Organic Electronics 22 (2015) 86–91

Contents lists available at ScienceDirect

Organic Electronics

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

Effect of the initial stage of film growth on device performance of organic transistors based on dinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophene (DNTT)

Hao Chang [a,b], Yunfeng Deng [a,b], Yanhou Geng [a], Tong Wang [a], Donghang Yan [a,*]

[a] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China
[b] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

ARTICLE INFO

Article history:
Received 18 January 2015
Received in revised form 19 March 2015
Accepted 27 March 2015
Available online 28 March 2015

Keywords:
Film growth
Organic epitaxy
Topography
DNTT
Organic thin-film transistors

ABSTRACT

The initial stage of organic film growth is considered to be vital for the carrier transport in organic thin-film transistors with bottom gate configuration. The same topographies of 40 nm dinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophene (DNTT) films on para-sexiphenyl (*p*-6P) monolayer and bare SiO_2 exhibited quite different field-effect mobilities, 1.9 and 0.1 $cm^2/V\,s$, respectively. The further investigation indicated there were different growth behaviors at their initial stages of film growth. Column islands with high density were observed on SiO_2, while lamina islands on *p*-6P monolayer due to the good diffusion ability and their good epitaxial relationship. The latter is beneficial to obtain high quality film with less boundaries and defects. The work demonstrated that the initial stage of film growth is an important factor to determine the device performance of organic transistors, which is significant to improve the device fabrication and optimize the device performance.

1. Introduction

Organic thin-film devices have drawn much attention for recent decades due to their potential application such as active-matrix flexible displays, radio-frequency tags, large-area sensors, medical apparatuses [1–7]. Recently, a series of heteroarene-based organic molecules have been synthesized and exhibited high mobility larger than 1 $cm^2/V\,s$, including dianthra-[2,3-b:2′,3′-f]thieno[3,2-b]thiophene (DATT), [1]benzothieno[3,2-b][1]benzo-thiophene (BTBT) derivatives and dinaphtho[2,3-b:2′,3′-f]thieno[3,2-b]thiophene (DNTT) [8–11]. Especially, C_8-BTBT showed the hole mobility up to 40 $cm^2/V\,s$ by solution process, which is one of the best results in organic semiconductor materials [12]. Therefore, they are worthy to be further investigated to improve the device fabrication and the device performance. Among these materials mentioned above, DNTT thin-film transistors showed prominent air stability since the transfer characteristics did not show a change after 72 days in air and dark condition [11,13]. In addition, it also showed good thermal stability. Furthermore, the hole mobility of DNTT single-crystal transistors is up to 8.3 $cm^2/V\,s$ with the current on/off ratio of 10^8 [14]. Therefore, the DNTT molecule is competitive as the candidate material in organic electronics [15–17]. However, there are scarcely investigations on the details of high quality DNTT film growth behavior, which is an essential role to obtain high device performance [18].

As for organic thin film transistors (OTFT), the thin-film quality usually plays a very crucial role to improve their device performance [19–21], especially the initial stage of growth process [22,23]. These several molecular layers (ML) of organic semiconductors adjacent to the dielectric layer are usually considered as the carrier transport path in OTFTs with bottom gate configuration which would also affect the subsequent film growth behavior [24,25]. Therefore, the investigation of initial stage of film growth would be more significant to obtain high quality film and better device performance. In this work, we investigated thin-film topography and device performance of DNTT transistors prepared on *para*-sexiphenyl (*p*-6P) and bare SiO_2, respectively. They exhibited the same topography but quite different hole mobilities, 1.9 $cm^2/V\,s$ for DNTT/*p*-6P and only 0.1 $cm^2/V\,s$ for DNTT/SiO_2. The selected area electron diffraction (SAED) patterns indicated the well epitaxial relationship between DNTT and *p*-6P, while the DNTT film on SiO_2 only showed polycrystalline diffraction ring pattern. The further investigation revealed the different growth behaviors at their initial stages of DNTT films grown on *p*-6P monolayer and SiO_2.

* Corresponding author.
E-mail address: yandh@ciac.ac.cn (D. Yan).

http://dx.doi.org/10.1016/j.orgel.2015.03.040
1566-1199/

2. Experimental

2.1. Fabrication and measurements of thin film transistors

Molecular structures of *p*-6P and DNTT were given in Fig. 1a. The DNTT and *p*-6P samples were synthesized according to Ref. [11] and Ref. [26], respectively. All the materials were purified twice by thermal gradient sublimation prior to experiments. Heavily doped n-type silicon wafers with a 300 nm thermal oxidation SiO_2 layer (dielectric capacitance 10 nF/cm^2) were used as substrates. The substrates were cleaned by acetone, alcohol, deionized water in order and then were dried at 150 °C for 30 min in the oven to eliminate the influence of the moisture. Firstly, about 3 nm *p*-6P (monolayer) was deposited on SiO_2 substrate forming continuous and flat monolayer at the substrate temperature of 170 °C. The DNTT thin films with various thicknesses were deposited on *p*-6P monolayer or bare SiO_2 at 70 °C. All thin films were deposited in vacuum chamber under the pressure of 10^{-4}–10^{-5} Pa at a rate of about 1 nm/min. Finally, the substrates with DNTT films were rapidly transferred to another vacuum chamber to define source and drain Au electrodes by a shadow mask at 10^{-4} Pa. The device configuration was shown in Fig. 1b. The channel length and width are 200 and 6000 μm, respectively.

Current–voltage measurements of OTFTs were performed with two Keithley 236 source–measurement units under ambient conditions at room temperature.

