# Current Trends in Shrinking the Channel Length of Organic Transistors Down to the Nanoscale

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In this Review article, we highlighted current trends in shrinking the channel length of organic field-effect transistors (OFETs) down to the nanoscale in three systems where sophisticated device fabrication has been integrated into the development of different electrodes with nanoscale gaps. The design principle is the combination of molecular design freedom and flexible molecular self-assembly with state-of-the-art device fabrication to realize organic field effect nano-transistors where molecular materials themselves behave as pivotal elements. Three different types of nanoscale electrodes are used for OFETs: metals, single-walled carbon nanotubes (SWCNTs), and graphenes. These electrodes are made by e-beam lithography as well as other complementary methods (shadow deposition, underetching, nanoimprinting, rubber stamping, and microcontact printing).

# 1. Introduction

Rising technical demands of modern information society (such as high-capacity performance, high-speed capability, high degree of integration, and low-power consumption) lead to the pressing need to scale down the characteristic dimensions of conventional Si-based optoelectronic devices. The feature size used in Intel and IBM is presently as short as 45 nm, which is well within the "nano" range.<sup>[1]</sup> This trend is expected to continue in the next decade. The ultimate goal is the single molecule/atom transistor (Fig. 1).<sup>[2–5]</sup>

Organic/molecular electronic devices have attracted broad attention over the past decade because of their inherent advantages, such as solution-processibility, light-weight, the possibility of large-area processing, low cost, and their flex-ibility.<sup>[6-12]</sup> Organic field-effect transistors (OFETs), in particular

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### DOI: 10.1002/adma.200900504

REVIEW

as one of the fundamental building blocks of electronic circuits, are one of the most important interests. In general, most OFETs are built from organic thin films as the active layers. Through great efforts in the past decade the performance characteristics of some OFETs are now comparable to those of amorphous silicon TFTs.<sup>[13]</sup> However, the conduction mechanisms in these organic thin films are still poorly understood. The nature of charge conduction in thin films of organic semiconductors may differ from that in bulk organic materials, owing to their sensitivity to the molecular packing, film morphology, and temperature.  $^{\left[ 14-17\right] }$  These factors work together and greatly influence the quality of organic thin

films. Previous studies have shown that charge transport in OFETs is dominated by defects such as traps and grain boundaries.<sup>[18–20]</sup> The resulting performance characteristics of the devices are significantly limited.

To probe the intrinsic properties of organic thin films, devices with defect-free active layers would be necessary. Remarkable attempts have been made to build OTFTs on micro/nanometer-scale organic crystals,<sup>[21–36]</sup> bulk organic crystals,<sup>[9,11,12,37,38]</sup> and large single grains.<sup>[39]</sup> Organic single crystals possess essentially perfect molecular ordering and are virtually free of grain boundaries, at least by comparison to the analogous organic thin films. The effective use of organic single crystals can afford micro/nanometer-sized organic single-crystalline transistors. However, it is a big challenge to design molecules that self-assemble in a predictive manner via weak Van der Waals forces into ordered high-quality single crystals over a large area and in a controllable way.<sup>[10,22,23,38]</sup> More work directed toward improving the performance of these devices is needed. Another important approach to minimizing defect density is to shrink the active channels by aggressively scaling down OFETs. From the view of the practical application, this approach is more useful since device miniaturization could make tremendous contribution to the integration of future optoelectronic circuits.<sup>[3,4]</sup>

Shrinking device dimensions down to molecular length scales of organic semiconductors offers new, defect-free charge



Figure 1. Illustration of a single molecule/atom transistor.





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transport regimes. This may lead to larger carrier mobilities, increased device speed, and enhanced ON/OFF ratio. Scaling down OFETs implies the reduction of the device dimensions, both the thickness of the devices (the semiconductor and/or insulator layers) and their lateral dimension (source-drain distance). Several attempts to reduce the semiconductor/ insulator thickness have been made using Langmuir–Blodgett (LB) films<sup>[40–42]</sup> and self-assemblied monolayer (SAMs) or

multilayers.<sup>[43-61]</sup> These studies utilized sophisticated molecular assemblies that spontaneously happen when the substrates are dipped sequentially into solutions of the active components to form an active part of OFETs, either the gate dielectric  $^{[44-46,49,51,52,60,61]}$  or the semiconductor layer  $^{[54,56-58]}$  In the former case, OFETs built on self-assemblied gate dielectric layers can function at a very low-operating voltage (as small as 2 V). This approach is attractive because it increases the capacitive coupling through the gate insulators and thus reduces the power dissipation. The big challenge, however, is to build molecular gate dielectric layers that minimize gate leakage currents. In the latter case, the electrical characteristics of the devices do not allow clear parameter extraction (in most cases) due to the inherent problems in the devices (such as the contact resistance and poor intermolecular  $\pi$ - $\pi$  stacking between molecules in the selfassemblied layers). It is possible to realize large-area SAM field effect transistors (FETs) if densely packed SAMs can be achieved. This possibility has been well demonstrated by the recent work by Edsger C. P. Smits et al.<sup>[58]</sup>

In this Review article, we will describe the current trends in shrinking the channel length of organic transistors down to the nanoscale in three systems in order to minimize defect density in the device materials. In each system sophisticated device fabrication is integrated into the development of different nanoscale electrodes. The incorporation of molecular self-assembly into the device fabrication allows us to build effective field effect nano-transistors. These three systems are i) nanoscale metal electrodes (made using electron beam (e-beam) lithogra-phy,<sup>[55–57,60–67]</sup> shadow deposition,<sup>[68]</sup> underetching,<sup>[69]</sup> nanoimprinting,<sup>[70]</sup> rubber stamping,<sup>[71]</sup> and microcontact printing,<sup>[72]</sup>, ii) single-walled carbon nanotube (SWCNT) electrodes,<sup>[5,54,73–79]</sup>

Table 1. Device characteristics of OFETs with nanoscale channel lengths.

