Chapter 1

Introduction

1.1 Overview of Organic Thin Film Transistors and Active-Matrix Pixel for Novel display Applications

Organic thin film transistors (TFTs) have attracted much attention over the last decade due to its low fabrication cost, low temperature process and compatibility with plastic substrate. The field effect of organic semiconductor was reported in 1970s. [1-2] However, since Koezuka and coworkers demonstrated the organic field effect transistors by electrochemically polymerized polythiophene in 1987, they have been treated as one of potential electronics elements [3-4]. Recently, organic TFTs has been improved dramatically, for instance, mobility, the most important index of properties of TFTs has raised several orders even over the level of amorphous silicon TFTs to 1-5 cm^2/vs. They could be widely used in electronics applications, such as radio frequency identification tags [5] , smart cards, microelectronics [6-10] or sensors [11]. Except those, the large area display is recognized as another key application. They are also the promising candidates to realize the flexible display technology.

In general, the organic semiconductors could divide into two catalogs. One is the family of conjugated polymers (or conducting polymers), with higher molecular weight and soluble in organic solvent. The regioregular poly(3-hexylthiophene) (RR-P3HT)[12-14] and poly(9,9'-dioctyfluorene-*co*-2,2'-bi-thiophene) [15,16] are the representatives. They could be processed by spin coating, ink jet printing, or other solution process. Hence the fabrication cost is very low. Moreover, the cost maybe

down to one tenth of traditional amorphous silicon TFTs by using roll-to-roll process. However, they suffer from the low performance of TFTs. The RR-P3HT TFTs could only reach the mobility order of 10^{-2} cm^2/vs. Another catalog is the family of small molecules. It has lower molecular weight and usually insoluble in organic solvent. Thus, they are processed by thermal sublimation or evaporation. Pentacene, a fused-ring polycyclic aromatic hydrocarbon, is the famous representative. It has better properties of TFTs with mobility of the order of 1 cm^2/vs and on/off current ratio above the order of 10^5.

Although organic TFTs have similar performance with amorphous silicon TFTs, they still surfers from some issues. For small molecular organic semiconductor, like pentacene, they are joined together by van der waals powers as forming a continuous film. Therefore, most pentacene films are loose, full of defects and contain many polycrystalline phase that are strongly dependent by lab. A suitable process control would enhance the dense and arrange the pentacene molecules in order. However, the mechanisms of forming a good quality and high dense pentacene film are still unknown and investigating.

The operation principle of organic TFTs are similar to amorphous or polycrystalline silicon TFTs. The current-voltage relation follows the charge sheet model. That would be detail described in section 1.1.1. In general, the carrier transport in organic semiconductors could roughly divide into two possible ways, the intra-molecular and inter-molecular. The intra-molecular carrier transport is mainly governed by the band-like energy distribution that is constructed by the specific π electron orbital of organic semiconductors. And the carrier transport behaviors of inter-molecules of pentacene are governed by thermal hopping. That deduces the low field effect mobility. Organic semiconductors usually have high band gap and high ionic potential, for instance, pentacene has a nearly 2 eV band gap and 5 eV of ionic

potential. Those make the pentacene TFT operation at high voltage and hard to form an ohmic contact with source/drain electrodes.

To solve these issues, many approaches were proposed. Such as the novel device structure that shorten the channel length to reduce the operation voltage, or doping the pentacene near the source/drain areas to increase its conductivity as well as lower down the barrier height between electrode with pentacene. The most direct way is to raise the pentacene quality by purification. It could get an intrinsic mobility almost 35 cm^2/vs by space-charge limited current method [17].

The other topic in this thesis is the novel active-matrix pixel structure. Except the applications to liquid crystal displays or organic light emitting displays, we try to apply the active-matrix pixel structure to the field emission display. Field emission display attracted much attention in 1990s due to its high brightness, good color performance, short response time and large viewing angle. In the beginning, the study focused on the spindt-type field emission display [18], however the reliability and high operation voltage issues retarded its proceedings. Until carbon-nanotube was found and took the place of spindt-type emission tips in recent years due to its low work function.[19] That leads to low turn-on electric field and low operation voltage. Even so, the carbon nanotube field emission display still suffers from low uniformity and possible reliability issues. Many methods were proposed to enhance the uniformity of carbon nanotube, such as by highly aligned carbon nanotube growth and multi-gates controlled. Here, the active-matrix pixel structure was adopted.

