Hydrophobic Nanostructured Glass Surfaces
Using Metal Dewetting Process

by

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Submitted to the
Department of Material Science and Engineering
in Partial Fulfillment of the Requirements for the Degree of

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Department of Material Science and Engineering
May 5, 2017

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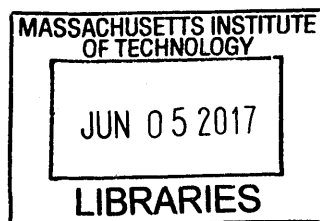
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ABSTRACT

This project aims to create a hydrophobic surface through a top down fabrication process of a nanostructure surface on a glass surface. The nanostructure is created through reactive ion etching utilizing silver as a mask. The silver mask is the result of a solid state thermal dewetting process which is controlled by varying the temperature and time of the process. Using this fabrication process, contact angles up to 137 degrees was achieved. Further surface modification resulted in contact angles exceeding 150 degrees. Superhydrophobic surfaces were made with the addition of a secondary roughness feature and the a PDMS coating.

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Introduction

When water falls onto a lotus leaf, it beads up and rolls right off picking up any dirt it encounters on the way. This self-cleaning property of a lotus leaf is known as the 'lotus effect'. The leaf's ability to repel water is due to its surface morphology (roughness) and chemistry (waxy coating). Using nature as inspiration, materials can be engineered to exhibit the lotus effect giving rise to surfaces with anti-fogging, anti-reflecting and anti-stick properties. There are many applications where such properties would be desired such as solar cells, roof tiles, water harvesting, separation technology, car windshields, satellite antennas and many more.

Background

Equilibrium state of a Droplet on a Surface

A surface is considered to be "wettable" when a liquid drop placed on it spreads over the surface. If the liquid instead beads up, the surface is considered to be "nonwettable". When this test is done with water, the wettable surface is considered hydrophilic and the nonwettable surface is considered hydrophobic.

The equilibrium shape of a liquid droplet on an ideal flat surface is governed by the surface free energies at the three phase interfaces of the droplet meets: the solid/liquid (γ_{sl}) interface, liquid/vapor(γ_{lw}) interface and solid/vapor (γ_{sv}) interface [1]. The balance of these forces per unit length (also known as surface tension γ) is given by Young's Equation (eqn. 1).

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} cos(\theta) \#(1)$$

where θ is the angle at which the liquid/vapor interface meets the solid. This is called the contact angle, which is often used as a measure of surface energy and surface wettability (Figure 1). A large contact angle characterizes a non-wetting surface in which the solid/gas interface has a low surface

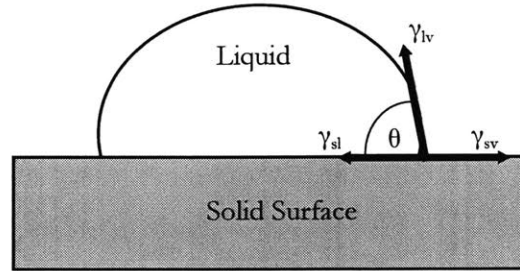energy whereas small angles characterizes a completely wettable surface which has a high surface energy.

Figure 1 The equilibrium shape of a liquid droplet on a surface with contact angle θ and the balance of 3 surface tensions at the interface

Surfaces with contact angles less than 90° are generally considered hydrophilic while those with contact angles greater than 90° are considered hydrophobic. If the contact angle exceeds 150°, then the surface is considered to be superhydrophobic. When tilted slightly water droplets will simply roll off a superhydrophobic surface. Just chemical modification of a surface using fluoropolymer coatings or silane layers can create water contact angles up to 120° [2]. To achieve a higher contact angle, there needs to be roughness in the structure of the surface [3].

A surface roughness or texture and its effect on contact angle are described by two models: the Wenzel and the Cassie Baxter. The Wenzel model describes a homogeneous wetting state where the water droplet penetrates into the grooves of the surface roughness while the Cassie-Baxter model describes a heterogeneous wetting state where the water droplet rests on both the solid substrate and air pockets [4]. For both models the water droplet must be sufficiently large compared to the scale of the roughness.

