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Novel Top-Contact Monolayer Pentacene-Based Thin-Film Transistor for Ammonia Gas Detection

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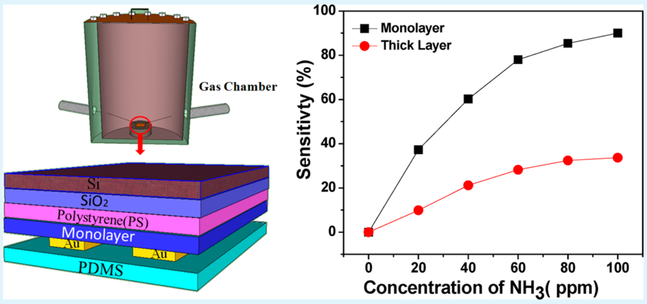
Supporting Information



ABSTRACT: We report on the fabrication of an organic field-effect transistor (OFET) of a monolayer pentacene thin film with top-contact electrodes for the aim of ammonia (NH_3) gas detection by monitoring changes in its drain current. A top-contact configuration, in which source and drain electrodes on a flexible stamp [poly(dimethylsiloxane)] were directly contacted with the monolayer pentacene film, was applied to maintain pentacene arrangement ordering and enhance the monolayer OFET detection performance. After exposure to NH_3 gas, the carrier mobility at the monolayer OFET channel decreased down to one-third of its original value, leading to a several orders of magnitude decrease in the drain current, which tremendously enhanced the gas detection sensitivity. This sensitivity enhancement to a limit of the 10 ppm level was attributed to an increase of charge trapping in the carrier channel, and the amount of trapped states was experimentally evaluated by the threshold voltage shift induced by the absorbed NH_3 molecular analyte. In contrast, a conventional device with a 50-nm-thick pentacene layer displayed much higher mobility but lower response to NH_3 gas, arising from the impediment of analyte penetrating into the conductive channel, owing to the thick pentacene film.

KEYWORDS: *pentacene, monolayer, field-effect transistor, top contact, NH_3, sensor*

INTRODUCTION

Since their discovery in the mid-1980s,[1] organic field-effect transistors (OFETs) have been remarkably improved. To date, there has been much effort devoted to obtaining satisfactory OFETs for practical applications on flexible circuits, electric papers, driving circuits for active matrix display, and sensors.[2−5] Sensors, according to their operation principles, can be assorted into optical sensors, electrical sensors, magnetic sensors, etc. Among electrical sensors, the OFET-based sensor may be one of the most promising candidates owing to its multiple choices of device design to satisfy the demand of low cost, low working temperature, portability, and disposable diagnostic sensors with high selectivity and sensitivity.[6,7] When an analyte is exposed to an OFET, a quantitative shift in device parameters such as the threshold voltage, the charge carrier mobility, and the drain current takes place, owing to the introduction of noncovalent interaction at the surface of an organic semiconductor, at the grain boundaries, and at the dielectric interface.[8] However, these interactions including van der Waals forces (dipole−dipole, dipole-induced dipoles) and hydrogen-bonding and hydrophobic interactions are usually weak enough when the sensors are purged in a cleaning gas. Therefore, a sensor can be utilized in a recirculated manner.

In particular, ammonia (NH_3) detection is of great research interest because of growing emphasis on environmental and health issues. A detection limit of NH_3 at the parts per million (ppm) level plays a pivotal role in different industries, viz., fertilizer manufacturer, coke manufacturer, livestock management, and fossil fuel combustion. The huge impact of NH_3 emission on human health and environment has accelerated prevalent scientific and technological progress in the field of NH_3 sensors.[9−11] Until now, there are limited reports on OFET-based NH_3 sensors.[12−14] Especially, there are several reports for ultrathin-film transistors via solution methods.[15,16] In the past, it was believed that direct exposure of the conduction channel to the environment may play a beneficial role in detection sensitivity. However, to enhance the credibility and fidelity of OFET-based sensors, there is still a need for an optimal fabrication process and a better understanding of the detection mechanism, as well as for the development of an inexpensive and presumably facile integration technique. In this paper, we report on a novel ultrathin-film OFET by using a single continuous pentacene molecular film via vacuum evaporation combined with a direct stamp top-contact metal electrode. A detection limit of the 10 ppm level for NH_3 gas can be achieved by reducing the organic thin film to a single monolayer by increasing charge trapping in the carrier channel.

