

Thin-Film Organic Electronic Devices

Howard E. Katz and Jia Huang

Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland 21218; email: hekatz@jhu.edu

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Key Words

sensors, organic semiconductors, diodes, dielectrics, conducting polymers

Abstract

We review recently published advancements in thin-film organic devices, ranging from the composition and properties of organic materials to be used in devices, to the applications of devices, with special emphasis on thin-film transistors, diodes, and chemical sensors. We present exemplary materials used in each kind of device, outline the physical mechanisms behind the functioning of the devices, and discuss the most advanced capabilities of the devices and device assemblies. Advantages to the selection of organic and polymeric materials, future prospects, and challenges for organic-based electronics are also considered.

INTRODUCTION

Many electronic devices commonly employed in CMOS circuitry have functional counterparts made from organic materials. Passive elements including conductive leads, antennas, gate dielectrics, interlayer dielectrics, and storage capacitors can all be fabricated from conductive and/or dielectric polymers. Transistors, diodes, sensors, transducers, and memory elements can incorporate semiconductors consisting of organic molecular solids and/or semiconducting polymers. Anticipated applications of these devices are in circuits of moderate complexity, such as display drivers, radio-frequency identification (RFID) tags, or pressure mapping elements (1–4). A few versions of portable or flexible displays that include organic materials are already available or planned for commercial release, including the Sony eBook[®], Amazon Kindle[®], and Polymer Vision Readius[®]. Development of complex organic-based circuitry for RFID tags has resulted in demonstrations of megahertz switching speeds (5, 6). New uses for organic semiconductors (OSCs), such as in wireless power distribution (7), have been proposed.

Organic materials to be used in devices can be grouped as permanent conductors and insulators, switchable conductors (semiconductors), and materials with added functionality beyond simple switching, such as chemical recognition, piezoelectricity, and hysteresis. These materials have long histories and thus have predictable behaviors when they are being considered for a given device application. But there have been many notable advances in the design and use of these materials in the past few years, and new capabilities and properties have been revealed. Such materials have been incorporated and combined to produce complex functionality that cannot always be duplicated in silicon. The processing options and mechanical flexibility of some of these materials open new opportunities for their use over large areas or in unusual topologies. This review describes some of these advances. Exemplary materials used in each device are presented, and the most advanced capabilities of the devices and device assemblies are discussed. The reader is encouraged to consider references cited in this review as leading references for further background on specific materials. We attempt to evaluate the prospects for application of these devices in anticipated future technologies.

Light-emitting diodes made with organic emissive materials have been extensively investigated and are already commercialized. Electrons and holes are injected from low- and high-work-function electrodes, respectively, and are made to recombine at a molecular subunit with high emission probability from its excited state, often a triplet state. Because of their advanced technological status, large existing literature, and rarity in logic circuits, these organic light-emitting diodes (OLEDs) are not covered in this review. Another emerging application of OSCs involves alternative photovoltaics. Bilayers, networks, and composites containing hole and electron transporters, some or all of which are organic or polymeric materials, are deposited as thin films in stacks with electrodes of different work functions. They simultaneously produce voltages of 0.5–1 V and significant current in response to solar radiation. This is another application that is developing its own extensive community and literature and that is not particularly connected to functional electronics, except perhaps as an integrated power source. The photovoltaics are also omitted from this review.

CONDUCTIVE POLYMERS

Conductive polymers are preferred materials for leads and contacts in organic devices because of their suitability for printing. There are three main classes of conductive polymers used for printed electronics: polythiophenes (and related polypyrroles), polyanilines, and insulating polymers filled with conductive nanostructures (**Figure 1**). Although such materials have been known for decades,

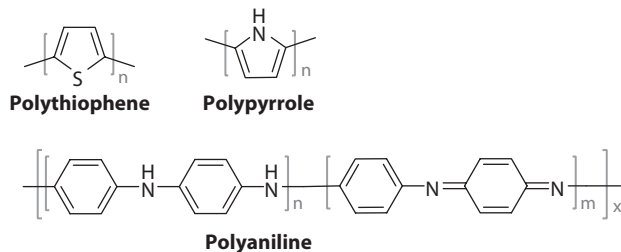


Figure 1

Structures of prototypical conducting polymers.

refinements continue to be made to optimize processability, conductivity, and transparency simultaneously. The term processability here refers to factors such as viscosity and surface energy that govern the fidelity and resolution of transferring these materials as conductive lines to arbitrary surfaces by conventional ink printing or by dry transfer of a line of solid material.

Poly(ethylenedioxythiophene) (PEDOT) is arguably the most widely employed conductive polymer for organic electronic device contacts (8). It is available commercially as a convenient aqueous dispersion from Bayer under the trade name Baytron[®]. The commercial formulation is often suitable for prototyping because of its ease of deposition and performance on both conductive substrates and nonconductive substrates (9–11). PEDOT has been employed as transistor source and drain in printed all-polymer transistors (12). Improved versions are often desired because of the need for higher conductivity, transparency, lower surface energy, higher viscosity, and/or greater chemical homogeneity. Therefore, numerous research groups have produced chemical variations of PEDOT by altering the main chain ring sequence, the nature of the dioxy substituents, or the counterionic component (8). By polymerizing a novel monomer solution in situ, researchers produced a film with conductivity of 170 S cm^{-1} (8). The process required a thermal conversion; other related electrochemical processes also require conductive substrates. In an especially intriguing variation, the sulfur in the PEDOT structure was replaced by selenium (13). The resulting polymer exhibited a pressed pellet conductivity in its doped state of 30 S cm^{-1} and showed clean spectroelectrochemistry.

