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Organic field-effect transistors as a test-bed for molecular electronics: A combined study with large-area molecular junctions

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The contact resistance of a transistor using self-assembled monolayer (SAM)-modified source and drain electrodes depends on the SAM tunnel resistance, the height of the injection barrier and the morphology at the contact. To disentangle the different contributions, we have combined here the transmission line measurements in transistors with transport measurements of SAMs in large-area molecular junctions. The tunnel resistance of the SAM has been independently extracted in two-terminal large-area molecular junctions. We show that the tunneling resistance of the SAM can be added linearly to the contact resistance of the transistor with bare Au electrodes, to account for the increased contact resistance in the SAM-modified transistor. The observed agreement is discussed. The manifestation of the SAM in the contact resistance shows that transistors can potentially be used as an experimental test-bed for molecular electronics.

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1. Introduction

The building block of organic electronic integrated circuits is the field-effect transistor (FET). Applications are envisaged in smart labels and active matrix displays [1]. The performance of the transistor depends on both charge injection and the transport of injected charges through the organic semiconductor [2]. The charge transport in organic semiconductors is theoretically well understood [3]. Experimentally, charge carrier mobilities close to unity (cm²/V s) have been reported both for holes and electrons [4]. A remaining challenge is understanding of the charge injection mechanism.

To inject charge carriers the Fermi level of the metal electrode has to be aligned with either the lowest unoccupied molecular orbital (LUMO) or the highest occupied molecular orbital (HOMO) of the organic semiconductor [5]. An offset between these levels yields an injection barrier, the presence of which deteriorates charge injection [6–8]. To reduce the injection barrier the work function of the electrodes has been modified by using polar self-assembled monolayers [9]. This dipole layer can be described as two parallel sheets of charge separated by the length of the molecule. The change in workfunction of the modified electrode follows from classical electrostatics [10]. By adapting the dipole moment of the molecule the workfunction can be tuned in a range of about 2 eV.

Although control of charge injection with SAMs in FETs has led to improved performance, enhancement of the extracted field-effect mobility and reduction of the contact resistance [8,11], the role of SAMs on the FETs’ performance is still elusive. In a thorough study, Stoliar et al. have investigated pentacene FETs with Au electrodes functionalized with alkanethiols. The extracted mobility increased with chain length up to \( n = 8 \) (\( n \) being the number of methylene units), and decreased exponentially for \( n \) larger than 8 [12]. This non-monotonic behavior,
together with a clear odd–even fluctuation in the extracted mobility, has been explained as the result of the interplay between a decreased hole injection barrier due to the dipole moment of the SAM, the tunneling assisted by the SAM and by an improved morphology of the pentacene at the interface with the SAM.

Firstly, we note that the mobility extracted from transistors is rather tolerant for injection barriers. Pentacene has been investigated using transistors with source and drain electrodes with widely different work functions: Au, Cu, Ni. The saturated output currents differed by less than an order of magnitude. Experimentally, injection barriers as high as 1 eV can be surmounted [13,14].

Moreover, deposition of organic materials that tend to form crystalline domains is particularly sensitive to the surface energy of the substrate. Application of a SAM alters the surface energy and can therefore change the morphology of the deposited semiconductor [15]. Changes in device mobility upon application of a SAM are therefore not necessarily due to a change in injection barrier but can be due to a different morphology [16].

Finally, insertion of a SAM on the electrodes introduces an additional resistance. The extra resistance depends on the molecular structure of the SAM, conjugated or non-conjugated, and its molecular length [17,18]. The resistance increases with the molecular length, \( L \), of the molecule as \( R \propto \exp(\beta L) \), where the tunneling decay coefficient \( \beta \) depends on the energy gap between the HOMO and the LUMO [19,20]. Although the charge transport through single molecules has typically been investigated in break junctions, in scanning probe geometries and in large-area molecular junctions, Stoliar et al. extracted the decay coefficient \( \beta \) from transistor measurements [12]. However, how the SAM’s resistance manifests in the overall resistance of the transistor remains unclear. It can be a simple series resistance or it can be a multiplication factor for the contact resistance.

Here, we combine electrical measurements in large-area molecular junctions and FETs to disentangle the different contributions of a SAM-modified electrode in the extracted mobility of a transistor. We used aliphatic SAMs because they are the benchmark for self-assembly. Aromatic SAMs can be applied to modify work-function and doping of a transistor. We used aliphatic SAMs to independently extract the contact resistance of the FET using the transmission line method (TLM). This step eliminates any parasitic currents from the top to the bottom electrode.