Parameters publications	$\mu~({\rm cm}^2/{\rm Vs})$	L (nm)	t <sub>ox</sub> (nm)	v <sub>D</sub> (V)	v <sub>G</sub> (V)	ON/OFF ratio	S mV/Dec	Current saturation?	Materials	Fabrication Method	Year
Collet et al. [60]	_	250	2	1.0	-1	10	300	n	n-Si	E-beam lithography	1998
Rogers et al. [72]	$1  imes 10^{-3}$	100	20	-5	-3	25	-	У	sexithiophene	Microcontact printing	1999
Collet et al. [61]	$3.6\times10^{-4}$	30	2	-1.5	-1.5	<10	350	n	sexithiophene	E-beam lithography	2000
Granstorm et al. [64]	$5  imes 10^{-4}$	400	150	-10	-30	100	-	n	sexithiophene	E-beam lithography	1999
Chwang et al. [65]	10 <sup>-4</sup>	500	150	-15	-15	100	-	n	sexithiophene	E-beam lithography	2000
Jones et al. [68]	_	50	100	0.1	0.4	-	-	_	polyaniline	Shadow deposition	1987
Austin et al. [70]	$8  imes 10^{-4}$	70	5	-3	-3	10 <sup>4</sup>	-	n	P3HT	Nanoimprinting	2002
Zaumseil et al. [71]	_	150	26	-2	-2.2	<100	_	n	Pentacene	Rubber stamping	2003
Wang et al. [66]	0.046	9	100	-5	-30	100	-	n	Pentacene	E-beam lithography	2004
Zhang et al. [62]	0.01	30	30	-2	-4	100	_	У	Pentacene	E-beam lithography	2003
Scheinert et al. [69]	$3 imes 10^{-5}$	700	50	-5	-5	10 <sup>4</sup>	400	n	P3HT	Underetching	2004
Tulevski et al. [56]	-	40	10	-3	-2.5	10	-	n	Tetracene	E-beam lithography	2004
Qi et al. [79]	_	6	10	-1	-3	10 <sup>3</sup>	400	n	Pentacne, P3HT	E-beam lithography	2004
Tsukagoshi et al. [78]	-	<500	200	-2	-10	10 <sup>3</sup>	-	n	Pentacene	E-beam lithography	2004
Lee et al. [63]	-	10	3	-0.3	-0.3	100	-	У	Pentacene	E-beam lithography	2005
Tulevshi et al. [55]	0.022	40-100	5	-3.6	-3.6	10 <sup>3</sup>	-	У	Pentacene	E-beam lithography	2006
Guo et al. [54]	≥l [a]	<10	300	-20	-20	10 <sup>3</sup>	500	У	HBC [b]	E-beam lithography	2006
Mottaghi et al. [57]	0.0035	50-1000	100	-0.5	-3	$1.8\times \text{I0}^{3}$	_	n	Oligothiophene	E-beam lithography	2007
Smits et al. [58]	0.01	750	200	-20	-20	10 <sup>6</sup>	-	У	Oligothiophene	Photolithography	2008
Guo et al. [80]	≥l [a]	<10	300	-20	-20	10 <sup>3</sup>	500	у	HBC [b]	E-beam lithography	2009
Cao et al. [81]	10 <sup>-3</sup>	100	300	-20	-5	10 <sup>5</sup>	20 V/Dec	n	Pentacene, P3HT	E-beam lithography	2009

[a] This mobility is only for comparison with other thin film transistors because it assumes a parallel capacitor model for the gate dielectric, which is not accurate here. [b] Contorted hexabenzocoronene.





**Figure 2.** A) A possible leakage path that would allow for transistor action without the current actually passing through the nanogap. Reproduced with permission from [63]. Copyright 2005, IEEE. B) The function of the two side guards is to suppress fringe currents. The white scale bar is 100 nm. Reproduced with permission from [66]. Copyright 2004, American Institute of Physics.

and iii) cut single-layer graphene sheets as 2D contacts.<sup>[81]</sup> We will describe the fabrication of these devices as well as some of their unique characteristics and sensitivities.

# 2. OFETs Based on Nanoscale Metal Electrodes

Traditionally, Si-based devices are made with metal electrodes, such as Au, Cu, and Pt, because of their high conductivities and their compatibility with industrial semiconductor processes. With great effort numerous approaches have been used to make nanoscale metal electrodes in order to achieve OFETs with submicrometer channel length. These methods include e-beam lithography,<sup>[55–57,60–67]</sup> shadow deposition,<sup>[68]</sup> underetching,<sup>[69]</sup> nanoimprinting,<sup>[70]</sup> rubber stamping,<sup>[71]</sup> and microcontact printing.<sup>[72]</sup> Device characteristics of OFETs made by each method are listed in Table 1. These results are promising and in principle demonstrate the possibility of realizing functional OFETs with channel lengths in the nanometer range and the wide capability for application in nanoscale/molecular electronics.

