

FEATURE ARTICLE

The Physical Chemistry of Organic Field-Effect Transistors

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This review covers fabrication and performance of organic-based field-effect transistors (FETs). The electronic states of organic solids, crystal growth processes, film alignment and morphology, and charge transport mechanisms are discussed. Discontinuities in the active layers and nonidealities in the device behavior are highlighted, and are presented as opportunities for further physical chemistry investigation.

Organic-based semiconductors in thin film form are projected to be active elements in plastic-based circuits, particularly those using field-effect transistors (FETs) as switching or logic elements.^{1,2} Such circuits are not expected to compete with silicon technology in the production of high-end products, such as computer memories, but rather as components of lower resolution, mass-produced items, such as identification tags, smart cards, and pixel drivers for displays. The performance of organic semiconductors, as judged by the fundamental characteristics of mobility and on/off ratio to be discussed below, may only approach that of amorphous silicon. On the other hand, these materials offer the advantages of facile processability and chemical tunability. The processing advantages can be gained most fully through the use of solution or liquid phase deposited semiconductors or by the use of extremely rapid sublimation or thermal transfer techniques compatible with a reel-to-reel fabrication mode.

A typical FET is constructed with the following basic components as shown in Figure 1A: electrodes (i.e., gate, drain, and source electrodes), a dielectric layer, and a semiconducting layer. The current flow between the drain and source electrodes (I_{DS}) is modulated by the applied gate voltage (V_G), as may be seen in the typical current–voltage plot in Figure 1B. An “off” state of a transistor is when no voltage is applied between the gate and the source electrodes ($V_G = 0$). I_{DS} is usually very low in the “off” state as long as the semiconducting material is not highly doped. When a voltage is applied to the gate, charges can be induced into the semiconducting layer at the interface between the semiconductor and dielectric layer, analogous to charging a capacitor. As a result, the drain-source current increases due to the increased number of charge carriers, and this is called the “on” state of a transistor. For p-channel transistors, holes are the major charge carriers while electrons are the major charge carriers for n-channel transistors.

The key parameters in characterizing a FET are its field-effect mobility and on/off ratio. Field-effect mobility quantifies the average charge carrier drift velocity per unit electric field, whereas on/off ratio is defined as the drain-source current ratio between the “on” and “off” states. Field-effect mobility can be deduced from eq 1, which describes the drain-source current characteristics in the saturation region of the current–voltage curve as a function of gate voltage. In eq 1, V_0 is the extrapolated

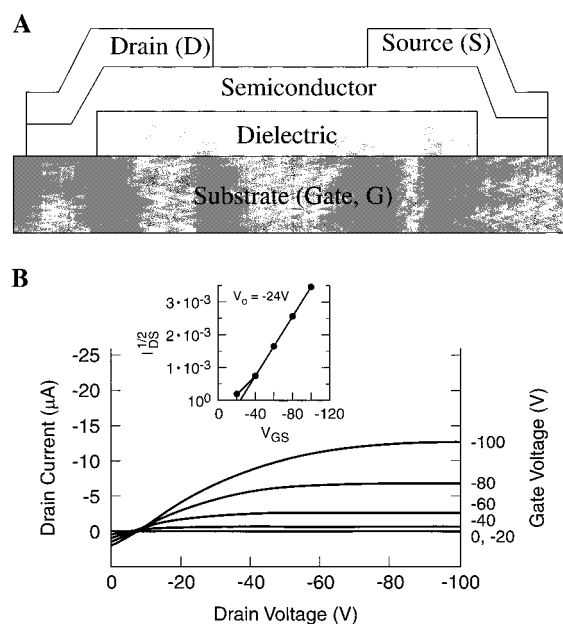


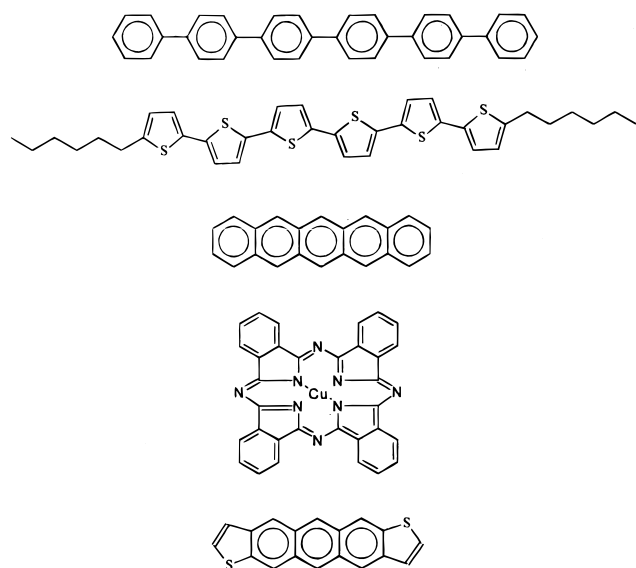
Figure 1. (a) Schematic diagram of a “top contact” FET. The gate electrode lies at the substrate–dielectric interface. The alternative “bottom contact” geometry has the source and drain on the semiconductor–dielectric interface. (b) Drain current versus drain voltage of a bis(benzodithiophene) FET with $W/L = 10$, deposited at a substrate temperature of 100 °C. The inset shows the plot of the square root of drain voltage versus gate voltage, used to calculate threshold voltage and mobility. The flatter parts of the curves, at the right of the main plot, indicate saturation currents. Copyright 1997 Wiley-VCH.

