CHAPTER-1

Introduction

1.1 Thesis Abstract

The research communities have focused a great deal of attention on developing and advancing organic thin-film transistors (TFTs) for various electronic and sensing applications. These TFTs have many potential applications in the era of memory devices, organic LEDs, gas sensors, medical applications and many more. With the continuous research progress and swift developments in deposition methodologies, there has been a noticeable advancement in the existing solution-processable, low -voltage, low-cost wide area-based TFTs to fulfill various electronic and sensing applications. Moreover, the organic semiconductor-based thin film transistors have gained more interest due to their ability to use in flexible electronics, such as flexible LEDs, displays, keyboards, smartphones, sensors, memories, etc., and in flexible smart cards, such as RFID (Radio Frequency Identification) tags, etc. Exploiting a broad advantage of TFTs, this thesis broadly discusses the advancement in the fabrication and characterization of organic semiconductor-based TFTs and their utilization in enhanced ammonia sensing/detection.

This thesis contains six chapters, which have been organized simply and concisely to explore the advancement in the fabrication and characterization of the Organic TFTs (OTFTs) and their applications as selective ammonia gas sensor. Each chapter begins with a brief description of its contents, followed by motivation for the research, and further supported by graphical illustrations.

The thesis briefly discusses the evolution of TFTs, the basic charge transport phenomenon in organic semiconductors, various deposition techniques, challenges in the deposition of organic semiconducting channel, and gate oxide film of organic TFTs in ***Chapter 1*****.** This chapter also outlines various architectures, charge transport mechanism in TFTs, application of OTFTs in gas sensing, literature survey/motivation behind OTFT-based ammonia sensors, and resources utilized in the device fabrication and sensing characterization/measurements.

***Chapter 2*, **dealing with the gas-sensing applications of organic polymer nanocomposite-based thin-film transistor in ammonia sensing application. This chapter explores the introduction of organic TFT in gas sensing application, device fabrication, followed by characterization properties of the thin film, various sensing results, and sensing mechanisms incorporated in fabricated organic polymer nanocomposite-based TFT for ammonia sensor. It has been found that the introduction of the 2D MoS_2 flacks in the P3HT polymer matrix enhances the sensing response of the polymer nanocomposite matrix towards ammonia gas at room temperature operation (25 ºC), and is almost independent of relative humidity (RH) variation.

In ***Chapter 3*,** a cost-efficient, minimal-wastage facile solution-processed floating film transfer method (FTM) has been discussed for the controlled morphological growth of organic semiconductor channel and further utilized for the gas sensing application. This chapter envisages a low-cost spin-deposited LaZrOx high-k dielectric layer for low-voltage OTFT device. The synthesized dielectric possesses a high band gap, low leakage current density, high stability, and the capability to generate a high saturated current even at low applied voltage. This chapter further explores various device characteristics and sensing results. It also investigates the device physics and sensing mechanism toward the target ammonia gas.

Chapter 4 includes novel high-k bilayer dielectric film and Au/P3HT nanocomposite organic semiconductor channel in the fabrication of organic TFT for ammonia sensing application. The introduction of TiO_2 and HfO_2 layers in the TiO_2/HfO_2 bilayer utilizes the advantages of both layers in terms of high dielectric constant (large capacitance per unit area) and high band gap (minimize leakage current density), which are further suitable for low voltage operation of the OTFT with the high saturated current. The bilayer dielectric also reduces the trap charge density at the dielectric/semiconductor interface and reduces the threshold voltage of the transistor. Moreover, introducing Au (gold) nanoparticles in the P3HT polymer matrix enhances the charge transport facility, the chain ordering, sensing response, and response/recovery time of the fabricated sensor towards ammonia gas.

Chapter 5 illustrates a novel high-k hybrid dielectric material as a gate oxide film and P3HT/g-C_3N_4 nanocomposite organic semiconductor channel for the fabrication of flexible organic TFT to obtain enhanced ammonia gas sensing performance. This work utilizes a hybrid ZrOx/PMMA/PMCF dielectric layer, which has the advantages of both the polymer dielectric (PMMA/PMCF) in terms of the smooth film (free form charge carrier scattering), flexible nature, etc., and the use of high-k inorganic dielectric (ZrOx) in terms of high dielectric constant (~ 22), etc. for the fabrication of low-voltage flexible organic TFT. In this chapter, the extensive study of the device and sensing characteristics of the fabricated flexible device has been thoroughly discussed. Moreover, the introduction of the 2D g-C_3N_4 in the pristine P3HT polymer matrix also demonstrates a better sensing characteristic due to improved π-π carriers' delocalization over the backbone of the polymer matrix.

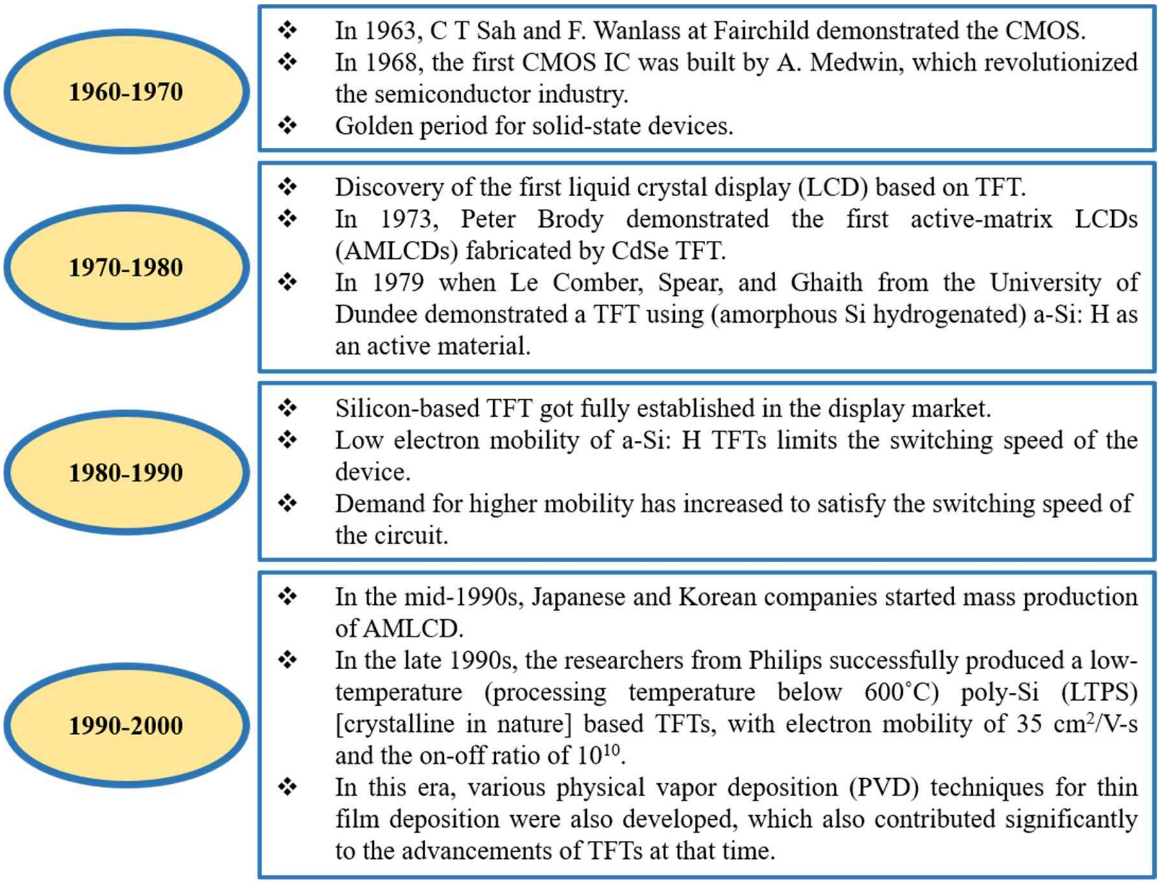
Chapter 6 presents a summary of the outcomes of the study undertaken during the work. The overall conclusion drawn from the study has been enunciated. The study revealed that it is possible to bring down the operating voltage of conventional OTFTs by using suitable high-k dielectric material as a gate oxide layer. It can also be concluded that with the suitable selection of organic polymers/nanocomposite materials and hybrid dielectric (Polymer/Inorganic) materials with certain optimization and deposition techniques, one can fabricate a cost-efficient, flexible organic TFT device in the area of electronic and sensing applications. This chapter further outlines the future scope of this extensive study.

1.2 Evolution of Thin Film Transistors

Thin film transistors are a special class of metal oxide semiconductor field effect transistors (MOSFETs), where the transistor is very thin as compared to the plane of the device. It can be fabricated by coating/growth of an active semiconductor layer, dielectric/oxide layer, and metallic contacts over any kind of rigid substrate. The substrate type includes silicon, glass, flexible PET (Polyethylene Terephthalate), etc., for device fabrication. Although the concept of the field effect transistor's idea was first patented by Julius Edger Lilienfeld in 1925 and in 1934 by Osker Heil, it began to receive significant attention over the late 1970s. The rising competition in the field of MOSFET, which uses the complex and costly fabrication process on a silicon substrate, motivated researchers to find an alternative to conventional MOSFETs. In addition to that, the necessity of low-cost portable electronics for large-area applications, such as in memories, displays, sensors, etc., motivated scientists to develop a low-cost, simple TFT device in the early 1970s [1]. The three scientists, Spear, Ghaith, and LeComber, described TFT in 1979 using hydrogenated amorphous silicon (a-Si: H) as a semiconductor material. After that, several active and dielectric layer modifications were done to obtain a reliable, high-performance TFTs device. In the 1980s, silicon-based TFTs gained a lot of attraction due to their large potential application in LCDs (liquid crystal displays) and proved itself as a very important device in the area of emerging electronics. Later, in the 1990s, TFTs with organic semiconductors as active layers were introduced with high electron mobility and performance [1]. Ever since, a lot of continuous research has been done on the fabrication optimization of organic semiconductors, gate dielectrics, etc., to improve the TFT device's performance and relative stability over a long time.

1.2.1. Development of Inorganic Oxide-based Thin Film Transistors

The first thin film transistor based on inorganic oxide was invented in 1962 from RCA Laboratories, Princeton, N. J. Paul K. Weimer, using a polycrystalline thin film of cadmium sulfide (CdS) as an active layer [2]. Later the cadmium sulfide was replaced with cadmium selenide film and obtained a better performance. The evolution of the thin film transistors is illustrated in **Figure 1.1**.



1960-1970

- In 1963, C T Sah and F. Wanlass at Fairchild demonstrated the CMOS.
- In 1968, the first CMOS IC was built by A. Medwin, which revolutionized the semiconductor industry.
- Golden period for solid-state devices.