Polyaniline is a second, relatively stable polymeric conductor, with a history that extends back for decades (14). Depending on the oxidation state, dopant type and level, and additives, the material may act as a hole conductor, a proton conductor, or both. It may be blended with insulating polymer matrices to yield composites with the desired mechanical and electrical properties simultaneously. The polymer partner can be introduced as a polyanion to counter the positive charge of active polyaniline (15). The morphology of individual polyaniline domains may be tuned from fibrular to particulate, depending on the intended deposition method and the need for a supporting matrix (16, 17).

Carbon nanotubes dispersed in polymer matrices confer a very wide range of conductivities, depending on nanotube surface treatments and dispersion methods (18). Some conductivity values exceed 1 S cm^{-1} . The required loading levels are just a few percent, considerably less than the levels needed for carbon black–polymer conductive composites (19). Suitable matrices include the transparent and widely available poly(methyl methacrylate) and polystyrene. Polyaniline represents another possible matrix; in that case, percolation requires only a close approach of nanotubes, rather than direct contact, and even lower loading levels are possible (20, 21). A polyaniline–nanotube composite with loading levels on the order of 1% was patterned by use of laser ablation–induced dry transfer to make conductive lines suitable for organic electronics (22).

Numerous other conductive fillers, such as gold and platinum particles, semiconductor quantum dots, carbon black, and transition-metal oxides, have been added to polyaniline (23–29).

A recent pair of papers argued that polyheterocycles are neither stable nor conductive enough to be relied upon as leads for organic transistors (30, 31) and therefore proposed an inorganic alternative comprising silver leads deposited as an electroless metal precursor ink. These leads were used to make bottom contact transistors with a thiophene-based polymeric semiconductor and showed low contact resistance and conductivity of thousands of Siemens per centimeter. Annealing above 150°C was required, which may have limited utility on plastic substrates. The need for higher-conductivity silver instead of a conductive polymer will likely be strongly dependent on the exact component dimensions. A 2- μm -resolution dry-transfer method was just demonstrated for silver electrodes (32).

DIELECTRIC POLYMERS

Composition and Properties

The most prominent role for insulating polymers in organic devices involves the gate dielectric for organic field-effect transistors (OFETs). Many common polymers can serve this function, including poly(methyl methacrylate), poly(vinyl phenol) and other polystyrenes, polyvinyl alcohol, polyimides, silicone network polymers, and parylene (Figure 2) (33, 34). Solution-based patterning of overlaying layers, including semiconductors and contacts, is eased by use of cross-linkable polymer dielectrics (35). Polymers are sometimes used as one of two dielectric layers whereby one is relied upon for dielectric strength or capacitance, whereas the other is designed to present a preferred interface for growth of an OSC. The polarity, viscosity, hydrophobicity, and roughness of polymer dielectrics all play roles in the quality of OSC films grown on them. A particular challenge is to pattern polymer dielectrics using efficient processes while retaining the physical and electronic features that lead to high-performance transistors. The BASF group recently led a collaboration that produced working transistor circuits using materials that were deposited in a roll printing process sequence, including dielectric polymers as transistor gate dielectrics (36). Higher-performance devices and circuits have been obtained with more precise lithographic

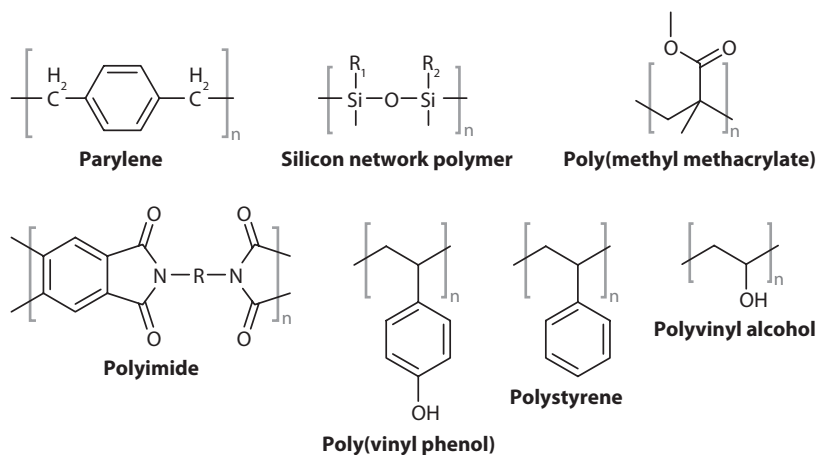


Figure 2

Representative dielectric polymers.

patterning techniques (37–39). Additional patterning complexity is needed for circuits based on multiple metallization layers. Communication among layers occurs through vias opened through dielectric layers. Thus, the dielectric layers need to be amenable to selective etching or dissolution in the vertical direction.

A more passive application of dielectric polymers, which is nevertheless vital for electrical energy management, involves their use as separators/isolators in storage capacitors (40–42). Hydrophobic polymers are sometimes selected because of their very high breakdown strength, whereas more polar alternatives provide higher dielectric constants. Inorganic and nanostructured additives, such as ferroelectric oxides and carbon nanotubes, are often added to produce composites with still higher dielectric constants. Part of the enhancement in such systems may arise from the polarization of the interfaces between the polymers and additive phases (43–45).