The Wenzel equation (eqn. 2) relates the apparent contact angle θ_W to Young's contact angle θ_Y. [5]

$$cos(\theta_W) = \frac{r\,\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} = r\,cos(\theta_Y)\ \#(2)$$

The roughness factor, r, is defined as a ratio of real rough surface area to the apparent nominal surface area. The real surface area is always larger than the nominal thus r is always greater than 1. Therefore, according to the Wenzel model any surface roughness will enhance both a hydrophilic surface and hydrophobic surface; making the hydrophilic surface more wettable and a hydrophobic surface less wettable.

The Cassie Baxter model states that on a rough surface air becomes trapped in the roughness grooves between the liquid droplet and the surface [5]. The trapped air prevents water from penetrating the crevices allowing the water droplet to rest partially on this air pocket (Figure 2b). The new contact angle θ_{CB} for this surface is defined in eqn. 3.

$$cos(\theta_{CB}) = r_f\, f\, cos(\theta_Y) + f - 1 \#(3)$$

where f is the fraction of the projected area of the solid surface that is wet and r_f is the roughness ratio of the wet area [4].
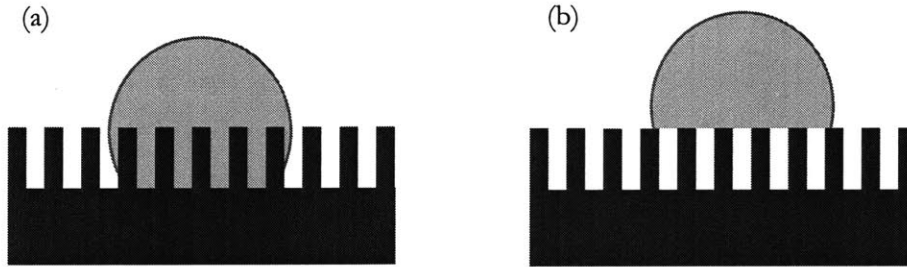

Figure 2 (a) Wenzel Wetting (b) Cassie-Baxter Wetting

The dimensions of the surface roughness features determine whether the Wenzel model or the Cassie-Baxter model will dominate the wetting state [6]. Murakami found that a surface roughness made of a pillar pattern with a low aspect ratio results in Wenzel wetting while a high aspect ratio resulted in Cassie-Baxter wetting. The Gibbs free energy of Wenzel wetting is lower than that of Cassie-Baxter wetting, so thermodynamically it is energetically favorable compared to Cassie-Baxter. However, there exists an energy barrier which makes the Cassie Baxter state meta-stable. The energy barrier can be overcome in a couple of ways: in a surface with low aspect ratio

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roughness, the droplet sags in the groove and touches the bottom substrate or the droplet becomes

unpinned and slides down due to increasing Laplace pressure inside the droplet [7].

Metal Dewetting

As deposited solid metal thin films are usually metastable. When heated to temperatures high

enough to overcome kinetics, these films will dewet or agglomerate to form isolated islands due to

the minimization of the total energy of the free surfaces of the film, substrate and the interface [8].

Dewetting can occur at temperatures well before the materials' melting point while the film remains

in the solid state as movement occurs via surface diffusion. [9] The process is dependent on the

material, temperature and film thickness.

Usually dewetting is an undesirable phenomenon in the fabrication and processing of

integrated circuits and nanosystems. However, sometimes there are applications that purposely use

dewetting such as particle arrays in sensors, catalysts formation and specifically for this project as a

template for patterning the substrate underneath.

The process of dewetting begins at holes (preexisting or formation of new ones) or at the

edge of the films. The rate of dewetting depends on the number of holes and the rate of growth of

the holes. Preexisting holes come from scratches, defects, containments or any other features found

on the substrate or created during the deposition process. New holes will form along grain

boundaries as grooves deepen and meet at places such as the grain boundary triple junctions [9].

