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Characterization of ultrahydrophobic hierarchical surfaces fabricated using a single-step fabrication methodology

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Abstract

Hydrophobic surfaces with microscale roughness can be rendered ultrahydrophobic by the addition of sub-micron scale roughness. A simple yet highly effective concept of fabricating hierarchical structured surfaces using a single-step deep reactive ion etch process is proposed. Using this method the complexities generally associated with fabrication of two-tier roughness structures are eliminated. Three two-tier roughness surfaces with different roughness parameters are fabricated and tested. The surfaces are characterized in terms of static contact angle and roll-off angle and are compared with surfaces consisting of only single-tier microscale roughness. The evaporation characteristics of a sessile droplet on the hierarchical surfaces is also assessed relative to comparable single-roughness surfaces. The robustness of the new hierarchical roughness surfaces is verified through droplet impingement tests. The hierarchical surfaces exhibit very high contact angle and lower contact angle hysteresis compared to the single roughness surfaces and are more resistant to wetting. The energy loss during impact on the surfaces is quantified in terms of the coefficient of restitution for droplets bouncing off the surface.

Keywords: hierarchical surface, ultrahydrophobic surface, single-step fabrication, hysteresis, evaporation, impingement, coefficient of restitution

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1. Introduction

The contact angle of a liquid droplet on a surface is determined by the surface energy as well as the surface morphology [1]. The morphology of the surface determines whether a droplet will remain in a Cassie (non-wetting) or a Wenzel (wetting) state (Figure 1a and Figure 1b, respectively). Dynamic switching from the Cassie to the Wenzel state can be attained by means of electrical actuation [2-5], application of pressure on the droplet, or dropping the droplet from a height [6]. Superhydrophobicity may be imparted to a surface by carefully engineering the surface topology and controlling the ratio of areas of the top surface of the pillars to the total base surface (ϕ), thereby controlling the extent of the liquid-air interface [7].

Ultrahydrophobic surfaces are non-wetting surfaces characterized by high contact angles ($> 150^\circ$), a low sliding angle, and low contact angle hysteresis (CAH) [8-11]. A large droplet contact angle is not the sole criterion to characterize the superhydrophobicity of a surface. It is important to design surfaces such that they are also robust enough to prevent impalement by droplets. A higher capillary pressure enhances the robustness of the air gap between the roughness elements of a surface [12]. Very high contact angles can be obtained by increasing the liquid-air interfacial area when a droplet is placed on the surface, *i.e.*, by increasing the air gap between the roughness elements. At the same time, an increased air gap results in reduced capillary pressure with a corresponding reduction in the external actuation force required for the Cassie to Wenzel transition. Transition of a droplet to its Wenzel state significantly increases the drag force incurred in transporting the droplet on the surface. Surfaces must therefore be optimized such that they sustain high contact angles with a low contact angle hysteresis, without compromising the capillary pressure of the surfaces. Sub-micron scale roughness coupled hierarchically with microscale roughness can render a surface ultrahydrophobic and impart improved non-wetting properties relative to single-tier roughness. Hierarchical roughness is commonly encountered in nature; the extreme water-repellent characteristic of lotus leaves arises from a double-roughness structure consisting of nanoscale waxes on microscale bumps [13].

Figure 1. Schematic illustration of droplet wetting states: (a) Cassie, and b) Wenzel.

Surfaces with such extreme hydrophobicity have important applications in the development of artificial self-cleaning surfaces and developing water-proof clothing [14] and offer a wide range of promising applications including their use in microfluidic-based technologies such as lab-on-chip devices, microelectromechanical systems (MEMS), and microarray biochips. An important heat transfer application lies in the development of surfaces for dropwise condensation. Dropwise condensation is desirable since the associated heat transfer coefficient is an order of magnitude higher than that with filmwise condensation. Dropwise condensation is, however, not readily achieved on single-tier roughness structures [15]. It was recently demonstrated that condensation on hierarchical roughness structures leads to condensation in the form of drops [16]. Since hydrophobic surfaces resist the formation of a liquid film, surface corrosion is also mitigated.

The wide range of applications of hierarchical hydrophobic surfaces has encouraged active research in this field. Different methods of fabricating such hierarchical surfaces [8, 17] to attain ultrahydrophobicity have been demonstrated in the literature. Fabrication of double-roughness structures typically involves the fabrication of the larger features on a substrate (by standard lithography methods) followed by the deposition of smaller roughness elements on these larger features [8, 17, 18]. Efforts at fabricating and testing robust superhydrophobic surfaces which can be easily fabricated and commercially used continue to be reported.

