Chapter 2

Different Tools and Techniques for Characterization of SnS Nanostructured Materials

The prepared SnS nanostructure materials have been characterized structurally by X-ray diffraction and Transmission electron microscopy. X-ray diffraction (XRD) measurements were performed by Bruker Axs D2 phaser SSD160 with Cu-kα radiation (λ=1.5405Å) in the range of 20° to 70°. A small drop of dispersed SnS nanocrystals have been taken on the thin carbon film supported on the copper grid and kept for some time for drying. Transmission electron microscopy (TEM) and HRTEM were carried out by JEOL JEM200 operating at 200KV. Selected area electron diffraction (SAED) pattern of the said samples were performed. The surface morphology of the grown samples has been characterized by FESEM using ZEISS MERLIN6105. The stochiometric analyses were performed by energy dispersive analysis of X-rays (EDAX). The Atomic force microscopy of as prepared samples was done by 5500 AFM (N9410S). Raman spectroscopy (Renishaw invia Raman microscope) was also carried out to identify the phases of the as prepared samples with an excitation wavelength of 532nm. UV-VIS absorption spectra of as prepared samples were measured by Shimadzu- Pharmaspec-1700 visible and ultraviolet spectrophotometer in the wavelength range 200nm-900nm at room temperature. PL spectra of as prepared SnS were obtained by Perkin Elmer LS55 Fluorescence Spectrometer. Time-Correlated Single Photon Counting (TCSPC) of the samples was performed by Delta flex-01-DD. For gas sensing measurements, SnS nanofilms have been grown from the dispersed SnS nanoparticles. The cleaned glass substrates have been dipped into the dispersed SnS nanoparticles in toluene for 72 hours. Silver electrodes were drawn on the sensor nanofilms. The resistance of the sensors were measured thoroughly through a simple electronic circuit

consisting of a power supply, a resistance, a Keithley Electrometer (6517) and proper electronic interface data acquiring system. I-V measurements of the fabricated heterojunction solar cell have been studied using a Keithley nanovoltmeter 2182a, source meter 2400, and 6221 ac/dc current source meter interface with LabVIEW program. Current (I)-Voltage (V) characteristics of the fabricated DSSCs based on SnS NPs were performed using Kiethly electrometer (6514).

2.1.   Principle of characterization

2.1.1.   Principle of X-ray diffraction (XRD)

X-ray diffraction (XRD) is a diagnostic technique for analyzing the crystal structure of materials. It gives the information about phase of crystals, lattice planes with orientation, lattice constant, average crystal size, crystalline behaviour, strain, crystal defects of the solid materials [181-182].

In 1912, the German physicist Max von Laue first discovered the phenomenon X-ray diffraction (XRD) within crystals which is behaved as a three-dimensional (3D) diffraction grating. After that, W. H. Bragg and W. L. Bragg discovered Bragg's law which relates the diffraction of monochromatic X-rays from the single crystal planes. X-ray diffraction (XRD) is basically a constructive interference pattern, occurs when a monochromatic X-rays are allowed to incident on the lattice planes, scattered from crystal planes. According to him, Bragg's diffraction condition can be expressed as $2d\sin\theta=n\lambda$, Where, λ is the wavelength of the incident ray, d is the interplaner spacing of the lattice planes, θ is the Bragg's angle and n is an integer.
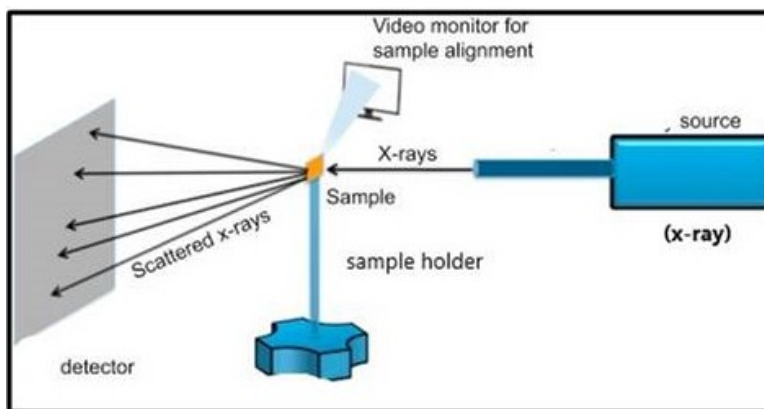
Fig. 2.1. X-ray diffraction measurement setup

