ULTRA-LOW POWER HYDROGEN SENSOR BY SUSPENDED AND PALLADIUM COATED SILICON NANOWIRE

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ABSTRACT

This paper reports silicon nanowire sensor decorated with palladium nanoparticles for the low temperature hydrogen detection with self-heating for fast response and recovery. Hydrogen gas responses of the palladium coated silicon nanowire (Pd-SiNW) were measured with Joule heating of Pd-SiNW. Even though the Pd-SiNW can detect hydrogen gas at room temperature, transient response is slow and even slower in humid conditions. Self-heating of the Pd-SiNW reduces the response and recovery times by consuming low power without any significant change of sensitivity. Power consumption is further reduced to sub-100 μW by suspending the Pd-SiNW from substrate. Humidity effect on hydrogen sensing was also reduced by Joule heating. Joule heated Pd-SiNW device is a promising hydrogen gas sensor to apply mobile device.

INTRODUCTION

Rapid growth in internet of things (IoT) markets has needed low-cost and low-power consumption devices for applying in various places. Accordingly, they are concerned about gas sensors for IoT devices because outdoor air monitoring is crucial than before. Gas sensors, such as electrochemical type sensor, optical type sensor and gas chromatography, are not suitable for integrating with the IoT devices due to high electric power consumption, bulky size and high cost. Semiconductor type gas sensors are the most likely candidate for miniaturized gas sensor because the device structure is simple [1]. However, it requires a few tens of mW to operate a microheater [2]. In other to reduce power consumption further, nanoscale semiconductor type sensors have been introduced.

Joule heated nano-structures were utilized for gas detection. Tin oxide nanowire [3], carbon nanotube [4] and silicon nanowire [5] were demonstrated to detect nitrogen dioxide gas and acetone vapor. The device fabrication processes of these works are not good for wafer-scale fabrication. However, the wafer-scale fabrication is mandatory for a competitive price in the market. Wafer-scale sensor fabrication processes have been introduced, but the processes were not reliable for producing uniform performance gas sensor [6, 7]. We utilized the well-defined top-down nanofabrication processes and physical vapor deposition method for cost-effective and reproducible gas sensor.

The concept of hydrogen gas sensing by Joule heating of palladium coated silicon nanowire (Pd-SiNW) was demonstrated in our previous paper [8]. This paper shows Joule heating power-dependent hydrogen sensing behavior and demonstration of suspended Pd-SiNW for ultralow power operation. There is a reduction of sensitivity on palladium resistor type sensors at increased temperature [9], however our device shows no significant sensitivity change by increasing Joule heating power. Humidity effect on palladium based hydrogen sensor was reduced by Joule heating in our work.

CONCEPT AND EXPERIMENTAL

Concept of Hydrogen Gas Sensing with Joule Heating

Figure 1 illustrates the working principle of palladium nanoparticles coated silicon nanowire for hydrogen detection and self-heating of Pd-SiNW for fast transient behavior. Hydrogen molecule is dissociated to hydrogen atoms on the palladium surface and hydrogen atoms are dissolved into palladium nanoparticles. Some hydrogen atoms are adsorbed at the interface between palladium nanoparticles and silicon dioxide with forming electric dipole and adsorption density of hydrogen depends on the concentration of hydrogen gas [10]. The electric conductivity of n-type silicon is increased through field effect of positive electric dipoles. Even though adsorption and desorption of hydrogen on palladium work at room temperature, the response time of hydrogen detection is decreased by increasing temperature of palladium. Joule

