

## *Chapter 1*

# **INTRODUCTION**

## INTRODUCTION

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### 1.1 Organic Electronics

Recently, low-cost organic electronics is an attractive and active area of research in the field of semiconductor technology. The invention of organic electronics offers flat and flexible platform to the electronic industries [Wang *et al.* (2011)]. Organic based electronic devices have a number of properties that can overcome a few major problems associated with inorganic semiconductor based electronic devices [Sun *et al.* (2005), Jeong *et al.* (2013)] therefore organic electronics is an emerging scientific area of global active research and prospective huge technological and commercial application.

Organic electronics possesses a number of advantages over conventional electronics. It is more flexible and light in weight. It does not require vacuum processing and lithography and requires low-cost substrates (plastic, paper, even cloth...) and conventional printing and patterning techniques for device fabrication. Therefore, it is a low-cost electronics. Organic electronics brings new glimmer to electronic systems and opens the door to many exciting and advanced new applications which would not be possible with silicon or copper [Jeong *et al.* (2013), Cataldo *et al.* (2013), Li *et al.* (2008), Kuo *et al.* (2005), Reese *et al.* (2004)]. It is one of the latest fascinating technologies that smoothens the progress of innovative electronic applications in various fields such as RFID-tags, flexible solar cells, interactive toys, rollable displays *etc.* which have entered the recent electronics market. OLEDs are one of the first few organic electronics appliances which entered the market with impressive enthusiasm in research and in public.

Organic electronics is biodegradable in nature because it consists of carbon atom; hence, it has possibility to blend with food and medical system where inorganic electronics are not applicable. As organic electronics is based on carbon-based semiconductors, the features of organic semiconductors can be tuned with chemistry (by changing their chemical composition) in order to get wide range of possibilities for novel applications. The popular applications of organic electronics are in the area of flexible displays as well as in printed electronics and photonics. A brief comparison between Organic and Inorganic Electronics [Wang *et al.* (2011), Sun *et al.* (2005), Jeong *et al.* (2013), Cataldo *et al.* (2013), Li *et al.* (2008), Kuo *et al.* (2005), Reese *et al.* (2004), Newman *et al.* (2004), Dodabalapur *et al.* (2006), Sundar *et al.* (2004), Zschieschang *et al.* (2003), Klauk *et al.* (2002)] has been presented in Table 1.1

**Table 1.1** Comparisons of Organic Vs Inorganic Electronics

Parameters	Organic Electronics	Conventional (Inorganic) Electronics
<b>Cost</b>	Low cost per unit area (\$5 / ft <sup>2</sup> )	High cost per unit area (\$100 / ft <sup>2</sup> )
<b>Capital Cost</b>	Low capital flexible plants	High capital dedicated plants
<b>Substrate area</b>	Large area	Small area
<b>Device Size</b>	10 ft x Roll to Roll	< 1m <sup>2</sup>
<b>Weight</b>	Light	Heavy
<b>Material</b>	Compatible with Flexible Plastic Substrate	Requires Rigid substrates
<b>Required Conditions</b>	Ambient Processing	Ultra Clean room
<b>Process required</b>	Continuous Direct Printing	Multi-step Photolithography

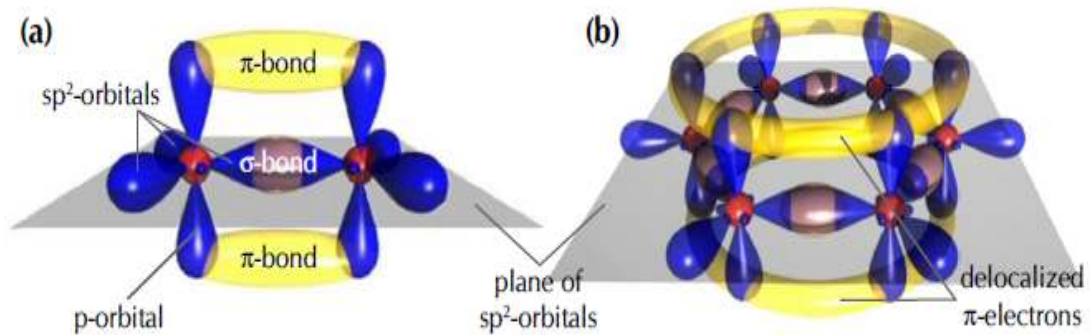
## 1.2 Organic Semiconductors (OSCs)

Organic materials can be simply prepared and processed at low price. These materials possess high strength and good flexibility. They are generally insulating in nature. However, low conductivity in iodine-doped oxidized polypyrrole was reported by Weiss *et al.* in 1963, and subsequently in 1977 high conductivity in iodine-doped oxidized polypyrrole was reported by MacDiarmid, Shirakawa and Heeger [Chiang *et al.* (1977)]. This study (discovery and development of conductive polymers) was rewarded by the Nobel Prize in chemistry in the year 2000. This research was the first step in the discovery of organic semiconductors. A lot of research work followed this discovery to develop novel organic semiconductors. The excellent chemical, mechanical and electrical properties of organic semiconductors provide flexible platform for the progress of efficient performance organic thin-film electronic devices such as organic field-effect transistors (OFETs) [Brabec *et al.* (2010)], organic solar cells [Fabiano *et al.* (2010)], organic light emitting diodes (OLEDs) *etc.* [Kalyani *et al.* (2012), Zhong *et al.* (2011)].

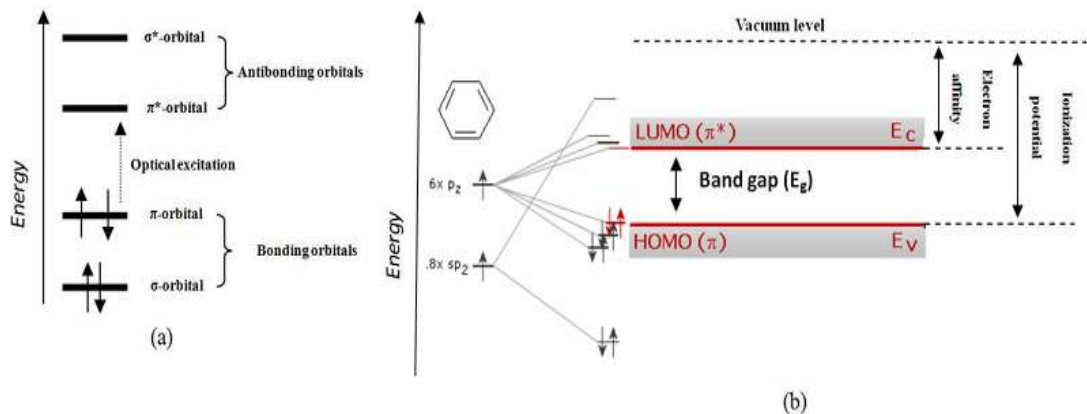
### 1.2.1 Conjugated Polymers

Polymers are characterized into two types: saturated and unsaturated polymers. Saturated polymers have single bonds, whereas unsaturated polymers have double bonds too. Conducting polymers are always unsaturated and exhibit semiconducting properties due to the presence of alternate single and double bonds in the polymer chain. Single C-C bonds in the polymer chain are  $\sigma$ -bonds and formed due to the overlapping of two  $sp^2$  hybridized orbitals, whereas, double C=C bonds are formed due to the sidewise overlapping of the remaining unhybridized  $p_z$  orbitals on each carbon atom. Such overlapping produces a different kind of orbitals which is known as  $\pi$ -bond. The sigma-pi model for ethylene and delocalized  $\pi$ -electron-system in a benzene ring is shown in Fig 1.1. Therefore, alternate single and double bonds in

polymer are called  $\pi$ -conjugate polymer system [Streetman *et al.* (2012), Cox *et al.* (1987)]. The  $\pi$ -electron density of conjugated polymers is divided into  $\pi$ -band and  $\pi^*$  band. Generally  $\pi$ -band is known as HOMO (Highest Occupied Molecular Orbital) which is completely filled and  $\pi^*$  band is known as LUMO (lowest Unoccupied Molecular Orbital) which is completely empty. In a polymer,  $\sigma$ -bond (covalent bond) forms the backbone of a polymer and the bond strength of  $\sigma$ -bond is higher compared to the  $\pi$ -bond (Van der waals force) strength of a conjugate polymer. The energy difference between  $\pi$  and  $\pi^*$  bands is known as the band gap of the polymer. Generally the range of energy band gap for the commonly known conjugate polymer is 1–4 eV [Cantatore *et al.* (2000)]. The energy band diagram for a conjugate polymer is shown in Fig. 1.2.



**Fig. 1.1** (a) The sigma-pi model for two  $sp^2$ -hybridised carbon atoms, as in ethylene, (b) Delocalized  $\pi$ -electron-system in a benzene ring consisting of six  $sp^2$ -hybridised carbon atoms [Kozel *et al.* (2006)].



**Fig. 1.2 (a)** The energy levels of a  $\pi$ -conjugated molecule, the lowest electronic excitation is between the bonding  $\pi$ -orbital and the antibonding  $\pi^*$ -orbital, **(b)** collection of molecular orbitals form bands separated by an energy gap [Teng *et al.* (2010)].

