Chapter 2

Experimental Techniques and Instrumentations

2.1. Introduction

This chapter summarizes detailed explanation of the experimental techniques required for the material synthesis, and fabrication of the OTFT devices sensor along with the apparatus and instruments used for fabrication and characterization. To examine the optical, structural, and morphological features of the quantum dots, polymer and polymer/nano-composite based thin films, a brief summary of the experimental setup and characterization techniques has been explained. The optical properties of materials are examined using room temperature ultraviolet-visible (UV-Vis) spectroscopy and Fourier transform infrared spectroscopy (FTIR). For structural, and morphological investigations Transmission electron microscopy (TEM), and Atomic force microscopy (AFM) have been used.

2.2. Material Synthesis

In this thesis, a hybrid material combination, polythiophene (PTh) based conjugated polymer with transition metal dichalcogenides (TMDs) based Quantum dots (QDs) were adopted for the fabrication of OTFT based ammonia sensors. PBTTT-C14 [Poly(2,5-bis(3-tetradecylthiophen-2yl)thieno(3,2-b)thiophene] have garnered significant attention from the research society because of its advanced structural and electrical properties, which provides solution processability and crystallization for significant charge transportation in organic electronic devices. Pure conducting polymers typically exhibit low sensitivity toward the target gas. TMDs based QDs are also potential material for their adaptable surfacial functionality and distinctive feature. Both materials can be combined to develop a hybrid OTFT ammonia sensor with exceptionally high sensitivity.

In this thesis work, PBTTT-C14 (Mol. Wt. >40,000), brought from Sigma-Aldrich Pvt. Ltd, has been utilized as CPs for OTFT fabrication. Besides, for the synthesis of MoS_2-QDs and WS_2-QDs, the hydrothermal method has been used, since this process is most frequently used for the synthesis of the TMDs based QDs and other nano-materials also. The primary focus of this thesis work is to develop an organic/inorganic hybrid p-n hetero-junction and homo-junction based high performing ammonia sensors, which can work at room temperature. Therefore, to identify a better composition of p-n organic/inorganic heterojunction that improves charge transport through the film in which hydrothermally synthesized QDs contributes as the n-type semiconductor in the polymer/QDs based heterojunction that highly enhances the overall sensitivity of the device. The hydrothermal synthesis of QDs is detailed in the respective chapters.

2.3. Device Fabrication

In OTFT device based gas sensor fabrication, the semiconductor channel plays an important role as the sensitive layer for the gas detection. In this work, an economical and facile technique called the Floating Film Transfer Method was chosen. This method requires no specialized instruments and generates minimal material waste. Before film fabrication, the substrates were cleaned by sequential sonication for 20 minutes each in deionized water, acetone, and isopropyl alcohol followed by a drying process. Fig. 2.1 displays the schematic of FTM technique. This FTM combines the Langmuir-Schaefer method with drop casting. This process involves casting a film over a liquid surface and then manually transferring the cast film over cleaned solid substrates. The FTM method requires a very high concentration solution of the material. To cast a film via FTM method, a polymer needs to dissolve in a volatile solvent (such as chloroform) which is required to float onto a non-volatile solvent that has a high boiling point. A micropipette is used to deposit a small amount (about 15 µl) of polymer solution onto the surface of a non-volatile blend of glycerol and ethylene glycol. Chloroform immediately evaporates after spreading across the liquid blend surface. The contrast between a liquid spreading on a surface and its adherence and cohesiveness determines how the solvent spreads. During this process, it is possible to calculate the spreading coefficient (S) of a solvent over a water surface in the following way:

$$S = \gamma_{\text{Liquid}} - \gamma_{\text{Solvent}} - \gamma_{\text{Solvent-Liquid}} \quad (2.1)$$

