Germanium coated silicon nanowires as human respiratory sensing device

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***Abstract*—We report on germanium coated silicon nanowires structures synthesized with metal assisted chemical etching and qualify their functionality as human respiratory sensor. The sensors were made from p-type single-crystalline (100) silicon wafers using a silver catalyzed top-down etching, afterwards coated by 50 nm germanium thin layer using a magnetron sputtering. The germanium post-treatment was performed by rapid thermal annealing at 450 and 700°C. The sensors were characterized by X-ray diffraction diffractogram and scanning electron microscopy. It is demonstrated that the sensors are highly sensitive as human breath detectors, with rapid response and frequency detectability. They are also shown to be a good candidate for human respiratory disease diagnoses.**

***Index Terms*—Silicon nanowire arrays, MACE, air flow sensors, humidity sensors**

I. Introduction

Sleep apnea syndrome is a potentially serious disorder during which breathing readily stops and starts with the occurrence of approximately 30 apneas during 7-8 hours of sleep. Increasing number of individuals suffer from sleep apnea complications, for instance hypertension and stroke, making sleep apnea a frequent cause of stroke. Therefore, respiratory monitoring of individuals posing sleep apnea syndrome is of prime importance.

In this context pressure and humidity sensors are of particular interest as they offer broad application in industry process control, environmental monitoring, clean rooms, medical or health care facilities, and more [1]–[3]. With rapid growth in technology, a vast variety of materials have been investigated for pressure and humidity sensing, to mention silicon nanowires (SiNWs), ZnO, GaN,TiO_2, carbon nanotubes, composite fibres/polymers(such as PDMS) combined with conductive nanostructure such as metals, carbon nanotubes and modified graphene [1], [2], [4]. However for these composite systems the long term sensing is not reliable as they tend to degrade in ambient atmosphere over time. Of these materials SiNWs pose superior characteristics due to its unique structural, electrical, optical, and thermoelectric properties [5], device compatibility, having larger surface area with high sensitivity to pressure and humidity.

It has been shown that SiNWs exhibit an anomolous piezoresistance effect, much higher than bulk silicon [6], and several sensors based on piezoresistance properties of SiNWs, prepared with metal assisted chemical etching (MACE) have also been proposed, for instance flexible pressure sensors [7], airflow sensing devices [8], or other pressure sensors [9]. Zhang et al [10], reported a flow sensor based on SiNWs NEMS sensors for a low pressure range which is critical for bio-compatible devices such as breath sensors. Additionally, stability, fast response and recovery time, and stabilized resistance baseline are important factors that most of the proposed sensors could not achieve [4]. Recently, a breath sensor based on periodic silicon nanorods was proposed [2]. In this paper we report a fabrication rout and characterisation of a low-cost, easy to fabricate, bio-compatible, and rapidly scalable breath sensor, based on random and interconnected SiNWs, coated with germanium nanoparticles.

II. Experimental

A. Materials and methods

Synthesis of arrays of random and interconnected SiNWs were fabricated on 10×10 mm^2 p-type, single-side polished, 525 μm thick Si (001) substrates, with resistivity of ρ of 0.1-0.5 Ωcm. A full description of synthesis process can be found in previous publication [5]. Briefly, a three step MACE process, with silver as metal, was performed as follows:

1) The Si substrate was deposited with Ag nanoparticles catalyst by immersing the substrate in a solution of 3 M HF and 2 mM $AgNO_3$ for 60 seconds.
2) To obtain vertically aligned SiNWs, after deposition of Ag nanoparticles, the substrate was etched by a HF:H_2O_2 (5M:0.4M) solution.
3) After etching the excess Ag nanoparticles were removed by immersing the sample in a 20% w/v HNO_3 solution.

Two structural schemes were utilized in this study including SiNWs and Ge-coated SiNWs either in as-synthesized or annealed state. For the Ge deposition, direct current magnetron sputtering was utilized at constant power of 30 W using a 5N-Ge target. Argon was utilized as working gas and the throttle valves were adjusted to stabilize the growth pressure of 0.7 Pa. After deposition, the sampler were subjected to rapid thermal annealing and ex-situ characterizations. JPilec JetFirst 150 was used to anneal the samples at 450 and 700°C under vacuum at 2×10^{-5} bar.

