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Electronic Properties of Organic Thin Film Transistors with Nanoscale Tapered Electrodes

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Materials Science and Engineering

by

Jeongwon Park

Committee in Charge:

Professor Sungho Jin, Co-Chair
Professor Andrew C. Kummel, Co-Chair
Professor Yu-Hwa Lo
Professor Yuan Taur
Professor William C. Trogler

2008
The dissertation of Jeongwon Park is approved, and it is acceptable in quality and form for publication on microfilm:

Co-Chair

Co-Chair

University of California, San Diego

2008
Dedicated to

my wife
“The future is not a result of choices among alternative paths offered by the present, but a place that is created--created first in the mind and will, created next in activity. The future is not some place we are going to, but one we are creating. The paths are not to be found, but made, and the activity of making them, changes both the maker and the destination.”

John Schaar
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La Jolla, June 2008
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2. Aging and recovery processes in Copper Phthalocyanine Thin Film Transistors (In preparation)


Patents / Technology disclosures:


Conference proceedings:

ABSTRACT OF THE DISSERTATION

Electronic Properties of Organic Thin Film Transistors with Nanoscale Tapered Electrodes

by

Jeongwon Park

Doctor of Philosophy in Materials Science and Engineering

University of California, San Diego, 2008

Professor Sungho Jin, Co-Chair

Professor Andrew C. Kummel, Co-Chair

Organic thin-film transistors (OTFTs) have received increasing attention because of their potential applications in displays, optoelectronics, logic circuits, and sensors. Ultrathin OTFTs are of technical interest as a possible route toward reduced bias stress in standard OTFTs and enhanced sensitivity in chemical field-effect transistors (ChemFETs). ChemFETs are OTFTs whose output characteristics are sensitive to the presence of analytes via changes in the channel mobility and/or threshold voltage induced by analyte chemisorption onto the channel materials. The fundamental understanding of charge transport properties of organic thin-films is critical for the applications. OTFT has been demonstrated by many groups; however, there has been much less progress towards more reliable contact structure between
organic materials and electrodes. This thesis investigates the electrical properties of metal phthalocyanine thin-film devices.

In chapter 1, the basic electrical properties in OTFTs are reviewed. In chapter 2, we have investigated the microfabrication process of OTFTs to control the contact morphology and the charge transport properties of phthalocyanine thin-film devices. In chapter 3, the channel thickness dependence of the mobility was investigated in bottom-contact copper phthalocyanine (CuPc) OTFTs. The current-voltage characteristics of bottom contact CuPc OTFTs with low contact resistance fabricated by the bilayer photoresist lift-off process were analyzed to determine the mobility, threshold voltage and contact resistance. The independence of measured electronic properties from channel thickness is due to the contact resistance being negligible for all channel thicknesses.

For practical applications, the aging and recovery process in CuPc OTFTs were investigated in chapter 4. An origin of the aging process on CuPc OTFTs has been investigated based on the responses of thick 1000ML CuPc OTFTs under a controlled atmosphere. The recovery process under 30 % relative humidity with pure dry air for 48 hours and pure dry air for 24 hours can improve the OTFTs performance with a good current saturation behavior, a high mobility, a low threshold voltage and a high current on/off ratio due to controlling dopants.

The bottom contact OTFTs with low contact resistance created in this work could serve useful in a variety of applications and initial results are presented for their use as displays, optoelectronics, logic circuits, and sensors.
CHAPTER 1: Introduction

1.1 History of organic semiconductor thin-films and electronic devices

After the world’s first transistor in 1947, inorganic field-effect transistors (FETs) have been the backbone of the semiconductor industry. However, organic thin-film transistors (OTFTs) have received increasing interest because of their potential applications in chemical vapor sensors due to a strong charge transport dependence on chemical environments.[1-6] Although the performance, such as carrier mobility, of organic semiconductor devices does not compete with those of single-crystalline inorganic semiconductors, such as Si, Ge, and GaAs, they still have considerable advantages in terms of large-area and low-cost manufacturing of the electronic devices, chemically sensitive field-effect transistors (ChemFETs) and sensors. For example, the unique processing characteristics and demonstrated performance of OTFTs suggest that they can be competitive candidates for existing or novel thin film transistor applications requiring chemical vapor sensing, structural flexibility and low temperature processing.

Research efforts on semiconducting conjugated organic thiophene oligomers, thiophene polymers, metal phthalocyanine (MPC) and the small pentacene molecule have led to dramatic improvements in the mobility of these materials by five orders of magnitude due to innovative chemistry and processing, as well as the increasing ability to control the self-assembly and ordering of oligomers, polymers, and nanocrystals over the last few decades, as shown in Figure 1.[7]
Figure 1. Performance of organic and hybrid semiconductors.[7]
1.2 Properties of organic thin film transistors

1.2.1 Structure

Organic semiconductor materials can function either as p-type or n-type. The most widely studied organic semiconductors have been p-type materials. Figure 2 and Figure 3 show some typical p-type and n-type organic semiconducting materials. The most widely studied organic semiconductor molecules are pentacene and thiophenes due to high mobilities.[3] The mobility of phthalocyanine (Pc) is relatively high (0.02 cm²/Vs) for a p-channel OTFT based on CuPc.[8] Moreover, the high chemical stability of copper phthalocyanine (CuPc) distinguishes this material from other high mobility organic semiconductors, like pentacene or rubrene. Table 1 lists the mobility and on/off current ratio measured from OTFTs as reported in the literatures for each one of the most promising organic semiconductors. The highest value of pentacene is similar to that of a-Si:H.
Figure 2. Molecular structures of common p-type organic semiconductors.[3]

α,ω-oligothiophene (m=4)
R = C_nH_{2n+1}; n = 0-8

Bis(dithienothiophene)

Pentacene

α,ω-dialkylantrahtadithiophene
R = C_nH_{2n+1}; n = 6, 12, 18

HT-poly(3-alkyl)thiophene
R = C_nH_{2n+1}; n = 6

Polyacetylene

Phthalocyanine
Figure 3. Molecular structures of common n-type organic semiconductors.[3]
Table 1. Mobility (µ) and on/off current ratio of OTFTs [9]

<table>
<thead>
<tr>
<th>Material</th>
<th>Mobility cm²/Vs</th>
<th>Ion /Ioff</th>
<th>W/L</th>
<th>Dep. method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper phthalocyanine</td>
<td>0.01-0.02</td>
<td>NR</td>
<td>NR</td>
<td>V*</td>
</tr>
<tr>
<td>Pentacene</td>
<td>2.7</td>
<td>10⁹</td>
<td>20-70</td>
<td>V</td>
</tr>
<tr>
<td>Polythiophene</td>
<td>~10⁻⁵</td>
<td>&gt;10²</td>
<td>NR</td>
<td>S**</td>
</tr>
<tr>
<td>Pentacene</td>
<td>1.5</td>
<td>10⁶</td>
<td>2.5</td>
<td>V</td>
</tr>
<tr>
<td>Pentacene</td>
<td>3.2</td>
<td>10⁹</td>
<td>250-1,000</td>
<td>V</td>
</tr>
<tr>
<td>Pentacene</td>
<td>0.21</td>
<td>&gt;10⁶</td>
<td>1,000</td>
<td>S</td>
</tr>
<tr>
<td>Pentacene</td>
<td>0.9</td>
<td>10⁶</td>
<td>1-20</td>
<td>S</td>
</tr>
<tr>
<td>Poly-3-hexylthiophene (P3HT)</td>
<td>0.96×10⁻⁴</td>
<td>NR</td>
<td>NR</td>
<td>S</td>
</tr>
<tr>
<td>Diphthalocyanine</td>
<td>10⁻³</td>
<td>NR</td>
<td>12</td>
<td>V</td>
</tr>
<tr>
<td>Polyacetylene</td>
<td>4×10⁻⁵</td>
<td>NR</td>
<td>180</td>
<td>S</td>
</tr>
<tr>
<td>Alpha-sexithienyl</td>
<td>3.3×10⁻⁴</td>
<td>NR</td>
<td>3.44</td>
<td>V</td>
</tr>
<tr>
<td>Poly(2,5 thiénylenevinylene)</td>
<td>0.22</td>
<td>NR</td>
<td>1,000</td>
<td>S</td>
</tr>
<tr>
<td>C60</td>
<td>0.3</td>
<td>NR</td>
<td>400</td>
<td>V</td>
</tr>
<tr>
<td>α-ω-hexathiophene</td>
<td>0.03</td>
<td>&gt;10⁶</td>
<td>21</td>
<td>V</td>
</tr>
<tr>
<td>Poly(3-hexylthiophene)</td>
<td>0.015-0.045</td>
<td>4×10⁻⁵-10⁻⁴</td>
<td>20.8</td>
<td>S</td>
</tr>
<tr>
<td>Pentacene</td>
<td>10⁻¹-10⁻²</td>
<td>~10⁵</td>
<td>&gt;150</td>
<td>S</td>
</tr>
<tr>
<td>Bis(dithienolthiophene)</td>
<td>0.05</td>
<td>10⁶</td>
<td>500</td>
<td>V</td>
</tr>
<tr>
<td>Pentacene</td>
<td>0.7</td>
<td>10⁷</td>
<td>11</td>
<td>V</td>
</tr>
<tr>
<td>BTET</td>
<td>0.001</td>
<td>NR</td>
<td>~17</td>
<td>S</td>
</tr>
<tr>
<td>α-ω-dihexyl-hexathiophene</td>
<td>0.13</td>
<td>&gt;10⁴</td>
<td>7.3</td>
<td>V</td>
</tr>
<tr>
<td>Poly-3-hexylthiophene</td>
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<td>10⁶</td>
<td>NR</td>
<td>S</td>
</tr>
<tr>
<td>DHa4T</td>
<td>0.039</td>
<td>NR</td>
<td>4</td>
<td>V</td>
</tr>
<tr>
<td>α-ω-Dialkyl thiophene</td>
<td>0.01</td>
<td>&gt;10⁴</td>
<td>NR</td>
<td>S</td>
</tr>
<tr>
<td>PAPSAH</td>
<td>2.14</td>
<td>36.6⁴</td>
<td>NR</td>
<td>S</td>
</tr>
<tr>
<td>ADT</td>
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<td>NR</td>
<td>1.5-4</td>
<td>V</td>
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<tr>
<td>Pentacene</td>
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<td>NR</td>
<td>NR</td>
<td>V</td>
</tr>
<tr>
<td>Pentacene</td>
<td>0.38</td>
<td>NR</td>
<td>4</td>
<td>V</td>
</tr>
</tbody>
</table>

*: Vapor based deposition method.

