

Bismuth Spheres Grown in Self-Nested Cavities in a Silicon Wafer

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Abstract: We have developed a one-step, hydrofluoric acid-free hydrothermal etching method that not only produces bismuth nano/micrometer-sized spheres but also prepares porous silicon with vertical holes. By controlling the heating temperature and time, nanoscale vertical-channeled porous silicon can be received. Our result indicated that the Bi clusters were formed first on the wafer surface. Then the etching of the Bi to the wafer creates the holes. Later, the Bi spheres went into the holes and expedited the etching process. A formation mechanism and chemical process have been proposed on the basis of experimental data. This simple chemistry approach may be of great scientific and technological importance for preparing porous silicon wafer.

1. Introduction

Bismuth is a semimetal with unusual electronic properties that results from its highly anisotropic Fermi surface, low carrier concentrations, and small effective carrier mass. Because of its large Fermi wavelength and long carrier mean free path, Bi has been extensively investigated for quantum transport and finite-size effects.¹ Bismuth nanostructures have been extensively pursued in studies of classical and finite size quantum effects for more than 20 years because of their very large magnetoresistance (MR)² and excellent thermoelectric properties.³ In recent years, synthesis and property characterization of bismuth nanostructures are attracting a lot of interest because of their potential applications as magnetic field sensor, thermoelectric cooler or power generator. Some groups have synthesized bismuth thin films, nanowires, nanotubes, nanoplates, and nanoballs through different synthesis routes.⁴

In this paper, we report a distinct and novel approach that integrates the synthesized Bi spheres with silicon wafer through a self-initiated etching process without using HF acid. This single step process not only receives the as-expected Bi structures, but also presents a simple etching method for preparing silicon surfaces that is different from the traditional methods for etching silicon. During the etching process, no current and no hydrofluoric acid was used. During the hydrothermal synthesis process, cavities were created inside a silicon wafer,

which were created by the bismuth microballs or nanospheres grown in situ inside the “nests” of the etched holes. Both the growth of the Bi spheres and the formation of nano/micropores occurred simultaneously. The chemical reactions and processes for this process have been proposed.

2. Experimental Section

The synthesis of the bismuth–silicon structure was conducted in a 22-mL Teflon-lined stainless steel autoclave. The preparation process comprises three steps. (1) The silicon wafers [(001) direction, 10 mm × 15 mm × 1 mm] were cleaned sequentially using H₂SO₄/H₂O₂ [H₂SO₄ (97%) + H₂O₂ (30%)] (90 °C, 30 min), deionized water (ultrasonic bath 10 min, 4–6 times, to pH 7), and ethanol (ultrasonic bath 10 min). (2) Bismuth hydroxide (0.01 mol/L) suspension was prepared. Analytical grade Bi(NO₃)₃·5H₂O (0.0005 mol, 98%, Alfa) was dissolved in 50 mL of deionized water to get bismuth nitric solution. Excessive ammonia hydroxide solution was dropped into the bismuth nitric solution to get bismuth hydroxide to precipitate. The precipitate was filtrated and washed with deionized water several times until the pH reached 7. Then, 0.01 mol/L bismuth hydroxide suspension was prepared by dispersing all of the precipitate in deionized water under ultrasonic irradiation for 60 min, and deionized water was added to 50 mL. (3) The hydrothermal process was conducted. The silicon wafer from step 1 was placed vertically into the bottom of an autoclave. Bismuth hydroxide suspension (2 mL) and 18 mL of deionized water were added into the autoclave. The autoclave was sealed and put into a furnace, which was preheated to 160–180 °C. After heating for different times, the autoclave was taken out and cooled to room temperature. The silicon wafer was taken out of the autoclave and washed with deionized water and then alcohol.

Characterization. X-ray diffraction was performed on a Philips X-ray diffractometer. Scanning electron microscopy (FE-SEM) (field emission LEO1530 at 5–10 K) and energy-dispersive X-ray spectroscopy (EDS) were used to investigate the chemical composition of the as-synthesized samples.

