Chapter-1

Introduction and Scope of the Thesis

1.1 Semiconducting Materials

1.1.1. Background of Semiconducting materials

Semiconducting materials laid the foundation of modern electronics, playing a pivotal role in the development and functionality of various electronic devices. Advancement of cutting- edge electronics technologies is not possible without the development of semiconducting materials suitable for appropriate applications. As technology continues to advance, the exploration and engineering of semiconducting materials, such as organic semiconductors, hold promise for pushing the boundaries of electronic performance and functionality. The versatility of semiconductors underscores their indispensability in powering the ever-evolving landscape of modern electronic technologies. This progress has set the stage for the imminent future, where quantum computers, Internet of Things (IoT) enabled electronic gadgets and wearable electronic devices are poised to reshape the technological landscape. Meanwhile, the integration of semiconductors into IoT devices and wearables is driving a paradigm shift in connectivity, data processing, and user interfaces, enabling a seamless and interconnected world [1][2]. Moreover, the unique properties of semiconductors have made them indispensable in a multitude of technological domains. Large-area displays, such as flat-panel TVs and monitors, leverage semiconductors for their ability to control individual pixels, providing vibrant and high-resolution visual experiences. In the realm of sensing applications, semiconductors are crucial components in sensors that detect changes in the environment and respond in terms of compatible output [3][4]. The ongoing exploration of new semiconducting materials continues to drive innovation, ensuring that these materials remain at the forefront of technological progress.

1.1.2. Definition of Semiconducting Materials

Semiconducting Materials are the materials that have the conductivity property between the metals and insulators. Typically, the energy band gap (E_g) between the conduction band (CB) and valance band (VB) is between 1 eV to 3 eV (**Figure 1.1**) [5]. Si and Ge are well-known semiconductors, used in semiconductor industries. Moreover, in recent decades, organic semiconductors have made significant strides in the domain of organic photovoltaics, contributing to the development of flexible and lightweight photodetectors and gas sensors.

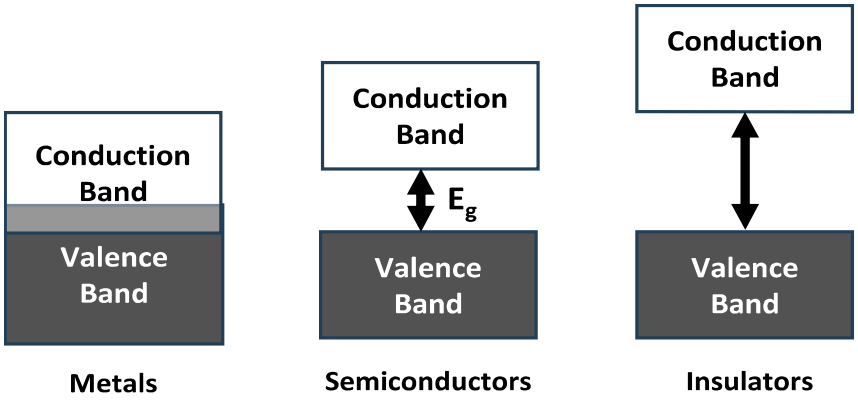

Figure 1.1 Band gap of metals, semiconductors, and insulators.

1.1.3. Applications of Semiconducting Materials

Semiconducting materials have a very broad range of applications. They are widely utilized in various machines, equipment, sensors and also in different electronic gadgets, wearable electronics etc. They are also important for wireless networking and optical communication devices. Furthermore, their compatibility with large-scale, low-cost manufacturing processes positions them as promising candidates for sustainable sensors/biosensors, photodetectors, and biomedical and health monitoring applications [6].

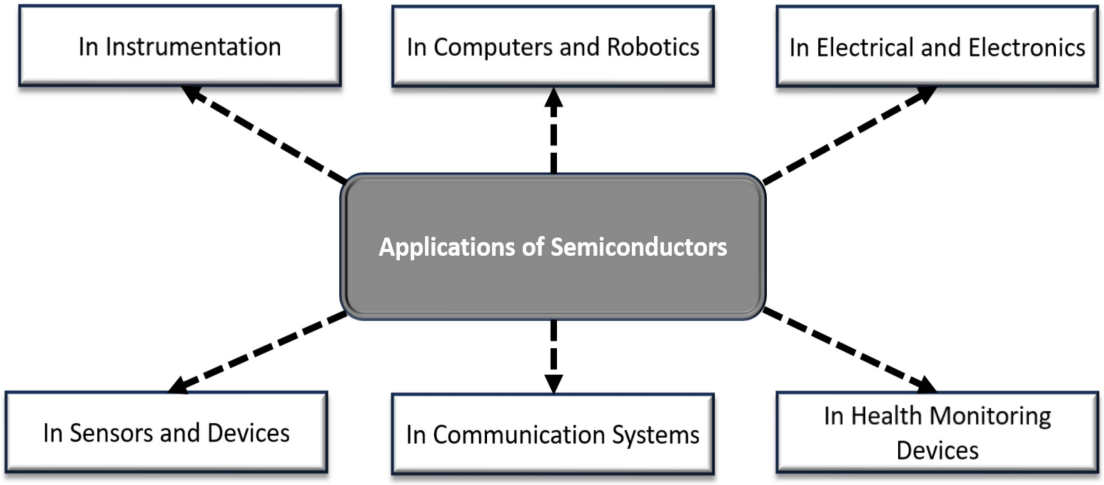

Figure 1.2 Broad area applications of semiconductor materials.

1.2 Classification of Semiconductor Materials

Based on the exceptional properties of elemental composition, structures, and doping profile of the semiconductor materials, they can be classified as shown in **Figure 1.3**. In the thesis work, we are only interested in the organic semiconductor-based device for sensing applications.

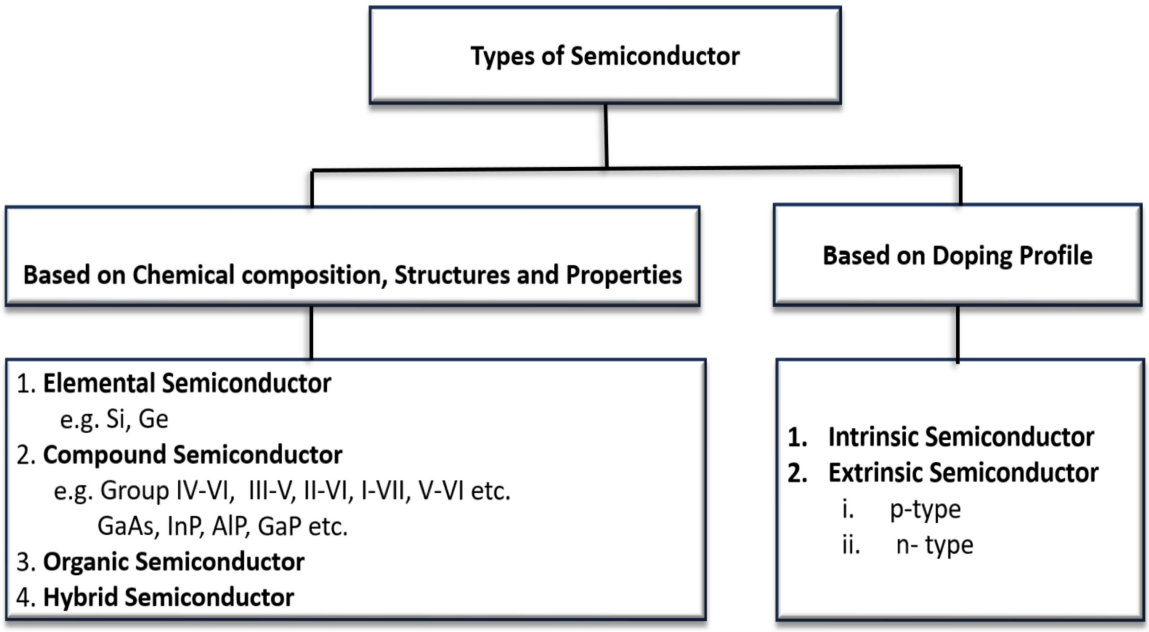

Figure 1.3 Classification of semiconducting materials.