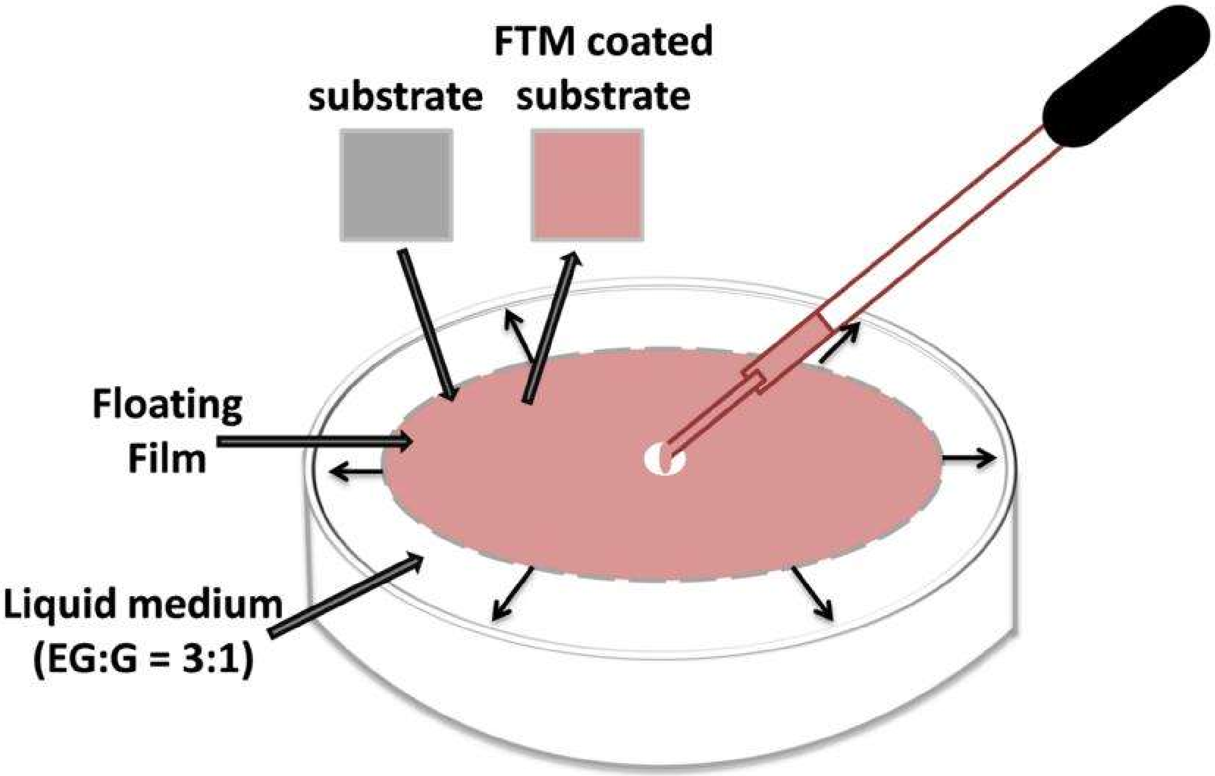

Fig. 2.1. Schematic representation of floating film transfer method (FTM) for film deposition.

where γ_{Liquid}, γ_{Solvent}, $\gamma_{\text{Solvent-Liquid}}$ are the surface tension of water, the surface tension of the solvent, and the interfacial tension between the two liquids, respectively. The spreading process is spontaneous when the spreading coefficient is positive. The spreading coefficient (S) of chloroform can be modified by changes in temperature or by altering the solvent. After the evaporation of chloroform, the polymer molecules stay on the surface due to its immiscibility in non-volatile solvents like glycerol and ethylene glycol, and this entire process results in the production of a good film.