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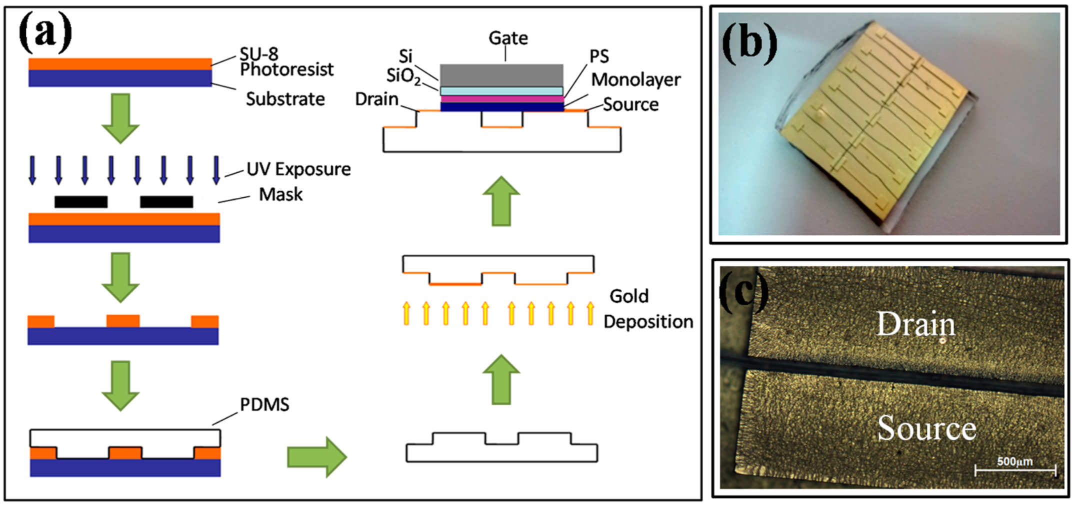

Figure 1. (a) Schematic diagrams of top-contact pentacene monolayer (1.5−4.5 nm) devices used for NH_3 gas sensing. Elastomeric polymer (PDMS) stamp replication from the SU-8 pattern was prepared with conventional photolithography. (b and c) Gold electrode on a PDMS stamp and the PDMS channel, respectively.

