Bridging Dimensions in Organic Electronics: Assembly of Electroactive Polymer Nanodevices from Fluids

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ABSTRACT

Processing and patterning of electroactive materials from solvents is a hallmark of flexible organic electronics,[1] and commercial applications based on these properties are now emerging. Printing and ink-jetting are today preferred technologies for patterning, but these limit the formation of nanodevices, as they give structures way above the micrometer lateral dimension. There is therefore a great need for cheap, large area patterning of nanodevices and methods for top-down registration of these. Here we demonstrate large area patterning of connected micro/nanolines and nanotransistors from the conducting polymer PEDOT, assembled from fluids. We thereby simultaneously solve problems of large area nanopatterning, and nanoregistration.

Scaling and controlling patterned feature sizes in all three dimensions is a necessity in the continued developments of organic electronics for enhancing the performance of individual devices and for increasing device density in circuits, just as for inorganic microelectronics. One of the main issues in the process of scaling feature sizes is that all of the combinations of low cost and large area manufacturing should simultaneously be met. This may be possible on the dimensions of 100 μm and above but imposes a number of patterning challenges when we enter the submicrometer regimes. We believe that the most promising schemes for solving these problems are those that take advantage of solvated electronic polymers for the creation of submicrometer features. Self-assembled printing (SAP) of nanogaps in organic field effect transistors (OFETs)[2,3] represent good examples of such schemes. However SAP does not solve the problem of higher device densities, which still is limited to the feature size limitation of printing.

A second issue that is deeply connected with the construction of low-cost organic nanoelectronics is that of registering and addressing of nanodevices, since integration and probing of nanodevices require large-scale electrode pads and interconnect lines, which should be aligned with nanoprecision. Top-down patterning for probing of nanostructures, through registration and alignment, cannot entirely solve this problem, since they are limited to small densities of nanodevices, increase complexity, cost, and the risk of degrading organic nanostructure materials, either mechanically or chemically (such as in photolithography methods). Even more importantly, top-down registration of nanostructures on flexible large areas is difficult due to the dimensional instability of large substrates such as plastics.[1] The use of large electrodes to address nanodevices also necessitates multiplexers, which can address signals to one out of many nanodevices. A standard geometry is the cross bar matrix, where devices are located at intersecting electrode lines. The multiplexer allowing selection of individual addresses must then be integrated at the micro/nanogap. For silicon nanoelectronics, suitable implementations of multiplexers based on field effects in nanowires have been proposed,[4,5] and a number of theoretical studies and alternative geometries have been proposed and analyzed.[6,7] The realization of similar structures in organic nanoelectronics with nanoarrays and crossbars could be based on dense nanoarrays of metallic polymers such as polyaniline (PANI) or poly(3,4-ethylenedioxythiophene) (PEDOT) with conductivities currently reaching 1000 S/cm. PEDOT will probably remain the most important class of material in organic electronic circuits in the near future.[8] PEDOT has been demonstrated as an active part in a number of device architectures, such as buffer layers in OLEDs and organic photovoltaics, as electrodes in OFETs, as transistor channels on planar substrates,[9,10] in e-textile,[11] as a multifunctional material in printed electronics,[12] and source−drain nanogaps and gate contacts in inkjet printed

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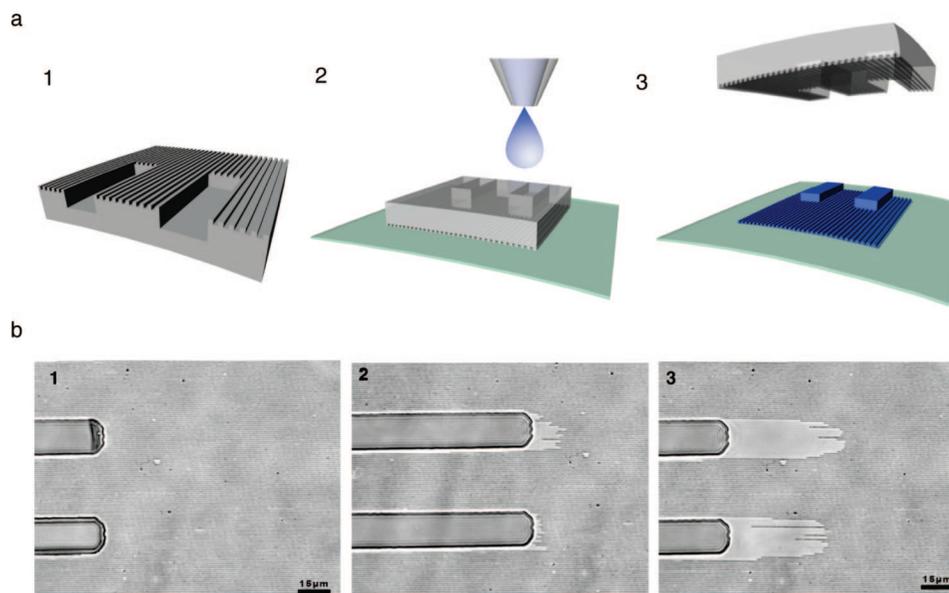‡ Center of Organic Electronics.
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Figure 1. (a) Schematic picture of molding in capillary patterning of PEDOT from aqueous solution using hybrid micro/nano-PDMS templates. (b) Optical micrographs taken at different time intervals (1−3) during the fluidic process of PEDOT inside bridged micro/nanochannels in PDMS, displaying continuous flow from the micro into the nanochannels. Scale bar is 15 μm.

