

ENGINEERING PHYSICS

MODULE – 5

Material Characterization Techniques and Instrumentation:**8 Hours**

Introduction to materials: Nanomaterials and nanocomposites. Principle, construction and working of X-ray Diffractometer, crystal size determination by Scherrer equation, Principle, construction, working and applications of Atomic Force Microscopy (AFM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Scanning tunnelling electron microscopy (STEM).

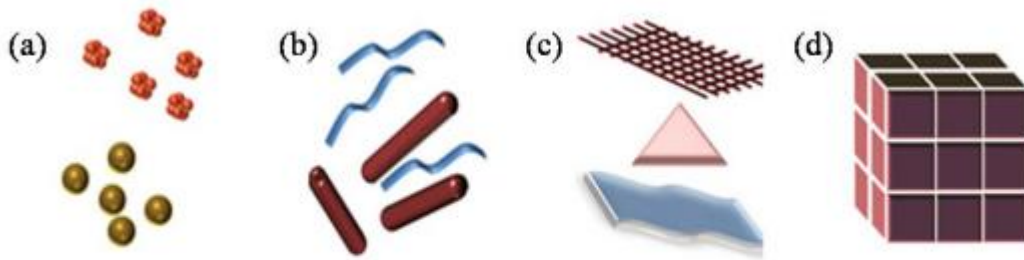
Nanomaterials

Materials having at least one dimension less than approximately 100 nanometers are classified as nanomaterials.

Nanomaterials are of increased interest because of the unique optical, magnetic, electrical, and other properties at this scale. These emergent properties have the potential for great impacts in electronics, medicine, and other fields.

Engineered nanomaterials 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. Also at the nano scale, quantum effects can become much more important in determining the materials properties and characteristics, leading to novel optical, electrical and magnetic behaviours.

Nanomaterials have extremely small size which having at least one dimension 100 nm or less. Nanomaterials can be nanoscale in one dimension (eg. surface films), two dimensions (eg. strands or fibres), or three dimensions (eg. particles). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nanotubes, dendrimers, quantum dots and fullerenes



Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.

Nanocomposite

Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm) or structures having nano-scale repeat distances between the different phases that make up the material.

The idea behind Nanocomposite is to use building blocks with dimensions in nanometre range to design and create new materials with unprecedented flexibility and improvement in their physical properties.

The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials. Size limits for these effects have been proposed:

1. <5 nm for catalytic activity
2. <20 nm for making a hard magnetic material soft
3. <50 nm for refractive index changes
4. <100 nm for achieving super paramagnetism, mechanical strengthening or restricting matrix dislocation movement

In mechanical terms, nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase or the aspect ratio (the ratio of its sizes in different dimensions). The reinforcing material can be made up of particles (e.g. minerals), sheets (e.g. exfoliated clay stacks) or fibres (e.g. carbon nanotubes or electrospun fibres). The area of the interface between the matrix and reinforcement phase(s) is typically an order of magnitude greater than for conventional composite materials. The matrix material properties are significantly affected in the vicinity of the reinforcement.

Ceramic-matrix nanocomposites

Ceramic matrix composites (CMCs) consist of ceramic fibers embedded in a ceramic matrix. The matrix and fibers can consist of any ceramic material, including carbon and carbon fibers. The ceramic occupying most of the volume is often from the group of oxides, such as nitrides, borides, silicides, whereas the second component is often a metal. Ideally both components are finely dispersed in each other in order to elicit particular optical, electrical and magnetic properties as well as tribological, corrosion-resistance and other protective properties.

Metal-matrix nanocomposites

Metal matrix nanocomposites can also be defined as reinforced metal matrix composites. This type of composites can be classified as continuous and non-continuous reinforced materials. One of the more important nanocomposites is Carbon nanotube metal matrix composites, which is an emerging new material that is being developed to take advantage of the high tensile strength and electrical conductivity of carbon nanotube materials. (eg. carbon nanotube metal matrix composites, boron nitride reinforced metal matrix composites and carbon nitride metal matrix composites).

Polymer-matrix nanocomposites

In the simplest case, appropriately adding nanoparticulates to a polymer matrix can enhance its performance, often dramatically, by simply capitalizing on the nature and properties of the nanoscale filler (nanofilled polymer composites). This strategy is particularly effective in yielding high performance composites, when uniform dispersion of the filler is achieved and the properties of the nanoscale filler are substantially different or better than those of the matrix. Nanoparticles such as graphene, carbon nanotubes, molybdenum disulfide and tungsten disulfide are being used as reinforcing agents to fabricate mechanically strong biodegradable polymeric nanocomposites for bone tissue engineering applications.

Magnetic nanocomposites

Magnetic nanocomposites can be utilized in a vast number of applications, including catalytic, medical, and technical. For example, palladium is a common transition metal used in catalysis reactions. Magnetic nanoparticle-supported palladium complexes can be used in catalysis to increase the efficiency of the palladium in the reaction.

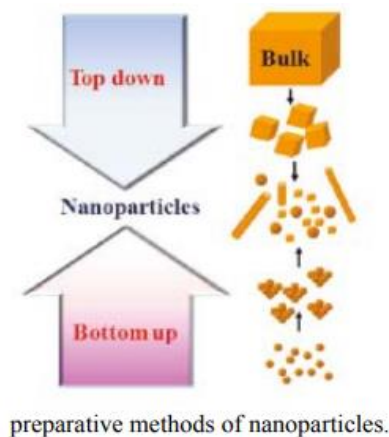
Magnetic nanocomposites can also be utilized in the medical field, with magnetic nanorods embedded in a polymer matrix can aid in more precise drug delivery and release.

Heat resistant nanocomposites

In the recent years nanocomposites have been designed to withstand high temperatures by the addition of Carbon Dots (CDs) in the polymer matrix. Such nanocomposites can be utilized in environments wherein high temperature resistance is a prime criterion

Nanomaterial - synthesis and processing

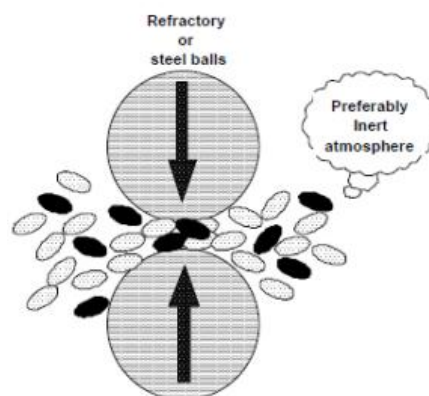
A nanometer is a billionth of a meter. Nanomaterials can be prepared by both the ‘bottom up’ or the ‘top down’ approaches. i.e. either to assemble atoms together or to dis-assemble (break, or dissociate) bulk solids into finer pieces until they are constituted of only a few atoms.



Examples:

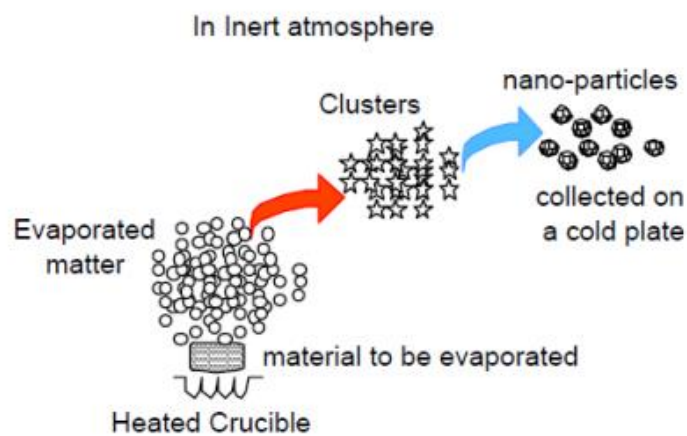
1. Mechanical grinding

Mechanical grinding or milling is a top down method and is typically achieved using high energy planetary ball. The energy transferred to the powder from 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

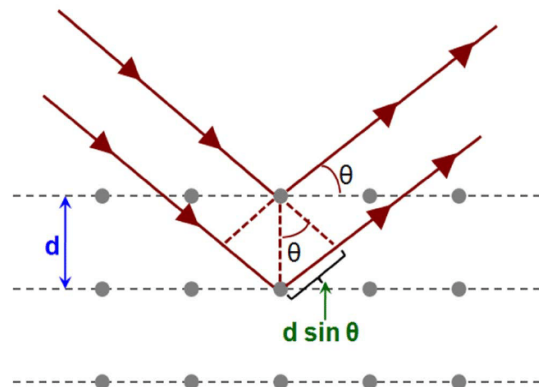


2. Physical Vapour Deposition

The simplest bottom up method to produce nanoparticles is by heating the desired material in a heat resistant crucible containing the desired material. This method is appropriate only for materials that have a high vapour pressure at the heated temperatures that can be as high as 2000°C. The atoms are evaporated into an atmosphere, which is either inert (e.g. He) or reactive (so as to form a compound). The hot atoms of the evaporated matter lose energy by collision with the atoms of the cold gas and undergo condensation into small clusters via homogeneous nucleation. And are collected on a cold plate.



