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Scanning photocurrent microscopy of electrons and holes in the pigment semiconductor epindolidione

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ABSTRACT

Photocurrent microscopy is used to characterize the kinetics of electrons and holes in organic field-effect transistors (FETs) with the hydrogen-bonded pigment epindolidione as active layer. The method relies on electrons and holes, generated on local illumination, which are provided after exciton splitting, to probe charge trapping. In the dark, hole conduction is observed for negative gate voltage while no electron conduction is observed for positive gate voltage. However, under illumination, a fast displacement current with 60 µs onset time and 1 ms exponential decay occurs for positive gate voltage, which can be explained by exciton splitting underneath the semitransparent top contact followed by subsequent electron trapping and hole extraction. Afterward, trapped electrons hop via further trap states within the film to the insulator into interface traps (13 ms exponential decay) which induce a positive threshold voltage shift in the FET transfer curves for hole transport. Photocurrent microscopy confirms that the displacement current occurs only for illumination under and near the semitransparent source/drain contacts, which act here as metal-insulator-semiconductor (MIS) diodes. For negative gate voltage instead, the photocurrent comprises an enhanced hole current in the FET channel between the contacts. In the channel region, the detrapping of holes at the interface with the insulator (3 ms time constant) enhances the transistor current at low frequencies < 1 kHz, whereas the displacement current between the contacts and the gate is observed only at frequencies > 10 kHz. Thus, we show here that photocurrent microscopy allows to identify the kinetics of electrons and holes in traps close to the contacts and in the FET channel of pigment transistors.

1. Introduction

Hydrogen-bonded pigments have emerged in recent years as a new class of organic semiconductors [1,2]. One representative is the pigment epindolidione (Epi), which is typically used as a yellow colorant in the printing and coating industry. Utilized as a semiconductor, Epi shows a hole transport mobility up to 1 $cm^2 V^{-1}s^{-1}$, combined with outstanding chemical stability in the pH range 3–10 [3,4]. Polycrystalline Epi films consist of linear chains of H-bonded molecules that are π-π stacked in a close, brick-wall arrangement, favoring charge transport between the individual Epi chains [3,5]. These properties allow for multidisciplinary applications with Epi thin films, such as photoelectrodes for H_2O_2 production or the bioconjugation with functional proteins in an aqueous environment [6,7]. Field-effect transistors (FETs) with a semiconducting Epi layer show bipolar charge transport of electrons or holes if proper metal contacts for charge injection are employed [3]. In Epi FETs, electron transport with reduced mobility of 2×10^{-3} $cm^2 V^{-1} s^{-1}$ is observed in N_2 atmosphere, suggesting that electron traps hinder the conduction at ambient conditions even further. The formation of defects in organic films can furthermore occur from interface effects, polymorphism, or mechanical strain [8,9]. A full picture of trap states and trap dynamics in Epi thin films is crucial for an optimization of the various devices produced with this material. As charge carrier trap states are a limitation of many organic semiconductor devices, elaborating methods for the evaluation of majority and minority carriers is a primary motivation behind this work. Following common descriptions of organic semiconductors, the high-mobility holes are here named majority charge carriers, and the low-mobility electrons are named minority charge carriers [10].

Using photoresponse microscopy measurements, we image the kinetics of electron and hole trap filling in p-type Epi transistors at ambient conditions. A variation of the applied drain voltage V_{DS} allows for using the tested devices in two operating modes, as FETs with $V_{DS} < 0$ V, or as metal-insulator-semiconductor (MIS) diodes with

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$V_{DS} = 0$ V [11]. Also, the gate voltage V_{GS} controls the charge distribution in the different device layers. For negative V_{GS}, holes are injected from the source/drain contacts into the Epi layer. Here, ohmic contacts but also injection barriers are possible, affecting the device performance strongly [12]. For positive V_{GS}, electrons are blocked at the source/drain-Epi interface. This electron barrier can induce a high electric field $E > 10^5$ V/cm in the Epi below the contacts, sufficient for charge separation in organic semiconductors [13].

The photoresponse microscopy maps for these different operation modes differ profoundly, and they show two major contributions. First, operated as FETs with negative V_{GS}, i.e. in hole accumulation, the devices show a conduction enhancement in the FET channel region due to de-trapping of holes. This de-trapping mechanism has previously been used for imaging of trap densities in pentacene films [14,15]. In addition to this FET photoresponse, a MIS photoresponse of Epi is observed, spatially confined to the area below the top contacts. We argue that this response stems from electron and holes obtained by exciton dissociation in the high-field region between the contacts and the gate. Subsequently, the generated charges move toward the contact and the gate insulator, similar to a time-of-flight setting. Time and frequency resolved measurements reveal fast and slow components due to different trapping behavior of majority and minority charge carriers (holes and electrons) for negative and positive V_{GS}, respectively. With pentacene devices, however, no significant photocurrent was observed for positive V_{GS} [14]. This missing contribution for pentacene could be owed to the ultrafast singlet fission and generation of triplet excitons in pentacene preventing charge separation [16]. Thus, photocurrent microscopy allows to identify electron and hole traps under the contacts and within the transistor channel. The method introduced here can be applied to a range of semiconductor materials, which show photoresponse in thin film geometry, including Perovskites, 1D and 2D materials [17–30].

The investigated Epi transistors were fabricated by deposition and formation of different functional layers in a bottom-gate/top-contact device geometry. A schematic of the transistor structure with electrical connections for biasing and measuring the drain-source current I_{DS} and the photocurrent I_{photo} is shown in Fig. 1. Further descriptions of the used materials and methods are provided in the **Experimental section**.

