PDMS-Coated Piezoresistive NEMS Diaphragm for Chloroform Vapor Detection

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***Abstract*—A polydimethylsiloxane (PDMS)-coated nanoelectromechanical systems diaphragm embedded with silicon nanowires (SiNWs) is proposed for chloroform vapor detection at room temperature. The PDMS film swells and leads to the deformation of micro-diaphragm when it is exposed to vapor. The SiNWs are connected in a Wheatstone bridge which is used to transform the deformation into a measurable output voltage. This sensor provides good linearity, sensitivity, and repeatability. The sensitivity of our sensor for chloroform vapor detection is 1.41 μV/V/ppm, while the power consumption is as low as 2 μW.**

***Index Terms*—Chloroform vapor sensor, nanoelectromechanical systems (NEMS) diaphragm, piezoresistive silicon nanowires (SiNWs), polydimethylsiloxane (PDMS) film.**

I. Introduction

CHLORINATED hydrocarbons are a group of serious environmental pollutants and are considered as a source of danger to the environment [1]. Prolonged exposure to these vapors could cause severe health effects such as eyesight disturbance, headache, lung congestion, kidney damage, cancer, and even death. Therefore, low-cost processing of appropriate sensors with well-sensing performance at low power consumption is urgently required to detect about chlorinated aliphatic hydrocarbon vapors. Numerous methods have been reported previously. A widely used conventional method for the detection of chlorinated hydrocarbon vapors is gas chromatography combined with mass spectrometry [2]. Although these common methods are accurate and reliable, they are indeed offline analysis, need bulky and expensive instrumentations, and are time consuming [3]. Semiconducting metal–oxide vapor sensors have been of great interest due to the easy detection of resistance changes via adsorption of vapor molecules [4]. However, these sensors show some negative characteristics, for example, lack of selectivity, interference from water vapor, and requirement of high operating temperature, which hamper their application on a large commercial scale [5]. Also, there are a number of reports on the application of quartz crystal microbalance (QCM) sensors for determination of chlorinated hydrocarbons in air. However, the sensitivity and detection limit value of QCM sensor are low [6], and those sensors are easy to be interfered by water vapor too. Recently, microelectromechanical systems (MEMS) structures such as microbridges [7], [8] and microcantilevers [9] have been used as detecting elements for vapor monitoring. Those MEMS vapor sensors show some excellent characteristics, for example, high sensitivity, small size, lightweight, low cost, low power consumption, and CMOS compatibility. By leveraging the advanced semiconductor process technology, nanoelectromechanical systems (NEMS) devices using piezoresistive silicon nanowires (SiNWs) have been reported as pressure sensor and flow sensor [10], [11]. With reported giant piezoresistive effect of SiNWs [12], SiNW NEMS sensors are considered as the most promising piezoresistive sensors. Attributed to the ultralow power consumption of SiNW NEMS sensors, the feasibility of having self-sustained NEMS sensors powered by microscale energy harvesters is promising in near future [13].

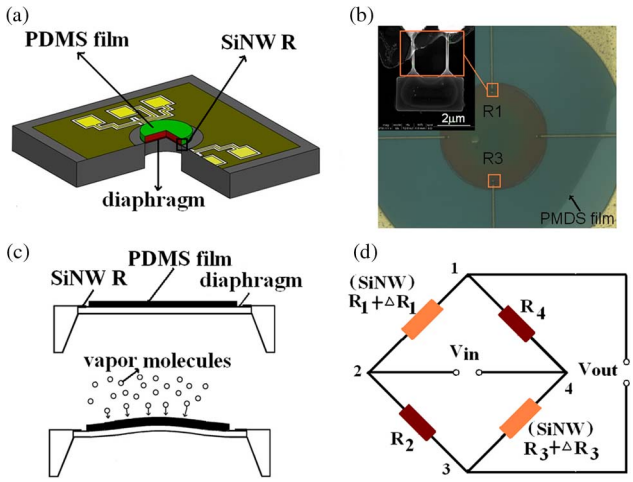

Fig. 1. (a) Schematic diagram of vapor sensor using SiNWs. (b) Optical photograph of the prepared sensor. Inset of (b) shows the zoom-in SEM photograph of the SiNWs. (c) Schematic illustration of the sensing mechanism of vapor sensor. (d) SiNWs are connected in Wheatstone bridge.

In this letter, a micro-diaphragm embedded with piezoresistive SiNWs and coated with a polydimethylsiloxane (PDMS) layer was characterized as a chloroform vapor sensor. The schematic diagram of the sensor is shown in Fig. 1(a). The photograph of the prepared sensor is shown in Fig. 1(b), where the zoom-in SEM photograph of two SiNWs is shown in the inset of Fig. 1(b). The swelling effect of the PDMS layer due

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to the absorption of vapor molecules from ambient causes the deformation of micro-diaphragm as shown in Fig. 1(c) and then elongates the SiNWs located at the edge of micro-diaphragm into a tensile strain state with the deformation. The SiNWs are further connected to form a Wheatstone bridge circuit such that the output voltage is measured as shown in Fig. 1(d).