**: Solution based deposition method.
1.2.2 Electrical properties of organic thin film transistors

OTFTs can be designed in a number of configurations as the active layer is usually deposited onto the gate dielectric. Figure 4 shows two typical schematic structures used in OTFTs. Charge carriers are accumulated by the gate capacitor and flow between the source and drain electrodes. The top-contact structure normally shows better performance than those with bottom contact structure due to low contact resistance. However, the top contact structure on Si wafer is difficult to fabricate after deposit organic materials using photolithography process. Therefore, bottom-contact structure is the dominate configuration for OTFTs in literature reports,[2, 3, 8, 10, 11] and the bottom contact structure is more suitable for device scaling and chemical sensing studies.[1, 5, 6, 12]
Figure 4. OTFT device configurations: a) Top-contact device, with source and drain electrodes evaporated onto the organic semiconducting layer through a shadow mask. b) Bottom-contact device, with the organic semiconductor deposited onto the gate insulator and the prefabricated source and drain electrodes using photolithography.[3]
Figure 5. Current-voltage characteristics of a bottom contact 12 ML CuPc OTFT with a channel length of 5 µm. (a) output characteristics (b) transfer characteristics for OTFTs obtained with the bilayer photoresist process, $V_{gs}=-10$ V.[13]
Typical current-voltage characteristics of a bottom contact 12 ML CuPc OTFT with a channel length of 5 µm is shown in Figure 5. [13] CuPc OTFTs exhibit p-type behavior (the majority carriers are holes). Thus, when the gate electrode is biased positively, the devices operate in the depletion mode. The field effect mobilities were extracted from the linear region based on equation (1.1) [14]

\[ I_d = \frac{nW}{L} \mu C_i (V_g - V_{th} - \frac{V_d}{2}) V_d, \]  

(1.1)

and in saturation region \((V_{ds} \gg (V_{gs} - V_{th}))\) based on equation (1.2) [14]

\[ I_{ds} = \frac{nW}{2L} \frac{\mu C_i}{(V_{gs} - V_{th})^2}. \]  

(1.2)

Here \(n\) is the number of fingers, \(W\) is the channel width, \(L\) is the channel length, \(C_i\) is the capacitance per unit area of the insulating layer, \(\mu\) is the field effect mobility, and \(V_{th}\) is the threshold voltage. The threshold voltages were extracted in the linear region by linearly extrapolating the transfer curves.

In the linear region, the overall device resistance \(R_{on}\) can be written as the sum of the intrinsic channel resistance \(R_{ch}\) and a contact resistance \(R_c\) according to equation (3), where \(\mu_i\) is the intrinsic mobility.[15]

\[ R_{on} = \frac{\partial V_d}{\partial I_d} \bigg|_{V_d \to 0} \mu_i = R_{ch} + R_c = \frac{L}{nWC_i \mu_i (V_g - V_{th})} + R_c, \]  

(1.3)

The contact resistance can be extracted by determining \(R_{on}\) from the linear region of the output characteristics.
1.2.3 Conduction mechanism in organic semiconductors

In inorganic semiconductors such as Si, Ge, and GaAs, the atoms are held together with very strong covalent bonds. In this case, the mobility is limited by lattice vibrations (phonons) that scatter the carriers and thus it is reduced as the temperature increases. In contrast, organic thin-films are held together by weak intermolecular interaction forces, typically van der Waals interactions. Therefore, organic thin-films contain a high density of trap states originated from either structural defects or impurities. Band transport is not applicable to disordered organic semiconductors, where carrier transport takes place by hopping between localized states and carriers are scattered at every step.

There are two existing analytical models describing the field-effect mobility in OTFTs: one is the variable range hopping model[16] and the other is the multiple trapping and release (MTR) model.[17, 18] According to the hopping model, the charge transport is by hopping of carriers between localized states. This model predicts a thermally activated mobility. Hopping is assisted by phonons and the mobility increases with temperature.[19] In the MTR model, the majority of the carriers are immobilized in the localized trap states. During their transit through the delocalized levels, the charge carriers interact with the localized levels through trapping and thermal release. The MTR model is currently the one most widely used to account for charge transport in amorphous silicon.
1.2.4 Chemical sensing properties

Organic semiconductors have found two main kinds of application in electronics so far: as materials for construction of various devices and as selective layers in chemical sensors.[20] Two-terminal chemiresistors and three-terminal ChemFETs have been utilized in chemical sensing. (Figure 6(a)) In the simplest form of a chemiresistor, small organic molecules or conducting polymers are deposited between a pair of electrodes on an insulating substrate. OTFTs or insulated gate field-effect transistor (IGFET) may be used as chemical sensors as shown in Figure 6. [20] The gaseous species act as either electron donor or electron acceptor and therefore change the device conductivity. In the OTFT structure, the gas species change the channel conductivity of the transistor. In the IGFET configuration, the gas species change the work-function of the organic thin-film, and therefore the current of the device.[21] In ChemFETs, particular attention must be paid to the quality of the contacts between the organic materials and the metal. If these are blocked, for example by thick insulating oxide, they are capacitive and cannot be chemically modulated.[22] Therefore, the bottom-contact OTFT fabricated in this work is an desirable configuration in chemical sensor.
Figure 6. Device configuration of organic chemical sensors. (a) Chemiresistor: B: bulk of the conducting polymer. S: surface. I: interface with the insulating substrate. C: interface with the contacts. (b)Thin-film transistor, (c) insulated gate field-effect transistor (IGFET).
1.4 Thesis Outline

In this thesis work, we have developed a practical device fabrication technique to obtain good OTFTs using the bilayer photoresist lift-off process. This thesis investigates the electrical properties of metal phthalocyanine thin-film devices. We have addressed the reliability and stability of OTFTs from both fundamental investigation and practical application perspectives. The bottom contact OTFTs with low contact resistance created in this work could serve useful in a variety of applications, and initial results are presented for their use as displays, optoelectronics, logic circuits, and sensors.

Chapter 1 gives a brief background on OTFTs including history, properties of OTFTs.

Chapter 2 discusses the microfabrication process of OTFTs to control the contact morphology and the charge transport properties of phthalocyanine thin-film devices that was used in this work.

Chapter 3 contains the channel thickness dependence of the mobility in bottom-contact copper phthalocyanine (CuPc) OTFTs, and discusses the current-voltage characteristics of bottom contact CuPc OTFTs with low contact resistance fabricated by the bilayer photoresist lift-off process.

Chapter 4 demonstrates the aging and recovery process in CuPc OTFTs For practical applications. An origin of the aging process on CuPc OTFTs has been investigated based on the responses of thick 1000ML CuPc OTFTs under a controlled atmosphere.
Chapter 5 gives a summary of the main results in the work, discusses some of the ongoing research, and what needs to be done in the future.

The following papers have been included in the thesis:


CHAPTER 2: Bilayer Processing for an Enhanced Organic-electrode Contact in Ultrathin Bottom Contact Organic Transistors

A bilayer lift-off process has been employed to fabricate optimal electrode contact geometry for statistical characterization of ultrathin OTFTs. For over 100 p-channel ultrathin (12MLs) copper phthalocyanine (CuPc) OTFTs, the bilayer photoresist lift-off process increased the field effect mobility by two orders of magnitude, decreased the contact resistance by three orders of magnitude, increased the on/off ratio by one order of magnitude, and the threshold voltage was decreased a factor of three compared to conventionally processed devices. The generality of the method was validated by fabricating OTFTs in four different phthalocyanines and CuPc OTFTs with 8 different channel thicknesses.

2.1 Introduction

Organic thin-film transistors (OTFTs) have received increasing attention because of their potential applications in displays, optoelectronics, logic circuits, and sensors such as the electronic nose.[23-28] Although the carrier mobility and other performance characteristic of organic semiconductor devices are low compared to single-crystal inorganic semiconductors, such as group IV semiconductors and compound semiconductors, OTFTs offer considerable advantages in lower processing temperature, larger area fabrication, and lower cost manufacturing. Semiconducting CuPc thin-films also have high chemical stability[2] and exhibit substantial responses to chemical analytes as chemiresistors.[1, 2, 4] Impedance spectroscopy has been used to identify analytes in metallophthalocyanine thin films.[5] Ultrathin OTFTs are of
technical interest not only as a means of studying intrinsic electrical properties of organic materials but also as a possible route toward reduced bias stress in standard OTFTs[12, 29] and enhanced sensitivity in chemical field-effect transistors (ChemFETs).[12] ChemFETs are OTFTs whose output characteristics are sensitive to the presence of analytes because when the analytes chemisorbs onto the channel materials, the channel mobility and/or threshold voltage are perturbed. Previous studies of the charge injection process from the metal contact to the conduction channel in OTFTs show that carriers conduct primarily through a few monolayers (MLs) above the gate dielectric.[30] Due to such a conduction mechanism, the contact between the electrode and the CuPc layer significantly affects the carrier transport behavior of organic films.[31] Therefore, it is desirable to find a practical fabrication method that provides minimal contact resistance for improved electrical properties.

This study reports a fabrication method for OTFTs which provides a low contact resistance between a CuPc channel and the source/drain electrodes. Contact resistance between the organic material and electrodes is a critical problem in bottom-contact OTFTs, an OTFT in which an organic channel layer is deposited on interdigitated source and drain electrodes. The channel profile becomes critical for ultrathin devices in which the organic channel thickness is smaller than the height of the electrodes. Careful tapering of the gold electrodes is required to avoid undercutting of the electrodes and thereby ensure excellent contact with the CuPc channel. Ultrathin thin channels are favorable for chemFETs because they exhibit far lower drift thereby making superior sensors.[6] We show that enhanced electrical properties can be achieved by employing a bilayer photoresist lift-off process [32-36] which sculpts the contact morphology at the edge of the electrodes. Statistical analysis of a large number
of devices of single layer and bilayer photoresist lift-off processes OTFTs revealed significantly different electrical properties. Large improvements in the electronic properties including the mobility, $I_{on}/I_{off}$ ratio, and threshold voltage were observed for bilayer photoresist lift-off processed OTFTs. The observed improvements in mobility, $I_{on}/I_{off}$ ratio and threshold voltage confirm the importance of the electrode-organic interface in bottom-contact OTFTs. The generality of the method was validated by fabricating OTFTs in four different phthalocyanines and CuPc OTFTs with 8 different channel thicknesses.

