Self-Cleaning Poly(dimethylsiloxane) Film with Functional Micro/ Nano Hierarchical Structures

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ABSTRACT: This paper reports a novel single-step wafer-level fabrication of superhydrophobic micro/nano dual-scale (MNDS) poly(dimethylsiloxane) (PDMS) films. The MNDS PDMS films were replicated directly from an ultralow-surface-energy silicon substrate at high temperature without any surfactant coating, achieving high precision. An improved deep reactive ion etching (DRIE) process with enhanced passivation steps was proposed to easily realize the ultralow-surface-energy MNDS silicon substrate and also utilized as a post-treatment process to strengthen the hydrophobicity of the MNDS PDMS film. The chemical modification of this enhanced passivation step to the surface energy has been studied by density functional theory, which is also the first investigation of C4F8 plasma treatment at molecular level by using first-principle calculations. From the results of a systematic study on the effect of key process parameters (i.e., baking temperature and time) on PDMS replication, insight into the interaction of hierarchical multiscale structures of polymeric materials during the micro/nano integrated fabrication process is experimentally obtained for the first time. Finite element simulation has been employed to illustrate this new phenomenon. Additionally, hierarchical PDMS pyramid arrays and V-shaped grooves have been developed and are intended for applications as functional structures for a light-absorption coating layer and directional transport of liquid droplets, respectively. This stable, self-cleaning PDMS film with functional micro/nano hierarchical structures, which is fabricated through a wafer-level single-step fabrication process using a reusable silicon mold, shows attractive potential for future applications in micro/nanodevices, especially in micro/nanoluidics.

INTRODUCTION

Poly(dimethylsiloxane) (PDMS) has attracted much attention in a wide range of fields due to its unique properties, such as transparency, flexibility, biocompatibility, and high-yield.1−6 Especially, the superhydrophobic PDMS has shown potential applications in self-cleaning devices and microfluidic systems.7,8 The capability of micro/nano hierarchical structures to enhance the material’s hydrophobicity has been demonstrated in previous research.9−13 Meanwhile, hierarchical structures also endow the material with some remarkable properties, such as strong adhesion when dry, antireflectance, and iridescent structural color.14−17 However, our understanding of the origin of the interaction of hierarchical structures during micro/nano integrated fabrication processes is still not satisfactory. The fabrication of a MNDS PDMS film (i.e., PDMS film with micro/nano hierarchical structures) conventionally contains two steps, microstructuring and nanostructuring, whose sequences can be changed for different processes.18−20 The contact angle of MNDS PDMS film fabricated using the two-step technique was reported to achieve 170°.18 In practical applications, an increased number of process steps will increase cost and may lead to process compatibility problems, making a single-step fabrication process for PDMS hierarchical structures very attractive. Some one-step techniques have been developed;21−23 however, a surfactant coating is conventionally required to prevent bonding between the PDMS and the replication mold during baking to cross-link the PDMS, which occurs due to high surface energy. Unfortunately, the surfactant coating will pollute the surface and also reduce the precision of PDMS replication due to the layer of surfactant coating the mold, especially for nanoscale structures. Another one-step method based on the combination of UV irradiation with a photomask also has been reported,24 while the nanotip is hard to form on the sidewalls due to the straight irradiation property of UV.

Besides increasing roughness via micro/nano hierarchical structures, plasma treatments have also been introduced to enhance the PDMS hydrophobicity.18,25−28 Although previous work has experimentally demonstrated that plasma treatment can effectively reduce surface energy, there is a lack of theoretical knowledge about the chemical modification mechanism. Here, we present a single-step process to fabricate superhydrophobic MNDS PDMS membranes replicated directly from ultralow-surface-energy MNDS silicon substrates without surfactant coating. An improved deep reactive ion etching (DRIE) process was developed to realize easily...
ultralow-surface-energy MNDS silicon substrates. The sharp reduction of surface energy and the formation of micro/nano hierarchical structures were realized simultaneously due to enhancement of the passivation step of the DRIE process. Therefore, thermal cross-linking at high temperatures (even above 180 °C) can be directly used during the PDMS molding process to enhance the pattern transfer precision, without requiring surfactant.

