

**Supplementary Materials for**

Wetting criteria of intrinsic contact angle to distinguish between hydrophilic and hydrophobic micro/nano-textured surfaces: Experimental and theoretical analysis with synchrotron X-ray imaging

**Authors**

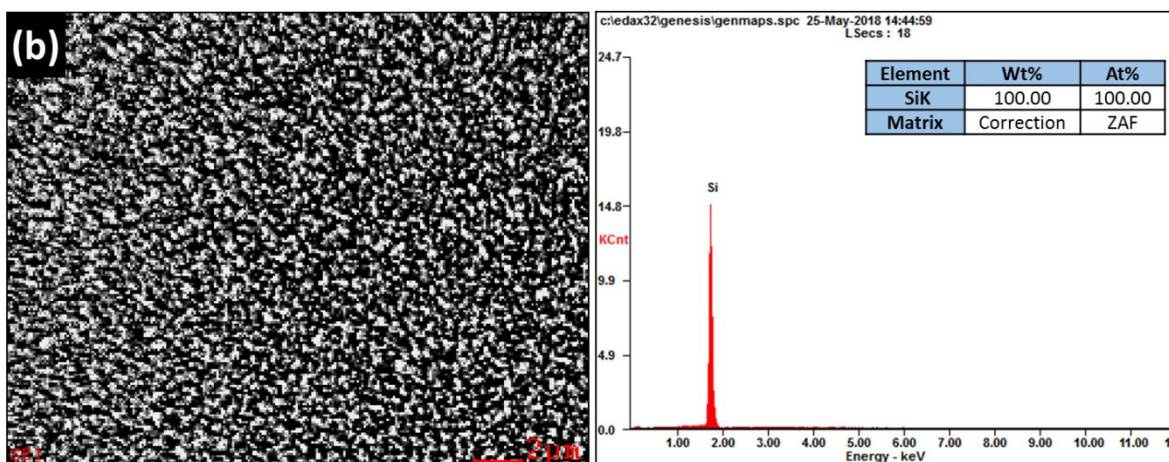
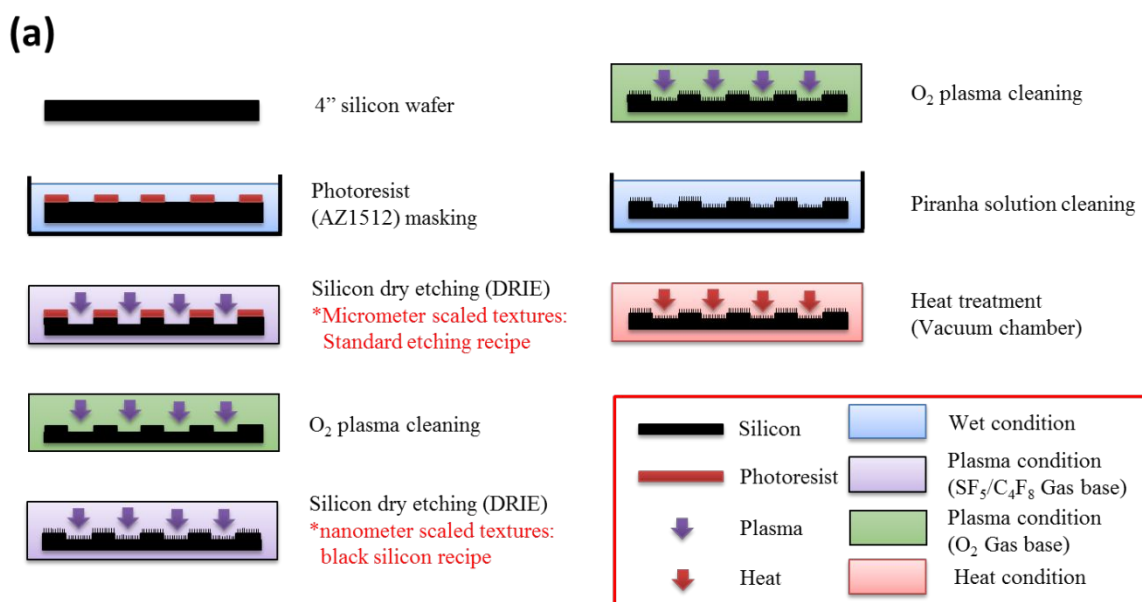
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- Section S1. Specific processes for preparation of test sections
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## Section S1. Specific processes for preparation of test sections