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(1) Du, X.; Tsai, S.; Maslov, D. L.; Hebard, A. F. *Phys. Rev. Lett.* **2005**, *94*, 166601(1–4).

(2) Lu, M. *Phys. Rev. B* **1996**, *53*, 1609–1615.

(3) Yang, F. Y.; Liu, K.; Hong, K.; Reich, D. H.; Searson, P. C.; Chien, C. L. *Science* **1999**, *284*, 1335–1337.

(4) Zhang, Z.; Sun, X.; Dresselhaus, M. S.; Ying, J. *Appl. Phys. Lett.* **1998**, *73*, 1589–1591. (b) Heremans, J.; Thrush, C. M.; Lin, Y. M.; Cronin, S.; Zhang, Z.; Dresselhaus, M. S.; Mansfield, J. F. *Phys. Rev. B* **2000**, *61*, 2921–2930.

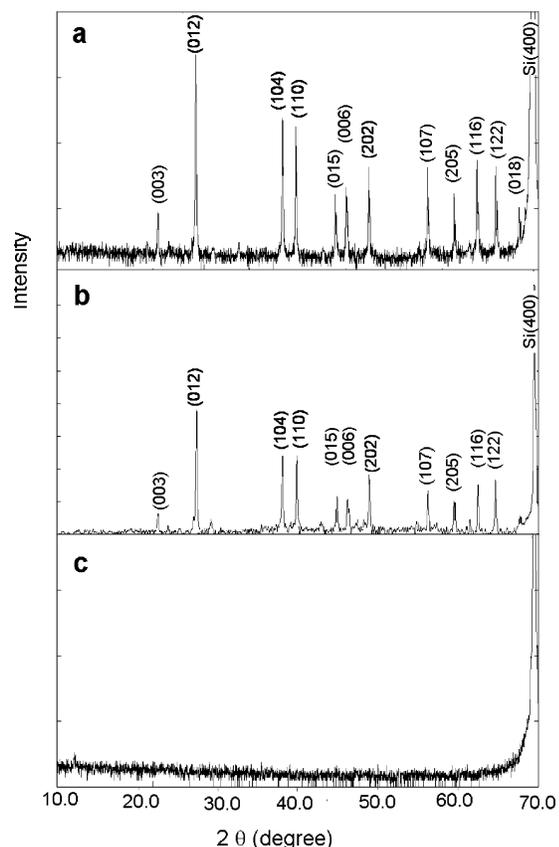


Figure 1. XRD patterns of the samples reacted at (a) 175 °C for 24 h, (b) 160 °C for 24 h, and (c) 160 °C for 48 h.

3. Results and Discussions

X-ray diffraction (XRD) patterns from the samples synthesized at 160 and 175 °C for 24 h show that the samples are composed of hexagonal bismuth (JCPD-85-1330) and single-crystal silicon with diamond structure (JCPD-80-0018). From the data presented in Figure 1, we can see that, besides of the {400} peak of silicon ((001) silicon wafer), all of the peaks in the XRD patterns are consistent with those of the standard XRD pattern of hexagonal bismuth. No other related compound, such as bismuth oxide or bismuth silicate, has been detected in the samples. In the pattern of the sample obtained at 160 °C for 48 h (Figure 1c), no crystalline compound was detected besides of silicon substrate.

Figure 2 shows SEM images of the sample on Si(001) synthesized at 175 °C for 24 h. Figure 2a is the morphology of the as-synthesized sample with low magnification. Many small balls 1.5–2 μm in diameter are distributed homogeneously on the surface of the silicon wafer. Each ball locates inside a hole nest created in the silicon. From Figure 2b, we can find that the holes are perfect circles, and all of the balls are trapped in the holes. The surface of silicon wafer looks like a lotus seedpod. On the surface of a ball grown in a hole (Figure 2c), we can see some rough areas with dots and some smooth areas with well-shaped patterns, which indicates that the ball may be crystalline. The smooth patterned area may be the growing planes with low-index facets, and the rough places may be the growing planes with higher index. The diameters of most balls are approximately the same, which are slightly smaller than the opening ends of the hole nests. For some balls, their sizes are

