Sol gel dielectrics for organic field effect transistors : investigations of device performance enhancement, molecular organization and interfacial chemistry effects

Cahyadi, Tommy

2008

Cahyadi, T. (2008). Sol gel dielectrics for organic field effect transistors : investigations of device performance enhancement, molecular organization and interfacial chemistry effects. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/13542>

<https://doi.org/10.32657/10356/13542>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**SOL GEL DIELECTRICS FOR
ORGANIC FIELD EFFECT TRANSISTORS:
INVESTIGATIONS OF DEVICE PERFORMANCE
ENHANCEMENT, MOLECULAR ORGANIZATION, AND
INTERFACIAL CHEMISTRY EFFECTS**

TOMMY CAHYADI

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2008

SOL GEL DIELECTRICS FOR ORGANIC FIELD EFFECT TRANSISTORS:
INVESTIGATIONS OF DEVICE PERFORMANCE ENHANCEMENT, MOLECULAR
ORGANIZATION, AND INTERFACIAL CHEMISTRY EFFECTS

TOMMY CAHYADI

2008

**SOL GEL DIELECTRICS FOR
ORGANIC FIELD EFFECT TRANSISTORS:
INVESTIGATIONS OF DEVICE PERFORMANCE
ENHANCEMENT, MOLECULAR ORGANIZATION, AND
INTERFACIAL CHEMISTRY EFFECTS**

TOMMY CAHYADI

School of Materials Science and Engineering

A thesis submitted to the Nanyang Technological University

in fulfillment of the requirement for the degree of
Doctor of Philosophy

2008

ACKNOWLEDGMENTS

“No progress is possible without the endeavors of people, and one cannot stop people from endeavors.” (Source unknown)

First of all, I would like to express my deep and sincere gratitude to my thesis advisor, Prof Subodh Gautam Mhaisalkar. He is not only a great scientist with deep vision but also and most importantly a kind person, who has always believed in me since the beginning. His wide knowledge in materials science and engineering and his logical way of thinking have been great value for me. With his encouragement and scientific excitement, I was able to make the right decisions in the most important moments of my research and I am glad to work with him.

I sincerely thank my co-advisor Dr Chen Zhikuan from IMRE who helped me start and carry on this project and provided me with the encouragement and solution at the unpredictable situations. I would also express my gratitude to Dr Ng Chee Mang, my mentor from Chartered Semiconductor Manufacturing, for his guidance and help, both academically and technically. I would like to thank Dr Lap Chan, our Special Project group advisor at Chartered, his passion for knowledge has inspired me to never stop learning.

Special thanks go to Prof Ananth Dodabalapur and his group members at UT Austin who helped me to get started with the organic electronics project. I would also like to thank Dr Qi Guojun and Huang Zhaohong from SIMTech for the assistance on the equipments at the earlier stage of this project. I am grateful to Prof Valipe Ramgopal Rao and Prof Rakesh Lal from IIT, Mumbai who were a constant source of invaluable knowledge and experience on electrical characterizations. Many thanks to Prof Beng S.

Ong for allowing me to learn valuable device fabrications from his previous group at XEROX Canada. Special thanks to Dr Wu Yiliang for providing support and guidance for the experiments, especially the PQT part.

This thesis involves a variety of characterization techniques, which became accessible because of the following people. I would like to thank Prof Shen Zexiang who let me use his Raman facility generously and Johnson Kasim who helped and coached me in the Raman measurements and analysis. I would also like to thank Yudi Setiawan for the TEM sample preparation training and for the TEM characterization. Thank you to Jiang Guo Dong for his help in providing me with the thermally grown silica.

This PhD journey has been exciting, unpredictable, and sometimes depressing. I would like to thank all members of Polymer Electronics group in MSE for providing support on this work and making the lab an enjoyable place to work. They include Nripan, Wei Lin, Willy, Phoebe, Ju Nie, Zongbin, Pei Si, Shripad, and Anup. Lastly, I am grateful for the assistance and friendship of present and previous MSE staff: Mastura, Yani, Sandy, Jing Li, Fiona, Irene, Xu Cheng, Swee Sing, Hui Fen, as well as Wunly for helping with the spelling error checking. The Special Project big family at Chartered, especially Batch 8, has also been a wonderful group of friends whose company has been encouraging and refreshing.

Finally, I would like to thank my parents and sisters for their constant support, understanding, care, concern, and encouragement. I would also like to apologize for the anxiety and trouble that I have caused in the few years.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	I
TABLE OF CONTENTS	III
SUMMARY	VI
LIST OF FIGURES	VIII
LIST OF TABLES	XIV
CHAPTER 1 INTRODUCTION.....	1
1.1 BACKGROUND.....	1
1.2 RESEARCH OBJECTIVES AND SCOPE.....	3
CHAPTER 2 LITERATURE REVIEW.....	6
2.1 ORGANIC SEMICONDUCTORS	6
2.1.1 Organic Molecular Crystals.....	10
2.1.2 Charge Transport in Organic Semiconductors	12
2.2 ORGANIC FIELD-EFFECT TRANSISTORS.....	14
2.2.1 Operation Principle.....	15
2.2.2 Fabrication of OFETs	18
2.3 GATE DIELECTRIC MATERIALS	19
2.3.1 Inorganic Dielectric Materials.....	20
2.3.2 Polymeric Dielectric Materials	22
2.3.3 Self-Assembled Mono- and Multilayers as Dielectric Materials	24
2.4 SOL-GEL GATE DIELECTRICS.....	25
2.4.1 Sol-Gel Method for Gate Dielectric in OFETs.....	25
2.4.2 Sol-Gel Process Steps: An Overview.....	26
2.5 PROGRESS IN OFETs PERFORMANCE	28
2.5.1 Routes to Performance Improvement	28
2.5.2 The Future of Improved Performance in OFETs	32
CHAPTER 3 EXPERIMENTAL PROCEDURES	34
3.1 SOL-GEL SYNTHESIS AND DEPOSITION	34
3.2 OFETs FABRICATION	35
3.2.1 Substrate Cleaning and Etching.....	36
3.2.2 Organic Semiconductors: Material and Purification.....	38

3.2.3	<i>Organic Thin Film Deposition</i>	39
3.2.4	<i>Metal Evaporation</i>	40
3.3	CHARACTERIZATION TECHNIQUES	40
3.3.1	<i>Atomic Force Microscopy (AFM)</i>	40
3.3.2	<i>Ellipsometer</i>	41
3.3.3	<i>Goniometer</i>	41
3.3.4	<i>Fourier Transform Infrared Spectroscopy (FT-IR)</i>	41
3.3.5	<i>Transmission Electron Microscopy (TEM)</i>	41
3.3.6	<i>X-ray Photoelectron Spectroscopy</i>	42
3.3.7	<i>Synchrotron X-ray Diffraction</i>	42
3.3.8	<i>Photoluminescence (PL)/Absorption/Raman Spectrum Measurement</i> ...	42
3.3.9	<i>Electrical Characterization</i>	43
	CHAPTER 4 RESULTS	44
4.1	SOL-GEL SILICA THIN-FILMS: BULK & SURFACE PROPERTIES	44
4.1.1	<i>Bulk Properties of Sol-Gel Silica Films</i>	45
4.1.2	<i>Surface Properties of Sol-Gel Silica Thin-Film</i>	48
4.2	OFET PERFORMANCE OF OSCs DEPOSITED ON SOL-GEL SILICA THIN-FILM AND THERMALLY GROWN SILICA	50
4.2.1	<i>Bulk vs Surface Effect of Sol-Gel Silica Thin-Film on Improved Transistor Performance</i>	55
4.2.2	<i>Sol-Gel Silica Thin-Film Bulk Properties Effect on Transistor Performance</i>	58
4.2.3	<i>Different Chemical Bonds in Sol-Gel Silica Thin-Film and Their Influence on Transistor Performance</i>	62
4.2.4	<i>Properties of Sol-Gel Silica Thin-Film and Their Effect on Ambient Performance</i>	64
4.3	MOLECULAR ORDERING INVESTIGATIONS ON OSCs DEPOSITED ON TOX VS SOL-GEL SILICA THIN-FILM	66
4.3.1	<i>Atomic Force Microscopy Study</i>	66
4.3.2	<i>X-ray Diffraction Study</i>	68
4.3.3	<i>Photoluminescence/Absorption Study</i>	70
4.3.4	<i>Raman Study</i>	73
	CHAPTER 5 DISCUSSION	77
5.1	SOL-GEL SILICA THIN-FILM PROPERTIES	77
5.2	IMPROVED OFETs PERFORMANCE ON SOL-GEL SILICA THIN-FILM ...	79
5.2.1	<i>Interrelation between Trapping Density and Transistor Performance</i> ...	79
5.2.2	<i>Correlation between Morphology, Molecular Ordering, and Enhanced Transistor Performance</i>	83
5.3	SOL-GEL SILICA DEVICE STABILITY	91
5.3.1	<i>Effect of Electret on Device Hysteresis</i>	91
5.3.2	<i>Chemistry and Trapping Effect on Device Hysteresis and Threshold Voltage Shift</i>	93

5.3.3	<i>Reversible Moisture Absorption and Desorption on Its Ambient Performance</i>	<i>95</i>
5.3.4	<i>Impact of Trapped Moisture on Transistor Charge Transport at Low Temperature</i>	<i>98</i>
CHAPTER 6 CONCLUSIONS		100
CHAPTER 7 FUTURE RECOMMENDATIONS		103
7.1	LARGE AREA PROCESSABILITY OF SOL-GEL SILICA DIELECTRICS....	103
7.1.1	<i>Control of Dense Silica for Strain-Free Stacked Dielectric Multilayers</i>	<i>103</i>
7.1.2	<i>Printing Method for Low Cost, Large Area Processing.....</i>	<i>104</i>
7.2	STABLE HIGH <i>K</i> PROPERTIES IN SOL-GEL SILICA THROUGH COLLOID-ALKOXIDE MIXTURE METHOD.....	105
7.3	PHOTOPHYSICS STUDY OF DEVICES FABRICATED ON FLEXIBLE SUBSTRATES	105
REFERENCES.....		106
APPENDIX A LIST OF ABBREVIATIONS		126
APPENDIX B AUTHOR’S PUBLICATION LIST		127

SUMMARY

The interfacial interactions between semiconductors and gate dielectrics have a profound influence on the device characteristics of field effect transistors (FETs). This thesis reports on the concept of introducing sol-gel silica as solution-processable inorganic gate dielectric with improved OFETs performance. The smoother film surfaces of sol-gel silica (~ 1.9 Å root-mean-square) and low surface energy (water contact angle of $\sim 75^\circ$) have been shown to allow effective modification of bottom layer topography without being limited by the chemistry required for self-assembled monolayer (SAM) functionalization, while simultaneously fine-tuning the dielectric surface, thus resulting in planarization of dielectric surface roughness in stacked gate dielectric applications.

Different sol-gel silica film thickness showed similar trends in improved performances indicating that this phenomenon clearly is a semiconductor-dielectric interface phenomenon, rather than a bulk dielectric effect. The dielectric-semiconductor interface, film morphology, and molecular ordering of the organic semiconductor molecules have a profound impact on mobility, threshold voltage, and other vital device characteristics of organic field-effect transistors. In this study, p-channel small molecule/polymer (evaporated pentacene and spin-coated poly(3,3''-didodecylquaterthiophene) – PQT) and n-channel fullerene derivative ({6}-1-(3-(2-thienylethoxycarbonyl)-propyl)-{5}-1-phenyl-[5,6]-C61 – TEPP-C61) show a significant enhancement in device mobilities ranging from $\sim 15\times$ to $\sim 45\times$ for all classes of semiconductors deposited on sol-gel silica gate-dielectric than on thermally grown silica. Atomic force microscopy, synchrotron X-ray diffraction, photoluminescence/absorption, and Raman spectroscopy studies provide comprehensive evidence that sol-gel silica dielectrics-induced enhancement in both p- and n-channel organic semiconductors is

attributable to enhanced molecular ordering/packing, and hence reduced charge trapping centers due to lesser chemical/physical defects at the dielectric-semiconductor interface.

The sol-gel silica effect on device stability, such as hysteresis, threshold voltage shift, and ambient performance, was also investigated. Vacuum and ambient studies of the hysteresis behavior and capacitance-voltage characteristics on single layer and varying thicknesses of bilayer dielectrics confirmed that blocking layers of thermal oxide could effectively eliminate the electret induced hysteresis, and that thin (25 nm) sol-gel silica dielectrics enabled elimination of nanopores thus realizing stable device characteristics under ambient conditions.

The low temperature study on the pentacene-based OFETs with sol-gel silica interfacial layer was compared to the OFETs without the sol-gel silica interfacial layer. It was found that there are a resultant of polarization effect in the sol-gel silica interfacial layer from the temperature dependent hysteresis and mobility observation. The polarization effect is ascribable to the water molecular dipoles and its behavior at low temperature.

Enhanced device performance with both p- and n-channel materials support the viability of using these materials and methodologies for large area printed electronics applications as dielectric layers or surface modifying layers to enable high mobilities coupled with low voltage applications in ambient environments.

LIST OF FIGURES

Figure 2.1 (a) Chemical structure of pentacene. Pentacene crystal structure in its single crystal: (b) view along the [100] axis (the layered structure can be seen) and (c) the herringbone arrangement within the layer, view along the long axis of the molecule. The unit cell orientation is also draw (after Ref. [37]).	11
Figure 2.2 OFET device configurations: (a) Top-contact device, with source and drain electrodes evaporated onto the organic semiconducting layer through a mask. b) Bottom-contact device, with the organic semiconductor deposited onto the gate insulator and the prefabricated source and drain electrodes. (After Ref. [2])	14
Figure 2.3 (a) Idealized energy level diagram of an organic TFT at $V_G = 0$ and $V_D = 0$. (b-e) Demonstrate the principle of field effect transistor operation for the case of (b) electron accumulation, (d) transport, (c) hole accumulation, and (e) transport. (After Ref. [81])	17
Figure 2.4 I - V curves for a FET operation. (Left) Output characteristics (I_D - V_D) for different applied gate voltage (V_G). The curves can be modeled by expression 2.1 and 2.3. (b) Transfer characteristics (I_D - V_G), semilogarithmic plot (left y-axis) and plot of $\sqrt{ I_D }$ - V_G (right y-axis). (After Ref. [2])	17
Figure 3.1 Flow chart of sol-gel silica synthesis and deposition	35
Figure 3.2 OFETs structures with top-contact configurations. [Gate = n-type Si wafer, TOX = thermally grown SiO ₂ , SG = sol-gel silica, OSC = organic semiconductor, Source/Drain = gold]	36

Figure 3.3 Chemical structures of pentacene, PQT, and TEPP-C61.	38
Figure 4.1 Effect of substrate cleaning on sol-gel silica film uniformity.	45
Figure 4.2 Infrared absorption spectrum of sol-gel silica thin-film.	46
Figure 4.3 TEM image of a cross-sectional specimen of sol-gel silica thin-film on Si wafer with average pores diameter of ~12 nm.	47
Figure 4.4 Contact angle measurements on (a) wet thermally grown SiO ₂ (TOX) and (b) sol-gel silica surface. AFM scans for (a) TOX and (b) sol-gel silica thin-film. The area size of the images was 1 x 1 μm ² . Line scans were scaled to the same z-axis (z = 2 nm) and x-axis (x = 1 μm) to aid better comparison.	49
Figure 4.5 XPS spectrum of sol-gel silica thin-film: (a) wide scan spectrum showing all elements present, (b) C 1s narrow scan spectra, (c) O 1s narrow scan spectra, and (d) Si 2p narrow scan spectra.	50
Figure 4.6 (a) Chemical structures of the organic semiconductors (OSCs) employed in this study. (b) Schematic diagram of OFET device structures. (c), (d), and (e) Output characteristics (I_D - V_D) for pentacene, PQT, and TEPP-C61 FETs on TOX and sol-gel dielectric structures respectively.	51
Figure 4.7 Transfer characteristics, μ_{eff} ($\propto$ transconductance), and channel conductance (g_D) plots for (a) pentacene, (b) PQT, and (c) TEPP-C61 FETs on TOX and sol-gel silica dielectric.	52
Figure 4.8 Transfer characteristics, μ_{eff} ($\propto$ transconductance), and channel conductance (g_D) plots for pentacene FETs on TOX and sol-gel dielectric indicate improved device characteristics on sol-gel dielectric and also an independence on the thickness of the sol-gel silica thin-film.	55

Figure 4.9 Localized charge densities of pentacene film on TOX and sol-gel silica dielectric show reduced localized charge states for different sol-gel thicknesses as compared with the reference TOX. Inset: Frequency dependence of the C_i measured at biasing voltage of -20 V (ac amplitude of 15 mV).	57
Figure 4.10 (a) Schematic structures of single and bilayer dielectric pentacene FETs. (b) The single layer (330 nm SG silica film) FET showed sweeping rate dependent hysteresis, lesser hysteresis with slower sweeping rates. (c) Transfer characteristics of FETs with and without 18nm TOX as the blocking layer between gate and 330 nm SG silica film (measured with sweeping rate of 0.01 V/s). (d) Capacitance-voltage (C - V) outputs of the MIS structures (single and bilayer dielectric) on n-type Si wafer (f = 100 kHz).	59
Figure 4.11 (a) Transfer characteristics of pentacene FETs (V_G = 1 V to -5 V, in steps of -1 V) with TOX and sol-gel dielectric; measured at temperatures of 130 K, 205 K, and 298 K. (b) Hysteresis plot from its I_D - V_G and MIS C - V curves, indicating different hysteresis direction for devices with TOX and sol-gel dielectric and also its temperature dependence. Note: Positive value for y-axis means clockwise hysteresis, and vice versa. The C - V curves were measured with ac amplitude of 15 mV.	61
Figure 4.12 (a) Chemical structures of TEOS and MTES. (b) Transfer characteristics of hybrid sol-gel silica pentacene FETs measured in linear region. There is observed V_{Th} shift and pronounced hysteresis with the MTES addition. (c) Capacitance-voltage (C - V) characteristics of MPIS (metal-pentacene-insulator-semiconductor) show the similar flat-band shift and hysteresis as observed from the transfer characteristics (measured at f = 100 kHz). (Note: F = forward scan, R = reverse scan).....	63

Figure 4.13 Response from pentacene devices on TOX and sol-gel dielectric in the saturation regime ($V_G = V_{DS} = -5$ V). Nitrogen gas with/without moisture were delivered to samples during the periods indicated by shades.	64
Figure 4.14 Morphology of pentacene film on (a) TOX and (b) sol-gel silica thin-film. (c) High resolution AFM image of pentacene on sol-gel silica along with (d) its surface profile indicating the terrace height (~ 1.5 nm) and the pentacene molecule orientation relative to the substrate ($\sim 20^\circ$).	67
Figure 4.15 Tapping-mode AFM phase images of PQT film on (a) TOX and (b) sol-gel silica thin-film.	67
Figure 4.16 AFM height images of TEPP-C61 film on (a) TOX and (b) sol-gel silica thin-film.	68
Figure 4.17 Synchrotron X-ray diffraction patterns of pentacene films on TOX and sol-gel silica. Inset: Calculations on crystalline size, structural disorder (g_{II}), and number of reflecting planes (N).	69
Figure 4.18 Synchrotron X-ray diffraction patterns of PQT films on TOX and sol-gel silica thin-film.	70
Figure 4.19 Synchrotron X-ray diffraction pattern of TEPP-C61 films on TOX and sol-gel silica thin-film.	70
Figure 4.20 PL spectra of pentacene film on TOX and sol-gel silica thin-film.	71
Figure 4.21 PL spectra were measured on the transistor samples, however the absorption spectra were obtained from PQT film deposited on microscopy glass slide and sol-gel silica coated glass slide, representing the TOX and sol-gel sample respectively.	72
Figure 4.22 PL spectra of TEPP-C61 film on TOX and sol-gel silica thin-film.	73
Figure 4.23 Raman spectra of pentacene films on TOX and sol-gel silica thin-film.	74

Figure 4.24 Raman spectra of PQT film on TOX and sol-gel silica thin-film. Inset: Smaller region of Raman spectra (1470 cm^{-1} to 1555 cm^{-1}) for better ν_1 mode visibility.	75
Figure 4.25 Raman spectra of TEPP-C61 film on TOX and sol-gel silica thin-film.....	76
Figure 5.1 Schematic cross-section of single sol-gel silica thin-film layer on Si wafer....	78
Figure 5.2 Schematic diagram of functional group electron trapping efficiency on TOX and sol-gel silica.....	82
Figure 5.3 Pentacene morphology on (a) TOX and (b) sol-gel silica with its height distribution analysis.	84
Figure 5.4 Schematic draw of PQT film morphologies on TOX and sol-gel silica. In these simplified pictures, the crystallites on TOX extend throughout the whole layer thickness and consist of fully extended chains. These crystalline whiskers are embedded into a disordered matrix. Film on sol-gel silica consists of small partially ordered domains with the average width smaller than the chain length, thus chains either fold back, extend into the disordered phase, or interconnect neighboring domains. (After Ref. [128])	87
Figure 5.5 Schematic cross section of OFET with sol-gel silica as the gate dielectric. The minus signs represent volume charges injected and trapped into sol-gel silica from the gate. The plus signs represent the induced positive charges accumulated at the semiconductor interface. The electron trapping results in H^+ . The upper part of sol-gel silica has denser structure, thus containing less water/-OH groups.....	92

Figure 5.6 Schematic energy level diagram of surface potential modification by surface (Si-CH ₃) ⁺ species for the pentacene FETs with hybrid sol-gel silica. (After Ref. [220]).....	95
Figure 5.7 (a) Transfer characteristics of bilayer dielectric pentacene OFET in ambient and vacuum. This phenomenon is reversible upon repeated measurements between ambient and vacuum for thick SG silica film (330 nm) on 80 nm TOX. The ambient stability is improved with thinner SG silica film (25 nm) (b) Capacitance-voltage (<i>C-V</i>) characteristics of MIS on n-type Si wafer for bi- layer structure with thick SG silica (330 nm) and thin SG silica (25 nm), measured at <i>f</i> = 100 kHz. (Note: F= forward, R= reverse)	96
Figure 5.8 Temperature dependent mobility for pentacene FETs with TOX and sol-gel silica film.....	99
Figure 7.1 Schematic draw of inkjet printed sol-gel silica film and the patterned pentacene to form the OFETs. Pentacene FETs fabricated on inkjet printed sol-gel silica have the improved performance, similar to devices fabricated on sol-gel silica film deposited by “conventional” technique (spin-coating).....	104

LIST OF TABLES

Table 2.1 Summary of OFET performance of p- and n-channel semiconductors.	8
Table 2.2 Comparison of characteristic features of organic molecular and covalent crystals. (after Ref. [91])	13
Table 2.3 Summary of the inorganic dielectrics (thickness d , capacitance C_i , dielectric constant k , breakdown field E_B) and their OFET characteristics. (After Ref. [8])	21
Table 2.4 Summary of the polymeric dielectrics (thickness d , capacitance C_i , dielectric constant k , breakdown field E_B) and their OFET characteristics. (After Ref. [8])	23
Table 2.5 Summary of the polymeric self-assembled dielectrics (thickness d , capacitance C_i , dielectric constant k , breakdown field E_B) and their OFET characteristics. (After Ref. [8])	25
Table 4.1 Device Characteristics of pentacene, PQT, and TEPP-C61 FETs on TOX and sol-gel silica thin film.....	53
Table 4.2 Pentacene device characteristics with TOX and sol-gel dielectric	56
Table 5.1 The ν_0 , ν_1 , and ν_2 vibrational mode analysis of Raman spectra from pentacene films on TOX and sol-gel silica. Inset: Schematic drawing of the ν_1 and ν_2 band coupling effect in pentacene unit cell.....	86

Chapter 1 INTRODUCTION

1.1 Background

Research in organic field effect transistors (OFETs) has gained great interest because of their potential applications in low cost and large area electronics [1-7]. To achieve these goals, the OFETs fabrication should ideally include low cost, high-throughput, and low temperature solution-patterning and deposition techniques, such as spin-coating, casting, or printing [8]. Thermally grown SiO₂ (TOX) as the gate dielectric is widely used as a substrate for the OFETs, mainly due to its superior electrical properties. However, for large area electronics applications, organic electronics on glass or flexible foil substrates, solution processed gate dielectrics are a necessity [6].

Organic dielectrics come naturally as the ideal choice for low cost, all plastic, and large area applications, however their low dielectric constants (k) makes very high voltage (> 20 V) operations essential. Self-assembled monolayers (SAMs) have been investigated as alternative dielectric materials for low voltage OFETs [9, 10]. Although self-assembled multilayers (SAMTs) [11] were introduced as more reliable dielectric materials with better device yields than SAMs, this approach is limited by the chemistry required for silane/phosphate coupling to the dielectric surface. Thus, the use of appropriate high- k inorganic materials would afford low voltage device applications, as well as its superior properties of being insoluble to the solvent used for the organic semiconductor deposition (in the case of bottom-gate structures). However, most high- k inorganic materials, such as Al₂O₃, TiO₂, Ta₂O₅, and Si₃N₄, require complex and expensive processes, higher temperature, and are not compatible with low cost, solution processed methodologies. To overcome this limitation, sol-gel based high- k dielectrics

have been proposed [12, 13], however concerns over interfacial compatibility with organic semiconductors (OSCs) remain [14].

Moreover, despite the fast developments in the field of organic electronics and dramatic improvement in knowledge and manipulation of molecular design [15-19] as well as heedful control of film growth conditions; it is recognized that chemical composition, surface functionalization, and surface morphology (roughness) of the gate dielectric [8, 14, 20, 21] critically influence mobility [14], hysteresis [22], threshold voltage (V_{Th}) [23] as well as the operating voltage. The hydroxyl bonds [24, 25] on gate dielectric surface together with alkali ions [26] in the gate dielectric layer are known to influence the device characteristics, particularly interface trapping and hysteresis. These trapped charges often lead to low mobility and a high degree of variability.

In spite of progress in OFETs resulting from an improved understanding of structure-property relationships of the organic semiconductors, a comprehensive understanding of the relationship between morphology, molecular ordering and their effect on device properties is still being developed. Investigations to further the fundamental understanding of the conduction mechanisms in organic semiconductors needs to focus in particular at the semiconductor-dielectric interface, since the charge carriers are thought to reside in the first few monolayers of the semiconductor film [1]. Accurate correlations between morphology, molecular packing, and the resulting electronic properties are essential in order to elucidate fundamental questions regarding charge transport in the organic semiconductors.

In addition to the microscopic properties correlation, particular attention must be paid to charge trapping in organic semiconductors as the charge carriers interact strongly with the lattice environment leading to polarization effects and tendency of charge carrier localization. This interaction facilitates charge carrier trapping, further narrowing the

bandwidths, and crucially affecting the transport properties. These complexities of current flow in organic materials, which are poorly understood, have increased the barrier to the development of the devices comprising these materials.

1.2 Research Objectives and Scope

To address the gaps in the literature identified above, namely the lack of suitable solution processable dielectrics and a lack of an in-depth understanding of the role of interfacial layers and molecular ordering on device performance; the main objectives of this thesis may be summarized as follows:

1. Study the applicability of sol-gel based dielectrics towards OFETs

Motivated by the various properties that gate dielectric materials require, such as solution-processability, high k , smooth and low surface energy, the thesis explores the fabrication of OFETs with solution-processed inorganic materials using sol-gel methodologies.

2. Investigate the impact of sol-gel dielectrics on device performance

A critical analysis of different factors that determine the interactions between gate dielectric and organic semiconductors in OFETs was evaluated in this thesis. The questions addressed concern sol-gel dielectric *surface* and *bulk* properties that influence the charge transport in organic semiconductors. In order to answer these questions, small molecule semiconductor (pentacene) was used mainly to allow this type of studies due to its higher degree of order than solution-processed polymers, thus it can be structurally characterized using diffraction and microscopy techniques. A systematic study of the gate surface chemistry, charge electret, and exposure to ambient conditions was carried to

analyze their effects on transistor characteristics, prior to the study of organic structural defects and molecular ordering. Polymer semiconductor (poly(3,3''-didodecylquaterthiophene) – PQT), and fullerene-derivative semiconductor ($\{6\}$ -1-(3-(2-thienylethoxycarbonyl)-propyl)- $\{5\}$ -1-phenyl-[5,6]-C₆₁ – TEPP-C₆₁) were also used to confirm the applicability of this sol-gel dielectric for enhanced device performance across a range of organic semiconductors in terms of majority charge carrier (p- or n-channel), core architectural characteristics (small molecule, polymer), core size (acene, buckyball), and processing methods (evaporation, solution).