1.1.1 The Basic Operation Mode and Principles of Organic Thin Film Transistors

Fig. 1.1(a)(b) show the standard two kind of organic TFTs configuration, (a) is

the inverted staggered type TFT and (b) is the inverted coplanar type TFT . Usually, the former was also called the top contact (TC) and the latter was called the bottom contact (BC) TFT. The organic p-type semiconductors commonly used have electrochemical oxidation potentials in the range 0 to +1 V versus SCE, which can be translated to ionization potentials in the range of 4.4 to 5.4 eV [20]. Thus high work function materials, such as gold with work function of 5.1 eV, Pt of 5.3 eV and Indium Tin Oxide (ITO) of 4.9~5.1 eV work fine as an ohmic contact. The mode of operation of such insulated thin film transistors has already been analyzed, following the knowledge developed for crystalline semiconductors and generalized to amorphous and polymer-based semiconductors [21,22]. Fig. 1.2(a) presents the schematic operation of organic TFTs, showing a lightly p-doped semiconductor; + indicates a positive charge; $\ominus$ indicates a negative charge. In Fig 1.2(b), the source electrode is grounded, and the insulated gate electrode is polarized negatively as V_G. The gate voltage is dropped over the insulator and over the semiconductor near the insulator/semiconductor interface, giving rise to band bending in the semiconductor, the accumulation region. The additional positive charge accumulated in this region is supplied by the ohmic source and drain contact. If the insulator has a capacitance per area C_i, then the accumulated charge per unit area is simply $(V_G-V_{th})C_i$, assuming that the V_G must overcome the built in voltage, presenting as threshold voltage V_{th} caused by unintentional charges in gate insulator and the voltage dropped across the semiconductor is negligibly. The semiconductor now contains positive charges both from doping and from the "field effect" which created the accumulation layer. If the latter charges are mobile and not trapped, then, when a small bias is applied on the drain electrode, a current larger than the ohmic current deduced by doping will be observed. An important parameter, mobility μ, is identified that govern the moving ability of accumulated charges under the influence of field effect. Accordingly, the

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relation between current-voltage could be deduced from charge sheet model in linear regime and presented as following:

$$I_{DS} = \frac{W\mu C_i}{L}(V_G - V_{th} - \frac{1}{2}V_D)V_D \qquad \text{if } (V_G - V_{th}) \leq V_D < 0 \qquad (1.1)$$

Where I_{DS} is source-drain current, V_D is the drain bias, and W/L is the channel width-to-length ratio. For higher V_D, exceed V_{th}, the channel pinch-off that means the channel depleted at the drain region, the saturation occurs and the current-voltage relation present as,

$$I_{DS} = \frac{W\mu C_i}{2L}(V_G - V_{th})^2 \qquad \text{if } 0 > (V_G - V_{th}) \geq V_D \qquad (1.2)$$

If a positive gate bias is applied, then the positive band-bending occurs in the semiconductor at the insulator interface, leading to depletion of charges (Fig. 1.2(c)). The positive doped induced charges within the depletion zone flow out the device through the source-drain contacts. When enlarging the gate bias, the depletion region will grow up into the semiconductor layer until eventually depleted the entire semiconductor layer. The depletion layer, W_{SC}, varying with the gate bias follows this equation:

$$W_{SC} = \frac{\varepsilon_s}{C_i}\left[\left(1 + \frac{2C_i(V_G - V_{fb})}{qN\varepsilon_s}\right)^{1/2} - 1\right] \qquad (1.3)$$

Where ε_s is the dielectric constant of the semiconductor, V_{fb} is the flat band potential, and N is the doping concentration. Therefore the pinch-off voltage, V_p, can be calculated by

$$Vp = \left(\frac{qNd^2}{2\varepsilon_s}\right)\left(1 + \frac{2Cs}{Ci}\right) \qquad (1.4)$$

where the C_s is the dielectric capacitance of the semiconductor layer, and d is the thickness of semiconductor layer. The equation is interesting since the dopant concentration N, can be obtained by the examination of the pinch-off voltage V_p. The

drain current in depletion regime, can also give by

$$I_{DS} = \left(\frac{Wdq\mu N}{L}\right)\left(1 - \frac{V_G - V_{fb}}{V_p}\right)V_D \tag{1.5}$$

allows very low drain leakage current to be reached for organic TFTs, which are needed for a high rectify ratio. The Fig. 1.3 (a)(b) show the as-obtained experiment output and transfer curves of an inverted coplanar type organic TFT utilizing ITO as electrodes without any correction, confirm the relevance of organic TFTs. The aforementioned refer to Kagan et al.[23] and Brown et al.[24].

1.1.2 The Carrier Transport in Organic Semiconductors

The organic semiconductor molecules are joined together by van der Waals power with energy smaller than 10 kcal mol^{-1}. This weak interaction energy of molecules may take responsibility for the low upper limit of carrier motilities, falls between 1–10 cm^2/vs by time-of-flight measurement [25], due to its value close to the vibration energy of molecules. Whereas in inorganic semiconductors that are joined by covalent bonds, the intermolecular bonding energy is strong such as 76 kcal mol^{-1} in silicon. Thus the carriers move as highly delocalized plane waves in wide band with high mobility.

