Buffered Oxide Etchant Post-Treatment of a Silicon Nanofilm for Low-Cost and Performance-Enhanced Chemical Sensors

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ABSTRACT: The high surface-to-volume ratio of nanostructured materials is the key factor for excellent performance when applied to chemical sensors. In order to achieve this by a facile and low-cost fabrication strategy, buffered oxide etchant (BOE) treatment of a silicon (Si)-based sensor was proposed. An n–n–n Si nanofilm structure was treated with a BOE, and palladium nanoparticles (PdNPs) were coated on the n-type Si channel surface via short-time electron beam evaporation to enable a highly sensitive and selective sensing of hydrogen (H₂) gas. The BOE treatment effect on lightly doped n-type Si was investigated, and the surface morphology of the etched Si was analyzed. Furthermore, the H₂ sensing characterization of PdNP-decorated Si devices with various BOE treatment times was systematically evaluated at room temperature. The results revealed that the surface of n-type Si is roughened by BOE treatment, which can further enhance the H₂-sensing performance of Pd-decorated Si. The elaborate study on the BOE-post-treated Si H₂ sensor showed that the performance enhancement was stable. The BOE treatment strategy was also applied to the nanopatterned Si sensors, which induced a clear performance enhancement for the H₂ sensing.

KEYWORDS: thin film sensor, hydrogen sensor, buffered oxide etchant, palladium nanoparticles, surface roughness

INTRODUCTION

Recently, rapid ongoing industrial development and potential applications in the oncoming era of internet of things (IoTs) put a massive emerging demand on the sensitive and selective detection of molecules for environmental monitoring, process control, safety, and medical diagnostics purposes.1–3 To date, silicon (Si)-based materials have been investigated as one of the most promising sensing materials for biological and chemical species.4–6 Nanostructured Si materials have attracted extensive attention since their introduction by Cui et al.7 because their large surface-to-volume ratio enables nanoelectronic devices with ultrasensitive response to target bio/chemical substances.8–10 Also, the electrical properties of Si could be easily controlled by the doping process, which makes it flexible and adaptable for various sensing applications.11 Meanwhile, Si itself shows no response to most of the bio/chemical species, and it can be easily decorated with various functional materials to generate the selective response to particular components.12–16 This enables an excellent selectivity of Si-based sensing devices compared with other nanomaterials such as metal oxides.17–21 Furthermore, the mechanical and chemical robustness, which gives an excellent long-term stability, is also an important merit of Si-based devices.22

The fabrication techniques for nanopatterned Si devices are categorized into bottom-up23–25 and top-down26–28 approaches. The bottom-up route has a high fabrication yield of nanostructures at low cost. However, it suffers from poor repeatability and difficulty of device integration.29 On the other hand, as for the standard top-down route, high-resolution lithography techniques such as electron beam (e-beam) lithography30,31 are needed to achieve nanoscale patterns. Although nanostructures down to a few nanometer dimensions could be achieved using this technique, high cost and low yield make it incompatible for cost-efficient mass production.19,22 Some recently reported novel methods including block copolymer lithography33 and nanosphere lithography34 are some alternative choices for overcoming the disadvantages of the conventional nanofabrication methods for nanopatterned Si-based sensor fabrication. However, there are still challenges to overcome to incorporate these lab-scale novel fabrication
methods into industrial-scale mass production. Along with these nanofabrication methods for the Si nanostructure patterning, surface roughing approach can be another way to go to increase the surface-to-volume ratio of Si nanofilm structures. In this paper, we proposed a buffered oxide etchant (BOE) postetching method to roughen the Si nanofilm with the aim of promoting a larger surface-to-volume ratio via the nanoporous surface structuring without using expensive nanopatterning or low-throughput nanomaterial assembly processes. A Si nanofilm structure was fabricated as the gas sensor framework, and palladium nanoparticles (PdNPs) were decorated on the Si channel surface via short-time e-beam evaporation to enable a highly sensitive and selective detection of H₂ gas. The H₂ sensing characterization of PdNP-decorated Si devices with various BOE treatment times for the Si nanofilm channel was evaluated at room temperature. The results revealed that the surface of the Si nanofilm is roughened by BOE treatment, which can in turn enhance the H₂ sensing performance of Pd-decorated Si nanofilms. In addition, the BOE postetching strategy was applied to the nanopatterned Si sensors, which induced clear performance enhancement for the H₂ sensors based on Pd-decorated nanopatterned Si structures.