2.2 Organic thin film transistor device fabrication

2.2.1 Substrate preparation

Bottom-contact OTFTs were prepared by either the standard, single layer lift-off processing or a bilayer lift-off processing, on thermally grown SiO$_2$ (thickness of 100 nm) on (100) n$^+$ Si substrates. The heavily doped Si substrate and the SiO$_2$ served as a common gate and gate dielectric, respectively. Figure 7 illustrates the fabrication process of the OTFTs using the single layer photoresist lift-off [Figure 7(a)] and the bilayer photoresist lift-off process [Figure 7(b)]. After cleaning the SiO$_2$ layer on the n$^+$ Si substrate, the photoresist layers are deposited by spin coating. In the bilayer photoresist lift-off process, we utilize two different types of photoresist material with distinct etching rates: polymethylglutarimide (PMGI) as the bottom resist layer and Microposit® S1805 photoresist as the top resist layer. The underlying polymethylglutarimide (PMGI) resist layer develops nearly isotropically and etches faster in the Microposit® MF319 developer solution (Shiplay Corp.) than the top layer S1805. The amount of undercut is precisely controlled by the etching rate of PMGI.
[see Figure 7(b)] This differential etching rate produces a bi-layer with reentrant resist profiles as illustrated in Figure 7(b).

Shown in Figure 7(c) and Figure 7(d) are the SEM images of typical electrodes after the single layer photoresist lift-off process and the bilayer photoresist lift-off process; a total of 10 electrodes, each on a different device, were examined by SEM and all of them had nearly identical structures to those displayed in Figure 7(c) and Figure 7(d). The contact angles between the electrodes and the SiO₂ were measured for 10 electrodes of each type. The contact angles are +133.2 ± 13.8 ° and +51.2 ±7.8 ° for the single layer lift-off and bilayer lift-off process devices, respectively. The SEM data show that the single layer lift-off process produces an electrode with elevated edges while the double layer lift-off process produces a tapered electrode with the edges in contact with the substrate surface.
Figure 7. Outlines of the OTFT fabrication process using (a) single layer photoresist process (b) bilayer photoresist process. SEM images of the electrodes (c) after single layer photoresist lift-off processing and (d) after bilayer photoresist lift-off processing.
The OTFT devices are isolated by the 100 nm silicon dioxide layer, and the source and drain electrodes are deposited with the use of electron beam evaporation at a rate of 1 Å/second. A 5 nm thick Ti adhesion layer was applied first, followed by deposition of 45 nm thick Au for a total electrode thickness of 50 nm. Figure 8 shows device geometry: The electrodes consist of 45 fingers with 5 μm channel spacing and an electrode width of 2 mm. Figure 9 shows a MPc sensor array containing six microsensors in a ceramic packaging chip.

Figure 8. Optical image of the interdigitated electrodes consisted of 45 fingers with 5 μm channel spacing and an electrode width of 2 mm.
Figure 9. Image of a MPc sensor array containing six microsensors (each consists of 50 nm thick Au electrodes, 45 interdigitated fingers, and 5 μm channel spacing, on a 1 μm thick SiO₂ substrate) and then wirebonded in a ceramic packaging chip.
2.2.2 Organic thin film growth by OMBE

The molecular structure of CuPc is schematically illustrated in Figure 10 CuPc was purchased from Sigma-Aldrich and purified via multiple zone sublimations at 400°C and 10^{-5} torr for over 50 h with a yield over 70%. Twelve monolayers (12 ML) of CuPc were deposited on six chips with six OTFTs devices per chip to assess reproducibility.

Figure 10. Molecular structure of CuPc
Figure 11. Organic molecular beam epitaxy (OMBE). (a) Single layer OMBE system, and (b) Multi-layer OMBE system.
The CuPc was deposited by organic molecular beam epitaxy (OMBE) in a UHV chamber (Figure 11) with a base pressure of $2 \times 10^{-10}$ torr. The film thicknesses were measured during deposition with a quartz crystal microbalance and calibrated after deposition by both atomic force microscopy and low angle XRD measurements using a Rigaku RU-200B diffractometer with Cu K$_\alpha$ radiation.[37]

2.1.3 Sample analysis of organic thin film transistors

Surface morphology was measured by atomic force microscopy (AFM) using a Nanoscope IV Scanning Microscope in tapping mode and a VEECO 200 kHz probe. The CuPc film exhibits a granular structure with slightly ellipsoidal grains of approximately 47 nm length along the long axis and an RMS (route-mean-square) roughness of 1.8 nm. Figure 12 shows the surface morphology of the 12 ML of CuPc deposited on the SiO$_2$ substrate. CuPc molecules on Au (111) at monolayer coverage were reported by Chizhov et al using Scanning Tunneling Microscopy (STM) as shown in Figure 13. [38, 39]
Figure 12. The AFM morphology of 12ML CuPc deposited on a SiO$_2$ substrate.

Figure 13. STM image of CuPc on Au (111) at monolayer coverage [38, 39]
Figure 14. XRD profile around the (100) peak of a 12ML CuPc film with SUPREX refinement using a single layer model.

The d spacing was 13.3 Å in accordance with the XRD measurements, which show that the phthalocyanine molecules are oriented perpendicular to the substrate surface, as shown in Figure 14. The deposition rate of the CuPc films ranged from 0.3 to 0.5 Å/sec, and the deposition pressure was 1x10⁻⁸ torr. The substrate temperature was kept at 25°C during deposition. The OTFTs were mounted on a temperature-controlled stage monitored with two thermocouples. After deposition, the devices were stored under vacuum below 10 mtorr until electrical measurements were recorded. (Figure 15)
Figure 15. Molecular structure of phthalocyanine (CuPc) and a schematic device structure of the thin film CuPc field effect transistor (G, gate; S, source; D, drain).
2.3 Results and Discussion

2.3.1 Current-voltage characteristics of OTFTs

The OTFT devices are isolated by the 100 nm silicon dioxide layer, and the source and drain electrodes are deposited with the use of electron beam evaporation at a rate of 1 Å/second. A 5 nm thick Ti adhesion layer was applied first, followed by deposition of 45 nm thick Au for a total electrode thickness of 50 nm. For the bilayer resist process, 18 chips each containing six devices were fabricated. For the single resist process, 13 chips each containing six devices were fabricated. By fabricating a total of 108 bilayer resist process devices and 78 single resist process devices, statistically significant characterization can be performed to compare the two fabrication processes.

Shown in Figure 16 are the cross-sectional views of OTFT structures and typical SEM images after depositing 12 ML of CuPc on the electrodes of Figure 7(c) and Figure 7(d); a total of 10 electrodes, each on a different device, were examined by SEM and 100% had nearly identical structures to those displayed in Figure 16. The contact angles between the electrodes and the SiO₂ after CuPc deposition are $+136 \pm 10.1 \degree$ and $+40 \pm 4.4 \degree$ for the single layer lift-off and bilayer lift-off process devices, respectively. As shown in Figure 16(a), the single layer lift-off processed devices have electrodes that are physically detached from the organic channel. Conversely, the bilayer lift-off processed devices shown in Figure 16(b) have a smooth contact between the source/drain metal electrodes and organic channel. These results illustrates that the bilayer resist lift-off process better controls the edge shape of the electrodes and could
influence the contract resistance to the organic channel especially for ultra-thin channels.

Figure 16. CuPc and electrode configurations in OTFTs. (a) Undesirable electrical separation of ultrathin organic layer from the electrode in single photoresist liftoff processing (top: schematic structure, bottom: the SEM image after depositing 12 ML CuPc), (b) Enhanced electrical contacts with bilayer photoresist lift-off processing (top: schematic structure, bottom: the SEM image after depositing 12 ML CuPc. The scale bar represents 200 nm).
The DC electrical properties were determined from I-V measurements with a HP 4155A semiconductor parameter analyzer. The OTFT devices were characterized in an optically isolated probe station at 25°C to minimize photocurrent. The single layer lift-off and bilayer lift-off devices were processed under identical conditions (as a single batch during thin film deposition) to minimize process variation effects on electrical properties. CuPc has a HOMO level (5.3 eV), which is close to the Au work function (5.0 eV), and Au is known to be a good hole-injection electrode. Figure 17(a) and Figure 17(b) show the representative plots of source-drain current ($I_{ds}$) versus source-drain voltage ($V_{ds}$) at different gate-source voltages ($V_{g}$) from +8 to -12 V. The negative gate voltage is consistent with a hole-accumulation process in both types of OTFTs (single layer lift-off vs bilayer lift-off). The output characteristics of the OTFTs using the single layer photoresist lift-off process show a p-type behavior with a lack of current saturation as shown in Figure 17(a). Comparing Figure 17(a) with Figure 17(b), it is evident that the bilayer photoresist lift-off process significantly increases the on-state current, from $0.7 \times 10^{-6}$ to $2.6 \times 10^{-5}$ amperes, under the same $V_{ds}$ (-15 V) and $V_{g}$ (-12 V) conditions. Furthermore, with the bilayer photoresist lift-off process, the linear region and the saturation region are observed clearly. Figure 17(c) and Figure 17(d) represent the typical transfer curves of OTFTs at a fixed $V_{ds}$ of -10 V for the single layer lift-off vs the bilayer lift-off devices. All the devices were p-channel transistors, and all the bilayer lift-off devices had good ohmic behavior at low voltages.
Figure 17. Current-voltage characteristics of OTFTs with a channel length of 5 µm. (a) OTFTs by conventional single layer photoresist process, (b) OTFTs with bilayer photoresist lift-off process. (c) transfer characteristics for OTFTs with single layer photoresist process and (d) transfer characteristics for OTFTs obtained with the bilayer photoresist process , $V_{ds} = -10 \text{ V}$. 
As shown in Figure 17, while the transfer curves from the bilayer lift-off devices are consistent with a well behaved OTFT, the transfer curves from the single layer lift-off devices are consistent with an OTFT with a poor on-off ratio and poor subthreshold performance. Most of devices fabricated with the single layer lift-off process showed little current modulation, with on-off ratios <10^4.