Bragg's law



Suppose, an X-ray beam is incident on a solid, making an angle θ with the planes of the atoms. These X-rays are diffracted by different atoms and the diffracted rays interfere. In certain directions, the interference is constructive and we obtain strong reflected X-rays. The analysis shows that there will be a strong reflected X-ray beam only if

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

where n is an integer. this equation is known as Bragg's law.

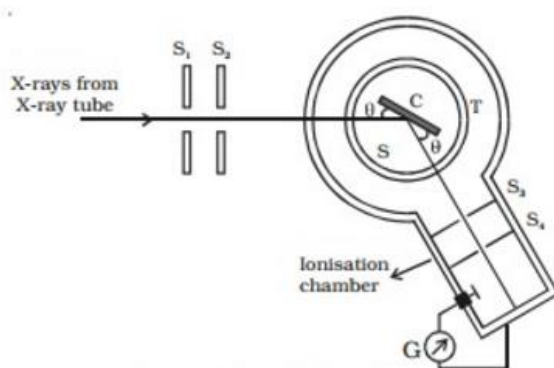
Braggs spectrometer

Braggs spectrometer used to determine the wavelength of X rays is shown in Fig. Braggs spectrometer is similar in construction to an ordinary optical spectrometer.

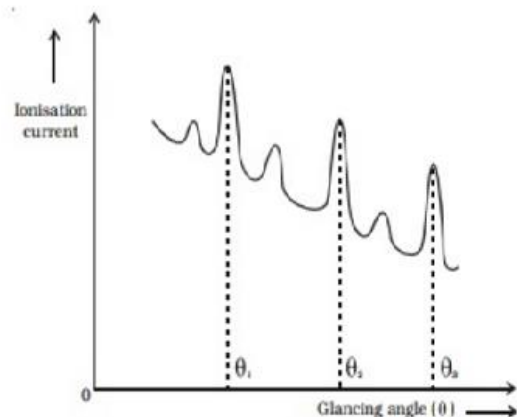
Xrays from an X-ray tube are made to pass through two fine slits S_1 and S_2 which collimate it into a fine pencil. This fine X-ray beam is then made to fall upon the crystal C (usually sodium chlo- ride crystal) mounted on the spectrometer table. This table is capable of rotation about a vertical axis and its rotation can be read on a circular graduated scale S . The reflected beam after passing through the slits S_3 and S_4 enters the ionization chamber. The X-rays entering the ionization chamber ionize the gas which causes a current to flow between the electrodes and the current can be measured by galvanometer G . The ionization current is a measure of the intensity of X-rays reflected by the crystal.

The ionization current is measured for different values of glancing angle . A graph is drawn between the glancing angle and ionization current.

For certain values of glancing angle, the ionization current increases abruptly. The first peak corresponds to first order, the second peak to second order and so on. From the graph, the glancing angles for different orders of reflection can be measured. Knowing the angle and the spacing d for the crystal, wavelength of Xrays can be determined.



Bragg's spectrometer



Plot of glancing angle and ionisation current

X-ray diffraction analysis (XRD) is a technique used in materials science to determine the crystallographic structure of a material. XRD works by irradiating a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that leave the material

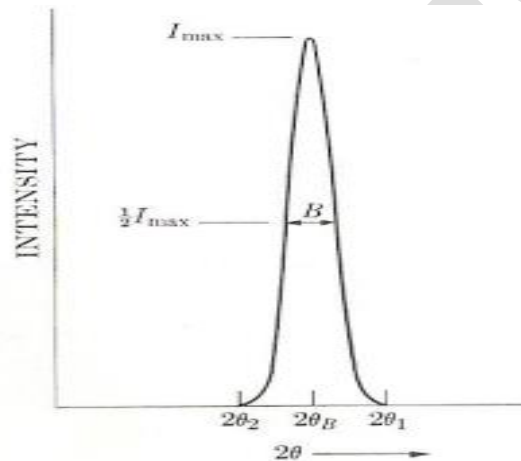
Scherrer formula

$t = 0.9 \lambda / B \cos \theta_B$ is known as the Scherrer formula

where: t- particle size

B- Full width Half Maxima (FWHM)

θ_B - Bragg's angle.



It is used to estimate the particle size of very small crystals from the measured width of their diffraction curves

Atomic Force Microscopy (AFM)

Atomic force microscopy or scanning force microscopy (SFM) is a very-high-resolution type of scanning probe microscopy (SPM), with demonstrated resolution on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction-limit. AFM consists of microscope cantilever with a sharp tip (probe) at its end used to scan the specimen surface. Instead of using an electrical signal, the AFM relies on forces between the atom on the tip and in the sample. The force present in the tip is kept constant and the scanning is done.

AFM Working Principle

The AFM principle is based on the cantilever/tip assembly that interacts with the sample; this assembly is also commonly referred to as the probe. The AFM probe interacts with the substrate through a raster scanning motion. The up/down and side to side motion of the AFM tip as it scans along the surface is monitored through a laser beam reflected off the cantilever. This reflected laser beam is tracked by a position sensitive photo-detector (PSPD) that picks up the vertical and lateral motion of the probe. The deflection sensitivity of these detectors has to be calibrated in terms of how many nanometers of motion correspond to a unit of voltage measured on the detector.

The detector of AFM measures the deflection (displacement with respect to the equilibrium position) of the cantilever and converts it into an electrical signal. The intensity of this signal will be proportional to the displacement of the cantilever.

Applications

The AFM has been applied to problems in a wide range of disciplines of the natural sciences, including solid-state physics, semiconductor science and technology, molecular engineering, polymer chemistry and physics, surface chemistry, molecular biology, cell biology, and medicine.

Applications in the field of solid state physics include

- (a) the identification of atoms at a surface,
- (b) the evaluation of interactions between a specific atom and its neighboring atoms, and
- (c) the study of changes in physical properties arising from changes in an atomic arrangement through atomic manipulation.

In molecular biology, AFM can be used to study the structure and mechanical properties of protein complexes and assemblies. For example, AFM has been used to image microtubules and measure their stiffness.

In cellular biology, AFM can be used to attempt to distinguish cancer cells and normal cells based on a hardness of cells, and to evaluate interactions between a specific cell and its neighboring cells in a competitive culture system. AFM can also be used to indent cells, to study how they regulate the stiffness or shape of the cell membrane or wall.

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is an analytical technique which uses Fourier transform to translate the raw data (interferogram) into the actual spectrum. This method is used to identify organic and inorganic materials in a given sample. This technique measures the absorption of infrared radiation by the sample material versus wavelength. The infrared absorption bands identify molecular components and structures.

Depending on the infrared absorption frequency range $600\text{--}4000\text{ cm}^{-1}$, the specific molecular groups prevailing in the sample will be determined through spectrum data in the automated software of spectroscopy. Fourier Transform Infrared Spectroscopy (FTIR) identifies chemical bonds in a molecule by producing an infrared absorption spectrum. The spectra produce a profile of the sample, a distinctive molecular fingerprint that can be used to screen and scan samples for many different components.

Principle: When a material is irradiated with infrared radiation, absorbed IR radiation usually excites molecules into a higher vibrational state. The wavelength of light absorbed by a particular molecule is a function of the energy difference between the at-rest and excited vibrational states. The wavelengths that are absorbed by the sample are characteristic of its molecular structure.

The electromagnetic spectrum consists of different regions corresponding to different energy (E), frequency (ν), and wavelength (λ) ranges as shown in Figure 1.

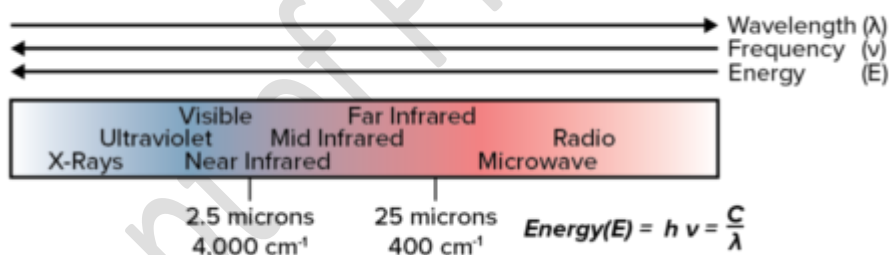


Figure 1

FTIR spectroscopy takes advantage of how IR light changes the dipole moments in molecules (Figure 2) that correspond to a specific vibrational energy.