Once a hole of critical size has formed capillary energies will grow the hole as the edges retract until

they eventually impinge and pinch off [9].

Materials Selection

Four metals were considered for this use in the metal dewetting process: silver, tin, copper

and gold. Tin and copper will oxidize in air upon heating so they were ruled out, leaving gold and

silver. Even though gold dewetting has been well studied, silver was ultimately selected because it

would make the process more cost effective. The substrate chosen for this process was fused silica because unlike tradition borosilicate glass, it does not contain the additives allowing for a higher etch rate.

Methods

Top Down Fabrication Process

The fused silica substrates were cleaned by a ten-minute sonication in acetone. A layer of silver was then deposited on the substrates using electron beam evaporation at a rate of 0.3nm/s. Each sample underwent a thermal dewetting process with a hot plate set at varying temperatures and times. Using the dewet silver as a mask, dry etching of the samples was done through reactive ion etching (RIE) using 30sccm CF_4 plasma at 100W RF power and 30mTorr. A five minute etch time was used to achieve approximately 150 nm etch depth with an etch rate of about 30 nm/min. This top down process is illustrated in Figure 2.
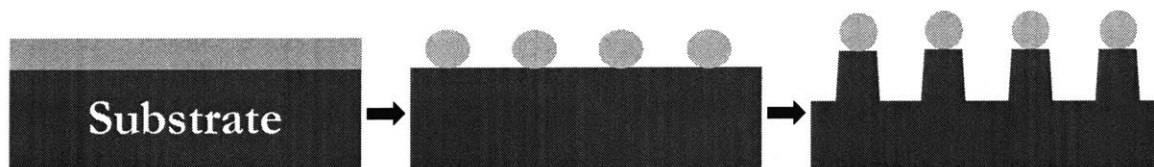
Characterization

Contact angle measurements are taken using the static sessile drop method. A drop of water is placed onto the surface and the contour of the drop is captured with a VCA Optima video contact angle system. A photo is recorded and the contact angle is then measured using VXE 2500 software.

Images of the surface were taken with a high resolution scanning electron microscope, a Zeiss Merlin at an acceleration voltage of 30 kV. The images were then processed using ImageJ to estimate area fraction of the surface.

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Results and Discussions

Mask Optimization

The etch mask was made from dewetting the silver film on the glass surface. To control the feature size of the mask, the temperature of thermal dewetting was varied from 120°C to 200°C in intervals of 20°C for 1, 2, 3, and 4 minutes. The resulting surface structures are shown Figure 5. These images are snapshot of the dewetting process at each temperature over time. At low temperatures such as 120 °C after one minute, the formation of holes is clearly seen and as time progresses the holes get larger in size and intersect. As the temperature increases while the time is held constant there is a similar pattern, after only one minute at 200 °C the area of growing holes are larger than that the silver area.
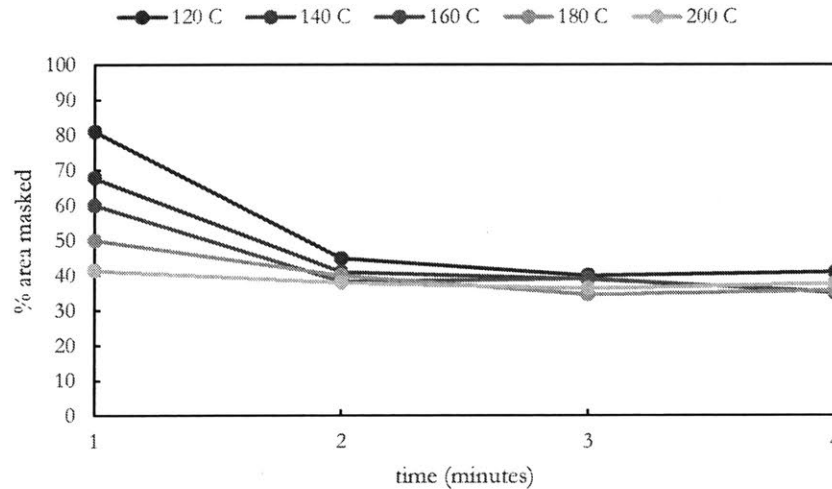