The conjugated organic materials contain the specific π electron orbital that makes the carriers possible to move intramolecular. In well-order organic semiconductors, the energy of excitation state and the steady states of π electron would extend and split to form a band-like energy scheme. The energy scheme is similar to that in inorganic semiconductor, LUMO (Lowest Unoccupied Molecular Orbital) like the conduction band and HOMO (Highest Occupied Molecular Orbital) as the velence band (See Fig. 1.4). The energy band structure make the carrier

transport demonstrate band-like behavior in some case.

However, band transport may not suit for disordered organic semiconductors, in which carrier transport is govern by hopping between localized states. It is thermal activated process and assisted by phonons. The mobility increases with temperature, although the overall mobility remains comparative low, usually much lower than 1 cm^2/vs. The discrimination between hopping and band transport is the organic semiconductor film of mobility around 1 cm^2/vs at room temperature. Many kinds of polycrystalline organic semiconductors like acene series, pentacene, rubrene, have mobility falling in the range. Sometimes, a temperature-independent mobility was found in some polycrystalline pentacene film [26]. This observation argued that the simply thermal activated hopping process governed the whole carrier transport behaviors in high quality polycrystalline pentacene film, despite that the defects rich film quality may cause mobility increase with temperature in some cases.

The understandings of carrier transport in a single crystalline organic semiconductor help us to understand the transport mechanism in a polycrystalline organic semiconductor film. It was believed that the carrier transport mechanism in single crystal is coherent band-like transport of delocalized states at low temperature. A high mobility for holes, 400 cm^2/vs, measured by time-of-flight in single crystal naphthalene at 4.2 K was observed [27,28]. The hole mobility increases from 1 cm^2/vs at room temperature to almost 400 cm^2/vs at 10 K following a power law of $\mu \propto T^{-n}$, n=2.79. This is a clear evidence of band transport in single crystalline organic semiconductor. On the other hand, the electron mobility was also found temperature-dependent below 100 K and following a power law of $\mu \propto T^{-n}$, n~1.5-1.7, in single crystal naphthalene [27,29,30]. However, between 100 K and 300 K, the electron mobility revealed a constant value [30,31], that has been treated as the

superposition of two independent carrier transport mechanisms. The first mechanism was thought as the tunneling of small molecular polaron (MP), that the carriers were treated as heavy polaron type qusiparticles formed by the interaction between carriers with intramolecular vibrations of the local lattice environment. In this model, the mobility followed the power law of $\mu_{MP} \propto aT^{-n}$. Another mechanism is the moving of small lattice polaron (LP) by thermal activated hopping, which followed an exponential dependence with temperature of $\mu_{LP} \propto \exp[-E_a / kT]$. The superposition of these two mechanisms could get good consistence with experiment data from room temperature to a few Kelvin degrees [30].

The basic understanding of carrier transport mechanism is very important in organic semiconductor. Although the ultrapure organic semiconductors demonstrated a coherent bandlike transportation, the most real organic semiconductor films were polycrystalline which contained many structure defects, such as in grain boundaries. Those defects dominated the carrier transport though affecting the energy barrier height in grain boundaries. .

In short summary, from above inference, the ways to enhance the carrier transport, or mobility, in organic semiconductors have two. One is to strengthen the intermolecular force of organic semiconductor to form a more rigid structure that would enhance the transport of delocalized carriers by lattice vibrations (phonons). Another is to build a structure that carrier transport only through intramolecular. That could be realized by long chain polymers or by very short channel length. Both them are not easy to mass production.

1.1.3 The structures of Pentacene

Pentacene ($C_{22}H_{14}$), a fused-ring polycyclic aromatic hydrocarbon, is one of the

promising candidates of organic semiconductors. Its schematic plot is shown in Fig. 1.5. There are ways to fabricated it as a continuous film such as the solution process, vapor phase deposition and thermal evaporation. Previous studies of the growth of single crystalline pentacene have shown that the pentacene molecular crystallized in a layer-by-layer structure with a herringbone arrangement, and giving a well defined 'layer periodicity': d(001) value of 14.4 Å (See Fig. 1.6(b)(c)). The single crystal pentacene is triclinic structure with a unit cell parameters of a=7.90 Å, b=6.06 Å, c=16.01 Å, α=101.9°, β=112.6°, γ=85.8° [32,33]. In 1991, Minakata et al. reported the pentacene as a film with a observed d(001) values of 15.4 Å [34-36] and 15 Å [37-38] different from the single crystal result of 14.4 Å. This was first mentioned by Dimitrikopoulos et al., who noted that the d(001) value of 15.4 Å should be attributed to another crystalline phase [39]. It was also the first time to observe the coexistence of two phases of pentacene, with d(001) values of 15.4 Å and 14.4 Å. The 15.4 Å and 14.4 Å polymorphs are commonly referred to as "thin film phase" and "single crystal phase". However, some recent studies demonstrated a single crystal phase of d(001) value of 14.1 Å [40-42]. The Mattheus et al. thus studied and observed that the polymorphs of pentacene would result four crystalline phases of d(001) values of 15.4 Å, 15.0 Å,14.4 Å, and 14.1 Å [42-45] which strongly depended on the fabrication temperature, surface energy, thickness, and so on. Some of these phases could be transformed each other by solvent or heat [46]. Different crystalline phases of pentacene would perform different electrical properties. In general, a single type crystalline phase is preferred rather than the coexistence of multi crystalline phases in pentacene, the former denoting better electrical properties.