2.4. Characterization Techniques

2.4.1. Ultraviolet-Visible Spectroscopy

UV-Vis spectro-photometry is an analytical technique that determines the absorption or reflectance of light in the ultraviolet and visible sections of the electromagnetic spectrum (typically from 200 nm to 900 nm). A schematic figure of UV-Vis spectrophotometer is depicted in Fig. 2.2. In this process the absorption of radiation in the UV-Vis region causes atomic excitation or the transition of a molecule from a low-energy ground state to an excited state. The interaction of light with matter provides crucial information regarding the electronic structure of chemical compounds. Conjugated polymers containing alternating single and double bonds in their backbone display unique UV-Vis absorption spectra, resulting from π-electron transitions within the conjugated system. The absorption maximum in the UV-Vis spectrum is proportional to the length of the conjugated system; longer conjugation moves absorption to longer wavelengths (lower energy). This characterization technique is important for understanding its electronic properties and potential applications in photo-detectors or solar cells.

When polymers are blended with nano-particles or other materials, (for example, in nano-composites) UV-Vis spectroscopy can be employed to monitor changes in absorption spectra indicating component interactions or dispersion within the blend. In general, for polymers this technique is very useful in assessment of functional groups, analysis of polymer blends and composites monitoring, degradation and stability etc.

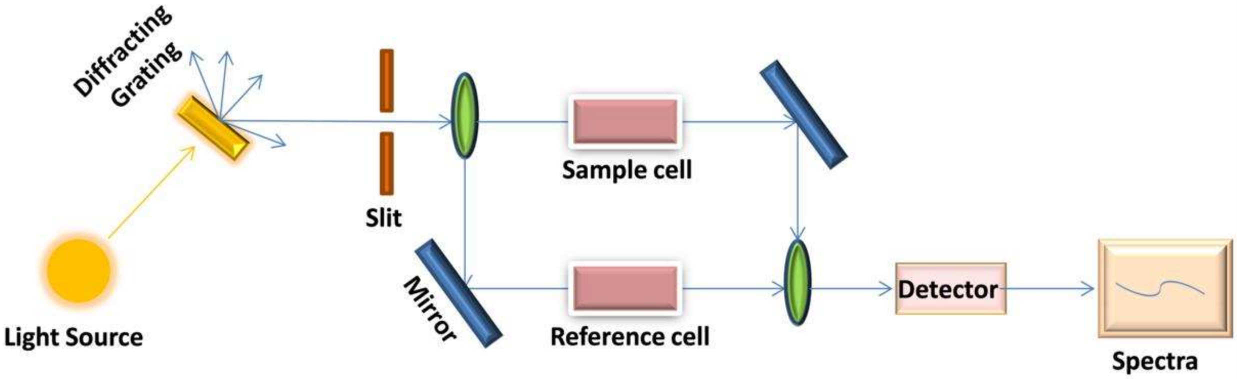

Fig. 2.2. Schematic illustration of UV-Vis spectro-photometer.

2.4.2. Fourier Transform Infrared Spectroscopy

The fundamental concept of FTIR is molecules absorb infrared light at certain frequencies that matches the modes of vibration of their bonds (C-H, C=O, N-H, etc.). The IR region is divided into three parts: near-IR, mid-IR, and far-IR. The mid-IR wave-numbers ranges from 4000-400 cm^{-1}. An absorption spectrum is produced when a sample is exposed to infrared light and its bonds absorb particular wavelengths. The Michelson interferometer (Fig. 2.3.), which includes a beam splitter, a stationary mirror, a moving mirror, a laser source, and a detector is the primary part of FTIR. Light from a source is split into two paths with the help of a beam splitter; one of the paths leads to an immovable mirror, while the other path leads to a moving mirror. An interference pattern is produced when the two beams are reflected from the mirrors and recombined at the beam splitter. This pattern is then transferred to the detector.

In Polymer Compositions, FTIR can be used to confirm the presence of specific monomers or additives in polymer blends or composites.

