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Influence of self-assembled monolayer dielectrics on the morphology and performance of α , ω -dihexylquaterthiophene in thin film transistors

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Three different ultrathin hybrid dielectrics based on self-assembled monolayers (SAMs) from phosphonic acid molecules were investigated on aluminum oxide. The impact of the underlying SAMs on the semiconductor morphology and transistor device performance was studied by reducing the film thickness of the subsequently deposited α , ω -dihexylquaterthiophene semiconductor to one monolayer and less. The nature of the SAM relates to the molecular orientation of submonolayer films, which is investigated by photoluminescence microscopy and atomic force microscopy. SAMs with high surface energy tend to induce a face-on growing of the semiconductor, whereas for SAMs with low surface energy an edge-on growth is favorable. © 2011 American Institute of Physics. [doi:10.1063/1.3560454]

Self-assembled monolayers (SAMs) provide a wide range of applications in the field of organic electronics and are well established as insulators in hybrid organic-inorganic dielectrics,^{1–4} in organic thin film transistors (OTFTs) or even as active semiconductor (SC) layer in transistor devices.^{5–7} The strong influence of SAMs on the channel performance in transistor devices and the possibility of active surface engineering based on functionalized or mixed-SAMs is a promising approach to achieve high performance OTFTs.^{8–11} In particular, in OTFTs, the dielectric-SC interface is of enormous importance.¹² As over 90% of the charge transport from source to drain electrode are carried directly at the interface of the organic SC and the dielectric, the molecular arrangement of the SC-molecules in the first few monolayers (MLs) of the SC determines the transistor performance.¹³

In this letter, we report on the results of bottom-gate, top-contact α , ω -dihexylquaterthiophene (DH4T) OTFTs. Three different phosphonic acid-SAMs were used to investigate the specific relation between the growth and morphology of the first ML of DH4T, influenced by the underlying SAM and the final impact on the TFT device performance.

The molecules n-decylphosphonic acid (C_{10} -PA), 16-phosphonohexadecanoic acid (PHDA), and 12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-pentadecafluorooctadecylphosphonic acid ($F_{15}C_{18}$ -PA), were chosen to form SAMs.¹⁴ Densely packed hybrid dielectrics were created on mildly plasma oxidized, activated aluminum-gate patterns (30 nm; evaporated through stencil mask on SiO_2 substrates) by self-assembly of the phosphonic acids from solution (4 mmol/l in 2-propanol, 72 h), following a recently described procedure.^{4,15,16} The SAM-formation and the surface energy of each dielectric stack was monitored by static contact angle measurements with three different liquids (water, diiodomethane, and formamide, dropsize=1.5 μ l) according to the Owens, Wendt, and Kaelble method.^{11,14,17} The capacity (C_i) and current density through the hybrid dielectric was determined in simple metal (Al)–insulator–metal (Au) cross bar structures with an area of 2500 μm^2 .

Transistor devices with a channel length of 20 μm and a width of 150 μm were fabricated on those substrates by evaporating a thin layer of 3 nm of DH4T on top of the dielectric surface through a stencil mask (2×10^{-6} mbar @ 0.1 $\text{\AA}/s$ @ $T_{\text{sub}}=60^\circ C$), followed by 30 nm gold to define source and drain electrodes. The 3 nm film thickness relates to an equivalent of 1.2 ML of DH4T according to a calculated molecular length of approximately 2.8 nm.¹⁸ All electrical measurements (at least five devices per sample) were recorded in ambient conditions using a *Micromanipulator* probe station with an *Agilent B1500A* SC device analyzer. Mobility values are calculated in the saturation regime using common parameter extraction methods and the measured C_i .¹⁹

In a second series of substrates the DH4T thickness was further reduced to 1 nm, which corresponds to a sub ML (with an app. surface coverage of 70%), in order to study the film growth and the morphology of the first ML. The sub ML-films were grown on SAM treated smooth AlO_x -films and investigated by atomic force microscopy (AFM, *Veeco Dimension III 3100*) in tapping mode and photoluminescence (PL) microscopy (*Olympus BX 51*, $\lambda_{\text{ex}}=400$ nm). AlO_x was grown by atomic layer deposition, providing a surface roughness below 0.6 nm (RMS @ 25 μm^2).²⁰

This setup provides a direct access to the interface region, where the impact of the SAM on the growing mode (during film formation) and the morphology of the resulting DH4T islands in the transistor channel can be attributed.