3. Investigate the contributions of morphology, structure, crystallinity, molecular ordering, inter-molecular interaction towards device performance

Although progress has been made in understanding the factors that influence OFET performance, there are still numerous areas of critical importance for which inconsistent explanations are found in the literature. Microstructural and molecular order information is essential to understand the role of trap densities in OFETs. Furthermore, the nature of interface traps is also dependent on intricate microstructural details of the semiconductor film itself. It is known that molecular orientation in the unit cells could be different even as the unit cell dimensions of the pentacene polymorph phases are identical [27]. This indicated that intermolecular order study has to be included if one aims to understand the molecular structure of the thin-film phase on different dielectric surfaces. In view of the changes in pentacene molecular orientation accompanying the change in μ_{eff} , it is unclear what role the in-plane π -system overlap plays in the field-effect transistor behavior, thus photoluminescence and Raman studies were employed to differentiate the solid-state packing of pentacene in the film since both exciton migration and carrier mobility are strongly modulated by the intermolecular overlap, leading to increase in bandwidth [28].

This study was also extended to solution-processed organic semiconductors with its higher complexity which included amorphous films (TEPP) as well as polymeric crystalline films (PQT).

Chapter 2 LITERATURE REVIEW

In this chapter, important concepts of organic semiconductors and recent developments of gate dielectrics in OFETs are reviewed. The organic semiconductor materials, crystal structures, and charge transports are presented in section 2.1. The principles and characteristics of OFETs are explained in section 2.2. In section 2.3, current gate dielectrics research and requirements are reviewed. A brief review of sol-gel method for solution-processed inorganic gate dielectrics is discussed in section 2.4. Finally, a summary of progress in OFETs performance is presented in Section 2.5.

2.1 Organic Semiconductors

Organic semiconductors are an intriguing fascinating class of materials with an extensive range of properties [29-31] that may be tuned by chemical functionalization and manipulation. Although organic semiconductors have been identified as early as the late 1940's [32], however important discoveries only occurred in more recent years (ca. 1974) in polyacetylene based conjugated polymers leading to the Nobel Prize in Chemistry in 2000 [33]. Rapid progress has been made as researchers are able to control the material properties at the molecular level to impose different molecular packing during growth, add side groups that enhance properties that improve charge transport [34, 35]. Past investigations were hindered by material instabilities (to environmental conditions and/or processing methods [36]) and structural defects that prevented the measurement and understanding of the intrinsic properties of the organic materials [37, 38]. The degradation is circumvented as a result of a better understanding of the material behaviors in different conditions (temperature, moisture, light) and interactions during processing.

Organic semiconductors are traditionally classified as polymers or small molecules. The former has the advantage of being amenable to specific deposition techniques that had been developed for long for conventional polymers. Their main drawback is that their performance is still lower than that of small molecules, which are typically deposited through thermal evaporation and currently offer mobilities higher than hydrogenated amorphous silicon [39].

As discussed later, organic field effect transistors function more as capacitors with the charge carriers being the majority carriers unlike the inversion regime carrier transport seen in inorganic semiconducting materials. Hole transporting p-channel materials still dominate in terms of performance over electron transporting n-channel materials (Table 2.1).

Pentacene is the material most extensively studied organic semiconductors for OFETs based on small molecules, with oligothiophenes and their derivatives being the next most important. The highest reported mobility is up to $6 \text{ cm}^2/\text{Vs}$ for the former [40] and $1 \text{ cm}^2/\text{Vs}$ for the later [41]. Major improvements have been achieved by modification of the insulator-semiconductor interface. Most devices are grown by vapor deposition on silicon oxide. Because of the different physical and chemical nature of both materials, their association may lead to highly disordered interfaces, thus leading to poor performance. Substrate heating and very slow deposition rate leads to better organization. A better alternative is by surface modification of self-assembled monolayer before organic layer deposition, with octadecyltrichlorosilane (OTS) giving good results with pentacene on silicon oxide. An alternative route is to use a polymeric dielectric, which resulted in high performance with sexithiophene derivatives [39].

Table 2.1 Summary of OFET performance of p- and n-channel semiconductors.

Ref.	Semiconductor [a]	μ (cm ² /Vs)	I_{ON}/I_{OFF}
<i>p-channel</i>			
[9, 10, 42]	6T	0.00021-0.034	$\sim 10^4$
[43]	BS8T2	0.006	$\sim 10^6$
[9, 10]	DE6T	0.2	
[9, 10]	DFHCO-4T	0.02	$\sim 10^3$
[44]	DH-5T	~ 0.03	
[9, 10]	DH-6T	0.02-0.04	$\sim 10^3$
[45]	Et-6T	0.03-0.05	$> 10^5$
[14]	F8T2	10^{-5} - > 0.02	10^2 - 10^6
[46]	Me ₂ -6T	0.02	
[47]	Me ₄ -Pentacene	0.3	10^3 - 10^5
[48]	P3BT	0.0002-0.04	
[49-52]	P3HT	0.001-0.2	10^2
[12, 13, 53-61]	Pentacene	0.08-3	10^2 - 10^8
[62, 63]	Pentacene-precursor	0.01-0.89	10^5 - 10^7
[34]	Pentacene-TIPSA	0.17	$\sim 10^5$
[15]	PQT-12	0.14	$\sim 10^7$
[14, 64]	PTAA	10^{-5} - > 0.01	10^3 - 10^5
[65]	PTTT-14	0.6-0.7	$\sim 10^7$
[66, 67]	Rubrene	1.5-20	
[68]	TFB	~ 0.0003	$\sim 10^4$
[43]	TS6T2	0.06	$\sim 10^5$
<i>n-channel</i>			
[69-72]	C ₆₀	10^{-4} -0.5	10^2 - 10^4
[73]	C ₈₄	0.0005	$\sim 10^3$
[74]	CuPc	0.01	
[75]	DFH-6T	0.01	10^5
[44]	FCuPc	~ 0.02	
[21]	FTTTTF	0.4	10^8
[76]	T3CN	0.2	$> 10^6$

[a] 6T, sexithiophene; C₆₀, fullerene; C₈₄, solution processable fullerene-derivative; CuPc, copper phthalocyanine; DFH-6T, oligothiophenes containing or substituted with carbonyl groups; DH-4T/DH-5T/DH-6T/Et-6T/Me₂-6T, hexyl-substituted thiophenes oligomers; FCuPc, perfluorophthalocyanine; F8T2, poly(9,9-dioctylfluorene-co-bithiophene); FTTTTF, mixed perfluoroarene-thiophene oligomers; P3HT, poly(3-hexylthiophene); PTAA, polytriarylamines; P3BT, poly(3-butylthiophene); Pentacene-precursor, soluble pentacene precursor; Me₄-Pentacene, soluble pentacene with methyl groups; Pentacene-TIPSA, soluble pentacene derivative; PQT, regioregular polyquarterthiophenes; TFB, poly[(9,9-dioctylfluorene-2,7-diyl)-*alt*-(phenylene-[*N*-(*p*-2-butylphenyl)iminophenylene])];

Polythiophenes are used for most work dealing with polymeric FETs due to their higher mobility, good solubility, and easy processability. After pioneering work on spin-coated poly(3alkylthiophene) (P3AT) [77], it is now established that the performance of polymeric FETs critically depends on the chemical and structural ordering of the chains at the dielectric-polymer interface. Exposure of films to air usually causes polymer doping degradation of the transistor and regioregular polyquarterthiophenes (PQTs) have therefore been developed to ensure processability, structural regularity, and extensive π -conjugation but with enhanced resistance to O_2 -doping [15]. Liquid-crystalline-like thieno[3,2-b]thiophenes polymers have shown to exhibit highly organized morphology and large crystal domains, hence good transistor stability under static storage and operation in dry N_2 ($\mu = 0.2\text{-}0.7\text{ cm}^2/\text{Vs}$) [65].

The compounds with the highest electron mobility are currently fullerene C_{60} [71, 72] and *N,N*-dialkyl-3,4,9,10-perylene tetracarboxylic diimide derivatives [78, 79], with values up to $0.5\text{ cm}^2/\text{Vs}$. Because C_{60} forms isotropic solids, the films do not require particular attention to control molecular orientation as in other organic materials. Solution-processable C_{60} - [80] and C_{80} - [73] functionalized materials have also been reported and hold great promise with their air stability. The other n-channel semiconductors are mostly based on oligothiophenes in which the molecular energy levels have been tuned by substitution with cyano, perfluoroalkyl/aryl, and alkyl/arylcarbonyl (Table 2.1).

2.1.1 Organic Molecular Crystals

Characteristics of organic semiconductors are the *intramolecular* bonds with the alternation of single (σ) and double (π) bonds, referred to as *conjugation*, where the hybridized sp^2 orbitals form the σ bonds and the nonhybridized p_z orbitals form the π bonds – delocalized over the molecule. The σ bonds are very strong and positioned lower in energy. The filled molecular orbitals (π -bonding orbitals) form the valence states where its highest energy orbital is called Highest Occupied Molecular Orbital (HOMO). The vacant orbitals (π^* -antibonding orbitals) form the conduction states where its lowest energy orbital is called Lowest Unoccupied Molecular Orbital (LUMO). The π -electrons are the main part of the intermolecular conduction in the organic semiconductors.

The crystal structures are determined by interplay between *dispersion* (van der Waals) forces between induced dipoles and *electrostatic* interaction between permanent multipoles (usually quadrupoles) [32, 81]. The two competing interactions promote different molecular stacking to minimize the energy, resulting in the characteristic organic molecular crystals interplanar distance of $> 3.4 \text{ \AA}$ [82]. The van der Waals interactions are optimized for “face-to-face” orientation of the molecules, resulting in the maximum π -overlap. On the other hand, the presence of quadrupolar moments favor the “edge-to-face” stacking, in which the hydrogen of one ring encounters the π -network of the adjacent molecule, resulting in herringbone arrangement, the most common crystal packing, in a layered fashion (Figure 2.1).

Figure 2.1 (a) Chemical structure of pentacene. Pentacene crystal structure in its single crystal: (b) view along the [100] axis (the layered structure can be seen) and (c) the herringbone arrangement within the layer, view along the long axis of the molecule. The unit cell orientation is also draw (after Ref. [37]).

Cofacial π -stacking in molecular crystals is hardly ever found. However, the different type and amount of π -overlap can be controlled by the nature, size, and position of the substituting group in the molecule backbone [83], leading to various stacking patterns, hence polymorphism (the existence of more than one crystal structure for a particular compound. This phenomenon is frequently driven by the growth conditions and/or subsequent treatment, substrate type, substrate temperature, and thickness of the film.

In pentacene ($\text{C}_{22}\text{H}_{14}$), a planar molecule composed of five benzene rings (Figure 2.1), there are four polymorphs detected [84, 85]. Its bulk phase, pentacene has a triclinic structure (space group $P\bar{1}$) and a density of 1.32 g/cm^3 with two molecules per unit cell arranged in a herringbone configuration. Vacuum-deposited thin films, however, differ from the bulk, forming a structure that has been referred to as the “thin film phase” [86]. The inter-planar spacing for thin film phase ($d_{001} = 15.4\text{ \AA}$) [86] is different from that in pentacene bulk crystals ($d_{001} = 14.5\text{ \AA}$) [87]. The bulk polymorph shown in Figure 2.1 has been found to coexist with the “thin film phase” on evaporated thin films beyond a certain critical thickness [37, 88].

2.1.2 Charge Transport in Organic Semiconductors

Organic semiconductors are *wide-band-gap* and *small bandwidth* semiconductors. Its HOMO-LUMO gap is in the range of 1-4 eV [32]. For pentacene, the absorption onset at 1.85 eV is assigned to the fundamental transition of solid pentacene that occurs between the HOMO and LUMO [89]. With such a large gap, it might be expected that the organic materials are insulators (an electron would have to acquire a large thermal energy to be excited from the HOMO level to the LUMO level). However, there are some effective methods that can generate charge carriers in the organic semiconductors: (a) injection of carriers from metallic electrodes (source-drain electrodes in the case of OFETs), (b) optical excitation (creation of electron-hole pairs as in the case of photovoltaics), and (c) electrostatic or chemical doping (mainly for conductor materials).

In organic molecular solids, the intermolecular forces are weak (van der Waals and electrostatic type) where their bonding energies are considerably lower than in covalent and ionic inorganic semiconductors [32, 90]. Table 2.2 compares the physical properties of organic molecular crystals with those of Si-type conventional semiconductors that are formed by strong covalent bonds [91]. For this reason, the mechanism of charge transport is fundamentally different where the charge carriers interact strongly with the lattice environment leading to polarization effects and inclination of charge carrier localization. Furthermore, the weak van der Waals interactions also result in small electronic bandwidth. This results in lower conduction for polymer ($\mu = 10^{-8}$ - 10^{-4} cm²/Vs) [24, 92] than for oligomers/small molecules ($\mu = 10^{-3}$ - 10^{-1} cm²/Vs) [93, 94] as polymer has higher disorder and is limited by hopping of charges between polymer chains, which can be depicted as self-exchange rates. The rate is affected by :[95, 96] (i) the electronic coupling between adjacent molecules (transfer integral) [97], which needs to be maximized, and (ii) the reorganization energy (λ_{reorg}), which needs to be small for

efficient charge transport. In the case of the embedded pentacene molecules, there is very little difference in λ_{reorg} with respect to an isolated pentacene molecule, indicating a weak dependence on intermolecular interactions [98], thus may be ignored in comparing substrate-induced intermolecular interactions.

Table 2.2 Comparison of characteristic features of organic molecular and covalent crystals. (after Ref. [91])

Organic molecular crystal (e.g., anthracene-type crystal)	Covalent crystal (e.g., Si-type crystal)
Weak van der Waals type of interaction (characteristic interaction energies $E_{\text{vdW}} = 10^{-3}$ - 10^{-2} eV)	Strong covalent type of interaction (characteristic interaction energies $E_{\text{cov}} = 2$ -4 eV)
Marked tendency of charge carrier and exciton localization	Pronounced charge carrier delocalization
Charge carriers and excitons as polaron-type quasiparticles	Charge carriers as free holes and electrons
Low charge carrier mobilities ($\mu \sim 1$ cm ² /Vs) and small mean free path ($l \sim a_0$ = lattice constant) at room temperature	High charge carrier mobilities and large mean free path ($l \sim (100 - 1000) a_0$) at room temperature
Large effective mass of charge carrier $m_{\text{eff}} = (10^2$ - $10^3) m_e$	Small effective mass of charge carrier $m_{\text{eff}} \leq m_e$
Hopping-type charge carrier transport dominant	Band-type charge carrier transport dominant
Excitons as molecular Frenkel-type quasiparticles	Excitons as Wannier-type quasiparticles
Low melting and sublimation temperatures, low mechanical strength, high compressibility	High melting and sublimation temperatures, high mechanical strength, low compressibility

Owing to the organic crystal polymorphism, the degree of cofacial configurations is particularly important as it accommodates the largest electronic splitting in the HOMO

and LUMO states, resulting in the higher charge carrier mobilities. Thus, a complete microscopic understanding will require the inclusion of further properties of the excitations in the consideration as intermolecular interactions. Furthermore, structural defects and chemical impurities present in the crystal lattice promote the localization of the charge carriers, either forming new states in the HOMO-LUMO gap – leading to electronic traps or scattering the charges, hence it decreases the mobility [99].

2.2 Organic Field-Effect Transistors

An OFET is analogous to its inorganic counterpart in basic design and function with several variants. It is basically a three-terminal device, in which a voltage applied to a gate electrode controls current flow between a source and drain electrode under an imposed bias. The structure of devices is dictated not only by its operating mode, but also by issues arising from its fabrication. The basic fabrication scheme consists of piling up thin films of the different elements. Because most organic semiconductors are fragile materials, the deposition of organic semiconductors on the insulator is much easier than the converse. Thus, the large majority of current OFETs are built according to the bottom-gate architecture, which in turn derives two alternatives as shown in Figure 2.1.

Figure 2.2 OFET device configurations: (a) Top-contact device, with source and drain electrodes evaporated onto the organic semiconducting layer through a mask. (b) Bottom-contact device, with the organic semiconductor deposited onto the gate insulator and the prefabricated source and drain electrodes. (After Ref. [2])

Their utility in this capacity is gauged by several key measures of their performance. The mobility, μ , describes how easily charge carriers can move within the active layer under the influence of an electric field and is, therefore, directly related to the switching speed of the device. This parameter can be extracted from current-voltage measurements, and would ideally be as large as possible. Typical values range from 0.1-1 cm^2/Vs for polycrystalline organic materials devices, with the best single crystal organic materials achieving mobilities of $\sim 15 \text{ cm}^2/\text{Vs}$ [67]. The on/off ratio, defined as the ratio of the current in the ‘on’ and ‘off’ states, is indicative of the switching performance of OFETs. A low off current is desired to eliminate leakage while in the inactive state. Ratios as high as 10^6 are suitable for most applications, and can be reached by the current generation OFETs [2].

2.2.1 Operation Principle

In stark contrast to inorganic materials, organics transport current by majority carriers, and an inversion regime does not exist. This key difference is related to the nature of charge transport in each of these semiconductors. In well-ordered inorganics, (e.g. single-crystal Si), the delocalization of electrons over equivalent sites leads to a band-type mode of transport, with charge carriers moving through a continuum of energy levels in the solid. In less-ordered organic materials, the proposed mechanism is hopping between discrete, localized states of individual molecules. The presence of impurities or inconsistencies in structure may result in ‘traps’ that alter the relative energy levels [25], and inhibit the flow of charge carriers as shown in Figure 2.3. It has been demonstrated that the use of hydroxyl-free gate dielectrics, such as BCB [24], can yield the ambipolar FET channel conduction in most conjugated organic semiconductors. Thus, there is

strong trapping of electrons but not holes, with FETs typically exhibiting p-channel, but not n-channel, even with proper work-function electrodes.

Another interesting aspect is the gate voltage-dependent mobility. Such dependence is predicted by the Vissenberg's model [100] based on the multiple trapping and release (MTR) model developed for a-Si:H [101]. Briefly, the dependence stems from the fact that as the gate voltage increases, injected charge-carriers tend to fill the traps, so trapping becomes less efficient and charge transport improves. It is also worth noting that there is gate voltage-dependent channel thickness despite the statement "all the induced charge resides in the first layer" [102], only true at high gate bias. Quantum mechanical calculations have shown that in short conjugated molecules the additional charge almost uniformly spreads over the whole entity [103], which leads to the conclusion that the actual distribution of charge-carriers in the film is not continuous; instead, it is in staircase shape, where the width of each step equals to one monolayer [39].

I - V characteristics of OFETs can be adequately described by models developed for inorganic semiconductors [90] to calculate the field effect mobility and other device parameters such as the current modulation (the ratio of the current in the accumulation mode over the current in the depletion mode, also referred to as I_{ON}/I_{OFF}), and the threshold voltage, V_{Th} . A typical plot of output characteristic (drain current I_D versus drain voltage V_D at various gate voltages V_G) and transfer characteristic (drain current I_D versus gate voltage V_G at constant drain voltages V_D) are shown in Figure 2.4.

Figure 2.3 (a) Idealized energy level diagram of an organic TFT at $V_G = 0$ and $V_D = 0$. (b-e) Demonstrate the principle of field effect transistor operation for the case of (b) electron accumulation, (d) transport, (c) hole accumulation, and (e) transport. (After Ref. [81])

Figure 2.4 I - V curves for a FET operation. (Left) Output characteristics (I_D - V_D) for different applied gate voltage (V_G). The curves can be modeled by expression 2.1 and 2.3. (b) Transfer characteristics (I_D - V_G), semilogarithmic plot (left y-axis) and plot of $\sqrt{|I_D|}$ - V_G (right y-axis). (After Ref. [2])

At low V_D , I_D increases linearly with V_D (linear regime) and is approximately determined from the following equation:

$$I_D = \frac{WC_i\mu}{L} \left(V_G - V_{Th} - \frac{V_D}{2} \right) V_D \quad (2.1)$$

where L is the channel length, W is the channel width, C_i is the capacitance per unit area of the insulating layer, V_{Th} is the threshold voltage, and μ is the field effect mobility, which can be calculated in the linear regime from the transconductance,

$$g_m = \left. \frac{\partial I_D}{\partial V_G} \right|_{V_D=const.} = \frac{WC_i}{L} \mu V_D \quad (2.2)$$

by plotting I_D versus V_G at a constant low V_D , with $-iV_D \ll -(V_G - V_{Th})$, and equating the value of the slope of this plot to g_m .

For $-V_D > -(V_G - V_{Th})$, I_D tends to saturate (saturation regime) due to the pinch-off of the accumulation layer, and is modeled by the equation

$$I_D = \frac{WC_i\mu}{2L} (V_G - V_T)^2 \quad (2.3)$$

In the saturation regime, μ can be calculated from the slope of the plot of $\sqrt{|I_D|}$ versus V_G . The calculated mobility in the saturation regime tends to be larger than the linear regime mobility due to the gate voltage-dependent mobility as previously discussed.

2.2.2 Fabrication of OFETs

Organic semiconductors are vastly different from their inorganic analogs in terms of melting point, solubility, and mechanical properties (Table 2.2). Owing to the fragility of organic materials, processing to incorporate them in electronic devices presents a challenge at this early stage, where it is commonly to have the organic semiconductor

film deposited at the last step of the process. Of course, such fabrication processes are not appropriate for taking advantage of the potential of organic materials for low cost, low temperature, and large area electronics. This triggers the interest to develop revolutionary methods that are simple and efficient to be used for the large scale applications.

Earlier work made use of screen-printing where major elements were deposited from solutions through stainless-steel mechanical masks [49, 104]. Although the devices fabricated by this method afforded similar performance with those fabricated by “conventional” technique, it has low space resolution, thus not suitable for highly integrated circuits fabrication. Microcontact printing using elastomeric stamps to print patterns of self-assembled monolayers (SAMs) are then used to improve the resolution down to 2 μm [105].

Similarly, the low resolution of inkjet printing, widely used alternative printing, was overcome by confining the spreading of the water-based ink with a pattern of repelling, hydrophobic regions that define the device dimensions [106]. However, both stamping and inkjet printing require liquid inks which may be a problem for conjugated polymers and small molecules. A dry process based on thermal imaging has been developed to enable the patterning of organic materials at high speed with micron size resolution, involving the transfer of a thin solid layer from a donor film on to a flexible receiver [107].

2.3 Gate Dielectric Materials

It has been long known that in insulated gate field - effect transistors, the role of gate insulator is at least as important as that of the active semiconductor. In OFETs, the conduction takes place at the surface of the semiconductor, the very first few monolayers [1], thus the device performance is limited by the quality of the interface between organic

and dielectric, and only in part by the bulk properties. Particularly important are the roughness of the semiconductor/dielectric interface [108], and the density of defects and impurities present in this region [24]. Thus, the performance of OFETs is very much dependent on the physical and chemical nature of the surface of the insulator. Besides its morphological effects, the nature of the insulator has also chemical and electrical consequences. This is evident from experiments, demonstrating that the gate dielectric can modify the charge density at the interface, hence a crucial effect on the operation of both small molecule [66] and polymeric [109] devices. The confluence of these two important gate dielectric effects has stimulated new research approaches. The three major dielectric classes used in OFETs, that is high- k inorganic, polymers, and self-assembled small molecules, are described in details below.

2.3.1 Inorganic Dielectric Materials

In this field, the driving force for inorganic dielectric materials is its high- k to increase the FET density on integrated circuits while preserving good insulator properties [110]. Table 2.3 shows the important metrics of inorganics dielectrics that has been used in OFETs researches. Although high- k dielectrics were used to increase the carrier density – thus increasing the charge carrier mobility, the OFET performance with this kind of gate dielectrics generally still leads to low mobility and a high degree of variability.

Table 2.3 Summary of the inorganic dielectrics (thickness d , capacitance C_i , dielectric constant k , breakdown field E_B) and their OFET characteristics. (After Ref. [8])

Ref.	Dielectric [a]	Method [b]	d (nm)	C_i (nF/cm)	k [c]	E_B (MV/cm)	Semicond. [d]	μ (cm ² /Vs)	I_{ON}/I_{OFF}	Year
[12, 13]	BZT BST Si ₃ N ₄	sputt.	122		17.3 16 6.2		Pentacene Pentacene Pentacene	0.32 0.4-0.5 0.6	10 ⁵	1999
[44]	Ta ₂ O ₅	anodiz.	70		23	4-5	DH-5T FCuPc	~0.03 ~0.02		2000
[50]	Ta ₂ O ₅	e-beam	100	180	21	>1	P3HT	~0.2		2002
[54, 55]	Al ₂ O _{3+x}	sputt.	270	22	7	~3	Pentacene	0.14	10 ⁶	2003
[64]	Al ₂ O ₃	anodiz.	120	60		~8	PTAA	3x10 ⁻⁵		2003
[56]	Ta ₂ O ₅	anodiz.	86	248	24		Pentacene	0.24	10 ⁴	2003
[74]	Ta ₂ O ₅	sputt.		66			CuPc	0.01		2003
[54]	SiO _x SiN _x	PECVD					Pentacene	0.2-0.4	~10 ⁸	2003
[51]	TiO ₂ Al ₂ O ₃	sputt.	97 93	373 79	41 8.4	~3	P3HT P3HT	5x10 ⁻³ 6x10 ⁻³	10 ² 10 ²	2004
[52]	Al ₂ O ₃	anodiz.	~7	600- 700	9- 11	~8	P3HT Pentacene	~10 ⁻³ 0.06-0.1		2004
[66]	Ta ₂ O ₅ -air	sputt.			25- 1		Rubrene	1.5-20		2004
[57]	Gd ₂ O ₃	IBAD	90	280	7.4		Pentacene	0.1	10 ³	2004
[61]	TiO ₂ +PαMS	anodiz.	8+10	228			Pentacene	0.8	10 ⁴	2005

[a] Abbreviations: BZT, barium zirconate titanate; BST, barium strontium titanate, PαMS, poly(α -methylstyrene).

[b] Dielectric deposition method. Abbreviations: sputt., sputtering; anodiz., anodization; PECVD, plasma-enhanced chemical vapor deposition; IBAD, ion-beam-assisted deposition.

[c] The capacitance was measured at different frequencies, thus there could be variance in k value due to ω dependence.

[d] Abbreviations: DH-5T, dihexylquinquethiophene; FCuPc, perfluorophthalocyanine; P3HT, poly(3-hexylthiophene); PTAA, polytriarylamine; CuPc, copper phthalocyanine.

It has been claimed that the dipole field present at the surface of high dielectric constant (high- k) insulators may enhance the formation of local states that in turn induce carrier localization and reduce-charge carrier mobility [66]. Hence, benefits have resulted from use of low- k organic dielectrics [109], as it can be seen for TiO₂ capped with an

ultrathin layer of PaMS as a gate insulator for 1 V operation [61]. It is worth remarking that such a conclusion is at variance with previous work that established interest in using high-capacitance insulators, which can be obtained by making use of high- k dielectrics [12]. Interest in high capacitances comes from the above mentioned gate voltage (i.e., charge density) dependence of the mobility as mentioned earlier. High capacitance means that high charge carrier concentration can be reached at low gate voltage; hence mobility is expected to be higher. The respective advantages of low- k and high- k dielectrics thus seem contradictory, and more work will be necessary to clarify this point [39].

2.3.2 Polymeric Dielectric Materials

Solution-processable materials are very attractive for applications in electronics, in part because films exhibiting good characteristics can often be formed simply by spin-coating, casting, or printing at room temperature and under ambient conditions. Gate dielectrics are not an exception. Polymeric gate dielectric materials are readily suitable to fulfill these requirements with its ability for chemical structure modification, thus tailored physical properties. The result is that polymers exhibiting a broad and complementary solubility and processability and dielectric properties (k values) can be selected for application in many electronic devices (Table 2.4) [8].

A similar strong correlation between the insulator k values and the field-effect mobility is observed as well for polymeric dielectric [42], as shown in Table 2.4. The higher k in polymeric dielectric is accompanied with hysteresis problem [21, 53]. Under ambient atmosphere, there is the peculiar behavior of a so-called hygroscopic insulator field-effect transistor (HIFET), where a hundredfold enhancement in I_{ON} were recorded at very low voltages (less than 1 V), depending on the relative humidity and the time of exposure [111]. The mechanism for the current enhancement was proposed to be due to

ionic processes that occur in the moisturized gate dielectric close to the semiconductor-dielectric interface.

