

Patterning of organic devices by interlayer lithography†

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We report a new lithographic procedure that enables the patterning of as-received semiconducting polymers and small molecules at the near micron level without causing discernible degradation of the patterned material. The method involves a minimum of processing steps, requires no modification of the active layer, and is compatible with both rigid and flexible substrates. The technique makes use of an intermediate resist layer between the substrate and the active layer, *i.e.* underneath the active layer, and involves the simultaneous patterning of the resist and active layers in a single expose/develop step. The technique has been successfully applied to the fabrication of flexible ITO-free light-emitting diodes and photodiodes, yielding peak quantum efficiencies of 8.8 cd A⁻¹ and 57% respectively comparable to similar devices fabricated on ITO-coated glass. It is also readily extendible to the patterning on a single substrate of multiple devices incorporating different component materials, *e.g.* the red, green and blue pixels of a colour display.

There is considerable interest in patterning techniques that allow well-defined geometric features to be produced in organic thin film structures at near micron resolution, reproducibly and at low cost. These techniques are of particular interest for optoelectronic devices based on organic semiconductors, where the ability to create densely packed regular arrays of components is important for many applications, including displays, imaging, electronics, communications and sensors. Conventional photolithographic techniques (such as those established for standard inorganic materials) often involve harsh chemical treatments and/or complicated wet processing steps that adversely affect the optical and electrical properties of typical functional organic materials (since the latter materials have a number of similarities to standard photoresists¹). In consequence, alternative non-damaging patterning techniques are being developed, including inkjet printing,² screen printing,³ sequential displaced shadow mask evaporation of small molecules,⁴ thermal transfer processes,^{5–7} laser assisted patterning^{8,9} and contact printing.¹⁰ However, these techniques variously suffer from insufficient resolution, poor scalability to larger substrate sizes, difficulty in ensuring pattern registration between sequential steps, and complex, costly, processing protocols that often require the development of new manufacturing equipment. To achieve adequate feature resolution for organic electroluminescent displays *via* inkjet printing, for instance, requires multi-step lithographic patterning of the substrate to produce well-like receptacles into which the polymer or

dendrimer ink droplets can be deposited. The corresponding shadow mask evaporation approach for small molecules involves a similar patterning of the substrate to provide separator banks and requires rigorous maintenance of the shadow mask to remove deposited residues that might otherwise cause cross-contamination between the red, green and blue pixels. In both cases, these requirements add considerable complexity and cost and are widely seen as obstacles to economic manufacturing.

In light of the above issues it remains the case that photolithography, *if* it could be carried out in a non-destructive manner, would be the preferred method for patterning functional organic materials due to its high-throughput parallel nature, its scalability to large-area substrates, and its use of established equipment and expertise. Accordingly, a number of researchers have sought to develop alternative photolithographic procedures that are compatible with organic materials. In the simplest of these approaches, patterning is carried out in the conventional manner until the final step when the photoresist is peeled away physically from the active layer, thereby obviating the need for aggressive etchants.¹¹ The adhesion between the active layer and photoresist however can be significant, rendering the active layer susceptible to physical damage when the photoresist is removed. To lessen this problem, DeFranco and co-workers reported the use of an inert sacrificial buffer layer of parylene-C between the active layer and the photoresist.¹² The parylene-C is deposited on the active layer by chemical vapour deposition (CVD) before deposition of the photoresist, and the patterning is then carried out in the usual manner, leaving at the penultimate step a patterned layer of the organic material coated with the sacrificial buffer layer. The parylene-C adheres only weakly to the organic layer and so is less liable to cause damage to the active layer when it is peeled away to expose the active layer.

DeFranco *et al.* also reported a modified version of the standard lift-off technique designed to be less-damaging to

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organic materials. In conventional lift-off lithography the photoresist is deposited directly on the substrate and used as a contact mask, *i.e.* the photoresist is patterned, the organic layer is then deposited in the voids of the photoresist, and the photoresist is then removed chemically, leaving the organic film patterned with the original void structure of the photoresist.¹² To avoid the use of aggressive reagents in the final step, DeFranco *et al* instead patterned a layer of parylene-C with the desired void structure using standard lithography. The organic layer is deposited in the voids, and the parylene-C is finally peeled away using a combination of Scotch tape and tweezers. This approach is effective on the laboratory scale but may not transfer readily to a manufacturing environment. More conventional lift-off approaches have also been used¹³ but these require elaborate re-optimisation of the process. In particular, re-selection of the resist and polymer solvents is required (in order to avoid interference) as well as reformulation of the lift-off solvent.