The field effect mobilities were extracted from the linear region[14] based on equation (1).

\[ I_d = \frac{nW}{L} \mu C_i (V_g - V_{th} - \frac{V_d}{2})V_d. \]  

(2.1)

Here \( n \) is the number of fingers, \( W \) is the channel width, \( L \) is the channel length, \( C_i \) is the capacitance per unit area of the insulating layer, \( V_{th} \) is the threshold voltage, and \( \mu \) is the field effect mobility.

The electrical parameters were measured on 79 OTFTs fabricated with the bilayer liftoff process and 41 OTFTs using the single layer lift-off process; the results are summarized in Table 2. 91% of the bilayer lift-off processed devices had measurable electronic properties; the failures of 9% of the devices were mostly due to gate leakage. We only obtained measurable electrical properties from 41 OTFTs out of 78 (53 %) for devices fabricated using the single layer lift-off process, primarily due to poor reliability of the contacts.

The field effect mobility values extrapolated from the linear region are 3.4 ± 4.9 \( \times 10^{-6} \) cm^2/Vs and 6.1 ± 1.3 \( \times 10^{-4} \) cm^2/Vs for the single layer lift-off processed and the bilayer lift-off processed devices, respectively. The large difference in extrapolated field effect mobility values is consistent with a non-negligible parasitic resistance associated with the channel-electrode contacts. Furthermore, there was one order of magnitude
difference in on/off ratio between the single layer lift-off processed and the bilayer lift-off processed devices ($6.0 \times 10^3$ to $4.5 \times 10^4$). This increase in mobility and on/off ratio is consistent with a lower contact resistance in the bilayer photoresist process devices. In the linear region, the overall device resistance $R_{on}$ can be written as the sum of the intrinsic channel resistance $R_{ch}$ and a contact resistance $R_c$ according to equation (2), where $\mu_i$ is the intrinsic mobility.[15]

$$R_{on} = \frac{\partial V^g_d}{\partial I_d} \bigg|_{V_d=0} = R_{ch} + R_c = \frac{L}{nWC_i \mu_i (V_g - V_{th})} + R_c,$$  \hspace{1cm} \hspace{1cm} \hspace{1cm} (2.2)

The contact resistance can be extracted by determining $R_{on}$ from the linear region of the output characteristics. The contact resistance values calculated from the linear region are $1.84 \pm 2.14 \times 10^8$ ohm and $9.61 \pm 3.90 \times 10^4$ ohm for the single layer lift-off processed and the bilayer lift-off processed devices, respectively. We note that the dramatic improvement in device performance was not only the result of reduced contact resistance, but also the result of improved threshold voltages. The threshold voltages were extracted in the linear region by linearly extrapolating the transfer curves between $V_g = -5$ to -15 V.[14] The threshold voltages are $+5.7 \pm 4.7$ V and $+2.2 \pm 1.1$ V for the single layer lift-off and bilayer lift-off processed devices, respectively.

As shown in Table 2, the analysis of the standard deviations of the electrical parameters show that the fractional standard deviation of the mobility and on-current, are lower for the bilayer lift-off processed devices compared to the single lift-off processed devices, which is consistent with the former process being more uniform. In OTFTs, because the charge carriers are transported in a few MLs adjacent to the gate oxide,[40] small changes in the electrode profile can produce large changes in the contact resistance and devices performance.
Table 2. Comparative electrical characteristics of organic thin film transistors based on single layer vs bilayer photoresist lift-off process. (Mobilities extracted from the linear region, on/off ratio obtained from the drain current for $V_g = 15$ V to $V_g = -15$ V. The on-state current was calculated from the drain current at fixed $V_g = -15$ V and $V_d = -10$ V). The electrical parameters were measured on 79 OTFTs fabricated with the bilayer liftoff process and 41 OTFTs using the single layer liftoff process.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Bilayer photoresist liftoff process</th>
<th>Mean</th>
<th>sd</th>
<th>sd (%)</th>
<th>se</th>
<th>se (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Threshold voltage (V)</td>
<td>2.23</td>
<td>1.09</td>
<td>49</td>
<td>0.12</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Mobility (cm$^2$/Vs)</td>
<td>6.08×10$^{-4}$</td>
<td>1.27×10$^4$</td>
<td>21</td>
<td>1.43×10$^{-5}$</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Contact Resistance (Ω)</td>
<td>1.15×10$^5$</td>
<td>3.65×10$^4$</td>
<td>32</td>
<td>5.27×10$^3$</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>$I_{on}$ (A)</td>
<td>-4.13×10$^{-5}$</td>
<td>7.37×10$^{-6}$</td>
<td>18</td>
<td>8.30×10$^{-7}$</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>$I_{on}/I_{off}$ ratio</td>
<td>4.5×10$^4$</td>
<td>6.0×10$^4$</td>
<td>132</td>
<td>6.7×10$^3$</td>
<td>15</td>
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</tr>
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</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Single layer photoresist liftoff process</th>
<th>Mean</th>
<th>sd</th>
<th>sd (%)</th>
<th>se</th>
<th>se (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Threshold voltage (V)</td>
<td>5.71</td>
<td>4.7</td>
<td>82</td>
<td>0.73</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Mobility (cm$^2$/Vs)</td>
<td>3.45×10$^{-6}$</td>
<td>4.91×10$^{-6}$</td>
<td>142</td>
<td>7.67×10$^{-7}$</td>
<td>22</td>
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<tr>
<td>Contact Resistance (Ω)</td>
<td>1.84×10$^8$</td>
<td>2.14×10$^8$</td>
<td>116</td>
<td>3.38×10$^7$</td>
<td>18</td>
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</tr>
<tr>
<td>$I_{on}$ (A)</td>
<td>-4.46×10$^{-7}$</td>
<td>7.02×10$^{-7}$</td>
<td>-157</td>
<td>1.1×10$^{-7}$</td>
<td>24</td>
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<tr>
<td>$I_{on}/I_{off}$ ratio</td>
<td>6.0×10$^3$</td>
<td>9.4×10$^3$</td>
<td>157</td>
<td>1.5×10$^3$</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>
2.2.2 Field effect mobility vs contract resistant of the OTFTs

To document the correlation between contact resistance and output current, the variation of the field effect mobility of OTFTs with (a) bilayer photoresist process and (b) single layer photoresist process as a function of contact resistance in shown in Table 2. The field effect mobility consistently decreased with increasing contact resistance in the bilayer lift-off processed OTFTs as shown in Figure 18. The correlation coefficient for the linear fit is -0.90. Additionally, the intrinsic mobility obtained from the zero contact resistance intersection of the linear fit to data for bilayer lift-off process devices was $8.9 \times 10^{-4}$ cm$^2$/Vs at room temperature, which is comparable to the best values of mobility of bottom contact CuPc OTFTs with 12 - 25 µm long channels and between 50 - 60 nm thick CuPc layers.[8] For single layer lift-off processed devices, we observed an exponential correlation between the field effect mobility and contact resistance. The strong correlation between contact resistance and mobility is consistent with the contact mobility being the primary cause of reduced electrical performance in these ultra-thin OTFTs.

In order to examine the consistency of the processing, histograms showing the distributions of threshold voltages, mobilities and on-state currents at $V_g = -15$ V and $V_{ds} = -10$ V for bilayer lift-off process OTFTs are displayed in Figure 19. The histograms show a narrow distribution of device characteristics. The relatively narrow distributions of electrical properties in the bilayer lift-off process devices are consistent with better control of the electrode profile in the first few nanometers above the surface.
Figure 18. (a) Variation of the field effect mobility of OTFTs with bilayer photoresist process and (b) variation of the field effect mobility of OTFTs with single layer photoresist process as a function of contact resistance.
Figure 19. Histograms showing statistical distribution of (a) threshold voltage, (b) mobility and (c) on-state current determined from analysis of 79 devices using bilayer photoresist lift-off process.
The generality of the method was validated by fabricating OTFTs in four different phthalocyanaines (CuPc, NiPc, H₂Pc and CoPc) and CuPc OTFTs with 8 different channel thicknesses (4ML to 1047ML). (see EPAPS document).\textsuperscript{17} The contact resistance values (mean +/- standard deviation) with different phthalocyanines are $9.6 \pm 3.9 \times 10^4$ ohm (CuPc 12ML), $4.8 \pm 3.4 \times 10^4$ ohm (NiPc 12ML), $2.5 \pm 0.7 \times 10^5$ ohm (H₂Pc 12ML), and $1.4 \pm 1.4 \times 10^5$ ohm (CoPc 12ML). The contact resistance values with different CuPc thicknesses are $3.9 \pm 3.9 \times 10^6$ ohm (4ML), $9.6 \pm 3.9 \times 10^4$ ohm (12ML), $1.60 \pm 0.4 \times 10^6$ ohm (36ML), $1.20 \pm 0.6 \times 10^6$ ohm (100ML), $5.4 \pm 2.6 \times 10^5$ ohm (150ML), $6.4 \pm 1.4 \times 10^5$ ohm (250ML), $6.9 \pm 0.9 \times 10^5$ ohm (494ML), and $2.8 \pm 1.6 \times 10^5$ ohm (1047ML) for the bilayer lift-off processed CuPc devices. The higher contact resistance of the 4ML CuPc devices may be due to incomplete film coverage above the third layer or differences in film texture.[6] As compared with the contact resistance on the single layer lift-off processed electrodes ($1.8 \pm 2.1 \times 10^8$ ohm, CuPc 12ML), the bilayer photoresist lift-off process on different phthalocyanines and different CuPc thicknesses decreased the contact resistance by between two and three orders of magnitude. Furthermore, all of fabricated OTFTs using the bilayer lift-off process showed the clear saturation behavior.

