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Effects of gate dielectric surface modification on phototransistors with polymer-blended benzothieno[2,3-*b*]benzothiophene semiconductor thin films

Darko Ljubic [a, b, 1], Victoria Jarvis [c], Chad S. Smithson [b], Nan-Xing Hu [b], Yiliang Wu [a, *], Shiping Zhu [a, **]

[a] *Department of Chemical Engineering, McMaster University, Hamilton, Ontario, L8S 4L7, Canada*
[b] *Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario, L5K 2L1, Canada*
[c] *Department of Chemistry and Chemical Biology, MAX Diffraction Facility, McMaster University, Hamilton, Ontario, L8S 4L8, Canada*

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ABSTRACT

In the present work, we investigated effects of the dielectric/semiconductor interface modification on the photoelectrical properties of phototransistors comprising a UV responsive semiconductor blend 2,7-dipentyl-[1]benzothieno[2,3-b][1]benzothiophene (C5-BTBT) and a linear unsaturated polyester (L-upe). Using various self-assembly monolayers with different end-groups at the dielectric/semiconductor interface we modulated the drain photocurrent and response times under the UV light illumination of phototransistors. Treatment of the SiO_2 dielectric surface with organosilanes led to the variation of the max mobility in the dark 0.10–0.18 $cm^2\ V^{-1}\ s^{-1}$ and under UV light 0.08–0.50 $cm^2\ V^{-1}\ s^{-1}$. Interestingly, detailed crystal structure analysis using 2D X-ray diffraction and photoelectrical characterization revealed that mobility in the dark predominantly depends on the alignment of C5-BTBT crystallites at the interface. Under UV light, the mobility increased with the electron withdrawing/donating nature of the SAM end-functional group. Additionally, chemical modification of the SiO_2 dielectric surface increased photocurrent relaxation/decay times upon UV light removal while retaining fast response times when exposed to UV light, which enhanced memory properties of fabricated phototransistors (fast UV response = writing and long relaxation = long data storage).

1. Introduction

The organic thin film transistor (OTFT) is an important building block of modern consumer electronics. Dynamic development of OTFTs over the past two and a half decades is justified by a variety of organic materials and their tunable properties for the fabrication of large-area electronics via printing, solution deposition, and melt processing [1]. OTFTs are successfully applied as backplanes for OLED displays, flexible e-paper, sensors, re-writable memory devices and radio frequency identification tags [2–4]. Furthermore, OTFTs are a great platform for phototransistors (PTs) that utilize the unique structure of field-effect transistors (FETs), thus, broadening their functionalities [5] [6].

When quantifying the performance of OTFTs, field-effect charge carrier mobility (μ_{FE}) is one of the most important properties and it has been constantly improved through molecular design and device engineering [7,8]. The mobility for small molecule based OTFTs reported to date is as high as 17.2 $cm^2\ V^{-1}\ s^{-1}$ for vacuum deposited tridecyl substituted [1]benzothieno[3,2-b][1]benzothiophene (asymmetric, C_{13}-BTBT) [9], and 43 $cm^2\ V^{-1}\ s^{-1}$ [10] for solution processed OTFTs based on C_8-BTBT. Recently Kim et al. [11] reported a thienoisoindigo-napthalene polymer based OTFT with an ultra-high mobility of 14.4 $cm^2\ V^{-1}\ s^{-1}$ utilizing a high-k polymer dielectric. FETs based on a-Si:H semiconductor have a mobility of ~1 $cm^2\ V^{-1}\ s^{-1}$, thus, OTFTs can largely exceed the performance of the Si-based FETs [12]. Constant improvements in performance and design of OTFT and PTs are critical to reaching higher-mobility, increased photosensitivity, and better environmental/operation stability [13–15].

Many research groups have reported different approaches for

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* Corresponding author.
** Corresponding author.
E-mail addresses: yiliang.wu@te.com (Y. Wu), shipingzhu@mcmaster.ca (S. Zhu).
[1] Visiting student at Xerox Research Center of Canada at Mississauga, Canada.

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mobility enhancement via i) semiconductor molecular design [16] and use of additives [17], or ii) control of molecular ordering in a crystal lattice and thin film morphology by altering processing conditions [18,19]. Furthermore, interface engineering using organosilanes, photochromic molecules, polymeric buffer layers and metal oxides is sought as an effective way to improve mobility while avoiding lengthy optimizations of fabrication conditions and complex chemical synthetic routes [20–23]. Active channel/dielectric interface is one of the most important interfaces in OTFTs that determines mobility. This is particularly true since OTFTs operate in accumulation mode, i.e. injected charge carriers are accumulated at the dielectric/channel interface when a bias voltage is applied, forming a conductive channel. Molecular ordering of the first few layers of semiconductor, at the active channel interface, determines overall mobility in the channel. It is demonstrated that mobility has a strong dependence on the presence of a self-assembled monolayer (SAM) and resulting surface energy of the dielectric [24,25]. The surface energy of the dielectric layer controls semiconductor crystal growth. It can be easily tuned by the SAM with different end-groups that can enhance molecular ordering at the interface and, thus, increase the mobility [26,27]. Additionally, the density of accumulated charge carriers at the interface has been demonstrated to be controlled by dipole moments of the end functional groups present in the SAM, which, in turn, improved OTFTs performance [28]. Dipole moments of the end functional groups in the SAM can also enhance mobility via built-in electric field affecting the threshold and the turn-on voltage of the OTFT [29].

