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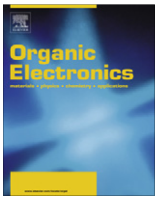

Bipolar charge transport in organic field-effect transistors: Enabling high mobilities and transport of photo-generated charge carriers by a molecular passivation layer

Andreas Opitz [a,b,*], Matthias Horlet [a], Marc Kiwull [a], Julia Wagner [a], Michael Kraus [a], Wolfgang Brütting [a]

[a] *Institute of Physics, University of Augsburg, Augsburg, Germany*
[b] *Institute of Physics, Humboldt University of Berlin, Berlin, Germany*

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ABSTRACT

High mobility bipolar charge carrier transport in organic field-effect transistors (OFETs) can be enabled by a molecular passivation layer and selective electrode materials. Using tetratetracontane as passivation layer bipolar transport was realised in the organic semiconductors copper-phthalocyanine, diindenoperylene, pentacene, TIPS-pentacene and sexithiophene and mobilities of up to 0.1 $cm^2/V\,s$ were achieved for both electrons and holes. Furthermore, the trap and injection behaviour was analysed leading to a more general understanding of the transport levels of the used molecular semiconductors and their limitations for electron and hole transport in OFETs. With this knowledge the transistor operation can be further improved by applying two different electrode materials and a light-emitting transistor was demonstrated.

Additionally, the effect of illumination on organic field-effect transistors was investigated for unipolar and bipolar devices. We find that the behaviour of photo-excited electrons and holes depends on the interface between the insulator and the semiconductor and the choice of contact materials. Whereas filling of electron traps by photo-generated charges and the related accumulation field are the reason for changes in charge carrier transport upon illumination without passivation layer, both types of charge carriers can be transported also in unipolar OFETs, if a passivation layer is present.

1. Introduction

Molecular or polymeric materials used as organic semiconductor in thin-film devices have traditionally been reported as either electron or hole transporting materials [1,2]. Most of the polymeric materials, like poly-phenylene-vinylenes or poly-thiophenes, and some classes of molecular materials, like acenes or phthalocyanines, are typical *p*-conducting materials, whereas fullerenes or fluorinated molecules are mainly *n*-conductive. By contrast, bipolar transport has been reported for high-purity single-crystals as measured by the time-of-flight (TOF) method [3]. In this technique electron–hole pairs are generated by light absorption close to an electrode and one of both carrier types, depending on the sign of the applied voltage, is transported through the whole crystal towards the counter electrode, where its arrival is monitored as transit time. The charge carriers in thin-film devices, however, are generated either by the field effect or by injection. Here the misalignment of the electrode work function to the respective transport levels can cause substantial injection barriers [4]. Furthermore, the transport in field-effect transistors is limited by trap states at the semiconductor/insulator interface. Especially the often used gate oxides,

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[*] Corresponding author at: Institute of Physics, Humboldt University of Berlin, Berlin, Germany.

E-mail addresses: Andreas.Opitz@hu-berlin.de (A. Opitz), Wolfgang.Bruetting@physik.uni-augsburg.de (W. Brütting).

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like silica or alumina, have electron traps at their surfaces in the form of hydroxyl groups [5]. By suppressing these interface traps and adjusting the injection barriers for both charge carrier types, injection and transport of electrons and holes are possible [5,6]. Thus bipolar transport is also observable in thin-film devices and hence not limited to single-crystals. Beside accumulation and injection the charge carriers in organic field-effect transistors (OFET) can be generated by photo excitation. As mentioned before for the TOF technique here both charge carrier types are generated inside the channel and can account for the transport.

In the following we will show that by applying an aliphatic interlayer bipolar transport in OFETs is possible with a variety of materials, including copper-phthalocyanine (CuPc), diindeno-perylene (DIP), pentacene (Pen), 6,13-bis(triiso-propylsilylethynyl)-pentacene (TIPS-Pen), and α-sexithiophene (6T), that have previously been described as *p*-type molecular semiconductors. Furthermore, we will discuss the influence of electrode materials for electron and hole injection, before considering *n*-type molecular semiconductors. From these observations and the comparison to the transport on bare oxides, limitations for electron and hole transport will be deduced. An improvement of ambipolar transport is achieved by additionally using different source and drain materials for simultaneous electron and hole injection. In the case of the molecular semiconductor DIP light emission from ambipolar OFETs was observed. Finally, the effect of illumination on charge carrier transport will be compared. Basic differences appear for unipolar transistors with and without passivation layer using DIP as active material which will be discussed.