Except the crystal structure properties of pentacene, the electrical properties of pentacene are also concerned. The ionization potential of pentacene is reported between 5.1 eV to 5.3 eV. And the band gap dependent on the crystal structure varied

from 2.2 eV to 1.96 eV. The data of dielectric constant of pentacene is quite different determined by different research groups. It was reported as 2, or 4. The 4 was adopted in this dissertation. That would be described in chapter 2.

1.2 Motivation

From the inference mentioned above, many unclear and unidentified mechanisms need to be studied for pentacene TFTs. Such as the definition of threshold voltage, field effect mobility behaviors and environment influence, all need be further considered. In the literature, most researchers extract the device parameters by fitting the charge sheet model equation (See Eqs. (1.1)(1.2)). In large bias regime, the organic TFTs were proved to follow Eqs. (1.1)(1.2) when the V_G exceed V_{th}. Nevertheless, in large gate bias region, the mobility was found dependent with gate bias. The detail mechanism was still under investigated. Dozens of researches proposed different theories to explain that, such as the trapping at localized gap states [47,48], potential barrier model [49], potential well model [50] and etc… The phenomena must be considered into the current-voltage relationship, and deduce an $\mu = \mu(V_G)$ item. Besides, the definition of V_{th} in Eqs(1.1)(1.2) was deduced from MOSFET, that may not suit for organic TFTs since most organic semiconductors are only proposed uni-polar operation and biased in accumulation mode. The physical meaning of threshold voltage in organic TFTs are questionable and difficulty to define [51,52]. In this thesis, we propose another point of view to analyze the definition and influence factor of threshold voltage.

The carrier transport in organic TFTs also attracts many interests. Its intrinsic mechanism is not clear yet. Organic films are very sensitive to the environment and are unstable in air [24,53-55]. Necliudov et al. [56,57] examined the instabilities of

the electrical characteristics and the 1/f noise behaviors of pentacene TFTs. They reported that atmospheric moisture causes pentacene TFT degradation. Brown et al. [24] found that the organic TFTs in air exhibit stronger hysteresis than those in a vacuum. Organic TFTs in air have higher off currents because the oxygen dopant [24,58] and/or moisture interact with organic films [59,60]. Recently, Zhu et al. [53] presented humidity sensors that use pentacene TFTs. Clearly, contact with compounds in air affects the transport characteristics of organic films. To find out the possible reason, and consider about the gate bias dependent mobility, the Levincen model and potential barrier model were used to estimate the trap density in the polycrystalline grain boundaries. That may explain the different pentacene film situation in air and in a vacuum.

In commercialization, the active-matrix display is an important application for organic TFTs. They allow the use of inexpensive, light-weight and mechanically rugged plastic substrates as alternatives to glass. Prototype display, each pixel of which is driven by pentacene TFTs [61] has been recently demonstrated. A polymer pixel engine has also been developed [62, 63], indicating the potential of organic TFT technology for use in display applications. However, the high operation voltage and photosensitivity of organic TFTs restrict the display type. Thus, most investigations on the use of organic TFTs to drive active-matrix liquid crystal displays focus on reflective displays, such as the polymer dispersed liquid crystal or electronic-ink displays [64]. These types of displays are suitable for operation at high voltage. But, the most popular and mature liquid crystal display is still the twist-nematic type liquid crystal display nowadays. We therefore try to realize an active-matrix twist-nematic liquid crystal display in this dissertation.

On the other hands, a novel active-matrix pixel structure was proposed to solve the non-uniform brightness and high turn-on voltage issues of carbon nanotube field

emission displays. The active-matrix addressing scheme was proposed before [65-67]. The high breakdown voltage transistor, like lateral diffused metal oxide transistor, was used to drive spindt-type field emission display. Since the carbon nanotube was used, the large scale process seems possible for field emission display technology in the future. So the active-matrix pixel structure driven by thin film transistors was proposed [68]. However it was only the impulse-type display; we try to realize another hold-type active-matrix carbon nanotube field emission display, here.