Analytical and experimental research has corroborated the strong effect of surface morphology on the impact behavior of a water droplet and its ability to bounce off the surface [14, 19-22]. Jung and Bhushan [14] demonstrated better water repellency on hierarchical surfaces as compared to single roughness elements. They formulated an expression for the critical velocity of the droplet (based on the Laplace pressure and Bernoulli pressure) beyond which it transitions to a Wenzel state on textured surfaces. Varanasi *et al.* [12] developed a pressure-balance model to arrive at a condition for droplet infiltration into the air gap between the surface structures. Denser textured surfaces were expected to provide greater capillary pressure and superior resistance to Wenzel wetting of impacting droplets.

The evaporation of a sessile droplet placed on a surface (and the transient evolution of the droplet shape) is influenced by its wettability as well its roughness. A comprehensive study of droplet evaporation on a hydrophilic surface and superhydrophobic single-roughness structures was reported by Dhavaleswarapu *et al.* [23] and McHale *et al.* [24], respectively. On both kinds of surfaces, the droplet was shown to follow three distinct phases while it evaporates: constant contact area mode, constant contact angle mode in which the contact angle remains almost fixed and the droplet interface slides, and mixed mode in which both the contact angle and the contact radius changes. Droplet evaporation on superhydrophobic lotus leaves and biomimetic polymer surfaces [25] has been reported to follow the constant contact angle mode in which the contact area also remains almost constant and there is a linear decrease in the height of the droplet till it evaporates. The droplet characteristics during evaporation are in fact dependent upon the contact angle hysteresis of the surface rather than the initial contact angle of the droplet [26].

The present work offers a one-step fabrication methodology for hierarchical, two-tier roughness surfaces. This methodology eliminates the complexities of producing the second sub-micron roughness layer. Pillars of square cross-section are carefully engineered so that the single-roughness features inherently maintain the droplets in a stable Cassie state. The double-roughness surfaces are fabricated with the same primary roughness as the single-roughness pillars using a single step DRIE method. The hydrophobicity enhancement imparted by the second roughness layer is quantified by comparing the properties of the double-roughness (DR) surfaces to those of single-roughness (SR) surfaces. The static contact angle and the roll-off angle of millimeter-sized sessile droplets on such surfaces are experimentally determined and compared to the results from the corresponding single-roughness substrates. The behavior of the contact angle and the contact diameter during the evaporation of sessile droplets on both single- and double-roughness surfaces is investigated in the absence of surface heating. Droplet impingement experiments are then conducted on the double-roughness surfaces to test the robustness of their hydrophobicity. Droplet dynamics on the double-roughness surfaces are explored and compared with droplet behavior on surface with single-roughness elements.

2. Sample preparation and experimental set-up

2.1. Sample Preparation

The fabrication procedure developed in the present work circumvents the conventional two-step process to create double-roughness structures. Silicon pillars constitute the larger roughness element. Photoresist residue forms on the pillars during the DRIE process; this residue is in the form of $\sim 1 \mu\text{m}$ strands stacked on top of the silicon pillars and provides the second-tier roughness. The advantage of this method is that a double-roughness surface is obtained with a single deep reactive ion etching step. All fabrication for this work was carried out at the Birck Nanotechnology Center at Purdue University.

Silicon wafers with $1 \mu\text{m}$ thermally grown oxide layers were used as the substrates. A layer of positive photoresist AZ 1518 was spin-coated and lithographically patterned on the wafer. A wet-etch process is used to selectively etch the oxide layer from the surface. The oxide layer along with the photoresist acts as the etch mask for the deep reactive ion etch (Bosch) process. The Bosch process uses SF_6 for etching and C_4F_8 for the passivation steps. During etching the silicon is selectively etched to form the pillars. A higher passivation time and a lower O_2 gas flow during etching aids in retaining a fraction of the polymers formed during passivation. This results in the small roughness elements on the pillars which lead to the second-tier roughness. Table 1 lists the process parameters used for fabrication of the double-roughness surfaces. The etch rate for silicon was observed to be approximately $4 \mu\text{m}$ per minute. A minimum of 4 minutes of etch time was required for the formation of the second-tier roughness structures.

