A highly selective hydrogen sensor based on self-heated polysilicon nanobelt device

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Abstract

In this report, a hydrogen (H₂) sensor based on polysilicon nanobelt device (PNB) was investigated. The PNB with $n^+/n^-/n^+$ structure was prepared by semiconductor fabrication process. A nanoscale template was formed via self-heating at the n^- region of the PNB, which was subsequently used for selectively evaporation of a palladium thin film for H₂ sensing measurement. The PNB device demonstrated high response to H₂ with limit of detection as low as 50 ppm, as well as high selectivity with no interference by hydrocarbon and toxic gases.

1. Introduction

Hydrogen (H₂) has long been considered as a clean energy carrier because it produces almost no pollution when burnt. That H₂ is the most plentiful element motivates it to play a bigger energy role and become widely used alternative to gasoline. One major challenge of using H₂ as a fuel comes from its highly flammable characteristic. In order to use H₂ in a safety manner, H₂ sensors have been developed extensively over the past decade. Great efforts have been made to satisfy the demands of H₂ sensors for sensitivity, selectivity, in addition to reducing sensor size, cost and power consumption [1]. Recently, silicon nanoribbons with sufficiently shallow thickness have been shown to be sensitive with surface charge and are therefore suitable for gas sensor [2]. Once the thickness of silicon channel approaches its Debye length, the charges on the sensing surface can fully deplete the conducting channel which produces a very large change in channel conductivity [3]. In this study, we report on a H₂ sensor based on polysilicon nanobelt (PNB) with $n^{+}/n^{-}/n^{+}$ structure. Localized Joule heating was applied to functionalize the PNB with palladium thin film. The device shows high sensitivity to H₂ over the concentration range from 50 ppm to 1%. The high selectivity of the device to H₂ was confirmed by the measurement in interference gases (butane and carbon monoxide).

2. Experimental

Device structure

The PNB device was fabricated by conventional lithography process [4]. The dimensions of the nanobelts are $13 \times 0.5 \times 0.059 \ \mum (L \times W \times D)$. The PNB was prepared with a doping profile n⁺/n⁻/n⁺ along the nanobelt. The n⁻ region of 2-µm length was implanted with $2.5 \times 10^{13} \ cm^{-2}$ of phosphorous at 20 keV. The n⁺ regions were implanted with $3 \times 10^{15} \ cm^{-2}$ of arsenic at 30 keV to form source/drain Ohmic contact. An oxide/nitride stack with thicknesses of 4/15 nm, respectively, was then deposited by LPCVD. After inter-level dielectric (ILD) deposition, dopants were activated at 930 °C for 30 min in a furnace. After forming the contact via, a metallization process was followed by forming gas annealing at 400 °C to maintain an Ohmic contact.

Functionalization of the PNB

The functionalization of the PNB for H_2 sensing purposes is summarized in Fig. 1. First, the PNB was sequentially cleaned in acetone and DI water to remove all the contaminations [Fig. 1(a)]. A thin layer of poly(methyl methacrylate) (PMMA) was spun on the device at 8000 rpm for 30 s [Fig. 1(b)]. The thickness of the PMMA layer was approximately 50 nm. Localized Joule heating was then carried out using an Agilent 4155B Pulse Generator to selectively ablate the PMMA layer at the n⁻ region of the PNB [Fig. 1(c)] [4]. The deposition of a 5-nm Pd layer was performed by e-beam evaporation at a deposition rate of 3 Å/s. Finally, the sample was lifted-off in acetone [Fig. 1(d)].

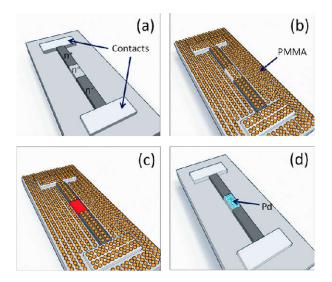


Fig. 1. Selectively functionalization of the PNB device by localized Joule heating: (a) a cleaned PNB; (b) a PNB coated with PMMA; (c) ablation of PMMA at n⁻ region at a Joule heating bias of 41 V; and (d) a PNB functionalized with Pd thin film by lift-off process.