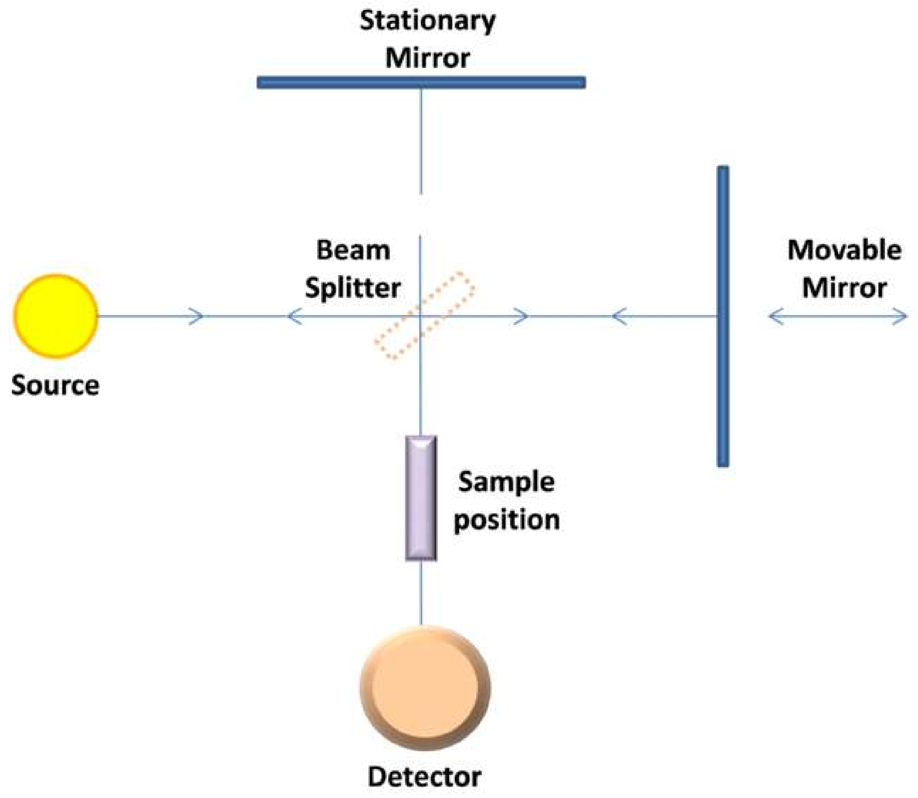

Fig. 2.3. Schematic representation of Michelson Interferometer.

2.4.3. X-ray diffractometer (XRD)

X-ray diffraction (XRD) analysis is a technique used in materials science to determine a substance's crystallographic structure. It measures the intensities and scattering angles of X-rays when a material is exposed to incident X-rays (Fig. 2.4). The results enable one to calculate the atomic distances inside the specimen's crystal lattice. XRD helps in understanding the crystalline arrangement of polymers to explain their properties. For example, polymers with a higher degree of crystallinity typically have higher tensile strength and stiffness. In polymer blends or composites, XRD can help identify interactions between different phases, phases with different crystallinities, or new crystalline phases formed by the combination of materials. Polymers can be measured in the form of thin films, powders, or fibers. Sample preparation might involve cooling or heating to study temperature-dependent structural changes. A typical XRD scan for polymers might cover a 2θ range from 5° to 60° or more, depending on the polymer and the desired resolution. Overall, XRD is a versatile procedure for studying both the crystalline and amorphous regions of polymers, and can provide insights into their molecular structure, crystallinity, and processing behavior.

