國立交通大學

顯示科技研究所

碩士論文

紫外光保護層於有機薄膜電晶體之研究 Ultraviolet Light Protective Layer for OTFTs Encapsulation

> 研 究 生:方俊傑 指導教授:冉曉雯 博士

中華民國 九十七年八月

紫外光保護層於有機薄膜電晶體之研究

研究生:方俊傑

指導教授:冉曉雯 博士

國立交通大學

顯示科技研究所碩士班

摘要

在這份論文中,我們製造N,N'bis(naphthalen 1 y)N,N'-bis(phenyl) 二氨基 聯苯(NPB)保護層保護有機薄膜電晶體(OTFTs)在紫外光照射之下免受退化。有 熱蒸鍍沉積的二氨基聯苯(NPB)薄膜之有機薄膜電晶體(OTFTs),它被發現在紫 外光照射下所導致的退化能顯著減少。例如,在大約紫外光照射 120 分鐘之後, 載子移動率的改變僅只 37 % 並且臨限電壓值的變動是在 10% 之內。相對地 , 沒有二氨基聯苯(NPB)薄膜的有機薄膜電晶體(OTFTs)遭受了嚴重的退化;載子 移動率大約減少 90%,而臨限電壓值卻增加超過了 40%。有機薄膜電晶體 (OTFTs)因紫外光所導致的退化在此也被討論;藉由原子力顯微鏡(AFM)的表面 形態分析和電子顯微鏡的化學分析(ESCA)得知,五環素(pentacene)薄膜表面的 氧化和破壞是影響有機薄膜電晶體(OTFT)特性退化的主要因素。我們認為,我 們的二氨基聯苯(NPB) 保護層是一個有用的方法保護五環素有機薄膜電晶體 (pentacene TFTs)。

Ultraviolet Light Protective Layer for OTFTs

Encapsulation

Student: Chun Chieh Fang

Advisor:Dr. Hsiao-Wen Zan

Display Institude

National Chiao Tung University

Abstract

In this thesis, we fabricated *N*,*N*-bis(naphthalen-1-y)-*N*,*N*'-bis(phenyl) benzidine (NPB) passivation to protect the organic thin-film transistors (OTFTs) from degradation under UV-light illumination. With a thermally-deposited NPB film on the OTFTs, it was found that UV-light induced degradation could be significantly reduced. For example, after about 120 minutes UV-light the change of field effect mobility was only 37 % and the change of threshold voltage was within 10%. On the contrary, the OTFTs without NPB film suffered serious degradation. The field-effect mobility was reduced by about 90%, and the threshold voltage was increased by more than 40%. UV-light induced degradation on OTFTs was also discussed; Through surface morphology analysis by atomic force microscopy (AFM) and electron Spectroscopy for Chemical Analysis (ESCA), the surface oxidation and destroyed pentacene

grains pentacene film was the dominative factor that influenced OTFT's properties. We conclude that our NPB passivation is a promising way to protect pentacene TFTs.

Finally, I would like to address that the work is conducted under the leading of my supervisor and also Mr. Kuo-His Yen, Ph. D student in our lab. The result is shared with all the co-workers in this research.



誌謝

丙年時間的飛逝,回首兩年前,滿懷著夢想與期望來到交大。在交大的求 學過程中,遇到了許多困難與考驗,這些考驗使自己在思想或能力上都成長許 多。首先要感謝我的指導教授冉曉雯老師,感謝冉老師帶領我進入 OTFT 的世 界,以及在研究路上不厭其煩的指導我,使我有機會在這塊領域著墨,並從研 究當中讓我了解到一個研究者該有的執著與專業。

感謝實驗室的博班學長:國錫學長、政偉學長、士欽學長、蔚宗學長、文 元學長,在這兩年來的幫助與鼓勵。尤其是國錫學長,在我這兩年來的研究生 涯裡,用心的教導我實驗方法以及提供實驗上的想法,並在心情低落時給予我 適時的開導,且不辭辛勞地協助我完成我的碩士論文。感謝實驗室的同學:武 衛、權陵、旻君、和璁以及志宇,這兩年來的互相打氣,互相砥礪。感謝實驗 室的學弟妹們:繁琦、鈞銘、祥瑞、淑玲、玉玫...等,在苦悶的研究生活裡, 添加了許多歡樂,有你們的陪伴,讓我在這兩年的研究生涯中更為甘甜回味。

最後感謝我的爺爺、奶奶、父母、老哥以及妹妹,感謝你們一路的陪伴與 支持,沒有你們,就不會有今日的我。

Contents

Abstract (Chinese)	Ι
Abstract (English)	II
Acknowledgement	IV
Contents	V
Figure Captions	VIII
Table Captions	XI

Chapter 1. Introduction	
1-1 Introduction of Organic Thin Film Transistors (OTFTs)	1
1-2 Motivation	3
1-3 Thesis Organization	4

Chapter 2. Theoretical Background of OTFTs

2-1 Introc	luction	7
2-2 Trans	portation Mechanisms of Organic Semiconductor	7
2-3 Penta	cene OTFTs with passivation layers	10
2-3-1 2-3-2	Environmental stability of pentacene thin-film transistors High energy UV-light illumination on pentacene thin-film	
	transistors	

2-4-1 Mobility 2-4-2 Threshold voltage	
2-4-3 Subtrieshod swing	
2-4-4 On/on ratio	
Chapter 3. Experiments	
3-1 OTFTs Fabrication	23
3-2 UV illumination experiments.	25
Chapter 4. Result and Discussion	
4-1 Degradation of pentacene OTFTs under UV-light illumination	28
 4-1-1Electrical properties of un-passivated OTFTs under UV-light illumination 4-1-2 Electrical properties of Gated-Four-Probes on un-passivated OTETs under UV-light illumination 	
4-1-3 Material analysis on pentacene films	
4-2 Ultraviolet light Protective Layer for OTFTs passivation	35
4-2-1 Transmittance and absorbing property of NPB passivation.	
4-2-2 Electrical properties of NPB-passivated OTFTs under UV-light illumination	
4-2-3Electrical properties of Gated-Four-Probes on NPB-passivated	
OTFTs under UV-light illumination	
4-3 Comparison of un-passivated OTFTs and NPB-passivated OTFTs	40
under UV-light illumination	
4-3-1 Electrical properties of un-passivated OTFTs and NPB-passivate	d
OTFTs under UV-light illumination	
4-3-2 Electrical properties of Gated-Four-Probes un-passivated OTFTs	5
and Gated-Four-Probes passivated OTFTs under UV illuminatio	n

Chapter 5. Conclusion.

5-1 Conclusion

References

Profile

68

60

58

ES.P. 1896

Figure Captions

Chapter 1

- Fig. 1-1 Energy curve spectra of solar radiation at sea level
- Fig. 1-2 Energy curve spectra of the low-pressure tube
- Fig. 1-3 Absorption spectra of pentacene films

Chapter 2

- Fig. 2-1 The X-ray diffraction (XRD) curves of pentacene film under different UV-light illumination times.
- Fig. 2-2 UV-degeneration of electrical properties on pentacene TFTs
- Fig. 2-3 The Fourier transform infrared spectroscopy (FTIR) spectrum of pentacene film under different UV-light illumination times
- Fig. 2-4 The structures of our flexible pentacene TFT with the SnO₂ encapsulation layer prepared by IBAD: (a) schematic cross section (b) photographic plan view

Chapter 3

- Fig. 3-1 The device structure of pentacene OTFTs with NPB passivation layer
- Fig. 3-2 The optical image of pentacene OTFTs with NPB passivation layer
- Fig.3-3 The image of UV illumination experiments

Chapter 4

Fig. 4-1 The transfer characteristics of pentacene OTFTs under different UV-light illumination times: Without passivation layer

Fig. 4-2 The R_{cont} and the R_{film} is plotted as a function of gate-voltage minus

threshold-voltage $(V_G - V_{th})$ of un-passivated OTFTs under UV-light illumination, respectively.

- Fig. 4-3 The $\triangle R_{cont}$ and $\triangle R_{film}$ and the percentage (%) of R_{cont} and R_{film} are further plotted as a function of UV-light illumination times at $V_G V_{th} = -25 \text{ V}$.
- Fig. 4-4 The X-ray diffraction (XRD) curves of pentacene film under different UV-light illumination times.
- Fig. 4-5 The Raman spectrum of pentacene film under different UV-light illumination times
- Fig. 4-6 The Fourier transform infrared spectroscopy (FTIR) spectrum of pentacene film under different UV-light illumination times are shown in Fig. (a) and Fig. (b)
- Fig. 4-7 The AFM images of pentacene films under different UV-light illumination times are shown in Fig. (a),. (b), (c), (d), (e), and (f).
- Fig. 4-8 Electron Spectroscopy for Chemical Analysis (ESCA) under different UV-light illumination times : (a) Oxygen (O1s) and Carbon (C 1s) (b) Oxygen (O1s), and (c) Carbon (C 1s).
- Fig. 4-9 Electron Spectroscopy for Chemical Analysis (ESCA) of depth profile under different UV-light illumination times
- Fig. 4-10 The performance of the OTFT before and after the passivation with (a)TiO₂ (b) NPB/Mg/TiO₂/PDMS (c)NPB
- Fig. 4-11 The transmittance and absorption spectra of the film are obtained as presented in Figure (a) and Figure (b), respectively
- Fig. 4-12 The initial transfer characteristics with un-passivated OTFTs and passivated OTFTs, respectively.