In addition, a number of researchers have used direct-write lithographies, in which the active material also serves as the resist. This can be achieved by chemical modification of the organic semiconductor^{14–17} or by loading with appropriate additives¹⁸ or, alternatively, precursor route synthesis methods may be used, with light exposure driving the conversion reaction to generate the desired (insoluble) conjugated polymer.¹⁹ In all of these approaches, the active layer is exposed using a photomask and the un-exposed soluble regions of the film are then removed using an appropriate developer.

The above procedures have been successfully applied to the patterning of functional organic materials but have clear limitations. The buffer method, for instance, involves a relatively large number of processing steps (including deposition of the parylene-C by CVD) and risks damaging the soft active layer when the buffer is peeled away. Similar issues arise for lift-off lithography and it is not clear that the technique can be readily extended to the patterning of multiple materials on a single substrate as required in a colour display. Direct-patterning techniques, by contrast, involve relatively few processing steps but they risk compromising the optoelectronic properties of the active layer (due to the retention of cross-linkable additives and/or incomplete consumption of reactive moieties) and significant effort is required to re-tailor the chemical structure of the organic layer to achieve resist-like properties. It is clear that an efficient and non-damaging photolithographic patterning strategy that can be successfully applied to existing functional organic materials, without the need to re-configure for each new material, would hold many attractions. In this manuscript we report just such a lithographic procedure which, moreover, involves a minimum number of processing steps, requires no modification of the chemical structure, uses standard processing solvents, and is compatible with both rigid and flexible substrates.

Our patterning technique, referred to here as *interlayer lithography*, makes use of an intermediate photoresist layer between the substrate and the functional organic layer to be patterned. The resist layer is exposed through a photomask either before or after deposition of the functional organic layer, thereby rendering the exposed regions of the resist soluble (in the case of a positive resist) or insoluble (in the case

of a negative resist) in an appropriate developer. The coated substrate is then transferred to the developer solution which removes the soluble parts of the resist layer together with the overlying parts of the functional organic layer, leaving a thin patterned film of the active material over a likewise patterned film of the resist material. The active layer and the photoresist layer are in effect simultaneously patterned in one expose/develop step, minimizing the number of processing steps. We stress that the insoluble regions of the photoresist remain in place at the end of the patterning process and hence the usual need for aggressive etchants or peeling of the photoresist is avoided. The placement of a photoresist *below* the layer to be patterned has proven to be highly effective in practice, allowing a variety of functional organic thin films (including conductors, semiconductors and insulators) and also standard metals to be readily patterned on a wide variety of substrate materials. The general principle of the patterning procedure is outlined schematically in Fig. 1, and full details are provided in the Experimental section at the end of the paper. In passing, we note that the approach we describe is not suited to situations where the material to be patterned requires high temperature (or otherwise harsh) deposition conditions that are incompatible with the limited durability of the pre-coated resist layer, as for instance would be the case for standard inorganic semiconductors. This is likely the reason why our technique is not found in the standard arsenal of lithographic patterning methods.

For the method to succeed the developer must penetrate the active layer but should not dissolve, crack, delaminate or otherwise unfavourably alter its physical or chemical properties. In addition, it is desirable that the resist layer should have good film-forming properties, simple processing requirements, high optical transmission, excellent chemical and thermal stability post-patterning, and good adhesion to both the substrate and the over-coated layer to be patterned. We have found that the commercially available resist SU8 together with the developer propylene glycol monomethyl ether acetate (PGMEA) meet these criteria extremely well. SU8 is a fully epoxidized bisphenol-A/formaldehyde novolac co-polymer which, in the presence of an appropriate photo-acid generator, becomes a negative resist capable of producing high aspect ratio (>20) features with vertical profiles.²⁰ SU8 can be deposited on a variety of substrate surfaces (including glass, silicon and various plastics), and in general other organic

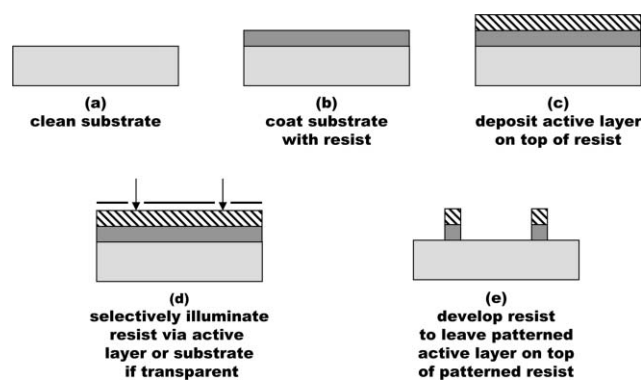


Fig. 1 Schematic diagram of the patterning method.

layers adhere well to it. Exposure to UV radiation cross-links the SU8 and converts it into an insoluble film.