Table 2.4 Summary of the polymeric dielectrics (thickness d , capacitance C_i , dielectric constant k , breakdown field E_B) and their OFET characteristics. (After Ref. [8])

Ref.	Dielectric [a]	Method [b]	d (nm)	C_i (nF/cm)	k [c]	E_B (MV/cm)	Semicond. [d]	μ (cm ² /Vs)	I_{ON}/I_{OFF}	Year
[42]	CYPEL	Cast		6	18.5		6T	0.034		1990
	PVA			10	7.8			0.00021		
[49]	PI	Print		20			P3HT	0.01-0.03		1997
[53]	PVP-CL	SC	260	~12	3.6	2-3	Pentacene	2.9	10^5	2002
	PVP-CP		380	~2	4.0	1-2		3.0	10^5	
[48]	CYPEL	SC	1200	8.85	12		P3BT	0.04		2004
	PVP		900	5.59	5			0.0002		
	PVA		500	17.8	10			0.03-0.003		
[58]	Polynorb.	SI-ROMP	~1200	~3			Pentacene	0.1-0.3	$\sim 10^2$	2004
[59]	PVP-CL	Cast	600-		3.5-		Pentacene	~0.25	$\sim 10^3$	2004
	nanoTiO ₂		700		5.4					
[68]	BCB	SC	50	235		>3	TFB	~0.0003	$\sim 10^4$	2004
[60]	CPVP-C _n	SC	~15	~300	~6	3-6	Pentacene	0.1	$\sim 10^4$	2005
	CPS-C _n		~15	~225	~3	3-6		0.08	$\sim 10^4$	

[a] Abbreviations: CYPEL, cyanoethylpullulan; PVA, polyvinylalcohol; PI, polyimide; PVP-CL, crosslinked polyvinylphenol; PVP-CP, polyvinylphenol copolymer; PVP, polyvinylphenol; Polynorb., polynorbornene; PVP-CL nanoTiO₂; PVP-crosslinked TiO₂ nanoparticles; BCB, divinyltetramethyldisiloxane-bis(benzocyclobutene); CPVP-C_n, crosslinked polyvinylphenol; CPS-C_n, crosslinked polystyrene.

[b] Dielectric deposition method. Abbreviations: Cast, casting; Print, screen-printing; SC, spin-coating; SI-ROMP, surface-initiated ring-opening metathesis polymerization.

[c] The capacitance was measured at different frequencies, thus there could be variance in k value due to ω dependence.

[d] Abbreviations: 6T, sexithiophene; P3HT, poly(3-hexylthiophene); P3BT, poly(3-butylthiophene); TFB, poly[(9,9-dioctylfluorene-2,7-diyl)-*alt*-(phenylene-[*N*-(*p*-2-butylphenyl)iminophenylene)]

An innovative approach to induce the higher k values was demonstrated by crosslinked melamine-PVP combined with TiO_2 nanoparticles, forming nanocomposites [59]. Moreover, polymeric dielectric could impose solubility issue – susceptible to attack by organic solvents that are commonly used during subsequent processing of devices, thus hybrid approach could be the solution to overcome disadvantages of each inorganic and polymeric dielectric.

2.3.3 Self-Assembled Mono- and Multilayers as Dielectric Materials

The use of self-assembled monolayers (SAMs) as ultrathin dielectric materials for OFETs was explored to reduce the operating voltage while at the same time maintaining the gate-induced charge carrier density at the channel (Table 2.5). Although the monolayers were demonstrated as an excellent electrical insulator, with leakage current densities as low as 10^{-8} A/cm^2 for an average field of 5.8 MV/cm, the film uniformity especially for large application is a challenge [9, 10].

Self-assembled multilayers (SAMTs) [11] were introduced as more reliable dielectric materials with better device yields than SAMs. This highly modular approach utilizes three-dimensional (3D) crosslinked dielectric SAMTs grown from solution via self-limiting sequential deposition of siloxane building blocks, highly polarizable layers, and siloxane capping layers. Importantly, the presence of the Si/SiO₂ interface underneath the SAMT layer strongly limits the maximum charge storage for MIS structure in the accumulation layer, resulting in underestimated C_i values. This result illustrates the strategic importance of having highly π -polarizable dipolar layers in enhancing SAMT k , while preserving excellent insulator properties. The laboratory device yields were reported to be > 95%, even so this approach is still limited by the chemistry required for silane/phosphate coupling to the substrate surface.

Table 2.5 Summary of the polymeric self-assembled dielectrics (thickness d , capacitance C_i , breakdown field E_B) and their OFET characteristics. (After Ref. [8])

Ref.	Dielectric [a]	d (nm)	C_i [b] (nF/cm)	E_B (MV/cm)	Semicond. [c]	μ (cm ² /Vs)	I_{ON}/I_{OFF}	Year
[9, 10]	OTS	2.8	153	9-12	6T	0.00036	$\sim 10^4$	2000
	PhO-OTS	2.5	900	14	DE6T	0.2		2004
					Pentacene	1.0	$\sim 10^4$	
	SAMT-I	2.3	400 [1100]	5-6	DH-6T	0.04	$\sim 10^3$	2005
	SAMT-II	3.2	710 [2500]	6-7	DH-6T	0.02	$\sim 10^3$	
	SAMT-III	5.5	390 [760]	6-7	DH-6T	0.06	$\sim 10^3$	
					6T	0.002	$\sim 10^3$	
					DFHCO-4T	0.02	$\sim 10^3$	
					FPcCu	0.003	$\sim 10^2$	

[a] Abbreviations: OTS, octyltrichlorosilane; PhO-OTS, OTS containing an aromatic (phenoxy) end group; SAMT, self-assembled multilayer.

[b] Values in brackets were measured in MIM structures. Dielectric constants were not reported in the literature as there could be discrepancies due to high series resistance and difficulty in getting the actual thickness of the dielectric stack.

[c] Abbreviations: 6T, sexithiophene; DE6T, diethyl-sexithiophene; DH-6T, (α,ω -dihexylsexithiophene); DFHCO-4T, (2,7-[bis(5-perfluorohexylcarbonylthien-2-yl)]-4H-cyclopenta-[2,1-*b*:3,4-*b'*]-dithiophen-4-one); FCuPc, perfluorophthalocyanine.

2.4 Sol-Gel Gate Dielectrics

In addition to the direct strategy of using one single material as the gate dielectric layer, several approaches with more complex/hybrid dielectric systems were studied. The work on sol-gel dielectric systems is basically driven by the motivation to increase the OFETs performance or to tune the electrical characteristics in a certain way, with prioritizing the simplicity and low-cost of organic electronics.

2.4.1 Sol-Gel Method for Gate Dielectric in OFETs

Silsesquioxane resins have been explored as the gate dielectric materials and could meet the stringent requirements for use in OFETS [7]. The low-molecular-weight precursors have the molecular formula $\text{RSiO}_{1.5}$, where R can be hydrogen or alkyl,

alkenyl, alkoxy, or aryl groups. The glass resin oligomers are soluble in common organic solvents which permit the use of various conventional liquid coating techniques, compatible with non-photolithographic, low-cost microcontact printing to produce films of the required thickness by adjusting the solution concentration. The low curing temperature permits the use in plastic substrates. The cured films have high dielectric strength, low leakage current, good hydrolytic and thermal stability along with high chemical resistance to many organic solvents.

Microcontact printing (μ CP, a versatile patterning technique for producing feature sizes as small as 1 μm [112]), has been shown with silsesquioxane dielectric material [7], top- and bottom-contact devices have performance comparable to those fabricated from conventional spin-casting method without the much delamination problem as observed for polymeric dielectric materials (such as non-crosslinked PMMA). The transparent glass resin dielectric has also been successfully employed in a flexible active matrix electrophoretic display over an area of 16 x 16 cm^2 without pin-holes allowing the operation of every single pixel in the display.

2.4.2 Sol-Gel Process Steps: An Overview

Three methods are used to make sol-gel monoliths: (1) gelation of a colloidal powder solutions, (2) hydrolysis and polycondensation of alkoxide precursors followed by hypercritical drying of gels, and (3) hydrolysis and polycondensation of alkoxide precursors followed by aging and drying under ambient conditions. In general, the sol-gel processes involved in making sol-gel-derived silica monoliths for all the three approaches can be illustrated as follows [113]:

Mixing. Colloidal powders or liquid alkoxide precursors (e.g., $\text{Si}(\text{OR})_4$, where R is alkyl) is hydrolyzed by mixing with water:

The hydrated silica tetrahedra interact in a condensation reaction, forming $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bonds:

Linkage of additional $\equiv\text{Si}-\text{OH}$ tetrahedral occurs as a polycondensation reaction and eventually results in a SiO_2 network. The H_2O and alcohol expelled from the reaction remains in the pores of the network. The hydrolysis and polycondensation reactions initiate at numerous sites within the precursors + H_2O solution as mixing occurs. When sufficient interconnected $\text{Si}-\text{O}-\text{Si}$ bonds are formed in a region, they respond cooperatively as colloidal (submicrometer) particles or a sol. The size of the sol particles and the cross-linking within the particles (i.e., density) depend upon the pH and R ratio ($R = [\text{H}_2\text{O}]/[\text{Si}(\text{OR})_4]$) among other variables.

Gelation. With time the colloidal particles and condensed silica species link together to become a three-dimensional network. The physical characteristics of the gel network depend greatly upon the size of particles and extend of crosslinking prior to gelation. At gelation, the viscosity increases and it could result in solid object.

Aging. Aging of a gel, also called *syneresis*, involves maintaining the cast object for a period of time, hours to days, completely immersed in liquid. During aging, polycondensation continues along with localized solution and reprecipitation of the gel network, which increases the thickness of interparticle necks and decreases the porosity. The strength of the gel thereby increases with aging. An aged gel must develop sufficient strength to resist cracking during drying.

Drying. During drying the liquid is removed from the interconnected pore network. Large capillary stresses can develop during drying when the pores are small (<20 nm). These stresses will cause the gels to crack catastrophically unless the drying process is

controlled by decreasing the liquid surface energy by addition of surfactants or elimination of very small pores (method 1), by hypercritical evaporation which avoids the solid-liquid interface (method 2), or by obtaining monodisperse pore sizes by controlling the rates of hydrolysis and condensation (method 3).

Dehydration or Chemical Stabilization. The removal of surface silanol (Si-OH) bonds from the pore network results in a chemically stable ultraporous solid. Porous gel-silica made in this manner by method 3 is optically transparent with interconnected porosity and has sufficient mechanical strength.

Densification. Heating the porous gel at high temperatures causes densification to occur. The pores are eliminated and the density ultimately becomes equivalent to fused silica. The densification temperature depends considerably on the dimensions of the pore network, the connectivity of the pores, and the surface area.

2.5 Progress in OFETs Performance

This section gives an overview of methods used to achieve higher mobilities in OFETs with pentacene as the vastly studied among organic molecules. Potential progress in understanding the nature of exceptional mobility in these devices will be pointed out and possible routes to stabilize device performances will be commented.

2.5.1 Routes to Performance Improvement

Optimization of pentacene FETs for mobility has led to some very promising results, however there is still a huge variation in the reported mobility – a good indication that there is still more to learn and that small processing differences can have large effects

on device performance. Thus, organic electronic performance continues to be a challenge in OFETs [114].

Purification. The importance of material purity is still somewhat debatable. It is generally accepted that higher purity correlates with higher performance and may also contribute to device reproducibility and stability, although careful studies are yet to be reported. Impurities can also affect the polarity of the OTFT. For example, iodine-doped pentacene is a p-type semiconductor [115] while alkaline metal-doped pentacene is an n-type semiconductor [116].

Interfacial Control. In general, the orientation of the pentacene molecules with respect to the substrate (especially for the first monolayer) is determined by the balance between the pentacene-substrate and pentacene-pentacene interactions [117, 118]. When pentacene is deposited onto flat, inert substrates such as some of the oxide or polymeric dielectrics, pentacene molecules stand nearly vertical on the substrate [2]. It is believed that the (001) plane has the lowest surface energy in pentacene crystals [119]. With a weakly interacting substrate where intralayer pentacene-pentacene interactions are stronger than pentacene-substrate interactions, pentacene will tend to form crystals with the (001) plane parallel to the substrate plane, leaving the lowest energy surface exposed.

On the other hand, if the substrate is a more reactive one, like clean Si [118] or clean metal [120], the interactions with the substrate become more important and may involve charge transfer at the interface. This makes pentacene molecules lay flat on the surface. A special case of inert substrates are those treated with self-assembled monolayers (SAMs). SiO₂ is often treated with SAMs prior to pentacene deposition to improve the field effect mobility [121] or to control the surface carrier density [122] in OTFTs. Growth mechanisms on treated substrates are less detailed in the literature but a few differences can be distinguished. On SiO₂ substrates, conventional cleaning

procedures such as wet chemistry or UV-ozone treatment leave a highly hydrophilic surface on which water adsorbs [117]. On the other hand, SAMs change the wetting properties of SiO₂ creating a hydrophobic surface. Surface roughness usually increases as well [123]. The role of the ad-layer of water during film growth on SiO₂ is not well understood yet. Pentacene grain sizes on SAMs are usually smaller than those on SiO₂ [124]. This is probably due to the increased roughness, although structurally, pentacene deposited on octadecyltrichlorosilane (OTS) seems to have a lower dislocation density ($0.5 \times 10^{11} \text{ cm}^{-2}$) than pentacene on SiO₂ ($0.9 \times 10^{11} \text{ cm}^{-2}$) for the same growth conditions. However, both, bulk and thin film phases are commonly found within films deposited on OTS [37, 125].

Structural Perfection. According to the standard nucleation and growth models, it is expected that the nucleation rate increases, and thus the size of the grains decreases, with increasing surface energy [39]. At this point, it is worth noting that the effect of grain size on OFETs performance is currently the subject of much debate. On the basis of polycrystalline conventional theories, it can be expected that mobility increases with grain size as charge transport in polycrystalline media is limited by grain boundaries, so that bigger grain size decreases the number of grain boundaries, leading to improved transport. Although similar observation has been reported earlier for oligothiophenes [126], several results prove the opposite is true for pentacene [124, 127] and polythiophenes [128].

In addition to the morphology observations, there is still much controversy regarding electronic transport in these organic molecular materials, although all of these materials have overlying similarity in their crystal structures – nearly all crystallize in a herringbone or herringbone-like structure in which molecules have consistently large overlap of their conjugated portions [91]. Possible explanations range from large π - π

overlap to near band-like structure, although a true picture is still evolving. The only irrefutable conclusion at this point is that herringbone-like structure seems to be conducive to higher field-effect mobilities in organic molecular crystals [114].

Device Architecture. In addition to improving structural order, reliable improvements of device performance have been demonstrated through optimization of device interfaces and architectures. The architectures are perhaps more easily addressed, and are also related to improving the structural order. Top-contact OFETs typically have the highest performance. This is most probably because of reduced contact resistance at the source and drain electrodes, related to reduced structural disorder at that interface due to dramatic morphology changes and/or dewetting of the semiconductor on/near the metallic source and drain electrodes [129].

The performance of bottom-contact devices, fairly easy to fabricate with traditional lithographic equipment, can also be improved by control of the interface of metallic source-drain electrodes. Simple SAMs on metal electrodes can alter the molecular growth, hence enhancing the crystallinity [129, 130]. The SAMs seems to serve as very thin layer which mask the characteristics of the metal and serve to minimize the transition from organic to metal. The SAM can often be chosen to improve charge injection, similar to electron transport and hole injection layers in OLEDs, in which a “buffer” material is used to reduce the charge injection barrier at certain device interfaces. SAMs have the added advantage of being chemically bound to the surface of the electrode material, thereby minimizing contributions of smaller-molecular-weight species migrating under high-field in OFETs [114].

2.5.2 The Future of Improved Performance in OFETs

In short, there are several well established routes to improving performance in OFETs. The first is to construct top-contact devices using simple methods such as shadow masking. Simply putting source and drain contacts on top of the semiconductor often results in increased mobility, simply because of improved contact resistance and crystalline order at the interfaces. A wide range of surface treatments, placed on bottom-contact source-drain electrodes and/or on gate dielectrics have also shown to be highly effective in raising mobility in OFETs [114]. The dielectric interface is likely to be a critical factor for real applications in flexible electronics. Many more experiments will be required in order to understand more fully on the interface phenomena, especially those able to separate morphology effects from others [14]. In addition, controlling and understanding deposition conditions and how they relate to structural order in the thin organic films have also contributed to improved devices [114].

Along with groups trying to understand and stabilize the performance of organic devices, there are also groups trying to find the alternatives, by combining the best attributes of variety materials, potential to optimize the material itself, which would block sensitivity to impurities or atmosphere could help to stabilize device performance. Further understanding of transport mechanisms and failure mechanisms in organic and how that relates to structure and purity could go a long way toward improving and stabilizing performance [114].

Lastly, understanding the specifications for intended applications and exact knowledge of the inadequacies of a chosen set of materials often lead to breakthroughs. The goal of the last ten years in the OFET community has been to make the best devices possible, where it has greatly improved device performance and has advanced the understanding of transport, architecture, and crystalline order in the devices. The goal for

the next ten years should be to understand the required performance levels for specific applications and to design materials, devices and systems to accommodate those requirements – in terms of both initial performance and device lifetime [114].

Chapter 3 EXPERIMENTAL PROCEDURES

This chapter contains a brief summary of experimental procedures for sol-gel dielectric synthesis and deposition, as well as the OFETs fabrication. Electrical characterizations of OFETs include current-voltage (I - V) and capacitance-voltage (C - V). Material characterizations of atomic force microscopy (AFM), X-ray diffraction (XRD), transmission electron microscopy (TEM), photoluminescence (PL), absorption, and Raman spectra were used extensively in this project.

3.1 Sol-Gel Synthesis and Deposition

Sol-gel (SG) silica solution was prepared by a two-step acid-base catalyst procedure by mixing tetraethylorthosilicate (TEOS, 99.9% purity), ethanol, water, and HCl in the following molar ratios: 1:10:3.5:0.003. After stirring at room temperature for 90 minutes, 150 μ l of the base catalyst (0.1 M NH_4OH) was then added into the solution. The solution was aged for three days under constant stirring at room temperature. The flow chart for synthesizing silica sol and its thin film deposition is shown in Figure 3.1.

The solution was filtered through a 0.2 μm PTFE membrane filter prior to spin coating at 2000 rpm on the substrate to form the sol-gel silica film of ~ 340 nm thickness. Various sol-gel silica thicknesses were also obtained from dilution of three-day aged solution by ethanol. All sol-gel silica films were dried at ambient conditions at 60°C with slow heating rate. It is widely known that the slow drying (evaporation) leads to a sufficient stress relaxation, reducing the stress stored in the shrinkage of the gel. Thus, the success in the formation of the thin silica film without fracture is attributed to the long

heating ramp-up time of 1 hour to reach the 60 °C. The films were further heated at 100°C, 10^{-7} mbar, before organic semiconductors film deposition.

Figure 3.1 Flow chart of sol-gel silica synthesis and deposition

An organic–inorganic hybrid gate dielectric layer has also been synthesized by a sol–gel process to investigate the influence of the silanol groups on the electrical performance of transistors. The precursor solution of organic–inorganic hybrid dielectric was synthesized using a mixture system of methyltriethoxysilane (MTES) and TEOS with different MTES/TEOS molar ratio of 1/9 and 1/4, while keeping the overall sol-gel reaction molar ratio constant.

3.2 OFETs Fabrication

The fabrication techniques of OFETs are divided into four sections. The first part describes the cleaning procedure for the substrate: SPM/SC-2/SC-1 clean or plasma clean, and the SiO₂ etching. The second part deals with the different organic materials used in this project as well as the pentacene purification process prior to its thermal evaporation. In third part, different organic thin-film depositions, such as thermal evaporation and

spin-coating, are discussed. The last part deals with metal source-drain electrodes deposition to form the top-contact. Figure 3.2 shows the various OFETs structures used in this project.

Figure 3.2 OFETs structures with top-contact configurations. [Gate = n-type Si wafer, TOX = thermally grown SiO₂, SG = sol-gel silica, OSC = organic semiconductor, Source/Drain = gold]

3.2.1 Substrate Cleaning and Etching

Prime grade silicon wafers (n-type Si) with various thermally grown SiO₂ (TOX) thickness (45, 100, 200 nm) were used as device substrates. Si wafer with thermally grown SiO₂ was cut into the appropriate size (1 inch x 1 inch or 3 cm x 2 cm).

SPM (Sulphuric Peroxide Mixture)/SC-2 (Standard Clean-2)/SC-1 (Standard Clean-1)

- The substrate was cleaned with Piranha solution ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 1 : 2$, to remove organic contaminants) for 8 minutes, and then rinsed with DI-water.

Note: The Piranha solution was left to stand for 8 minutes before using it. This is to allow for the stabilization of the exothermic reaction taking place.

- Standard Clean-2 (SC-2) solution ($\text{HCl} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1 : 1 : 10$) was used to remove the metallic contaminations. It was then cleaned for 10 minutes, followed by rinsing with DI-water, and dried using N₂ gas.

- c. Standard Clean -1 (SC-1) solution ($\text{NH}_4\text{OH} : \text{H}_2\text{O}_2 : \text{H}_2\text{O} = 1 : 1 : 5$) was used to further clean the organic residue. The decontamination works based on sequential oxidative desorption and complexing with SC-1. It was then cleaned for 10 minutes, followed by rinsing with DI-water, and dried using N_2 gas.
- d. The substrates were then baked on a hotplate at 120°C to remove any IPA residue present.

Plasma Clean

- a. The substrate was then cleaned with IPA for 10 minutes, and then rinsed with IPA and blown dry.
- b. Subsequently, the substrates were plasma-cleaned for 2 minutes on medium-settings power (700 V DC, 15 mA DC, 10.5 W, Plasma Cleaner PDC-32G-2, Harrick Plasma).
- c. All substrates were immersed in DI-water for 10 minutes to passivate the SiO_2 surface with hydroxyl bonds. The substrates were then rinsed with DI-water, isopropyl alcohol (IPA), and blow dried with N_2 gas.
- d. The substrates were then baked on a hotplate at 65°C to remove any IPA residue present.

Etching of Silicon Dioxide

A very selective chemical for SiO_2 (i.e., does not etch silicon at all) is hydrofluoric acid (HF). If used directly, such etchant has a too fast and vigorous action on the oxide, making very difficult the undercut and the linewidth control. For such reason, HF is universally used as a “buffered” solution, which can keep the etch rate low and constant,

by moderating the pH level of the bath. This allows the etching time to be reliably correlated to the etching depth.

The industry standard buffered hydrofluoric acid solution (BHF) has the following formulation:

6 volumes of ammonium fluoride (NH_4F) to 1 volume of HF (40% solution)

The following etching reaction holds:

3.2.2 Organic Semiconductors: Material and Purification

The semiconductors pentacene, purified through vacuum sublimation prior to usage, and {6}-1-(3-(2-thienylethoxycarbonyl)-propyl)-{5}-1-phenyl-[5,6]-C61 (TEPP-C61) were purchased from Aldrich and American Dye Source (ADS) respectively, while the poly(3,3'-didodecylquarterthiophene) (PQT; $M_w = 22,900 \text{ g mol}^{-1}$, $M_n = 17,300 \text{ g mol}^{-1}$ relative to polystyrene standard) was synthesized in-house at Xerox per the synthesis route reported previously [15]. Figure 3.3 shows the chemical structures of all the three molecules.

Figure 3.3 Chemical structures of pentacene, PQT, and TEPP-C61.

Pentacene was needed to be purified prior to usage to remove contaminants such as water and 6,13-pentacenequinone. Without pre-purification of the pentacene, pentacenequinone will sublime together with the host molecule. The procedures are as follows:

- a. The quartz tube was cleaned with IPA to remove impurities, and then blow-dried with N₂ gas.
- b. Sufficient pentacene was loaded into the tube.

Note: If the ambient air is very dry, there is a tendency for the pentacene powder to be “attracted” to tube walls because of electrostatic charging. Thus, a special apparatus is needed to shield the pentacene when it is being transported to the end of the tube.

- c. The tube was wrapped with heating tape and insulating tape, and left with a narrow exposed part. The exposed part was the site where purified pentacene would be deposited.
- d. The system was pumped down for 1 hr until a pressure of $\sim 10^{-3}$ torr was reached.
- e. Heating of the powder was done by setting the heating tape at 110 V and 1.8A for 1 hour.
- f. The purified pentacene was sublimed onto the top of the quartz tube which is unheated and was scrapped carefully from the walls of the tube by using a weighing paper-shielded spatula.

3.2.3 Organic Thin Film Deposition

Deposition of pentacene was performed in a thermal evaporation system from BOC Edwards (model Auto 306 coating system) with OLED heating source in alumina

crucible. The 500 Å pentacene film was evaporated under a vacuum of 10^{-7} mbar; at substrate temperatures of 100°C, and deposition rates of 0.5 Å/ s.

Thin films were also deposited by spin-coating 3 mg/ml PQT in dichlorobenzene at 1000 rpm for 140 s, followed by annealing in vacuum at 140°C, while 10 mg/ml of TEPP-C61 solution in chloroform was prepared to deposit films at 1000 rpm, 120 s, followed by annealing in N₂ at 120°C.

3.2.4 Metal Evaporation

On top of organic semiconductor films, gold source-drain electrodes were vacuum-deposited by shadow mask evaporation to obtain top-contact geometry. Although low work function metals are usually used for n-channel material to achieve good ohmic contact, here gold electrodes were used for TEPP-C61 FETs as it has been observed that gold electrode can also provide decent ohmic contact for n-channel materials [73].

3.3 Characterization Techniques

3.3.1 Atomic Force Microscopy (AFM)

Instrument : DIMENSION™ 3100 Series, Scanning Probe Microscope

The pentacene film morphology was characterized in tapping mode. AFM scans were performed both in ambient condition using scan size of 1 and 5 μm and a scan rate of 0.8 Hz. The internal gain and proportional gain were 0.4 and 0.6 respectively.

3.3.2 Ellipsometer

Instrument : M-44 Ellipsometer, J. A. Woollam Co., Inc. with WVASE 32™

Software

Ellipsometry for thickness measurements was carried out by using wavelength from 450 to 950 nm, and an incident angle of 60° and 65°. Readings were taken on the samples to get the sol-gel silica thickness, and the thickness was calculated by using SiO₂ on Si model.

3.3.3 Goniometer

Instrument : Goniometer

The contact angle was measured at atmospheric temperature of ~23 °C and humidity of 58 % with DI water droplets. Contact angle goniometry (CAG) is used to examine the general hydrophilicity or hydrophobicity of a surface, indicating the incorporation of functional groups,

3.3.4 Fourier Transform Infrared Spectroscopy (FT-IR)

Instrument : Perkin-Elmer System 2000

The infrared spectra data of the sol-gel dielectric on a bare n-type wafer were obtained using the Spectrum v200 software with 4 scans per sample over the range of 4000 – 400 cm⁻¹.

3.3.5 Transmission Electron Microscopy (TEM)

Instrument : JEOL JEM-2100F Field Emission Electron Microscope equipped with double-tilt holder, CCD, and TV-rate camera

The high resolution TEM (HRTEM) images were performed at 200 kV with a high contrast objective aperture of 20 μm in diameter corresponding to a nominal point-to-point resolution of 1.7 Å. The samples were prepared by grinding a stack of epoxy-glued sol-gel silica coated Si wafer to a thickness of $\sim 100\ \mu\text{m}$. The thinned sample was then stuck on a Cu grid before dimpling to a thickness of $\sim 20\ \mu\text{m}$. Afterwards, the sample was ion-milled from both sides to electron-transparent thickness regimes (20-100 nm).

3.3.6 X-ray Photoelectron Spectroscopy

Instrument : VG ESCALAB 220I – XL Imaging XPS

A monochromatic Al K α X-ray source at 1253.6 eV was used. C 1s, O 1s, Si 2p, Au 4f levels were recorded at an electron take-off angle of 90°.

3.3.7 Synchrotron X-ray Diffraction

Instrument : X-ray diffraction system with synchrotron X-ray at Singapore
Synchrotron Light Source (SSLS)

Thin films of organic semiconductors were analyzed with beamline of 8.04 keV over the 2θ range of 2° to 30°.

3.3.8 Photoluminescence (PL)/Absorption/Raman Spectrum Measurement

Instrument : Confocal Raman microscope WITec CRM200 (PL/Raman)
Shimadzu UV-2501 PC UV-vis (absorption)

PL, absorption, and Raman spectra were recorded in ambient conditions. Absorption spectra of organic thin-film were obtained using transmission set-up with the sol-gel silica coated/uncoated microscope glass slide as the baseline. Confocal Raman microscope was used for the PL and Raman study. A double-frequency Nd:YAG excitation laser with

wavelength of 532 nm was coupled into the system with single mode fiber. The power of the laser on the sample can be adjusted with linear continuous variable filter. The PL and Raman signals were collected via backscattering configuration (Olympus 100X objective lens, NA 0.95) to a TE-cooled CCD with laser spot dimension of ~500 nm.

3.3.9 Electrical Characterization

Instrument : Desert Cryogenics probe station coupled with Keithley 4200-SCS and a HP4284 LCR meter

All electrical measurements were done in a Desert Cryogenics probe station with a base pressure of 5×10^{-5} mbar. The position of each probe arms can be adjusted precisely via a three dimension (x, y, z axis) translation stage. This probe station is also equipped with a stage that can be cooled with liquid nitrogen or liquid helium. Combined with a silicon diode temperature sensor and a Lakeshore L-331 controller, this system allows low temperature electrical characterization over temperatures ranging from 4.2 K to 400 K. The I - V and C - V characteristics were measured using a Keithley 4200-SCS semiconductor parametric analyzer and a HP4284 LCR meter respectively.

Chapter 4 RESULTS

In this chapter, the sol-gel silica thin-film is experimentally identified for its bulk and surface properties. OFETs with different organic semiconductors have been fabricated to study the effect of sol-gel silica thin-film and TOX as the gate dielectric materials. Finally the morphology, molecular level ordering, and structural disorder is studied by means of atomic force microscopy (AFM), X-ray diffraction (XRD), photoluminescence/absorption spectra, and Raman spectra.