Figure 4 Percent of area masked of SEM images of sample surfaces processed under different temperatures conditions

Each SEM image was converted to a binary image and the 2D planar area of the silver regions over the total image area was calculated, which is the f value used in the Cassie-Baxter equation. As seen in Figure 4 and Figure 5 after the first minute the differences in the hole sizes and dewetting

progress is quite different across the five temperatures. As time progresses the differences get less pronounced and the ratio of silver area to the total area appears to stabilize around 40%.
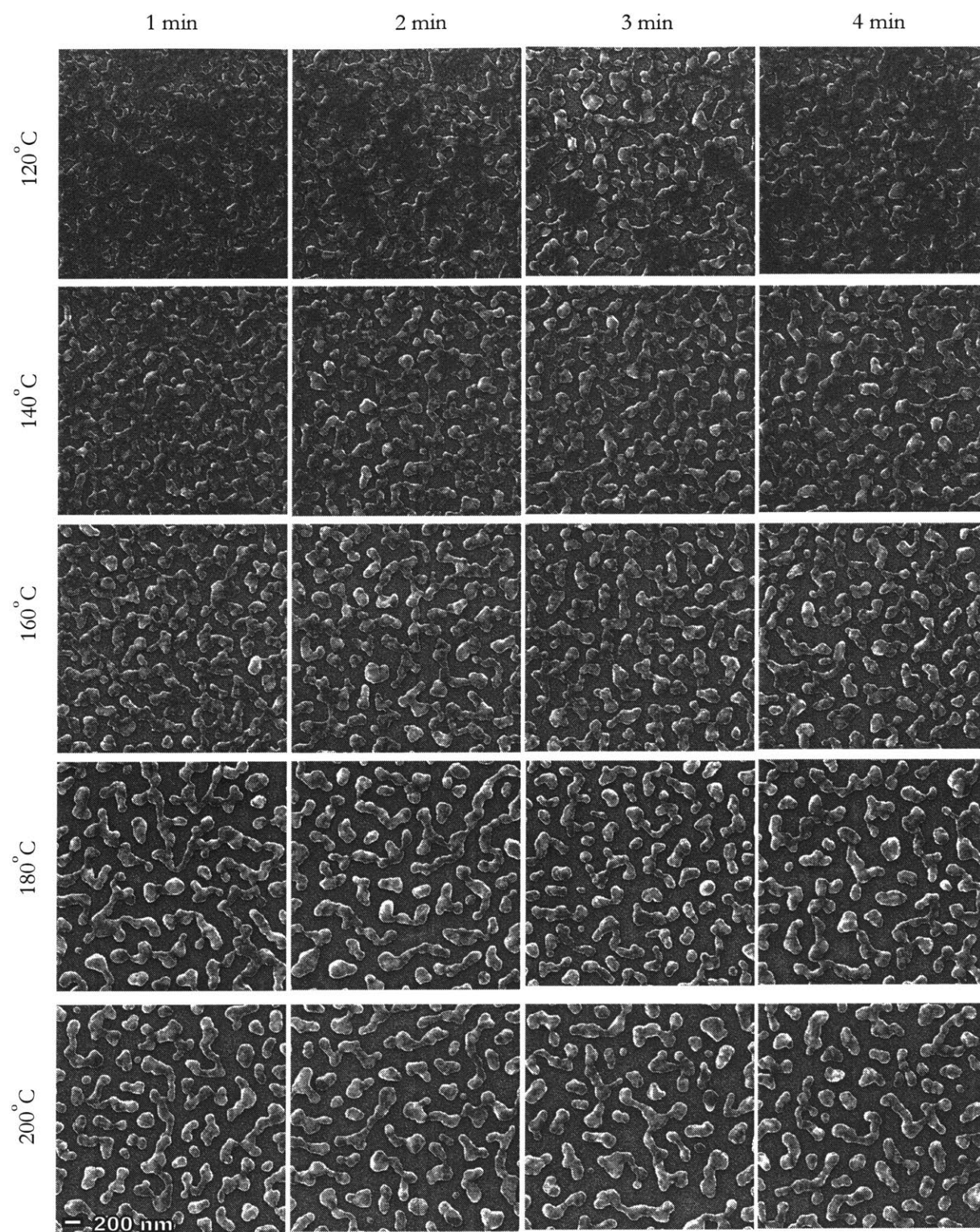
Figure 5 SEM images of the surface after thermal dewetting at 120ºC, 140ºC, 160ºC, 180ºC and 200ºC over a total of 4 minutes in one minute intervals.
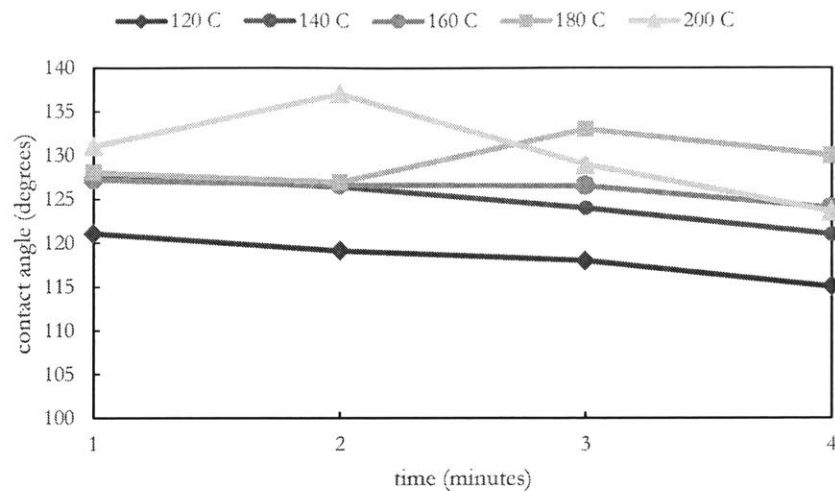
Figure 6 Contact angle measurements surface of samples after processing under different temperature and times settings

