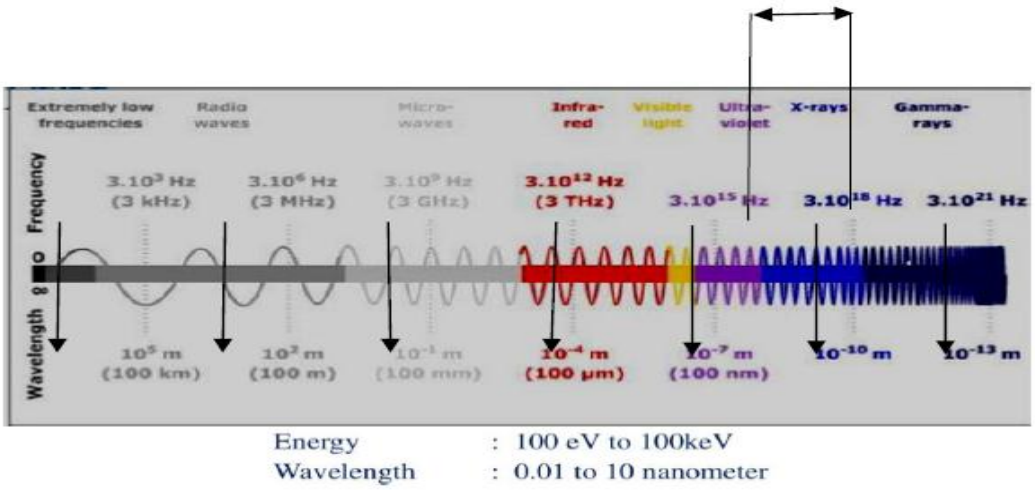
Powder X-ray diffraction (XRD):

- X-rays are electromagnetic radiation with typical photon energies in the range of 100 eV to 100 keV. For diffraction applications, only short wavelength x-rays in the range of a few angstroms to 0.1 Å are used.



Energy : 100 eV to 100keV
Wavelength : 0.01 to 10 nanometer

-These x-rays with short wavelengths are comparable to the interplanar distances; hence, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials.

How do you get x-ray?

-X-rays are high-energy photons that are produced when electrons make transitions from one atomic orbit to another.

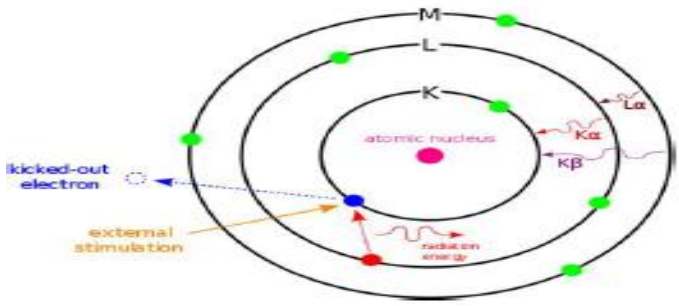
-These transitions can be generated via the **photoelectric effect** as shown.

-If you send a photon into an atom with energy greater than the **binding energy** of an electron in that atom, the photon can knock that electron out of its orbit, leaving a hole (or vacancy).

-This hole can then be filled by another electron in the atom, giving off an x-ray in the transition to conserve energy.

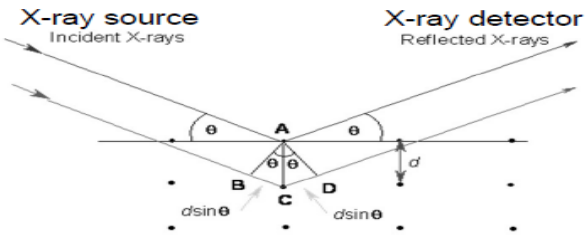
-Many different atomic electrons of different binding energies can fill this hole, so you would expect to see many energy peaks in an x-ray spectrum.

-Electron transitions to the K shell of an atom are called K X-rays, and transitions to the L shell are called L X-rays.



- It is used for identifying the crystalline phases, lattice parameter, and estimating crystallite size. It is based on the elastic scattering of X-ray photons by atoms in a periodic lattice. A beam of X-rays (wavelength λ ~ 0.5–2Å) hits the catalyst sample, and is diffracted by the crystalline phases in the catalyst according to Bragg's law, where n =1, 2, . . . , d is the spacing between atomic planes in the crystalline phase, and Θ is the diffraction angle.

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



Difference in path length = BC + CD

$BC = CD = d_{hkl}\sin\theta_{hkl}$

Difference in path length = $2d_{hkl}\sin\theta_{hkl}$

Must be an integral number of wavelengths, $n\lambda = 2d_{hkl}\sin\theta_{hkl}$

(n = 1, 2, 3, ...)