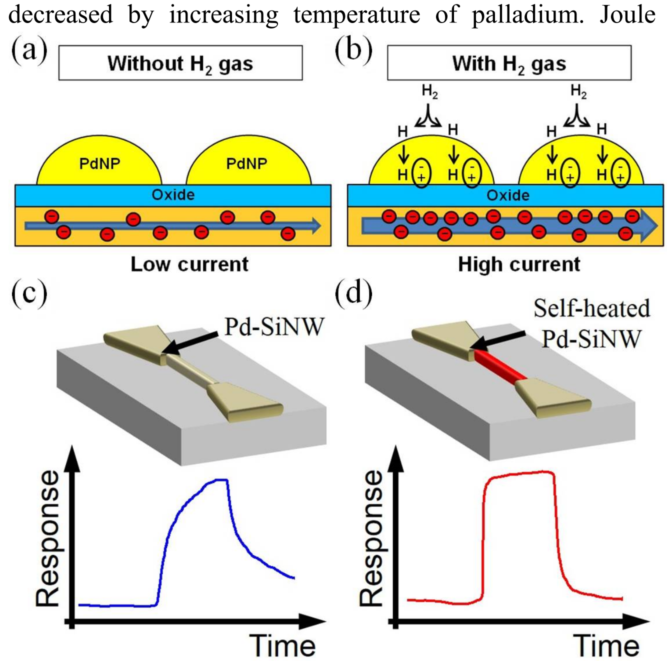

Figure 1: Working principle of the Pd-SiNW for hydrogen gas detection and Joule heating effect on Pd-SiNW sensor.

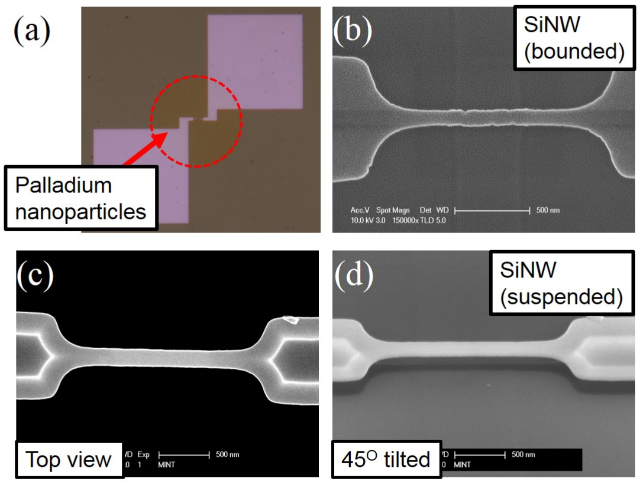

Figure 2: Optical microscope and scanning electron microscope images of bounded Pd-SiNW and suspended Pd-SiNW.

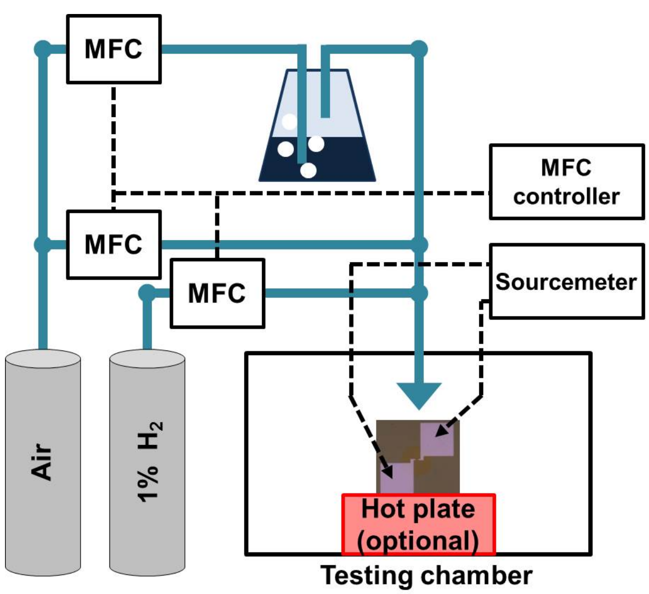

Figure 3: Schematic image of gas test set-up.

heating of silicon nanowire is an efficient method to increase the temperature of palladium nanoparticles. Joule heating suppresses the slow transient response in humid air, which occurs due to the blocking the palladium surface by water molecules.