Table 1.1 Advantages and disadvantages of inorganic materials

Advantages	Disadvantages
❖ Exhibit high mobility (1-1500 cm^2/V-sec). ❖ Generally have stability at high temperatures. ❖ Generally have good solubility in water. ❖ Exhibit relatively low melting/boiling points.	❖ Demand additional processing for device fabrication. ❖ Exhibit inflexible frameworks and are hence unsuitable for adaptable and wearable technology.

Inorganic and organic semiconductors represent distinct classes of materials with unique characteristics, each playing a crucial role in the modern era of electronics. Inorganic semiconducting materials have been the bedrock of the electronics industry for decades due to their excellent thermal and stability properties. Although, inorganic semiconductive materials have several advantages but suffer from high-temperature processibility, mechanically inflexible nature, etc. The advantages and disadvantages of the organic and inorganic semiconductors are given in **Table 1.1.** The drawbacks and limitations of inorganic semiconductive materials can be overcome by suitable organic semiconductive materials **(Table 1.1).** Organic semiconducting materials are a new class of materials which are composed of carbon-based molecules, bringing flexibility, lightweight, and cost-effectiveness to the forefront. Their properties make them ideal for applications such as flexible electronics, organic photovoltaics, and wearable devices. While inorganic semiconductors remain integral to mainstream technologies, the rise of organic semiconductors and their advantages reflect a growing emphasis on versatility and adaptability, ushering in a new era where both classes of materials contribute synergistically to the diverse landscape of electronic applications. The present thesis focuses on the inherent applications of organic semiconductors in photodetector and gas sensing applications for industrial and commercial uses.

1.3 Organic Semiconducting Materials

Organic semiconducting materials are well-known structural materials with remarkable electrical properties. They are establishing the foundation for a new approach to electronic devices that can be processed for large-area applications. Furthermore, their device performance parameters can be tuned by modifying the chain structure and thin film processing conditions [7].

- In 1950, **H. Inokuchi** and his team discovered the first conducting organic molecule [8]. Later, it was discovered that these organic molecules can also be used as semiconductors such as Si and Ge. **W. Helfrich** and **W.G. Scheider** studied anthracene and found that organic molecules can also be used in photonic applications, and subsequently, this property of the anthracene was utilized to develop an organic light-emitting diode (LED) [9][10].
- In 1977, **Shirakawa, Heeger** and group**,** first time discovered the organic conductive polymer 'polyacetylene', for which they were conferred the Nobel Prize in 2000 [11]. After that, various organic polymers such as PTCDA **(**perylene tetracarboxylic dianhydride), PTB7, P3HT etc. were discovered [12].
- In 1986, **H. Koezuka, A. Tsumura and Tsuneya Ando** fabricated the first organic field-effect transistor (OFET) using polythiophene polymer which opened a new horizon to explore organic materials-based devices for multiple applications [13].
- Another remarkable success was achieved in 1987 when **Ching Tang and Steven Van Slyke** discovered the first **Organic Light-Emitting Diode (OLED)** at Kodak Lab [14][15]. This device was able to emit light at 5 volts only, which has opened the doors for low voltage operated devices.

The distinctive characteristics of organic polymers, such as their weak intermolecular interactions, low dielectric constants, and the extensive range of available molecules,

determine the possible applications of organic polymer semiconductors for investigating and harnessing solid-state phenomena.

The advent of organic conducting materials has emerged a new field of study i.e. organic electronics with new possibilities for electronic device fabrication and their applications in sensing, biomedical, and other various applications. Several devices are fabricated using organic polymers/molecules: diodes, OLED, OFET, OPV devices, etc. The organic polymer-based device has also wide area applications in display applications, light sensing, gas sensing, biomedical applications, flexible electronic devices, solar cells, etc [6][16][17].

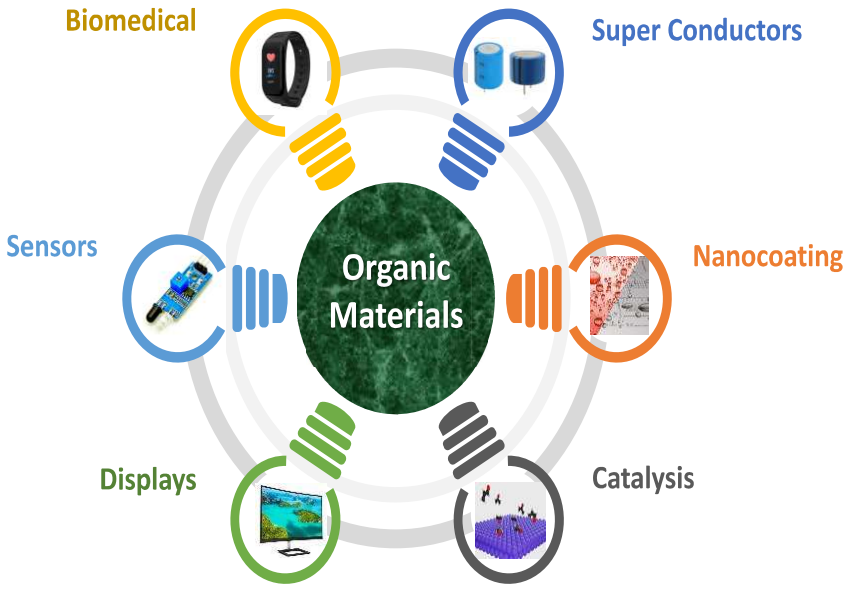

Figure 1.4 Broad area applications of organic semiconducting material-based devices.

1.3.1. Types of Organic Semiconducting Materials

The molecular arrangement and structure of organic semiconducting materials are key parameters for deciding the properties of these materials. Based on these properties organic materials can be classified into two classes:

1. Small Molecules Organic Semiconductors
2. Polymers Organic Semiconductors

- Small molecule OSCs, often in the form of oligomers, consist of individual, well-defined molecules with relatively low molecular weights. In small molecule OSCs, the carbon atoms combine to create long conjugated chains with benzene as a fundamental unit, or in other words, the small molecules consist of carbon atoms that are finite in number. The small molecules exhibit high crystallinity, facilitating efficient charge transport, but may pose challenges in terms of processing thin films and processes with sophisticated vacuum deposition techniques.
- Conversely, polymer OSCs consist of long-chain macromolecules, offering enhanced solution processability and flexibility. The extended and flexible nature of polymer chains allows for better control over thin-film morphology, influencing the overall performance of organic electronic devices. The comparison between small molecule organic semiconductors and polymer semiconductors is given in **Table 1.2** [18].
- The selection between small molecule OSCs and polymer OSCs depends on specific application requirements, with each class contributing uniquely to the evolving landscape of organic electronic technologies. Some common organic semiconducting materials are listed in **Table 1.3** with their applications [19][20][21][18].

Table 1.2 Comparison between small molecule and polymers type of organic materials

Small Molecule Organic Semiconducting Materials	Organic Polymer Semiconducting Materials
❖ Shows poor solubility in common organic solvents, therefore, requires complex vacuum deposition processes for deposition	❖ Shows good solubility in common organic solvents
❖ Uniform Film	❖ Relatively better quality, uniform film
❖ Minimal control over the structural and morphological aspects of the film.	❖ Highly controlled morphological and structural characteristics of the film.
❖ Vacuum evaporation of the small molecule organic semiconductor produces an excellent quality film with better electrical characteristics, but the method is expensive and time-consuming.	❖ When compared to small molecules of organic semiconductors, film quality and electrical characteristics are inferior.
❖ The film progresses towards the crystalline property.	❖ Amorphous in nature, however, crystallinity can be enhanced by specific deposition processes.

Table 1.3 Types of organic semiconducting material, some examples and their applications [22][23].

Organic Semiconducting Material		Examples of Polymers (Acronym)
Small Molecule Organic Semiconductors	Thiophene & Discotic Liquid Crystals	❖ Hexabenzocoronene ❖ DNTT ❖ Triphenylene
	Oligoacenes	❖ Perylene diimide ❖ Triphenylene
Organic Polymer Semiconductors	Polyparaphenylene, Polyparaphenylene Vinylene, and derivatives	❖ PPP ❖ PPV
	Polythiophene (PT) and derivatives	❖ P3HT ❖ PQT C-12 ❖ Polyanilines (PANI) ❖ PTB7 ❖ PBTTT C-14

1.3.2. Comparison of Organic and Inorganic Semiconducting Materials

Inorganic semiconductors have some limitations which can be overcome by organic semiconductors. **Table 1.4** represents the material, fabrication and electrical properties of organic and inorganic semiconductors.

