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SUPERHYDROPHOBICITY OF HIERARCHICAL ZNO NANOWIRE COATINGS (POSTPRINT)

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AFRL/RXAN**

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Superhydrophobicity of hierarchical ZnO nanowire coatings†

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Hierarchical superhydrophobic surfaces were constructed by growing various lengths of ZnO nanowires on micro-scale Si pyramids produced by chemical etching. The nano-size effect on wettability of nano/micro complex structures has been investigated by adjusting the ZnO nanowire length. As the nanowire length on the Si pyramid surface increases, a transition from the Wenzel state to the Cassie state occurs. A water contact angle as high as 169.1°, with a contact angle hysteresis less than 1.3°, was formed by growing ZnO nanowires of a suitable length on Si micro-pyramids. Compression and impact experiments further demonstrate the robust superhydrophobicity of ZnO nanowire–Si pyramid hierarchical structures.

Introduction

Superhydrophobic surfaces have promising industrial and biological applications, such as self-cleaning windshields for automobiles,¹ stain resistant textiles,² anti-biofouling paints for boats,³ optics,⁴ and optoelectronics.⁵ Superhydrophobicity causes a high water contact angle ($\sim 160.4^\circ$) and low contact angle hysteresis ($<5^\circ$) which leads to water repellency and self-cleaning characteristics.^{6–14} It has been shown that hierarchically structured artificial surfaces demonstrate these superhydrophobic properties.^{15–18} For example, in the water repellent biological systems, they usually show two levels of hierarchical structures.¹⁹ The size of one set of surface structure is on the order of several micrometers while the other is in the range of tens to hundreds of nanometers, which have been shown in the lotus leaves⁶ and water strider's legs.²³ Recent studies have shown that surfaces with hierarchical structures are crucial to retain the Cassie–Baxter state in liquid drops.^{20–23} Additionally, Cha *et al.* investigated the superhydrophobicity of surfaces consisting entirely of micro-pillars or nano-pillars as well as surfaces with a mixture of both.²⁴ It was found that the superhydrophobic robustness of the surface with dual roughness was

significantly enhanced compared to that of other surfaces. However, the impact force of actual raindrops striking such surfaces, which exerts a higher pressure on the surfaces, has not yet been investigated.

Two models considering the roles of the surface area and trapped air have been proposed by Wenzel²⁷ and Cassie–Baxter²⁰ to explain the effects of surface topography on the enhancement of hydrophobicity. In the Cassie state, air trapped beneath the drop is conducive to lifting the drop from the surface, but increasing the air fraction at the surface may harm the state stability.²⁸ Consequently, most Cassie states are unstable under external pressure, resulting in invasion and a subsequent loss of superhydrophobic properties.^{7,29} A robust Cassie state could be achieved in theory by reducing the microstructure scale or increasing the Young's contact angle.^{30–32} Therefore, it is necessary for the stability of the Cassie state to create a nano-structured superhydrophobic state to improve the Young's contact angle on other types of microstructured surfaces.

In this study, we present a novel hierarchical superhydrophobic surface by hybridizing ZnO nanowires with Si micro-pyramids (ZNSP). The ZnO nanowires are hydrothermally grown on Si micro-pyramids (SP), formed by anisotropic etching of the Si (100) surface. We demonstrate that the length of ZnO nanowires plays an important role in the surface superhydrophobicity, while simulated raindrop impact experiments illustrate the establishment of a robust Cassie state caused by the dual scale surface roughness.

