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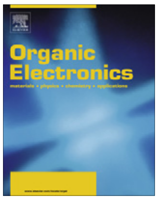

Vacuum-processed polyethylene as a dielectric for low operating voltage organic field effect transistors

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ABSTRACT

We report on the fabrication and performance of vacuum-processed organic field effect transistors utilizing evaporated low-density polyethylene (LD-PE) as a dielectric layer. With C_{60} as the organic semiconductor, we demonstrate low operating voltage transistors with field effect mobilities in excess of 4 cm^2/Vs. Devices with pentacene showed a mobility of 0.16 cm^2/Vs. Devices using tyrian Purple as semiconductor show low-voltage ambipolar operation with equal electron and hole mobilities of ~0.3 cm^2/Vs. These devices demonstrate low hysteresis and operational stability over at least several months. Grazing-angle infrared spectroscopy of evaporated thin films shows that the structure of the polyethylene is similar to solution-cast films. We report also on the morphological and dielectric properties of these films. Our experiments demonstrate that polyethylene is a stable dielectric supporting both hole and electron channels.

1. Introduction

Highly stable and trap-free dielectrics are crucial in the fabrication of high-performance organic field effect transistors (OFETs) [1]. Owing to its excellent insulating properties (band gap of ~8.8 eV) [2], and extremely low conductivity ($\sim 1 \times 10^{-18}\,\Omega^{-1}\,cm^{-1}$) [3], low toxicity, chemical inertness, stability, and ease of large-scale processing [4–6], polyethylene (PE) represents an interesting choice for the dielectric layer in organic devices. Polyethylene is the leading plastic material available today, with a global consumption of about 83 million metric tons in 2010 [7]. Deposition of polyethylene by vacuum processing technique was first reported by Madorsky in 1951 [8], and subsequently its film formation, molecular weight distribution and adherence properties on metal substrates briefly investigated [9–12]. Despite one report of successful polyethylene solution-processing for OFETs [13], to the best of our knowledge, vacuum-processed polyethylene for the fabrication of organic devices has never been explored. In this article, we show that vacuum processed polyethylene represents a viable dielectric layer for the fabrication of organic field effect transistors operating at voltages as low as 0.5 V.

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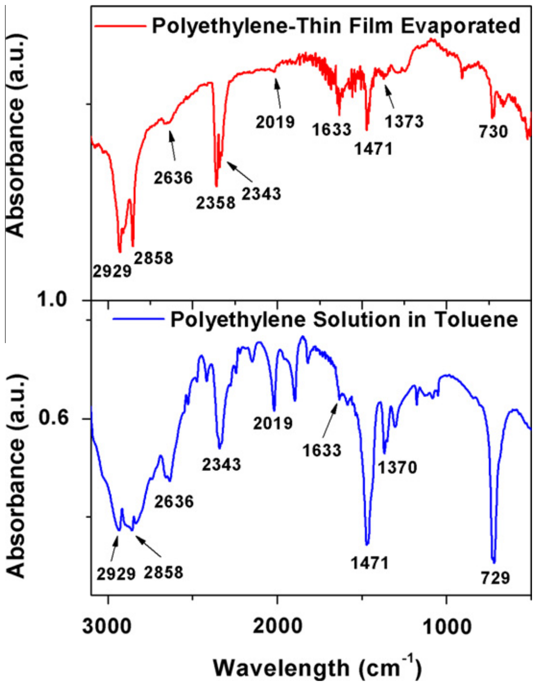

Fig. 1. Grazing-angle middle-infrared spectrum of vacuum-processed thin films of low-density polyethylene and solution processed low-density polyethylene in toluene. The vibration modes are assigned according to the literature.

2. Experimental

2.1. Preparation and/or purification of materials

Low-density polyethylene (LDPE) in pellet form was purchased from Sigma–Aldrich and used without further purification. Prior to the vacuum evaporation, LDPE pellets were melted in a quartz crucible and degassed in vacuum below the sublimation point for a period of 10–12 h. Fullerene C_{60} was purchased from MER USA and purified by thermal gradient sublimation. Pentacene was purchased from Aldrich and used as received. Tyrian purple (6,6′-dibromoindigo) was synthesized according to previously reported procedures [14] and purified by sublimation. Glass slides (1.5 × 1.5 cm) were cleaned with detergent and next in base piranha solution prior to aluminum gate electrode evaporation.

