FABRICATION OF A TRANSPARENT STRUCTURED SUPEROMNIPHOBIC SURFACE USING A MULTIPLE PARTIAL EXPOSE METHOD

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ABSTRACT

A novel approach which uses a multiple partial exposure method to fabricate a transparent structured superomniphobic surface with doubly re-entrant structures by using negative thick photoresist SU-8 as the material is proposed. By using gray-tone lithography, the doubly re-entrant structures can be formed only via a standard lithography process. The gray-tone lithography for fabricating the doubly re-entrant structures is achieved by depositing three appropriate thicknesses of Ti film on glass substrate that acts as the gray-tone mask. The proposed transparent surface with the doubly re-entrant structures successful suspend all the tested liquid even the completely wetting liquid, such as silicon oil with the surface tension of 20.9 mN/m. This approach provides a simple, flexible and low-cost solution for fabricating superomniphobic surface, and it also has the potential to integrate with either flexible or nonflexible substrate for different applications.

INTRODUCTION

Super-repellent surface can be classified to superhydrophobic for repelling high surface tension liquids, such as water, or superomniphobic for repelling low surface liquids, such as oils and alcohols.[1, 2] In common approach, super-repellent surface were achieved by roughing the hydrophobic material to trap the gas. In 2014, Liu and Kim first proposed that the material's inherent wettability, depicted by the intrinsic contact angle, is irrelevant when dealing with a completely wetting liquid.[3] Based on the theory they proposed, a surface with doubly re-entrant structures, which was formed by hydrophilic material, was developed to superrepel all available liquids. However, the surface with doubly re-entrant structures has been demonstrated the powerful liquid repellency, but the surface was opaque and nonflexible based on the proposed silicon-based fabrication.

In this work, a novel approach to fabricate a transparent superomniphobic surface with doubly re-entrant structures is proposed. The proposed multiple partial exposure method is applied to the negative thick photoresist SU-8 to form the doubly re-entrant structures. A gray-tone mask with three difference thicknesses metal is fabricated for modulating exposure dosage, which makes the doubly re-entrant structures to be formed only after a standard lithography process. This approach provides a simple, flexible and low-cost solution to fabricate the structured superomniphobic surface without any other process (i.e., depositing hydrophobic material).

METHOD

Structured surface for liquid suspension

The surface microstructures can be categorized by their sidewalls angle (α, with respect to the horizontal surface), such as (i) simple structures with a positive downward slope (i.e., $90° \leq \alpha < 180°$), as shown in figure 1(a), (ii) re-entrant structures with a negative downward slope (i.e., $0° \leq \alpha < 90°$), as shown in figure 1(b), and (iii) doubly re-entrant structures with an upward slope (i.e., $-90° \leq \alpha < 0°$), as shown in figure 1(c). The structure's sidewall angle determines the theoretical range of intrinsic contact angle that to generate an upward suspension force from the surface tension of liquid for liquid suspension.[3] Figure 1(a) illustrates that the suspension upward force can be generated on the simple structures (i.e., $90° \leq \alpha < 180°$) for nonwetting liquids (i.e., $\theta_0 > 90°$) in the condition of $90° \leq \alpha < \theta_0$. Figure 1(b) illustrates that the upward force can be generated on the re-entrant structures (i.e., $0° \leq \alpha < 90°$) for wetting liquids (i.e., $\theta_0 < 90°$) in the condition of $0° \leq \alpha < \theta_0$. Figure 1(c) illustrates that the upward force can be generated on the doubly re-entrant structures (i.e., $-90° \leq \alpha < 0°$) for all liquids (i.e., $\theta_0 \geq 0°$) in the condition of $-90° \leq \alpha < 0° \leq \theta_0$.

