A SIMPLE FABRICATION METHOD FOR DOUBLY REENTRANT OMNIPHOBIC SURFACES VIA STRESS INDUCED BENDING

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ABSTRACT

We developed omniphobic, doubly reentrant surfaces fabricated with a simple method suitable for use with traditional microfabrication processes. Intrinsic stresses in deposited layers of silicon nitride induced bending of a singly reentrant microstructure, creating the doubly reentrant geometry. Due to the use of standard microfabrication processes, this approach may be extended to a variety of materials and feature sizes, increasing the viability of applying omniphobic doubly reentrant structures for use in areas such as superomniphobicity, anti-corrosion, heat transfer enhancement, and drag reduction.

INTRODUCTION

Doubly reentrant microstructures enable omniphobic surfaces that repel even completely wetting (i.e., low surface tension) fluids without the use of low-surface-energy coatings [1-3]. Such surfaces have use in a range of applications such as anti-fouling[4], chemical shielding [5], heat transfer enhancement [6], drag reduction [7], self-cleaning [8], and water purification [9]. In order to achieve omniphobicity, reentrant microstructures with characteristic length smaller than the liquids capillary length are required [1]. The level of reentrance necessary depends on the fluid's intrinsic contact angle, θ , with the surface material (Figure 1a). The black arrow in the figure represents the contact line force. In order for liquid to be repelled, a component of the contact line force must act in the vertical direction. Therefore, a regular microstructure without reentrance only repels liquids with $\theta > 90^\circ$. This large intrinsic contact angle is not possible for many liquids on solid surfaces or requires chemical modification for many others. Adding reentrant geometry can reduce the necessary contact angle to below 90° . However, for a small θ , the vertical component of the contact line force is also small, making it difficult to repel highly wetting liquids. Therefore, to repel all liquids, including those with a small contact angle, a large degree of reentrance is required (i.e., doubly reentrant), which has been difficult to fabricate at the necessary characteristic length scales (100s of microns or smaller). Due to these difficulties, the fabrication of doubly reentrant surfaces has been limited in materials used, i.e., specialized polymers [2], or required complex fabrication techniques, i.e., high temperature

Figure 1: Types of microstructures along with corresponding intrinsic contact angle, θ , for which the structure can practically repel liquid. The black arrow represents the contact line force that prevents liquid from entering the structure, which must act in the vertical direction in order to repel the liquid. To successfully repel liquids with low contact angle, doubly reentrant surfaces are necessary.

oxidation of silicon (not suitable for other materials) and multiple etch steps [1].

In this work, we developed a simple fabrication method using traditional microfabrication processes and demonstrated omniphobicity of the surface. The method relies on intrinsic stresses of deposited materials to induce bending of singly reentrant structures to create doubly reentrant geometry. Because this fabrication technique is based on singly reentrant surfaces, for which robust, scalable processes are already well-developed [10-12], it enables simple fabrication of doubly reentrant structures for a wide variety of materials.

RESULTS

The level of double reentrance, α , influences the component of contact line force that acts in the vertical direction, F_y , which prevents liquid from entering the structures and maintains omniphobicity. Figure 2 shows the vertical component of F , for different θ and α , normalized by the theoretical maximum that occurs when the force is completely vertical, $F_{y,max}$, and is defined as:

$$F_{norm} = \frac{F_y}{F_{y,max}} = \frac{P\gamma \sin(\theta + \alpha)}{P\gamma} \quad (1)$$

where P is the length of the contact line (determined by microstructure geometry), and γ is the surface tension of the liquid. If the sum of θ and α is greater than 90° , then $F_{norm} = 1$ due to the fact that a maximum occurs in F_y for a contact angle below the intrinsic value, which is still a stable state. This is why the curves for different θ reach a stable value of 1 with increasing α . This figure highlights a number of key points. First, in order to produce adequate repellency of fluids with $\theta = 0^\circ$, α must be larger than 0 . Second, the repellency force increases with α , which creates a more

Figure 2: The normalized vertical component of the contact line force for different contact angle, θ , and level of reentrance, α . For a perfectly wetting liquid, α must be greater than 0° for the surface to have repellency. The maximum is reached when $\theta + \alpha = 90^\circ$.

robust omniphobicity, but reaches its maximum value when $\theta + \alpha = 90^\circ$. We note that though the maximum repellency is reached at $\theta + \alpha = 90^\circ$, a lesser value of α may still produce adequate repellency.