Experimental

N-type silicon (100) wafers with resistivity of 3–10 Ω cm were used as substrates. The wafers were etched in a solution of KOH (3 wt%), distilled water and isopropyl alcohol (10% vol%) at 95 °C for 50 min. Subsequently, a 10 nm ZnO seed layer was

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† Electronic supplementary information (ESI) available: Additional information related to slides of movies displaying movement of a simulated raindrop on the different nanoscale hierarchical structure surfaces. Simulated raindrops consisted of 4 μ L water drops released from rest at a height of 5 cm. See DOI: 10.1039/c3ta14102k

Table 1 Contact angles and contact angle hysteresis on smooth silicon and hierarchical structure surfaces after perfluorooctyl tri-chlorosilane (PFOS) treatment (error: $\pm 0.5^\circ$)

Samples	Contact angles (degree)	Contact angle hysteresis (degree)	Nanowire length (nm)
Si	113.7	>60	—
SP	126.5	>60	—
SPS	128.2	>60	—
ZNSP-10 min	134	>60	15
ZNSP-15 min	157	15.5	61
ZNSP-20 min	165.7	8.4	101
ZNSP-25 min	166.7	3.4	137
ZNSP-30 min	169.1	1.3	445
ZNSP-1 h	168.1	2.1	790
ZNSP-1.5 h	167.2	2.5	1106
ZNSP-2 h	166.7	3.4	1284

deposited on the pyramid structured silicon substrate surface by RF-magnetron sputtering. The Si pyramid-ZnO seed layer (SPS) was then annealed in air for 1 h at 300 °C. Finally, the substrates were held vertically and immersed in an 150 mL of aqueous solution, heated to 95 °C, containing zinc acetate dehydrate (Zn-AD, purity 99.6%, 0.01 mol L⁻¹) and hexamethylenetetramine (He-T, purity 99%, 0.01 mol L⁻¹). The growth times were 10 min, 15 min, 20 min, 25 min, 30 min, 1 h, 1.5 h, and 2 h, respectively, corresponding to samples of ZnO nanowire-Si pyramid 10 min (ZNSP-10 min), ZNSP-15 min, ZNSP-20 min, ZNSP-25 min, ZNSP-30 min, ZNSP-1 h, ZNSP-1.5 h and ZNSP-2 h. The average length of every sample under different growth conditions (Table 1) was measured from 100 random ZnO nanowires in two different areas in four SEM pictures.

Contact angle measurements were performed with a Rame-Hart goniometer equipped with a CCD camera for image capture. Each contact angle was measured repeatedly five times with a 4 μ L droplet at different places on the sample and the mean value was recorded. Scanning electron microscopy (SEM) was used to investigate the surface morphology. After fabrication of the nano/microstructures, surface fluorination was performed in a 10 mM perfluorooctyl trichlorosilane (PFOS) solution. The dynamic behavior of the water drops on the sample surfaces was examined using a JVC GZ-HD 30U high-definition camera.

Results and discussion

Si micro-pyramids were prepared by noble-metal-free anisotropic etching of Si substrates along the (100) orientation as illustrated in Fig. 1a and b.^{25,26} The dissolution of the Si (100) surface is initiated by OH⁻ in a nucleophilic attack, as shown in Fig. 1a and a Si-OH bond is formed with the evolution of H₂. The ligands' electronic attraction dissociates these Si bonds forming Si(OH)₆²⁻ as the final etching product while the etched Si micro-pyramid surface terminates with Si-H bonds. It should be noted that the (110) surface etching is the similar process as the (100) surface. However, the chemical dissolution rate of (111) oriented Si surfaces is negligible as a result of insufficient

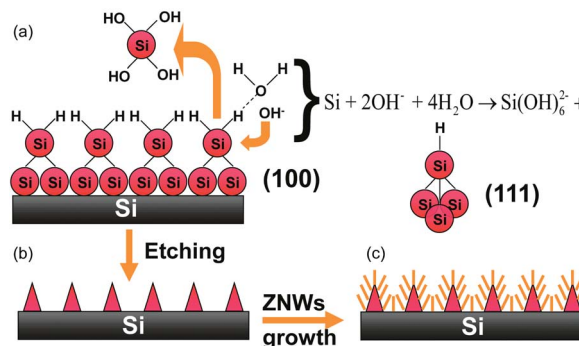


Fig. 1 Schematic of fabrication of the nano- to micro-structural hierarchy. (a and b) Etching process in KOH solutions. (c) ZnO nanowires (ZNWs) grown on the Si pyramid surfaces.

polarization of the Si bonds by one -OH group, as shown in Fig. 1. As a result, the micro-pyramid structures were formed by dissolving the Si (100) and (110) surfaces while reserving the (111) surface.