To illustrate the technique, we begin by describing the patterning procedure as applied to films of the conducting polymer Baytron P. Baytron P is a high conductivity formulation of poly(2,5-ethylenedioxythiophene) : polystyrenesulfonate (PEDOT : PSS) from H.C. Starck GmbH that is commonly used as the hole injecting contact in organic light-emitting diodes. Two commercially available formulations of PEDOT : PSS were used here, Baytron P and Baytron P VPAI 4083, which differ in their PEDOT : PSS ratios and have resistivities of $\sim 1 \Omega \text{ cm}$ and $\sim 500\text{--}1000 \Omega \text{ cm}$ respectively. SU8 is an effective interlayer resist for PEDOT : PSS and mediates the deposition of high quality films of hydrophilic Baytron P even on hydrophobic substrates. Two types of SU8 were used in this work, SU8-2 and SU8-10, which yield films of different thickness due to their different viscosities. Our patterning procedure is shown to work with a variety of substrate materials, including glass, silicon, electrical circuit board (flame retardant woven glass reinforced epoxy resin, FR4) and flexible poly(ethylene terephthalate) (PET) films.

In the case of opaque substrates (e.g. Si and FR4), the SU8 must be illuminated through the overlying functional organic layer or before this layer is deposited. In the case of transparent substrates (e.g. glass and PET), patterning may additionally be achieved with illumination through the substrate. This creates the option of using the substrate itself to define the pattern. In such an approach, the desired pattern is pre-written onto the substrate, creating in effect a “self-aligning mask” which removes the usual need for a mask aligner (in conventional patterning procedures, a mask aligner is required to achieve accurate registration between the mask and the substrate). In all cases, we were able to successfully pattern PEDOT : PSS with better than $2 \mu\text{m}$ resolution (the limit of our tests to date), indicating the generality of the patterning technique and its suitability for many applications. Optical micrographs of patterned SU8-10/Baytron P on (a) glass, (b) silicon, (c) PET and (d) FR4 are shown in Fig. 2. In the cases of glass and FR4 board, for illustrative purposes only, the procedure was used to pattern the SU8-10/Baytron P in the shape of numerical digits of approximate dimensions $250 \times 375 \mu\text{m}$.

To determine whether the patterning procedure was suitable for device applications, we compared the characteristics of patterned PEDOT : PSS on SU8-coated glass with those of unpatterned PEDOT : PSS on glass. Four key parameters were investigated: optical transmission, surface roughness (morphology), electrical conductivity and work function. The optical transmission in the visible wavelength region was approximately 80% for both samples, indicating that the presence of the thin SU8-2 layer does not noticeably affect the total optical transmission (see Fig. S11 in ESI† for transmission spectra). This is an important consideration for displays, photodetectors and other optoelectronic applications where light is required to enter or exit the device structure through the substrate. The mean surface roughness was determined by atomic force microscopy and found to be similar for the two films, namely 1.53 and 1.55 nm for glass/Baytron P and glass/SU8/Baytron P respectively, indicating that the patterning

