

The path to ubiquitous and low-cost organic electronic appliances on plastic

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Organic electronics are beginning to make significant inroads into the commercial world, and if the field continues to progress at its current, rapid pace, electronics based on organic thin-film materials will soon become a mainstay of our technological existence. Already products based on active thin-film organic devices are in the market place, most notably the displays of several mobile electronic appliances. Yet the future holds even greater promise for this technology, with an entirely new generation of ultralow-cost, lightweight and even flexible electronic devices in the offing, which will perform functions traditionally accomplished using much more expensive components based on conventional semiconductor materials such as silicon.

Interest in organic electronics stems from the ability to deposit organic films on a variety of very-low-cost substrates such as glass, plastic or metal foils, and the relative ease of processing of the organic compounds that are currently being engineered by hundreds of chemists. The most advanced organic electronic systems already in commercial production are high-efficiency, very bright and colourful thin displays based on organic light-emitting devices¹ (OLEDs). Significant progress is also being made in the realization of thin-film transistors^{2–4} (TFTs) and thin-film organic photovoltaic cells^{5–8} for low-cost solar energy generation. Yet the ultimate test of this technology lies less in the reliability and performance of the organic components, which in some cases has already approached or even exceeded the requirements of a particular application, but rather in the ability to manufacture products at very low-cost. Although the cost of the organic materials used in most thin-film devices is low, in electronics the materials cost rarely determines that of the end product, where fabrication and packaging costs typically dominate. Hence, the successful application of this interesting materials platform will depend on capturing its low-cost potential through the innovative fabrication of devices on inexpensive, large-area substrates.

This suggests that conventional semiconductor device fabrication technologies need to be adapted to handle the large-area substrates spanned by organic macroelectronic circuits, and to be compatible with the physical and chemical properties of these fascinating compounds. Also, solids based on organic compounds are typically bonded by weak van der Waals forces that decrease as $1/R^6$, where R is the intermolecular spacing. This is in contrast to inorganic semiconductors that are covalently bonded, whose strength falls off as $1/R^2$. Hence, organic electronic materials are soft and fragile, whereas inorganic semiconductors are hard, brittle, and relatively robust when exposed to adverse environmental agents such as moisture and the corrosive reagents and plasmas commonly used in device fabrication. The apparent fragility of organic materials has also opened the door to a suite of innovative fabrication methods that are simpler to implement on a large scale than has been thought possible in the world of inorganic semiconductors. Many processes involve direct printing through use of contact with stamps, or alternatively via ink-jets and other solution-based methods.

Here I describe several recent advances in organic electronic devices, focusing particularly on the specialized processing techniques used in their realization. The discussion begins with a description of the unique electronic and optical properties of organic materials that make them interesting as technological substances. This is followed by a discussion of the methods of film deposition and patterning using techniques that have been

developed to maintain the very low costs inherent in these material systems. The promise of organic electronics through the production of ubiquitous, low-cost and robust devices filling niches not occupied by silicon-based electronics should become readily apparent through the understanding of the unique properties that characterize these potentially high-performance materials.

Essential properties of organic semiconductors

Like all organic materials, organic semiconductors are carbon-rich compounds with a structure tailored to optimize a particular function, such as charge mobility or luminescent properties. Organic electronic materials (Fig. 1) can be classified into three categories: 'small molecules', polymers and biological materials. 'Small molecule' is a term broadly used to refer to those compounds with a well-defined molecular weight. The material shown, Pt-octaethylporphyrin (PtOEP), is a metallorganic complex that has

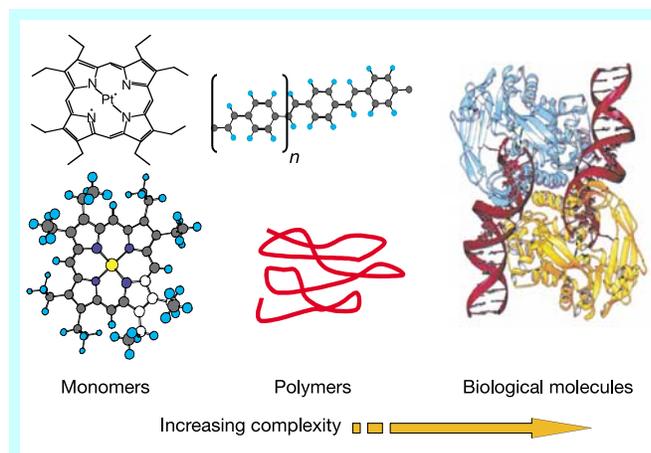


Figure 1 Various types of organic electronic materials, ranged in order of increasing complexity from left (simplest) to right (most complex). Monomeric compounds (left), typified by the metallorganic phosphor PtOEP shown here, are single compact molecular units with a well-defined molecular weight that are generally, although not always, deposited in vacuum. Dendrimers are larger variants of small-molecular-weight compounds. Next in complexity are polymers (centre), forming chains of repeating monomeric units. The chains are not of a well-defined length, and thus their molecular weight varies over a considerable range. Polymers are generally, although not always, deposited from liquid solution. Finally, the most complex materials are of biological origin (right), consisting of proteins and strands of DNA. Currently, there are no clear demonstrations of the utility of these complex structures for use in electronic applications.

been optimized to provide deep red phosphorescent emission when placed in an OLED⁹. Other small-molecular-weight materials include low-generation dendrimers and other oligomers^{10,11}. In contrast, polymers are long-chain molecules consisting of an indeterminate number of molecular repeat units. The molecule shown is poly(*p*-phenylene vinylene), or PPV. Like PtOEP, PPV is an emissive organic semiconductor used in OLEDs^{12–14}. At the high end of the complexity scale are organic materials of biological origin (in contrast to PtOEP and PPV, which are synthetic). As yet there are no clear applications that exploit the optical or electronic properties of these most complicated structures, although considerable investigation into the understanding and utilization of photosynthetic complexes is currently under way^{15,16}. This Review concerns only monomeric and polymeric materials, as they are in the most advanced state of development for electronic and photonic applications.

