FABRICATION OF SUSPENDED NANOWIRES USING SUSPENDED CARBON NANOTUBES AS TEMPLATE FOR GAS SENSING

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ABSTRACT

We developed a novel approach to fabricate suspended metal- and metal oxide nanowires using carbon nanotubes (CNTs) as sacrificial template. As a potential application that harnesses the unique properties of suspended nanowires, sensitive chemical sensors were demonstrated. The suspended CNTs template was synthesized on the side wall of the electrodes by chemical vapor deposition (CVD), followed by the deposition of nanomaterials on top of the CNTs by evaporation. The CNTs template was completely removed during the oxidation process while the remained nanowires had the identical geometry to the CNTs. Because all the fabrication procedure consists of dry and batch processes, it is possible to mass-produce the sensors without contamination or damage of the nanowires. The fabricated WO_3 nanowire-based sensor successfully detected 100 ppm of NO_2 at a temperature of 300 °C. The sensing performance of the sensor is attributed to the high surface area of the suspended morphology and small diameter of the nanowires.

INTRODUCTION

Over the past few decades, the 1-D nanostructures represented by nanowires, nanotubes, and nanorods have been widely studied, and are still continuously promising for the applications of electronics [1, 2], optoelectronics [3, 4], energy harvesting devices [5, 6] and sensors [7, 8]. Number of fabrication methods for 1D-nanostructures have been reported so far, such as vapor-liquid-solid (VLS) [9, 10], hydrothermal process [11, 12], and template-assisted method [13-15]. Among them, template-assisted method has been used in various fields, since it has many advantages including easy fabrication, low cost, and high throughput. Although alumina template, the most popularly adopted one, was used to fabricate diverse nanowires made of Ga_2O_3, In_2O_3, TiO_2 and Fe_2O_3 [16-18], there are some limits in this approach. First, the diameters of the fabricated nanowires are usually larger than 80 nm. Second, large-area synthesis of the template is difficult, which significantly lowers the throughput. Third, it is difficult to remove the alumina template completely.

Since the discovery by Iijima in 1991 [19], CNTs have attracted much interest as physical templates because they are easily mass-produced and removed at the temperature above 400°C. Rao and co-workers fabricated ZrO_2, Al_2O_3, V_2O_5, SiO_2 and MoO_3 nanotubes by sol-gel process on the surface of CNTs, followed by oxidation of the CNTs [20-22]. However, high cost and toxicity of metal alkoxides used in this approach, as well as long processing time, limited the usage of this technique. Liu et al. synthesized Fe_2O_3 and Cr_2O_3 nanotubes by supercritical chemical deposition using CNTs as template [23, 24]. Du et al. fabricated In_2O_3, NiO, SnO_2, Fe_2O_3 and CuO nanotubes using layer-by-layer assembly on the CNTs template in combination with oxidation of CNTs [25]. Later, the same group fabricated Co_3O_4 nanotubes using CNTs as templates and $Co_4(CO)_{12}$ as a precursor in organic solvent [26]. However, all the above template-based processes conducted in solvents are also limited in material choice, contamination and difficulty of device-integration. i.e., there are only a limited number of solution-processible metal oxide that may be formed as nanostructure; nanostructures could be easily contaminated, damaged or broken during the solution processes; additional complicated processes such as positioning and integrating nanostructures to electrodes, are needed to apply the nanostructures for devices.

Here, we introduce a technique to mass-produce suspended nanowires using evaporation of metals and metal oxides on the suspended CNTs template. The CNTs are oxidized and selectively removed leaving only the suspended nanowires. The suspended CNT network template is self-adjusted between two electrodes [27, 28], and thus, a two-terminal device in which the nanowires connect the two electrodes is easily formed. Unlike the previous researches, wide variety of materials can be formed as nanowires, as long as the material is deposited by evaporation. All of the fabrication steps are performed in dry condition, and thus the nanowires can maintain suspended state without any contamination. Fabricated WO_3 nanowires were tested to detect low concentration of NO_2 at 300 °C under atmospheric pressure.