OFETs.[3] Downscaling of patterns in PEDOT, or similar classes of conducting polymers, is therefore of high priority in the future development of organic electronics. Although attention and analysis has been paid to[13,14] the electrical behavior of single conducting polymer chains,[14,15] little attention has been paid to the demonstration of low-cost, large-area patterning, and electrical function of nanostructures of conducting polymers at high density, nor to the necessity of the molecular design requirements of highly conducting polymers for meeting demands for cheap nanopatterning from solution.

Here we demonstrate a solution to both the problems of patterning and registration of large area organic nanoelectronics. This is done by demonstrating large area patterning of connected micro- and nanolines in PEDOT directly from fluids, combined with large area assembling of nanotransistors on the nanopatterns, allowing for the realization of multiplexer architectures.

The methods used here for large area nanopatterning of organic electronic materials are based on the powerful tools of soft lithography (SL).[16] SL tools are promising in the future development of nanoelectronics and feature sizes as small as 0.5−5 nm have already been demonstrated.[17] Molding is an interesting SL technique since it allows patterning of organic electronic materials deposited directly from fluids[18] without any additional step that could degrade the material. Molding allows patterning in both micro- and nanodimension with good feature size control especially in the planar directions, allowing for construction of dense nanostructures such as dense arrays of nanolines. Molding in capillaries from fluidics has been used for the patterning of organic electronic materials such as carbon electrodes,[19] PEDOT(PSS) grating structures,[20,21] and micro- and nanostructures in PANI.[22] The electrical characterization and device assembly of these large area patterns are however up to date all on the microscale. One reason for this is probably,

as mentioned above, the problem of registration of individual nanostructures. The mechanical instabilities of large area substrates and the chemical sensitivity of conducting polymers such as PEDOT complicates the alignment and assembly of conventional electrical micropads, necessary for nanoprobing, onto single nanostructures over large areas. Since PEDOT is a multifunctional material and can be used as both electrode and transistor channel material, we have the possibility to use micropads of PEDOT seamlessly connected to nanostructures in the same material for probing purposes. Here we use this possibility in combination with a three-dimensional capillary molding method[23] for one-step patterning of connected micro- and nano-PEDOT lines in dense arrays. The templates for making these patterns comprise dense nanoline arrays that are aligned and seamlessly connected to arrays of microlines.

