CHAPTER 1

Introduction and Scope of the Thesis

1.1 Organic Electronics

The development of solid state electronic devices was started with the concept of rectification effect observed by Ferdinand Braun in 1874 [1] followed by the invention of point contact diode for detecting radio waves by Jagadis Chandra Bose in 1901 [2]. The real breakthrough in the research of semiconductor devices took place with the invention of point-contact transistor by John Bardeen, William Shockley and Walter Brattain at Bell Laboratories in December, 1947 [1], [3]. Subsequently, several important devices such as the rectifying diodes, junction FETs, bipolar junction transistors (BJTs), metal oxide semiconductor field-effect transistors (MOSFETs), thin film transistors (TFTs) etc. have been developed and explored for implementing various modern day's electronic circuits and systems [3]. Various materials such as Si, Ge, III-V compounds (e.g. GaAs, AlGaAs, GaN etc.) and II-VI compounds (e.g. ZnO, TiO_2, SnO_2 etc.) have been widely used for fabricating most of the semiconductor devices for electronic, optoelectronic and sensing applications [4], [5]. Apart from the above mentioned conventional semiconductors, the organic semiconductors or conducting polymer compounds have drawn special attention in recent times for developing large area flexible electronic devices for various electronic, optoelectronic and sensing applications due to their low-cost, low-temperature processing, room-temperature operation, environment-friendly nature and possibility of fabricating electronic devices with much larger area than the conventional semiconductor based devices [4], [6]–[9].

The first organic junction device using vacuum deposition of organic materials namely indigo, chloranil, chloranil/p-phenylenediamine complex, and phenazine was reported in 1964 [10]. The conducting polymer, polyacetylene based first junction device was reported in 1979 [11] followed by first metal-insulator-semiconductor (MIS) transistor was reported in 1982 [12]. A brief timeline regarding the development of various important electronic devices has been given in Figure 1.1. Nowadays, organic electronics is an emerging area of research for developing organic electronic devices which can replace the conventional inorganic semiconductor based devices for all types of commercial applications [6], [13]. In 2017, the US based marketing research institute named *IDTechEx* has forecasted that the total market share for printed, flexible and organic electronics may grow from \$29.28 billion in 2017 to \$73.43 billion in 2027 [14]. A significant part of the development of organic electronic devices and circuits includes the growth and development of low-cost and large area flexible electronic

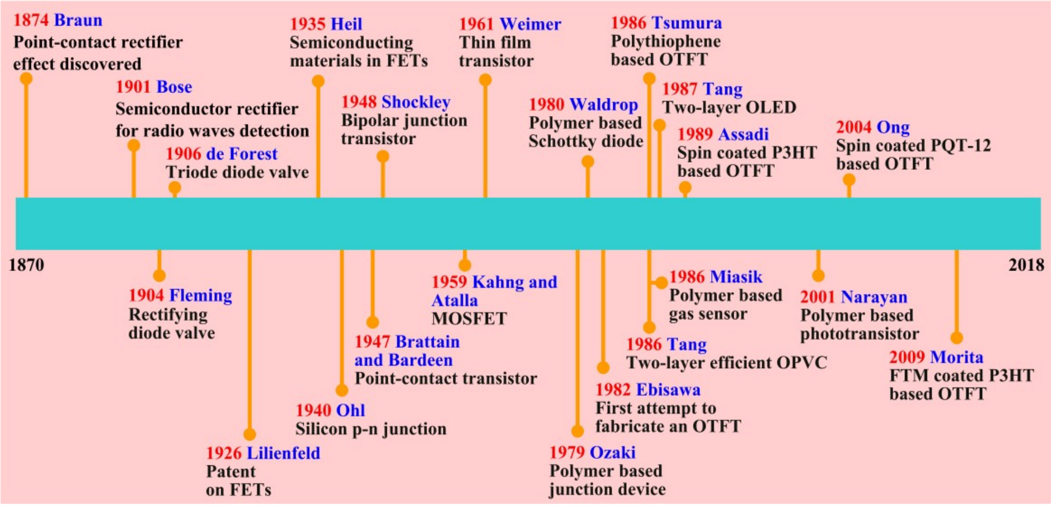


Figure 1.1: Historical development of electronic devices: starting with the point-contact device to the organic materials based thin film devices.

sensors for smart monitoring systems.

Organic electronics possesses many advantages over convention solid-state semiconductor (inorganic) electronics [15]. Some of them are: (i) organic electronic materials are inherently low-cost due to their easy synthesis techniques, (ii) large-area organic electronic devices can be fabricated at low-temperatures using low-cost fabrication processes, (iii) organic semiconductors are inherently biodegradable nature which makes the organic electronic devices enviro-friendly, (iv) organic electronic devices yield the minimum electronic wastes due to their non-toxic and biodegradable characteristics [8], and (v) the properties of the organic conducting polymers can be tuned/modified by changing the carbon bonds through synthesis routes to make them suitable for novel applications by the optimized film/device engineering. As a result of the above mentioned important properties of the organic semiconductors, we can easily fabricate low-cost and large-area organic electronic devices with a wide range of room-temperature operating characteristics suitable for many exciting and advanced applications including transparent display [16], interactive toys [17], RFID-tags [6], flexible sensors [7] and solar cells [18]. In the present thesis, we have explored some organic conducting polymer based thin film devices for gas sensing and optoelectronic applications.

1.2 Organic Semiconductors

The research on the organic semiconductor (OSC) was started with the synthesis of polyaniline by the anodic oxidation of aniline in 1862 [19]. Organic polymers made of carbon and hydrogen atoms along with a few heteroatoms such as sulphur, nitrogen, oxygen etc. are adopted as materials for organic electronics [20]. Such organic materials have high strength and good flexibility [21]. However, the conductivity of organic semiconductors was not found to be encouraging at the earlier investigations. Bolto et al. [22] observed a low conductivity (~2.2 S/m) in iodine-doped oxidized polypyrrole synthesized in 1963. In 1977, Shirakawa et al. [23] synthesized iodine-doped polyacetylene with a reasonably good conductivity (~3800 S/m) for which Nobel Prize was awarded in the year 2000. The conductivity of various available organic materials from a very low conductivity (i.e. insulator) to a very high conductivity (i.e. conductor) is shown in Figure 1.2. The semiconducting properties of the organic polymers are of great interests to the researchers for the development of organic electronic devices for electronic and sensing applications.

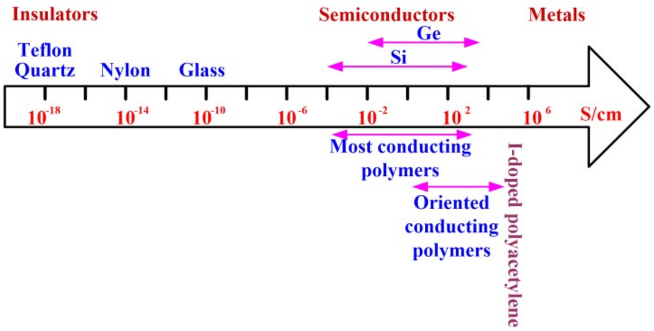


Figure 1.2: Comparison of the conductivity of conducting polymers to the inorganic counterparts.

1.2.1 Conjugated Polymers

The organic polymers with large molecular weight are mainly preferred for organic electronic devices due to their suitability for low-cost solution process-based fabrication techniques. These organic polymers are categorised into saturated and unsaturated polymers. The polymers containing only C-C bonds but no C=C in the polymer chain are called saturated polymers while the unsaturated polymers contain at least one C=C bond [24]. The unsaturated polymers with alternate C-C bonds (σ-bonds) and C=C bonds (π-bonds) in the polymer chain are called *conjugated polymers* which are electrically conducting in nature. Conjugation in the polymers is the overlap of one p-orbital with another across an intervening σ bond. The σ-bonds and π-bonds form two different orbitals: σ and π bonding and σ* and π* anti-bonding orbitals. The σ-orbital is at the lowest energy level and filled, whereas the σ*-orbital is at the highest energy level and empty. The bonding and anti-bonding in σ-orbital form strong net attractive interactions among the nuclei which holds the molecule together. On the other hand, a little attractive interaction exists in π-bonds which results in weak splitting to form π- and π*-orbitals. Similar to the σ-orbital, π-orbitals are filled but π*-orbitals are empty. As a result, molecular orbitals in semiconducting polymers playing similar roles of valence band and conduction band respectively in conventional semiconductors. The highest occupied molecular orbital consisting of π-orbitals is called the HOMO while the lowest unoccupied molecular orbital consisting of π*-orbitals is called the LUMO. The energy difference between the HOMO and LUMO is termed the HOMO–LUMO gap which plays the similar role to the bandgap energy in the inorganic semiconductors. The simplified energy levels and band diagram of a conjugated polymer is compared to those of a conventional inorganic material [24] is shown in Figure 1.3.

