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Introduction

Today we live in a fast-growing electronic world, where computers are acting as the backbone for our efficient and comfortable work experience. On average, today a working person is surrounded by more than 1000 processors. This all started with the invention of the transistor in 1948 by John Bardeen, William Shockley and Walter Brattain at Bell Labs and since then the semiconductor industry is growing expeditiously. In the year 1965, Gordon Moore predicted that the number of transistors will double in an integrated circuit every two years [Moore,1998]. With the need for miniaturization of chips, the statement became the roadmap to the growing semiconductor industries and the number of transistors on chips has tremendously increased over time, where the count was ~ 8000 in 1974 which is now 39.54 billion transistors in a commercially available microprocessor. The technology node has immense advancement where it was ~8000 nm process in 1974 and which has reached to 7 nm in 2019.

Silicon electronics has solved many challenges related to our increased electronics use, but there are limitations to what silicon electronics can do. There is a need for alternative electronics that can be used for large-area flexible electronics without using costly fabrication tools and can be processed at low temperatures so that the application area can be broadened. In addition, the methodologies and resources use in silicon electronics manufacturing concerns the negative environmental impact and there is a need for technology that can reduce the electronic waste at the end of the life span of the devices. Considering the need, organic electronics seems to be the best possible alternative to conventional silicon technology in terms of solving the problems discussed above. The use of organic materials will provide a platform for the electronic world to be more environmentally friendly and reducing production costs. In this chapter, the salient feature of organic electronics and its importance in today's electronics world is discussed.

1.1 ORGANIC ELECTRONICS

In the last few decades' electronics based on the electroactive organic compounds have gained a lot of attention and are termed as organic electronics. The special electronics uses organic materials and their properties for the world of electronics in a way that was unimaginable until now with the silicon technology. The ability to tailor the electrical, optical and mechanical properties of the electroactive organic materials has broadened the application area to a wide range.

The capability to process at low temperature with simple solution processing techniques makes the production of organic-based electronic devices feasible even in the resource-limited regions of the world where necessary infrastructure is unavailable. The organic devices are not comparable to the conventional silicon technology when high electrical performance and stability of the devices are of prime importance. However, in the applications where the nominal electrical performance with low-temperature processing and low production cost is required organic electronics is dominating and the best replacement to conventional silicon technology and has the potential to change the way how our society interacts with electronics.

1.1.1 Evolution of Organic Electronics

Up to the mid of the 20th century the semiconducting properties, metallic conductivity, superconductors were the domain of inorganic science and solid-state inorganic science only and organic materials were considered only as insulators with a wide range of application in the insulating and packaging industry. Inspiring from the discovery of the transistor there were initial reports on the organic semiconductor with decent dim conductivity in the 1950s [Akamatu et al.,1954, Gutmam and Lyons,1967]. Later in 1963 McNeill and coworkers reported high electrical conductivity in polypyrrole [McNeill et al.,1963]. The blue light emission from anthracene single crystal was reported by pope and coworkers in the same year [Pope et al.,1963]. The materials used in their studies have shown semiconducting behavior but with very low performance and at that time they were considered to have a low potential for future applications.

In 1964, articles published by William Little on the possibility of excitonic superconductivity gave inspiration to the researches in the field and the organic electronics thus advances with various findings from semiconductors to metals to superconductors [Little,1964, Little,1965]. In 1977, the finding on the variable electrical conductivity of the conjugated polymer polyacetylene played a huge role in revolutionizing organic electronics [Chiang et al.,1977]. In the year 2000, for the discovery of conductive polymers, the Chemistry Nobel Committee awarded A. J. Heeger, A. G. MacDiarmid and H. Shirakawa Nobel prize in chemistry [Chiang et al.,1977, Shirakawa et al.,1977]. The electroactive organic materials thus developed have been used in various potential applications and devices. The high performance electroluminescent organic vacuum evaporated dye films [Tang and VanSlyke,1987, Tang et al.,1989], organic field-effect transistors with polythiophene [Koezuka et al.,1987, Tsumura et al.,1988] and small conjugate oligomers were demonstrated in the late 1980s [Garnier et al.,1990]. The first conjugated polymer-based light-emitting diode (PLED) was demonstrated by Burroughes and coworkers in 1990 [Burroughes et al.,1990]. Apart from organic light-emitting diodes, organic field-effect transistors (OFETs)[Mannsfeld et al.,2010, Meager et al.,2014] and circuits based on OFETs [Di et al.,2013, Khim et al.,2013, Li et al.,2018], solar cells [Liu et al.,2016, Chen et al.,2017], photodiodes [Lamprecht et al.,2005, Ng et al.,2008, Rauch et al.,2009], and lasers[Gaal et al.,2003] with organic materials have been widely explored and the technology has been developed a lot. These findings were the stepping stones towards the development of organic electronics to the commercial level. Today using organic electronic devices in the commercially available product is no more a dream, rather the industry has already left its footprints in the organic electronic device industry with cellphones using organic light-emitting displays is one of its examples.

Printed electronics, flexible large-area electronics, polymer electronics, plastics electronics, etc. are some of the names today use for organic electronics. The technology is using a combination of low-cost materials, printing technology, and large-area processing capabilities with environmentally friendly processes to open up new fields of application. Radiofrequency identification (RFID) tags, flat panel display drivers, solar cells, smart packaging, printable batteries, foldable displays, flexible sensors, printable circuits are examples of the advancement of the organic electronics technology till date [Tang,1986, Dodabalapur et al.,1998, Sirringhaus et al.,1998, Sekitani et al.,2009, Mannsfeld et al.,2010, Myny et al.,2010, Wu et al.,2014, Liu et al.,2016, Zang et al.,2016]. The technological achievements in the field in such a short span shows the interest of the research community in this fast-growing field and its development. The success and growth of particular technology can be said by its revenue generated in the real world. The organic electronics market is expected to reach USD 87.21 billion by 2024 and the organic displays are the largest revenue-generating segment of the technology with 65-75 % of the total market revenue. The main devices where the organic light-emitting displays used are TVs, tablets, cell phones, etc. The graph of revenue generation and demand for organic electronics based devices are continuously growing. An example of which is shown in Figure 1.1, where the market captured by printed electronics components and the future estimation of the 3D printed electronics is shown. Such a high demand for the commercial market shows why the researchers around the world are putting continuous efforts in the development of this technology. The foldable organic light-emitting diodes and printable light-emitting diodes are capturing huge attention and are on a verge of commercial growth. The organic electronics technology has traveled a long way and there is huge scope for the industry to grow with an immense number of products to come in the future and is thus called the futuristic technology.

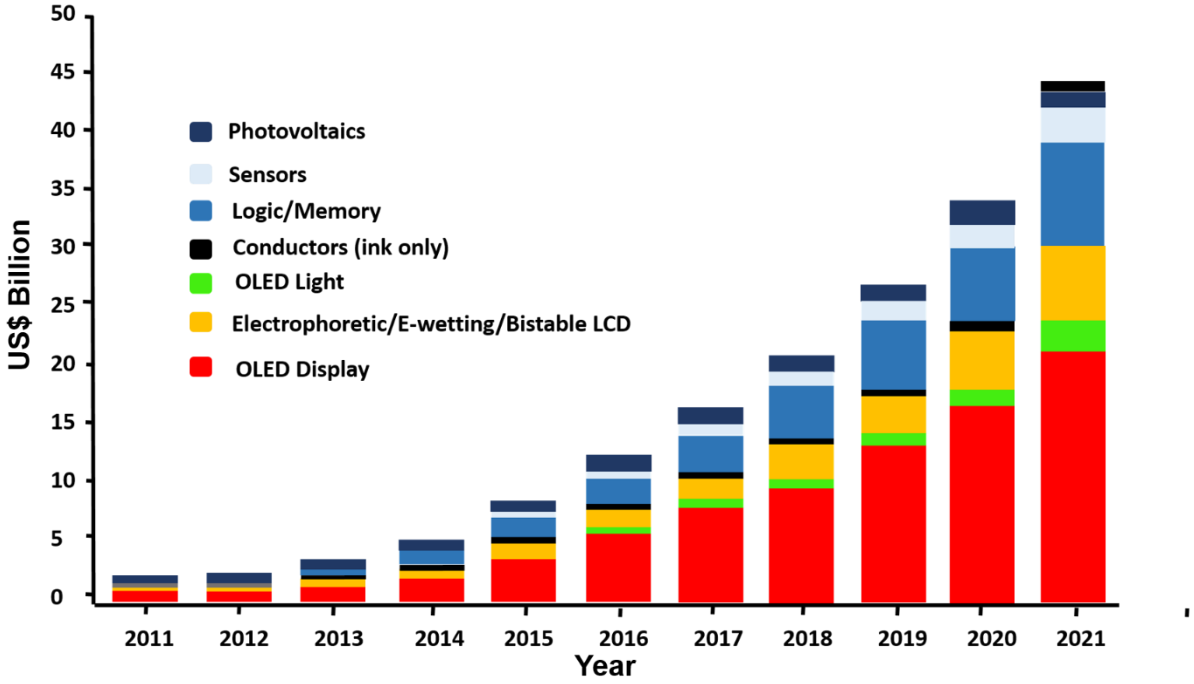

Figure 1.1 : Graph showing continuous growth in the printed electronics market and expected demand in the future (Source: IDTechEx Market research).

