Highly enhanced charge injection and bulk transport in organic gap-type diodes via one-pot treatment process: experiment and simulation

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The gap-type diode is a basic component of organic field-effect transistors. In the critical voltage range above 10 V, the gap-type diode works in the same way as a sandwich-type diode adapted for organic light-emitting diodes and organic photovoltaic cells. However, the gap-type diode is rarely studied, and compact modelling is not often found in previous reports that deal with this type of an organic diode. Enhanced bulk transport is exhibited using the one-pot treatment of self-assembled monolayers (SAMs) for an SiO_2 surface and an Au contact metal in the gap-type organic diode. Charge-injection improvement via the SAM treatment on Au induces higher bulk transport. This phenomenon is analysed mainly through compact modelling.

1. Introduction: Organic electronic devices have attracted considerable attention owing to their low cost, flexibility and large-area processing capability [1]. The demand for organic electronics in flat-panel displays (FPDs) such as liquid crystal displays and organic light-emitting diodes (OLEDs) has increased and continues to do so owing to the organic electronics' strong capability of replacing conventional processes in the FPD industry. Moreover, flexible electronics can become indispensable when wearable devices appear in the commercial marketplace; for example, electronic wristbands such as the Fitbit or Galaxy Gear.

A number of structures exist for the implementation of organic electronic devices, including thin films. Organic field-effect transistors (OFETs) present a new approach to building electronics that are mechanically flexible, span large areas and integrate with organic materials. The recent development of OFETs may underpin devices such as artificial skin [2–4]. OFETs can be manufactured at low temperatures, thereby allowing integrated circuits to be made on plastic substrates. These substrates cannot withstand the high processing temperatures used for silicon-based devices. Organic materials can be processed in a soluble manner [5–7] so that the ability to print organic OFETs increases the possibility of inexpensive large-area electronics. Furthermore, because most organic semiconductors are sensitive to specific chemical and/or biological agents [8], OFETs are excellent in sensor applications. The characteristics of mechanical flexibility, large area production and chemical specificity render OFETs intrinsically suitable for integration with organic materials such as biochemical sensors [9], actuators [10] and artificial muscles [11].

Recently, a remarkable increase in the carrier mobility of an OFET was realised using newly synthesised materials. However, the probable improvement in charge transport in an organic diode and/or an OFET is substantially restricted by limited charge injection due to an energy-level mismatch between the metal electrodes and the organic semiconductors. Further investigation is required to enhance the performance of OFETs and to understand the role of charge injection in transport. This investigation is carried out without considering the effect at the dielectric/semiconductor interface that is induced by the emergence of a gated channel near the interface.

For the investigation, we introduced a gap-type structure of diodes with two planar metal electrodes in the semiconductor [12]. As the charge injection was one of the most crucial issues in this investigation, metal electrodes were used to exclude the effect of the gate electrode on the bottom contact configuration of the OFET. Surface modification that involves a silane-anchored, self-assembled monolayer (SAM) leads to an enhanced charge injection, via a simultaneous treatment process for the SiO_2 and Au surfaces in one pot. Thus far, the SAM treatment has been conducted for SiO_2 and Au surfaces with two different sequential processes. We applied a one-pot process enabling mass production that is cost-effective and simple to realise. As a result, improved electronic transport was observed by examining the current–voltage measurement. In addition, a thorough electrical analysis was carried out through two-dimensional (2D) compact modelling based on a finite element method (FEM).

2. Experimental method and details: The configuration of the gap-type diode, using thin-film transistors without a gate electrode, is illustrated in Fig. 1*a*. Octadecyltrichlorosilane (ODTS), which is illustrated in Fig. 1*b*, was purchased from Sigma-Aldrich and used without further purification. To deposit SiO_2 on Au, to activate the Au surface, a UV/ozone pretreatment was carried out for 1 min. Subsequently, Si wafer substrates with SiO_2 on them were dipped into an ODTS solution in hexane to render their surfaces hydrophobic. Then, the Si wafer substrates were vacuum evaporated at a base pressure of 2×10^{-5} mbar, with a nominal thickness of 25 nm at a deposition rate of 0.1 A/s, on the SiO_2 substrate. By contrast, for the treatment of the ODTS on SiO_2 without standing on Au, the deposition of Au was followed by an ODTS treatment. Pentacene was vacuum evaporated at a base pressure of 10^{-6} mbar. The thickness of the film was 40 nm, as measured by a calibrated quartz microbalance. The space between the two electrodes of the diode is defined by a distance of 50 mm and a width of 2500 mm. The current–voltage (I–V) characteristic was measured with a Keithley 4200 parameter analyser.

