Simple fabrication of Si nanowire and its biological application

Y.T. Cheng\(^1\), Y.H. Cho\(^1\), N. Takama\(^1\), P. Löw\(^2\), C. Bergaud\(^2\), and B.J. Kim\(^1\)

\(^1\) Institute of Industrial Science, The University of Tokyo 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan
\(^2\) LAAS-CNRS, Toulouse, France

E-mail: bjoonkim@iis.u-tokyo.ac.jp

Abstract. A novel, relatively simple and cost effective method is reported to fabricate suspended silicon nanowires. This method allows for the production of suspended silicon nanowires using anisotropic wet etching and thermal oxidation of single crystalline silicon. The dimensions of the silicon nanowires fabricated with the proposed method are evaluated. The vibration properties of the nanowires obtained by heterodyne laser doppler interferometer show the potential of being nanomechanical sensors.

1. Introduction

Nanowire has attracted much interest as essential parts for functional electronics devices because of its potential applications in nanoelectronics [1-3] and highly sensitive biosensor [4-5]. Although research focused on the fabrication of nanowire using synthesis-based bottom-up approach [3] has led to considerable achievements to date, the shortcomings have also been detailed nowadays. In contrast, top-down approaches provide many superior advantages over previously described bottom-up approaches [2, 6, 7]. For instance, top-down approaches can produce silicon nanowire precisely at designed locations in devices using nanolithography or micromachining process on a bulk silicon substrate. However, nanolithography-based top-down fabrication utilized in previous studies uses high-cost facilities, such as electron beam lithography. Therefore, because of the serial processes required for nanolithography, it is not simple to do mass production. In the case of the micromachining methods of bulk silicon substrates to fabricate nanowires, some methods have been reported: anisotropic wet etching of single crystalline silicon [8] and silicon thinning using silicon thermal oxidation [9-10]. In these methods, the silicon-on-insulator (SOI) substrates were indispensably utilized for nanowire fabrication. The top-down approaches for nanowire fabrication may limit the uniformity in the width of nanowires.

Here, we report a simple and cost-effective fabrication process to fabricate suspended silicon nanowire only using conventional MEMS processes including anisotropic wet etching and local thermal oxidation processes without nanolithography techniques. Due to the anisotropic etching of \(<100>\) single crystalline silicon substrate in KOH solution, uniform and well-defined silicon nanowires with sub-micro diameter were obtained. Because the top surface of Si nanowires is expected to remain relatively flat after finally fabricated, it is supposed to be possible to measure the resonant frequency with heterodyne laser doppler interferometer [11]. This approach also provides us a direction of applying nanowires as mechanical sensors.
Recently, silicon nanowires have been utilized as the core element of field-effect transistor and demonstrated high capabilities. G. Zheng, et al. developed and characterized high performance silicon nanowire field effect transistors in 2004 [15]. One promising approach for the direct label-free and electrical detection of biomolecules is to use field-effect transistors (FETs) because the conductance of a nanosized channel changes upon binding of small quantity of charged biomolecules to probe receptors grafted onto the channel surface. In addition, it should be possible to exploit the massive knowledge that exists for the chemical modification of oxide surfaces, for example, from studies of silica, planar chemical/biological sensors, to create semiconductor nanowires modified with receptors for many applications. On the other hand, nano electro mechanical systems (NEMS), particularly nanomechanical resonators vibrating at high frequency, are being actively explored for applications including, resonant sensors for ultrahigh-resolution mass sensing, force detection, quantum electromechanics, electromechanical signal generation and processing, etc. The development of high frequency silicon nanowire electromechanical resonators has shown a potential for applications in resonant sensing, quantum electromechanical systems, as well as biological sensing.

Therefore, although the direction of applications in this article does not focus on the electrical characterization of nanowires such as FET sensor, the measurement of mechanical property may show a potential direction of applications of utilizing this suspended silicon nanowire. In this article, the basic process of fabricating the suspended Si nanowire on silicon substrates is demonstrated. The measurement of resonant frequency of final fabricated Si nanowire is also carried out. Moreover, the fabricated Si nanowires are to be used as submicrometer local heater with additional electrodes from both sides of nanowire for joule heating. Then, high spatial resolution of surface temperature mapping in dry an even liquid environment using our fluorescent thermometry method [14] will be investigated through these suspended silicon nanowire arrays.

