Nanoparticles with solution-process for dielectric applications in organic thin-film transistors

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**NANOPARTICLES WITH SOLUTION-PROCESS FOR
DIELECTRIC APPLICATIONS IN ORGANIC THIN-FILM
TRANSISTORS**

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SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

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School of Chemical and Biomedical Engineering

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Summary

The PhD thesis presented here mainly focuses on investigation of the solution-processed dielectrics from organic-capped inorganic nanoparticles for high-performance organic TFTs. To study the feasibility of solution-processable organic/inorganic nanoparticles for dielectric application in organic transistors, oleic acid-capped titanium dioxide (OA-TiO₂) nanoparticles were synthesized through solution-phase chemical routes and the as-synthesized OA-TiO₂ nanoparticles were well-dispersed into an organic solvent followed by spin-coating a homogeneous film without any further treatments. These nanoparticle films show a dielectric constant (k) of about 5.3 and low leakage current density of $\sim 3 \times 10^{-8}$ A/cm² under an electric field of 1 MV/cm. Bottom-gate poly(3,3''-didodecylquaterthiophene) (PQT-12) and top-gate pentacene TFTs fabricated with OA-TiO₂ nanoparticle dielectrics demonstrate good performance with mobilities of about 0.05 ± 0.02 cm²/Vs and 0.2 ± 0.05 cm²/Vs, respectively, with on/off ratios of 10^3 - 10^5 .

In order to improve the k values of the dielectric nanoparticles, a series of solution-processable OA capped barium titanate (BTO), strontium titanate (STO), and barium strontium titanate (BST) hybrid nanoparticles were synthesized. The dielectric constant k of the OA-BTO and OA-STO nanoparticle films is tunable in the range of 4.1 to 9.3 by altering the molar ratio of oleic-acid surfactant to synthesis precursor. For the OA-BST nanoparticle films, with constant molar ratio of oleic-acid surfactant to synthesis precursor, the k values vary in the range of 5 to 9.6 in terms of different Ba²⁺/Sr²⁺ molar ratios of the nanoparticles. Low-voltage modulated high-performance organic TFTs were

fabricated using the high- k nanoparticle films as the dielectric component. Flexible bottom-gate pentacene TFTs exhibit outstanding device performance with field-effect mobilities, μ , in the range of 2.0-3.5 cm²/Vs and on/off ratios of $\sim 10^4$ at low gate voltages. Top-gate PQT-12 TFTs also show high device performance with μ of 0.05-0.1 cm²/Vs and on/off ratios of 10^3 - 10^4 .

Studies on the gate voltage-dependent mobility of the devices reveal that only a low gate electric field is needed to achieve the saturated mobility for the OA-BST based pentacene organic TFTs. The low-voltage operation of the transistors could be attributed to a low density of trapped states at the interfaces between the organic semiconductors and the nanoparticle dielectric films.

A universal strategy for the design of solution-processable high- k dielectric nanoparticles for low-voltage high-performance organic TFTs is proposed. This research provides a series of promising dielectric materials for fabrication of superior organic TFTs through a solution process and fundamentally suggests that low trapped state density at the semiconductor/dielectric interface may be an important factor in achieving low-voltage modulation in organic TFTs.

In summary, this work not only demonstrates nanoengineering approaches to synthesize solution-processable nanostructure dielectric materials for performance-enhanced organic TFTs, but also explores the possible mechanism of the charge carrier transport at the dielectric/semiconductor interface, which has great significance in organic electronics physics. The success of this work renders a universal approach for the fabrication of high- k nanoparticle dielectrics possible and may have potential applications in printable electronic circuits.

Chapter 1 Introduction

1.1 Introduction

Organic field-effect transistors (FETs) or thin-film transistors (TFTs) have received significant research interest for their advantages such as low material cost, high mechanical flexibility, light weight, and low-temperature fabrication process¹. Organic TFTs are also expected to have broad promising applications in integrated circuits for large-area, low-cost and flexible electronics, such as flat-panel displays, radio frequency identification (RFID) tags, smart cards, and disposable sensors. Publications in the field of organic transistors have continually increased every year, as noted by the Institute for Science Information's (ISI) web of science, from 80 in 1999 to 302 in 2003 and 1,018 in 2008². With the remarkable progress made in organic materials, processing, and device physics, organic TFTs appear to be moving toward potential commercialization. Numerous organic materials used as active components in organic TFTs have been developed to improve processability and device performance, which is generally benchmarked against that of amorphous silicon TFTs with field-effect mobilities of 0.5-1 cm²/Vs and on/off current ratios of 10⁶-10⁸². The mobilities of organic TFTs as high as 5 cm²/Vs have been achieved in the case of vacuum-deposited small molecules³ and 0.6 cm²/Vs for solution-processed polymers⁴.

Earlier integration of organic TFTs into electronic circuits was accomplished by some of the pioneers in organic electronics, such as Lucent technology,⁵ Philips⁶ and IBM^{7,8}. Since then, continuous results from integrated organic TFTs have been reported and the capabilities of these new electronic materials are extended

with new explorations. Inverters and ring oscillators fabricated with pentacene-based TFTs have been demonstrated by Kelley and coworkers. A more complex RFID tag was designed and fabricated in their later work ⁹. Gelinck et al. have demonstrated flexible active-matrix monochrome electrophoretic displays and shift registers comprising solution-processed organic transistors on 25- μm -thick polyimide substrates ¹⁰. Rogers et al. have fabricated prototype flexible paper-like displays on a plastic substrate with pentacene-based TFTs as the backplane circuits ¹¹. Someya et al. have developed electronic artificial skins (E-skins) that utilized flexible, large-area networks of pressure and thermal sensors based on organic transistor-active matrices ¹². Very recently, Bao and coworkers have successfully demonstrated the sensing capability of organic TFTs in aqueous environments, attributing to the possibility of low-voltage driven operation and high stability of the organic TFT devices ¹³⁻¹⁵.

Semiconductors, insulators and electrodes are the three key elements used to construct an organic TFT device. Tremendous research interest has been given to organic semiconducting materials for understanding of charge transport and device performance enhancement. Recently, the critical role of the dielectric material in organic TFT performance has been recognized and reported in many publications. Besides a required superior organic semiconductor material, a suitable gate dielectric material may be the key to realize low-power consumption of the devices ¹⁶. Transportation of free carriers in the channel has been found to be confined within several monolayers in the semiconductor near the semiconductor/dielectric interface ¹⁷. The dielectric surface properties, such as surface energy and roughness, have great impact on molecular structural

ordering (especially in the first few layers) of the semiconductor film deposited on top of the dielectric surface in a bottom-gate geometry and the number of trapped states at the semiconductor/dielectric interface. Highly ordered semiconductor films are important for high device mobilities¹⁸⁻²⁰. The trap sites, such as hydroxyl (-OH) functional groups, at the semiconductor/dielectric interface can immobilize the induced charge carriers resulting in low mobility and unstable device performance²¹. Other important properties for a practical dielectric in organic transistor application include high dielectric capacitance, high dielectric breakdown field, low leakage current, good stability and easy processability. In the past decade, a number of different dielectrics have been studied involving inorganic^{22, 23}, organic^{24, 25}, inorganic/organic nano-composites²⁶, and self-assembled monolayers²⁷ with the goal of developing high-capacitance low-leakage films, which are easy to process and compatible with electrode and semiconductor materials. The development in new dielectric materials and inexpensive processing capabilities will expedite the realization of commercial electronics driven by organic transistors. There is also a great challenge to gain a physical fundamental insight into the role of organic dielectrics in organic TFT performance.

1.2 Motivations

Although the carrier mobilities of organic semiconductors are now comparable to or surpass those of amorphous Si, this is still generally achieved at very high operating voltages, typically greater than 30-50 V²⁸. Organic TFTs employing such large-bias operation are impractical for use as the driving circuits due to excessive power consumption. SiO₂, a benchmark gate dielectric, is widely used

for evaluating new organic materials due to its excellent insulating properties (high dielectric strength and low leakage current)^{29, 30}. Furthermore, its surface is very smooth, providing a compatible platform for semiconductor deposition; techniques related to SiO₂ deposition and modification can be borrowed conveniently from well-developed silicon technologies^{31, 32}. To reduce the operating voltage of the organic TFTs, high-capacitance gate dielectric is generally needed to permit greater charge injection into the semiconductor layer at a given gate voltage. Although the thickness of SiO₂ has been successfully reduced to 10-20 nm, high leakage current is problematic. High dielectric-constant (k) metal oxide complex are attractive alternatives to SiO₂ and can provide high gate capacitance at higher thickness with reasonable leakage. The deposition of the inorganic films is usually carried out in vacuum systems at a high cost. Recently, anodization process is reported to be a possible solution to make high quality metal oxides with large coverage. Organic TFTs with pentacene as the active layer and anodized Ta₂O₅ ($k = 24$) as the gate dielectric show a mobility of 0.36 cm²/Vs operated under 5V³³.

Polymeric dielectric materials such as polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(vinyl phenol) (PVP), etc., with the great advantage of solution-processability, have been widely used in organic transistors. However, these materials normally possess low k properties ($k = 2 - 4$)³⁴. In order to achieve high capacitance, the thickness of the films has to be reduced to nanoscale dimensions, where the defects in the films could cause significant leakage currents. Even with the successful demonstration of spin-on ultrathin cross-linked polymers (thickness as low as 40 nm)^{25, 35}, the requirements for high-quality pinhole-free films in large areas are still critical

issues for practical applications. Inorganic/polymer blends have been attempted for solution-processed high- k dielectrics. The effective permittivity of two-component systems can be modelled using the volume fraction of each component according to Power-Law relationships: $\varepsilon_c^\beta = \phi_I \varepsilon_I^\beta + (1 - \phi_I) \varepsilon_2^\beta$, where ε_c , ε_I and ε_2 are the complex dielectric permittivity of the composite system, the filler and the matrix respectively, ϕ_I is the volume fraction of filler component of the composite system, and β is a dimensionless parameter representing the shape and orientation of the filler particles within the bulk composite³⁶. Incorporating high- k inorganic materials at relevant inorganic volume fraction into polymeric materials will result in high- k composites with the flexibility of polymeric materials. However, the homogenous distribution of the inorganic nanoparticles is challenging. Recently, the use of inorganic colloidal nanoparticles via wet-chemistry as nanocomposite dielectrics in organic TFTs has been reported by Maliakal et al²⁶. While, complicated synthesis procedures to form TiO₂-polystyrene core-shell nanorods are employed in their work. Very recently, Tan et al. published their work on solution-processable sol-gel silica gate dielectrics³⁷. However, sophisticated fabrication processes to form three layers of silica nanoparticle films are needed to prevent the gate leakage problems. Hence, there is a tremendous need to investigate new dielectric materials that provide simple solution processability and cater for high device performance.

1.3 Objectives of the study

The objectives of this research are encapsulated in four specific tasks as follows:

- 1) To investigate the feasibility of solution-processable organic/inorganic

nanoparticles for dielectric application in organic TFTs. Organic/inorganic core-shell nanoparticles have been synthesized for various applications such as fluorescent labels in bio-sensors or bio-imaging³⁸, catalysts in chemical reactions³⁹, optical dyes in photovoltaic devices⁴⁰, carriers in drug delivery systems⁴¹, conductive inks⁴², etc. The organic capping layers not only avoid the aggregation of the nanoparticles and offer good solubility/dispersibility of the nanoparticles in common solvents, in the electronic aspect, but also serve as the insulating layer since most of the organic/polymer materials are good insulators.

2) To improve the k values of the dielectric nanoparticles for low-voltage high-mobility organic TFTs. High- k dielectric materials are important to realize low-voltage operation of organic TFTs. Due to the high permittivity and low losses, perovskite oxides are largely used in electronic industry for many applications. Different perovskite oxide composites will be used as the core materials and modulation of k values of the core-shell nanoparticles will be manipulated by altering the composition and ratio of the inorganic core elements.

3) To develop a general strategy for the design of solution-processed nanoparticles for dielectric applications in high-performance organic TFTs.

4) To study the relation of the surface properties of the nanoparticle gate dielectrics to gate-dependent mobilities in order to gain fundamental physical insights into the role of organic dielectrics in device performance.

1.4 Organization

This dissertation is devoted to the study of solution-processed organic/inorganic core/shell nanoparticle dielectrics for low-voltage high-mobility organic thin-film transistors. This dissertation is organized in the following manner:

Chapter 1 provides the background and overview of the motivation and objectives of this PhD research.

In chapter 2, the literature on organic thin-film transistors (organic TFTs) is summarized. In particular, the basic concepts of organic TFTs, development of organic semiconductor and dielectric materials in organic TFTs, and the fabrication process of organic TFTs are reviewed.

Chapter 3 describes the experimental procedures involved in this study in detail. Fabrication of organic TFTs and characterization methods of the materials and devices are introduced.

Chapter 4 demonstrates the application of solution-processed titanium dioxide nanoparticles as the gate dielectrics in organic TFTs.

In chapter 5, low-voltage organic TFTs based on high- k oleic acid (OA)-capped barium titanate or strontium titanate nanoparticle film dielectrics are developed.

In chapter 6, a strategy for the design of organic-capped perovskite nanoparticles as gate dielectrics in organic TFTs is proposed and their examples are illustrated. The interfacial properties between the semiconductor and nanoparticle dielectric are studied and their impact on the device performance is discussed.

Finally, in chapter 7, a general conclusion is given and some perspectives on possible future research are summarized and proposed.

Chapter 2 Literature review

This chapter reviews the technologies and scientific developments in organic thin-film transistors (TFTs). First, an overview of the concepts and development history of organic TFTs is given in section 2.1. Semiconductor layer, dielectric layer and the electrode contacts are the three key components in an organic TFT. The material properties, interfacial properties, and fabrication process all have great impact on the final performance of an organic TFT device. The critical role played by individual components and the interfaces between them will be discussed in detail in sections 2.2 and 2.3. Finally, an overview of the development and advantages of the fabrication process for constructing organic TFTs will be given in section 2.4.

2.1 Organic thin-film transistors

Organic field-effect transistors (organic FETs) or organic thin-film transistors (organic TFTs) have been extensively developed since its first demonstration using an electrochemically-deposited polythiophene as the active channel by Tsumura in 1986⁴³. Organic TFTs offer the combined attractions of being light weight, having a low-temperature processability, mechanical flexibility, and an amenability to manufacture by a low-cost, large-area, high-throughput reel-to-reel printing process⁴⁴. From the scientific aspect, organic FETs have been a unique tool for investigating the charge transport mechanism in organic materials¹⁶. The performance of the best organic materials is now competitive to that of the amorphous silicon TFTs commonly used as the pixel-switching elements in active matrix flat-panel displays⁴⁵. Currently, organic FETs have already shown promising applications in flexible “electronic paper” displays¹⁰.

^{46, 47}, radio frequency identification (RFID) tags ⁴⁸⁻⁵⁰ for consumer goods packaging and labelling, and portable electronic sensors ⁵¹.

2.1.1 Geometry and operation of organic TFTs

The main components of the organic TFT device are an organic semiconductor layer, an insulating layer, and three contact electrodes. Various configurations of the organic TFTs have been identified ⁵²⁻⁵⁴ and Figure 2.1 illustrates the three most popular geometries of the organic TFTs. Based on the position of the gate electrode, a transistor has either a bottom-gate or top-gate configuration. Depending on the position of the source-drain electrodes, the structure can be further configured as top contact, where source and drain electrodes are patterned and deposited on top of the organic semiconductor layer, or bottom contact, where organic semiconductors are deposited onto the pre-fabricated source and drain electrodes. The distance between source and drain electrodes, termed as channel length (L), typically ranges from 5 to 100 μm , and channel widths (W) are usually between 1 and 3 mm.

Figure 2.1 Cross-sectional view of a (a) bottom-gate bottom-contact, (b) bottom-gate top-contact, and (c) top-gate bottom-contact organic transistor. (d) Relevant voltages and geometry illustration. S: source, D: drain, G: gate, L: channel length, and W: channel width.

The source is always connected to ground, and the voltage applied between the source and drain is referred to as drain voltage (V_D). The basic operation of an organic TFT involves the modulation of current flow through the organic semiconductor film from source to drain at a given V_D by an applied voltage to the gate electrode (V_G) with respect to source. The semiconductor film and the gate electrode are capacitively coupled through a thin layer of insulator such that application of a sufficient high V_G induces charge in the semiconductor film. P-type or n-type behavior in organic TFTs depends on two properties: the ability of the semiconductor materials to transport hole (p-type) or electrons (n-type), and the ability to inject and retrieve charge carriers to and from the highest

occupied molecular orbital (HOMO) (hole, p-type) or the lowest unoccupied molecular orbital (LUMO) (electron, n-type) levels of the organic semiconductor materials. Generally, n-type semiconductors have a higher electron affinity and p-type semiconductors have a lower ionization potential ⁵⁵.

The operation principle of an organic TFT is generally clarified in the simplified energy-band diagrams ^{56, 57} shown in Figure 2.2. Figures 2.2(a) and 2.2(d) show the band alignment at gate/insulator/semiconductor interfaces and source-drain contacts/semiconductor interfaces when $V_G = 0$ V. The Fermi levels of the gate metal and the semiconductor are similar, and there is no band bending. Most organic TFTs operate in an accumulation mode ^{58, 59} in which the device is normally ‘off’ when there is no voltage applied to the gate. If a drain bias (V_D) is applied, there is no intrinsic conduction of the organic materials, except that carriers generated by non-intentional doping flow through the channel region, which is the source-drain off current and is proportional to the bulk conductivity of the organic semiconducting thin film. In the case of a p-channel organic TFT, upon the application of a negative gate bias, positive charges are induced in the channel and accumulate at the semiconductor/dielectric interface, resulting in the bending of both HOMO and LUMO as shown in Figure 2.2(b). If the gate-electric field is large enough, the HOMO becomes resonant with the Fermi levels of the contacts and holes can then flow from the contacts into the HOMO. As a result, free carriers (holes) can flow in the channel from source to drain in response to an applied V_D , Figure 2.2(e). The electric current is modulated by the amount of induced charges that are proportional to the gate bias (V_G) and the capacitance (C_i) of the insulator. Under this condition, the organic TFT is said to be in the on state.

However, not all the induced charges are free to move, thus contributing to the current. Defects in the semiconductor film form the trap sites for the charge carriers, so that the induced charge carriers have to fill all the traps first to be able to flow through the channel. On the other hand, if the organic material is unintentionally doped (e.g. impurities), considerable conductivity can be observed at $V_G = 0$. Furthermore, mismatch between the Fermi level of the contact and the HOMO of the organic semiconductor results in charge transfer between the contact and semiconductor, causing a dipole and band bending in the organic material^{32, 57}. A nonzero V_G is necessary to achieve the flat-band condition, referred to as flat-band voltage (V_{FB}). To account for these various situations described above, a parameter, threshold voltage (V_T or V_{th}) that is necessary to induce mobile charges, is introduced. For a p-type material, deep traps shifts V_T negatively^{60, 61}, doping shifts V_T positively, and mismatch between the HOMO and contact Fermi level may shift V_T in either direction depending on the nature of the misalignment⁶².

Similar principles apply in the case of n-type organic TFT operation. A positive gate bias causes both HOMO and LUMO levels to bend downward and electrons to accumulate at the semiconductor/dielectric interface shown in Figure 2.2(c). When the gate electric field is large enough, the LUMO becomes resonant with the Fermi levels of the contacts and the mobile electrons can flow from the contacts into the LUMO, Figure 2.2(f), resulting in an electronic current between source and drain upon application of a drain voltage. These field-induced charges are confined within several monolayers (~ 5 nm) in the semiconductor film near the dielectric/semiconductor interface, as observed by Dodabalapur from thiophene oligomer α -hexathienylene (α -6T) based transistors of which the

field-induced conductivity did not increase when the thickness of the active material was raised from 5 to 150 nm⁶³. As shown in Figure 2.2(e) and 2.2(f), the free carriers are always injected from the source contact into the active channel regardless of the sign of the gate voltage.

