This chapter describes the brief introduction, theories and applications of various characterization tools used throughout the research work. These characterization tools include UV-visible Spectroscopy, X-ray Diffractometer (XRD), X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FT-IR), Transmission Electron Microscopy (TEM), Photoluminescence spectroscopy, Scanning Electron Microscopy (SEM), and Atomic Force Microscope (AFM).

UV-visible spectrophotometer and photoluminescence spectrophotometer have been used to study the optical properties especially the fibril growth information in the case rr-PQT-12 and rr-pBTTT-C14. XRD is used to investigate the evidence of fibril formation. On the basis of this instrument, an increase in intensity is expected due to increasing in crystallinity that causes high extent of scattering factors. TEM and SEM are used to crosscheck the morphology of polymers upon a set of given experimental conditions. AFM is used to investigate the diameter, morphology and thickness of as-prepared films. Since the vibrational frequencies of all individual functional groups are different. Therefore, FTIR is used to investigate the presence of different functional groups based on their vibrational frequencies in the modified materials. Similarly, Raman is used to investigate the presence of stacking of layers and functional groups present on the surface of sheet. XPS is used to get the information related to all elements present in the modified material along with their possible oxidation states. This experimentation clears the bonding state of different elements. Cyclic voltammetry (CV) setup is used investigate the extent of charge storage capability near the working electrode under the influence of applied potentials in three electrode system. The core backgrounds of each experimental technique are explained one by one in next section.

2.1 UV visible spectroscopy

It is an instrument that works of absorption, transmission or reflectance mode on exposure to the specific concentration of samples in the part of the ultraviolet and the full, adjacent visible range of spectra's. In this process, the electrons are excited from their ground state to higher excitation states by absorbing the proper amount of aforesaid range of radiations. It is also called electronic spectroscopy because it involves electronic transition. The intensity of absorption of radiations as a function of wavelength of light absorbed is plotted and the graph gives an idea of electronic transition taking place in the molecule. From these electronic transitions information we can depict the structure of molecules.

Single beam spectrophotometer:

In this type of spectrophotometer, one beam of light passes through the sample and the intensity of the light reflected from a reference are measured without the sample. Abloch diagram for such kind of arrangement is shown in Fig. 2.1.

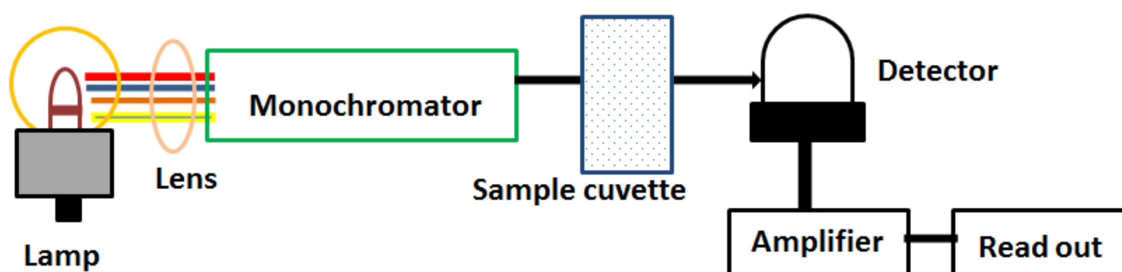


Fig. 2.1 Block diagram of single beam spectrophotometer [Bordoloi (2018)].

Double beam spectrophotometer:

In this type of spectrophotometer, source light is splitted in two beams, one beam passes through the sample cell, while the other passes through the reference cell. Detector measures the ratio of the two beams and chart recorder. To understand this phenomenon, a ray diagram is shown below in Fig. 2.2.

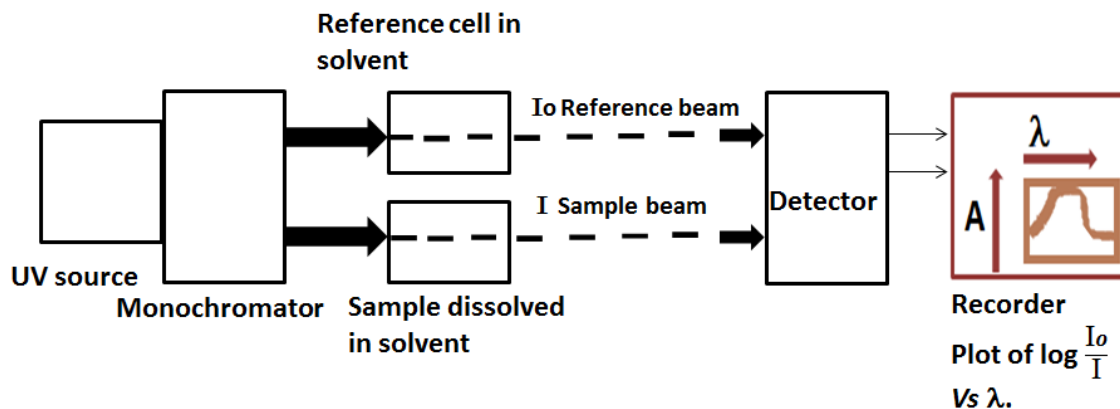


Fig. 2.2 Block diagram of double beam spectrophotometer.