The contact resistance values with different CuPc thicknesses and different phthalocyanaines (CuPc, NiPc, H₂Pc and CoPc) are shown in Table 3. The contact resistance can be extracted by determining $R_{on}$ from the linear region of the output characteristics at fixed gate voltage ($V_{gs} = -12V$). SD is the standard deviation.
Table 3. Comparative contact resistance ($R_c$) of OTFTs based on bilayer photoresist lift-off process with different CuPc thicknesses and different phthalocynaines.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Thickness (MLs)</th>
<th>$R_c$ Mean (W)</th>
<th>SD</th>
<th>No. of devices</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuPc</td>
<td>4 ML</td>
<td>$3.90 \times 10^6$</td>
<td>$3.90 \times 10^6$</td>
<td>8</td>
</tr>
<tr>
<td>CuPc</td>
<td>12 ML</td>
<td>$9.60 \times 10^4$</td>
<td>$3.90 \times 10^4$</td>
<td>79</td>
</tr>
<tr>
<td>CuPc</td>
<td>36 ML</td>
<td>$1.60 \times 10^6$</td>
<td>$3.90 \times 10^5$</td>
<td>8</td>
</tr>
<tr>
<td>CuPc</td>
<td>100 ML</td>
<td>$1.20 \times 10^6$</td>
<td>$5.80 \times 10^5$</td>
<td>10</td>
</tr>
<tr>
<td>CuPc</td>
<td>150 ML</td>
<td>$5.40 \times 10^5$</td>
<td>$2.60 \times 10^5$</td>
<td>3</td>
</tr>
<tr>
<td>CuPc</td>
<td>250 ML</td>
<td>$6.40 \times 10^5$</td>
<td>$1.40 \times 10^5$</td>
<td>7</td>
</tr>
<tr>
<td>CuPc</td>
<td>494 ML</td>
<td>$6.90 \times 10^5$</td>
<td>$9.40 \times 10^4$</td>
<td>3</td>
</tr>
<tr>
<td>CuPc</td>
<td>997 ML</td>
<td>$3.10 \times 10^5$</td>
<td>$1.30 \times 10^5$</td>
<td>4</td>
</tr>
<tr>
<td>CuPc</td>
<td>1047 ML</td>
<td>$2.80 \times 10^5$</td>
<td>$1.60 \times 10^5$</td>
<td>3</td>
</tr>
<tr>
<td>NiPc</td>
<td>12 ML</td>
<td>$4.83 \times 10^4$</td>
<td>$3.41 \times 10^4$</td>
<td>3</td>
</tr>
<tr>
<td>H2Pc</td>
<td>12 ML</td>
<td>$2.52 \times 10^5$</td>
<td>$6.76 \times 10^4$</td>
<td>3</td>
</tr>
<tr>
<td>CoPc</td>
<td>12 ML</td>
<td>$1.37 \times 10^5$</td>
<td>$1.35 \times 10^5$</td>
<td>3</td>
</tr>
</tbody>
</table>
2.3 Summary

In summary, ultrathin, organic thin film transistors (OTFTs) with significantly improved properties have been produced using a bilayer lift-off photoresist process. About two orders of magnitude improvement in the field effect mobility, one order of magnitude larger on/off ratio ($6.0 \times 10^3$ to $4.5 \times 10^4$), and a factor of three lower threshold voltage were obtained using the bilayer photoresist lift-off process. The results were consistent with a careful tapering of the electrodes being a requirement for high performance in ultra-thin OTFTs. The observed improvements in mobility, $I_{on}/I_{off}$ ratio and threshold voltage indicate the crucial role of interface contacts in charge transport in bottom-contact OTFTs.

CHAPTER 3: Channel Thickness versus Mobility in Copper Phthalocyanine Thin Film Transistors with Nanoscale Tapered Electrodes

The channel thickness dependence of the mobility was investigated in bottom-contact copper phthalocyanine (CuPc) OTFTs. A bilayer lift-off process has been employed to fabricate sculpted electrode contacts to nearly eliminate contact resistance. The current-voltage characteristics of bottom contact CuPc OTFTs fabricated with the bilayer photoresist lift-off process were analyzed to determine the mobility, threshold voltage and contact resistance. In contrast to all previous studies, the mobility and the threshold voltage were found to have only a small variation with channel layer thickness between 12 monolayers (MLs) and 1000 (±5%) ML. Channel film thickness dependence was consistent with the charge transport process in OTFTs being confined to the first few MLs above the gate dielectric and the doping resulting primarily from O₂ adsorption at the air/MPC interface. The independence of measured electronic properties on channel thickness differs from previous studies and may be attributed to the contact resistance being negligible due to the tapering of the bottom contact electrodes in the present study.

3.1 Introduction

Organic thin film transistors (OTFTs) have attracted much attention because of their application in chemical sensors and electronic devices. Recently, it has been shown that contact resistance and contact stability are crucial for device performance.[3, 10, 11, 30, 41] Phthalocyanines (MPcs) represent one of the most promising class of OTFTs. They have been employed as gas sensors (chemFETs) because of their excellent film growth properties, advantageous electronic properties, and chemical
stability.[1-3, 5, 6, 12, 42] Although important progress has been made in determining the role of deposition conditions on MPc OTFT device performance,[43-47] only a limited number of systematic studies have been reported concerning the dependence of device performance on electrode geometry.[11, 13, 48] Several studies have shown that OTFTs have mobilities which depend strongly on film thickness,[49-51] but this is in conflict with the hypothesis that all conductivity occurs in the first few MLs above the gate dielectric.[13, 52]. Possible explanations for the strong variation of channel mobility with film thickness include variation in MPc channel doping, contact resistance, and morphology with film thickness. The present work shows that true channel mobility is nearly thickness independent for films more than 12 ML thick, which is consistent with nearly all the conductivity occurring in the first few monolayers.

3.2 Experimental details

3.2.1 Electrode fabrication

Substrate-gated, bottom-contact OTFTs were fabricated by bilayer photoresist photolithography and lift-off processing[13] on (100) n⁺ Si substrates with 100 nm SiO₂, the gate dielectric, from Nova Electronic Materials, Ltd. The electrodes were fabricated on a SiO₂ surface by a two step spin-coating process (300 nm polymethylglutarimide (PMGI) as the bottom resist layer and 2 µm Microposit® S1818 photoresist as the top resist layer) and photolithographically patterning both resists in a single step.
Figure 20. SEM images of electrode. (a) Metal electrode deposition on the interdigitated pattern using bilayer photoresist photolithography, (b) High magnification of the dotted area of (a), and (c) cross-section image of a 4ML CuPc layer on the Au electrode after liftoff.
As shown in Figure 1(a) and Figure 20(b), a reentrant profile is produced by the differential development rate of the two components of the bilayer resist. Source and drain contacts were fabricated by electron beam deposition at a rate of 1 Å/second of a 5nm Ti adhesion layer and a 45 nm of Au layer followed by lift-off patterning. The electrodes consist of 45 pairs of gold fingers, with a 5 μm gap and an electrode width of 2 mm. Six pairs of electrodes were grown on each substrate to verify OTFT reproducibility.

3.2.2 Thin Film Deposition

CuPc was deposited by organic molecular beam epitaxy (OMBE) at ~0.5 Å/sec under high vacuum (base pressure < 1x10^{-8} torr), with the substrate temperature during deposition held constant at 25°C. CuPc was obtained from Sigma-Aldrich and zone purified at 400°C and 10^{-5} torr for over 50 h with a yield over 70%. CuPc films with thicknesses ranging from 4MLs to 997MLs were deposited on chips with six OTFT devices per chip to assess reproducibility. Shown in Figure 20(c) is the cross-sectional SEM images of typical electrodes after depositing 4ML thick CuPc films, which is the thinnest film thickness in this study. The film thicknesses were monitored during deposition with a quartz crystal microbalance (QCM). The QCM was calibrated with both atomic force microscopy (AFM) and low angle XRD measurements employed a Rigaku RU-200B diffractometer with Cu Kα radiation to guarantee accurate control of the film thickness. XRD revealed the films deposited at 25 °C to be textured α phase. The CuPc molecules in the bulk of the film are oriented perpendicular to the substrate
surface with 13.3 Å for the d spacing.[37] After deposition, electrical measurements of the devices were recorded within one hour.

3.3 Results and Discussion

The bilayer lift-off process was employed to fabricate optimal electrode contact geometry for CuPc OTFTs with low contact resistance. 12 ML devices fabricated using the two different electrode geometries were used to show the dependence of contact geometry on the contact resistance. The contact resistance was determined using D.C. electrical measurements, scanning Kelvin probe microscopy (SKPM), and the transfer line method (TLM). Subsequently, the electrical properties of CuPc OTFTs with sculpted contacts were measured as a function of the channel CuPc layer thickness from 4 MLs to 1000 (±5%) MLs. Minimizing the contact resistance provides electrical measurements that reflect the channel mobility dependence on the channel thickness.