Piezoelectric Properties

A more active use of dielectric polymers includes their applications as pressure sensors, which convert mechanical displacement to an electrical signal, and actuators, which convert voltage differentials to mechanical distortions. The former are referred to as piezoelectric sensors, and the latter as artificial muscles. Polymers that have alignable dipolar monomer units, often displaying ferroelectric transitions, can be used in such devices. Once aligned, a film of such a polymer has a net voltage across it. Maintaining this voltage in the face of a change in thickness necessitates current being driven across an external circuit because of the accompanying capacitance change. If current cannot flow, then the voltage differential must change because the polarization is kept constant. The polarization can be read directly as a voltage signal in response to the dimensional change, or the polarization can be amplified if it alters the gate voltage of a powered transistor (4, 46, 47). Any realignment of the dipole arrays in response to applied electric fields results in a large change in electrical polarization of the polymer and is thus associated with a large dielectric constant. The energy stored during this realignment process represents a third application embodiment for this class of polymers. The best-known examples of these piezoelectric/ferroelectric polymers are based on 1,1-difluoroethylene monomers, sometimes with added comonomers in the polymer chains (Figure 3) (29, 48). Cross-linked polymers with conductive additives below the percolation threshold can also be used in place of piezoelectrics for the pressure-sensing application (4, 47). Both the switchable polarization and the high capacitance have been employed to confer tunable and reduced turn-on voltages when ferroelectric polymers were used as organic transistor gate dielectrics (49–51). Very recent work has also employed polymer gate dielectrics for organic

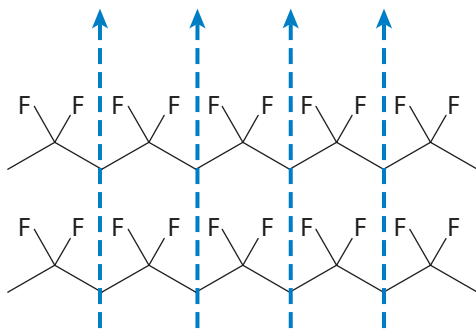


Figure 3

Structure of poly(vinylidene fluoride) illustrating additive dipoles.

transistors in which static charge altered the polarization state (52). Thus, distinct transistors made from identical materials and with identical layouts can serve different functions in circuits because of their tuned turn-on voltages and charge carrier mobilities. At a given gate voltage, the static charge can alter the output current by two orders of magnitude and can alter the voltage-dependent mobility by one order of magnitude. The difference in states of these transistors can be used in principle as a memory element or, more practically, as a tool for circuit tuning.

ORGANIC AND POLYMERIC SEMICONDUCTORS

Classes of *p*-Channel Organic Semiconductors

The number of research groups devoting significant effort to the synthesis of OSCs has grown from just a few in the late 1990s to many dozens at the present time. There are now hundreds of compounds that have been demonstrated as hole-transporting (*p*-channel) semiconductors in field-effect transistors (FETs). The preference for holes is determined by the highest occupied molecular orbital (HOMO) energy levels relative to contact work functions and environmental quenchers. It would be futile to list all the compounds individually because new ones are reported each month. Many exhibit field-effect mobilities on the order of 0.1 to 2 cm² Vs⁻¹, at or exceeding the value generally associated with amorphous silicon (which is an electron transporter used as a relatively inexpensive semiconductor for display applications). The main classes of hole-carrying molecular solid OSCs include fused rings (such as pentacene, thienothiophene, benzodithiophene, dithienoanthracene, and tetracene), short oligomeric chains of rings (various combinations of thiophenes, phenylenes, thiazoles, and pyrroles), ethylene and ethynylene groups, and selenophenes. A few such structures are shown in **Figure 4**. Side chains provide additional morphology, processing, and reliability control (53–67). Outstanding mobility, >10 cm² Vs⁻¹, has been established for a unique single crystal, rubrene (54, 68). Some very recent examples of organic *p*-channel semiconductor solids are cited here (69–80); these are intended as the most recent practical entrants into the literature and only hint at the variety of organic structures now being considered. There has also been great recent progress in the design of polymeric hole-transporting semiconductors based on thiophene copolymerized with single- and fused-ring comonomers (81, 82). The structures of the comonomers, along with the judicious sizing and placement of side chains, promote self-assembly of chains that facilitate charge transfer among them and thereby increase charge carrier mobility across a bulk film (83–88).

n-Channel Organic Semiconductors

There are considerably fewer molecular structures that have been identified as preferentially electron-carrying (*n*-channel) transistor semiconductors, although the list has grown rapidly in the past two years and now approaches 100 total compounds. *n*-OSCs are needed to take advantage of the greater power efficiency of complementary transistor circuits, as well as to develop devices that relay on *p-n* junctions, such as thermoelectric modules and solar cells. Pi frameworks that can be the basis of *n*-OSCs must provide sufficient stability of injected electrons relative to environmental quenchers such as oxygen and synthesis residues in and around OSCs. For thermodynamic stability of the radical anion to oxygen and water, the reduction potential of an *n*-OSC would need to be more positive than the standard calomel electrode (SCE) (89). A challenge of using such materials would be to prevent their accidental doping by environmental agents that would render them permanently conductive. The lowest unoccupied molecular orbital (LUMO) energy levels of most conjugated organic compounds lie outside the preferred ranges for electron transport.

