Organic field-effect transistors with electroplated platinum contacts

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Recent developments in organic transistor semiconductors and engineering have led to a situation where the performance of state-of-the-art organic transistors (organic field-effect transistors) often is limited by the resistance at the metal/semiconductor contacts, rather than the semiconductor channel. This letter shows that organic transistor contacts can be improved by the most important industrial process for the deposition of noble metals, electroplating. The advantages of electroplating over vacuum-based techniques such as evaporating and sputtering, in particular for the deposition of platinum (Pt), are discussed. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1797540]

A key element in organic field-effect transistor (OFET) research has traditionally been the organic semiconductor material itself. However, when Bürgi *et al.*[1] have directly mapped the lateral potential distribution in the channels of working OFETs, they have found that a substantial part of the externally applied drain voltage drops across the metal-semiconductor contact, rather than the transistor channel. This "parasitic" voltage drop leads to a lowering of the effectively applied drain voltage, and consequently, reduced drain saturation current and longer switching times. The relative importance of contact resistance increases with increasing charge carrier mobility μ in the semiconductor, and decreasing channel length L. As OFET materials and engineering methods for short channels progress, contact resistance rapidly becomes the most serious limitation of OFET performance, and needs to be addressed.

The metalorganic semiconductor contact may either be ohmic or non-ohmic (barrier-type), depending on the relative position of metal work function, and semiconductor ionization potential (electron affinity) for p-type (n-type) semiconductors. For ohmic contacts (e.g., gold on polythiophene), voltage drops are equal at source and drain, while for non-ohmic contacts (e.g., chromium on polythiophene), voltage drop at the source is larger than at the drain due to the additional impedance of the injection barrier.[1] To minimize parasitic voltage drops, we desire a cost-effective method to prepare ohmic contacts.

Ohmic injection into p-type organic semiconductors requires high work function metals. Consequently, platinum (Pt) would be an ideal choice, as it displays extremely high work function $\Phi_{Pt}=5.65$ eV.[2] However, Pt has not frequently been used for practical OFET contacts. First, Pt has a very high melting point and is therefore difficult to evaporate, and second, it is very expensive. Evaporation or sputtering are very wasteful procedures, with most of the metal deposited on the shadowmask or bell-jar, rather than the target electrodes.

In this contribution, we demonstrate Pt OFET contacts prepared by electroplating. Electroplating is the electrochemical reduction of metals from solutions of their salts, and is a major industrial process for the surface finish of metals.[3] Here, we have prepared contacts of the low work function metal titanium (Ti) (Goodfellow, 99.99%; $\Phi_{Ti}=4.33$ eV)[2] by shadowmask evaporation of 50 nm onto commercially available wafers of 100 nm SiO_2 on n-doped (arsen) Si (University Wafer, resistivity: $10^{-3}-5\times10^{-3}$ Ω cm, orientation: 100), which are frequently used as gate insulator/gate contact test substrates in OFET research. Ti will act as the "base metal" for electroplating. Previous to Ti evaporation, the SiO_2 surface had been coated with poly(α-methylstyrene). For the coated gate insulator, we have measured a capacitance of $C_i=21.3$ nF/cm^2. For the fabrication of diodes rather than OFETs, we have also prepared Ti contacts on polyester substrate. For electroplating, either one or both Ti contacts were connected to the cathode of a galvanostat, and were immersed into an electrolytic cell filled with a 10 g/L solution of dinitrosulfatoplatinum(II) (received from Johnson Matthey plc, UK) that was kept at room temperature and was stirred continuously. As counter-electrode, we used a solid Pt anode. A constant current of 1 mA/cm^2 was applied for 120 s, resulting in the deposition of reduced, metallic Pt onto Ti. With the help of the known efficiency factor close to 1, we estimate the thickness of the Pt deposit as ~110 nm. Note that Pt is deposited only onto Ti electrodes connected to the cathode, nowhere else on the substrate or the electrolytic cell. Consequently, there is no waste; any unused Pt remains in solution and can be used for later plating. After plating, substrates were washed thoroughly in de-ionized water. Finally, bottom-contact diodes and OFETs were completed by evaporation of pentacene to a thickness of approximately 50 nm under 10^{-6} Torr vacuum. Devices were characterized with the help of Keithley 2400 source-measure units.

