1
Introduction

The conventional silicon technology has been widely used in the semiconductor industry since 1960. In year 1965, Gordon E. Moore predicted that the number of transistors in an integrated circuit doubles in approximately every two years [Moore, 1998]. Since then, Moore's law has been the basis for the roadmap of the silicon microelectronics industry, and the number of transistors per chip has steadily increased from ~10^3 in 1971 to more than 10^8 in today's silicon chips [Wikipedia, 2014].

Silicon integrated circuits are at the heart of many modern electronic devices that have made human lives easier and more convenient to a great extent. Many things around us have greatly benefited from silicon technology, such as desktop computers, laptops, digital cameras, smart phones, the Internet, tablet devices, music players, and many other electronic devices that contain silicon integrated circuits. However, silicon technology is not a suitable choice for flexible, large-area, light-weight, and low-temperature electronics.

Therefore, for the past three decades, researchers have extensively been exploring the field of organic electronics, which is a suitable technology for such applications. In this Chapter, firstly the historical perspective, advantages, and applications of organic electronics are discussed, followed by a discussion of the electronic properties and the charge-transport mechanism of organic semiconductors. The techniques used for processing of organic semiconductors are given in this Chapter. Motivation to work in the field of organic electronics and a brief discussion about the work involved in the construction of this thesis are given in the last part of this Chapter.

1.1 ORGANIC ELECTRONICS

Organic electronics is an exciting and emerging field with a wide-range of large-area, low-cost, light-weight, and low-temperature electronic applications. The uniqueness of organic electronics are, the simple fabrication process, the low-temperature processing, and the ability to fabricate organic devices on flexible plastic substrates. The fabrication of organic electronic devices does not require high-end clean room laboratories and involves comparatively simple manufacturing processes, such as spin coating, evaporation, drop-casting, and printing which makes organic electronics cost-effective and favorable to be used for future electronics.

Among the crucial discrete components of organic electronic circuits or systems are organic thin-film transistors (TFTs). Depending on the exact application, the TFTs have to provide a sufficiently large electric current in order to drive other components of the system, such as an organic light emitting diode (OLED). The drain current of an organic TFT is proportional to the charge-carrier mobility. Although the charge-carrier mobility of organic TFTs is relatively small compared to that of bulk silicon, it has recently approached to that of the hydrogenated amorphous silicon (a-Si:H) TFTs (~1 cm²/Vs). This thesis primarily focuses on the flexibility, performance, stability, and reliability aspects of organic TFTs.

1.1.1 Historical Perspective

Historically, organic materials have been known to be insulators, and have found widespread use in plastics, packaging, and insulation. In silicon electronics processing, for example, organic materials are routinely used as a photoresists in optical lithography, enabling the continuous shrinking of the device dimensions from 10 μm in 1971 to 20 nm in 2014 [Shaw and Seidler, 2001]. In 1963, a high electrical conductivity of 1 S/cm was observed in polypyrrole [McNeill *et al*, 1963]. In the same year, the emission of blue light from single-crystals of the organic semiconductor anthracene was reported [Pope *et al*, 1963].

In 1977, the discovery of a large, tunable electrical conductivity in the conjugated polymer polyacetylene played a huge role in the early development of organic electronics. The doping of polyacetylene results in a new class of conducting polymers, due to the increase of the electrical conductivity by 11 orders of magnitude [Chiang *et al*, 1977]. For the discovery of doped polyacetylene, A. J. Heeger, A. G. MacDiarmid and H. Shirakawa received the Nobel Prize in chemistry in 2000. The use of organic materials for the active layer of photoconductors for xerographic applications was demonstrated in 1978 [Bean and Miller, 1978]. In the 1980s, the first efficient organic solar cell and the first efficient organic light-emitting diode were developed at Kodak [Tang, 1986; Tang and VanSlyke, 1987]. The first organic TFT based on a thin film of polythiophene as the active layer was reported in 1987 [Koezuka *et al*, 1987]. These contributions fueled an enormous amount of further research work towards the development of more efficient organic electronic devices, considering their various advantages.

1.1.2 Advantages

Organic electronics, which is also known as flexible or plastic electronics, has a number of distinct advantages over conventional silicon technology. Some of the most important advantages of organic electronics compared with silicon are:

(a) Low-temperature Processing

The temperature required for the processing of organic semiconductors is typically below 100°C and hence much lower compared to the processing temperatures required for silicon (see Table 1.1). This is an important advantage, since it allows the deposition of organic semiconductors and hence the fabrication of organic electronic devices on flexible plastic substrates, such as polyethylene naphthalate (PEN) and polyethylene terephthalate (PET), which have the glass transition temperature in the range of 70 – 130°C.

Table 1.1 : Comparison of Different Silicon-based Semiconductor Materials with Organic Semiconductors in terms of Typical Processing Temperature and Charge-carrier Mobility

Semiconductor Material	Temperature Process	Charge-carrier Mobility (μ)
Single-crystalline Si	>800°C	~500 cm^2/Vs
Polycrystalline Si	~600°C	~50 cm^2/Vs
Hydrogenated amorphous Si	~300°C	~1 cm^2/Vs
Organic semiconductors	RT to ~100°C	~1 cm^2/Vs

