Response enhancement mechanism of NO$_2$ gas sensing in ultrathin pentacene field-effect transistors

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**A B S T R A C T**

By optimization of structural and physical–chemical properties at a precision level of molecules, organic sensing devices seek to realize the state of the art in monolayer based device applications. In our work, pentacene ultrathin film transistor has been integrated into the implement of a gas sensor based on an increase in its mobility and a shift of its threshold voltage. A limit of detection of pentacene monolayer field-effect transistor was found to be at sub ppm level when it is applied for detection of NO$_2$. Compared with a thick layer sensor device, the pentacene monolayer NO$_2$ sensor has boosted up sensing response with three orders of magnitude. An enhancement of high selectivity and response mechanism can be understood with a reasonable description emphasizing on the 2D transport characters and a series of gauzy interplay for monolayer pentacene film with NO$_2$ analyte.

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1. Introduction

In recent years, much research efforts have been devoted to gas sensors due to the fact of severe air pollution. NO$_2$, a main pollutant arising from combusted fuel, can cause photochemical smog, acute pulmonary, acid rains, edema, and irritation of eyes and is even suspected to cause cancer [1–3]. To date, commercial NO$_2$ sensors are usually bulky, have low selectivity and high power consumption. Therefore, it is highly desirable to develop novel gas sensors that are endowed with efficient manufacturing, high throughput, and good device performance such as high sensitivity/selectivity, light weight and low power consumption.

As a sensor alternative, organic field effect transistor (OFET) has been demonstrated and continuous demand for electronic sensor technology is a motivating initiator for its development. A typical OFET gas sensor is achieved by non-covalent bond interaction between analytes and organic semiconductors. The field effect mobility, on/off ratio, threshold shift and change in conductivity used to characterize the sensing response of an OFET sensor for a given gaseous analyze constitute the output parameters. Therefore, an enhancement interaction between the electronic sensors with them is foreseen as a core element in intriguing OFETs capable of detecting and delivering such responses.

Recently, the investigation of ultrathin transistors has got attention as an attractive research subject especially in sensor technology due to its prominent properties such as quick adsorption, diffusion and desorption thus facilitating high performance sensors which are significantly desired for uses. Furthermore, it provides a chance to clarify response mechanism with a deep insight into physics of device as the conductive channel locates at the interface between organic semiconductors and the dielectric [4]. The ultrathin transistors-based sensors allow fabrication of devices by direct investigation of film morphology effect on device physics, thus opening the door for enhanced sensitivity and less recovery time, low cost and accelerating the interaction between conductive channel and the analyte. Zhang et al. fabricated the ultrathin film organic transistors by spin coating method [5]. Yang described the ultrathin organic transistors for chemical sensing [6], Li et al. reported high performance ammonia sensor using ultrathin organic semiconductor film [7]. Hetero-structure of PTCDI-Ph and ultrathin film of p-6P based NO$_2$ sensor in organic filed effect transistors had shown a good sensitivity [8]. However, few deep response mechanisms were discussed in these works and there were few reports for connecting the highly sensitive OFET-based sensors with its two dimensional (2D) transport characters.

This paper aims to implement novel organic semiconductor gas sensors and decipher the structural chemistry of pentacene ultrathin film and proposed mechanism for interaction between NO$_2$ gas analyte and pentacene ultrathin film. The threshold shift, drain...
current and mobility variations as a consequence of NO₂ analyte are described more relevantly. The limit of detection of our ultrathin pentacene device is 100 ppb (at sub ppm level), which is much higher than pentacene thick layer counterpart. The selectivity of our ultrathin pentacene device is not taken as for granted, rather we discriminated our monolayer devices for CO, CO₂, N₂O and NH₃ gases as well.