threshold voltage, μ is the field-effect mobility, W is the channel width, L is the channel length, and C_i is the capacitance per unit area of the insulating layer. The slope of a plot of $I_{DS}^{1/2}$ vs V_G is equal to the square root of $WC_i/(2L\mu)$, from which field-effect mobility can be calculated.

$$I_{DS} = \frac{WC_i}{2L} \mu (V_G - V_0)^2 \quad (1)$$

The “on/off” ratio depends strongly on the gate voltage used for calculation. Comparisons of on/off ratios can be made only

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when the same gate voltages are used for both “on” and “off” states. The values quoted in this article are generally measured for gate voltages between 0 V (“off” state) and 100 V (“on” state). For a high performance FET, the field-effect mobility and on/off ratio should be as high as possible. For example, field-effect mobilities of greater than 0.1 cm^2/Vs and on/off ratio greater than 10^6 are needed for the driving circuits in liquid crystal displays.

Great progress has been made in the development of semiconducting organic thin films. The initial demonstration of transistor activity in these films was with a narrow group of p-channel thiophene oligomers³ (referred to as αnT where n indicates the number of 2,5-linked thiophene rings) and polymers.^{4,5} The reported mobilities were on the order of 0.01 cm^2/Vs or less, and on/off ratios (where off refers to zero volts between source and gate) were <100 . During the past few years, a much broader selection of molecular solids and polymers has been developed, all with mobilities well above 0.01 cm^2/Vs and achievable on/off ratios greater than 1000 versus zero gate field. p-Channel compounds in this category include poly(phenylene)s,⁶ end-substituted thiophene oligomers,^{7,8} pentacene,⁹ phthalocyanine¹⁰- and thiophene¹¹-based fused ring compounds, and regioregular poly(3-alkylthiophene)s.¹² Typical chemical structures of molecular semiconductors are displayed in Chart 1. Transistor assemblies such as ring oscillators have been constructed with pentacene as the active material,¹³ and hybrid FET-LED “smart pixels” have been made operational.¹⁴ Furthermore, some of the newer compounds have displayed n-channel activity, including C_{60} ,¹⁵ perfluoro copper phthalocyanine,¹⁶ and lower-mobility naphthalene¹⁷ and perylene¹⁸-based compounds, enabling all-organic complementary circuit (inverter and ring oscillator) fabrication for low-power applications.¹⁹ Several reviews have appeared that summarize the results, focusing on molecular design from the organic chemistry perspective, and device characteristics from the electrical engineering perspective.^{20–23,25}

The organic semiconductors that display the best mobility, on/off ratio, uniformity over large areas, and reproducibility have been deposited by vacuum sublimation. However, some recent efforts in this field have focused on processes for solution deposition of small molecules⁸ and polymers,^{12,24} as well as integration of these processes with other nonlithographic device fabrication techniques.²⁵ Mostly preliminary results have been

reported for the solution-phase deposition of molecular solids as TFT semiconductors,^{8,11,26,27} with one more elaborate study involving spin-coating under very specific conditions.²⁸ Greater progress has been demonstrated with polymeric semiconductor solutions, especially regioregular poly(hexylthiophene) (mobilities 0.01–0.1 cm^2/Vs), and lower mobility poly(thienylene-vinylene) prepared with an in situ conversion step, from which complex circuits were fabricated.¹ Large-area coverage and uniformity are easier to achieve with polymer solutions, although the spin-coating and unusual temperatures that are sometimes required are not ideal in a reel-to-reel process. However, it is difficult to purify polymers to the level required for high mobilities and on/off ratios, and batch-to-batch variability has been observed. Smaller molecules, on the other hand, can be purified to the level where on/off ratios above one million can be obtained in accumulation mode, without the rigorous exclusion of O_2 .

Although the semiconductor investigations have provided the most novel discoveries, materials development and optimization will be required for the dielectric and electrode materials as well. For example, a recent advance in the design and deposition process of high dielectric constant inorganic gate insulators (in place of the more usual SiO_2 , polyimide, poly(methyl methacrylate), or poly(vinylphenol)) has enabled the demonstration of FETs that operate at significantly reduced voltage.²⁹ Work functions of source/drain contacts (e.g. gold, silver paste, carbon black, and polyaniline) strongly influence the current–voltage relationships of FETs, much as they do in the case of LEDs. Newer microcontact printing techniques provide a conceivable route to devices with high width/length ratios and therefore higher current outputs than are attainable with conventional shadow masking and screen printing. Some of the most pressing issues in the field of organic electronics involve the interfaces between the active materials and the conducting or insulating layers.

