Photoluminescence Spectroscopy

Photoluminescence (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. If a light particle (photon) has an energy greater than the band gap energy, then it can be absorbed and thereby raise an electron from the valence band up to the conduction band across the forbidden energy gap. In this process of photoexcitation, the electron generally has excess energy which it loses before coming to rest at the lowest energy in the conduction band. At this point the electron energy eventually falls back down to the valence band. As this happens, the energy it loses is converted back into a luminescent photon which is emitted from the material. Thus the energy of the emitted photon is a direct measure of the band gap energy, Eg. The process of photon excitation followed by photon emission is called photoluminescence

There are many types of photoluminescent process

Resonant radiation: when a photon of a particular wavelength is absorbed and equivalent photon is immediately emitted. This process is extremely fast about 10ns, and no significant transition of the internal energy of the chemical substrate between absorption and emission occurs.

Fluorescence: When the chemical substrate undergoes internal energy transitions before re-emitting the energy from the absorption. This process is also fast, but some of the original energy is dissipated so that the emitted light photons are of lower energy than those absorbed.

Phosphorescence: In phosphorescence the energy from absorbed photons undergoes intersystem crossing into a state of higher spin multiplicity, generally a triplet state. When the energy is trapped in the triplet state, transition back to the lower singlet energy states is forbidden quantum mechanically. This leads to a slow process of radiative transition back to singlet state that last from minutes to hours. The lifetime of phosphorescence is usually from 10^{-4}- 10^{-2} s, much longer than that of Fluorescence. Therefore, phosphorescence is even rarer than fluorescence, since a molecule in the triplet state has a good chance of undergoing intersystem crossing to ground state before phosphorescence can occur.

A spectrometer is an instrument used for measuring the intensity of light as a function of wavelength. Spectrometers usually contain a diffraction grating (or prism) to disperse the light, thereby spreading out the light of differing wavelengths into different positions. The spectrometer unit has an internal CCD (charged coupled device) silicon detector, essentially a digital camera detector, to measure the light intensity at various positions along its length.

From the emission patterns, photoluminescence spectroscopy is used in other fields of analysis, especially semiconductors.

Band gap determination:

Band gap is the energy difference between the lowest state in the conduction and the highest state in the valence bands, in semiconductors. The spectral distribution of PL from a semiconductor can be analyzed to nondestructively determine the electronic band gap and this provides a means to quantify the elemental composition of compound semiconductor.

Impurity levels and defect detection:

Radiative transitions in semiconductors 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 PL spectrum at low sample temperatures often reveals spectral peaks associated with impurities contained within the host material. Fourier transform photoluminescence microspectroscopy, which is of high sensitivity, provides the potential to identify extremely low concentrations of intentional and unintentional impurities.

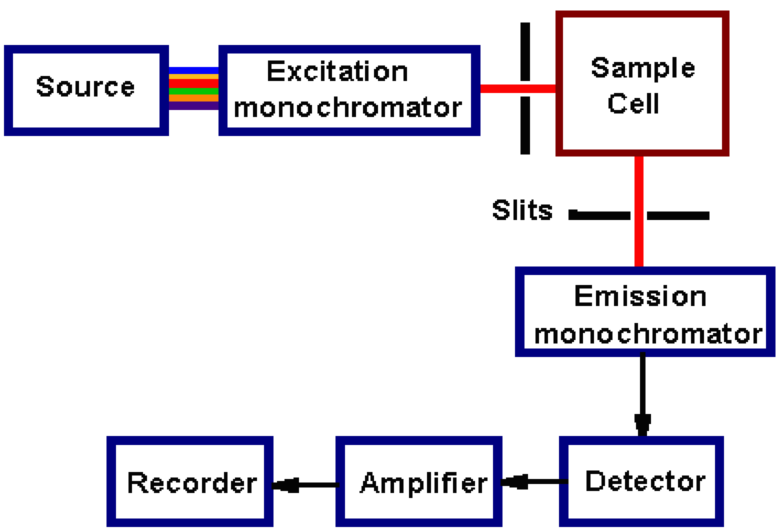
Surface structure and excited states:

Photoluminescence is very sensitive to surface effects or adsorbed species of semiconductor particles and thus can be used as a probe of electron-hole surface processes.

Recombination mechanisms:

Recombination mechanism, can involve both radiative and non-radiative processes. The quantity of PL emitted from a material is directly related to the relative amount of radiative and non-radiative recombination rates. Nonradiative rates are typically associated with impurities and the amount of photoluminescence and its dependence on the level of photo-excitation and temperature are directly related to the dominant recombination process. When samples is exposed to photons, the photoexcitation of electrons from the valence band to conduction band occurs and, the electrons losses excess energy through non-radiative relaxation before falling to the lowest energy in the conduction band. The electrons may radioactively recombine with holes of the valence band and if the sample is completely free of impurities i.e. pure an exciton gets formed between these two carriers with a small binding energy. The characteristic of the energy levels is the energy of the emitted photons due to band-to-band transition, an exciton recombination or any other possible transitions. If the sample is impure or doped, radiative recombination also may occur via shallow donor or acceptor levels. In case of impure sample three types of transition may occur, conduction band to acceptor level, donor level to valence band and donor level to acceptor level.

Thus, analysis of photoluminescence pattern can give information about the impurity, energy transfer, band gap of the material.



Instrumentation of Photoluminescence