To understand the effect of nanowire length on the contact angle, ZnO nanowires were grown under conditions similar to our previous work³³ which demonstrated that a low concentration of the Zn(II) precursor is crucial for growing ZnO nanowires with smaller diameters. Reaction times were varied to produce different nanowire lengths and SEM images of the hybrid ZnO-Si hierarchical nano/microsurface are shown in Fig. 2. Fig. 2b-d show ZnO nanowire-Si micro-pyramid hierarchical structures grown with reaction times of 0 min, 20 min, 30 min, and 120 min, corresponding to the length of ZnO nanowires 0 nm, 101 nm, 445 nm, and 1284 nm, respectively. As can be seen from these images, the growth of ZnO nanowires on the Si micro-pyramids is hierarchical, highly ordered, and vertically aligned. The cross-sectional SEM images of hierarchical surfaces on the Si (111) surface are shown in Fig. 2e-i. When the reaction time of ZnO nanowires was increased from 10 min to 2 h, the corresponding nanowire length is increased from 15 nm to 1284 nm while the diameters of the ZnO nanowires are consistently ~ 20 -30 nm. The relationship between the ZnO nanowire length and the growth time, t , is shown in Fig. S2 of the ESI.† The results indicate that it is possible to control the length of the nanowires by controlling the growth time on the Si micro-pyramid-ZnO seeds. Consequently, the contact angles and contact angle hysteresis on the hierarchical surfaces could be finely tuned by controlling the length of the ZnO nanowires grown on the surfaces of the pyramid structures.

The contact angles and contact angle hysteresis on the Si, SP, SPS and ZNSP surfaces are shown in Fig. 3a, and the corresponding surface contact angles are 113.7°, 126.5° and 128.2° (Table 1), respectively, indicating these surfaces in the Wenzel state. Initially, the contact angle on the hierarchical surfaces first increased up to a time, t_{max} , of 30 min and then decreased slightly with increasing growth time (Fig. 3b). Meanwhile, the contact angle hysteresis initially decreased but then began to increase. For the ZNSP samples grown for 10 min to 25 min, the increase of the contact angle and reduction of the contact angle hysteresis may have been caused by the growth of ZnO

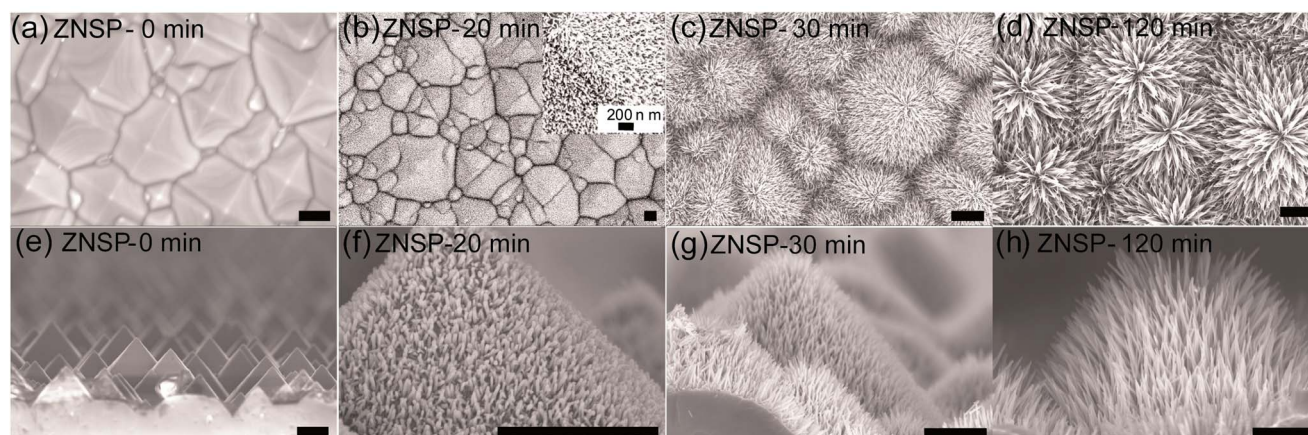


Fig. 2 Hierarchical structure surfaces with (a) ZnO seed layer on silicon pyramid surfaces, and (b–d) ZnO nanowire–Si pyramid (ZNSP) hierarchical structures grown at reaction times of 20 min, 30 min and 2 h, respectively, on the Si (111) surface. (e–h) Corresponding cross-sectional images of (b–d). The scale bar is 1 μm .