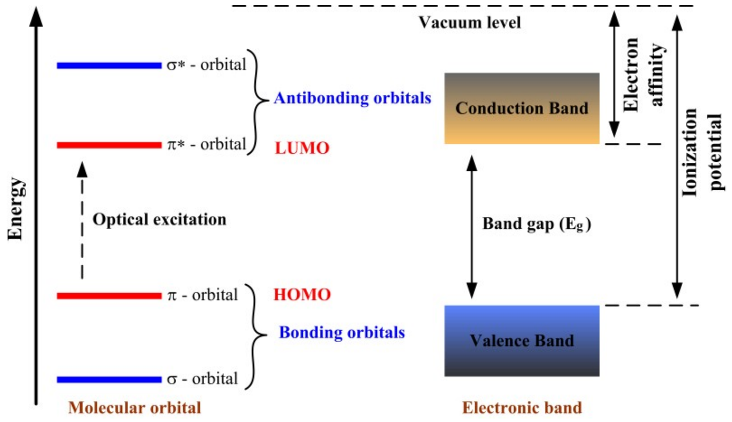


Figure 1.3: The energy levels distribution of a π-conjugated polymer in comparison with convention inorganic materials.

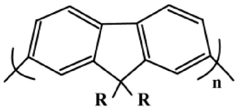
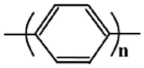
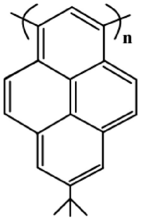
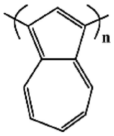
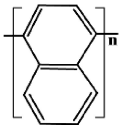
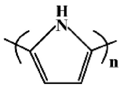
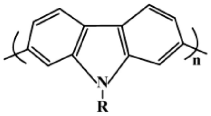
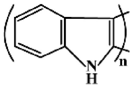
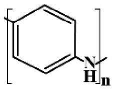
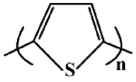
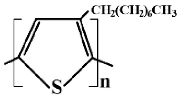
1.2.2 Conjugated Polymers as Semiconductor

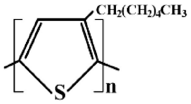
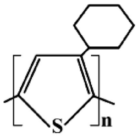
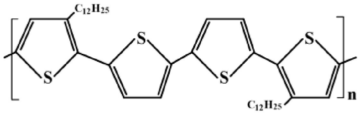
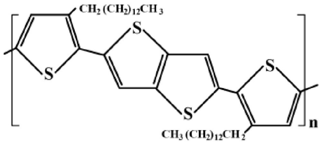
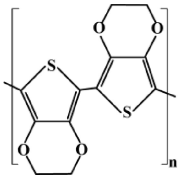
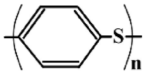
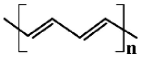
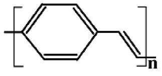
The conjugated polymers as semiconducting materials are of great interests for various electronic, optoelectronic and sensing applications due to their several advantages such as low-cost, light weight, and good flexibility over inorganic semiconductors and small-molecule organic semiconductors [25]. The soluble polymer semiconducting materials can be easily processed and printed (without requiring the conventional photolithography for patterning) for fabrication of large-scale printed electronics [25], [26]. In addition, the electrical properties of the conjugated semiconducting polymers can be fine-tuned by using suitable organic synthesis methods and by advanced dispersion techniques [27], [28]. Most of the conjugated polymers have energy band gap of less than 3 eV [29] and hence they can work as an active semiconducting material for the fabrication of organic electronic devices. The molecular structures of some commonly used organic semiconductors are shown in Table 1.1. Among the listed conjugated polymers, the polythiophene group is widely investigated as a semiconducting polymer for the organic electronic devices. The poly(3, 3‴-dialkylquarterthiophene) (PQT-12) is an improved and modified version of Poly(3-hexylthiophene) (P3HT) in the polythiophene group has been projected as a promising semiconducting organic material for various sensing applications due to its high charge mobility and enhanced air stability as compared to other polymers in the polythiophene group [30]–[34]. That why, the PQT-12 polymer has been explored in the present thesis for gas sensing and optoelectronic applications.

1.2.3 Conduction Mechanism in Conjugated Polymers

We discussed that the HOMO and LUMO levels in organic semiconductors are is roughly similar to the valence band maximum and the conduction band minimum in

Table 1.1: List of conjugated polymer families and their derivatives.

Polymers main chain contains		**Polymer families**		**Molecular structures**
Aromatic cycles	**No heteroatom**	Poly(fluorene)s		
		Polyphenylenes		
		Polypyrenes		
		Polyazulenes		
		Polynaphthalenes		
	Nitrogen-containing	Poly(pyrrole)s (PPY)		
		Polycarbazoles		
		Polyindoles		
		Polyanilines (PANI)		
	Sulphur-containing	Poly(thiophene)s (PTs)	PT	
			P3OT	

			P3HT	
			P3CHT	
			PQT-12	
			PBTTT	
			PEDOT	
		Poly(p-phenylene sulfide) (PPS)		
Double bonds		Poly(acetylene)s (PAC)		
Aromatic cycles and double bonds		Poly(p-phenylene vinylene) (PPV)		

inorganic semiconductors [35]. Thus, the LUMO and LUMO play significant roles in deciding the charge carrier transport and hence the electrical properties of the organic semiconductors. The electrons in the LUMO of a donor site can transfer to the empty LUMO of an electron accepting site whereas the holes from an acceptor site are transferred to HOMO level [24]. The electronic coupling among these sites is necessary but not sufficient for the completion of charge transfer in organic semiconductors. The description of charge transport phenomenon depends on various complicated coupling/interaction mechanisms in the conjugated polymers. Some major transport models [24] for organic semiconductors are described briefly in the following.

1.2.3.1 Band Transport

The charge transportation takes place through a band if the interaction energy with the nearest neighbour is large enough as compared to any other energy due to dynamic/static disorder. This band transport can appear only if the available bands are wider than the uncertainty of the charge carrier's site energy [24], [36]. If the mobility exceeds about 5 $cm^2V^{-1}s^{-1}$ then the band transport model is dominant in organic semiconductors. However, most of the organic semiconductors have measured mobilities at or near room temperature in the order of 1 $cm^2V^{-1}s^{-1}$ where the band transport is negligible.

1.2.3.2 Hopping Transport

The hopping transport is dominated when any of the other energies due to the effects of dynamic/static disorder are significant compared to the neighbouring interaction energy [24]. In this case, a charge carrier is localized at individual sites and succeeds by a sequence of non-coherent transfer events termed as hopping motion. This is commonly used model to explain the charge carrier transport in organic materials and is generally accepted for the description of the conductivity in disordered organic semiconductors [37], [38].

1.2.3.3 Polaronic Transport

If the organic semiconductor is perfectly ordered then the electronic coupling among the transport sites is very small as compared to electron-phonon coupling [24]. Also, the charged molecules are coupled to the nearby molecules, so the inter-molecular displacements and polarization effects change the van der Waals energy between the molecules. This charge then forms a tiny quasi-particle termed as polaron by the lattice deformation. The formed polaron jumps from one site to another site. Therefore, the transport takes place through inter-site is polaron hopping.

1.2.3.4 Disorder-Controlled Transport

The charge transport mechanism in the disordered organic semiconductor is highly complicated as the sites (donor/acceptor) are neither equally spaced nor iso-energetic. Thus, the movements of polarons are asymmetric, which is not similar to perfect polaronic transport. Thus, the Gaussian disorder model (GDM), also known as Bässler model is used to explain the charge carrier mobility in a disordered organic semiconductor on a microscopic level [38]. This model is based upon charge carriers hopping among multiple sites that used the Gaussian distribution of energy and inter-site spacing.

