

# Introduction

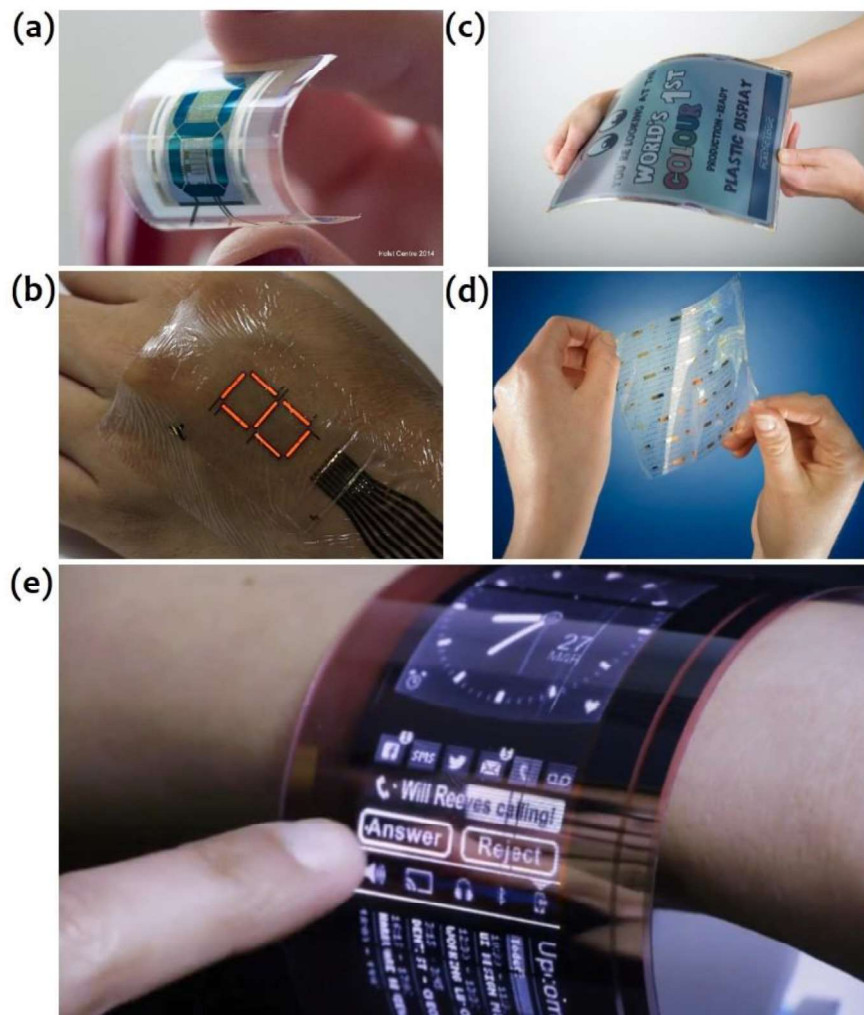
A new electronics era started after invention of Transistor in 1948 by John Bardeen, William Shockley and Walter Brattain at Bell Labs. However, after the realization of a Metal oxide semiconductor field-effect transistor (MOSFET) in 1960, and Complementary metal oxide semiconductor (CMOS) configuration in 1963, the semiconductor industry forged ahead at an unprecedented rate towards CMOS technology. The requirements for reducing costs and improving performance led to scaling down of device dimensions. Gordon Moore predicted in 1965 that the number of transistors in an integrated circuit will double approximately every two years. Silicon based microelectronics technology witnessed a huge growth with transistor density increasing from ~8000 in 1974 to ~10,000,000,000 in 2015 while the technology node improved from 8000 nm process in 1974 to 20 nm in 2015. Speed of such devices exhibited a huge leap with clock frequency rising from 2 MHz in 1974 to as large as 4133 MHz in 2015. Many products inevitable in our daily life such as computers, phones, cameras, music players and display screens are the results of this advancement in the microelectronics technology.

However, conventional CMOS or silicon based microelectronics technology is not suitable for large area, flexible, or printable electronics, where low process temperatures are desired. There exist viable alternatives to achieve the above mentioned goals with a fair enough performance compromise in device performance. Organic electronics is the prime among all the alternatives of conventional technology. In this chapter, various aspects related to organic electronics, brief overview of their physics, salient features, description of organic transistors and their applications have been strategically discussed.

## 1.1 ORGANIC ELECTRONICS

Conventional silicon based electronic technology has made tremendous advancement in previous few decades. Traditional silicon based devices are superior to their many competitors as far as electrical performance and stability are concerned. However, when low cost and simplified processing are the prime desires in an application with nominal electrical performance, it is then when alternative technologies like organic electronics lead the pathway of research and development. Light emitting diodes, transistors and solar cells are some of the broad domains where organic electronics has proved its potential to become a viable alternative of conventional inorganic devices. Successful demonstration of futuristic sensing devices, flat panel displays, radio frequency identification tags and printable circuits with these organic devices in relatively short period of time are some of the main accomplishment of the organic electronics technology [Caironi and Noh, 2015, Cicoira and Santato, 2013, Klauk, 2006, Logothetidis, 2014, Meller and Grasser, 2009, Sun and Dalton, 2008, Wöll, 2009]. Figure 1.1 shows some of the applicative products based on above technology and developed on flexible platforms. These achievements are also the evidences of profound research interest of the scientific research community in this technology and its development. Not only the scientific research, but the commercial interest in the organic electronics technology has also noticeably scaled up. Global market of organic electronics is expected to rise at an astonishing rate of 32.6% from 2012 to 2018, and total market value is predicted to cross \$ 75 billion by 2020 [Das, 2016, Rohan, 2014, Singh, 2014]. Major portion of the organic electronics market is dominated by

organic light emitting diodes and related displays. Other commercial organic electronic products include conductive inks, photo-voltaics, sensors, batteries and memory elements. Besides low cost and convenient processing, organic electronics also provides the feature of large area applicability of processing techniques. These aspects are some of the reasons for large investment by industries in the organic electronics market. Research progress and market growth are the driving factors for each other, which will keep the pace of technological advancement maintained.

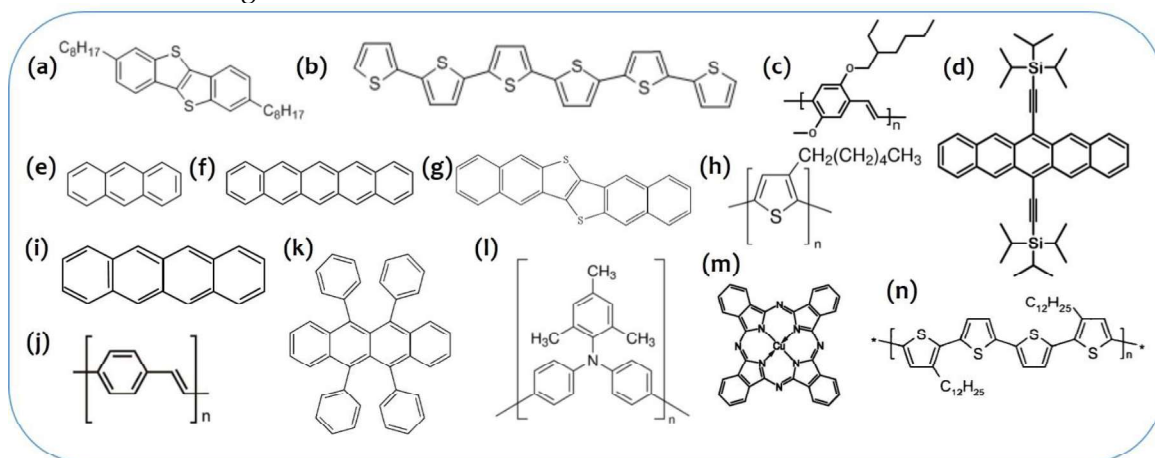


**Figure 1.1:** Applications of flexible organic electronics; (a) a flexible seven segment display (Image source: electroiq.com). (b) An ultra-thin and wearable LED display (Image source: www.independent.co.uk). (c) A flexible color e-reader display with OTFT back plane (Image source: Plastic logic). (d) An ultra-flexible organic circuitry (Image source: www.printedelectronicworld.com). (e) A wearable flexible AMOLED display (Image source: Plastic logic).