#### 2.1. E-beam Lithographic Method

E-beam lithography is the most commonly used technique to fabricate nanoscale metal electrodes. OFETs with sub 100 nm channel lengths have been reported. For example, by using e-beam lithography and lift-off techniques,  $\text{Collet}^{[60,61]}$  and Zhang

et al.<sup>[62]</sup> have reported the fabrication of organic thin-film transistors with a channel length as short as 30 nm. OFETs with even smaller channel lengths (10 nm) were also fabricated by Subramanian's group.<sup>[63]</sup> However, in such devices with small W/L ratio, a significant portion of the measured drain current may actually result from fringe current rather channel current, through the path illustrated in Figure 2. To suppress spreading current in devices, Wang et al.<sup>[66]</sup> employed a new pair of guarding electrodes, which are as close as 20 nm to the two sides of the channel (Fig. 2B), to improve the FET properties of pentacene thin film transistors with sub 10 nm channel lengths. Such OFETs based on nanoscale metal electrodes are very interesting for studying the intrinsic properties of organic thin films, and they can operate at low voltage (Table 1). Their current-voltage characteristics exhibit

the similar p-type FET behaviors. Typical field-effect mobilities of these nanodevices are the order of  $10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> (Table 1). At this early stage these studies show that it is possible to realize functioning OFETs with the channel length down to the nanoscale, and that their electrical characteristics exhibit good performance, comparable to macroscopic OFETs.

Previous reports of organic thin-film devices have shown that the first few molecular layers of organic semiconductor at the oxide interface are the locus of charge injection and are responsible for current modulation.<sup>[14,43,44,64,65]</sup> It is very important to explore the subtle correlation between structures, assemblies, and properties of the first layer of organic semiconductors. Little work has been devoted to the use of the first layer or self-assembled monolayer (SAM) as an active part of OFETs due to the great challenge of achieving uniform SAMs with dense packing. Recently, Tulevski et al.<sup>[56]</sup> demonstrated a new class of organic semiconductor that spontaneously forms upright monolayers on gate oxides. They found that a tetracene derivative covalently forms dense, upright monolayers on the surface of the aluminum oxide dielectric layer (Fig. 3A). The rigid, covalent attachment provides a direct method for using the dielectric surface structure as an adjustable parameter to tune the monolayers' self-assembled structure and therefore their electrical properties. After these monolayers spontaneously selforganize into the active layer in nanoscale field-effect transistor (FET) devices with prepatterned source-drain electrodes separated by less than 100 nm (Fig. 3B, C), the resulting devices showed the p-type, hole transporting properties (Fig. 3D). This work opens up a new avenue for studying the intrinsic properties of SAM as the active layer in nanoscale thin-film organic transistors. Moreover, the SAM-based nanodevices could act as highly sensitive environmental and molecular sensors since the first layer of the active channel is exposed to the environment.

As the authors mentioned, this work still suffers from two factors: one is the sharp decrease in the yield of the devices with l > 60 nm, and the other is the nonlinear I/V curves and the failure of the current saturation (Fig. 3D). These issues can be ascribed to the problems of poor long-range organization of



**Figure 3.** a) Molecular structure of an end functionalized tetracene and schematic of bonding and orientation of it on aluminum oxide. b) SEM image of the nanodevices. c) SEM image of the 40 nm gap. d) Source–drain *I/V* curves at different gate biases [ $G_V = 0$  (red) to -2.5 V (dark green) in -0.5 steps]. Inset: Tapping mode AFM image of the 40 nm device. Reproduced with permission from [56]. Copyright 2004, ACS.

the organic monolayer, poor charge injection from contacts, and increased contact resistance. However, the recent work by Mottaghi<sup>[57]</sup> and Zhang et al.<sup>[62]</sup> demonstrated sub 100 nm OFETs which do show saturated current output currents, indicating that these observed nonidealities may not be intrinsic to nanoscale OFETs. In Mottaghi's work OFETs are built on an SAM formed from bifunctional molecules comprising a short alkyl chain linked to an oligothiophene moiety that acts as the active semiconductor.<sup>[57]</sup> Platinum/titanium source and drain electrodes are patterned by e-beam lithography, with a channel length ranging between 20 and 1000 nm. Although ill-defined *I/V* curves were recorded, attributed to a poor electrical contact between platinum and the oligothiophene moiety in most cases, a few devices did offer well-defined curves with a clear saturation.

Indeed, these problems mentioned above can be solved by considered molecular designs as nicely demonstrated by further work of Tulevski<sup>[55]</sup> and Smits et al.<sup>[58]</sup> Tulevski et al. used structurally and electronically similar semiconductors to form SAMs on the surface of the source and drain electrodes in order to eliminate the grain boundaries that give rise to deleterious traps and poor electronic coupling (Fig. 4A).<sup>[55]</sup> Using e-beam lithography, FET test structures were built on highly doped silicon wafers (having 5 nm of thermally grown silicon oxide) (Fig. 4B, C). These monolayers form a template on the metal surface and provide better electronic coupling between the electrode and the semiconductor (Fig. 4A). Because the



**Figure 4.** a) Illustration of surface modification to form a template that recognizes a complementary surface. b) Schematic of the device structure. c) SEM image of devices and single device channel (inset). d) Structures of compounds used to modify the electrodes. Reproduced with permission from [55]. Copyright 2006, ACS.

