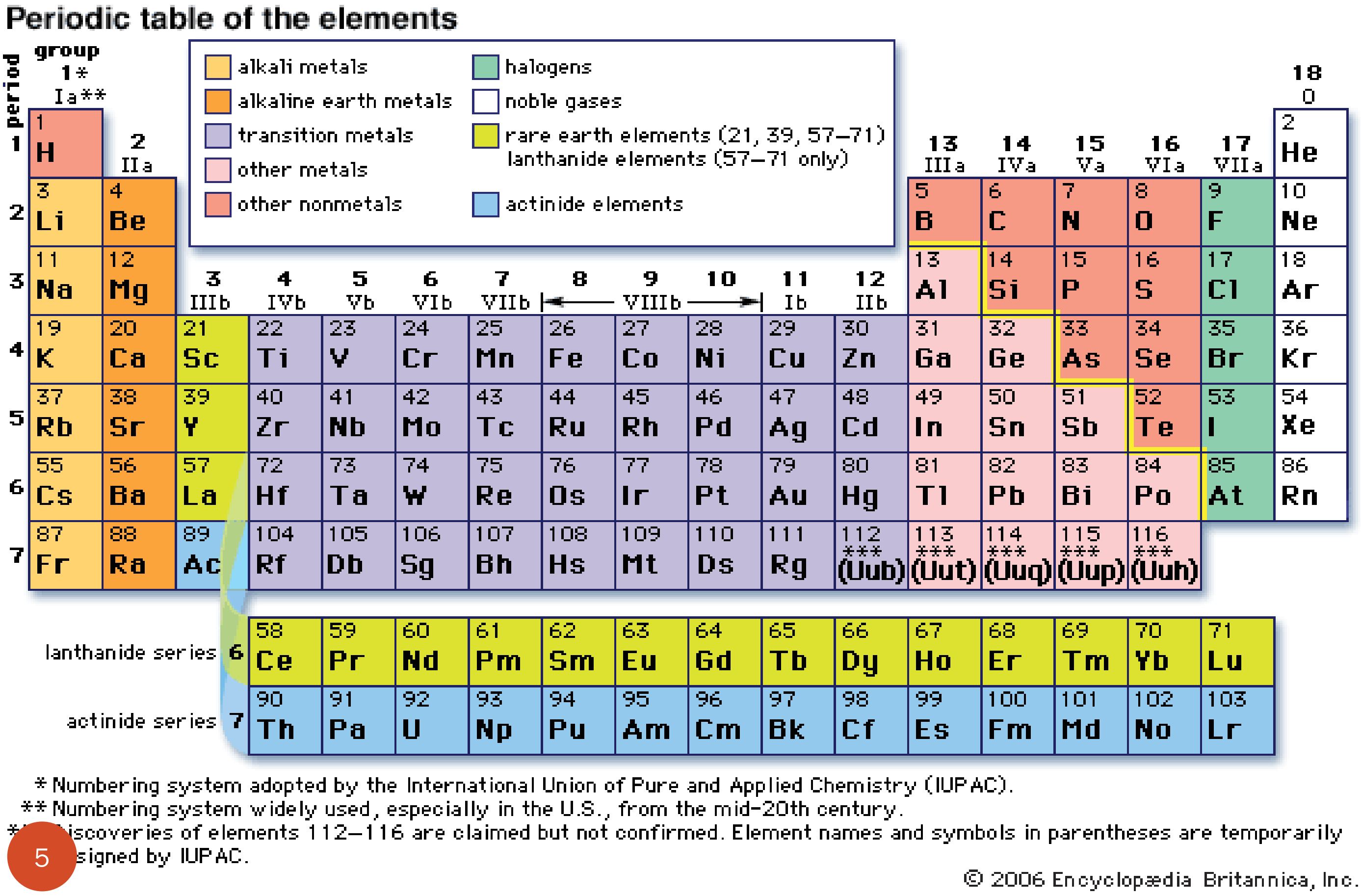
Atomic Particles

- Atoms are made up of protons, neutrons, and electrons. These classical subatomic particles consist of fundamental or elementary particles of matter. Since they are also particles of matter, they have size and mass.
- The protons and neutrons are collectively known as nucleons.
- The electron is a subatomic particle, symbol e− or β− , tiny ,very light particles. Electrons surround the nucleus, have a relatively small mass but occupy a large volume of space outside the nucleus.
- Neutrons are uncharged particles found within the nucleus.

- The proton and electron are exactly the same size but different charge.
- Atoms are extremely small ad diameter of the single atom can vary from 0.1- 0.5 nanometers. One carbon atom is approximately 0.15 nm in diameter.
- Atomic size is decrease following the increase of group number, and increase following the increase of period number.

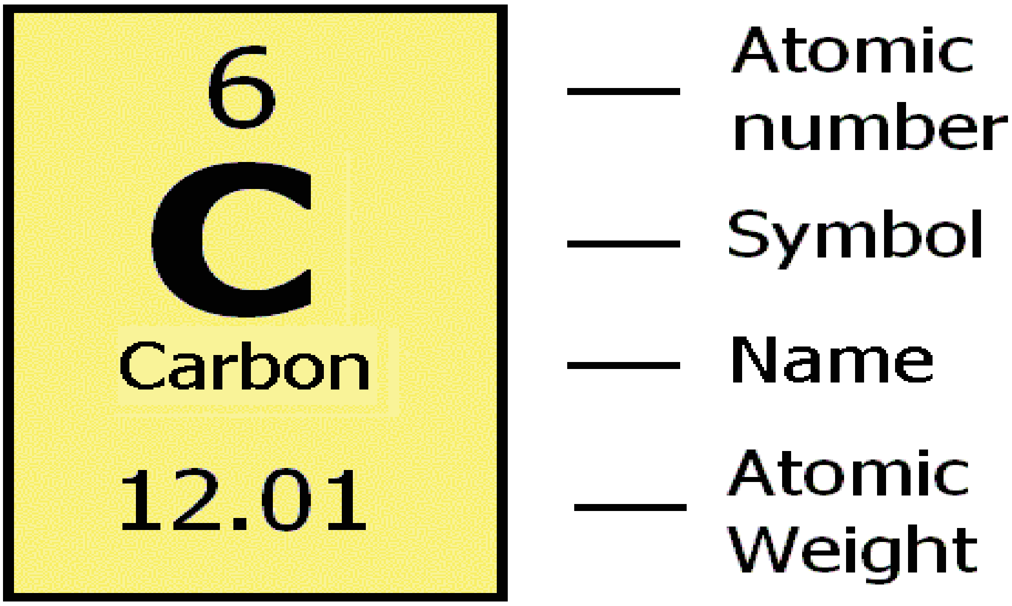


Periodic Table of Elements



- The periodic table, also known as the periodic table of elements, is a tabular display of the chemical elements, which are arranged by atomic number, electron configuration, and recurring chemical properties. The horizontal rows of the table called periods, generally have metals on the left and non-metals on the right.
- The vertical columns, called groups, contain elements with similar chemical behaviors.

How do you read the PERIODIC TABLE?



The periodic table of elements arranges all of the known chemical elements in an informative array. Elements are arranged from left to right and top to bottom in order of increasing atomic number. Order generally coincides with increasing atomic mass.

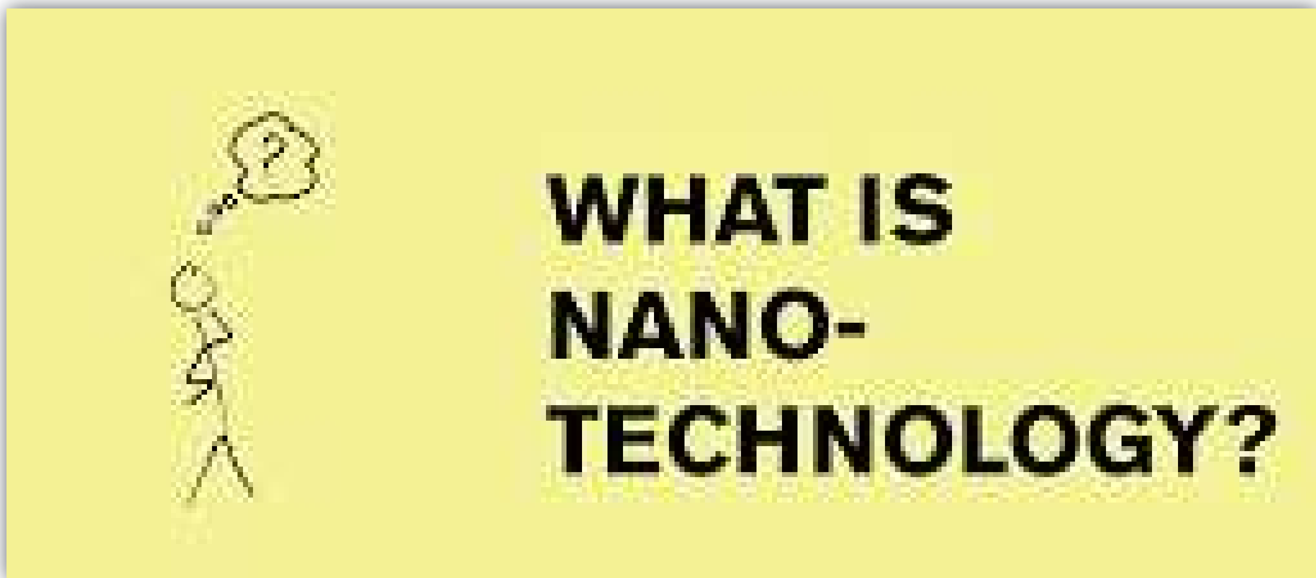
The rows are called periods. The period number of an element signifies the highest energy level an electron in that element occupies. The number of electrons in a period increases as one moves down the periodic table; therefore, as the energy level of the atom increases, the number of energy sub-levels per energy level increases.

Elements that occupy the same column on the periodic table (called a "group") have identical valance electron configurations and consequently behave in a similar fashion chemically. For instance, all the group 18 elements are inert gases.

NANOTECHNOLOGY

Outline

- What Is Nanotechnology?
- Focuses on classification
- Methods of preparation, characterization, application, advantages of nanoparticles and health perspectives.



- **Nano** : derived from the Greek language means dwarf(small man)
- In standard international units (SIU) is prefix denotes a fraction of 10-9 a given unit like nanometer, nano gram, nano litter … etc.
- **Nanotechnology:** is a combination of physical and chemical science ideas with
- Biological Sciences.
- **Nanotechnology:** a technology capable of achieving high degrees of accuracy in functions and sizes the shapes of materials and their components.

- In nano Technology a subatomic particle called electron play a very important role.
- Another word, nano chemistry is mainly about studying the impact of electron on material properties at micro level.

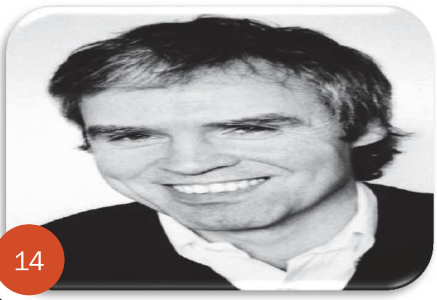
What Are Nano Materials ?

- Nano material are material possessing grain sizes one the order a billionth of the mater (10M).
- Nano materials research literally exploded in mid – 1980 s

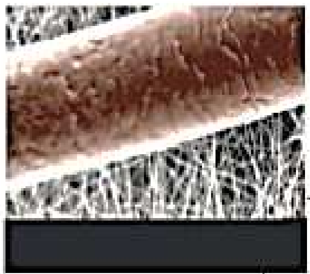
❖ *Preface*

"Nanotechnology has given us the tools to play with the ultimate toy box of nature - atoms and molecules. Everything is made from them and the possibilities to create new things appears limitless"

Horst Stormer (Nobel Prize Winner in Physics-1998).

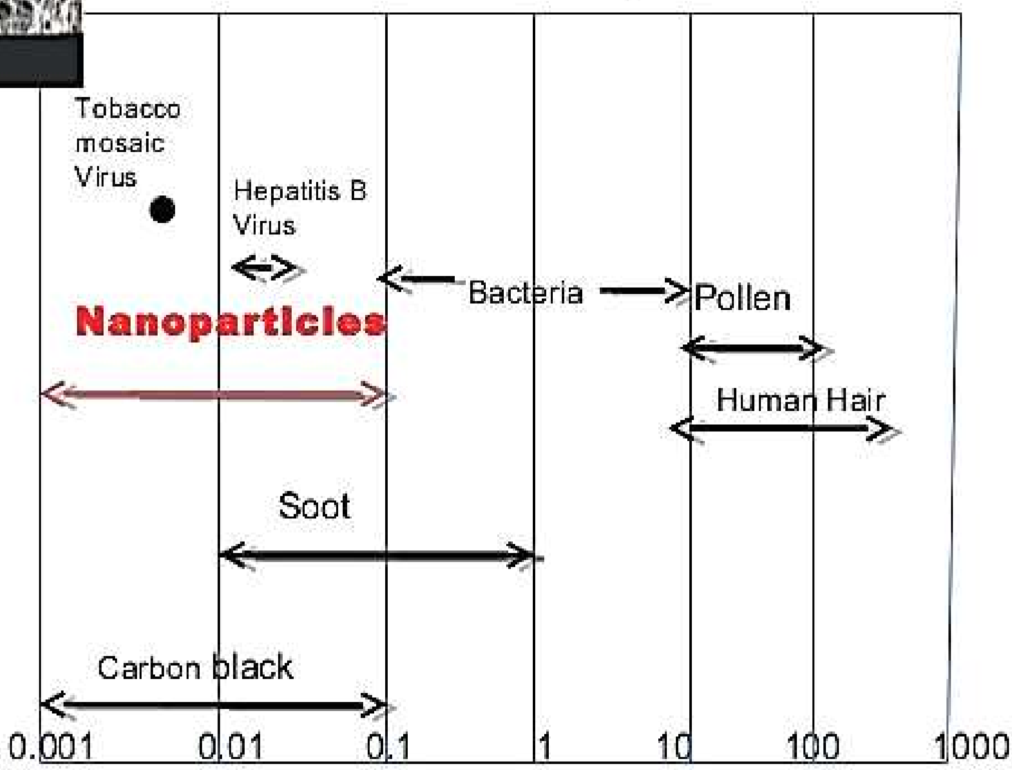


Some compounds, when manufactured in nanometer sizes, acquire unique properties They are not available when they are in significant size, although they are identical chemical composition in both cases, the nano metric material is infinitely small it a quires extraordinary electrical, optical and magnetic properties as a result for the new order taken by the atoms.