Table 1. DRIE process parameters.

Parameters	Value	
	etching	passivation
Switching time	5 sec	3 sec
Gas flow	450 sccm SF_6 15 sccm O_2	200 sccm C_4F_8
RF coil power	1500 W	1000 W

The surfaces are then spin-coated with 0.1% solution of Teflon-AF 1600 (DuPont, Wilmington, DE) in FC-77 (3M, St. Paul, MN) to impart hydrophobicity. The thickness of the Teflon layer is approximately 50 nm and hence the overall roughness of the primary roughness as well as the sub-micron roughness is not affected by the Teflon coating. The single-roughness surfaces SR-1, SR-2, and SR-3 used for comparison against the results from double-roughness surfaces are fabricated with the primary geometrical parameters held identical to those for the double-roughness surfaces DR-1, DR-2, and DR-3, respectively, using the negative photoresist SU-8 with standard lithography. The pillars are subsequently coated with Teflon to impart superhydrophobicity. The pillar geometry of the double-roughness surfaces fabricated is outlined in Table 2. The table also shows the two parameters utilized to quantify the primary surface roughness, namely, $\phi = \left(\frac{a^2}{p^2} \right)$ and $r_m = \left(1 + \frac{4ah}{p^2} \right)$, where a is the width of the square pillars, p is the pitch, b is the width of the air gap between the pillars such that $p = a + b$, and h is the height of the primary roughness elements. The dimensions of the pillars are chosen such that

the Cassie state is energetically more favorable [2]. Figure 2 shows SEM images of the double-roughness surfaces 1, 2, and 3.

Table 2. Parameters of the hierarchical surfaces.

Surface	Pillar size, a (μm)	Pillar pitch, p (μm)	Pillar height, h (μm)	ϕ	b/a	r_m	Sub-micron roughness, R_a (μm)
DR-1	27	42	32	0.41	0.56	2.96	0.33
DR-2	13	25	32	0.27	0.92	3.66	0.27
DR-3	33	47	32	0.49	0.42	2.9	0.33

Figure 2. SEM images of hierarchical surfaces a) DR-1, b) DR-2, and c) DR-3. The images to the right show the static shape of a 3 μl water droplet placed on the corresponding surface.

2.2. Experimental Setup

Deionized (DI) water droplets of volume $3 \mu\text{l} \pm 0.1 \mu\text{l}$ are used for all the characterization experiments (except the droplet impingement tests). The static contact angle of the droplets on the surfaces is measured using a goniometer (Model 590, Rame Hart), equipped with an automated tilt stage. For the droplet roll-off experiments, the stage is tilted slowly (0.8 deg/sec) to prevent inadvertent addition of momentum to the droplet. Images are simultaneously captured to analyze the advancing and the receding contact angles and the roll-off angle (α , the tilt angle at which droplet motion is initiated) of the droplet on the substrate (Figure 3). Three sets of tests are carried out on each substrate. The reported static contact angle is the average of the contact angles measured at five different locations on the substrate. The deviation in static contact angle is within $\pm 2^\circ$. The roll-off results are repeatable to within the standard deviation as described in a later section.

The droplet evaporation experiments help to characterize the behavior of the droplet contact line and the contact angle during evaporation on the hierarchical surfaces. Experiments are carried out without external heating under controlled temperature and humidity conditions of 21°C and 32%, respectively. A $3 \mu\text{l}$ droplet of water dispensed using a carefully calibrated microsyringe on to the test surfaces is visualized using the goniometer imaging system till it evaporates completely. A cold light source used for backlighting ensures improved contrast but does not affect the droplet evaporation rate. The contact diameter and the contact angle are measured during evaporation on the DR surfaces and compared to the evaporation characteristic of a droplet on the SR surfaces.

Finally, droplet impingement tests are carried out on the double- and the single-roughness surfaces to quantify the enhanced superhydrophobicity under impact imparted to the substrate by the secondary roughness layer. Droplet impingement was also tested with a smooth hydrophobic silicon substrate coated with Teflon to provide a baseline for comparison. A single droplet of volume $4.40 \mu\text{l} \pm 0.25 \mu\text{l}$ is released from a height of 10 mm and 100 mm by means of a high-precision automated dispensing system fitted with a micro-syringe as shown in Figure 4. The impact dynamics of the droplet are visualized with a high-speed camera (1024 Photron PCI) at 3000 to 3750 frames per second. As in evaporation experiments, backlighting is used along with a diffuser for improved contrast. The images are subsequently analyzed using MATLAB [27] and Image J (an image processing program available from the National Institutes of Health). The advancing and the receding interface of the droplet, as well as the velocity at which the droplet leaves the substrate, are tracked.