This review aims to highlight some of the physical chemistry behind the fabrication and performance of organic-based FETs. The relevant subtopics span a wide range, and include the electronic states and energy levels of organic solids, the kinetics and mechanism of crystal growth, the occurrence and effect of defects and impurities, charge carrier transport mechanisms, surface alignment, and polymer morphology, entanglement, and phase separation. It will become obvious that our understanding of these phenomena is insufficient to fully explain some device characteristics, or optimize device design. Thus, in addition to providing a brief summary of what has been uncovered, opportunities for further physical chemistry investigation are also highlighted.

Crystal Packing and Intrinsic Mobility in Single Crystals

Organic semiconductors are molecular solids that rely upon weak electronic interactions among discrete molecular constituents for charge migration pathways, and are thought to follow a “localized” charge transport model. This is in contrast to inorganic semiconductors such as silicon and germanium, in which charge may move within a three-dimensional covalent network.²³ Energies for injecting charge into molecular solids are determined primarily by molecular orbital energy levels. For FET operation, holes are conveniently injected into compounds with oxidation potentials at or slightly below 1 V vs the standard calomel electrode (slightly above 5 eV below vacuum energy). Electrons are injected somewhat below 0 V, or approximately 4 eV below vacuum. Lower potentials for oxidation and higher potentials for reduction would further ease

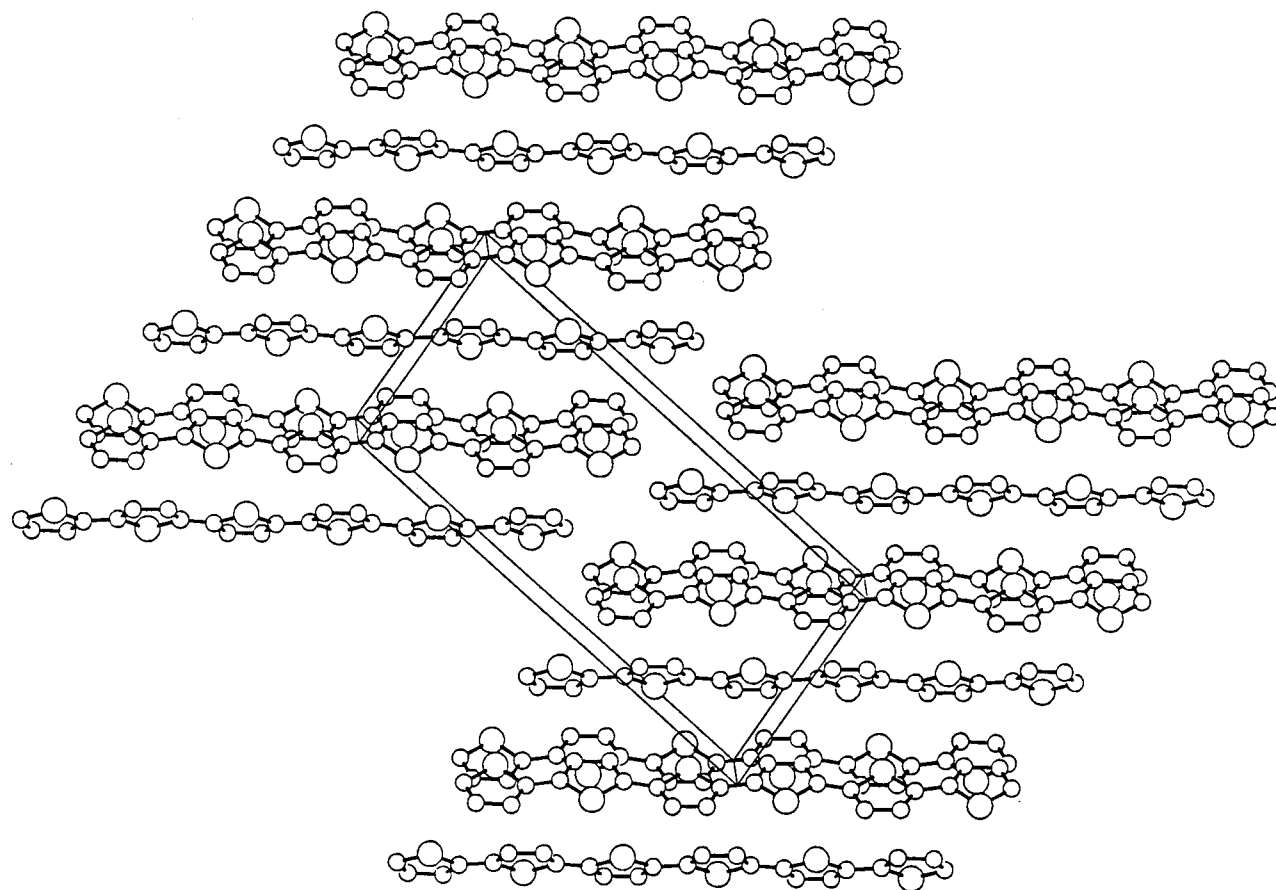


Figure 2. Packing diagram of α -6T single-crystal high-temperature polymorph, showing the herringbone motif. Copyright 1995 Materials Research Society.

