Fabrication of template with dual-scale structures based on glass wet etching and its application in hydrophobic surface preparation

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Template-based methods are a commonly used way to prepare superhydrophobic surfaces, in which, one of the critical issues, is template fabrication. In this work, a template with a dual-scale hierarchical structures fabrication method is investigated, in which, using the Cr and photoresist as etching mask, the fused silica glass substrate is etched in a buffered hydrofluoric solution. Optical photos and atomic force microscopy (AFM) scans show that the excellent ordered and uniform microstructures with a feature size less than 4 µm combining with the nanostructures with a feature size of about 20–30 nm on the etched surface have been fabricated, indicating hierarchical structures being obtained. Then the template with dual-scale structures is used as a master template and experiments of pattern transferring to PDMS and photoresist by cast moulding and by imprint lithography, respectively, have been conducted. The duplicating fidelity is characterised through optical photos and AFM scans. The contact angles of water on various fabricated surfaces are characterised and the influence of the surface roughness on wettability has been discussed.

1. Introduction: Wettability is one of the important properties of solid surfaces from both fundamental and practical aspects. Solid surfaces with special wettabilities possess great advantages in practical applications including the fabrication of microfluidic devices, the prevention of the adhesion of snow to antennas and the self-cleaning of traffic signals [1, 2]. Theoretical and experimental results show that micro and nanostructures play a key role in the wetting of a surface, regardless of chemical composition [3, 4]. However, constructing surfaces by mimicking the multiscaled structures of natural biological surfaces still remains a challenging project.

As the microfabrication techniques improve our ability to probe the physics down to micrometre length scales, many different synthesis strategies have been developed to fabricate functional surfaces with micro and nanostructures, in which, lithographic methods, plasma treatment, self-assembly and self-organisation, chemical deposition, layer-by-layer deposition, colloidal assembly, phase separation and electrochemical micromachining can be used as candidate techniques [1]. In terms of constructing dual-scale hierarchical structures, much excellent work has been done. By combining anisotropic wet etching with deep reactive ion etching (DRIE) process and by coupling black silicon process with DRIE, Zhang's research team has fabricated micro/nanodual-scale structures which show robust and stable hydrophobicity with the contact angle (CA) of ∼160° [5, 6]. Jiang and Yuan's group has reported an effective fabrication method combining DRIE and galvanic etching for silicon with micro/nanohierarchical structures and the wettability of the as-prepared surface has been analysed theoretically [7]. In addition, with a combination of dual lithography and DRIE, Ma *et al.* [8] have fabricated nano/nanodual-scale hierarchical structures with high-aspect-ratios. Metallic surfaces with special wettability exhibit some important applications such as anti-corrosion, friction reduction and liquid transportation. Combining electrochemical micromachining with ZnO nanostructures growth via the wet-chemical route, multi-level structures on tin–bronze substrate have been fabricated successfully [9]. Although these method promise regularity of microstructures and uniform nanostructures, they are multistep and time-consuming. Therefore a general, inexpensive and operationally convenient method is highly demanded, which would be very advantageous for large-scale industrial production.

Template-based methods are a commonly used way to prepare superhydrophobic surfaces which includes preparing a featured template master, then moulding the replica and finally removing the templates. Usually, the surface processed by lithography can be treated further by plasma etching to achieve complex roughness with multilayers and then used as a featured template to produce replicas. The critical issue of this process is the fabrication template with multi-scale hierarchical structures. Zhang *et al.* [10] have presented a template fabrication method involving silicon wet etching and improved DIRE and using the micro/nanodual-scale silicon mould, superhydrophobic hierarchical PDMS structures have been fabricated. However, since the silicon is lighttight, the silicon mould does not apply to commonly used light-cured polymer.

Glass offers high chemical and heat resistance, high electrical isolation, a large optical transmission range and low optical absorption and can be used for a variety of materials modelling by either heat or light curing. In this reported work, templates with dual-scale hierarchical structures have been fabricated based on fused silica glass wet etching. Then the template is used as a master template for PDMS cast moulding process and imprint lithography. The CAs of water on various fabricated surfaces by the template-based method are characterised and the influence of the surface roughness on wettability is discussed.