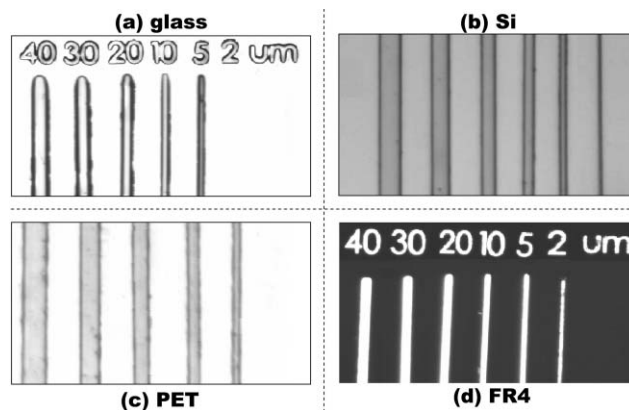


Fig. 2 Optical micrographs of patterned SU8-10/Baytron P on (a) glass, (b) silicon, (c) PET and (d) electrical circuit board (glass epoxy FR4 board). The widths of the patterned lines are 40, 30, 20, 10, 5 and $2 \mu\text{m}$. In the case of glass and FR4 board, for illustrative purposes only, the procedure was used to pattern the SU8-10/Baytron P into the shape of numerical digits of dimensions $250 \times 375 \mu\text{m}$. Note, in order to obtain reasonable sized images of the numerical digits, a lower magnification was used for the films on glass and FR4 than for those on silicon and PET. As a result, the line thicknesses appear somewhat broader for the latter two samples.

procedure does not appreciably increase the roughness of the PEDOT : PSS film (see Fig. S12 in ESI† for AFM images and typical cross-sectional profiles for the two samples). Furthermore, the electrical properties of the PEDOT : PSS remain favourably undiminished by both the patterning process and the presence of the underlying photoresist. For instance, using the Kelvin probe technique, the work function was determined to be $4.91 \pm 0.18 \text{ eV}$ for unpatterned Baytron P on glass compared with 5.06 ± 0.11 for Baytron P on patterned SU8-2 coated glass; and, using the four point probe technique, the conductivity was determined to be $2.54 \pm 0.38 \text{ S cm}^{-1}$ for Baytron P on glass compared with $3.81 \pm 0.25 \text{ S cm}^{-1}$ for Baytron P on patterned SU8-2 coated glass. The slightly higher conductivity measured for the patterned film is desirable for device applications and is considered to be due to the removal of surface contaminants by the developer.

A critical requirement of any patterning procedure for device applications is that the patterned material should be functionally undamaged. To establish whether this is indeed the case, we fabricated polymer light-emitting diodes on flexible PET substrates. The devices used a Baytron P anode patterned in the manner described above and a 1 : 1 blend by weight of poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) and poly(9,9-dioctylfluorene-co-*N*-(4-butylphenyl)diphenylamine) (TFB) as the active layer. The devices had the following structure: PET ($100 \mu\text{m}$)/SU8-2 ($1.2 \mu\text{m}$)/PEDOT : PSS (150 nm)/TFB : F8BT (90 nm)/LiF (1 nm)/Al (100 nm). Fig. 3 shows the current density–voltage–luminance (J – V – L) characteristics for a typical device. The turn-on voltage of the device was $\sim 2 \text{ V}$ and a luminance of 100 cd m^{-2} was obtained at $\sim 3.5 \text{ V}$. The peak power efficiencies were 13.7 lm W^{-1} and 8.8 cd A^{-1} , comparable to ITO devices with the same structure. These values also compare very reasonably with the typical efficiencies ($\sim 20 \text{ lm W}^{-1}$) obtained in a corporate environment for polymer LEDs fabricated on rigid

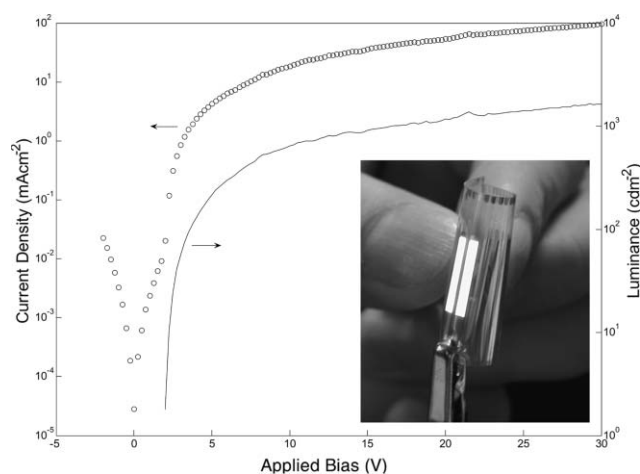


Fig. 3 The current density–voltage (open circles) and luminance–voltage (line) characteristics of a typical LED fabricated on a flexible PET substrate. The inset shows a photograph of a similar device in operation (see text for details).