## 1.2 ORGANIC SEMICONDUCTORS

Organic semiconductors are the most important class of materials in the domain of organic conducting materials. Organic semiconductors are the essential constituents of various organic electronic devices such as organic field-effect transistors (OFETs), organic light emitting diodes (OLEDs), Organic solar cells etc [Klauk, 2006, Li, 2011, Weidner, 2008, Bernards *et al.*, 2010]. The first highly conducting organic material (chemically doped polyacetylene) was discovered in 1977 by group of Hideki Shirakawa, Alan Heeger, and Alan MacDiarmid [Shirakawa *et al.*, 1977]. Since then, plethora of organic semiconductors have been synthesized and used for research and commercial purposes. Some of the widely researched organic

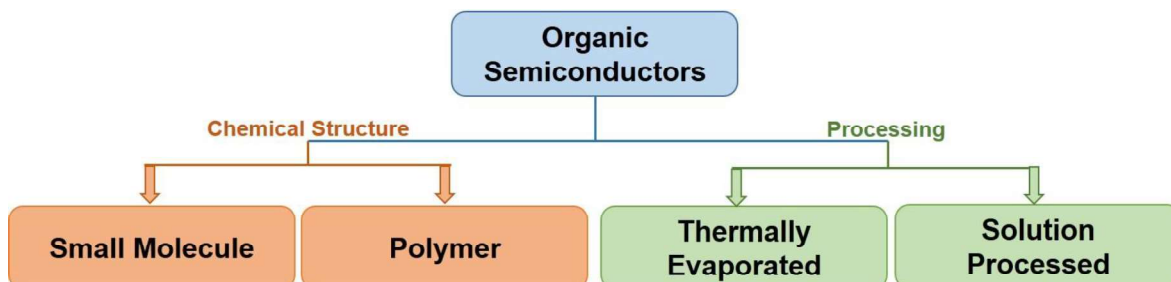
semiconductors are shown in Figure 1.2. Properties of organic semiconductors can be artificially tailored to suit the applicability, which is one of the main merit over their inorganic counterparts. This advantage of organic semiconductors has led to tremendous research interest of both organic chemistry and electronics fraternity, in the synthesis and applications of numerous novel organic semiconductors.



**Figure 1.2:** Chemical structure of various organic semiconductors; (a) C8-BTBT. (b) Sexithiophene. (c) MEH-PPV. (d) TIPS-pentacene. (e) Anthracene. (f) Pentacene. (g) DNNT. (h) P3HT. (i) Tetracene. (j) PPV. (k) Rubrene. (l) PTAA. (m) CuPC. (n) PQT-12.

### 1.2.1 Classification

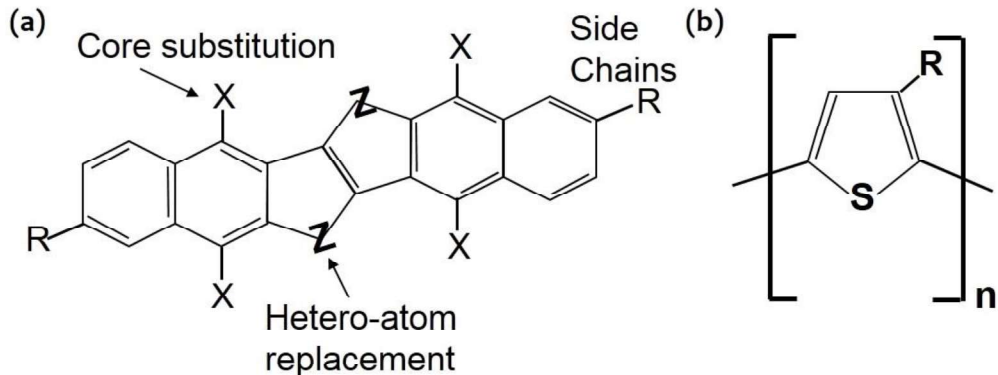
A very general categorization strategy of organic semiconductor is shown in Figure 1.3. Based on chemical structure, organic semiconductors can be primarily classified into two categories, small molecule semiconductors and polymeric semiconductors [Klauk, 2006, Weidner, 2008].



**Figure 1.3:** Classification of organic semiconductors.

In small molecule based organic semiconductors, the elemental conducting unit is a conjugated core, having countable number of carbon atoms. These conjugated units are arranged in a particular packing style in the final film which determines the efficiency of the inter-molecular charge transport in the semiconductor film. On the other side, in polymeric organic semiconductors, a conjugated monomeric unit repeats itself many times to make a single semiconducting chain. Both inter-chain and intra-chain charge conduction mechanisms in the polymeric semiconductors are more complex than small molecule semiconductors, because of higher degree of structural disorder in the semiconducting chains [Klauk, 2006, Weidner, 2008]. General chemical structures of a small molecule and polymeric organic semiconductors are shown in Figure 1.4. Further, on the grounds of processing, organic semiconductors can be categorized in two classes, vacuum processed and solution processed organic semiconductors. Vacuum processed organic semiconductors are generally small molecule semiconductors

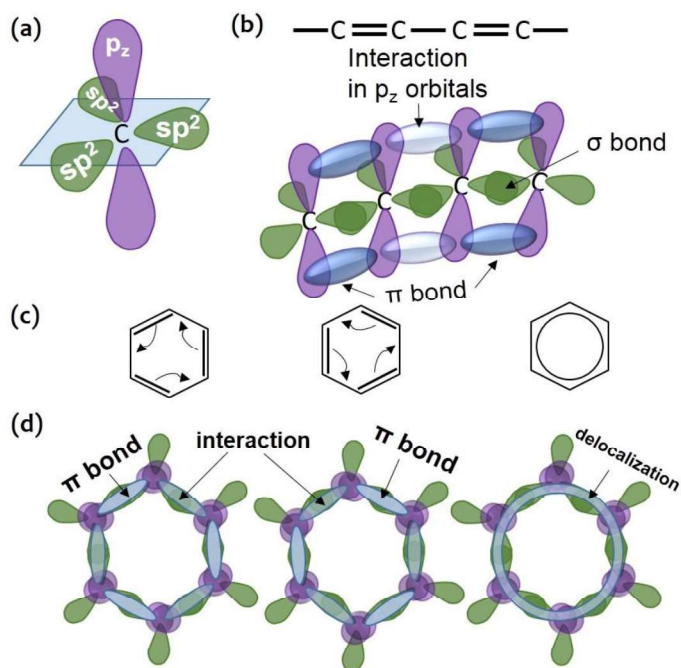
without any side chain on the main conjugated core. These types of semiconductors are generally insoluble in common organic solvents and hence are commonly thermally evaporated using vacuum systems. Whereas the solution processed organic semiconductors can be either small molecule or polymeric structurally, having a side chain substitution to render them soluble in organic solvents [Klausk, 2006, Logothetidis, 2014, Li, 2011, Weidner, 2008]. The solubility of these semiconductors in solvents, which depends on the net dipole moment of the molecule [Reichardt and Welton, 2011], affects the properties of the final film very critically.