1.1.2 Advantages

Organic electronics also termed as large-area electronics, which is growing at such a fast pace in the field and seems to be a good replacement to conventional silicon technology. Despite having relatively low electrical performance, the growing technology has a lot of scope in the market and is competing with the conventional technology market because of its unique electronic device properties that are impossible to achieve through the silicon technology. Some of the major advantages of the technology are listed below:

(a) Solution Processability

The major advantage of organic electronics technology is the solution processability of most of the organic materials. The organic semiconductors can also be processed through a high vacuum deposition system like sputtering, thermal evaporation systems, organic molecular beam deposition, and organic physical vapor deposition. But utilizing such a sophisticated instrument does not fulfill the core motive of the organic electronics that is producing electronic devices at low cost. Solution processability allows the organic semiconductors to convert in the form of inks by dissolving in various solvents and the obtained inks can easily be patterned in various ways with the use of printers to obtained various circuits. Imagine plotting a drawing of a particular circuit on software and developing it using a printer. Such easy processing of semiconductors is a major factor in obtaining high throughput, easily processed electronic devices. The solution casting of organic material can be done in numerous ways like spin coating, dip coating, blade coating, spray coating, and screen printing etc.

(b) Low-Temperature Processing

Organic electronics is also termed as printed and foldable electronics. Thus the technology mainly focuses on substrates like plastics, paper, cloth, etc. The glass transition temperature of most of these flexible substrates is < 150 °C. This means processing over 150 °C, the substrate loses its integrity. The processing temperature for most of the organic electronic devices fabrication is < 100 °C, which makes these substrates compatible with this futuristic technology and the temperature processing requirements are much lesser compared to the single-crystalline Si (>800 °C), polycrystalline Si (~ 600 °C) and the hydrogenated amorphous Si (~300 °C). The organic materials thus can be processed from room temperature to 100 °C and do not require complex processing equipment.

(c) Flexibility and Roll to Roll Processing

The soft nature of the organic semiconductors allows them to be processed on bendable and foldable plastic and other flexible substrates. The mechanical flexibility itself highly broadens the application area of organic electronics. The flexibility properties are used to make electronic skin with tactile sensing properties that can be used in robotics and other applications where flexible touch sensors are required that were impossible to be built by existing silicon technology. The soft nature of these carbon-based materials makes them compatible with various curved and movable surfaces. The flexible nature also favors the production of organic devices through the roll to roll processing, where the fabrication is almost similar to printing a newspaper with high speed. The roll to roll processing cuts down the processing cost to a large extent and allows the bulk production at a faster rate. The organic devices fabricated on a flexible PET substrate and the roll to roll processing is shown in Figure 1.2.

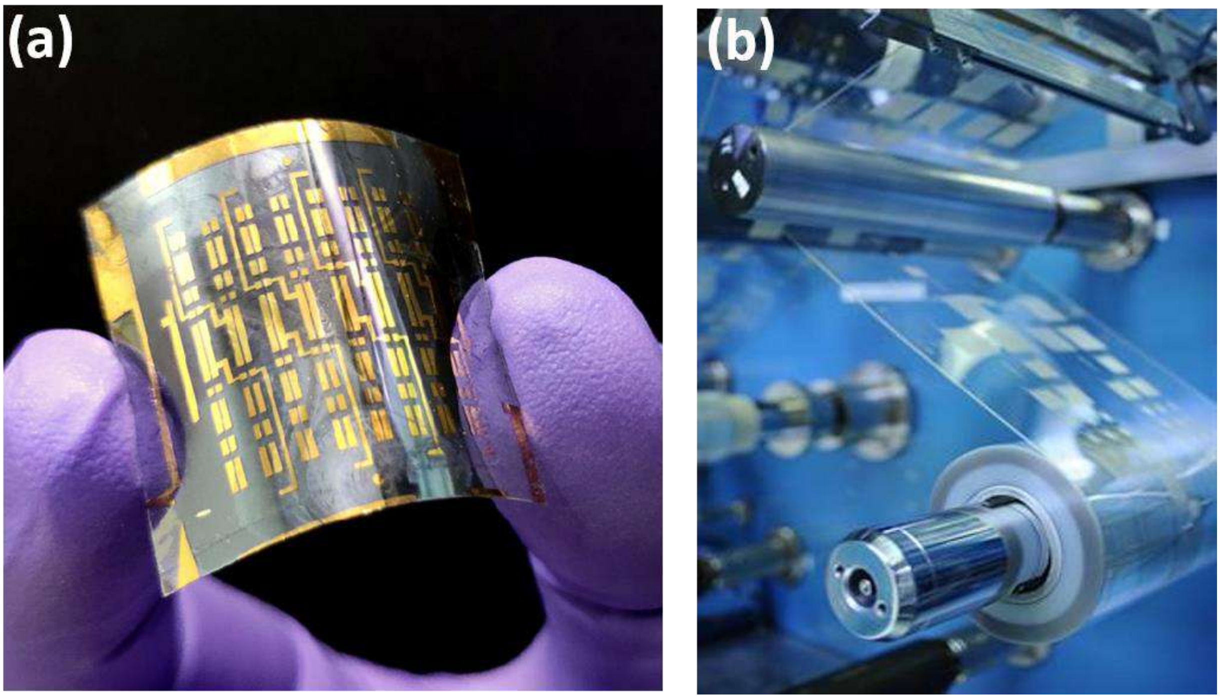

Figure 1.2 : (a) Digital image of the fabricated organic electronics devices on flexible Polyethylene Terephthalate (PET) substrate demonstrating the mechanical flexibility of organic electronics. (b) Roll to roll processing use in fabricating organic electronic devices (Source: vttresearch.com).

(d) Low Manufacturing Cost

Technology is said to be successful not only by its nature of producing products with ease but also by the development of products that are accessible to the common population and are affordable in their budget. Organic electronics not only change the way how people look at the technology but also promises to reach the sector of the population that cannot afford basic facilities by producing products at a much cheaper cost. This technology does not necessarily require a cleanroom with sophisticated instruments. In addition, it requires simple processing techniques like spin coating, drop-casting, printing, etc. that reduce the budget requirement. Also, the materials used in the process are nowadays available in bulk, which further reduces the manufacturing cost. This low-cost processing allows the manufacturing of the organic electronic devices even in resource-limited regions of the world. Around 1.2 billion people in the world don't have access to electricity and they rely on batteries or kerosene. The development of organic electronics is fruitful in such areas. One of the examples of such low-cost technological advancement is the indigo program run by Elight19 a UK based company that works on the organic solar cell. In the program, the company has provided solar power energy to rural areas with organic printed solar cells. The program was named as pay-as-you-go which eliminates the high initial cost of solar power systems. The consumers have to pay in the week by week system until they own the system and the cost per week was less than their cost that was put on kerosene for a week and also environmentally friendly than kerosene. Once the total product cost is paid the usage was free of cost. The advantages of low-cost productivity and various other advantages discussed above are the motivation of the researchers to carry out research in this futuristic technology.

1.1.3 Applications

The soft nature of organic electronics made it possible to be processed at a variety of substrates that have the benefit of mechanical flexibility. This core advantage broadens the application area of the technology and changes the perspective of the world to this growing technology. Some of the major applications are organic light-emitting diodes (OLEDs), flexible displays, thin-film transistors, Radiofrequency Identification tags (RFIDs), intelligent packaging, energy-efficient lightning, organic memory devices, etc. Figure 1.3 shows some of the available products of organic electronics that are developed on flexible platforms.

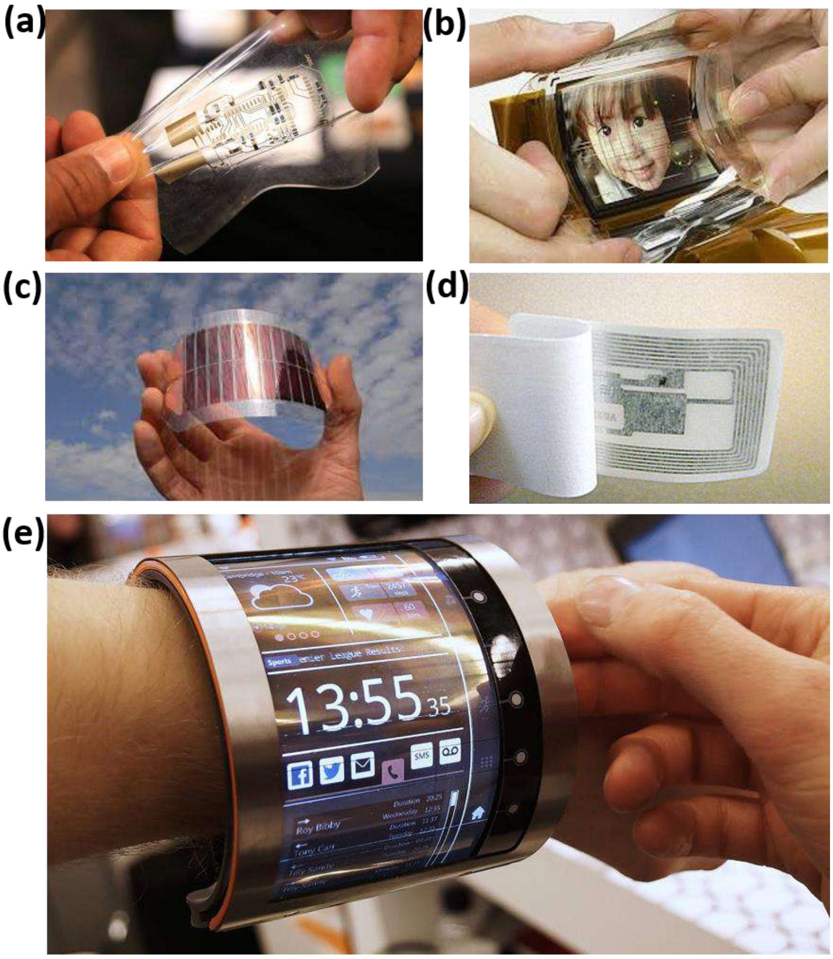

Figure 1.3 : Applications of organic electronics on flexible platforms. (a) Circuit board printed on a flexible substrate (Source: wsj.com). (b) Bendable organic light-emitting display (Source: prweb.com). (c) An organic solar panel on a flexible substrate (Source: ise.fraunhofer.de). (d) Printed flexible RFID tag (Source: elechouse.com). (e) wearable organic light-emitting display (Source: theconversation.com).

