Materials for Printed Organic Thin-Film Transistors

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Abstract

Printed organic thin-film transistors (OTFTs) have received great interest as potentially low-cost alternative to silicon technology for application in large-area, flexible, and ultra-low-cost electronics. The development of printable materials including semiconductor, conductor, and gate dielectric are essential to enable this technology transition. The Xerox efforts in design and development of thiophene-based polymeric semiconductors, metal nanoparticles as printable conductors, and a dual-layer robust gate dielectric materials for all solution-processed high-performance OTFTs will be reviewed in this paper.

Introduction

OTFTs have received profound interest in recent years for their potential as low-cost alternatives to α-silicon transistors for large-area and flexible electronics. The economic advantage of OTFTs stems from low-cost fabrication, using common solution-based deposition techniques such as spin coating and ink jet printing. Although significant progresses have been made in the last decade, challenges and issues in materials, printing processes, and device integration remain and need to be addressed. Among these challenges, material readiness is the key to enable practical applications. In this article we will discuss Xerox Research Centre of Canada's efforts in materials design and development for all-printed OTFTs.

Semiconductor development

One of the critical materials for OTFTs is the channel semiconductor which dictates the transistor performance. Functionally capable organic semiconductors for low-cost OTFTs are rare as most semiconductors are either insoluble or very sensitive to air under ambient conditions. Material insolubility precludes the use of liquid patterning and deposition while air sensitivity requires manufacturing in inert atmospheres - both of these restrictive requirements invariably lead to increased cost, thereby may nullify the fundamental economic advantage of OTFTs. One exemplary semiconducting polymer is regioregular poly(3-hexyl thiophene) (HT-P3HT). OTFTs fabricated in air with HT-P3HT generally exhibited much lower performance than those made in an inert atmosphere.[1,2] This was primarily due to the sensitivity of HT-P3HT to atmospheric oxygen. HT-P3HT forms a lamellar structural order in solid state with all its thienylene moieties along the polymer backbone in coplanarity by intermolecular alkyl side-chain interaction, which results in a highly delocalized π-conjugated system. This electron-rich, highly extended π-conjugated structure is susceptible to photoinduced oxidative doping by atmospheric oxygen. Nevertheless, the fact that HT-P3HT was capable of achieving high mobility and current on/off ratio in OTFTs made in an inert atmosphere or in the dark demonstrated its excellent intrinsic field-effect transistor (FET) properties. These results suggested that an approach to a high-performance polymer semiconductor was possible if appropriate structural features could be incorporated into regioregular polythiophene to control its π-conjugation for air stability without compromising FET properties.

Studies of regioregular polythiophenes at Xerox Research Centre of Canada are driven by the objective of achieving functionally capable OTFTs using simple solution processes under ambient conditions. This could be accomplished using a structurally engineered thiophene-based system through proper deployment of the following design principles: i) sufficiently long alkyl side chains to provide solution processability; ii) structural regularity to enable molecular self-organization from solution deposition; and iii) proper control of π-conjugation to achieve good air stability and high mobility. Of the three design principles, building stability against oxygen doping in a semiconductor structure without compromising its mobility is perhaps the most demanding.

Poly(3,3'''-dialkyl-quaterthiophene) (Figure 1, **1**), PQT, represents one of the regioregular polythiophene systems which satisfies the design principles.[3] PQT comprises two alky side-chains at C-3 and C-3''' positions of its repeating units, thus, enabling an alternating syn-trans distribution of side-chains along polymer backbone in the stretched-out coplanar conformation. With appropriate alkyl side-chain substitution, PQT would be expected to exhibit excellent solution processability as well as self-assembly ability. PQT has a repeating length of about 15.5 Å. Thus, the *d*-spacing of alkyl side-chains oriented in the same direction in the extended coplanar conformation of PQT is approximately 12 Å, since the side-chains are tilted at an angle of ~50° against the backbone. This 12 Å spacing together with a sufficiently long alkyl side-chain would enable PQT to self-assemble more efficiently through intermolecular side-chain interdigitation. The result would be a strongly held lamellar structure, enabling a long-range lamellar π-stacking order in the solid state. The unsubstituted thienylene moieties of PQT, which are expected to assume certain torsional deviations from coplanarity, would cut down on the π-conjugation to provide the needed photo-oxidative stability.

