Gas Dielectric Transistor of CuPc Single Crystalline Nanowire for SO₂ Detection Down to Sub-ppm Levels at Room Temperature

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Sulfur dioxide (SO₂) is one of the most dangerous air pollutants that impair environment and human health. SO₂ in air is released during the burning of fossil fuels and plays one major role in the formation of acid rain. The repeated exposure to low levels of SO₂ can cause permanent pulmonary impairment for humans. The long and short-term exposure limits for SO₂ gas are 2 and 5 ppm, respectively, and the U. S. Environmental Control Agency has set the acceptable limit for SO₂ in ambient air at a level of 0.5 ppm. It is of great importance to measure low concentration of SO₂ in air accurately and fast for human health protection and air-quality monitoring.

Semiconductor resistor sensors are, for more than 30 years, one of the most common used gas sensors to detect toxic and flammable gases such as NO₂, H₂S, CO, NH₃, and H₂ because of their distinguished merits such as low cost, long lasting, high sensitivity, and good reliability, etc. Organic field-effect transistor (OFET) is another alternative semiconductor sensing technology with advantages over resistors, and has attracted much attention only recently. The sensitivity can be dramatically enhanced by changing the source-drain current (I_SD) of OFET when operating the sensors in the sub-threshold regime, as a result of the current modulation by the extra gate electrode. Another advantage of OFET sensors is that the sensing response can be enhanced by integrating them in oscillator and adaptive amplifier circuits. These advantages combined with low cost and light weight of organic semiconductors ensure that OFET sensors have attracted much attention for the detection of a wide range of gases.

However, only few efforts have been made to develop the semiconductor SO₂ sensors and almost all of them are resistor-type (a detailed performance list for the reported semiconductor SO₂ sensors is shown in Supporting Information Table S1). The semiconductor materials are mainly focused on metal oxide, such as SnO₂, WO₃, and TiO₂. Most reported semiconductor SO₂ sensors require an operating temperature of 200–600 °C, demonstrate a sensitivity lower than 50%, face challenges in low concentration detection, or suffer from a slow response and recovery time of over 10 min.

In this communication, an OFET based on gas dielectric and CuPc single crystalline nanowire as a novel SO₂ sensor with complete recovery and room-temperature detection is reported. To the best of our knowledge, this is the first demonstration of SO₂ gas sensing based on OFETs. The sensitivity is characterized by the enhanced field-effect mobility and is as high as 764% in 20 ppm SO₂. The detect limitation is down to sub-ppm levels (0.5 ppm) with high sensitivity (119%) and high resolution (100 ppb). The exposed conductive channel is shown to be responsible for the sensitivity to SO₂.

Figure 1a shows a schematic image of the gas dielectric field-effect transistor (FET) sensor based on CuPc nanowire and the adsorption of SO₂ molecules on CuPc nanowire surface in ambient N₂ environment (not to scale). Figure 1b is the SEM image of the device. The device is fabricated by the “gold film stamping” method (Figure S1), and has the stable field-effect characteristics (Figure S2). Figure 1c shows five cycles of the real-time I_SD responding to the dynamic switches in pure dry N₂ and the different SO₂ concentration (0.5–20 ppm) at room temperature (test details are available in Supporting Information Figure S3). I_SD changes fast and reversibly when the atmosphere is changed, and fully restores its original value after SO₂ is removed. No heating is required in the whole test process. The limit of detection (LOD) is down to 0.5 ppm, which is in a class with the highest detection limit for the semiconductor SO₂ sensors reported so far (Table 1). The response and recovery times of the device in 0.5 ppm SO₂ are only 3 and 8 min, respectively. Considering that the switch time of the SO₂ concentration is over 0.5 min in our equipment, the real response and recovery times are expected to be shorter than the measured results. Figure 1d shows the sensitivity (S) of the gas dielectric FET as a function of SO₂ concentration at room temperature. The sensitivity is calculated by S = (I.SO₂ - I.N₂)/I.N₂ × 100%, where I.SO₂ and I.N₂ are the current in pure N₂ and SO₂ containing atmosphere, respectively. With the increase of the SO₂ concentration, the sensitivity first increases linearly, and then trends to saturation. The sensitivity of the device in 0.5 ppm SO₂ is as high as 119%. Considering that 0.5 ppm is the control limit of our equipment, it can be predicted that the real LOD is much lower than 0.5 ppm. Combined with the linear sensitivity dependence on the concentration, the nominal range of the device is expected to be 0–5 ppm. The sensitivity change in the linear region from 0.5 to 5 ppm is 20% per 100 ppb SO₂, corresponding to a concentration resolution of 100 ppb. Therefore, our device is applicable for the detection of SO₂ at very low concentration. At the same time, the notable