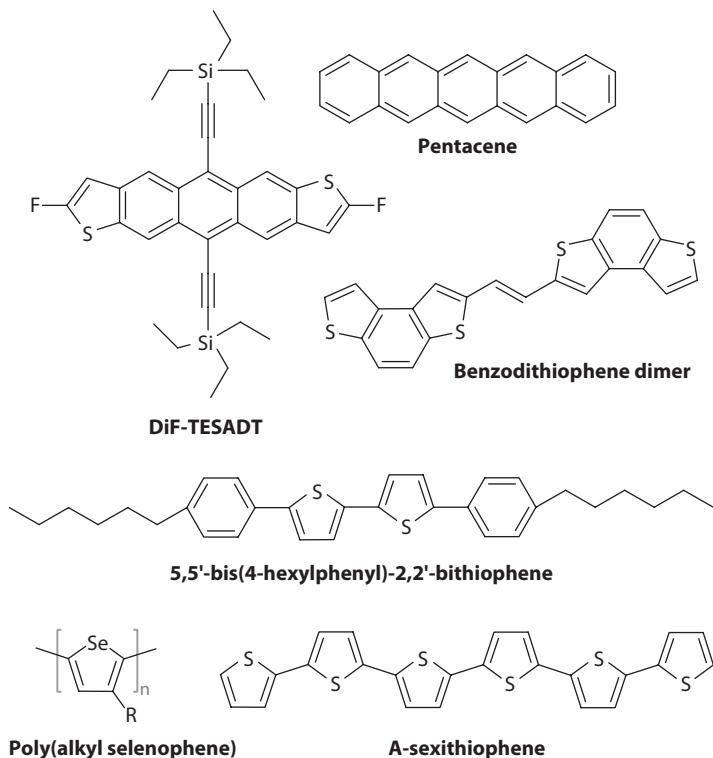


Figure 4

Some *p*-channel semiconductors.

In 2000, Katz et al. (90, 91) showed that thermally evaporated thin films of various *N,N'*-disubstituted naphthalenetetracarboxylic diimides (NTCDIs) (**Figure 5**) demonstrated high field-effect electron mobilities both in vacuum and in air. These materials exhibited mobilities on the order of $10^{-1} \text{ cm}^2 \text{ Vs}^{-1}$, even in air. Fluoroalkyl chains remote from the core play a role in allowing the compounds to be employed in air, although the exact mechanism remains unproven (92). Even a single CF_3 group on a small side chain such as benzyl greatly increased air stability (90, 93–95). More recently, other researchers have demonstrated high mobilities from other large-cross-section side chains such as cyclohexyl (96); substitution of the NTCDI core with electron-withdrawing groups to increase thermodynamic stability of radical anions (97–99); and use of extended diimides such as perylenetetracarboxylic diimides (PTCDIs) (99–107), anthracenedicarboximides (108, 109), and higher rylenes (110). A series of PTCDIs with small substituents such as core-chloro, core-fluoro, *N*-heptafluorobutyl, and *N*-phenethyl showed mobilities of $0.1\text{--}0.7 \text{ cm}^2 \text{ Vs}^{-1}$, with some retaining most of the mobility in air (102, 104, 105). A noteworthy electron-transporting polymer with a mobility of approximately $0.01 \text{ cm}^2 \text{ Vs}^{-1}$ was made by copolymerizing a PTCDI with dithienothiophene (111).

The most recently reported *n*-OSCs include trifluoromethyl-substituted fused rings (112), fused heterocyclic diones (113), perfluoroalkyl-substituted acenes (114), and naphthalenetetracarboxylic diimides with elaborated fluoro-substituted side chains (115). These build on a library of other *n*-OSCs that include oligothiophenes (116–119) substituted with perfluoroacyls, perfluorophenyls, polycyanovinyls, difluoromethylenes, aza heterocycles (120–123), perfluoropentacene (124) and aza-acenes (125), and terthienoquinoids (116, 126–129). With organosilane surface

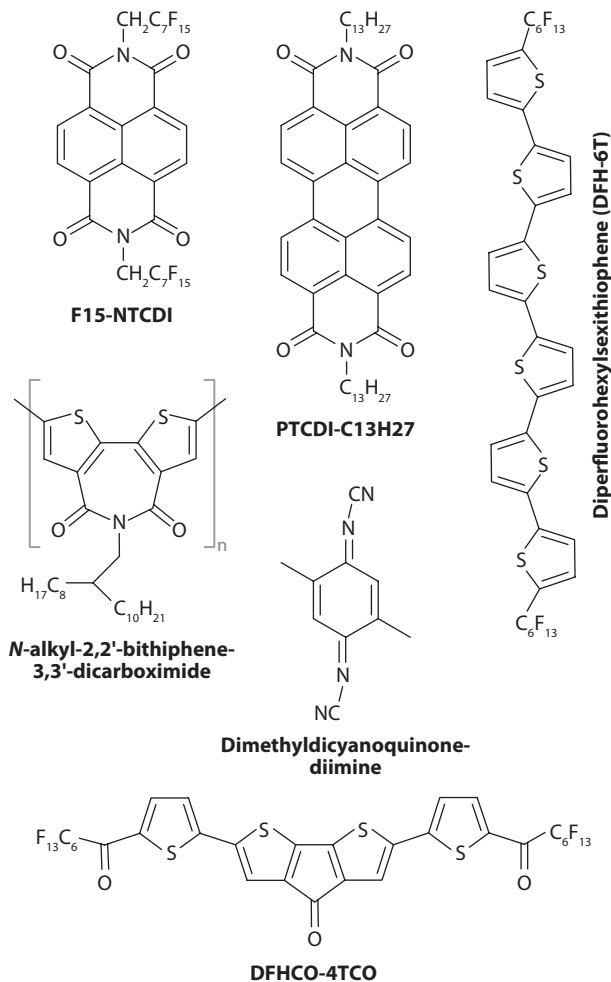


Figure 5

Some recently discovered *n*-channel semiconductors.

modifications and high-vacuum measurement, mobilities of 0.1–1.2 cm² Vs⁻¹ were observed from oligomers with aza ring positions and CF₃ termini, although other parts of the oligomer structure were sulfur rich and seemingly electron donating (121, 122, 130). Carbonyl functionalized quaterthiophenes and anthracenedicarboximides have yielded maximum mobilities of 0.34 cm² Vs⁻¹ in vacuum (109, 131). Fluoro-substitution remains a common theme among most of these compounds. Carbonyl functional groups are also effective in lowering the energies of injected electrons, whereas some other functional groups such as nitro and oxadiazole seem to be less beneficial (132).