After a systematic study of the replication process, the key process parameters of baking temperature and baking time are obtained. In the meantime, the interaction of hierarchical multiscale structures of PDMS (i.e., the effect of the morphology of microscale structure on the formation of nanoscale structure) during the micro/nano integrated fabrication process has been experimentally observed for the first time, which is also investigated using the finite element simulation. A post-DRIE process only consisting of passivation steps, which is actually C4F8 plasma treatment, was utilized to enhance the hydrophobicity of PDMS. The chemical modification mechanism of the C4F8 plasma treatment was studied by density functional theory at the molecular level for the first time. Hierarchical PDMS pyramid arrays intended for application as functional structures for light-absorption coating layer and V-shaped grooves for directional transport of liquid droplets have also been developed. Finally, the static contact angle (CA) of MNDS PDMS film fabricated using the optimized process parameters achieved up to more than 160°, while the CA hysteresis was reduced to below 10°. The stability of the superhydrophobic MNDS PDMS film produced in this work was demonstrated by squeezing and impact tests.

EXPERIMENTAL DETAILS

Ultralow-Surface-Energy Silicon Mold. The MNDS silicon mold was prepared by two steps, microstructure fabrication followed by nanostructure formation. Photolithography and KOH wet etching were used to fabricate microstructures with inverted pyramids and V-shaped grooves. Next, an improved DRIE process was used to directly realize nanostructures atop the microstructure produced in the previous steps, forming the final MNDS silicon mold. An inductively coupled plasma (ICP) etcher (Surfacing Technology Systems plc, Multiplex ICP 48443) was used, with SF6 and C4F8 for etching gas and passivation gas, respectively.

By optimizing the DRIE process parameters, especially enhancing the passivation steps, the polymer deposited during the passivation step cannot be completely removed by the next etching step, and the residual nanoscale polymer will protect the substrate as a self-mask and form high-density nanotips [Figure 1a(II−IV)]. Here, compared with our previous work,29−31 the improved DRIE process is further optimized and followed by a post-DRIE process [Figure 1a(V)]. This post-DRIE process, which is actually based on this improved DRIE process but only made up of passivation steps, is utilized to further reduce the mold surface energy. The detailed process parameters have been given in Table S1 of the Supporting Information. As a result of the minimized liquid–solid contact area and the fluorocarbon layer deposited during the DRIE process, this silicon mold shows superhydrophobicity, and its surface energy is sharply reduced to be ultralow.13

Micro/Nano Hierarchical PDMS Film. Commercial PDMS product (Sylgard 184, Dow Corning Corp.) was used for structure replication. The MNDS silicon substrate was dipped into a liquid PDMS mixture consisting of base and curing agent in the mass quantity ratio of 10:1. Then the samples were placed into vacuum chamber evacuated to a pressure below 1 × 10−2 Pa for 15 min to...
remove the interface bubbles between PDMS mixture and silicon substrate. Subsequently, the samples were heated at the high temperature from 60 to 95 °C, in order to cure the liquid PDMS into a solid PDMS membrane. After this thermal cross-linking, the PDMS film was simply peeled off from the substrate [Figure 1 a(VI–VII)]. The micro/nano dual-scale structures on the silicon (i.e., inverted pyramids and V-shaped grooves) were effectively transferred directly onto the PDMS film (Figure 2) without surfactant coating.

Figure 2 shows photos and SEM images of surface-micro/nanostructured PDMS membranes and their corresponding molds (i.e., surface-micro/nanostructured silicon substrate). The structural parameters and geometry morphology of microstructures are well-designed to realize specific functions. The post-DRIE process was also used as plasma treatment to enhance the superhydrophobicity of surface-micro/nanostructured PDMS. The passivation gas (i.e., C4F8) flow was 50 sccm, while the etching gas (i.e., SF6) flow was set to be 0 sccm.