1.3 Thesis outlines

This dissertation is organized as follow:

In Chapter 2, the basics of pentacene grain growth mechanism was studied. The growth of pentacene with different substrate temperature and pretreatment layer was investigated. The different device configurations were also studied. Then we focused on the study of properties of the inverted staggered type pentacene TFTs utilizing gold as source/drain electrodes with different pentacene thickness. The device parameters extraction methods of pentacene TFTs were investigated. Different methods such as the constant current method, maximum transconductance (Gm) method, square root methods, and capacitance-voltage measurement were used to extract the threshold voltage. And a bulk traps dependent threshold voltage model is proposed to explain the threshold voltage shift. It is consistent with theory.

In Chapter 3, the atmospheres effect on pentacene TFTs was studied. The humidity was found to seriously degrade the carrier transport in pentacene. The field effect mobility in linear and saturation regions were extracted and analyzed in detail, respectively. The gate bias dependent mobility was analyzed by grain boundary potential barrier model in different atmospheres. The trap density in grain boundaries
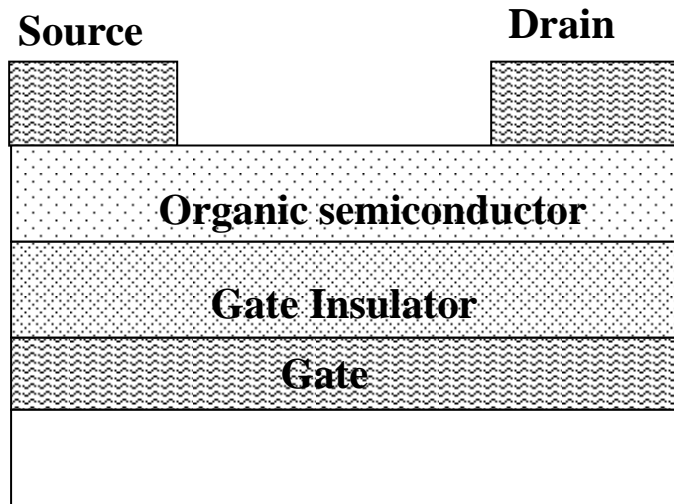
was extracted and discussed.

In Chapter 4, to further consider the criteria of pentacene TFTs for display applications, the device uniformity in local area, gate stress reliability, sensitivity to illumination, and passivation effect were all measured. The criteria were summarized and integrated into the active-matrix pixel design for driving a liquid crystal display. This display was realized and functions successfully.
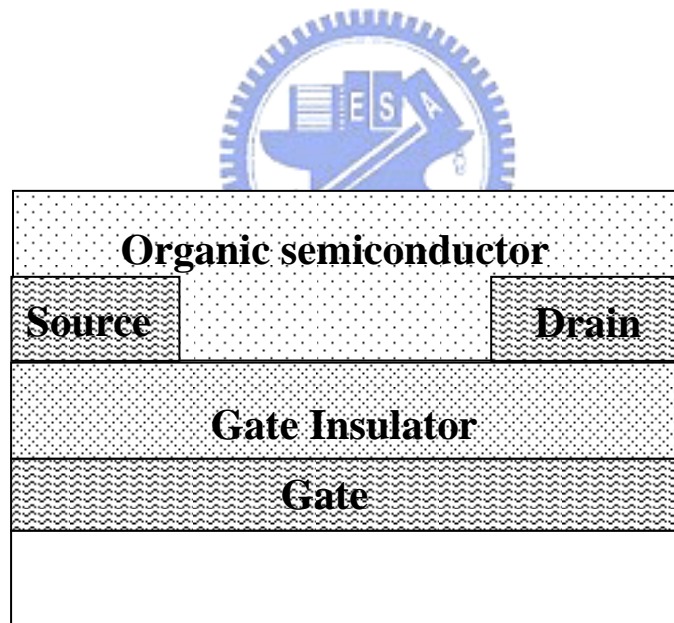
In Chapter 5, a novel active-matrix pixel design was proposed. The high performance and thermal stable low-temperature poly silicon TFTs were used to drive a diode carbon nanotube field emission display. Two TFTs and one storage capacitor were adopted in one pixel. This pixel structure could perform a hold type active-matrix display. This display were fabricated and demonstrated in this chapter.

In Chapter 6, conclusions as well as some recommendations for further study are given.

Source   **Drain**

Organic semiconductor

Gate Insulator

Gate

(a)

Organic semiconductor
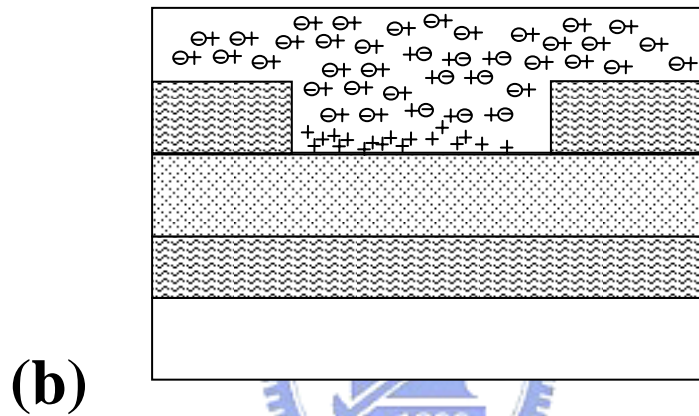
Source   Drain

Gate Insulator

Gate

(b)

Fig.1.1   (a) Cross section view of inverted staggered type organic TFTs.

