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Photoactive self-assembled monolayers for optically switchable organic thin-film transistors

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We investigate the photoconductive and photovoltaic effects in organic thin-film transistors with thin hybrid dielectrics composed of aluminum oxide and self-assembled monolayers (SAMs). By using SAM molecules with an electro-optical functionality tuning of the photoinduced charge transfer at the interface of semiconductor and SAM upon illumination with laser light can be achieved. Control of the threshold voltage by the SAM composition enables the optical operation of the transistors without applying a gate voltage and affects the dynamics of photoinduced charge transfer. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4804595>]

Research in the field of organic thin-film transistors has achieved significant improvements of the performance and reliability of such devices during the last years and has made an entrance of this technology into market applications viable.^{1–4} Since most organic materials applied in thin-film transistor devices are based on extended π -conjugated systems the absorption of visible light and the resulting photoconductive and photovoltaic effects may cause a strong impact on the device characteristics.^{5,6} The understanding and the control of these effects are essential in order to prevent malfunction of the devices in ambient light. On the other hand, taking advantage of these features enables the realization of photosensitive transistors that can be used, e.g., for light detection and light induced switches.^{6–12}

Among the different approaches to fabricate organic thin-film transistors, the use of self-assembled monolayers as part of a thin hybrid dielectric has proven to be a promising route to realize flexible, low-power consuming organic thin-film transistors and circuits with a promising stability.^{13,14} Moreover, it has been shown that applying molecules with electron acceptor functionality in a self-assembled monolayer (SAM) on a thick SiO₂ dielectric leads to a large photosensitivity in combination with pentacene as the semiconductor.^{15,16}

In the present work we have integrated molecules with self-assembly properties containing C₆₀ head groups into SAMs deposited on a thin aluminum oxide (AlO_x) dielectric to investigate the photoinduced charge transfer in pentacene and α,ω -dihexylsexithiophene (DH6T) transistor devices operated at low voltages. We show that SAMs are a versatile tool to tune the photoinduced charge transfer by modifying the properties of the dielectric/semiconductor interface.

Bottom-gate top-contact thin-film transistor devices were fabricated on silicon substrates with 100 nm thermal SiO₂. The device layout is shown in Fig. 1(a). 30 nm of aluminum were evaporated through a shadow mask to form the gate electrodes. A thin aluminum oxide layer was generated by an oxygen plasma treatment in a Diener Electronic Pico (200W) at 0.2 mbar for 3 min. The hybrid dielectric was

formed by immersing the samples into the SAM solution (concentration of 0.05 mmol/l) for 3 days. The three differently composed SAMs used in this investigation are depicted in Fig. 1(a). SAM 1 was created by pure tetradecyl phosphonic acid (1). SAM 2 was formed by stoichiometric mixing [1-methoxy-3-(18-76 phosphonic acid hexyloxy)-methano]-1,2-dihydro[60]fullerene (2), a photoactive molecule with electron acceptor functionality based on C₆₀, and

FIG. 1. (a) Device layout and schematics of the three different SAM compositions. (b) UV/Vis spectra of 35 nm pentacene (red) and 30 nm DH6T (blue) evaporated on quartz glass and wavelengths of the laser diodes indicated by vertical lines in the diagram.

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tetradecyl phosphonic acid. The molar ratio in the solution of molecules (1) and (2) was approximately 99:1. A pure SAM of the fullerene derivative [1-methoxy-3-(18-76 phosphonicacid octadecyloxy)-methano]-1,2-dihydro[60]fullerene (3) was designated as **SAM 3**. The average water static contact angles were 111° for **SAM 1**, 109° for **SAM 2**, and 73° for **SAM 3**. The organic semiconductors were thermally evaporated onto the hybrid dielectric with a rate of $0.1 \text{ \AA/s}$ to form films with a thickness of 35 nm (pentacene) or 30 nm (α,ω -dihexylsexithiophene). Top drain and source electrodes were formed by deposition of a 10 nm thick gold layer through a gate aligned shadow mask creating devices with a channel length of $10 \mu\text{m}$ and a channel width of $150 \mu\text{m}$.

The normalized absorption spectra of thin layers of pentacene and DH6T evaporated on quartz glass are shown in Fig. 1(b). Illumination of the transistor devices was performed by a laser module (Thorlabs MCLS1) equipped with laser diodes of 658 nm or 406 nm wavelength (indicated in Fig. 1(b) with vertical lines). The laser beam was coupled out through a fiber perpendicular to the sample surface and focused on the sample surface through a fiber port. The illumination intensity was determined by a power meter (Thorlabs PM100D console with S120VC photodiode power sensor).