- Fig. 4-13 The transfer characteristics of pentacene OTFTs under different UV-light illumination times: Covered with NPB passivation layer.
- Fig. 4-14 Figures. (a) and (b) presents the variation of the linear regime field-effect mobility and threshold voltage under UV-light illumination.
- Fig. 4-15 The variation of the linear regime field-effect mobility under UV-light illumination.(the literatures with SnO₂ film)
- Fig. 4-16 The R_{cont} and the R_{film} is plotted as a function of gate-voltage minus threshold-voltage ($V_G - V_{th} = -25V$) of un-passivated OTFTs and NPB-passivated OTFTs under UV-light respectively.



Table Captions

Chapter 2

 Table 1
 Summary list of current studies on OTFT passivation

Chapter 4

Table 2The transfer characteristics of the OTFTs before and after passivation with TiO_2 NPB, NPB/Mg/TiO_/PDMS layers compared with literatures



Chapter 1 Introduction

1-1 Introduction of Organic Thin Film Transistors (OTFTs)

The concept of using organic materials as semiconductors layer in transistors are realized at least since the 1980s [1,2]. Recently, pentacene has received enormous attention as the most promising organic semiconductor for flexible displays, smart cards, radio frequency- identification tags, and various kinds of organic sensors[3-6]. Organic TFTs with mobility exceeding $1 \text{ cm}^2/\text{v.s}$ and an on/off ratio greater than 10^6 have been developed; these values are comparable to hydrogenated amorphous silicon transistors (a-Si:H TFT) [7]. Nevertheless, there are still several issues to be considered before pentacene TFTs are launched into real applications: minimizing threshold voltage hysteresis, improving gate voltage stress resistance, and avoiding the environmental contamination or high-energy ultraviolet (UV)-induced degradation on the pentacene film.[8-10] Among these issues, the UV-induced degradation of pentacene is probably the most immediate and serious. Many studies reported the UV-degeneration effects on pentacene TFTs that were illuminated by a high energy UV with energy over 3.9 eV (wavelength shorter than ~320 nm). Though in a normal sea-level solar radiation the UV portion is very small(See Fig 1-1)[9-16]. The

light-source such as fluorescent lamps and even the mercury light were the common source of UV-light. The low-pressure tube will emit short-wavelength radiation (185nm and 253.7nm from mercury vapor) which may cause damages to organic films(See Fig 1-2).However, in the present studies the details for UV degradation of device characteristics are still not well-understood. The performance of pentacene TFTs under high energy UV is also not reported. According to Jeong-M. Choi's research[11], when a high energy UV strikes the initial crystalline pentacene, it is likely that the pentacene channel gradually loses its crystallinity, enhancing the molecularlike character of constituent pentacenes inside as shown in Fig. 1-3.. In contrast, the energy of 364 nm UV is not high enough to generate crystalline defects in the pentacene channel. Light with energy larger than the energy gap of the 44444 respective semiconductor leads to a degradation of the devices.[15].Hence, it is important to discuss the device degradation under high energy UV illumination.

On the other hand , the stability of OTFTs is one of the major concerns. This is because, OTFTs or any other organic devices tend to easily degrade when they are directly exposed to ultraviolet (UV) lights with energy over 3.9 eV (wavelength shorter than \sim 320 nm)[13-15]. Although, Woo Jin Kim et.al[10] have reported on the fabrication of flexible pentacene thin-film transistors (TFTs) encapsulated with an ultraviolet (UV) protecting SnO₂ thin film that has been prepared by ion-beam-assisted deposition (IBAD). However, the SnO2 encapsulation involves ion beam processes that might cause a little damage on organic pentacene layer. In view of these facts, it is important to develop a protection technique for organic-based devices.

1-2 Motivation

In this experiment, we try to investigate that UV-light induced degradation on OTFTs. By the gated-4-probes OTFTs, the organic film properties and mental-contact effects can be studied separately. Moreover, it is conjected from material analysis to find what may be the dominative factor that influenced OTFT's properties.

Finally ,we proposed on the fabrication of pentacene TFTs encapsulated with NPB thin-film that protect the organic thin-film transistors (OTFTs) from degradation under UV-light illumination. NPB film has high transparent property and does not damage on organic pentacene layer during the passivation process.

1-3 Thesis Organization

In Chapter 1, we make a brief introduction to the demands on OTFTs, passivation layer, and motivation of the thesis. In Chapter 2, we introduce the

transportation mechanisms of organic semiconductor, and parameter extraction. In Chapter 3, the fabrication and the structure of OTFTs are presented. In Chapter 4, the transmittance property of NPB passivation film , the transfer characteristics of un-passivated OTFTs and passivated OTFTs under UV-light illumination, and effects of UV light illumination on our OTFTs are investigated. Finally, we will make a conclusion in Chapter 5.





Fig. 1. Spectral energy curve of solar radiation at sea level and extrapolated outside the atmosphere, as given by Pettit (1951). The darkened areas represent gaseous absorption in the atmosphere.





Fig. 1-2 Energy curve spectra of the low-pressure tube (www.kingo-light.com.tw/kimo/INDEX/PAGE3/Book/UV-根據臭氧的表面處理.pdf)



FIG. 2. (Color online) Absorption spectra of thermally evaporated 50-nm-thick pentacene films illuminated by (a) 254 nm UV and (b) 364 nm UV over the periods of 0, 1, 2, and 3 h.



Chapter 2

Theoretical Background of OTFTs

2-1 Introduction

A large number of conjugated polymers, oligoacenes, and fused aromatics have been used to be the active layers of OTFTs. Most of these organic or polymer semiconductors are p-type material. Recently, many molecular semiconductors, such as pentacene, thiophene oligomers, and regioregular poly(3-alkyl-thiophene) are proposed. The most significant difference between distinguishing those devices fabrication is the deposition method. Among the p-type material , pentacene ($C_{22}H_{14}$) is a rod-like aromatic molecule composed of five benzene rings, shows the highest mobility (>1cm²/v-sec), owning to highly ordered films with proper dielectric properties and growth conditions. Hence, pentacene ($C_{22}H_{14}$) is a promising candidate for future electronic devices and an interesting model system [17].

2-2 Transport Mechanisms of Organic Semiconductor

Carrier transport in the organic semiconductors have been investigated on the theory and modeling in the past years [18]. Organic conductors are conjugated materials, where the π -electrons are conducted intra the molecular. In conjugated

molecules , the properties of charge transport are intrinsically correlated with their crystalline structure, where the π delocalized carriers are responsible for the intra-molecular conduction. However, the nature of van der Waals bonding between discrete molecules is thought to be the limitation of the carrier transport, and the transport is usually described by "localized model " Hence, the carrier transport is described by different models than the covalent-bonded semiconductors. In covalent-bonded semiconductors, carriers move as highly delocalized plane waves in wide bands and have a very high mobility. But in weak-bonded organic semiconductors, the high-mobility model is no longer valid.

Recently, two principal types of theoretical model are used to describe the transport in organic semiconductors : "The band-transport model" and "The hopping models". However, band transport may not suit for some disordered organic semiconductors, in which carrier transport is govern by the hopping between localized states. Hopping is assisted by phonons and the mobility increases with temperature. Typically, the mobility is very low, usually much lower than 1cm²/V-sec. The boundary between "band transport" and "hopping" is divided by materials mobilities (~1cm²/V-sec) at room-temperature (RT) [19]. Many kinds of polycrystalline organic semiconductors , such as several members of the acene series including pentacene, rubrene, have RT mobility larger than 1cm²/V-sec. [20] Sometimes,

temperature-independent mobility was found in some polycrystalline pentacene devices [20]. Thus, this observation argued that the simply thermal activated hopping process governed the whole carrier transport behaviors in high quality polycrystalline pentacene film, despite that the temperature independent mobility has been observed in exceptional cases [21].

