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Silicon nanowires based resistors as gas sensors

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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 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 SiO₂ 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 based resistors as gas sensors for ammonia (NH₃) and smoke detection.

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 sensors was reported by Lieber's group in 2001 [3]. As SiNWs synthesis can be compatible with 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 non intentionally doped 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 ($< 600^{\circ}\text{C}$) silicon technology resistors fabrication and their ability as sensitive units for gas (ammonia) and ambience (smoke) detections is demonstrated.

2. Silicon nanowires synthesis and resistors fabrication

2.1 VLS SiNWs based devices

The VLS mechanism was proposed in 1964 as an explanation for silicon whisker growth from the gas phase in the presence of a liquid gold droplet placed upon a silicon substrate [9]. Such mechanism is described following three steps: i) preparation of a liquid alloy droplet (catalyst) upon the substrate from which a wire is to be grown, ii) introduction of the substance to be grown as a vapor (precursor gas), which absorbs on the liquid surface, and diffuses into the droplet, and iii) supersaturation and nucleation at the liquid/solid interface leading to axial crystal growth.

Au-catalyst VLS SiNWs were synthesized and integrated into resistors. In this way, a heavily phosphorous *in-situ* doped amorphous silicon layer was first deposited by LPCVD (Low Pressure Chemical Vapor Deposition) 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 was performed at 600°C under vacuum to get a highly doped polycrystalline silicon (polysilicon) film. This film was patterned by Reactive Ion Etching (RIE) to define the geometry of the comb shape electrodes (interdigitated structure shown in Fig.1(a)). Au thin film (≤ 5 nm) was then deposited by thermal evaporation and locally removed using a lift off technique in order to define precise location for SiNWs growth (Fig.1(b)). High density Au-catalyst non intentionally doped VLS-SiNWs network was then synthesized by LPCVD technique at 460°C and 40 Pa using silane (SiH_4) as precursor

gas. Due to the length of the SiNWs which can exceed 20 μm , bridges and contacts between SiNWs ensure the connection of these two heavily *in-situ* doped polysilicon islands leading to the formation of resistors in a 3D configuration (Fig.1(c)). This synthesis results in a tangled growth of 100 nm diameter SiNWs insuring electrical contact between the two doped electrodes (Fig.1(d)). LPCVD parameters were chosen in order to avoid silicon deposition on areas uncovered with Au thin film.

Previous study [10] of electrical behavior of such VLS SiNWs based resistors showed that the global electrical resistance results from the contribution of the silicon NWs. In addition, such electrical resistance value is both dependent on the length and the number of effective conductive paths [11] (difficult to estimate).

2.2 Spacer method SiNWs based devices

The sidewall spacer method is commonly used in submicron scale device silicon technology to insulate device active area. In our case, the spacer at nanometric scale made of silicon constitutes the nanowire. This method is an alternative way to synthesize SiNWs in a 2D configuration (Fig.2).

At first, a dielectric film A was deposited and patterned into islands by conventional UV lithography. Then, an undoped polysilicon layer was deposited by LPCVD technique. Silicon film was deposited in an amorphous state at 550°C and 90 Pa, and then crystallized by 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 (Fig 2(a)). The feasibility of this technological step was previously reported [12]. Thus, non intentionally doped polysilicon NWs with a 100 nm curvature radius were synthesized (see Fig.2(b)). This method allows the fabrication of parallel SiNWs network over a large area. Such polysilicon NWs were integrated into resistors devices in coplanar structure. In this case, contacts

electrodes were made of thermally evaporated aluminum and defined by wet etching (Fig.2(c)). Finally a thermal annealing in forming gas (N₂:H₂) was carried out to ensure good electrical contacts. Resistors were fabricated with 10 μm length parallel SiNWs.

3. Results and discussion

3.1 Methodology

Performances of SiNWs based resistors are characterized measuring static electrical characteristics I-V using HP4155B semiconductor parameter analyzer. The resistance ($R=V/I$) is deduced from the slope of the linear I-V curves for each device previously reported [11, 12]. R-values are then reported as function of time for devices under exposure to ammonia or smoke. Prior to measurements, devices were submitted to high diluted hydrofluoridric acid (2 %) aqueous solution to remove the native oxide on the SiNWs surface in order to promote chemical species adsorption. Then, SiNWs based devices were put into a vacuum chamber. The electrical measurements were carried out at room temperature with an all or nothing protocol: it means after evacuating the chamber ($P=10^{-4}$ mbar) ammonia (or burnt incense stick smoke) was introduced without any carrier gas. Ammonia partial pressure during SiNWs based resistors exposure is about 200 mbar.