charge injection but would also make doping much more likely. In fact, given the closeness of the reduction potential of oxygen and the oxidation potential of p-channel semiconductors, it is likely that most of the high mobility hole carriers are slightly doped by oxygen from the air, and some oxygen-derived off current is to be expected.^{22,30}

Spectroscopic evidence is that these orbitals are not extensively delocalized over many molecules.³¹ Once injected, the mobility of the charges is determined by the degree to which the charge-accepting orbitals of neighboring molecules overlap, subject to attenuation by traps and barriers. Unlike the case of solid state inorganic materials, movement of charge from one molecule to another is phonon-assisted, so that mobility generally increases with temperature in organic solids.²¹ However, in some exceptional cases, the high magnitude (ca 1 cm²/Vs) and small temperature dependence of the mobility suggest that the charge localization–delocalization boundary may be approached. For example, a pentacene sample displaying mobility of 1.5 cm²/Vs shows essentially no mobility dependence on temperature below 120 K.³²

One reason for the promise shown by semiconducting crystalline solids is the high degree of structural organization in these materials, enforcing a significant and uniform degree of orbital overlap.²³ This overlap is usually due to an edge-to-face interaction characteristic of a herringbone geometry, as illustrated for the prototypical compound α -6T in Figure 2. Numerous thiophene oligomers and condensed ring compounds share this crystal packing motif,^{31,33} as shown by crystal structures of compounds as large as α -6T,^{34,35} α -8T,³⁶ and pentacene.³⁷ However, an interesting exception has been recently reported, a dithienothiophene dimer that packs in parallel, face-to-face stacks.³⁸

Most recent results suggest that the mobility of films of unsubstituted thiophene oligomers increases with length, up to the octamer.³⁹ It is appealing to attribute this trend to the increased intermolecular overlap achievable with the larger molecules. However, the different concentrations of dopants present in the various materials, and the greatly increased susceptibility of the shorter radical cations to environmental quenching³ leave open the possibility that the mobility increase is not entirely due to π overlap. The difficulties in selectively synthesizing and purifying a compound as insoluble and easily oxidized as α -8T and in accounting for injection barriers have made confirmation of this result elusive.^{3,40} More convincing comparisons can be made among single crystal semiconductor samples, which presumably are the most chemically and morphologically pure samples obtainable. The mobilities of α -4T and α -6T in single crystal form, determined both by measurement of space charge limited current and field effect current, are 0.05 and 0.5 cm²/Vs, respectively, the result expected from increased overlap of the longer molecules.⁴¹ Pentacene, which has the highest thin film mobility reported to date, also displays the strikingly high single crystal mobility of nearly 2 cm²/Vs. The obstacles to obtaining these data are considerable, and include the fragility of the crystals, their unevenness that decreases the intimacy of contact and dielectric interfaces, and the series resistance imposed by the necessity of traversing the low mobility direction (long axis) of the crystal in certain geometries.³⁴ A schematic diagram of the experimental setup used to characterize these crystals is shown in Figure 3.

Materials in Real Devices

It is a tempting goal to utilize single-crystal mobilities in thin film devices. However, single-crystal character in an organic

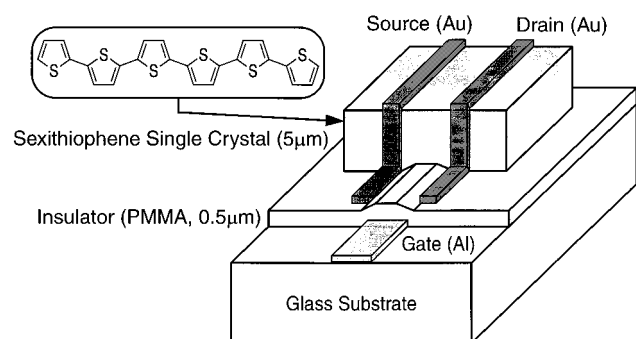


Figure 3. Schematic view of the FET made with an α -6T single crystal on a poly(methyl methacrylate) insulating layer. Used with permission from ref 34. Copyright 1996 Wiley-VCH.

semiconducting film is very rare,^{42,43} and to our knowledge, unknown in a film deposited from solution. Most semiconductor depositions instead lead to polycrystalline coverage.