The organic electronics open up new possibilities and applications in the field, one of the most important application is the use of organic thin-film transistors in the flexible active matrix display circuitry. Organic transistors are the basic building block for organic electronics circuits. Some of the other important applications of organic electronics where organic field-effect transistors used are listed below:

(a) Organic Displays

The key revenue-generating part of the organic electronics market is organic displays. The organic light-emitting diodes (OLEDs) are made of one or many layers sandwiched between two electrodes in which one of the electrodes is transparent through which the light is emitted. When power is applied to the electrodes they emit bright light. OLEDs are emissive displays they do not require any backlight to work rather they produce their own light via electroluminescence to display images. Thus the OLED display circuitry requires less space and is thinner as compared to the LCD displays. These displays are more energy-efficient and consume less power when compare to the displays that require a backlight. The OLED displays are not only energy-efficient and thinner, rather the low-temperature processing of organic electronics and the development of organic TFTs based pixel driver circuits allows them to be fabricated on a variety of flexible substrates which broadens the application area of these displays with the aid of transparency, foldability, rollability in the displays. These displays are commercially utilized all around the world. For example, Samsung galaxy cellphone series uses OLED displays and it covers a large cellphone sector. The latest example of this technology is the foldable smartphone launched by Samsung (Samsung galaxy fold) that utilizes the AMOLED display. Figure 1.4 shows some of the examples of these displays.

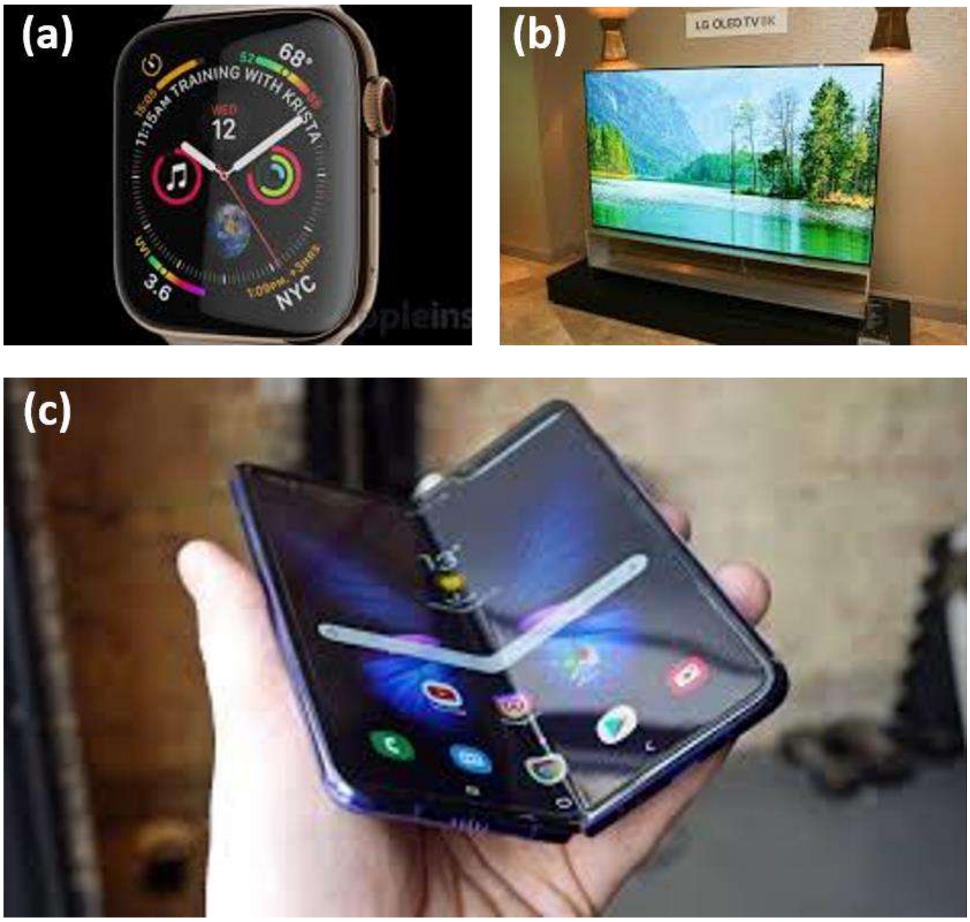

Figure 1.4 : Devices that use OLED displays (a) Apple 4 series watch with an OLED display (Source: appleinsider.com). (b) LG 88-inch 8k OLED TV (Source: cnet.com). (c) Samsung foldable smartphone Samsung galaxy fold with AMOLED display (Source: techradar.com).

(b) Radio Frequency Identification Tags

Radio Frequency Identification Tag is a device used to transmit information from a transponder to the reader device. RFIDs are used in tracking of consumer goods, electronics product codes for logistics, identification cards of employees, electronic ski-pass, and many other automation applications. It is a passive device, which means it does not contain any power source, rather it gets activated when it comes in a range of particular frequency of the reader (high radio frequency of 13.56 MHz) and the stored information is thus transmitted from the RFID tag to the reader. The RFID tags are the combination of integrated digital logic circuitry and memory, which is connected to an antenna for transmitting the information. The RFID market is very large and its cost-effectiveness is a major concern in further expansion of its use.

Printed RFIDs can be very cost-effective and a good substitute to the standard RFID tags where a silicon chip is mounted on the substrate and connected to the antenna. The antenna can be printed using conductive inks. If the internal circuitry uses organic thin-film transistors than the complete RFID tag can be printed. Along with the advantage of low cost, the printed RFID will also have flexibility, smaller thickness, and better ecological properties compared to the standard RFID tags. Researchers are working on the development of printed organic RFID tags. The first printed RFID tag was presented by PolyIC in the year 2007, which was working at a high frequency of 13.56 MHz. Since then many researchers came up with improve performance of printed RFID tags. Along with the advantage of printing, there are many challenges in printed RFIDs in terms of performance, memory size reading distance, etc. Thus a lot of research is still needed in improving the performance of organic field-effect based printed RFID tags and with the maturity of the technology the application areas of printed RFID tags are increasing and the performance is expected to meet that of the conventional RFID tags.

(c) Sensors

Organic electronics has a wide range of application in low-cost sensors. Sensors are the means of detecting any stimuli. They detect some physical quantity (any stimuli) and the detected parameter is seen in terms of change in the electrical signal. Flexible electronics sensors can be used in a variety of applications like mounting flexible sensors on the body of the athletes, continuous health monitoring of patients, etc. To understand the relation between the wide organics electronics technology and the sensors, let us understand what is required for a sensor. The sensor consists of material that reacts to particular stimuli that can be either environmental change, temperature, pressure etc. Thus, the organic flexible electronics use materials that are compatible with the printed technology to develop low cost printed sensors. Organic thin-film transistor-based biological, temperature, pressure, chemical and environmental sensor have shown promising results in the field. These sensors have advantages of mechanical flexibility, affordable cost, low-temperature deposition and the ability to be produced by the roll to roll processing to produce in high volumes. These advantages are the motivation for the researchers to develop further low-cost and easily processable sensors based on organic TFTs.

1.2 ORGANIC SEMICONDUCTORS

Organic semiconductors as by their name suggest are the semiconducting materials with carbon and hydrogen being their basic constituents. They are the most important class of materials in the conducting organic materials list with a wide range of applications in devices like organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), organic solar cells, etc. In the initial development stage of organic conducting polymers, the first discovery that has shown highly conducting nature in organic material was in chemically doped polyacetylene way back in 1977 by Hideki Shirakawa, Alan Heeger, and Alan MacDiarmid. Since then a lot of organic semiconductors materials have been synthesized, developed and introduced for use in various commercial products. The conducting properties of the organic semiconductor materials can be tailored to a large range depending on the need of a particular application, which is one of its major merit over its inorganic counterparts.

1.2.1 Classification

The general classification of organic semiconductors can be given on the basis of different basic units. They are classified as small molecule organic semiconductors (Oligomers) and polymer organic semiconductors. In the small molecule organic semiconductors, the carbon atoms form large molecules of long conjugated chains with benzene as a typical basic unit, or in other words, the small molecules have carbon atoms that are countable in number. Also, the molecular weight of small molecules organic semiconductors is less (< 1000g/mol) and well defined. The arrangement of the conjugated units in the finally obtained film in the device defines the efficiency of the intramolecular charge transport in small molecule semiconductors. Small molecule organic semiconductors are generally deposited through high vacuum thermal evaporation technique which provides uniform semiconducting films.