Although much emphasis has been placed on the differences between the properties of small-molecular-weight organic thin films and polymers for organic electronic applications, there are in general more similarities than differences in both their electronic and optical properties, with the main distinction being in the methods of thin-film deposition and device preparation. In both polymers and small molecules, the excitonic state dominates their optical properties¹⁷. Here, an exciton is a molecular excited state that is mobile within the solid—that is, it can hop from molecule to molecule, or in the case of polymers, from chain to chain as well as along the polymer backbone until it recombines, generating either light (in a radiative process) or heat (under non-radiative circumstances). The most dominant species in organic electronic devices is the Frenkel exciton—a tightly bound (~ 1 -eV binding energy) electron–hole pair that is generally localized on a single molecule at a time¹⁸. In addition, in highly ordered molecular crystals, more weakly bound charge-transfer (CT) excitons are found in the optical spectra. These equally mobile states are generally spread over one or more neighbouring molecules, and owing to their larger diameters, are more weakly bound (~ 10 – 100 meV) than Frenkel states.

Similarly, charge carrier (electron or hole) transport can occur via hopping between molecular sites, or from chain to chain. In this case, the carrier mobilities are quite low compared with inorganic semiconductors whose room temperature values typically range from 100 to 10^4 cm² V⁻¹ s⁻¹ (ref. 19). In contrast, in highly ordered molecular materials where charges hop between closely spaced molecules forming a crystalline stack, mobilities of $\mu \approx 1$ cm² V⁻¹ s⁻¹ have been observed at room temperature^{20–22}. This apparently is an approximate upper bound, with the mobility ultimately limited by thermal motion between neighbouring molecules. In more disordered molecular systems and polymers, the mobilities are only 10^{-3} to 10^{-5} times this upper limit^{23–25}. However, deposition (generally by spinning) of polymers onto substrates prepared by rubbing or other ‘direction-inducing’ processes can lead to alignment of the chains, thus increasing the charge mobility over that of completely randomly disordered films²⁶. A further strategy for reducing disorder in molecular systems as well as in polymers is by templating ordered epitaxy-like growth using crystalline substrates that impose their lattice order onto the adsorbed organic films^{27,28}. However, this latter approach may also result in a prohibitive increase of device fabrication complexity, or may be limited to only a few organic materials and substrates that are not necessarily optimal for use in a particular application.

The low mobility leads to low electrical conductivity σ , given by $\sigma = ne\mu$, where n is the charge carrier density and e is the electronic charge. Thus, typical conductivities of organic materials are $\sigma \approx 10^{-6}$ S cm⁻¹. In addition to low conductivity, low mobility also results in a very low charge carrier velocity, $v = \mu F \approx 10$ cm s⁻¹, where F is the electric field of $\sim 10^5$ V cm⁻¹, typical of many devices^{29,30}.

Owing to the low conductivity and carrier velocities that are

intrinsic to organic thin-film semiconductors, one would expect that very-low-bandwidth operation of common optoelectronic devices such as transistors, OLEDs and photodetectors would provide a significant, if not fatal, limitation to their application in modern electronic systems. Although in many cases this is indeed true, the applications open to organic electronics are not targeted at simply replacing conventional electronics niches served by materials such as crystalline silicon. For example, very-low-bandwidth (~ 10 -kHz) organic thin-film transistors (OTFTs) may find application in display back planes or low-cost ‘disposable’ electronics, such as building entry cards and other radio-frequency identification inventory control devices^{31,32}. In addition, by using the thin vertical dimension (normal to the substrate plane) and the high crystalline order inherent in some molecular thin-film systems, very short carrier transit distances, and hence response times, can be obtained, leading to surprisingly high bandwidths. This has recently been demonstrated using multiple-layer organic photodetectors with bandwidths approaching 450 MHz (ref. 33). Further possibilities for exploiting the short vertical dimensions have also been demonstrated in polymer OTFTs by depositing polythiophene derivatives into a ‘V’-shaped channel microcut into a flexible poly(ethylene terephthalate) substrate³⁴.

The viability of organic electronics, therefore, lies not in the displacement of existing applications niches currently filled by conventional semiconductors, *per se*, but rather in capturing the low cost and enormous variability inherent in organic systems that are otherwise not accessible. Success in achieving very-low-cost electronics hinges almost entirely on the ability to deposit and fabricate organic electronic devices using methods that represent a revolutionary departure from those commonly used by the current high-performance electronics industry. Hence, a great deal of current research has focused on depositing films and patterning devices on a large scale (leading to ‘macroelectronic’ applications), avoiding the need for labour-intensive techniques such as photolithography that today dominate the cost structure of conventional electronics.

