



Facile dielectric surface-modification methodology for high-performance polymer transistors via thermal evaporation of polydimethylsiloxane



Seong Hoon Yu, Jangwhan Cho, Kyu Min Sim, Dae Sung Chung*

School of Chemical Engineering and Material Science, Chung-Ang University, Seoul, 156–756, South Korea

ARTICLE INFO

Article history:

Received 18 August 2015
Received in revised form
6 September 2015
Accepted 9 September 2015
Available online xxx

Keywords:

Dielectric surface-modification methodology
Thermal evaporation
Organic thin-film transistors
Polydimethylsiloxane

ABSTRACT

Here we demonstrate a novel surface-modification methodology for dielectric layers to be used for high-performance organic field-effect transistors (OFETs). Instead of conventional solution-processed polymeric thin films or self-assembled monolayers such as octadecyltrichlorosilane, we introduce thermally evaporated thin films of polydimethylsiloxane (PDMS) processed at atmospheric conditions. The thermally evaporated PDMS (TEP) thin film possesses various merits compared to other surface-treated films in terms of surface hydrophobicity, smoothness, reproducibility, and large-area deposition. From surface energy analyses, X-ray photoelectron spectroscopy, near-edge X-ray absorption fine structure spectroscopy, grazing incident X-ray diffraction, and atomic force microscopy analyses, we prove the overall superiority of TEP over other surface-treated films for OFETs. Using a conventional semiconducting polymer of poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene) (PBTTT), OFETs with TEP dielectric layers are demonstrated to have higher charge carrier mobility, better on/off ratio, and superior reproducibility compared to OFETs with other buffer layers. The relationships between dielectric surface properties and OFET performance are fully discussed in conjunction with the above-mentioned analyses. In addition, the reproducibility of the TEP-based OFET is demonstrated by long-term fabrication and measurement analyses.

© 2015 Published by Elsevier B.V.

1. Introduction

Organic electronics are becoming increasingly common and can be found in everyday life in applications such as organic light-emitting diodes [1–3]. In the field of polymer field-effect transistors (PFETs), impressive development has occurred recently regarding charge carrier mobility, based on the design and synthesis of novel donor–acceptor copolymeric semiconductors [4–10]. By adopting a co-planar backbone structure with efficient intramolecular charge transfer, the charge carrier mobility of such donor–acceptor copolymers in the organic field-effect transistors (OFETs) geometry routinely exceeds $5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [4–6], a realistic minimum requirement for typical voltage compensation circuits to operate at sufficient speed [11]. In conjunction with other inherent merits, such as flexibility and processability at low temperatures and in solution, polymeric semiconductors now possess properties

that rapidly expand their potential field of application. Nonetheless, unresolved issues remain, related to the large-area reproducibility of high charge-carrier mobility and operational stability under constant current stress.

One representative methodology for overcoming such issues of reproducibility and stability in OFETs is the modification of dielectric surfaces by introducing a high-coverage buffer layer [12–15]. In most cases, the introduction of the buffer layer enhances the charge carrier mobility by adjusting the interfacial properties between the semiconducting and dielectric layers [14,15]. Dielectric surface modification can tune the electronic disorder of the adjacent semiconductor layer as well as the electrostatic interactions between the buffer and semiconductor layers [14]. For example, adding an octadecyltrichlorosilane self-assembled monolayer (OTS-SAM) to a SiO_2 dielectric layer decreases the electronic disorder in the semiconductor compared to pristine SiO_2 , while electrostatic interaction is minimized [14]. Therefore, OTS-SAM is a preferred buffer layer in OFETs, not only to enhance reproducibility but also to increase charge carrier mobility, once high surface coverage is established. In addition to OTS,

* Corresponding author.

E-mail address: dchung@cau.ac.kr (D.S. Chung).

polydimethylsiloxane [15] (PDMS) or CYTOP [16] are also known to enhance the performance of OFETs. One common factor among these preferred buffer layers is very low surface energy ($<20 \text{ mN m}^{-1}$). In this case, the adhesion energy between the semiconductor and buffer layer is usually lower than the semiconductor cohesion energy, and thus the semiconductor molecules tend to cluster together, forming well-ordered crystalline grains and increasing charge carrier mobility. From a different point of view, the low surface energy and high hydrophobicity of these buffer layers can also promote the edge-on orientation of alkyl chain-based polymeric semiconductors, thus benefitting in-plane charge transport, rather than the face-on orientation. In addition, low-surface-energy buffer layers can enhance the reliability and stability of the resulting device by repelling oxygen and water molecules from the interface and covering interfacial defects [17].

In spite of the remarkable merits of such low-surface-energy buffer layers, some practical issues remain in the use of these materials. For example, because of the nature of wet chemistry in producing OTS-SAM, the adsorption behavior of OTS molecules can be significantly influenced by the reaction solution conditions, such as temperature, humidity, and pH [18]. This is a critical drawback in the commercial application of OTS treatments, in which the bulk production of uniform devices is requested. In the case of low-surface-energy polymeric buffer layers, cross-linking the buffer layer or using orthogonal solvents is necessary to prevent the upper-deposited semiconductors from affecting the dielectric/semiconductor interfaces. Consequentially, the addition of a PDMS buffer layer requires a delicate and time-consuming cross-linking procedure [19]. Otherwise, functionalized polymers with orthogonal solvents are necessary, such as the expensive CYTOP. Therefore, the development of a facile dielectric surface-modification method that does not rely on solution-phase deposition is necessary to facilitate the near-future commercial application of OFETs.