(b) Cross section view of inverted coplanar type organic TFTs.

$V_G = V_D = 0$

(a)

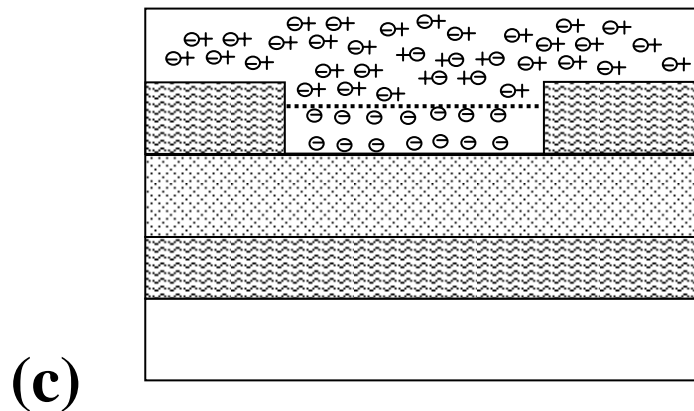$V_G < V_D < 0$

(b)

$V_G > 0, V_D = 0$

(c)
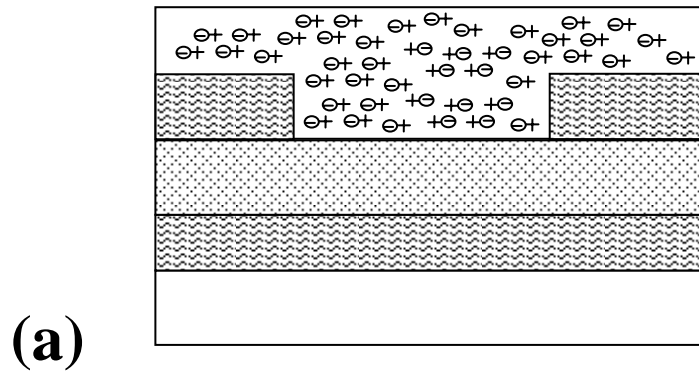
Fig 1.2 (a)Schematic of operation of organic TFTs, showing a lightly p-doped