The initial electrical characterization of the devices was carried out in a dark environment in ambient air. The bias range in all transfer measurements was held constant for each semiconductor. The sweeps were recorded with an integration time of 20 ms, steps of 50 mV (pentacene) or 40 mV (DH6T) and swept from positive to negative bias and back. The saturation mobilities (μ_{sat}) of pentacene devices were approximately $0.05 \text{ cm}^2/\text{Vs}$ for **SAM 1** and **SAM 3**, and $0.04 \text{ cm}^2/\text{Vs}$ for **SAM 2**. DH6T transistors exhibited μ_{sat}

values of approximately $0.02 \text{ cm}^2/\text{Vs}$ for **SAM 1** and **SAM 2**, and $0.01 \text{ cm}^2/\text{Vs}$ for **SAM 3**.¹⁷

Fig. 2 shows representative transfer measurements for all devices in the saturation regime at $V_{DS} = -2 \text{ V}$. Each sample was first measured under dark conditions (solid line). The characteristic under illumination ($\lambda = 658 \text{ nm}$) was recorded immediately after switching on the laser and is represented by the dashed line. The samples were illuminated during the whole sweep with a constant intensity of 10 mW/cm^2 .

Independently from the SAM applied in the hybrid dielectric, the pentacene transistors show a clear response upon illumination (see first line in Fig. 2 for pentacene transistors). The resulting shift of the transfer curve to more positive bias and the occurrence of hysteresis are related to trapping of photo-generated charges at the interface of semiconductor and dielectric, as described for other systems.^{18,19} By adapting this explanation to our pentacene transistors, this implies that photoinduced charges can accumulate at the AlO_x surface even through the densely packed tetradecyl phosphonic acid SAM (**SAM 1**—thickness of approximately 1.95 nm (Ref. 20)). As a result of this, the threshold voltage (V_{TH}) is shifted by approximately 1 V to positive bias. The increase in gate current, especially when electrons are attracted to the gate electrode at positive bias, supports this interpretation. Note that a complete passivation of the interface that is able to block photoinduced charges requires thicker spacer layers of organic materials.^{18,19} While adding 1 molar percentage of the Fullerene molecule to the SAM does not lead to a significant increase of the V_{TH} shift, the use of a pure Fullerene SAM in the dielectric (**SAM 3**) produces a slightly larger V_{TH} shift upon illumination (1.2 V). That might indicate an increased electron transfer from

FIG. 2. Transfer characteristics for pentacene (a)–(c) and DH6T (d)–(f) in the dark (solid lines) and under illumination with $\lambda = 658 \text{ nm}$ and 10 mW/cm^2 (dashed lines) in the saturation regime at $V_{DS} = -2 \text{ V}$. Inset in (d) shows a transfer characteristic under illumination with $\lambda = 406 \text{ nm}$.

pentacene to the Fullerene moieties, in accordance with previous reports of Park *et al.*^{15,16} For DH6T we can observe an additional effect (see second line in Fig. 2 for DH6T characteristics). Due to the larger optical band gap of DH6T (2.42 eV (Ref. 21)) compared to pentacene (1.86 eV (Ref. 22)), illumination with the 658 nm laser does not lead to generation of photoinduced charges; hence, no effect on the characteristic can be observed. However, using laser light with 406 nm wavelength and an intensity of 10 mW/cm² provides suitable energy for photoinduced charge transfer through the SAM, as shown in the inset in the characteristic of DH6T on SAM 1 in Fig. 2. Introducing only 1% of the photoactive C₆₀ moieties into the alkyl SAM (SAM 2) enables photoinduced charge transfer between C₆₀ and DH6T and leads to a large shift of the transfer curve upon illumination with the 658 nm laser. We attribute this effect to photoexcitation of the C₆₀ moiety with a reported optical bandgap of 1.7 eV.²³ DH6T transistors with a pure Fullerene SAM (SAM 3) exhibit large positive V_{TH} values of approximately 1.5 V due to the large negative dipole moment of the SAM molecule and the electrical charging during operation.^{24,25} Illumination of the samples does not change the characteristic significantly in the turn-on behavior. In this case the contribution of photoinduced charges is almost negligible since the Fullerene SAM is already saturated with trapped electrons in the dark.

