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Realization of large-scale sub-10 nm nanogratings using a repetitive wet-chemical oxidation and etching technique

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Abstract

Despite many efforts to create nanogratings to exploit exceptionally enhanced nano-sized effects, realizing sub-10 nm nanogratings on a large area still remains a great challenge. Herein, we demonstrate fabrication of an inch-scale sub-10 nm nanogratings with simple and reliable features, by employing a repetitive wet-chemical oxidation and etching technique. We found that a few atomic layers of the silicon surface are naturally oxidized in a nitric acid (HNO_3) solution, which enables the surface of the silicon to be etched with 1.0 nm resolution by selectively removing the oxide layers. By combining this high-precision etching technique with silicon nanogratings previously prepared by conventional methods, we successfully demonstrated a sub-10 nm silicon nanogratings on an inch-scale wafer.

Keywords: Nanograting, Sub-10 nm, Large-scale, Self-limiting oxidation, Wet-chemical digital etching, Repetitive wet-chemical oxidation and etching

Background

Nanogratings are a three-dimensional array of regularly spaced nanoscale line structures. They have received a great deal of attention because their anisotropic form factor is desirable for high performance electrical [1] and optical [2, 3] devices. The recent development of nanofabrication technologies has made it possible to fabricate nanowire- [4] and nanogap-arrays [5], utilizing the shape of nanogratings, so that nanogratings have becoming increasingly useful for various applications. In particular, many researchers have found that the properties of a material can be dramatically improved when the pattern size is reduced to tens of nanometers and below [6, 7]. There have been a considerable number of studies focused on fabricating small nanogratings on large areas to realize high performance devices.

To fabricate the nanograting substrate, researchers have suggested various methods based on conventional photolithography, including KrF [8], immersion [9], and spacer [10] lithography. Even though hundreds of nanometer scale grating patterns have been successfully fabricated, it is difficult to fabricate grating patterns with dimensions of tens of nanometers because of resolution limitations [11]. Improved technologies, such as direct self-assembly [12, 13] and e-beam lithography [14], have been developed that can fabricate devices on the tens of nanometer scale. However, they still have fabrication difficulties including stability, and yield on large areas.

In a successful effort to produce tens of nanometer-scale nanogratings over a large area, we previously developed a pattern downscaling technology based on multiple spacer lithography and pattern-recovery techniques [15]. As a result, highly compact and continuous 100 nm pitch silicon nanogratings were successfully fabricated on 8-inch wafer, and the method allowed us to fabricate various material-based nanowires easily with extremely high aspect ratio (4,000,000:1). However, this technique also has a resolution limitation, which prevents it from being used for superior nano-scale phenomena [6, 7]. Thus, it is still necessary to develop a method to fabricate a smaller

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dimension nanogratings on a large area with stable and simple features.

In this paper, we demonstrate a large-scale sub-10 nm silicon nanogratings. To realize the sub-10 nm grating, we developed a nitric acid (HNO_3) based surface oxidation/etching technique, based on a conventional wet-chemical solution process. We determined that the moderate reactant used for silicon oxidation exists stably at the azeotropic point of HNO_3 and the oxidation is self-limiting within a few nanometer range. As a result, ultra-accurate silicon etching (1.0 nm level) can be achieved by selectively removing the oxidized surface.

By combining our multiple spacer lithography/pattern recovery technique and the developed HNO_3 based silicon etching techniques, we successfully fabricated sub-10 nm silicon nanogratings on an inch-scale level. The developed method is based on conventional photolithography and low temperature wet-chemical solutions with nanoscale controllability, which is highly useful for achieving various nanostructures such as nanodots, nanosquares, and nanoshells, and their applications.

Approach

The proposed method employed a nanoscale digital etching process, based on activating only the surface layer and then selectively removing the activated layer [16–18]. Previously, oxidant solutions such as hydrogen peroxide (H_2O_2) and mixture of H_2O_2 and acid solution have been typically used as the oxidant solutions in the wet-chemical digital etching technique. However, they are not suitable for the pattern reduction of large-scale substrates, because of their weak oxidizing power or non-uniform reactivity [19, 20].