Measurement and Analysis. The static contact angle and the stability of superhydrophobicity of micro/nano dual-scale PDMS surfaces were measured by an OCA 20 video-based contact angle meter (DataPhysics Instruments GmbH). The physical mechanism of the effect of baking temperature and time on pattern transfer was analyzed using an atomic force microscope (Dimension ICON, Bruker Corp.) and a scanning electron microscope (Quanta 600F, FEI Co.). The interaction of hierarchical multiscale structures was studied by finite element simulation (COMSOL). Density functional theory (DFT) calculations were performed to investigate the chemical modification of the enhanced passivation steps.

RESULTS AND DISCUSSION

Due to both the minimized liquid–solid contact area and the fluorocarbon layer deposited during the DRIE process, the surface energy of MNDS silicon substrate is sharply reduced. Consequently, the intermolecular force between PDMS and the ultralow-surface-energy mold is significantly weakened, and the undesirable bonding of PDMS to silicon substrate that would otherwise occur at high temperature was prevented, even for temperature higher than 180 °C. Therefore, the MNDS PDMS structures could be easily replicated from silicon substrate without surfactant coating. A major advantage of this method is that the precision of the pattern replication is improved, as surfactant coating is not required. The MNDS structures, including nanostructures, are completely transferred onto the PDMS surface, even onto the inclined surface shown in Figure 2. The high-yield of this single-step fabrication process has been demonstrated by fabricating 4 in. silicon mold and PDMS film, as shown in Figure 2. Additionally, the fluorocarbon layer deposited during the DRIE process also helps protect the mold surface, which is undamaged after replication for ~50 times (Figure 1b,c). This polymer layer has two main effects on the silicon mold. One is serving as a protective layer to cover and protect the micro/nano hierarchical structures on the silicon substrate. The other is sharply reducing the surface energy of the silicon mold and thus resulting in the ultralow interface force between PDMS and silicon mold. Thus, the damage to the silicon mold, when peeling PDMS from it, is dramatically reduced. Therefore, this wafer-level single-step fabrication process also shows an attractive reusability.

Surface-Nanostructured PDMS Film. There are two key factors affecting the transfer result when replicating surface-micro/nanostructured PDMS structures from a silicon mold. Baking temperature is one of the key factors. When the PDMS base solution and the curing agent are mixed and heated, the PDMS mixture is solidified to form the PDMS film. Within a certain range, the higher the baking temperature, the greater the mechanical strength of the PDMS film. Thus, the MNDS PDMS structures baked at higher temperature are stronger and less likely to be destroyed when they are peeled off from the mold, which results in better pattern transfer. In our experiments, this relationship has been demonstrated in the baking temperature range from 60 to 85 °C. The SEM and AFM images of surface-nanostructured PDMS samples illustrate that the pattern transfer precision improves as the
baking temperature increases from 60 to 85 °C [Figures S1 (panels I, II) (Supporting Information) and 3a–c].

In Figure S1 of the Supporting Information, the surface-nanostructured PDMS film baked at 60 °C is smoother than that of the sample baked at 85 °C. In Figure 3, the average roughness (i.e., $R_a$) of surface-nanostructured PDMS sample increases during the baking temperature range from 60 to 85 °C.

$$R_{a60°C} (=76.2) < R_{a80°C} (=87.6) < R_{a85°C} (=93.7)$$

(1)

$$R_a = \frac{1}{N} \sum_{j=1}^{N} |Z_j|$$

(2)

in which $N$ is the number of nanostructures and $Z_j$ is the nanostructure height of number $j$.