ITO-coated glass substrates.⁹ In addition, the current efficiency remained high (above 4 cd A^{-1}) up to 8 V, at which bias the luminance reaches 500 cd m^{-2} . The inset to Fig. 3 shows an unencapsulated flexible substrate device with pixel size $2 \text{ mm} \times 8 \text{ mm}$ working under ambient conditions. The device emits bright yellow light with CIE 1931 coordinates of (0.455, 0.535), and continues to function without any obvious problems even when rolled up tightly with a bending radius $r_B < 4 \text{ mm}$. This compares favourably with devices fabricated on ITO-coated flexible substrates, for which the anode resistance is found to increase sharply when $r_B < 8 \text{ mm}$ due to micro-cracking.²¹

In addition, we have successfully fabricated flexible polymer photodiodes with patterned Baytron P anodes, using a 1 : 1 blend by weight of poly(3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6) C_{61} (PCBM) as the active layer and Al as the cathode. The current–voltage response of a typical device is shown in Fig. 4 for 550 nm incident light of intensity $0.7 \mu\text{W}$. The devices exhibited high peak external quantum efficiencies of $\sim 57\%$, indicating that they can be used as sensitive photodetectors. The peak quantum efficiency compares favourably with values of 65–70% for conventional P3HT/PCBM devices on ITO-coated glass.²² The marginally lower efficiencies we obtain are primarily due to our use of a flexible substrate, which limits the (post-patterning) annealing temperature to $120 \text{ }^\circ\text{C}$. This is only marginally above $110 \text{ }^\circ\text{C}$, the glass transition temperature of P3HT,²³ and significantly below the typical temperatures of 140 to $155 \text{ }^\circ\text{C}$ used when fabricating devices on glass.^{22,24}

The method may be further extended to the patterning on a single substrate of multiple devices based on different component materials, *e.g.* the red, green and blue (RGB) pixels of a full colour display. As a proof of principle demonstration, we fabricated a simple three-pixel RGB element on a glass substrate. SU8-10 was used as the photosensitive intermediate layer and three typical polyfluorene derivatives, denoted for simplicity PF-Blue, PF-Green and PF-Red, were selected as

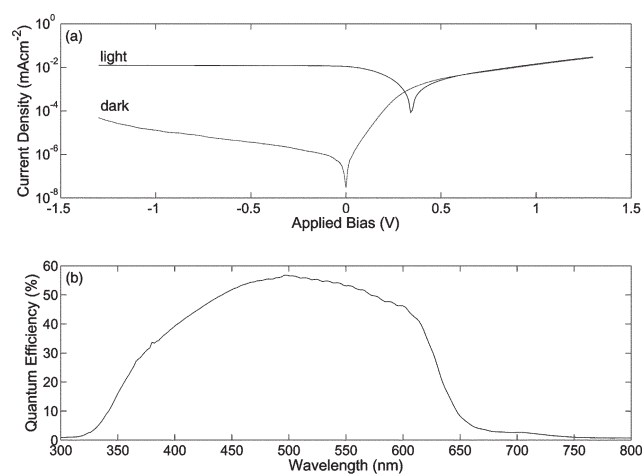


Fig. 4 (a) The current density–voltage characteristics of a typical photodiode fabricated on a flexible PET substrate in the dark and under $0.7 \mu\text{W}$ 550 nm illumination. (b) The photocurrent action spectrum for the same device.

the active materials. The method used is shown schematically in Fig. 5 and includes the following key steps: (a) successive deposition of the photosensitive material (1), Baytron P (2), Baytron P VP AI 4083 (3), and the first polyfluorene (4) on the substrate; (b) exposure of the photosensitive material *via* a photomask (5) with UV radiation (350–400 nm); (c) treatment with developer to remove the unexposed soluble part of the photosensitive material along with the unwanted portion of the overlying organic layers; (d) successive deposition of the photosensitive material, Baytron P (2), Baytron P VP AI 4083 (3), and the second polyfluorene (6); (e) exposure of the photosensitive material *via* a photomask (5) with UV radiation; (f) treatment with developer to remove the unexposed soluble part of the photosensitive material along with the unwanted organic layers; (g)–(i) repeat of steps (d)–(f) with the third polyfluorene (7), again using a photomask (5) to enable selective UV exposure. The device was completed in step (j) by thermal evaporation of 1 nm LiF followed by 100 nm of aluminium (8). (We note that in the above description, the three polyfluorene materials may be deposited in any order.) Importantly, the multicolour patterning utilises relatively few lithographic steps and uses an identical process for each colour, without the need to change the interlayer resist, the deposition solvent or the developer solution each time.