Figure 3. Schematic diagram of the sessile droplet and the angles measured.

Figure 4. Experimental setup for droplet impingement test.

3. Results and discussion

3.1. Static Contact Angle and Roll-off Angle

When a droplet gently placed on a substrate is in its Cassie state (Figure 1a), the static contact angle θ_c can be approximated using the Cassie equation [1] as

$$\theta_c = \cos^{-1}(-1 + \phi(1 + \cos \theta_0)) \quad (1)$$

where θ_0 is the Young's contact angle on the smooth surface (measured to be 120° for water droplet on a smooth surface coated with Teflon). Table 3 lists the predicted and experimentally observed static contact angles of the droplet on the single-roughness surface and the observed static contact angles on the double-roughness surfaces. Good agreement is observed between the theoretical contact angles from the Cassie expression (1) and the experimentally observed contact angles. The observed value of contact angle on the double-roughness surfaces is greater than 160° . This significant increase in the static contact angle of the droplet on the double-roughness surfaces relative to the single-roughness surfaces (Table 3) is the first proof of their enhanced ultrahydrophobicity due to the presence of the sub-micron features.

Table 3. Static contact angle measured on the test surfaces.

	Static contact angle	
	predicted	observed
SR-1	142 ⁰	142 ⁰ ± 3.5 ⁰
SR-2	150 ⁰	147 ⁰ ± 3.0 ⁰
SR-3	139 ⁰	144 ⁰ ± 2.0 ⁰
DR-1	–	161 ⁰ ± 2.5 ⁰
DR-2	–	160 ⁰ ± 2.0 ⁰
DR-3	–	161 ⁰ ± 1.5 ⁰

Before a droplet begins to move on an inclined surface, the droplet shape changes such that the forces acting at the triple contact line balance the gravitational force. The roll-off angle (α) decreases with an increase in droplet volume due to the increase in the gravitational force (mg) acting on the droplet [28]. Droplet roll-off experiments are carried out both on the double-roughness and single-roughness surfaces to determine the reduction in the contact angle hysteresis as well as enhancement in the roll-off characteristics due to the second layer of roughness. The capillary length of a water droplet defined as $\left(\frac{\gamma}{\rho g}\right)^{1/2}$ is equal to 2.7 mm. The

characteristic length scale (diameter) of the 3 μ l water droplet used in the experiments is approximately equal to 1.79 mm and is less than the capillary length. This implies that the effect of gravity can be considered negligible and the droplet assumed to be of spherical-cap shape [29]. Also, this results in the surface forces being more dominant in comparison to the gravitational forces in determining the rolling tendency of the droplets.

The roll-off angle is observed to be very high on the single-roughness surfaces. For SR-2 ($b/a = 0.92$), the roll-off angle is 51⁰ ± 3⁰, while for SR-1 ($b/a = 0.56$) and SR-3 ($b/a = 0.42$), the droplet did not roll off even at an inclination angle of 90⁰. For the very small droplets employed in the experiments, the gravitational force is unable to overcome the surface tension force acting at the triple contact line of the droplet. This is consistent with the observations of Varanasi *et al.* [12] who reported that for a b/a ratio less than 1, a 1 μ l droplet did not roll off. The test was repeated for SR-1 and SR-3 using a larger droplet volume of 5 μ l. In this case the droplet did roll off, but again, at a very high roll-off angle of 37⁰. For SR-2, the roll-off angle reduced to 32⁰ when a droplet volume of 5 μ l was used, which is consistent with the observation of Bhushan and Jung [28].

The droplet rolled off at a much lower tilt angle on the double-roughness surfaces. A 3 μ l droplet rolled off at an inclination angle of 8.3⁰ from DR-1, 9.5⁰ from DR-2, and 3.7⁰ from DR-3. Thus the presence of the secondary roughness layer reduces the roll-off angle drastically in all cases. Figure 5a shows a comparison between the roll-off angle of water droplets on the single roughness and double roughness surfaces. It is noted that 3 μ l droplets were used in all experiments, with the exception that a 5 μ l droplet was used for SR-1 and SR-3.