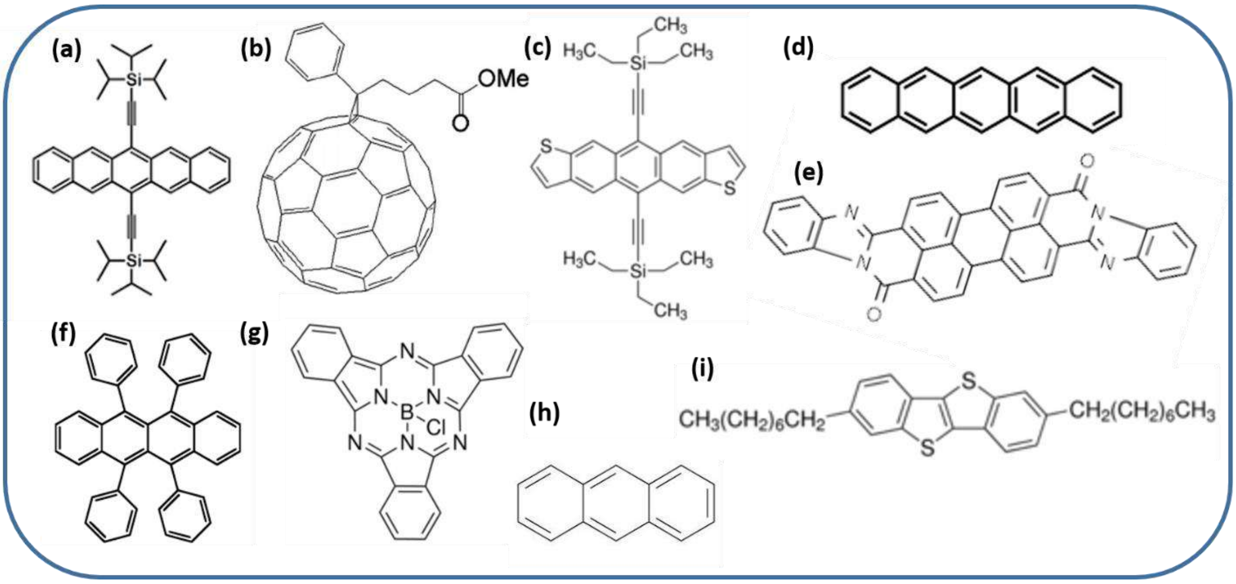

Figure 1.5 : Chemical Structure of various small molecule organic semiconductors (a) TIPS-pentacene (b) $PC_{60}BM$ (c) TES-ADT (d) Pentacene (e) PTCBI (f) Rubrene (g) SubPC (h) Anthracene and (i) C8BTBT.

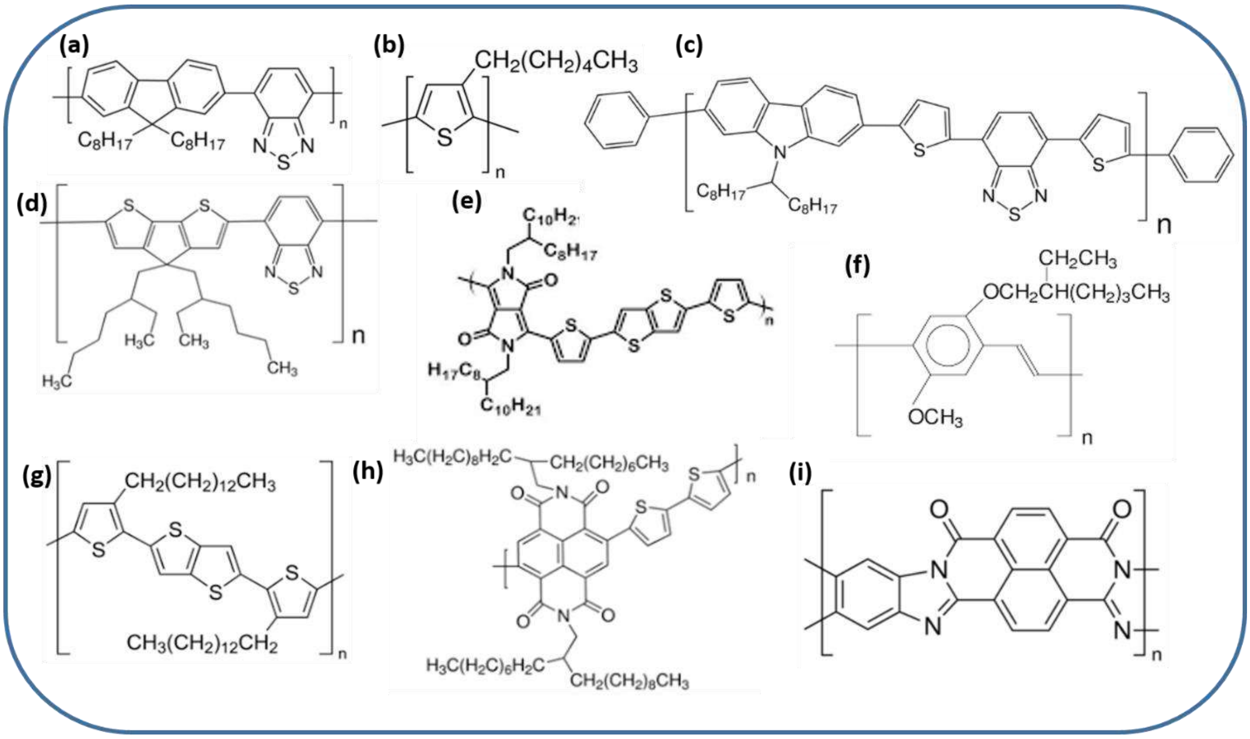

Figure 1.6 : Chemical structure of various polymeric organic semiconductors (a) F8BT (b) P3HT (c) PCDTBT (d) PCPDTBT (e) PDPP-TTT (f) MEH-PPV (g) PBTTT (h) P(NDI2OD-T2) and (i) BBL.

On the other hand, in the polymer organic semiconductors, a single monomeric unit repeats itself several times to form a long chain and the molecular weight of these polymeric chains is higher (>1000g/mol) and also not properly defined. In addition, the intra-chain and inter-chain charge transport are also complex in polymers because of large structural disorder in the semiconducting chains. The polymer organic semiconductors have an advantage as they can easily be deposited through solution processing techniques such as drop casting, spin coating, blade coating, spray coating, etc., but the uniformity of film remains a concern. Thus a tradeoff between the uniformity of films and deposition ease has to be adopted before selecting a kind of organic semiconductor for a particular application. Some of the commonly exploited small molecule and polymer organic semiconductors are listed in Figures 1.5 and 1.6 respectively.

1.2.2 Conduction Mechanism

The semiconducting or conducting properties in organic molecules are attributed to the interaction between carbon-carbon atoms and their ability to form a double bond. When two carbon atoms interact to form a molecule, the orbitals in each carbon atom can hybridize into sp, sp^2 and sp^3 orbitals. Those organic molecules constituted of sp^2 hybridize orbitals called conjugated organic materials. One of the simplest examples of bond formation in carbon atoms is represented for the ethylene molecule in Figure 1.7. In the represented molecule each of the carbon atoms consists of one p_z orbital and three of sp^2 hybridize orbitals to form σ bonds. A conjugated molecule consists of alternate single and double bonds and with the overlapping of wave function of p_z electrons, two orbitals are known as bonding also referred as π (represents the highest occupied molecular orbital (HOMO)) and antibonding orbitals also referred as π^* (represents the lowest unoccupied molecular orbital (LUMO)) are formed. In an alternating single and double bond chain, the electrons associated with the single bond are bound whereas the electrons associated with the double bond (the π electrons) are delocalized and these π electrons are delocalized along with the whole conjugated system. These delocalized π electrons turn the organic material into an organic semiconductor. When molecules exist together in a bulk material, the intermolecular interaction leads to broadening of HOMO-LUMO levels and it results in energy bands. The gap between the HOMO and LUMO levels is termed as the energy gap of the particular material.

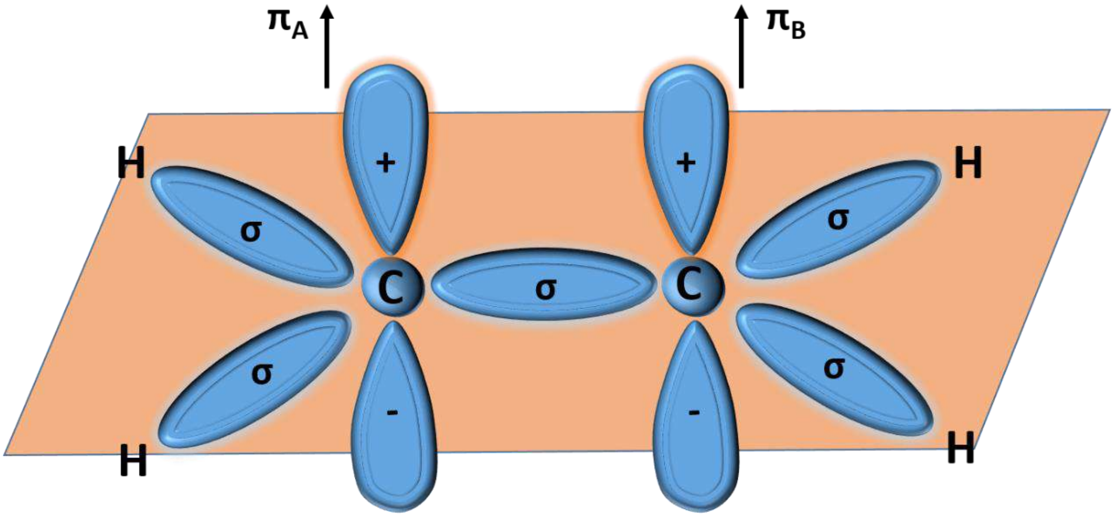

Figure 1.7 : An ethylene molecule.