### RESULTS AND DISCUSSION

The fabrication process for the Si nanofilm sensor device is schematically illustrated in Figure 1. A silicon-on-insulator (SOI) wafer, with a 60 nm thick Si device layer and 400 nm thick buried Si oxide layer, was used as the substrate for the sensor fabrication. A high-concentration arsenic (As) doping process was applied at the source and drain regions (n⁺-Si) by ion implantation, while the channel area was protected by the photoresist (PR) as a doping mask, followed by cleaning of the protection layer residue and a low-concentration phosphorus (P) doping process to the entire active area. Thus, an n⁺-n-n⁺ Si structure was formed as the framework of the sensor device.
The contact electrodes, consisting of a gold conducting layer and chrome adhesion layer, were made by conventional UV photolithography, e-beam evaporation, and a lift-off process. A PR pattern was then formed through another UV photolithography process to open the channel area while protecting other areas in the later BOE treatment process. After that, the chips were immersed into the BOE solution for the post-treatment, and the PR protection layer was then removed using acetone and rinsed with deionized (DI) water. Finally, the BOE-treated Si nanofilm was surface-decorated with PdNPs via short time e-beam evaporation to achieve highly selective sensing response to H2 gas. With the preset deposition thickness of 1 nm, a dispersive nanoparticle layer rather than a continuous layer was formed on the Si surface, which is due to higher surface energy of Pd compared with the native oxide layer on Si.

To understand the effect of BOE treatment on the n-type doped Si nanofilm, the surface morphology was characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The AFM imaging results shown in Figure 2 indicate that the Si surface becomes rougher dramatically with the longer BOE treatment time initially from 0 to 5 min (Figure 2a–c). Quantitatively, the roughness indicated as the value of root mean square was increased from 0.25 nm for the original SOI Si surface to 0.73 nm for 3 min BOE treatment and to 1.38 nm for 5 min BOE treatment, respectively. With further increase in BOE treatment time up to 10 min (Figure 2d), more "small islands" were etched away, while the "big islands" were retained, and the overall surface roughness did not increase significantly further with a measured value of 1.3 nm for 10 min BOE-treated Si surface. It is generally known that the crystalline Si structure is not damaged significantly by BOE or concentrated hydrofluoric acid (HF). However, some researchers have observed that a slight attack of 5:1 buffered HF on the n’ polysilicon occurs, causing surface roughening. Therefore, it is supposed that the crystalline structure of Si on the surface was partially destroyed by the ion implantation process and did not fully recover during the rapid thermal annealing process, which makes the Si structure slightly attackable by BOE. These defects caused by the doping process may accelerate the oxidation of the Si structure by the soluble O2 and water molecules in the BOE solution, especially near the defects, which accelerates the BOE etching effect for the doped Si structures. Although the actual mechanism of the BOE etching effect on our n-type doped Si nanofilm device is not fully understood, the measured AFM results are congruent with our assumption above: initially, BOE attacks those defects of the crystalline Si generated by the doping process, giving a rough Si surface with a lot of "small islands". Ultimately, BOE removes all the related defects while nonattacked parts are left as the "big islands".

To apply this BOE etching effect to the Si-based chemical sensors, Si nanofilm sensors were fabricated using a SOI substrate, as illustrated in Figure 1. The BOE treatment was applied to the Si channel region, while the other area was covered with the PR layer, and we could observe the etching effect clearly by optical microscopy with surface roughing, which occurs especially at the edge of the Si channel (Figure S1). The electrical properties of the Si nanofilm device with different BOE treatment times was measured by the probe system and semiconductor analyzer, and the results are presented in Figure S2. The resistance increasing with longer BOE treating time is also congruent with our hypothesis that the n-type doped Si is attacked by the BOE solution.