Light source: Hydrogen lamp, Tungsten lamp, Deuterium lamp.

Solvents: Methanol, Ethanol, Hexane and Water etc.

Cells: Quartz and other clear materials which are not absorb UV radiation.

The UV-visible spectrophotometer, model no. EPOCH2C, Biotech Instrument Inc. USA, has been used throughout the work.

2.2 Photoluminescence spectroscopy

Photoluminescence spectroscopy is a contactless, versatile, nondestructive, powerful optical 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. Thus photoluminescence is the spontaneous emission of light from a material under optical excitation. 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 non-radiative 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. PL spectroscopy gives information only on the low lying energy levels of the investigated system. In semiconductor systems, the most common radiative transition is between states in the conduction and valence bands, with the energy difference being known as the bandgap. During a PL spectroscopy experiment, excitation is provided by laser light with an energy much larger than the optical band gap. The photo excited carriers consist of electrons and holes, which relax toward their respective band edges and recombine by emitting light at the energy of the band gap. Radiative transitions in semiconductors may also involve localized defects or impurity levels therefore the analysis of the PL spectrum leads to the identification of specific defects or impurities, and the magnitude of the PL signal allows determining their concentration.

The photoluminescence spectrophotometer is an analytical instrument used to measure and record the fluorescence of a sample. While recording the fluorescence, the excitation, emission or both wavelength may be scanned. With additional accessories, variation of signal with time, temperature, concentration, polarization, or other variables may be monitored. Fig. 2.3 shows the block diagram of fluorescence spectrometer. Fluorescence spectrometers use laser sources, which contains wavelength selectors, sample illumination, detectors and corrected spectra.

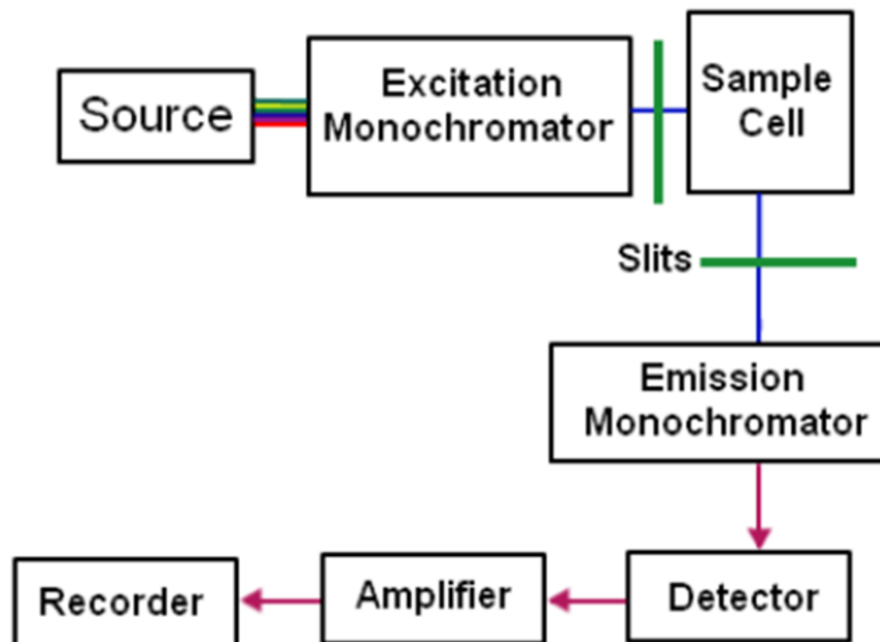


Fig. 2.3 Block diagram of photoluminescence spectroscopy [Nikita (2015)].

Photo luminescence analysis has been carried out on PL spectrophotometer model no. Perkin Elmer, LS-50B, USA.

2.3 Atomic force microscopy

The working principle of AFM is based on the measurement of the forces between the probe and the sample in terms of their mutual separation. AFM uses a sharp tip attached to the end of a cantilever which rasters across the selected area while a laser and photodiode are used to monitor the tip force on the surface. A feedback loop between the photodiode and the piezo crystal maintains a constant force during contact mode imaging and constant amplitude during tapping mode of imaging. Since, an AFM relies on contact rather than current, so many nonconductive materials can be examined using this instrument. When the tip is brought close to sample, a number of forces may operate. The forces contributing most to the movement of an AFM cantilever are the coulombic and van der Waals interactions. In columbic interaction, strong, short range electrostatic repulsive force

between electron clouds of tip & sample as separation decreases repulsion increases, while the vander Waals interaction is the longer range attractive forces. A simplified block diagram is shown in the Fig 2.4.

