Hybrid manufacturing of electrochemical transistors

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Abstract

We report on a hybrid manufacturing approach for electrochemical transistors (ECTs) based on conventional printing, digital printing, laser processing, and post-press technologies. A careful selection of the conductive, dielectric and semiconductor materials with respect to their optical properties allows for a significant reduction of registration problems that apply when structuring is done only by additive techniques, enabling fabrication of ECTs on large areas. We produced a matrix of 50x17 ECTs on format DIN A4 (210 x 297 mm^2). The prototype components based on this technology operate at gate voltages in the range of 1 V and show on-off ratios of 10^2.

Introduction

Manufacturing of printed transistors has to cope with the challenge to reliably deliver devices operating at appropriate low voltages and high on-off ratios. For organic thin-film transistors, a strategy to achieve reasonably operating voltages is to significantly decrease the transistor channel lengths. However, at the same time, the costs of manufacturing must not significantly exceed the ones of usual graphically printed items. The requirement of reduction in feature size down to the (sub-)micron scale, however, increases the equipment costs as it drives the demand for the involved patterning techniques towards and beyond their usual resolution limits. Another limiting factor for roll-to-roll manufacturing of complex devices such as organic thin-film transistors is the quality of the multilayer registration between the individual process steps.

The field of printed electronics aims for this goal as it relies on processing in ambient conditions (without vacuum) and often promotes additive patterning from solution such as printing However, at the same time, in-depth control of the interface properties between the substrate and the individual deposited layers (and amongst them) has to be provided. In contrast to graphical printing where the quality of a several-micron-sized halftone element as smallest unit of a patterned functional layer is defined by its bulk absorption properties according to Lambert-Beers law, for printed electronics components, the level of understanding how manufacturing parameters relate to film morphology relate to device performance are much more demanding. [1]

Materials and Methods

Figure 1 shows a schematic illustration of the architecture of an electrochemical transistor (ECT) chosen for this study. It represents a stack geometry which – in contrast to other studies – deals with a fabrication of these components based on printing techniques. This conquest started with Nilsson et al. on all-printed ring oscillators [2], Mannerbro et al. on fully inkjet-printed ring oscillators [3], and finally with Kaihovirta et al. who used flexo printing for source, drain and gate on pre-patterned substrates [4]. All these approaches used a lateral device architecture, motivated by the fact that all electrodes and layers can be deposited immediately on one substrate by the respective printing techniques. However, in a lateral geometry, due to the persistent limits of resolution and registration in mass and digital printing, the variability of the devices with respect to important parameters (e. g. switching time) is limited.

Our combined approach introduced in this paper merges additive and subtractive technologies which makes it possible to return to a vertical stack of functional layers. It builds on a self-alignment in the manufacturing of the channel between the source and drain electrodes which is not susceptible to particular registration challenges. It also gives rise to smaller feature sizes.

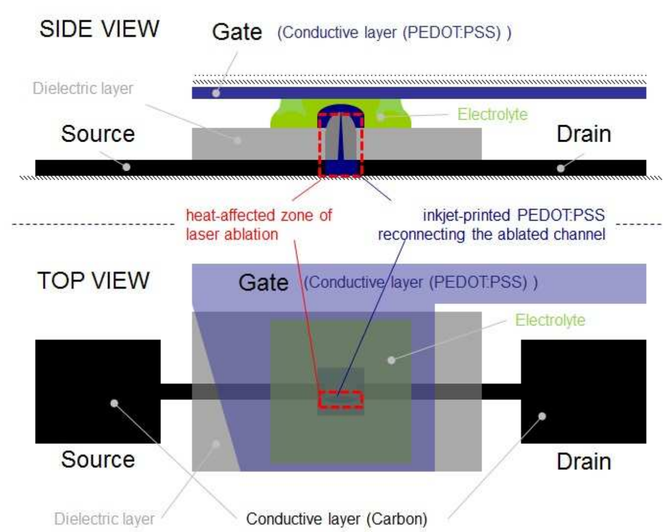

Figure 1: Side view and top view of the vertical stack to build an individual electrochemical transistor (ECT) by printing and laser ablation.

In particular, in our approach, the first two layers of the devices (conductive layer as conjectural source-drain structure and a dielectric layer) were printed at Printed Electronics Arena (Norrköping, Sweden) using a semiautomatic screen printer and both thermal and UV-based drying systems. A commercial polymer foil (PET, sheets of mm, thickness 125 um) was used as substrate. To minimize alignment problems especially during the thermal drying steps between the printing passes, the foil substrates were preshrunk in a ventilated oven at elevated temperatures prior to printing.