monolayer functionality is complementary to the structure of the molecular semiconductor (Fig. 4D), well-behaved devices with a channel length as short as 40 nm can be readily achieved. Smits and co-workers<sup>[58]</sup> demonstrated SAM field effect transistors (SAMFETs) with long-range intermolecular p-p coupling in the monolayer. A prerequisite for successful SAMFETs is a dense and ordered semiconducting monolayer. The key point in this work was the use of liquid-crystalline molecules consisting of a p-conjugated mesogenic core separated by a long aliphatic chain from a monofunctionalized anchor group in order to achieve dense packing (Fig. 5A). They claimed that monofunctional anchoring groups are crucial in order to prevent defects. They chose  $\alpha$ -substituted quinquethiophene as the core of the semiconducting molecule. This core molecule was functionalized with aliphatic chains because these oligothiophenes have charge carrier mobilities several orders of magnitude higher than the corresponding  $\beta$ -substituted molecules, and they show a good compromise between solubility and charge carrier mobility. Smits et al. reported that the resulting SAMFETs, which had 40 µm channel lengths, are quite reproducible, and they exhibit a bulk-like carrier mobility and large current modulation (Fig. 5B). Furthermore, they combined the SAMFETs into logic gates as inverters and demonstrated real logic functionality by constructing a 15-bit code generator. This work is an important step toward realizing functional self-assembled integrated circuits through bottom-up approaches.

A new e-beam lithographic technique has been created to fabricate nanoscale metal electrodes (Fig. 6A–D).<sup>[67]</sup> This is a self-aligned lithographic process able to produce large numbers of nanogaps with remarkably high yield and precision. The substrate for this process is a clean silicon wafer that has a surface of 20 nm thermal SiO<sub>2</sub> surmounted with a 5 nm layer of ZrO<sub>2</sub>. A 3 nm-thick layer Pt is deposited by electron-beam lithography, followed by 2.5-7 nm of Al (Fig. 6A). The key to this process is that the thin native aluminum oxide layer forms an overhang structure over the Pt electrode after lift-off (Fig. 6B). The second electrode is 2.5 nm Pt deposited by electron beam evaporation overlapping with the first electrodes (Fig. 6C). The portion of the second Pt deposit that overlaps with the alumina along with the alumina and aluminum are removed by wet etching. This exposes the nanogaps that were formed during the shadowed Pt deposition (Fig. 6D). The size of the gap is determined by the thickness of the aluminum oxide layer, which scales with the aluminum film thickness for these ultrathin films. Figures 6E, F, and G show the nanogaps prepared by this method with  $\sim$ 3, 5, and 10 nm. This unique technique is important for exploring the intrinsic properties of nanoscale OFETs; it could be a reliable electrical test-bed by providing large numbers of nanoscale metal electrodes with remarkably high yield and precision.





Figure 5. a) X-ray reflectivity (XRR) of the SAM on silicon dioxide. The solid red line is the fit to the experimental data. The inset shows the chemical structure of the molecule and the thicknesses, root-mean-square (r.m.s.) roughness values and electron densities obtained from the fit. The measurements reveal a layer thickness equivalent to one monolayer. b) Output characteristics for the corresponding SAMFET. The gate voltage was varied from -5 to -20V in steps of -5 V. Reproduced with permission from[58]. Copyright 2008, Nature Publishing Group.

#### 2.2. Other Methods

In addition to e-beam lithography, a large number of approaches have been developed to make nanoscale metal electrodes in order to achieve OFETs with submicrometer channel lengths. For example, Wrighton and co-workers<sup>[68]</sup> used multistep shadow deposition techniques to prepare molecule-based transistors with the source–drain electrodes separated by 50 nm (Fig. 7A). Rogers et al.<sup>[72]</sup> integrated near-field photolithography with microcontact printing and shadow masking to demonstrate complementary inverter circuits from OFETs with 100 nm channel length. Scheinert et al.<sup>[69]</sup> developed an underetching technique to define submicrometer channel length polymer FETs (Fig. 7B). The transistors with submicrometer channel length show the operating voltage as low as 5 V with a low inverse subthreshold



**Figure 6.** a) A line of Al on Pt is deposited by e-beam lithography on a silicon wafer coated with  $ZrO_2$ . b) Air in the ambient oxidizes aluminum to produce an overhanging aluminum oxide layer. c) Evaporation of the counter electrode produces platinum separated by the amount of aluminum oxide overhang. d) Dissolving the aluminum/aluminum oxide layer give closely spaced platinum electrodes. e) SEM showing a 3 nm gap; the part in the red rectangle is enlarged 200%. F) SEM showing a 5 nm gap. G) SEM showing a 10 nm gap. Reproduced with permission from ref. [67]. Copyright 2007, Wiley-VCH.

slope of 0.4–0.5 V/dec, on–off ratio of 10<sup>4</sup>, and without short-channel effects. Austin and Chou<sup>[70]</sup> successfully fabricated 70 nm channel length polythiophene transistors using nanoprinting lithography (Fig. 7C). Finally, Zaumseil et al.<sup>[71]</sup> used a high-resolution rubber stamping technique to define channels down to 150 nm and built pentacene transistors (Fig. 7D). The good performance of all the devices and their low-voltage operation make them and the fabrication procedures attractive for many applications.