2. Experimental

Pentacene (99% pure) purchased from Sigma Aldrich was used without further purification. All reagents (ethanol, acetone, HCl, H₂O₂) used were analytical grade. The used deionized water was prepared using Milli-Q Millipore (Bedford, MA, USA) purification system and the resistivity of water was about 18 MΩ cm⁻¹. The elastomeric polymer (PDMS) stamp replication from SU-8 pattern was prepared using conventional photolithography as illustrated in our previous work [16]. After cleaning Si wafer with ethanol, acetone and HPM (HCl:H₂O₂:H₂O = 1:1:6) a negative photo-resist of SU-8 was spin coated. The substrate was heated for few minutes. After exposing UV through photo-mask, the SU-8 thin film was developed. An elastomeric polymer (PDMS) was poured onto SU-8 mold. PDMS was peeled off from SU-8 mold after the curing process. An 80 nm thick gold electrodes were evaporated on polymeric stamp as metal electrodes with channel length \( L = 100 \mu m \) and width \( W = 3000 \mu m \). In the fabrication of device, heavily doped silicon with thermally grown SiO₂ of thickness 300 nm was used as substrate. Toluene solution of polystyrene (PS) was spin coated on SiO₂ as hybrid dielectric layer. After that pentacene monolayer film of 1–4 nm was deposited by Auto 306 (BOC Edward Co.) with a deposition rate of 1.25 nm/min evaporated at a vacuum pressure of 10⁻⁵ Pa. The morphology of pentacene monolayer film was characterized by a Nanoscope III (Vecco Co.) atomic force microscopy with tapping mode. The schematic diagram of device for NO₂ sensor is shown in Fig. 1a. The sensing chamber was kept at 1 atm pressure to provide inert atmosphere of N₂. The diluted NO₂ gas was introduced into the sensing chamber using mass flow controller (MFC). The current–voltage characteristic of pentacene monolayer OFETs were measured by Keithley 4200 SCS instrument at room temperature.

3. Results and discussion

The carrier transport in OFETs involves charge migration through conducting channel within a grain and across the grain boundaries. OFETs are interfacial devices and dielectric layer interfacial properties influence the carrier transport hence its mobility. The charge carrier mobility in OFETs is normally determined by the molecular orientation, grain size and grain boundaries especially located at the dielectric/semiconductor interface [9–13]. Each of them usually plays a vital role in the OFET sensing processes. The modulation in mobility and drain current occurs when analyte interact with conductive region. The interacted analyte may act as either dopants or traps for charge carrier [14]. For charge transport in OTFT, a continuous and highly ordered semiconducting layer is prerequisite, while for gas sensors, ultrathin thickness of the active layer is accessible so that it can reduce the time of absorption/desorption of analyte with a good electrode contact from the device conductive channel [15]. It is noteworthy that continuous ultrathin film growth is rather a challenging task. We have reported the fabrication of novel top contact pentacene ultrathin field effect transistor in a controllable manner (as explained in our previous work) [16]. To avoid the penetration of direct evaporation of gold into monolayer film we fabricated flexible electrodes.

The schematic diagram of monolayer pentacene device is shown in Fig. 1a. The charge carrier mobility evaluated from transfer curve in the saturation regime (as shown in Fig. 1c) can be obtained using the equation [17]:

\[
\mu = \frac{V_{th} - 0.45V}{V_{DS} - V_{th}} \times \frac{(10^6)^{2}}{V_{DS} - V_{th}}
\]
where \( W \) and \( L \) are channel width and length while \( V_{GS} \) is gate voltage, \( V_{th} \) is threshold voltage, \( C_{i} \) is dielectric capacitance per unit area, \( \mu \) is mobility and \( I_{DS} \) is drain current. The mobility of our top contact ultrathin pentacene device is 0.038 cm²/Vs and threshold voltage is −35.5 V and on/off is 10⁶. Typical transfer (\( V_{DS} = −60 \), \( V_{GS} = −60 \)) and output curves of ultrathin pentacene device are illustrated in Fig. 1 and d, respectively. AFM image as shown in Fig. 1b indicates morphology of pentacene ultrathin film.

