

Super-hydrophobic and/or Super-hydrophilic Surfaces Made by Plasma Process

Lei Chen*, Gerard Henein, J. Alexander Liddle

Center for Nanoscale Science and Technology, National Institute of Standards and Technology
Stop 6201, 100 Bureau Drive, Gaithersburg, MD 20899, USA

*leichen@nist.gov

ABSTRACT

In this paper, a simple, fast, all-plasma surface modification (APSM) process, which can form super-hydrophobic and/or super-hydrophilic surfaces is introduced. The APSM process includes plasma-induced surface nano-pattern formation, substrate etching and surface chemical modification. By using this process, large area super-hydrophobic or super-hydrophilic surfaces can be fabricated easily. The wetting properties can be switched between super-hydrophobic and super-hydrophilic by simply changing the plasma chemistry. By using a stencil mask to selectively modify areas on the surface with different chemicals, both super-hydrophobic and hydrophilic areas can be created on a single surface. APSM is an environmentally friendly and economic process which can be used in a variety of applications.

Keywords: Super-hydrophobic, Super-hydrophilic, Plasma, Nano-pattern, Surface

A super-hydrophilic surface is a one with contact angle of water less than 5° while a super-hydrophobic surface is a one with contact angle larger than 150° . Those extreme wetting characteristics have opened up an entirely new field for manipulating and controlling the interaction of liquids with surfaces. Normal chemical surface modification cannot achieve super-hydrophobic and/or super-hydrophilic properties. Wenzel⁽¹⁾ and Cassie-Baxter⁽²⁾ first pointed out that it is possible to significantly enhance the wetting characteristics of a surface by introducing roughness at the right length scale. Based on these theories, a variety of approaches have been developed to roughen the surface with lithographically- defined micro/ nano structures⁽³⁾, micro/nano-porous⁽⁴⁾ and other surface textures. Both super-hydrophobic⁽⁵⁾ and super-

hydrophilic⁽⁶⁾ surfaces have been demonstrated by covering the textured surfaces with suitable chemicals^(5, 6). However, most of these processes are either too expensive, time consuming, require the use of harsh chemicals, or cannot be easily scaled-up to create large-area uniform surfaces.

Plasma induced surface pattern formation has been studied in our laboratory and other places⁽⁷⁾. In this study, a photo-resist (S1813) was spin-coated on a Si wafer. This polymer resist was then exposed to a fluorine (F) and oxygen (O) mixture plasma to induce polymer re-deposition on Si substrate.

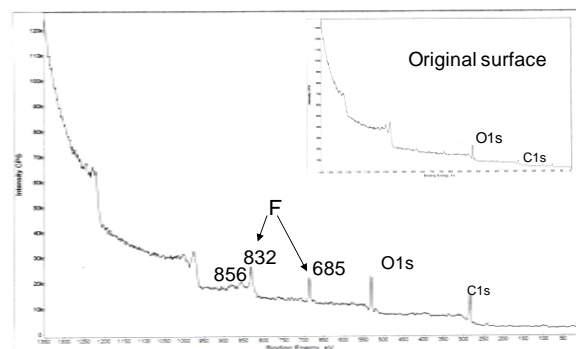


Figure 1. XPS spectra of the polymer surface treated by CHF_3 and O_2 plasma with the spectra of original surface as a reference.

X-ray photoelectron spectroscopy (XPS) analysis indicates that the chemical composition of the re-deposited polymer is different from the original polymer photo-resist thin film (figure 1). The new re-deposited polymer consists of carbon (C) and fluorine (F) species. In the plasma, the photo-resist surface can be activated by ion bombardment or F etching. The reactive polymer species can bond with the CF_x plasma species to form a new fluorinated polymer.

Atomic force microscope (AFM) characterization shows that the re-deposited polymer

generated by the plasma reaction is not a smooth thin film but appears as separated pillars. The detailed image (figure 2), indicates that the pillars are in fact open tubes standing perpendicular to the surface, with a diameter less than 100nm.