The hydrophobic samples with C_{10} -PA-SAM exhibit a surface energy of about 22 mN/m, and the partially fluorinated molecule ($F_{15}C_{18}$ -PA) features a surface energy of only 9 mN/m.^{11,16,17} In contrast, the hydrophilic PHDA and the AlO_x reference sample feature an increased surface energy of about 53 mN/m (hydroxyl groups on the surface). The corresponding capacitances (C_i) and leakage current densities (J at 2 V) for the reference (only AlO_x of ~ 3.6 nm thickness and $\epsilon=4.5$) are 1.15 $\mu F/cm^2$ and 70 $\mu A/cm^2$. With SAM treatment the values are decreased by almost one order of magnitude to 0.82 $\mu F/cm^2$, 9 $\mu A/cm^2$ for the C_{10} -PA sample and 0.71 $\mu F/cm^2$, 2 $\mu A/cm^2$ for the PHDA sample. The sample with the longest phosphonic acid,

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FIG. 1. (Color online) (Top) Electrical transfer characteristic of organic TFTs with hybrid gate dielectric based on different SAM molecules and 3 nm of DH4T SC film. (Bottom) Height profile of a nominally 3 nm thick DH4T film on $F_{15}C_{18}$ -PA (left) and PHDA (right). (Inset) AFM images of the corresponding samples.

$F_{15}C_{18}$ -PA, and the thickest hybrid dielectric, respectively, exhibits the lowest capacity of $0.42 \mu\text{F}/\text{cm}^2$ and leakage current density of $2 \mu\text{A}/\text{cm}^2$, confirming the good isolating properties of the SAM.^{11,14,15}

Typical transfer characteristics are presented in Fig. 1. Despite a DH4T thickness of only 3 nm, all devices exhibit a transistor performance with a typical p-type behavior and operate at low voltages ($V_{\text{DS}} = -1 \text{ V}$, $V_{\text{GS}} \leq -3 \text{ V}$) with ON/OFF ratios in the range of 10^3 and I_{D} values of at least 10 nA, indicating that connected pathways between source and drain are existent. Generally, the reduced film thickness of DH4T leads to more negative values for V_{th} compared to thicker films of tens of nanometers due to reduced defect density.²¹ For the reference sample (AlO_x -dielectric), the lowest ON/OFF ratio (10^2) and a threshold voltage of -1.6 V was obtained. The V_{th} of the SAM-treated devices varies over a range of 1.3 V and strongly depends on the used SAM-molecule. Devices with $F_{15}C_{18}$ -PA for example cause a threshold voltage of -0.4 V . The V_{th} of devices with PHDA is -1.3 V (V_{th} of C_{10} -PA devices: -1.5 V). In general, the V_{th} -shift is addressed to rely on dipole moments of the SAM-molecules or field-induced charging of interface traps during operation (bias stress effect).^{9,22} For the reference sample a corresponding field effect mobility (μ) of $0.003 \text{ cm}^2/\text{V s}$ was calculated, for the SAM treated samples $\mu = 0.018 \text{ cm}^2/\text{V s}$ (PHDA), and a maximum value of $\mu = 0.024 \text{ cm}^2/\text{V s}$ was obtained for both, the $F_{15}C_{18}$ -PA- and C_{10} -PA- samples.

Corresponding studies on OTFTs (SC film thickness $> 30 \text{ nm}$), introducing SAMs with CH_3 -, NH_2 -, or F-functionalization, feature similar trends in V_{th} shift and charge carrier mobilities.^{9,10} As the charge transport occurs

FIG. 2. (Color online) (Top) PL images ($\lambda_{\text{ex}} = 400 \text{ nm}$, $\lambda_{\text{em}} > 455 \text{ nm}$) of 1 nm DH4T film on smooth ALD (AlO_x) substrates treated with $F_{15}C_{18}$ -PA (left) and PHDA (right). Schematic of the proposed SC morphology and the resulting PL signals.

directly at the SC-dielectric interface, aspects like morphology, grains, and molecular orientation become more crucial for transistor devices with only 3 nm active layer thickness. The morphology and the growth mode of a sub ML film of DH4T on different SAM-surfaces were studied via PL microscopy and AFM.