4.1 Sol-Gel Silica Thin-Films: Bulk & Surface Properties

It was found that the film smoothness and pinhole density were strongly affected by the substrate cleanliness, thus surface properties. Without any cleaning, the resulting sol-gel silica film is very non-uniform on examination using AFM (Figure 4.1a, RMS roughness ~ 3.5 nm). The film evidenced many pinholes that could have resulted from poor wetting and/or dirty surface. Superior sol-gel silica films were obtained when the silicon substrates were cleaned prior to sol-gel silica deposition as the cleaning process generates a highly hydrophilic surface, which should enhance the wettability and adhesion of the sol-gel silica. Figure 4.1b is AFM image of sol-gel silica on cleaned substrates. It can be seen that very smooth films were formed after the plasma etch (RMS ~ 0.2 nm). No-pinhole was found with sol-gel silica over a large area ($10\ \mu\text{m} \times 10\ \mu\text{m}$).

Figure 4.1 Effect of substrate cleaning on sol-gel silica film uniformity.

Thermally grown SiO_2 (TOX) was used as the gate dielectric in control sample because it is a widely used substrate for OFETs and its properties have been widely known. Thus, the study of bulk properties and surface properties of sol-gel silica thin-film was made in reference to TOX properties. Bulk and surface properties study on sol-gel silica thin-film will be presented in the following sections.

4.1.1 Bulk Properties of Sol-Gel Silica Films

The capacitance of *metal-insulator-semiconductor* (MIS, gold-TOX or SG silica/TOX-n-type Si) were measured in vacuum, yielding $C_i = 76.6 \text{ nF/cm}^2$ and 17.1 nF/cm^2 for 45 nm TOX and $\sim 390 \text{ nm}$ SG silica/45 nm TOX respectively. The dielectric constant k for the SG silica thin-film in SG silica/TOX stack was calculated to be ~ 9 , which is much higher than the dielectric constant of TOX ($k = 3.9$). Higher k for TEOS based sol-gel materials has been reported due to moisture trapping in pores [131].

Figure 4.2 Infrared absorption spectrum of sol-gel silica thin-film.

The infrared spectroscopy has been used to analyze the presence of moisture in the sol-gel silica thin-film. In the spectra, the broad peak located in the range of 3000-4000 cm^{-1} , indicated by the number 1, corresponds to the fundamental stretching vibrations of different hydroxyl groups. The broadness suggests different local environments for the OH groups as it is necessary to recognize that “water” is present in two forms: free water within the ultraporous gel structure (i.e., physisorbed water) and hydroxyl groups associated with the gel surface (i.e., chemisorbed water) [113]. The band at about 1630 cm^{-1} , indicated by the number 2, is assigned to the deformation mode of H_2O molecules trapped in the pores [132]. In the range of 400 to 1500 cm^{-1} , the spectrum shows several bands located at about 570, 800, and 1080 cm^{-1} , identified, respectively, with the number 6, 5, and 3, are the bond-rocking, the bond-bending, and the bond-stretching bands in the SiO_2 lattice. The broad 1080 cm^{-1} band with its shoulder could mean that there is different siloxane environment in the SiO_2 network structure of the sol-gel silica thin-film. Considering the chemistry of the film synthesis, the siloxane would exist both as Si-O-Si for the skeletal network and as Si-OR for the internal surface coverage [133]. The

band located at about 950 cm^{-1} , indicated with the number 4, is assigned to the stretching vibrations of silanol groups $[\text{Si}(\text{OH})]$ [132].

Figure 4.3 TEM image of a cross-sectional specimen of sol-gel silica thin-film on Si wafer with average pores diameter of $\sim 12\text{ nm}$.

Figure 4.3 shows a TEM image of a cross-sectional sol-gel silica thin-film on Si wafer. The sol-gel silica thin-film appears to have porous structures, comprising the bulk of the film thickness. The pore diameters range from $\sim 9\text{ nm}$ to $\sim 15\text{ nm}$, giving average of $\sim 12\text{ nm}$. The pores are rather uniform in its distribution and sizes as it is known that two-step acid-base catalyzed sol-gel process (initial polymerization under acidic conditions and further gelation under basic conditions) exhibit hierarchical structures and complex network topology with smaller and narrower pore size distribution [134]. In addition to

these porous structures, the sol-gel silica thin-film has a darker contrast layer appearing on the surface region and the area near the surface. This distinct layer of ~ 30 nm thickness could be correlated with the denser layer of silica networks, as similarly observed for plasma treatment-induced outer denser layers [135].

4.1.2 Surface Properties of Sol-Gel Silica Thin-Film

As surface energy is an important parameter for optimum organic molecules growth/ordering, contact angle measurements were done on both TOX and sol-gel silica thin-film surface (Figure 4.4a and b). Lower surface energy was observed for sol-gel silica surface with its water contact angle of $\sim 70^\circ \pm 5^\circ$, while water contact angle of TOX was $\sim 40^\circ \pm 3^\circ$.

AFM image of sol-gel silica (Figure 4.4d) reveals a negligible distribution of pores and crack-free surface. This suggests a closed-pore structure of the sol-gel silica thin film. Cracking and shrinkage commonly associated with ORMOSIL type materials [136] due to the breakage of the single and double carbon bonds were not observed in this study primarily because of the slow heating rates and considerably lower processing temperatures ($60 - 100^\circ\text{C}$). The resulting surface roughness of sol-gel silica thin-film deposited on TOX and TOX film, as measured by AFM, were $\sim 1.9 \text{ \AA}$ and $\sim 3.1 \text{ \AA}$, respectively (Figure 4.4c and d).

Figure 4.4 Contact angle measurements on (a) wet thermally grown SiO_2 (TOX) and (b) sol-gel silica surface. AFM scans for (a) TOX and (b) sol-gel silica thin-film. The area size of the images was $1 \times 1 \mu\text{m}^2$. Line scans were scaled to the same z -axis ($z = 2 \text{ nm}$) and x -axis ($x = 1 \mu\text{m}$) to aid better comparison.

XPS measurement was done to study the surface chemical species responsible for the low surface energy of sol-gel silica thin-film. Figure 4.5 shows the wide scan spectra of all elements present on the film. There was no Cl or N species that was used as the catalyst in the synthesis stage. The resultant peak positions of the elements were corrected with the Au $4f_{7/2}$ peak as an external standard. In general, all the spectra show broad and asymmetric lines, indicating overlaps of more than one bonding state. In the C $1s$ spectra (Figure 4.5b), at least two bonding states were observed, one is the typical hydrocarbon (C-C/H) and the other with higher binding energy is carbonyl species (C-O). Comparing these to crystalline SiO_2 such as pure quartz [137], the sol-gel silica thin-film exhibited a lower binding energy of Si $2p$ by $\sim 0.5 \text{ eV}$ while the position of O $1s$ is relatively comparable. Considering its synthesis chemistry, Si $2p$ and O $1s$ peaks would exist both as Si-O-Si for the skeletal network and as Si-OR or Si-OH [138]. From its hydrophobic surface properties, the Si-OR may be the species attributing to the different siloxane

environment, hence the centroid peak position shift. Furthermore, it has been shown that low $[\text{H}_2\text{O}]/[\text{TEOS}]$ ratio (< 5) for the sol-gel synthesis will inhibit the full hydrolyzation in the solution [132]. The $[\text{H}_2\text{O}]/[\text{TEOS}]$ used in this experiment was 3.5.

Figure 4.5 XPS spectrum of sol-gel silica thin-film: (a) wide scan spectrum showing all elements present, (b) C 1s narrow scan spectra, (c) O 1s narrow scan spectra, and (d) Si 2p narrow scan spectra.

4.2 OFET Performance of OSCs Deposited on Sol-Gel Silica Thin-Film and Thermally Grown Silica

Three different organic semiconductor molecules: pentacene, PQT, and TEPP-C61 were deposited on TOX and sol-gel dielectric as shown in Figure 4.6. The devices on TOX dielectric were used as control samples. Typical output characteristics (drain

current-drain voltage, I_D - V_D) show the standard linear and saturation regions and the I_D scaled nicely with increasing gate voltages (V_G) with minimum hysteresis and good ohmic contact as there is no gradual increase (shoulder) at very low drain bias, confirming the good quality of the dielectric material. At the same V_D , the I_D of OFETs on sol-gel silica was higher than OFETs on TOX.

Figure 4.6 (a) Chemical structures of the organic semiconductors (OSCs) employed in this study. (b) Schematic diagram of OFET device structures. (c), (d), and (e) Output characteristics (I_D - V_D) for pentacene, PQT, and TEPP-C61 FETs on TOX and sol-gel dielectric structures respectively ($V_G = 5$ V to -20 V, in steps of -5 V for pentacene and PQT, while $V_G = -5$ V to 30 V, in steps of 5 V for TEPP-C61).

The transfer characteristics in the saturation regime, the effective mobility, and the channel conductance also showed improved performance for OFET on sol-gel silica (Figure 4.7). The effective mobility was estimated from the gate voltage sweep at low drain voltage ($|V_D| = 1$ V) [139] or its transconductance from Equation 2.2, while the channel conductance was calculated from:

$$g_D = \left. \frac{\partial I_D}{\partial V_D} \right|_{V_G = \text{const}} = \frac{W}{L} \mu_n C_i (V_G - V_{Th}) \quad (4.1)$$

where L is the channel length, W is the channel width, C_i is the capacitance per unit area of the insulating layer, V_{Th} is the threshold voltage, and μ is the field effect mobility.

Figure 4.7 Transfer characteristics, μ_{eff} ($\propto$ transconductance), and channel conductance (g_D) plots for (a) pentacene, (b) PQT, and (c) TEPP-C61 FETs on TOX and sol-gel silica dielectric.

The saturation mobility (μ_{sat}) for devices on TOX and sol-gel silica were 0.07 and 0.95 cm^2/Vs for pentacene, 0.003 and 0.133 cm^2/Vs for PQT, and 0.002 and 0.041 cm^2/Vs for TEPP-C61, respectively (Table 4.1), showing significant improvements in its carrier mobility between $\sim 15\times$ to $\sim 45\times$ higher for all three molecules with devices fabricated on sol-gel silica under identical processing conditions.

Table 4.1 Device Characteristics of pentacene, PQT, and TEPP-C61 FETs on TOX and sol-gel silica thin film

OSC ^a	Dielectric	μ_{sat}^b	V_{Th}^c	s.s. ^d	$I_{\text{ON}} * L^e$	$I_{\text{ON}}/I_{\text{OFF}}^f$	C_i^g	$N_{\text{trap}}^{\text{max h}}$
Pentacene	TOX (200nm)	0.07	-6.13	547	-55	7.73×10^5	17.1	8.97×10^{11}
Pentacene	TOX(45nm)+ SG(342nm)	0.95	-3.63	289	-1062	4.07×10^6	26.6	6.59×10^{11}
PQT	TOX(45nm)	0.003	-7.31	1360	-7	5.97×10^4	76.7	1.07×10^{13}
PQT	TOX(45nm)+ SG(365nm)	0.133	-3.36	1057	-78	1.43×10^4	16.6	1.78×10^{12}
TEPP-C61	TOX(100nm)	0.002	16.60	2398	12	7.57×10^3	34.6	8.69×10^{12}
TEPP-C61	TOX(100nm)+ SG(343nm)	0.041	16.58	2861	100	4.09×10^3	15.0	4.51×10^{12}

^aOSC = organic semiconductor. For Pentacene and PQT, W/L = 500 μm /150 μm , while for TEPP-C61, W/L = 2000 μm /200 μm

^bUnit is $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$

^cUnit is V

^dUnit is mV decade⁻¹

^eUnit is $\mu\text{A} \mu\text{m}$

^f I_{ON} was taken at $V_{\text{G}} - V_{\text{Th}} = -13 \text{ V}$ (for Pentacene and PQT), or 13 V (for TEPP-C61) and I_{OFF} was taken at $V_{\text{G}} = 0 \text{ V}$

^gUnit is nF cm^{-2}

^hUnit is cm^{-2}

On-off current ratio ($I_{\text{ON}}/I_{\text{OFF}}$) values are comparable for TOX and sol-gel dielectric devices of all three molecules due to higher I_{OFF} for sol-gel dielectric device, despite its higher μ_{sat} and I_{ON} . Interestingly, the I_{OFF} is barely affected by the gate leakage current (similar gate leakage currents were observed for both devices) and by gate capacitance (C_i , similar or lower C_i was measured for sol-gel dielectric than TOX), indicating a variable degree of enhanced conductivity in the semiconductor channels themselves.

The subthreshold swing (s.s) and threshold voltage (V_{Th}) for pentacene device with sol-gel silica were 289 mV/decade and -3.63 V; whereas those for pentacene device with TOX were 547 mV/decade and -6.13 V. For PQT, the s.s and V_{Th} were 1057 mV/decade and -3.36 V on sol-gel silica, and 1360 mV/decade and -7.31 V on TOX. Similarly, the s.s and V_{Th} on sol-gel silica were 2861 mV/decade and 16.58 V for TEPP-C61 device on sol-

gel silica, and 2398 mV/decade and 16.60 V for TEPP-C61 device on TOX. Thus, the $s.s.$ and V_{Th} for devices on sol-gel dielectric were better than those for devices on TOX (especially for pentacene and PQT), despite its similar or lower capacitances (C_i) than TOX.

The shift in $s.s$ and V_{Th} could be related to difference in trap density, which can be estimated by relative V_{Th} shifts with respect to that in reference samples [140], the difference between V_{Th} and V_{ON} in the same device [141], or from its $s.s$ [140]. As V_{Th} is a fitting parameter derived from $I_{DS}^{1/2}$ - V_G curve, trap density is more reliable to be extracted from its $s.s$, less dependent on the aforementioned artifacts[21]. Thus, the maximum trap density can be estimated from [140]:

$$N_{trap}^{max} = \frac{C_i}{q} \left[\frac{qs.s \log e}{k_B T} - 1 \right] \quad (4.2)$$

where k_B is Boltzmann's constant, T is temperature, e is the base of the natural logarithm, q is the electronic charge, $s.s$ is the reciprocal subthreshold slope (in V/decade), and C_i is the capacitance/area of the gate dielectric. The estimated trap densities for the various semiconductor dielectric pairs are tabulated in Table 4.1. The devices on sol-gel dielectric show lower trap densities than the devices on TOX for all three molecules. It may be noted that PQT on sol-gel displays the highest improvement in the mobility (~45x higher) and has the largest difference in the trap density (~10x lower), while the pentacene film on sol-gel has the lowest improvement in the mobility (~15x higher) and has the smallest difference in the trap density (~1.4x lower).

4.2.1 Bulk vs Surface Effect of Sol-Gel Silica Thin-Film on Improved Transistor Performance

In Si MOSFET technology, it is known that the shift in $s.s$ and V_{Th} could be due to the difference in C_i value or trapped charges in the gate dielectric bulk or interface [90]. TOX of similar equivalent oxide thickness (EOT) to sol-gel dielectric stack (sol-gel silica on TOX) has been used in order to avoid the capacitance related artifact of threshold voltage shift (Table 4.1). Varying sol-gel silica thin-film thicknesses has been done to investigate its role in improved device performance whether it is bulk effect or interface effect (Figure 4.8).

Figure 4.8 Transfer characteristics, μ_{eff} ($\propto$ transconductance), and channel conductance (g_D) plots for pentacene FETs on TOX and sol-gel dielectric indicate improved device characteristics on sol-gel dielectric and also an independence on the thickness of the sol-gel silica thin-film.

Table 4.2 shows the device characteristics of pentacene devices fabricated on TOX and sol-gel dielectric with various sol-gel silica thin-film thicknesses. With decreasing sol-gel silica film thicknesses, increased gate capacitances, increased channel carrier concentrations, and subsequent increases in mobilities may be expected [12]. An increase in I_D with higher C_i was observed; however, the μ_{sat} , μ_{eff} , and channel conductance were not affected by the sol-gel silica thin-film thickness or by the related increase in the C_i , showing only a small variation in values of 0.87-1.24 cm^2/Vs and $\sim 1 \mu\text{S}$ at $V_G = -20 \text{ V}$, respectively. These observations strongly suggest that the improved mobilities (compared with TOX devices) are not contributed by the bulk effect, but indicating that this phenomenon is clearly a semiconductor-dielectric interface phenomenon [142].

Table 4.2 Pentacene device characteristics with TOX and sol-gel dielectric

Dielectric	μ_{sat} (cm^2/Vs)	V_{Th} (V)	s.s (mV/dec)	$I_{on} * L$ @ $V_G - V_{Th} = -13 \text{ V}$ ($\mu\text{A} \mu\text{m}$)	I_{on}/I_{off} @ $V_G - V_{Th} = -13 \text{ V}$	C_i (nF/cm^2)
TOX (200 nm)	0.07	-6.13	547	-55	7.73×10^5	17.1
TOX (45 nm) + SG (342 nm)	0.95	-3.63	289	-1062	4.07×10^6	26.6
TOX (45 nm) + SG (311 nm)	1.00	-5.20	321	-1245	3.22×10^6	29.6
TOX (45 nm) + SG (265 nm)	1.24	-5.45	334	-1756	4.71×10^6	33.9
TOX (45 nm) + SG (117 nm)	0.97	-3.64	246	-1964	3.00×10^6	46.5
TOX (45 nm) + SG (63 nm)	0.87	-3.52	229	-1609	7.02×10^6	43.7

To elucidate the surface phenomenon further, capacitance-voltage ($C-V$) behavior was analyzed at frequencies ranging from 300 Hz to 1 MHz, for metal-pentacene-oxide-

silicon capacitors (Figure 3). The value of the C-V slope at varying frequencies has been related to the density of the localized charges (N_A) [143] through Mott-Schottky relations, where variation of the capacitance in the depletion regime is determined by [144, 145]:

$$\frac{\partial\left(\frac{1}{C^2}\right)}{\partial V_G} = \frac{2}{q\epsilon_0\epsilon_{semi}N_A} \quad (4.3)$$

The C_i of different sol-gel silica film thickness showed higher capacitance than the C_i of the thermal oxide based capacitors under the same frequency, suggesting that there were fewer states with localized charges in the sol-gel silica - pentacene films. For the entire range of test frequencies, the pentacene films on sol-gel silica have lower N_A than the pentacene films on TOX. Aside the slight sol-gel silica thin-film thickness dependent, which can be explained due to some level contribution from the increased C_i , there is a clear indication that the sol-gel silica-pentacene interface has reduced localized fixed charge or trap states.

Figure 4.9 Localized charge densities of pentacene film on TOX and sol-gel silica dielectric show reduced localized charge states for different sol-gel thicknesses as compared with the reference TOX. Inset: Frequency dependence of the C_i measured at biasing voltage of -20 V (ac amplitude of 15 mV).

4.2.2 Sol-Gel Silica Thin-Film Bulk Properties Effect on Transistor Performance

For OFETs on TOX and sol-gel silica, similar hysteresis characteristics were observed (Figure 4.7) and agrees favorably with recent reports by other research groups [21, 25, 108, 146]. Hysteresis is known due to impurities and trapped charges, such as hydroxyl groups that can capture electrons [147], at the semiconductor-dielectric interface and/or those in the bulk of the dielectric, as well as the inherent properties of the dielectric [148]. In a recent study [149], a bilayer dielectric employed in the fabrication of FETs yielded evidence of the hysteresis being bulk-related rather than interface-related. In polymer, inorganic, as well as the hybrid dielectric film based OFETs, hysteresis is believed to be related to electron injection from the gate to –OH groups; however, the extrinsic origin of charge trapping for an enlarged hysteresis, V_{Th} instabilities, and higher off current in relation with the –OH groups is far from understood [150-152].

In this section, the effect of –OH groups on the electrical performances of pentacene OFETs with sol-gel silica thin-film in SG and SG/TOX dielectric systems (Figure 4.10a) are studied so as to investigate their charge trapping mechanism. The transfer characteristics of the device with the 330 nm SG silica film (single layer dielectric), measured in vacuum, exhibit a metastable clock-wise hysteresis (Figure 4.10b). The hysteresis and drain currents of the devices are significantly influenced by the sweeping rates. With the sweeping rate decreasing from 0.125 to 0.01 V/s, a significant decrease in hysteresis whereas an increase in the maximum drain current (I_{ON}) was observed. The origins of these observations may be related to trapping of electrons injected from the gate (space charge electret) [153] or polarization of the dielectric (dipolar electret) [154].

Figure 4.10 (a) Schematic structures of single and bilayer dielectric pentacene FETs. (b) The single layer (330 nm SG silica film) FET showed sweeping rate dependent hysteresis, lesser hysteresis with slower sweeping rates. (c) Transfer characteristics of FETs with and without 18nm TOX as the blocking layer between gate and 330 nm SG silica film (measured with sweeping rate of 0.01 V/s). (d) Capacitance-voltage (C - V) outputs of the MIS structures (single and bilayer dielectric) on n-type Si wafer ($f = 100$ kHz).

To confirm the mechanism responsible for the hysteresis and I_{ON} change, a thermally grown SiO₂ (TOX) layer was introduced underneath the 330 nm SG silica film to form the bilayer dielectric. If the origin of the hysteresis was related to dipolar electrets, the bilayer dielectric FET would still show the clock-wise hysteresis because the TOX would not affect the interaction of the polarization field with the pentacene channel as it was located beneath the SG silica film. However, as evidenced by Figure 4.10c, the introduction of TOX all but suppresses the hysteresis in the bilayer FETs. This observation verifies that the cause of the clockwise hysteresis is related to space charge electrets creation as electrons from the Si gate are injected into the SG silica film; thus

leading to charge storage within the SG silica bulk film [151, 153]. The charge trapping mechanism was further examined by its capacitance-voltage (C_i - V) characteristics (Figure 4.10d) in the metal-insulator-semiconductor (MIS) configuration on n-type Si wafer. Similar to the observations in the I_D - V_G characteristics (Figure 4.10b and c), the single layer sol-gel dielectric displays a positive threshold voltage (V_{Th}) shift in the MIS C_i - V scans; further suggesting the existence of negative oxide charge present in the SG silica film. In contrast, the bilayer dielectric MIS capacitor exhibits negligible hysteresis, similar to the transfer characteristics as seen in Figure 4.10c.

Furthermore, Figure 4.10c shows that the forward bias characteristics for both devices remain the same although the I_{ON}/I_{OFF} increases with the bilayer dielectric, signifying a bulk rather than interface (dielectric-semiconductor) traps phenomenon [155]. The change in I_{ON}/I_{OFF} could be attributed to the decrease in the gate leakage current (I_G) with TOX as the blocking layer (Figure 4.10c). There is also slight decrease in the I_{ON} of bilayer dielectric FET, thus the hole mobility ($\mu_h = 0.67 \text{ cm}^2/\text{Vs}$) for bilayer dielectric was calculated to be lower than that of the single layer dielectric ($\mu_h = 2.08 \text{ cm}^2/\text{Vs}$). However, its lower effective capacitance per unit area ($C_i = 16.3 \text{ nF/cm}^2$ for bilayer dielectric, compared to $C_i = 29.3 \text{ nF/cm}^2$ for single layer dielectric), due to absence of the space-charge electret field and thicker gate dielectric, along with the low gate leakage current are recognized to make significant contribution to this reduced hole mobility.

The transfer characteristics in the saturation regime for pentacene devices with TOX and sol-gel dielectric were also measured at different temperatures (Figure 4.11). It was observed that the switch-on voltage (V_{SO}) of the device with sol-gel dielectric is lower in magnitude than that with TOX (0.2 V for sol-gel dielectric device vs -1.0 V for the TOX device) and the V_{SO} were consistently lower than those of the reference TOX device at

any measured temperatures and were almost temperature independent for both OFETs. Although the early switch-on voltage is commonly contributed to Si-OH groups (preferentially trapping electrons rather than holes) [25], however the sol-gel silica has low surface energy surface due to the presence of inherently involved alkyl-terminated surfaces in the sol-gel silica network, as previously discussed in Section 4.1.2. Thus, the nature of traps might be other chemical/physical defects, rather than the silanol functionalities on dielectric surface.

Figure 4.11 (a) Transfer characteristics of pentacene FETs ($V_G = 1$ V to -5 V, in steps of -1 V) with TOX and sol-gel dielectric; measured at temperatures of 130 K, 205 K, and 298 K. (b) Hysteresis plot from its I_D-V_G and MIS $C-V$ curves, indicating different hysteresis direction for devices with TOX and sol-gel dielectric and also its temperature dependence. Note: Positive value for y-axis means clockwise hysteresis, and vice versa. The $C-V$ curves were measured with ac amplitude of 15 mV.

It was also observed that there are different hysteresis direction and temperature dependent in the sol-gel and TOX devices, with the latter displaying anticlockwise hysteresis which could be due to pentacene structural defects [156]. The hysteresis window is temperature dependent, increasing in width with increase in temperature, suggesting the temperature-activated trap states. However, the sol-gel dielectric device has different hysteresis direction, clockwise hysteresis, and its hysteresis window is increasing with temperature, followed with decrease in its window at temperature close to room temperature. In other words, the low temperature charge transport for sol-gel dielectric device could be dominated by mechanisms influenced by the sol-gel silica properties.

4.2.3 Different Chemical Bonds in Sol-Gel Silica Thin-Film and Their Influence on Transistor Performance

It is known that silicon oxide films can be doped with carbon to lower the hydrolization-induced polarity, hence lower k -value, with the main dopants used to date have been carbon in the form of alkyl groups [157-162]. In this connection, an organic-inorganic hybrid sol-gel silica of tetraethylorthosilicate (TEOS) and methyltriethoxysilane (MTES) (Figure 4.12a) was synthesized to study the effect of different chemical groups on the transistor performance. With higher [MTES]/[TEOS] ratio, higher water contact angle from $\sim 50^\circ$ to $\sim 80^\circ$ and lower dielectric constant from ~ 9 to ~ 7 , for [MTES]/[TEOS] = 0% and 20% respectively, were observed, proving the presence of the methyl group (CH_3) was unaltered, because the methyl group is neither reacted with any chemical group nor decomposed during the drying (100°C).

Figure 4.12 (a) Chemical structures of TEOS and MTES. (b) Transfer characteristics of hybrid sol-gel silica pentacene FETs measured in linear region. There is observed V_{Th} shift and pronounced hysteresis with the MTES addition. (c) Capacitance-voltage (C - V) characteristics of MPIS (metal-pentacene-insulator-semiconductor) show the similar flat-band shift and hysteresis as observed from the transfer characteristics (measured at $f = 100$ kHz). (Note: F = forward scan, R = reverse scan)

Figure 4.12b shows the transfer characteristics of the pentacene FETs fabricated using hybrid sol-gel silica with different $[\text{MTES}]/[\text{TEOS}]$ of 10% and 20%. The field-effect mobilities were similar to all three devices although there is observed negative V_{Th} shift with increasing $[\text{MTES}]/[\text{TEOS}]$ ratio and clockwise hysteresis with $[\text{MTES}]/[\text{TEOS}]$ of 1/4. The threshold voltage depends on various factors such as the flat-band voltage due to the work function difference between the gate electrode and semiconductor, the gate dielectric capacitance, and the trap states residing in both the gate dielectric and semiconductor [142]. The work function difference could be neglected as it is identical for all three transistors, having the same electrode and semiconductor materials. In this regard, the capacitance and trapped charge density difference may influence the V_{Th} shift. It is suggested that the Si-CH₃ bonds results in the V_{Th} shift and hysteresis. In the previous section, it was mentioned that silanol groups can act as trap sites for electron, thus here Si-CH₃ could act as trap sites for charges as well.

4.2.4 Properties of Sol-Gel Silica Thin-Film and Their Effect on Ambient

Performance

The performance of dielectrics in ambient conditions and the influence of moisture on dielectrics are important considerations in their study as suitable dielectrics. The influence of moisture has been documented in dielectrics such as poly(4-vinylphenol) (PVP) and poly(vinyl alcohol) (PVA). The hydroxyl (-OH) groups within PVP/PVA films or moisture has been linked to its large hysteresis [163, 164] and increase in drain currents related to polarization in the dielectric [165]. The influence of -OH groups and the effect of moisture have also been reported in inorganic [150]/organic-inorganic hybrid [22] gate dielectrics with high polarizability (or high dielectric constant, k), that results in hysteresis and negative V_{Th} shift [14]; however, the extrinsic origin of charge trapping for an enlarged hysteresis, V_{Th} instabilities, and higher off-current in ambient air is far from understood [150-152].

Figure 4.13 Response from pentacene devices on TOX and sol-gel dielectric in the saturation regime ($V_G = V_{DS} = -5$ V). Nitrogen gas with/without moisture were delivered to samples during the periods indicated by shades.