To form an ultra-fine silicon oxide uniformly over a large area, we engineered the proper nitric acid (HNO_3) solution to be used as the oxidant solution for the wet-chemical digital etching. HNO_3 is a well-known oxidizing agent which generates nitric oxide (NO) and nitrogen dioxide (NO_2) with singlet oxygen as the reactive oxygen species. Silicon oxidation process using nitric acid follows self-limiting oxidation process in which the thickness of the oxide is saturated and does scarcely change after a certain period of time, and it is schematically shown in bottom of Fig. 1. In the nitric acid oxidation process, diffusion of this reactive oxygen species promotes oxidation of the surface of the silicon, until the diffusion of the oxidizing agent equilibrates with the stress induced by volume expansion during the oxidation process [21–23]. This saturates the oxide thickness at a fixed and predictable value. To guarantee accuracy and ensure the reliable growth of the saturated oxide, the azeotropic point (120 °C, 68 wt%) of the HNO_3 solution was utilized [24]. Process conditions could be maintained throughout the experiments because the temperature and concentration of the HNO_3 solution stabilized at this azeotropic point. Moreover, the highest throughput was achievable at this point, since the oxidation process is accelerated at high temperature.

Experiment

The overall process is schematically shown in Fig. 1. The wet-chemical digital etching was carried out by repetitive HNO_3 oxidation and oxide etching. First, the HNO_3 solution at azeotropic point should be prepared for experiments. By heating any concentration of HNO_3 solution, it can reach the azeotropic point with change of boiling point according to its concentration. When the boiling point of HNO_3 solution is kept constant at 120 °C, it means that HNO_3 solution reached the azeotropic point, so its concentration is kept constant at 68%. While continuously heating the HNO_3 solution on hot plate to keep the solution at the azeotropic point, nanostructured substrate (100 nm pitch nanogratings) was immersed into the HNO_3 solution for a sufficient time over 5 min until the oxide thickness is saturated. After the oxidation process was finished, the shallow oxide was then removed using diluted hydrofluoric acid (HF, 0.1 wt%) solution. It is necessary to completely rinse the substrate after each process in order to prevent contamination. By alternately immersing the prepared nanograting substrate into these two solutions, the width of the nanogratings was progressively thinned as the number of process cycles increased. The dimensions could be completely controlled, and were used to realize sub-10 nm structures.

Results and discussion

The first objective was to identify the saturation time and thickness of the silicon in the HNO_3 solution. This would reveal the resolution of the proposed method that could be achieved in a single size reduction cycle. The oxide thickness was investigated by spectroscopic ellipsometer (M2000D, Woolam) and high-resolution transmission electron microscopy (HR-TEM; TecnaiTM G2 F30 super-twin, FEI), and the results are shown in Fig. 2.

As the oxidation time increased, the oxide thickness continued to increase until it reached the saturation point at about 5 min. After 5 min of oxidation, the oxide thickness saturated at around 1.8 nm and we confirmed that further oxidation up to 30 min did not increase the thickness. The saturated oxide thickness after 5 min of oxidation was also confirmed using HR-TEM imagery, and the results agreed with the value obtained from spectroscopic ellipsometry. Based on this identification, we set the oxidation time to over 5 min for each repeated oxidation cycle.

Fig. 1 Schematics of the fabrication process. **a** Ultra-thin nanogratings were produced from initial nanogratings by repetitive oxidation and etching cycles. One cycle consists of an oxidation process in nitric acid and an etching process in diluted hydrofluoric acid. **b** Growth of silicon oxide with respect to time in the oxidation process; silicon oxide grows until the saturation point, and then remains at a constant saturated thickness (Tox, sat) after this saturation time