Figure 1 shows the current–voltage characteristic of a planar diode on polyester substrate, where one of the contacts was Ti plated with Pt (Pt–Ti), the other was left untreated Ti. The diode displays linear current–voltage (C/V) characteristics, but clearly rectifies with rectification ratio $r\approx300$ measured at ±50 V (note that r is rather independent of voltage due to linear C/V). Apparently, in forward bias (Pt−Ti+/Ti−), contact resistance is low due to the good injection of holes from Pt into pentacene, but in reverse bias, current is limited by the high hole injection barrier at the Ti/pentacene contact.

Figures 2(a) and 2(b) show the output characteristics of an OFET with asymmetric source/drain contacts: One contact was Pt–Ti, the other Ti. Since Figs. 2(a) and 2(b) refer to

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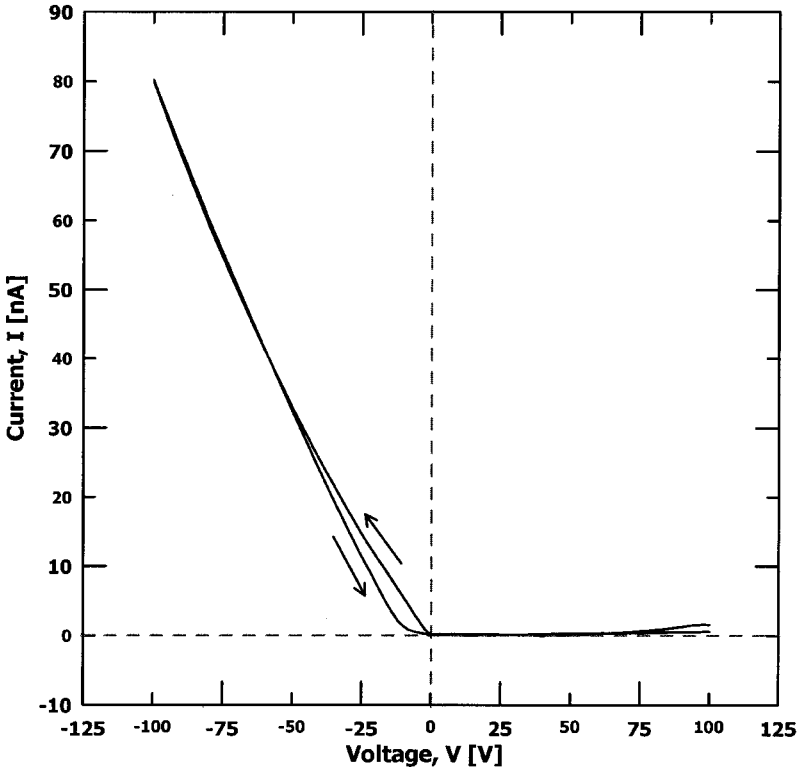

FIG. 1. C/V characteristics of a (Pt-plated Ti)/pentacene/Ti diode. Length/width of pentacene channel was 80 μm/2 mm. Double lines refer to ramping voltage up/down, respectively.

the same device, we can accurately compare respective results. In Fig. 2(a), the Ti contact is used as source S (i.e., Ti is connected to ground), and Pt–Ti as drain D (i.e., Pt–Ti is connected to $V_D<0$: "reverse bias"). In Fig. 2(b), Pt–Ti is used as S, Ti as D ("forward bias"). Between them, Figs. 2(a) and 2(b) show a highly biased OFET; note the different drain current scales. The poor quality of the Ti/pentacene contact is evident from the extremely low drain currents even at high drain and gate voltages, as seen in Fig. 2(a). Drain saturation current is severely contact-limited, and scales linearly with gate voltage, rather than quadratically, as expected for channel-limited OFETs. In forward bias [Fig. 2(b)], however, for a given gate- and drain voltage, drain currents are (200–300) times higher than in reverse bias, and drain saturation current scales quadratically with gate voltage. Nichols *et al.*[4] have previously observed somewhat asymmetric behavior in OFETs with photolithographically produced asymmetric S/D contacts (Pd/Ni), but asymmetry is much stronger here due to the very poor quality of the Ti contact. When carrier mo-