The understanding of carrier transport in single-crystal of organic semiconductors will help us to describe the transport mechanism in polycrystalline organic semiconductors. The coherent band-like transport of delocalized carriers becomes the prevalent transport-mechanism in the single crystals of organic pentacene, tetracene, under the low-temperature semiconductors, such as environments. A very high hole mobility values has been measured by time-of-flight experiments [22]. Thus, the temperature dependence of the carrier mobility was found below 100K and following with a power law of $\mu^{\infty} T^{n}$, n~1, [23], in single crystals of organic semiconductors, consistent with the band-transport model. However, between 100K and 300K, the carrier mobility show a constant value [23], that has been described as the superposition of two independent carrier transport The first mechanism was small molecular polaron (MP). According mechanisms. to this model, the carriers were treated as the heavy; polaron-type; quasi-particles. It is formed by the interaction of the carriers with intra-molecular vibrations of the local

lattice environment, and move coherently via tunneling. In this model, the mobility follows the power law $\mu_{MP}=aT^{-n}$. The other involves a small lattice polaron (LP), which moves by thermally activated hopping and exhibits a typical exponential dependence of mobility on temperature : $\mu_{LP}=bexp[-Ea/kT]$. The superposition of these two mechanisms could get a good consistence with experimentally measurement of temperature-dependence mobility from room temperature to a Kelvin degrees (K) [24].

Finally, the exact nature of the charge carrier transport in organic molecular crystals is still not well-understood, which has been the focus in many theoretical studies [25].

2-3 Pentacene OTFTs with passivation layers

Organic thin-film transistors (OTFTs) have received increasing attention recently in place of conventional inorganic electronics because of advantages in their lower cost and simpler packaging, relative to conventional inorganic electronics, and their compatibility with flexible substrates[26-27]. For the commercial value of many applications based on organic devices, stability and performance of organic materials are important[27]. This is because that OTFTs or any other organic devices tend to easily degrade when they are directly exposed to ambient air with some degree of humidity[28-30] or when exposed to UV-lights with energy over 3.9 eV (wavelength shorter than 320 nm)[13-15]. In view of these facts, it is important to develop a protection technique for organic-based devices.

2-3-1 Environmental stability of pentacene thin-film transistors

Recent studies on the environmental stability of OTFT indicate that some specific gases such as H₂O and O₂ affect the TFT performance significantly.[28-30] For example, H₂O remarkably degrades the performance of the OTFT without encapsulation layers in ambient air. This is because that H₂O can diffuse into the grain boundaries and crystal lattice, and they capture charges generated in the channel because of its polar nature.[27,28,30] This results in the decrease in the on-current and field-effect mobility. On the other hand, in case of O₂, because of its electronegativity, it attracts the electrons from the pentacene molecules and generates holes.[31] Jurchescu et al. [31] suggested that oxygen accumulates holes within the pentacene layers by solving one-dimensional Fick's second law. The dislocations in the pentacene crystal lead to accessible vacant orbital and enhance the chemical reactivity.[32] In other words, oxygen diffused to the grain boundaries does not contribute to form the accumulation of holes, but change pentacene into pentacenequinone by oxidation.[32] Therefore, in order to enhance the stability of devices, some encapsulation layers capable of preventing H₂O or O₂ in air from

penetrating through the organic layers have been employed.[33] SiOx, SiNx, AlOx, AlOxNy, SnO₂ and SiOxNy are common amorphous oxides used as an inorganic gas barrier[33-36]. Furthermore , parylene , polyvinylalcohol(PVA), photosensitive acryl ,and polydimethylsiloxanes(PDMS) are common organic materials used as an organic gas barrier[37-43].(The passivation layers summarized in Table1) .This is because these passivation layers which can perform the function of a gas barrier.[44] However, during the deposition process of the passivation layer, some serious damage might be induced on the organic layers. This damage would be caused by energetic ions, X-rays, or electron beams.[33,45-46]Therefore, finding a simple and suitable way to passivate or package organic devices has become an important subject.

manna

2-3-2 High energy UV-light illumination on pentacene thin-film transistors

Many previous studies reported the UV-degeneration effects on pentacene TFTs when samples illuminated by a high-energy UV with energy over 3.9 eV (wavelength shorter than ~320 nm)[9-16]. In Woo Jin Kim 's research[10], according to X-ray diffraction data as shown in Fig.2-1, they indicates that the UV-induced-degradation of device characteristics is directly correlated to the degradation of pentacene crystallinity against UV radiation. Furthermore, in Jeong-M. Choi's research[11], according to the UV-degeneration of electrical properties on pentacene

TFTs(SeeFig.2-2), they signifies that the deep UV damaged the pentacene crystalline channel layer from the surface to the channel/gate oxide interface, generating excessive defects in the whole layer thickness. In particular, it is suspected that the deep UV may additionally cause a surface oxidation of organic pentacene, generating deep level defects near the surface in the vicinity of oxygen molecules in air. Finally in Woo Jin Kim 's research[12], as shown in Fig.2-3. absorption peaks characteristic of pentacene have decreased in intensity, and only a very weak and ill-defined broad feature between 1600 cm⁻¹ and 1800 cm⁻¹ (region of C–O stretching modes) appears in the spectrum, which may indicate the formation of a variety of oxidized intermediate species (the tiny sharp absorptions in this region are due to residual water vapour in the spectrometer). Therefore, they indicates that the chemical reactions 411111 occurring in pentacene thin films in the presence of reactive oxygen species. As mentioned above, it is important to discuss the degradation of UV-light illumination on OTFTs.

On the other hand ,in order to protect the organic thin-film transistors (OTFTs) from degradation under UV-light illumination , Woo Jin Kim et.al[10] have reported on the fabrication of flexible pentacene thin-film transistors (TFTs) encapsulated with an ultraviolet (UV) protecting SnO_2 thin film that has been prepared by ion-beam-assisted deposition (IBAD). However, the SnO2 encapsulation involves ion

beam processes that might cause a little damage on organic pentacene layer. Therefore, before the IBAD processes , they were attempted on thermally evaporated buffer SnO2 on the top dense SnO2.(see.Fig2-4.) This makes the process complicated. In our research, a simple approach was demonstrated to protect organic devices from the damage of strong UV illumination.

2-4 Parameter Extraction

In this section, the methods of extraction the mobility, the threshold voltage, the subthreshold swing, the maximum interface trap density, and the is characterized, respectively.

2-4-1 Mobility

Generally, the linear mobility (for $V_D < V_G - V_{th}$) can be extracted from the

transconductance maximum g_m in the linear region:

$$g_m = \left\lfloor \frac{\partial I_D}{\partial V_G} \right\rfloor_{V_D = cons \tan t} = \frac{WC_{OX}}{L} \mu V_D$$
(2.1)

The saturation mobility (for $V_D > V_G - V_{th}$) can also be extracted from the slope of the curve in the squared drain-current versus the gate-voltage diagram:

$$\sqrt{I_D} = \sqrt{\frac{W}{2L} \,\mu C_{OX}} \left(V_G - V_{TH} \right) \tag{2.2}$$



2-4-2 Threshold voltage

Threshold voltage is related to the operation voltage and the power consumptions of an OTFT. We extract the threshold voltage from equation (2.2), the intersection point of the squared drain-current versus gate-voltage.

2-4-3 Subthreshold swing

Subthreshold swing is also important characteristics for device application. Its is a factor to estimate how rapidly the device switches from the off state to the on state in the region of exponential current increase. It is defined by:

$$S = \frac{\partial V_G}{\partial (\log I_D)} \Big|_{V_D = \text{constant}} , \text{ when } V_G < V_T \text{ for p-type.}$$
(2.3)

Moverover, the subthreshold swing also represents the interface quality and the defect density [26], the maximum interface state trap-density can be extracted by :

$$N_{SS} = \left[\frac{S \cdot \log(e)}{kT/q} - 1\right] \cdot \frac{C_i}{q}$$
(2.4)

A high-performance TFTs will show a lower subthreshold swing.

2-4-4 On/off ratio

Devices with high on/off current ratio represent large turn-on current and small off current. It determines the gray-level switching of the displays. High on/off current ratio means there are enough turn-on current to drive the pixel and sufficiently low off current to keep in low power consumption.

2-4-5 Gated four-probes for resistance

During the standard three-terminal current-voltage measurements, the channel potential was monitored *in situ* at two points in the channel via the potential probes. At a constant V_D , V_G was swept and the channel potential was measured at each V_G step. Knowing the channel potential at two points, V_1 and V_2 , a linear extrapolation of the potential profile to each contact was performed. The potential drops at the source and drain, ΔV_S , ΔV_D and ΔV_{Film} , were calculated according to the following equations:

$$\Delta V_{s} = \left[V_{2} - \frac{(V_{1} - V_{2})}{(L_{2} - L_{1})} (L - L_{2}) \right] - V_{s}$$
(2.5)

$$\Delta V_{D} = V_{D} - \left[V_{2} + \frac{(V_{1} - V_{2})}{(L_{2} - L_{1})} L_{2} \right]$$

$$\Delta V_{Film} = \frac{(V_{1} - V_{2})}{(L_{2} - L_{1})} L$$
(2.6)
(2.7)

where V_s , V_D , V_1 , and V_2 are the voltages at the source, drain, and potential probes, respectively. L_1 , L_2 , and L are the distances from the drain electrode to the first potential probe, the second potential probe, and the source electrode, respectively. where ΔV_{Film} is the actual voltage drop across the film.