ORGANIC DEVICES

Organic Field-Effect Transistors

An OFET is basically a capacitor, with a sandwich-like structure consisting of gate, dielectric, and semiconductor layers. Two metal contacts, the source and drain electrodes, are connected

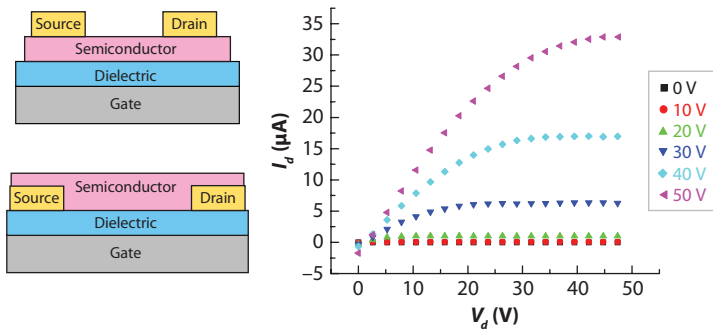


Figure 6

Layouts of organic field-effect transistors (OFETs) and current-voltage curves for various gate voltages of a typical organic transistor.

electrically to the semiconductor film, as shown schematically in **Figure 6**. This structure was initially developed for amorphous silicon transistors (133). For testing purposes, a conductive substrate is used as mechanical support and also acts as gate electrode. Insulating oxide or polymeric insulators coated on the gate, with or without surface treatment, act as dielectric layers. OFETs are usually operated in accumulation mode, with the source always grounded. Without applied gate voltage V_g , the intrinsic conductivity of most OSCs is low; when a source-drain voltage V_d is applied between two electrodes, very little current can flow through the semiconductor thin film, and the device is in the OFF state. When a gate voltage V_g is applied on the gate, a potential gradient is built in the capacitor structure, and charges then accumulate at the dielectric-semiconductor interface. Those charges are mostly mobile and lead to the formation of conducting channels between source and drain, charges move in response to the applied V_d , and the transistor is in the ON state.

Most OSCs are not intentionally doped so that charges are actually injected and extracted from source and drain electrodes. For most cases, there is mismatch between the Fermi level of metal electrodes and HOMO (LUMO) of p -channel (n -channel) semiconductors, which induces charge injection barriers. A nonzero V_g is required to shift the molecular orbital energy levels of semiconductors up or down so that the molecular orbitals become resonant with the Fermi level of metal electrodes and reduce the charge injection barriers. In addition, there are always trap states in the semiconductor film that are induced from impurities and defects (including grain boundaries), as well as molecules like H_2O and O_2 adsorbed from the environment. A nonzero V_g must be applied to fill these trap states before charges can be transported in semiconductor films. The threshold voltage V_t was defined to account for all those effects. In other words, V_t is the minimum gate voltage needed to turn on the organic thin-film transistor device.

With the gradual-channel approximation, the source-drain current I_d of the organic thin-film transistor device is given by Equation 1 (134, 135):

$$I_d = \frac{W}{L} C \mu \left[(V_g - V_t) - \frac{V_d}{2} \right] V_d, \quad 1.$$

where μ is the carrier mobility, C is the capacitance of the dielectric insulator per unit area, and W and L are channel width and length, respectively.

When $V_d \ll (V_g - V_t)$, the $V_d/2$ term is negligible, and I_d is linearly proportional to V_d ; the device is operating in the linear region. When V_d is increased to be comparable with V_g , there is no potential difference between the gate and the semiconductor near the drain electrode, and the mobile charges at that area are depleted. Further increases in V_d will induce a larger depleted

region in the conduction channel, and the source-drain current I_d is saturated and does not increase with increased V_d . In that case, the device is operating in the saturation region. This relationship is described by Equation 2, which was obtained from Equation 1 by assuming $V_d = V_g - V_t$. The drain current in the saturation region is called saturation source-drain current, denoted as $I_{d,\text{sat}}$:

$$I_{d,\text{sat}} = \frac{W}{2L} C \mu (V_g - V_t)^2. \quad 2.$$

Charge mobility μ defines the velocity per unit applied to the electric field of charge carriers. Mobility μ is usually a function of gate voltage. Although the charge transport mechanism in OSCs is still not fully understood, several models have been developed to interpret the gate voltage dependence of mobility (135–138). In general, there are traps distributed in OSCs. When gate voltage is increased, more traps are filled by the injected charges, leaving fewer traps retarding the movement of charges. Hence, charges move faster at higher gate voltage, which is consistent with the fact that mobility usually increases with increased gate voltage for most OFETs reported. In cases in which mobility does not seem to increase with increased gate voltage, contact resistance may have a relatively stronger effect on output currents at higher gate voltages, diminishing the apparent mobility.