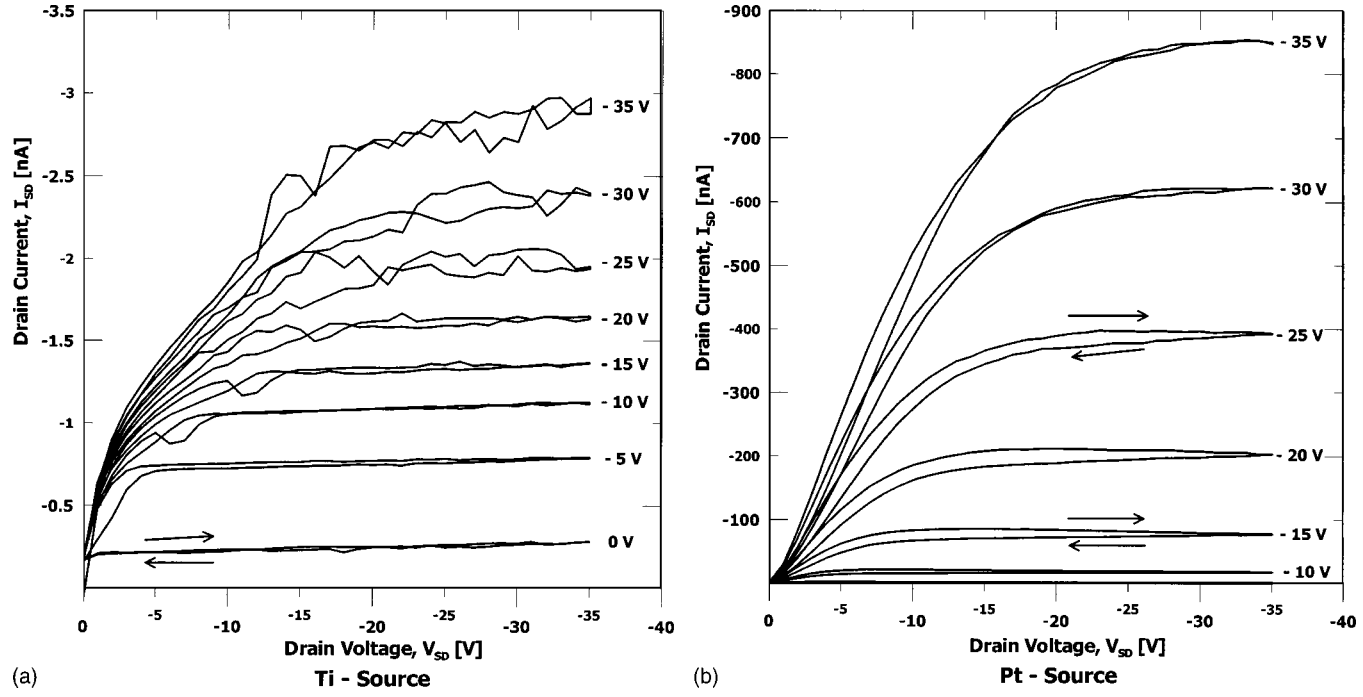

FIG. 2. Output characteristics of the OFET with asymmetric contacts. Channel length/width was 80 μm/2 mm. (a) Ti as source/Pt-plated Ti as drain. (b) Pt-plated Ti as source/Ti as drain. Double lines refer to ramping drain voltage up/down. Note the different drain current scales.