# 3. OFETs Based on SWCNT Electrodes

Since their discovery,<sup>[82]</sup> carbon nanotubes have been regarded as one of the best nanostructural materials derived from bottom-up chemical synthesis.<sup>[3,4]</sup> Carbon nanotubes have the simplest

chemical composition and atomic bonding configuration but exhibit perhaps the most extreme diversity and richness among nanomaterials in structures and structure-property relations.<sup>[83,84]</sup> SWCNTs are 1D ballistically conducting nanowires that are intrinsically the same scale as molecules. They are easy to process for nanofabrication. SWCNTs are formed by folding up a graphene sheet into a cylinder along a certain lattice vector. This hints at useful conduction via the  $\pi$ -bonding network. Ultimately SWCNTs are composed of carbon six-membered rings, and therefore we propose that a high-quality contact can be formed between SWCNT electrodes and molecules. As a result of all of these features. SWCNTs should be ideal point contacts for testing the intrinsic properties of various molecular devices with molecular sizes in all dimensions.<sup>[5,54,73–79]</sup>

We form SWCNT electrodes by cutting them by precise local oxidation through a polymethylmethacrylate (PMMA) mask.<sup>[73]</sup> The mask is created by e-beam lithography. This process leaves two ends that are separated by a





**Figure 7.** Schematic illustrations of building thin film transistors by multistep shadow mask technique a), underetching lithography b), nanoprinting lithography c), and rubber stamping technique d). Reproduced with permission from [68–71]. Copyright 1987, ACS, and copyright 2004, 2002, and 2003, AIP, respectively.

gap of  $\leq$ 10 nm (Fig. 8A, B). This method differs from the formation of SWCNT electrodes by electrical breakdown, which has been used recently to realize pentacene nanotransistors by Qi and Tsukagoshi et al.<sup>[78,79]</sup> In both cases, applying a high current through the channel disconnected each single-walled or multi-walled carbon nanotube that bridged the two metal leads. Organic materials were then thermally evaporated to bridge the gap. This formed ultra small OFETs having nanoscale channel lengths (Fig. 8). These two studies have proven that carbon nanotubes can be novel electrodes for a variety of molecular devices.

In order to fabricate SWCNT electrodes we prepare an array of SWCNT transistors and spin-coat this array with a blanket layer of PMMA. Then we open a window (<10 nm) on top of individual SWCNT transistors using ultra high-resolution e-beam lithography. We then cut the nanotubes through the window via oxygen plasma ion etching (Fig. 9A, B). We control the degree of cutting, and therefore the gap size, by varying the time of the



**Figure 8.** Individual carbon nanotubes as electrodes for small OFETs. A) Schematic drawing of a cut SWCNT with a sub-10-nm gap to be used as source (S) and drain (D) electrodes of an organic FET and AFM image of a cut SWNT with a vapor-deposited pentacene crystallite bridging a cut SWNT. B) Cross-sectional view of device structures of the pentacene nanotransistor with carbon nanotube electrodes. Reproduced with permission from [78–79]. Copyright 2004, ACS, and copyright 2004, AIP, respectively.

exposure to the oxidant. Figure 9C shows an AFM image of one nanogap. Given the imaging convolution of the AFM tip size, an upper bound on the size of a typical gap in these micrographs is  $\sim$ 10 nm. This strategy allows molecules to be wired into the SWCNT circuits through robust amide linkages, avoiding the common problems related to thiol molecules inserted between gold electrodes. The amide linkages are so robust that the devices can endure external stimuli and chemical treatments. Utilizing this method, we have tested a number of different types of molecular wires.<sup>[73–77]</sup> We have made different types of molecular electronic devices that are able to switch conductance as a function of pH,<sup>[73]</sup> detect the binding between protein and substrate,<sup>[76]</sup> photoswitch the conductance between conjugated and nonconjugated states,<sup>[77]</sup> and measure the conductance differences between complementary and mismatched DNA strands.<sup>[74]</sup> Detailed below are the new applications of this strategy in organic electronics. We have demonstrated that

SWCNTs can function as efficient point contacts for nanoscale FETs. We made FETs out of both monolayers<sup>[54]</sup> and self-assembled columns<sup>[80]</sup> of polycyclic aromatic hydrocarbons. These devices are ultrasensitive to their chemical environment, temperature, and light.<sup>[54,80]</sup>

#### 3.1. Chemoresponsive Monolayer Transistors

It is a formidable challenge to make organic monolayer transistors because when the semiconducting layers of typical OFETs are scaled down to a monolayer their properties





**Figure 9.** A) Very fine cutting of SWCNTs with oxygen plasma introduced through an opening in a window of PMMA defined with e-beam lithography. B) The results of oxidative opening of the tubes are point-contacts that are functionalized on their ends and separated by as little as  $\sim$ 2 nm. C) AFM image of the gap cut into the SWCNT. Inset: height profile of the isolated tubes. Reproduced with permission from [73]. Copyright 2006, American Association for the Advancement of Science.

generally become poor, presumably due to discontinuities or defects in the films.<sup>[54,56–58]</sup> However, this problem could be circumvented by chemically functionalizing the molecular semiconducting material such that the molecules both assemble laterally and attach themselves chemically to the substrate (Fig. 10).<sup>[54]</sup> We have found that monolayers of molecules behave as p-type semiconductors when they are incorporated into FETs wired by SWCNT electrodes. The devices show both large current modulation and high gate efficiency. Contorted hexabenzocoronenes (HBCs) (Fig. 10A) were chosen because these compounds self-organize into molecular stacks with useful semiconducting properties. Acid chloride functionality was chosen for its well-known ability to bind to the silicon oxide surface. Owing to their good solubility, high-coverage monolayers with  $\sim 0.7$ molecules per square nm on silicon oxide can be easily formed. The surface reaction between the carbonyl chlorides of the HBCs and the oxygens of the silicon oxide produces an ester, imparting significant stability to the monolayers (Fig. 10B). Surface X-ray reflectivity data can be fit well to a box-model of three layers (Fig. 10B), which implies an HBC monolayer, composed of an ester layer and the HBC core, whose thickness is approximately 12.2 Å. These reflectivity results are in agreement with the results from UV-vis absorption that show that the molecules of the monolayer are essentially upright and tightly packed on the silicon oxide surface. Another striking feature of the X-ray scattering is the extremely high electron density (0.54  $e^{-}/Å^{3}$ ) for the HBC layer. The tight packing of these molecules and their high  $\pi$ -electron density imply useful electronic properties of the monolayer. To aid in the subsequent analysis of the devices, we only use those that are wired using metallic SWCNTs.