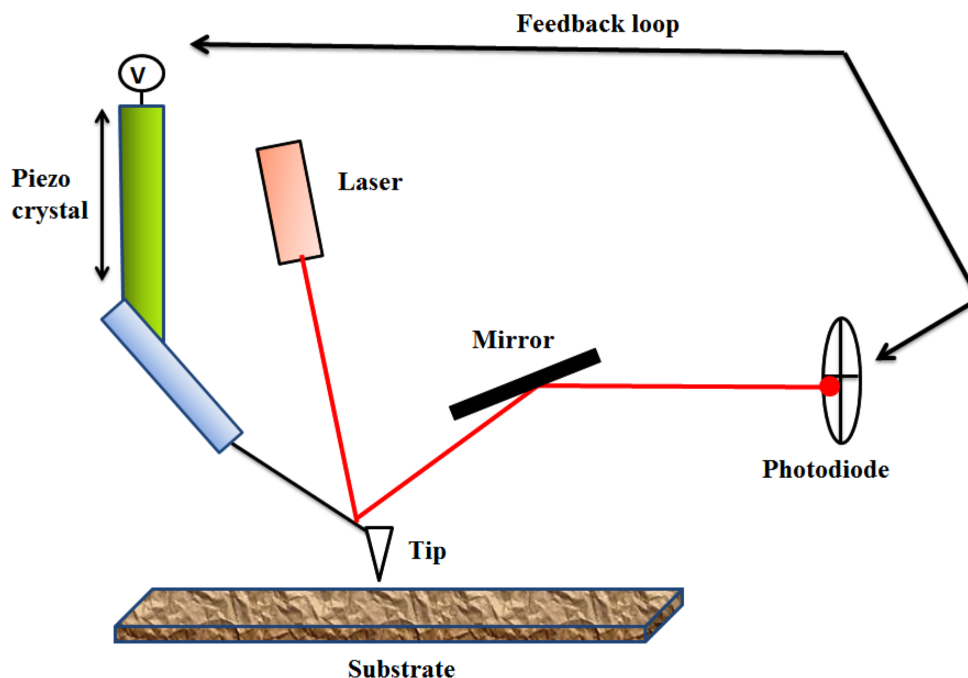


Fig. 2.4 Schematic of working principle of atomic force microscopy used for surface analysis.

We performed AFM measurements on NT-MDT, NTGRA, Prima, Russia.

2.4 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) technique is used for the surface characterization up to 2 to 5 nanometers (nm) depth of the materials. XPS was developed in 1960s by Kai Siegbahn, who got the Nobel Prize in physics in 1981 for his research. XPS is used to study the chemical elements and chemical bond present between them. XPS can be used to analyze all the elements except hydrogen and helium and requires ultrahigh vacuum (UHV) conditions i.e. 10-9 millibar (mbar). XPS is based on the photoelectric effect and involves

irradiation of a sample with X-rays of sufficient energy that results in the excitation of the electrons in the bound states (shown in Fig. 2.5).

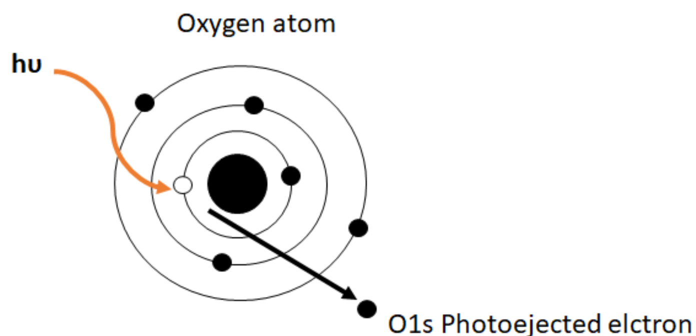


Fig. 2.5 Physical process involved in XPS and photoelectron emission [Embong (2011)].

In a typical XPS measurement, surface analysis involves the irradiation of sample with a high energy primary beam mostly comprised of photons or electrons in UHV and their impact on the surface results in the formation of secondary beam made of ejected electrons. Some of photo-ejected electrons are in elastically scattered through surface while others undergo prompt emission without any loss of energy into the surrounding vacuum, they are captured by the electron analyzer to get their respective kinetic energy. XPS spectrum is the plot of intensity (count/sec) *vs.* Binding energy (eV) which covers the scan from 0 to 1200 eV binding energy base on the phenomenon shown in equation (1).

$$\mathbf{S + h\upsilon \longrightarrow S^{*+} + e^{-}} \quad \text{.....................(1)}$$

Here, 'S' can be a molecule, atom or an ion and 'S^{*+}' is their respective excited state. The kinetic energy of photo ejected electrons 'E_K' is measured with an electron analyzer, hence binding energy of the electron 'E_b' can be measured by using following equation (2) where,