In order to examine the effect of moisture on the drain current, the devices were exposed to nitrogen gas with and without moisture (wet and dry N_2). The end of the gas delivery tube was placed close to samples so that when gas was turned on the samples were exposed to the local ambient created by the flow. In the case of pentacene FET with TOX, the magnitude of drain current decreased when subject to nitrogen gas flowing through the water reservoir (Figure 4.13), which made the device performance more humid than the normal air. The decrease of the drain current is partly attributed to trapping at the grain boundaries caused by the water molecules [166]. After changing to dry N_2 , nitrogen gas without flowing through the water reservoir, the drain current showed rapid increase followed by plateau, when the bias stress effect was balanced with the recovery by means of charge carrier releasing from water molecule induced traps. Wet N_2 was injected again, and repetitive behavior was observed.

The opposite pattern was obtained from pentacene FET with sol-gel dielectric (Figure 4.13). The drain current increased further after being exposed to the wet N_2 indicating the overall polarization of the sol-gel silica thin-films further increased owing to increased water molecules. Then, upon delivery of dry N_2 , the decrease in drain current is more strongly marked. The fastest response from device with TOX or the slowest response from device with sol-gel silica to reach plateau is due to the different water molecules diffusion rate, where water molecules need longer time to diffuse into the sol-gel silica, passing through the pentacene film first. The effect on sol-gel silica could also indicate that the bias stress can be vastly overwhelmed by the polarization in sol-gel silica [165].

4.3 **Molecular Ordering Investigations on OSCs Deposited on TOX vs Sol-Gel Silica Thin-Film**

Interplay amongst dielectric-semiconductor interfacial morphology & surface chemistry, bulk molecular order of OSCs, and electronic transport are yet to be elucidated, as previously mentioned in Section 2.5.1; particularly for different classes of OSCs such as evaporated vs solution-processed p- or n-channel molecules. In this section, various material characterization techniques are employed to give a systematic study of the morphology, crystallinity, molecular ordering, and structural disorder of the three OSCs deposited on sol-gel silica and compared to the pristine thermally grown SiO₂ (TOX).

4.3.1 **Atomic Force Microscopy Study**

The morphology of the pentacene on TOX has a smaller grain size in the range of $\sim 0.5 \mu\text{m}$ with formation of only few smaller and irregular terraces (Figure 4.14a), while the morphology of pentacene on sol-gel silica exhibits a grain size of $\sim 1.5 \mu\text{m}$ (Figure 4.14b). The grains also exhibited a terraced-structure, with a series of 12-14 terraces (Figure 4.14c and d). The terrace height was determined to be about $15 \text{ \AA}$ and is close to the length of the pentacene molecule ($16.01 \text{ \AA}$). This suggested that the long axis of the pentacene molecule was inclined by about $\sim 20^\circ$ from the normal to the substrate.

AFM phase images (Figure 4.15) show clear morphological differences between PQT films on TOX and sol-gel silica. The PQT film on the TOX dielectric forms well-defined nanorods, while the PQT film on sol-gel dielectric does not display any distinct features. It is presumed that polymer chains may have enough mobility to relax after the shear induced by the AFM stylus, thus height image is not plausible [167]. Figure 4.16

shows AFM height images of TEPP-C61 on TOX and sol-gel silica. Pinholes morphology without clear crystalline domains was observed for both films on TOX and sol-gel silica.

Figure 4.14 Morphology of pentacene film on (a) TOX and (b) sol-gel silica thin-film. (c) High resolution AFM image of pentacene on sol-gel silica along with (d) its surface profile indicating the terrace height (~ 1.5 nm) and the pentacene molecule orientation relative to the substrate ($\sim 20^\circ$).

Figure 4.15 Tapping-mode AFM phase images of PQT film on (a) TOX and (b) sol-gel silica thin-film.

Figure 4.16 AFM height images of TEPP-C61 film on (a) TOX and (b) sol-gel silica thin-film

4.3.2 X-ray Diffraction Study

The X-ray synchrotron source (S-XRD) patterns for 500 Å thick pentacene layers (Figure 4.17), exhibit a series of $(00l)$ lines, indicating a highly textured material with peaks corresponding to the thin film phases of pentacene with interplanar spacing of 15.5 Å, agreeable to the terrace step height as observed from its AFM image (Section 4.3.1). The mean crystalline domain size perpendicular to the plane (hkl) ($\bar{L}_{hkl}$), the degree of structural disorder (g_{II}), and the average number of reflecting planes ($\bar{N}$) can be calculated from the half width of the diffraction peaks, according to the α^* law or paracrystal theory [168, 169], from the following expression:

$$(\delta s)_0^2 = (\delta s)_c^2 + (\delta s)_{II}^2 = \frac{1}{\bar{L}_{hkl}^2} + \frac{\pi^4 g_{II}^4 m^4}{\bar{d}_{hkl}^2} \quad (4.4)$$

where $(\delta s)_0 = 2 \cos \theta \delta \theta / \lambda$ is the overall broadening, excluding instrumental broadening, θ is the diffraction angle, $\delta \theta$ is in radians, λ is the X-ray wavelength, $(\delta s)_c$ indicates the broadening associated with the crystalline domain size, $(\delta s)_{II}$ measures the broadening associated with the second kind of crystal structure distortions, m is the diffraction order, and $\bar{d}_{hkl}^2$ is the mean spacing between (hkl) planes. Furthermore, for a

wide range of partially ordered materials, $\sqrt{\bar{N}}g_{\parallel}$ value is about 0.15 ± 0.05 [170], where $\bar{N}$ is the average number of reflecting planes of the crystal in the film.

Figure 4.17 Synchrotron X-ray diffraction patterns of pentacene films on TOX and sol-gel silica. Inset: Calculations on crystalline size, structural disorder ($g_{\parallel}$), and number of reflecting planes (N).

The $\bar{L}_{hkl}$ were calculated to be 519 Å and 595 Å, while the $g_{\parallel}$ were determined to be 1.85 % and 1.40 % for pentacene film on TOX and sol-gel dielectric respectively. The instrumental broadening was not subtracted from the S-XRD peak width, thus the calculated crystallite size represents the lower bound [86]. Number of reflecting planes $\bar{N}$ was estimated to be 66 and 115 ML (monolayers) on TOX and sol-gel dielectric.

Despite undefined PQT film morphology on sol-gel silica, the (100) and (200) S-XRD peaks display significantly higher intensities than those for the TOX (Figure 4.18); implying well-ordered packing of the conjugated backbones, thus better lamellar π -stacking order [15]. The S-XRD observations suggest that the nanorods formation does not necessarily ensure better intermolecular interaction. Likewise the absent of crystalline domains from AFM images, there are no S-XRD peaks for TEPP-C61 films on both TOX and sol-gel silica, indicating their amorphous phase in nature (Figure 4.19).

Figure 4.18 Synchrotron X-ray diffraction patterns of PQT films on TOX and sol-gel silica thin-film.

Figure 4.19 Synchrotron X-ray diffraction pattern of TEPP-C61 films on TOX and sol-gel silica thin-film.

4.3.3 Photoluminescence/Absorption Study

Photoluminescence spectra of pentacene (Figure 4.20) exhibits a number of excitation structures between 1.8 eV and 2.6 eV with the most pronounced peak is at 1.81 eV. The energetically lowest single excitation at 1.81 eV has been modeled based on molecular Frenkel excitons (including Davydov splitting) or a charge transfer excitation, or a mixture of both [171]. It was also observed that there is suppression of the 2 eV and

2.15 eV peaks in pentacene films on sol-gel compared to that on TOX. Since the excitations above 1.81 eV are purely electronic in origin and not due to vibrations [171], they may be attributed to nonequilibrium recombinations.

Figure 4.20 PL spectra of pentacene film on TOX and sol-gel silica thin-film.

For PQT films, emergence of redshifted 0-1 peak in the photoluminescence spectrum for PQT on sol-gel dielectric against PQT on TOX (Figure 4.21) is observed, while the 0-0 peak (1.98 eV) intensity relative to 0-1 peak intensity is lower for PQT on sol-gel dielectric (0.24), compared to 0.33 for PQT on TOX. The emergence of the redshifted species has been reported to be correlated with the formation of crystallites [172-174], similarly the loss of 0-0 peak intensity with time has been indicated as energy diffusion to more ordered domains which carry lower 0-0 intensity [175].

Within an H aggregate model, magnitude of interchain coupling can be estimated from the ratio of the 0-0 and 0-1 absorbance peaks [175]. With $S = 1$, one finds:

$$\frac{A_{0-0}}{A_{0-1}} \approx \frac{n_{0-1}}{n_{0-0}} \left(\frac{1 - 0.24W/E_p}{1 + 0.073W/E_p} \right)^2 \quad (4.5)$$

where n_{0-i} is the real part of the refractive index at the 0- i peak. E_P is the phonon energy of the main oscillator coupled to the electronic transition. Absorption spectra (Figure 4.21) indicates an increase in A_{0-0}/A_{0-1} ratio from 0.538 for PQT on microscopy glass slide representing the TOX surface to 0.576 for PQT on sol-gel silica coated glass slide surface. Using $E_P = 0.18$ eV, a refractive index ratio of ~ 0.97 [176], Equation 4.5 yields the free exciton bandwidths (W) of 156 meV and 139 meV respectively.

Figure 4.21 PL spectra were measured on the transistor samples, however the absorption spectra were obtained from PQT film deposited on microscopy glass slide and sol-gel silica coated glass slide, representing the TOX and sol-gel sample respectively.

The PL measurements were also done on TEPP-C61 films and its results are shown in Figure 4.22. There are two aspects to notice from these spectra. First, the observed peak is broad and there is no splitting as observed for crystalline C_{60} film [177], implying an amorphous film [178], as confirmed by the XRD spectra (Figure 4.19). Second, there is redshift for the PL spectrum for TEPP-C61 film on sol-gel dielectric, compared to TEPP-C61 film on TOX.

Figure 4.22 PL spectra of TEPP-C61 film on TOX and sol-gel silica thin-film.

4.3.4 Raman Study

The Raman peaks at 1158 cm^{-1} and 1177 cm^{-1} (Figure 4.23) originate from the C-H in-plane vibration of the pentacene molecule. There is down-shift for both peaks of pentacene film on sol-gel silica, implying that pentacene molecules are more homogeneous, thus leading to a lower molecular relaxation energy [179, 180]. The peak at 1158 cm^{-1} may be deconvoluted to consist of three vibrational modes at: 1158 cm^{-1} (ν_0), 1154 cm^{-1} (ν_1), and 1162.5 cm^{-1} (ν_2). The ν_1 band has been associated with in-phase intermolecular coupling (twinning) vibrations of different pentacene molecules in a unit cell, while the ν_2 band has been associated with the out-of-phase intermolecular coupling of different pentacene molecules in one (00 l) plane and its adjacent (00 l) plane [181, 182].

Figure 4.23 Raman spectra of pentacene films on TOX and sol-gel silica thin-film.

Figure 4.24 shows the Raman spectra of PQT film on both TOX and sol-gel dielectric. The ν_1 mode is known to be related to the π -conjugation, with higher peak positions (larger wavenumbers) and larger widths correlated with longer conjugation lengths and wider distribution of conjugation lengths [183]. Higher peak positions (1518 cm⁻¹ vs 1510 cm⁻¹) and narrower widths of the ν_1 peak (36 cm⁻¹ vs 51 cm⁻¹) were observed for the PQT films on sol-gel dielectrics. The ν_2 band represents the symmetric stretching mode of C=C bond ring, the most intense intrinsic Raman mode of PQT. There is observed increase in intensity of this band for PQT on sol-gel dielectric than that on TOX. The $Q1$ and $Q2$ band intensities on the other hand, are almost the same on both dielectrics. These bands are contributed to doping levels [184, 185], hence signifying the equivalent doping levels for both films which were deposited under the same processing conditions.

Figure 4.24 Raman spectra of PQT film on TOX and sol-gel silica thin-film. Inset: Smaller region of Raman spectra (1470 cm^{-1} to 1555 cm^{-1}) for better ν_1 mode visibility.

Despite its amorphous phase, the Raman spectra show some features related to its intramolecular modes (Figure 4.25). Although Raman studies of TEPP-C61 are not reported in the literature, reports for C₆₀ molecules suggest that the intramolecular tangential $A_g(2)$ mode at 1467 cm^{-1} is insensitive to the substrate-induced structural difference as its shift is normally accounted to the charge transfer between the metal and C₆₀ molecules or its oxidation state [186]. In this study, the $A_g(2)$ modes do not show any change on TOX or sol-gel dielectrics showing a behavior similar to the C₆₀ films. On the other hand, the H_g (eight modes) Raman active wavenumbers in C₆₀ molecules are known to be broadened by structural disorder due to ionic or covalent bonding to other species [186] and as well as surface effects [187]. Modes $H_g(7)$ and $H_g(8)$ are sensitive to electron-phonon coupling. The FWHM of $H_g(7)$ mode at 1431 cm^{-1} was 27 cm^{-1} and 17 cm^{-1} for TEPP-C61 film on TOX and sol-gel dielectric respectively. The FWHM of H_g

(8) mode at 1569 cm^{-1} was also observed to be more broadened for TEPP-C61 film on TOX (29 cm^{-1}), compared to the film on sol-gel dielectric (25 cm^{-1}).

Figure 4.25 Raman spectra of TEPP-C61 film on TOX and sol-gel silica thin-film.

Chapter 5 DISCUSSION

This chapter is divided into three sections. The first section describes the sol-gel silica thin-film process and its implications in the resulted structure as gate dielectric for OFETs. The second section will discuss the improved performance of OFETs on sol-gel silica thin-film, compared to OFETs on thermally grown silica in electrical terms, material terms, and the correlation between both. The last section will be focused on assessing data on the transistor device stability with an emphasis on the effect of sol-gel silica bulk properties. The chemical effects of sol-gel precursors on the device performance will be evaluated as well in this section.

5.1 Sol-Gel Silica Thin-Film Properties

A key point of the sol-gel silica thin-film is the high k value and at the same time having low surface energy. These sol-gel silica thin-film properties could be schematically drawn in Figure 5.1. Porous silica comprising majority Si-OH and H-O-H bonds gives rise to its high k , while the dense silica comprising majority Si-O-C bonds relative to Si-O-H bonds gives rise to the low surface energy as evidenced by the FT-IR, TEM, contact angle, and XPS data (Section 4.1).

Figure 5.1 Schematic cross-section of single sol-gel silica thin-film layer on Si wafer.

The sol-gel silica films used in this study were cured by thermally condensing a commercially available precursor (TEOS) in two steps, first at temperature of 60 °C in ambient air and second at temperature of 100 °C in high vacuum. Use of these mild conditions yields films that have not completely cured and have hydroxyl (-OH) groups present mainly in the bulk sol-gel silica. To achieve complete dehydration, it is necessary to recognize that “water” is present in two forms: free water within the ultraporous gel structure (i.e., physisorbed water) and hydroxyl groups associated with the gel surface (i.e., chemisorbed water). This dehydration of physisorbed water is completely reversible from 25 °C to 170 °C. Only by using very high curing temperatures (i.e., 400 °C) or extended curing time at temperatures in the range of 100-200 °C, would the concentration of hydroxyl groups be sufficiently decreased for use in low dielectric constant applications [7, 113]. It was observed that the sol-gel silica thin-film has lower contact angle of only ~50° after the first curing step, compared to contact angle of ~75° after the second curing step, although the presence of these hydroxyl groups allows the surface to be modified by applying silane reagents whenever it is necessary.

High vacuum and heat (100 °C) causes further dehydration of physisorbed water and partial chemisorbed water, mainly at the surface and area near the surface.

Simultaneously with the removal of physisorbed and chemisorbed water, the structure and texture of the gels evolves: the isolated hydroxyl groups on the pore surface react with each other, bringing particles together, thereby eliminating pores within the sol-gel silica, forming the densified layer. If the surface water is unable to be desorbed prior to pore closure, it is trapped inside the densified gel [113]. Consequently, this produces the characteristics of $\sim 75^\circ$ contact angle, yielding a low energy surface without the need of any silane treatment. In addition, the required high temperature (up to 400°C) for complete dehydration signifies that the high k property of sol-gel silica thin-film is stable and suitable for the organic electronics processes and applications.

5.2 Improved OFETs Performance on Sol-Gel Silica Thin-Film

The effect of sol-gel silica dielectrics on its field-effect transistor performance has been studied with three different OSCs: evaporated small molecule p-channel pentacene, solution-processed polymeric p-channel PQT, and solution-processed fullerene derivative n-channel TEPP-C61 (Figure 4.6). These OSCs cover a broad selection in terms of majority charge carriers, core architectural characteristics (small molecule, polymer), core size (acene, buckyball), and processing methods (solution, evaporation). Devices fabricated on thermally grown SiO_2 (TOX OFETs) were used as reference.

5.2.1 Interrelation between Trapping Density and Transistor Performance

The device characteristics of all three molecules with devices fabricated on the sol-gel dielectric have been shown to have significant improvements in its effective carrier mobilities (between $\sim 15\times$ to $\sim 45\times$ higher), as well as higher effective mobility (μ_{eff} , derived from its transconductance in linear regime) and increased channel conductance as

shown in Figure 4.7, compared to devices fabricated on TOX layer dielectric under identical processing conditions. Apart from the increased carrier densities related to the presence of polarized dielectrics [165, 188]; improved interfacial ordering and grain size [126, 189] as well as interfacial trap densities [142, 190, 191] may be considered as contributing factors to the improved device characteristics.

From the pentacene study on different sol-gel silica thin-film thicknesses (Section 4.2.1), it was observed that there are similar trends in improved performances with different sol-gel silica film thicknesses, indicating this phenomenon is clearly a semiconductor-dielectric interface phenomenon rather than the bulk dielectric polarization effect. The improvement could be readily related to the larger pentacene grains [126, 189] observed on sol-gel silica thin-film ($\sim 1.5 \mu\text{m}$), compared to $\sim 0.4 \mu\text{m}$ grain size on TOX (Figure 4.14), and this morphology did not change with changing sol-gel thicknesses. This may be readily attributed to the similar smoothness (rms roughness $\sim 1.9 \text{ \AA}$) and low surface energy (water contact angles $\sim 75^\circ$) observed for the sol-gel silica films with different thicknesses, inducing and facilitating molecular ordering of pentacene layer [14, 192] (TOX has rms roughness of $\sim 3.1 \text{ \AA}$ and water contact angle of $\sim 40^\circ$), confirming the surface dielectric effect. It has also been reported that mobility can be improved by reduction in surface scattering mechanisms that may occur in the presence of a smoother interface [193].

The role of the sol-gel silica in improving the semiconductor-dielectric interface is also evident in the improvement of threshold voltage (V_{Th}) and subthreshold swing ($s.s$); further suggesting the superior surface properties of the sol-gel silica thin-film. The calculated trap densities from its $s.s$ show consistently lower trap densities for the devices on sol-gel dielectric than the devices on TOX for all three molecules (Table 4.1). It may be noted that PQT on sol-gel displays the highest improvement in the mobility ($\sim 45\times$

higher) and has the largest difference in the trap density ($\sim 10\times$ lower), while the pentacene film on sol-gel has the lowest improvement in the mobility ($\sim 15\times$ higher) and has the smallest difference in the trap density ($\sim 1.4\times$ lower). The Mott-Schottky analysis confirms the device on sol-gel silica have lower localized fixed charge or trap states (N_A) than the device on TOX, for the entire range of test frequencies (Section 4.2.1).

Surface and deep level traps can form within the semiconductor grains as well as the dielectric–semiconductor interfaces, leading to lower device currents and shifts in the turn-on voltage [127]. The low temperature measurements of pentacene FETs with and without sol-gel silica thin-film show that the origin of the traps is at the semiconductor–insulator interface from the observation on the temperature independence of switch-on voltage (V_{SO}) [194], hence the reduced interfacial trap densities is considered as one of the contributing factors to the improved device characteristics.

Sources of traps are considered to be localized at impurities, semiconductor–dielectric interface, and/or chemical/physical defects [81]. Considering that each semiconductor film is concurrently deposited on sol-gel and on TOX, traps due to impurities may be neglected. Trap density has been largely attributed to differences in the dielectric–semiconductor interface chemistry with Si-OH groups (preferentially trapping electrons rather than holes), suppressing mobility in electron-dominated charge transport and introducing extra holes at the semiconductor–dielectric interface for charge balance and a positive V_{Th} shift for hole-dominated charge transport [24, 25]. Although it looks instinctive to attribute the positive V_{Th} shift in the pentacene and PQT sol-gel FETs to these electron-trapping Si-OH groups, however the sol-gel silica surface is more hydrophobic, thus lesser Si-OH groups on the surface as discussed earlier in Section 5.1 (Figure 5.2).

Figure 5.2 Schematic diagram of functional group electron trapping efficiency on TOX and sol-gel silica.

Additionally, all of the semiconductors exhibit the same polarity on both thermally grown SiO₂ and sol-gel silica, and dielectric-induced ambipolar behavior was not observed as previously reported for pentacene on PVA [195]. Thus, the nature of traps might be other chemical/physical defects, rather than the silanol functionalities. Microstructural and molecular order information is thus essential to understand the origins of the enhanced device performance in the sol-gel FETs. Moreover, one order of increase in mobility with decreasing surface roughness has been reported and that the roughness is known to inhibit the growth of uniform, large crystal domains of polycrystalline materials [108].

5.2.2 Correlation between Morphology, Molecular Ordering, and Enhanced Transistor Performance

Although earlier it was mentioned that the improvement in pentacene devices is agreeable in common terms with improved morphology [6, 127, 193]; however contributions and interplay amongst dielectric-semiconductor interfacial morphology & surface chemistry, bulk molecular order of OSCs, and electronic transport are yet to be elucidated; particularly for different classes of OSCs such as evaporated vs solution-processed p- or n-channel molecules. In this section, a detailed discussion of the OFET response characteristics of three OSCs deposited on sol-gel silica and compared to the pristine thermally grown SiO₂ (TOX) is reported so as to investigate the different molecular order of small conjugated molecule (pentacene), polymer (poly(3,3'-didodecylquaterthiophene) – PQT), and fullerene-derivative ({6}-1-(3-(2-thienylethoxycarbonyl)-propyl)-{5}-1-phenyl-[5,6]-C61 – TEPP-C61), resulting in polycrystalline or amorphous thin films, with the improved device performance of p/n-type majority charge transport. The questions addressed here include: confirming the applicability of this sol-gel dielectric for enhanced device performance across a range of OSCs, effect of sol-gel dielectric on semiconductor-dielectric interface/morphology, and correlation between OSCs solid-state packing and device performance.

Pentacene. It has been shown that pentacene films deposited on the sol-gel silica dielectric showed an increase in grain size from ~0.4 μm on TOX to ~1.5 μm on sol-gel dielectric (Figure 4.14). Smoother [108], lower surface energy [14, 192] dielectrics are known to induce and facilitate molecular ordering of pentacene and the sol-gel surface seems to have facilitated the growth of larger pentacene grains.

The calculated $\bar{L}_{hkl}$ from their S-XRD FWHM peaks shows the similar trend in increase grain size, and the pentacene film on sol-gel silica is more ordered (g_{II} was

determined to be 1.85 % and 1.40 % for pentacene film on TOX and sol-gel dielectric respectively), corroborated by the stronger intensities of the S-XRD diffractions peaks for pentacene on sol-gel silica. The better terrace structured of pentacene film on sol-gel silica is confirmed by the number of reflecting planes $\bar{N}$, estimated to be 66 and 115 ML (monolayers) on TOX and sol-gel dielectric, agreeable to its height distributions obtained from their AFM images (Figure 5.3).

Figure 5.3 Pentacene morphology on (a) TOX and (b) sol-gel silica with its height distribution analysis.

Although it is widely reported that larger grain sizes (reduced grain boundaries) contributes to improved mobility, however, it is also known that use of surface modifiers such as octyltrichlorosilane (OTS) leads to improved mobilities despite smaller grain sizes [124]. Coalescence studies of first and second layers leading to a uniform film before bulk film growth [21] and the reports indicating different molecular orientations within identical pentacene polymorphs [27] further underline the fact that improved device performance may not be explained solely via improvements in film morphologies. Thus photoluminescence (PL) and Raman studies were employed to investigate the correlation between morphology observation, intermolecular order, and solid-state packing since both exciton migration and carrier mobility are strongly modulated by the intermolecular overlap, leading to increased bandwidth [28].

Comparing the excitation energy (1.81 eV) from the PL spectra to pentacene HOMO-LUMO gap ($E_g=1.88$ eV for thin film phase [196]) enables its assignment to the electron-hole pair creation [197]. The suppression of the 2 eV and 2.15 eV peaks (and nonequilibrium recombinations) in pentacene films on sol-gel may be attributed to larger grain sizes and larger cluster heights, similar to a report on island growth studies in pentacene films [198].

Charge mobility of organic materials may be depicted as hopping transport (at room temperature), which is affected by [95, 96]: i) the electronic coupling between adjacent molecules (transfer integral) [97], which needs to be maximized, and (ii) the reorganization energy (λ_{reorg}); which may be ignored in the case of pentacene thin films [98] in comparison with substrate-induced intermolecular interactions. Thus, Raman spectra of pentacene was used to investigate the correlation between the intermolecular couplings and the carrier transport within pentacene films [181]. The Raman peaks at 1158 cm^{-1} and 1177 cm^{-1} (Figure 4.23) originate from the C-H in-plane vibration of the pentacene molecule, with a down-shift for both peaks of pentacene film on sol-gel silica, implying that pentacene molecules are more homogeneous, thus leading to a lower molecular relaxation energy [179, 180]. The peak at 1158 cm^{-1} may be deconvoluted to consist of three vibrational modes at: 1158 cm^{-1} (ν_0), 1154 cm^{-1} (ν_1), and 1162.5 cm^{-1} (ν_2) as shown in Table 5.1. The pentacene film deposited on sol-gel dielectric shows a stronger ν_1 relative to the ν_0 band intensity and the corresponding spectral area ratio of ν_1 to ν_0 bands (A_{ν_1}/A_{ν_0}) was 0.89, compared to 0.50 for pentacene film on TOX, implying strong in-phase (intralayer) intermolecular interaction between pentacene molecules. The surface property/chemistry of sol-gel silica seemingly promotes an enhanced in-phase intermolecular coupling and π -orbital overlap thus leading to an improved carrier transport.

Table 5.1 The ν_0 , ν_1 , and ν_2 vibrational mode analysis of Raman spectra from pentacene films on TOX and sol-gel silica. Inset: Schematic drawing of the ν_1 and ν_2 band coupling effect in pentacene unit cell.

Sample	ν_0 band		ν_1 band		ν_2 band		A_{ν_1}/A_{ν_0}	A_{ν_2}/A_{ν_0}
	λ_{max} (cm^{-1})	A	λ_{max} (cm^{-1})	A	λ_{max} (cm^{-1})	A		
Pc on TOX	1157.9	4.27	1153.9	2.15	1162.5	0.58	0.50	0.14
Pc on SG silica	1157.3	2.01	1153.0	1.79	1160.4	0.35	0.89	0.17

PQT. The reasons behind the improved device performance of PQT, a solution processed polymeric semiconductor, were also probed using AFM, PL/Absorption, and Raman spectroscopy. Polythiophenes are known to show varying crystallinity, conformation and packing of polymer chains with varying molecular weights and solvents used for the formation of thin films [128, 199-201]. The PQT film on the TOX dielectric forms well-defined nanorods, while the PQT film on sol-gel dielectric does not display any distinct features (Figure 4.15). However, the S-XRD pattern of PQT on sol-gel dielectric display significantly higher peak intensities than those for the TOX (Figure 4.17); implying well-ordered packing of the conjugated backbones, thus better lamellar π -stacking order [15]. The S-XRD observations suggest that the nanorods formation does not necessarily ensure better intermolecular interaction, as the nanorods are reportedly distributed highest in a region closer to the film surface and are thought to be embedded in a disordered or amorphous matrix [128] (Figure 5.4). The lack of distinct features in the PQT on sol-gel dielectric may suggest that the nanorods formed may consist of smaller ordered domains along with a conformational change with chains either folding back, extending into the disordered/amorphous phase, or interconnecting with neighboring domains [128], and furthermore, a well-resolved (010) S-XRD presence for the PQT on sol-gel dielectric further affirming this aggregates in the film. Thus, the

transport properties of PQT are more significantly determined by the overall crystallinity of the samples and not only by the packing of the chains in the individual crystallites [128].

Figure 5.4 Schematic draw of PQT film morphologies on TOX and sol-gel silica. In these simplified pictures, the crystallites on TOX extend throughout the whole layer thickness and consist of fully extended chains. These crystalline whiskers are embedded into a disordered matrix. Film on sol-gel silica consists of small partially ordered domains with the average width smaller than the chain length, thus chains either fold back, extend into the disordered phase, or interconnect neighboring domains. (After Ref. [128])

The PQT film on sol-gel dielectric differs not only by their structural properties but also by their optical properties (Figure 4.21). The emergence of redshifted 0-1 peak in the photoluminescence spectrum for PQT on sol-gel dielectric correlates well with the small partially ordered domains with its conformational change as the chains extend and planarize [174] forming aggregates in the film [175]. This results in thermal relaxation, characteristic of van der Waals-bonded organic molecules, leading to an enhanced orbital overlap over a longer effective conjugation path [202]. Since 0-0 peak (1.98 eV) is attributed to nonradiative recombination due to extrinsic defects [203], the observed

lower 0-0 peak intensity relative to 0-1 peak intensity (0.24) for PQT on sol-gel dielectric, compared to 0.33 for PQT on TOX, signifies that the PQT film on the thermal oxide dielectric has more defects and suggests that the defects are of interchain structural nature, contributing to the observed lack of crystallinity.