(b) Mechanical Flexibility

Organic semiconductors are compatible with mechanically flexible substrates, such as plastics and paper. This compatibility of organic semiconductors has led to the development of mechanically flexible and bendable electronics. In addition, organic semiconductors are soft materials, which make them bendable, flexible, and rollable. An example of flexible and bendable organic electronics is shown in Figure 1.1, where organic devices and circuits were fabricated on a flexible PEN substrate (during this thesis).
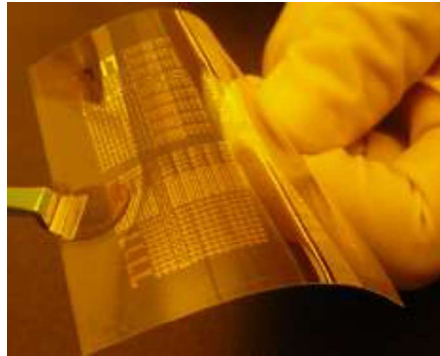

Figure 1.1 : Photograph of Organic TFTs Fabricated on a Flexible Polyethylene Naphthalate (PEN) Substrate showing the Mechanical Flexibility of Organic Electronics

(c) Low Cost

The processing of organic semiconductors does not require high-end clean rooms, and the fabrication techniques involved in the processing of organic semiconductors, such as: spin-coating, drop-casting, evaporation and printing are comparatively cost-effective techniques. Now-a-days, many organic semiconductors are already commercially available in bulk quantities, which further reduce the cost of production of organic electronic devices and systems. The low fabrication costs, along with the other benefits mentioned earlier, have motivated many research institutes, academia, and industries to perform research in this field.

1.1.3 Applications

The extensive research in the field of organic electronics has led to a variety of applications, such as OLEDs, organic photovoltaics, and organic TFTs. Some of the applications are given below in this Section. One of the most important applications is the integration of organic TFTs in the pixel driver circuits of flexible active-matrix flat-panel displays. In the present display technology, amorphous silicon (a-Si) or polycrystalline silicon (poly-Si) TFTs are typically used for the realization of the pixel driver circuits of active-matrix flat-panel displays. Due to their low process temperature, organic TFTs open up the possibility of realizing flexible (*i.e.*, rollable or foldable) active-matrix displays.

In addition to flexible displays, organic TFTs can also be used in many other types of electronic applications, such as radio frequency identification (RFID) tags, sensors (chemical, biological, pressure and others), and smart cards. Some of the applications which involve the use of TFTs are:

(a) Flexible Displays

An important development in the display technology is of Active-Matrix Organic Light-Emitting Diode (AMOLED) displays. AMOLEDs are revolutionizing the display technology

due to their smaller-weight, better image quality, and smaller power consumption compared with Active-Matrix Liquid-Crystal Displays (AMLCDs). In AMOLED displays, organic semiconductors are used as the electroluminescent components, *i.e.* as the OLEDs. The first commercialized OLED television, 55" was launched in December 2011 by LG (see Figure 1.2(a)). It weighs only 3.5 kg and is only 4 mm thick. However, all currently available AMOLED displays use inorganic TFTs for the pixel driver circuits and therefore fabricated on rigid, breakable glass substrates.

The realization of flexible displays requires the development of organic TFTs for the pixel driver circuits. However, for organic TFTs to be integrated in flexible display backplanes, lot of research is still required for improving the performance and reliability of these TFTs. In this thesis work (Chapter 4), the stability and reliability of high-performance organic TFTs are compared to those of a-Si:H TFTs.
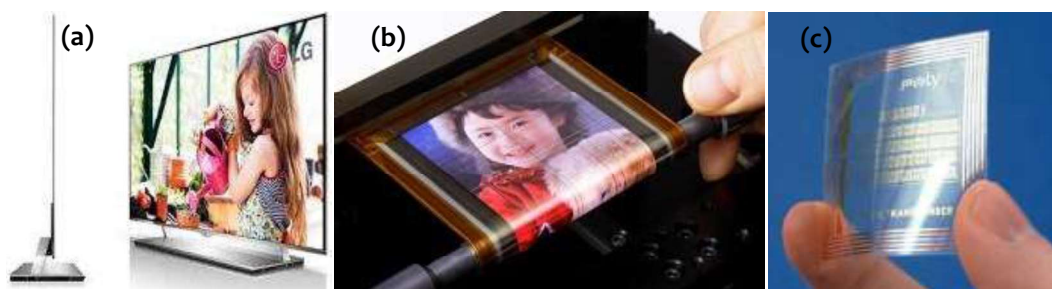

Figure 1.2 : Photograph of the (a) First 55" AMOLED Television Launched by LG in December 2011 [Source : OLED, 2014]; (b) First 4.1" Organic TFT Driven AMOLED Display Demonstrated by Sony, and [Source : Sony, 2010] (c) Organic RFID Tag PolyID by PolyIC [Source : RFID, 2014]

Many research institutes and companies are investing money into the research and development of organic-TFT-driven flexible displays, which helps improving the field of organic electronics. One example is the development of the first rollable organic-TFT-driven AMOLED display by Sony. It has a screen size of 4.1" diagonal and a thickness of 80 µm and has the capability of reproducing moving images even when it is repeatedly being rolled around a thin cylinder (see Figure 1.2(b)). However, this flexible display is not yet suitable for commercialization because of several challenges faced by organic TFTs, as discussed in Chapter 2.

(b) Radio Frequency Identification Tags

One of the potential applications of organic electronics is flexible, low-cost RFID tags. Low-cost RFID tags are essential for electronically identifying and tagging commercial products without increasing their final cost. RFID tags consist of a digital integrated circuit and an antenna. The antenna is usually fabricated by lithographic patterning of a thin electroplated copper film or by printing a conducting metal inks on to the substrate surface. In most of the RFID tags available today, the integrated circuit is a small silicon chip attached to the substrate and connected to the antenna. If the integrated circuit can be fabricated using organic TFTs, then the complete RFID tag (antenna and circuit) will be mechanically flexible as well as of low cost.