'W' is work function of the spectrometer. A block diagram of modern photo electron spectroscopy for chemical analysis is shown in Fig. 2.6.

$$E_b = h\upsilon - E_K - W \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

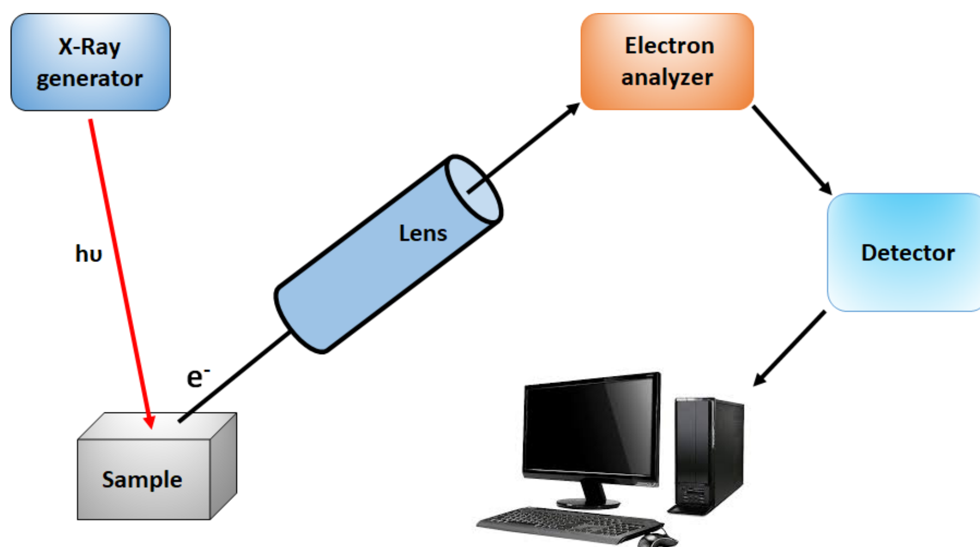


Fig. 2.6 Block diagram of modern electron spectroscopy for chemical analysis.

XPS measurement was carried out using K-Alpha™ X-ray Photoelectron Spectrometer (XPS) System (Thermo Fisher Scientific, USA)

2.5 Scanning Electron Microscopy

Scanning electron microscope is widely used for examining the surface morphology of the samples. It gives the detail about topography texturing, grain size, void content, particle agglomeration, compositional contrast, and compositional information about the sample. The basic principle of scanning electron microscopy is to scan a specimen with a focused electron beam of kilo Volt energy. An image is formed by scanning a cathode ray tube in synchronism with the beam and by modulating the brightness of this tube with beam-excited signals.

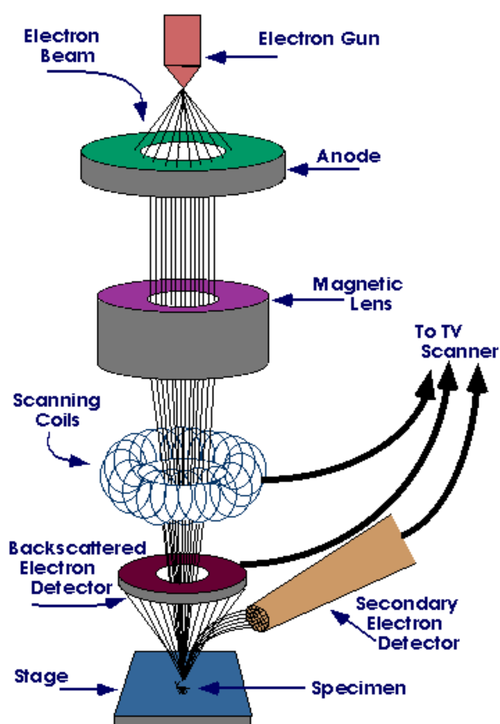


Fig. 2.7 Schematic diagram of scanning electron microscope [Ankan (2015)].

Fig. 2.7 shows the schematic diagram of the scanning electron microscope. SEM consists of an electron gun, an electromagnetic lenses system and a set of detectors. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample. Once the beam hits the sample, electrons and X-rays are ejected from the sample. Detectors collect these X-rays, backscattered electrons, and secondary electrons and convert them into a signal that is sent to a screen similar to a television screen. This produces the final image.

We have used Nova Nano SEM 450, FEI Company of USA (S.E.A.) PTE, LTD, for HR-SEM imaging.