The grain size and continuity of polycrystalline semiconducting films are strongly dependent on the substrate temperature during deposition. Low temperatures produce very fine grains that pose numerous boundaries and discontinuities in a film. High temperatures lead to much larger grains, but sometimes

these are separated by spaces that pose insurmountable barriers to charge transport, as shown in Figure 4.^{44,45} Generally, there is an optimal temperature, somewhat above ambient but well below the melting or sublimation point, where grain boundaries are not too numerous and intergrain connections are still semiconducting. Observation of continuous or discontinuous morphology by microscopy is directly correlated to high or low charge mobility assessed by device characteristics. Local continuity and alignment homogeneity can be improved through thermal annealing,²³ but this procedure leads to cracking on a macroscopic scale due to coefficient of thermal expansion mismatches between semiconductor and substrate.⁴⁶

Assessments of morphology using microscopic methods are limited in that the most important morphology is that of the first few monolayers of a FET film. Both experimental evidence and computer simulation have established that the injected charge (the channel) is confined to a region very near the dielectric interface.⁴⁷ Probes of roughness and discontinuity on the top of a film that is several times thicker than this region will only hint at the morphology of the region where almost all of the charge is transported.

New surface analytical and electrical microprobe techniques allow the treatment of small domains of polycrystalline films

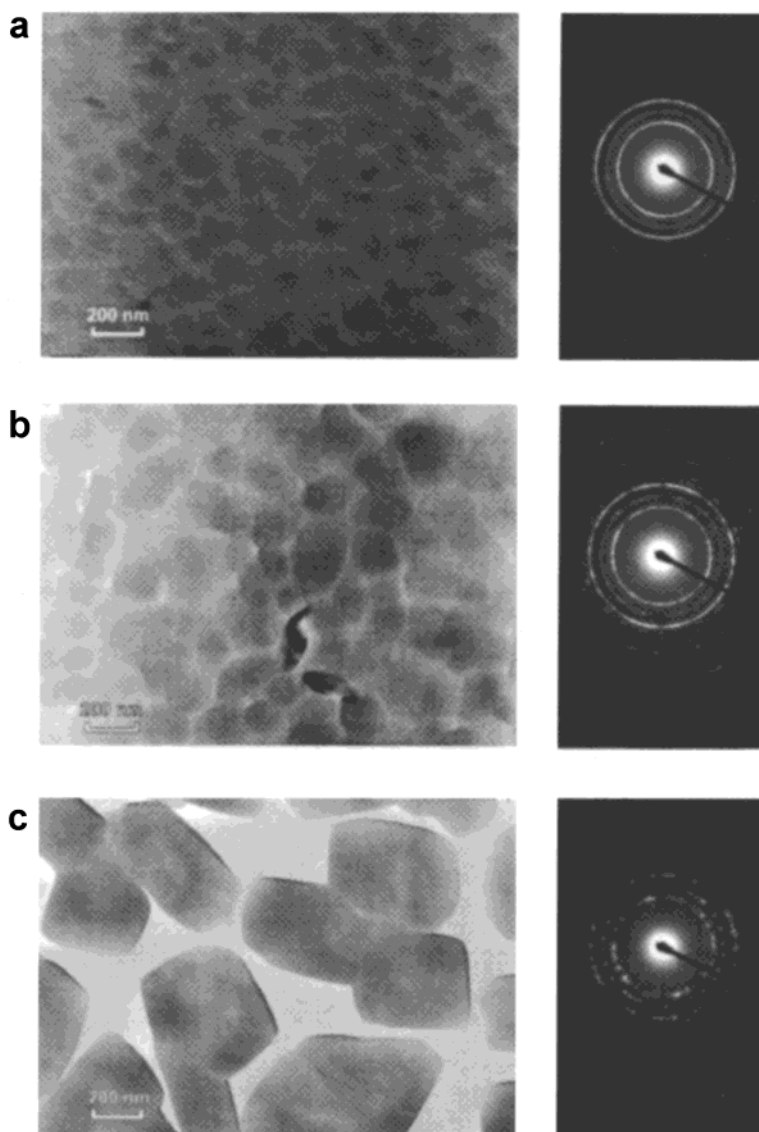


Figure 4. Transmission electron micrographs and selected area diffraction patterns of anthradithiophene films deposited at substrate temperatures of (a) 25 °C, (b) 85 °C, (c) 100 °C. Copyright 1998 American Chemical Society.

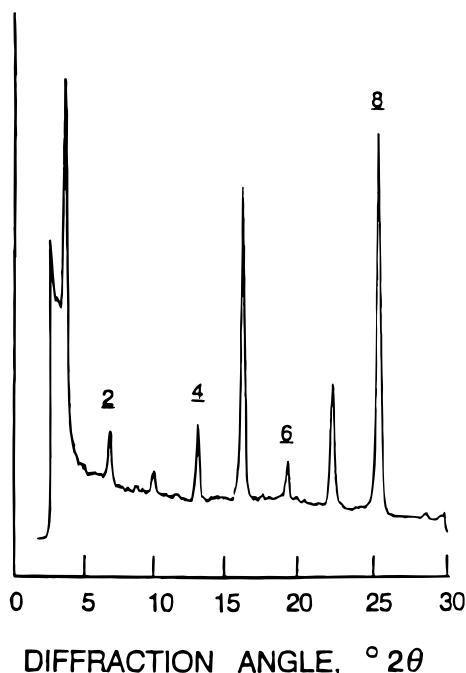


Figure 5. X-ray diffractogram of dihexyl- α -4T films deposited on Si/SiO₂ by sublimation at ambient temperature. Copyright 1998 American Chemical Society.