Fig. 2a shows the transfer characteristics at room temperature for various concentrations of NO₂ gas analyte. The plots show increase in drain current with increasing the concentration of NO₂ analyte. The sensitivity response of these devices to NO₂ analyte was evaluated by using the following equation:

\[
\% \Delta S = \left( \frac{I_{DS} - I_{DS0}}{I_{DS0}} \right) \times 100
\]  

The concomitant change in threshold voltage and mobility are used to characterize the sensing property. It is anticipated that these effects result in change of drain current. The change in threshold voltage and mobility with different concentration of NO₂ analyte exposure is illustrated in Fig. 2b. The sensitivity increase with respect to various concentrations is plotted in Fig. 2c along with increase in drain current. The sensitivity presents an increase over 1300% by enhancing on current \( I_{DS0} \) and mobility change with even exposure of a small amount of 2 ppm NO₂. When the exposure amount of NO₂ increases to 10 ppm, the sensitivity keeps on increasing to around 3000% and then goes to saturation with further NO₂ exposure. The sensing response of thick layer pentacene devices is 10⁷ orders less than ultrathin devices. The enhanced mobility in our ultrathin devices, by controlling the gas ambience, could provide opportunities to improve the performance of OFETs.

The limit of detection is expressed as a concentration corresponding to the smallest signal that can be detected with reasonable certainty for a given analytical procedure. Using Fig. 2c for concentration dependent sensitivity response of the monolayer pentacene OFET, we can extract the limit of detection using following equation [18].

\[
Y_{LOD} = \left\{ \frac{-ab + \sqrt{a^2b^2 - (b^2 - \eta^2\Delta b^2)(a^2 - \eta^2\Delta a^2)}}{b^2 - \eta^2\Delta b^2} \right\}^{\frac{1}{2}}
\]  

In this study, the value of \( \eta = 2.58 \) corresponding to 99% confidence level is shown in Fig. 2d. The \( \eta \) is the confidence factor used in statistical calculation to estimate mean and standard deviation more reliably that is why also named as reliability factor. The value of limit of detection is 100 ppb (sub-ppm level). To the best of our knowledge, this sensitivity is the highest for any pentacene based sensors because of its ultrathin thickness.

To confirm the reproducibility of our ultrathin OFET sensors, nine cycles were carried out at 0.5 ppm concentrations (shown in Fig. 3a). The excellent performance under varying NO₂ concentrations and good reproducibility make our sensor suitable for a trace analysis and quantitative detection. The response/recovery time for 0.5 ppm NO₂ is less than 20 s.

We also accomplished experiments for CO, CO₂, N₂O and NH₃ gases. The CO, CO₂, N₂O gases did not show any response for monolayer pentacene devices but NH₃ showed response as described in our previous work. Remarkably the sensitivity of NO₂ gas is the highest among all gases we analyzed (Fig. 3b) which provide potential strategy to suppress the poor selectivity for organic semiconductor sensors.

To study the response mechanism for such an ultrathin NO₂ sensor, understanding of the decisive factors of transport in organic field effect transistors is imperative. As our device is of few monolayer, prospect of NO₂ analyte to reach on these interfaces is tremendous. The high sensitivity response of ultrathin devices can be attributed to a synergy enhancement effect combining a strong electron affinity of NO₂ and a pure 2D transport character where grain boundaries are highlighted.

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**Fig. 2.** (a) Transfer curves of monolayer film exposed with different concentration of NO₂ gas analyte. (b) Threshold voltage and mobility change with respect to concentration of NO₂. (c) The sensitivity percentage change and drain current change for different concentration of NO₂. (d) Limit of detection calculation.
NO₂ being a strong electron acceptor absorb electron thus generates holes while interacting with pentacene film. Therefore, carrier concentration of devices becomes high in the devices which are exposed to NO₂ molecules. The initially injected carriers first fill the traps under the transport band or transport energy level and then move to flow current. The carrier concentration is found to be mobility dependent by power law $\mu (n) \propto n^a$ which is consistent with energetic disorder model [19]. The charge carrier mobility is dependent on carrier concentration [20–22] which means higher the carrier concentration larger is the charge carrier mobility.