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merits such as quantitative detection, direct electrical readout, and simplified correction process and auxiliary circuits are expected for our OFET because of its linear sensitivity in low concentration range. It is worth noting that many sensing parameters of our devices present excellent values, such as sensitivity, LOD, response time, recovery time, resolution, and operating temperature.\(^1,9\) Some of them are comparable to the commercialized solid electrolyte sensors.

For FETs, there are a few fundamental parameters to evaluate their performance, including mobility $\mu$, threshold voltage $V_T$, on-state current $I_{on}$, off-state current $I_{off}$, sub-threshold slope $SS$, etc, which reflect the transport processes of carriers in FET and depend on the properties of semiconductor, dielectric, electrode, device configuration, and fabrication technique. These parameters can be used to study the response mechanism of FET sensor.\(^{10}\) Figure 2a is the transfer curves of the gas dielectric FET in different SO$_2$ concentration. The multiple parameters of the FET can be extracted from Figure 2a, and their percentage changes are presented in Figure 2b as a function of SO$_2$ concentration by $P = (P_{SO2}/P_{N2})/P_{N2} \times 100\%$. It is found that $V_T$ and $I_{off}$ show the weak change lower than 5% and $SS$ decreases 22% in 20 ppm SO$_2$ (Figure 2c). However, both $I_{on}$ and the mobility present dramatically change with the increase of over 750% in 20 ppm SO$_2$. The enhanced mobility in our device could open up opportunities to improve the performance of OFETs by the controlled gas ambience.

The synchronous change of $I_{on}$ and mobility as shown in Figure 2b suggests that the mobility determines the response of our device to SO$_2$, in contrast to most reported FET sensors in which the shift of the threshold voltage is used to characterize the gas sensing.\(^6,11\) To study the response mechanism of our sensors, it is important to understand the decisive factors of the field-effect mobility. Based on the widely accepted theory of the carriers transport in organic semiconductor, the effective field-effect mobility is related to shallow traps at the semiconductor/dielectric interface, and can be well described by the standard multiple trap and release (MTR) model with the following equation:\(^{12}\)

$$\mu = \mu_0 \frac{\tau_{diff}}{\tau_{diff} + \tau_r}$$

\(^1\) Figure 1. a, b) The schematic and SEM images of gas dielectric FETs based on CuPc Nanowire. The channel length $L = 3.3 \, \mu m$, the width $W = 210 \, nm$ (width of the nanowire), and the thickness of the dielectric $d = 200 \, nm$. c) Real-time $I_{SD}$ change of device to various SO$_2$ concentration (0.5, 2, 5, 10 and 20 ppm) at $V_C = -10 \, V$ and $V_{SD} = -15 \, V$ at room temperature. The blue line corresponds to SO$_2$ concentration (right y-axis). d) Sensitivity of device as a function of SO$_2$ concentration at $V_C = -10 \, V$ and $V_{SD} = -15 \, V$ at room temperature. The red line is the linear fitting result in low concentration SO$_2$.