Figure 1a (1) shows a schematic of a PDMS replica of these templates (see Supporting Information for construction details on the micro/nanotemplates and for more information on PDMS instability). The PDMS replica is used for patterning of different PEDOT materials directly from aqueous solution using the SL technique of molding in capillaries, as shown schematically in Figure 1a, where the aqueous PEDOT solutions migrates into the microchannels purely through capillary force action and continues into the connected nanochannels (Figure 1a (2),b). The persistence of fluidics principles in both micro- and nanodimension allows continuous flow and eventually deposition of material as the solvent evaporates, creating connected patterns of PEDOT throughout the entire relief structure, and most interestingly resulting in seamlessly connected patterns at the most critical part, the bridge between the micro- and nanodomains. Patterning of both PEDOT/PSS and the newly developed form of alkoxysulfonate PEDOT (PEDOT-S)[24] were tested.
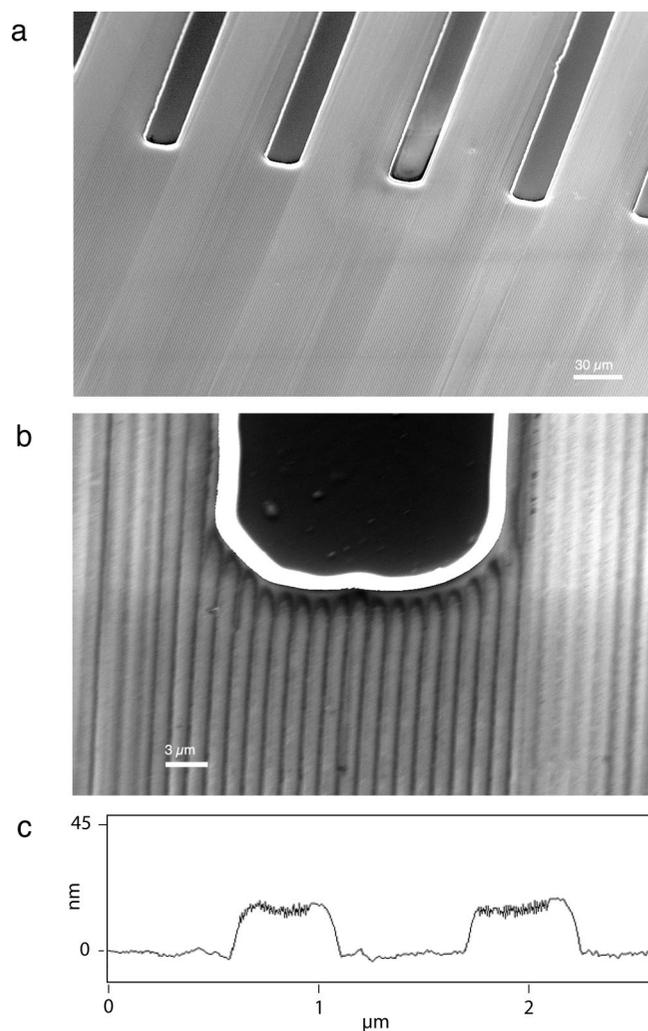
Figure 2. (a) SEM graph showing a number of bridged micro/nano-PEDOT-S patterns on a silicon substrate. (b) SEM graph of a single micro/nanobridge in PEDOT-S, more clearly showing the seamless connection of the micro/nanolines. (c) AFM section analysis graph of two neighboring PEDOT-S nanolines from the arrays depicted in panels a and b.

Figures 2a,b show SEM pictures of patterned PEDOT-S structures where parts of the large-area patterns and the connected structures of the micro/nanobridge are clearly visible. The length of patterned nanolines extend into the millimeter dimensions resulting in connected PEDOT lines with a large width to length ratio exceeding 1000, where each small segment of the nanolines is easily accessible through the microbridge.

The capillary filling time over large areas is relatively fast (minutes), and we believe that optimization of these techniques[25−27] can further enhance patterning times. This patterning procedure could be successfully demonstrated for different substrates including plastic sheets, glass, and silicon.

Electrical characterization of the nanolines is performed by simple mechanical probing of the bridged microlines. Current−voltage measurements are performed along each group of nanolines containing ≈20 nanolines connected to each microline and over large lengths (≈500 μm) along the nanolines in order to study continuity of electrical paths along these lines.
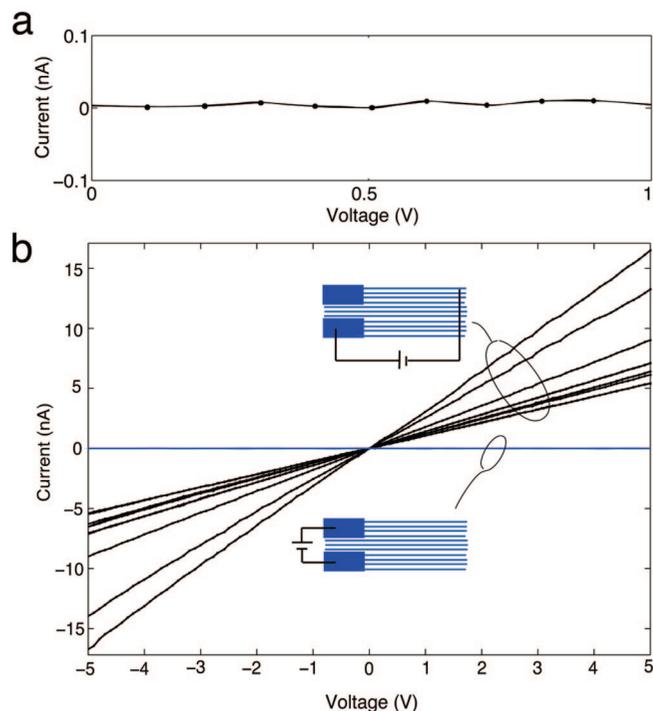
Figure 3. (a) $I-V$ measurements, showing no conduction, measured through 0.5 mm long nanolines patterned in PEDOT/PSS (Bayer PH 500, 5% DMSO). (b) $I-V$ measurements through seven different nanoline groups, patterned in PEDOT-S on a plastic sheet. Each group is connected to and probed via a bridged microline (back lines). $I-V$ measured between four different neighboring microlines (blue lines).