Figure 5. (a) The roll-off angle, and (b) contact angle hysteresis for the single-roughness surfaces (SR-1, SR-2, SR-3) and the double-roughness surfaces (DR-1, DR-2, DR-3).

Contact angle hysteresis refers to the difference between the advancing and the receding contact angles of a droplet and depends upon the surface roughness/irregularities. When the substrate is inclined, the advancing and receding angles of the droplet modulate so as to overcome the surface tension force acting at the triple contact line and the contact line pinning due to surface structures. This explains the lower contact angle hysteresis shown in Figure 5b for SR-2 which has a b/a ratio higher than SR-1 and SR-3. The contact angle hysteresis (CAH) provides an estimate of the energy loss due to impact/interaction with the structured surface. The CAH is reduced significantly; for the DR-2 surface, this reduction is by 12.4° for a droplet of $3\ \mu\text{l}$ volume (Figure 5b). The CAH is due to the pinning of the contact line on some of the sub-micron roughness features during initiation of rolling. The temporal evolution of the advancing and the receding contact angles on the double-roughness surfaces prior to roll-off illustrates that the advancing contact angle remains almost fixed at its static contact angle value while the receding

contact angle decreases prior to the droplet roll-off (Figure 6). For the single-roughness surfaces, the advancing contact angle increases while the receding contact angle decreases before the droplet starts rolling.

Figure 6. Temporal evolution of advancing and receding contact angles during roll-off on single-roughness surfaces (SR-1, SR-2, SR-3) on the left and double-roughness surfaces (DR-1, DR-2, DR-3) on the right.

3.2. Droplet Evaporation

The double-roughness surfaces were further characterized via droplet evaporation experiments under controlled environmental conditions without bottom heating as previously described. An initial droplet volume of 3 μl was used in all the experiments. The experimental observations are reported in terms of the non-dimensional contact diameter (normalized with respect to the initial contact diameter) and contact angle of the droplet as it evaporates. Figure 7a and Figure 7b show the time evolution of the evaporating droplet on SR-1 and DR-1, respectively. The experimental observation are reported in terms of the non-dimensional time τ ; $\tau = t/T$, where t is the time instant and T is the total time taken for the complete evaporation of the droplet.

Figure 7. Instantaneous images of an evaporating sessile droplet placed on a) SR-1, and b) DR-1.

The droplet evaporation on the single-roughness surfaces (SR-1, SR-2, and SR-3) occurred in three distinct phases: constant contact area mode, constant contact angle mode and the mixed mode (Figure 8a, Figure 9a) as discussed in [24]. In the first phase the droplet contact angle reduces while the droplet contact line is pinned. Subsequently the contact line is de-pinned; the droplet interface starts sliding with a constant contact angle. The interesting observation here is that sliding of the contact line begins when the contact angle is equal to the receding contact angle. This observation is similar to that in the case of hydrophilic surfaces [23] and smooth hydrophobic surfaces. For all the three surfaces under consideration this angle is in close agreement with receding angles obtained from the roll-off experiments (Table 4). In case of the single-roughness surfaces the droplet remains in the Cassie state while evaporating except at the very end of the process when the droplet enters the air gaps and goes into the Wenzel state. Such an effect is delayed with two-tier roughness.

On the double-roughness surfaces, the droplet evaporates in the mixed mode, that is, the contact diameter as well as the contact angle change continually during the entire evaporation process. The change in contact angle is minimal; on DR-2, the CA varies from 165° to 157° till $\tau = 0.87$, after which the contact angle rapidly reduces. For DR-1, the contact angle reduces to 142° (corresponding to $\tau = 0.89$) in contrast to the behavior of SR-1 in which the contact angle decreases to 125° within a time of $\tau = 0.41$. Hence the reduction in contact angle is smaller compared to that of the single-roughness surfaces (Figure 9, Figure 10). The contact diameter has a continuous sliding motion as illustrated by the time evolution of the surface profiles in Figure 8. The contact angle behavior is qualitatively similar to that observed on lotus leaf surfaces [25].