\(^2\) Figure 2. a) Transfer characteristics of gas dielectric FET based on CuPc nanowire to various SO$_2$ concentration (0, 0.5, 2, 5, 10 and 20 ppm) at room temperature. b,c) Parameters percentage variation at different SO$_2$ concentration extrapolated from $I_{SD}$-$V_C$ curves (in Figure 2a). d) Mobility and trap density in semiconductor/dielectric interface of device as a function of SO$_2$ concentration.
where $\mu_0$ is the intrinsic trap-free mobility, $\tau_D$ is the average carrier retention time in shallow traps, and $\tau_{\text{diff}}$ is the average time of carrier diffusion between shallow traps. In the devices with the low density of shallow traps, $\tau_{\text{diff}} > \tau_D$, and $\mu = \mu_0$. However, in the trap-dominated devices, $\tau_{\text{diff}} < \tau_D$, and $\mu = \mu_0$ ($\tau_{\text{diff}}/\tau_D < \mu_0$). In our experiment, the mobility of the CuPc device is $-0.005 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is not only lower than that of our previously reported result ($0.75 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),[33] but also far lower than the reported highest mobility by Kloc’s group (1 cm$^2$ V$^{-1}$ s$^{-1}$).[14] Therefore, high-density shallow traps are located at the semiconductor/dielectric interface in our sensor.

The density of trap states $N$ can be characterized by the sub-threshold slope $SS$ with the equation:[13]

$$SS = \frac{kT}{q} \ln 10 \left(1 + \frac{qN}{C} \right)$$

where $k$ is Boltzmann’s constant, $T$ is temperature, $q$ is electronic charge. $1.6 \times 10^{-19}$ C and $C$ is the dielectric constant. According to the transfer curves in Figure 2a, the SS is extracted from the slope of the log($I_{\text{on}}/I_{\text{off}}$) versus $V_G$ curve in the sub-threshold region with $V_G$ from the switch-on voltage to the threshold voltage.[13] The calculated SS of the gas dielectric CuPc nanowire FETs in N$_2$ is 2.78 V/decade, from which an shallow trap density of $1.3 \times 10^{12}$ cm$^{-2}$ V$^{-1}$ can be obtained using Equation (2). It is comparable with the CuPc thin film FETs on the order of $2 \times 10^{12}$ cm$^{-2}$ V$^{-1}$.[13] and is one order higher than that of our gas dielectric CuPc nanowire devices with the mobility over 0.5 cm$^2$ V$^{-1}$ s$^{-1}$. It further confirms the presence of the high shallow trap density in the conductive channel, i.e., the CuPc nanowire/gas dielectric interface, for our sensor.

Based on the transfer curves in Figure 2a, the mobility and the density of the shallow trap at the semiconductor/dielectric interface in the different SO$_2$ concentration are extracted and shown in Figure 2d. The notably improved mobility can be observed by introducing SO$_2$ gas into the N$_2$ ambient. Both the mobility and the shallow trap density show the steep change in the low SO$_2$ concentration and then trend to saturation in the high SO$_2$ concentration. The similar rule of the shallow trap density as for the mobility on the SO$_2$ concentration suggests that the compensation of the SO$_2$ molecules into the shallow traps is the possible reason for the notably changed mobility. Since SO$_2$ is a polar molecule with the positive charge on S atom side, its positive side probably interacts with the conduction channel. However, for the gas dielectric devices, all the surfaces of CuPc nanowire, in particular, the surface as the conductive channel in the semiconductor/dielectric interface, are exposed to the detected gas (Figure 1a). Therefore, it is an ideal method to investigate the response of the conductive channel of FETs to the atmosphere environment by comparing the gas and solid dielectric FETs.