The role of impurities

It is commonly observed that the purity of the starting material is central to assuring high-performance and high-reliability electronic device operation. In organic electronics, the types of impurities and their effect on performance may differ substantially from those affecting inorganic semiconductor devices. Substitutional lattice impurities such as boron or phosphorous can change the conductivity of the host inorganic semiconductor (for example, silicon) by several orders of magnitude if introduced at only the parts per billion level, because each impurity atom disrupts the valence states of the neighbouring lattice atoms. However, no equivalent ordered lattice or bond-sharing exists in organic solids. The van der Waals forces that bond organic crystals, and also provide the cohesive force between neighbouring polymer chains, do not involve sharing of electrons between nearest-neighbour molecules³⁵. Thus, impurities do not necessarily form electrically active substitutional defects. Yet, impurities may act as deep traps, extracting charge or acting as recombination sites within the thin film, or if ionic, they may still contribute charge to the surrounding crystal. Hence, although impurities act in remarkably different ways compared to an ordered inorganic semiconductor, they nevertheless can strongly influence the conductive properties of an organic material.

Indeed, intentional doping of molecular organic materials using the n-type dopants Pyronin B (ref. 36), 4-phenanthridinolato-Li (ref. 37) or Li (ref. 38), and p-type dopants such as F₄-TCNQ and FeCl₃ (refs 39–41), have been shown to increase the conductivity of small-molecular-weight films by several orders of magnitude compared with undoped organic layers. More frequently, however, dopants such as oxygen or even water can enter the organic film through unintentional exposure to the environment, leading to

degradation of the device performance over extended periods of operation^{42–46}. Also, molecular impurities such as fractions that are co-deposited with the desired organic semiconductor can disrupt the molecular stacking order, resulting in a significant reduction in charge carrier mobility.

Because polymer chains in solution have a dispersity of molecular weights whose mean values are often $>10^5$, depending on the length of the polymer chain, there are few strategies for purifying the material based on molecular weight alone. Chromatography and other 'distillation' processes are commonly used to achieve the highest level of purity⁴⁷, although attaining $<1\%$ impurity concentrations remains a challenge. In contrast, small-molecule materials have well-defined molecular weights, allowing for straightforward separation of the host from the impurities. One common means for accomplishing this is via thermal gradient sublimation²⁷, whereby the organic source material is heated in a vacuum furnace, and then allowed to condense downstream in a cooler region of the furnace. The low- and high-molecular-weight impurities each condense in a different temperature zone from the desired source material, making separation of these components possible. Using sublimation techniques, fractional impurity concentrations as low as 10^{-4} are potentially achievable, although it remains an important challenge to measure this quantity precisely because of the complex role that impurities play in affecting the properties of the host material.

Deposition of organic semiconductors

As noted previously, the principal distinction between polymers and small-molecular-weight organic thin films is the different methods used in their deposition and patterning.

Solution deposition of polymer thin films

In general, polymers are solution processed, uniformly applied across the entire wafer substrate by spin-on or spray-on methods. The solvent is then 'driven off' by evaporation after deposition. This technique can lead to very uniform films ~ 100 nm thick, as required in most devices such as OLEDs and OTFTs. Although there are several advantages to this method of film application, such as very-high-speed deposition over large substrate areas, there are also potential shortcomings. Primarily, the solvents used for one polymer layer can, and often do, attack previously applied layers, thereby limiting the complexity (and often as a consequence, the performance) of the structure that can be achieved⁴⁸. This limitation is most frequently overcome by functionalizing or blending polymers to perform the many different tasks required to meet all of the performance criteria demanded by a particular application. For example, in an OLED where both charge conductivity and luminescence efficiency must be simultaneously maximized, the polymer can itself be functionalized, or it can be blended with other polymers (or even small-molecular-weight materials and dendrimers) to achieve both properties in a single layer⁴⁹. Unfortunately, this can often lead to compromises, in which one performance parameter is traded off against another in the interest of low cost and fabrication simplicity.

A more serious shortcoming of full-surface deposition is the inability to locally pattern the electronic device. An example where substantial in-plane patterning must be applied is in fabricating colour displays based on a triad of closely spaced red (R), green (G) and blue (B) polymer OLEDs. The R, G and B sub-pixels must be separately contacted and energized such that their intensities can be individually controlled to achieve both the desired colour and intensity grey-scale⁵⁰. Unfortunately, using spin-on or spray-on methods, the entire substrate is coated with only a single material, requiring different strategies for such a lateral functionalization. One emerging patterning strategy is ink-jet printing^{51–54}. Micrometre-high polymer walls are prepatterned onto the substrate surface, thereby forming a region that defines the ~ 50 – 100 - μm pixel diameter (Fig. 2). This is followed by ejecting a droplet of the

solvated polymer from a micrometre-scale nozzle from a modified ink-jet printer. The droplet lands at the base of the well, spreading out to form a structure of dimensions determined by the well itself. This is done for each of the three colour sub-pixels, with adjacent wells in the triad each filled with polymers that are functionalized to produce the desired R, G and B colour emission (see Fig. 2). The process can be very rapid, generating a mobile phone display in only a few seconds.