The most common mechanism accepted for charge conduction in organic semiconductors is the charge hopping mechanism, despite the fact that distinctly purified crystals of some organic semiconductors have demonstrated an enhancement in mobility similar to inorganic semiconductors with lowering the temperature. Contrary to inorganic materials, the intermolecular forces between molecules in organic semiconductors are weak van der wall interactions and thus the charge transport between two molecules is phonon-assisted or in other words, the lattice vibration assisted and thus can be thermally activated. Therefore, the charge transport in organic semiconductors is driven by a hopping transport process. The hopping processes basically referred to the transferring of charge from one molecule to another. When a charge is localized on a molecule for a long period which is enough to persuade the nuclei to relax and attain its optimal geometry, the lattice around the molecule deforms and resulted in the formation of polaron. In a simpler way, it can be said that polaron hopping is a self-assisted electron transfer process where the charge hops from an ionized site to the nearby neutral site and so on and the continued process is responsible for the observing carrier mobility in organic semiconductors. The rate of charge hopping is represented by Eq. (1.1).

$$k_{hopping} = \frac{4\pi^2}{h}\frac{1}{\sqrt{4\pi k_B T}}t^2\, exp\left(-\frac{\lambda}{4k_B T}\right) \qquad (1.1)$$

Where T is the temperature, t is the transfer integral and λ is the reorganization energy, h and k_B are the Planks and Boltzmann constants respectively. With the interaction of individual conjugated chain to another isolated chain, there exists a splitting of electronic level which is represented by the transfer integral. As for as the organic semiconductors are concerned the splitting of electronic levels is associated with the HOMO and LUMO levels. The higher the HOMO bandwidth, the higher will be the mobility of holes in the semiconductor. Figure 1.8 shows the schematic representation of the interaction between bonding and antibonding energy levels of ethylene molecules. The transfer integral in Eq. (1.1) represents the ease of charge transfer from one molecule to another which in other words reflects the strength of the interaction.

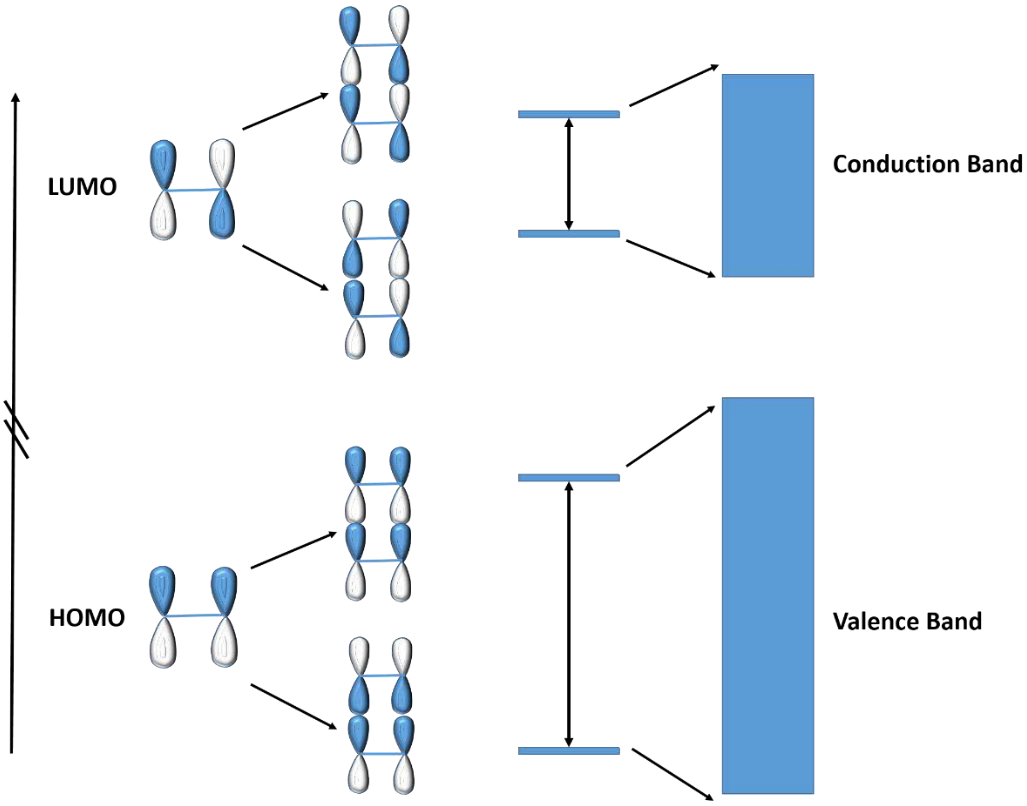

Figure 1.8 : Bonding-antibonding interaction of energy levels between the pair of ethylene molecules.

On the other hand, the reorganization energy represents the strength of phonon-electron interaction and this quantity needs to be minimized for efficient charge hopping in organic semiconductors. This parameter is basically the sum of geometrical relaxation energies of a molecule and its nearest neighbors with the movement of charge carriers. The crucial parameter to define the efficiency of charge hopping or charge transfer in the mobility of the charge carriers. In the absence of any field around the charge carriers, they undergo random movement and thus the net resulted movement is zero. When a field is applied the charge carriers start moving in a particular direction and gain acceleration. The average position of the charge carrier's changes and thus attain a drift velocity. The ratio of the attain drift velocity (v) to the applied field (E) is called the mobility ($\mu = v/E$) of charge carriers. The quantity signifies how fast the charge carriers can move in a medium when a field is applied.

1.3 ORGANIC FIELD-EFFECT TRANSISTORS

An organic field-effect transistor (OFET) is an electronic device that uses organic semiconductor material for the active layer. OFETs are the main elements in organic electronic devices and are the basic building blocks for many applications namely the RFID tags, active-matrix displays, circuits and various low-cost environmental and biological sensors. OFETs are receiving much attention for flexible electronic applications because of their solution processability, low manufacturing cost, low-temperature processing and ability to be processed in large areas. Initial work on OFETs was started in 1983 by Ebisawa where the device was made using polyacetylene as an active semiconductor. A couple of years later Tsumura demonstrated an OFET with polythiophene as an active layer and a large modulation in current was observed in these devices. These initial OFETs were based on polymeric semiconductor films which were deposited by spin coating or screen printing. The achieved mobility was of the order of 10^{-5} cm^2 V^{-1} s^{-1}. In terms of electrical performance OFETs have traveled a long way and today the mobility values higher than 10 cm^2 V^{-1} s^{-1} are achievable. Although the performance of OFETs is much lower compared to Si-based devices, however, this future technology is in high demand because of its broad range of applications and its ability to be fabricated on various unconventional and bendable substrates.

1.3.1 Device Architectures

The device architecture of OFETs is much simpler as compared to the conventional MOSFET. It is a three-terminal device namely gate, source and drain. On the basis of the position of these terminals with respect to the organic semiconducting film, the OFET device structures can be classified and they can either be coplanar or with staggered architecture. The cross-sectional view of four different types of OFET architectures is shown in Figure 1.9. The first architecture is known as bottom gate top contact (BGTC), the second one is called bottom gate bottom contact (BGBC) and the other two are top gate bottom contact (TGBC) and top gate top contact (TGTC) respectively. In the bottom contact devices, the organic semiconductor is deposited over the gate insulator and source-drain electrode, whereas in top contact devices source-drain electrodes are generally deposited over organic semiconductors through a shadow mask. OFETs with the same materials but with different structures can show a drastic change in their electrical performance.

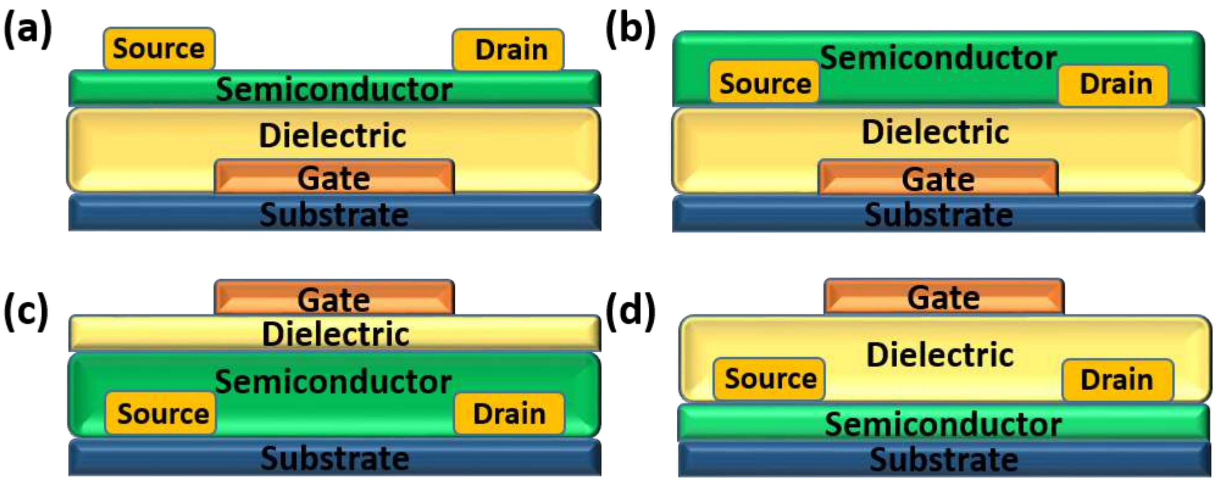

Figure 1.9 : OFET device architectures; (a) Bottom gate top contact. (b) Bottom gate bottom contact. (c) Top gate bottom contact. (d) Top gate top contact.