2. Fabrication procedure
The fabrication process is demonstrated with the capability of fabricating suspended nanowires reproducibly. The processes include photolithography, anisotropic wet etching, and local thermal oxidation of silicon and removal of silicon dioxide. Nanowires were obtained by a simple process flow where wire lines with widths of 3 μm were patterned by employing UV lithography and following anisotropic wet etching and thermal oxidation of silicon. The nanowire fabrication was performed on n-type (100)-oriented substrates being characterized by a specific resistance of 1-10 Ωcm.

Flow chart of the suspended silicon nanowire fabrication process is shown in Figure 1. The silicon substrates were prepared by depositing a 100-nm-thick silicon nitride layer (Figure 1b) by low-pressure chemical vapor deposition (LPCVD). This silicon nitride layer was used as a masking layer in the silicon anisotropic wet etching and thermal oxidation processes (Figure 1d). Then, the photolithography process is carried out to define the silicon wire patterns in micrometer scale on the silicon substrates (Karlsus aligner) (Figure 1c). The open areas on the silicon substrate obtained simultaneously in the previous process were anisotropically etched to an appropriate depth using KOH solution (40 w%, 60 ℃). Consequently, silicon columns aligned along the (111) direction were obtained (Figure 1e). Local oxidation of silicon (LOCOS) was then performed at 1100 ℃ in order to grow SiO2, which was used as etching mask in the 2nd KOH solution for the reduced silicon wire structures, later (Figure 1f-i). The 2nd photolithography was carried out to cover and protect part of the structure (Figure 1g). After selective etching of silicon dioxide layer, additional KOH solution etching was carried out to release silicon wires from the substrate (Figure 1h-j). Finally, the rest silicon dioxide and silicon nitride was removed by BHF solution (Figure 1k).
Figure 1. The schematic view of fabrication process for the suspended silicon nanowires. (a-b) preparation of the silicon substrates, (c-d) silicon columns definition by lithography and RIE, (e-f) determination of width of wires, (g) partially protecting wire structures, (h) selective etching of silicon dioxide to produce silicon dioxide mask, (i-j) determination of thickness of wires, (k) removal of rest silicon dioxide and silicon nitride.

3. Results

3.1. Dimensions of suspended Si nanowires

The dimensions of suspended silicon nanowires are decided in three processes, which are the first anisotropic KOH solution etching, thermal silicon oxidation and the second anisotropic KOH solution etching process. The field-effect scanning electron microscopy (FE-SEM) images of the suspended Si nanowires are shown in Figure 2.

In this fabrication procedure, three different sorts of length of wires were designed, which are 50, 20 and 10 μm, respectively. Due to the crystallographic characteristics and wet anisotropic etching, the final length of nanowires was shortened to be approximate 44, 10 μm and less (non-suspension). The final length (44 and 10 μm) is shorter than the designed length (50 and 20 μm). The shorten amount were around from 3 to 5 μm at one end of nanowire, as shown in Figure 3. The shortage in length of suspended silicon nanowire mainly comes from the anisotropic 2nd. KOH solution etching process and partially from the 1st. KOH etching process.

The designed width of wires on the mask is about 3 to 3.3 μm. After side-silicon etching of anisotropic KOH solution etching and thermal oxidation processes, the width of fabricated suspended silicon nanowires is expected to be 100 to 300 nm. However, due to the difficulty of keeping KOH solution etching rate stable, the width of fabricated silicon nanowires is approximately 550 nm, which becomes wider than what of was expected. Thickness of nanowire is determined by the duration of 2nd. KOH solution etching (figure 1 (i-j)). In 2nd. KOH solution etching, it was expected to etch silicon for
around 5.5 μm to obtain a nanowire with 0.5 μm in thickness. However, the final thickness was around 0.35±0.2 μm. The error was supposed to be from unstable etching rate at the nano-scale reactive surface. A more stable wet etching system is supposed to be necessary in the following fabrication processes.

![Figure 2](Image)

**Figure 2.** Field-emission scanning electron microscopy (FE-SEM) images of the fabricated suspended silicon nanowires. The designed length is (a-b) 50 μm, (c-d) 20 μm and (e-f) 10 μm. Due to the natural angle between crystallographic planes, the virtual length of suspended silicon nanowire is around 44 μm, 10 μm in the 50-μm and 20-μm cases, respectively. In the 10 μm case, the wires were not suspended because of insufficient space.