Ink-jet printing requires precise control of the polymer chemistry to satisfy all the electrical and optical demands of a high-performance display. In addition, the polymer ink must have the appropriate mechanical properties, such that there is uniform coverage across the well diameter, as the applied voltage across the OLED, and hence the local current density, is strongly dependent on layer thickness. The process, therefore, places additional demands on the polymer inks over those for materials applied by conventional solution processing. Yet, early results with ink-jet printing of organic electronic devices have been quite promising⁵³. For example, Toshiba has recently demonstrated its application to the fabrication of a full-colour polymer display with a 17-inch diagonal dimension. Although several problems related to pixel yield and operational lifetime of the display require further work before practical, cost-effective components can be realized, the demonstration of the

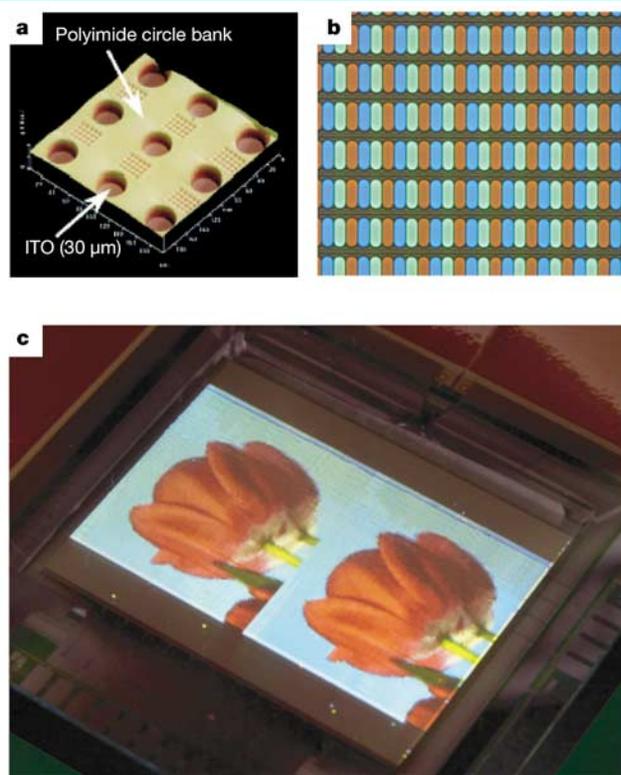


Figure 2 Ink-jet printing and the fabrication of full-colour polymer organic light-emitting device (OLED) displays. **a**, An atomic force micrograph of the polymer dams, or 'circle banks' prepatterned onto the substrate to receive and confine the polymer droplet from the ink-jet head, thereby forming a well defined polymer light-emitting device pixel, in this case with a diameter of $30\ \mu\text{m}$. Accurate positioning of the ink-jet nozzle to ensure hitting the circle bank 'target' that contains the indium tin oxide (ITO) anode ($30\ \mu\text{m}$ diameter), thereby forming the OLED, remains a challenge. From ref. 53. **b**, Three-colour triad of ink-jet-printed pixels, forming a prototype full-colour display (**c**). The individual $66 \times 200\ \mu\text{m}$ pixels in (**b**) are shown emitting fluorescent light after optical excitation. The full colour, 2-inch-diagonal ink-jet-printed display consists of a 128×160 array of polymer pixels, each pixel having dimensions of $60 \times 200\ \mu\text{m}$. Images in **b** and **c** courtesy of Philips Electronics.

patterning technology over such a large spatial scale suggests that ink-jet printing offers many possibilities for fabricating very-large-scale and complex organic electronic circuits that will be produced at a cost unapproachable using conventional semiconductor device fabrication methods.

Vapour-phase deposition of small molecules

Thermal sublimation in vacuum is the most common means for depositing small-molecular-weight thin films²⁷. This process involves the heating of the source material in a vacuum chamber, with the substrate located several centimetres distant, usually placed above the source. This ‘bottom up’ geometry prevents the source material from spilling out of the sublimation boat, and also avoids contamination of the substrate by flaking of material previously deposited onto the vacuum chamber wall, thereby creating dust that would ordinarily land on the substrate surface if a ‘top down’ deposition geometry were used. Vacuum thermal evaporation (VTE) is widely used in the processing of inorganic semiconductor devices because of the precision with which layer thicknesses can be controlled (typically to within ± 0.5 nm), and the relative simplicity of the process. One particular advantage of VTE is its ability to grow an unlimited number of layers, each optimized for a different function, to complete the device structure. This flexibility in device design is an inherent feature of ‘dry processing’—that is, the several material layers that are deposited to form a device structure do not physically interact because there is no solvent that might transport material and chemically attack the predeposited film. This compatibility between layers provides for enormous flexibility in choosing materials and structures to be used in complex, modern electronic devices.

Nevertheless, there are several shortcomings to VTE: it can be wasteful of material, and it is difficult to maintain a uniform deposition rate because the organic material sources are typically thermally insulating. Hence, they are only heated in regions where the organic source is in contact with the resistively heated boat, creating pockets in the source powder that occasionally collapse under gravity, resulting in spitting or rapid changes in evaporation rate. Nevertheless, commercial production of organic displays is primarily based on VTE, and very-large-area full-colour displays (with 20-inch-diagonal displays recently announced by IBM, and 13-inch-diagonal displays demonstrated by Sony, among others) have been demonstrated using this process. One such display is shown in Fig. 3a, along with a conceptual view of a future ‘universal communication device’ consisting of computer and communication electronics contained in a very compact appliance also containing a lightweight and rugged display deposited on a flexible substrate^{55,56}. Indeed, the ability to deposit organics onto a wide range of substrates without regard for the lattice-matching conditions that limit the materials choices of conventional semiconductor devices opens up many opportunities for applications based on this technology.