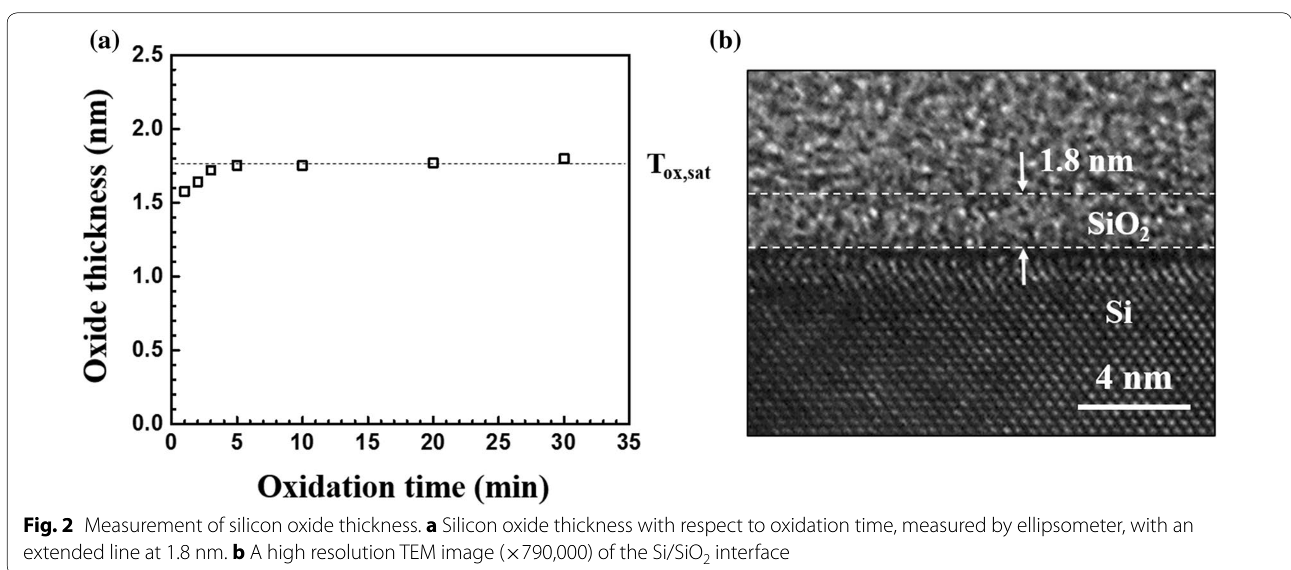

Fig. 2 Measurement of silicon oxide thickness. **a** Silicon oxide thickness with respect to oxidation time, measured by ellipsometer, with an extended line at 1.8 nm. **b** A high resolution TEM image (×790,000) of the Si/SiO_2 interface

The accurate resolution of the proposed method was established by measuring the etching depth of the silicon based on the number of repeated oxidation and etching cycles. Using a flat silicon wafer with a patterned Cr masking layer, the surface of the silicon was selectively oxidized and etched for several cycles. The resulting depth profile was measured using atomic force microscopy (AFM; XE-100, PSIA), and the detailed experiment method is shown in Fig. 3.

AFM measurement was carried out after repeating the size reduction cycles 5, 10, 15, 20 times respectively. As expected, the depth increased proportionally with the number of repeated cycles, and the extracted etching depth per cycle from linear fitting was 1.0 nm. Note that the smaller etching depth of silicon compared with the produced oxide thickness can be explained with the conventional model of silicon volume expansion during the oxidation process. As can be seen in Fig. 3a, about half of the oxide is formed under the silicon surface. This phenomenon is well-known and originated from the fact that oxide molecular density is about half of that of silicon. This is why the silicon etching depth is about half of the oxide thickness [25]. Furthermore, when surface roughness was compared between the initial and etched surfaces, no noticeable change could be observed. This means the silicon surface was uniformly oxidized and etched with each repeated cycle.

The proposed size reduction method was then applied to fabricate nanogratings. The prepared substrate had a 100 nm pitch nanograting pattern with a 40 nm line and a 60 nm space, as a scanning electron microscope (SEM; Sirion, FEI) image shown in Fig. 4a. After the substrate was immersed in the HNO_3 solution for 5 min to form a saturated oxide layer, TEM observation was carried out. The cross-sectional TEM images shown in Fig. 4b indicate the entire surface of the nanogratings was uniformly oxidized, which can be attributed to the self-limiting oxidation process of the wet-chemical oxidizing agent. We can also infer from these results that only the width of the nanogratings can be thinned as the size reduction cycles progress, while other dimensions, such as the height and pitch of the nanogratings are maintained.