$\lambda = 2d_{hkl}\sin\theta$

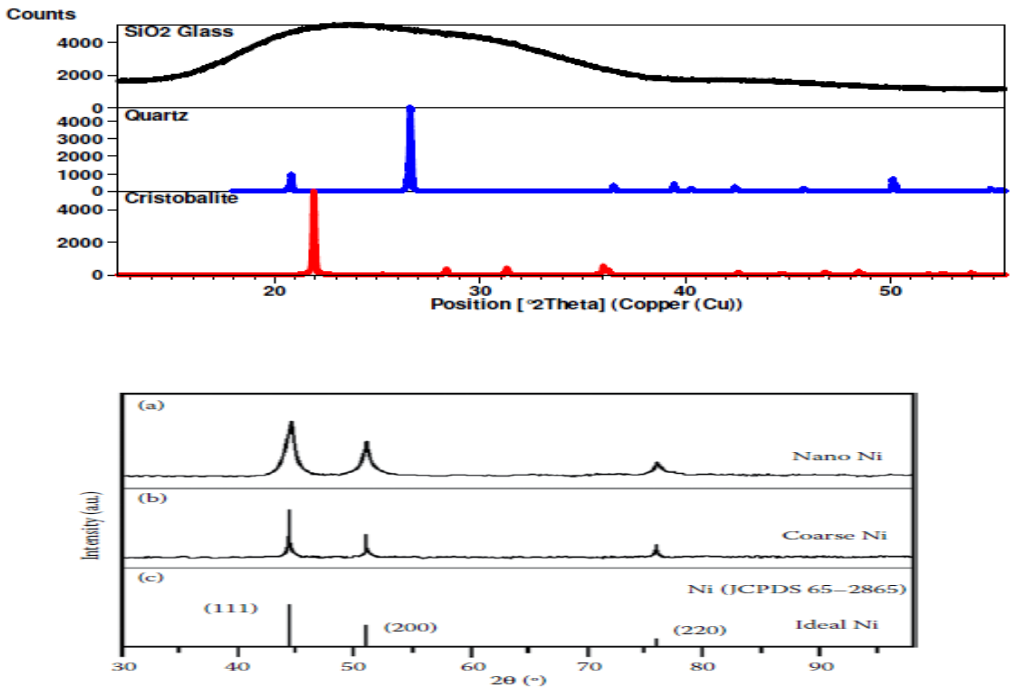
Bragg Equation

- The intensity of the diffracted X-rays is plotted as a function of the diffraction angle and the sample orientation. This diffraction pattern is

used for identifying the crystalline phases and measuring the size and lattice spacing of the crystallites.

- Crystalline phases of unknown samples can be identified by comparing the X-ray diffraction pattern with known patterns of metals and oxides (the International Centre for Diffraction Data, ICDD database, lists approximately 100 000 diffraction patterns of solids).

- Since XRD is based on interference between reflecting X-rays from lattice planes, it requires sufficient long-range order. Noncrystalline catalysts, such as silica/alumina gels used for hydrocarbon cracking, will show either broad and weak diffraction lines or even no diffraction at all.



Powder XRD patterns of (a) ideal Ni, (b) coarse-grained bulk Ni, and (c) Ni nanopowder.

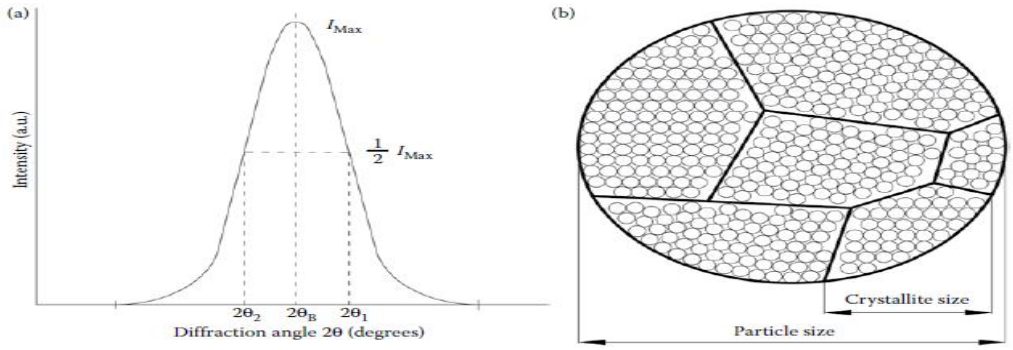
- As shown in Figure, ideal (free from defects) crystalline materials provide sharp diffraction lines and the real crystalline materials exhibit diffraction peaks with slight peak broadening at the base of diffraction lines compared to that of ideal materials. However, in case of finite sized

crystals (size <1000 Å), where the number of diffracting planes is limited (nanomaterials), the diffraction peak will broaden significantly due to the insufficient number of planes causing destructive interference at the diffraction angles other than Bragg's angle. This peak broadening helps in determining the crystallite size of nanomaterials. In contrast to this, amorphous materials show broad hump in the XRD pattern due to an almost complete lack of periodicity of atoms or ions.

