Conciliating surface superhydrophobicities and mechanical strength of porous silicon films

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ABSTRACT

Hydrophobic surfaces on Mechanical stable macroporous silicon films were prepared by electrochemical etching with subsequent octadecyltrichlorosilane (OTS) modification. The surface morphologies were controlled by current densities and the mechanical properties were adjusted by their corresponding porosities. Contrast with the smooth macroporous silicon films with lower porosities (34.1%) and microporous silicon with higher porosities (97%), the macroporous film with a rough three-dimension (3D) surface and a moderate pore to cross-section area ratio (37.8%, PSi2') exhibited both good mechanical strength (Yong' modulus, shear modulus and collapse strength are 64.2, 24.1 and 0.32 GPa, respectively) and surface superhydrophobicity (water contact angle is $158.4 \pm 2°$ and sliding angle is $2.7 \pm 1°$). This result revealed that the surface hydrophobicities (or the surface roughness) and mechanical strength of porous films could be conciliated by pore to cross-section area ratios control and 3D structures construction. Thus, the superhydrophobic surfaces on mechanical stable porous films could be obtained by 3D structures fabrication on porous film with proper pore to cross-section area ratios.

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1. Introduction

Superhydrophobic surfaces are functional surfaces that may have important applications not only in scientific research but also in our daily life [1], e.g. microfluidic devices [2], window's glass and commercial vessels [3,4]. Up to now, the research mainly concentrated on the preparation and stimuli-responsive effects [5]. However, except for the bonding of organic molecules to their substrates, the mechanical properties of the substrates and the films fabricated on, and the adhesive forces between them were rarely concerned [6]. Under the particular application environment, the fluids (shear or impact behaviors) may have significant impact on their surfaces and challenge their durability. For example in a microchannel with a height in the size of $1 \mu m$, the corresponding shear stress of water (τ) in laminar flow mode may run up to 18 MPa [7,8], when the Reynolds number (Re) get to 1500 [9]. Therefore, the mechanical properties or the adhesive forces are essential for the applications of this kind of functional surfaces and should be considered. Porous film, especially porous silicon (PSi) with available pore size from nano- to micrometer [10] is a wonderful platform for this special scientific research. But there is a misunderstanding that superhydrophobic surfaces must be constructed on porous films with high porosities, which is actually caused by the mixing up of two concepts: surface roughness and film porosity. In order to clarify this point, in this report, we fabricated superhydrophobic surfaces on macroporous silicon films by electrochemical etching of silicon, combing with subsequent OTS modification. Pore to cross-section area ratio (r_p), defined as the porosity (p) on special cross section area in 2D, is also introduced for this aim. Due to the absence of film interfaces, we just focus on the mechanical properties of PSi films, which can be adjusted by their porosities.

