CHAPTER 5

CHARACTERIZATION TECHNIQUES

Nanoparticle characterization is necessary to establish understanding and control of nanoparticle synthesis and applications. Characterization is done by using a variety of different techniques, mainly drawn from materials science. Common techniques are electron microscopy (TEM, SEM), atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy, dual polarization interfererometry and nuclear magnetic resonance (NMR).

5.1 MORPHOLOGY ANALYSIS INSTRUMENTS

Common instruments used in the identification, analysis and description of the structure of nanomaterials are electron microscopy (TEM, SEM), atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD), etc.

5.1.1 Scanning Electron Microscopy (SEM)

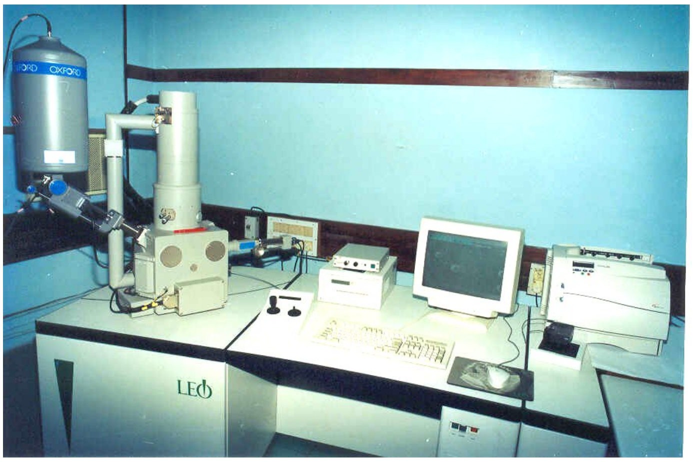

Fig 5.1 Scanning Electron Microscope.

Scanning Electron Microscopy is extremely useful for the direct observations of surfaces because they offer better resolution and depth of field than optical microscope. The Scanning Electron Microscope creates the magnified images by using electrons instead of light waves. The SEM shows very detailed 3-dimensional images at much higher magnifications than is possible with a light microscope. The images created without light waves are rendered black and white. In a very brief way SEM works under vacuum in a column where an electron gun emits a beam of high-energy electrons. This beam travels downward through a series of magnetic lenses designed to focus the electrons to a very fine spot. Near the bottom, a set of scanning coils moves the focused beam back and forth across the specimen, row by row. As the electron beam hits each spot on the sample, secondary electrons are knocked loose from its surface. A detector counts these electrons and sends the signals to an amplifier. The final image is built up from the number of electrons emitted from each spot on the sample. A detailed explanation of how a typical SEM functions:

1. The "Virtual Source" at the top represents the electron gun producing a stream of monochromatic electrons.
2. The stream is condensed by the first condenser lens (usually controlled by the "coarse probe current knob"). This lens is used to both form the beam and limit the amount of current in the beam. It works in conjunction with the condenser aperture to eliminate the high-angle electrons from the beam.
3. The condenser aperture constricts the beam by eliminating some high-angle electrons.
4. The second condenser lens forms the electrons into a thin, tight, coherent beam and is usually controlled by the "fine probe current knob".
5. A user selectable objective aperture further eliminates high-angle electrons from the beam.
6. A set of coils then "scan" or "sweep" the beam in a grid fashion (like a television), dwelling on points for a period of time determined by the scan speed (usually in the microsecond range).
7. The final lens, the Objective, focuses the scanning beam onto the part of the specimen desired.
8. When the beam strikes the sample (and dwells for a few microseconds) interactions occur inside the sample and are detected with various instruments.
9. Before the beam moves to its next dwell point these instruments count the number of interactions and display a pixel on a CRT whose intensity is determined by this number (the more reactions the brighter the pixel).

