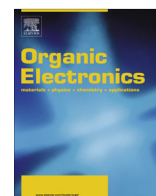




ELSEVIER

Contents lists available at ScienceDirect

Organic Electronics

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

Carboxylic acid mediated self-assembly of small molecules for organic thin film transistors

Kwan Hang Lam^{a,b}, Thelese Ru Bao Foong^{b,*}, Jie Zhang^b, Andrew Clive Grimsdale^a,
Yeng Ming Lam^{a,*}

^aSchool of Materials Science and Engineering, Nanyang Technological University, Blk N4.1, Nanyang Avenue, Singapore 639798, Singapore

^bInstitute of Materials Research and Engineering (IMRE), Agency for Science Technology and Research (A*STAR), 3 Research Link, Singapore 117602, Singapore

ARTICLE INFO

Article history:

Received 17 December 2013

Received in revised form 19 March 2014

Accepted 29 March 2014

Available online xxxx

Keywords:

Self-assembly

Hydrogen-bonding

Small molecule

Organic field-effect transistor

Spin coat

ABSTRACT

A p-type small molecule bearing dicarboxylic acid functional group (–COOH) is synthesized and evaluated for field-effect transistor properties. We discover and report for the first time, that the –COOH groups assist in the passivation of surface traps on the dielectric layer and *simultaneously* facilitate the self-assembly of the molecules via inter-molecular hydrogen bonding resulting in crystalline active channels. A 9-fold decrease in the threshold voltage was observed for the transistors made using the –COOH functionalized molecule, QT-DA, compared to its ester analogue, QT-ES, providing an evidence of surface passivation. This resulted in an increase in the hole mobility of QT-DA by up to 2 orders of magnitude. It was shown that QT-DA adopts a vertical alignment with respect to the substrate due to preferential interaction between the –COOH groups and the SiO₂ surfaces.

© 2014 Published by Elsevier B.V.

1. Introduction

Conjugated small molecules present a viable approach to solution processable organic thin film transistor (OTFT) as it has the advantages of a definite molecular weight, ease of purification and good batch-to-batch reproducibility. Fabrication of OTFTs involves the deposition of a semi-conducting organic layer on SiO₂/Si substrates where the thermally grown SiO₂ acts as the gate insulator. The SiO₂ layer and other metal oxide gate insulators often contain charge trapping sites due to the presence of hydroxyl (–OH) groups and surface defects [1,2]. Since charge generation and transport in OTFTs occur close to the semiconductor/insulator interface, any imperfection at that interface can result in high threshold voltages that in turn affect charge carrier mobilities. A common method

to overcome this problem is to passivate the SiO₂ surface with self-assembled monolayers (SAMs) such as hexamethyldisilazane (HMDS) [3,4], octadecyltrichlorosilane (OTS) [5–7] and other types of silanes. Silanes are widely used for surface functionalization as they form covalent bonds with the SiO₂ surface. Other than silanes, alkane-phosphonic acids have also been used to treat substrates due to their good binding properties to metal oxide surfaces [8]. However, the use of molecules that can both passivate the substrate and simultaneously form the active channel is a relatively new and unique area of research that is worth exploring. In this work, we report the synthesis of carboxylic acid functionalized at the α - and ω -position of the semiconducting small molecule that function both as the dielectric passivating layer as well as the active channel material. The bi-functional configuration was selected so that one of the carboxylic acid groups can anchor onto and passivate the dielectric surface via hydrogen bonding or proton transfer onto the lattice oxygen atom while the other acid group can assist in the

* Corresponding authors. Tel.: +65 67904260 (Y.M. Lam).

E-mail addresses: foongtrb@imre.a-star.edu.sg (T.R.B. Foong), ymlam@ntu.edu.sg (Y.M. Lam).

<http://dx.doi.org/10.1016/j.orgel.2014.03.041>

1566-1199/© 2014 Published by Elsevier B.V.

structural ordering and extending the packing range of the small molecules via inter-molecular hydrogen bonding. The above functionalities are achieved in a single spin coating step. The interaction of carboxylic acid groups with inorganic oxide surfaces has been reported for both dye-sensitized solar cells and SAMs [9–12]. A recent computational study by Bauer et al. shows that the most stable attachment mode for –COOH on inorganic oxides is the monodentate linkage [13]. We employ the simple quarterthiophene as the semiconducting core due to its well-reported success in small molecule OTFTs [14–17].

A similar concept for SAM field effect transistors (SAM-FETs) where a semiconducting small molecule with a mono-functionalized anchoring group was used as the active layer has been demonstrated [18–20]. In SAMFETs, short channel lengths in the order of submicrometer range were commonly required for current modulation due to limitations in long-range intermolecular π – π interactions between the molecules. In the SAMFETs fabrication, a common practice was to immerse the substrate into a dilute SAM solution to effect the functionalization and self-assembly. However, previously a pyrene-phosphonic acid molecule was reported to be able to self-assemble onto hydrophobic surfaces via spin-coating [21]. Recently, Hutchins et al. have shown that in situ functionalization and assembly during spin coating could also be realized [20]. Leveraging on the SAMFETs concept, we propose that a bi-functionalized molecule will be able to simultaneously result in passivation layers and ordered thin films with good charge transport properties that can be characterized with larger micron-scale channel lengths. Although moieties other than carboxylic acid (e.g. phosphonic, sulfonic acids and amine groups) may also bind well to oxide surfaces we chose carboxylic acid due primarily to its ease of synthesis for this proof-of-concept study.

