Materials Science & Engineering B 226 (2017) 107–113

Contents lists available at ScienceDirect

Materials Science & Engineering B

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

Thickness modulation on semiconductor towards high performance gas sensors based on organic thin film transistors

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ARTICLE INFO

Keywords:
Organic thin film transistor
Copper phthalocyanine
Gas sensor
Thickness modulation

ABSTRACT

Copper phthalocyanine (CuPc)-based organic thin film transistors (OTFTs) with various thicknesses of organic semiconductor were fabricated, and the corresponding gas sensing performance was systematically evaluated. In situ measurements of OTFTs under nitrogen dioxide (NO_2) exposure showed a remarkable sensitivity enhancement from 7% to 241% by simply decreasing CuPc film thickness from 40 to 10 nm. CuPc films were analyzed by atomic force microscopy and grazing incidence X-ray diffraction. The results showed that thinner CuPc film, which enhances the interplay of CuPc film and NO_2 analyte, is beneficial for NO_2 diffusion and smaller CuPc grain formation, resulting in considerable sensing performance improvement.

1. Introduction

Since the discovery of organic thin film transistors (OTFTs) in the mid-1980s, they have been receiving intriguing attention because of their inherent merits, such as low fabrication costs, lightweight, and compatibility with a wide range of applications including flexible electronic papers, display backplanes, radio frequency identification tags, and logic circuits [1–5]. Especially in recent years, with extensive reports on molecular synthesis, functional group modification, and semiconductor heterojunction design, organic materials (organic small molecules and polymers) are representing an emerging field in functional electronic devices because of their ability to deliver high flexibility and high electrical performance [6–10]. Moreover, the incorporation of organic materials promoted various efficient preparation techniques, including spin coating and spray coating [11–13]. Benefiting from these achievements, OTFTs are taking an increasingly important place in the domain of sensing applications [14,15]. OTFT-based sensors can efficiently detect many kinds of analytes, such as temperature, moisture, light intensity, pressure and various types of harmful gases [16,17]. Compared to conventional semiconductor resistor-based sensors, OTFT-based sensors can translate the detected signals into multiple electrical parameters, such as charge carrier mobility (μ), current on/off ratio (I_{on}/I_{off}), threshold voltage (V_{th}), and channel current. Moreover, because an OTFT-based sensor is the combination of a sensor and an amplifier, a slight modulation in gate bias may change the response (signal-to-noise ratio) of the device by several orders of magnitude, which provides the potential for ultra-low limit of gas detection [18,19].

Notably, OTFT-based gas sensors are manifesting their application with broad concern in the fields of environmental monitoring, disease diagnostics, and chemical processing [20]. To date, lots of progress have been made to improve the sensing properties by applying functional materials, adjusting film morphologies, adopting innovative device structures, and so on [21–25]. Among abundant methods that can effectively enhance the detecting ability of OTFT-based sensors, the utilization of an ultrathin organic semiconductor is a simple and practical strategy.

It is widely recognized that the first few molecular layers of organic semiconductor at the organic/dielectric interface play the most essential role in determining the charge transport in OTFTs [26,27]. Analyte molecules that diffuse into the conducting channels are expected to strongly affect the charge transport. Therefore, the sensing performance enhancement of OTFT-based sensor relies not only on the physical and/or chemical interactions between analytes and semiconductors but also on the analyte molecule's diffusion efficiency. Hence, the thickness modulation of organic semiconductor layer has been put forward as one of the most facile, yet efficient, techniques to fabricate highly sensitive OTFT-based gas sensors. In recent years, a series of works have been performed on OTFT-based gas sensors with an ultrathin organic semiconductor layer [28,29]. By using a versatile strategy for the growth of dendritic microstripes with 4–6 molecular layers (6.5–11 nm in thickness) by a dip-coating process, Li et al. recently reported an OTFT sensor based on dialkyl tetrathiapentacene, which exhibits considerably enhanced sensitivity of over 100 folds to 50 ppm ammonia (NH_3) with

