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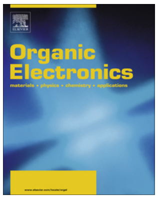

Separating the impact of oxygen and water on the long-term stability of n-channel perylene diimide thin-film transistors

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ABSTRACT

A detailed understanding for the mechanisms that control degradation of the electrical performance of organic thin-film transistors (TFTs) during exposure to various environments, such as oxygen and humidity, is still developing. This is particularly true for n-channel organic TFTs. Here we present an investigation of the long-term stability of n-channel TFTs based on the small-molecule organic semiconductor N,N′-bis(2,2,3,3,4,4,4-heptafluorobutyl-1,7-dicyano-perylene-(3,4:9,10)-tetracarboxylic diimide (PDI-FCN_2) during storage in dry nitrogen, dry air, wet nitrogen and ambient air. By monitoring the electrical characteristics of the TFTs over a period of six weeks, we are able to show that the degradation of the electrical parameters (charge-carrier mobility and the simultaneous shift of the threshold voltage) is caused by two distinct mechanisms with different time constants. Exposure to oxygen or nitrogen (in the absence of humidity) causes the carrier mobility to drop by a factor of two and the threshold voltage to shift towards more positive values within 20 days, possibly due to a slight rearrangement of the conjugated molecules within the semiconductor layer. Storing the TFTs in saturated water vapor or in ambient air causes the threshold voltage and the carrier mobility to change much more rapidly, within just one day. The observed degradation in ambient air can be explained by an electrochemical instability of the radical anion of the organic semiconductor.

The electrical performance of organic thin-film transistors (TFTs) has seen substantial improvements over the past few years. For example, the field-effect mobility of organic TFTs has been increased up to about 40 cm^2/Vs [1]. But a large carrier mobility is only one of the factors that are important for the commercial applicability of organic TFTs. The long-term stability of the carrier mobility (and that of the other electrical TFT parameters, including the on/off current ratio, the threshold voltage, and the subthreshold slope) is also a critical requirement. The mechanisms by which the carrier mobility of organic TFTs degrades during long-term storage in ambient air (or in other environments that contain oxygen and/or humidity) are still under debate, and only some aspects of this degradation are understood.

For example, if the organic molecules are susceptible to oxidation (as is the case with pentacene [2]), oxidation of the molecules may lead to the loss of π-conjugation, so that the oxidation products no longer participate in charge transport, or they may form charge traps, both of which will cause the carrier mobility to drop. But even if the conjugated molecules are stable against oxidation, the carrier mobility of organic TFTs can degrade during long-term exposure to oxygen and/or humidity, for example as a result of the intercalation of oxygen and/or water into the organic semiconductor layer or due to the oxygen- or water-induced formation of charge traps at the semiconductor/dielectric interface. Water was unambiguously identified to lead to a degradation of the carrier mobility of pentacene transistors, both in the case of polycrystalline thin films of pentacene [3,4] as well as in the case of pentacene single-crystals [5]. This water-induced mobility degradation was attributed to the generation of scattering sites by the intercalation of water either into the crystals [5] or into the grain boundaries of the polycrystalline films [3]. Furthermore, it was shown that water leads to an increase of the off-state drain current of pentacene TFTs, possibly by introducing mobile species into the semiconductor film [3,4]. Unlike the effects of water, for which there seems to be some consensus, as described above, the effects of oxygen on the electrical parameters of pentacene FETs are still controversially discussed in literature.

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Observations range from the oxygen-induced generation of trap states deep in the bandgap that degrade either the entire current–voltage characteristics [6] or only the subthreshold behavior [7] to an oxygen-induced increase of the on-state drain current [5] that was attributed to a change of the work function of the gold source/drain contacts of the TFTs [8]. Interestingly, the opposite effect, i.e., an oxygen-induced decrease of the on-state drain current along with a positive shift of the threshold voltage have also been reported for pentacene TFTs [9].

For p-channel TFTs based on semiconducting polymers, de Leeuw and co-workers have developed a theory to explain the often-observed shift of the threshold voltage during prolonged negative gate-bias stress by an electrolytic generation of protons from water at the semiconductor/dielectric interface [10].

For n-channel organic TFTs, significantly fewer studies have been conducted so far [11]. Aguirre et al. showed the degradation of electron transport due to the redox reaction between solvated oxygen in single-walled carbon nanotube FETs [12]. Hang et al. showed for polymer FETs based on poly{[N,N′-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5′-(2,2′-bisthiophene)} (P(NDI2OD-T2)) that both oxygen and water form traps in this semiconductor [13]. This observation is in agreement with previous reports by Di Pietro et al. [14] who found that the exposure of P(NDI2OD-T2) to oxygen leads to the formation of an oxygen/P(NDI2OD-T2) complex that acts as an electron trap with an energy level of 0.34 eV below the LUMO level, and that this trap state has a negative effect on the electron mobility [14]. Di Pietro et al. also found that in the presence of water (or water and oxygen), electron traps in the form of OH^- groups are created that cause a decrease of the carrier mobility and a positive shift of the threshold voltage [14,15].