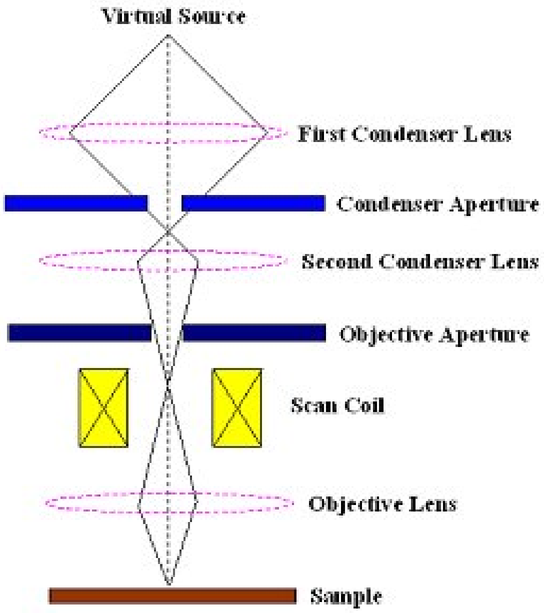

Fig 5.2 Schematic shows the diagram of Scanning Electron Microscope.

5.1.2 X-Ray Diffraction (XRD)

X-ray Generation & Properties X-rays are electromagnetic radiations with typical photon energies in the range of 100 eV - 100 keV. For diffraction applications, only short wavelength x-rays (hard x-rays) in the range of a few angstroms to 0.1 angstrom (1 keV -120 keV) are used. Because the wavelength of x-rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic x-rays can penetrate deep into the materials and provide information about the bulk structure. X-rays are produced generally by either x-ray tubes or synchrotron radiation. In a x-ray tube, which is the primary x-ray source used in laboratory x-ray instruments, x-rays are generated when a focused electron beam accelerated across a high voltage field bombards a stationary or rotating solid target. As electrons collide with atoms in the target and slow down, a continuous spectrum of x-rays are emitted, which are termed as Bremsstrahlung radiation. The high-energy electrons also eject inner shell electrons in atoms through the ionization process. When a free electron fills the shell, an x-ray photon with energy characteristic of the target material is emitted.

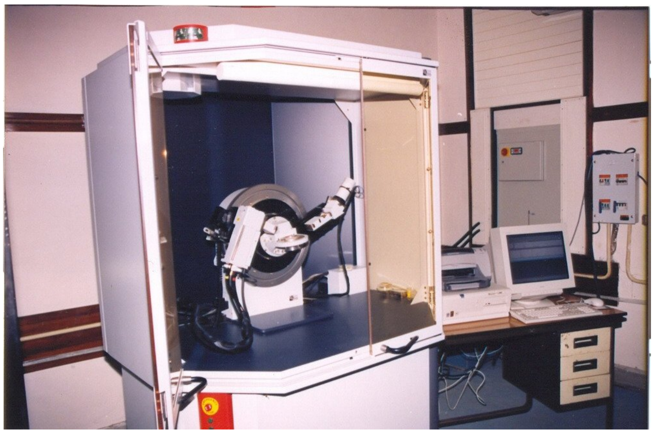

Fig 5.3 Advance X-Ray Diffractometer.

Lattice Planes and Bragg's Law

X-rays primarily interact with electrons in atoms. When x-ray photons collide with electrons, some photons from the incident beam will be deflected away from the direction where they original travel, much like billiard balls bouncing off one another. If the wavelength of these scattered x-rays did not change (meaning that x-ray photons did not lose any energy), the process is called elastic scattering (Thompson Scattering) in that only momentum has been transferred in the scattering process. These are the x-rays that we measure in diffraction experiments, as the scattered x-rays carry information about the electron distribution in materials. On the other hand, in the inelastic scattering process (Compton Scattering), x-rays transfer some of their energy to the electrons and the scattered x-rays will have different wavelength than the incident x-rays. Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern therefore allows one to deduce the distribution of atoms in a material. The peaks in an x-ray diffraction pattern are directly related to the atomic distances. Fig. 5.4 shows incident x-ray beam interacting with the atoms arranged in a periodic manner as shown in 2 dimensions. The atoms, represented as spheres in the figure, can be viewed as forming different sets of planes in the crystal.