2. Experimental details

2.1. Template fabrication

2.1.1 Materials: In this work, polished quartz glass plates with a size of 50 mm × 50 mm × 1.5 mm were used. This is a fused silica material which, besides SiO_2 (99.8%), consists of small amounts of $Na_2O + K_2O$ (0.1%) and Fe_2O_3 (0.1%). The evaporated Cr metal film combined with a thin layer of positive tone photoresist EPG 533 (Everlight Chemical Industrial Co., Taiwan) is used as the etching mask. The buffered hydrofluoric acid with hydrochloric acid as an etching agent additive (HF: NH_4F: HCl = 0.5 mol l^{-1}:

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0.75 mol l^{-1}: 0.15 mol l^{-1}) was used as etching solution. All the chemicals used were reagent grade and processing solutions were prepared using deionised (DI) water.

2.1.2 Glass wet etching: The process flow is as depicted in Fig. 1. It is divided into the following steps.

Cr film sputter coating. First, the samples were rinsed with acetone (10 min) followed with ethanol for 10 min in an ultrasonic rinser and then the glass was immersed in concentrated H_2SO_4 (98%) for 10 min. Before further processing, the substrate was rinsed in DI water and baked in an oven (100°C) for 10 min to remove residual water. After that, a thin Cr metal layer with a thickness of 100 nm is sputtered on the glass wafer substrate through the conventional chrome photomask fabrication technique.

Photoresist coating, lithography and developing. In the steps shown in Figs. 1*b–e*, a common positive resist process was used for the etching mask patterning. A thin layer (about 5 μm) of photoresist was spin-coated and baked (70°C) for 10 min and then the ultraviolet (UV) lithography was performed with an exposurer (ABM 350//NOV/DCCD, USA). The developing of the resist was accomplished in 1 min by immersing the exposed sample into the developer (5 wt% NaOH) and agitation. After rinsing in DI water and drying by N_2 gas, the post baking of the resist was carried out at 100°C for 30 min to harden the etching mask.

Cr film through-mask etching. The metal layer of the unmasked portion was etched away with a Cr etch. The etch has the composition of ceric ammonium nitrate and perchloric acid ($(NH_4)_2[Ce(NO_3)_6]$): $HClO_4$ = 0.2 mol l^{-1}:0.45 mol l^{-1}) and reveals an etch rate of approximately 40 nm/min at room temperature (23 ± 0.5°C). After Cr film etching, rinsing, drying and baking process as mentioned above were carried out again to harden the etching mask.

Etching. The etching was performed in an ultrasonic setup. The agitation of the etching solution affects the glass dissolution because of the continuous renewal of the etching solution at the critical etching areas, which resulted in an etching rate of 0.4 μm/min at a room temperature.

Nanostructure fabrication. After mask layer of the photoresist and Cr film were stripped off, the glass wet etching was conducted again for 10 s and then the nanostructure was obtained in the region of substrate protected previously by the etching mask, which results in the transparent template with dual-scale hierarchical structures.

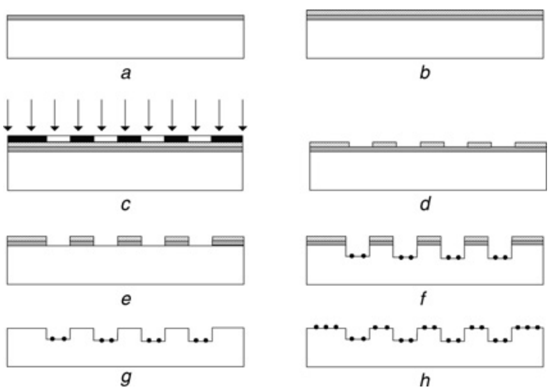

Figure 1 *Fabrication process of template with dual-scale hierarchical structures*
a Cr film sputtering
b Photoresist coating
c UV exposure
d Development
e Cr wet etching
f Glass wet etching
g Etching mask removal
h Flood wet etching

2.2. Dual-scale structures replication: Two materials with different wettable property involving PDMS and photoresist made in-house [11] were chosen to investigate the effect of surface roughness on wettability. The PDMS (ESSIL 291) from Axson Corporation was chosen to serve as the hydrophobic material because of its fine self-adaptability and low surface energy. The process is described briefly as follows: after thoroughly mixing prepolymer and the curing agent in a ratio of 10:1 by weight, the mixture is degassed for the first time to eliminate the trapped air bubble and then poured onto the glass master, then the mixture is evacuated for the second time to help the liquid mixture stuff into the channels of the master, finally the mixture is cured at a given temperature in an oven under normal atmosphere and the resulting PDMS with a replicated pattern on its surface is peeled off from the master [12].