Apart from these commonly used charge transport models used for the explanation of conduction mechanism in organic semiconducting polymers, various other theories/models (e.g. the delocalized band transport model [15], the multiple trapping and release model [15], the tunneling model [17] and many others) are also being developed for the better understanding of physics behind the conduction mechanism in the organic semiconductor. Some models are also used in combination to realize a better representation of charge transport in the organic semiconductor. It may be mentioned that the charge transport is affected by the trapping effects and morphologies of organic semiconductor films. These trapping sites can be induced in the organic semiconductor by either structural defects or unintentionally/intentionally added dopant molecules. The morphologies are controlled by various film deposition techniques.

1.2.4 Thin Film Deposition Techniques for Conjugated Polymers

The thin film deposition of the organic semiconductor is an important part for the fabrication of various organic electronic devices. The conjugated polymers are soluble in a number of non-polar solvents such as chloroform, chlorobenzene, dichlorobenzene, toluene etc. Thus, the conjugated polymers (which are used as semiconducting materials) can be easily deposited in the form of thin films on substrates by low-temperature solution processing techniques. In this method, a homogeneous solution of conjugated polymer is first obtained by adding it to an appropriate solvent. The resultant solution is deposited on the desire substrates in the form of thin films by using various deposition techniques such as drop-casting, spin-coating, dip-coating, Langmuir-Blodgett and floating-film transfer method (FTM). The spin coating and FTM are considered to be better thin film deposition techniques over others to obtain a highly smooth organic semiconductor thin film with a better morphology and orientation at lower-deposition cost [39]. That is why, the said two deposition techniques have been explored for the fabrication of organic thin film devices investigated in this thesis work.

Spin coating is a commonly used method for the deposition of the organic semiconductor due to its compatibility with all types of solution, better repeatability of obtained thin film, and fast processing [40]–[42]. This method utilises the centrifugal force for uniform spreading of the solution to form the thin films on the desired substrates. The thickness and quality of the obtained thin films depend on the concentration and viscosity of the solution, rotation speed, acceleration and time. The wettability of substrates such as the surface type, hydrophobic or hydrophilic, play also a significant role in deciding quality of the deposited thin films. The commonly employed steps followed in the spin coating method for the polymer film deposition is illustrated in Figure 1.4. The substrate is first placed on the spin coater and then the solution in the form of micro-drops is placed at its centre. Then the substrate is rotated at an optimized speed to spread out the excess solution over the substrate by centrifugal force. The process may be followed multiple times unless the desired film thickness is achieved. The spin-coater used for the fabrication of polymer films is the TSE-system GmbH (model SPM-150LC), Germany.

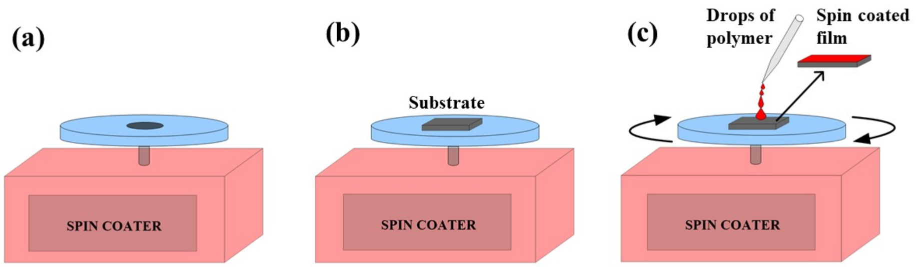


Figure 1.4: Spin-coating process steps (a) Coating unit (b) Sample on coating unit and (c) Coating on the sample and spin coated film.

Floating-film transfer method (FTM) is a relatively new deposition technique used for organic semiconductor thin films [43]. The technique involved is similar to Langmuir-Blodgett film deposition method with the exception that no surface-pressure is applied to obtain film in this case [44], [45]. The FTM technique was originally proposed by Morita et al. [43] but it has been later optimized by others [39], [46]–[48] to achieve a well oriented and self-assembled thin film of any organic semiconductor. The procedure for achieving the FTM film on a desired substrate is illustrated in Figure 1.5. In this technique, a floating film of the desired polymer is created on a liquid substrate made of a hydrophilic solution. A very small quantity of polymer solution prepared by using a hydrophobic solvent is dropped on the hydrophilic liquid substrate so that the polymer solution can spread uniformly over the surface of the liquid substrate to form a floating film. The film is then stamped on the cleaned surface of the desired substrate as demonstrated in the figure. Once the film is transferred to the desired substrate, the solvent of the polymer solution is evaporated by heating at appropriate temperature. Finally, a well-assembled and well-orientated polymer film is prepared on the desired substrate by this method.

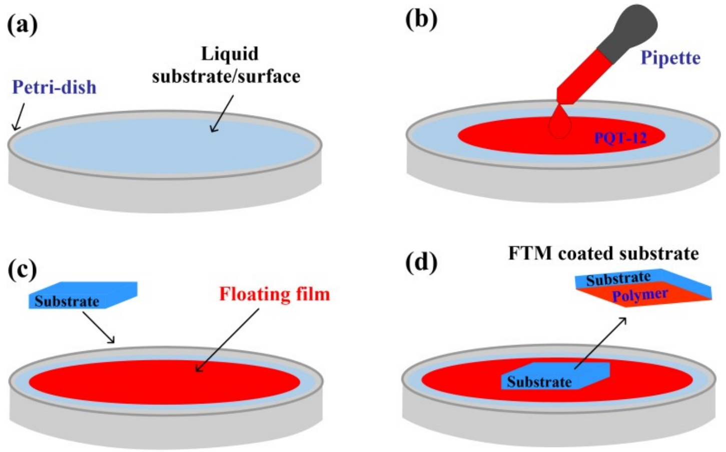


Figure 1.5: FTM set-up and process of thin film deposition (a) Hydrophilic liquid substrate (surface) in petri-dish, (b) Drop of conducting polymer on the liquid surface, (c) Floating polymer film on liquid surface and (d) Stamping of polymer film.

1.2.5 Thin Film Characterization of Conjugated Polymers

The conjugated polymer film is characterized for its various properties such as surface morphology, roughness, surface structures, molecular orientation, conduction levels, reflectance, absorbance, luminance etc. Various film characterization techniques used in the present thesis are briefly introduced in the following.

1.2.5.1 Scanning Probe Microscopy

Scanning probe microscopy (SPM) is a tool for studying the surface morphology of polymer films. A physical probe (tip) is used to scan over the surface of the sample for collecting surface profile data. The basic block diagram of the SPM and its operation [49] is illustrated in Figure 1.6. Three most common techniques employed for scanning probe are: scanning tunnelling microscopy (STM), atomic force microscopy (AFM), and near-field scanning optical microscopy (NSOM). The STM measures the electrical current (tunnelling current) between the tip and the surface of the sample for the imaging while the interaction force between the tip and the surface of the sample is measured in the AFM. The force in the AFM depends on the sample type, probe tip and the distance between them. The NSOM is a type of microscopy technique which used the properties of evanescent waves that breaks the far field resolution limit for nanostructure investigation. Among these techniques, the AFM is more versatile and suitable for all type of samples. It is operated in various modes such as non-contact, contact and intermittent contact (tapping). The thickness of the thin film can also be measured using AFM by making a sharp step in the film. The surface roughness/morphology and thickness of the polymer film studied in this thesis have been investigated by the AFM from NT-MDT Services and Logistics Ltd. (model NTEGRA Prima), Ireland.