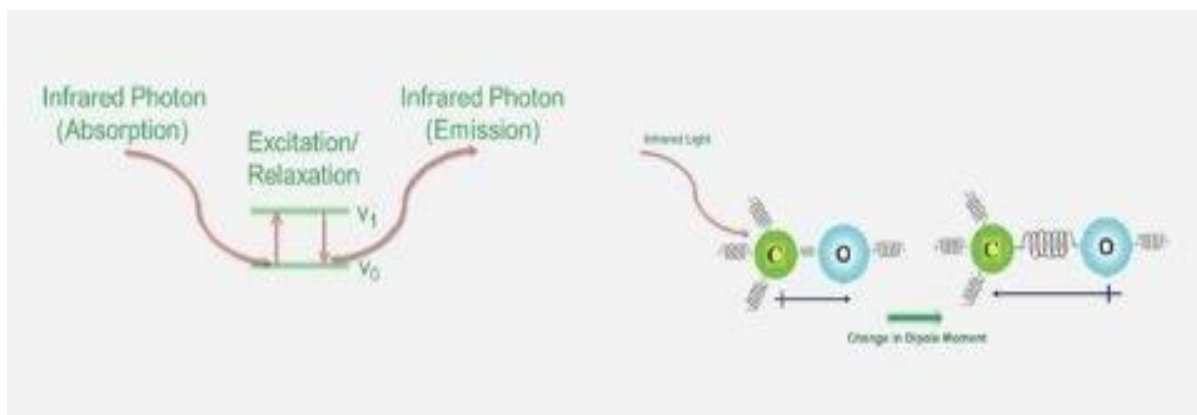


Figure 2

Vibrational energy corresponds to two variables: reduced mass (μ) and bond spring constant (k) and is given by the relation

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad [1]$$

The values of k are shown in Figure 3. There is an increase of 800 cm^{-1} from C-C, C=C to C≡C as shown in Figure 3. Substituting atoms in a C-C bond with nitrogen and oxygen causes a shift of 100 cm^{-1} (Figure 3). By looking at the two series, it can be seen that bond strength alters the wavenumbers more than mass.

C - C	1,400 cm^{-1}	Increasing k	$\tilde{\nu} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$	C - C	1,400 cm^{-1}	Increasing μ
C = C	1,600 cm^{-1}			C - N	1,350 cm^{-1}	
C ≡ C	2,200 cm^{-1}			C - O	1,300 cm^{-1}	

Figure 3

Since every functional group is composed of different atoms and bond strengths, vibrations are unique to functional groups, and classes of functional groups (e.g. O-H and C-H stretches appear around 3200 cm^{-1} and 2900 cm^{-1} , respectively). A correlation chart with various functional group vibrations can be seen in Figure 4. Since the collection of vibrational energy bands for all of the functional groups a molecule is unique to every molecule, these peaks can be used for identification using library searches of comprehensive sample databases.

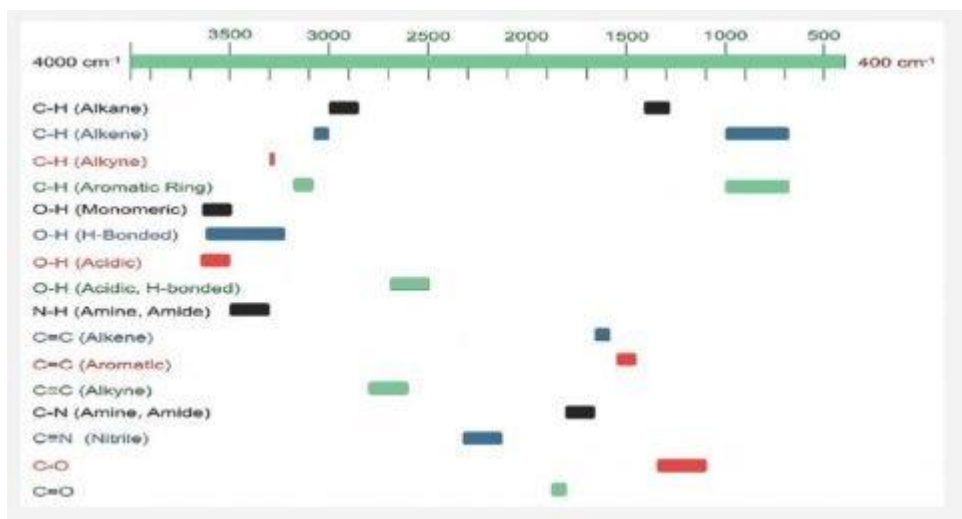


Figure 4

Construction:

The three major parts of an FTIR are the source, interferometer, and detector (Figure 5).

Source: The source is typically a broadband emitter such as a mid-IR ceramic source (50-7,800 cm^{-1}), a near-IR halogen lamp (2,200 – 25,000 cm^{-1}), or a far-IR mercury lamp (10-700 cm^{-1}).

Interferometer:

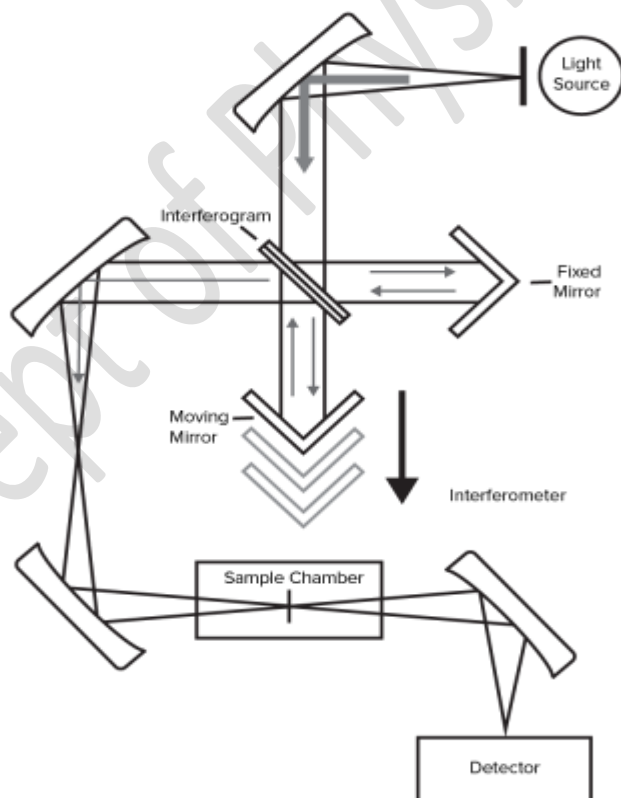


Figure 5

The interferometer is the heart of FTIR and consists of a beam splitter, a stationary mirror, a moving mirror, and a timing laser. The beam splitter splits the light from a source into two paths with half the light going to a stationary mirror and the other half going to a moving mirror. In many FTIR systems, the beam splitter is placed at 45 degrees to the incident beam, but for high throughput applications, a low angle interferometer is preferred as the P and S polarizations converge close to the Brewster's Angle. Common beam splitter materials are KBr (375 – 12,000 cm^{-1}) for mid-IR, Quartz (4,000 – 25,000 cm^{-1}) for near-IR, and Mylar (30 – 680 cm^{-1}) for far-IR.

HeNe lasers are the industry norm due to their excellent wavelength stability compared to solid-state or diode lasers. This laser stability allows for spectral additions, library searches, and other functions that need high wavenumber accuracy.

Detectors: convert photons into measurable electric signals to be sent to the computer. Common detectors include room temperature DLaTGS (220 to 15,000 cm^{-1}) for routine analysis, liquid nitrogen cooled MCT (450 to 12,000 cm^{-1}) for high sensitivity applications, Si-photodiodes (10,000 to 25,000 cm^{-1}) for visible and near-IR, and silicon bolometers (10 to 650 cm^{-1}) for the far-IR.

Working:

FTIR analysis measures the range of wavelengths in the infrared region that are absorbed by a material. This is accomplished through the application of infrared radiation (IR) to samples of a material. The sample's absorbance of the infrared light's energy at various wavelengths is measured to determine the material's molecular composition and structure.

The beams from the moving and stationary mirrors are recombined back at the beam splitter and steered toward the sample. The difference in the path of the mirrors causes constructive and destructive interference over the course of time it takes for the moving mirror to make a pass. The signal versus mirror position (and, thus, time) is called an interferogram. A laser is used to determine the position of the moving mirror using the precisely known wavelength of the laser (Figure 6).

The light then is steered through the sample and onto a detector where the time domain signal is converted to the frequency domain via a Fast Fourier Transform. The power of the beam (P_0) is attenuated by the sample by absorbance by the sample (P_0), Figure 7. The relationship between power, transmittance, and absorbance is given in Figure 7.

