Rendering superhydrophobic laser-induced rough surfaces by transferring on them hydrophobic polymeric nanoparticles

Ilker Bayer[*], Fernando Brandi[**], Roberto Cingolani[**], and Athanassia Athanassiou[*,**]
[*] Center for Biomolecular Nanotechnologies @UNILE, Istituto Italiano di Tecnologia (IIT), Via Barsanti 1, 73010 Arnesano, Lecce, Italy, athanassia.athanassiou@iit.it
[**] Italian Institute of Technology (IIT), via Morego 30, 16152 Genova, Italy

ABSTRACT

By using nanosecond pulsed UV laser irradiation surfaces of polished and unpolished silicon/SiO_2 wafers were patterned to induced certain degree of roughness to control their wetting properties from superhydrophilic to superhydrophobic. By varying the laser fluence, it is possible to control in a systematic and reproducible way the surface roughness, and thus the wettability properties of the silicon/SiO_2 surfaces. In particular, in our experiments the laser beam was focused using a cylindrical lens with focal length 75 mm, and the fluence used was between 0.5 and 2.0 J/cm^2. The silicon wafers were placed in liquid, methanol or distilled water, with 5 mm of liquid covering them. The wafers were moved in precise steps using a x-y translation stage. After the laser treatment, submicron (~ 150 nm) Teflon® particles were deposited onto the rough surfaces by a dry-transfer technique to modify the surface hydrophobicity. In this way highly hydrophilic patterned surfaces could be rendered hydrophobic to superhydrophobic depending on the underlying roughness.

Keywords: laser patterning, superhydrophobic, Teflon, micro and nanostructuring

1 INTRODUCTION

Micro and nanostructuring have been extensively used recently in order to control the wettability properties of surfaces, with emphasis to the possibility of making them either superhydrophilic or superhydrophobic [1]. Such increased research interest is due to the wide range of applications in which these surfaces can be applied, such as biological scaffolds, self-cleaning surfaces, microfluidics, lab-on-chip devices, coatings for automotive and aerospace vehicles, and textiles [2–4]. To generate micro or/and nanostructures, and thus tailor the wettability of diverse surfaces, several physical and chemical patterning approaches have been employed, including photolithography, electron-beam etching, templated electrochemical deposition, plasma treatment, and selective growth of nanotubes, atomic force microscopy, soft lithography, laser micromachining and microsphere nanopatterning. Electron beam etching induces high amounts of heat and damage to the surface, while photolithography involves multiple steps and requires the use of chemicals. Atomic force microscopy can be used to mechanically etch the surface, but the procedure is slow and is not suitable for large areas. Soft lithography techniques such as microcontact printing, micromolding, microtransfer molding and replica molding, imprinting and injection molding have been extensively used due to their low thermal effect, cost and large area applicability. However, these techniques involve multiple steps and require specialized masters. Microsphere nanopatterning, in which laser light is focused through a layer of self-assembled microparticles is able to form submicron periodic patterns with a number of disadvantages including control of particle assembly and additional patterning over the processed particles. Laser micromachining, on the other hand, has a number of advantages such as fast material-processing speed, large scan area and single-step capability.

Surface patterning using nano and femtosecond laser has many applications such as fabrication of MEMS/NEMS, CMOS, 3D-microstructures, microtrenches, microchannels, microholes, periodical submicron gratings and nanophotonics. It can also be used for patterning of magnetic and transparent thin films which can be used for microelectronics applications such as fabrication of flat panel displays and hard disk drives. In this work we demonstrate the possibility to alter the wettability properties of silicon/SiO_2 surfaces, by UV nanosecond pulsed laser irradiation, to render them initially superhydrophilic. By varying the laser fluence, it is possible to control in a systematic and reproducible way the surface roughness, and thus the wettability properties of the silicon/SiO_2 surfaces (Figure 1).

