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Printable organic and polymeric semiconducting materials and devices

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Solution-processable organic and polymeric semiconducting materials are active materials used for electronic devices such as thin film field-effect transistors (FETs). These materials are more likely to have practical advantages when coupled with low cost approaches to patterning that are compatible with them. Material requirements for high performance solution based FETs are discussed. Also described are structural, morphological, and processing factors that influence device performance. Finally, methods and schemes of printing workable devices are surveyed.

1 Introduction

There has been great interest recently in the development of electronic circuits and displays using various printing methods such as screen-printing,[1] ink-jet printing,[2–5] and microcontact printing.[6–8] This trend is driven by the demand for low-cost, large area, flexible and lightweight devices. For these purposes, organic and polymeric semiconducting materials have been widely pursued since they offer numerous advantages for easy processing (*e.g.* spin-coating, printing, evaporation), good compatibility with a variety of substrates including flexible plastics, and great opportunities for structural modifications.[9–14] In addition, these materials can be processed at much lower substrate temperatures (less than 120 °C) and with little or no vacuum involved, as compared to the high substrate temperatures (greater than 900 °C) and high vacuum needed for typical inorganic semiconducting materials.

Organic and polymeric semiconductors are the core materials for constructing thin film field-effect transistors (FETs), which comprise the basic building blocks for microelectronics. Instead of competing with conventional silicon technologies, printable FETs may find niche applications in low-cost memory devices, such as smart cards and electronic luggage tags, and large area driving circuits for displays. The demonstration of such devices relies heavily on high-performance solution-processable organic and polymeric materials along with novel printing processes. In this article we will review the current status in transistor material discovery and device printing developments.

2 Materials

In this section a brief introduction will be given on the operation of FET devices and different materials necessary for fabricating printable FETs. Emphasis will be directed to various solution processable organic/polymeric semiconducting materials. Extensive reviews on vacuum sublimed oligomeric organic semiconductors can be found elsewhere;[10–13] therefore, these materials are not the focus of this review.

A typical FET has the device structure shown in Fig. 1. The current flow between the drain and source electrode is low when no voltage is applied between the gate and the drain electrodes as long as the semiconducting material is not highly doped. This state at which the gate voltage is zero is called the 'off' state of a transistor. 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. 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. Therefore, to construct a FET, materials ranging from insulating (dielectric material), semiconducting, to conducting are required. 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. They both depend strongly on the gate voltage used for calculation. Comparisons of on/off ratios can be made only 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 ('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 mobility of greater than 0.1 $cm^2 V^{-1} s^{-1}$ and on/off ratio greater than 10^6:1 are needed for the driving circuits in liquid crystal displays.

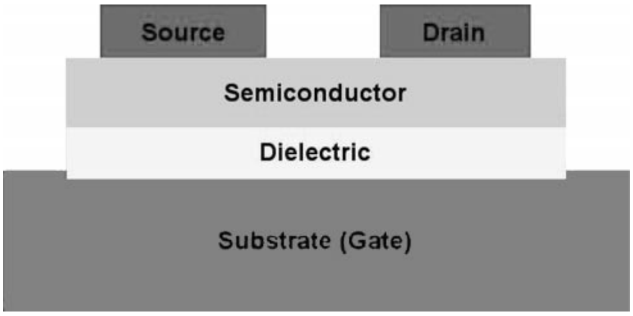

Fig. 1 Scheme of a typical FET device.

2.1 Solution processable oligomeric semiconductors

As noted above, several reviews have been published concerning FETs based on organic molecular solid semiconducting compounds.[10,12,13] Classes of suitable compounds have been surveyed, and methods for evaluating their device performance have been described. Theoretical approaches for understanding both the charge injection (switching-on) process and the passage of current through the switched-on FET have been elucidated. The semiconductors must satisfy stringent criteria relating to both the injection and current-carrying phenomena, as discussed below.

First, the frontier orbital energies of the individual molecules (perturbed by their placement in a crystalline solid) must be at levels where electrons may be added or removed at accessible applied voltages, across interfaces with conductors of reasonable work function. These orbital energies have been probed in solution using electrochemistry,[15] and in thin films *via* photoelectron spectroscopy.[16–19] Analysis of junctions of two organic solids and of organic materials on inorganic substrates has further defined these levels, and helped us understand factors such as molecular orientation relative to the junction interface that may ease charge injection.

Second, the crystal structure of the solid must provide sufficient overlap of the frontier orbitals to allow charge to migrate among neighboring molecules without excessive barriers. Charge transport in organic semiconductors generally occurs by a molecule-to-molecule hopping mechanism, rather than through a spatially extended band. Consequently, an activation barrier is associated with each intermolecular electron (or hole) transfer. In the absence of orbital overlap, this barrier, multiplied over the entire device, can become formidable, considering that a FET length typically spans 10^4–10^6 molecules. Structural features in the crystal including π-stacking and intimate edge-to-face contacts are suggestive of significant overlap, as has been shown for the α-6T and bis(dithienothiophene) crystal structures illustrated in Fig. 2.[20,85] Mobility is the highest in directions of significant intermolecular interaction, while it is vanishingly small in directions where molecules are insulated from one another. Impurities and defects that decrease the perfection of the crystal and thereby the overlap can in principle lower the mobility.

Third, the domains of the crystalline semiconductor must continuously span the source and drain contacts, oriented so that the high mobility directions are parallel to the directions of desired current flow. Ideally, this would be accomplished by preparing single crystal thin films larger than the device size. In rare cases this can be achieved through sublimation under specific conditions.[21] More generally, polycrystalline films are deposited, where many grains are traversed in crossing the device. While the grains are generally incommensurate, it is desirable that the inter-grain contact not impose a substantial series resistance, and a highly interconnected, fine grain morphology seems to be the most favorable in this regard. This principle has been dramatically illustrated in the case of bis(benzodithiophene) (Fig. 3)[22] and copper phthalocyanine.[23] While fewer boundaries would result from larger grains, such boundaries seem to be more deleterious. In the limiting case of grains separated by empty space the boundaries are catastrophic, because of the essentially infinite resistance of voids.

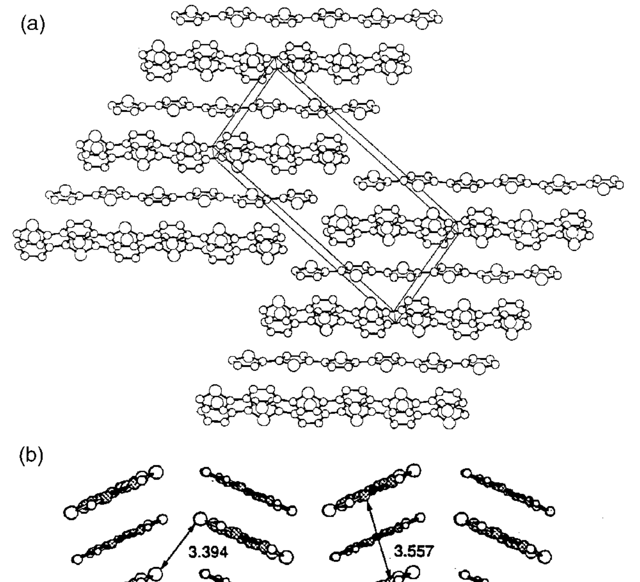

Fig. 2 Crystal packing diagrams for (a) α-6T, from ref. 85, (b) bis(dithienothiophene), from ref. 20, ©American Chemical Society.

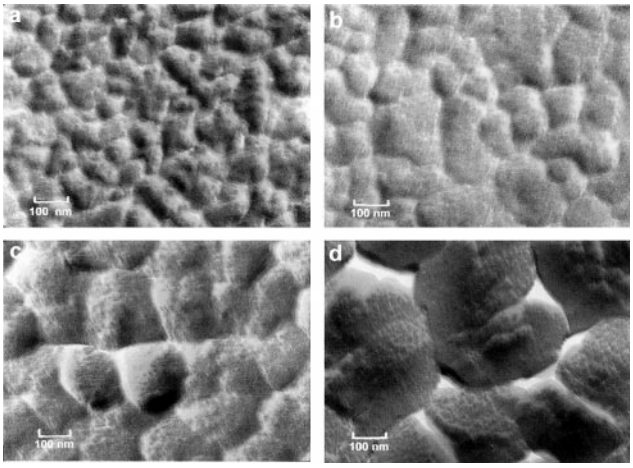

Fig. 3 Transmission electron micrographs from bis(benzodithiophene) films deposited on substrates held at (a) 25, (b) 75, (c) 100, (d) 125 °C, from ref. 22, ©Wiley-VCH.