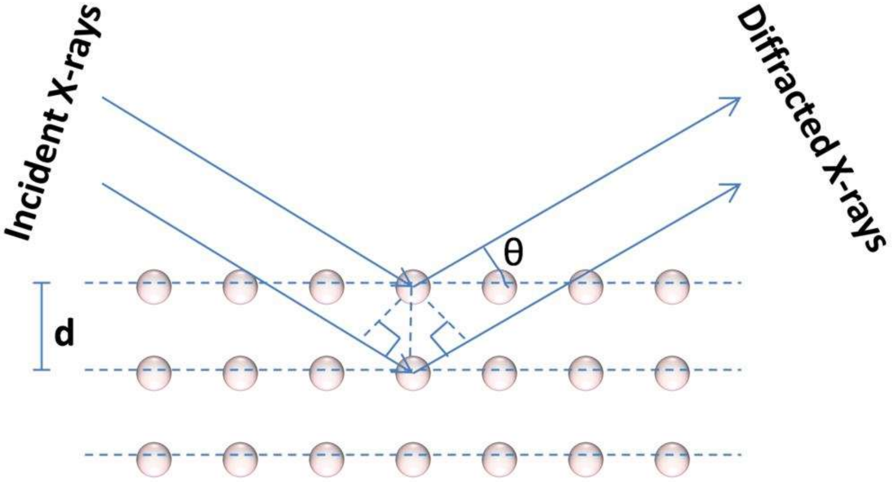

Fig. 2.4. Schematic diagram for X-ray diffraction

2.4.4. Atomic Force Microscopy (AFM)

AFM is a powerful tool for investigating the surface properties of materials at the nano-scale. AFM offers complete insights into the surface morphology, mechanical features, and nano-mechanical behavior of samples. AFM operates by scanning a sharp tip (typically made of silicon or silicon nitride) across the surface of a sample in a controlled manner. The interaction between the tip and the sample's surface is measured through the deflection of a cantilever. AFM can be performed in several modes, each providing different information about the sample's surface. A tapping mode AFM schematic is displayed in Fig. 2.5.

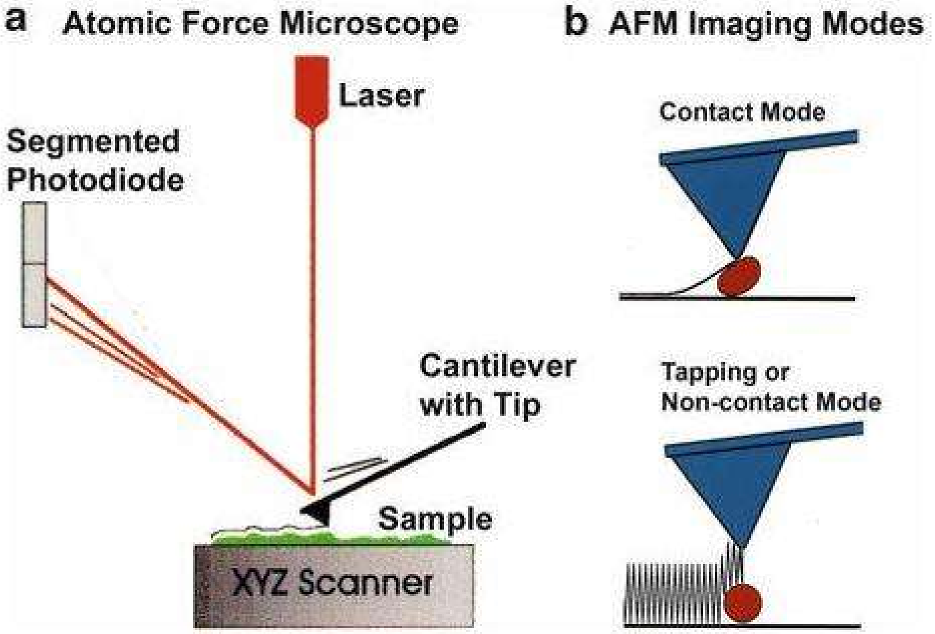

Fig. 2.5. Schematic of tapping mode AFM used for surface roughness measurements (image credit) [99].

Tapping Mode AFM is the most widely used study for polymer surface, in which the tip taps the surface without remaining in constant contact that reduces the likelihood of damaging soft or delicate polymer surface. This mode is particularly useful for studying soft polymers, allowing for the observation of surface topography without excessive force. These AFM micrographs can distinguish micro-phase separated regions in polymer blends, copolymers or nano-composites providing insights into the domain structure, size and distribution of components. Besides, AFM micrographs can reveal crystalline regions in semi-crystalline polymers by observing the periodic structures on the surface, such as lamellae. Therefore, an AFM is a useful instrument in assessing the surface roughness, thin film morphology and adhesion features of polymer films and coatings, which is important for applications like organic electronics and photo-voltaics.

