國立交通大學

電機學院微電子奈米科技產業研發碩士班

碩士論文

探討製程變異於有機電晶體之影響

Study of process variation on P3HT-Based OTFTs

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探討製程變異於有機電晶體之影響

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摘　要

本論文研製之 P3HT 有機電晶體，是利用溶劑式製程方式，故須將其粉末(溶質)，經選用適當的溶劑與調配比例，使得 P3HT 能均匀得溶於溶劑之中，再使用旋鍍製程方式，沉積形成 P3HT 薄膜；此薄膜當成有機主動層(*p*-type)，進而應用於有機電子相關產品。

P3HT 於有機材料中，被分類為共軛高分子；因具有自我組織的性質，而形成高分子長鏈，因製程方式不同，所得實驗結果和薄片(lamella)排列也不盡相同。經本論文實驗結果：首先藉由氯仿溶液與調配濃度百分比為 0.1% 之比例，能讓 P3HT 完全溶解於其中，不會因溶解度的關係而降低其效能；相反的，利用二甲苯卻得到相對不理想之結果，因較差的溶解度關係所造成。製程時，猜測搭配較少的比例與揮發慢的溶劑，可以提供相對較長排列時間，使得微結構分子，有較恰當的排列方式，進而得到較高之結晶性，而使的移動率相對的提高。接著探討不同規則區域性(Regioregularity_RR)和分子量(Molecular weight)，兩種溶質同樣溶於氯仿中，經電性與物性分析結果，知道分子量差異比 RR 值來的重要。再經由 1500 轉速、烘烤(Curing)溫度為 150℃與時間維持 3 分鐘下的製程條件，具有比較好的電性結果，這也利用歐傑電子(Auger)和表面元素(ESCA)分析發現，氧分子含量都有相對

比較低的情況，但是透過 FTIR，並無見到氧分子所造成的結果，猜測：其的存在是利用物理吸附非鍵結，故無法被偵測到。

已知基本製程條件後，由於蕭特基接面會有較高的能位障產生，此位能障位於金屬和有機物間，然而，藉由金(GOLD)的金屬材料和適當厚度的附著層(Adhesion layer)，可因功函數接近 HOMO 和其化學屬性的關係，得到相對比較小阻值結果，另一方面，使用表面處理(HMDS)，讓分子可更有效排列與增加結晶性，而提高移動率與越接近零之起始電壓(Threshold Voltage)。

論文的最後，研究 P3HT 有機材料的穩定性，因為大氣環境對有機物來說是一種挑戰。實驗結果顯示，製程而成的電晶體，卻在存放一個月左右，即可明顯見到退化現象。可是再利用後段長壓退火，以通入氮氣方式，進行 180℃和 30 分鐘的退火，可以有效改善效能，這樣的效果一樣可在低分子量見到；同時發現，經過一連續製程步驟之元件，再經退火處理後，On/off 比例值可達到 6~8x10^6 次方，經由歐傑電子之縱深分析，適當退火可更有效使氧分子被驅離出薄膜；可惜的是，移動率並沒有因此而提升和起始電壓有往負值方向移動。最後利用定電壓和時間 STRESS 方式，發現只供給 Drain -60 伏電壓下，P3HT 的 ID 電流，會隨時間上升而增加，且已達開啟電流，此時，卻未發現閘極電流隨著上升的情形。但再次量測基本電性時，發現整個 OFF 電流，受 STRESS 後，有上升趨勢，間接猜測是，因為氧分子，經由 STRESS 時，再次進入薄膜，而可能導致的結果。

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ABSTRACT

A procedure is studying and using the solution-process to fabricate P3HT-based organic thin film transistor. Using appropriated solvent and weight percentage is needed. And then the P3HT solution will be spun and deposited to be as active layer for organic electronic.

P3HT organic material is to be classified to conjugated polymer. One of advantages is a property of self-organization and based on this structure to form a long chain. This long chain will be formed a lamella structure. If this lamella were packing closely, it would result a high regioregularity, which could obtain high mobility. Due to different process method, this lamella will be formed edge-on or face-on result. In my experiment, First of all, using chloroform to be a solvent with 0.1 weight percentages to fabricated OTFT can obtain better performance than xylene made, due to solubility and like dissolves like. Subsequently, we study the difference between regioregularity and molecular weight, two solutes were purchased from two different companies, dissolved them in the same solvent, chloroform. The result is that the difference of molecular weight is more importance than regioregularity. Moreover, fabricated by spin speed at 1500rpm and curing at 150℃ for 3 minutes can exhibit optimized result and in the meantime, observe that the oxygen concentration is less and less in the thin film analyzed by Auger electronic and ECSA surface elemental.

Known a basic process procedure, there is a Schottky barrier between metal and organic material resulting less the current transport. However, S/D deposited with gold and an appropriated adhesion layer can reduce this barrier height, due to their closest work function

and surface chemical property. In addition to previous results, to use surface treatment (HMDS) is a good idea to improve the packing and ordering for strong chain interaction and lead to exhibit high mobility and approximate to $V_G=0$ of threshold voltage.

In end of this thesis, we discuss about stability characteristics. Storage in the atmosphere, all of organic material will degrade as time goes by. This result is the same as P3HT polymer when it has been stored for one month. But the off current can be “healed” by annealing process at 180℃ for 30 minutes in furnace with N_2 flow. Extra, low molecular weight comes to the same thing. Meanwhile, a device undergoing a serious process procedure can obtain a better performance, too. The on/off ratio is improved from $6x10^4$ to $8\sim6x10^6$; suspect that oxygen molecule can be driven off during annealing process. Unfortunately, the mobility is not to be improved and reduce down to $0.3x10^{-3}$ from $6x10^{-3}$ slightly and Vth is shifted to more negative, due to chain torsion. Last, constant voltage stress is applied to see how the drain current change. During stress, the drain increases with stress time going by when only drain electrode is applied at -60 voltages. There is no any gate current to be observed. We find out that the basic electrical result of the same device is changing after stress. A slight movement in off current, compared with just annealing one. So we suspect that the oxygen may diffuse into the film during stress.

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Chapter 1

Introduction and motivation

1.1 Overview of organic semiconductor

Organic thin-film transistors based on solution-processed and semiconducting conjugated polymers have highly promising and feature technological properties, due to its high mobility. Polymer, it also follows in complex microstructures. Indeed, using solution-processed process is one of method to suppress cost, cohering with the low cost requirement, and simple process procedure. For application, it can apply to large area, flexible panel, flat-panel display, and identification tags **[1.1] [1.2] [1.3]**.

In the early 1970, the conducting conjugated polymer has known as polyacetylene, PA, with it repeat unit $(C_2H_2)_n$ and announcement **[1.4]**. It is one class of conjugated polymer, which consists of the hydrocarbon. After doping appropriated oxygen (oxidation), its conductivity was reached to 10^3 S/cm, compared with un-doped one. Table 1-1 shows common organic polymer. What a great history. The theory of transporting is that the charge is transporting (hopping) along main chain, which is composed of sequences of alternating single (named sigma bond) and double bond (pi bond). Those bonds are composed of outer value electron between atoms or between atoms and other covalent bond, which sharing of pairs of electrons. The pi bond, which electron could gathers around mostly, can provide a conductive path to let the carrier "move". Greatest thanks for those inventors. They were awarded the Noble Prize for this contribution. General speaking, There are many methods to changing the conductivity such as electropolymerization and By now, by such investigated result it appealingly make many researches join in, improve its chemical properties, and many study result were published. The disadvantage of PA is unstable when it exposes in the atmosphere, due to the moisture and humidity so that its value of existence should be concerned.

Polythiophene is one of extended conjugated polymer by using a concept of polyacetylene. Replacing of benzene with sulfuric acid provided. Due to its conductivity and electroactivity, in the past two decades, Polythiophene is known for its environmental stability, structural versatility, and combination of original electronic properties **[1.5]**. Controlling structural regularity for improving high electrical conductivity is major problem. The result of finest optimized electrochemical synthesis is quest for. A analysis through optical properties of polymer and the electrochemical have illustrated that the conductivity increase with decreasing band gap from 2.20 to 1.90 eV **[1.6]**.

In 1985, R. L. Elsenbaumer et al **[1.7]** reported that they were subsubstituted at beta position of a monomer of thiophene to 3-alkylthiophene and then using a method of chemical or electrochemical, like $AuCl_3$ or $FeCl_3$ …etc to copolymerize to poly-3-alkylthiophene (P3AT). This exhibits a conductor and optical property and it can be dissolved in organic solvents at room temperature. It is easy to form a thin film. This P3AT also exhibits a good stability.

P3AT is a typical polymer with a result of regioregularity, which improves the property of polythiophene. Due to 3-alkylthiophene is dissymmetry, leading to three types of dyad structure as head-to-tail, head-to-head, and tail-to-tail isomers, as shown in **Fig. 1-1[1.8]**. the fact of asymmetry is that both the α-position of oxidation potential and the difference between α- and D-position will decrease as the number of ring boosting. HH coupling structure is undesired because of steric hindrance, which is based on van der Waals force (discuss in chapter 2). This kind of steric hindrance makes a random chain packing and interaction, causing unstable conjugated system and low chain length. Side chain, alkyl, impede packing in solid state. In contract, HT coupling will reflect to self-organization and obtain a better ordering. Ordering will affect packing. Notice that short-range attraction in the interaction will appear anisotropic, when they pack themselves. Because lowest packing potential energy will be in regular arrangement, local chain will show as orientation dependent **[1.9]**. Some researchers are effort to produce high regioregularity by 2, 5-linked repeat unit such as McCullough et al. **[1.10]** and Rieke et al. **[1.11]**. Of course, the other position substituted like 2, 4- and 2, 3-coupling resulted in a problem of steric hindrance.

For 3-alkylthiophenes and other 3-substituted monomers, the observed effects were electrosynthesis conditions. There are so many ways to obtain HT-PATs. Notice that Polythiophene itself could not be dissolved, and the reason for substituted alkyl side chain is to make it soluble.

1.2 Conducting mechanize of conjugated polymer

Although this conducting theory is not clear, it is known that they are insulator or weak conductor of semiconductor as its natural. The molecular structure can be formed by atomic, which bind by covalent bond. Many interchain of molecules are bonded together by chemical bond, like van der Waals force with smaller than 10 kcal mol^{-1}. A long chain composed of each single molecule is monomer and there are hounded or thousand in a chain. After doping, meaning remove or inject electron, it will become a conductor or semiconductor. Therefore, it can explain by a theory of the classical semiconductor of band structure. The number of molecular orbital will increase with the number of atomic bonding to molecule. When these many orbital are spaced together, they will form a continue energy band. For instance, Polyacetylene **[1.12]** as degree of polymerization increase, the π and π^* orbital of CH will accumulate successively, energy distance between two neighbor orbits of different molecules is closing (overlapping) and finally, forms a energy band as shown in **Fig. 1-2**.

At the equilibrium, the highest occupied molecular orbital is named HOMO and the lowest unoccupied molecular orbital is named LUMO. There are similar as conducting band and valence band. The bandgap energy Eg between the bottom of LUMO band and the top of HOMO band is the width of forbidden energy gap. General speaking, in traditional material, it regard the band gap within 0eV, no gap, as a conductor, insulators are characterized by a large bandgap and the bandgap of conjugated polymer is around 1~3.5eV and that is a reason for organic semiconductor.

The feature of conjugated polymer is that the polymer chain is composed of many monomers by covalent bond. Secondary covalent bond are named π-bond, which is composed of carbon-carbon of single- and double bond with interacting each other and above π electron orbits the charge can travel along major chain or hopping to neighbor orbits for transport. The mobility can be obtained by this phenomenon. When the distance of carbon and carbon in main chain is the same, the π-electron is to be delocalized completely and then the band gap will be shorter and increase conductive. If the π-electron were delocalized as possible, it would reduce the band gap between conductor band and valence band. So far, the best way is adding a substitute radical in main chain to pull or add electron. The experimental results illustrate that it not only shorts the bond length between molecules, but also increase the feature of double bond **[1.13][1.14]**. Because the observed polycrystalline is studied, traps will attribute to defects and grain boundaries and dominate the transport.

1.3 Conjugated polymer of operation of thin-film transistor

The are several methods to deposit organic semiconductor of P3HT such as dip coating, speed-coating, drop coating, and print process **[1.15]**. Recently, the solution-process P3HT can be deposited by vacuum evaporation **[1.16]**, like small polymer. OTFT device performance can be affected by controlling external process procedure, like deposit rate and temperature. These results will reflect to morphology and electrical result. Post-deposition treatments, such as annealing and capping a protect layer, also preserve and improve molecular ordering, respectively. In this thesis, we use solution-process to deposit P3HT thin film onto SiO_2 surface and the device structure is bottom gate and bottom contact, as shown in **Fig. 1-3 (b)**. Because of less step of lithographic and prevent organic will be affected by metal evaporating step. **Figure 1-3(a)** shows a bottom-gate and top contact structure, which report a better performance for limitation of organic materials. Of course, all of them have own advantage and disadvantage and within the basic MOSFET architecture.

Basically, the structure is a three-terminal device, where a voltage applied at gate electrode to adjust current flow, source contact is used as the voltage reference, and drain electrode will operate device in linear region (small voltage) and saturation region (larger V_{DS}). There are several situation of operation, for instance, p-type semiconductor will be demonstrated. First, all three electrode are applied a zero voltage. The charge in semiconductor is in thermal equilibrium and there are no current. Second, A positive voltage is applied at gate electrode, the electron in the semiconductor will be induced and move to the interface of semiconductor and insulator. This situation is called depletion region. The width of depletion region, Wd, can be calculated by an equation below,

$$W=\frac{\epsilon_s}{C_i}\left[\left(1+\frac{2C_i^2V_g}{qN_A\epsilon_s}\right)^{1/2}-1\right] \qquad (1\text{-}1)$$

Where NA is the charge carrier density and ε_s is the permittivity of the semiconductor **[1.17].** Third, the accumulation region is form by applied a negative gate biased. Induced charge is hole carrier, which treated as transporting carrier and forming channel path. And also, the drain voltage is also applied. The current starts flow from source to drain. There are uniform charges per unit area in the channel. When the gate voltage increases the proportioned current will be obtain. Fourth, the drain voltage is applied only, the gate a voltage difference will become positive, and then a depletion region will be formed.

1.4 Organization of this thesis

In my thesis of organization, I hope states reasonable and logically.

a.) **Chapter two**: we describe about solvent related to solubility and polarity. Because we are used solution-process throughout all my experiment, solvent study is needed. Next, electrical result can be related to solvent and weight percentage directly. We also pick up one optimized term to discuss next chapter. Organic is temperature-dependent material, because of its chemistry properties. The effect of the glass transits temperature and the melting point is a factor for concerning. So how many times and temperature are needed when the molecular can interact and order each other by thermal diffusion.

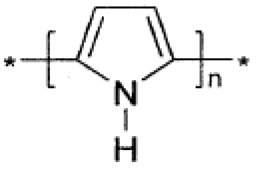
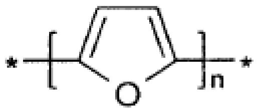
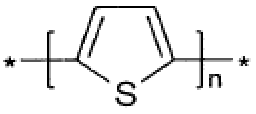
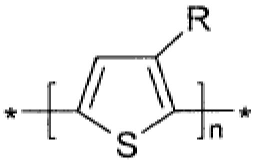
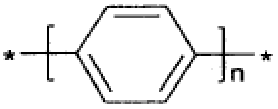
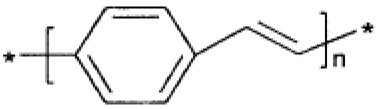
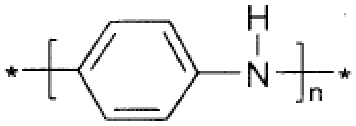
b.) **Chapter three**: A study of metal material, its chemical property and work function difference, is discussed. The thickness of an adhesion layer, different metal material and surface treatment, they are all objection we investigate.

c.) **Chapter four**: stability is a challenge for organic material, due to air and temperature are most impact and very sensitive in the device. What kind of elemental in air could affect it? We need to know and deal with that problem.

d.) **Chapter five**: the conclusion and future work will be involved.

Description of analyzed result above is supported by physical analysis as far as possible.

Table 1-1 Common organic polymer

Polymer name	Chemical structural
Polyacetylene(PA)	
Polypyrrole(PPY)	
Polyfuran(PF)	
Polythiophene(PT)	
Poly-3-alkylthiophene	
Poly-p-phenylene(PPP)	
Poly-p-phenyl vinylene(PPV)	
Polyaniline(PAN)	

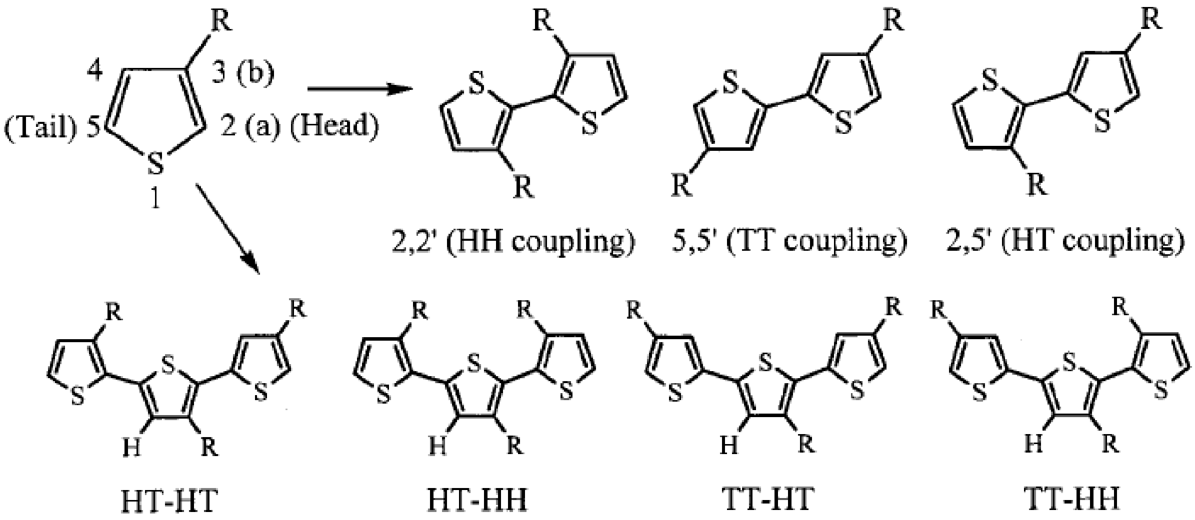


Figure 1-1 The coupling and its connect method of the 3-substituted thiophene [1.8].

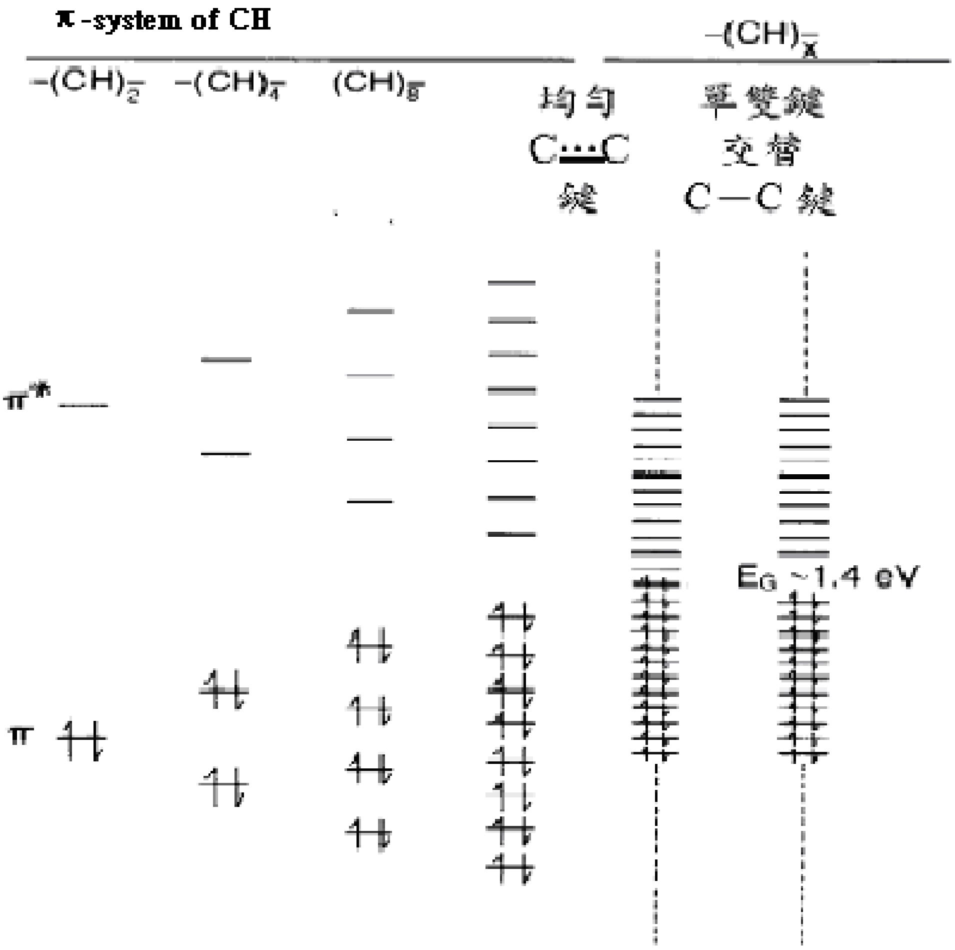


Figure 1-2 Steps of forming an energy band in Polyacetylene.

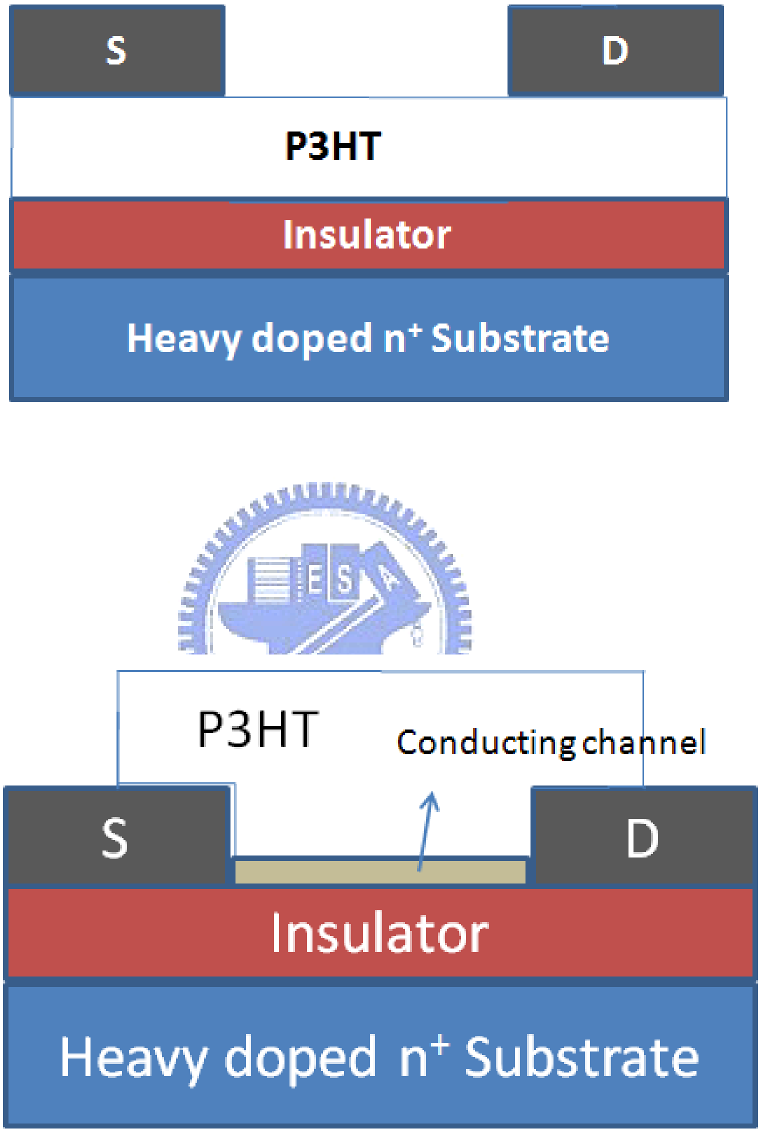


Figure 1-3 Device structure of (a) bottom-contact and bottom-gate, (b) Top contact and bottom-gate.

Chapter 2

Synthetic effect in P3HT fabrication

2.1 Introduction and motivation

Organic thin-film transistors based on solution-processed, semiconducting conjugated polymers have highly promising technological properties, resulting in complex microstructures.

The P3HT transistor is easily affected by intrinsic and external factors such as regioregularity, molecular weight, solvent, temperature, and many related process factors, leading to different result of electrical parameter and chemical property. For instance, from solvent point of view, besides the evaporate rate will affect crystalline [**2.1**]; the solubility is also an index for soluble conjugate polymer in liquid. The reason can be explained that new binding force is high enough to attacks old one, make molecular interaction break, so that the solute can be dissolved well. Another relation of solution process with solution adjustment is the weight percentage. The weight percentage is not only related to supersaturation of solvent itself but also it has a viscosity, which will reflect the thickness of thin film obviously [**2.2**].

From the molecular weight of view, the variation of molecular weight follows a morphology and phase. Many labs are observed the mobility value differently and accuse for this factor. Its molecular weight with mobility values increasing from 1.7×10^{-6} to 9.4×10^{-3} $cm^2 V^{-1} S^{-1}$**[2.3] [2.4]**. But there is a curious thing; MW can be obtained by different solvent. It seems lose the base line of experiment. And all of external process effects include curing time, curing temperature and speed spin…etc. During curing process, many factors are involved. Those factors from molecular interaction to each segment of chain reaction are important for transporting and further affect in device performance. Of course, the device as quenched to room temperature is another important thing.

We present here a study of related to upper description from solution adjustment to the difference of MW, try to explain each result systematically from theory to physical property, and all related investigation will be illustrated by electrical and physical analysis. We also try to develop the optimized terms.

2.2 Poly (3-Hexylthiophene), P3HT – an organic semiconductor

For this thesis work, the organic semiconductor utilized as active layer was poly (3-Hexylthiophene) (P3HT) with its repeat unit $(C_{10}H_{18}S)_n$. It is based on the polythiophene, aromatic compound, and the alkyl group, hexylkyl, take replace and incorporated into a polymer chain of 3-position. The molecular formula of P3HT represents $(C_{10}H_{18}S)_n$; C, H, S represents carbon, hydrogen, and sulfur, respectively. "n" is represented a repeat unit, as shown in **Fig. 2-1 (a) [2.5]**. Two P3HT radicals can be incorporated into a polymer chain by a forming covalent bond. Due to side chain and sulfur, the self-organization is asymmetry, leading to Head-to-head (the position of covalent is 2-5) coupling and another is head-to-tail (the position of covalent is 2-2) coupling. In **Fig. 2-1(b)**, they are composed of one single radical and others, resulting to two type of result, regio-regular and regio-random. A region-random of P3HT is consisting of head-to-head and tail-to-tail in coupling and a region-regular is only consisting of head-to-tail in coupling. The value of region-regular can be calculated by equation **[2.6]**:

$$regioregul\,arity(\%) = \frac{HT\,(value)}{HT\,(value) + HH\,(value)} \times 100\% \qquad (2\text{-}1)$$

Where HT is a value of head-to-tail, and HH is head-to-head. High regioregularity means that the couple of forming type is mostly like head-to-tail. In this type, it can obtain high crystalline and ordering, due to regularity of molecular structure make molecular chain fit into the crystal lattice. Thus, the transporting carrier moved in π system along main chain, due to molecular orbital (electron cloud) is easy and increases a probability of intramolecular mobility. The coupling of head-to-tail can be more stabilizer than head-to-head one, because side chain of head-to-head structure may too close to make chain torsion and low chain conjugated length or unfavorable coplanarity. The transport will be interrupted along main chain and low the value of mobility. By different sublimed or purity process method, the different rr-P3HT value can be obtained, for instance, following the McCullough rout, P3HT with regioregularity of 91% and 95% was obtained. Or the sample of highest regioregularity was 96% HT, synthesized by the Rieke rout **[2.7]**. Indeed, many researches in this field with different regioregularity have a relative to the mobility.

Self-organization in P3HT is one of advantages, and it results in a lamella structure with two-dimensional conjugated sheets formed by interchain stacking **[2.8]**. In **figure 2-2**, the lamella has two type of lying ways onto the substrate, edge-on and face-on, respectively. It depends on the process methods (drip-casting or spin-casting). X-Ray Diffraction (XRD) studies are also supported. It synthesized that organic thin film transistors made with 81% head-to-tail P3HT by spun from chloroform had mobilities in the range of around 10^{-5} to 10^{-4} $cm^2\ V^{-1}s^{-1}$. Contrariously, highly head-to-tail value of 91% had mobilities around 10^{-2} to 10^{-1} $cm^2\ V^{-1}s^{-1}$. The result is responsible for the structural order in the polymer layer. For instance, high density of packing and ordering will increase the hopping opportunity to neighbor chain. Moreover, X-ray studies show that layer as spun at lower speed or drip-casting from highly rr-P3HT value exhibited an orientation order of the lamella with edge-on to the substrate and the direction of pi-pi stacking is in perpendicular to substrate. In contrast, the film as spun with high speed with low region-regularity P3HT (81%) has parallel the substrate and its pi-pi system is perpendicular to substrate. They are opposed to each other.

Before a lamella of polymer chain forms, the conformation order of molecule about rotation may occur at a single bond. This phenomenon is due to thermal energy provides and the material itself has lower rotational barriers, making the chains flexible so that polymer molecular can rotate all the time.

In our experiment, P3HT thin films are deposited by spin costing in the environment of atmosphere. Before it spun onto substrate, it needs to be dissolved. There are two different solutions in this experiment, chloroform and xylene.

2.3 Fabrication Process

The standard baseline process for fabricating P3HT thin film transistors in this thesis is described below. The substrate in this work was n^{++} silicon, although FETs were also successfully fabricated on the flexible or glass substrate.

The steps of process flow are shown in the **Fig. 2-3** and are described in detail below:

1. Silicon wafers are cleaned through RCA standard process, and this n^{++} silicon substrate (0.002~0.004Ω-cm) act as gate electrode.
2. Silicon di-oxide is deposited by APCVD Wet-Oxidation. This thermal oxidation SiO_2 remains at 980℃ in the deposition chamber. The thickness is around

200nm, which measured by n&K system.

3. Gold Source/drain electrodes are defined on the photo resist-coated (FH6400L) dielectric by lithography by electron beam deposition. Titanium (Ti) is used to be an adhesion (sticking) layer for firmly sticking gold and dielectric. And then photoresist (P.R.) will be removed by life-off process in acetone with vibrations in ultrasonic for 5min.
4. Poly (3-hexylthiophene), P3HT is spun onto gate dielectric and S/D electrodes. The substrate remains at room temperature during deposition. Typical background process of solution is described,
   A.) P3HT solute will be dissolved by xylene and chloroform, respectively. Weight percentages are classed as 0.01wt%, 0.05wt%, 0.1wt%, 0.3wt%, 1wt%, and 2wt%.
   B.) All solutions were filtered through a 0.20 μm pore-size PTFE membrane syringe filter before use.
   C.) For spin coating, the film is deposited from solution by two kind of spin rate:
   first, at a spin rate of 500rpm for 10s (for uniformity);
   second, at spin rate of 1500rpm for 25s (for thickness).
   D.) All samples will be curing on hot plate at 150℃ for 3min, and quench to room temperature in air.

Upper experimental terms are summarized in **Table 1-1 experimental table** for reference.

Before the active layer of P3HT is deposited, all samples are cleaned by soaking in acetone with vibrations in supersonic oscillator for 5min. the reason for this is removing the residual organic and particle contaminants on the channel region.

A typical FET pattern is shown in **Fig.2-4**. Involved channel width/length are 75/50, 600/50, and 26400/50 (μm/μm), respectively. There are two kinds of layouts used in fabrication of P3HT FETs, linear-like and figure-like. The channel length of linear-liked are in a range of 10~100μm, and the width are in a range of 75~3700μm. The channel length and width of finger-liked is fixed at 50μm and 26400μm.

All of electrical measurements and extraction were performed using an HP4156 semiconductor parameter analyzer, which was set in a shield box in atmosphere. The surface morphology of P3HT transistor was observed by atomic force microscope (AFM), device cross sections were observed by scanning electron microscopy (SEM).

Regioregular P3HTs were purchased from FEM Inc. (MW=55K, RR=90~93%), and

Aldrich Chemical Company (MW=17K, RR>98.5%). Different regioregularity and molecular weight will be discussed later.

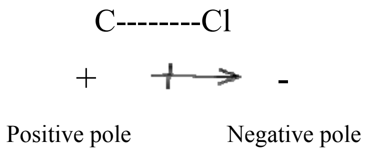
2.4 Different solvents, solubility and weight percentage

2.4.1 Result and discuss

Initially, there are so many P3HT precipitations in xylene solvent when it is dissolved to be a solution and the same situation is observed in chloroform with weight percentage higher than 1wt%. The solute of P3HT can be dissolved in chloroform easily, whereas xylene had poor solubility. Further, solvents and solutions will be gelled, although it is reported that both of them can dissolve P3HT solute. Two likelihood reasons for this are that "supersaturation" and "like dissolves like".

For supersaturation, this explanation is based on fundamental chemical. It defines that contains more of the dissolved material than could be dissolved by the solvent under normal circumstances, meaning each of solution has its supersaturation nearly. If the proportion of solute is lower a level, solvent could dissolve them easily. Thereagainst, if the proportion of solute is beyond, it would not easy to dissolve.

For like dissolves like, it is related to polarity. Polar compounds dissolve in polar compounds and non-polar dissolve in non-polar. The types of intermolecular forces dictate these results. Moreover solution is a homogeneous physical mixture of solvent and solute. The solute particle sizes are ions, atoms, molecules or small combinations of these units. Basically, polarity of material compounds are decided by polarity of molecules and polarity of molecules are responsible for its polarity of bonds. Let us start off the solvent. Chloroform ($CHCl_3$) has 3 bonds with chlorine (two of them symmetrical; see **Table 2-2**), and one with hydrogen. Chlorine, like many of its neighbors on the right side of the periodic table, is very electronegative: it pulls electrons towards its nucleus, like so:



Thus, it is a polar bond. The two symmetrical chlorine-carbon bonds "balance out" this pulling, so that no net pull occurs. The remaining chlorine-carbon bond is not "balanced out" by the less-polar hydrogen-carbon bond, resulting in a net polarity, with the "-" end towards the chlorine atom. Xylene (Paraxylene, C_8H_{10} ($C_6H_4C_2H_6$)) is low-polarity **[2.9]**. Although the side chain is less-polar (C is negative pole and H is positive pole), they are located at each side. According to this result, the polar of CH3 bonds balance out and its polarity is low.

At room temperature, xylene solution will gel within a few minutes. In addition, when devices were fabricated in xylene and exceeded 0.3wt%, the solution was not easy to pass through a 0.20 μm pore-size PTFE membrane, due to precipitation should block. About chloroform, it will dry out within several weeks, depending on low wt% ratio.

The ratio of weight percentage was defined as:

$$\text{wt\%} = (\text{grams solute} / \text{grams solution}) \text{ X } 100\% \qquad (2\text{-}2)$$

There are two equations for calculating weight percentage, but their results are the same.

2.4.2 Electrical results

A set of transistors was fabricated with different weight percentages. Each new transistor set was measured and added to the plot in following figures. Although there is a vibration across these devices, the trend of measured result is stable fairly.

Figure 2-5 shows the transfer characteristic of P3HT transistors from different weight percentages and solvents. For P3HT in xylene, as you can seen in **Fig. 2-5 (a)**, the result of 0.01wt% and 0.05wt% indicates that the data it is near a limit of measured machine, so a obtained curve may not be true, and there is no yield within 0.05wt% when measure. We suspect that thin film is not to be formed so that obtained result is poor. In **figure 2-6 (a)**, AFM surface morphology illustrates that the roughness of P3HT transistor in xylene with 0.01%wt is close to SiO_2 one. For 0.1wt% in xylene and 0.01wt% in chloroform as shown in **Fig. 2-6 (b)**, the surface morphology reaches around 3.5nm. It indicates that the roughness of exhibited performance is around 3 nm, but the roughness of xylene with 0.01wt% is below that. In addition to phase data, our think, thin film forming should be an issue.

Low weight percentage, 0.1wt% and 0.3wt%, the device turn on approximately at Vg=0. In chloroform devices, as shown in **Fig. 2-5(b)**, lower weight percentage exhibits the same condition, except 0.01wt% and 0.05wt%, and they exhibit a similar curve to 0.1wt%. Despite their result are closed to 0.1wt%, but it is not good enough for on current. As following P3HT in both solvent with weight percentage increasing, the turn-on voltage is shifted toward to positive values. In other words, the off-current is increasing when weight percentage boots. Two possible reasons for this condition are that first, the precipitation and impurity more and more in active layer with high weight percentage could exhibit a defect, when the solvent reach its own supersaturation.

Second, weight percentage can be affected by the viscosity so that the thickness is an index for supporting this result. As you observed in **figure 2-7**, indeed, the thickness increases with weight percentage rising (the rest of part of thickness, P3HT in xylene and chloroform, please refer to **Table 2-3**). It could involve more the number of defects in the film. Additionally, those defects can act as trap center, and transport carrier will be trapped during the device operating in accumulation region. Trapped carrier will be released by applied a reverse voltage.

About on-current, it increases with weight percentages booting clearly. **Figure 2-8** shows the surface morphology, which scanning by AFM. P3HT transistor in xylene observed a clear line-like structure onto the SiO_2 after spun. The line-like structure, named nanofibrillar, is consisted of nano-rod. This nano-rod is relative to ligands, which is control agent. The component will affect growth of nanorod. Apparent result also observed with 2 weight percentage. We suspect that the P3HT thin film is a long-chain polymer with lamella layer structure. The carrier is transferring through pi bond, which located at above sigma bond, and also it is source of electrons cloud. With 2 weight percentage, there is a possible chance to form a clear and long line. In contract, less weight percentage, like 0.1wt%, cannot form that. The result agrees from the data published by Yang et al. [**2.10**], who explains that long nonafibrils are composed of nanorods with width of ~22nm. He also suggests that all of long nanofibrils exists grain and grain boundaries. On the other hand, these grain and grain boundaries can be a trapping and releasing center so that affects the result of off current further.

Nanofibrillar provide a conductive path, and transfer carrier can go through it easily. Also it improves a chance of hopping transfer. Surprisingly, this data has not agreed with P3HT transistor in chloroform, as shown in **Fig. 2-9**. Nanofibrils are not clearly and even short in sample of 2 weight percentage, compared with samples in xylene. In contrast, in low weight percentage sample, nanofibrillar is to be formed, due to its boiling points. Xylene solvent has high boiling point around 138~139℃, and about chloroform, it is around 60.5~61.5℃ (obtained from the MSDS of Aldrich-sigma company).