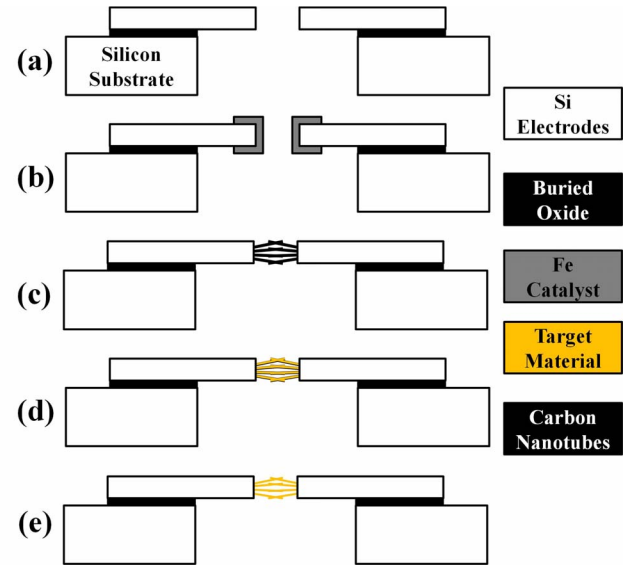

Figure 1: Fabrication process of the sensor. (a) Fabrication of MEMS electrodes on SOI substrate (b) Deposition of Fe catalyst by evaporation (c) Synthesis of suspended CNTs by CVD process (d) Deposition of target material on top of CNTs (e) Removal of CNTs through annealing process.

FABRICATION

The nanowires formation process is comprised of the following three steps: growing CNTs between two electrodes, depositing the material of which the nanowires will consist later onto the CNTs template, removing the CNTs template. For the fabrication of nanowires-based sensors, silicon microelectrodes were firstly patterned on a silicon-on-insulator (SOI) wafer by photolithography and etching (Figure 1(a)). Secondly, Fe catalyst was deposited by evaporation on the two separated electrodes through the opening of the shadow mask (Figure 1(b)). CNTs were then grown by CVD, filling the gap between the two electrodes as shown in Figure 1(c). The CNTs grown on each of the two separated electrodes come into contact with each other in the middle of the gap [27, 28]. After synthesizing CNTs, a material to be formed as nanowires was deposited on CNTs through the shadow mask by evaporation (Figure 1(d)). Figure 1(e) shows the suspended nanowires after removal of CNTs through annealing process. Nanowires fabricated in this way connect two electrodes just like CNTs did and two-terminal device was formed easily without any additional positioning or assembly process.

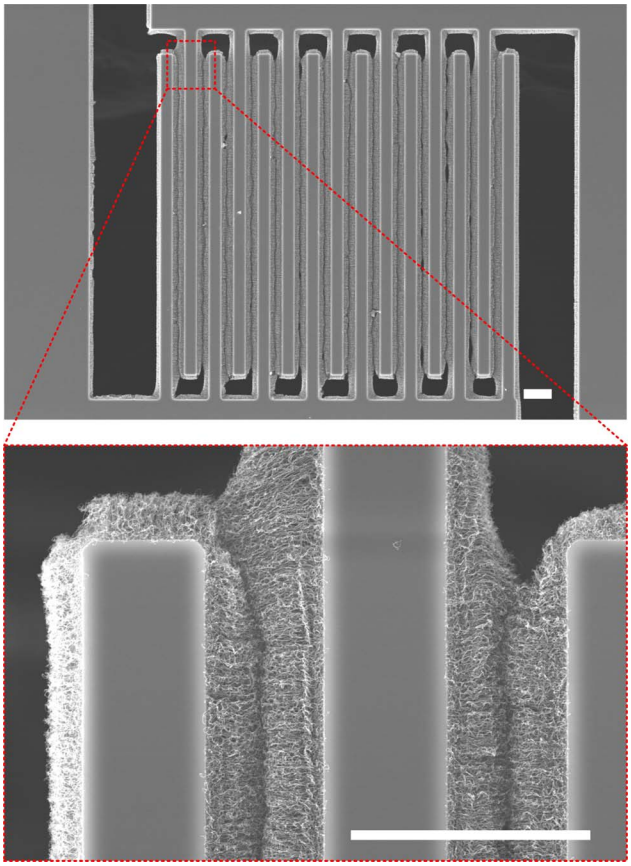

Figure 2: SEM images of the suspended WO_3 nanowires between the two separated electrodes after the removal of the CNTs. WO_3 nanowires remained with the shape identical to that of original CNTs after all the CNTs were oxidized at 600 °C for 6 hours. The scale bars in both figures are 50 µm.

