Organic Electronics 27 (2015) 18–23

Contents lists available at ScienceDirect

Organic Electronics

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

Molecular-scale charge trap medium for organic non-volatile memory transistors

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ARTICLE INFO

Article history:
Received 18 June 2015
Received in revised form
21 August 2015
Accepted 21 August 2015
Available online xxx

Keywords:
Organic non-volatile memory transistor
Triphenylene
Charge trap layer
Small molecule

ABSTRACT

In this work, we introduce a molecular-scale charge trap medium for an organic non-volatile memory transistor (ONVMTs). We use two different types of small molecules, 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and 2,3,6,7,10,11-hexamethoxytriphenylene (HMTP), which have the same triphenylene cores with either hydroxyl or methoxy end groups. The thickness of the small molecule charge trap layer was sophisticatedly controlled using the thermal evaporation method. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) analysis revealed that there were negligible differences in the chemical structures of both small molecules before and after thermal deposition process. The ONVMTs with a 1-nm-thick HHTP charge trap layer showed a large hysteresis window, approximately 20 V, under a double sweep of the gate bias between 40 V and −40 V. The HMTP-based structure showed a negligible memory window, which implied that the hydroxyl groups affected hysteresis. The number of trapped charges on the HHTP charge trap layer was measured to be 4.21×10^{12} cm^{-2}. By varying the thickness of the molecular-scale charge trap medium, it was determined that the most efficient charge trapping thickness of HHTP charge trap layer was approximately 5 nm.

1. Introduction

Over the last two decades, organic electronics have been intensively researched due to their distinct advantages, such as their low cost, applicability to large areas, easy processing, light weight, and flexibility [1,2]. Many studies focused on organic electronic devices such as organic light emitting diodes (OLEDs), organic photovoltaic cells (OPVs), organic field effect transistors (OFETs) and organic nonvolatile memory devices (ONVMs). Among these, organic non-volatile memory transistors (ONVMTs) are attractive because of their multiple functionalities, such as switching, data storage, and nondestructive reading [3,4].

ONVMTs can be classified based on their operating mechanisms or device structure, such as ferroelectric or floating gate (polymer electrets, metal nanoparticles, metal thin film) type ONVMTs [5–7]. Among these, floating gate type ONVMTs have been extensively studied not only because of their well-known operational mechanism but also because of the relatively simple fabrication processes involved in their production. As a charge trapping medium, the floating gate is located between the blocking and tunneling layers in typical back gate type OFETs. The ONVMTs generally have two different states at certain gate bias conditions by injecting charges (hole or electron) from the semiconductor to the floating gate through the tunneling layer, thus exhibiting a source-to-drain current (I_{ds}) change or a threshold voltage (V_{th}) shift. Recently, there have been many studies on materials that can be used for the floating gate layer. The memory performance was successfully tuned by controlling the metal-based nanoparticle species, size, and density or by using a multi-stack charge trapping layer [8,9]. Polymer electret layers were applied as a potential charge trapping or detrapping layer for ONVMTs [3,10].

Among many types of floating gate materials, recently, the organic molecular materials have been widely investigated. Burkhardt et al. demonstrated OTFT memory with a C_{60}-functionalized phosphonic acid self-assembled monolayer as the charge storage component [11]. While, Paydavosi et al. demonstrated OTFT

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http://dx.doi.org/10.1016/j.orgel.2015.08.020
1566-1199/

memory using thermally evaporated organic dye molecules as a charge trap layer [12]. Recently, Chang et al. reported a new strategy for fabricating heterostructure double floating-gate memory devices using discrete sub-micrometer-scale single-crystal C_{60} needle and copper phthalocyanine (CuPc) nanoparticle trapping sites [13].

As the simplest chemical unit, a small molecule system is a good platform for studying the effect of chemical moiety [14,15]. For example, 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) holds great interest as a starting material for preparing materials such as discotic liquid crystals and semiconductors from doped hexaalkoxytriphenylenes or in applications that take advantage of the molecular properties that the triphenylene nucleus possesses [16]. The HHTP, which have six hydroxyl end groups, is one of the candidates for the charge trap materials. Because electron trapping is related to the hydroxyl group which has electron withdrawing property in a polymeric dielectric, hydroxyl terminated gate dielectrics are responsible for the threshold voltage shift of organic transistors [17–19]. Comparing with other charge trap materials, the HHTP has many attractions, including the following: It is easy to control its thickness precisely through the thermally evaporation process. Thus, we can easily tuned amount of charge trap site. The synthetic procedure of HHTP is relatively simple and the cost is lower than other charge trap materials such as fullerene (C_{60}), copper phthalocyanine (CuPc), Au nanoparticles. Also, the HHTP has well controlled end functional group (hydroxyl group) and it can modulate electronic property of the device through the molecular structure engineering. In addition, HHTP is able to solution process because it is reasonably soluble in organic solution.