RFID tags are being developed as replacements for optically detected barcode tags, because RFID tags store a significantly larger amount of information, can be reprogrammable, and are suitable for long-distance communication without the line-of-sight requirement of barcode tags.

Many companies and research laboratories are actively working on the development of flexible organic RFID tags. One such company is PolyIC, which has demonstrated a flexible RFID tag based on organic TFTs (Figure 1.2(c)) [PolyIC, 2014]. The Holst Centre research lab reported the development of a 13.56 MHz organic RFID tag, in 2009. In 2010, the Holst Centre, Interuniversity Microelectronics Centre (IMEC) and Toegepast Natuurwetenschappelijk Onderzoek (TNO) demonstrated an RFID tag chip based on dual-gate organic TFTs operating at a low voltage (~10 V). Nonetheless, a lot of research is still needed for the commercialization of flexible and low-cost organic-TFT-driven RFID tags.

(c) Sensor Devices

Organic-TFT-based sensors have shown promising results for biological, chemical, pressure and environmental sensing applications. Some specific examples are: gas, pressure and thermal sensors [Torsi *et al*, 2000; Sekitani *et al*, 2010]. Organic-TFT-based sensors can be produced on conformable, flexible and large-area substrates [Sekitani *et al*, 2010]. The advantages, such as high sensitivity, mechanical flexibility, low cost, simple fabrication, and biocompatibility, make organic-TFT-based sensors an exciting field for research.

1.2 ORGANIC SEMICONDUCTORS FOR TRANSISTOR

Organic semiconductors can be classified into oligomers (small molecules) and polymers on the basis of their molecular weight. The molecular weight of oligomers is small and well-defined, whereas the molecular weight of polymers is less well-defined, because it depends on the length of the backbone and the number of repeat units. Both oligomers and polymers have their own advantages and drawbacks.

Polymers can be easily processed by solution based deposition techniques, such as spin-coating, drop-casting, blade-coating, solution-shearing, inkjet printing and gravure printing, which potentially leads to lower production costs compared with vacuum-based deposition approaches. In contrast, oligomers are often deposited by thermal sublimation in vacuum, which has been shown to produce higher performance and better uniformity of the devices. Hence there is a tradeoff between the ease of fabrication and the level of device performance and reproducibility.

Depending on the dominant type of charge carriers in the transistor, organic semiconductors can be classified as p-channel (hole), n-channel (electron), and ambipolar semiconductors [Klauk *et al*, 2003; Tiwari *et al*, 2012; Rödel *et al*, 2013].

One of the most important parameters of an organic semiconductor is the charge-carrier mobility. When the applied electric field (E) is small, the charge carriers drift through the semiconductor at a velocity (v_{drift}), which is proportional to electric field (E), so the charge-carrier mobility (μ) can be written as follows,

$$\mu = {}^{v_{drift}}\!/_{E} \tag{1.1}$$

where μ is the charge-carrier mobility of organic semiconductor.

A lot of research is devoted to the designing and synthesis of new organic semiconductors with larger charge-carrier mobility and better environmental and operational stability. Figure 1.3 shows the development of the charge-carrier mobility of organic TFTs based on various solution-processable and vacuum-processable organic semiconductors since 1984. This plot shows that during the past 20 years, the charge-carrier mobility of organic TFTs has been improved from ~10^{-5} cm²/Vs to about 10 cm²/Vs. High charge-carrier mobility is important,

because it is one of the parameters that determine the drain current and the switching frequency of the TFTs.
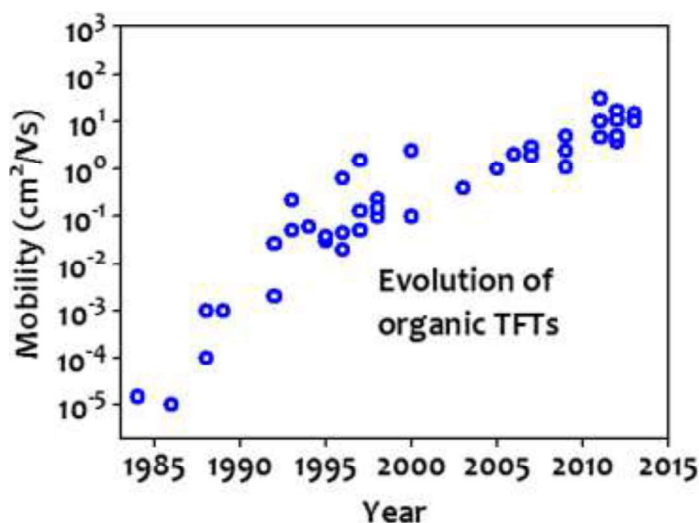

Figure 1.3 : Historic Development of the Charge-carrier Mobility of Organic TFTs based on various Organic Semiconductors (Data Points Taken from [Source : Dimitrakopoulos and Malenfant, 2002; Sirringhaus, 2014])

In this thesis, six different small-molecule organic semiconductors (oligomers) are used to fabricate organic TFTs on flexible plastic substrates and characterize their performance and stability. Four of these semiconductors are hole-transporting (p-channel) materials and two of them are electron-transporting (n-channel) materials, and they are further discussed in Chapter 3.

