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Membranes

Converting Free-Standing Porous Silicon into Related Porous Membranes**

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Porous materials with high surface-to-volume ratios have been used in a wide variety of applications in bioengineering, catalysis, environmental engineering, and sensor systems.[1–4] Porous materials related to silicon, such as Si_3N_4[5–7] and SiC,[8,9] possess adequate mechanical strength, possible high separation flux, and high chemical and thermal stability, and they have potential applications as gas filters, separation membranes, and catalyst supports at high temperature. Porous Zn_2SiO_4 has potential applications in gas-sensor and optoelectronic nanodevices.[10] Several methods, such as sol–gel process,[11] solid–gas reactions,[12] tape casting,[13] and liquid-phase sintering with additives,[14,15] have been used to fabricate porous materials derived from silicon. However, little has been reported on the fabrication of such free-standing porous membranes with high specific surface area and a wide range of adjustable pores. Herein, we demonstrate a simple, low-cost, effective method to fabricate free-standing porous membranes related to silicon, such as Si_3N_4, SiC, and Zn_2SiO_4, by in situ conversion of porous silicon films. The resultant membranes inherit the morphology and microstructure of the mother porous silicon films.

Figure 1 outlines our approach for the synthesis of derivatized porous membranes. A free-standing porous silicon (PS) film, obtained by electrochemical etching of monocrystalline p-type silicon,[16] is heated at high temperature in a furnace filled with active species A, which is formed by the decomposition of raw materials. The active species will react with the Si atoms on pore walls of PS to form Si_xA_y. With extended heating, the whole PS film transforms into porous compound Si_xA_y.

First, we tried to produce membranes of two-element compounds containing Si. We took Si_3N_4 membranes as an example. In this case, A in Figure 1 represents the active species N. We have converted free-standing PS films in situ into porous Si_3N_4 membranes through nitridation at 1250 °C using NH_3 as the N source. Figure 2 shows a series of X-ray diffraction (XRD) patterns taken from the converted membrane products nitridized for 1, 2, 3, and 4 h. The PS membrane is not converted after nitridizing for 1 h at 1250 °C (Figure 2 a), but it begins to convert to Si_3N_4 after nitridation for 2 h (weak peaks of hexagonal Si_3N_4 appear, Figure 2 b). Finally, the PS membrane is completely converted into Si_3N_4 after nitridation for more than 3 h (Si peaks disappear, and all the peaks can be indexed to α-Si_3N_4; Figure 2 c, d). Figure 3 shows the results of X-ray photoelectron spectroscopy (XPS) analysis of the converted Si_3N_4 membrane nitridized for 4 h. The Si 2p spectrum (Figure 3 a) exhibits two peaks around 101.45 and 103.78 eV, corresponding to Si–N and Si–O bonds, respectively. The N 1s spectrum (Figure 3 b) shows a peak at 396.29 eV, corresponding to N connected to three Si atoms. Therefore, the converted membrane contains Si–N bonds, further indicating that the PS film has been transformed into a Si_3N_4 membrane.

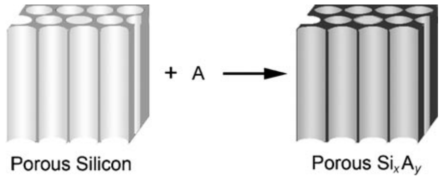

Figure 1. Schematic depiction of the synthesis of a silicon-derived porous membrane. Porous silicon is first obtained by electrochemical etching and is then treated with active species A to form the porous compound Si_xA_y.

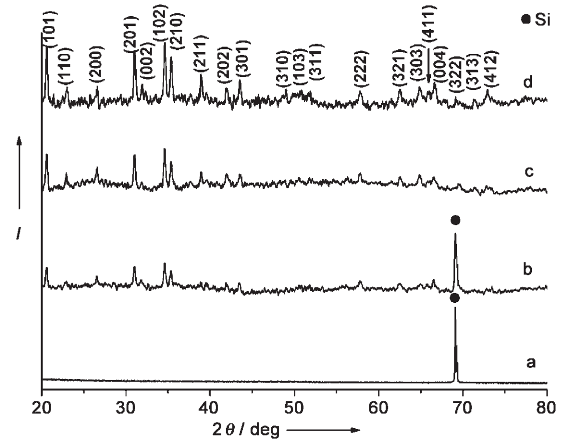

Figure 2. XRD patterns of the converted porous Si_3N_4 membranes after nitridation for a) 1 h, b) 2 h, c) 3 h, and d) 4 h.

