Chapter 1

Introduction and Literature Review

1.1. Introduction

In recent decades there has been a significant amount of research on organic electronics due to their affordable, lightweight, easily processed nature and mechanical flexibility [1-3]. There has been demonstration of a variety of devices, such as organic field-effect transistors (OFETs) [4, 5], organic light-emitting diodes (OLEDs) [6], photo-voltaics (OPVs) [7] and bio (chemical) sensors [8, 9]. OLEDs, which were designed for solid-state lighting and flat panel display applications currently, exist in consumer electronics, such as mobile phones, automotive audio systems, and other devices. The evolution of organic thin-film transistors (OTFTs) is aimed at utilizing them in disposable electronics and display backplanes, including RFID tags, smart cards, and sensor arrays. Photo-voltaics (OPVs), which includes solar cells and photo-detectors have also drawn significant research efforts and advanced to a great extent during the last decade [10, 11].

In the expanding electronic industries, organic semiconductors have become crucial for producing inexpensive, flexible, and portable electronic components. The efficiency of organic semiconductors is intimately correlated with their purity, crystallinity, and molecular packing much like that of typical inorganic semiconductors. The formation of organic semiconductor crystals is ascribed to weak van der Waals interactions among molecules, unlike inorganic semiconductor crystals that rely on covalent bonds between atoms [12, 13].

Organic semiconducting films possess flexible intermolecular forces, enabling the development of innovative electronic devices that are impractical with traditional, brittle inorganic semiconductors [14]. Over the past several decades, significant progress has been made in the synthesis of both n-type and p-type organic semiconductor channels. These materials can be processed through vapor deposition or solution-based methods and have demonstrated higher on/off ratios and charge carrier mobilities compared to those of amorphous silicon (on/off ratio ~ 10^5 and charge carrier mobility ~1 cm^2/v.sec.) [15, 16].

1.2. Conducting polymers

Conducting polymers, a unique group of materials in which the creation of lightweight electronic devices with relatively easy processing compared to their inorganic equivalents attained enormous attention. They have recently gained attention in the wearable electronics industry due to their flexibility and minimal stiffness when conducting electricity. In 1977, the work "Synthesis of Electrically Conducting Organic Polymers: Halogen Derivatives of Polyacetylene, (CH)x" in "Chemical Communications" established a novel discipline of chemistry, "Electrically Conducting Polymers". Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa's discovery of polyacetylene, a conductive material similar to metal, changed the way people think of polymers. In recognition of their transformative contribution, **the Nobel Prize in Chemistry 2000** was awarded jointly to **Heeger, MacDiarmid, and Shirakawa** for "the discovery and development of electrically conducting polymers [17]. The discovery that plastics and polymers may carry electricity has led to important advancements in research. Later, several additional conjugated polymeric materials and their derivatives were discovered to be electrically conductive [18-22]. Polyaniline (PANI), polypyrrole (PPy), and polythiophene (PTh) are the most studied polymers due to their diverse electrical conductivity, ease of synthesis, exceptional redox characteristics, inexpensiveness, stability, and potential relevance in energy storage, super-capacitors, gas sensors and as corrosion resistant materials [23-27]. Some of the examples of commonly used organic semiconductors are given in Fig. 1.1.

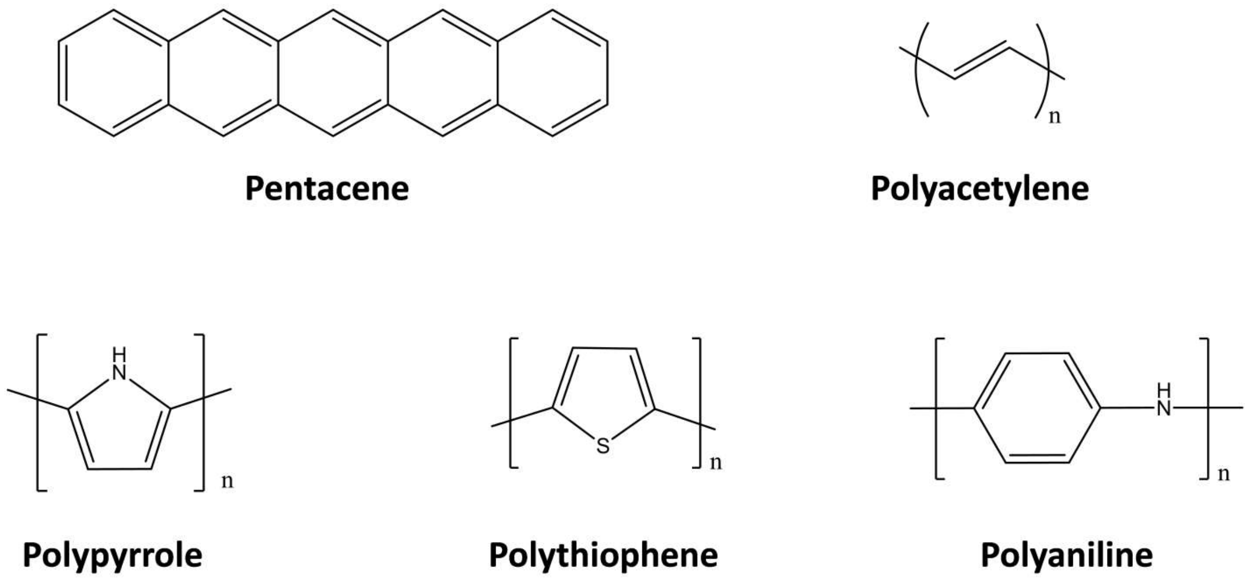

Fig. 1.1. Examples of the some commonly used organic semiconductors.

Using conducting polymers to create nano-composites has gained popularity in recent times. Such nano-composites are two-phase systems with at least one phase having nanometer-sized dimensions. Hybrids of organic polymers (like PANI, PPy, PTh etc.) with metal oxides and carbonaceous materials are extremely interesting nanocomposite systems [28-31]. Combining conducting polymers with nano-structured particles can create polymer nano-composites with unique properties, making them ideal for new and innovative applications. These nano-composites can take several forms, including nano-fibers, nano-rods, and thin films etc. [32-34]. The potential to tune the electrical conductivity of conducting polymers over several orders of magnitude by varying the synthetic parameters (dopant, solvent, oxidation states and synthetic processes etc.) is one of the most fascinating characteristics. Conducting polymers can be easily oxidized or reduced due to their extensive π-systems. Controlling the oxidation and reduction processes allow for exact changes to the optical and electrical characteristics of these polymers.