2. Experimental

Organic field-effect transistors (OFET, for cross-sectional structure see Fig. 1a) were prepared on highly doped silicon wafers with 320 nm thermally grown oxide. Additionally a layer of the insulating long chain alkane tetratetracontane (TTC, $C_{44}H_{90}$, purchased from Sigma–Aldrich, used as received, chemical structure shown in Fig. 1d) was deposited by thermal evaporation [7] (thickness about 10 nm) to separate the charge carrier transport in the molecular semiconductor from the silicon oxide surface. The layers were smoothed by thermal annealing at 60 °C for 2 h as shown earlier [8]. Unfortunately TTC shows a good solubility in most organic solvents. So spin coating of an organic semiconductor layer like poly(3-hexylthiophene) or 6,13-bis(triisopropylsilylethynyl)-pentacene (TIPS-Pen) on top of the TTC film dissolves the TTC molecules and removes the passivation layer. Up to now, TTC can be used as passivation layer only for evaporated semiconductors.

The semiconducting materials were deposited with a film thickness of 25 nm as active layer on top of a TTC layer by thermal evaporation. The molecular semiconductors copper-phthalocyanine (CuPc), α-sexithiophene (6T), perfluorinated CuPc (F_{16}CuPc, all purchased from Sigma–Aldrich), diindenoperylene (DIP, from S. Hirschmann, University of Stuttgart), and Buckminster fullerene C_{60} (purchased from Creaphys) were purified by temperature gradient sublimation at least once; in contrast pentacene (Pen) and TIPS-Pen were used as received from Sigma–Aldrich. The molecular structures are displayed in Fig. 1b and c. Various electrode materials (aluminium, silver, gold, tetracyanoquinodimethane-tetrathiafulvalene – TTF-TCNQ) have been used to analyse transistors in top contact geometry. The metal layers had a thickness of 50 nm and the organic metal TTF-TCNQ a thickness of 150 nm. Furthermore FETs with two different electrode materials were prepared by a parallactic shadow mask displacement technique [9] (see Fig. 6a). Thereby the Al layer was evaporated at first and afterwards, with a slight lateral shift, the TTF-TCNQ layer [10]. The whole processing was carried out under high vacuum or under inert atmosphere. Electrical characterisation was also performed under high vacuum conditions. The measured transfer characteristics have been analysed by the transfer length method using various channel lengths between 50 and 150 μm [7,11].

The surface morphology of evaporated films was determined by scanning force microscopy (SFM) in non-contact mode. Strong differences are observed for the growth behaviour of the molecular semiconductors on top of the TTC passivation layer. Exemplarily the surface morphology is shown in Fig. 2 for a TTC film as well as for a CuPc film and a DIP film deposited on top of the TTC layer. TTC forms a well crystallized film with a monolayer thickness of about 6 nm, which is close to the length of the molecules [7]. While CuPc grows only on top of the TTC islands, the DIP grains are exceeding the individual TTC islands [8,10]. Additionally, preferred orientations of the CuPc grains can be seen. They are aligned perpendicular to each other. The growth of CuPc on TTC can be considered as some kind of “pseudo-epitaxial” growth [7].

3. High mobility ambipolar transport

Measured transfer characteristics of OFETs with CuPc, DIP, Pen, TIPS-Pen, and 6T as normally “*p*-type” molecular semiconductors are presented in Fig. 3. For all these semiconductors electron and hole transport, i.e. bipolar transport, is observed. Typical electrode materials for achieving bipolar transport are silver or gold for CuPc and DIP, silver or aluminium for Pen and TIPS-Pen as well as silver for 6T. If low-work function metals, like Ca or in some cases Al, are used, even unipolar *n*-channel transistors can be fabricated with CuPc and DIP, while the use of the organic metal TTF-TCNQ allows for achieving unipolar *p*-channel FETs. These results show that TTF-TCNQ must have a different interface behaviour than ordinary metals. Even if the reported work function of TTF-TCNQ [12] is comparable to the values of Au [6], TTF-TCNQ only allows for hole injection, whereas Au allows for both electron and hole injection. The reason for this behaviour might be related to energy level alignment of the here used top contacts together with diffusion of the evaporated metal atoms and associated damages of the organic material [7]. By contrast, only *n*-channel transistors could be achieved for the typical “*n*-type” materials C_{60} and F_{16}CuPc, even with TTF-TCNQ as electrode, as shown by transfer characteristics in Fig. 4. As summarised in Table 1 the determined mobilities for