For workfunction measurements, Au substrates were prepared by thermal evaporation of 150 nm of Au on ther-
mally grown SiO₂ substrate with 1 nm of Cr as an adhesion layer. After the self-assembly process the work function of bare and SAM-modified metals were measured using a Kelvin probe in a nitrogen-filled glove box.

2.3. Device characterization

Electrical measurements on FETs were all carried out in a probe station under high vacuum ($10^{-6}$ mbar) with a Keithley 4200-SCS Semiconductor Characterization System. In the case of large-area molecular junctions, the probe station was pressurized at $10^{-6}$–$10^{-7}$ mbar for at least 6 h before the measurements to remove any residual water absorbed in the PEDOT:PSS layer. The recorded current densities were averaged for approximately 40 devices with different diameters.

3. Results and discussion

We measured large-area molecular junctions with self-assembled monolayers of both PFDT and HDT, processed in identical conditions. In large-area molecular junctions the tunneling resistance can be evaluated by measuring the tunneling current [17]. Fig. 2 shows the tunneling current density versus applied voltage for PFDT and HDT junctions. The values are averaged over more than 40 devices. We calculated the normalized resistance in the Ohmic regime ($R_S$, resistance $\times$ area, $\Omega \mu m^2$) at 0.1 V bias, corresponding to an electric field of 70 MV/m. The resistance scales linearly with device area for junctions of 5–100 μm in diameter, resulting in identical $R_S$ values. For HDT and PFDT SAMs the corresponding tunnel resistances were determined as $2.7 \times 10^5 \Omega \mu m^2$ and $9.7 \times 10^5 \Omega \mu m^2$, respectively.

We used bottom contact/bottom gate (BC/BG) transistors to extract the contact resistance in the FETs as a function of gate bias. In the coplanar BC/BG structure, charges are directly injected into the accumulation layer at the semiconductor/dielectric interface, whereas in the staggered bottom contact/top gate (BC/TG) configuration, the source and drain electrodes are separated from the channel by the semiconducting layer, which yields a series resistance. Direct evaluation of SAM’s tunnel resistance in BC/TG is then hampered by the presence of the additional resistance. Moreover, the current crowding effect in BC/TG impedes a good estimation of the effective contact area.

To unambiguously rule out the influence of an injection barrier we first focus on PFDT treated Au electrodes. The workfunction of bare Au was measured as 4.7–4.8 eV and that of the PFDT-treated Au electrode as 5.5 eV. The HOMO energy of MEH-PPV is approximately 5.1 eV. Therefore
both bare Au and Au/PDFT electrodes form an Ohmic contact with MEH-PPV for hole injection.

The output characteristics are presented in Fig. 3. There is no hysteresis. The mobility determined for both transistors in the linear regime at small source drain bias is comparable and amounts to $3 \times 10^{-4} \text{cm}^2/\text{V s}$, in good agreement with reported mobility values. A similar value for the saturated mobility was determined from the transfer characteristics (not shown), which shows that the channel resistance of the transistors with bare Au and Au/PDFT electrodes is the same.

Fig. 3 shows that the output current using Au/PDFT electrodes for all gate voltages is smaller than that using bare Au electrodes. The total device resistance is comprised of the channel resistance plus the contact resistances. To verify that the lower output current for Au/PDFT originates from an increased contact resistance, we derived the contact resistance using the TLM method by using transistors with various channel lengths [25]. The contact resistances derived from the TLM scaling analysis are presented in Fig. 4 as a function of gate bias. The contact resistance decreases with increasing negative gate bias as commonly observed [14,26,27]. At low bias the charges are injected into an undoped semiconductor yielding a high contact resistance. With increasing gate bias the semiconductor gets electrostatically doped, and the contact resistance decreases. The contact resistance has been presented as a function of mobility [26]. The determined value of the contact resistance in accumulation of about $10^9 \Omega \text{cm}$ is lower than expected for a transistor with a mobility of $3 \times 10^{-4} \text{cm}^2/\text{V s}$, confirming the absence of any injection barrier.

Fig. 4 shows that the contact resistance increases when the Au source/drain electrodes are modified with a PDFT SAM. In order to relate the calculated contact resistance with the measured resistance of the PDFT SAM in molecular junctions, we renormalized the contact resistance to the injection area in transistors. The renormalized contact resistance (presented in Fig. 4 right axis) is taken as the contact resistance times the thickness of the accumulation layer which is typically estimated as about 2 nm [28].