Figure 2.2 Idealized energy-band diagrams at gate/insulator/semiconductor interface⁷ and source-drain electrodes/semiconductor interfaces of an organic TFT in off state (a, d) when V_G , $V_D = 0$ V, and in p-channel operation for hole accumulation (b) and transportation (e), and in n-channel operation for electron accumulation (c) and transportation (f).

It is noticed that two electric fields orthogonal to each other, induced by V_G and

V_D respectively, are involved in the transistor operation. Figure 2.3 describes the impact of the two electric fields on the charge transport in a p-channel organic transistor¹⁶. If a negative V_G is applied, positive charges accumulate at the semiconductor/insulator interfacial plane. When $V_D = 0$, the density of the negative charge carriers will be uniform along the channel, as shown in Figure 2.3(b). The application of a negative V_D will cause nonuniform distribution of the electric field in the channel. As a result, the area charge density induced at a given position x along the channel is proportional to the voltage difference $V_G - V(x)$, and, as long as $|V_D|$ is less than $|V_G - V_T|$, the charge concentration forms a linear gradient in the channel from source ($x = 0$) to drain ($x = L$), as indicated by the red line in Figure 2.3(b). As V_D is increased, the carrier concentration profile becomes increasingly nonuniform and results in quadratic I-V characteristics. When $V_D = V_G - V_T$, the position in the channel next to the drain electrode is at the same potential as the gate, giving rise to complete depletion of free carriers in this region, which is referred to as pinch-off condition. As long as the channel length L is much longer than the width of the depletion region, further increases of V_D will not increase the drain current I_D , which means that the drain current saturates.

Equations (2.1) and (2.2) give the drain current in the linear and saturation regions, respectively.

$$I_D = \frac{WC_i\mu}{L} \left(V_G - V_T - \frac{V_D}{2} \right) V_D, \quad |V_D| < |V_G - V_T| \quad (2.1)$$

$$I_{D,sat} = \frac{WC_i\mu}{2L} (V_G - V_T)^2, \quad |V_D| > |V_G - V_T| \quad (2.2)$$

where W , L , C_i and μ are the channel width and length, capacitance per unit area of the dielectric layer, and the field-effect mobility, respectively.

Figure 2.3 (a) Cross-sectional view of a p-channel organic TFT with the carrier concentration profile (represented by the colored region in the channel) and the corresponding voltages. (b) Schematic illustration of the charge induced in the channel under different V_D . The grey line represents uniform charge density induced along the channel when $V_D = 0$, the red line represents the linear gradient of the charge concentration along the channel when $|V_D| < |V_G - V_T|$; the blue line represents the quadratic charge profile when $V_D = V_G - V_T$, (channel pinched-off), and the green line represents the charge depletion near the drain contact with a saturated I_D when $|V_D| > |V_G - V_T|$.

2.1.2 Parameter extraction

Parameters used to describe the performance of an organic transistor are usually field-effect mobility (μ), threshold voltage (V_T or V_{th}), on/off ratio, and subthreshold swing (S). Equations (2.1) and (2.2) are the two commonly used methods for mobility extraction. The extracted μ values are normally in the range of 10^{-3} - 10^{-1} cm^2/Vs , but mobilities as high as 1 - 10 cm^2/Vs have been reported for pentacene TFTs⁶⁴. Figure 2.4 shows an example of the output and transfer characteristics of a bottom-gate bottom-contact organic transistor on a heavily doped n-type silicon substrate with thermally grown SiO_2 (100 nm) as the gate insulator and poly(3,3''-didodecylquaterthiophene) (PQT-12) as the active layer.

Figure 2.4 (a) Output characteristics and (b) transfer characteristics and $|I_D|^{1/2}$ vs. V_G of a bottom-gate poly(3,3''-didodecylquaterthiophene) (PQT-12) TFT on silicon substrate with channel length of 20 μm and channel width of 9000 μm .

Equation (2.1) shows the drain current in the linear region, where $|V_D| < |V_G - V_T|$. For $|V_D| \ll |V_G - V_T|$, the term $V_D/2$ is negligible, such that I_D is approximately linear as a function of V_G or V_D at a given V_D or V_G respectively. The slopes of the two corresponding curves are referred to as the transconductance (g_m) and conductance (g_d), respectively, as defined in Equations (2.3) and (2.4) below.

$$g_m = \frac{dI_D}{dV_G} = \frac{WC_i\mu}{L} V_D \quad (2.3)$$

$$g_d = \frac{dI_D}{dV_D} \sim \frac{WC_i\mu}{L} (V_G - V_T) \quad (2.4)$$

Therefore, the field effect mobility in the linear region (linear mobility) can be calculated from either g_m or g_d when $|V_D| \ll |V_G - V_T|$.

By taking the square root of the drain current in the saturation region, Equation (2.2) becomes

$$\sqrt{I_{D,sat}} = \sqrt{\frac{WC_i\mu}{2L}} |V_G - V_T| \quad (2.5)$$

Therefore, the device mobility in the saturation region (saturated mobility) can be calculated from the slope of the linear part of the $\sqrt{I_{D,sat}}$ vs. V_G plot. The threshold voltage (V_T) can be obtained from the intercept of a straight line through the linear part of the $\sqrt{I_{D,sat}}$ vs. V_G plot on the V_G axis (where $I_D = 0$) as shown in Figure 2.4(b). The current on/off ratio, defined as the ratio of I_D in the

on ($V_G > V_T$) and off ($V_G = 0$ V) states, indicates the switching performance of the device. A low off current is desirable to ensure that the transistor is in a true off state; this can be accomplished by minimizing the doping level of the organic semiconductor. However, due to non-intentional doping, polycrystalline organic active layers normally exhibit some conduction. The true off state is achieved by applying a small V_G with inverted sign, which depletes the carriers in the channel. The logarithmic plot of I_D vs. V_G , shown in Figure 2.4(b), gives an on/off ratio of $\sim 8 \times 10^4$. The gate voltage at which the drain current starts to increase exponentially is defined as the turn-on voltage (V_O or V_{on}). In most devices, V_O does not coincide with V_T . In the case of a p-channel transistor, the threshold voltage is generally associated with the donor state density at energy level near the HOMO of the organic material (shallow states)⁶⁴, while the turn-on voltage is related to acceptor states closer to the middle of the bandgap of the organic material (deep states)⁶⁵⁻⁶⁷. Another important parameter that can be obtained from the logarithmic plot of I_D vs. V_G is the subthreshold swing (S).

$$S = \frac{dV_G}{d(\log I_D)} \quad (2.6)$$

S is a measure of switching speed (how rapidly the device can switch from the off state to the on state in the region of exponential current increase) and is typically quantified in V/decade or mV/decade⁶⁸. The subthreshold swing is also related to the shallow-trap density: a large subthreshold swing generally implies a large concentration of shallow traps.

2.1.3 Contact resistance

Contact resistance at the interface between source/drain electrode and organic semiconductor has a great impact on the performance of organic TFTs^{62, 69, 70}. Especially for a short channel (channel length $L < 5 \mu\text{m}$) transistor, where the contact resistance becomes comparable to the channel resistance, the contact resistance should be taken into consideration.

The transmission line model (TLM) was first developed for amorphous silicon thin-film transistor⁷¹ to access the channel and contact resistance independently and is widely applied in the estimation of the contact resistance in organic TFTs nowadays^{69, 70}. The total device resistance between the source and drain can be divided into the channel resistance and the contact resistance. When the device is operated in the linear region with very small V_D ($|V_D| \ll |V_G - V_T|$), where there should be most pronounced contact effects, the total device resistance R_{total} is given by

$$R_{\text{total}} = \frac{V_D}{I_D} = R_{\text{ch}} + R_c = \frac{L}{WC_i\mu(V_G - V_T)} + R_c \quad (2.7)$$

where R_{ch} is the channel resistance that can be derived from the channel conductance given by equation (2.4), and R_c is the contact resistance. From Equation (2.7), R_{total} is a function of L for the width-normalized devices at a given V_G . The contact resistance can be extracted from the plot of R_{total} as a function of L . The intercept of the linear fit of R_{total} at zero channel length gives the contact resistance.

The contact resistance can be affected by the energy alignment⁷²⁻⁷⁴ and film

morphology of organic semiconductors⁷⁵⁻⁷⁹ at the electrode/semiconductor contacts. To improve the performance of organic TFTs, it is desirable to reduce the contact resistance. The top-contact organic TFTs normally show better performance than those of bottom contact organic TFTs⁸⁰ due to more efficient charge injection. In a top-contact device, the molecular ordering of the active layer is mainly affected by dielectric/semiconductor interfaces and the ordered structures pack continuously and uniformly through the entire film. However, in a bottom-contact device, the continuity of ordered molecular packing is usually disrupted at the border of the electrodes due to the interfacial interaction between organic semiconductor and electrode contacts⁶⁹. This results in an inefficient charge carrier transport through the discontinuous molecular ordering region and lowers the device performance. In order to improve the device performance of bottom-contact pentacene based thin-film transistors (TFTs), self-assembled monolayers (SAMs) of alkanethiol have been used to modify the surfaces of gold (Au) electrodes, resulting in improved grain size and ordering of pentacene near the electrodes⁷⁵⁻⁷⁷. On the other hand, SAMs have been demonstrated to be a versatile technique to modulate Schottky barrier height at metal/semiconductor contacts^{18, 57, 62, 69, 81-84}. By chemisorbing SAMs of molecules with an intrinsic electric dipole moment and forming a highly ordered molecular layer of the same dipole orientation on a metal surface, Schottky barrier height at a metal/semiconductor contact can be lowered or raised to significantly affect the charge injection⁶².

2.2 Organic semiconductors

Continuous and significant progress has been made in the development of

organic semiconductor materials over the past decades. The device mobility has been improved by five orders of magnitude since the early reported organic TFTs. Table 2.1 summarizes the performance characteristics of some p-type and n-type organic semiconductors for organic TFTs. High mobility is mostly obtained from vacuum deposited small molecules with highly ordered structures; the highest device mobility is reported from pentacene based TFTs with an average of $5 \text{ cm}^2/\text{Vs}$ ^{19, 85}. The devices with solution-processed semiconductors, especially those fabricated in ambient condition, generally demonstrate relatively poor performance⁸⁶. The results reveal the significance of molecular ordering on the device performance and imply great difficulties in forming ordered structures of semiconductors by the solution process⁸⁶.

Most of the organic thin-film transistors demonstrate p-channel, but not n-channel, behavior even with the appropriate low-work-function electrodes, except for a few special high-electron-affinity^{81, 87-90} or low-bandgap⁹¹ organic semiconductors⁹². However, recent studies have discovered n-channel conduction in most conjugated polymers, which are well-studied as p-type semiconductors, by using hydroxyl-free gate dielectrics⁹². The results show that electron mobilities are considerably higher in these materials than previously thought. Ambipolar behavior (both p- and n-type) is even observed in some devices and this greatly enriches the selectivity of suitable materials for organic complementary metal-oxide semiconductor (CMOS) circuits^{93, 94}.

Table 2.1 Typical organic semiconductors with organic TFTs characteristics.

Semiconductor	Mobility (cm ² /Vs) (deposition condition)	On/off	Ref
p-type
Rubrene	2.4 (vacuum)	10 ⁶	95
Pentacene	3.3 (vacuum)	10 ⁶	96
α, ω -dialkylsexithiophene	1.1 (vacuum)	10 ⁴	97
poly(9,9-dioctylfluorene-co-bithiophene) (F8T2)	0.02 (solution)	10 ⁶	98
Poly(3-hexylthiophene) (P3HT)	0.1 (solution)	10 ⁵	99
n-type
perfluoropentacene	0.11 (vacuum)	10 ⁵	100
F ₁₆ CuPc	3 × 10 ⁻³ (vacuum)	10 ⁵	101
α, ω -diperfluorohexylquaterthiophene (DFH-4T)	0.22 (vacuum)	10 ⁶	102

Two types of p-channel organic semiconductors, which are used as the template active layer for constructing the organic thin-film transistors studied in this dissertation, will be addressed in detail. They are pentacene and polythiophenes. The former are small molecules that are normally vacuum-deposited, while the latter are polymers that can be solution-processed.

2.2.1 Pentacene

Pentacene is one of the most reliable benchmark materials for vapor-deposited thin film transistors, primarily due to routinely obtainable TFT mobilities in excess of $1 \text{ cm}^2/\text{Vs}$. The interplay between thin-film growth, morphology, and the device performance of the transistors based on pentacene and other vapor-deposited small conjugate molecules (such as tetracene (naphthacene)^{103, 104}, rubrene¹⁰⁵, oligoacenes¹⁰⁶, and oligothiophenes^{97, 107, 108, 109-118}) has been studied extensively¹⁰⁹⁻¹¹⁸. It is well established that the mobility and charge transport depends on the morphology of the polycrystalline thin film¹¹⁹. In pentacene TFTs, the coplanar rings of the molecules have to be nearly perpendicular to the substrate surface and form a well ordered thin-film phase in order to facilitate charge transport^{30, 111}. Many parameters, including the nature of the substrate^{30, 111}, the substrate temperature during deposition^{109, 111}, the deposition rate^{109, 111}, and device geometry¹²⁰, affect the morphology of the deposited film. Gundlach et al. investigated the TFT performance with pentacene films deposited at elevated temperature at low-to-moderate deposition rates, and the high mobility of $0.7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with on/off ratio of 10^8 is achieved from pentacene films of high degree ordering molecules with micrometer-sized and larger dendritic grains²⁰. Films deposited at low temperature or by flash

evaporation have small grains and poor molecular ordering and yield TFTs with low mobility¹²¹.

In general, highly hydrophobic (low surface energy) and smooth surfaces are favorable for the morphology that facilitates charge transport. The stability of pentacene TFTs has been investigated by several groups. It is found that the adsorption of H₂O into the pentacene layer is the main cause for the degradation of devices. The pentacene TFTs are stable over months in vacuum. In large-area flexible electronics, materials that are suitable for solution processes, such as spin-coating, are desirable to lower manufacturing costs. Soluble precursor routes¹²²⁻¹²⁸ to pentacene and pentacene derivatives¹²⁹ have been explored. Afzali and co-workers have developed such a precursor that can be heated at moderate temperatures and converted to pentacene, and the devices with this precursor-converted pentacene show mobilities as high as 0.89 cm²/Vs and on/off ratio about 10⁷¹²⁸.

2.2.2 Polythiophenes

Polythiophenes represent the most widely studied materials for polymer-based organic TFTs. Alkyl-side chains are generally introduced to enhance the solubility of the polymers in common organic solvents for film deposition through a solution process such as spin-coating. Charge transport in organic materials is through charge carrier tunnelling (hopping) between localized states that are disordered both in space and in energy¹³⁰. Hence, grain boundary effects may reduce the mobility significantly if the grain density is high, resulting from small crystal domains. Amorphous or disordered materials exhibit low mobility whereas semiconductor materials of highly ordered structures with large crystal

domains generally demonstrate good capabilities of charge transport^{95, 131}. Therefore, many research groups have examined the effects of modifying molecular parameters (regioregularity¹³², molecular weight¹³³, and side-chain length¹³³) and processing conditions (solvent power^{134, 135}, film thickness^{136, 137}, doping level¹³⁸, thermal annealing^{134, 135}, and the film-forming method⁹⁸).

Ong and coworkers have found that in the polythiophene system, a sufficiently long alkyl side-chain would provide the solubility needed for processing, while structural regioregularity helps to promote molecular self-assembly and achieve a desirable structural order for charge transport⁸⁶. On the other hand, regioregular alkyl-substituted polythiophenes such as the head-to-tail poly(3-alkylthiophene)s with a long alkyl side-chain are able to self-organize from solution when deposited on appropriate substrates¹³⁹. Regioregular head-to-tail poly(3-hexylthiophene) (HT-P3HT) based TFTs have shown excellent mobility of 0.1 cm²/Vs and on/off ratio about 10⁶ if fabricated and measured in an inert atmosphere¹⁴⁰. However, polythiophene transistors have relatively high off currents and poor on/off ratios in air, because it is sensitive to moisture and is prone to ambient oxidative doping. In addition, the devices tend to degrade gradually with time and cycling. The oxidation of semiconducting conjugated polymers greatly depends on their positions of HOMO levels, referred to as the ionization potentials (IPs), which are associated to their effective π -conjugation lengths. For polythiophenes, coplanarity of the thienylene moieties along the polymer backbone leads to extensive π -conjugation and, thus, a lower IP, and a greater tendency to be oxidatively doped^{141, 142}. Shorter effective π -conjugation lengths can be obtained by deviations from coplanarity, resulting in higher IPs and greater resistance

against oxidative doping^{141, 142}. New polythiophene materials are hence designed for better air stability to address the problem of degradation^{18, 140, 143-145}.

Poly(3,3''-dialkylquaterthiophene)s (PQTs), a class of solution-processable regioregular polythiophenes developed by Ong and coworkers^{18, 143}, affords excellent TFT performance under ambient conditions. No precautionary measures need to be taken in excluding oxygen, moisture, or light during device fabrication. For example, PQT-12 has an ionization potential 0.1 eV lower than that of P3HT and a wider bandgap, indicating that it has greater stability against photoinduced oxidative doping. Bottom-gate top-contact TFT devices with PQT-12 active channel layers fabricated by spin coating techniques under ambient conditions yield an average mobility of 0.07-0.12 cm²/Vs and on/off ratio over 10⁷ after an annealing process at 120-140 °C in vacuum. The annealing process helps the self-organization of PQT-12 into highly ordered lamellar π - π stacking structures, which are oriented to the substrate manipulated through proper alignment layers, resulting in improved device mobility^{18, 143}.

2.3 Gate dielectrics

The gate dielectric separates the active semiconductor layer from the gate electrode. Actually, there are two interfaces playing roles in the operation of organic TFTs: 1) dielectric/gate electrode interface, where the injection of static charge or dynamic charge into the dielectric should be prevented. The injected charge from the gate electrode can have adverse effects on threshold voltage change with time and cause hysteresis of current on voltage. Therefore, high-quality pinhole-free dielectric layer is necessary to prevent gate leakage

currents, and 2) semiconductor/dielectric interface, which plays an essential role in the performance of organic TFTs. In most organic TFT structures, where bottom-gate geometry is employed, the semiconductor is deposited on top of the dielectric. The molecular structural ordering and morphology of the organic semiconductor films (especially in the first few layers), which is thought to be most critical to the performance of organic semiconductors, greatly depends on the surface properties of the dielectric layer. A great deal of research has been conducted to engineer the semiconductor/dielectric interfaces to improve the performance of organic TFTs. Besides the interfacial properties, other important properties of a dielectric in an organic TFT are dielectric breakdown fields (E_b), capacitance per area (C_i), and leakage currents.

The current between source and drain is directly proportional to the induced charges ($C_i V_G$) at the dielectric/semiconductor interface as indicated in Equations (2.1) and (2.2). C_i is given by $\frac{k\epsilon_0}{t}$, where ϵ_0 , k and t are the vacuum permittivity, dielectric constant and thickness of the dielectric layer, respectively. High capacitance of gate dielectric, which can be achieved by either reducing the thickness or increasing the dielectric constant of the gate dielectric layer, is of great importance in reducing the operating voltage, thus the power consumption, of the transistor devices with the same semiconductor material and device dimensions.

Dielectric materials for organic TFTs have received significant attention recently^{28, 146}. The main objective has been to develop high-capacitance films using simple deposition techniques with materials that form good interfaces with

organic semiconductors.