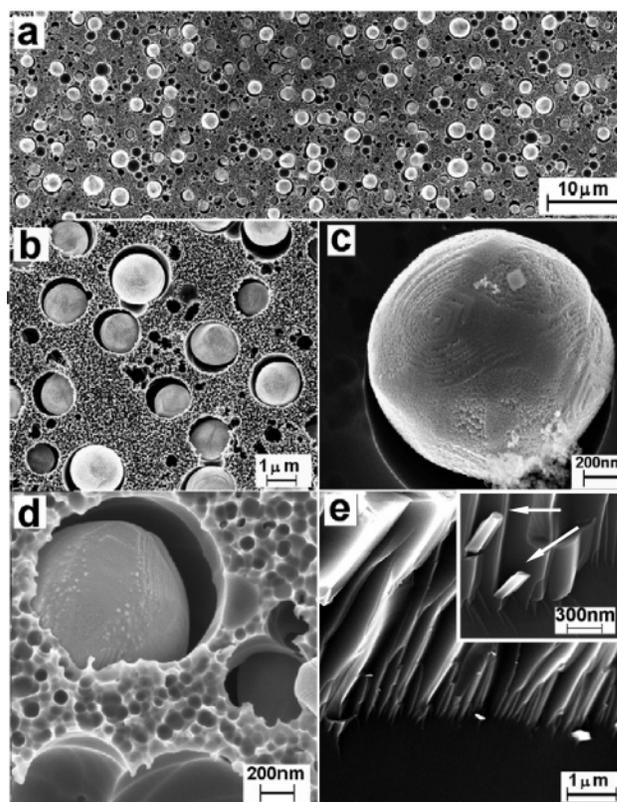


Figure 2. SEM images of the sample on Si(001) synthesized at 175 °C for 24 h. (a, b) Top view of the ball–hole structures on the wafer at different magnifications. (c, d) Top view of two individual balls. (e) SEM image acquired from a fractured sample synthesized at 175 °C for 48 h. Inset: Cylinders found at the bottom of the holes (marked by arrows).

larger than the opening ends of the holes and they are “trapped” inside (Figure 2d). This observation indicates that the balls were formed inside the holes and/or they were responsible for creating the holes as they grew, but they cannot be placed in or fall in after the holes were formed. Thus, the balls and the holes were formed simultaneously as the reaction proceeds. Figure 2e is the SEM image acquired at a fraction side of the sample synthesized at 175 °C for 48 h. We can see that the etching depth is about 5 μm. From the inset of Figure 2e, we can see that there is a cylinder about 100 nm in diameter at the bottom of each etching hole.

To confirm the chemical composition of the balls and the surface of the wafer of the sample, EDS was performed in SEM. Figure 3 shows EDS spectra from the balls at different circumstances. The only detectable element by EDS from the balls/polyhedra is bismuth. This supports the XRD result that the balls are hexagonally structured bismuth crystals. At the rough area between the holes of the wafer, besides of the main element Si, there is a small amount of oxygen and bismuth. A small amount of silicon oxide should exist at the surface of the silicon wafer, and the minor Bi could come from the tiny Bi sphere below the surface and/or the Bi balls located away from the beam illuminated area, due to the large interaction volume (~1–2 μm) of the electron beam with the sample. Carbon element detected by EDS should be from ethanol molecules absorbed on the surface of the samples during washing with alcohol.

To receive nanosized bismuth balls and holes, samples were prepared at lower temperature for different times (Figure 4).