2.6 Transmission electron microscopy

In transmission electron microscopy (TEM), high energy electron beam (100-400KeV) is transmitted through the ultra-thin (<100nm). A TEM image is formed from the interaction of the electrons transmitted through the specimen and the image is further magnified and focused onto an imaging device, such as a fluorescence screen, on a layer of photographic, or to be detected by a sensor such as a CCD camera. At top of the microscope, electron gun emits the electron which travels through the vacuum in column of microscope and focused into very thin beam by electromagnetic lenses (Fig. 2.8.). The electron beam then travels through the specimen, depending on the materials, some electron scattered and transmitted electron through the specimen hit the fluorescence screen which give rise to shadow image of the specimen with its different part displayed in varied darkness according to their density and chemical structure. TEM are used to analyze the morphology, compositions of specimen and to get the crystallographic information.

The electron beam used to analyze the specimen is of high energy and wavelength associated with the electron is of order of inter atomic distance. In this case, the atomic planes in specimen behave like a diffraction grating for incident electron beam. These electrons diffracted in particular direction depending on the crystal structure of specimen which produces a spot on tem image. This type of analysis is known as selected area diffractions pattern [William and Carter 2009)].

We have utilized transmission electron microscope (TEM)-FEI-Tecnai 20 U Twin with EDX and Tecnai 20 G2 operated at 200 KeV, for the structural characterization of different Polymeric materials/ nanomaterials.

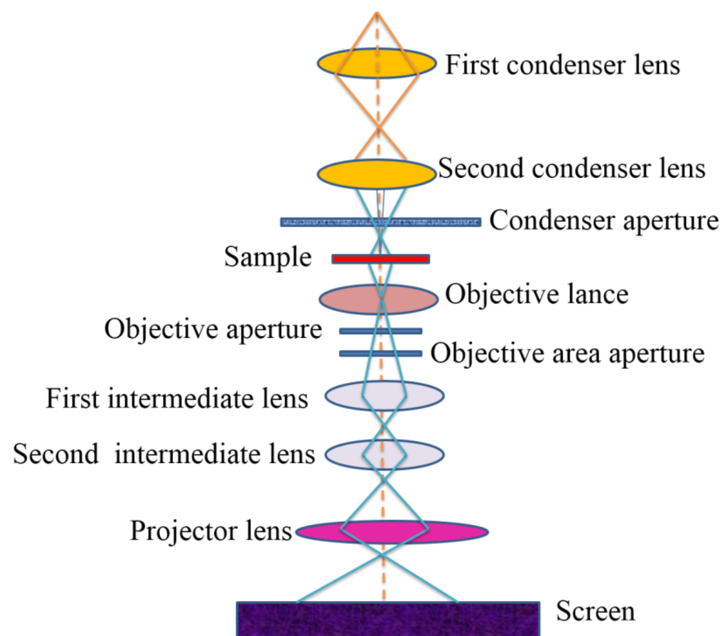


Fig. 2.8 Schematic diagram of transmission electron microscope.

2.7 Fourier transforms infrared spectroscopy

IR (Infrared) spectroscopy is a technique which is mostly used by the organic chemist. This technique utilizes infrared radiation, which is a part of the electromagnetic spectrum and lies between microwave and visible regions. IR spectra are recorded by an instrument known as IR spectrometer. A block diagram of FT-IR spectroscopy is shown in Fig. 2.9. It is used to study the detailed information about the structure and purity of a compound. The IR region is categorized into three parts: the near, mid and far. The wavenumber of mid-IR range is 4000-400 cm^{-1}. IR radiation is absorbed by organic compound and transformed into molecular vibrational energy. Infrared radiation is exposed to a molecule in IR spectroscopy. When the energy of radiation equals the specific molecular vibrational energy, absorption occurs. In the IR spectrum, the wavenumber is plotted the on X-axis and % transmittance is plotted on the Y-axis. We performed optical measurements with Perkin-Elmer 783 spectrometer.

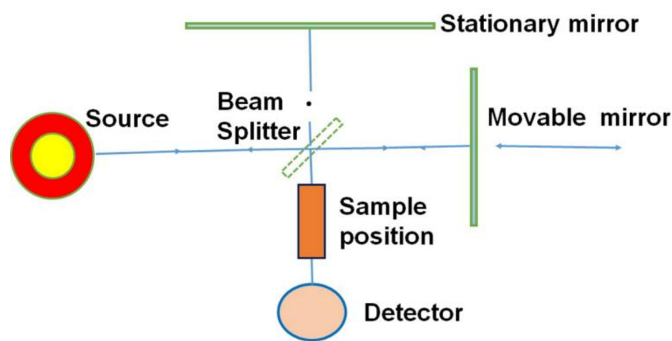


Fig. 2.9 Block diagram of FT-IR spectroscopy [Okamoto (2018)].