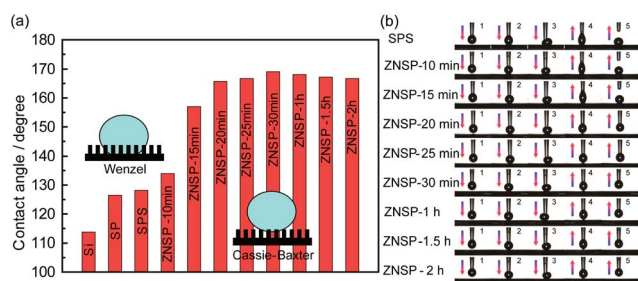


Fig. 3 (a) Contact angles on silicon and hierarchical structure surfaces after perfluorooctyl trichlorosilane (PFOS) treatment. (b) Water drop motion behaviors on modified sample surfaces. A series of vertical row images are about 4 μL water drops on SPS and ZNSP surfaces after modified by PFOS to render a hydrophobic surface. At first, the water drop approaches the sample surface, and then begins to touch. In the 3rd row, extra force on the water by pressing the tubule and the shape of the water turned into an ellipse. At last, the tubule was pulled back. 4th row is the critical states of the water, which was pulled back by tubule exerted force and sample surfaces' liquid–solid surface tension. 5th row is the final state. The water drops stick to the sample surfaces (SPS, ZNSP-10 min, -15 min), or pull back without any loss (ZnSP-20 min, -25 min, -30 min, -1 h, -1.5 h, and -2 h). The arrow represents the motion direction of the water drops.

nanowires on the SP surfaces.²⁷ For ZNSP samples grown for 30 min to 2 h, the decrease of the contact angle and the increase of contact angle hysteresis could be attributed to the elongation of the ZnO nanowires and their potential overlap. These two features occupy the space between the Si pyramids thus decreasing the liquid–air contact area.

The behavior of a water drop on the sample surface was investigated. As illustrated in Fig. 3b, a 4 μL water droplet suspended on the end of a tubule was brought into contact with the sample surface (column 1 of Fig. 3b). Column 2 shows the water droplet as it began to touch the surface with the tubule exerting a force on the top of the droplet. As shown in column 3, the shape of the water droplet became elliptical on the control surface while a spherical shape was maintained on the superhydrophobic surface. Interestingly, the water droplet did not

spread out even when it was pressed. In the 4th column, the tubule was gradually retracted from the sample surfaces. The SPS, ZNSP-10 min and ZNSP-15 min sample surfaces bound tightly to the water droplet and pulled it off of the end of the tubule unlike the other surfaces which left the droplet on the tubule. The measured contact angle for the SPS sample was 128.2° and the contact angle hysteresis was larger than 60°. The ZNSP-10 min sample shows a similar contact angle of 134° and a contact angle hysteresis of >60° (Table 1), which could be caused by the short length of the nanostructures on the SP surfaces.³² The contact angle on ZNSP-15 min sample achieved angles as high as 157°, a superhydrophobic surface, but the droplet adhesion force from the sample surface was greater than that from the tubule, making the droplet stick to the sample surface. As the length of ZnO nanowires increased beyond that of the 15 min samples the water droplet was easily retracted with the tubule without leaving any remnants on the sample surface (Column 5 Fig. 3b). This effect is of great importance in applications involving transport of micro-droplets.³⁴ The robustness of superhydrophobic surfaces is critical to achieve commercially viable applications of these surfaces in such diverse areas such as antifouling, self-cleaning, and water-resistant coatings.

