Fabrication of silicon pyramid/nanowire binary structure with superhydrophobicity

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1. Introduction

Wettability is a very important aspect of surface property and is governed by both the surface chemical composition and surface structure [1–10]. A closely related phenomenon in nature is the “lotus effect”, referring to surfaces with water contact angle larger than 150°, which was found in the leaves of lotus, taro, and haulm, etc. [1–3]. These surface properties have a very significant application in microelectromechanical system (MEMS), anticorrosion, resisting water coalescence, fog condensation, and self-cleaning system [4–7]. In addition, the hydrophobic surface offers much promise for the formation of high-performance micro-/nano-structured surfaces with multifunctionality that can be used in optical, photoelectric, microelectronic, catalytic, and biomedical applications [9–13].

Silicon nanowires have attracted much attention in recent years due to their potential applications in MEMS, solar cell, and nanoscale electronic/optoelectronics device [14–16]. If we could take some actions and fabricate special structure with superhydrophobicity besides the excellent semiconductor properties, applications of silicon nanowire will be greatly extended. Many efforts have been made to obtain the hydrophobic silicon surface by a variety of methods, like the deep silicon dry etching [17], chemical etching [18], and X-ray lithography [19]. Constructing the hierarchical structure also proved to be an efficient approach in creating silicon surface with high contact angles and small contact angle hysteresis [20–23]. In this study, we present a simple and low-cost method to fabricate silicon pyramid/nanowires binary structure and obtain a superhydrophobic surface with contact angle of 162° and small sliding angle less than 2° after chemical treatment.

2. Experimental details

In author’s experiment, p-type silicon (100) wafers with resistivity of 1–30 Ω cm were used as substrate. Before experiment, the silicon wafer was thoroughly washed in ultrasound bath contained acetone and ethanol for 5 min each to remove the organic compound of the surface. The silicon pyramid/nanowires binary structure was fabricated by two-step chemical etching process. The silicon surface shows a stable superhydrophobicity with high contact angle of 162° and small sliding angle less than 2° after being modified with octadecyltrichlorosilane (ODTS). The binary roughness of pyramid/nanowire structure presents a stable composite interface of silicon–air–water and responsible for the superhydrophobicity of silicon surface.

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ABSTRACT

A pyramid/nanowire binary structure is fabricated on the silicon surface via a NaOH anisotropic etching technique followed by a silver-catalyzed chemical etching process. The silicon surface shows a stable superhydrophobicity with high contact angle of 162° and small sliding angle less than 2° after being modified with octadecyltrichlorosilane (ODTS). The binary roughness of pyramid/nanowire structure presents a stable composite interface of silicon–air–water and responsible for the superhydrophobicity of silicon surface.

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2 min at room temperature to fabricate the pyramid/nanowire binary structure. The concentrations of HF and H₂O₂ were 4.6 M and 0.44 M, respectively. Finally, the silver film was removed by immersing the silicon wafer into a mixture solution of ammonia and hydrogen peroxide (NH₃:H₂O₂:H₂O = 1:1:5).

Octadecyltrichlorosilane (ODTS) was employed as hydrophobic material to reduce the surface free energy of silicon surface. Prior to the contact angle measurement, the as-prepared silicon substrates were immersed into 5 ml hexane solution containing 24 µl ODTS for 5 min followed by heating for 1 h in air. The morphologies and structures of samples were examined by using LEO 1550 field emission scanning electron microscope (FESEM). The contact angle measurement was carried out with a Dataphysics OCA-20 contact angle system at room temperature in ambient atmosphere and further touching a water droplet toward the underlying surface until the water droplet can be pulled down to the sample surface. Each measurement was repeated five times to verify the reproducibility of the data.

3. Results and discussion

Fig. 1 shows FESEM images of three kinds of morphologies fabricated on Si substrates. Fig. 1a and b are typical FESEM images of the textured silicon surface after treated with the mixture solution of NaOH, IPA, and hydrazine hydrate at 85 °C for 1 h. As can be seen from the high magnification of FESEM, the silicon surface consists of sharp pyramid structures with size ranging from 5 µm to 50 µm and height between 5 µm and 15 µm, which is similar to previous report [24]. The density of the silicon pyramid structure increases with the prolonged anisotropic