2.8 Raman spectroscopy

Raman spectroscopy is a totally non-invasive, quick and non-destructive characterization technique, totally non-invasive, label-free technique which excites vibrations of molecular bonds, has been widely used to characterize two-dimensional material (such as graphene, transition metal dichalcogenides (TMDCs). Although infrared spectroscopy can excite these vibrational bonds but it relies on low power sources and noisy detectors. Raman spectroscopy can afford information on the layer order, adsorbates, stacking surface the strength of in interactions layer etc. The phase of material we can find using Raman spectroscopy (like 1T and 2H phase of the MoS_2). Raman spectroscopy is highly valuable to biomedical research and also to find the cancer cell in human body. In Raman spectroscopy generally uses a laser wavelength of 532 nm (diode-pumped frequency doubled Nd:V) or 785 nm (AlGaAs diode) due to that , a good lateral resolution of better than half the wavelength (250–350 nm) is observed. This sub-cellular resolution is similar to that achieved in fluorescence imaging, and is so superior to the low resolution (~0.1–10 mm) achievable with medical diagnostic. A schematic of the apparatus is shown in Fig. 2.10. The set-up shows the illuminating laser (green laser). When a spot is illuminated at the sample, the Raman-shifted light (red line) is separated out from the laser light by a

dichroic mirror, and dispersed along a vertical line on CCD detector. When the Light is passed through a spectrometer, which disperses the light into a spectrum which is recorded with a cooled CCD camera.

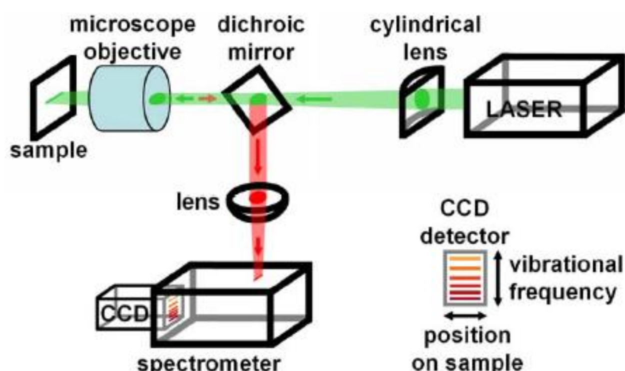


Fig. 2.10 Schematic diagram of Raman spectrometer [Downes (2010)].

Raman spectroscopic measurements were conducted using a Micro Raman Spectrometer (Renishaw, Germany) at 180° scattering geometry with 514.5 nm line of Ar^+ laser of 50 mW to investigate the effect of the Ag film on the rr-PQT-12 layer.

2.9 Cyclic Voltammetry

It is an electrochemical technique that measures the current (or voltage) which is produced in the electrochemical cell under the applied voltage (or current) condition where voltage (or current) is exceeded to that of predicted by Nernst Equation. In the three electrode system, potentio-dynamic CV is performed by cycling the applied potential of fixed scan rate between working and counter electrode and measuring the resulting current with respect to that of reference electrode. A block diagram for electrode connection is shown in Fig. 2.11. A cyclic voltammogram can be obtained by measuring the current at the working electrode during the scan of a range of potential.

A CV system consists of a potentio-galvano stat (PG-STAT), electrolysis cell connected via wire. The electrolysis cell consists of a reference electrode, working electrode, counter electrode, and electrolytic solution. The working electrode's potential is varied linearly with time, while the reference electrode maintains a constant potential. The counter electrode conducts electricity from the signal source to the working electrode. The purpose of the electrolytic solution is to channels' the ions between the electrodes during oxidation and reduction. A potentiostat is an electronic device which uses a dc power source to produce a potential which can be maintained and accurately determined and allowing small currents into the system without changing the voltage. Similarly, PG-STAT allows both application of dc or ac power and measurement of current or voltage.

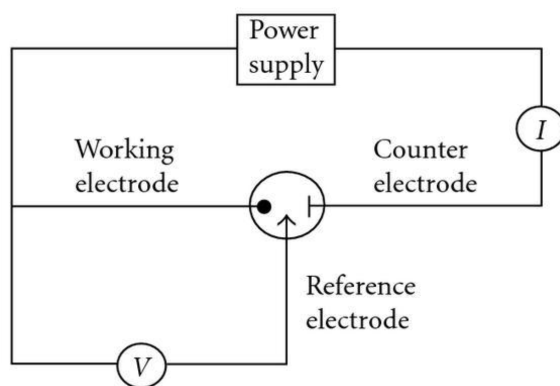


Fig. 2.11 Block diagram of three electrode connections.

The electrochemical response have been collected by using cyclic voltammetry (CV) Autolab (PGSTAT101, Metrohm, Netherlands) and Ω Metrohm, 797 VA, Computrace Trace analyzer, Switzerland, using three electrode assembly.

2.10 Dual channel source meter

A source meter unit, interfaced with computer, is an effective instrument in order to measure the I-V response, by varying small step of voltage range while recording the

current density through device. A voltage (V) is applied between the electrodes using voltmeter and corresponding current (J) is measured using ammeter. The set used in measurement have current measurement range from 10^{-2} A to 10^{-12} A with maximum voltage 200V. The measurements were performed at dark condition in ambient.