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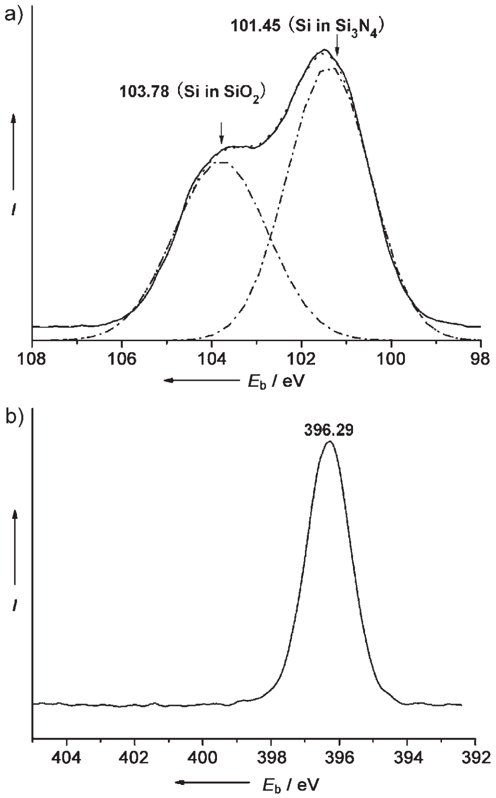

Figure 3. XPS spectra of the converted Si_3N_4 membrane nitridized for 4 h: a) Si 2p and b) N 1s.

Scanning electron microscopy (SEM) images (Figure 4) of the converted Si_3N_4 membrane nitridized for 4 h reveal that the membrane is about 50 μm thick with pore diameters of 1–2 μm. The top view (Figure 4a) shows perpendicular pores distributed on the planar surface of the Si_3N_4 membrane. The cross-sectional view (Figure 4b) reveals that the pores are roughly cylindrical, with small variations along the pore walls. The resultant porous Si_3N_4 membrane inherits the morphology and microstructure of the mother PS film (see the Supporting Information, Figure S1).

Figure 5 shows the room-temperature photoluminescence (PL) spectrum of the porous Si_3N_4 membrane after nitridization for 4 h using an excitation wavelength of 275 nm. The spectrum can be well fitted by three Gaussian peaks. The bands at 435 nm (2.85 eV) and 535 nm (2.32 eV) may be caused by defects in the Si_3N_4 membrane.[17,18] The UV emission band at 350 nm is similar to that observed for thermally oxidized PS and SiO_2 powder,[19] which can be attributed to radiative recombination from oxygen excess defects.

To extend our approach to porous membranes of other two-element compounds containing Si, we tried to convert free-standing PS films into porous SiC membranes through carbonization at 1350 °C for 2 h using ethanol as the source of active C species. The XRD pattern and XPS analysis (see the Supporting Information, Figures S2 and S3) confirm that the PS film has been fully converted into the SiC membrane. The obtained SiC membrane (Supporting Information, Figure S4) also retains the 3D morphology features of the PS film. The PL spectrum (Supporting Information, Figure S5) from the converted porous SiC membrane reveals two peaks, a UV peak centered at 322 nm (3.85 eV), possibly originating from oxygen excess defects,[19] and a blue emission at 430 nm (2.88 eV) attributed to radiative recombination of excited carriers.[20,21]

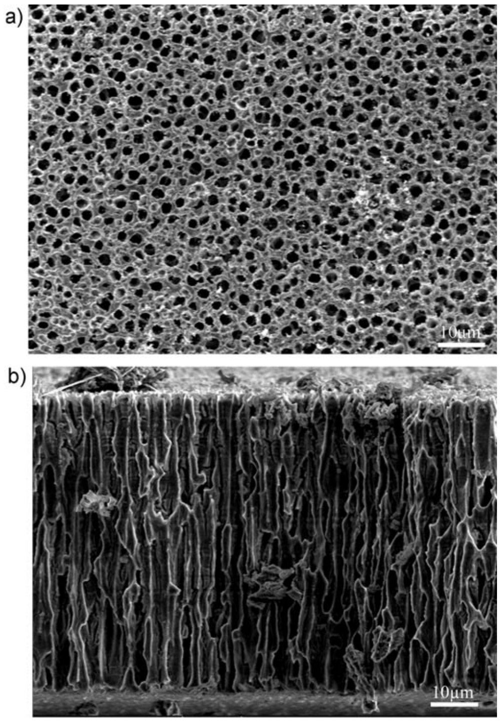

Figure 4. SEM images of the porous Si_3N_4 membrane nitridized for 4 h; a) top view and b) cross-sectional view.