Finally, the decrease in the line width of the nanogratings based on the increasing number of cycles is illustrated in Fig. 5. The width distribution was investigated statistically by measuring the length of 50 peaks of the nanogratings. Every five additional cycles reduced the line width of the nanogratings by about 10 nm. This agrees with the AFM

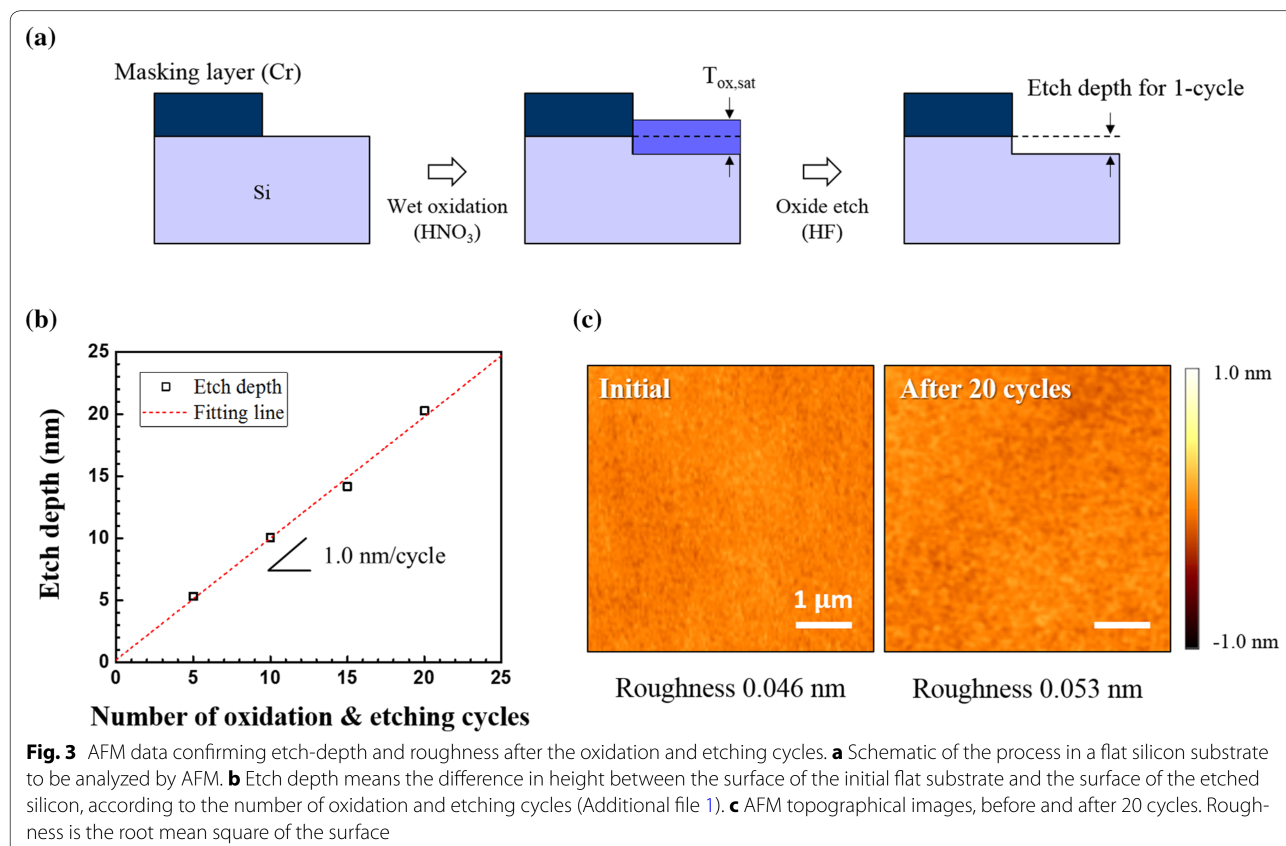

Fig. 3 AFM data confirming etch-depth and roughness after the oxidation and etching cycles. **a** Schematic of the process in a flat silicon substrate to be analyzed by AFM. **b** Etch depth means the difference in height between the surface of the initial flat substrate and the surface of the etched silicon, according to the number of oxidation and etching cycles (Additional file 1). **c** AFM topographical images, before and after 20 cycles. Roughness is the root mean square of the surface