as miniature single crystals. Exact thicknesses and birefringences of such domains have been determined using optical polarization microscopy combined with atomic force microscopy.⁴⁸ Electrical properties of such domains have been observed using conducting probe atomic force microscopy, leading to detailed descriptions of various grain boundary and contact resistances.⁴⁹ For example, substantial mobility in single α -6T grains of monolayer thickness and distinct grain boundary resistance in α -6T grain “dimers” have been measured.⁵⁰

Just as there is an optimal, elevated temperature for the preferred morphology at low vacuum deposition rates, low deposition rates on heated substrates also lead to maximized film orientation during vacuum deposition.^{39,40} A thermodynamically equilibrated film is produced that features nearly perpendicular alignment of individual molecules with respect to the substrate. A signature of this kind of alignment is the observation of strong X-ray diffraction peaks corresponding to the first and higher order reflections of layer planes separated by the approximate length of the long axis of the molecule, as exemplified by Figure 5. The reasons for this alignment, observed in a wide range of compounds, are not fully understood, and the dynamics are hardly understood at all.⁵¹ A tradeoff among intermolecular, π surface–substrate, and molecule edge–substrate interactions along with entropies of packing may be invoked. Lower deposition temperatures, on the other hand, lead to a “kinetic film” incorporating various proportions of parallel aligned and disordered molecules.²³ Examination of these temperature dependencies is complicated by the polymorphism of many semiconductors that depends on deposition temperature and rate.⁴⁴ Deposition dynamics are even more complex when molecules are nucleated and deposited from solution, where various solvent–solute and solvent–surface interactions create many more pathways for film formation and makes the alignment of the film less predictable. In addition, all of the uncertainty regarding sites and rates of nucleation and crystal growth is much more of an issue when attempting to cast films from solution. The incorporation of medium-sized terminal alkyl substituents, especially *n*-hexyl, imparts a liquid crystal-like

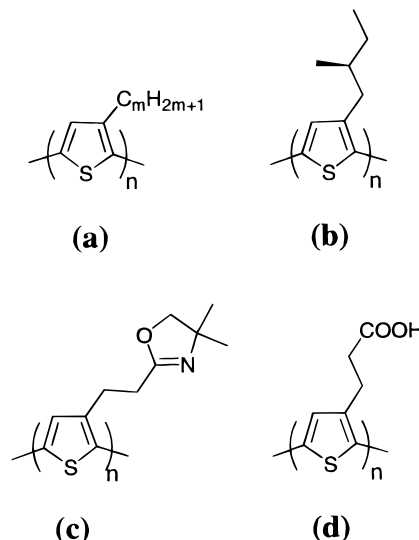


Figure 6. Chemical structures of regioregular polythiophenes.

behavior to many rigid ribbon-shaped molecules, including oligomers and fused ring compounds, and increases their propensity for perpendicular alignment and the formation of large ordered domains, both from vapor phase and solution.^{7,21,23,40} On the other hand, it is possible to deposit some of these molecules with purely *parallel* alignment on very nonpolar surfaces such as metals, graphite, and fluoropolymers, but FETs have not been extensively investigated in these situations.⁵²

In contrast to the high mobility molecular solids, where molecules generally adapt an edge-on orientation with the longest molecular axis perpendicular to the substrate surface,⁵³ polymeric semiconducting materials favor a different conformation where the polymer backbones are parallel to the substrate surface with the alkyl chains between the backbones assembled in an interdigitated fashion, directed perpendicular to the substrate.¹² Nevertheless, in both cases the π -stacking direction is in the plane of the substrate and facilitates charge carrier transport in the plane.

The highest field-effect mobility (0.1 cm²/Vs) among soluble polymers has been obtained with regioregular poly(3-hexylthiophene) (PHT).^{12,24} Transistors made from regioregular poly(3-alkylthiophene)s with various side chains, such as octyl (POT) and dodecyl (PDT) substituents, have also been fabricated and their electrical characteristics have been studied.⁵⁴ POT has a similar field-effect mobility as PHT, while PDT has a much lower mobility of the order of 10^{−6} cm²/Vs. The degree of π -overlap does not seem to be affected by longer side chain length as indicated by similar electron diffraction patterns for all polymers. The higher volume fraction of insulating side chains for PDT may contribute to its low field-effect mobility.