In contrast, when the baking temperature is higher than 85 °C, the pattern transfer precision declines with further temperature increase. We believe that the difference between baking temperature and room temperature affects the PDMS replication due to thermal expansion and contraction. The larger the temperature difference, the greater the thermal contraction. Therefore, the baking temperature and the temperature difference from room temperature have opposite effects on the pattern transfer. According to the experiments shown in Figure 3, the balance point occurs at the temperature of 85 °C.

$$R_{a60°C} (=76.2) < R_{a95°C} (=78.4) < R_{a100°C} (=87.6)$$

(3)

The static contact angle (CA) of surface-nanostructured PDMS films has also been investigated, which shows the same trend. In Figure 4a, the peak contact angle occurs at 85 °C. The PDMS with pyramids increase as baking temperature increases in the range from 60 to 85 °C, reaches a peak at 85 °C, and then decreases from 85 to 95 °C. Interestingly, the CA curve of MNDS PDMS with V-shaped grooves shows an opposite trend, as is shown in Figure 4. According to the finite element simulation shown in Figure 5, we believe that the effect of the microstructure morphology on the nanostructure formation induces these opposite trends.

When a MNDS PDMS film with V-shaped grooves is peeled off from the mold, the stress distribution is different from that for a film with pyramid arrays. For the MNDS PDMS film with pyramid arrays, the stress only distributes at the bottom of the microscale pyramid; thus, the nanoscale holes experience close to no stress and will keep their original profile during the peeling off process. In contrast, for V-shaped grooves, much larger stress (as indicated in Figure 5 by the yellow-red color) occurs at the nanoscale holes, which will enlarge the aspect ratio of the nanoscale holes during the peeling off process. Logically, this effect of the stress on the aspect ratio of nanoholes will be larger when the PDMS film is softer. As is known, the Young’s modulus of the PDMS film will become larger when the baking temperature is higher. Therefore, when the groove-type MNDS PDMS film is baked at lower temperature, the stress effect will make the aspect ratio of nanoholes larger and subsequently increase the CA. Thus, the interaction of hierarchical multiscale structures (i.e., the effect of the microstructure morphology on the nanostructure formation) explains the opposite curve trend of the groove-type MNDS PDMS in Figure 4.

**Plasma Treatment.** The same improved DRIE process without etching gas flow was used as the plasma treatment to enhance the superhydrophobicity, which is also called the post-DRIE process [Figure 1a(V)]. The fluorocarbon layer deposited in the passivation steps can further reduce the surface energy of PDMS samples, thereby strengthening the water-repellent effect. To understand the chemical mechanism behind the effect of C4F8 plasma treatment on the PDMS surface energy, we study the interaction of fluorocarbon polymer deposited by C4F8 plasma and PDMS with H2O by optimizing two model complexes, CF3(CF2)4CF3 · H2O and (CH3)3SiOSi(CH3)2OSi(CH3)3 · H2O, respectively, at the DFT level (see Video S1 and computational details in the Supporting Information).32 For convenience of statement, we denote the two model complexes by MCF · H2O and MNDS · H2O, respectively. The two optimized stable complexes are shown in Figure 6. Obviously, in the MCF · H2O complex, water binds to one terminal F atom and forms a hydrogen bond in a monodentate fashion with a H···F bond length of 2.45 Å. While in MNDS · H2O, water binds to one O atom and also forms a hydrogen bond with a H···O bond length of 1.89 Å. The hydrogen-bond interaction in MNDS · H2O is higher than that in MCF · H2O by about 7 kcal/mol; i.e., the H2O is more attracted by PDMS than the fluorocarbon polymer, due to the stronger electrostatic attraction in the former. The Mulliken charge analysis in Figure 6 shows that the O atom carries more negative charge than the F atom, i.e., −0.97 vs −0.45, and vice versa for the two H atoms involved in the hydrogen bonds.

