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Laser printing of n- and p-type semiconductors for complex organic thin film transistors

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Abstract. With the goal to study complex organic thin film transistor (OTFT) architecture, thin films of semiconductors and of metallic materials have been laser printed. The n-type copper hexa deca fluoro phthalocyanine ($F_{16}CuPc$) and p-type copper phthalocyanine (CuPc) semiconductors have been used to form the active layers. The materials have been successively transferred onto a receiver substrate by laser pulses in the picosecond regime. The latter substrate has formed the gate and the dielectric of the transistor. The three materials have been then combined in a multilayer stack prepared by the successive depositions of the materials by thermal evaporation under vacuum and then laser have been printed in a single step.

1. INTRODUCTION

Organic semiconductors (OSC) are the main piece in the OTFT devices. They offer unique opportunities in low-cost microelectronics. The development of facile and cheap fabrication processes represents tasks of major importance and laser-based processes offer versatile alternatives toward organic devices operating on flexible supports where usual techniques, such as inkjet or roll-to-roll printing, cannot be used because of the lack of solubility of the organic semiconductor or in the case of complex device architectures. In this paper, we report a Laser-Induced Forward Transfer (LIFT) technique on organic n- and p-type semiconductors with the goal to achieved a complex transistor configuration: the ambipolar transistor [1].

Since its development by Bohandy et al. [2], the feasibility of LIFT for the deposition of inorganic and organic materials been repeatedly demonstrated. This technique reveals itself particularly effective for the precise micro deposition of a large variety of materials, for instance of liquids [3], nanotubes [4], polystyrene microbead [5], organic light emmiting diodes (OLED) [6] ceramic [7], polymer [8] and especially sensitive materials as DNA [9], cells in liquid media [10].

2. EXPERIMENTAL SETUP

Under the action of a single laser pulse of a Nd:YAG picosecond laser (continuum leopard SS-10-SV) operating at 355 nm ($\tau = 50$ ps), a small part of the desired materials was transferred from a donor to a receiver substrate, placed in close contact. The receiver substrate was based on a silicon (Si) wafer oxidized by a 300 nm thick layer of silicon dioxide (SiO2) (C_i of 12 nF/cm^2) purchased from Vegatec (France) and used as gate and dielectric in OTFT devices, respectively. The fluence was controlled

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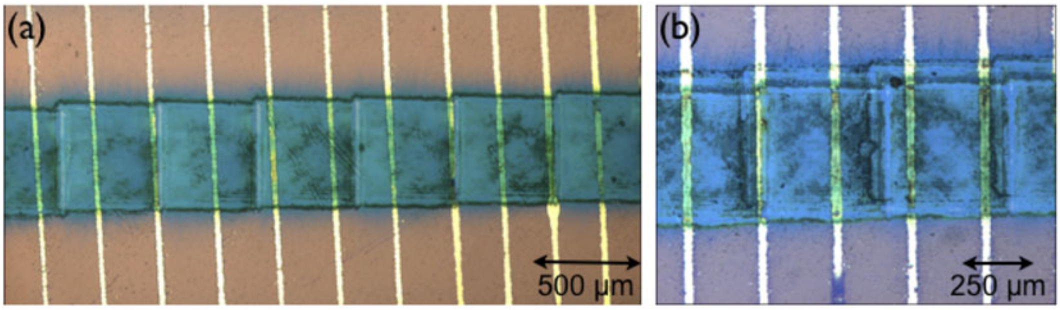

Figure 1. (a) Horizontal lines of CuPc and F_{16}CuPc with perpendicular lines of silver nanoparticles ink between them, (b) small offset on the overlapping of the CuPc and the F_{16}CuPc deposits.

with calibrated polarization devices. A square mask is used to select an optimally homogeneous part of the beam, which is imaged on the material to be transferred by a converging lens (spot size on the sample: $500 \times 500\,\mu m^2$). A camera with a magnification objective allowed monitoring the deposition process and controlling the precise design of the transistor configuration. The accurate positioning of the sample was obtained by micrometric translation devices. The experiments have been performed under ambient conditions of temperature and pressure. Current-voltage characteristics of the transistors have been measured at room temperature in air with a Hewlett-Packard 4140B pico-amperemeter DC voltage source using a Labview®program.