- The Debye–Scherrer equation used to calculate the crystallite size of the sample from the full width at half maximum (FWHM) of a diffraction peak broadening using the Debye–Scherrer equation:

$$t = \frac{K\lambda}{\beta_c \cos\theta}$$

where t is the crystallite size and β_c is the FWHM. The value of Scherrer's constant (K) for diffractions with different crystallographic Miller indices (hkl) of a cubic crystal lattice varies between 0.9 and 1.15, and it is generally taken 0.9 for a cubic materials for simplicity.



Crystal structure

-Intermolecular attraction is in minimum in the gaseous state and this disappears completely when the gas is ideal. The interaction is stronger in liquids and is strongest in solids.

-the attractive interaction between the molecules tries to keep them together and the thermal motion is opposed to that. Hence, it is possible

to change a substance from one state to another by changing its temperature. If the liquid is allowed to cool slowly, the molecules will arrange themselves in an orderly manner and this will finally result in a **crystalline solid**. If cooling is rapid, the molecules will not be able to arrange themselves in order. Rapid densification will give a glass or an **amorphous solid**.

Crystal: a solid composed of atoms, ions or molecules arranged in a pattern periodic in three dimensions.

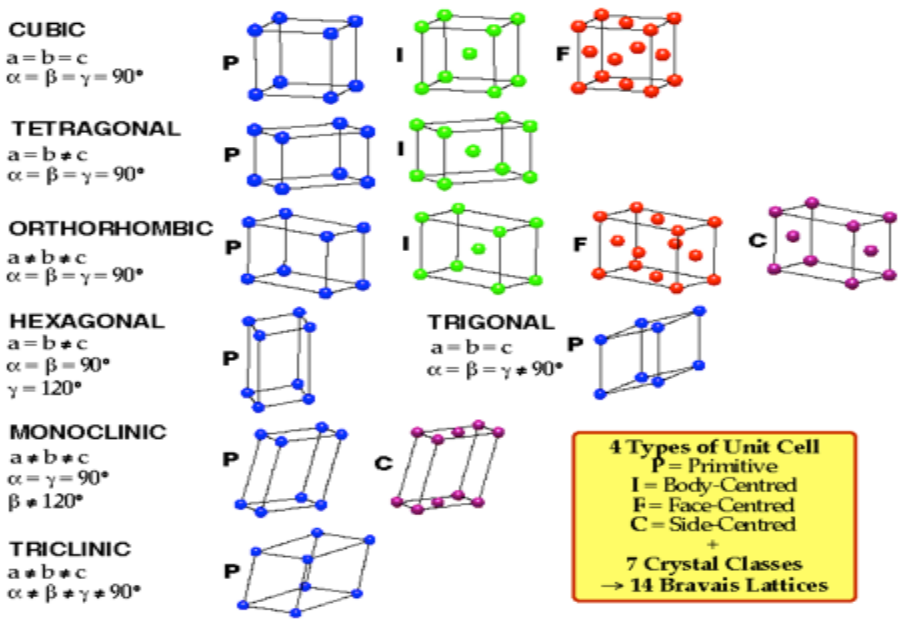
Single crystals

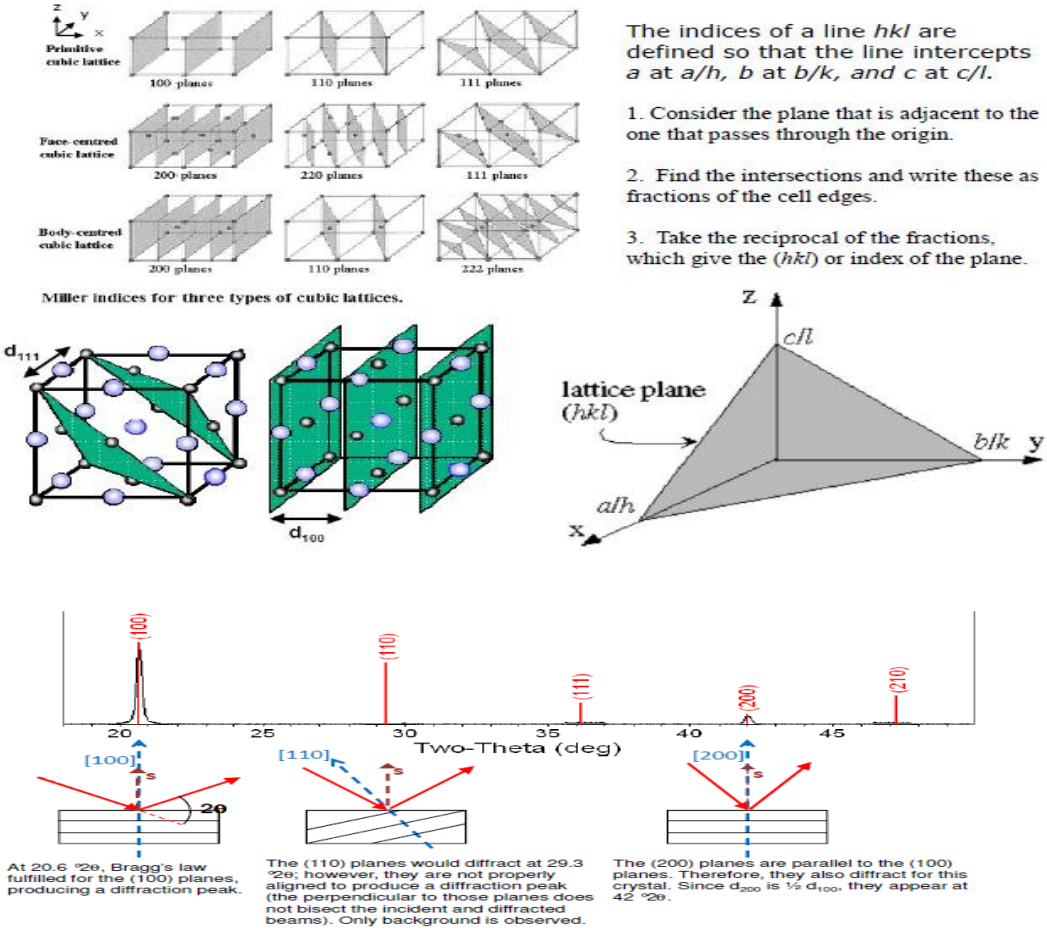
Crystalline solids →

Polycrystalline

Not all solid are crystalline, however, some are amorphous, like glass, and do not have any regular interior arrangement of atoms, ions, or molecules.

Crystal Systems:





Small-angle X-ray scattering (SAXS):

Small-angle X-ray scattering (SAXS) works similarly, but while XRD covers the10–180° scattering range, SAXS deals with 2Θ angles 0.1 deg to 5 deg. This enables the determination of catalyst particle size in the 50–500 nm range. In some cases, SAXS can also be used for determining the particles surface area, giving comparable results to BET adsorption studies.

- Small-angle X-ray scattering (SAXS) is an analytical technique that measures the intensities of X-rays scattered by a sample as a function of the scattering angle.

- From Bragg's law it is understood that with decreasing scattering angle, increasingly larger structural features are being probed. A SAXS signal is observed whenever a material contains structural features on the length scale of nanometers, typically in the range of 1-100 nm.

- On the other hand, wide-angle X-ray scattering (WAXS), also known as wide-angle X-ray diffraction (WAXD), probes for structures in the material on the much smaller length scale, that of interatomic distances. Small angle X-ray scattering and wide angle X-ray scattering (SAXS and WAXS) are complementary techniques.