1970-1980

- Discovery of the first liquid crystal display (LCD) based on TFT.
- In 1973, Peter Brody demonstrated the first active-matrix LCDs (AMLCDs) fabricated by CdSe TFT.
- In 1979 when Le Comber, Spear, and Ghaith from the University of Dundee demonstrated a TFT using (amorphous Si hydrogenated) a-Si: H as an active material.

1980-1990

- Silicon-based TFT got fully established in the display market.
- Low electron mobility of a-Si: H TFTs limits the switching speed of the device.
- Demand for higher mobility has increased to satisfy the switching speed of the circuit.

1990-2000

- In the mid-1990s, Japanese and Korean companies started mass production of AMLCD.
- In the late 1990s, the researchers from Philips successfully produced a low-temperature (processing temperature below 600˚C) poly-Si (LTPS) [crystalline in nature] based TFTs, with electron mobility of 35 $cm^2/V\text{-}s$ and the on-off ratio of 10^{10}.
- In this era, various physical vapor deposition (PVD) techniques for thin film deposition were also developed, which also contributed significantly to the advancements of TFTs at that time.

Figure 1.1 Evolution of inorganic oxide-based thin-film transistors.

1.2.2. Development of Organic Thin Film Transistors

The invention of conjugated polymers opened a new era of research to manufacture cost-effective devices for electronic and sensing applications. The excellent solubility of the conjugated polymers in some organic solvents opened advancement in the cheap, facile fabrication methodologies to fabricate solution-processed, low-cost electronic devices for various applications in the semiconductor industries [3]. The solution-processed methods can reduce the fabrication process complexities and minimize the fabrication cost compared to the inorganic semiconductor-based devices. Early in the 1960s, Martin Pope and his colleagues [4] conducted interesting research on the ground- and excited-state electronic structure of organic compounds of anthracene. Shirakawa and his team's later demonstration of successful synthesis and controlled doping of semiconducting polymer in the 1970s [5] gave the research community the impetus to conduct such a large volume of investigation on these materials and their commercial exploitation by the industry in the recent decades. The first organic field-effect transistor based on a thiophene polymer was announced in 1986 by Mitsubishi Electric researchers (H. Koezuka, A. Tsumura, and Tsuneya Ando) [6]. Soon after, this development and discovery of conductive polymer became so interesting that Shirakawa and his team members were awarded Nobel Prize in 2000. Since then, organic semiconducting materials have propelled the development of several electronic devices over the ensuing decades. These include OTFTs, electrochemical cells, solar cells, organic light-emitting diodes (OLEDs), organic memories, printed organic circuits, organic photodetectors, and organic biosensors. Moreover, with the ever-increasing demand and advancement in the semiconductor industries for cost-effective electronic products for consumers, organic semiconductor-based devices have indeed greatly advanced in their applications.

1.3 Organic Semiconductors in TFTs

Organic semiconductors are classified as: (1) Small molecule organic semiconductors and (2) Conductive polymer semiconductors. Small molecule organic semiconductors are generally not soluble in common organic solvents and can't be deposited by simple solution-processed methods. Over the small molecule organic semiconductors, conductive polymer organic semiconductors are generally dissolved in common organic solvents (except polar solvents (Alcohol, H_2O) and some non-polar solvents (Toluene, Benzene, Octane, and Hexane), etc.), This makes polymer semiconductors suitable for solution-processed cost-efficient deposition methods. **Table 1.1** shows the organic semiconductor molecule classifications and their applications in electronic industries.

Table 1.1 Organic Semiconductor Classifications and their Applications

Organic Molecules		**Examples (Acronym)**	**Applications**
Small Molecule Organic Semiconductors	Oligoacenes [7]	❖ Pentacene [8] ❖ TIPS Pentacene ❖ Rubrene [9] ❖ Tetracene [10]	▪ Well-defined crystal structures ▪ OLEDs ▪ OTFTs
	Thiophene & Discotic Liquid Crystals	❖ DNTT [11] ❖ Hexabenzocoronene [12] ❖ Triphenylene [13] ❖ Perylene diimide [14]	▪ OTFTs ▪ Based on 2D, disc-like molecules ▪ Electron and/ hole transport
Conductive Polymer Semiconductors	Polythiophene (PT) and Derivatives [15]	❖ P3HT [16] ❖ PBTTT C-14 [17] ❖ PQT [18] ❖ PTB7 [19] ❖ PCPDTBT ❖ Polyanilines [20] ❖ PEDOT ❖ Polycarbazoles [21]	▪ OTFTs ▪ OLEDs ▪ Electroluminescent Devices ▪ Solar Cells ▪ Biosensors ▪ Chemical Sensors
	Polyparaphenylene, Polyparaphenylene Vinylene, and their Derivatives	❖ PPP [22] ❖ PPV [23]	▪ high luminescence quantum yield ▪ light-emitting applications ▪ OLEDs

P3HT *- Poly(3-hexylthiophene-2,5-diyl),* ***DNTT****-Dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene,* ***PBTTT C-14****-Poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene],* ***PTB7****-Poly({4,8-bis[(2-ethylhexyl)oxy-benzo[1,2-b:4,5-b']dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}),* ***PCPDTBT****- Poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b;3,4-b']dithiophene)-alt-4,7(2,1,3-benzothiadiazole)],* ***PEDOT*** *- Poly(3,4-ethylenedioxythiophene),* ***PPP****- Pristine Poly(para-phenylene),* ***PPV****- polyparaphenylenevinylene .*

Table 1.2 explains the difference between small molecules and organic polymer semiconductors [24][25].

Table 1.2 Difference between Small Molecule and Polymer Semiconductors

Sl.no.	Small Molecule Organic Semiconductors	Organic Polymer Semiconductors
1	❖ Not soluble in common solvents, needs special vacuum deposition techniques.	❖ Soluble in common organic solvents.
2	❖ Film quality using vacuum evaporations is superior, better electrical properties, but costly and time-consuming process.	❖ Film quality and electrical properties are inferior compared to small molecule organic semiconductors.
3	❖ Crystalline in nature.	❖ Amorphous in nature generally, but crystallinity can be improved with some special deposition techniques.

1.3.1. Charge Carrier Transport Model in Organic Semiconductors

Over the last three decades, there were extensive studies have been done to investigate the charge carrier transport theory of organic semiconductors. But the charge transport theory of organic semiconductors remains a complex and ambiguous topic and needs more research [26]. The charge transport theory of organic semiconductors can be explained by the molecular orbital theory (Highest Occupied Molecular Orbital (HOMO)/ Lowest Unoccupied Molecular Orbital (LUMO) theory) [27]. The Molecular Orbital (MO) theory was first proposed in the 20th century to explain the brief study of the charge transport phenomenon by approximating the state of bonded electrons as a liner combination of atomic orbitals (LCAO). According to this theory; when two atoms with the same energy are brought closer together, the energy level of the atoms gets perturbed and split, creating different molecular energy levels.

The energy level with higher energy is called LUMO and with the lower energy is called HOMO. The position of the energy levels can't be determined exactly but it is approximated by LACO method [28][29]. Based on the LACO method, each molecule has a set of molecular orbitals, and the molecular orbital wave function (ψ_j) follows the weighted sum of 'n' constituent orbitals X_i, The expression for the molecular orbital wave function is given by-

$$\psi_j = \sum_{i=0}^{n} C_{ij} X_i \tag{1.1}$$

In other words, for the diatomic dipole (atomic orbital of two atoms, atom X, atom Y) having wave function ψ_X and ψ_Y , respectively when bought nearer leads to the formation of the molecular orbital wave function ψ_j is given by-

$$\psi_j = \psi_X \pm \psi_Y \tag{1.2}$$

Generally, the reinforcement of the two electrons of the molecular wave function results in bonding molecular orbitals, while the repulsive force of the electrons wave function results in antibonding molecular orbitals. The superposition of the two atomic orbitals split into bonding (σ) and antibonding (σ_*) orbitals are shown in **Figure 1.2**.

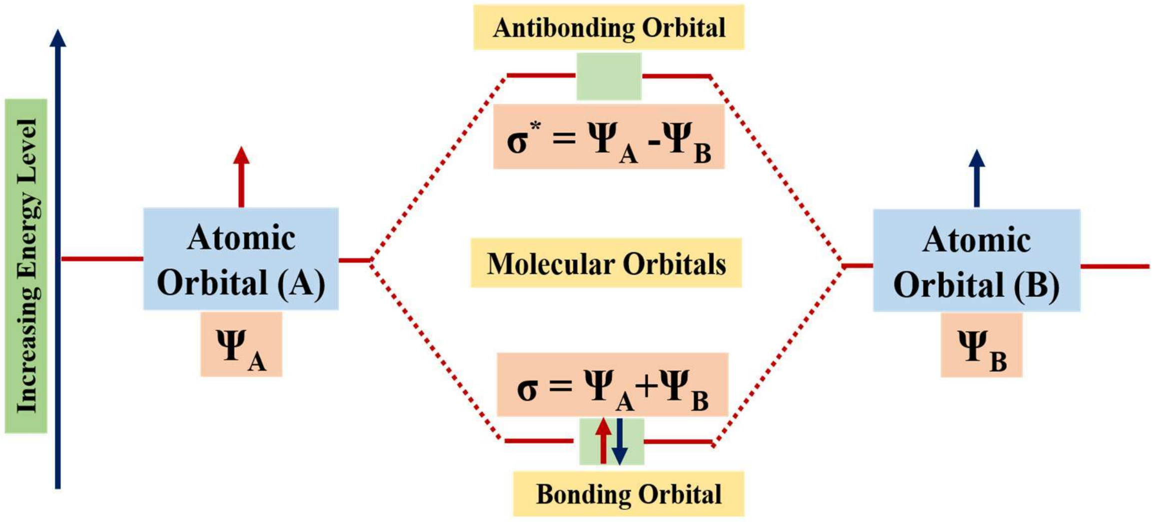


Figure 1.2 Bonding and antibonding formation in the diatomic hydrogen atom.

The molecular bonding and antibonding orbitals are given by the addition and substation of the wave function as –

$$\sigma = \psi_X + \psi_Y \tag{1.3}$$

$$\sigma_* = \psi_X - \psi_Y \tag{1.4}$$

Further, the molecular orbitals can be further classified into two categories: (1)- sigma bond and (2) pie bond. The sigma and pie bond formation is demonstrated in **Figure 1.3(a)** by overlapping the two 'p' orbitals. The symmetrical overlapping results in bonding and vice versa. The antibonding molecular orbitals pass with higher energy levels due to the repulsive nature of the wave function. The concept of bonding and antibonding of the molecular orbitals are important aspects of defining the band gap of the organic semiconductors. Excitation of carriers occurs in an organic semiconductor from the bonding to the anti-bonding orbital of the conjugated electron system. The antibonding π*-orbital shows the LUMO bonding, while the π-orbital shows the HOMO of an organic semiconducting molecule. The band gap of organic semiconductors is typically determined by the energy difference between the HOMO and LUMO energy levels, as illustrated in **Figure 1.3(b)**.