2.2. Device fabrication

A 1 mm wide, 100 nm thick aluminum gate was evaporated onto 1.5 × 1.5 cm glass slides and subsequently anodized by immersing in citric acid solution and passing a step voltage (up to a maximum of 40 V) at a constant current of 0.06 mA. Polyethylene, pentacene, C_{60}, and tyrian purple were evaporated at a pressure of 10^{-6} mbar in an organic materials evaporator; the evaporation rate was 0.2 Å/s for polyethylene and 1 Å/sec for pentacene, C_{60}, and tyrian purple. 100 nm-thick aluminum contacts were used in the case of C_{60}; gold source-drain contacts (100 nm) were used for pentacene and tyrian purple.

2.3. Materials and device characterization

FTIR measurements were performed using a Bruker Optics spectrometer (EQUINOX 55) on polyethylene samples (both sublimed and solution-processed) on aluminum-coated glass slides, the latter functioning as the reflection element for the grazing-angle FTIR measurement. AFM investigation was performed using a Digital Instruments Dimension 3100 microscope working in tapping mode. Steady-state current–voltage measurements were performed with an Agilent E5273A instrument in a glove box under nitrogen. Dielectric spectroscopy measurements were done with a Novocontrol impedance analyzer.

3. Results and discussion

Polyethylene was evaporated at a pressure of 10^{-6} Torr. Compared to polyaniline, which sublimes in high vacuum directly from the solid phase [15,16], low-density polyethylene first melts and then evaporates. We found it critical to degas the melt for a significant time before opening the shutter and starting the layer deposition. The crucial steps in producing high quality films of polyethylene are (1) extensively degassing the melt from volatile species and/or impurities before proceeding to the actual evaporation and (2) evaporating the material at a temperature not exceeding 350 °C. It was reported in [9] that at temperatures of 350 °C lower molecular weight components ($MW \leqslant 1000$) evaporate due to 'scissoring' of the polyethylene chains; at higher temperatures larger fragments are known to sputter from the source.

To verify the chemical structure of the evaporated films, grazing-angle Fourier transform infrared (FT-IR) spectra

Table 1
Observed peaks and literature-reported peaks for polyethylene.

Observed peaks (cm^{-1})	Vibration mode	Literature reported peaks (cm^{-1})	
		Gulmine et al. [25]	Mirzataheri et al. [26]
2929	CH_2 asymmetric stretching	2919	2918
2856	CH_2 symmetric stretching	2851	2851
1633	C=C stretching	Reported in [9]	
1472	Scissor (bending) vibration	1473	1464
1373	Wagging deformation	1377	1377
1352	Wagging deformation	1351	–
1288	Twisting deformation	1306	–
721, 730	Rocking vibration of $-(CH_2)_n-$	720, 731	719, 720

