Porous silicon prepared from monolithic porous silica glass using a two-step magnesiothermic reduction

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Abstract
Magnesiothermic reduction to convert silicon dioxide into silicon is difficult to control because the reduction often proceeds through the formation of magnesium silicide. To improve the yield of silicon, we have applied a two-step magnesiothermic reduction to produce porous silicon from a monolithic porous silica glass substrate. At the first step, the porous silica glass substrate with pore size of approximately 40 nm was reacted with magnesium at 525°C for 6 hours, in which magnesium silicide was formed in the several tens of micrometers-deep surface layer, while the inside of the substrate remained unreacted. Subsequently, in the second step, the product was heat-treated at 650°C for 72 hours to produce silicon. In this step, the obtained magnesium silicide reacted with the unreacted silica glass and the intermediate products, which consist of silicon in the intermediate oxidation states generated in the first step of the reaction. The obtained silicon retained the characteristic porous structure of the initial porous silica glass. The sample also retained the monolithic shape of the initial substrate, even after being divided into several pieces. In addition, we found that periodical layered structures were generated in the course of the reduction procedure. We successfully obtained a monolithic porous silica glass sample, the surface region of which consists of porous silicon.

KEYWORDS
glass, phase separation, porous materials, silica, silicon

1 | INTRODUCTION

In metallurgical and industrial settings, silicon is typically prepared from silicon dioxide through carbothermic reduction, in which the reduction reaction usually proceeds at temperatures above 1700°C, yielding liquid silicon.¹⁻⁴ For silicon dioxide reductions, however, reagents other than carbon can be potentially used.¹⁻⁷ Among these, magnesium has been one of the most attractive options: the magnesiothermic reduction usually proceeds at temperatures in the 500-900°C range, and silicon dioxides are reduced, in the solid state, to silicon.⁵⁻⁷ Consequently, this reaction has received much attention not only because it is energy-efficient but also because it converts silicon dioxide into silicon while retaining the morphology of silicon dioxide.⁸ In fact, magnesium is an excellent reductant and the magnesiothermic reduction for titanium oxide and complex oxides containing titanium has also been well studied.⁹⁻¹¹
Sandhage and coworkers applied the magnesiothermic reduction to nanostructured silicon dioxide microcrystallites from diatoms and obtained porous silicon with the nanostructure of the microcrystallites.12–14 Since then, various types of silicon dioxides with nanometer-size structures have been successfully converted to silicon retaining morphologies similar to those of the original silicon dioxides.12–28 Silicon dioxides can be obtained from natural resources15–20 or by synthesis through various techniques, including the sol-gel and polymer-template methods.21–31

For the porous silicon prepared from porous silicon dioxides, one of the most attractive uses is as anode materials for lithium-ion batteries.17–19,28,32–36

We previously reported that we could obtain silicon from pulverized porous silica glass samples, which in turn were prepared from sodium borosilicate glass samples by the heat treatment for phase separation and acid leaching of the borate-rich phase.37 The obtained silicon retained the characteristic porous morphology of the starting porous silica glass. Since the porous silica glass samples were obtained from monolithic borosilicate glass by acid leaching, porous silica glasses of various shapes can be prepared. Furthermore, the pore structure, for example, the pore size and distribution, can be controlled by adjusting the composition of the original borosilicate glass and the heat treatment conditions for phase separation and acid leaching.38–40 Therefore, taking porous silica glass as a starting material, we expect to obtain porous silicon with well-defined pore structure and morphology through the magnesiothermic reduction. However, porous silicon has not yet been obtained from monolithic porous silica glass through the magnesiothermic reduction.