3.3.1 Optimal CuPc OTFTs with low contact resistance

The current (I) – voltage (V) characteristics were measured with a HP 4155A semiconductor parameter analyzer at 10V/s sweep rate in an optically isolated probe station at 25°C to minimize photocurrent. Figure 21(a) and Figure 21(b) show the representative output characteristics (source-drain current (I_{ds}) versus source-drain voltage (V_{ds})) of 12ML CuPc OTFTs at different gate-source voltages (V_{gs}) from +4V to -12 V for a single layer photoresist lift-off processed device and a bilayer photoresist lift-off processed device[13].
Figure 21. Output characteristics of 12ML CuPc OTFTs with 5µm channel length. (a) electrodes fabricated with the single layer photoresist and (b) tapered electrodes fabricated with the bilayer photoresist liftoff process. The insets show the cross-section of the SEM images and the electrode layout for each device.
The insets in Figure 21 show the cross-sectional SEM image and the electrode geometry for each device (note: six devices of each type were fabricated; the data shown in Figure 21 are representative of all these devices). The output characteristics of the 12ML CuPc OTFTs using the single layer photoresist lift-off process show a nonlinear behavior at low $V_{ds}$ and no apparent current saturation (Figure 21(a)), which is consistent with a large contact resistance between the CuPc channel and the source/drain electrodes due to the poor electrode shape.[53] Conversely, with the bilayer photoresist lift-off process the linear region and the saturation region are observed clearly. Over 100 of the bilayer photoresist lift-off devices had good saturation behavior at high $V_{ds}$, as shown in Fig 2(b), which is consistent with a low contact resistance from the nanoscale tapered edge shape of the bilayer processed electrodes. To quantify the role of electrode shape, the contact resistances were extracted for single and bilayer processed OTFTs from the linear region of the output curves.[15] The contact resistance values differed by 200x: at $V_{ds} = -1\text{V}$ and $V_{gs} = -12\text{V}$ the contact resistances are $1.84 \pm 2.14\times10^8 \Omega$ and $9.61 \pm 3.90\times10^4 \Omega$, respectively, for the single layer lift-off processed and the bilayer lift-off processed devices.[13]

To further confirm the low contact resistance in bilayer processed 12ML CuPc OTFTs, the contact resistance was calculated using the transfer line method (TLM)[15] from 12 ML OTFTs with channel lengths from 5 to 160 µm (see Figure 22). In this method, the total resistance is assumed to be the sum of the channel resistance and contact resistance. The TLM contact resistance on 12 ML CuPc OTFTs was $3.7\times10^5\Omega$ at $V_{gs} = -12\text{V}$, which is comparable to the value obtained from the I-V characteristics, considering the differences in drain voltage and channel length between the two
methods. To further characterize the role of contact resistance in the poor output characteristics of the single layer processed devices, the surface potentials on the 12 ML single and bilayer processed devices were measured by SKPM (Nanoscope IV Scanning Microscope in tapping mode with a VEECO 200 kHz probe).[54, 55] SKPM uses an atomic force microscope (AFM) tip to map the potential between the source and drain electrodes as a function of gate and source-drain voltages. This allows the contact resistance to be quantified by measuring perturbations to the potential at the source-channel and channel-drain interfaces. [56-58] The bilayer photoresist lift-off processed devices have small symmetric potential drop of 1V across the source and drain contacts compared to 8V on the source contact side of the monolayer photoresist lift-off processed devices.[59] The bilayer photoresist lift-off processed device potential drops are sufficiently small that the output characteristics can be employed to calculate the channel mobility accurately. By minimizing the barrier to carrier injection, the bilayer photoresist lift-off process has effectively eliminated contact resistance in the CuPc OTFTs, providing nearly ideal I-V characteristics in the linear region as shown in Figure 21(b).
Figure 22. Resistance as a function of channel length from 5 to 160 μm with 12ML CuPc OTFTs at $V_{ds} = -10\text{V}$ and gate voltages ($V_{gs}$) from -4 V to -12 V. The y-axis intercepts correspond to the contact resistance of CuPc OTFTs.
3.3.2 Thickness effects (AFM, IV)

Figure 23 shows the film morphology of the channel layer with 4ML to 997ML CuPc film thickness on devices fabricated with the bilayer photoresist lift-off process. The 1.3 nm step height of the molecular islands corresponds to standing CuPc molecules. For a 4 ML thickness, CuPc has a continuous film up to the third layer and contains grains of about 21 nm in diameter as shown in Figure 23(a). For thicker films, such as 494 ML in Figure 23(e) and 997 ML in Figure 23(f), the growth mechanism competes with various coarsening (reconstruction) processes and results in large island formation. The root-mean-square (RMS) surface roughness increases linearly from 0.7 nm to 62 nm for the 4ML and 997ML CuPc films, respectively, but is always a small fraction of the film thickness. The conductivity of CuPc thin films depends on the O2 doping level. The CuPc films are primarily doped by O2 at the metal centers exposed to air at the MPc/air interface,[60, 61] and oxygen acts as an electron acceptor in p-type CuPc films.[62]

\[
\text{CuPc} + \text{O}_2 \rightarrow \text{CuPc}^+ + \text{O}_2^- \quad (3.1)
\]

O2 bonds to the metal center of the phthalocyanine molecule; therefore, the potential number of doping sites can be estimated by counting the number of exposed surface metal centers. Unfortunately, the exact structure of the surface layer is not precisely known.[63] Since the films are in the α phase, a perfect surface with bulk-like termination would have no exposed metal centers; in this case all the exposed metal centers would be at grain boundaries and step edges. Although AFM can determine the
size of individual MPc grains, it cannot resolve monoatomic steps. It is possible that the monoatomic step density is thickness independent while the RMS roughness is thickness dependent. Furthermore, it is possible that there is a surface reconstruction in which the top-layer lies flat with exposed metal center as observed for t-t-butyl-FePc/Au(111). [63]

Figure 23. AFM images (1 X 1 um) of a CuPc layer on SiO$_2$ with different CuPc thicknesses. (a) 4ML, (b) 36ML, (c) 150ML, (d) 250ML, (e) 494ML, and (f) 997ML. RMS roughness is linear with film thickness at a rate of 0.06 nm/ML. Grain size follows a power law of about 1/10 with thickness of film.
Figure 24 presents the representative current-voltage characteristics of our fresh OTFTs and illustrates the OTFT performance with different film thicknesses for 118 different devices [7 (4ML), 79 (12ML), 7 (36ML), 12 (100ML), 6 (250ML), and 7 (997±5%ML)] fabricated with the bilayer photoresist lift-off process. These output characteristics were measured on at least 6 duplicates for each device, and the output current at saturation at high gate voltages had a standard deviation less than 33% for all thicknesses. The current-voltage characteristics are similar for devices ranging from 12MLs to 997MLs. This is consistent with a charge transport mechanism in which all the carriers conduct in the first few MLs near the gate dielectric.

In order to examine the consistency of the processing, histograms showing the distributions of on-state currents at $V_g = -12$ V and $V_{ds} = -15$ V for the bilayer lift-off processed OTFTs are displayed in Figure 25. The histograms show a narrow distribution of device characteristics with different CuPc thicknesses. The relatively narrow distributions of electrical properties in the bilayer lift-off process devices are consistent with control of the electrode profile in the first few nanometers above the surface.
Figure 24. Output characteristics of fresh CuPc OTFTs with different CuPc thicknesses. (a) 4ML, (b) 12ML, (c) 36ML, (d) 100ML, (e) 250ML, and (f) 997ML.
Figure 25. Histograms showing statistical distribution of (a) on-state current at $V_{ds} = -15V$, $V_g = -12V$, (b) contact resistance, (c) threshold voltage, and (d) mobility from analysis of 7 (4ML), 10 (12ML), 7 (36ML), 10 (100ML), 6 (250ML), and 4 (997ML) devices using the bilayer photoresist lift-off process.
The field effect mobilities and threshold voltages can be obtained from the device characteristics in saturation region \((V_{ds}>> (V_{gs}-V_{th}))\) based on Eq. (3.2) [14]

\[ I_{ds} = \frac{nW}{2L} \mu C_i (V_{gs} - V_{th})^2. \]  

(3.2)

Here \(n\) is the number of fingers, \(W\) is the channel width, \(L\) is the channel length, \(C_i\) is the capacitance per unit area of the insulating layer, \(V_{th}\) is the threshold voltage, and \(\mu\) is the field effect mobility. Figure 26 shows variation of the on-current (at \(V_{ds}=-10V, V_{gs}=-15V\)), contact resistance, the mobility and the threshold voltage for all the devices for each thickness. The variation in on-current is from \((-4.1 \pm 0.5) \times 10^{-6} \text{ A}\) (4ML) to \((-34.7 \pm 5.7) \times 10^{-6} \text{ A}\) (997ML). The contact resistance varies from \((2.9 \pm 2.6) \times 10^{6} \text{ \Omega}\) (4ML) to \((3.1 \pm 1.3) \times 10^{5} \text{ \Omega}\) (997ML). The threshold voltage ranges between \(2.3 \pm 3.3V\) (4ML) and \(3.4 \pm 0.9V\) (997ML). The mean device properties are plotted versus the log of the channel thickness in Figure 26. The mobility is about \(4 \times 10^{-4} \text{ cm}^2/\text{Vs}\) with a small random variation (<2x) with film thickness except in the 4 ML CuPc OTFTs as shown in Fig. 7(c). The one order of magnitude lower mobility of the 4 ML CuPc devices compared to 12 ML CuPc devices may be due to incomplete film coverage or differences in oxygen doping.[6] A similar dependence on the CuPc thickness was also seen for the variations in the threshold voltages, as shown in Figure 26(d). Though the RMS roughness increased from 1.8 nm to 62 nm for the 12 ML and 997ML CuPc films, as shown in Figure 23, the mobility and the threshold voltage were found to have only a small variation (less than 2x) over 36x change in film roughness and island size.
This is consistent with the extent of oxygen doping in grain boundaries having a negligible influence on the mobility for fresh devices. Instead, the density of oxygen doping sites in fresh devices is independent of film thickness and RMS roughness. The data suggests that for charge transport process in OTFTs, carriers conduct primarily through the first few MLs above the gate dielectric and that the number of oxygen adsorption sites varies little with RMS roughness. For all film thicknesses, the threshold voltage varies by less than 1V (30%); this again is consistent with grain boundaries playing a minimal role in the threshold voltage for fresh devices.
3.4. Summary

The contact resistance and thickness dependences of bottom-contact copper phthalocyanine (CuPc) OTFTs were investigated. In contrast to previous studies, the mobility and the threshold voltage were found to have only a small variation over 12 ML to 1000 (±5%) ML CuPc channel film thicknesses. This is consistent with the charge transport process in OTFTs being confined to the first few MLs above the gate dielectric and the doping resulting primarily from O₂ adsorption at exposed metal centers on MPc molecules at the air/MPc interface. The independence of measured electronic properties from channel thickness in this study versus previous studies is attributed to the contact resistance being negligible for all channel thicknesses with the use of tapered bottom contact electrodes.