When ultra-small point contacts, separated by molecular length-scales, are used as the source and drain electrodes (Fig. 10C), transistors can be made from monolayers of these molecules. These transistors have high gate efficiency and large ON/OFF ratios. These electrically active monolayers of HBCs behave as p-type semiconducting films. Figure 10D and E show the transistor characteristics for a monolayer of HBCs. These devices are very stable; they can be cycled many times despite the high levels of current through these self-assembled stacks. The carrier mobility is very high ( $\geq 1 \text{ cm}^2 \text{ V}^{-1} \cdot \text{s}^{-1}$ ). In such a device using SWCNT S/D electrodes separated by  $\leq$ 10 nm, owing to their 1D nature, the electric field from the back gate could focus on the SWCNT junction regions and efficiently penetrate into the middle of the semiconductor channel, thus leading to the observed high gate modulation. Another possibility is that the gate voltage does change the properties of the contact. However, it is logically very difficult to separate the behavior of the contact from the behavior of the semiconductor, since the device must be a combination of the two (plus the other elements: the dielectric, etc.). We suppose that the synergistic effects of surface attachment of

HBC molecules, the upright conformation, the close packing, and the particular 1D nature of SWCNT electrodes produce the high-performance FET behavior. This study demonstrates a clear example of how the ever-reducing dimensions of top-down device fabrication can be tailored to mesh with the expanding length scales of bottom up self-assembly.

Since the electrical current in OFETs travels through the first few layers of molecules near the oxide interface, these monolayer devices can detect certain types of molecules. In other words, the active channel of such a monolayer device is exposed to the environment and is available for analyte recognition. Figure 11 shows the transistor characteristics for the device shown in Figure 10D and E after dipping into a solution of the well-known electron acceptor TCNQ. Given the affinity of TCNQ for the molecules such as coronene, it likely acts as a dopant for the stacks by accepting  $\pi$ -electrons. This would explain the shift in voltage threshold to more positive values and the increase of the OFF-current by roughly an order of magnitude. These results form the basis for a new type of environmental and molecular sensors. What is left unclear is how this doping occurs: whether it is through an intercalation of the TCNQ or some other associative mechanism.

#### 3.2. Photoresponsive Nanoscale Columnar Transistors

In order to make the photoresponsive transistors<sup>[80]</sup> we used the liquid crystalline material tetra(dodecyloxy)hexabenzocoronene





**Figure 10.** A) HBC molecules synthesized with groups to bind the surface of silicon oxide. B) Model with three color-coded layers and their thicknesses. C) Monolayers of self-assembled stacks being probed with SWCNT electrodes separated by only a few nanometers. D) Transistor output,  $V_G = 0$  to -5 V in -1V steps. E) Transfer characteristics for the device,  $V_D = -2V$ . Reproduced from [54].

After TCNQ

(HBC) (Fig. 12A). This compound self-organizes into columnar nanostructures with the similar size as the diameter of SWCNTs. Single-column transistors are formed when ultrasmall point

Before TCNQ







#### Drain Current (A) Drain Current (A) -6 -6 -4 -2 -2 0 0 0.0 -1.0 -2.0 -3.0 -4.0 -5.0 0.0 -1.0 -2.0 -3.0 -4.0 -5.0 Source-Drain Voltage (V) Source-Drain Voltage (V) D) B) 10-8 (V) 10<sup>-9</sup> 10<sup>-10</sup> (V) 10<sup>-10</sup> (V) 10<sup>-8</sup> 10<sup>-9</sup> 10<sup>-10</sup> 10<sup>-10</sup> 10 100x10<sup>-6</sup> 100x10<sup>-6</sup> 80 80 (II<sub>D</sub>I)<sup>1/2</sup> (A<sup>1/2</sup>) (II<sub>D</sub>I)<sup>1/2</sup> (A<sup>1/2</sup>) 60 60 10<sup>-11</sup> - 10<sup>-11</sup> 40 40 10<sup>-12</sup> 20 10<sup>-12</sup> 20 0 0 10<sup>-13</sup> 10-13 0 -2 -4 2 0 -2 -4 2 Gate Voltage (V) Gate Voltage (V)

C)

-10x10

**Figure 11.** The device shown in 10 D and E after the assembly of a monolayer of HBCs on the SiO<sub>2</sub> surface of a silicon wafer with SWCNT electrodes. A) Transistor output,  $V_G = 0$  to -5 V in -1V steps. B) Transfer characteristics for the device,  $V_D = -2$  V. C) Transistor output,  $V_G = 0$  to -5 V in -1V steps, for the same device after treatment with a TCNQ solution. D) Transfer characteristics for the device,  $V_{SD} = -2$  V. Reproduced from [54].



A) -10x10





**Figure 12.** A schematic of how HBCs can be assembled to form single-column transistors and measured by SWCNT point contacts. A) The structure of contorted liquid crystalline tetra (dodecyloxy)hexabenzocoronene (HBC). B) Device structure of single column transistors with SWCNT-metal junctions protected by HSQ. C) Device structure of single column transistors made by drop-casting. Only the nanogaps between SWCNT electrodes are covered by HBCs. D) An optical microscopy image of a device whose SWCNT-metal junctions have been protected by HSQ. E) An optical microscopy image of a device produced by drop-casting HBCs exactly on the nanogaps. Reproduced from [80].

device structure. It is very clear that the tiny drop of organic semiconducting materials is not connected to any metal electrode. In both of the cases charge exclusively passes through SWCNT-molecule-SWCNT junctions, identifying that these nanojunctions play a key role in the electronic characteristics of the devices.