In the magnesiothermic reduction, the reaction that converts silicon dioxide into silicon is represented as the following equation,

\[
\text{SiO}_2 + 2\text{Mg} \rightarrow \text{Si} + 2\text{MgO.} \tag{1}
\]

The standard Gibbs free energy change, \(\Delta G_1\), is estimated as \(-260\) kJ/mol for this reaction at 600°C, indicating that the reaction proceeds spontaneously from the thermodynamic aspect.41 The standard Gibbs free energy changes of reactions 1-4 are provided in the supplemental file. It should be noted, however, that the obtained silicon is further reduced to magnesium silicide in the following reaction:

\[
\text{Si} + 2\text{Mg} \rightarrow \text{Mg}_2\text{Si}, \tag{2}
\]

for which the standard Gibbs free energy change, \(\Delta G_2\), is \(-65\) kJ/mol at 600°C.41 Thus, silicon dioxide is expected to be readily reduced to magnesium silicide if a sufficient amount of magnesium is present.

In fact, in the reduction of a silica glass substrate and quartz embedded in a magnesium powder, the reaction proceeds from the surfaces of the starting materials, and the reaction products are magnesium silicide and magnesium oxide.42–44 It has been reported that an intriguing structure, in which magnesium silicide-rich and magnesium oxide-rich layered phases are periodically arranged, is formed in this reaction.42–44 However, the generation of silicon has not been observed. In the case of the reduction reaction in which the amount of the supplied magnesium is significantly limited, silicon dioxide is effectively converted into silicon. Actually, it was demonstrated that silica and/or silicate glass substrates were reduced to silicon by magnesium thin films deposited on the substrates.

We have investigated the reaction process of the magnesiothermic reduction, in which a silica glass substrate is reduced by a magnesium film that is deposited on the substrate surface.47,48 The reduction was performed at various conditions by varying the reaction temperature, duration, and thickness of the deposited magnesium film. The relationship between the reaction conditions and the reaction products was closely examined. From these experiments, we concluded that the complete reduction of silicon dioxide to magnesium silicide shown in Equation (3) quickly proceeds in the magnesiothermic reduction at the surface of the silica glass substrate. Thus, we hypothesized that the silicon is generated from the reaction between the magnesium silicide produced in the reduction reaction and the unreacted silica glass, as shown in Equation (4).

\[
\text{SiO}_2 + 4\text{Mg} \rightarrow \text{Mg}_2\text{Si} + 2\text{MgO}. \tag{3}
\]

\[
\text{SiO}_2 + \text{Mg}_2\text{Si} \rightarrow 2\text{Si} + 2\text{MgO}. \tag{4}
\]

Magnesium silicide is not stable when in contact with silicon dioxide. Since the reaction in Equation (4) has a negative Gibbs free energy change, \(\Delta G_4\), \(-195\) kJ/mol at 600°C, the reaction proceeds spontaneously.41

From these observations, we have proposed a two-step reaction scheme for the magnesiothermic reduction of monolithic silicon dioxide. In the first step, silicon dioxide is reduced by reacting with magnesium to magnesium silicide. In the subsequent second step, the produced magnesium silicide reacts with the unreacted silicon dioxide to produce silicon. We successfully prepared silicon from a silica glass substrate through this two-step reaction.48

In the present work, the two-step magnesiothermic reduction was applied to monolithic porous silica glass samples that were prepared from a borosilicate glass through the heat treatment for phase separation and acid leaching of the borate-rich phase.
2 | EXPERIMENTAL PROCEDURES