The source-drain structures and the dielectric layer were deposited in two individual passes with commercially available ink materials. For the conductive layer (source-drain) structure, a commercial carbon paste was mixed with a commercial thinning liquid. For the dielectric layer, a UV-sensitive and cross-linkable commercial material was used.

First, the conductive layer was printed with one screen and dried in a conveyor-belt-fed drying system at elevated temperatures. Second, the dielectric layer was printed and cured in a conveyor-belt UV dryer. The screen printing parameters were set and adjusted in detail until a homogeneous deposition was reproducibly achieved. Besides a visual homogeneity of the printed structures, the criterion for homogeneity was the observation that the conductivity of the individual source-drain structures was in the range of (10 +/- 5) kOhm, measured with a standard digital multimeter. This value was determined for a number of source-drain structures (components) on the substrate sheet between the test prods of distance 1 cm.

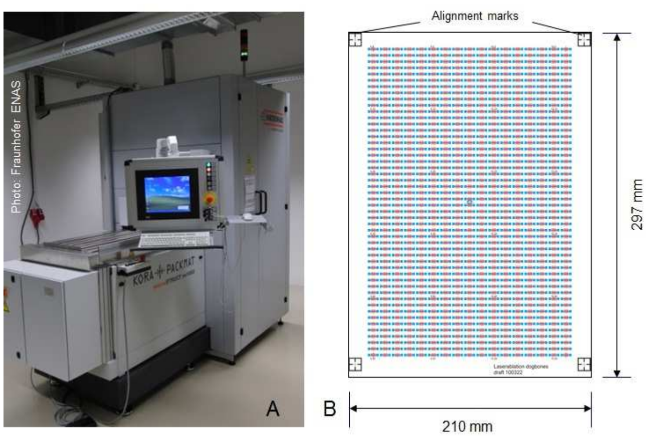

Figure 2: A. microSTRUCT 1060 (3d-micromac AG, Chemnitz, Germany) for laser micromachining of sheet-based substrate materials; B. matrix of 50x17 individual ECTs on a DIN A4 sheet of PET.

For the laser treatment, an industrial laser patterning setup (microSTRUCT 1060, 3d-micromac AG, Chemnitz, Germany) was used (see Figure 2). The machine is particularly designed for sheet-fed laser treatment of large-area substrates for printed and polymer electronics devices. It consists of a conveyor belt for the transport of the printed sheets and a closet for laser machining with an area of operation of (700 x 700) mm2. Alignment of the fed sheets is done by an optical inspection system. The plant uses a compact and air-cooled pulsed Ytterbium Fiber Laser (IPG Laser GmbH, Burbach, Germany) with an average power of 30 Watts at a wavelength of 1064 nm, a maximum repetition rate of 200 kHz and nominal pulse duration of 100 ns. A bendable, metal-coated fiber guides the laser beam into the closet. The positioning of the laser beam on the sample is carried out with a mirror-based long-distance scanner system (focal length 820 mm; SCANLAB AG, Puchheim, Germany).

A PC interface card controls the synchronous and continuous operation of the mirrors and the laser in real time via an automation code, and this option was used to control the movement of the scanner during laser operation (mark speed) and hence the distances of the laser pulses incident on the substrate. The other relevant laser parameters were kept constant (wavelength 1064 nm, repetition rate 200 kHz, average power 30 W). Disconnection of the source-drain structures was verified by a digital multimeter.

Inkjet printing was performed using a Dimatix DMP-2800 printer (Fujifilm Dimatix Inc., Santa Clara, USA). The printing setup consisted of several piezoelectric inkjet printheads with a nozzle diameter of 21.5 µm and a nominal drop volume of 10 pL. All samples were printed at ambient conditions (22.5 ± 0.8 °C and 40 ± 3 % relative humidity). The DMP was applied in multi-nozzle mode, with a clear distance between the nozzle and the substrate maintained at 1 mm. The PEDOT:PSS ink was prepared from commercially available Clevios HC Jet P (Lot No. JOF6903-6b; H.C. Starck GmbH, Leverkusen) mixed with in deionized water (ca 9:1) and treated with ultrasound prior to filling the printing cartridges. The printing pattern was designed to overfill the particular cross section and to yield efficient reconnection (pattern area 2x2 mm, drop space 15 um, nominal film volume 0.17 uL). After printing, the samples were dried at elevated temperatures for a few seconds (see Figure 3).

