Applied Surface Science 303 (2014) 456–464

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Local wettability tuning with laser ablation redeposits on PDMS

Stijn van Pelt*, Arjan Frijns, Rajesh Mandamparambil, Jaap den Toonder

Department of Mechanical Engineering, Eindhoven University of Technology, The Netherlands

ARTICLE INFO

Article history:
Received 7 January 2014
Received in revised form 13 February 2014
Accepted 3 March 2014
Available online 12 March 2014

Keywords:
Excimer laser
Ablation
PDMS
Superhydrophobic
Redeposits
Sticky

ABSTRACT

In this paper, we present a method to locally control the wettability behavior of PDMS surfaces by excimer laser ablation. In the ablation process, a micrometer scale roughness is formed in the irradiated regions while a nanometer scale roughness is formed by the redeposits surrounding the irradiated regions. The increase in surface roughness results in a change of the wettability behavior of the PDMS surface. By using a hexagonal pattern and tuning the patterning pitch, two different wetting behaviors were realized. A pitch smaller than 300 μm resulted in a superhydrophobic surface with an advancing contact angle of $\theta_{adv} = 165^\circ$ and a receding contact angle of $\theta_{rec} = 160^\circ$. A pitch between 300 and 500 μm resulted in a sticky superhydrophobic surface with $\theta_{adv} = 120–150^\circ$ and $\theta_{rec} = 80^\circ$. The contact angle hysteresis for the latter was larger than for untreated PDMS resulting in very sticky surfaces with high sliding angles. This gives the method great versatility since the two wetting behaviors are very different. By combining both behaviors, local surface features like pinning sites, non-wetting sites, barriers and guides can all be fabricated by a single method. As an application demonstrator of the method, we show that drops can be caught and released depending on size and tilting angle by creating slippery surfaces with sticky barriers. Additionally, the method is ideal for rapid prototyping as it consist of only a single step. It is a direct write method requiring no lithographic mask. Also the process works in ambient atmosphere, so it can be used for temperature or pressure sensitive applications.

1. Introduction

Controlling the wettability of solid surfaces has been a topic that has received a lot of scientific interest lately. Surfaces are superhydrophobic when they have a strong water-repellency and water drops tend to easily roll off. This can be used to control for instance clogging, fouling, self-cleaning and condensation behavior. Many potential applications exist for this phenomenon: self-cleaning windows, clothing, microfluidics, etc. Methods to realize this behavior are often based on examples found in nature, like lotus leaves and certain butterfly wings [1].

A surface is considered superhydrophobic if it has a water contact angle of $\theta > 150^\circ$ [2]. Generally, high drop mobility is also associated with superhydrophobic behavior, meaning low hysteresis with a sliding angle of $\alpha < 10^\circ$ for drops of 5 μl. The sliding angle is defined by the minimal tilting angle of the surface for a drop to roll off. A drop that moves over a surface will have different contact angles at the front and back. This is defined by the larger advancing contact angle θ_{adv} at the front and the smaller receding angle θ_{rec} at the back. The contact angle hysteresis θ_{hys} is defined by the difference between the advancing and receding contact angle. The larger this hysteresis is, the less likely a drop will start to slide off a tilted surface [3].

Superhydrophobic surfaces have very low hysteresis so both the advancing and receding contact angle are >150° and the surface is "slippery". So called "sticky" superhydrophobic surfaces show very high advancing contact angles of $\theta_{adv} > 150^\circ$ but have a sliding angle of $\alpha > 10^\circ$ because of a large hysteresis [4,5]. This phenomenon requires a high surface tension for the solid–liquid interface. Superhydrophobic surfaces can be realized by increasing surface roughness at the micro/nano-scale, especially hierarchical geometries with elements of different length scales have been used [6].

Techniques that increase the contact angle of a surface are of chemical or geometrical nature or a combination of the two. Chemical techniques change the nature of the material that the drop comes into contact with, thereby increasing the surface tension of the interface. Methods include plasma treatment [7], sol–gel, fluorination [8], silanization, adsorption of polymer or proteins and lipid coatings [9]. However these methods are often complex, difficult to pattern and may not be stable on long time scales [10]. Geometrical techniques increase the surface roughness and thereby

* Corresponding author. Tel.: +31 402472186.
E-mail addresses: s.v.pelt@tue.nl, stijnovic@gmail.com (S. van Pelt).

http://dx.doi.org/10.1016/j.apsusc.2014.03.025

change the total surface area that the drop comes into contact with. It can result in the Wenzel [11] state where the liquid is in contact with the whole surface or in the Cassie-Baxter [12] state where air is trapped in the roughness features below the drop. Both states result in an increase of the apparent surface tension. Methods to create the surface topography include (soft) lithography and particle deposition. Lithographic methods offer the versatility to create a non-uniform wettability but are complex, time-consuming and expensive. Particle deposition techniques are simple but can only be used to create surfaces with uniform wettability.

Crick et al. [13,14] used an aerosol assisted deposition method to create a PDMS surface with a microscale roughness. By controlling the temperature of the substrate between 210 °C and 330 °C, they were able to control the geometry of the growing film. This resulted in static contact angles of up to 167°. The higher temperatures resulted in sliding angles of 10–15° whereas lower temperatures resulted in sticking drops even at 90° for drops of 60 μl. This process however is suitable for large surfaces. To make it local, laser modification could be used. Graubner et al. [15] report photochemical modification of PDMS by irradiation at 172 nm making it hydrophilic. Also they investigated PDMS modification by excimer laser ablation at different wavelengths, resulting in the formation of ablation products [16]. Jin et al. [17] showed an ablation process to make PDMS superhydrophobic using ablation patterning to change the surface microscale roughness. Wagterveld et al. [18] used a similar process on SU-8 but they added an additional plasma coating step after creating the microscale roughness by ablation. Yong et al. [19–21] have shown a similar process using femtosecond laser ablation to make PDMS superhydrophobic. They show control of both the contact angle and sliding angle between 110–160° and 1–90° respectively by changing the ablation parameters.

