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Shifted transfer characteristics of organic thin film and single crystal FETs

K.P. Pernstich*, C. Goldmann, C. Krellner, D. Oberhoff, D.J. Gundlach, B. Batlogg

Laboratory for Solid State Physics, ETH Zürich, CH - 8093 Zürich, Switzerland

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Abstract

The threshold voltage and the turn-on voltage of pentacene thin film transistors (TFT) can be shifted by covering the gate insulator with a self assembled monolayer (SAM) of organosilane molecules. In this article we present experimental evidence identifying the SAM-induced modifications of the surface potential as the main cause for the shifted characteristics. To this end, FETs have been produced both on thin films and on single crystals. In the "flip-crystal" method for fabricating FETs, the single crystals of rubrene were placed onto prefabricated structures comprising a gate electrode, gate insulator and source/drain contacts. Prior to attaching the crystals, the SiO_2 gate insulator was treated with different organosilane molecules that form SAMs on the gate insulator. Depending on the molecule's dipole moment, shifts of the characteristics by up to 40 V in V_g are measured. This behavior can be explained in a simple energy level diagram where the surface potential of the gate insulator is changed by the built in electric dipole field of the self assembled monolayer.

Keywords: Turn-on voltage; Surface treatment; SAM-induced charge; Surface potential; Contact potential

1. Introduction

The demonstration of organic transistors and ring oscillators fabricated on paper [1] expands the range of substrates that can be used to fabricate organic electronics. To further increase the applicability of organic materials in commercial products, versatile and easy production schemes are necessary. Equally important is a basic understanding of the physical mechanisms. In the past, notable improvements of the mobility in thin film transistors (TFT) made from the prominent organic material pentacene were achieved by either treating the gate insulator surface, or by using different insulator materials. It has been shown that treating the gate insulator with the silane coupling agent (SCA) octadecyltrichlorosilane (OTS) results in a mobility of pentacene thin film transistors of $> 2\,cm^2/V\,s$ [2]. By using cross-linked polyvinylphenol as a gate insulator, a mobility of $3\,cm^2/V\,s$ was achieved [3] and by using poly-α-methylstyrene the mobility could be further increased to $5\,cm^2/V\,s$ [4]. While some parameters for these improvements are well established, a detailed explanation is still missing.

In this article we report on the effect of treating the surface of the gate insulator with different silane coupling agents. As we will show, the different SCAs cause a shift of the transistor turn-on voltage and of the threshold voltage for specific chemical endgroups of the SCA, resulting in a significant mobile charge carrier density in the transistor channel even without an applied gate voltage. The built-in electric field of the SAM mimics an externally applied gate voltage. Additionally we observe that the SCAs also influence the trap density which is reflected by the subthreshold characteristic.

2. Experimental

Fig. 1(a) shows the schematic device structure of the top contact pentacene TFTs, fabricated on heavily doped and oxidized silicon wafers. Prior to the pentacene deposition the wafers were treated with a 3 mM solution of the various SCAs in anhydrous toluene as described in detail previously [5]. The studied SCA molecules are shown in Fig. 2 and form self as-

* Corresponding author. Tel.: +41 1 633 3626; fax: +41 1 633 1072.
E-mail address: kurt.pernstich@solid.phys.ethz.ch (K.P. Pernstich).

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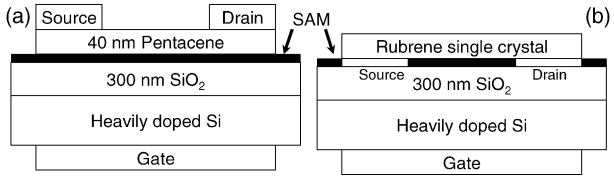

Fig. 1. Schematic device structure of the top contact pentacene TFTs (a) and the rubrene single crystal FETs (b).

sembled monolayers (SAMs) on the SiO_2 gate insulator with a measured capacity of 11.5 nF/cm^2. A 40 nm thick pentacene film was deposited at a rate near 2 nm/min using purified starting material. During the deposition, the wafers were heated to a temperature of 50 °C. Gold source and drain contacts were evaporated through shadow masks, completing the transistors. All TFTs have a channel width of $W = 600\,\mu m$ and a channel length varying from $L = 30$ to$150\,\mu m$.

To fabricate single crystal transistors as illustrated in Fig. 1(b), we employed a "flip-crystal" technique, described in detail previously [6], which was slightly modified for this experiment: 20 nm thick source and drain contacts were deposited on clean silicon wafers prior to the treatment with the SCAs and no treatment of the gold contacts was made. Rubrene single crystals were grown as described in [7] and the single crystal field effect transistors (SC-FETs) were completed by placing the rubrene crystals onto the prefabricated substrates.