Typical size of small particles

Particle size µm



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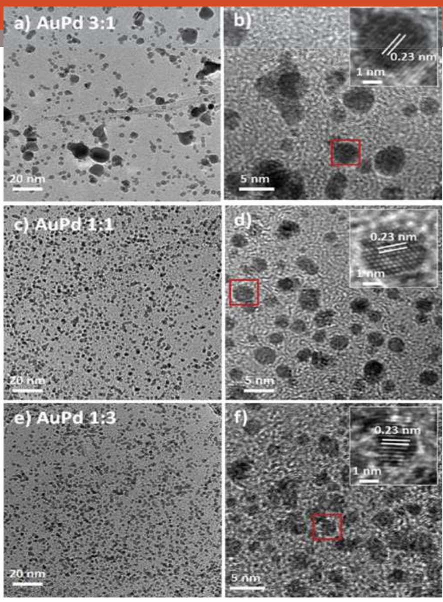

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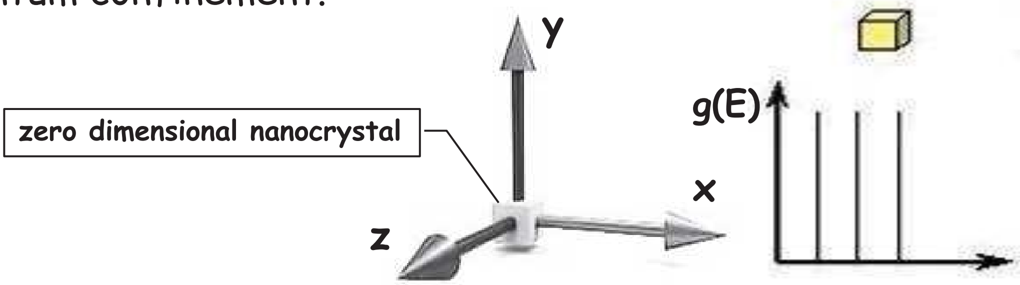
Lecture (2)

Nanomaterial's Classification

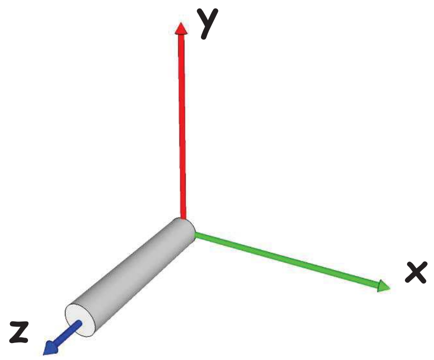
1. According to the dimensions.

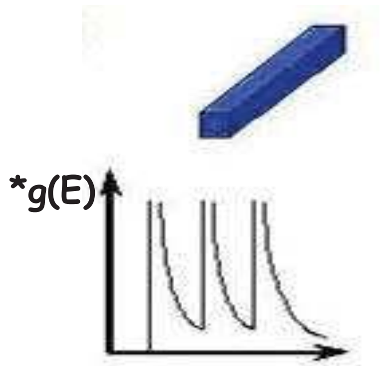
Any crystalline particle must take three dimensions (x, y, and z), this method of classifying the nanoparticles depends on how many none nano dimensions (micro or macro scale) of the x, y, z are existed.

- **The (0D) zero dimensions nanomaterial:** are those have all three dimensions are at nanoscale or there is no micro dimension like quantum dots (ZnO, PbS) nanogold, in another way those nanocrystals exhibit three quantum confinement because this effect appers with nanoscale only, so (0D) nanocrystals have three quantum confinement.



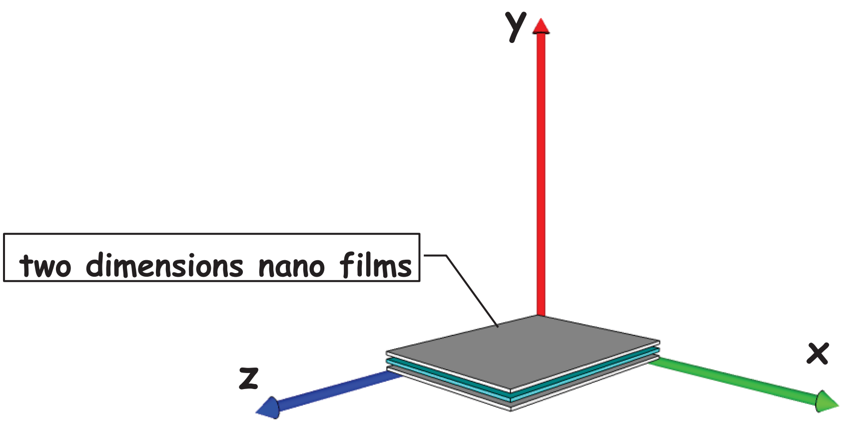
- **The (1D) one dimensions nanomaterial:** are those have only on dimension at micro scale like length, and other remain dimensions such as carbon nanotubsw, Ni wires, Fe nanorods, … etc, are at nanoscale but these nanomaterials exhibit two quantum confinement (**is change of electronic and optical properties when the material sampled is of sufficiently small size - typically 10 nanometers or less**

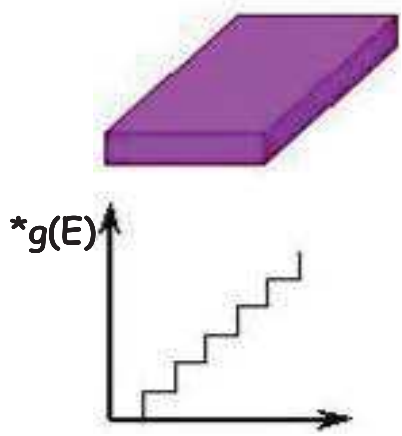




*Quantum dot density of state g(E)

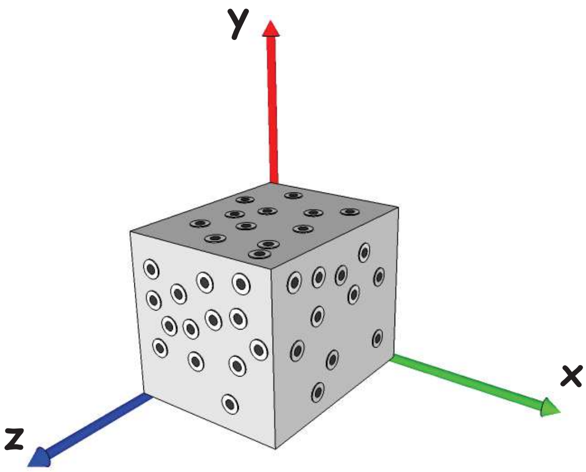
- **The (2D) two dimensions nanomaterial:** (have two micro dimensions) like nano films (Ag, Au, …etc.) while there is only one direction for the quantum confinement.

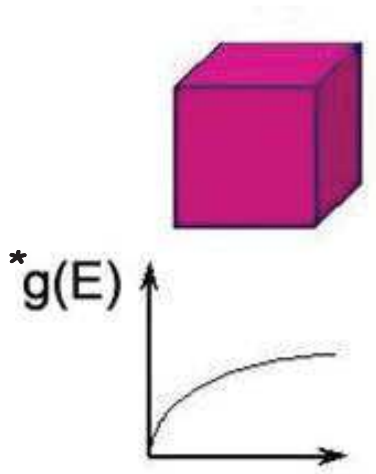




*Quantum dot density of state g(E)

- **The (3D) three dimensions nanomaterial:** all dimensions are micro-size like composite and clusters (polymers with nanoparticles), (polystyrene with nano MgO).

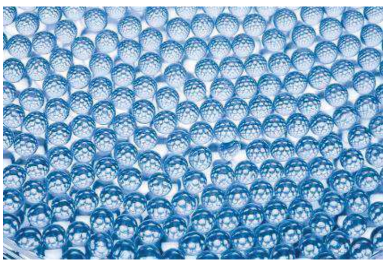




**Quantum dot density of state g(E)*

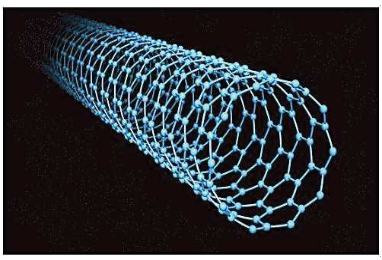
2. According to the shape.

- **Nano particales or nano spheres:** like quantum dots(ZnO,PdS),nano gold Electronics - Gold



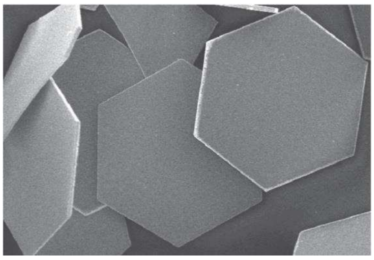
Silicon Nano particales

- **Nanotubes or nano wires or nano rods:** like carbon nanotubes W, Ni wires.



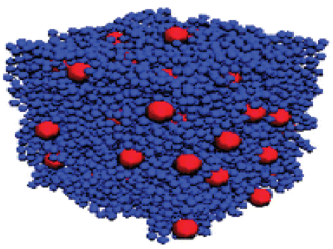
Carbon nano tube

- **Nano scale thin films or ultra-thin films:** like nano films (Ag, Au,…)



Nano scale thin films

- **Nano composites:** a material comprised of many nano scale inclusions such as nano particles

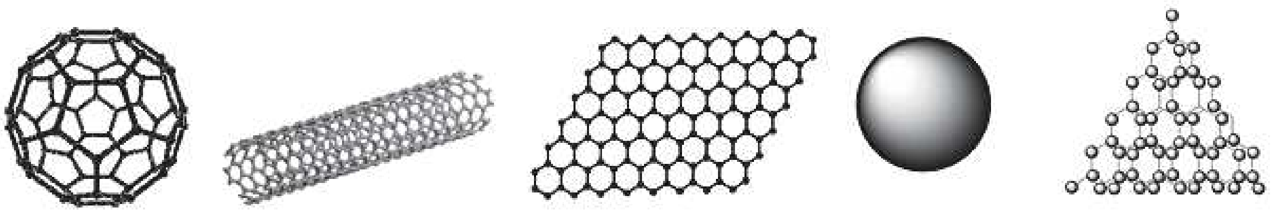


Polymer Nano composites

3. According to the composition

Another way can be noticed in some literature for the nomenclature the nanomaterial according to their element composition.

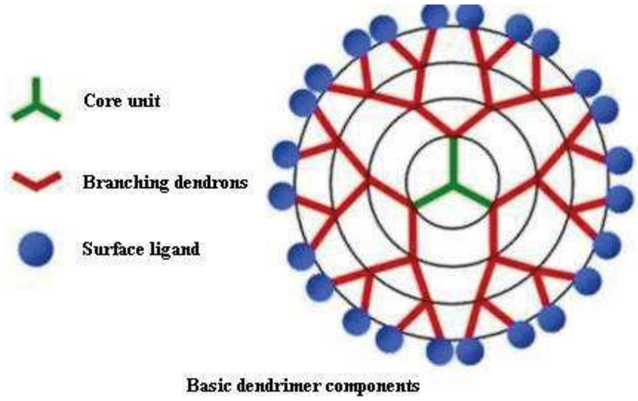
- **Carbon Based Nanomaterial:** (hollow spheres, ellipsoids, or tubes. spherical and ellipsoidal, carbon nano tubes/Fullerence).

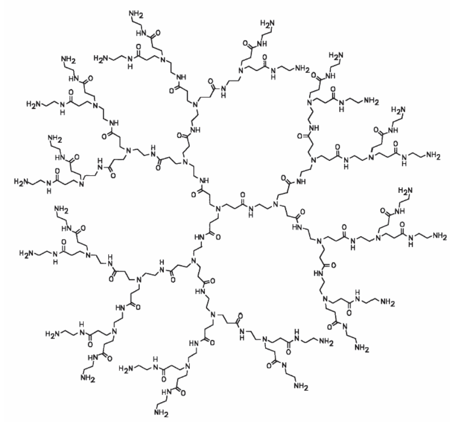


Fullerene | Carbon nanotubes (CNTs) | Graphene | Carbon dots (Cdots) | Nano-diamonds (NDs)

- **Metal Based Nanomaterials**: These are metal based materials that are commonly regarded as quantum dots, nanogold, nanosilver and oxides with metal bases.