The ammonia or smoke detector response, S_g , is defined as:

$$S_g = \frac{R_g - R}{R_g} = \frac{I - I_g}{I} \quad (1)$$

where R (I) and R_g (I_g) are the resistance (current) values for devices in vacuum and reactive ambient respectively.

3.2 Chemical species detection

The chemical responses of these SiNWs based resistors to ammonia or incense smoke exposure are presented in function of exposure time in Fig.3 and 4 respectively. For each SiNWs based device deduced values of S_g are summed up in Table 1.

Upon exposure to ammonia cycling tests (Fig.3), time dependence change of the electrical resistance is found to indicate a quasi reversible trend suggesting that SiNWs could be reusable after exposure. For the two types of non doped SiNWs based devices, electrical resistance decreases because ammonia species act as donor of electrons (reducing agents) at the SiNWs surface [13]. Under incense smoke exposure, the cycling tests show a decrease of the electrical resistance (Fig. 4), which shows that chemical species adsorbed at the SiNWs surface mostly act as reducing agents. However, the reversibility is not effective because it is lower after the second cycle. This may be related to the chemical species contained in the incense smoke. Indeed, the gas products from burning incense include CO, CO₂, NO₂, SO₂... The lower value observed for the two types of SiNWs based resistors after the second cycle suggests that some of these species might not be desorbed after exposure.

As the gas molecules adsorption occurs at the SiNWs surface, electrons are transferred to the SiNWs crystal core. Such interactions induce significant changes in the carriers transport along the nanowires and SiNWs electrical resistance in different possible cumulative ways. First, as the SiNWs conductance can be modulated by an applied voltage [13,14], positively charged gas molecules (electron donors) binded on SiNWs surface can modulate their conductance by changing the volume of the conductive layer. In this case, ammonia and incense smoke may act as chemical gates. In other words, it means that the Fermi level of the Si nanowires is shifted reducing the sample electrical resistance. This phenomenon may occur on the two SiNWs structures. Moreover, carrier transport strongly depends on structural nanowires defects. So, we have to consider effects of grain boundaries (spacer method – SiNWs) and contact resistance

between nanowires (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 [15]. For the two types of SiNWs based devices, the electrical resistance decrease under ammonia or incense smoke exposure suggests that electrons transfer and potential barriers lowering effects may dominate. In such case, the higher measured relative responses for poly-SiNWs based resistors could be related to the higher defects density for the polysilicon SiNWs due to their polycrystalline texture, promoting a higher chemical species adsorption. However, the lower relative responses for VLS SiNWs based resistors could be explained by another reason: gold impurities embedded within NWs bulk during the process growth. Such impurities might act as recombination centers, and therefore they could be responsible of a lowering of the electrons transfer effect related to chemical species detection.

These first qualitative results show the potential usefulness of the two kinds of nanowires as sensitive units for high sensitive gas sensors applications operating at room temperature.

4. Conclusion

In summary, we report the SiNWs synthesis using bottom up or top down approaches, over a large area and with high density, without requiring costly lithographic tools. These nanowires, integrated into resistors electrically tested, show their sensitivity under exposure to ammonia and smoke due to ambient charged species detection. The first results serve as proof-of-concept for a new kind of SiNWs as promising sensitive units for high performance room temperature chemical sensors compatible with classical integrated silicon technology. Further work will focus on the SiNWs surface functionalization for sensing different kinds of gases as well as on the optimization of the surface/volume ratio to get high sensitivity sensor.

Acknowledgments

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Figure captions

Figure 1: Key device fabrication steps of the SiNWs based resistors (VLS method). (a) Definition of the comb shape electrodes geometry on a SiO₂ capped substrate. (b) Thin film Au local deposition after lift off technique. (c) Growth of Au-catalyst VLS SiNWs by LPCVD. (d) SEM top view observation of VLS SiNWs based resistor.

Figure 2: (a) Fabrication of polysilicon NWs by the sidewall spacer formation technique. (b) SEM pictures of 100 nm radius curvature polysilicon NWs cross section view. (c) Spacer method 10 μm length polysilicon NW based resistor.

Figure 3: Electrical resistance variations versus time under ammonia exposure cycling test (a) VLS – SiNWs, (b) polysilicon nanowires (spacer method).