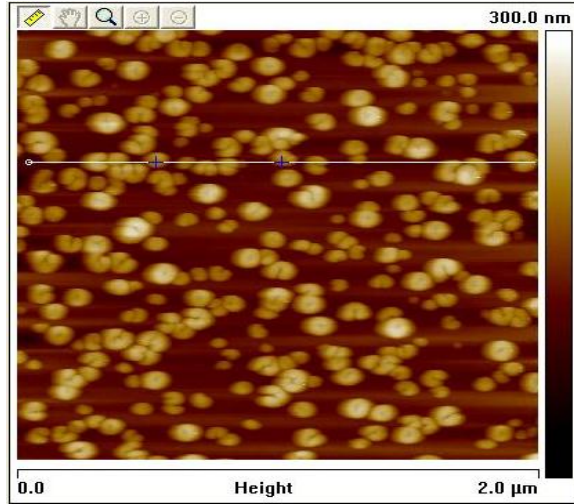


Figure 2. AFM of the surface pattern induced by plasma polymer re-deposition

These plasma-generated polymer nano-tubes can be used as a mask to etch the underlying substrate. In this study, the Si substrate was etched using a gas-chopping etching process, alternating between etch and deposition steps. Etching the substrate in this way adds additional degrees of freedom that can be used to tailor the aspect ratio of the surface topography to vary the surface roughness and achieve the required super-wetting properties. According to the simulations done by Johnson and Dettre⁽⁸⁾, the water contact angle varies with the surface roughness. For example, on a hydrophobic surface, where water is conformal with the topography, both the contact angle and contact angle hysteresis (difference between receding contact angle and the advancing contact angle) increase as the surface roughness increases. However, when the roughness factor exceeds a critical level, the contact angle continues to increase while the hysteresis starts decreasing due to a decrease of the water surface contact area and an increase in the amount of air trapped at the interface between the surface and the water droplet. This decrease in hysteresis results from a change in the dominant wetting behavior from the Wenzel state to the Cassie state⁽⁵⁾. Figure 3 shows Si nano-needles etched by using the surface patterns

produced by the plasma polymer re-deposition as a mask.

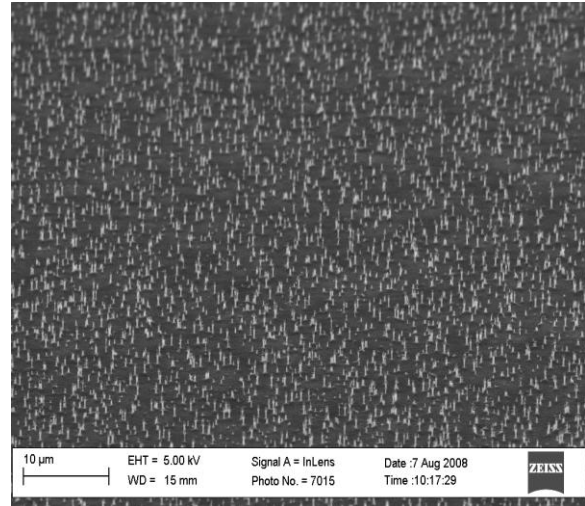
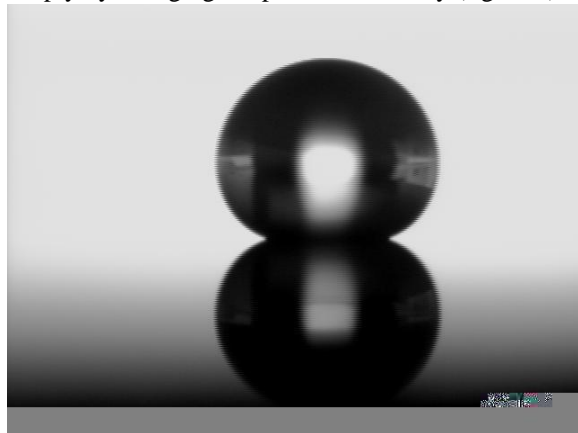


Figure 3. Scanning Electron Microscope image of the Si nano-needles formed by using the deposited polymer as mask