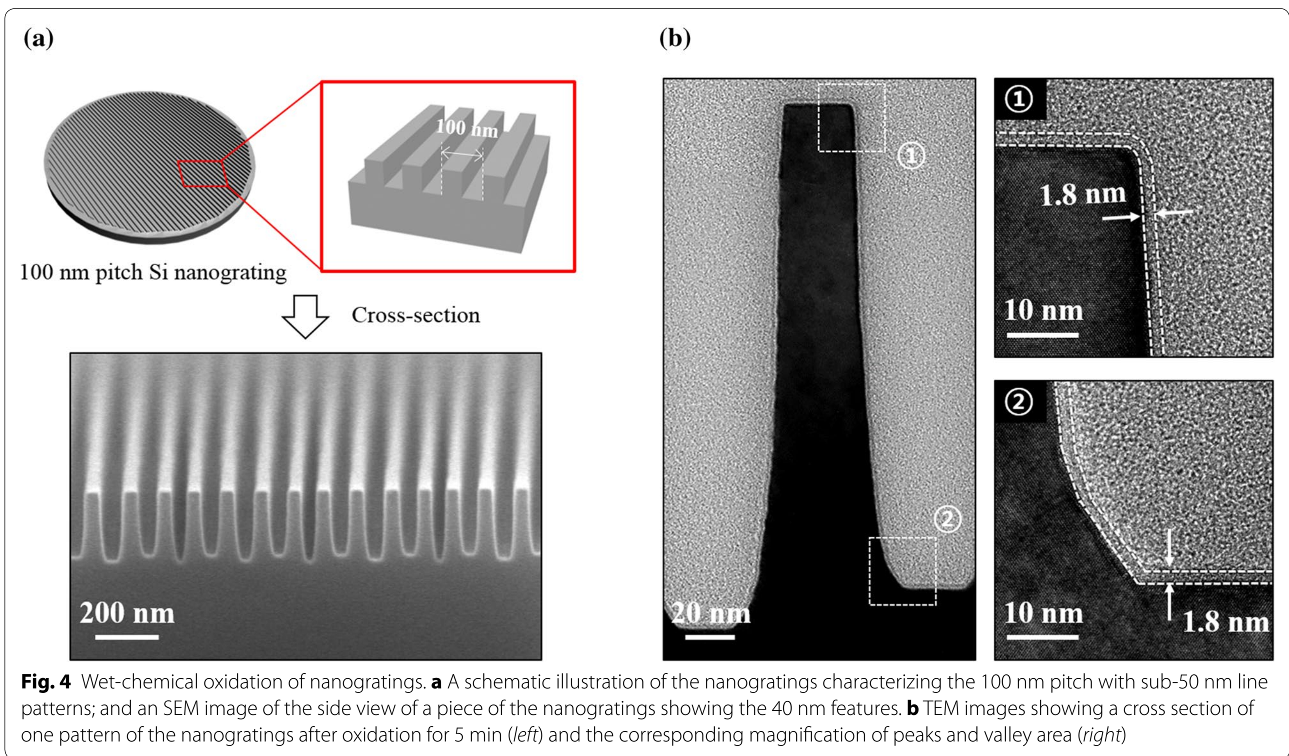

Fig. 4 Wet-chemical oxidation of nanogratings. **a** A schematic illustration of the nanogratings characterizing the 100 nm pitch with sub-50 nm line patterns; and an SEM image of the side view of a piece of the nanogratings showing the 40 nm features. **b** TEM images showing a cross section of one pattern of the nanogratings after oxidation for 5 min (*left*) and the corresponding magnification of peaks and valley area (*right*)

