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Silicon nanowires synthesis for chemical sensor applications

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Abstract

Silicon nanowires (SiNWs) are synthesized following two methods: i) the VLS (Vapor-Liquid-Solid) growth technique (bottom up approach), and ii) the sidewall spacer fabrication (top down approach) commonly used in microelectronic industry. The VLS growth technique uses gold nanoparticles to activate the vapor deposition of the precursor gas and initiate a 100 nm diameter SiNWs network growth. In the case of the sidewall spacer method, a polysilicon layer is deposited by LPCVD (Low Pressure Chemical Vapor Deposition) technique on SiO_2 wall patterned by conventional UV lithography technique. Polysilicon film is then plasma etched. Accurate control of the etching rate leads to the formation of spacers with a 100 nm curvature radius that can be used as polysilicon NWs. Each kind of nanowires is integrated into resistors fabrication. Electrical measurements show the potential usefulness of these SiNWs as chemical sensors.

Keywords: Silicon nanowires ; synthesis ; chemical sensor ;

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1. Introduction

Semiconducting nanowires are currently attracting much attention as promising components for future nanoelectronic devices such as nanowire field effect transistors [1], photonic and optoelectronic devices [2], and more particularly as chemical or biological sensors [3-5]. The need of a fast and precise detection of early disease symptoms, as well as the need of environment safety, becomes now the main leitmotiv of the societal development. The incorporation of semiconducting nanowires into chemical and biological sensors applications receives a great interest. As their surface can be sensitive to charged species combined with their high surface to volume ratio, semiconducting nanowires are the subject of intense research activities for high sensitivity chemical sensor fabrication.

The first application of silicon nanowires (SiNWs) in biological and chemical sensor was reported by Lieber’s group in 2001 [3]. As SiNWs synthesis can be compatible to the established Si technology, SiNWs based sensor integration will allow a lower manufacturing cost, in addition to the advantageous electronic features of embedded detection and signal processing in silicon technology. The intrinsic reliability of the well-known semiconductor CMOS (Complementary Metal Oxide Semiconductor) process also guarantees a reproducible and reliable diagnosis.

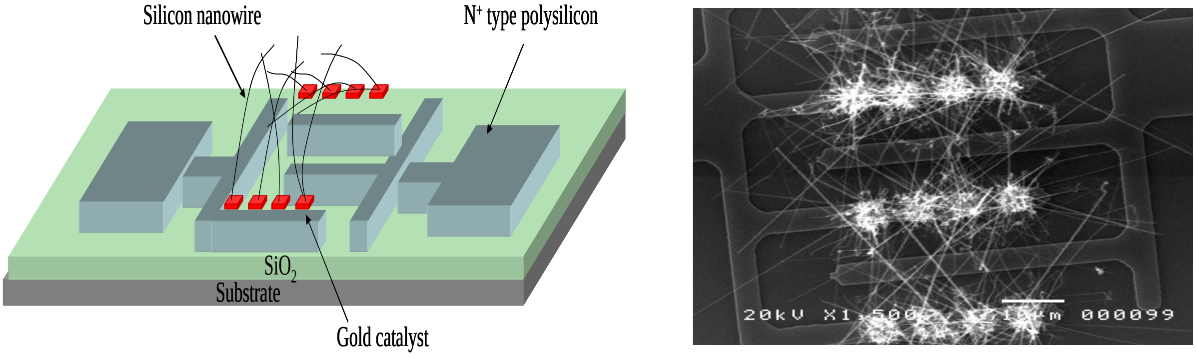
SiNWs can be prepared by the top-down approach, using various advanced methods such as e-beam [5], AFM [6] or deep UV [7] lithography. The main disadvantage of these advanced lithographic tools with nanometer size resolution rests on the high cost generated. An alternative way to synthesize SiNWs is the bottom-up approach that usually employs metal catalytic growth. The most commonly used growth technique is the VLS (Vapor-Liquid-Solid) method using metallic nanoparticles. The metal catalyst used is usually gold although other metals are also employed [8]. However, this approach suffers from the difficulty in precisely positioning the device.

In this work, two types of SiNWs are synthesized, without requiring costly lithographic tools, following the VLS growth technique (bottom up approach), and the sidewall spacer realization (top down approach) commonly used in microelectronic industry. These SiNWs are integrated into low temperature (< 600°C) silicon technology resistors fabrication and their ability as sensitive unit for ambiance detection is demonstrated.