1.2.1. Intrinsic π-Conjugated polymeric materials

Conjugated polymers are organic polymer molecules consisting of alternating single and multiple bonds (double bonds). The π-electrons in double bonds are distributed throughout the polymer chain, not just over a single C atom. Such organic polymers can conduct current in their intrinsic form and are commonly used as solution processable organic semiconductor for various electronics device applications including OTFT, OLED etc. It is known that the electronic interactions between the unit cells of a polymer lead to the creation of electronic bands. The lowest unoccupied levels are recognized as Lowest Unoccupied Molecular Orbital (LUMO), which is akin to the conduction band, while the highest occupied electronic levels make form a valence band referred as Highest Occupied Molecular Orbital (HOMO), which is akin to valence band. The intrinsic electrical properties of these materials are dependent upon the width of the band gap (Eg), which is the forbidden energy band between the HOMO and LUMO.

1.2.2. Thiophene-containing conjugated polymers

Among the most commonly employed building blocks for conjugated polymer production is the thiophene ring, which has garnered significant attention from researchers as potential active elements in organic electronic devices. Since thiophene chemistry has been well-established and explored for a long period of time, extensive and fascinating structural variants allow for the tuning of the electrical characteristics in a broad range.

Early studies on substituent-free polythiophenes were conducted in the 1980s for FET applications, and the results showed only 10^{-5} cm^2/Vs of mobilities [35]. Several PT derivatives have already found usage throughout the field of electronics, and many are being investigated for potential application in electronic devices. The basic chemical structure of some polythiophene derivatives are displayed in Fig. 1.2.

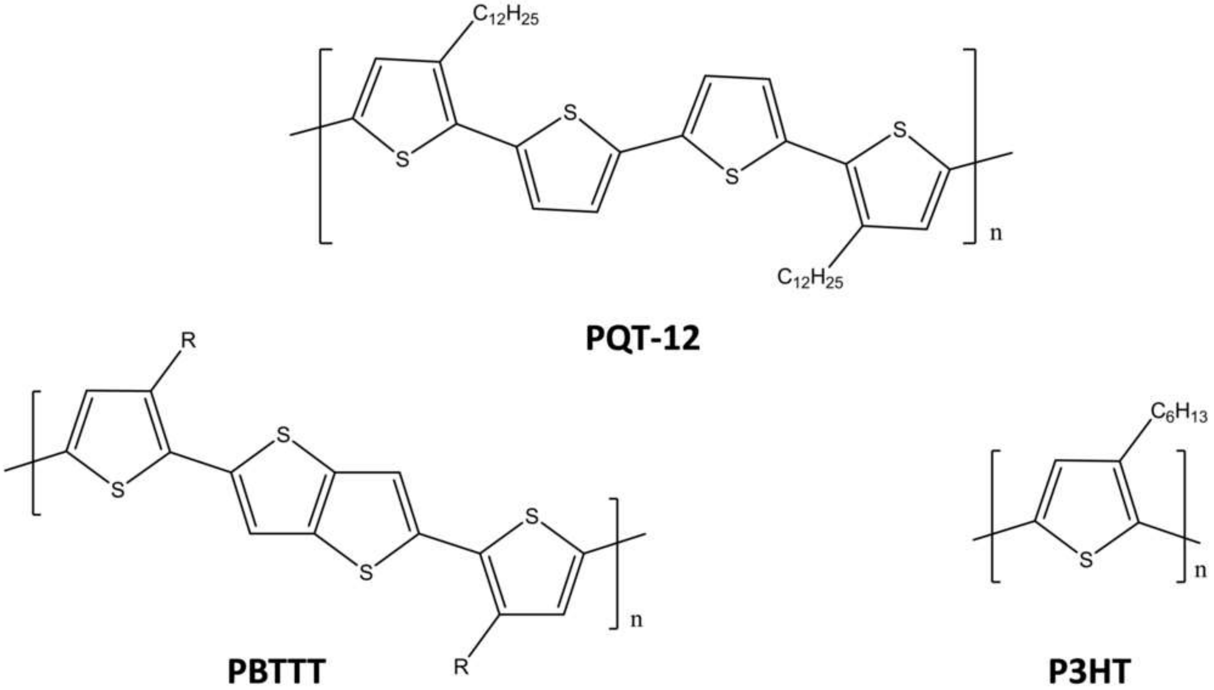

Fig. 1.2. Basic chemical structures of polythiophene derivatives.

1.2.3. Charge transport in organic semiconductors

Organic semiconducting materials are generally classified into small molecules and conductive polymers. Since polymers have higher molecular weights than their counterparts, their mobility is observed to be lower. The semiconductor grains need to be larger in order to get greater mobility. The potential to create conducting characteristics is maintained by conjugated polymers, which are sp^2-hybridized linear carbon chains. The carbon atom is in a double bond with the sp^2-$2p_z$ structure. The creation of a σ bond is caused by the intramolecular contact of two carbon atoms overlapping their sp^2-orbitals [36]. On the other hand, two p_z-orbitals result in π and π* (bonding and anti-bonding) orbitals.

The localization of states brought on by non-crystalline structure and the presence of imperfections have an impact on organic materials. The hopping of charges among these localized and discrete states of a molecule is the process that produces conduction. The standard models of charge transfer can be expanded and modified because they are amorphous in nature. Multiple trapping and release (MTR) and variable range hopping (VRH) models are commonly used to describe charge transfer in organic materials.

Charge hopping between localized states overcomes energy differences by phonon emission or absorption. Miller et al. studied the rate of single phonon jumps to mimic hopping in inorganic semiconductors [37]. Vissenberg et al. [38] studied how energy distribution and hopping distance affect carrier mobility in amorphous transistors. The multiple trapping and release model assumes that extended states are accessible to charge transfer. However, most injected carriers entrap on multiple occasions in confined states within the forbidden gap. The release of carriers thermally through theses states results in effective mobility, as defined

$$\mu_{Ef} = \mu_0 aexp\left(-\frac{E_{tr}}{K_b T}\right) \tag{1.1}$$

Where, μ_0 is the material's intrinsic mobility, K_B denotes the Boltzmann constant, Etr represents the energy level of a single trap, and T is the temperature.

1.3. Evolution of thin film transistor (TFT)

The technology of thin film transistor has advanced rapidly during the last few years, particularly in large-area, large-scale, low-temperature production. Recent technological developments in thin film transistors (TFT) suggest the availability of new information appliances in the future that will complement modern information infrastructures and lifestyles. Approximately thirty years ago, thin-film transistors were first made available for the use in liquid crystal display applications. The main benefits of thin-film transistor technologies over conventional silicon complementary metal-oxide-semiconductor (CMOS) transistors are their direct integration onto a range of flexible substrates due to their capacity to be produced on large substrates at lower processing temperatures and at low-priced per unit area [39].