X-ray diffraction pattern of the powder samples was also obtained by Debye Scherrer. When the monochromatic X-rays are allowed to incident upon the powder sample, these X-rays are scattered from the specific crystal planes making an angle θ with the incident X-rays beam and satisfying Bragg's diffraction condition. These scattered X-rays are then detected by detector, processed and counted. Since the sample is rotating by an angle 2θ, all the possible diffraction peaks are obtained in those 2θ value at which Bragg's diffraction condition is satisfied. The average grain size D of the crystalline materials are obtained by the Debye Scherrer's formula expressed as

$$D = \frac{0.9\lambda}{\beta_{1/2}\cos\theta}$$

Where, λ is the wavelength of X-rays which is 1.5405Å, $\beta_{1/2}$ is the full width half maximum (FWHM), θ is the Bragg angle. X-ray diffraction (XRD) measurements of the prepared samples were recorded by Bruker Axs D2 phaser SSD160 with Cu-kα radiation (λ=1.5405Å).

2.1.2. Principle of Transmission Electron Microscope (TEM)

Transmission electron microscopy (TEM) is a popular technique in which a high energetic beam of electrons is transmitted through a thin foil specimen to create an image. An image is developed with the interaction of electrons and sample during the transmitting of the beam of electrons through the specimen. Then the image is magnified as well as focused on the imaging device, such as a fluorescent display/sensor [183]. TEM image can assist to study

the inner structure and investigate the features of the sample in atomic scale region. It is used to evaluate crystal size, morphology, crystal structure as well as elemental composition of the nanomaterials.
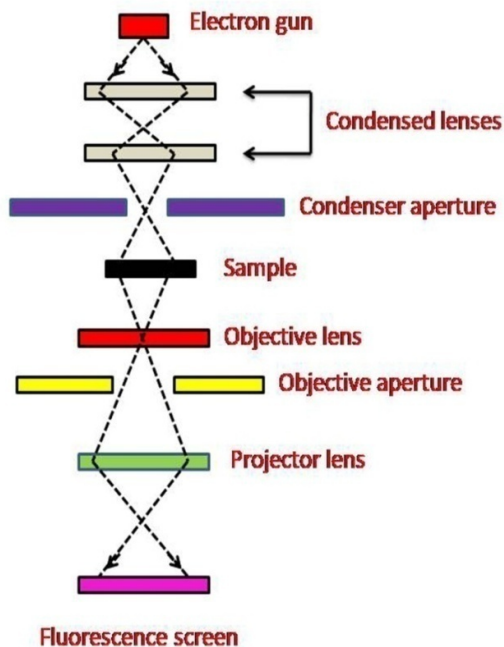
**Fig. 2.2.** Block diagram of Transmission Electron Microscope.

Fig. 2.3. Image of Transmission Electron Microscope.

Selected area electron diffraction (SAED) is a useful technique in TEM test to achieve diffraction patterns that can be obtained through the scattering of electron beam by the lattice. The electrons are diffracted by the lattice planes, and therefore satisfy Bragg's law. So, one can index the spots on diffraction pattern and recognize the phases of the sample as well as their crystalline behaviour [184]. The selected area diffraction pattern is formed on the screen at the back focus plane of the objective lens. The transmission electron microscope (TEM) and HRTEM of the grown nanoparticles were investigated by JEOL JEM200 operating at 200 KV.

2.1.3. Principle of Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a flexible and influential microscopy technology to study the samples in nanoscale order. The atomic force microscopy can deliver not only image in three-dimensional (3D) topographic map but also it supplies various types of surface information for scientists and engineers. It also produces various types of height information, friction, and magnetism of the samples in the order of angstrom [183].