A polycationic liquid with mobile anions was chosen as the electrolyte, formulated to an aqueous ink and printed with an overfill (pattern area 3x3 mm, drop space 20 um, nominal film volume 0.23 uL) under similar conditions as the PEDOT:PSS ink. Alternatively, manual deposition of microdroplets was applied. A commercial PEDOT:PSS-coated plastic foil (Orgacon EL-350, AGFA; total thickness 175 um; thickness of the PEDOT:PSS layer 200 nm) was applied as top electrode before the electrolyte was dry after deposition. The pieces were cut on a sheet plotter and placed with the conductive side in contact with the printed electrolyte. A reasonable mechanical stability of the device was given once the electrolyte was dry, but to allow for a robust handling during the device characterization, the gate electrode was additionally fixed with tape.

The deposited layers were characterized using optical microscopy and scanning electron microscopy. Reconnection of the source-drain structures with inkjet-printed PEDOT:PSS was verified with a digital multimeter. The current-voltage characteristics of the entire components were taken with a parameter analyzer equipped with manual probe heads. The individual transistor components were cycled in the range V_{DS} = {0 … -1.5 V} for the source-drain voltage and V_G = {0 … 1.5 V} for the gate voltage. The time-dependent current switching characteristics were obtained by coupling of two digital sourcemeters (Keithley 2400), operating as waveform generator and measurement device, respectively. More details on the manufacturing workflow will be reported elsewhere.

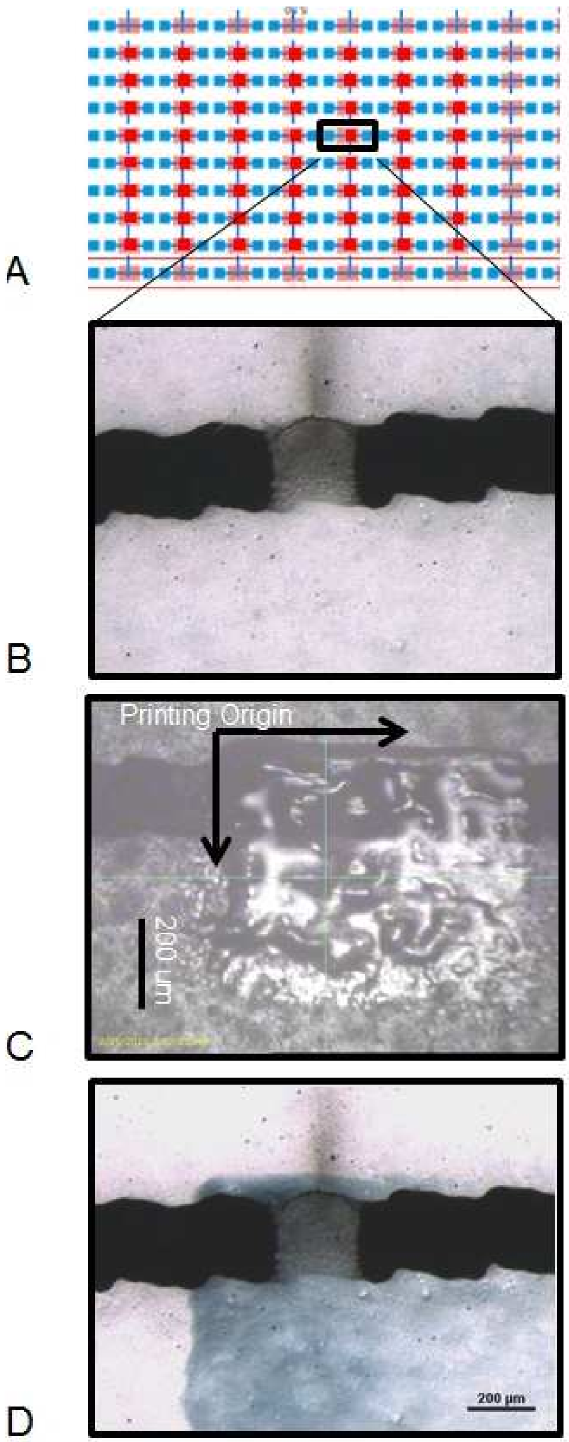

Figure 3: A source-drain structure (black bar, top view) which was laser-ablated through a transparent dielectric layer (not visible) allows reconnection by inkjet-printed PEDOT:PSS through capillaries induced A. Principle sketch (part of the 50x17 matrix); B. Microscope image of source-drain structure after laser-ablation, C. … after inkjet-printing of PEDOT:PSS ink; D. … after drying of PEDOT:PSS ink.