2.1 | Preparation of monolithic porous silica glass

Porous silica glass was prepared from borosilicate glass through heat treatment for phase separation and acid leaching of the borate-rich phase, as described below. Borosilicate glass with a composition, 65SiO₂·25B₂O₃·10Na₂O (mol%), was prepared from a batch mixture with an appropriate composition of reagent grades SiO₂, B₂O₃, and Na₂CO₃. The mixture was melted in a platinum crucible at 1400°C for 1 hour, and was then poured into carbon molds for vitrification. Before the glass was cooled to room temperature, it was moved into a furnace and heat-treated at 620°C for 18 hours. The as-quenched glass was still transparent. After the heat treatment, however, the glass became translucent. This indicates that phase separation was induced by the heat treatment. The phase-separated glass was cut into glass substrates with a size of 5 × 30 mm² and thickness of 2 mm, and for each substrate, both sides were polished. The glass substrates were immersed in a 0.5 mol/L HNO₃ aqueous solution at 95°C for 48 hours, to leach the borate-rich phase. The acid-treated glass samples were rinsed in deionized water and dried at 700°C for 1 hour to obtain monolithic porous silica glass samples. For these samples, the mass ratio of the porous silica glass to the original borosilicate glass was 63.8%. The samples during each step of the preparation procedure from the original glass to the porous silica glass are shown in Figure S1 in the supplementary file; the X-ray diffraction (XRD) patterns for these samples are also shown.

2.2 | Two-step magnesiothermic reduction of the prepared porous silica glass

The magnesiothermic reduction was performed using the two-step reaction scheme that was mentioned in Introduction. The procedures are illustrated in Figure 1. In the first step, the prepared porous silica glass substrates of the size of 5 × 30 mm², thickness of 2 mm, and approximately 0.45 g were embedded in the 1.8 g of magnesium coarse powders in stainless tubes of outer diameter, 3/8 in; length, 60 mm, under an Ar atmosphere (Figure 1A). The magnesium coarse powder (reagent grade, supplied from FUJIFILM Wako Pure Chemical Co.) was used as received. For each stainless tube, both ends were sealed using Swagelok® stainless caps. Then, the tubes were heated at 525°C for 3 to 72 hours.

After the heat treatment for the first step of the reaction, the reacted porous silica glass substrates were removed from the stainless tubes. The substrates were then heat-treated in the second step of the reaction in silica glass tubes, outer diameter, 10 mm; inner diameter, 8 mm (Figure 1B). Then, each tube was sealed in vacuum using an H₂-O₂ burner. The heat treatment was performed at 650°C for 72 hours. The samples that were obtained after the second step of the reaction were rinsed in a 1.2 mol/L HCl solution (Figure 1C).
2.3 | Characterization

The prepared samples were characterized using an X-ray diffractometer (XRD, Rigaku MiniFlex) with Cu Kα X-ray source operated at 40 kV, 15 mA, and a scanning electron microscope (SEM, JEOL JSM-7600F), equipped with an energy dispersive X-ray spectrometer (EDX, Oxford INCA). The SEM observation and EDX elemental analyses were performed under a 15.0-kV acceleration voltage. The pore size distributions were measured using a mercury porosimeter (SHIMADZU AutoPore III9400). The XPS spectra were obtained using a JEOL X-ray photoelectron spectrometer (JPS-9010) with Al Kα radiation (1486.6 eV). The spectra were acquired with pass energy of 10 eV for narrow scan and calibrated using the C 1s peak at a binding energy of 285.0 eV. The decomposition of the spectral curve was performed by a least-square fit with Gauss-Lorentz functions after the removal of Shirley-type background.

3 | RESULTS

3.1 | Characterization of the monolithic porous silica glass

Figure 2 shows the SEM images and the EDX results for porous silica glass. The images show a typical interconnected pore structure, characteristic of the porous silica glass prepared from a phase-separated borosilicate glass through the spinodal decomposition. The average pore size was estimated to be 40 nm, based on the sharp peak in the pore size distribution (Figure 6). This is consistent with the SEM image (B) in Figure 2. The atomic ratios calculated based on the EDX measurement results shown in Figure 2 (inset) were Si: Na: O = 30.5:0.14:69.3. From the atomic ratios of Si and Na, and from the mass ratio of the porous silica glass to the original borosilicate glass (63.8%), the composition of the porous glass was calculated as 97.9SiO2.1.9B2O3.0.2Na2O, assuming that the silica content in the borate-rich phase is negligible.