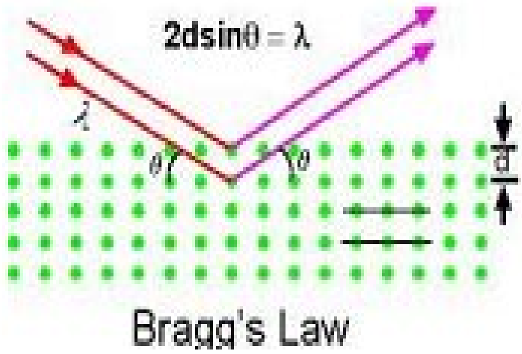

Fig 5.4 X-ray reflections from a crystal

For a given set of lattice plane with an inter-plane distance of d, the condition for a diffraction (peak) to occur can be simply written as: 2d sinθ = n λ, which is known as the Bragg's law. In the equation, λ is the wavelength of the x-ray, θ the scattering angle, and n an integer representing the order of the diffraction peak. The Bragg's Law is one of most important laws used for interpreting x-ray diffraction data. It is important to point out that Bragg's Law applies to scattering centers consisting of any periodic distribution of electron density. In other words, the law holds true if molecules or collections of molecules, such as colloids, polymers, proteins and virus particles, replace the atoms.

Powder Diffraction Powder XRD, Debye-Scherer method is particularly used for characterizing samples in the present work. As the name suggests, the sample is usually in a powdery form, consisting of fine grains of single crystalline material to be studied.

The technique is used also widely for studying particles in liquid suspensions or polycrystalline solids (bulk or thin film materials). The term 'powder' really means that the crystalline domains are randomly oriented in the sample. Therefore when the 2-D diffraction pattern is recorded, it shows concentric rings of scattering peaks corresponding to the various d spacing in the crystal lattice. The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material. For example, the diffraction lines of graphite would be different from diamond even though they both are made of carbon atoms. This phase identification is important because the material properties are highly dependent on structure. Powder diffraction data can be collected using either transmission or reflection geometry. Because the particles in the powder sample are randomly oriented, these two methods yield the same data.

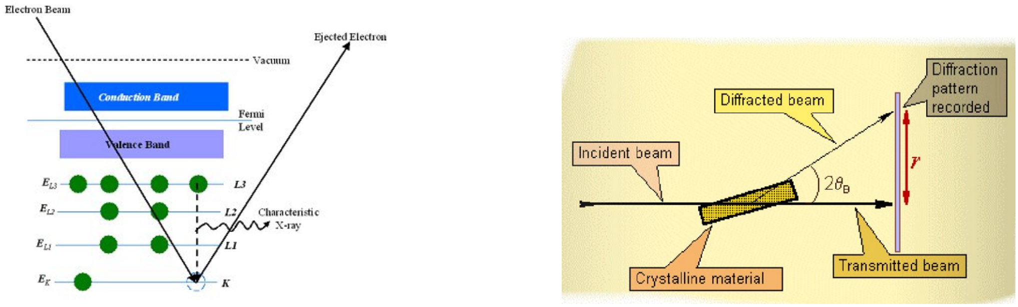

Fig 5.5 Schematic shows the processes that contribute to the generation of X-rays.

Scherer formula is used to calculate the X-ray particles diameter.

$$D = \frac{0.9 \times \lambda}{\beta \cos \theta}$$

Where D is crystallite size, λ is the wavelength of X-ray used, β is the full width at half maximum (FWHM) of diffraction peaks (in radians) and θ is the Bragg angle.

Applications of XRD

- XRD is a nondestructive technique.
- To identify crystalline phases and orientation.
- To determine structural properties such as lattice parameters (10-4Å), strain, grain size, expitaxy, phase composition, preferred orientation (Laue) order-disorder transformation, thermal expansion.
- To measure thickness of thin films and multi-layers.
- To determine atomic arrangement.
- Detection limits: ~3% in a two phase mixture; can be ~0.1% with synchrotron radiation