Table 1.4 Comparison between organic and inorganic semiconducting materials

Comparison of Organic/Inorganic Semiconducting Materials		
Parameters	**Organic semiconducting Materials**	**Inorganic semiconducting Materials**
Processing Temp.	Low Temperature	High Temperature
Stability	Less Stable	Highly Stable
Flexibility	Flexible	Inflexible
Mobility	Low Mobility	High Mobility
Differences in terms of various Electrical Parameters		
Binding Energy	Weak (Van der Waals force)	Strong (Covalent bonds)
Polarization	Relatively strong	Relatively weak
Carrier Mobility	~1	~1000

Organic polymers offer a range of advantages that make them highly attractive for various applications in the field of materials science. Some of the important distinct properties of organic semiconducting materials are as mentioned below:

1. The main advantage of organic semiconductors is assembled into a fully flexible film on any substrate which leads to better charge transportation in the fabricated device.
2. Organic semiconducting materials have very good solubility in organic solvents, thereby best suitable for solution processing device fabrication approach. These solution-processable methods are cost-effective and scalable for large industrial manufacturing.
3. Organic polymers are best suitable for low-temperature fabrication methods. The low-temperature method has the inherent advantage of the organic polymer for the fabrication of flexible organic devices on PET (Polyethylene Terephthalate) or plastic substrate.
4. Their inherent mechanical flexibility and tunable properties of materials with tailored electronic, optical, and mechanical characteristics. In organic materials, the photonic properties can be finely tuned via chemical synthesis. These tunability

properties of the polymers can be suited for various broad-area sensing applications.

5. Organic polymer's thin coating can be easily grown over large areas and a variety of substrates, including mechanically flexible substrates. Associated with the simple processing steps, the fabricated device has a major potential for low-cost fabrication.
6. Semiconducting or conducting (doped semiconducting) polymers, can be doped with other materials to prepare as 'inks' for thin-film printing technology. [25][26].
7. The sustainable and environmentally friendly aspects of many organic polymers further contribute to their appeal, making them key players in the development of innovative technologies for the modern era.

1.4 Charge Transport Mechanism in Organic Semiconducting Material

The structure of organic semiconducting materials consists of a polymer backbone with alternatively arranged single and double carbon-carbon bonds. This alternation of the single and double bonds is called conjugation. The double-bond carbon atoms show sp^2 hybridization.

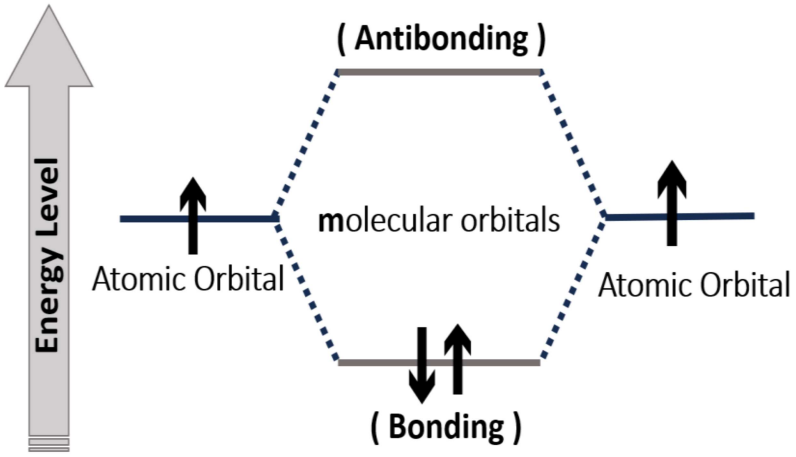

Figure 1.5 Splitting of molecular orbitals in organic semiconducting materials [28].

The charge transportation in π-conjugated organic materials is determined by one type of charge carrier, either electrons or holes. In strong electron acceptors or p-doped

polymers, charge-carrier transportation is done by holes as carriers [27]. In organic semiconductors, the separation of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels are formed due to the interaction of adjacent atomic orbitals which is analogous to the valence band and conduction band in inorganic materials (**Figure 1.6**) [21][29].

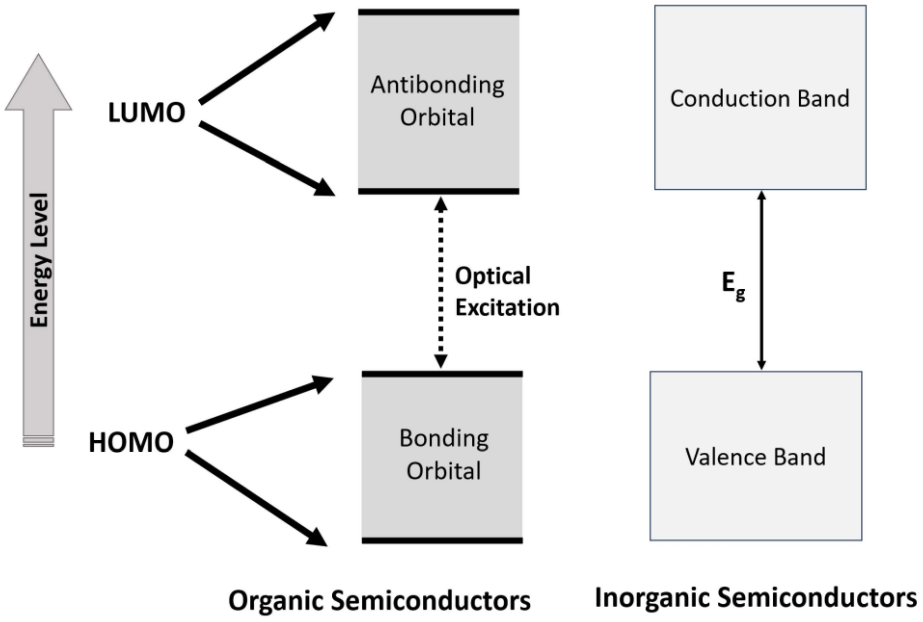

Figure 1.6 HOMO and LUMO levels and bandgap representation in organic/inorganic semiconducting materials [29].

- In organic materials, charge transportation can be described by Intra-chain charge transfer, Inter-chain charge transfer, and the Hopping method [30][31].

1.5 Thiophene Based Organic Polymers

Thiophene-based oligomers and polymers are organic semiconductors that exhibit an extensive variety of features such as charge conduction in the oxidized or reduced states ("doped" states) for optical sensing by illumination of a suitable wavelength of light. These compounds demonstrate significant variation in their structure and are primarily synthesized to modify molecular structures that may be useful for understanding the structural relationship during material properties optimization required for sensing

applications [32]. The incredible adaptability of thiophene-based materials is attributed to the extensive options of ring functionalization and chain extension from a few rings forming monodisperse oligomers to a large number of ring-forming polydisperse polymers which can tune the device properties for broad area applications.

1.5.1. Advantages of thiophene based Organic Semiconductors

1. Thiophene semiconductors offer structural variation, which provides tuning of electronic properties over a wide range of optoelectronic applications.
2. Thiophenes are chemically stable materials in open air. Therefore, suitable for the fabrication of highly stable devices for sensing applications.
3. Thiophenes exhibit unique arrangement and stacking properties on solid surfaces, which make them perfect for organic electronics.
4. These materials have very promising electronic, and optical properties with good charge transport and self-assembly properties.
5. The main significance of thiophene-based molecules is their low cost and processability at low temperatures, mechanical flexibility, ability to be applied on flexible substrates, and high charge transport characteristics that can be utilized for high-performing devices.
6. Thiophene exhibits smaller band gaps because of sulfur molecules as compared to other five-membered oxygen and nitrogen-containing heterocycles. Owing to a narrow band gap these thiophene molecules can transfer effective charge between donor and acceptor molecules.

1.5.2. PTB7 and its distinctive Properties

PTB7 is a low-bandgap conducting polymer with high mobility which is widely used for the fabrication of solar cells [33][34][35] and photodetectors [36] using low-cost solution methods. The PTB7 polymer has the unique qualities stated

below, which make it a preferred choice for device fabrication and its broad area application in sensing:

1. PTB7 has very good solubility in chloroform, chlorobenzene, and dichlorobenzene which makes it outstanding for solution processing or sol-gel method of deposition.
2. PTB7 exhibits excellent promising electronic and optical properties (Absorbance: ~ 665 nm) which offers an ideal choice for visible range photodetector.
3. PTB7 has good charge transport properties and self-assembly properties.
4. PTB7 shows high mobility as $\mu_p = 1\times10^{-3}$ $cm^2/V\text{-}s$ at room temperature contributing to enhanced device performance.