### 1.2.2 Conjugated Polymers as Semiconductors

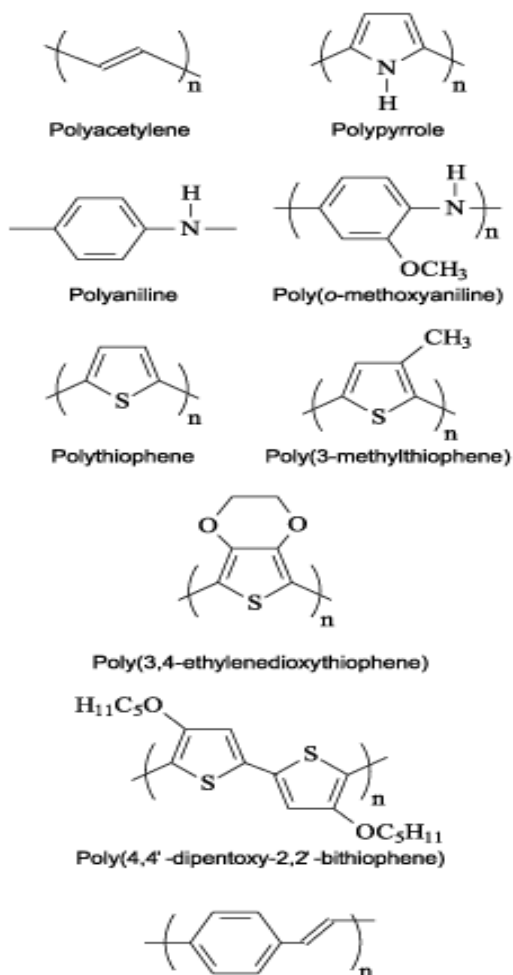
An essential condition for a polymer to be an organic semiconductor is that it must have conjugate bonds. Organic semiconductors are generally carbon based materials having alternate single and double bonds and exhibit similar conducting properties as inorganic semiconductors. They may be single molecules, oligomers (small chains) or polymers [Garnie *et al.* (1997)]. Compared to silicon technology, organic semiconductors exhibit a few interesting advantages. A comparison between organic and conventional semiconductors [Li *et al.* (2008), Garnie *et al.* (1997), kagan *et al.* (2003), Dimitrakopoulos *et al.* (2001), Huang *et al.*, Shur *et al.* (1984), Kelley *et al.* (2003), Ling *et al.* (2004), Brown *et al.* (1997)], is given in the Table 1.2.

**Table 1.2** Comparisons between Organic and Inorganic Semiconductors

Organic Semiconductors	Inorganic Semiconductors
Weaker intermolecular bonding (van-der-waals bonded)	Covalent bonding
Direct band gap material	Silicon is indirect band gap material (no light emission is possible)
Their production is easy	It has complex production process
Excellent flexibility	Stiff
Easily processable	Processing is difficult
Compatible with plastic substrates	Brittle, hence, incompatible with plastic substrates

Processable at low temperature	Requires high temperature for processing
Provide large coverage area at low cost	Very expensive to process onto large area substrates
Low mobility	High mobility

Organic semiconductors are used as active elements in organic electronics and optoelectronic devices such as organic light emitting diodes (OLED), organic solar cells, and organic field effect transistors (OFET). Organic semiconductors have many structures. Structures of few organic semiconductors are given in Fig. 1.3.



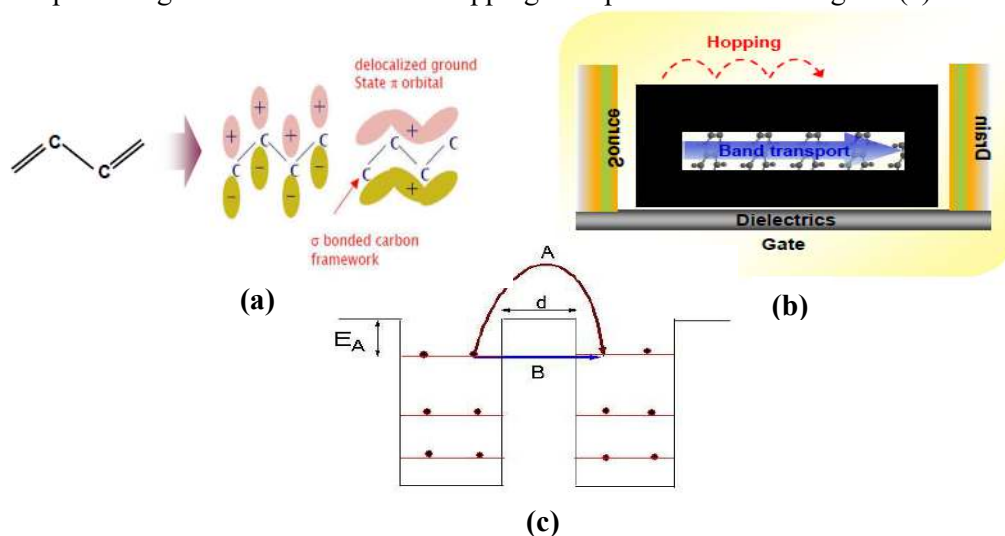
**Fig. 1.3** Structures of few organic semiconductors [Cantatore *et al.* (2000)]

### 1.2.3 Conduction Mechanism in Organic Semiconductors

Carrier transport mechanisms in organic semiconductors are mainly through tunneling and/or hopping of the thermally-assisted charge carriers between adjacent localized states and mobility gaps [Christos *et al.* (2002)]. OSCs have alternate double and single bonds, and if all the carbons of an organic semiconductor lie in the same plane, then, the  $\pi$ -electrons overlap and become delocalized as shown in the Fig. 1.4 (a). These delocalized states permit charge carriers to move through them for current conduction. The charge carriers can transport in two ways for the conduction.

**Band Transport:** In this type, the carrier transport takes place from HOMO to LUMO by  $\pi$ -orbital overlap in energy band of an organic semiconductor as shown in Fig 1.4 (b). Such type of carrier transport occurs in the crystalline stable organic semiconductors.

**Hopping Transport:** It is a type of tunnel effect among the neighbor molecules assisted by phonons (lattice vibration). Such type of charge transport occurs in the amorphous organic semiconductors. Hopping transport is shown in Fig 1.4 (c).



**Fig. 1.4** (a) Overlapping of  $\pi$ -electrons along the chain, (b) Hopping and band transport [Lee (2011)], (c) Hopping and tunneling between the two delocalized states [Hamadani (2007)].



### 1.2.4 Doping of Organic Semiconductors

Generally, organic semiconductors are intrinsically insulators; therefore, they show poor conductivity (less than  $10^{-8}$  S  $\text{cm}^{-1}$ ). This drawback can be simply overcome by doping. Dopants increase the mobile charge carrier density which results in improvement in conductivity of organic semiconductors. The conductivity of organic semiconductors can be easily modified from insulator to good conductor by altering the dopant type, doping level, polymer regioregularity and blending of organic semiconductors with various organic nanofillers and other semiconductors. Examples for n-doped and p-doped polymers are shown respectively in Fig. 1.5, and Fig. 1.6 [Pron *et al.* (2002)].

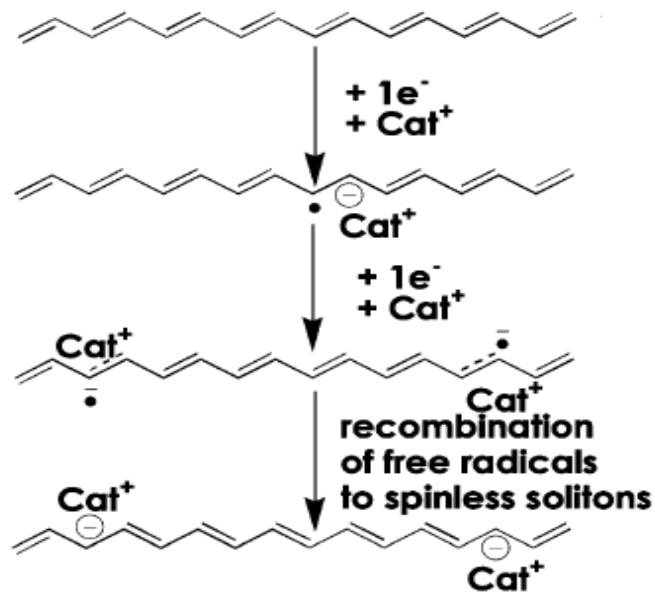


Fig. 1.5 n-type doping of poly(acetylene) [Pron *et al.* (2002)]

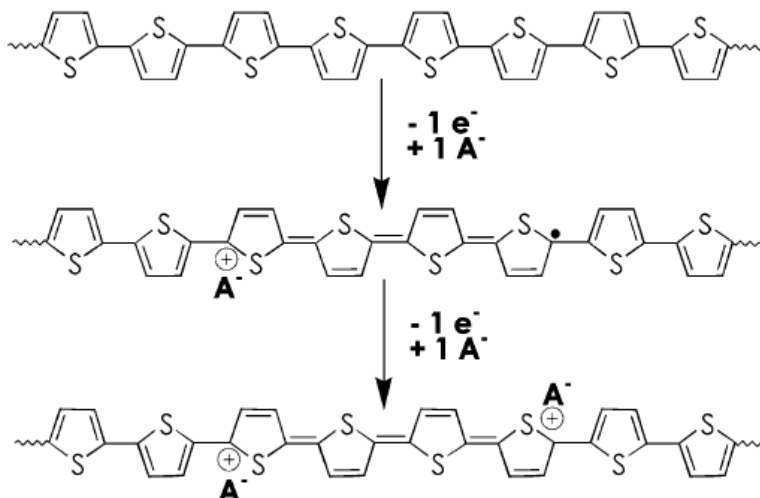


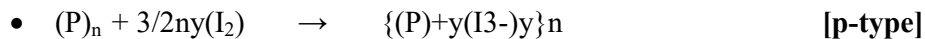
Fig. 1.6 p-type doping of poly(thiophene) [Pron *et al.* (2002)]

#### 1.2.4.1 Doping Methods

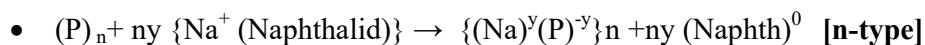
Generally there are four type of doping methods used for the doping of organic semiconductors [Menke (2013), Marius *et al.* (2010), McGehee *et al.* (1999)].

##### (a) Chemical Doping

This type of doping involves oxidation for p-type doping and reduction for n-type doping of organic semiconductor as described below



Other dopants may be  $ClO_4^-$ ,  $SO_4^-$ , halides ( $X^-$ ),  $BF_4^-$  etc



Other dopants may be alkali metal ions,  $Ca^{++}$  etc.

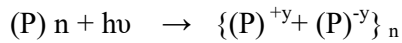
##### (b) Electrochemical Doping

In this technique an electrode supplies redox charges to the OSCs. Here, the doping level can be controlled by controlling the voltage applied between the organic semiconductor and the electrode as described below.