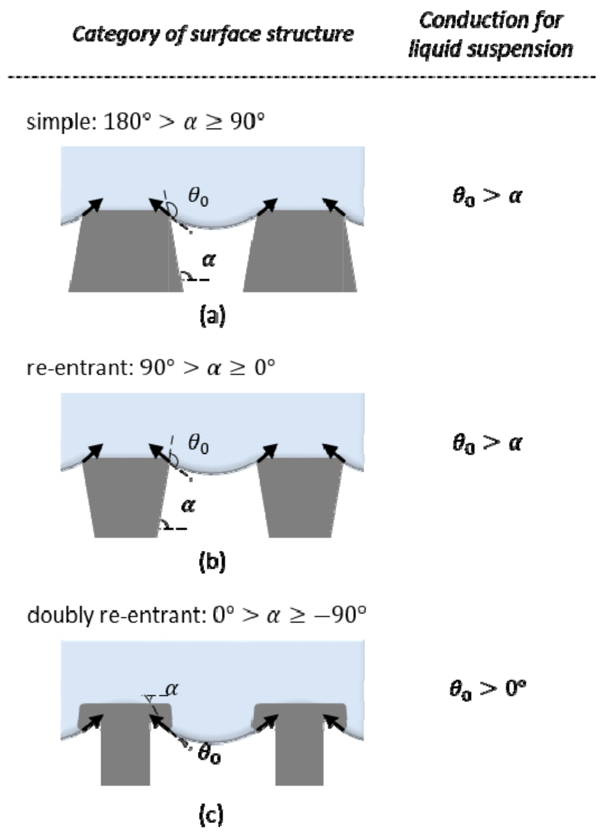

Figure 1: Relationship between intrinsic contact angle θ_0 and different surface structures for successful liquid suspension. (a) Simple structures require contact angle larger than the sidewall angle in order to have an upward suspension force. (B) Re-entrant structures also require contact angle larger than the sidewall angle in order to have an upward suspension force. (C) Doubly re-entrant structures always provide an upward suspension force and thus can theoretically suspend any, even perfectly wetting liquid.

Fabrication process

The partial exposure method has been demonstrated to enhances the fabrication capability of three dimensional (3D) photoresist microstructures.[4, 5] For the negative photoresist, only photoresist suffering the exposure dosage over the threshold value will be formed the structures during the post-exposure bake (PEB) and the development, so the doubly re-entrant topology with the multi-level steps on the back side can be achieved by patterning the photoresist from the front side via dosage control. Here, a batch process using a partial expose method in front side is employed to fabricate the transparent structured superomniphobic surface with the doubly re-entrant topology. The doubly re-entrant topology is achieved by incorporating a gray mask in the front-side exposure. By using gray-tone lithography, the doubly re-entrant structures can be formed only via a standard lithography process.

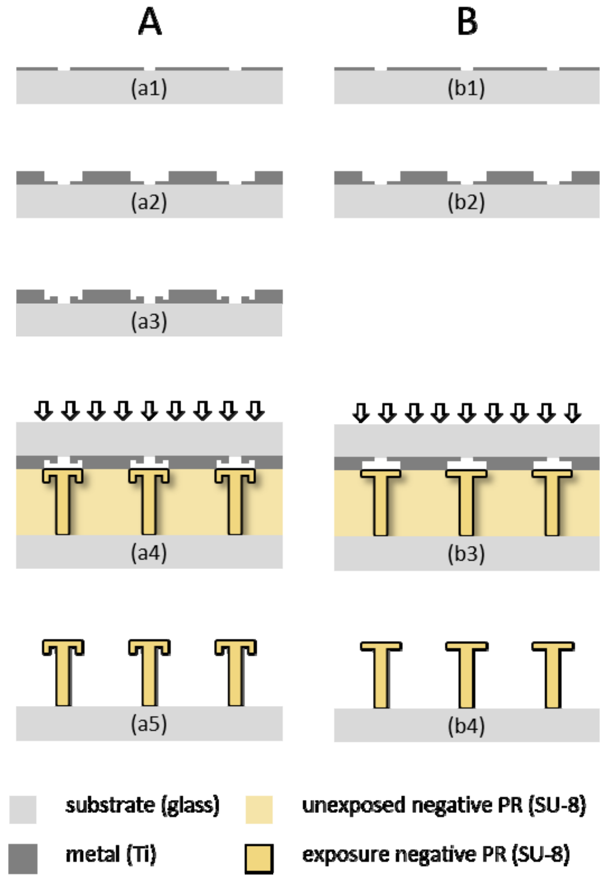

Figure 2: Fabrication process of doubly re-entrant topology and re-entrant topology by multiple partial exposes method. Process of doubly re-entry topology: (a1) defining a thin Ti film as 1st gray-tone area, (a2) defining the thick Ti film as opaque mask, (a3) defining other thin Ti film as 2nd gray-tone area, (a4) coating SU-8 and completing full exposure by one exposure, and (a5) development. Process of re-entrant topology: (b1) defining a thin Ti film as gray-tone area, (b2) defining a thick Ti film as opaque area, (b3) coating SU-8 and completing full exposure by one exposure, and (b4) development.