In this thesis, we are primarily interested in organic polymer semiconductors due to their low-temperature processibility and conjugative 'π' bond [30]. The formation of the conjugated polymers is due to the hybridization of the 'C' atoms and results in the delocalization of the 'π' bonded electron over the neighboring C atoms. The low mobility of the organic semiconductors is due to the localization of the active carriers. The basic bonding and antibonding phenomenon in organic semiconductors and the band gap of the organic semiconductor have been illustrated below [31].

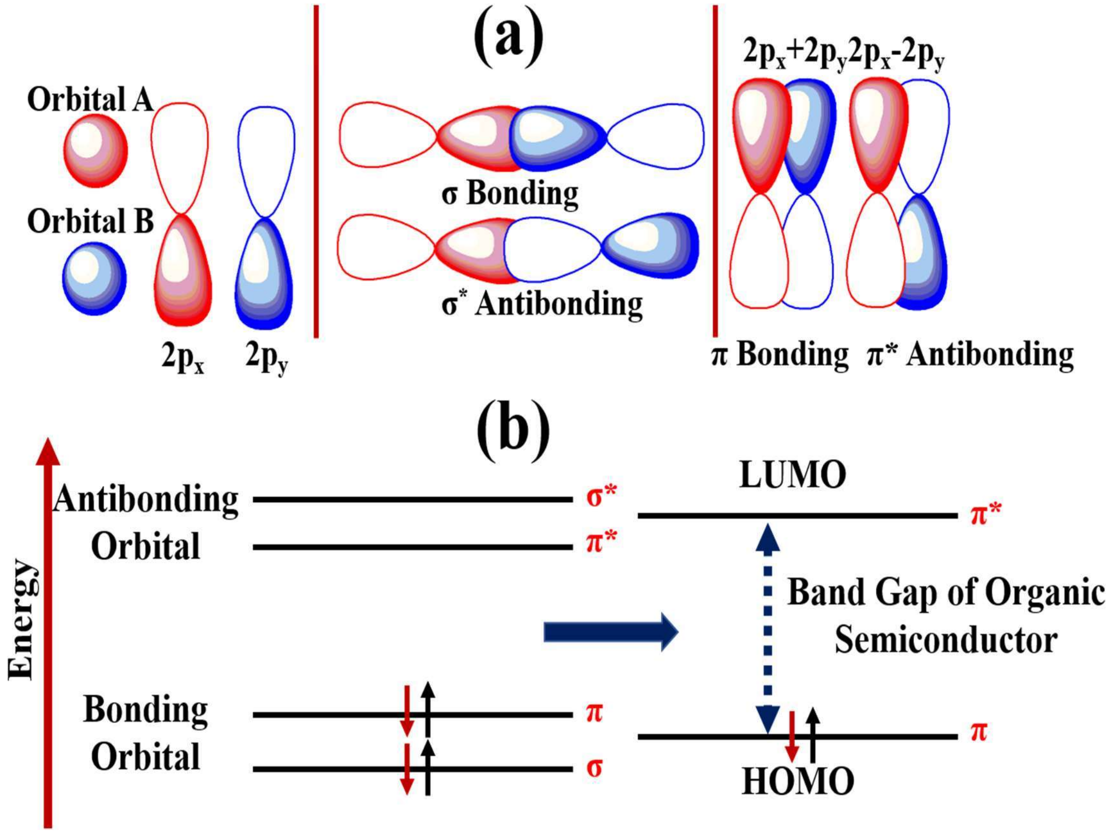


Figure 1.3 (a) Interaction of molecular orbitals and formation of sigma and pie bond, (b) The energy levels of a π- π conjugated molecule and representation of bandgap of an organic semiconductor.

1.3.2. Advantages of Organic Semiconductors

A qualitative investigation has been carried out in this section to explore the advantages and disadvantages of organic semiconductors over inorganic semiconductors. The important parameters to inspect the quality of the organic semiconductors are tabulated in **Table 1.3.** Organic semiconductors have various advantages in terms of low-temperature processing, low cost, and flexible film, but they suffer from low mobility and poor stability compared to inorganic semiconductors [32][33]. **Table 1.3** illustrates the comparison between organic semiconductors and inorganic semiconductors over various parameters [34].

Table 1.3 Comparison between Organic and Inorganic semiconductors

Comparison table of Organic/Inorganic semiconductors		
Parameters	**Organic semiconductors**	**Inorganic semiconductors**
Processing Temp.	Low Temperature	Mostly High Temperature
Flexibility	Flexible	Inflexible
Stability	Less Stable	Highly Stable
Mobility	Low Mobility	High Mobility
Transparency	Less Transparent	Highly Transparent
Differences in terms of various Electrical parameters		
Exciton	Frankel	Wannier
Charge Transport	Hoping	Band to Band
Carrier Mobility	~1 cm^2/V. sec.	~1000 cm^2/V. sec.
Charge Carriers	Localized	Delocalized
Binding Energy	(Weak) Van der Waals	(Strong) Covalent
Polarization	Strong	Weak

1.3.3. Organic Thin Film Deposition Methods

This section will cover the different techniques for the growth of the thin film over the various substrates. The primary advantage of choosing the organic semiconductor P3HT in our work is that it offers the ability to work with a range of substrates, including flexible ones, due to its low-temperature processibility. Additionally, the P3HT polymer film is highly sensitive to gases such as ammonia, making it suitable for sensing applications. Here, we can use various substrates, such as PEN, PET, Silicon, etc., for device fabrication with organic semiconductors. **Figure 1.4** shows the various thin film deposition methods used to fabricate thin film semiconducting devices [35].

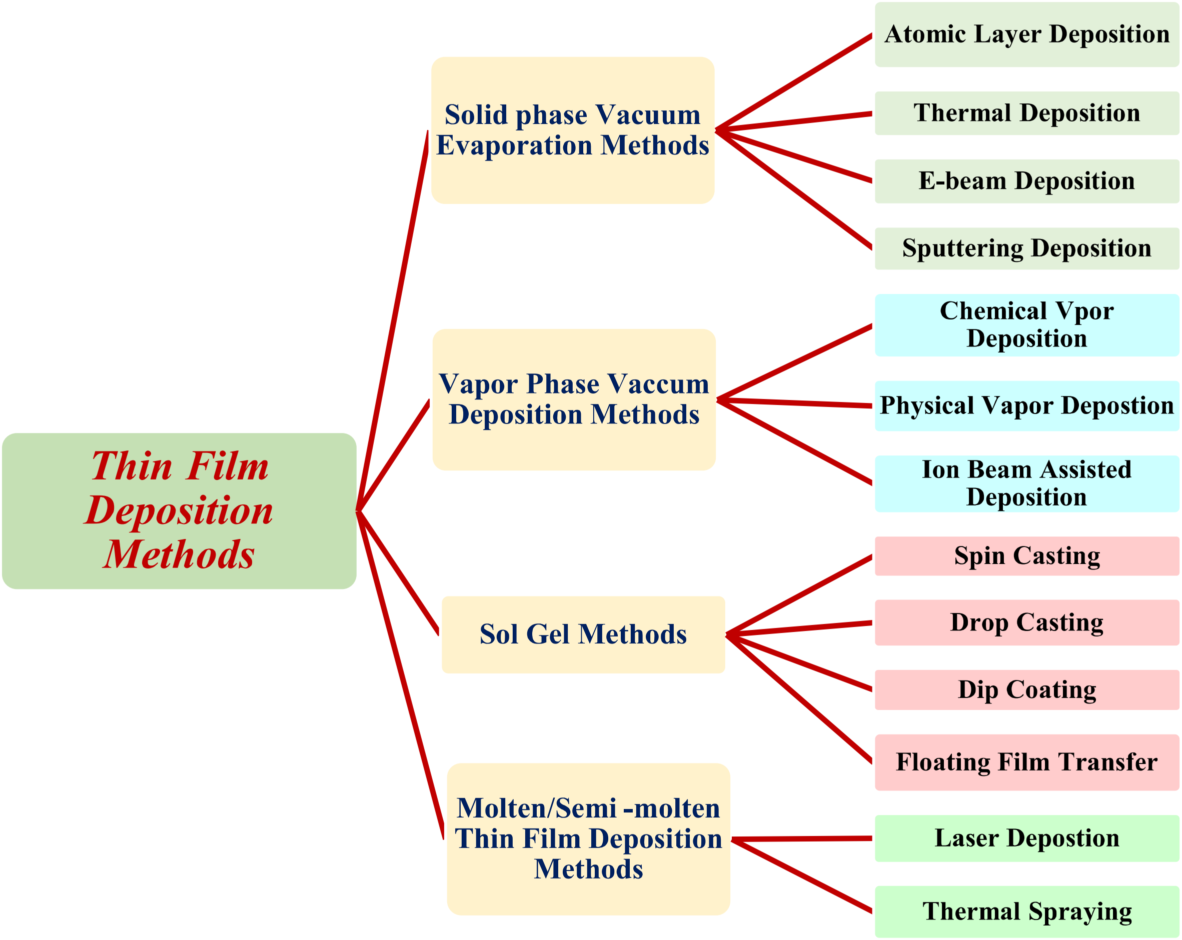


Figure 1.4 Classification of thin film deposition methods.

Polymeric semiconductors are generally preferred for sol-gel deposition methods due to their excellent solubility, low cost, and minimal wastage compared to other deposition methods. We have used the FTM (Floating Film Transfer) method in all work for semiconductor film deposition. The advantage of the FTM technique over other deposition methods is that it is a low-cost, solution-processed method with minimal material wastage. A brief idea about the FTM method is demonstrated below-

Floating Film Transfer (FTM) Method

The FTM is a self-assembled growth technique for polymer film at an air-liquid interface, proved itself as an advantageous technique in terms of easy fabrication steps, minimal wastage, and large-scale production over any kind of substrate [15]. The FTM techniques precisely control the polymer chain ordering, crystalline behavior, and thickness of the self-oriented film over the substrate. Primarily this technique has been optimized for the thiophene family polymers (P3HT, PBTTT, PQT12). These thiophene derivatives go for self-assembly while minimizing steric hindrance during thin film formation due to the regioregular grafting of an alkyl side chain. Many factors, including the solubility of polymers in nonpolar solvent, the surface free energy of the solvent, relative thermal conductivity, relative viscosity, temperature gradient, density fluctuation, spreading coefficient, and evaporation flux, affect the growth of polymer crystals in floating film on a liquid subphase/substrate. First, we focus on the surface energy for the growth of pristine P3HT polymer over the liquid substrate of Ethylene glycol and Glycerol with a 1:1 ratio. A basic schematic is shown in **Figure 1.5**.