2.3.1 Inorganic gate dielectrics

Thermally grown SiO₂ (gate insulator) on heavily doped Si (gate electrode) has been widely used in benchmark test devices for its ready availability from conventional Si technology. Many research groups have investigated the effects of surface treatment of SiO₂ on the performance of organic transistors, looking at the surface morphology of semiconductor film, number of trap states and dipoles at the dielectric surface^{32, 147, 148}. Self-assembly monolayers (SAMs), such as hexamethyldisilazene (HMDS), octadecyltrichlorosilane (OTS), other silanes, or alkanephosphonic acid, which can interact with the Si-OH groups at the SiO₂ dielectric surface, are effective in reducing the surface energy, promoting crystallization of the organic semiconductor, and improving the performance of the organic TFTs. In addition to morphology effects, SAMs can prime the dielectric to provide a more uniform interface. One of the most effective treatments, OTS, is not only bonded to the substrate but also cross-linked laterally. Due to the high density of interchain cross-linking, it may also reduce the surface roughness. Pentacene field-effect mobilities between 0.6 and 2.1 cm²/Vs have been obtained for organic TFTs using OTS-treated silicon dioxide layer, which are better than those obtained for organic TFTs without OTS treatment¹⁴⁹. Ong et al. observed current increase from PQT-12 deposited on octyltrichlorosilane (OTS-8) treated SiO₂ compared to that on untreated SiO₂ substrate¹⁸. On the other hand, SiO₂ has relatively low dielectric constant ($k = 3.9$) and substantial tunnelling currents when very thin films are employed. There exists strong motivation for the development of an alternate,

high-dielectric constant metal oxide gate dielectric as a replacement for low- k SiO₂.

Dimitrakopolous et al. employed sputtered barium zirconate titanate (BZT, $k = 17.3$), barium strontium titanate (BST, $k = 16$), and Si₃N₄ ($k = 6$) films as gate insulators and investigated the gate-bias dependence of the field-effect mobility in pentacene TFTs. The pentacene transistors with the high- k gate dielectrics demonstrated mobilities of more than 0.3 cm²/Vs and current modulation of 10⁵ at operating voltages as low as 5 V. The mechanism enhancing the TFTs carrier mobility is found to be related to the charge carrier density in the channel region rather than the gate electric field ⁸.

Wang et al. used high- k titanium dioxide (TiO₂, $k = 41$), Al₂O₃ ($k = 8.4$), and TiO₂-SiO₂ bilayers as gate insulators for regioregular P3HT based TFTs ¹⁵⁰. TiO₂ and Al₂O₃ were deposited by sputtering, whereas SiO₂ was deposited by plasma-enhanced chemical vapor deposition (PECVD). Good modulated transistor characteristics were obtained with saturation at low driving voltages (~ -2 V) and with carrier mobilities of 1.3×10^{-2} cm²/Vs. A significant improvement in the TFTs characteristics was observed with deposition of a top layer of thin SiO₂ film; the field-effect mobility increased to 5.4×10^{-2} cm²/Vs, the on/off ratio increased from 10² to 6×10^4 , and the leakage current decreased by a factor of 10².

Very recently, Yang et al. demonstrated P3HT-based transistor with PVP/TiO₂ bilayer as a gate dielectric ¹⁵¹. The TiO₂ layers were processed from TiO₂ nanorod suspension and cured at low temperature; subsequently, another layer

of cross-linking PVP was applied. The polymer capping at the surface could further smooth the TiO₂ dielectric surface and eliminate the leakage current from grain boundaries in TiO₂ films. The resulting devices could operate with a supply voltage of less than 10 V with the mobility and on/off ratio of 0.014 cm²/Vs and 10³, respectively.

Electrochemical anodized Ta₂O₅ ($k = 24$) and Al₂O₃ ($k = 9-11$) were demonstrated as gate insulators by several groups^{22, 33}. This technique is attractive since it can be carried out at room temperature in aqueous solution, which is compatible with flexible plastic substrates, and is potentially suitable for reel-to-reel processing. Pentacene and P3HT based TFTs with OTS modified Al₂O₃ showed mobilities of $1.1-1.4 \times 10^{-3}$ and 0.06-0.1 cm²/Vs, respectively.

2.3.2 Polymeric gate dielectric materials

Another class of gate insulators for organic TFTs is polymer dielectrics. Polymeric dielectric materials offer great flexibility and freedom to build both bottom and top gate devices by using solution coating techniques and printing. Most organic polymers are insulators, and among them, some show excellent insulating properties with exceedingly low leakage currents. Furthermore, proper processing methods can generate very smooth and reproducible polymer films that can form excellent contact with organic semiconductor materials and assist in structure ordering of the semiconductor materials as a template. For the deposition of a multilayered structure with solution processes, orthogonal solvents are desirable to avoid mixing and to achieve a trap-free interface. In addition, insoluble cross-linked polymers are often preferred. Wetting of the underlying surface is important to get pinhole-free films to avoid gate leakage.

Some common polymers used as gate dielectrics in organic TFTs are illustrated in Figure 2.5.

Figure 2.5 Chemical structures of some polymeric dielectric materials for organic TFTs. [†]Copyright (2005) National Academy of Sciences, U.S.A. ¹⁵².

Poly(vinyl phenol) (PVP) is one of the most widely used polymer dielectrics for organic electronics applications ^{24, 153-158}, due to its excellent solubility in common organic solvents (such as ethanol, acetone, propylene glycol monomethyl ether acetate (PGMEA), etc.) and film-forming properties that result in a homogenous film with a smooth surface. A wide range of formulations and resulting film thickness (10 nm to 1 μ m) are possible ¹. In addition, this polymer can be crosslinked to form chemically and mechanically robust polymer films with proper cross-linkers. Several crosslinking agents have

been identified for PVP. The most commonly used is methylated poly(melamine-co-formaldehyde) (MPMF), whose methyl groups are coupled with the hydroxyl groups of PVP during the curing process. A thermal treatment at 150 °C is required to start the crosslinking reaction and efficient crosslinking takes place at 200 °C. Lim et al. studied the hysteresis behavior of pentacene TFTs with PVP gate dielectrics mixed with different concentrations of MPMF (0-125 wt% to PVP). Reduced hysteresis behavior of the devices was observed with increased amount of MPMF, as a result of the reduced electron trappings related to the –OH groups in the polymeric gate dielectrics¹⁵⁹.

To reduce the cross-linking temperature for applications that cannot afford a process temperature of 200 °C, alternative effective crosslinking agents have been searched for. A photo-initiator has been attempted to initiate the crosslinking reaction under UV illumination, which opens the opportunity to produce directly patterned dielectrics¹. The electrical characteristics of pentacene TFTs based on these films are compatible with those on thermally cross-linked PVP gate dielectrics¹.

Marks' research group synthesized novel bifunctional-silane based cross-linkers having tuned reactivity with respect to hydroxyl-containing dielectric polymers, such as PVP. They studied the kinetics of the coupling reaction of chloro- (Cl-), acetoxy- (OAc-), dialkylamino- (NMe₂-), and methoxyl (OMe-) silanes with 4-isopropylphenol (PhOH), a hydroxylated reactant, to relate the crosslinking reaction rate to the surface morphological properties, film robustness, and dielectric characteristics of the cross-linked polymer blend (CPB) films fabricated with the various silane crosslinkers¹⁶⁰. The CPB formulations with

PVP and silane crosslinking reagents are readily fabricated via spin-coating and gravure-printing on various gate contact materials such as n^+ -Si, ITO, and Al, and curing at low temperature ($\sim 110^\circ\text{C}$). This results in stable, insoluble, pin-hole-free films with excellent insulating properties (leakage current densities of 10^{-7} - 10^{-8} A/cm² at 2 MV/cm) and tunable capacitance values (from 5 to ~ 350 nF/cm²). Organic TFTs with these new CPB dielectric films exhibit good performance at low-operating voltages ($\pm 3\text{V}$) for both p- (pentacene) and n-type (DFHCO-4T) ¹⁶¹ organic TFTs. Organic TFTs on spin-coated dielectric films exhibited mobilities of 0.12-0.49 and 0.02-0.52 cm²/Vs for pentacene and DFHCO-4T, respectively, and on/off ratios of 10^4 - 10^6 . Organic TFTs on gravure-printed dielectric films showed mobilities of 0.3-0.9 cm²/Vs and on/off ratios of 10^4 - 10^5 for both pentacene and DFHCO-4T devices. The humidity-dependent dielectric properties and the corresponding pentacene TFT performance were investigated for the different CPB compositions. The results showed that moisture absorbed in the dielectric films appeared to induce additional charge carriers, resulting in increased gate leakage and source-drain current as well as in apparent mobility.

Very recently, Roberts et al. evaluated the thermal crosslinking of PVP at low temperature (60-120 °C) with a variety of commercially available, ambient stable bifunctional anhydrides, acylchlorides, and carboxylic acids ²⁵. They studied the influence of the cross-linker material, concentration, processing conditions, and surface treatment on the insulating physical and electronic properties. Ultra-thin crosslinked PVP films showed high capacitance of 152-180 nF/cm² with the dielectric constants between 4.0 and 4.8 for 22 nm thick films, leakage current

density below 10^{-6} and 10^{-8} A/cm² for 22 and 56 nm films, and breakdown voltages of 3-4 V for 20-25 nm films. Films of 50 and 150 nm thickness could withstand biases of 10 and 25 V, respectively, yielding average breakdown strength of 1.7-2.0 MV/cm. Pentacene TFTs fabricated on these crosslinked PVP films gave the highest mobility of 3 cm²/Vs under the gate bias of 2 V with on/off ratio of 10^5 , achieved from OTS modified PVP crosslinked with 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (HAD). Subsequently, low-voltage organic TFTs were demonstrated on flexible ITO/PET substrates and aluminium foil with DDFTTF¹⁶² as the active layer and two-layer PVP-HAD film as the gate insulator. The devices showed reasonably stable performance with a $\mu \sim 0.2$ cm²/Vs and on/off ratio of 1.8×10^4 upon physical stress from bending.

A siloxane-based compound, divinyltetramethyldisiloxanebis-(benzocyclobutene) (BCB) has been recently demonstrated as a promising dielectric material for organic TFTs³⁵. Solid film formation via a thermal ring opening and then a [4+2] Diels-Alder cycloaddition/polymerization occurred, making it pinhole-free even down to a few tens of nanometers in thickness with a dielectric breakdown strength of about 3 MV/cm⁹². The monomer of BCB can be spin-coated and thermally cured at 150-200 °C in an inert atmosphere. A recent report using BCB as a dielectric states n-type conduction has been observed for semiconducting polymers such as polyfluorene and poly(p-phenylenevinylene), which have otherwise been considered exclusively p-type semiconductors⁹². Electron mobilities in the order of 10^{-3} to 10^{-2} cm²/Vs have been measured in these conjugated polymers. It is proposed that n-type

conduction in these polymeric semiconductors has not been observed previously due to trapping of electrons at the dielectric/semiconductor interface by hydroxyl groups revealed from infrared ray (IR) spectroscopy investigation ³⁵. These findings highlight the critical nature of the dielectric/semiconductor interface and its role in modifying the performance of the semiconductor.

Fabrication of high-k ultrathin dielectrics is being investigated by vapor-deposition methods. Atomic-layer chemical vapor deposition (ALCVD) is considered particularly promising among these methods, since this is the only feasible method to control the thickness and composition of ultrathin metal oxide films in a layer-by-layer fashion ¹⁶³. Recently, atomic-layer-deposited (ALD) HfO₂ combined with spin-cast epoxy has been demonstrated as a high-capacitance (up to 330 nFcm⁻²) bilayer dielectric for low-voltage TFTs in which the active components are networks of single-wall carbon nanotubes (SWNTs) ¹⁶⁴. The high-capacitance, hysteresis-free, and low-temperature processability of this bilayer dielectric makes this process a promising technique for producing low-voltage organic TFTs in general.

The ability to deposit parylene C dielectrics using vapor phase deposition methods makes it very useful for sensitive semiconductors (in the case of top gate devices) such as single crystals. Researchers at Rutgers and Bell Labs have made extensive use of this dielectric in single-crystal field-effect transistors ¹⁰⁵. Using parylene C as a top gate dielectric, a double gate TFT device was generated in which the mobility at top and bottom interfaces of a single pentacene film was measured. Top gate mobility was 0.1 cm²/Vs compared to 0.4 cm²/Vs for bottom gate device. The roughness of the top interface was

considered as the reason for the decreased mobility of the top gate device.

Top gate devices composed of poly(ethylene oxide) (PEO)-lithium perchlorate have been reported¹⁶⁵. These polymer electrolyte gate dielectrics exhibit extremely high capacitances ($\sim 5 \mu\text{F}/\text{cm}^2$), exceeding even the best values reported for inorganic dielectrics. The large capacitances are reported to be due to redox chemistry at the semiconductor–dielectric interface. However, detailed understanding of this phenomenon will require further research effort. Hysteresis effects and low mobilities for both n- and p-type semiconductors are observed, but the authors of the study believe these gate dielectric films may be useful in transistor-based sensing applications where switching speed is less critical¹⁶⁵.

As dielectric films get thinner, the potential for pinhole defects increases, resulting in significant leakage currents. In order to achieve the thinnest dielectric films, great attention must be devoted to the organization of the film. Self-assembled monolayers (SAMs) and multilayers have been demonstrated to be successful dielectrics in organic TFTs. In an initial work by Vuillaume and coworkers, a simple OTS chain (2.8 nm thick) was grafted onto the surfaces of p-doped Si substrates covered with a 1.0-1.5 nm thick native oxide. The authors demonstrated for the first time that this monolayer acts as an excellent electrical insulator with leakage current as low as $10^{-8} \text{ A}/\text{cm}^2$ for an average field of 5.8 MV/cm. Halik et al. reported pentacene transistors with a SAM, consisting of 18-(phenoxyoctadecyl)trichlorosilane (PhO-OTS), as the dielectric layer¹⁶⁶. The PhO-OTS monolayer (2.5 nm thick) was self-assembled on a natively oxidized silicon surface in a one-step process either from solution or from vapor. The

strong π - π interaction between the phenoxy groups provides a densely packed surface, resulting in a very low leakage current ($\sim 5 \times 10^{-7}$ A/cm² at 1 V) and a large breakdown field (~ 14 MV/cm). The closely packed surface also prevented the pentacene molecules penetrating into the SAM dielectric layer. The pentacene TFTs operated under applied voltages of less than 2 V and exhibited mobilities of ~ 1 cm²/Vs, on/off ratios of $\sim 10^6$, and threshold voltages of -1.3 V. Yoon et al. developed a strategy to form ultra-thin self-assembled multilayers (SAMTs) (2.3-5.5 nm) as reliable dielectric materials for organic TFTs¹⁵². The 3-dimensional (3-D) crosslinked dielectric multilayers were formed by means of a sequential layer-by-layer solution phase deposition of molecular silicon precursors (which were α,ω -difunctionalized hydrocarbon chains (Alk), highly polarizable stilbazolium layers (Stb), and octachlorotrisiloxane capping layers (Cap)), resulting in smooth, nanostructurally well defined, pinhole-free, strongly adherent, thermally stable organosiloxane thin films having exceptionally large electrical capacitances (up to 2,500 nF/cm²)¹⁵², excellent insulating properties (leakage current densities as low as 10^{-9} A/cm²), and single-layer dielectric constant (k) of ~ 16 . These 3-D self-assembled multilayers enable organic thin-film transistors to be operated at very low supply voltages (source-drain, gate, and threshold voltages of < 1 V), which are compatible with a broad range of vapor- or solution-deposited p- and n-type organic semiconductors¹⁵².

2.3.3 Hybrid dielectric materials

Chen et al. studied nanocomposite dielectrics consisting of crosslinked-PVP combined with TiO₂ nanoparticles. Due to the nanoscale size of the TiO₂, it can disperse well in organic solvent, in which PVP is soluble. After sufficient

stirring, a stable TiO_2 colloid was obtained that was able to go through a $1\ \mu\text{m}$ filter easily. The colloids were spin-coated, and the films were baked at $120\ ^\circ\text{C}$ for 5 minutes and $200\ ^\circ\text{C}$ for 20 minutes. The dielectric constants of the films having 600-700 nm thickness increased from 3.5 to 5.4 with an increase in TiO_2 concentration from 0 to 7 wt%. The films containing TiO_2 are much rougher than the neat PVP films, with a root-mean-square (rms) roughness of $\sim 13\ \text{nm}$ (for the 7wt% sample) versus $0.3\ \text{nm}$ for the neat PVP films. Pentacene based TFTs on these materials showed mobilities of $\sim 0.25\ \text{cm}^2/\text{Vs}$. However, the on/off ratios remained low ($\sim 10^3$) even though higher on currents were obtained for higher capacitance films with higher TiO_2 concentrations. This result was attributed to the greater leakage currents through the gate in the case of rougher films. Schroeder et al. demonstrated nanoparticle-filled high- k polymer gate insulators with PVA or its random copolymer, poly(vinyl alcohol)-co-poly(vinyl acetate)-co-poly(itaconic acid) (PVAIA) mixed with BaTiO_3 nanoparticles¹⁶⁷. The capacitance of the PVAIA/ BaTiO_3 film was $62.5\ \text{nF}/\text{cm}^2$ at a thickness of $170\ \text{nm}$, which corresponds to a k value of 12, about twice the dielectric constant of pristine PVAIA ($k = 6$). The pentacene TFTs with this insulator showed mobility and on/off ratio of $0.12\ \text{cm}^2/\text{Vs}$ and 5×10^3 , respectively, at $4\ \text{V}$ operating voltages, and a subthreshold swing as low as $220\ \text{mV}/\text{decade}$. With a reduced loading of BaTiO_3 in the PVAIA insulator, the dielectric constant was only 9 and the mobility of the transistor was higher, at $0.4\ \text{cm}^2/\text{Vs}$. For the PVA/ BaTiO_3 insulator, the capacitance of the $160\ \text{nm}$ thick film was $61\ \text{nF}/\text{cm}^2$, corresponding to a dielectric constant of 10. A higher mobility of 0.35 and on/off ratio of 10^4 was obtained. The smoothest surface was obtained from PVAIA/ BaTiO_3 films with less nanoparticles loading, and it appeared that the

more polar co-monomers of PVAIA do help in distributing the nanoparticles better. The result revealed that both the increased surface roughness of the highly filled PVAIA polymer film, as well as the rather reactive co-monomers, reduced the mobility of the pentacene semiconducting layer.

Several groups tend to use organic/inorganic core shell nanoparticles as high- k gate dielectrics in flexible organic TFTs. Maliakal et al. reported core-shell nanoparticle architectures with titanium dioxide as the high capacitance core, and polystyrene as the shell. In this work, oleic-acid stabilized TiO_2 nanoparticles (TiO_2 -OLEIC) and phosphonate-terminated polystyrene were synthesized separately, before polystyrene coated titanium oxide nanoparticles (TiO_2 -PS) were produced through ligand exchange reaction. By comparing the average diameter of the TiO_2 -OLEIC (13nm) to the TiO_2 -PS (23nm), it was suggested that the change in diameter of ~ 10 nm was a result of functionalization with PS. This is consistent with expectations for the attachment of a layer of PS, and supports the conclusion that the polystyrene chains form a shell around the titanium oxide core that is roughly 1 coil thick. The TiO_2 -PS was spun from chlorobenzene solution (10-20% weight/volume) to form films with thicknesses ranging from 0.5 to 1.25 μm . The volume % of titanium dioxide in these films was calculated to be 18.2%. The dielectric constant of the 1.25 μm -thick film is ~ 8 . Pentacene TFTs based on this film operated at low threshold voltage (-2 V), and exhibited reasonably high mobilities of $\sim 0.18 \text{ cm}^2/\text{Vs}$. The on/off ratio (535) is reasonably high for these unpatterned pentacene devices ($W/L = 9.4$), indicating low leakage currents through the dielectric.

More recently, Kim et al. reported high- k nanocomposite thin films utilizing high volume fractions (up to 37 vol%) of phosphonic acid-modified BaTiO₃ nanoparticles dispersed in crosslinkable PVP. Pentacene TFTs utilizing these thin films as gate insulators exhibit a large on/off current ratio $\sim 10^6$ due to the reduced leakage current (10^{-8} A/cm²). In addition, the surface roughness of the underlying nanocomposite films has a great influence on the saturation mobility of the pentacene layer. By combining high volume fraction nanocomposites with a thin smoothing layer of a pure polymer, a saturation mobility of 0.17 cm²/V s and an output current of 10^{-5} A were obtained.