The contact angle of each of the 20 samples was measured on five locations in each sample and the average value plotted in Figure 6. The largest contact of 137° achieved was the sample heated at 200°C for 2 minutes. All samples had contact angles above 120° which is considered a decent hydrophobic surface. The 120 °C samples had the lowest contact angles and the 140 °C and 160 °C temperature samples gave very similar measurements. The average contact angle of uncoated fused silica as received was 46.3° and after only depositing 15 nm of silver the contact angle increased to 100.3 ° as seen in Figure 7. Keeping the silver mask on the surface increases the contact angle. Once the silver is removed, the contact angle will drop about 5-7 degrees.
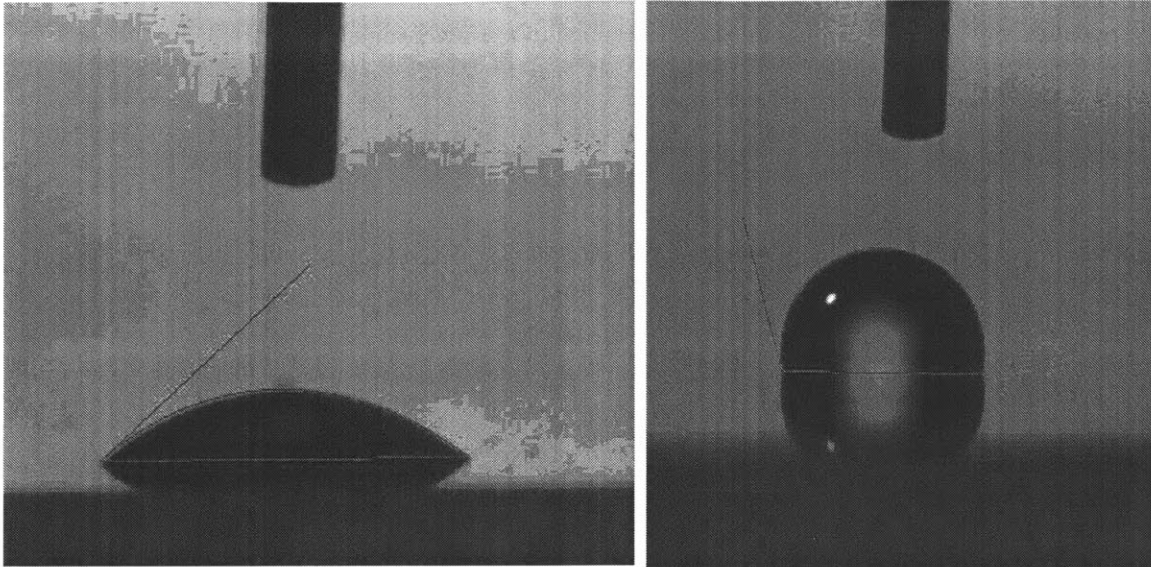
Figure 7 Left: Contact angle of 46 degrees on fused silica as received; Right: contact angle of 100 degrees after silver deposition