Fabrication Processes of Palladium Coated Silicon Nanowire

Figure 2 shows optical microscope and scanning electron microscope images of bounded and suspended Pd-SiNW. Silicon nanowires were fabricated by conventional CMOS compatible processes with silicon on oxide (SOI, top silicon = 40 nm and buried oxide = 400 nm) wafer. 160 nm width of silicon nanowire was defined by reactive ion etching with photoresist patterned by deep ultraviolet lithography and oxygen plasma reduction. Then, channel region of 500 nm long was covered by photoresist and source and drain regions were doped by ion implantation (arsenic, energy = 25 keV and dose = 5×10^{15} cm^{-2}). Additional doping for channel region was conducted by ion implantation (phosphorus, energy = 15 keV and dose = 1×10^{14} cm^{-2}) and rapid thermal annealing at 1000 °C for 10 sec in nitrogen environment was utilized for activating dopants. The additional doping process was needed for operating Joule heating of silicon nanowire at low voltage. Silicon nanowires were suspended from substrate by etching the buried oxide layer via buffered oxide etchant for 100 seconds. Palladium nanoparticles were decorated on the bounded and suspended silicon nanowire by depositing 1 nm thick of palladium via physical vapor deposition method. 1 nm thick of palladium layer is formed into nanoparticles rather than thin film on the silicon oxide surface [11].

Gas Sensing Set-Up

Figure 3 shows schematic image of gas test set-up. Hydrogen gas concentration was controlled from 0 % to 1 % by mixing air and 1 % of hydrogen gas (mixed in air). Electric current of Pd-SiNW was measured by a sourcemeter (Keithley 2635B). The Pd-SiNWs were mounted on a probing stage inside a custom-built gas chamber. Humid air was generated by bubbling dry air through water and the relative humidity of mixture gas was adjusted by ratio of dry air and humid air. Mixing ratio of dry air, humid air and hydrogen gas was controlled by mass flow controllers (MFCs) and the relative humidity of the mixture gas was measured by a commercial humidity sensor. The sourcemeter and the MFCs were controlled by personal computer and Labview® software.

RESULTS AND DISCUSSION

Figure 4 shows the hydrogen gas responses of the bounded Pd-SiNW with applying Joule heating power. Electrical signal of Pd-SiNW was stabilized in dry air for 200 sec before exposing hydrogen gas and measured electrical current was normalized by the stabilized current. Electrical current of Pd-SiNW was increased, when the Pd-SiNW was exposed to hydrogen gas, and higher current was observed at higher concentration of hydrogen gas. It is evident that 1 nm thick palladium film is not a major current path because electrical conductivity of palladium is decreased after exposing hydrogen gas. Therefore, electrical signal of Pd-SiNW was governed by dipole formation as explained in the previous section. Sensitivity of Pd-SiNW was defined by $S = (I_{H2}-I_{air})/I_{air} \times 100$ (%) where I_{H2} is a saturated current after exposing hydrogen gas and I_{air} is the stabilized current. Response time and recovery time are defined by the periods from 0 % sensitivity (i.e. after exposing hydrogen gas) to 80 % sensitivity and 100 % sensitivity (i.e. turn off hydrogen gas) to 20 % sensitivity, respectively. Response time and recovery time are faster as increasing Joule heating power, on the other hand, sensitivities are not significantly affected. Response time and recovery time are comparably shorter than hydrogen gas response of palladium nanowire because nanoparticle has higher surface-to-volume ratio than nanowire. Sensitivities of Joule heated palladium nanowire