Even where the morphology is favorable, mobility can be reduced by the action of traps, either from the environment or the dielectric layer. Since the semiconductors are generally deposited as 100–1000 Å films, and the channel region where most of the charge is injected is thinner still,[24] FETs are particularly sensitive to traps. The thinness of the channel charge layer has been verified both by experiment and computer simulation, portrayed in Fig. 4. The combined effects of traps and hopping barriers can severely diminish FET mobility relative to mobility obtained in macroscopic single crystals of identical compounds.[25] In the best cases, such as with pentacene, this mobility lowering is less than an order of magnitude, but the thin film mobility of other compounds, including α-4T,[26] is greatly attenuated. Sometimes, the orbital energies and chemical reactivities that lead to trap sensitivity also create barriers at electrodes, so that the apparent effects on mobility due to traps and electrode series resistance are difficult to distinguish.[27]

Several of the vacuum-deposited semiconducting organic compounds are readily available commercially, including the *p*-channel compounds pentacene[28] and copper phthalocyanine,[29] and *n*-channel copper hexadecafluorophthalocyanine.[30] Lower mobility compounds such as naphthacene[31] and naphthalenetetracarboxylic dianhydride[32] can also be obtained for comparison purposes. Chemical structures of some of these compounds are presented in Fig. 5. Buckminsterfullerene (C_{60})

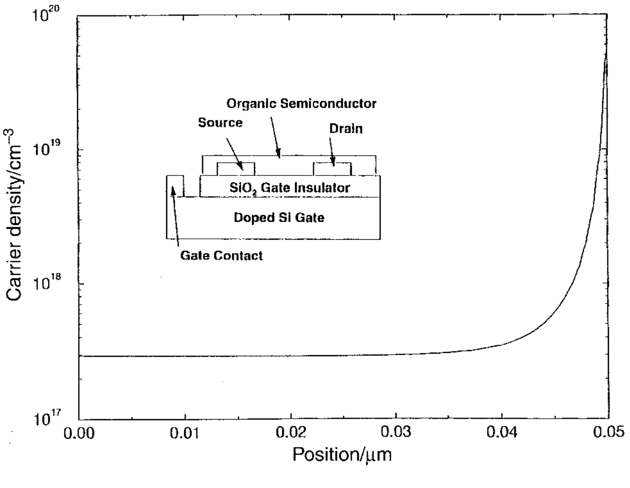

Fig. 4 Surface charge density as a function of position for a 0.05 μm film of α-6T on 0.3 μm of SiO_2, where 0.05 μm designates the semiconductor–oxide interface, and a gate voltage of 60 V is applied (from ref. 24, ©IEEE).

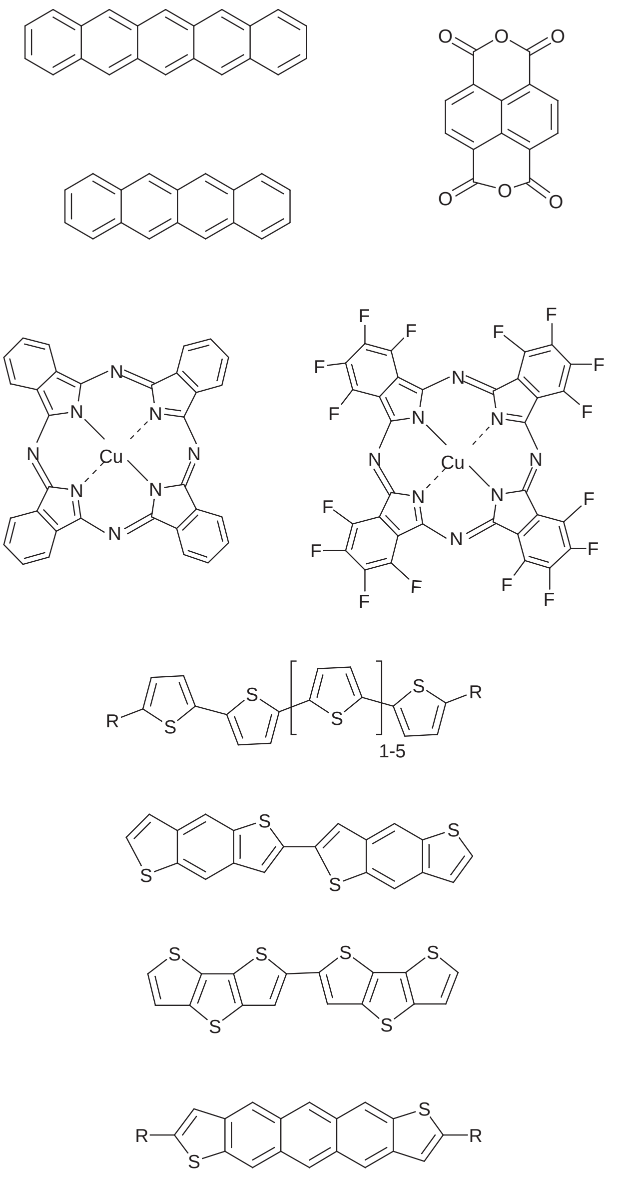

Fig. 5 Molecular structures of typical organic semiconducting compounds.

is an air-sensitive *n*-channel material that is commercially available, but requires extensive refinement.[33] Other materials, encompassing the widely used thiophene oligomers and fused ring compounds containing embedded thiophene, are specially synthesized.[34–42] While unsubstituted oligomers can be prepared in just one or two steps from purchasable starting materials, end-substituted and ring-closed compounds often require more extensive synthesis. As described below, the terminal substitution is important in providing materials suitable for liquid phase deposition. New procedures have been developed for producing the compounds and ensuring adequate purity for use in devices. Synthetic sequences that allow for purification of intermediates, and isolation processes that comprise both recrystallization and sublimation, have both proven valuable in obtaining pure products.

The challenge of fabricating semiconducting films from solution that match the characteristics of those made by vacuum sublimation is centered on the kinetics and thermodynamics of crystal assembly. Vapor growth processes are characterized by a single state (vapor) that competes with the solid phase, and limited movement of surface-bound molecules after condensation. Solution deposition, on the other hand, involves many more states, of solvation and aggregation, as well as solvent-mediated equilibration mechanisms, that make the desired morphology less accessible and/or stable.

Of course, an initial requirement is that the semiconducting compounds be soluble. Since most of the parent semiconducting conjugated systems are highly rigid and therefore virtually insoluble, substituents are affixed to increase solubility. Even so, the solubility can still be sparing, and the first reports of thienyl molecules and related compounds deposited from solution in FET configurations are marked by low mobilities and small areas of coverage.[37,41,43] Compounds with substitution at middle positions, such as adjacent to thiophene–thiophene bonds, or with highly branched substituents, are considerably soluble, but are also incapable of forming solids with extensive intermolecular overlap.[44–46] Linear, terminal substitution, on the other hand, actually increases the propensity of chromophores to form ordered films.[38]

The best compromise between orbital overlap and solubility is found in the moderately long thiophene oligomers dihexyl-α-4T and -α-5T, whose solubility in common solvents exceeds 0.1% and which form solution-fabricated thin films with mobility considerably higher than 0.01 $cm^2\ V^{-1}\ s^{-1}$.[47,48] The tetramer has been employed in a spin-coating process on both SiO_2 and poly(methyl methacrylate) (PMMA) dielectrics to produce devices with promising on/off ratios. Rapid evaporation of the chloroform solvent, induced by a substrate held above the boiling point of the solvent, was found to be essential in this process. The pentamer, on the other hand, was cast from higher boiling solvents onto mildly heated substrates under gentle vacuum, conditions first uncovered by working with dihexyl-α-6T. One device made from dihexyl-α-5T had an on-current >300 μA. In another relevant experiment, FETs were made by spin-coating a thiophene oligomer incorporating internal ethylenic linkages.[49]

Additional factors that uniquely influence solution deposition of small molecules are related to both the physical and chemical attributes of the liquid–solid interface. The spreading or contraction of solutions situated on dielectric substrates, and the speed of motion of the boundary of pools of solution as they evaporate, are governed by the wetting properties of the solvent on the substrate, and on the solid film that is eventually deposited. For example, in the dihexyl-α-4T experiment described above suitable morphologies were obtained when the dielectric surface was first modified with octadecylsilyl groups.

Contamination of the semiconductor by impurities arising from the solvent, or transferred into the film through the solvent, are processes that simply cannot occur in vapor phase deposition, and can lead to decreased on/off ratios if not prevented. Dihexyl-α-6T films cast from chlorobenzene can have on/off ratios of 10:1 when ‘reagent grade’ solvent is used, and 1000:1 when the solvent is carefully distilled, under otherwise identical conditions. While mobilities on polymer dielectrics are often comparable to those obtained on the flatter, more homogeneous SiO_2, on/off ratios are much more susceptible to lowering by impurities that are extracted from polymer dielectrics. Minimization of these impurities will be required in order to realize the full benefits of ‘all-organic’ or ‘all-printed’ electronics.