RESULTS AND DISCUSSION

Scanning electron microscope (SEM) images of the suspended WO_3 nanowires are shown in Figure 2. The nanowires connect the two interdigitated electrodes (IDEs), where each finger measures 20 µm in width, 300 µm in length and 20 µm in height, while the gap between each finger is 20 µm. Since the IDEs are suspended, the CNTs are also suspended between the IDEs. The shape of WO_3 nanowires shown in the figure is similar to that of CNTs, which implies that the nanowires were not damaged or deformed during the oxidation process. The nanowires are suspended similarly as the CNTs were, which makes it possible to avoid the formation of gas boundary layers around the sensor or unnecessary electrical crosstalk with the substrate.

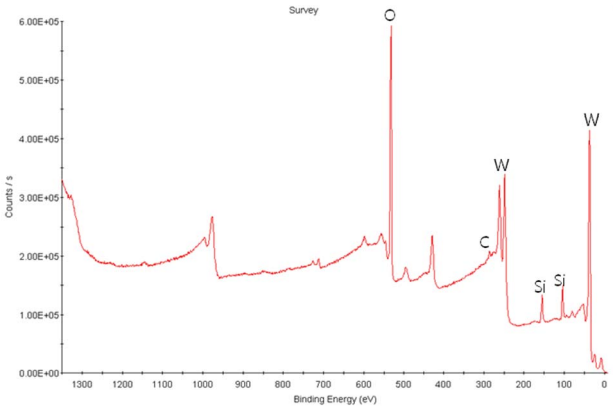

Figure 3: X-ray photoelectron spectroscopy (XPS) data after oxidizing all the CNTs.

It is well known that CNTs are oxidized into CO_2 at the temperature above 400 °C [29]. X-ray photoelectron spectroscopy (XPS) was carried out after oxidation of the CNTs template at 600 °C for 6 hours to verify that the CNTs were removed. Figure 3 shows the XPS data on WO_3 nanowires after the oxidation process. C peak appeared between the binding energies of 282 and 292 eV, and the peak magnitude was only a very small fraction of other species such as O, W and Si. This much of C is usually considered as a contaminant deposited on the surface of the material, which reveals that CNTs were removed completely as expected.

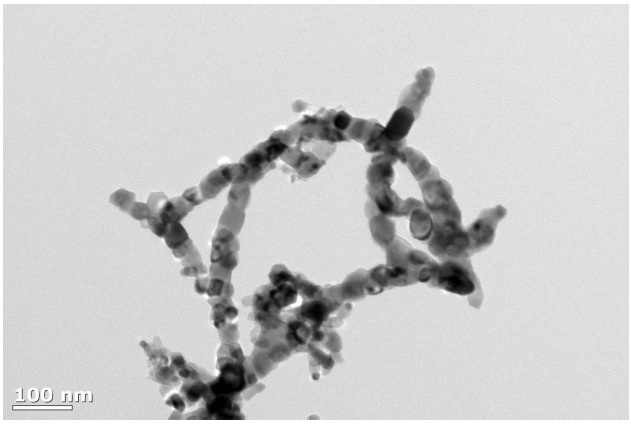

Figure 4: Transmission electron microscopy (TEM) image of WO_3 nanowires after the oxidation of CNTs. CNTs were removed completely and WO_3 maintained its nanowires shape after the oxidation process.

Evidence of complete removal of the CNTs can also be confirmed by Transmission electron microscopy (TEM) inspection. Figure 4 presents the TEM image of WO_3 nanowire after the oxidation process. As shown in the figure, WO_3 maintains the nanowire shape after the oxidation process, while the CNTs are completely removed.