**Figure 1.4:** General chemical structure of small molecule (a), and polymeric (b) organic semiconductors.

### 1.2.2 Structure

As the name suggests, organic semiconductors primarily contain carbon and hydrogen as their elemental constituents. The feature which distinguishes organic semiconductors from other organic compounds is the  $\pi$ -conjugation at intra-molecular level. All organic semiconductors have a conjugated core, having double bonds at alternate positions. Each carbon atom in a conjugated core is  $sp^2$  hybridized [Klausk, 2006, Weidner, 2008].



**Figure 1.5:** (a)  $sp^2$  hybridized orbitals in carbon atom. (b) Orbital level interactions in a small unit in a  $\pi$  conjugated molecule. (c) Canonical structures of benzene molecule. (d) Interactions in molecular orbitals of benzene and subsequent delocalization of  $\pi$  electrons.

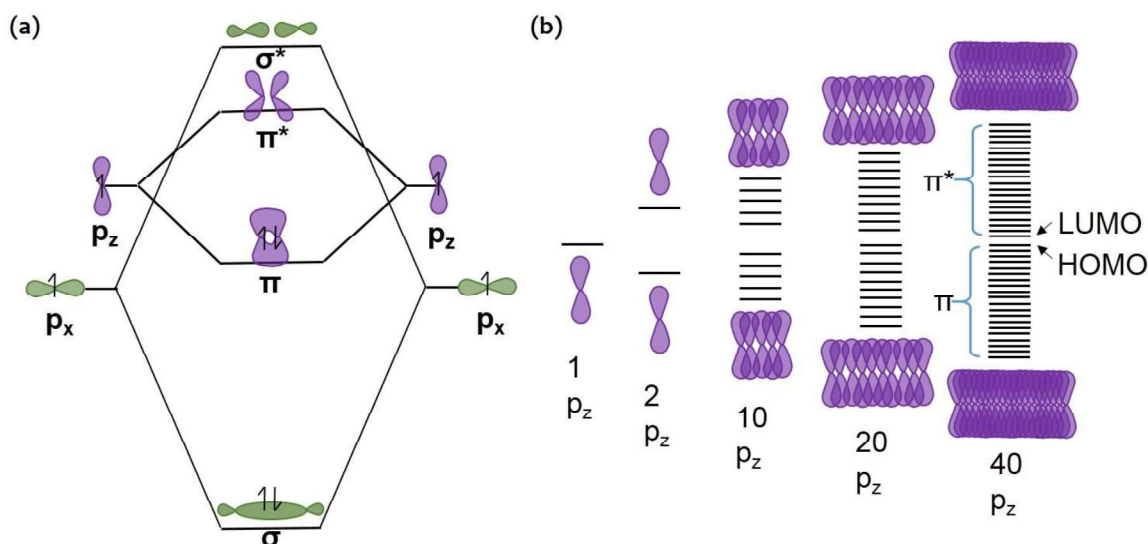
In Figure 1.5(a),  $sp^2$  hybridized atomic orbitals and  $p_z$  atomic orbital of a carbon atom are illustrated. Each of the three  $sp^2$ -hybridized molecular orbital of carbon overlaps with three

other molecular orbitals of its neighbors to make three  $\sigma$  bonds, leaving a  $p_z$  orbital in a plane perpendicular to plane of conjugated core. The overlapping in the electronic clouds of the two adjacent  $p_z$  orbitals leads to formation of a  $\pi$ -bond. In addition, there is a substantial interaction in  $p_z$  orbitals of carbon atoms bonded by a  $\sigma$  bond only. The formation of  $\sigma$  and  $\pi$  bond due to interaction of atomic orbitals is depicted in Figure 1.5(b). This interaction in the electronic clouds of  $p_z$  orbitals extends over whole molecule or polymeric chain and form an extended  $\pi$ -conjugated system.  $\pi$  conjugation enables  $\pi$  electrons to traverse beyond their  $\pi$ -bond within the molecule and outside the molecule.  $\pi$  conjugation and delocalization is explained in Figure 1.5(c) and 1.5(d) with the example of a benzene molecule. This delocalization of  $\pi$  electrons paves the foundation of charge transport in the organic semiconductors [Klauk, 2006, Logothetidis, 2014, Li, 2011, Weidner, 2008].

### 1.2.3 Physics

According to orbital theory, electronic wave functions of molecular orbitals are formed through linear combination (Addition and subtraction) of wave functions of atomic orbitals. The number of molecular orbitals formed is always equal to the atomic orbitals participating. The molecular orbital resulting from the sum of two atomic wave functions is known as bonding molecular orbital and has lower energy than the participating atomic orbitals. On the other hand, the molecular orbital obtained from the subtraction of the atomic wave functions is known as anti-bonding molecular orbital and has higher energy than the participating atomic orbitals [Liberles, 1966].

When two atomic orbitals of  $sp^2$  hybridized carbon atoms combine linearly,  $\sigma$ -bonding and  $\sigma^*$ -antibonding molecular orbitals corresponding to  $\sigma$  bond are formed. Simultaneously, due to combination of two adjacent  $p_z$  orbitals,  $\pi$ -bonding and  $\pi^*$ -antibonding molecular orbitals are also formed, which corresponds to  $\pi$  bond. However, due to weaker overlapping of  $p_z$  orbitals,  $\pi$  bond is weaker than the  $\sigma$  bond. Therefore, the energy of the  $\sigma$ -bonding is lower than that of  $\pi$ -bonding, while energy of the  $\pi^*$ -antibonding is lower than that of the  $\sigma^*$ -antibonding [Klauk, 2006, Weidner, 2008], which is graphically illustrated in Figure 1.6(a). Molecular orbitals in a conjugated molecule like benzene or pentacene are also formed similarly. In the bulk phase of the organic semiconductor, the merger of all the molecular orbitals of the individual molecules results into creation of quasi-bands, similar to inorganic semiconductors. In organic semiconductors, energy levels corresponding to HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) are defined, in contrast to continuous valence band and conduction bands in inorganic semiconductors. These are the energy levels that electrons must acquire to become a free carrier. The HOMO is the energy level at the top of a continuous band of occupied states, whereas the LUMO is the first available energy level in the unoccupied band [Klauk, 2006, Weidner, 2008]. Formation of HOMO and LUMO energy levels in organic semiconductors is shown in Figure 1.6(b). The energy gap between HOMO and LUMO levels is similar to energy band gap of inorganic semiconductors. The band gap of organic semiconductors lies generally between 1 to 4 eV.