The dual-scale structures replication on photoresist has been implemented through imprint lithography. The process begins with substrate cleaning. Then the UV-sensitive resist is coated onto the substrate. The template bearing patterned relief structures is imprinted on the resist, displacing the liquid-state photoresist and the patterned area is filled with the resist. Then the exposure of UV light through the back side of the template cures the photoresist. Finally, the template is separated from the substrate, leaving a relief image on the photoresist surface that is a replica of the template pattern [11].

2.3. Wettability characterisation: The CA which is usually modelled by either Cassie's or Wenzel's theory has been commonly used to represent the surface wettability. Hence, the CAs of a drop of liquid resting on prepared surfaces were measured with the contact angle system (OCA20, Dataphysics, Germany). Based on the data obtained, the surface morphological effect on wettability is discussed.

3. Results and discussion

3.1. Wet etching mechanism and the effect of etchant composition and glass composition on etched quality: The first step in controlling the etch rate and etch quality is to understand the material dissolution process and the relationship between the ionic composition of the solution and the etch rate. The overall chemical reaction involved in the dissolution of SiO_2 in HF solutions is generally described as

$$SiO_2 + HF \rightarrow SiF_4 + 2H_2O \quad (1)$$

in which the SiF_4 is in gas state in the common condition and will react with hydrofluoric acid soon before vapourisation in solution

$$4SiF_4 + 3H_2O + 2HF \rightarrow 3H_2SiF_6 + H_2SiO_3 \quad (2)$$

The replacement of the first oxygen by a fluorine ion is a slow and rate-determining reaction step. The subsequent reaction steps to remove the SiF unit from the SiO_2 network are much faster. The reaction equations mentioned above is just a simplified presentation. In fact, the dissolution reaction is a complex function of the active ions concentration in the solution, the pH value, the material composition and the additives [13, 14]. It is generally accepted that the dissolution reaction is governed by the absorption of the two reactive species: HF and HF_2^-. H^+ ions introduced by adding strong acids to the etch solution adsorb on the surface and catalyses the dissolution reaction. In the following text, the effect of the strong acids addition and the glass composition on the etched results quality is discussed.

As is in our previous work [11], the hydrochloric acid is also used as an etching agent additive in this Letter. However, the intention of adding the hydrochloric acid is different. In the previous work, the soda-lime glass used is a multicomponent mixture which, besides SiO_2 (72%), consists of CaO (7.2%) and MgO (4%). Since there exist the insoluble reaction resultants, CaF_2 and MgF_2 during etching, the purpose of the hydrochloric acid is to transform the CaF_2 and MgF_2 into soluble products $CaCl_2$ and $MgCl_2$, respectively, and then avoid the etching mask effect of the precipitated particles [11, 15]. By contrast, etching of the fused silica glass used in this work will not result in insoluble reaction products. The effect of the hydrochloric acid is to decrease the pH value of the etchant to improve the stability of the photoresist etch mask since the developer of the photoresist used is NaOH based and it is found that the photoresist mask was prone to be eroded in the buffered hydrofluoric acid with no additive. When the hydrochloric acid is added, the etching mask stability and then the etched edge quality are improved.

3.2. Effect of the hierarchical structure on wettability: It is believed that the wettability is governed by two factors. One is the chemical factor, and the other is the geometrical factor of the solid surfaces. Theoretical and experimental results show that even a material with the lowest surface energy (6.7 mJ/m^2 for a surface with regularly aligned closest-hexagonal packed-CF_3 groups) gives a water CA of only around 120° [16]. For higher hydrophobicity, a proper surface roughness is required. In the following part of this Section, wettable behaviour on various surface roughness is discussed.