Many researches group [**2.11**] [**2.12**] reported that the elongated nanocrystals are strongly affected by solvent-evaporation rates and costing solvents. This is due to its low boiling point and rapid evaporation speed. For high weight percentage in our study, it is not enough time to interact and self-aggregation in molecule before P3HT dry out. This results a short nanofibrillar on SiO_2 surface. For low weight percentage, it is probably that small number of molecule with semidry situation could self-organize to form the thermodynamic structure and efficiently to form nanofibrillar by nano-rod.

In fact, one more suspect is that higher weight percentage can obtain thicker film. General speaking; a solvent will be dried out from outer (surface of a film). Self-organization inward film is on progressing when the surfaces of organic film dry out. So based on this reason, it may understand that on current increases with higher weight percentages.

Figure 2-10 shows the output characteristics of typical device with different weight percentage and solvents. The P3HT transistors show MOSFET-like characteristics, and they are obtained for negative bias. It indicates that P3HT behaves as p-type semiconductor. For small negative source-drain voltage (V_{SD}) the FET operates in the linear region, and observed from result shows an ohmic contact. When the source-drain voltage increases, the gate field is no longer uniform, and accumulation area is formed. Beyond a certain V_{SD}, the current becomes saturated. The shape of I-V curves are identical, but the magnitude is quite difference. Let the output characteristics of chloroform values minus xylene ones and the result shows in **Fig. 2-11**. It is indicated that the performance of P3HT field effect transistor in chloroform has a better result than that in xylene ones, and no matter what weight percentages, P3HT transistors dissolved in chloroform obtained the same result.

2.4.3 Field effect mobility, on-off ratio, and threshold voltage

For mobility, while the mobility can be calculated in several different ways, the field-effect mobility was extracted from the transistor characteristics as suggested below, using the equations developed in chapter 1. Although the P3HT transistor various across these samples. All mobility were measured at V_{SD}=-10V (linear region) and V_{SD}=-60V (saturation region) as following discuss.

The data in **figure 2-12** shows the normal trend which involved three types of device dimensions. In **Fig. 2-12 (a)**, in the beginning of weight percentage about P3HT FETs in chloroform are larger than that in xylene, which is almost one order of magnitude. Two reasonable explanations are that first, poor solubility in xylene leads to many precipitations and defects in the film. The precipitations may interrupt and form a barrier height for transporting carriers. Defects may to be a trap center to trap carrier (electron) and those will form a scattering. Second, with high boiling point, solvents will evaporate slowly so that it is enough time for ordering. In contract, solvents with low boiling point and less weight percentage, like chloroform, can provide more time to order crystal orientation and interaction between molecular and molecular, and then improve chain packing and pi-pi stacking can be stronger. After crystalline structure improves, transport carrier can hop easily.

In the case of xylene, the field-effect mobility increases when weight percentage is boosting. This is due to nanofibrillar are formed potentially with high weight percentage, which can provide more electron sources (refer to 2.4.1 section).

Besides, P3HT field effect transistor in chloroform exhibit a raising trend under 1wt%. Unfortunately, an anti-trend in nanofibrillar, compared with P3HT solution in xylene, shows less nanofibrils on to $SiO_{2.}$ The worse case is in P3HT FETs with 2 weight percentage, and the field-effect mobility dropped down to almost two orders of magnitudes. It seems a large resistor to black hopping. Two suspect reasons are that first, removing solvent and impurity cause a pinhole; second, almost nanofibrils-free makes it worse.

Among the plotted weight percentage, the highest mobility, μ_{FE} (sat.) = 0.011 cm^2/Vs, was obtained at V_D=-60V from P3HT solution in chloroform with 1wt%. The best mobility in the research field is 0.1 cm^2/Vs. This thickness of active layer is 219nm.

For On-Off ratio, **Figure 2-12 (b)** shows the on-off ratio versus weight percentage, which involved xylene and chloroform solvents. P3HT FETs in xylene is keeping in around 10^3, which means that it won`t change with increasing weight percentage. But P3HT in chloroform cannot sustain at a fixed level. Observed data can understand that on-off ratio decreases seriously with increasing weight percentage. This result is dominated by off-current (refer to section 2.4.2).In this study, if the high off current with 2 weight percentage could be reduced, on-off current will get a great improvement. Among the plotted weight percentage, the highest value, 10^4, was obtained at P3HT in chloroform with 0.1wt%, which was extraction during operating in linear region. The best on-off ratio in the research field is 10^6.

For threshold voltage, the way to obtain V_{TH} is that a MOSFET with source terminal connected to ground, the drain current is measured with various gate biases. Drain terminal is applied a small value to make sure it operate in linear region. The expression of drain current is written as below:

$$I_D = \frac{W}{L}\mu C_{ox}\left[V_D\left(V_G - V_T\right) - \frac{V_D^2}{2}\right] \tag{2-4}$$

For small drain bias the above expression is:

$$I_D = \frac{W}{L}\mu C_{ox} V_D \left(V_G - V_T\right) \tag{2-5}$$

Where W is channel width, L is channel length, Cox is capacitor per unit area. The equation (2-5) predicted that at a constant drain voltage by plotting I_D-V_G, a straighten line must be obtained. The inflexion point of the I_D-V_G plot is the point where the transconductance reaches its maximum. The threshold voltage is found at the intercept of tangent in the inflexion point with the V_G axis [**2.13**]. The result of the V_{TH} extraction method is shown in **Fig. 2-13 (a)** for device operating in the linear region. When the device operates in the saturation, the method to extraction the V_{TH} is not the same. The drain current is measured at different values of V_G, and at drain voltages that ensure the operation of the transistor in the saturation region: $V_D \geqq \max(V_G)$ or $V_{DG} > 0$. The drain current obeys the same square law in saturation region.

$$I_D = I_{DSS} = \frac{W}{L} C_{ox}\mu \frac{1}{2}\left(V_G - V_T\right)^2 \tag{2-4}$$

In **Fig.2-13 (b)** is represented the extraction way to obtain V_{TH}, resulting in a straighten line that intercepts the V_G axis in V_{TH}.

By plotting threshold voltage versus weight percentage, which is presented in the **figure 2-14**, P3HT FETs with 0.01wt%, 0.05wt%, 0.1wt%, 0.3wt%, and 1wt%, the value of V_{TH} is smaller than 2wt% sample. The threshold voltage of in lower 1 weight percentage sample is low. A large V_{TH}, 496V, is obtained in 2wt% sample. Due to P3HT FETs in chloroform are normally on device, and it is hard to turn off. So applied a large bias at gate is to turn it off. General speaking, it does not to do so. As device scaling, small device has a trend in the future. If a large bias were applied, it would cause damage on device. Observing and zooming in 0.1 and 0.3 weight percentages, summarized in **Table 2-4**, the value of V_{TH} is approaching zero. For device scaling, expect for the device dimension of 600/50(μm) with 0.1wt% in both xylene and chloroform, the rest of them are approached zero for threshold voltage.

2.5 Regioregularity and molecular weight

Both regioregularity and molecular can affect P3HT FETs performance. For those effects, there are many reports to investigate that without keeping the same datum, for example, the obtained molecular weight are made and dissolved in different solvents. In this section, the material of P3HT will be dissolved in the same solvent, which is chloroform. In the beginning, the material of rr-P3HT (MW=55K, RR=90~93%) were purchased from FEM Inc, and Aldrich Chemical Company (MW=17K, RR>98.5%). All data were claimed by own companies. Although the material brought from different companies, a technology in making this material, like purity, is the same. Before go further, according to the results of the section 2.4.2, experimental terms and fabricated process flow are the same as below: weight percentage is fixed at 0.1wt%, and P3HT solute was dissolved in chloroform solvent.

Regioregularity value is based on purification method (refer to section 2.2), and MW is described below: the molecular formula is shown in **Fig. 2-15**. The molecular weight can be calculated based on its individual atoms number, and then summed all of them. The molecular formula of P3HT is $(C_{10}H_{18}S)n$, n is repeat unit of molecular, and their individual atom number are C=12, H=1, S=32. Total number in the brace is 170. n=100 (MW=17K) and n=323.5 (5~60K) are derived from molecular weight, for instant, MW=17K, there are hundreds monomer to compose of a long chain. The difference is known, and electrical result will be a goal.

In **Fig. 2-15**, all performance of high weight percentages is better than low one, even in off current. This result is suspect that a fixed a chain length, 50nm, high molecular could reach that easily, due to much repeat unit can perform the self-organization with less grain boundaries. For low molecular weight, first, it needs more three times of repeat unit to get the same result, compared to high molecule, and if low molecular weight would reach 50nm length, it would need more and more nanorods to gather around. Additionally, more of grain boundaries would be involved in the film. The rest of electrical parameters are summarized in the **Table 2-5**. The result in high molecular weight is higher one order of magnitude than low ones. It is possible to anticipate output characteristics in high molecular is better, and exhibit a good performance in both the linear and saturation regions, which is shown in the **figure 2-16**. From observed electrical result in my study, molecular weight is more important than the regioregularity.

2.6 Effect of various curing temperature

2.6.1 Fabrication process

All process procedure is the same as section 2.3. There is only one difference point, which is curing temperature. Curing temperature is varying in a range, 50℃, 100℃, 150℃, 200℃, and then set the device on hot plate for fixed 3 minutes. P3HTs were purchased from FEM Inc. (MW=55K, RR=90~93%).

2.6.2 Results and discuss

A set of transistors was fabricated with different curing temperatures. Over all of transistor were measured and plotted in **Fig.2-3**. Although the P3HT deposition conditions varied across these samples, the fabricated procedure is all the same.

The worse situation happed in both xylene and chloroform solvents at temperature 50□, which showed a large off current in **Fig. 2-17(a)**, and leaded to a small value of on-off ratio. As you seen in **Fig. 2-17(b)**, it shows typical On-Off ratios values versus the temperature with vary dimension devices. At temperature 50 degree, most low value of off current obtained in our study is around 10^2. Even in a situation of 100℃, compared with 150℃. Two possible reasons are suspected that first, at low temperature, 50℃; it is not enough to let the remnant solvents remove, the impurity drive off, which occupied the volume. In **Fig. 2-18**, a three-dimension analysis of surface morphology scanned by AFM can observe a hill-like surface, which could involve defects. When P3HT solution becomes a solid film, it involved many factors remind upper. Those factors lead to a low level of on-off ratio.

Electron Spectroscopy for Chemical analysis, ESCA, illustrated that the counts of oxygen in chloroform at 50℃ has second high level count in **Fig. 2-19.** The oxygen (1s) concentration is obtained during process producers, such as mixing with solvent and solute, spin, and even it exists in atmosphere. The rest of elemental, sulfur and carbon, are the same, besides the case of xylene solvent. Sulfur (2p) and carbon (1s) cannot be detected in this analysis at this temperature fully. We doubt that the sulfur and carbon are less in the bulk of P3HT organic semiconductor, and this could be a reason for low mobility. Utilizing xylene to be a solvent is not appropriate.

Brian et al. **[2.14]** reported that annealing at 40-60 degree the concentration of oxygen is reduced, intermediate value of oxygen concentration is obtained at temperature of 80 ℃, and the concentration reached its lowest level when temperature is adding over 100 degree. This illustrated that anneal at low temperature the impurity will embed in the films, and could not been dedoped out off so that a production is formed within the pi-pi* gap. It will trap and de-trap the transport carriers.

Second, it is about physical property of polymer itself. During curing process, the temperature set at 50 degree, for P3HT polymer, it is near or under the glass transition temperature so that it is too low to provide energy. In general, the temperature could provide thermal energy, from heat source became kinetic energy, and causes a change in polymer such as intermolecular forces (bonding force are stronger between molecular and molecular, it needs to provide a thermal energy for polymer motion, which related to well-order, and enhance crosslink or interaction molecular each other), free volume of polymer (impurity or remnant solvents occupied the free volume, and the space of motion in polymer reduced) **[2.15] [2.16] [2.17]**.

Moreover, the molecular of polymer are not to have any segmental motion and dimensional change. A temporary distortion in covalent bond is occurred only. As you seen, the off current reduces with the temperature increasing, and these changes make on-off ratio increase between 100~150 degree. Summarized reasons are remnant solvent removeral, impurities dedope, polymer gained thermal energy to re-order, and free volume reduced and then polymer could fit.

As curing temperature over 150 degree, both of field-effect mobility and on-off ratio decade dramatically, as shown in **Fig.2-20**. Curing at this temperature will be a challenge for P3HT organic polymer, due to organic is sensitive for temperature. Surface morphology is changing to more flatter. It indicates that remnant solvent will be removed and dedoped the impurity so that the volume has been changed. Also, at such temperature, pinhole could be formed, due to remnant solvent was dry out so fast, meanwhile P3HT solutions formed a solid film, and the voids could not be filled in time. For hopping carrier, pinhole treats as a barrier height in the channel.

The rigidity-flexible and conformation of organic polymer could be affected by temperature. P3HT has low energy barrier to rotation, molecular can rotated easily, which results high the flexibility of molecular. This rotation occurred at carbon single bond in main-chain structure with side-chain structure. It could not happen at heterocyclic of polythiophene. The reason is that the carbon double bond and polythophene had strongly bond energy. To break these double bonds needs higher bond dissociation energy. When P3HT molecule rotates with side-chain structure, the conformation will change to eclipsed conformation. Side structure is alkyl group; each side-alkyl aggressive or too close, the excluded force of van der Waals force (steric hindrance) could be form, as shown in **Fig. 2-21**, resulting low conjugality, stability, and low coplanarity. Low conjugality reduced the length of main chain, and affected the hopping carrier in the channel. This result is the same as section 2.4.3. There is an analogy with Brain et al.

For P3HT FETs in xylene, it is hard to measure the characteristics in 26400/50 dimension. In fact, using xylene to be a solvent seems not an appropriated choice. There are 8 transistors at each dimension, and most of them cannot be measured. This is reason for a few current yields.

2.7 Effect of various curing time

2.7.1 Fabrication process

Basically, all the process procedure is the same as section 2.3. There is only one difference, which is curing time. After the P3HT solutions in both xylene and chloroform spun onto SiO_2, the device will be cured in 3 and 15 minutes, respectively. To see how curing time difference to affect electrical parameter.

2.7.2 Result and discuss

Figure 2-22 shows a transfer characteristic of P3HT FETs spin-coated from different curing time. Both P3HT FETs in xylene and in chloroform exhibit that the performance of fixed at 3 minutes are better than 15 minutes, which is one order of magnitudes in on current. About the off current, it just exhibits a little change. The window of off current shows a vibration across those samples in our experiment.

According to the results, the suspect reason is that for long-duration curing time at 15 min, it could provide thermal energy from substrate for elemental oxygen, which would diffuse into the interface between organic active layer and silicon di-oxide. It embedded in the conducting channel and reduced the performance. This suspect could be supported by Auger depth analysis system in the **Fig.2-23**. Although the density of carbon and oxygen are much in the environment, measured data is very clear. Initially, the material of P3HT film exist four atomics, including carbon, oxygen, silicon, and sulfur (an atomic of hydrogen cannot be detected due to auger electron spectroscopy can detect atomic number lower 3). The atomic percentage in the bulk and conducting channel are rising, especially in 15min sample. Further, the concentration of oxygen for curing 3 minutes is higher than that of 15 minutes. It can be supported by different slope, although the sampling point is less in 3 min sample. The concentration of sulfur is the same. Indeed, the existence of oxygen is embedded in the film. The existence of oxygen embedded in the film could be a trapping and de-trapping center (refer to section 3.2.2). The source of oxygen are coming from all of process procedure such as solute, solution, the atmosphere, and baking on hot plate.

2.8 Effect of various spin speed

2.8.1 Fabrication process

Basically, all the process procedure is the same as section 2.3. There is only one difference, which is spin speed. Before the P3HT FETs in both xylene and chloroform will be cured in 3 minutes, the spin speed will be set 1500rpm and 3000rpm, respectively. To see how spin speed difference to affect electrical parameter and physical property.

2.8.2 Result and discuss

Figure 2-24 shows a transfer characteristics of different spin speed with 0.3wt% in xylene and 0.1, 0.3wt% in chloroform including two different dimension of 26400/50 (μm) and 75/50 (μm). As you can see, a large off current was obtained at 3000rpm with 0.1, 0.3wt% in chloroform obviously, and spin speed at 1500rpm obtains small effect. For transistor in xylene at 3000rpm, the performance and yield were quite low so that obtained data is not good.

A reasonable thickness shows in **Figure 2-25**. The thickness of P3HT transistor in chloroform with 0.1wt% is 36nm. Actually, the film is thinner than observed result. About

P3HT transistor in xylene is around 81nm. The viscosity is an index for this result. AFM topography shows a very rough and aggregated surface for 3000rpm, which observed both P3HT transistors in xylene and chloroform, as shown in **Fig. 2-26**. Contrarily, AFM topography for 1500rpm shows more flat surface without large area of aggregated. According to this result, we may suspect that the diffusion rate of oxygen in thin film is higher than thick one.

2.9 Summary

A.) P3HT in chloroform has got a better solubility. The result is based on "like dissolves like" and "high solubility". Both chloroform solvent and P3HT powder have polarity, but remind here, there is still a supersaturation when wt% reaches 2%.

B.) Apparently, on-current increases as wt% rises. This is due to a clearly nano-friballer attaches onto SiO_2 surface, forming a conducted path. Also Off current increases as wt% increase. The reason for this is that the thick active layer involves more number of defects.

C.) Samples of P3HT in chloroform with 0.1wt% are optimized for the better condition of electrical and solution. The highest field-effect mobility is $2x10^{-3}$ cm^2 V^{-1} S^{-1} (in linear region).

D.) The value of molecular weight is more importance than regio-regular value. The difference in electrical result is around one order of magnitude (both on and off current).

E.) 150℃ for 3min is an optimized curing temperature, due to the number of embedded oxygen is lowest. Lower and higher curing temperature could make more oxygen concentration and chain torsion and then obtained poor performance.

F.) Short spin speed will obtain a better performance than rapid one and more rough surface morphology for rapid speed. This may a root-cause for large off current.

Table 2-1 Experimental table

Solvent	Wt%	RPM	PB time(min)	PB temp(℃)	Treatment	Metal
Xylene	0.1% 0.3% 1 % 2 %	1st 10s 500RPM a.)2nd 25s 1500RPM b.) 2nd 25s 3000RPM	3 15	50 100 150 200	W/O and W/ HMDS	Ti/Au Ti/Pd Ti/Ni Ti/Pt Only Ti
Chloroform						

Table 2-2 Polarity of solvent and solute with the polarity.

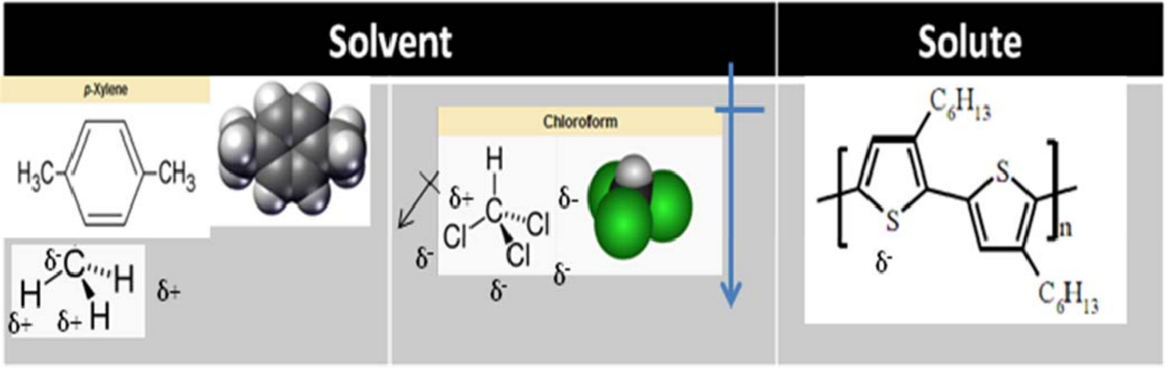
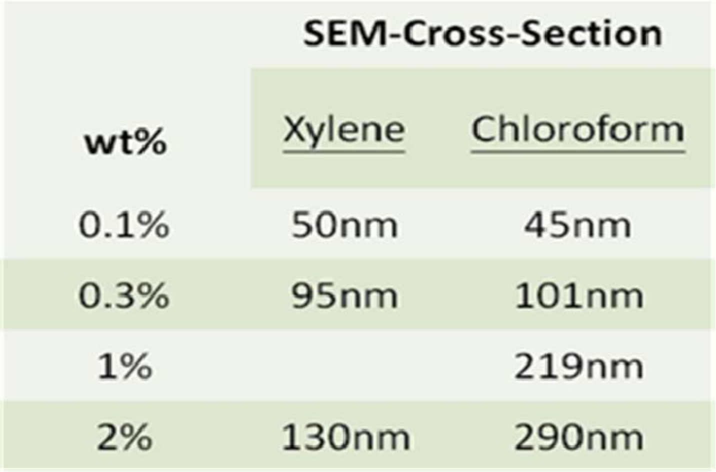
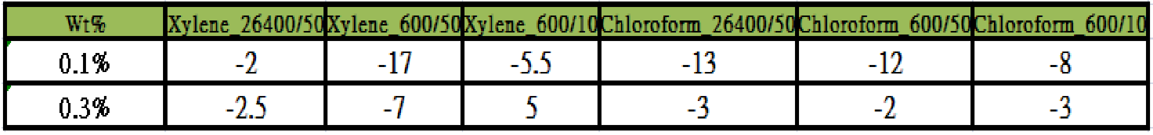


Table 2-3 The thickness of P3HT transistors with different weight percentages and solvents



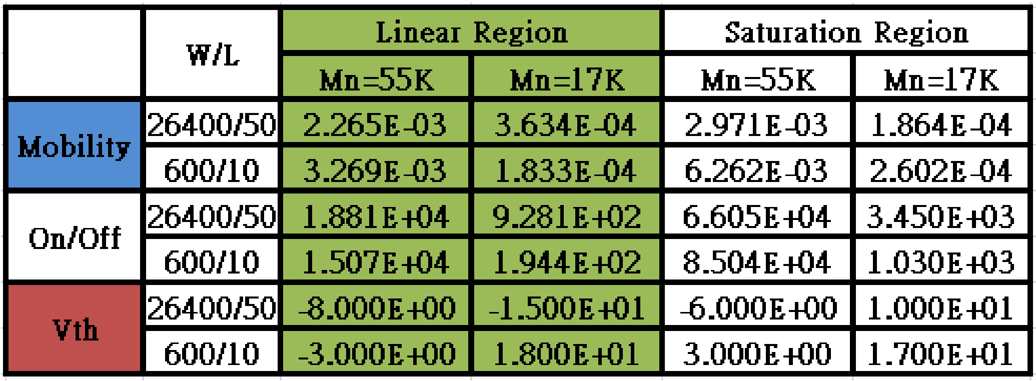
wt%	SEM-Cross-Section	
	Xylene	Chloroform
0.1%	50nm	45nm
0.3%	95nm	101nm
1%		219nm
2%	130nm	290nm

Table 2-4 Threshold voltage of P3HT transistors with 0.1 and 0.3 weight percentages.



Wt%	Xylene_26400/50	Xylene_600/50	Xylene_600/10	Chloroform_26400/50	Chloroform_600/50	Chloroform_600/10
0.1%	-2	-17	-5.5	-13	-12	-8
0.3%	-2.5	-7	5	-3	-2	-3

Table 2-5 List of electrical parameter in different molecular weight



	W/L	Linear Region		Saturation Region	
		Mn=55K	Mn=17K	Mn=55K	Mn=17K
Mobility	26400/50	2.265E-03	3.634E-04	2.971E-03	1.864E-04
	600/10	3.269E-03	1.833E-04	6.262E-03	2.602E-04
On/Off	26400/50	1.881E+04	9.281E+02	6.605E+04	3.450E+03
	600/10	1.507E+04	1.944E+02	8.504E+04	1.030E+03
Vth	26400/50	-8.000E+00	-1.500E+01	-6.000E+00	1.000E+01
	600/10	-3.000E+00	1.800E+01	3.000E+00	1.700E+01

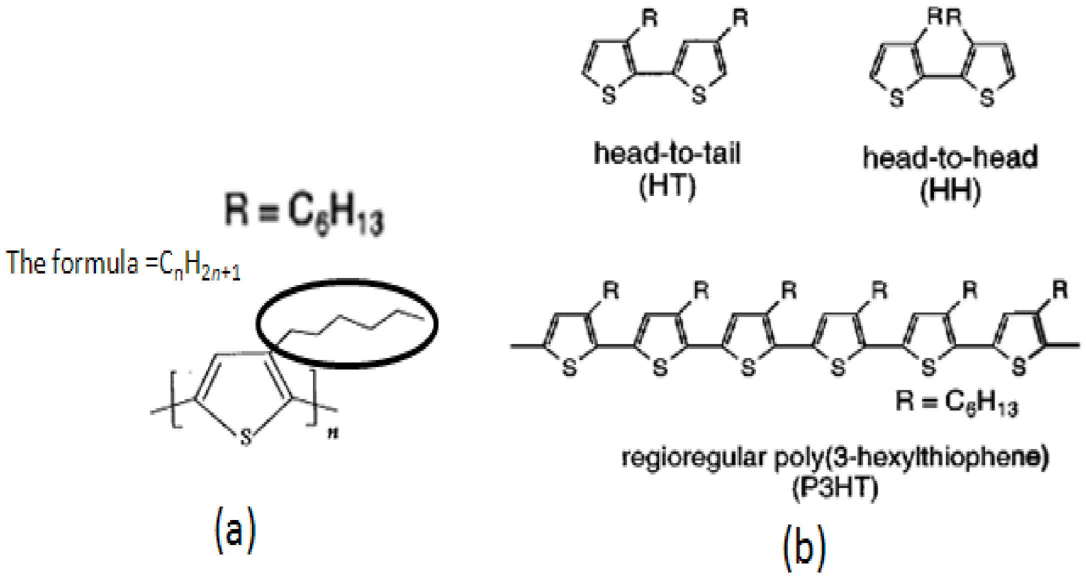


Figure 2-1 Poly (3-hexylthiophene) P3HT Chemical structure (a) monomer, (b) Organization.

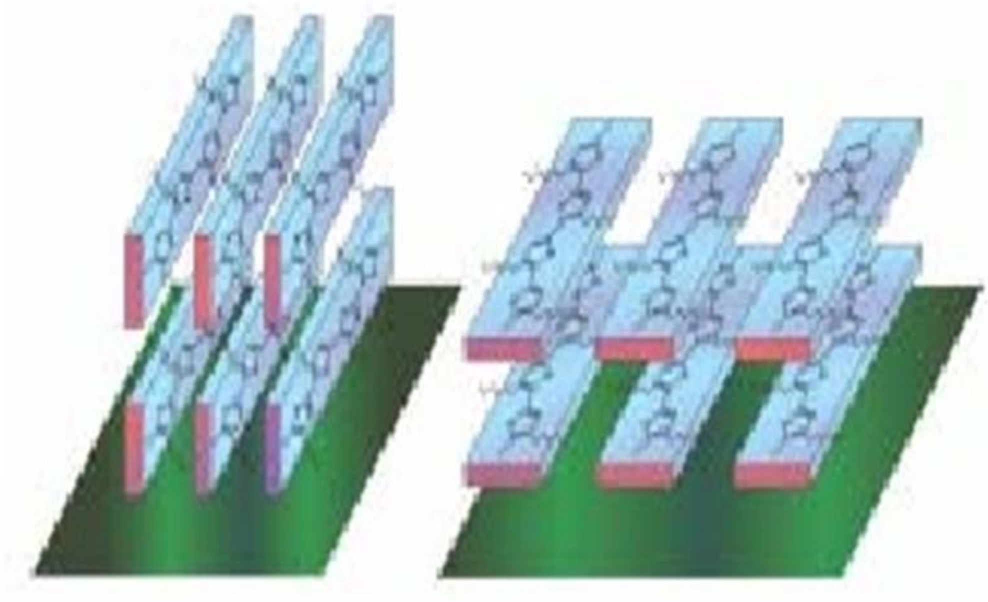


Figure 2-2 P3HT Lamella (a) edge-on (b) face-on [2.2].

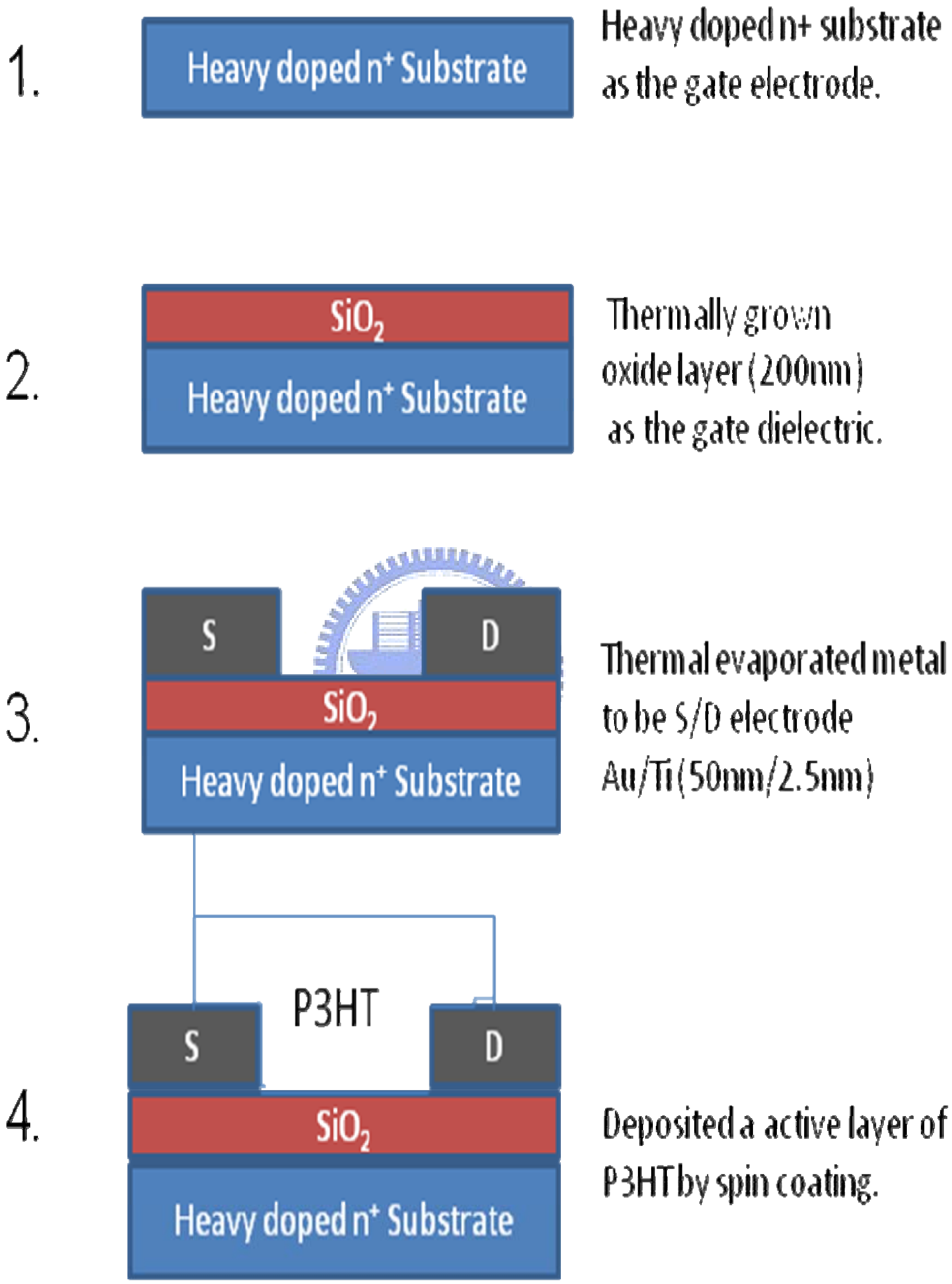


Figure 2-3 Fabrication process for bottom contact organic thin film transistors

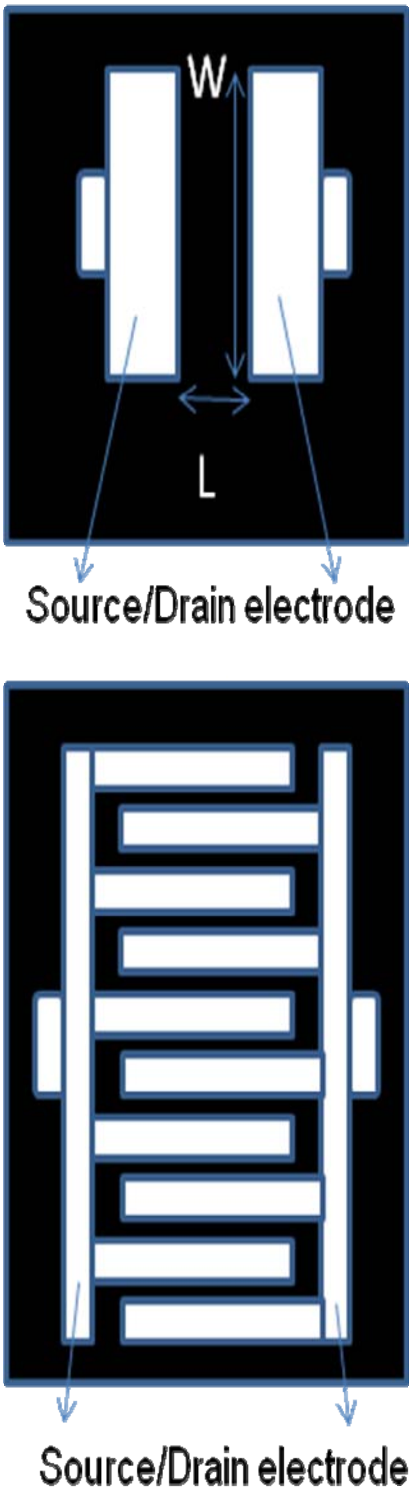


Figure 2-4 Micrograph of bottom contact P3HT FET, (a) linear type (b) Finger-like.

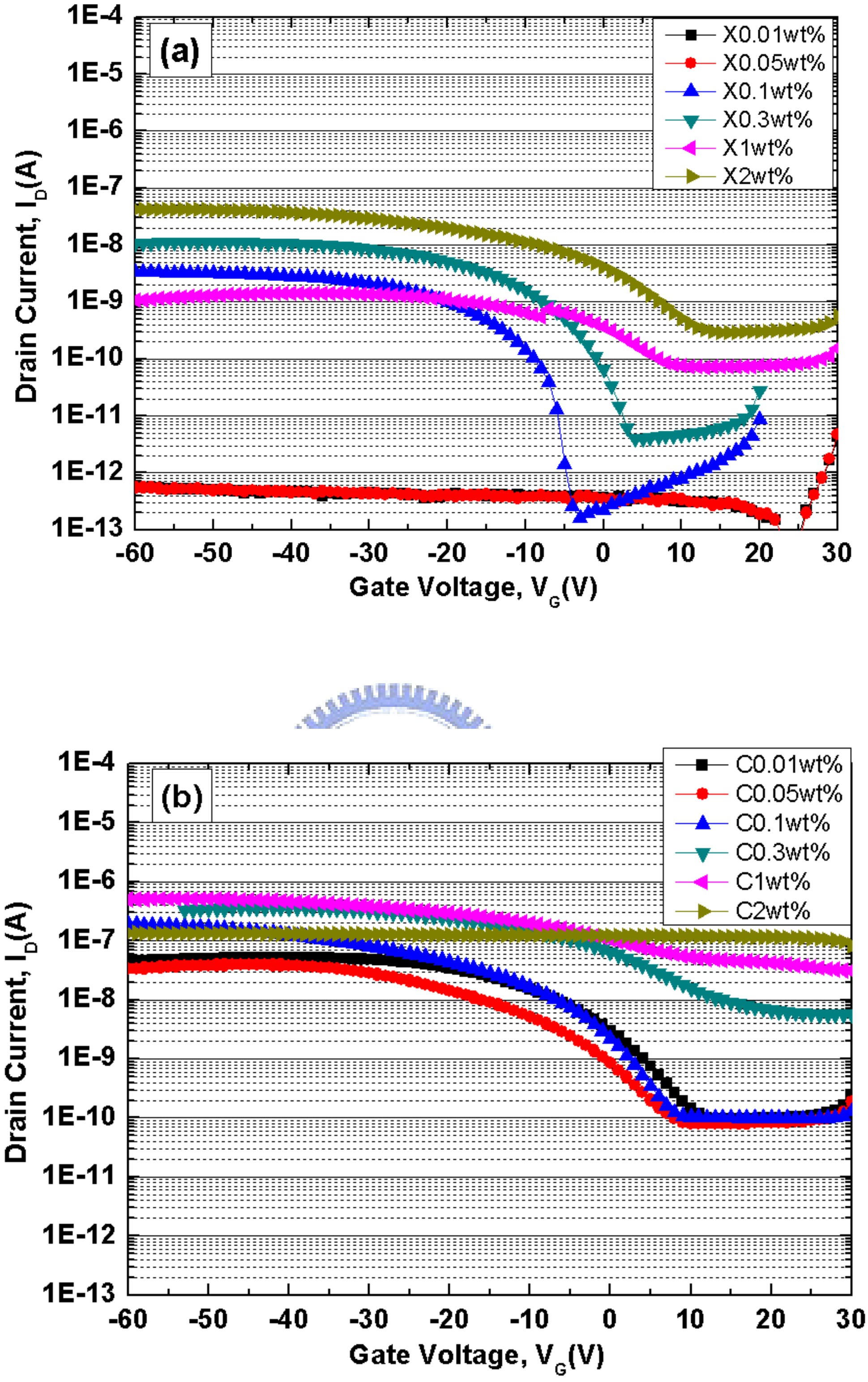
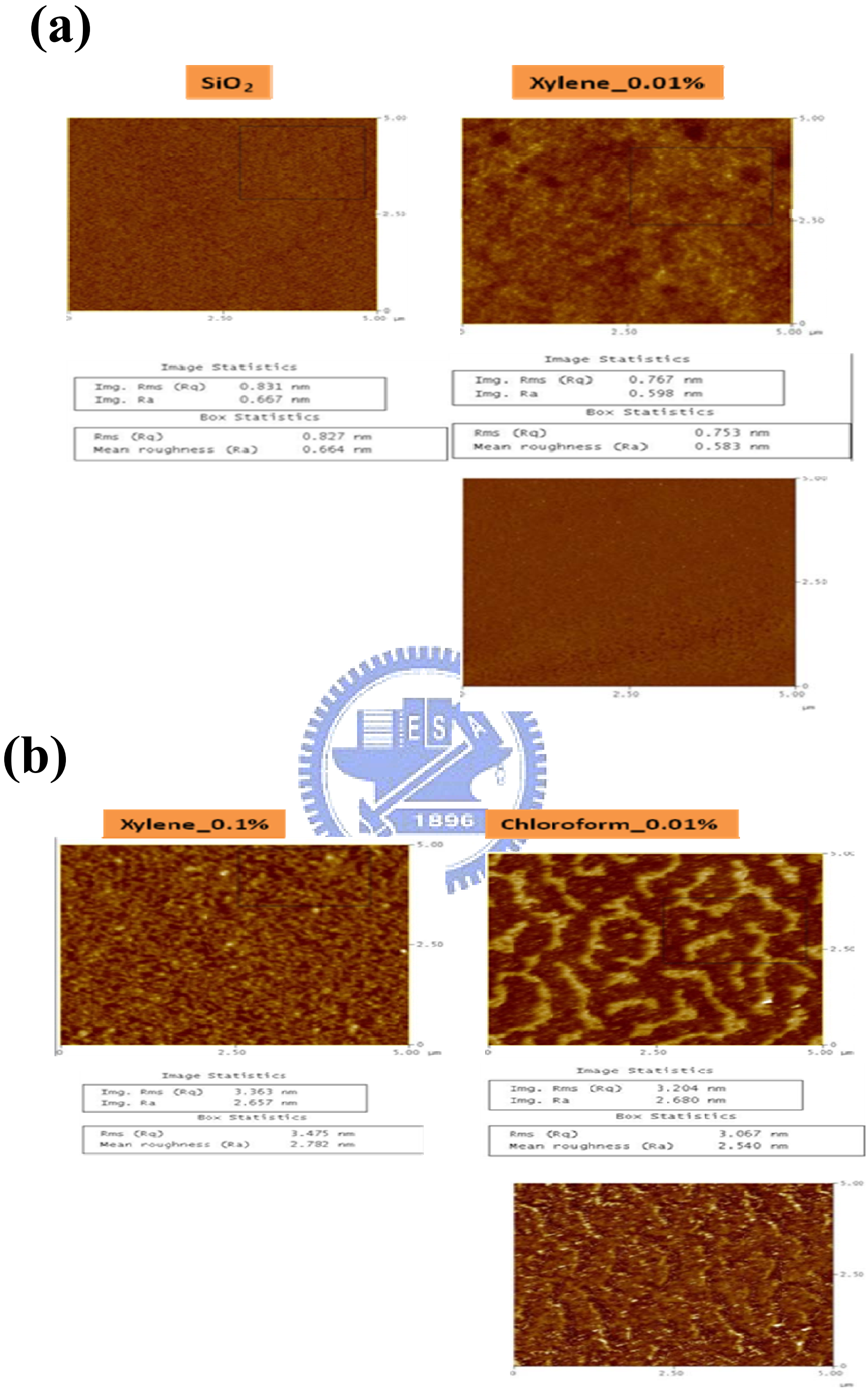


Figure 2-5 Transfer characteristics of P3HT FETs spin-coated from different weight percentages and solvents, (a) spin-coated from Xylene, (b) spin-coated from chloroform.