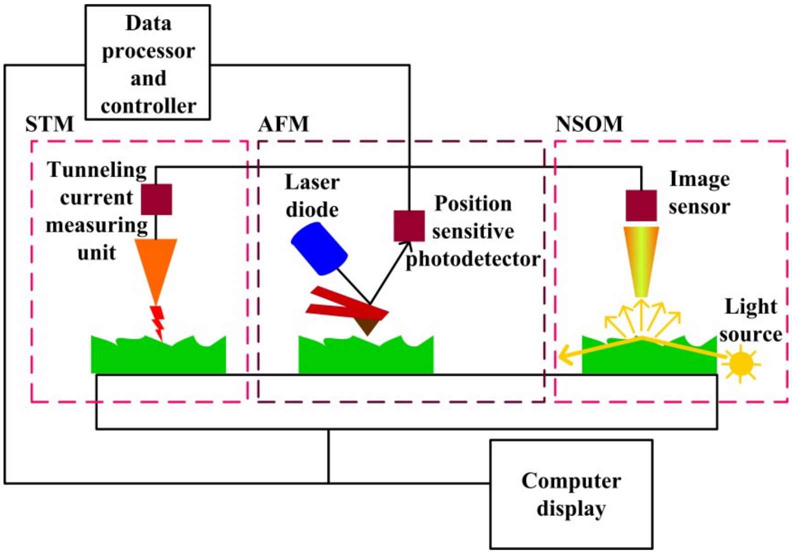


Figure 1.6: Working process of SPM (STM, AFM, and NSOM) measurement.

1.2.5.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) captures the image of the surface of a sample through scanning with a focused beam of high-energy electrons [49]. The high-energy electrons of the bear are allowed to interact with the sample's surface to produce various signals which are analysed to extract various information related to the surface topography, morphology and composition of the films. This technique is used for the surface investigation with a resolution of up to 0.5 nm (~100 kX magnification) in a variety of applications. The elemental identification and quantitative composition of the samples are measured using the in-built energy dispersive X-ray analyzer (EDX or EDA) of the SEM system. The basic operation of SEM with a schematic representation is shown in Figure 1.7 (a). The surface morphology of the PQT-12 film considered in this thesis is investigated by SEM from Carl Zeiss Microscopy Ltd. (model EVO MA 15/18), UK.

1.2.5.3 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is used to acquire the high-resolution images of the surface of the thin film samples or a suspension on the grid [49]. A focused beam of high-energy electrons is transmitted through the thin samples to interact with their atoms and provide various interesting information about the crystal structure along with dislocations and grain boundaries in the structures. Since electrons have a much smaller wavelength than light, so the resolution obtained from the TEM image is up to ~0.1 nm with ~500 kX magnification which is many times larger than that obtained from optical image. The size, shape, quality and density of quantum dots, wires and wells are also analysed using these high-resolution TEM images. Thus, the TEM technique can be used to predict the finest details of the internal structure of the thin films. The information about the crystallographic properties of the thin film can be determined by using the selected area electron diffraction pattern (SAED) measurement by exploring the wave nature of electron (instead of its particle nature). The operation and schematic of TEM is shown in Figure 1.7 (b). The TEM system used for our study in the present thesis is the Tecnai G2 20 TWIN from FEI, USA.

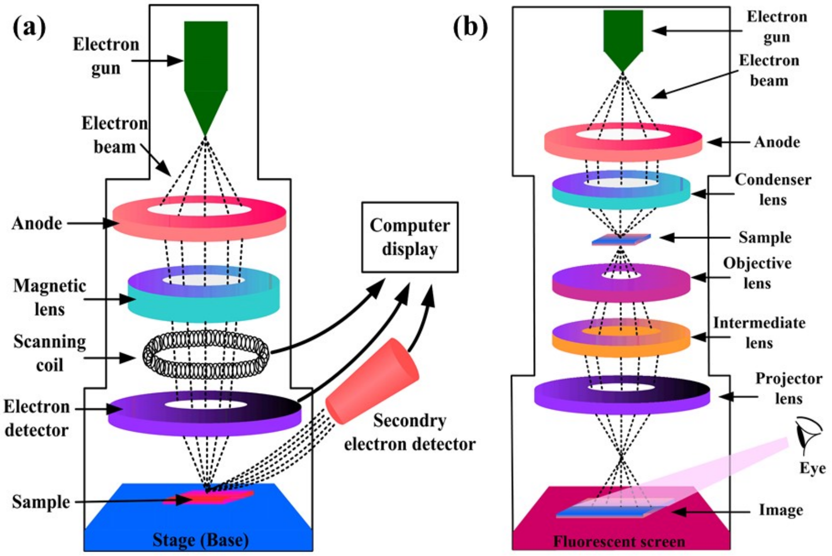


Figure 1.7: Set-up and working of (a) SEM measurement and (b) TEM measurement.

1.2.5.4 X-Ray Diffraction

X-ray diffraction (XRD) is a powerful material characterization tool applicable for fluids, powders and crystals. In this method, an X-ray beam incident on the surface of the sample to interact with the material in a non-destructive manner [49]. The wavelength of X-rays is of the order of atomic level, smaller than the visible light. Thus, the X-rays with low-wavelength has high energy which is capable to penetrate the matter. When X-rays are penetrated inside any material/matter, the uniform spacing of atoms in the material/matter produces an interference pattern due to diffraction phenomenon. The resolution of the X-ray diffraction pattern is described by the Bragg equation (*2d sinθ=nλ*) [49]. The X-ray spectroscopic measurement technique is used for the identification of various crystalline phases of the materials and their quantitative analysis. The operation and working principle of XRD is illustrated Figure 1.8 (a). The SmartLab X-Ray Diffractometer from Rigaku, Japan is used for the XRD measurements of the thin films investigated in this thesis work.

1.2.5.5 Cyclic Voltammetry

Cyclic voltammetry (CV) is a commonly used electrochemical tool to acquire qualitative information about various reactions and properties of the materials [50]. It is used to measure electrochemical properties of various materials in solution or in the solid-state phase (thin films on an electrode). It is very simple and straightforward technique in which electrochemical potentials relative to a known internal standard is determined under reversible redox behaviour of analytes. The obtained results of CV are the primary source of information about the orbital energy levels of different materials for electronics or other applications. The current at the working electrode is measured and plotted against the applied potential at the working electrode to obtain the cyclic voltammogram trace. The basic schematic of the cyclic voltammetry measurement is

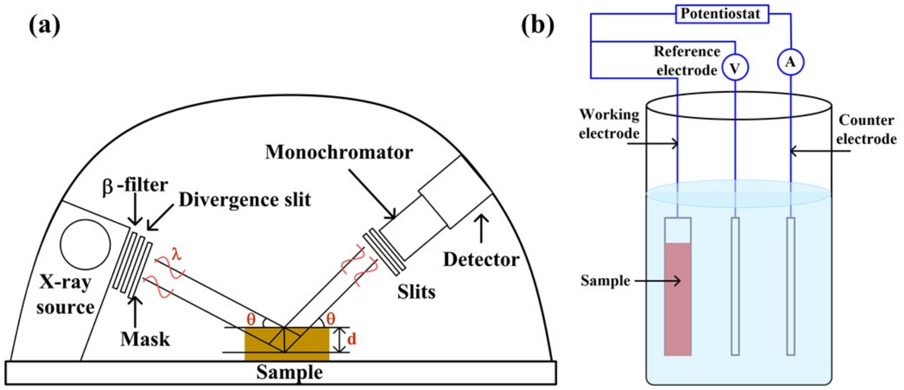


Figure 1.8: Set-up and working of (a) XRD measurement and (b) Cyclic voltammetry measurement.

shown in Figure 1.8 (b). The CV measurements have been carried in this thesis using the electrochemical workstation (CHI-7041C) from CH Instruments Inc., USA.

1.2.5.6 Fourier Transform Infrared Spectroscopy

The Fourier transform infrared spectroscopy (FTIR) techniques is used extensively for obtaining the infrared spectrum of absorption or emission of both the organic and inorganic materials [49]. The technique identifies the chemical bonds in the molecules by measuring the absorption of infrared radiation (IR) through the sample versus wavenumber. The absorbed infrared radiation excites the molecule of the sample into the higher vibrational state. The tool is also used to detect functional groups and illustrating covalent bonding information of the sample. The operating principle of an FTIR spectrometer is illustrated in Figure 1.9 (a). The chemical bond disturbance in the polymer film is investigated by FTIR spectroscopy (Alpha FTIR Spectrometer, Eco-ATR) from Bruker, USA.

1.2.5.7 Spectrophotometry

Spectrophotometry is a technique to measure the reflectance and transmittance of the thin films [49]. Based on the obtained reflectance and transmittance, the thickness of the film is also calculated using the refractive index and extinction coefficient of the material. The calculation is optimized by using the discrete Fourier transform (DFT) and fast Fourier transform (FFT) algorithms along with the material characteristics. The operating principle of the spectrophotometry is illustrated in Figure 1.9 (b). The reflectance, transmittance and the thickness of polymer film are measured in the present thesis by the spectrophotometry reflectometer (F20-UV) from Filmetrics, USA.