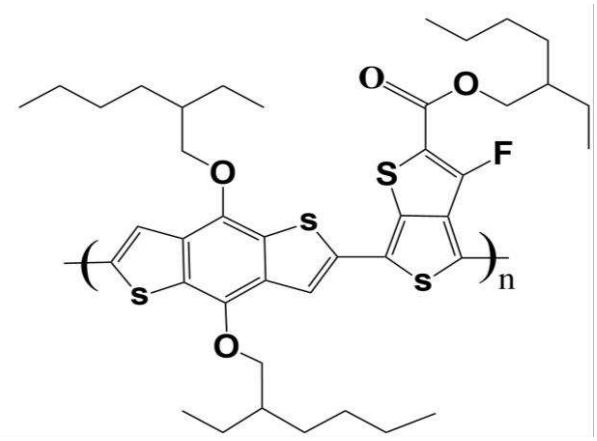

Figure 1.7 Chemical structure of PTB7.

1.6 Basics of Photodetectors

Photodetectors are optoelectronic devices that convert light signals into electrical signals. Based on the region of application, photodetector can be divided into 4 categories[37]:

1. UV Photodetector
2. Visible Photodetector
3. IR Photodetector
4. Broadband Photodetector

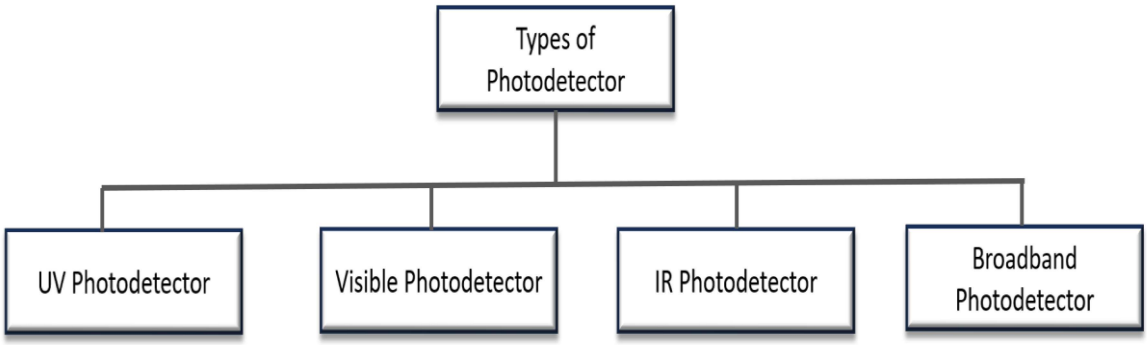

Figure 1.8 Classification of photodetectors.

The performance of the Photodetector can be qualified based on the following parameters [38][39]:

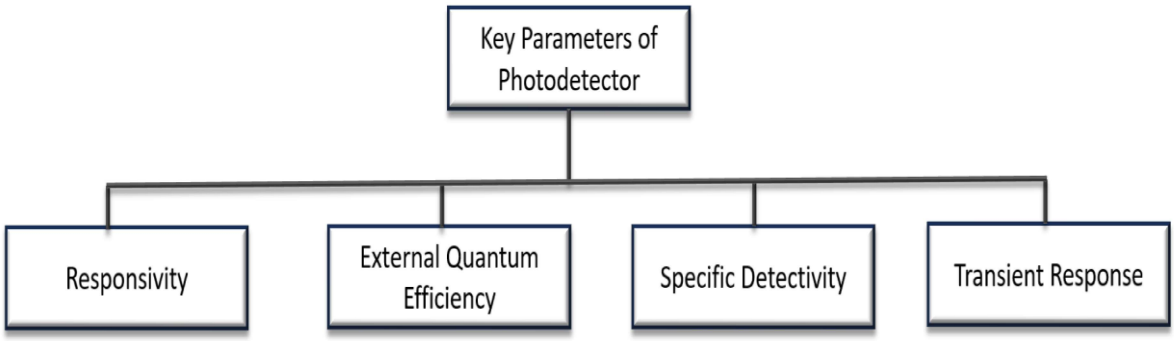

Figure 1.9 Figure of merits of photodetector.

1. Responsivity (R)

It is an important metric for performance measurement in any photodetector. It is determined as the ratio of generated photocurrent and the incident/absorbed optical power. It is calculated by the following formula:

$$Responsivity\ (R) = \frac{Photocurrent}{Incident\ Optical\ Power} = \frac{I_{ph}}{P_{in}}\ (A/W) \qquad (1.1)$$

2. External Quantum Efficiency (EQE)

It plays a significant role in deciding the efficiency of a photodetector. EQE is expressed as the no. of charge carriers collected by the external circuit to the no. of photons that fall on the photodetector device. It is related to responsivity as below expression:

$$EQE\ (\%) = 1240\frac{R}{\lambda} \times 100 \tag{1.2}$$

where λ is the wavelength (in nm) of the incident optical light.

3. Specific Detectivity (D*)

Specific detectivity is defined as the minimum power of the incident optical signal that the device can detect and reflect as an output response. Specific detectivity is computed by the formula below:

$$D^* = \frac{R}{\sqrt{2eJ_d}} \qquad (Jones) \tag{1.3}$$

Specific detectivity is measured in **Jones**. J_d, is the dark current density and e is the charge of an electron.

4. Transient Response (t_r, t_f)

Transient analysis of photodetector signifies the response time and recovery time of any photodetector. Rise time is the duration in which the detector produces a response when exposed to appropriate light to the response. Similarly, the recovery time is the duration in which the photodetector is again ready to respond according to input light.

The device structures used in this thesis for photodetection are represented in **Figure 1.10**. These structures can be broadly classified into two types [6]:

1. Metal-Semiconductor-Metal (MSM) Devices
2. Vertical Structure Devices

1. Metal-Semiconductor-Metal (MSM) Devices

Metal-semiconductor-metal is a two-terminal, symmetric device structure. In the MSM structure, both contacts are of schottky type in nature, which behaves as the back-

to-back schottky diode. This MSM structure exhibits high responsivity compared to other photodetector device configurations.

2. Vertical Structure Devices

These are also two terminal devices also known as photodiodes. When the light falls on active material the excitons are generated, which are collected to the respective electrodes constituting photocurrent. These vertical device structures offer better transient responses compared to other device structures.

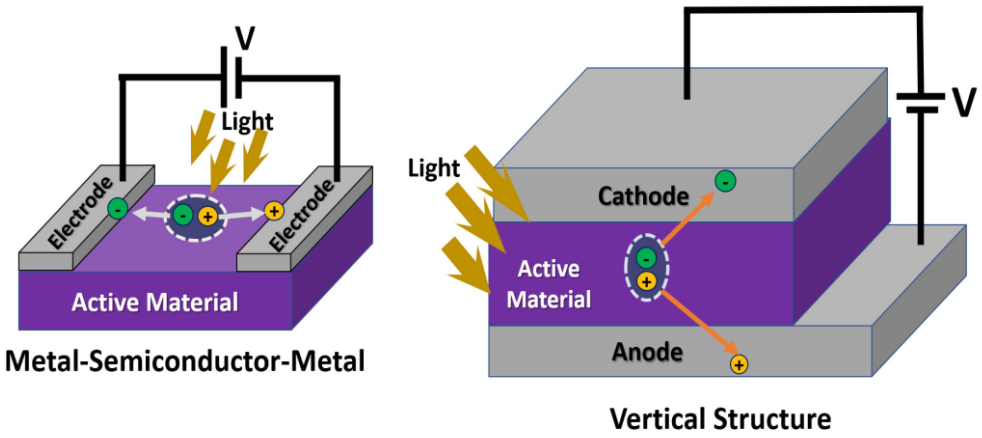

Figure 1.10 Structures used for photodetectors.

1.6.1. Working Mechanism of Photodetectors

A photodetector is a light-dependent device. When the photodetector is exposed to light of suitable energy, it absorbs the light and accordingly photocurrent is generated in the device. The working of the photodetector can be described in the following steps [37][40]:

- When the photodetector is exposed to light, the incident photon energy gets absorbed in the active layer.
- After absorption of photon light charge excitons are generated at the interface.
- These charge excitons are separated and transported to an external circuit that constitutes photocurrent in the device.