Another key point is the large sensitivity of the ultrathin devices. As proved in our previous work of electric field dependent mobility [23], in pentacene based monolayer transistors the grain boundaries play a vital role in the charge transport progress. The charge carriers will inevitably go into grain boundaries without upper grains acting as a bridge over grain boundaries, which make the transport feature of grain boundary more dominate. A large amount of trap states are distributed in grain boundaries as they are sites of much more disorder. As illustrated in Fig. 4, in monolayer devices the gas molecules interact directly with the grain boundaries, generating large number of holes. These holes enter quickly into localized states making the extra holes to transport smoothly through the energy level with higher density of states, thus increasing the charge carrier mobility. Conversely in thick layer devices, the grain boundaries in first monolayer are covered by the grains of upper layer. The charge carriers present in the first monolayer will go through a specific path to connect to grains in the second layer, making the grain boundaries less important in charge transport. Additionally, the increase in number of holes will not have much influence on the mobility within the grains as the grains near the conductive channel are not directly exposed to the gas analyte, in a consequence not influencing the grain boundaries too.

The above analysis can be further consolidated by the analysis of trap density. During the exposure of NO₂ analyte large amount of deep traps in the grain boundaries are massively filled, or equivalently the NO₂ analyte reduces the trap density, decreasing the trapping probability of injected holes by gate voltage, which can be reflected by sub threshold swing (SS):

$$SS = \frac{\partial V_D}{\partial (\log_{10} I_D)}$$

From the sub-threshold swing the effective trap density can be extracted by equation [24]:

$$N = \frac{C}{q} \left( \frac{qSS}{kT \ln 10} - 1 \right)$$

Fig. 3. (a) Time response of nine successive cycles of NO₂ sensor of pentacene monolayer device. (b) Pentacene monolayer device selectivity for five different gases.

Fig. 4. (a) The schematic images of the monolayer device with DOS. (b) Monolayer device with NO₂ analyte exposure. (c) Thick layer with NO₂ analyte exposure.
Fig. 5. Sub-threshold swing (SS) and trap density change for various concentration of NO$_2$.

where $k$ is Boltzmann's constant, $T$ is absolute temperature, $q$ is electronic charge and $C$ is the dielectric capacitance. It is clear from Fig. 5 that the exposure of NO$_2$ analyte decreases the trap density.

The trap density extracted from SS in N$_2$ atmosphere is 1.13E12 cm$^{-2}$ while for 2 ppm NO$_2$ is 4.23E11 cm$^{-2}$. The trap density for different concentration of NO$_2$ are evaluated and shown in Fig. 5. The trap density shows an abrupt change with NO$_2$ exposure. We also carried out experiments for thick layer pentacene film but the sensitivity was poor (three orders of magnitude less) as compared to monolayer counterpart. The increase in mobility and positive shift of threshold voltage in ultrathin pentacene film can also be understood by change in density of trap states due to NO$_2$ exposure.

4. Conclusion

In conclusion, NO$_2$ gas sensing with ultrathin pentacene film with near one whole monolayer coverage has shown excellent sensor performance including high sensitivity, fast response/recovery time, good selectivity, low concentration detection capability, excellent reproducibility. The ultrathin pentacene devices allow direct adsorption of the gas molecules in the conductive channel and decrease the carrier trap density, thus increasing the mobility. More physical explanation is resorted to the combination of strong electron affinity ability of NO$_2$ and grain boundary dominated 2D transport. This study may pave a boulevard towards developing highly sensitive room temperature NO$_2$ semiconductor sensor and enhanced mobility provides promising route in improving the performance of OFETs.

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