Figure 2A shows the detailed fabrication procedures of the doubly re-entrant topology as the proposed transparent superomniphobic surface. A gray-tone mask for fabricating the doubly re-entrant topology is achieved by depositing three thicknesses of metal film (Ti) on the glass substrate to modulate light transmitted. First, a thinner metal film is deposited and patterned by the lift-off process on a soda lime glass substrate as the 1st gray-tone area for modulating exposure dosage, as shown in figure 2(a1). A thicker metal film is also subsequently defined at the desired locations by sputtering as the opaque area, as shown in figure 2(a2). Then, another metal film is also deposited and patterned by the lift-off process as the 2nd gray-tone mask for modulating exposure dosage, as shown in figure 2(a3). After fabricating the gray-tone mask, the fabrications of transparent structured superomniphobic surface are carried out on soda lime glass substrates, and the commercially available negative thick photoresist (SU-8 3025, Microchem) is used here. After cleaning the glass substrate, the photoresist is spin-coated and then soft-baked. After rehydration, the photoresist is exposed, as shown in figure 2(a4). Finally, the doubly re-entrant topology is formed during the PEB and the development, as shown in figure 2(a5).

Furthermore, a comparison surface with the re-entrant topology can also be achieved by patterning the photoresist from the front side via dosage control. The detail fabrication procedures of fabricating the re-entrant topology is shown in figure 2B. Similar to fabricate the doubly re-entrant topology, a gray-tone mask for fabricating the re-entrant topology is achieved by depositing two thicknesses of metal film (Ti) on the glass substrate to modulate the light transmitted. First, a thinner metal film is deposited and patterned by the lift-off process on a soda lime glass substrate as the gray-tone area for modulating exposure dosage, as shown in figure 2(b1). A thicker metal film is also subsequently defined at the desired locations by sputtering as the opaque area, as shown in figure 2(b2). Then, the fabrications of the comparison surface are also carried out on soda lime glass substrates, and the commercially available negative thick photoresist (SU-8 3025, Microchem) is also used here. After substrate cleaning, photoresist spin-coating, soft-baking and rehydration, the photoresist is exposed and then PEB, as shown in figure 2(b3). Finally, the re-entrant topology is formed during the development, as shown in figure 2(b4).

FABRICATOIN RESULTS

For fabricating the doubly re-entrant topology, the gray-tone mask is achieved by depositing three thicknesses of Ti film, such as 40 nm, 55 nm and 90 nm, on the glass substrate to modulate light transmitted. After fabricating the gray-tone mask, the fabrications of transparent structured superomniphobic surface are carried out on soda lime glass substrates, and the commercially available negative thick photoresist (SU-8 3025, Microchem) is used here. After cleaning the glass substrate, the photoresist around 110 μm thick is spin-coated and then soft-baked at 95 ℃ for 20 min. After rehydration for over 20 min, the photoresist is exposed to the dosages of 750 mJ/cm^2 and then PEB at 65 ℃ for 1 min and 95 ℃ for 6 min. Final development is performed for 10 min with a Microchem

SU-8 developer, followed by a second spray/wash with Isopropyl Alcohol (IPA) for another 10 s. Figure 4A shows the SEM of the fabrication results of the proposed transparent superomniphobic surface with doubly re-entrant topology. We designed a surface with an array of doubly reentrant structures, as shown in figure 3(a1). And, the doubly re-entrant structures with an upward slope (i.e., -90°≤α<0°) is successful fabricated, as shown in figure 3(a2). In the preview theoretically, the upward force can be generated on the doubly re-entrant structures (i.e., -90°≤α<0°) for all liquids (i.e., $\theta_0 \geq 0°$) in the condition of $-90° \leq \alpha < 0° \leq \theta_0$. In addition, figure 3(a3) and figure 3(a4) shows the other dimensions of the doubly re-entrant topology fabricating by multiple partial expose method.