2 EXPERIMENTAL DETAILS

The UV laser beam was focused using a cylindrical lens with focal length 75 mm, and the fluence used was between 0.5 and 2.0 J/cm^2. The silicon wafers were placed in liquid, methanol or distilled water, with 5 mm of liquid covering them. The wafers were moved in precise steps using a x-y translation stage. After the laser treatment, submicron (~ 150 nm) Teflon® particles were deposited onto the rough surfaces by a dry-transfer technique, which allows to the particles to be positioned among the rough structures. The Teflon® particles are stably deposited onto the laser-treated structures, since post treatment with different solvent was impossible to remove them. Static water contact angle and

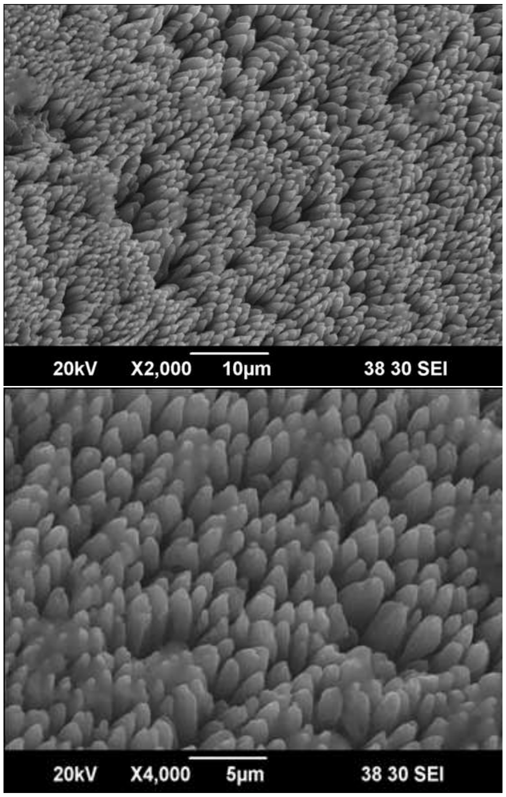

Figure 1. SEM images from a laser-treated area on a silicon wafer

contact angle hysteresis measurements were made on the treated surfaces using a Kruss contact angle goniometer. A homemade setup was used to tilt the surfaces in order to measure advancing and receding contact angles before the droplets started sliding off the surfaces. Up to 10 measurements were taken for both static and advancing and receding contact angles on the Teflon treated surfaces.

3 RESULTS AND DISCUSSION

The laser patterning technique used in this study is ideally suited for the generation of micron sized protruding structures on polished or unpolished silicon wafers. Figure 2 displays an atomic force microscope (AFM) topography of a patterned surface using the UV nanosecond laser at a fluence of 1.0 J/cm^2. Pyramid-like roughness features appear as a result of laser machining. Roughness analysis indicates that the base of the pyramids is about 2 micron wide and the top is 0.5 micron wide. We found that morphology of these feature namely the size, depth and the frequency of distribution of these micro pyramids strongly depend on the laser fluence and the application technique. In the present case, the samples are prepared by irradiating the wafer with a line focus beam (about 20 mm long and 0.2 mm wide) while rotating the wafer. The line focus is set radially

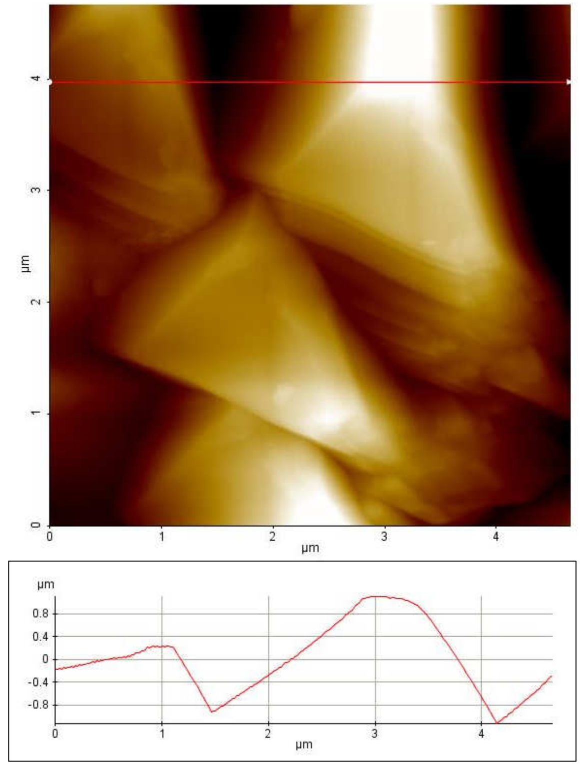

Figure 2. (Top): Non contact mode atomic force microscope image of a silicon surface irradiated with a laser of 1.0 J/cm^2 fluence. (Bottom): Typical roughness profile of the surface which is made up of these pyramids. The dimensions of these features are approximately 2 micron wide base and 0.5 micron wide top.