Figure 8 shows the superposed images of droplet profiles to illustrate the behavior of the wetted diameter of the droplet as it evaporates on the two different types of surfaces (SR-2, DR-2). As can be seen from Figure 8, the droplet contact diameter continuously shrinks while evaporating on the double-roughness surface, whereas the contact line is pinned during the first phase on the single roughness surface. The asymmetry in the latter case (SR-2) is due to pinning of droplet contact line on one side. Among the three double roughness surfaces considered in the

study, DR-2 exhibits the minimum resistance to sliding of the contact line while evaporating (Figure 10).

Table 4. Comparison of the contact angle corresponding to the initiation of sliding of droplet interface and the receding contact angle.

Single-roughness surface	Contact angle corresponding to contact line sliding during evaporation (deg)	Receding contact angle from roll-off experiments (deg)
SR-1	125	128
SR-2	133	129
SR-3	122	122

Figure 8. Evolution of the surface profile of an evaporating sessile droplet placed on a) SR-2 and b) DR-2 (the numbers represent the time instant in min).

Figure 9. Variation of contact angle and contact diameter with respect to non-dimensional time (τ) during evaporation on a) single-roughness and b) double-roughness surfaces.

Figure 10. Variation of contact angle with non-dimensional contact diameter on a) single-roughness and b) double-roughness surfaces.

3.3. Droplet Impingement Dynamics

Droplet impingement is the most demanding test of the water repellency of a surface under dynamic conditions. During droplet impingement on a structured surface the forces acting on the droplet that are responsible for wetting the air gaps are the Laplace pressure (P_L) and the Bernoulli or dynamic pressure (P_D), which can be written as

$$P_L = \frac{2\gamma}{R}$$

$$P_D = \frac{1}{2} \rho V^2$$

where γ is the surface tension of the liquid, R is the radius of the droplet, ρ the density of the liquid, and V is the velocity of the droplet just before impact. The capillary pressure (P_c) of the air gap in the surface offers the main resistance to droplet impalement of the surface and is inversely related to the space between the pillars

$$P_c = -\gamma \cos \theta_0 \frac{4a}{p^2 - a^2}$$

where θ_0 is the initial contact angle, a is the width of the pillars and p is the pitch. The transition criterion from the Cassie to Wenzel states upon droplet impingement is determined by the relative magnitude of P_c , P_L , and P_D . While surfaces with larger solid fraction (ϕ) have higher capillary pressure owing to the decreased air gap, the larger solid fraction also results in a lower contact angle and a lower roll-off tendency of the droplet on such surfaces as observed in the roll-off experiments. It is therefore essential to select an optimum value of ϕ while designing surfaces for higher contact angle and the required water repellency. The presence of a second layer of roughness elements helps enhance the static contact angle and water repellency of surfaces.

The study of droplet impact was carried out on the six superhydrophobic surfaces using droplets of volume $4.40 \pm 0.25 \mu\text{l}$ in all the tests and impingement heights of 10 mm and 100 mm. The relative importance of the kinetic energy of the impinging droplet and the surface tension force may be compared using the Weber number [22] defined as $We = \rho V^2 R / \gamma$. For the droplet impingement heights of 10 mm and 100 mm, We is equal to 2.8 and 27.6, respectively.

The behavior of the droplet upon impact can be understood based on two main stages. In the first stage, the droplet interface advances to attain the maximum wetted diameter. During this phase the kinetic energy of the droplet is stored as deformation energy in the droplet. In the second stage, the droplet retracts and the stored energy helps it rebound off the surface. The first stage (spreading of the droplet) is an inertia-driven phenomenon. Subsequent retraction and bouncing of the droplet off the surface is the basic test for the water repellency of the surface. Figure 11 shows images of the droplet at different instants when the droplet impingement height is 10 mm. For this impingement height with $We = 2.8$, the droplet bounced off both the single- and double-roughness surfaces, but there are differences between these sets of surfaces in terms of the contact angle of the droplet while it is retracting on the substrates, the contact time (total time the droplet is in contact with the substrate), and the droplet height attained after it bounces back.

Figure 11. Images of the droplet profile at different time instants upon impingement from a height of 10 mm on the (a) smooth hydrophobic surface, (b) SR-2, and (c) DR-2.