The EL emission spectra for the three pixels are shown in Fig. 6 and are essentially the same as those of the individual red, green and blue LEDs fabricated on separate substrates. The multicolour devices still require some additional optimisation as the drive voltages are relatively high. (See Fig. S13 in ESI† for the current–voltage–luminance characteristics). For instance, to achieve a brightness of 100 cd m^{-2} drive voltages of 7.8 V, 7 V and 8.2 V were required for the red, green and blue pixels respectively. This is primarily because the emitters were deposited directly onto un-annealed PEDOT : PSS, whereas standard PEDOT : PSS handling protocols recommend prolonged annealing at temperatures above $120 \text{ }^\circ\text{C}$ before deposition of the organic layer in order to improve the conductivity and work function.²⁵ This, however,

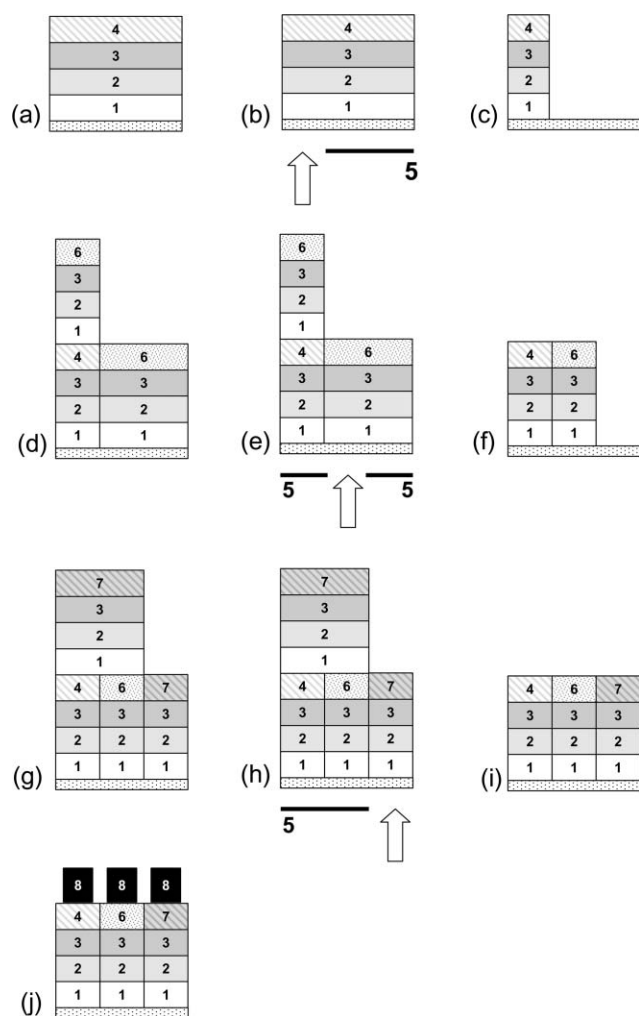


Fig. 5 Schematic diagram representing the procedure for patterning multiple devices, incorporating different component materials, on a single substrate, e.g. the red, green and blue pixels of a colour display. See main text for details. The numeric labels correspond to the following materials: (1) SU8 resist; (2) Baytron P; (3) Baytron P VP AI 4083; (4) the blue-emitting polyfluorene; (5) a photomask; (6) the green-emitting polyfluorene; (7) the red-emitting polyfluorene; and (8) aluminium-capped LiF.

causes partial conversion of the SU8 resist and, in so doing, risks compromising the patterning resolution. In ongoing studies, we are evaluating alternative resist materials which are fully compatible with standard PEDOT : PSS handling procedures.

The same procedure should be straightforwardly extendable to a full colour display by preparing a plurality of red, green, and blue pixels arranged in an appropriate spatial pattern. The ultimate spatial resolution and feature density remain to be established but the experiments performed to date (c.f. Fig. 2) are encouraging in relation to typical display requirements. For instance, feature sizes of order $60 \mu\text{m} \times 200 \mu\text{m}$ are typical for QVGA active matrix portable displays, easily achievable using the technique described here. In the case of passive and active matrix displays, it may be advantageous for the photoactive intermediate layer to be conductive in order to provide an electrical connection between the patterned