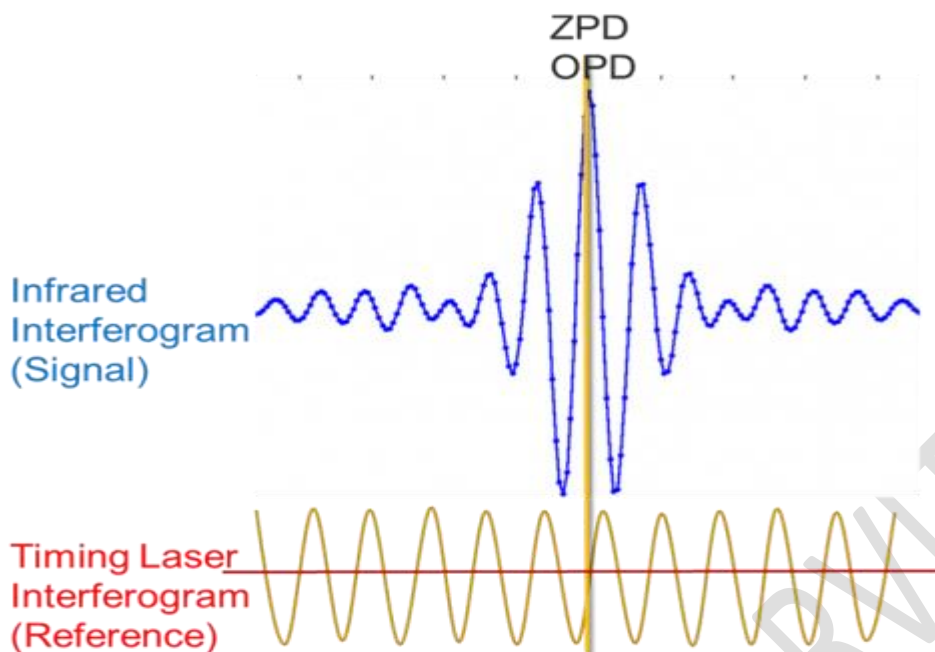


Figure 6

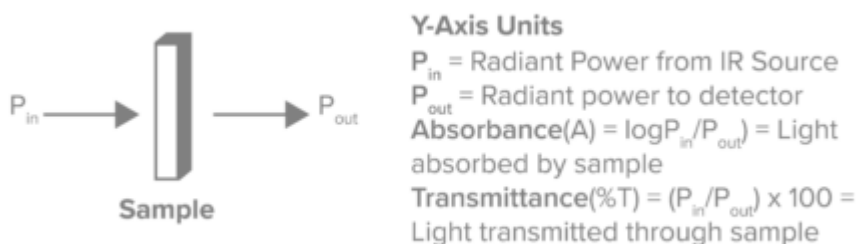


Figure 7

Unknown materials are identified by searching the spectrum against a database of reference spectra. Materials can be quantified using the FTIR materials characterization technique as long as a standard curve of known concentrations of the component of interest can be created. FTIR Analysis can be used to identify unknown materials, additives within polymers, surface contamination on a material, and more. The results of the tests can pinpoint a sample's molecular composition and structure.

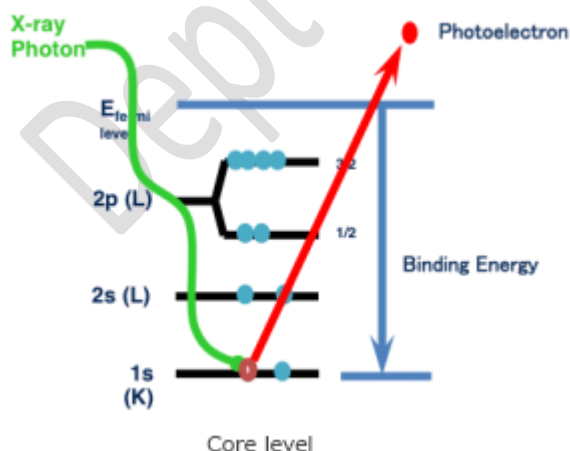
A simple device called an interferometer is used to identify samples by producing an optical signal with all the IR frequencies encoded into it. The signal can be measured quickly.

Then, the signal is decoded by applying a mathematical technique known as Fourier transformation. This computer-generated process then produces a mapping of the spectral information. The resulting graph is the spectrum which is then searched against reference libraries for identification. With the microscope attachment, samples as small as 20 microns can be analysed. This allows quick and cost-effective identification of unknown particles, residues, films or fibres. FTIR testing can also measure levels of oxidation in some polymers or degrees of cure in other polymers as well as quantifying contaminants or additives in materials.

Application: FTIR is an effective analytical instrument for detecting functional groups and characterizing covalent bonding information. FTIR spectrometers (Fourier Transform Infrared Spectrometer) are widely used in organic synthesis, polymer science, petrochemical engineering, pharmaceutical industry and food analysis. In addition, since FTIR spectrometers can be hyphenated to chromatography, the mechanism of chemical reactions and the detection of unstable substances can be investigated with such instruments.

X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is used to determine quantitative atomic composition and chemistry. A sample is irradiated with monochromatic x-rays, resulting in the emission of photoelectrons whose energies are characteristic of the elements within the sampling volume. An XPS spectra is created by plotting the number of electrons versus their binding energy.



Principle: Based on Einstein's photoelectric effect. Many materials emit electrons when light shines upon them and ore electrons with kinetic energy E_k are ejected by incident X-rays.

$$E_K = h\nu - E_b - \phi_{sp}$$

E_K = kinetic energy

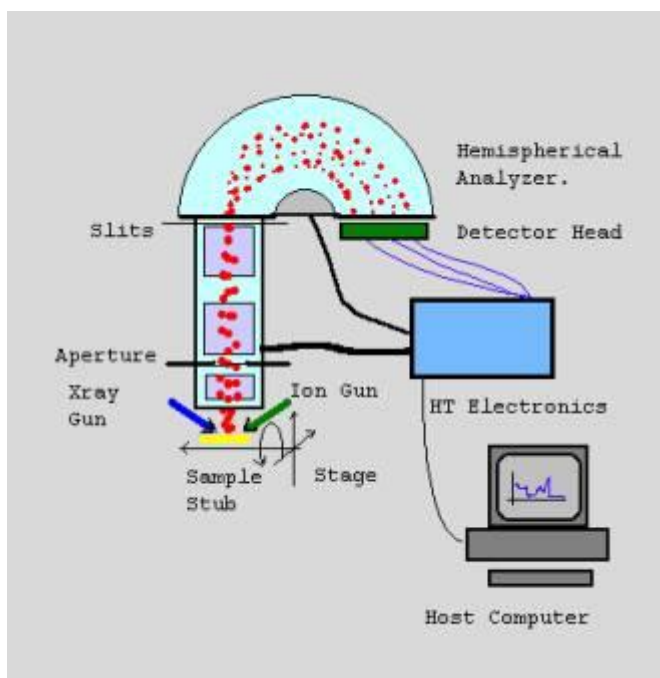
E_b = binding energy

h = Planck's constant

ν = frequency of X-rays

ϕ_{sp} = spectrometer work function

Construction: The logical components of an XPS instrument are shown below.

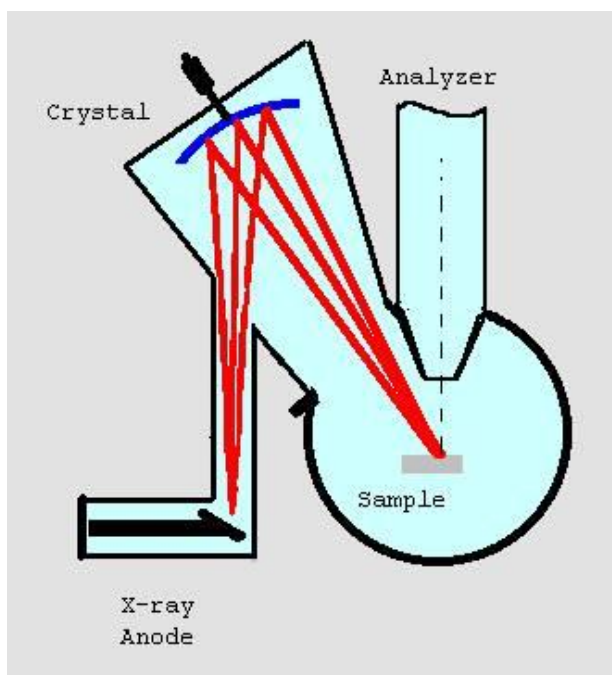


X-rays illuminate an area of a sample causing electrons to be ejected with a range of energies and directions. The electron optics, which may be a set of electrostatic and/or magnetic lens units, collect a proportion of these emitted electrons defined by those rays that can be transferred through the apertures and focused onto the analyzer entrance slit. Electrostatic fields within the hemispherical analyzer (HSA) are established to only allow electrons of a given energy (the so-called Pass Energy PE) to arrive at the detector slits and onto the detectors themselves.

Electrons of a specific initial kinetic energy are measured by setting voltages for the lens system that both focus onto the entrance slit the electrons of the required initial energy and retards their velocity so that their kinetic energy after passing through the transfer lenses matches the pass energy of the hemispherical analyzer. To record a spectrum over a range of initial excitation

energies it is necessary to scan the voltages applied to these transfer lenses and the prescription for these lens voltages is known as the set of lens functions. These lens functions are typically stored in some configuration file used by the acquisition system.

A hemispherical analyzer and transfer lenses can be operated in two modes, namely, Fixed Analyzer Transmission (FAT), also known as Constant Analyzer Energy (CAE), or Fix Retard Ratio (FRR) also known as Constant Retard Ratio (CRR). In FAT mode, the pass energy of the analyzer is held at a constant value and it is entirely the job of the transfer lens system to retard the given kinetic energy channel to the range accepted by the analyzer. Most XPS spectra are acquired using FAT.