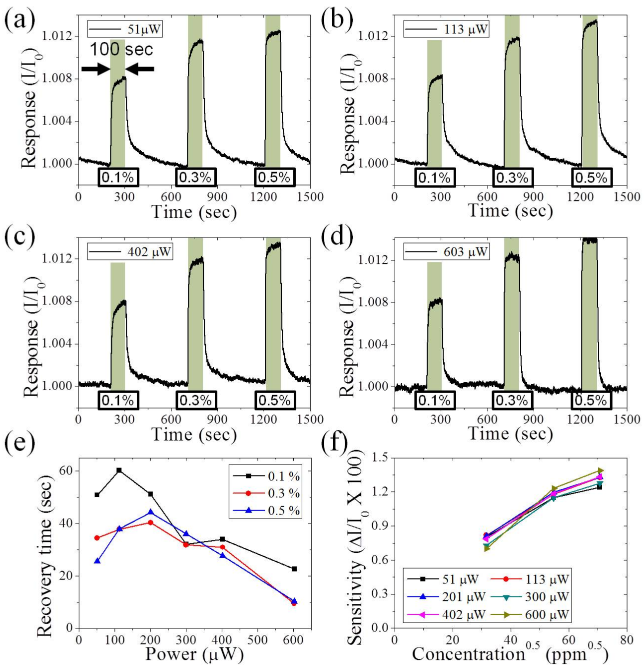

Figure 4: (a-d) Hydrogen gas sensing response of bounded Pd-SiNW with Joule heating power of 51 μW, 113 μW, 402 μW and 603 μW, (e, f) recovery time and sensitivity of Joule heated Pd-SiNW.

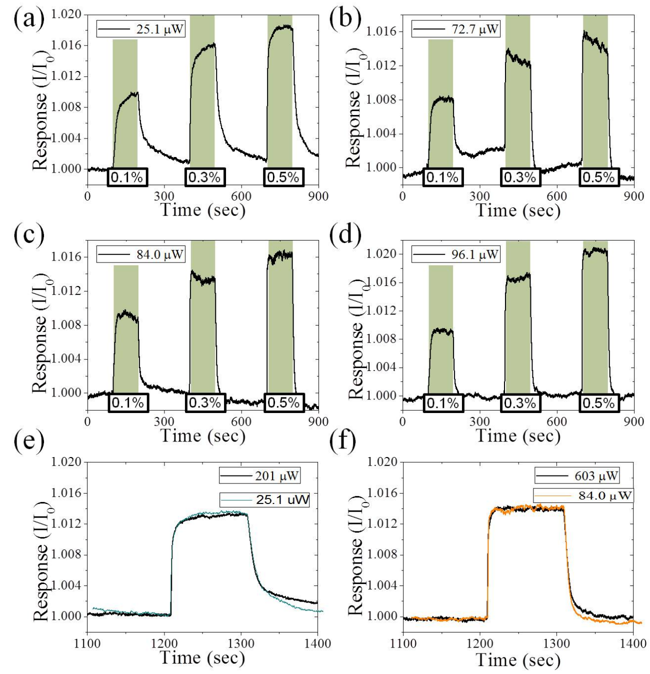

Figure 5: (a-d) Hydrogen gas sensing responses of suspended Pd-SiNW with Joule heating power of 25.1 μW, 72.7 μW, 84.0 μW and 96.1 μW, (e, f) comparison of responses of bounded and suspended Pd-SiNWs.

were smaller as increasing power (i.e. temperature) however sensitivities of Pd-SiNW were not reduced as increasing Joule heating power.

Figure 5 shows the hydrogen gas responses of suspended Pd-SiNW with applying Joule heating power and compared with the bounded Pd-SiNW. Power consumption of the suspended Pd-SiNW was much smaller than the bounded Pd-SiNW because heat dissipation through the substrate is reduced. Sensitivities of the suspended Pd-SiNW were increased as increasing Joule heating power and higher than the bounded Pd-SiNW. The reason that the suspended Pd-SiNW showed higher sensitivity is not understood. Transient behaviors of the bounded and suspended Pd-SiNWs were compared as shown in the figure 5 (e, f). Similar transient behaviors of the bounded and suspended Pd-SiNWs indicate that temperatures of Joule heating are the same for suspended and bounded Pd-SiNWs [3]. The transient behaviors depict that temperatures of bounded Pd-SiNW at 201 μW and 603 μW are the same as bounded Pd-SiNW at 25.1 μW and 84 μW, respectively. This means that the suspended Pd-SiNW operated at ~8 times lower Joule heating power than the bounded Pd-SiNW with similar gas sensing performance.

In the ambient condition of living area, humidity changes and affects the sensing performance. Humidity effects on the Pd-SiNW during hydrogen gas detection were investigated as shown in the figure 6. Slow transient behavior and high sensitivity were observed in humid condition at low Joule heating power. Transient response was recovered as same as no humidity condition by applying 4 V (620 μW) to the Pd-SiNW. We believe that slow transient behavior is caused by blocking the adsorption and desorption sites of hydrogen molecule on palladium surface and fast transient behavior in Joule heated Pd-SiNW is due to vaporization of water molecules. Sensitivities at Joule heating power of 620 μW were not significantly affected by changing relative humidity. Therefore, the Pd-SiNW sensor can detect hydrogen without interference from humid air.