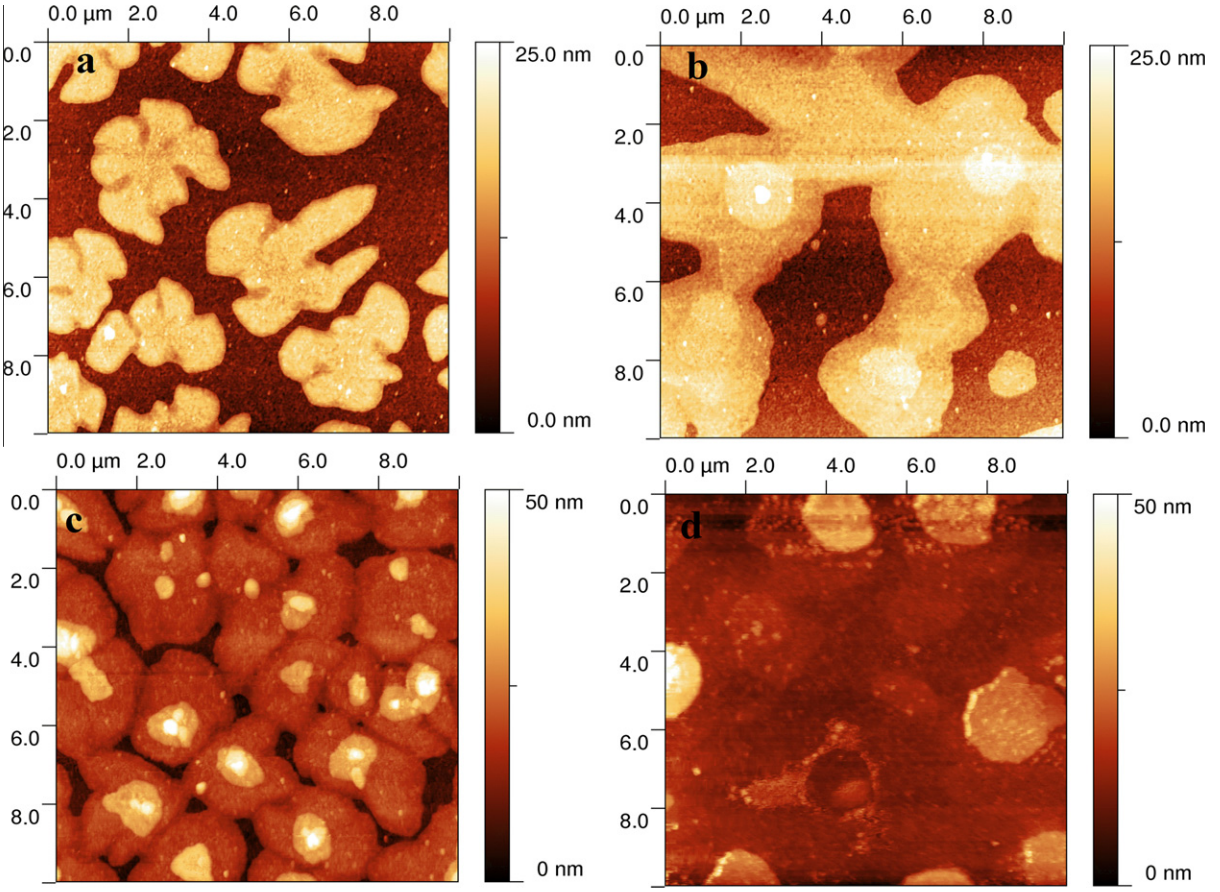

Fig. 2. Atomic force microscopy images of vacuum-processed polyethylene films on aluminum oxide gate dielectric showing island formation and coalescence of the film: (a)10 nm thick film; (b) 10 nm thick film annealed at 110 °C for 15 min; (c) 20 nm thick film; (d) 20 nm thick film annealed at 110 °C for 15 min. The latter melted film forms a closed layer.

were obtained and compared with literature values for polyethylene foils and with the spectra of polyethylene solution-processed from toluene. An FT-IR spectrum of vacuum-processed polyethylene thin films is shown in Fig. 1a and b. In good correlation to the peaks reported in literature for polyethylene [25,26], characteristic peaks have been recorded at 2929 and 2858 cm^{-1} due to the asymmetric and symmetric stretching vibrations of CH_2 groups. Beside these two peaks, the peak generated by the bending vibration was observed at 1472 cm^{-1}. Table 1 shows a correlation of peaks we found in the vacuum-processed films with those reported in the literature for LD-PE foils. Additionally, we found in both solution-cast and evaporated film a vibration at ~1633 cm^{-1}, corresponding to C═C bonds, indicated that there is some unsaturation in the chains. This has been reported in [9].

Atomic force micrographs of vacuum processed polyethylene films are presented in Fig. 2a–d and show that polyethylene condenses on the aluminum oxide surface as individual islands (Fig. 2a) that finally coalesce and grow with subsequent material deposition (Fig. 2c). The evaporation of a 10–15 nm thick polyethylene film results in the formation of islands with a typical size of 3–4 nm and a root-mean-square (rms) roughness measured along the top of each island of ~1 nm. The condensed polyethylene islands can be easily smeared out by heating the sample at a temperature above the melting point of

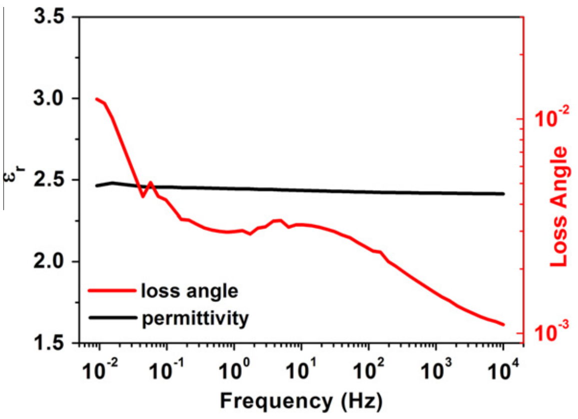

Fig. 3. Relative permittivity of a 250 nm-thick film of evaporated polyethylene. A constant capacitance and very low losses over a wide range of frequencies suggest that thin films of evaporated polyethylene can act as trap-free dielectric layers in organic field effect transistors.