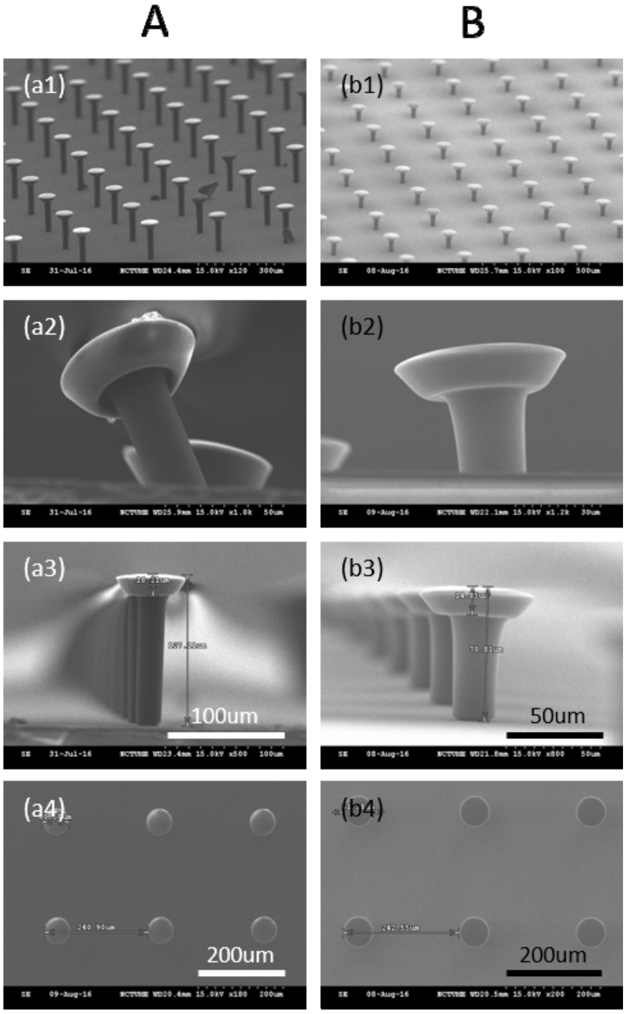

Figure 3: SEM of the doubly re-entrant structures and the re-entrant structures. The doubly re-entrant structures: (a1) bird view, (a2) bottom-angled view, (a3) side view, and (a4) top view. The re-entrant structures: (b1) bird view, (b2) bottom-angled view, (b3) side view, and (a4) top view.

For fabricating the re-entrant topology, a gray-tone mask is achieved by depositing two thicknesses of Ti film, such as 40 nm and 90 nm, on the glass substrate to modulate light transmitted. After fabricating the gray-tone mask, the fabrications of the comparison surface are also carried out on soda lime glass substrates, and the commercially available negative thick photoresist (SU-8 3025, Microchem) is also used here. After cleaning the glass substrate, the photoresist around 70 μm thick is spin-coated and then soft-baked at 95 ℃ for 20 min. After rehydration for over 20 min, the photoresist is exposed to the dosages of 750 mJ/cm^2 and then PEB at 65 ℃ for 1 min and 95 ℃ for 6 min. Final development is performed for 10 min with a Microchem SU-8 developer, followed by a second spray/wash with IPA for another 10 s. Figure 4B shows the SEM of the fabrication results of the re-entrant topology. We also designed a surface with an array of re-entrant structures, as shown in figure 3(b1). And, the re-entrant structures with a negative downward slope (i.e., 0°≤α<90°) is successful fabricated, as shown in figure 3(b2). In the preview theoretically, the upward force can be generated on the re-entrant structures (i.e., -90°≤α<0°) for wetting liquids (i.e., $\theta_0<90°$) in the condition of $0° \leq \alpha < \theta_0$. In addition, figure 3(b3) and figure 3(b4) shows the other dimensions of the doubly re-entrant topology fabricating by multiple partial expose method.

TESTING RESULTS

Transparent structured superomniphobic surface

Figure 4 shows a photograph of the proposed transparent structured superomniphobic surface with doubly re-entrant structures with droplets. Even if the paper is covered by the proposed surface, the words on the paper are still visible and distinguishable.

Figure 4: Photograph of the proposed transparent structured superomniphobic surface with doubly re-entrant structures with droplets.

Liquid repellency testing

To evaluate the liquid repellency, three difference liquids are used, such as DI water with surface tension of 72.8 mN/m, Phosphate-buffered saline (PBS) with surface tension of 69.5 mN/m, and silicon-oil with surface tension of 20.9 mN/m. The intrinsic contact angle of three tested liquids on a smooth SU-8 surface is measured, such as DI water of ~81.3°, PBS of ~72.7° and silicon oil of ~0°, as shown in figure 5(a1), figure 5(a2) and figure 5(a3), respectively. Figure 5(b1), figure 5(b2) and figure 5(b3) shows the testing results of liquid repellency on the re-entrant structures. The surface with re-entrant structures successfully suspends the tested wetting liquid (i.e. DI water and PBS). Figure 5(c1), figure 5(c2) and figure 5(c3) show the testing results of liquid repellency on the doubly re-entrant structures. The surface with the doubly re-entrant structures successfully suspended all the tested liquid, even the completely wetting liquid (i.e. silicon oil, ~0°).

