Surface doping in pentacene thin-film transistors with few monolayer thick channels

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(Received 8 June 2012; accepted 28 June 2012; published online 17 July 2012)

Molecular surface doping was studied for organic thin film transistors consisting of an active layer of few monolayers pentacene, as prepared by physical vapor deposition. *In situ* transport measurements with different dopants revealed both positive (tetrafluoro-tetracyanoquinodimethane – F₄TCNQ) and negative (manganese(III)-tetraphenylporphyrin-chloride), as well as zero value (cobalt(II)-tetraphenylporphyrin and fullerene) gate threshold shifts. For F₄TCNQ, a high doping efficiency of 25% was observed. The maximum gate threshold shift was more than halved with pentacene thickness increasing from 2.5 to 5 monolayers, indicating that the doping effect decays above ~2.5 monolayers. Charge transfer has been discussed based on complementary x-ray photoelectron experiments. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4737214>]

Doping is essential to tune electronic transport in semiconductor materials and is an important parameter which needs to be controlled in order to improve device performance and to realize specific functionalities.¹ Doping in inorganic semiconductors normally requires incorporating donor or acceptor atoms which form covalent bonds with the host crystal. In organic semiconductors consisting of small molecules such as pentacene (Pn), the doping effect occurs via charge transfer between neighboring molecules interacting through a weaker, non-covalent bond.^{2,3} Since the dominant transport mechanism in organic semiconductors is through charge carrier hopping, in contrast to band transport in inorganic semiconductors, doping in organic semiconductors may be of comparably limited efficiency and spatial range. However, recent reports showed that doping is effective to boost electrical transport in organic semiconductors. This effect occurs on the micrometer-scale for the contact-resistance of thin-film transistors (TFTs)^{4–6} and on the nanometer scale for Ohmic transport in Pn nano-islands self-assembled across nano-gap devices.^{4,7} Temperature dependent transport measurements in doped TFT devices demonstrated key effects for strong organic acceptor dopants in the Pn matrix: First, the injection barrier height at the Au-Pn interface is reduced and second, acceptor states are created, which lie near the current carrying states in the highest occupied molecular orbital (HOMO) edge of Pn.⁷

In this letter, we study the surface doping of Pn TFTs with a few monolayer (ML)-thick channels in order to further elucidate the molecular doping mechanism. Although surface doping is of limited effect for conventional semiconductor materials except for hydrogen terminated diamond,⁸ hydrogen terminated silicon,⁹ carbon nanotubes,^{10,11} and graphene,¹² we show for ML-thin Pn channels that surface doping exhibits a high doping efficiency and is strongly

affected by the channel thickness and the non-uniformity and disorder of the channel.

We used Pn TFTs with 2.5–10 ML thick channels with a bottom-contact geometry, Figs. 1(a) and 1(b). The TFTs were fabricated with channel lengths between 5 and 200 μm and channel widths of 400 μm on heavily doped silicon wafers with 150 nm thermal oxide. The source and drain electrodes consist of 100 nm-thick Au with a 10 nm-thick Ti adhesion layer between the oxide and the Au. The channel width was defined by a resist pattern, which serves as an on-chip shadow mask for the Pn channel deposition. A double-layer resist process ensured the electrical isolation between devices. We exposed the chip surface to oxygen plasma before loading the chip into the Pn deposition chamber.^{4,7} The chip was then transferred into the chamber with minimal exposure to the ambient atmosphere.¹³ This procedure proved to be essential for reproducible thin film growth as reflected in well-reproducible electrical characteristics. After loading the chip into the vacuum system, we evacuated the chamber down to $(1 - 5) \times 10^{-8}$ mbar before deposition of the Pn and the molecular dopants and before subsequent *in situ* transport investigations of the such prepared exploratory TFT devices.