3.2 | Magnesiothermic reduction

Figure 3 shows the images and the XRD patterns of the studied samples after the each step of the two-step magnesiothermic reduction. The first step of the reaction was performed at 525°C for 6 hours. After the first step of the reaction, the sample became black and was divided into several pieces, but each piece retained the substrate-like shape. Based on the SEM observations and the EDX measurements of the sample cross section (not shown), we conclude that magnesium migrated to the depth of 59 μm and the reaction proceeded from
the surface of the sample to this depth. The XRD patterns in Figure 3 were obtained from the surfaces of the monolithic samples, while the XRD patterns in Figure 4 were obtained for the pulverized samples corresponding to the samples shown in Figure 3. The patterns in Figure 4 show strong halos, attributed to the unreacted silica glass. The XRD pattern in Figure 3a, measured after the first step of the reaction, shows the diffraction lines assigned to Mg$_2$Si and MgO. In both the diffraction patterns in Figures 3a and 4a, no diffraction lines assigned to crystalline silicon were detected, indicating that silicon crystallites were hardly generated in the first step of the reaction. The sample was heat-treated at 650°C for 72 hours, as the second step of the reaction. In the XRD pattern acquired after the second step of the reaction (Figure 3b), the diffraction lines assigned to Mg$_2$Si were not observed although the lines assigned to MgO were almost unchanged. Instead of the diffraction lines of Mg$_2$Si, the lines attributed to crystalline silicon were detected. Such variations in the diffraction patterns were observed for the pulverized samples, as shown in Figure 4b, in which the diffraction lines assigned to silicon were clearly observed instead of the lines assigned to Mg$_2$Si. After the subsequent acid treatment, because MgO was removed, the XRD pattern (Figure 3c) contained only the diffraction lines assigned to crystalline silicon. The diffraction patterns in Figure 4c shows tiny but clear diffraction lines of crystalline silicon. Since halo signals were detected in the XRD patterns, we concluded that the porous silica glass remained in the unreacted raw state. Note that the obtained substrates retained the shape of the original monolithic silica glass substrate.

The XRD patterns for the samples treated under other conditions in the first step of the reaction, for example, at 525°C for 3 and 48 hours, are shown in Figure S2. The XRD patterns for the samples, taken after the first step of the reaction, showed the diffraction lines that were assigned to Mg$_2$Si and MgO, while no diffraction lines assigned to crystalline silicon were detected, as shown in Figures 3 and 4. The intensities of these diffraction lines increased as reaction duration increased. After the second step of the reaction and the subsequent acid treatment, diffraction lines that were assigned to crystalline silicon were detected, although halos were observed as well, indicating the presence of the unreacted silica glass.

The SEM images and the EDX results for the samples after the second step of the reaction and the subsequent acid treatment are shown in Figure 5. The characteristic porous structure of the porous silica glass was retained, although part of the structure was lost. The EDX results indicated that the atomic fractions of Si, O, and Mg were 86.5 at%, 13.0 at%, and 0.56 at%, respectively, in the surface region of the
sample after the acid treatment. Based on these results, we concluded that SiO₂ was almost completely reduced to Si in the surface region of the monolithic porous silica glass. The measurements of the pore size distributions using the mercury porosimeter were performed for the samples that were treated in the acid solution and dried in vacuum after the second step of the reaction. Although some parts of the unreacted silica glass remained inside the sample, the pore size distributions were measured using the mercury porosimeter for the samples without removing the unreacted part of silica. The measured pore size distributions and accumulated pore volume are shown in Figure 6A,B, respectively, along with the corresponding results for the porous silica glass samples that were used as the starting materials. A weak but clear peak is observed at approximately 34 nm for the obtained samples after the acid rinse. The average pore size for the obtained samples is similar to that for the initial porous silica glass samples, as can be inferred by comparing the pore size distributions. Thus, the preservation of the pore structure was also ascertained by the pore size distributions. The oxygen signal in the EDX data was weak, compared with that for the porous silica glass, indicating that the silicon was predominantly present on the surfaces of the samples.