1.2.1 Electronic Properties

The reason for the electrical conductance in organic semiconductors is the presence of delocalized π-electrons. The molecular structure of one popular small-molecule organic semiconductor, pentacene, is shown in Figure 1.4. In pentacene, each carbon atom exhibits sp^2 hybridization, forming three localized σ-bonds with neighboring carbon and hydrogen atoms and one delocalized π-bond with all the other carbon atoms. In the schematic molecular structure, the π-bonds are illustrated as alternating single and double bonds between adjacent carbon atoms. The presence of delocalized π-electrons is called conjugation, and organic semiconductors are also referred to as conjugated semiconductors.

Figure 1.4 shows two of the resonance forms of pentacene, with the single and double carbon-carbon bonds depicted in alternating positions. Unlike, the localized σ-electrons, which do not contribute to charge conduction, the delocalized π-electrons are responsible for the electrical conductivity of organic semiconductors. In the ground state, the 11 π-orbitals with the lowest energies are occupied with two π-electrons per orbital, and the 11 π-orbitals with the highest energies are empty. The difference in energy between the highest occupied molecular orbital (HOMO); similar to the ionization energy of the semiconductor and lowest unoccupied molecular orbital (LUMO); similar to the electron affinity of the semiconductor, is called the HOMO-LUMO gap.
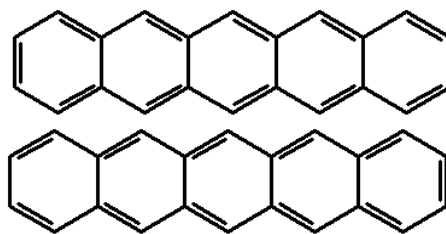
Figure 1.4 : Chemical structure of Pentacene showing Two of the Resonance Forms

1.2.2 Charge Transport Mechanism

Most organic semiconductors have a relatively large HOMO-LUMO gap. For example, the HOMO-LUMO gap of pentacene is about 2 eV [Winlder and Houk, 2007]. At room temperature and in the absence of chemical doping, the density of free charge carriers and hence the electrical conductivity at room temperature are therefore typically very small, so that organic semiconductors behave mostly like insulators at room temperature. However, the density of free charge-carriers and thereby the conductivity can be increased over several orders of magnitude by applying an external electric field. The mechanism of the charge transport in organic semiconductors is fundamentally different from that in inorganic semiconductors, because the van der Waals bonds by which the molecules in organic semiconductors are held together are substantially weaker (~10^{-3} eV per molecule) than the covalent bonds (~2 eV) by which the atoms in inorganic semiconductors are bound to each other. Unlike the covalent bonds in inorganic semiconductors, which involve the formation of shared electron pairs between the atoms, the van der Waals interactions between the molecules in organic semiconductors are due to the (much weaker) electrostatic forces between spontaneously induced molecular dipoles.

The charge transport mechanism in crystalline semiconductors can be explained by assuming that the charge carriers move exclusively in extended electronic states in the valence band (VB) or in the conduction band (CB). The VB represents the highest occupied energy band and the CB represents the lowest unoccupied energy band. In this case, the conductivity increases with the number of free electrons in the CB (or with the number of free holes in the VB). Free charge-carriers can be generated in the semiconductor by promotion of electrons from the VB to the CB (e.g., by thermal activation or by absorption of photons with sufficient energy), or they can be injected into the semiconductor under the influence of an applied electric field (see Figure 1.5).

Within this picture of perfectly coherent band transport in crystalline semiconductors, the charge-carrier mobility (and hence the electrical conductivity) is limited only by the scattering of the charge-carriers with thermally induced lattice vibrations (phonons). The charge-carrier mobility in crystalline semiconductors therefore generally decreases with increasing temperature. The electrical conductivity (σ) is proportional to both the density of free charge-carriers (n) and to the charge-carrier mobility (μ) and is given as,

$$\sigma = n \cdot q \cdot \mu \qquad\qquad (1.2)$$

where q is the elementary charge, (1.602×10^{-19} As).

In contrast, the charge transport in disordered semiconductors, such as a-Si:H and most organic semiconductors, is considered to be due to the hopping of the charge-carriers between localized electronic states and is thus explained in the context of discrete energy levels, rather

than extended energy band (see Figure 1.5). Since the hopping rate is thermally activated, the charge-carrier mobility in disordered semiconductors therefore generally increases with increasing temperature. The electrical conductivity is therefore proportional to the density of charge-carriers in the lowest unoccupied energy level (n_{band}) [Servati $et\ al$, 2006] and is given as,