Compression experiments revealed that the ZNSP-hierarchical structure surfaces that were grown for 20 min to 2 hours exhibited superior robustness of their superhydrophobicity (Fig. 3). Additionally, impact experiments were performed to further support this observation. In these impact experiments water droplets were released onto the different surfaces to observe their stickiness and rebound ability. Several 4 μL droplets were released from a height of 5 cm, and the impact velocity was approximately 1 m s⁻¹ (ESI†). For the SP, SPS, ZNSP-10 min, ZNSP-15 min and ZNSP-20 min surfaces the drops collided with and stuck to the surface. However, for the ZNSP-25 min, -30 min, -1 h, -1.5 h, and -2 h surfaces, the drops struck and then rebounded from the surface. These results reveal that the hierarchical structures with enough nanoscale-length (equal to or larger than 137 nm) improved the robustness of the Cassie

state for the superhydrophobic surfaces. To examine more violent impacts, the drop height was raised to 20 cm. This increased the impact velocity to approximately 2 m s^{-1} . These results were similar to those using a drop height of 5 cm for the SP, SPS, ZNSP-10 min, ZNSP-15 min, and ZNSP-20 min surfaces. Although water drops fragmented into smaller drops for the ZNSP-25 min, -30 min, -1 h, -1.5 h and -2 h surfaces they all still rebounded from the surface. Therefore, it is suspected that the nanowires contribute to the enhanced non-wetting properties of the hierarchical structure under conditions of violent impingement.

The composite interface (air–water and solid–water interfaces) with the air trapped structure is a key factor to creating superhydrophobicity. Fig. 4 shows the geometry involved with water contact surface structure with inclined walls. On an inclined structure surface, one effective way to increase the Laplace pressure, thus promoting superhydrophobicity, is to generate nanostructures on the SP surfaces.¹⁵ The Laplace pressure can be expressed as²⁵

$$\Delta p = p - p_o = -\frac{\gamma \cos(\theta - \alpha)}{R_o + h \tan \alpha} \quad (1)$$

where γ is the surface tension of water, θ is the Young's contact angle of liquid on the surface, α is the inclination angle as illustrated in Fig. 4, R_o is half the distance between base edges of two adjacent inclined walls, p is the pressure on the liquid side of the meniscus, and p_o is the atmospheric pressure. According to eqn (1), the Laplace pressure is amplified when an enhanced contact angle θ can be generated on the pyramid side wall surfaces. This effect can be achieved by forming a nano-scale secondary structure. Additionally, the extended three-phase contact line on smooth surfaces is segmented into smaller contact lines on ZnO nanowire surfaces. As a result, the solid–liquid contact fraction was reduced and ultimately resulted in a robust and stable superhydrophobic state. Such effects cannot be achieved readily by structures with only one micron size-pyramids.

Zheng *et al.*³² recently studied the effects of hydraulic pressure on the transition from the Cassie–Baxter to Wenzel states. From a consideration of the balance between the pressure and surface tension across the suspended inter-nanowire liquid–air interface, it was found that the smaller nanowire diameter

could improve endurance to hydraulic pressure. The critical pressure p_c for the Cassie–Wenzel transition is given by