1.7 Basics of Gas Sensors

Gas sensors are electronic devices that identify the presence of different gases around them. Typically, these sensors are used to monitor the harmful/toxic gases in industries, or workplaces, the environment monitoring and food quality measures. In this thesis, the fabricated device is studied for ammonia gas detection, which harms human health if exceeds the safety guidelines [41].

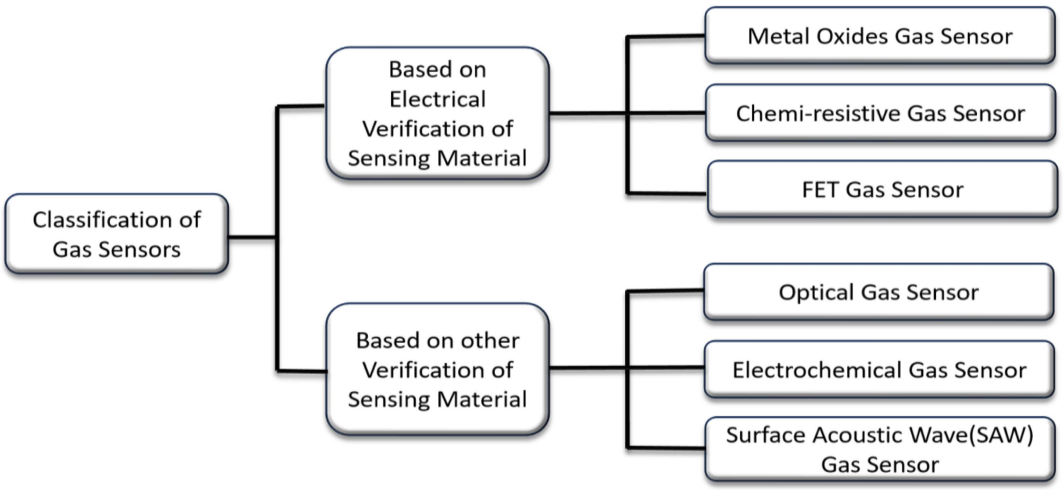

Figure 1.11 Classification of gas sensors.

Some gas sensors are based on the electrical properties of sensing materials which measure the change in the electrical properties of the sensing material after interaction of the specific gas, while other properties of the sensing material such as refractive index, optical absorbance etc. can also be verified for gas sensing. Based on the different verifications, gas sensor classification is presented in **Figure 1.11** [42][41][43].

The performance and efficiency of the gas sensors are measured on the following key parameters shown in **Figure 1.12** [44][45]:

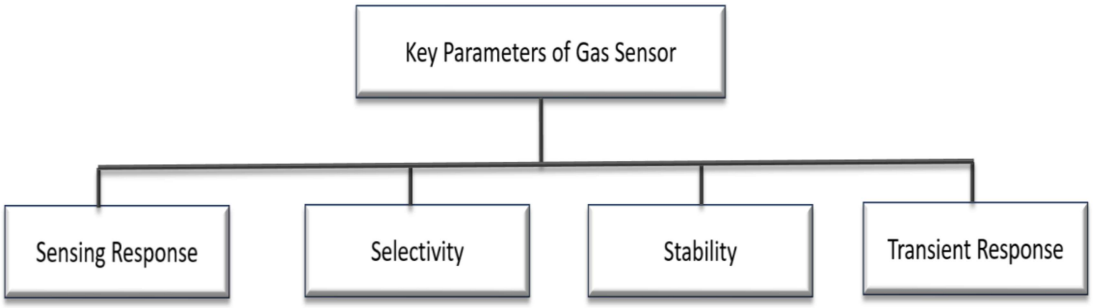

Figure 1.12 Figure of merits of gas sensors.

1. Sensing Response

This is also called the sensitivity of the gas sensor. It is expressed as the ratio of change in sensing parameters (i.e., resistance, current etc.) in the presence of a target gas.

$$\%\, S = \frac{Change\ in\ sensing\ parameter}{sensing\ parameter\ in\ reference\ condition\ or\ in\ air} \qquad (1.4)$$

$$= \frac{I_{air} - I_{gas}}{I_{air}}$$

where I_{air}, I_{gas} represent device current in air/reference atmosphere and device current after target gas exposure.

2. Selectivity

It is the ability of the gas sensor which discriminate the specific gas out of a mixture of gases. It is crucial for the identification of a particular class/ species of the analyte gas.

3. Stability

Stability measures the gas response of the gas sensor repeatability over time. Also, the humidity affects the sensing response of the gas sensor. Extreme exposure to humidity may surpass the response of the gas sensor.

4. Transient Response

Transient analysis of the sensor describes the response time and recovery time of the gas sensor. Response time is the time that measures the response from 10% to 90% of its

final value when interacting with the target gas. Similarly, the recovery time can be explained by the time duration in which the gas sensor is again ready for sensing response.

1.7.1. Working Mechanism of Gas Sensors

The working principle of the gas sensor is enlightened by two phenomena [42][46]:

1. Physisorption
2. Chemisorption

Physisorption is the physical interaction of the target gas molecule with the sensing material. There is no chemical change in the sensing molecules with gas atoms. The gas molecules adsorb/desorb at the active sites of the sensing layer through reversible vander walls (weak intermolecular) forces.

Chemisorption is a chemical interaction between the sensing surface and target gaseous molecules which results in higher bonding energy. Chemisorption can be further described as associative chemisorption and dissociative chemisorption.

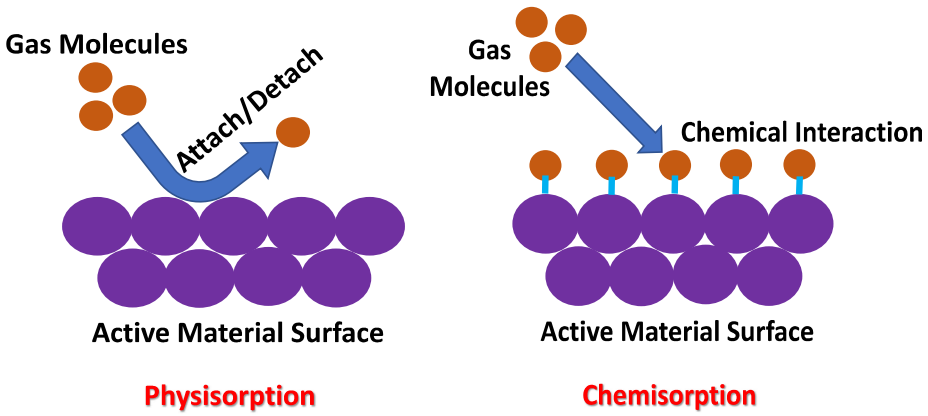

Figure 1.13 Gas sensing mechanism: (a) physisorption and (b) chemisorption.

The selection of the sensing material and the exposed gas display the different electrical behaviour during measurement. **Table 1.5** shows the relation between the

nature of the target gas with the sensing material and the effect on resistance after gas exposure[47].

Table 1.5 Resistance of the device according to the type of material used and target gas

Resistance Response with Type of Materials and Nature of Gas Exposed		
Classification	**Nature of Gas**	**Device current**
n-type	Reducing Gas	Increasing
	Oxidizing Gas	Decreasing
p-type	Reducing Gas	Decreasing
	Oxidizing Gas	Increasing

In this thesis, ammonia gas sensing is examined by an active layer of PTB7 polymer equipped with ZnO nanostructures at room temperature.

1.8 Instruments used for Device Fabrication and Characterization

There are various steps involved in the device fabrication. In the first step devices are fabricated followed by the thin film analysis using FESEM, and AFM characterizations. For photodetector application optical characterization is also performed to measure the maximum absorbance region of the active material. Finally, the fabricated devices are used for electrical parameters measurement and light/gas sensing applications.