Following the creation of the substrate surface roughness, plasma treatments were used to modify the surface chemistry to create the desired super-wetting characteristics. To produce a super-hydrophobic surface, a C_4F_8 plasma thin film coating process was developed. The plasma causes the fragmentation of the C_4F_8 monomers⁽⁹⁾ and the resulting CF_x radicals can form a fluorinated polymer deposition. On a flat wafer surface, this hydrophobic coating exhibits a 97° contact angle with water. However, when the same coating was applied to the Si nano-needle patterned surface, the water contact angle increased to greater than 150° (figure 4a). Low-hysteresis, Cassie super-hydrophobic behavior was observed, with water droplets on the coated Si nano-needle surface rolling off even at very small tilt angles. To create a super-hydrophilic surface, an O_2 plasma was used to oxidize the surface of the Si nano-needles to SiO_2 . A normal, flat hydrophilic SiO_2 surface has an 18° contact angle with water, but the nano-needle patterned Si surface exhibits super-hydrophilic behavior, with a contact angle less than 5° (figure 4b).

It is clear that the Si nano-needles on surface can enhance the wetting effects of chemical modification. Using the identical surface topography, a surface can be engineered to have either super-

hydrophobic or super-hydrophilic properties. The behavior of the surface coating can be reversed simply by changing the plasma chemistry (figure 4).



(a)



(b)

Figure 4. Super-hydrophobic (a) and super-hydrophilic (b) surfaces made by APSM process. Surface (a) treated by C_4F_8 plasma, surface (b) treated by O_2 plasma.

By using a stencil mask to selectively remove the fluorinated thin film coating and oxidize the surface with oxygen plasma, a hydrophilic array on a super-hydrophobic surface has been demonstrated (figure 5).

The APSM process can potentially be used in a variety of applications including self-cleaning glass, stain-resistant textiles, anti-fogging windows, microfluidic chips, drug delivery systems, and protein concentrators⁽¹⁰⁾.

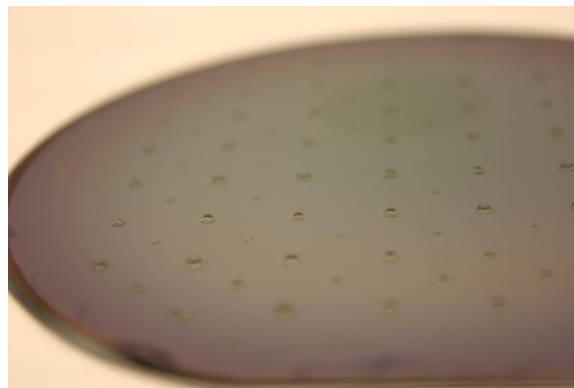


Figure 5. Water droplet array on a fluorinated super-hydrophobic surface selectively modified by oxygen plasma through a stencil mask.

References:

- [1] (a) R. N. Wenzel, *Ind. Eng. Chem.* **1936**, 28, 988.
(b) R. N. Wenzel, *J. Phys. Colloid Chem.* **1949**, 53, 1466.
- [2] A. B. D. Cassie; S. Baxter, *Trans. Faraday Soc.* **1944**, 40, 546.
- [3] G. McHale; N. J. Shirtcliffe; S. Aqil; C. C. Perry; M. I. Newton, *Phys. Rev. Lett.* **2004**, 93, 036102/1.
- [4] N. J. Shirtcliffe; G. Mchale; M. I. Newton; C. C. Perry; P. Roach, *Chem. Commun.* **2005**, 3135.
- [5] L. Zhai; Fevzi C. Cebeci; Robert E. Cohen and Michael F. Rubner; *Nano Letters*, **4** (7), 1349 - 1353, (2004).
- [6] F. C. Cebeci; Z. Wu; L. Zhai; R. E. Cohen; M. F. Rubner; *Langmuir* 22, 2856-2862 (2006)
- [7] S.M. Rossnagel, J.J. Cuomo, W.D. Westwood "Handbook of Plasma Processing Technology" by Noyes Publications (1990)
- [8] R. E. Johnson; R. H. V. Dettre, *Ad. Chem. Ser.* **1963**, 43, 112.
- [9] R. d'Agostino, "Plasma polymerization of Fluorocarbons," in: Plasma Deposition, Treatment, and Etching of Polymers, New York: Academic Press, (1990)
- [10] X. Yu; Z. Wang; Y. Jiang; F. Shi; X. Zhang; *Adv. Mater.* 17, 1289-1293. (2005)