Despite being patented in 1925 by Julius Edger Lilienfeld and in 1934 by Osker Heil, the field effect transistor concept only received significant attention in the late 1970s. Examining numerous device architectures and semiconductor materials, the thin film transistor (TFT) was forced to take second place due to competition from silicon-based metal oxide semiconductor field effect transistors (MOSFETs). The early 1970s observed scientists considering alternatives to crystalline silicon due to the need for economical electronics for large-area applications. TFT technology is therefore a leader in this situation. The three scientists Spear, Ghaith, and LeComber first described TFT in 1979 using hydrated amorphous silicon as a semiconductor material. The use of active channel layer material is then modified in a number of ways by technology in order to obtain notable switching ratios and carrier mobility. Since the mid-1980s, silicon-based TFTs have effectively impacted large area liquid crystal display (LCD) technology and have grown to be the key component of organic light emitting diode and active matrix LCD applications. Meanwhile, organic semiconductor channel layer-based TFTs with electron mobility comparable to hydrated amorphous silicon are launched in the 1990s [40]. It appears that this kind of TFTs could be an appropriate match for integration on flexible substrates. However, they also have lower carrier mobility, which restricts their use in circuits that need to operate at high current and fast speed.

1.3.1. Architecture of thin film transistor (TFT)

There are four OTFT configurations exist based on the manner in which source, drain and gate electrodes are arranged in relative to the semiconductor layer. Based on the electrode positions, TFT may be designed into four fundamental structures: bottom gate bottom contact (BGBC), top gate top contact (TGTC), bottom gate top contact (BGTC), and top gate bottom contact (TGBC).

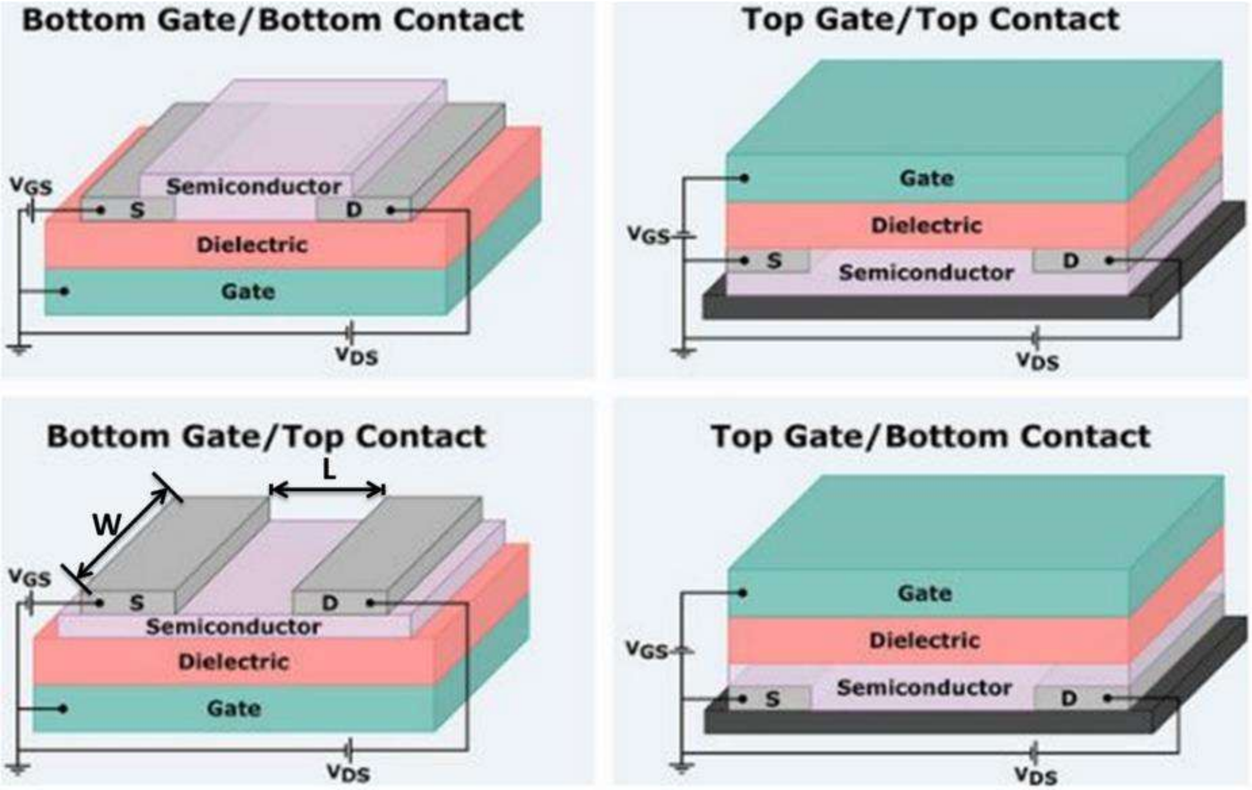

Fig. 1.3. TFT configurations: (a) Bottom-gate bottom-contact; (b) Top-gate top-contact; (c) Bottom-gate top-contact; and (d) Top-gate bottom-contact (image credit) [41].

It is fascinating that different TFT configurations (Fig.1.3.) can use the same materials and have remarkably distinct device characteristics. Thin film transistor is a unique category of field effect transistor that is manufactured by depositing thin films onto a supporting substrate that include the dielectric layer, active semiconductor channel, and metallic contacts.

A thin film transistor resembles a plate capacitor made up of an organic semiconducting layer and a gate electrode. In the operation, when a gate voltage is pulsed, a conductive channel is created when the carriers gather close to the interface between the organic and dielectric layers. Following the injection of carriers into the organic layer from the source electrode, transport occurs to the drain electrode via the conductive channel. Fig. 1.4 displays a more comprehensive illustration of the TFTs' operating concept.

1. **Linear regime:** The concentration of charge carriers in the transistor channel is constant when source-drain bias is not applied. Applying a small source-drain voltage ($V_D \ll V_G - V_T$) causes the charge concentration to be distributed.
2. **Pinched off:** The channel is "pinched off" when the source-drain voltage is raised to a point where $V_D = V_G - V_T$. In the conductive channel close to the drain electrode, there is no longer any potential difference between the gate and the drain electrode; this is termed as the "pinched off" voltage. Additionally, a depletion area forms close to the drain electrode, where no charge carriers remain.
3. **Saturation regime:** Although increasing the source-drain voltage further causes the depletion region to expand and the channel to slightly shorten, it does not significantly enhance the current. The transistor functions in the saturation regime in this situation.