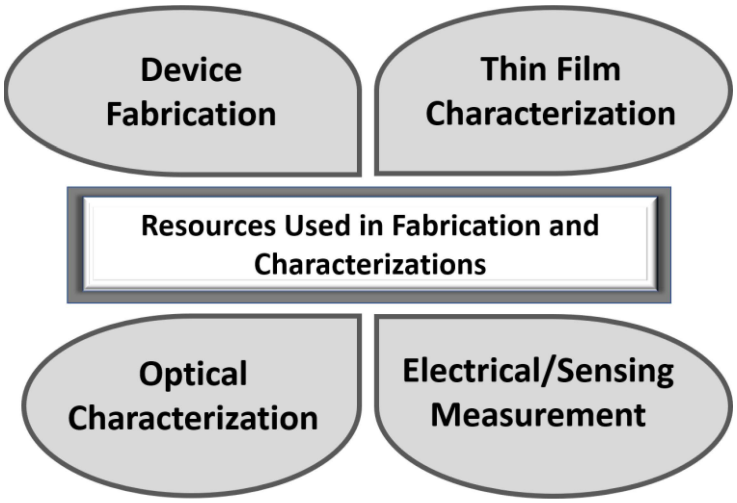

Figure 1.14 Various steps involved in device fabrication and characterization.

1.8.1. Thin Film Deposition Techniques

The typical thin film deposition techniques are shown in **Figure 1.15**. Organic semiconducting materials (OSM) have the advantage of better solubility to achieve thin films. Therefore, OSM are best suitable for solution-processible approaches for device fabrication. We have mainly opted for the spin coating and floating film transfer method to obtain a thin film of our polymer. Spin coating and FTM methods and explained in **Figure 1.16**. **Table 1.6** demonstrates a comparison study of the spin coating and FTM method for thin film deposition.

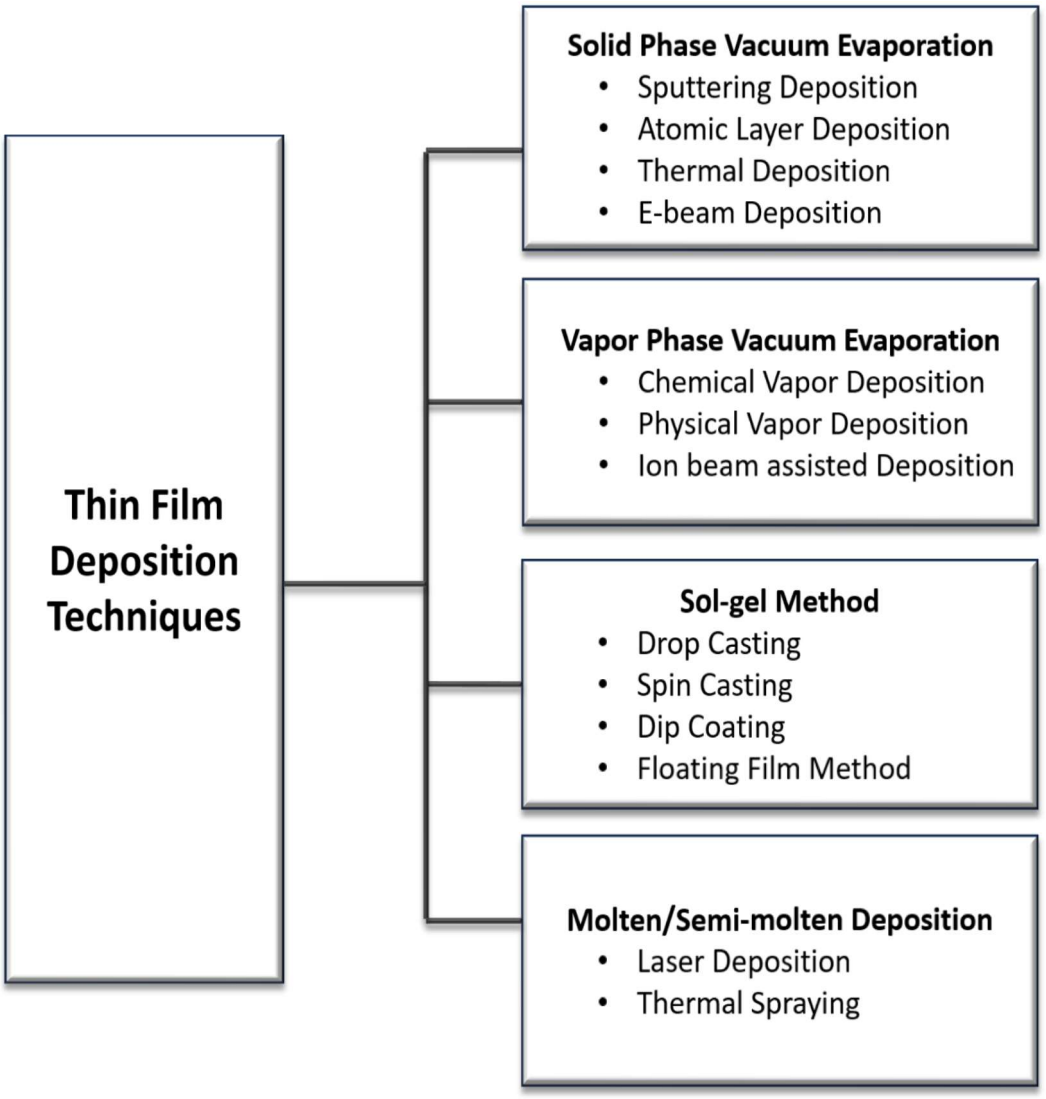

Figure 1.15 Various thin film deposition techniques.

- Spin Coating is a widely used and versatile technique for thin film deposition method on a substrate. In this method, a solution of the material is spun at high speed, centripetal force and a surface tension of the liquid works together which creates a thin coating of the material over the substrate. Spin coating is a very popular method of film coating which is scalable for large-area production. The process is illustrated in **Figure 1.16** in detail for explanation.
- The concentration of the solution, viscosity, speed of rotation, and time duration of rotation are key parameters to optimize the quality and thickness of the film coating.

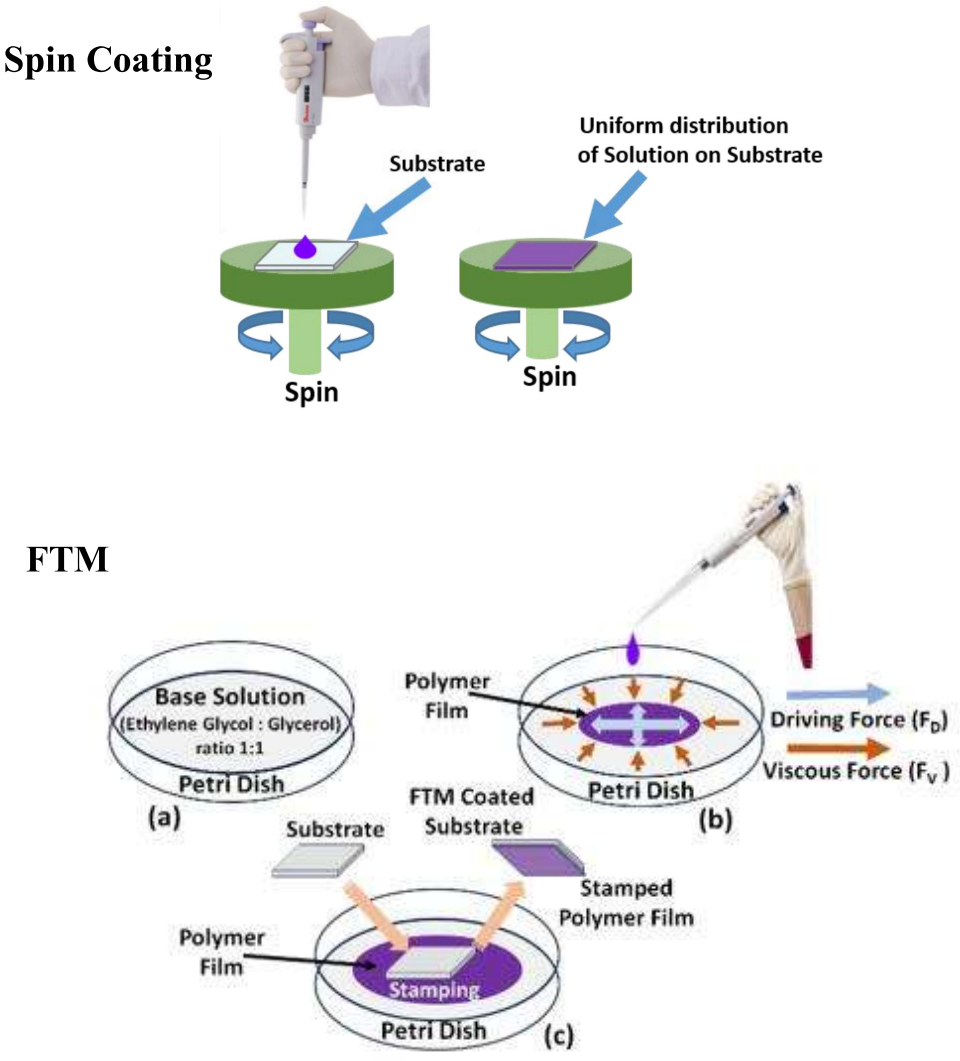

Figure 1.16 Spin coating and FTM method of thin film deposition.