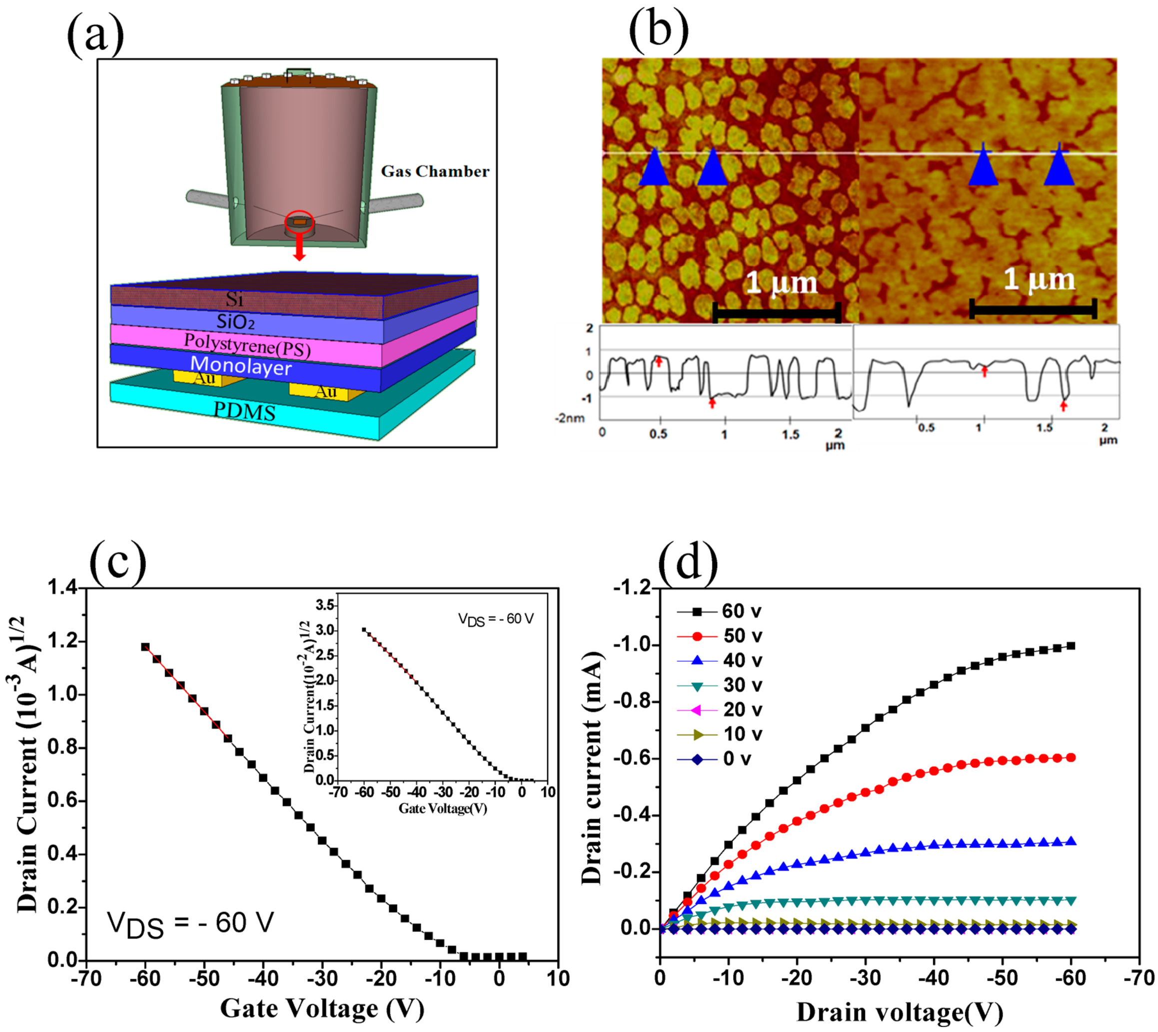

Figure 2. (a) Schematic representation of a top-contact pentacene monolayer (with thickness of 1.5−4.5 nm) device with exposure of NH_3 gas for the gas sensor. (b) AFM image of a monolayer, with its height profile showing different coverages of the monolayer film. (c) Transfer characteristics of a top-contact pentacene monolayer device at a gate voltage of −60 V [the inset shows the transfer curve of a thick-layer (50 nm) pentacene film]. (d) Output curves of a pentacene monolayer device.

EXPERIMENTAL DETAILS

The top-contact electrodes made by a flexible stamp method are fabricated as follows. A silicon wafer was cleaned with ethanol, acetone, and HPM ($HCl:H_2O_2:H_2O = 1:1:6$) and then heated at 150 °C for 10 min. A negative photoresist of SU-8 with a thickness of 200 μm was spin-coated onto the silicon wafer. The substrate was heated at 65 °C for 15 min and at 95 °C for 45 min and cured at room temperature for 5 min. UV was exposed through the photomask. The SU-8 thin film was developed to yield the pattern followed by cleaning with isopropyl alcohol and deionized water. An elastomeric polymer, poly(dimethylsiloxane) (PDMS), was poured onto the SU-8 mold and cured at room temperature for 6 h. PDMS was detached from the SU-8 mold after the curing process, and an elastomeric polymer stamp was prepared. A 100-nm-thick gold electrode was evaporated on this elastomeric polymer stamp as metal electrodes with channel length L = 250 μm and width W = 3000 μm. All of the fabrication processes are schematically shown in Figure 1.