2. Experimental

2.1. Preparation of PSi films

As received silicon wafers (100 orientation, n-type, resistivity $3–5 \Omega$ cm) were cleaned in acetone ultrasonic bath. Then, they were electrochemically etched in Teflon cells (efficient etching area: $1 cm^{-2}$) containing 5% HF ethanol solution (40% HF and anhydrous ethanol with volume ratio in 1:7) with constant current densities for 30 min (room temperature). A tungsten-iodine lamp (220 V, 35 W) and graphite plate were used as backside illumination source and counter electrode, respectively. After that, the PSi samples were rinsed with copious deionized water (18 MΩ) and dried in a N^2 stream. Two PSi samples were prepared: one is in
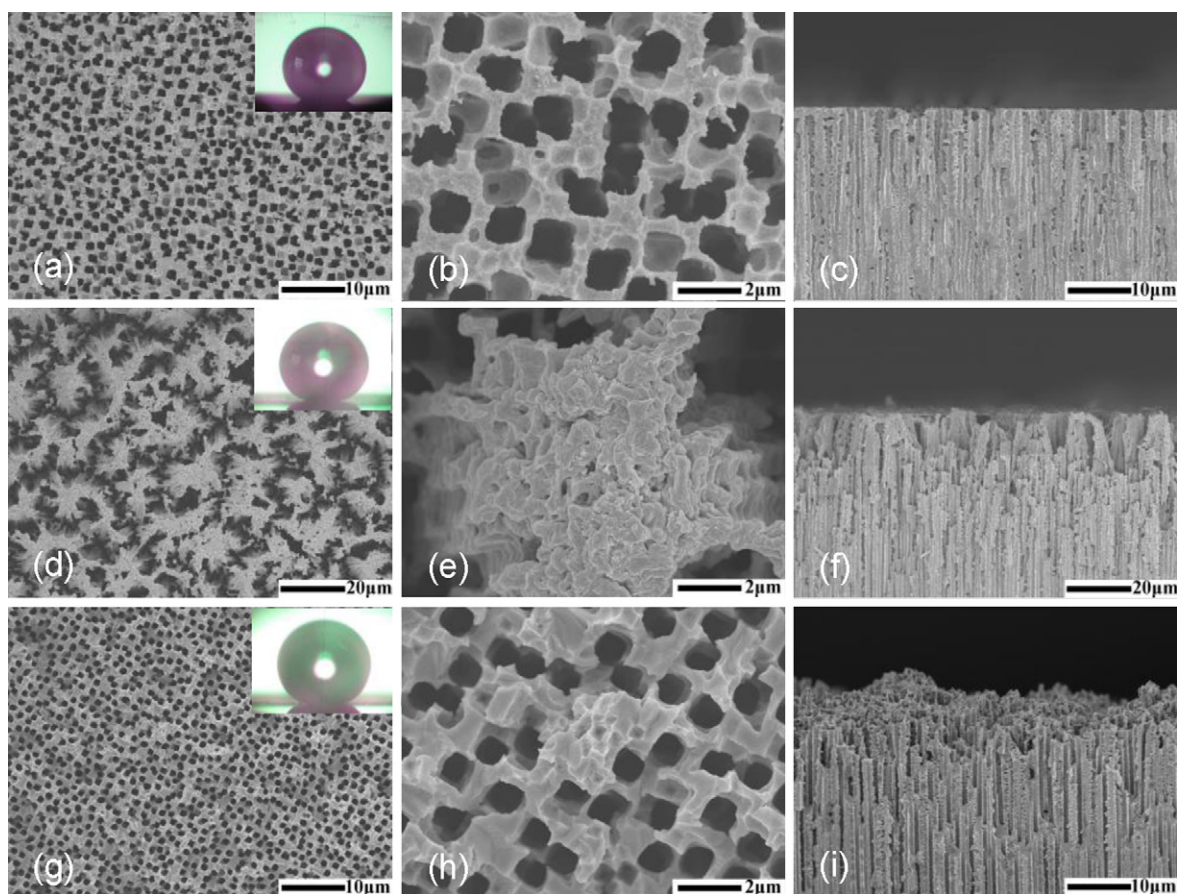
Fig. 1. FE-SEM images of the hydrophobic PSi films prepared by electrochemical etching under galvanostatic condition: (a–c) 10 mA cm^{-2} (PSi1); (d–f) 60 mA cm^{-2} (PSi2); (g–i) 60 mA cm^{-2}, with subsequent ultrasonic cleaning (PSi2′). The water drops' profiles on the corresponding surfaces are shown as the insets.

20 mA cm^{-2} (PSi1), another is in 60 mA cm^{-2} (PSi2). Because the top layer is fragile, PSi2 was cleaned in 1:1 C$_2$H$_5$OH/deionized water ultrasonic bath (Bransonic, Branson 200: 40 kHz, 220 V, 19 W) for 10 min, which was named PSi2′ in the context.

2.2. Surface modification of PSi films

After treated with piranha solution (3:1 concentrated H$_2$SO$_4$/30% H$_2$O$_2$, 90 °C, 1 h), PSi samples were modified in 3 mmol/L OTS/toluene solution at room temperature for 10 h. One silicon sample without electrochemically etch was used as a reference, which is also modified with OTS. After that, all of the samples were cleaned in acetone for three times.

2.3. Characterization of PSi films

The morphology of the porous silicon films was investigated with a field-emission scanning electron microscopy (FE-SEM, JSM-6701F, JEOL) at 5.0 kV. Their porosities were calculated from the weight loss and total qualities of porous films, which is a function of density and film thickness (the effective etching area is 1 cm^2). Water contact angle and sliding angle were measured on an optical contact angle meter (Kyowa Scientific Co., Ltd.) at ambient temperature. The XPS spectrum were investigated on a spectrometer (PHI-5702, Physical Electronics, Inc.) using an Al KR X-ray source (1486.7 eV). The energy scale was internally calibrated by referencing to the binding energy (E_b) of the C 1s peak of a carbon contaminant at 284.6 eV.