(a) SiO2

Image Statistics
Img. Rms (Rq) 0.831 nm
Img. Ra 0.667 nm

Box Statistics
Rms (Rq) 0.827 nm
Mean roughness (Ra) 0.664 nm

(a) Xylene_0.01%

Image Statistics
Img. Rms (Rq) 0.767 nm
Img. Ra 0.598 nm

Box Statistics
Rms (Rq) 0.753 nm
Mean roughness (Ra) 0.583 nm

(b) Xylene_0.1%

Image Statistics
Img. Rms (Rq) 3.363 nm
Img. Ra 2.657 nm

Box Statistics
Rms (Rq) 3.475 nm
Mean roughness (Ra) 2.782 nm

(b) Chloroform_0.01%

Image Statistics
Img. Rms (Rq) 3.204 nm
Img. Ra 2.680 nm

Box Statistics
Rms (Rq) 3.067 nm
Mean roughness (Ra) 2.540 nm

Figure 2-6 AFM synthetic result of P3HT in chloroform and xylene with different weight percentages, (a) SiO_2 and xylene 0.01wt%, (b) xylene 0.1wt% and chloroform 0.01wt%.

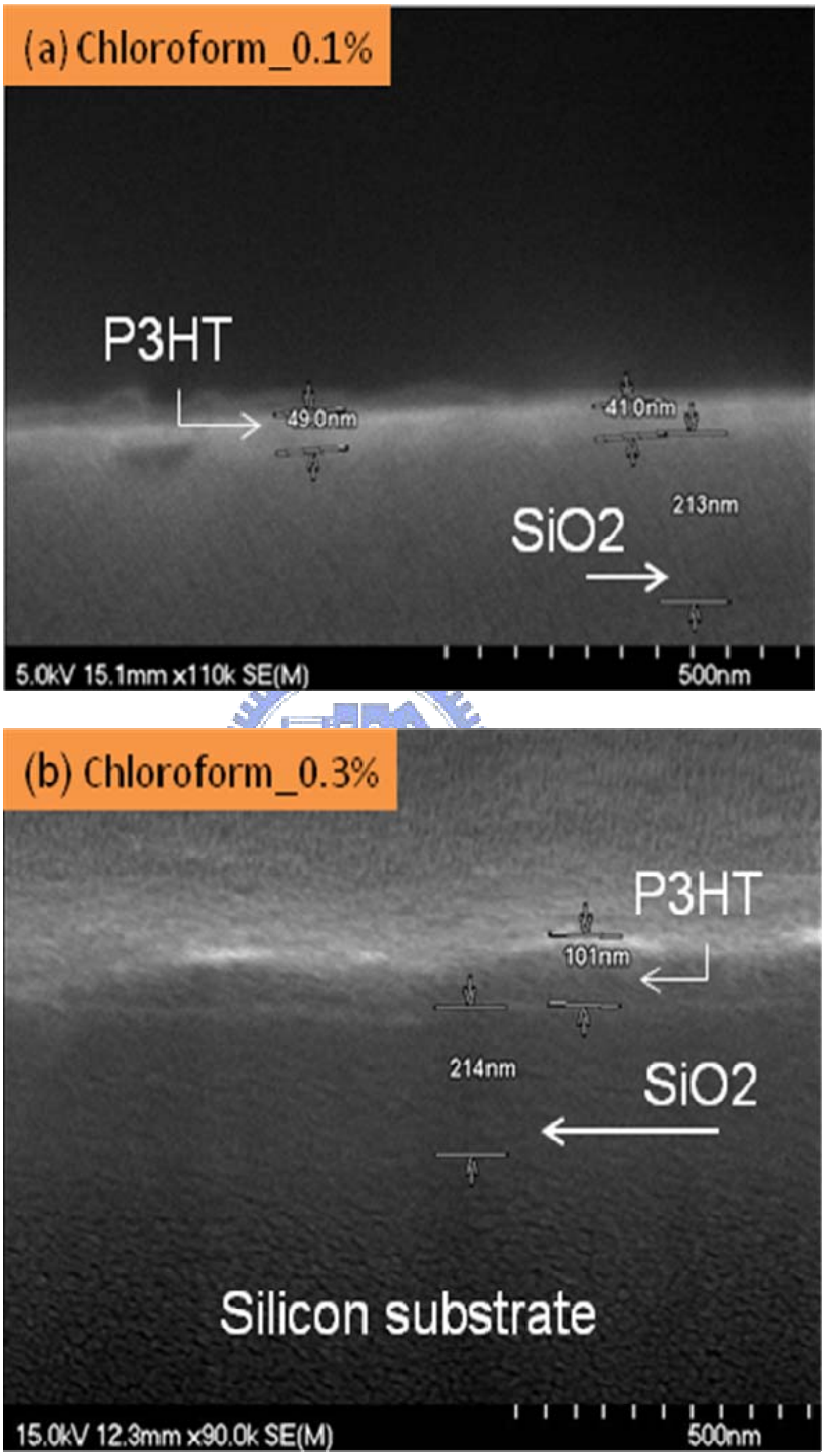


Figure 2-7 SEM cross-section of P3HT in chloroform FETs spin-coated from different weight Percentages, (a) 0.1wt%, (b) 0.3wt%.

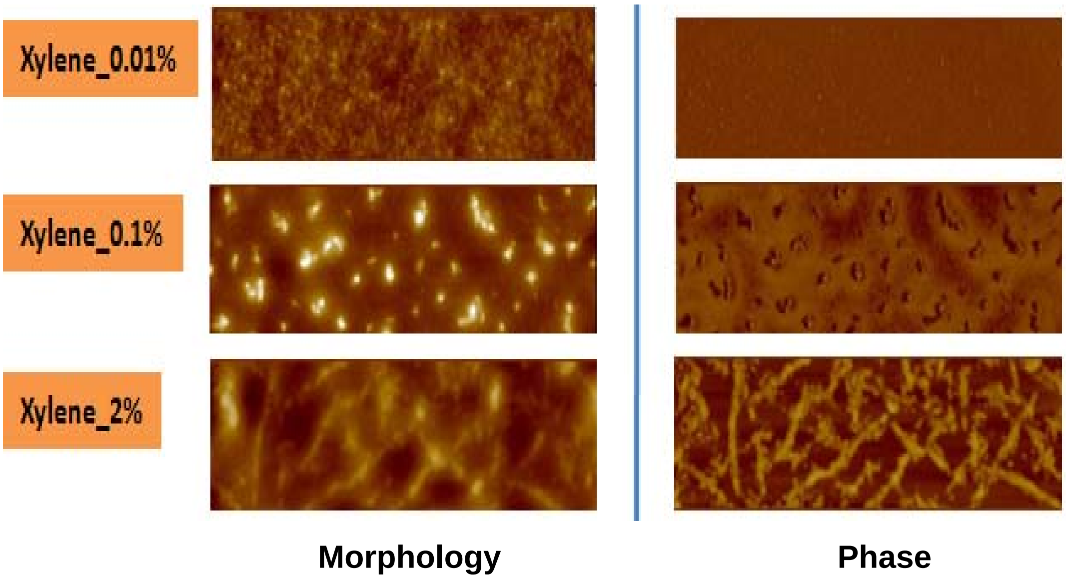


Figure 2-8 AFM topography of small scale scanning of P3HT in xylene with 0.01wt%, top, 0.1% middle and 2wt%, bottom.

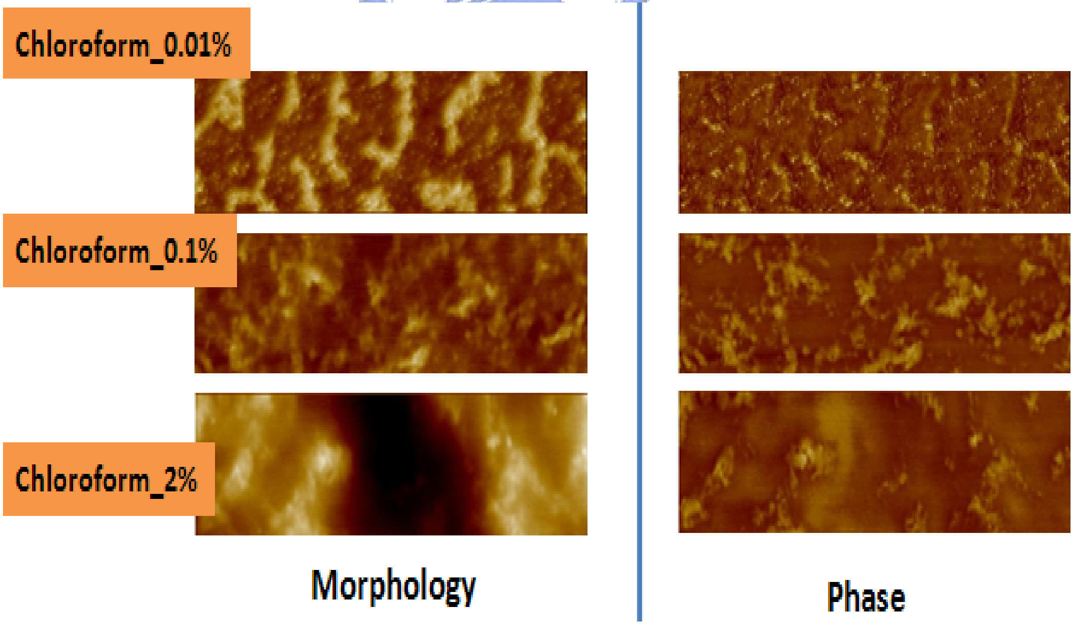


Figure 2-9 AFM topography of small scale scanning of P3HT in chloroform with 0.1wt%, top, 0.1% middle and 2%wt%, bottom.

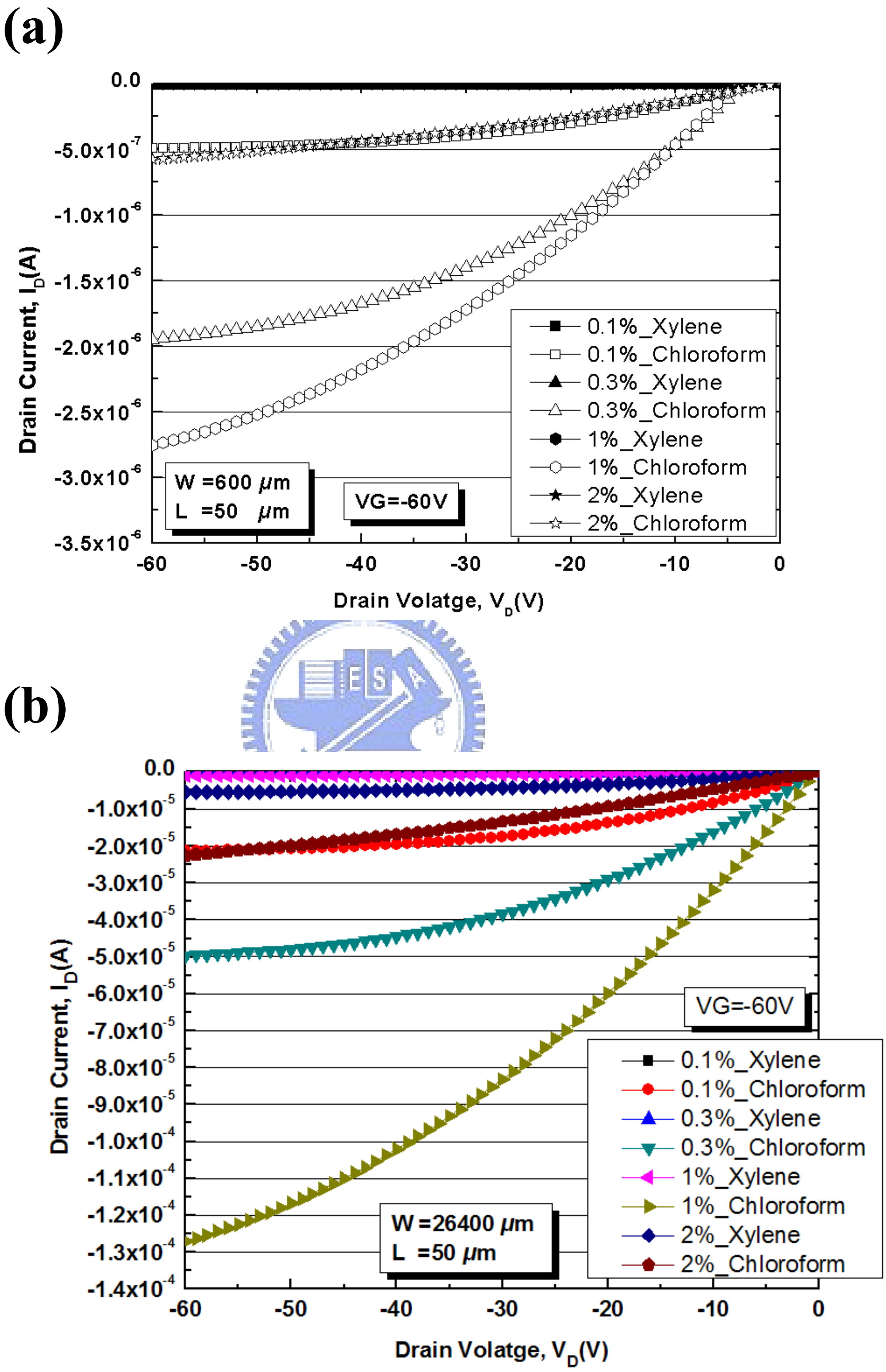


Figure 2-10 The output characteristics of typical device with different weight percentage and solvents, (a) 600/50, (b) 26400/50 μm.

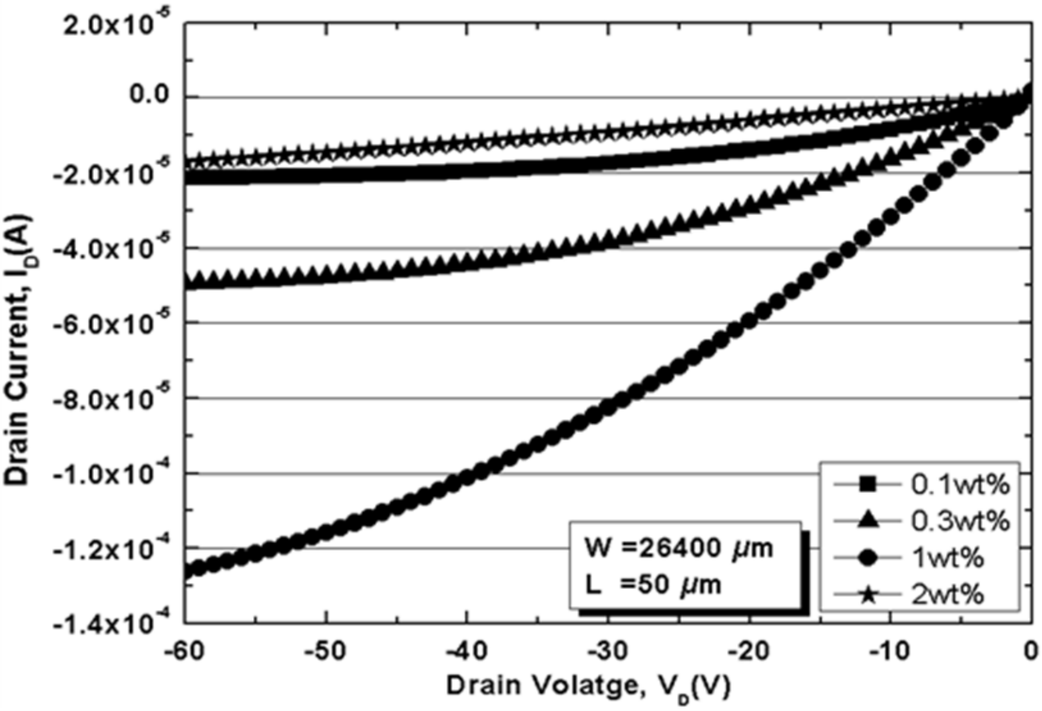


Figure 2-11 Output characteristics different with various weight percentages.

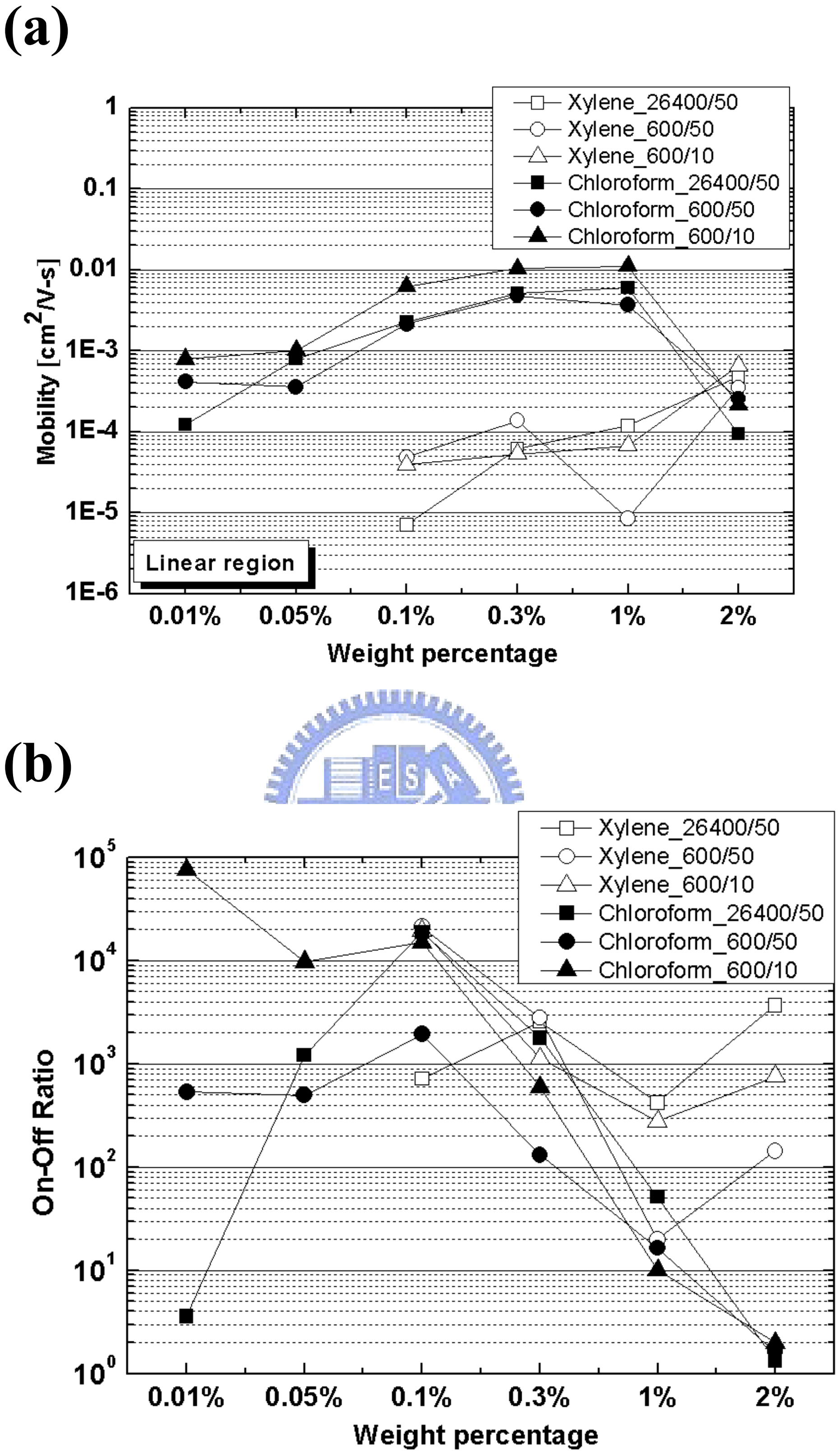


Figure 2-12 The mobility of P3HT FETs with various weight percentages and solvents (a) Field-effect mobility (b) On-Off ratio.

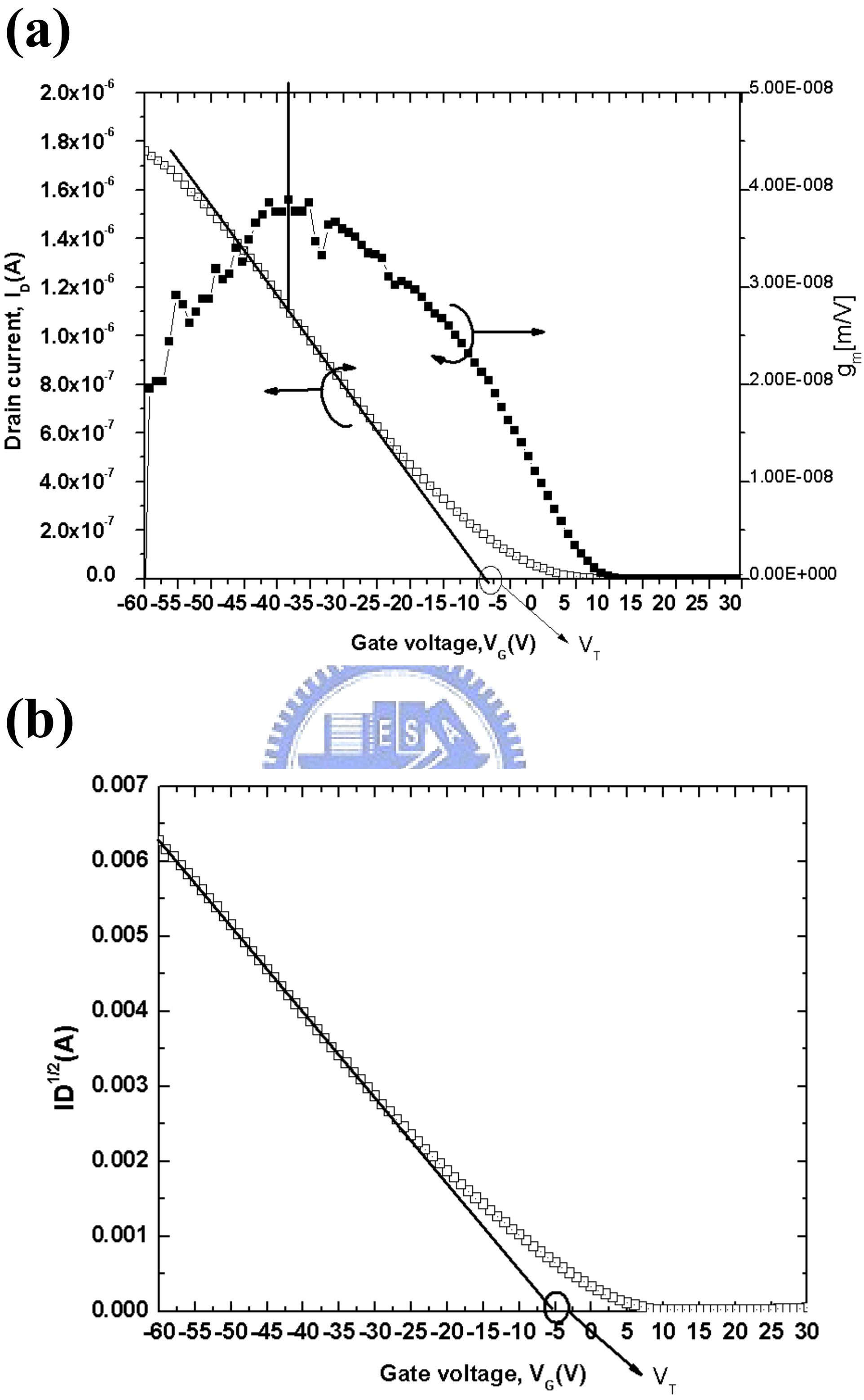


Figure 2-13 The VT extraction using the linear extrapolation method for device operated in the linear region (a) in saturation region (b).

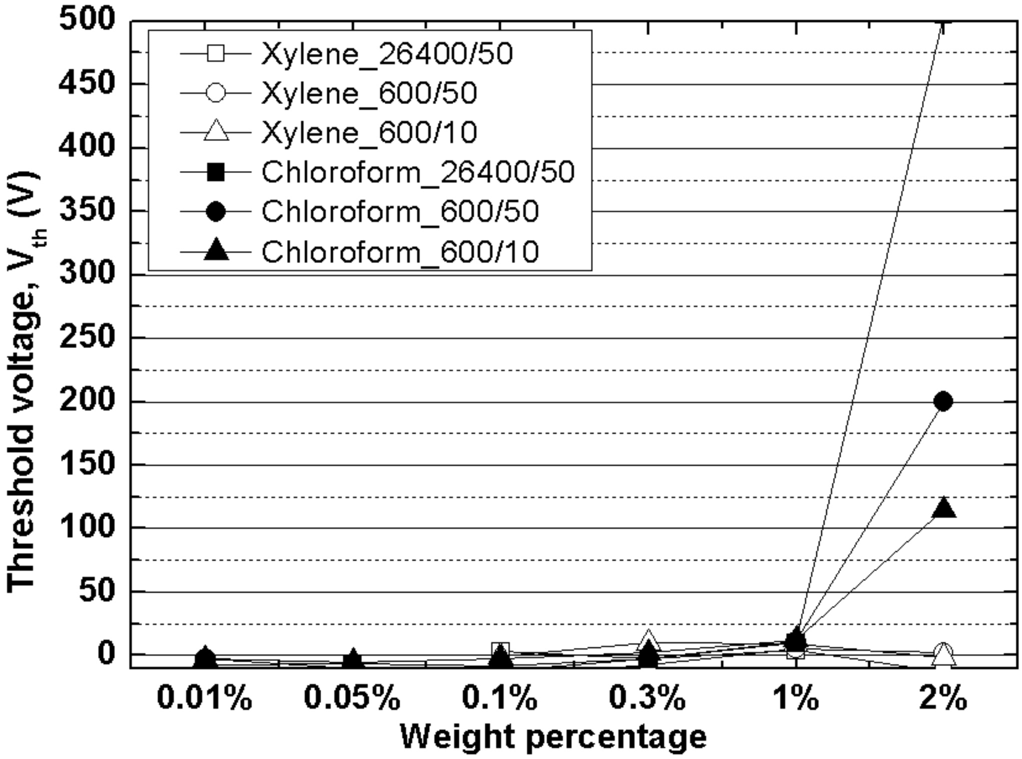


Figure 2-14 Threshold voltage of P3HT FETs of with various weight percentages and solvents.

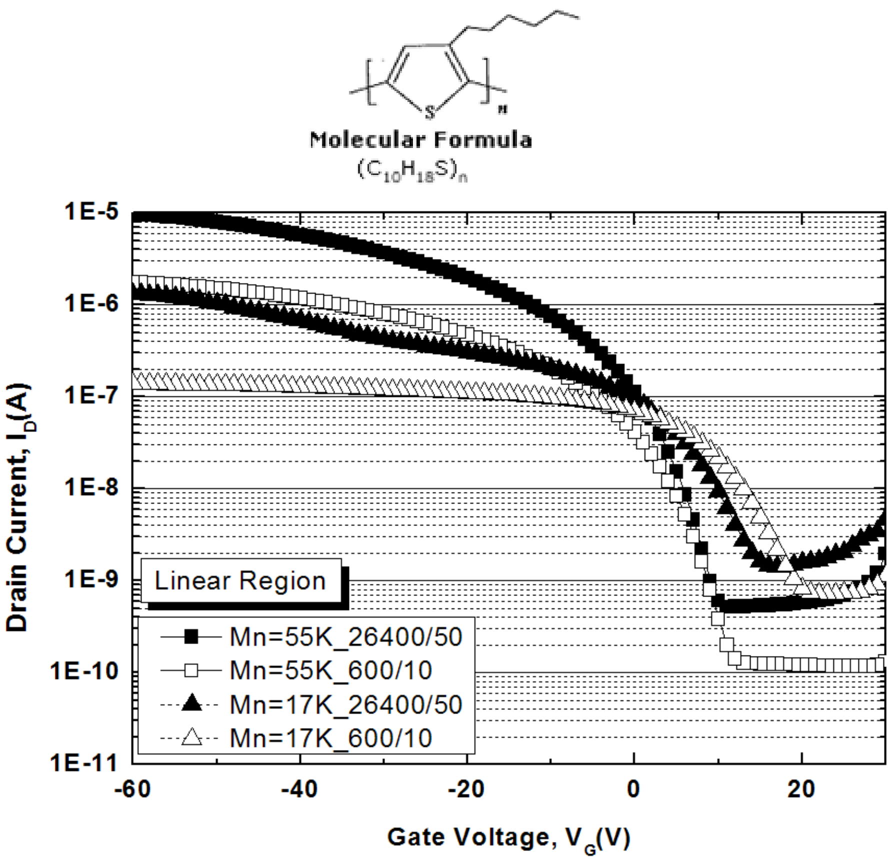


Figure 2-15 Transfer characteristics of P3HT FETs spin-coated from different MW, top insert is Molecular structure including its formula.

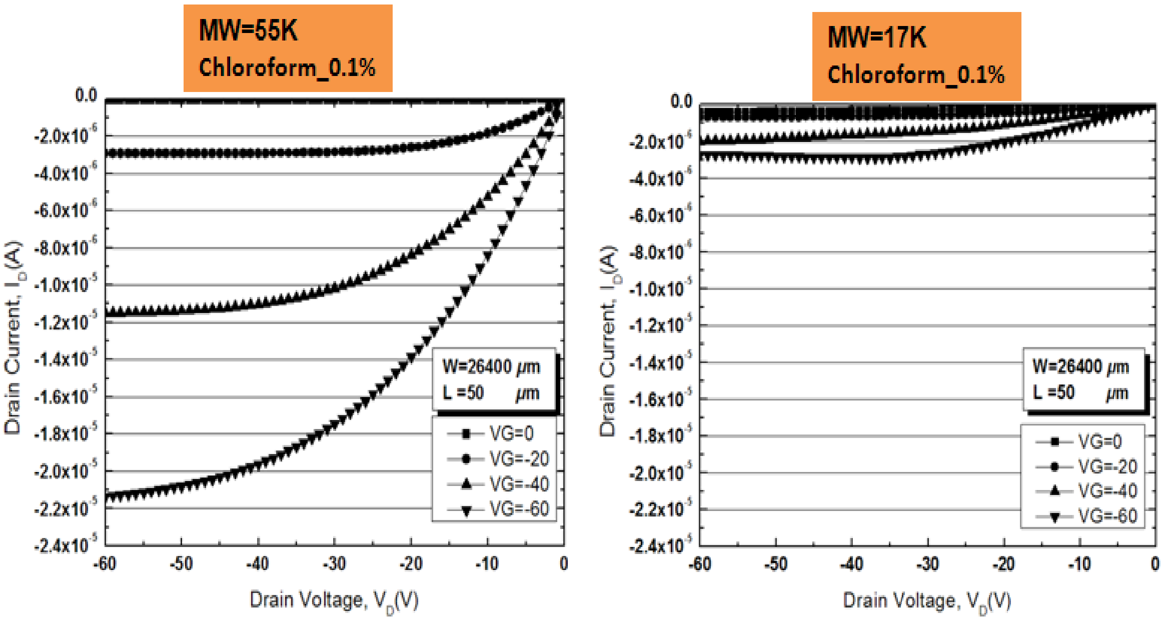


Figure 2-16 The output characteristics of typical device with different molecular weight MW=55K, left, MW=17K, right.

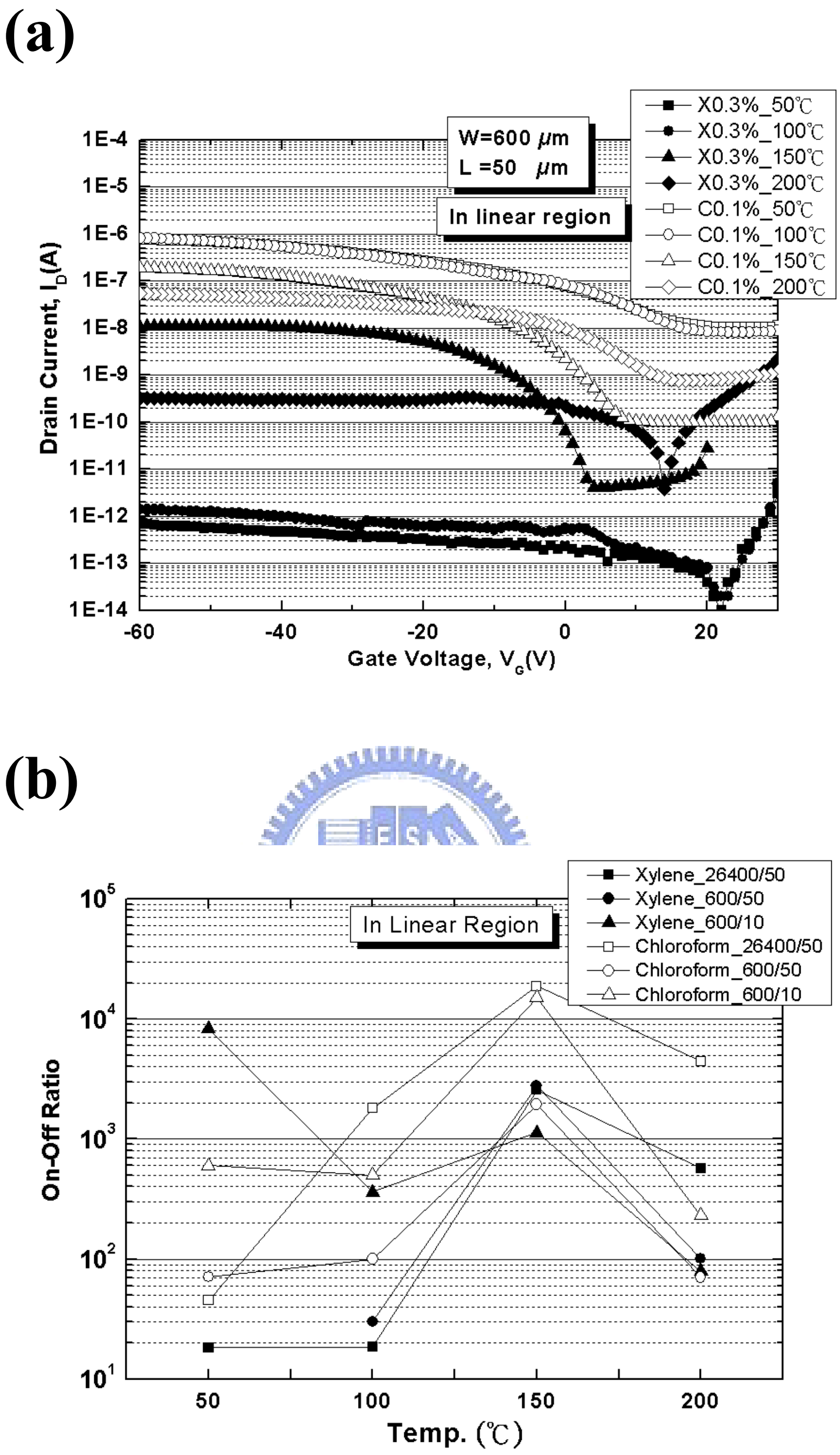


Figure 2-17 Transfer characteristics of P3HT FETs spin-coated from different curing temperatures and solvents, (a) 600/50. A typical On-Off ratio versus the temperature with vary dimension device (b).