**Figure 1.6:** (a) Linear combination of two  $p_x$  and two  $p_z$  atomic orbitals to form bonding ( $\sigma$  and  $\pi$ ) and antibonding ( $\sigma^*$  and  $\pi^*$ ) molecular orbitals respectively. (b) Linear combination of many  $p_z$  orbitals to form energy bands.

### 1.3 CHARGE TRANSPORT

In organic semiconductors, molecules interact with each other by relatively weak van der Waals forces. Therefore, electrons of  $\sigma$  bond are largely restricted within the individual molecules. However, due to interaction of adjacent  $\pi$  orbitals, corresponding electrons are delocalized in a large range, covering the entire molecule and beyond. Intra-molecular delocalization of electrons is generally weaker and is largely dependent on the molecular packing style. Increasing degree of  $\pi$ - $\pi$  interaction/overlapping leads to an enhanced delocalization and ultimately an efficient charge transport [Klauk, 2006, Meller and Grasser, 2009, Wöll, 2009]. This inter-molecular and intra-molecular delocalization pave the foundation of charge transport in the organic semiconductors.

Mechanism of charge transport in organic semiconductors is significantly different than their inorganic counterparts and is not fully understood yet. In silicon based devices, charge transport can be explained using band transport model. However, the band transport is applicable for high purity organic semiconductors at very low temperatures. Organic semiconductors inherently have high degree of disorder, which limit the applicability of band transport in practical situations [Klauk, 2006, Inokuchi, 1989, Klauk, 2012]. In addition, the one-electron approximation used in the band theory for inorganic semiconductors is no longer valid for organic semiconductors, as the polarization in these materials is a many-electron phenomenon [Eiduss and Silinsh, 2012]. For these reasons, the band model cannot fully explain the charge transport in organic semiconductors. Further grain imperfections and different molecular packing motifs make the charge transport in these materials really complicated to understand. Despite numerous complexities, several charge transport models for organic semiconductors have been proposed. Some of the widely studied transport mechanisms are briefly discussed below.

#### 1.3.1 Hopping Model

When the mean free path of the charge carriers becomes shorter than the atomic distance, then hopping becomes the main charge transport mechanism between localized states. This happens generally in low conductivity materials such as amorphous or organic semiconductors, in the absence of long range order. Carrier mobility for this type of transport can be expressed as following,

$$\mu = \mu_0 \exp \left[ \left( -\frac{T_0}{T} \right)^{\frac{1}{\alpha}} \right] \quad (1.1)$$

where  $\alpha$  is an integer ranging from 1 to 4. The second term signifies that hopping is a thermally activated process [Holstein, 1959].

### 1.3.2 Small Polaron or Energy Transfer Model

When transferring energy is thermodynamically more viable than charge, then it occurs by transferring the energy through a polaron. A polaron is formed from deformation of a molecule under influence of a charge particle. From the Holstein model, small polaron, the mobility of organic semiconductor can be described as

$$\mu = \sqrt{\frac{\pi}{2}} \frac{ea^2}{\hbar} \frac{J^2}{\sqrt{E_b}} (kT)^{-3/2} \exp \left( -\frac{E_b}{2kT} \right) \quad (1.2)$$

Where  $E_b$  is polaron binding energy, which is defined as the energy gain of an infinitely slow carrier due to the polarization and deformation of lattice.  $J$  is electron transfer energy and  $a$  is lattice constant [Holstein, 2000].

### 1.3.3 Multiple Trap and Release Models

In this model, a high concentration of localized energy states, which act as charge traps, are associated with a narrow delocalized band. When charge carriers interact with these states, they are trapped and released. This model is based on several assumptions. First, the carriers interacting with the localized states are trapped with a probability close to 1. Second, the release of trapped carriers is thermally controlled. The effective mobility can be given as a function of delocalized band mobility, trap density and thermal energy as following

$$\mu = \mu_0 \alpha \exp \left[ -\frac{E_t}{kT} \right] \quad (1.3)$$

Where  $\mu_0$  is delocalized band mobility,  $E_t$  is the trap density, and  $kT$  thermal energy.  $\alpha$  is the ratio of the effective density of states between the trap level and the delocalized band edge [Le Comber and Spear, 1970].

### 1.3.4 Grain Boundary Models

The Grain boundary model is a widely used hypothesis to explain the charge transport in polycrystalline materials [Chung-Chen *et al.*, 2004, Gundlach *et al.*, 2008]. In this model, it is assumed that the grain boundary has negligible thickness compared to the grain size. Since the barrier height for charges at the grain boundary plays very important role in the charge transport, the mobility of the polycrystalline materials considerably depends on the Fermi energy. The effective mobility  $\mu_{\text{eff}}$  in polycrystalline materials can be expressed as following,

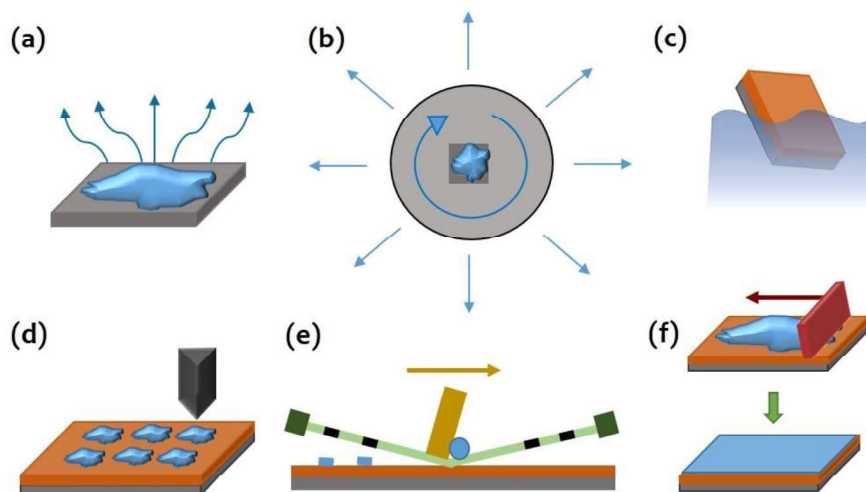
$$\frac{1}{\mu_{\text{eff}}} = \frac{1}{\mu_0} + \frac{1}{\mu_{\text{GB}}} \quad (1.4)$$

where  $\mu_0$  is the bulk mobility inside the grain, and  $\mu_{\text{GB}}$  is the grain boundary mobility [Ahmed *et al.*, 1985].

## 1.4 SOLUTION PROCESSING

In almost every practical electronics application, deposition of a thin film of the active material by a physical scheme with thickness ranging from a few nanometers to few micrometers is required. On similar lines, thin films of organic materials can be deposited either from evaporation processing based on vacuum systems or from solution processing [Weidner, 2008, Brütting and Adachi, 2012]. Vacuum processing requires thermal evaporation of materials in high vacuum systems and physical transport of evaporated material closer to substrate where it is deposited. Main vacuum processing techniques include organic molecular beam deposition

[Kowarik *et al.*, 2008] and organic physical vapor deposition [Laudise *et al.*, 1998]. Other techniques such as sputtering [Depla *et al.*, 2010] and laser based schemes [Norton, 2006] are seldom used in practice because of the thermal damage they cause to organic films. All the vacuum techniques provide good control over thin film properties and very widely used for practical purposes. However, they do not seem to fulfill the requirements of low cost and simplicity as promised by organic electronics, and apparently do not fall in the category of simplified low cost future technologies. On the other side, solution processing of organic materials offers all the advantages featured by organic electronics. In this type of processing, a liquid precursor of the organic material is prepared in a volatile solvent, which can be deposited on substrate in several ways [Allard *et al.*, 2008]. Some of the deposition schemes based on solution processing are illustrated in Figure 1.7.