To avoid many of the shortcomings of VTE, an alternative method for depositing molecular organic thin films called organic vapour phase deposition (OVPD) has recently been introduced^{57,58}. This technique differs from VTE in that evaporation occurs in a hot-walled reactor vessel in the presence of an inert carrier gas such as nitrogen or argon that is also maintained at a temperature sufficiently high to induce evaporation of the source material (see Fig. 4). These apparently simple differences from VTE have numerous consequences: evaporation in the presence of a carrier gas transforms the pickup of material into an equilibrium process, as opposed to the non-equilibrium conditions extant in VTE. That is, in VTE, the rate of material evaporation (and hence arrival rate of molecules at the substrate surface) follows an exponential dependence, $r = r_0 \exp(-\Delta H_{\text{vap}}/kT_{\text{cell}})$, where ΔH_{vap} is the enthalpy of vaporization of the source organic, k is Boltzmann’s constant, and T_{cell} is the source cell temperature. In contrast, in OVPD the carrier

gas becomes saturated with the organic source material, which is then carried downstream to the cooled substrate where it enters a boundary layer of nearly stagnant flow. Depending on the pressure and temperature within the reactor, transport can be ‘diffusion limited’, whereby the molecule entering the thick boundary region suffers many collisions in a purely random process before reaching the substrate surface where physisorption occurs. At lower molecular partial pressures or higher gas flow velocities, the boundary layer thickness is decreased, and transport becomes ‘kinetically limited’—that is, the rate of arrival of the molecules at the substrate is determined by the flow field of the gas that entrains them towards the surface.

Differences in molecular kinetic energy and momentum inherent in the diffusive and kinetic regimes lead to considerable differences in, and hence control over, the resulting thin-film morphology. For example, in the channels of pentacene OTFTs grown by OVPD, the crystallite size of the pentacene can vary from only a few tens of nanometres when grown under highly kinetic conditions, to several micrometres when grown in the diffusive regime⁴ (Fig. 4). This variability arises because under equilibrium diffusive growth, molecules arriving at the surface can find their lowest-energy configuration with respect to neighbouring molecules, thus forming an ordered, self-assembled crystal structure. Under kinetic growth conditions, the molecules arrive rapidly at an aggressively cooled substrate, and are forced to ‘stick’ in positions that they assume at the time of arrival, hence leading to greater crystalline disorder. The result of this control is an increase in transistor field-effect hole

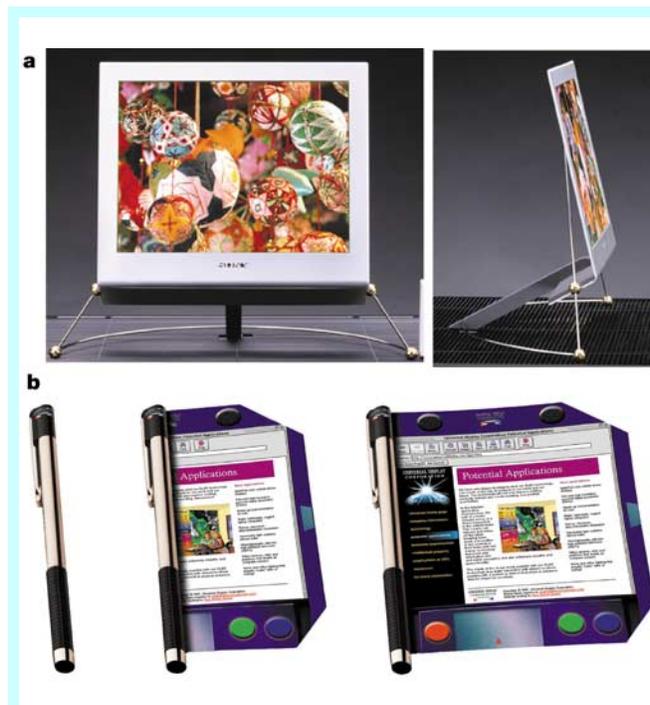


Figure 3 Organic emissive displays in the present and the future. **a**, A full colour, 13-inch diagonal small-molecular-weight OLED display. The display is only 2 mm thick, and uses top emitting OLEDs on an active transistor matrix backplane. The display supports full motion video images, and can be viewed at very oblique angles (right) without incurring a significant change in colour or contrast. Images courtesy of Sony Corp. A principal advantage of organic electronic devices is their ability to be deposited onto any substrate, including flexible and robust plastic sheets. **b**, A conceptual view of a future organic electronic flexible display that when not in use is rolled up into a pen-like device containing computational and wireless communication electronics. This lightweight and potentially low-cost electronic appliance is enabled by the high-resolution flexible display technology now being developed by the organic electronics community. Images courtesy of Universal Display Corp.

mobility under diffusion-limited growth by over an order of magnitude when compared to that obtained for kinetically grown crystals. Indeed, the highest hole mobilities obtained for pentacene TFTs grown by both OVPD and VTE are $\mu_{\text{eff}} \approx 1.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, comparable to electron mobilities in amorphous silicon TFTs^{3,4}.

