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Letter

High-resolution direct-writing of metallic electrodes on flexible substrates for high performance organic field effect transistors

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ABSTRACT

We report on organic field-effect transistors (OFETs) with sub-micrometer channels fabricated on plastic substrates with fully direct-written electrical contacts. In order to pattern source and drain electrodes with high resolution and reliability, we adopted a combination of two digital, direct writing techniques: ink-jet printing and femtosecond laser ablation. First silver lines are deposited by inkjet printing and sintered at low temperature and then sub-micrometer channels are produced by highly selective femtosecond laser ablation, strongly improving the lateral patterning resolution achievable with inkjet printing only. These direct-written electrodes are adopted in top gate OFETs, based on high-mobility *holes* and *electrons* transporting semiconductors, with field-effect mobilities up to 0.2 $cm^2/V\,s$. Arrays of tens of devices have been fabricated with high process yield and good uniformity, demonstrating the robustness of the proposed direct-writing approach for the patterning of downscaled electrodes for high performance OFETs, compatibly with cost-effective manufacturing of large-area circuits.

1. Introduction

After several years of study and research, the synthesis of advanced organic semiconductors with increasing charge-carrier mobility has recently led to the realization of high performance solution processable Organic Field Effect Transistors (OFETs) with field-effect mobilities exceeding 1 $cm^2/V\,s$, preluding to their adoption in a variety of commercial applications [1–11]. The integration of OFETs in more complex electronic systems such as drivers for flat-panel displays [12,13], radio-frequency identification tags [14,15] and complementary and pseudo-complementary logic circuits [16–23] has already been demonstrated. Furthermore, the compatibility of organic materials with polymeric flexible substrates [24,25] and their low temperature processing are attracting great interest as they pave the way for ubiquitous integration of cheap, flexible, large-area electronic applications [26] produced with low cost manufacturing techniques, such as common graphical arts printing [27–31]. However, one of the main limitations towards the development of high-performance logic circuits based on printing techniques is still represented by the low resolution patterning capability of state-of-the-art printing tools, which severely limits the minimum achievable lateral features [32]. This represents a strong fundamental limit given that the highest operation frequency in an OFET and its driving capability are strongly dependent on its channel length (L) [33,34]. While conventional photolithography, etching and thermal evaporation techniques are widely reported in the literature on organic electronics for high-resolution patterning of electrodes, the multi-step nature of the processes and high vacuum conditions are not compatible with the large-area manufacturing of low-cost electronic circuits. Therefore suitable fabrication techniques, which maintain the compatibility with cost-effective fabrication of large-area flexible and plastic electronic devices, but capable of a finer patterning, have to be developed.

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Promising results in this direction have been recently achieved with various roll-to-roll compatible techniques, such as femtoliter gravure printing [35], reverse offset printing [36] and roll-to-roll nanoimprint lithography [37], which offer the advantage of a high throughput. Besides these methods, digital direct-writing techniques, though limited by a lower throughput, are being extensively investigated as well since they do not require the fabrication of a cliché and allow for fast prototyping. "Drop-on-demand" DOD inkjet printing [38] is among the most promising direct-writing methods which have been explored to develop high-resolution printed electronics [39,40]. The additive, non-contact and mask-less nature of the process permits the direct deposition of soluble inks avoiding the wastage of precious materials, favored by the recent development of a wide range of low-sintering temperatures highly-conducting inks [41–43]. While DOD inkjet is a very flexible tool and allows for one of the smallest lateral features achievable with standard graphical art tools, this is in any case limited to few tens of micrometers, due to rheological properties of inks which do not allow to reduce the nozzle diameter below $\sim$10 μm, and to the broadening of the ink on the substrate [44,45]. Dramatic improvements in the patterning resolution have been obtained from the development of new printing techniques (such as Electrohydrodynamic jet printing, eJET [46,47]) or from the combination of inkjet printing with higher resolution patterning processes (such as Self-Aligned Printing [48,49], Laser Processing [50–54] or dip-pen-like dragging [55]). In particular Laser Processing in general presents all the advantages of a direct-writing process (i.e. maskless and data-driven) and thanks to the availability of stable femtoseconds pulsed laser systems, it allows strongly improved resolution in material processing with high reliability [56–58]. Interesting works regarding femtosecond laser-induced high-resolution sintering of metal nanoparticles have been recently reported in literature [59,60]. By means of this process, conductive lines with a lateral width lower than 1 μm have been demonstrated. However, different parameters are involved in the process (metal nanoparticles formulation, melting temperature and laser beam parameters) and multiple steps are necessary for the achievement of the final result (deposition and drying of the nanoparticles, slow laser scan and washing of the non-sintered nanoparticles).