Figure 3 shows our fabrication process. Thin films of silicon nitride with intrinsic stresses were deposited on the polished silicon wafer with an STS PECVD system, which allowed stresses in the deposited material to be controlled (i). Next, features were defined with photolithography (ii). A 2.5 μm thick layer of Microposit S1823 was spin coated on the wafer and exposed using an MLA150 Maskless Aligner. The resist was developed in CD-26 for 90 seconds. Structures were then etched with DRIE (iii). An STS ICP RIE was used to etch the silicon nitride layers. Subsequently, an SPTS Rapier DRIE was used to etch the underlying silicon. Finally, an isotropic silicon etch was used to undercut the thin films of silicon nitride (iv). Both XeF_2 and SF_6 were successfully used for the isotropic etch due to the etch selectivity between silicon nitride and silicon. Due to the intrinsic stresses in the nitride films, tunable bending (based on film thickness, stress, and undercut distance) occurred and formed the doubly reentrant surface.

Figure 3: Fabrication method of doubly reentrant structures. i: Deposition of films with tensile and compressive stress. Silicon nitride was deposited with PECVD in this study. The film stresses induce bending in the final fabrication step to create the doubly reentrant geometry. Stresses and film thicknesses were chosen based on modeling of the bending ii: Etch mask defined using standard photolithography. iii: Deep reactive ion etch (DRIE) of structures. iv: Isotropic silicon etch with SF_6 in the DRIE to create doubly reentrant feature due to stress induced bending.

Figure 4a shows a cross-section SEM of a fabricated doubly reentrant stripe-textured hoodoo (type of reentrant surface with parallel lines as features) surface with $\alpha = 62^\circ$. The bottom film of silicon nitride was 100 nm thick and low stress (less than 50 MPa), while the upper layer was 100 nm and had compressive stress (763 MPa measured using an FLX-2320 S), which induced the bending. Finite element analysis was used to choose the necessary film thicknesses, stresses, and geometry (Figure 4b) to achieve a high level of double reentrance, and showed reasonable agreement with fabricated surfaces. For stresses achievable in PECVD silicon nitride, this required the length, L , of the undercut to be between 10 and 100 times larger than the combined thickness of the deposited films. This ratio between film thicknesses and undercut length is a key parameter and will vary depending on material choice.

Figure 4: a: Cross-section SEM of the fabricated doubly reentrant ($\alpha = 62^\circ$) stripe-textured hoodoo surface. b: COMSOL model used to predict surface bending based on stresses and film thicknesses. This model determined the necessary stresses and thicknesses to realize a doubly reentrant surface with significant bending. For silicon nitride, this required the ratio of the length of the feature undercut, L , to the combined film thicknesses to be between 10 and 100, where 100 is shown in this figure.

We characterized the apparent advancing and receding contact angle of the fabricated surface for a variety of liquids using the experimental setup depicted in Figure 5. A syringe was used to add and remove liquid from a droplet on the surface. A collimated light source behind the droplet illuminated it while a DSLR camera recorded video as the droplet grew and shrunk. The video was then used to extract the advancing and receding contact angles in ImageJ.

Figure 5: Schematic of experimental setup for characterizing contact angle. A syringe is used to add and remove liquid from a droplet on the surface, creating an advancing and receding contact line, respectively.

Images of the apparent advancing contact angle of both water, with a surface tension of 72.8 mN/m and FC 40, a common refrigerant with a very low surface tension of 16 mN/m, are shown in Figure 6. Due to the double reentrant structures and surface omniphobicity, both fluids were repelled regardless of the liquid surface tension.

Figure 6: Images of advancing contact angle on the stripe-textured hoodoo surface, both parallel and perpendicular to the stripe for both water and FC 40. Both fluids were repelled due to the surface omniphobicity.