The results for PEDOT-S (Figure 3b) show Ohmic behavior over these large aspect ratios (length/width >1000) proving electrical connectivity across the entire lines and also further proving the seamless connection at the micro/nanobridge. The difference in conductance between each subgroup of nanolines could be a result of deviations in height along the lines and also possible breaks; however, a deviation of only 3−4 times between different groups would require a surprisingly small number of breaks, especially considering the high width/length aspect ratio of the nanolines.

Very small currents were measured perpendicular to the microlines, proving that the nanolines are separated (see blue curve in Figure 3b). AFM measurements (Figure 2c) also show further evidence for the lack of material between the lines.

By assuming that the material in each line has the same conductivity as the bulk conductivity of PEDIT-S 1 S/cm,[24] choosing for each nanoline the height $h = 20$ nm and width $w = 500$ nm from AFM measurement (Figure 2c), and choosing the length $l = 0.5$ mm (which is the length over which the resistances were measured), then the calculated resistance is $(1/s)l/(wh) = 500$ MΩ. This is slightly lower than the measured resistance from the $I-V$ values, suggesting that there are small deviations of the resistance along the nanolines, probably due to geometrical variations.

Figure 3a shows an $I-V$ measurement made on same structure as Figure 3b, where instead the commercial water-

soluble PEDOT/PSS (Bayer PH500 with 5% DMSO) instead is used (tests both with and without secondary dopants full chemical name DEG and dimethylsulfoxide (DMSO) were made). The graph shows that we cannot measure any conductivity at all through PEDOT/PSS structures, although their height profile in AFM does not show any visible differences as compared to PEDOT-S nanolines. The reason for this discrepancy between the two PEDOT materials is probably the presence of the nonconducting PSS polymers in the PEDOT/PSS polymer blend, which is absent in the pure PEDOT-S polymer system. The PSS forms partially segregated structures, and previous measurements have shown surface-segregated PSS layers with thicknesses up to 4 nm.[28] The segregation effect could be more complex in the case of molding in capillaries and also occur in planar dimension, leading to breaks in the electron paths already for these nanostructures with 500 nm width and 20−30 nm heights. This might explain the lack of demonstration of large area submicrometer patterning of functional PEDOT wires in the literature. On the other hand, PEDOT-S cannot form segregated nonconducting shells or islands, and electron paths are most probably always available through inter- and intrachain hopping throughout the bulk at these nanodimensions. This observation supports our statement that downscaling of conducting polymer electronics is not just a matter of patterning technique.

The nanoline arrays are further used for the large area top-down assembly of nanotransistors. The transistors are created by mechanically placing a microfiber, coated with thin films of PEDOT and a solid polymer electrolyte, perpendicular to the nanowire array and thereby simultaneously creating millions of electrochemical nanotransistors along every microfiber/nanoline junction (see Figure 4a). This hybrid transistor assembly is inspired by textile assembly methods.[11] The microlines are used as common drain contacts to each subgroup of parallel-connected nanotransistors, and a common source is used for all nanotransistors at a very large distance of ≈0.5 mm from the microlines. The electrical characteristics of two different micro/nanotransistor groups are shown in Figure 4b. The behavior of these transistors is similar to those previously demonstrated on both microwires[11,29] and nanonetworks,[30] showing current saturation[31] and a clear depletion mode operation at very low gate voltages (<1 V). The low on currents result from the large distance between the S−D pads, which is necessary in a multiplexer design (see below) and therefore demonstrated here.