To further functionalize the Si structure, PdNPs were decorated onto the Si surface, enabling the structure with highly selective and sensitive response to H2 gas, because Si itself is inert to most of the chemical/gas components, and Pd can be specifically responsive to H2. These PdNPs were formed on the Si surface by short time e-beam evaporation (with preset thickness of 1 nm). The related AFM images are shown in Figure 3a–c, indicating that the formed PdNPs is about 1–4 nm high, with diameters ranging from several nanometers to ∼50 nm. To further prove that the PdNPs were successfully decorated on the Si surface, we checked the Si sample and without short-time Pd evaporation by X-ray photoelectron spectroscopy (XPS), as displayed in Figure 3d–f. These analytical results show that the Si sample had strong Pd 3d characteristic spectra at 335.4 and 340.2 eV after the Pd evaporation.
To evaluate the BOE etching effect on the sensing performance of the Pd-decorated Si nano-film-based H₂ sensor, we used the Si structure with different BOE etching times of 0, 3, 5, 10, and 15 min, as presented in Figure 4. Because the lower flammable limit (LFL) of H₂ gas is 4% in air, and the alarm concentration is set to 10% of the LFL based on the requirement from the US Department of Energy,²⁹ we tested the H₂ sensing performance of our sensors at a concentration range from 0.1 to 0.8%. The original current sensing data of these samples are illustrated in Figure 4a under the same applied voltage of 0.05 V, which gives a current value of ∼20 μA and a power consumption of ∼1 μW for our sensors, which is appropriate for the low-power gas-sensing applications. The general working mechanism of the Pd-decorated Si device is illustrated in Figure S3, including a typical sensing signal. To quantitatively compare the sensing performances of these sensors, the response was defined as the percentage change in the current value over the original current value \[ S = 100 \times (I - I_0)/I_0 \] (%). The results show that the response of the Pd-decorated Si nano-film sensor is dramatically improved by the BOE treatment of the Si structures for various H₂ gas concentrations tested, as shown in Figure 4b. A closer view of the sensing performance at 0.8% H₂ for the Pd-decorated Si nano-film sensor is illustrated in Figure 4c. The response to 0.8% H₂ was initially \( S = 0.49\% \) (±0.054%, standard deviation) for Pd-decorated Si without BOE treatment, while it dramatically increased to \( S = 3.74\% \) (±0.135%) after 3 min of BOE etching. It further improved to \( S = 5.85\% \) (±0.119%), 6.66% (±0.147%), and 7.07% (±0.159%) for 5, 10, and 15 min of BOE etching, respectively. The overall comparison for response and response time for these 5 conditions is shown in Figure 4d,e, respectively, where the error bar shows the standard deviation of measurement from three individual samples fabricated at the same time. From these results, we could observe that treatment longer than 5 min did not increase the roughness quite significantly, while the H₂ response kept increasing for 10 and 15 min. This phenomenon can be well-explained by the presumption we made above on...
The response improvement became less significant dramatically increased with initial BOE treatment time, and Figure S4. To quantify the response speed of H$_2$ gas sensors, significantly, while the latter mechanism does not have the nano films cannot make significant effects because the etching of the Si nano film is very slow. Based on the experimental results observed, it is presumed that the defects of the crystalline Si structure appear more on the surface layer. Initially, the response enhancement was caused by both the surface roughening and the etching of Si, where the surface roughening was the dominant effect. However, the slight response increment after relatively longer BOE treatment time was mainly due to the slow reduction of the nano film thickness. The former mechanism increases the surface-to-volume ratio dramatically, while the latter mechanism does not have significant effects because the etching of the Si nano film is very slow. Based on the experimental results observed, it is presumed that the defects of the crystalline Si structure appear more on the surface layer. Initially, the response enhancement was caused by both the surface roughening and the etching of Si, where the surface roughening was the dominant effect. However, the slight response increment after relatively longer BOE treatment time was mainly due to the slow reduction of the nano film thickness. The former mechanism increases the surface-to-volume ratio dramatically, while the latter mechanism cannot make significant effects because the etching of the Si nano film becomes slower. Therefore, the response dramatically increased with initial BOE treatment time, and the response improvement became less significant with further BOE treatment (longer than 5 min). The response improvement by BOE etching is schematically illustrated by the enhanced Pd gating effect on the roughened Si surface in Figure S4. To quantify the response speed of H$_2$ gas sensors, the response time was defined as the time needed to reach from 0 to 80% of the final response value. The experimental results show that the response time becomes relatively shorter for BOE treatment periods of 3 and 5 min, but it becomes significantly longer for 15 min of BOE treatment. The response speed in the same ambient environment is only related to the morphology especially the dimension considering that the Pd formed as a particle shape on the Si surface. Although it is hard to directly check the morphology of Pd particles on the BOE-etched rough Si surface device simply by AFM, with the experimental results on the responding speed of the sensors, we still can give a reasonable assumption that Pd forms relatively larger size particles in the 15 min BOE-etched Si case, while it forms relatively small size particles in the 3 and 5 min BOE-etched Si case. Finally, 5 min of BOE treatment was chosen for further experiments because both high response speed and response are achieved. To further illustrate the sensing performance of the sensor with the 5 min BOE treatment condition, we conducted a repeated sensing test from 0.1% H$_2$ to 0.8% H$_2$ and the results indicated a good repeatability, as depicted in Figure 4f. To check the lower limit of the detection, we also tested the sensor performance of the 5 min etched film sensor for lower H$_2$ concentration cases from 100 to 2000 ppm, as illustrated in Figure S5, which showed that the sensor gave a clear responding signal of about 1.15% current change for 100 ppm. Therefore, the Si film sensor with 5 min BOE treatment has a lower limit of detection (LOD) below 100 ppm. Along with the experimental results, we also estimate the LOD by the signal-to-noise approach, which is generally the concentration with response at three times of the noise standard deviation. The estimated LOD with linear response range is about 45 ppm, which is illustrated in Figure S5d.