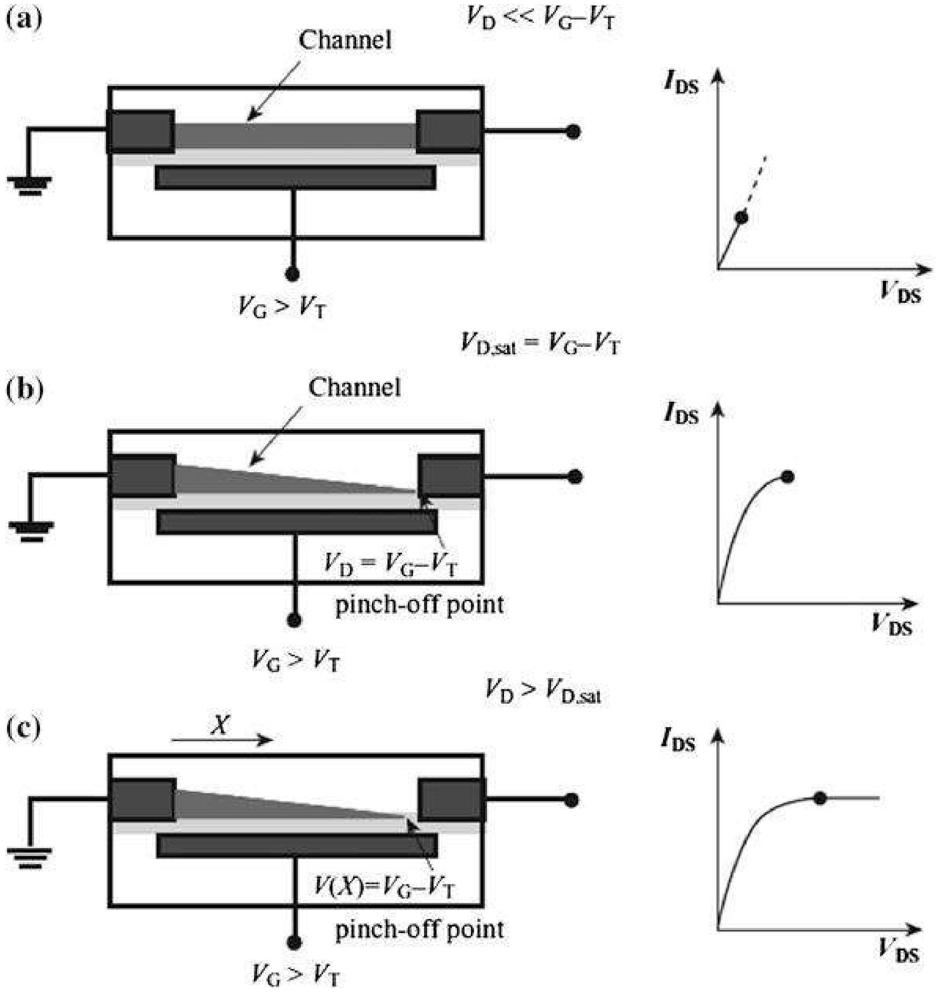

Fig. 1.4. Schematic work principles of thin film transistor: (a) linear regime; (b) start of saturation regime at pinch-off; (c) saturation regime and corresponding current–voltage characteristics (image credit) [42].

The electrical properties of TFT are typically measured using two characteristics and four device parameters.

These two electrical characteristics (Fig. 1.5) are:

1. Output characteristics (I_{DS}-V_{DS})
2. Transfer characteristics (I_{DS}-V_{GS})

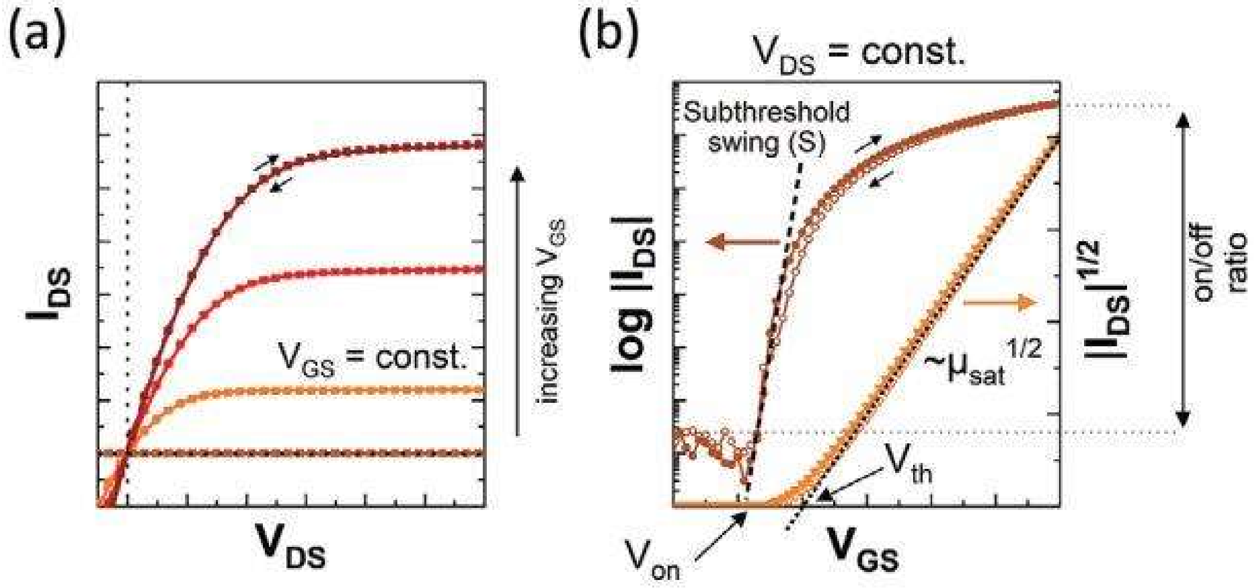

Fig. 1.5. Typical (a) Output characteristics and (b) transfer characteristics of a TFT to extract the device parameters (image credit) [43].

And four device parameters are:

1. **Charge carrier mobility (μ):** It represents the drift velocity of the carrier at the unit electric field. μ can be divided into two categories: the commonly utilized charge carrier mobility of the saturation regime and the charge carrier mobility of the linear regime. The two μ classifications are determined using the following equations:

For linear regime

$$I_{DS} = \frac{W\mu C}{L}(V_G - V_{Th})V_D \tag{1.2}$$

For saturation regime:

$$I_{DS} = \frac{W\mu C}{2L}(V_G - V_{Th})^2 \tag{1.3}$$

Where, μ is the field-effect mobility, W is the channel width, L is the channel length, and C is the insulator's capacitance, V_G is the gate voltage, V_{Th} is the threshold value, and V_D is the drain voltage.

2. **Current ratio (Ion/Ioff):** The ratio of the highest possible on-state current value to the lowest possible off-state current value. OTFTs typically exhibit on/off ratios ranging from 10^4 to 10^6.
3. **Threshold voltage (V_{Th}):** The minimum gate voltage essential to turn on the transistor is termed as the threshold voltage. Typically the value of V_{th} is 0 V to 0.4 V for OTFTs.
4. **Subthreshold slope (SS):** The subthreshold slope is a crucial factor in device performance. It is a measurement of the effectiveness with which a voltage differential applied to the gate can turn off the transistor. It is typically expressed as the reciprocal value of the subthreshold swing Ss-th.

$$S_{S-th} = \ln(10)\frac{kT}{q}\left(1+\frac{C_{\mathrm{dep}}}{C_{\mathrm{ox}}}\right) \tag{1.4}$$

Where, kT/q is the thermal voltage, C_{ox} is the gate oxide capacitance and C_{dep} is the depletion layer capacitance.