As well as allowing the control of crystalline morphology by the saturated pickup of the source material, OVPD is also a relatively dust-free process, because the chamber walls are maintained at a temperature high enough to prevent readsorption. This also leads to very-high-efficiency material use, as the only cold region in the reactor where molecular adsorption can occur is the substrate. Finally, none of the non-uniformities in evaporation rate common to VTE affect growth by OVPD, simply because the source material is infused with the carrier gas, making the entire source isothermal,

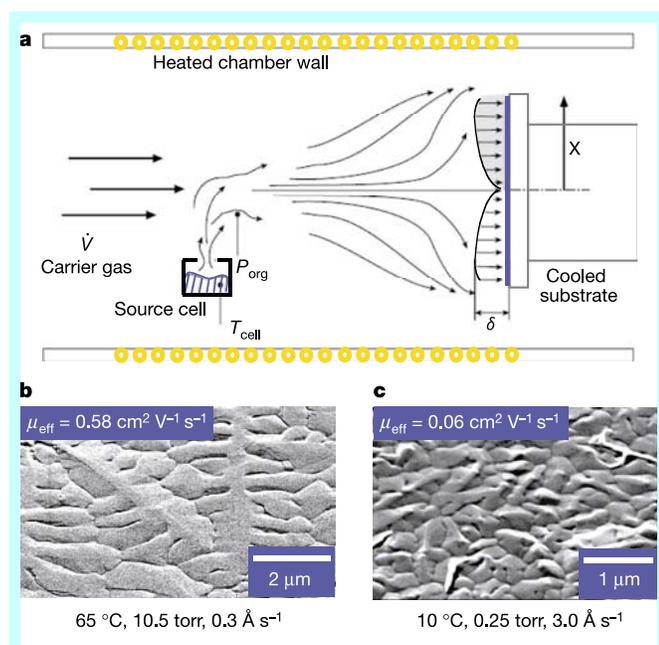


Figure 4 The process of organic vapour-phase deposition (OVPD) for the growth of organic electronic devices. **a**, A schematic cross-section of a hot-walled OVPD reactor showing the growth process. Growth occurs by infusing a hot boat containing the organic source material with an inert carrier gas. The gas becomes saturated with the organic vapours and carries them downstream to a cooled substrate where they physisorb onto its surface. Shown immediately in front of the substrate is a hydrodynamic boundary layer of thickness δ . Depending on the reactor pressure and rate of molecular pickup by the carrier gas, the boundary layer thickness can be varied from very thin (in which case the growth rate is considered kinetically limited), whereby the nearly ‘ballistic’ transport of molecules to the surface dominates) to several millimetres thick (corresponding to diffusion-limited growth, whereby the molecules suffer many collisions within the boundary layer, thereby controlling the growth process). Because the walls of the chamber are hot, adsorption occurs only on the substrate, resulting in extremely high-efficiency use of materials. Further, the pickup of molecular species results in saturation of the inert carrier gas, resulting in highly controlled growth rates. Here, \dot{V} is the gas volumetric flow velocity, P_{org} is the partial pressure of the organic material in the gas stream, T_{cell} is the temperature of the organic source cell, and X is the position as a function of distance from the substrate axis. **b**, **c**, The growth regime affects the morphology of a pentacene film. The conditions in **b** correspond to diffusion-limited growth (high substrate temperature and chamber pressure, slow growth rate) resulting in very large crystalline domains. In a thin-film transistor, these domains can span the entire device active region from source to drain contacts, leading to a high field-effect hole mobility of $\mu_{\text{eff}} = 0.58 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. For kinetically grown films (**c**) (low substrate temperature and chamber pressure, and high growth rate), the crystallite size is considerably smaller than in **b**. In this case, transport from source to drain is primarily limited by scattering from grain boundaries between the individual crystallites, resulting in a tenfold decrease in hole mobility. From refs 4 and 58.

independent of its thermal conductivity.

As in the solution-based application of polymers, simple deposition either by VTE or OVPD results in the full surface of the substrate being uniformly coated. In both OVPD and VTE, therefore, the most common means for achieving patterned growth as required for display pixellation is to deposit the material through a shadow mask placed in close ($\sim 1 \mu\text{m}$) proximity to the substrate surface. The mask has an array of apertures whose dimensions match that of the desired deposit diameter, with the minimum feature size approximately equal to that of the mask thickness (for example, $\sim 20\text{--}75 \mu\text{m}$). Indeed, under highly controlled conditions, the smallest features achieved using shadow masks are⁵⁹ $1\text{--}5 \mu\text{m}$.

An analogue to ink-jet printing, known as organic vapour-jet printing (OVJP), has also been proposed and developed for use with small-molecular-weight materials^{59,60}. Like OVPD, the solvent is a hot inert carrier gas that vaporizes the organic source, creating a flow of volatilized molecules. These molecules pass through a nozzle, after which they are deposited onto a cold substrate placed in close proximity ($\sim 10\text{--}100 \mu\text{m}$) to the nozzle tip. This process replaces the liquid solvent used in ink-jet printing with an inert carrier gas, thereby eliminating many of the mechanical properties of the liquid (such as meniscus formation leading to thickness non-uniformities), and does not require polymer wells to be formed on the substrate to spatially contain the liquid droplet. Like ink-jet printing, OVJP is at its very earliest stages of development, and as yet there are no clear demonstrations that this technology will eventually find use in the large-scale production of low-cost organic electronic circuits and systems.