It is noteworthy that the construction of these transistors only requires simple micromechanical alignment of the microsized gate wire, and that the bridged micro/nanoconnection alleviates probing of the nanochannels. Furthermore the high length to width ratio of the nanowires allows for the fabrication of several microgates along each single nanowire with only one necessary alignment step at the microscale. On the basis of the demonstrated bridged micro/nanoline- and nanotransistor arrays, a multiplexer circuit can be designed that allows direct electrical addressing of each single nanowire in the dense array from a low number of addressing points at the microdimensions. Figure 4c shows
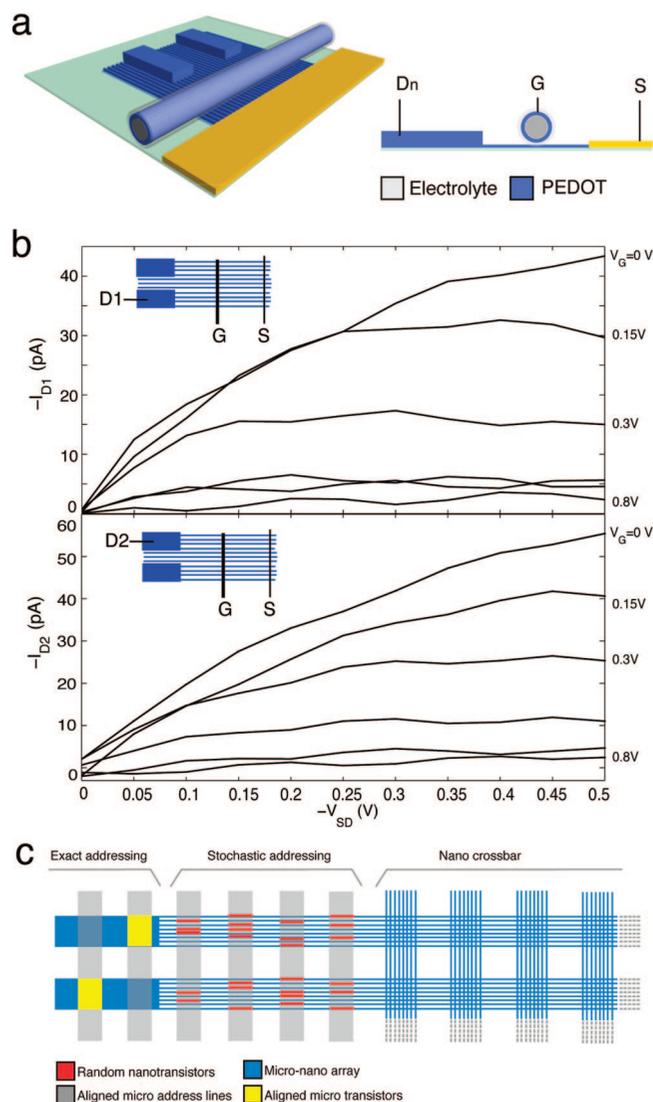

Figure 4. (a) Three-dimensional schematic picture of hybrid-transistors constructed on top of nanolines and contacted through the microbridge, and schematic cross-section of the same transistors, where S, D, and G contacts are all on the microdimension. S = source, D = drain, and G = gate. (b) Transistor curves for two different nanotransistor groups as shown schematically in panel a. (c) Schematic of a proposed multiplexer architecture based on bridged PEDOT micro/nanoarrays, aligned microtransistors and randomly placed nanotransistors, where the multiplexer addresses nanocrossbars.

a schematic of a proposed architecture of a multiplexer and a dense nanocrossbar that can be addressed with two such multiplexers. In this multiplexer, parts of the crossbar junctions comprise micro/microjunctions, and the ease of exact transistor patterning and registration at these dimensions results in a multiplexer subsegment that can uniquely address each microline. Such micromultiplexers have already been demonstrated.[11] Unique addressing of the remaining nanoline segments, each bridged to one uniquely addressed microline, requires similarly a number of nanotransistors placed along the nanowires, as we have demonstrated here. As exact pattering of each nanotransistor is incompatible with low-cost large area patterning, instead stochastic assembly of nanotransistors along the wires would require no nanoalign-

ment and would still be sufficient to uniquely address each nanoline. The function of such stochastic multiplexer architectures have theoretically been proven.[32] The dimensions of the demonstrated PEDOT micro/nanoarrays fulfill the request for assembly of multiplexers and nanocrossbars with the proposed architecture shown in Figure 4c (see Supporting Information for more detailed calculations).

The demonstrated large area patterning of PEDOT-S nanoarrays is an important step toward the miniaturization of low cost flexible organic electronics where we simultaneously solve the problem of large area patterning and registration. The bridged micro/nanotemplates can be applied to other soft lithographical applications, including optofluidics, and laboratory on chip.

The concept of bridged micro/nanofluidics patterning could also be extended to include multiphase laminar flows and combinations of mesoscopic self-assembled organic nanostructures,[33] and nanofluidics for directing and registration of molecular structures into determined circuit design patterns.

Further development of randomly aligned nanotransistors could allow realization of low-cost, large area, addressable, dense nanocrossbar architectures. These could comprise molecular junctions, where PEDOT has proven to be a strong candidate as crossbar material,[34] or high density PEDOT memories.[35]

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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