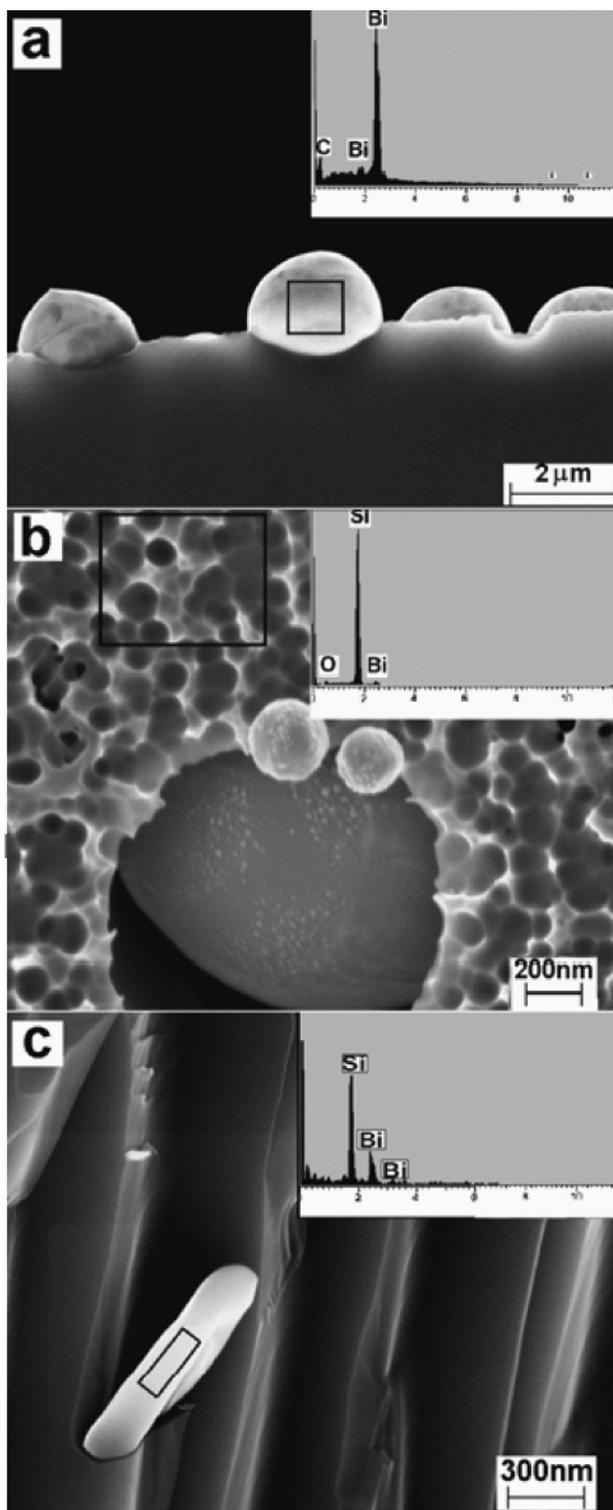


Figure 3. Energy dispersion spectra acquired in SEM from (a) a ball, (b) the rough surface area between the holes, and (c) a cylinder at bottom of an etched hole.

After reacting at 160 °C for 15 h (Figure 4a), small spheres 150–200 nm in diameter can be found on the surface of the silicon wafer. However, no obvious etching holes can be found. After reacting for 24 h (Figure 4b), the etching holes were formed, and the spheres directly sat on the holes. The depth of the holes increases with the increase of hydrothermal time. Figure 4c shows the surface of the silicon wafer synthesized at

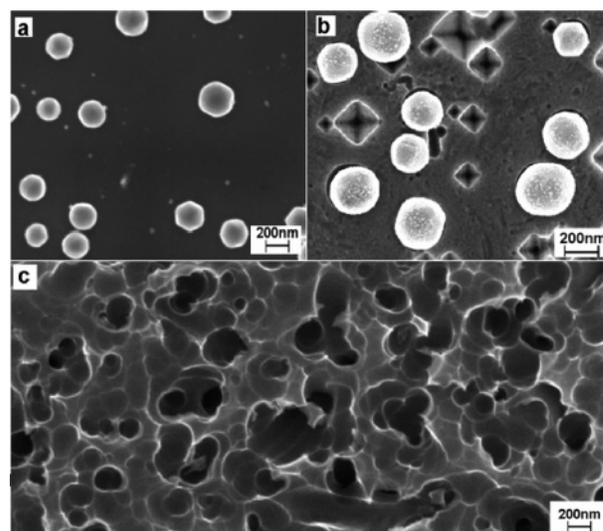


Figure 4. Top view of the samples reacted at 160 °C for (a) 15 h, (b) 24 h, and (c) for 48 h.