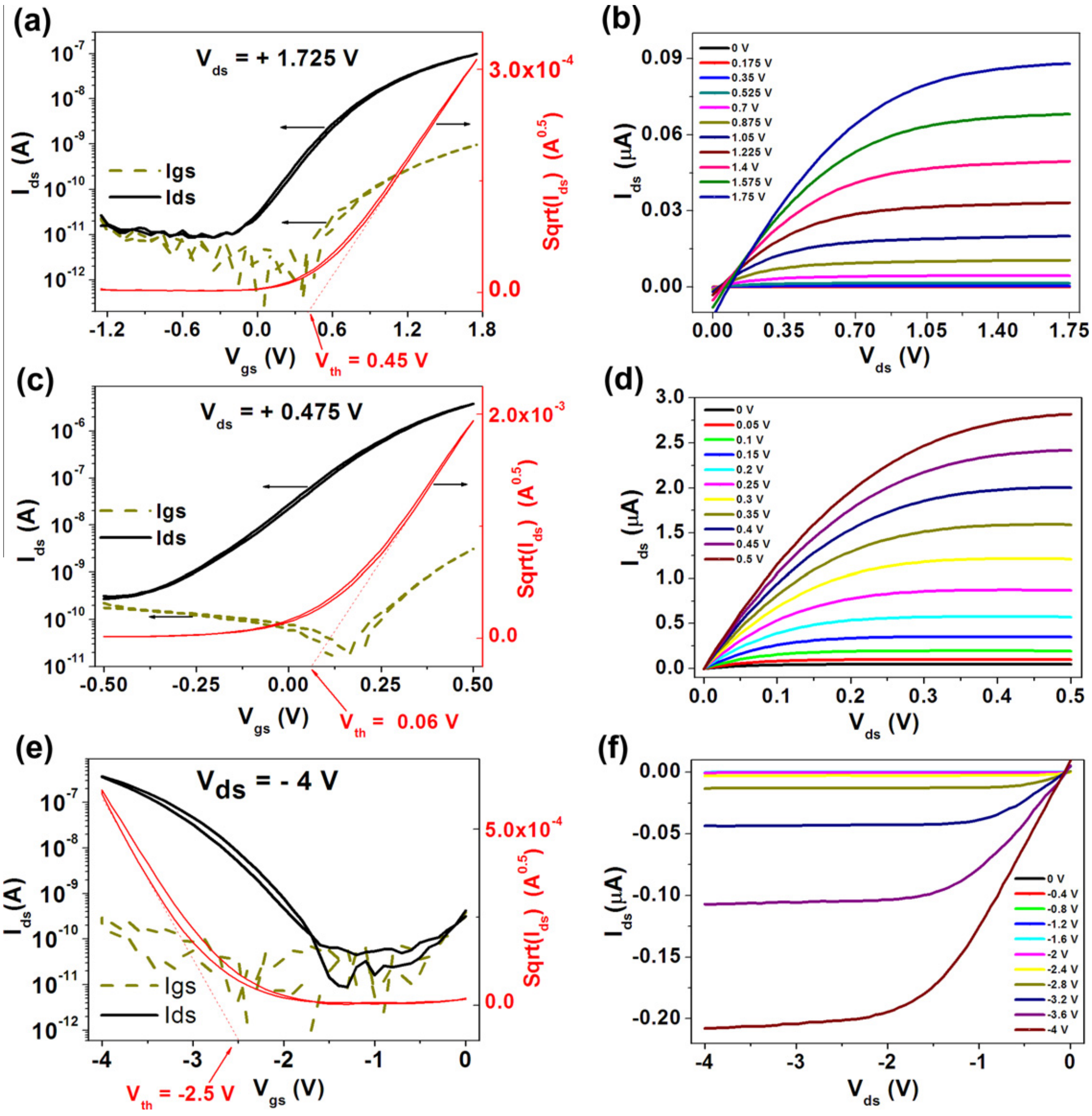

Fig. 4. Transfer and output characteristics of field effect transistors with polyethylene dielectric layers: (a and b) 250 nm vacuum processed polyethylene dielectric and C_{60} semiconductor. Channel design: L = 75 μm, W = 2 mm. Dielectric capacitance per area C_{0d} = 8.5 nF/cm^2, mobility μ_e = 0.55 cm^2/Vs; (c and d) 55 nm AlO_x and 20 nm vacuum-processed polyethylene dielectric and hot wall epitaxially-grown C_{60} semiconductor. Channel design: L = 35 μm, W = 7 mm. Dielectric capacitance per area C_{0d} = 60.4 nF/cm^2, mobility μ_e = 4.4 cm^2/Vs; (e and f) 8 nm AlO_x and 20 nm vacuum processed polyethylene dielectric and pentacene semiconductor. Channel design: L = 75 μm, W = 2 mm. Dielectric capacitance per area C_{0d} = 96 nF/cm^2, mobility μ_h = 0.16 cm^2/Vs.

polyethylene (~105 °C) for 30 min (Fig. 2b and d). Alternatively, the glass slides can be heated *in situ* during the evaporation process of the dielectric material to allow for a complete coverage and passivation of the aluminum oxide dielectric layer.