***p-n* Semiconductor Junction Diodes**

Although diodes are seemingly less glamorous than FETs and have received much less attention from the organic electronics community, they also have a role to play in organic-based circuitry. Solution-deposited diodes could be useful elements of printable RFID and signal generation circuits. Such diodes are considered important enough for the RFID application that an IEEE standards working group has been formed to develop evaluation methods for them (announced at <http://grouper.ieee.org/groups/1620/2/>). In 2000, the Philips Corporation obtained a patent on an organic transponder, for which rectification was achieved by use of diodes of undefined composition (139). The 3M group demonstrated a prototype organic RFID circuit based entirely on OFETs, in which radio-frequency input is coupled directly to the logic circuitry without a rectification stage (140). The IMEC research center fabricated a 50-MHz RFID rectifying Schottky diode with pentacene as the sole semiconductor by utilizing the work function difference between gold and aluminum (6). Besides the RFID application, which may be problematic because of the circuit complexity and fierce competition from silicon-based components, organic diodes may exhibit useful sensitivities that would be independent of FET responses, such as for temperature (4, 141) and chemical sensors (142). **Figure 7** shows a current-voltage plot for a hybrid diode.

The physics of inorganic semiconductor diodes has been thoroughly treated in textbooks (143, 144). Doping profiles affect carrier concentrations, the nature of the depletion layer at the *p-n* interface, the junction breakdown voltages, and device speeds. Carrier mobilities control both the saturation current density of the *p-n* junction and the series resistance of the bulk semiconductors on either side of the junction. Carrier density and trapping (145) play a key role in controlling diode function; for example, such effects in the depletion layer are a significant source of deviation of diodes from ideal behavior. A large number of alternative inorganic *p-n* junction diodes have been reported, whereas organic/inorganic and all-OSC junctions have received relatively less attention (146).

There is some understanding of the electronic properties of the organic *p-n* junction, although this knowledge is limited compared with our understanding of inorganic *p-n* junctions and should be developed further considering the impact of organic *p-n* junctions on OLEDs and solar cells (147, 148). An early diode was fabricated through solution deposition of

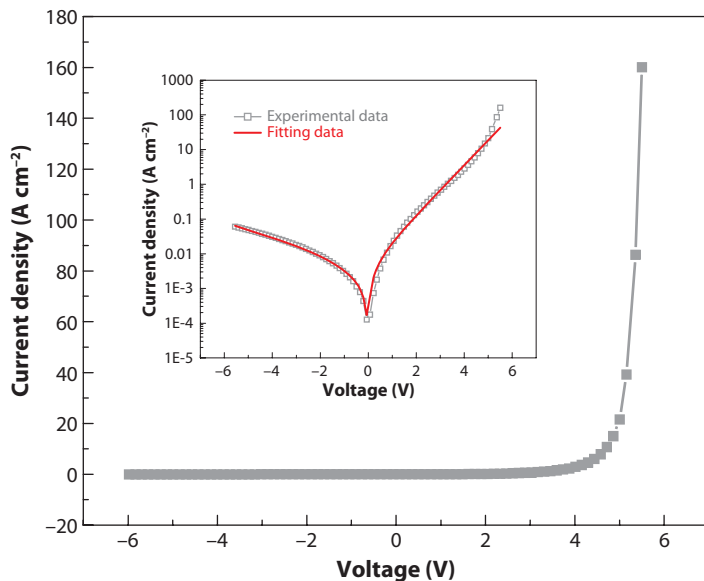


Figure 7

Current-voltage plots (linear and log scales) for a pentacene-ZnO *p-n* junction diode.

poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEHPPV) and vapor deposition of poly(3,4-dicyanothiophene) with gold electrodes on both sides (149). There, rectifying character was assigned to the *p-n* junction. Both dark rectification and photoconductivity were observed. An internal electric field was seen, but its origin was not completely defined. Ink-jet printing of a similar diode, with a cyano-substituted MEHPPV as electron carrier, was demonstrated elsewhere (150). An interfacial carrier density was observed in tris(8-hydroxyquinoline)aluminum (ALQ3) adjacent to the hole carrier *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine by use of bias-dependent capacitance measurements (151). Diodes using naphthalene tetracarboxylic dianhydride (NTCDA) and polymeric hole carriers operated as expected (152), with electron injection into the NTCDA defining the forward bias direction.

A molecular solid homojunction (**Figure 8**) was made from two layers of zinc phthalocyanine, one layer with an *n*-dopant and another layer with a *p*-dopant (153). The importance of this experiment was that the device had a degree of epitaxy between the layers, as in the case of inorganic diodes composed of two layers of the same semiconductor, differing only in the nature of the doping in each layer. In the case of the phthalocyanine diode, an insulating layer was inserted between the doped layers to prevent tunneling through the heterojunction. A built-in potential of 0.8 V was determined through use of capacitance-voltage measurements, although this was not strictly a junction potential because of the insulating layer. In a related device, the junction voltage at the interface of copper phthalocyanine and its perfluorinated analog increased charge carrier density and led to ambipolar transport when the two semiconductors were stacked in a bilayer (154).

The Katz group (155) recently prepared *n*-ZnO/*p*-pentacene and *n*-ZnO/poly[5,5'-bis(3-dodecyl-2-thienyl)-2,2'-bithiophene] (*p*-PQT-12) vertical *p-n* junction diodes on indium tin oxide (ITO)-coated glass. The current densities were 160 A cm⁻² and 350 A cm⁻², respectively, which were comparable to those of other recent organic vertical diodes. The DC rectification ratio at ± 5.5 V was approximately 3×10^3 for the ZnO/pentacene diode, and the turn-on voltage was