3.3 Chemical state of silicon

Figure 7 shows the Si 2p and Mg 2s XPS spectra of the samples after the first step of the reaction and after the second step of the reaction performed at 525°C for 3 hours, while the second step of the reaction amounted to the heat treatment at 650°C for 72 hours. For the sample after the first step of the reaction, the spectrum was also obtained after Ar-ion sputtering. The spectrum of the porous silica glass is also shown for comparison. The Si 2p line peaking at 103.7 eV in the spectrum of the porous silica glass is assigned to Si⁴⁺. In the spectrum before the Ar-ion sputtering for the sample after the first step of the reaction, a weak and broad band, ranging from 97 eV to 105 eV, was observed for the Si 2p core level, while an intense peak at 89 eV was observed for Mg 2s. After the Ar-ion sputtering, however, a clear band consisting of at least two lines appeared at the Si 2p core level. The decomposition of the band illustrated in the inset showed that the Si 2p signal consisted of three lines, peaking at 101.2, 99.3, and 97.8 eV, which were assigned to Si²⁺, Si⁰, and Si⁴⁻, respectively.47,50 The intensity ratios of these lines were 61%, 4%, and 35%, respectively. From the XRD patterns in Figure S2A,a, the observed crystalline materials were Mg₂Si and MgO in the sample after the first step of the reaction. Thus, the Si 2p peak at 97.8 eV, assigned to Si⁴⁻, corresponds to the silicon of Mg₂Si. The silicon atoms in the other oxidation states were present in amorphous states, such as silicon monoxide, SiO.

3.4 Magnesium incorporation depth and periodically layered structures

Magnesium incorporation depth was estimated based on the depth profiles of the elements observed using the SEM-EDX for the cross sections of the samples after the first step of the reaction performed at 525°C for various durations, from 6 to 72 hours. The dependence of the magnesium incorporation
depth on the reaction duration is shown in Figure 8. The depth increased slowly during the first approximately 20 hours, and then increased in a parabolic manner. This dependence suggests that the process of magnesium incorporation into the porous glass substrate becomes diffusion-limited after a certain transient time. In fact, as shown in the inset, the diffusion depth increased proportionally to the square of the reaction time, \( t \), less the transient time, \( t_0 = 22.5 \) hours.

By inspecting the reaction zone more closely into which magnesium was incorporated, some interesting periodic concentration profiles were identified. Figure 9 shows the SEM images and the concentration profiles of Mg, Si, and O along the depth dimension, for the sample (A) after the first step of the reaction applied at 525°C for 48 hours and the sample (B) after the subsequent second step of the reaction with the heat treatment at 650°C for 72 hours. The sample after the second step of the reaction was not applied with the acid treatment. In the concentration profiles as shown in Figure 9B for the sample after the second step of the reaction, clear periodic changes, with the wavelength of approximately 1.5 μm, can be observed. Interestingly, the variations for Mg and O are in phase, while that for Si is in the antiphase to the other two elements. The concentration profiles in Figure 9A for the sample after the first step of the reaction do not exhibit clear periodicity, compared with those in Figure 9B. However, the profile of Si varies with the periodicity of approximately 1.2 μm. Furthermore, in the some regions of the Mg and O profiles, the variations are similar to that of Si. It is noteworthy that the amounts of Si and Mg increase, while the amount of O decreases, in the parts marked with arrows.