The most prominent advantage of the template-based method is that the template can be used repeatedly once it has been fabricated. The pattern quality on the template is significant for the subsequent process. Fig. 2 gives the picture of the structure and surface roughness on the fused silica glass substrate etched under optimised etching conditions. Figs. 2*a* and *b* are optical photos (Keyence, Japan) of the etched microstructures taken at a magnification of 175 and 450, respectively, which show excellent regularity and uniformity of the microstructures etched through the optimised etching conditions in this work. Figs. 2*c* and *d* give the atomic force microscopy (AFM) scans (Veeco, USA) of the etched structure profile and etched surface roughness, respectively, which indicate that besides the ordered microstructures, the unordered nanostructures with a feature size of about 20–30 nm on the etched surface have also been obtained under the conditions of wet etching and ultrasound stirring. Fig. 2*e* is the measured results along the direction denoted by arrowhead in Fig. 2*b*. From these images, it can be seen that by manipulating the etching conditions, a grid of highly ordered microstructures with a top width of about 4 μm and a period of 60 μm and unordered nanostructures on the etched surface have been fabricated successfully.

The excellent chemical, heat and optical properties of the glass mean that it can be used for a variety of materials modelling by either heat or light curing. Before the cast process is performed, the glass template has been etched again in the same hydrofluoric acid without the etching mask for 10 s and the nanostructures appear on top of the protrusion portion of the glass template which has been protected by the etching mask previously. Then the pattern on the glass surface was replicated through the cast moulding process and imprint lithography, which results in the negative relief image of the pattern on the glass master template surface on the PDMS and the photoresist surface. The topographical structures on PDMS surface are shown in Fig. 3. From the AFM image, it can be seen that the patterns with high fidelity on PDMS surface have been replicated from the glass master template.

To investigate the relationships between wettability and the surface topographical property under the Wenzel contact condition at the solid–liquid interface, photoresist films having different surface roughness, namely the smooth surface, the surface with nanostructured roughness and the surface with dual-scale structures were prepared. The photoresist used in the experiments is made in-house, the compositions of which is previously mentioned [11]. Fig. 4 shows the pattern on the photoresist surface with hierarchical structures replicated from the glass template master.

The wetting of a solid by a liquid is characterised by the CA, which is the angle between the solid–air and the liquid–air interfaces. The greater the CA, the more hydrophobic is the material. Fig. 5 illustrates the wettability of various surfaces characterised by CA. By comparing Figs. 5*a–f*, we can deduce that the surface texturing results in a CA increase of a water droplet on a hydrophobic substrate surface and a CA decrease on a hydrophilic substrate surface, which is qualitatively consistent with the basic tenet that surface roughness is known to amplify surface wettability.

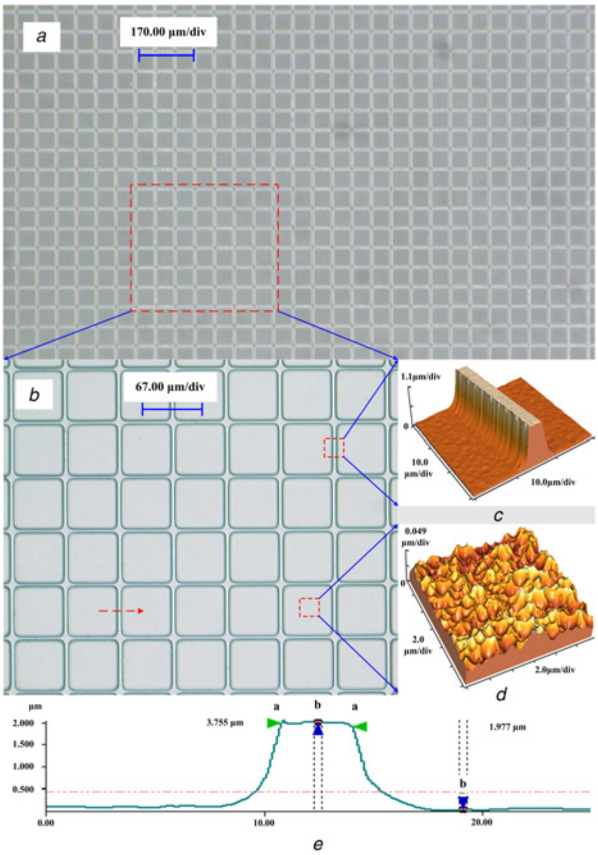

Figure 2 *Optical photos and AFM images of etched microstructure array on glass substrate surface*