As a channel semiconductor in OTFTs, fabricated under ambient conditions and annealed at 120–140 ºC, PQT-12 (**1a**, R = *n*-dodecyl), it exhibited excellent FET properties. The output characteristics showed no noticeable contact resistance, very good saturation behavior, and clear saturation currents which were quadratic to the gate bias. The device switched on nicely at around 0 V with a subthreshold swing of 1.5 V dec^{-1}. Extracted mobility of up to 0.2 $cm^2 V^{-1} s^{-1}$ and on/off ratio of 10^6-10^8 were obtained.[3] The ability to achieve high mobility and extremely high on/off ratio in the OTFTs fabricated under ambient conditions affirmed the significantly greater environmental stability of PQT-12.

While the spin coated OTFTs with PQT-12 semiconductor provide high mobility and on/off ratio, those fabricated by inkjet printing show a greater variability in performance. This may be attributable to the tendency of PQT-12 solution to gel at room temperature, leading to non-uniformity in the jetted semiconductor layers. This gelling complication would be expected to present serious practical challenge to OTFT fabrication, and undermine a cost-effective manufacturing feasibility. Through our studies of solution behaviors of PQT, a PQT-12 nanoparticle material to circumvent this difficulty had been successfully developed.[4] PQT-12 nanoparticles, when dispersed in a suitable liquid medium, formed a stable nanoparticle ink which enabled printing of reproducible, functionally capable semiconductor layers for OTFTs. Active-matrix OTFT array backplanes for flat-panel displays using inkjet printed PQT-12 nanoparticles exhibited a FET mobility of 0.05 - 0.10 cm^2 V^{-1}s^{-1}, and a current on/off ratio of ~10^6, which were very similar to those of spin-coated devices.[5]

A simple approach to structurally optimizing polythiophene systems such as PQT to improve FET properties is to shorten the spacing between its pendant side-chains to strengthen intermolecular side-chain interdigitation. This could readily be accomplished through fusion of two adjacent thienylene moieties of PQT structure into thienothiophene to form poly(2,5-bis(2-thienyl)-thieno-thiophenes **2** and **3** (Figure 1). Poly(2,5-bis(3-dodecylthiophen-2-yl)-thieno[3,2-*b*]thiophene) **2a** (R = n-dodecyl) was reported to provide a FET mobility of 0.2–0.6 cm^2 V^{-1}.s^{-1} and a current on/off ratio of 10^6 when measured under a nitrogen atmosphere.[6] Latest studies provided a mobility of 0.3 cm^2 V^{-1}.s^{-1} even after annealing at 180 ºC in a nitrogen glove box.[7]

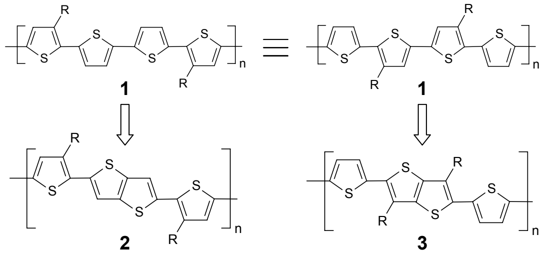

***Figure 1**. Fusion of two adjacent thienylene units in PQT to form poly(2,5-bis-(3-alkylthiophen-2-yl)-thieno[3,2-b]thiophene **2** and poly(2,5-bis(2-thienyl)-3,6-dialkylthieno[3,2-b]thiophene **3**.*

The other modified PQT with close side-chain spacing, poly(2,5-bis(2-thienyl)-3,6-dipentadecylthieno[3,2-*b*]thiophene) **3a** (PBT-15, R = n-pentadecyl), also provided about the same FET mobility.[8] The HOMO level of PBT-15, as determined by cyclic voltammetry, was 5.23 eV from vacuum, which was much lower than that of **2a** (5.1 eV). The low-lying HOMO together with a large band gap was expected to confer on PBT-15 greater air stability. DSC analysis of PBT-15 showed only a sharp endotherm at 148 °C on heating, arising from backbone melting. This was much lower than that of **2a** at 244-251°C.[6] This disparity arose from the alkyl side-chain placement on the thieno[3,2-*b*]thiophene instead of thienylene moieties, thus allowing its thienylene units substantial torsional deviations from coplanarity with the molecular plane in the solid state. This gave rise to a much lower backbone melting temperature than **2a**, thus enabling PBT-15 to be annealed at ~ 150°C - a temperature which is compatible with the dimensional stability and structural integrity of plastic substrates. The OTFT devices incorporating PBT-15 semiconductor annealed at ~ 150 °C showed excellent FET characteristics with the mobility up to 0.25 cm^{2}V^{-1}.s^{-1} and a current on/off ratio of 10^7.