Here we introduced thermally evaporated PDMS (TEP) thin films as buffer layers in OFETs, constructed by the heat-assisted thermal evaporation of solid PDMS at atmospheric conditions without vacuum-processing. With the vapor-deposition process, no cross-linking procedure was required and thus more efficient device fabrication was possible, while both low surface energy and high surface coverage were ensured with high reproducibility. Various surface characterization tools such as X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure spectroscopy (NEXAFS), grazing incident X-ray diffraction (GIXD), and atomic force microscopy (AFM) analyses were used in conjunction with the calculation of adhesion energy to demonstrate the superior surface properties of TEP. High performances in OFETs using poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno [3,2-b]thiophene) (PBTTT) as the semiconductor layer were demonstrated; the performances were similar to that of OFETs with OTS buffer layers. Using long-term device fabrication and measurement experiments, we demonstrated the overall superior reproducibility of TEP over OTS-SAM.

2. Experimental

TEP deposition: To prepare the source of TEP, solid PDMS was obtained by curing. Cubic-shaped PDMS solids ($\sim 0.2 \text{ cm}^3$) were put in a closed jar with a Si wafer located on top by facing each other. Careful sealing was performed for the successful deposition of TEP at the target temperature.

Device fabrication: The fabrication of OFETs with PBTTT was completed by spin-coating the PBTTT solution in chloroform (0.5 wt %) onto the Si/SiO₂ (100 nm) substrate treated with TEP or OTS. To further enhance the molecular order between PBTTT chains, the prepared films were annealed at 170 °C for 30 min and then slowly

cooled. Finally, the OFET geometry was completed by depositing Au source-drain electrodes onto the annealed films.

Characterization: To evaluate the surface free energy of OTS and TEP as well as their adhesion energy with PBTTT, contact-angle measurements were conducted using home-built set-up. Contact angles of water and diiodomethane were measured and used to calculate the surface free energy (γ_s) based the following equation [20].

$$1 + \cos\theta = \frac{2(\gamma_s^d)^{0.5}(\gamma_{lv}^d)^{0.5}}{\gamma_{lv}} + \frac{2(\gamma_s^p)^{0.5}(\gamma_{lv}^p)^{0.5}}{\gamma_{lv}}$$

where γ_{lv} is the surface energy of the test liquid and superscripts *d* and *p* refer to the dispersive and polar components, respectively. The adhesion energy was calculated following the previous method reported by Effertz and coworkers [15]. The GIXD measurements were performed using the PLS-II 3C beamline at the Pohang Accelerator Laboratory (PAL) in Korea. All NEXAFS and XPS measurements were performed at room temperature at the 4D beamline of the Pohang Light Source II (PLSII). We used the partial-electron-yield detection mode for NEXAFS spectra by recording the sample current normalized to a signal current measured simultaneously using Au mesh under ultrahigh vacuum. We used a p-polarized synchrotron photon beam ($\sim 85\%$) with an energy of 279–325 eV with a spectral energy resolution of $\Delta E = 150 \text{ meV}$ and a $\sim 5 \text{ nm}$ probing depth for surface-sensitive measurements. The corresponding electrical characteristics of the transistors were measured using 4156A Precision semiconductor parameter analyzers (Agilent Technologies).

3. Results and discussion

In Fig. 1(a), the experimental set-up for the deposition of TEP is described, following the previous report [21]. For the formation of a TEP layer with 10 nm thickness, the PDMS was treated for 30 min at 300 °C. Depending on the operating temperature, the deposition time could be further decreased. Fig. 1(b) shows the XPS spectra of TEP deposited onto a bare Si substrate in comparison to the blank Si substrate. The significantly larger XPS signal around 153 eV, corresponding to the binding energy in TEP, compared to the spectrum of bare Si, is attributed to the increased portion of PDMS Si 2s groups in the surface [22]. Simultaneously, as shown in the inset, the appearance of a new feature at 100.05 eV that corresponds to Si–C and the great enhancement of the feature at 102.8–103.5 eV, including Si 2p and siloxane signals, also strongly suggest the formation of TEP on the Si substrate [23]. The surface free energy was obtained by means of contact angle measurement to calculate and compare the adhesion energy between PBTTT and TEP to the cohesive energy of PBTTT [15] (Table 1). The surface free energy of 30.6 mN m^{-1} of PBTTT and 19.9 mN m^{-1} of TEP led to the adhesion energy of 48.65 mN m^{-1} , which is lower than the cohesion energy of PBTTT (61.2 mN m^{-1}). This is very similar to the case of OTS-SAM, with the surface free energy of 19.8 mN m^{-1} . Consequently, PBTTT molecules prefer to stack together rather than adsorbing to the TEP layer. In other words, by utilizing TEP as a buffer layer, PBTTT can form large lamellar crystalline domains, leading to π – π stacking. In addition, because of the low surface energy, a high degree of edge-on orientation is expected, similar to the case of OTS-SAM.

To confirm the molecular orientation and degree of crystalline order of PBTTT on TEP, GIXD studies were performed on both OTS- and TEP-based PBTTT thin films. As summarized in Fig. 2, both PBTTT films reveal well-ordered, edge-on orientations with lamellar packing of (100) up to (400) planes along the out-of-plane direction, as well as very clear π – π peak along the in-plane

Download English Version:

<https://daneshyari.com/en/article/7701188>

Download Persian Version:

<https://daneshyari.com/article/7701188>

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