Thermal transfer of organics

Patterned deposition is based on the thermal imaging dry transfer (using, for example, a laser or other localized heat source) of a

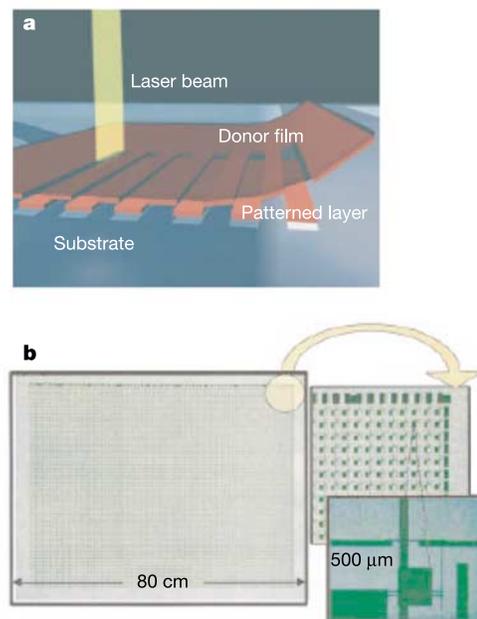


Figure 5 Laser-induced thermal imaging transfer of active organic semiconductor materials to a substrate. **a**, A ‘donor’ film is pre-loaded with the organic thin film, which is then locally transferred by thermal ablation using a laser. From ref. 63. **b**, Micrograph of a $50 \times 75 \text{ cm}$ array of pentacene organic thin-film transistors whose source and drain contacts were patterned using laser-induced thermal imaging. The various images show different magnifications from (clockwise) the full panel, a small segment containing approximately 100 TFTs, and a single TFT with a gate length of $\sim 20 \mu\text{m}$. From ref. 52.

polymer or small-molecular-weight material from a ‘donor’ or material source sheet, to the ‘receiver’ or target substrate, and is also attracting interest⁶¹. The transfer occurs by ablation of materials that are predeposited onto the donor sheet held in contact with the substrate (Fig. 5). In one demonstration of this method, high-conductivity, $5 \times 2.7 \mu\text{m}$, polymer contacts loaded with single-walled carbon nanotubes used for the source and drain of a pentacene transistor were transferred using an infrared diode laser as the ablation source⁶². The pentacene channel was applied by routine VTE deposition, thereby spanning the gap between source and drain. A $50 \times 75 \text{ cm}$ printed transistor backplane has been fabricated using thermal imaging, suggesting its utility for producing large-area organic circuits (Fig. 5). This technique, however, is not confined to the deposition of contacts, but can be applied to the transfer of the active semiconductor layer as well⁶³. For example, a blend of a blue-light-emitting polymer and a hole transport layer was transferred to a receiving substrate using laser ablation, creating well-formed and high-resolution blue-emitting OLEDs. The transferred material must be optimized such that its resistance to thermal degradation and mechanical properties are suitable for this

so-called laser-induced thermal imaging process. Although this optimization can lead to compromises in device performance, laser-induced thermal transfer of organics is showing early promise as a route for realizing practical macroelectronic integrated circuits.

Direct patterning of organic electronic devices

To capture the low-cost potential of organic thin films inherent in their low-temperature deposition on substrates such as glass, plastic or metal foils, it is imperative that these processes be complemented by similarly inexpensive device patterning and fabrication methods. For this reason, researchers have long sought innovative and fault-tolerant methods for patterning thin organic films that are simple and do not result in the destruction of these often fragile or environmentally sensitive materials.

In addition to patterning during deposition using techniques such as ink-jet or OVJP, methods have also been developed to pattern the organics into circuits after deposition. These methods include direct nanoimprinting of the polymer⁶⁴, lithographically induced self assembly⁶⁵, microcutting of the cathode metal after deposition onto the underlying active organic materials⁶⁶, photocrosslinking of polymer regions to form conducting contacts to organic thin-film transistors, followed by creating vertical interconnects between circuit levels (or ‘vias’) using metal ‘pins’³², lamination of contacts onto the organic surface from soft rubber stamps⁶⁷, and cathode formation by cold welding from stamps^{68,69}.

Cold welding is the binding of two clean surfaces, each containing a film of the same metal, on contact or on application of a moderate pressure (Fig. 6). To pattern contacts and interconnects, one starts by forming a ‘stamp’ in a soft material such as poly(dimethylsiloxane) (PDMS), where the desired pattern is embossed onto the stamp surface⁶⁸. Then an adhesion-preventing coating is placed on the stamp, followed by the deposition of the metal at a thickness needed for the cathode or other metallic interconnect. Before the cold-welding step, the organic layers forming the desired electronic device are deposited across the full surface of the substrate in the normal sequence. This is capped with a very thin ($\sim 5 \text{ nm}$)

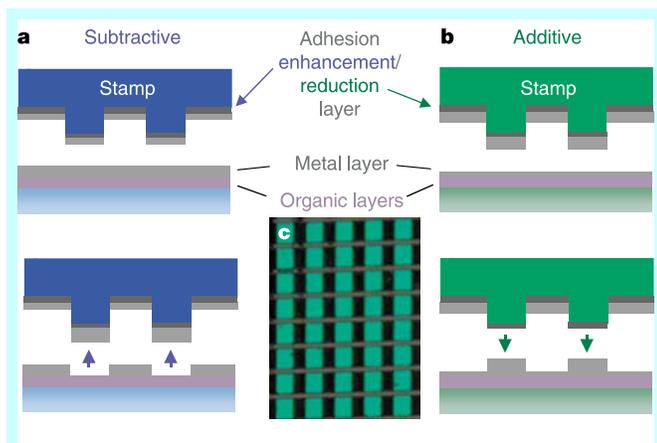


Figure 6 Direct micro/nanopatterning of an organic electronic device by cold welding.