Figure 3b shows the transfer curves of the solid dielectric FETs in different SO$_2$ concentration. According to Figure 3b, the $\mu$, $V_T$, $I_{\text{on}}$, $I_{\text{off}}$, SS in different SO$_2$ concentration are calculated, and the percentage changes of these parameters are obtained and shown in Figure 3c. Figure 3b presents the overlapped transfer curves in the SO$_2$ concentration lower than 5 ppm, suggesting no obvious response in low level of SO$_2$ for the solid dielectric FET. When the concentration is higher than 5 ppm, the solid dielectric FET exhibits weak response. The LOD decreases by over one order of magnitude (from 10 to 0.5 ppm) when the device configuration is changed from solid to gas dielectric. Based on the $I_{\text{on}}$, the sensitivity at $V_G = -10$ V is only about 40% in 30 ppm SO$_2$ (Figure 3c). In comparison, the gas dielectric FET shows the sensitivity of about 800% in the same SO$_2$ concentration (Figure 2b). The histogram in Figure 3d clearly presents the dramatically improved sensitivity in different SO$_2$ concentration when the dielectric is changed from solid to gas state.

The compared results of the gas dielectric FETs with the solid dielectric counterparts indicate that the exposed channel is responsible for the dramatically improved sensing properties, which is in good agreement with the theoretical calculation in Figure 2d. For the resistor sensors, the current passes through the whole semiconductor section which acts as the conductive channel. However, the conductive channel of the FETs is located in a few molecular layers at the interface between the semiconductor and the dielectric.[16] It is possible that the gas adsorption in the conductive channel of FETs has the far larger influence than on the upper and side surface of the semiconductor layer. However, the conductive channel of the traditional solid dielectric FETs is capped by the semiconductor layer and the solid dielectric. In contrast, the gas dielectric makes the conductive channel exposed to the detected gas (as shown in Figure 1a), which facilitates the direct interaction between the gas molecules and the conductive channel resulting in the improvement of the sensing performance. Such a response mechanism endows the gas dielectric CuPc single crystalline nanowire FET with good sensitivity to other gases also, for example, NO$_2$. The selectivity, which is still challenging for semiconductor sensors, should be achieved for practical applications. Our preliminary results show the different OFET parameter change for SO$_2$ and NO$_2$, which provides a potential strategy to overcome the problem in poor selectivity for semiconductor sensors.[10] The sensing behavior of other gases will be investigated as well, and further systematic work is in progress.

In conclusion, the room-temperature gas dielectric CuPc nanowire FET SO$_2$ sensors with high sensitivity, low detection limit, fast response and complete recovery have been fabricated. The detect limitation is down to sub ppm levels (0.5 ppm) with the sensitivity of 119% and high resolution of 100 ppb. The sensitivity is as high as 764% in 20 ppm SO$_2$. The device shows a linear response in the range of 0.5–5 ppm. The response and recovery time in 0.5 ppm SO$_2$ are only 3 and 8 min,
respectively. The multiple parameter measurement indicates that the mobility change determines the response of the sensors. The high performance of the sensor originates from the exposed conductive channel by using a gas dielectric. It allows for the direct absorption of the gas molecules in the conductive channel, and decreases the shallow trap density. The excellent SO₂ sensing performance, which stems from the notably enhanced mobility, provides a promising route both to developing highly sensitive room-temperature semiconductor SO₂ sensors and improving the performance of the OFETs.

**Experimental Section**

Single crystalline nanowires of CuPc were synthesized by physical vapor transport method as previously described.[1] The PMMA in anisole was spin-coated onto the surface of the substrate with patterned Au/Ti electrodes as the dielectric. Electron Beam Lithography was used to remove part of the PMMA and to create a gap with width of 3–10 micrometers. The individual single-crystal nanowire and the Au films were successively transferred by the mechanical manipulation with the micropipettes of a Cascade 150M probe station with an optical microscope under ambient condition. The field-effect and the gas response properties of the devices were recorded with a Keithley 4200 SCS in a hommade stainless steel chamber at room temperature. Pure dry N₂ and SO₂ controlled by gas flowmeters are introduced to the chamber through stainless tube. SEM images were obtained on a Philip XL30 instrument.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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