2.4.5. Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) is a powerful microscopy technique, which is used in material science for the analysis of the microstructure of materials at the atomic or nanoscale level. TEM provides high-resolution images and allows for the examination of the internal structure of materials, including phases, defects, crystallography and interfaces. In TEM, a beam of electrons is transmitted through a thin sample. These electrons interact with the material and are scattered, forming an image based on the density and atomic arrangement of the material. A TEM instrument is commonly equipped with EDX detectors, allowing for elemental investigations of the sample by detecting characteristic X-rays emitted from the material when it is bombarded with electrons. TEM can also perform electron diffraction, enabling the study of the crystallographic structure and orientation of materials. This provides important information about grain boundaries, dislocations, and other structural features.

Samples for TEM must be extremely thin (typically less than 100 nm), which often involves complex sample preparation techniques. For this thesis work, I performed TEM study of the polymer and polymer composites for their structural analysis. The thin films of the polymer or composite materials have been transferred onto the carbon coated Cu grid via FTM methods, to understand the detailed microstructure of the film that is used for OTFT fabrication.

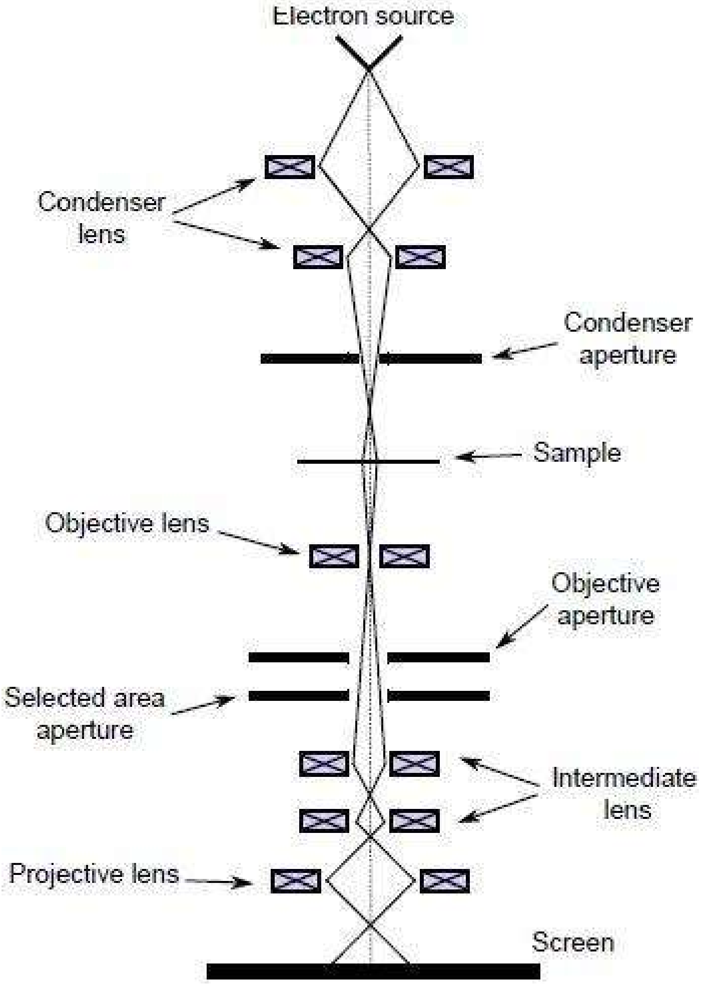

Fig. 2.6. Ray diagram of transmission electron microscope in image mode (image credit) [100].