TFTs can be operated in either enhancement or depletion mode, depending on whether a gate voltage is needed to initiate channel conduction. The channel conductance is low for an enhanced mode of operation, when there is no gate voltage applied. For this mode to be accomplished, the channel must have a low carrier density. In the case of an enhancement mode, a channel must be created. The channel is enhanced as the gate source voltage rises. Then, the drain current flows when voltage is applied between the drain and source terminals. In contrast, the drain current will flow for zero gate source voltage in the depletion mode if the drain source voltage is applied.

1.3.2. Organic TFT (OTFT)

Organic thin film transistors (OTFTs) are gaining interest due to their potential uses in smart cards, flexible screens, and ID tags. The first organic transistor, developed in 1984, uses an electrolyte as the gate media [44]. Tsumura et al. reported the first OTFT in 1986, and it demonstrated clear transistor behavior [35]. Because of its simpler fabrication method, OTFTs are gaining popularity in comparison to traditional silicon technology.

The OTFT has multiple functional layers of organic semiconductor (OSC), gate dielectric, and electrode that contribute considerably to its operation. The device's effectiveness depends on its layers; therefore selecting the right materials and ensuring compatibility are essential throughout assembly. The OSCs play an essential character to the OTFT's performance since charge transport happens there. Consequently, to enhance the performance of OTFT, high-quality OSCs are required. The two primary groups into which OSCs can be divided are small molecules and conducting polymers. There are two common methods for depositing the OSC layer including solution-based procedures and vapor deposition. When it comes to OSCs, p-types OSCs have higher mobility than n-types. This happens because of the small band gap and low work function of materials in p-type OSCs resulting in a lower hole injection barrier compared to electron injection [45]. Additionally, electron transport can lead to charge trapping in the OSC layer, thus impacting the OTFT's performance [46].

Significant progress has been achieved in the past decade to create new organic semiconductors that will enhance transistor performance [47-49]. Stability, effective charge injection at the contacts, ordered molecular arrangement of the semiconductor channel, and the interface of metal and dielectric with semiconductor are some significant performance influencing elements that are improving over the time to fill the gap for their commercial applications. Several research investigations have been performed to use small molecules and polymers as the active layer of OTFTs.

1.4. Conjugated polymer thin film deposition methods

One of the fundamental procedure for easily and extensively preparing organic electrical devices is solution processing. Compared to Si-based electronics, organic electronics have an advantage since their processing feature makes the process both energy-efficient and inexpensive. However, arbitrary mixing and molecular alignment during solid phase condensation results in a range of film morphologies in organic-semiconductor films made using the solution technique. The most popular technique for creating CP thin films is spin coating, yet their use is still restricted on an industrial scale by issues including high material waste and surface roughness [50]. Meanwhile, a number of thin-film fabrication methods have been developed, including capillary action [51], flow coating [52], and slide coating [53] etc. For the large-scale manufacture of organic electronic devices, intriguing issues like an easy fabrication method with thickness homogeneity and the ability to fabricate multilayer thin films still need to be resolved.

As the film morphology changes the electronic characteristics also varies significantly. Therefore, the process of casting, which creates the film of organic semiconductors, is very essential in maximizing the potential of these materials. The inherent anisotropy of OSCs with respect to their geometric and electronic structures is linked to the origin of this diverse film morphology. So, in order to utilize the benefit of its anisotropy, the CP orientation methodology with an easy and rapid approach is highly demanded. In this thesis work, the Floating Film

Transfer Method (FTM) has been used for depositing CPs that has been used as a conducting channel of OTFT. A concise description of this method is specified in the following section.

1.4.1. Floating Film Transfer Method (FTM)

A unique thin film fabrication approach, to offer a cooperative solution to issues with the spin-coating and other methods is the Floating Film transfer method. Floating thin film deposition of CPs from low boiling point (BP) solvents, such as chloroform, onto an orthogonal liquid substrate, not only improves device performance, besides it also helps attain molecular orientation for several CPs with potential applications in anisotropic optoelectronics [54, 55]. The technique holds significance because it uses a liquid substrate to cast thin films. A homogenous film is formed by the mobile surface that liquid substrate gives the solidifying components to join with one another. Specifically, after spreading the solution on the liquid substrate, floating-film solidification occurs instantly if a volatile solvent like chloroform is utilize for the casing solution. In this instance, a floating film formed during spreading and solidification, which caused the film to compress due to the movement of the liquid substrate and result in an orientated floating film. Numerous variables, including the solvent's volatility, the solution's spreading speed, and the material’s solidification speed, will impact the orientation properties in dynamic FTM. Earlier a great number of research shows the orientation of π-conjugated polymers has a direct relation with molecular packing that influences device performance[56].

It has been shown that the aligned conjugated polymers display superior charge transport capabilities in electronic devices w.r.t the amorphous phase of those polymeric films [57, 58]. Therefore, these FTM grown films are expected to improve device performance significantly w.r.t the conventional spin coating thin films.

1.5. Applications of OTFTs

Organic semiconductors offer new prospects for lightweight, flexible, and environmental friendly electronics. They provide greater flexibility for shaping, manufacturing, and customization than inorganic materials. Organic compounds with π-π bonding have higher conductivity for holes and electrons [59] [60]. OSCs have revolutionized our understanding of electronics by offering a substitute to traditional inorganic-based devices and enabling ultrathin, lightweight, and flexible devices due to their special characteristics of electrical, chemical, and mechanical capabilities. Organic materials have become competing substitutes for photovoltaic cells (OPV), organic light-emitting diodes (OLEDs), and organic thin-film transistors (OTFTs) [6, 61, 62]. Particularly, OTFT provide a straightforward platform in terms of construction and is suited well with flexible circuits, inexpensive radio-frequency identification (RFID) cards, and biological or chemical sensors in particular [9, 49, 63].

OTFT-based sensors are commonly utilized for a range of applications, such as drug delivery, food preservation, in-situ medical diagnostics, environmental monitoring, and the detection of chemical warfare agents. Aside from organic materials, electronic detection-based sensors are perfect for an extensive variety of detection applications, ranging from big biological molecules in complex settings to diluted compounds in vapor.

A chemical binding event can be easily measured, amplified, analyzed and it can be converted into an electric signal. These sensors offer an alternative to costly, heavy equipment with lengthy sampling and analysis times that limits current technologies. Instead, they can lead to low-cost, portable detection units that consume less power and should be easy to integrate with other devices. These different applications of OTFTs are summarized in Fig. 1.6.