It is noteworthy that the electrical properties of these devices improve significantly after annealing. Before the devices were



**Figure 13.** Device characteristics of a device before and after annealing. A) Transistor output,  $V_G = 0$  to -3 V in -0.6 V steps. (B) Transfer characteristics for the device,  $V_D = -3 V$ . C) Transistor output,  $V_G = 0$  to -11V in -2.2 V steps for the same device after the treatment of heat. B) Transfer characteristics for the device,  $V_D = -11V$ . Reproduced from [80].

annealed, we found that the yield of the working devices was low ( $\sim$ 10%) and the maximum current within the measured scale is quite small as shown in Figure 13A, B, while after heating the yield of the working devices increased to ~60%. Another significant difference is the maximum current after annealing, which increased by a factor of over two orders at  $V_{\rm D} = -3$  V (Fig. 13C, D). These molecular transistors, which have the 1D ballistic SWCNTs as point contacts, exhibit high-current modulation and a high ON/OFF ratio. The ON/OFF ratio is as high as 10<sup>3</sup>; this is difficult to achieve in ultrasmall devices with metallic S/D electrodes. This is because of the synergistic effects of the 1D nature of SWCNT electrodes in the devices and self-assemblied columnar nanostructures of HBCs.

Another significant advantage is that we can use SWCNTs as point contacts to measure the photoconductivity of an individual, 1D liquid crystalline columnar core. This is because the size of these columnar nanostructures perfectly matches the diameter of SWCNT

electrodes. In Figure 14A and B we compare the electrical characteristics of the same annealed device made by drop-casting in the dark and under the irradiation of visible light. The measured photoconductivity originates from photoexcitations that are restricted in the 1D hexaradialene-core by the insulating alkoxyphenyl cladding. When the devices are held at fixed source-drain bias and gate bias by switching on/off light, the reversible photocurrent of the devices can be monitored in the

real time (Fig. 14C). We also found that the device photoresponsiveness is universal since we used another organic semiconductor (dithiophenylpentacene) to observe the similar phenomenon. These studies demonstrate that efficacious stimuli-responsive single column transistors should have the potential for applications in ultrasensitive devices for environmental sensing and solar energy harvesting.

# 4. OFETs Based on 2D Graphene Electrodes

Graphene, a newly isolated form of carbon,<sup>[85,86]</sup> has a set of remarkable electronic and physical properties that make them ideal for use in nanoelectronics<sup>[87–89]</sup> and its discovery has led to a flood of worldwide research interest.<sup>[90–99]</sup> As an electrode for nanoscale electrical devices graphene is attractive because it is a very thin (single-atom thick), two-dimensional semimetal that is easily available in very high crystallographic quality. We suggest that graphene may prove to be another type of electrode for making a wide



**Figure 14.** Device characteristics of a device made by drop-casting in the dark and under irradiation with visible light after annealing. A) Transistor output,  $V_G = 0$  to -20 V in -4 V steps. B) Transistor output,  $V_G = 0$  to -20 V in -4 V steps for the same device after the treatment of heat. C) The drain current as a function of time while the same device is held at -20 V source-drain bias and -8 V gate bias by switching on/off light. Reproduced from [80].

variety of molecular devices (Fig. 15A) and might improve the performance of nano-OFETs.<sup>[81]</sup>

The fabrication of three-terminal, graphene-based transistors is described in the literature.<sup>[85–89]</sup> The identification of the single graphene sheets obtained by a repeated peeling-off technique is performed by a combination of optical and atomic force microscopy. After device fabrication by e-beam lithography, we oxidatively cut individual graphene sheets using another ultrafine lithographic process and oxygen plasma etching. This produces nanogaps between the graphene half-sheets (Fig. 15B). We controlled the fabrication procedure to give a gap size in the range



**Figure 15.** A schematic of how graphene sheets function as 2D electrodes to measure the electrical conductance of organic semiconductors. A) Device structure of P3HT transistors made by dip-coating. Only the nanogaps between graphene sheets are covered by P3HT. B) Optical micrographs and atomic force microscopic image of a representative device. The thickness of graphenes used here is ~0.8 nm, a single layer of graphene. The gap size between the graphene ends is ~100 nm. Reproduced with permission from [81]. Copyright 2009, Wiley-VCH.



**Figure 16.** Device characteristics of a representative P3HT thin film transistor based on 2D graphene contacts made by dip-coating from its dilute chloroform solution (~0.25 mg mL<sup>-1</sup>). A) Transistor output,  $V_G = 100$  to -5 V in -21 V steps. B) Transfer characteristics for the device,  $V_D = -20$  V. The field effect mobility  $\mu$ , calculated in the red regime, is  $\sim 1.4 \times 10^{-3}$  cm<sup>2</sup> V<sup>1</sup> · s<sup>1</sup> at  $V_D = -20$  V.  $L = \sim 100$  nm and  $W = \sim 4 \,\mu$ m. Reproduced with permission from [81]. Copyright 2009, Wiley-VCH.

of 100–150 nm, which is the shortest channel length that can yield an efficient field effect from the global back-gate. We then dip-coated thin films of organic semiconductors (P3HT) within and across the gap between the graphene half-sheets. By applying gate bias voltage ( $V_{\rm G}$ ), we can fine-tune the carrier density in the devices.