$$\sigma_{disordered} = n_{band} \cdot q \cdot \mu \tag{1.3}$$

where n_{band} depends on the density of charge-carriers which are trapped and contribute to the conduction when they are excited to the extended states due to the application of a bias or due to external excitation (temperature), and also on the mechanism involved in the charge-transport.
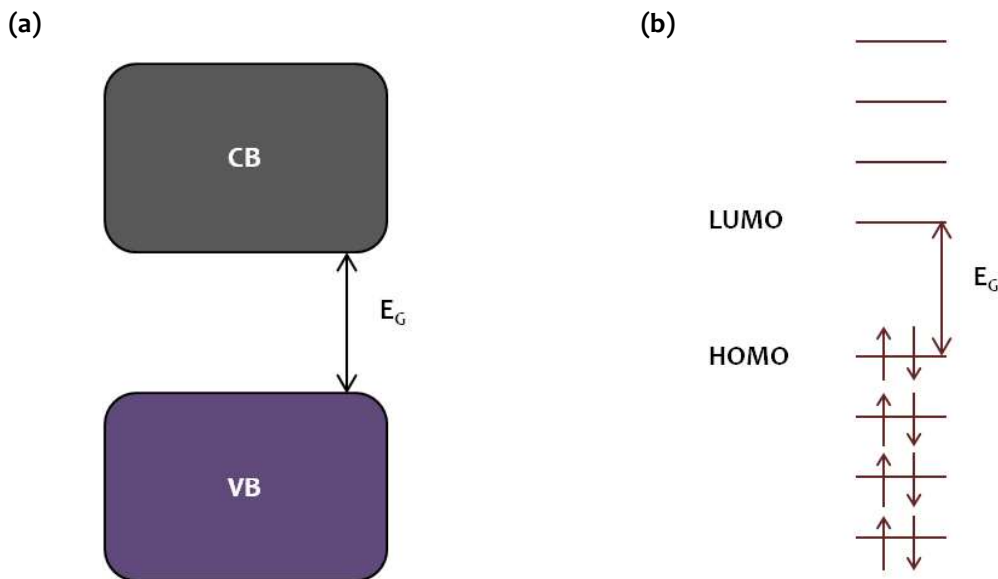

Figure 1.5 : Schematic diagram showing the Charge-carrier Transport in (a) an Ordered Semiconductor using the Band Model, and (b) a Disordered Semiconductor using Discrete Energy Levels, where E_G is the Energy Gap

The charge-carrier mobilities in organic TFTs span a wide range, depending on the semiconductor and on the technique by which the semiconductor is deposited [Klauk, 2010]. Consequently, a variety of models have been proposed to quantitatively explain the charge-transport over such a wide range of mobilities. The most commonly cited charge-carrier transport models for organic semiconductors are: the nearest-neighbor hopping model, variable range hopping (VRH) model, and the multiple trapping and release (MTR) model, which will be discussed in this Section. Hopping is referred to as the transfer of charge-carriers between localized electronic states by a combination of quantum-mechanical tunneling and thermal activation under the influence of an applied electric field. Hopping was introduced in the treatment of doped semiconductors by Kasuya and Koide in 1958, further studied by Miller and Abraham in 1960, and later extended to amorphous semiconductors in 1979 by Mott and Davis [Singh and Shimakawa, 2003].

(a) Nearest Neighbor Hopping

According to this model, charge-carriers are transported from one localized occupied state to the nearest unoccupied state having the same energy level [Blythe and Bloor, 2008]. In such cases the probability of a charge-carrier (e.g., electron) to hop between two localized state (*i.e.,*

from a to b) depends on the spatial separation between the two states (d_{ab}) [Baranovski, 2006] and is given as,

$$P_{ab} = v_o \cdot \exp\left(\frac{2d_{ab}}{\alpha}\right) \tag{1.4}$$

where α is the distance between the two localized states a and b, and v_o is the characteristics frequency associated with the hopping between the two states. In disordered materials, v_o is assumed to be due to the interaction between the electrons and the phonons, and the phonon frequency is often assumed to be on order of 10^{13} s^{-1} [Baranovski, 2006]. If the energy barrier between the two states is sufficiently small, the thermal energy (kT) may be sufficient for the charge-carriers to hop from one state to the other. On the other hand, if the energy barrier is large, the energy required to overcome the barrier may be transferred from phonons [Blythe and Bloor, 2008]. The electrical conductivity due to hopping between two nearest neighboring states [Baranovski, 2006] is given as,

$$\sigma_{org} = \sigma_o \cdot \exp\left(\frac{-E_h}{kT}\right) \tag{1.5}$$

where σ_o is the conductivity between two states without any barrier, E_h is the energy required to cross the barrier, k is the Boltzmann constant, and T is the absolute temperature.

(b) Variable Range Hopping

The variable range hopping (VRH) model was developed by Mott and can be viewed as an improved version of the nearest neighboring hopping model. It was first applied to organic semiconductors in 1998 [Vissenberg and Matters, 1998]. The VRH model is not limited to hopping between neighboring states, and it also considers the energy difference between the states involved in the hopping for the determination of the hopping probability. In this case, the probability of a charge-carrier (*i.e.*, and electron) to hop between two localized states (*i.e.* from a to b) not only depends on the spatial separation between the two states (d_{ab}), but also on the energy difference between the two states [Bässler, 1993] and is given as,

$$P_{ab} = v_o \cdot \exp\left(\frac{2d_{ab}}{\alpha}\right) \cdot \exp\left(\frac{E_a - E_b}{kT}\right) \tag{1.6}$$

where E_a and E_b are the energies associated with the two states. The diffusion coefficient (D) in one direction can be calculated as $D = \frac{P_{ab} \cdot d^2}{6}$ [Madan and Shaw, 1988], and using Einstein's equation, the charge-carrier mobility is given as: $D = \frac{kT}{q} \cdot \mu$. In Eq.(1.3), the charge-carrier density is given as the product of the density of states at the Fermi energy and the range of allowable energies $n_{band} = N(E_F) \cdot kT$ [Morigaki, 1993]. Hence,

$$\sigma = \frac{1}{6} \cdot N(E_F) \cdot q^2 \cdot P_{ab} \cdot d^2 \tag{1.7}$$

This model is useful to describe the charge-carrier transport in disordered (amorphous) materials having the charge-carrier mobility smaller than about 10^{-2} cm^2/Vs [Klauk, 2010].