- SAXS method is one of the most versatile techniques for the structural characterization of nanomaterials. The samples may be solid objects, powders, gels or liquid dispersions, and they may be amorphous, crystalline or semi-crystalline. Measurements require only minimal sample preparation and can often be done in situ.
-Typical samples that can be studied by Small-angle X-ray scattering include:

- Liquid nanoparticle dispersions / colloids

- Nanopowders

-Nanocomposites

-Polymers

-Surfactants

-Microemulsions

-Biomacromolecules

-Liquid crystals

-Mesoporous materials

From the evaluation of the measured scattering profiles a wide range of information about the structure and properties of the materials can be obtained, such as:

-Nanoparticle size distribution

-Particle shape

-Particle structure (e.g. core-shell)

-Specific surface area

-Agglomeration behavior of nanoparticles

-Pore size distribution

-Liquid crystalline phases

IR Spectroscopy

Infrared spectroscopy is the most widely used technique for studying the surface chemistry of heterogeneous catalysts. It can give information about the catalyst structure, as well as about the species adsorbed on the catalyst surface.

- By using probe molecules like CO, NO and NH_3, information is obtained about the nature and environment of atoms and ions exposed on the surface.

- IR spectroscopy of solid catalysts can be performed either by transmission of the IR beam through a thin section of the solid, or by its reflection from the surface. The energy of these vibrations depends on the nature and bonding of the molecules. The vibrational frequencies of surface groups and probe molecules are identified by comparing their "fingerprints" with literature databases.

- IR spectroscopy has two important advantages: - It is nondestructive and noninvasive, and it can be adapted to measurements at high temperatures and pressures. This means that IR studies can be done under real process conditions, and even, with today's advanced computers, using on-line analysis.

- By using reactive probe molecules, you can qualify and quantify the type and number of active sites. For example, pyridine vapor is used for titrating Brønsted acid sites on solids, and the changes in the acid absorption bands are easily monitored using diffuse-reflectance infrared Fourier-transform spectroscopy (DRIFTS).

- IR spectroscopy can even be used for detecting the way that molecules are adsorbed on the catalyst surface. CO, for example, can form different adcomplexes on metal surfaces (Figure 4.19): linear (u_1, 2000–2130 cm^{-1}); bridged between two metal atoms (u_2,1860–2000 cm^{-1}); triply bridged(u_3,1800–1920cm^{-1});and even quadruply bridged (u_4, 1650–

1800cm^{-1}). The linear configuration is common for most group VII metals, while bridged configurations are found more with group VIII metals.

