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Copper phthalocyanine and Hexadecafluorophthalocyanine Enhancing Nitric Oxide Gas Sensitivity of *p*-Si NWs FETs

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Abstract

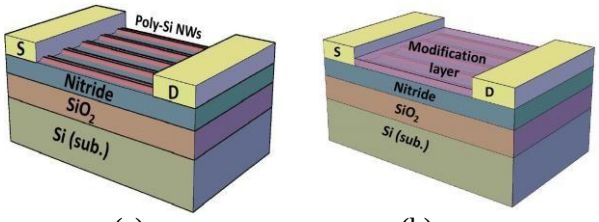
Copper phthalocyanine (CuPc) and copper hexadecafluorophthalocyanine (F16CuPc) were thermally deposited for surface modify the poly-Si nanowires field effect transistors (*p*-Si NWs FETs) for nitric oxide (NO) gas sensor. In particular, CuPc modified layer was found enhancing the detection toward low nitric oxide (NO) gas levels from 10 to 100 ppb. The experimental results suggested that over 30% enhancement can be found compared to the un-modified *p*-Si NWs FETs.

1. Introduction

Human breath contains various gases besides carbon dioxide and water vapor. Some species are considered as biomarkers for specific diseases. Ammonia (NH_3) in human breath, for example, is a typical symptom of server liver cirrhosis. Increasing nitric oxide (NO) concentration in breath also indicates airway inflammatory disorders such as asthma. The NO concentration in breath is found higher (25~50 ppb) when the initial stage of asthma than a healthy people (< 25 ppb.) It can be detected as five times more than its normal levels several hours before an asthma attack (100 ppb).[1] In this study, the poly-Si nanowires field effect transistor (NWs FETs) modified with copper phthalocyanine (CuPC), and copper hexadecafluoro-phthalocyanine (F16CuPC) are fabricated for NO gas sensor. The NWs FETs device has several advantages such as compact size, simple manufacturing process, low cost, low power consumption, short response time, and large surface-volume ratio [3-4]. When NO molecules accumulate on the chip, charge is transferred to the near the surface, and the electrical properties of the device are changed which achieves the purpose of detecting NO.

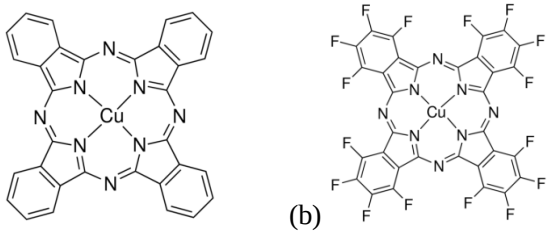
2. Experiments

The N-type poly-Si NWs FETs is a bottom gate FET which is shown in Fig.1 (a). Each poly-Si NWs FETs consists ten nanowires (NWs) with channel length (l) and width (w) of 2 μm and 80 nm, respectively [5]. The organic compound modified thin film was evaporated on the NWs surface by thermal coating to enhance the sensing properties, as shown in Fig.1(b). Both copper phthalocyanine and copper hexadecafluorophthalocyaine were purchased from Sigma Aldrich. Their chemical structures are shown in Fig. 2. The thickness of deposition film was controlled at ~3 nm with coating rate under 1Å /min. The experiment was conducted in the airtight chamber and controlled under a pressure of 500 torr with relative humidity 20%. The specific NO gas concentration was injected by mass flow controller (MFC). The electrical characteristic of Poly-Si NWs FETs was measured by a Keithley 2636 chip analyzer.



(a) (b)

Fig. 1 Scheme of the poly-Si NWs FETs (a) normal device; and (b) surface modified device



(a) (b)

Fig. 2 Chemical structure of (a) Copper phthalocyanine; and (b) Copper Hexadecafluorophthalocyanine

3. Result and Discussion

Metallophthalocyanine (MPC) complexes have been widely used as electrocatalysts for many reactions. These complexes could potentially be used as a NO sensor with the N-type poly-Si NWs FETs. The I_D-V_G curves of the normal device under various NO gas concentrations are shown in Fig. 3. The drain current was slightly decreased as the NO concentration increased. The NO molecule is considered as the electron acceptor which caused the charge to be easily transferred from gate channel to the target molecule.

