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Mixed self-assembled monolayer of molecules with dipolar and acceptor character—Influence on hysteresis and threshold voltage in organic thin-film transistors

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In this report, we investigate the impact of the molecular dipole moment and redox active head groups (C_{60}) in pure and mixed self-assembled monolayers (SAMs), which serve as an ultra-thin hybrid dielectric layer in low-voltage operating organic thin-film transistors. We show that the dipole of the SAM-forming molecules affects the threshold voltage, while the concentration of redox-active C_{60} moieties determines the hysteresis in devices with α,α' -dihexyl-sexithiophene and pentacene as organic semiconductors. © 2012 American Institute of Physics. [doi:10.1063/1.3682301]

Self-assembled monolayers (SAMs) are now well established organic components of thin hybrid dielectrics in organic thin-film transistors (OTFTs). Their nanometer-scale thickness and the possibility of tuning the channel interface by varying the molecular structure lead to high performance and ultra-low power operation.^{1–3} The molecular structure of the component molecules of the SAMs and in particular their permanent molecular dipoles influence the turn-on characteristics of OTFTs with ultra-thin hybrid dielectrics strongly. Also on thicker gate dielectrics decorated with SAMs, effects on device characteristics have been observed.^{4–6} Both positive and negative shifts in the threshold voltage (V_{TH}) were obtained using molecules with negative or positive dipoles, respectively. In this respect, positive and negative denote dipoles with their negative ends directed towards the substrate surface or semiconductor, respectively. This effect is due to the additional electrical field of the dipolar SAM-molecules, which reduces or enhances the applied gate field.⁷ Furthermore, it can be used to control V_{TH} continuously in p- and n-type OTFTs by varying the stoichiometric composition of SAMs that consist of mixtures of molecules with different dipoles.^{8,9} However, in many cases, the V_{TH} shift caused by SAM dipoles is overlaid with other changes in the device characteristics. For instance, the appearance and nature of hysteresis during operation are typically attributed to the dielectric layer, whereas variations of the charge-carrier mobility are associated with the semiconductor and changes in its arrangement on the dielectric surface (grain size, orientation, etc.).^{2,5} Thus, molecular rearrangements or charging of the dielectrics are reasonable causes for hysteresis. Charging in particular leads to a change of the dielectric permittivity and thus to a shift in V_{TH} , as used exquisitely in floating-gate memory transistors.^{10,11} The large variety of molecules that form SAMs allows ones that have approximately equal dipole moments but different abilities to attract and trap

charges to be synthesized. Using such molecular dielectrics in operating devices helps distinguish between the effects of molecular dipoles and the ability to trap charge on V_{TH} -shift and hysteresis.

In order to explore this approach, we have investigated a series of thin-film transistor devices using pure and mixed SAMs of 12,12,13,13,14,14,15,15,16,16,17,17,18,18,18H-pentadecafluoro-octadecyl phosphonic acid **1** ($F_{15}C_{18}$ -PA) and a C_{60} -terminated octadecyl phosphonic acid [1-methoxy-3-(18-phosphonicacid octadecyloxy)-methano]-1,2-dihydro[60]fullerene **2** ($C_{60}C_{18}$ -PA) in hybrid AlO_x /SAM dielectrics (Figure 1). These molecules are shown by density-functional theory (DFT) calculations (defined in the supporting information) to have large total dipole moments (2.79 D for **1** and 4.05 for **2** in their extended conformations) but very similar components along the molecular axes (see below), so that the dipole effect can be minimized.¹² They were used in combination with two different p-type organic semiconductors (pentacene and α,α' -dihexyl-sexithiophene

FIG. 1. (Color online) Schematic cross section of a fully patterned bottom-gate top-contact transistor with AlO_x /SAM hybrid dielectrics (top-left). Chemical structure of SAM-forming molecules and direction of the molecular dipole component perpendicular to the surface (top-right, arrow heads show negative ends of the dipoles). Schematic sketch of pure and mixed SAM hybrid dielectrics composed of **2** and **3**.

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(Hex-6T-Hex)). A second device series of pure and mixed SAM dielectrics of octadecyl phosphonic acid **3** (C_{18} -PA, calculated dipole moment = 1.07 D) and **2** ($C_{60}C_{18}$ -PA) was used in TFTs with Hex-6T-Hex in order to investigate the effect of their different dipole moments in the SAM with as few extraneous perturbations as possible. The devices were fabricated in a fully patterned bottom-gate, top-contact configuration on SiO_2 substrates (Figure 1) according to procedures described recently.^{9,13} We used an excess of the alkyl or fluoroalkyl molecules (**3** or **1**) over **2** ($C_{60}C_{18}$ -PA) to prepare the mixed SAMs by adjusting the stoichiometries of the solutions of the compounds and used two different mixed SAMs with molar ratios of 99:1 and 95:5. The low molar content of **2** ($C_{60}C_{18}$ -PA) was chosen because the C_{60} head-group of approximately 1 nm diameter covers a larger surface than **3** or **1** and therefore contributes proportionately more strongly to the surface area. This leads to pronounced changes in device characteristics, even at low C_{60} content.⁹ The SAM composition was tracked with static contact angle (SCA) measurements and confirmed by other methods.¹⁴ A schematic cross section of the channel region is shown in Figure 1.