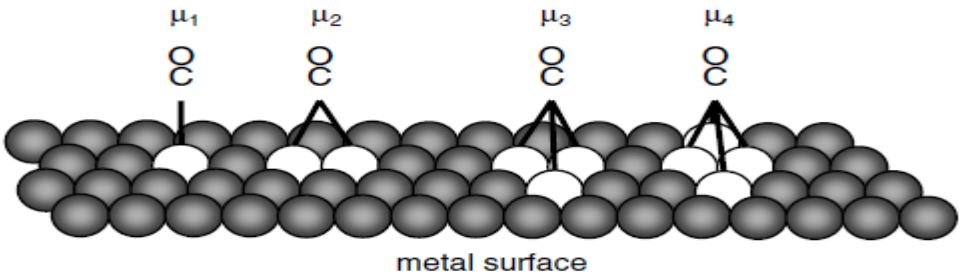


Figure 4.19 The four different adsorption configurations of CO on metal surfaces can be distinguished by their IR activity.

Examples of Applications:

– Detection of Brønsted acid and Lewis acid surface groups with chemisorbed pyridine

– Ethylene chemisorption on isolated Pd atoms by means of matrix-isolation techniques (metal vapor, 10–30 K, xenon matrix, high vacuum): detection of chemisorption complexes

– Proof of metal oxo compounds (Mo,V) as oxidation catalysts

– IR bands of chemisorbed NO for the characterization of supported metal catalysts, e. g., Mo/Al_2O_3, $Pt–Re/Al_2O_3$, cracking catalysts.

Electron Microscopy:

- Optical microscopes do not have sufficient resolution to picture the particle morphology. The smallest distance between two objects that can be resolved is described by the Rayleigh criterion:

$$d = 0.62\frac{\lambda}{n\sin\theta}$$

where d is the resolution, λ the wavelength, n the refractive index of the medium and θ the angle of the collected light.

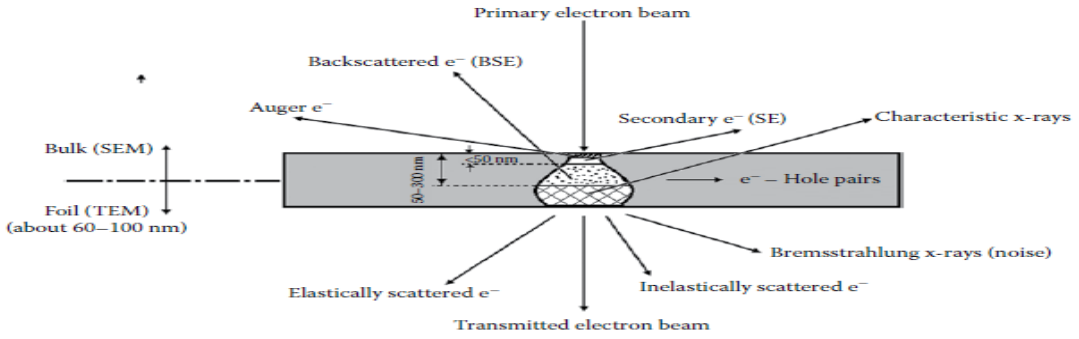
- Using an acceleration voltage of 200 keV gives the electrons a wavelength of ~1 pm which gives a much higher resolution compared to optical microscopes where the wavelength is ~100 nm.

From De Broglie relation**,** we can write:

$\lambda = h / \sqrt{2meV} = 12.3 / \sqrt{V}$ **; (for V in kV, λ in Å)**

V of 60 kV, λ = 0.05 Å

- Electron microscopy became one of the most important techniques to characterize the material's morphology on the nanometer to atomic scale. -There are two main types of electron microscopes: SEM and TEM. When a high-energy primary electron beam enters a specimen, electrons undergo elastic scattering and inelastic scattering along with transmitted beam (in case of thin foil). The interactions of primary electrons with a specimen's atoms generate several signals such as secondary electrons (SEs), backscattered electrons (BSEs), Auger electrons, Bremsstrahlung (continuous) x-rays, characteristic x-rays, etc. (Figure).

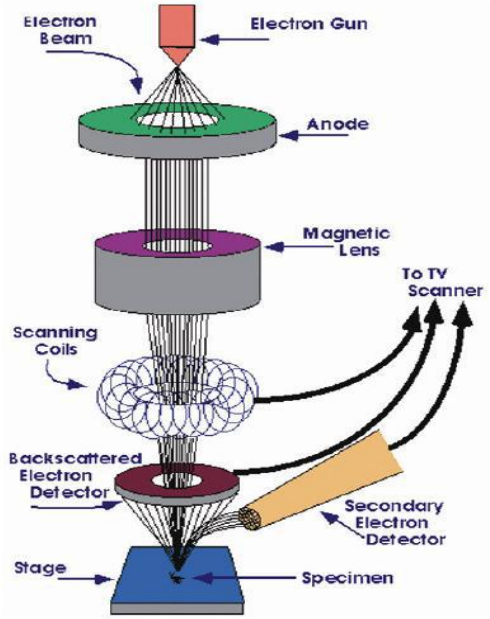


Typical schematic diagram showing the interaction zone between the primary electron beam and specimen surface

Scanning Electron Microscopy (SEM):

- When the electron beam (energy 5–30 keV) impinges on the specimen, many types of signals are generated. Most of the electrons are scattered at large angles (from 0° to 180°); these elastically scattered electrons are usually called BSE. Some electrons are scattered inelastically due to the loss in kinetic energy upon their interaction with orbital shell electrons, these electrons are called SEs.

