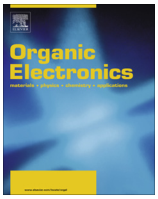
Organic Electronics 21 (2015) 149–154

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Interface engineering for improving optical switching in a diarylethene-channel transistor

Ryoma Hayakawa[a], Matthieu Petit[b], Kenji Higashiguchi[c,d], Kenji Matsuda[c,*], Toyohiro Chikyow[a], Yutaka Wakayama[a,*]

[a] International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan
[b] Aix Marseille University, CNRS, CINaM-UMR 7325, F-13288 Marseille, France
[c] Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
[d] PRESTO, Japan Science and Technology Agency, Kawaguchi 332-0012, Japan

ARTICLE INFO

Article history:
Received 9 December 2014
Received in revised form 18 February 2015
Accepted 7 March 2015
Available online 9 March 2015

Keywords:
Interface engineering
Optical switching
Photochromic channel layer
Thin film transistor

ABSTRACT

Photochromic diarylethene (DAE) molecules were employed as the channel layer of a field-effect transistor, where the drain current was effectively modulated by the reversible phase transition between a semiconductor (closed-ring) and an insulator (open-ring) under ultraviolet or visible light irradiation. Our goal was the further improvement of optical switching properties by interface engineering. First, we reduced the hole injection barrier by introducing an α-sexithiophene (6T) thin film at the interface between the source–drain electrodes and the DAE channel layer. As a result, the threshold voltage of the DAE-FETs was greatly reduced from −64 to −4 V. Second, we improved the optical switching performance by the surface treatment of a SiO_2 gate insulator with poly(methyl methacrylate) (PMMA). The drain current was unchanged even after 10 cycles of optical switching in contrast to the rapid degradation found with untreated DAE transistors. The combination of these improvements and interdigitated source–drain electrodes eventually resulted in a light irradiation driven on/off ratio of over 10^3. Significantly, the light-induced on/off ratio was comparable to that driven by an electrical field, which satisfies the requirement for industrial optical applications. Our findings will provide useful ways of realizing high-performance optical switching transistors.

1. Introduction

Organic field-effect transistors (OFETs) are key elements for developing printable and flexible electronic circuits [1–4]. In the last decade, great progress has been made as regards their performance. A carrier mobility of 0.1–16 cm^2 V^{-1} s^{-1} has been achieved even in solution processed OFETs [5–8]. Recently, the development of optical switching OFETs with photochromic molecules, including diarylethene (DAE), azobenzene and spiropyran (SP), has attracted considerable attention with a view to providing a new direction for organic electronics [9–17]. In most cases, these photochromic molecules are doped as “photoresponsive additive parts”, but are not used directly as “transistor channels”. This is because the employed molecules are basically nonconductive. Photochromic molecules or their self-assembled monolayers (SAMs) are introduced at the interface between organic semiconductors and gate insulator layers or doped into polymeric semiconductors to change the carrier transport through host organic semiconductors. In these devices, the drain currents through organic semiconductors have been reversibly controlled by light irradiation depending on photochromic reactions. For example, Zhang et al. introduced spiropyran (SP) SAMs at the interface between a pentacene transistor channel and a SiO_2 gate insulating layer [9]. Crivillers et al. inserted an azobenzene-SAM at the interface between source–drain (S–D) electrodes and *N*,*N*′-1H,1H-perfluorobutyl dicyanoperylenecarboxydiimide (PDIF-CN_2) to modulate the carrier injection barrier with light irradiation [10]. On the other hand, Orgiu et al. used a mixed layer consisting of diarylethene (DAE) molecules and a poly(3-hexylthiophene) (P3HT) semiconductor as a transistor channel, where the photochromic molecules worked as optically controllable dopants [14]. Although various kinds of device structures with photochromic molecules have been proposed as described here, the light-induced current modulations were relatively small (less than 500%). This is because the channel and photochromic layers are separated, and thus the photoisomerizations induce only slight

---

[*] Corresponding authors.

E-mail addresses: kmatsuda@sbchem.kyoto-u.ac.jp (K. Matsuda), WAKAYAMA.Yutaka@nims.go.jp (Y. Wakayama).

http://dx.doi.org/10.1016/j.orgel.2015.03.011
1566-1199/

fluctuations in the carrier transport, which makes it difficult to manipulate the transistor properties effectively.

Another approach for overcoming the small modulations in the drain currents, which has rarely been attempted, is the direct use of photochromic molecules as transistor channels, that is, the photochromic molecule should be compatible with the organic semiconductor [18,19]. Arlt et al. demonstrated OFETs based on *N*,*N*′-diphenyl-*N*,*N*′-bis[4-(phenylazo)phenyl]-4,4′-diaminobiphenyl (AZOPD) thin films [18]. Although the AZOPD thin films worked as p- or n-type transistor channels, the on/off ratio obtained by light irradiation was as low as 250%. Karimi-Alavijehe et al. employed π-conjugated stilbene oligomers for the transistor channels [19]. The OFET achieved an extremely high carrier mobility of 0.1 $cm^2\,V^{-1}\,s^{-1}$ and a high light-induced on/off ratio of 10 (10^3%) by making use of the *cis–trans* photoisomerization of the semiconducting oligomers. However, *cis–trans* photoisomerization is strongly affected by the operating temperature. The modulated drain current rapidly returned to its original value about 30 s after the incident light was turned off even at room temperature.