Figure 4: Electrical resistance variations versus time under smoke exposure cycling test (a) VLS – SiNWs, (b) polysilicon nanowires (spacer method).

Table caption

Table 1: Summary of the relative responses to ammonia and smoke for VLS and polysilicon SiNWs based resistors.

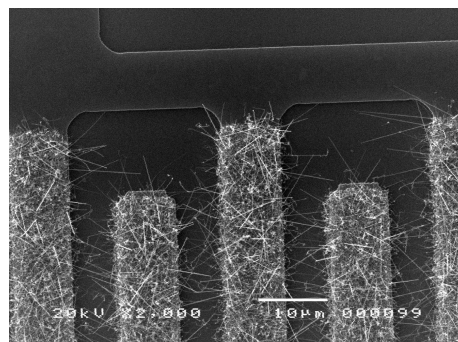
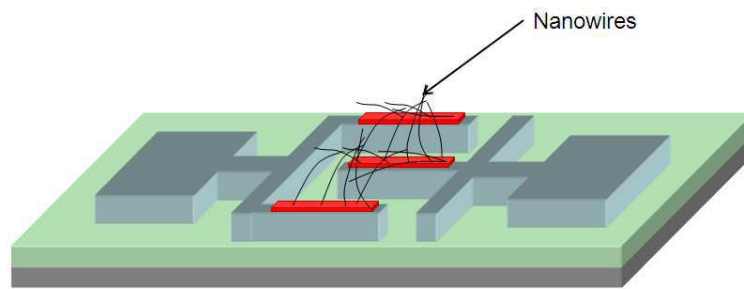
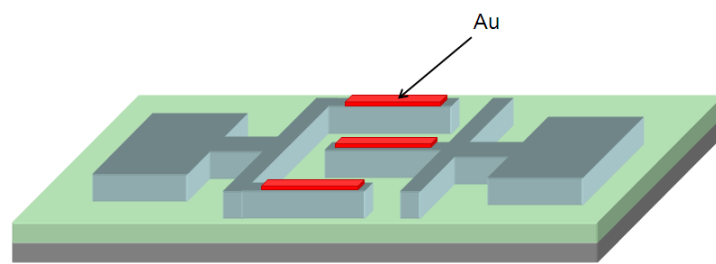
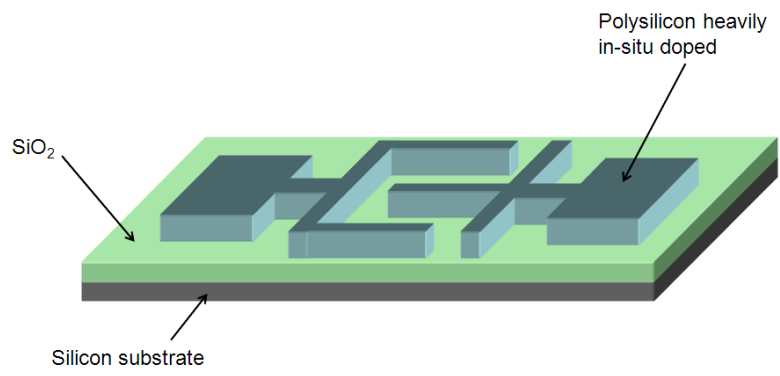