Monochromator

Energy Resolution

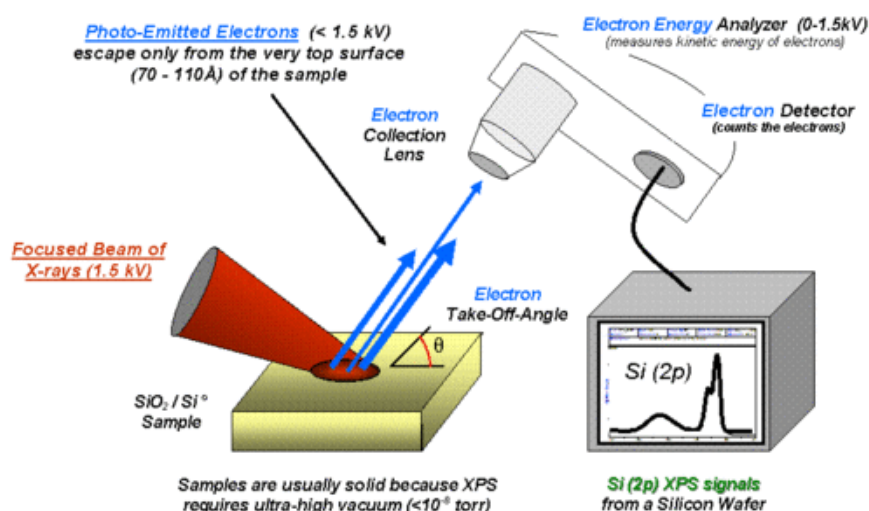
A number of factors influence the energy resolution achieved within a spectrum. The diameter of the analyzer, the pass energy and the spread of energies in the X-ray source play a major role in determining the full width half maximum (FWHM) for a given photoelectric line. Sample dependent considerations are also important where localized charging may broaden lines regardless of the precision built into the instrument and therefore effective charge neutralization is an important part of any system.

Small Area Analysis

Electrons are dispersed through the hemispherical analyzer so that different energy electrons arrive at different positions in the radial direction; further, they are also spatially dispersed

around the circumference of the sphere. This relationship has been exploited by the Scienta ESCA300 and SPECS delay-line-detector systems, where images can be recorded that show both energy dispersion and spatial information in the form of sets of line-scans. VG ESCALABS 220i instruments use additional lenses at the entrance slit and before an imaging detector, which perform a Fourier transform and the inverse operation to allow an energy-resolved stigmatic image to be recorded through a hemispherical analyzer whilst operating in deflection mode.

Working:



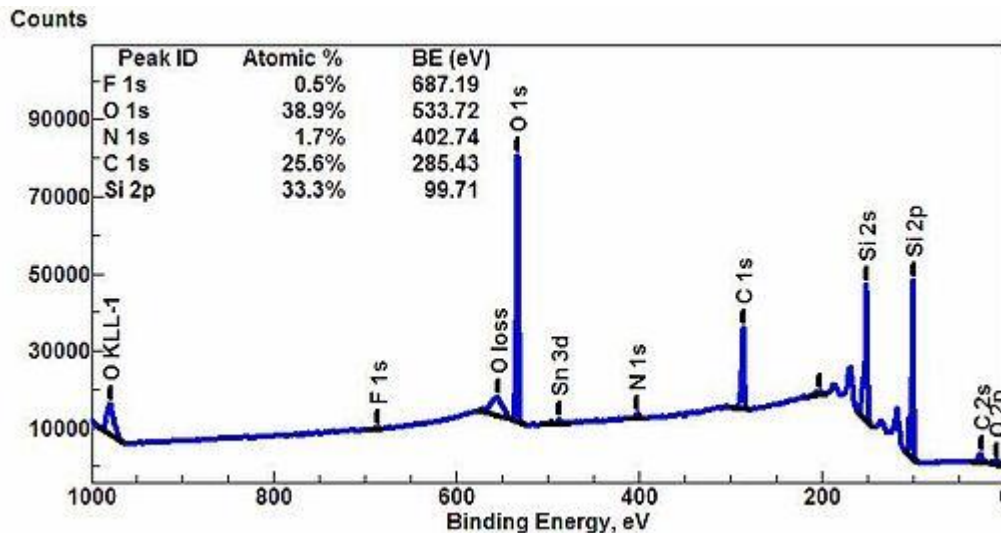
X-rays (photons) are shot onto a sample, and when electrons in the sample absorb enough energy, they are ejected from the sample with a certain kinetic energy. The energy of those ejected electrons is analyzed by a detector and a plot of these energies and relative numbers of electrons is produced. Electrons of different energies follow different paths through the detector which allows the computer to differentiate the electrons and produce the spectra seen below.

Atoms present in compound being tested by XPS are determined according to the equation:

$$E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi)$$

Here, binding energy is the energy of an electron attracted to a nucleus; photon energy is the energy of X-ray photons being used by the spectrometer, and the kinetic energy is the energy of the ejected electrons from the sample. The work function is a correction factor for the instrument and correlates to the minimum energy required to eject an electron from an atom. The work function and photon energy are known and the kinetic energy is measured by the

detector. That leaves the binding energy as the only unknown, which can then be determined. As electrons are in orbitals farther from the nucleus, less energy is required to eject them, so the binding energy is lower for higher orbitals. Electrons contained in different subshells (s,p,d, etc.) have different energies as well. By showing the energy of electrons emitted from a material, XPS allows for the composition of a material to be determined.



Additionally, chemical shifts can be determined using XPS. This is owing to the fact that binding energy doesn't only depend on the shell of the electron. It also depends on the environment, that is, the bonds that the atom in question partake in. Therefore, a primary carbon would have a slightly different binding energy than a carboxyl carbon, for example.

Applications:

XPS is useful for investigating almost all surface problems. XPS data can be used to solve problems with existing surface interactions, or to investigate new materials. It is used for **biological** applications like in the analysis of a Wound Dressing and the characterization of Chemical Gradients and Antibody Immobilization. It is used in surface Chemical-State Analysis of catalyst. It is used in Defect Analysis and to analyze Contact Lens Samples. It is used in the surface analysis of oxides, Polymers and in the field of microelectronics.

Scanning Electron Microscopy (SEM)

Principle: A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The

electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample. The electron beam is scanned in a raster scan pattern (raster scanning, is the rectangular pattern of image capture and reconstruction in television) , and the position of the beam is combined with the intensity of the detected signal to produce an image. In the most common SEM mode, secondary electrons emitted by atoms excited by the electron beam are detected using a secondary electron detector. The number of secondary electrons that can be detected, and thus the signal intensity, depends, among other things, on specimen topography. Some SEMs can achieve resolutions better than 1 nanometer. Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples. Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyse the same materials repeatedly.

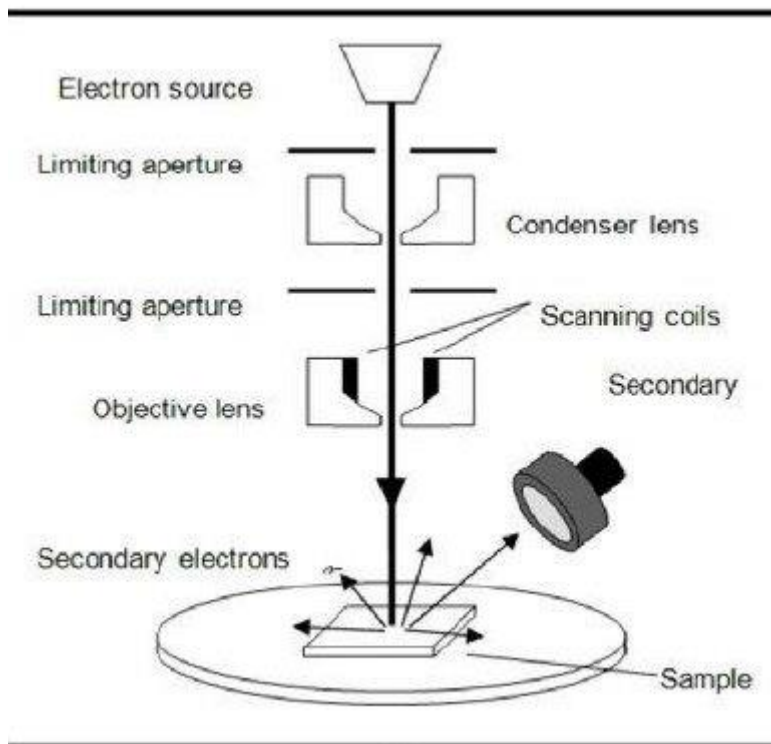
Construction: Essential components of all SEMs include the following:

Electron Source ("Gun"): electron microscopes employ an electron beam for imaging. In SEM, two types of electrons are primarily detected:

- backscattered electrons (BSE),
- secondary electrons (SE),

Backscattered electrons are reflected back after elastic interactions between the beam and the sample. Secondary electrons, however, originate from the atoms of the sample: they are a result of inelastic interactions between the electron beam and the sample.

The electron beam travels through the electron column, which consists of a set of lenses that focus the beam onto the sample surface. Electron microscope lenses can be electrostatic or magnetic, depending on whether they use an electrostatic field or a magnetic field to focus the electron beam.



Deflectors

Electrons are negatively charged particles and travel through the electron column at high energy and high speed. One way to deflect these particles is to let them travel through an electric field generated by two plates at potential $+U$ and $-U$, as shown in Fig. 1a.

Under the influence of the electric field, the electron is deflected at an angle that depends on the electron energy, the electric field applied in between the plates, and the length of the plates. The faster, or the more energetic the electron, the smaller the deflection angle. The higher the electric field and the longer the plates, the bigger the deflection angle. A device consisting of two plates at different potential is called a deflector.