The bulkiness of the side chains has a direct effect on the degree of π -overlap and field-effect mobility of the substituted regioregular polythiophenes.⁵⁵ Poor molecular ordering and low crystallinity have been observed for regioregular polythiophenes with bulky (Figure 6a) or carboxylic-substituted side chains (Figure 6d), and the resulting transistor devices showed low field-effect mobilities (less than 10^{−5}–10^{−4} cm²/Vs).⁵⁵ In another example, a chiral alkyl-substituted regioregular polythiophene (Figure 6b) has shown crystallinity. However, the π – π overlap distance between the polythiophene backbones increases substantially (i.e. to ca. 4.3 Å vs 3.8 Å for PHT) after the introduction of methyl branches in the side chains. The field-effect mobility of this polymer is reasonably high compared to many solution-processable conjugated polymers (i.e., of the

order of 10^{-3} cm²/Vs), but it is still an order of magnitude lower than regioregular PHT. These results indicate that the nature of the side chains has a critical impact on the self-assembly, crystallization, and semiconducting properties of regioregular poly(3-alkylthiophene) derivatives. High crystallinity and high transistor performance are obtained only with regioregular polythiophenes that contain nonsterically hindered linear side chains.

The interchain hopping mechanism for charge transport requires that the pi-frameworks of molecules be highly overlapped. Preferably, most of the polycrystalline domains have similar molecular orientations in the plane of current flow. Efforts have been made to direct polymer chain orientation in thin films for transistor applications using Langmuir–Blodgett (LB) technique⁵⁶ and utilizing highly oriented friction-transferred poly(tetrafluoroethylene) (PTFE) on a SiO₂ substrate.⁵⁷ In both cases, regioregular PHT was the active semiconducting material. While there are indications of anisotropic alignment of polymer chains by optical measurements, the electrical measurements have not been conclusive. No anisotropic electrical properties were observed for PHT LB films, possibly due to the nonuniformity and cracking typical for nonamphiphilic polymer LB films.⁵⁶ Friction transferred PTFE has a high density of ridges and grooves on the ten-nanometer scale running along the friction transfer direction. Solvent cast PHT deposits with a significant tendency for the polymer chain axis to align along the PTFE friction transfer direction. The field effect mobility was found to be highly anisotropic, with the larger mobility along the PTFE friction transfer direction. Both intrinsic as well as topological factors may cause this anisotropy.⁵⁷

Electronic Effects in Real Devices

Contact resistance has a major influence on the characteristics of some devices. For example, this resistance may mask a mobility that increases with gate voltage, as the resistance becomes a dominant circuit element. Both work function mismatches between metal and semiconductor and chemical reactivity of metals with the semiconductors may contribute to this resistance. It is not believed that gold poses a particularly high barrier to p-channel compounds,²² but this is a problematic assumption for n-channel compounds and even for the higher band gap p-channel materials such as α -4T. This resistance is not gate bias dependent, as it originates far from the dielectric interface where the gate voltage has its main effect, especially in top contact devices. It has been shown that intercalation of a “charge injecting” material at the source and drain electrode interfaces, for example, TCNQ at the α -4T–gold interface, lessens this effect and increases the apparent mobility.^{39,58} A variety of spectroscopic techniques have been used to probe the injection barriers between organic semiconductors and both metallic and semiconducting inorganic materials,^{59,60} but clear, universal dependencies on metal work function, interface dipole, and/or organometallic surface reactions have yet to emerge.

A different sort of series resistance can arise from short-channel effects.^{47,61} In some situations (low channel length, high source-drain voltage), a depletion region is formed near the source and/or drain contacts that occupies a significant fraction of the channel length. Conduction in this region is space charge limited, rather than channel mediated, and can be modeled by a parasitic resistance placed in series with the channel. An equivalent circuit incorporating this resistance is shown in Figure 7. A more dramatic kind of “short-channel” effect is observed when the channel length is below 50 nm, on devices where the dielectric is a single, 2-nm-thick alkylsilane monolayer.⁶²

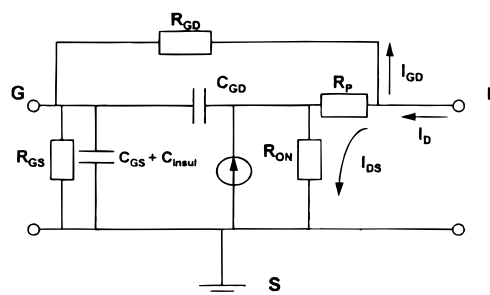


Figure 7. Equivalent circuit for a FET including parasitic elements. S, D, and G refer to source, drain, and gate electrodes, and R, C, and I indicate resistance, capacitance, and current, respectively. The resistance of the FET in its “on” state is R_{ON} , while the parasitic resistance is R_P . Copyright 1995 American Institute of Physics.

Traps are a particular problem in fabricating n-channel semiconductor devices, because oxygen itself is reduced easily enough to act as an electron trap when devices are operated in air.²¹ In addition, the protons of water can hydrogen-bond to functional groups such as carbonyls attached to the semiconductors, especially in their radical anion forms, also leading to trapping. There is very little chemical understanding of the effect of specific dielectric surface functional groups on the mobility of the overlying semiconductor, but one can easily imagine the creation of electronic inhomogeneities by such groups. The fact that such defects would be present at the exact layer where most channel conduction occurs would exaggerate their influence on device performance.