All electrical measurements were carried out using a HP 4155 A parameter analyzer with the samples kept in an inert atmosphere.

3. Results and discussion

The output characteristics for pentacene transistors with various SCA layers are shown in Fig. 3 for *zero* gate voltage. The magnitude of the drain current reflects the mobile charge carrier concentration at zero gate bias for the different treatments. Obviously there is a significant density of mobile charge carriers present in the TFT channel, even at zero gate bias.

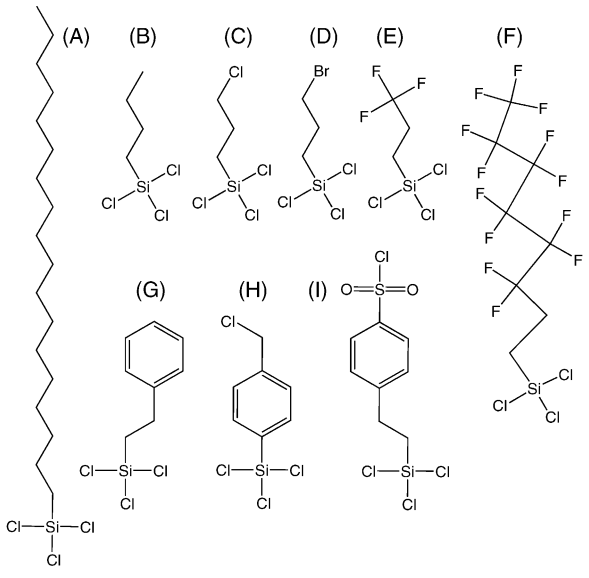

Fig. 2. Molecular structure of the studied silane coupling agents.

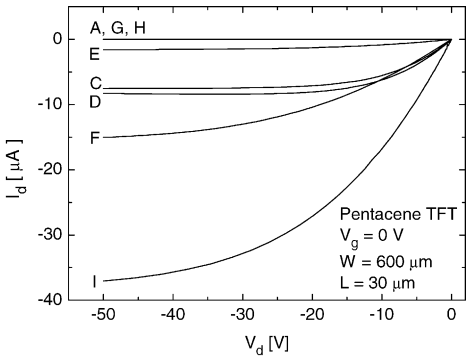

Fig. 3. Output characteristics of TFTs with several surface treatments at zero gate bias. The drain current indicates different mobile charge carrier concentrations for various treatments.

Listed in Table 1 are the main device parameters measured on transistors with various SCAs. The charge carrier mobility μ and the threshold voltage V_t were extracted from a plot of $\sqrt{I_d}$ versus V_g (not shown). The turn-on voltage V_{to} and the normalized subthreshold swing S were extracted from the transfer characteristic plotted as $\log|I_d|$ versus V_g. The extraction procedure is described elsewhere [5].

For all SCA treatments except (E), (F) and (I) the mobility is $> 0.5\,cm^2/V\,s$ (cf. Table 1). The turn-on voltage is slightly negative for the phenyl treatment (G) and positive for all the other treatments. A negative turn-on voltage implies that the transistor is completely switched off at zero gate bias. From the difference between threshold voltage and turn-on voltage a trap density can be estimated [5]. Another indication of the trap density is the initial subthreshold swing S, which is steep for treatments (A), (B), (G) and (H) and shallow for treatments (E), (F) and (I). The remaining treatments (C) and (D) show an intermediate subthreshold swing.

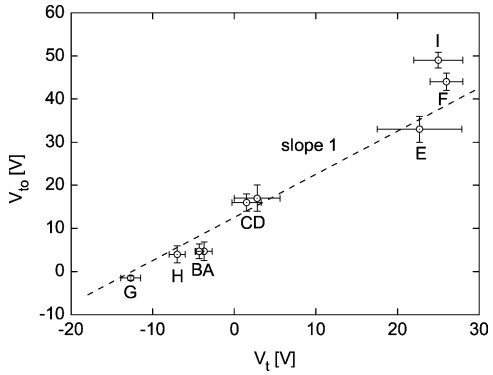

Fig. 4. Turn-on voltage versus threshold voltage: except for the treatments (F) and (I) the turn-on voltage shifts by the same amount as the threshold voltage. Treatment (F) and (I) also show a significantly modified transfer characteristic (Fig. 6) compared to OTS.