Advancing and receding contact angle measurements were conducted for liquids with a wide range of surface tensions (FC-40, ethanol, isopropanol, ethylene glycol, and water) in Figure 7. The observed contact angles agree well with theoretical values [11]. For the stripe-textured hoodoo surfaces the advancing contact angle perpendicular to the stripes, $\theta_{adv,perpendicular}$, is given by:

$$\cos\theta_{adv,perpendicular} = -1 \quad (2)$$

which gives an expected value of 180° . The observed values are slightly lower due to vibrations in the laboratory causing the droplets to partially relax. The advancing contact angle parallel to the stripes, $\theta_{adv,parallel}$, is given by:

$$\cos\theta_{adv,parallel} = r\phi\cos\theta - (1 - \phi) \quad (3)$$

where r is the roughness of the wetted solid (taken as 1 in this work due to the thin nitride films), and ϕ is the local areal solid fraction of the advancing droplet, 0.5 for the surface demonstrated here. This gives a predicted value of 90° , similar to the experimentally observed values. Finally, the receding contact angle in both the parallel and perpendicular directions, θ_{rec} , is given by:

$$\cos\theta_{rec} = r\phi\cos\theta - (1 - \phi) \quad (4)$$

For the stripe-textured surface used here the predicted receding angle is the same as the advancing angle parallel to the stripes, leading to a low contact angle hysteresis, which is necessary for liquid shedding. Furthermore, due to the doubly reentrant geometry the fluid properties do not appear in equations 2 through 4. Therefore, measured contact angles in Figure 7 are independent of the liquid contacting the surface, which agrees well with observed values. The advancing contact angles on a flat silicon nitride surface are also shown. Despite the nearly perfectly wetting liquids used, they were still successfully repelled.

Figure 7: Apparent advancing and receding contact angle of liquids with different surface tension, γ , both parallel and perpendicular to the stripe. Receding angle was the same in both directions. Advancing contact angle on a flat silicon nitride surface is also shown. All fluids were repelled, highlighting the omniphobicity, which can only be achieved with doubly reentrant geometry.

We are currently working to demonstrate different material sets and types of reentrant geometry (other than stripe-textured). Though silicon nitride was used in this work, other materials also have controllable stresses (including metals, oxides, nitrides, and polymers) and are potential material choices. Table 1 lists a variety of materials and residual stresses observed in literature after growth/deposition with different techniques such as chemical vapor deposition (CVD), plasma-enhanced chemical vapor deposition (PECVD), magnetron sputtering, spin coating, and atomic layer deposition (ALD). Although this incomplete list represents candidate materials, further research should be done to determine necessary deposition parameters, how stresses in the films may evolve with time, as well as what α may be achieved. Furthermore, in order to fabricate the reentrant geometry, etch selectivity between the deposited material and the underlying substrate is necessary, which may limit material choices.

Table 1: Possible materials, deposition techniques, and residual stresses reported in the literature. A negative stress is compressive.

Material	Deposition Technique	Residual Stress [MPa]	Reference
Silicon nitride	PECVD	300 to -600	[13]
Metals	Sputtering	1000 to -2000	[14]
Parylene	CVD	50 to 20	[15]
Polyimide	Spin coat	30	[16]
Aluminum Oxide	ALD	500 to 200	[17]

CONCLUSIONS

This fabrication procedure simplifies the ability to create doubly reentrant surfaces. Stress induced bending of singly reentrant geometry into doubly reentrant geometry was achieved by relying on intrinsic stresses of deposited silicon nitride films. Finite element analysis (FEA) was used to predict the necessary stresses, film thicknesses, and undercut length, L , to achieve a high level of reentrance. A stripe-textured hoodoo surface was fabricated and

good agreement was observed with the FEA model. Due to the high level of reentrance achieved ($\alpha = 62^\circ$), the fabricated surface was able to repel all tested liquids with surface tension ranging from 16 to 72.8 mN/m, including liquids with very small intrinsic contact angle on silicon nitride. Furthermore, the observed contact angles matched well with predicted values based on previously developed models. Due to the use of standard microfabrication processes, the process developed here expands the potential materials sets, and widens the potential application of doubly reentrant omniphobic surfaces.

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