In this work we demonstrate that by combining inkjet printing (IP) of metallic inks with low sintering temperature and femtosecond laser ablation (FLA), electrodes arrays with sub-micrometer gaps can be reliably fabricated in a three steps only process and integrated as source and drain contacts in high-performance downscaled OFETs. The combination of IP and FLA provides enhanced patterning capabilities, while being compatible with manufacturing of cheap and large-area electronic circuits. In fact, while similar approaches based on metallic nanoparticles inks and continuous or nanoseconds pulsed lasers were proposed in the past [61–63], the adoption of femtosecond pulses with an ultra-short time width ($\tau_{pulse} \sim 10^{-13}$ s), lower than the heat transfer time constant ($\tau_{heat} > 10^{-11}$ s), in combination with low sintering temperature inks, makes this process compatible with different substrates, from glass to polymeric ones, and materials, such as metallic films, thus opening vast possibilities for the manufacturing of electronic devices on different media. Based on this approach, arrays of tens of both *n*-type and *p*-type OFETs with sub-micron channels could be fabricated on flexible substrates with a good yield and uniformity of the ON currents, thus being adoptable for the fabrication of high performance organic complementary logic circuits.

2. Experimental

125 μm thick PEN Teonex Q65FA (DuPont Teijin Films) was adopted as a flexible substrate, while tests on rigid substrates were performed on microscope glass slides with a coating of cross-linked PMMA. PMMA was cross-linked by adding a 1,6-bis(trichlorosilyl)hexane in a *n*-butyl acetate solution [64]. A silver ink (InkTec Tec-IJ-060) was printed with a Dimatix Materials Printer DMP-2831 using 10 pL volume drops cartridges. Silver lines with variable width, from 100 μm to 200 μm, were printed using a two voltage levels waveform. The sintering step of the silver electrodes was performed at 150 °C for 10 min to achieve metallic lines with a low resistivity of approximately $2 \times 10^{-7}\ \Omega$ m, one order of magnitude higher than in bulk silver. The ablation process was carried out at 515 nm, with the second harmonic of a mode-locked Yb:KGW (ytterbium doped potassium gadolinium tungstate) laser at 1030 nm (Pharos) characterized by an ultra-short pulses width of approximately 280 fs, and a repetition rate of 500 kHz. Samples were fixed on a highly precise, programmable, 3-dimensional moving stage (Aerotech ABL1000), with a resolution of 2.5 nm, a maximum travel speed of 300 mm/s, a maximum limit in vertical direction of 50 mm and a maximum limit in horizontal directions (*x* and *y*) of 100 mm and 150 mm respectively. 50× and 100× objectives (Mitutoyo Plan Apo NIR) were used during the whole experimental activity. The scan velocity of the beam was fixed at 15 mm/s.

A top-gate/bottom-contacts architecture (Fig. 1a), which provides superior transistor performances [65], was used for OFETs fabrication. Source and drain electrodes were fabricated by scanning the femtosecond laser on a single printed silver line and by dividing it into two electrically insulated contacts. The sub-micrometer ablated cut was used as the channel of OFETs.

For *n*-type devices, after filtering through a 0.2 μm PTFE filter, a 1,2-dichlorobenzene solution (15 g/l) of poly{[N,N′-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5′-(2,2′-dithiophene)}, abbreviated as P(NDI2OD-T2) [66], was deposited by spin-coating at 1000 rpm for 90 s in a nitrogen atmosphere, then annealed for 10–15 h at 120 °C on a hot plate in a nitrogen atmosphere. A $\sim$350 nm thick PMMA dielectric (M_w = 120 kg/mol, Sigma–Aldrich) was spun from an *n*-butyl acetate solution (60 g/l, filtered with a 0.45 μm PTFE filter) in nitrogen atmosphere at 2000 rpm for 60 s. After the dielectric deposition, the devices were annealed in nitrogen, on a hot-plate, at 80 °C for 4 h.