One advantage of less easily doped semiconductors, such as α-4T derivatives, is their increased imperviousness to the effects of chemical contamination. To some extent, this advantage applies to most of the well characterized small-molecule FET semiconductors relative to polymeric semiconductors that have been considered for this application. Not only can molecular solids be purified by crystallization and chromatography to a level not attainable with polymers, they are generally more stable to electrochemical modification, and are attractive for these reasons. On the other hand, the obstacles to fabricating uniform, continuous films of small molecules are much greater than for polymers, whose solution viscosity, entropically driven phase separation, and solid state entanglement result in bulk physical properties more favorable for thin films.

2.2 Solution processable polymeric semiconductors

The frontier orbital energy and morphological requirements for polymeric semiconductors are similar to those discussed above for oligomeric materials. Polymers have the advantages of good film forming properties. However, in contrast to oligomeric materials, they are more difficult to purify because they cannot be subjected to vacuum sublimation, and it is also very difficult to purify them *via* chromatography. In addition, it is more challenging to create the desired ordered structures from polymers. Most polymers tend to form amorphous films, where intermolecular π overlap is poor, resulting in low field-effect mobilities.

A novel class of polymer, which has been shown to have reasonably high mobility, is regioregular poly(3-alkylthiophene) (Fig. 6a).[1,50–52] The regioregularity refers to the position of the alkyl substituents.[53] For regioregular poly(3-alkylthiophene)s all the substituents are on the 3 position, while a regiorandom polymer can have substituents on both the 3 and 4 positions. As a result, regiorandom polyalkylthiophenes do not have well ordered morphology and their mobilities are usually in the range of 10^{-6} to 10^{-4} cm^2 V^{-1} s^{-1}.[54,55] However, improvement of mobility to about 10^{-2} cm^2 V^{-1} s^{-1} has been observed with films prepared by slow dipping from the solution of a regioirregular random copolymer of poly(3-methylthiophene)-co-poly(3-hexylthiophene).[56] The relative high mobility in this case may be attributed to the better alignment of polymer chains induced by the external force applied during dipping.

For regioregular poly(3-alkylthiophene)s, the evidence from both X-ray diffraction (Fig. 7a) and electron diffraction (Fig. 7b) is that such polymers can self-order as thin films and produce a high degree of three-dimensional ordering of the polymer chains.[50,57] There is a preferred molecular orientation when a thin film of this polymer is cast onto a substrate (either on a flat SiO_2 surface or a polymeric dielectric film of polyimide or PMMA). The polymer backbone in the resulting film has been observed to be parallel to the substrate with the alkyl chains between the backbones in an interdigitated fashion, directed perpendicular to the substrate.[50,57] Hence, the π-stacking direction is in the plane of the substrate and facilitates charge carrier transport in the plane.

The nature of the sidechains has been found to have a great effect on transistor performance.[50,51] First, the length of linear alkyl substituents needs to be between three and twelve carbons.[50] If the alkyl chain is too long the film matrix could be dominated by the insulating alkyl substituents, resulting in low mobilities of the films. On the other hand, if the alkyl chain is too short the polymer has low solubility and it is difficult to form uniform smooth films.

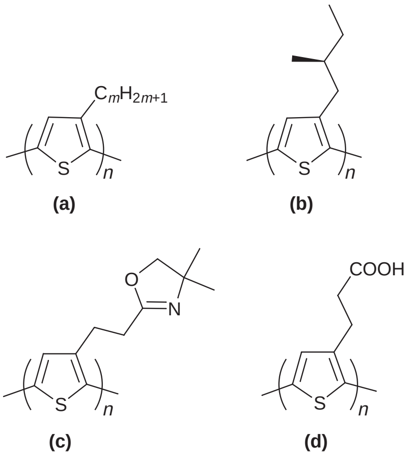

Fig. 6 Chemical structures of 3-substituted regioregular polythiophenes.

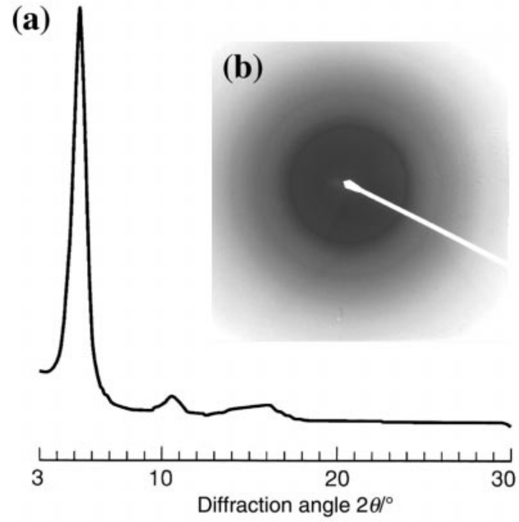

Fig. 7 X-Ray diffraction (a) and electron diffraction (b) patterns of regioregular poly(3-hexylthiophene), from ref. 29, ©American Institute of Physics.

Second, the bulkiness of the sidechains has a direct effect on the morphology and field-effect mobility of the polymer.[51] Poor molecular ordering and low crystallinity have been observed for regioregular polythiophenes with bulky (Fig. 6c) or carboxylic-substituted sidechains (Fig. 6d), and the resulting transistor devices showed low field-effect mobilities (less than 10^{-5} to 10^{-4} cm^2 V^{-1} s^{-1}).[51] In another example, a chiral alkyl-substituted regioregular polythiophene (Fig. 6b) has shown better crystallinity. However, the π–π overlap distance between the polythiophene backbones increases substantially (*i.e.* to *ca.* 4.3 *vs.* 3.8 Å for regioregular poly(3-hexylthiophene) (PHT)) after the introduction of methyl branches in the sidechains. 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} cm^2 V^{-1} s^{-1}), but it is still an order of magnitude lower than that of regioregular PHT. These results indicate that the nature of the sidechains 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 non-sterically hindered linear sidechains.

Besides the above factors, the field-effect behavior of regioregular poly(3-alkylthiophene)s is also strongly dependent on the solvents utilized in film formation.[50] Various high purity organic solvents have been used to fabricate transistor devices of poly(3-hexylthiophene) (PHT), and the field-effect mobility varies significantly with the choice of solvents. For example, a field-effect mobility close to 0.1 cm^2 V^{-1} s^{-1} is obtained when using chloroform as solvent while the mobility is only 6×10^{-4} cm^2 V^{-1} s^{-1} if THF is used.[50] Since similar conductivity at zero gate voltage has been observed for films prepared from various solvents, it is believed that the occurrence of higher mobility from certain solvents is not a result of higher dopant concentration as described by Brown *et al.* for doped amorphous materials.[58] Instead, it might be due to the difference in film quality when different solvents are used. With certain solvents, different degrees of film discontinuity may be obtained depending on the solubility of the polymer and nature of the solvent.

Even though the dielectric materials are not the focus of this paper, it should be pointed out that the chemical nature of polymer dielectrics not only affects the field-effect mobility but also plays an important role in the long-term reliability of polymer transistors. Detailed studies are yet to be done to understand the interfacial interaction between various polymer dielectrics and semiconductors. Preliminary data have shown that polymer dielectrics with less reactive functional groups tend to have better long-term performance.[59] Fig. 8 shows the current–voltage characteristics of FET devices after being stored under a nitrogen atmosphere in the dark for three months. In these devices, PHT was the semiconducting layer and three kinds of polymers were used as the dielectric layer. The more reactive poly(4-vinylphenol) device showed much higher leakage current and lower mobility after one month while all fresh devices showed almost identical performance. The dramatic difference in the long-term FET device performance may have to do with the interfacial reaction, which may take place between the dielectrics and semiconductor and corrode the interface where current flows.