(c) Multiple Trapping and Release

The multiple trapping and release (MTR) model was originally developed to describe the charge transport in hydrogenated amorphous silicon, a-Si:H [Le Comber and Spear, 1970] and was later adapted by G. Horowitz to explain the charge-carrier transport in polycrystalline organic semiconductors [Horowitz *et al*, 1999]. According to this model, charge-carriers move with the same mobility at an energy level above the mobility edge. The localized electronic states (*i.e.*, carrier traps) are mainly situated in the mobility gap (see Figure 1.6) and can be

categorized into deep states and tail states [Powell, 1989]. In a-Si:H, the deep states are the result of the large density of dangling bonds, and their energy is deep in the energy gap between the VB and the CB (see Figure 1.6), whereas the tail states are due to structural disorder and cause the broadening of the CB and the VB and the formation of tails of localized states/traps below the CB mobility edge and above the VB mobility edge (see Figure 1.6). These localized states/traps limit the mobility of the charge-carriers.
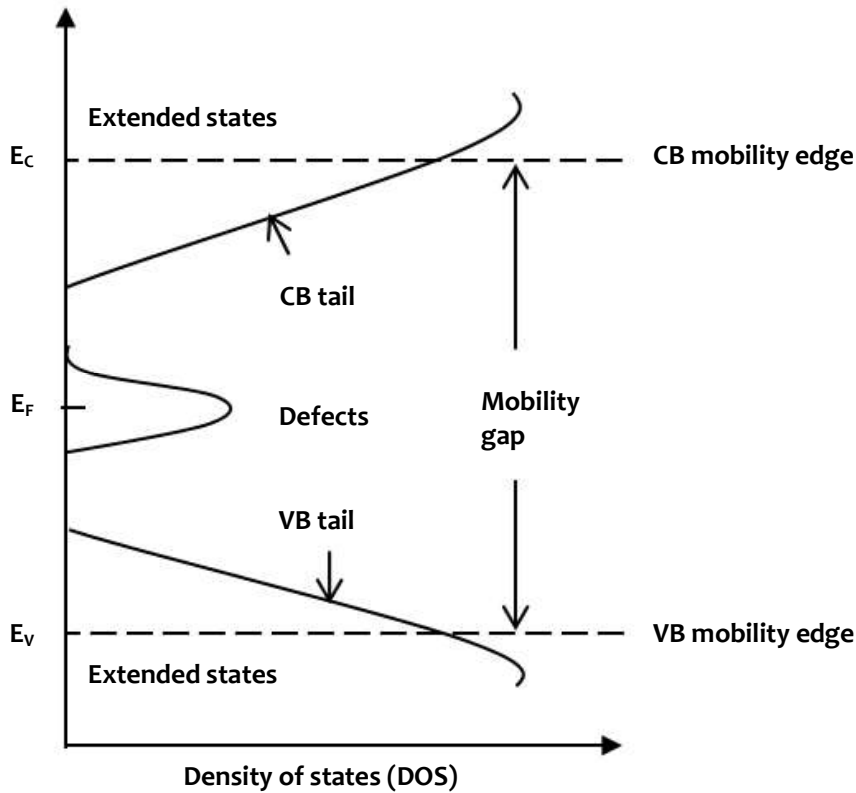

Figure 1.6: Schematic diagram showing the Existence of the Mobility Edge in a Disordered Semiconductor [Source : Liu, 2013]

In organic semiconductors, disorder results from chemical impurities (e.g., synthetic byproducts, oxidation products) and structural defects (e.g., grain boundaries, vacancies) and leads to the formation of localized electronic states (*i.e.*, carrier traps) in the HOMO-LUMO gap. During transport, the charge carriers interact with the localized states through trapping and thermal release. The trapping of charge-carriers occurs instantaneously when a free carrier approaches a localized state, while the release of trapped carriers is thermally activated.

The trapping and release of the charge-carriers have a large impact on the mobility of the charge-carriers. Therefore, the charge-carrier mobility depends not only on the mobility in the delocalized band (μ_o), but also on the ratio between the effective density of states at the band edge and the density of trap states (α) and the energy difference between the trap level and the mobility edge (E_T) [Horowitz, 1998; Horowitz *et al*, 1999],

$$\mu = \mu_o . \alpha . \exp\left(\frac{-E_T}{kT}\right) \qquad (1.8)$$

This model also explains the dependence of the charge-carrier mobility on the applied gate bias and the temperature. This model is useful to describe the charge-carrier transport in polycrystalline organic semiconductors having charge-carrier mobilities greater than about 0.1 cm^2/Vs [Klauk, 2010].

1.2.3 Processing Techniques

Various processing techniques can be used for depositing thin films of organic semiconductors, depending on whether the materials are solution processable or not. As we have already discussed, polymers are typically solution-processable, and thus be deposited by various solution-processing techniques such as spin-coating, drop-casting, and printing. Small molecules (*i.e.* oligomers) are usually deposited by sublimation in vacuum. In this Section, various techniques used for depositing thin films of organic semiconductors are discussed.