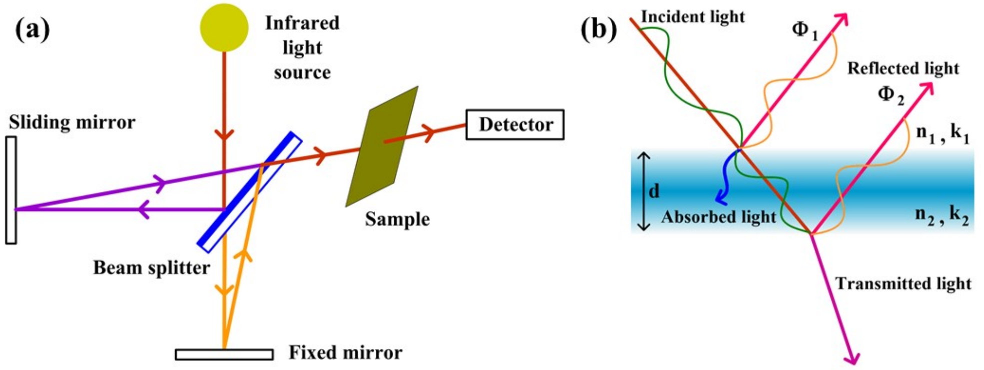


Figure 1.9: Working principle of (a) FTIR spectroscopy and (b) Spectrophotometry.

1.2.5.8 UV-Visible Spectroscopy

Ultraviolet-visible (UV-Vis) spectroscopy is used to measure the optical absorption characteristics of the materials [51]. It is observed that atoms and molecules of a matter undergo electronic transitions from the ground state to the excited state when it is irradiated with the electromagnetic spectrum. In the case of a conjugated polymer containing π-electrons or non-bonding electrons (n-electrons), these electrons excite to higher anti-bonding (π*) molecular orbital after absorbing energy in the form of ultraviolet or visible light. Therefore, the UV-Vis spectrophotometer is also used to measure the absorption characteristics of a material. It is also used to measure the approximate bandgap energy of the material. It measures the absorbance characteristics from transmittance (T) characteristics as $A = -\log (T)$. The obtained absorbance spectrum can be used to match for the identification of the functional group of a material. The schematic diagram of a UV-Vis spectroscopy is shown in Figure 1.10 (a). The UV-Vis spectroscopy (Lambda-25) from Perkin Elmer, USA has been used for the thin film characterization in the present thesis.

1.2.5.9 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is used to analyse the electronic structure of materials in a contactless and non-destructive manner [52]. Visible along with adjacent light is directed to a sample through a monochromator, where it is absorbed to excite the material to a higher electronic state through photo-excitation. After relax, the excited electrons return again to lower energy levels and emit light which is called photoluminescence. The energy of the emitted photons (i.e. photoluminescence) depends on the energy difference between the excited state and the equilibrium state. The PL spectroscopy is used to extract various information of materials such as material quality, defect detection, impurity levels, bandgap determination, recombination mechanisms etc. The schematic for photoluminescence spectroscopy measurement is shown in Figure 1.10 (b). The PL measurement has been carried out in the present thesis by using spectrometer (FLS 980) from Edinburgh Instruments, UK.

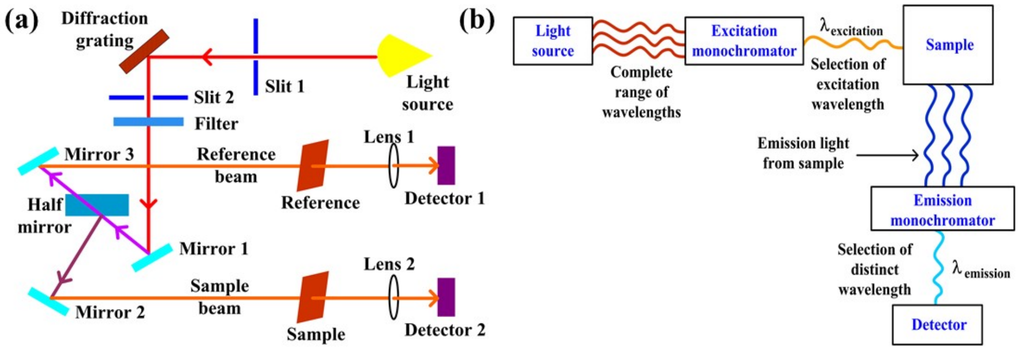


Figure 1.10: Working principle of (a) UV-Vis spectroscopy and (b) Photoluminescence spectroscopy.

1.3 Organic Thin Film Devices

Like conventional semiconductors, the organic semiconductors have also been explored for fabricating various electronic device structures for applications including sensors [7], [9], photodetectors [4], photovoltaic cells [18], light emitting devices [6], memory devices [53], display devices [16] etc. Various organic polymer based device structures such as Schottky diodes [54], [55], p-n junction diodes [56], metal-semiconductor-metal (MSM) diodes [12], and thin film transistors [30], [31] have been reported in the literature. We will now briefly introduce the basic two and three terminal device structures and their basic fabrication steps in the following.

1.3.1 Basic Fabrication Steps for 2-Terminal and 3-Terminal Devices

Since the diodes and transistors are the basic electronic device structures, the organic thin film devices (OTFDs) are broadly divided into two sub-classes: 2-terminal devices and 3-terminal devices. The diodes, MSM, metal-insulator-semiconductor (MIS) capacitors etc. are two terminal devices, whereas the thin film transistors (TFTs) are three terminal devices. The organic thin film devices may use the film of semiconducting, conducting and insulating organic films. The thin films of conjugated polymers or semiconducting polymers are generally fabricated by the solution processed techniques such as the spin coating and dip coating. The conducting films for the electrodes are obtained by depositing metals using physical vapour deposition methods like the thermal evaporation, electron-beam evaporation, sputtering etc. The polymer based insulating thin films are used for the dielectric layer in the electronic devices. For silicon based organic devices, the organic thin films are normally deposited on a silicon dioxide layer grown on the silicon substrate using dry oxidation method.

Two terminal devices are relatively simple for fabrication and characterization. The organic semiconductor based two terminal device structures such as Schottky diode, p-n junction diode, MSM and MIS are shown in Figure 1.11. The p-type conducting polymers form the Schottky barrier contact with low work-function metal and ohmic contact with high work-function metal as in Schottky diode. Like the conventional semiconductors, the Schottky or ohmic contact between a metal and the conductor polymers also depend of the work-functions of the metals and polymers. In general, the p-type conducting polymers form the Schottky contacts with low work-function metals whereas they form ohmic contacts with the high work-function metals [57]. The reverse situation occurs in case of an n-type conducting polymers. The organic thin film transistors (OTFTs) are 3-terminal devices which have enhanced internal gain with

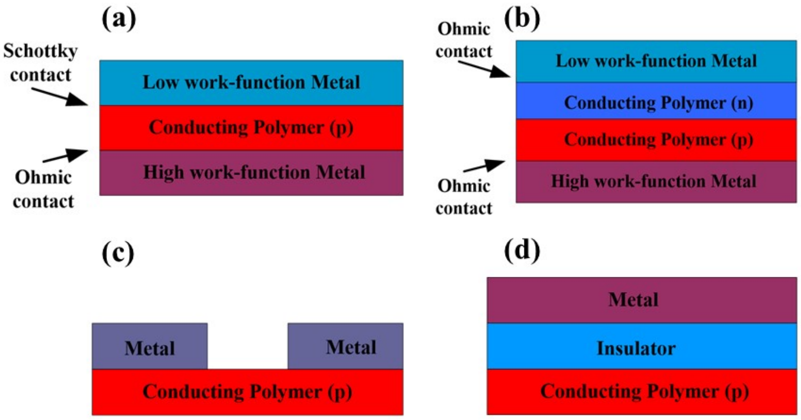


Figure 1.11: Device structure of (a) Schottky diode, (b) p-n diode, (c) MSM, and (d) MIS.

