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VLS silicon nanowires based resistors for chemical sensor applications

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Abstract

Silicon nanowires (SiNWs) based resistors are fabricated in two different structures: i) inter-digital comb-shaped structure and ii) V-shaped groove structure. The SiNWs used are synthesized by VLS (Vapor-Liquid-Solid) mechanism using gold as metal catalyst and carried out by LPCVD (Low Pressure Chemical Vapor Deposition). For the former structure, tangled SiNWs network interconnects the inter-digital comb-shaped heavily doped electrodes. For the latter structure, tangled SiNWs network is locally synthesized inside a predefined V-shaped groove. Compared with the inter-digital structure, the V-shaped structure is more compatible with planar technology. Thanks to the high surface-to-volume ratio of SiNWs, high-efficiency surface modification can be obtained. The quantitative dynamic measurements under exposure to a wide range of gas (ammonia) concentration (from 175 ppm to 700 ppm) were performed and demonstrated high performance of the SiNWs based resistors as sensitive chemical sensors.

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Keywords: VLS; silicon nanowires; gas sensor; ammonia;

1. Introduction

Owing to their physical and electrical properties, silicon nanowires (SiNWs) are currently attracting much attention as promising components for future nanoelectronic devices such as nanowire field effect transistors [1], photovoltaic devices [2] and bio-chemical sensors [3]. SiNWs can be prepared by both top-down and bottom-up approaches. As one of the main bottom-up approaches (self assembly method) to

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fabricate silicon nanowires, the VLS method enables to achieve mass production of silicon nanowires avoiding using high costly advanced lithographic tools. However, the difficulty in controlling the growth orientation of the nanowires restricts the planar compatibility. In this case, nanowires need to be selectively collected and manipulated to be assembled in a planar layout.

SiNWs present various advantages such as high surface to volume ratio, possibility of surface functionalization, and synthesis compatible with large area silicon technology (< 600°C), which leads to the development of innovative sensors. Main interest of SiNWs rests on their high surface that can be sensitive to charges. In this work, two different structures are fabricated: inter-digital comb-shaped structure which is achieved in a 3D configuration; and V-shaped groove structure which is compatible with planar technology. The two mentioned structures are used to fabricate devices acting as sensor for ambiance detection (ammonia) at room temperature.

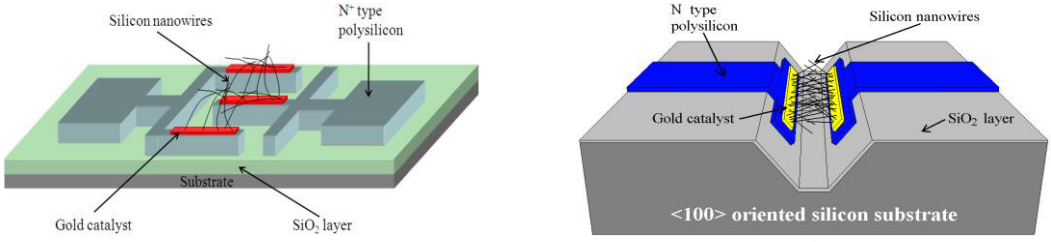
2. VLS silicon nanowires synthesis and devices fabrication

High density Au-catalyst VLS-SiNWs network is synthesized by LPCVD at 460°C and 40 Pa using silane as precursor gas [4]. Such SiNWs are integrated into resistors as shown in figure 1.

For the inter-digital comb-shaped structural device, a heavily phosphorous *in-situ* doped amorphous silicon layer is firstly deposited by LPCVD technique at 550°C and 90 Pa on a substrate (silicon wafer or glass substrate) capped with a SiO_2 buffer layer. Subsequent solid phase crystallization is performed by thermal annealing at 600°C under vacuum to get a highly doped polycrystalline silicon (polysilicon) film. This film is then patterned by Reactive Ion Etching (RIE) to define the geometry of the inter-digital comb-shaped electrodes (fig 1.a). Au thin film (< 5 nm) is then deposited by thermal evaporation and locally removed using a lift off technique in order to define precise location for SiNWs growth. The final step consists in the growth of VLS SiNWs by LPCVD technique.