The AFM consists of cantilever with a very fine sharp tip that interacts with the surface of the sample. As the tip comes close to the surface, an attractive force in between the sample surface and the AFM tip deflects the cantilever through the sample surface. This cantilever deflection has been detected with a laser beam which is reflected by the cantilever. The reflected laser beam is captured by a position-sensitive photo diode (PSPD) and generates the topographic map of the sample surface feature. The Atomic force microscopy of as prepared SnS nanoparticles was studied by 5500 AFM (N9410S).
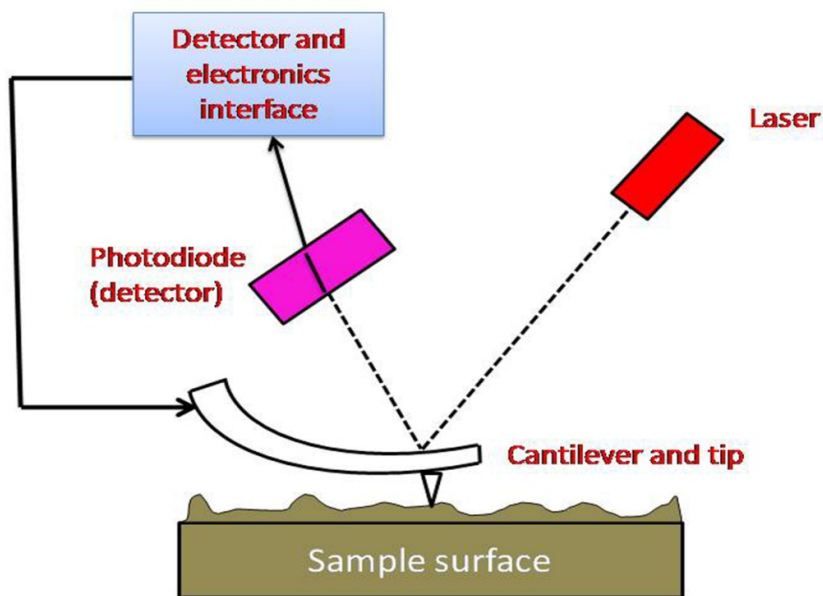
Fig. 2.4. Schematic diagram of atomic force microscopy (AFM)

2.1.4. Principle of Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique that exploits the interaction of photons with matter to achieve the chemical and structural information of the materials. The basic mechanism of the Raman spectroscopy is based on light scattering process. Raman spectroscopy provides the information about molecular vibrations, chemical bonding, crystal and molecular structure, crystallographic orientation, biological imaging etc. [185].
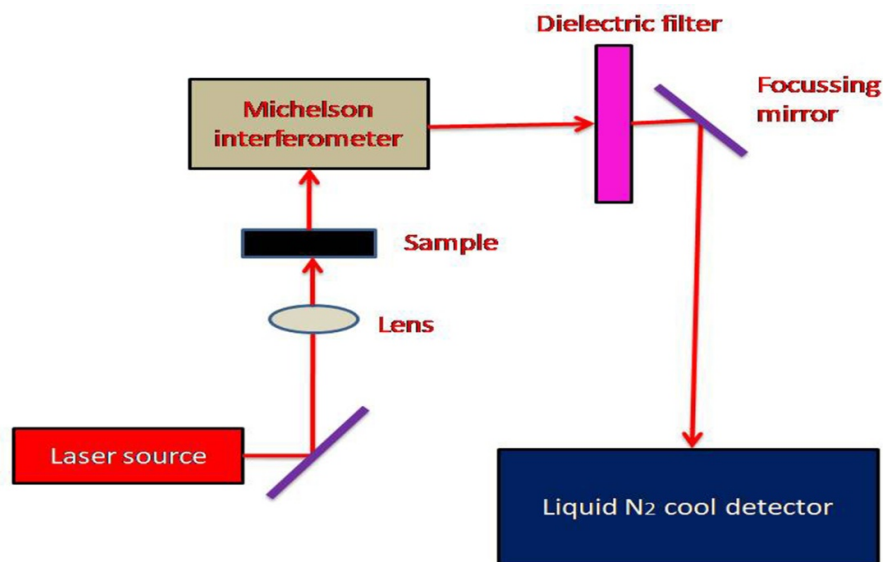

Fig. 2.5. Block diagram of Raman Spectroscopy

When a monochromatic light is passed through the different medium such as gas, liquid, or solid, then the photons interacts with molecules of the samples. The maximum number of photons are scattered with the identical frequency as the incident photons. This is expressed as elastic scattering / Rayleigh scattering. A few numbers of these photons will scatter with different frequency than the incident photon. This process is described as inelastic scattering / Raman effect. In 1930, Sir C.V. Raman got Nobel Prize in Physics for this work. The Raman Scattering study can be explained by quantum mechanical phenomenon. When the incident photons interact with a molecule of the sample, the molecule shifted to the higher energy state and then calm down to the vibrational energy level which is different than the beginning

state and produces a photon. The difference between the incident photon energy and the

scattered photon energy is called Raman shift. If the change in frequency of the scattered

photon is less than the frequency of incident photon, the scattering is termed as Stokes

scatter. Again, if the change in frequency of the scattered photon is higher than the frequency

of incident photon, the scattering is called as anti-Stokes scatter [186]. Raman spectroscopic

measurement of the samples were analysed through Renishaw invia Raman microscope.