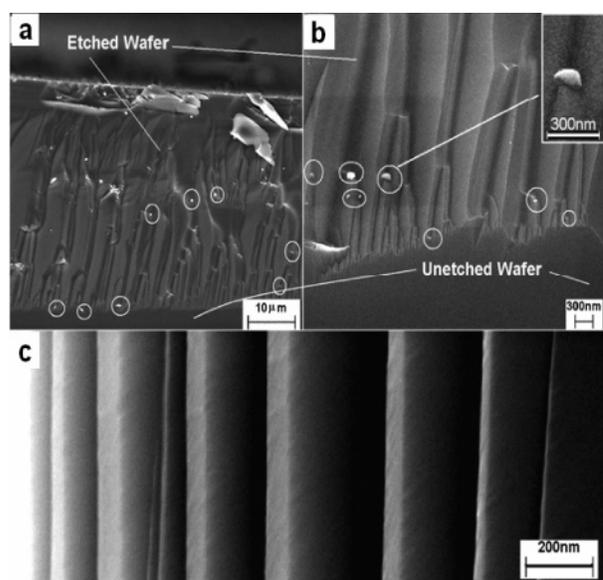


Figure 5. (a, b) Cross sectional view of the sample reacted at 160 °C for 48 h and (c) uniform, vertically etched holes obtained at 165 °C for 72 h through a well-dispersed suspension of bismuth hydroxide.

160 °C for 50 h, which have many deep holes of ~200 nm in diameters on the surface of the wafer, but surprisingly there are no Bi spheres on the surface. Then, the silicon wafer was fractured to see its cross-section (Figure 5a,b). The depth of the etched holes is over 30 μm , and nanosized Bi particles of about 100–150 nm in size, as indicated by circles, were found at the bottoms of the holes. The diameter of the spheres is slightly smaller than that in Figure 4b, and the lower half of the nanospheres is not a standard sphere shape. At the same time, the diameter of the hole at the bottom is slightly smaller than that at the opening end. By adjusting the etching condition, we can get uniform etched holes in the silicon wafer. The conditions for successfully achieving the etching are as follows: the concentration of bismuth hydroxide suspension is 0.005 mol/L, and before being added into autoclave, the suspension was dispersed with ultrasonic irradiation for 40 min. The autoclave was heated at 165 °C for 72 h. The diameters of most of the vertical holes (over 90%) are 150–190 nm, and

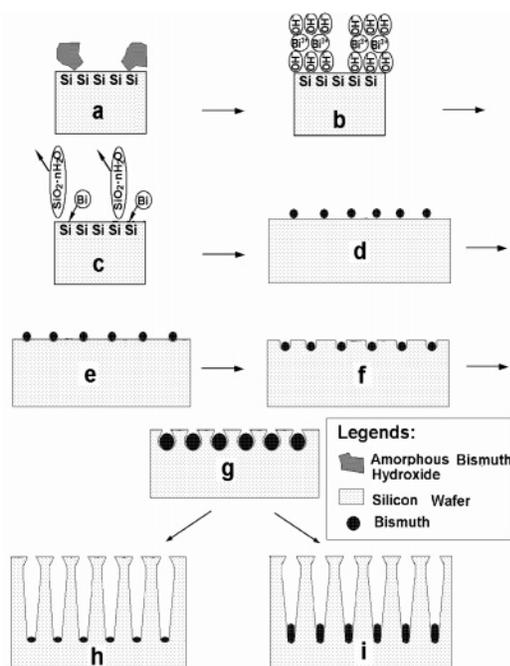


Figure 6. A schematic model illustrating the formation of bismuth spheres and the bismuth-sphere-catalyzed chemical etching of silicon (see the text for details).