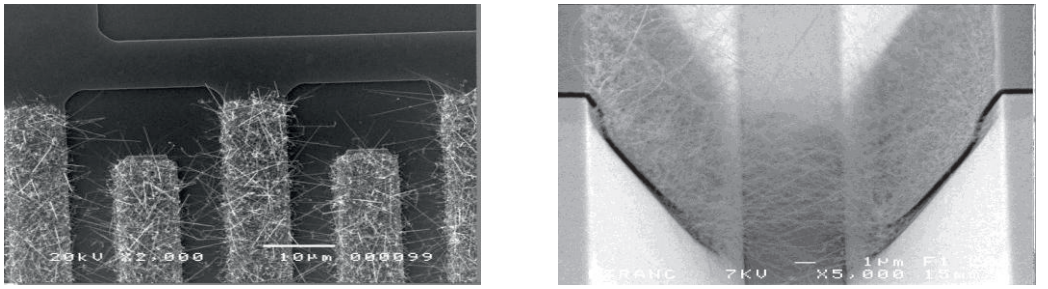
The V-shaped groove device is processed on a <100> oriented silicon wafer. A technological process based on Tetra-Methyl Ammonium Hydroxide (TMAH) wet etching [5] is used to achieve a V-shaped groove. At first, a 1-µm-thick SiO_2 layer is grown by wet thermal oxidation and patterned by wet etching to be used as hard mask. In this case, because of a higher etching rate of (100) plane than (111) plane, a V-shaped groove is achieved by using a 50% diluted TMAH solution at 80°C. Then a 70-nm-thick buffer SiO_2 layer and a heavily phosphorus doped polysilicon layer are deposited successively. The polysilicon layer is then patterned and dry etched to define the geometry of the electrodes (fig 1.b). The following steps to synthesize the SiNWs are identical to those used for the inter-digital comb-shaped device.

Due to the length of the SiNWs which can exceed 20 µm, bridges and SiNWs crossing contacts ensure the electrical connection between these two heavily doped polysilicon islands leading to the formation of resistors in a 3D configuration. This synthesis results in a tangled growth of about 150 nm diameter SiNWs. Depending on the device structure, SiNWs network is synthesized over the substrate surface (fig 2.a) or inside the predefined V-shaped groove (fig 2.b). Therefore, the latter structure is more compatible for planar technology.



(a) (b)

Fig. 1. Schematic views of the (a) Inter-digital comb-shaped, and (b) the V-shaped groove VLS-SiNWs based resistors.



(a) (b)

Fig. 2. SEM pictures of the (a) Inter-digital comb-shaped and (b) the V-shaped groove VLS-SiNWs based resistors.

3. Results

Previous results demonstrated the feasibility of such SiNWs based resistors [4]. Performances of these devices are characterized measuring the current using a pico-ammeter (Keithley 2636A) whereas the voltage of the dc source is fixed at 1V. The deduced R-values are then reported as function of time for devices under exposure to ammonia. Prior to measurements, a highly diluted hydrofluoridric acid (2 %) aqueous solution based wet etching is used to remove the native oxide on the SiNWs surface in order to promote chemical species adsorption. Then, SiNWs based devices are put into a vacuum chamber. Electrical measurements are carried out at room temperature and the pressure is monitored at 500mbar regardless of the gas (ammonia) flow injection. Before beginning the sensing measurement, a degassing process is carried out at 200°C for one hour. The sample is then cooled down to room temperature.

At first, a flow of nitrogen gas is injected continuously into the chamber during few minutes to guarantee current baseline leveled off. Then, a flow of ammonia is injected with the chosen dilution of NH_3/N_2 during a few minutes. Then, the gas injection is cut off and the gas mixture of NH_3/N_2 is evacuated by pumping. During the whole period of measurement, gas mixture is exchanged all the time whereas the concentration of the gases is kept constant.