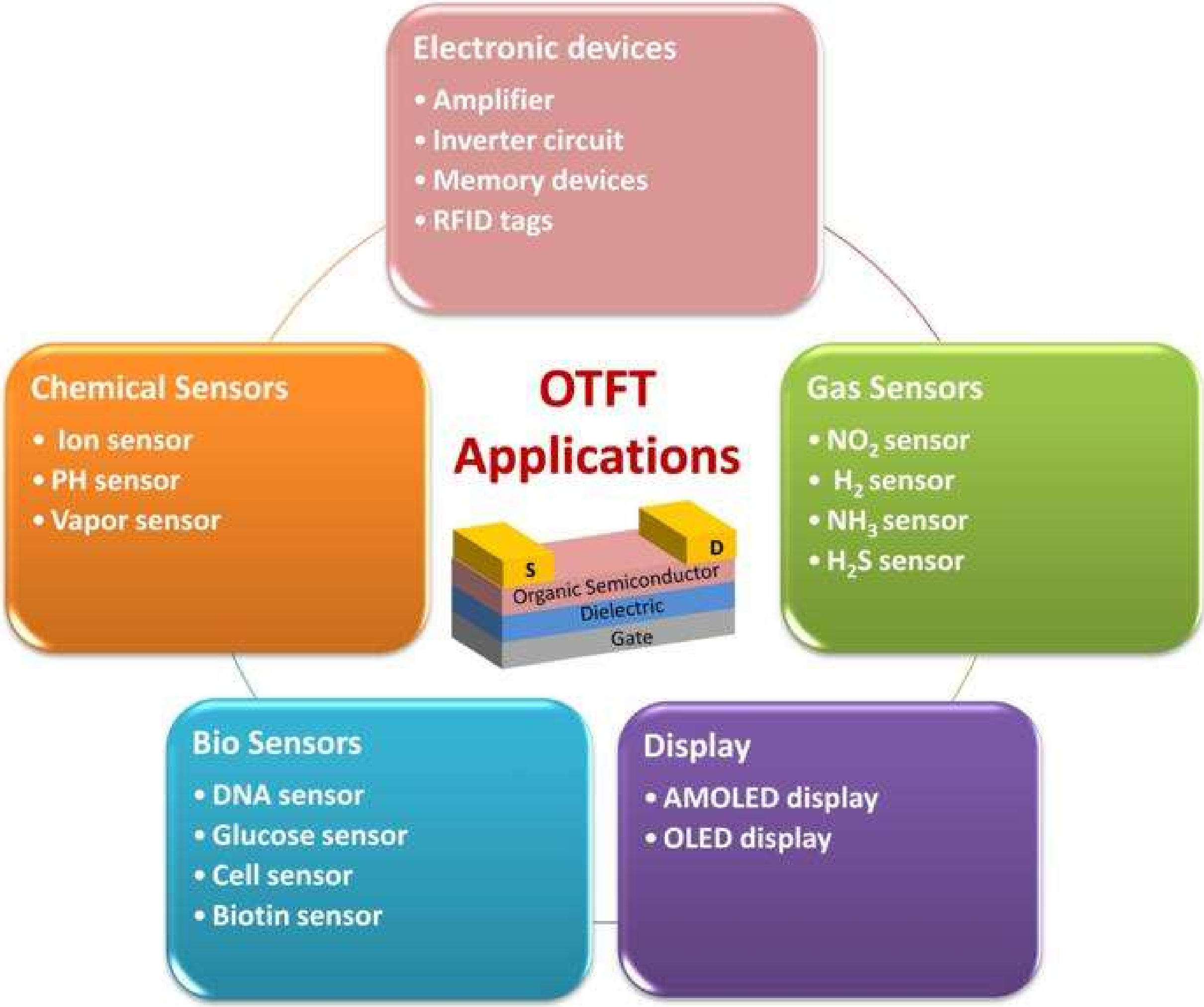

Fig.1.6. Summarizes the typical OSCs for OTFT applications.

The progress of novel and highly sensitive sensors has become imperative due to the growing worries about the protection of the environment and living things, as well as the widespread need for extremely accurate process monitoring. The unique redox chemistry of conducting polymers and their nano-composites has led them be considered as noble sensing materials. Hybrid materials incorporating CPs and a range of inorganic components including carbons (graphene and carbon nano-tubes), metal nano-particles, and metal oxide nanostructures also exhibit enormous potential for highly developed sensors because of the modulation of redox features, improved surface adsorption, and electronic interactions. In terms of construction and design, organic thin-film transistors (OTFT) provide an easy-to-use platform for electronic sensors by which a chemical binding event can be easily measured, amplify, analyzed, and converted into an electric signal.

1.5.1. Gas sensors

Rapid industrialization and the world's population growth are major contributors to the rapidly rising levels of air pollution, which have harmful effects on both the human health and the environment. Notably, the World Health Organization's (WHO) 2018 air quality database reports that 7 million people die annually as a result of living in hazardous environments where 9 out of 10 people have exposure levels to toxic chemicals over the allowed limits [64]. The primary cause of the environmental changes leading to a raise in temperature of the Earth, is air pollutants such NO_2, COx, and CH_4 etc. In addition to polluting gases, the environment also contains a number of other dangerous gases, such as NH_3, H_2, and H_2S, which can explode when combined with air in specific amounts. In addition to these poisonous gases, another class of dangerous chemicals that poses a risk to human health is the vapors of several volatile organic compounds (VOCs), including ethanol, toluene, formaldehyde, acetone, and triethylamine (TEA). Thus, sensing of these gases is essential for environmental study, medical diagnosis, industrial emission monitoring, agriculture, public protection and safety. Gas sensors that are highly sensitive, portable, and cost-effective are therefore in high demand.

Traditional methods of gas leak detection, which generate devices that give off an auditory alert to aware people to harmful or toxic gas leaks, are essentially unreliable because of the need for precise real-time investigations of the gas concentration. However, from the past few decades, centuries have been utilized numerous gas sensor technologies such as catalytic, optical, electrochemical, semiconductor and acoustic gas sensors to detect different gases. A number of factors determine the performance characteristic of each sensor, such as selectivity, sensitivity, detection limit, reaction time and recovery time.

Metal-oxide sensors (MOSs) have been commercially successful for a number of useful applications, such as hand-held ethanol sensors for cases of drunk driving, hydrogen and methane sensors for the protection of laborers in mines and industries, and gas sensors for acetone and toluene that are used to diagnose lung cancer and diabetes [65]. For these real-world sensing applications, SnO_2, TiO_2, WO_3, ZnO, CuO, CdO, and In_2O_3 have all received a lot of attention. These all kind of gas sensors has a high sensitivity; however their relatively high operating temperature requires more cost for maintenances and operations. Thus, in recent decades, new alternatives have been investigated as sensing materials to address the abovementioned problems, such as carbon nanomaterials (CNMs) [66-68]. CNMs can reach great sensitivity because of their large surface area for absorption. CNMs, or carbon nanotubes, graphene, and its variants, have excellent electron transport qualities and minimal electronic noise. Additionally, CNMs gas sensors allow for fast UV light recovery. Furthermore, their durability makes them perfect for creating flexible and portable devices that are highly sensitive [69-71]. Despite pristine CNMs having a lot of benefits, they also possess several noteworthy disadvantages, like poor repeatability, low selectivity, and non-uniformity of the functional groups on graphene derivatives or CNT walls [72, 73]. The 2D inorganic materials have a number of advantages, including ultra-high surface area, surface functionality, high stability and solution-based processibility [74, 75]. Nevertheless, these materials have drawbacks, like the fact that they are poisonous and non-biocompatible. Owing to these constraints, there is a significant emphasis within the scientific community on investigating organic semiconductors [7, 76].