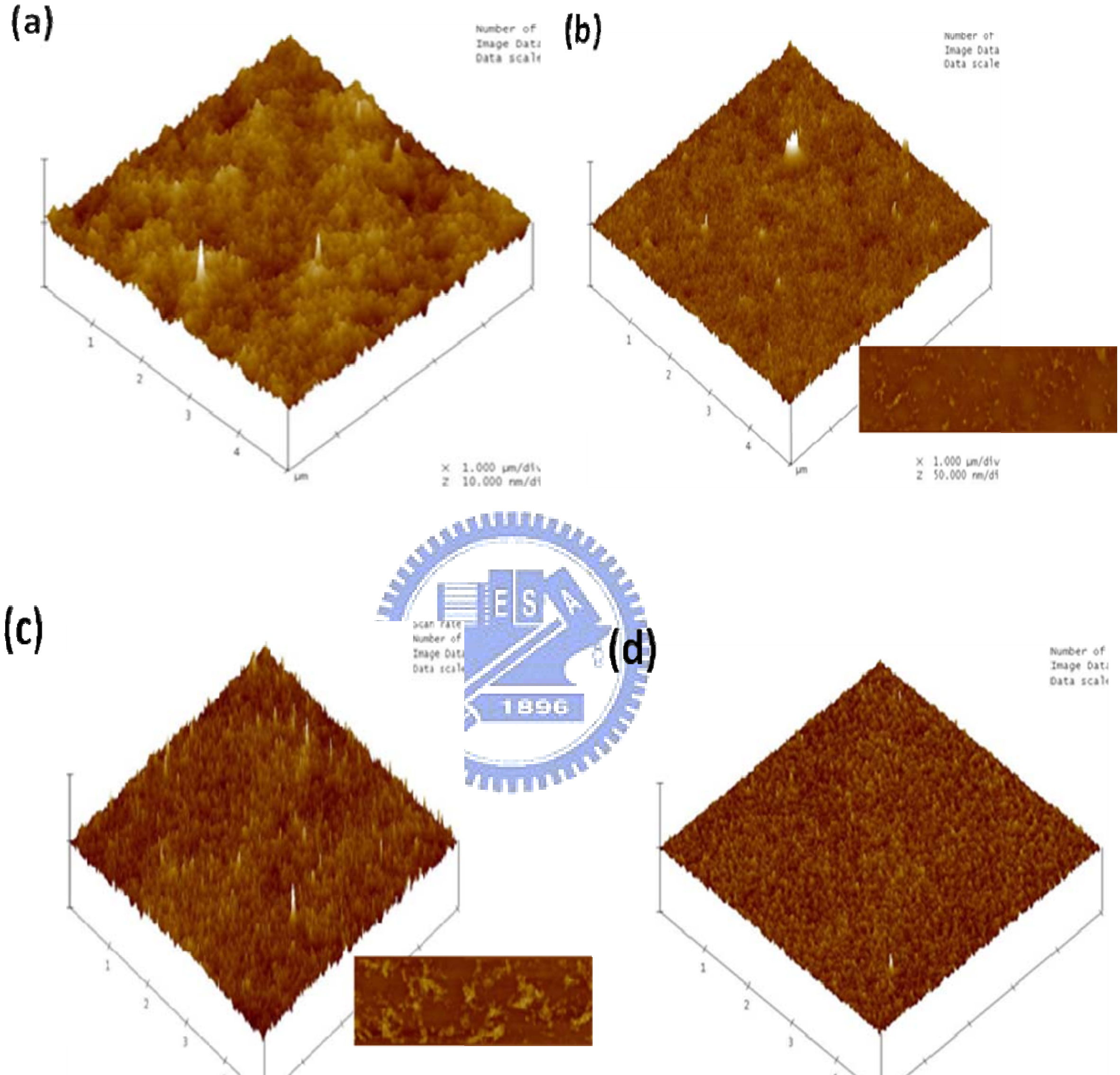


Figure 2-18 Atomic force morphology: 3D analysis from different curing temperature (a) 50℃, (b) 100 ℃(c) 150 ℃, (d) 200 ℃.

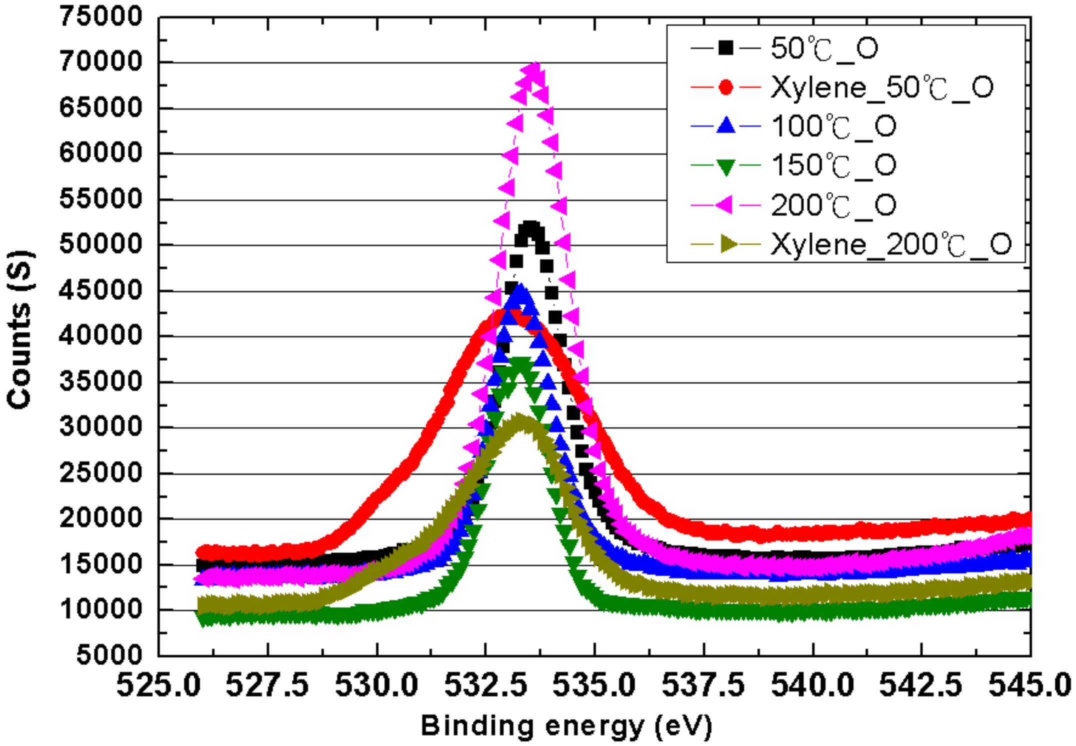


Figure 2-19 ESCA surface elemental analysis: elemental counts versus binding energy with various temperatures (a) Oxygen concentration

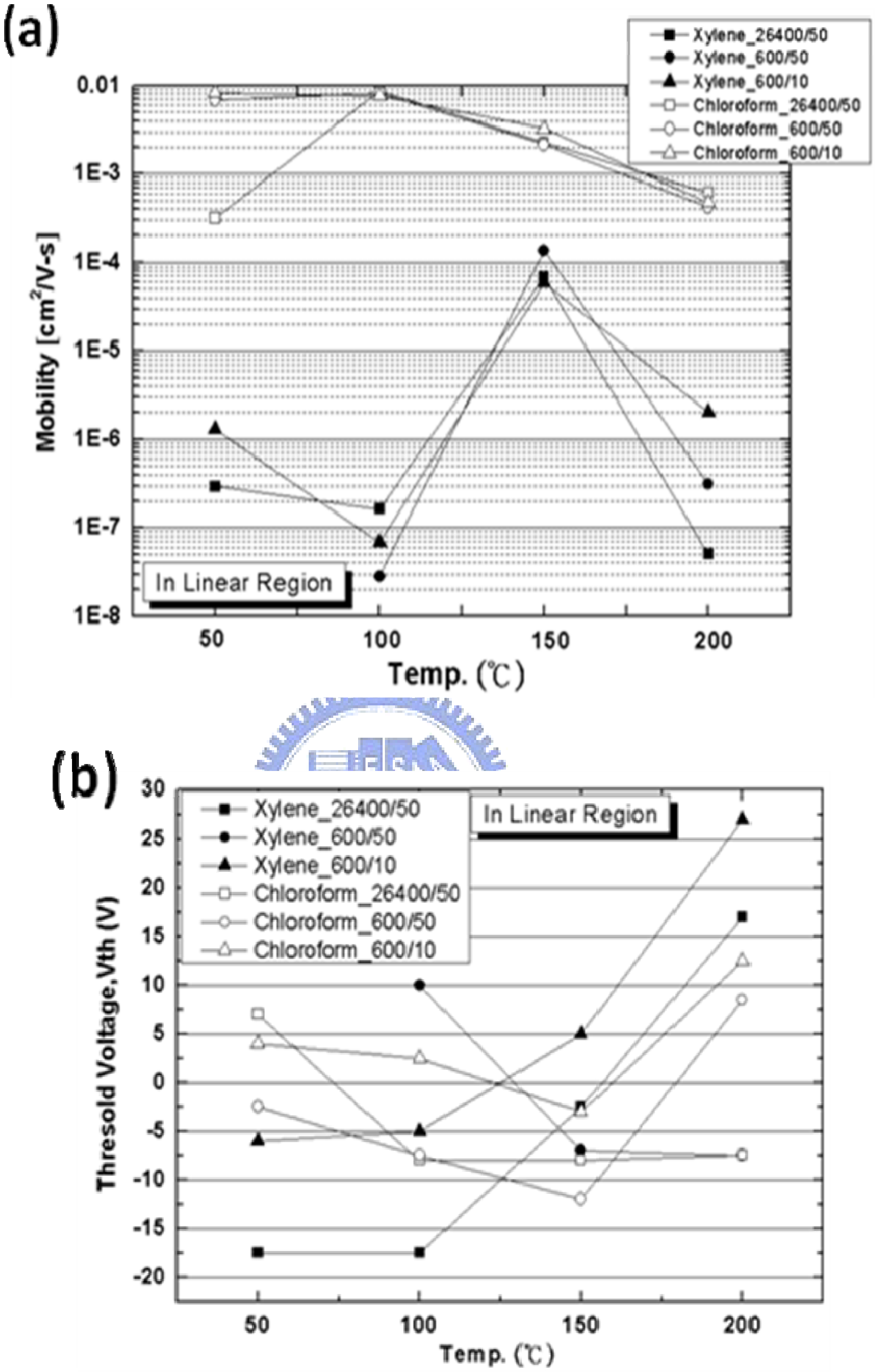


Figure 2-20 Electrical parameters: field-effect mobility of P3HT FETs with varies dimension devices. (a) threshold voltage versus temperature (b).

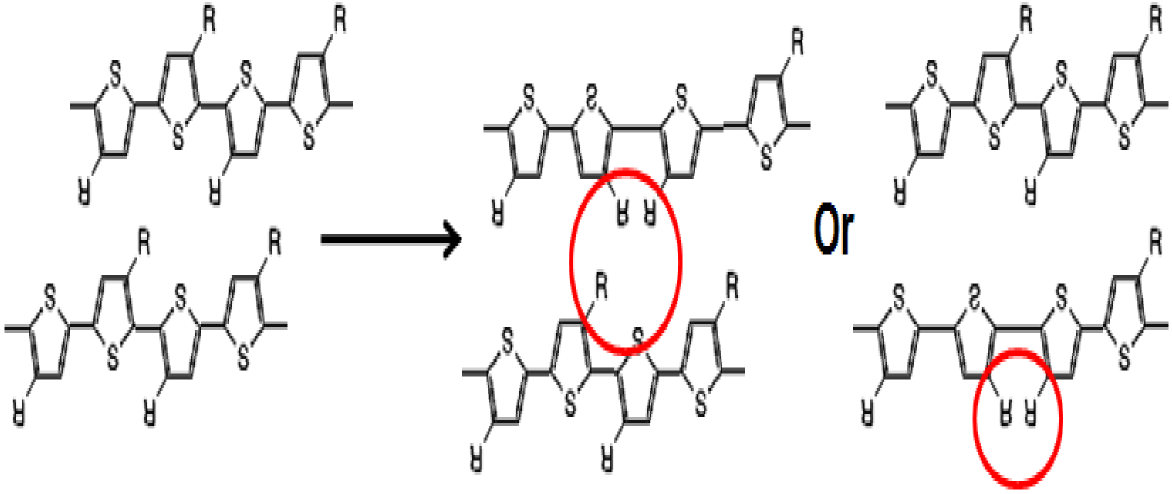


Figure 2-21 rr-P3HT molecular chain and its probability behavior of steric hindrance

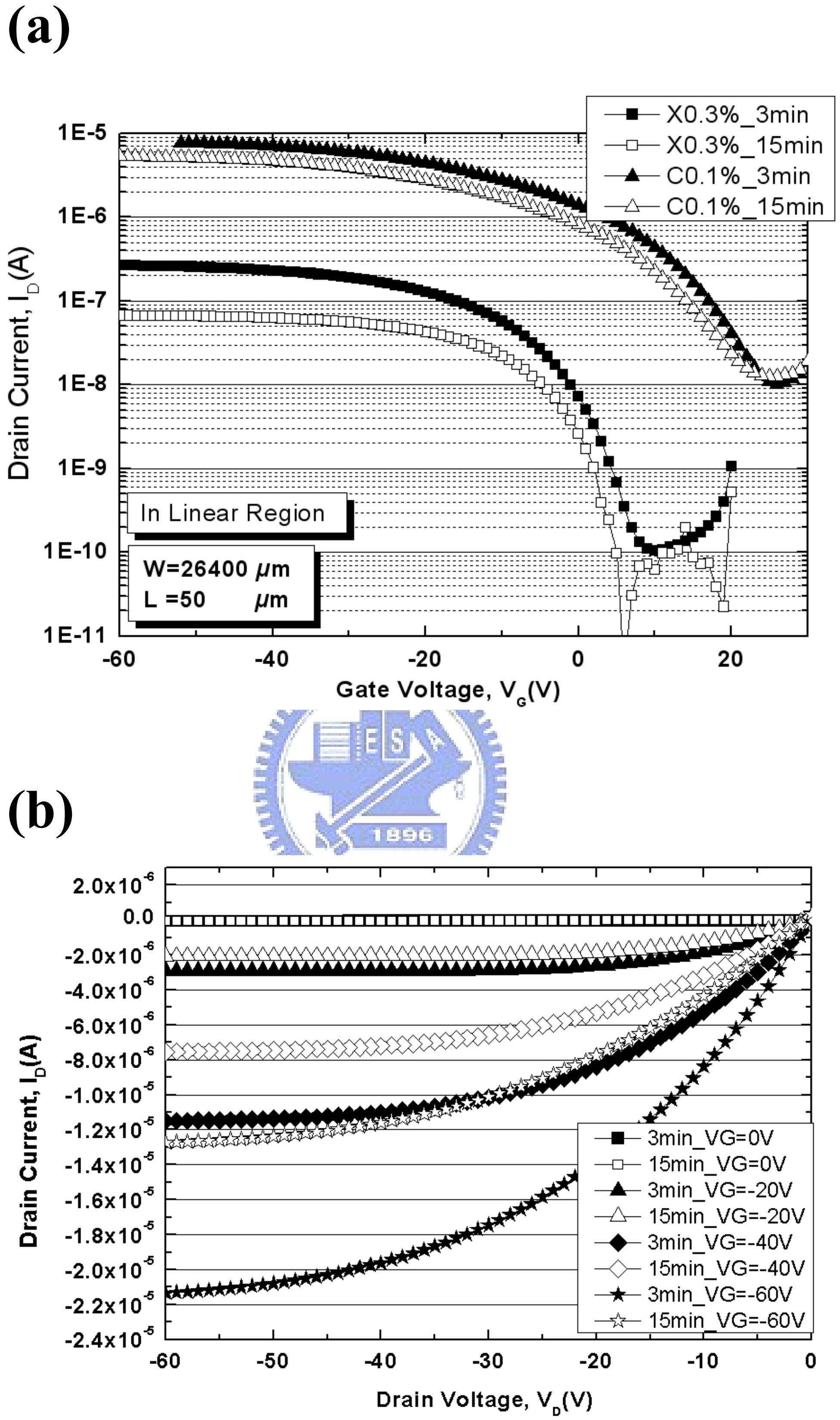
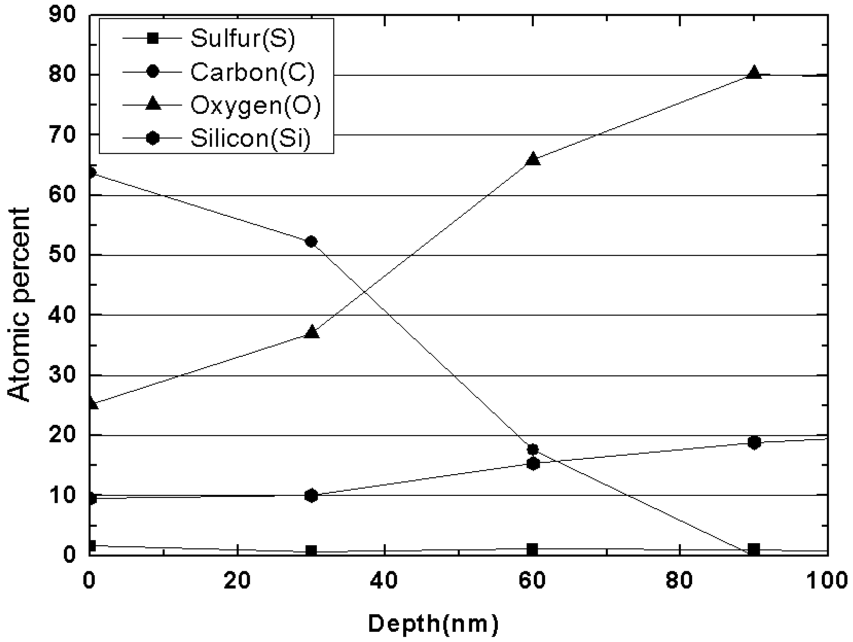


Figure 2-22 P3HT FETs from different curing time and solvents (a) transfer characteristics (b) output characteristics.

(a)



(b)

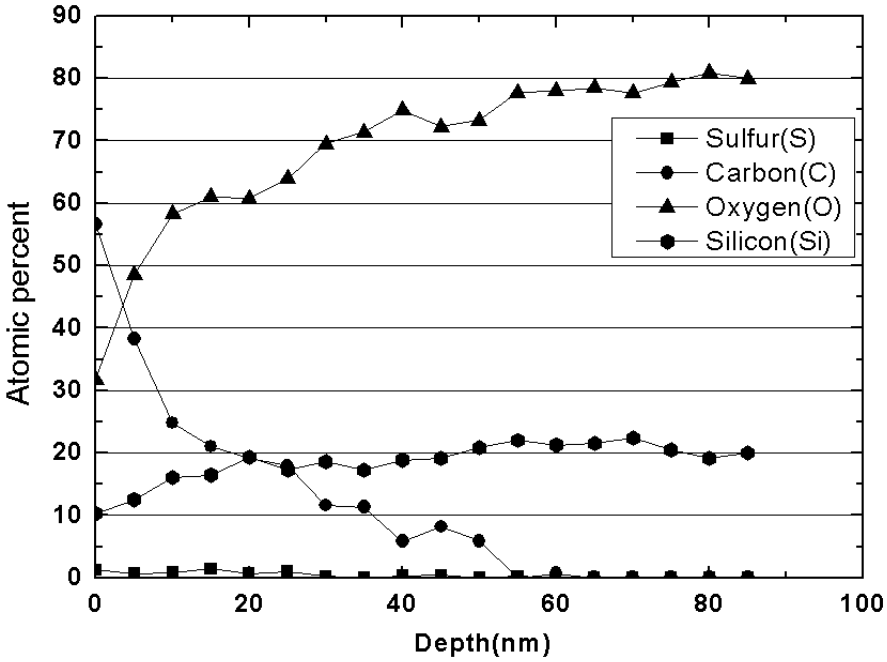


Figure 2-23 Auger depth analysis of PFETs compared with (a) curing for 3min (b) curing for 15min.

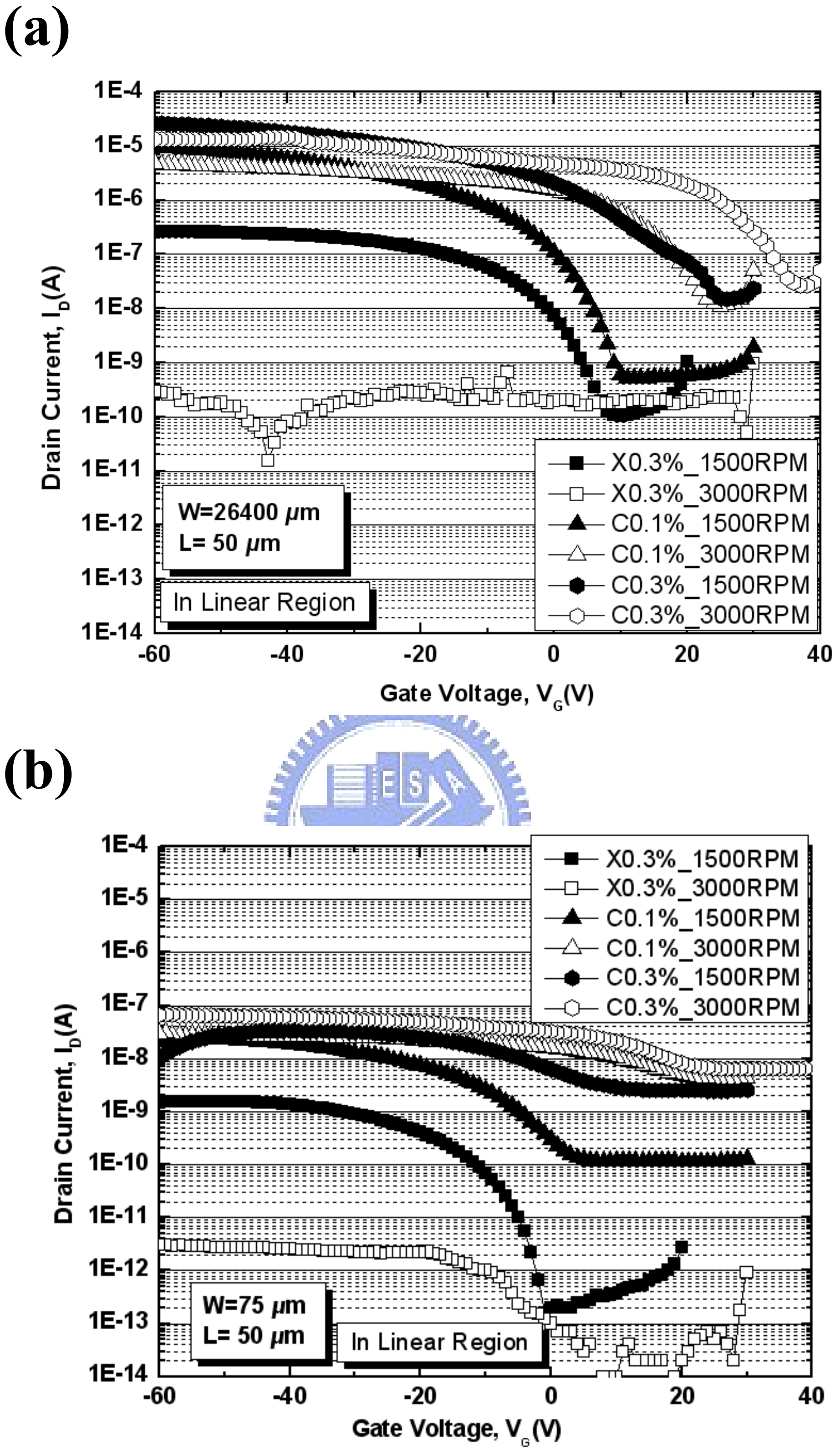


Figure 2-24 Transfer characteristics of different spin-speed with 0.3wt% in xylene and 0.1, 0.3wt% in chloroform including two different dimensions (a) 26400/50 (μm) and (b) 75/50 (μm).

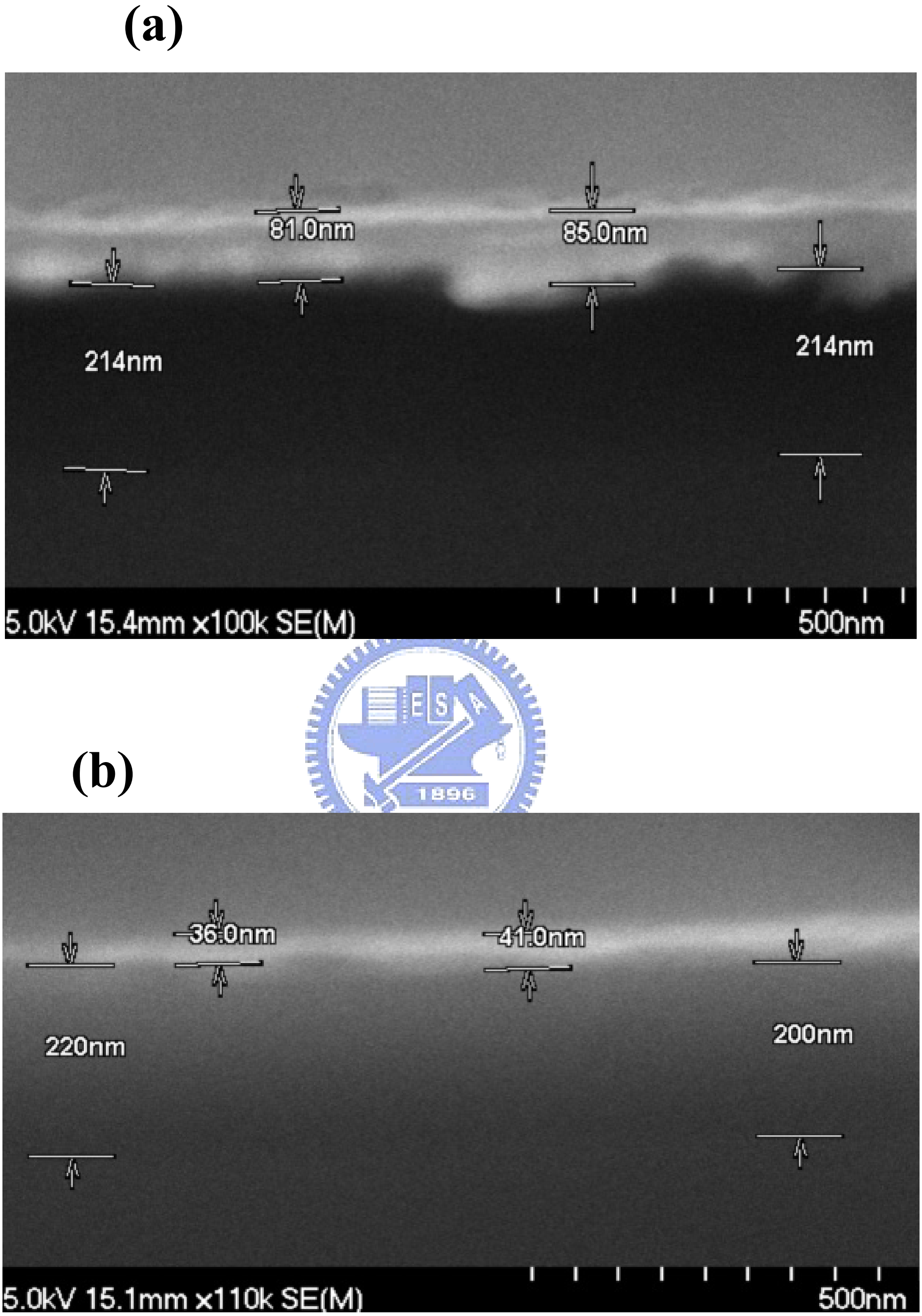


Figure 2-25 SEM cross-section of P3HT FETs spin speed at 3000rpm (a) xylene 0.3wt% (b) chloroform 0.1wt%.

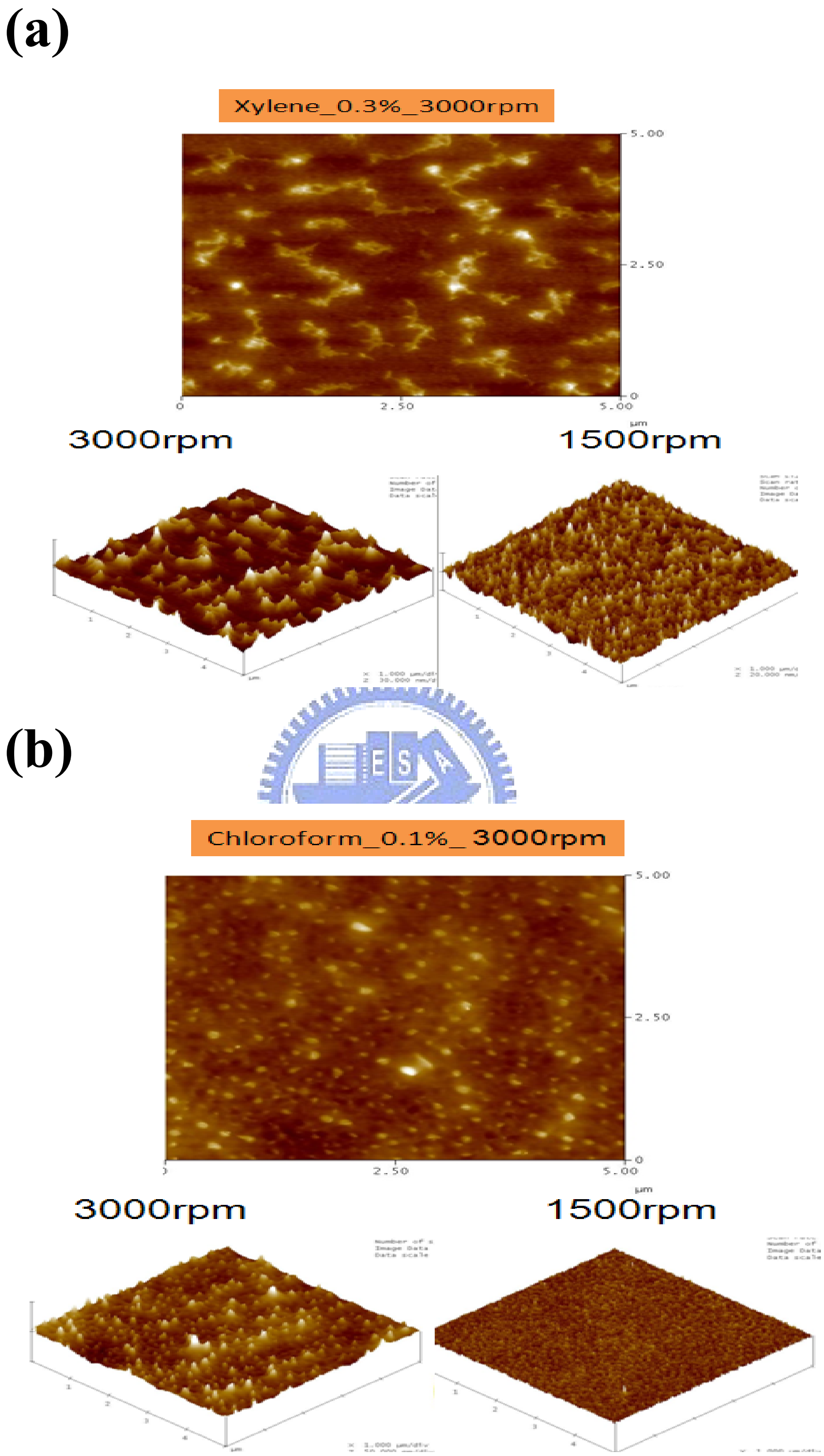


Figure 2-26 Atomic force morphology: the morphology and 3D analysis from different spin speed (a) transistor in xylene (d) transistor in chloroform.

Chapter Three

Surface treatment of gate dielectric and contact metal

3.1 Introduction and motivation

There are two resistances in the P3HT transistor; channel resistance and contact resistance. This will reflect in device scaling, just like MOSFET device does. When device scaling down, the resistance will be enhanced. That result responses in lowing the mobility. Until now, this problem in organic thin film transistor is hardly summoned. Limitations by contact resistance are getting serious **[3.1] [3.2] [3.3]**.

Figure 3-1 shows the mobility value and output characteristic with channel reducing. It is not serious about that issue, and we suspect that nanofibrillar is formed in short channel appropriately so that scaling down issue is not apparent. Conducting channel in the interface between insulator and organic semiconductor is a major rule of transporting carrier. If this surface was roughness, the scattering would be enhanced. And also, random and disorder of molecule will increase a difficult in accumulated carrier.

Additionally, the different metal material has its own work function value. P3HT in accumulation region is transported by holes and the semiconductor is *p*-type. So it needs a level of metal material located in closing to HOMO level, or it lead to poor inject current. The issue is named Schottky barrier.

Major path of carrier transport is near insulator and organic semiconductor. The roughness, no matter at SiO_2 or thin film, it may cause a scattering when the carrier transport. Also, there are several issues for bottom contact such as surface roughness on insulator and hydroxide. All description above will be a concern for the performance.

In this thesis we will study related metal material, the thickness of Ti adhesion and surface treatment how they affect the electrical result.

3.2 Effects of the thickness of adhesion layer

3.2.1 Fabrication Process

The standard baseline process for fabricating P3HT thin film transistors in this thesis is described below. The substrate in this work was n^{++} silicon, although FETs were also successfully fabricated on the flexible or glass substrate.

The steps of process flow are shown in **Fig. 2.3** in chapter two and are described in detail below:

1. Silicon wafers are cleaned through RCA standard process, and this n^{++} silicon substrate (0.002~0.004Ω-cm) to be gate electrode.
2. Silicon di-oxide is deposited by APCVD Wet-Oxidation. This thermal oxidation SiO2 remains at 980℃ in the deposition chamber.
3. Gold Source/drain electrodes are defined on the photo resist-coated (FH6400L) dielectric by lithography by electron beam deposition. Titanium (Ti) is used to be an adhesion layer for firmly sticking gold and dielectric. And then photoresist (P.R.) will be removed by life-off process in acetone with vibrations in super for 5min.
4. Poly (3-hexylthiophene) (P3HT) is spun onto gate dielectric and S/D electrodes. The substrate remains at room temperature in the deposition place. Typical background process is that,
   A.) P3HT will be dissolved by chloroform, respectively. Weight percentage is 0.1wt%.
   B.) All solutions were filtered through a 0.20 μm pore-size PTFE membrane syringe filter before use.
   C.) For spin coating, the film was deposited from solution by two steps: first, at a spin rate of 500rpm for 10s (for uniformity) and second, at spin rate of 1500rpm for 25s (for thickness).
   D.) Curing temperature is 150℃ and then set the device on hot plate for curing for fixed 3 minutes.

Before the active layer of P3HT is deposited, all samples were cleaned by soaking in acetone with vibrations in supersonic oscillator for 5min. the reason for this is that remove the residual organic and particle contaminants on the channel region. Regioregular P3HTs were purchased from FEM Inc (MW=55K, RR=90~93%).

In this experiment, the thickness of Titanium (Ti) is 2.5nm, 10nm and Ti only without Au metal, respectively to see how they affect the electrical result. Moreover, the metal material of source and drain will be deposited by gold (Au) and palladium (Pd)

3.2.2 Result and discuss

Figure 3-2 shows a transfer characteristic of P3HT FETs with source and drain of Ti/Au and Ti/Pd and channel length and width is 26400/50μm. The Ti adhesion layer is an important index for injection barrier. In **Fig. 3-2(a)**, the thickness of Ti adhesion layer is 2.5nm, which could help gold to stick (adhesion) onto silicon di-oxide without affecting electrical characteristic. Deposited thicker Ti adhesion layer, 10nm, onto silicon dioxide may affect the performance of on current, which dropped down one order of magnitude. Even worse, for using Ti adhesion to be a contact metal, it exhibits a very poor performance. Further, we compare experiment of reference (EOR) sample with several different dimensions using Ti only metal in the **Fig. 3-2(b)** and **figure 3-3.** The same result is occurred. The suspect reason is that the work function of Ti is around 4.33eV and it is located at middle of HOMO and LUMO band gap, leading to a large injection barrier for transporting carrier so that a poor performance could be obtained. **Figure 3-4** shows the diagram of work function difference and band bending result. The best adhesion layer of Ti for contact metal in my study is 2.5nm. The extraction on maximum mobility of P3HT transistor with the thickness of Ti/Au obtaining from 50nm/2.5nm is around 0.0023 cm^2/ Vs. Consequently, an appropriated adhesions layer like 2.5nm in our study were good for performance of P3HT FETs, and no matter what metal materials, large injection barrier would be exist between Ti and P3HT active layer. Using Ti to be a contact metal material seems not good for injection carrier.

3.3 Surface treatment of silicon di-oxide gate dielectric

3.3.1 Fabrication Process

Two sets of devices were fabricated for each experiment: (a) untreated control devices, (b) devices treated with Hexamethyl Disilazane (HMDS)：$(CH3)_3Si-NH-Si\ (CH3)_3$. Except for treatment of HMDS dielectric prior to P3HT deposition, the fabrication process was exactly the same described in the previous section 3.2.1.

The first set of devices (a) was fabricated using the standard baseline process with no surface treatment of the silicon di-oxide prior to P3HT deposition, which named experiment of reference (EOR). The second set of devices (b) was coating a surface treatment HMDS for 5 minutes in the vacuum oven, which temperature sets at 150℃. Physical characteristics of the silicon di-oxide surfaces and P3HT morphology was performed using several techniques. Electrical data was obtained from characterization of the FET devices. The results of those two experiments (EOR and W/ HMDS) are analyzed in the following sections.

3.3.2 Result and discus

Figure 3-5 shows transfer characteristics for typical device with two dimensions treated and untreated. Both dimensions show the same result: first, off current reduced when the device was treated with HMDS. And the untreated device exhibit large off current. Second, the value of threshold voltage is changing also. **Table 3-1** shows the increase of on-off ratio both in the linear and saturation region.

Treated devices were to modify the silicon di-oxide surface in order to improve P3HT growth. The first few layers in particular are most important in transistor operation, since in the accumulation region carriers are concentrated at the interface between a gate dielectric and organic active layer **[3.5]**. A more hydrophobic surface is expected to result in better packing of the P3HT molecules as shown in **Fig.3-6 [3.6]**. The theory illustrate that a hydrophobilic surface become to a hydrophobic surface, due to treated device takes replaces the hydroxyl groups at silicon di-oxide surface with methyl or alkyl groups by given a temperature, which will cause a transfer between NH in HMDS and OH in SiO_2 surface. The co-product is NH_2 and it will be evaporated away, reminds the rest of radical function, resulting in a small surface energy, as shown in **Fig 3-7**. From contact angle measurements, in **figure 3-8**, shows the increase in contact angle from 54.8° in the untreated silicon di-oxide to 90.3° in the treated HMDS surface (The gate dielectric surfaces were characterized using contact angle goniometry). Well order in the surface could enhance a high density of chain packing, and result a reduction in passivating defects. AFM result shows that the surface roughness of P3HT has changed after treats with HMDS, as shown in **Fig. 3-9**. This reason could be supported by the gate leakage, as shown in **Fig.3-10**. The leakage current through the HMDS-treated silicon di-oxide is decreased by almost one order of magnitude.

In **figure 3-5 (b)**, as you seen, the improved performance both in linear region and saturation region with surface treatment can be obtained. The extraction of mobility is summarized in **Fig. 3-11 (a)**. Although the value of improvement is large, and treated with HMDS onto silicon di-oxide in all of dimensions are better than untreated ones. Highest mobility with treated dimension, 600/10(μm), is around 3.94×10^3 $cm^2/$ Vs, compared to without treat HMDS is 3.72×10^3 $cm^2/$ Vs. In additional, the treated transistors turn on approximately at Vg=0. The turn-on voltage is shifted toward to more negative values as shown in **figure 3-11(b)**.

All of data illustrate that SiO2 surface treats with HMDS can improve device performance at all.

3.4 The ideal metal material

3.4.1 Fabrication Process

The standard baseline process for fabricating P3HT thin film transistors in this thesis is the same as section 3.2.1. The difference is that involved metal material are Gold (Au=5.1 eV), Nickel (Ni=5.15eV), Palladium (Pd=5.12 eV), Platinum (Pt=5.65 eV), Titanium (Ti=4.33 eV).Work function of all metal material are summarized in **Table 3-2 [3.7].** The metal material of source and drain will be made with those metal and compare to the performance. All thickness of them is 50nm and Ti acts as an adhesion layer with a thickness of 2.5nm. A comparison of experiment named experimental of reference (EOR), which untreated with HMDS and its metal material is Ti/Au.

