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Short Communication

Self-sealing SiO_2 pores on silicon formed by oxidation of microporous silicon

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ABSTRACT

Self-sealing silicon pores with size of 140–160 nm are formed by electrochemical etching. The microporous silicon (MPS) covers the openings and side walls of straight silicon pores (SSPs). The self-sealing SiO_2 pores with diameters of 195–205 nm are fabricated from the self-sealing SSPs in an aqueous alkaline medium containing magnesium via oxidation of MPS. The thicknesses of the surface layers covering the SSPs and SiO_2 pores are 200 nm and 140 nm, respectively, and the depth of the pores is more than 60 μm. The SiO_2 making up the sub-micron pores has a nanoporous structure which allows water and hydrogen molecules to pass through in an aqueous solution.

1. Introduction

SiO_2 pores have potential applications in separation, functionalization, guiding of highly charged ions, and so on [1–6]. It can be used in organic–inorganic nanocomposite materials by grafting with organic groups [6,7] and to separate colloids, particles, and microorganisms in aqueous solutions [2,6,8]. Owing to the diverse functionalities, a wide range of SiO_2 pore size and hydrophilic surface is needed. Nanoporous and mesoporous SiO_2 has been fabricated by direct synthesis in surfactants [3,5,7,9] and the cross-section of the SiO_2 pores is limited to about 10 nm or less by the size of the surfactant aggregates [10]. Sub-micrometer SiO_2 pores with size between 100 nm and 1 μm have attracted attention in recent years due to the demand of big pores in separation and functionalization. Sub-micrometer SiO_2 pores can be prepared by colloidal crystallization [10], supercritical fluids [5], and thermal oxidation of silicon pores [4]. Macroporous silica with a multilamellar structure is synthesized by mixed-surfactant-based synthesis [8], but it is still a challenge to fabricate hierarchically ordered macro–mesostructures efficiently [6].

Microporous silicon (MPS) can be oxidized by OH^- in water to form silicon oxide. For instance, a transparent silicon dioxide film is formed when microporous silicon is placed in an aqueous alkaline medium containing Mg [11]. Electrochemical etching has been shown to be an effective method to produce macro- or micro-pores in silicon. Microporous silicon can be formed on straight macropore walls on p-type silicon [12–14] and microporous silicon covering the top opening of straight macropores in n-type silicon [13–15]. This offers a new method to prepare sub-micrometer SiO_2 pores by oxidizing porous silicon produced by electrochemical etching. Crystalline silicon can be used as the substrate to improve the hardness of the SiO_2 pores and the $Mg + H_2O$ system yields a better hydrophilic surface with Si-OH bonds [11].

In this work, microporous silicon covering both the pore wall and opening is prepared by electrochemical etching in an HF solution. Sub-micrometer SiO_2 pores are formed by oxidizing the microporous silicon on crystalline silicon and the SiO_2 shows a nanoporous structure. The pores are characterized and the mechanism is discussed.

2. Experimental details

The straight silicon pores (SSP) with MPS covering the top opening and pore wall were prepared on 1–60 Ω-cm n-type (100) silicon by electrochemical etching in an HF and ethanol mixture using a 2-electrode configuration with graphite as the counter electrode under room light. The volume ratio of HF (48%) to ethanol and etching current were 1:1.2 and 120 mA, respectively, with a limiting voltage of 50 V to avoid higher voltage puncturing of the surface nanostructure. The etched area was about 3 cm^2 and etching time was 10 min. The etched sample was put in water containing the Mg alloy (AZ31) which provided OH^- ata pH value of 7–8. The reaction under alkaline conditions is:

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$$2H_2O + Mg \rightarrow Mg^{2+} + 2OH^- + H_2 \quad \text{reaction.} \tag{1}$$

The prepared MPS had many Si-H dangling bonds [11,16] and MPS reacted with OH^- to form SiO_2:

$$-\text{Si-H} + H_2O = -\text{Si-OH} + H_2 \quad \text{reaction and} \tag{2}$$

$$-\text{Si-Si} - \text{OH} + H_2O = -\text{Si-O-Si-OH} + H_2 \quad \text{reaction.} \tag{3}$$

Mg was not detected by X-ray photoelectron spectroscopy (XPS) meaning that the OH^- produced in reaction (1) served as a catalyst in reactions (2 and 3). The MPS was oxidized to SiO_2 to form the self-sealing SiO_2 pores. Oxidization of MPS in Mg + H_2O proceeded slowly for several hours. The SiO_2 was removed by 5% HF and finally the silicon macropores were obtained from the SSP.

To characterize the inner structure of the etched samples, ion beam sputtering was used to remove the surface covering the pores. The current and voltage of argon ions were 14 mA and 1.9 kV, respectively. The sputtering time was 20 min and the sputtering rate was about 30 nm/min. The difference in the sputtering rates of silicon, MPS, and SiO_2 helped to distinguish the structures and no chemical reaction occurred during ion sputtering.

A power supply (ITECT IT6123) was used to electrochemically etch n-type silicon. Ion beam sputtering was performed in a plasma immersion ion implantation system offering multiple functions such as ion implantation and film deposition. Scanning electron microscopy (SEM, JEOL JSM-6335F) and field-emission scanning electron microscopy (FE-SEM, JEOL JSM 7001F) were utilized to characterize the structures of the samples. Au was evaporated on the samples prior to electron microscopy examination. X-ray photoelectron spectroscopy (XPS) was performed to determine the chemical shifts.