A PL image ($\lambda_{\text{em}} > 455 \text{ nm}$) of a 1 nm DH4T film on different SAMs is presented in Fig. 2. In this example, the AlO_x substrate was coated with a low surface energy SAM ($F_{15}C_{18}$ -PA, left) and with a high surface energy SAM (PHDA, right). At the left side ($F_{15}C_{18}$ -PA) a very weak PL intensity is observed, in contrast to a high emission intensity at the PHDA side. It is well known that a strong PL emission is obtained, when the light is efficiently coupled to the photoactive π -system.²³ For thiophene systems such as sexithiophene²⁴ or quaterthiophene,²⁵ a strong PL emission is observed for molecules lying flat (face-on) on the surface but almost no emission occurs, when the molecules stand on their long molecular axis (edge-on), perpendicular to the surface.²⁴ The PL intensities in Fig. 2 indicate that DH4T tends to orient face-on on high surface energy SAMs (PHDA) but edge-on on low surface energy SAMs ($F_{15}C_{18}$ -PA).

To further investigate and prove this hypothesis, AFM images of those layers have been recorded. Typical height signals of the investigated sub-ML films are shown in Fig. 3. For hydrophobic $F_{15}C_{18}$ -PA samples, a dewetting behavior is observed, leading to small separated DH4T islands. The morphology on C_{10} -PA with slightly increased surface energy occurs as coalescent network of small grains. Large, roundish, or jagged areas are observed for the hydrophilic reference and for the PHDA samples. The profile analysis of the deposited DH4T islands results in step heights of about 3 nm for samples with low surface energies ($F_{15}C_{18}$ -PA and C_{10} -PA) and values of about 1 nm for samples with high surface energy (AlO_x reference and PHDA).

These results indicate dominant intermolecular interactions (π - π -stacking) between molecules stand on low energy surfaces ($F_{15}C_{18}$ -PA and C_{10} -PA), leading to islands with defined step heights of about 2.8 nm, corresponding to the length of DH4T. On high energy surfaces the molecules lie flat on the substrate, with their π -systems parallel to the substrate (effective light coupling) as the molecule-surface interaction dominates over the intermolecular interaction.

FIG. 3. (Color online) AFM height signals of 1 nm DH4T film on different SAM, (a) $F_{15}C_{18}$ -PA, (b) C_{10} -PA, (c) PHDA, and (d) reference AlO_x [tapping mode, height scale (a), (b) is 5 nm and (c), (d) is 2.5 nm].

Morphological AFM studies of the 3 nm DH4T layer (Fig. 1) on $F_{15}C_{18}$ -PA yield a three dimensional growth of a terracelike morphology with a constant step height of about 3 nm. AFM images on PHDA samples indicate an almost closed first layer with a step height of about 1 nm (face-on). Subsequent DH4T layers on this first layer grow edge-on (step height of 2.8 nm), as the π - π -interactions dominate over the interaction with the now covered and thereby changed surface.^{26,27} In PL images of thicker films (3 nm and >10 nm), no difference in emission intensity depending on the underlying SAM is observed. The surface energy measured on those thick DH4T films is 23 mN/m, similar to hydrophobic samples (C_{10} -PA samples), also indicating a similar orientation in thick films on all substrates.

As the transistor devices were fabricated with a 3 nm film of DH4T, the device performance can be attributed directly to the morphology of the first ML. For low surface energy samples, DH4T molecules orient edge-on from the beginning of the deposition process, featuring a well ordered first ML, resulting in higher charge carrier mobilities. In the case of high surface energy samples, the first ML grows face-on and leads to less effective π - π -stacking of the subsequent layer. Furthermore, the face-on DH4T may induce more charge trapping defects within the interface or may contribute to the hybrid dielectric, resulting in lower charge carrier mobility.

In conclusion, three different hybrid dielectrics based on phosphonic acid molecules were tested in OFETs with 3 nm of DH4T SC in order to study their impact on the device performance. The maximum charge carrier mobility for devices with hydrophobic, low surface energy dielectrics was related to the observed morphology of sub ML-films. As the charge transport occurs directly in the first two ML of the SC, the orientation of the molecules has a strong impact on the device performance. Face-on orientation of the first ML seems less favorable than edge-on orientation, even if the subsequent layers grow edge-on. The molecular orientation critically depends on the relative strength of molecule-substrate interaction versus intermolecular interaction, which can be tuned actively by introducing SAMs with different surface energies.

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