- The FTM is a solution approach to achieve a self-assembled thin film of polymers with certain advantages viz. easy fabrication steps, and almost no wastage of polymer. This FTM technique produces a very good polymer chain assembly with optimized thickness control of the film. FTM is preferred to the polymers with high molecular weight (>30000 wt.) because of good solubility properties (**Figure 1.16**).
- A thin film is obtained from a low surface energy solvent (polymer in chloroform) over a base solution of a high surface energy solution (mixture of Ethylene Glycol: Glycerol**,** ratio 1:1), which is shown in **Figure 1.16**. There is a surface pressure gradient between the interface of both high and low surface energy solvents [48].

Since Spin coating and FTM both are solution processing methods, both have their advantages and disadvantages summarized in **Table 1.6**.

Table 1.6 Comparison of spin coating and FTM for thin film deposition

Spin Coating	FTM
❖ More wastage of material during deposition	❖ Minimal wastage of material
❖ Can be used for large-scale manufacturing	❖ Better for small-scale production
❖ Require a deposition setup	❖ Does not require any setup
❖ Produces good quality film	❖ Produces high-quality uniform film
❖ Can be used for rigid and flexible substrates	❖ Can also be used for rigid and flexible substrates

1.8.2. Summary of Fabrication and Characterization Process

A complete device fabrication and characterization includes several steps from material synthesis to final device parameters measurement. A brief introduction of the instruments used in the device fabrication in this thesis is summarized in **Figure 1.17**.

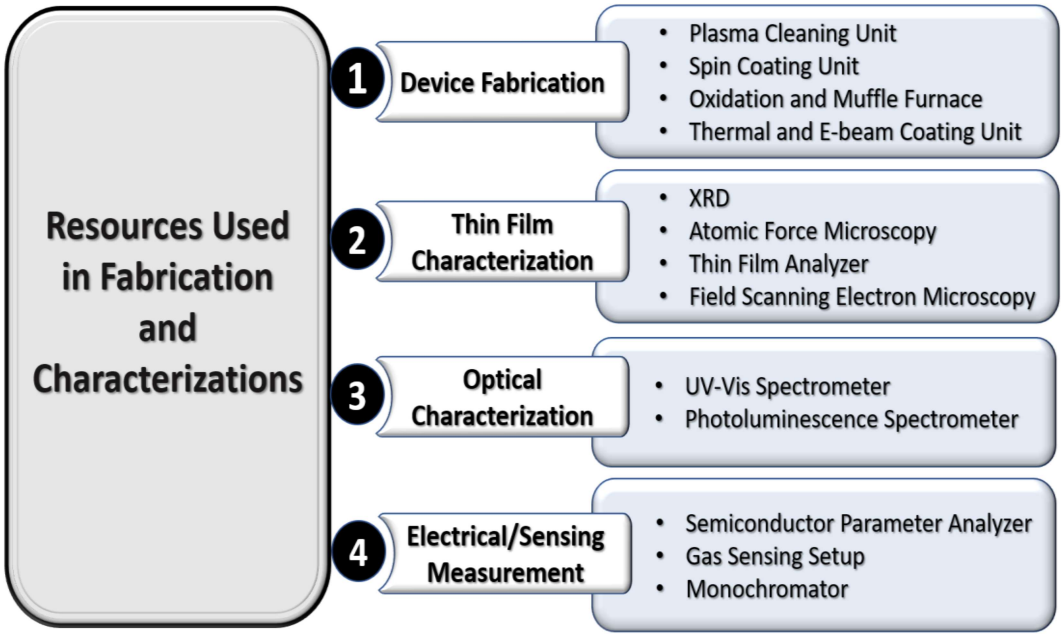

Figure 1.17 Resources used in fabrication and characterizations of devices used in this thesis.

1.9 Literature Review on Organic Semiconductor Materials-based Devices

In 1964, J. E. Meinhard reported organic material-based rectifying junctions by depositing organic compounds using vacuum deposition method [49]. After that H. Shirakawa et al. [11] reported high conductivity organic polymer 'polyacetylene' in 1977. In 1979, rectifying junctions were fabricated by M. Ozaki and his group using polyacetylene polymer [50]. After that, the mechanism of metal-polyacetylene schottky contact was proposed by J.R. Waldrop and his team in 1981[51]. In 1983, Ebisawa et al. [52] investigated the I-V and C-V measurements for analyzing the electrical properties of the organic polymer polyacetylene/polysiloxane interface. They have fabricated the metal-semiconductor-metal structure for device measurement. Later, various devices such as schottky diodes [53][54] and MSM diodes [55][56] have been reported by using different conjugated polymers and polythiophene family polymers. Several conjugated polymers have been explored by researchers and found that the polythiophene family polymers exhibit relatively better air stability, good solubility,

good quality thin film for light sensing [16][6][57] and gas sensing [58][59][60] devices compared with other organic polymer-based devices.

1.9.1. Organic Polymer-based Visible/White Light Photodetector

Thiophene derivative polymers such as PQT-12 and P3HT have been investigated by researchers as MSM [61][62], vertical structure [63] and organic field effect transistors [64] for optoelectronic applications. These organic polymer-based devices have been studied as organic photodetectors [17], organic light-emitting diodes (OLEDs) [65], and organic photovoltaics [66]. Several research groups have explored the OTFT-based device for visible light sensing [67][68][69].

Some researchers have fabricated two-terminal-based organic photodiode/inverted devices for visible photodetection applications [70]. Schilinsky et al.[71] have fabricated heterojunction visible photodetector, but high dark current was present in this fabricated device. Then, Ramuz et al. [72] reported an organic polymer-based low-dark current visible range photodiode using P3HT polymer. Armin and group [73] have reported a photodiode structure for visible light detection by optimizing the thickness of polymer active layer. Park et.al. [74] used PBDTT-8ttTPD: PC71BM and P3HT: PC71BM as active materials for visible light photodetector. Armin et.al.[75] have reported heterojunction structures using PCDTBT: $PC_{70}BM$ and DPP-DTT: $PC_{70}BM$ organic materials to realize a visible light detector. Zafar et.al. [76] fabricated PEDOT: PSS/VOPc-PhO: PCDTBT structure-based photodetector for visible range detection.

Zeng et al. [77] have reported a vertical structure-based photoactive layer of conjugated polymer for broadband light detection. Chen et al.[78] have fabricated P3HT composite-based OTFT for white light sensing. Several research groups have

explored organic composite-based devices for broadband light sensing applications [79][80][81][82][83].

Recently, Upadhayay et. al [36] have reported a two-terminal PTB7 thin film-based vertical device for visible light sensing. Also, R. K. Upadhyay et.al [84] have published PTB7 bilayer device for white light sensing.

All the above-mentioned devices have been fabricated by spin coating method of thin film deposition. These spin-coated thin films can be further improved for better self-assembly/orientation of carbon chains by adopting another emerging solution processing method i.e. floating film transfer method (FTM) [85][23]. Tiwari et al. [86] have reported a detailed comparative study in terms of surface morphology, optical properties and electrical characteristics of spin-coated thin film devices and FTM deposited thin film devices and obtained better performance by FTM deposited device.

Therefore, PTB7 thin film devices in MSM and vertical configuration are studied in this present thesis for visible/white light sensing.

1.9.2. Organic Polymer based Ammonia Gas Sensor

Ammonia is a widely used gas in industrial production of pharmaceuticals, fertilizers and beverages [87][88]. In these industries, ammonia is exposed to the environment and human resources involved in production. Ammonia exposure beyond the safety guidelines by OSHA (Occupational Safety and Health Administration) has a catastrophic impact on human health [41]. It can cause lung damage, and blindness also [89]. Therefore ammonia sensors are mandatory devices used in industries for safety regulations.