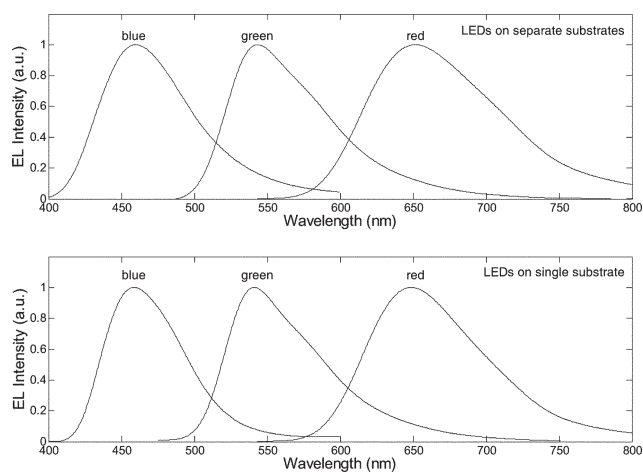


Fig. 6 Comparison of the electroluminescence spectra for both (a) individual red, green and blue LEDs fabricated on separate substrates and (b) the sequentially patterned red, green and blue pixels on a single substrate.

light-emitting material and the underlying matrix. In the case of SU8 photoresist, this might be favourably achieved by the addition of conductive dopants such as Ag nanoparticles²⁶ to the photoresist solution or by blending with an appropriate conducting polymer.^{27,28} This is the subject of ongoing investigations.

In summary, we have developed a simple and reliable method of selectively patterning thin film organic conductors, semiconductors and insulators on both rigid and flexible substrates. The technique permits patterned arrays of organic devices to be fabricated at near-micron resolution, at low cost, and using facile processing. The patterning procedure can be applied to flexible plastic substrates and hence should be compatible with roll-to-roll manufacturing techniques. The utility of our method was demonstrated by fabricating flexible-substrate polymer LEDs and polymer photodiodes with PEDOT : PSS anodes. The resultant devices showed good performance, comparable to equivalent devices fabricated using ITO coated glass substrates. The technique was also shown to allow the fabrication of multi-element structures, in which red, green, and blue pixels were produced on a single substrate by sequential patterning. The latter structure represents the first stage in establishing a new lithographic fabrication scheme for full colour organic electroluminescence displays. The small number of process steps required (and their generality) is potentially very attractive.

Experimental

PEDOT : PSS patterning

The patterning procedure was first demonstrated using Baytron P, a high conductivity formulation of PEDOT : PSS produced by H.C. Starck GmbH. The various substrate materials (glass, Si, glass epoxy FR4 board, PET flexible film) were cleaned by sonication in a detergent solution, followed by successive washing in de-ionised water, acetone and isopropanol. They were then dried with nitrogen and left on a heated stage at $80 \text{ }^\circ\text{C}$ for one hour to drive off any residual solvent.

SU8 from MicroChem Corp. was spin-coated onto the substrates using a two-step spin-coating process, in which the sample was first ramped from stationary to 500 rpm at an acceleration of 100 rpm s^{-1} , then ramped to 3000 rpm at an acceleration of 300 rpm s^{-1} and held for 40 s. Two kinds of SU8 were tested: SU8-2 and SU8-10. In the case of SU8-2, the films were soft-baked on a level hot plate at $65 \text{ }^\circ\text{C}$ for one minute and at $95 \text{ }^\circ\text{C}$ for a further minute. An aqueous dispersion of the PEDOT : PSS was filtered through a $0.45 \text{ }\mu\text{m}$ PTFE filter and spin-coated onto the SU8 layer at a speed of 2000 rpm for 180 seconds. After spin-coating in class 1000 clean room conditions, the films were left to dry naturally in the same environment. The films were subsequently irradiated for 20 seconds from one side using an UV lamp (200 W cm^{-2} at a distance of 12 cm) through a photomask. The substrates were then placed onto a level hot plate to carry out a post-exposure bake at $65 \text{ }^\circ\text{C}$ for one minute, followed by $95 \text{ }^\circ\text{C}$ for another minute. Unexposed SU8 was removed by soaking and sonicating, for between one and three minutes in SU8 developer, namely propylene glycol monomethyl ether acetate (PGMEA), and/or acetone. In the case of SU8-10, the same procedure was used except that the soft baking conditions were $65 \text{ }^\circ\text{C}$ for two minutes and $95 \text{ }^\circ\text{C}$ for five minutes, and the post-exposure bake conditions were $65 \text{ }^\circ\text{C}$ for one minute and $95 \text{ }^\circ\text{C}$ for a further two minutes.