- $(P)_n + ny \{ Li^+ (BF_4^-) \}_{solu} \rightarrow \{(P)^{+y}(BF_4^-)^y\}_n + ny Li$  (as anode) **[p-type]**
- $(P)_n + ny Li$  (as anode)  $\rightarrow \{(Li^+)_y(P)^{-y}\}_n$  **[n-type]**

### (c) Photo Doping

Here the excess free carriers are generated due to the absorption of photons ( $h\nu > E_g$ ) by the organic semiconductor. Photo doping can be doped by photo-excitation; the organic semiconductor is locally oxidized and nearby reduced by photo-absorption and charge separation (electron-hole pair creation) as described below.



Where  $y$  is the number of photo excitation (depends upon the pump rate in competition with the recombination rate).

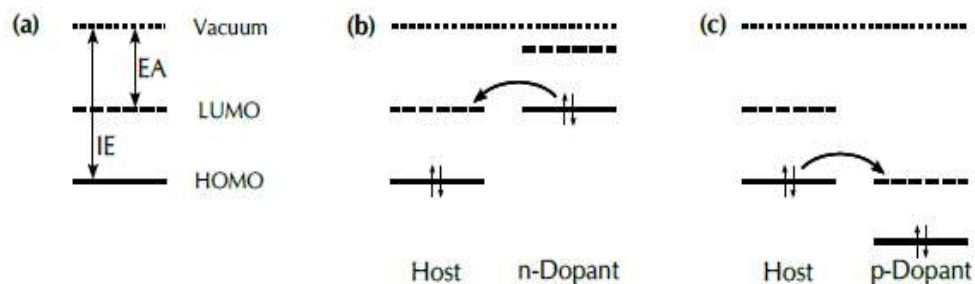
### (d) Interfacial Doping

Current carrying charge carriers can be injected into the organic semiconductors at the interface with a metal contact.

#### 1.2.4.2 Doping Mechanism

Generally, doping is a two step process. In the first step, the dopant gets ionized and transfers an electron (or a hole) to the host material by leaving a hole (or an electron) at the dopant molecules. Then, the electron (hole) has to dissociate against the coulomb attraction of the hole (electron) left on the dopant [Menke (2013)]. This doping principle is valid for both conventional as well as organic semiconductors. In the first step of the molecular doping of an organic semiconductor, an appropriate dopant molecule is required. Ionization energy (IE) is the energy difference between the HOMO and the vacuum level, as shown in Fig. 1.7, which requires removing the least bound electrons from the molecules. On the other hand, electron affinity (EA) is the energy difference

between the LUMO and the vacuum level. A dopant molecule with a low IE is expected to donate electrons and so used as an n-dopant, while p-dopants usually have high EA and allow accepting the electrons.



**Fig. 1.7** Doping mechanisms in OSCs (a) Energy levels of OSCs, (b) n-doping: an electron is transferred from the HOMO of the dopant to the LUMO of the host, (c) p-doping: an electron is transferred from the HOMO of the host to the LUMO of the dopant, generating a hole at the host.

In the second step of doping, generated charge pairs get dissociated. It is easy to dissociate generated charge carriers in conventional semiconductor due to their higher dielectric constants ( $\epsilon \approx 10$  to  $15$ ) compared to OSCs ( $\epsilon \approx 3$  to  $5$ ) [Riede *et al.* (2011)]. Hence, the coulomb force of attraction between the doping generated charge carries is stronger in the case of OSCs.

## 1.2.5 Thin-Film Deposition

### 1.2.5.1 Organic Semiconductor Deposition

A lot of organic thin-film deposition techniques have been reported in the literature [Ling *et al.* (2004), Nicholson *et al.* (2010), Bai *et al.* (2007), D. Arnaud (2012)]. Generally, organic thin-film is deposited either by dry methods (Vacuum Thermal Evaporation, Organic Vapor Phase Deposition, and Organic Molecular Beam Deposition) or by wet methods (Drop casting, Spin coating, Doctor Blade, Dip coating, Langmuir-Blodgett, Spray coating *etc.*). It depends on the solubility as well as nature of organic materials i.e. polymer or oligomer. Film deposition

techniques highly influence the performance of an organic device. The mobility of an OFET highly depends on the channel film uniformity, morphology, and thickness. Smooth and large grains size and  $\pi$ - $\pi$  stacking of organic molecules in the same direction in a deposited thin-film improve the conductivity of the film and provide high device performance.

### **Spin Coating**

It is a very common and easy thin-film deposition technique generally used in laboratories in order to deposit very uniform film. Soluble nature of organic semiconductors increases the application of this film deposition technique. In this technique, few drops of material solution is kept at the centre of the substrate which is placed on a spin coating equipment and the spin coater is rotated at a high speed for few seconds so that the solution spreads uniformly in the form of a very thin film on the substrate due to centrifugal force. The excess solution is thrown out from the substrate edge. Spin coating provides good uniformity and reproducibility in the thin-film.

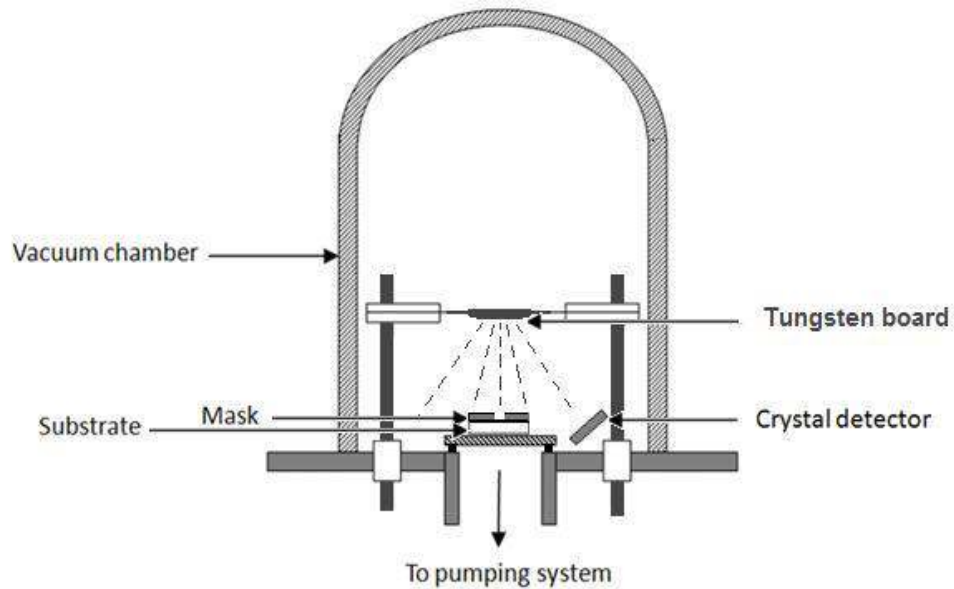
The thickness of the deposited film mostly depends on the viscosity and density of the solution as well as rotation speed, radial velocity and coating time. This technique is easy and suitable to deposit thin-film of thickness approximately 10 nm and above. Therefore, this film deposition technique is preferred and is used in this thesis for the deposition of organic semiconductor layer for the OFET devices.

#### **1.2.5.2 Metal Deposition**

##### **Thermal Vacuum Coating Technique**

This deposition technique is generally used in laboratories to deposit thin-film of metals or organic molecules. Here, source material deposition takes place at

very low pressure or very high vacuum ( $P < 10^{-6}$  to  $10^{-5}$  torr). This high vacuum prevents the source atoms interacting with surrounding air molecules.



**Fig. 1.8** Schematic diagram of a resistive thermal evaporation system

A schematic diagram of thermal evaporation unit is shown in Fig. 1.8. Here a vacuum of  $10^{-5}$  to  $10^{-6}$  torr is created in the vacuum chamber in two steps; initially up to  $10^{-3}$  torr by a rotary pump and then upto  $10^{-6}$  torr by a diffusion pump. The substrate and the source material are loaded in the vacuum chamber in the beginning. The source material in the form of a wire is wrapped around the tungsten board which is resistive heated to evaporate the source material.

The generated target material vapor moves toward the substrate in straight-line path. After arrival at the substrate, heat of vaporization from the vapor gets absorbed by the substrate and condensed vapor molecules form thin-film upon the substrate. The advantage of using this deposition technique are-

- Good adhesion between the thin film and substrate.
- Deposition of very thin layers, and multiple layers of different materials.

- High chemical purity.
- Control over mechanical stress in the film.
- Low gas entrapment.

Deposition rate can be controlled by controlling the current through the tungsten board. Deposited thin-film thickness is measured through the crystal detector which is already inbuilt in the vacuum thermal deposition system.

### 1.2.6 Morphology of Organic Semiconductors

The various properties of an organic semiconductor highly depend on its thin-film morphology. Organic thin-film has several structural morphologies mainly nanostructures such as nanorods, nanobelts, nanowires, nanofibers, nanotubes, nanoribbons *etc.* which play important roles in the molecular level study of a material. A number of structural morphologies with some unique properties and different shape and size can be developed simply by changing synthesis method, amount of chemicals, thin-film deposition methods and environmental conditions. The ordering in the morphology highly depends on the intermolecular interaction force, conformations, and  $\pi$ - $\pi$  stacking between the molecules. These structural morphologies enhance the organic devices performance drastically due to improvement in their charge transportation properties. Nowadays, nanostructures have achieved significant progress in fundamental research and their promising applications in the modern organic electronics due to their outstanding electrical, optical, mechanical, and electronic performances. [Jean *et al.* (2002), Botiz (2024)] Generally, carrier transport in a material is very much sensitive to structural defects, such as molecular disorder and grain boundaries. Therefore, currently one dimensional-aligned nanostructures such as nanofibers, nanocomposites *etc* are

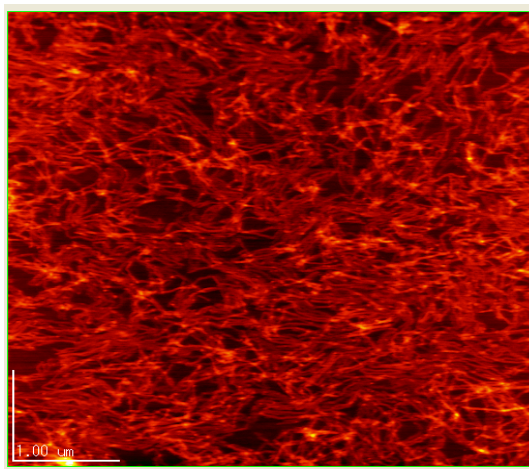
preferred to get high performance of organic devices such as solar cells, light-emitting diodes, OFETs, sensors, and several other types of microcircuits.