Fig. 2.6. Image of Raman spectrophotometer instrument

2.1.5. Principle of Absorption Spectroscopy

Ultraviolet–visible spectroscopy (UV–Vis) is referred to absorption spectroscopy or

reflectance spectroscopy in the ultraviolet and visible spectral regions. This means it utilizes

light in the visible and adjacent [near–UV and near- infrared (NIR)] ranges. The basic

principle of UV-Vis absorption spectroscopy is mainly based on the absorption of ultraviolet

(UV) light or visible (VIS) light by the molecules of the samples which gives the production

of spectroscopic image. Therefore, spectroscopy is interconnected to the interaction between

light as well as matter. When the light is absorbed by the matter, the excited electrons are

jumped to the higher state and then de-excitation to the lower state which gives rise to distinct spectrum [187].
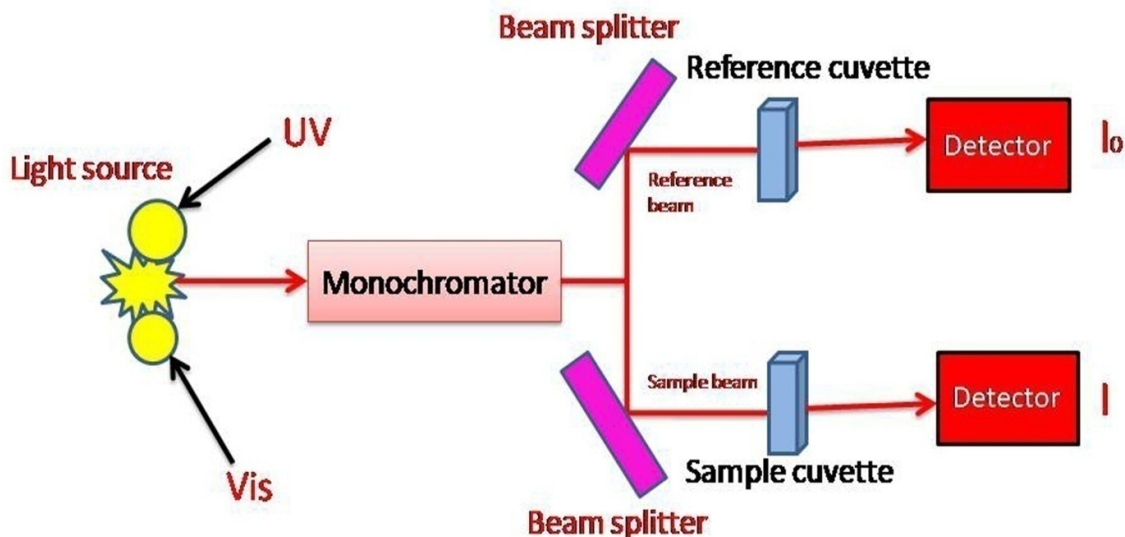

Fig. 2.7. Schematic diagram of optical absorption spectrophotometer

UV-vis absorption spectroscopy techniques are broadly applied in analytical chemistry for the measurements of various analytes as like as metal ions, conjugated organic compounds as well as biological macromolecules. These measurements are usually done in dispersed solution. The basic components of a UV-vis absorption spectrophotometer are (i) a light source of ultraviolet (UV) and visible (VIS) (ii) a sample cuvette (iii) a monochromator and (iv) a proper detector. The ultraviolet /visible light source (white light) is incident into a monochromator and separated its constituent wavelengths by diffraction grating. The monochromatic light (single wavelength) is then divided in equal intensity into two by a beam splitter. Then, one of the beam passes through a sample cuvette and other through the reference cuvette. At the end, the intensity of both transmitted light beams are measured through a proper detector and then compared.

The intensity of transmitted beam through reference is indicated by I_0 where as the transmitted beam through the sample is indicated by I. According to Beer Lambert law, the transmitted beam intensity through the sample is expressed as,

$$I = I_0 \, e^{-\alpha x}$$

$$\alpha = \frac{1}{x} \, ln \left(\frac{I_0}{I} \right)$$

Where α is the absorption coefficient and x is the optical path length.

