

HIGHLY ALIGNED SUSPENDED NANOWIRE ARRAY FOR SELF-HEATING TYPE GAS SENSORS

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ABSTRACT

A unique array structure of highly aligned and suspended palladium nanowires was demonstrated for application in self-heating type hydrogen gas sensors. Unlike conventional devices which employ randomly distributed bottom-up grown nanowires, in this study a top-down method which enables controllable and uniform device fabrication was used to produce the highly aligned nanowire array. Moreover, by suspending the array, heat loss through the substrate was eliminated, leading to a more efficient self-heating and rapid gas sensing response. As a result, with only a few milliwatts of power, the self-heated gas sensing device exhibited a considerably faster response time upon exposure to hydrogen gas than the device operating at room temperature.

INTRODUCTION

In recent years, nanowires have attracted considerable interest as building blocks for fabricating self-heating type gas sensors. The high surface-to-volume ratio of the nanowires allows a large number of gas molecules to be adsorbed on the nanowire's surface, and this creates a more sensitive, measurable response to small concentrations of target gases. In addition, the nanowires' extremely low heat capacity proportional to their mass reduces the amount of electric power required to heat the sensing elements to their optimum operating temperature. For these reasons, there have been a considerable number of studies exploring ways of utilizing the self-heated nanowires as sensing elements, to realize high performance gas sensors that can operate with minimum power dissipation.

Preparing the nanowires is the most important process step when developing nanowire-based self-heating type gas sensors. Until now, the conventional approaches of producing nanowires have been based on chemical synthesis methods such as electrospinning [1], vapor-liquid-solid growth [2], hydrothermal growth [3] and so on. However, manipulating nanowires that have been grown with the bottom-up methods still remains a significant challenge, and only proof-of-concept devices have been demonstrated using single or randomly distributed nanowires [4], [5]. Although the nanowires synthesized for self-heating type gas sensors have been experimentally demonstrated to have excellent properties, a systematic design for using the nanowires in structural devices has not yet been developed, and is essential for their practical use.

APPROACH

To ensure reliable and reproducible device fabrication, the number and sizes of the nanowires need to be precisely

controlled. In this respect, a highly aligned nanowire array is the preferred format for sensing elements, because the array makes it easy to define the dimension of the active area with high precision. In addition to precisely controlling the nanowires, another important issue is optimizing the nanowire device structure to ensure efficient self-heating. Since most of the heat generated in a nanowire can be lost through substrate conduction, a suspended structure can dramatically enhance the energy efficiency of the self-heating, by eliminating a major pathway of heat loss.

With these factors in mind, we propose a highly aligned, suspended nanowire array as the optimum structure for the sensing elements of a self-heating type gas sensor. The proposed structure was realized by developing appropriate nanowire fabrication and integration techniques, based on a top-down approach. While bottom-up grown nanowires inevitably have an irregular shape and are randomly distributed, the top-down approach allows the number and sizes of nanowires to be precisely controlled.

As a first demonstration, palladium, a well-known hydrogen gas sensing material, was employed to realize the proposed structure. The FEM simulation results shown in Fig. 1 confirm the superior self-heating capability of the proposed structure. It should be noted that the bulk, not the nanoscale, parameter of palladium was used in this simulation, and therefore the estimated temperature may deviate from the experimentally obtained value. Nevertheless, the self-heating performance of the fabricated devices was confirmed using IR thermal imagery and measurements of the gas sensing response.

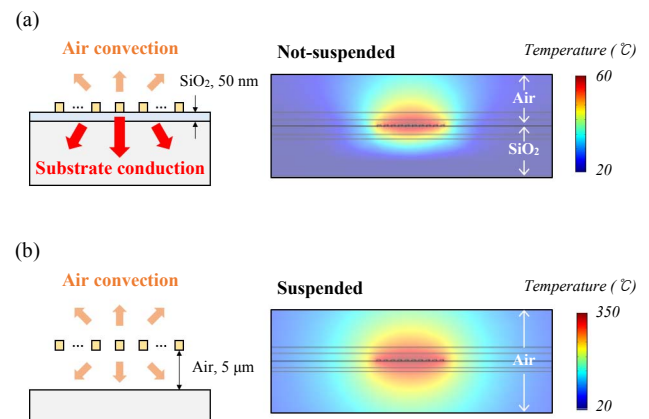


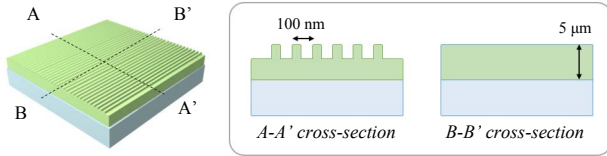
Figure 1: Estimated temperature of self-heated palladium nanowires by FEM simulation. (a) not-suspended, (b) suspended case. Each nanowire consumes 40 μW .