Secondary Roughness

To increase the hydrophobicity, a secondary roughness was added through two different methods. Prior to silver deposition, one sample was sandblasted to create a microscale roughness. Another sample was recoated and processed in the same manner. Figure 7and Figure 8 shows the resulting structures from a top and tilted view.
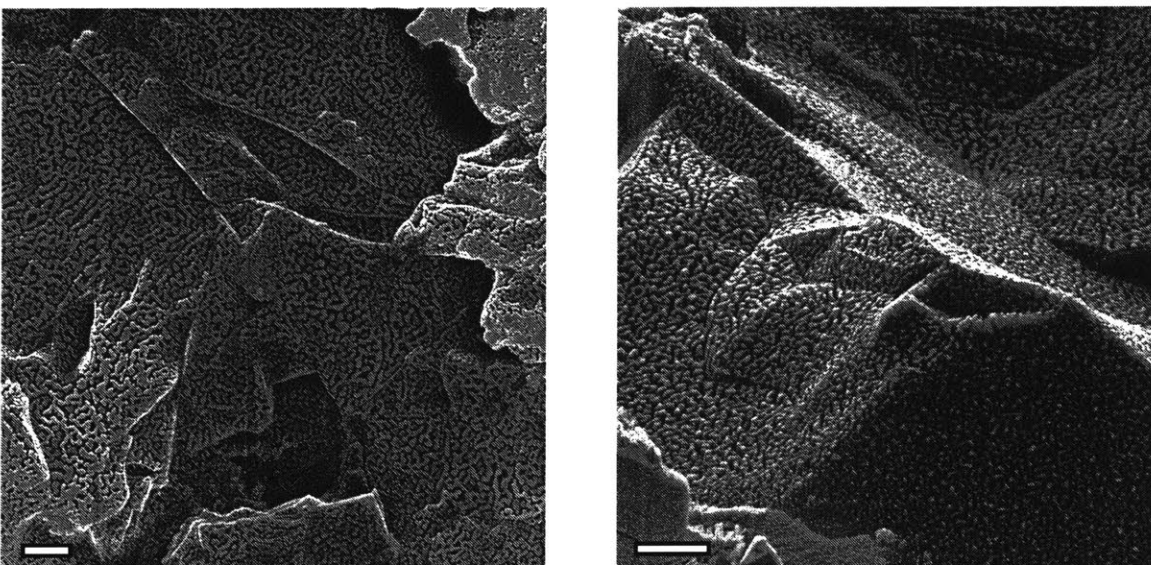

Figure 8 Left: Top down SEM image of surface after nanostructuring a sandblasted surface; Right: tilted SEM image of the same surface