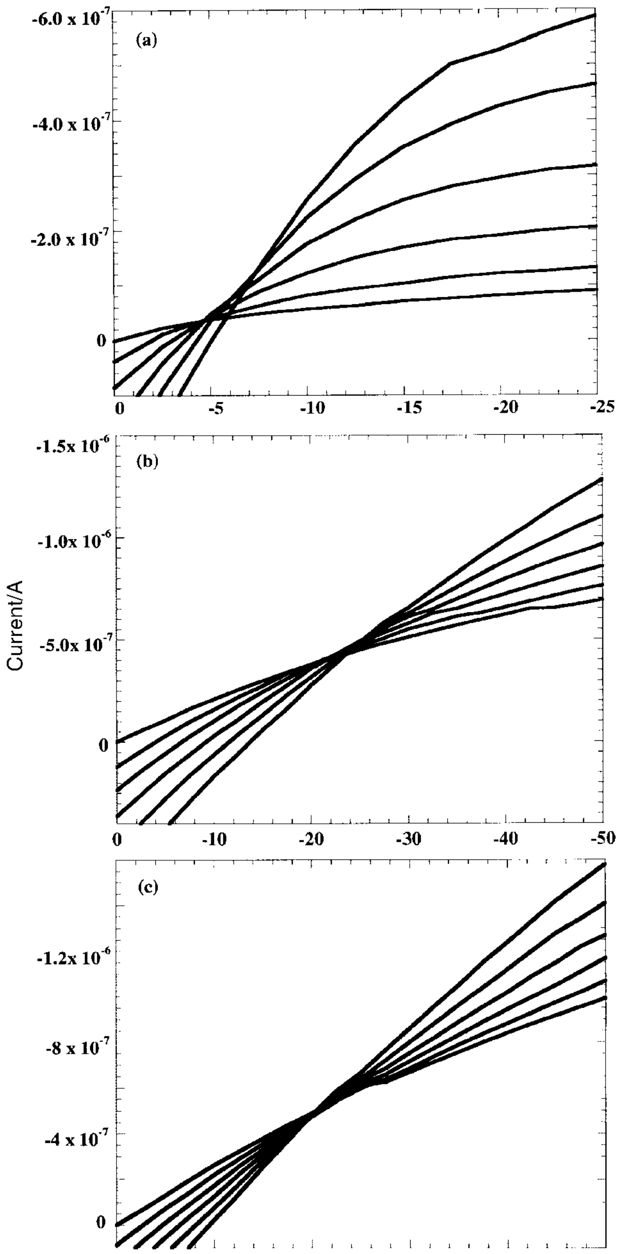

Fig. 8 Current–voltage characteristics of FET devices fabricated on various polymer dielectrics after storage under a nitrogen atmosphere in the dark for three months: (a) polyimide purchased from Japan Synthetic Rubber Co. (OPTIMER AL 3046); (b) polyimide from AMOCO Co. (AMOCO Ultradel®); (c) poly(4-vinylphenol) from Aldrich Chemical Co.

One difficulty that is often associated with polymer semiconductors is that they are difficult to purify. The residue impurities can either dope the polymer, which can lead to low on/off ratios, or act as traps that result in lower mobilities. The on/off ratios of regioregular poly(3-alkylthiophene)s have not been satisfactory. For devices prepared and measured in air the on/off ratio is at most several hundreds.[50] However, with various sample treatments an on/off ratio close to 10^4 can be achieved. Useful treatments include: (1) thermal annealing under vacuum (150 °C, 10^{-5} Torr) or forming gas (150 °C) to remove oxygen or reduce oxidized sites;[50,59] (2) ammonia gas treatment to form immobile quaternary species;[50] (3) surface treatment to suppress doping caused by impurity or surface reactive groups from the dielectric layer.[52,59] The intrinsic on/off ratio of regioregular PHT can reach as high as 10^6:1 when samples were prepared under a nitrogen atmosphere on hexamethyldisilazane (HMDS) treated SiO_2 dielectrics, overcoated with a reducing layer of SiO_x, and measured under vacuum.[52] The low on/off ratio for PHT with no special treatment is due to its relatively low bandgap and it is easily doped by oxygen and other oxidative impurities. For practical applications, it is desired that the as-prepared or simply treated devices have reasonable on/off ratios. These kinds of devices could then be encapsulated to maintain their performance. More material improvements are necessary to reduce the intrinsic dopability of regioregular poly(3-alkylthiophene)s but still maintain the high self-assembly property.

The degradation of polythiophene-related polymers is believed to be associated with photo-oxidation of the thiophene ring by singlet oxygen, which breaks apart the conjugated backbone.[59,60] Proper encapsulation should prevent or slow down the degradation from photo-oxidation. For PHT devices without encapsulation, it is found that storage under a nitrogen atmosphere with exclusion of UV light virtually maintains the same transistor performance for many months.[59]

3 Printing of organic and polymeric transistors

Solution-processable materials are attractive for applications in electronics in part because films with good characteristics can often be formed simply by casting at room temperature in open air. This capability, however, only has practical advantage when coupled with low cost approaches to patterning that can be applied directly to these materials or to those that are compatible with them. Conventional techniques, such as photolithography or electron beam lithography, are not typically suitable because they are expensive and generally require multiple processing steps with resists, solvents and developers that can be difficult to use in straightforward ways with organic active materials. Nevertheless, recently described photolithographic processes that rely not on resists but on the photochemical conversion of polymers from non-conducting into conducting states or from luminescent to non-luminescent ones produced impressive complex organic circuits[61] and patterned light emitting devices.[62] Similar approaches will likely be important in the future, but they may also retain the high costs associated with photolithography and may be less flexible than other methods in the materials that can be processed. This part of the review focuses on four non-photolithographic approaches that we believe to be promising for patterning organic electronics, including some with demonstrated capabilities in this area: screen printing, ink-jet printing, microcontact printing,[63–65] and micromolding in capillaries.[66–68] Here, we give an overview of each of these methods and describe their use for generating simple patterns of organic/polymeric materials and, in a few cases, complete working devices such as thin film transistors (TFTs) or light emitting devices (LEDs).

We also present brief descriptions of how these techniques might be combined and matched to form a complete system for patterning all layers in practical devices.

3.1 Screen printing

Screen printing is a simple and environment-friendly method to produce electronic circuitry and interconnections. In this method, patterns are generated by using a 'doctor blade' to squeeze ink through predefined screen masks. It is a purely additive method in which an ink is deposited and patterned in a single step, with printed lines as fine as 125 μm. This printing process can significantly reduce the time and cost associated with photolithography.

The first screen-printed transistor has been demonstrated by Garnier *et al.*[69] In those transistors, only the electrodes (gate, drain and source electrodes) were printed separately on each side of a sheet of polyester film, which acts as the dielectric layer. This film with electrodes was then taped to a plastic substrate followed by vacuum deposition of an organic semiconductor layer (dihexyl-α-6T). For practical applications, it is desirable that all the necessary components are printed in a continuous process. Therefore, liquid-phase processable organic semiconductors need to be used so that low-cost large area electronics with flexible plastic substrates for display or data storage can be realized using printing techniques.

Recently, the first high performance plastic transistors have been demonstrated in which all the essential components are printed directly onto plastic substrates using screen printing.[1] A scheme of procedures for producing printed plastic transistors is shown in Fig. 9. An ITO-coated poly(ethylene terephthalate) film is used as the plastic substrate on which the ITO layer acts as the gate electrode. A polyimide layer is printed through a screen mask onto the ITO surface. An organic semiconductor layer consisting of regioregular poly(3-hexylthiophene) is then put down by spin-coating, casting, or printing using chloroform as the solvent. Finally, the device is completed by printing the drain and source electrodes using a conductive ink through another screen mask. By using this procedure, many devices with different shapes or geometries can easily be obtained in large quantities simply by printing through suitable screen masks.

The typical printed devices fabricated with regioregular PHT are *p*-channel devices, which operate both in accumulation and depletion mode. The field-effect mobilities of transistors fabricated using screen printing are typically between 0.01 and 0.06 $cm^2 V^{-1} s^{-1}$. These values are comparable to the results obtained for regioregular poly(3-hexylthiophene) by using a Si substrate and SiO_2 as the dielectric layer with photolithographically defined gold electrodes.

The finest feature size which can be obtained by screen printing is still relatively large, in the range of 75 to 100 μm. It has been proposed that plastic devices with large feature sizes may be stacked to take up less space since they are lightweight and can be fabricated onto thin plastic substrates. However, for the simplicity of circuit design and high-speed requirements, it is desired that the feature size of printed plastic circuits be as small as possible, preferably smaller than 10 μm. In addition, screen printing requires relatively high viscosity inks. Low viscosity inks may flow prematurely or uncontrollably through the screen and cause poor resolution. Since the concentration of an organic/polymeric semiconducting material is in the range of several hundred parts per million, the viscosity of the dilute solution is almost the same as that of the organic solvent itself. Therefore, screen-printing may be most suited for high viscosity solutions and pastes of high molecular weight dielectric polymers, conducting polymers, and conducting pastes, where relatively large feature sizes (greater than 75 μm) over large areas are desired.