2.2. Topographies and crystalline structures

2.2.1. Atomic force microscope (AFM)

The thin film topographies were imaged by a SPI 3800/SPA 300HV (Seiko Instruments Inc., Japan) with the tapping mode. A 150 μm scanner and a commercially available SiN_4 cantilever with a spring constant of 15 N/m were used in all experiments.

2.2.2. X-ray diffraction (XRD)

The out-of-plane XRD patterns were taken from a D8 discovery thin-film diffractometer with Cu Kα radiation (λ = 1.54056 Å). The selected voltage and current were 40 kV and 40 mA, respectively. And the in-plane XRD patterns were carried out at Shanghai Synchrotron Radiation Facility (SSRF) on beamline BL14B1 with λ = 1.24 Å.

2.2.3. SAED measurements

Carbon films as support layers was deposited on DNTT/*p*-6P/SiO_2 substrates, then they were separated from the SiO_2 surface by soaking into the 10% HF solution, finally, they were transferred on a copper grid for measurements. Au was directly deposited on copper grid for demarcation if necessary. The SAED was imaged by a JEOL JEM-1011 transmission electron microscope operated at 100 kV. To provide a weaker-intensity beam and high contrast of the image, dark field was used during the measurement.

3. Results and discussion

3.1. Transistor performance and film topographies

The output curves of DNTT/*p*-6P and DNTT/SiO_2 transistors were given in Fig. 1c and d, and the thickness of DNTT films were about 40 nm. Under the gate voltage V_G = −50 V, the saturation current was about 250 μA for the DNTT/*p*-6P device, which was nearly 10-fold larger than that of device based on DNTT/SiO_2. The field effect mobility of DNTT/*p*-6P transistor extracted from the saturation region of the transfer curve (Fig. 1e) has reached to 1.9 cm^2/V s, while the corresponding value was only 0.1 cm^2/V s for the DNTT/SiO_2 transistor.

To explore the difference in their carrier mobilities, the topographies were imaged by AFM, as shown in Fig. 2. However, their film topographies are similar, consisting of dendritic domains, and hard to be indistinguishable from each other.

3.2. Crystlline structure and epitaxial relationship

The crystalline structures of DNTT films were further investigated. Unfortunately, the out-of-plane and in-plane XRD patterns (Fig. 3) were still similar for the 40 nm DNTT films on *p*-6P monolayer and bare SiO_2 substrates. The diffraction peaks of out-of-plane XRD patterns were indexed to (001), (002), (003), (004), (005) lattice planes, which indicated that the crystallographic *c*-axis was perpendicular to the substrates. And in-plane XRD patterns demonstrated that ab plane was parallel to the substrate. Therefore, DNTT molecules showed the same packing arrangement on *p*-6P and bare SiO_2 substrate.

To further obtain the in-plane structure information in microscale, SAED measurement was performed for these two kinds of films, and the corresponding patterns were shown in Fig. 4. For the different DNTT domains grown on same *p*-6P domain, they have showed same orientation relationship with *p*-6P, which was corresponding to commensurate epitaxial relationship that b^* axis of DNTT parallel to the a^* axis of *p*-6P with $(001)_{p\text{-}6P}//(001)_{DNTT}$, $[100]_{p\text{-}6P}//[010]_{DNTT}$, $[010]_{p\text{-}6P}//[100]_{DNTT}$ as shown in Fig. 4a. This good epitaxial relationship may originate from their similar lattice parameters (given in Table 1) and molecular structures, consequently, DNTT molecules were easy to arrange along one direction on *p*-6P domain, and highly ordered DNTT crystalline film was obtained on *p*-6P monolayer. However, the diffraction pattern showed significant difference for the DNTT film grown on SiO_2. As shown in Fig. 4b, no regular set of diffraction pattern was observed. On the contrary, many diffraction spots with same d value formed diffraction ring pattern, which indicated DNTT molecules had arranged in many orientations on SiO_2 substrate, and the DNTT domains consisted of many small crystals.

This result demonstrated that DNTT film grown on one *p*-6P domain could be considered as a single-crystal film with same orientation. Although the similar surface topography, the DNTT film grown on SiO_2 consisted of many small crystals smaller than 1 μm. Hence, DNTT film grown on *p*-6P could form higher quality film than that grown on SiO_2 substrate, which is the possible clue to achieve higher carrier mobility.

3.3. Growth modes of DNTT films on different substrates

To further confirm the conclusion given by SAED, we observed the topography evolution of DNTT films grown on two substrates at different stages. First, *p*-6P monolayer was deposited on bare SiO_2 and formed large-area continuous and flat film with a root mean square (RMS) roughness of 0.8 nm (Fig. 5a). The smooth surface is beneficial to the subsequent growth of DNTT film. Then, the DNTT film of 0.8 ML was deposited on *p*-6P monolayer and bare SiO_2 under the same conditions, respectively. The density of DNTT domains on SiO_2 is obviously higher than that on *p*-6P monolayer, certainly the domains on *p*-6P are much larger than that on SiO_2 substrate (Fig. 5b and c).

With the increase of film thickness, the DNTT film showed lamina islands on *p*-6P monolayer, while DNTT molecules tended to form isolated tall column islands on SiO_2 substrate. The RMS roughness was 1.6 nm for DNTT film of 5 nm (~3 ML) on *p*-6P monolayer (Fig. 6a) and that was 7.8 nm on SiO_2 (Fig. 6b). According to their height profiles, the amplitude is only several nanometers for DNTT film grown on *p*-6P monolayer, and that