However, even using this process at this moment, the fabricated nanowire arrays have very uniform widths and thickness in the same substrates. When SOI substrate, which has already well defined thick silicon on top, is used to fabricate nanowires by our method, it can be more easily obtained to control critical dimension of nanowire arrays.
The length of suspended silicon nanowire is 44 μm, which is shorter than the designed length of 50 μm on mask.

3.2. Characterization of nanowires: resonant frequency

These nanowires can be used as mechanical sensors. A rectangular wire suspended across a gap is expected to have a resonance frequency $f_n$ that scales with the dimensions of the wire and with the size of the gap according to equation (1), where the $\lambda_n$ is a constant of order unity which equals to 4.73 under the condition of two ends fixed, $L$ is the length suspended which was measured with FE-SEM images, $E$ is Young’s modulus which equals to 110GPa, $I$ is the moment of inertia, $\rho$ is density which equals to 2330Kg/m³ at 298K, and $A$ is cross section area of nanowire. The calculated value of the 1st. mode resonant frequency of the selected wire in 44-μm (Figure 2, a) is 1.96 MHz. The calculated value of the selected 10-μm wire (Figure 2, c) is 39.1 MHz.

$$f_n = \frac{\lambda_n^2}{2\pi^2} \sqrt{\frac{EI}{\rho A}}$$  (1)

The measurement were done with a Heterodyne laser Doppler interferometer built by Prof. H. Kawakatsu’ group in the University of Tokyo. [16]. The measurement with suspended Si nanowire was carried out in air condition. A HP-8752C Network Analyzer was used to control the frequency of the excitation laser diode. The nanowires were excited by a laser diode and measured with a He-Ne laser beam. The frequency of He-Ne laser light changed after being reflected by the nanowire, which was caused by the vibration of nanowire (Doppler effect). For focusing the laser beams on the nanowires, 50, 20 and 10 times of magnification lens were equipped on the sample stage. A camera and a TV set were installed and used to observe the focusing process through magnification lens. Different optical elements allowed the construction of an interference image around a base frequency of 1.08 GHz. The characteristic interference image was captured by an avalanche photodiode and the resulting electrical signal filtered and demodulated with a delay line. The resulting signal is equivalent to the speed of the cantilever. This signal was connected and transferred into the Network Analyzer that can handle with a frequency range from 300 kHz to 3 GHz. The scanning frequency range can be selected freely in this range. The data can be acquired through the General Purpose Interface Bus (GPIB) of the Network Analyzer with a personal computer running a Labview program.

The measurement in liquid (DI water) condition was also tried. Nevertheless, due to the limitation of measurable frequency range (max 5 MHz) of BPF (band-pass filter), the measurement in liquid condition was not available so far.
First resonant frequency of nanowires with 44 and 10 μm in length were measured in air. For the first example, the measured frequency of the 850 nm-in-width, 540 nm-in-thickness and 44 μm-in-length nanowire was 1.64 MHz. For the second example, the measured frequency of the 570 nm-in-width, 670 nm-in-thickness and 10 μm-in-length nanowire was 21.75 MHz. There is 16.3% deviation from calculated value to measured one. The calculated value of the selected 10-μm wire (Figure 2, c) is 39.1 MHz, which showed 44% deviation from calculated value to measured one, as shown in Table 1.

| Measured length (μm) | Measured width (nm) | Measured thickness (nm) | Measured 1st resonant frequency (MHz) | Calculated 1st resonant frequency (MHz) | Deviation |
|----------------------|---------------------|-------------------------|---------------------------------------|----------------------------------------|-----------|
| 44                   | 850                 | 540                     | 1.64                                  | 1.96                                   | 16.30%    |
| 10                   | 570                 | 670                     | 21.8                                  | 39.1                                   | 44.24%    |

Because of the low uniformity of the thickness of nanowires observed (Figure 4), the 16.3% and 39% difference was supposed to be as a result of low uniformity of thickness. The improvement of wet etching system was also thought to be one of possible approaches to have higher uniformity of wire thickness. The high performance of vibration properties shows the potential of being used as mechanical sensors [12].

**Figure 4.** Side view of suspended silicon nanowire (10-μm case) clearly shows the low uniformity of thickness, especially at the two ends.