The stability of the 5 min BOE-treated Si nanofilm sensor was characterized by measuring the sensor responses to 0.8% H$_2$ right after fabrication, after 2 weeks and after 1 month of fabrication, as shown in Figure 5a, with the corresponding real time sensing data illustrated in Figure 5b. Between these tests, the sensor was stored in regular ambient conditions (room temperature and humidity). The response results indicated that the sensor response does not have significant degradation after 1 month of fabrication. The selectivity of the 5 min BOE-treated Si nanofilm sensor was investigated among H$_2$ and other potential interfering gases including hydrogen sulfide (H$_2$S), carbon monoxide (CO), and nitrogen dioxide (NO$_2$) at their critical concentrations according to the permissible exposure limits by the Occupational Safety and Health Administration (OSHA) of the United States. The response comparison is summarized in Figure 5c, with the corresponding real time sensing data illustrated in Figure 5d.
confirms a high selectivity of the sensor. This can be attributed to the inertness of Si and highly selective reaction of Pd with H₂.

Table 1 shows the comparison for the important parameters of the Pd-loaded Si-based H₂ sensors reported recently regarding the materials used, fabrication method and performance parameters on response, responding/recovery speed, lower LOD, selectivity, and operating temperature. From the table, we could see that our reported sensor has an overall good sensing performance with a facile fabrication method compared with the existing H₂ sensors with Pd−Si materials. Moreover, our reported BOE treatment method can also be...
easily implemented in the existing technology to further improve the performance with an effective and cost-efficient process.

To further widen the applications of the simple BOE treatment method we proposed in this paper, we applied this method to the patterned Si nanomesh structures. This Si nanomesh structure was fabricated by nanosphere lithography, which is a facile and cost-effective method to achieve nanometer-scale structures. The fabrication procedure is illustrated in Figure S6, and further details of the fabrication method can be found in our previous work.32 The schematic process of the PdNP-decorated and BOE-treated Si nanomesh structure is illustrated in Figure 6a, showing the change in the cross-section, which is further linked with the surface-to-volume ratio, during the BOE treatment process. The polystyrene nanosphere monolayer pattern displayed in Figure 6b was used to pattern the Si structure later. The fabricated Si nanomesh structure has a minimum width of 50 nm, as the information shown in Figure 6c and a close-up view in Figure 6d. The responses of these nanopatterned Si structures with 0, 1, and 2 min BOE treatment periods to 0.1, 0.2, 0.5, and 0.8% H2 were investigated, and the results are shown in Figure 6e with a close-up view of response comparison to 0.8% H2 in Figure 6f. As compared in Figure 6g, the response to 0.8% H2 increased from 15.8% (±0.31%) of the Si nanomesh sensor without BOE treatment to 19.5% (±0.29%) and 27.5% (±0.23%) with 1 and 2 min BOE treatment periods, respectively. The response times are shown in Figure 6h correspondingly. This result verifies that the facile BOE treatment method is also applicable to the performance enhancement of the nanopatterned Si structures, which massively broadens the potential applications of our method.