To exclude the possibility of charge transporting directly through the junctions between Au electrodes and P3HT thin films, we performed concentration-dependent experiments. Based on the results, we are confident that the current path of the devices is through graphene electrodes bridged by P3HT. It is

remarkable that these molecular transistors, which utilize the 2D single-layer graphene electrodes, display high current modulation and high ON/OFF ratio. The ON/OFF current ratio is as high as that of macroscopic organic FETs ( $\sim 10^5$  in Fig. 16A, B). The calculated carrier mobility ( $\mu$ ) is quite good (around  $1.4 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> · s<sup>-1</sup>, even without optimization). Both of these values are comparable to those obtained from bulk organic FETs based on metal electrodes.<sup>[14,100-104]</sup> Furthermore, because of the tight interatomic sp<sup>2</sup> bonds existing in their intrinsic structure without any defects, graphene-based electrodes are quite stiff, thus ensuring robust devices, even under source-drain voltage biases as high as -20 V. This strongly suggests that cut 2D planar graphene sheets can function as efficient electrodes, realizing all the functions of macroscopic metal electrodes at the nanometer scale.

These graphene-based transistors are sensitive to visible light because of the presence of photoactive organic materials. Figure 17 shows the electrical photoresponses of the same device in Figure 16A made by dip-coating from the dilute chloroform solution of P3HT. The reversible photocurrent, presumably originating from the photoexcited states of the molecules, was stable without any degradation for many measurement cycles even in the presence of oxygen and moisture in the air.

4DVANCED





**Figure 17.** A) Time trace of the drain current for the same device used in Figure 3, showing the reversible photocurrent while the device was held at -2V source-drain bias and -2V gate bias by switching on/off light. B) A representative full switching cycle showing the quick saturation process in drain current of the device under light irradiation. Reproduced with permission from [81]. Copyright 2009, Wiley-VCH.

The calculated responsivity of the device is very high, approximately 8.3 A/W ( $W = \sim 100 \text{ nm}$  and  $L = \sim 4 \mu \text{m}$ ,  $V_D = -2 \text{ V}$  and  $V_G = -2 \text{ V}$ ) at an intensity of 30 mW cm<sup>-2</sup>, in comparison with conventional photodetectors (typically less than 1 A/W), using the conventional model for the calculation.<sup>[105,106]</sup>

To identify the reliability and generality of the device photoresponsiveness, we used the junction-protected devices to fabricate pentacene nanotransistors.<sup>[81]</sup> We also observed the quick, stable photoinduced current increase of the device upon exposure to visible light under the same conditions. This study demonstrates that 2D planar graphene sheets can serve as powerful electrodes due to the 2D planar nature and the high electrical conductivity of semimetallic graphenes. Furthermore, because of their 2D compatibility with existing CMOS architectures, graphenes might be simply integrated into CMOS technology and find a broad application in developing integrated ultrasensitive devices at the nanometer scale.

#### 5. Conclusion

Recent advances in current trends in shrinking the channel length of OFETs down to the nanoscale are presented. To minimize defect density, remarkable attempts have been made to build nano-OTFTs in three systems. In each case sophisticated device fabrication has been integrated into the development of different electrodes with nanoscale gaps. The principle is the combination of molecular design freedom and flexible molecular self-assembly with state-of-the-art device fabrication to construct organic field effect nano-transistors where molecular materials themselves behave as pivotal elements. In the first system, e-beam lithography is the most commonly used technique to make nanoscale metal electrodes with high yield and precision. Other methods, including shadow deposition, underetching, nanoimprinting, rubber-stamping, and microcontact printing, are complementary and powerful for making miniaturized OFETs. In the second system, we detailed a general methodology of forming SWCNT electrodes with 1-10 nm gaps as point contacts. These OFETs based on SWCNT electrodes, which are formed from both monolayers and self-assembled columns of polycyclic aromatic hydrocarbons, are ultrasensitive to their chemical environment, temperature, and light. In the third

system, we report on a recent study of making photoresponsive field effect nano-transistors using cut single-layer graphene sheets as 2D contacts. Nanoscale organic transistors based on graphene contacts show high-performance bulk-like FET behaviors, proving that graphene is another type of powerful electrodes for making a wide variety of molecular devices.

Shrinking device dimensions are attractive because it allows for probing the intrinsic behavior of organic materials and increasing the FET performance, such as carrier mobility, on-current, low-operating voltage, and device speed. However, such size reduction has met with a number of difficulties that limit the performance of the devices. Nonidealities have been observed including the degradation of

gate effects, the lack of the *I*/*V* current saturation, and the strong deviation from square-law behavior that are ascribed to increased contact resistance, poor charge injection from contacts, ballistic transport, and space charge limited current. To achieve functional OFETs, one should try as best as possible to comprehensively understand the device fabrication process as an integral one. The holistic consideration of the appropriate choice of contact materials, interface structures, and device design may enable the realization of optimized nanoscale organic devices. Another formidable issue in molecule-based electronics is a great shortage of efficient integration strategies. More research is necessary to bridge hard electronics with the vast store of the soft molecular world.

#### Acknowledgements

We acknowledge primary financial support from FANEDD (no. 2007B21), MOST (2009CB623703), and NSFC (grant no. 50873004, 20833001, 50821061). C. N. and M. L. S. acknowledge financial support from the Nanoscale Science and Engineering Initiative of the National Science Foundation under NSF Award Number CHE-0641523 and by the New York State Office of Science, Technology, and Academic Research (NYSTAR).

> Received: February 13, 2009 Published online: July 17, 2009

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