Figure 12 shows the temporal variation of the wetted diameter of the droplet when it is in contact with the surface corresponding to the impingement height of 10 mm. The time instant at which the droplet is just about to touch the substrate is taken as the initial time instant ($t = 0$). The droplet takes 2.67 ± 0.33 ms to reach its maximum wetted diameter irrespective of the surface parameters and the maximum wetted diameter is approximately equal to 1.2 times the droplet diameter as shown in Figure 12. However, the rate at which the interface of the droplet retracts before bouncing off the surface varies depending on the nature of the surface. This reflects the correlation between the contact angle hysteresis and the residence time of the droplet on the surface during impact. The droplet takes the least time to detach from surface DR-2 ($t = 10$ ms) and the contact time is maximum for SR-3 ($t = 12.3$ ms). The higher the CAH, the longer is the time the droplet takes to detach from the substrate. For tests with the 10 mm drop height, the droplet takes 12.27 ± 0.76 ms to bounce off the single-roughness surface whereas the time is reduced to 10.33 ± 0.67 ms for the double-roughness surfaces (DR-1, DR-2, DR-3). This difference is mainly attributed to the higher energy loss upon impact on SR surfaces (resulting from greater CAH) as compared to DR surfaces. As stated earlier, the hysteresis is greater when only one tier of roughness elements is present, with a correspondingly higher loss of energy. The contact time varies between surfaces and is slightly different from the characteristic time scale

(based on the balance between inertia and capillarity) given as $\tau = (2.6 \pm 0.1) \left(\frac{\rho R^3}{\gamma} \right)^{1/2}$ by

Okumura *et al.* [30]. The characteristic time scale for the droplet is 10.1 ms. The deviation from this time scale primarily in case of the single roughness surfaces is mainly because of the contact angle hysteresis on the surfaces. This is because the energy loss due to contact angle hysteresis is neglected in the derivation of the contact time. A more sparse distribution of pillars than those considered in the present work would yield contact times closer to the characteristic time scale due to the corresponding decrease in the contact angle hysteresis, as has also been observed by Li *et al.* [31].

Figure 12. Variation of the wetted diameter of the droplet on the SR and DR surfaces corresponding to the droplet impingement height of 10 mm.

The other difference between the single and double-roughness surfaces is observed in the contact angle that the droplet interface makes with the substrate while retracting, and the wetted diameter of the droplet just prior to detachment from the surface. Table 5 summarizes the contact angle and the wetted diameter of the droplet before it detaches from the double-roughness and single-roughness surfaces. The droplet bounces off the hierarchical surfaces at a much higher contact angle than in case of single-roughness surface, thus indicating a Cassie jump. This further explains the lower energy loss of the droplet upon impact on the double roughness surfaces. The lower wetted diameter and the lower contact angle prior to detachment indicates the pinch-off phenomenon on the single roughness surface (Figure 11a) which is not seen in case of the double-roughness surfaces.

Table 5. Contact angle and wetted diameter of the droplet prior to detachment from the substrate.

Double-roughness surface	Contact angle prior to detachment (deg)	Wetted diameter (mm)
DR-1	146.5	0.23
DR-2	144.7	0.27
DR-3	135	0.13
SR-1	124.4	0.20
SR-2	125.3	0.20
SR-3	113.9	0.13

The coefficient of restitution is defined as $COR = \sqrt{\frac{h_2}{h_1}}$ where h_2 is the height to which the

droplet bounces up and h_1 is the initial height from which the droplet is released. h_2 is given by the maximum distance between the center of mass of the droplet bouncing off the surface and the substrate. The coefficient of restitution of a surface is used as a quantitative measure of the reduction in energy loss of the droplet on the double-roughness surface. Figure 13 shows the maximum height attained by the droplet when it is dropped from a height of 10 mm on to the DR surfaces, SR surfaces, and a smooth surface (silicon wafer coated with Teflon). The droplet height follows a parabolic profile with respect to time after rebounding from the surface. The droplet oscillates in air (determined in terms of the position of its center of mass) after bouncing off the surface, suffering energy loss due to viscous dissipation as observed by Richard and Quéré [22]. A frequency analysis of the droplet oscillation in air can predict one primary oscillation frequency which varies according to the substrate; such analysis is, however, beyond the scope of the present study. The height h_2 reached by the droplet after impingement and the corresponding COR are shown in Table 6. The COR for DR-2 is 0.67, as compared to a value of 0.54 for SR-2 and 0.52 of SR-1. The droplet did not bounce off the smooth surface at the droplet impingement height of 10 mm (resulting in a COR of 0 for this surface). The higher coefficient of restitution on the double-roughness surfaces as compared to the single-roughness and the smooth surfaces illustrates their superior hydrophobicity. This is a cumulative effect of the reduction in the viscous dissipation of the droplet, and lower contact angle hysteresis during droplet retraction.