starting slightly from the center of the wafer, thus the actual shot dose, i.e. number of laser shots per unit surface, is changing along the radius. The static water contact angle on this surface is quite low (25^o) and it is highly hydrophilic. When submicron Teflon particles are applied to the surface by using a dry-transfer technique, the surface morphology as well as the wetting of the original surface are altered completely. Figure 3 shows an AFM topographic image of the Teflon transferred surface, the original topography of which is shown in figure 2. Note that the pyramidal roughness features are covered with submicron roughness. The topology shows superimposition of submicron roughness on the micron scale roughness features. Since Teflon is intrinsically hydrophobic, the Teflon transferred surface also becomes hydrophobic but due to the underlying roughness the static contact angles exceed that of smooth Teflon surface which is around 110^o. Detailed static water contact angle and contact angle hysteresis measurements showed that these surfaces are not self cleaning due to relatively high contact angle hysteresis which on average is around 35^o. We have also fabricated other surfaces in which the average pyramid shaped roughness size and width are greater than 2 μm. These surfaces are more hydrophobic and contact angle hysteresis is less than 35^o which will be discussed as future work.

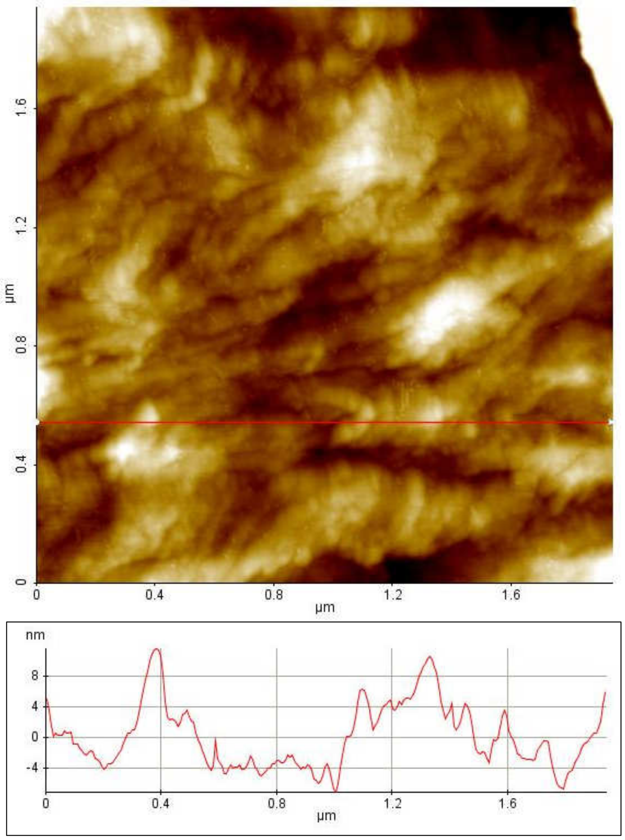

Figure 3. (Top): Submicron Teflon transferred surface morphology obtained by a non contact AFM measurement corresponding to the surface seen in Figure 2. (Bottom): Nanoscale surface roughness profile as a result of Teflon transfer.

In figure 4 detailed static water and contact angle measurements are presented for Teflon transferred surfaces. As seen, static contact angles center around 130^o for all surfaces on average. Contact angle hysteresis on the other hand is approximately 35^o on average. Note that highly hydrophobic polymers such as polydimethyl siloxane (PDMS) resins do present very high contact angle hysteresis close to 90^o. Although the surfaces in their present state do not display lotus effect (contact angle hysteresis being less than 15^o), they still display superior hydrophobicity compared to smooth Teflon or PDMS surfaces. Within the laser fluence range studied, the dry Teflon transfer technique results in surfaces with almost identical hydrophobicity. The main reason for this is attributed to the fact that the dry transfer technique creates about 1.5 micron thick Teflon films using the 150 nm Teflon powder. In one way this decreases the micro roughness from ~ 1.6 microns to 15 nm as seen in the bottom image of Figure 3. Additional work in our laboratories is underway in order to increase the surface roughness features on the silicon wafers.