The novel conception that plastics or polymers can conduct electricity gave rise to a fascinating field of study, and substantial progress has been made in this area. Later, it was investigated that a wide variety of added conjugated polymeric materials and their derivatives exhibited electrical conductivity [18, 22, 77]. Among these polymers, researchers are most interested in polyaniline (PANI), polypyrrole (PPy), and polythiophene (PTh) because of their extensive array of electrical conductivity from insulating to metallic, their ease of synthesis, special redox properties, good stability, affordability, and potential uses in a range of industries, including supercapacitors, gas sensors, corrosion protection, and energy storage [78, 79].

Due to the redox characteristics, PANI, PPy, and PTh are commonly employed as sensing materials [80-82]. Electronic conduction can be controlled through doping or dedoping, resulting in conducting or non-conducting states. The electrical conductivity of these polymers is determined by the amount and type of dopant employed, which creates charge carriers for conduction. The conductivity of a doped polymer is affected by any analytic interactions that change the amount and charge carrier's movement along the chain, as well as hopping across chains. Chemical-vapor sensing materials rely on this fundamental chemical principle. CPs based sensors exhibit higher sensitivity and rapid response/recovery times, particularly at ambient temperatures [83-85].

1.5.2. Influencing factors of Conducting Polymers/Nano-composites in gas sensing response

Understanding the phenomena of doping and dedoping as well as the impact of adding nano-particles on the surface area and electronic features of the polymer or polymer/nano-composites is crucial for developing high performance gas sensors by conducting polymer nano-composites.

1. Electrical Conduction

A conjugated backbone of polymer facilitates the mobility of charge carriers, which is necessary for conductivity. Compared to regular polymers, conjugated polymers are more readily oxidized or reduced. Owing to the π-conjugated structure, "doping" is used to enhance electrical conductivity, which creates additional charge-carriers in the form of free electrons or holes. In this thesis work, carrier modulation of CPs thin film channel of OTFT via doping or dedoping method for detecting the analyte gas like NH_3 has been utilized.

2. Doping Process

The function of dopant is to either remove or supply electrons or works as charge transfer agents to the polymer. Doping (p-type oxidation or n-type reduction) can significantly enhance the electronic conductivity of the polymer. The doping reaction can be presented as follows:

$$\textbf{Oxidation:}\ P + n\,X^{+}A^{-} \longrightarrow [P : n\,X^{+}]\,[nA^{-}] \quad \text{(p - type doping)} \tag{1.5}$$

$$\textbf{Reduction:}\ P + n\,X^{+}A^{-} \longrightarrow [P : n\,A^{-}]\,[n\,X^{+}] \quad \text{(n - type doping)} \tag{1.6}$$

Where, P represents a polymer chain segment. The process begins with the formation of a soliton or polaron (cation or anion), followed by a second electron transfer to generate a dication or dianion, also known as a bipolaron.

3. Dedoping Process

Doping can also be reversed, a process known as dedoping, in which a doped polymer like p-type doped reacts with a reducing substance to return to its higher resistive state. Through a charge-transfer reaction, the dedoping agent diffuses into the polymer matrix and neutralizes the charge carriers partly of the system. The procedure could entail chemical processes that result in neutralization via charge transfer among the dedoping agent and the carbonium ion or/and dopant. Thermal treatments can also have an impact on dedoping as seen in the case of PTh. Numerous techniques, including optical spectroscopy, x-ray diffraction, electrical conductivity measurements, can be used to study the kinetics of dedoping.

4. Surface Area Aspects

The sensing signal is often caused by the functional groups on the polymer surface. Porous or meso-porous materials contain a larger amount of exposed functional groups and therefore show stronger reactions, however, inter-coiled or compressed polymeric structures will respond poorly because they have fewer unexposed functional sites. The entire surface area of the polymer nanocomposite is significantly impacted by the addition of nano-particles to the polymeric system. Conducting polymer solution-cast films usually show low porosity, while electrochemical deposition of polymers has the potential to create high porosity that can maximize the surface area [86, 87]. Under ideal circumstances, the in situ polymerization process for the creation of polymer nano-composites usually results in the polymer wrapping nano-particles, and increasing the surface area of the sensing material that results in improved sensitivity of the sensor [88, 89].

5. Role of Environmental Conditions

The conductivity of polymers increases with rising temperature and humidity. Therefore, investigation of device performance with different temperature and humidity are very important studies. The interaction with the analyte molecules to the CPs and their adsorption on the detecting surface of the film are important processes to understand the sensing mechanism which are highly dependent on temperature. Since low temperatures are more favorable for adsorption, any increase in temperature will cause the equilibrium to shift and favor analyte desorption [90, 91]. Therefore, sensitivity decreases as temperature rises. On the other hand, because of the higher reaction rate caused by rising temperatures, the sensitivity of redox reaction-based sensors increases. In real terms, sensors are highly sensitive to humidity, and in that situation, water vapor acts as an analyte. Because the reaction of sensing material to the analyte gas and humidity is identical, the data from the sensor may be deceptive, when there is humidity present [91].

1.6. OTFT based gas sensors

π-Conjugated organic semiconductors have demonstrated a unique combination of charge-transport properties and low-temperature, solution-based processing capabilities. These characteristics have led to promising potential and play a critical role in enabling essential charge-transportation in the two-dimensional accumulation layer of a TFT. For the design and fabrication of electronic gas sensors, OTFT offers an inexpensive and accessible platform. The detection of gases with OTFTs involves a change in electronic performance when gas molecules react with the active transport layer of organic semiconductors (Fig. 1.7).

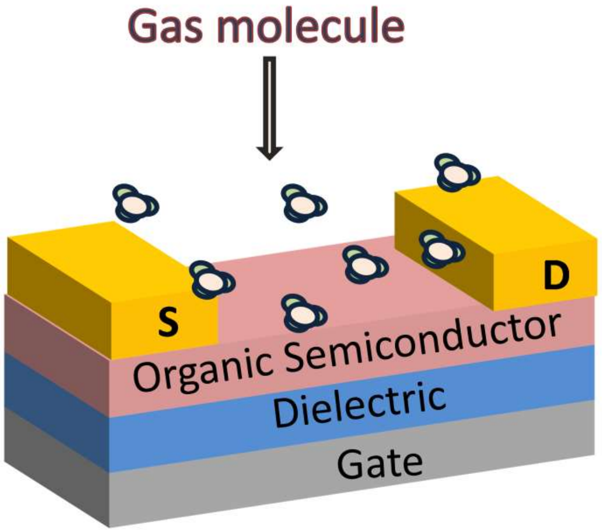

Fig.1.7. BGTC OTFT assembly with gas molecule interaction.