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http://dx.doi.org/10.1016/j.mseb.2017.08.019
Received 16 May 2017; Received in revised form 21 July 2017; Accepted 17 August 2017
Available online 17 September 2017

short response/recovery time of 27–36 s/4–10 s [30]. Moreover, Misbah et al. reported the fabrication of a monolayer pentacene OTFT device aiming at nitrogen dioxide (NO_2) detection, which had boosted up sensing response with three orders of magnitude as compared to a conventional thick layer device [31]. However, systematic study and specific analysis toward the correlation between semiconductor layer thickness and sensing properties have scarcely been reported.

Herein, the dependence of sensing properties of OTFTs on organic semiconductor thickness is studied in detail by fabricating NO_2 OTFT sensors with a series of different thicknesses of copper phthalocyanine (CuPc). By characterizing the sensing performance of OTFTs under various NO_2 concentrations and analyzing the film properties of CuPc with different thicknesses, we identify that sensing properties were remarkably enhanced by decreasing the CuPc film thickness, as expected. This is considered to be mainly attributed to the increase in gas-generated carriers in conducting channel. The observed substantial enhancement in sensing performance, which was induced by thickness modulation, paves a promising way for the fabrication of superior low-cost OTFT-based gas sensors.

2. Material and methods

2.1. Device preparation

Fig. 1 shows the schematic of a bottom-gate top-contacted OTFT. The OTFT devices were constructed on indium tin oxide (ITO)-coated glass, which acted as both substrate and gate electrode. Prior to the fabrication procedure, the substrates were successively ultrasonically cleaned in acetone, deionized water, and isopropyl alcohol. The substrates were then UV–ozone treated for 10 min. After that, Poly(methyl methacrylate) (PMMA) (Sigma-Aldrich, average Mw ~ 120,000) dissolved in anisole at a concentration of 10 wt% was spin coated on the ITO substrates at 1500 rpm for 1 min and then dried in an oven at 120 °C for 1 h. The resulting PMMA dielectric was 520 nm thick with a capacitance of 6.32 nF/cm^2. Subsequently, CuPc (Sigma-Aldrich, triple-sublimed grade, > 99.95% trace metals basis) layers with thicknesses ranging from 10 to 40 nm were deposited onto the dielectric layer by thermal evaporation at a rate of 0.2–0.3 Å/s under 3×10^{-4} Pa. Finally, source and drain electrodes of 50 nm gold (Au) were thermally deposited on the CuPc film under 3×10^{-3} Pa. The Au electrodes were patterned using a shadow mask with a channel length and width of 100 μm and 1 cm, respectively [14]. The electrical characteristics of all devices were analyzed using a Keithley 4200-SCS Source Meter in N_2. V_{th} was extracted in the saturation regime from the highest slope of

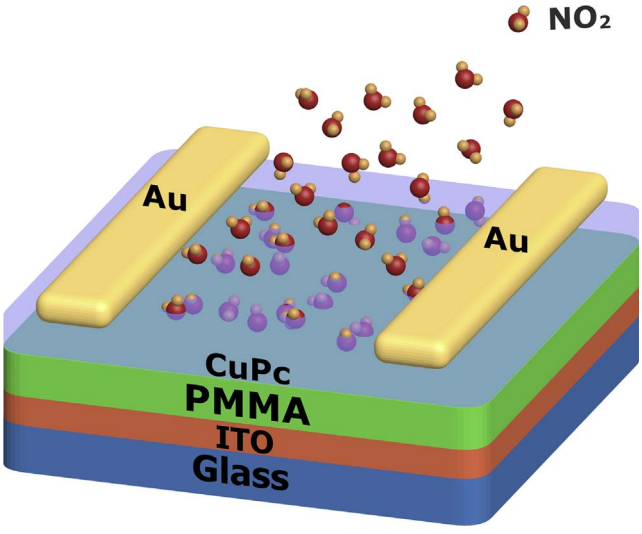

Fig. 1. Schematic of OTFT-based gas sensors.