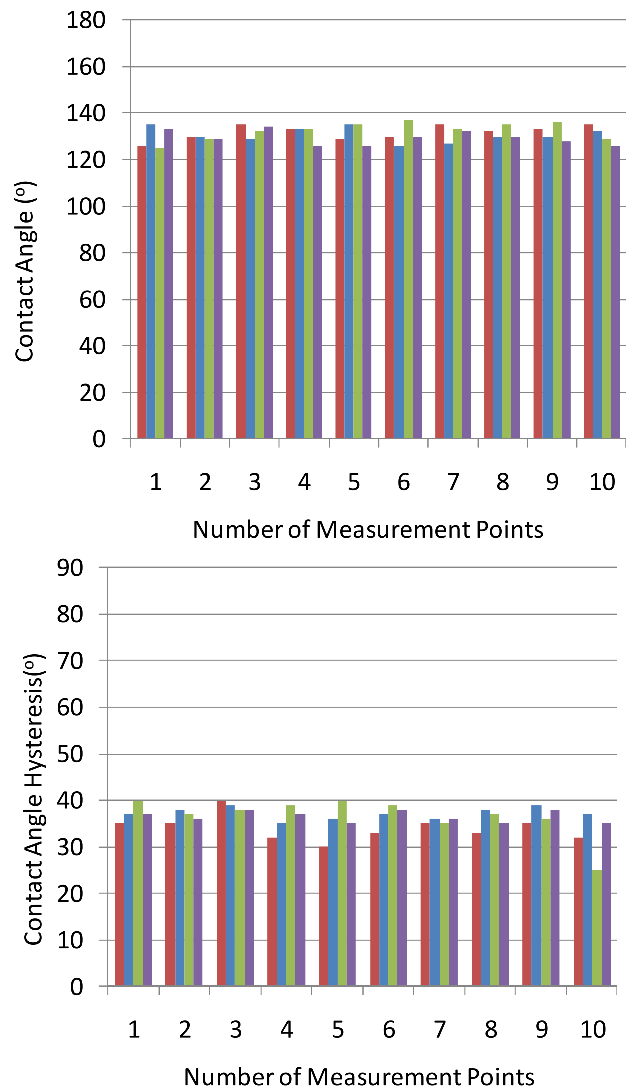

Figure4. Static water contact angle (top panel) and water contact angle hysteresis on Teflon transferred laser patterned surfaces. Different colors in the graphs indicate surfaces created using different laser fluences. Ten random measurements were taken on each surface to investigate the wetting homogeneity on the surfaces.

4 CONCLUSIONS

Both polished and unpolished silicon wafers were micro-machined using a nanosecond UV laser to create micron sized pyramidal structures. These surfaces were highly hydrophilic at the beginning due to the Wenzel effect caused by laser machining. The surfaces were rendered superhydrophobic applying submicron Teflon particles using a dry transfer technique. Contact angles as high as 130^o were measured on these surfaces with contact angle hysteresis around 35^o. Further work is underway in order to create a lotus effect on these surfaces by tuning some parameters of the laser patterning and dry transfer technique.

5 REFERENCES

[1] V. Zorba, L. Persano, D. Pisignano, A. Athanassiou, E. Stratakis, R. Cingolani, P. Tzanetakis and C Fotakis, Nanotechnology 17 3234 (2006).
[2] A. Nakajima, A. Fujishima, K. Hashimoto and T. Watanabe, Adv. Mater. 11 1365 (1999).
[3] Z. Yoshimitsu, A. Nanajima, T. Watanabe and K. Hashimoto, Langmuir 18 5818 (2002).
[4] N. A. Patankar Langmuir 19 1249 (2003)
[5] N. J. Shirtcliffe, S. Aqil, C. Evans, G. McHale, M. I. Newton, C. C. Perry and P. Roach, J. Micromech. Microeng. 14 1384 (2004).
[6] L. Huang, S. P. Lau, H. Y. Yang, E. S. .P Leong and S. F. Yu J. Phys. Chem. B 109 7746 (2005).
[7] L. Rizzello, S. Shiv Shankar, D. Fragouli, A. Athanassiou, R. Cingolani and P. P. Pompa, Langmuir 25 6019 (2009).
[8] P. N. Bartlett, J. J. Baumberg, P. R. Birkin, M. A. Ghanem and M. C. Netti, Chem. Mater. 14 2199 (2002).