We monitored the Pn deposition by a water-cooled quartz crystal microbalance. A deposition rate of 0.2–0.5 ML/min was used and the thickness of the layer was controlled by different exposure times. The thickness and the morphology of the Pn layer were checked by atomic-force microscope (AFM) as well as by scanning electron microscope (SEM) (see Ref. 14). We were able to resolve terraces of 0–3 ML Pn on SiO₂ by SEM and by AFM. For a 6-ML-thick film on SiO₂/Si, we measured x-ray diffraction (XRD) at the Materials Science Beamline¹⁵ of Swiss Light Source, which showed that the layer height of 1 ML corresponds to 1.53 nm.¹⁶ Therefore, the Pn channel on the SiO₂ layer consists of upright standing Pn molecules. This is in agreement with earlier reports of the thin film phase of Pn on SiO₂.¹⁷ The ML step height of ~1.5 nm measured by AFM was in agreement with the value obtained by XRD.¹⁴ As shown in

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FIG. 1. (a) Scanning electron microscope (SEM) image of a 1.1 ML Pn TFT. The channel (right) is covered by a compact ML and by islands on top of it. On the electrode (left), Pn forms separated islands. (b) Sketch of the device geometry with the electrical connections. (c) *In situ* monitoring of the channel formation. The drain-source current I_{ds} is measured by applying a drain-source bias V_{ds} of -1 V and a gate bias V_g of -5 V while evaporating Pn. Above the threshold channel thickness of ~ 1 ML, I_{ds} increases further until it levels off for a coverage of ~ 6 ML (not shown).

the SEM images of Fig. 1(a) for a 1.1 ML-thick Pn channel and of Figs. 3(b)–3(d) for thicker Pn channels, the first monolayer formed a relatively smooth film, but from the second layer on, the channel consisted of an ensemble of ~ 0.5 μm-scale grains. On the Au electrodes, the morphology of the film was entirely different because of the modified adhesion of the Pn on the Au surface¹⁸ as one can see from the left side of Fig. 1(a). This difference in the Pn thin film morphology required careful patterning of the electrode edge for good electrical contact and transistor characteristics.¹⁶

In Figure 1(c), we show a typical relation between the channel thickness and the drain-source current I_{ds} for the drain-source bias V_{ds} of -1 V and the gate-source bias V_g of -5 V. Because of the formation of a continuous first monolayer, I_{ds} increased abruptly when the channel thickness reached ~ 1 ML. When the film thickness was further increased, I_{ds} increased gradually in agreement with our previous observation that contact resistance reduces and the mobility increases for thicker films.⁴ The drain-source current saturated at around 6 ML, demonstrating that the charge carrier flow is confined within the first few MLs at the Pn-SiO₂ interface^{19,20} in similarity to other organic TFT's.^{21,22}

In the TFT experiments, we measured the transfer characteristics of Pn TFTs in the un-doped state and after surface-doping *in situ* without breaking the vacuum. As dopants, we used 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄TCNQ), which is a strong acceptor molecule,²³ two different porphyrin molecules, manganese(III)-tetraphenylporphyrin-chloride (MnTPPCL) and cobalt(II)-tetraphenylporphyrin (CoTPP), and fullerene (C₆₀). The deposition rate for the doping molecules was 0.02 ML/min for dopant levels below ~ 0.01 nm⁻² and was 0.3 ML/min above. We

FIG. 2. Changes of the transfer characteristics for 2.5 ML Pn TFTs doped with different amounts (in nm⁻²) of (a) F₄TCNQ and (b) MnTPPCL. The effect of the dopant molecules is characterized in terms of the shift of $V_{g,th}$, which is defined as the intercept of the fit of the data in the linear regime (straight lines) with the abscissa. $V_{g,th}$ shifts to positive values by doping with F₄TCNQ. This indicates an increased hole density in the Pn channel (a) and (c). By doping with MnTPPCL, the opposite effect is observed (b) and (c). The dashed lines in (c) indicate an activation ratio η of 0.25. No changes are recorded by doping with C₆₀ or CoTPP (c). The specific effect of the dopant molecules can be already noticed at doping concentrations below 0.1 nm⁻² which correspond to a sub-ML coverage of dopants on top of the 2.5 ML Pn channel.

present the TFT transport characteristics for devices with a channel length of 60 μm. The results we obtained for channel lengths between 40 μm and 200 μm were comparable (not shown). The surface coverage of molecules expressed in ML depends on the size and the packing of the molecules. Assuming the least packed case (i.e., with the dopants lying flat), we estimated that the doping coverage was less than a complete ML for concentrations below ~ 0.6 nm⁻² of MnTPPCL and CoTPP and below ~ 1 nm⁻² of F₄TCNQ and C₆₀.