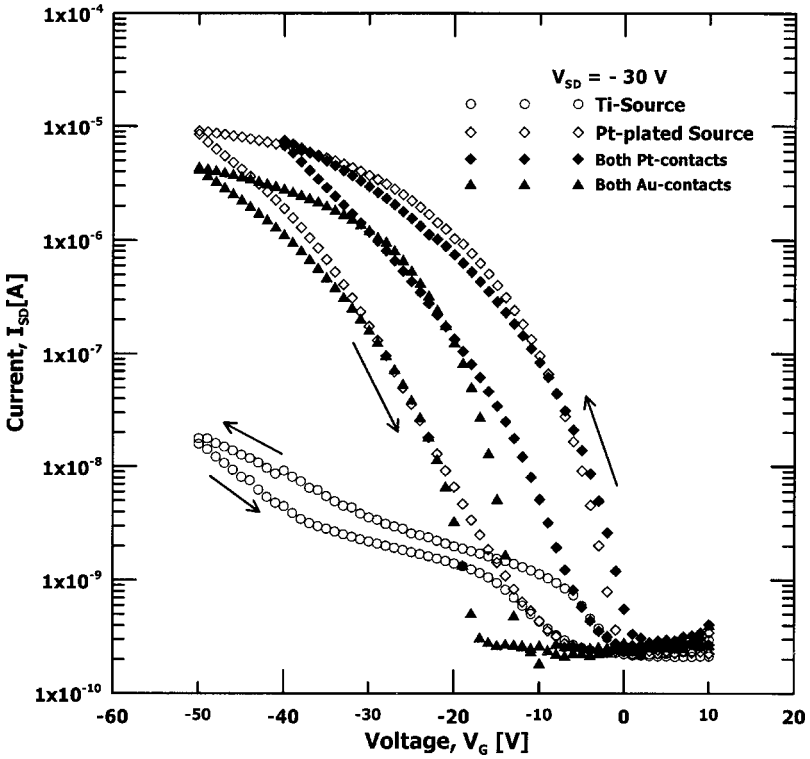

FIG. 3. Transfer characteristics of the OFET with asymmetric contacts in forward (◇) and reverse (○) bias. Also shown, transfer characteristics of different OFETs: both contacts made from Pt-plated Ti (◆) and both contacts completed by the evaporation of Au (▲). Channel length/width was 80 μm/2 mm for all OFETs, V_{SD} =−30 V.

bility is extracted from the slope in a plot of $\sqrt{I_D}$ against V_G at $V_D=V_G$, the result is $\mu=3.4\times10^{-2}$ cm^2/V s in forward bias; extracting a mobility in reverse bias is not sensible as saturation current does not scale quadratically with gate voltage. The forward bias mobility of pentacene found here is not particularly high compared to the best known pentacene mobilities. However, substrate was not heated during evaporation, channel length was rather long, which may result in moderate mobility because of numerous pentacene grain boundaries, and bottom contacts were used which generally lead to lower OFET mobilities.[5]

In forward bias [Fig. 2(b)], we also note some hysteresis between ramping drain voltage up/down. We believe this results from difficulties in the extraction of holes at the drain. Under atmosphere, Ti spontaneously forms a thin "native" oxide layer of TiO_2 on its surface. This oxide layer protects Ti from further oxidation, and is vital for its use as base metal in the acidic plating bath, as this otherwise would dissolve Ti. However, the oxide layer is insulating and will form a capacitance in series with the semiconductor channel. We believe the charging/discharging of this capacitance during ramping drain voltage up/down causes the hysteresis observed in the output characteristics.

Figure 3 shows the transfer characteristics of the OFET with Ti/Pt–Ti contacts both in forward and reverse bias, together with the transfer characteristic of the OFETs that had both *S* and *D* with plated Pt–Ti and evaporated Au. All the devices have bottom contacts structure. Again, the limitations of using unplated Ti as source are immediately obvious. Also, we find that for the device with both *S* and *D* Pt-plated, the transfer characteristic displays less hysteresis than for a device with Pt–Ti *S*/Ti *D*. This, we believe, results from the removal of the capacitive impedance that is present at unplated Ti contacts. The OFET with both contacts plated displays mobility $\mu=3.2\times10^{-2}$ cm^2/V s, that is virtually identical to the mobility found for the asymmetric OFET in forward bias. Inverse subthreshold slope is 4 V/dec and on/off ratio at least 10^5 (notice that the measurement of "off" current is limited by the 0.2 nA constant current offset of our Keithley 2400 Source Measure Unit). For comparison purposes, Fig. 3 also contains transfer characteristics of an OFET with both Au contacts completed by evaporation. The Au device has performed slightly worse than the Pt device.

In summary, we have shown that electroplating of platinum (work function $\Phi=5.65$ eV) onto a low work function base metal can significantly improve the quality of OFET contacts. Electroplating has a number of advantages over evaporation and sputtering in terms of simplicity and cost effective use of expensive metals. Should it be desired, asymmetric contacts can be prepared with ease, resulting in OFETs with strong bias. Also, we have shown that not only carrier injection at the source, but also carrier extraction at the drain may be a factor impacting on OFET performance.

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