II. Fabrication and Experimental Setup

The fabrication of the micro-diaphragm starts with a (100) single-crystal silicon-on-insulator wafer. After photolithography, the photoresist is trimmed to reduce the critical dimension to around 100 nm for the following silicon etching. The dimension of SiNWs is further reduced down by thermal oxidation process. Diaphragm embedded with SiNWs is obtained, while an average cross section and the length of SiNWs are 90 nm $\times$ 90 nm and 2 μm, respectively. The piezoresistive characteristics of SiNWs are obtained by P-type implantation using BF^{2+} with a dosage of 10^{14} ion/cm^2 and followed by annealing for activation. Then, a 400-nm SiO_2 is deposited as passivation layer. After via opening and metallization, a 2.5-μm SiN_x layer is further deposited to compensate the initial compressive stress introduced by SiO_2 layer. By using backside deep reactive-ion etching, the micro-diaphragm is further released. Finally, the PDMS layer is coated on micro-diaphragm by spin-coating method. The radius and thickness of micro-diaphragm are 100 and 3 μm, respectively, and the thickness of PDMS layer is 30 μm.

The experiments are carried out at room temperature. The testing chamber is a 1-L glass container where the sensor is mounted inside the container. The initial resistances of 2-μm-length SiNWs are 90 kΩ. The supply voltage of Wheatstone bridge is 0.2 V to avoid Joule effect in the SiNWs. Before the experiment began, the chamber is purged with dry air. Organic solvent is taken by a microsyringe and then injected into the testing chamber to adjust the concentration level inside. The concentration of vapor could be precisely controlled by syringe and is calculated in parts per million according to its density, purity percent, and volume. During the testing, the output voltage of the sensor is monitored by the digital millivoltmeter (KEITHLEY 2000, USA).

III. Results and Discussion

A typical response of the vapor sensor is shown in Fig. 2. As can be seen, for the sensor without the PDMS layer, the chloroform vapor concentration does not affect the output voltage; in contrast, the output voltage of the sensor with PDMS layer increases rather linearly with increasing concentration of chloroform vapor. The corresponding maximum SiNW resistance change in chloroform vapor within our measurement range is $+0.56\%$, showing that the SiNW is elongated by the tensile stress [11]. The sensitivity of the sensor is defined as the ratio of output voltage change to vapor concentration change divided by the input voltage of Wheatstone bridge. Through linear fitting, the sensitivity of the vapor sensor is extracted as 1.41 μV/V/ppm. In our measurement, the minimum detectable concentration of chloroform vapor is 10 ppm within the setup limitation. The vapor sensor has a slightly higher detection limit than that of membrane FET-type

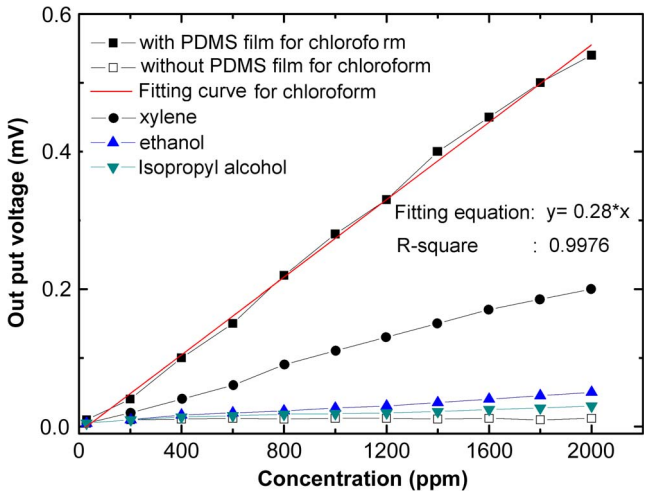

Fig. 2. Response of the vapor sensor in various organic vapors.

gas sensors [14], [15]. Therefore, further studies are required to reduce the detection limit of sensor in the future. In our previous work [8], the maximum sensitivity for ethanol vapor is reported as 0.01 μV/V/ppm, which used polymer-coated silicon diaphragm embedded with microscale piezoresistors. Moreover, the previously derived minimum detectable concentration of vapor is 200 ppm using the same kind of millivoltmeter. Compared with our previous data, the new NEMS vapor sensor using SiNWs as the piezoresistive sensing elements has better sensitivity and lower minimum detectable concentration of vapor. Moreover, this new sensor has a low supply voltage that the total power consumption below 2 μW is achieved. Such value of the power consumption is less than 1/1000 of the power consumption reported in [8]. This feature of ultralow power consumption of vapor sensor renders this device a niche position for applications in wireless sensor network. More specifically, it will be useful for long-term environmental monitoring.