$|I_d|^{1/2}$ vs. V_g plots, while μ, which reflects the migration ability of the carrier in semiconductor under a specific electric field, was calculated using Eq. (1) as follows:

$$|I_d| = (W/2L)\mu C_i(V_g - V_{th})^2 \quad (1)$$

where L and W are the channel length and width, respectively, and C_i is the capacitance (per unit area) of the dielectric. V_g is the gate voltage and I_d is the drain–source current.

2.2. Film characterization and sensor test

The morphologies of CuPc films were characterized by atomic force microscopy (AFM) (Bruker; Dimension Edge; Tip Model: RFESP, Cantilever Parameters: T = 3 μm, L = 225 μm, W = 35 μm, f_c = 75 kHz, K = 3 N/m; Longitudinal resolution: 0.01 nm; Transverse resolution: 0.1 nm) in tapping mode. Grazing incidence X-ray diffraction (GIXRD) measurement was made using a Rigaku SmartLab Thin-film Diffraction Workstation equipped with a high-intensity 9-kW copper rotating anode X-ray source, which was coupled to a multilayer optic device. The impinging angle was 0.5 degree. Samples were placed horizontally with surface normal direction upward because of the default settings of the apparatus: incident slit size 0.1 × 5 mm, soller slits 0.5 degree, and a resolution of less than 5%. The OTFT sensors were stored in an airtight chamber (approximately 2 mL). N_2 and 200 ppm standard NO_2 gas, purchased from Sichuan Tianyi Science & Technology Co., were mixed by mass flow controllers (S48 300/HMT, Beijing BORIBA METRON Instruments Co.) to form appropriate concentrations of NO_2 and introduced into the test chamber simultaneously. The flow rate was fixed at 100 sccm (standard cm^3 per min). The devices were exposed to each concentration of gas for 5 min before measurement.

3. Results and discussion

The representative transport characteristics of all OTFTs were measured with the gate voltage (V_g) sweeping between 20 and −40 V, with a step size of 1 V, and a source–drain voltage (V_d) of −40 V, as shown in Fig. 2(a). The output characteristics are presented in Fig. 2(b), with V_d ranging between −40 and 0 V and V_g varying from 0 to −40 V, with a step of −5 V. Parameters including saturation current (I_{on}), μ, turn-on voltage (V_{on}), and I_{on}/I_{off} were extracted or calculated from the transport curves. Notably, V_{on} represents the point where the source–drain current ($-I_d$) starts to steeply increase, which can be more easily distinguished than V_{th} in the transport curves.

As shown in Fig. 2(a), the device with 10 nm CuPc exhibited the lowest I_{on}/I_{off} of about 8.9×10^2 and the most negative V_{on} of −16.9 V. An enhancement in I_{on} and a positive shift of V_{on} occurred with an increase in CuPc film thickness. The device with 40 nm CuPc had the best electrical performance with a high I_{on}/I_{off} of 9.8×10^3, which is one magnitude higher than that of the device with 10 nm CuPc. Moreover, a relatively low V_{on} of −4.6 V was also obtained. In addition, the mobility calculated by Eq. (1) showed an increase from 1.58×10^{-3} cm^2/Vs (10 nm CuPc) to 4.26×10^{-3} cm^2/Vs (40 nm CuPc). The electrical parameters of these devices are summarized in Table 1. V_{th}, which served as a parameter in the calculation of μ, were −19.1 V (10 nm), −11.8 V (20 nm), −8.16 V (30 nm), and −7.31 V (40 nm).

Subsequently, these devices were exposed to different concentrations of NO_2 in a test chamber for a certain period. In situ measurements of the transport curves were made before and after the exposure, and multiple relative parameters were extracted from the curves. NO_2 concentration in the sensing test procedure varied from 0 to 30 ppm. The transport curves of all kinds of devices in different NO_2 concentrations are depicted in Fig. 3. It is obvious that the sensing performance was remarkably enhanced with the decrease in CuPc film