Regioregular thiophene polymers such as PQT-12 and PBT-15 with well-spaced alkyl side-chain distributions self-organized into highly crystalline lamellar π-π stacking structural orders via intermolecular side-chain interdigitation upon thermal annealing followed by slow cooling. Although the temperatures are often sufficiently low to be compatible with plastic substrates, such steps are time consuming and it would be not desirable for high speed roll-to-roll manufacturing processes. As stated earlier, HT-P3HT self-assembled readily at room temperature into a highly crystalline state when deposited from solution without additional thermal assistance.[2] This was primarily made possible by the sterically crowded side-chain distribution along the backbone of HT-P3HT, which rendered ordering via intermolecular side-chain end-to-end interaction energetically favorable. Accordingly, it is envisaged that a plausible approach to achieving low-temperature structural ordering in a polymer semiconductor was to build a regioregular system with a crowded pendant side-chain distribution along the backbone. Such a system would be expected to self-assemble into crystalline states by adopting an end-to-end side-chain interaction much like that in HT-P3HT.

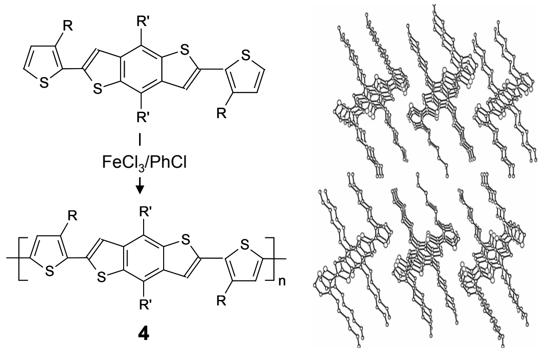

***Figure 2.** Synthesis of PBTBT, and single crystal structure of 4,8-dihexyl-2,6-bis(3-hexylthiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (monomer of **PBTBT-6**) showing end-to-end side-chain interaction.*

Benzodithiophene bithiophene copolymer (**4**), PBTBT, was selected to verify this hypothesis (Figure 2).[9] PBTBT possessed a crowded pendant alkyl side-chain distribution along the backbone, and would behave much like HT-P3HT in self-organization through end-to-end side-chain ordering as indicated in the single crystal structure. Meanwhile, it was thermally and oxidatively very stable, and its relatively large and planar molecular structure would help promote co-facial π-π stacking which is beneficial to charge transport. X-ray-diffraction measurement of a spin-coated thin film of PBTBT-6 (4a, R=R'=n-hexyl) showed only a strong primary diffraction pattern (100) at 2θ=5.6° (*d*-spacing of 16.1 Å), demonstrating a well-organized lamellar layered structure which was oriented normal to substrate. Highly organized nature of PBTBT-6 in a thin film was also manifested by the formation of extraordinarily large crystal domains of ~1 μm in width and > 1 μm in length as visualized in the AFM images.

In line with the ability to achieve high crystalline orders in solution-cast thin films via end-to-end side-chain interaction, PBTBT-6 exhibited excellent FET characteristics as channel semiconductors in OTFTs. Specifically, the output behaviors followed closely the metal oxide-semiconductor FET gradual channel model, showing very good saturation with no observable contact resistance. The transfer characteristics displayed a near-zero turn-on voltage, a small threshold voltage of -5.9 V, and a subthreshold slope of ~ 2 Vdec^{-1}. The extracted saturation mobility was up to ~ 0.25 $\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$ (on/off ratio: 10^5 - 10^6) without requiring post-deposition annealing.[9]

Printable conductor development

Conductor materials are equally important as they have decisive impacts on the OTFT characteristics. For proper functioning of an OTFT, the electrode materials need to meet certain electrical and materials requirements including: i) energetically compatible with the organic semiconductor layer to form an ohmic contact for efficient charge injection, ii) chemically inert towards the semiconductor and dielectric layers to avoid adverse effects due to chemical interactions, iii) electrically robust enough to withstand the electrical stress of high applied voltage and generated large current, iv) readily processable at a reasonably low temperature to enable the use of plastic substrate. Earlier work on printable conductors focused on organic materials such as polyaniline[10] and PEDOT/PSS.[11] In addition to their potential thermal and electrical instabilities, they have very low conductivity (<10 $\mathrm{S.cm}^{-1}$). In view of processability, conductivity, and electric stability, metal electrodes derived from solution-deposited precursor compositions would be ideal.