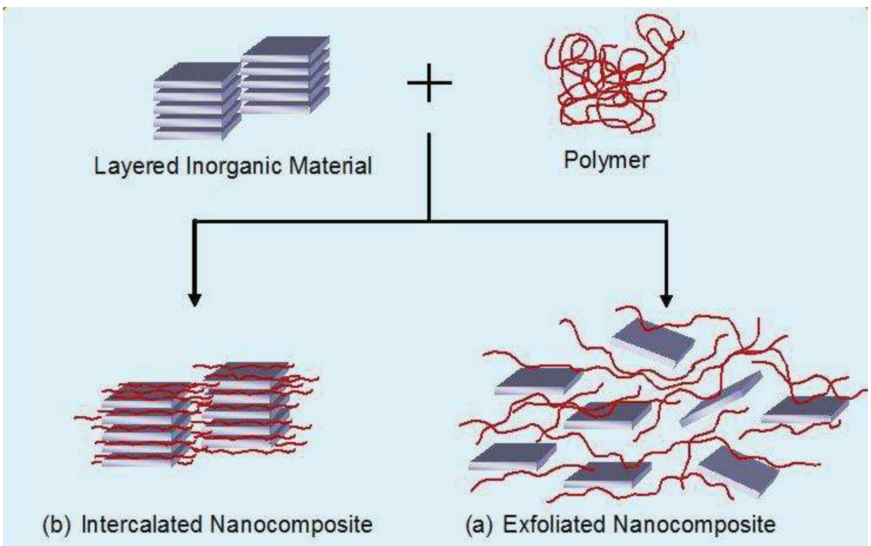
- **Dendrimers:** Branched components that form polymers like polyimidomethyimethaacrlate (PMMA)



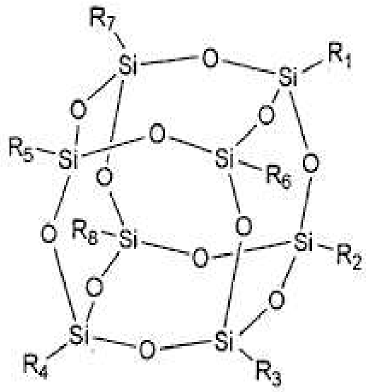


- **A nanocomposite:** is a matrix to which nanoparticles have been added to improve a particular property of the material. The properties of nano composites have caused researchers and companies to consider using this material in several fields.

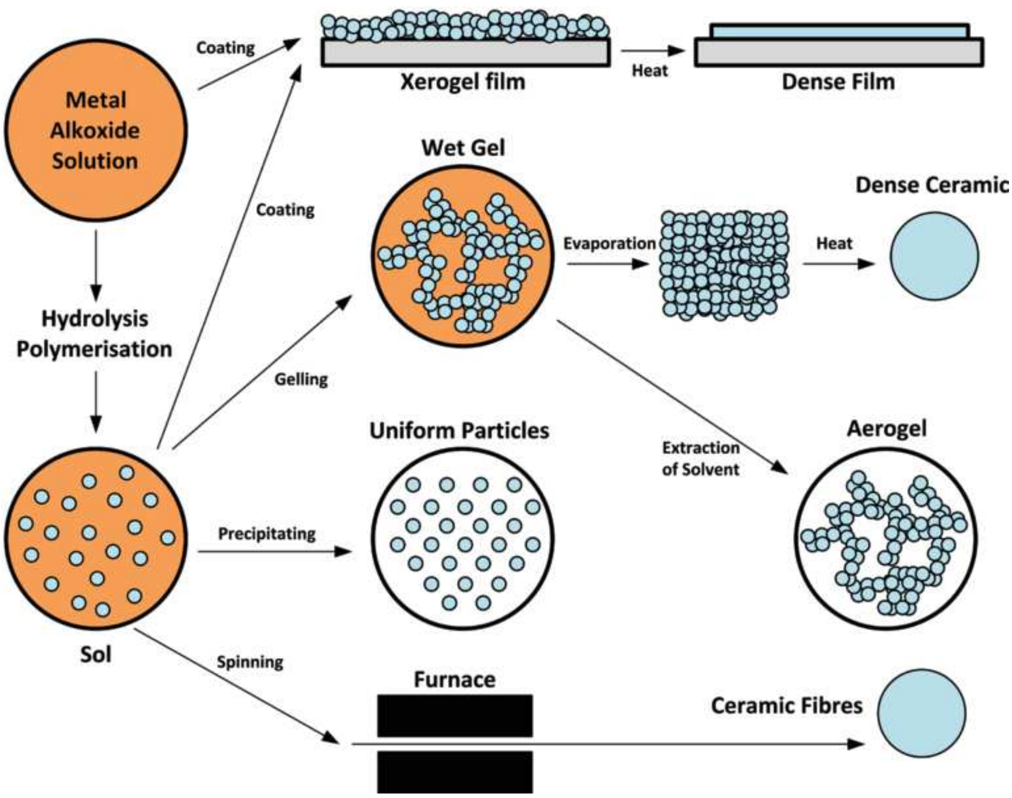
Typically ,nano composition are clay, polymer or carbon, or a combination of these materials with nanoparticle building blocks.



- **Inorganic-organic Hybrid nano particle's** (polyhedral Silsesquioxanes.



- **Nano-intrermediates:** like metal alkoxides (titaniumisoperoxide), metal organic compounds ,as their uses in producing nano materials by sol gel process.



Schematic representation of the different stages and routes of the sol-gel technology

A survey of applications:

The following survey of nanocomposite applications introduces to many of the uses being explored, including:

- Producing batteries with greater power output. Researchers have developed a method to make anodes for lithium ion batteries from a composite formed with silicon nanospheres and carbon nanoparticles. The anodes made of the silicon-carbon nanocomposite make closer contact with the lithium electrolyte, which allows faster charging or discharging of power.
- Producing structural components with a high strength-to-weight ratio. For example an epoxy containing carbon nanotubes can be used to produce nanotube-polymer composite windmill blades. This results in a strong but lightweight blade, which makes longer windmill blades practical. These longer blades increase the amount of electricity generated by each windmill.
- Using graphene to make composites with even higher strength-to-weight ratios. Adding graphene to epoxy composites may result in stronger/stiffer components than epoxy composites using a similar weight of carbon nanotubes. Graphene appears to bond better to the polymers in the epoxy, allowing a more effective coupling of the graphene into the structure of the composite. This property could result in the manufacture of components with higher strength-to-weight ratios for such uses as windmill blades or aircraft components.

Preparation methodologies

There are two major approaches to fabricate the nano materials (preparation , synthesizing)

1. Top-Down approach:

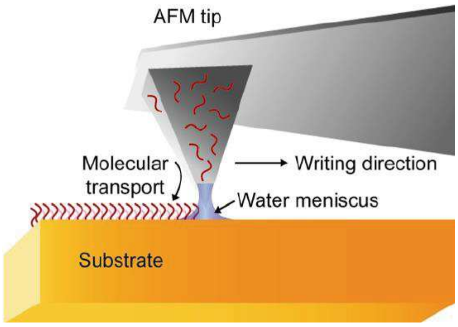
Top-Down approaches refers to slicing or sequential cutting of a bulk material to get nano sized particles.

a. **Grinding/ Milling**

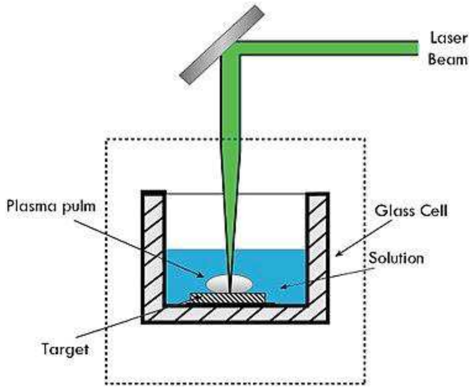
b. **Nanolithography:** is the branch of nanotechnology concerned with the study and application of fabricating nanometer-scale structures, meaning patterns with at least one lateral dimension between 1 and 1,000 nm :

- *Conventional Mask*
- *Scanning E-beam, I-beam*
- *Soft nano printing*
- *Spherical.*

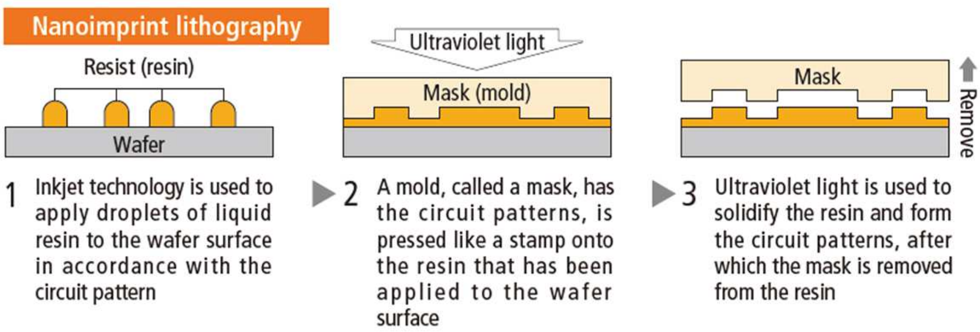
c. **Laser ablation**



Soft Nano-printing



Laser ablation



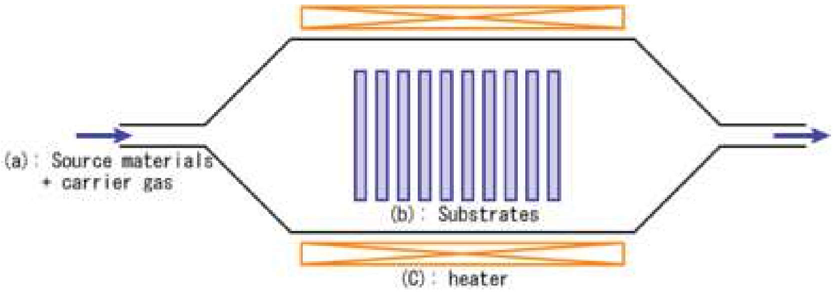
Conventional mask

2. Bottom-up approach:-

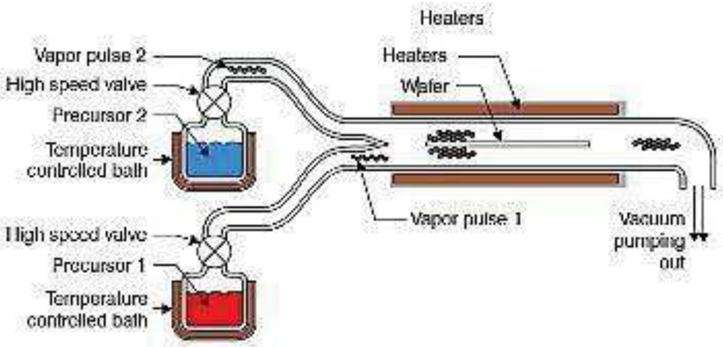
Bottom-up methods start with atoms or molecules to form nanomaterials:

a. Gaseous phase methods

- *Chemical vapour deposition (CVD), and Metal-Organic Chemical Vapour Deposition*
- *Inert-gas Condensation (IGC)*
- *Molecular-beam epitaxy (MBE), and Metal oxide vapour-phase epitaxy (MOVPE)*
- *Atomic layer deposition (ALD)*
- *Flame pyrolysis*
- *Thrombolysis*
- *Ion implantation*



Chemical vapour deposition (CVD)



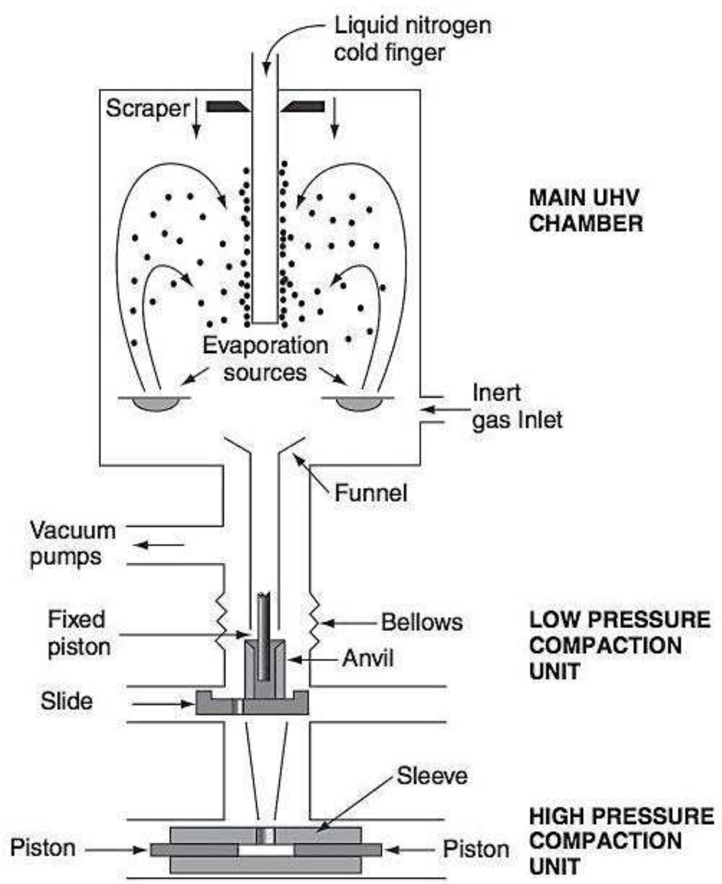
➢ *Inert-gas condensation method*

The inert gas evaporation-condensation (IGC) technique, in which nanoparticles are formed via the evaporation of a metallic source in an inert gas, has been widely used in the synthesis of ultrafine metal particles since the 1930s

This method is old, has been used in the manufacture of carbon black, an ink pigment, since ancient times. The application to the production of truly nano scaled powders is relatively recent. The technique employed now for the formation of nano powders, in reality, dicers from that used to produce carbon and lampblack primarily in the choice of atmospheric composition and pressure and in the use of a chemically reac tive source.