Cui et al. attempted to use self-assembled silica nanoparticles (diameter ~ 45 nm) to form the gate dielectric layer for organic TFTs¹⁶⁸. Vapor-deposited pentacene was employed as the semiconductor. The devices were operated under 5 V, and gave the field-effect mobility of 0.05 cm²/Vs and slope of 1.4 V/decade. This low-temperature and low-cost electrostatically driven nano self-assembly could be an alternative solution-process to construct insulating layers in organic TFTs.

Very recently, Cahyadi et al. reported using sol-gel silica nanoparticles as the gate dielectrics, and p-channel small molecule/polymer (evaporated pentacene and spin-coated PQT) and n-channel fullerene derivative TEPP-C61 based transistors were demonstrated¹⁶⁹. The sol-gel silica solution was prepared and spin-coated on the thermally-grown SiO₂ (TOX) substrate to form sol-gel dielectric films, which were dried in ambient conditions at 60 °C and further heated at 100 °C under 10^{-7} mbar before organic semiconductor deposition. The organic transistors showed significant enhancement in device mobilities ranging from ~ 6 to ~ 45 times higher for all classes of semiconductors deposited on the

so-gel silica gate-dielectric than on pristine/octyltrichlorosilane(OTS-8) treated thermally grown silica, which is attributed to better molecular ordering and reduced charge trapping centers due to less structural defects at the dielectric/semiconductor interface.

Table 2.2 summarizes recently reported organic/inorganic composites for the dielectric application in organic TFTs.

Table 2.2 Dielectric properties of organic/inorganic hybrid materials.^a

Dielectric materials	Method (deposition)	v.v %	C _i (nF/cm ²)	t (nm)	k	I _L (A/cm ²)	E _B (V/cm ²)	Device	OSC (process)	μ (cm ² /Vs) (V _G , V _D)	On/off	V _T (V)	S (V/dec)	ref
PVP/TiO ₂	blending	12.4	6.8	700	5.4	--	--	BG, TC	Pentacene (vapor)	0.24 (-40V)	10 ³	-7	--	170
TiO ₂ -PS	Core-shell nanocomposites (SC)	18.2	5.7	1250	8	--	2×10 ⁴	BG, TC	Pentacene (vapor)	0.18±0.03 (-12V,-20V)	535	-2	--	26
PVA/BaTiO ₃	Blending (SC)	--	61	160	10.9	5×10 ⁻⁷	2×10 ⁶	BG, TC	Pentacene (vapor)	0.35 (4V)	10 ⁴	-0.7	0.21	167
PVAIA/BaTiO ₃	Blending (SC)	--	62.5	170	12	4×10 ⁻⁶	2×10 ⁶	BG, TC	Pentacene (vapor)	0.12 (4V)	5×10 ³	-0.12	0.22	167
(PS-PEO-PS) [EMIM][TFSI]	Solid polymer electrolytes (SC)	--	~ 2×10 ⁴	9000	--	--	--	TG, BC	P3HT	1.8 (-4V, -1V)	~ 10 ⁵	--	0.1	171
									PQT-12	1.6 (-4V, -1V)	~ 10 ⁵	--	--	
									F8T2	0.8 (-4V, -1V)	~ 10 ⁴	--	--	
(PS-PMMA-PS) [EMIM][TFSI]	Solid polymer electrolytes (aerosol jet printing)	--	~ 2×10 ⁴	10000	--	--	--	TG, BC	P3HT (printing)	2±0.7 (-2, -1.5)	~ 10 ⁵	--	--	171
BaTiO ₃ -PEGPA /PVP	blending	37	31	406	14	~ 10 ⁻⁸	2×10 ⁵	BG, TC	Pentacene (vapor)	0.04 (-10V)	6×10 ⁴	-1.96	0.67	172

^a Abbreviations: SC, spin-coating; BG, bottom-gated; TG, top-gated; BC, bottom-contact; TC, top-contact;

Table 2.2 Dielectric properties of organic/inorganic hybrid materials. (cont.)

Dielectric materials	Method (deposition)	v.v %	C _i (nF/cm ²)	t (nm)	k	I _L (A/cm ²)	E _B (V/cm ²)	Device	OSC (process)	μ (cm ² /Vs) (V _G , V _D)	On/off	V _T (V)	S (V/dec)	ref
BaTiO ₃ -PEGPA /PVP+PVP	bilayer	--	42	251	12	<10 ⁻⁸	2×10 ⁵	--	--	0.17 (-10V)	2.3×10 ⁵	-1.1	0.3	172
SiO ₂ trilayer	Sol-gel	--	303	29	9.8	5×10 ⁻⁸	1×10 ⁶	BG, TC	Pentacene (vapor)	3.5 (-3V)	5×10 ³	-0.77	0.267	37
BaTiO ₃ filled polymer + P105	Lux Print 8153E	--	--	10000-15000 + 100-600	--	--	--	BG, TC	PTAA (SC)	3×10 ⁻³ (-60V)	10 ³	±8V	--	173
(SiO ₂ /PDDA) ₈	Spin coating LBL SA	70	~ 17.7	300	6	--	--	DG, BC	Pentacene (vapor)	0.1 (-15V,2.5V)	3.8×10 ³	-2.2V	1.3	174

2.3.4 Fabrication process

In the early days of organic thin-film transistors, much of the techniques used in device fabrication have been borrowed from well-developed inorganic metal-oxide-semiconductor FET (MOSFET) fabrication processes, such as thermal oxidation, thermal evaporation, optical lithography and lift-off metallization techniques. However, in an effort to lower the fabrication costs, these techniques have been adapted and new ones especially suited for organic transistors are developed. In general, organic semiconductors can be deposited either from vapor or from solution phase depending on their vapor pressure and solubility¹⁷⁵. As mentioned earlier, device performance may vary greatly depending on the deposition conditions due to the variations in the molecular structures and thin film morphology. It is known that the current flow in an organic TFT is mainly confined within the first several monolayers (~ 5 nm) of semiconductor film away from the semiconductor/dielectric interface. The typical semiconductor thickness required for an organic TFT is in the range of 20-50 nm. A thinner film may have incomplete surface coverage¹⁷⁶. For bottom-contact devices, a thicker semiconductor layer usually does not affect the charge carrier mobility even though the device off-current may increase for materials with a higher unintentional doping. For top-contact devices, a thicker layer may lead to higher resistance for the charge carriers to travel from the source electrode to the semiconductor/dielectric interface, where the majority of the current flow occurs.

A brief discussion on different deposition methods are discussed below.

2.3.4.1 Vacuum Evaporation

The technique of vacuum thermal evaporation has been used by a number of researchers to fabricate organic transistors, which have produced devices with the highest reported mobilities^{47, 96, 177}. This technique begins by heating the organic material until it vaporizes. Evaporation is then carried out under high or ultra-high vacuum conditions with a pressure in the range of 10^{-8} to 10^{-6} torr. Under such condition, impurities are usually removed and high purity of the material can be achieved. The vapor is then captured onto a prefabricated substrate where the thickness can be controlled by the amount of exposure time and the evaporation speed.

For organic small molecules and oligomers that are solution-insoluble, vacuum thermal evaporation is an ideal deposition method. Currently, the best mobility for organic semiconductors has been reported for vacuum-deposited pentacene films⁸⁵. Vacuum thermal evaporation has the advantages of forming films with high film-uniformity and good reproducibility. Multilayer deposition and co-deposition of several organic semiconductors can be carried out without the concerns of damage to the previous layer from delamination or dissolution during subsequent deposition steps. However, this method has a relatively high material consumption and incurs a high initial cost for equipment setup. Although this does lead to better devices, the expense of the equipment and the process is comparatively high, which has led many research groups to investigate alternative and cheaper methods of fabrication.

2.3.4.2 Solution deposition

To realize truly the advantages of organic materials in device fabrication, liquid

phase processing is strongly desired. Deposition methods based on solution-processable materials (including semiconductors, insulators and electrodes) are not limited by the size of the vacuum chamber and no pumping down time is required. They are compatible with large-area thin-film fabrication and therefore results in lower production cost per device. Several techniques are used for solution deposition of organic materials.

Spin Coating. In this process, the material in its liquid state is deposited onto the wafer that is held to a spindle by a vacuum. After deposition of the liquid, the whole assembly is spun at a high speed (round per min, rpm) to obtain the desired final thickness of organic semi-conducting material. This is a very simple process, but it also requires a subsequent process to pattern the organic material. The solvent dries relatively quickly, allowing less time for molecular ordering. Nevertheless, the film uniformity is good. Transistors fabricated using spin coat thin films have typically shown smaller mobilities than the evaporated forms of the same materials. For example, for pentacene, mobility of $\sim 0.015 \text{ cm}^2/\text{Vs}$ has been reported for spin coated films¹⁷⁸ versus $2.4 \text{ cm}^2/\text{Vs}$ for single crystal films.

Drop Casting. Basically, drop casting is very similar to spin coating. The organic material will first be dissolved in a suitable organic solvent and then be dripped onto a prefabricated substrate. A great advantage of this method is the ease of administering the organic semiconductor onto the substrate, as it does not involve complicated equipment associated with the manufacturing of transistor devices. However, the thickness of the organic semiconductor cannot be controlled easily.

Printing. Organic deposition methods have also been borrowed from other technologies. Several groups such as Motorola, Philips Electronics, Plastic Logic and others have been researching the use of modified ink jet printers to pattern organic transistors^{125, 126, 179-181}. A particular advantage of this process is the ability to print directly onto a transparency which acts as the flexible substrate. This technology can allow anybody to quickly prototype a design and develop their own circuits. However, it is limited in scope to current ink-jet technology resolution. The highest resolution printers create droplets that are 1200 x 1200 dpi (dots per inch) in size. This translates to a minimum geometry of 25 x 25 μm , which is much larger than current CMOS based micro processing technology. Furthermore, because of the space between the print head and the substrate, there is difficulty in controlling the absolute edge resolution due to some splashing. This creates further limitations on transistor geometries due to the difficulty in controlling the deposition of the material.

Soft lithography is another approach for high resolution, large volume patterning of surfaces at low cost. The stamp used to transfer the patterns is the key component in soft lithography. Crosslinked poly(dimethylsiloxane) (PDMS) is commonly used as an elastomeric stamp to produce conformal contact between the stamp and the substrate surface¹⁸²⁻¹⁸⁴.

Chapter 3 Experimental methodology and techniques

3.1 Synthesis approach of organic-capped inorganic nanoparticles

The synthesis of organic-capped inorganic nanoparticles studied in this dissertation was conducted by solution-phase chemical routes (sol-gel techniques) at low temperature (100 °C), involving hydrolysis of the perovskite precursors with oleic acid (OA) as surfactant. The sol-gel technique provides the means of producing high-purity nanoscale materials of a specific and variable size. The detailed synthesis procedures, properties of the synthesized nanoparticles, and preparation of the nanoparticles suspensions will be described in Chapter 4, 5 and 6.

3.2. General considerations for device fabrication

3.2.1 Capacitors

To investigate the dielectric properties of the OA-capped nanoparticles films, metal-insulator-metal (MIM) capacitor structures were fabricated on indium tin oxide (ITO) coated glass substrates (sheet resistance of 12Ω/sq), which were cleaned with detergent and deionized (DI) water (Q-Grad ®1, Millipore Corporation, USA) assisted by sonication, and subsequently treated with oxygen plasma for 2 min. OA-capped nanoparticle suspensions were spin-coated (SCS G3P-8 programmable spin coater, USA) on treated ITO substrates under 500-1000 rpm for 45 s at ambient condition. The thickness of the nanoparticle films was adjusted by the concentration of the suspension and the spinning speed. A suitable concentration and spinning speed was selected for individual OA-capped nanoparticles suspension to produce films with reasonable

capacitance, leakage current and breakdown voltage for incorporation into transistor devices. Silver top contacts of ~ 100 nm in thickness and 4 mm^2 in area were deposited on the nanoparticle films through a shadow mask by physical vapour deposition (PVD) at a rate of $120 \text{ \AA/min}$ under 10^{-7} torr. The residual solvent in the nanoparticle films was evaporated completely during this period in a high vacuum environment.

3.2.2 Pentacene TFTs

Bottom-gate pentacene TFTs with nanoparticle dielectrics were fabricated on ITO coated polyester (ITO/PET) films (sheet resistance of $100 \Omega/\text{sq}$) or Al coated glass (Al/SiO_2) substrates. OA-capped nanoparticle suspensions in toluene ($\sim 40 \text{ mg/g}$) were spin-coated to deposit nanoparticle dielectric films on the substrates. Pentacene (Aldrich, 99.99%) films of ~ 40 nm were deposited by thermal evaporation on the nanoparticle films held at temperature at a rate of $\sim 42 \text{ \AA/min}$ under 10^{-8} torr and Au source-drain electrodes of 50 nm thickness were subsequently deposited through a shadow mask at a rate of $30 \text{ \AA/min}$ under 10^{-7} torr. The channel length (L) varies from $70 \text{ }\mu\text{m}$ to $200 \text{ }\mu\text{m}$ and the channel width (W) is 2 mm. The device configuration is illustrated in Figure 3.2(a).

In addition, bottom-gate top-contact pentacene devices were also fabricated on a heavily-doped n-type (n^{++}) silicon wafer with a 100-nm-thick top-layer of SiO_2 as insulator. The SiO_2 surfaces were treated in Piranha solution (98% H_2SO_4 (Aldrich): 30% H_2O_2 (Aldrich), v/v = 3:1) at 80°C for 30 min, then rinsed with excess DI water, and blow dried under a high-purity nitrogen stream. It is believed that Piranha solution treatment on the substrates could introduce abundant hydroxyl groups ($-\text{OH}$) on the SiO_2 surface¹⁸⁵ for further

functionalization via silanization. The substrates were then immersed in 10 mmol octyltrichlorosilane (OTS-8) (Aldrich) solution in hexane (Aldrich, HPLC) for 30 min at room temperature (RT), rinsed with hexane followed by isopropanol (Aldrich, HPLC) to remove the unreacted OTS-8 molecules, and blow dried with nitrogen before pentacene deposition. The treatment scheme on the SiO_2 surface is shown in Figure 3.1.

Figure 3.1 OTS-8 modified SiO_2 surface (OTS- SiO_2): (a) SiO_2 surface, (b) Piranha solution treatment brings Si-OH groups onto SiO_2 surface, and (c) OTS-8 covalently bonded onto the oxide surface.

3.2.3 PQT-12 TFTs

PQT-12 TFTs were fabricated on an n^{++} silicon wafer with 100 nm thermally grown SiO_2 as the bottom gate insulator. Gold/titanium (Au/Ti: 50 nm/1 nm) source-drain contacts were patterned using a lift-off technique and deposited by electron-beam evaporation under 1×10^{-6} torr. The channel length ranged from 5 μm to 100 μm with the same channel width of 9000 μm . The substrates were cleaned successively by ultrasonication in acetone, methanol, and de-ionized (DI) water, followed by treatment in Piranha solution at 80 °C for 30 min, then rinsed with excess DI water, and dried with nitrogen. The Piranha solution treatment on the substrates could reduce the contact resistance dramatically for the bottom-contact organic TFTs⁷⁰. Subsequently, the substrates were treated with 10 mmol OTS-8 solution in hexane at room temperature for 30 min, rinsed with hexane followed by isopropanol, and then dried with a stream of nitrogen gas. PQT-12 semiconductor layers were deposited by spin-coating the PQT-12 solution in dichlorobenzene (0.5 wt %) (Xerox Research Centre, Canada) at 1000 rpm for 2 min with a resulting thickness of about 60 nm. The prepared semiconductor film was then dried, annealed at 125 °C for 30 min, and cooled down to room temperature overnight in a vacuum oven. The bottom-gate geometry was used to characterize the performance of PQT-12/OTS- SiO_2 TFTs.

The top-gate devices were made by spin-coating OA-capped nanoparticle suspensions in toluene (~ 40 mg/g) on PQT-12 semiconductor layers under ambient condition. Since the annealed PQT-12 film is insoluble in toluene, the deposition of the nanoparticle films from the suspension in this orthogonal solvent should not damage the underlying PQT-12 films. The top gate contact

was accomplished by depositing 100 nm thick silver on the nanoparticle dielectric films under 10^{-7} torr (Figure 3.2(b)).

Figure 3.2 Device configurations of (a) bottom-gate pentacene and (b) top-gate PQT-12 TFTs with OA-capped nanoparticles as dielectrics.

3.3 Electrical characterization

3.3.1 Capacitance characterization

To determine the dielectric constants of the organic-capped nanoparticles, the capacitance-frequency characteristics of the nanoparticle films were measured at ambient atmosphere with the MIM capacitor structures using an LCR meter (HP 4284 Precision LCR meter, USA) with a probe station (Summit 11751B-6 system, Cascade Microtech, USA). The dielectric constant k was calculated by the following equation: $k = \frac{C_i * t}{\epsilon_0}$, where C_i , t , and ϵ_0 are the unit area capacitance, the thickness of the film, and vacuum permittivity (8.85×10^{-12}

F/m), respectively. Thickness of the film was measured with Atomic force microscope (AFM) (SPM 3100, Veeco Instruments Inc., USA) operated in tapping mode with a scan rate of 0.5 Hz.

Polarization of the gate dielectric materials with respect to an applied DC bias has great impact on the performance of the transistor devices and slow polarization may cause significant hysteresis of the drain current on the gate voltage. To examine the polarization behavior of the OA-capped nanoparticles films, the capacitance-voltage characteristics of the fabricated MIM capacitors were measured under a DC sweep voltage for both forward (from negative to positive) and reverse (from positive to negative) conditions at fixed frequency at ambient atmosphere.

3.3.2 Leakage current characterization

An important concern with any gate dielectric material is gate leakage. The leakage current of the dielectric layer was measured with the capacitor structures similar to those used for capacitance-voltage (C-V) measurements using an Agilent 4157B Semiconductor Parameter Analyzer System (USA) with a probe station. It is known that moisture absorbed by polymer dielectric films could induce significant leakage problems. Leakage currents of the nanoparticle films were reduced when measured under a stream of nitrogen. Figures 3.3(a) and 3.3(b) show the examples of the leakage current density of the OA-capped nanoparticles films studied in this thesis (OA-SrTiO₃ film: 400 nm in thickness; OA-Ba_{0.1}Sr_{0.9}TiO₃ film: 450 nm in thickness) at different humidity levels adjusted by purging high-purity nitrogen into the chamber of the probe station at different flow rate. The humidity level inside the chamber was measured

with a humidity meter. The leakage current was reduced by almost 40 times when the humidity was reduced from $\sim 50\%$ to $\sim 26\%$.

Figure 3.3 Leakage current density vs electric field of the nanoparticle films: (a) OA-SrTiO₃ [OA]/[P] = 1 (400 nm thick) and (b) OA-Ba_{0.1}Sr_{0.9}TiO₃ (450 nm thick) at different humidity levels.

3.3.3 Transistor device characterization

The electrical characterization of the organic TFTs based on OA-capped nanoparticle dielectrics as well as SiO₂ dielectrics were performed on a probe station under a stream of nitrogen, using an Agilent semiconductor parameter analyzer. For the output characteristic of an organic TFT, the drain current was measured during drain-source voltage ramped from 0 to a negative value at discrete gate voltages. The transfer characteristic was measured by scanning the gate voltage for discrete drain-source voltage in the linear regime ($|V_D| \ll |V_G|$) and the saturation regime ($|V_D| > |V_G - V_{th}|$), respectively. V_{th} was determined by extrapolating the fitting line for $|I_{D, sat}|^{1/2}$ vs. V_G to zero current. Turn on voltage

(V_{on}), which is the voltage at which subthreshold current starts increasing exponentially, and the on/off ratio was extracted from the $I_{D,sat}$ vs. V_G characteristic plotted on a semi-logarithmic scale. The saturation mobilities and the subthreshold swing (S) of the devices were calculated using Equation 2.2 and Equation 2.6, respectively.