■ CONCLUSIONS

In summary, we propose a facile BOE treatment method to an n-doped Si nanofilm, which can induce an effective surface roughing phenomenon and further increase the surface-to-volume ratio of the Si structures. To illustrate that this proposed method can be used for fabricating high-performance chemical sensors, we further functionalized the Si surface with PdNPs, making it a highly selective H2 sensor. The performance test illustrated that 5 min BOE treatment for the Si nanofilm, along with surface decoration with PdNPs, can give a fast, stable, highly sensitive, and selective response to H2 gas. This method was further utilized for Si nanomesh structures, which also gave further performance improvement of the Si nanomesh sensors, broadening the application of our method to the nanostructured devices. It is expected that our approach can be useful for the fabrication of cost-effective, highly selective Si-based chemical and other stimulus-responsive sensors linked with a massive emerging application field for the coming IoTs world.

■ EXPERIMENTAL SECTION

Fabrication of Si-Sensing Devices. The sensor devices reported in this paper were fabricated using lightly boron (B)-doped p-type SOI wafers (resistivity: 10–20 Ω·cm). The thickness of the top Si layer was reduced to about 60 nm via thermal oxidation and wet etching of SiO2, and that for the buried oxide layer was about 400 nm. The active area, including the source, drain, and channel, was patterned through the conventional UV photolithography and reactive-ion etching for the Si layer using O3 and SF6. To make a metal contact, the source and drain areas were doped by arsenic (As) ion implantation with a dose of 5 × 1015 cm−2, giving an impurity concentration as high as 1023 cm−3 (n+–Si), while the channel area was protected by the PR mask. The PR residue was later removed by oxygen plasma ashing and piranha solution cleaning. A low-concentration phosphorus (P) ion implantation was applied to the entire active device area with a dose of 1 × 1015 cm−2, giving an impurity concentration of about 1018 cm−3 (n–Si) in the channel area. Metallic contacts consisting of Cr/Au (10/200 nm) were then formed by electron beam (e-beam) evaporation and the lift-off process.

BOE Post-Treatment. After the Si device was fabricated from the process explained above, the chips were immersed into the 6:1 BOE solution for different periods. The channel area was opened to the BOE solution, while other areas were covered with a PR protection layer to prevent the possible attack on the source and drain areas. The treated samples were then rinsed in DI water to remove the BOE residue. Afterwards, the PR pattern was dissolved in acetone, rinsed by flowing DI water, and dried by N2 flow.

PdNP Decoration. E-beam evaporation was used for the Pd nanoparticle formation on the surface of the Si nanofilm. A thickness of 1 nm with a deposition rate of 0.2–0.3 Å/s was set for the deposition.

Gas Sensing Test. The gas sensing performance of the fabricated sensor was tested in a sealed chamber with a probe station inside. A schematic of the gas test setup is shown in Figure S7. The real-time channel current was recorded using a SourceMeter (Keithley 2635B) when the target gas with certain concentrations was injected into the chamber. The mixture of N2 and O2 gases with a volume ratio of 4:1 was used to represent the air environment, which represents the basic state of the sensor. The composition and concentration of the test gas were controlled by adjusting the flow rate of the corresponding mass-flow controllers (MFCs), while the total flow rate was maintained at 500 sccm. The relative humidity (RH) level of the testing environment is in a dry condition with RH about 5%. The current SourceMeter and all MFCs were controlled by the LabView interface. For each testing condition, three individual samples were used.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c08977.

Optical images and SEM images of the BOE-etched Si surface; I–V curve of the devices with different BOE etching times; schematic illustration of H2 gas sensing mechanism for Pd-decorated Si-sensing devices; schematic illustration of BOE treatment for a Si nanofilm device with and without Pd decoration; lower H2 concentration sensing performance; fabrication process for the Si nanomesh structure by nanosphere lithography; and gas sensing test setups (PDF).

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Author Contributions

M.G. and I.P. conceived the idea. M.G., Z.J.-Z., H.K., M.J., and P.L., T.K., K.K., and I.C. contributed to experimental work of device fabrication, characterization, and the H2 sensing performance test. M.G. and I.P. wrote the initial manuscript. J.H.-J. and I.P. supervised this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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