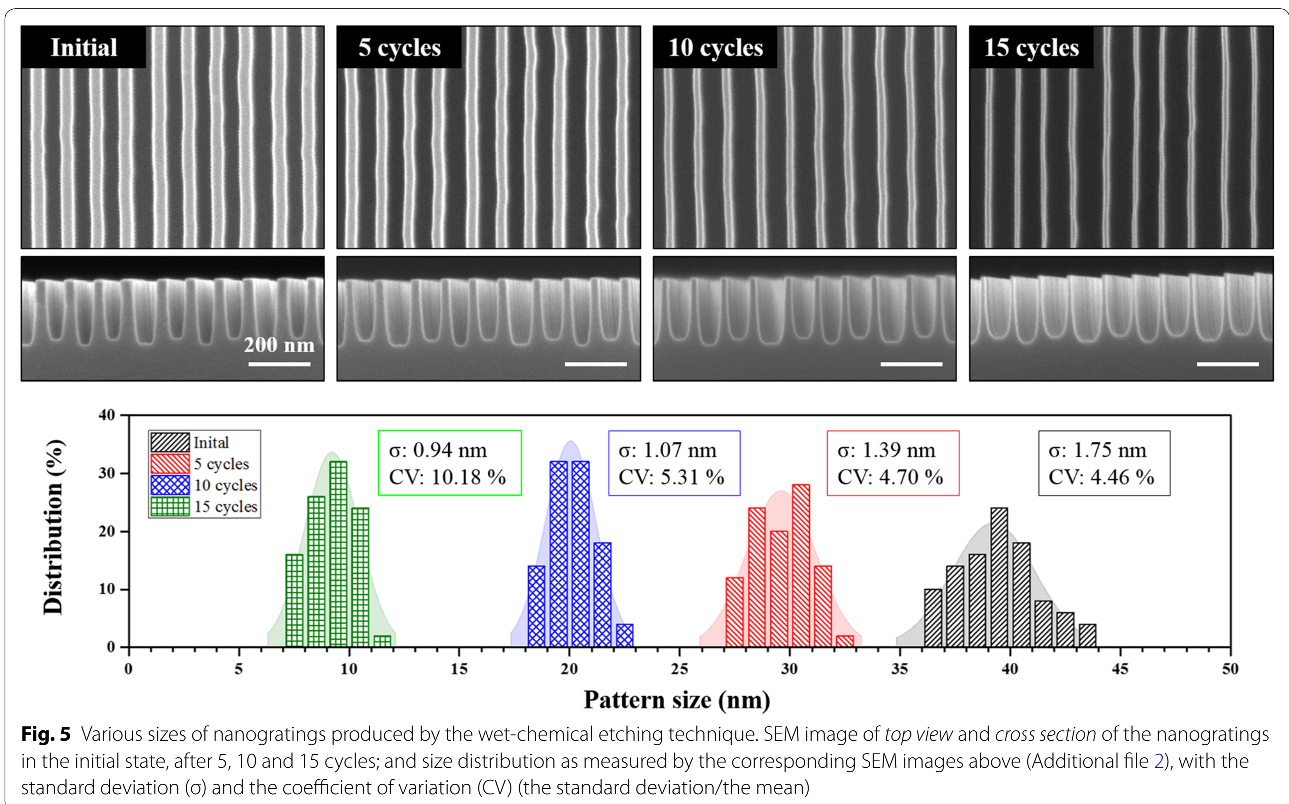

Fig. 5 Various sizes of nanogratings produced by the wet-chemical etching technique. SEM image of *top view* and *cross section* of the nanogratings in the initial state, after 5, 10 and 15 cycles; and size distribution as measured by the corresponding SEM images above (Additional file 2), with the standard deviation (σ) and the coefficient of variation (CV) (the standard deviation/the mean)