Table 1

Treatment	μ (cm^2/V s)	V_t (V)	V_{to} (V)	S [(V/dec)(nF/cm^2)]
(A) Octadecyltrichlorosilane	0.96(16)	−3.7 (1.0)	4.7	10.4
(B) Butyltrichlorosilane	0.61(11)	−4.3 (0.5)	4.7	12.6
(C) 3-Chloropropyltrichlorosilane	0.71(09)	1.5 (1.8)	16	20.7
(D) 3-Bromopropyltrichlorosilane	0.74(13)	2.8 (2.8)	17	23
(E) Trichloro(3,3,3-trifluoropropyl)silane	0.03(01)	22.7 (5.2)	33	56.3
(F) 1H,1H,2H,2H-Perfluorooctyl-trichlorosilane	0.15(02)	26 (2.0)	44	56.3
(G) Phenethyltrichlorosilane	0.71(11)	−12.7 (1.2)	−1.5	10.4
(H) 4-(Chloromethyl)phenyltrichlorosilane	0.56(12)	−7 (1)	4	13.8
(I) 2-(4-Chlorosulfonylphenyl)ethyltrichlorosilane	0.36(05)	25 (3)	49	50.6

Mean value (standard deviation) of the electrical properties of the TFTs incorporating various self assembled monolayers. μ is the charge carrier mobility, V_t the threshold voltage, V_{to} the turn-on voltage and S the normalized subthreshold swing.

In Fig. 4 the turn-on voltage is plotted versus the threshold voltage. The dashed line with a slope of one indicates that the turn-on voltage and the threshold voltage are shifted by the same amount. Treatments (F) and (I) are an exception. A detailed look at the difference between the threshold voltage and the turn-on voltage reveals small differences that might be due to different trap densities as discussed below.

For molecules similar to the investigated ones shown in Fig. 2, a permanent electric dipole moment of order 1-2 Debye has been reported [8,9]. When assembled into a monolayer, a net effective dipole results that changes the surface potential. The relationship between dipole moment and surface potential change has been studied experimentally [8,9]. Typical values are in the range of a few tenths of a V for SAMs on an insulator [9], and approximately 1 V for SAMs on a metal surface [8]. Assuming the thickness of the monolayer to be 1.5 nm, the built-in electric field of the SAM produces a field strength of 1–10 MV/cm. To produce the same field across the 300 nm thick SiO_2 gate insulator a gate voltage between 30 and 300 V is necessary.

Considering the dipole field of the SAM, a schematic energy level scheme shown in Fig. 5(a) may explain the working of the transistors: the vacuum level of the pentacene and the SiO_2 without the SAM are aligned [10] and the position of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [11] in the bulk are at 2.5 and 5 eV from the vacuum level [10]. Due to the built in electric field the SAM's effect is similar to a gate bias, bending the HOMO and the LUMO levels at the interface between gate insulator, SAM, and pentacene. Therefore mobile charge carriers can accumulate, observed as a finite current at zero gate bias.

The SAM-induced surface potential shift can be viewed as a modified contact potential that results in a (mobile) surface charge density, and might be depicted as in Fig. 5(b): the negative charge on the SCA molecules induces a mirror charge in the organic material which could be generated via thermal processes. The positive charges on the SCA molecules induce a mirror charge in the SiO_2. If additional charge is present on the SiO_2 surface, it can also influence the charge carrier concentration. In Fig. 5(b) the fixed (negative) oxide charge is marked with squares and the holes induced by this oxide charge are marked with circles. The density of trapped charge on the oxide depends on the preparation conditions of the SiO_2. Controlling the effective surface charge by passivation with OTS for instance, seems necessary to establish good control over the threshold voltage and the turn-on voltage respectively, which is of major importance for the design and the fabrication of devices.

In addition to the built-in electric field of the SAM, one might also have to consider a partial charge transfer between the organic material and the SAM. Holes could accumulate in the transistor channel if electrons are transferred from the active layer to the SAM. The details of such a transfer how-

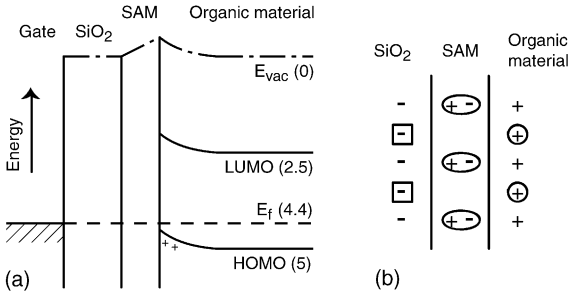

Fig. 5. Schematic energy level diagram of organic FETs with a SAM (a). Without a SAM the vacuum levels of the pentacene and the SiO_2 are aligned while the SAM rises the surface potential of the gate insulator. The numbers are given in eV and are taken from [10]. (b) Illustration of the charge distribution in the FETs. The holes in the organic material are induced by the SAM as well as by charge trapped on the gate insulator.