In the subtractive process (a), the organic layers comprising the active electronic device are deposited across the full substrate surface, followed by the deposition of the unpatterned metallic contact. A hard ‘stamp’ is then fabricated, whose raised regions correspond to the regions of the finished device where cathode metal is removed. The stamp is first coated with an adhesion ‘enhancement’ layer, followed by deposition of the same metal used as a contact metal to the organic electronic device. The stamp is then brought into a pressure contact with the substrate, such that the metal on the stamp and substrate form an intimate metallic bond, or cold weld. Pressing harder causes the metal at the edge of the stamp to fracture, allowing for lift-off of the metal under the stamp when it is separated from the substrate. The amount of pressure that needs to be applied to cause a fracture at the edge of the stamp increases with the thickness of the metal. Note that no pressure is applied to a device whose active region is under the metal contact (for example, a detector or an OLED). In the additive process (b), the metal layer that is predeposited onto the organic layer surface is very thin (typically $\sim 5 \text{ nm}$). This is the ‘strike layer’. Unlike the subtractive process, the desired thickness of the metal contact is deposited onto the stamp itself, not the organic layers. Further, before deposition on the stamp, the stamp surface is coated with an ‘adhesion reduction layer’ that ensures that the metal can easily lift away from the stamp after separation from the substrate. The stamp and substrate are then brought into pressure contact where cold welding once more occurs and the metal on the stamp is left behind, directly forming the contact pattern. The thin residual strike layer between the contacts is then removed by gentle etching by a reactive gas or by simple sputtering. Using soft stamps, this process requires very low pressures that are not dependent on metal thickness (no fracture is required). The pattern definitions achievable using these processes are $< 10 \text{ nm}$ in many cases. In c is shown a segment of a passive matrix OLED display patterned using the subtractive process. The green regions are pixels emitting light when electrically addressed. From refs 68 and 69.

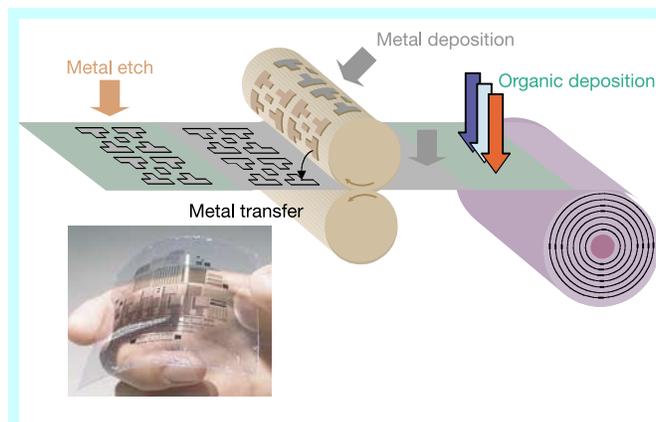


Figure 7 Conceptual diagram of continuous and very-low-cost manufacture of organic electronic devices. Starting with a roll of plastic substrate, the organic materials forming the device active regions are first deposited either from the liquid or vapour phase, and then a metal ‘strike layer’ (such as in Fig. 6) is deposited. The film is then passed between rollers with an embossed pattern representing the ultimate electrode scheme required on their surfaces. These rollers then directly pattern the electrodes, again as in Fig. 6. In the final step, the strike layer metal is removed by dry etching, completing the circuit. The sheets are eventually coated to eliminate degradation from exposure to the environment, and then packaged to suit the desired application. The lower photograph shows a fully processed wafer foil containing all-polymer transistors and integrated circuits, showing recent progress in achieving this vision of the future. Photograph courtesy of T. Jackson, Pennsylvania State University.

unpatterned metal film, such as LiF/Al/Au, that ultimately forms part of the injecting cathode into the organic heterostructure. This thin layer is known as the 'strike layer'.

In bringing the stamp and substrate into contact and under weak pressure (typically 1 atm), the metal on the stamp cold-welds to the same metal which is also used for the strike layer (Fig. 6). Here, noble metals are preferred, as they do not form thick oxides that might prevent bonding when brought into contact with the second metal surface. As the stamp is lifted away from the surface, its thick metal layer is left behind, bonded to the strike layer owing to the cold weld. Finally, the strike layer between the metal pattern remaining after stamping is removed, using a plasma or other light etching step. This technique has been shown to result in high-quality organic electronic devices with pattern resolutions approaching 10 nm.

The organic future

The opportunities for the use of organic thin films in modern electronic circuits are rapidly expanding, based on the very high-performance and unique functionality offered by these principally carbon-containing semiconductors. However, their practical implementation in electronic applications will ultimately be decided by the ability to produce devices and circuits at a cost that is significantly below that needed to manufacture conventional electronic circuits based on, for example, silicon. If successful, these low-cost fabrication processes will ultimately result in the 'printing' of large-area organic electronic circuits using roll-to-roll or web-based methods, where low-temperature deposition of the organics is followed by metal deposition and patterning in a continuous, high-speed process analogous, perhaps, to processes used in the printing of documents or fabrics (Fig. 7). However, much work must be done before such an ambitious goal can be realized. Although many innovative technologies have been developed relating to the fabrication of thin-film organic devices with high performance and long operational lifetime, very few of these technologies have left the laboratory and found their way into a manufacturing environment. Indeed, only the simplest fabrication technologies have so far been implemented on manufacturing lines: spin-coating of polymers over broad substrate surfaces to create monochrome displays, or in the case of small molecules, vacuum deposition through shadow masks resulting in full colour displays. Yet even these early demonstrations are impressive. As the more sophisticated and versatile methods currently being developed in the laboratory make their way into the manufacturing environment, we can expect that organic electronic circuits whose functions are only now being envisioned will one day revolutionize the technological world in which we live. □

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