The characterised device performance was then compared with the results obtained from compact modelling. The simulation was

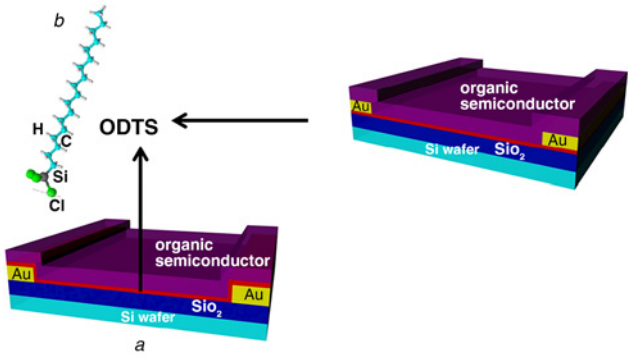

Figure 1 *Schematic of organic semiconductor-based gap-type diode with and without ODTS treatment on Au (Fig. 1a), and chemical structure of ODTS (Fig. 1b)*

carried out using a 2D device simulation software package, Silvaco ATLAS, with an organic module [13].

3. Results and discussion: A deionised (DI) water-contact-angle measurement on the ODTS–Au substrate confirmed the development of a hydrophobic ODTS layer. In fact, the ODTS treatment is quite effective in acquiring a high-quality film of pentacene grown on the SiO_2 surface. We found that after the UV/zone pretreatment, ODTS not only emerged on the SiO_2 surface but also on the Au surface. This phenomenon has not been exploited thus far, and it is regarded as an undesirable process although the silane-anchored SAM may appear on the Au surface during several pretreatments on Au [14]. Treatments such as UV/ozone and O_2 plasma are able to both activate the surface of SiO_2 and facilitate the growth of approximately 1.5 nm of AuO_x on the Au surface [14]. In general, this thin layer of AuO_x is not sufficiently stable to be supported by itself. However, the silane SAM treatment renders AuO_x that may still stay on the Au surface. As shown in Fig. 2, we found a 101° DI water contact angle when measuring the surface energy of Au after the ODTS treatment. In general, the DI contact angle of a bare Au surface ranges from 70° to 80°, depending on the cleaning method used on the bare Au [15–16].

Organic gap-type diodes based on Au electrodes, with and without the ODTS treatment, were fabricated. The current–voltage (I–V) characteristics are shown in Fig. 3. Essentially, those two devices have ODTS-treated SiO_2. Moreover, the treatment proceeds in the same batch, so that the bulk property of pentacene grown on the SiO_2 surface is defined to the same quality of the film. The change occurs solely at the interface of the electrode/semiconductor. This treatment on Au electrodes may induce a better surface morphology with higher grains of pentacene molecules,

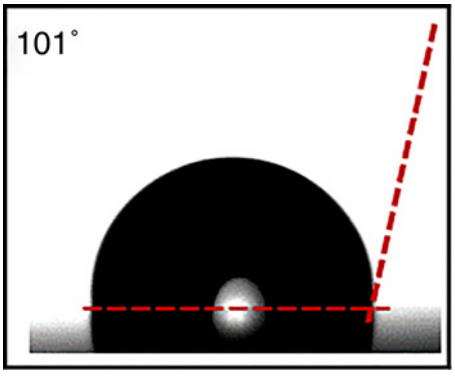

Figure 2 *Contact angle using DI water on Au surface after ODTS treatment*

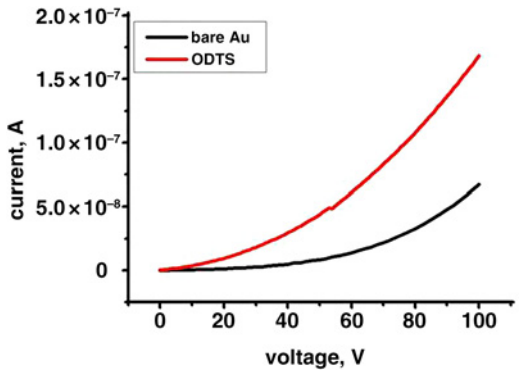

Figure 3 *Current–voltage characteristic of gap-type diode with and without ODTS treatment*

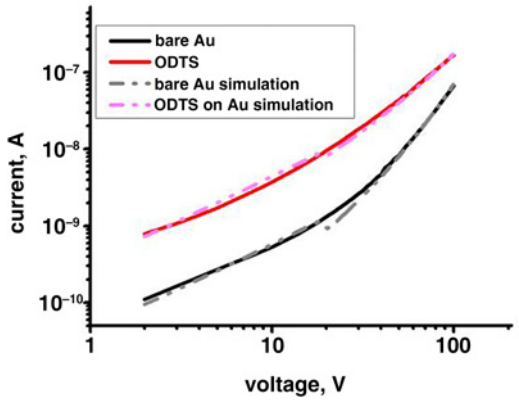

Figure 4 *Log–log plot of current–voltage characteristics (solid lines) of gap-type diode with and without ODTS treatment and their reproduction via device simulation (dashed lines)*

with a potential to overcome the dipole barrier between metal electrodes and their organic semiconductor counterparts, and passivation against oxygen doping on the interface. Thus, charge injection from the Au electrodes to pentacene is facilitated on the basis of the points mentioned above. Fig. 3 depicts that a simple pretreatment on Au is able to produce a predominant difference in the diode current of more than 20 V.