3.4.2 Result and discuss

Basically, all data and figure will be arranged from low work function to high work function, and compare to all of measured result.

Three metal materials with approximate work function will be discussed. They are Au=5.1 eV, Ni=5.15eV, Pd=5.12 eV, respectively. The result shows in **Fig. 3-12** with different dimensions. An apparent difference for nickel has poor performance, large off current and small on current. We suspect that a mismatch in work function between Ni and P3HT enhanced this result, and a large injection barrier for transport carrier reduced ability of hopping. And also a chemical surface property of Ni between metal and active layer was not reactive, leading to a poor electrical results. Because a good metal material could help the P3HT molecules to order onto surface, enhancing chain packing, stronger molecules interaction.

Competitions between metal materials are Au and Pd. For this, we observe and compare all related device dimension (not show here). Indeed, for off current, they are so close to each other. Initially, we have already known that their work function difference is comparable. Next, we compare the mobility and threshold voltage as shown in **Fig. 3-13** and **Fig. 3-14**. Honestly, from observed result, the mobility calculated from Gold is higher than Pd one, and its threshold voltage is approaching to zero. For physical analysis, AFM 3D result shows in **figure 3-15.** No matter what P3HT thin film spun on channel or metal, the surface roughness of Au metal is lower than Pd metal. This result is similar with section 2.4 in chapter two. Higher surface roughness and more cluster gathering could exhibit larger off current. So we suspect that this is not related with work function, due to their value are all close. One of reason for that is surface chemical property, which could affect the performance. **Figure 3-16** shows the output characteristic. In linear region, enlarged figure below, obtained current with Pd metal will be higher than Au. This indicates that device fabricated with Pd metal has an apparent situation of normally on. It would be considerable issue if it fabricated.

Additionally, the interface between metal and organic has high roughness surface, as shown in **Fig. 3-17**. This could be formed as spun. For evaporated organic like small polymer, the small grain will be located at this interface, which may an existence of high resistance **[3.8]**.

Fig. 3-18 shows the leakage current compared with the HMDS-treated, Au metal and Pd metal, resulting a decrease by almost one order of magnitude in positive. We still have not a reasonable explanation for it. Compared metal materials are putting together in **figure 3-19**. The result is the same as description in previous.

3.5 Summary

A.) For P3HT transistor in my study, scaling down issue seems not affected, because the nano-fibrillar can be formed in short channel.

B.) The thickness of adhesion layer, Ti, is a proportional to the performance. The better thickness is 2.5nm for both Au and Pd source/drain metal, due to injected barrier is not low when applying a biased voltage.

C.) Indeed, using surface treatment, HMDS, could modify surface property of SiO2 and improve chain packing and then increase the electrical parameters such as the mobility, on/off ratio and threshold voltage.

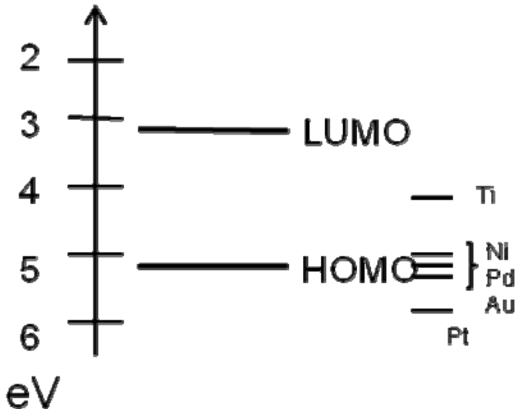
D.) Metal material with close to work function difference may not obtain the same performance. Gold can exhibit a better result, higher mobility. It also related to surface chemical property and contact resistance. The lowest surface roughness is gold metal, compared with Pd.

Table 3-1 Electrical parameters of w/o and w/ surface treatment and operating in linear and saturation region.

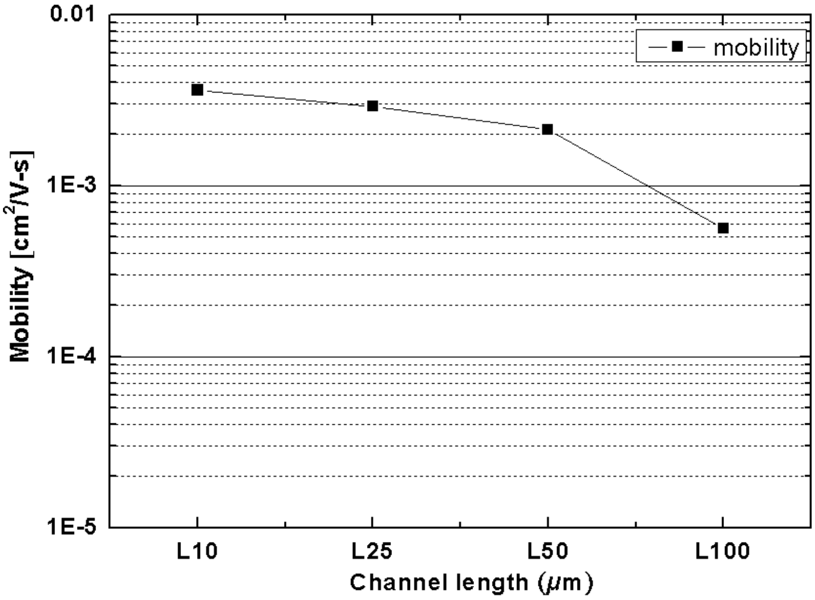
		Linear region		Saturation region	
	W/L	w/o HMDS	w/ HMDS	w/o HMDS	w/ HMDS
On/off ratio	26400/50	1.88E+04	2.13E+04	6.60E+04	8.70E+04
	600/10	1.51E+04	3.24E+04	8.50E+04	1.91E+05
Mobility	26400/50	2.60E-03	3.07E-03	2.60E-03	3.50E-03
	600/10	3.62E-03	3.84E-03	3.72E-03	3.94E-03
Vth	26400/50	-14	-12.5	-6	-3.5
	600/10	-8	-5	2.5	3

Table 3-2 Metal element and its work function, left, and Position set, right.

Metal element	Work function(eV)
Ti	4.33
Ni	5.1
Pd	5.12
Au	5.15
Pt	5.65



(a)



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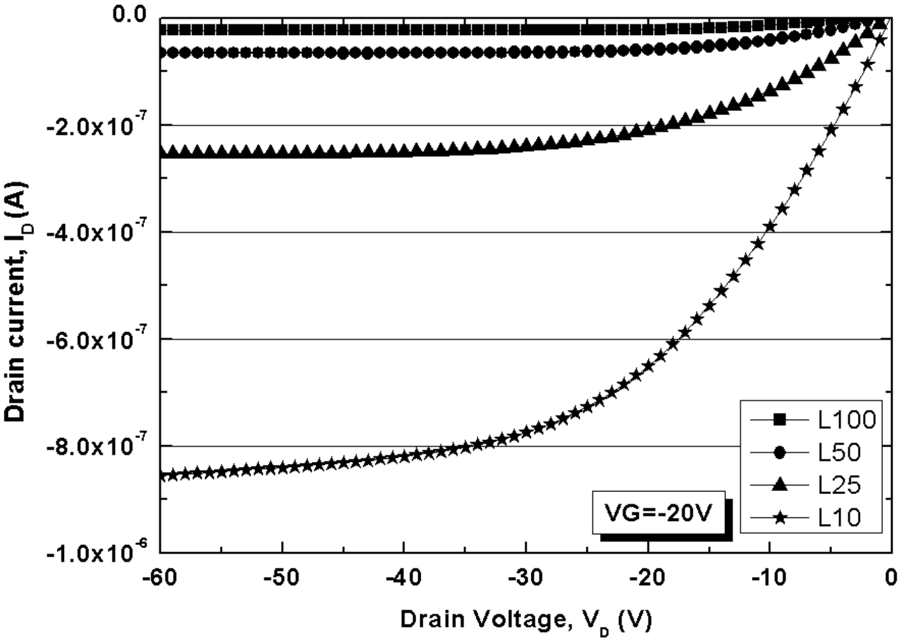


Figure 3-1 Scaling down issue in P3HT transistors (a) the mobility (b) the output characteristic with different channel length.

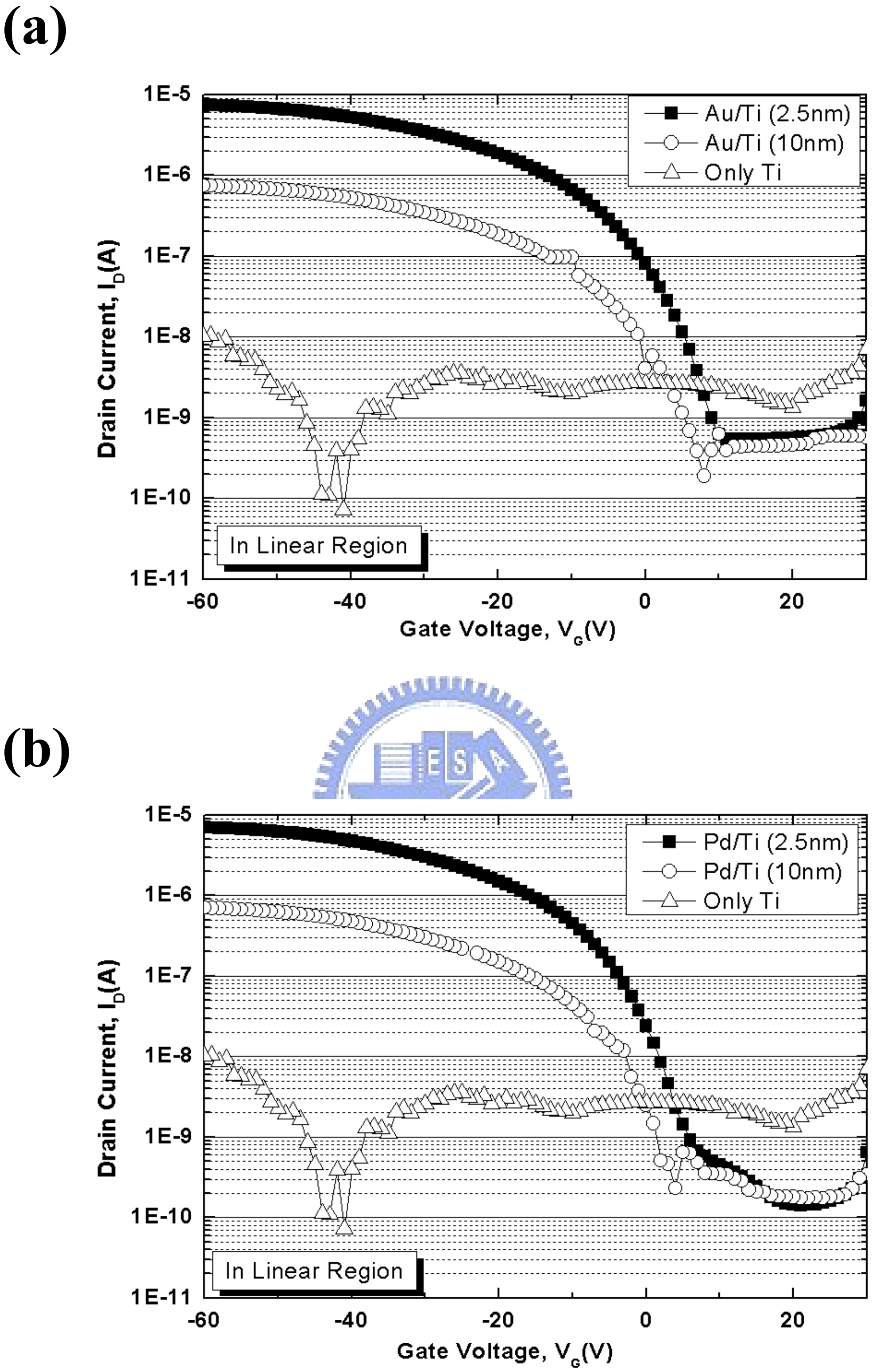


Figure 3-2 Transfer characteristics of different Ti thickness with (a) Au metal, (b) Pd metal

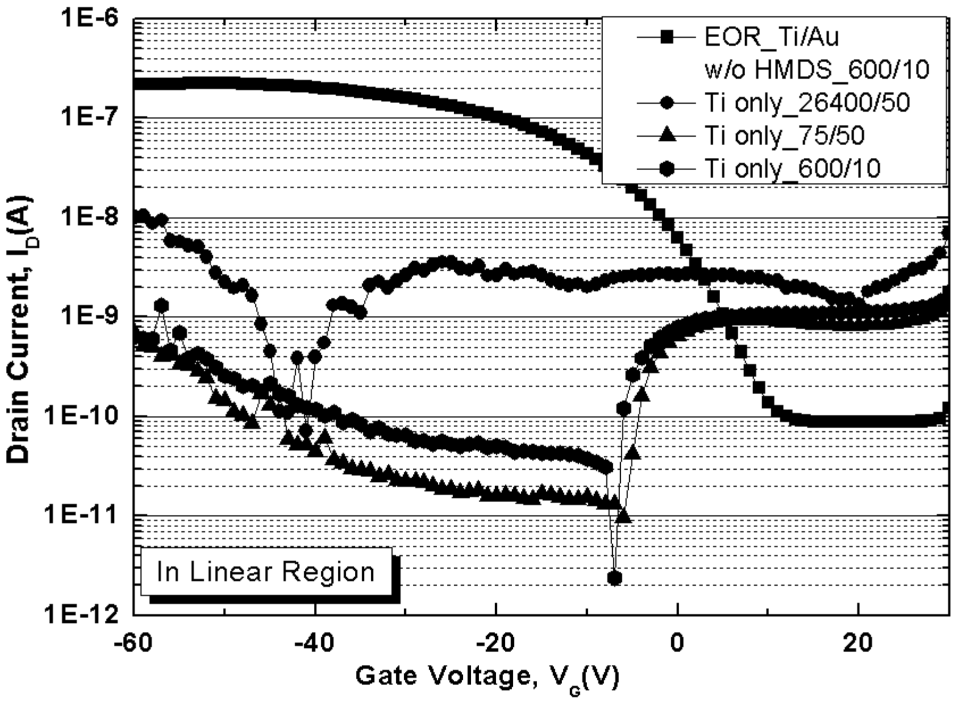


Figure 3-3 Transfer characteristics of Ti only with different device dimension.

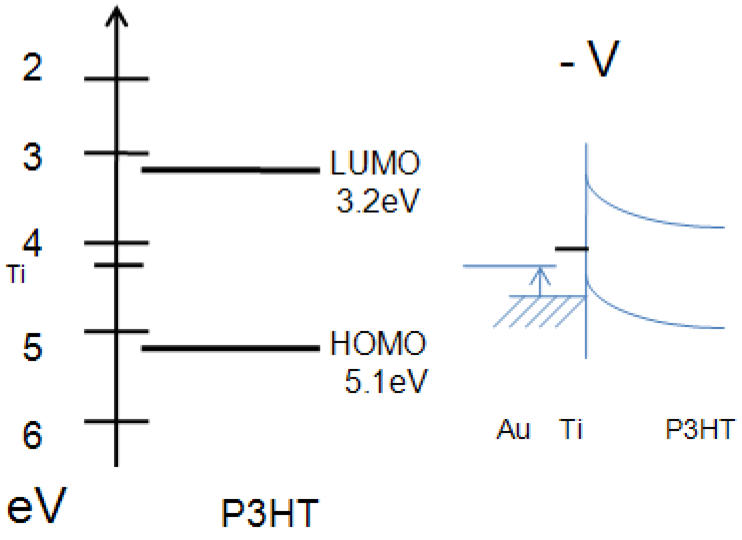


Figure 3-4 Work function difference of Ti and band bending result.

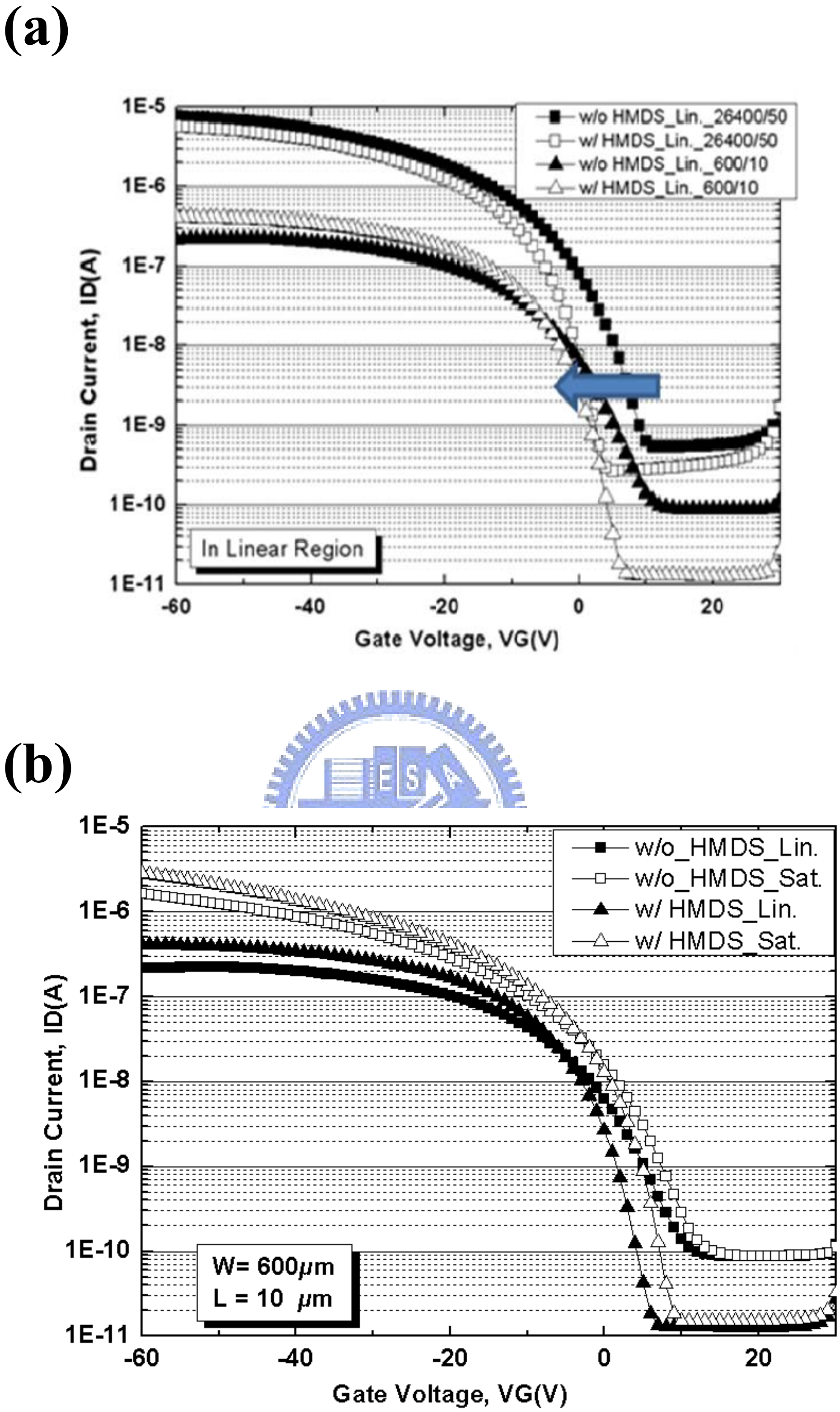


Figure 3-5 Transfer characteristics (a) w/ and w/o surface treatment, (b) the device operates in the linear and saturation region w/ and w/o surface treatment.

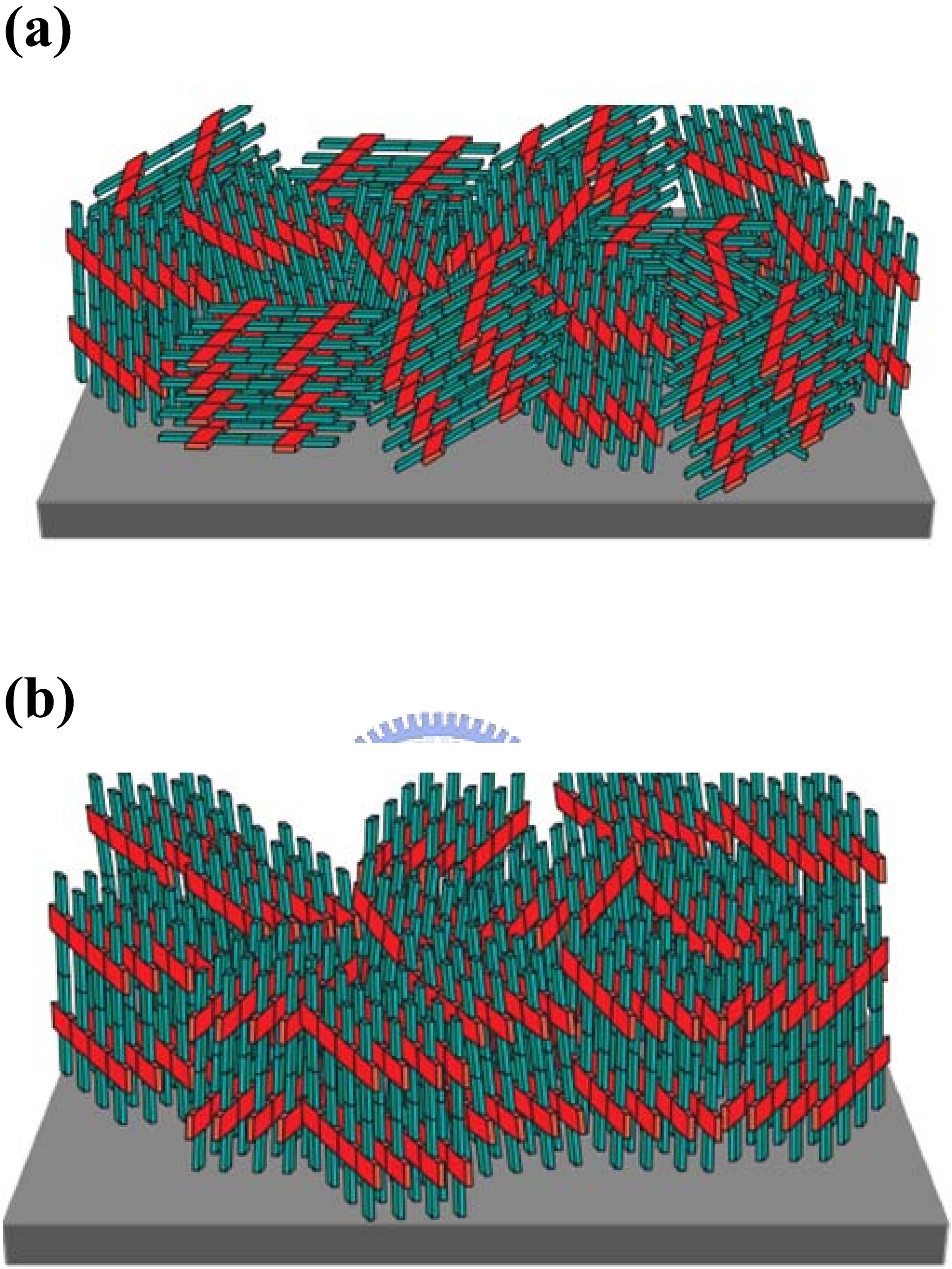


Figure 3-6 The molecular ordering and packing way (a) w/o and (b) w/ surface treatment.

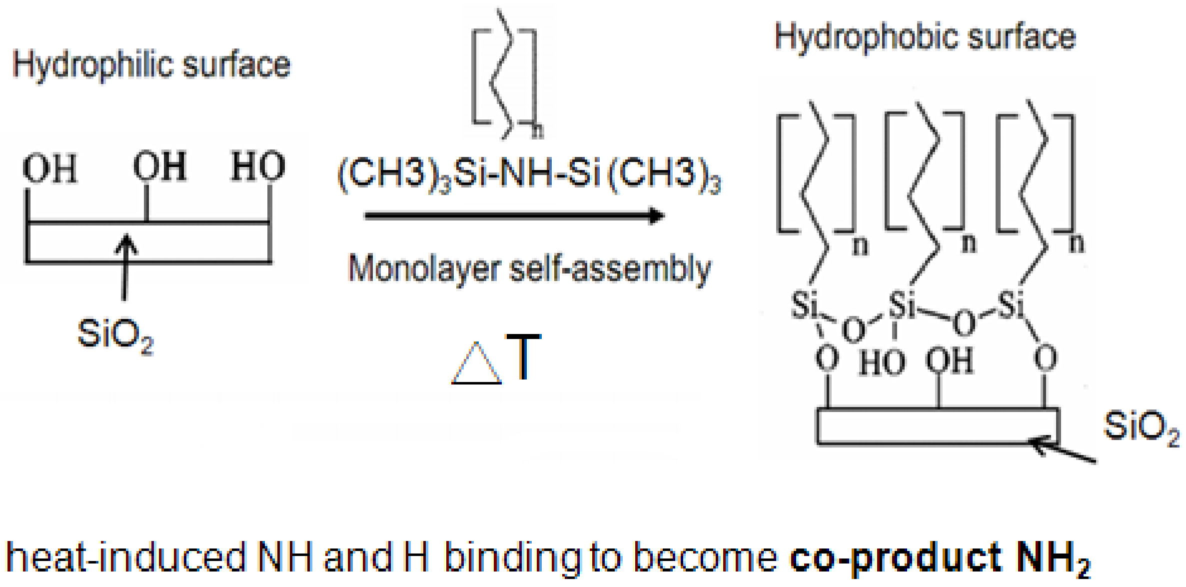


Figure 3-7 The theory of surface treatment of HMDS from hydrophilic to hydrophobic surface.

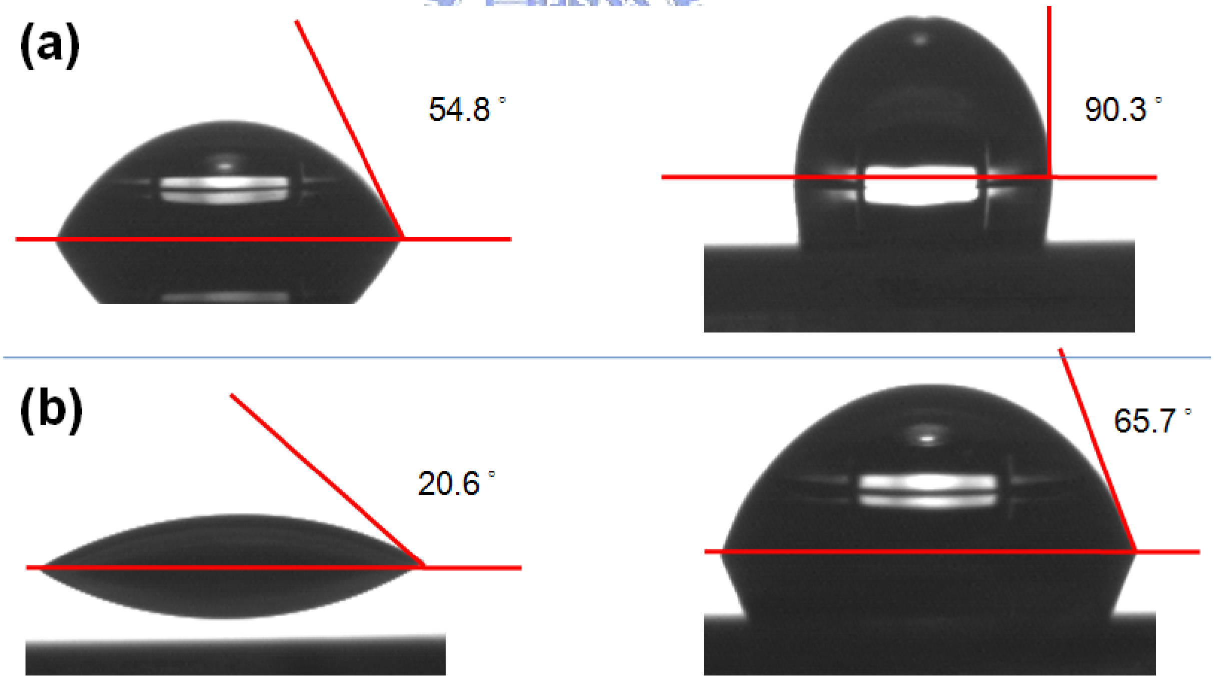
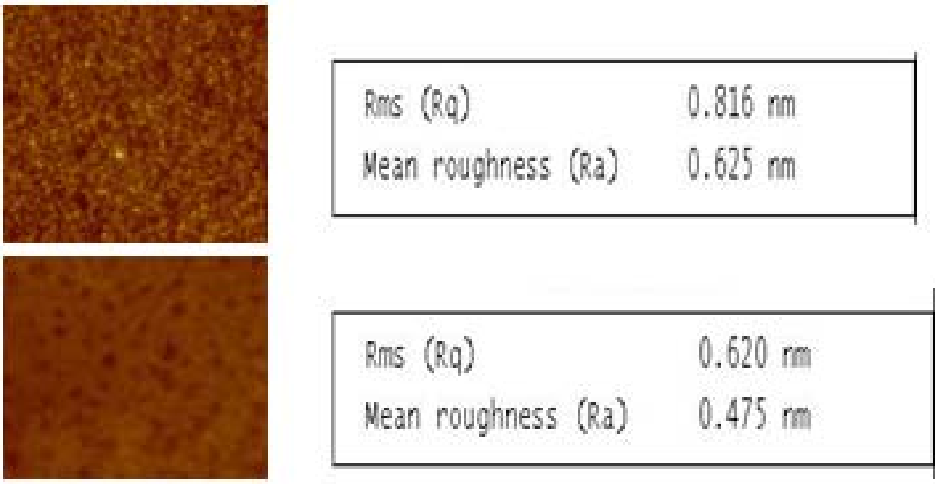


Figure 3-8 Contact angle value on surface of silicon di-oxide (a) water, and (b) ethylene glycol.



Rms (Rq) 0.816 nm
Mean roughness (Ra) 0.625 nm

Rms (Rq) 0.620 nm
Mean roughness (Ra) 0.475 nm

Figure 3-9 AFM surface roughness of w/o, top, and w/, bottom, surface treatment.

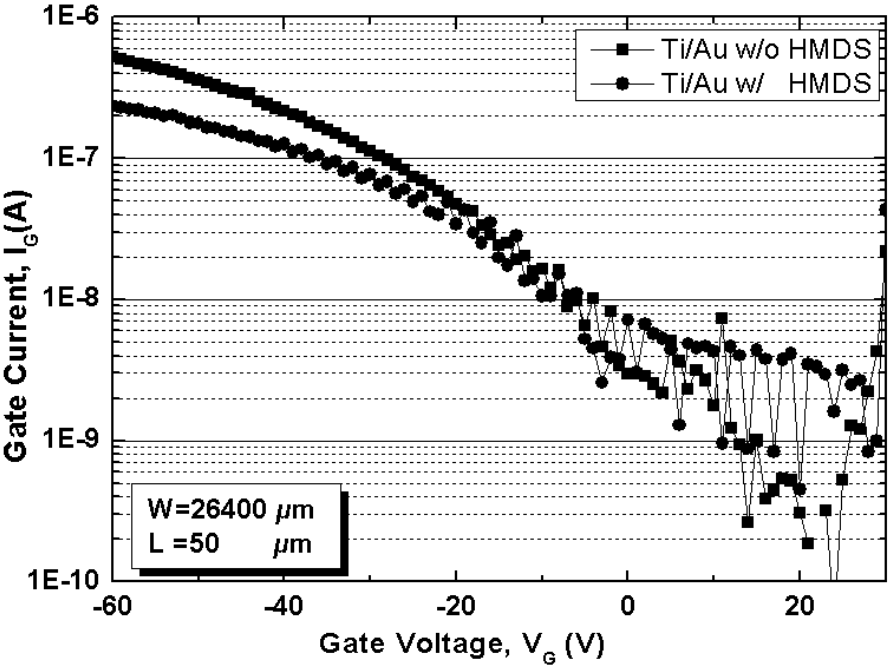


Figure 3-10 Gate leakage current characteristics of typical device w/ and w/o surface treatment.

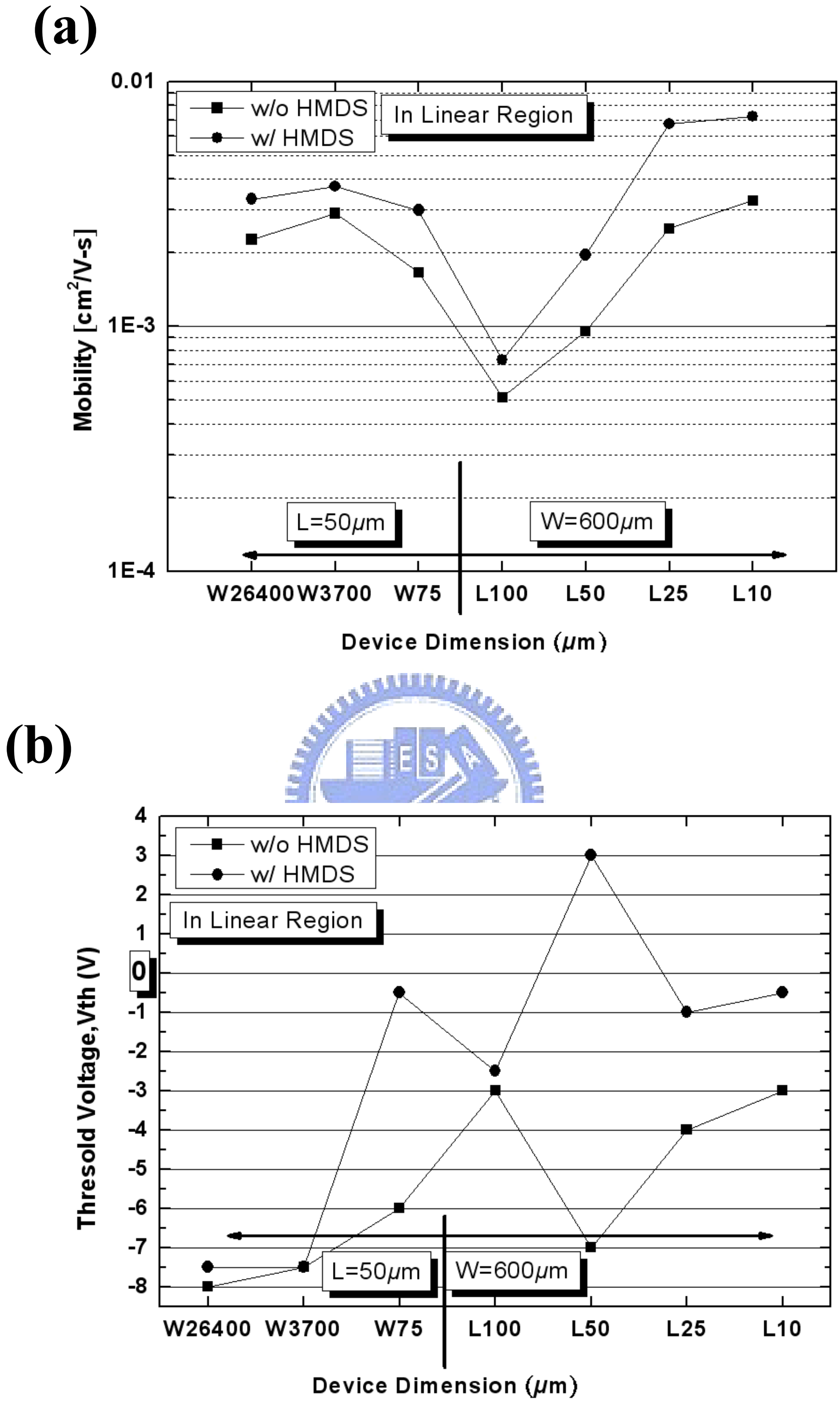


Figure 3-11 Typical electrical characteristic w/ and w/o surface treatment (a) the extraction of the mobility (b) threshold voltage with all device dimensions.

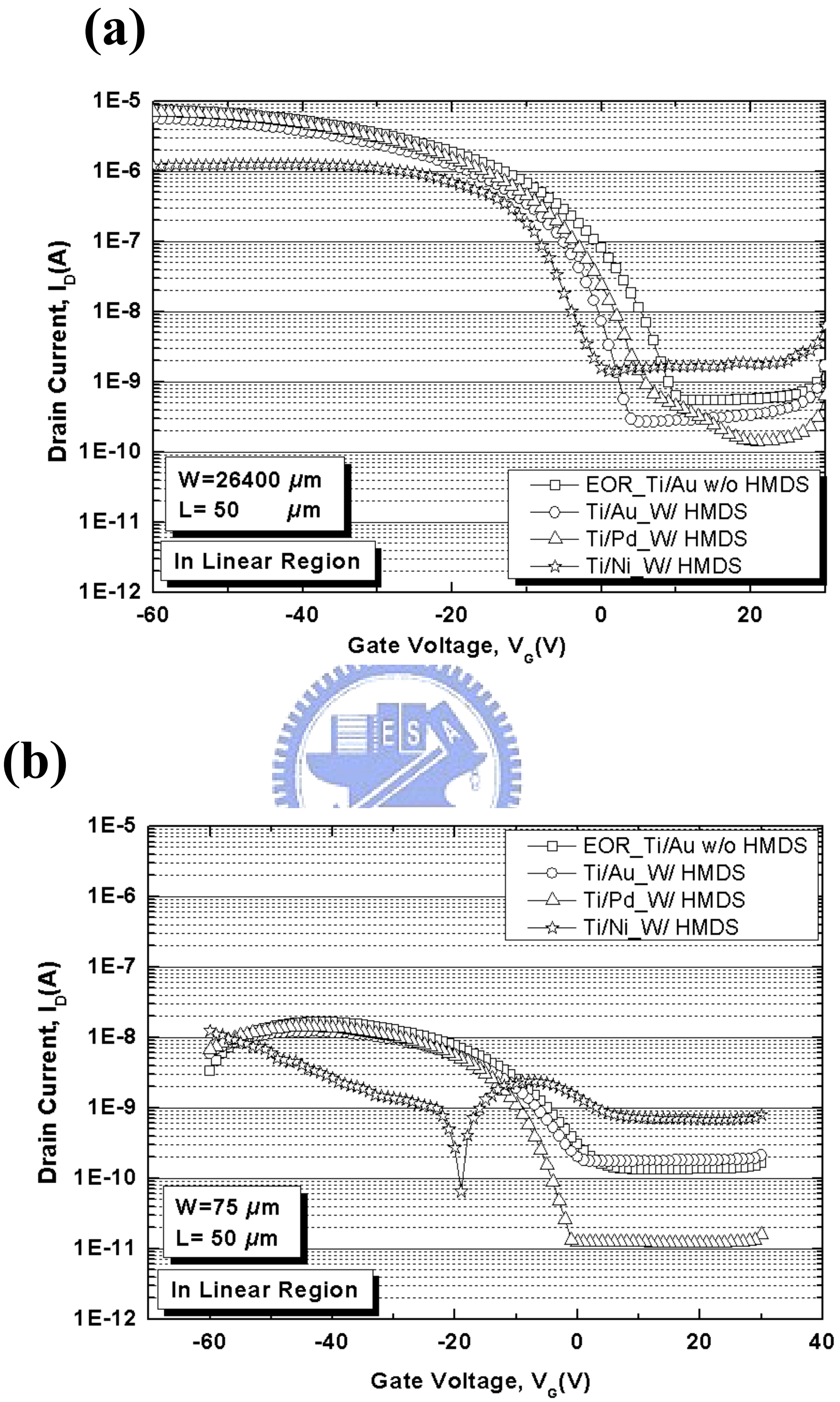


Figure 3-12 Transfer characteristics with different S/D metal (a) W/L=26400/50, (b) W/L=75/50.