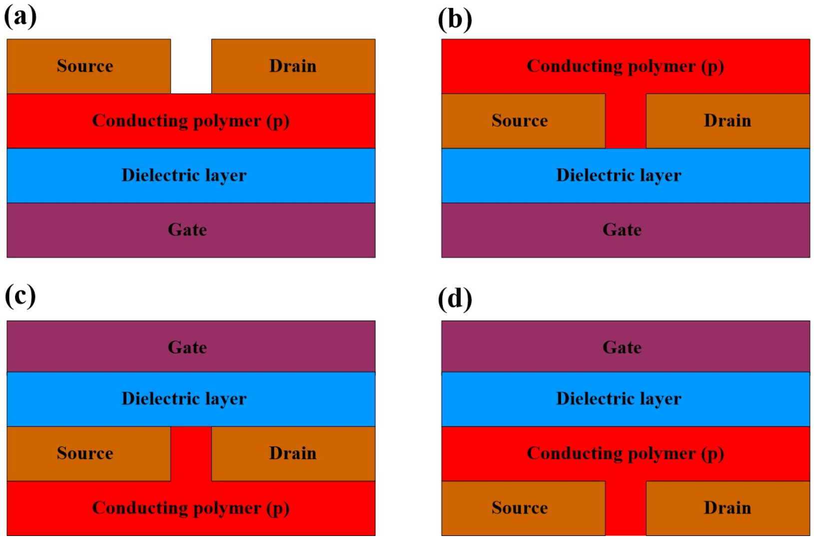


Figure 1.12: Different OTFT structures: (a) Bottom-gate top-contact, (b) Bottom-gate bottom-contact, (c) Top-gate top-contact, and (d) Top-gate bottom-contact.

multiparameter characteristics [58]. The OTFTs are widely used for various sensing applications [9], [58]. Based on the position or the combination of gate and source/drain contacts, the transistors have four structures as shown in Figure 1.12. Among the transistor structures shown in Fig. 1.12, the bottom-gate top-contact based structure are used for various electronic and sensing applications due to their better performance parameters [9], [59].

1.3.2 Organic Device Characterization Tools

Like other semiconductor devices, the electrical characteristics of organic thin film devices are measured using semiconductor parameter analyser (SPA) (Make: Keysight, Model: B1500A). The two terminal devices such as Schottky diodes, p-n junction diodes and MSM diodes can be characterized with the help of two 'source and measuring units (SMUs)', whereas the transistor characterization requires the SPA with minimum three 'SMUs'. The SPA is used to measure the current-voltage (*IV*), capacitance-voltage (*CV*), current-time (*I-t*), resistance-time (*R-t*) characteristics of the devices. The measurement set-up for the electrical characterization of the organic devices using SPA is shown in Figure 1.13. The electrical characterization setup can further be extended for various sensing applications considered in the present thesis.

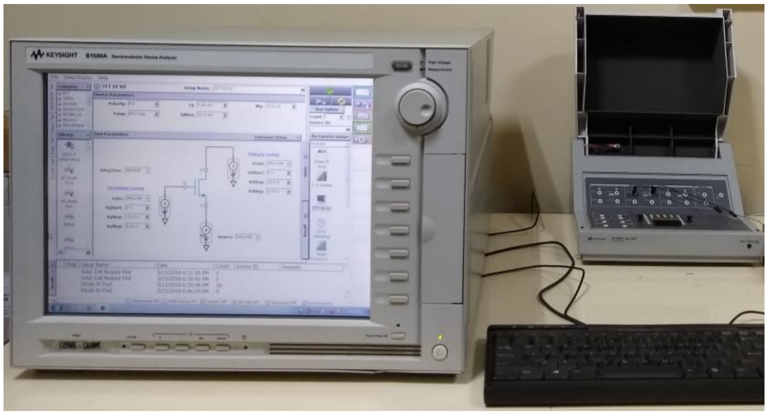


Figure 1.13: Semiconductor parameter analyser for the measurement of various electrical parameters.

1.3.3 Organic Thin Film Device Applications

The organic thin films are used for various electronic, gas sensing and optoelectronic applications such as in the chemical sensors (gas/biological), light sensors (photodetector), light emitting diodes (LEDs), solar cells (photovoltaic), display, and memory devices. The clusters of organic device applications listed in the OE-A Roadmap [60] is shown in Figure 1.14. We have explored the PQT-12 organic semiconductor for gas sensing and light sensing applications which are briefly introduced in the following.

Figure 1.14: Clusters of organic device application from OE-A Roadmap.

1.3.3.1 Gas Sensors

Gas sensors are used for the detection of various hazardous gases such as ammonia, nitrogen dioxide, carbon monoxide and many more gases/vapours [61], [62] which may cause severe health disorders in the human body. Their concentrations are measured to take the needful actions once they cross the danger limit. Many gasses can't be detected by our nose but can be easily detected by the electronic sensors. Therefore, the gas sensors are sometimes called an “electronic nose (E-nose)”. The E-nose works similarly as the human nose as illustrated in Figure 1.15. The obtained data from the gas sensor are processed, compared using neural system analysis with help of known data and finally, the information regarding the type of gases and their concentrations are obtained. The inorganic materials (mainly metal oxides and their nanostructures) [62]–[66] as well as organic conducting polymers [9], [67]–[75] are used for the fabrication of the gas sensors. Although, the metal-oxides especially using SnO_2 [76] are mostly used in commercial gas sensor, but their high fabrication cost due to the requirement of very expensive set up [9], poor selectivity [62] and poor room temperature response have greatly encouraged the researchers for developing low-cost and low-temperature based gas sensors using conducting polymers [9], [67]–[75]. Thus, the conjugated polymer-based thin film devices are extensively explored for low cost detection of hazardous gases by means of a change in electrical response of the device.

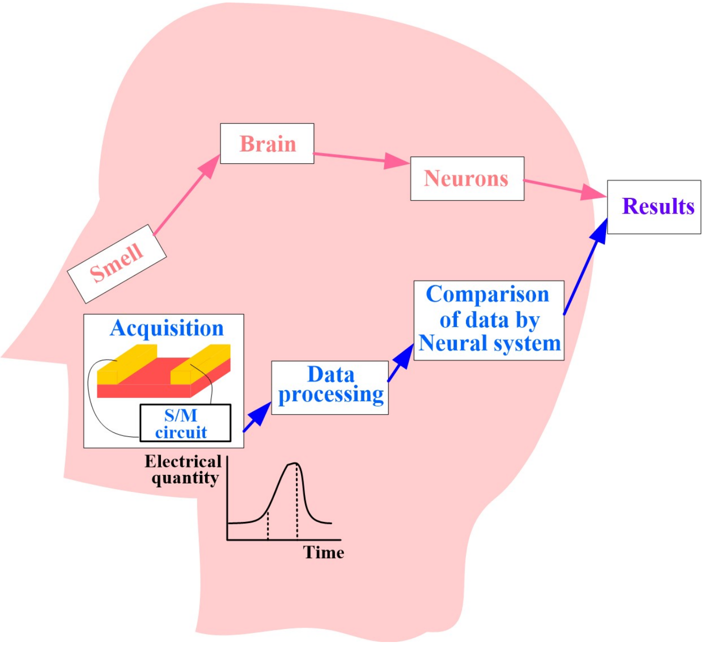


Figure 1.15: E-nose and its processing with respect to the human nose.

The working of thin film devices as gas sensor is mainly based on chemisorption and/or physisorption of the gases [9]. When the gases interact with a conducting polymer film, the gases are adsorbed in the polymer film and change the conductivity of the film. This change in conductivity is either happened due to base de-doping in case of reducing gases or dipole charge interaction in case of oxidising gases [75], [77]. Commonly, reducing gases behave as electron donors which start doping and de-doping in the p-type conjugated polymer films when they are exposed to the gases. This results in the enhanced traps sites on the surface of the polymer thin films thereby reducing the transportation of holes and hence increasing the film resistance [77], [78]. However, when the films are exposed to oxidising gases, a partial positive charge is developed in p-type conjugated polymers because of charge transfer due to dipole charge interaction [40]. This charge transfer reduces the trap sites for the holes and enhances the conductivity of the film [58]. It may be mentioned that the gas response in conducting polymer based sensors is highly dependent on polymer film thickness, device structure and any doping to the polymer [79], [80]. Thus, we have explored PQT-12 using film/device engineering for sensing ammonia, nitrogen dioxide gases and other interference gases.