According to Marangoni flow, a solvent with a low surface energy would spontaneously spread over a solvent with a greater surface energy. This flow theory has been utilized here for the self-assembly/oriented growth of P3HT conductive polymer over the liquid substrate (Ethelene Glycol: Glycerol= 1:1 ratio). At the interface of the surrounding materials, the surface pressure gradient is produced by the dropping of a low surface energy solvent (P3HT in chloroform solution in our work) over a high surface energy solvent, and this surface pressure gradient causes low surface energy solvent to spread spontaneously in the direction of the severely stressed surface as shown in **Figure 1.5 (a)**.

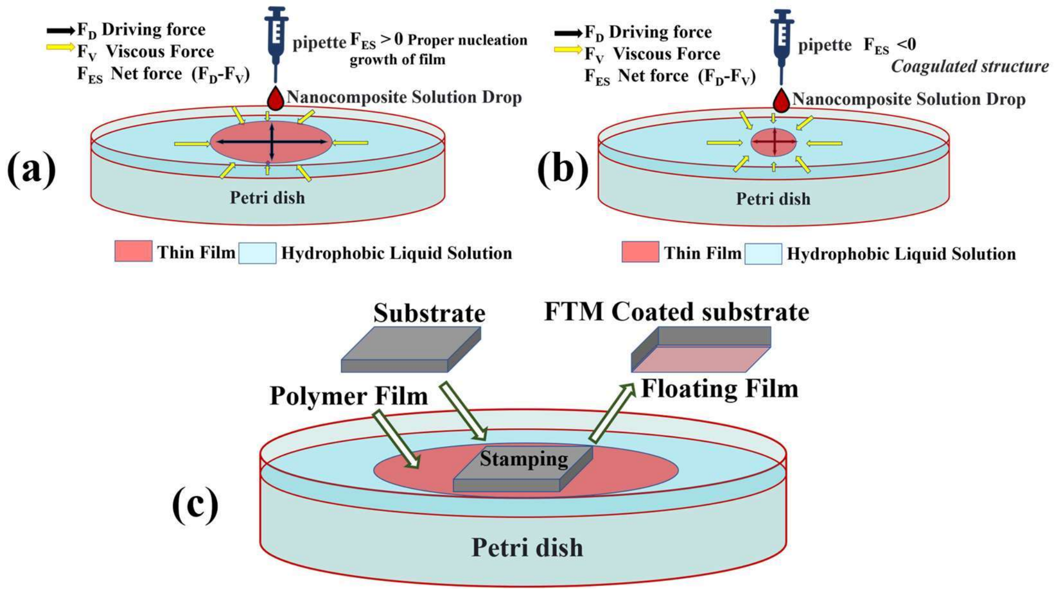


Figure 1.5 Floating film transfer methods, (a) Nucleation growth of the polymer thin film (suitable for film deposition), (b) Coagulated thin film (not suitable for film deposition), (c) Thin film transfer over the hydrophobic substrate.

Here the two forces are working on the spontaneous growth of the thin film- (1) Driving force and (2) Viscous force. The driving force is responsible for the nucleation growth of the film over the liquid subphase (with high surface energy), and the viscous force works against the driving force for spontaneous spreading. The spreading equation governed by the equation F_{ES} (Effective Spreading Force) = FD (Driving force) – FV (Viscous force) for the nucleation growth of the film, and the spreading coefficient to the thin film can be given as-

$$\gamma = \gamma_1 - \gamma_2 - \gamma_{12} \tag{1.5}$$

γ_1 – Surface tension of the liquid substrate effective towards outside

γ_2 – Surface tension of the thiophene solution in chloroform effective towards inside

γ_{12} – Signifies the surface tension developed at the interface boundaries of the liquids

Only through ultrafast evaporation and simultaneous solidification of the polymeric solution, it is possible to produce an air-processable, self-assembled, large-area thin film over the liquid substrate. For the spreading of the polymer solution over the liquid hydrophobic substrate, the driving force should be greater than the viscous force. In other words, F_{ES} should be greater than '0' ($F_{ES}>0$). If the driving force is less than the viscous force, the nucleation spreading of the polymer solution is not possible, or spreading forms a coagulated/drop structure shown in **Figure 1.5 (b)**. Optimizing the concentration of the polymeric solution and concentration of the liquid subphase/substrate allows to fabricate a compact, large area, high-quality self-assembled polymer thin film. The thin film over the liquid hydrophobic subphase/substrate can easily be lifted over any kind of hydrophobic substrate shown in **Figure 1.5 (c)**. The complete processes of the film spreading and film lifting over the hydrophobic substrate are shown in **Figure 1.5**.

1.4 Gate Dielectrics in TFTs

1.4.1. Classification of Gate Dielectrics

The gate oxide dielectrics are classified in **Figure 1.6**. The various types of dielectrics have their own advantages and disadvantages. **Table 1.4** demonstrate the properties of the different class of dielectric materials. Here in the thesis, we have focused on inorganic dielectrics (high-k and high band gap) and hybrid dielectrics (high-k, high band gap, flexible nature) for the fabrication of low-voltage TFTs.

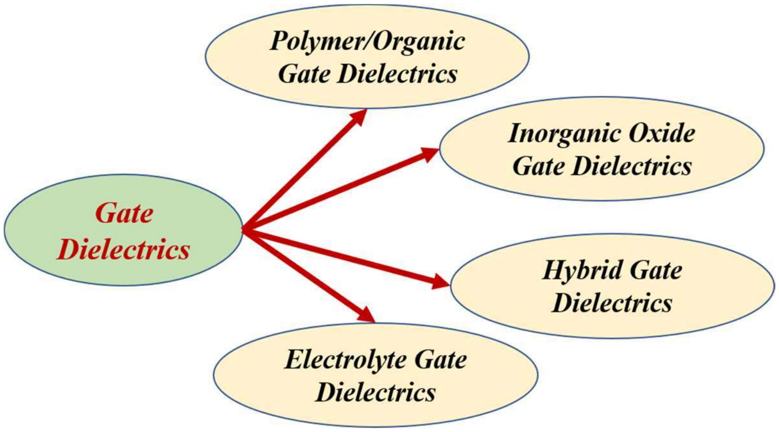


Figure 1.6 Classification of gate dielectric materials.

Table 1.4 Difference between various types of Dielectric Materials

Gate Dielectrics	Properties
Inorganic Oxide Gate Dielectrics	❖ Usually belong to the IIA, IIIA, IIIB, IVB, and VB group Metal Oxides. ❖ High dielectric constant. ❖ Generally, it requires a high temperature for synthesis. ❖ Inorganic Oxides are brittle in nature. ❖ High dielectric strength. ❖ Mechanical inflexibility/Brittle in nature.
Organic/Polymer Gate Dielectrics	❖ Low dielectric constant. ❖ Low-temperature solution processibility. ❖ Mechanical flexibility. ❖ Smoother surface.
Hybrid Gate Dielectrics	❖ Usually consists of polymer/inorganic blend materials. ❖ High dielectric constant with mechanical flexibility. ❖ High surface smoothness.
Electrolyte Gate Dielectrics	❖ Consists of ion gels, ionic liquids, polyelectrolytes, and polymer electrolytes.

Reference-[36]

1.4.2. Selection Criteria of the Gate Dielectrics

A proper selection of the Gate dielectric material plays a vital role in the performance of the OTFT. A suitable dielectric material must follow the following parameters for satisfactory low-voltage operation of TFTs [37]–[39].

- ❖ It's dielectric constant (k) should be in the range of 10 - 30 and have a large free Gibbs energy (0 to -50 kJ/mol favorable).
- ❖ The dielectric/oxide materials must be a good insulator (Band Gap $E_g > 5$ eV.), and there will be a sufficient band offset between Si (Silicon) and dielectric interface ($E_{offset} > 1$ eV.) (for deposition over Silicon substrate).
- ❖ Good interface quality between oxide semiconductor interface, low trap charge density, and a smooth dielectric film ($\sigma_{rms} < 1$ nm favorable).

Over the last few decades, conventional SiO_2 has proven to be the best choice for a dielectric gate material, as it offers advantages such as low surface roughness, a defect-free oxide film, high thermal strength, high band gap, etc. [40]. The defect-free SiO_2 films possess with low carrier scattering, which improves the mobility of the charge carrier and enhances the drain current of the TFT devices. Although conventional SiO_2 has proven itself as a good choice for gate dielectric material, due to the miniaturization of the devices or technology shrinks in the semiconductor industries. For that, it is necessary to shrink down the dielectric gate thickness and operating voltage of the transistors. The problem associated with the conventional SiO_2 is that it became very leaky in sub-10 nm thickness, and its dielectric constant is very low ($k = 3.9$). With the advancement in the semiconductor industries, when the dielectric thickness is scaling down, the areal capacitance increases (favorable for low voltage operated TFTs), but the dielectric leakage current also increases. So, there is always a trade-off between the thin film transistors' areal capacitance and leakage current [41][42].

These problems/trade-offs can be suppressed by utilizing suitable high-k dielectric materials. The high-k dielectric materials maintain their areal capacitance even at high dielectric thickness due to their high dielectric constant (k), but there is an inverse relationship between the band gap and the ‘k’ value of the dielectric materials [36]. So, it is necessary to find a suitable dielectric material with a high-k value (>10) and a large band gap (>5 eV.). In the thesis (chapters 3, 4, and 5), we have reported a high-k inorganic dielectric thin film of a suitable band gap, high-k value, and improved surface roughness. The relation between the inorganic dielectric constant (k) and the band gap is plotted in **Figure 1.7**. **Figure 1.7** clearly illustrates that there is an inverse relationship between the band gap and dielectric constant in the inorganic dielectric materials.