In its basic form, the method consists of evaporating a metallic source, using resistive heating (although radio frequency heating or use of an electron or laser beam as the heating source are all equally effective methods) inside a chamber which has been previously evacuated to about 10^{-7} torr and backfilled with inert gas to a low pressure

The metal vapour migrates from the hot source into the co oler inert
gas by a combination of convective flow and diffusion and the evaporated atoms collide with the gas atoms within the chamber, thus losing kinetic energy.
Ultimately, the particles are collected for subsequent consolidation, usually by deposition on a cold surface.

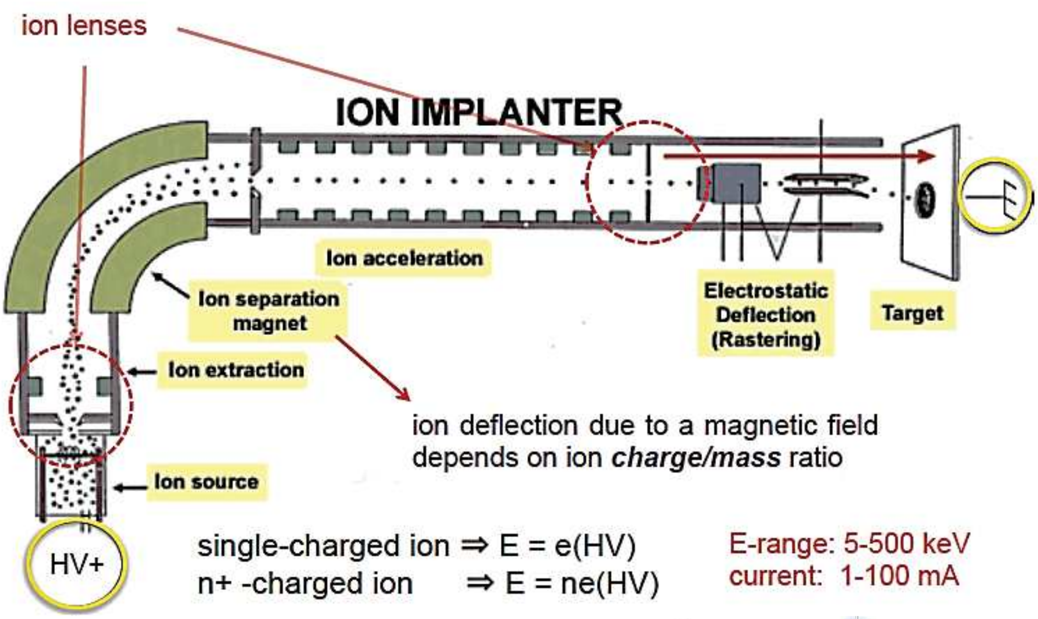


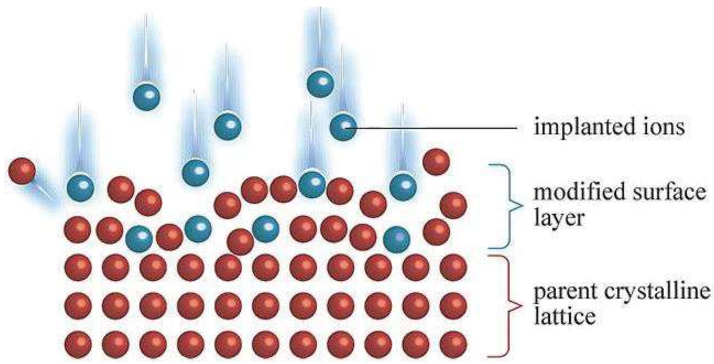
Inert-gas condensation method

➢ Ion implantation:

bombardment of a solid target with an energetic ion beam (typically 1keV - 1MeV) ⇒ ions penetrate through the material, slow down by transferring their energy to the target atoms/electrons and eventually stop at a certain depth (~0-1µm) below the surface.
It is basically a surface or near-surface processing technique. Due to their stronger interactions with target atoms, ions penetrate much less in matter than electrons, for the same energy.

❖ ***Why ion implantation ?***
To modify/improve properties (physical, chemical) of materials in a thin (50nm-1µm) surface layer





➢ *Chemical vapour deposition (CVD)*

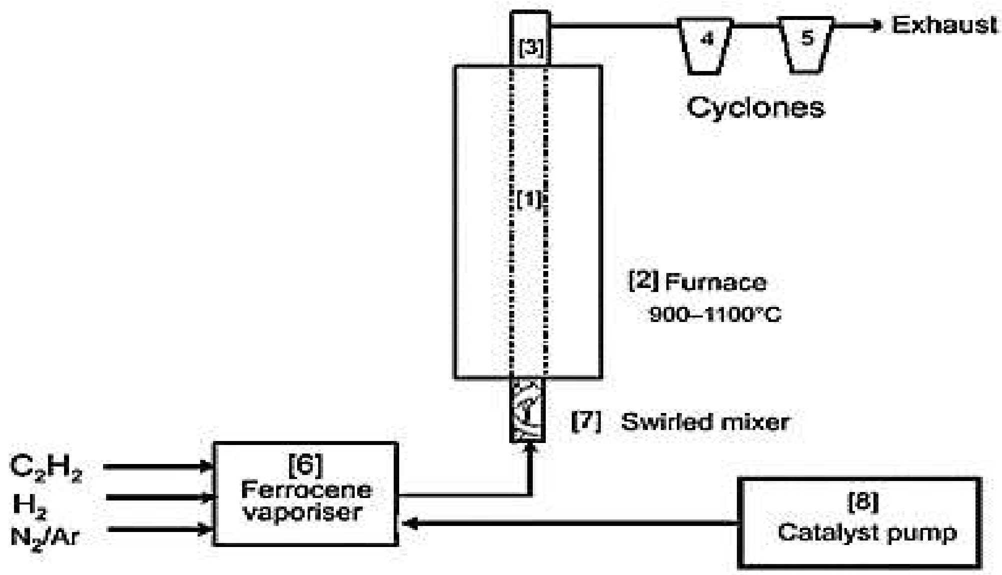
- *can also take place due to a chemical reaction between some reactants on the substrate. In this case reactant gases (precursors) are pumped in to a reaction chamber(reactor). Under the right condition (T,P), they undergo a substrate. The by products are pumped out.*
- *Chemical vapour deposition (CVD) is a deposition method used to produce high quality, high-performance, solid materials, typically under vacuum. The process is often used in the semiconductor industry to produce thin films*

Advantages:

- *High growth rates possible.*
- *Can depots material which hard to evaporate .*
- *Good reproductively.*
- *Can growth epitaxial films.*

Disadvantages:

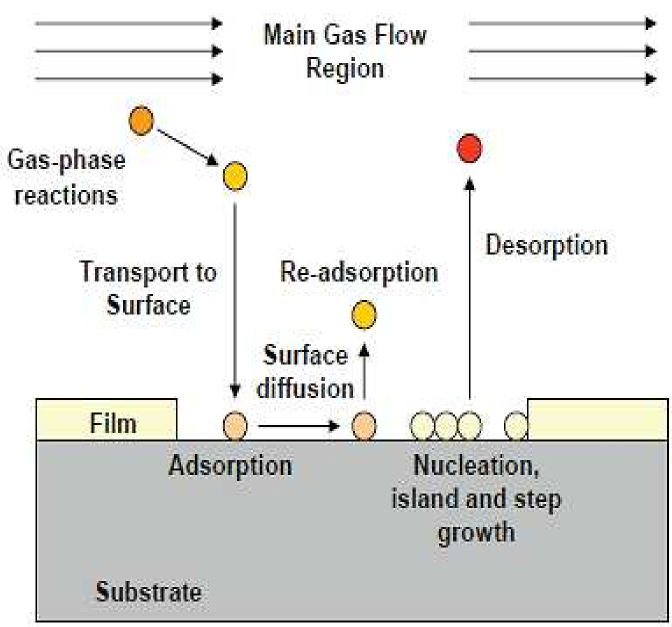
- *High temperatures.*
- *Complex processes.*
- *Toxic and corrosion gases.*



Chemical vapour deposition (CVD)

Fundamental CVD Processes

- *Convective and diffusive transport of reactants to the reaction zone.*
- *Gas phase reactions.*
- *Transport of reactants to the substrate surface.*
- *Chemical and physical adsorption.*
- *Surface reactions leading to film formation.*
- *Desorption of volatile by products.*
- *Convective and diffusive transport of by-products away from the reaction zone.*



CVD Reaction Types – I :-

Pyrolysis

– *Thermal decomposition of gaseous species on hot substrates.*

$$SiH_{4\,(g)} \rightarrow Si_{(s)} + 2H_{2\,(g)}$$ at 650 °C

$$Ni(CO)_{4\,(g)} \rightarrow Ni_{(s)} + 4CO_{(g)}$$ at 180 °C

-Also can deposit, Al, Ti, Pb, Mo, Fe, B, Zr, C, Si, Ge, SiO_2, Al_2O_3, MnO_2, BN, Si_3N_4, GaN, $Si_{1-x}Ge_x$

Reduction

– *Use hydrogen gas to reduce halides, carbonyl halides and oxyhalides*

$$SiCl_{4\,(g)} + 2H_3 \rightarrow Si_{(s)} + 4HCl_{(g)}$$ at 1200 °C

$$WF_{6\,(g)} + 3H_2 \rightarrow W_{(s)} + 6HF_{(g)}$$ at 300 °C

$$MoF_{6\,(g)} + 3H_2 \rightarrow Mo_{(s)} + 6HF_{(g)}$$ at 300 °C

Also can deposit, Al_2O_3, TiO_2, Ta_2O_5, SnO_2, ZnO

CVD Reaction Types – II :-

Oxidation

– *Using oxygen gas to produce oxides.*

$$SiH_{4\,(g)} + O_2 \rightarrow SiO_{2\,(s)} + 2H_{2\,(g)} \quad \text{at } 450\ °C$$

$$2AlCl_{3\,(g)} + 3H_2 + 3CO_2 \rightarrow Al_2O_{3\,(s)} + +3CO + 6HCl_{(g)}$$

Also can deposit TiO2 , Ta2 O5 , SnO2 , ZnO

Compound Formation

– *A variety of carbide, nitride and boride films can be formed.*

$$SiCl_{4\,(g)} + CH_4 \rightarrow SiC_{(s)} + 4HCl_{(g)} \quad \text{at } 1400\ °C$$

$$BF_{3\,(g)} + NH_3 \rightarrow BN_{(s)} + 4HF_{(g)} \quad \text{at } 1100\ °C$$

CVD Reaction Types – III :-

Disproportionation

– *A solid metal can be deposited when there exists two valence states for a metal with different stable temperatures.*
– *Requires mass transfer between hot and cold ends.*

$$2GeI_{2\,(g)} \underset{600\ °C}{\overset{300\ °C}{\Longleftrightarrow}} Ge_{(s)} + GeI_{4\,(g)}$$

Reversible Transfer

– *Depending on the temperature, you can get deposition or etching*

$$As_{4\,(g)} + As_{2\,(g)} + 6GaCl_{(g)} + 3H_2 \underset{850\ °C}{\overset{750\ °C}{\Longleftrightarrow}} 6GaAs_{(s)} + 6HCl_{(g)}$$

2.Bottom-up approach:- Contin ....