### 1.2.6.1 Organic Semiconducting Nanofibers

Organic semiconducting nanofibers of controlled dimensions along with ordered structure boosts the organic electronic device performance. There are lot of techniques such as self-assembly, gel-based printing, dip-pen nanolithography, polymerization in nanoporous templates, electro-spinning, directional epitaxial solidification, whisker method, thermal annealing, and Langmuire Blodgett method which have already been reported for the nanofibers formation [Sun *et al.* (2011), Jiang *et al.* (2011), Wang *et al.* (2012), Jo *et al.* (2012), Colangelo *et al.* (2012)]. Among these techniques, electro-spinning is a cost-effective method to produce controlled morphology of organic nanofibers at large scale. Self-assembling is another easy and cost effective technique for the formation of nanofibers. In this technique, polymer nanofibers, nanotubes or microwires are formed by the aggregation and  $\pi$ - $\pi$  stacking of organic molecules with a strong intermolecular force in a conjugated polymer solution. These nanostructures are supposed to enhance the carrier mobility along with other various properties of conjugated polymers which support these materials as good candidates for the applications of hybrid organic electronic devices. The formation of nanofibers strongly depends on various factors like temperature, solvent, concentration of the solution *etc.* Recently, unidirectional alignment of nanofibers proposed super performance organic devices, but alignment of nanofibers is still a challenging issue. Unidirectional nanofibers enhance the carrier mobility due to end to end charge carrier transportation and that's why aligned nanofibers play a very important role to improve the performance of organic devices. From a variety of



organic semiconductors, P3HT is a commonly studied semiconductor for the purpose of research and device applications due to its high mobility and solubility. Click coupling and self assembling are the two easy and inexpensive techniques to prepare P3HT-nanofibers. The nanofibers quantity and dimensions generally depend on solvent, solution concentration and the time period for which solution is preserved at a constant temperature. The range of diameter of organic conjugated nanofibers is 50 to 500 nm. The atomic force measurement (AFM) image of P3HT-nanofiber is shown in Fig. 1.9



**Fig. 1.9** AFM image of P3HT-nanofibers

#### 1.2.6.2 Organic Semiconductor Nanocomposites

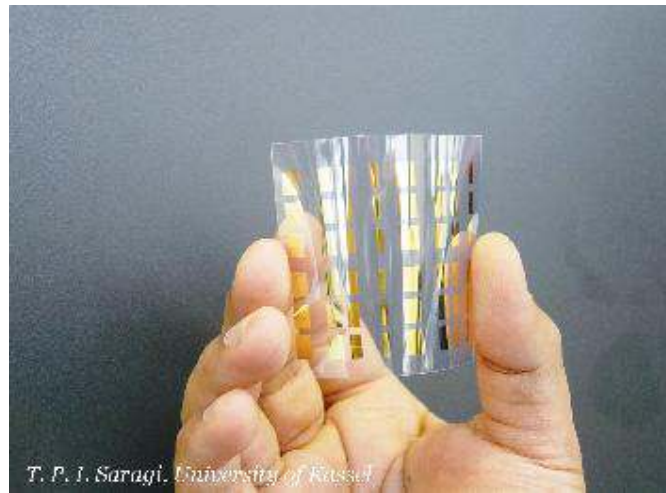
Nanocomposites are the materials having amazing property combinations which provide excellent device performance. Organic semiconducting nanocomposites are the multiphase materials which are prepared by insertion of one or more nanoscale (1-100 nm) fillers of dimensions 0-D, 1-D and 2-D into organic semiconductor matrix to attain desired properties which are not available in matrix or filler alone. In the organic semiconducting nanocomposites, organic semiconductor which is the host material transfers stresses to the other fillers and protects them from the environment. However, dispersed nanofillers enhance the

thermal, optical, mechanical and electrical properties of the matrix [Camargo *et al.* (2009)]. Nanofillers may be fibers, nanographite, spheroids, nanotubes, platelets, *etc.* The characteristics of nanocomposites strongly depend on the quality as well as quantity of dispersed nanofillers in the organic semiconductor matrix. They also depend on the scattering of nanofillers, nature of bond formed among the nanofillers and matrix, and fraction of nanofillers to the matrix. The smaller size nanofillers have high surface to volume ratio which results in high surface energy [Jeon *et al.* (2010)]. It is expected that incorporated nanofillers improve the bonding among the organic semiconductor and fillers by providing high interfacial energy. This improved bonding enhances the mechanical property of the nanocomposite material. The electrical properties of the nanocomposite material appear enhanced owing to the improved compactness of the organic semiconductor, which enhances the coupling among the nanoparticles through the grain boundaries. Organic semiconducting nanocomposites are applicable in several hybrid organic electronic devices such as electroluminescent devices, displays, smart windows, chemical sensors, batteries, light emitting diodes, thin film transistors, and memory devices [Bounioux *et al.* (2011), Obreja *et al.* (2013)].

### 1.3 Organic Field-Effect Transistors

Organic Field Effect Transistors (OFETs) are basic building block elements for flexible organic electronics, and are fabricated in a layered structural design. The transistor uses some organic semiconducting material rather than silicon as its active channel. Fig. 1.10 shows the picture of recent OFETs fabricated on the flexible substrate. OFET consists of three terminals (source, drain, and gate) along with an organic semiconducting film and an insulating layer. Gate electrode is isolated from the channel;

however, source and drain are connected with the channel film. The current flow through OFET channel can be controlled by the gate supply.



**Fig. 1.10** Picture of today's [Saragi *et al.* (2004)]

Nowadays OFETs are receiving great interest as potential alternatives to conventional FETs. Fabrication of conventional FETs requires high processing costs, complex fabrication system (ultra-clean condition, high-vacuum deposition, and photolithography) and costly materials; whereas, OFETs are light-weight, low-cost devices and have flexible fabrication [Kumar *et al.* (2014), Wakayama *et al.* (2014), Ebisawa *et al.* (1983), Tsumura *et al.* (1986), Brown *et al.* (1997), Jung *et al.* (2009), Chen *et al.* (2007), Verilhac *et al.* (2009)]. Even though OFETs are not going to replace the existing conventional FETs to lead the electronics industry, but such transistors are very much useful in the area of applications where low-cost, large-area, and flexibility has more importance than switching speed of the transistors. Comparison between OFET and conventional FET is given in the Table 1.3.

**Table 1.3** Comparison between OFETs and conventional FETs

Parameters	Organic FET	Conventional FET
Fabrication	Easy	Complex
Cost	Low-cost	Expensive
Process temperature	Low	High
Plastic Compatibility	Excellent	Under development
Mobility	Low	High

### 1.3.1 Review of Progress in Performance of OFETs

OFETs Fabricated initially showed poor field-effect mobility which underwent continuous improvement with time with the improvement of fabrication methodology and synthesis of novel materials. The first work on the OFET was started in 1983 by Ebisawa using polyacetylene as an active channel material [Wakayama *et al.* (2014)]. Few years later, in 1986, polythiophene based OFET with mobility of  $10^{-5}$  cm<sup>2</sup>/Vs was demonstrated by Tsumura [Ebisawa *et al.* (1983)]. In 1997, mobility of poly(thienylene vinylene) based OFET was measured to be  $3.5 \times 10^{-4}$  cm<sup>2</sup>/Vs [Brown *et al.* (1997)]. Further, in 2003, two order improved mobility for poly[(9,9-dioctylfluorenyl-2,7-diyl)-cobithiophene] based FET was achieved and the value reported was  $1 \times 10^{-3}$  cm<sup>2</sup>/Vs along with ON/OFF ratio of  $10^6$  [Jung *et al.* (2009)]. In 2007, mobility for P3HT [Poly(3-hexylthiophene)] based FET was measured to be  $2.5 \times 10^{-3}$  cm<sup>2</sup>/Vs along with poor ON/OFF ratio [Chen *et al.* (2007)]. In 2009, quite high field-effect mobility for TFB Pol [9,9-dioctylfluorene-co-N-(4-butylphenyl)-diphenylamine] based OFET was estimated and the value was found to be  $2 \times 10^{-2}$  cm<sup>2</sup>/Vs [Verilhac *et al.* (2009)]. Nowadays, growth of novel materials, surface treatment methods, and thin-film fabrication techniques has improved the

performance of OFETs drastically. A high mobility of  $0.34 \text{ cm}^2/\text{Vs}$  was estimated for poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophenes based FET in 2010 [Wang *et al.* (2010)]. Further in 2012, an OFET device fabricated with a very high molecular-weight DPP-DTT-based polymer showed excellent FET performance with mobility and ON/OFF ratio of  $10.5 \text{ cm}^2/\text{Vs}$  and  $10^6$  respectively [Li *et al.* (2012)].

The performance of OFET has been improving continuously. The amazing improvement in the OFET performance was due to development of novel organic active semiconducting channel materials, device structures, and thin film deposition techniques. OFET key parameters such as ON/OFF current ratio, mobility, threshold voltage, trans-conductance *etc* strongly depend on the device fabrication factors – (1) controlled processing parameters (deposition rate, film forming method, channel dimension, annealing process, deposition thickness, solvent power, heat treatment), (2) selection of suitable materials for electrodes, substrate, and dielectric, and (3) selection of active channel material of high purity, molecular weight, and high regioregularity. The optimized materials and fabrication conditions provide very good OFET performance. The mobility can be improved by simply controlling the molecular ordering in channel film material in order to get high carrier transport from source to drain electrode. In 2013 a high mobility of  $11 \text{ cm}^2/\text{Vs}$  for TIPS-pentacene based FET was reported [Kurihara *et al.* (2013)]. Recently, in July-2014, an excellent carriers mobility for poly(thienoisindigo-alt-naphthalene) based FET was reported and found to be  $14.4 \text{ cm}^2/\text{Vs}$  [Kim *et al.* (2014)]. This value exceeds the benchmark mobility values for amorphous silicon semiconductors. The improvement in mobility through the years can be observed through Table 1.4 [Abanoz *et al.* (2014)] which shows the highest mobility since 1964 to 2014 reported for OFETs fabricated using various deposition methods.