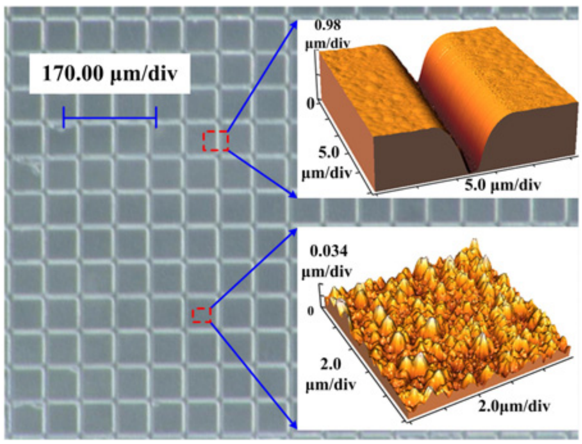

Figure 3 *Patterns on PDMS surface replicated from the fused silica glass master*

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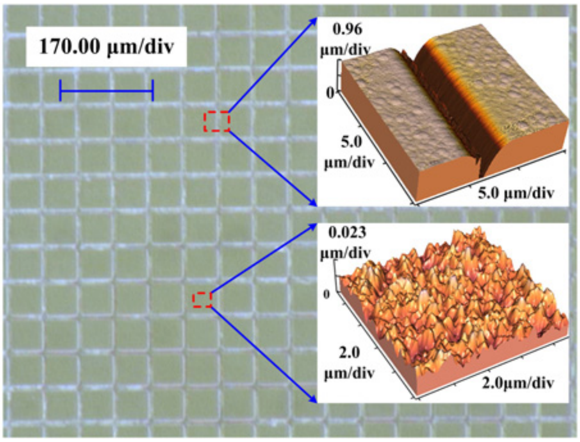

Figure 4 *Pattern on photoresist surface replicated from glass master through imprint lithography*

3.3. Theoretical analysis: The underlying theories interpreting the surface wetting property are mainly focused on the Young equation, the Wenzel equation and the Cassie-Baxter equation. Wenzel's and Cassie's formulas predict different CAs for a droplet on the same rough surface. Cassie's theory is based on the hypothesis that a composite surface is formed between a liquid droplet and a rough surface. In Cassie's approach, it is assumed that the liquid forms a composite surface on the rough substrate, the liquid does not fill the grooves on the rough surface but instead traps air under it [17, 18]. In this case

$$\cos\theta_c = \phi_s(\cos\theta_e + 1) - 1 \quad (3)$$

where θ_c is the apparent CA assuming a composite surface. θ_e is the equilibrium CA of the liquid drop on the flat surface which is the so-called intrinsic CA and ϕ_s is the area fraction of the liquid–solid contact.

In Wenzel's approach, it is assumed that the liquid fills up the grooves on the rough surface. In this case

$$\cos\theta_r = r\cos\theta_e \quad (4)$$

where r is the ratio of the actual area of liquid–solid contact to the projected area on the horizontal plane.

Based on the theory above, the effect of surface roughness on wettability is analysed quantitatively. If only the ordered microstructure on the fabricated surface is considered, the analytical geometry model is as shown in Fig. 6, in which w is the groove width and g is the gap between the adjacent grooves. According to formula (3) and formula (4), the theoretical CA of a droplet on