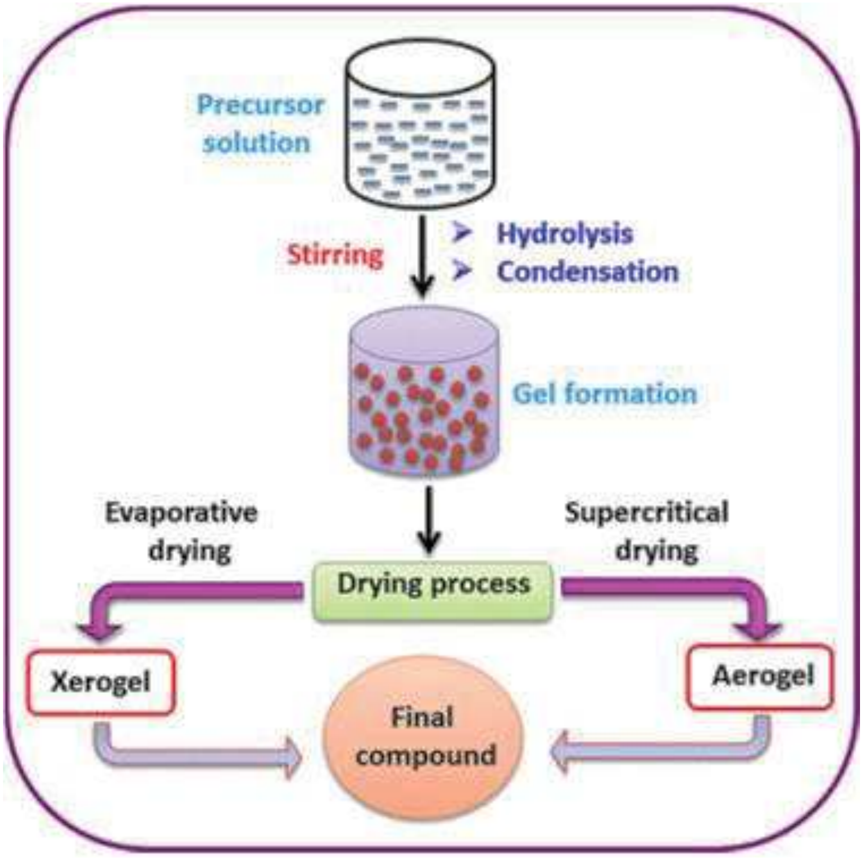
b. Liquid phase methods:

- *Molecular self-assembly (MSA)*
- *Superamolecular chemistry*
- *Chemical bath deposition (CBD)*
- *Sol - gel process*
- *Single crystal growth*
- *Electrodeposition/electroplating*
- *Anodizing*
- *Molten salt Hydrothermal*
- *Polyol*
- *Colloidol*
- *Water-oillmicroemulsions*
- *electrolysis*

➢ Sol - gel process

sol-gel method is one of the well-established synthetic approaches to prepare novel metal oxide nps as well as mixed oxide composites. this method has potential control over the textural and surface properties of the materials. sol-gel method mainly undergoes in few steps to deliver the final metal oxide protocols and those are ***hydrolysis, condensation, and drying process.***

The formation of metal oxide involves different consecutive steps, initially the corresponding metal precursor undergoes rapid hydrolysis to produce the metal hydroxide solution, followed by immediate condensation which leads to the formation of three-dimensional gels. Afterward, obtained gel is subjected to drying process, and the resulting product is readily converted to Xerogel or Aerogel based on the mode of drying.

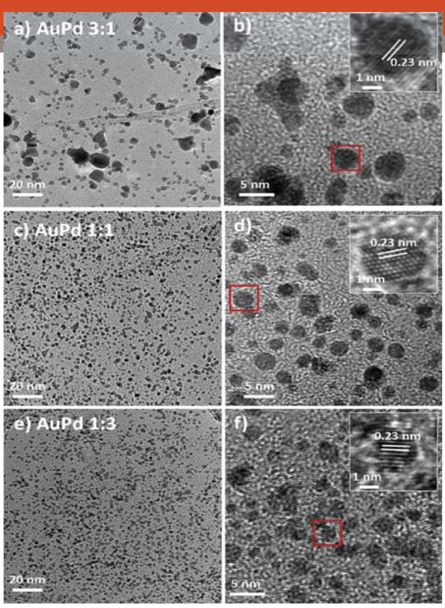


- *If the structure is maintained, an aergel is formed. If the structure collapses ,is formed.*
- *Normal drying of the gel leads to structure collapse due capillary forces drawing the wall of the pores together, and reducing the pore size.*
- *Cracking may occur when the tension in the gel is so large that is can not shrink anymore.*
- *A method was needed where dust was reduced(compared to the ceramic method) and which needed a lower sintering temperature.*
- ***The main benefits of sol-gel processing are the high purity and uniform nanostructure achievable at low temperatures.***
- ***To dissolve the compound in a liquid in order to bring it back as a solid in a controlled manner***

Sol-gel method can be classified into two routes, such as aqueous sol-gel and nanoaqueous sol-gel method depending on the nature of the solvent utilized.

- nanoparticles are designed for use as conductors from printable inks to electronic chips.1 As the world of electronics become smaller, nanoparticles are important components in chip design. Nano scale gold nanoparticles are being used to connect resistors, conductors, and other elements of an electronic chip.

NANOMATERIALS



Dr.SANAA TAREQ SARHAN

Lecture (3)

Characterization Techniques For Nanotechnology

Over the past few decades nano size and nano dimensional materials whose structures exhibit significantly novel and improved physical, chemical and biological properties, phenomena, and functionality due to their nanoscaled size, have drawn much interest. Nanotechnology is an emerging interdisciplinary area that is expected to have wide ranging implications in all fields of science and technology such as material science, mechanics, electronics, optics, medicine, plastics, energy, aerospace, etc. Nanophasic and nanostructured materials are also attracting a great deal of attention of the textile and polymer researchers and industrialists because of their potential applications for achieving specific processes and properties, especially for functional and high performance textiles applications.

characterizing these nano sized materials is also an developing field posing lot of challenges to scientists and technologists. Thus, nanotechnology encouraged the researches activities on the discovery and invention of sophisticated nano characterization techniques to allow a better control of morphology.

Some of these techniques used for analysis and characterization of nanaomaterials include:-

Some of these techniques used for analysis and characterization of nanomaterials include:-

1) Diffraction Analysis techniques :-

a) X-ray Diffraction Analysis (XRD)

b) Electron Diffraction.

c) Small Angle X-ray Scattering (SAXS).

d) Small Angle Neutron Scattering (SANS).

2) Electron Microscopy techniques :-

a) Scanning Electron Microscope (SEM)

b) Transmission Electron Microscope (TEM).

3) Scanning Probe Microscope techniques :-

a) Atomic Force Microscope (AFM)

b) Scanning Tunnelling Microscope (STM).

Characterization Information's

❖ **Crystallographic information's ➡ (XRD,SEM, AFM)**

How the atoms are arranged in the object.

❖ **Topography ➡ (SEM, AFM)**

the surface features of an object or "How it looks", its texture.

❖ **Morphology ➡ (SEM,TEM, AFM)**

The shape and size of the particles making up the object.

❖ **Composition ➡ (XRD,*XRF, **AAS)**

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

*X-ray fluorescence, ** Atomic absorption spectroscopy (AAS)

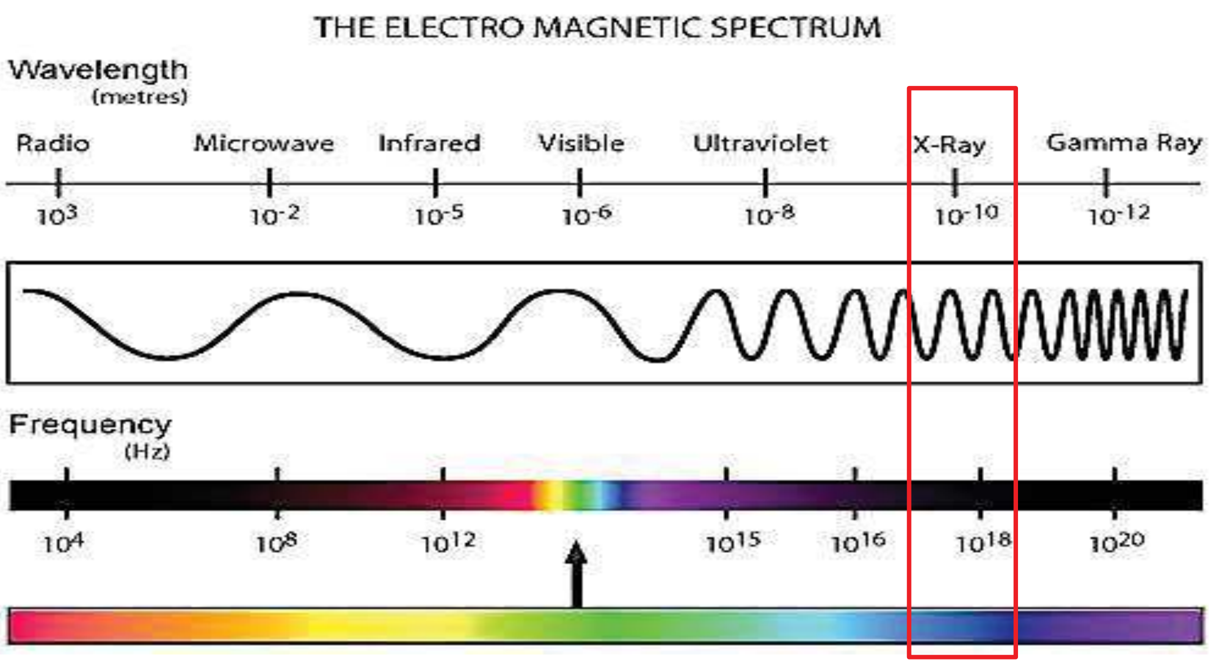
1. X-ray Diffraction Analysis (XRD)

The X-ray diffraction is a crystallographic technique applied to obtain all the data associated to the crystalline phase existing in the solid sample selected to characterize the bulky phases, to detect the bulk transformation and its kinetics, and also to determine particle size.

X-ray are **electromagnetic waves** with wave length in the range of interatomic **distance (0.1-100Å).**

This match of length scales makes them suitable for the study of crystalline materials. For single-phase materials the crystal structure can be obtained directly using x-ray diffraction (XRD). With the help of a database of known structures XRD can be used for phase identification. Also crystal size, strain and preferred orientation of polycrystalline materials can be measured.

The related technique of x-ray reflection enables accurate determination of film thickness.



The uses and the applications of x-ray for nanotechnology

1. Phase identification.
2. Texture or preferential orientation.
3. Crystallite size and residual stress.
4. In-situ temperature and pressure studies.
5. High resolution diffraction.
6. Layer thickness measurements.

Principles

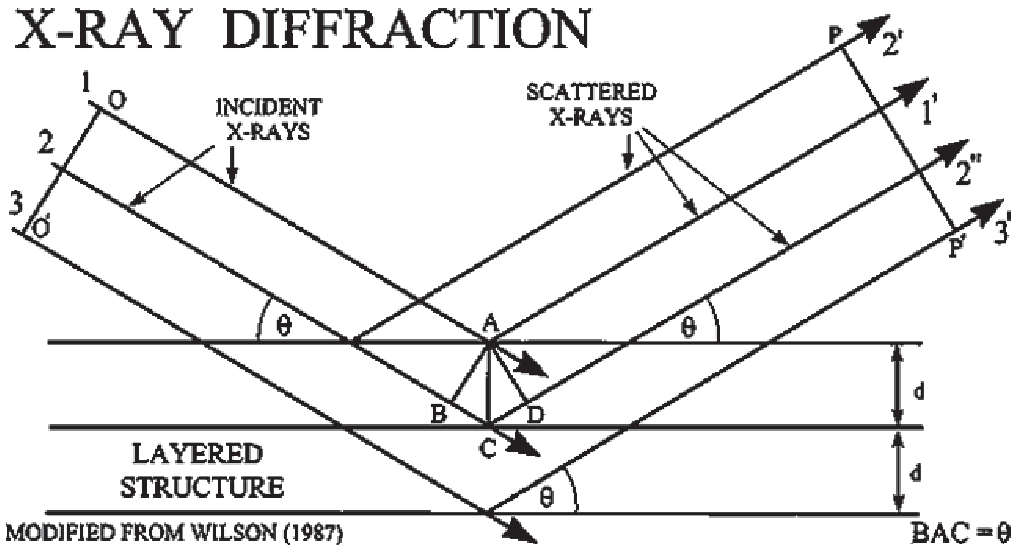
When x-ray radiation is directed on a sample, the x-rays are scattered "diffracted" by electrons present in the material, if the atoms in the material are arranged in a regular structure, i.e. if the material is crystalline, this scattering results in maxima and minima in the diffracted intensity. The single maxima follow **Bragg's law:**

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

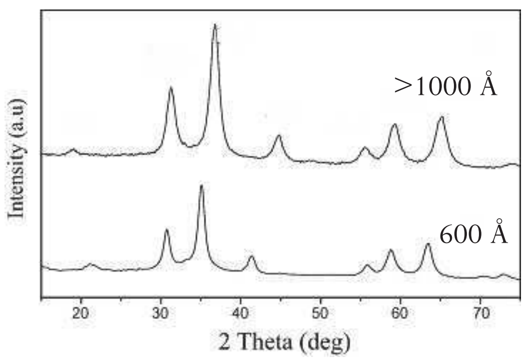
Example:- $\lambda = 1.54\,Å,\;\; 2\theta = 38$

$$\Rightarrow\; d= 1{,}34Å/\,(2*\sin\,(38/2)) = 2.35\,Å$$

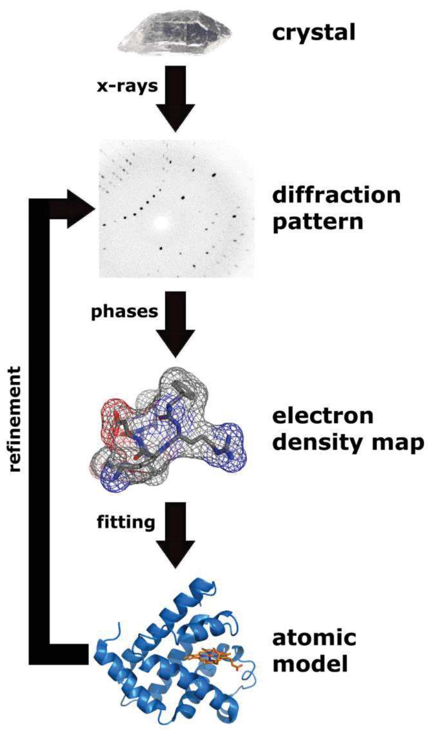
Where:- n is an integer
λ is the X-ray wavelength
d is the distance between crystal lattice planes
θ is the diffraction angle.