Fig. 4 clearly shows that a prominent enhancement of charge injection leads to a high current in the transport region of more than 10 V through a log–log plot of the I–V characteristics. The dashed lines represent the simulated results of each device. These results are in good agreement with the experimental I–V curves. In the range under 10 V, hole injection with the ODTS treatment on bare Au depicts a current ten times higher than that observed in the case of the treatment on Au. As the applied bias increases, the variance of current on those two diodes remains high. Compact modelling gives us strong evidence on hole-injection-induced bulk transport within the organic semiconductor,

Table 1 Major parameters used in simulation of I–V characteristics

Used parameters	Value
Au work function	5.1 eV
bandgap of pentacene	2.2 eV
permittivity	3.9
electron affinity	2.8
doping concentration	1.0×10^{16}
N_C and N_V	2.0×10^{21}

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Table 2 Physical parameters to differentiate between the electrical property of organic diodes with bare Au and with ODTS-treated Au in the regime of injection and transport for the simulation of *I–V* characteristics

Parameters		ODTS only on SiO_2		ODTS on all	
		Injection	Transport	Injection	Transport
bulk defect, pentacene	HA	2.44×10^{20}	2.44×10^{20}	2.44×10^{20}	2.44×10^{20}
	TCA	2900	2900	2900	2900
	HD	1.27×10^{18}	6.7×10^{17}	1.27×10^{18}	6.7×10^{17}
	TCD	3000	3000	3000	3000
interface defect, gold-pentacene	HA	4.0×10^{14}	4.0×10^{14}	1.0×10^{15}	1.0×10^{15}
	TCA	3000	3000	2550	2550
	HD	1.11×10^{14}	1.11×10^{14}	1.11×10^{13}	1.11×10^{13}
	TCD	3000	3000	2300	2300
zero-field mobility		1.0	0.014	0.5	0.022
field-dependent factor of hole		1.8×10^{4}	7.8×10^{2}	1.8×10^{4}	2.9×10^{3}

as well as on the underlying physics of injection-assisted transport [17].

The basic equations of density of states (DOS), which were adapted in compact modelling as decision factors, are given in the following equations:

$$g_{\mathrm{A}}(E) = \frac{H_{\mathrm{A}}}{kT_{\mathrm{CA}}} \exp\left(\frac{E - E_c}{kT_{\mathrm{CA}}}\right) \quad (1)$$

$$g_{\mathrm{D}}(E) = \frac{H_{\mathrm{D}}}{kT_{\mathrm{CD}}} \exp\left(\frac{E_v - E}{kT_{\mathrm{CD}}}\right) \quad (2)$$

where $g_{\mathrm{A}}(E)$ is the acceptor-like conduction-band density of states, $g_{\mathrm{D}}(\mathrm{E})$ is the donor-like valence-band density of states, k is the Boltzmann constant, H_{A} is the acceptor trap density of states, H_{D} is the donor trap density, T_{CA} is the acceptor trap characteristic temperature and T_{CD} is the donor trap characteristic temperature.

The terms in the DOS were incorporated in the drift–diffusion equation to describe charge concentration. We then solved the drift–diffusion equation using the FEM utilising terminal. The role of charge injection is expressed by the control of the DOS at the interface of the Au electrodes and the semiconductor in the simulation. The augmented acceptor trap DOS (H_{A}) in the diode with bare Au reflects a disturbed charge injection. By contrast, a diminished acceptor trap DOS in the diode with the ODTS-treated Au stands for facilitated charge injection. The acceptor trap characteristic temperature (T_{CA}) is also varied to fine-tune the simulated current level. The values of the major parameters are listed in Table 1. The work function of Au is 5.1 eV (as is widely known), the bandgap of pentacene is 2.2 eV with 5.0 eV of the highest occupied molecular orbital and 2.8 eV of the lowest unoccupied molecular orbital that electron affinity denotes. The doping concentration of pentacene is 10^{16} cm^{-3}. The total DOSs of the conduction band (N_{C}) and valence band (N_{V}) are both 2×10^{21} cm^{-3}.

Table 2 lists the parameters used to differentiate the charge injection effect for two different diodes, with and without the ODTS treatment. The various donor traps DOS (H_{D}) exhibited different electronic states of the bulk semiconductor. This occurred because of the variation in the charge concentration within the injection regime under 10 V and the transport regime over 10 V. To express mobility, we adapted the Poole-Frenkel conduction model to express the physics of trap-dominant transport [18]. Mup0 is the zero-field mobility of the hole and e0p.pfmob is the field-dependent factor for hole charge carriers.

4. Conclusion: Enhancing the injection property of a charge carrier results in improved transport in a bulk semiconductor. Moreover, a newly developed process of one-pot treatment of SAMs results in a higher current using a simple process. This promises to facilitate an improvement in the electrical performance in OFETs, OLEDs and OPVs, where gap-diode structures can be applied. Compact modelling segments injection and transport, so that the qualitative analysis in the simulation clearly shows an enhanced charge transport in a bulk semiconductor. A direct implementation of the techniques used here will be simply confirmed in three terminal devices such as OFETs soon. Device design may be able to be optimised according to the pre-conducted compact modelling before the fabrication.

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