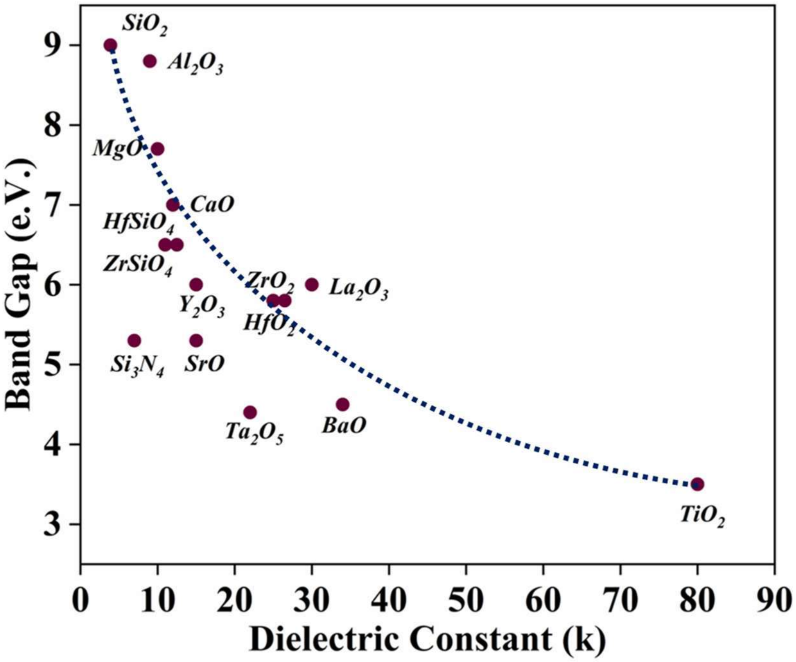
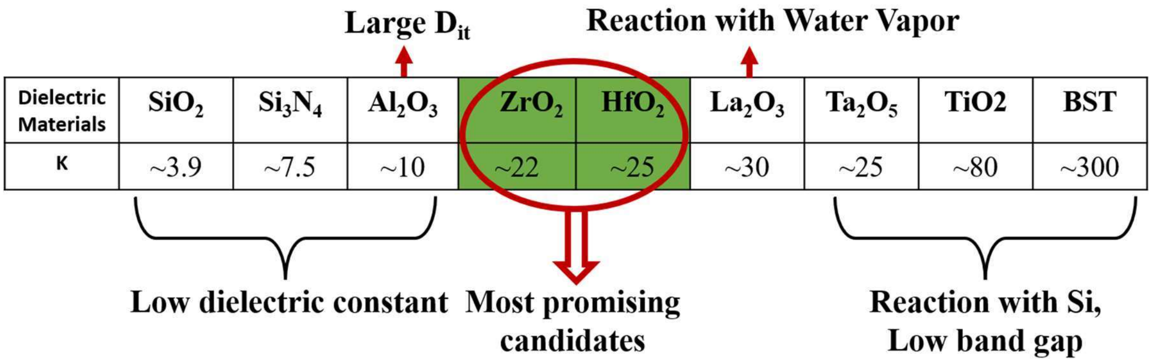


Figure 1.7 Band gap vs. dielectric constant of common gate dielectric materials.

Figure 1.7 shows that the dielectric ZrO_2, HfO_2, and La_2O_3 are the best choice for gate dielectric materials. But the problem with the La_2O_3 is that it suffers from a strong reaction with water vapor/moisture, which deteriorates the device's performance in terms of relative stability as it is highly sensitive to a humid environment. Thus, we can say that the ZrO_2 and HfO_2 are the best choices for gate dielectric materials with a high-k value of ~25 (in pristine form) (**Figure 1.8**).



Dielectric Materials	SiO_2	Si_3N_4	Al_2O_3	ZrO_2	HfO_2	La_2O_3	Ta_2O_5	TiO2	BST
K	~3.9	~7.5	~10	~22	~25	~30	~25	~80	~300

Figure 1.8 Selection of promising candidates for the gate oxide/dielectric film in TFTs.

1.4.3. Deposition Methods of Inorganic Oxide Dielectrics in TFT Fabrication

Currently, gas phase and processible solution methods have been widely used for the deposition of inorganic dielectric film. Gas phase deposition methods (ALD, PLD, and CVD) are time-consuming and costly but give superior quality dielectric film over solution processible deposition methods (spray coating, dip coating, spin coating). In our work, we have utilized thermal oxidation and low-cost spin coating methods for the development of the gate oxide film. The gate dielectric film thickness in the solution-processed method has been optimized by rotation speed, spin time, and concentration of the dielectric solution in the fabrication process.

1.4.4. Challenges and Trade-offs in Inorganic Oxide Dielectric Deposition

Although the inorganic dielectrics pass with high-k, high stability, and areal capacitance, there are various challenges associated with high-quality oxide film growth. Some of the challenges are given below-

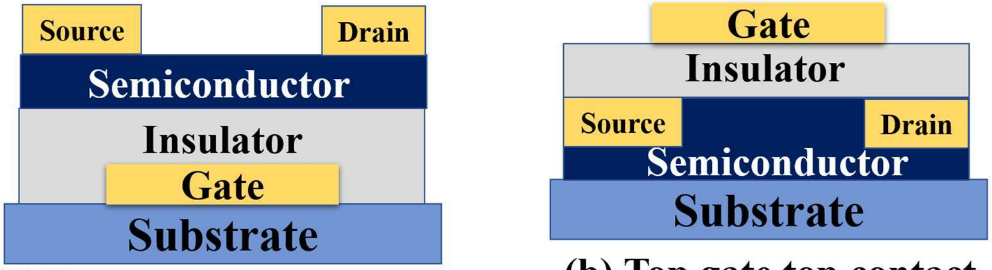
- In general, inorganic dielectric fabrication steps involve a high-temperature annealing process. The high-temperature processing makes them unsuitable for flexible electronics. By some optimized techniques, depositing a low-temperature processed oxide film such as UV cured (cost-efficient, requires no special arrangements) and various vacuum deposition methods (costly and requires deposition setups) is possible.
- The dielectric/organic semiconductor interface properties must be treated with any self-assembled monolayer (SAM) material to enhance the grain quality of organic semiconductors.
- The surface roughness plays a vital role in OTFT's performance. A good dielectric

film must be smoother for reliable and high-performance OTFTs. The inorganic dielectric generally passes with poor surface roughness compared to polymer dielectrics. So, it is necessary to optimize the material properties and fabrication process to get a dielectric/oxide film with low RMS surface roughness.

- The dielectric materials with high surface roughness suffer from high carrier scattering, reducing the transistor's effective field effect mobility.
- The trap charge density and dangling bonds in the inorganic dielectric films are high. So, it is necessary to minimize/optimize the necessary processing steps and surface treatment to encounter these problems.

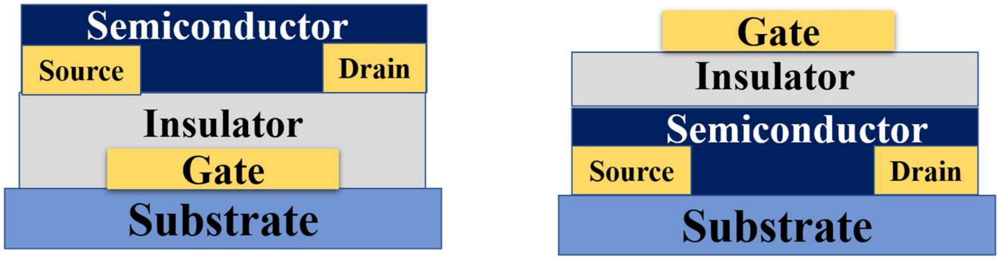
1.5 Schematic and Charge Transport Mechanism in TFTs

The basic architecture of TFTs consists of a gate, source, drain terminals, active semiconductor, and dielectric layer. These terminals and layers can be arranged in a certain pattern to fabricate different architectures of the TFTs. Each architecture has its own advantages and disadvantages [36][43]. The different architecture of TFTs is shown in **Figure. 1.9**. The three terminals of the TFTs are clearly shown in the various architectures **(a, b, c, d)**. When the gate electrode is located below the insulating layer or dielectric layer, these architectures are called bottom gate architectures (**Figure. 1.9(a)** and **Figure. 1.9(c)**). On the other hand, architectures, where the gate electrode is deposited on top of the insulator or dielectric layer, are referred to as top gate architectures (**Figure. 1.9(b)** and **Figure. 1.9(d)**). Similarly, architectures, where the source and drain are defined at the top of the semiconductor layer, are called top contact architectures (**Figure. 1.9(a)** and **Figure. 1.9(b)**). Conversely, when the source and drain are deposited below the semiconductor layer, these architectures are referred to as bottom contact (**Figure. 1.9(c)** and **Figure. 1.9(d)**).



(a) Bottom gate top contact

(b) Top gate top contact



(c) Bottom gate bottom contact

(d) Top gate bottom contact

Figure. 1.9 Different architectures of organic thin film transistors.

The bottom gate top contact (BGTC) architecture is the most popular because of its easy fabrication process and low contact resistance, making it widely used for TFTs fabrication [44].

It has been noticed that the architecture of the TFTs is a very important factor in maintaining its performance. **Table 1.5** compares the properties of different architectures in detail.

Table 1.5 Advantages and Disadvantages of Different TFT Architectures

Device Architecture	Advantages	Disadvantages
Top Gate	❖ The gate electrode and source/drain electrode can be deposited on top of the device by printing processes or any other deposition techniques with high printing resolution. ❖ A gate insulator and a gate electrode on top of the active layer can provide an encapsulation effect against any environmental effect, which increases the stability of the device.	❖ The top gate structure is difficult to fabricate. ❖ The surfaces of source/drain electrodes in a top gate bottom contact device may influence the film morphology. ❖ Required to develop a compatible mask for the Organic semiconductor layer.

	❖ In top-gate TFTs, high-quality active layer films can be deposited on top of flat substrates, so the morphology of the active layer film is independent of the surface of the dielectric material.	
Bottom Gate	❖ The bottom gate structure is simpler in fabrication. ❖ Thermal annealing of the dielectric layer over the gate does not damage the Organic Semiconductor layer.	❖ Requires a proper passivation layer for the Organic semiconductor channel to enhance the stability and lifetime of the OTFT.
Top Contact	❖ The top contact structure offers lower contact resistance due to the large injection area for charge carriers in the channel.	❖ Complex fabrication process and a chance of contact penetration in the deposited film.
Bottom Contact	❖ Suitable for low-cost, flexible electronic applications.	❖ High metal contact resistance. ❖ The presence of a barrier increases the subthreshold swing and lowers the field effect mobility.

References- [45]–[49]

A typical TFT output characteristic can be explained by a charge carrier injection mechanism, which is given below [50]. A TFT (Thin-Film Transistor) has a gate, source, drain, and active (channel) layer. In the present thesis, the active layer consists of a gas-sensitive material for sensing applications. The source and drain terminal of the TFTs are used for charge carrier injection, and these charge carriers move through the channel in the parallel direction of the gate dielectric layer. The charge injection mechanism can be illustrated by alignment in the work function of metal contact and HOMO/LUMO energy level [50]–[53], as shown in **Figure 1.10**. The corresponding highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the semiconductor relative to the fermi level of the source and drain contacts are shown in **Figure 1.10**. The charge carriers' injection depends upon the injection barrier (difference between work function (φ) and HOMO level for the p-type channel, the difference between work function (φ) and LUMO level for n-type channel) [51] offers at the metal/semiconductor interface. If the gate bias is zero and a small source to drain voltage is applied, the conduction process does not occur due to no mobile charge carriers present in the semiconductive channel.