Figure 1

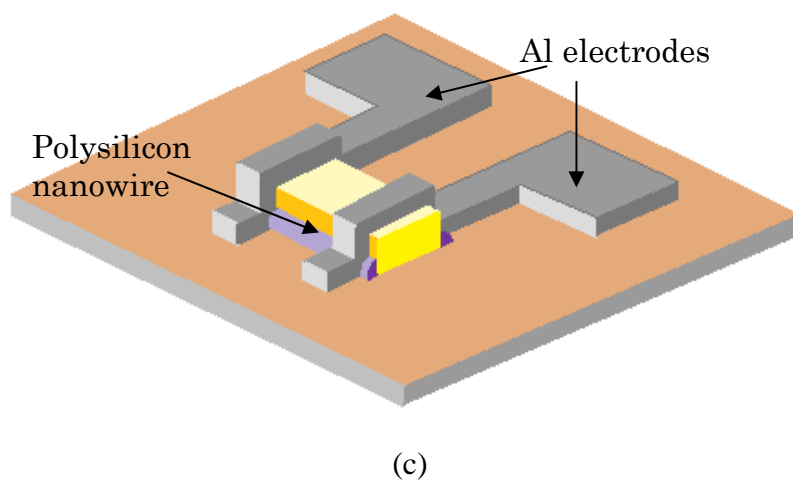
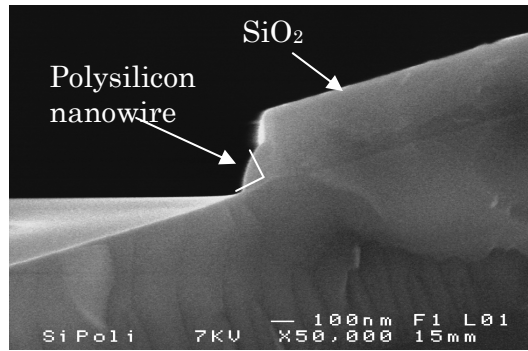
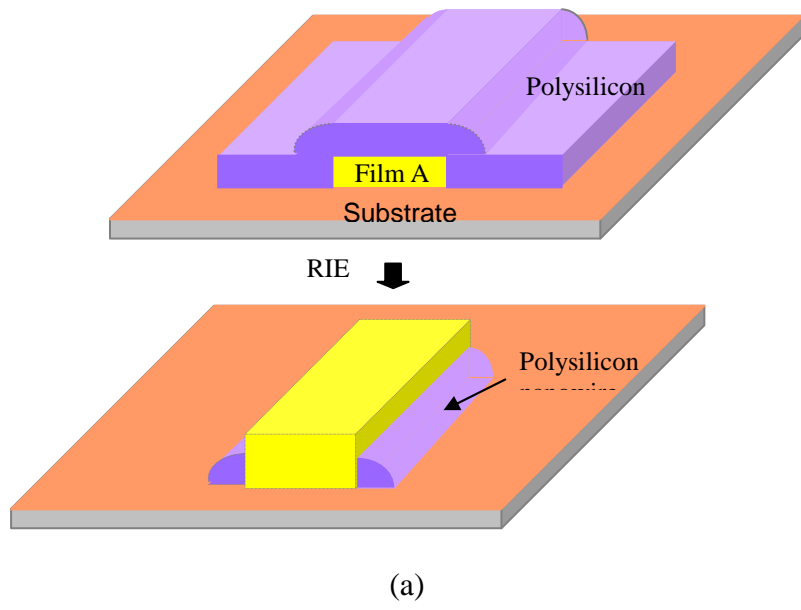
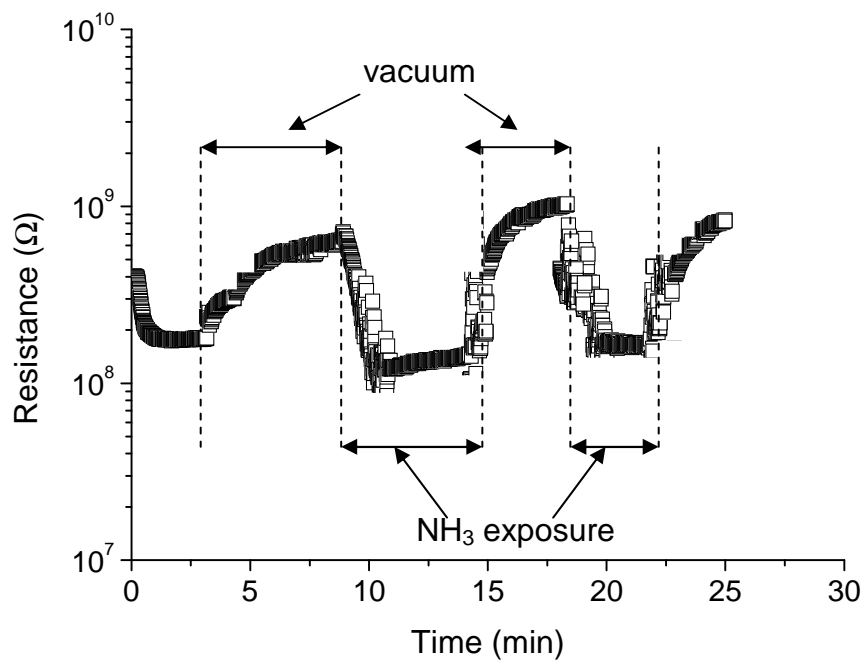
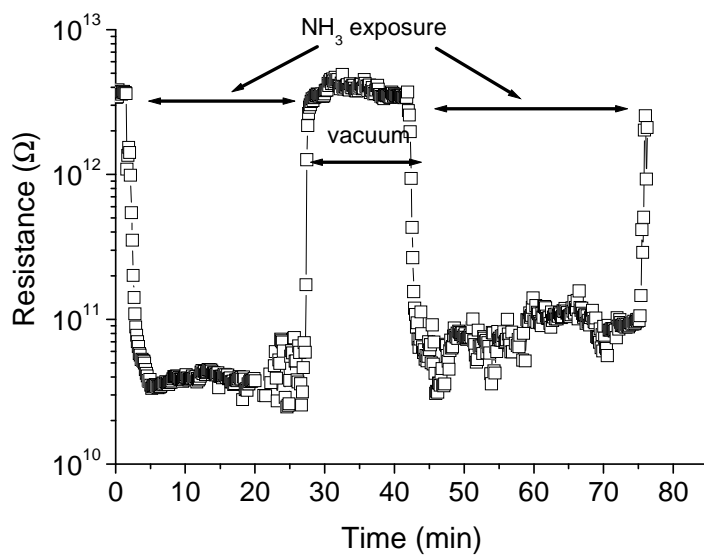