$$p_c = -\frac{4\gamma f_s \cos \theta_y}{f_g D} \quad (2)$$

where γ is the surface tension of the water drop, θ_y is the drop contact angle on a flat surface, D is the average diameter of the nanowires, and f_s and f_g are the solid and gas fractions, respectively. For a pressure p greater than p_c , the drop is impaled and the Wenzel state is preferred over the Cassie–Baxter state. For the best superhydrophobic sample, ZNSP-30 min, the density of the nanowires was $2.0 \times 10^{13} \text{ m}^{-2}$,³³ and the average diameter D was 30 nm. Thereby, f_s and f_g were 0.016 and 0.984, respectively. According to eqn (2), the critical pressure was $6.34 \times 10^4 \text{ Pa}$. This critical pressure is higher than the impact pressure of $4.20 \times 10^4 \text{ Pa}$ for a large raindrop with diameter of 5.76 mm, whose terminal speed is about 9.17 m s^{-1} .³⁵ This means that the superhydrophobic surfaces with the hierarchical structures are robust enough to withstand the impact of a large, high-speed raindrop and can avoid the transition from a Cassie state to a Wenzel state. We attribute the superior robustness of the ZNSP hierarchical structure to the presence of the nanowires on the surface of the pyramids and bottom surface between the pyramids. When a falling drop comes into contact with the nanowires, the nanowires resist the spreading of the drop because of the superhydrophobic contact angle. Furthermore, the drop has only a small contact area with the side or bottom surface, and it can be restored to rest on the tops of the pyramid after releasing the outward pressure (Fig. 4b). In contrast, spreading over the microstructures of silicon-pyramids until the contact angle approaches the Young's contact angle, leads to impalement of the drop.

Contact angle and contact angle hysteresis are mainly governed by the surface structure and surface chemical composition. The water contact angle on the plane ZnO thin film modified by fluorination is less than 120° ,³⁶ but reached as high as 169° on the ZNSP surface. The largest variance in the contact angle is due to the surface hierarchical morphology of ZNSP. Beside the important morphology effect on contact angle, the surface free energy also plays a significant role. The contact angle on the surface of as-grown ZNSP-30 min is less than 5° (Fig. S3(a)†), and immediately transform to 169° modified by PFOS (Fig. S3(b)†). In order to evaluate ZnO nanowires' stability on the Si surface, an abrasion resistance of the ZNSP surface is investigated (Fig. S4†). A polishing cloth (Allied High Tech Products, Inc.) is served as the abrasion surface, and the ZnO nanowire surface is polished facing the abrasion cloth material. The surface of ZnO nanowires is moved along one direction, while a pressure ($\sim 5000 \text{ Pa}$) is simultaneously applied normal to the sample surface. This process can be repeated many times on the surface. After the abrasion testing, the ZnO nanowire surfaces do not exhibit the clear wear trace (as shown in Fig. S4†), which provides the potential for hierarchical ZnO coating in self-cleaning surface applications.

Conclusions

In summary, we have demonstrated the preparation of superhydrophobic surfaces by growing ZnO nanowires on silicon

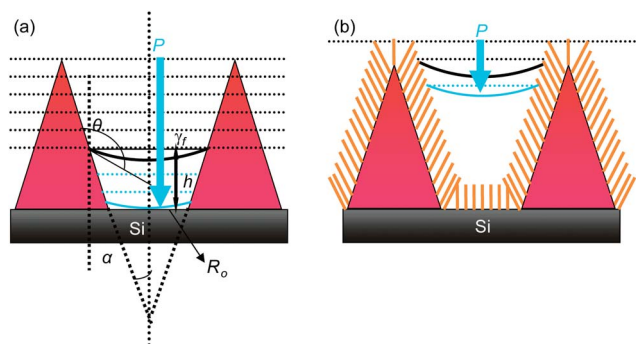


Fig. 4 Water contact at (a) SP and (b) ZNSP surfaces with inclined side walls.

pyramid structures. Additionally the effect of ZnO nanowire length on the hydrophobicity of these surfaces was investigated, and it was found that the length of ZnO nanowires played an important role in the surface hydrophobicity. With an optimized length of 445 nm, the maximum water contact angle reached 169.1°, while the contact angle hysteresis was only 1.3° for the ZnO nanowire–Si pyramid hierarchical structures grown at a reaction time of 30 min (ZNSP-30 min). Compression and impact experiments indicated that the hierarchical structures are robust when the length of nanowires was equal to or larger than 137 nm. As two important semiconductor materials, Si and ZnO have been widely used in sensors, piezo-nanogenerators, and solar cells. The hierarchical structures of ZnO nanowires grown on Si pyramid surfaces exhibiting superhydrophobicity in this work will have promising applications in the next generation photovoltaic devices and solar cells.

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