1.3.3.2 Light Sensors (Photodetectors)

Like any semiconductor, the organic semiconductors can be also used for photodetection applications. The thin film electronic devices using conjugated polymers as active material can be explored for sensing light with wide range of wavelengths in the optical spectrum. The conductivity of the organic film is increased when it is exposed to the light in the similar manner as that occurs in the conventional semiconductors as demonstrated in Figure 1.16. When the light is incident on the organic film of the organic photodetectors, the extra charge excitons pairs are generated in the active semiconducting thin film [81]–[85] as shown in the figure. This generation of charge pairs are the function of the intensity and wavelength of the incident light. The generated photo-excitons enhance the charge carrier density in the polymer film thereby increasing the conductivity of the semiconducting polymers (e.g. PQT-12) used as the active materials in the detectors.

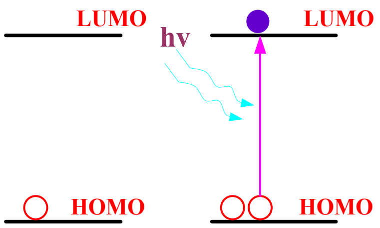


Figure 1.16: Generation of charge excitons in conducting polymer under light exposure.

1.4 Literature Review

The objective of the present thesis is to investigate the gas sensing and photodetection properties of organic semiconducting polymer based thin film devices. In order to outline the scope of the thesis, we will now review some important literature on the organic thin film devices and their applications in the following sub-sections.

1.4.1 Review of Organic Thin Film Devices

One of earliest work on the organic thin film devices (OTFDs) is the organic thin film rectifying junction which was reported by J. E. Meinhard as early as in 1964 [10]. The junction was fabricated by vacuum deposition of various complexes such as indigo, chloranil, chloranil/p-phenylenediamine complex, and phenazine. After the discovery of high conductivity in doped polyacetylene [23], Ozaki et al. [11] have reported the organic junction device using pure and doped polyacetylene polymers in 1979. The polymer based Schottky diodes [57] have been reported using polyacetylene polymer in 1980. Ebisawa et al. [12] demonstrated the properties of both the metal-semiconductor (i.e. semiconducting polymer)-metal (MSM) and TFT devices in a single device structure using polyacetylene polymer. Later, several conjugated organic materials including polyacetylene polymer have been explored for the fabrication of different types of OTFDs including Schottky diodes [55], [86], MSM diodes [87], [88], and TFTs [89], [90]. Among various conjugated polymers, polythiophenes derivatives have been widely explored for the OTFDs due to their easier processing, better material stability, better thin film quality and higher mobility than other available materials for gas sensing [9], [40], [91]–[93] and light sensing applications [4], [94], [95]. Kaneto et al. [96] reported polythiophene thin film based devices as early as in 1983. Poly(3-hexylthiophene) (P3HT), one of the derivatives of polythiophenes, have been explored for various organic thin film diodes [54] and transistor structures [55], [97]. Wang et al. [98] fabricated the P3HT based TFTs using three different deposition techniques namely the spin coating, drop casting and dip coating. They [98] observed the highest field effect mobility in the dip coating based OTFT due to structural ordering of the P3HT polymer. Yang et al. [99] observed enhanced field-effect mobility due to crystalline structure orientation of the P3HT film in OTFTs. Kumari et al. [100] and Couderc et al. [101] observed improved charge transportation in the P3HT/CdSe nanocomposite films due to decrease in trap energy and increase in hole mobility. Chiu et al. [102] observed an improvement of the electrical and optical performance in the P3HT/CdSe@ZnSe QDs nanocomposite film based TFTs over the TFTs with conventional P3HT films. Chen et al. [103] observed a better electrical performance in the TFTs using composites of P3HT and CdSe QDs than that of the TFTs with a conventional P3HT film. Morita et al. [43] introduced the FTM technique for fabricating an oriented P3HT film for the improvement of electrical performance of the OTFTs. Others researchers [39], [47] have optimized the FTM technique for improving the performance of the P3HT based OTFTs.

Consistent efforts were made to improve the material stability and film quality of polythiophenes by using molecular engineering techniques [30], [98], [99]. Ong et al. [30] from Xerox Research Centre proposed a new polymer, called poly(3, 3‴-dialkylquarterthiophene) or poly(3, 3‴-didodecylquarterthiophene) or simply PQT-12 in 2004 using a structural modification of polythiophenes. They used the material for fabricating a bottom-gate top-contact TFT and achieved an average field effect mobility of 0.07-0.12 $cm^2V^{-1}s^{-1}$. Chabinyc et al. [104] reported the field effect mobility of ~0.3 $cm^2V^{-1}s^{-1}$ in a PQT-12 based TFT with a short channel length of 3 μm. They [104] also observed that the saturation characteristics of OTFTs with channel lengths below 20 μm were largely affected due to the short-channel effects (SCEs). However, the transistors with channel lengths above 20 μm had ideal characteristics largely supported by the gradual channel approximation model of the field effect transistors (FETs). Wu et al. [105] reported the thin film transistor using the controlled orientation of liquid-crystalline PQT-12 polymer and achieved a field effect mobility of 0.18 $cm^2V^{-1}s^{-1}$. This improved performance in transistor characteristics was attributed to the well-aligned edge-on orientation of PQT-12 polymer and an arrays of parallel lamellar π-π stacks with their lamellar (100) axes normal to the surface [105]. Later, Ong et al. [31] reported the maximum field effect mobility of 0.2 $cm^2V^{-1}s^{-1}$ in TFTs using structurally ordered PQT-12 nanoparticles. The effect of relative humidity (RH) on the performance of PQT-12 based TFTs was investigated by Chabinyc et al. [32]. They [32] found a slight reduction in the field effect mobility with the increase in %RH. Cai et al. [106], [107] reported that the performance of the PQT-12 based TFTs could be improved further by using gold source/drain contacts after treating it in piranha solution or monolayer of alkanethiol. The stability and electrical performance improvement due to deposition technique have been observed by Constantinescu et al. [108] in the pulsed laser evaporated PQT-12 film based TFTs. The TFTs using various composites of PQT-12 polymer with different nanomaterials such as carbon nanotube (CNT), graphene and F4TCNQ etc. have also been investigated by the researchers [16], [109]–[111].

Besides the TFTs, PQT-12 polymer has also been employed in MSM [67], pn junction diodes [56], and Schottky diodes [45], [112], [113] fabricated on different substrates. The heterojunction diode of PQT-12 (p-type) and ZnO (n-type) [56] with improved response over their homo junctions has also been reported in the literature.

1.4.2 Review of OTFDs Based Gas Sensors

Conducting polymers such as polyacetylene, polypyrrole, poly-N-methylpyrrole, poly-5-carboxyindole, polyaniline, polythiophene derivatives and many more are found sensitive to chemicals and gases [9], [40], [93], [114], [115]. Thus, the conducting polymer based OTFD gas sensors have been used for sensing various health hazardous gases such as ammonia (NH_3), nitrogen dioxide (NO_2) and many more organic gas/vapours [9], [40], [58], [93], [114]. It may be mentioned that even a small amount of ammonia gas (<100 ppm) [116] or nitrogen dioxide gas (<1 ppm) [117] is hazardous to the health if inhaled for a long time. Thus, many works have been reported on the conducting polymer based NH_3 and NO_2 gas sensors. Miasik et al. [93] reported a poly(pyrro1e) based MSM gas sensor using interdigitated gold electrode for detecting both the NH_3 and NO_2 gases. A poly(pyrro1e) based MSM device was reported by Chougule et al. [118] for ammonia gas sensing application. Polyaniline-TiO_2 nanocomposite based thin film MSM type ammonia sensor have been reported with improved response over the conventional polyaniline based gas sensors [119], [120]. Later, different conjugate polymers, especially the derivatives of polythiophene have been largely explored for the ammonia [72], [121]–[123] and nitrogen dioxide [40], [124] gas sensing applications due to their better stability over other conjugated polymers [9], [40], [91], [92], [94], [125]. Among various derivatives of the polythiophene, P3HT has been widely explored for ammonia [72], [121], [126]–[128] and nitrogen dioxide [41], [42], [58], [72], [78], [121], [129] gas sensing applications. The composites of P3HT with other materials (e.g. ZnO, RGO, PCBM, MoS_2) have also been used for gas sensing applications [122], [124], [126], [127], [130]–[135]. Recently, PQT-12 has been reported to be a good contender to the P3HT polymer due to its better stability and electrical performance over P3HT based devices [33], [136]. Dai et al. [33] have reported a better stability in the ammonia response in the PQT-12 based sensors than that of P3HT based ammonia sensors. A PQT-12 based printable OTFT ammonia gas sensor fabricated on a flexible substrate has been reported by Besar et al. [68]. Vieira et al. [67] reported that PQT-12 composites with CNT based MSM ammonia sensors have better performance over the pristine PQT-12 based ammonia sensors. However, PQT-12 is relatively a new material with superior features over the P3HT. Further, the material is less explored for gas detection applications. Thus, there is an ample opportunity for exploring the PQT-12 material for detecting various hazardous gases especially NH_3 and NO_2 gases which is the prime objective of the present thesis.