4. Further study
In various and prosperous fields of silicon nanowire applications, those applications for being used as nano-scale thermometer or sensing nano-scale temperature distribution have been supposed to have high potential in the future research. Fluorescent molecules, such as Rhodamine B or nanocrystals, have been used as monitoring interface to characterize local temperature distribution [13]. Nevertheless, nickel and silicon nanowires used in the previous research were not suspended from substrates, which resulted in obvious heat diffusion from wires to substrates. This phenomenon may cause overheating in the system and unnecessarily waste energy. Hence, our contribution will be utilized to deal with applying suspended nanowires for nanoscale heat source. By utilizing Rhodamine B as temperature monitoring interface, the localized temperature controlling will be carried out. A nano-scale temperature controlling system is also expected to be available for high efficient biosensors. Finally, this nano-scale temperature sensing and controlling system will be expected to be one of the tools to discover part of thermal-mechanical biomolecular physic or biosensors with local temperature control.
5. Summary
A novel fabrication process has been studied via anisotropic KOH solution etching and local thermal oxidation. Relatively uniform and well-defined suspended silicon nanowires were obtained by controlling the duration time of anisotropic wet etching and thermal oxidation. The 1st mode resonant frequency of one of the 50 μm-length nanowire was measured by laser doppler interferometer way. The measured frequency of this suspended Si nanowire with 850 nm in width and 540 nm in thickness was 1.64 MHz. The measured value is in a good agreement with the calculated one. The result from the resonant frequency measurement of nanowire shows us the potential of utilizing them as nanomechanical resonators or sensors as well. In the near future, they are also supposed to be applied for nano-scale heat source and high spatial resolution mapping of temperature distribution by utilizing fluorescent molecules as monitoring interface for biomolecular research.

Acknowledgments
This research is partially supported by Sharp Corporation, Nara and KAKENHI Kiban C (Grants-in-Aid for Scientific Research C, 19510126) from the Japanese Society of Promotion of Science (JSPS). The authors would like to thank Prof. H. Kawakatu and Mr. K. Nakagawa in IIS, The University of Tokyo, for help with the measurement of the resonant frequency and fruitful advices. We also acknowledge the laboratories of Prof. H. Fujita for their support regarding experimental equipment and cleanroom facilities.

References
[1] X. Duan, C. Niu, V. Sahi, J. Chen, J. Parce, S. Empedocles, J. Goldman, Nature, 425, 274 (2003)
[2] Y. Cui, C. M. Lieber, Science, 291, 851 (2001)
[3] A. M. Morales, C. M. Lieber, Science, 279, 208 (1998)
[4] Y. Cui, Q. Wei, H. Park, C. M. Lieber, Science, 293, 1289 (2003)
[5] G. Zheng, F. Patolsky, Y. Cui, W. U. Wang, C. M. Lieber, Nature Biotech., 23, 1294 (2005)
[6] A. Hochbaum, R. Fan, R. He, P. Yang, Nano Lett., 5, 457 (2005)
[7] A. M. Morales, C. M. Lieber, Science, 279, 208 (1998)
[8] E. Stern, J. F. Klemic, D. A. Routenberg, P. N. Wyrembak, D. B. Turner-Evans, Nature, 445, 519 (2007)
[9] J. Kedzierski, J. Bokor, C. Kisielowski, J. Vac. Sci. Technol. B, 15, 2825 (1997)
[10] K. Kakushima, T. Watanabe, K. Shimamoto, T. Gouda, M. Ataka, H. Mimura, Y. Isono, G. Hashiguchi, Y. Mihara, H. Fujita, Japanese Journal of Applied Physics, 43, 4041 (2004)
[11] G. M. Kim, S. Kawai, M. Nagashio, H. Kawakatsu, and J. Brugger, J. Vac. Sci. Technol. B, 22, 1658 (2004)
[12] N. A. Melosh, A. Boukai, F. Diana, B. Gerardot, A. Badolato, P. M. Petroff, J. R. Heath, Science, 300, 112 (2003)
[13] H. F. Arata, P. Löw, K. Ishizuka, C. Bergaud, B.J. Kim, H. Noji, H. Fujita, Sens. Actuators B, 117, 339 (2006)
[14] P. Löw, B.J. Kim, N. Takama, and C. Bergaud, Small, DOI 10.1002/smll.200700581, (2008)
[15] G. Zheng, W. Lu, S. Jin, C. M. Lieber, Advanced Materials, 16, 21, 1890 (2004)
[16] S. Nishida, T. Sakurada, D. Kobayashi, S. Meguro and H. Kawakatsu, Seisannkenkyu, 58 (2) 161 (2006)