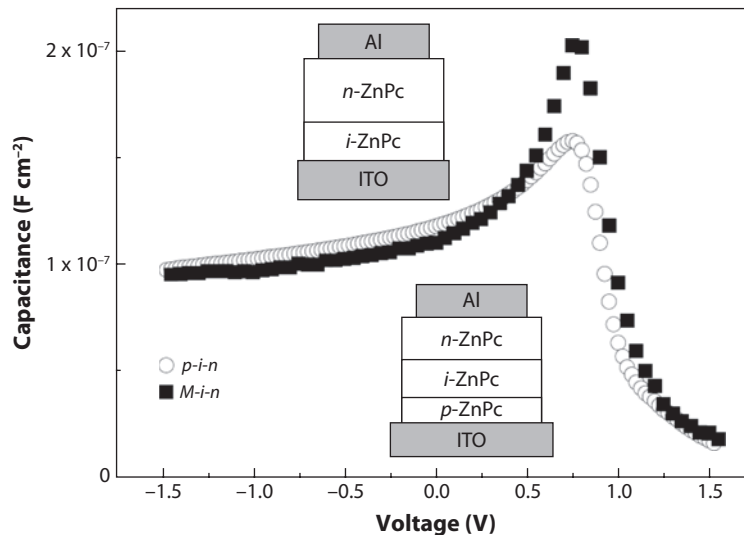


Figure 8

Capacitance-voltage plot showing the built-in potential of vertical phthalocyanine multilayers. From Reference 153.

approximately 1 V. The current density for the *n*-ZnO/*p*-PQT-12 diode reached 350 A cm^{-2} . With respect to open-atmosphere measurements, the response speeds of these devices are much higher than the previously reported organic vertical Schottky diode. Strong rectification is detected with frequencies on the order of 10 MHz, measured as wave outputs from oscillating inputs via an oscilloscope rather than as an integrated output over macroscopic time. This performance enhancement is attributed partly to the commensurate sizes of the ZnO grains (tens of nanometers) and domains of the OSCs deposited on top, as well as the overall high mobilities of the semiconductors (155).

Organic Thin-Film Transistor Sensors

Organic thin-film transistors offer great potential for applications in chemical and biological sensing for homeland security, environmental monitoring, industry manufacturing, and medical/biological detection. Besides the advantages of being easily processable, low cost, and compatible with plastic substrates, another essential advantage of sensors based on organic thin-film transistors is that the OSC compound can be chemically functionalized via covalently bonded side groups, which can make the adsorption of analytes of interest more favorable, thereby improving the selectivity of the sensor. Compared with inorganic devices, the binding chemistry of adding functional groups is better defined for OSCs, and synthetic chemistry provides great freedom to introduce various side groups to make the sensor more sensitive to analytes of interest, ranging from toxic or explosive vapors to biologically/medically important molecules. Two types of organic thin-film transistors have been studied extensively: sensors based on OFETs and sensors based on organic electrochemical transistors (OECTs).

For OFET sensors, analyte molecules diffuse into grain boundaries of the semiconductor film and interact with semiconductors in the conduction channel. Those analyte molecules can have various effects on organic OFETs, such as doping or quenching-induced charge-carrier-density

variation and dipole-induced trapping and retarding of charges. Those interactions alter the threshold voltages and the mobilities of devices and hence change the current flow through thin OSC films between source and drain electrodes.

Various approaches have been demonstrated to improve the sensitivity, selectivity, stability, and response speed of OFET sensors. Ultrathin OFET sensors with semiconductor layers only several molecular monolayers thick have exhibited enhanced sensitivity and response speed that are orders of magnitude higher than for conventional thick OFETs (156, 157). The first few molecular monolayers of OSCs define the conduction channels of OFETs. For OFET sensors with only a few molecular monolayers of semiconductors, the conduction channels are exposed to the environment. Analyte molecules can interact directly with the conduction channel without having to diffuse through a thick semiconductor film and hence enhance the sensitivity and response speed of OFET sensors by orders of magnitude. In addition to the improved sensitivity and selectivity of the OFET sensors, the application of ultrathin semiconductor films was also reported to improve the baseline stability of sensors (158).

A major challenge of OFET sensors is to achieve selective and specific detection. Organic transistors with functionalized receptor layers play an essential role in the improvement of the selectivity of OFET sensors. For example, alkyl- and alkoxy-substituted polythiophene exhibited a selective response to analyte vapors in terms of analyte alkyl chain length and analyte dipole moment, respectively (159). In addition, bilayer blend OFET sensors with a hydroxyl-functionalized semiconductor incorporated into a receptor layer above the OSC film exhibited an improved response to phosphonate vapors compared with a single-component device without functionalized receptor layers (160).

Although increasing progress has been made in improving the selectivity of OFET sensors, further enhanced specific detection of analytes with similar chemical structure or physical properties remains an open issue, for example, to discriminate analytes with potential interference analytes and, even more precisely, to discriminate among exposures to different optical isomers of the same chemical skeleton. Recently, Torsi et al. (161) demonstrated that bilayer OFET sensors endowed with chiral side groups exhibit different responses upon exposure to optical isomers in the tens-of-parts-per-million concentration range (**Figure 9**). Here the receptor layer with built-in enantioselective properties played a key role in achieving chiral differential detection (161).

Arrays of sensors with different sensitivities/responses to individual analytes have also been used to improve the selectivity of sensors. Metal-free phthalocyanines and phthalocyanines with Co, Ni, and Cu metalation were used as active materials of chemical sensors and show contrasting oxidation/reduction behaviors to the H_2O_2 owing to the catalytic redox contrast in the sensor array (162).