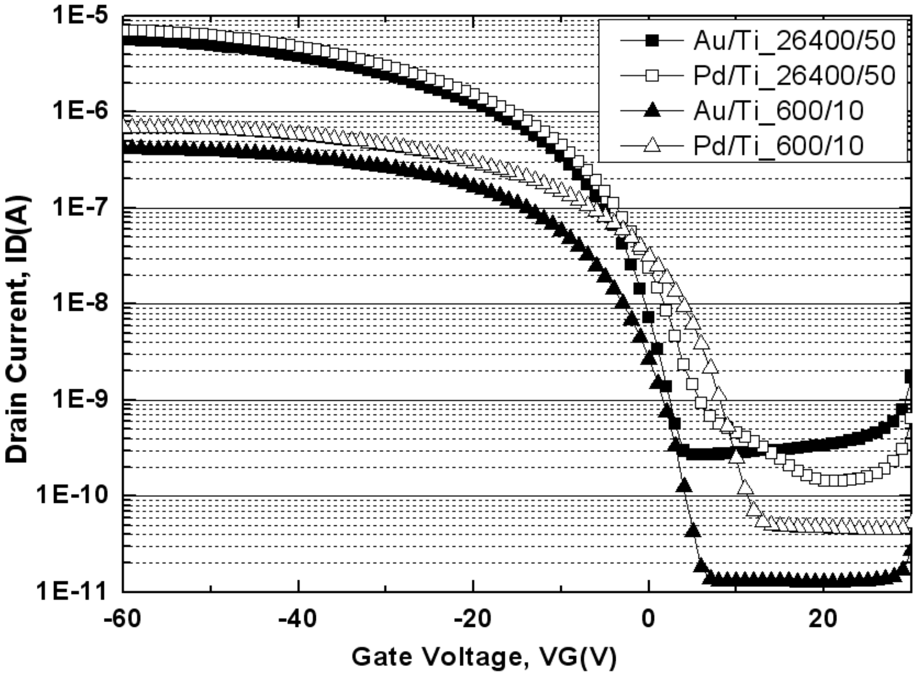
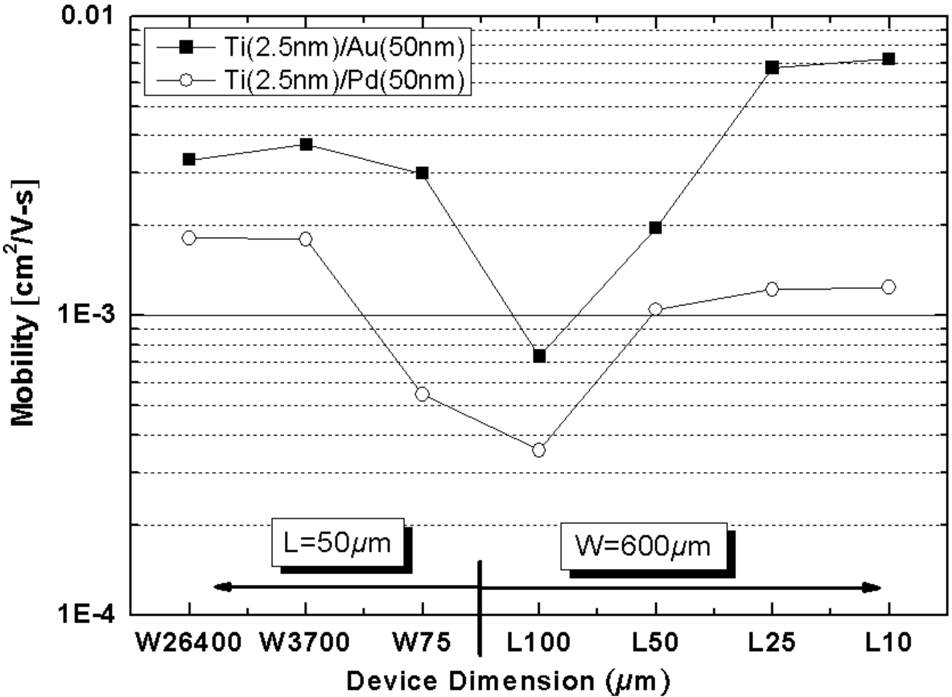


Figure 3-13 Transfer characteristics with different S/D metal (a) W/L=26400/50, (b) W/L=600/10.

(a)



(b)

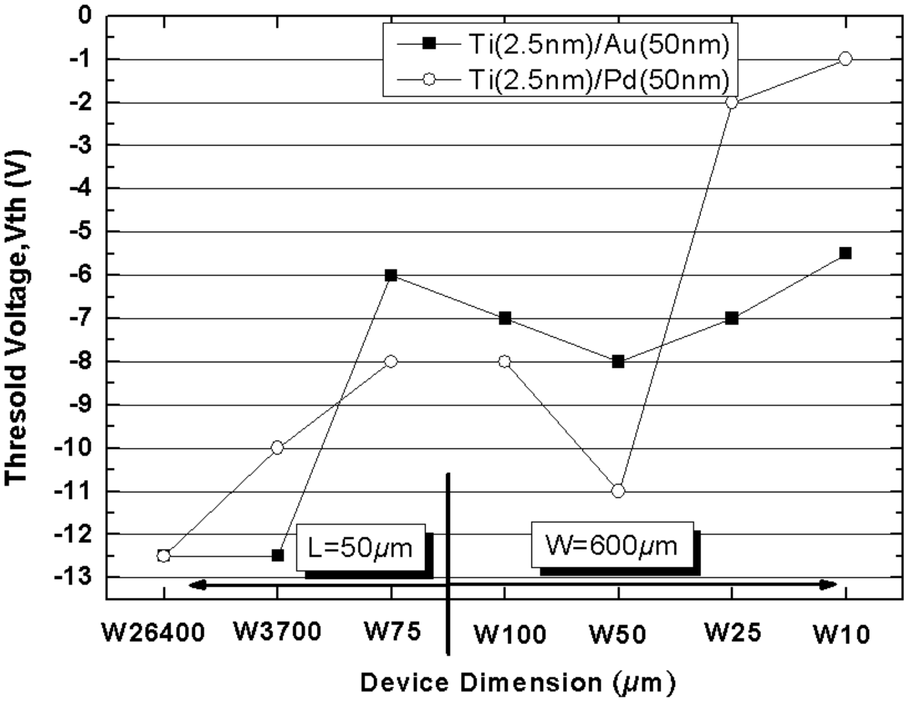


Figure 3-14 Electrical characteristics with different S/D metal (a) the mobility, (b) threshold voltage.

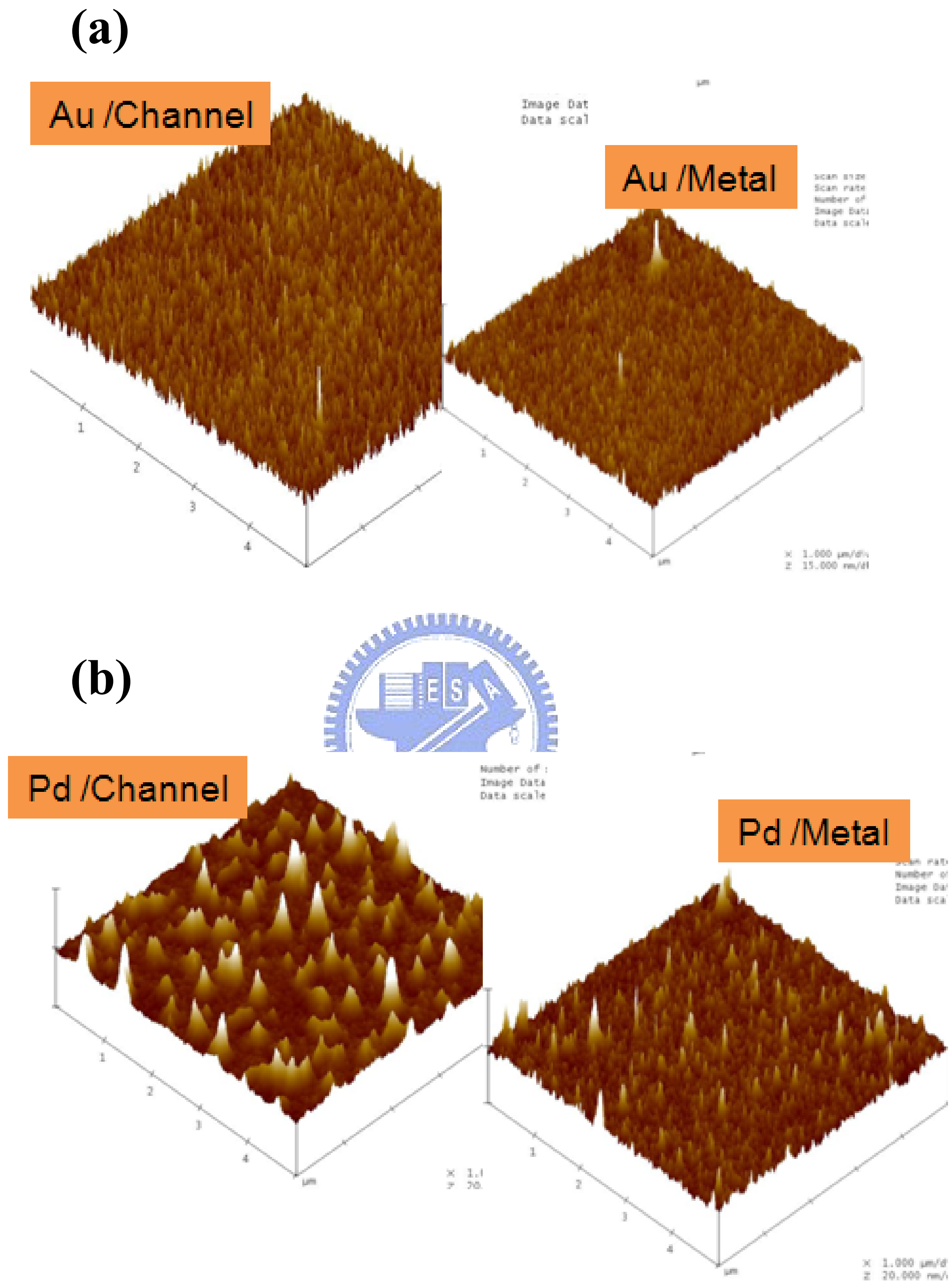


Figure 3-15 AFM: 3D analysis, P3HT film on channel and metal, respectively, (a) Au, (b) Pd.

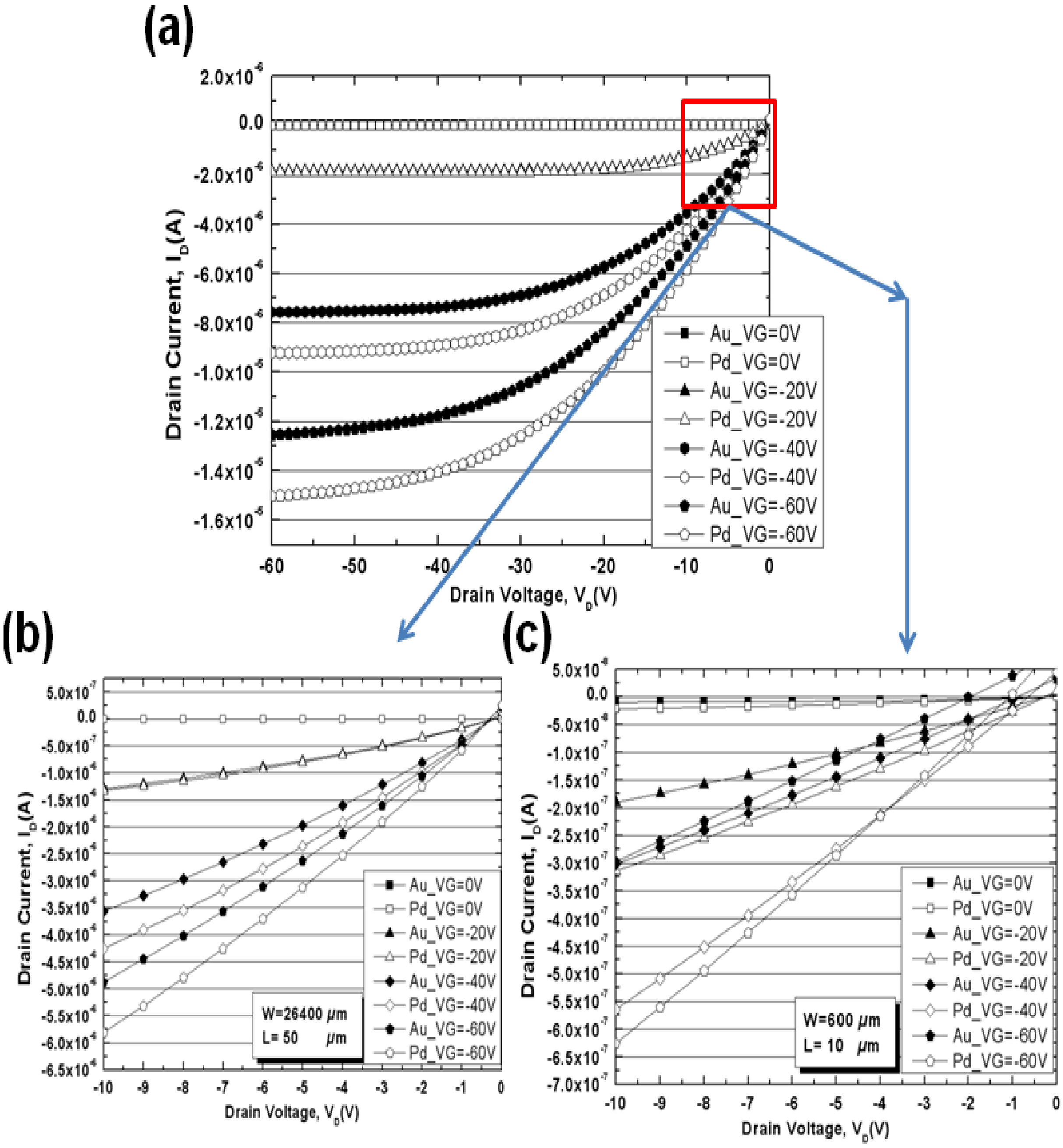


Figure 3-16 The output characteristic result compared with Au and Pd metal. (a) W/L=26400/50, (b) W/L=600/10 in linear region.

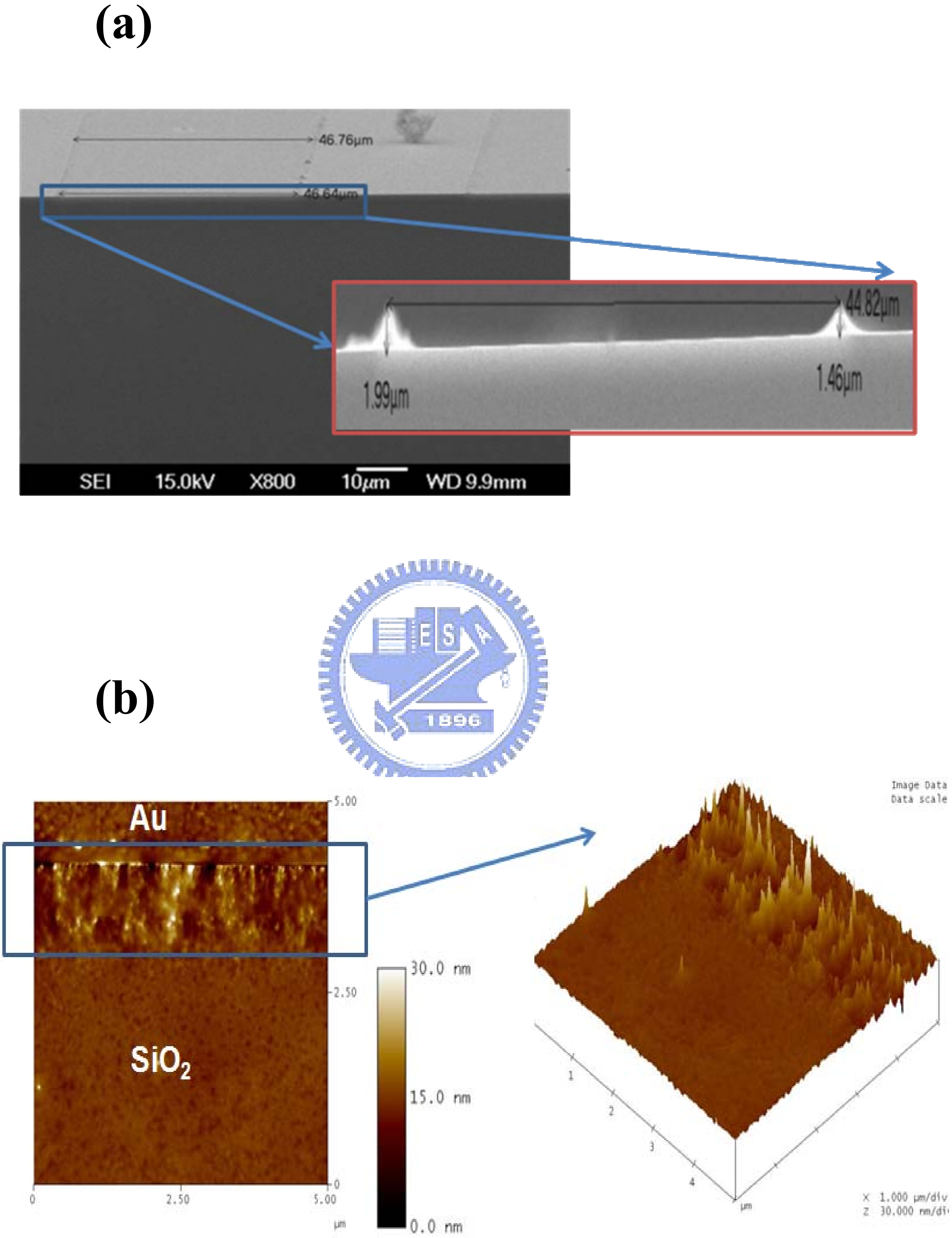


Figure 3-17 High hill-like regions between metal and organic interface. (a) SEM, (b)

AFM.

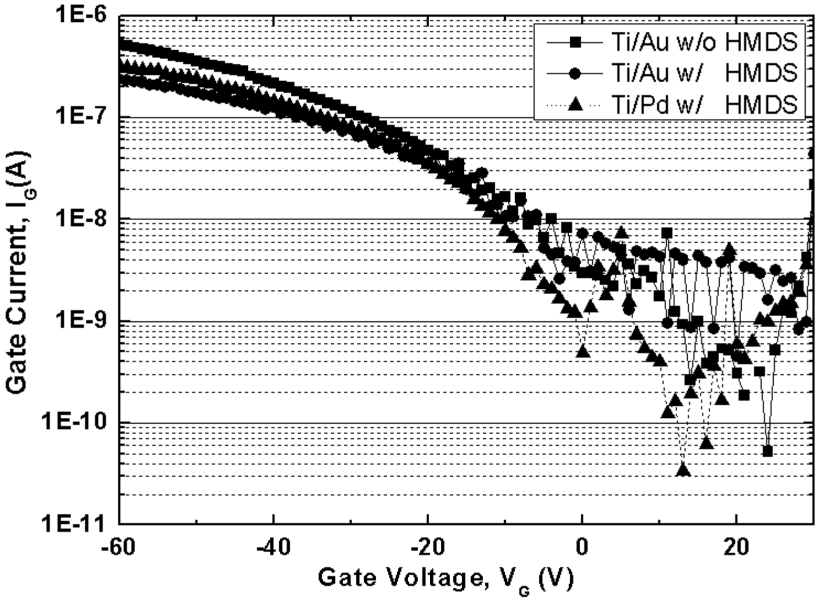


Figure 3-18 Gate leakage current characteristics of typical device with different metal materials.

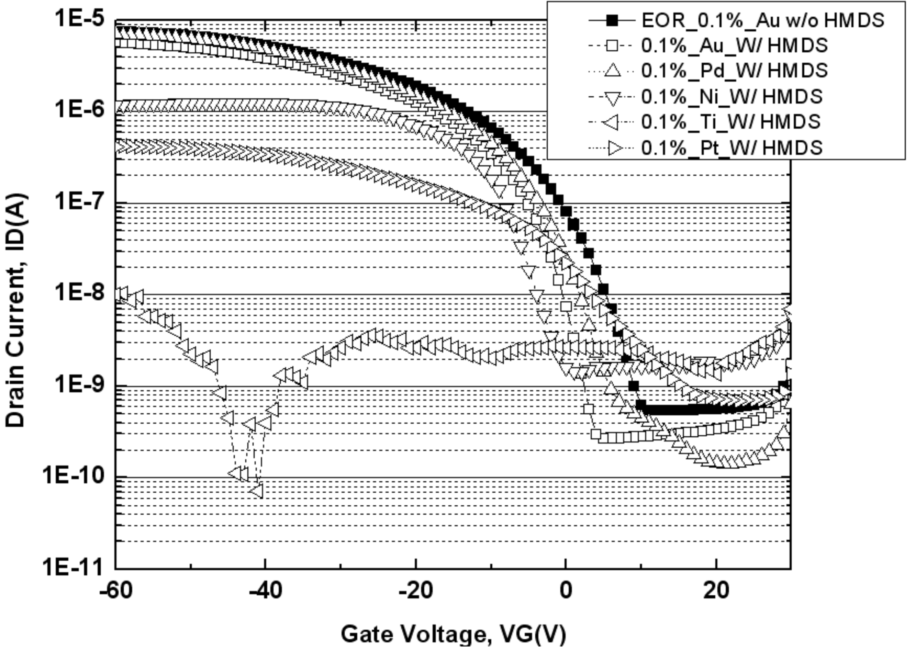


Figure 3-19 The transfer characteristics of P3HT FETs with different metal materials.

Chapter Four

Stability characterization of P3HT OTFT

4.1 Introduction and motivation

Indeed, the transistor made by P3HT is interesting and useful. However, its poor environmental stability is notorious **[4.1]**, which results degradation in performance such as the mobility, on-off ratio and positive shifting threshold voltage. This problem is caused by influence of humidity and oxygen. Recent studies for environmental stability illustrate that H_2O can diffuse into the grain boundaries and crystal. It can trap charges generated in the channel. Also the oxygen in the film will not contribute to form the accumulation of holes, but increase the barrier height. Others environmental influence such as temperature and light can affect the life time of conjugated polymers.

There are some groups to study how storage time extends without affecting the P3HT properties. Majewski and Song **[4.2]** reported that the immersion of devices in the polar solvent, acetone and water, could protect the thin film and not to be attack by oxygen without affecting the performance. This is final goal apparently.

Using annealing process could drive out impurities, remnant solvent and also could strong molecular interaction and then improve the mobility. But how to control the temperature is an art, due to that too high or low annealing temperature will be affecting the organic material property. So an appropriated temperature is major role, in addition to annealing time and environments are also needed.

Stability could be predicted by stress method. So many stress methods such as dynamics voltage or constant voltage as a function of time are used **[4.3]**.

In this work, we study self life time of P3HT conjugated polymer in transistor and use annealing process to see how it improves the mobility. In addition to utilizes constant voltage to stress the transistor and to try to understand its root-cause.

4.2 Storage life time

Notice that good measured results should be similar with origin data, no matter how long it stored [**4.4**]. However, it is inevitable that organic life time can be affected by temperature, humidity, light, and oxygen. There are so many different factors of environmental influences.

This measurement of shelf life time is exhibited on transistors. Three samples are randomly chosen from a box, which stored in the atmosphere in clean room. They are separated from sunlight and stored for one, two, and three months, respectively until 97/06/05. The measured data will be compared with those transistors that measured in the beginning. All experiments are performed using optimized transistor terms, which are P3HT transistor in chloroform with 0.1 weight percentage (refer to chapter 2 and 3).

Figure 4-1 shows the transfer characteristics of PFETs after fabrication and samples stored for one, two, three months later. Three samples exhibit a passable result and characteristics totally. Obviously, there is a situation, both on and off current are degraded. This result can be supported and summarized in **Table 4-1**. Every sample in our study has degradation for on-off ratio. In the C0329 sample, the on-off ratio degraded from 1.54×10^4 to 8.30×10^2. Most degradation of breadth is in C0411 sample, and its on-off ratio degrades down to 9.96×10^1. This on-off ratio is decreased seriously after fabricated two months, but the mobility is still high enough for this sample. For on current degradation, no matter what sample, all on current degraded slightly. It is a change obviously for off current. Basically, on-off ratio is decreased, which responsible for off current. Corresponding to the off current of random sample increased on an average of 16%. Arrows in the figure can point out. As shown in **Fig.4-2**, delta value is calculated by using stored value to divide by fresh one. There is a trend to indicate that it is degradation with all related electrical parameters, like mobility, drain current and on-off ratio when the device stored a few month. According to this result, we suspect that the influence of H_2O, O_2 and O_3 should be top three **[4.5] [4.6] [4.7]**.

Those suspect compounds include basic elemental, oxygen. Due to organic property is similar with atmosphere such as hydrocarbon, and it combine with organic material easily. After combination onto surface, oxygen elemental could diffuse into the bulk and even into conducting channel by grain boundary and dislocation. As existence in the film, they will capture charges generated in the channel because of its polar nature and electronegativity. It attracted the electrons from P3HT molecules and generates holes. Clearly, attracted electrons could make a scattering of carrier, which could drive transporting carrier away from a straighten path so that lower the number of transporting carrier. Also the mobility decreases with impurity concentration increasing because of enhanced impurity scattering. This can explain in the decrease of on current. About the off current, due to electron-hole pair is generated. The oxygen attract electron toward itself in a covalent bond, as remind, the hole will be generated and formed as “extra” carriers, relatively. For off current, it treats as exceed carrier, and hard to deplete, which signify that it needs higher vertical electron field to induce electron forming depletion region. In other words, semiconducting devices are hard to be turn off, this is a reason why off current increases. Additionally, we found out an interesting situation. The result of self life time could be enhanced (stressed) by utilizing long duration curing time as shown in **figure 4-3**. There is an obviously trend that a change of on and off current is similar with self life time one.

Of course, this affected by oxygen can be reduced by using the encapsulation process, which acts as a capping layer to protect the organic material surface. This application can avoid a contact with atmosphere, but notice that the material of encapsulation cannot destroy and harm P3HT conjugated polymer when it uses.

4.3 Heat treatment: Annealing process

4.3.1 Fabrication Process

Basically, all the process procedure is the same as section 3.2.1 in chapter 3. There are only two differences, which are annealing temperature and time. The annealing temperature will be involved in a range from 50 degree to 250 degree, interseptal 50. After the P3HT solutions in chloroform spun onto SiO_2 as a device and it will be annealing for 30 minutes and 3 hours, respectively. Notice that all annealing process is in a furnace with N2 flow rate of 10 liter/min. it is based on upper experiment, oxygen elemental is an affect for P3HT organic material, and we will not use O_2 flow or without any gas when annealing process.

4.3.2 Result and discuss

The motivation is that use different annealing temperature and time difference to see which one will affect electrical parameter mostly. This process of vary annealing temperature could caused a change in on and off current. **Figure 4-4** shows the transfer characteristics of PFETs with annealing process and set the temperature in a range, 50℃~250℃. Obviously, on and off current come to the same things, both decrease with annealing temperature increasing, especially in a state of off current. As annealing temperature at 50℃, the electrical result resembles in a un-anneal measured data, and seems not help for ordering. We suspect that annealing at this temperature could not reach glass transition temperature so that there is no phase segregate, thermally diffusion and free volume changing. Origin bond could unchange [**4.8**]. Besides, in the bulk of P3HT could involve some thermally-activated defects.

Annealing above the glass transition temperature can help the polymer in reducing the free volume and residual solvent so that will be an impact in ordering or agglomerating films. Off current measured by electrical result starts a change as temperature increase. During 100~200℃, off current drops theatrically, and the device turn on approximately at Vg=0, which means the threshold voltage also shifts to negative. Finally, annealing above 250℃, whole device turn-on curve shifts to more negative. The threshold voltage obtained by calculated is -18V. it is increased by 58.3%, compared with annealing at 150℃. Indeed, there is a trend that threshold voltage is shifting to more negative. In addition to on current, it notoriously decreases. The mobility of PFETs with annealing process including vary annealing temperature as shown in **figure 4-5**, which indicates that there is no change in mobility before annealing at 200℃. Annealing temperature over 250℃ and it drops.

AFM result shows that the image statistics and section analysis indicate a rough surface morphology from 0.872nm to 1.604nm, as shown in **Fig. 4-6.** From this point of view, higher roughness, we suspect that the retention of solvent will be evaporated by thermal heating, ran off to the surface film into environment and remained some pits, whereas whole thin film has already became a solid state. The possible of reflow is not distinctness. Annealing process impacts the P3HT films thus leading to a change. In other words, the film could be reorganized toward to more disordering with annealing temperature increasing. Further, phase results observe that annealing at 150℃ could preserve a structure of nano-fibrillar, and it pave on the surface of SiO_2 randomly. In contract, annealing at 250℃ can observe the nano-rod only. It illustrates that annealing at this high temperature could cause a nano-fibrillar becoming to nano-rod. Notice that we still have any clearness, for instance, this result could cause by itself or removal solvent. Meanwhile, thermal heating induces a diffusion of molecules.

Here, we have found out an interesting thing in annealing temperature at 250℃. According to H. Yang report [**4.9**], the melting temperature, measured by DSC, is 216℃. Notionally, at this temperature, re-crystallite behavior is possible. So it may improve and modify the degree of order of P3HT film, compact packing and obtain a higher mobility. On the other hand, we obtained an anti-trend for on current. Even we don`t obtain that result for 200℃. Of course, the exact measurement of the equilibrium melting point is complex, due to it involves kinetic factor, structural factors and impure environment of crystallites [**4.10**]. And the crystallite is related with molecule structure, which is related with interchain of interaction. This result is worth a think.

Further study for annealing, we exam the device at 180℃ for 30 minutes and 3 hour. **Figure 4-7** displays the transfer characteristics of PFETs with annealing process for 30min and 3hr, compared with un-anneal samples. In **figure 4-7(a)**, the sample of un-anneal to anneal means that it has ever measured under atmosphere environment and then undergoes annealing process. Other samples, starting with fresh-, are undergoing a serious of continue process without interrupting to measure. As you can see, there is no obvious change for on current and this process procedure improves off current only. Large off current obtained for sample of un-anneal, un-anneal to anneal and fresh anneal 3hr, compared with annealing process for 30 min. Longer annealing (3hr) will be affected the electrical parameter, we suspect that the appropriate time of annealing could reduce defects, which could formed by grain boundary and oxygen elemental. In **Fig. 4-7(b)** shows electrical parameter of On-off ratio, comparison of w/o and w/ annealing process. The device with annealing process can obtain higher one order of magnitude, compared with un-anneal one.

Unfortunately, the mobility is not to be improved by annealing process, as shown in **Fig. 4-8 (a)**. It is not a result what we expected. This result agrees with Wang et al. [**4.11**]. They are measured in nitrogen environment and obtained a decrease of mobility and on/off ratio increases. This interpretation is that even measurement in nitrogen could obtain a data like that and still more measurement in the atmosphere environment. Maybe this result is not considerable. In **Fig 4-8 (b)**, the threshold voltage with annealing is shifted to more negative, which sustains at a level of -15V, but the un-anneal sample is approaching to 0V.

We utilize ESCA and Auger depth analysis to try to figure out these related elementals. From ESCA data, in **Fig.4-9**, oxygen concentration for 30min and 3hr reduce dramatically. Further, in **figure 4-10**, auger depth analysis tells a notoriously different between before and after annealing process. The sample without annealing process contains large percentage of oxygen in the surface and even near the conducting channel and the number almost reach to about hundred percent. But the sample with annealing process involves less and less oxygen percentage in the surface and near conducting channel. Those data indicate that annealing process can drive off the elemental oxygen powerfully and involved oxygen device obtain a poor performance. So oxygen in the films may act as a role of defect to trap carrier and increases scattering and acceptor-like so that it obtains a poor result. Notice that an unclear result for large off current in annealing for 3hr still not figures out, although oxygen concentration is less than annealing for 30min.

Figure 4-11 shows the output characteristics of typical device with un-annealing and annealing process for 30min. The entire performance with annealing process improves almost one order of magnitude at every gate biased. Still one curious result shows in gate leakage (circle). In **figure 4-12**, it suppresses gate leakage after annealing, but it is not understand what root-cause is. Additionally, **figure 4-13** shows an average value of annealing process. Obviously, annealing for 30 min is better than un-annealing and annealing for 3hr.

In this case, we realize that annealing process could drive off the most of oxygen and reduce off current. Next, we demonstrate that stored device, low molecule device and skip curing device how can be affected by annealing for off current. First, in **figure 4-14(a)**, in c0411 fresh sample obtained a transfer characteristic, stored after 2 months later, the performance is getting worse obviously, but off current could be improve by annealing process. In low molecule weight sample, we could obtain the same result. Likewise, annealing process could amend off current even it has stored for a while. The improvement is driving off the oxygen from the films, based on ECSA and Auger depth data we saw. Second, we tried to skip curing on hot plate, and then put it in furnace for annealing directly. The result from electrical analysis is that off current with skipping curing is not good as a sample go through fully process. The difference is about one half orders of magnitude. This can be observed by various device dimensions, as shown in figure **4-14(b)**.

4.4 Temperature dependence & constant voltage stress

4.4.1 Temperature dependence

Figure 4-15 illustrates the electrical characteristics obtained for un-annealing and annealing process. Both samples were fabricated and measured in air. The transfer characteristic with un-annealing sample shows a stable behavior as measured temperature increasing, compared with annealing sample. On current exhibits a change slightly and off current increases with measured temperature increasing, which indicted as arrow in figure. Comparison of annealing sample in **figure 4-15 (b)**, on current behavior is changing slightly, but off current shows an apparently change. This change is almost degrading for three orders of magnitude. Off current degrades from 10^{-12} (A) becoming to 10^{-9}(A). **Figure 4-16** responses this result. The electrical characteristic of on-off ratio with un-annealing exhibits an almost horizontal level with various device dimensions as measured temperature increase. Notice that on-off ratio is calculated by equation of drain current and each line is varying depends on its own dimension. The On-off ratio with annealing process is a high order initially. However, after the measured temperature increases, the device is affected and degraded dramatically, for instance, the lowest point is $3.57\text{x}10^{2}$ in W/L=600/10, the dropped range is very serious. The rest of electrical parameter is mobility and threshold voltage. In **figure 4-17**, from the observed data, there is on seriously change for both un-annealing and annealing process sample. They are sustained in a fixed level before 100℃ and the value is around $1\sim2\text{x}10^{-3}\text{cm}^{-2}/\text{V-s}$. When measured temperature increases to 150℃, there is a slightly degradation. Also, threshold voltage is shifting to more positive, after annealing process is especially apparent**,** as shown in **Fig. 4-18**. Basically, un-annealing sample can sustain around 0V, but it is not ideal for annealing sample from -15V at 25℃ to 12.5V at 150℃.

It is based on the result of auger depth analysis previously, we suspect that due to undergoing annealing process, the oxygen is driven off from the thin film so that there are less and less existence of oxygen concentration. The measurement environment is in air, the oxygen could diffuse from air into the film again by measured temperature. This starting from scratch and fill up suddenly could affect the performance mostly. In contrast, for un-annealing process sample, the concentration of oxygen has already existed for a certain numbers so that it is not change extremely.

4.4.2 Constant voltage stress

This is a test for stability to see how the device performances change. It could have a meaning in reliability. The voltage of three terminals, V_G, V_D, and V_S, in **figure 4-19** top insert, will be change and keep in a voltage level as function of time goes by. The device dimension of W/L=600/10 is chosen for test; due to short channel length can enhance the result quickly. Of course, we will measure each of basic performance such as the transfer and output characteristics before and after stress for making sure the device work.

In **figure 4-19 (a)**, in the beginning, three terminals will be applied a zero voltage biased, meaning ground. The measured drain voltage is very close to 10^{-13}~10^{-14} amps. For this value, we don`t think that the lowest value is right and it may a noise of this machine because the value of 10^{-12}~10^{-13} (A) is open-short measurement. This confirms that there is no current flow when all terminals are grounded. Second, source and drain terminal are grounded, only gate terminal is applied -20V biased. The drain current keeps in 10^{-8} level. After stress around 10^3 S, the drain current is degraded slightly and we observe the gate current increases slightly in **figure 4-20 (a)**. Third, V_D=-60V and source and gate electrode are grounded. This time, we have a surprised result. The drain current is approaching to turn on with stress time increasing, compared with **figure 4-19(b)** and the gate current is not increasing, as shown in **Fig.4-20(b)**. Horizontal field could forces the carrier to transport and form a conducting path, because we also measure the source current, similar with drain current. Forth, we try to decrease and suppress this leakage (current) by formed a vertical field (V_G=10). Unfortunately, the outcome (red) is not expected. It still has the same situation. Fifth, we "pull" source terminal up to the same level like drain terminal (V_S=V_D=-60V), and gate terminal is keeping at 10V. We can observe that this leakage is reducing successfully and gate current is not change, in **Fig.4-20(c)**. Finally, gate electrode is grounded and remind source and drain biased at -60V. The drain current sustains in a fixed level. The device is leaking to gate current, due to gate current is increasing in **Fig.4-20(d)**. According to step from third to sixth, it seems horizontal field has a stronger effect then vertical field. But the different between gate biased and source/drain biased is six times and the drain current is 10^{-8} (A) initially at step two so that we cannot judge.

Next, we utilize some sample to undergo annealing process. Due to annealing can improve structure ordering, morphology and free volume such as interaction of intermolecular (please refer to section 4.3).

Figure 4-21 shows constant voltage stress versus time measurement of comparison of before and after annealing. In sample with annealing process can suppress drain leakage in the beginning, although it still has drain leakage with stress time increasing. It is biased a voltage at drain for -60V and drain current suppress around two orders of magnitude. When stress time increase, there is about one order of magnitude in average suppress. The sample with annealing for 3hr obtained the same result, but it became worse than 30 min one with stress time increasing, which are shown in **figure 4-21 (b)**. Still its performance is better than un-annealing sample. In addition, we set the chunk temperature to 150℃ when stress the sample. The performance has the same situation with un-annealing.

We suspect that electron can travel through source and drain by the defect in the film, which could form by high free volume, remnant solvent and elemental oxygen. After annealing process, those are being driven off the film and also improve the interaction of intermolecular. But the real root-cause is undergoing.

4.5 Summary

A.) Self life time is really a problem for P3HT organic material. It seems the performance will be degraded at each minutes. The suspect reason is oxygen in the thin film. Oxygen, due to electronegativity can cause accept like.