We opted for the use of the n-type copper hexadecafluorophthalocyanine (F_{16}CuPc) and the p-type copper phthallocyanine (CuPc) [11], known as chemically and photochemically robust OSC. We used the organic semiconductor materials directly as supplied by Sigma Aldrich (France). The OSC were prepared by thermal evaporation under vacuum (2×10^{-6} mbar at room temperature) on UV-transparent quartz suprasil.

Source and drain electrodes were made to complete the donor substrates. Charges are injected from the source electrode into the semiconductor. A good ohmic contact is expected when the work function of the injecting metal is close to the HOMO level of the CuPc (-5 eV) and the LUMO level of the F_{16}CuPc (-4.8 eV). A previous study has shown that gold (-4.90 eV) electrodes are systematically destroyed during the laser transfer of a multilayer stack made by CuPc and gold electrodes [12]. In this study, we chose to use silver. Silver (Ag) with Ef ≈ 4.52 eV should be able to inject both holes and electrons in p- and n-type organic semiconductors, respectively.

3. RESULT AND DISCUSS

3.1. Step by step fabrication

Previous study showed that well-resolved homogeneous pixels were obtained from 100 nm thick CuPc and F_{16}CuPc film printed at the low fluence of 0.10 and 0.13 J/cm^2, respectively [13,14]. We first transferred the CuPc, in juxtaposing the pixels lines were formed. To form the silver electrodes, we opted for the silver nanoparticles ink (Cabot). Donor substrates were prepared by spin-coating the ink (20 s at 3000 rpm) on UV-transparent quartz substrates (suprasil). Well-resolved silver lines were laser printed by juxtaposing deposits of silver nanoparticles ink [13]. The channel length (L) was set at 250 μm. Once transferred, the lines were annealed with the CuPc at 150 °C in order to evaporate the residual solvent contained in the ink and to create a good conduction of the silver nanoparticles. The lines exhibited an average resistivity of 10 $\mu\Omega$ cm. The top contact transistors so-created showed performances of (4–8) $\times 10^{-5}$ cm^2 V^{-1} s^{-1} for the mobility, +20 V for the threshold voltage (V_T) and (3–4) $\times 10^2$ for the On/Off current ratio. Finally the F_{16}CuPc was transfer on these transistors to cover the CuPc lines.

All these lines were precisely defined and no damage was observed. The so-obtained transistors are shown in figure 1(a) The overlap of the F_{16}CuPc deposits on the CuPc pixels was precisely controlled. For example, the figure 1b exhibits the same construction with a small offset of 50 μm of the F_{16}CuPc pixels.

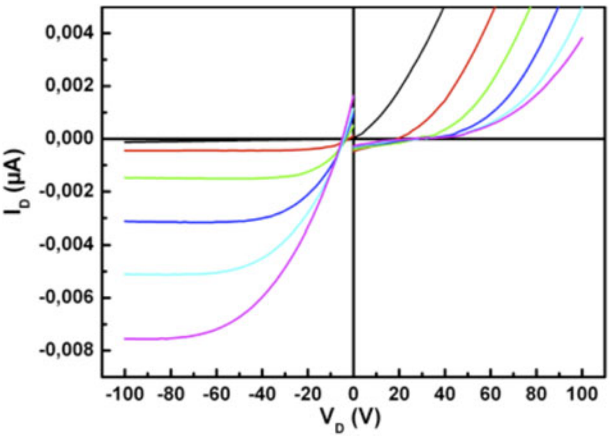

Figure 2. Output characteristic for OTFTs based on CuPc and F_{16}CuPc as active layers and silver nanoparticles ink all laser printed by LIFT.

OTFT devices were characterized at room temperature in ambient atmosphere. Output characteristics are shown in figure 2 . Only the p-type CuPc exhibits a transistor effect. The electrical parameters are 4×10^{-5} cm^2 V^{-1} s^{-1} for the mobility and $4 + 20$ V for V_T. The transfer of the F_{16}CuPc does not degrade or interact in the electrical performance of the CuPc transistors. On the other side, n-type F_{16}CuPc were non operative. Ambipolar transistor were reported with smaller thicknesses (30 nm) of both OSC layers and it seems that 100 nm is too thick to allow the transport of the charge in the OSC of the top. Valid depositions of these OSCs with a thickness of less than 100 nm are not possible by LIFT. Improve performances have been obtained for the laser printed generation of OTFTs using multilayer donor substrates composed by CuPc and silver electrodes [12]. We chose to combine the two OSCs with the electrodes in one donor substrate to obtain a stack with a total thickness of 100 nm. Moreover when the laser ablation occurs on the material to be transferred, one side of the film undergoes a direct laser irradiation inducing some damages (chemical changes, roughness). The modifications induced by the laser interaction can clearly decreases the contact quality. As the quality of the interfaces between all the constituents is essential for both injection and carrier of the charges, we studied the transfer in a single step of both organic active layers already equipped with metallic source/drain electrodes.