Relative permittivity as a function of probe frequency of a ~250 nm thick films of vacuum-processed polyethylene is presented in Fig. 3. The impedance spectrum shows that vacuum processed polyethylene has a constant capacitance and very low losses over a wide range of frequencies, suggesting that thin films of evaporated polyethylene can act as trap-free dielectric layers in organic field effect transistors. From the dielectric spectroscopy data, a dielectric constant of 2.4 is calculated from the high-frequency geometric capacitance regime, agreeing closely with reported values [17]. It has been proposed that a low dielectric constant results in occurrence of reduced energetic disorder at the dielectric/organic semiconductor interface, recommending polyethylene as a candidate for the development of high mobility organic field effect transistors, suggested before by Veres et al. and Hulea et al. [18,19].

Transfer and output characteristics of transistors with 250 nm thick evaporated polyethylene dielectric and C_{60} as active organic semiconductor are presented in Fig. 4a and b in a bottom-gate, top-contact OFET geometry. The transfer characteristic is hysteresis-free, a fact that was also reported previously for other dielectric materials like adenine, cytosine and thymine [20,21]. The respective

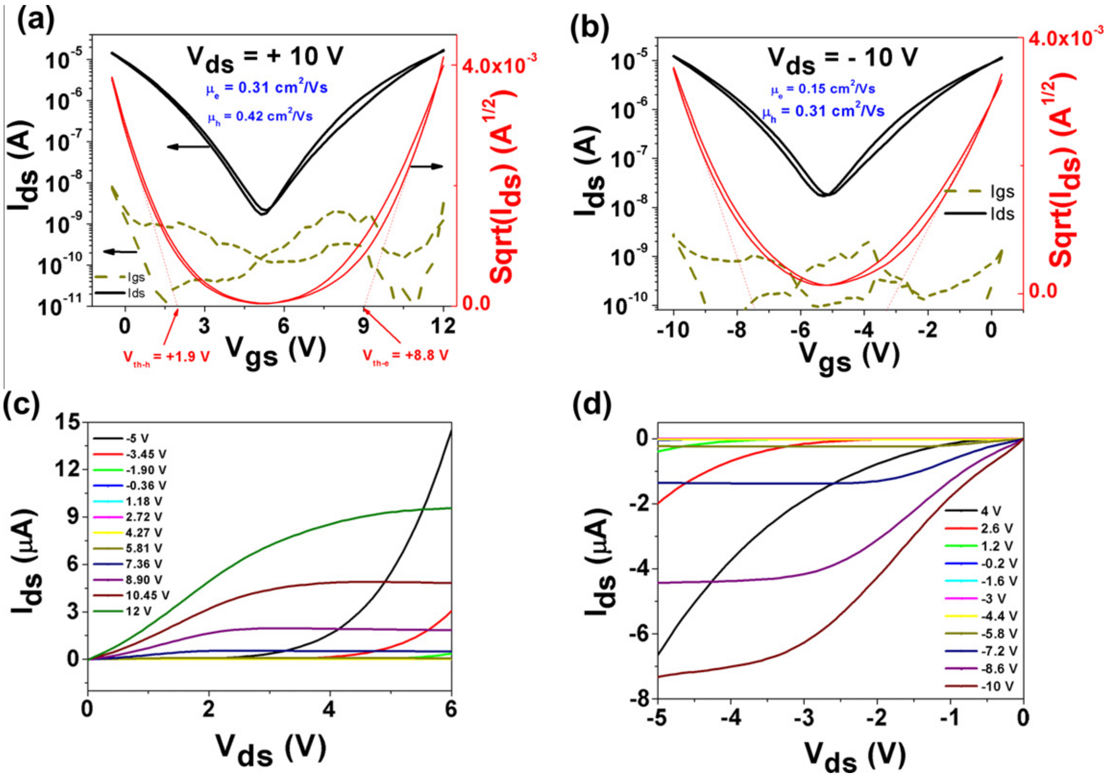

Fig. 5. (a and b) Transfer and (c and d) output characteristics of an tyrian purple based OFET on evaporated polyethylene-passivated aluminum oxide dielectric on glass substrate. Thicknesses: aluminum oxide 30 nm, polyethylene 15 nm, tyrian purple 50 nm, gold source and drain electrodes 100 nm. Channel dimensions: $L = 35$ μm, $W = 5$ mm. Dielectric capacitance per unit area, $C_{0d} = 90.3$ nF/cm^2. Field effect mobility: $\mu_h = \mu_e = 0.31$ cm^2/Vs.

OFET dielectric capacitance per unit area, C_{0d}, is 8.5 nF/cm^2 and the semiconductor mobility calculated in the saturation regime is 0.55 cm^2/Vs. An improved transistor performance with respect to operating voltage is obtained if polyethylene is used as a passivation layer for the electrochemically-grown aluminum oxide dielectric layer. As an example shown in Fig. 4c and d, a 20 nm-thick polyethylene layer was evaporated on ~55 nm-thick aluminum oxide, followed by C_{60}. The dielectric capacitance of the combined dielectric was 60.4 nF/cm^2 and the operating voltage of the OFET was ~0.5 V for a mobility of the semiconductor material as high as 4.4 cm^2/Vs. The origin of higher mobility in fullerene when a thin passivation layer of polyethylene is used as opposed to a thick layer is not yet clear.

The evaporated polyethylene dielectric also supports a hole transport channel. As an example shown in Fig. 4e and f, pentacene was thermally-evaporated on the combined AlO_x-polyethylene dielectric layer, with 8 nm of electrochemically-grown aluminum oxide passivated with 20 nm of polyethylene. Although not fully optimized, the operating voltage of this device was only 4 V and the semiconductor mobility ~0.16 cm^2/Vs, for a dielectric capacitance of 96 nF/cm^2. The electron and hole mobility values obtained for the OFETs with C_{60} and pentacene channels deposited on polyethylene dielectric scale favorably with the values reported in the literature for other dielectrics [16,20–23].