(a) Spin-coating

Spin-coating is used to deposit thin films of various solution-processable materials on flat substrates. In this technique the substrate is held by vacuum on the chuck of the spin-coater and a small amount of material to be deposited as a film is dropped in the centre of the substrate. The substrate is then rotated at a high rate to distribute the material uniformly on the substrate surface. The final thickness of the film depends on various factors, such as the rate and the duration of the rotation, the concentration and the viscosity of the solution, and the rate at which the solvent evaporates. Meyerhofer *et al* reported that the thickness of the film (h) can be estimated from the solution parameters [Aegerter and Mennig, 2004; Meyerhofer, 1978] using the following equations,

$$h \ = \ x \cdot \left(\frac{e}{2(1-x)K} \right)^{\frac{1}{3}} \tag{1.9}$$

$$e = C \cdot (\omega)^{1/2} \text{ and } K = \rho\omega^2/3\eta \tag{1.10}$$

where x is the effective solid content of the solution, e and K are the evaporation and flow constants, C is a proportionality factor that depends on the flow of the air and on the diffusivity of the solvent molecules in air, ω is the rotation rate, and ρ and η are the density and viscosity of the solution [Aegerter and Mennig, 2004]. The higher the rate at which substrate rotates, the lower the final thickness of the film, and vice-versa. Advantages of this technique are the good uniformity of the films, the ability to control the film thickness by adjusting the process parameters (rate of rotation, concentration, and viscosity of the solution, etc.) and the excellent reproducibility of the process. The shortcomings of this technique are the significant material wastage, the fact that this technique is not suitable for large substrates, and the fact that it is a batch process.

(b) Drop-casting

Drop-casting is another type of processing technique used for depositing a thin film of solution-processable organic semiconductors. In this technique, the solution to be deposited is dropped on the substrate, using a pipette/dropper/syringe, and then the substrate is left to dry (to allow the solvent to evaporate). The thickness of the final film depends on the concentration and viscosity of solute and solution. It is reported that the films deposited by this technique can have high molecular ordering for some solution-processable organic semiconductors [Park *et al*, 2007]. Use of this technique involves simple processing and efficient use of the material to be deposited. The shortcomings of this technique are the poor repeatability, uniformity, and thickness-controllability.

(c) Printing

Printing is also one of the advanced processing techniques used for depositing solution-processable organic semiconductors. There are various types of printing techniques, such as inkjet printing, microcontact printing, and screen printing. All of these techniques use solution-processable organic semiconductors as inks for creating specific structures/patterns on the substrate. There are many reports that highlight the advantages of printing, such as the ability to coat large substrate, low cost, easy processing, and good reproducibility [Sirringhaus *et al*, 2000; Teichler *et al*, 2013]. Challenges for printed organic transistors include the reproducible formation of very thin films, the achievable patterning resolution, and the device performance.

(d) Vacuum Evaporation

Vacuum evaporation is mainly used for the deposition of thin-films of oligomers. In this technique, a high vacuum (pressure less than about 10^{-6} Torr) is maintained in the process chamber before starting the deposition process. A low background pressure in the chamber is necessary to limit, and achieve a long mean free path for the source material to be deposited. The schematic diagram of a vacuum evaporation system is shown in Figure 1.7.
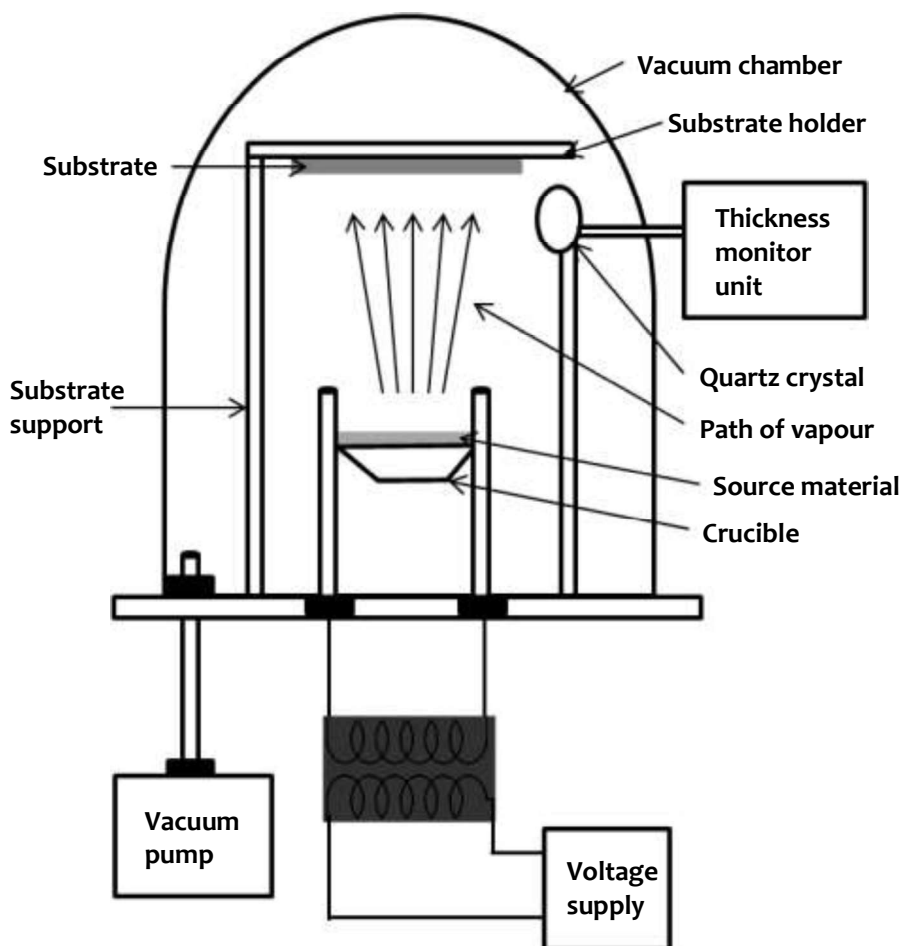

Figure 1.7 : Schematic diagram of the Vacuum Evaporation System

The source material (in solid or powdered form) is placed in the metal crucible. The crucible is resistively heated by applying a voltage to it to evaporate the source material from the crucible, resulting in the deposition of the atoms/molecules on the surface of the substrate. The

rate at which the evaporation of the target material (E_R) takes place is proportional to the vapor pressure (P_T) of the target material [Plummer, 2000]and is given as,

$$E_R = 5.83 \times 10^{-2}.A_T.P_T.\sqrt{\frac{m}{T_T}} \qquad\qquad\qquad (1.11)$$

where A_T is the area of the target, m is the gram molecular mass, and T_T is the temperature at which evaporation of the target material occurs.