3.2. Multilayer printing

The multilayer donor substrate was made as well. The CuPc was prepared by thermal evaporation under vacuum (2×10^{-6} mbar at room temperature) on UV-transparent quartz suprasil. The thickness was set at 50 nm. Then 30 nm of silver were evaporated under high vacuum through a mask (1×10^{-6} mbar at room temperature). The channel length (L) was varied from 30 to 200 μm. Finally 20 nm of F_{16}CuPc was evaporated under high vacuum (2×10^{-6} mbar at room temperature). Figure 3 illustrates the LIFT step process. Homogeneous and well-defined deposits were obtained from the laser printing of these multilayer substrates at the fluence of 0.13 J/cm^2, figure 3(b). Splashes and ejected debris outward were limited and the electrodes are fully conductive all along their length. A resistivity of 3 $\mu\Omega$ cm was measured. No damage or crack was observed in the whole structure. Despite the good quality of the laser printed pixel, very low current were observed in n and p configuration. Mobilities of the order of 10^{-8} cm^2 V^{-1} s^{-1} were measured. Very high leakage currents were observed for both semiconductors. The quality of the interface between both semiconductors is a crucial parameter for a good carrier of the charge in an ambipolar transistor configuration. Some damages probably occured inside the layers and at this interface. Further studies will be done on the optimization of the transfer, of both OSCs thickness and in the influence of the position of the semiconductors in the ambipolar transistor architecture.

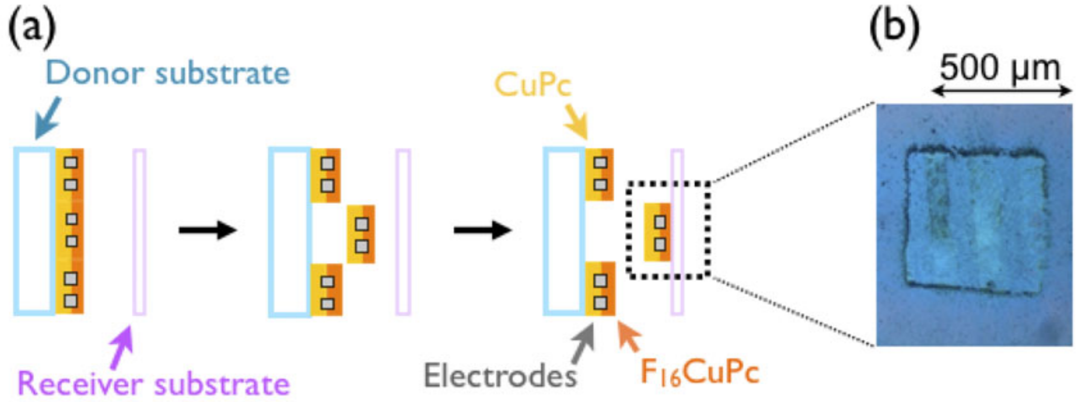

Figure 3. (a) Principe of the multilayer LIFT printing made by CuPc (yellow), silver electrodes (gray) and $F_{16}CuPc$ (orange). (b) Printed pixel at 0.13 J/cm^2.

4. CONCLUSION

This work demonstrates that the Laser-Induced Forward Transfer technique is effective to transfer different material layer of materials to build an accurate complex architecture. Ambipolar transistor need very thin layers of semiconducting materials, which is particularly difficult to obtain with the LIFT technique. Very thin semiconducting and metallic layers were successfully laser printed in a multilayer system. The results showed that is difficult to maintain the electrical performances of both semiconductor layers. Future studies will focus on the use of an intermediary sacrificial layer with the unique role to absorb the photons and provide the mechanical push to the transfer material. This layer will protect the multilayer system from damages due to laser irradiation. This technique has been already successfully applied for OLED printing [6].

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