![Fig. 1. Low and high magnification of FESEM images of the silicon surface textured by pyramid structure (a and b); pyramid/nanowire binary structure (c–e) and nanowires structure (f).](image)
etching chemical etching duration. At initial etching stage of 5 min, the density of pyramid structure is so low. After the etching duration extends to 1 h, the density of pyramid structure increases evidently and the overall coverage of pyramid structure reaches as high as 95% over the whole silicon wafer, see Fig. 1a. Compared with the sample produced in NaOH–IPA system, the presence of hydrazine hydrate greatly increases the coverage of pyramid structure and the experimental reproducibility. The morphologies of silicon surface change obviously after the silver-catalyzed chemical etching process. Fig. 1c shows the FESEM image of the silicon surface after treated in etching solution containing HF and H₂O₂. It is obvious that the flocy pyramid structure was not as sharp as that seen in Fig. 1a. Actually, a thin layer of nano-structure is grown on the pyramid structure after silver-catalyzed chemical etching process of 2 min, see Fig. 1d. FESEM image with higher magnification, as shown in Fig. 1e, indicates that the pyramid structure is covered by a thin layer of nanowire with diameter less than 100 nm and length of ca. 400 nm. A remarkable phenomenon is that most of nanowires grow perpendicularly to every face of the tetrahedron which may be correlated to the preferred etching direction. It is evident that the nanowire grown on the pyramid structure increases not only the specific surface area of the silicon surface, but also the trapping effect for sun light. Raman spectrum, as shown in Fig. 2 (solid line), recorded from the pyramid/nanowire structure shows a typical characteristic band of silicon nanowire. Compared with the characteristic Raman band of single crystal silicon and/or silicon pyramid structure at 520.3 cm⁻¹ (dot line), the Raman band of silicon nanowire (solid line) shows an obvious lower shift and asymmetric broadening, which maybe related with the phonon quantum confinement effect of silicon nanowire [25]. Combined with the black color of fabricated sample, big specific surface area, and the good ability for light trapping and absorption [26], it is believed that this pyramid/nanowire binary structure will have a potential application in solar cell. This will be an exploring area for the next step. Anyway, a pyramid/nanowire binary structure was fabricated by an anisotropic etching technique followed by silver-catalyzed chemical etching process. This study focuses on the hydrophilic/hydrophobic properties of this pyramid/nanowire binary structure. For the purpose of comparison, FESEM image of the silicon nanowires structure produced by silver-catalyzed chemical etching is also presented, see Fig. 1f.

Octadecyltrichlorosilane was employed as hydrophobic material to reduce the surface free energy of silicon surface. During the chemical treatment process, we use the minimum amount of ODTS to reduce the shield for the properties of silicon nanowire and present a superhydrophobic surface. Fig. 3a–c shows the optical images of 7 μl water droplet on ODTS modified silicon pyramid structure, nanowires structure and pyramid/nanowire binary structure, respectively. The silicon surface with pyramid structure modified by ODTS has contact angle of 134 ± 2° (top image of Fig. 3a), indicating a non-superhydrophobic surface. The silicon surface with nanowires structure modified by ODTS presents high contact angle of 151 ± 2° (top image of Fig. 3b). It is surprising that the contact angle of silicon surface covered with pyramid/nanowire binary structure greatly increases after treated by ODTS, and reaches as high as 162 ± 2° (see top image of Fig. 3c). However, the high contact angle does not mean that the modified silicon surface has excellent superhydrophobic property. Previous report emphasized that contact angle hysteresis is more important in characterizing hydrophobicity than the maximum achievable contact angle [27]. Measurement of contact angle hysteresis, which is the difference