Gold nanoparticles were first studied as solution-printed, high-conductivity contacts for OTFTs.[12] Gold is particularly appealing as the electrode material for OTFTs since it forms excellent ohmic contact with most p-type organic semiconductors such as PQT-12. A dispersion of alkanethiol-functionalized gold nanoparticles in an organic solvent was used to print electrode features. The printed features were annealed at a relatively low temperature of 140°C to yield gold electrodes with conductivities (1.0×10^5 $\mathrm{S\ cm}^{-1}$) resembling those from vacuum deposition. OTFTs using the gold source and drain electrodes of this nature and the PQT-12 semiconductor exhibited no contact resistance, high FET mobility to 0.15 $\mathrm{cm}^2\mathrm{V}^{-1}\mathrm{s}^{-1}$, high current on/off ratio of 10^7, and a low threshold voltage (-6 V). All these results are in agreement with those observed for the devices using vacuum deposited gold electrodes.

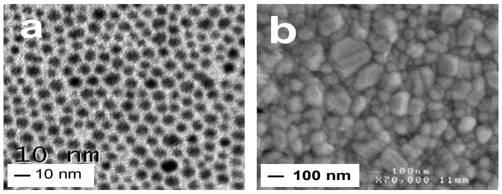

Figure 3. (a) TEM image of Ag nanoparticles on carbon grid. (b) SEM image of Ag film after annealing a spin cast Ag nanoparticle film at 160 °C for 30sec.[13]

The high cost of gold may negate its merits for low-cost printed OTFTs, particularly when used as interconnect or gate electrodes. Liquid-processed silver materials accordingly represent an appealing alternative. We developed a facile synthesis of stable silver nanoparticle having particle size of < 10 nm,[13] which involved reduction of silver acetate with substituted hydrazine(e.g. $\mathrm{PhNHNH_2}$) in the presence of 1-alkylamine (e.g. $\mathrm{C_{16}H_{33}NH_2}$) in refluxing toluene. Silver nanoparticles prepared in this manner were stable at room temperatures and were soluble in common organic solvents. Transmission electron microscopic (TEM) measurements showed that the particle size was < 10 nm (Figure 3a). UV-vis absorption spectrum showed a plasmon band at ~415 nm, indicative of metallic silver. When spin coated as thin films or printed as electronic features, these 1-alklamine-stablized silver nanoparticles disintegrated readily on heating at 120 – 160 °C to form conductive layers or elements with high conductivity of 2 – 4 × 10^4 $\mathrm{S\ cm}^{-1}$. OTFTs with printed silver source/drain electrodes of this nature gave high mobility of 0.05 – 0.08 $\mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$, high current on/off ratio of 10^6 – 10^7. These are similar to those of reference OTFTs with vacuum-deposited silver electrodes (mobility ~ 0.06 $\mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$; on/off ratio ~ 10^6 – 10^7).

The fact that polythiophene-based OTFTs with silver source/drain electrodes, both from vacuum deposition and silver nanoparticles above, afforded lower FET mobilities than OTFTs having gold electrode is a consequence of inefficient charge carrier injection caused by contact resistance often observed in OTFTs. Silver has a work function of 4.3 eV which is lower than HOMO level of most p-type organic semiconductor. To resolve the energetic mismatch of silver electrode with regioregular polythiophene semiconductors, a novel approach via *in-situ* modification of electrode/semiconductor interfacial properties using acid stabilized silver nanoparticles to enable ohmic contact formation was developed.[14] The rationale for this approach was based on the following considerations: i) Xerox's studies revealed that some stabilizers or their thermally transformed entities remained on the surface of annealed silver nanoparticle films since the latter exhibited larger advancing water contact angles than those from vacuum deposition; ii) regioregular polythiophene OTFTs with PEDOT/PSS-coated copper source/drain electrodes provided significantly higher mobility than those with untreated copper electrodes; and iii) if the stabilizer of silver nanoparticles had the ability to dope polythiophenes in much the same manner as PSS to PEDOT, then the annealed silver electrodes from these silver nanoparticles would be rendered energetically compatible with polythiophene semiconductors. Since carboxylic acids can readily dope polythiophenes and increase their conductivity, the carboxylic acid-stabilized silver nanoparticles such as those stabilized with oleic acid would represent ideal precursors for this purpose. Oleic acid-stabilized silver nanoparticles afforded highly conductive elements upon proper annealing. The annealed silver film exhibited a water contact angle of 112°, indicating a highly hydrophobic characteristic, in contrast to that of vacuum deposited silver film with a contact angle of 54°. OTFTs using source/drain electrodes prepared from these silver nanoparticles and PQT-12 semiconductor provided excellent field-effect characteristics (mobility of 0.12 $\mathrm{cm}_2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$ and on/off ratio of 10^7) which are in line with those of OTFTs with vacuum-deposited gold electrodes, despite a significant difference between the work function of silver and the HOMO level of PQT-12.