In this paper, we will present a single step method to fabricate both slippery and sticky superhydrophobic patterns on polydimethylsiloxane (PDMS) surfaces using an excimer laser. PDMS is often used in biomedical and microfluidic applications, but untreated it is only slightly hydrophobic. Using our method, special patterns can be made that can be used for wettability control and in particular for sophisticated drop manipulation, for instance by making local barriers, gradients or anisotropic patterns. As an application demonstrator of the method, we show that drops can be caught and released depending on size and tilting angle by creating slippery surfaces with sticky barriers. The method is ideal for rapid prototyping because it is a single step, direct write method.

2. Methods

2.1. Fabrication

PDMS resin (Sylgard 184) and curing agent were mixed in a 10:1 ratio. It was then mixed and defoamed using a Thinky ARE-250 mixer. The mixture was poured into a glass Petri dish to form 2 mm thick membranes. After baking overnight at 80 °C, the membranes were manually released using tweezers.

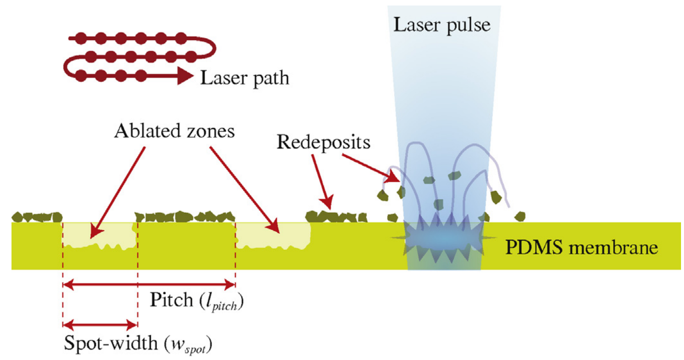


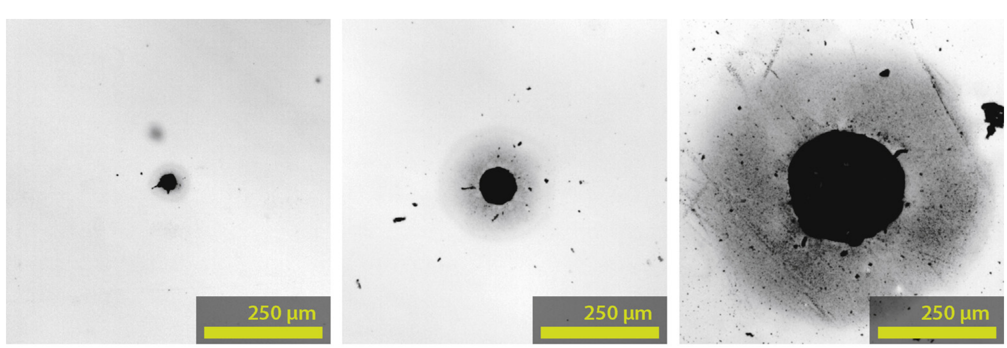
Fig. 1. Schematic of the ablation patterning process.

The PDMS samples were irradiated with an excimer laser operating at a wavelength of 248 nm, a pulse length of 20 ns, a pulse frequency of 150 Hz and a tophat beam profile. A mask was used to shape the beam, resulting in a circular spot. Ablations spots were formed on the PDMS surface, surrounded by redeposition areas. In Fig. 1, a schematic representation of the process can be found. The spot-width w_{spot} could be varied between 30 and 250 μm, see Fig. 2. The fluence was measured with a power meter, it fluctuated between 453 and 641 mJ/cm^2. To get a cumulative effect, multiple pulses were fired consecutively at the same location, this is defined by the number of shots per location n_{spl}.

Irradiation of the PDMS samples shows different stages. After 10–20 shots, chemical transformations become visible in the form of dark spots, see Fig. 3(a). Because of the low linear absorption coefficient (~2 cm^{-1}) [16] of PDMS at the wavelength of the laser, the light is absorbed evenly across the thickness of the irradiated sample. Therefore, the chemical transformations do not only take place on the surface. By further irradiation, these spots increase in size, thereby increasing the absorption. After 30–40 shots, the surface ruptures and redeposits can be seen in an area around the spot with roughly 3 times the radius of the spot, see Fig. 3(b). After further irradiation, more redeposition occurs but the irradiated zone shows no further visual changes, see Fig. 3(c and d).

After irradiation, redeposits of two different length scales can be found, see Fig. 4. The larger ones vary in size between 5 and 50 nm and are distributed randomly and far away from each other. The smaller redeposits vary between 50 and 500 nm and are densely packed, covering the entire redeposition surface.

Depending on the number of shots per location, the amount of redeposits varies. In Fig. 5 an indirect measurement of the roughness can be seen. This was done by comparing the grayscale levels



(a) spot-width: 30μm (b) spot-width: 75μm (c) spot-width: 250μm

Fig. 2. Optical micrographs of ablated spots with different spot-widths and 200 shots per location. The redeposition area is proportional to the spot-width.