The optical band gap energy of the materials can be estimated the Tauc relation

$$(\alpha h\nu)^2 = C \, (h\nu - E_g) \qquad \text{for direct band gap energy}$$

$$\text{and } (\alpha h\nu)^{1/2} = C \, (h\nu - E_g) \qquad \text{for indirect band gap energy}$$

Where C is a constant, E_g is the band gap energy of the sample and α is the absorption coefficient of the sample. Optical absorption study of the dispersed samples was studied in the visible wavelength range using a Shimadzu Pharmaspec 1700 UV–Vis Spectrophotometer.

Fig. 2.8. Image of absorption spectrophotometer instrument

2.1.6. Principle of Photoluminescence Spectroscopy (PL)

Photoluminescence (PL) is a process in which a substance absorbs energy (photon) in some form and then re-emits the fraction of it's in the visible region. 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. When the chemical substance undergoes internal energy transitions before re-emitting the energy (emission) from the absorption result, the phenomenon is known as fluorescence. It is also termed as radiative transition between states of like spin multiplicity. The created photon in this case is said to be red shifted and the loss of energy is shown in Jablonski diagram [188].
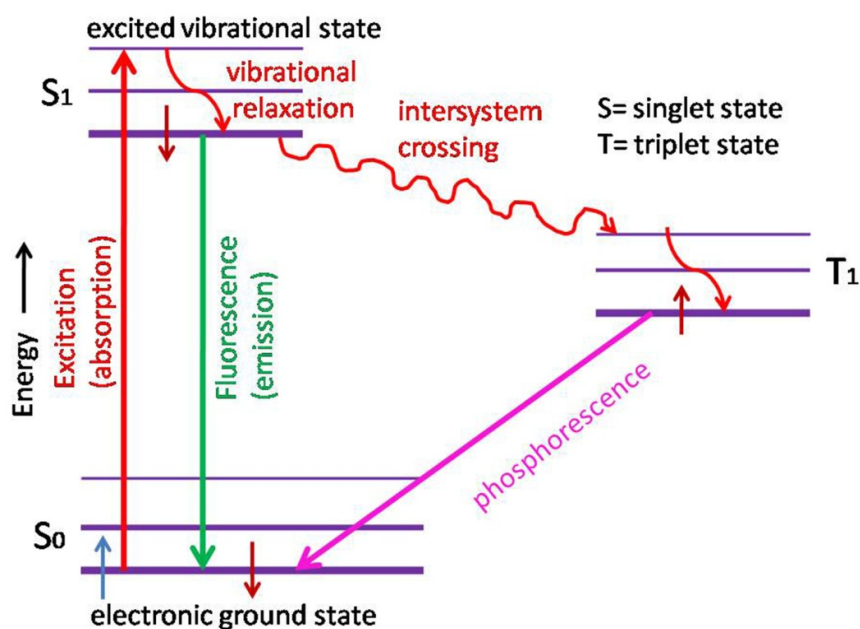

Fig. 2.9. Jablonski diagram

Photoluminescence (PL) is a significant method to detect the physical and chemical properties of a material. The spectral as well as time distributions of emission spectra are connected to electronic transition inside the semiconducting samples. In the photoluminescence spectroscopy study, a light source from xenon lamp is incident into

sample for excitation to the higher energy state and then emitted photons are collected by lens. These collected photons are passed through spectrometer and then detected properly by photo detector. The block diagram of the Photoluminescence spectroscopy (PL) is depicted in fig. 2.10.
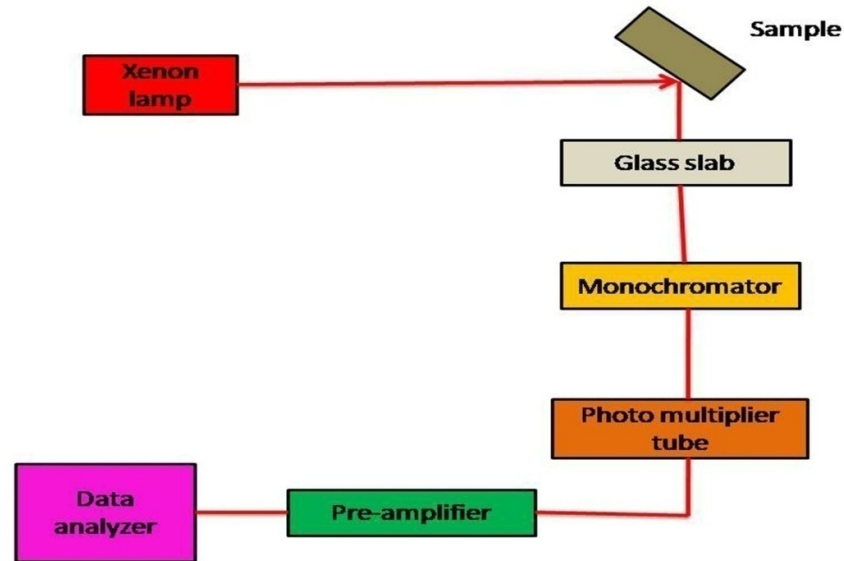
Fig. 2.10. Schematic diagram of Photoluminescence spectrophotometer