The most studied effect of SAM on mobility and overall performance of OTFTs was reported for pentacene and P3HT based OTFTs in the dark [30]. To the best of our knowledge, little or no effort was made to investigate the effect of dielectric surface modification using organosilanes on the performance of solution processed PTs. There is a lack of knowledge about the influence of the dielectric surface treatment on charge carrier generation/separation, drain photocurrent, subthreshold characteristics, field-effect mobility, and response times of PTs under the light illumination. This is very important for the design, development, and operation optimization of PTs used as sensors and optically writable memory devices.

Herein, we report on the effects of the dielectric surface treatment with eight different SAMs on the photoelectrical characteristics of field-effect hole mobility and PT performance under UV light ($\lambda = 365$ nm and 3 mW cm^{-2}) and in the dark. The semiconductor system was a previously reported blend of linear unsaturated polyester (L-upe) and 2,7-dipentylbenzo[*b*]benzo[4,5]thieno[2,3]thiophene semiconductor (C5-BTBT) (Fig. 1a) [31]. We employed a variety of organosilanes with different end-groups to form SAM covalently bonded to the SiO_2 dielectric surface via a silanization reaction (Fig. 1b). Additionally, PTs with a bare SiO_2 dielectric (referred as OH groups) were fabricated and characterized as well. Based on findings in the work reported previously [31], that electron withdrawing (EW)/electron donating (ED) functional groups present in the channel significantly affect photoelectrical characteristics of UV responsive PTs, we purposely selected organosilanes with functional groups having strong EW/ED properties. Moreover, we compared the performance of those PTs to that of devices having a bare SiO_2 or an electroneutral SAM.

Detailed analyses of photoelectrical properties of L-upe + C5-BTBT PTs (top-contact-bottom-gate structure, Fig. 1c) revealed that organosilane treatment of the SiO_2 dielectric surface significantly affected mobility under UV light and drain photocurrent relaxation times when UV light was removed. Mobility under UV light in the L-upe + C5-BTBT PTs was strongly correlated to the molecular electronic properties of the SAMs. The stronger the electron withdrawing group, the higher the mobility under UV light. Besides, a small variation of mobility in the dark in all PTs was attributed to the alignment of C5-BTBT crystallites normal to the substrate governed by the interface nature due to surface treatment, as confirmed by 2D X-ray analysis. Our approach enabled an effective way to control charge carrier mobility and overall performance of the dielectric/small molecule semiconductor blend-based PTs via simple chemical modification of the dielectric surface for potential memory and sensors applications. This approach offers not only insights into charge transport in PTs but directions for the better device design and its operation optimization/enhancement while utilizing already established light responsive semiconductive systems.

2. Experimental

2.1. Materials

Surface modifying agents (organosilanes): hexamethyldisilazane (CH_3), trichloro(phenethyl)silane (R′-Ph), (3-Chloropropyl)trimethoxysilane (R″-Cl), (3-aminopropyl)trimethoxysilane (R″-NH_2), (3-mercaptopropyl)trimethoxysilane (R″-SH), trichloro(phenyl)silane (Ph), and 4-(chloromethyl)phenyltrichlorosilane (Ph-CH_2-Cl) were purchased from Sigma Aldrich (Canada), except for 2-(4-chlorosulfonylphenyl)ethyltrichlorosilane (R′-Ph-SO_2Cl), which was purchased from Gelest (Morisville, PA, US). Acetone, chloroform, and isopropanol were purchased from Caledon (Canada) while anhydrous toluene and 1,1,2,2-tetrachloroethane (TCE) were obtained from Sigma Aldrich (Canada). All organosilanes and solvents were used as received. Analytical grade small molecule semiconductor 2,7-dipentylbenzo[*b*]benzo[4,5]thieno[2,3]thiophene (C5-BTBT) was synthesized following the reported procedures [32,33]. Linear unsaturated polyester (L-upe, MW = 50000), comprised of propoxylated bisphenol A and fumaric acid monomer units, was kindly supplied by the Xerox Research Center of Canada. Chemical structures of the active channel materials and organosilanes are displayed in Fig. 1a. Highly n-doped silicon wafers (Ø4 inch) with 200-nm thermally grown SiO_2 as a dielectric layer were purchased from Silicon Quest International (San Jose, CA, USA).

2.2. Preparation of L-upe + C5-BTBT blend

The L-upe + C5-BTBT blend (1:1) was prepared according to our previously reported procedure [31] summarized in Supp. Info (Section 1.1). We purposely used a 1:1 blend ratio since our previously studies showed that this ratio gave the best quality thin films formed by spin-coating onto HMDS modified Si wafers [33].

2.3. Modification of SiO_2 dielectric surface and phototransistors fabrication

Substrates (1 × 1 inch) were thoroughly cleaned in cold acetone and isopropanol, followed by a 5 min sonication in a sonication bath, successively in hot acetone, isopropanol then chloroform. The final cleaning step was treatment with plasma/UV for 2 min in plasma cleaner PDC-32G (Harrick Plasma, USA). Thereafter, the substrates were soaked in DI water for 10 min to saturate active sites on the surface of SiO_2, forming hydroxyl end groups. Air dried substrates (two for each type of organosilanes) were immersed in a freshly prepared organosilane solution in toluene (0.12 mol L^{-1}). Silanization reaction was optimized to carry out for 30 min at 60 °C. Upon completion, the substrates were rinsed with fresh toluene, sonicated (sonication bath) also in fresh toluene for 2 min to remove any excessive layers of organosilane on the surface of SiO_2, rinsed again with toluene and air dried. The result was a SAM covalently bonded to the substrate(s) via strong Si_s—O—Si bonds

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