FIG. 3. (a) Threshold shift as function of the F₄TCNQ doping concentration for 2.5, 5, and 10 ML Pn channel thickness. The reduced threshold shift for thicker channels indicates that surface doping can efficiently influence the channel transport when the channel thickness is below ~ 2.5 ML. (b)–(d) show the SEM (top) and AFM (bottom) data for 2.5, 5, and 10 ML Pn, respectively.

In Figures 2(a) and 2(b), we show the evolution of the transfer characteristics of Pn TFTs with increasing F₄TCNQ (Fig. 2(a)) and MnTPPCL (Fig. 2(b)) doping. These data were measured at a fixed V_{ds} of -5 V on two different Pn TFTs. Both were manufactured with 2.5 ML-thick Pn channels and showed similar transfer characteristics in the pristine state. Fig. 2(a) shows that F₄TCNQ doping shifted the transfer characteristics in the positive V_g direction as a direct consequence of the acceptor doping. In the case of MnTPPCL doping, the transfer characteristics shifted in the negative V_g direction. To quantify these shifts, we defined the gate threshold voltage $V_{g,th}$ as the intercept of the linear fit of the transfer characteristics (see lines in Figs. 2(a) and 2(b)) with the V_g axis. We summarized the relation between $V_{g,th}$ and the surface doping concentration in Fig. 2(c) for F₄TCNQ and MnTPPCL. The corresponding results obtained for CoTPP and C₆₀ are also presented in Fig. 2(c). For F₄TCNQ concentrations p_a below ~ 0.1 nm⁻², $V_{g,th}$ increased proportionally with the increase of p_a and then gradually saturated at higher p_a . Combining this data with the gate capacitance C_g of ~ 23 nF/cm², we found that this proportional increase of $V_{g,th}$ corresponds to a ~ 0.25 efficiency η of the doping, given by $d(C_g V_{g,th}/e)/dp_a$. We note that the activation ratio for a F₄TCNQ acceptor molecule to supply a hole into Pn, equal to $\sim \exp(-E_a/(k_B T))$, is 4×10^{-3} and a factor of ~ 60 lower than the observed η , where E_a equal to 0.14 eV is the energy of the acceptor level of F₄TCNQ with respect to the center of the Pn HOMO in the density of states (Ref. 7), k_B is the Boltzmann constant, and T is the room temperature. Also from the slope of the above described linear fit to the transfer curve, we found that the field-effect mobility was $(5.5 \pm 0.2) \times 10^{-2}$ cm²/(Vs) for pristine and doped TFTs with p_a up to 0.05 nm⁻². This shows that the change of the film quality by the surface doping was minimal. In contrast to the case of F₄TCNQ doping, the origin of the negative $V_{g,th}$ shift by the MnTPPCL is unclear. We did not observe a significant $V_{g,th}$ shift when we deposited a similar porphyrin molecule, CoTPP, or an *n*-type semiconductor C₆₀.²⁴ Fig. 2(c). Interestingly, the efficiency of this apparent *n*-type doping of MnTPPCL was found to be of the same order of magnitude as the *p*-type doping efficiency of F₄TCNQ (Fig. 2(c)).