B. Characterization

The samples were characterized using X-ray diffraction (XRD) measurements using a Panalytical X'pert diffractometer (CuKα, 0.15406 nm) and scanning electron microscopy

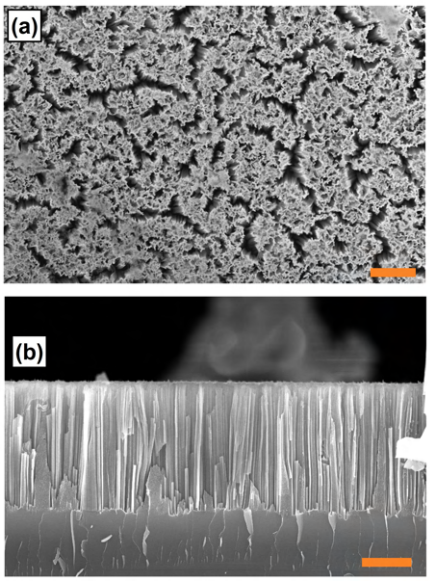

Fig. 1. (a) Top-view and (b) cross-sectional SEM micrograph of SiNWs obtained by MACE. The scale bar provided is 2μm.

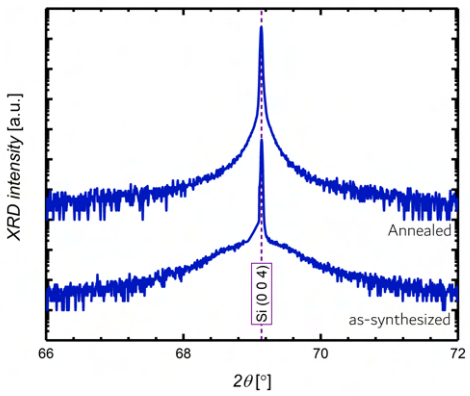

Fig. 2. XRD diffractorgram along Si (004) atomic plane obtained over SiNWs based structures both in un-annealed (lower plot) and annealed (upper plot) state.

(SEM, Zeiss Supra 35). A detailed description regarding X-ray diffraction analysis is provided in our previous work [11]. For electrical measurements, two co-planar Au-contacts, 2×10 mm^2 each, with 250 nm thickness, were deposited on the surface of the samples via a hard mask using an electron beam evaporator (Polyteknik Cryofox Explorer 600 LT). The distance between the two contacts was 6 mm.

III. Results and Discussion

A. Structure characterization

Figure 1 shows (a) top view and (b) cross-sectional view of SiNWs obtained after 20 min etching. The top view image indicates that the wires are interconnected, forming a bundled rigid structure. Such bundle formation may take place because of capillary forces acting during the drying process following the wet-etching step. In the cross-sectional image one can see that the length of the wires is relatively homogeneous, around 5.5 µm. The XRD diffractogram obtained over structures (i.e.), SiNWs annealed and un-annealed (UA) around (004) atomic plane. Fig. 2, shows a variation in FWHM of peak, which is strongly influenced by strain-relaxation related phenomena [12]. For (UA) SiNWs the XRD plot showed a peak along with broad hump, which when annealed at 700°C showed a sharp feature. Such an effect can be attributed to structural defects and consequent strain relaxation phenomena in nanowires, which arise due to bending and torsion as has been well-documented in a study by Romanitan *et. al.* [12].

B. Respiratory sensing

The human respiratory sensing was investigated using various SiNWs based sensors, as shown in Fig. 3. All structures were tested for three different breathing modes i.e., normal, rapid, and deep breathing, and are labeled respectively in Fig. 3. In order to show the repeatability of the measurements, two breathing sequences are shown for each mode. For SiNWs (both annealed and UA) there is a significant drift in the resistance baseline with time (indicated by arrow), unlike Ge-coated SiNWs in both UA-state and annealed at 450 and 700°C. We attribute this difference to the higher Ge-hole mobility as compared to Si. Additionally, for the bare SiNWs and for two samples coated with Ge, UA and annealed at 450°C, the amplitude of the resistance waves caused by breath is higher than for the Ge-SiNWs annealed at 700°C. However, the sensitivity to capture detailed features of the resistance oscillations, with lower response and recovery time, along with several non-periodic kinks during exhaling and inhaling breathing cycles, may vary between our samples. Such detailed features in breathing profile can be visualized in the differential plots in Fig. 4(a-c). We can see differences that may possibly be related to breathing details, but also to internal sample behavior, such as delayed response, hysteresis, or other transient phenomena to be studied separately [13].

The sensor samples were mounted on a ceramic chip having patterned interdigital Au-electrode. Thin Al-wires were attached between co-planar contacts on sample and electrodes on ceramic chip. The sample was than mounted firmly on to philtrum using a double-sided tape, while the thin coaxial cables between the signal processing unit and sample were properly dressed within a canula tube to avoid any loose connections and/or interference with unintended objects. A schematic illustration of setup is shown in Fig. 5(a).