Results and Discussion

During the manufacturing process according to the workflow outlined above, the morphological characterization revealed that laser ablation indeed is a sufficient technique to reliably disconnect the printed absorptive conductive structure through the transparent dielectric superlayer, at least provided several conditions with respect to the chosen pulse energy and scan velocity were met. We further observed that it is possible to reliably reconnect the ablated conductive structure through the transparent dielectric layer by inkjet printing of a conductive ink (PEDOT:PSS). We ascribe this possibility to the fact that the ablation process takes place only in the black conductive layer. However, due to the complex hydrodynamics of this non-equilibrium process there occur capillary cracks even in the dielectric which allow the liquid PEDOT:PSS to proceed to the source-drain channel created by the ablation process.

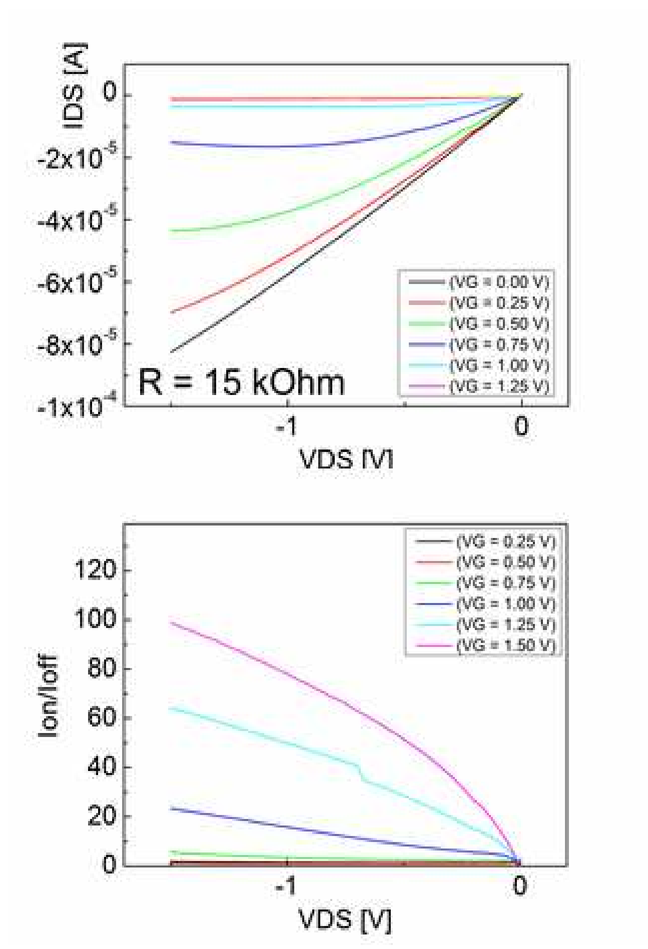

Figure 4: Example for the current-voltage characteristics (upper graph) and the on-off ratio (lower graph) as a function of source-drain voltage of an ECT fabricated according to our hybrid manufacturing approach.

Figure 4 shows that the ECTs manufactured in our hybrid approach reliably switch in the applied ranges V_{DS} = {0 … -1.5 V} and V_G = {0 … 1.5 V}. The on-off ratios are typically in the range of 100. For the best devices, an on-off ratio of 600 was measured. The switching times obtained by transient electric measurements were determined to be 200 ms and below are possible. Further details on these processes as well as the manufacturing yield are currently under investigation.

Summary

We have successfully implemented a hybrid manufacturing approach for electrochemical transistors (ECTs) using both additive and subtractive techniques. With the introduction of laser ablation into a traditional printing workflow it was possible to rely onto the device geometry of a vertical stack. This solution circumvented typical challenges of all-printed devices such as limited feature resolution and registration problems. The transistors obtained operated at voltages in the 1.5 V range and at reasonable on-off ratios and switching times.

Acknowledgements

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Author Biography

Thomas Blaudeck received his Diploma (M. Sc.) (2002) and his PhD in Experimental Physics from Chemnitz University of Technology (2007). In the following, as a postdoctoral researcher the group of Prof. Reinhard R. Baumann (Digital Printing and Imaging, Chemnitz University of Technology, Chemnitz, Germany) he was involved in the EU-projects PolyNet and PRODI (2008-2010) around the topic "Manufacturing and Production Equipment for Large-Area, Organic and Printed Electronics".

In February 2011, he joined the Organic Electronics group with Prof. Magnus Berggren at Linköping University (Sweden) as a postdoctoral researcher in the field of printed electronics.