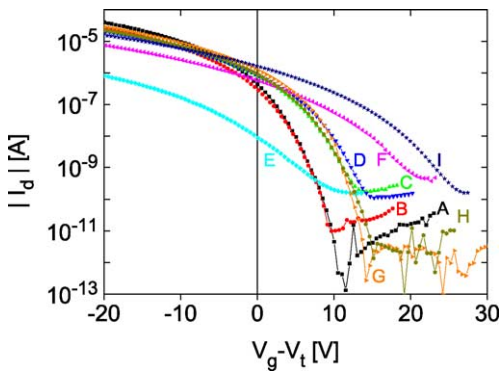

Fig. 6. Transfer characteristics of TFTs with self assembled monolayers of various silane coupling agents. The curves are aligned at the threshold voltage to visualize the differences in subthreshold behavior.

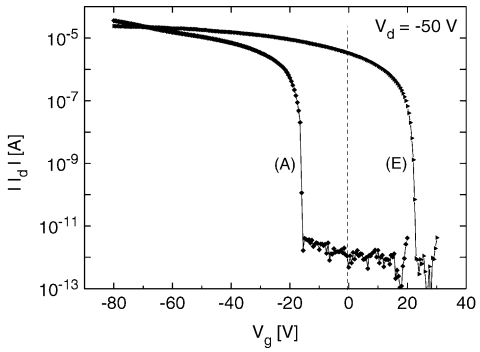

Fig. 7. Comparison between the transfer characteristics of rubrene crystal based FETs on gate insulators treated with OTS (A) and with (E). The turn-on voltage differs by ≈ 40 V.

ever, are not well established. The electronic levels, and in particular the possible dipole strength, for a single molecule will be different from those in a monolayer formed by the same molecules [12]. Therefore a self consistent treatment of the energy levels including SiO_2, SAM and the organic material could decide whether or not partial charge transfer occurs at the interface between gate insulator, SAM, and organic semiconductor.

Fig. 6 shows the transfer characteristic of the pentacene TFTs as $\log|I_d|$ versus $V_g - V_t$. In this representation the differences in subthreshold behavior are emphasized. A similar behavior in terms of turn-on voltage is measured for all treatments except (F) and (I), while in terms of the subthreshold swing the treatments (E), (F) and (I) differ significantly from the remaining treatments. Additionally, an increased off current was measured for treatments (C,D,E,F,I) which is consistent with a higher bulk trap density [13], possibly due to a poor molecular ordering of the films [5].

Since the subthreshold behavior strongly depends on the trap density and distribution respectively, the differences in subthreshold behavior can be attributed to different trap densities. The question arises about the origin of these additional trap states. Previously we investigated the influence of the film morphology on the value of V_t and V_{to} by depositing the pentacene at different substrate temperatures [5]. This results in films with different microstructure and *no clear trend* was observed for either V_t or V_{to}. Since the difference $V_t - V_{to}$ does vary for the different treatments, this could be an indication that the SAMs induce new trap states. Possible mechanisms are discussed in [5].

The most direct evidence for the central role played by the SAM's dipole field in shifting the characteristics is provided by single crystal experiments: rubrene single crystals were placed onto prefabricated substrates treated with OTS (A) or with (E). The resulting transistors are of high quality with essentially the same steep subthreshold characteristics, and a charge carrier mobility $> 1\,cm^2/V\,s$. The transfer characteristics are shown in Fig. 7. At an operating voltage of $V_d = -50\,V$ a large difference of the turn-on voltage was measured: $-15\,V$ for the OTS (A) treated transistor and $+24\,V$ for the transistor treated with (E). This clearly indicates that the major shift of the turn-on voltage is due to the presence of the SAM. Takeya et al. [14] recently reported similar results for SC-FETs. If interpreted in terms of a surface potential difference only, the shift of V_g by approximately 40 V would correspond to a difference of the surface potential by $\Delta V \approx 0.2\,V$.

4. Conclusions

We have shown that treating a transistor's gate insulator with different silane coupling agents can shift the threshold voltage and the turn-on voltage of organic FETs. The shift occurs for transistors made of both pentacene thin films and rubrene single crystals. Of special interest is the treatment with phenethyltrichlorosilane that results in transistors that are completely switched off at zero gate bias and show a mobility comparable to transistors treated with OTS. The observed shifts are consistent with a change of the surface potential resulting from the built-in dipole field of the SCA molecules.

Acknowledgments

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