5.1.3 Atomic Force Microscopy (AFM)

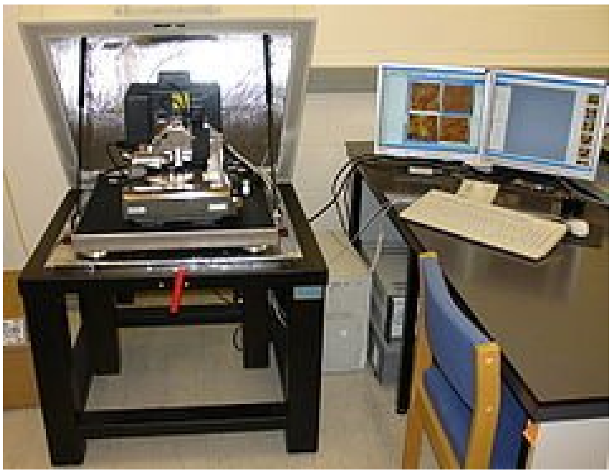

Fig 5.6 A commercial AFM setup

Atomic Force Microscopy (AFM) is a form of scanning probe microscopy (SPM) where a small probe is scanned across the sample to obtain information about the sample's surface. The information gathered from the probes interaction with the surface could be as simple as physical topography or as diverse as measurements of the material's physical, magnetic, or chemical properties. These data are collected as the probe is scanned in a raster pattern across the sample to form a map of the measured property relative to the X-Y position. Thus, the AFM microscopic image shows the variation in the measured property, e.g., height or magnetic domains, over the area imaged.

The AFM probe has a very sharp tip, often less than 100Å diameter, at the end of a small cantilever beam. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law.

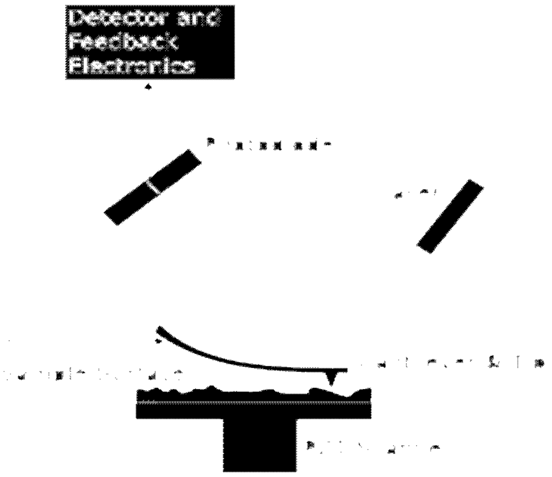

Fig 5.7 Block diagram of atomic force microscope

Typically, the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes as shown in Figure above. Using a Wheatstone bridge, strain in the AFM cantilever due to deflection can be measured, but this method is not as sensitive as laser deflection or interferometry.

If the tip was scanned at a constant height, a risk would exist that the tip collides with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample. Traditionally, the sample is mounted on a piezoelectric tube that can move the sample in the z direction for maintaining a constant force, and the x and y directions for scanning the sample. Alternatively a 'tripod' configuration of three piezo crystals may be employed, with each responsible for scanning in the x,y and z directions. This eliminates some of the distortion effects seen with a tube scanner. The resulting map of the area $s = f(x,y)$ represents the topography of the sample. Areas as large as about 100 µm squares to less than 100 nm square can be imaged. The AFM can be operated in a number of modes, depending on the application. In general, possible imaging modes are divided into:

Contact Mode AFM - The AFM probe is scanned at a constant force between the probe and the sample surface to obtain a 3D topographical map. When the probe cantilever is deflected by topographical changes, the scanner adjusts the probe position to restore the original cantilever deflection. The scanner position information is used to create a topographical image. Lateral resolution of <1 nm and height resolution of <1 Å can be obtained.

Intermittent Contact (Tapping Mode) AFM - In this mode, the probe cantilever is oscillated at or near its resonant frequency. The oscillating probe tip is then scanned at a height where it barely touches or "taps" the sample surface. The system monitors the probe position and vibrational amplitude to obtain topographical and other property information. Accurate topographical information can be obtained even for very fragile surfaces. Optimum resolution is about 50 Å lateral and <1 Å height. Images for phase detection mode, magnetic domains, and local electric fields are also obtained in this mode.

Image Analysis - Since the images are collected in digital format, a wide variety of image manipulations are available for AFM data. Quantitative topographical information, such as lateral spacing, step height, and surface roughness are readily obtained.