When the intensity of detected X-rays is plotted as a function of angle θ an X-ray diffraction pattern is obtained, which is characteristic for the sample material thin layers of only a few nanometers can be investigated. Phase identification can be done by matching the XRD pattern with reference patterns of pure substances. The width of diffraction peak is influenced by the crystallite size: a large crystallite size causes sharp reflections, whereas a small size leads to broad reflections. The effect crystal size can have an XRD pattern is shown in the next figure.



Working Steps Of XRD Flow Chart



Crystal (regular array of atoms) is mounted on Goniometer

⬇

Bombarded with X-ray while rotating

⬇

Production of diffraction pattern of regularly spaced spot

⬇

The 2-D images taken at different rotation at converted to 3-D models of the electron density map by the method of Fourier Transform

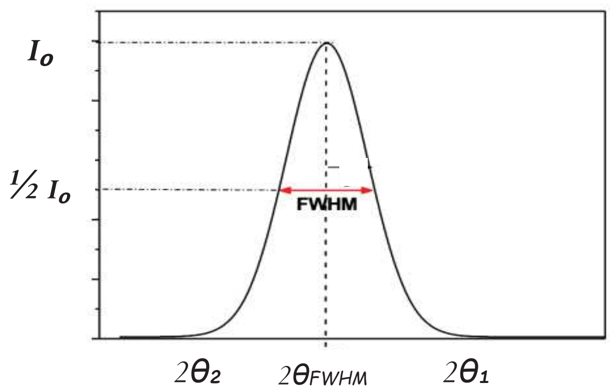
Calculation of crystalline size (thickness) by Scherrer equation

$$Crystallite\ size\ \ t = \frac{(K \times \lambda)}{(B \times \cos\theta)}$$

Where;

K	Sherrer constant.
λ	the X-ray wavelength.
B	(FWHM) the full width peak at the half of maximum.
θ	the diffraction angle.

Note: 20% -30% accuracy at best.

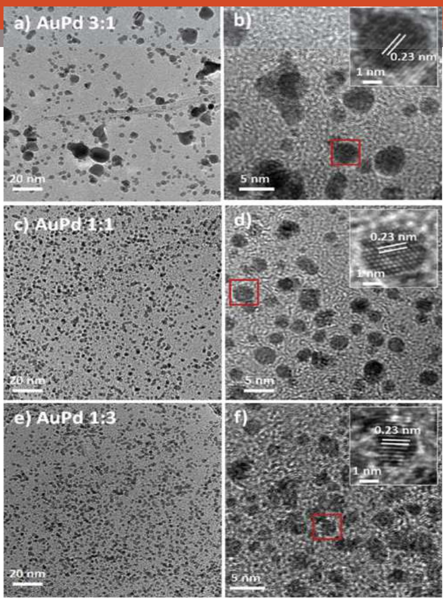


Example: λ= 1.54 Å, 2θ= 98.25, FWHM= 0.1°

B=(0.1°) ×π/180= 0.00174

t=0.89×λ/(B cosθ_B)= 0.89×1.54 Å/ (0.00174 × cos(98.25/2))= 1200Å

NANOMATERIALS



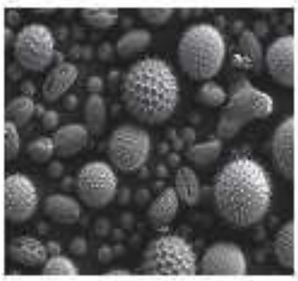
Dr.SANAA TAREQ SARHAN

Lecture (4)

2. Electron Microscope (SEM,TEM)

The scanning electron microscope (SEM) uses a focused **beam of high-energy electrons to generate a variety of signals at the surface of solid specimens**. The signals that derive from electron-sample interactions reveal information about the sample including **external morphology** (texture), chemical composition, and **crystalline structure** and **orientation of materials making up the sample.**

Scanning Electron Microscopy (SEM)



In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; **this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions using energy dispersive X-ray spectrometry (EDS), crystalline structure, and using electron backscatter diffraction (EBSD).**

Scanning Electron Microscopy (SEM) Instrumentation - How Does It Work? Essential components of all SEMs include the following:-

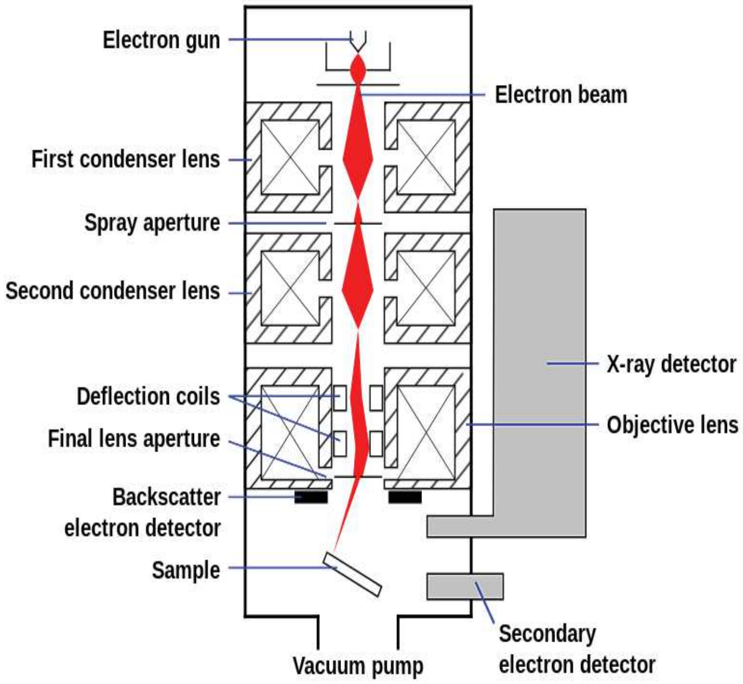
- Electron Source ("Gun").
- Electron Lenses.
- Sample Stage.
- Detectors for all signals of interest.
- Display / Data output devices.

Infrastructure Requirements:-

- Power Supply
- Vacuum System
- Cooling system
- Vibration-free floor

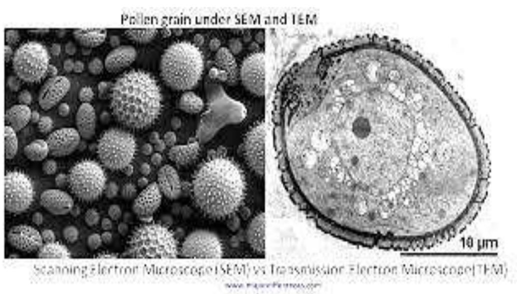
Room free of ambient magnetic and electric fields SEMs always have at least one detector (usually a secondary electron detector), and most have additional detectors.

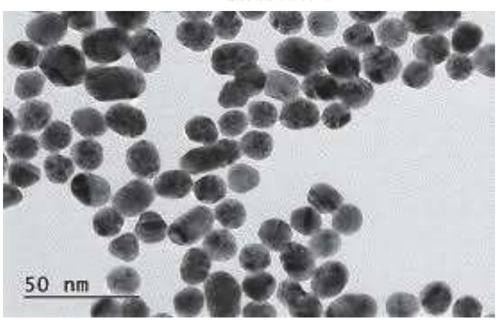
The disadvantages of a Scanning Electron Microscope start with the size and cost. SEMs are expensive, large and must be housed in an area free of any possible electric, magnetic or vibration interference. Maintenance involves keeping a steady voltage, currents to electromagnetic coils and circulation of cool water.



3. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM, an abbreviation which can also stand for the instrument, a transmission electron microscope) is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image.





TEMs consist of the following components:-

- An electron source.
- Thermionic Gun.
- Electron beam.
- Electromagnetic lenses.
- Vacuum chamber.
- 2 Condensers.
- Sample stage.
- Phosphor or fluorescent screen.
- Computer.

Advantages

A Transmission Electron Microscope is an impressive instrument with a number of advantages such as:

- TEMs offer the most powerful magnification, potentially over one million times or more.
- TEMs have a wide-range of applications and can be utilized in a variety of different scientific, educational and industrial fields.
- TEMs provide information on element and compound structure.
- Images are high-quality and detailed
- TEMs are able to yield information of surface features, shape, size and structure.
- They are easy to operate with proper training.

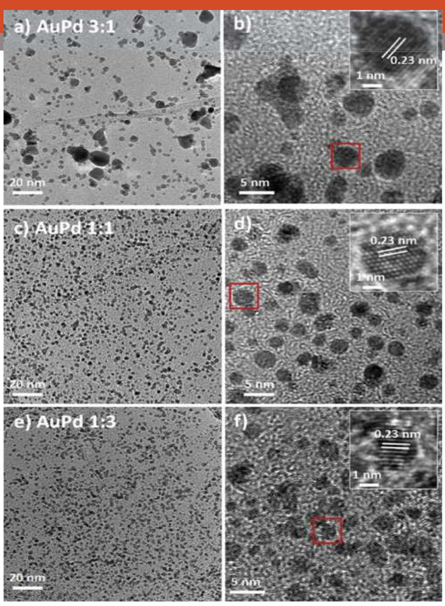
Disadvantages

Some cons of electron microscopes include:

- TEMs are large and very expensive.
- Laborious sample preparation.
- Potential artifacts from sample preparation.
- Operation and analysis requires special training.
- Samples are limited to those that are electron transparent, able to tolerate the vacuum chamber and small enough to fit in the chamber.
- TEMs require special housing and maintenance.
- Images are black and white.

Electron microscopes are sensitive to vibration and electromagnetic fields and must be housed in an area that isolates them from possible exposure.
A Transmission Electron Microscope requires constant upkeep including maintaining voltage, currents to the electromagnetic coils and cooling water.

NANOMATERIALS



Dr.SANAA TAREQ SARHAN

Lecture (5-6)

Scanning Electron Microscope (SEM)	Transmission Electron Microscope (TEM)
Used to produce **excellent images of the surfaces** of cells and small organisms. Excellent for studying surface morphology of the organisms, cells or any suitable material under study.	Used to study **the ultra-structure of the cell and its components**. It can see objects as small as a protein molecule or even at nano level. Provides details about internal composition of cells or any suitable material under study.
Electron beam **scans over** the surface of the sample	Electron beam **pass through** the sample
Based on scattered electrons or produces images by detecting secondary electrons which are emitted from the surface due to excitation by the primary electron beam.	Based on transmitted electrons or produces images by detecting primary electrons transmitted from the sample.
Comparatively low resolution than TEM; Resolution: 2nm(Average), 0.2nm (Special).	High Resolution; Resolution: 10 nm (Average), 0.5nm (Special)
Magnifying power: 100,000X	Magnifying power: 5,000,000X
Specimen contrast: by electron adsorption	By electron scattering.
Produces three-dimensional black and white images	Produces two-dimensional black and white images
Preparation technique: easy	Skilled, very thin sample is required
Specimen mounting: Aluminium stubs	Thin films on copper grids
Field of view: Large	limited

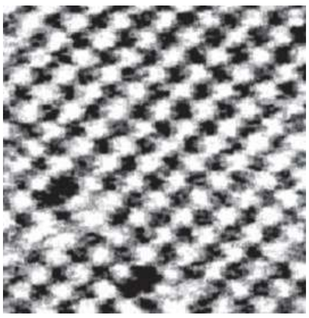
3. Scanning Probe Microscopy

What are scanning probe microscopes?

Scanning probe microscopes (SPMs) are a family of tools ,(SPM) techniques offer unique possibilities to investigate local surface properties of material with a high resolution in the Nano scale and used to make images of Nano scale surfaces and structures, including atoms. **There are several types of SPMs**:-

- ### Atomic force microscopes (AFMs):-

Measures the electrostatic forces between the cantilever tip and the surface. The tip may be dragged across the surface, or may vibrate as it moves. The interaction force will depend on the nature of the sample, the probe tip and the distance between them.



SPM Image of Sodium Chloride

▪ Scanning Tunnelling microscopes (STMs):-

Measures a weak the electrical current flowing between tip and the sample as they are held a very distance apart.

Thus, SPM is a common tool in nano science and nanotechnology , which provides important information on surface topography, surface stiffness, surface magnetization, and many other sample-specific information.

▪ SPM technologies share the concept of :

Scanning an extremely sharp tip (typically 3–50nm radius of curvature) across the object surface.

This tip is mounted on a flexible cantilever, allowing the tip to follow the surface profile. When **the tip moves in proximity to the investigated** object, **forces of interaction between the tip and the surface influence the movement of the cantilever.**

These movements are detected by selective sensors .various interactions can be studied depending on the mechanics of the probe.

Operating

In real space, direct sample information is gained and frequently displayed in a pictorial way, which allows an easy understanding. The samples do not require a special pretreatment or a partial vacuum but can be observed in air at standard temperature and pressure or under more complex sample environments

NOTES:-

- On the other hand, SPM measurements are limited to rather small sample surface areas and have difficulties in accessing buried interfaces.
- The remaining limitations are more serious: it is still difficult to achieve information with SPM, for example, about the surface structure, on a larger surface area.
- An extensive mapping of the sample is either impossible or at least not economical. As a consequence, advanced scattering.

How do they work?