With the knowledge of the total current flowing through the device and the potential drops across the film and contacts, the resistance of the source contact, drain contact, and the film can be calculated using Ohm's Law, when devices operation in linear region.

$$R_{S} = \frac{\Delta V_{S}}{I_{D}}$$

$$R_{D} = \frac{\Delta V_{D}}{I_{D}}$$

$$R_{F} = \frac{\Delta V_{F}}{I_{D}}$$

$$(2.9)$$

$$(2.10)$$

$$=\frac{\Delta V_{F}}{I_{D}}$$
(2)





Fig. 2-1 The X-ray diffraction (XRD) curves of pentacene film under different UV-light illumination times.

```
(Electrochem. Solid-State Lett. Vol 9, pp.G251 2006)
```



FIG. 1. (Color online) (a) Drain current-drain voltage $(I_D - V_D)$ characteristics of pristine (left), the high energy 254 nm UV treated (middle), and the low energy 364 nm UV treated (right) TFTs with SiO₂ dielectrics. (b) $\sqrt{-I_D}$ vs V_G and log $(-I_D)$ vs V_G (inset) curves at V_{DS} =-30 V obtained from our OTFTs with SiO₂ dielectrics.

Fig. 2-2 UV-degeneration of electrical properties on pentacene TFTs (Appl. Phys. Lett. , Vol. 90, pp.113515 2007)



Fig. 2. (a) Infrared spectra of a 12 nm thick pentacene film on SiO₂ (a) in its pristine state and (b) after 13 h UV exposure in air. The wiggles below $\sim 1000 \text{ cm}^{-1}$ are caused by the electronics of the spectrometer. (c) Infrared spectrum of a 12 nm thick 6,13-pentacenequinone film on SiO₂.

Fig. 2-3 The Fourier transform infrared spectroscopy (FTIR) spectrum of pentacene film under different UV-light illumination times



(Surface Science, Vol.600, pp. 4004. 2006)

Fig. 2-4 The structures of our flexible pentacene TFT with the SnO₂ encapsulation layer prepared by IBAD: (a) schematic cross section (b) photographic plan view

(Electrochem. Solid-State Lett. Vol 9, pp.G251 2006)

Table 1 Summary list of current studies on OTFT passivation

paper	作者	研究單位	passivation material	Mobility cm ² /Vs	期刊	年份
High-quality thin-film passivation by catalyzer-enhance d chemical vapor deposition for organic light-emitting diodes	Han-Ki Kim	Department of Information and Nano Materials Engineering, Kumoh National Institute of Technology Yangho-dong, Gumi, Gyeongbuk 730-701, Korea	SiNx (CECVD)		APPLIED PHYSICS LETTERS 90, 013502	2007
Air-Stable Operation of Organic Field-Effect Transistors on Plastic Films UsingOrganic/Met allic Hybrid Passivation Layers	Tsuyoshi SEKITANI_ and Takao SOMEYA	Quantum Phase Electronics Center, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan	Parylene (coater)	0.58	Japanese Journal of Applied Physics Vol. 46, No. 7A, , pp. 4300–4306	2007
Solvent Effect of the Passivation Layer on Performance of an Organic Thin-Film Transistor	Seung Hoon Han, Jun Hee Kim	Department of Information Display and Advanced Display Research Center, Department of Chemistry and Advanced Display Research Center, and Kyung Hee University, Seoul 130-701	PA, PVA/ D-PVA, PVA/D-PVA /PA, and parylene-C.	0.43	Electrochem ical and Solid-State Letters, 10 _5_ J68-J70	2007

paper Lifetime of organic thin-film transistors with organic passivation layers	作者 Seung Hoon Han, Jun Hee Kim, and Jin Janga_	研究單位 Department of Information Display and Advanced Display Research Center, Kyung Hee University, Seoul 130-701, Korea	passivation material Acryl+PVA	Mobility cm ² /Vs 0.8	期刊 APPLIED PHYSICS LETTERS 88,073519	年份 2006
Transistor performance of top rough surface of pentacene measured by laminated double insulated-gate supported on a poly(dimethylsiloxa nes) base structure	Mang-mang Ling and Zhenan Bao	Department of Chemical Engineering, Stanford University, Stanford, California 94305	PDMS	0.1-0.2	APPLIED PHYSICS LETTERS 88, 033502	2006
Photolithographic ally defined polythiophene organic thin-film transistors	Flora M. Li,a_ Yuri Vygranenko, Sarswati Koul, and Arokia Nathan	Department of Electrical and Computer Engineering, 1896 University of Waterloo, Waterloo, Ontario N2L 3G1, Canada	SiNx (PECVD)	10 ⁻³ to 10 ⁻⁵	J. Vac. Sci. Technol. A 24,,3, May/Jun	2006
High mobility top gated pentacene thin film transistors	Christopher R. Newman, Reid	Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis	Parylene (laboratory- made CVD apparatus.)	0.1	J.Apply. Phys .vol 98, pp.084506	2005

paper	作者	研究單位	passivation material	Mobility cm ² /Vs	期刊	年份
Encapsulation of Organic Field-Effect Transistors with Highly Polarizable Transparent Amorphous Oxide	Woo Jin KIM, Won Hoe KOO,	Department of Metallurgical Engineering, Yonsei University, Seoul 120-749, Korea	SnO2 (IBAD)	0.8	Japanese Journal of Applied Physics Vol. 44, No. 37, , pp. L 1174–L 1177	2005
Suppression of DC bias stress-induced degradation of organic field-effect transistors using postannealing effects	Tsuyoshi Sekitani, Shingo Iba,	Quantum-Phase Electronics Center, School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan	Parylene (poly-chloro -para-xylyle ne _dix-SR, Daisankasei Co., Ltd.)	0.27-0.36	APPLIED PHYSICS LETTERS 87, 073505	2005
Patterning pentacene organic thin film transistors	Ioannis Kymissis, Christos D. Dimitrakopoul os,	IBM Research, T. J. Watson Research Center, Yorktown Heights, New York 10598	parylene (vapor deposited)	0.08	J. Vac. Sci. Technol. B 20.3., MayÕJun	2002
Characterisation of aluminium oxynitride gas barrier films	Erlat, A.G.; Henry, B.M.; Ingram	Department of Materials, Uni_ersity of Oxford, Parks Road, Oxford OX1 3PH, UK	AlOxNy		Thin Solid Films Vol.388,pp. 78	2001

Chapter 3 Experiments

3-1 OTFTs Fabrication

A cross-sectional view and photographic plan view of pentacene OTFTs fabricated in this experiment is shown in Fig.3-1and Fig.3-2. The detail fabrication processes are as follows:

Step 1. Preparation of Substrates

A p-type, single crystal silicon wafer (100) was used as the substrate and the gate electrode. After RCA cleaning, a 1000Å thermally-grown SiO₂ layer was deposited by furnace. After the SiO₂ deposition, we try to remove the SiO₂ layer from the wafer of unpolished-side. The etching-solution we used is buffered oxide etching (B.O.E.). Hence, the wafer of unpolished-side without SiO₂ layer can serve as a gate-electrode. Finally, the substrate was cleaned in ultrasonic tank by the sequence of: de-ionic water (5 minutes), acetone (1 minutes), and de-ionic water (5 minutes).

Step 2. Spin-coated PMMA on SiO₂

After substrate cleaning, we spin the solution-based Polymethylmethacrylate (PMMA) onto the substrate to modify the surface. The content of solution-based PMMA is a mix of PMMA and anisole with a concentration (10%) .Consequently, we

try to remove the residual solvent. The substrate is then baked on hot-plate at 90° C about 30 minutes.

Step.3 Growth of Pentacene film and Electrodes

The pentacene powder used in this experiment was obtained from Aldrich and its purity was about 99%. The deposition of pentacene film is started at a pressure around 1×10^{-6} torr. The deposition-rate is controlled at ~0.5Å/sec and the thickness of pentacene film was about 100nm, monitored by the quartz crystal oscillator. The pentacene film region is defined through the shadow-mask and the substrate temperature is controlled at room temperature(RT) during the pentacene film deposition.

After the pentacene deposition, a 100-nm-thick gold (Au) layer was deposited through shadow masks to serve as source/drain electrodes. The channel width (W) and length (L) of the Gated-four-probed OTFTs were 800µm and 1200µm, respectively.