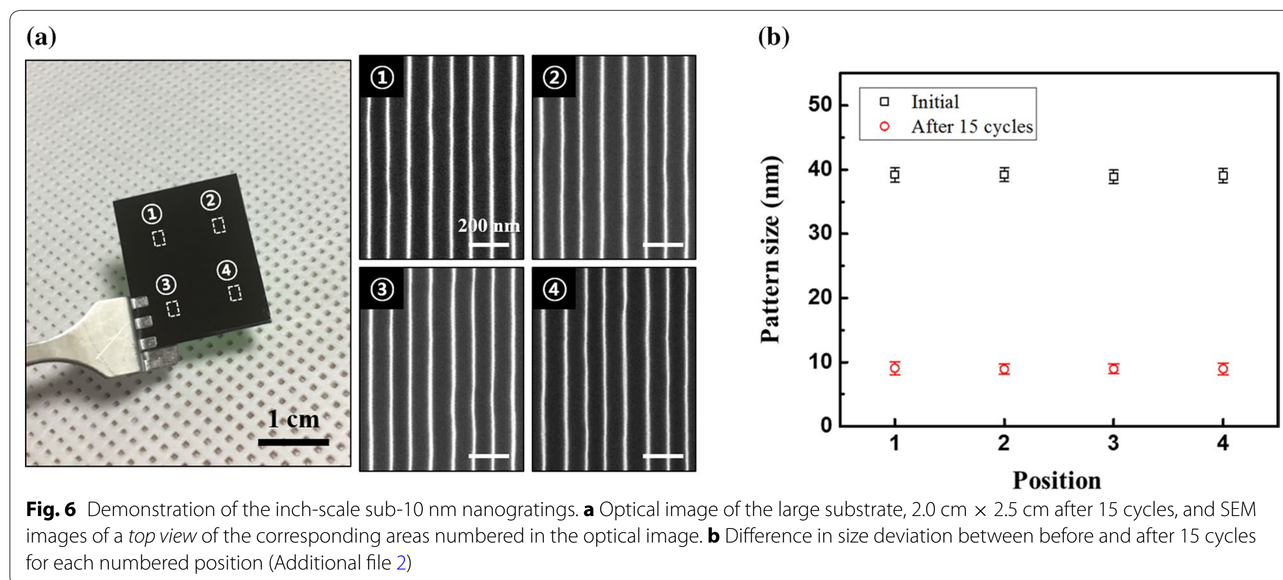

Fig. 6 Demonstration of the inch-scale sub-10 nm nanogratings. **a** Optical image of the large substrate, 2.0 cm × 2.5 cm after 15 cycles, and SEM images of a *top view* of the corresponding areas numbered in the optical image. **b** Difference in size deviation between before and after 15 cycles for each numbered position (Additional file 2)

measurement results, that each cycle reduced both sidewalls of the nanogratings by 1.0 nm. For each cycle, about 2 nm of width was reduced from the original pattern. With this high level of resolution, the dimensions of the nanostructure could be precisely controlled and thinned to the targeted sub-10 nm size, by determining the number of size reduction cycles. In addition, the standard deviation of the pattern size decreases as increasing the number of oxidation and etching cycles, and the coefficient of variation, on the other hand, increases as the number of processes. The reason of this tendency requires further investigation. However, since the standard deviation stays within 2 nm and the coefficient of variation (the standard deviation/the mean) is about 10% at 15 cycles of etching, it means that sub-10 nm patterns could be manufactured stably through the proposed method.

To verify the large-scale applicability of the proposed method, we conducted the same experiments on a 2 cm by 2.5 cm area and observed the position dependent manufacturing result. Optical and SEM images were obtained after applying the size reduction method for 15 cycles, as illustrated in Fig. 6. The statistical investigation of 20 peaks of the nanogratings for each divided position confirmed that all of the surfaces were uniformly reduced, regardless of their position on the wafer. This result is again attributed to the use of the self-limiting oxidation of the wet-chemical oxidant in our proposed method.

Conclusion

We realized a sub-10 nm nanogratings on a large-scale wafer by employing a wet-chemical digital etching technique. The introduced HNO_3 based wet-chemical digital etching technique can remove silicon at a resolution of 1.0 nm per cycle, because the HNO_3 oxidizes only a few atomic layers of silicon surface per cycle. Saturation of the silicon oxide thickness means that this technique can be used to uniformly etch the surface of a large area. A previously prepared sub-40 nm nanogratings on inch-scale wafer was reduced to a precisely controlled sub-10 nm using this technique. Furthermore, the nanoscale size reduction technique developed in this work can be applied to any kind of silicon nanostructures, in addition to nanogratings. The sub-10 nm structures produced by this method have great potential for a variety of applications in high performance electronics, optoelectronics and sensing devices.

Additional files

Additional file 1. Z-drive profiles measured by AFM; the datasets state the measured values of graph in Fig. 3b.

Additional file 2. Pattern size distribution of nanogratings measured from SEM images; the datasets state statistical values of graphs in Fig. 5 and Fig. 6b.

Authors' contributions

MSJ and KWC carried out design, fabrication, measurement and analysis of the results, and drafted the manuscript. SMH performed analysis of results and participated in editing the manuscript. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

Availability of data and materials
The datasets supporting the conclusions of this article are included within the article and its additional files.

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