SPMs are a very powerful family of microscopes, sometimes with a resolution of less than a nanometre. (A nanometre is a billion the of a meter.) An SPM has a probe tip mounted on the end of a cantilever. The tip can be as sharp as a single atom. It can be moved precisely and accurately back and forth across the surface, even atom by atom. When the tip is near the sample surface, the cantilever is deflected by a force. SPMs can measure deflections caused by many kinds of forces, including mechanical contact, electrostatic forces, magnetic forces, chemical bonding, van der Waals forces, and capillary forces. The distance of the deflection is measured by a laser that is reflected off the top of the cantilever and into an array of photodiodes (similar to the devices used in digital cameras).

SPMs can detect differences in height that are a fraction of a nano meter, about the diameter of a single atom.

The tip is moved across the sample many times. This is why these are called"scanning" microscopes. A computer combines the data to create an image.

The images are inherently colorless **because** they are measuring properties other than the reflection of light. However, the images are often colorized, with different colors representing different properties (for example, height) along the surface.

Scientists use SPMs in a number of **different ways, depending on the information they're trying to gather from a sample**. The two primary modes are ***contact*** *mode* and **tapping mode.** In contact mode, the force between the tip and the surface **is kept constant.** This allows a scientist to **quickly** image a surface.

In tapping mode, the cantilever oscillates, intermittently touching the surface. Tapping mode is especially useful when a scientist is imaging a soft surface. **There are several types of SPMs**. Atomic force microscopes (AFMs) **measure the electrostatic forces** between the cantilever tip and the sample. Magnetic force microscopes (MFMs) **measure magnetic forces.** And scanning tunnelling microscopes (STMs) **measure the electrical current flowing between the cantilever tip and the sample.**

A.Atomic force microscopes (AFMs)

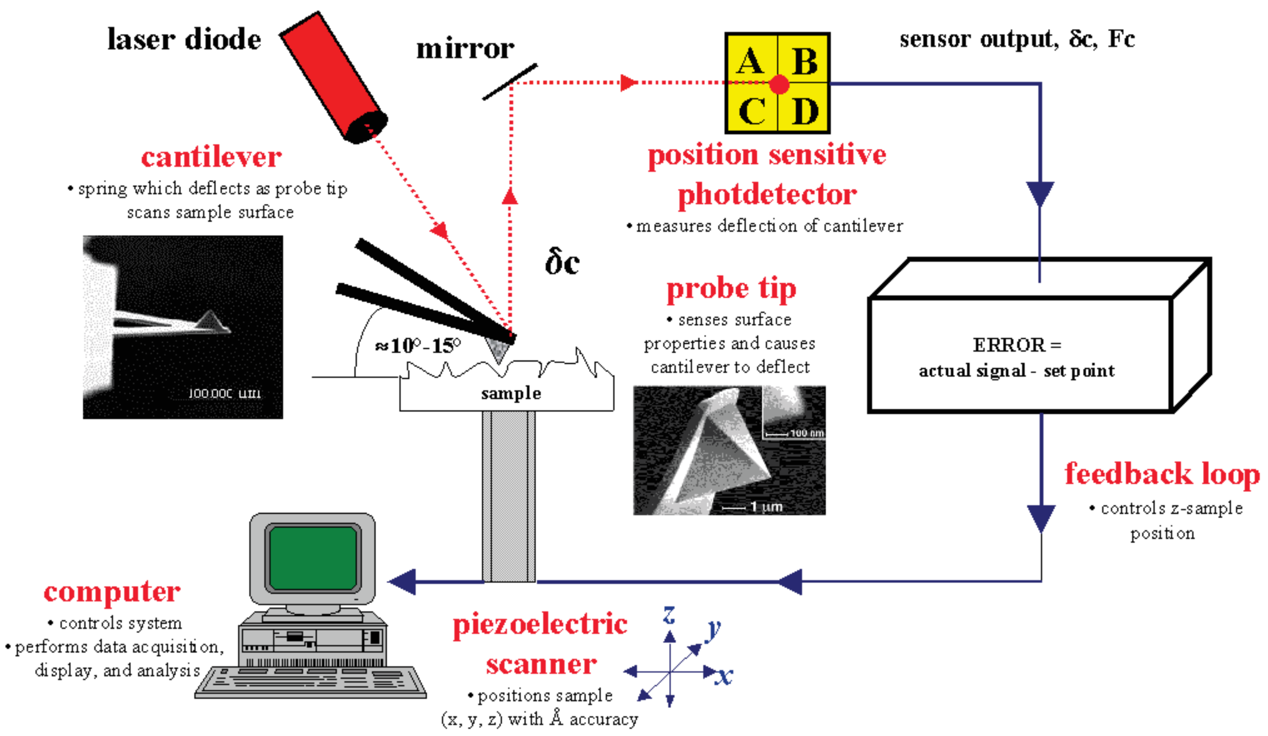
Measures the interaction force between the tip and surface. The tip may be dragged across the surface , or may vibrate as it moves the interaction force will depend on the nature of the sample ,the probe tip and the distance between them.

B.Scanning Tunnelling Microscopy(STM):

measures a weak electrical current flowing between tip and sample as they are held a very distance apart.

Atomic Force Microscopy (AFM) :

General Components and Their Functions

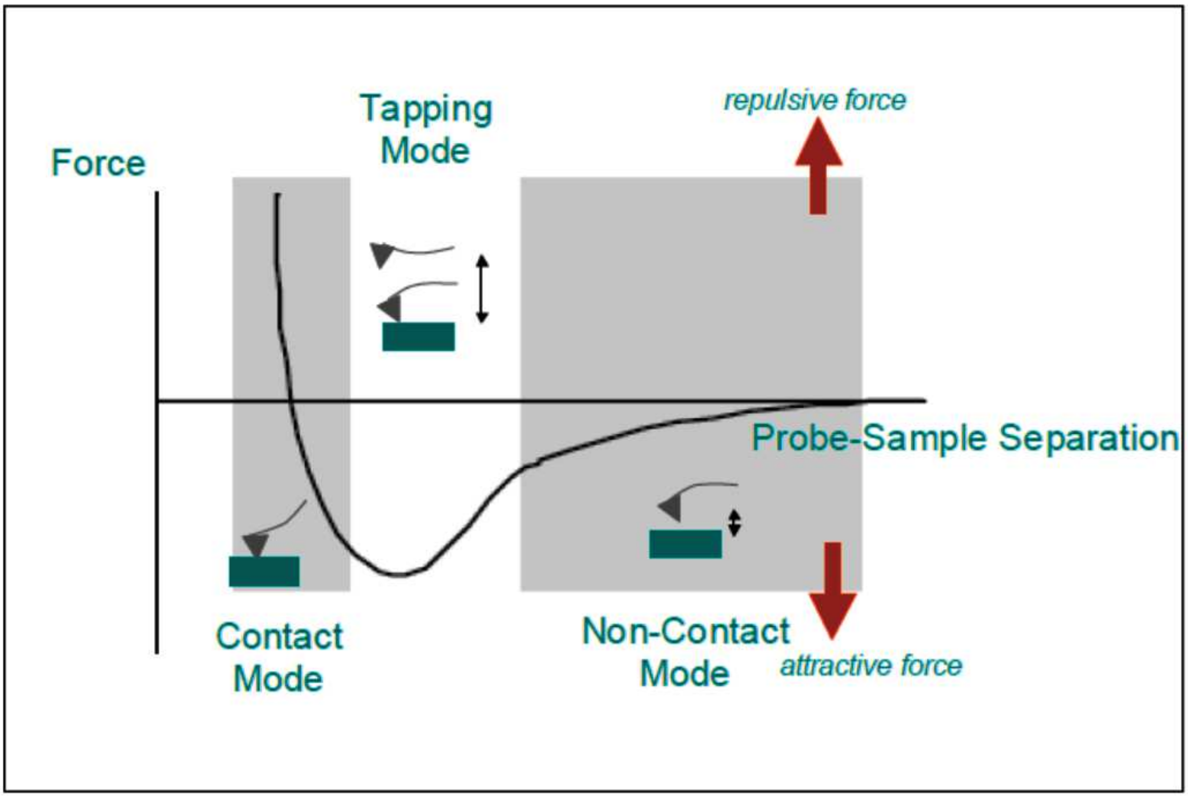


HOW DOES THE AFM WORK?

AFM provides a 3D profile of the surface on a nanoscale, by measuring forces between a sharp probe (<10 nm) and surface at very short distance (0.2-10 nm probe-sample separation).

The probe is supported on a flexible cantilever. The AFM tip "gently" touches the surface and records the small force between the probe and the surface.

Beam deflection system ,using a laser and photodetector to measure the beam position. Because the atomic force microscopy relies on the forces between the tip and sample ,therefore these force is important for proper imaging .**The force is not measure directly but can calculated the deflection of the lever using HOOK's law.**



Plot of force as a function of probe-sample separation.

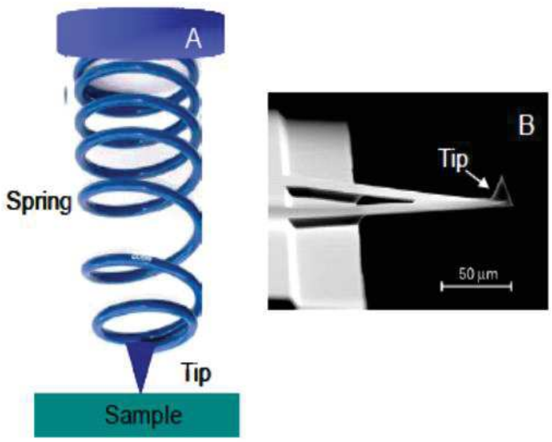
The probe is placed on the end of a cantilever (which one can think of as a spring). The amount of force between the probe and sample is dependant on the **spring constant** (stiffness) of the cantilever and the distance between the probe and the sample surface. This force can be described using **Hooke's Law**:

$$F = K.X$$

F = Force

k = spring constant

x = cantilever deflection



a) Spring depiction of cantilever b) SEM image of triangular SPM cantilever with probe (tip). (Image from MikroMasch)[1]

The spring constant of cantilever (typically ~ 0.1-1 N/m) is less than surface, the cantilever bends and the deflection is monitored.

This typically results in forces ranging from nN (10) to µN (10^{-6}) in the open air.

What are probes made of?

Probes are typically made from $Si_3\ N_4$, or Si. Different cantilever lengths, materials, and shapes allow for varied spring constants and resonant frequencies.

A description of the variety of different probes can be found various vendor sites. Probes may be coated with other materials for addition .SPM applications such as chemical force microscopy (CFM) and magnetic force microscopy (MFM).

Modes of Operation

There are 3 primary imaging modes in AFM:

1) **Contact AFM:** < 0.5 nm probe-surface separation.

2) **Intermittent contact (tapping mode AFM):** 0.5-2 nm probe-surface separation.

3) **Non-contact AFM:** 0.1-10 nm probe-surface separation.

Primary Modes of Imaging:

1. Contact Mode AFM:

(repulsive VdW) When the spring constant of cantilever is less than surface, the cantilever bends. The force on the tip is repulsive. By maintaining a constant cantilever deflection (using the feedback loops) the force between the probe and the sample remains constant and an image of the surface is obtained.

Advantages : fast scanning, good for rough samples, used in friction analysis.

Disadvantages: at time forces can damage/deform soft samples (however imaging in liquids often resolves this issue).

2. Intermittent Mode (Tapping):

The imaging is similar to contact. However, in this mode the cantilever is oscillated at its resonant frequency, (see the next figure). The probe lightly "taps" on the sample surface during scanning, contacting the surface at the bottom of its swing .By maintaining a constant oscillation amplitude a constant tip-sample interaction is **Oscillation Amplitude**:20-100 nm maintained and an image of the surface is obtained.

Advantages : allows high resolution of samples that are easily damaged and/or loosely held to a surface; Good for biological samples.

Disadvantages: more challenging to image in liquids, slower scans peeds needed

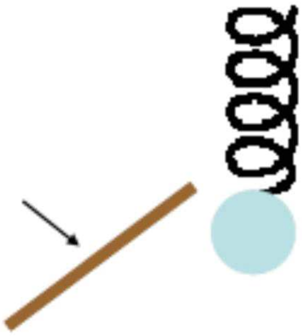
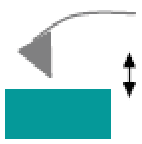


Figure shows **Resonant frequency** is a natural frequency of vibration determined by the physical parameters of the vibrating object. For example if you hit a spring with a mass at the end (probe) the main response will be a bob up and down at its natural frequency.

3. Non-contact Mode:



the probe does not contact the sample surface, but oscillates above the adsorbed fluid layer on the surface during scanning. The force between the tip and sample (attractive VdW).

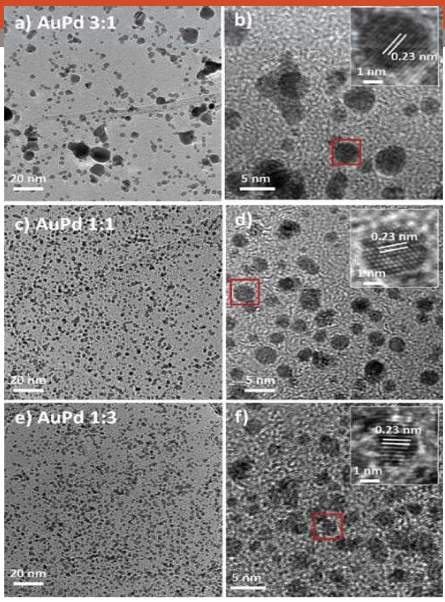
(Note: all samples unless in a controlled UHV or environmental chamber have some liquid adsorbed on the surface).