4 | DISCUSSION

In the magnesiothermic reduction, monolithic silicon dioxides, such as quartz crystal and silica glass substrates, are reduced to magnesium silicide starting from the surfaces of these initial materials, when magnesium is sufficiently supplied in the reaction.42–44 For such the monolithic silicon dioxides, the reaction with magnesium is diffusion-limited. The diffusion of magnesium in the reaction zone may proceed faster than the diffusion of magnesium in the unreacted silicon dioxides. Then, given the sufficient amount of magnesium, the reduction in the reaction zone may proceed to magnesium silicide via silicon. The reduction in monolithic porous silica glass is also regarded as a reaction that is limited by the magnesium diffusion. Since the rate of the reduction is not necessarily the same throughout the entire reaction zone, silicon in various oxidation states from \( \text{Si}^{4+} \) to \( \text{Si}^{0} \), and \( \text{Si}^{2+} \) exists in the reaction zone. This is shown in the Si 2p XPS spectra in Figure 7, in which the peaks assigned to \( \text{Si}^{2+} \) and \( \text{Si}^{0} \) other than \( \text{Si}^{4+} \) are observed as predominant components. In the second step of the reaction, the reaction product is heat-treated without magnesium. Since magnesium is not supplied to the reaction zone, the reduction of silicon does not proceed any more. Instead of the reduction, \( \text{Si}^{2+} \) in \( \text{Mg}_2\text{Si} \) reacts with silicon in the intermediate oxidation states and \( \text{SiO}_2 \); the former is present in the reaction zone, while the latter is predominantly located at the diffusion front of magnesium. The final goal of the reaction in the second step is that crystalline silicon is generated.

Periodic variations in the concentrations of magnesium, silicon, and oxygen were observed in the depth dimension for both
samples after the first and second steps of the reaction. These concentration variations imply periodically layered structures parallel to the surface of the monolithic porous silica glass. Such layered structures were clearly observed in the products of the magnesiothermic reduction in a silica glass substrate and quartz. Chen et al proposed a model, in which stresses induced by the diffusion of magnesium drive the generation of such structures. In that study, it was reported that Mg$_2$Si-rich and MgO-rich phases with typical thicknesses 0.5-3 μm were alternatively generated. The concentrations of individual elements were estimated as 54Mg-37O-9Si and 62Mg-16O-22Si (at%) for MgO-rich and Mg$_2$Si-rich phases, respectively. From this estimation, the difference between the magnesium concentrations in the two phases was small (under 15%), while the difference between the concentrations of oxygen and silicon was more than twofold. The concentration profiles in Figure 9A also show similar variations, in which the concentration variations for silicon are clearly observed, while those for magnesium are obscure. The variations for oxygen are in the antiphase to those for silicon. In the SEM images, crystallite-like grains were observed. The XRD patterns indicated that Mg$_2$Si and MgO are present in the samples after the first step of the reaction. Thus, the observed grains may be Mg$_2$Si crystallites because the concentration of silicon is higher in the grains.

Of note, the periodic variations in the concentrations of Mg, Si, and O were much clearer in the samples after the second step of the reaction and before the acid treatment. The XRD patterns show the presence of silicon and MgO crystallites in these samples. These observations suggest alternation of silicon-rich and MgO-rich phases, with the periodicity of approximately 1.5 μm. The mechanisms underlying the generation of such structures are unclear. However, these structures are probably owing to the periodic structures observed in the samples after the first step of the reaction. The pores derived from the porous structure of the initial silica glass material were not observed in the samples after the second step of the reaction that were not subjected to the acid treatment. This can be explained by noting that the pores might have filled up and become covered by the MgO byproducts. The MgO by-product was removed by the acid treatment, promoting the appearance of the pore structures.

5 CONCLUSIONS

We applied two-step magnesiothermic reduction to a monolithic porous silica glass substrate, converting the surface region of the porous silica glass substrate to porous silicon.
Although the substrate was divided into several pieces, the resulting product retained the shape of the substrate and the produced silicon retained the characteristic pore morphology of the initial porous silica glass substrate. Additional ongoing studies seek to improve the reduction conditions for obtaining products that better retain the morphologies of the initial silicon dioxide substrates. Since porous silica glasses are generated according to various shapes and morphologies, this two-step magnesiothermic reduction is expected to be used for producing porous silicon with various shapes and morphologies.

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SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section.

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