**Figure 1.7:** Some common solution processing techniques; (a) Drop casting. (b) Spin coating. (c) Dip coating. (d) Inkjet printing. (e) Screen printing. (f) Blade coating.

Drop casting involves simple pouring of semiconductor liquid precursors [Bharti and Tiwari, 2016]. In spin coating, liquid precursor is dispensed on substrate and rotated at high speed to achieve uniformity [Ossila, 2016]. In dip coating, thin film is deposited by dipping the substrate in the precursor [Diao *et al.*, 2013]. In inkjet printing, small droplets of solution are ejected and deposited on substrate in a fixed patterned way [Sturm *et al.*, 2000]. In screen printing, the solution is pressed through a patterned screen on a substrate [Thaidigsmann *et al.*, 2013]. Blade coating requires the solution to be scraped with a blade on the substrate [Chen *et al.*, 2011]. These processes offer several process parameters to control the final film quality. Each of these processes has some advantages and disadvantages which are related to time elapsed in the process, material consumption and overall film quality. The main disadvantage of solution processing is the absence of a universal processing method viable with all the materials. Selection of an optimal solution processing method depends on several factors ranging from kind of material to final device application.

## 1.5 ORGANIC FIELD-EFFECT TRANSISTORS

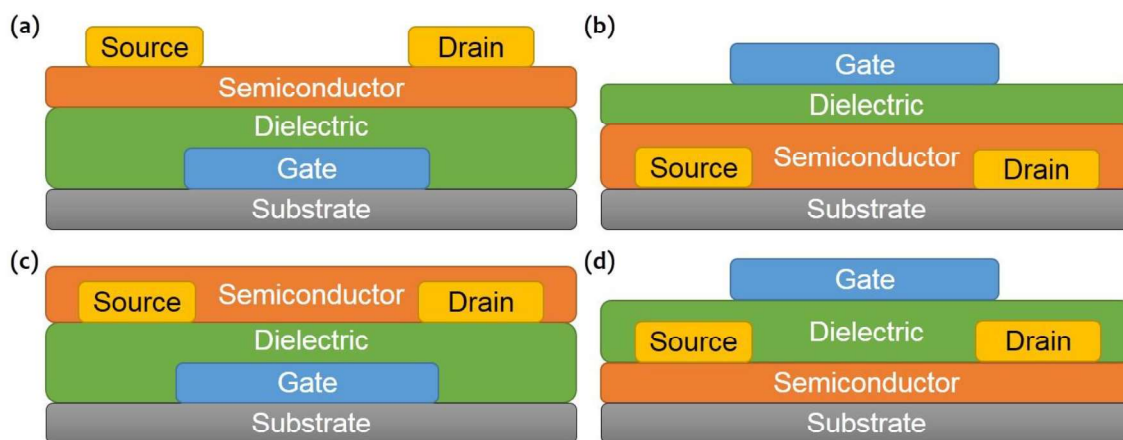
Organic field-effect transistors (OFETs) are the key devices in the organic electronics technology being the building blocks in numerous applications including flat panel displays [Lisong *et al.*, 2005], circuitry [Xu *et al.*, 2015], RFIDs [Myny *et al.*, 2010] and sensors [Torsi *et al.*, 2013]. First OFET was reported by Koezuka and coworkers in 1987 using a thiophene based polymer [Koezuka *et al.*, 1987]. Since then, several physical, chemical and electrical aspects of OFETs have been investigated in great detail. This exploration has resulted into significant improvement in device performance with mobility values rising from  $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [Babel and



Jenekhe, 2003] to more than  $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [Niazi *et al.*, 2015]. Though the performance of OFETs is lower than Si-based devices, OFETs are still in high demand because of broad range of applications and the ease with which they can be fabricated on variety of substrates including bendable plastics, papers and textiles.

### 1.5.1 Device Architectures

Structure of an OFET is slightly different than a conventional MOSFET. An OFET is a three terminal device with gate, source and drain as its three terminals. The conductivity in the channel region is controlled by applying the potential on gate, source and drain terminals. Opposite to conventional MOSFET structure, OFETs do not have physically defined source and drain regions, however, have source-drain contacts in form of metallic thin films. OFETs are generally fabricated on inert substrates. Based on relative position of dielectric layer and source-drain contacts, four different types of device architecture are possible, which are shown in Figure 1.8. First type of architecture is the bottom gate top contact. Second architecture is known as bottom gate bottom contact. Third and fourth types are top gate bottom contact and top gate top contact respectively [Klauk, 2006].

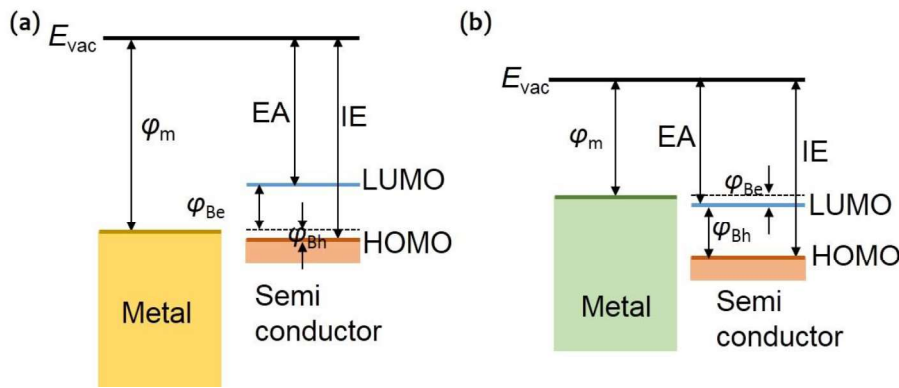


**Figure 1.8:** OFET device architectures; (a) Bottom gate top contact. (b) Top gate bottom contact. (c) Bottom gate bottom contact. (d) Top gate bottom contact.