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**Fig. 3.** Optical images of water droplet on the silicon surface with pyramid structure (a), nanowires structure (b) and pyramid/nanowire binary structure (c) after being modified by ODTS. Top optical image of (a–c) is the optical image of water contact angle on the corresponding structure, respectively; bottom images of (a–c) is captured image during the sliding angle measurement on the corresponding structures, respectively; and middle images of (a–c) present a visualization of the advancing and receding contact angles on the corresponding structures by dragging the water droplet from left to right, respectively.
between the advancing and receding contact angle, involves the adding or withdrawing the water from the drop and accurately measuring the contact angle. In our experiments, both of the contact angle hysteresis of silicon surface with pyramids and nanowires structure is more than $30^\circ$. However, the contact angle hysteresis of silicon surface with pyramid/nanowires binary structure is approximately closed to $0^\circ$, indicating a superhydrophobic surface. The contact angle hysteresis could also be indirectly reflected by moving the droplet on the silicon surface. Here, we use the syringe tip to drag the water droplet along corresponding modified textured surface and allow a visualization of the adhesion between the droplet and silicon surface (see middle image of Fig. 3a–c, respectively). From middle image of Fig. 3a, we can see that the water droplet undergoes a severe deformation under dragging of syringe tip. This implies that modified silicon surface with pyramid structure provides high adhesion to water and shows a high contact angle hysteresis. As a result, the surface has a high sliding angle and the water droplet still stays pinned to the surface when the sample is tilted to any angle, even upside down (see bottom image of Fig. 3a). For the modified silicon surface with nanowires structure, an obvious deformation of the water droplet is observed under dragging of syringe tip, which also indicating a high contact angle hysteresis, see middle image of Fig. 3b. This is why the droplet still stays on the modified silicon surface when the surface is tilted to $45^\circ$, see bottom image of Fig. 3b. However, for the modified silicon surface with pyramid/nanowire binary structure, no distortion is observed in the shape of water droplet during the dragging process (see middle image of Fig. 3c). The contact angle hysteresis of modified pyramid/nanowire surface is approximately closed to $0^\circ$. As a result, the water sliding angle is so small (less than $2^\circ$, see bottom image of Fig. 3c). Interestingly, it is very difficult to place a water droplet with the volume less than $7 \mu l$ on the modified pyramid/nanowire binary structure surface even a sharp syringe tip was used. A sequence of photographs records the touching behavior of $5 \mu l$ water droplet on the silicon surface. Fig. 4a displays the sequential photographs of water droplet shape at the initial state, exacting contacting state, tight/severe contacting state under pressure, and final state. It can be seen that no obvious change is observed in the water droplet shape between the initial state and exact contacting state. Similar phenomenon is also observed when the water droplet is in tight or severe contact with silicon surface. More interestingly, the water droplet still hangs on the syringe tip and no remaining water was observed on the silicon surface when the substrate was removed from the water droplet. Based on this phenomenon, we successfully use the syringe tip to move the water droplet from the left side to the right side of the sample surface, see Fig. 4b. This is far different from that observed in modified pyramid surfaces and nanowires structure, demonstrating that modified binary structure surface has the very low adhesion and very small contact angle hysteresis. In addition, all the as-prepared surfaces show the stable hydrophobic properties over a wide range of pH from 1 to 14, as shown in Fig. 5, especially for the modified pyramid/nanowire binary structure which shows stable contact angle as high as $162^\circ$ even in the corrosion environments containing acid, basic solutions. The value of water contact angle still remained essentially constant after 3 months storage in air and/or heated at 200 °C, indicating that the pyramid/nanowire structure has long-term stability. All of these advantages will greatly extend the application of silicon and silicon nanowire as engineering materials with superhydrophobic surface in the wide range.

The wetting behavior of material has been widely investigated and two theories, including Wenzel model (Eq. (1)) and Cassie model (Eq. (2)) have been constructed [28,29].

$$\cos \theta_r = r \cos \theta$$

$$\cos \theta_r = f_1 \cos \theta - f_2$$

where $\theta$, and $\theta_r$ are the water contact angle on rough surface and flat surface, respectively, and $r$ is the surface roughness factor; $f_1$ and $f_2$ are the fractional interfacial areas of the porous structures and of
the air in the interfaces among the porous structures, respectively. Total of $f_1$ and $f_2$ is 1.

Both of two models can be used to achieve a high water contact angle by fabricating textured surface with different scales structures and chemical treatment. However, only the Cassie state shows a superhydrophobic surface with low contact angle hysteresis and small sliding angle. Fig. 6 shows the possible schematic diagram of the water droplet on the pyramid structure and pyramid/nanowire structure. For the modified pyramid structure, it shows a higher water contact angle than that of pristine silicon surface because of increase of surface roughness, which is consisted with the Wenzel model. However, it is not a superhydrophobic surface because the water droplet almost completely fills the valleys of the pyramid structures where they contact (see Fig. 6a). As a result, the water droplet is still pinned to the silicon surface; even the sample is upside down. In fact, it is not the finite value of contact angle but the contact angle hysteresis which decides the surface superhydrophobicity. According to Eq. (3) [30], the minimum force needed to start a drop moving a solid surface is closely related with the difference between advancing contact angle $\theta_A$ and receding contact angle $\theta_R$

$$F = \gamma_{LV}(\cos \theta_R - \cos \theta_A)$$

where the $F$ is the critical line force per unit length of the drop perimeter, $\gamma_{LV}$ is the surface tension of the liquid, and $\theta_R, \theta_A$ are the receding and advancing contact angles, respectively.