**Table 1.4.** Improvement in Field-effect Mobility of OFET since starting (1083) to recent (2014)

Year	Mobility ( $\text{cm}^2/\text{Vs}$ )	Material (deposition method) (v) = vacuum deposition (s) = from solution (s.c.) = macroscopic single crystal OFET
1964	Not reported	Cu-phthalocyanine (v) (first demonstration of field effect in small organic molecules)
1983	Not reported	Polyacetylene (s) (first demonstration of field effect in polymers)
1984	$1.5 \times 10^{-5}$	Merocyanine
1986	$10^{-5}$	Polythiophene (s)
1988	$10^{-4}$ $10^{-3}$ $10^{-4}$	Polyacetylene (s) Phthalocyanine (v) Poly(3-hexylthiophene) (s)
1989	$10^{-3}$ $10^{-3}$	Poly(3-alkylthiophene) (s) $\alpha$ -sexithiophene (v)
1992	0.027 $2 \times 10^{-3}$	$\alpha$ -sexithiophene (v) Pentacene (v)
1993	0.05 0.22	$\alpha$ - $\omega$ -dihexyl-sexithiophene (v) Polythienylenevinylene (s)
1994	0.06	$\alpha$ - $\omega$ -dihexyl-sexithiophene (v)
1995	0.03 0.038	$\alpha$ -sexithiophene (v) Pentacene (v)
1996	0.02 0.045 0.62	Phthalocyanine (v) Poly(3-hexylthiophene) (s) Pentacene (v)

1997	1.5 0.13 0.05 0.01	Pentacene (v) $\alpha$ - $\omega$ -dihexyl-sexithiophene (v) Bis(dithienothiophene) (v) <i>trans-trans</i> -2,5-Bis-[2-5-(2,2'- bithienyl)ethenyl]thiophene (BTET) (v)
1998	0.1 0.23 0.15	Poly(3-hexylthiophene) (s) $\alpha$ - $\omega$ -dihexyl-quaterthiophene (v) Dihexyl-anthradithiophene
2000	0.1	$\alpha$ - $\omega$ -dihexyl-quinquethiophene (s)
2002	0.89	Pentacene from precursor (s)
2003	3.4	Pentacene (v)
2004	15.0	Rubrene (s.c.)
2005	0.7	Rubrene (s)
2005	1.0	Triethylsilyl derivative of anthradithiophene (s)
2005	1.8	5,5'-bithiazole with trifluoromethylphenyl end groups (n-type) (v)
2006	2.0	2,7-Diphenyl[1]benzothieno[3,2-b]benzothiophene (or DPh-BTBT) (v)
2007	1.8	TIPS-pentacene (s)
2007	15.0 - 40.0	Pentacene (s.c.)
2007	43.0	Rubrene (s.c.)
2007	10.0	Hexamethylenetetrafulvalene (HMTTF) (s.c.)
2007	10.0	titanyl phthalocyanine (TiOPc), $\alpha$ -phase (v)
2009	8.3	dinaphtho[2,3- <i>b</i> :2',3'- <i>f</i> ]thieno[3,2- <i>b</i> ]-thiophene (DNNT) (s.c.)
2011	31.3	2,7-dioctyl[1]benzothieno[3,2- <i>b</i> ][1]Benzothiophene

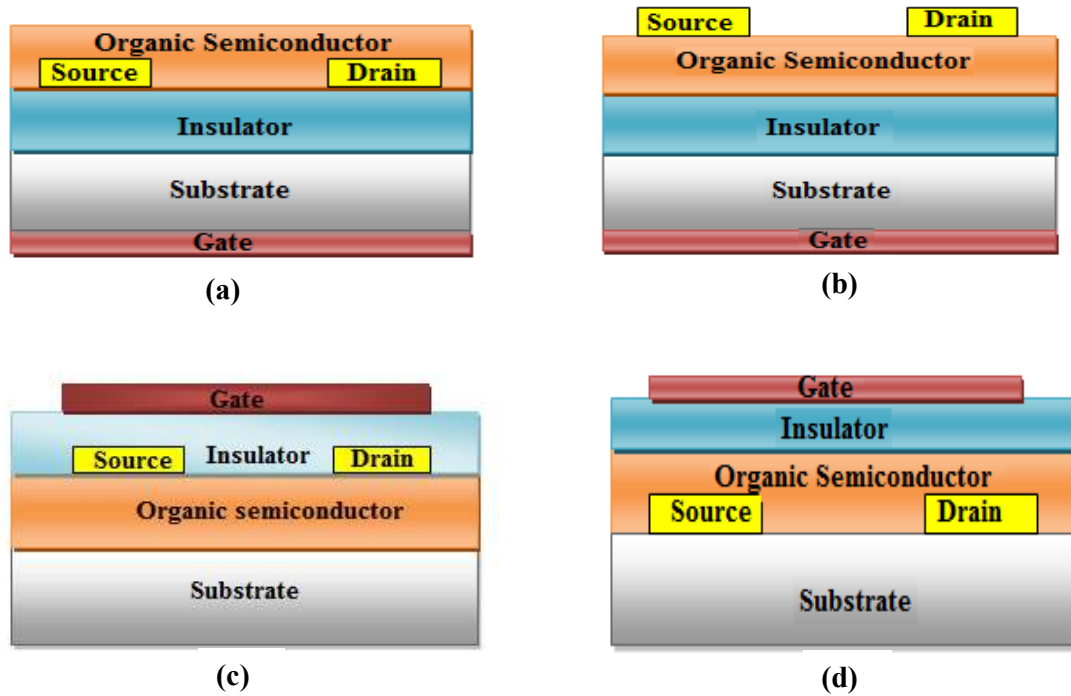
		(C8-BTBT), (s.c.), (ink-jet printed), (s)
2011	4.6	TIPS-pentacene (s), with strained lattice
2011	8.0	C10-DNTT (v)
2011	11.0	C10-DNTT (s)
2011	16.0	dianthracen-[2,3- <i>b</i> ]:2',3' <i>f</i> ]thieno [3,2- <i>b</i> ]thiophene (DATT) (s.c.)
2012	4.3	Hexacene (s.c.)
2012	17.2	Asymmetric C13-BTBT (v)
2012	10.5	Alternating D-A polymer with donor moiety, dithienylthieno[3,2- <i>b</i> ]thiophene (DTT) and acceptor moiety, N-alkyl diketopyrrolo-pyrrole (DPP) (s)
2013	11.0	TIPS-pentacene (s), OTFTs with single crystal domains and nonequilibrium crystal structure
2013	15.6	End-substituted <i>bis</i> (benzothieno)naphthalenes (BBTN) (v)
2014	14.4	(D{A} polymer semiconductor: poly(thienoisoindigo-alt-naphthalene) (PTIIGNp) (s)

### 1.3.2 Device Architectures

The fundamental structures of OFETs are either staggered or coplanar type [Gelinck *et al.* (2000), Lee *et al.* (2014)] and each structure has two distinct configurations. The cross-sectional diagrams for four different types of OFET configurations are given in the Fig. 1.11. In the staggered structure, semiconductor lies in between the insulating layer and the plane having both (source and drain) electrodes [Lee *et al.* (2014)]. The staggered configurations of OFETs are shown in



Fig. 1.11 (b) and (d). On the other hand, in coplanar structures, both electrodes (source and drain) and accumulated active channel are located in the same plane which should be at the interface of the insulator and semiconductor [Lee *et al.* (2014)]. The coplanar configurations of OFETs are shown in Fig. 1.11 (a) and (c).



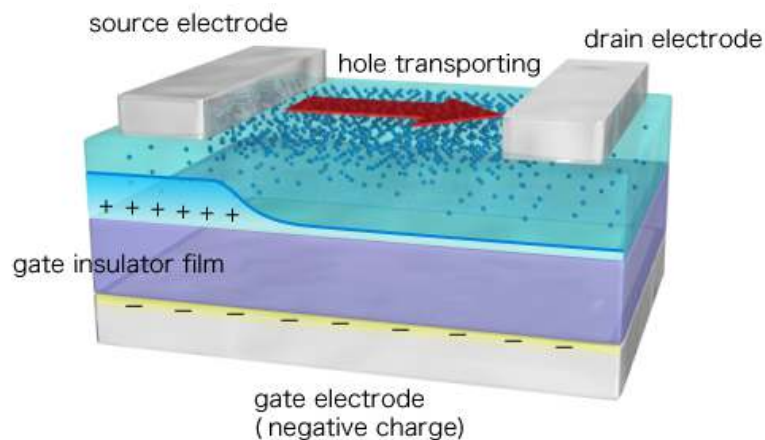
**Fig. 1.11** Cross-sectional view of different OFET device configurations (a) Bottom-gate, bottom-contact (Coplanar), (b) Bottom-gate, top-contact (Staggered), (c) Top-gate, Top-contact (Coplanar), (d) Top-gate, bottom-contact (Staggered).