Electron Lenses:

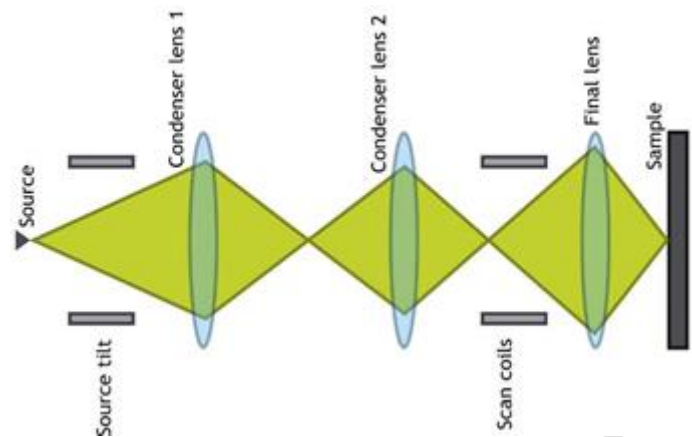
Electrostatic lenses consist of metallic plates connected to high voltage with an aperture that the electron beam travels through. Single-aperture lenses consist of a single metallic plate at high voltage and can often be found in electron sources.

lens.

Magnetic lenses

Magnetic lenses use the Lorentz force, that is proportional to the electron charge and velocity, to deflect electrons. Magnetic lenses consist of a metallic body (called the ferromagnetic circuit) that ends with two pole pieces.

The magnetic field is given by a coil positioned at the top of the ferromagnetic circuit, as shown in Fig. 3. The strength of the lens can be altered by varying the magnetic field B . This is done by modifying the geometry of the pole piece, namely the distance between the pole pieces, and the current flowing into the coils (excitation).



Magnetic lens schematic.

SEMs always have at least one detector (usually a secondary electron detector), and most have additional detectors. The specific capabilities of a particular instrument are critically dependent on which detectors it accommodates.

Infrastructure Requirements:

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

Room free of ambient magnetic and electric fields

Electron — matter interactions: the different types of signals which are generated

Working: At the heart of a scanning electron microscope is a high-energy electron source positioned above a series of condenser lenses and apertures which focus these electrons into a beam. The position of this beam is altered by sets of deflection or scanning coils before the final lens aperture. A sample is placed in the path of the electron beam which is continuously deflected into a raster scanning pattern by the deflection coils.

When electrons impact a surface, they generate secondary and backscattered electrons (BSE), as well as x-rays. BSE and x-ray detectors in the sample chamber acquire these signals, which are characteristic of the sample's elemental composition, morphology, and crystalline

structure. Scanning electron microscopy can subsequently be used for imaging the elemental composition of a sample surface and determining topographical sample features with a significantly increased resolving power.

Scanning electron microscopy can generate 3D chemical surface maps of a sample with a magnifying capacity of up to 50,000x. This offers high lateral resolution ranging from millimeters to nanometres ($>10\text{nm}$), while energy dispersive x-ray (EDX) analysis provides chemical detection limits of 1000 – 3000 parts per million (ppm).

Application: The SEM is routinely used to generate high-resolution images of shapes of objects (SEI) and to show spatial variations in chemical compositions: 1) acquiring elemental maps or spot chemical analyses using EDS, 2) discrimination of phases based on mean atomic number (commonly related to relative density) using BSE, and 3) compositional maps based on differences in trace element "activators" (typically transition metal and Rare Earth elements) using CL. The SEM is also widely used to identify phases based on qualitative chemical analysis and/or crystalline structure. Precise measurement of very small features and objects down to 50 nm in size is also accomplished using the SEM. Backscattered electron images (BSE) can be used for rapid discrimination of phases in multiphase samples. SEMs equipped with diffracted backscattered electron detectors (EBSD) can be used to examine microfabric and crystallographic orientation in many materials

Scanning electron microscopy is a robust analytical tool with a broad range of practical applications in the commercial, analytical, and industrial spaces. It is broadly used for quality control (QC) and good-bad testing of pharmaceutical products and has proven useful for detecting and identifying unknown contaminants in manufactured goods.

Transmission Electron Microscopy (TEM)

Transmission electron microscopes (TEM) are microscopes that use a particle beam of electrons to visualize specimens and generate a highly-magnified image. TEMs can magnify objects up to 2 million times. In order to get a better idea of just how small that is, think of how small a cell is. It is no wonder TEMs have become so valuable within the biological and medical fields.

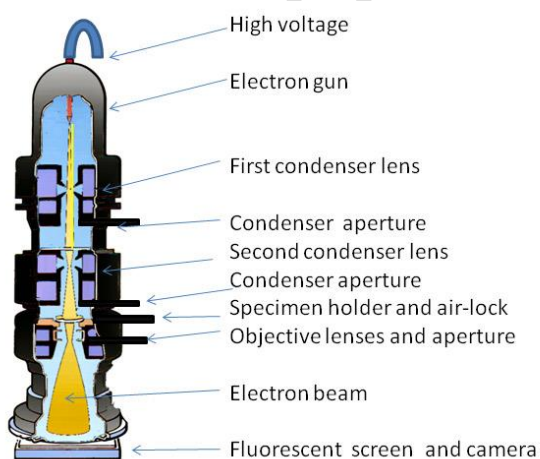
The transmission electron microscope is a very powerful tool for material science. A high energy beam of electrons is shone through a very thin sample, and the interactions between the

electrons and the atoms can be used to observe features such as the crystal structure and features in the structure like dislocations and grain boundaries. Chemical analysis can also be performed. TEM can be used to study the growth of layers, their composition and defects in semiconductors. High resolution can be used to analyze the quality, shape, size and density of quantum wells, wires and dots.

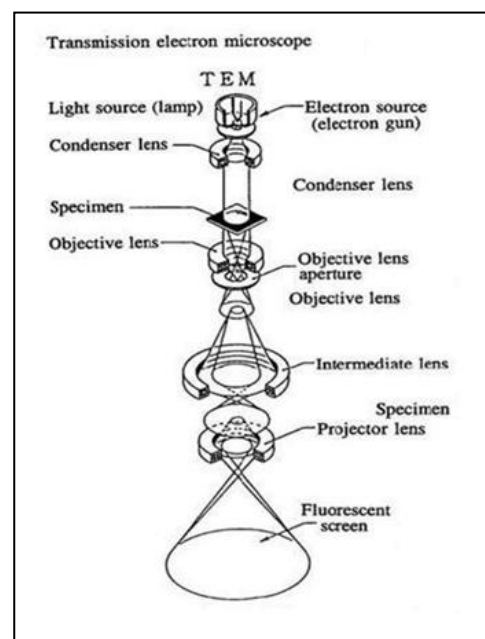
The TEM operates on the same basic principles as the light microscope but uses electrons instead of light. Because the wavelength of electrons is much smaller than that of light, the optimal resolution attainable for TEM images is many orders of magnitude better than that from a light microscope. Thus, TEMs can reveal the finest details of internal structure - in some cases as small as individual atoms.

Principle: TEMs employ a high voltage electron beam in order to create an image. An electron gun at the top of a TEM emits electrons that travel through the microscope's vacuum tube. Rather than having a glass lens focusing the light (as in the case of light microscopes), the TEM employs an electromagnetic lens which focuses the electrons into a very fine beam. This beam then passes through the specimen, which is very thin, and the electrons either scatter or hit a fluorescent screen at the bottom of the microscope. An image of the specimen with its assorted parts shown in different shades according to its density appears on the screen. This image can be then studied directly within the TEM or photographed. Below is shown a diagram of a TEM and its basic parts.

Construction:



Working:



In a transmission electron microscope, an electron gun, fires a beam of electrons. The gun accelerates the electrons to extremely high speeds using electromagnetic coils and voltages of up to several million volts.

The electron beam is focused into a thin, small beam by a condenser lens, which has a high aperture that eliminates high angle electrons. Having reached their highest speed, the electrons zoom through the ultra-thin specimen and parts of the beam are transmitted depending on how transparent the sample is to electrons.

The objective lens focuses the portion of the beam that is emitted from the sample into an image. Another component of the TEM is the vacuum system, which is essential to ensure electrons do not collide with gas atoms.

A low vacuum is first achieved using either a rotary pump or diaphragm pumps which enable a low enough pressure for the operation of a diffusion pump, which then achieves vacuum level that is high enough for operations. High voltage TEMS require particularly high vacuum levels and a third vacuum system may be used.

The image produced by the TEM, called a micrograph, is seen through projection onto a screen that is phosphorescent. When irradiated by the electron beam, this screen emits photons. A film camera positioned underneath the screen can be used to capture the image or digital capture may be achieved with a charge-coupled device (CCD) camera.

Imaging

The beam of electrons from the electron gun is focused into a small, thin, coherent beam by the use of the condenser lens. This beam is restricted by the condenser aperture, which excludes high angle electrons. The beam then strikes the specimen and parts of it are transmitted depending upon the thickness and electron transparency of the specimen. This transmitted portion is focused by the objective lens into an image on phosphor screen or charge coupled device (CCD) camera. Optional objective apertures can be used to enhance the contrast by blocking out high-angle diffracted electrons. The image then passed down the column through the intermediate and projector lenses, is enlarged all the way.