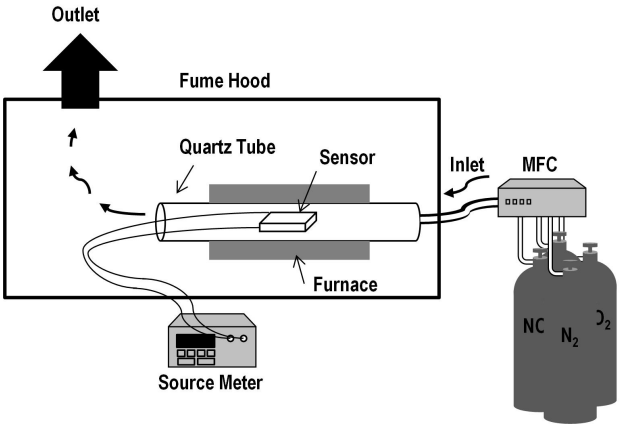

Figure 4: Experimental setup for gas sensing. Total gas flow rate is maintained constantly by a mass flow controller (MFC) to minimize the effect of the flow rate change.

The sensing performance of the fabricated sensor was tested by exposing it to a mixture of NO_2 and nitrogen gases at atmospheric pressure and temperature of 300 °C. Figure 4 is a schematic diagram showing the sensing setup used in the experiment. The flow rate of each gas was tightly controlled by MFC to evaluate the precise responsiveness of the sensor to different concentration of NO_2. In order to minimize the effect of the resistance change caused by the possible fluctuation of flow rate, total gas flow rate was constantly set to 500 sccm.

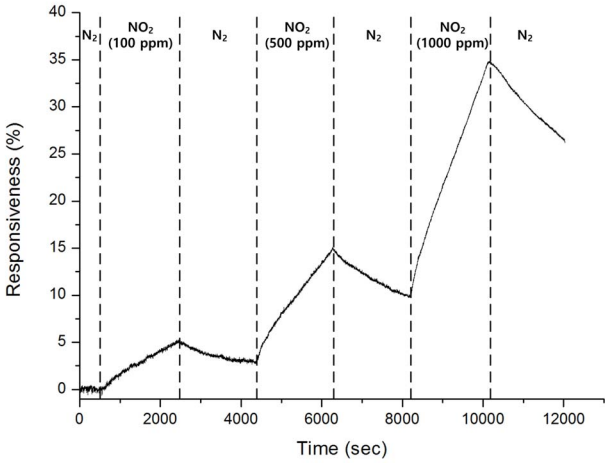

Figure 5: The responsiveness versus time for the suspended WO_3 nanowires at the exposure to different concentration of NO_2 gas from 100 ppm to 1,000 ppm.

Figure 5 shows the responsiveness of the suspended WO_3 nanowires to various NO_2 concentrations from 100 to 1,000 ppm. The responsiveness is defined as $(R_g - R_i) / R_i \times 100\%$, where R_i and R_g are the resistances of the sensors before and after the exposure to NO_2, respectively. At the exposure to NO_2 gas, absorbed molecules result in an increase of electrical resistance of WO_3 nanowires. When the NO_2 gas is turned off, molecules are desorbed and the resistance of the nanowires decreases. As the concentration of NO_2 decreases, the amount of NO_2 molecules absorbed to WO_3 nanowires is reduced, resulting in the decrease in responsiveness. The responsiveness of the sensor was 36.5, when nanowires were exposed to the mixture of 1,000 ppm NO_2 and nitrogen.

CONCLUSIONS

In conclusion, we fabricated suspended nanowires made of WO_3 using suspended CNTs as the template and by removing the CNTs. Compared to existing template-based methods, our approach contains several notable advantages. First, wide variety of material choice is possible to form suspended nanowires as long as the material can be physical vapor-deposited. Second, all of the fabrication steps, synthesizing CNTs, depositing materials and oxidizing the CNTs, are dry process, which allows the formation of two-terminal devices based on suspended nanowires without contamination. Finally, no additional integration process such as placement or assembly of nanowires between the electrodes is necessary since the nanowires are directly formed between the electrodes. WO_3 nanowires fabricated by this technique were used to demonstrate the NO_2 sensor application. Utilizing the versatility in material choice to generate suspended nanowires integrated to the microelectrodes, various sensors or sensor arrays with high sensitivity could be batch-fabricated.

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