Kiethley 2612A, dual channel system source meter has been utilized for the device I-V characteristics.

2.11 Device fabrications

The device is fabricated in two modes *viz.* Sandwich structure as represented as ITO/Polymer/Al (for Schottky diode) and Al (20 µm length)/3.0 mm width channel/Al (20 µm length) over SiO_2 (source -drain) as shown schematically in Fig 2.12 .

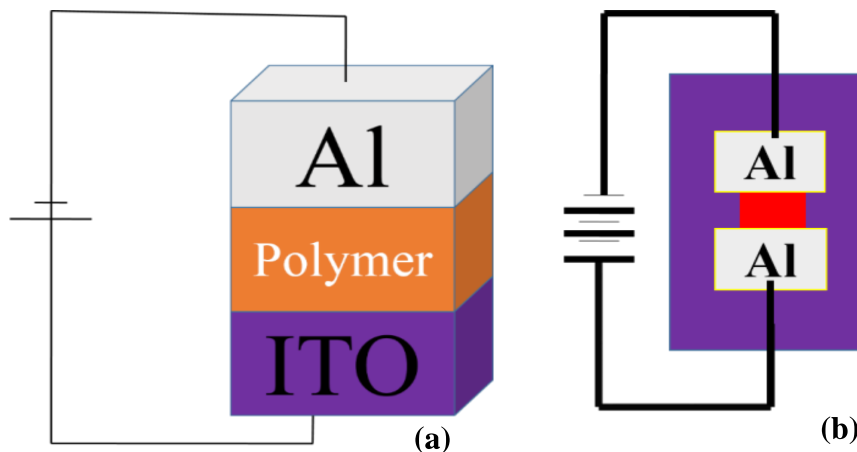


Fig. 2.12 Schematic representations of devices.

The device fabrication consists of following steps:

(a) Substrate cleaning step:

ITO and Si/SiO_2 are used as substrate for device fabrication. The substrate were cleaned using DI water, acetone, chloroform for 20 minutes each using ultrasonic bath. The cleaned substrata was the backed for 20 minutes in vacuum oven at 50^0C.

(b) Thin film depositions

Spin coating and FTM technique has been used for depositions of polymer films over desired substrate.

(c) Electrode depositions (Vacuum thermal Evaporations)

Vacuum thermal evaporation is a common method for thin film deposition of desired thickness over a given substrate. In this method, the source material is evaporated in a high vacuum. Here, the vacuum allows vapor particles to travel directly to the target object (substrate), where they condense back to a solid state. A schematic diagram vacuum thermal evaporations unit is shown in Fig. 2.13. Vacuum thermal evaporations techniques have been used in present study to deposit metal electrode thin films. In this process, materials are vaporized at low pressure approx. 10^{-6}torr by heating the filament according to material to be evaporated. An electric variac is used to monitor the temperature of the filament by controlling the current. There are several parameters which can be varied during the deposition of film such as depositions rate, film thickness, substrate temperature and deposition angle etc. [Mahan 2000].

The diffusion pump backed by rotary pump was used to create vacuum inside the chamber. The thickness of film is controlled by using the quartz crystal micro balance. These processes offer a very clean method of depositions of metal film as electrodes.

