Extended Abstracts of the 2016 International Conference on Solid State Devices and Materials, Tsukuba, 2016, pp891-892

PS-11-01

A High Sensitivity Gas Sensor for Nitric Oxide: Poly-Si Nanowire FETs with Phthalocyanine Complexes Surface Modification

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Abstract

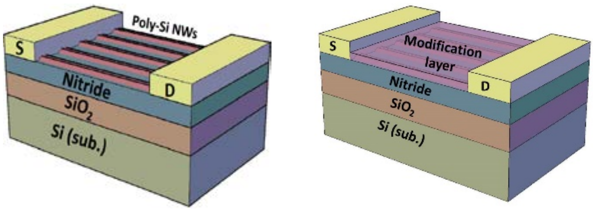
Noninvasive nitric oxide (NO) gas sensor based on polycrystalline silicon nanowire field effect transistors (poly-Si NWFET) with acceptor layer modification of transition metal phthalocyanine (Pc) complexes (Pc and NiPc) was fabricated in this study. The improved detection limit of $NO_{(g)}$ was 10 ppb, and linear range was measured from 10 ppb to 100 ppb. The results are applicable for asthma detection and monitoring.

1. Introduction

Poly-Si NWFETs have great potential for gas sensor application due to their low processing cost, ease of large area fabrications, flexibility on substrates, and high sensitivity [1]. In particular, the high sensibility of the target molecules at low concentration is a requirement for the breath diagnostic system. Elevated levels of fraction of exhaled nitric oxide (F_ENO) is a typical symptom of asthma. The American Thoracic Society (ATS) released a clinical guideline that suggested 25 ppb and 50 ppb as clinically significant cut points of F_ENO between low, intermediate and high F_ENO levels respectively, which may thereby be used to monitor inflammation levels in asthma. Monitoring F_ENO levels over time may be a useful noninvasive marker for evaluating response to or failure of medical therapy in COPD, pulmonary hypertension, and cystic fibrosis as well [2]. In this study, a nitric oxide gas sensor based on poly-Si NWFET modified with organic acceptor layers, phthalocyanine (Pc, or H_2Pc), and nickel phthalocyanine (NiPc) (see Fig. 2) is fabricated. The acceptor layer modified poly-Si NWFET targets the detection of low concentration (10 ppb) nitric oxide gas.

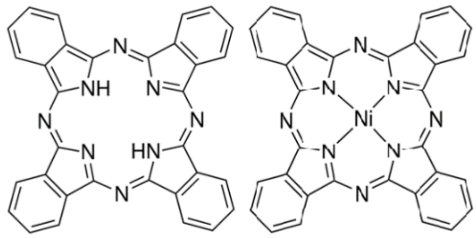
2. Experiment Methods

The n-type poly-Si NWFET consists of ten nanowires, the length (l) and width (w) is 2 μm and 80 nm respectively, and a bottom gate (see Fig. 1 (a)). The organic acceptor layer of 3.5-nm uniform thickness is thermally evaporated on the oxygen passivated poly-Si NWFET (see Fig. 1 (b)). Electric properties of poly-Si NWFET were measured by Keithley 2636 semiconductor analyzer. $NO_{(g)}$ concentration was controlled in the chamber by adjusting the mass flow controller. General procedure for measuring the electric properties of poly-Si NWFET is placed under various $NO_{(g)}$ concentrations (0, 10, 25, and 100 ppb, diluted with $N_{2(g)}$) at 650 Torr with relative humidity at 40 ± 2% at room temperature.



(a) (b)

Fig. 1 Schematic of the (a) poly-Si NWFET (b) modified poly-Si NWFET



(a) (b)

Fig. 2 Chemical structure of (a) Pc, and (b) NiPc

3. Results and Discussions

NO is known to chemisorb into silicon surface defects (ex. missing dimer) and grain boundaries [3].The I_{DS} current decreased significantly with larger V_{th} after exposure to 10 ppb of $NO_{(g)}$, and further decreased with higher concentrations. This indicated that $NO_{(g)}$ (an strong electron withdrawing gas) interacted with the n-type poly-Si surface causing electron reduction (i.e. electron trapping) and ionized impurity scattering in the active layer (nitride) (see Fig. 3).