Chapter 4 Organic-Capped Titanium Dioxide Nanoparticles for Dielectric Applications in Organic Thin-Film Transistors ^a

4.1 Introduction

Recently, soluble TiO₂ nanorods have been synthesized as the precursors of TiO₂-polystyrene core-shell nanorods, which were processed as high-*k* dielectrics for organic TFTs ^{26, 186}. The multi-step synthesis of TiO₂-polystyrene core-shell nanorods involved the synthesis of soluble oleic-acid capped TiO₂ nanorods, the synthesis of phosphonate terminated polystyrene via atom transfer radical polymerization, and the ligand exchange reaction between oleic acid and phosphonate terminated polystyrene. Due to the complexity of the TiO₂-polystyrene nanorods synthesis, it will be desirable to produce soluble TiO₂ nanoparticles from one-step synthesis and apply them directly as homogeneous gate dielectric films in organic electronics.

In this work, oleic acid-capped titanium dioxide (OA-TiO₂) nanoparticles were synthesized and prepared as solution-processable dielectrics. Both top-gate and bottom-gate organic thin-film transistors were successfully demonstrated with OA-TiO₂ nanoparticle films as the gate insulating layers.

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4.2 Material synthesis and preparation

4.2.1 Synthesis of OA-TiO₂ nanoparticles

The synthesis of OA-capped TiO₂ (OA-TiO₂) was described somewhere else¹⁸⁷ and the process is illustrated in Figure 4.1. In detail, 127 ml oleic acid (OA) (Aldrich, 90%) was dried at 120 °C for 1 h under vigorous stirring and argon atmosphere, and then cooled down to 100 °C. 9 ml titanium isopropoxide (Aldrich, 97%) and 5 ml triethylamine (Aldrich, 99%) in 18 ml ethylene glycol (Aldrich, 99.8%, anhydrous) were subsequently added into the OA under argon atmosphere at 100 °C. The subsequent mixture was maintained under argon atmosphere at 100 °C for 48 h. After the reaction, the solution was allowed to cool down to room temperature and OA-TiO₂ nanoparticles were readily precipitated when the solution was poured into excess ethanol (Aldrich, 99.8%). The supernant was decanted and the white precipitate was collected by centrifugation at 6000 rpm and washed 6 times by ethanol to remove surfactant residuals. The collected OA-capped TiO₂ nanoparticles were then easily dispersed in chloroform (Aldrich, HPLC) to form yellow transparent dispersion. The as-obtained TiO₂ nanoparticle dispersion was stable for a few weeks, after which some precipitation was observable. The resultant transparent dispersion could then be stable for more than half a year for use.

Figure 4.1 Synthesis of OA-TiO₂ nanoparticles

Inorganic weight and volume fraction of the nanoparticles were determined as following procedures: 1) a portion of the as-synthesized OA-TiO₂ nanoparticles was dried in vacuum overnight, subsequently annealed at 500 °C for 30 min under nitrogen gas. The inorganic titania residue was determined to have a weight fraction of 0.38 of the dry OA-TiO₂ nanoparticles. 2) Inorganic volume fraction (%volume of TiO₂/total volume) (f) can be obtained by the following equation: $f = (\text{weight fraction TiO}_2 / \text{density of TiO}_2) / [(\text{weight fraction TiO}_2 / \text{density of TiO}_2) + (\text{weight fraction of OA} / \text{density of OA})]$, where the density of TiO₂ and OA was estimated to be 3.84 g/cm³ and 0.89 g/cm³, respectively. Hence, the OA-TiO₂ nanoparticles have an inorganic volume fraction of 0.138. The permittivity of the OA-TiO₂ nanoparticles can be predicted by the linear Power law mixture model³⁶: ϵ_{TiO_2} and ϵ_{OA} is the

permittivity of bulk TiO_2 ($k = 41^{150}$) and OA ($k = 2.3^{188}$), respectively.

$$\varepsilon_{\text{OA-TiO}_2}^\beta = f \times \varepsilon_{\text{TiO}_2}^\beta + (1-f) \times \varepsilon_{\text{OA}}^\beta \approx 7 \text{ for } \beta = 1.$$

4.2.2 Preparation of OA-TiO₂ nanoparticle suspensions

The OA-TiO₂ nanoparticles suspension in chloroform obtained previously is very viscous with a concentration of 8 wt% and needs to be diluted for use. To assess the feasibility of different solvents for solution process of the nanoparticles, the pristine OA-TiO₂ NPs suspension in chloroform was diluted with another solvent (x) of the same weight as chloroform in the suspension ($\text{CHCl}_3 : x = 1 : 1$ (w/w)). The testing solvents include toluene, heptane, cyclopentanone (CP), and methyl ethyl ketone (MEK). All the solvents were HPLC grade and purchased from Aldrich. The mixture was stirred at room temperature for 24 hrs before use and the final suspension with concentration of 5 wt%, 3.3 wt%, 2.5 wt%, and 2 wt%, respectively, was used for further tests.

4.3 Material characterization analysis

The dispersion of OA-TiO₂ nanoparticles in organic solvent has been carefully treated. Figure 4.2 shows digital images of (a) TiO₂ nanoparticles obtained from Aldrich in CHCl_3 , (b) vacuum-dried OA-capped TiO₂ dispersed in CHCl_3 , (c) ethanol-wetted OA-TiO₂ (40-60 wt% of ethanol) nanoparticles dispersed in CHCl_3 , and (d) ethanol-wetted OA-TiO₂ nanoparticles dispersed in toluene. The TiO₂ nanoparticles obtained from Aldrich cannot be dispersed in CHCl_3 , as well as other organic solvents. When the OA-TiO₂ nanoparticles are vacuum-dried to remove ethanol after washing, the dry OA-TiO₂ nanoparticles exhibit very poor dispersion in CHCl_3 and other organic solvents, even when assisted by

sonication. As shown in Figures 4.2(c) and 4.2(d), the ethanol-wetted OA-TiO₂ (without vacuum drying) nanoparticles can be well-dispersed in CHCl₃ and toluene to produce a transparent light-yellow solution. The OA-TiO₂ suspensions in chloroform and toluene are stable over months with negligible precipitation. The poor dispersion of vacuum-dried OA-TiO₂ nanoparticles is probably due to the irreversible aggregation of nanoparticles.

Figure 4.2 (a) Aldrich-TiO₂ nanoparticles in chloroform (1 wt%), (b) vacuum-dried OA-TiO₂ nanoparticles in chloroform (1 wt%), (c) ethanol-wetted OA-TiO₂ nanoparticles in chloroform (5 wt%), and (d) ethanol-wetted OA-TiO₂ nanoparticles in toluene (5 wt%).

Elemental analysis, using energy-dispersive X-ray spectroscopy (EDS) attached to the field emission scanning electron microscope (FESEM) (JSM-6700F, JOEL, Japan), confirms the presence of Ti, and O in the OA-TiO₂ ensembles as shown in Figure 4.3. The platinum (Pt) element is from the conductive coating for SEM.

Figure 4.3 EDS spectra of OA-TiO₂ nanoparticle films.

High-resolution transmission electron microscope (HR-TEM) (JEM-2100F, JOEL, Japan) was used to get the TEM images of the nanoparticles. The samples for TEM measurement were prepared by dropping the dilute nanoparticle suspensions in toluene onto 300 mesh copper grids and kept in vacuum for solvent evaporation. Figure 4.4(a) shows the transmission electron microscopy (TEM) image of the OA-TiO₂ nanoparticles. The particles are not able to be clearly identified implying poor crystallization of the inorganic cores and existence of a relevant fraction of amorphous materials¹⁸⁷. This is consistent with the XRD analysis (not shown here) where no peaks are observable. From the HRTEM image (left inset in Figure 4.4(a)), the anatase (101) lattice plane¹⁸⁷ is observed from the core of a single nanoparticle and the size of the particle is of 4-8 nm allowing total solubility in organic solvents.

The prepared OA-TiO₂ nanoparticles suspensions in different solvents were spin coated onto silicon substrates to form transparent films. The surface properties of the films were characterized. For nanoparticle dispersion in CHCl₃

(denoted as OA-TiO₂/CHCl₃), as well as the dispersion diluted with heptane or MEK, no homogeneous nanoparticle films can be obtained in a large area on silicon substrates with the surface area of $2.6 \times 2.6 \text{ cm}^2$ and structural defects are observable. AFM was used to characterize the surface morphology. The surface morphology of small regions of $\sim 4 \text{ }\mu\text{m}^2$ on the OA-TiO₂/CHCl₃ film is rather smooth with a surface root mean square roughness (R_{rms}) of around 0.5 nm as shown in Figure 4.4(b). The insert in Figure 4.4(b) gives the histogram of the bearing analysis, which is a useful method of plotting and analysing the distribution of the surface height/depth over a sample¹⁸⁹, and the bearing width (full width at half maximum: W) of the histogram is a good measure of the surface roughness^{190, 191}. The OA-TiO₂/CHCl₃ film shows a bearing width of 1.2 nm. For the OA-TiO₂ nanoparticles dispersion in CHCl₃-toluene (CHCl₃ : toluene = 1: 1 (w/w)) and CHCl₃-CP (CHCl₃ : CP = 1: 1 (w/w)), respectively, homogeneous nanoparticle films can be obtained on the silicon or ITO coated glass substrates in large areas ($2.6 \times 2.6 \text{ cm}^2$). Figures 4.4(c) and 4.4(d) show the AFM morphology images and histogram of bearing analysis (inset) of the resulting nanoparticle films on silicon substrates. The OA-TiO₂/CHCl₃-toluene film also shows a very smooth surface morphology ($R_{rms} = 0.6 \text{ nm}$, $W = 1.3 \text{ nm}$) and the nanoparticle suspension is stable over months with negligible precipitation, which means toluene is introduced into the nanoparticle dispersion in CHCl₃ without compromising the nanoparticle dispersion. On the other hand, the OA-TiO₂/CHCl₃-CP film shows higher surface roughness of 1.3 nm and broader bearing width of 3 nm, and it is found that the suspension becomes thicker after two weeks storage and is finally gelatinized one month later. Hence, toluene is a suitable solvent for dispersing the OA-TiO₂ nanoparticles and

subsequent solution process to form uniform and smooth films. The surfaces of the homogeneous nanoparticle films exhibit low surface energy with a water contact angle of about $95 \pm 3^\circ$ measured with FTÅ 200 (First Ten Angstroms, USA).

Figure 4.4 (a) Representative TEM images of OA-TiO₂ nanoparticles and AFM height-images of representative OA-TiO₂ nanoparticle films obtained from (b) CHCl₃ suspension, (c) CHCl₃ and toluene suspension, and (d) CHCl₃ and cyclopentanone (CP) suspension on silicon substrates, respectively. The inserts in (a) are the high-resolution TEM image of a representative single OA-TiO₂ nanoparticle (left corner) and the diffractive pattern of OA-TiO₂ nanoparticles (right corner). The inserts in (b), (c) and (d) are the respective histogram of bearing analysis of each image.

4.4 Electrical properties of OA-TiO₂ films

By spin-coating the OA-TiO₂ nanoparticles suspensions in toluene of different

concentrations on pre-cleaned ITO coated glass at the same spinning condition (RT, 1000 rpm for 45 s), films of different thickness were obtained. The concentration of the nanoparticle solution and corresponding film thickness is listed in Table 4.1, which shows that lower concentration solution results in thinner film due to the reduced viscosity of the diluted solutions. To characterize the electrical properties of the films, MIM structures were fabricated as mentioned in *Chapter 3.2.1*. By reducing the film thickness, the capacitance of the dielectric films can be increased. On the other hand, the leakage current is also increased, which leads to high off current and low on/off ratio of the organic TFTs. Table 4.1 lists the film thickness and the corresponding dielectric strength of the OA-TiO₂ nanoparticle films, and it shows that the thickness of the films can be reduced to about 300 nm with low-leakage current density; a further reduction in thickness could result in a significant increase in leakage current density, which would make the film unsuitable for use as gate dielectrics in organic TFTs.

Table 4.1 Dielectric properties of OA-TiO₂ nanoparticle films of different thickness

Solvents	Concentration (wt%)	Thickness (nm)	Capacitance (nF/cm ²)	Electric field (MV/cm)	Current density (A/cm ²)
CHCl ₃ -CP	3	640	7.5	1	2.76×10^{-8}
	2	390	11.2	1	4×10^{-7}
	1.5	320	13.5	0.5	2×10^{-7}
	1	280	15.2	0.2	6.9×10^{-6}
CHCl ₃ -Toluene	5	650	7.2	1	1.4×10^{-8}
	3	470	9.6	1	2×10^{-8}

Figure 4.5(a) shows the frequency-dependent dielectric constant of the

nanoparticle films. The dielectric constant of the nanoparticle films at 10^3 Hz is about 5.3 and shows a slight frequency-dependent drop ($\sim 6\%$) at the frequency of 10^6 Hz. The declining trend of dielectric constant drop with increasing frequency is similar to those of nanocomposites containing TiO_2 nanoparticles^{26, 167, 170}. The homogeneous OA- TiO_2 films show a dielectric constant enhancement of more than twice that of bulk oleic acid ($k = 2.3$)¹⁸⁸ and this value is lower than the predicted permittivity of the nanoparticles. This could be due to the overestimation of the TiO_2 permittivity in the calculation since the inorganic core materials of OA- TiO_2 were not highly crystallized. The current density-voltage/electric field (J-V/E) characteristics of the nanoparticle film (650 nm) are shown in Figure 4.5(b). The leakage current density is about $3 \times 10^{-8} \text{ A/cm}^2$ at $E = 1 \text{ MV/cm}$, which is about one order of magnitude lower than those of SiO_2 dielectrics¹⁷⁷, cross-linked polyvinylphenol (PVP) dielectrics¹⁷⁷, and the nanocomposite containing barium titanate (BaTiO_3) nanoparticles¹⁶⁷ under the same electric field. Recently, A. Maliakal et al. reported nanocomposite films containing TiO_2 -polystyrene core-shell nanorods as dielectrics for bottom-gate pentacene TFTs^{26, 186}. The nanocomposite dielectrics show a dielectric constant of about 8.2 and a dielectric-breakdown field of about $2 \times 10^4 \text{ V/cm}$, which is significantly lower than that ($> 1 \times 10^6 \text{ V/cm}$) of OA- TiO_2 nanoparticle films in this work. The OA- TiO_2 nanoparticles were directly solution-processed as dielectric layers, neglecting the multi-step nanocomposite synthesis. The higher electrical strength observed here probably arises from the excellent homogeneity of the nanoparticle films. The dielectric constant of nanoparticle films in this work is relatively lower; this is probably due to the low volume ratio of inorganic TiO_2 nanoparticles component, which is only 0.138 as

estimated, and the relative low dielectric constant of oleic acid ($k = 2.3$)¹⁸⁸.

Figure 4.5 (a) Dielectric constant vs frequency and (b) current density vs voltage/electric field plots of OA-TiO₂ nanoparticle dielectrics (650 nm) sandwiched between ITO glass substrates and silver top-contacts

4.5 Organic TFTs characterization

Top-gate PQT-12 TFTs and bottom-gate pentacene TFTs with the OA-TiO₂ films as the gate dielectric layer were fabricated according to the procedures

described in *Chapter 3.2.2* and *3.2.3*, respectively. A 680-nm-thick OA-TiO₂ nanoparticle film ($C_i \approx 7 \text{ nF/cm}^2$) was used in the device fabrication. Figure 4.6(a) shows the output characteristic ($I_D - V_D$) of a representative PQT-12 TFT. The corresponding plots of transfer curves and $|I_D|^{1/2}$ versus V_G characteristic are shown in Fig. 4.6(b). The PQT-12 TFTs with OA-TiO₂ nanoparticle dielectrics exhibit an average device mobility of $0.05 \pm 0.02 \text{ cm}^2/\text{Vs}$, with a current on/off ratio of about 10^4 - 10^5 and a threshold voltage of about -3.6 V. The breakdown voltage of the device is -40 V. When the PQT-12 TFTs are operated under $V_D = -3 \text{ V}$ and $V_G \leq -10 \text{ V}$, the devices exhibit a device mobility of about $0.02 \text{ cm}^2/\text{Vs}$ with an on/off ratio of about 10^4 , suggesting an operational capability of PQT-12 TFTs under low driven voltage.

The output characteristics and transfer curves of the pentacene TFTs are shown in Figures 4.6(c) and 4.6(d). The devices exhibit an average device mobility of $0.2 \pm 0.05 \text{ cm}^2/\text{Vs}$. The on/off ratio is about 2×10^3 , V_{th} is around -24 V and the device breakdown voltage is -60V. The higher breakdown voltages obtained from bottom-gate pentacene TFTs than those from top-gate PQT-12 TFTs are attributed to fewer defects in the OA-TiO₂ films when deposited onto smooth ITO surfaces rather than organic semiconductor surfaces. The device performance of pentacene TFTs with OA-TiO₂ nanoparticle dielectrics is comparable to those of high-performance pentacene TFTs with the same device configuration using SiO₂ dielectrics^{192, 193}. The results indicate that the OA-TiO₂ nanoparticles can be easily solution-processed as thin-film dielectrics for high performance organic TFTs of top-gate or bottom-gate configuration.

Figure 4.6 (a) and (c) Output characteristics, (b) and (d) transfer curves, and $V_G - (-I_D)^{1/2}$ characteristic of PQT-12 and pentacene TFTs with OA-TiO₂ nanoparticle dielectric films of about 680 nm.

4.6 Conclusions

In summary, oleic acid-capped titanium dioxide (OA-TiO₂) core-shell nanoparticles have been successfully developed as promising solution-processable dielectrics for organic thin-film transistors (TFTs). The

nanoparticle dielectrics exhibit stable dielectric constant (5.0-5.3) in the frequency region of 10^2 - 10^6 Hz and low leakage current density for organic TFTs. Using the OA-TiO₂ nanoparticle dielectrics, organic TFTs of top-gate and bottom-gate configuration are successfully demonstrated with PQT-12 and pentacene semiconductors. This research provides a facile method (single-step synthesis) to produce high- k solution-processable inorganic nanoparticles and demonstrates that such nanoparticles could be promising materials for dielectric application in organic TFTs.

Chapter 5 Organic-Capped Barium Titanate and Strontium Titanate Nanoparticles for Dielectric Applications in Low-Voltage Organic Thin-Film Transistors ^a

5.1 Introduction

Low-voltage transistor operation is of great interest for low-power applications, portable electronics, and bio/chemical detection in aqueous media. My previous work has demonstrated that homogeneous dielectric films can be obtained from spin-coating oleic-acid stabilized TiO₂ nanoparticles suspension¹⁹⁴. However, the dielectric constant achieved is still modest (k of about 5.3) and the pentacene based transistors with this dielectric material exhibited a mobility of ~ 0.2 cm²/Vs and an on/off ratio of $\sim 2 \times 10^3$ operated under -45 V. Inorganic colloidal nanoparticles that can be directly solution-processed into high- k inorganic films, without need for sophisticated nanocomposite synthesis or blending with polymer materials, are urgently needed to fully exploit the simplicity and economic advantages associated with organic TFTs ¹⁹⁴.

In this work, a series of solution-processable oleic acid (OA) capped barium titanate (OA-BaTiO₃) and strontium titanate (OA-SrTiO₃) nanoparticles with high dielectric constants ($k = 4.1 - 9.3$) were synthesized for low-voltage organic thin-film transistors (TFTs). With excellent dispersibility in organic solvent, the nanoparticle suspensions are directly solution-processed as the dielectric component in organic TFTs by spin-coating on various substrates. The

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suitability of nanoparticle dielectrics for organic TFTs using pentacene in bottom-gate configuration and poly(3,3''-didodecylquaterthiophene) in top-gate configuration is also demonstrated. The bottom-gate pentacene TFTs exhibit outstanding device performance with field-effect mobilities, μ , in the range of 2–4 cm²/Vs and on/off ratio of $\sim 10^4$ at low gate voltage. Top-gate Poly(3,3''-didodecylquaterthiophene) TFTs also show high device performance with μ of 0.05–0.1 cm²/Vs and on/off ratios of 10^3 – 10^4 . The organic TFTs show surprisingly low-voltage driven function and theoretical consideration of the trapped state density at the semiconductor/dielectric interfaces is suggested to account for the low-voltage function of organic TFTs.