- The SEs as well as BSEs are widely used for SEM topographical imaging. Both SEs and BSEs signals are collected when a positive voltage is applied to the collector screen in front of the detector. In contrast, when a negative voltage is applied on the collector screen, only BSEs signal is captured and the low-energy SEs is repelled. The electrons captured by the scintillator/photomultiplier are then amplified and used to form an image in the SEM.



-The spatial resolution of the SEM depends on various parameters: working distance, acceleration voltage (or wavelength of electrons), beam size, and probe current. A typical SEM has an image resolution of 5–10 nm, but a modern state-of-the-art SEM like field emission SEM is capable of providing an image resolution of 1 nm.

-SEM is often combined with energy-dispersive x-ray (EDX) spectroscopy detector to get the elemental composition of the nanomaterials.

- A specimen for SEM analysis can be in any form (powder or pieces) and size, which is easily fitted on specimen holder.

- SEM requires electrically conductive specimen to avoid the surface charging of specimens, and dehydration for biological samples to prevent the destroying of the surface morphology.

-However, the presence of a metal oxide layer and insulating phases in metallic specimens may also generate surface charging. The charging of the specimen can be prevented by applying a thin (i.e., 10–20 nm) conductive film onto specimen surfaces by either vacuum evaporation or sputtering in a vacuum chamber. Gold and gold–palladium are commonly used as the target material.

- Alternatively, conductive coating is not needed if one uses very low-accelerating voltages (0.5–2.0 kV), depending upon the sample material. In such cases, the electron hitting the sample surface and those being ejected (SEs and BSEs, respectively) balance and thus there is no charge accumulation on the surface. The technique, also called low-voltage scanning electron microscopy (LVSEM), is now being widely used for polymers.

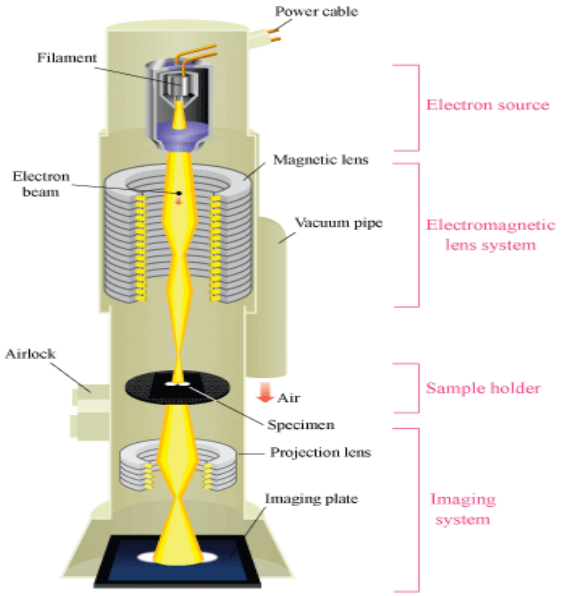
Transmission Electron Microscopy:

-TEM utilizes high energy (100 keV to 1 MeV) electron beam to provide morphology, composition, and crystallographic information from a sample.

- In TEM, images are produced by focusing an electron beam on a very thin specimen (thickness of 60–100 nm) which is partially transmitted and carries information about the specimen.

-As the electrons travel through the sample, they are either scattered or are transmitted unaffected through the sample. The diffracted electrons, deflected away from the optical axis of the microscope, are blocked using an aperture and thus the transmitted electron beam generates a contrast on the fluorescent screen or a charge-coupled-device (CCD) camera, and generates an image with varying contrast.

- Modern high-resolution TEM (HRTEM) goes down to a resolution better than 0.2 nm (i.e., <0.2 nm). The higher the operating voltage of a TEM instrument, the greater is its lateral spatial resolution. A TEM with 400 keV has point-to-point resolutions better than 0.2 nm. TEM can offer magnification up to 5 million times at maximum.



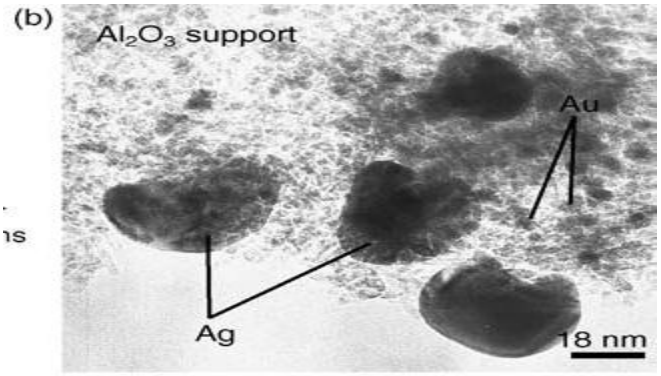
-TEM is used to determine directly the size of nanoparticles or nano-crystallites and the interfaces in nanocomposites. For example, the interface between the nickel (Ni) with size of ca. 30–50 nm and titanium nitride (TiN) has been clearly observed.