1.3.2 Basic Working Principle

Before discussing the working principle of OFET we first have to analyze the metal-insulator-semiconductor (MIS) structure. The energy level diagram of the MIS structure in two different operating modes with the p-type semiconductor is shown in Figure 1.10. The energy band diagram drawn here is with the assumption of ideal MIS structure, which implies that the insular material is not conducting and the fermi level (E_F) of the metal and the semiconductor are completely aligned. In other words, the bend bending was nil before the application of any voltage and is represented in Figure 1.10 (a) in the equilibrium condition. The lowest edge of the conduction band (E_C) is represented as the lowest unoccupied molecular orbital (LUMO) of the organic semiconductor and the highest edge of the valence bend (E_V) is represented as highest occupied molecular orbital (HOMO) of the organic semiconductor. When the equilibrium is broken by applying the external field the bend bending occurs depending on the polarity of the field applied. When a negative gate voltage is applied ($V_{GS} < 0$), bend start moving upwards, the HOMO level starts coming closer to E_F which implies the accumulation of holes at the interface and thus the dielectric: semiconductor is filled with holes as shown in Figure 1.10 (b). When the polarity of gate voltage changes, means gate voltage is positive ($V_{GS} > 0$) downward bend bending takes place and the number of charge carriers starts decreasing until the channel is fully depleted. The number of electrons starts increasing compared to the holes and the device is now in the inversion region.

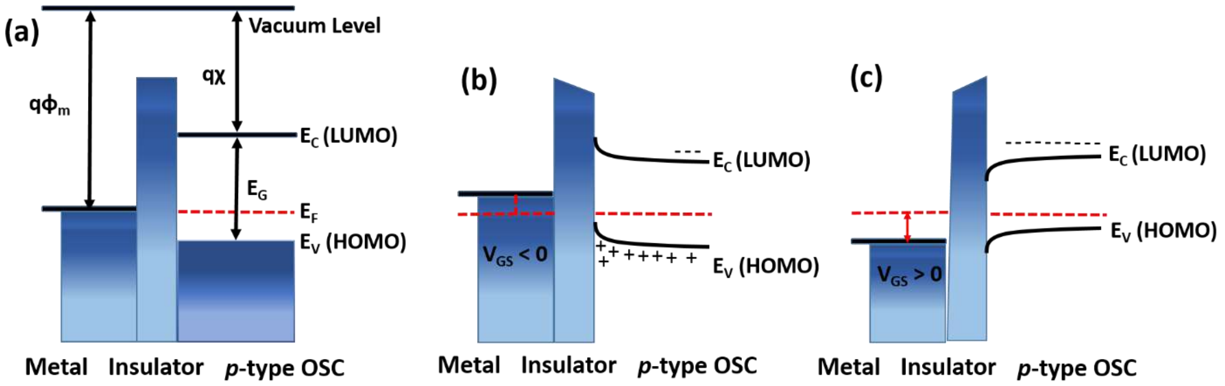

Figure 1.10 : Schematic representation of energy band diagram of ideal MIS structure with p-type OSC under (a) equilibrium, under application of (b) negative bias and (c) positive bias.

Compared to conventional MOSFET, the working of OFETs differs in the operating mode as the conventional MOSFET can be operated in depletion or inversion mode, whereas the OFETs are generally operated in accumulation mode. The basic working of the OFET is explained by considering a p-type OFET shown in Figure 1.11. In a p-type OFET, both the gate terminal and the drain terminal are negatively biased whereas the source terminal is grounded. With the application of negative potential at the gate terminal, holes started getting accumulated in the close vicinity of the dielectric: semiconductor interface. There can be various traps at the crucial interface which needs to be filled for the current to rise in the transistor. Thus a sufficient voltage needs to be applied to witness noticeable current in OFET and the minimum voltage that is needed to turn on the device is termed as the threshold voltage. With the small drain voltage applied, there exists a small current proportional to the applied drain voltage and the transistor is said to be operated in the linear region. With further increase in drain voltage when $V_{DS} > |V_{GS} - V_{TH}|$, the channel starts pinching off from the drain side and the current saturates. The level of current in this region depends on the gate bias, with further increase in drain voltage the current will not change much. The device is said to be operated in the saturation regime in this region.

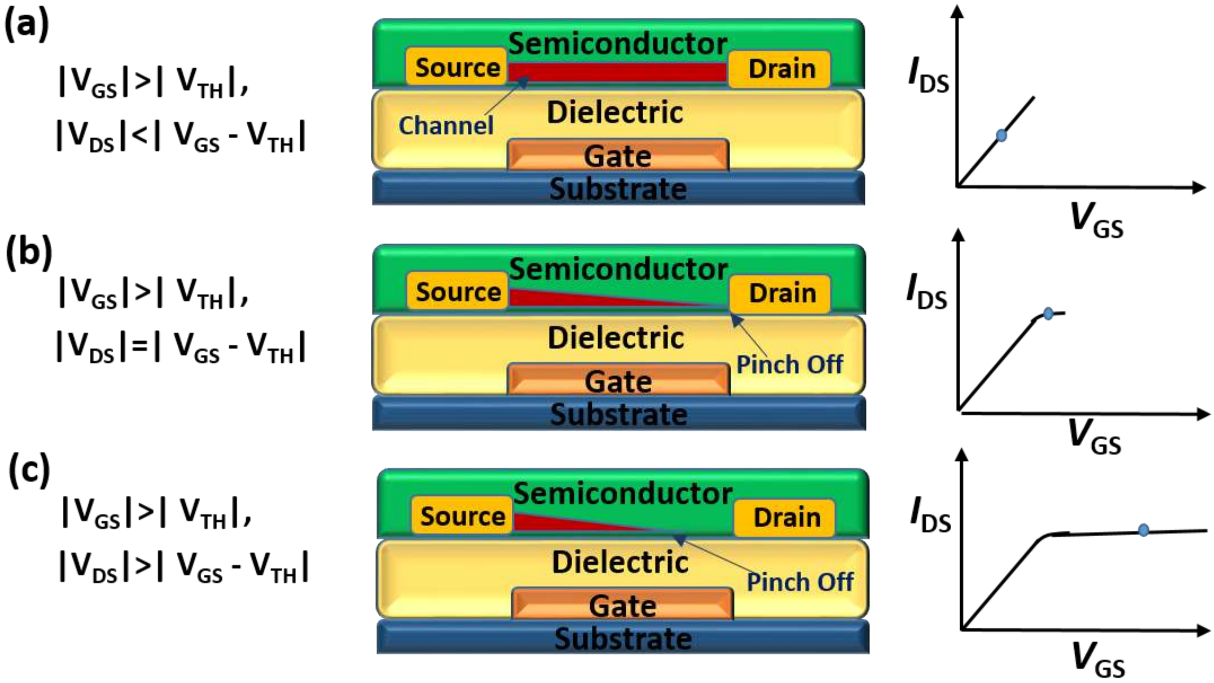

Figure 1.11 : Operating Principle of OFET in (a) linear regime, (b) onset of saturation, and (c) saturation regime.

1.4 FLEXIBLE OFETs

One of the core advantages associated with organic electronics is its flexible nature, which broadens the application area of the devices. OFETs fabricated on flexible substrates have a wide range of applications as they can be used in wearable sensors, foldable displays, biomedical devices, smart identification cards and other emerging applications with the potential of the roll to roll processing. In the last few decades, a lot of research has been carried out focusing on high performance and operational stability of flexible OFETs fabricated on plastic substrates. Plastic has the advantage of smooth surface suitable for organic device fabrication, thus in spite of being costlier than its other counterparts, it is widely explored globally. The electrical performance of OFETs fabricated on plastic substrate is summarized in Table 1.1.

Table 1.1 : Summary of various studies reporting high-performance OFETs on the plastic substrate. Subs: Substrate; Dev. Str.: Device Structure; OSC.: Organic semiconductor; Op. Vol.: Operating Voltage; Flex. Test: Flexibility Test.

Subs.	Dev. Str.	Dielectric	OSC.	Op. Vol. (V)	μ (cm^2 V^{-1}s^{-1})	V_{TH} (V)	I_{ON}/I_{OFF}	Flex. Test	Reference
Kapton/ PET	BGBC	PVP	Rubrene Single crystal	60	4.6	-2.1	10^6	Yes	[Briseno et al.,2006]
Polyimide	BCTC	AlO_x	Pentacene	2	0.5	-	10^6	Yes	[Sekitani et al.,2010]
PET	TGBC	CYTOP	TIPS-pen and poly(triaryl amine) blend	60	1.13 ±0.05	-5 to -10	10^4	Yes	[Smith et al.,2009]

Mylar	BGBC	Mylar	TIPS-pen.	50	0.14	Near Zero	~10^5	Yes	[Yi et al.,2012]
PES	TGBC	CYTOP/Al_2O_3	TIPS-pen. and PTAA blend	8	0.24 ± 0.08	−1.3 ± 0.1	~10^5	yes	[Hwang et al.,2011]
Polyimide	BCBC	Polyimide	Pentacene	100	0.55	-	10^5	No	[Ji et al.,2013]
PET	BGTC	ODPA/Annealed ZrO2	PBTTT-C14	3	0.18 ± 0.03	-0.75	10^5	No	[Park et al.,2013]
PET	BGTC	HfO2/PVP	TIPS-pen	10	0.12	-0.2	10^4	Yes	[Raghuwanshi et al.,2016]
PEN	BGBC	PVP	TIPS-pen.	< 1	0.95 ± 0.12	−0.19 ±0.03	2.5 × 10^4	No	[Conti et al.,2017]
PEN	TGBC	PMMA	P-29-DPP-SVS	80	2.98 ± 0.19	-38.04 ± 3.49	1.61 × 10^2	Yes	[Ryu et al.,2015]
Polyimide	BGTC	TiO_2	Pentacene	1	0.12	-0.2	10^4	-	[Sung et al.,2015]
PET	TCBC	PMMA/ PAA	PIDT-BT Doped with TCNQ	5	0.69	−0.61	10^4	Yes	[Yin et al.,2018]
PET	BGTC	PMMA/ PVP/PMMA	Pentacene	5	0.72	−3.04	2.3× 10^4	Yes	[Ling et al.,2019]
Parylene C	BGTC	Polyimide	TIPS-pen. and PS Blend	1	0.04	-	7.7× 10^5	Yes	[Park et al.,2019]
PEN	BGBC	PVC	TIPS-pen. and PS Blend	5	0.37	-	10^5	No	[Ding et al.,2017]
PEN	BGTC	PVA	P3HT and PSS	40	0.25	-	10^3	No	[Kwon et al.,2014]
PEN	BGTC	PMMA	P3HT	30	0.007	5.4		No	[Song et al.,2017]
PEN	BGTC	AlO_x	DNTT	3	2.52	-0.66	2× 10^4	Yes	[Kaltenbrunner et al.,2013]
Non-birefringent plastic	BGTC	PMMA	Pentacene	10	0.6 ±0.1	-1	10^5	No	[Vaklev et al.,2014]
PET	BGTC	Al_2O_3	Pentacene	3	0.65	-1.3	10^5	Yes	[Sun et al.,2019]