The image strikes the phosphor screen and light is generated, allowing the user to see the image. The darker areas of the image represent those areas of the sample that fewer electrons are transmitted through while the lighter areas of the image represent those areas of the sample that more electrons were transmitted through.

Typical accelerating voltages for a biological TEM range up to 125,000 Volts.

Abbe's equation: $d = 0.753/\lambda V^{1/2}$

d = resolution in nm

λ = half aperture angle

V = accelerating velocity

Resolution is defined as the distance at which two points or objects can be distinguished.

Therefore as λ approaches zero we say that the resolution is increased.

DeBroglie's formula:

$\lambda = h/mv$

h = Plank's constant

(6.626×10^{-23} ergs/ sec)

m = mass of the electron

v = electron velocity

DeBroglie's formula states that if the accelerating voltage is increased, electron velocity will increase as will resolution.

Application: This technology can be used in various industries from medical research where it is employed to investigate viruses and bacteria, for example, to forensic science, gemology and materials science.

What Are the Differences Between a TEM and a Light Microscope?

Although TEMs and light microscopes operate on the same basic principles, there are several differences between the two. The main difference is that TEMs use electrons rather than light in order to magnify images. The power of the light microscope is limited by the wavelength of light and can magnify something up to 2,000 times. Electron microscopes, on the other hand, can produce much more highly magnified images because the beam of electrons has a smaller wavelength which creates images of higher resolution. (Resolution is the degree of sharpness of an image.) Figure 2 compares the magnification of a light microscope to that of a TEM.

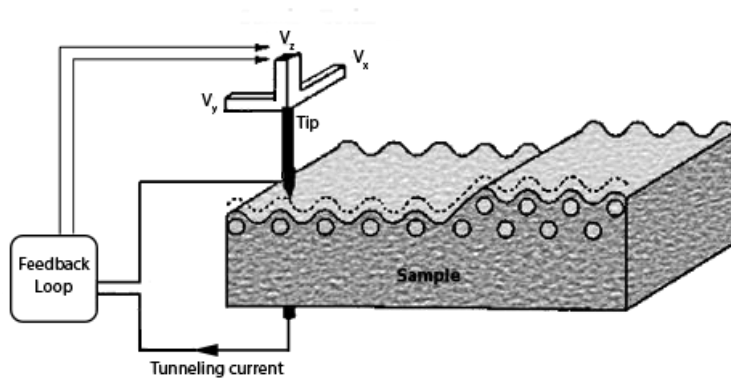
Scanning tunnelling electron microscopy (STEM)

Scanning tunneling microscopy (STM) is a powerful instrument that allows one to image the sample surface at the atomic level. Scanning transmission electron microscopy (STEM) combines the principles of transmission electron microscopy and scanning electron microscopy and can be performed on either type of instrument. Like TEM, STEM requires very thin samples and looks primarily at beam electrons transmitted by the sample. One of its principal advantages over TEM is in enabling the use of other of signals that cannot be spatially correlated in TEM, including secondary electrons, scattered beam electrons, characteristic X-rays, and electron energy loss.

Like SEM, the STEM technique scans a very finely focused beam of electrons across the sample in a raster pattern. Interactions between the beam electrons and sample atoms generate a serial signal stream, which is correlated with beam position to build a virtual image in which the signal level at any location in the sample is represented by the gray level at the corresponding location in the image. Its primary advantage over conventional SEM imaging is the improvement in spatial resolution.

Principle:

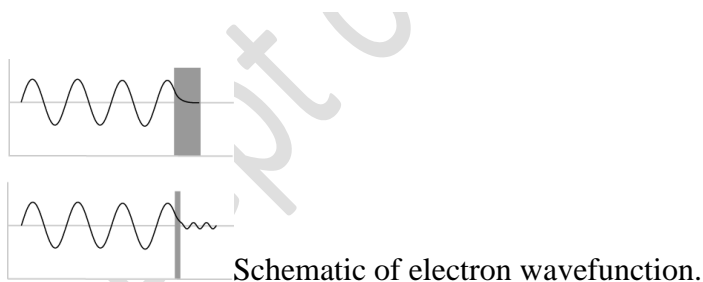
The STM is based on several principles. One is the quantum mechanical effect of tunneling. It is this effect that allows us to “see” the surface. Another principle is the piezoelectric effect. It is this effect that allows us to precisely scan the tip with angstrom-level control. Lastly, a feedback loop is required, which monitors the tunneling current and coordinates the current and the positioning of the tip. This is shown schematically below where the tunneling is from tip to surface with the tip rastering with piezoelectric positioning, with the feedback loop maintaining a current setpoint to generate a 3D image of the electronic topography:



Tunneling

Tunneling is a quantum mechanical effect. A tunneling current occurs when electrons move through a barrier that they classically shouldn't be able to move through. In classical terms, if you don't have enough energy to move "over" a barrier, you won't. However, in the quantum mechanical world, electrons have wavelike properties. These waves don't end abruptly at a wall or barrier, but taper off quickly. If the barrier is thin enough, the probability function may extend into the next region, through the barrier! Because of the small probability of an electron being on the other side of the barrier, given enough electrons, some will indeed move through and appear on the other side. When an electron moves through the barrier in this fashion, it is called tunneling.

Quantum mechanics tells us that electrons have both wave and particle-like properties. Tunneling is an effect of the wavelike nature.

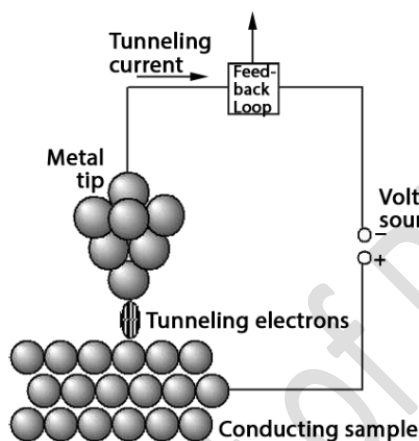


The top image shows us that when an electron (the wave) hits a barrier, the wave doesn't abruptly end, but tapers off very quickly – exponentially. For a thick barrier, the wave doesn't get past.

The bottom image shows the scenario if the barrier is quite thin (about a nanometer). Part of the wave does get through and therefore some electrons may appear on the other side of the barrier.

Because of the sharp decay of the probability function through the barrier, the number of electrons that will actually tunnel is very dependent upon the thickness of the barrier. The current through the barrier drops off exponentially with the barrier thickness.

To extend this description to the STM: The starting point of the electron is either the tip or sample, depending on the setup of the instrument. The barrier is the gap (air, vacuum, liquid), and the second region is the other side, i.e. tip or sample, depending on the experimental setup. By monitoring the current through the gap, we have very good control of the tip-sample distance.



Feedback loop and electron tunneling for scanning tunneling microscopy (STM).

Piezoelectric Effect

The piezoelectric effect was discovered by Pierre Curie in 1880. The effect is created by squeezing the sides of certain crystals, such as quartz or barium titanate. The result is the creation of opposite charges on the sides. The effect can be reversed as well; by applying a voltage across a piezoelectric crystal, it will elongate or compress.

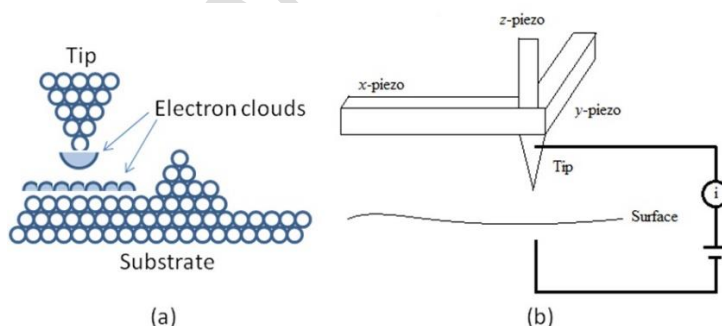
These materials are used to scan the tip in an scanning tunneling microscopy (STM) and most other scanning probe techniques. A typical piezoelectric material used in scanning probe microscopy is PZT (lead zirconium titanate).

Feedback Loop

Electronics are needed to measure the current, scan the tip, and translate this information into a form that we can use for STM imaging. A feedback loop constantly monitors the tunneling current and makes adjustments to the tip to maintain a constant tunneling current. These adjustments are recorded by the computer and presented as an image in the STM software. Such a setup is called a constant current image.