These configurations are also referred by the position of source and drain electrodes with respect to semiconductor as top contact and bottom contact configurations and by the position of gate contact as top gate and bottom gate configurations. A thin insulating layer is deposited as gate insulator on the top of the substrate. The source and drain electrodes are deposited by using lithography or Ni-shadow mask technology. The electrical performance of the top-contact type OFET is superior compared to bottom-contact type OFETs. It is because the contact area of

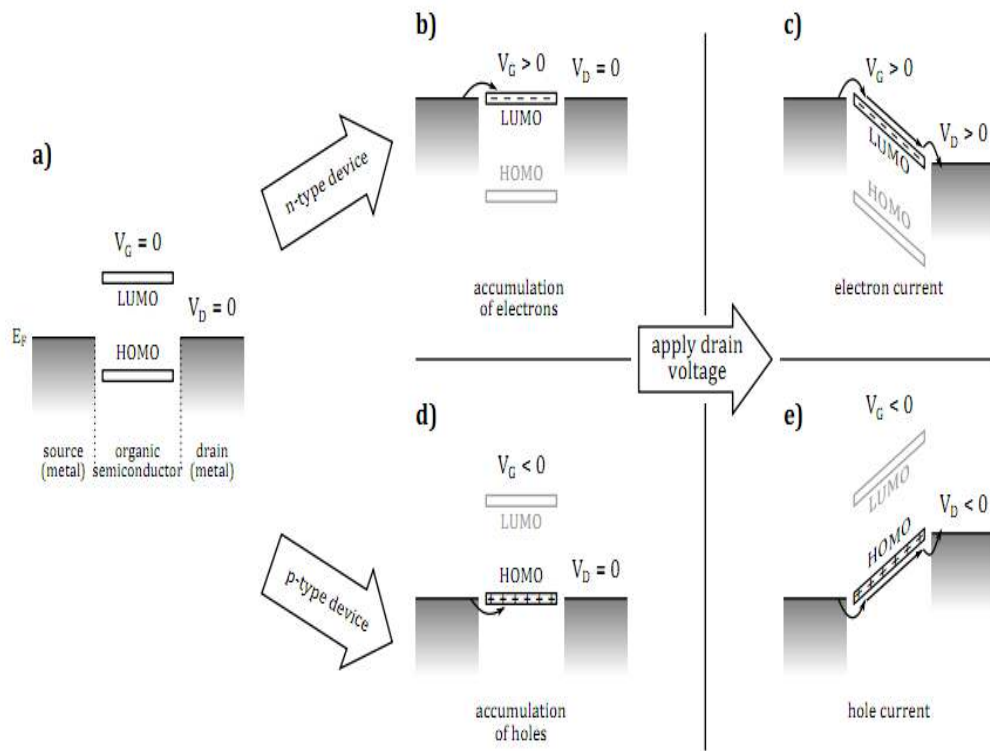
electrodes and semiconducting film is more in the top-contact type OFET configurations compared to bottom-contact type OFETs. So, large number of current carriers can be injected from the source electrode to the organic semiconductor and hence the current flow through the channel of top-contact type OFETs is higher compared to the current through bottom-contact type OFETs.

### 1.3.3 Operating Principle

The operating principle of an OFET is very similar to the operation of a conventional MOSFET; however, the channel formation concept is somewhat different. The channel in an OFET is formed due to the accumulation of the charge carriers in the bulk of the semiconductor as shown in the Fig. 1.12, while, in a MOSFET the inversion process is responsible for the formation of conduction channel between S/D electrodes. The operation of an OFET is explained in brief with the help of simplified energy band diagram drawn for the Fermi level of source/drain electrodes and HOMO/LUMO of organic semiconductor as shown in Fig. 1.13.



**Fig. 1.12** OFET Operation [Vukmirovic *et al.* (2011)]



**Fig. 1.13** Energy-band diagram showing operating principle of OFETs [Schaer, 2010]

**Case 1.** At  $V_G = 0$  V,  $V_D = 0$  V; no charge carriers will be induced at the interface of organic semiconductor/insulator. It is due to the intrinsic undoped nature of organic semiconductors. A small current through the device will flow only due to direct injection of charge carriers from source/drain electrodes. The magnitude of this current is very small due to the high resistance offered by the organic semiconducting material and long distance between the electrodes (source, and drain).

**Case 2.** If  $V_G < 0$  V,  $V_D < 0$  V; a number of positive charge carriers get accumulated at the interface of the semiconductor and dielectric layer and form a thin (in nm) p-type conduction channel between source/drain electrodes. Negative applied gate potential shifts the electrodes Fermi level towards the HOMO of organic semiconductor. If the Fermi-level of the electrodes will be far away from the HOMO

level of the semiconductor then the carrier injection/extraction will be difficult and results in low current due to large contact barrier between the electrodes and organic semiconductor. However, if the electrodes Fermi level will be sufficiently close to the LUMO level of the organic semiconductor, the carriers can transfer easily by applying a voltage  $V_{DS}$ , and the transistor work in the switched ON mode. This type of OFET is called p-type OFET.

Hence, a high work function metal should be selected for the electrodes (such as gold  $\Phi_{Au} = 5.1$  eV) to get high holes injection by applying a negative source-drain voltage.

**Case 3. At  $V_G > 0$  V,  $V_D > 0$  V;** If a positive potential is applied to the gate terminal, electrons get induced at the interface of the semiconductor and dielectric, and form a thin conducting n-channel between electrodes. The amount of accumulated electron density depends on the strength of the voltage applied to the gate terminal. Positive applied gate voltage shifts the Fermi level of the metals towards the LUMO of organic semiconductor. If the Fermi level of the electrodes get matched with the LUMO level of the organic semiconductor then the efficiently electrons flow start from the metal electrode to the semiconductor. This device works as n-type OFET. For an n-type OFET, low work function metals are selected for the electrodes such as samarium ( $\Phi_{Sm} = 2.7$  eV), magnesium ( $\Phi_{Mg} = 3.66$  eV), or calcium ( $\Phi_{Ca} = 2.87$  eV). These metals are generally unstable in atmosphere. So, in the past years, some new n-type organic semiconductors were synthesized by great effort in order to work with air stable electrodes. It is also interesting to know that until a few years ago, researchers had trouble in using n-type materials as the bottom-gate top-contact configuration using Si/SiO<sub>2</sub> as respective substrate and dielectric. This was recently attributed to the formation of –OH groups on the SiO<sub>2</sub> surface

which act as traps for electrons, thus hindering the charge transport mechanism. The use of organic dielectric free of –OH groups at their surface solved this problem [Schaur (2010)].

### 1.3.4 Current-Voltage (I-V) Characteristics

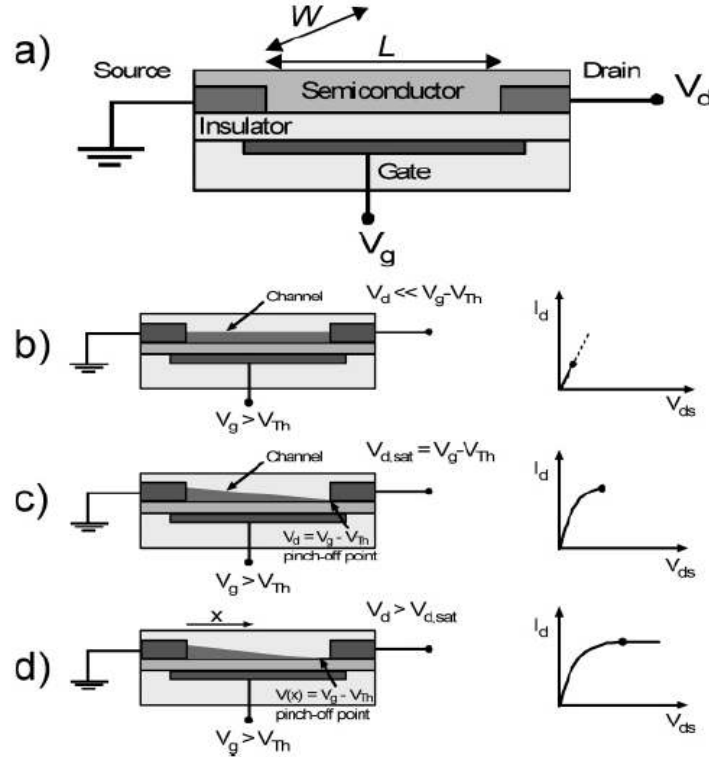
The electrical characteristics of an OFET can be clearly understood by the conventional FET theories [Sze (1981)]. The output characteristics is the variation of drain to source current ( $I_{DS}$ ) with the drain to source voltage ( $V_{DS}$ ), at a constant gate to source voltage ( $V_{GS}$ ) above the threshold voltage. This characteristic shows two distinct operating regions, *viz.*, linear region and saturation region separated by pinch off. Initially, as the applied voltage  $V_{DS}$  increases, the current  $I_{DS}$  through device increases linearly, but, for a particular value of  $V_{DS}$ , the  $I_{DS}$  gets saturated and that  $V_{DS}$  voltage is called “pinch off” voltage. Above pinch off voltage,  $I_{DS}$  will be independent of  $V_{DS}$ .

**Case 1:** If  $V_{DS} \ll V_{GS} - V_{TH}$ , the semiconductor of the device channel behaves as resistor, therefore, the variation of current is linear for this voltage conditions. The expressions for the  $I_{DS}$  in the linear region is given as

$$I_{DS,linear} = \frac{W}{L} C_{OX} \mu_{sat} (V_{GS} - V_{TH}) V_{DS}$$

Where, L is the channel length, W is the channel width,  $\mu_{sat}$  is the field-effect carrier mobility,  $V_{TH}$  is the threshold voltage,  $C_{OX}$  is the capacitance per unit area of the insulating layer and  $I_{DS}$  is the drain to source current. In this region, the channel conductivity depends on by how much value the gate voltage is in excess of threshold voltage.

**Case 2:** If  $V_{DS} = V_{GS} - V_{TH}$ , the voltage at the drain with respect to gate just exceeds the threshold voltage and hence pinch-off occurs. Maximum  $I_{DS}$  will flow through the device channel.