- HRTEM is used to determine the size of the extremely small nanoparticle and the distance between the atomic planes. For example, cubic titanium carbide (Ti44C56) nanoparticle with size of ca. 12–18 nm has the atomic planes distance of 0.25 nm for the (111) planes.

- The TEM can provide information on the particle size, size distribution, and morphology of the nanoparticles. This is the only technique in which the individual particles are directly observed and measured.

- TEM can also be used to see degree of dispersion or aggregation of the nanoparticles (or particulates) in the matrix.

- HRTEM can provide thickness of the shell on the core-shell NPs, due to the contrast differ form the core and shell.
- Similar to SEM, the TEM attached with EDX detector makes it suitable for analytical techniques including elemental mapping.
- A conventional TEM can magnify ·300 000, with a resolution of 0.5 nm, whereas a high-resolution apparatus can magnify ·1000 000, giving atomic resolution.
- The contrasts in the image reflect the different scattering processes, and the interactions between the transmitted electrons and different atoms in the sample (typically, the metal has a much higher electron density than the support, and appears darker in the TEM image). Thus, supported metal particles appear as dark spots, while the support itself appears as a lighter background (see the example of Au and Ag nanoparticles supported on g-alumina in Figure 4.17b).



TEM image (showing gold and silver nanoparticles supported on ɣ-alumina

Atomic Force Microscopy (AFM):

An AFM operates by measuring the attractive or repulsive forces between the fine tip with size of the order of nanometers (20–50 nm or less) and sample. These forces vary with the spacing between the tip and sample and cause the cantilever to deflect when the cantilever drags the tip over

the sample. An image of the surface topography is generated by measuring the deflection of cantilever.

- The tip made of silicon or silicon nitride is attached to a cantilever. As the tip is brought into close proximity of a sample surface, van der Waals force between the tip and the sample leads to a deflection of the cantilever. The force is measured either by recording the bending of a cantilever on which the tip is mounted (i.e., contact mode) or by measuring the change in resonance frequency due to the force (i.e., tapping mode).

- For two bodies held at a distance of one to several tens of nanometers, van der Waals forces usually dominate the interaction force between them. Van der Waals forces (F) are usually attractive and rapidly increase as atoms, molecules, or bodies approach one another. As a first approximation, the force can be described by using the following equation:

$$F = \frac{-H \times R}{(6 \times d^2)}$$

where H is the material-dependent Hamaker constant (is a physical constant that can be defined for a van der Waals body–body interaction), R is the radius of the tip, and d is the distance between the tip and the specimen surface.

- The forces can be derived from the deflection Δz of a cantilever (or spring), on which one of the material sheets is mounted. According to Hooke's law, the force can be represented by the following equation:

$$F = c\Delta z$$
$$(c = E \times w \times t^3 / 4l)$$

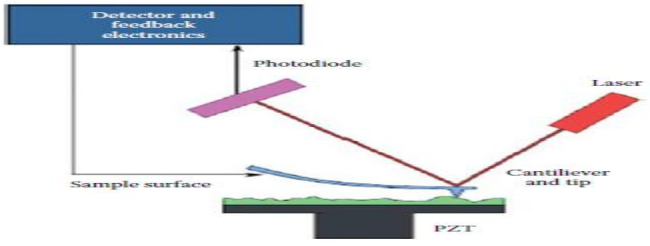
where E is Young's modulus (it is a mechanical property that measures the stiffness of a solid material and it is a constant for each materials)

and *w*, *t*, and *l* are the width, thickness, and length of the cantilever, respectively. For example, a cantilever made of aluminum foil with size of 4 mm (length) × 1 mm (width) × 10 μm (thick) would have a spring constant of ~1 N/m. This cantilever can measure a force as small as 10^{-10} N and thus can measure the deflection of ~0.1 nm easily. Precise control of the tip/sample interactions is now possible with PicoForce AFM.

In contrast to STM:

- AFM can also analyze the electrically insulating samples.
- It hardly needs any sample preparation.
- It has a drawback of investigating only the surface structures. For example, in case of oxidized semiconductor surface, the AFM shows the image of oxide.
- AFM monitors the force exerted between top surface of the sample and the bottom of the probe tip.

In AFM, a laser beam is focused on the top of the cantilever, which is reflected into photodiode. Differences in the reflected beam are measured by split photodiode and recorded as change in topography. The photodiode detector is able to resolve the probe motion <1 nm. The bending of the cantilever obeys Hooke's law for small displacements, and the force between the tip and the sample can be calculated. If the whole apparatus is raster-scanned across the surface, then an image of the specimen can be generated.