This method is not applicable for polymers, because polymers tend to decompose at high temperatures [Li *et al*, 2011]. The morphology of the film deposited using this technique depends on the temperature, the surface energy, the roughness of the substrate, and on the rate of deposition. With this technique, high-quality ordered films can be deposited. This technique provides good control over the thickness of the film to be deposited [Zhang *et al*, 2009; Zschieschang *et al*, 2010; Zschieschang *et al*, 2011]. The spin-coating, drop-casting, and printing techniques are usually used for the processing of solution-processable polymers. In this study, small molecules are used as organic semiconductor (discussed in Chapter 3), deposited by the vacuum evaporation technique.

1.3 MOTIVATION FOR THIS WORK

Organic electronics has the potential to enable certain electronic applications that are not possible with silicon electronics, most notably applications that require (or at least benefit from) the possibility to fabricate the transistors at low temperatures on flexible, light weight plastic substrates over large area.

The further development of organic transistors and their future commercialization demand a lot more research work in order to address a variety of remaining challenges, such as the design and development of new organic semiconductors with improved charge-carrier mobility, the development of more efficient fabrication techniques, improvement in the performance of the devices by optimizing the various interfaces, and improvements in the device reliability. The device reliability includes the air stability, the bias-stress stability, and the mechanical stability.

It has been known for a long time that some of the parameters of organic TFTs (and also of some inorganic TFTs), such as the threshold voltage, the drain current, and the subthreshold slope change over time when constant voltages are continuously applied for long duration [Riedl *et al*, 2007; Wang *et al*, 2008; Tiwari *et al*, 2009; Zschieschang *et al*, 2009]. This phenomenon is called bias-stress instability. The instability of the device performance is obviously a critical reliability concern, especially for TFTs that are operated on the state continuously for longer duration. Examples are flexible information displays, RFID tags, and sensor devices. Hence, a detailed understanding of the bias-stress effect in organic TFTs is essential. Since the bias-stress stability of organic TFTs is greatly affected by the choice of the organic semiconductor, it is necessary to quantitatively assess the bias-stress stability whenever a new organic semiconductor is being considered for application in organic TFTs. To address these issues, various experiments were performed as part of this thesis, such as investigations of the shelf-life stability, bias-stress stability, and charge trapping dynamics of organic TFTs based on half a dozen promising small-molecule organic semiconductors. One of the causes of the bias-stress effect is the trapping of charge-carriers at various interfaces. Hence, a detailed study using the displacement current measurement technique was performed on organic TFTs based on various combinations of organic semiconductor and contact metal in order to estimate the charge-carrier injection, extraction, and trapping in organic TFTs.

1.4 ORGANIZATION OF THE THESIS

This thesis is organized as follows:

Chapter 1 presents an introduction to organic electronics. It gives the historical perspective, advantages and applications of organic electronics. The second Section of this Chapter focuses on the progress of the organic semiconductors used for the fabrication of organic transistors, and their electronic properties. The various mechanisms involved in the charge transport of organic semiconductors are also discussed. Finally, the processing techniques involved in depositing the films of organic semiconductor are discussed.

Chapter 2 summarizes the evolution, details, and operation of transistors. The structure and operation of Metal Oxide Semiconductor Field-effect transistor (MOSFET) is presented in the beginning, which is followed by the details related to the a-Si:H transistors. The evolution, architecture, and operation of organic TFTs are discussed. The strategy involved in the extraction of the important parameters for the evaluation of fabricated organic TFTs is also discussed here and the Chapter ends with the discussion on the challenges faced in achieving high-performance organic TFTs.

Chapter 3 shows the demonstration of low-voltage flexible organic TFTs. Firstly, the organic semiconductors investigated in this study are introduced. Then the fabrication process involved in the production of organic TFTs on flexible substrates is discussed. Finally, the electrical characteristics (*i.e.* transfer and output) of these organic TFTs are shown along with their air stability and the effect of continuous scans on the transfer characteristics.

Chapter 4 is devoted on the Bias-stress stability of flexible low-voltage organic TFTs. The introduction to Bias-stress and its mechanism is given in this Chapter. The influence of gate-source and drain-source voltages on the electrical stability of organic TFTs is given. The comparison between different organic semiconductors based TFT are made on the basis of their Bias-stress stability. The comparison between the stability of the organic and a-Si:H TFTs is also made in order to benchmark the stability of organic TFTs in comparison with different materials or technologies.

Chapter 5 is focused on the study of the charge-carrier dynamics of organic TFTs using displacement current measurement (DCM) technique. Firstly, the device structure required to conduct displacement current measurement with its operation principle are discussed. The experiments were conducted with this measurement technique on various organic semiconductor and metal contacts based devices to estimate the charge-carrier trapping dynamics in organic TFTs.

Chapter 6 gives a detailed summary of this thesis work with an outlook for the possible future work which can be conducted in the direction related to this thesis.