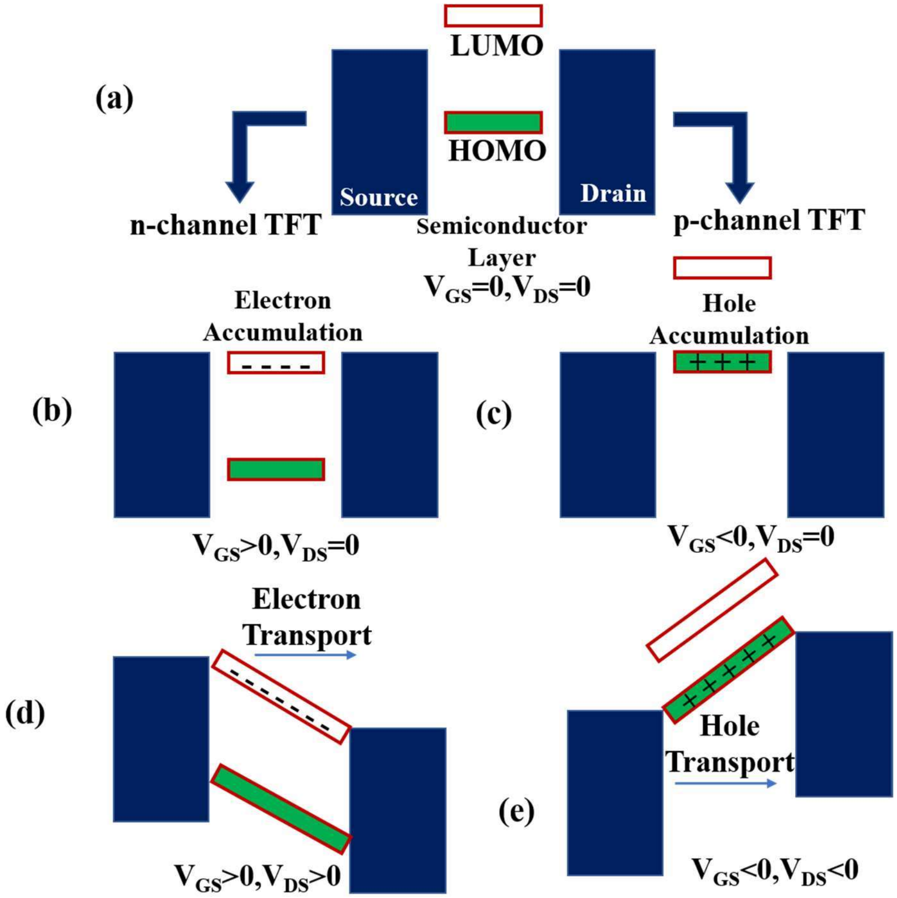


Figure 1.10 Thin film transistor operation on the application of electric field, (a) Ideal energy level diagram of TFT at $V_{GS}=0$, $V_{DS}=0$ (b) Electron accumulation at $V_{GS}>0$, $V_{DS}=0$, (c) Hole accumulation at $V_{GS}<0$, $V_{DS}=0$ (d) Electron transport at $V_{GS}>0$, $V_{DS}>0$, (e) Hole transport at $V_{GS}<0$, $V_{DS}<0$.

Let us consider an n-type TFT; a large electric field can be developed at the interface when a specific positive gate bias has been applied with drain voltage $V_{DS} = 0$ and $V_{DS} > 0$. The applied voltage offers a large electric field, causing a shifting of LUMO and HOMO levels down with respect to the Fermi level of metal contact (as its potential is externally controlled), which reduces the potential barrier for charge carrier injection. With a sufficiently large electric field at the gate, carriers can flow from the contact to the LUMO. In addition to this, a sufficient drain-to-source voltage will cause current to flow from the source to the drain [51], [54]–[56], as shown in **Figure 1.10**. The vice-versa mechanism has been followed in the case of p-channel organic TFTs. The energy level diagram for p-channel TFT and n-channel TFT is illustrated in **Figure 1.10**.

The output characteristics of bottom gate top contact TFTs are shown in **Figure 1.11**. The three respective **Figures**, **Figure 1.11(a)**, **Figure 1.11(b)**, and **Figure 1.11(c),** show the linear region, pinch-off region, and saturation region of the transistor. In the case of n channel TFT, when a positive gate voltage ($V_{GS}>0$) is applied at the gate/insulator interface, an equal amount of opposite charge induces near the semiconductor/insulator interface. With no source to drain voltage applied, the charge density will be uniform across the channel. It is illustrated in **Figure 1.11(a)**. With an applied positive potential at the drain terminal with respect to the source, the induced charge will no longer be uniform; rather, it is a function of 'x' (along the channel), as shown in **Figure 1.11(b)**. The induced charge at a distance 'x' from the source terminal can be given by-[50][57]

$$q_{ind}(x) = n(x)et = C_{ox}\big(V_{GS} - V_{TH} - V(x)\big) \tag{1.6}$$

Where 'n(x)' represents the density of charges in the channel (q/cm^3), 'e' is electron charge (1.6×10^{-19} coulomb), 't' is the thickness of the charged layer, 'C_{ox}' represents the capacitance of dielectric layer, V_{GS} shows the gate to source voltage and 'V_{TH}' is the threshold voltage of the TFT, respectively.

The average value of the induced charge density can be given by -

$$q_{ind}(x) = n(x)et = C_{ox}\left(V_{GS} - V_{TH} - \frac{V_{DS}}{2}\right) \tag{1.7}$$

'$q_{ind}(x)$' is the induced areal charge density at the center of the channel, and V_{DS} represents drain to source potential, respectively.

To the right of the center, the charge density will be lower, and on the left side, the charge density will be higher. From Ohm's law of conductivity-

$$J = \sigma E$$

$$\frac{I_{DS}}{tW} = \sigma \frac{V_{DS}}{L} \Rightarrow I_{DS} = \frac{W}{L}\left(n_{ind(Avg)}et\right)\mu V_{DS} \tag{1.8}$$

Where 'σ' represents carrier conductivity, 'W' and 'L' are the width and length of the channel, 'μ' shows the carrier mobility, and '$n_{ind(Avg)}$' is the average carrier concentration in the channel, respectively.

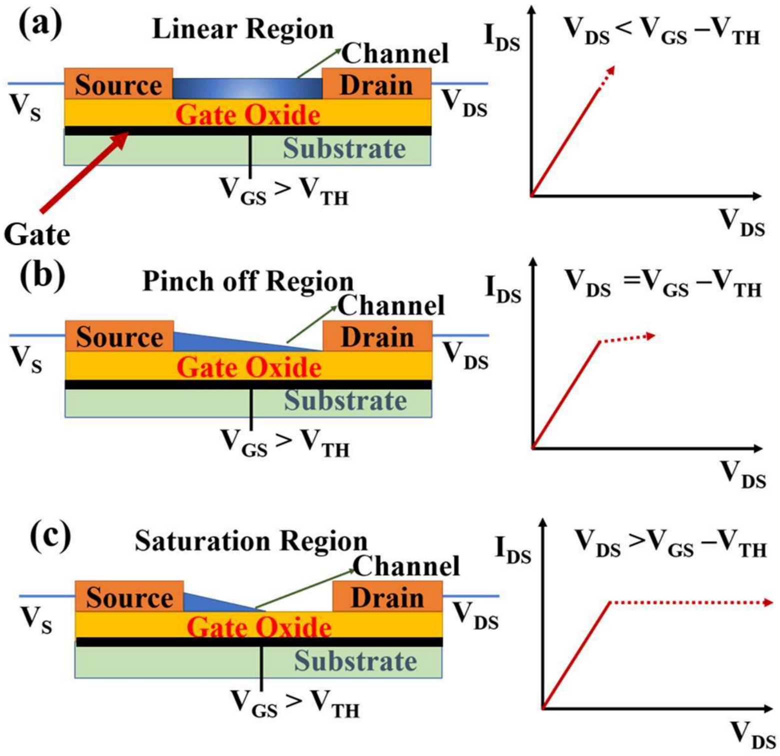


Figure 1.11 I_{DS}-V_{DS} (Drain characteristics) of n-channel TFT (a) Linear Region (b) Channel pinch-off region (c) Saturation region.

The drain current (I_{DS}) of a TFT in the linear regime can be given by [50][58][59]

$$I_{DS} = \frac{W}{L} C_{ox}\mu\left(V_{GS} - V_{TH} - \frac{V_{DS}}{2}\right)V_{DS};\ |V_{DS}| < |V_{GS} - V_{TH}| \tag{1.9}$$

And the drain current in the saturation regime can be given by [58]

$$I_{DS} = \frac{W}{2L} \mu\, C_{ox}(V_{GS} - V_{TH})^2; \quad |V_{DS}| > |V_{GS} - V_{TH}| \tag{1.10}$$

The above equations show that TFT works as a voltage-controlled current source. The vice-versa mechanism has been followed in the case of p-channel organic TFTs.

1.6 OTFTs Applications

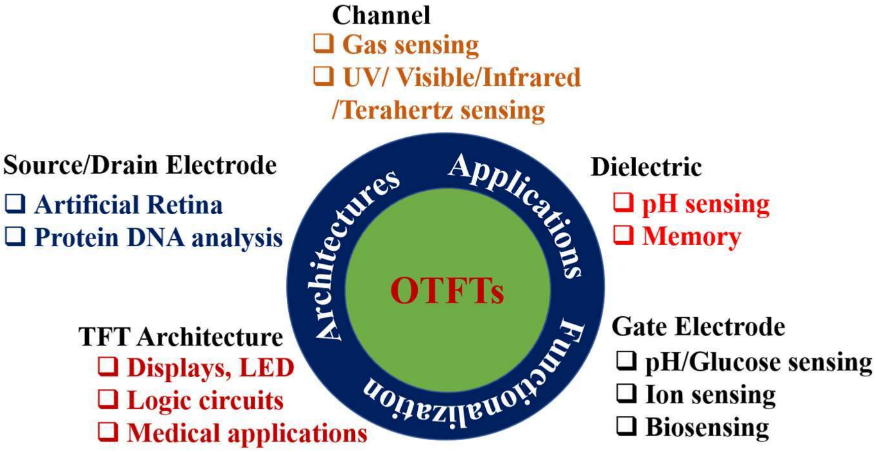


Figure 1.12 Applications of OTFTs.