2. Results and discussion

First, we discuss the photoresponse for global illumination of the Epindolidione devices in FET mode ($V_{DS} = -10$ V). The transfer curves in the dark and under illumination are shown in Fig. 2. A full set of transfer and output curves is shown in the Supplementary Information. Typical for p-type organic semiconductors, these transfer curves allow to define two distinct operating conditions. At positive gate voltages V_{GS}, no significant current was measured. At sufficiently negative gate voltages, a linear increase of $I^{1/2}$ indicates that a conductive hole channel formed. In the fabricated transistors, the work function difference between the Al gate and Au top contacts induced a negative threshold voltage V_{th}, calculated with a linear fit on $I_{DS}^{1/2}$ vs. V_{GS}.

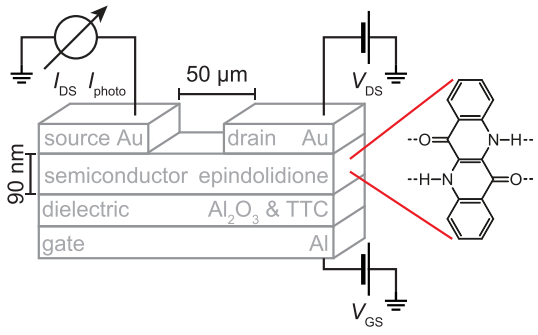

Fig. 1. Schematic of the transistor geometry with the pigment semiconductor epindolidione, building hydrogen-bonds between neighboring molecules.

The effect of global illumination on the transfer curves is investigated with the following experiment, shown in Fig. 2a: Starting in the dark with $V_{GS} = -15$ V at a chosen $I_{DS,0}$, the gate voltage was gradually increased to $V_{GS} = 5$ V (A), with a sweep rate of 1 V/1.13 s. Then, a blue laser with $\lambda = 488$ nm wavelength uniformly illuminated the transistor with 2 mW cm^{-2} for 2 s (B). Afterward, again in the dark, the gate voltage was gradually decreased to $V_{GS} = -15$ V (C), followed by a waiting time, here 140 s, until I_{DS} reached the starting value $I_{DS,0}$. The consecutive control experiment in dark showed only a slight increase of I_{DS}. The extracted transfer curves in Fig. 2b show a significant hysteresis, *i.e.* a transfer curve shift toward more positive V_{GS} due to illumination [31]. This bias stress is quantified by calculating the threshold voltage difference between the sweeps C and A, here $\Delta V_{th} = 2.1$ V for the illumination time $t = 2$ s. In contrast, only little bias stress, $\Delta V_{th} = 0.25$ V, was observed in the dark. The extracted voltage shifts ΔV_{th} for different illumination times (ms to s) are drawn in Fig. 2c and show a substantial increase for longer illumination. By comparing the dark value to ΔV_{th} under illumination, we could detect light-induced bias stress for illumination times as low as 2 ms, or 4 µJ cm^{-2}. Often, bias stress is induced by localized charges, *i.e.* filled trap states, at the semiconductor-dielectric interface. Trap filling can be quantified by the relation $\Delta Q = -c\ \Delta V_{th}$. Here, a positive ΔV_{th} is induced by the negative charge of trapped electrons [31]. In the dark, only little bias stress was observed because the high energy barrier between the work function of Au and the lowest unoccupied molecular orbital (LUMO) of Epi prohibits electron injection, so that electron traps cannot be filled from the contacts [3].

As a 30 nm thick Au layer shows 13% transmission at $\lambda = 488$ nm [32], the incoming light reached the Epi layer below the Au contacts, creating excitons. Thus, it is reasonable to assume that the trapped electrons, causing the bias stress upon illumination, originate from exciton splitting in the high field between the blocking top contact and the gate.

In the following, the kinetics of bias stress is further analyzed with time-resolved current measurements, recording the transient response of I_{DS} on global illumination. These measurements are shown in Fig. 3a) and **b)** for $V_{GS} = 5$ V and $V_{GS} = -15$ V, respectively. Here, the transistor was exposed to pulsed light with a pulse frequency $f = 48$ Hz, i.e. switching every 10.4 ms between full illumination and dark; gray areas mark the times during illumination. For light exposure at $V_{GS} = 5$ V, I_{DS} reached its maximum value of 3.5 nA within 60 µs and decreased slowly to a finite value above zero. Switching from light to dark, I_{DS} peaked equally fast at a minimum value of −1.6 nA and likewise decreased to a finite value above zero. For $V_{GS} = -15$ V, an average current of −2.78 µA was measured. Here, the current changed on the ms time scale from −2.74 µA in the dark to −2.82 µA during illumination. Both time-resolved current measurements follow a bi-exponential behavior, depicted by the red lines, with two decay time constants $\tau_1 = 1$ ms and $\tau_2 = 13$ ms for $V_{GS} = 5$ V, and $\tau_1 = 0.6$ ms and $\tau_2 = 3$ ms $V_{GS} = -15$ V. Such a bi-exponential behavior of a transient current implies that several effects contribute [33]. Assuming an uncharged Epi layer for $V_{GS} = 5$ V in the dark due to the blocking top contact, illumination created excitons, and the electric field between the top contacts and the gate could then separate these electron-hole pairs. The observed displacement current suggests that the electrons were driven against the electric field to the Epi-TTC interface, filling electron traps in bulk Epi or at the interface. The holes were extracted at the contacts.

Within this scenario, the fast component with rising time < 60 µs and decay constant $\tau_1 = 1$ ms represents the initial displacement current due to electrons and holes moving in the Epi layer and from electron trapping in bulk Epi, in close vicinity of where the excitons were split. After this initial process, a slower displacement current follows, namely due to electron hopping from bulk traps toward the Epi-TTC interface ($\tau_2 = 13$ ms). The decrease to a finite value above zero could originate from a leakage in the dielectric, or from an overall