Figure 7 shows the comparison between hydrogen gas sensing responses of Pd-SiNW using Joule heating and an external heater. Hydrogen gas responses at 201 μW and 40 °C and 503 μW and 60 °C of Joule heating power and

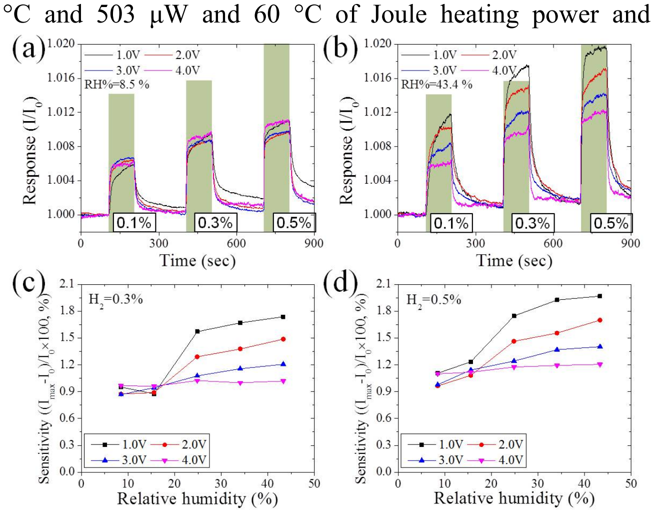

Figure 6: Humidity effects on hydrogen gas sensing: (a, b) Joule heating power-dependent hydrogen sensing response, (c, d) sensitivity versus relative humidity corresponding to Joule heating voltage.

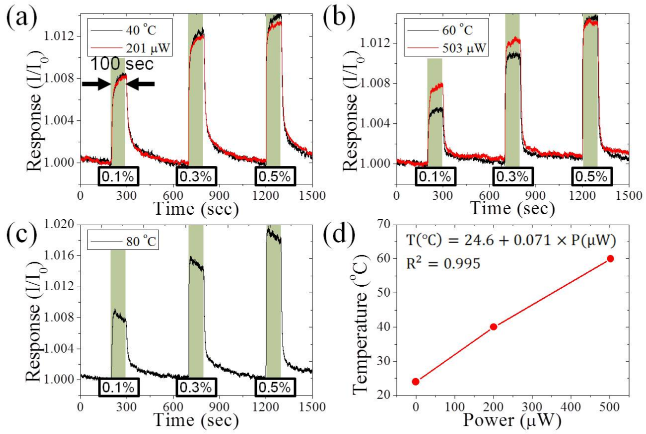

Figure 7: Temperature and Joule-heating-power dependent hydrogen gas responses of Pd-SiNW and comparison between (a) 201 μW and 40 °C and (b) 503 μW and 60 °C, (d) relation between Joule heating power and temperature.

temperature of external heater, respectively, showed similar transient behavior. Thus, we concluded that the temperature of Joule heating powers at 201 μW and 503 μW were 40 °C and 60 °C, respectively. Also, we can obtain the relationship between Joule heating power and temperature as shown in figure 7 (d).

CONCLUSION

We demonstrated the Pd-SiNW for fast detection of hydrogen gas operated at ultra-low power by using Joule heating of suspended structure. Silicon nanowires were fabricated by top-down fabrication processes and palladium nanoparticles were decorated on the silicon nanowires by a physical vapor deposition method. Joule heating power-dependent hydrogen responses of Pd-SiNW were observed and power consumption was reduced by utilizing the suspended Pd-SiNW. Also, humidity effect on the Pd-SiNW for hydrogen detection was characterized with respect to Joule heating power and reduced by Joule heating. The sensor device has advantages of mass production and integration with electric circuit because conventional CMOS processes are utilized and palladium nanoparticles are coated by a physical vapor deposition method.

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