Figure 2

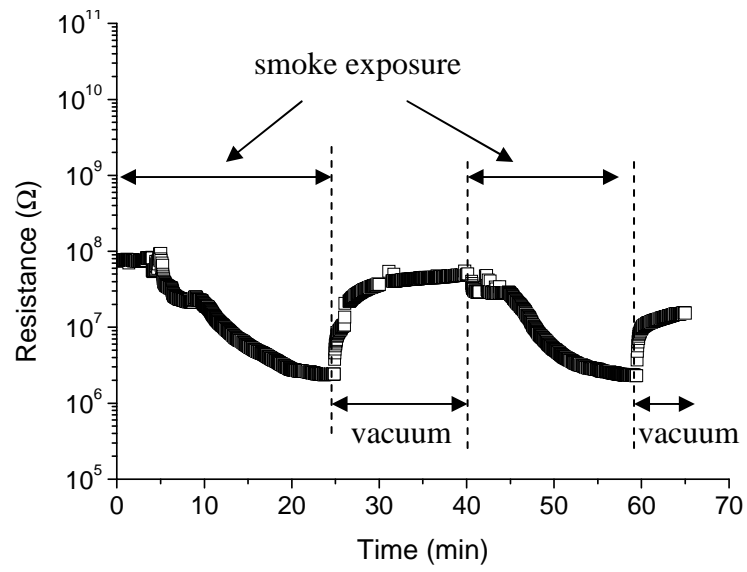


(a)

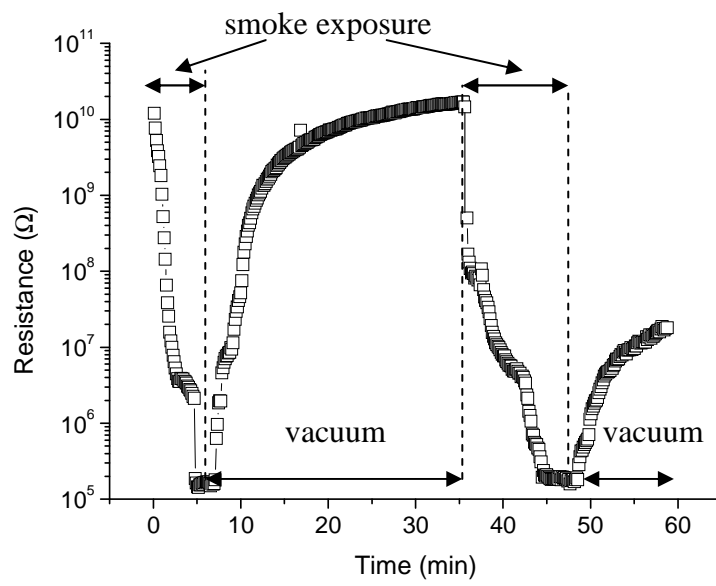


(b)

Figure 3



(a)



(b)

Figure 4

	S_g (%) (NH ₃)	S_g (%) (smoke)
VLS SiNWs based resistors	~ 2000	~ 2×10 ⁴
Polysilicon SiNWs based resistors	~ 10 ⁴	~ 10 ⁷

Table 1