The data discussed in the following were obtained from transfer measurements recorded with an integration time of 50 ms, steps of 40 mV, 2 s hold time and swept from positive to negative bias. Clockwise and anticlockwise hysteresis refer to a transfer characteristic that is shifted to more positive bias and to more negative bias in the backward measurement, respectively. The reference series with Hex-6T-Hex and **3:2** (C_{18} -PA: $C_{60}C_{18}$ -PA) as pure and mixed SAM dielectrics exhibited a clear shift in V_{TH} from -880 mV to $+770$ mV with increasing $C_{60}C_{18}$ -PA content and showed a rising anticlockwise hysteresis from ~ 5 mV to 350 mV

(Figure 2). These two types of behavior can be attributed to the different dipoles of the molecules and charging of the fullerenes, respectively, during device operation.⁹ The very small component of the molecular dipole moment of **3** (C_{18} -PA) along the molecular axis (0.28 D) reduces the applied gate field slightly and leads to a relatively strong negative V_{TH} of -880 mV. The component of the dipole moment of **2** ($C_{60}C_{18}$ -PA) along the molecular axis is -2.43 D. Consequently, the applied negative gate field is enhanced, and the devices operate with a more positive V_{TH} , which depends on the amount of C_{60} within the mixed SAMs.^{7,8}

In contrast, the Hex-6T-Hex series with pure and mixed SAMs of **1** and **2** ($F_{15}C_{18}$ -PA and $C_{60}C_{18}$ -PA) gave completely different results. All TFTs operated with a distinctly positive V_{TH} ($+600$ mV for pure $F_{15}C_{18}$ -PA, $+1100$ mV for **1:2** (99:1), $+1000$ mV for **1:2** (95:5), and $+800$ mV for pure **2** ($C_{60}C_{18}$ -PA) SAM dielectrics). V_{TH} remained positive (close to $+770$ mV from the reference series with pure **2**) and did not depend significantly on the stoichiometric composition of the SAM (Figure 2). However, the hysteresis depended strongly on the SAM composition, and increased from a clockwise hysteresis of -10 mV for pure **1** ($F_{15}C_{18}$ -PA) to an anticlockwise one of 400 mV for pure **2** ($C_{60}C_{18}$ -PA). Although the total dipole moments of **1** (2.79 D) and **2** (4.05 D) differ significantly, their components along the molecular axes are very similar (-2.27 and -2.43 D, respectively), so that the dipole effect should be minimal. However, whereas **1** is redox-inactive, the C_{60} head group of **2** is a strong reversible electron acceptor (electron affinity = 2.68 eV).¹⁵ We therefore suggest that the hysteresis results from charging the C_{60} during operation and should therefore depend on the concentration of C_{60} in the SAM. We recently showed that mixed SAMs of **3** (C_{18} -PA) and **2** ($C_{60}C_{18}$ -PA) can act as charge-storage dielectric layers in

FIG. 2. (Color online) Transfer characteristics of devices with pure and mixed SAM hybrid dielectrics composed of C_{18} -PA: $C_{60}C_{18}$ -PA and Hex-6T-Hex (top-left), of $F_{15}C_{18}$ -PA: $C_{60}C_{18}$ -PA and Hex-6T-Hex (top-right), of $F_{15}C_{18}$ -PA: $C_{60}C_{18}$ -PA and pentacene (bottom-left). Relationship between the molar composition of the SAM dielectrics and the device parameters (threshold voltage and hysteresis) (bottom-right).

TABLE I. Electrical characteristics of devices with pure and mixed SAM hybrid dielectrics composed of F₁₅C₁₈-PA and C₆₀C₁₈-PA. Data for Hex-6T-Hex transistors with dielectrics composed of C₁₈-PA and C₆₀C₁₈-PA (in parentheses) is taken from Ref. 9.

		F ₁₅ C ₁₈ -PA (C ₁₈ -PA)	99:1	95:5	C ₁₈ C ₆₀ -PA
Hex-6T-Hex	SAM SCA water (°)	121.5	121	120	75
	Capacitance (μF cm ⁻²)	0.5	0.5	0.55	0.71
	Mobility (cm ² V ⁻¹ s ⁻¹)	0.03	0.025	0.035	0.035
	V _{TH} (V)	0.6 (−0.9)	1.1 (−0.3)	1 (0.2)	0.8 (0.8)
Pentacene	Max. hysteresis ^a (mV)	−10 (5)	5 (45)	60 (230)	400 (350)
	Mobility (cm ² V ⁻¹ s ⁻¹)	0.16	0.055	0.009	0.13
	V _{TH} (V)	−0.5	−0.5	−0.7	−0.7
	Max. hysteresis ^a (mV)	−50	−30	180	400

^aClockwise hysteresis is dedicated to negative signs and anticlockwise hysteresis to positive signs.

organic TFTs.⁹ We note that using mixed SAMs of **1** (F₁₅C₁₈-PA) and **2** (C₆₀C₁₈-PA) (99:1) as the charge-storage dielectric layer in organic TFTs shows a similar effect, with the major difference that the retention time of the ON-state (charged C₆₀) is reduced to less than 2 min (as opposed to several hours), as shown for **3:2** (99:1).⁹ This result is not surprising considering the unfavorable Coulomb interaction of the negatively charged C₆₀ with the surrounding electron-rich fluoroalkyl environment of the F₁₅C₁₈-PA.