However, it does not mean that the longer the plasma treatment, the better the improvement of superhydrophobicity. As the cycle of plasma treatment increases, the thickness of the fluorocarbon layer increases, covering the nanostructures, decreasing the roughness, and leading to the deterioration of hydrophobicity, as is shown in Figure 7. The largest CA of
surface-micro/nanostructured PDMS film is achieved after two-cycle plasma treatment. The structural parameters are also optimized to further enhance the superhydrophobicity, and the optimized length and space are 13 and 4 μm, respectively. After optimizing the plasma treatment cycle (i.e., the post-DRIE process) and the structural parameters, CA of up to more than 160° was achieved, CA hysteresis reduced to below 10°, and the rolling angle was below 5°. Therefore, this surface-textured PDMS film after plasma treatment shows remarkable superhydrophobicity.33,34

**Functional Micro/Nano Hierarchical Structures and Stable Superhydrophobicity.** Two types MNDS PDMS films were specifically designed and produced for the light-absorption coating layer and directional transport of liquid droplets. Pyramid arrays were used to enhance light absorption and minimize reflectance in decades due to the multireflectance by inclined sidewalls of the pyramid.35–37 Here the pyramid-type MNDS PDMS film show more potential for future applications as an effective light-absorption coating layer for optical microsystems due to the high-efficiency light-trap by the combination of microscale pyramid arrays and nanoscale holes. Additionally, the groove-type MNDS PDMS shows an anisotropic wettability (Figure 8), which makes it an attractive material with which to realize the directional transport of liquid droplets.

The stability of the superhydrophobic properties and the self-cleaning capability of the material were demonstrated by a squeezing test and an impact test (Figure 9). These two tests were carried out 2 weeks after the fabrication process was

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**Figure 5.** The FEA study of the stress behavior of the micro/nano dual-scale PDMS surface peeled off from the ultralow-surface-energy mold.

**Figure 6.** The study of the interaction between water molecule and PDMS samples (a) before and (b) after the post-DRIE process (i.e., C6F13 plasma treatment) via optimization of model complexes (CH3)3SiOSi(CH3)2O and CF3(CF2)4CF3 at the density functional theory level. In these two stable complexes, the bond lengths of hydrogen bonds, i.e., H···O and H···F, and the Mulliken charge on these four atoms are given.

**Figure 7.** The effect of the post-DRIE process (i.e., C6F13 plasma treatment) cycle on CA of surface-micro/nanostructured PDMS (3 μL), and SEM images of MNDS PDMS film after (I) two cycles and (II) 10 cycles plasma treatment, respectively.

**Figure 8.** The measured CA of MNDS PDMS film with V-shaped grooves in the horizontal and the normal direction (volume of 2 μL), and photos of ink droplets (volume of 15 μL) on different MNDS PDMS surfaces.
completed. In Figure 9a, during the vertical movement process of the platform, although the water droplet is pushed, squeezed, and pulled sequentially, it still remains on the injector tip. In Figure 9b, when the water droplet drops from the injector tip and impacts the sample surface, it bounces several times along the 10° inclined surface.

### CONCLUSIONS

In this paper, we present a self-cleaning PDMS film with functional micro/nano hierarchical structures and also a wafer-level single-step fabrication process. The key feature of the single-step fabrication process is the use of a reusable ultralow-surface-energy silicon mold. An optimized DRIE process with enhanced passivation steps is employed to fabricate ultralow-surface-energy silicon molds and also the micro/nano hierarchical structures atop them simultaneously. After a systematic study of key process parameters of PDMS pattern replication, the interaction of hierarchical dual-scale structures during micro/nano integrated fabrication process is investigated, and the stress concentrations that lead to this effect are analyzed by finite element simulation. The mechanism by which an enhanced passivation step using C₂F₆ plasma treatment can reduce the PDMS surface energy is studied by using density functional theory. After the optimization of the post-DRIE process, the superhydrophobic stability and the self-cleaning properties of PDMS film are experimentally demonstrated. This single-step process to fabricate superhydrophobic micro/nano hierarchical PDMS structures is low-cost, large-scale, and precise, which leads to strong potential for applications in microfluidics.

### ASSOCIATED CONTENT

Supporting Information

Figure S1, Table S1, and Video S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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### ABBREVIATIONS USED

PDMS, poly(dimethylsiloxane); DRIE, deep reactive ion etching; MDNS, micro/nano dual-scale; DFT, density functional theory; CA, contact angle; SEM, scanning electron microscope.

### REFERENCES