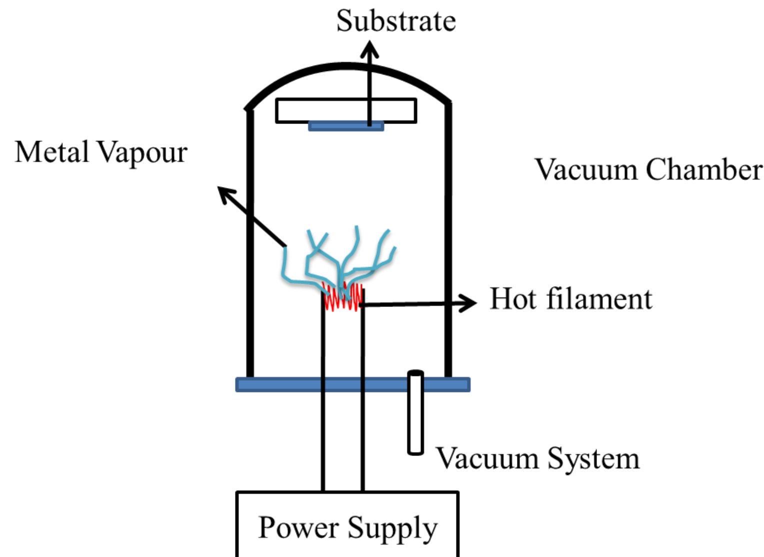
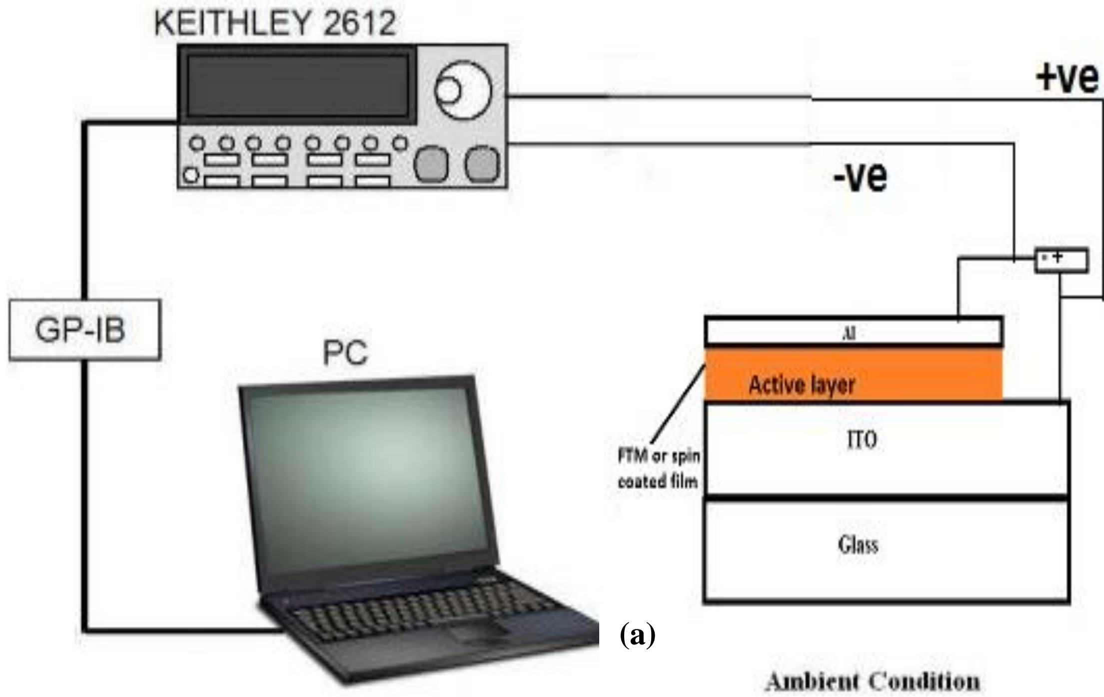


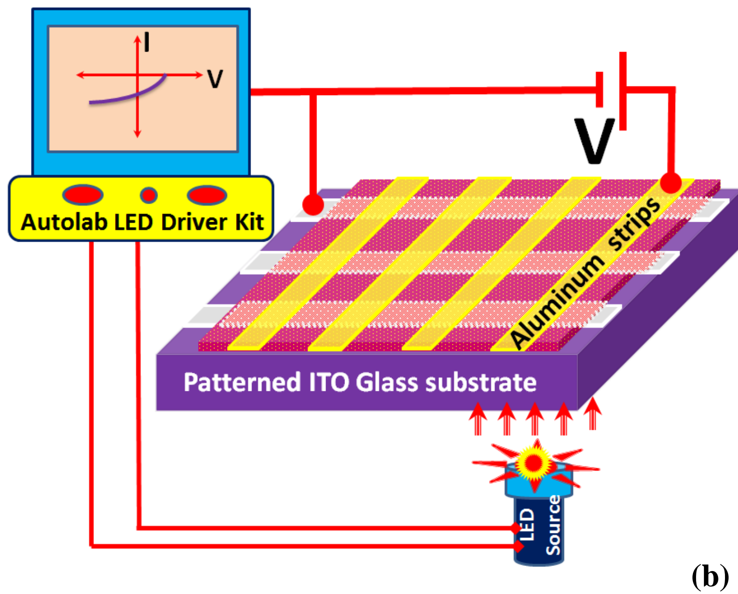
Fig. 2.13 Schematic diagram of vacuum thermal evaporations unit.

2.12 Device measurement

Fig. 2.12 shows the schematic diagram of sandwiched structure of ITO/rr-PQT-12/Al (a), and source -drain structure (MSM structure; Au/semiconducting materials/Au, without providing the gate voltage), Au/20 μm length and 3mm width channel/ Au over SiO_2 (b). The measurement of as fabricated device (Schottky diode) is done in two probe measurement using source meter (Kiethley model no.2612A, dual channel system) as schematically shown below in Fig. 2.14 (a).

For the measurement of the photovoltaic characteristics (current-voltage characteristics in presence of various LED lights), the Optical Bench associated with Autolab LED driver kit (Metrohm, Switzerland), under illumination of different wave length such as Red-627nm, Blue-470nm, and Green-530nm (as schematically shown in Fig. 2.14 (b)) .





(b)

Fig. 2.14 Block diagram of I-V measurement system (a) in case of diode (Schottky) application (b) in case of photodetector application.