semiconductor; + indicates a positive charge; Θ indicates a negative charge.
(b) Development of a positive accumulation layer when a negative gate bias
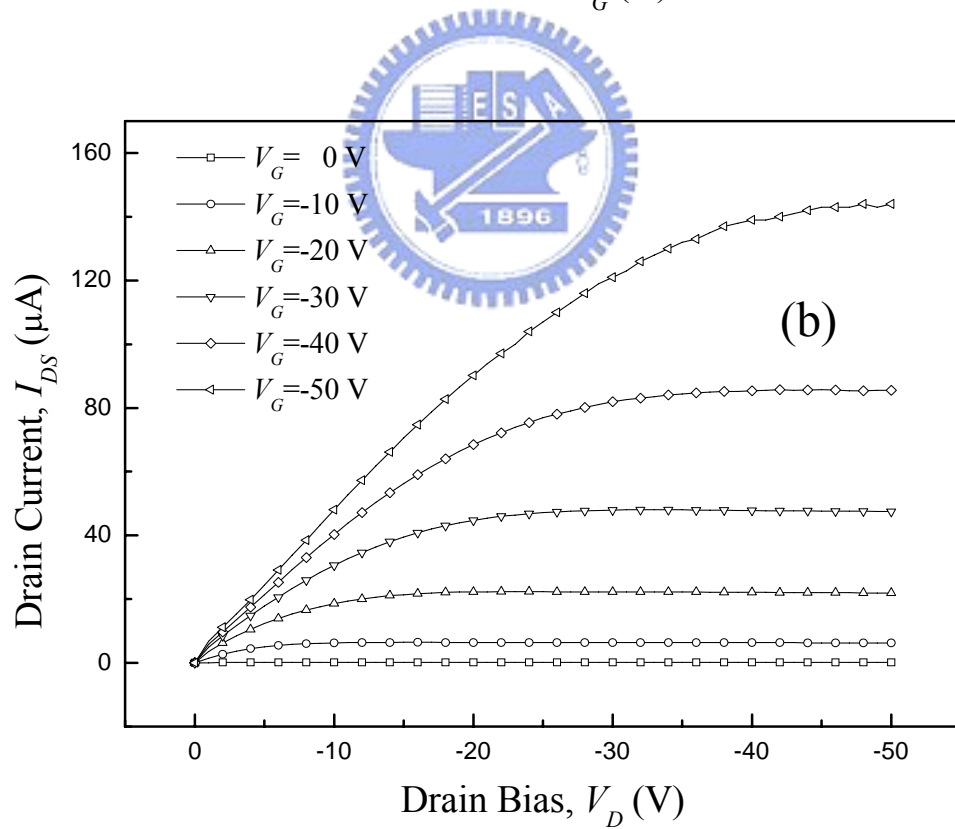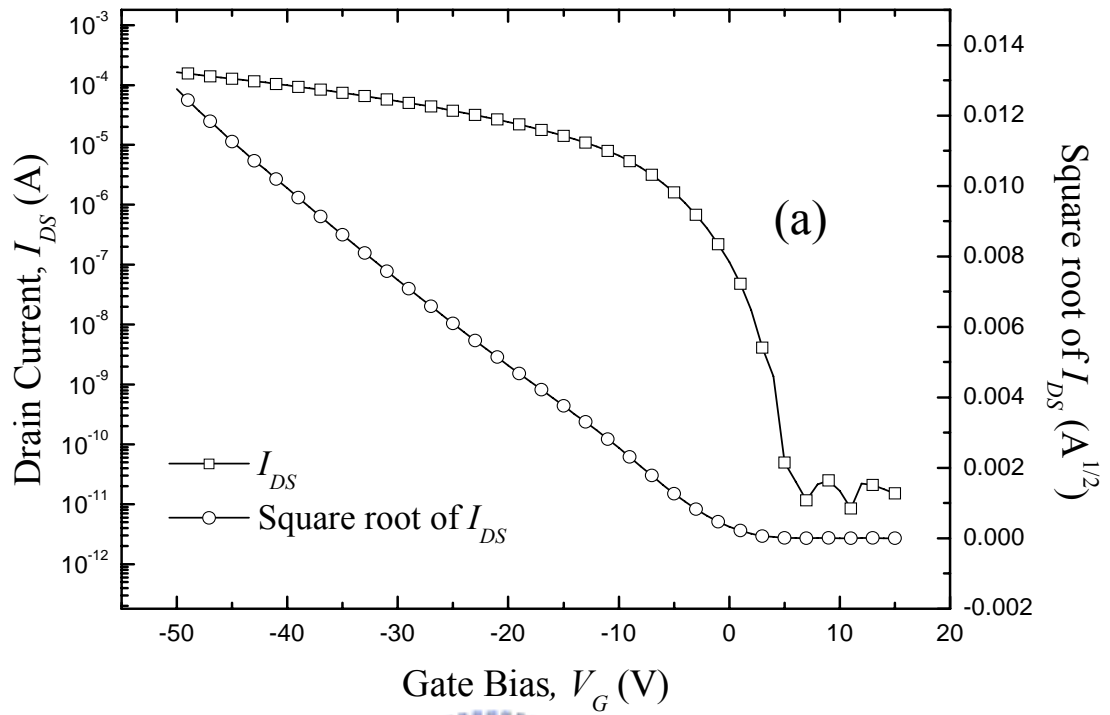is applied. (c) Development of a depletion region when a negative gate bias
is applied.