Step.4 Passivation layer deposition

The NPB film was then deposited on the top of the device by thermal evaporation at room temperature (RT) at a pressure around 1×10^{-6} torr to a film thickness of about 600 nm. Afterward, by using e-gun evaporation system, the multiple thin-film layers, which made by oxide(100nm) and metal(100nm) layers, can be continuously deposited on the NPB film at a pressure around 3×10^{-6} torr.
Finally, we spin the PDMS onto the device to passiviate the OTFTs. The substrate is then baked on hot-plate at 50°C about 90 minutes.

The current-voltage (I-V) characteristics of our pentacene OTFTs were obtained from the semiconductor parameter analyzer Keithley 4200-SCS and Keithley 2636 in the dark at room temperature(RT).

3-2 UV illumination experiments

In Figure.3-3, we show the image of UV illumination experiments. The UV (Jelight Company, GLS-144 UV Lamp) illumination experiments were performed with un-passivated and passivated pentacene OTFTs under a strong UV (175-254 nm) with an optical power density of 0.043mW/cm². The UV light was continuously illuminated onto our un-passivated and passivated pentacene OTFTs for periods of 0,

10, 20, 40, 80, and 120 minutes.



Fig. 3-1 The device structure of pentacene OTFTs with NPB passivation layer



Fig. 3-2 The optical image of pentacene OTFTs with NPB passivation layer



Fig. 3-3 The image of UV illumination experiments.



Chapter 4

Result and Discussion

4-1 Degradation of pentacene OTFTs under UV-light

illumination

In this experiment, we try to investigate that UV-light induced degradation on OTFTs and by the gated-4-probes OTFTs, the organic film properties and mental-contact effects can be studied separately. Moreover, it is conjected from material analysis to find what may be the dominative factor that influenced OTFT's properties



4-1-1 Electrical properties of un-passivated OTFTs under UV-light illumination

First , the figures. 4-1 show the transfer characteristics of un-passivated OTFTs under UV-light illumination. After about 120 minutes UV-light illumination, the turn-on current (I_D) at V_G = -45V of un-passivated OTFTs was significantly reduced from 0.38 μ A to 0.028 μ A. It is clear that un-passivated OTFTs almost lost the drain current .

These UV-light illuminations effects are again observed from the plots of I_D vs V_G and $Log_{10} I_D$ vs V_G as presented in Fig. 4-1, where we can evaluate the field effect

hole mobilities, threshold voltage, subthreshold swing, and on/off current ratios, respectively. After about 120 minutes UV-light illumination , the pentacene OTFTs without the passivation layers exhibited significantly reduced in field effect mobility from 0.47 cm²/V s to 0.039 cm²/V s; the threshold voltage was significantly changed from -12.2V s to -16.2V ; the subthreshold swing was significantly changed from 2.36 V/decade s to 4.78 V/decade ; the on/off current ratio was significantly reduced from 10^6 to 10^3 when the off current was defined at V_{GS} = 0 V.

It is evident that the degradation of un-passivated OTFTs was significantly reduced under high energy UV-light illumination.

4-1-2 Electrical properties of Gated-Four-Probes on un-passivated OTFTs under UV-light illumination

From potential-probes on channel, the voltage-drops at the source electrode (ΔV_s) , drain electrode (ΔV_D) , and within the pentacene film (ΔV_{film}) can be estimated by:

$$\Delta V_{s} = [V_{1} - \frac{(V_{2} - V_{1})}{(L_{2} - L_{1})} \cdot L_{1}] - V_{s}$$
$$\Delta V_{D} = V_{D} - [V_{2} + \frac{(V_{2} - V_{1})}{(L_{2} - L_{1})} \cdot (L - L_{2})]$$
$$\Delta V_{film} = \frac{(V_{2} - V_{1})}{(L_{2} - L_{1})} \cdot L$$

 V_1 and V_2 is the voltage measured from the first potential probe (near the source

electrode) and second potential probe (near the drain electrode), respectively. L_1 and L_2 is the distance from the first potential probe to source electrode and the second potential probe to drain electrode. *L* is the channel length. V_D and V_s is the drain voltage and source voltage, respectively. The total contact resistance (R_{cont}) and film resistance (R_{film}) can also be estimate by:

$$R_{cont} = \frac{\Delta V_S + \Delta V_D}{I_D}$$
$$R_{film} = \frac{\Delta V_{film}}{I_D}$$

As shown in Fig. 4-2, we show the he contact resistance and pentacene resistance by the gated-four-probes of un-passivated OTFT under UV-light illumination. When the UV-light illumination times increases, both the R_{cont} and the R_{film} will increase.

To study the effects of UV-light illumination on OTFT devices, the $\triangle R_{cont}$

and $\triangle R_{film}$ is further plotted as a function of UV-light illumination times at $V_G - V_{th} = -25$ V in Fig 4-3(a). After about 120 minutes UV-light illumination, the R_{cont} will approach a maximum value about $4.9 \times 10^6 \Omega$, which is smaller than the value of R_{film} around $8.1 \times 10^7 \Omega$. The Fig. 4-3(b) shows the percentage (%) of R_{cont} and R_{film} versus UV-light illumination times, respectively. It is clear that the percentage (%) of R_{film} is as high as about 90% under different UV-light illumination times. Thus, the OTFT characteristics should be mainly dominated by the pentacene film properties rather than the contact properties.

4-1-3 Material analysis on pentacene-OTFTs

From the transfer characteristics of pentacene OTFTs under UV-light illumination, it is important to discuss the degradation of UV-light illumination on OTFTs. Therefore, we try to investigate the pentacene film properties under different UV-light illumination times firstly. In Fig. 4-4, we show the x-ray diffraction (XRD) curves of pentacene film under different UV-light illumination times. All pentacene films show the (001) signal with a peak value about 5.73° (degree). The higher order signal of (002) and (003) peak is also observed with a values about 11.47° (degree) and 17.21° (degree), respectively. According to the XRD analysis[47], it implies that the pentacene films under different UV-light illumination times are almost identical. It is clear that pentacene crystallization was not significantly 4411111 changed after UV-light illumination. Consequently, we also try to verify the pentacene film by the Raman spectrum. With the Raman spectrum analysis, the conformational transition during carrier transport [47]. The pentacene vibration-modes of C-HC-C(around 1155-1179cm-1) and (around 1353-1380cm-1) bindings are plotted in Fig. 4-5. According to the Raman spectrum analysis, the result also reveals that the intermolecular coupling was not be changed even if the pentacene films under different UV-light illumination times. Finally, we also show fourier transform infrared spectroscopy (FTIR) spectrum of the pentacene

films under different UV-light illumination times. The FTIR spectrum of 100nm thick pentacene films on SiO2 (see Fig. 4-6) displays a number of strong absorption bands, which can be identified according to the literature [12,48]: 729 cm⁻¹ and 903 cm⁻¹ are out-of-plane C-H bending modes, 1296 cm-1 a ring stretching mode, and 3004 cm⁻¹correspond to C-H in-plane stretching modes. According to the FTIR spectrum analysis, the bonding of pentacene films was not be changed even if the pentacene films under different UV-light illumination times. Based on these material analysis, the crystalline, molecular coupling, and the absorptive properties of pentacene film under different UV-light illumination times should be almost identical. It is clear that deep UV do not damage the pentacene crystalline channel layer from the surface to the channel/gate oxide interface, and not generating excessive defects in the whole layer thickness.

In order to study the effect of UV-light illumination on OTFTs, we verified the effects of UV-light illumination on thin-film properties. In Fig. 4-7, we show the AFM images of pentacene films under different UV-light illumination times. Before illumination, the dendritic pentacene grains could be observed. Beside, the monolayer edges also clearly appeared. However, after illumination, several knobs appeared on the dendritic pentacene grains[12]. The monolayer edges were blurred. Pentacene grain slightly changes were observed among these AFM images. Therefore, deep

UV cause a surface damage of organic pentacene which UV-light illumination times increases.

It is not clearly understood why UV cause a degradation of pentacene TFTs. However, it is conjectured from electron Spectroscopy for Chemical Analysis (ESCA) was used to examine the changes of thin film chemical bonding. The pentacene vibration-modes of carbon (C) signal (around 285eV) and oxygen (O) signal (around 532eV) bindings are plotted in Fig. 4-8(a). The carbon (C) signal of pentacene films is further plotted as a function of binding energy in Fig. 4-8(b), which were illuminated by UV-light with different times. Significantly, the carbon signal significantly decreased, additionally, a carbon-oxygen (O) related signal around 290eV appear after UV-light illumination[49]. We also show the oxygen signal in Fig. 4-8 (c). We found 411111 pentacene film without UV-light illumination showed a very low oxygen signal. However, when pentacene film was exposed to UV-light illumination, the oxygen signal significantly increased. This implied that UV-light illumination may result in a photo-induced oxidation of organic pentacene. This will result in changed bonding between the benzene ring and oxygen. The added oxygen in the pentacene film severely influenced OTFT performance.