DEMONSTRATION

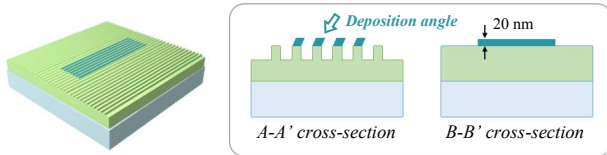
Device Fabrication

Here, we used a top-down approach based on the glancing-angle deposition (GLAD) technique on a nanograting substrate to achieve a perfectly-aligned nanowire array [6]. To accurately define the gas sensing area, a photolithographic patterning process was conducted on the top of a nanograting substrate made of polyurethane acrylate (PUA). Then, GLAD processing with palladium was used to form the perfectly-aligned gas sensing nanowire array, by applying a lift-off technique. Once the electrodes were formed with another lift-off patterning process, the PUA under the nanowire array was etched away by oxygen plasma treatment. In this final step, the fabricated electrodes served as both etch mask and posts for supporting the suspended nanowires. It should also be noted that the PUA layer is used as a template for fabricating the nanowires, as well as a sacrificial layer for suspending the nanowires. A schematic description of the overall fabrication process is summarized in Fig. 2, including the specific dimensions used for the experiments.

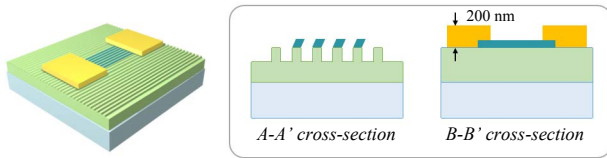
(1) Preparation of nanograting substrate made of PUA



(2) 1st lift-off patterning of Pd nanowire array (GLAD)



(3) 2nd lift-off patterning of Au electrodes



(4) O₂ plasma treatment for suspending the array

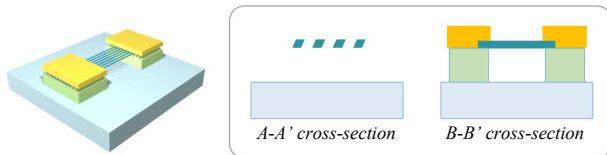


Figure 2: Fabrication process developed to realize a highly aligned suspended nanowire array, based on a top-down approach.

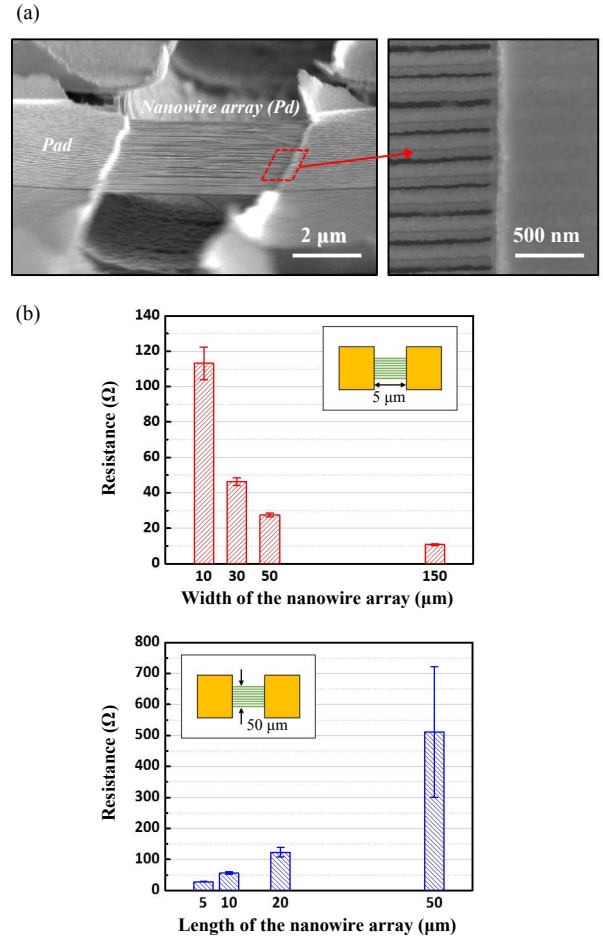


Figure 3: (a) Scanning electron microscope images and (b) electrical resistance obtained from the fabricated devices.

Scanning electron microscope images of the fabricated device are shown in Fig. 3 (a). The nanowires are suspended between two pads, while maintaining their perfect order.

To evaluate the reliability and reproducibility of the developed fabrication process, the electrical resistance of 30 randomly selected devices was measured for each geometry. Since well-established photolithographic processes were used to fabricate the highly aligned and patterned nanowire array, controllable and uniform device fabrication was achieved, as demonstrated in Fig 3 (b).

Evaluation of Self-Heating Type Gas Sensors

To evaluate the self-heating capability of the fabricated devices with the proposed structure, two types of devices were prepared: those that were not suspended and those that were suspended. The IR thermal images shown in Fig. 4 verify that the suspended device self-heated to a higher temperature with the same applied power. Note that heat loss through the substrate in the case of the not-suspended device can be clearly visualized in Fig. 4 (a) by the rise of temperature in the surrounding substrate.