Typical applications

- 3-dimensional topography of IC device
- Roughness measurements for chemical mechanical polishing
- Analysis of microscopic phase distribution in polymers
- Mechanical and physical property measurements for thin films
- Imaging magnetic domains on digital storage media
- Imaging of submicron phases in metals
- Defect imaging in IC failure analysis
- Microscopic imaging of fragile biological samples
- Metrology for compact disk stampers

5.2 OPTICAL PROPERTY ANALYSIS INSTRUMENTS

An optical instrument either processes light waves to enhance an image for viewing, or analyzes light waves (or photons) to determine one of a number of characteristic properties.
Optical properties measurements, instrumentation, and analytical tools for interactive analysis of targets and backgrounds can be studied obtained with the help of these instruments. Some of them are discussed below.

5.2.1 Ultraviolet and Visible Spectroscopy (UV-VIS)

The instrument used in ultraviolet-visible spectroscopy is called a UV-VIS spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_o). The ratio I/ I_o is called the *transmittance*, and is usually expressed as a percentage ($\%T$). The absorbance, A, is based on the transmittance:

$$A = -\log(\%T)$$

It involves the spectroscopy of photons in the UV-visible region. It uses light in the visible and adjacent near ultraviolet (UV) and near infrared (NIR) ranges. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state.

An ultraviolet-visible spectrum is essentially a graph of light absorbance versus wavelength in a range of ultraviolet or visible regions.

Fig 5.8 Schematic shows an UV/Vis spectrophotometer

The instrument needs to generate UV-visible radiation, select the wavelength of interest, and measure the amount absorbed after it has been passed through the sample. The schematic diagram above shows the major constituents in a simple instrument. Such light sources cover the wavelength range beyond 320 nm, but to reach further down into the UV regime, an additional source is essential. Deuterium arc lamp is used for this purpose, which gives a continuous spectrum below 400 nm.

Applications

- UV/Vis spectroscopy is routinely used in the quantitative determination of solutions of transition metal ions and highly conjugated organic compounds.
- Solutions of transition metal ions can be colored (i.e., absorb visible light) because the electrons within the metal atoms can be excited from one electronic state to another.
- Organic compounds, especially those with a high degree of conjugation, also absorb light in the UV or visible regions of the electromagnetic spectrum. The solvents for these determinations are often water for water soluble compounds, or ethanol for organic-soluble compounds. Organic solvents may have significant UV absorption.

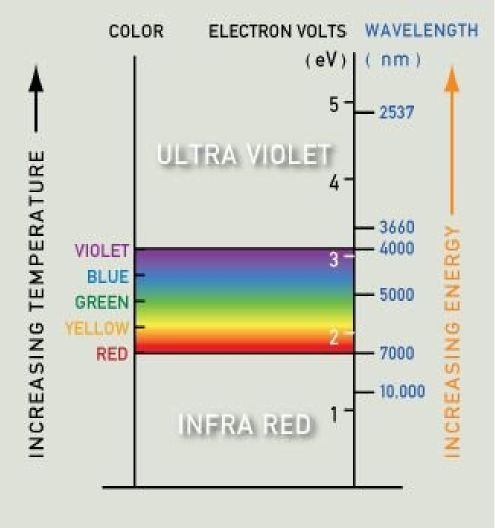

Fig 5.9 Temperature VS Wavelength Curve

Noble metal nanoparticles absorb strongly in the visible region due to surface plasmon resonance, which was discussed briefly earlier. Hence the UV–Visible absorption spectroscopy is a primary characterization tool to study the metal nanoparticles formation.

5.2.2 Photoluminescence Spectroscopy (PLS)

Introduction

Photoluminescence spectroscopy is a contactless, non-destructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. One way this excess energy can be dissipated by the sample is through the emission of light, or luminescence. In the case of photo-excitation, this luminescence is called photoluminescence. The intensity and spectral content of this photoluminescence is a direct measure of various important material properties. Photo-excitation causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light (a radiative process) or may not (a nonradioactive process). The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process.