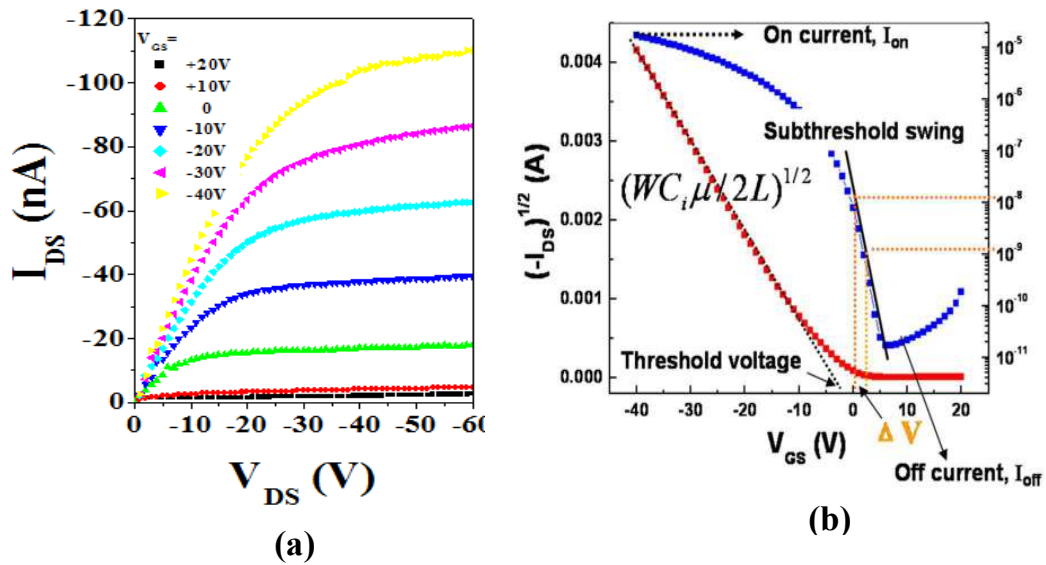


**Fig. 1.14** Working of an OFET (a) Schematic structure of OFET with applied voltages, (b) linear region, (c) "Pinch-off" condition, (d) saturation region [Chen, 2009]

**Case 3:** If,  $V_{DS} \gg V_{GS} - V_{TH}$ , the current flow through the channel will get saturated. It is because some area of the channel is occupied by the wedge shape depletion layer formed inside the active channel as shown in Fig. 1.14, remaining channel width (effective channel width) allow to flow the maximum carriers from source to drain which cause  $I_{DS,sat}$  flow through the device. The expressions for the  $I_{DS}$  in the saturation region is given below

$$I_{DS,sat} = \frac{W}{2L} C_{OX} \mu_{sat} (V_{GS} - V_{TH})^2$$

The I-V characteristics of a normally on-type p-channel OFET is shown in the Fig. 1.15. The output characteristics are drawn between drain current and drain voltage at various fixed gate voltage as shown in Fig. 1.15 (a), and transfer characteristic is drawn among drain current versus gate voltage at a fixed drain voltage as shown in Fig. 1.15 (b).



**Fig. 1.15** The I-V characteristics of a typical OFET (a) Output Characteristics, (b) Transfer Characteristics

A normally on type p-channel OFET works in accumulation mode for negative supply at gate and drain electrodes, however, it works in depletion mode for the positive applied voltage at the gate and the drain terminals. The OFET key performance parameters can be extracted from the I-V characteristics.

### 1.3.5 Performance Parameters

The application of an OFET strongly depends on its various key performance parameters such as field-effect carrier mobility ( $\mu$ ), ON/OFF current ratio, transconductance ( $g_m$ ), and the threshold voltage ( $V_{TH}$ ), sub-threshold slope ( $SS$ ) etc.

An OFET shows high performance only if it has high field-effect mobility, high ON/OFF ratio and low off current, free of charge traps and other defects, low threshold voltage and subthreshold slope, environmental, electrical and thermal stability, and low cost processing. These parameters are strongly affected by many issues, such as materials of different layers, morphology and grain size of the semiconductor film and structural dimensions.

**(a) Mobility:** The mobility indicates the average charge carrier drift velocity per unit electric field. It determines how proficiently carriers move in the conduction channel. It also determines the processing speed of a device. High mobility provides large on-current which is fundamental requirement for the memory applications. Generally *n*-type organic semiconductors exhibit low mobility compared to *p*-type organic semiconductors due to their large band gaps. Nowadays, many researchers are concentrating to improve the mobility of *n*-type organic semiconductors, in order to successfully realize complementary logic circuits. Mobility of organic transistor enhances with the increase in the gate overdrive voltage, therefore, it is called field dependent mobility [Kumar *et al.* (2014), Fu *et al.* (2009), Marinov *et al.* (2009), Carranza *et al.* (2012), Deen *et al.* (2001)]. Mobility of organic semiconductor improves significantly day by day due to discovery of novel materials and by optimization of the fabrication techniques which raise the opportunity of realizing organic devices for high speed applications such as graphics, the games, and animation.

**(b) Threshold Voltage ( $V_{TH}$ ):** Threshold voltage is the least gate voltage needed for accumulation of the charge carriers at the OSC/insulator interface in order to form a conducting channel between the source, drain electrodes. It measures the switching performance of a device. It is highly influenced by the dielectric constant



of the insulator, device channel length, doping concentration, thicknesses of the organic semiconductor thin-film, and the dielectric layers. The reduced threshold voltage can be obtained by lowering the channel length, increasing the active thin-film thickness, and decreasing the insulating layer thickness. Smaller  $V_{TH}$  is helpful in decreasing the device power consumption; therefore, it is advantageous in the production of portable devices.

**(c) ON/OFF current ratio:** It is calculated by taking the ratio of the maximum  $I_{DS}$  in the accumulation mode and the minimum  $I_{DS}$  in the depletion mode. Insulator of high dielectric constant and small thickness and low doping concentration of organic semiconductor film are the main features in order to get high ON/OFF ratio [Sirringhaus *et al.* (1997)]. Reducing the thickness of semiconductor and dielectric layers provide a high “ON” and low “OFF” current respectively, which increases the  $I_{ON}/I_{OFF}$  ratio. High ON/OFF ratio is the basic requirement for the display applications and also allow larger noise margin in digital circuits to enhance the reliability of the circuit. Generally short channel devices are fabricated in order to get high ON/OFF current ratio.

**(d) Sub-Threshold Slope:** A sub-threshold slope (SS) is the ratio of change in the gate biasing to the change in the drain current in logarithmic scale that can be expressed as

$$SS = \frac{\partial V_{GS}}{\partial \log_{10} I_{DS}}$$

It is a measure of trap density, impurity concentration, and interface states which have a strong effect on the switching performance of the transistor. By varying the gate and drain biasing, huge deviation in the sub-threshold slope is observed owing

to variation in the channel conductivity. The sub-threshold of an OFET is very much related to the mobility increment for carrier hopping. Smaller trap density provides steeper slope which exhibits good switching characteristics [Ha *et al.* (2011)]. Sub-threshold slope is an essential parameter to determine a proficient application of a transistor.

### 1.3.6 OFET Applications

Nowadays OFETs are very attractive and are gaining great deal of attention due to their low-weight, low-cost, and flexible fabrication properties. It is used as fundamental element in tremendous modern micro and nano electronics. It has huge applications in the fabrication of digital switches, large-area display devices, electronic artificial skin, smart digital gadgets, smart cards, integrated circuits, RF identification tags, and sensors [Brabec *et al.* (2001), Urien *et al.* (2007), Han *et al.* (2011)]. One area where OFETs have been effectively used is in e-inks, electronic barcodes and papers. OFETs have an important area of application in the backplanes of flexible displays. Use of conventional electronics in the backplanes is inflexible, more expensive, and un-printable. Therefore, application of OFETs in backplanes provides flexible displays along with many new features. It has been proved that OFETs have wide range of applications from sophisticated medical diagnostics to the smart textiles. Recently OFETs have their promising and potential application in the area of sensing as “electronic nose” and are use as chemical, physical, and biological sensors. It is because OFET sensors have various benefits over the other kinds of sensors such as easy fabrication, signal amplification, high sensitivity, miniaturization, and for multisensory arrays. Organic semiconductors can easily interact with dissimilar analytes. Fig.1.16 and 1.17 show some typical applications of OFETs

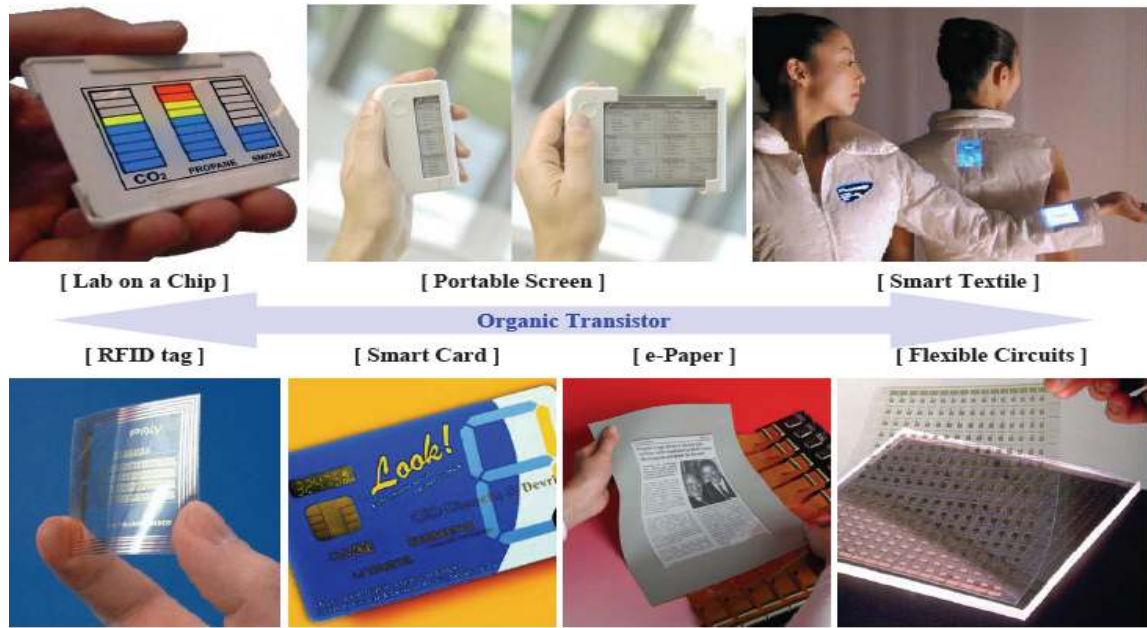


Fig. 1.16 Applications of OFETs [Chen (2011), Anthopoulos (2011), Kanicki (2011)]



**Fig. 1.17 (a)** LG Electronics: the world's largest OLED HDTV presented at the 2012 Consumer Electronics Show (CES) in Las Vegas, it has a display size of 55 inches, weighs a mere 7.5 kg and is only 4 mm thick [Electronics (2012)], **(b)** Sony: a rollable full color 4.1 inches OLED display driven by OFETs, being wrapped around a thin cylinder [Sony (2010)], **(c)** Polymer Vision: 'Radius', a flexible electrophoretic (e-ink) display fabricated on plastic substrates using OFET backplanes [Polymer vision (2008)], **(d)** Poly IC GmbH & Co. KG: roll-to-roll printing organic RFID tags on plastic substrates [Poly IC (2012)].