Surface wetting conditions are generally expressed using the chemical composition and geometric morphology of the surface. The chemical composition is quantitatively defined using the intrinsic contact angle, which is an apparent contact angle on an ideal smooth surface, and the geometric morphology is quantitatively defined as the roughness ratio  $f$ , which is the ratio of the wetted area  $A_{wetted}$  to the projected area  $A_{projected}$ . To verify the intrinsic contact angle for distinguishing between hydrophilic and hydrophobic textured surfaces, test sections to measure the surface wetting conditions quantitatively were prepared using a micro-electro-mechanical-systems technique. Photolithography and a conventional etching method were used to prepare the uniformly arrayed micro-textured surfaces. First, micro-dot patterns were marked with photoresist on a 4 inch double-sided polished silicon wafer; then, micro-posts were fabricated by a deep reactive-ion etching machine on the patterned silicon wafer. For preparation of the nano- and micro/nano-textured surfaces, the black silicon method was used due to the difficulties in fabricating nanometer scaled patterns using photolithography on flat and micro-textured surfaces. During the photolithography and deep reactive-ion etching process, the photoresist and fluorine passivation essentially remain on the surfaces of the structures, leading to hydrophobicity of the surface. Therefore, these hydrophobic residues were cleaned with  $O_2$  plasma (1,000 W, 10 minutes) and piranha solution ( $H_2O_2$ :  $H_2SO_4$  = 2:1 volume ratio, 20 minutes). After these cleaning processes, hydroxyl groups remain on the surfaces, which are likely to introduce experimental error because this functional group makes the test sections temporarily hydrophilic. Hence, the test sections were baked in a vacuum chamber under high temperature (220 °C, -0.1 MPa, 1 day) to remove the hydroxyl groups on the surfaces. The specific fabrication and cleaning processes for preparation of the test sections are shown in Fig. S1. a. After the fabrication and cleaning processes, as shown in Fig. S1. b, the clarity of the prepared surfaces was confirmed by energy-dispersive X-ray spectroscopy.