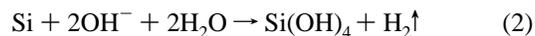
the thicknesses of the walls between two adjacent holes are 20–50 nm (see Figure 5c). This process can give a similar etching result comparing to that of the metal-catalysis etching, for which a layer of metal was deposited on the surface of the silicon wafer, and the metal layer was transferred as a layer of nanoballs by heating the wafer. But the traditional corrodent, HF, was still used for etching. Vertical nanoholes of 50–150 nm in diameters are formed because of catalysis effect of the metal nanoballs.⁵ The etching method proposed in the current paper is much simpler and less toxic than the traditional ones.

Our result indicated that the Bi spheres were formed first on the wafer surface. Then the etching of the Bi sphere to the wafer creates the holes. Later, the Bi spheres fell into the holes and continued the etching process. On the basis of the data, we proposed a formation mechanism (Figure 6) for the etched holes and bismuth spheres in the holes.

When bismuth hydroxide suspension is added into the water in the autoclave, a layer of amorphous bismuth hydrothermal particles may be adsorbed on the surface of the wafer, which is located at the bottom of the autoclave (Figure 6a). When the autoclave is placed into the furnace, which is preheated to 160 or 175 °C, water in autoclave is overheated and forms supercritical water. The dissolvability of bismuth hydroxide particles in the supercritical water is thus increased because of the novel dissoluble ability of supercritical water.⁶

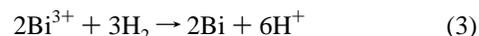


Therefore, the local concentration of OH^- at the surface of the wafer, where the bismuth hydroxide particles are adhered, should be much higher than that at other places (Figure 6b). Therefore, reaction between silicon and hydroxide ion should occur immediately on the surface of the wafer.



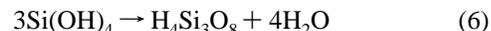
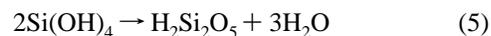
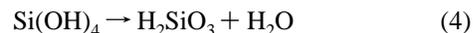
The electrochemical etching mechanism of hydroxide ions on silicon wafer with applied voltage has been investigated extensively.⁷ In the present work, however, we did not apply any electric field on the wafer, and all of the processes were conducted under a hydrothermal condition.

The hydrogen atoms formed from reaction 2 have strong reducing ability. It is easily to reduce the Bi^{3+} ions formed in reaction 1. The electrode standard potential of Bi^{3+} is +0.317,⁸ thus, it is easily reduced by hydrogen:



Bismuth atoms reduced by hydrogen accumulate at the surface of the silicon and become crystalline nuclei (Figure 6c). At the same time, hydrogen ions formed in reaction 3 enter the solution. With the hydrothermal process continuing, the pH value decreases (dropping to 5–6 after hydrothermal process).

The as-forming soluble Si(OH)_4 molecules released from the surface enter the water. Because Si(OH)_4 is not stable in water, it is easily condensed into $x\text{SiO}_2 \cdot y\text{H}_2\text{O}$.⁹



In fact, H_2SiO_3 could not exist at temperatures over 0 °C, and $\text{H}_4\text{Si}_3\text{O}_8$ is difficult to form during a very short period of time.¹⁸ Therefore, the Si(OH)_4 from reaction 2 should become $\text{H}_2\text{Si}_2\text{O}_5$. But $\text{H}_2\text{Si}_2\text{O}_5$ is not stable at a temperatures over 160 °C, and it decomposes into water and silicon oxide at higher temperatures:



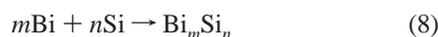
The silicon oxide formed from reaction 7 should be amorphous, and a small amount of amorphous silica should adhere on the surface of the wafer (Figure 6d). This is the reason we