### 1.5.2 Operating principles

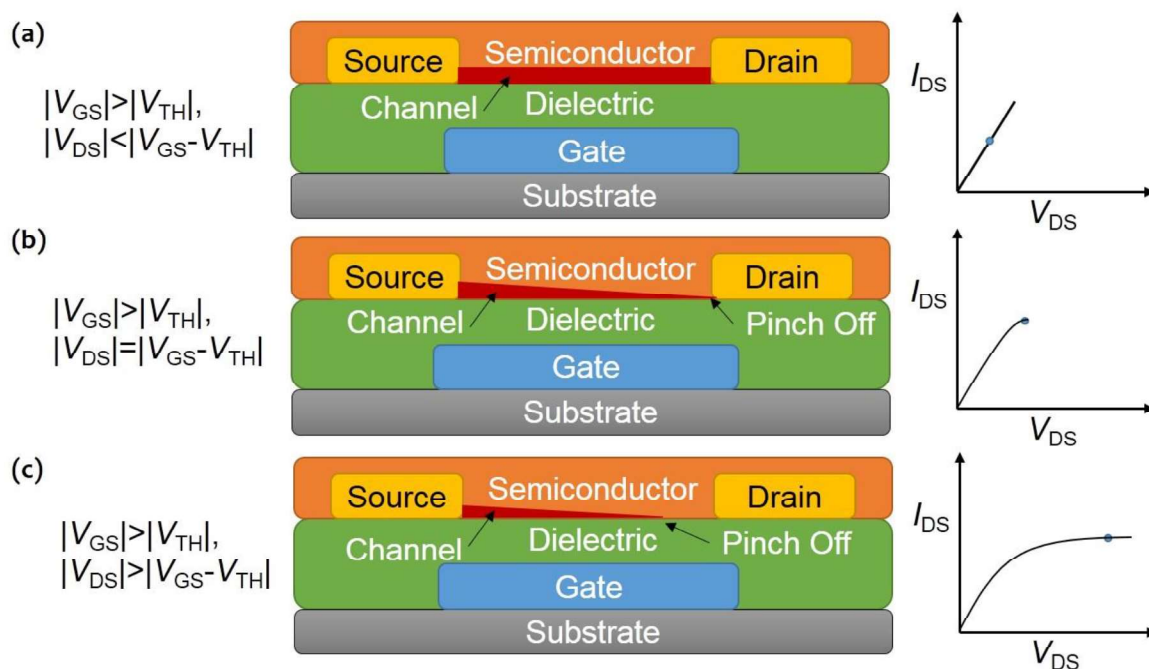
Some of the theories related to charge transport in organic semiconductors have already been reviewed briefly in section 1.3. However, before discussing the operating principles of OFETs, it is of vital importance to understand the basics of charge injection at semiconductor-metal interface. Semiconductor-metal interface critically governs the device performance by regulating the amount of the charge injected from metal to semiconductor [Klauk, 2006].

Charge injection from metal to semiconductor is dependent on energy level alignment between Fermi level of metals and HOMO or LUMO levels of the organic semiconductors. For p-type organic semiconductors (hole conduction), HOMO level of the organic semiconductors should match with the Fermi level of a high work function metal like gold or platinum [Brütting and Adachi, 2012]. Similarly, for n-type organic semiconductors (electron conduction), LUMO level should match with Fermi level of a low work function metal like calcium or magnesium. This is schematically illustrated in Figure 1.9. The injection barrier (amount of energy level mismatch between HOMO/LUMO and Fermi energy of metal) has to be overcome by appropriate means for an efficient charge injection and high performance in devices.



**Figure 1.9:** Metal-semiconductor energy band diagram for p-type (a), and n-type (b) organic semiconductors.

Figure 1.10 shows a bottom-gate bottom contact p-type OFET. When a negative potential is applied on the gate terminal and source is grounded, charges are accumulated in the semiconductor layer in the close vicinity of dielectric-semiconductor interface. However many traps and defect sites are present on the interface, and these sites have to be filled before the current can pass through the transistor. Therefore, a gate voltage higher than a certain offset voltage has to be applied to observe significant current in the transistor. This offset voltage is known as the threshold voltage of the device. When no potential is applied on the drain terminal, no current flows from the drain terminal of the device. When a small negative drain bias is applied, current flows through the drain terminal due to linear potential gradient. This region is known as the linear region of the OFET operation, as the current flowing is proportional to the applied drain bias. When the applied drain bias exceeds the difference of the applied gate bias and the threshold voltage, the channel starts pinching off from the drain side. Now only a constant saturated current can flow from the channel, value of which depends on the gate bias. Further increase in drain bias does not increase the drain current. This mode of operation of OFETs is known as saturation region [Klaauk, 2006].



**Figure 1.10:** Operating principle of an OFET in linear mode (a), onset of saturation (b), and saturation mode (c).

## 1.6 FACTORS AFFECTING PERFORMANCE OF OFETS

High electrical performance and stability are the prime objectives for OFETs to be deployed in practical applications. However, there are several factors which regulate the performance of OFETs and need to be given significant attention. These factors are sequentially presented in Figure 1.11. First factor is the properties of materials used as dielectric, semiconductor and metals. Dielectric constant of the insulator determines the operating voltage of the device [Ortiz *et al.*, 2010], whereas HOMO/LUMO levels of organic semiconductor and work function of the metal regulate the charge injection [Klauk, 2006]. Second factor is the properties of deposited film of semiconductor which include molecular packing motif and degree of crystallinity. Molecular packing motif determines the efficiency of inter-molecular charge transport [Kalita *et al.*, 2015, Reig *et al.*, 2015]. A More dense arrangement of semiconductor molecules leads to larger degree of  $\pi$ - $\pi$  overlapping and extended delocalization of electrons which results in an efficient charge transport. Crystallinity is the quantitative measure of order in the film, with higher crystallinity indicating higher order in the film and vice-versa. Higher degree of crystallinity will also lead to an efficient charge transport and a high performance device [Bharti and Tiwari, 2016]. Third factor is the quality of the functional interfaces in the device: dielectric-semiconductor and metal-semiconductor interface. Since the charge transport takes place in the few monolayers in the organic semiconductors in the vicinity of dielectric-semiconductor interface, the quality of this interface is very critical to device performance [Brütting and Adachi, 2012]. Presence of traps and defects at this interface is detrimental to the device performance. Similarly, the injection barrier at metal-semiconductor interface also limits the amount of charge injected into the semiconductor [Klauk, 2006]. Hence, efforts are needed to obtain a dielectric-semiconductor interface with enhanced uniformity and a metal-semiconductor interface with minimum injection barrier. Fourth factor is the processing conditions used for active layer deposition. A semiconductor can off course be deposited by different deposition techniques, however, never demonstrates similar performances. In addition, change in process parameters also cause a huge variation in device performance. All the different deposition techniques and process parameters actually change the interfacial conditions, surface morphology and grain properties, which brings a vast disparity in performances of devices with the same semiconductor. Fifth factor is the device architecture. Performances of OFETs of the same semiconductor in different architectures are different, which is due to different contact resistances and interfacial conditions. All of the above issues have to be given significant consideration when performance is a major concern.

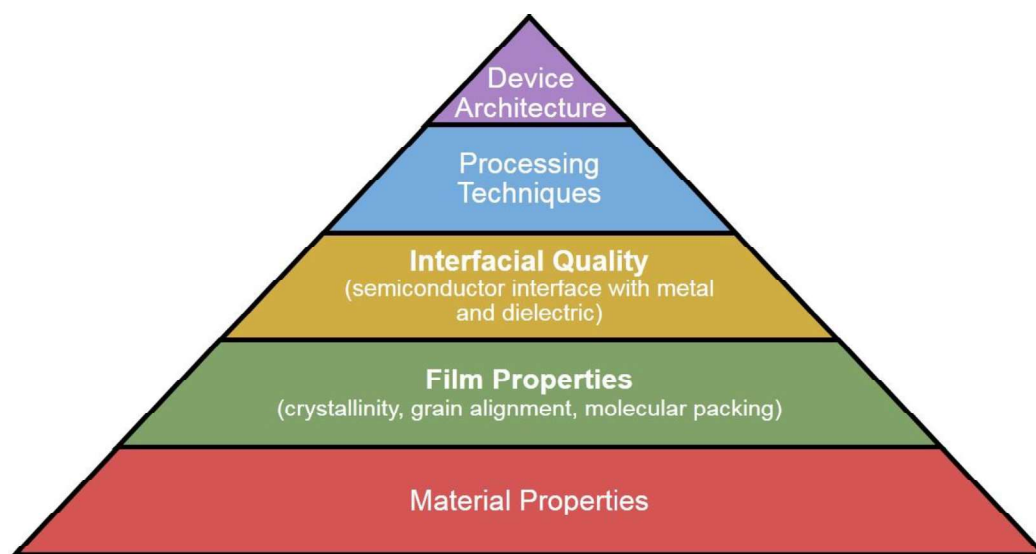


Figure 1.11: Various factors affecting performance of devices.