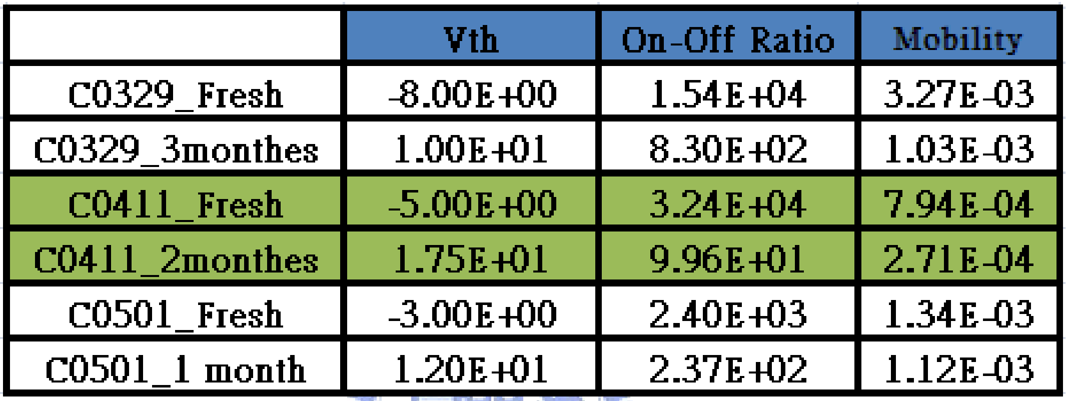
B.) Using annealing process can drive off the impurity such as the embedded oxygen and improve off current and suppress gate current. Even the stored device and low MW obtain the same result. This result can be supported by auger depth analysis and ESCA data. The optimized annealing temperature and time in my research are 150℃ and 30min, respectively.

C.) The device skipping curing process may affect electrical characteristic.

D.) The variation of measured temperature will follow a problem of oxygen diffusion by thermal heat from chunk. This may affect the device with annealing, although the mobility is still stable. Besides, on-off ratio and threshold voltage.

E.) A basic constant voltage stress will be function to enhance a leakage between source and drain electrode as function of stress time. The worse case is by applying a V_D= -60V. This leakage cannot be suppressed by applying VG= 10V. The root-cause is still undergoing. We found out that the sample undergoing annealing could suppress that efficiently.

Table 4-1 Threshold value and On-off ratio value with samples stored one, two, three months later.



	Vth	On-Off Ratio	Mobility
C0329_Fresh	-8.00E+00	1.54E+04	3.27E-03
C0329_3monthes	1.00E+01	8.30E+02	1.03E-03
C0411_Fresh	-5.00E+00	3.24E+04	7.94E-04
C0411_2monthes	1.75E+01	9.96E+01	2.71E-04
C0501_Fresh	-3.00E+00	2.40E+03	1.34E-03
C0501_1 month	1.20E+01	2.37E+02	1.12E-03

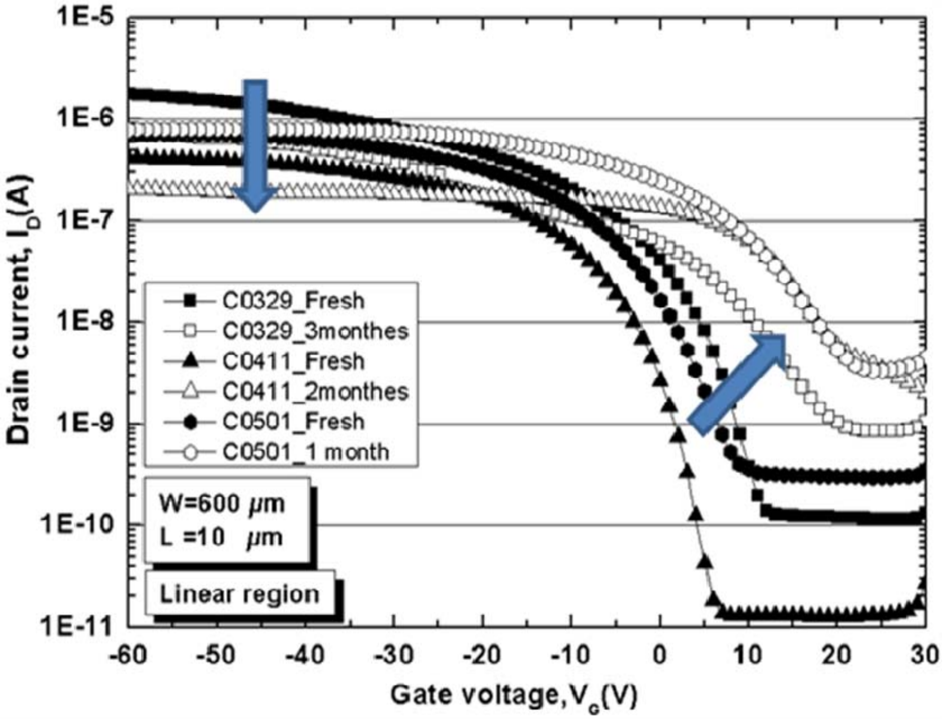


Figure 4-1 The transfer characteristics of PFETs after fabrication and samples stored one, two, three months later.

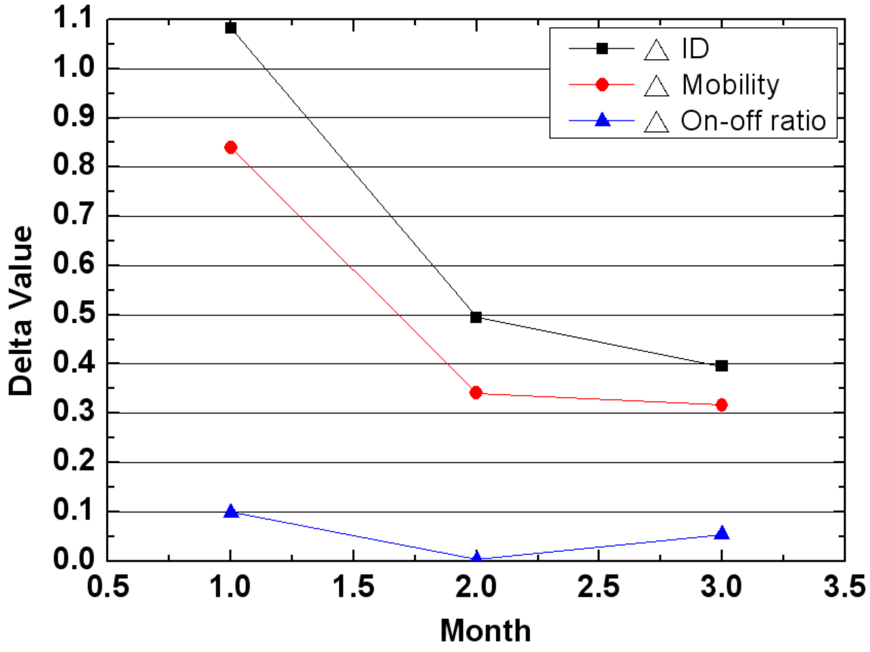


Figure 4-2 The variation of electrical parameters of PFETs after fabrication and samples stored one, two, three months later.

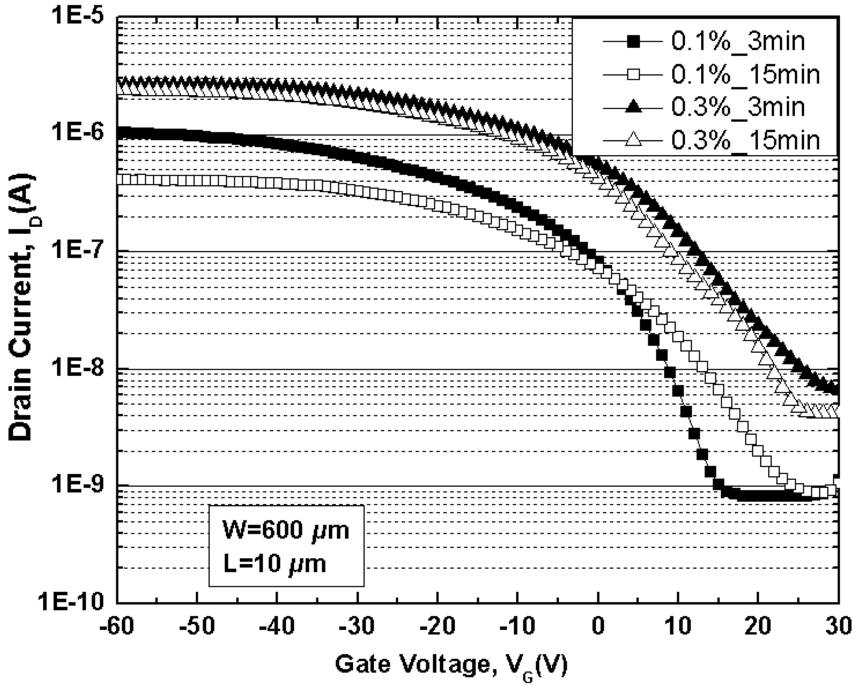


Figure 4-3 The variation of electrical parameters of PFETs after fabrication and samples stored one, two, three months later.

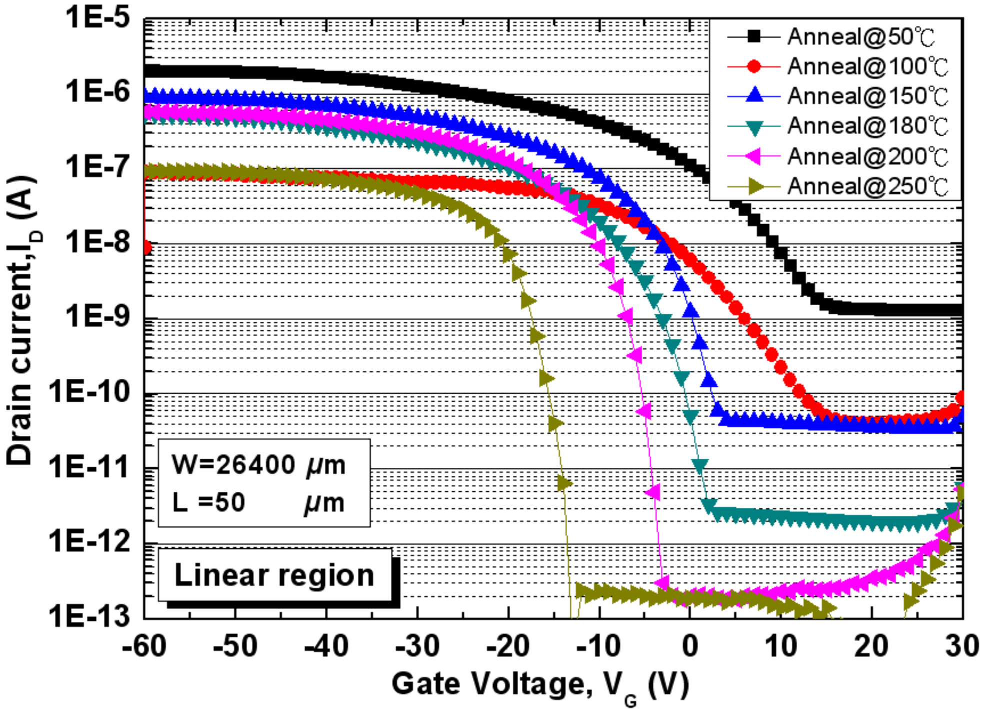


Figure 4-4 The transfer characteristics of PFETs with annealing process in a range from 50°C~250°C.

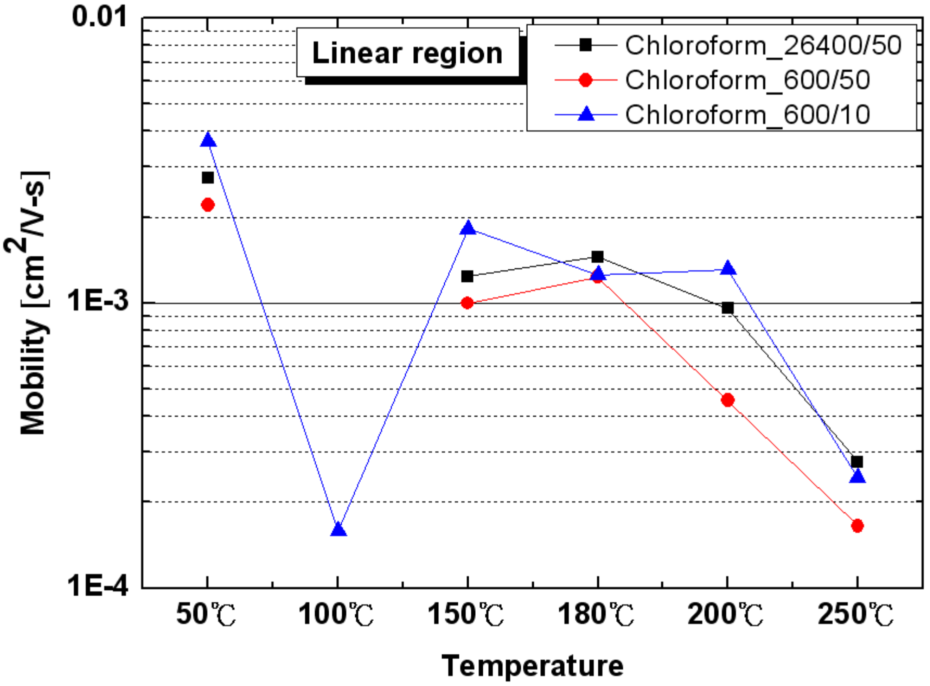
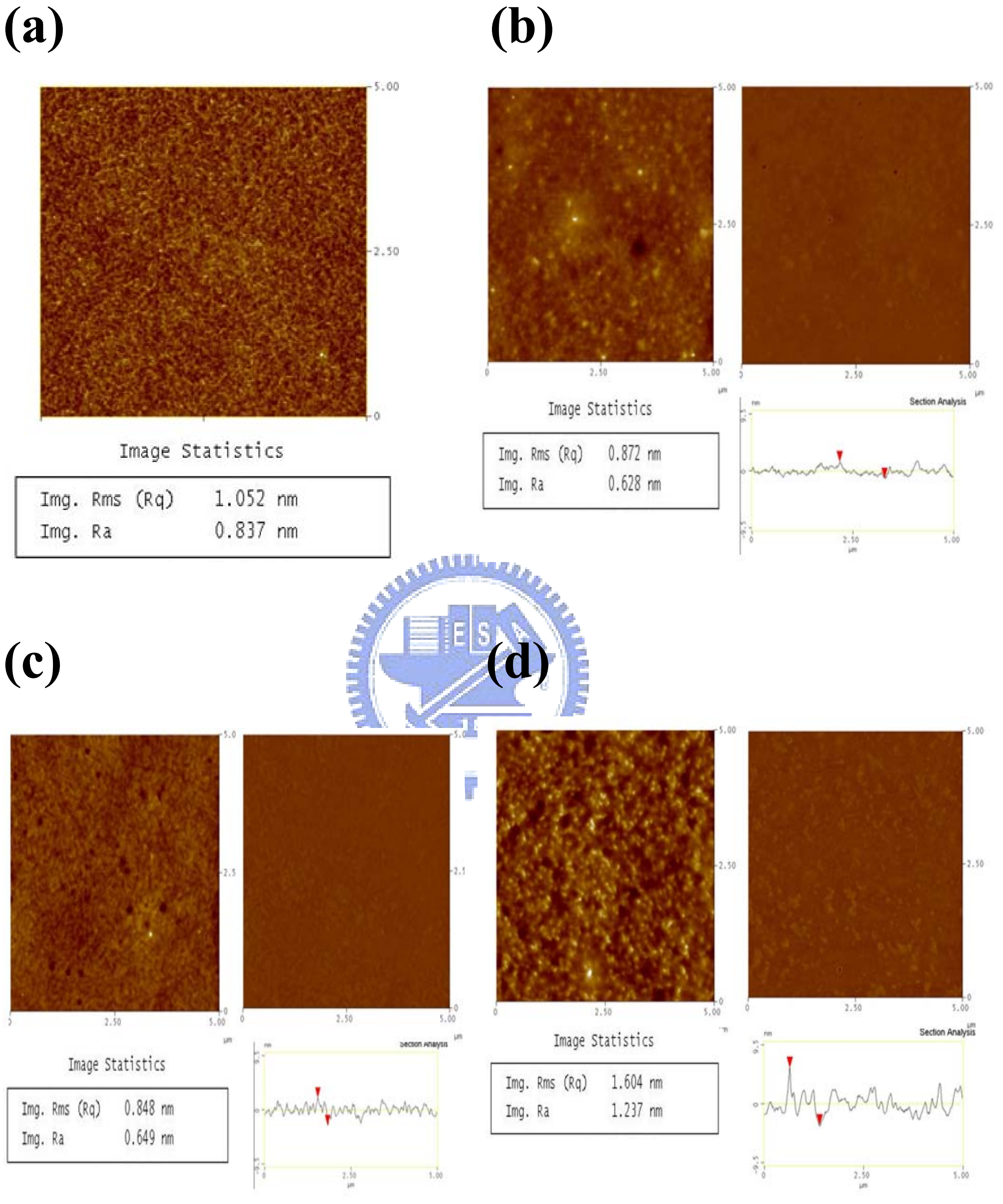


Figure 4-5 The mobility of PFETs with annealing process including vary annealing temperature.



(a) Image Statistics

Img. Rms (Rq) 1.052 nm
Img. Ra 0.837 nm

(b) Image Statistics

Img. Rms (Rq) 0.872 nm
Img. Ra 0.628 nm

(c) Image Statistics

Img. Rms (Rq) 0.848 nm
Img. Ra 0.649 nm

(d) Image Statistics

Img. Rms (Rq) 1.604 nm
Img. Ra 1.237 nm

Figure 4-6 AFM multi-analysis of morphology(top left), phase, image statistics and section curve (a) un-anneal, (b) annealing at 50 °C, (c) annealing at 150 °C, (d) annealing at 250 °C.

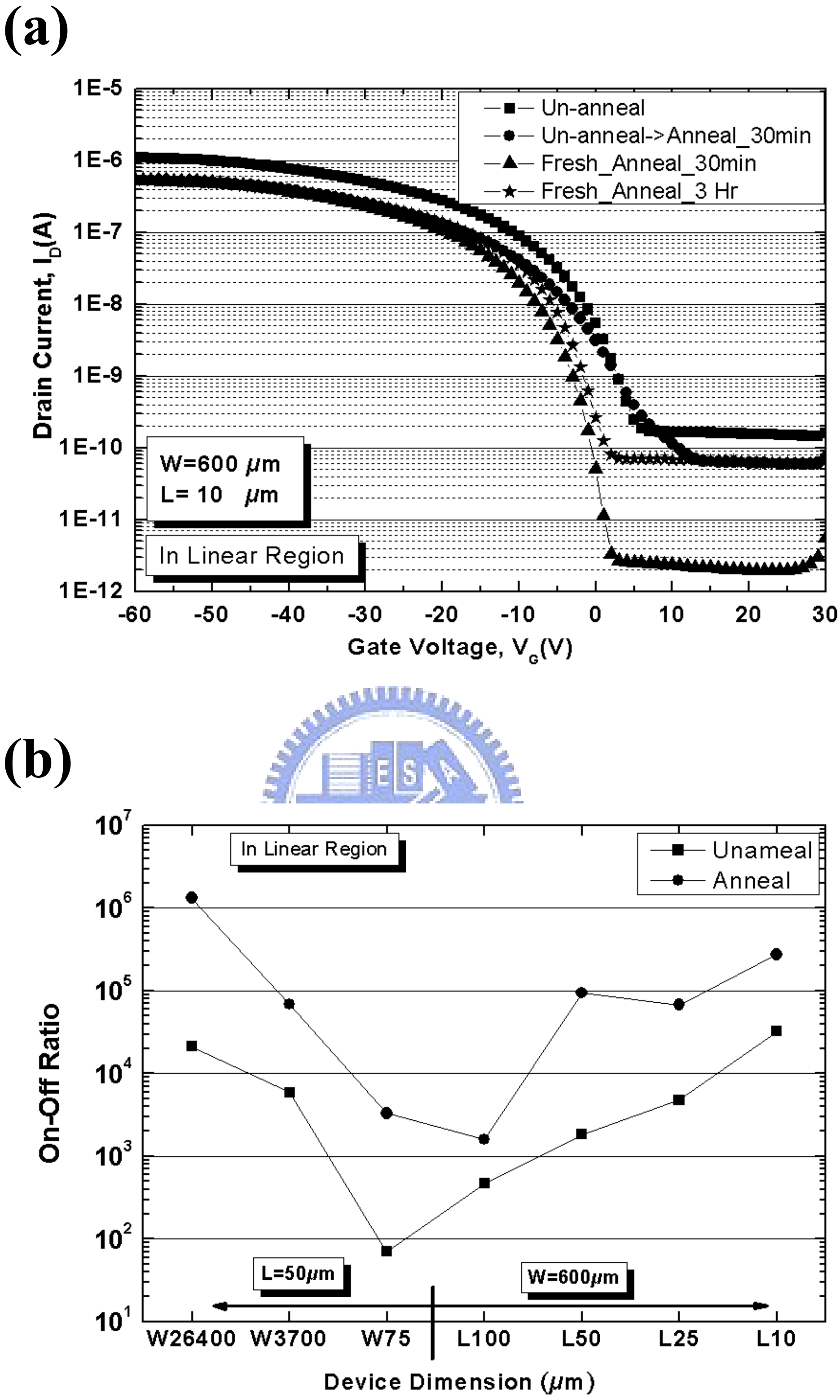


Figure 4-7 The transfer characteristics of PFETs after annealing process for 30min and 3hr (a), electrical parameter of On-off ratio, comparison of w/o and w/ annealing process

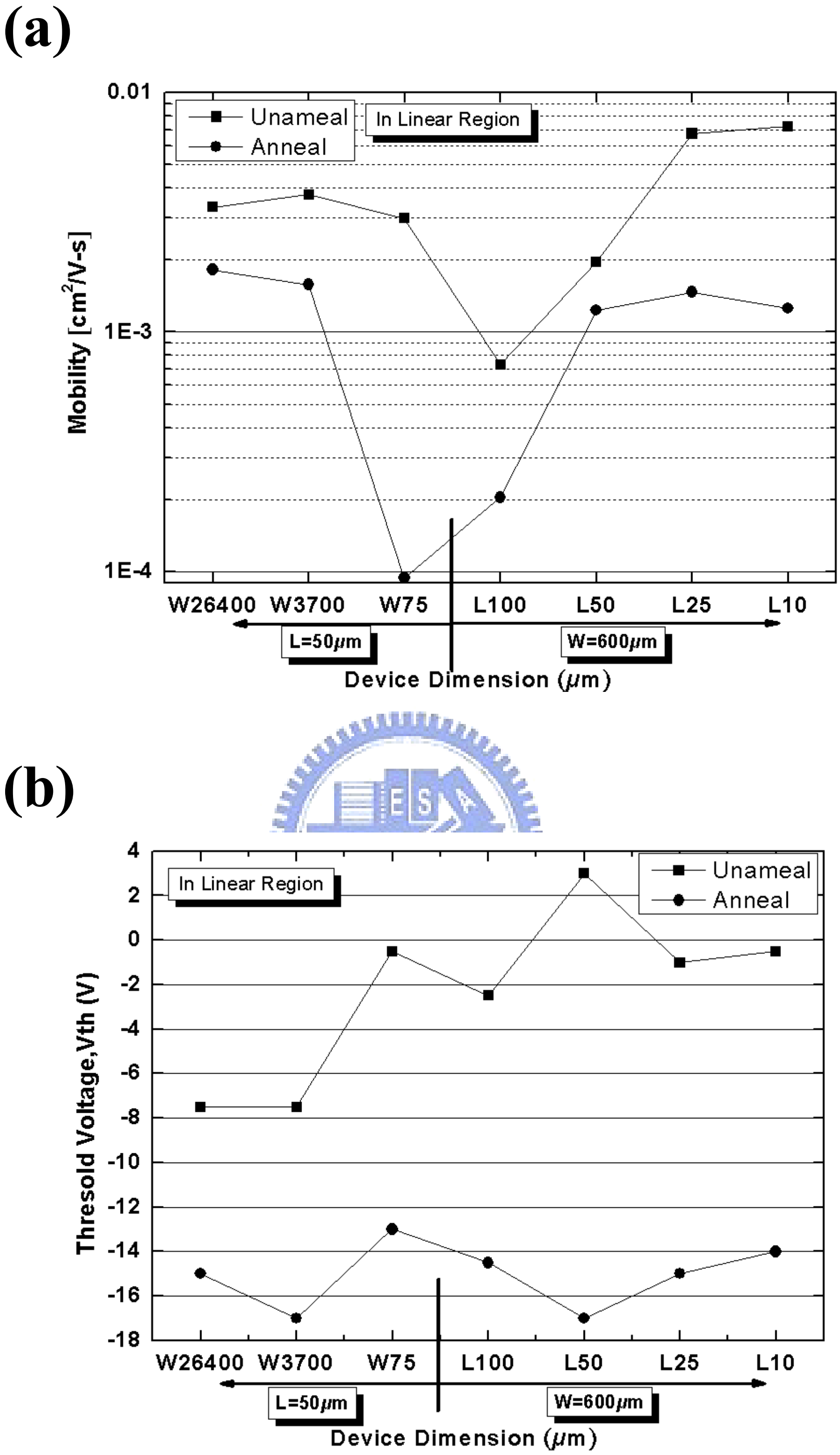


Figure 4-8 The mobility of PFETs compared with before and after annealing process for 30min (a), electrical parameter of Vth, comparison of before and after annealing process (b).

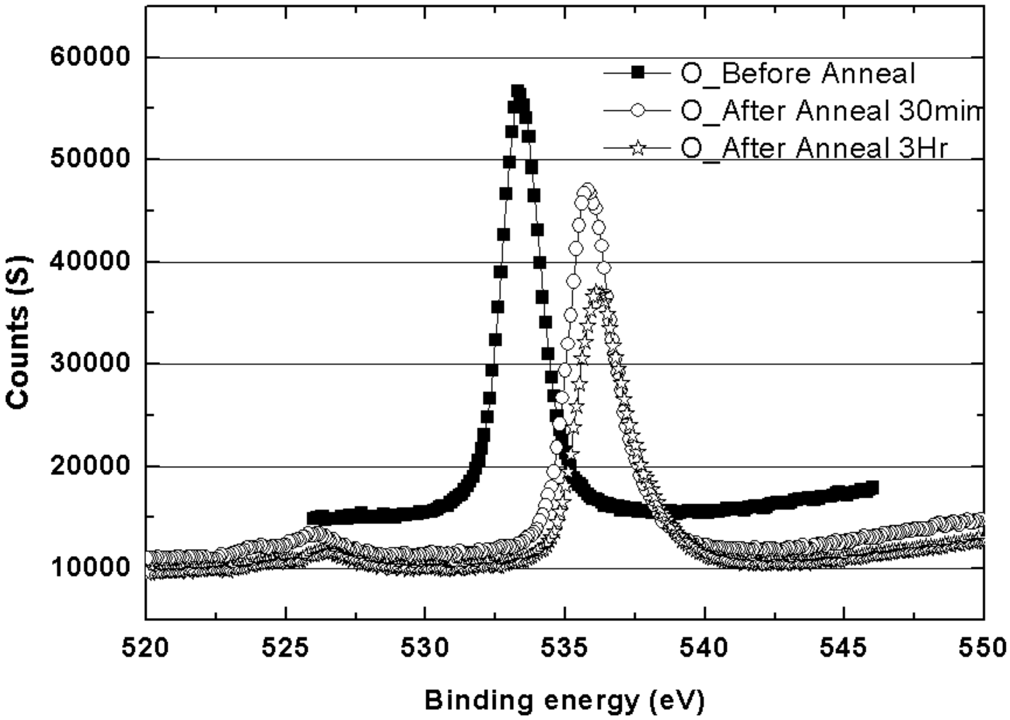


Figure 4-9 ESCA of PFETs compared with before and after annealing process for 30min and 3hr.

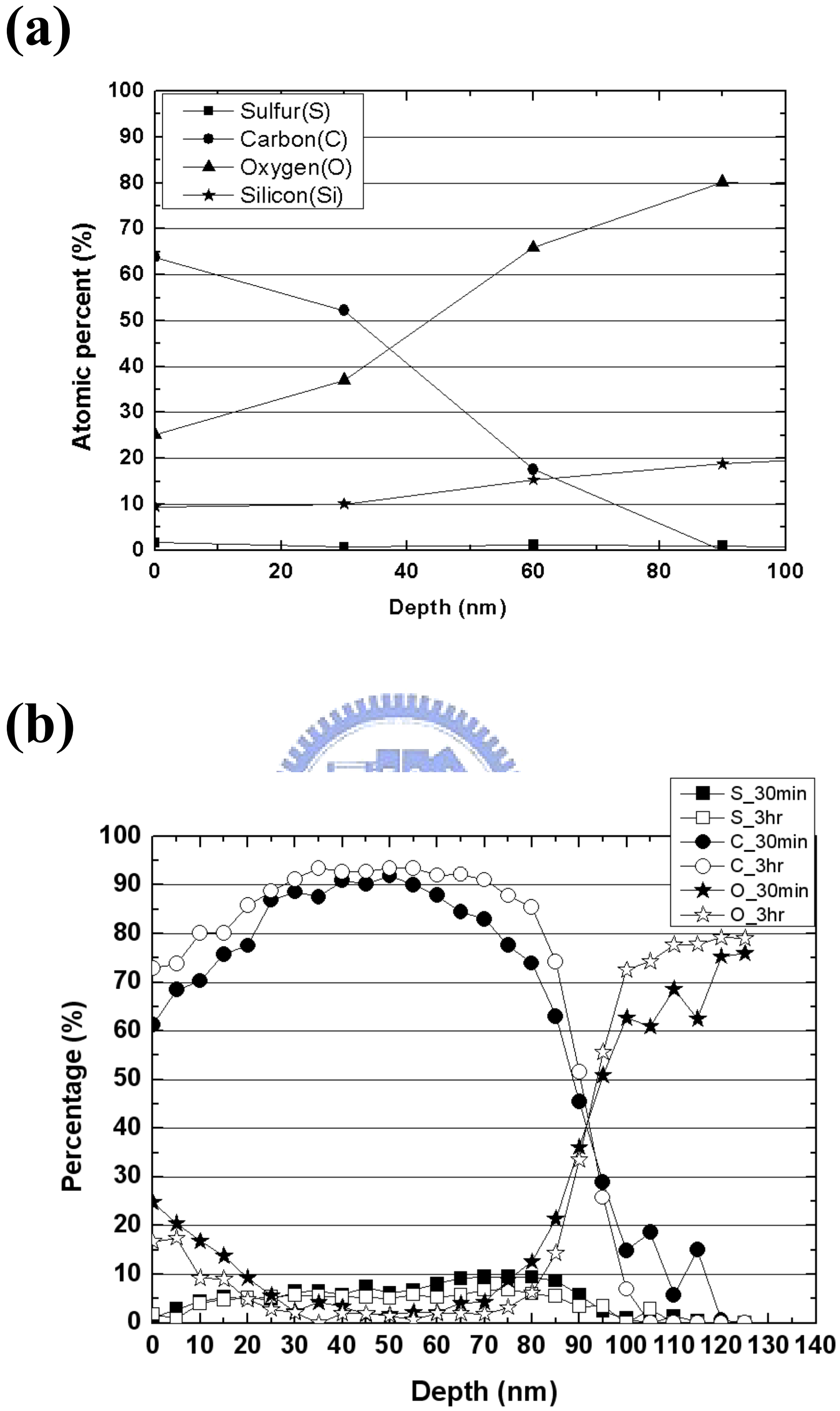


Figure 4-10 Auger depth analysis of PFETs compared with before annealing (a) and after annealing process for 30min and 3hr (b).

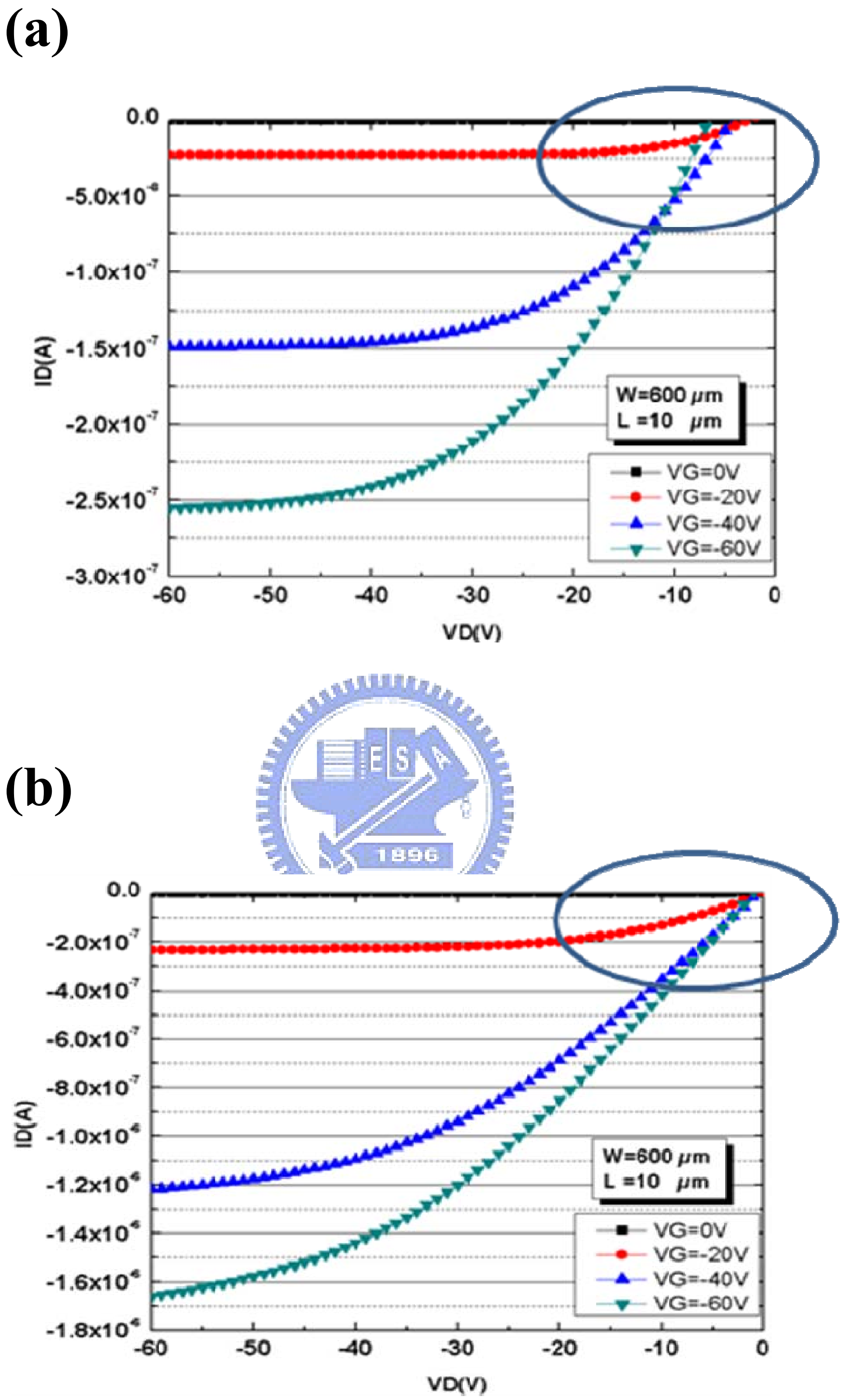


Figure 4-11 The output characteristics of typical device, (a) before anneal, (b) after anneal for 30min.

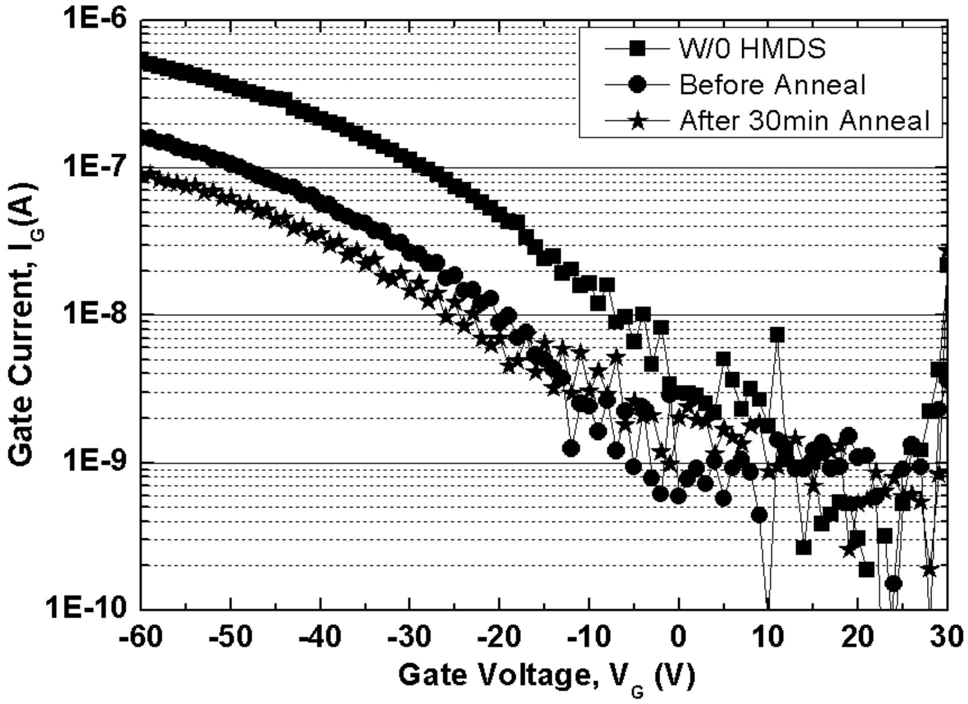


Figure 4-12 Gate leakage current characteristics of typical device with before anneal, and after anneal for 30min.

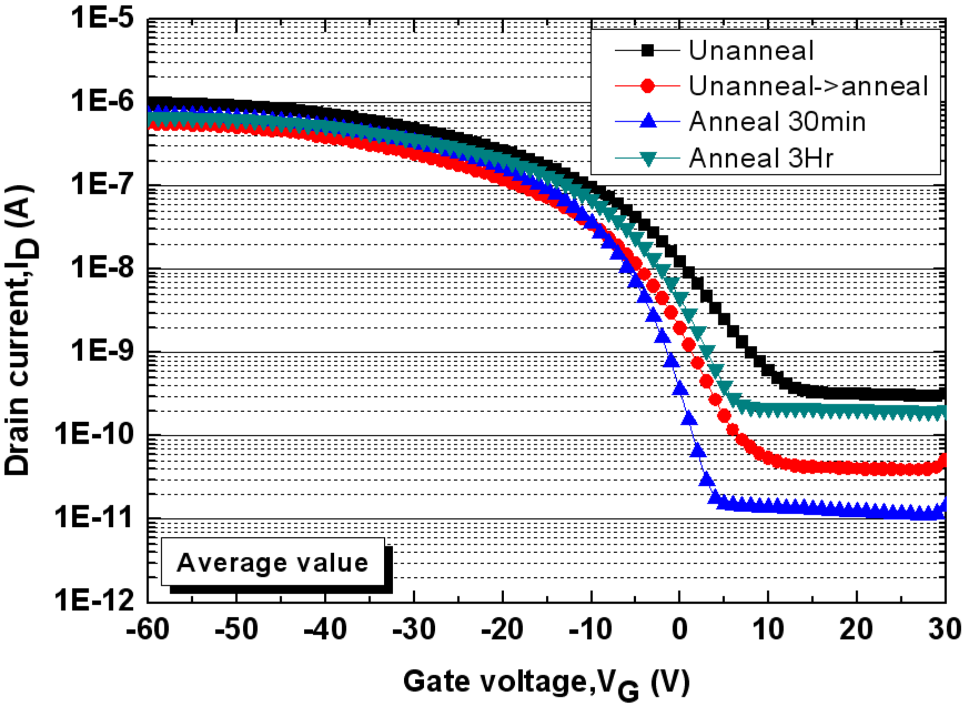


Figure 4-13 The transfer characteristics of typical device with an average of before anneal, and after anneal for 30min and 3 hr.