The gate bias dependence of the field effect mobility may be correlated with the presence of mobile charges, as reflected in the hysteresis of drain current–gate voltage plots for unsubstituted thiophene oligomers.³⁹ The varying mobility may reflect a distribution of states into which charges are injected, with the states characterized by a range of energy barriers for release of the charge, or detrapping. At different degrees of charge injection, a further incremental charging may fill higher mobility states than had been the case for lower-voltage charging, or simply contribute to an overall increase in charge density that increases the probability of hopping events.⁶³ It is also possible that the injection of a quantity of charge alters the activation energy distribution of the remaining unfilled states, so that a gate-dependent mobility may be intrinsic to the material.^{22,64} There may even be a significant relaxation time associated with the reorganization of a film to its most stable mobility state following charge injection or filling of deep traps.²² A sharp increase in mobility at a particular gate voltage can appear as a threshold voltage well into the accumulation regime. This may be observed in polymers as well as small molecule solids.²⁴

Increases in mobility through intentional doping of polymers and small molecules, especially in disordered solids, may be explained in similar ways. In addition, the dipoles created through intermolecular charge transfer from dopants to semiconductors must affect the transport energetics.^{63,65} It seems that a variety of high and low mobility materials show augmented mobility in the presence of dopants in the form of diffused gases from the ambient, included metals, or counterions introduced during synthesis.^{3,23,66} This doping can be photoassisted.³⁰ Such mobility increases are not particularly useful, since conductivity increases faster than mobility when dopants are introduced (except possibly from metal islands), and the on/off ratio suffers, eventually decreasing to unity.⁶³ The relationship between the conductivity and mobility increase is similar for a wide variety of compounds with intrinsic mobilities below 0.001 cm²/Vs, as

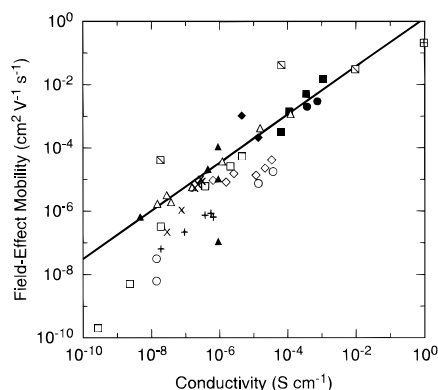


Figure 8. Dependence of field-effect mobility on film conductivity, where each kind of mark represents a different amorphous organic semiconductor. Used with permission. Copyright 1994 Elsevier Science.

suggested by the plot in Figure 8.^{22,63} Furthermore, some of the carriers introduced via dopants are so deeply trapped as to contribute little to the mobility.^{3,63,67} Conductivity that arises from dopants is depletable in some cases, resulting in a threshold or turnon voltage opposite in sign from the accumulation regime.⁶⁸ Clearly, the relationship among doping, charge density, and mobility remains somewhat controversial, and further work is needed to sort out the effects.³⁹

A more useful means of attaining the higher mobility that seems to arise from higher injected charge density is by decreasing the thickness and increasing the dielectric constant of the gate dielectric. It has been convincingly shown²⁹ that for a given voltage, the effective mobility in "as received" pentacene increases with the capacitance of the dielectric, and does not increase independently as a function of the gate field. Thus, the higher gate capacitance enables higher on currents at specific voltages, not only because of the linear dependence of current on capacitance but also because of the potential of accessing a higher mobility regime of the semiconductor through the increased channel charge density. It is interesting that a particularly strong gate bias dependence of the mobility is observed in pentacene converted from a soluble precursor, where impurities are almost surely retained.⁶⁴

Conclusions

Organic semiconductors now possess sufficient mobilities and on/off ratios, at least under certain conditions, for serious consideration in useful circuits. Simple processing techniques have been developed that can be readily applied to manufacturing. Circuits with complex functionality have been demonstrated, and their performance has been modeled both at the single device and total circuit levels. Nevertheless, our understanding of aspects of both materials and electronic issues is primitive. The realization of a competitive technology based on organic electronics will require far greater phenomenological insight and control of variables than we now possess.

Much of the required increase in our knowledge base will depend on additional physical chemical studies. For example, a correlation of mobility with single crystal structure would greatly aid in material design and selection. Advances in deposition process will come from a greater awareness of the dynamics of growth and alignment of crystalline thin films, especially from solution. The vast array of polymer morphology engineering techniques based on phase separation effects and intermolecular interactions could be brought to bear on the polymer optimization. Ancillary electrical effects, such as time-dependent trapping and detrapping and injection barriers need

to be addressed, and the intrinsic or extrinsic nature of these effects needs to be determined. Clearly, opportunities abound for a wide range of physical chemistry investigations of organic FETs.

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