In this study, we introduced a charge trapping moiety (−OH) to a small molecule (2,3,6,7,10,11-hexahydroxytriphenylene (HHTP)) and applied the small molecule as the charge trap layer of pentacene-based ONVMTs. The effect of the chemical moiety (−OH vs. $-OCH_3$) on charge trapping and the resulting electrical and memory behavior are studied. In particular, by varying the thickness of the small molecule layer between the organic tunneling and blocking layer, we calculate the amount of trapped charges on different thicknesses of the small molecule layer at both fixed gate bias range and electrical field. In addition, we estimated the optimum thickness of a molecular-scale charge trap medium for ONVMTs and the charge trap efficiency of the small molecule (HHTP) layer.

2. Experimental details

The ONVMTs were fabricated on heavily doped p-type Si substrates with a 100-nm-thick thermally grown SiO_2 layer. The substrate was cleaned by ultrasonication in acetone and isopropanol. As a charge trapping layer, the hexasubstituted triphenylenes were prepared according to the reported synthetic procedure [20], using the trimerization reaction of veratrole in the presence of $FeCl_3$ to give 2,3,6,7,10,11-hexamethoxytriphenylene (HMTP) [21]. 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) was prepared via the demethylation of HMTP using HBr and acetic acid [16]. The charge tunneling layer was prepared from a poly(methyl methacrylate) (PMMA) (Sigma–Aldrich, $M_w = 120{,}000$) solution in toluene at a concentration of 3 mg/ml, spin-coated at 4000 rpm for 40 s, and then annealed on a hotplate at 120 °C for 15 min in a nitrogen-filled glove box. The thickness of the PMMA film was approximately 10 nm. For an organic semiconductor, a 50-nm-thick pentacene layer (Sigma–Aldrich) was deposited by thermal evaporation at approximately 10^{-7} torr. Finally, 50-nm-thick gold electrodes were deposited by thermal evaporation through a shadow mask as source and drain contacts, where the channel length (L) and channel width (W) were 100 and 1000 μm, respectively. The electrical characteristics of the transistors were measured using both HP4145B and Keithley 4200SCS semiconductor parameter analyzers. Atomic force microscopy (AFM) images were obtained using a Veeco Dimension 3100. X-ray photoelectron spectroscopy (XPS) analysis was performed by K-Alpha (Thermoscientific). Fourier transform infrared (FTIR) analysis was carried out using a PerkinElmer Spectrum GX.

3. Results and discussion

The main difference in the chemical structures of the disk-shape small molecules is the six chemical moieties at the ends of triphenylene cores, as shown in Fig. 1(a) and (b). Due to the charge trapping effect of the hydroxyl group, hydroxyl-containing organic materials are considered potential charge trap layers for ONVMTs. By inserting the HHTP and HMTP between the organic tunneling and blocking layers on conventional back gate organic transistors, we investigate the effect of the chemical moiety on the electrical behavior of ONVMTs. To control the thickness of small molecule layers in a sophisticated manner, HHTP and HMTP were thermally evaporated and deposited on the silicon oxide (blocking layer). To form the organic tunneling layer on the thermally deposited small molecules, we chose a solvent (toluene) that was orthogonal to both small molecules. After the thermal deposition of the pentacene layer and the Au electrode, the final structure of the ONVMTs was $p^{++}Si/SiO_2$/small molecule/PMMA/Pentacene/Au, as shown in Fig. 1(e).

3.1. Surface properties of small molecule charge trap layers

The morphologies of individual layers of the ONVMTs were characterized by AFM (see Supporting Information Fig. S2). Surface topography of the thermally deposited HHTP layer on SiO_2 is an important factor in its application as a charge trap layer in ONVMTs. A uniform and smooth surface of the charge trap layer, with angstrom scale roughness, provides a better interface for the coating of the organic tunneling layer. It is possible to apply a uniform electrical field between the gate and source electrodes and expect the quantitative control of tunneling and trapping of charges in ONVMTs under different gate bias conditions. Compared with other spin-coating-based organic charge trap layers, such as polymer electrets, our thermally deposited small molecules have a similar film quality, which makes it even easier to control the film thickness because it exhibits an RMS value of 0.537 nm (see Supporting Information Fig. S2(a)). In addition, a 10-nm-thick organic tunneling layer (PMMA) also maintains its very smooth surface, with an RMS value of 0.581 nm (see Supporting Information Fig. S2(b)). As a channel layer of a p-type organic semiconductor, pentacene was thermally deposited on the PMMA, and the film had typical terrace-like structures (see Supporting Information Fig. S2(c)). For comparison, HMTP was also inserted between the organic tunneling and blocking layers (see the supporting information).

For a further analysis of the small molecule charge trap layer, we investigated the chemical structure of HHTP and HMTP using XPS and FTIR analysis, as shown in Fig. 2 (see Supporting Information Fig. S3). XPS is a highly sensitive and semi-quantitative analysis method that is valuable for probing the surface element compositions of materials. The survey scan of HHTP is shown in Fig. 2(a). The C1*s* and O1*s* peaks correspond to the main constituent elements of these materials, and the C/O ratio provides the quantitative information of surface bond types. The C/O ratio in HHTP was 3.05. The C1*s* XPS deconvolved spectra of HHTP are shown in Fig. 2(b). The C1*s* peaks of HHTP are assigned to C–C/C=C in the aromatic rings (284.7 eV) and to C–O in the hydroxyl groups (286.3 eV). In Fig. 2(c), the O1*s* peak of HHTP reveals the binding