To further find where the photo-induced oxidation of organic pentacene is, electron Spectroscopy for Chemical Analysis (ESCA) depth profile was plotted in Fig. 4-9. We can compare the carbon (C) signal and oxygen (O) signal, which were illuminated by UV-light with different times. Significantly, in the thickness of pentacene film thiner than 10 nm, the carbon signal significantly decreased. In contrast, the oxygen signal significantly increased. It is clear that UV-light illumination cause a surface oxidation of organic pentacene, generating deep level defects near the surface in the vicinity of oxygen molecules in air.[13]

According to charge transport mechanisms of pentacene OTFTs[50], all the charge of the conducting channel resides in the first monolayer next to the insulator-pentacene interface; in other words, the charges located close to the interface have the highest mobility, which reinforces their contribution to the conductivity of the conducting channel. Consequently, the conventional field-effect mobility gives a relatively good estimate for the actual mobility at the interface. However , the electron Spectroscopy for Chemical Analysis (ESCA) depth profile result further verify surface oxidation of pentacene film severely degraded OTFT performance. Therfore , it is clear that the charge of the conducting channel not just located in the first monolayer next to the insulator-pentacene interface ,but also in whole pentacene layer.

4-2 Ultraviolet light protective layer for OTFTs passivation

In order to protect the organic thin-film transistors (OTFTs) from degradation under UV-light illumination , we proposed on the passivation of pentacene TFTs using two kinds of passivation layers : TiO2, *N'*-bis(naphthalen-1-y)-*N*,*N'*-bis(phenyl) benzidine (NPB)/Mg/TiO₂/PDMS and NPB.

For UV-light illumination , the TiO2 thin film have strong absorption property. Therefore , we used the TiO2 thin film to protect the organic thin-film transistors (OTFTs) from degradation under UV-light illumination. However, in figure 4-10(a) ,we shows the performance of the OTFT before and after the passivation with TiO₂ . It is clear that there is a significant increment in the off-current after the passivation. We signifies that UV-light illumination on the TiO₂ thin film, occurring the chemical reactions in TiO2 thin film. Furthermore, during the deposition process , x rays, and electron beams damages the pentacene active layer, resulting in the degradation of the field-effect mobility from 0.38 to 0.32 cm²/V.s, This result coincides with the previous report on the X-rays and electron beams effect on pentacene OTFT.[45-46]

Therefore, in order to avoid OTFT degradation during the passivation process and the off current decrease, we proposed on the passivation of pentacene TFTs with NPB/Mg/TiO₂/PDMS. By using e-gun evaporation system, the multiple thin-film layers, which made by oxide and metal layers, can be continuously deposited on OTFTs. These multiple thin-film layers were low optical transparency and high gaseous resistance, which will act as the protective layers to avoid OTFT degradation under UV-light (wavelength: 175-254 nm) soaking. However, in figure 4-10(b), we shows the performance of the OTFT before and after the passivation with NPB/Mg/TiO₂/PDMS. It is clear that although the off-current does not change after the passivation. But during the deposition process, X-rays, and electron beams damages the pentacene active layer[45-46], resulting in the degradation of the field-effect mobility from 0.44 to 0.35 cm²/V.s, so that the drop was 0.09 cm²/V s.

Therefore, in order to avoid OTFT degradation during the passivation process , we proposed the NPB film as the passivation for pentacene TFTs .Because the NPB film have highly transparent property.[51]. Furthermore, in figure 4-10(c), we shows the transfer characteristics of the OTFT before and after passivation with NPB layer. Before passivation , the device shows a mobility about $0.47 \text{cm}^2/\text{v-sec}$, a threshold voltage about -12.2V, a subthreshold swing about 2.36 V/decade , and a on/off ratio about 10^6 . On the other hand, the OTFTs with NPB passivation show a similar mobility about 0.48 cm²/v-sec, a lower threshold voltage about -11 V, a larger subthreshold swing about 2.4V/decade, and a lower on/off ratio about 10^4 . It is interesting that with NPB passivation , the threshold voltage will be reduced , the subthreshold swing will be increased, and the on/off ratio will be reduced. But the field effect mobilities almost remains unchanged. Therefore, it is clear that during the passivation process, the NPB film does not damage on organic pentacene layer.

The transfer characteristics of the OTFTs before and after passivation with TiO₂ NPB, NPB/Mg/TiO₂/PDMS layers compared with literatures which have summarized in Table 2. It is clear that the transfer characteristics of the OTFTs before and after passivation with NPB layer almost remains unchanged. This result for passsivation layer of pentacene OTFTs is our unique finding .Therefore, the NPB film as the passivation layer to protect the organic thin-film transistors (OTFTs) from degradation under UV-light illumination.

4-2-1 Transmittance and absorbing property of NPB passivation

To verify the UV protective properties of the NPB passivation, the transparent and absorptive properties are important demands. In this experiment, the NPB film with thickness about 600 nm was deposited on guartz glass by thermal evaporation, the spectrum of the film presented in Figure 4-11(a) and Figure 4-11(b), respectively. During the visible wavelength of the spectrum, the NPB film displays a transmittance about as high as 80%, and based on the plot of the squared angular frequency absorption coefficient ($\alpha^2 \omega^2$) vs. photon energy (ev) ,the estimated optical bandgap of NPB film was around 2.9 eV[10]. It is clear that the NPB film is highly transparent[51]. It should be a good passivative layer for covering the OTFTs, especially for in the application of displays.

4-2-2 Electrical properties of passivated OTFTs under UV-light illumination

In Figures. 4-12, we show the transfer characteristics of passivated OTFTs under UV-light illumination. After about 120 minutes UV-light illumination, the turn-on current (I_D) at V_G= -45V of un-passivated OTFTs was slightly changed from 0.4 μ A to 0.23 μ A. It is clear that passivated OTFTs still showed a high current level of 0.23 μ A while the un-passivated one almost lost the drain current (that decreased from 0.38 μ A to less than 0.028 μ A)

These UV illuminations effects are again observed from the plots of $I_D vs V_G$ and $Log_{10} I_D vs V_G$ as presented in Fig. 4-12, where we can evaluate the field effect hole mobilities, threshold voltage, subthreshold swing, and on/off current ratios, respectively. After about 120 minutes UV-light illumination , the pentacene OTFTs with the passivation layers exhibited slightly reduced in field effect mobility from 0.48 cm²/V s to 0.30 cm²/V s; the threshold voltage was slightly changed from -11V

to -12V ; the subthreshold swing was slightly changed from 2.40V/decade to 3.96 V/decade ; the on/off current ratio was slightly reduced from 10^4 to 10^3 when the off current was defined at $V_{GS} = 0$ V. Evidently, with NPB passivation, the UV light induced degradation was reduced.

4-2-3 Electrical properties of Gated-Four-Probes on NPB-passivated OTFTs under UV-light illumination

In Figures. 4-13, we show the he contact resistance and pentacene resistance by the gated-four-probes of passivated OTFT under UV-light illumination, respectively. When the UV-light illumination times increases, both the R_{cont} and the R_{film} will slightly increase. It is clear that the NPB film will protected pentacene OTFTs effectively from high energy UV illumination

4-3 Comparison of un-passivated OTFTs and NPB-passivated OTFTs under UV-light illumination

4-3-1 Electrical properties of un-passivated OTFTs and

NPB-passivated OTFTs under UV illumination

The field effect mobility vs UV illumination period plotted and summarized in Fig. 4-14(a). The field-effect mobility of un-passivated OTFTs significantly degraded from 0.47 cm² /V s to 0.04 cm² /V s while the NPB passivated one does slightly degrade from 0.48 cm² /V s to 0.30 cm² /V s. The NPB-passivated TFT shows a gradual degradation of mobility while the un-passivated one does very rapid degradation. Similar results were reported with SnO₂ thin film.(See Fig.4-14(b)).

In Figures. 4-15 presents the variation of the linear regime threshold voltage, under different UV-light illumination times. The relative change from -12.2V s to -16.2V in the threshold voltage of un-passivated OTFTs, as the UV-light illumination times are increased, are much larger than the relative change (from -11V s to -12V) in the NPB-passivated OTFTs, as stated above.

It is evident that the NPB film have protected pentacene OTFTs effectively from high energy UV illumination

4-3-2 Electrical properties of Gated-Four-Probes un-passivated OTFTs and Gated-Four-Probes passivated OTFTs under UV illumination

As shown in Fig. 4-16, the R_{cont} and the R_{film} is plotted as a function of gate-voltage minus threshold-voltage ($V_G - V_{th} = -25$ V) of un-passivated OTFTs and passivated OTFTs under UV-light illumination, respectively. When the UV-light illumination times increases, both the R_{cont} and the R_{film} will increase. But the R_{cont} and the R_{film} of un-passivated OTFTs shows a significantly increases while the NPB passivated one does slightly increase. It is clear that the NPB film will protected pentacene OTFTs effectively from high energy UV illumination.