(5) Song, D. W.; Shen, W. N.; Dunn, B.; Moore, C. D.; Goorsky, M. S.; Radetic, T.; Gronsky, R.; Chenb, G. *Appl. Phys. Lett.* **2004**, *84*, 1883–1885. (b) Hasegawa, Y.; Ishikawa, Y.; Komine, T.; Huber, T. E.; Suzuki, A.; Morita, H.; Shirai, H. *Appl. Phys. Lett.* **2004**, *85*, 917–919. (c) Yang, B.; Li, C.; Hu, H.; Yang, X.; Li, Q.; Qian, Y. *Eur. J. Inorg. Chem.* **2003**, 3699–3702. (d) Wang, J.; Wang, X.; Peng, Q.; Li, Y. *Inorg. Chem.* **2004**, *43*, 7553–56. (6) Peng, K.; Wu, Y.; Fang, H.; Zhong, X.; Xu, Y.; Zhu, J. *Angew. Chem.* **2005**, *117*, 2797–2802.

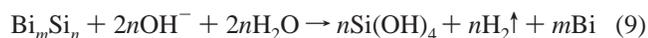
(7) Yahya, R. B.; Hayashi, H.; Nagase, T.; Ebina, T.; Onodera, Y.; Saitoh, N. *Chem. Mater.* **2001**, *13*, 842–847. (8) Xia, X. H.; Ashruf, C. M.; French, P. J.; Rappich, J.; Kelly, J. J. *Phys. Chem. B* **2001**, *105*, 5722–5729. (9) Serp, J.; Lefebvre, P.; Malmbeck, R.; Rebizant, J.; Vallet, P.; Glatz, J. P. *J. Nuclear Mater.* **2005**, *340*, 266–270. (10) Caven, R. M.; Lander, G. D. *Systematic Inorganic Chemistry*; Blamkie & Son Limited: London, 1936; pp 257–95. (11) Massalski, T. B.; Murray, J. L.; Bennett, L. H.; Kacprzak, L. *Binary Alloy Phase Diagrams*; American Society of Metals: Metals Park, OH, 1996; pp 538–539. (12) Tada, T.; Kanayama, T.; Koga, K.; Weibel, P.; Carroll, S. J.; Seeger, K.; Palmer, R. E. *J. Phys. D* **1998**, *31*, L21–L24. (13) Schuster, R.; Kirchner, V.; Allongue, P.; Ertl, G. *Science* **2000**, *289*, 98–101. (14) Peng, K.; Wu, Y.; Fang, H.; Zhong, X.; Xu, Y.; Zhu, J. *Angew. Chem.* **2005**, *117*, 2797–2802. (15) Tujino, K.; Mutsumara, M. *Adv. Mater.* **2005**, *17*, 1045–1047. (16) Kendall, D. L. *Appl. Phys. Lett.* **1975**, *26*, 195. (17) Glembocki, O. J.; Stahlbush, R. E.; Tomkiewicz, M. *J. Electrochem. Soc.* **1985**, *132*, 145. (18) Raisch, P.; Haiss, W.; Nichols, R. J.; Schiffrin, D. J. *J. Phys. Chem. B* **2001**, *105*, 12508–12515.

can detect a small amount of oxygen, but no crystalline silicon oxide can be detected by XRD on the rough place on the surface of the silicon wafer. It should be noted that the amorphous silica forms in the solution, and the adhered amorphous silica is located on the surface of the wafer, which does not lower the etching speed.

From the bismuth–silicon binary phase diagram,¹⁰ we can see that the melting point of bismuth is only 271 °C, which is much lower than that of silicon (1412 °C). The as-reduced bismuth atoms should be very active, and at the same time, silicon atoms on the surface of the silicon wafer in supercritical water should be more active than those under a normal condition; therefore, the silicon atoms will be “attracted” out of its silicon lattice by the active as-reduced bismuth atoms to form temporary congruent melting clusters:



From the Bi–Si phase diagram, we found that silicon and bismuth cannot form a stable compound. Therefore, silicon atoms in the bismuth–silicon clusters are easily released and react with OH^- , as shown in reaction 2, resulting in more hydrogen atoms.