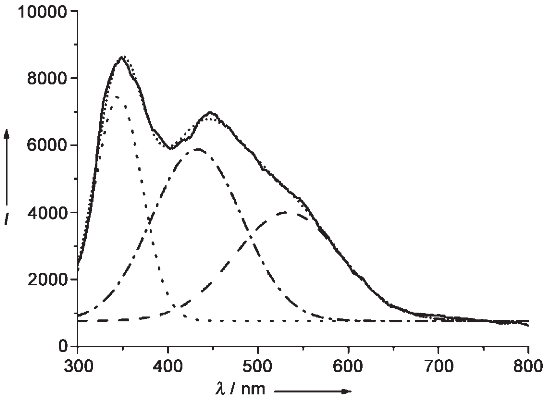

Figure 5. PL spectrum of the porous Si_3N_4 membrane obtained after nitridization for 4 h. ——: experimental spectrum; -----, ———, —•—•: component peaks; •••••: calculated combination of component peaks.

Finally, we tried to extend our approach to porous membranes of Si-based compounds containing three elements. To illustrate this concept, we converted free-standing PS films into porous Zn_2SiO_4 membranes at 1100 °C for 3 h using Zn powder as the source for active Zn species and O_2 as the source for active O species. The XRD pattern (Supporting

Information, Figure S6) indicates complete conversion of PS to Zn_2SiO_4. The resultant porous Zn_2SiO_4 membrane (Supporting Information, Figure S7) also retains the morphology of the mother PS films. Element distributions inside a broken fragment of the porous Zn_2SiO_4 membrane were imaged with energy-dispersive X-ray spectroscopy (EDS) mapping (Supporting Information, Figure S8b–d). This analysis reveals that O and Si atoms are uniformly distributed in the Zn_2SiO_4 membrane, while Zn appears less evenly distributed, thus indicating that the converted membrane comprises both Zn_2SiO_4 and SiO_x components. A high-resolution TEM (HRTEM) image taken from the edge of this broken fragment (Supporting Information, Figure S8e) shows a lattice fringe spacing of about 0.738 nm, corresponding to the (101) plane of Zn_2SiO_4. The corresponding selected area electron diffraction (SAED) pattern taken along the $[\bar{1}101]$ zone axis (Supporting Information, Figure S8f) can be indexed to rhombohedral Zn_2SiO_4 with (110) and (101) planes. EDS analysis (Supporting Information, Figure S8g) also indicates that the membrane is composed of Zn, Si, and O. The PL spectrum (Supporting Information, Figure S9) from the converted Zn_2SiO_4 membrane shows an emission band at 425 nm attributed to Zn_2SiO_4 and a peak at 320 nm possibly originating from oxygen excess defects.[19]

In summary, we have demonstrated a general method to fabricate free-standing porous membranes of Si-derived compounds, including Si_3N_4, SiC, and Zn_2SiO_4, by in situ conversion of PS films. The resultant porous membranes inherit the morphology and microstructure of the mother PS films. As the morphology, porosity, and thickness of PS films can be controlled by etching in HF,[22] the converted membranes can be produced with desired morphology and structures. Such membranes might have potential applications as gas filters, separation membranes, and catalyst supports. The in situ conversion method reported herein might be exploited to fabricate porous membranes of other materials.

Experimental Section

PS film was obtained by electrochemical etching of a monocrystalline p-type silicon (100) substrate (boron-doped, 8–15 Ω cm) at 2 mA cm^{-2} for 3 h in a 1:1 (v/v) mixture of aqueous HF (49 % hydrofluoric acid) and ethanol. During the final stage of the etching process, a current density of 400 mA cm^{-2} was applied for 1 min to separate the PS film from the silicon substrate.

Synthesis of the Si_3N_4 membranes: The as-prepared free-standing PS films were loaded in a ceramic boat and put into the hot zone of a horizontal tubular furnace. Before heating, Ar (99.999 %) was let in for 1 h to expel oxygen from the furnace. The system was then heated to 1250 °C in 15 min and held at this temperature for different periods of time (1–4 h). A constant gas flow of NH_3 (99.999 %) at a flow rate of 10 sccm (standard cubic centimeter) was maintained during the heating process.

Synthesis of the SiC membranes was similar. The system was heated to 1350 °C in 15 min and held at this temperature for 2 h. A constant gas flow of Ar (99.999 %), serving as carrier gas, passed through ethanol at a flow rate of 10 sccm and was maintained during the heating process. After the reaction was terminated and the furnace was cooled to room temperature, the products were exposed to air and heated at 600 °C for about 4 h to get rid of superfluous carbon on the resultant membrane surface.