Humidity is a potential interfering factor for OFET sensors. Most OFETs exhibit degraded performance in a humid environment (163–165). Furthermore, developing OFET sensors that are suitable for aqueous systems remains a big challenge. Recently, Bao et al. (166) reported a way to circumvent this aqueous-incompatible problem by the application of ultrathin gate dielectric layers and OSCs containing long aliphatic side groups. Ultrathin, cross-linked gate dielectric polymers enable low-voltage transistor operation in aqueous media, and OSCs containing long aliphatic side groups are considered to be less sensitive to H_2O owing to the close-packed hydrophobic surfaces. OFET sensors made from 5,5'-(7-dodecyl-9H-fluoren-2-yl)-2,2'-bithiophene (DDFTTF) exhibited stable operation in aqueous media and achieved detection at the hundreds of part-per-billion concentration level.

Although most OFET sensors use crystalline OSC films, OFETs functioning with amorphous semiconducting polymers can also detect NO_2 . The threshold voltage, rather than the charge mobility, shows the strongest sensing response, which is attributed to the absence of grain

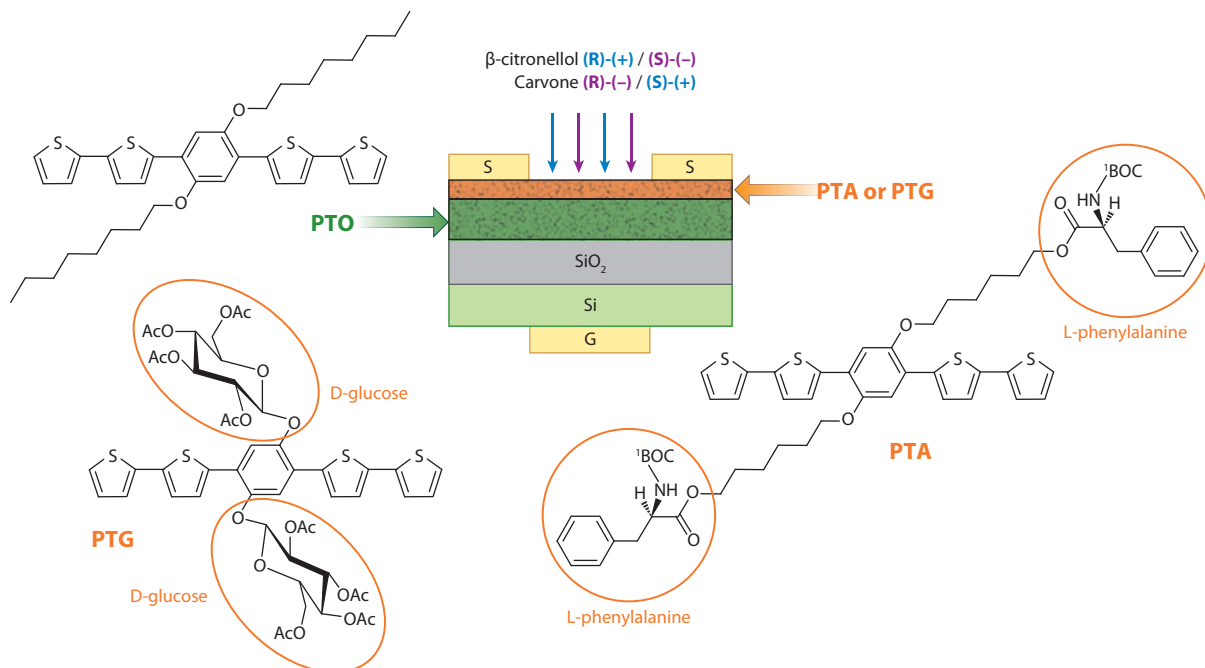


Figure 9

Bilayer organic field-effect transistor sensors endowed with chiral side groups (*orange circles*). Redrawn from Reference 161 with permission.

boundaries (167). Cao and coworkers (168) reported in situ fabrication of organic polymer sensors with polymer semiconductor and gold electrodes fabricated simultaneously by soft lithography techniques, which combined nanotransfer printing and solventless polymerization inside stamp channels.

Device sizes of OFET sensors also play an important role in chemical vapor detection. Dodabalapur and colleagues (169) reported scaling behavior of the sensing response. When the dimension of OFET sensors was reduced to the nanoscale, the sensor behaved differently from large-scale devices (169). Pentacene OFET sensors with a long channel length showed a decrease in source-drain current upon exposure to 1-pentanol vapor, whereas an increase in the current was observed for a device with a channel length of less than 150 nm.

Besides OFETs, sensors based on OECTs have been widely studied as biological sensors. For OECT sensors, an electrolyte layer, instead of the insulator layer typically in OFETs, was inserted between the OSC layer and the gate electrode. Source-drain current is modulated by electrochemical doping/dedoping of the semiconductor by ions from the electrolyte layer. A small change in the ion concentration can induce a large change in the source-drain current (170). Malliaras and colleagues (171, 172) have demonstrated the use of OECT sensors in the detection of glucose at concentrations down to 1 μM and observed reversible responses.

FUTURE PROSPECTS

The devices described in this review, and the materials used to make them, have been rigorously demonstrated to function in individual devices. The next great challenge in organic electronics is to

scale up their function in terms of numbers and degree of interconnection. For example, although circuits with multiple different types of transistors have been arduously produced, they now need to be made more elegantly and to perform more elaborate information processing. Arrays of sensors need to be diverse enough to discriminate among related analytes in a “fingerprint” sense. The energy losses of organic circuits, such as energy losses from contact resistance and hysteresis, need to be better controlled, and conversely, opportunities to use organic electronics in energy harvesting need to be sought. Finally, to realize applications such as artificial skin and plastic-based robotics, it will be necessary to combine the elementary functions of individual organic devices into coordinated, higher-order operations on single substrates.

DISCLOSURE STATEMENT

The authors are not aware of any biases that might be perceived as affecting the objectivity of this review.

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Errata

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