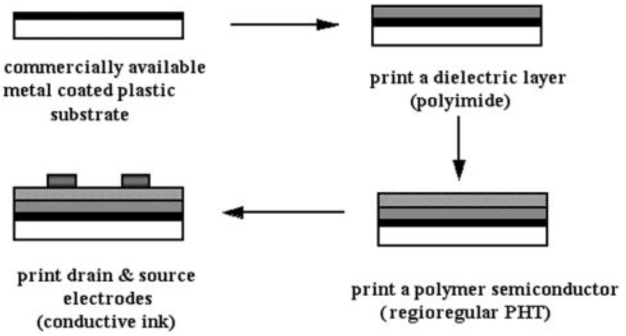

Fig. 9 Procedures of screen-printing of an 'all-printed' plastic transistor.

3.2 Ink-jet printing

In ink-jet printing liquids are ejected from a nozzle onto a substrate. Solidification of the liquid by evaporation of solvent, for example, yields patterned thin solid films. Two methods of depositing ink onto a substrate are typically used, impulse and continuous printing.[70] Continuous printing utilizes an ultrasonic nozzle to emit a stream of electrostatically charged droplets. A steering voltage controls the placement of the ink on the substrate. Impulse, or drop-on-demand, printing is more commonly used and exists in two forms:[71] piezoelectric systems that use nozzles pulsed by electrical signals to eject small droplets of an ink onto a substrate, and thermal-bubble systems that launch inks onto substrates by rapid heating. Printing with piezoelectric nozzles is attractive for organic/polymeric electronics because it does not require heating of inks that may be sensitive to elevated temperatures. It is compatible with a variety of organics, and has been demonstrated in the patterning of simple organic LEDs.[2–5] It can also form inorganic structures that may be useful for circuits that use organic active layers: dielectric glasses can be formed from printed sol–gel precursors[72] or colloidal suspensions,[73] and conducting lines can be generated by electroless plating onto printed palladium catalysts.[74] Although we are not aware of the use of ink-jet techniques to form working circuits or electronic devices such as TFTs, we believe that the capabilities demonstrated in the patterning of LEDs and other structures indicate that it may be useful for patterning gates, source/drain electrodes, dielectric layers and other essential circuit components. Ink-jet printing is attractive partly because it is intrinsically an additive technique. Like screen-printing, it does not require sacrificial resist or liftoff layers, and deposits materials only where they are needed. The patterning itself is purely serial, however. A multitude of nozzles that can operate in parallel may be required to achieve the high speeds that will be essential for low cost manufacturing. At this early stage of development it is difficult to determine the ultimate resolution of ink-jet patterning. The smallest features that have been formed in organic LEDs, for example, are ≈150 μm dots;[2] this resolution is similar to that demonstrated with TiO_2[73] and electroless copper.[74] Although the dimensions of the nozzles can be significantly (<2 times) smaller than these features, the printed drop typically splashes and flows in uncontrolled ways when it impacts the solid surface upon which it is printed. The viscosity of the ink and its ability to wet and bind to the substrate, therefore, both affect the resolution. For impulse printing heads, the trajectory of the droplet as it travels from the nozzle to the substrate is also not typically well controlled. As a result, the 150 μm dots demonstrated in organic LEDs are likely considerably smaller than the sizes of reproducible features (lines or spaces, for example) that consist of many interconnected printed droplets. For coarse LEDs or large displays the existing ≈150 μm resolution may be acceptable; it also may be adequate for patterning certain components of organic circuits. In its current form, however, it is likely insufficient for patterning source/drain electrodes for TFTs, for example, where features with better than ≈ 5 μm edge resolution will be required for commercially significant applications of known organic semiconductors. In addition to resolution, other challenges for the development of ink-jet techniques as generally useful tools for patterning organics include (i) producing ink-jet deposits with uniform thickness,[4] (ii) improving the reproducibility of the shapes and sizes of printed droplets, (iii) eliminating pin-holes in printed layers,[2,3] (iv) expanding the range of viscosities of solutions that can be printed. All of these shortcomings are related more to engineering aspects of the current design of ink-jet printers than to fundamental limitations of the technique. We believe, therefore, that the future of ink-jet printing for patterning in organic electronics is promising.

3.3 Micromolding in capillaries (MIMIC) and microcontact printing (μCP)

Screen and ink-jet printing both have the advantage that many technological aspects of these methods are relatively well developed for applications similar to, but distinct from, organic electronics. As noted above, however, neither currently has the resolution necessary for patterning the finest features that are required for useful organic circuits (typically the separation between source/drain electrodes). Some of our recent work focuses, therefore, on investigating methods for patterning features that are smaller than those that can be produced with existing forms of ink-jet and screen printing. We recently studied the suitability of new high resolution lithographic techniques that use elastomeric stamps and molds[64,65] for patterning source/drain electrodes for applications in organic electronics. These methods are attractive because they are low cost, can be used directly with many organic materials, and have demonstrated resolution that comfortably satisfies the requirements for nearly all realistic applications of organic electronics. Although many aspects of these techniques are less developed than those of screen and ink-jet printing, research applications of them to several areas of conventional microelectronics now exist, primarily in the Whitesides group at Harvard[75,76] and the Nuzzo group at UIUC.[77,78] Below we summarize our use of micromolding in capillaries (MIMIC) and microcontact printing (μCP) for defining source/drain electrodes for high performance organic TFTs. In each case, we define some of the limitations of these methods, and give an overview of our other related work in this area.

Fig. 10 illustrates how MIMIC can be used to define source/drain electrodes. Casting and curing a prepolymer of polydimethylsiloxane (PDMS) against patterned photoresist produces an elastomeric mold. (Many molds can be generated from a single pattern of photoresist, and each mold can be used many times.) The mechanical flexibility of the mold enables conformal, liquid-tight sealing against the surface to be patterned. This conformal contact generates an array of capillary channels. Liquid applied to access holes in the mold wicks into the channels. Solidification by evaporation of solvent or photochemical or thermal conversion followed by removal of the mold completes the fabrication of microstructures that have the geometry of the original pattern of photoresist. The dimensions of the channels, which are defined by the patterned photoresist, can be significantly less than 1 μm. In order for fluid to flow through them on reasonable timescales, however, dimensions larger than a few microns are required and the inks must have a sufficiently low viscosity. The distance of separation between the source and drain electrodes (which is the most important dimension for this application), on the other hand, is not limited by this consideration, and can be substantially less than 1 μm. We have used MIMIC to form conducting carbon electrodes from liquid carbon paint ($\approx 2\%$ solid carbon in ethanol) and polyaniline (PA) electrodes from solutions of polyaniline in *m*-cresol.[7] In both of these cases, evaporation of solvent from the filled capillary channels forces flow of solution from the reservoirs into the channels. If the channels fill with solids before solution from the reservoirs is exhausted a tightly packed microstructure of carbon or polyaniline in the geometry of the mold is produced. We combined this molding approach to form source/drain electrodes with screen printing to define patterns of dielectrics and semiconductors, and fabricated arrays of working TFTs.[7] Transistors formed using MIMIC and screen printing have electrical properties that are identical to those fabricated with conventional photolithographic techniques.

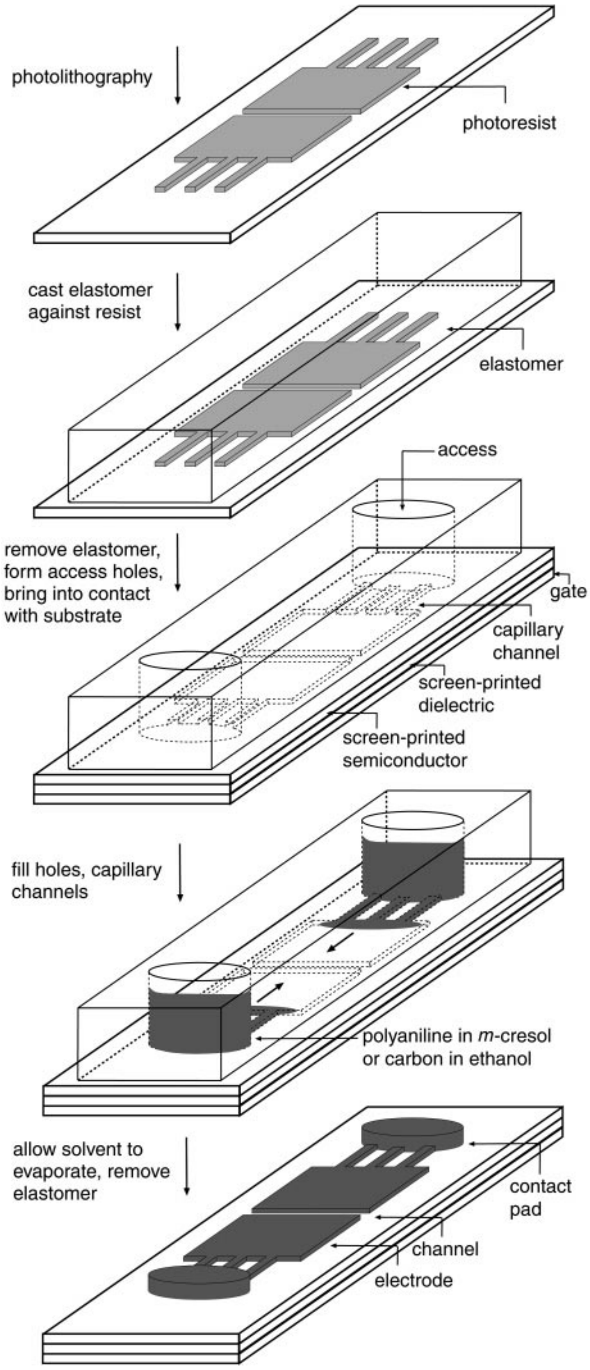

Fig. 10 Schematic illustration of molding procedures for defining high resolution source/drain electrodes on top of semiconductor, dielectric and gate layers patterned with screen printing. Conducting inks wick into capillary channels formed by contact of an elastomeric mold with the surface to be patterned. Removal of the mold after the solvent evaporates completes the fabrication (ref. 7, ©American Institute of Physics).