The modified silicon surface with pyramid/nanowire binary structure shows not only high water contact angle of 162° but also low contact angle hysteresis. As a result, this modified silicon surface present excellent superhydrophobicity with small water sliding angle lower than 2°. According to the previous report [31,32], we believe that the binary roughness of pyramid/nanowires structure should responsible for the superhydrophobicity of modified silicon surface. By constructing the nanowire on the top of pyramid structure, the pyramid/nanowire binary structure provide and maintain a stable composite interface between the water droplet, pyramid/nanowire binary structure and the air pockets or bubbles trapped in the valleys between the pyramid and nanowires structures, see Fig. 6b. According to the Eq. (2), the $f_2$ value of rough surface with pyramid/nanowire binary structure is estimated to be 0.933 on the premise that actual contact angle $\theta_r$ and Young’s contact angle $\theta$ are 162° and 107°, respectively (see Table 1), which means that the air occupies about 93.3% of the contact area between water droplet and binary structure. For the silicon surface with simplex pyramid structure, however, the air fraction is only 41.4%. This implies that the pyramid/nanowire binary structure dramatically decrease the contact area between silicon and water droplet. The original three phase contact line (Si–water–air) is broken into smaller fragment and energy barrier for the water droplet motion is lowered by the nanowire constructed on the pyramid structure. The water droplet thus moves freely on the top of pyramid/nanowire binary structure without any deformation. As a result, the surface achieve a stable Cassie state, exhibits a high contact angle, low contact angle hysteresis, small sliding angle and thus is a superhydrophobic surface. It is obvious that the nanowire constructed on the pyramid structure plays a significant role in the transformation from Wenzel state of pyramid structure to Cassie state of pyramid/nanowire binary structure, and the superhydrophobicity is only achieved on the silicon surface with pyramid/nanowire binary structure. It should be noted that the aspect ratio of the micro-sized pyramids and/or nanowires, which depend on the duration of the first and second chemical etching process, respectively, is also

<table>
<thead>
<tr>
<th>Structure</th>
<th>Pyramid structure</th>
<th>Nanowire structure</th>
<th>Pyramid/nanowire binary structure</th>
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<tbody>
<tr>
<td>$f_1$</td>
<td>0.414</td>
<td>0.177</td>
<td>0.067</td>
</tr>
<tr>
<td>$f_2$</td>
<td>0.586</td>
<td>0.823</td>
<td>0.933</td>
</tr>
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Fig. 5. Contact angle–PH curves of silicon surface with different surface textured structures; the volume of water droplet is 7 μl.

Fig. 6. Supposed schematic diagram of water droplet on (a) silicon pyramid structure and (b) silicon pyramid/nanowire binary structure.
critical for the hydrophobicity of the silicon surface. The short duration of first chemical etching will produce the low density of pyramid structure; induce the low coverage of silicon pyramid/nanowires binary structure and high coverage of nanowires grown on the flat substrate after silver-catalyzed chemical etching process. As a result, a non-superhydrophobicity surface with high water contact angle and high sliding angle is obtained. Therefore, for the desired superhydrophobic silicon surface, the first chemical etching duration must be long enough to obtain the high density silicon pyramid structure. However, for the long duration of the silver-catalyzed chemical etching process, the silicon nanowires which constructed on the pyramid structure will aggregate together and become the silicon nanowires bundles because of their flexibility and length. This will greatly decrease the air trapping effect of pyramid/nanowires structure, and also give a non-superhydrophobic surface. In brief, a stable and high density of pyramid/nanowire binary structure is required for the superhydrophobicity of silicon surface.

4. Conclusions

In this study, large area of pyramid/nanowire binary structure was fabricated on silicon surface based on two-step chemical etching process. After being modified by ODTS, the silicon surface shows a stable superhydrophobicity with high contact angle, low contact angle hysteresis, as well as small sliding angle, even in the wide of PH range. This is related to the binary roughness of pyramid/nanowire binary structure, which presents a stable composite interface of silicon–air–water, decreases the adhesion of a liquid droplet to the silicon surface, and thus reduces the water contact angle hysteresis. Combined with the excellent properties of silicon nanowire and surface superhydrophobicity, we expect that the pyramid/nanowire binary structure will extend the application of silicon nanowire in solar cell and corrosive environment.

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