The pretreatment of sand blasting the surface resulted in a contact angle of 140.5 which is about 10 degrees higher than without the pretreatment.
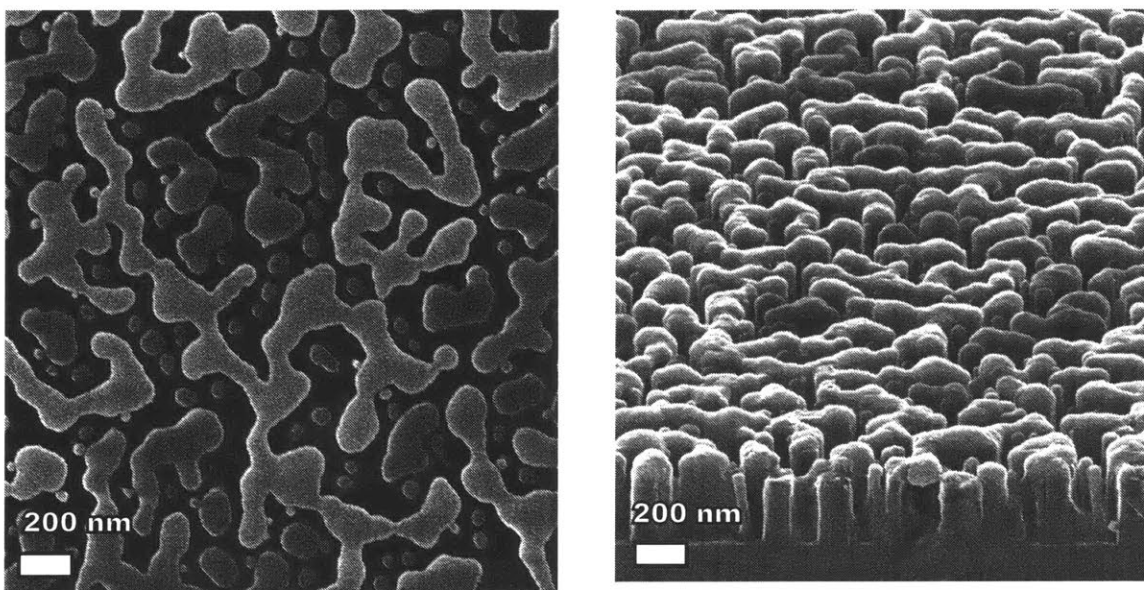

Figure 9 Left: Top Down SEM Image of the surface after a second structuring process; Right: Tiled SEM Image

The sample that was dewet at 200°C for 1 minute was selected for a second deposition and was dewet under the same conditions. The contact angle measured after the repeat processing were within the error of measurement (1-3 degrees) meaning it did not change the hydrophobicity of the surface.

Chemical Coating

A PDMS coating was added to the surface in an attempt to increase hydrophobicity even more. A solution of PDMS-OH with molecular weight of 0.8 kg/mol in toluene solution 1.5 wt% was applied to the surface through spin coating at 4,000 rpm. The sample was then annealed at 170°C for seventeen hours. As seen in Figure 10 the coating increased the contact angle of flat untreated fused silica by 64° going from 60° to 124°. A sample with a primary roughness created by dewetting the silver at 200°C for 3 min experienced an increase in contact angle of about 17° going from 125° to 142°. Finally, the sample with secondary roughness from sand blasting became