Absorption spectra (Figure 4.21) indicates an increase in A_{0-0}/A_{0-1} ratio from 0.538 for PQT on microscopy glass slide representing the TOX surface to 0.576 for PQT on sol-gel silica coated glass slide surface, yielding the free exciton bandwidths (W) of 156 meV and 139 meV respectively. The interchain coupling (J where $W = 4J$) [204, 205] was estimated to be 39 meV and 35 meV for PQT film on TOX and sol-gel dielectric respectively. Thus, the PQT film on sol-gel dielectric is expected to have longer conjugation length and higher degree of interchain order than that on TOX, comprehending that lower J increases the conjugation length [175].

To further explore the physical validity of the better conjugation length, Raman spectra (Figure 4.24) was analyzed to confirm the conformational change and the π -conjugation length [183]. Higher peak positions (1518 cm^{-1} vs 1510 cm^{-1}) and narrower widths of the ν_1 peak (36 cm^{-1} vs 51 cm^{-1}) were observed for the PQT films on sol-gel dielectrics, indicating longer conjugation lengths and wider distribution of conjugation lengths [183]. The intensity increase of ν_2 band for PQT on sol-gel dielectric is possibly due to its more ordered conformational state as this is related to the symmetric stretching mode of $C=C$ bond ring.

Study of TEPP-C61 provides a comparison between p-type and n-type semiconductors and also between polycrystalline and amorphous materials and their compatibility with the sol-gel dielectrics. The AFM images demonstrate pinholes morphology without any crystalline domains for both films on TOX and sol-gel dielectric, with observed lesser pinholes density in the TEPP-C61 film on sol-gel

dielectric (Figure 4.16). These pinholes could raise the carriers scattering effect, thus affecting the charge transport in the channel.

The PL measurements were also done on TEPP-C61 films and its results are shown in Figure 4.22. The amorphous phase of TEPP-C61 is confirmed from the observed broad peak and no splitting on their spectra, as observed for crystalline C₆₀ film [177], and also confirmed by their S-XRD spectra (Figure 4.19) [178]. The redshift for the PL spectrum for TEPP-C61 film on sol-gel dielectric, compared to TEPP-C61 film on TOX, may be attributable to lesser structural defects and more closely packed molecules [206], likewise for PQT film on sol-gel.

The features in TEPP-C61 Raman spectra are related to its intramolecular modes (Figure 4.25), rather than its intermolecular mode due to its amorphous film. The intramolecular tangential $A_g(2)$ mode at 1467 cm^{-1} does not show any change on TOX or sol-gel silica as its shift is normally accounted to the charge transfer between the metal and C₆₀ molecules or its oxidation state [186]. On the other hand, modes $H_g(7)$ and $H_g(8)$ are sensitive to electron-phonon coupling. The broadened FWHM of $H_g(7)$ and $H_g(8)$ mode for TEPP-C61 film on sol-gel silica, compared to that of TEPP-C61 on TOX, suggests that the TEPP-C61 film deposited on sol-gel has lesser structural disorder. This is agreeable to literature as these H_g Raman active wavenumbers in C₆₀ molecules are known to be broadened by structural disorder due to ionic or covalent bonding to other species [186] and as well as surface effects [187].

The stronger intermolecular coupling, as observed in pentacene, yields stronger cofacial configurations, promoting the larger electronic splitting in the HOMO and LUMO states, hence impacting higher charge carrier mobilities. However, localized intermolecular coupling, indicated by nanorods formation as in the case of PQT on TOX, is not enough to yield better carrier mobility as there is discontinuous charge carrier path

from one nanorod to another nanorod, which needs to travel through the amorphous region. This results in smaller conjugation length and wider distribution of conjugation length. Even more for amorphous case, certain degree of structural disorder, hence smaller electronic coupling, could affect the transport property to a great extent, as shown from TEPP-C61 study, and the small difference in structural disorder could be detected well from the PL and Raman study.

In other words, this electronic coupling between adjacent molecules, quantified by the *transfer integral* (t), is modulated by the molecular arrangement and directly associated with the electronic mobility [207-209], influenced by the intermolecular separation distance, the molecular overlap, the length of the molecule, and, in the case of herringbone structures, the rotation of molecular planes [209]. The direct relation between the morphology and mobility, as a result of scattering by defects, impurities, and phonons (lattice vibrations), could be described by following equation [210]:

$$\mu = \frac{e\tau}{m^*} \quad (5.1)$$

where τ is the time between two consecutive scattering events, and m^* is the effective mass. Thus, the mobility increases with the degree of structural order.

In the present study, the sol-gel silica dielectric surface properties depict similar effect as self-assembled monolayer (SAM) functionalizations. Various SAMs, such as hexamethyldisilazane (HMDS) [211], octadecyltrichlorosilane (OTS) [124, 154, 212], or other silanes [154], have been shown to generally enhance OFET performance. This strategy has been extended to dielectric surface modification using spin-coated organic thin film, such as poly(α -methylstyrene) (PaMS) [64], poly(methyl methacrylate) (PMMA) [74], as well as poly(methyl silsesquioxane) (pMSSQ) [213], behaving similarly as SAMs by influencing the film morphology and microstructures along with interface traps.

5.3 Sol-Gel Silica Device Stability

Structural defects and chemical impurities in gate dielectrics have been demonstrated to have a significant role in the device stability of inorganic MOSFETs. The semiconductor layer also contains defects and impurities as previously discussed in Section 5.2.2, but there are significant differences between their effects and how they can be controlled compared with gate dielectric layer. The discussion in this section will be limited to the effects of gate dielectric defects and chemical impurities on the electrical performance of OFETs.

5.3.1 Effect of Electret on Device Hysteresis

Hysteresis in Si MOSFET technology is known due to the impurities and trapped charges, such as hydroxyl groups that can capture electrons [147], at the semiconductor-dielectric interface and/or those in the bulk of the dielectric, as well as the inherent properties of the dielectric [214]. For all OFETs, especially pentacene and PQT OFETs, on TOX and sol-gel silica (Figure 4.7), similar hysteresis characteristics were observed and agreed favorably with recent reports by other research groups [25, 108, 146, 155]. The gate-swing hysteresis is attributable to electron traps (electrochemical traps such as surface hydroxyl groups [24]) at the organic-channel/inorganic-dielectric interface, where the trapping and detrapping of electrons is likely to occur during the bias swing.

In Section 4.2.2, a bilayer dielectric (SG/TOX) employed in the fabrication of FETs yielded evidence of the hysteresis being bulk-related rather than interface-related, related to trapping electrons injected from gate by the hydroxyl groups inside the pores (space charge electret), similar to a recent study [149]. Sol-gel silica films are known to trap moisture in nanopores inside its bulk [113] ensuing in higher k values compared with TOX [131]. Cross-sectional transmission electron microscopy (XS-TEM) observations

reveal the presence of these nanopores ($\sim 10\text{-}12$ nm in diameter) and also a denser silica layer on its surface (Figure 4.3). The hydroxyl groups contained in the nanopores near the Si substrate interact with the high electron density, resulting from the negative gate bias voltage, and form electron trapping centers creating charge electrets, as illustrated in Figure 5.5. Due to the denser silica layer and the vacuum condition during measurement (drying out the physical and surface water from the area near the surface), the trapping of electrons from the channel to the sol-gel silica is negligible.

Figure 5.5 Schematic cross section of OFET with sol-gel silica as the gate dielectric. The minus signs represent volume charges injected and trapped into sol-gel silica from the gate. The plus signs represent the induced positive charges accumulated at the semiconductor interface. The electron trapping results in H^+ . The upper part of sol-gel silica has denser structure, thus containing less water/ -OH groups.

Similar to the mechanism in Si-FETs, these charge traps, which may be referred to as border traps, are spatially separated from the Si/sol-gel silica film interface; but however, are close enough to exchange charge with the underlying Si gate. These respond slowly to the applied voltage sweep [215] and thus result in the sweep rate dependent transfer characteristics (Figure 4.10).

The complexity of sol-gel silica-induced hysteresis is further explored from the low-temperature study. Figure 4.11 shows the temperature-dependent hysteresis direction and window. It is commonly known that rich –OH group in clean TOX surface could act as the electron trapping sites that are largely responsible for the anti-clockwise hysteresis in OFETs. For sol-gel OFETs, the hysteresis window starts to increase at ~200 K and decrease at ~273 K. The ~200 K is related to the transition temperature of super-cooled water or glassy water, where there is co-existence of water solid and liquid form starting at around this temperature and the liquid form proportion increases along with the increasing temperature [216]. Thus, the polarization of water molecule dipole could be the mechanism responsible for the observed temperature-dependent hysteresis, where upon freezing down to 100 K in this experiment, the water molecule dipoles are randomly oriented; and upon increasing the temperature, above its glassy water temperature, the water molecule dipoles could be alternated and aligned easily. This polarization is also observed for C - V curves of MIS (metal: gold – insulator: bi-layer dielectric – semiconductor: Si substrate) structures as shown in Figure 4.11b.

In other words, the sol-gel silica dielectric could induce hysteresis through electron-trapping from the –OH groups on its surface (interfacial trapping), bulk trapping (space charge electret), and polarization (dipolar electret), occurring only for low temperature. For single layer sol-gel silica (without TOX as blocking layer), the space charge electret-induced hysteresis could superimpose the hysteresis from its interfacial electron trapping.

5.3.2 Chemistry and Trapping Effect on Device Hysteresis and Threshold Voltage Shift

Different functional groups at the dielectric-semiconductor interface is known to influence the device characteristics and its stability under an electric field [21]. In this

section, the discussion will be limited to the effects of different functional groups from sol-gel precursors on the electrical performance of OFETs. Carbon in the form of alkyl groups [157-162] has been used as dopant to lower the hydrolization-induced polarity. In Section 4.2.3, different precursor concentrations of methyltriethoxysilane (MTES) have been mixed into the tetraethylorthosilicate (TEOS)-based sol-gel solution. In this regard, the dielectric constant difference and the water contact angle difference with different MTES concentration may influence the observed threshold voltage shift and hysteresis, which is attributed to the methyl group.

It is known that the Si-CH_3 can trap holes injected from the electrode under a positive gate bias, forming a positively charged species, $(\text{Si-CH}_3)^+$ [217]. The $(\text{Si-CH}_3)^+$ species located at the interface between the dielectric and semiconductor can develop an electric field, which induces a negative shift of the threshold voltage. The positively charged surface species of $(\text{Si-CH}_3)^+$ tends to repel the holes (h^+) present in the channel region of the semiconductor. This electrostatic interaction subsequently modifies the surface potential at the junction between the dielectric and semiconductor [218, 219], resulting in downward bending of the HOMO and LUMO bands (Figure 5.6a). This downward band bending should be overcome in order to form the transport pathway of carriers and further negative voltage is required to flatten the band bending (Figure 5.6b). Then, as the applied negative gate voltage increases, the upward bending of HOMO and LUMO bands is enhanced, in turn reaching the threshold voltage (Figure 5.6c) [220]. Therefore, because of the higher surface electric field originating from the presence of more surface $(\text{Si-CH}_3)^+$ species, more negative gate voltage has to be applied to switch on the transistor based on the hybrid sol-gel silica film with different MTES concentration.

Figure 5.6 Schematic energy level diagram of surface potential modification by surface $(\text{Si-CH}_3)^+$ species for the pentacene FETs with hybrid sol-gel silica. (After Ref. [220])

It was observed that increasing the MTES concentration to 20% not only shift the threshold voltage further to the negative value but also induce hysteresis. The observed negligible hysteresis for 10% MTES concentration, this could be due to the competing different polarities of $(\text{Si-O})^-$ from silanol groups and $(\text{Si-CH}_3)^+$ from methyl groups. Increasing the MTES concentration, the $(\text{Si-CH}_3)^+$ will increase, thus it will dominate the charge trapping centers over the negatively charged $(\text{Si-O})^-$ species. The clockwise hysteresis in its transfer characteristic was observed as well in its capacitance-voltage characteristic (Figure 4.12b and c). The trapped holes may require positive gate bias to release them from their trap charge centers, hence the flatband voltage shift for the C - V curve upon reversing the bias [147].

5.3.3 Reversible Moisture Absorption and Desorption on Its Ambient

Performance

The effect of $-\text{OH}$ groups and moisture on the electrical performances of pentacene FETs with TOX and sol-gel dielectric has been previously shown in Section 4.2.4 and is further studied in this section by measuring the transfer characteristics in vacuum and ambient conditions so as to investigate the ambient moisture effects. The physisorbed water in the silica network could be evacuated through vacuum dry process, dehydrating

the pores adjacent to the surface, hence this create further distance between the trap sites and the active layer. From the transfer characteristics measured under ambient conditions (Figure 5.7a), the pentacene FET with 330nm sol-gel silica is always on and could not be turned off, even upon application of V_G up to +20 V. This could be due to the moisture and hydrogenous species in the ambient, as observed as well from dry/wet N_2 gas measurements (Figure 4.13). Although the physisorbed water was removed, the silica networks still contained a very large concentration of chemisorbed water on the surface of the pores as its dehydration process requires high drying temperature from 170 °C up to 400 °C [113], thus enabling the reversible moisture absorption and desorption in the sol-gel silica thin-film. In addition to this, akin to the extrinsic source of the space-charge electrets formation, moisture may lead to the formation of SiOH ($Si-O-Si + H_2O \Leftrightarrow 2SiOH$) species under the influence of an electric field [221].

Figure 5.7 (a) Transfer characteristics of bilayer dielectric pentacene OFET in ambient and vacuum. This phenomenon is reversible upon repeated measurements between ambient and vacuum for thick SG silica film (330 nm) on 80 nm TOX. The ambient stability is improved with thinner SG silica film (25 nm) (b) Capacitance-voltage ($C-V$) characteristics of MIS on n-type Si wafer for bi-layer structure with thick SG silica (330 nm) and thin SG silica (25 nm), measured at $f=100$ kHz. (Note: F= forward, R= reverse)

These reversible moisture effects, which have also been reported in the PVP film [163, 165], could be illustrated from its significantly higher capacitances of the 330 nm sol-gel silica dielectric, in ambient conditions (Figure 5.7b). The increase in k of the sol-gel silica film from $k \approx 10$ in vacuum to $k \approx 21.5$ in ambient likewise signifies that dipolar polarization of the water molecules in sol-gel silica is very fast and responds readily to the measuring frequency. Moreover, the hysteresis of C_i - V characteristics is negligible, suggesting that there are negligible interfacial traps or the traps are shallow in nature, responding very fast to the measuring frequency.

Standard transfer characteristics, including a high on/off ratio in ambient conditions, was brought about in the pentacene FETs by resorting to a sol-gel silica thickness of 25 nm. Thinner sol-gel silica results in a negligible nanoporous sol-gel silica bulk layer while retaining the same denser silica skin layer on its surface, yielding a lower k value of ~ 4.5 . However, it could also be observed that there is a slight increase in I_{ON} and I_{OFF} ; and positive V_{Th} shift, compared to the 330 nm sol-gel silica FET measured in vacuum. This could be ascribed to the higher C_i ($\propto 1/d$) and the reduced charge electrets in the thin nanoporous sol-gel silica layer. The ability of these devices to operate in ambient also confirms a strong reversible hydrolysis and electrostatic charging effect rather than an electrochemical doping mechanism recently reported in polymer electrolytes [222].

Additionally, the effect of the polarization in sol-gel silica is superimposed on the drain current along with the OFETs bias stress effect, as observed in Figure 4.13 where the drain current either increases or decreases slower than TOX device. This could lead to inaccurate estimation of device performance if device characterization is conducted in an ambient with considerable humidity, especially important when the devices are designed for sensing applications since the water molecules polarize the dielectric and can screen out the response from analytes of concern [165].

5.3.4 Impact of Trapped Moisture on Transistor Charge Transport at Low Temperature

The temperature dependence of the mobility of pentacene FETs with TOX and sol-gel silica between 100 K and 300 K is shown in Figure 5.8. The mobilities of both pentacene FETs decrease with decreasing temperature. At 100 K, the mobility of the sol-gel silica FET reached down to $\sim 3 \times 10^{-6} \text{ cm}^2/\text{Vs}$, which is five orders of magnitude lower than the mobility at 300 K ($0.35 \text{ cm}^2/\text{Vs}$), and there are two different temperature dependent mobility slope as well. On the contrary, temperature dependence of the mobility of the TOX FET is more moderate/steep: the mobility at 100 K ($\sim 6 \times 10^{-4} \text{ cm}^2/\text{Vs}$) maintained the value about two orders magnitude less than that at 300 K ($\sim 0.02 \text{ cm}^2/\text{Vs}$). The activation energy (E_a) of both pentacene FETs is described by the multitrapped and release (MTR) model and is given by [223]:

$$\mu = \mu_0 \exp\left(-\frac{E_a}{k_b T}\right) \quad (5.2)$$

where μ_0 is the free carrier mobility, E_a is the activation energy to escape from trap states to delocalized states, and k_b is the Boltzmann constant.

The temperature dependent mobility of pentacene FET with TOX follows the Arrhenius-like law, with an apparent activation energy (E_a) of 53 meV, compatible with literature values [6], which could be activation energy for shallow traps due to grain boundaries and line dislocations in the pentacene film [156]. However, the temperature dependent mobility of pentacene FET with sol-gel silica is not monotonic, consisting two different E_a . The E_a of 200 – 100 K (93 meV) indicates similar value with TOX device, although the mobility is lower for sol-gel device for this temperature range. This could be due the bias dependent activation energy as the total effective gate electric field for sol-gel device is lower than that of TOX device due to thicker dielectric stack of SG/TOX (C_i

= 15.7 nF/cm² vs 115 nF/cm² at RT for sol-gel dielectric and TOX respectively) and also the random water molecule dipoles in the solid state for this temperature range. This bias dependent activation energy is explained as the shift of Fermi level at different temperatures through energetically distributed traps, which results in an implicit dependence of the mobility on the gate bias [224].

Figure 5.8 Temperature dependent mobility for pentacene FETs with TOX and sol-gel silica film.

The sudden mobility increase at $T > 200$ K with higher E_a of 329 meV for sol-gel device is related to the water molecule transformation from its solid state to transform into its supercooled water transition phase (part of the solid-state starts to become liquid-state). This polarization of water molecule dipoles will induce additional effective gate bias, thus the Fermi level of the semiconductor moves in the density of states (DOS), as a result of charge accumulated in the pentacene layer, reaching the mobile states [6]. Thus, the concentration of mobile carriers will be increased; hence the channel conductivity as well as charge carrier mobility ($\mu \sim \sigma^\delta$ [225]) will be increased as well [224]. This is confirmed by the increase in off-current (I_{OFF}) with temperature in the transfer characteristic of sol-gel device (Figure 4.11).

Chapter 6 CONCLUSIONS

Through various designed investigations, improvements in device performance and understanding of the structural order on the molecular level, together with the knowledge on the influence of gate dielectric bulk and surface traps have been achieved. This section summarizes the conclusions and original contributions stemming from this thesis.

Sol-Gel Silica Thin-Films. Smooth (rms roughness $\sim 1.9 \text{ \AA}$) and low surface energy ($\sim 70 \pm 5^\circ$) of sol-gel silica thin-film with various thicknesses could be produced through the conventional solution processing methods, making them amenable to low-cost, large area applications. This lower surface energy is contributed from the presence of non-hydrolyzed Si-OR, where R is alkyl groups. These results suggest that the sol-gel silica based dielectrics may be employed as surface treatment layers especially for rough surfaces encountered in flexible substrates or in applications that necessitate the use of low temperature solution processed dielectrics. The higher k value of ~ 9 -18 is observed for $\sim 340 \text{ nm}$ thick sol-gel silica film, contributed from the hydroxyl groups present in the porous bulk film. This high k value will enable lowering of driving voltage, as present, the transistors are often operated in the range of 50-100 V.

Improved OFETs Performance with Sol-Gel Silica Dielectrics. The improved OFETs performance (charge carrier mobility, threshold voltage, and subthreshold swing) for various organic semiconductors: p-channel (small molecule pentacene and polymeric poly(3,3''-didodecylquarterthiophene) - PQT), and n-channel fullerene derivative ($\{6\}$ -1-(3-(2-thienylethoxycarbonyl)-propyl)- $\{5\}$ -1-phenyl-[5,6]-C61 – TEPP-C61), by employing sol-gel silica dielectric, has been shown, with a significant enhancement in device mobilities ranging from $\sim 15\times$ to $\sim 45\times$ for all three organic semiconductors. The independence of device performance on the sol-gel silica films thickness indicates that

this is a surface phenomenon, rather than bulk dielectric effect, and the reduced localized fixed charge states as computed from the frequency dependent C-V characteristics suggest reduced trap densities in the sol-gel silica based OFETs.

Correlation between Morphology, Molecular Ordering, and Enhanced Device Performance with Sol-Gel Silica Dielectric. The low surface energy sol-gel silica promotes in-plane π -stacking order along with improved crystallinity for pentacene and PQT, whereas provides a reduced pin-hole density film for the amorphous TEPP-C61. Photoluminescence / absorption and Raman studies have highlighted that in addition to the effect of crystal structure and grain size; solid-state packing, intermolecular interactions, and better molecule structural order are of great significance in comprehending the improved mobility, threshold voltages, sub-threshold swings, and lower interface trap densities. Films deposited on sol-gel dielectrics showed more homogeneous and better in-phase intermolecular coupling in pentacene; longer π -conjugation length and higher degree of interchain order in PQT; and lesser structural defects and more closely packed molecules for TEPP respectively.

Sol-Gel Silica Properties and Their Effects on Device Stability. The electret effect has been studied in sol-gel silica dielectric films in pentacene FETs. Studies with cross-sectional TEM and with a blocking layer consisting of thermally grown oxide confirmed that the electret mechanism is related to electron injection into the hydroxyl groups contained within the nanopores of the sol-gel silica film. The sol-gel silica bilayer film undergoes a reversible hydrolysis reaction in ambient and as a result there is an always on characteristics for these devices. Thin sol-gel silica films (25 nm) eliminate the nanoporous hygroscopic regions of the films while facilitating the use of these dielectrics in printed electronics applications as interface layers or surface modifying layers to enable high mobilities coupled with low voltage applications in ambient environments.

The lower interfacial trapping density of pentacene on sol-gel silica film also has been confirmed from low temperature measurements. In addition, this experiment provides insight into the gate-dielectric effect on charge transport, especially at low temperatures. The hysteresis of sol-gel silica device indicates that there is a polarization phenomenon due to dipoles attributable to water molecules. The presence of polarization effected by these water molecules present inside the sol-gel bulk film was further confirmed by the temperature dependent mobility measurements.

Additionally, moisture absorption and desorption could affect the device stability when operated in ambient conditions. It has been shown that this moisture effect could be eliminated by controlling the porous bulk thickness relative to the denser silica thickness. Chemical dopings, alkyl groups, to the gate dielectric using hybrid inorganic-organic sol-gel silica have been shown to affect the transistor performance. The threshold voltage tenability and hysteresis-free device could be obtained with optimized control of MTES concentration.

In summary, it may be concluded that significant device enhancements were demonstrated by a sol-gel based dielectric which is applicable to a broad range of organic semiconductors. The applicability of these dielectrics for ambient environment operations highlight the viability of these materials for large area printed electronics applications. Fundamental understanding of the molecular ordering and interactions investigated in this study will further contribute to optimizing device performance and deployment of these materials and devices in printed electronics applications

Chapter 7 FUTURE RECOMMENDATIONS

Stemming from this thesis study, the following future works are recommended to further exploit the advantages of the sol-gel silica as gate dielectric in organic field-effect transistors and the advantages of optical study on correlation between molecular ordering and its impact on various aspects of organic electronics.

7.1 Large Area Processability of Sol-Gel Silica Dielectrics

Consequently, sol-gel silica dielectric has been demonstrated as a viable dielectric layer to enhance device performance of *p*- and *n*-channel organic semiconductors which may be evaporated or spin coated and may form either amorphous or crystalline thin films by its beneficial surface properties without the necessity for additional self-assembled monolayer (SAM) functionalization or surface modification layer. In printed electronics applications, it is imperative that dielectrics be compatible with flexible substrates, amenable to ambient operation, and be deposited by means that are scalable to large area applications.

7.1.1 Control of Dense Silica for Strain-Free Stacked Dielectric Multilayers

The stacked dielectric approach has been shown as the preferred way in this thesis for the sol-gel silica thin-film applicability as gate dielectric in OFETs with negligible bulk dielectric-induced hysteresis, in which thermally grown silica in SG/TOX stack has been used as blocking layer. Conforming to large area process, a solution-processable blocking layer is needed and the dense silica layer formation could be utilized to form the dielectric stack with thermally strain-free due to matching thermal expansion coefficient.

A thin-thick-thin sol-gel silica film stack could be obtained by controlling the dense silica formation through heat treatment [113, 134] or plasma densification [135] respectively. The thin film next to gate electrode will provide enough charge blocking due to silica densification control, while the thick film will provide the high k properties with its porous bulk film, and the thin film next to the semiconductor layer will provide additional capping effect for more robust device stability against the moisture.

7.1.2 Printing Method for Low Cost, Large Area Processing

The sol-gel dielectrics described herein have been successfully inkjet printed on flexible substrates. The improved device performance as well as ambient operations could be obtained from the pentacene FETs with inkjet printed sol-gel silica (Figure 7.1). This preliminary result confirms the applicability of sol-gel silica as gate dielectric in OFETs with its superior surface properties with other printing method for the large scale applications, such as screen-printing [49, 104] and microcontact printing [105].

Figure 7.1 Schematic draw of inkjet printed sol-gel silica film and the patterned pentacene to form the OFETs. Pentacene FETs fabricated on inkjet printed sol-gel silica have the improved performance, similar to devices fabricated on sol-gel silica film deposited by “conventional” technique (spin-coating).

7.2 Stable High k Properties in Sol-Gel Silica Through Colloid-Alkoxide

Mixture Method

Although controlling heat treatment time or temperature [113] could adjust the hydroxyl groups; however this hydrolization-induced polarity effect could be replaced with high k nanoparticles (NP) embedded in the sol-gel silica network for better device stability and at the same time harvesting the superior surface properties of sol-gel silica thin-film. The high k NP of controlled size and size distribution prepared by sol-gel method could be obtained to form its colloidal suspension, then added to the hydrolysis-polymerization of $\text{Si}(\text{OC}_2\text{H}_5)_4$ with ammonia solution. The thin film could be spin-coated on the substrate to form the high- k NP-embedded silica matrix, wherein its success in fabrication may depend on the initial size, size distribution, concentration of high- k NP, and thermal expansion coefficients to control the roughness, k value, and uniformity.

7.3 Photophysics Study of Devices Fabricated on Flexible Substrates

The optical studies on organic semiconductor films could create venues for quick and non-destructive probing method of the organic semiconductor film quality by PL/absorption or Raman scattering methods and provide insights into device process control and various stability testing issues. Examples of future works include studies on the impact of various organic semiconductor deposition methods, subsequent film treatments, or subsequent processing steps on molecular ordering and stability, the properties of heterolayer structures/hybrid blending of organic semiconductors, the bending strain effect on organic molecular ordering and device performance for flexible applications, and the understanding of device stability for ambient performance and sensing mechanisms.

REFERENCES

- [1] Horowitz, G. (2004). Organic thin film transistors: From theory to real devices. *J. Mater. Res.*, 19, 1946.
- [2] Dimitrakopoulos, C.D. and Malenfant, P.R.L. (2002). Organic thin film transistors for large area electronics. *Adv. Mater.*, 14, 99.
- [3] Nelson, S.F., Lin, Y.-Y., Gundlach, D.J., and Jackson, T.N. (1998). Temperature-independent transport in high-mobility pentacene transistors. *Appl. Phys. Lett.*, 93, 1854.
- [4] Street, R.A., Knipp, D., and Völkel, A.R. (2002). Hole transport in polycrystalline pentacene transistors. *Appl. Phys. Lett.*, 80, 1658.
- [5] Verlaak, S., Arkipov, V., and Heremans, P. (2003). Modeling of transport in polycrystalline organic semiconductor films. *Appl. Phys. Lett.*, 82, 745.
- [6] Knipp, D., Street, R.A., and Völkel, A.R. (2003). Morphology and electronic transport of polycrystalline pentacene thin-film transistors. *Appl. Phys. Lett.*, 82, 3907.
- [7] Bao, Z., Kuck, V., Rogers, J.A., and Paczkowski, M.A. (2002). Silsesquioxane resins as high-performance solution processible dielectric materials for organic transistor applications. *Adv. Funct. Mater.*, 12, 526-531.
- [8] Facchetti, A., Yoon, M.-H., and Marks, T.J. (2005). Gate dielectrics for organic field-effect transistors: New opportunities for organic electronics. *Adv. Mater.*, 17, 1705.
- [9] Fontaine, P., Goguenheim, D., Deresmes, D., Vuillaume, D., Garet, M., and Rondelez, F. (1993). Octadecyltrichlorosilane monolayers as ultrathin gate insulating films in metal-insulator-semiconductor devices. *Appl. Phys. Lett.*, 62, 2256.
- [10] Collet, J., Tharaud, O., Chapoton, A., and Vuillaume, D. (2000). Low-voltage, 30 nm channel length, organic transistors with a self-assembled monolayer as gate insulating films. *Appl. Phys. Lett.*, 76, 1941.
- [11] Yoon, M.-H., Facchetti, A., and Marks, T.J. (2005). Octadecyltrichlorosilane monolayers as ultrathin gate insulating films in metal-insulator-semiconductor devices. *Proc. Natl. Acad. Sci. U.S.A.*, 102, 4678.