Photoinduced shifts of the threshold voltage and the increase of hysteresis are related to trapping at the dielectric interface and are therefore assisted by the gate-source field.¹⁸ Thus, the photosensitivity of the drain current depends strongly on the gate voltage.⁶ In the OFF-state, the increase of drain current upon illumination is dominated by the transition of photoinduced charge carriers into the dielectric due to the applied gate-field. In the ON-state, photo induced charges can contribute to the drain current. The photosensitivity P defined as

$$P = \frac{I_{light} - I_{dark}}{I_{dark}} \quad (1)$$

reaches maximum values of approximately 1.5×10^6 for pentacene on SAM 1 and 3×10^4 for DH6T on SAM 2 determined at the onset voltage (V_{on}).

If the onset voltage of a transistor is shifted close to 0 V by a proper SAM treatment,²⁴ it becomes possible to operate the transistor effectively only by illumination with the laser light, without applying a gate voltage. This is shown for a pentacene transistor with SAM 3 and a DH6T transistor with SAM 2 in Fig. 3. The output characteristics at $V_{GS} = 0$ V show that modulation of the drain current can be controlled simply by varying the illumination intensity. Therefore, SAMs offer the possibility to reduce and to tune the gate voltage needed for modulation of photoinduced drain currents. The output characteristic for the DH6T transistor shows a more pronounced modulation behavior than the pentacene transistor. This difference in the modulation behavior could be addressed to the dynamics of the photoinduced charge transfer at the interface. Characteristic time scales for trapping of charges in the dielectric are in the range of several seconds.^{16,26} Therefore, the contribution of photoinduced charges due to trapping should be rather small within the time scale of the

FIG. 3. Output characteristics for pentacene on SAM 3 (a) and DH6T on SAM 2 (b) at $V_{GS} = 0$ V and under different illumination intensities with the 658 nm laser.

output measurement (1 s). Hence, the main contribution is attributed to the photoconductive effect which relies on the fast charge transfer between electron donor and electron acceptor within the lifetime of excitons (850 ps for pentacene).²⁷

The time dependency of the photocurrent and the switching behavior was investigated at $V_{DS} = -2$ V and $V_{GS} = 0$ V for pentacene on SAM 3 and DH6T on SAM 2 and at $V_{DS} = -2$ V and $V_{GS} = -1$ V (V_{GS} close to V_{on}) for the pentacene transistor with SAM 1 (Fig. 4). The laser was

FIG. 4. Ratio of photocurrent and dark current as a function of time and switching behavior for pentacene on SAM 3 (black) and SAM 1 (green) and DH6T on SAM 2 (red). The resolution of the measurement was 8 ms, the 658 nm laser with an intensity of 30 mW/cm² was turned on after approximately 13 s.

switched on in all measurements after approximately 13 s. The initial increase of the drain current by a factor of 50 for the pentacene transistor with **SAM 3** and the DH6T transistor can be ascribed to the photoconductive effect, while the subsequent slower increase can be related to trapping of charges as mentioned above.

According to a method applied by Park *et al.*,¹⁶ we have fitted the time-dependent characteristic of the drain current after the initial increase with an exponential function, which gave time constants of 5 s for the DH6T transistor and 3.2 s for the pentacene transistor with **SAM 3**. These are much lower than the time constant of 32 s that was obtained for pentacene on thick SiO₂ modified with a C₆₀-SAM.¹⁶ Due to the absence of C₆₀ acceptor states, the photoconductive effect for the pentacene sample with **SAM 1** is considerably smaller (increase of $I_{\text{photo}}/I_{\text{dark}}$ by a factor of approximately 20 upon illumination) than for the other two devices. Moreover, the characteristic for this sample exhibits a very shallow subsequent increase of the current (Fig. 4). Therefore, incorporating acceptor moieties into the SAM of our transistor devices not only increased the photosensitivity due to increased photoconductive effect but also accelerated trapping of charges in the dielectric compared to a densely packed alkane SAM.

We have demonstrated the versatility of thin hybrid dielectrics composed of AlO_x and SAMs to tune the optical response of organic thin-film transistors, which relies on fast charge transfer between an electron donor and acceptor and on trapping of charges at the interface of semiconductor and dielectric. If the energy of the light source is larger than the bandgap of the π -conjugated chromophore, photoinduced charge transfer results in a shift of the characteristic to more positive bias. SAMs provide the possibility to manipulate the charge carrier density in the semiconductor and can therefore be used to reduce and to tune the voltages needed to switch the transistors optically. In best case phototransistors can be realized in a two electrode setup without electrical gating. An improvement of the switching behavior can be realized by incorporating strong electron acceptors, e.g., C₆₀ into the SAM. This also enables phototransistor operation even without a photoresponse of the semiconductor at the excitation wavelength. In general, SAM modifications of the interface have an impact on the dynamics of the photoinduced charge transfer, which has to be considered for predicting the behavior of the transistor characteristics under illumination.

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