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Letter

High-resolution spatial control of the threshold voltage of organic transistors by microcontact printing of alkyl and fluoroalkylphosphonic acid self-assembled monolayers

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ABSTRACT

A dense array of 500 organic TFTs with two different threshold voltages arranged in a checkerboard pattern has been fabricated. The threshold voltages were defined by preparing self-assembled monolayers (SAMs) of either an alkyl or a fluoroalkylphosphonic acid on the gate-oxide surface of each TFT, using a combination of microcontact printing from an elastomeric stamp and dipping into a solution. The threshold voltages are -1.01 ± 0.15 V for the TFTs with the fluoroalkyl SAM and -1.28 ± 0.23 V for the TFTs with the alkyl SAM. ToF-SIMS analysis shows that the two SAMs can be patterned with a pitch of 10 μm and without significant cross-contamination. Cross-sectional TEM and NEXAFS characterization of the SAMs indicate that the properties of the SAMs prepared by microcontact printing and dipping are essentially identical.

1. Introduction

Continuous improvements in the performance, reproducibility, and reliability of organic thin-film transistors (TFTs) have recently fueled the development of more complex applications for organic TFTs, such as flexible and stretchable active-matrix displays [1,2], microprocessors [3], radio-frequency identification (RFID) tags [4], and sensor arrays [5,6].

An important requirement for the realization of robust integrated circuits based on organic TFTs is the ability to control the electrical properties of the TFTs. For example, in static random access memory (SRAM), the ability to set the threshold voltage of each TFT of the memory cells individually can greatly enhance the static noise margin and can be helpful in suppressing inadvertent switching events.

The threshold voltage of organic TFTs can be controlled, for example, by adjusting the thickness of the gate dielectric [7], by introducing controlled channel doping [8], by implementing a floating-gate structure [9], or by functionalizing the surface of the gate oxide with an organic self-assembled monolayer (SAM) [10]. The use of SAMs appears particularly promising, because of the availability of a wide range of SAMs with different properties [11,12], the reproducibility and tunability of the process [13,14], and the excellent stability of the SAMs [15,16]. Depending on the chemical structure of the SAM and the specific interactions at the interface between the SAM and the organic semiconductor, the threshold voltage of the TFTs is affected by the dipole moment of the SAM and/or by the space-charge layer induced by the SAM, so that depending on the combination of SAM and organic semiconductor, a robust, permanent and well-defined shift of the threshold voltage can be obtained [17].

The most popular method for preparing SAMs is by dipping the substrate into a liquid solution of the self-assembling molecules, which leads to the chemisorption of the molecules on the surface of the substrate and the spontaneous formation of a well-ordered monolayer [10–18]. A fundamental limitation of the dipping method is that it usually covers the entire substrate with the same SAM, making it difficult to create a dense pattern of more than one type of SAM on the same substrate. However, for certain applications, such as complementary circuits based on p-channel and n-channel organic TFTs that benefit from different gate-oxide modifications for each type of TFT [19], it is beneficial to be able to pattern more than one type of SAM on the same substrate. This will require the spatially resolved formation of each SAM on the

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substrate, which can be accomplished, for example, by microcontact printing [20–23], microwriting [24], lithography with ultraviolet radiation [25], or combinations thereof [26].

Controlling the threshold voltages of organic TFTs in a complex pattern for large-scale integrated circuits requires a precise and deterministic process that can be applied to individual transistors with micron-scale resolution over large areas. In a previous study we demonstrated the formation of two different SAMs (an alkyl and a fluoroalkylphosphonic acid SAM) on the same substrate by microcontact printing [27], but with limited resolution and without the ability to pattern the SAMs in an arbitrary geometry.

Here we report on the fabrication and characterization of a dense array of 500 organic TFTs using two different patterned SAMs, so that each TFT has one of two different threshold voltages, depending on the type of SAM prepared on the gate-oxide surface of that transistor. The first SAM was prepared by microcontact printing, and the second SAM was prepared by dipping. A lateral resolution of 5 μm was achieved, and no significant contamination of the SAMs was observed by time-of-flight secondary ion mass spectrometry (ToF-SIMS).

2. Experimental

Five different alkyl and fluoroalkylphosphonic acids with three different chain lengths were employed in this work: *n*-octylphosphonic acid (HC_8-PA), *n*-decylphosphonic acid (HC_{10}-PA), *n*-tetradecylphosphonic acid (HC_{14}-PA), 3,3,4,4,5,5,6,6,7,7,8,8,8-terdecylfluoro-*n*-octylphosphonic acid (FC_8-PA) and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecylfluoro-*n*-decylphosphonic acid (FC_{10}-PA).

Microcontact printing was performed using a polydimethylsiloxane (PDMS) stamp with raised and recessed regions arranged in a checkerboard pattern with a pitch of either 10 μm (for the structural characterization of the SAMs) or 3–4 mm (for the TFT array). To fabricate the stamp, a layer of a positive photoresist (JSR-PFR 7790G-27cp) was spin-coated onto an oxidized silicon wafer (spin-coating conditions: 700 rpm for 1 s, followed by 2000 rpm for 30 s) and baked at a temperature of 110 °C for 90 s. This silicon wafer serves as the master for the fabrication of the PDMS stamp. The photoresist was exposed to a checkerboard pattern using an LED Maskless Lithography System (PMT Cooperation) at the scan speed of 0.6 mm/s. The resist pattern was developed in an aqueous solution of tetramethyl ammonium hydroxide (2.38% NMD) for 60 s. After rinsing with pure deionized water, the resist was baked at a temperature of 110 °C for 200 s and coated with a fluoropolymer to facilitate the later release of the PDMS mold. PDMS diluted with hexane was then poured onto the resist pattern, degassed, and vulcanized at room temperature. Finally, the PDMS stamp was peeled from the silicon master.