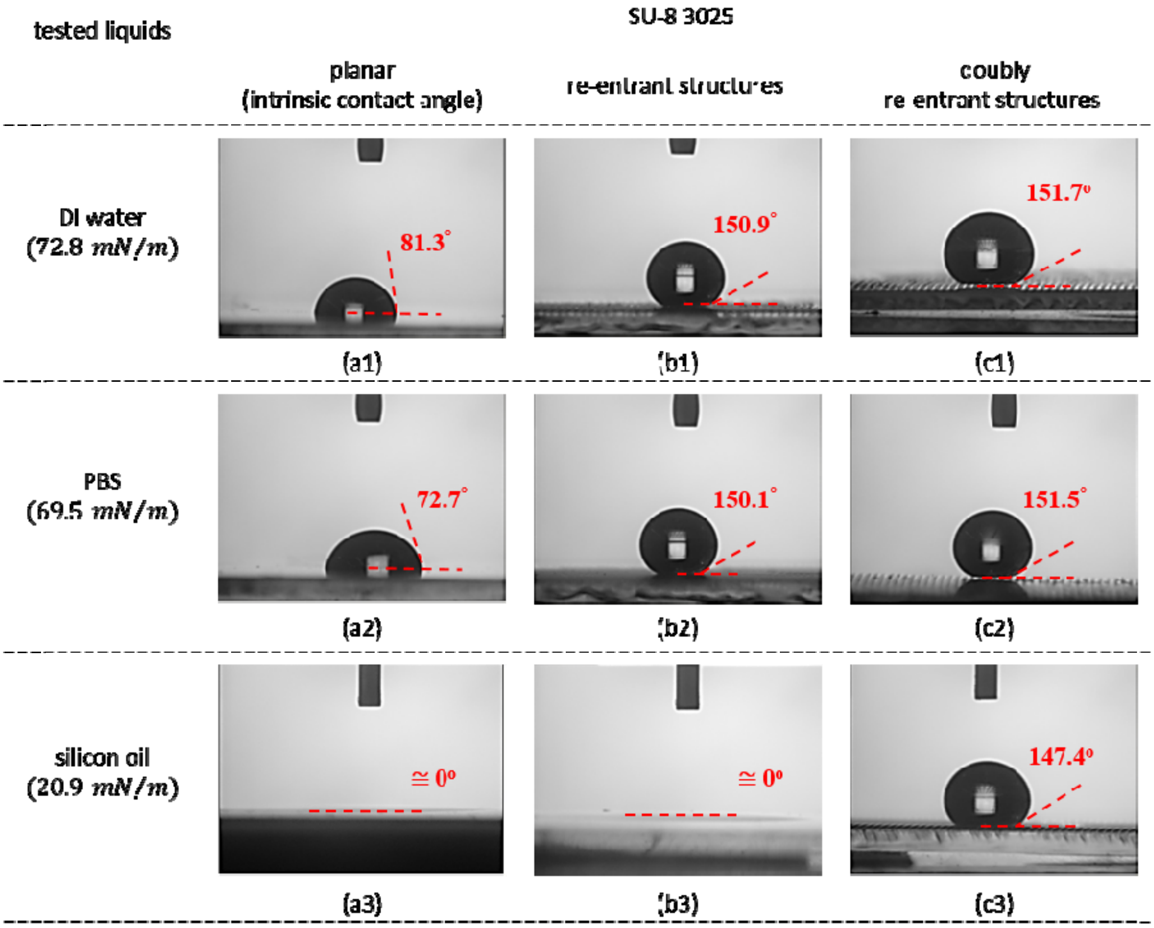

Figure 5: Testing results of liquid suspension and comparison.

CONCLUSIONS

This investigation proposes a simple approach to fabricate a transparent superomniphobic surface with the doubly re-entrant structures by using the negative thick photoresist SU-8 as the material. A gray-tone mask with three difference thicknesses metal is fabricated for modulating exposure dosage. By using gray-tone lithography, the doubly re-entrant structures can be formed only via a standard lithography process. For comparison, a surface with re-entrant structures is also fabricated by similar method. The surface with re-entrant structures successfully suspends the tested wetting liquid (i.e., DI water with intrinsic contact angle of 81.3° and PBS with intrinsic contact angle of 72.7°). The surface with the doubly re-entrant structures successfully suspended all the tested liquid, even the completely wetting liquid (i.e., silicon oil with intrinsic contact angle of ~0°). This approach provides a simple, flexible and low-cost solution to fabricate the structured superomniphobic surface without any other process (i.e., depositing hydrophobic material), and it also has the potential to integrate with either flexible or nonflexible substrate for different applications.

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