Fig.4-1 The transfer characteristics of pentacene OTFTs without NPB passivation layer under different UV-light illumination times

Un-passivated OTFT



Fig. 4-2 The variation of the linear regime resistance of un-passivated under different UV-light illumination times



Fig. 4-3(b) The percentage (%) of R_{cont} and R_{film} versus UV-light illumination times



Fig. 4-4The X-ray diffraction (XRD) curves of pentacene film under different
UV-light illumination times.



Fig. 4-5 The Raman spectrum of pentacene film under different UV-light illumination times



Fig. 4-6(b) The Fourier transform infrared spectroscopy (FTIR) spectrum of pentacene film:1200nm-3200nm





(a) UV 0 min

(b) UV 10 mins



(c) UV 20 min

(d) UV 40 mins



(e) UV 80 min

(f) UV 120 mins

Fig. 4-7 The AFM images of pentacene films under different UV-light illumination times are shown in Fig. (a) ,. (b) , (c) , (d) ,(e) ,and (f).



Fig. 4-8(a) Electron Spectroscopy for Chemical Analysis (ESCA) under different UV-light illumination times : Oxygen (O1s) and Carbon (C 1s)



Fig. 4-8(b) Electron Spectroscopy for Chemical Analysis (ESCA) under different UV-light illumination times :Carbon (C 1s)



Fig. 4-8(c) Electron Spectroscopy for Chemical Analysis (ESCA) under different UV-light illumination times : Oxygen (O 1s)



Fig. 4-9 Electron Spectroscopy for Chemical Analysis (ESCA) of depth profile

under different UV-light illumination times



Fig. 4-10(b) The performance of the OTFT before and after the passivation with NPB/Mg/TiO₂/PDMS



Fig. 4-10(c) The performance of the OTFT before and after the passivation with

NPB





Fig. 4-11(a) The transmission curve of NPB film (600nm) was plotted as a



Fig. 4-11(b) The absorption spectrum of NPB fim was plotted as a function of

energy



Fig. 4-12 The transfer characteristics of pentacene OTFTs with NPB passivation layer under different UV-light illumination times

NPB-passivated OTFT



Fig. 4-13 The variation of the linear regime resistance of NPB-passivated under different UV-light illumination time



Fig. 4-14(b) The variation of the linear regime field-effect mobility under UV-light illumination.(the literatures with SnO₂ film)
(Electrochem. Solid-State Lett. vol 9, pp.G251 2006)



Fig. 4-16 The resistance vs UV illumination period plotted and summarized

Table 2The transfer characteristics of the OTFTs before and after passivationwith TiO2,NPB, NPB/Mg/TiO2/PDMS layers compared with literatures

<i>µ</i> (cm ² /V-sec)	SnO ₂ Woo Jin KIM [10]	PVA/acryl Seung Hoon Han [TiO ₂ 35]	NPB/Mg/TiO ₂ /PDMS	NPB
before passivation	0.37	0.98	0.38	0.44	0.47
after passivation	0.34	0.8	0.32	0.35	0.48



Chapter 5 Conclusion

5-1 Conclusion

In conclusion, the highly transparent NPB film was used as the passivation layer for pentacene OTFTs. After the passivation process, the OTFTs threshold voltage was reduced, the subthreshold swing was increased, and the on/off ratio was reduced, but the field-effect mobility was almost unchanged. It was clear that the NPB passivation will not damage the organic pentacene film.

The device degradation under UV-light illumination was prevented after capping the thermally-deposited NPB film. The high energy UV-light (175~254nm wavelength) was constantly applied onto the passivated device. After several periods time of 10, 20, 40, 80, and 120 minutes, the field-effect mobility of NPB passivated OTFTs gradually degraded from 0.48 to 0.30cm²/Vs. However, the other device without passivation will rapidly become invalid, and showed a larger threshold-voltage shift than the passivated OTFTs. The NPB film is suitable to protect the pentacene OTFTs from UV-light illumination.

We also discussed the effects of UV-light illumination on OTFTs. Through the analysis of atomic force microscopy (AFM), x-ray diffraction spectrum (XRD) and

electron Spectroscopy for Chemical Analysis (ESCA), we found the changes in both chemical properties and surface morphologies were significantly. The oxidation signal and destroyed pentacene grains were significantly appeared on the surface of pentacene film and seemed to be a dominated factor that influenced the OTFTs performance. Based on these experiment results, it may be supposed that the performance degradation was strongly related to changes in chemical bonding and grain morphology, but rather than changes inside the thin-film bulk.



References

- [1] A. Tsumura, K. Koezuka, and T. Ando, "Macromolecular electronic devices: Field-effect transistor with a polythiophene thin film", Appl. Phys. Lett. Vol.49, pp.1210 (1986).
- [2] J. H. Burroughes, C. A. Jones, and R. H. Friend, "Polymer diodes and transistors: new semiconductor device physics", Nature, Vol. 335, pp.137 (1988)
- [3] Kazuhito Tsukagoshi, Jun Tanabe, Iwao Yagi, Kunji Shigeto, and Keiichi Yanagisawa, "Organic light-emitting diode driven by organic thin film transistor on plastic substrates", J.Apply. Phys. Vol 99, pp.064506 (2006)
- [4] Alejandro L. Briseno, Qian Miao, Mang Mang Ling, Colin Reese, Hong Meng, Zhenan Bao,and Fred Wudl, "Hexathiapentacene: Structure, Molecular Packing, and Thin-Film Transistors", J. Am. Chem. Soc. Vol.128, pp.15576 (2006)
- [5] R. Rotzoll, S. Mohapatra, V. Olariu, R. Wenz, M. Grigas, K. Dimmler, O. Shchekin, and A. Dodabalapur, "Radio frequency rectifiers based on organic thin-film transistors", Appl. Phys. Lett. Vol.88, pp.123502 (2006)
- [6] Michael C. Hamilton, Sandrine Martin, and Jerzy Kanicki, "Thin-film organic polymer phototransistors", IEEE Trans. Electron Devices. Vol 51, pp.877 (2004)
- [7].Y. Y. Lin, D. J. Gundlach, S. F. Nelson, and T. N. Jackson, "Pentacene organic
thin-film transistors-molecular ordering and mobility ", IEEE Electron Device Lett. Vol. 18, pp. 87 (1997).

- [8] C. R. Kagan, A. Afzali, and T. O. Graham, "Operational and environmental stability of pentacene thin-film transistors", Appl. Phys. Lett. Vol.86, pp.193505 (2005).
- [9] D. K. Hwang, J. H. Park, J. Lee, J.-M. Choi, J. H. Kim, E. Kim, and S. Im, "Improving resistance to Gate Bias Stress in Pentacene TFTs with Optimally Cured Polymer Dielectric Layers", J. Electrochem. Soc. Vol. 153, G23 (2006)
- [10]W. J. Kim, W. H. Koo, S. J. Jo, C. S. Kim, H. K. Baik, D. K. Hwang, K.
 Lee, J. H. Kim, and S. Im, "Ultraviolet-Enduring Performance of Flexible Pentacene TFTswith SnO₂ Encapsulation Films", Electrochem. Solid-State .Lett. Vol 9, pp.G251 (2006).
- [11] Jeong-M. Choi, D. K. Hwang, Jung Min Hwang, Jae Hoon Kim, and Seongil Im, "Ultraviolet-enhanced device properties in pentacene-based thin-film transistors", Appl. Phys. Lett., Vol. 90, pp.113515 (2007)
- [12] A. Vollmer *, H. Weiss, S. Rentenberger, I. Salzmann, J.P. Rabe, N. Koch "The interaction of oxygen and ozone with pentacene ", Surface Science , Vol.600 ,pp. 4004–4007. (2006)
- [13].A. Maliakal, K. Raghavachari, H. Katz, E. Chandross, and T. Siegrist,

"Photochemical Stability of Pentacene and a Substituted Pentacene in Solution and in Thin Films", Chem.Mater., Vol. 16, pp. 4980 (2005).