* Dimension of the nanowire array: 5 μm length, 150 μm width

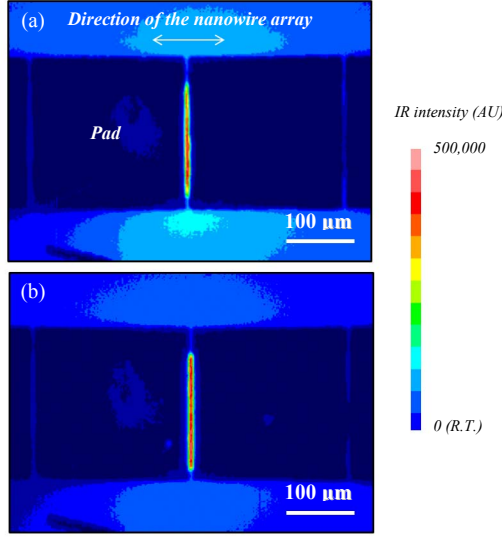


Figure 4: IR thermal images of fabricated (a) not-suspended, and (b) suspended devices when 0.2 V was applied.

Finally, the performance of the devices as self-heating type hydrogen gas sensors was examined, as shown in Fig. 5. Both the not-suspended and suspended devices showed a faster response time as the applied power was increased. However, the enhancement was more dramatic in the suspended device, which further verifies the superior self-heating capability of the suspended structure design.

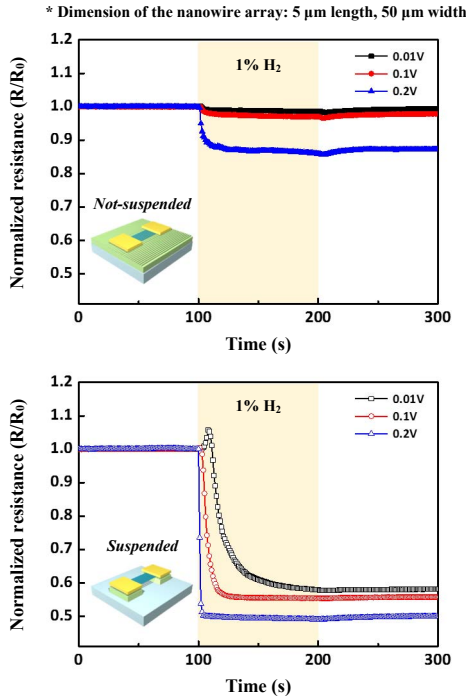


Figure 5: Gas sensing response of fabricated (a) not-suspended, and (b) suspended devices upon exposure to hydrogen gas according to the various applied voltages.

Table 1: Extracted gas sensing performance from the measurement results in Fig 5 (a), the not-suspend device. Temperature was estimated through FEM simulation.

| Applied voltage (Power) | Estimated temperature | Sensitivity | Response time |
|------------------------------|------------------------|-------------|---------------|
| 0.01 V (~ 10 μW) | 20 $^{\circ}\text{C}$ | 1.4 % | 62 s |
| 0.1 V (~ 1 mW) | 47 $^{\circ}\text{C}$ | 2.9 % | 43 s |
| 0.2 V (~ 4 mW) | 129 $^{\circ}\text{C}$ | 13.3 % | 14 s |

Table 2: Extracted gas sensing performance from the measurement results in Fig 5 (b), the suspended device. Temperature was estimated through FEM simulation.

| Applied voltage (Power) | Estimated temperature | Sensitivity | Response time |
|------------------------------|------------------------|-------------|---------------|
| 0.01 V (~ 10 μW) | 21 $^{\circ}\text{C}$ | 42.1 % | 43 s |
| 0.1 V (~ 1 mW) | 113 $^{\circ}\text{C}$ | 44.6 % | 14 s |
| 0.2 V (~ 4 mW) | 393 $^{\circ}\text{C}$ | 51.1 % | 2 s |

The specific gas sensing performance was extracted and is shown in Tab. 1 and Tab. 2. For the suspended device, the initial response time of 43 seconds upon exposure to 1 percent hydrogen gas was reduced to just 2 seconds by operating the gas sensor with 4 milliwatts of power. These results show that the highly aligned and suspended nanowire array demonstrated first here is very promising as an optimal gas sensing element.

CONCLUSION

A highly aligned suspended nanowire array was realized with palladium and evaluated as a self-heating type hydrogen gas sensor. The development of a nanowire fabrication and integration technique, based on a top-down approach, enabled controllable and uniform device fabrication. By eliminating heat loss through the substrate, the suspended nanowire structure exhibited greatly enhanced self-heating energy efficiency. As a result, the self-heated devices achieved a dramatically faster response time while operating with only a few milliwatts of power. Furthermore, the unique structure and manufacturing technique developed in this work can be extended to other gas sensing materials, by simply depositing the desired target material on the nanograting substrate. This method opens a way of realizing arrays of ultra-low power, high performance chemo-resistive gas sensors that can monitor various harmful gases in our living environment.

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