Heavily doped silicon wafers with thermally grown SiO_2 of 300 nm were used as substrates. The substrates were cleaned sequentially with deionized water, pure ethanol, acetone, piranha solution ($H_2SO_4:H_2O_2 = 7:3$), a hot ammonia (NH_3)/hydrogen peroxide solution (NH_3:hydrogen peroxide:water = 1:1:5), deionized water, and pure ethanol. Polystyrene (Alfa Aesar; molecular weight = 100000) was dissolved in toluene with a concentration of 0.5 wt %, then spin-coated onto the substrate at 3000 rpm by a spin processor (Laurell Technologies Co.), and then cured at 85 °C for 10 h in a vacuum oven to remove residual solvent. Pentacene (purchased from Sigma-Aldrich and used without further purification) films with 1−3 monolayers (1.5−4.5 nm in thickness) and with 50 nm thickness were deposited in an Auto 306 (BOC Edward Co.) thermal evaporation system with a deposition rate of 1.2 nm/min at a vacuum pressure of 7×10^{-5} Pa. The substrate temperature was kept at room temperature, and the nominal thickness of the films was measured by a quartz crystal. The morphology of the films (2 × 2 μm) was characterized by a Nanoscope III (Vecco Co.) atomic force microscope with tapping mode. The current−voltage characteristics of the OFETs were measured by a Keithley 4200SCS instrument at ambient temperature.

To test the sensing property of NH_3 gas, the OFETs were biased at a drain voltage of −60 V while keeping the gate voltage sweeping from +10 to −60 V. Before starting the gas sensing, the chamber was pumped with a mechanical pump to less than 1 Torr and then N_2 was purged into the chamber up to 1 atm to provide an inert atmosphere. NH_3 gas was introduced to check the OFET detection sensitivity. Different concentrations of NH_3 from 10 to 100 ppm were introduced into the chamber by diluting NH_3 into N_2 using a needle valve in a controlled manner. The exposure time of NH_3 gas into the chamber was 1 min. To prove that our device can work under a real environment, an experiment was performed in our cleaning room, keeping 50 ppm concentration of NH_3 in vacuum and in air (keeping the humidity around 25%). When the device was exposed to air, the drain current decreased a little (negligible), which ensured that our sensor is appropriate for practical applications (Figure S2 in the Supporting Information, SI). Because of the limitations of our experimental setup, we cannot go below 10 ppm. The recovery of the sensor was checked after NH_3 was pumped from the system and filled again with N_2. The devices almost recover to their original positions because desorption of the analyte occurs.

RESULT AND DISCUSSION

In OFET-based devices, chemical sensing arises from a change in the conductivity as an analyte interacts with the active transport layer. In fact, the conducting channel of a field-effect transistor device locates at the interface between the organic semiconductor and the gate dielectric, so the thin-film thickness of a few monolayers can accelerate the interaction between the conductive channel and the analyte more effectively than their thick counterpart.[17] However, growth of a continuous ultrathin film is still a challenging task because of the necessary compromise of thickness for practicable device fabrication. Especially, a high-quality source and drain contacts with ultrathin molecular films remain big challenges. Here, for the first time, we report the successful growth of ultrathin pentacene films with 1−3 monolayers (1.5−4.5 nm) via vacuum evaporation and the formation of a direct source and drain metal top contacts in an adaptable strategy to achieve a high response for NH_3 gas detection.

Figure 2a shows schematically the device configuration of the top-contact monolayer pentacene-based OFET. For an ultrathin-film channel consisting of several pentacene monolayers, the charge-carrier-transport properties depend on the semiconductor molecular packing, dielectric chemistry, electrode, device configuration, and fabrication technique.[18] For practical applications of OFET, it is necessary to increase the charge carrier mobility by optimizing the molecular packing during deposition and reducing the effect of contact resistance.[19] One possible way to attain this goal is to maintain a two-dimensional layer-by-layer growth mode for the early growth stage and avoid the diffusion of metal atoms into the thin organic semiconductor layer during fabrication of the source and drain contacts. In this sense, the bottom contact configuration is not suitable because it will deteriorate the molecular packing. Because the diffusion of metal electrodes can cause permanent damage to the ultrathin organic layer during high-temperature deposition of metal onto an organic film, conventional formation of S/D contacts using vacuum evaporation is prohibited.[20] Instead, a series of organic transistors having several monolayers are fabricated on a flexible substrate (PDMS) with S/D electrodes by conventional photolithography, as illustrated in Figure 1a. Using this novel method, the molecular ordering of a single monolayer film was successfully maintained. The gold deposited by thermal evaporation acts as an electrode on the PDMS stamp, which comes in direct contact with the S/D electrodes of the elastomeric stamp through van der Waals bonding, as shown in Figure 1b,c.