Although the current version of the micromolding approach has sufficient resolution, it lacks the speed and flexibility in patterning (*i.e.* non-interconnected circuit patterns are difficult to form directly) for a manufacturable solution to lithography for organic electronics. One can, however, conceive of extensions of the technique that use screen and ink-jet printing, for example, to deliver inks to access holes strategically placed across a complex circuit pattern defined by a large mold. We are currently exploring this and other approaches to overcome the limited flexibility in patterning that exists with the basic MIMIC technique.The same strategies may also increase the speed of patterning by reducing the total distance that ink must flow through and solidify in capillary channels.

In addition to the MIMIC approach we are also exploring other methods. One of these is μCP, a technique that we believe is particularly attractive because it has many characteristics necessary for the type of rapid, large volume reel-to-reel processing that is often considered important for cost-effectively exploiting organics in microelectronics. Briefly, μCP uses elements similar to the molds used for MIMIC to define, by contact printing, patterns of self-assembled monolayers (SAMs) that can then be used as resists to prevent removal of material or as initiators to guide material deposition.[63–65] Generally, this technique yields the best results when inks of alkanethiols are used to define monolayer etch resists on the surfaces of ultrathin layers of gold ($<\approx 40$ nm) or silver ($<\approx 300$ nm).[79–82] The resolution of features that can be etched into the underlying thin films in these cases is remarkably high: ≈ 30 nm features have been demonstrated in 15 nm films of gold.[8] Large areas can be patterned rapidly: printing requires contact of the stamp with the surface for less than ≈ 0.5 s, areas of many square centimeters can be stamped at once, and etching is completed in 0.5–5.0 min, depending on the thickness of the metal. Although neither gold nor silver is particularly useful for conventional microelectronics, gold is a good material for source and drain electrodes in organic transistors because it is chemically inert and allows excellent ohmic contacts with many organic semiconductors. Ultrathin electrodes are attractive from a cost standpoint, especially when gold is used: the materials cost of an unpatterned 200 Å film of Au is ≈ 0.04 ¢ cm^{-2}, a value that is conceivably acceptable, depending on the details of the economics. Its sheet resistance, $\approx 3\ \Omega$, is much smaller than that of the photoprocessable conducting polymers (≈ 1 kΩ) used in recent work on plastic integrated circuits.[61]

Our recent work[8] with μCP for organic electronics demonstrates: (i) methods for fabricating and using cylindrical 'roller' stamps mounted on fixed axles for printing, in a continuous reel-to-reel fashion, high resolution source/drain electrodes in ultrathin gold, (ii) methods for efficiently removing the SAM from the printed gold to allow ohmic contact with useful organic semiconductors, and (iii) materials and fabrication sequences that can efficiently exploit these printed electrodes for working organic TFTs. Fig. 11 shows the steps for microcontact printing gold electrodes, and for preparing them for use in organic TFTs. Fig. 12a shows how the electrodes can be used in an 'upside down' fabrication sequence to produce working TFTs. In this sequence the semiconductors, dielectrics and gate electrodes are deposited on the printed electrodes by simply casting these materials from solution, an approach that is clearly compatible with the screen and ink-jet printing techniques described previously. The characteristics of TFTs formed using these techniques (Fig. 12b) are equivalent to those of devices fabricated using photolithography. In a manufacturing sequence that uses this approach, source drain electrodes and appropriate interconnections could be printed onto a metallized plastic sheet; other solution-processable components of the circuits could then be cast on this sheet using relatively minor modifications of existing low resolution techniques such as screen or ink-jet printing. In a future publication we will describe the successful application of MIMIC, μCP and other new approaches to the fabrication of TFTs monolithically integrated with organic LEDs, and simple working circuits with features as small as 0.1 μm.

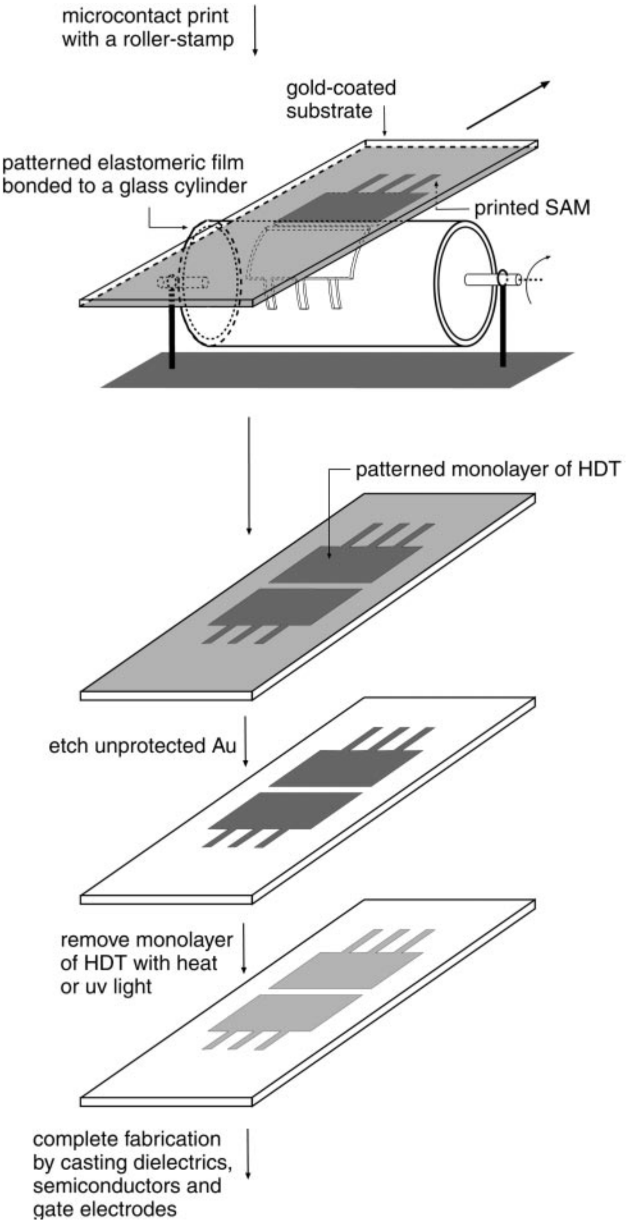

Fig. 11 Schematic illustration for using microcontact printing with a cylindrical, 'roller', stamp to define source/drain electrodes for organic transistors. Printing defines a patterned self-assembled monolayer (SAM) of hexadecanethiol on the surface of an ultrathin layer of gold. Exposing the printed gold to an aqueous ferrocyanide etch removes the gold that is not protected by the SAM. Removing the SAM after the etch yields conducting patterns of gold that are well suited for use in organic electronics (ref. 8, ©Wiley-VCH).