## 1.7 SENSORS BASED ON OFETS

There are several applications in which OFETs have been successfully integrated including flexible displays [Lisong *et al.*, 2005], organic circuitry [Xu, Liu, Khim and Noh, 2015] and sensors [Torsi *et al.*, 2013]. OFETs based sensors also are of special interest to the scientific community because of their applications in sensing a wide range of external stimuli which include pressure, chemical, biological, gas, light, humidity and radiation. Electronic skin (e-skin) [Nawrocki *et al.*, 2016] and electronic nose (e-nose) [Wedge *et al.*, 2009] are the example of OFET based pressure sensors. These devices detect pressure and force in static or dynamic mode. In pressure and temperature-sensitive artificial skin used in the robotics technology, pressure-sensitive rubber and thermal sensors are used collectively [Grossard *et al.*, 2013]. Operational Concept of OFET based chemical and gas sensors is similar. Analyte molecules get adsorbed in different locations in the active layer, especially in the grain boundaries. These foreign molecules act as charge trapping/detrapping sites and alter potential barrier between grains, which brings change in the on current and threshold voltage of the device [Zhang *et al.*, 2015]. OFETs as efficient bio-sensors have also been explored in great detail, where the OFETs have been used in two different configuration; ion sensitive OFETs (ISOFETs) and electrolyte gated OFETs (EGOFETs) [Kergoat *et al.*, 2012, Sokolov *et al.*, 2009]. In ISOFETs, a given electrolyte and insulator are in contact. The external gate electrode is immersed into the electrolyte and the drain current is determined by the potential of the electrolyte-insulator interface. It is viable to sense several biomolecules, by using a particular electrolyte, sensitive to a given analyte. In EGOFETs, organic semiconductor layer is in direct contact with a thin layer of electrolyte. Upon application of gate potential, electrical double layer is formed in the electrolyte. A low voltage operation is possible due to high capacitance density of the electrolyte. In addition, incorporation of the bio-receptor as a part of transistor structure has also been explored. Due to light sensitive nature of organic semiconductors, OFETs have also been extensively used as photo-detectors. Upon exposure to the light, excitons (bound pairs of electron and hole) are generated, which eventually dissociate into free charge carriers. More mobile carriers are collected at drain terminal increasing the drain current, whereas less mobile carriers gets trapped on the dielectric-semiconductor interface causing a threshold voltage shift [Baeg *et al.*, 2013, Wakayama *et al.*, 2014]. Performance advancement has led to improved photo-response of OFETs comparable to inorganic photo-detectors. Functional concept of humidity sensors is similar to chemical sensors, where water molecules get trapped in the grain boundaries of organic semiconductor and the electrical performance of OFETs are altered [Park *et al.*, 2013, Subbarao *et al.*, 2016]. Area of Radiation sensors based on organic devices is relatively a novel area. Conceptually, high energy radiation can alter the semiconductor morphology and thus the electrical performance, which can be calibrated in the form of electrical response [Raval *et al.*, 2013].

## 1.8 CURRENT STATUS

An extensive research advancement has been observed in the field of OFETs and related applications in past few years. Though the contribution of research and development of previous two decades is enormous and is the foundation of current stage of organic electronics, however, to ascertain the current trends of device performance, a brief overview of some of the main research outcomes related to high performance OFETs is presented in Table 1.1.

**Table 1.1:** Comparative summary of various studies reporting high performance OFETs in previous five years. OSC: Organic semiconductor; Subs: Substrate; Dielec: Dielectric; Dep. Method: Deposition Method; Op. Vol: Operating Voltage; Cap: Capacitance Density

OSC	Subs.	Dielec.	Dep. Method	Op. Vol. (V)	$\mu_{avg}$ ( $cm^2 V^{-1}s^{-1}$ )	$\mu_{max}$ ( $cm^2 V^{-1}s^{-1}$ )	$V_{TH}$ (V)	$I_{ON}/I_{OFF}$	Cap. (nF/cm <sup>2</sup> )	Ref.
C8BTBT: PMMA	Si	SiO <sub>2</sub>	PASVA	40	1.1 ±0.78	3.8	-14.9 ±6.65	10 <sup>4</sup>	30	[Kumatani et al., 2012]
TIPS-PEN	Si	SiO <sub>2</sub>	Micro-tubes, Drop cast	60	1.2	1.73	-	10 <sup>6</sup>	10.8	[Kim et al., 2012]
TIPS-PEN: PTAA	Glass	Al <sub>2</sub> O <sub>3</sub> /PVP	Spin cast	12	1.89 ±0.49	2.82	-11.9 ±1.9	-	2.94	[Hwang et al., 2012]
TIPS-PEN	Si	SiO <sub>2</sub> /BCB	Droplet pinning	80	2.4 ±0.6	3.8	-6 to -35	10 <sup>5</sup>	10	[Li et al., 2012]
TIPS-PEN	Si	SiO <sub>2</sub> /OTS	Inkjet Printing, SVA	60	-	1.7	-	-	-	[Kim et al., 2012]
TIPS-PEN:PS	Glass	PVA	Spin Cast	2-5	-	1	-	-	12.2	[Feng et al., 2013]
TIPS-PEN	Si	SiO <sub>2</sub> / PVP	Spray Cast	40	0.122	0.35	11.3	>10 <sup>4</sup>	6.2	[Shao et al., 2013]
DPP-TT	Glass	PMMA	Bar coating	60-80	1.64 ±0.41	2.83	-41.6 ±2.5	-	-	[Khim et al., 2013]
TIPS-PEN	Si	SiO <sub>2</sub>	Zone cast	100	-	0.67	-18.9	6.3 × 10 <sup>4</sup>	-	[Su et al., 2013]
C6-DNT-VW	Si	SiO <sub>2</sub>	Solution crystallization	100	6.2 ±1.62	9.5	-42 to -65	10 <sup>6</sup> -10 <sup>7</sup>	-	[Okamoto et al., 2013]
TIPS-PEN	Si	SiO <sub>2</sub> / PTS	FLUENCE	100	8.1 ±1.2	11	-	10 <sup>6</sup> -10 <sup>8</sup>	-	[Diao et al., 2013]
C8BTBT: PS	Glass	PVP-HDA	Off-center spin cast	20-40	25	43	-1.4 to -11.5	10 <sup>3</sup>	-	[Yuan et al., 2014]
TIPS-PEN	Si	SiO <sub>2</sub> / PTS	fluidic channel	40	0.71	2.18	-	10 <sup>5</sup> -10 <sup>7</sup>	-	[Kim et al., 2014]
TIPS-PEN	Si	SiO <sub>2</sub>	Lateral confinement	40	2.02 ±0.68	2.70	-	1.04 ×10 <sup>6</sup>	10	[Giri et al., 2014]