Atomic force microscopy (AFM) is used to characterize the morphology of monolayer pentacene devices. The morphology of the semiconductor layer and consecutive monolayer evolution with an increase in coverage are shown by two different AFM images. Because of the quasi-Stranski-Krastanov growth mechanism for the pentacene molecule deposited on suitable dielectrics, the early grown layer is proven to show a growth feature of a two-dimensional layer-by-layer mode. We carried out experiments for film structure analysis of 1, 2, and 4 monolayer pentacene thicknesses, as shown in Figure 2b. The evolution of morphology of all thicknesses proves that islands grow up to coalesce each other under a diffusion-mediated growth mode.[21] Figure 2a represents the pentacene monolayer film with a gas characterization chamber. We also did some experiments with direct thermal evaporation of gold metal as the S/D electrode on the pentacene monolayer film but the devices showed high off current and very low on current due to diffusion of metal into the monolayer film.

From the transfer curves shown in Figure 2c, the monolayer pentacene-based device in a N_2 atmosphere exhibits well-defined field-effect transistor behavior owing to both the ordered molecular packing of the ultrathin film and a low-temperature process in metal contacts to keep the monolayer film intact. We have also investigated the ultrathin OFET performance with a change of the active layer thickness. The trend is that, with increasing thickness of the organic thin film,

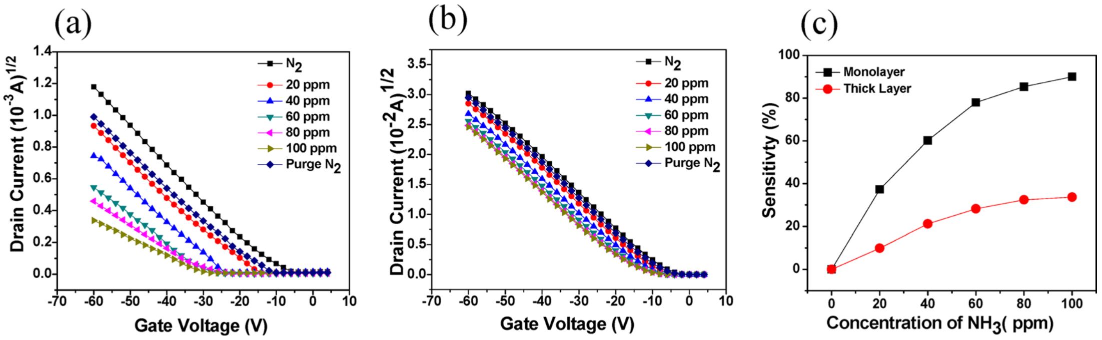

Figure 3. (a) Transfer curves of top-contact pentacene monolayer devices in different concentrations of NH_3 gas. (b) Transfer curves of top-contact pentacene thick-layer devices in different concentrations of NH_3 gas. (c) Sensitivity S_{FET} of monolayer and thick-layer devices with different concentrations of NH_3 gas.

the sensitivity decreases. The charge carriers are generated and transported within the first few monolayers in contact with the gate dielectric in OFETs. In ultrathin-film OFETs (1−4 monolayers), exposure to the environment will affect the OFET response as molecules either adsorb onto or approach the charge-transport layer. It becomes favorable in sensing application. Though promising progress has been made in the fabrication of monolayer pentacene devices within the last decades,[22,23] we optimized the growth and fabrication processes to achieve a top-contact pentacene monolayer device with high performance and sensitivity for the first time.

To evaluate the performance of field-effect transistors in a saturation regime, a few fundamental parameters are calculated by

$$I_{DS} = \frac{\mu C_i W}{2L}(V_{GS} - V_{th})^2 \tag{1}$$

where I_{DS} is the drain current, W and L are the channel width and length, respectively, μ is the mobility, V_{th} is the threshold voltage, C_i is the dielectric capacitance, and V_{GS} is the gate−source voltage. These parameters can be used to analyze the responsivity characters of an OFET sensor. The mobility and threshold voltage of monolayer pentacene-based devices are 0.01 $cm^2/(V\ s)$ and −11.8 V, respectively. The mobility and threshold voltage of a thick-layer pentacene film of 50 nm are also evaluated as 1.4 $cm^2/(V\ s)$ and −2.9 V, respectively, as shown in the inset of Figure 2c. The drain current from the monolayer OFET is 2 orders of magnitude smaller than that of the thick-layer OFET. The small drain currents usually do not benefit a conventional OFET, but they are well suited to explore a high sensing response to a gas molecular analyte.