Over the last few decades, the scientific community has shown considerable interest in solution-processed TFTs because of their potential applications in sensors, displays, numerous electronic circuits, etc. [60]–[64]. The flexible, low-temperature processing, large area coverage and cost -efficient properties of the organic semiconductors made them viable choice for broad area flexible electronic and sensing applications. Organic TFTs are well-suited for smart cards, flexible displays, and storage applications due to their flexibility, low power consumption, and cost-effectiveness. Smart cards with organic TFTs can be used for secure identification, access control, contactless payment, and other data storage and processing in real-life applications. The flexibility and low power consumption of organic TFTs make them ideal for wearable electronics, such as smartwatches, fitness trackers, or electronic textiles, and they also can be used in various healthcare monitoring applications such as glucose detection [60]–[64]. OTFT offers multi-parameter characteristics to characterize the device's performance in various real-time applications in terms of mobility, threshold voltage, sub-threshold swing, etc. [65][66]. The simple structure of the OTFTs, small size device, and uniformity over a large surface make it useful for large-area applications at a lower processing cost. Based on some crucial key parameters, some frequent applications of the TFTs are given in **Figure 1.12**.

1.6.1. Introduction to Gas Sensing Applications

In the past few decades, with the rapid growth of the automobile, chemical, fertilizer industries, etc., efficient miniaturized, cost-efficient electronic gas sensors have become essential to detect toxic analytes and prevent fatal accidents and causalities [16]. Electronic gas sensors have diverse applications, particularly in indoor/outdoor air quality monitoring, medical diagnosis, food quality analysis, and chemical industries. So, the detection of these odorful, odorless, flammable, toxic, and corrosive gases needs highly reliable, non-invasive sophisticated, cost-efficient sensors in current days [16][67]. Gas sensors also have a wide range of applications at manufacturing sites, laboratories, aircraft, and in household applications.

Simply, a sensor is a device that detects a change in the physical/chemical properties of the sensing material and produces a sensing response. The response can change one or more properties of sensing materials, such as mass, electrical conductivity, capacitance, etc. A sensor has three primary components (**Figure 1.13**) [68]:

- Detection unit,
- Transducer,
- Processing unit.

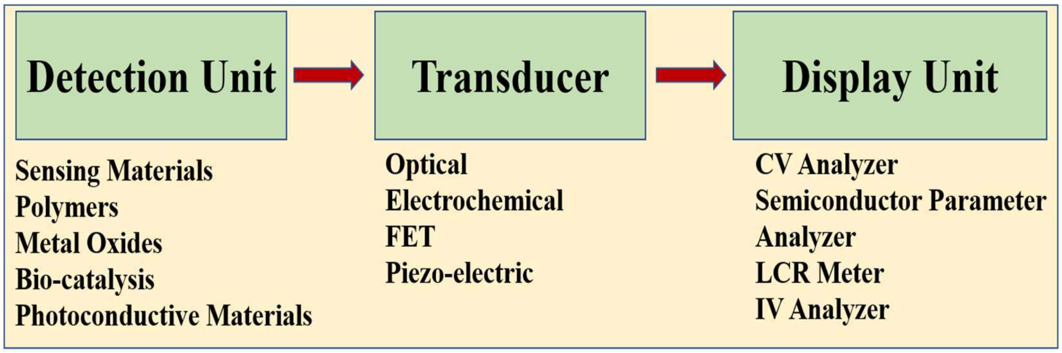


Figure 1.13 Schematic of basic sensing mechanism.

The sensor's detection unit, referred to here as the sensing materials, is the component that interacts with the gas analyte and responds to changes in its chemical/physical properties. The interaction may be chemical, as in the case of doping an organic semiconductor, or physical, as in the case of photo-excitation. The transducer unit converts/changes the detecting unit into measurable signals, often electrical signals. The display unit (third unit) is the supporting hardware and software required to transform the transducer signal into an output that can be analyzed in the form of electrical data over the display/screen unit. In short, the gas sensing devices generally use the concentration of the gas analytes, respond to changes in the physical/chemical properties of the sensing material, and transduce into a compatible signal for the display unit. A specific/selective sensor has versatile applications like: ammonia sensors for fish freshness [69], the fertilizer industry, CO_2 in vehicular environmental pollution, LPG detectors for domestic gas pipelines, etc. In addition to that, the gas sensors also have a vital role in medical diagnoses, such as the presence of acetone concentration in uremia and liver cirrhosis can be used to diagnose diseases such as diabetes and lung cancer, presence of ammonia concentration can be used to diagnose renal failure [70], presence of hydrogen sulfide concentration in breath analysis can diagnose periodontal disease [71], etc.

The broad application of the sensing devices motivates us to develop a sophisticated, cost-efficient, non-invasive ammonia gas sensor for various industrial and commercial applications. The beauty of the gas sensors is that the output can be analyzed easily, recorded for further analysis, and supported by low-end electronic applications. Several gas sensors operating according to various principles and transduction mechanisms have been identified in sensing applications. These sensors can be classified as follows-

(a) Classification of the Gas sensors

The most used gas sensors can be divided into two major categories. The first is based on the electrical verification of sensing materials, and the second is based on other kinds of verification (non-electrical based) of sensing materials. Further, the electrical verification of the sensing materials can be classified as Metal Oxide (MO)-based sensors, Chemiresistive based gas sensors, and FET gas sensors. And other, based on non-electrical verification of sensing materials, can be classified as Optical Gas sensors, Electrochemical sensors, and Acoustic wave sensors [72][73] (**Figure 1.14**).

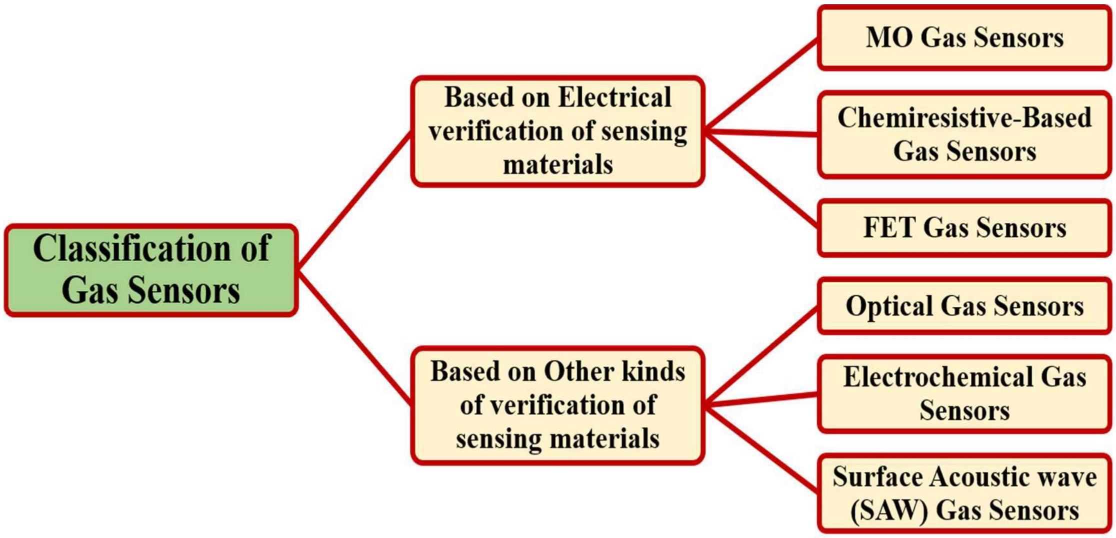


Figure 1.14 Classification of gas sensors.

Various types of sensors have their own advantages/disadvantages, elaborated in **Table 1.6**.

Table 1.6 Sensor Types and their Advantages and Disadvantages

Sensor Type	Sensing Materials	Operating Temp.	Advantages	Disadvantages	Ref.
MO Gas Sensors	n,p-type metal oxides*	Micro-heater (240-400 °C)	Low cost, Simple fabrication, morphology control	High operating temp., bulky size, high power consumption	[73]
Chemiresistive based Gas Sensors	Polymers **	RT	RT operation, simplicity, rapid response, Low LOD	Costly, less stable, less time span	[74]
FET based Gas Sensors	Active materials (usually polymer/ metal oxides with low band gap)	RT/Micro heater (25-112 °C)	Low power dissipation, portability, compact size compatible with CMOS, low LOD, rapid response	Sensitive to ambient conditions.	[75]
Optical Gas Sensors	Gas-sensitive materials $^{\Delta}$	RT	Detecting flammable gases, low LOD, low drift	High-cost, bulky, precise light source	[76]
Electrochemical Gas Sensors	Electrolytes $^{\Delta\Delta}$	- RT	Low energy linear output, high resolution, selectivity, and repeatability	Low response time, cross response issues i.e., humidity, high drift	[77]
SAW Gas Sensors	Metal oxide/ piezoelectric materials/ polymers	RT	Excellent response time and sensitivity, low cost, small size	Complicated electronic circuits, Require transducers	[78]

**- n, p-type semiconductors- (n-type ZnO, TiO_2, MgO, CaO, etc.) (p-type PdO, NiO, TeO_2, etc.)*

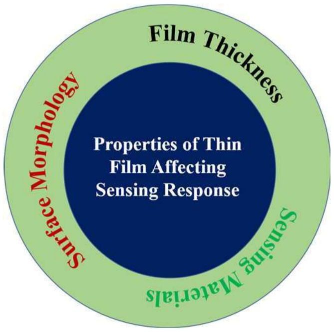
***- Polymer- Polyaniline, Polypyrrole, Polythiophene, PBTTT, P3HT, DNTT, etc.*

Δ - Thin nanofilms or nanostructures fabricated onto the waveguide

ΔΔ – Usually solid or liquid electrolytes.

(b) Properties of the Thin Film Affecting Gas Sensing Response

Thin films used for enhanced sensing response towards ammonia gas typically possess specific properties and characteristics that make them suitable for the sensing purpose. The properties of the thin film are very crucial for high-performing device as well as in sensing applications. The thin film properties can be tuned for enhance performance by the surface morphology, film thickness and sensing materials for the gas sensing [16][18][19]. Here are some key features as follows -



Surface Morphology

Surface area: Thin films are fabricated to have a large surface area relative to their volume. This provides suitable condition for interaction between the gas molecules and the film, increasing the chances of gas adsorption and detection and thereby enhances sensing response.

Porosity: Thin films can be engineered to have a porous structure with interconnected voids or pores. This enhances gas diffusion and promotes the interaction of gas molecules into the film, leading to improved sensing capabilities.

Film Thickness

The thickness of the thin film should be optimized to enhance the sensing response. It should be thin enough to allow rapid gas diffusion and interaction with the sensing material yet thick enough to provide sufficient coverage and sensitivity.