Fig. 5(b) shows the response of a sensor (Ge coated SiNWs annealed at 700°C) to periodic monitoring of the human breathing. It can be observed that the sensor can efficiently detect the different breathing states i.e., in our case normal, rapid, and deep breathing, Fig. 5(c). We want to emphasize that the fabrications of our samples is considerable simpler than those with complex multi-step process and materials [4], [14]–[16], particularly composite fibres or polymers combined

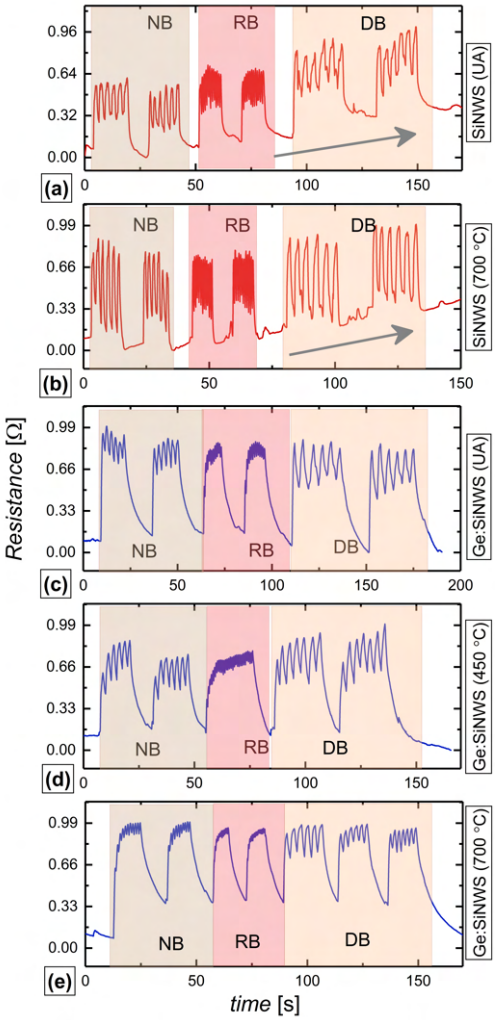

Fig. 3. Room-temperature resistance change as a function of time for (a) UA-SiNWs (b) SiNWs annealed at 700°C, (c) UA-Ge:SiNWs and annealed Ge:SiNWs at (d) 450°C and (e) 700°C, respectively, under normal (NB), rapid (RB), and deep (DB) breathing, also represented as highlighted regions.

with conductive nano-materials like metals, carbon nano tubes or graphene, which are often unstable and tend to degrade in ambient atmosphere over time.

Our sensors were able to capture breathing patterns without losing any features. It is to mention here that the waveform obtained during breathing is assumed to mimic the intended breath modes, while a discontinuity between waves may indicate a potential menace. Therefore, our sensors can provide a possible indication of risky situation, for instance in case of sleep apnea, or other breathing threats like f.ex. choking and asthma. Moreover, our samples were tested for re-usability, after aging them for four weeks. The samples were also tested for longer and repeated breathing cycles. A longer breathing sequence is shown in Fig. 6, as a differential plot (dR/dt vs time), for NB and RB breathing modes, where the inset in the NB plot shows the repeatability of the signal.

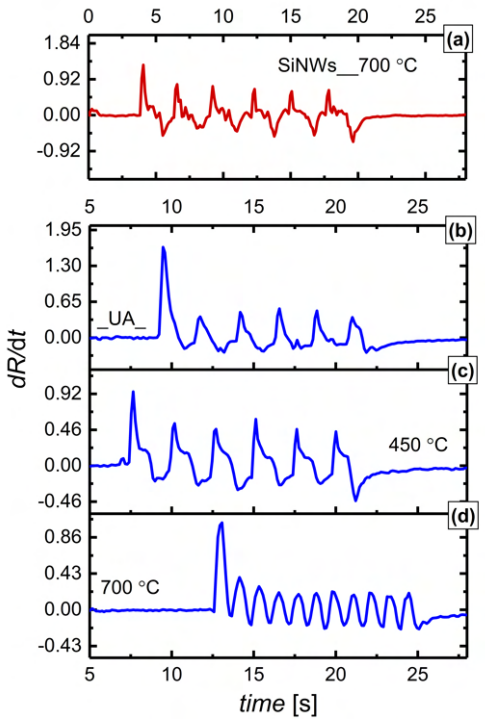

Fig. 4. Differential plots obtained from Fig. 3 of NB states for (a) SiNWs annealed at 700C°C (b) UA-Ge:SiNWs and annealed Ge:SiNWs at (c) 450 °C and (d) 700°C, prospectively.