Among these various efforts, we have proposed utilizing DAE thin films themselves as the channel layers in OFETs (Fig. 1(a)) to realize both a large light-induced modulation in the drain current and a long retention time with a varied drain current [20]. For this purpose, we synthesized a diarylethene molecule derivative, 1,2-bis(2-methyl-5-(4-biphenyl)-3-thienyl)hexafluorocyclopentene, to allow us to manage the transistor properties by alternating ultraviolet (UV) and visible (Vis) light irradiation. The essential parts of this molecule are the biphenyl rings attached on either side of the main part. The molecule can induce a large change in a π-conjugated system with accompanying photoisomerization between open-ring and closed-ring isomers, leading to considerable variation in the conductivity. In previous work, we proved that DAE films with closed-ring isomers work as p-type transistor channels. The transistor channel was then completely off when the DAE molecules changed into open-ring isomers. Namely, we successfully induced a phase transition from semiconductor (closed-ring isomer) to insulator (open-ring isomer) by light irradiation. The on/off ratio of the drain current caused by light irradiation was 10^2 (10^4%). Furthermore, the modulated drain current was quite stable and maintained even after a week in dark conditions. On the other hand, our proposed OFETs have some problems. The transistor property was poor; the threshold voltage was as high as −64 V and the carrier mobility was restricted to the 10^{-6}–10^{-5} $cm^2\,V^{-1}\,s^{-1}$ range. Another problem is that the modulated drain current degraded rapidly with repeated optical switching.

In this paper, we describe how we improved the optical switching performance in DAE transistors by employing interface engineering. The introduction of an α-sexithiophene (6T) thin film between S–D electrodes and a DAE channel contributed to a reduction in the injection barrier for the hole carriers, and the resulting decrease in the threshold voltage from −64 to −4 V. The surface treatment of a SiO_2 gate insulator with poly(methyl methacrylate) (PMMA) prevented degradation in the optical switching. The drain current remained almost constant even after 10 cycles of repeated optical switching. Moreover, interdigitated S–D electrodes effectively increased the on-current to improve the optical on/off ratio to over 10^3 (10^5%).

2. Experimental

Fig. 1(a) shows the configuration of a top-contact and bottom-gate DAE transistor. Fig. 1(b) and (c) shows the molecular structures of 6T and DAE, respectively. A DAE derivative, 1,2-bis(2-methyl-5-(4-biphenyl)-3-thienyl)hexafluorocyclopentene, was synthesized to change the transistor properties with alternating UV and Vis light irradiation. A highly doped p^+-Si (001) wafer with a 200-nm-thick SiO_2 layer was used as a substrate. The Si wafer and the oxide layer acted as a gate electrode and a gate insulator, respectively.

First, 1 wt.% of PMMA dissolved in toluene was spin-coated on a SiO_2 surface (6000 rpm for 1 min at room temperature), followed by thermal annealing at 120 °C for 1 h to evaporate any residual solvent. The surface roughness was comparable to that of the bare SiO_2 surface (Fig. S1(a) and (b) in Supporting Information). The PMMA layer thickness was estimated to be 10 nm by X-ray reflection measurement (Bruker, D8 Discover). Subsequently, 25-nm-thick DAE films were grown on the PMMA-covered SiO_2 substrate through a shadow mask in a vacuum deposition system. The base pressure was below 5×10^{-7} Pa. The substrate temperature was optimized at 40 °C (Fig. S2(a) in Supporting Information). X-ray diffraction measurement showed that the DAE fimls thus prepared had amorphous structure (Fig. S2(b) in Supporting Information). Then, 6T and Au thin films were sequentially deposited through a common shadow mask onto the DAE film. The patterns of Au and 6T layers were aligned with an accuracy of 20 μm. The 6T film thickness was varied in the 1.5–6 nm range. The Au film thickness was fixed at 50 nm. Two different kinds of S–D electrode patterns were used, namely parallel and interdigitated. The channel length (L) and width (W) were respectively 50 and 400 μm for the parallel electrode, and 100 and 51,000 μm for the interdigitated electrode. The W/L ratio for the interdigitated electrode was about 60 times larger than that for the parallel electrode.

To determine the energy-level diagram of the Au/6T/DAE multiple structure, the HOMO levels of the 6T and DAE layers and the work function of Au were estimated by employing photoelectron spectroscopy in air (Rikken Keiki, AC-3) [21]. The details are described in the Supporting Information.

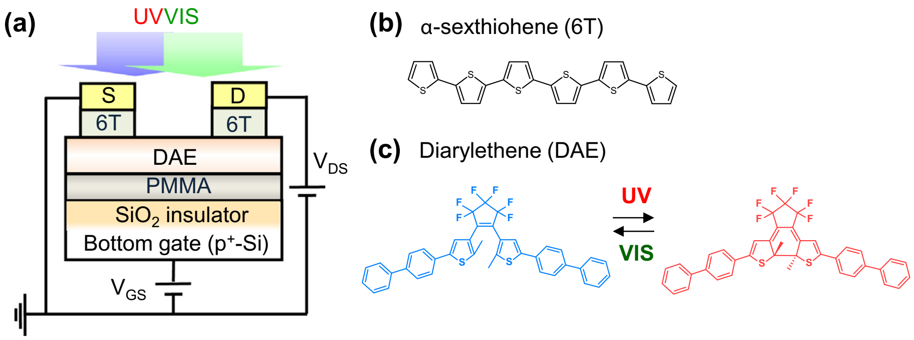


Fig. 1. (a) A schematic illustration of a top-contact and bottom-gate-type DAE transistor formed on a PMMA-coated SiO_2 surface, where a DAE thin film works as transistor channel. A 6T layer is introduced at the interface between the S–D electrodes and DAE films. (b) Molecular structure of α-sexithiophene. (c) Photoisomerization reaction between open-ring and closed-ring isomers in DAE molecules.