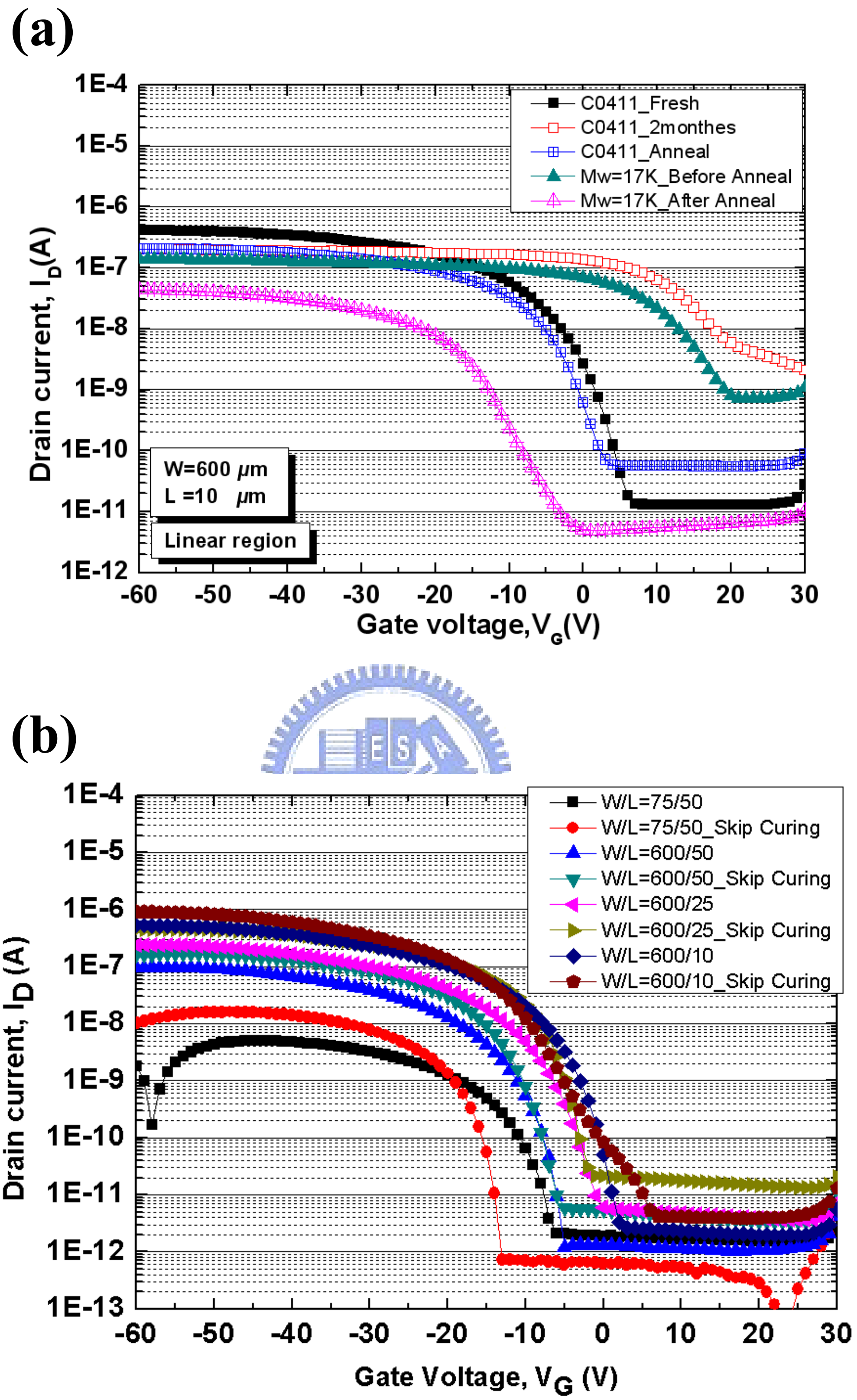


Figure 4-14 The output characteristics with stored device and low molecule comparison of before anneal and after anneal for 30min (a), skip curing and go anneal directly (b).

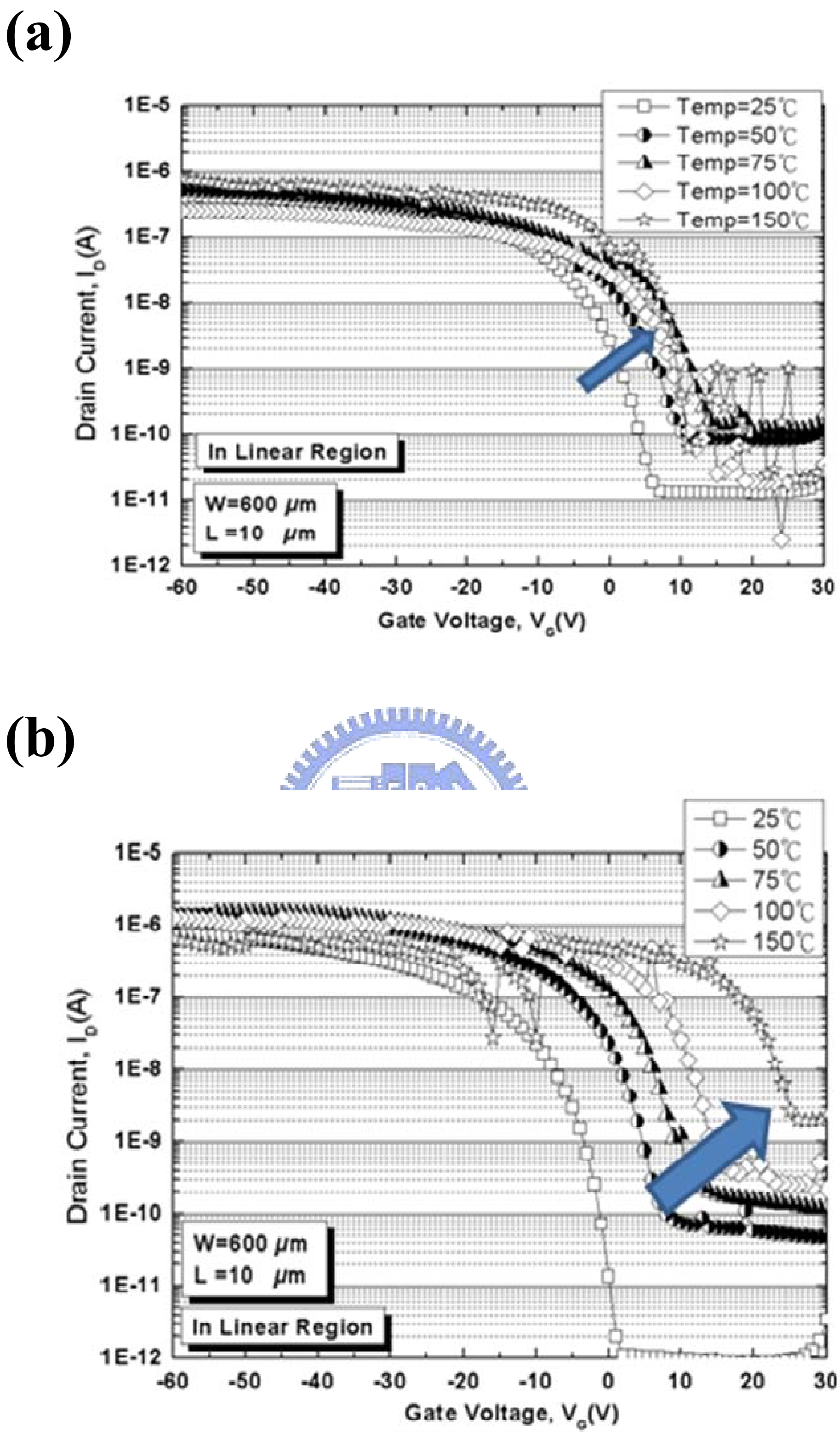


Figure 4-15 The transfer characteristics with various temperature measurements (a) before annealing, (b) after annealing.

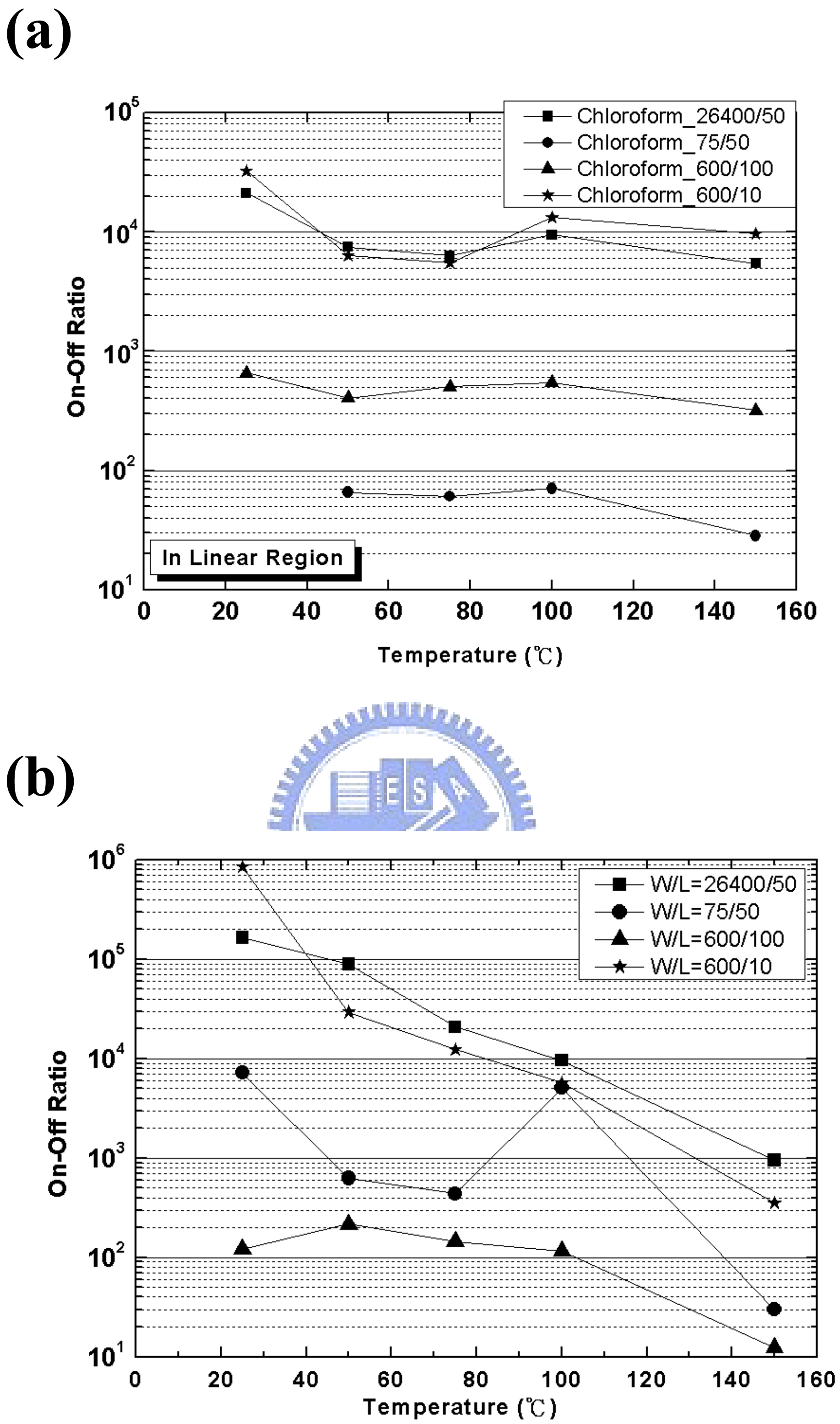


Figure 4-16 The electrical characteristics of on-off ratio versus various temperature measurements (a) before annealing, (b) after annealing.

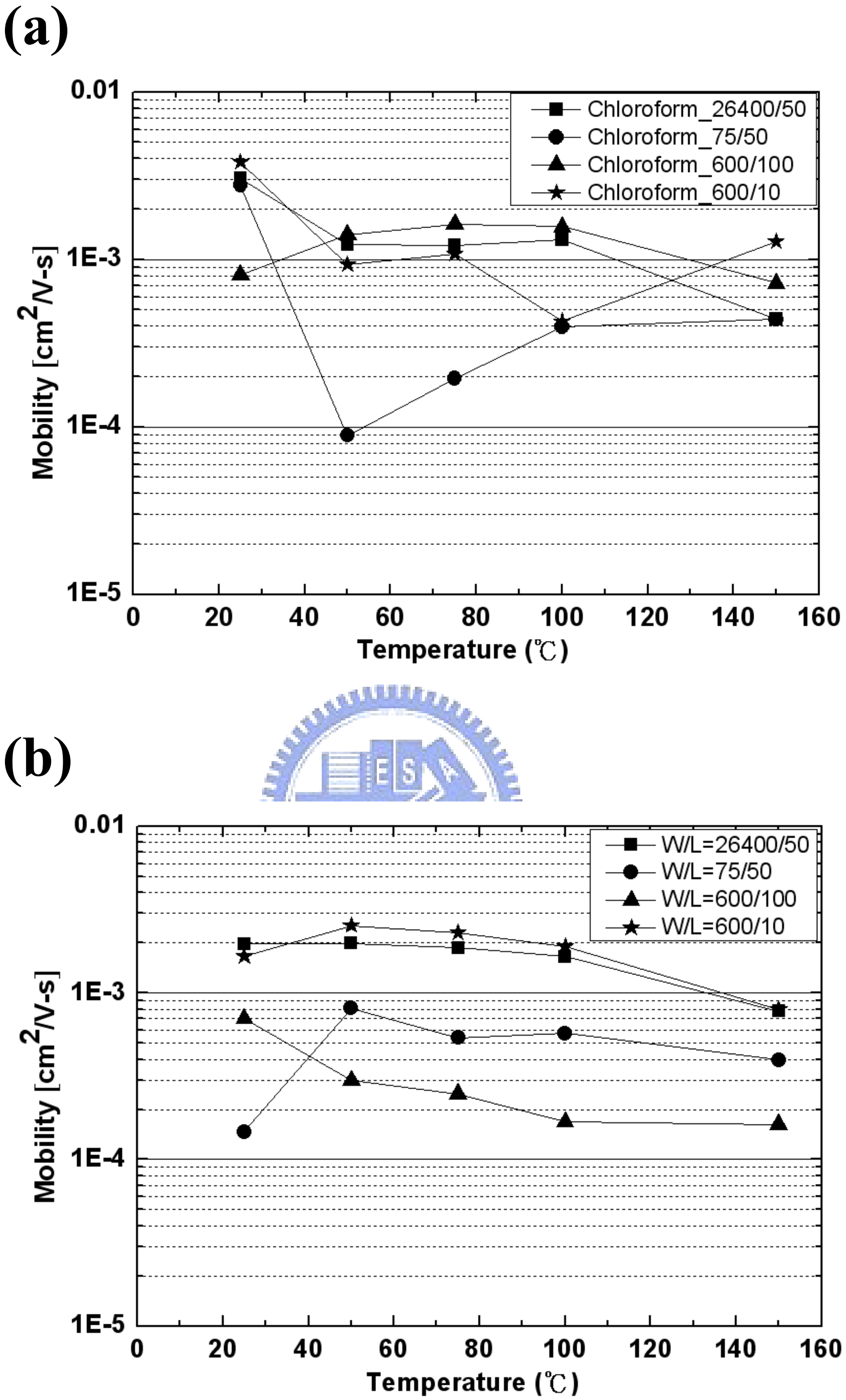


Figure 4-17 The electrical characteristics of mobility versus various temperature measurements (a) before annealing, (b) after annealing.

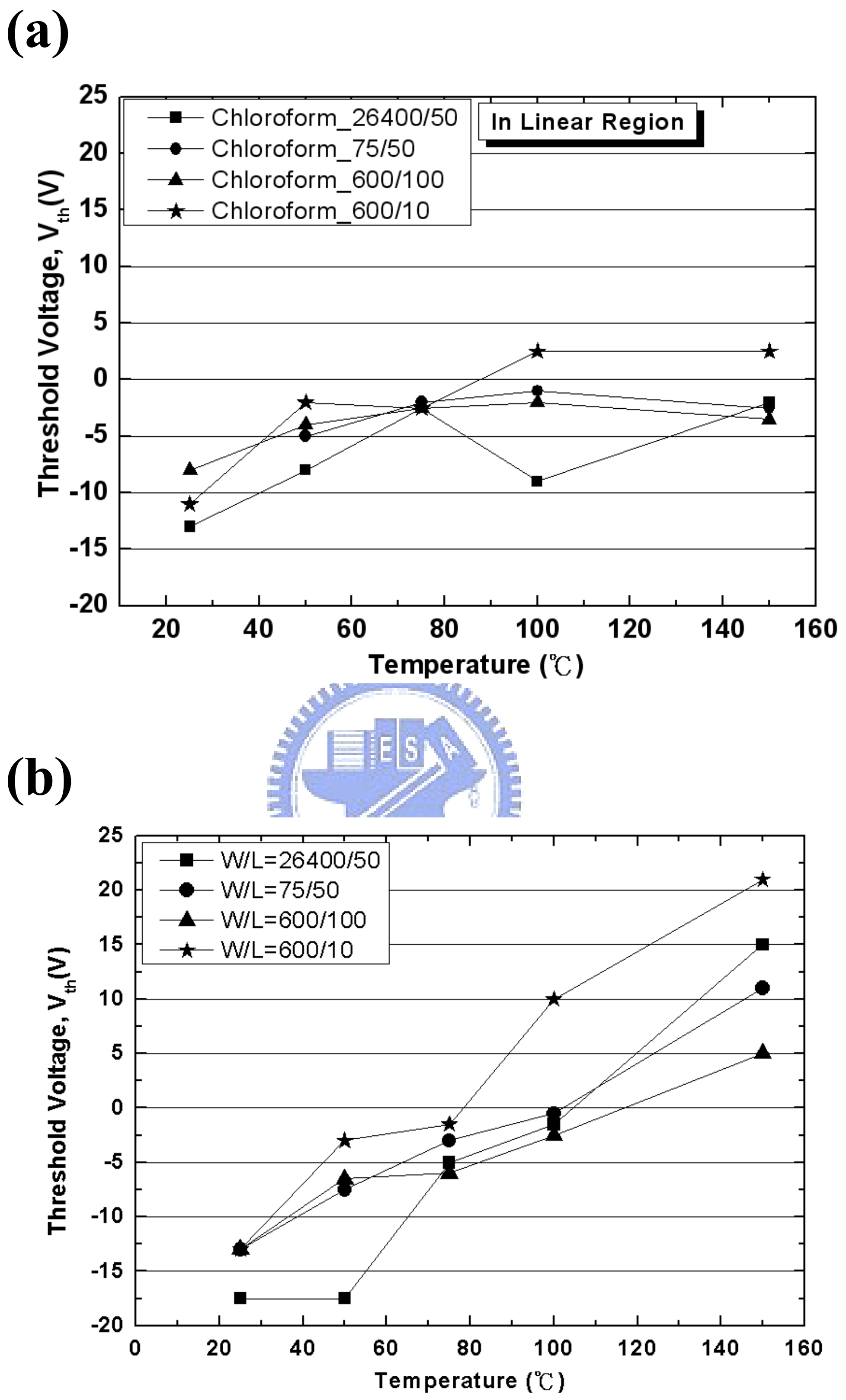


Figure 4-18 The electrical characteristics of Vth versus various temperature measurements (a) before annealing, (b) after annealing.

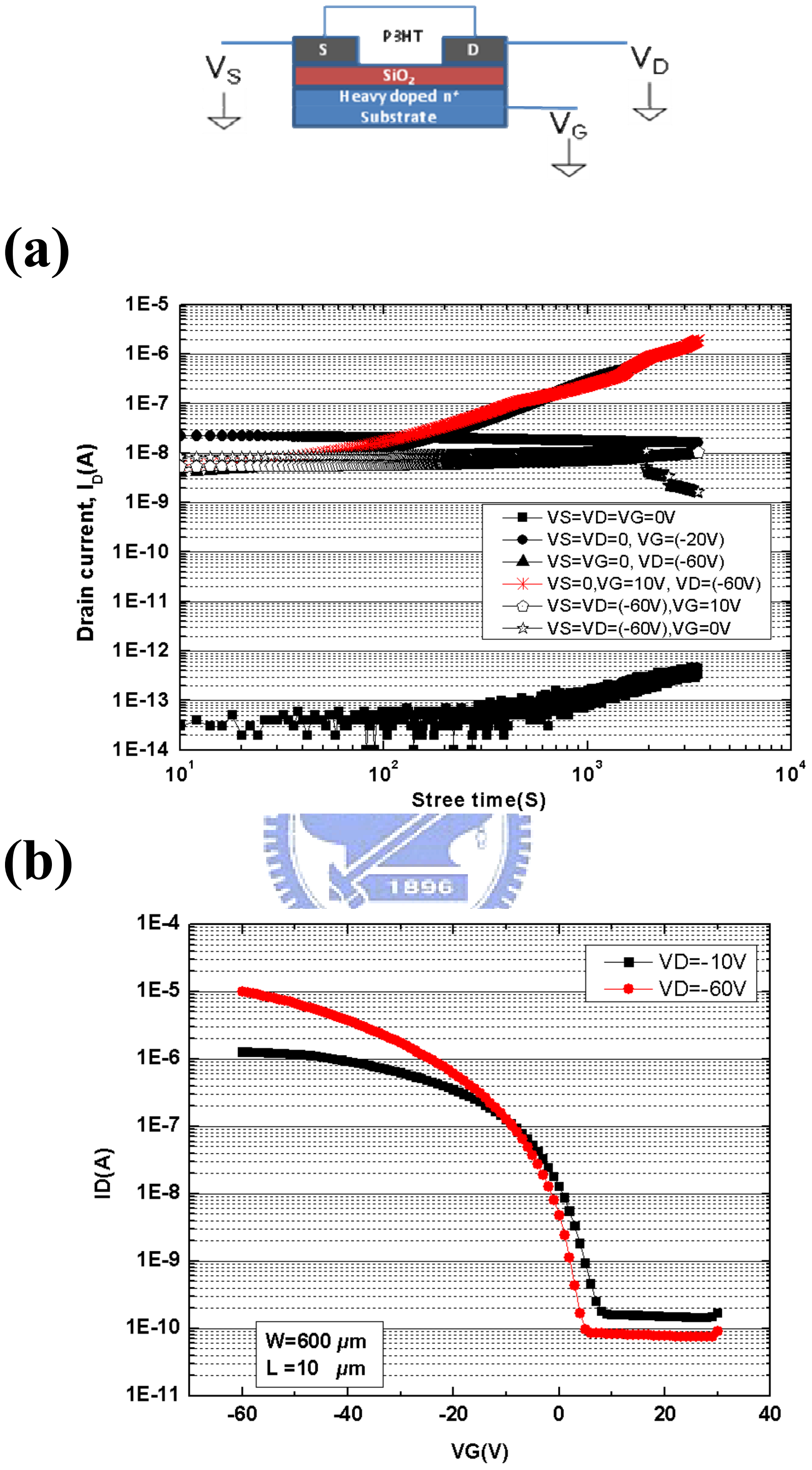


Figure 4-19 Constant voltage stress versus time measurement (a) varies terminal voltage stress, (b) the transfer characteristics. Top insert is varying terminal.

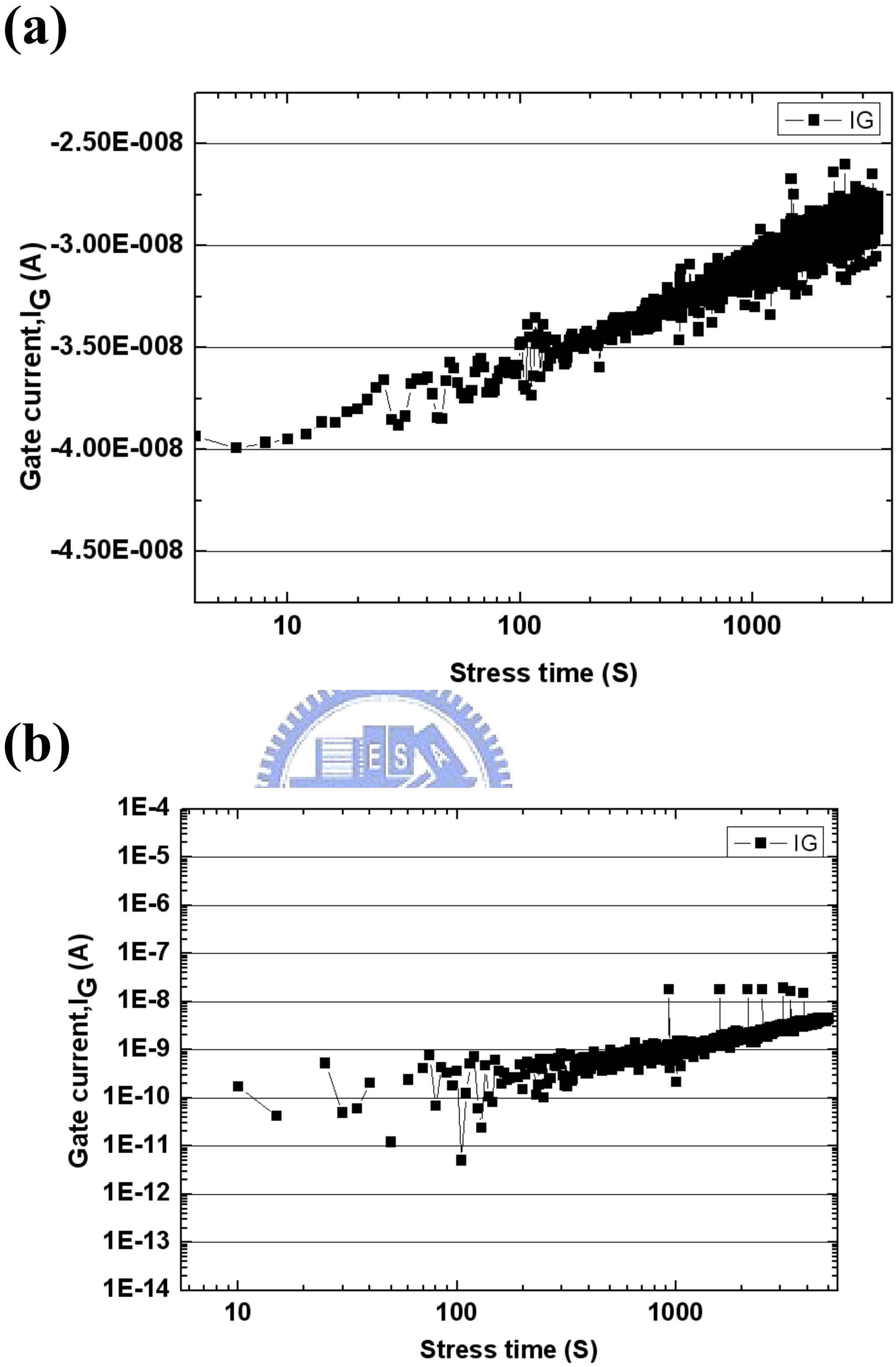
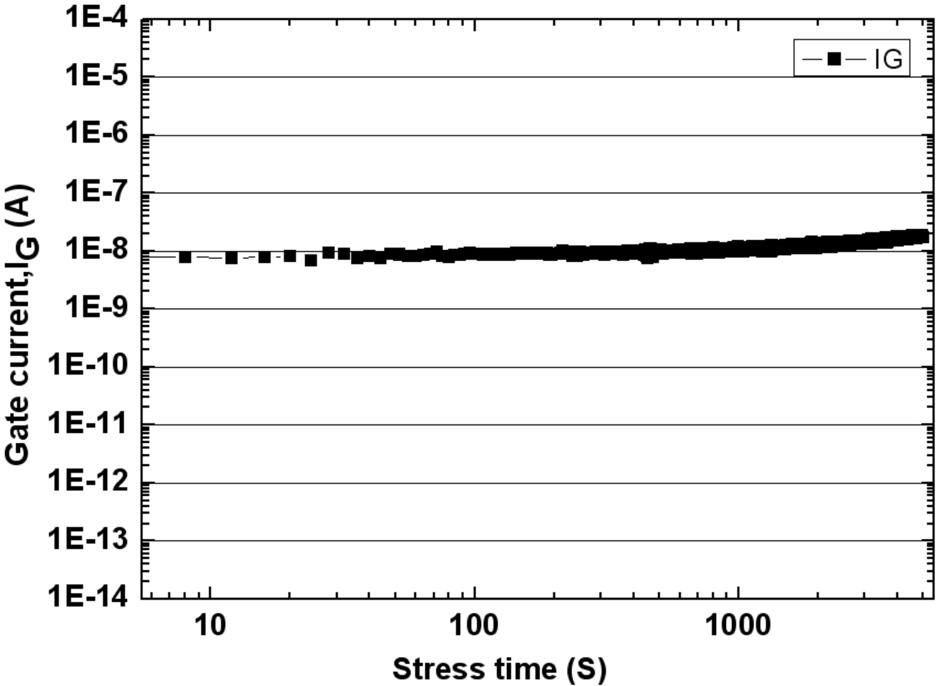


Figure 4-20 The gate current as function of stress time, (a) VG=-20V and VS=VD=0V, (b) VG=VS=0V and VD=-60V

(c)



(d)

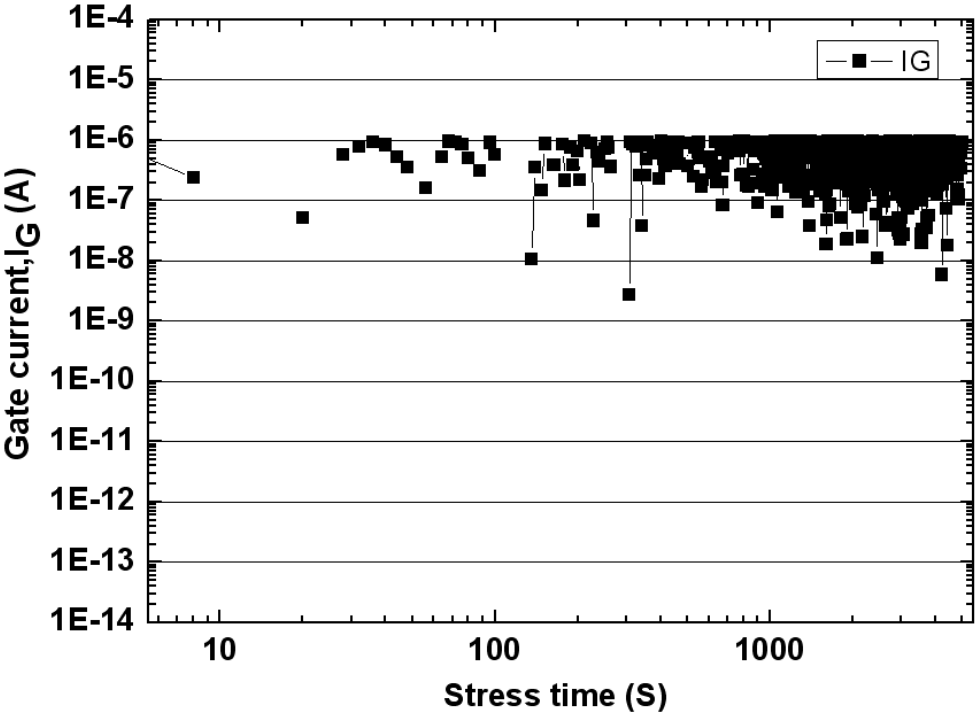


Figure 4-20 The gate current as function of stress time, (c) VG=10V and VS=VD= -60V, (d) VG=0V and VD=VS= -60V(continued).

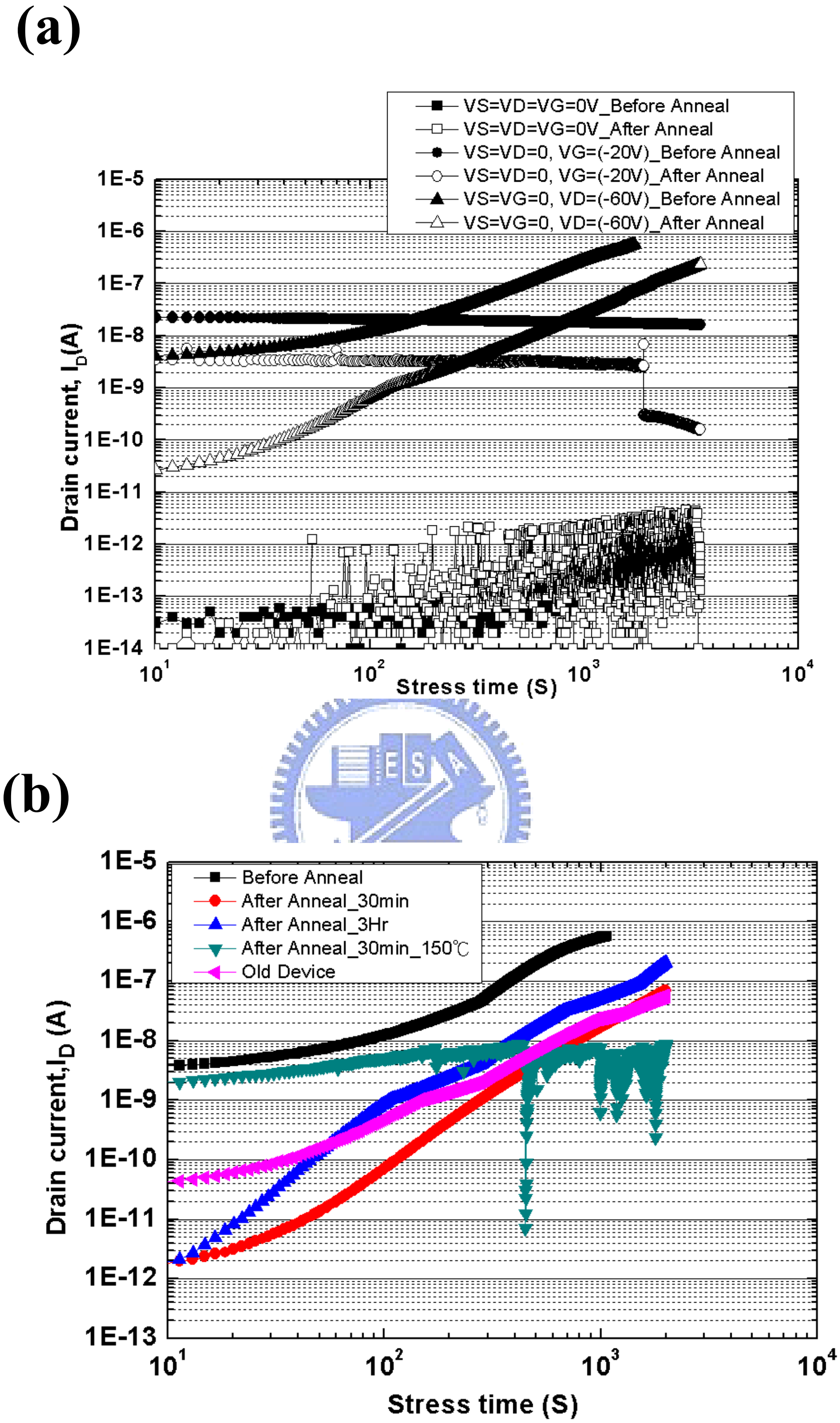


Figure 4-21 Constant voltage stress versus time measurement of comparison of before and after annealing (a) varies terminal voltage stress, (b) 30 min and 3hr.

Chapter Five

Conclusion and future work

5.1 Conclusion

In the beginning, all of related process procedure about P3HT material will be discussion in this thesis, starting from solution to stability characteristics. In chapter 2, to use xylene and chloroform as a solvent is studies to dissolve P3HT in solution. About solubility issue, we try to explain by elemental chemistry and organic chemistry and understand that in addition to supersaturation, the theory of like dissolve like is worth to think. The selection of solvent for solution process is very important. An appropriated solvent with slow evaporated rate and high boiling point is not only to dissolve the P3HT solute completely for less participation, but also provide an enough time for packing and ordering of backbone. As we previous discussion, P3HT solute dissolved in chloroform can obtain higher solubility then xylene solution, although boiling point of chloroform is not high. The solubility is a key for good performance in my experiment. On and off current increase with weight percentage increasing. On current is affected by nano-fibrillar and off current is related to the thickness of thin film.

Next, we used curing temperature at 150℃ on hot plate for 3 minutes can obtain a good performance, due to the impurity such as remnant solvent and oxygen could be driven off, which can be supported by auger electron and ESCA analysis. Besides, fabricated P3HT transistor with slow spin-speed can obtain a flat surface morphology and good performance, compared with high spin-speed rate.

After understanding an impact of basic process flow, we use the optimized condition in my study to discuss the influence of contact resistance. By using a thickness 2.5nm of Ti adhesion layer and deposited with gold metal material have a better performance, because of lowest injection barrier. Additionally, the devices treated with HMDS have an improvement. This surface treatment will modify the SiO_2 surface from hydrophobilic to hydrophilic and contact angle is changing from 54.8° to 90.3°. Due to NH molecule in HMDS will react with OH^- on SiO_2 surface, become a co-product and go away.

Last, in chapter 4, we observed that the device stored in air, the performance will degrade. This effect is caused by oxygen molecule, which will cause an acceptor-like result. Not only affect off current, act as trapping center, but also electron scattering, deviate from strengthen line. This “bad” result can be improved by annealing process with N_2 flow rate. Annealing at 180℃ for 30min, under this environment can suppress the interaction between oxygen and P3HT thin film. We use constant voltage stress to test P3HT transistor and discover that the worse case is by applying V_D= -60V only. The drain current increase with stress time increasing. We check the gate current out and it is not change. The same transistor will be tested a basic characteristics such as transfer char., find out off current will increase after stress, compared with un-annealing one. We suspect that this problem could be caused by oxygen diffusion.

5.2 Future work

In my experiment, there are so many indirect suspects and unknown answers. Further study is required to fully understand the contribution of improving gate leakage in chapter 3, and how the stress affect drain current…etc. We need to obtain clear evidence. Or modifications of P3HT intrinsic property or change material of active layer could exhibit better result.

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