5.2 Materials synthesis

5.2.1 Synthesis of barium titanium glycolate and strontium titanium glycolate

Barium titanium glycolate ($\text{BaTi}(\text{C}_2\text{H}_4\text{O}_2)_3 \cdot 4\text{C}_2\text{H}_6\text{O}_2 \cdot \text{H}_2\text{O}$) (BTG) and strontium titanium glycolate ($\text{SrTi}(\text{C}_2\text{H}_4\text{O}_2)_3 \cdot 4\text{C}_2\text{H}_6\text{O}_2 \cdot \text{H}_2\text{O}$) (STG) as the precursors were synthesized referring to the literature ¹⁹⁵. In a typical preparation, 78 mmol barium oxide (Aldrich, 97%) or strontium oxide (Aldrich, 99.9%) fine powder was added into 60 mL ethylene glycol in a 250 mL round-bottom flask. The reaction mixture was vigorously stirred until the added fine powder was dissolved and then diluted with 80 mL 2-propanol. Titanium isopropoxide (18 mL) was then added into the reaction mixture with vigorous stirring for 1h. The product precipitated from the solution was collected by centrifugation, washed with 2-propanol, and dried in vacuum for further use.

5.2.2 Synthesis of OA capped barium titanate and strontium titanate

In a 250 mL three-neck flask, a mixture of 50 mL diphenyl ether (Aldrich, 99%) and 5-45 mmol oleic acid was dried at 120 °C for 1h under argon atmosphere with vigorous stirring. After the mixture was cooled down to 100 °C, 5 mmol barium titanate glycolate or strontium titanate glycolate was added to the mixture under vigorous stirring until the added precursors was dissolved. 1.8 g 30% hydrogen peroxide in water (Aldrich) was then injected into the mixture slowly (vigorous exothermic reaction). The mixture was maintained in a closed system at 100 °C and stirred under a mild reflux with water for 48 h in an inverse micelle condition. After the reaction mixture was cooled down to room temperature, the product was readily precipitated upon addition of an excess of ethanol to the reaction mixture. The resulting precipitate was collected by centrifugation and repeatedly washed with ethanol to remove the surfactant residuals. The ethanol-wetted precipitate was dispersed into toluene by sonication. By low-speed centrifugation (5000 rpm) for 5 min, non-dispersed precipitate was isolated from the suspension to give clear light-yellow suspensions of OA-capped nanoparticles, which were stored at room temperature for characterizations and device fabrication.

5.3 Materials characterization analysis

Figures 5.1(a) and 5.1(b), respectively, show the digital photographs of a series of dispersions of OA-BaTiO₃ and OA-SrTiO₃ nanoparticles, which were synthesized with [OA]/[P] (P, precursor) molar ratios ranging from 1 to 9. For all [OA]/[P] ratios, the as-synthesized nanoparticles of different [OA]/[P] ratio are well-dispersed in toluene, giving clear nanoparticle suspensions. As shown

respectively in Figures 5.1(a) and 5.1(b), the OA-BaTiO₃ and OA-SrTiO₃ suspensions (~ 40 mg/ml) darken from left to right with increasing [OA]/[P] ratio which can be explained by the number of particles per unit volume of the suspension, expressed by $n = \frac{c}{\frac{4}{3}\pi r^3 \times \rho}$, where n is the number of particles

per unit volume of the suspension, c is the concentration of the nanoparticles in the suspension, and r and ρ are the radius and density of the as-synthesized nanoparticles, respectively. The concentrations of the nanoparticles in all dispersions are controlled at ~ 40 mg/ml. When [OA]/[P] ratio increases, the radius (r) and density (ρ) of the OA-capped nanoparticles become smaller leading to higher number (n increases) of particles per unit volume; as a result, the dispersion is darker. The nanoparticle suspensions in toluene have been stable for more than one year, with negligible precipitation at the time of writing of this thesis.

Figures 5.1(c) and 5.1(d) show transmission electron microscopy (TEM) images of representative OA-BaTiO₃ and OA-SrTiO₃ nanoparticles of [OA]/[P] = 1 with core sizes of 3-5 nm and high-resolution TEM lattice images of single OA-BaTiO₃ and OA-SrTiO₃ nanoparticles of [OA]/[P] = 1 (Figure 5.1(c) and 5.1(d) inserts). As the [OA]/[P] ratio increases to 9, the nanoparticle core size decreases gradually to 2-3 nm. The size distribution of the as-synthesized nanoparticles was analyzed with a Zetasizer Nano system (Malvern, UK). The sample concentration was ~ 2 mg/ml in toluene and measurements were made at room temperature in sealed quartz cuvettes. The results are shown in Figures 5.1(e) and 5.1(f). The inserts give the mean size of the nanoparticles with respect

to $[OA]/[P]$ ratios. The sizes measured for the samples are significantly larger than that determined by TEM. The difference can be interpreted as the thickness of the oleic-acid capping layer. The results also reveal that the nanoparticle size decreases with increased $[OA]/[P]$ ratio.

Figure 5.1 Digital images of clear (a) OA-BaTiO₃ and (b) OA-SrTiO₃ nanoparticle suspensions in toluene (~ 40 mg/g), and from left to right in (a) and (b), the nanoparticle formulations are $[OA]/[P] = 1, 2, 3, 5,$ and 9 . Representative TEM images of (c) OA-BaTiO₃ ($[OA]/[P] = 1$) and (d) OA-SrTiO₃ ($[OA]/[P] = 1$) nanoparticles, and the scale bars are 10 nm. The insets in (c) and (d) are high-resolution TEM images of a representative single OA-BaTiO₃ and OA-SrTiO₃ nanoparticles, respectively, and the insert scale bars are 2 nm. Size distribution of (e) OA-BaTiO₃ and (f) OA-SrTiO₃ with different $[OA]/[P]$ ratios. The insets in (e) and (f) are mean size of OA-BaTiO₃ and OA-SrTiO₃ nanoparticles vs. $[OA]/[P]$ ratios, respectively.

The EDS results confirm the presence of Ba or Sr, Ti, and O in the corresponding OA-BaTiO₃ and OA-SrTiO₃ ensembles of all [OA]/[P] ratios.

Figure 5.2 gives the EDS spectra of OA-BaTiO₃ and OA-SrTiO₃ with [OA]/[P] = 1. The element Pt in the spectra is from the coating for SEM.

Figure 5.2 EDS spectra of (a) OA-BaTiO₃ ([OA]/[P] = 1) and (b) OA-SrTiO₃ ([OA]/[P] = 1) nanoparticle films.

The organic surfactant, OA, is critical for good dispersion of the inorganic nanoparticles in organic solvent. The surface immobilization of OA onto inorganic core nanoparticle surfaces is confirmed with Fourier transform infrared (FT-IR) spectroscopy. Attenuated total reflectance Fourier transform

infrared (ATR-FT-IR) spectra were collected with a Nicolet 5700 spectrometer equipped with a Smart Orbit diamond ATR unit (Thermo, USA) at a resolution of 1 cm^{-1} . Figure 5.3 presents representative FT-IR spectra of OA-BaTiO₃ and OA-SrTiO₃ nanoparticles and a comparison spectrum of OA. Both OA-capped nanoparticle samples (Figures 5.3(a) and 5.3(b)) and the OA sample (Figure 5.3(c)) exhibit strong absorption peaks at 2923 and 2853 cm^{-1} which are due to the intense anti-symmetric and symmetric C-H stretching vibrations, respectively, of the -CH₂- groups¹⁹⁶. A weak absorption band at 3010 cm^{-1} , attributable to the olefinic C-H stretching vibration¹⁹⁶, is also observable in Figures 5.3(a)-5.3(c). It suggests that the carbon-carbon double bond in OA could be preserved during nanoparticle synthesis, although cross-linking or polymerization of OA cannot be ruled out. The free C=O stretching vibration leads to a strong absorption peak at 1709 cm^{-1} in the OA spectrum. This feature is absent from the spectra of OA-capped nanoparticles. In contrast, two characteristic absorption peaks at 1545 and 1403 cm^{-1} are apparent in the nanoparticle spectra, due to the COO⁻ anti-symmetric and symmetric stretching vibrations, respectively, of carboxylate anions complexed with surface metal centers of the nanoparticles^{187, 197}. The frequency difference ($\Delta\nu \approx 142\text{ cm}^{-1}$) between the two absorption bands suggests that the binding mode of carboxylate on the inorganic core nanoparticle surfaces may be in the chelating bidentate form¹⁹⁸. These results suggest that the stabilizing OA ligands are effectively bonded to the surfaces of the inorganic core nanoparticles and that free OA is nearly absent in the nanoparticle suspensions.

Figure 5.3 FT-IR spectra of representative (a) OA-BaTiO₃ ([OA]/[P] = 1), (b) OA-SrTiO₃ ([OA]/[P] = 1) nanoparticles, and (c) oleic-acid (OA).

Given the excellent dispersion of OA-BaTiO₃ and OA-SrTiO₃ nanoparticles in toluene, homogenous and transparent nanoparticle films (280-350 nm in thickness) are easily deposited, via spin-coating under ambient condition, on indium tin oxide (ITO) coated glass, ITO coated polyethylene terephthalate (PET), and silicon wafer substrates. The spin-coated films are dried in a vacuum at room temperature. The surfaces of the resulting nanoparticle films are smooth. As shown in Figure 5.4, films made with OA-BaTiO₃ and OA-SrTiO₃ nanoparticles formulated with [OA]/[P] = 1 have root-mean-square roughness (R_{rms}) values of about 7 nm over a 25 μm^2 area, determined with AFM. Films made with nanoparticles of higher [OA]/[P] molar ratios show reduced surface roughness, with R_{rms} values in the range of 0.5-4 nm. The size of the

nanoparticles should be controlled around 10 nm in order to get a smooth nanoparticles film. In addition, the resulting film surfaces have characteristics of low surface energy with water contact angles of 95-103 °.

Figure 5.4 Atomic force microscopy (AFM) images of (a) OA-BaTiO₃ of [OA]/[P] = 1, (b) OA-BaTiO₃ of [OA]/[P] = 3, (c) OA-SrTiO₃ of [OA]/[P] = 1, and (d) OA-SrTiO₃ of [OA]/[P] = 9 thin films spin-coated on silicon substrates. The X, Y, and Z scales are 5, 5, and 0.5 μ m, respectively. (e) and (f) are rms vs. [OA]/[P] plots for OA-BaTiO₃ and OA-SrTiO₃ films, respectively.

5.4 Electrical properties of nanoparticles films

5.4.1 Effects of [OA]/[P] ratio on k

To evaluate their dielectric properties, homogeneous OA-BaTiO₃ and OA-SrTiO₃ nanoparticle films are sandwiched between ITO coated glass substrates (bottom-electrodes) and vacuum-deposited aluminium (Al) films (top-electrodes) to form capacitors. The dependence of the dielectric constant on the volume fraction of the nanoparticles is investigated. Figure 5.5 shows plots of the dielectric constant (obtained at 100 Hz) and inorganic volume fraction vs. [OA]/[P] molar ratio for these films. For the lowest molar ratio nanoparticle formulation, [OA]/[P] = 1, the OA-BaTiO₃ and OA-SrTiO₃ films exhibit dielectric constants of 9.3 and 7.1, respectively, which are 4- and 3-times that of bulk OA ($k = 2.3$)¹⁸⁸. The inorganic BaTiO₃ and SrTiO₃ volume fractions are estimated to be 0.16 and 0.18 for OA-BaTiO₃ and OA-SrTiO₃ nanoparticles with [OA]/[P] = 1 respectively, assuming the densities of pure BaTiO₃, SrTiO₃, and OA to be 6.08, 4.81, and 0.89 g/cm³ respectively. When the [OA]/[P] ratio is increased in the synthesis, the inorganic BaTiO₃ and SrTiO₃ volume fractions decreases gradually to about 0.14 and 0.09 at [OA]/[P] = 9, respectively. The decrease of inorganic volume fraction with increased [OA]/[P] ratio is probably due to the fact that the size of the synthesized inorganic cores decreases with increased [OA]/[P] ratio, which have previously been used to control the size of inorganic nanoparticles in nanoparticle synthesis^{187, 198}. As the [OA]/[P] molar ratio increases from 1 to 9, the k values of OA-BaTiO₃ and OA-SrTiO₃ nanoparticle films decreases significantly from 9.3 to 4.1 and 7.1 to 4.5, respectively. The trend of k variation with [OA]/[P] molar ratio is consistent with the inorganic volume fraction variation. This phenomenon is consistent

with other reports of nanocomposite materials^{26, 186}, for which k decreases as the volume fraction of the inorganic component decreases. This demonstrates that the dielectric constant of the nanoparticles can be tuned by varying the geometric parameters as a result of varying the surfactant/precursor ratios in the synthesis.

Figure 5.5 Dielectric constant (k) and inorganic volume fraction (f) vs. $[OA]/[P]$ molar ratio plots. The k values are determined at a frequency of 100 Hz.

5.4.2 Capacitance vs. frequency

The frequency-voltage dependent capacitance of the nanoparticle films is further studied. Figures 5.6(a) and 5.6(b) present the unit area capacitance of the OA-BaTiO₃ and OA-SrTiO₃ nanoparticle thin films (280-350 nm in thickness) of different $[OA]/[P]$ ratios vs. frequencies, respectively. The capacitances of the

nanoparticle films decrease slightly when the frequency increases from 10^2 to 10^6 Hz. The capacitance is constant over the DC bias sweep range (± 10 V) and there is no polarization behaviour observed for both OA-BaTiO₃ and OA-SrTiO₃ nanoparticle films as shown in Figure 5.6(c).

Figure 5.6 Capacitive characteristics of OA-BaTiO₃ and OA-SrTiO₃ nanoparticle films. Capacitance vs. frequency plots of (a) OA-BaTiO₃ and (b) OA-SrTiO₃ nanoparticle films. (c) is capacitance vs. voltage plot of nanoparticle films from OA-BaTiO₃ ([OA]/[P] = 1) and OA-SrTiO₃ ([OA]/[P] = 1) under 10^3 Hz.

5.4.3 Insulating properties

On the other hand, the OA-BaTiO₃ and OA-SrTiO₃ dielectric films (except for the OA-BaTiO₃ film with [OA]/[P] = 9) exhibit good insulating properties with low leakage current densities and reasonable electrical strength. As shown in Figures 5.7(a) and 5.7(b), the as-spin-coated nanoparticle films generally give electric current densities of 10^{-5} – 10^{-7} A/cm² at electric fields in the range of 0.5–1 MV/cm, and electrical strength > 1 MV/cm. The single exception to this is the OA-BaTiO₃ nanoparticle film with [OA]/[P] = 9, which has a relatively low electrical strength, ≤ 0.3 MV/cm.

Figure 5.7 Current densities vs. electric field plots of (a) OA-BaTiO₃ and (b) OA-SrTiO₃ nanoparticle dielectric films.

5.5 Organic TFTs performance

Bottom- and top-gate organic TFTs were fabricated with nanoparticle dielectric thin films ($k \geq 5$) to assess the utility of these materials as device components. Figures 5.8(b) and 5.8(d) show representative transfer characteristics and $|I_D|^{1/2}$ vs. V_G plots of bottom-gate pentacene TFTs with OA-BaTiO₃ and OA-SrTiO₃ dielectrics. The OA-BaTiO₃ thin film of approximately 330 nm in thickness was made with the [OA]/[P] = 1 formulation ($k \sim 9.3$) and the OA-SrTiO₃ thin film of approximately 340 nm was made with the [OA]/[P] = 2 formulation ($k \sim 5.9$). As shown in Figure 5.8(b), the pentacene TFTs with OA-BaTiO₃ dielectrics on the PET substrates exhibit a field-effect mobility of about 3.5 cm²/Vs, with an on/off ratio of about 2×10^4 under low operating voltages of $V_D = V_G = -2$ V. The subthreshold swing (S) of the device is about 106 mV/dec and the breakdown voltage is -15V. With OA-SrTiO₃ dielectrics, the bottom-gate pentacene device, in Figures 5.8(c) and 5.8(d), is operated with higher voltages of $V_D = V_G = -10$ V. It gives field-effect mobility of ~ 3.0 cm²/Vs and on/off ratios of $\sim 2 \times 10^4$ with a subthreshold swing of ~ 517 mV/dec and breakdown voltage of -30V. The pentacene TFTs with the selected OA-BaTiO₃ and OA-SrTiO₃ dielectrics on plastic substrates typically show field-effect mobilities of 2.0 - 3.5 cm²/Vs under operating voltages of $|V_D| = |V_G| \leq 10$ V.

Figure 5.8 Output characteristics, transfer characteristics, and $|I_D|^{1/2}$ vs. V_G plots of bottom-gate pentacene TFTs based on ((a) and (b)) OA-BaTiO₃ ([OA]/[P] = 1, $k = 9.3$, and channel width/length ($W/L = 13$) and ((c) and (d)) OA-SrTiO₃ ([OA]/[P] = 2, $k = 5.9$, and $W/L = 45$) nanoparticle dielectrics. The sweep rates in transfer characteristics are 0.55 and 0.45 V/s for pentacene/ OA-BaTiO₃ and pentacene/OA-SrTiO₃ devices, respectively. The background image in (b) is a photograph of the pentacene TFTs with OA-BaTiO₃ dielectric demonstrating its mechanical flexibility.

For comparison, pentacene TFTs were fabricated with the same device configuration, but using 100 nm SiO₂ dielectrics on heavily-doped n-type Si wafers. The SiO₂ surfaces were pretreated with octyltrichlorosilane (OTS-8). Similar to the OA-capped nanoparticle film, OTS-8-treated SiO₂ (OTS-SiO₂) surfaces have low surface energy (water contact angle of $\sim 98^\circ$) and alkyl-chains at the top-most surfaces, which may induce similar molecular arrangement and orientation of vapor-deposited pentacene on the respective substrates¹¹². The pentacene devices with OTS-SiO₂ dielectrics show an average field-effect mobility of only $\sim 0.38 \text{ cm}^2/\text{Vs}$ with an on-off ratio of about 10^3 under drain and gate voltages of 35 V (Figure 5.9). The pentacene/OA-BaTiO₃ TFT has performance metrics far superior to those of the comparison device using OTS-SiO₂ dielectrics. Compared to the pentacene/OTS-SiO₂ device, the pentacene/OA-BaTiO₃ device in Figure 5.8(b) has almost one-order of magnitude higher field-effect mobility, and this is obtained under operating conditions of more than one-order of magnitude lower gate-field (E) and charge per unit area (Q) at the semiconductor/dielectric interface. It is also notable that the pentacene/OA-BaTiO₃ TFTs show low-voltage function with high device performance similar to the behaviour of organic TFTs with ultra-thin ($< 50 \text{ nm}$) cross-linked polymer or polymer blend dielectrics^{13, 153, 160, 199, 200}, despite the much lower capacitance values ($15\text{-}25 \text{ nF}/\text{cm}^2$) of the nanoparticle dielectric films compared to those ($200\text{-}400 \text{ nF}/\text{cm}^2$) of ultra-thin cross-linked polymer or polymer blend dielectrics.

Figure 5.9 Performance of bottom-gate pentacene TFTs with OTS-SiO₂ dielectric films (100 nm).