The sensing response of these devices to NH_3 gas was tested in a homemade vacuum probe stage, as described in the Experimental Details section. Figure 3a displays the transfer curves of the monolayer pentacene OFET with different NH_3 concentration. The drain current changes quickly when the atmosphere is changed. A detection limit of better than 20 ppm for monolayer OFET has been unambiguously demonstrated. The sensitivity S_{FET}, defined as the percentage change in the drain current, is presented by

$$S_{FET} = (I_{NH_3} - I_{N_2})/I_{N_2} \times 100\% \tag{2}$$

Here I_{NH_3} stands for the drain current under various concentrations of a NH_3 atmosphere and I_{N_2} stands for the drain current under an inert atmosphere. The sensitivity increases with the concentration of NH_3 gas, as shown in Figure 3c. It is noted that the drain current nearly restores its original value after NH_3 is purged. We carried out experiments for confirmation of the device reversibility. In this case, the device was exposed to 50 ppm concentration of NH_3 and measurements were done for 1 min. The same experiment was subsequently repeated three times at the same conditions. The measurements indicated that there is only a small variation in the current values even after the third time of exposure. We found that after all regeneration the current remains almost the same although with a decrease of 6.7% (Figure S1 in the SI).

For comparison, the sensing performance of a thick film (50 nm) of pentacene is tested in Figure 3b, which shows significantly lower response to NH_3 gas than that of a monolayer device. The comparison of the sensing performances of ultrathin and thick films with different concentrations of NH_3 gas is shown in Figure 3c. The error bar of Figure 3c is also calculated and displayed in Figure S3 in the SI. We extended the exposure time of NH_3 gas for 10 min. Even with increasing exposure time, the thick layer does not allow much analyte to the interface compared to our monolayer film device. So, the sensitivity of the thick layer is much less than that of the monolayer device. In the case of monolayer pentacene-based OFET, the charge carriers become more influenced by environmental effects than the thick layer. This can easily be understood because thick films create barriers for the interaction of the analyte with the conductive channel of the organic semiconductor; therefore, they show low sensing behavior.

To investigate the sensing mechanism, it is necessary to determine the factors that affect the drain current when NH_3 gas is let in and out. In fact, the structural deviation from the perfect arrangement and thermal motion of the molecule result in electronic trap states in the film, which is expected to be of an intrinsic nature of an organic small molecule. For the specific situation in the monolayer film, a high density of structural defects is found within grain boundaries, where the trap states can be induced because of both extrinsic and intrinsic defects. The intrinsic defects deduced from the bias-stress measurements for the sample grown under the similar conditions[24] are in the range of 10^{12} cm^{-2}. These defects cause charge carrier trapping and reduce the drain current and the effective field-effect mobility. When exposed to a polar molecular atmosphere (NH_3 in our case), because of their dipole nature, the analyte molecules present on the grain boundaries behave as extrinsic defects and trap the mobile charge carriers from the channel and hence yield a disorder dipole−charge interaction. Usually the trap density of extrinsic defects is much smaller than that of intrinsic defects, when the analyte molecules are few. In order to enhance the detection sensitivity, extrinsic defects need to be compared with or surpass intrinsic defects.[25]

Figure 4a displays the sensing mechanism of monolayer and thick-layer pentacene-based OFETs. Because eq 1 shows that the changes in the drain current are affected by the mobility and/or threshold voltage, we investigated the transfer curves before, during, and after NH_3 gas exposure (Figure 3a) and also determined the device parameters such as the mobility and threshold voltage from the series transfer curves. The data are also summarized in Table 1. When NH_3 gas is exposed, a mobility decay of about 60% occurs and the threshold voltage shifts negatively from −11.8 to −29.2 V. This shift in the threshold voltage is assigned to the presence of additional trapped charges Q_t owing to the introduction of extrinsic defects of analyte molecules at the pentacene−dielectric interface, as shown in Figure 4a. The shift of the threshold voltage with a change in the concentration of NH_3 gas of the monolayer device is shown in Figure 4b, and we deduced the trapped charge density from the threshold voltage. These trapped charges in the pentacene film influence the local electric field and become the cause of the threshold voltage shift.