The fact that evaporated polyethylene dielectric layers afford both electron and hole channels, suggests that the material can be used for developing ambipolar organic field effect transistors. In our recent work, excellent results were obtained when evaporated polyethylene was used in combination with novel ambipolar organic semiconductors like indigo or tyrian purple [22,24]. Such an example is given in Fig. 5a–d, where tyrian purple is used as an ambipolar semiconductor and evaporated polyethylene is employed as a passivation layer for electrochemically-grown aluminum oxide dielectric. The channel used in the above case had a width, $W = 5$ mm and length, $L = 35$ μm. The reason for opting to fabricate devices with a wide channel configuration was to demonstrate that 15 nm of vacuum processed polyethylene successfully passivated the large area of aluminum oxide gate. The OFET shows a clear print of ambipolarity with both electron and hole channel formation and superlinear increase in the source-drain current at low gate voltages (Fig. 5). The transistor was measured with both positive as well as negative $V_{ds} = \pm 10$ V. The calculated field effect mobility for both positive and negative source-drain voltages is displayed in the insets of Fig. 5a and b. However, considering the electron mobility calculated in the regime of positive V_{ds} and the hole mobility calculated in the regime of the applied negative V_{ds}, the calculated electron and hole mobilities were both ~0.3 cm^2/Vs.

Further studies are in progress to investigate the effect of polyethylene on OFET long-term stability. The high chemical stability and inertness of polyethylene recommends its use in long-lifetime devices.

4. Conclusions

We demonstrate that vacuum-processed polyethylene represents an excellent dielectric layer for the development of high performance organic field effect transistors. Polyethylene has outstanding insulating properties, given by its high band gap of ~8.8 eV and its extremely low conductivity of $\sim 1 \times 10^{-18}$ S/cm. Its chemical stability is an additional attractive feature. Vacuum-evaporated layers of polyethylene can perform either as a stand-alone dielectric or in combination with aluminum oxide to obtain efficient charge transport in OFETs. The best C_{60} devices built in our lab showed operating voltages as low as 0.5 V and field effect mobilities of ~ 4.4 cm^2/Vs. In addition, the possibility that both electrons and holes can be transported at the interface polyethylene-organic semiconductor, as demonstrated by tyrian purple, recommends vacuum-processed polyethylene as a suitable dielectric for organic integrated circuits based on ambipolar OFETs.

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