3. Results and discussion

The surface morphology of PSi was investigated by FE-SEM and their wettabilities were analyzed on an optical contact angle meter. As shown in Fig. 1a and b, the surface of PSi1 are covered by many macropores with diameters in the size of 1.3 μm and etch pits with diameters in the range of nano- and micrometer. Water contact angle (CA) on such a surface is 144.4 ± 2° (the inset of Fig. 1a), which indicate that the PSi1 surface was hydrophobic. However, when the sample was tilted, water drops pinned on the surface, and when it was turned over, they did not fall off. In this case, we define the sliding angle (SA) was 180°. It means that the 2D surface (Fig. 1c) with macropores is not rough enough for PSi1 surfaces to be superhydrophobic, despite r_p is bigger than p (0.341) owing to the existence of etch pits on the surface. In contrast, "island" microstructures with irregular shapes are observed on PSi2 surfaces (Fig. 1d). Their diameters are in the range of 10–30 μm and the heights are about 19 μm (Fig. 1f). On the top of these structures, many pores and cavities in the size of nano- and micrometer (Fig. 1e) can be seen. When modified with OTS molecules, the PSi2 surface was superhydrophobic. Water CA and SA were 158.0 ± 2° (the inset of Fig. 1d) and 2.3 ± 1°, respectively. In contrast with PSi1, these results reveal that the "island" microstructures on PSi2 surface are important to its wettability (here, r_p and p are not efficient for wettability evaluation, due to surface cracking), which is coincident with the literatures [11]. However, these structures are fragile and can be destroyed easily by ultrasonically cleaning and the sample without the fragile layer is named PSi2′. As shown in Fig. 1g, lots of protuberances
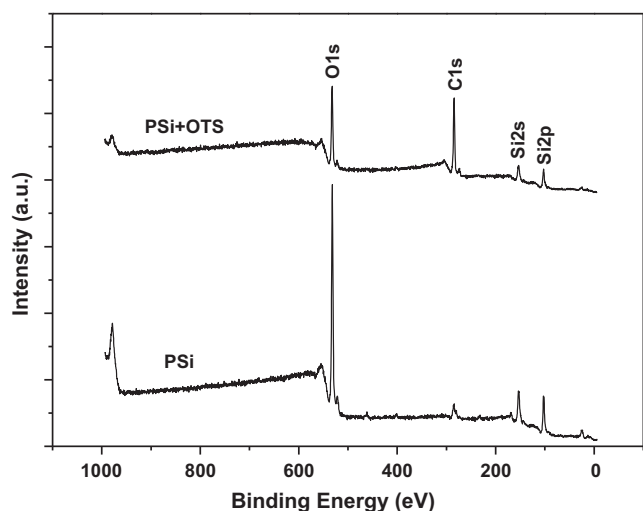
Fig. 2. XPS spectra of PSi2′ film, before and after OTS modification.

are observed on the pore skeleton of PSi2′. Their diameters are in the range of 5–10 μm and heights are around 10 μm (Fig. 1i). The Pores with nearly square shape cover the whole surface and their diameters are about 1 μm. Many steps appear on the pore skeleton and etch pits in micrometer and particles in nanometer still can be seen on the porous skeleton (Fig. 1h). Water CA and SA of PSi2′ with 3D microstructures are $158.4 \pm 2°$ (the inset of Fig. 1g) and $2.7 \pm 1°$, respectively. It is to say that PSi2′ surface, with rough 3D surface still has superhydrophobicity, despite r_p is moderate and almost equal to its porosity (0.378). The surface composition of PSi2′ before and after OTS modification was analyzed by XPS spectrometer and their spectra are shown in Fig. 2. The increase of C 1s peak intensity and decrease of Si 2s, Si 2p and O 1s peaks intensity revealed that OTS were bonded to the PSi2′ surface. These results indicate that the superhydrophobic surfaces on silicon have been successful produced by electrochemical etching and subsequent OTS modification. Surface 3D structure construction and r_p control are all important to their wettability.

Except for the surface wettabilities, the mechanical properties of superhydrophobic materials are also important in practical applications. We all known that the PSi films prepared by electrochemical etching have the same composition with their substrates and the corresponding mechanical properties can be controlled by etching current densities or their porosities. The ultra-high porosity of PSi without cracks that had been prepared by supercritical drying is 97% [12] and water CA on a smooth silicon surface with OTS modification is $107.4 \pm 2°$. According to Cassie's equation [13],

$$\cos \theta' = f \cos \theta - (1 - f), \tag{1}$$

the apparent CA of a rough surface θ' could be obtained from the intrinsic CA of the smooth surface θ with the same material and the fraction of the solid/water interface f. Assuming

$\theta = 107.4°$ and $f = 0.03$ (the corresponding porosity p is 97%), the resulting apparent CA (θ') for such a PSi surface with OTS modification is as big as $168.2°$. Unfortunately, the film with such high porosity could not survive the capillary stress produced by water evaporation at ambient atmosphere and therefore not suitable for practice application as superhydrophobic surface. In order to obtain superhydrophobic surface with high mechanical strength, we use macroporous silicon as the platform. The porosity of PSi1 film we prepared here at $20 \, \text{mA cm}^{-2}$ is 34.1%. Assuming the PSi film is isotropic, the Yong' modulus (E^*), shear modulus (G^*) and collapse strength (σ^*) of PSi can be calculated approximately as that of cellular material as follows [14,15]:

$$E* = E_s(1 - p)^2, \tag{2}$$

$$G* = \frac{3}{8}E_s(1 - p)^2, \tag{3}$$

$$\sigma* = 0.65\sigma_s(1 - p)^{3/2}, \tag{4}$$

where E_s and σ_s are the Yong's modulus and collapse stress of bulk silicon, and p is the porosity of PSi. If $E_s = 166 \, \text{GPa}$ and $\sigma_s = 1 \, \text{GPa}$ for bulk silicon [15], and $p = 0.341$ for PSi1, the Yong' modulus (E^*), shear modulus (G^*) and collapse strength (σ^*) of PSi1 σ^* are 72.1, 27.0 and 0.35 GPa, respectively. But the 2D surface with macropores is not rough enough for PSi1 to be superhydrophobic, as mentioned above (water CA: 144.4°). These results seem to indicate that surface superhydrophobicity and film mechanical strength are contradictory in respect of porosity. In fact, film mechanical strength is determined by its porosity, while surface wettability, to be more exact surface roughness, is related to r_p and surface 3D structures. If the porosity was moderate and not varied with film thickness, that is to say that mechanical strength could be guaranteed, the surface wettability still could be adjusted through 3D structure construction. In order to enhance the roughness of PSi surfaces, we increased the current density to $60 \, \text{mA cm}^{-2}$. According to the literature [16], the pore forming and electropolishing behaviors both participated in the electrochemical etching process and the resulting film were porous with a thin skeleton. With the capillary stress, the pore skeleton cleaved and the "island" structures formed on the surface, as shown in Fig. 1d. Because the macropore diameter on PSi2′ surface is about 1 μm, according to Laplace' formula:

$$P = \frac{2\gamma_{LV}}{r}, \tag{5}$$

the capillary stress produced by water evaporation is only 0.29 MPa, where the surface tension of water γ_{LV} is $72 \, \text{mJ m}^{-2}$. It is to say that the "island" microstructures of PSi2 were formed under this condition and destroyed by the subsequent ultrasonic cleaning. However, the porosity of PSi2 measured with the same method as PSi1 is 47.8% and the corresponding collapse strength calculated from equation 4 is as big as 0.25 GPa (other mechanical parameters are shown in Table 1). The remarkable reduction of collapse strength is due to the gradient variation of porosity and the branched pores formed on the primary pores ([0 0 $\bar{1}$]) along the direction of [1 0 0], [$\bar{1}$ 0 0], [0 1 0] and [0 $\bar{1}$ 0], as shown in Fig. 1f.

Table 1
Surface wettabilities and mechanical properties of monocrystalline silicon and PSi films with OTS modification.

Sample	CA (°)	SA (°)	p (%)	E^* (GPa)	G^* (GPa)	σ^* (GPa)
Si	107.4 ± 2			166[a]		1[a]
PSi1 ($20 \, \text{mA cm}^{-2}$)	144.4 ± 2	180	34.1	72.1	27.0	0.35
PSi2 ($60 \, \text{mA cm}^{-2}$)	158.0 ± 2	2.3 ± 1	47.8	45.2	17.0	0.25
PSi2′ ($60 \, \text{mA cm}^{-2}$, with ultrasonic cleaning)	158.4 ± 2	2.7 ± 1	37.8	64.2	24.1	0.32

[a] From Ref. [15].

This result reveals that the formation of 3D structures is important for porous films to be superhydrophobic. Since the up-layer of PSi2 film was not mechanical stable, we removed it by ultrasonic cleaning. SEM images in Fig. 1g–i show that the remained surface is still rough with lots of protuberances on the pore skeleton. Based on the porosity at 37.8%, the calculated Yong' modulus, shear modulus and collapse strength of PSi2′ are 64.2, 24.1 and 0.32 GPa (Table 1), respectively. Due to the existence of branched pores, as that in PSi2 film, all those value of PSi2′ may also be reduced, but they are better than PSi2. This result demonstrates that film mechanical properties and surface superhydrophobicities could be conciliated through 3D structures construction on porous films with appropriate r_p.

4. Conclusion

In summary, superhydrophobic surfaces (water CA: $158.4 \pm 2°$, SA: $2.7 \pm 1°$) on macroporous silicon films with moderate porosity (37.8%) and excellent mechanical properties (Yong' modulus, shear modulus and collapse strength are 64.2, 24.1 and 0.32 GPa, respectively) were prepared successfully by electrochemical etching combining with organic monolayer modification. SEM analysis and fundamental calculation revealed that the 3D microstructures are important for macroporous silicon films to be mechanical stable and at the same time to possess surface superhydrophobicities. To reasonably coordinate surface 3D structures and pore to cross-section area ratios is an efficient solution for superhydrophobic surface construction on mechanical stable films. We hope those results will be benefit to the practical applications of superhydrophobic surfaces, especially those with mechanical requirements, such as microfluidic.

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