Here we investigate the stability of the electrical parameters of n-channel TFTs based on the small-molecule semiconductor N,N′-bis(2,2,3,3,4,4,4-heptafluorobutyl-1,7-dicyano-perylene-(3,4:9,10)-tetracarboxylic diimide PDI-FCN_2, Fig. 1a) in four different environments: dry nitrogen, dry air, wet nitrogen and ambient (humid) air. Conjugated molecules of this type are known to be inert with respect to photo-oxidation [16], so in evaluating the degradation processes we will assume that the molecules themselves remain intact and that the observed degradation occurs only within the semiconductor film.

PDI-FCN_2 was selected for this study because of its superior combination of performance [17] and air stability [17] and was synthesized by previously reported methods [17]. TFTs were fabricated by vacuum deposition of a 30 nm thick layer of the organic semiconductor onto a doped silicon wafer covered with a 100 nm thick thermally grown SiO_2 gate dielectric passivated with a self-assembled monolayer (SAM) of octadecyltrichlorosilane (OTS). The OTS SAM was prepared from the vapor phase by placing the oxygen-plasma-activated substrate along with a small amount of OTS into a desiccator continuously purged with dry nitrogen, and heating the desiccator to a temperature of 150 °C in an oven for about 4 h. Compared with the preparation of OTS SAMs from solution, the vapor-phase method can be helpful in preventing the undesirable polymerization of OTS. The silicon wafer serves both as the substrate and as the gate electrode of the TFTs. During the vacuum deposition of the organic semiconductor, the substrate was held at a temperature of 120 °C in order to allow the molecules to form a well-ordered polycrystalline film [18]. Gold source and drain contacts were then deposited by vacuum evaporation through a shadow mask. A schematic cross-section of the devices is shown in Fig. 1b.

In order to ensure good process uniformity, all TFTs employed in this study were fabricated on the same substrate within the same deposition run. After deposition of the source/drain contacts onto the semiconductor layer, the substrate was divided into four pieces, and several TFTs on each piece were electrically characterized. Devices were then stored for 42 days in desiccators under four different environments: Dry nitrogen (relative humidity 5%), dry air (relative humidity 5%), wet nitrogen (relative humidity >97%) and ambient air (relative humidity ~50%). The desiccators were not intentionally protected from the weak yellow laboratory light. For the electrical measurements, which were performed in ambient air under yellow light, the samples were briefly removed from the desiccators. In order to make sure that the observed evolution of the carrier mobility and the threshold voltage was not affected by the operation of the transistors in the laboratory ambient [19], we monitored for the first five days also TFTs that had not been previously measured. It was found that the evolution of the carrier mobility of pristine TFTs and of TFTs that had been previously measured were identical. We can therefore safely assume that the observed degradation was not induced by the electric fields applied during the measurements, but stems from processes that occur in the absence of externally applied voltages. Also, the applied gate-source voltage was always limited to 30 V in order to minimize bias-induced shifts of the threshold voltage or changes in the hysteresis in the transfer characteristics.

Fig. 2 shows the transfer characteristics of the TFTs measured immediately after device fabrication and the transfer curves recorded after the TFTs had been stored for 42 days in dry nitrogen, dry air, wet nitrogen and ambient air (for the plots showing the square root of the drain current, please refer to the Supplementary data). During these 42 days, we periodically measured the transfer characteristics and extracted the saturation mobility and the threshold voltage (compare Fig. 3). As can be seen, the carrier mobility of all TFTs decreases and the threshold voltage

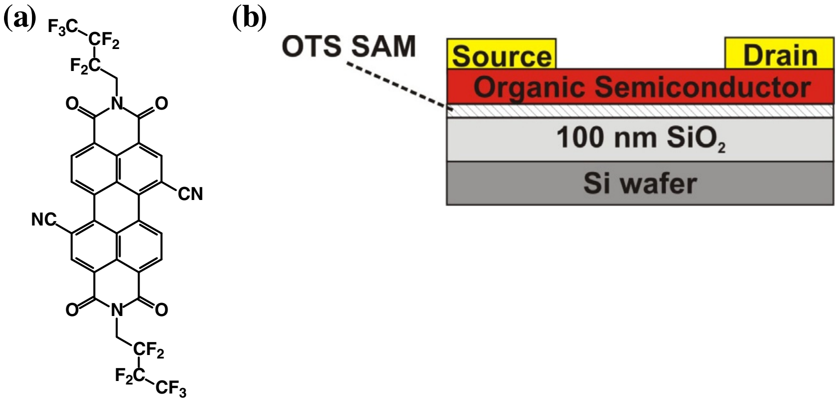

Fig. 1. (a) Chemical structure of the organic semiconductor PDI-FCN_2 (b) schematic cross-section of the thin-film transistors.