The X-ray diffraction (XRD) spectra of the pentacene films on OA-BaTiO₃ and OA-SrTiO₃ films were recorded at room temperature on a Bruker AXS X-ray diffractometer (USA) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) with a θ - 2θ scan configuration. Figure 5.10 shows that both diffraction patterns exhibit very strong (001) diffraction peaks with d_{100} spacing of 1.52 nm, indicating the thin-film conformation of the pentacene films on the surfaces of OA-capped nanoparticles films^{176, 201}. Figure 5.11 shows the surface morphology of pentacene on OA-BaTiO₃ surface and OTS-SiO₂ surface. The pentacene crystalline grains are smaller on OA-BaTiO₃ than on OTS-SiO₂. The formation of larger grains in a bulk film, with the attendant lower areal density of grain boundaries, may benefit the charge transport in semiconductor films⁷. The AFM results suggest that the higher device performance on OA-BaTiO₃ dielectric than on OTS-SiO₂ dielectric may not be due to the morphology of the pentacene thin

films.

Figure 5.10 X-ray diffraction (XRD) patterns of pentacene films (35nm) vacuum-deposited on (a) OA-BaTiO₃ and (b) OA-SrTiO₃ film surfaces, respectively.

Figure 5.11 AFM images of pentacene films of 35 nm deposited on (a) OA-BaTiO₃ and (b) OTS-SiO₂ substrates, respectively.

These phenomena can be understood through consideration of the trapped state

density at semiconductor/dielectric interfaces in a trapping model²⁰², which has been successfully applied to describe pentacene-based TFT behavior^{60, 203, 204}. The trapped state density can be estimated with the relation $N_{trap} = C_{in}|V_{on}-V_{th}|/q$, where N_{trap} , C_{in} , V_{on} , V_{th} and q are the trapped state densities, insulator capacitance per unit area, turn-on voltage, threshold voltage, and the electron charge, respectively^{60, 205}. Table 5.1 lists the estimated trapped state density for TFTs with the semiconductor/dielectric interfaces studied here. The pentacene TFTs with OTS-SiO₂ dielectrics has a trapped state density of about $1.34 \times 10^{12} / \text{cm}^2$, which is consistent with values for OTS-treated SiO₂ dielectrics reported in the literature⁶⁰. For the pentacene device with OA-BaTiO₃ (Figure 5.8(b)), the trapped state density is estimated to be $3.4 \times 10^{10} / \text{cm}^2$, nearly 40 times lower than that of TFTs with OTS-SiO₂. Much lower (10 fold less) trapped state density ($1.16 \times 10^{11} / \text{cm}^2$) is also estimated for the device with OA-SrTiO₃ dielectric (Figure 5.8(d)).

Another model ($N_{trap}^{max} \approx C_{in}[qS \log(e)/k_B T - I]/q$, where N_{trap}^{max} , S , k_B , T , and e are the maximum trapped state density, subthreshold swing, Boltzmann's constant, temperature, and the base of the natural logarithms, respectively¹⁹²) leads to similar inferences that the devices with OA-BaTiO₃ and OA-SrTiO₃ dielectrics in Figures 5.8(b) and 5.8(d) have trapped state densities more than one-order of magnitude lower than that of devices with OTS-SiO₂ dielectrics. Fundamentally, less numbers of charge carriers are needed to fill the localized states in the devices with low trapped densities; it is reasonable that the pentacene TFTs with nanoparticle dielectrics could be operated under low gate voltage with high device performance. These results suggest that OA-BaTiO₃

and OA-SrTiO₃ dielectrics may match pentacene films in forming excellent semiconductor/dielectric interfaces with low trapped state density.

Low-voltage TFTs are also demonstrated in top-gate PQT-12 with OA-BaTiO₃ (~ 290 nm, [OA]/[P] = 2, $k \sim 6.8$) and OA-SrTiO₃ (~ 330 nm, [OA]/[P] = 1, $k \sim 7.1$) nanoparticle dielectrics. Figures 5.12(b) and 5.12(d) are representative transfer characteristics and $|I_D|^{1/2}$ vs. V_G plots of the top-gate PQT-12 TFTs. The devices give field-effect mobility of ~ 0.06 and on/off ratio of about 10^4 for OA-BaTiO₃ and mobility of ~ 0.1 cm²/Vs and on/off ratio of about 10^3 for OA-SrTiO₃ under low-voltage operation ($V_D = V_G = -3$ V) and current modulation of more than 10^3 for gate voltage variations of about 4 V. Low trapped state density values ($< 1 \times 10^{11}$ /cm², Table 5.1) are also suggested for these PQT-12 TFTs.

Table 5.1 Performance of bottom-gate pentacene and top-gate PQT-12 TFTs, as well as bottom-gated pentacene TFTs with 100 nm OTS-SiO₂ on n⁺⁺ Si substrates for comparison.

Device	Interface	μ (cm ² /Vs)	C (nF/cm ²)	V_{th} (V)	V_{on} (V)	N_{trap} ($\times 10^{11}$ /cm ²)
Bottom-gate Pentacene TFTs	Pentacene/OTS-SiO ₂	~ 0.38	34	-13.5	-7.2	13.4
	Pentacene/OA-BaTiO ₃	~ 3.5	25	-0.87	-0.65	0.34
	Pentacene/OA-SrTiO ₃	~ 3.0	15.4	-6.12	-4.91	1.16
Top-gate PQT-12 TFTs	PQT-12/OA-BaTiO ₃	~ 0.06	21	0.23	0.92	0.90
	PQT-12/OA-SrTiO ₃	~ 0.1	20	0.32	0.59	0.46

Figure 5.12 Output characteristics, transfer characteristics, and $|ID|^{1/2}$ vs. V_G plots of top-gate PQT-12 TFTs with ((a) and (b)) OA-BaTiO₃ ([OA]/[P] = 2, $k = 6.8$, and $W/L = 1800$) and ((c) and (d)) OA-SrTiO₃ ([OA]/[P] = 1, $k = 7.1$ and $W/L = 1800$) nanoparticle dielectrics. The sweep rate in transfer characteristics are 0.75 and 0.90 V/s for PQT-12/ OA-BaTiO₃ and PQT-12/OA-SrTiO₃ devices, respectively.

Hysteresis and its dependence on sweep rate are well known in most organic TFTs. Figures 5.8(b), Figure 5.8(d), Figure 5.12(b), and Figure 5.12(d) show the transfer characteristics of devices using OA-capped nanoparticle dielectrics with

forward (positive to negative) and reverse (negative to positive) sweeps. Considerable hysteresis is observed for pentacene and PQT-12 TFTs based on OA-capped nanoparticle dielectrics with sweep rates in the range of 0.45 – 0.90 V/s. The hysteresis is probably associated with the trapping of electrons injected from the gate ^{157, 206}. As shown in Figure 5.13, the hysteresis for TFTs with OA-capped nanoparticle dielectric is substantially suppressed by slowing the sweep rate from 0.45 V/s to 0.08 V/s. Hysteresis has been widely observed in organic TFTs using polymeric high- k dielectric materials, such as poly(vinyl alcohol) ^{24, 207}, poly(4-vinyl phenol) ¹⁵⁵, polymer electrolyte (polyethylene oxide containing $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$) ¹⁶⁵, as well as sol-gel silica dielectrics ²⁰⁸. The trapping of injected electrons from the gate and insufficient ion migration velocity accounts for the hysteresis of these dielectrics. For polymer electrolytes and sol-gel silica dielectrics, a sweep rate of about 0.01 V/s is necessary to suppress or eliminate hysteresis behaviour ^{165, 208}. Much reduced hysteresis has been demonstrated in pentacene TFTs with inorganic oxide dielectrics from the anodization of Ta (Ta_2O_5) and Ti (TiO_2) ^{209, 210}. The device mobilities of these low-voltage pentacene TFTs were less than $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, although these dielectric surfaces had been treated by a silane to reduce the surface trapping centres for charge carriers. It has been demonstrated that inserting a blocking oxide layer between the gate and crosslinked PVP or PVA dielectrics is effective to diminish the charge injection from the gate, leading to noticeably reduced hysteresis in the pentacene based transistors performance ^{24, 155}.

Figure 5.13 Reduction of sweep rate significantly reduces hysteresis of a PQT-12 based TFT with OA-capped nanoparticle dielectric.

5.6 Conclusions

In summary, a series of soluble OA-BaTiO₃ and OA-SrTiO₃ nanoparticles were synthesized and applied as dielectrics in low-voltage organic TFTs. The nanoparticles are well-dispersed in organic solvent, which facilitates low-temperature solution-phase processing and fabrication of low-cost flexible organic TFTs on plastic substrates. High-performance low-voltage organic TFTs in bottom- and top-gate device configurations are demonstrated using high-*k* nanoparticle films as dielectric layers. Pentacene TFTs had mobilities of 2.0–3.5 cm²/Vs with on-off ratios of about 10⁴ under < 10 V and PQT-12 TFTs had mobilities of 0.05–0.1 cm²/Vs with on-off ratios of about 10³–10⁴ under 3 V. This work provides a facile method for synthesis of high-*k* solution-processed

perovskite nanoparticle-based dielectrics. This research also suggests that trapped state density at the semiconductor/dielectric interface may be a critical factor in enabling low-voltage operation of organic TFTs.

Chapter 6 Organic-Capped Hybrid-Nanoparticles for Dielectric Applications in High-Performance Organic TFTs ^a

6.1 Introduction

Nowadays it is recognized that the semiconductor/dielectric pairs are essential for organic TFT device performance since the charge transport is confined in several monolayers of semiconductor molecules near the semiconductor/dielectric interfaces ^{116, 211-213}. Various dielectric materials, such as polymers ^{160, 214, 215}, inorganic high-*k* materials ^{22, 210}, and inorganic/polymer blends ^{156, 186, 216, 217} have been incorporated into semiconductor/dielectric pairs for organic TFTs; however, it still remains a great challenge for the dielectric materials to meet the requirements of solution-processability, flexibility, low-voltage operation (≤ 10 V), and high charge mobility ($\mu \geq 1$ cm²/Vs).

To fulfill the above requirements of dielectric materials for organic TFTs, dielectric materials oleic-acid (OA) capped barium strontium titanate (BST) core-shell hybrid nanoparticle was designed and synthesized according to the following principles (as illustrated in Figure 6.1): I) high-*k* inorganic nanoparticle cores can provide high-*k* property, which facilitates charge accumulation in the channel, II) organic surfactants, such as oleic acid, capping the surfaces of inorganic nanoparticle cores can enable well-dispersion of the inorganic nanoparticles in organic solvents and improve solution-processability of nanoparticles suspension, III) effective functional groups of organic

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surfactants can stabilize the inorganic nanoparticles and avoid nanoparticle aggregation, and IV) chemical inertness of surfactant end groups (pointing out from inorganic nanoparticle surfaces) may deter possible electrochemical interactions and minimize trapped state density at the semiconductor/dielectric interfaces.

Figure 6.1 Schematic illustration of core-shell hybrid nanoparticles for dielectric application in organic TFTs.

OA-capped BST (OA-BST) nanoparticles with a molar formula $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ in which x varies from 0.1, 0.2, and so on, till 0.9 molar%, are synthesized and characterized by high-resolution transmission electron microscopy (HRTEM) measurements. The nanoparticles are further well dispersed in organic solvent to fabricate uniform thin films by spin coating. The dielectric constants of the films with different $\text{Ba}^{2+}/\text{Sr}^{2+}$ molar ratio of the nanoparticles are characterized.

Bottom-gate pentacene and top-gate poly(3,3''-didodecylquaterthiophene) (PQT-12) TFTs are fabricated using these nanoparticle dielectric films to investigate the electric transport performance. The gate voltage-dependent mobility of these devices is studied to explore the possible mechanism of the electrical transport at the dielectric/semiconductor interface.

6.2 Synthesis of OA-capped barium strontium titanate (BST) nanoparticles

The barium titanium glycolate and strontium titanium glycolate of overall 5 mmol with systematically adjusted $\text{Ba}^{2+}/\text{Sr}^{2+}$ molar ratios were transferred into a dry mixture of 50 mL diphenyl ether and 5 mmol stabilizing agent OA at 100 °C under argon atmosphere. A 1.8 g 30 wt% hydrogen peroxide solution was injected slowly into the solution (vigorous exothermic reaction) to avoid possible splashing hazard caused by boiling. The solution was maintained in a closed system and stirred at 100 °C over 48 h to promote further hydrolysis and formation of the OA-capped nanoparticles. After the reaction, the solution was cooled down to room temperature and the nanoparticles were readily precipitated with excess ethanol. The precipitate was washed 6 times with ethanol and the absorbed OA removed by centrifuge.

Figure 6.2 Synthesis of OA-BST nanoparticles

6.3 Material characterizations analysis and electrical properties

Figure 6.3(a) shows the HRTEM image of OA- $\text{Ba}_{0.1}\text{Sr}_{0.9}\text{TiO}_3$ nanoparticles and the inset is the corresponding selected-area electron diffraction (SAED) pattern. Lattice structures can be observed and identified from the cores of the nanoparticles. The size of the nanoparticles is 5-8 nm. From zeta potential measurements, the size of OA- $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ($x = 0.1, 0.2, \dots, 0.9$) nanoparticles is in a range of 6-10 nm, which is very close to the theoretical value in terms of the nanoparticle structure shown in Figure 6.3(b). Figure 6.3(c) shows that very clear nanoparticle dispersions in non-polar organic solvents (such as toluene) are produced. The dispersions are stable for more than one year without gelatinization or agglomeration. However, if the nanoparticles are dried, it would be hard for them to re-disperse into the organic solvent as discussed in the previous work¹⁹⁴. Thin films (300-400 nm in thickness) obtained from spin-coating the nanoparticle suspensions are homogenous and smooth, with a

surface root-mean square roughness (R_{rms}) ranging from 3.5-5.5 nm as shown in Figure 6.4. The surfaces are hydrophobic with water contact angles of 93-105 °.

Figure 6.3 (a) HRTEM image of OA- $\text{Ba}_{0.1}\text{Sr}_{0.9}\text{TiO}_3$ nanoparticles and inset is the corresponding selected-area electron diffraction (SAED) pattern. (b) OA- $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ nanoparticle size distribution from zeta potential measurements and inset is the mean size for different nanoparticles. (c) Digital images of clear OA- $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ nanoparticle suspensions in toluene (~ 40 mg/g), where $x = 0.1, 0.2$, and so on, till 0.9 from left to right.

Figure 6.4 AFM images and surface roughness of OA-Ba_xSr_{1-x}TiO₃ (x = 0.1, 0.2, ..., 0.9) nanoparticle films deposited on silicon substrates.

It is known that the capacitance of a capacitor is more prominent at lower frequencies. The typical frequencies for characterizing the gate dielectric materials in organic transistors are in a range of 10^2 - 10^6 Hz^{199, 218}. The capacitance of the MIM capacitors was measured with DC sweep voltage of ± 10 V at fixed frequencies in the range of 10^2 - 10^6 Hz (Figure 6.5(a)), indicating that the capacitance only decreases slightly with an increase in the frequency. Figure 6.5(b) gives the relation of capacitance vs. voltage for the OA-Ba_{0.1}Sr_{0.9}TiO₃ film. No polarization behavior is observed for all OA-BST films. This is different from the highly crystallized perovskite oxides that normally possess ferroelectric properties²¹⁹. The dielectric constant k values at 100 Hz calculated

for different OA-BST nanoparticles are shown in Figure 6.5(c), indicating that the OA-Ba_{0.1}Sr_{0.9}TiO₃ has a dielectric constant of ~ 9.6 . With increasing Ba²⁺ loading while reducing Sr²⁺ contents in the compound, the k drops to 6.1 for OA-Ba_{0.2}Sr_{0.8}TiO₃ and then to 5.6 for OA-Ba_{0.3}Sr_{0.7}TiO₃. Films with OA-Ba_{0.4}Sr_{0.6}TiO₃ to OA-Ba_{0.9}Sr_{0.1}TiO₃ exhibit dielectric constants in the range of 5 to 6. This result suggests that a small difference in the Ba/Sr molar ratio of the nanoparticles at low values ranging from 0.1 to 0.4 can result in significant k changes of nanoparticle films. The spin-coated OA-BST nanoparticle films (350-450 nm) show leakage current densities in the range of 10^{-8} - 10^{-6} Acm⁻² when the electric field across the capacitor is 0.7-1 MVcm⁻¹ (Figure 6.5(d)).

Figure 6.5 Electrical characteristics of spin-coated OA-BST nanoparticle films. (a) Plots of capacitance vs. frequency in the range of 10²-10⁶ Hz for OA-BST films (380-510 nm). (b) Plots of capacitance vs. voltage for OA-Ba_{0.1}Sr_{0.9}TiO₃ film (~ 410 nm) at different frequencies. (c) Comparison of k (measured at 10² Hz) for different OA-BST nanoparticles. (d) Current densities vs. electric field plots.

6.4 Organic TFTs characterization

6.4.1 Low-voltage operation

Figures 6.6(a) and 6.6(b) give a set of representative transfer curves for both forward and reverse gate bias scans (scan rate: ~ 0.7 V/s) and the $|I_D|^{1/2}$ vs. V_G plots for forward condition of bottom-gate pentacene TFTs and top-gate PQT-12 TFTs, respectively. Both bottom- and top-gate TFTs have the selected OA-BST

nanoparticles as gate dielectrics. The OA-BST based pentacene TFTs exhibit field-effect mobilities of $1 - 2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with on/off ratios of 10^3 at low operating voltages of $V_D = V_G = -2.5 \text{ V}$. The breakdown voltages of the devices are -12V . PQT-12 TFTs operated under higher voltage $V_D = V_G = -5 \text{ V}$ have field-effect mobilities of $0.01 - 0.1 \text{ cm}^2/\text{V}^{-1}\text{s}^{-1}$, on/off ratios of 10^3 and breakdown voltages of -20V . The corresponding output characteristics of the devices in Figure 6.6(c) clearly demonstrate the typical linear/saturation behavior.

Hysteresis of I_D - V_G is observed with a positive shift in V_{th} ($\Delta V_{th} = 0.6\text{-}0.9 \text{ V}$). Hysteresis is often observed in organic TFTs with high- k polymeric dielectric materials, such as poly(vinyl alcohol) ²⁴, polymer electrolyte ¹⁶⁵, as well as sol-gel silica dielectrics ²⁰⁸, which is probably due to the trapping of electrons injected from the gate ²⁰⁶. The hysteresis can be suppressed effectively by lowering the scan rate ^{21, 208}.

Figure 6.6 Representative transfer characteristics and $|I_D|^{1/2}$ vs. V_G plots of organic TFTs with OA-BST nanoparticle films as gate dielectrics. (a) Bottom-gate pentacene TFTs, channel width/length (W/L) = 11, 45, 13, and 20 for sample OA- $\text{Ba}_{0.1}\text{Sr}_{0.9}\text{TiO}_3$ (21 nFcm^{-2}), OA- $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ (9.8 nFcm^{-2}), OA- $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (16.1 nFcm^{-2}), and OA- $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ (16.8 nFcm^{-2}), respectively. (b) Top-gate PQT-12 TFTs, channel width/length (W/L) = 900 for OA- $\text{Ba}_{0.1}\text{Sr}_{0.9}\text{TiO}_3$ (21.8 nFcm^{-2}), OA- $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ (10.1 nFcm^{-2}), OA- $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (12.8 nFcm^{-2}), and OA- $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (12.7 nFcm^{-2}), respectively. (c) Output characteristics of the selected devices in: (a) the bottom-gate pentacene TFT, gate voltage increases from 0 to -4 V in steps of -1 V, and (b) the top-gate PQT-12 TFT, gate voltage increases from 0 to -6.4 V in steps of -1.6 V, respectively.

The morphology and crystallinity of the pentacene films on the respective substrates were examined using AFM and XRD. Figure 6.7 shows the AFM images with the section height profiles of the corresponding pentacene films grown on OTS-SiO₂ and OA-BST nanoparticle films. The pentacene films show similar structures with the grain size around 160 nm on SiO₂ substrate and 120-140 nm on OA-BST nanoparticle films.