PET	BGTC	PMMA/PVP	Pentacene	50	1.51	-20.1	10^5	Yes	[Yi et al.,2015]
AryLite polyester	BGTC	PMMA	TIPS-pen.	40	0.062	~ -4 V	~10^5	No	[Yu et al.,2013]
PET	BGTC	PMMA and PAA blend	PIDT-BT	10	0.064 ± 0.002	−2.06	>10^3	Yes	[Liu et al.,2018]
PET	BGTC	HfO2	TIPS-pen. and PS blend	5	0.5 ± 0.3	-0.5 ± 0.3	~10^5	Yes	[Bharti et al.,2016]
PET	BGTC	STO	Pentacene	5	1.1	-1.1	~10^5	No	[Yadav and Ghosh,2016]
PEN	BGTC	PMMA	TIPS-pen. and PMMA blend	5	0.87	-0.81		Yes	[Onojima et al.,2020]
PET	BGTC	HPCPS	C8-BTBT single crystal	4	33.4	-1.1	10^5	Yes	[Chen et al.,2019]
PET	BGTC	PAA + PI copolymer	Pentacene	3	5.6	-3	1.4× 10^6	Yes	[Ji et al.,2018]

It can be observed from Table 1.1 that because of the progress in the research and development in the area of flexible electronics very high performing OFET devices with good mechanical stability can be fabricated on plastic substrates. However, it is known that plastic is made from the bi-products of the oil industry and its bio-degradation takes place very slowly. With the increasing plastic technology, the plastic waste is also increasing dramatically thus these plastic substrates have a negative impact on the environment. In the OFETs fabrication the substrate occupies the large part of the device, so there is need to improvise the biodegradability of the substrate to reduce the negative impact on environment. In recent years, with increasing awareness on environmental pollution researches have tried making devices on substrates which leaves fewer footprints at the end of their lifespan. Paper is one of the most common unconventional substrates which are available at low cost and is naturally renewable. However, fabricating devices on paper is challenging because it suffers from severe microscopic surface non-uniformities. This challenge can be addressed in number of ways such as by choosing device architecture which is less sensitive to the substrate roughness or by utilizing a planarization layer prior to device fabrication or by selecting some specialize paper which is already engineered for surface roughness with inherent smooth surface. Some of the OFET devices fabricated on paper and the kind of planarization techniques used are summarized in Table 1.2.

Table 1.2 : Summary of various studies on OFETs fabricated on paper substrate. Surface Mod.: Surface Modification.

Type of Paper	Surface mod.	Dev. Str.	Dielectric	OSC.	Op. Vol. (V)	μ (cm^2 V^{-1}s^{-1})	V_{TH} (V)	I_{ON}/ I_{OFF}	Ref.
Photo Paper	Parylene	BGBC	polyimide /SiO2	P3HT	50	0.086	-11.9	10^4	[Kim et al.,2004]
Cotton-fiber paper	Polymer Barrier Coatin	BGBC	PVP	Pentacene	30	0.2	-5	10^6	[Eder et al.,2004]
Paper	Special Coating	TGBC	Cytop	F8T2	60	-	-	10^2	[Trnovec et al.,2009]
Fine Paper	Multi-layer Coating	TGBC	PVP	P3HT	1	-	-	10^1-10^2	[Bollström et al.,2009]
Fine Paper	Multi-layer Coating	-	-	P3HT/PLAA	2	-	-	10^6	[Pettersson et al.,2014]
Bank Note	-	BGTC	AlOx/SAM	DNTT	3	0.57	-1 to -1.4	10^5	[Zschieschang et al.,2011]
Bank Note	-	BGTC	AlOx/SAM	F_{16} CuPc	3	0.005	-	10^4	[Zschieschang et al.,2011]
Bank Note	PDMS	BGTC	P(VDF-TrFE)	Pentacene	15	0.12	-0.5	10^3	[Khan et al.,2012]
Photo Paper	Parylene	BGTC	Cytop/ PMMA	C8-BTBT	40	1.3	-2.6	10^8	[Li et al.,2012]
Bank Note	-	BGTC	PAN/PS	PDI-C8	15	0.23	8.5	10^7	[Zhang et al.,2013]
Printing Paper	Chitosan	-	P(VDF-HFP): [EMI][TSFA]	P3HT	2	0.97	0.67	10^4	[Qian et al.,2015]
Xerox Paper	-	BGTC	Parylene	DNTT	30	0.39	0.9	10^4	[Peng and Chan,2014]
Aramid paper	UV-curable polymer	BGTC	Cytop	DNTT	60	0.25	−35.73 ± 1.28	10^7	[Shin et al.,2019]
printer paper	-	BGTC	Parylene	DNTT	80	0.33	-1.22	10^8	[Peng et al.,2014]

Photo Paper	-	BGTC	Parylene	Pentacene	60	0.09	20-30	10^5	[Zocco et al.,2014]
Photo Paper	Parylene	TGBC	Cytop	C 8 -BTBT	40	2.5	-	10^6	[Minari et al.,2014]
Packing paper	PVP	BGBC	PVP	pBTTT	40	0.086	0.88	10^4	[Grau et al.,2014]
Nano-Paper	-	BGTC	PMMA	NTCDI-F15	80	0.0043	-	10^2	[Huang et al.,2013]
Nano-Paper	Olefin polymer	BGBC	EPRIMA, AL-X6	Merck Lisicon S1200	20	0.83	-	10^8	[Fujisaki et al.,2014]
Nano-Paper	Al_2O_3	TGBC	Cytop/ Al_2O_3	TIPS pentacene/PTAA	10	0.11	−2.1 ±0.7	2.4 × 10^3	[Wang et al.,2015]
Nano-Paper	-	BGTC	ICCN	C_8-BTBT	10	.072	−1.26	7 × 10^3	[Dai et al.,2018]
Nano-Paper	-	BGTC	ICCN	NTCDI-F15	10	.0098	0.16	2.30 ×10^3	[Dai et al.,2018]
Nano-Paper	-	BGTC	ICCN	PQT-12	10	.021	0.28	2.97 × 10^3	[Dai et al.,2018]
p_e:smart paper	Multiple Layers	TCBC	EP-NS/MMAcoMAA	PTAA	30	.087	11.8 ± 0.39	10^2	[Mitra et al.,2017]
Starch Paper	-	BGTC	Parylene-C	Pentacene	40	0.37	−21.3	4.9 × 10^5	[Jeong et al.,2018]
Starch Paper	-	BGTC	Parylene-C	PTAA	40	0.013	−13.0	6.9 × 10^4	[Jeong et al.,2018]
Starch Paper	-	BGTC	Parylene-C	DNTT	40	0.36	−15.7	1.6 × 10^5	[Jeong et al.,2018]
Clean Room Paper	-	BGTC	AlOx/SAM	DNTT	2	1.6	-0.8	10^6	[Zschieschang and Klauk,2015]

It is evident from Table 1.2 that despite the high surface roughness of the paper substrate, high performing OFET devices can be fabricated by utilizing planarizing techniques. However, despite so many reports on a paper substrate, the study of the device on paper with external stress remains underexplored. Extensive investigation of this facet of device performance is imperative to address for productive fostering of the field and to cater the increasing demand of solutions to futuristic applications by the route of the unconventional substrate. In the current study, the optimized device's components were utilized and the devices were fabricated on a low-cost paper substrate which is engineered to have an inherent smooth surface, low absorption and provide excellent thermal and mechanical stability. In addition to further smoother the surface we have used PVA as a planarizing layer. The devices were then studied for performance stability under environmental and electrical stress.