This chapter, in full, has been prepared for “Channel Thickness versus Mobility in Copper Phthalocyanine Thin Film Transistors with Nanoscale Tapered Electrodes”, (In preparation) by J. Park, J. E. Royer, C. Colesniuc, J. S. Lee, F. I. Bohrer, A. Sharoni, T. Gredig, S. Jin, I. K. Schuller, W. C. Trogler, A. C. Kummel. The dissertation author was the primary investigator and author of this paper.
CHAPTER 4: Aging and Recovery Processes in Copper Phthalocyanine Thin Film Transistors

The aging and recovery processes in CuPc OTFTs were investigated by measuring the device characteristics of OTFTs with channel thickness between 4ML and 1000ML in dry clean air, moist clean air, and ambient air environments. While the aging process in ambient air for thicker CuPc OTFTs causes a loss of saturation behavior at high drain voltage, the aging process is greatly diminished in thinner CuPc OTFTs. However, the aging process is nearly absent in dry clean air for CuPc OTFTs of all thicknesses. Thick channel devices which had been aged in ambient air to the point of losing all saturation behavior could be restored to proper saturation behavior by exposure to clean moist air. The data is consistent with aging resulting from trace strong ambient oxidant adsorption in the grain boundaries.

4.1 Introduction

The recent demand for low cost, versatile electronic devices has stimulated interest in organic thin film transistors (OTFTs).[3, 17] Application of OTFTs as chemical sensors has shown promise in development of electronic noses (e-noses) and in nerve agent detection.[1, 64, 65] A major concern for OTFTs is long-term stability of the organic films.[29, 66] Developing OTFTs that can maintain sufficient stability in open environments remains a significant issue to be addressed before organic electronics can become commercialized. Although a few mechanisms have been
proposed to explain this instability [8, 67, 68], a limited number of studies have been reported concerning the dependence of the environment on OTFTs with channels of different thickness of metal phthalocyanines (MPc).[8, 62, 67-69] A systematic approach to isolating the cause of device degradation (“aging”) in copper phthalocyanine (CuPc) OTFTs can provide insight to the interactions of CuPc films with atmospheric agents.

4.2 Experimental details

*Electrode fabrication:* Metal electrodes consisting of Ti (5nm) and Au (45nm) were patterned on a heavily doped (100) n+ Si wafers (common gate) with thermally grown 100nm SiO$_2$ (insulator) from Nova Electronic Materials, Ltd using photolighography and a bilayer photoresist lift-off process.[13] In the bilayer photoresist lift-off process, two different types of photoresist material with distinct etching rates are utilized (50:50 mix polymethylglutarimide (PMGI) solution with equal volumes of pure PMGI SF13 and PMGI SF3 solutions to create about 300 nm height undercut layer as the bottom resist layer and Microposit® S1818 photoresist as the 2 µm height top resist layer). The underlying PMGI resist layer develops nearly isotropically and etches faster in the Microposit® MF319 developer solution (Shiplay Corp.) than the top layer S1818. Therefore, the amount of undercut is precisely controlled by the etching rate of PMGI. The electrodes consist of 45 pairs of interdigitated gold fingers forming a 5µm channel length and 2mm channel width. Six pairs of electrodes were grown on each substrate to verify reproducibility and increase yield.
**Thin Film Deposition:** CuPc was purchased from Sigma-Aldrich and purified via multiple zone sublimations at 400°C and 10^{-5} torr for over 50 h with a yield over 70%. CuPc films between 4 monolayers (MLs) and 1000 MLs thickness were deposited on chips with six OTFTs devices per chip to assess reproducibility. The CuPc was deposited by organic molecular beam epitaxy (OMBE) in a UHV chamber with a base pressure of 2x10^{-10} torr. The deposition rate of the CuPc films ranged from 0.3 to 0.5 Å/sec, and the deposition pressure was 1x10^{-8} torr. Substrate temperature during deposition was held constant at 25°C. The OTFTs were mounted on a temperature-controlled stage monitored with two thermocouples.

**Film Characterization:** After CuPc deposition, the electrode shapes were measured by field emission scanning electron microscope (FESEM). Surface morphology was measured by atomic force microscopy (AFM) using a Nanoscope IV Scanning Microscope in tapping mode and a VEECO 200 kHz probe. The film thicknesses were measured during deposition with a quartz crystal microbalance and calibrated after deposition by both atomic force microscopy and low angle XRD measurements using a Rigaku RU-200B diffractometer with Cu K_{\alpha} radiation. XRD revealed the films deposited at 25°C to be textured α phase. The d spacing was 13.3 Å in accordance with previous measurements that show that the phthalocyanine molecules are oriented perpendicular to the substrate surface.[37]

**Aging and recovery experiment:** To verify if water has a role in the charge trapping, the water content of the ambient atmosphere was decreased by purging with dry N\textsubscript{2} gas
or with pure dry air. Water vapor was introduced into the chamber by bubblers immersed in a Haake F8 constant temperature (15°C) bath and mass flow controllers. A constant total flow rate of 500 sccm (standard cm³ per minute) was applied during the dosing/purging cycle. Under these conditions, the number of trapped charges is dramatically reduced and their kinetics is slowed down significantly. The DC electrical properties were determined from I-V measurements. The OTFTs were characterized in an optically isolated probe station at 25°C to minimize photocurrent. Voltage was swept with 10V/s.

4.3 Results and Discussion

In this work, bottom contact OTFTs were prepared with channel thicknesses of 4ML to 1000 (±5%) ML CuPc films to investigate the effect of aging as a function of the channel thickness. Schematic cross-sections of the bottom contact OTFTs fabricated by the bilayer photoresist lift-off process[13] are shown in Figure 27. A thicker CuPc layer will have taller, high surface area gain boundaries which allow for more adsorption sites of oxidants (O₂, NOₓ, O₃) from the ambient air than a thinner CuPc layer. Three dimensional atomic force microscopy (AFM) images of (a) 4 ML CuPc and (b) 997 ML CuPc films are shown in Figure 28. Root-mean-square (RMS) roughnesses are 0.7 nm and 64.4 nm for 4ML CuPc and 997ML CuPc, respectively. The RMS roughness increases sublinearly with film thickness. For the thicker film, the RMS roughness is only 5% of the film thickness consistent with a film of small densely packed crystallites separated by tall gain boundaries.
Figure 27. Cross section of device structures (a) with a thin CuPc layer and (b) with a thick CuPc layer. For this devices, L(channel length) = 5 µm, W (channel width) = 2000 µm, the number of fingers is 45.
Figure 28. High resolution three-dimensional AFM images of (a) 4ML CuPc and (b) 997ML CuPc with 1 µm by 1 µm size.
OTFTs based on CuPc exhibit p-channel field-effect transistor behavior with distinct linear and saturation regions of operation, as shown by the I-V characteristics in Figure 24. The lower source-drain current of the 4 ML CuPc devices may be due to incomplete film coverage above the third layer or differences in film texture [6, 13]. After 14 days in ambient air, the source-drain currents were significantly increased for both 4ML (Figure 24(b)) and 997ML (Figure 24(e)) CuPc OTFTs. The aging effects are evident in two obvious I-V characteristics: increased drain-source current at $V_g = 0$ V and degraded saturation behavior. The aging is more dramatic in the 997ML CuPc OTFTs as seen in the output characteristics after 14 days in the ambient air (Figure 24(e)). The correlation between the film thickness and the effects of aging is consistent with gas adsorption induced trap states and fixed charge in the grain boundaries.[69] To remove the traps and fixed charge, the devices were stored in a high vacuum ($10^{-7}$ torr) chamber for 4 days. After 4 days in a high vacuum chamber, the 4ML CuPc OTFT recovered its initial I-V characteristics as shown in Figure 24(c), while the 997ML CuPc OTFT retains poor I-V saturation behavior with a high threshold voltage as shown in Figure 24(f), consistent with these devices having high fixed charge and trap densities [70-72].
Figure 29. Output characteristics of 4ML CuPc ((a), (b) and (c)) vs 997ML CuPc ((d), (e) and (f)) OTFTs. (a) and (d) as-prepared fresh devices, (b) and (e) after aging in the ambient air for 14 days, (c) and (f) after additional aging in a high vacuum (10^{-7} Torr) chamber for 4 days.

On-state current of OTFTs with different CuPc channel thickness at $V_{ds} = -15$V, $V_g = -12$V before aging and after aging in ambient air for 14 days are given in Figure 30. Before aging in ambient air, the current-voltage characteristics are independent of CuPc thickness (30ML to 1000ML), consistent with a charge transport mechanism in which all the carriers conduct in the first few MLs near the gate dielectric.[6, 52] However, the on-state current after aging in the ambient air for 14 days increases with increasing CuPc thickness consistent with the increase in on-current resulting from ambient induced doping (negative fixed charge and high trap density) in grain boundaries.[62]
Figure 30. On-state current with different CuPc thickness at $V_{ds} = -15V$, $V_g = -12V$ before aging and after aging in the ambient air for 14 days. Some error bars are less than the size of the data points.
Since the effects of aging were most dramatic in the thick CuPc devices, they were used for isolating the cause of aging in ambient air. Exposure of 1000ML thick CuPc OTFTs to a sequence of environments including ambient air, clean dry air (20% O<sub>2</sub>/N<sub>2</sub>), water vapor and N<sub>2</sub> isolated the causes of device degradation in thick CuPc OTFTs. Figure 31(a) shows the normalized on-state current with I<sub>max</sub> = -2.33 x 10<sup>-5</sup>A of 1000ML CuPc OTFTs at V<sub>ds</sub> = -15V, V<sub>g</sub> = -12V under different environments. Vapor pressure data was used with the Clausius-Clapeyron equation to calculate the concentration of water dose in parts per million (ppm). A dose of 8440ppm water vapor in N<sub>2</sub> or clean dry air carrier gas was used to create a relative humidity of roughly 30%. Four environments were employed: I. 30% relative humidity with pure N<sub>2</sub> for 3.5 hours; II. N<sub>2</sub> for 13 hours; III. Clean dry air for 17 hours; IV. 30% relative humidity with clean dry air at 25 °C for 3.5 hours. To verify reproducibility of the OTFT response to each environment, three devices were subject to an identical exposure cycle.