3. Results and discussion

Fig. 1 depicts the SEM image of the sample produced using 40 mA/cm^2 and volume ratio of HF to ethanol of 1–1.2. The etched surface is uniform and disordered pores are formed using the optimized etching parameters. The pore opening is not clear due to the surface cover. The pore density is 0.65–0.85 μm^{-2} which is higher than those reported previously [17–19]. Fig. 2(a) and (b) depict the cross-section of the SSPs and SiO_2 pores. Fig. 2(a) shows that the breakdown of the space charged region and current burst play key roles in the surface and deep etching, respectively [17–19]. Fig. 2(b) shows that the SiO_2 pores are obtained by oxidizing the

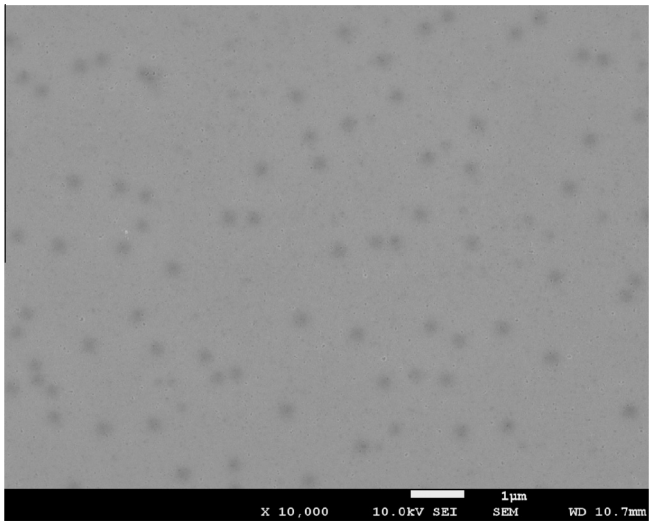

Fig. 1. SEM image of the sample produced using 40 mA/cm^2 and a volume ratio of HF to ethanol of 1–1.2.

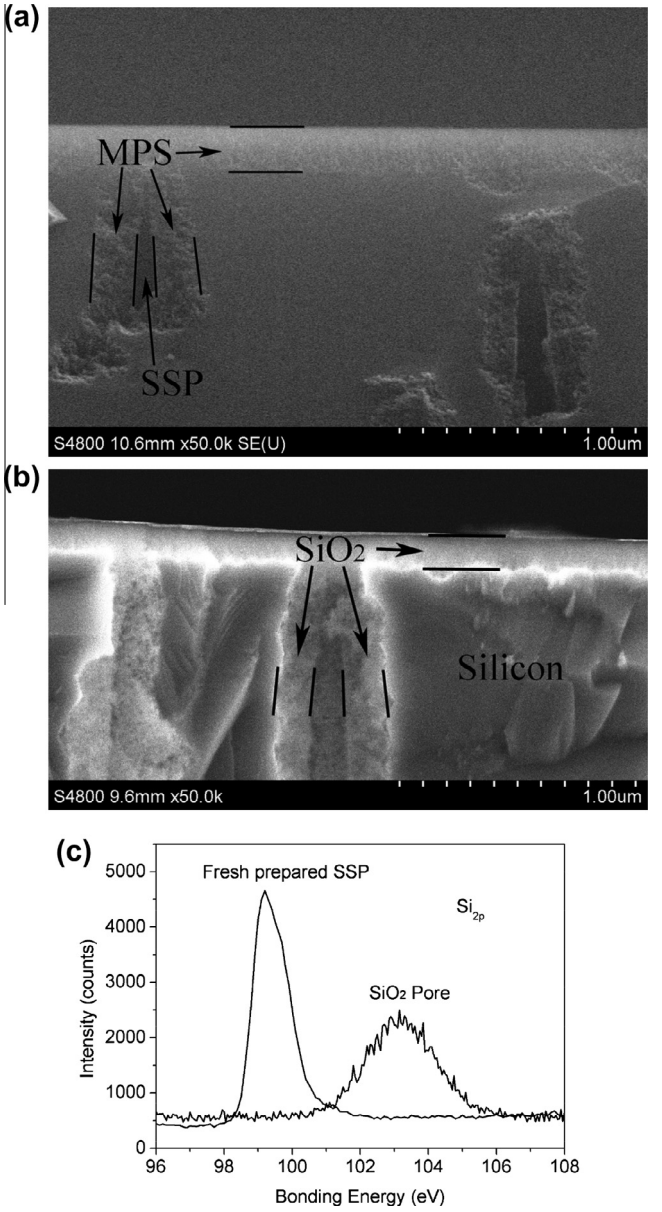

Fig. 2. Cross-section images: (a) SSPs and (b) SiO_2 pore. (c) Si_{2p} XPS spectra of surfaces of SSP and SiO_2 pore samples.

MPS covering SSP in (Mg + H_2O), indicating that water can pass through the surface oxide layer to oxidize the MPS at a depth. Fig. 2(c) displays the Si_{2p} XPS spectra of the surfaces of the freshly prepared SSP and SiO_2 pores. The Si_{2p} peaks of the SSP and SiO_2 pore samples are at 99.2 eV and 103.2 eV, respectively, confirming the formation of SiO_2. The O/Si atom ratio is 2.13 which implies the existence of extra O due to bonded H_2O. Complete conversion of MPS into hydrated dioxide in the alkaline solution can be inferred from infrared spectra [11] and results in the literature [16]. As shown in Fig. 2(a), the surface and side wall of the SSPs are covered by MPS and it is different from the published structures [12–14]. The SSPs underneath the surface MPS has a pore tip where current burst begins during electrochemical etching. As shown in Fig. 2(b), the SiO_2 pores have a similar self-sealing structure. However, the thicknesses of the surface layers on SSP and SiO_2 pores are 200 nm and 140 nm, respectively, and the SiO_2 pore diameter is bigger. This confirms a shrinkage of 30% when the sample is exposed to air compared to surface MPS due to the porosity of