Schematic diagram of AFM

-AFM provides a 3-D surface profile of a sample without any special surface preparation and high vacuum.

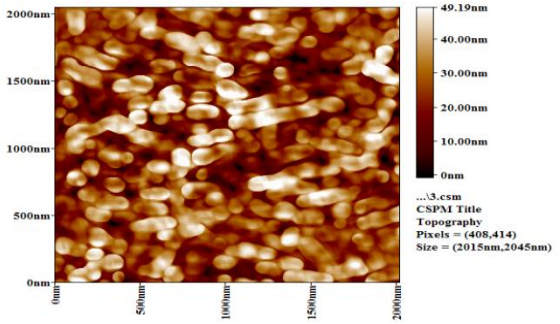
- It is a nondestructive technique, whereas electron microscopy uses high-energy electron beams which may destroy the organic parts of a hybrid sample.

-AFM shows a maximum height on the order of micrometers and a maximum area of around 100 × 100 μm. Its scanning speed is quite low compared to SEM.

-AFM provides atomic-level resolution because of the force of interaction between the atoms of the tip and the sample.

- In contrast to TEM and SEM, AFM reveals a range of information about the biomolecule, and the nanomaterial–biomolecule interaction on a single particle basis.

-AFM can examine nonconductive, wet, and soft samples in physiological environments.



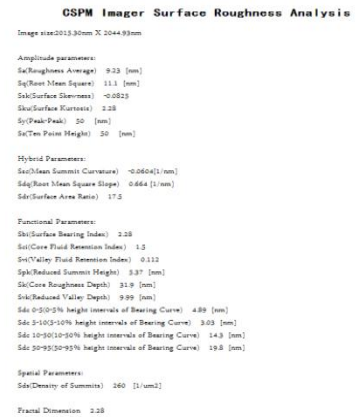

CSPM Imager Surface Roughness Analysis

Image size:2015.30nm X 2044.93nm

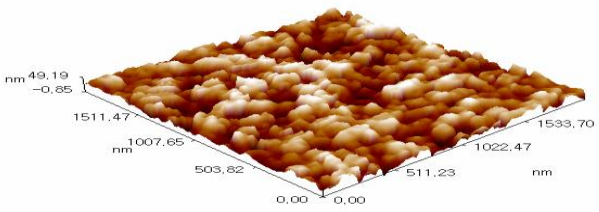
Amplitude parameters:
Sa(Roughness Average) 9.33 [nm]
Sq(Root Mean Square) 11.1 [nm]
Ssk(Surface Skewness) -0.0825
Sku(Surface Kurtosis) 2.28
Sy(Peak-Peak) 50 [nm]
Sz(Ten Point Height) 50 [nm]

Hybrid Parameters:
Ssc(Mean Summit Curvature) -0.0604[1/nm]
Sdq(Root Mean Square Slope) 0.664 [1/nm]
Sdr(Surface Area Ratio) 17.5

Functional Parameters:
Sbi(Surface Bearing Index) 2.28
Sci(Core Fluid Retention Index) 1.5
Svi(Valley Fluid Retention Index) 0.112
Spk(Reduced Summit Height) 5.37 [nm]
Sk(Core Roughness Depth) 31.9 [nm]
Svk(Reduced Valley Depth) 9.99 [nm]
Sds 0-5(0-5% height intervals of Bearing Curve) 4.89 [nm]
Sds 5-10(5-10% height intervals of Bearing Curve) 3.03 [nm]
Sds 10-50(10-50% height intervals of Bearing Curve) 14.3 [nm]
Sds 50-95(50-95% height intervals of Bearing Curve) 19.8 [nm]

Spatial Parameters:
Sds(Density of Summits) 260 [1/um2]

Fractal Dimension 2.28



SPM Scanning Probe Microscope

Granularity Cumulation Distribution Report

Sample:3	**Code:**Sample Code
Line No.:lineno	**Grain No.:**313
Instrument:CSPM	**Date:**2019-07-08

Avg. Diameter:76.92 nm	**<=10% Diameter:0 nm**
<=50% Diameter:70.00 nm	**<=90% Diameter:110.00 nm**

Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
50.00	11.18	11.18	95.00	3.51	79.55	140.00	0.32	97.44
55.00	10.54	21.73	100.00	3.51	83.07	145.00	0.32	97.76
60.00	7.67	29.39	105.00	3.19	86.26	155.00	0.32	98.08
65.00	9.27	38.66	110.00	1.92	88.18	160.00	0.96	99.04
70.00	9.27	47.92	115.00	1.92	90.10	170.00	0.32	99.36
75.00	10.54	58.47	120.00	2.88	92.97	180.00	0.32	99.68
80.00	5.11	63.58	125.00	3.19	96.17	190.00	0.32	100.00
85.00	6.71	70.29	130.00	0.32	96.49			
90.00	5.75	76.04	135.00	0.64	97.12