Fig. 1.3 The properties of an inverted coplanar pentacene TFT utilizing ITO as electrodes with channel width 10000 μm and channel length 57μm. (a) The transfer curve of V_D= -50 V. (b) The output curves.
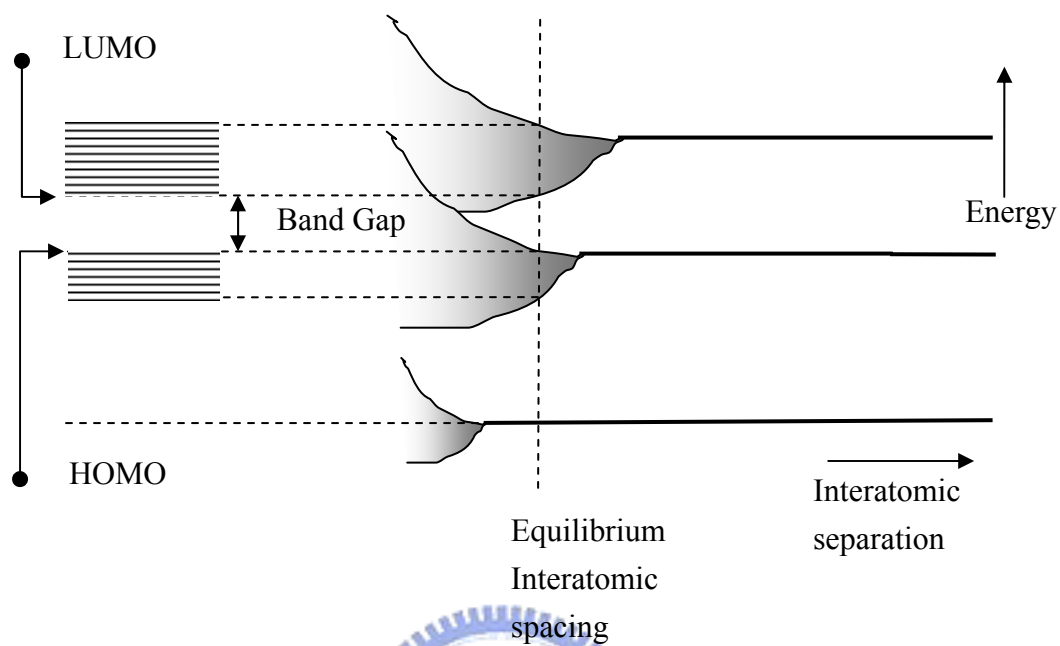
Fig 1.4 The energy band diagram shows the formation of LUMO (Lowest Unoccupied Molecular Orbital) and HOMO (Highest Occupied Molecular Orbital) in organic semiconductor.
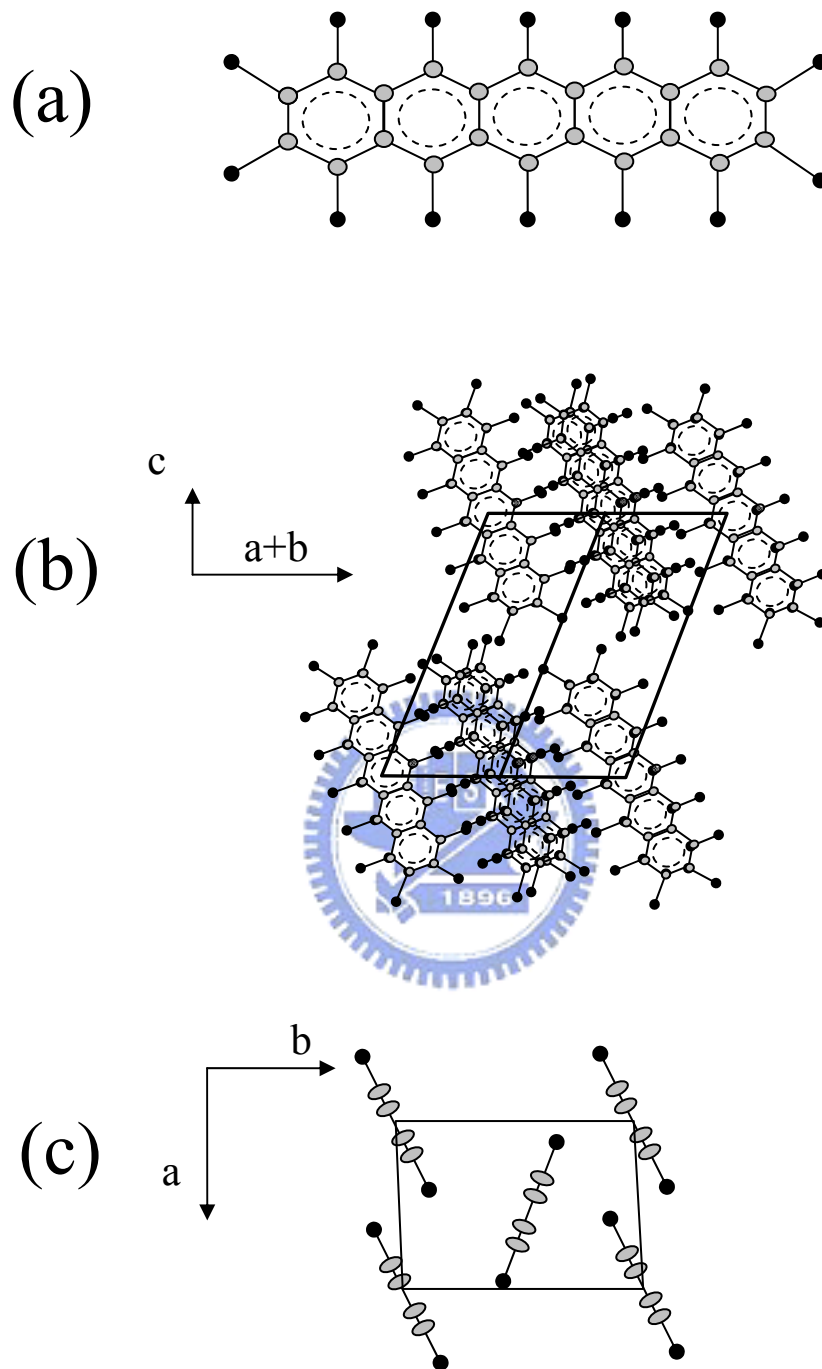
Fig 1.5 (a) The schematic plot of a pentacene molecules. (b) The crystal structure of the layer by layer pentacene crystallization in the direction of [110] axis. (c) Top view along the long axis.