4 Summary and future outlook

In this article solution processable organic/polymeric semiconducting materials are surveyed. Several potentially useful printing methods are reviewed. The concept of printed high performance organic/polymeric electronic devices has been demonstrated. There are yet many issues that need to be addressed. In the material aspect there have been soluble organics and polymers which have mobilities and on/off ratios very close to those of amorphous Si. However, large area uniform coverage still tends to be difficult to achieve for organics[47] while the existing polymers generally have low

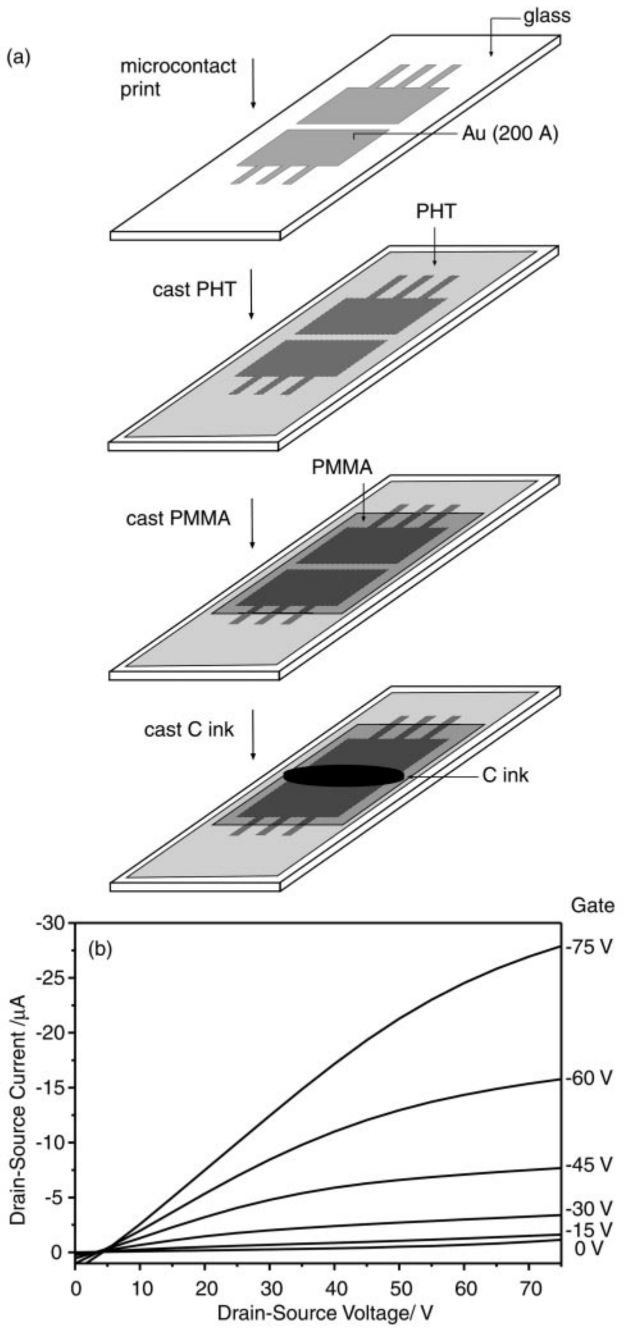

Fig. 12 Fabrication sequence suitable for using printed patterns of thin gold to produce working organic transistors. In the approach illustrated, low resolution patterning of dielectric, semiconductor and gate layers on top of high resolution printed gold electrodes produces arrays of thin film transistors. The bottom frame shows the good performance of a typical device that was fabricated in this manner.

on/off ratios unless special fabrication conditions are followed.[52] New materials with improved performance and processability should be explored. In addition, better understanding is needed of the chemical structure–performance–processability relationships by systematic material design and characterizations. All the soluble semiconducting materials discussed in this article are *p*-channel materials. Logic families constructed with complementary metal oxide semiconductor (CMOS) circuits require both *p*- and *n*-channel active materials. Organic analogs based on CMOS circuits are particularly desirable because they have very low static power dissipation and can retain their operating characteristics for a long time.[83,84] No transistor has been fabricated so far from a solution of any *n*-channel organic semiconductor. There are clear needs for such materials to realize all-printable CMOS circuits.

On the printing side the printed devices have only been demonstrated on laboratory scales. The possibility of producing the above devices in a manufacturing setting needs to be addressed. It is most likely that several types of printing methods need to be combined to meet various resolution requirements for all the components. The printing methods described here are only a few which have shown feasibility in printing organic/polymer based devices. High resolution and small feature size (less than 10 μm) printing methods are the most challenging and will require extensive development. There are other printing methods, such as direct laser writing and thermal heat transfer, *etc*., that can achieve printing resolution equivalent to or better than 10 μm, however, their feasibility for printing workable organic/polymer devices has yet to be demonstrated.

Finally, it is extremely important that future research be carried out to address reliability issues of organic electronic devices and understand their degradation mechanisms both of active materials and at interfaces. For many low-end applications, the devices may not need to have long operating time, but a certain shelf-life will still be necessary. For these reasons suitable encapsulation methods need to be explored.

5 References

1 Z. Bao, Y. Feng, A. Dodabalapur, V. R. Raju and A. Lovinger, *Chem. Mater.*, 1997, **9**, 1299.
2 J. Bharathan and Y. Yang, *Appl. Phys. Lett.*, 1998, **72**, 2660.
3 S. C. Chang, J. Bharathan and Y. Yang, *Appl. Phys. Lett.*, 1998, **73**, 2561.
4 T. R. Hebner, C. C. Wu, D. Marcy, M. H. Lu and J. C. Sturm, *Appl. Phys. Lett.*, 1998, **72**, 519.
5 T. R. Hebner and J. C. Sturm, *Appl. Phys. Lett.*, 1998, **73**, 1775.
6 J. A. Rogers, Z. Bao and L. Dhar, *Appl. Phys. Lett.*, 1998, **73**, 294.
7 J. A. Rogers, Z. Bao and V. R. Raju, *Appl. Phys. Lett.*, 1998, **72**, 2716.
8 J. A. Rogers, Z. Bao, A. Makhija and P. Braun, *Adv. Mater.*, 1999, in the press.
9 R. F. Service, *Science*, 1997, **278**, 383.
10 H. E. Katz, *J. Mater. Chem.*, 1997, **7**, 369; Z. Bao, in *Semiconductive Polymers*, eds. B. Hseih, Y. Wei and M. E. Galvin, American Chemical Society, Washington, D.C., 1999.
11 A. J. Lovinger and L. J. Rothberg, *J. Mater. Res.*, 1996, **11**, 1581.
12 H. E. Katz, A. Dodabalapur and Z. Bao, in *Oligo- and Polythiophene-based Field-effect Transistors*; ed. D. Fichou, Wiley-VCH: Weinheim, 1998.
13 G. Horowitz, *Adv. Mater.*, 1998, **10**, 365.
14 A. R. Brown, C. P. Jarrett, D. M. de Leeuw and M. Matters, *Synth. Met.*, 1997, **88**, 37.
15 P. Garcia, M. Pernaut, P. Hapiot, V. Wintgens, P. Valat, F. Garnier and D. Delabouglise, *J. Phys. Chem.*, 1993, **97**, 513.
16 I. G. Hill, A. Rajagopal, A. Kahn and Y. Hu, *Appl. Phys. Lett.*, 1998, **73**, 662.
17 T. Shimada, K. Hamaguchi, A. Koma and F. S. Ohuchi, *Appl. Phys. Lett.*, 1998, **72**, 1869.
18 S. Hiller, D. Schlettwein, N. R. Armstrong and D. Wohrle, *J. Mater. Chem.*, 1998, **8**, 945.
19 Y. Hirose, W. Chen, E. I. Haskal, S. R. Forrest and A. Kahn, *J. Vac. Sci. Technol., B*, 1994, **12**, 2616.
20 X. C. Li, H. Sirringhaus, F. Garnier, A. B. Holmes, S. C. Moratti, N. Feeder, W. Clegg, S. J. Teat and R. H. Friend, *J. Am. Chem. Soc.*, 1998, **120**, 2206.
21 Y. Y. Lin, D. J. Gundlach and T. N. Jackson, *Device Research Conference, Santa Barbra*, 1996, 175.
22 J. Laquindanum, H. E. Katz, A. Dodabalapur and A. J. Lovinger, *Adv. Mater.*, 1997, **9**, 36.
23 Z. Bao, A. J. Lovinger and A. Dodabalapur, *Adv. Mater.*, 1997, **9**, 42.
24 M. Alam, A. Dodabalapur and M. Pinto, *IEEE Trans. Electron Devices*, 1997, **44**, 1332.
25 J. H. Schon, C. Kloc, R. A. Lauudise and B. Batlogg, *Appl. Phys. Lett.*, 1998, **73**, 3574.
26 R. Hajlaoui, D. Fichou, G. Horowitz, B. Nessakh, M. Constant and F. Garnier, *Adv. Mater.*, 1997, **9**, 557.