Using a **feedback loop** to monitor changes in the amplitude due to attractive VdW forces the surface topography can be measured

Advantages: VERY low force exerted on the sample(10^{-12} N), extended probe lifetime. The advantage of tapping the surface is improved lateral resolution on the soft samples. Lateral forces such as drag.

Disadvantages: generally lower resolution; contaminant layer on surface can interfere with oscillation; usually need ultra high vacuum (UHV) to have best imaging

NANOMATERIALS



Dr.SANAA TAREQ SARHAN

Lectures (7-8)

- **Scanning -Tunnelling microscopes (STMs):-**

The scanning-tunneling microscope (or STM), Figure (1) , is one of the most powerful microscopes available. It provides atomic-scale resolution of surfaces and is also being developed to move atoms on surfaces. STM relies on the fact that electrons near surfaces have wave functions which decay into the vacuum outside the surface boundary.

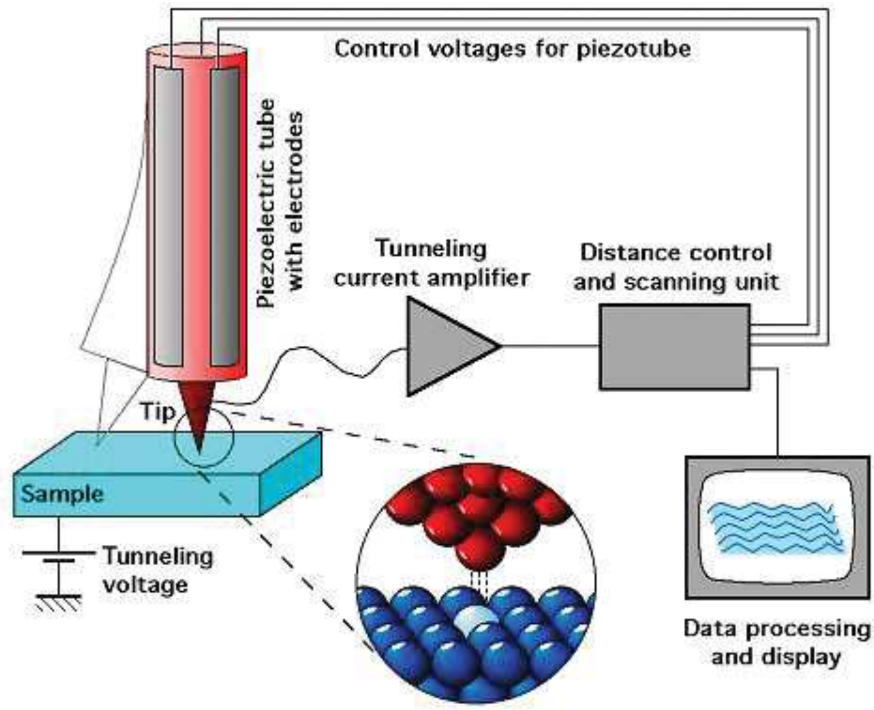


Figure (1) schematic view of STM

The microscope consists of a conducting tip connected to a current-measuring circuit. **When the tip is in close proximity to the surface (~1 nm), the decaying wave function from the surface could overlap with the tip, the surface electron has a finite probability of being in the tip. Since the latter is conducting, the electron under a voltage field (~1–10 V) can then move creating a current. This current is known as a tunnelling current whose magnitude (as for all tunnelling currents) is very sensitive to the surface tip separation (the region in between effectively acting as a barrier)**:

The scanning-tunnelling microscope (or STM), can be used to carry out chemical reaction on the surfaces .This relies on a tip (sample interaction).The force can be either attractive or repulsive.

APPLICATIONS OF NANOMSTERILS

The unique properties of nanomaterial's encourage belief that they can be applied in wide range of fields are included;

1. **Large surface area to volume:**
   Better catalytic efficiency through higher surface-to-volume ratio.
2. **Electrical conducting:**
   Increases **electrical conductivity** in ceramic and magnetic nanaocomposites, **increases electric resistance in materials**.
3. **Chemical properties:**
   Corrosion protection for machinery.
4. **thermal properties:**
   Equipment, heat resistance for turbines and engines, thermal insulation equipment and construction materials, etc.
5. **Wetting properties:**
   Antigraffiti, antifouling, lotus-effect, self-cleaning surfaces for textiles, and ceramics, etc.
6. **magnetic properties:**
   increases magnetic coercivity* up to a critical grain size super-paramagnetic behaviour.
   *(*the resistance of a magnetic material to changes in magnetization, equivalent to the field intensity necessary to demagnetize the fully magnetized material*)

7. **Mechanical properties:**
   Improving hardness and toughness of materials and alloys ductility and super-plasticity of ceramic.
8. **Optical properties:**
   Spectral shift of optical absorption and fluorescence properties, increases quantum efficiency of semiconductor crystals.
9. **Biological properties:**
   increases permeability through biological barriers (membranes, blood-brain barrier), etc. Improving biocompatibility.

Current and emerging applications of nanotechnology

Electronic, optoelectronic magnetic applications	Biomedical, pharmaceutical cosmetic applications	Energy, catalytic structural applications
• Chemical-mechanical polishing. • Electro conductive coatings • Magnetic fluid seals and recording media • Multilayer capacitors • Optical fibbers • Phosphors • Quantum optical devices	• Antimicrobials • Biodetection and labelling • Biomagnetic separations • Drug delivery • MRI contrast agents • Othopedics/implants • Sunscreens • Thermal spray coatings	• Automotive catalyst • Membranes • Fuel cells • Photocatalysts • Scratch-resistant coatings • Structural ceramics • Solar cells

Automotive industry	Chemical industry	**Engineering**
• Lightweight constructions • Painting (filters, base coat, clear coat) • Catalyst • Tires (fillers) • Sensors • Coatings for wind, screen and car bodies	• Fillers for paint systems • Coating system based on nanocomposites • Impregnation of papers • Switchable adhesive • Magnetic fluids	• Wear protection for tools and machines (anti blocking coatings, scratch resistant coatings on plastic parts, etc.) • Lubricant- free bearings

Electronic industry	**Construction**	Medicine
• Data memory (MRAM, GMR, HD) • Displays (OLED, FED) • Laser diodes • Glass filters • Optical switches • Filters (IR-Bloking) • Conductive, antistatic coating	• Construction materials • Thermal insulations • Flame retardants • Surface-functionalised building materials for wood, floors, stone, facades, tiles, roof tiles, etc. • Facade coatings • Groove mortar	• Drug delivery systems • Active agents • Contrast medium • Medical rapid tests • Prostheses and implants • Antimicrobial agents and coatings • Agents in cancer therapy

Textile/fabric/non-wovens	**Energy**	Cosmetics
• surface-processed textile • Smart clothes	• Fuel cells • Solar cells • Batteries • capacitors	• Sun protection • Lipsticks • Skin creams • Tooth past

Food and drink	household	**Sports /outdoor**
• Package materials • Storage life sensors • Addvitive • Clarification of fruit juices	• Ceramic coatings for irons • Odors catalyst • Cleaner for glass, ceramic, floor, windows.	• Ski wax • Antifogging of glasses/ goggles • Antifouling coating for ships/boats • Reinforced tennis rackets and balls

Examples of the established applications of nanomaterials

Nanofluids:

Materials with special nano properties are introduced in many applications, as example, the nanofluids, which they are new class of fluids that consist of a base fluid with nano-sized particles (1-100nm) suspended within.

Nanofluids applications:

1. Transportation (Engine cooling)
2. Electronic cooling (electric transforms cooling)
3. Defens and Space
4. Nuclear systems cooling
5. Heat exchanger
6. Biomedicine
7. Other application(heat pipes ,fuel cell, solar water heating , chillers, domestic refrigerator , diesel combustion, drilling, thermal storage….etc)

Notice

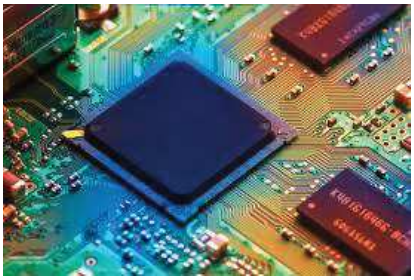
In more details and according to the types of application the following points can be descripted:

1. Electronics

Microelectronics

Definition - What does Microelectronics mean?

Microelectronics is a subdivision of the field of electronics that deals with very small and microscopic elements to manufacture electronic components. Microelectronics has been rapidly evolving as the most in-demand field of electronics because of the ever-increasing demand for inexpensive and lightweight equipment.



Microelectronics is a field in electronics that utilizes tiny or micro components to manufacture electronics. As demand for small and less expensive devices grows, the field continues to expand.

Semiconductor material such as silicon, CNT and graphite **are the most commonly used elements in the manufacturing of microelectronic devices due to their varied electronic properties.** These include transistors, capacitors, inductors, resistors and diodes as well as insulators and conductors. Equipment and expertise used in manufacturing of microelectronic devices is not widely available, causing microelectronic devices to generally be more expensive than devices that do not utilize microelectronics.

The resolution of televise ion or a monitor improves with reduction of pixel size .The use of nanocrystalline materials can greatly enhance resolution and may significantly reduce cost. Also a flat panel display is a television, monitor or other display device that uses a thin panel design instead of a traditional **cathode ray tube** (CRT) design. A flat panel display constructed with nanomaterial may possess screens are much lighter and thinner, and can be much more **portable than traditional televisions and monitors.** They also have higher resolution than older models.

Thin carbon NTs have ideal geometry for electron emission due to their smallest atomistic tip radius that result in turn to a high electric field strength.

Moreover CNTs are being widely studied because of their unique structure and extraordinary properties. The mechanical properties and chemical inertness, associated with structure dependent electronic properties and high aspect ratio make CNTs suitable for several innovative technologies.

CNTs are known exhibit: the high strength, melting temperature; resistance aggressive media; as graphite, and are able to work in technical vacuum.

The application of CNTs as electron field emitters has been widely investigated ever since it was firstly demonstrated in 1995. Indeed, the above recalled properties make CNTs excellent emitters, suitable for many applications such as high-resolution electron microscopes as well as electron beam lithography, X-ray tubes and flat panel displays.

High energy density batteries:

New nanometerial show promising properties as anode and cathode material in lithium –ion batteries, having high capacity and better cycle life than their larger- particle equivalents intercalation. Among them are : Aerogel intercalation electrode material , nanocrystalline alloys, Nano sized composite materials, carbon nanotube and Nano sized transition metal.

High sensitivity sensors:

Due to their surface area and increased reactivity , nanomaterial could be employed as sensors for detecting various parameters, such as electrical resistivity ,chemical activity magnetic permeability ,thermal conductivity and capacitance.

2. Transportation and telecommunication

Car tires:

Nanoparticle of carbon black ranging between 10nm-500 nm act as a filler in the polymer matrix of tires and are used for mechanical reinforcement.

Car bumpers:

Clay particle based composites containing plastics and man-sized clay are used to make car exterior that are lighter and twice as resistant to scratches than usual materials.

3. Imaging

Scanning microscope imaging:

SWCNTs have been used as probe tips for atomic microscopy imaging of antibodies, DNA, etc. Nanotubes are ideal probe tips for scanning microscopy due to their small diameter (which is maximize resolution). High aspect ratio, and stiffness.

Molecular-recognition AFM tips:

SWCNTs with attached biomolecules are attached to AFM tips, and used for "molecular-recognition" in order to study chemical forces between molecules.

4. Biomedical applications

Nano scaffolds:

Nano fiber scaffolds can be use to regenerate central nervous system cells and possible other organs. Experiments performed on a hamster with severed optic tract demonstrated the regeneration of axonal tissue initiated by a peptide nanofibers scaffold.

Antimicrobial nano powders and coatings:

Antimicrobial nanopowders, possess antimicrobial properties. When these powders contact cells of E.coli, or other bacteria species and viruses, over 90% are killed within a few minutes. Due to their antimicrobial effect, nanoparticle of silver and titanium dioxide (<100 nm) are assessed as coatings for surgical makes.

Bio separation:

Nanotube membranes can act as channels for highly selective transport of molec and ions between solutions that are present on both side of the membrane. For example, membrane containing nanotubes with inside diameters of molecular dimensions (less than 1 nm) separate small molecules on the basis of molecular size, while nanotubes with larger inside diameters(20 -60 nm) can be used to separate proteins.

Drug delivery

The ability of nanoparticles to target and penetrate specific organs and cell contributes to their toxicity. However, this ability may be exploited in nanomedicine. Nanospheres composed of biodegradable polymer can incorporated drugs, allowing the timed release of the drug as polymer degrades. When particles are set to degrade in acid microenvironment, such as tumor cells or around inflammation sites, this allows site-specific or targeted drug delivery.

5. cosmetics

Titanium dioxide and zinc oxide become transparent to visible light when formed at the nanoscale. However, are able to absorb and reflect UV light, being currently used in sunscreens and in the cosmetic industry.

6. coatings

Nanomaterials have been used for every thin coatings for decades if not centuries. Today, thin coatings are used in a vast range of applications including architectural glass, microelectronic, anti counterfeit, devices, optoelectronic device, and catalytically active surfaces, structured coatings.