TIPS-PEN	Si	SiO <sub>2</sub>	Non-isotropic solvent evaporation	40	0.52	0.63	-3.5 ±1.1	4.8 × 10 <sup>5</sup>	6.0 ±0.4	[Pitsalidis et al., 2014]
PTDPPTF T4	Si	SiO <sub>2</sub>	Solution shearing	60-100	3.13 ±0.55	3.94	-15 ±6	10 <sup>6</sup>	10	[Lee et al., 2014]
Pentacene	PET	PMMA/PVP	Thermal Evap.	50	-	1.51	-20.1	10 <sup>5</sup>	-	[Yi et al., 2015]
PTDPPTF T4	Si	ePVDF-HFP	Spin coating	5	1.09 ±0.44	2.11	-0.67 ±0.31	2 × 10 <sup>4</sup>	8.4	[Wang et al., 2015]
diF-TESADT: PS	Si	SiO <sub>2</sub>	Blade coating	10	-	6.7	<1	> 10 <sup>5</sup>	9.5 - 11	[Niazi et al., 2015]
TIPS-PEN: PαMS	Si	SiO <sub>2</sub>	Blade Coating	10-60	-	4.6	-	-	-	[Niazi et al., 2016]
DPPT-TT	Si	SiO <sub>2</sub>	Slot-die coating	60	-	4.6-7.2	-	-	-	[Chang et al., 2015]
PDFDT	Glass	PMMA	Bar Coating	80	1.41	2.19	-50.7 ±14	2.5 × 10 <sup>4</sup>	6.20	[Nketia-Yawson et al., 2016]
diF-TESADT: PTAA	Glass	Cytop	Electrostatic Spray	60	1 ±0.3	1.7	-7.9 ±2.8	10 <sup>3</sup>	2.2	[Pitsalidis et al., 2016]
C8BTBT: C16IDTBT	Glass	Cytop	Spin	25-200	9.4	13	-	> 10 <sup>3</sup>	-	[Paterson et al., 2016]
TIPS-PEN	Si	SiO <sub>2</sub> /BCB	nano-wire array	100	6.91	9.71	-56.9	1.8 × 10 <sup>6</sup>	10.1	[Kim et al., 2016]
C10-DNBDT-NW/PMMA	Si	SiO <sub>2</sub>	Continuous edge-casting	30	10.6	17	-	-	26.8	[Soeda et al., 2016]

It can be observed from the Table that progress in the research and development in the area of semiconductor materials and processing has brought significant improvement in the performance of the devices. The mobility has been improved by more than an order in the last decade with mobility values ranging up to 43 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. In addition, small molecule based semiconductors like TIPS-pentacene, diF-TESADT and C8BTBT have been increasingly preferred over polymer based organic semiconductors for producing high performance OFETs due to their inherent high mobility and stability. However, most of these high performance OFETs are still being fabricated on rigid substrates like silicon or glass. Most of these OFETs have incorporated polymeric dielectrics in the OFET architecture to achieve a fine quality of dielectric-semiconductor interface. Various novel solution based deposition methods like

droplet pinning, spray coating, bar coating, zone casting, slot-die coating have been proposed in past few years, which have contributed towards performance advancement in OFETs. Though, the performance has been improved, relatively lesser attention has been paid to reduce the operating voltage of the devices and no significant advancement has been observed with respect to operating voltage of the device. In most of the studied devices, operating voltage varies from 30 to 100 V. The maximum mobility higher than  $40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  has been achieved, however at high operating voltages. In addition, the current on-off ratios have been shown to lie in ranges of  $10^4$  to  $10^6$  for most of the OFETs.

## 1.9 RESEARCH FOCUS AND THESIS ORGANIZATION

A remarkable advancement has been observed in the last decade in the research related to organic materials, their synthesis, exploration of various physical and chemical properties, electrical performance of related devices and several applications. Dissemination of these research outcomes has given a profound thrust to research interest in the domain of organic materials and related applications. There are plethora of research arenas in organic devices and applications, which deal with numerous aspects related to physics, chemistry and processing of materials.

One of the focuses of the current work is to produce high performance field-effect transistors on rigid and flexible platforms by means of improving the crystallinity of the active semiconductor layer and interface quality at the junction of dielectric and semiconductor layers. Nonetheless, selection of an appropriate organic semiconductor material is very crucial for accomplishment of these research aims. With high priority goals of affordability and easy processing, selection criterion points out towards solution processed organic semiconductors. In solution processed semiconductors also, search was restricted to small molecule semiconductors due to their superior performance as compared to polymeric semiconductors. Among many high performance small molecule solution processed semiconductors like C8-BTBT, TES-ADT, TIPS-pentacene, diF-TES-ADT; TIPS-pentacene was selected as the semiconductor material for this research work due to several reasons. First, TIPS-pentacene is a derivative of pentacene, the most exhaustively explored organic semiconductor. Second, it is highly air stable. Third, it has the inherent property of making large semiconductor crystals on solvent evaporation. With TIPS-pentacene as the active semiconductor layer, following research aims were set,

- To boost the electrical performance of the OFETs by improving crystalline order in the active layer and quality of dielectric-semiconductor interface.
- To achieve the merits of superior performance at low operating voltages on flexible substrates.
- To deploy high performance flexible devices in sensing applications.

To achieve the first goal, the improvement in the crystallinity has been sought by solvent and polymer additives in the TIPS-pentacene solution. Second objective has been achieved with TIPS-pentacene:polymer blend flexible OFETs, which operate at lower voltages than corresponding rigid OFETs. Third aim has been fulfilled by employing the flexible OFETs as visible and ultra-violet light detecting elements.

This thesis has been organized as following:

Chapter 2 provides the fundamental conceptual background of various processing and characterization techniques used in the study. In addition, a brief overview on characteristics parameter extraction techniques for OFETs is given.

Chapter 3 presents the effect of structural dissimilarity of solvent additive from the main solvent on the crystallinity of the active layer and resulting device performance.

Chapter 4 presents a comparative analysis of electrical performance and stability of two different types of OFETs; neat TIPS-pentacene on  $\text{SiO}_2$  dielectric and TIPS-pentacene:PS blends on  $\text{SiO}_2$  dielectric.

In chapter 5, two device strategies (neat TIPS-pentacene on HfO<sub>2</sub>/PVP and TIPS-pentacene:PS blend on HfO<sub>2</sub>) have been realized on flexible PET substrates and compared for electrical performances.

Chapter 6 reports on high performance, TIPS-pentacene:PS blend flexible OFETs. Apart from being operated on low voltages, a high degree of electro-mechanical stability in these OFETs has also been demonstrated.

Chapter 7 presents the photo-response of low voltage TIPS-pentacene OFETs with HfO<sub>2</sub>/PVP gate dielectric under red, green and blue illumination. In addition, the effect of UV irradiation on the performance of flexible OFETs has also been investigated.

Chapter 8 summarizes the research work done in this thesis and provides conclusion and options for future extension.

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