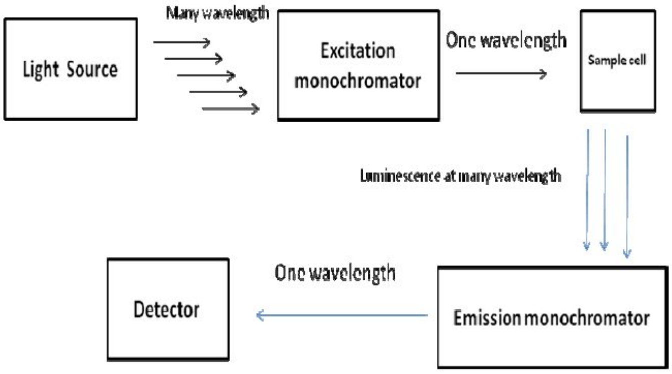

Fig 5.10 Schematic diagram of photoluminescence

The energy of the emitted photon is a direct measure of the band gap energy, E_g. The process of photon excitation followed by photon emission is called *photoluminescence*.

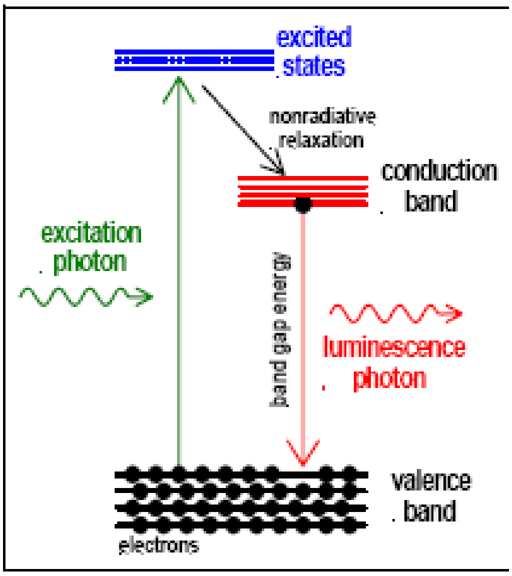

Fig 5.11 Energy band diagram

Photoluminescence (abbreviated as PL) is a process in which a substance absorbs photons (electromagnetic radiation) and then re-radiates photons. Quantum mechanically, this can be described as an excitation to a higher energy state and then a return to a lower energy state accompanied by the emission of a photon. This is one of many forms of luminescence (light emission) and is distinguished by photoexcitation (excitation by photons), hence the prefix *photo*. The period between absorption and emission is typically extremely short, in the order of 10 nanoseconds. Under special circumstances, however, this period can be extended into minutes or hours.

Main processes of luminescence:

(1) Absorption of excitation energy and stimulation of the system into an excited state
(2) Transformation and transfer of the excitation energy
(3) Emission of light and relaxation of the system into an unexcited condition

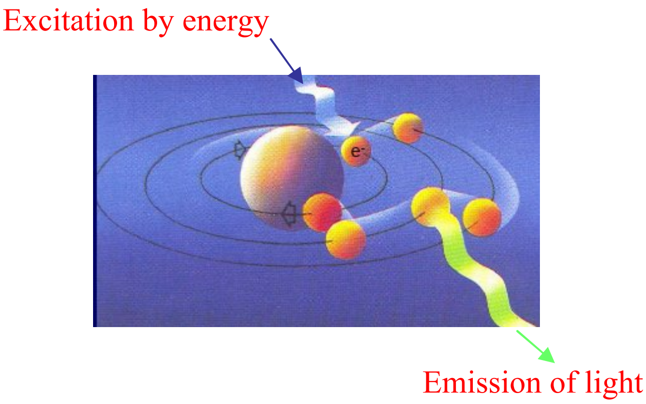

Fig 5.12 Schematic model of luminescence processes

Applications

- The most common radiative transition in semiconductors is between states in the conduction and valence bands, with the energy difference being known as the band gap. Band gap determination is particularly useful when working with new compound semiconductors.
- Impurity Levels and Defect Detection
- Radiative transitions in semiconductors also involve localized defect levels. The photoluminescence energy associated with these levels can be used to identify specific defects, and the amount of photoluminescence can be used to determine their concentration.
- The return to equilibrium, also known as "recombination," can involve both radiative and nonradiative processes. The amount of photoluminescence and its dependence on the level of photo-excitation and temperature are directly related to the dominant recombination process. Analysis of photoluminescence helps to understand the underlying physics of the recombination mechanism.

In general, nonradiative processes are associated with localized defect levels, whose presence is detrimental to material quality and subsequent device performance. Thus, material quality can be measured by quantifying the amount of radiative recombination.