Researchers have explored various conducting polymers such as polyacetylene, polypyrrole, and polythiophene derivatives to develop low-cost, highly sensitive

devices for ammonia sensing [58][90][91][92]. In this quest, Miasik et al. used polypyrrole device for ammonia sensing. Later, Chougule et al. [93] also fabricated a polypyrrole thin film for room temperature ammonia sensing. Some researchers have explored nanostructures with polyaniline thin film to improve sensing response over pristine polyaniline sensors [94][95]. Later, polythiophene derivative polymers P3HT and PQT-12 have been extensively explored for room-temperature ammonia sensing. Tiwari and group [96] have reported P3HT-based organic thin film transistors (OTFTs) for low-concentration ammonia detection at room temperature. Xie et al. [97] fabricated an ammonia sensor using P3HT bilayer film-based OTFT device to improve the transient response of the fabricated device. Zongbiao and group [98] have fabricated a P3HT composite film-based ammonia sensor. Further, other composites of P3HT have been studied for ammonia sensing applications [99][100][101][102]. Ming-Zhi Dai and group [103] have compared PQT-12 and P3HT vertical junction devices for ammonia sensing. Kumar et.al. [91][104] have investigated PQT-12 based thin film transistors for room-temperature ammonia sensing. Verma et. al. [45] have fabricated a P3HT composite-based thin film transistor to sense ammonia gas at room temperature.

Most of these organic polymer-based devices have been fabricated as organic thin film transistors, which is a three-terminal device. OTFTs fabrication involves an additional insulating (dielectric) layer for gate contact, which is obtained by complex fabrication steps. Moreover, the measurement of these OTFTs needs a sophisticated measurement setup. On the other hand, two-terminal-based device structures are easy to fabricate and do not require complex measurement setup.

Recently, PTB7 has been reported as a promising choice for ammonia sensing at room temperature. PTB7 is the least explored thiophene derivative polymer for ammonia gas sensing. Chen et al. [105] have reported PTB7-based two-terminal device

for room temperature ammonia sensing. The fabricated device has shown good sensing response. Therefore, PTB7 thin film-based nanostructured MSM device has been studied in this thesis for room temperature ammonia sensing application.

1.10 Thesis Motivation

Following the discovery of organic polymers, researchers were inspired to dwell on new areas of electronic devices. Organic materials-based devices have many meritorious properties than conventional metal oxide devices. However, these organic semiconducting materials are not explored much for their potential applications as electronic devices and sensors. Particularly, the synthesis of organic polymers can be tailored for a variety of photodetector applications, including UV, visible, and broadband photodetectors. These photodetectors are widely used in daily life. Infrared photodetectors are used in security systems, UV photodetectors are helpful for phototherapy and disinfection, and visible photodetectors are needed for visible communication systems.

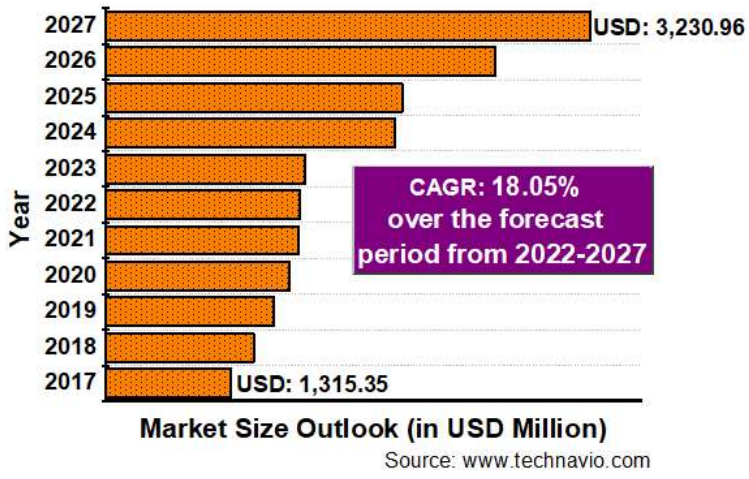

Figure 1.18 Photodetectors market demand forecast and analysis 2023-2027.

Due to the numerous applications of photodetectors, **Technavio** forecasted the market demand for photodetectors with a CAGR of 18.05% between 2022 and 2027 (according

to the study on the global ultraviolet sensor market, released in 2022). The enormous demand for photodetectors served as a significant impetus for research in this area and the investigation of appropriate materials and fabrication techniques for highly efficient, inexpensive, and easily processable photodetectors.

These new-generation semiconducting materials are also explored for gas-sensing applications to detect various toxic and harmful gases in the atmosphere and industries. These gas sensors were fabricated using various materials as an active layer.

According to the market survey report of **precedence research** (2022), gas sensors demand is forecasted with CAGR of 8.50% from 2023-2032 (**Figure 1.19**). These organic material-based gas sensors offer the advantages of low-cost production, flexibility, and high sensitivity. By exploring the fabrication processes and optimizing the sensor performance, this research aims to contribute to the development of more efficient and reliable gas sensing devices.

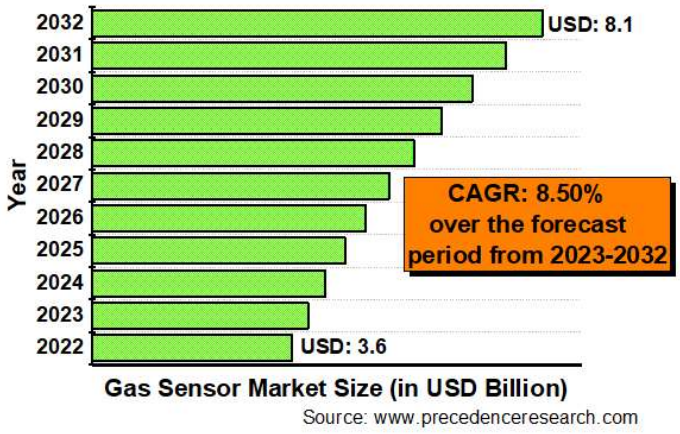

Figure 1.19 Gas sensor market size, growth, trends, report 2023-2032.

1.11 Thesis Objective

Based on the literature review, it was found that the PTB7 thin film has been majorly explored for solar cell applications. However, PTB7 is also a promising material for optoelectronic and gas-sensing applications. Therefore, the research work

in this thesis is carried out with the following objectives:

- To explore the various device structures for PTB7-based thin film devices.
- To explore the wet-processing low-cost device fabrication methods.
- To study the PTB7-based MSM device for white light sensing.
- To explore the PTB7-based heterojunction device for light sensing applications.
- To analyze the PTB7 and nanostructures for ammonia sensing application.

1.12 Scope of the Thesis

This thesis aims to extensively study of thiophene family member PTB7-based heterojunction and nanostructured morphology-based devices for light detection and ammonia sensing applications, respectively. The thesis includes the fabrication and characterizations of two terminal thin film devices for sensing applications.

Chapter 2 consists of the article on the fabrication of metal-semiconductor-metal (MSM) based visible light photodetector using PTB7 as an active material. These visible-light photodetectors are useful in short-range optical communications. The thickness of the polymer film was optimized by the spin coating technique. The schottky contact, with Al (aluminium) metal, was made by the thermal deposition process with the help of an interdigitated shadow mask. A boron-doped p-type Si wafer with an insulating layer of SiO_2 (300nm) was used as a substrate in the fabrication process of this device.

Chapter 3 describes the vertical structure-based white light detector using PTB7 polymer as an active layer. An efficient solution deposition method FTM has been used to achieve the polymer thin film.

Chapter 4 discusses the PTB7 and ZnO nanorod-based room temperature ammonia sensor. The reported gas sensor is effective in sensing very low concentrations of ammonia gas at room temperature. In the proposed device structure, PTB7 film on

ZnO nanorods works as the nanorods of polymer film. The fabricated sensor has potential application for domestic as well as industrial usage for harmful ammonia detection. Also, the device does not require any operating temperature like metal oxide gas sensors for effective operation, which reduces the extra cost of sensor manufacturing for commercial production.

Chapter 5 contains the conclusion of this thesis work. The thesis includes the light and gas sensing devices fabricated using PTB7 polymer. Facile, low-cost solution techniques i.e., spin coating and FTM have been adopted as active material coating. At last, this chapter ends with the future extension of the work in broad area applications in other domains summarized in this thesis.