- [12] Dimitrakopoulos, C.D., Kyminis, I., Purushothaman, S., Neumayer, D.A., Duncombe, P.R., and Laibowitz, R.B. (1999). Low-voltage, high-mobility pentacene transistors with solution-processed high dielectric constant insulators. *Adv. Mater.*, 11, 1372.
- [13] Dimitrakopoulos, C.D., Purushothaman, S., Kyminis, J., Callegari, A., and Shaw, J.M. (1999). Low-voltage organic transistors on plastic comprising high-dielectric constant gate insulators. *Science*, 283, 822-824.
- [14] Veres, J., Ogier, S., and Llyod, G. (2004). Gate insulators in organic field-effect transistors. *Chem. Mater.*, 16, 4543.
- [15] Ong, B.S., Wu, Y., Liu, P., and Gardner, S. (2004). High-performance semiconducting polythiophenes for organic thin-film transistors. *J. Am. Chem. Soc.*, 126, 3378.
- [16] Wu, Y., Li, Y., Gardner, S., and Ong, B.S. (2005). Indolo[3,2-*b*]carbazole-based thin-film transistors with high mobility and stability. *J. Am. Chem. Soc.*, 127, 614.
- [17] Letizia, J.A., Facchetti, A., Stern, C.L., Ratner, M.A., and Marks, T.J. (2005). High electron mobility in solution-cast and vapor-deposited phenacyl-quarterthiophene-based field-effect transistors: Toward n-type polythiophenes. *J. Am. Chem. Soc.*, 127, 13476.
- [18] Tang, M.L., Okamoto, T., and Bao, Z. (2006). High-performance organic semiconductors: Asymmetric linear acenes containing sulphur. *J. Am. Chem. Soc.*, 128, 16002.
- [19] Kline, R.J., DeLongchamp, D.M., Fischer, D.A., Lin, E.K., Richter, L.J., Chabinyc, M.L., Toney, M.F., Heeney, M., and McCulloch, I. (2007). Critical role of side-chain attachment density on the order and device performance of polythiophenes. *Macromolecules*, 40, 7960.
- [20] Yang, C., Shin, K., Yang, S.Y., Jeon, H., Choi, D., Chung, D.S., and Park, C.E. (2006). Low-voltage organic transistors on a polymer substrate with an aluminum foil gate fabricated by a laminating and electropolishing process. *Appl. Phys. Lett.*, 89, 153508.
- [21] Yoon, M.-H., Kim, C., Facchetti, A., and Marks, T.J. (2006). Gate dielectric chemical structure-organic field-effect transistor performance correlations for electron, hole, and ambipolar organic semiconductors. *J. Am. Chem. Soc.*, 128, 12851.

- [22] Katz, H.E., Hong, X.M., Dodabalapur, A., and Sarpeshkar, R. (2002). Polarizable gate organic field-effect transistors. *J. Appl. Phys.*, 91, 1572.
- [23] Takeya, J., Nishikawa, T., Takenobu, T., Kobayashi, S., Iwasa, Y., Mitani, T., Goldmann, C., Krellner, C., and Batlogg, B. (2004). Effects of polarized organosilane self-assembled monolayers on organic single-crystal field-effect transistors. *Appl. Phys. Lett.*, 85, 5078.
- [24] Chua, L.-L., Zaumseil, J., Chang, J.-F., Ou, C.-W., Ho, P.K.-H., Sirringhaus, H., and Friend, R.H. (2005). General observation of n-type field-effect behaviour in organic semiconductors *Nature*, 434, 194.
- [25] Gu, G., Kane, M.G., Doty, J.E., and Firester, A.H. (2005). Electron traps and hysteresis in pentacene-based organic thin-film transistors. *Appl. Phys. Lett.*, 87, 243512.
- [26] Reiß, S., Krumm, H., Niklewski, A., Staemmler, V., and Wöll, C. (2002). The adsorption of acenes on rutile $\text{TiO}_2(110)$: A multi-techniques investigation. *J. Chem. Phys.*, 116, 7704.
- [27] Schiefer, S., Huth, M., Dobrinevski, A., and Nickel, B. (2007). Determination of the crystal structure of substrate-induced pentacene polymorphs in fiber structured thin films. *J. Am. Chem. Soc.*, 129, 10316.
- [28] Curtis, M.D., Cao, J., and Kampf, J.W. (2004). Solid-state packing of conjugated oligomers: From π -stacks to the herringbone structure. *J. Am. Chem. Soc.*, 126, 4318.
- [29] Friend, R.H., Gymer, R.W., Holmes, A.B., Burroughes, J.H., Marks, R.N., Taliani, C., Bradley, D.D.C., Dos Santos, D.A., Bredas, J.L., Logdlund, M., and Salaneck, W.R. (1999). Electroluminescence in conjugated polymers. *Nature*, 397, 121.
- [30] Dodabalapur, A., Katz, H.E., Torsi, L., and Haddon, R.C. (1995). Organic heterostructure field-effect transistors. *Science*, 269, 1560.
- [31] Kagan, C.R., Mitzi, D.B., and Dimitrakopoulos, C.D. (1999). Organic-inorganic hybrid materials as semiconducting channels in thin-film field-effect transistors. *Science*, 286, 945.
- [32] Pope, M. and Swenberg, C.E. (1999). *Electronic processes in organic crystals and polymers*. 2nd ed., New York: Oxford University Press.

- [33] Chiang, C.K., Park, Y.W., Heeger, A.J., Shirakawa, H., Louis, E.J., and MacDiarmid, A.G. (1977). Electrical conductivity in doped polyacetylene *Phys. Rev. Lett.*, 39, 1098.
- [34] Anthony, J.E., Brooks, J.S., Eaton, D.L., and Parkin, S.R. (2001). Functionalized pentacene: Improved electronic properties from control of solid-state order. *J. Am. Chem. Soc.*, 123, 9482.
- [35] Wu, Y., Liu, P., Gardner, S., and Ong, B.S. (2005). Poly(3,3"-dialkylterthiophene)s: Room-temperature, solution-processed, high-mobility semiconductors for organic thin-film transistors. *Chem. Mater.*, 17, 221.
- [36] Chabinye, M.L., Street, R.A., and Northrup, J.E. (2007). Effects of molecular oxygen and ozone on polythiophene-based thin-film transistors. *Appl. Phys. Lett.*, 90, 123508.
- [37] Ruiz, R., Choudhary, D., Nickel, B., Toccoli, T., Chang, K.C., Mayer, A.C., Clancy, P., Blakely, J.M., Headrick, R.L., Iannotta, S., and Malliaras, G.G. (2004). Pentacene thin film growth. *Chem. Mater.*, 16, 4497.
- [38] Drummy, L.F., Kübel, C., Lee, D., White, A., and Martin, D.C. (2002). Direct imaging of defect structures in pentacene nanocrystals. *Adv. Mater.*, 14, 54.
- [39] Horowitz, G. (2006). Organic transistors. In H. Klauk (Ed.), *Organic electronics: Materials, manufacturing and applications*. Weinheim: Wiley-VCH.
- [40] Kelley, T.W., Muires, D.V., Baude, P.F., Smith, T.P., and Jones, T.D. (2003). High performance organic thin film transistors. *MRS Symp. Proc.*, 771, 169.
- [41] Halik, M., Klauk, H., Zschieschang, U., Schmid, G., Ponomarenko, S., Kirchmeyer, S., and Weber, W. (2003). Relationship between molecular structure and electrical performance of oligothiophene organic thin film transistors. *Adv. Mater.*, 15, 917.
- [42] Peng, X., Horowitz, G., Fichou, D., and Garnier, F. (1990). All-organic thin-film transistors made of alpha-sexithienyl semiconducting and various polymeric insulating layers. *Appl. Phys. Lett.*, 57, 2013.
- [43] Usta, H., Lu, G., Facchetti, A., and Marks, T.J. (2006). Dithienosilole- and dibenzosilole-thiophene copolymers as semiconductors for organic thin-film transistors. *J. Am. Chem. Soc.*, 128, 9034.
- [44] Tate, J., Rogers, J.A., Jones, C.D.W., Vyas, B., Murphy, D.W., Li, W.J., Bao, Z., Slusher, R.E., Dodabalapur, A., and Katz, H.E. (2000). Anodization and microcontact printing on electroless silver; solution based fabrication procedures

- for low voltage electronic systems with organic active components. *Langmuir*, 16, 6054.
- [45] Murphy, A.R., Frechet, J.M., Chang, P., Lee, J., and Subramanian, V. (2004). Organic thin film transistors from a soluble oligothiophene derivative containing thermally removable solubilizing groups. *J. Am. Chem. Soc.*, 126, 1596.
 - [46] Barbarella, G., Zambianchi, M., Antolini, L., Ostojia, P., Maccagnani, P., Bongini, A., Marseglia, E.A., Tedesco, E., Gigli, G., and Cingolani, R. (1999). Solid-state conformation, molecular packing and electrical and optical properties of processable b-methylated sexithiophenes. *J. Am. Chem. Soc.*, 121, 8920.
 - [47] Meng, H., Bendikov, M., Mitchell, G., Helgeson, R., Wudl, F., Bao, Z., Siegrist, T., Kloc, C., and Chen, C.H. (2003). Tetramethylpentacene: Remarkable absence of steric effect on field effect mobility. *Adv. Mater.*, 15, 1090.
 - [48] Parashkov, R., Becker, E., Ginev, G., Riedl, T., Johannes, H.-H., and Kowalsky, W. (2004). All-organic thin-film transistors made of poly(3-butylthiophene) semiconducting and various polymeric insulating layers. *J. Appl. Phys.*, 95, 1594.
 - [49] Bao, Z., Feng, Y., Dodabalapur, A., Raju, V.R., and Lovinger, A.J. (1997). High-performance plastic transistors fabricated by printing techniques. *Chem. Mater.*, 9, 1299.
 - [50] Bartic, C., Jansen, H., Campitelli, A., and Borghs, S. (2002). Ta₂O₅ as gate dielectric material for low-voltage organic thin-film transistors. *Org. Electron.*, 3, 65.
 - [51] Wang, G., Moses, D., Heeger, A.J., Zhang, H.-M., Narasimhan, M., and Demaray, R.E. (2004). Poly(3-hexylthiophene) field-effect transistors with high dielectric constant gate insulator. *J. Appl. Phys.*, 95, 316.
 - [52] Majewski, L.A., Schroder, R., Grell, M., Glarvey, P.A., and Turner, M.L. (2004). High capacitance organic field-effect transistors with modified gate insulator surface. *J. Appl. Phys.*, 96, 5781.
 - [53] Klauk, H., Halik, M., Zschieschang, U., Schmid, G., Radlik, W., and Weber, W. (2002). High-mobility polymer gate dielectric pentacene thin film transistors. *J. Appl. Phys.*, 92, 5259.
 - [54] Ha, W.H., Choo, M.H., and Im, S. (2002). Electrical properties of Al₂O₃ film deposited at low temperatures. *J. Non-Cryst. Solids*, 303, 78.

- [55] Lee, J., Kim, J.H., and Im, S. (2003). Pentacene thin-film transistors with $\text{Al}_2\text{O}_{3+x}$ gate dielectric films deposited on indium-tin-oxide glass. *Appl. Phys. Lett.*, 83, 2689.
- [56] Iino, Y., Inoue, Y., Fujisaki, Y., Fujikake, H., Sato, H., Kawakita, M., Tokito, S., and Kikuchi, H. (2003). Organic thin-film transistors on a plastic substrate with anodically oxidized high-dielectric-constant insulators. *Jpn. J. Appl. Phys.*, 42, 299.
- [57] Kang, S.J., Chung, K.B., Park, D.S., Kim, H.J., Choi, Y.K., Jang, M.H., Noh, M., and Whang, C.N. (2004). Fabrication and characterization of the pentacene thin film transistor with a Gd_2O_3 gate insulator. *Synth. Met.*, 146, 351.
- [58] Rutenberg, I., Scherman, O.A., Grubbs, R.H., Jiang, W., Garfunkel, E., and Bao, Z. (2004). Synthesis of polymer dielectric layers for organic thin film transistors via surface-initiated ring-opening metathesis polymerization. *J. Am. Chem. Soc.*, 126, 4062.
- [59] Chen, F.-C., Chu, C.-W., He, J., Yang, Y., and Lin, J.-L. (2004). Organic thin-film transistors with nanocomposite dielectric gate insulator. *Appl. Phys. Lett.*, 85, 3295.
- [60] Yoon, M.-H., Yan, H., Facchetti, A., and Marks, T.J. (2005). Low-voltage organic field-effect transistors and inverters enabled by ultrathin cross-linked polymers as gate dielectrics. *J. Am. Chem. Soc.*, 127, 10388.
- [61] Majewski, L.A., Schroeder, R., and Grell, M. (2005). One volt organic transistor. *Adv. Mater.*, 17, 192.
- [62] Brown, A.R., Pomp, A., Hart, C.M., and de Leeuw, D.M. (1995). Logic gates made from polymer transistors and their use in ring oscillators *Science*, 270, 972.
- [63] Afzali, A., Dimitrakopoulos, C.D., and Breen, T.L. (2002). High-performance, solution-processed organic thin-film transistors from a novel pentacene precursor. *J. Am. Chem. Soc.*, 124, 8812.
- [64] Majewski, L.A., Schroeder, R., and Grell, M. (2004). Flexible high capacitance gate insulators for organic field effect transistors. *J. Phys. D: Appl. Phys.*, 37, 21.
- [65] McCulloch, I., Heeney, M., Bailey, C., Genevicius, K., MacDonald, I., Shkunov, M., Sparrowe, D., Tierney, S., Wagner, R., Zhang, W., Chabinyc, M.L., Kline, R.J., McGehee, M.D., and Toney, M.F. (2006). Liquid-crystalline semiconducting polymers with high charge-carrier mobility. *Nat. Mat.*, 5, 328.

- [66] Stassen, A.F., de Boer, R.W., Iosad, N.N., and Morpurgo, A.F. (2004). Influence of the gate dielectric on the mobility of rubrene single-crystal field-effect transistors. *Appl. Phys. Lett.*, 85, 3899.
- [67] Sundar, V.C., Zaumseil, J., Podzorov, V., Menard, E., Willet, R.L., Someya, T., Gershenson, M.E., and Rogers, J.A. (2004). Elastomeric transistor stamps: Reversible probing of charge transport in organic crystals. *Science*, 303, 1644.
- [68] Chua, L.-L., Ho, P.K.-H., Sirringhaus, H., and Friend, R.H. (2004). High-stability ultrathin spin-on benzocyclobutene gate dielectric for polymer field-effect transistors. *Appl. Phys. Lett.*, 84, 3400.
- [69] Kastner, J., Paloheimo, J., and Kuzmany, H. (1993). *Solid state sciences*. New York: Springer.
- [70] Haddon, R.C., Perel, A.S., Morris, R.C., Palstra, T.T.M., and Hebard, A.F.C. (1995). C₆₀ thin film transistors. *Appl. Phys. Lett.*, 67, 121.
- [71] Jarret, C.P., Pichler, K., Newbould, R., and Friend, R.H. (1996). Transport studies in c₆₀ and c₆₀/c₇₀ thin films using metal-insulator-semiconductor field-effect transistors. *Synth. Met.*, 77, 35.
- [72] Kobayashi, S., Takenobu, T., Mori, S., Fujiwara, A., and Iwasa, Y. (2003). Fabrication and characterization of c₆₀ thin-film transistors with high field-effect mobility. *Appl. Phys. Lett.*, 82, 4581.
- [73] Anthopoulos, T.D., Kooistra, F.B., Wondergem, H.J., Kronholm, D., Hummelen, J.C., and de Leeuw, D.M. (2006). Air-stable n-channel organic transistors based on a soluble c₈₄ fullerene derivative. *Adv. Mater.*, 18, 1679.
- [74] Yuan, J., Zhang, J., Wang, J., Yan, X., Yang, D., and Xu, W. (2003). Bottom-contact organic field-effect transistors having low-dielectric layer under source and drain electrodes. *Appl. Phys. Lett.*, 82, 3967.
- [75] Facchetti, A., Deng, Y., Wang, A., Koide, Y., Sirringhaus, H., Marks, T.J., and Friend, R.H. (2000). Tuning the semiconducting properties of sexithiophene by α,ω -substitution - α,ω -diperfluorohexylsexithiophene: The first n-type sexithiophene for thin-film transistors. *Angew. Chem. Int. Ed.*, 39, 4547.
- [76] Pappenfus, T.M., Chesterfield, R.J., Frisbie, C.D., Mann, K.R., Casado, J., Raff, J.D., and Miller, L.L. (2002). A pi-stacking terthiophene-based quinodimethane is an n-channel conductor in a thin film transistor. *J. Am. Chem. Soc.*, 124, 4184.
- [77] Sirringhaus, H., Brown, P.J., Friend, R.H., Nielsen, M.M., Bechgaard, K., Langeveldvoss, B.M.W., Spiering, A.J.H., Janssen, R.A.J., Meijer, E.J., Herwig,

- P., and de Leeuw, D.M. (1999). Two-dimensional charge transport in self-organized, high-mobility conjugated polymers *Nature*, 401, 685.
- [78] Katz, H.E., Lovinger, A.J., Johnson, J., Kloc., C., Siegrist, T., Li, W.J., Lin, Y.-Y., and Dodabalapur, A. (2000). A soluble and air-stable organic semiconductor with high electron mobility. *Nature*, 404, 478.
- [79] Malenfant, P.R.L., Dimitrakopoulos, C.D., Gelorme, J.D., Kosbar, L.L., Graham, T.O., Curioni, A., and Andreoni, W. (2002). N-type organic thin-film transistor with high field-effect mobility based on a n,n'-dialkyl-3,4,9,10-perylene tetracarboxylic diimide derivative. *Appl. Phys. Lett.*, 80, 2517.
- [80] Waldauf, C., Schilinsky, P., Perisutti, M., Hauch, J., and Brabec, C.J. (2003). Solution-processed organic n-type thin-film transistors. *Adv. Mater.*, 15, 2084.
- [81] Newman, C.R., Frisbie, C.D., da Silva Filho, D.A., Bredas, J.L., Ewbank, P.C., and Mann, K.R. (2004). Introduction to organic thin film transistors and design of n-channel organic semiconductors. *Chem. Mater.*, 16, 4436.
- [82] Williams, K.A., Veenhuizen, P.T.M., de la Torre, B.G., Eritja, R., and Dekker, C. (2002). Nanotechnology carbon nanotubes with DNA recognition. *Nature*, 420, 761.
- [83] Anthony, J.E., Eaton, D.L., and Parkin, S.R. (2002). A roadmap to stable, soluble, easily crystallized pentacene derivatives. *Org. Lett.*, 4, 15.
- [84] Mattheus, C.C., Dros, A.B., Baas, J., Meetsma, A., Boer, J.L.d., and Palstra, T.T.M. (2001). Polymorphism in pentacene. *Acta Crystallographica Section C*, 57, 939-941.
- [85] Mattheus, C.C., de Wijs, G.A., de Groot, R.A., and Palstra, T.T.M. (2003). Modeling the polymorphism of pentacene *J. Am. Chem. Soc.*, 125, 6323.
- [86] Dimitrakopoulos, C.D., Brown, A.R., and Pomp, A. (1996). Molecular beam deposited thin films of pentacene for organic field effect transistor applications. *J. Appl. Phys.*, 80, 2501.
- [87] Campbell, R.B., Robertson, J.M., and Trotter, J. (1962). The crystal structure of hexacene, and a revision of the crystallographic data for tetracene and pentacene. *Acta Cryst.*, 15, 289.
- [88] Bouchoms, I.P.M., Schoonveld, W.A., Vrijmoeth, J., and Klapwijk, T.M. (1999). Morphology identification of the thin film phases of vacuum evaporated pentacene on SiO_2 substrates. *Synthetic Metals*, 104, 175.

- [89] Kim, K., Yoon, Y.K., Mun, M.-O., Park, S.P., Kim, S.S., Im, S., and Kim, J.H. (2002). Optical properties of solid pentacene. *J. Superconductivity*, 15, 595.
- [90] Sze, S.M. (1981). *Physics of semiconductor devices*. 2nd ed., USA: John Wiley & Sons
- [91] Silinsh, E.A. and Capek, V. (1994). *Organic molecular crystals*. New York: AIP Press.
- [92] Meijer, E.J., de Leeuw, D.M., Setayesh, S., van Veenendaal, E., Huisman, B.H., Blom, P.W.M., Hummelen, J.C., Scherf, U., and Klapwijk, T.M. (2003). Solution-processed ambipolar organic field-effect transistors and inverters. *Nat. Mat.*, 2, 678.
- [93] Gundlach, D.J., Lin, Y.Y., Jackson, T.N., Nelson, S.F., and G., S.D. (1997). Pentacene organic thin-film transistors - molecular ordering and mobility. *IEEE Electron Device Letters* 18, 87-89.
- [94] Podzorov, V., Pudalov, V.M., and Gershenson, M.E. (2003). Field-effect transistors on rubrene single crystals with parylene gate insulator. *Appl. Phys. Lett.*, 82, 1739.
- [95] Marcus, R.A. (1993). Electron transfer reactions in chemistry. Theory and experiment *Rev. Mod. Phys.*, 65, 599.
- [96] Gruhn, N.E., da Silva Filho, D.A., Bill, T.G., Malagoli, M., Coropceanu, V., Kahn, A., and Brédas, J.L. (2002). The vibrational reorganization energy in pentacene: Molecular influences on charge transport. *J. Am. Chem. Soc.*, 124, 7918.
- [97] Brédas, J.L., Calbert, J.P., Da Silva Filho, D.A., and Cornil, J. (2002). Organic semiconductors: A theoretical characterization of the basic parameters governing charge transport. *Proc. Natl. Acad. Sci. U.S.A.*, 99, 5804.
- [98] Bromley, S.T., Torrent, M.M.-., Hadley, P., and Rovira, C. (2004). Importance of intermolecular interactions in assessing hopping mobilities in organic field effect transistors: Pentacene versus dithiophene-tetrathiafulvalene. *J. Am. Chem. Soc.*, 126, 6544.
- [99] Jurchescu, O.D., Baas, T., and Palstra, T.T.M. (2004). Effect of impurities on the mobility of single crystal pentacene. *Appl. Phys. Lett.*, 84, 3061.
- [100] Vissenberg, M.C.J.M. and Matters, M. (1998). Theory of the field-effect mobility in amorphous organic transistors *Phys. Rev. B*, 57, 12964.

- [101] Le Comber, P.G. and Spear, W.E. (1970). Electronic transport in amorphous silicon films *Phys. Rev. Lett.*, 25, 509.
- [102] Dodabalapur, A., Torsi, L., and Katz, H.E. (1995). Organic transistors: Two-dimensional transport and improved electrical characteristics. *Science*, 268, 270.
- [103] Sancho-Garcia, J.C., Horowitz, G., Brédas, J.L., and Cornil, J. (2003). Effect of an external electric field on the charge transport parameters in molecular organic semiconductors. *J. Chem. Phys.*, 119, 12563.
- [104] Garnier, F., Hajlaoui, R., Yassar, A., and Srivastava, P. (1994). All-polymer field-effect transistor realized by printing techniques *Science*, 265, 1684.
- [105] Xia, Y. and Whitesides, G.M. (1998). Soft lithography. *Angew. Chem. Int. Ed.*, 37, 550.
- [106] Sirringhaus, H., Kawase, T., Friend, R.H., Shimoda, T., Inbasekaran, M., Wu, W., and Woo, E.P. (2000). High-resolution inkjet printing of all-polymer transistor circuits *Science*, 290, 2123.
- [107] Blanchet, G.B., Loo, Y.L., Rogers, J.A., Gao, F., and Fincher, C.R. (2003). Large area, high resolution, dry printing of conducting polymers for organic electronics. *Appl. Phys. Lett.*, 82, 463.
- [108] Fritz, S.E., Kelley, T.W., and Frisbie, C.D. (2005). Effect of dielectric roughness on performance of pentacene tfts and restoration of performance with a polymeric smoothing layer. *J. Phys. Chem. B*, 109, 10574.
- [109] Veres, J., Ogier, S., Leeming, S.W., Cupertino, D.C., and Khaffaf, S.M. (2003). Low-k insulators as the choice of dielectrics in organic field-effect transistors. *Adv. Funct. Mater.*, 13, 199.
- [110] Kingon, A.I., Maria, J.-P., and Streiffer, S.K. (2000). Alternative dielectrics to silicon dioxide for memory and logic devices *Nature*, 406, 1032.
- [111] Sandberg, H.G.O., Baecklund, T.G., Oesterbacka, R., and Stubb, H. (2004). High-performance all-polymer transistor utilizing a hygroscopic insulator. *Adv. Mater.*, 16, 1112.
- [112] Rogers, J.A., Bao, Z., Makhija, A., and Braun, P. (1999). Printing process suitable for reel-to-reel production of high-performance organic transistors and circuits. *Adv. Mater.*, 11, 741.
- [113] Hench, L.L. and West, J.K. (1990). The sol-gel process. *Chem. Rev.*, 90, 33.

- [114] Kelley, T. (2006). High-performance pentacene transistors. In H. Klauk (Ed.), *Organic electronics: Materials, manufacturing and applications*. Weinheim: Wiley-VCH.
- [115] Minakata, T., Imai, H., and Ozaki, M. (1992). Electrical properties of highly ordered and amorphous thin films of pentacene doped with iodine. *J. Appl. Phys.*, 72, 4178.
- [116] Minakata, T., Ozaki, M., and Imai, H. (1993). Conducting thin films of pentacene doped with alkaline metals. *J. Appl. Phys.*, 74, 1079.
- [117] Ruiz, R., Nickel, B., Koch, N., Feldman, L.C., Haglund, R.F., Kahn, A., and Scoles, G. (2003). Pentacene ultrathin film formation on reduced and oxidized si surfaces. *Phys. Rev. B*, 67, 125406.
- [118] Meyer zu Heringdorf, F., -J., Reuter, M.C., and Tromp, R.M. (2001). Growth dynamics of pentacene thin films. *Nature*, 412, 517.
- [119] Verlaak, S., Steudel, S., Heremans, P., Janssen, D., and Deleuze, M. (2003). Nucleation of organic semiconductors on inert substrates. *Phys. Rev. B*, 68, 195409.
- [120] Wang, Y.L., Ji, W., Shi., D.X., Du, S.X., Seidel, C., Ma, Y.G., Gao, H.J., Chi, L.F., and Fuchs, H. (2004). Structural evolution of pentacene on a ag (110) surface. *Phys. Rev. B*, 69, 075408.
- [121] Lin, Y.-Y., Gundlach, D.J., Nelson, S.F., and Jackson, T.N. (1997). Pentacene-based organic thin-film transistors. *IEEE Trans. Elect. Dev.*, 44, 1325.
- [122] Kobayashi, S., Nishikawa, T., Takenobu, T., Mori, S., Shimoda, T., Mitani, T., Shimotani, H., Yoshimoto, N., Ogawa, S., and Iwasa, Y. (2004). Control of carrier density by self-assembled monolayers in organic field-effect transistors. *Nat. Mat.*, 3, 317.
- [123] Shankar, K. and Jackson, T.N. (2004). Morphology and electrical transport in pentacene films on silylated oxide surfaces. *J. Mater. Res.*, 19, 2003.
- [124] Shtein, M., Mapel, J., Benziger, J.B., and Forrest, S.R. (2002). Effects of film morphology and gate dielectric surface preparation on the electrical characteristics of organic-vapor-phase-deposited pentacene thin-film transistors. *Appl. Phys. Lett.*, 81, 268.
- [125] Nickel, B., Barabash, R., Ruiz, R., Koch, N., Kahn, A., Feldman, L.C., Haglund, R.F., Jr., and Scoles, G. (2004). Dislocation arrangements in pentacene thin films. *Phys. Rev. B*, 70, 125401.