Gate dielectric materials development

Another key component for printed OTFTs is printable dielectric materials which play a decisive role in the functioning of

OTFT devices. Often requirements for dielectric layer differ depending on the type of semiconductor, since the interfacial interactions of semiconductor layer with gate dielectric are specific. For example, while the octyltrichlorosilane self-assembled monolayer on thermal SiO_2 surface enhances the semiconductor performance of PQT-12,[15] utilization of untreated native SiO_2 surface has led to reductions in mobility and on/off ratio by as much as up to three orders of magnitude.

An effective approach to a solution processed dielectric design to enable all-solution processed, high-performance OTFTs for flexible electronic applications was demonstrated. This is through a dual-layer dielectric structure comprising of a UV-crosslinked poly(4-vinyl phenol)-co-poly(methyl methacrylate) (PVP-PMMA) bottom layer for low gate leakage, and a thermally crosslinked polysiloxane top layer of for example poly(methyl silsesquioxane) (pMSSQ) for good compatibility with semiconductor.[16] The partially crosslinked pMSSQ which can be readily generated from methyltrialkoxysilane in an appropriate solvent is solution processable and its solution viscosity can be adjusted to suit various solution deposition techniques such as spin coating and inkjet printing. After deposition, the pMSSQ layer can then be fully crosslinked thermally at a temperature which is compatible with common commercial plastic substrates for fabrication of flexible integrated circuits.

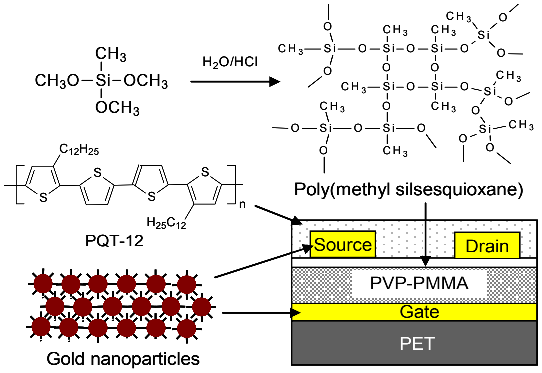

Figure 4. *Schematic depiction of formation of poly(methyl silsesquioxane) from methyltrimethoxysilane and its incorporation as a dielectric top layer in an all-solution processed OTFT device on PET.[16]*

The uncoated PVP-PMMA surface, with a high concentration of surface hydroxy groups, was hydrophilic and exhibited a water contact angle of ~78°. After treatment with pMSSQ, a hydrophobic surface with a water contact angle of ~ 98° was obtained. This contact angle is identical to the case when a hydrophilic native SiO_2 surface is modified with octyltrichlorosilane.

Finally**,** all-solution processed OTFTs on flexible substrate using the dual-layer gate dielectric, together with gold nanoparticles as electrodes and PQT-12 as semiconductor layer were demonstrated. The OTFT devices exhibited ideal FET behaviors--the output characteristics showed no observable contact resistance, very good saturation behavior, and clear saturation currents which were quadratic to gate bias. The devices showed a mobility of 0.15 $cm^2\ V^{-1}\ s^{-1}$ and current on/off ratio of 10^6, and exhibited small hysteresis effect. Compared to the devices with the non-modified UV-cured PVP-PMMA dielectrics, the improvements were phenomenal, with mobility by as much as 50 times and on/off ratio by 2 orders of magnitude. The performance characteristics of these OTFTs were very consistent and reproducible, with little transistor-to-transistor variations, which would be critically important for large-area electronic device fabrication where hundreds of thousands of transistors may be involved.

Summary

In conclusion, we have shown that Xerox designed and developed novel thiophene-based polymer semiconductors not only possess high field-effect mobility (0.1-0.4 $cm^2V^{-1}s^{-1}$) but also resolve two critical issues for roll-to-roll manufacturing OTFT devices: the air-stability for open air printing and simple processing without time-consuming thermal annealing. Xerox developed conductive materials based on metal nanoparticles could be processed at a plastic-compatible temperature to yield high conductivity of 10^4-10^5 S cm^{-1}. OTFTs with electrodes printed from the nanoparticles exhibited identical performance to their counterparts employing vacuum evaporated metal contacts. Together with Xerox developed robust and low-leakage dual-layer gate dielectric which also has a good compatibility with the semiconductors. The integration of these solution-processable materials into high-performing OTFTs on flexible substrate has been successfully demonstrated.

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