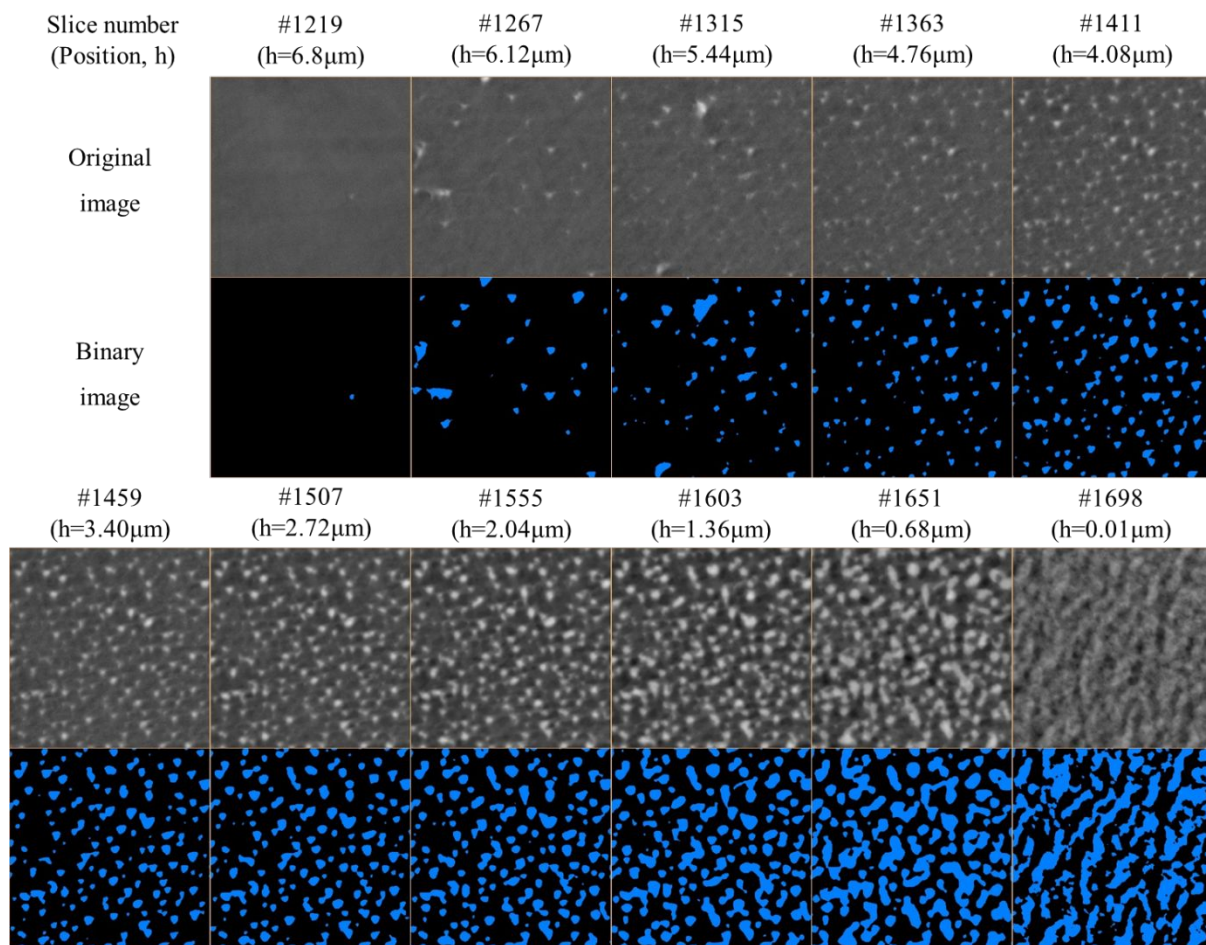
**Figure S1. (a)** Specific recipe to fabricate and clean test sections **(b)** Analysis of energy dispersive X-ray spectroscopy (nanometer scaled textures)

## Section S2. Synchrotron X-ray tomography for nanometer-scaled pillars

We calculated the surface parameters of nanometer-scaled pillars (generally known as ‘black silicon’), including the area, volume, average diameter, distance, and height using synchrotron X-ray tomography. The nano-pillars at the top of micro-pillars were investigated through nanoscopic imaging. Nanoscopic projection and computed tomography (CT) scanning of the samples were carried out using a monochromatic synchrotron X-ray (6.78 keV) at the Pohang Accelerator Laboratory (PAL) 7C beam line. The optical components for sample positioning were ULTRAlign, Gothic Arch XYZ stages (Newport, San Jose, CA, USA) and picomotor actuators (New Focus; Newport). Synchrotron X-ray tomographic data were acquired with a set up reported previously (Lim et al. 2014) [S1]. The specimen was mounted on a computer-controlled precision stage that rotates through 360°. For the specific volume (6.5 [width] × 6.5 [column] × 6.8 [height] μm<sup>3</sup>), a total of 721 images were collected at 0.5° increments with an exposure time of 5s/projection. Three-dimensional images of the specimen were obtained by applying a filtered back-projection algorithm to the projection image, using the OCTOPUS software package (Ghent University, Ghent, Belgium). Finally, Amira software (VSG Inc., Burlington, MA, USA) was used for reconstruction (volume segmentation and rendering). On the basis of the reconstructed images, for the Wenzel state, the roughness ratio is defined as the ratio of the wetted area to that of the projected area for nanometer-scaled pillars on the specific volume. For the Cassie-Baxter state, since nanometer-scaled pillars have a circular cone shape, the roughness ratio is defined as the averaged value of 10 points in the height direction for the nanometer-scaled pillars on the specific volume as shown in Fig. S2.

### Reference

[S1] J. Lim, H. Kim and S. Y. Park, Hard X-ray nanotomography beamline 7C XNI at PLS-II, *J. Synchrotron Rad.* **2014**, 21, 827-831.



**Figure S2.** Cross sections of the nano-textured surface along the height (10 positions)