- [126] Horowitz, G. and Hajlaoui, M.E. (2001). Grain size dependent mobility in polycrystalline organic field-effect transistors. *Synthetic Metals*, 122, 185-189.
- [127] Knipp, D., Street, R.A., Völkel, A.R., and Ho, J. (2003). Pentacene thin film transistors on inorganic dielectrics: Morphology, structural properties, and electronic transport. *J. Appl. Phys.*, 93, 347.
- [128] Zen, A., Saphiannikova, M., Neher, D., Grenzer, J., Grigorian, S., Pietsch, U., Asawapirom, U., Janietz, S., Scherf, U., Lieberwirth, I., and Wegner, G. (2006). Effect of molecular weight on the structure and crystallinity of poly(3-hexylthiophene). *Macromolecules*, 39, 2162.
- [129] Wang, J., Gundlach, D.J., Kuo, C., and Jackson, T.N. (1999). High mobility polymer thin film transistors based on copolymers of thiophene and 3-hexyl thiophene. *41st Electronic Mater. Conf. Dig.*, 16.
- [130] Kyymissis, I., Dimitrakopoulos, C.D., and Purushothaman, S. (2001). High-performance bottom electrode organic thin- film transistors. *IEEE Trans. Elect. Dev.*, 48, 1060.
- [131] Yu, S., Wong, T.K.S., Hu, X., and Yong, M.S. (2005). Dielectric and mechanical properties of surface modified organosilicate films. *J. Sol-Gel Sci. and Tech.*, 35, 69.
- [132] Martinez, J.R., Ruiz, F., Vorobiev, Y.V., Péres-Robles, F., and González-Hernández, J. (1998). Infrared spectroscopy analysis of the local atomic structure in silica prepared by sol-gel. *J. Chem. Phys.*, 109, 7511.
- [133] Bertoluzza, A., Fagnano, C., Morelli, M.A., Gottardi, V., and Guglielmi, M. (1982). Raman and infrared spectra on silica gel evolving toward glass. *J. Non-Cryst. Solids*, 48, 117.
- [134] Brinker, C.J. (1990). Structure of sol-gel-derived glasses. *Glass science and technology*. Boston: Academic Press, Inc.
- [135] Mascia, L. and Zhang, Z. (1997). Dense outer layers formed by plasma treatments of silica coatings produced by the sol-gel method. *J. Mater. Sci.*, 32, 667.
- [136] Vorotilov, K.A., Vasiljev, V.A., Sobolevsky, M.V., and Sigov, A.S. (1998). Thin ormosil films with different organics. *J. Sol-Gel Sci. and Tech.*, 13, 467.
- [137] Chastain, J. (1992). *Handbook of x-ray photoelectron spectroscopy*. Minnesota: Perkin-Elmer.
- [138] Jo, M.-H., Park, H.-H., Kim, D.-J., Hyun, S.-H., Choi, S.-Y., and Paik, J.-T. (1997). SiO₂ aerogel film as a novel intermetal dielectric. *J. Appl. Phys.*, 82, 1299.

- [139] Sze, S.M. (2002). *Semiconductors devices: Physics and technology*. 2nd ed., New York: Wiley.
- [140] McDowell, M., Hill, I.G., McDermott, J.E.B., S. L., and Schwartz, J. (2006). Improved organic thin-film transistor performance using novel self-assembled monolayers. *Appl. Phys. Lett.*, 88, 073505.
- [141] Pernstich, K.P., Haas, S., Oberhoff, D., Goldmann, C., Gundlach, D.J., Batlogg, B., Rashid, A.N., and Schitter, G. (2004). Threshold voltage shift in organic field effect transistors by dipole monolayers on the gate insulator. *J. Appl. Phys.*, 96, 6431.
- [142] Kagan, C.R. and Andry, P. (2003). *Thin-film transistors*. 1st ed., New York: Marcel Dekker.
- [143] Zhao, N., Marinov, O., Botton, G.A., Deen, M.J., Ong, B.S., Wu, Y., and Liu, P. (2005). Characterization of mos structures based on poly(3,3"-dialkyl-quaterthiophene). *IEEE Transactions on Electron Devices*, 52, 2150-2156.
- [144] Meijer, E.J., Mangnus, A.V.G., Huisman, B.H., 't Hooft, G.W., de Leeuw, D.M., and Klapwijk, T.M. (2004). Photoimpedance spectroscopy of poly(3-hexyl thiophene) metal-insulator-semiconductor diodes. *Synth. Met.*, 142, 53.
- [145] Marinov, O., Deen, M.J., Yu, J., Vamvounis, G., Holdcroft, S., and Woods, W. (2004). Low-frequency noise in polymer thin-film transistors. *Inst. Elect. Eng. Proc. -Circuits Devices Syst.*, 151, 466.
- [146] Hwang, D.K., Lee, K., Kim, J.H., Im, S., Park, J.H., and Kim, E. (2006). Comparative studies on the stability of polymer versus SiO_2 gate dielectrics for pentacene thin-film transistors. *Appl. Phys. Lett.*, 89, 093507.
- [147] Nicollian, E.H. and Brews, J.R. (1982). *Mos (metal oxide semiconductor) physics and technology*. New York: Wiley.
- [148] Schroder, D.K. (1998). *Semiconductor material and device characterization*. 2nd ed., New York: Wiley.
- [149] Park, S.Y., Park, M., and Lee, H.H. (2004). Cooperative polymer gate dielectrics in organic thin-film transistors. *Appl. Phys. Lett.*, 85, 2283.
- [150] Koo, J.B., Ku, C.H., Lim, S.C., Kim, S.H., and Lee, J.H. (2007). Hysteresis and threshold voltage shift of pentacene thin-film transistors and inverters with Al_2O_3 gate dielectric. *Appl. Phys. Lett.*, 90, 133503.

- [151] Park, D.-W., Lee, C.A., Jung, K.-D., Park, B.-G., Shin, H., and Lee, J.D. (2006). Low hysteresis pentacene thin-film transistors using SiO_2 /cross-linked poly(vinyl alcohol) gate dielectric. *Appl. Phys. Lett.*, 89, 263507.
- [152] Lee, C.A., Park, D.W., Jin, S.H., Park, I.H., Lee, J.D., and Park, B.-G. (2006). Hysteresis mechanism and reduction method in the bottom-contact pentacene thin-film transistors with cross-linked poly(vinyl alcohol) gate insulator. *Appl. Phys. Lett.*, 88, 252102.
- [153] Huang, C., West, J.E., and Katz, H.E. (2007). Organic field-effect transistors and unipolar logic gates on charged electrets from spin-on organosilsesquioxane resins. *Adv. Funct. Mater.*, 17, 142.
- [154] Salleo, A., Chabinyc, M.L., Yang, M.S., and Street, R.A. (2002). Polymer thin-film transistors with chemically modified dielectric interfaces. *Appl. Phys. Lett.*, 81, 4383-4385.
- [155] Yoon, M.-H., Kim, C., Facchetti, A., and Marks, T.J. (2006). Gate dielectric chemical structure-organic field-effect transistor performance correlations for electron, hole, and ambipolar organic semiconductors. *J. Am. Chem. Soc.*, 128, 12851-12869.
- [156] Puntambekar, K., Dong, J., Haugstad, G., and Frisbie, C.D. (2006). Structural and electrostatic complexity at a pentacene/insulator interface. *Adv. Funct. Mater.*, 16, 879.
- [157] Maex, K., Baklanov, M.R., Shamiryan, D., Iacopi, F., Brongersma, S.H., and Yanovitskaya, Z.S. (2003). Low dielectric constant materials for microelectronics. *J. Appl. Phys.*, 93, 8793.
- [158] Han, S.S., Kim, H.R., and Bae, B.S. (1999). Deposition of fluorinated amorphous carbon thin films as a low-dielectric-constant material. *J. Electrochem. Soc.*, 146, 3383.
- [159] Oh, K.S., Jing, S.Y., Choi, C.K., Lee, K.M., and Lee, H.J. (2001). Formation and characteristics of fluorinated amorphous carbon films deposited by CF_4/CH_4 icpcvd. *J. Korean Phys. Soc.*, 39, 291.
- [160] Lim, S.W., Shimogaki, Y., Nakano, Y., Tada, K., and Komiyama, H. (1999). Changes in orientational polarization and structure of silicon dioxide film by fluorine addition. *J. Electrochem. Soc.*, 146, 4196.

- [161] Kim, J.Y., Hwang, M.S., Kim, Y.H., Kim, H.J., and Lee, Y. (2001). Origin of low dielectric constant of carbon-incorporated silicon oxide film deposited by plasma enhanced chemical vapor deposition *J. Appl. Phys.*, 90, 2469.
- [162] Wang, M.R., Rusli, Yu, M.B., Babu, N., Li, C.Y., and Rakesh, K. (2004). Low dielectric constant films prepared by plasma-enhanced chemical vapor deposition from trimethylsilane. *Thin Solid Films*, 462-463, 219.
- [163] Noh, Y.H., Park, S.Y., Seo, S.-M., and Lee, H.H. (2006). Root cause of hysteresis in organic thin film transistor with polymer dielectric. *Org. Electron.*, 7, 271.
- [164] Lim, S.C., Kim, S.H., Koo, J.B., Lee, J.H., Ku, C.H., Yang, S.Y., and Zyung, T. (2007). Hysteresis of pentacene thin-film transistors and inverters with cross-linked poly(4-vinylphenol) gate dielectrics. *Appl. Phys. Lett.*, 90, 173512.
- [165] Jung, T., Dodabalapur, A., Wenz, R., and Mohapatra, S. (2005). Moisture induced surface polarization in a poly(4-vinyl phenol) dielectric in an organic thin-film transistor. *Appl. Phys. Lett.*, 87, 182109.
- [166] Li, D., Borkent, E.J., Nortrup, R., Moon, H., Katz, H.E., and Bao, Z. (2005). Humidity effect on electrical performance of organic thin-film transistors. *Appl. Phys. Lett.*, 86, 042105.
- [167] Derue, G., Coppée, S., Gabriele, S., Surin, M., Geskin, V., Monteverde, F., Leclère, P., Lazzaroni, R., and Damman, P. (2005). Nanorubbing of polythiophene surfaces. *J. Am. Chem. Soc.*, 127, 8018.
- [168] Wyckoff, R.W.G. (1971). *Crystal structures*. 2nd ed., New York: Interscience.
- [169] Hosemann, R. and Hindeleh, A.M. (1995). Structure of crystalline and paracrystalline condensed matter. *J. Macromol. Sci. Phys.*, B34, 327.
- [170] Hindeleh, A.M. and Hosemann, R. (1988). Paracrystals representing the physical state of matter. *J. Phys. C: Solid State Phys.*, 21, 4155.
- [171] Grobosch, M., Schuster, R., Pichler, T., and Knupfer, M. (2006). Analysis of the anisotropy of excitons in pentacene single crystals using reflectivity measurements and electron energy-loss spectroscopy. *Phys. Rev. B*, 74, 155202.
- [172] Rumbles, G., Samuel, I.D.W., Magnani, L., Murray, K.A., DeMello, A.J., Crystall, B., Moratti, S.C., Stone, B.M., Holmes, A.B., and Friend, R.H. (1996). Chromism and luminescence in regioregular poly(3-dodecylthiophene). *Synth. Met.*, 76, 47.

- [173] Theander, M., Svensson, M., Ruseckas, A., Zigmantas, D., Sundström, V., Andersson, M.R., and Inganäs, O. (2001). High luminescence from a substituted polythiophene in a solvent with low solubility. *Chem. Phys. Lett.*, 337, 277.
- [174] Yue, S., Berry, G.C., and McCullough, R.D. (1996). Intermolecular association and supramolecular organization in dilute solution. 1. Regioregular poly(3-dodecylthiophene). *Macromolecules*, 29, 933.
- [175] Clark, J., Silva, C., Friend, R.H., and Spano, F.C. (2007). Role of intermolecular coupling in the photophysics of disordered organic semiconductors: Aggregate emission in regioregular polythiophene. *Phys. Rev. Lett.*, 98, 206406.
- [176] Brown, P.J., Thomas, D.S., Köhler, A., Wilson, J.S., Kim, J.-S., Ramsdale, C.M., Sirringhaus, H., and Friend, R.H. (2003). Effect of interchain interactions on the absorption and emission of poly(3-hexylthiophene). *Phys. Rev. B*, 67, 064203.
- [177] Ebbsen, T.W., Mochizuki, Y., Tanigaki, K., and Hiura, H. (1994). Direct observation of c_{60} exciton. *Europhys. Lett.*, 25, 503.
- [178] Chikamatsu, M., Nagamatsu, S., Yoshida, Y., Saito, K., and Yase, K. (2005). Solution-processed *n*-type organic thin-film transistors with high field-effect mobility. *Appl. Phys. Lett.*, 87, 203504.
- [179] Cheng, H.L., Mai, S., Chou, W.Y., and Chang, L.R. (2007). Influence of molecular structure and microstructure on device performance of polycrystalline pentacene thin-film transistors. *Appl. Phys. Lett.*, 90, 171926.
- [180] Cazayous, M., Sacuto, A., Horowitz, G., Lang, P., Zimmers, A., and Lobo, R.P.S.M. (2004). Iodine insertion in pentacene thin films investigated by infrared and raman spectroscopy. *Phys. Rev. B*, 70, 081309.
- [181] Cheng, H.L., Chou, W.Y., Kou, C.W., Tang, F.C., and Wang, Y.W. (2006). Electric field-induced structural changes in pentacene-based organic thin-film transistors studied by *in situ* micro-Raman spectroscopy. *Appl. Phys. Lett.*, 88, 161918.
- [182] Farina, L., Brillante, A., Della Valle, R.G., Venuti, E., Amboage, M., and Syassen, K. (2003). Pressure-induced phase transition in pentacene. *Chem. Phys. Lett.*, 375, 490.
- [183] Kim, H.-J., Kim, D.-C., Kim, R., Kim, J.H., Park, D.-H., Kim, H.-S., Joo, J., and Suh, Y.D. (2007). Confocal Raman spectroscopy of single poly(3-methylthiophene) nanotubes. *J. Appl. Phys.*, 101, 053514.

- [184] Furukawa, Y. (1996). Electronic absorption and vibrational spectroscopies of conjugated conducting polymers. *J. Phys. Chem.*, 100, 15644.
- [185] Chen, F., Shi, G., Zhang, J., and Fu, M. (2003). Raman spectroscopic studies on the structural changes of electrosynthesized polythiophene films during the heating and cooling processes. *Thin Solid Films*, 424, 283.
- [186] Dresselhaus, M.S., Dresselhaus, G., and Eklund, P.C. (1996). Raman scattering in fullerenes. *Journal of Raman Spectroscopy*, 27, 351.
- [187] Manaila, R., Belu-Marian, A., Macovei, D., Brehm, G., Marian, D.T., and Baltog, I. (1999). Evidence for metal- c_{60} interface interaction from raman spectroscopy. *Journal of Raman Spectroscopy*, 30, 1019.
- [188] Qiu, Y., Hu, Y., Dong, G., Wang, L., Xie, J., and Ma, Y. (2003). H_2O effect on the stability of organic thin-film field-effect transistors. *Appl. Phys. Lett.*, 83, 1644.
- [189] Carlo, A.D., Piacenza, F., Bolognesi, A., Stadlober, B., and Maresch, H. (2005). Influence of grain sizes on the mobility of organic thin-film transistors. *Appl. Phys. Lett.*, 86, 263501.
- [190] McDowell, M., Hill, I.G., McDermott, J.E., Bernasek, S.L., and Schwartz, J. (2006). Improved organic thin-film transistor performance using novel self-assembled monolayers. *Applied Physics Letters*, 88, 073505.
- [191] Lee, J., Kim, J.H., Im, S., and Jung, D.-Y. (2004). Threshold voltage change due to organi-inorganic interface in pentacene thin-film transistors. *Journal of Applied Physics*, 96, 2301-2304.
- [192] Wu, Y., Liu, P., and Ong, B.S. (2006). Organic thin-film transistors with poly(methyl silsesquioxane) modified dielectric interfaces. *Applied Physics Letters*, 89, 013505.
- [193] Steudel, S., Vusser, S.D., Jonger, S.D., Janssen, D., Verlaak, S., Genoe, J., and Heremans, P. (2004). Influence of the dielectric roughness on the performance of pentacene transistors. *Appl. Phys. Lett.*, 85, 4400-4402.
- [194] Meijer, E.J., Tanase, C., Blom, P.W.M., van Veenendaal, E., Huisman, B.-H., de Leeuw, D.M., and Klapwijk, T.M. (2002). Switch-on voltage in disordered organic field-effect transistors. *Appl. Phys. Lett.*, 80, 3838.
- [195] Singh, T.B., Meghdadi, F., Gunes, S., Marjanovic, N., Horowitz, G., Lang, P., Bauer, S., and Sariciftci, N.S. (2005). High-performance ambipolar pentacene organic field-effect transistors on poly(vinyl alcohol) organic gate dielectric. *Adv. Mater.*, 17, 2315.

- [196] Parisse, P., Ottaviano, L., Delley, B., and Picozzi, S. (2007). First-principles approach to the electronic structure in the pentacene thin film polymorph. *J. Phys.: Condens. Matter.*, 19, 106209.
- [197] Park, S.P., Kim, S.S., Kim, J.H., Whang, C.N., and Im, S. (2002). Optical and luminescence characteristics of thermally evaporated pentacene films on si. *Appl. Phys. Lett.*, 80, 2872.
- [198] He, R., Tassi, N.G., Blanchet, G.B., and Pinczuk, A. (2005). Fundamental optical recombination in pentacene clusters and ultrathin films. *Appl. Phys. Lett.*, 87, 103107.
- [199] Kline, R.J., McGehee, M.D., Kadnikova, E.N., Liu, J., Fréchet, J.M.J., and Toney, M.F. (2005). Dependence of regioregular poly(3-hexylthiophene) film morphology and field-effect mobility on molecular weight. *Macromolecules*, 38, 3312.
- [200] Yang, H., Shin, T.J., Yang, L., Cho, K., Ryu, C.Y., and Bao, Z. (2005). Effect of mesoscale crystalline structure on the field-effect mobility of regioregular poly(3-hexyl thiophene) in thin-film transistors. *Adv. Funct. Mater.*, 15, 671.
- [201] Ong, B.S., Wu, Y., Liu, P., and Gardner, S. (2005). Structurally ordered polythiophene nanoparticles for high-performance organic thin-film transistors. *Adv. Mater.*, 17, 1141.
- [202] Janssen, R.A.J., Smilowitz, L., Sariciftci, N.S., and Moses, D. (1994). Triplet-state photoexcitations of oligothiophene films and solutions. *J. Chem. Phys.*, 101, 1787.
- [203] Ziemelis, K.E., Hussain, A.T., Bradley, D.D.C., Friend, R.H., Rhe, J., and Wegner, G. (1991). Optical spectroscopy of field-induced charge in poly(3-hexyl thienylene) metal-insulator-semiconductor structures: Evidence for polarons. *Phys. Rev. Lett.*, 66, 2231.
- [204] Spano, F.C. (2005). Modeling disorder in polymer aggregates: The optical spectroscopy of regioregular poly(3-hexylthiophene) thin films. *J. Chem. Phys.*, 122, 234701.
- [205] Spano, F.C. (2007). Erratum: "modeling disorder in polymer aggregates: The optical spectroscopy of regioregular poly(3-hexylthiophene) thin films" [*J. Chem. Phys.* 122, 234701 (2005)]. *J. Chem. Phys.*, 126, 159901.
- [206] Morita, T., Takashima, W., and Kaneto, K. (2007). Characteristics of field effect transistors based on fullerene derivatives. *Jpn. J. Appl. Phys.*, 46, L256.

- [207] Troisi, A. and Orlandi, G. (2006). Charge-transport regime of crystalline organic semiconductors: Diffusion limited by thermal off-diagonal electronic disorder. *Phys. Rev. Lett.*, 96, 086601.
- [208] Cheng, Y.C., Silbey, R.J., da Silva Filho, D.A., Calbert, J.P., Cornil, J., and Brédas, J.L. (2003). Three-dimensional band structure and bandlike mobility in oligoacene single crystals: A theoretical investigation. *J. Chem. Phys.*, 118, 3764.
- [209] Cornil, J., Beljonne, D., Calbert, J.P., and Brédas, J.-L. (2001). Interchain interactions in organic π -conjugated materials: Impact on electronic structure, optical response, and charge transport. *Adv. Mater.*, 13, 1053.
- [210] Ashcroft, N.W. and Mermin, N.D. (1976). *Solid-state physics*. Philadelphia: Saunders College.
- [211] Sirringhaus, H., Tessler, N., and Friend, R.H. (1998). Integrated optoelectronic devices based on conjugated polymers *Science*, 280, 1741.
- [212] Lin, Y.Y., Gundlach, D.J., Nelson, S.F., and Jackson, T.N. (1997). Stacked pentacene layer organic thin-film transistors with improved characteristics. *IEEE Elect. Dev. Lett.*, 18, 606.
- [213] Liu, P., Wu, Y., Li, Y., Ong, B.S., and Zhu, S. (2006). Enabling gate dielectric design for all solution-processed, high-performance, flexible organic thin-film transistors. *J. Am. Chem. Soc.*, 128, 4554.
- [214] Schroder, D.K. (1998). *Semiconductor material and device characterization*, 2nd ed. Vol. Chap. 6. New York: Wiley.
- [215] Fleetwood, D.M., Winokur, P.S., Reber, R.A., Meisenheimer, T.L., Schwank, J.R., Shaneyfelt, M.R., and Riewe, L.C. (1993). Effects of oxide traps, interface traps, and border traps on metal-oxide-semiconductor devices. *Journal of Applied Physics*, 73, 5058.
- [216] Maréchal, Y. (2007). *The hydrogen bond and the water molecule: The physics and chemistry of water, aqueous and bio media*. Amsterdam: Elsevier.
- [217] Zakirov, A.S., Navamathavan, R., Kim, S.H., Jang, Y.J., Jung, A.S., and Choi, C.K. (2006). Electro-physical properties of a si-based mis structure with a low- k sioc(-h) film. *J. Korean Phys. Soc.*, 49, 1293.
- [218] Pernstich, K.P., Hass, S., Oberhoff, D., Goldmann, C., Gundlach, D.J., Batlogg, B., Rashid, A.N., and Schitter, G. (2004). Threshold voltage shift in organic field effect transistors by dipole monolayers on the gate insulator. *J. Appl. Phys.*, 96, 6431.

- [219] Ishii, H., Sugiyama, K., Ito, E., and Seki, K. (1999). Energy level alignment and interfacial electronic structures at organic/metal and organic/organic interfaces. *Adv. Mater.*, 11, 605.
- [220] Jeong, S., Kim, D.-C., Park, B.K., Lee, S., and Moon, J. (2007). Influence of silanol groups on the electrical performance of organic thin-film transistors utilizing organosiloxane-based organic-inorganic hybrid dielectrics. *Nanotechnology*, 18, 025204.
- [221] Shackelford, J.F. and Masaryk, J.S. (1976). The thermodynamics of water and hydrogen solubility in fused silica. *Journal of Non-Crystalline Solids*, 21, 55.
- [222] Panzer, M.J. and Frisbie, C.D. (2007). Polymer electrolyte-gated organic field-effect transistors: Low-voltage, high-current switches for organic electronics and testbeds for probing electrical transport at high charge carrier density. *J. Am. Chem. Soc.*, 129, 6599.
- [223] Horowitz, G. (1998). Organic field-effect transistors. *Adv. Mater.*, 10, 365.
- [224] Horowitz, G., Hajlaoui, M.E., and Hajlaoui, R. (2000). Temperature and gate voltage dependence of hole mobility in polycrystalline oligothiophene thin film transistors. *Journal of Applied Physics*, 87, 4456.
- [225] Brown, A.R., de Leeuw, D.M., Havinga, E.E., and Pomp, A. (1994). A universal relation between conductivity and field-effect mobility in doped amorphous organic semiconductors. *Synth. Met.*, 68, 65.

Appendix A LIST OF ABBREVIATIONS

AFM	atomic force microscope (microscopy)
C-V	capacitance-voltage
FE	free exciton
FET	field-effect transistors
FT-IR	Fourier transform infrared spectroscopy
FWHM	full-width-at-half-maximum
HOMO	highest occupied molecular orbital
I-V	current-voltage
LUMO	lowest unoccupied molecular orbital
ML	monolayer
MOS	metal oxide semiconductor
MOSFET	MOS field-effect transistor
nm	nanometer
OFET	organic field-effect transistor
ORMOSIL	organically modified silica (silicates)
OSC	organic semiconductor
P α MS	poly(α -methylstyrene)
PL	photoluminescence
PMMA	poly(methyl methacrylate)
PQT	poly(3,3''-didodecylquarterthiophene)
RMS	root-mean-square
RT	room temperature
SG	sol-gel
S-XRD	synchrotron X-ray diffraction
TEPP-C61	{6}-1-(3-(2-thienylethoxycarbonyl)-propyl)-{5}-1-phenyl-[5,6]-C61
TEM	transmission electron microscope (microscopy)
TFT	thin-film transistor
TOX	thermally grown silica (SiO ₂)
UV	ultraviolet
XPS	X-ray photoelectron spectroscopy

Appendix B AUTHOR'S PUBLICATION LIST

JOURNAL ARTICLES

- (1) Enhancement of carrier mobilities of organic semiconductors on sol-gel dielectrics:
Investigations of molecular organization and interfacial chemistry effects

Manuscript in preparation

- (2) Hybrid sol-gel silica as tunable gate dielectric in pentacene-based field-effect transistors

Manuscript in preparation

- (3) Origin of Gaussian Density of States Broadening in Organic Field-Effect Transistors with Sol-Gel Silica Gate Dielectric

Manuscript in preparation

- (4) Low Temperature Processed Inorganic Gate Dielectrics for Plastic Substrate based Organic Field Effect Transistors

H. S. Tan, T. Cahyadi, Z. B. Wang, A. Lohani, Z. Tsakadze, Sam Zhang, F. R. Zhu, and S. G. Mhaisalkar

IEEE Electron Device Letters 29, 698 (2008)

- (5) Electret mechanism, hysteresis, and ambient performance of sol-gel silica gate dielectrics in pentacene field-effect transistors

T. Cahyadi, H. S. Tan, S. G. Mhaisalkar, P. S. Lee, F. Boey, Z. -K. Chen, C. M. Ng, V. R. Rao, and G. J. Qi,

Applied Physics Letters 91, 242107 (2007)

- (6) Investigations of enhanced device characteristics in pentacene-based field effect transistors with sol-gel interfacial layer

T. Cahyadi, J. N. Tey, S. G. Mhaisalkar, F. Boey, V. R. Rao, R. Lal, Z. H. Huang, G. J. Qi, Z. -K. Chen, and C. M. Ng

Applied Physics Letters 90, 122112 (2007)

- (7) Improved pentacene device characteristics with sol-gel SiO₂ dielectric films

T. Cahyadi, H. S. Tan, E. B. Namdas, S. G. Mhaisalkar, P. S. Lee, Z. -K. Chen, C. M. Ng, and F. Y. C. Boey

Organic Electronics 9, 455 (2007)

- (8) A simple and direct method for interface characterization of OFETs

P. Srinivas, S. P. Tiwari, T. Cahyadi, S. G. Mhaisalkar, and V. R. Rao

Proceedings of 14th IEEE International Symposium on the Physical and Failure Analysis of Integrated Circuits (IPFA), 11-13 July 2007, Bangalore, India

CONFERENCE PRESENTATIONS

- (1) Improved transistor characteristics of p-type and n-type organic semiconductor films on sol-gel silica as gate dielectric

T. Cahyadi, B. T. Tan, Z. -B. Wang, S. G. Mhaisalkar, Z. -K. Chen, and C. M. Ng

International Conference on Materials for Advanced Technologies, Singapore (2007)

- (2) Improved interface properties and device characteristics of p-type and n-type organic semiconductor films on sol-gel silica as gate dielectric

T. Cahyadi, S. G. Mhaisalkar, Z. -K. Chen, and C. M. Ng

The E-MRS 2007 Spring Meeting, Strasbourg, France (2007)

- (3) A simple and direct method for interface characterization of OFETs

P. Srinivas, S. P. Tiwari, T. Cahyadi, S. G. Mhaisalkar, and V. R. Rao

14th IEEE International Symposium on the Physical and Failure Analysis of Integrated Circuits (IPFA), Bangalore, India (2007)

- (4) Fabrication of high performance OTFT using liquid crystalline poly(3,3'-didiodecylquaterthiophene) with novel solution processed dielectric

T. Cahyadi, E. B. Namdas, N. Mathews, T. Qian, S. G. Mhaisalkar, Z. Chen, and B. S. Ong

The E-MRS 2006 Spring Meeting (E-MRS – IUMRS – ICEM 06), Nice, France (2006)

PATENT

Solution-Processed Inorganic films for Organic Thin Film Transistors

E. B. Namdas, T. Cahyadi, S. G. Mhaisalkar, P. S. Lee, Z. -K. Chen, Y. M. Lam, and L. Song

PCT Patent Application, 21 May 2007