Photoluminescence spectroscopy study is usually utilized to determine the impurity as well as defect states/levels, analysis of recombination mechanism, surface configuration, and detection of excited states. The quality of materials is also measured from the PL spectroscopy study. PL spectra of the dispersed samples are recorded using Perkin Elmer LS 55 Fluorescence Spectrophotometer.

Fig. 2.11. Image of Photoluminescence spectrophotometer instrument

2.1.7. Principle of Time-Correlated Single Photon Counting (TCSPC)

Time-Correlated Single Photon Counting (TCSPC) is a useful and popular technique for the measurements of fluorescence decay lifetime in the order of picoseconds to microsecond. A laser source with appropriate wavelength which is equal to the fluorescence excitation has been used. It is mainly based on the detection of a single photon at a definite time in which excitation pulse of laser source is directly proportional to the fluorescence intensity at the same time. The TCSPC instrument consists of a laser source, optical components, electronics components and emission detector. A short pulse of the laser source is employed to excite the carriers of the samples to the higher energy state. The time gap in between the excitation pulse and the coming of the initial photon at the emission detector is estimated. The TCSPC electronics interface composed of two inputs visualize START signal pulse and STOP signal pulse. The measurement of time (along x-axis) for one more START – STOP sequence can be represented in a histogram. A schematic diagram of the TCSPC is depicted below [189-190].
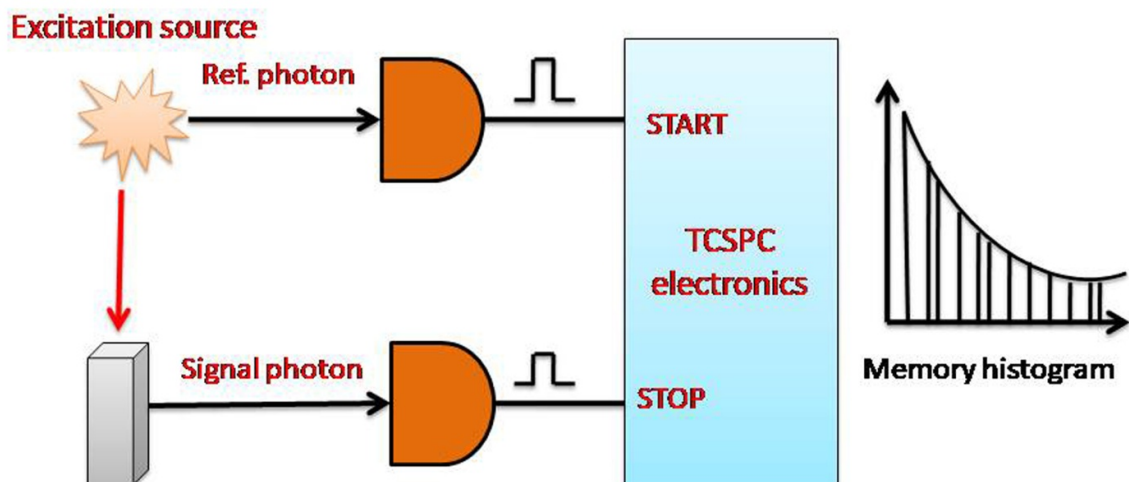
Fig. 2.12. Block diagram of TCSPC

With a greatly repetitive source of light millions of START – STOP cycles can be determined in a short time. The resulting histogram of photons counts vs. channels represents the form of the fluorescence (FL) decay. A single pulse towards the TCSPC electronics produces via single emission of photon. Single photons are detected by the photo-detectors. These are generally photomultipliers. The fluorescence decay lifetime of the carriers were determined from the following formula

$$\tau_{av} = \sum \frac{\alpha_i \tau_i}{\alpha_i}$$

Where $\tau's$ are the decay components and α's are the respective amplitudes of life time components. Time-Correlated Single Photon Counting (TCSPC) of the prepared samples recorded by Delta flex-01-DD.