2. Experimental

Heavily doped p-type silicon wafers with about 200 nm thick thermally grown SiO₂ were used as substrates for the top contact OTFTs. The substrates were cleaned by ultrasonication in acetone for 10 min and in isopropanol for another 10 min. The substrates were then rinsed with deionized (DI) water and dried with pressurized N₂ and treated with UV-ozone heated for 20 min at 100 °C prior to surface silanization or direct deposition of active layers. The quarterthiophene with dicarboxylic acid, QT-DA, and the diester analogue, QT-ES molecules were dissolved in THF and CHCl₃ respectively at a concentration of 4 mg/mL and spin-coated on the substrates at 3000 rpm for 1 min. The source and drain electrodes were deposited by thermal evaporation of gold (ca. 80 nm) through a shadow mask. OTFT testing was performed on a probe station equipped with an optical microscope and a Keithley 4200 parameter analyzer. Monolayer samples of QT-DA was obtained by spin coating a 0.2 mM solution at 2000 rpm on a UV-ozone treated SiO₂/Si substrates followed by spin rinsing. Determination of step height was achieved from voids present. The highest occupied molecular orbital (HOMO) level of the molecules were obtained from thin

film samples by the photoelectron spectroscopy in air (PESA) using a Riken Keiki AC-2 spectrometer. Film thicknesses were measured using a step profiler KLA Tencor P-10 while atomic force microscopy (AFM) images were collected from Digital Instruments Nanoscope IIIa in tapping mode. Molecular modeling was carried out using energy minimization with molecular mechanics (MM2) using the ChemBio Office ChemBio 3D Ultra, v. 11.0 (CambridgeSoft, Cambridge, MA) [22–24]. X-ray diffraction (XRD) was conducted on the Bruker General Area Detector Diffraction System (GADDs) with a Cu K α radiation and a 2D detector. Scans were collected for a 2θ range of 2–30° with scan duration of 10 min. The synthesis and detailed materials characterization of QT-DA and QT-ES are reported elsewhere [25].

3. Results and discussion

Fig. 1 shows the molecular structure of quarterthiophene with dicarboxylic acid, QT-DA, and its diester analogue, QT-ES. QT-ES was used as a comparison to investigate the effect of incorporating –COOH functional groups. Materials characterizations of the final compounds are provided in Supporting Information.

The highest occupied molecular orbital (HOMO) level for both molecules was estimated using Photo-Electron Spectroscopy in Air (PESA) while the lowest unoccupied molecular orbital (LUMO) level was calculated from the optical band-gap. The HOMO/ LUMO levels for QT-DA and QT-ES were –5.18/–3.11 eV and –5.50/–3.31 eV respectively [25]. The HOMO levels for both molecules make them suitable as hole transport materials. Field effect transistor behaviour of these QT molecules was investigated via the bottom gate, top contact device configuration. The substrates used were heavily p-doped conductive silicon wafers with a layer of thermally grown SiO₂ (~200 nm) on the surface as the gate dielectric. No silane treatment of the SiO₂ layers was done prior to the deposition of the channel materials. Instead, we exposed the substrates to UV-ozone treatment for 20 min to remove surface contaminants and increase the density of anchoring sites for molecule–substrate interaction [26]. QT-DA and QT-ES were spin-coated from THF and CHCl₃ respectively using a concentration of 4 mg/mL at 3000 rpm for 1 min. A layer thickness of approximately 70 nm was obtained and annealing was done prior to gold source and drain deposition to evaluate the effects of thermal annealing. Annealing temperatures were chosen to be between the crystallization and melting temperatures (not shown in paper) of the materials and they were 75 °C and 100 °C for QT-ES and QT-DA respectively. p-Channel characteristics were observed for both QT molecules (Fig. 2) and the hole mobilities were calculated from the saturation regime of the transfer curves with an applied drain voltage of –70 V. The hole mobility of QT-ES was 2.6×10^{-5} cm²/Vs (averaged) and 3.2×10^{-5} cm²/Vs (champion data) with I_{ON}/I_{OFF} ratio of approximately 10² and a threshold voltage (V_{th}) of –28 V. The hole mobility of QT-DA showed a significant improvement over that of QT-ES (up to 2 orders of magnitude) -2.7×10^{-4} cm²/Vs

Download English Version:

<https://daneshyari.com/en/article/10566296>

Download Persian Version:

<https://daneshyari.com/article/10566296>

[Daneshyari.com](https://daneshyari.com)