Synthesis of Zn_2SiO_4 membranes: The as-prepared free-standing PS films were preoxidized in air at 300 °C for about 3 h and then loaded in a ceramic boat with Zn powder (0.65 g, 99 %) placed upstream and put into the hot zone of a horizontal tubular furnace. The system was heated to 1100 °C in 15 min and held at this temperature for 3 h. A constant gas flow of Ar/O_2 (5:1) was kept at 12 sccm during the heating process.

The converted products were characterized by X-ray diffraction (XRD, X'Pert Pro MPD), X-ray photoelectron spectra (XPS, Thermo ESCALAB 250, using $Al_{K\alpha}$ radiation as the excitation source), scanning electron microscopy (SEM, Sirion 200), and transmission electron microscopy (TEM, JEOL 2010). Photoluminescence (PL) spectra of the products were also recorded (Edinburgh luminescence spectrometer FLS 920; excitation source: Xe lamp).

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[1] M. E. Davis, *Nature* **2002**, *417*, 813.
[2] T. K. Maji, R. Matsuda, S. Kitagawa, *Nat. Mater.* **2007**, *6*, 142.
[3] X. D. Wang, C. J. Summers, Z. L. Wang, *Adv. Mater.* **2004**, *16*, 1215.
[4] J. V. Ryan, A. D. Berry, M. L. Anderson, J. W. Long, R. M. Stroud, V. M. Cepak, V. M. Browning, D. R. Rolison, C. I. Merzbacher, *Nature* **2000**, *406*, 169.
[5] H. D. Tong, H. V. Jansen, V. J. Gadgil, C. G. Bostan, E. Berenschost, C. J. M. V. Rijn, M. Elwenspoek, *Nano Lett.* **2004**, *4*, 283.
[6] J. Yang, J. F. Yang, S. Y. Shan, J. Q. Gao, T. Ohji, *J. Am. Ceram. Soc.* **2006**, *89*, 3843.
[7] A. Díaz, S. Hampshire, *J. Eur. Ceram. Soc.* **2004**, *24*, 413.
[8] Y. F. Shi, Y. Meng, D. H. Chen, S. J. Cheng, P. Chen, H. F. Yang, Y. Wan, D. Y. Zhao, *Adv. Funct. Mater.* **2006**, *16*, 561.
[9] I. K. Sung, Christian, M. Mitchell, D. P. Kim, P. J. A. Kenis, *Adv. Funct. Mater.* **2005**, *15*, 1336.
[10] X. H. An, G. W. Meng, Q. Wei, L. D. Zhang, *Cryst. Growth Des.* **2006**, *6*, 1967.
[11] G. Q. Jin, X. Y. Guo, *Microporous Mesoporous Mater.* **2003**, *60*, 207.
[12] Z. C. Liu, W. H. Shen, W. B. Bu, H. R. Chen, Z. L. Hua, L. X. Zhang, L. Lei, J. L. Shi, S. H. Tan, *Microporous Mesoporous Mater.* **2005**, *82*, 137.
[13] Y. Inagaki, Y. Shigegaki, M. Ando, T. Ohji, *J. Eur. Ceram. Soc.* **2004**, *24*, 197.
[14] J. F. Yang, Z. Y. Deng, T. Ohji, *J. Eur. Ceram. Soc.* **2003**, *23*, 371.
[15] J. Ihle, M. Herrmann, J. Adler, *J. Eur. Ceram. Soc.* **2005**, *25*, 987.
[16] W. Sun, N. P. Kherani, K. D. Hirschman, L. L. Gadeken, P. M. Fauchet, *Adv. Mater.* **2005**, *17*, 1230.
[17] G. Pacchioni, D. Erbetta, *Phys. Rev. B* **1999**, *60*, 12617.
[18] C. M. Mo, L. D. Zhang, C. Y. Xie, T. Wang, *J. Appl. Phys.* **1993**, *73*, 5185.
[19] G. G. Qin, L. Lin, J. Q. Duan, G. Q. Yao, *Appl. Phys. Lett.* **1996**, *69*, 1689.
[20] H. Mimura, T. Matsumoto, Y. Kanemitsu, *Appl. Phys. Lett.* **1994**, *65*, 3350.
[21] T. Matsumoto, J. Takahashi, T. Tamaki, T. Futagi, H. Mimura, Y. Kanemitsu, *Appl. Phys. Lett.* **1994**, *64*, 226.
[22] M. Rocchia, S. Borini, A. M. Rossi, L. Boarino, G. Amato, *Adv. Mater.* **2003**, *15*, 1465.