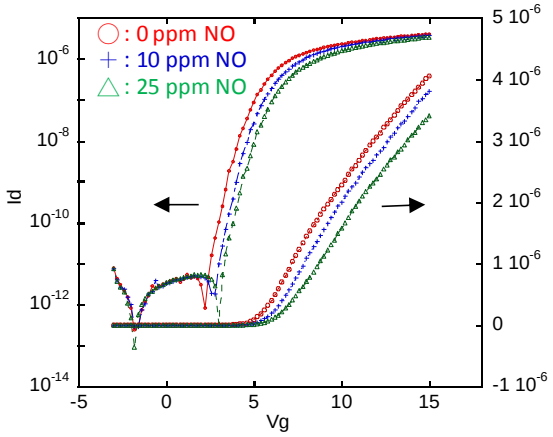


Fig. 3 The I_D-V_G curve of poly-Si NWs FETs under various NO concentrations.

The I_D-V_G curves of the surface modified poly-Si NWs FETs are shown in Fig. 4. From Fig. 4 (a) and (b), the drain current of the CuPC modified device greatly decreased with NO concentration from 0 ppb to 25 ppb. When the NO molecule was reduced, the center metal changed oxidation states upon interacting with the NO molecule and it recovered its initial oxidation state by accepting electrons from the gate channel. However, the F16CuPC modified device didn't show the same response due to the high electronegativity of surrounding florine atoms, so the redox reaction did not take place after gas exposure, which caused less transfer of charge.

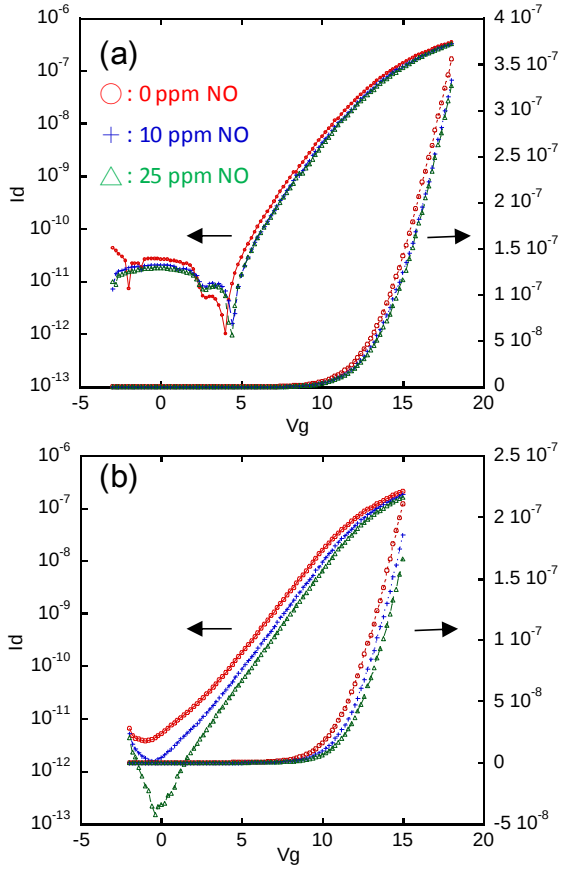


Fig. 4 The I_D-V_G curve of surface modified poly-Si NWs FETs under various NO concentration in the (a) F16CuPC ; and (b) CuPC devices

To quantify the sensing ability of poly-Si NWs FETs for NO gas, we used the drain current ratio which can be expressed the standard of sensing ability as defined in eq. (1).

$$Current\ Ratio = \frac{I_{D(NO)}}{I_D(base)} \quad \text{.....eq. 1}$$

Table I. Current ratio of each modified poly-Si NWs FETs

20% RH	0 ppb	10 ppb	25 ppb
Bare NWs	1	0.93	0.84
CuPC modified	1	0.78	0.67
F16CuPC modified	1	0.94	0.91

Bare NWs device shows around 15% decrease of current ratio at 25 ppb. Two organic materials above were used to increase sensing properties towards NO molecule. CuPC modified device shows 33% decrease at 25 ppb when the F16CuPC modified device only shows 9% decrease of current ratio. As the results, the CuPC complex has significantly improved the NO gas sensing properties.

4. Conclusions

In this paper, we have investigated the gas sensing properties of a surface modified N-type poly-Si NWs FETs. The sensor elements with the F16CuPC film showed slight change of current ratio after NO exposure, which means thin film blocked the reaction between target gas and sensor. However, the sensor elements with the CuPC film exhibited a distinct response to NO gas even at 10 ppb, the current ratio even decreased 33% when the NO gas concentration reached 25 ppb.

Acknowledgements

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