To support our hypothesis of a dipole related V_{TH}-shift and hysteresis caused by dielectric charging, we have related the measured values of V_{TH} for Hex-6T-Hex transistors with the theoretical density of dipoles. Assuming a homogeneous electric field in the SAM dielectric, the voltage shift caused by the SAM, ΔV_{SAM} is given by

$$\Delta V_{SAM} = \frac{ND}{\epsilon_0 \epsilon_{SAM}}, \quad (1)$$

where N is the packing density, D the dipole moment along the molecular axis, and ϵ_{SAM} the dielectric constant of the SAM molecule.¹⁶ The measured difference in threshold voltage for pure SAMs of molecules **3** (C₁₈-PA) and **1** (F₁₅C₁₈-PA) ($\Delta V_{TH\ 1-3} = V_{TH\ SAM\ 1} - V_{TH\ SAM\ 3} = 1.5$ V) agrees with the one calculated from Eq. (1) ($|\Delta V_{SAM\ 1-3}| = 1.5$ V), if $N = 3.5 \times 10^{14}$ cm⁻² is assumed for both molecules. This value is reasonable as it is slightly lower than the theoretical maximum packing SAM density of alkyl phosphonic acids (4.35×10^{14} cm⁻²).^{17,18} The dielectric constants ϵ_{SAM} (2.5 for **3** and 2.2 for **1**) were obtained from capacity measurements of the hybrid dielectric AlO_x/SAM stack at 10 kHz. The same estimation for molecules **3** (C₁₈-PA) and **2** (C₆₀C₁₈-PA) led to a discrepancy between measured ($\Delta V_{TH\ 2-3} = 1.7$ V) and theoretical values ($|\Delta V_{SAM\ 2-3}| = 1.2$ V), obtained with $N = 3.5 \times 10^{14}$ cm⁻² and $\epsilon_{SAM} = 3.2$ for molecule **2**. However, as the packing density of pure **2** is certainly lower than that of pure alkane SAMs, the difference between $\Delta V_{TH\ 2-3}$ and $|\Delta V_{SAM\ 2-3}|$ is expected to be even larger. Assuming that the contribution of trapped electrons to a shift of V_{TH} for the sample with pure **3** is negligible because of the expected high packing density of this SAM molecule, we assign the larger value of $\Delta V_{TH\ 2-3}$ to the redox properties of the Fullerene. Charging of this moiety leads, therefore, to the experimentally observed hysteresis and the additional shift of V_{TH} to more positive values.

For further corroboration of our hypothesis, we fabricated a series of TFTs with pentacene as semiconductor with **1** and **2** as pure and mixed SAM dielectrics. All pentacene TFTs of this series showed a narrow distribution of V_{TH} between −500 mV and −700 mV (Figure 2, Table I), while we typically obtained a more negative V_{TH} of approximately −1200 mV for pentacene TFTs with n-alkyl-PA in hybrid dielectrics.¹³ No significant shift of V_{TH} or dependence of the shift on the C₆₀-content was observed, but the hysteresis changed from clockwise −50 mV (pure **1**) to anticlockwise 400 mV (pure **2**) with increasing C₆₀-content. In contrast to the series with Hex-6T-Hex, in which the devices exhibited an almost constant charge-carrier mobility of 0.03 ± 0.005 cm²/Vs independent of the SAM composition, the pentacene devices with pure SAMs show good charge-carrier mobility of 0.16 cm²/Vs (**1**) and 0.13 cm²/Vs (**2**), but the mixed SAMs show dramatically reduced mobility (to 0.009 cm²/Vs). We assume that this impact on the mobility is related with a more sensitive thin film-growth behavior of pentacene (according to disturbed surfaces) compared to the alkyl-substituted Hex-6T-Hex on mixed SAMs.¹² However, the trends obtained with pentacene devices support the distinction between V_{TH}-shift and operation hysteresis and their assignment to the dipole and charge-trapping effects, respectively, outlined above.

In summary, we have shown that in SAM hybrid dielectrics, the dipole moment of the molecules and thereby the dipole field of the SAMs determines the threshold voltage, whereas an electrically chargeable unit of the molecule (e.g., C₆₀) leads to hysteresis. In randomly mixed SAMs composed of molecules that combine dipolar and/or chargeable properties, the device characteristics V_{TH} and hysteresis depend on the concentrations of the components of the mixed SAMs.

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