1.4.3 Review of OTFDs Based Photodetectors

Like the conventional semiconductors, the conjugated polymers have also been investigated for photodetection applications [4], [18], [137], [138]. K. S. Narayan and N. Kumar [81] reported the first phototransistor using conjugated polymer P3OT in 2001. Later, various conjugated polymers and their structurally ordered films have been investigated for enhancing photoresponse of the devices [53], [82], [95], [139]–[144]. Thin films of various composites of conjugated polymers have also been used in TFTs for photodetection applications [103], [145], [146]. Pal et al. [53] reported a regioregular P3HT based high performance phototransistor with the maximum responsivity of 250 AW^{-1} under white light illumination. Bhargava and Singh [147] reported that the FTM-coated P3HT film based OTFT has better electrical and optical response characteristics than those of the OTFT using a conventional spin-coated P3HT film. Recently, optical properties of PQT-12 polymer have drawn considerable attention for photodetection application [83], [148]–[150]. Wasapinyokul et al. [149] have observed a good responsivity of 6.6 AW^{-1} in the PQT-12 polymer based thin film phototransistors. Lee et al. [151] have used PQT-12/PEO composite polymer for fabricating a flexible phototransistor on PET textile substrate. They [151] have observed a responsivity of as high as 930 mAW^{-1}. However, there is an ample opportunity for enhancing the photoresponse characteristics of the PQT-12 based TFTs for future generation flexible photodetectors.

1.4.4 Major Observation from the Literature Survey

In this section, we will summarise the major observations derived from the literature survey as given in the following:

- The organic thin film devices using conducting polymers are of great interests for flexible electronic applications due to their high strength and good flexibility, easy and low-cost synthesis technique, enviro-friendly bio-degradable nature and low-temperature fabrication processing [8], [15], [17].
- Among various conducting polymers, the polymers of polythiophene groups are largely investigated for various sensing applications due to their higher stability, better suitability for solution processing, and higher carrier mobility than other conducting polymers [30], [31], [33], [147], [152].
- The PQT-12 conducting polymer, which is a derivative of polythiophene, has been reported to be a good contender to the widely used P3HT for various sensing applications [33]. Note that PQT-12 is a polymer chain engineered version of P3HT, which has higher stability and higher mobility than P3HT [30], [31], [105]. It is relatively a new material which has not been explored extensively so far for electronic, gas sensing and optoelectronic applications.
- PQT-12 is sensitive to various health hazardous gases [33], [67], [68]. There is an ample opportunity for exploring the PQT-12 material based 2-terminal MSM and TFT devices for hazardous gas sensing applications.
- Besides hazardous gases, the PQT-12 is also sensitive to the green light [83], [149]. Thus, the PQT-12 polymer is believed to be explored for green light detection.
- Colloidal composites of PQT-12 and quantum dots have not been explored for the gas sensing applications.

1.5 Challenges in OTFDs for Sensing Applications

It is already mentioned earlier that conducting polymers based electronic devices are continuously gaining popularity due to their low fabrication cost in addition to the inherently flexible and biodegradable nature. However, while the bio-degradable nature of organic devices is good for the environment, it provides challenges in maintaining a stable electrical characteristic of the organic devices over a longer period. Further, the inherently lower mobility of the organic materials over the inorganic semiconductor puts another challenge in achieving good electrical characteristics of the organic thin film devices. A number of efforts have been made for enhancing the stability and carrier mobility of the organic materials by employing polymer chain engineering and thin film engineering techniques. The film deposition technique also plays a major role in determining the electrical, optical and gas sensing properties of the PQT-12 thin films.

1.6 Motivation and Problem Definition

It has been already discussed that organic electronic devices have many challenges related to the synthesis and fabrication of highly stable conducting polymer thin films with high stability for various sensing applications. Because of the relatively superior features of PQT-12 over the widely used P3HT material, the PQT-12 is believed to be having a wide opportunity for various sensing applications. In view of the above, the objective of present thesis is to investigate the electrical, gas sensing and photodetection properties of some PQT-12 thin film based organic MSM and TFT devices fabricated by spin coating and FTM based thin film deposition techniques. Attempt has also been made to improve the electrical and gas sensing performance of the organic TFTs (OTFTs) by using composites of PQT-12 and CdSe quantum dots. Characterization of the organic thin films, optimization of film thickness and heat treatment of the films are believed to play key roles in optimizing the electrical and sensing characteristics of the organic thin film devices.

1.7 Scope of the Thesis

The present thesis deals with the fabrication and characterization of some PQT-12 polymer-based devices for gas sensing and photodetection applications. The thesis consists of SIX chapters including the present chapter. The contents of the remaining FIVE chapters are briefly described in the following:

Chapter-2 deals with the investigation of gas sensing properties of the PQT-12 polymer film-based metal-semiconductor-metal (MSM) structure. The MSM device includes an optimized PQT-12 film of 80 nm as the active sensing material deposited on polyamide substrate by spin-coating method. An interdigitated gold electrode structure has been used in the MSM device under study. After the PQT-12 film characterization, the suitability of the PQT-12 based flexible MSM device under study for sensing of various hazardous gases such as ammonia, nitrogen dioxide and other interferences has been studied in details.

Chapter-3 reports the fabrication and characterization of PQT-12 and CdSe QDs composites based organic thin film transistor (OTFT). Two types of OTFTs have been fabricated: One OTFT contains a conventional spin-coated pristine PQT-12 thin film while the other has used PQT-12/CdSe QDs composite as the active channel material of the OTFTs. In both the OTFTs under study, the films have been deposited on the SiO_2 layer obtained by dry oxidation of the cleaned Si substrates. Properties of the two types of films have been studied in details. Then the electrical and ammonia sensing characteristics of the OTFT containing the composite of PQT-12/CdSe QDs have been compared with those of the OTFT containing the spin-coated pristine PQT-12 thin film. The suitability of the OTFT for the detection of ammonia gas has primarily been studied.

Chapter-4 deals with the fabrication and characterization of a PQT-12 thin based OTFT fabricated by the floating-film transfer method (FTM). The performance parameters of the FTM based OTFT have been compared with the OTFT containing the conventional spin-coated PQT-12 film as discussed in Chapter-3. The SiO_2 coated Si substrates considered in Chapter-3 have also been used for the fabrication of the FTM film based OTFT under consideration in the present chapter. The properties of the FTM based PQT-12 films have been compared with those of the spin-coated films. Finally, ammonia gas sensing properties of the proposed OTFT (using FTM based PQT-12 film) have been compared with those of the spin-coating PQT-12 film based OTFT device.

Chapter-5 investigates the green-light detection properties of the OTFTs fabricated by FTM technique as studied in Chapter-4. The optical properties of both the spin-coated and FTM coated PQT-12 films have been studied by UV-Vis spectroscopy and photoluminescence spectroscopy techniques. Finally, the photoresponse characteristics of the OTFTs fabricated using FTM technique have been measured for an incident light with 540 nm wavelength and 5 $\mu W/cm^2$ intensity.

Finally, **Chapter-6** summarizes the major objectives and concludes the major findings of the present thesis. This chapter also outlines some future scope of works related to this thesis.