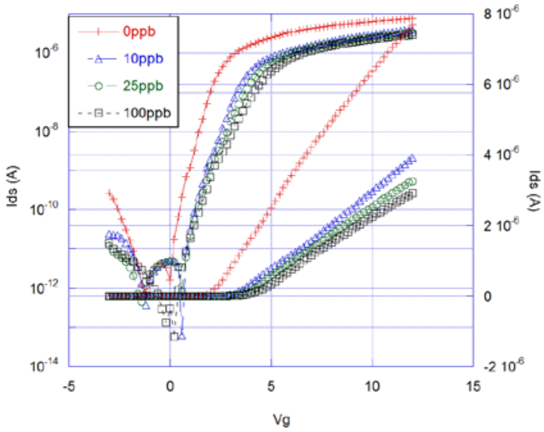
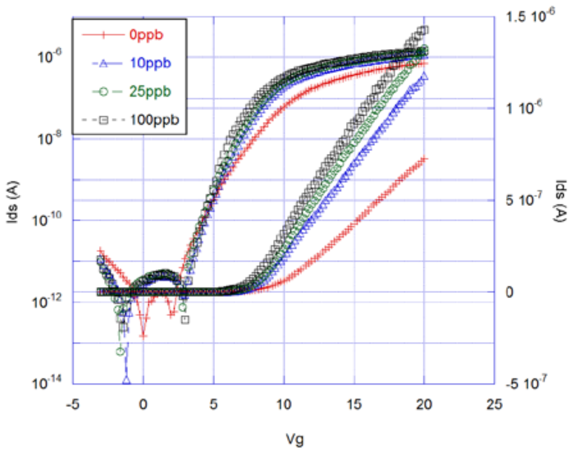


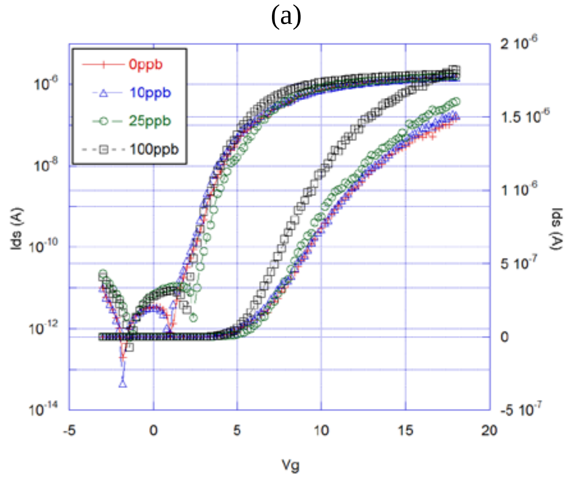
Fig. 3 Electrical properties of unmodified poly-Si NWFET under $NO_{(g)}$ concentration of 0, 10, 25, 100 ppb.

On the contrary, the surface modified acceptor layer poly-Si NWFET attained significant increase in I_{DS} current and decreased V_{th} when exposed to $NO_{(g)}$ (See Figure 4. (a) and (b)). Suggested by molecular properties and experimental results of electrical properties, $NO_{(g)}$ molecule physisorbs to Pc and NiPc organic layer (i.e. phthalocyanine), however, while NiPc is suggested not to undergo any observable redox reactions with $NO_{(g)}$ [5], Pc formed hydrogen bonding (N-H) with $NO_{(g)}$ in the central cavity. Here, Figure 4. and Table 1. indicate that while the current ratio of NiPc acceptor layer is relatively linear with respect to nitric oxide gradient and without evident signs of saturation, the Pc acceptor layer showed early signs of saturation with higher levels of $NO_{(g)}$.

The electrostatic attraction may be applied to explain the result. While bonded onto the organic acceptor layer, the $NO_{(g)}$ molecule pulls the electrons away, leaving the acceptor layer electrically positive which significantly enhanced the electron density of the n-type active layer near the acceptor layer due to electrostatic attraction as suggested in previous literature [6].



(a)



(b)

Fig. 4 Electrical properties of poly-Si NWFET with acceptor layer (a) Pc, and (b) NiPc under $NO_{(g)}$ concentration of 0, 10, 25, 100 ppb.

To quantify the nitric oxide sensing ability of poly-Si NWFETs, the drain-source current ratio (CR) is adopted, which is defined as Eq. (1).

$$\textbf{Current Ratio} = \left.\frac{I_{DS[NO=Xppb]}}{I_{DS[baseline]}}\right|_{V_{GS}\,(fixed)} \qquad \textbf{(1)}$$

where $I_{DS[NO=Xppb]}$ and $I_{DS[baseline]}$ were drain-source current measured under specific $NO_{(g)}$ concentration and zero $NO_{(g)}$ concentration (pure $N_{2(g)}$), respectively.

Table 1 summarized the sensitivity results on unmodified poly-Si NWFET and the acceptor layer (Pc and NiPc) modified poly-Si NWFETs at the selected gate voltage.

Table I. Current ratio of modified poly-Si NWFETs

	10ppb	25ppb	100ppb
Unmodified	0.53	0.50	0.49
Pc	2.18	2.54	3.03
NiPc	1.10	1.27	1.80

3. Conclusions

In this study, an ultrasensitive nitric oxide poly-Si NWFET gas sensor has been fabricated. Compared with the unmodified poly-Si NWFET, the acceptor layer modified poly-Si NWFET has significantly improved the nitric oxide sensing behavior. The results open a non-invasive way to monitor airway inflammation in asthma patients.

Acknowledgements

The authors would like to acknowledge the financial support by Ministry of Science and Technology of the Republic of China under Grant No. MOST 104-2221-E-009-174.

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