Figure 13. Maximum height attained by the droplet after recoil from the surface for a droplet impingement height of 10 mm (t – instantaneous time; t_{contact} – time instant when the droplet just detaches from the substrate).

Table 6. Droplet impingement summary on the textured surfaces.

Surface	Coefficient of Restitution		
	1	2	3
DR	0.66	0.67	0.62
SR	0.52	0.54	0.49

The droplet impingement experiments are repeated with the droplet being released from a height h_I of 100 mm, resulting in an impingement velocity of 1.4 m/s and a corresponding $We = 27.6$. Figure 14 shows the instantaneous images of droplet impact on DR-3 and SR-3 for this droplet release height; time t is defined as zero when the droplet is just about to touch the substrate. At this impingement velocity the droplet deforms significantly as it spreads on the surface. Figure 15 shows the temporal variation of the diameter of the droplet on surfaces 2 and 3, both for single- and double-roughness. As for the smaller release height of 10 mm, the droplet interface attains its maximum wetted diameter and then recedes. The droplet takes 2.27 ± 0.15 ms to reach its maximum wetted diameter in this case. This maximum wetted diameter on both single- and double-roughness surfaces is 2.3 times the initial droplet diameter, which is significantly larger than in the case of the shorter release height ($h_I = 10$ mm), where the ratio was

1.2. The subsequent retraction profiles of the droplet interface on the single- and double-roughness surfaces are, however, different, and the secondary roughness on the DR surfaces serves to reduce the contact time.

Prior to bouncing off the surface, the droplet is highly elongated for $h_I = 100$ mm, and the non-uniform energy distribution in the droplet results in smaller droplets being detached from the elongated droplet while bouncing off the substrate. While the droplet bounces off completely from the double-roughness surfaces (at $t = 10.4$ ms for DR-3), a pinch-off is observed in the case of the single-roughness surfaces: a very small part of the droplet is stuck to the single-roughness surface (SR-3) as shown in Figure 14 at $t = 12.8$ ms. The higher retraction time (difference between the time instant of maximum spread and time instant when the droplet finally detaches from the substrate) on single-roughness surfaces, i.e., 8.13 ms on SR-2 and 10.53 ms on SR-3 compared to 6.73 ms on DR-2 and 8.13 ms on DR-3, indicates the reduction in total energy loss on the double-roughness surfaces fabricated.

Fragmentation occurs at the top of the droplet to form smaller droplets while bouncing off the substrate at this high Weber number ($= 27.6$). The smaller droplets formed (Figure 14) are released at a much higher velocity reaching a much larger height, and are not captured in the window size of the images. Hence the coefficient of restitution, which depends upon the final height of the center of mass of the droplet, is not calculated for this droplet release height.

SR-3

DR-3

Figure 14. Instantaneous images of droplet impingement for a droplet release height of 100 mm on (a) SR-3, and (b) DR-3.

Figure 15. Droplet wetted diameter corresponding to the droplet impingement height of 100 mm on (a) SR-2, and DR-2, and (b) SR-3, and DR-3.

4. Conclusion

A simple, one-step fabrication methodology for developing ultrahydrophobic double-roughness surfaces is presented. A single-step deep reactive ion etch method is employed to fabricate the hierarchical roughness structures; the second layer of roughness caused by the photoresist residue is stable and is an easy way to enhance the surface hydrophobicity. Significant improvement of the surface hydrophobicity is observed in terms of the non-wetting characteristics when the second layer of roughness elements is introduced as compared to surfaces with a single level of roughness in the form of micropillars. Larger static contact angles with a water droplet, smaller roll-off angles, and reduced contact angle hysteresis are demonstrated with the hierarchical surfaces relative to the single-roughness surfaces. The surfaces are also shown to better withstand the impact pressure from an impinging water droplet. A coefficient of restitution of approximately 0.65 is achieved with the double-roughness surfaces when the droplet impingement height is 10 mm. The double-roughness nature of the fabricated surfaces preserves the robustness of the air gap between pillars even under impingement of a droplet released from a height of 100 mm.

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