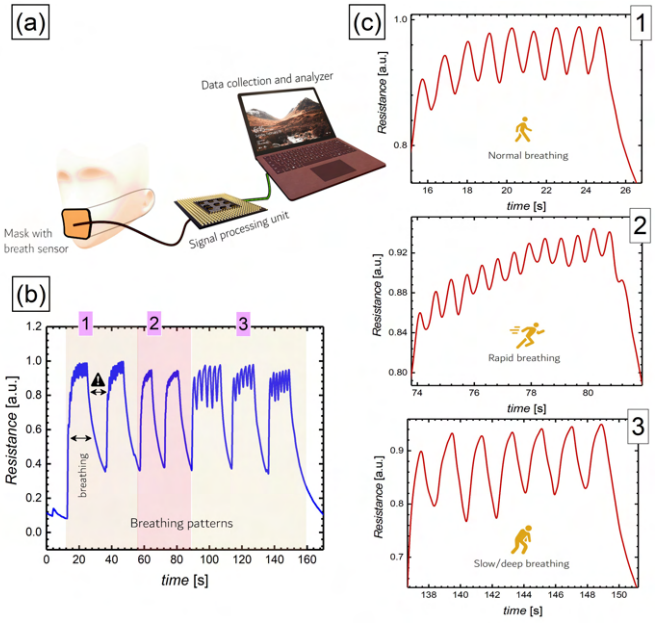

Fig. 5. (a) Schematic of the respiratory setup utilized. (b) The breathing response in real time recorded using annealed (700°C) Ge:SiNWs. (c) The data marked as 1, 2 and 3 expanded.

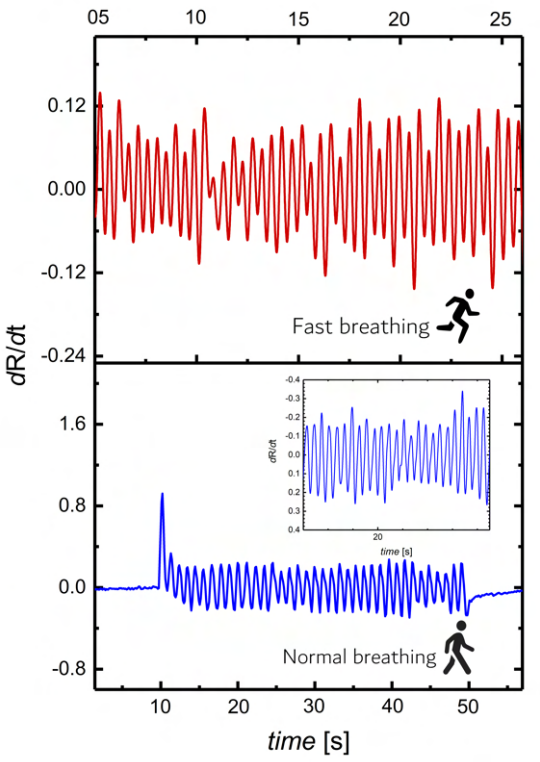

Fig. 6. Differential plot for Ge:SiNWs structure annealed at 700°C, 5 min, under RB (upper plot) and NB (lower plot) modes for an increased number of cycles. The sensor was tested again under similar condition for repeatability the results from which are shown in an inset for NB mode.

IV. Conclusion

In conclusion, we synthesized random arrays of SiNWs by MACE for application in respiratory sensing. The obtained structure were characterized via XRD and SEM showing SiNWs of $\sim$ 5.5 μm, bundled together. The structures were further treated either by rapid thermal annealing and/or coated with Ge films with aim to increase the sensitivity and efficiency. It was observed that SiNWs coated with Ge and annealed for 5 min at 700°C resulted in higher efficiency, faster response, and improved signal profile, without any baseline drift in resistance. We have demonstrated the fabrication of portable, easy to fabricate, and wearable sensor with a great potential for application in devices intended to monitor a human respiratory profile and for other possible applications of pressure sensing.

Acknowledgment

This work was supported by Reykjavik University Ph.D. fund no. 220006 and the Icelandic Research Fund Grant no. 218029-051. We are grateful to Rodica Plugaru and Neculai Plugaru for discussions.

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