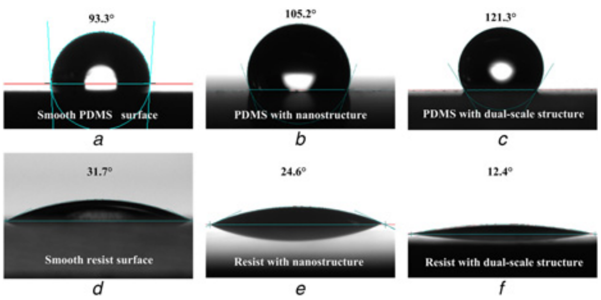

Figure 5 *CAs of water on PDMS and photoresist surface with various roughness*
a 93.3° *b* 105.2° *c* 121.3°
d 31.7° *e* 24.6° *f* 12.4°

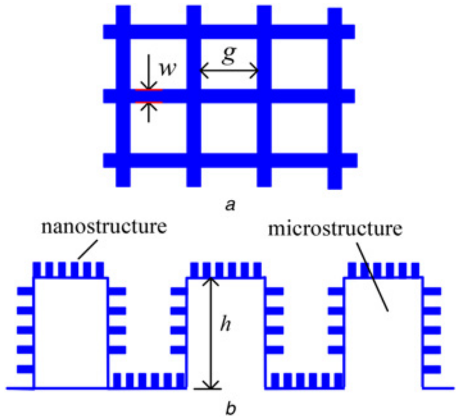

Figure 6 *Schematic illustration for geometry size of the fabricated microstructure array*
a Top view
w – width of the groove
g – gap between two adjacent grooves
b Cross-section view

the artificial surface can be calculated with the following expression

$$\cos\theta_c = s^2g^2(\cos\theta_e + 1) - 1 \quad (5)$$

$$\cos\theta_w = (1 + 4s^2hg)\cos\theta_e \quad (6)$$

where $s = 1/(w+g)$.

The PDMS used in this work is hydrophobic. Taking the CA on a smooth PDMS substrate surface as the intrinsic CA θ_e approximately and substituting the value of $w = 10$ μm (top width of the groove), $g = 50$ μm, $s = 0.017$ into the formula (5), we can obtain the theoretical CA $\theta_c = 108.6°$. Compared with the experimental result shown in Fig. 5*c*, the measured CA is much larger than the theoretical value. The result is probably attributed to the existence of the nanostructures on the sample surface. Similarly, photoresist used in this work is hydrophilic and the theoretical CAs of a droplet on the rough resist surface can be predicted by Wenzel's formula, viz., formula (6). Taking the CA on smooth resist surface as the approximate intrinsic CA and substituting the value of $h = 1.977$ μm, $w = 10$ μm, $g = 50$ μm, $s = 0.017$ into formula (6), the theoretical CA $\theta_w = 18.4°$ is obtained. The measured CA value is smaller than the calculated one, which is also probably ascribed to the roughness effect because of the nanostructures on the glass surface.

In addition, compared with the unitary scale, the surface with the hierarchical structure shows a larger CA. Besides, it is believed that the dual-scale structures can help establish stable and robust superhydrophobicity owing to the kinetics of droplet movement and the themodynamics of wetting [19].

4. Conclusion: Wettability on a solid surface plays a significant role in daily life and many industry applications. Theoretical and experimental results show that micro and nanostructures on the surface can influence the surface wettability significantly. Thus constructing novel surfaces with multiscaled roughness has become an increasingly hot research topic. Template-based methods are a commonly used way to prepare superhydrophobic surfaces. In this Letter, a template with a dual-scale hierarchical structures fabrication method is investigated, in which, using the Cr and photoresist as the etching mask, the fused silica glass substrate is etched in a buffered hydrofluoric solution and an ordered microstructures array is obtained. Optical photos and AFM scans show that the excellent ordered microstructures with a feature size less than 4 μm combining with the nanostructures with a feature size of about 20–30 nm on the etched surface have been fabricated. Then the template with dual-scale structures is used as the master template for pattern replication on the PDMS and resist without the routine steps of nanostructures formation by plasma etching. The duplicating fidelity is characterised through optical photos and AFM scans. The CAs of water on surfaces with different wettability properties are characterised and the influence of the surface roughness on wettability is discussed. The glass wet etching techniques can be used for imprint template fabrication as in this Letter and it is also used for fabricating microelectro-optical–mechanical system (MEOMS) components or microfluidic chips.

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