Fig. 2 also shows the typical response of this sensor in various organic vapors. The output voltage of sensor is measured when it is exposed to chloroform, xylene, ethanol, and isopropyl alcohol. The corresponding sensitivities in these vapors are extracted as 1.41, 0.51, 0.11, and 0.07 μV/V/ppm, respectively. The largest response is observed for the sensor in chloroform and then followed by the sensor in xylene, whereas little response is observed from the sensors in ethanol and isopropyl alcohol. The result shows that the sensor has obvious selectivity for chloroform and xylene against ethanol and isopropyl alcohol. The selectivity of sensor should be attributed to the swelling coefficient of PDMS film in organic vapors [8]. The PDMS film has different swelling ratios in various organic solvents. Fig. 3 shows that the swelling ratios of the 30-μm-thick PDMS film in chloroform, xylene, ethanol, and isopropyl alcohol solvents are approximately 1.1, 0.48, 0.05, and 0.04, respectively, after saturation. It could be reasonably expected that the PDMS film exhibits higher swelling coefficient in chloroform and xylene vapors than it is in ethanol and isopropyl alcohol vapors as well. Combining with previous sensitivity data, the sensitivities of the sensor are in an approximately linear relationship with the swelling coefficients in different solvents as shown in Fig. 3 inset. The results show that the

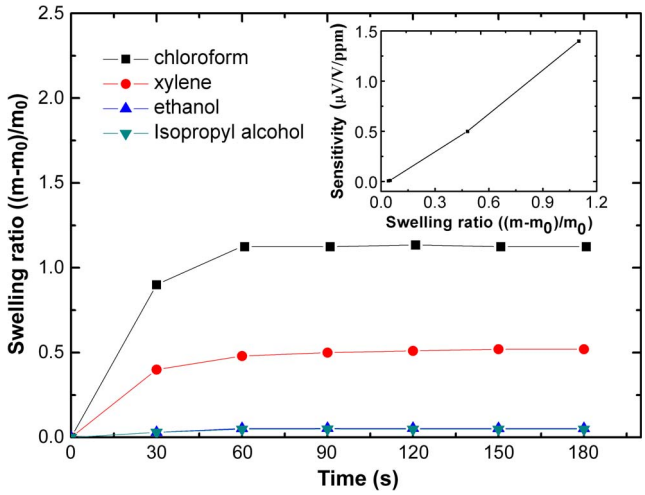

Fig. 3. Swelling ratio of PDMS film in various organic solvents. Inset shows the relationship between the sensitivity of sensor and the swelling ratio of PDMS in different solvents.

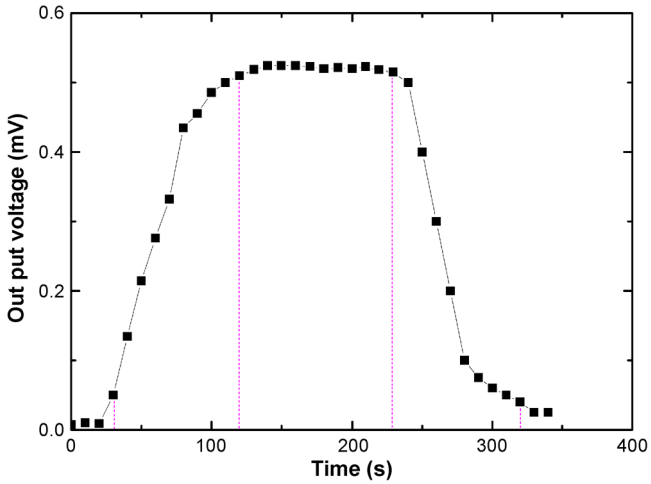

Fig. 4. Response–recovery curves of the sensor in chloroform at 2000 ppm.

sensitivity and selectivity of the sensor coated with PDMS layer for the detection of various vapors depend on the swelling coefficients of PDMS film in various vapors. In other words, the swelling ratio of polymer film in organic solvents is a key factor in choosing the sensitive film for other organic vapor sensor.

The sensor was tested in chloroform vapor at 2000 ppm. The response–recovery curves of the sensor are shown in Fig. 4. The response time and recovery time of the sensor are approximately 85 and 90 s, respectively.

To characterize the repeatability of sensor, the experiment was repeated several times under the same experimental conditions for the chloroform vapor concentration ranging from 200 to 2000 ppm. Here, we define the repeatable error as the ratio of maximum voltage output deviation to full-scale voltage output value, while the derived maximum repeatable error is $\pm 1.7\%$. The test results show that our new vapor sensors provide good repeatability.

Finally, reliability is of importance for the vapor sensor. The chloroform vapor sensor using PDMS as sensing film has good response characteristic even after a long time usage. The PDMS has good aging stability which is often used as the medical polymer material and electrical packaging material, and the degradation of PDMS is usually caused by heat, light, and radiation [16]. Therefore, we can use appropriate packaging to protect PDMS in the practical applications.

IV. Conclusion

The proposed NEMS vapor sensors have demonstrated good sensitivity and extremely low power consumption for the detection of chloroform vapor. This kind of vapor sensor also has advantages including scalability, ultracompact footprint, low cost, and CMOS-IC process compatibility. In addition, by changing the vapor-absorption polymer layer, we can apply the same approach to detect other organic vapors. Furthermore, a sensor chip with cascaded micro-diaphragms coated with various vapor-absorption polymer films can be used as an electronic nose for identification and determination of volatile organic compounds in environmental monitoring applications.

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