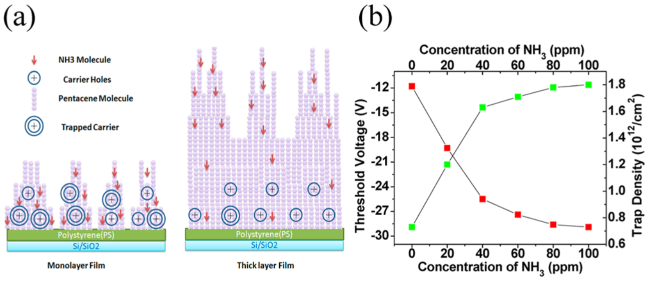

Figure 4. (a) Sensing mechanism of monolayer and thick-layer devices by a schematic illustration. (b) Threshold voltage (V_{th}) (Red square) of the monolayer device as a function of the NH_3 concentration, as well as the trap density (Green square) of the monolayer device extracted from the threshold voltage according to eq 4

Table 1. On Current, Mobility, Threshold Voltage, and Trap Density of a Monolayer Device Exposed to Different Concentrations of NH_3

NH_3 concentration (ppm)	on current (10^{-6} A)	mobility [(10^{-3}) cm^2/(V s)]	threshold voltage (V)	trap density (N) 10^{12}/cm^2
0	1.39	10	−11.8	0.73
20	0.872	8.0	−19.3	1.20
40	0.552	6.0	−25.5	1.63
60	0.297	4.8	−27.4	1.71
80	0.210	4.0	−28.6	1.78
100	0.111	3.7	−28.9	1.80

This effect can be evaluated by the following equation:[26]

$$Q_t = \Delta V_{th} C_g \tag{3}$$

where C_g is the dielectric capacitance per unit area. The trapped charge carrier density can be estimated as[27]

$$\Delta n = \Delta V_{th} C_g / q \tag{4}$$

that is, 7.37×10^{11} cm^{-2} in a N_2 atmosphere, 1.20×10^{12} cm^{-2} in 20 ppm of NH_3, 1.63×10^{12} cm^{-2} in 40 ppm of NH_3, 1.71×10^{12} cm^{-2} in 60 ppm of NH_3, 1.78×10^{12} cm^{-2} in 80 ppm of NH_3, and 1.80×10^{12} cm^{-2} in 100 ppm of NH_3, and is shown in Figure 4b.

We assume that the trapped charges may have some chemical reaction with a pentacene molecule as in the case of oxygen,[28] resulting in device performance degradation. However, this degradation is essentially reversible when exposed to nitrogen gas owing to weak molecular van der Waals interaction. In the case of a thick film, the structural interconnection is large; the thickness of the film reduces analyte diffusion into the active channel area, which results in a low sensing response.

CONCLUSION

In conclusion, a novel fabrication technique for an ultrathin organic film grown via vacuum deposition, combined with the direct soft-imprinting gold electrodes, has been developed enabling an OFET gas sensor to realize much higher sensing response to NH_3 gas, having a monolayer device with top-contact configuration, than the conventional counterpart with a 50-nm-thick active layer. This sensitivity enhancement was attributed to an increase of charge trapping in the transport channel. The trap density and its influence on transport in devices before and after exposure to a NH_3 molecular analyte have been systematically analyzed, and the possible mechanism has also been proposed. Our results offer great promise for the realization of high sensitivity up to a detection limit of the 10 ppm level on sensor devices and may stimulate researches for optimizing the design of OFETs for better functional applications.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Information about the recovery of a device and its reproducibility, comparison of transfer curves of 50 ppm concentration in vacuum and air, and error bars of Figure 3c for thick-layer and monolayer sensitivity. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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