2.5. Device fabrication

The Gas sensor device fabrication is done in the bottom gate top contact (BGTC) mode transistor configuration. The gas sensitive film is fabricated via FTM method over the Si/SiO$_2$ substrate while source-drain contact electrodes are deposited by thermal evaporator. These processes consist of following steps;

2.5.1. Substrate Cleaning

The Si/SiO_2 substrates were used where 300 nm SiO_2 works as a gate dielectric of the device. Before polymer or composite film deposition, the substrates are cleaned with soap solution and sonicated in an ultrasonic bath cleaner for 20 minutes sequentially in deionized-water, acetone and iso-propanol followed by the drying process in nitrogen atmosphere.

2.5.2. Polymer or composite thin film depositions

After the drying process, the polymer or polymer-composite layer is deposited via the pre-explained FTM method as described earlier.

2.5.3. Source-Drain electrode deposition

Thermal evaporation is one kind of physical vapor deposition, which is used to deposit thin films of materials onto surfaces, such as glass, metal, or plastic. This is done by evaporating the material by heating the substance to its boiling point or sublimation point in a vacuum chamber and then condensing the vapor onto the surface. This process requires careful control of temperature, pressure, and other factors. This technique can be used to deposit a large range of materials, including metals, insulators, and semiconductors. The thickness of the film or coating is in Angstroms to microns range and can be a single material or multiple layers of the different materials. Fig. 2.7 represents a schematic diagram of vacuum chamber of a thermal evaporation system.

In this method, materials are heated to an elevated temperature on the filament in order to evaporate them at lower pressure of about 10^{-6} Torr. An electric variac (current controller) is employed to monitor the filament's temperature. The vacuum inside the chamber is created by diffusion pump, backed by a rotary pump. A quartz crystal micro balance is utilized to regulate the film's thickness. Thermal evaporation can produce high-purity materials with minimal contamination. This instrument has been used to deposit gold electrodes on polymer or composite thin film that works as source drain of the OTFTs.

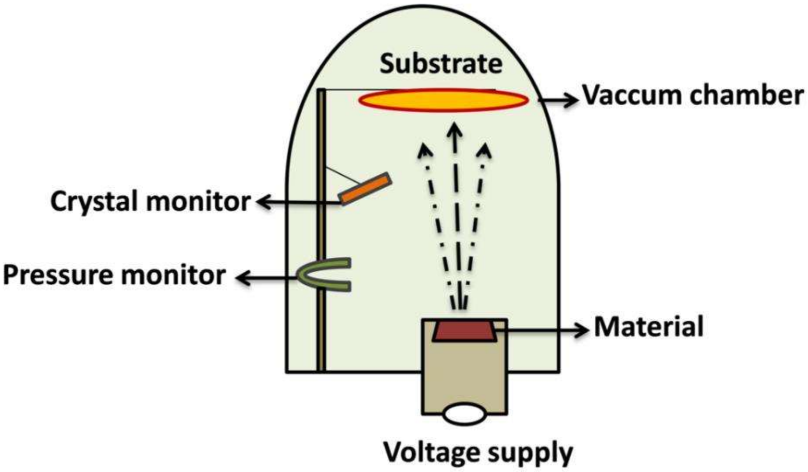

Fig. 2.7. Schematic of vacuum chamber of thermal evaporations system.

2.5.4. Gas Sensing Set-up

A controlled atmosphere gas sensing assembly is designed for the investigations of the ammonia sensing properties of the fabricated OTFT device sensors. A schematic presentation of this set-up is shown in Fig. 2.8. There are two inlets and one outflow on the gas assembly. Ammonia gas is injected through the first inlet, while dry air is injected through the second. Mass flow controllers (MFC) are used for the controlled circulation of the gases in chambers. There is a gas mixing chamber for the mixing of gases. A semiconductor parameter analyzer (Keysight, B1500A) is connected to the gas chamber via a probe station. The purpose of the exhaust pump is to flushing out air from the chamber. Ammonia gas with different concentrations is injected into the gas chamber under the controlled flow of dry air, and the consequential variations in drain current are measured using electronic measurements.