The potential use of these SiNWs as sensitive units to ammonia detection was checked by measuring the detection response, S_g, defined as:

$$S_g = \left|\frac{R_g - R}{R_g}\right| = \left|\frac{I - I_g}{I}\right| \qquad (1)$$

where R (I) and Rg (Ig) are the resistance (current) values for devices under nitrogen and reactive ambience, respectively.

Figure 3 shows results of dynamic measurements carried out on both structures that consist in exposing SiNWs under various ratio of ammonia (from 175 ppm to 700 ppm) at room temperature. Upon exposure, S_g ($\Delta R/R_g$) increases significantly with an increase in concentration for both VLS SiNWs resistors.

For the chemical and biological sensors, the large surface-to-volume ratio enables SiNWs sensors to have promising performances. The mechanism of such sensors is explained in two main theories, charge exchanging effect and chemical gating effect. The charge exchanging effect means that there could be charges exchange between the adsorbed molecules and the SiNWs. It means that the NH_3 molecules adsorbed on the surface of the SiNWs could transfer charges following the equation: $NH_3 \rightarrow NH_3^+ + e^-$ due to the reducing effect (electron donor) of ammonia. This phenomenon could directly inject electron carriers into the SiNWs, thus decreasing the resistance [6]. Moreover, as SiNWs conductance can be modulated by an applied voltage [6, 7], positively charged gas molecules (electron donors) bound on

SiNWs surface can modulate their conductance by changing the volume of the conductive layer. In this case, the adsorbed gas molecules, NH_3^+ may act as chemical gates which shift the Fermi level of the undoped SiNWs in the upper part of the band gap and reduces the resistance of the VLS SiNWs based device.

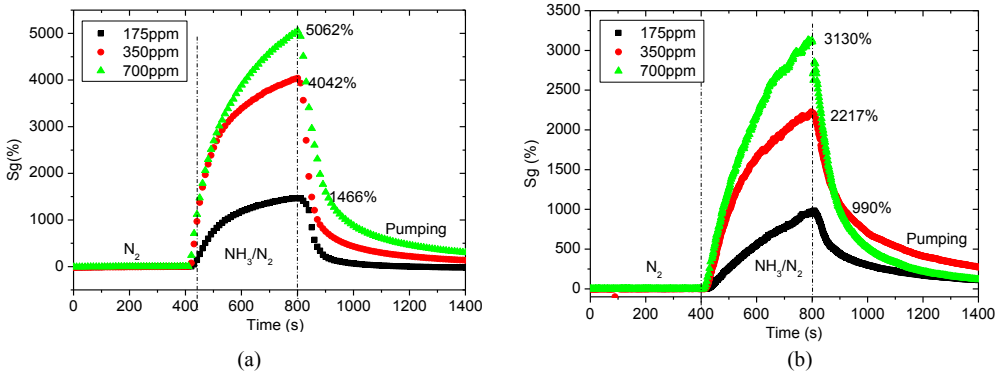


Fig. 3. Sg (ΔR/Rg) variation as a function of exposure time to different concentrations of NH_3/N_2 ranging from 175 to 700 ppm for, (a) Inter-digital comb-shaped, (b) V-shaped groove SiNWs resistors.

4. Conclusion

In summary, we report two different resistors based on VLS SiNWs, inter-digital comb-shaped structure and V-shaped groove structure used as gas (ammonia) sensors. The high performance under exposure over a wide range of ammonia concentration at room temperature was monitored, which illustrates the possibility of these simple devices to act as a new kind of chemical sensors. Moreover, the V-shaped groove based resistor provides possibility to assemble with a capping PDMS (poly-dimethyl siloxane) mold and compatibility for planar integration, because the space between the PDMS mold and the etched groove channel could confine the analytes, and most of the SiNWs are located inside the V-shaped groove.

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