COMSOL simulation

Joule heating of the devices was simulated by COMSOL Multiphysics software. The resistivity of the n⁺ regions is $8.125 \times 10^{-5} \Omega \cdot m$, while that of n⁻ region is $6.578 \times 10^{-3} \Omega \cdot m$. The temperature coefficient of resistance was determined using an Agilent 4155B semiconductor parameter analyzer to be $-4.53 \times 10^{-4} \text{ K}^{-1}$ [5].

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Hydrogen sensing measurement

The device was bonded and wired to a printed circuit board for H_2 testing. The measurements were conducted at room temperature. Dry air was used as carrier gas while H_2 was diluted to a certain concentration before being introduced to the flow cell. Gas flow rate was monitored by mass flow controller and was fixed at 180 sccm. The device bias and current were controlled by Labview program. The response to H_2 was defined as the percentage of the relative current change over the baseline ($\Delta I/I_0$).

3. Results and Discussions

Sensitivity to hydrogen

The H₂ performance of the PNB device functionalized with Pd was measured at 10 V bias. At this high bias, the temperature of the device is obtained from COMSOL simulation to be 39.5 °C. The H₂ concentration was examined over the range from 50 ppm to 1% [Fig. 2(a)]. Prior to H₂ exposure, dry air was purged in the test chamber to obtain the baseline. Hydrogen was introduced for 5 min, followed by dry air to allow the device to recover. When exposed to H₂, a dipole moment was generated at the interface between Pd and insulator layer that accounts for an increase in the current through the device. The $\Delta I/I_0$ values versus H₂ concentration are presented in Fig. 2(b). The response increases with H₂ concentration, and exhibited an approximately 4% change in current at concentration as low as 50 ppm.

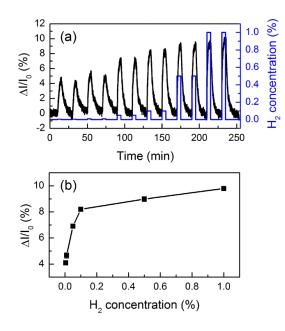


Fig. 2. Hydrogen sensing performance of PNB device: (a) the real time responses to increasing concentration of H_2 , including 0.005, 0.01, 0.05, 0.1, 0.5 and 1% of H_2 (each concentration with two pulses); (b) summary of the response versus concentration.

Selectivity to hydrogen

A measurement on the selectivity of the Pd-decorated PNB sensor was carried out using a hydrocarbon (C_4H_{10})

and a toxic gas (CO). The applied bias was 10 V and the total gas flow rate was maintained at 180 sccm. As clearly indicated in Fig. 3, the response of PNB device to H_2 was not influenced by interference gases. The high selectivity to H_2 of the self-heated PNB sensor may be originated from the elevated working temperature that is effective for detaching interference species from the surface of Pd and/or the use of Pd as H_2 catalyst.

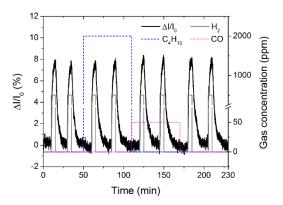


Fig. 3. The responses of the PNB device when exposed subsequently to 500 ppm H_2 , mixture of 500 ppm H_2 and 2000 ppm C_4H_{10} , mixture of 500 ppm H_2 and 50 ppm CO, and 50 ppm H_2 . Black solid line refers to the $\Delta I/I_0$ value and corresponds to the left *y*-axis. Light brown solid, blue dash and pink dot lines refer to H_2 , C_4H_{10} and CO concentrations, respectively and correspond to the right *y*-axis.

3. Conclusions

Localized Joule heating was acquired to selectively functionalize the double-junction $n^+/n^-/n^+$ PNB with Pd at n^- region for H₂ sensing application. The PNB device was prepared by conventional semiconductor fabrication process. The Pd-catalyzed PNB device presented here meets the requirements of a H₂ sensor, namely, easy fabrication and manipulation, reliable sensing performance, and no cross-sensitivity with interference gases.

Acknowledgements

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