Device fabrication

PET substrates were coated with a $1.2 \text{ }\mu\text{m}$ layer of SU8-2. A 110 nm layer of Baytron P (a high conductivity formulation of PEDOT : PSS from H.C. Starck GmbH) was deposited on top of the SU8-2, and the two layers were patterned in the manner described above. The patterned substrate was then spin-coated with 40 nm of Baytron P VP AI 4083—a low conductivity formulation of PEDOT : PSS, also supplied by H.C. Starck GmbH which yields a clean upper surface that is able to form a good contact with the active light-emitting layer. The inclusion of this layer results in devices of substantially higher quality than those using Baytron P alone. The conductivity of Baytron P VP AI 4083 is high compared to that of the active layer, and therefore does not adversely affect turn-on voltages. However, its conductivity is insufficient to cause appreciable cross-talk between adjacent pixels; consequently there was no need to pattern this layer. The coated substrate was annealed at $120 \text{ }^\circ\text{C}$ for 20 minutes in a dry nitrogen atmosphere. Polyfluorene derivatives, poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) and poly(9,9-dioctylfluorene-co-*N*-(4-butylphenyl) diphenylamine) (TFB) were used as emitting and hole transport materials, respectively. A 90 nm mixed layer of TFB : F8BT was spin-coated on top of the PEDOT : PSS layer from a 1 : 1 blend by weight of the two components in xylene. The films were dried at $60 \text{ }^\circ\text{C}$ for two hours in a dry nitrogen atmosphere. Finally, top contacts of LiF (1 nm) and Al (100 nm) were thermally deposited through a mask onto the polymer film in vacuum (2×10^{-6} mbar). The overlap of patterned Baytron P and the metal cathode defined the emitting area ($\sim 1.5 \text{ mm}^2$). The same procedure was used to pattern the Baytron P for the photodiodes. For these devices, a 160 nm mixed layer of 1-(3-methoxycarbonyl)propyl-1-phenyl-(6,6) C_{61} (from Nano-C Inc.

(USA)) and poly(3-hexylthiophene) was deposited (after annealing the PEDOT : PSS) from a 1 : 1 blend by weight of the two components in dichlorobenzene. Finally, 100 nm Al was deposited onto the polymer layer; the active area was again $\sim 1.5 \text{ mm}^2$. The completed devices were thermally annealed at $120 \text{ }^\circ\text{C}$ in a nitrogen atmosphere for 30 min prior to use.

Multicolour device fabrication

10% Solutions by weight of PF-red, PF-green and PF-blue were separately prepared in toluene. PET substrates were coated with a $15 \text{ }\mu\text{m}$ layer of SU8-10. Layers of Baytron P and Baytron P VP AI 4083 were sequentially spin-coated at 2000 rpm for 3 min on top of the SU8-10 and allowed to dry in a normal clean room atmosphere. The combined thickness of the two PEDOT : PSS layers was about 150 nm. A layer of PF-red was spin-coated at 1500 rpm from a 10% solution by weight in toluene. The SU8-10 was then exposed and developed as described for the PEDOT : PSS above, leaving a 80–100 nm patterned layer of PF-red on top of similarly patterned layers of Baytron P VP AI 4083, Baytron P and SU8-10. The layered film was thermally annealed at $120 \text{ }^\circ\text{C}$ in a dry nitrogen atmosphere for 30 min. The same procedure was repeated for PF-green and then finally for PF-blue, again resulting in films of thickness 80–100 nm (note, the specific order in which the red, green and blue pixels are deposited is unimportant.) Finally, top contacts were deposited onto the polymer films as described for the single-colour LEDs above. The active area for each pixel was about 1.3 mm^2 .

Measurements

The UV patterning was carried out using a Mercury short arc lamp (OSRAM GmbH) and an appropriate photo mask. Atomic force microscope images were obtained using a Burleigh SPM. The work functions were measured using the Kelvin probe technique (Kelvin Control 07 from Besocke Delta Phi GmbH). The conductivities of the films were measured using a four point probe technique. The current–voltage characteristics of the LEDs were measured with a Keithley 2410 Source-Meter. The LED luminance was measured with a TOPCON Luminance Meter. The photodiode characteristics were measured using a Keithley 236 source measure unit, and a 150 W Xe lamp coupled to a Digikrom 240 monochromator was used for illumination. All device measurements were carried out in nitrogen at room temperature.

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