- [14].K. A. M. dos Santos, P. A. Z. Suarez, and J. C. Rubim, "Photo-degradation of synthetic and natural polyisoprenes at specific UV radiations", *Polym Degrad. Stab.*, Vol.90, pp.34 (2005).
- [15]. H. Heil, G. Andress, R. Schmechel, H. Von Seggern, J. Steiger, K. Bonard, and R.Sprengard ,"Sunlight stability of organic light-emitting diodes ", J. Appl. Phys., Vol.97, pp.124501 (2005).
- [16]AndrewA.Lacis"A parameterization for the absorption of solar radiation in the earth atmosphere", Journal of the atmospheric sciences, Vo31, pp.118(1973)
- [17] Yanming Sun, Yunqi Liu, and Daoben Zhu, "Advances in organic field effect transistors", J.Mater.Chem., Vol.15, pp.53(2005)
- [18] R.A.Street, D.Knipp, and A.R.Volkel, "Hoke transport in polycrystalline pentacene transistors", Appl. Phys. Lett., Vol. 80, pp.1658 (2002)
- [19] G. Horowitz, "Organic field-effect transistors", Adv. Mater., Vol. 10, pp. 365, (1998).
- [20] Y.-Y. Lin, D. J. Gundlach, S. F. Nelson, and T. N. Jackson, "Stacked pentacene layer organic thin-film transistors with improved characteristics", IEEE Electron Device Lett, Vol. 18, pp 606, (2000).

- [21]S. F. Nelson, Y.-Y. Lin, D. J. Gundlach, and T. N. Jackson, "Temperature-independent transport in high-mobility pentacene transistors", Appl. Phys. Lett., Vol. 72, pp. 1854, (1998).
- [22] W. Warta, and N. Karl, "Hot holes in naphthalene: High, electric-field-dependent mobilities", Phys. Rev. B, Vol. 32, pp. 1172, (1985).
- [23] L. B. Schein, C. B. Duke, and A. R. McGhie, "Observation of the Band-Hopping Transition for Electrons in Naphthalene", Phys. Rev. Lett., Vol 40, pp. 197,

(1978).

- [24] E. A. Silinsh, A. Klimkans, S. Larsson, and V. Cápek, "Molecular polaron states in polyacene crystals Formation and transfer processes", Chem. Phys., Vol 198, pp. 311 (1995).
- [25] O. Ostroverkhova, D. G. Cooke, S. Shcherbyna, R. F. Egerton, F. A. Hegmann, R.R. Tykwinski, and J. E. Anthony, "Bandlike transport in pentacene and Functionalized pentacene thin films revealed by subpicosecond transient photoconductivity measurements", Phys. Rev. B, Vol. 71, pp. 035204, (2005).
- [26] C. D. Dimitrakopoulos, D. J. Mascaro, "Organic thin-film transistors : A review of recent advances", IBM J. RES. & DEV., Vol. 45, , pp. 11-26, (2001)
- [27] Jung Hun Lee, Gi Heon Kim, Seong Hyun Kim, Sang Chul Lim, Yong Suk Yang, Jiyoung Oh, Ji Ho Youk, Jin Jang, Taehyoung Zyung "The novel encapsulation

method for organic thin-film transistors", Current Applied Physics ,Vol 5, pp. 348–350 (2005)

- [28] D. Li, E. J. Borkent, R. Nortrup, H. S. Moon, H. Katz, and Z. Bao, "Humidity effect on electrical performance of organic thin-film transistors" Appl.Phys. Lett. Vol.86, pp.042105 (2005).
- [29]Y. Qiu, Y. Hu, G. Dong, L. Wang, J. Xie, and Y. Ma, "H₂O effect on the stability of organic thin-film field-effect transistors" Appl. Phys. Lett. Vol.83, pp.1644 (2003).
- [30]R. Ye, M. Baba, K. Suzuki, Y. Ohishi, and K. Mori, "Effects of O₂ and H₂O on electrical characteristics of pentacene thin film transistors" Thin Solid Films Vol.464,pp.437 (2004).
- [31]O. D. Jurchescu, J. Baas, and T. T. M. Palstra, "Electronic transport properties of pentacene single crystals upon exposure to air"Appl. Phys. Lett.Vol. 87, pp.052102 (2005).
- [32]O. D. Jurchescu, J. Baas, and T. T. M. Palstra, "Effect of impurities on the mobility of single crystal pentacene" Appl. Phys. Lett. Vol.84, pp.3061(2004).
- [33]Woo Jin KIM, Won Hoe KOO, "Encapsulation of Organic Field-Effect Transistors with Highly Polarizable Transparent Amorphous Oxide ", J.J.Apply. Phys.vol 44, pp.L1174 (2005)

- [34]A. G. Erlat, B. M. Henry, J. J. Ingram, D. B. Mountain, A. McGuigan,
 - R. P. Howson, C. R. M. Grovenor, G. A. D. Briggs, and Y. Tsukahara, "Characterisation of aluminium oxynitride gas barrier films"

Thin Solid Films Vol.388,pp. 78 (2001).

- [35] Han-Ki Kim, "High-quality thin-film passivation by catalyzer-enhanced chemical vapor deposition for organic light-emitting diodes", Appl. Phys. Lett. Vol.90, pp.013502 (2007)
- [36] Flora M. Li, Yuri Vygranenko, Sarswati Koul, and Arokia"Photolithographically defined polythiophene organic thin-film transistors", J. Vac. Sci. Technol. Vol 24 pp.3(2006)
- [37]Tsuyoshi SEKITANI and Takao SOMEYA, "Air-Stable Operation of Organic Field-Effect Transistors on Plastic Films UsingOrganic/Metallic Hybrid Passivation Layers ", J.J.Apply. Phys .Vol 46, pp.4300 (2007)
- [38] Seung Hoon Han, Jun Hee Kim, "Solvent Effect of the Passivation Layer on Performance of an Organic Thin-Film Transistor", Electrochemical and Solid-State Letters, Vol.10, pp.J68-J70(2007)
- [39] Seung Hoon Han, Jun Hee Kim, and Jin Janga, "Lifetime of organic thin-film transistors with organic passivation layers", Appl. Phys. Lett. Vol.88, pp.073519 (2006)

- [40] Mang-mang Ling and Zhenan Bao, "Transistor performance of top rough surface of pentacene measured by laminated double insulated-gate supported on a poly(dimethylsiloxanes) base structure", Appl. Phys. Lett. Vol.88, pp.033502 (2006)
- [41] Christopher R. Newman, Reid"High mobility top gated pentacene thin film transistors", J.Apply. Phys .vol 98, pp.084506 (2005)
- [42] Tsuyoshi Sekitani, Shingo Iba, "Suppression of DC bias stress-induced degradation of organic field-effect transistors using postannealing effects", Appl. Phys. Lett. Vol.87, pp.073505(2005)
- [43] Ioannis Kymissis, Christos D. Dimitrakopoulos, "Patterning pentacene organic thin film transistors", J. Vac. Sci. Technol. B Vol.20.pp.3(2002)
- [44] Woo Jin Kim, Won Hoe Koo, Sung Jin Jo, Chang Su Kim, and Hong Koo Baik,"Passivation effects on the stability of pentacene thin-film transistors with SnO2prepared by ion-beam-assisted deposition ", J. Vac. Sci. Technol. BVol.23.pp.6(2002)
- [45] V. Bulovi, P. Tian, P. E. Burrows, M. R. Gokhale, and S. R. Forrest"A surface-emitting vacuum-deposited organic light emitting device", Appl. Phys. Lett., Vol. 70, pp. 2954, (1997).
- [46] L. S. Hung, C. W. Tang, M. G. Mason, P. Raychaudhuri, and J.

Madathil"Application of an ultrathin LiF/Al bilayer in organic surface-emitting diodes", Appl. Phys. Lett., Vol. 78, pp. 544, (2001).

- [47] Horng-Long Cheng, Yu-Shen Mai, Wei-Yang Chou, and Li-Ren Chang, "Influence of molecular structure and microstructure on device performance of polycrystalline pentacene thin-film transistors", Appl. Phys. Lett., Vol. 90, pp. 171926, (2007).
- [48] Y. Hosoi, K. Okamura, Y. Kimura, H. Ishii, M. Niwano, "Infrared spectroscopy of pentacene thin film on SiO2 surface", Appl. Surf. Sci.Vol.244,pp. 607 (2005).
- [49] S. Li,1 E. T. Kang, Z. H. Ma and K. L. Tan, "XPS investigation of electrode/polymer interfaces of relevance to the phenylene vinylene polymer-based LEDs ",Surf. Interface Anal. Vol 29, pp.95 (2000)
- [50] Gilles Horowitz, "Organic thin film transistors: From theory to real devices", J.Mater. Res., Vol. 19, pp. 1946 (2004)
- [51] Y. Yuan, D. Grozea, S. Han, and Z. H. Lu, "Interaction between organic semiconductors and LiF dopant", Appl. Phys. Lett. Vol.85, pp.4959 (2005).

簡歷

姓名:方俊傑

出生年月日:中華民國七十二年十一月十九日

住址:嘉義縣中埔鄉中埔村 20 巷 87 弄 12 號

學歷:

私立逢甲大學電機系



(2002.09~2006.06)

國立交通大學顯示科技研究所碩士 (2006.09~2008.06)

論文題目:

紫外光保護層於有機薄膜電晶體之研究

Ultraviolet Light Protective Layer for OTFTs Encapsulation