2. Silicon nanowires synthesis and devices fabrication

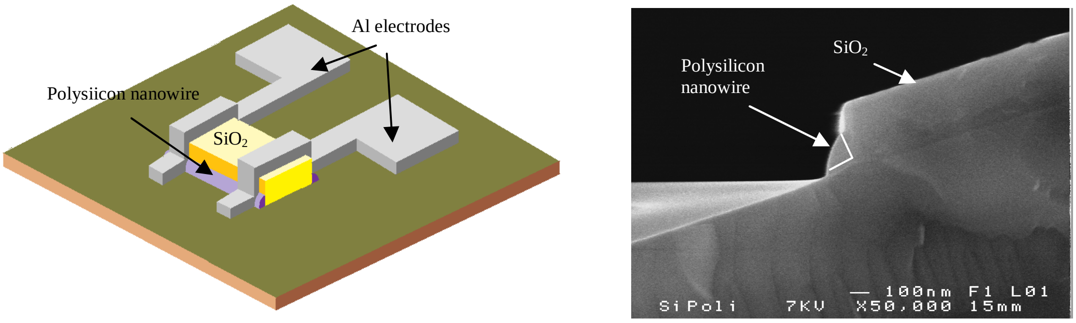
High density Au-catalyst VLS-SiNWs network is synthesized by LPCVD (Low Pressure Chemical Vapor Deposition) technique at 480°C and 40 Pa using silane as precursor gas. Such SiNWs are integrated into resistors (figure 1). First, a heavily phosphorous *in-situ* doped amorphous silicon layer is deposited 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 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 comb shape electrodes (interdigitated structure shown in figure 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. 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 100 nm diameter SiNWs. LPCVD parameters are chosen in order to avoid silicon deposition on areas uncovered with Au thin film (figure 1 (b)).

The sidewall spacer method is an alternative way to synthesis SiNWs in a 2D configuration. At first, a dielectric film A is deposited and patterned into islands by conventional UV lithography. Then an undoped polysilicon layer is deposited by LPCVD technique. Silicon film is deposited in an amorphous state at 550°C and 90 Pa, and then crystallized by a thermal annealing under vacuum at 600°C during 12 hours. Accurate control of the polysilicon layer RIE rate leads to the formation of nanometric size sidewall spacers that can be used as nanowires. The feasibility of this technological step was previously reported [9]. Thus, 10 µm length polysilicon NWs with a 100 nm curvature radius are synthesized and integrated into resistors devices in coplanar structure (figure 2). In this case contacts electrodes are made of thermally evaporated aluminum and defined by wet etching. Finally a thermal annealing in forming gas (N_2:H_2) is carried out to ensure good electrical contacts.



(a) (b)

Fig. 1. VLS-SiNWs based resistor: (a) schematic view; (b) SEM picture (100 nm diameter SiNWs grow from Au deposited on local areas on half teeth)



(a) (b)

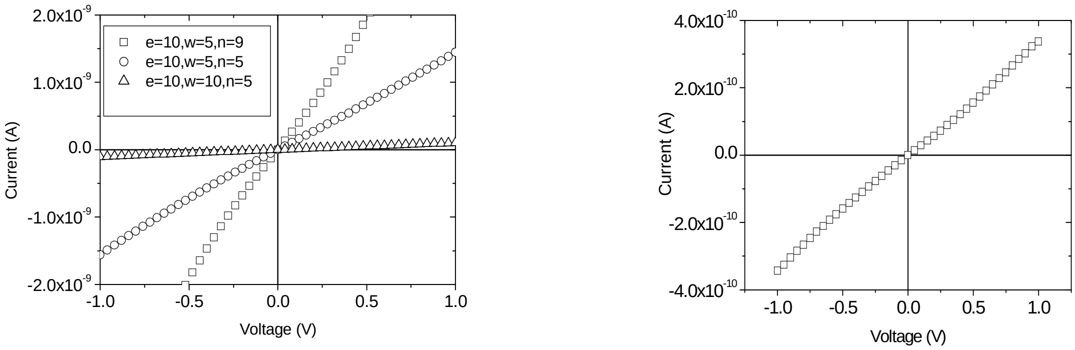
Fig. 2. Spacer method polysilicon NW based resistor: (a) schematic view; (b) SEM picture of 100 nm curvature radius polysilicon NW (cross section view)

3. Results

For SiNWs based resistors electrical sensitivity measurements, samples are placed in an isolated chamber at room temperature. Static electrical characteristics I(V) are collected using a HP 4155 B semiconductor parameter analyzer. Control humidity in air environments are achieved using a humidity/temperature measuring system Testo 635.