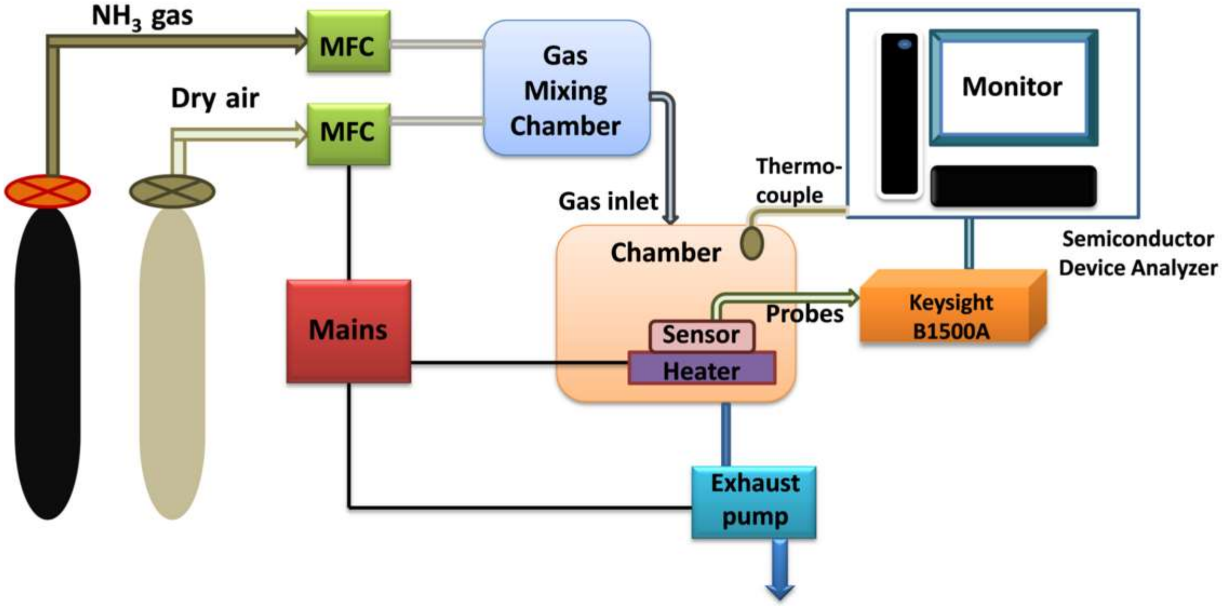

Fig. 2.8. Schematic diagram of Gas sensing set-up.

By analyzing a range of parameters with the help of gas sensing set-up, we can evaluate the performance and characteristics of gas sensors under different environmental conditions. The key parameters for gas sensing are:

- **Sensitivity -** The ability of a sensor to detect low concentrations of a specific gas. High sensitivity is essential to detect trace gases.
- **Selectivity -** The sensor's capability to detect a target gas in the presence of other interfering gases. A high selectivity ensures the sensor responds mainly to the gas of interest and not to other substances.
- **Response Time -** The time taken by the sensor to respond to a gas concentration change. A short response time is crucial for real-time monitoring of gases.

- **Recovery Time -** The time required for the sensor to return to baseline or normal readings after the gas exposure is removed. A quick recovery time is desirable for continuous monitoring and avoiding signal drift.
- **Limit of Detection -** The lowest concentration of a gas that the sensor can reliably detect. This determines how sensitive the sensor is at detecting very low levels of a gas.
- **Stability and Long-Term Performance -** The ability of a sensor to maintain its performance over time, especially under varying environmental conditions.

The above parameters help in evaluating the sensor's sensitivity, accuracy and response to various gases. These parameters collectively determine the performance and suitability of a gas sensor for different applications such as air quality monitoring, industrial safety, environmental monitoring and medical diagnostics.