The bismuth atoms disposed of as the bismuth ball and can repeat reaction 8 at the bottom of the holes. During the further etching process, bismuth atoms attract and release silicon atoms and play the role of an etching catalyst. Bi^{3+} ions transported by supercritical water are neutralized by the charges from the hydrogen atoms, forming bismuth elemental atoms, which epitaxially deposit on the surface of bismuth nuclei, increasing their sizes to small nanospheres (Figure 6d).

All of the above reactions repeat during the hydrothermal process, and the surface of the silicon wafer was etched to form holes gradually (Figure 6e). Because of the catalysis function of the bismuth spheres, silicon atoms in contact with the spheres are easily etched, and the depth increases with increasing etching time (Figure 6f). The diameter and depth of the holes increase, and at the same time, the bismuth nanospheres grow with increasing reaction time (Figure 6g). During the reaction process, the sphere preserves its position at the bottom of the etched hole. Finally, the concentration of H^+ in the hole is much higher than that outside of the hole, preventing Bi^{3+} from entering into the hole. At equilibrium, although the etching processing can continue and lead to an increase in hole depth, the diameter of the hole and the size of the sphere in the hole do not increase. At last, a porous structure of silicon is received. The hole is deep, and the bismuth sphere sinks to the bottom of the hole. Therefore, we cannot detect bismuth in the sample prepared at 160 °C for 48 h. Because there are a small amount of bismuth atoms left on the wall of the hole and no additional bismuth atoms coming into the hole during the “catalysis” process of a bismuth ball, the ball becomes smaller after a long etching. This may be the reason the ball becomes smaller and the diameter

of the hole decreases slightly at the bottom of the hole after reaction for 48 h (see Figure 5). In addition, because the formation and decomposing of temporary congruent melting clusters, some bismuth atoms are moved from the front area to the part behind the ball. Therefore, the shape of the balls should change. For the big balls, the diameters shrink and they become cylinders. For the nanospheres, their diameter should change slightly, and they become thick disks.

The experimental procedure demonstrated above opens a new, simple chemical approach for etching silicon wafers, which offers some advantages in comparison to the existing etching technology that normally uses HF. The bismuth element left in the holes can be removed by nitrate acid, because silicon does not dissolve in nitrate acid and bismuth does. As is well-known, standard and advanced lithography are based on hydrofluoric acid etching.¹¹ The corrodents of most electrochemical etching, chemical etching, and macromachining technology on silicon wafer are also related to HF.^{12,14} Although hydroxide solution is often used as a corrodent in electrochemical etching of silicon wafers,¹⁵ a layer of oxide is easily formed on the surface, resulting in a sharp drop in etching rate and the anodic current;¹⁶ the etching process has to be interrupted to remove the oxide with HF. Although careful control of the potential of the n-type silicon wafer during the etching process can prolong the time before forming the passivation layer on the etched surface, it is still difficult to totally prevent the formation of the oxide layer.¹⁷ As of now, almost all of the etching methods for silicon wafer cannot totally avoid the use of corrosive and toxic hydrofluoric acid, which are toxic not only for the operators but also for the environment. Therefore, the demonstration of a simple and nontoxic etching method without hydrofluoric acid is an important part of the current work.

4. Conclusions

In this paper, we have developed a one-step, hydrofluoric acid-free hydrothermal etching method that not only produces bismuth nano/micrometer-sized spheres but also prepares porous silicon with vertical holes. By controlling the heating temperature and time, nanoscale vertical-channeled porous silicon can be received. Our result indicated that the Bi clusters were formed first on the wafer surface. Then the etching of the Bi on the wafer creates the holes. Later, the Bi spheres went into the holes and expedited the etching process. A formation mechanism and chemical process have been proposed on the basis of experimental data. This simple and nontoxic chemistry approach may be of great scientific and technological importance for preparing porous silicon wafers.

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