1.5 OPERATIONAL STABILITY

Along with achieving high performance in OFETs, operational stability is another major concern for OFETs to be deployed in practical applications. Many efforts have been made in the last few decades to improvise the long term stability of devices. Various organic semiconductors with high mobilities were developed which have an air-stable nature. However, utilizing air-stable semiconductors is not the only requirement of stable OFETs, there are various factors that affect the stability of OFETs. The first factor is the material used for semiconductor, dielectric and metal contacts. All these materials should have an intrinsic stable nature. A material which itself degrade with time or bias, cannot be a good candidate for the overall stable device. The second factor is the quality of films and functional interfaces in the devices. For OFETs, smoother and uniform the quality of films, better will be the performance and stability of the device. The various functional interfaces such as the dielectric: semiconductor and metal: semiconductor interface plays a crucial role in determining the stability. As most of the charge carriers are accumulated in the few monolayers at the dielectric: semiconductor interface, thus the interface plays a crucial role in defining the stability of the device. The poor quality dielectric: semiconductor interface provides a large number of trapping sites to the charge carriers, which get trapped to the sites and the phenomenon eventually leads towards unstable device performance. Similarly, the quality of the metal-semiconductor interface defines the barrier to the injecting charge carriers from metal to semiconductor and limits the amount of charge carrier injection which also limits the stability of the device. Hence efforts need to put on improvising the uniformity of various films and reducing the barrier height for maximum charge injection. The third factor is the processing techniques used for the deposition of the various layer in device fabrication. The quality of the films obtained varies drastically with the processing technique. For instance, a semiconducting layer can be deposited by various methods such as drop-casting, spin coating, dip coating etc. However, the same material deposited with different techniques provides different device performance and stability. The process parameters also change the stability by a large margin. All these factors such as the processing techniques or process parameters eventually affect the interfacial conditions of the device, which define stability. Another major factor is the architecture of the device used. The device fabricated with the same materials in different architecture provides different performance and stability. For example, a semiconducting film in a BGTC architecture is more exposed to the environment compared to the same film in a TGBC architecture and thus the different environmental exposure results in different stability conditions.

For all the factors affecting the stability, their remedies need to be taken care of before fabricating a stable device. The chosen semiconducting material should be less prone to environmental conditions. Dielectric material with hydroxyl groups may lead to charge trapping at the dielectric: semiconductor interface, thus utilizing hydroxyl free dielectrics or strategies through which the direct contact of the hydroxyl group with the charge carriers is avoided, should be used, which limits the charge trapping at the interface and provide a stable device. The devices will also encounter various external stimuli such as humidity, temperature and electrical stress applied, which affect the performance and stability. One example of this is when an external bias is applied in OFET their electrical characteristics changes with time. Say if we use an OFET that is used to switch ON a current, for example, to drive a pixel in a display, will switch off in some time. The problems arise due to the change in threshold voltage of the OFETs due to charge trapping at various regions of the active layer film. The effect is called the bias stress effect. Various remedies to improve the stability of OFETs are used in this thesis work. In the current study, TIPS-pentacene is chosen as the organic semiconducting layer because of its inherent air-stable nature. The semiconductor material is also blended with insulating polymer PS to improvise the dielectric: semiconductor interface and helps in decreasing the interfacial traps. Other factors affecting the stability were also considered to obtain high performance and operationally stable OFET devices.

1.6 LOW OPERATIONAL VOLTAGE

The last section was dedicated to factors affecting the operational stability of OFETs and what are the remedies that can be used. Another critical issue in OFETs for practical application is the operational voltage. The major target applications of OFETs are dedicated to low-cost RFID tags and the electrophoretic displays which require low threshold voltage. In addition, to use these devices in the portable application, where the devices run through a battery, the operating voltage needs to be lowered. Lowering the operating voltage is the pursuit of the goal because the operating voltage is still high that leads to high power consumption in these devices. To understand what are the possibilities through which the operating voltage can be reduced let's understand the standard drain current equation of OFETs

$$I_{\mathrm{DS}} = \mu C_{\mathrm{ox}} \frac{W}{L}\left[\left(V_{\mathrm{GS}} - V_{\mathrm{TH}}\right)V_{\mathrm{DS}} - \frac{V_{\mathrm{DS}}^2}{2}\right] \tag{1.2}$$

Where μ is the field-effect mobility, C_{ox} is the capacitance density, V_{TH} is the threshold voltage of the device and W and L are the channel width and length respectively. Looking at the equation it can be observed that the operating voltage at a given drain current can be reduced by three paths. Either the dimension factor (W/L) or the capacitance density or the mobility of the device must increase accordingly. The first cannot be altered much as the channel length is limited with processing techniques such as shadow mask or printing etc. Also with reducing channel length, the contact resistance starts dominating over the channel resistance and the device inhibits saturation. Channel width, on the other hand, cannot be increased above an extent because with time the dimensions of the device are shrinking to accommodate a large number of devices in a small area. Mobility is the inherent property of the material and that cannot be increased above a particular limit. The only and important parameter left in hand to reduce the operating voltage is by increasing the capacitance density of the dielectric stack, which in turn is directly proportional to the dielectric constant of the material used and inversely proportionally to the thickness of the dielectric stack. The use of an ultrathin dielectric stack may lead to high leakage current, which eventually degrades the device performance and undesirable for practical applications. Utilizing high-k organic, inorganic or hybrid dielectric stack is one of the most efficient means to reduce the operating voltage requirement.

Polymeric dielectrics are the first choice for OFETs because of their solution-processable nature and the ability to provide better quality semiconductor: dielectric interface. Some of the most common polymeric dielectric used are poly(4-vinylphenol) (PVP), polyvinyl alcohol (PVA), polymethylmethacrylate (PMMA), etc. which provide high performance in devices but the operating voltage still remains high because of their low dielectric constant. On the other hand, high-k inorganic dielectrics which are typically deposited by atomic layer deposition, chemical vapor deposition or sputtering can significantly increase the surface charge density at the dielectric: semiconductor interface but these dielectrics also suffers from poor quality dielectric: semiconductor interface. Thus to obtain high performing and low operating voltage devices, procedures need to be adopted that utilize the benefits of both the solution-processable polymeric dielectrics and high-k inorganic dielectrics. In the current study, to improve the performance and to reduce the operating voltage requirement, various strategies have been used. The semiconductor material is blended with insulating polymer and has been used over the high-k inorganic dielectric layer. The blend solution improves the charge transport in the used organic semiconductor, whereas the high-k dielectric reduced the operating voltage. In addition, hybrid dielectric stack for OFETs and high-k dielectric deposited at room temperature were also demonstrated for high performance low operating voltage OFET devices.

1.7 RESEARCH FOCUS AND ORGANIZATION OF THESIS

The advancement in the field of organic electronics in the past few decades is noteworthy. Various organic materials have been synthesized, and their physical and chemical properties for their utilization in high-performance devices and circuits have been studied by researchers globally. The development in the field led it to be called as the future technology. Organic field-effect transistors are the key elements in most of the organic electronics applications and the key useful aspect of OFETs is their relatively low processing temperatures. The important facet of the technology allows these devices to be fabricated on a variety of unconventional substrates like plastic, paper, cloth, etc., and thus the devices can be used in a broad range of applications that couldn't be possible with the conventional Si-based technology. Successful realization of these devices on the unconventional substrates and achieving high performance and operational stability is still a challenging task and a plethora of research arenas still need to be explored for the commercialization of products on unconventional substrates. It has been known that the electrical parameters of OFETs like the threshold voltage, drain current, etc. decays with time. Thus special focus needs to be given in improving the operational stability of these devices.

The main focus of the thesis is to achieve high performance and operational stability in low voltage operated OFETs and their realization on unconventional substrates. The performance requirement of OFETs was tried to be achieved through improvisation in the dielectric: semiconductor interface. This crucial interface is also engineered for operational stability. With the said aim in mind, the very first task was to select an organic semiconductor for conducting various studies. TIPS-pentacene which is a small molecule organic semiconductor was selected because of its solution processability, inherent air-stable nature and ability to form semiconductor: polymer insulator blend with a variety of insulating polymers. After selecting the active semiconductor following research aims were set;

- Achieving high performance in solution-processable OFETs by blending organic semiconductor with insulating polymer and analyzing the effect of mixing ratio of semiconductor: polymer blend in device performance.
- To achieve low operating voltage by exploring dielectrics with high dielectric constant and which are processable at a low temperature so the devices can be fabricated on low-cost flexible plastic substrates.
- Exploring the bilayer hybrid dielectrics for high performance and long term operationally stable OFETs.
- Realization of high performing devices on the unconventional substrate.

The thesis has been organized as follows:

Chapter 1 presents an introduction to organic electronics mainly focusses on its evolution with time, advantages and core applications. The second section of the chapter focusses on device structures of OFETs and its working principle, the need for unconventional substrates and state of the art OFETs devices on the unconventional substrates. The rest of the chapter focusses on the factors affecting the operational stability and the remedies to cure them. In addition, the importance of low operational voltage and the methods to achieve it are discussed.

Chapter 2 provides methods for cleaning various substrates and fundamental working principles of various processing and characterization tools used in the study. The chapter also enlightens about various OFET parameter extraction methods and how the analysis of operational stability is being carried out in various studies.

Chapter 3 presents the effect of semiconductor: polymer blend mixing ratio on the electrical performance of OFETs. The study on the mechanical stability of the blend OFETs was also discussed.

Chapter 4 is devoted to reducing the operating voltage by proposing room temperature deposited high-k dielectrics for flexible OFETs. The chapter presents the optimization of various dielectric deposition parameters on a rigid platform. Later the electromechanical stability of devices with the optimized dielectric on a flexible substrate is discussed.

Chapter 5 is focused on exploring the bilayer organic/inorganic hybrid dielectric layer for OFETs on low-cost polyimide (Kapton tape) substrate. The device electrical characteristics were first discussed in the pristine state. Later the device performance with different bilayer dielectric stack was discussed for long term air stability. Finally, external load inverter circuits were discussed for the stable bilayer dielectric devices.

Chapter 6 deals with the planarization of unconventional paper substrate and then the realization of low voltage operated paper OFETs with bilayer dielectric and TIPS-pentacene:PS blend as an active layer. Along with low voltage operation, long term stability under extreme humid and environmental conditions is also demonstrated. Finally, the paper-based phototransistors under UV illumination are discussed.

Chapter 7 summarizes the research work carried out in the thesis and provides conclusion along with discussing the possible future extension of the work

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