An array of 500 organic TFTs with a pitch identical to that of the PDMS stamp and covering an area of $4 \times 4\ cm^2$ was fabricated on a 50 μm thick flexible polyimide substrate. The TFTs were fabricated in the bottom-gate, top-contact device structure. 40 nm thick aluminum gate electrodes were deposited by thermal evaporation in vacuum through a shadow mask. The surface of the aluminum gate electrodes was exposed to a oxygen plasma to form a 4 nm thick layer of aluminum oxide (AlO_x). The freshly grown AlO_x surface is characterized by a large density of hydroxyl groups, thus providing an excellent template for the formation of high-quality phosphonic acid SAMs [15,16,27]. FC_8-PA and HC_8-PA SAMs were chosen for the TFTs, because in a preliminary experiment, TFTs with these two SAMs had shown better electrical performance than TFTs with FC_{10}-PA and HC_{10}-PA SAMs (see Fig. S2 and Table S1).

The process to pattern the two SAMs on the same substrate by a combination of microcontact printing (for the first SAM) and dipping (for the second SAM) is illustrated in Fig. 1. To prepare the first SAM, the PDMS stamp was immersed into a 2-propanol solution of FC_8-PA (1 mM) for 5 min, then dried with nitrogen. The stamp was then aligned with respect to the array of gate electrodes on the polyimide substrate and brought into contact with the substrate for 10 min. This leads to the transfer and chemisorption of FC_8-PA molecules from the raised regions of the stamp onto the surface of the plasma-oxidized gate electrodes, thus covering the gate electrodes of half of the TFTs of the array with FC_8-PA molecules. After removing the PDMS stamp from the substrate, the substrate was immersed into a 2-propanol solution of HC_8-PA (1 mM) overnight. This leads to the self-assembly of an HC_8-PA monolayer on those plasma-oxidized gate electrodes that had not been previously covered with FC_8-PA molecules during the microcontact-printing step, thus producing a checkerboard pattern of TFTs with FC_8-PA and HC_8-PA SAMs. Finally, the substrate was rinsed with 2-propanol and annealed at a temperature of 100 °C for 10 min in order to stabilize the monolayers [28].

After the formation of the two SAMs, a 30 nm thick layer of the small-molecule organic semiconductor dinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophene (DNTT) [29,30] and 50 nm thick Au source and drain contacts were vacuum-deposited through shadow masks. The TFTs have a channel length of approximately 40 μm and a channel width of 1000 μm. All electrical measurements were performed in ambient air at room temperature.

3. Structural characterization of the SAMs

Cross-sectional transmission electron microscopy (TEM), time-of-flight secondary ion mass spectroscopy (ToF-SIMS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy were performed to characterize the morphology, the molecular composition and the molecular orientation of the SAMs. For these experiments, the SAMs were prepared on silicon substrates covered with a 100 nm thick layer of thermally grown SiO_2, a 40 nm thick layer of aluminum, and a 4 nm thick layer of oxygen-plasma-grown AlO_x.

The cross-sectional TEM images were obtained using a Hitachi High-Tech H-9000UHR microscope at an acceleration voltage of 300 kV. Fig. 2a shows the cross section through a $Si/SiO_2/Al/AlO_x$/ SAM stack with an HC_{14}-PA SAM prepared by microcontact printing, Fig. 2b shows the cross section through a $Si/SiO_2/Al/AlO_x$/ SAM stack with an HC_{14}-PA SAM prepared by dipping, and Fig. 2c shows the cross section through a $Si/SiO_2/Al/AlO_x$ stack without SAM. Although the interface between the AlO_x layer and the SAM is difficult to discern, the images indicate that the total dielectric thickness is larger by about 1 nm in Fig. 2a and b than in Fig. 2c. The thickness of the HC_{14}-PA SAMs is expected to be about 1.7 nm [31], *i.e.*, 70% larger than the increase in thickness indicated by the TEM cross-sectional images, but this deviation may be due to the fact that the interfaces between the various layers are not perfectly smooth, that the density of the SAM is smaller than that of the layers below and above the SAM, and that the TEM image is the result of electron absorption along the entire thickness of the specimen. Both the SAM prepared by microcontact printing and the SAM prepared by dipping appear continuous and without apparent defects.

Fig. 3 shows ToF-SIMS images of a checkerboard pattern of an FC_{10}-PA SAM prepared by microcontact printing followed by the preparation of an HC_{10}-PA SAM by dipping. The checkerboard pattern has a pitch of 10 μm. Fig. 3a–c show the spatial distributions of the measured intensities of the $Al_3O_6H_2$ signal, the F signal and the CH signal on the substrate surface, respectively. In principle, there are two conceivable contamination paths: one is the unintended desorption of the first SAM from the AlO_x surface during the dipping process (during which the second SAM is formed), and the other is the unintended adsorption of molecules during the dipping process onto the first SAM (formed previously by