In a simple approximation, we can reconstruct the contact resistance of the PDFT modified transistors by simply adding the tunnel resistance of the PDFT SAM as measured in large-area molecular junctions, to the renormalized contact resistance as determined in transistors using bare Au electrodes. The calculated curve is presented in Fig. 4 by the red line. A good agreement with the extracted contact resistance of the PDFT modified transistor is obtained. At low gate bias, the contact resistance is dominated by charge injection into the undoped semiconductor. At higher gate bias, in accumulation, the contact resistance is dominated by the series resistance of the SAM.

To substantiate the analysis above, we varied the chemical nature of the SAM. We investigated transistors with HDT modified Au electrodes. The workfunction amounted to 4.1 eV yielding an injection barrier with MEH-PPV of approximately 1 eV. The contact resistance as a function of gate bias was obtained from TLM analysis and presented in Fig. 4. Despite the barrier of about 1 eV, the values are comparable to those of bare Au and PDFT treated electrodes. Transistors are tolerant for injection barriers due to the image-force lowering of the barrier caused by the high electric field at the source contact [29]. We added the measured tunnel resistance of HDT molecular junctions to that of renormalized contact resistance using bare Au electrodes. The blue line in Fig. 4 shows that a good agreement is obtained with the extracted contact resistance of transistors using HDT-modified electrodes. We note that, the agreement is surprising because resistance and Ohm’s law are based on scattering and diffusive transport rather than tunneling. A tentative explanation is given below.

The absolute value of the resistance in a molecular junction depends on the nature of the electrical contacts to the molecule [30]. Strongly-coupled chemisorbed contacts
yield lower resistances than weakly-coupled physisorbed contacts [31,32]. Furthermore, the metal work function and the composition of the chemical anchoring group can change the resistance [32,33]. Here we have determined the SAM resistance from molecular junctions that consist of a chemisorbed Au–S bottom contact, an alkane backbone and a physisorbed SAM/PEDOT:PSS top contact. The junction thickness is smaller than the electron coherence length and, therefore, Ohm’s law is not obeyed. The electrical transport is by non-resonant tunneling. The resistance of a single molecule follows from e.g. multi barrier models yielding a resistance that is factorized with the contacts.

The total resistance of the transistor is the sum of the channel resistance and the contact resistance. At low bias the resistance is dominated by the channel resistance of the semiconductor. At high gate bias however the contact resistance dominates. In accumulation the semiconductor channel is electrostatically ‘doped’ by the gate voltage. Therefore, at sufficiently high gate voltage there are so many charge carriers in the channel that the semiconductors becomes degenerate and that it starts to act like an electrode at the SAM modified contact. The contact at low gate bias can be treated as a metal–insulator–semiconductor (MIS) tunnel junction. At high gate bias however the contact behaves as a MIM tunnel junction, similar as in the large-area molecular junctions [34]. Here we add the absolute value of the SAM resistance as a series resistance to the total resistance of the transistor without SAM. The resistance of the molecular junction is factorized with the PEDOT:PSS resistance [35]. However, when using highly conductive PEDOT:PSS and optimized processing the absolute resistance derived agrees with that of break junction and C-AFM measurements [36]. The agreement obtained here might be due to the fact that the junction consists of metal/SAM/doped semiconductor. Therefore, the SAM resistance is clearly manifested in the contact resistance of the transistors. Hence a SAM-modified transistor can be used as an experimental test-bed for molecular electronics as first proposed by Stoliar et al. [12].

The tunnel resistance of the PFDT SAM has been independently extracted in two-terminal large-area molecular junctions. We show that in first order approximation the tunneling resistance of the SAM can be added linearly to the contact resistance of the bare Au transistor, to account for the increased contact resistance in the PFDT-modified transistor. The analysis has been verified by using different SAMs.

The SAM modified contact at low gate bias can be treated as a metal–insulator–semiconductor (MIS) tunnel junction. At high gate bias however the contact behaves as a MIM tunnel junction, similar as in the large-area molecular junctions.

The agreement obtained here shows that the SAM resistance is clearly manifested in the contact resistance of the transistors. Hence SAM-modified transistors can potentially be used as a gauge to measure electrical transport through single molecules.

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