To study the influence of the surface doping on the TFTs with different channel thickness, we furthermore measured the relation between the Pn channel thickness and the positive $V_{g,th}$ shift induced by the F₄TCNQ doping. Fig. 3(a) shows the results obtained for three Pn TFTs with channel thickness of 2.5, 5, and 10 ML. The mobility of the TFTs measured without and with doping up to 0.05 nm⁻² was $(4.4 \pm 0.2) \times 10^{-1}$ cm²/(Vs) and $(2.1 \pm 0.1) \times 10^{-1}$ cm²/(Vs) for 5 ML and 10 ML Pn TFTs, respectively. We found that, upon increasing the channel thickness from 2.5 to 5 ML, the maximum $V_{g,th}$ shift at ~ 1 nm⁻² F₄TCNQ dropped by more than a factor of 2. This demonstrates that a F₄TCNQ molecule can efficiently influence the channel transport when the channel thickness is in the order of 2.5 ML or below. The experiment showed that the 10 ML channel was also influenced by the surface doping leading to a similar $V_{g,th}$ shift as what we observed for the 5 ML channel. We consider that this similarity is caused by the diffusibility of the F₄TCNQ and the spatial thickness variation of the Pn channel. In fact, SEM and AFM inspection of these Pn films,

Figs. 3(b)–3(d), showed a strong non-uniformity of the films; ensembles of ~ 0.5 μ m-scale grains are clearly visible. In particular, at some grain boundaries, our AFM measurement showed zones with Pn thickness of 0–2 ML which may attract F₄TCNQ molecules and thereby influence the charge carriers.

It is not apparent why a negative $V_{g,th}$ shift was observed for MnTPPCL but not for CoTPP. This is even less apparent because the HOMO energy levels of these two molecules are similar, -6.5 eV for CoTPP (Ref. 25) and -5.91 eV for MnTPPCL (derived from ultraviolet photoelectron spectra (see Ref. 14)). The transfer of an electron from MnTPPCL HOMO to Pn LUMO at -2.8 eV (Ref. 26) is therefore difficult. In contrast, the fact that the LUMO of F₄TCNQ at -5.2 eV (Ref. 26) is below the HOMO of Pn at -5.0 eV (Ref. 26) is compatible with the *p*-type doping of F₄TCNQ by the electron transfer from Pn to F₄TCNQ, although the actual acceptor level is located above Pn-HOMO.⁷

As a complementary experiment, we characterized Pn films doped by these molecules (see Ref. 14) by x-ray photoelectron spectroscopy (XPS). This was done for Pn films deposited on Au(111) single-crystal substrates with Pn thickness comparable to the 2.5 ML on SiO₂. From the XPS data of the F₄TCNQ doped Pn, we observed a chemical shift of the nitrogen core level, providing evidence for charge transfer between F₄TCNQ and Pn.¹⁴ However, the XPS data of the MnTPPCL-doped Pn indicated no chemical shift for Mn2p, Cl2p, and N1s core levels, indicating the absence of the charge transfer and chemical reaction between MnTPPCL and Pn. This is in contrast to the case when MnTPPCL is evaporated on certain metal surfaces. For example, when MnTPPCL is deposited on Co, it becomes Mn(II)TPP by losing Cl, as evidenced by the observation of Mn²⁺ instead of Mn³⁺ and the chemical shift of the Cl2p core level.²⁷ Although the Pn molecular stacking and film morphology of the Pn films on Au(111) differs from the Pn TFT channels deposited on the SiO₂, we expect XPS to give a qualitative indication for the presence or lack of the charge transfer between Pn and the molecular dopants.

We therefore tentatively ascribe the origin of the apparent *n*-type doping of MnTPPCL in absence of charge transfer to the molecular dipole moment and its ordering on the Pn. Complete elucidation of this process including the difference of the Pn crystal structure of the TFT sample and the XPS sample requires further research and is beyond the scope of this Letter.

In conclusion, our experiments showed that the surface doping can be highly efficient to modify the performance of organic semiconductor devices on the nanoscale. The fact that the detailed molecular structure crucially determines the doping effect highlights the enormous potential of realizing functional organic semiconductor devices engineered by chemical tuning of guest molecules.

We acknowledge R. Schelldorfer for AFM user support and design and construction of the experimental apparatus, B. D. Patterson for his help with the XRD measurements, N. Baumann for his help with the preparation of the multi-pin feedthrough, and C. Schönenberger for helpful discussions. The XRD data presented in the supplemental material has been obtained at the Material Science Beamline of the Swiss Light Source (SLS) at Paul Scherrer Institut. This work was partially supported by the Swiss National Center (NCCR) on Nanoscale Science.

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