As can be seen from the XRD patterns shown in Figure 6.8, all the pentacene films exhibit regularly spaced diffraction peaks, indicating that the pentacene molecules are packed orderly and oriented along the long axis vertical to the plane of the dielectric surface. Both strong (001') and weak (001) diffraction peaks, representing the "thin-film phase" and "bulk phase" respectively, are observed, indicating that the pentacene films contain multiple phases but the thin-film conformation is dominating. The d001' spacing is calculated to be 1.5 nm and (1.46 ± 0.01) nm for pentacene films grown on OTS-SiO₂ and OA-BST nanoparticle films, respectively.

Figure 6.7 AFM images of pentacene films of 40 nm deposited on (a) OTS-SiO₂, (b) OA-Ba_{0.1}Sr_{0.9}TiO₃, (c) OA-Ba_{0.3}Sr_{0.7}TiO₃, and (d) OA-Ba_{0.8}Sr_{0.2}TiO₃ substrates, respectively.

Figure 6.8 X-ray diffraction (XRD) patterns of pentacene films (40 nm) vacuum-deposited on (a) OTS-SiO₂, (b) OA-Ba_{0.1}Sr_{0.9}TiO₃, (c) OA-Ba_{0.3}Sr_{0.7}TiO₃, and (d) OA-Ba_{0.8}Sr_{0.2}TiO₃ substrates, respectively.

6.4.2 Gate dependent mobility

The device mobility is known to be gate-voltage dependent in organic TFTs^{17, 116}. The dependency of the mobility of both pentacene and PQT-12 TFTs with OA-BST dielectrics on different gate voltages was studied in order to gain an insight into the fundamentals of organic TFT mobility. For comparison, the investigations of this dependency were also conducted on devices with OTS-SiO₂ dielectrics. To minimize the gate stress effect, 5 min rest was allowed between two consecutive measurements for each device. Normalized mobility is used to obtain a clearer picture of how the mobility varied with V_G for different

devices by neglecting the mobility difference caused by the device variation. It is defined as the actual mobility at corresponding V_G over the saturated (maximum) mobility obtained from the same device. The mobilities vs. gate voltage dependencies are plotted in Figures 6.9(a) and 6.9(b) for pentacene TFTs and PQT-12 TFTs, respectively. The saturated mobilities together with other characteristics of the devices are listed in Table 6.1.

The pentacene/OA-BST TFTs all demonstrated a mobility plateau (1-3.5 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) at much lower driven voltages of around -5 V compared to the pentacene/OTS-SiO₂ TFTs, where the mobility plateau is not observed even at the gate voltage of -50 V and the highest mobility is only $\sim 0.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. It can be seen that the OA-BST based pentacene TFTs exhibit superior performance over the pentacene TFTs on OTS-SiO₂. The mobility plateau occurs at a driven voltage of around -12 V for top-gate PQT-12/OA-BST TFTs (0.03-0.04 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$), while taking place at a high operating voltage (-55 V) for bottom-gate PQT-12/OTS-SiO₂ TFTs ($\sim 0.09 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). The lower device μ_{max} of the top-gate PQT-12 TFTs may be related to the high surface roughness of the PQT-12 films²²⁰. Rougher semiconductor surfaces and possible moisture adsorption at the interface during fabrication in an atmospheric environment could degrade the device mobility^{44, 146, 221}.

Figure 6.9 Gate dependent mobility of the organic TFTs with OA-BST nanoparticle films as gate dielectrics. (a) Bottom-gate pentacene TFTs, channel width/length (W/L) = 24, 11, 13, and 20 for sample OTS- SiO_2 , OA- $\text{Ba}_{0.1}\text{Sr}_{0.9}\text{TiO}_3$, OA- $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ and OA- $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ respectively. (b) Top-gate PQT-12 TFTs, channel width/length (W/L) = 90, 180, 90, and 90 for sample OTS- SiO_2 , OA- $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$, OA- $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$, and OA- $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$ respectively.

Table 6.1 Device performance of bottom-gate pentacene and top-gate PQT-12 TFTs.

Organic semiconductor	Dielectric	Dielectric thickness (nm)	$\mu_{\max}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	V_G (V)	C_i (nFcm^{-2})	V_{th} (V)	S (Vdec^{-1})	$N_{trap}^{\max}$ (cm^{-2})
Pentacene	OTS-SiO ₂	100	0.54	-50	34	-9.8	0.778	2.06×10^{12}
	Ba _{0.1} Sr _{0.9} TiO ₃	420	2.7	-5	21	-2.5	0.232	3.88×10^{11}
	Ba _{0.5} Sr _{0.5} TiO ₃	330	3.42	-5	16.1	-1.14	0.216	2.7×10^{11}
	Ba _{0.8} Sr _{0.2} TiO ₃	330	1.38	-3	16.8	-0.8	0.277	3.9×10^{11}
PQT-12	OTS-SiO ₂	100	0.089	-55	34	-9	0.989	3.37×10^{12}
	Ba _{0.3} Sr _{0.7} TiO ₃	505	0.04	-12	10.1	2.8	2.05	2.15×10^{12}
	Ba _{0.5} Sr _{0.5} TiO ₃	420	0.03	-13	12.8	-0.73	1.26	1.64×10^{12}
	Ba _{0.8} Sr _{0.2} TiO ₃	495	0.04	-12	11.3	0.4	1.08	1.23×10^{12}

The dependency of field-effect mobility on gate voltage can be described by the multiple trapping and release (MTR) model^{8, 17}, which has been generally used to describe the charge transport behavior in organic TFTs. This model assumes that there is a large density of trapped states (localized states) in the forbidden band gap of the semiconductors. As gate voltage increases, the deepest trapped states are filled first as the Fermi level approaches the delocalized band edge (such as the highest occupied molecular orbital (HOMO) in pentacene). The threshold voltage is reached when all deep trapped states are filled and the local Fermi level overlaps the energy level that thermally activated carriers can occupy. This condition could be described as the equilibrium state between trapped and mobile carriers. If all the trapped states are filled at a higher voltage,

any subsequently injected carriers are free to move into the delocalized band and the field-effect mobility will be independent of the gate voltage.

According to this model, there are two important factors significantly influencing the channel mobility: one is the number of charge carriers induced, which can be denoted by the unit area carrier charge (Q_s), and the other is the number of trapped states to be filled. Usually, the first factor is of more concern since higher k insulators could achieve sufficient number of charge carriers to fill all the trapped states at lower gate voltages⁸. Interestingly in the experimental results, as shown in Table 6.1, the OA-BST dielectrics have a unit area capacitance of 10-21 nFcm⁻², which is much lower than those of the high- k materials (80 nm Al₂O₃¹¹⁶: 90nFcm⁻², 270 nm TiO₂/PVP/PαMS²¹⁶: 34.4 nFcm⁻², 250 nm ZrO₂-OTMS²²²: ~ 68 nFcm⁻², HfO₂²¹⁸: 0.69 μFcm⁻²) and even SiO₂ (100 nm: ~ 34 nFcm⁻²). The gate-voltage-accumulated charge carriers known to be confined very closely to the semiconductor/insulator interfaces should be much smaller in pentacene/OA-BST systems than those dielectric systems reported for low-voltage high-performance devices^{116, 216, 218, 222}. However, the mobility of the pentacene/OA-BST TFTs is almost one order higher under less than one tenth of the gate field (E). It is very likely that the trapped state density at the semiconductor/insulator interfaces plays the key role in the high-mobility and low-voltage performance of OA-BST based pentacene devices.

It is known that the trapped states at semiconductor/dielectric interfaces are attributable to interfacial chemical defects, such as Si-OH species, which can influence the charge transport by trapping/scattering charge carriers at the

interfaces^{8,53,54}. These trapped states are critical to organic transistors, since the charge transport channel is believed to be within the several semiconductor monolayers adjacent to the dielectric surfaces. The maximum interface trapped state density can be estimated using $N_{trap}^{max} = \frac{C_i}{q} \left[\frac{qS \log e}{k_B T} - 1 \right]$ ^{205, 223} where k_B , T , e , q , S and C_i are Boltzmann's constant, temperature, the base of the natural logarithm, the electron charge, the reciprocal subthreshold swing, and the dielectric capacitance per unit area, respectively. The calculated maximum trapped densities of the devices at the maximum mobility condition are also summarized in Table 6.1.

Clearly, S and threshold voltages (V_{th}) for the pentacene/OA-BST devices are much better than those for the pentacene/OTS-SiO₂ devices. The pentacene/OA-BST devices have maximum trap densities in the range of $2.7\text{-}3.9 \times 10^{11} \text{ cm}^{-2}$, almost one order lower than those for OTS-SiO₂ devices ($2.06 \times 10^{12} \text{ cm}^{-2}$). The top-gate PQT-12/OA-BST devices exhibit higher maximum trap densities in the range of $1\text{-}2 \times 10^{12} \text{ cm}^{-2}$, which could be the reason for the lower μ_{max} and higher subthreshold swings obtained on these devices as discussed above. However, these values are still less than those of bottom-gate PQT-12/OTS-SiO₂ devices ($3 \times 10^{12} \text{ cm}^{-2}$). It is expected that a lower concentration of trapped states in the gap would require less number of compensating charge carriers and low-voltage operation with high mobility could be achieved on the OA-BST dielectrics based organic TFTs. In comparison to cross-linked PVP dielectric films with a similar capacitance per unit area ($10\text{-}20 \text{ nFcm}^{-2}$)¹⁷⁷ used in organic TFTs, the OA-BST dielectrics have the advantage of enabling much lower-voltage device operation. In addition, the

dielectrics developed in this work do not need the post-annealing for cross-linking required by the polymer based ones. These results suggest that the trapped state density at semiconductor/dielectric interfaces is important for enabling low-voltage high performance organic TFTs and should also be taken into consideration when designing the proper dielectric materials for organic TFTs.

In Figures 6.10(a)-6.10(j) the Fourier transform infrared (FT-IR) spectra of OA and OA-Ba_xSr_{1-x}TiO₃ nanoparticles for all samples display two strong peaks at 2922 and 2853 cm⁻¹, which are attributed to the intense antisymmetric and symmetric C-H stretching vibrations¹⁹⁶ of the -CH₂- groups in the hydrocarbon moiety. The weak absorption band at 3006 cm⁻¹, attributable to the olefinic C-H stretching vibration¹⁹⁷, is also clearly observable. The strong adsorption peak at 1708 cm⁻¹ shown in Figure 6.10(a), associated with free C=O stretching vibration, is absent in the spectra for OA-capped nanoparticles (Figures 6.10(b)-6.10(j)). While two strong characteristic bands centered at 1550 and 1404 cm⁻¹ appear in Figures 6.10(b)-6.10(j). These two absorption bands can be characteristically attributed to the COO⁻ antisymmetric and symmetric stretching vibrations of carboxylate anions complexed with the metal surface^{197, 198}. The results suggest that OA as the stabilizing ligands have effectively bound to the surfaces of the inorganic nanoparticle cores and nearly no free OA is present in the nanoparticle suspensions.

It has been shown that alkyl chains on modified dielectric surfaces can substantially reduce the interfacial trap density^{32, 148, 192}, which is principally attributed to interfacial chemical functionalities/species such as Si-OH for SiO₂

dielectrics, in conjunction with adsorbed H_2O and adventitious carbon contamination^{224, 225}. It has been found that silanol groups cannot be completely removed by such self-assembled alkyl layers²²⁶. On the other hand, for the OA-BST nanoparticles, the alkoxide precursors are readily reactive with carboxylic acids to produce OA surfactant-capped BST nanoparticles, thus resulting in significantly lower density of metal-OH species on the nanoparticle surfaces^{187, 227}. In addition, the near absence of $-\text{COOH}$ groups on the nanoparticle surfaces could hinder possible electrochemical reactions and minimize the trapped state density at the semiconductor/dielectric interface when the charge carriers are transported⁹².

Figure 6.10 FT-IR spectra of representative (a) oleic-acid (OA), (b)-(j) OA- $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ nanoparticles where $x = 0.1, 0.2$, and so on, till 0.9 , respectively.

6.5 Conclusions

In summary, solution-processable OA-Ba_xSr_{1-x}TiO₃ (OA-BST) nanoparticles with x varying from 0.1, 0.2, and so on, till 0.9 molar%, were synthesized for dielectric application in low-voltage organic TFTs. The dielectric constant of the spin-on OA-BST films vary in a range from 5 to 9.6 with different Ba/Sr molar ratios in the nanoparticles. Bottom-gate pentacene and top-gate PQT-12 TFTs with the OA-BST films as gate insulators were fabricated. The studies on the gate dependence of mobility in the devices show that very high device mobilities (1.4-3.4 cm²V⁻¹s⁻¹) can be obtained at low operating voltages (< -5 V) for pentacene TFTs. Low-operating voltages (~ -12 V) are also demonstrated on PQT-12 TFTs with the mobility of ~ 0.1 cm²V⁻¹s⁻¹ and on/off ratios of 10³-10⁴. This prominent device performance on the OA-BST nanoparticle dielectrics is found to be attributable to the very low trap densities (< 3.9 × 10¹¹ cm⁻²) at the semiconductor/insulator interface, which is more than one-order lower than that obtained in the OTS- SiO₂ devices.

Chapter 7 General conclusion and future work

7.1 General conclusion

In this dissertation, the advancement of organic thin-film transistors in recent years has been reviewed thoroughly. The details including basic concepts of organic thin-film transistors (organic TFTs), organic materials developed, and issues in organic TFTs are presented and the device performance based on different gate dielectrics is compared and discussed. It is still a challenging issue to manufacture low-voltage high-performance organic TFTs at low cost. The development of new insulating materials and solution-processing capabilities will greatly aid in the realization of commercial electronics driven by organic transistors.

The feasibility of the organic/inorganic nanoparticles with a solution process for dielectric applications in organic TFTs has been studied and investigated in this project. Oleic acid-capped titanium dioxide (OA-TiO₂) nanoparticles were synthesized through solution-phase chemical routes, and a solution process was used to form homogeneous dielectric films for organic TFTs of top-gate and bottom-gate configurations. These nanoparticle films show a dielectric constant of about 5.3 and a low leakage current density of 3×10^{-8} A/cm² under an electric field of 1 MV/cm. Poly(3,3'-didodecylquaterthiophene) (PQT-12) and pentacene TFTs with the OA-TiO₂ dielectrics exhibited mobilities of 0.05 ± 0.02 and 0.2 ± 0.05 cm²V⁻¹s⁻¹, respectively, with on/off ratios of 10³-10⁵. This material is a new kind of material used in dielectrics formed through a solution process in printable organic TFTs.

To obtain better device performance at low-voltage operation, the dielectric constant (k) of the dielectric nanoparticles is improved by employing higher k inorganic core materials, such as barium titanate (BTO), strontium titanate (STO), and barium strontium titanate (BST) hybrid, and oleic acid acting as the capping layer to form core-shell structured nanoparticles. The dielectric constant k of the OA-capped BTO (OA-BTO) and OA-capped STO (OA-STO) nanoparticle films is tunable in the range of 4.1 to 9.3 by altering the molar ratio of oleic-acid surfactant to synthesis precursor. For the OA-capped BST (OA-BST) nanoparticle films, the k values vary in the range of 5 to 9.6 according to different Ba/Sr molar ratio of the nanoparticles. Low-voltage modulated high-performance organic TFTs are fabricated using the high- k nanoparticle films as the dielectric components. Flexible bottom-gate pentacene TFTs exhibit outstanding device performance with the field-effect mobility, μ , in the range of $2.0 - 3.5 \text{ cm}^2/\text{Vs}$ and on/off ratios of about 10^4 at low gate voltage. Top-gate PQT-12 TFTs also show high device performance with μ of $0.05 - 0.1 \text{ cm}^2/\text{Vs}$ and on/off ratios of $10^3 - 10^4$.

The performance of the devices composed of different types of nanoparticles dielectrics studied in this thesis is listed in Table 7.1.

Table 7.1 Device performance of bottom-gate pentacene and top-gate PQT-12 TFTs.

Organic semiconductor	Dielectric	Dielectric thickness (nm)	$\mu_{\max}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	V_G (V)	C_i (nFcm^{-2})	V_{th} (V)	S (Vdec^{-1})	$N_{trap}^{\max}$ (cm^{-2})
Pentacene	OA-TiO ₂	680	0.2	-45	7	-24	1.44	5×10^{11}
	OA-BaTiO ₃ [OA]/[P] = 1	330	3.5	-2	24.9	-0.87	0.106	6×10^{11}
	OA-SrTiO ₃ [OA]/[P] = 2	340	3	-10	15.4	-6.12	0.517	5.6×10^{11}
	Ba _{0.8} Sr _{0.2} TiO ₃	330	1.38	-3	16.8	-0.8	0.277	3.9×10^{11}
PQT-12	OA-TiO ₂	650	0.05	-30	7	-3.6	3.14	2×10^{12}
	OA-BaTiO ₃ [OA]/[P] = 2	290	0.06	-3	21	0.23	0.5	1.6×10^{12}
	OA-SrTiO ₃ [OA]/[P] = 1	330	0.1	-3	19	0.32	0.6	1.9×10^{11}
	Ba _{0.8} Sr _{0.2} TiO ₃	495	0.04	-12	11.3	0.4	1.08	1.23×10^{12}

Theoretical studies on the gate voltage-dependent mobility of the devices show that only a low gate electric field is needed to achieve the saturated mobility for the OA-BST based pentacene organic TFTs. This low-voltage operation of the transistors could be attributed to a low density of trapped states at the interfaces between the organic semiconductors and the nanoparticle dielectric films.

This research provides a universal strategy to design high- k dielectric nanoparticles for low-voltage high-performance organic TFTs. A series of promising dielectric materials for fabrication of superior organic TFTs through a solution process are synthesized and fundamentally suggest that a low trapped state density at the semiconductor/dielectric interface may be an important factor in achieving low-voltage modulation in organic TFTs.

In summary, this work not only investigates nanoengineering approaches to synthesize solution-processable nanostructured dielectric materials for performance enhanced organic TFTs, but also explores the possible mechanism of the charge transport at the dielectric/semiconductor interface, which has great significance in organic electronics physics. The success of this work leads to a universal approach for developing high- k nanoparticle dielectrics that may have potential applications in printable electronic circuits.

7.2 Recommendations for future work

Organic thin-film transistors (TFTs) are of great interest for applications in low-cost and disposable electronics. To enable low-cost manufacturing of flexible organic TFTs, most of the research work has focused on solution-processable organic semiconductors and dielectrics for low cost

manufacture. In this work, the dielectric constant of the organic-capped nanoparticles can be tuned by varying the inorganic core components or by controlling the size of the nanoparticle during synthesis with different surfactant/precursor molar ratios. The effects of the capping layer on the dielectric properties of the core-shell nanoparticles could also be an interesting topic to investigate in order to gain a better understanding of the mechanism of the dielectric nanoparticles for high performance. In future work, oleic acid can be replaced by the phosphate of varying lengths of alkyl chains through a ligand exchange process. Hence, the thickness of the capping layer can be adjusted and their impact on the device performance can be studied.

On the other hand, bifunctional molecules can be an option for use as a surfactant to inorganic nanoparticles. The molecule can have a carboxyl group at one end, and a hydroxyl group at the other end. The carboxyl groups may bind to the nanoparticle surfaces and the hydroxyl groups will be used for cross-linking purposes. The surfactant may be introduced to inorganic nanoparticle surfaces during synthesis or via a surface-ligand exchange process after synthesis. After the cross-linking, the thickness of nanoparticle dielectric films would be further reduced to nanoscale dimensions (~ 100 nm) and this will lower the power consumption of devices. In addition, the dielectric films are also expected to be highly resistant to organic solvent as well as being able to adhere robustly to the substrates, which could be compatible with solution-deposition of organic semiconductors.

Furthermore, printable electronic circuits based on organic transistors with the developed nanoparticle dielectrics can be demonstrated in a number of practical

applications.

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