27 L. Torsi, A. Dodabalapur and H. E. Katz, *J. Appl. Phys.*, 1995, **78**, 1088.

28 Y. Y. Lin, D. J. Gundlach, S. F. Nelson and T. N. Jackson, *IEEE Trans. Electron Devices*, 1997, **44**, 1325.

29 Z. Bao, A. J. Lovinger and A. Dobabalapur, *Appl. Phys. Lett.*, 1996, **69**, 3066.

30 Z. Bao, A. J. Lovinger and J. Brown, *J. Am. Chem. Soc.*, 1998, **120**, 207.

31 G. Horowitz, X.-Z. Peng, D. Fichou and F. Garnier, *Synth. Met.*, 1992, **51**, 419.

32 J. G. Laquindanum, H. E. Katz, A. Dodabalapur and A. J. Lovinger, *J. Am. Chem. Soc.*, 1996, **118**, 11331.

33 R. C. Haddon, A. S. Perel, R. C. Morris, T. T. M. Palstra, A. F. Hebard and R. M. Fleming, *Appl. Phys. Lett.*, 1995, **67**, 121.

34 P. Bauerle, in *Oligo- and Polythiophene-based Field-effect Transistors*; ed. D. Fichou, Wiley-VCH: Weinheim, 1998.

35 H. E. Katz, L. Torsi and A. Dodabalapur, *Chem. Mater.*, 1995, **7**, 2235.

36 Y. Wei, Y. Yang and J.-M. Yeh, *Chem. Mater.*, 1996, **8**, 2659.

37 H. E. Katz, J. G. Laquindanum and A. J. Lovinger, *Chem. Mater.*, 1998, **10**, 633.

38 F. Garnier, A. Yassar, R. Hajlaoui, G. Horowitz, F. Deloffre, B. Servet, S. Ries and P. Alnot, *J. Am. Chem. Soc.*, 1993, **115**, 8716.

39 H. E. Katz, A. Dodabalapur, L. Torsi and D. Elder, *Chem. Mater.*, 1995, **7**, 2238.

40 H. E. Katz, A. J. Lovinger and J. G. Laquindanum, *Chem. Mater.*, 1998, **10**, 457.

41 J. Laquindanum, H. E. Katz and A. J. Lovinger, *J. Am. Chem. Soc.*, 1998, **120**, 664.

42 W. Li, H. E. Katz, A. J. Lovinger and J. G. Laquindanum, *Chem. Mater.*, 1999, **11**, 458.

43 H. Akimichi, K. Waragi, S. Hotta, H. Kano and H. Sakaki, *Appl. Phys. Lett.*, 1991, **8**, 1500.

44 D. Fichou, in *Oligo- and Polythiophene-based Field-effect Transistors*, ed. D. Fichou, Wiley-VCH, Weinheim, 1998.

45 J. K. Herrema, J. Wildeman, F. van Bolhuis and G. Hadziioannou, *Synth. Met.*, 1993, **60**, 239.

46 A. Yassar, F. Garnier, F. Deloffre, G. Horowitz and L. Ricard, *Adv. Mater.*, 1994, **6**, 60.

47 W. Li and H. E. Katz, unpublished results.

48 F. Garnier, R. Hajlaoui, A. El Kassmi, G. Horowitz, L. Laigre, W. Porzio, M. Armanini and F. Provasoli, *Chem. Mater.*, 1998, **10**, 3334.

49 C. D. Dimitrakopoulos, A. Afzali-Aradakani, B. Furman, J. Kymissis and S. Purushothaman, *Synth. Met.*, 1997, **89**, 193.

50 Z. Bao, A. Dodabalapur and A. J. Lovinger, *Appl. Phys. Lett.*, 1996, **69**, 4108.

51 Z. Bao and A. J. Lovinger, *Chem. Mater.*, 1999, in the press.

52 H. Sirringhaus, N. Tessler and R. H. Friend, *Science*, 1998, **280**, 1741.

53 R. D. McCullough, S. Tristram-Nagle, S. P. Williams, R. D. Lowe and M. Jayaraman, *J. Am. Chem. Soc.*, 1993, **115**, 4910.

54 J. Paloheimo, P. Kuivalainen, H. Stubb, E. Vuorimaa and P. Yli-Lahti, *Appl. Phys. Lett.*, 1990, **56**, 1157.

55 A. Assadi, C. Svensson, M. Willander and O. Inganas, *Appl. Phys. Lett.*, 1988, **53**, 195.

56 J. Wang, Y. Y. Lin, W. Qian and T. N. Jackson, MRS conference, Boston, MA, 1–4th December, 1998, Symposium R4.4.

57 T. J. Prosa, M. J. Winokur and R. D. McCullough, *Macromolecules*, 1996, **29**, 3654.

58 A. R. Brown, D. M. deLeeuw, E. E. Havinga and A. Pomp, *Synth. Met.*, 1994, **68**, 65.

59 Z. Bao and A. L. Lovinger, *Chem. Mater.*, 1999, in the press.

60 T. Caronna, M. Forte, M. Catellani and S. V. Meille, *Chem. Mater.*, 1997, **9**, 991.

61 C. J. Drury, C. M. J. Mutsaers, C. M. Hart, M. Matters and D. M. de Leeuw, *Appl. Phys. Lett.*, 1998, **73**, 108.

62 K. Tada, M. Onoda and H. Nakayama, *Jpn. J. Appl. Phys.*, 1998, **37**, L1181.

63 A. Kumar and G. M. Whitesides, *Appl. Phys. Lett.*, 1993, **63**, 2002.

64 D. Qin, Y. Xia, J. A. Rogers, R. J. Jackman, X.-M. Zhao and G. M. Whitesides, 'Microfabrication, Microstructures and Microsystems', in *Topics in Current Chemistry*, A. Manz and H. Becker, Eds., Springer, Berlin, 1998, pp. 1–20.

65 Y. Xia and G. M. Whitesides, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 550.

66 E. Kim, Y. Xia and G. M. Whitesides, *Nature* (*London*), 1995, **376**, 581.

67 E. Kim, Y. Xia and G. M. Whitesides, *J. Am. Chem. Soc.*, 1996, **118**, 5722.

68 Y. Xia, E. Kim and G. M. Whitesides, *Chem. Mater.*, 1996, **8**, 1558.

69 F. Garnier, R. Hajlaoui and A. Yassar, *Science*, 1994, **265**, 1684.

70 R. H. Leach, *The Printing Ink Manual*, 4th edn., Van Nostrand Reinhold International, New York, 1989; J. A. G. Drake (Editor), *Chemical Technology in Printing and Imaging Systems*, Royal Society of Chemistry, London, 1993.

71 W. Gerhatz, (Editor), *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, 1989.

72 A. Atkinson, J. Doorbar, A. Hudd, D. L. Segal and P. J. White, *J. Sol-Gel Techol.*, 1997, **8**, 1093.

73 S. J. Kim and D. E. McKean, *J. Mater. Sci. Lett.*, 1998, **17**, 141.

74 P. Shah, Y. Kevrekidis and J. Benziger, *Langmuir*, 1999, **15**, 1584.

75 J. Hu, R. G. Beck, T. Deng, R. M. Westervelt, K. D. G. Maranowski and G. M. Whitesides, *Appl. Phys. Lett.*, 1997, **71**, 2020.

76 J. Hu, R. G. Beck, R. M. Westervelt and G. M. Whitesides, *Adv. Mater.*, 1998, **10**, 574.

77 N. L. Jeon, J. Hu, G. M. Whitesides, M. K. Erhardt and R. G. Nuzzo, *Adv. Mater.*, 1998, **10**, 1466.

78 N. L. Jeon, P. Clem, D. Y. Jung, W. Lin, G. S. Girolami, D. A. Payne and R. G. Nuzzo, *Adv. Mater.*, 1997, **9**, 891.

79 J. L. Wilbur, A. Kumar, E. Kim and G. M. Whitesides, *Adv. Mater.*, 1994, **6**, 600.

80 Y. Xia, X. M. Zhao and G. M. Whitesides, *Chem. Mater.*, 1995, **7**, 2332.

81 Y. Xia, E. Kim and G. M. Whitesides, *J. Electrochem. Soc.*, 1996, **143**, 1070.

82 H. A. Biebuyck, N. B. Larsen, E. Delamarche and B. Michel, *IBM J. Res. Dev.*, 1997, **41**, 159.

83 A. Dodabalapur, J. Laquindanum, H. E. Katz and Z. Bao, *Appl. Phys. Lett.*, 1996, **69**, 4227.

84 Y. Y. Lin, A. Dodabalapur, R. Sarpeshkar, Z. Bao, W. Li, H. Katz and V. R. Raju, *Appl. Phys. Lett.*, 1999, **74**, 2714.

85 T. Siegrist, R. M. Fleming, R. C. Haddon, R. A. Laudise, A. J. Lovinger, H. E. Katz, P. Bridenbaugh and D. D. Davis, *J. Mater. Res.*, 1995, **10**, 2170.

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