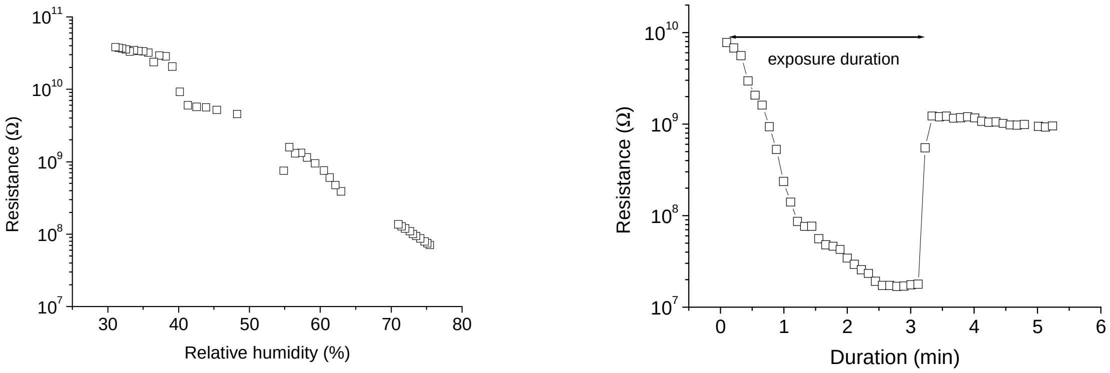
Typical I(V) characteristics of the two different SiNWs based resistors plotted in figure 3 show the feasibility of such SiNWs based devices. The chemical sensitivity of these SiNWs based resistors to smoke and humidity in air is displayed in figure 4. Upon exposure, resistance is found to dramatically decrease over 3 orders of magnitude for the two SiNWs based resistors. These results indicate that VLS-SiNWS and polysilicon NWs are extremely sensitive to humidity and smoke respectively. In addition, the electrical response of polysilicon NWs under smoke exposure is quasi reversible suggesting that SiNWs could be reusable after exposure.

As the gas molecules adsorption occurs at the SiNWs surface, effects are electrically transferred to the crystal bulk. Such interactions induce significant changes in the carrier transport along the nanowires and may affect SiNWs resistance in different possible cumulative ways. First, as the SiNWs conductance can be modulated by an applied voltage [10], gas molecules binded on SiNWs surface can modulate their conductance by changing the volume of the conductive layer. In this case, smoke and water vapor may act as chemical gates. In other words, it means that the Fermi level of the Si nanowires is shifted reducing the sample resistance. This phenomenon may occur on the two SiNWs structures. Moreover, carrier transport depends on structural nanowires defects. So, we have to consider effects of grain boundaries (spacer method – SiNWs) and contact resistance between nanowires-



(a) (b)

Fig. 3. I(V) characteristics of the SiNWs based resistors: (a) VLS method (current depends on the space between teeth, w, and the number of teeth, n) ; (b) spacer method.



(a) (b)

Fig. 4. (a) Resistance variations versus relative humidity of the SiNWs based resistor (VLS method), (b) Resistance variations versus exposure duration to smoke of the polysilicon NWs based resistor (spacer method)

VLS - method). Through charge exchange, gas molecules adsorbed may play a significant role in decreasing the potential barrier height at the tunnel junction of two crossed SiNWs (VLS method) or the potential barrier height at the grain boundaries between two grains (spacer method). Previous work reported such effect [11].

4. Conclusion

In summary, we report the SiNWs synthesis using bottom up and top down approaches. These nanowires, integrated into resistors electrically tested, show their sensitivity under exposure to smoke and humidity due to ambient charged species detection. The results serve as proof-of-concept for a new kind of SiNWs as sensitive units for high performance integrated chemical sensors. Further work will focus on the SiNWs surface functionalization as well as on the optimization of the surface /volume ratio to get high sensivity sensor.

Acknowledgements

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