After 3.5 hours of exposure to 30% relative humidity with pure N<sub>2</sub> or with clean dry air at 25 °C, a 1000ML CuPc OTFT loses about 50% of its current at V<sub>ds</sub> = -15V, V<sub>g</sub> = -12V. However, recovery of the on current (V<sub>ds</sub> = -15V, V<sub>g</sub> = 0V) occurs upon exposure to 30% humidity with pure N<sub>2</sub> or with clean dry air. The data is consistence with previous reports that conductance of phthalocyanine films decreases upon exposure to water vapor.[1, 4, 73] Water vapor causes current losses for all CuPc films because it is an electron donor and the channel is p-type. This reduction of the CuPc film occurs at the air/CuPc interface or in the grain boundaries.[73] While desorption from the air/CuPc interface is relatively rapid, diffusion out of grain boundaries is slow.
for 1000 ML thick channels so prolonged exposure in a water-free environment is required for full recovery of the 1000ML thick channel OTFTs from exposure to water. Exposure to pure N₂ gas for 13 hours and clean dry air for 17 hours increases the output current by removing water molecules or trace strong oxidants. Oxygen in clean dry air (environment III, Figure 31(a)) further increases the CuPc film conductivity acting as the primary dopant in clean dry air for p-type CuPc films since it acts as an electron acceptor.[62]

\[ \text{CuPc} + \text{O}_2 \rightarrow \text{CuPc}^+ + \text{O}_2^- \] (4.1)

Figure 31(b) shows the I-V output characteristics of a fresh device exposed to ambient air for 45 minutes. Figure 31(c) shows the I-V output characteristics after exposure to clean dry air for 17 hours. Figure 31(d) shows the output characteristics after exposure to N₂ with 30% relative humidity at 25 °C for 3.5 hours. Figure 31(e) shows the I-V output characteristics after exposure to four cycles of gas sequences. As shown in Figure 31(b), the output characteristics of the initial CuPc OTFTs after exposure to ambient air for 45 minutes shows higher source-drain current at \( V_g = 0 \)V than the same device after dosing in various combination of water, clean dry air, and clean wet air as shown in Figure 31(e); this is consistent with the elevated threshold voltage being due to trace strong oxidants (for example O₃ and NOₓ) in ambient air and not due to any combination of O₂ and H₂O. [67, 74] After exposure to clean O₂, the linear region and the saturation region have higher source-drain currents for all gate voltages and negligible source-drain currents at \( V_g = 0 \)V as shown in Figure 31(e). These results suggest that O₂, H₂O and O₂/H₂O products are not responsible for the aging process in ambient air.
Figure 31. (a) Normalized on-state current with $I_{\text{max}} = -2.33 \times 10^{-5} \text{A}$ of 1000ML CuPc OTFTs with different environments at $V_{\text{ds}} = -15 \text{V}$, $V_{\text{g}} = -12 \text{V}$ (I. 30% relative humidity with N$_2$ at 25 °C for 3.5 hours; II. N$_2$ for 13 hours; III. Clean dry air for 17 hours; IV. 30% relative humidity with clean dry air at 25 °C for 3.5 hours). The output characteristics are shown at four points in the dosing sequence: (b) at the starting point where devices have been in the ambient air for 45 minutes after deposition, labeled “start”, (c) after exposure under clean dry air for 17 hours, labeled “1st”, (d) after exposure under 30% relative humidity with N$_2$ at 25°C for 3.5 hours, labeled “2nd”, and (e) after exposure to four complete gas sequences, labeled “End”.
To confirm that trace strong oxidants are responsible for the aging process, fully aged 1000 ML CuPc OTFTs were exposed to 30% relative humidity with clean dry air at 25 °C for 48 hours and pure dry air for 24 hours. The exposure sequence included H₂O because dosing with dry air could not restore the devices as shown in Figure 32.

Recovery was demonstrated on three fully aged devices with similar initial output characteristics; the deviation in saturation current between devices was less than 20% at both the beginning and end of the recovery sequence. Figure 33(a) shows the representative plots of source-drain current (I_{ds}) versus source-drain voltage (V_{ds}) at different gate voltages (V_{g}) from 0 to -12 V for fully aged 1000ML CuPc OTFTs which had been exposed to ambient air for more than two weeks. The device performance of the recovered 1000ML CuPc OTFTs is shown in Figure 33(b) after exposure to the clean controlled atmospheres for 3 days; the long time for recovery is due to thick devices being employed. Fully aged 1000ML CuPc OTFTs (Figure 33(a)) show a p-type behavior with a lack of current saturation and a high drain-source current at V_{g} = 0V (i.e. a large positive threshold voltage). Conversely, after exposure to the clean controlled atmospheres, the devices have relatively good saturation behavior even at high gate voltage and a low threshold voltage as shown in Figure 33(b). The variation of the source-drain current with time at V_{ds} = -15V with V_{g} = -12V and at V_{ds} = -15V with V_{g} = 0V under 30 % relative humidity with clean dry air and clean dry air at 25 °C are shown in Figure 33(c) and Figure 33(d), respectively. The source-drain current at V_{ds} = -15V with V_{g} = 0V was found to have only a small variation after decreasing under the humid environment as shown in Figure 33(d).
Figure 32. (a) Source-drain current at $V_{ds} = -15V$, $V_{g} = -12V$ and at $V_{ds} = -15V$, $V_{g} = 0V$ in clean dry air at 25 °C for 41 hours. (b) output characteristics of fully aged 1000ML CuPc OTFTs under ambient air, (c) output characteristics of fully aged 1000ML CuPc OTFTs after exposure to pure dry air for 41 hours.
Figure 33. (a) output characteristics of fully aged 1000ML CuPc OTFTs under ambient air, (b) output characteristics of fully aged 1000ML CuPc OTFTs after exposure to the clean controlled atmospheres under 30% relative humidity with clean dry air at 25 °C for 48 hours and pure dry air for 24 hours, (c) On-state current at $V_{ds}=-15V$, $V_{g}=-12V$ during the recovery test under 30% relative humidity with clean dry air at 25 °C for 48 hours and pure dry air for 24 hours, and (d) Source-drain current at $V_{ds}=-15V$, $V_{g}=0V$ under 30% relative humidity with clean dry air at 25 °C and clean dry air.

The recovery process was able to lower the threshold voltage by about 35x (from 6.22V to 0.17V), improve the on/off ratio by about 200x (from 7.6 to 1.5×10^3), and decrease the current slope at saturation by about 100 x (from 2 ×10^-6 A/V to 7×10^-8 A/V at $V_{g}=-6V$). These results are consistent with the aging effect being due to trace
strong oxidants in air reversibly adsorbing in grain boundaries to create fixed charge and trap states; the results are also consistent with the reversal of aging requiring water vapor since H₂O is also a strong chemisorbate.

4.4 Summary

In summary, the aging and recovery process in CuPc OTFTs were investigated by studying the I-V output characteristics of CuPc OTFTs in ambient air and in controlled atmospheres. The primary aging effects in ambient air include a large increase in off state current, a large positive threshold voltage, and a loss of saturation behavior even at high gate voltage. In controlled atmospheres of clean air with and without H₂O, none of the typical aging effects are observed consistent with O₂ and H₂O not playing a direct role in the aging process. The aging process in the ambient air is much more pronounced for thicker CuPc OTFTs than thin CuPc OTFTs. While the output current at high gate voltage is independent of channel thickness between 4ML and 1000ML, after aging the output current scales with channel film thickness; this is consistent with aging being due to adsorption of trace oxidants (for example O₃ and NOₓ) at grain boundaries causing an increase in fixed charge and trap states.[68, 75] The adsorption of the strong oxidant is reversible since the fully aged devices can be restored to proper working devices by prolonged exposure to clean air with H₂O.

This chapter, in full, has been prepared for “Aging and recovery processes in Copper Phthalocyanine Thin Film Transistors”, (In preparation) by J. Park, J. E. Royer, C. Colesniuc, F. I. Bohrer, A. Sharoni, S. Jin, I. K. Schuller, W. C. Trogler, A. C. Kummel. The dissertation author was the primary investigator and author of this paper.
CHAPTER 5: Summary, Conclusions, and Future Work

In summary, ultrathin organic thin film transistors (OTFTs) with significantly improved properties have been produced using a bilayer lift-off photoresist process. About two orders of magnitude improvement in the field effect mobility, one order of magnitude larger on/off ratio ($6.0 \times 10^3$ to $4.5 \times 10^4$), and a factor of three lower threshold voltage were obtained using the bilayer photoresist lift-off process. The results were consistent with a careful tapering of the electrodes being a requirement for high performance in ultra-thin OTFTs. The observed improvements in mobility, $I_{on}/I_{off}$ ratio and threshold voltage indicate the crucial role of interface contacts on charge transport in bottom-contact OTFTs.

Second, the contact resistance and thickness dependences of the bottom-contact copper phthalocyanine (CuPc) OTFTs were investigated. In contrast to all previous studies, the mobility and the threshold voltage were found to have only a small variation over 12 ML to 1000 (±5%) ML CuPc channel film thickness consistent with the charge transport process in OTFTs being confined to the first few MLs above the gate dielectric and the doping resulting primarily from O$_2$ adsorption at exposure metal centers on MPc molecules the air/MPc interface. The independence of measured electronic properties from channel thickness is due to the contact resistance being negligible for all channel thicknesses.

Finally, the aging and recovery process in CuPc OTFTs were investigated. We see clearly from the output characteristics an aging process on CuPc OTFTs in the ambient air. The aging process in the ambient air for thicker CuPc OTFTs is more significant than thinner CuPc OTFTs, which shows a poor current saturation behavior.
This may be due to aging induced traps in grain boundaries. The responses on 1000ML CuPc OTFTs in a controlled atmosphere at room temperature show the origin of the aging process on CuPc OTFTs. The main effect of aging in the ambient air might be due to NOx or ozone doping effect in the CuPc channel layer from the ambient air.[68, 75] The recovery process under 30 % relative humidity with pure dry air for 48 hours and pure dry air for 24 hours can improve the OTFTs performance with a good current saturation behavior, a high mobility, a low threshold voltage and a high current on/off ratio due to controlling dopants.

The potential applications for OTFTs are still great and it is believed that there will be real world devices that contain them at some point. Hopefully the control over contact geometry, aging and recovery of OTFTs demonstrated in this work will help take another step towards OTFTs making their way into everyday life.
REFERENCES