## 1.4 Features of Each Layer of OFET in Order to Provide High Performance

### 1.4.1 Organic Semiconductors

Energy level of organic semiconductors should have good match with the energy level of S/D electrodes for efficient charge injection from electrodes to semiconductor. It should be prepared by using good synthesis technique in order to get organic semiconductor of high molecular weight, high regioregularity and should have good film forming properties to reduce the grain boundary in the thin-film. It should also produce polycrystalline film of highly molecular orientation for the fast carrier transports in the grains parallel to the dielectric surface. Organic semiconductors should have good self-assembling ability on the insulator surface to form high molecular oriented films. It should be highly pure in order to decrease the charge trapping sites, and dopants which increase the conductivity in the off state. Organic semiconductors should have good thermal, electrical, and environmental stability.

### 1.4.2 Gate Dielectrics

Accumulation and movement of charge carriers in an OFET occur at the gate insulator and organic semiconductor interface. Therefore, the device performance is highly influenced by the characteristics of interface and dielectric materials. The OFET parameters are strongly dependent on the chemical structure and properties of the organic semiconductor as well as gate insulator. In order to get high performance in OFETs, gate dielectric materials should offer few important properties listed below [Lee *et al.* (2009), Veres *et al.* (2004), Facchetti *et al.* (2005), Das *et al.* (2012), Sing *et al.* (2006)]

- High dielectric constant for low-voltage operation and low leakage current.
- Good heat and chemical resistance.

- Smooth surface roughness to reduce carrier scattering at the organic semiconductor/dielectric interface.
- Pinhole free thin film formability with high breakdown voltage and long term stability.
- Comparable with organic semiconductor in interfacial properties.

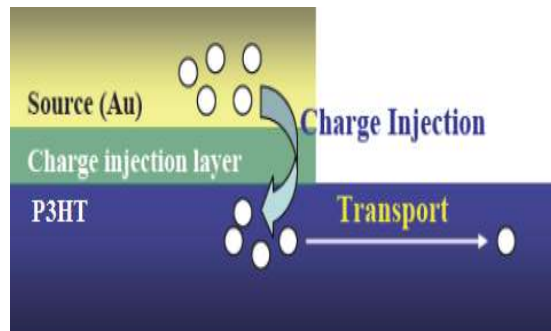
Dielectric constant helps to determine the capacitance of the insulating layer of thickness  $d$ . The expression for the capacitance is  $C_i = \frac{\epsilon_0 \epsilon}{d}$ , where,  $\epsilon_0$  is the free space permittivity, and  $\epsilon$  is the permittivity of the gate insulator. The charge induced in the channel is highly dependent on the capacitance value. Therefore, to get sufficient charges in the device channel, dielectric thickness should be less or the value of dielectric constant should be high. High dielectric constant provides high polarization; so charge carrier density gets enhanced which results in high carrier mobility. In general, thermally grown silicon dioxide ( $\text{SiO}_2$ ) is used as gate dielectric for OFET fabricated at heavily doped silicon substrate ( $\text{Si}/\text{SiO}_2$ ). Many research groups reported [Dinelli *et al.* (2006)] that treatment of  $\text{SiO}_2$  ( $\epsilon = 3.9$ ) surface (e.g., with octyltrichlorosilane (OTS) or hexamethyldisilazane (HMDS)) strongly influence the device performance by changing the semiconductor film morphology, amount of trap states, and dipoles present at the surface. Apart from  $\text{SiO}_2$ , there are lot of metal oxides such as  $\text{Ta}_2\text{O}_5$  ( $\epsilon = 10$ ) [Majewski *et al.* (2003)] and  $\text{Al}_2\text{O}_3$  ( $\epsilon = 10$ ) with high dielectric constant that are available for OFET application.

### 1.4.3 Source/Drain Electrodes

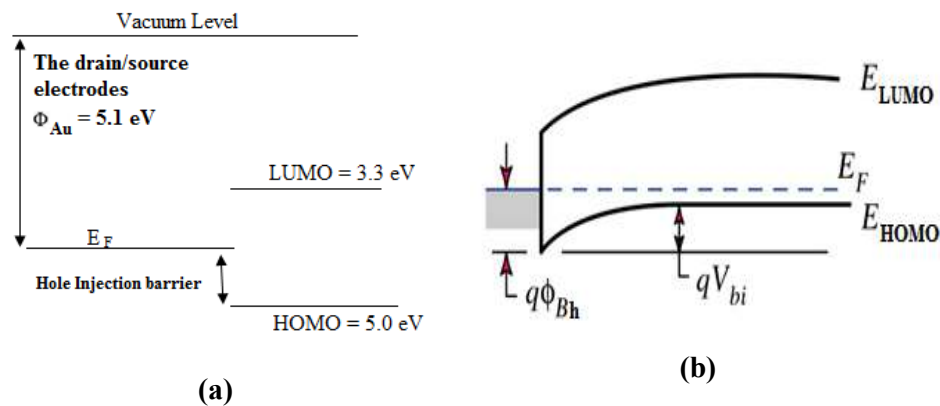
Generally electrodes (source, drain) of OFETs consist of metals like Au, Pt, Ag, Al, or Pd, and are deposited using thermal vacuum evaporation technique. Normally gold (Au) is preferred over other metals for S/D electrodes in polymer FETs due to

its high work function (5.4 eV) and low injection barrier. The efficient carrier injection at the interface of the metal and semiconductor is shown in Fig. 1.18. In order to get high performance in OFET, S/D electrodes should exhibit the properties [Dong *et al.* (2013), Yu *et al.* (2012), Michaelson *et al.* (1977), Waldrop *et al.* (1984), Wondmagegn *et al.* (2009), Alborghetti *et al.* (2012), Li *et al.* (2004), Gupta *et al.* (2005)] listed below-

- Work function of the electrodes should be matching with that of the organic semiconductor.
- It should offer high resistance against oxidation.
- It should be process compatible and should have good adhesion property.
- It should have high conductivity and low diffusivity.
- It should have high carrier injection capability, and low contact resistance.



**Fig. 1.18** Carriers injection at the metal and semiconductor interface



**Fig.1.19** Energy band diagram of gold and P3HT (a) before contact, (b) after the contact

The energy band diagram for of gold and P3HT is shown in the Fig 1.19,  $\phi_{Au}$  is the work function of gold,  $E_F$  is the Fermi energy level, and  $V_{bi}$  is the build in potential. The hole injection barrier should be small as small as possible for the efficient carrier injection from the electrode to the semiconductor.

### 1.5 Challenges in OFETs

The main challenges in the OFETs are low mobility, poor stability, and bulky device dimension, although these challenges are continuously improving since last two decades by optimization of fabrication methodology and synthesis of some novel materials. The mobility can be simply improved by using extremely pure organic semiconductor as impurities work as charge carrier trap centers. The molecules in the active thin-film should be highly oriented in order to produce crystalline domains for efficient charge carrier transport through the OFET channel. HOMO/LUMO of the particular molecules should be at that levels where hole/electrons can be induced at accessible applied electric fields. Recently, mobility has been improved from the order of  $10^{-5}$   $\text{cm}^2/\text{Vs}$  to  $10$   $\text{cm}^2/\text{Vs}$ . OFETs are not supposed to fight with conventional FETs for production of high-speed devices but they can be a component of low speed and low resolution mass produced items. Other limitations are also overcome day by day by developing new materials and methodology.

### 1.6 Motivations

The discovery of organic semiconductors has opened many new possibilities and flexibility for the electronic industries due to their special features. OFETs are investigated for applications of large area, flexible, low-cost, and disposable production that conventional FETs could not reach. Even though OFETs cannot replace the inorganic FETs to lead the electronics industry, but there are still many advantages that conventional FETs do not exhibit. Although the mobility of OFETs are too low

compared to poly-Si based FETs, still these transistors are very much useful in the area of applications where fabrication cost, mass production, and flexibility are more important than the switching speed of the transistors. Recently, the mobility of p-type OFET was found to be  $14 \text{ cm}^2/\text{Vs}$  [Kim *et al.* (2014)], and it can undoubtedly increase further by optimization of fabrication methodology and synthesis of novel materials.

### 1.7 Goal of the Research

In this work it was planned to fabricate top contact “normally ON-type” P3HT based FETs with the objective to improve their electrical performance by simply changing the morphology and doping of organic semiconductors deposited at the FET active channel.

### 1.8 Organization of the Thesis

According to the motivations and objectives of the study this thesis is structured into seven chapters.

In **Chapter 1** a brief presentation of the basic knowledge of organic semiconductors and Organic Field Effect Transistors are discussed. Motivations and goal of the thesis as well as important features of each layer of OFETs in order to get high performance are also described here.

**Chapter 2** introduces a brief outline of the materials, synthesis of P3HT, experimental methods regarding the OFET fabrication and electrical as well as structural characterization used in this study.

**Chapter 3** presents the fabrication and characterization of lab synthesized P3HT based field effect transistors.

**Chapter 4** discusses how to improve the mobility of OFETs by changing the active channel thin-film morphology due to incorporation of graphene flakes into the semiconductor.



Further, **Chapter 5** describes the methods to enhance the transport property of the channel film by simply changing the morphology of the P3HT as nanofibres for enhancing the overall performance of the OFET device.

**Chapter 6** discusses P3HT doping technique to improve the OFET performance. Here the effect of TCNQ doping has been discussed. This chapter further discusses the drawback associated with high doping and how to overcome this by coating of an ultra thin-film of aluminum in the highly doped device channel.

**Chapter 7** describes the conclusions of the whole work done in this study along with future scope.