In addition, for very flat surfaces, the feedback loop can be turned off and only the current is displayed. This is a constant height image

The key physical principle behind STM is the tunneling effect. In terms of their wave nature, the electrons in the surface atoms actually are not as tightly bonded to the nucleons as the electrons in the atoms of the bulk. More specifically, the electron density is not zero in the space outside the surface, though it will decrease exponentially as the distance between the electron and the surface increases (Figure 8.3.38.3.3 a). So, when a metal tip approaches to a conductive surface within a very short distance, normally just a few Å, their perspective electron clouds will starting to overlap, and generate tunneling current if a small voltage is applied between them, as shown below



then we consider the separation between the tip and the surface as an ideal one-dimensional tunnelling barrier, the tunnelling probability, or the tunnelling current I , will depend largely on s , the distance between the tip and surface,

In a typical STM operation process, the tip is scanning across the surface of sample in x-y plain, the instrument records the x-y position of the tip, measures the tunneling current, and control the height of the tip via a feedback circuit. The movements of the tip in x, y and z directions are all controlled by piezo ceramics, which can be elongated or shortened according to the voltage applied on them.

Normally, there are two modes of operation for STM, constant height mode and constant current mode. In constant height mode, the tip stays at a constant height when it scans through the sample, and the tunneling current is measured at different (x, y) position. This mode can be applied when the surface of sample is very smooth. But, if the sample is rough, or has some large particles on the surface, the tip may contact with the sample and damage the surface. In this case, the constant current mode is applied. During this scanning process, the tunneling current, namely the distance between the tip and the sample, is settled to an unchanged target value. If the tunneling current is higher than that target value, that means the height of the sample surface is increasing, the distance between the tip and sample is decreasing. In this situation, the feedback control system will respond quickly and retract the tip. Conversely, if the tunneling current drops below the target value, the feedback control will have the tip closer to the surface. According to the output signal from feedback control, the surface of the sample can be imaged.

Construction:

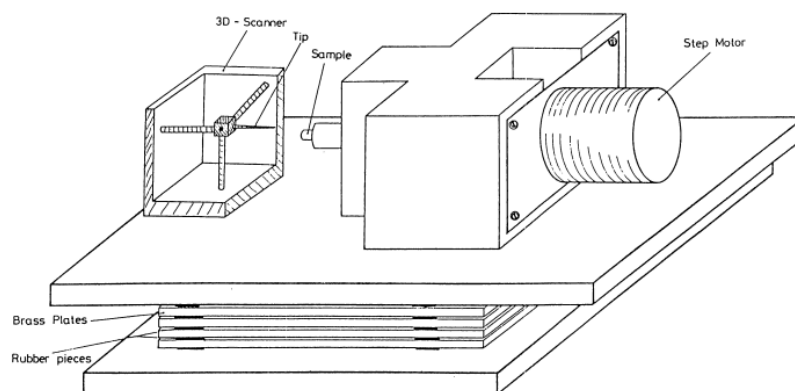
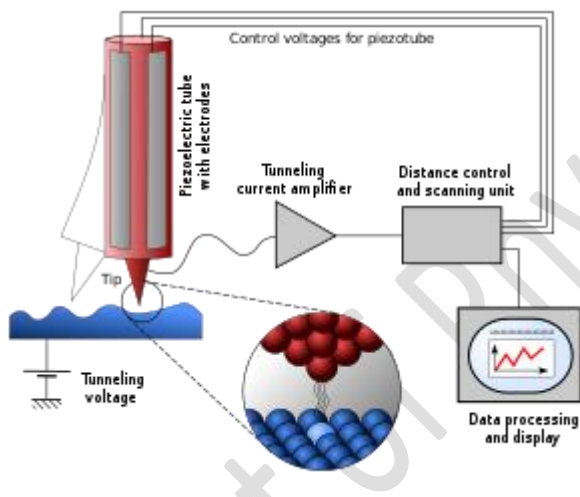
The main components of a scanning tunneling microscope are the scanning tip, piezoelectrically controlled height (z axis) and lateral (x and y axes) scanner, and coarse sample-to-tip approach mechanism. The microscope is controlled by dedicated electronics and a computer. The system is supported on a vibration isolation system.

The tip is often made of tungsten or platinum-iridium wire, though gold is also used. Tungsten tips are usually made by electrochemical etching, and platinum-iridium tips by mechanical shearing. The resolution of an image is limited by the radius of curvature of the scanning tip. Sometimes, image artefacts occur if the tip has more than one apex at the end; most frequently double-tip imaging is observed, a situation in which two apices contribute equally to the tunneling. While several processes for obtaining sharp, usable tips are known, the ultimate test of quality of the tip is only possible when it is tunneling in the vacuum. Every so often the tips

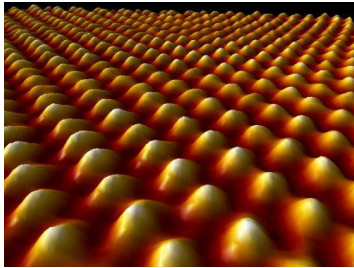
can be conditioned by applying high voltages when they are already in the tunneling range, or by making them pick up an atom or a molecule from the surface.

In most modern designs the scanner is a hollow tube of a radially-polarized piezoelectric with metallized surfaces. The outer surface is divided into four long quadrants to serve as x and y motion electrodes with deflection voltages of two polarities applied on the opposing sides. The tube material is a lead zirconate titanate ceramic with a piezo constant of some 5 nanometers per volt. The tip is mounted at the center of the tube. Because of some crosstalk between the electrodes and inherent nonlinearities, the motion is calibrated and voltages needed for independent x, y and z motion applied according to calibration tables.

Maintaining the tip position with respect to the sample, scanning the sample and acquiring the data is computer controlled. Dedicated software for scanning probe microscopies is used for image processing as well as performing quantitative measurements.

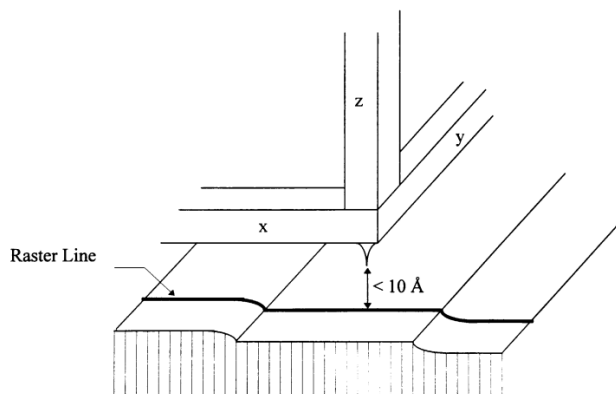


Working: The scanning tunneling microscope (STM) works by scanning a very sharp metal wire tip over a surface. By bringing the tip very close to the surface, and by applying an electrical voltage to the tip or sample, we can image the surface at an extremely small scale – down to resolving individual atoms.



With scanning transmission electron microscopy (STEM), a highly-focused electron probe is raster-scanned across the material, and various types of scattering are collected as a function of position. The transmitted electrons at high scattering angle can be collected to form high-resolution, chemically sensitive, atomic number (Z-) contrast images. The x-rays generated can be collected using an energy-dispersive X-ray spectroscopy (EDS) detector and used to form high spatial resolution compositional maps. Electron energy losses can be detected using a Gatan image filter (GIF) to map the compositional and electronic properties of materials.

The scanning tunneling microscope is essentially a very sensitive profilometer that uses quantum mechanical tunneling as the sensing method. A small metallic probe, usually made of tungsten or a platinum-iridium alloy, is scanned across a sample surface by piezoelectric transducers .



These transducers provide motion in three orthogonal directions. A saw tooth waveform rasters the probe in the x-direction, while a ramp voltage advances the raster signal in the y-direction. With this notation the probe-sample distance is on the z-axis. A third voltage adjusts this z distance so that the probe and sample remain separated by a few angstroms creating a small vacuum potential barrier. By overlapping the electron wavefunctions in the metallic probe and the sample, tunneling current flows when a bias is applied between the probe and sample. Amplifying this tunneling current and comparing it to a set point value creates a signal suitable for feedback on the voltage applied to the z piezoelectric transducer. This feedback loop created by the tunneling current and the z piezoelectric transducer voltage maintains a constant separation distance between the probe and the sample as scanning occurs, creating an array of z voltages that represent a contour plot of the sample.

Application: STM provides a powerful method to detect the surface of conducting and semi-conducting materials. Recently STM can also be applied in the imaging of insulators, superlattice assemblies and even the manipulation of molecules on surface. More importantly, STM can provide the surface structure and electric property of surface at atomic resolution, a true breakthrough in the development of nano-science. In this sense, the data collected from STM could reflect the local properties even of single molecule and atom. With these valuable measurement data, one could give a deeper understanding of structure-property relations in nanomaterials.

QUESTION BANK:

1. Differentiate between nanomaterials and nanocomposites.
2. Explain any three types of nanocomposites.
3. Explain top down and bottom up processes of nanomaterial synthesis with examples.
4. What is Bragg's law?
5. Explain the construction and working of Bragg's spectrometer.
6. Write down the Scherrer formula and explain it.
7. What is the principle of Atomic Force Microscopy?
8. Explain the construction and working of AFM.

9. Explain the principle, construction and working of a FTIR spectroscope.
10. Explain the principle, construction and working of an X-ray Photoelectron Spectroscope.
11. Explain the principle, construction and working of a scanning electron microscope.
12. Explain the working principles of electron lens and magnetic lens.
13. Explain the principle, construction and working of a transmission electron microscope.
14. Explain the principle, construction and working of a Scanning tunnelling microscope.