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superhydrophobic after the coating. So much so that the contact angle could not be measured since the water droplet would rather stay on the dispensing tip than the sample surface (Figure 10).
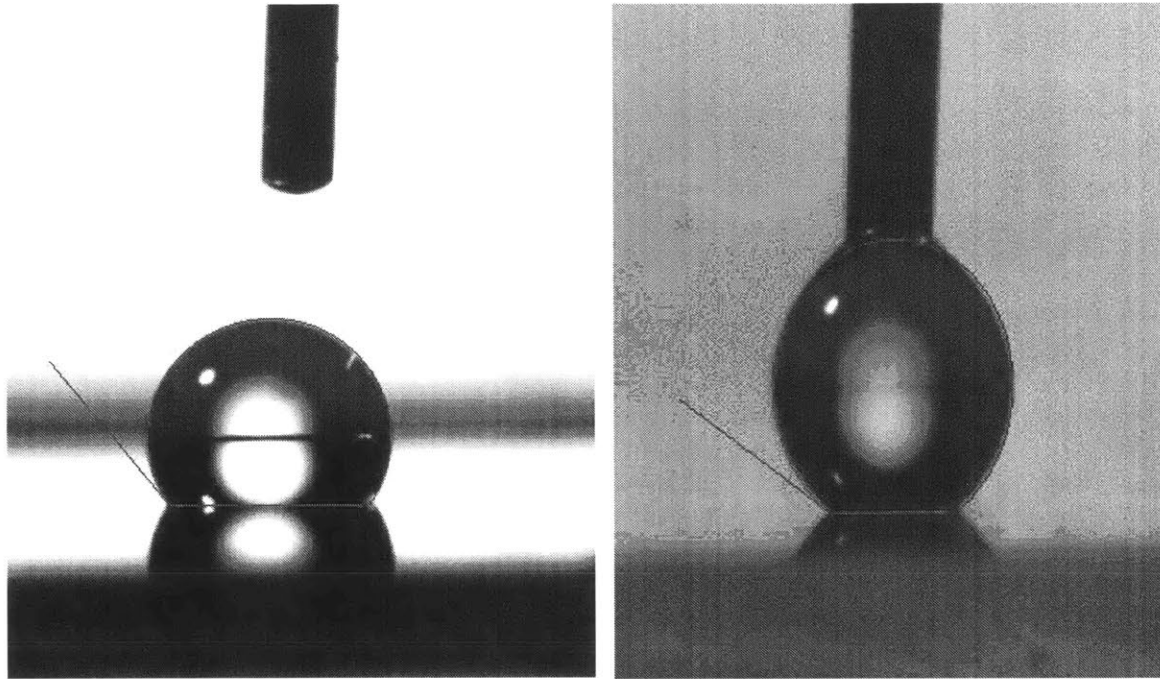

Figure 10 (a) surface with roughness before PDMS coating contact angle of 125 degrees (b) after PDMS coating contact angle of 142 degrees

Process Cost

This process of a top down fabrication method using a mask for surface patterning was designed to be a scalable, fast and lost cost method for structuring surfaces to possess hydrophobic characteristics. Silver costs about $485 per kilogram[1] . With a 15 nm thick coating it will be about $0.05 per meter squared. The cost of fused silica is $3 per meter squared. The dewet using a hot plate for a few minutes in air is minimal cost, which can be estimated to be about $0.15. Thus the total cost per meter squared is about $3.20. The processing time in total is only 40 minutes per run including the vacuum pump down times. The equipment used in processing are commonly found in the semiconductor industry (the deposition of silver need not be done with ebeam or high vacuum

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[1] price estimate from silverprice.org

sputtering machines; a simple sputtering device such as those used for SEM sample preparation would suffice). Additionally, there are numerous methods available for silver reclamation and thus can be reused.

Conclusions

A top down process utilizing silver dewetting produced hydrophobic surfaces. By adjusting the temperature and time of the dewet process of the silver thin film, the mask was optimized allowing the fabrication of a surface with a contact angle of 137°. The addition of a secondary roughness from sand blasting prior to processing produced a surface that was very hydrophobic with a contact angle of 140°. The surfaces were further improved with the addition of a PDMS coating making the surface superhydrophobic.

Further Work

Further study can be conducted on varying the thickness of the silver film and the resulting dewetted structure. The durability of the surface structure can be investigated and potentially improved through ion exchange or other methods. The optical properties of the nanostructured glass could also be explored. Finally, this process can be applied to different materials substrates. The cost of fused silica was the 93% of the estimated cost so modifying this process to work with borosilicate glass or plastic substrates would lower the cost significantly.

Acknowledgements

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