At constant bias conditions, in which the gate bias (V_G) and source-drain bias (V_{DS}) are fixed to facilitate current flow across the channel, are commonly used to monitor the transformation of the drain current during the exposure of analyte gas to the channel. The interaction or binding of gas molecule with the CPs of the channel that varies the source-drain current (I_{DS}), is eventually dependent on the gas concentration, and bias conditions of the OTFT [92]. Therefore, some of the important characteristics of the sensor depend on the rate of variation in drain current (I_{DS}) with analyte gas concentration under certain bias conditions that determines the quality of the sensors. The gas response of the OTFT sensor is dependent on the variation in drain current before and after the exposure of the analyte gas and is represented as:

$$R = \frac{|I_{DS,Air} - I_{DS,Gas}|}{|I_{DS,Air}|} \times 100\% \tag{1.7}$$

An advantage of transistors over conventional two-terminal chemi-resistors is the presence of an additional gate electrode, which modulates the conductivity of the sensing material and provides an active sensing window along with integrated signal amplification. Multi-parametric analysis is also a further beneficial feature of the drain current modulation. This implies that changes in a number of parameters, including threshold voltage (V_T), conductivity, On/Off ration and mobility (μ) can be employed to monitor the analyte event.

The semiconductor film morphology, which works as the active site for the gas molecule interaction of the OTFT is a key player in gas sensing applications. Till date a number of techniques for depositing the organic semiconductor layer have been identified including the two important processes as thermal evaporation and spin coating [93]. In the case of a thermal evaporator system, the morphology of the deposited film is influenced by several deposition parameters such as substrate temperature, deposition rate, and film thickness, which have a major impact on the film properties and consequently, affect the performance of the OTFT sensor [94, 95]. However, in solution based coating the key variables that affect the film's morphology are the solvent, concentration of the polymer solution, and temperature etc.

1.7. Motivation of the thesis on Ammonia sensor

Ammonia (NH_3) is a pungent and colorless gas, which is commonly found in agricultural, industrial, and environmental contexts. It is toxic and hazardous compound that poses significant health and safety risks. When it released into the atmosphere in large quantities, can contribute to air pollution and environmental degradation. On the other hand, Ammonia, is a key chemical used in many industrial processes, including fertilizer production, and has significant potential as an energy carrier, especially for use in fuel cells or as a hydrogen carrier. Any leaks or exposure can be harmful to workers and the surrounding environment. Thus, effective detection of ammonia is important for mitigating its harmful effects and ensuring compliance with environmental and health safety standards.

1. Environmental and Health Impact of Ammonia

Nowadays, human activity is the primary source of direct or indirect ammonia emissions into our atmosphere. Major artificial sources include intensive livestock farming, where manure decomposition releases significant amounts of ammonia and industrial processes, particularly in the production of fertilizers and refrigeration systems. Ammonia is flammable at high concentrations, which is a major disadvantage. Inhaling lower concentrations of this gas can cause soreness in the nose and coughing due to its suffocating odor. At higher concentrations, it can also cause burning sensations in the throat and nose. In severe circumstances, it might completely harm the respiratory system and can cause long-term health issues. Vytenis published documentation of an actual NH_3 explosion that occurred in West Texas in 2013, leaving 200 persons injured and 15 dead [96].

Agriculture-related emissions of atmospheric ammonia (NH_3) are a major cause of acidification. NH_3 directly affects the respiratory health of people who engage in handling animals. These health effects may include a decline in eye and throat discomfort, rise in coughing and phlegm production and lung function. According to current research, agricultural ammonia may have a direct impact on young children's early onset of asthma [97]. Ammonia is a major component of fine particulate matter ($PM_{2.5}$), which contributes to respiratory problems and other health issues. When ammonia enters water bodies, it can lead to eutrophication, which degrades water quality and harms aquatic life. Ammonia (NH_3) gas undergoes an exothermic reaction with water, resulting in ammonia-induced corrosion in various metals, including copper (Cu), zinc (Zn), and their alloys.

2. Industrial Relevance

The global need for green hydrogen is set to expand as it plays a key role in reducing emissions, enhancing energy security and driving the transition to a sustainable low-carbon economy. In the context of green hydrogen, ammonia is often considered as a possible storage and transport medium due to its high hydrogen content. Many countries are exploring ammonia as a means to import and export hydrogen, as ammonia is easier to liquefy, store, and transport than hydrogen in its pure form. However, the production, storage, and transportation of ammonia come with safety risks, particularly related to its toxicity and potential environmental impact. This is where the global need for ammonia sensors is likely to grow significantly in the coming years and play a vital role in the widespread adoption of ammonia-based hydrogen storage technologies [98]. The importance of ammonia sensing in hydrogen storage can be understood in several key areas:

- **Safety Concerns:** If ammonia leaks into storage or transportation systems, it poses significant safety risks. Ammonia is toxic and corrosive, and its presence could lead to hazardous working conditions, so early detection and monitoring is critical to prevent accidents. By regularly sensing ammonia concentrations, it is possible to detect leaks early and reduce the risk of more severe system failures.
- **Optimizing Hydrogen Storage Systems:** Ammonia as a hydrogen carrier can be stored and transported at relatively low pressures or even in liquid form at moderate temperatures. Ammonia is synthesized and then decomposed to release hydrogen when

needed. Ammonia sensing helps to monitor the integrity and efficiency of the storage system and ensures that ammonia is released at the appropriate time for hydrogen usage.

- **Regulatory Compliance:** Many countries have stringent environmental and safety regulations for ammonia emissions, especially in industrial settings where hydrogen is stored or used. Low-concentration ammonia sensing ensures compliance with these regulations by providing real-time data on ammonia concentrations, which is necessary for reporting and controlling emissions.

Ammonia is also widely used in industrial processes, including in the production of fertilizers, explosives, refrigeration systems and in various chemical manufacturing operations. In many of these industries, ammonia is handled in large quantities, creating potential safety hazards and ammonia sensors will help in real-time monitoring of ammonia concentrations for ensuring the safety of workers and preventing accidents.

In summary, the growing need for reliable ammonia detection technologies driven by environmental concerns, industrial applications, and safety regulations, there is a need for cost-effective, portable and real-time ammonia sensors that are sensitive, selective and capable of continuous monitoring in a variety of environments. Therefore, this thesis work broadly explores and motivates the development of room temperature operating OTFT based high performance ammonia gas sensors fabricated by a low cost solution process technique. This work explores the ammonia-sensing capabilities of organic/heterojunction and homojunction based OTFTs based sensors. Moreover, the thesis chapters thoroughly examined the sensitivity, selectivity, stability and plausible mechanism of the sensor in response to ammonia gas concentrations at room temperature.