Sensing Material

The thin film is typically composed of a sensing material that undergoes a measurable change in its electrical, optical, or physical properties upon exposure to target gas. This material may be a metal oxide, a conducting polymer, or a composite material designed to exhibit a high sensitivity and selectivity towards the target analyte.

1.6.2. Motivation of the Thesis on Ammonia Sensors

In the past decades, the necessity to fabricate a novel gas sensor with high performance and excellent sensing characteristics, employed in diverse applications such as in industries, medical applications, air quality control, etc. [79]–[82]. Ammonia (NH_3) proved to be one of the most reactive, toxic, colorless, pungent-smelling soluble alkaline gas [83][84], which can affect the environment and is dangerous for all living/non-living organisms. In general, a low concentration (low ppm) of ammonia exposure over a long time can cause permanent blindness, throat infection, serious illness, eye irritation, and other lung diseases [85]–[87]. The emission of ammonia not only affects human and animal health but also affects semi-natural systems. The excess amount of nitrogen emission from the reaction of ammonia and oxygen can cause eutrophication and acidification of water bodies, which leads to some harmful effects such as: low BOD levels, species composition changes, etc. [88]–[92]. Currently, NH_3 has been considered among highly processed toxic inorganic chemicals (processed approx. over 200 million tons per year), emanating from both natural and artificial sources. Some of the artificial sources are the decomposition process of manure, agriculture, and the fertilizer industry. Recently, it was estimated that about 90% of ammonia gas had been produced solely from livestock waste and agricultural activities. The rest of the ammonia gas is produced from industrial coolants, refrigeration, pharmaceutical industries, etc. [93][94]. Ideally, the concentration of this toxic analyte ammonia should be maintained within a certain limit (<5 ppb) for an excellent atmospheric environment [95][96]. The maximum permissible limit for a safe level of this gas in the environment, in accordance to OSHA (occupational safety and health administration), is less than 35 ppm as a 15 minutes' Time Weighted Average (TWA) [86]. In accordance with NIOSH (National Institute for Occupational Safety and Health), the small duration exposure limit of ammonia is not permitted to exceed over 35 ppm during any 15 minutes in a whole working day and 50 ppm during any 5 minutes in a day. A concentration above the safe level can cause life-threatening illnesses such as throat infection, skin irritation, eye irritation, and other lung diseases [97]. Also, NH_3 can be one of the prominent pollutant gases due to its corrosive, toxic, and explosive nature. So, the accurate measurement of NH_3 in the environment is necessary to avoid fatal accidents and other life-threatening illnesses caused due to overexposure to ammonia gas [98].

This thesis broadly explores and motivates the fabrication and characterization of thin film transistors for ammonia detection to prevent fatal accidents and causalities at various emission sites. The thesis also includes an advancement in the device fabrication process to fabricate low voltage, cost-efficient, low power TFTs for ammonia sensors on rigid silicon as well as on flexible ITO PET substrate. Moreover, the thesis chapters thoroughly investigate the sensing results and sensing mechanism behind conductive polymer/conductive polymer nanocomposite-based organic TFTs for ammonia sensing at room temperature.

Emission Sources of Ammonia

The major artificial sources of ammonia emission in the environment are (a) agriculture fertilizer, (2) livestock management, (3) fossil fuel combustion, (4) refrigeration, and industrial coolants. On the other hand, natural sources of ammonia emission are caused by the breakdown of organic waste matters, animal and human waste, nitrogen fixation processes, gas exchange with the atmosphere, forest fires, etc. Nowadays, most of the ammonia emission is mainly due to anthropic activities. Among all, livestock waste and agriculture fertilizers are the primary sources of ammonia (NH_3) emission. Ammonia is the main constituent of Nitrogen fertilizer production as it can be used directly in fertilizer or manufacturing of urea or ammonium nitrate [99][100]. According to the National Emissions Inventory, US EPA, 61% of the total ammonia is emitted by livestock management, and 31% of the total ammonia is emitted by fertilizer application (**Figure 1.15**). The other main source of ammonia emission is due to NOx emission from fossil fuel combustion [101]. However, Nitrogen oxide emission can be controlled with the help of post-combustion control methods, which include SCR (selective catalytic reduction) and SNCR (selective non-catalytic reduction). In these processes, excess urea or NH_3 can be used to control nitrogen oxide emissions [101]. Ammonia nitrification, denitrification, leaching, volatilization, runoff, etc., are several mechanisms through which inorganic ammonia is emitted [97][102]. Various sources which can emit ammonia analyte are illustrated in **Figure 1.15**.

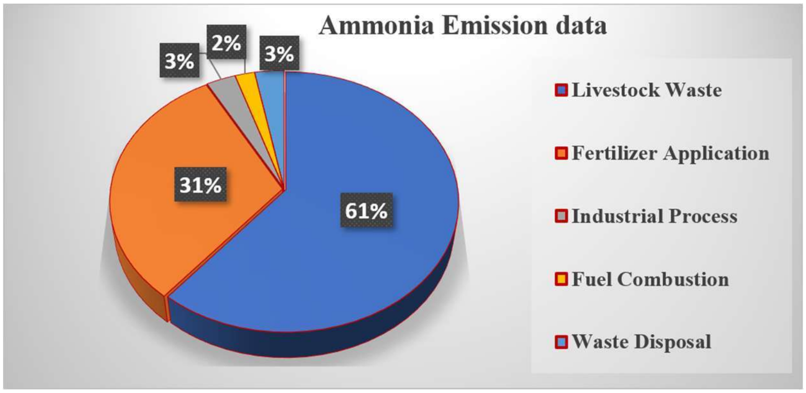


Figure 1.15 Ammonia emission data.

1.7 Resources utilized in Device fabrication and Sensing characterization

The equipment/tools in the device fabrication process, film characterization process, and electrical/sensing measurement setup are illustrated in **Figure 1.16**.

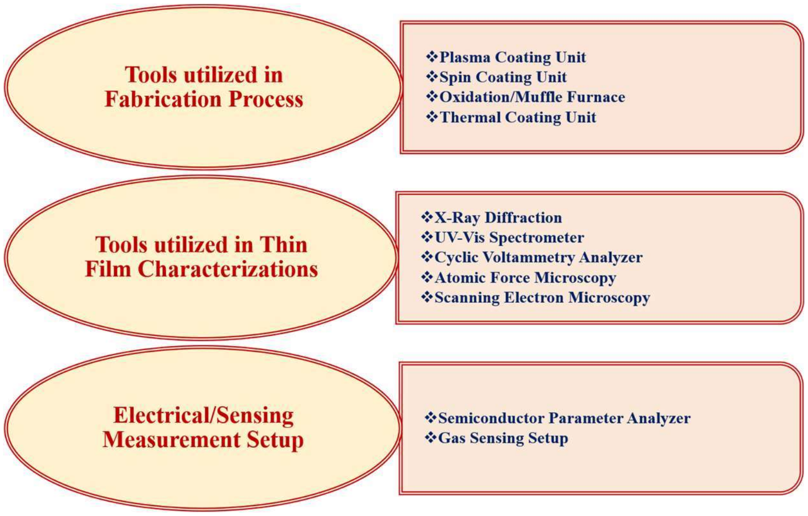


Figure 1.16 Resources utilized in OTFT fabrication and characterization.

1.8 Outlines of the Thesis

The thesis aims to extensive study of organic thin film transistors (OTFTs) fabrication and characterization for ammonia sensing applications. This study has attempted to resolve the fabrication complexity using a simple, cost-efficient, minimal-wastage floating film transfer method (FTM) to fabricate organic TFTs. With the advancement in the fabrication technologies and techniques to fabricate low voltage operated devices on a silicon substrate or low voltage transparent devices on a flexible substrate, this thesis also includes the fabrication optimization associated with device fabrication methodologies on silicon/flexible substrate and utilizes their application in ammonia sensing.

The thesis is divided into six chapters to cover the extensive investigation of the fabrication and film/sensing characterization topics during my Ph.D. program. The thesis covers the introduction section, the fundamental mechanism of organic semiconductors, the operation of the TFT devices, fabrication facilities utilized in the OTFT fabrication, and fabricated OTFTs for ammonia sensing application. The thesis chapters are organized as follows-

Chapter 1. The introduction of various topics including the thesis abstract and the evolution of TFTs have been explained in this chapter. The topics covered are as follows.

- *Thesis Abstract*
- *Introduction on TFTs*
    - *Organic Semiconductors and their Deposition Methods*
    - *Gate Dielectrics and their Deposition Method and Complexities*
- *Schematic and Charge Transport Mechanism in TFTs*
- *Broad Area Application of OTFTs*
- *Resources utilized in OTFT Fabrication and Characterization*
- *Outlines of the Thesis*

Chapter 2: explores the importance of organic polymers for the fabrication of organic TFTs, which has unique properties for ammonia sensing. This chapter has investigated an organic polymer nanocomposite P3HT/MoS_2-based organic thin-film transistor (OTFT) with the following research highlights.

- *Device Fabrication Steps*
- *Thin Film Characterization*
- *Electrical and Sensing Parameters*
- *Device Results and Sensing Mechanism*
- *Conclusion*

Chapter 3: explores the importance and application of low-voltage operated organic TFT for ammonia sensing application. In this chapter, an organic polymer P3HT-based solution-processed, cost-efficient, low voltage operated organic thin-film Transistor (OTFT) has been investigated with the following research highlights.

- *Device Fabrication Steps*
- *Thin Film Characterization*
- *Electrical and Sensing Parameters*

- *Device Results and Sensing Mechanism*
- *Conclusion*

Chapter 4: explores the importance of bilayer high-k dielectric for low-voltage operated organic TFTs for ammonia sensing application. The chapter elucidates the investigation on a metal nanoparticle-doped P3HT layer, which has been utilized to enhance ammonia sensing at room temperature. In this chapter, an organic polymer nanocomposite Au-doped P3HT-based organic thin film transistor (OTFT) has been investigated with the following research highlights.

- *Device Fabrication Steps*
- *Thin Film Characterization*
- *Electrical and Sensing Parameters*
- *Device Results and Sensing Mechanism*
- *Conclusion*

Chapter 5: explores the fabrication and characterization of a hybrid (polymer-inorganic composite) dielectric-based flexible organic thin film transistor for ammonia sensing application. The chapter includes a synthesis of flexible high-k hybrid dielectric-based gate oxide and polymer/2D nanocomposite-based organic semiconductor channel for enhanced ammonia sensing application. The essential research highlights of the chapter are as follows-

- *Device Fabrication Steps*
- *Thin Film Characterization*
- *Electrical and Sensing Parameters*
- *Device Results and Sensing Mechanism*
- *Conclusion*

Chapter 6: concludes the summary and future scope of the research work presented in the previous chapters.