A 3-dimensional rippled nanoshell structure (a hollow pillar with wriggly sidewall morphology) is demonstrated for superhydrophobicity. As a control group, a straight nanoshell structure without a rippled shape was also prepared. The rippled structure showed improved superhydrophobicity with a large contact angle and a small sliding angle compared to the straight nanoshell structure. These enhancements originate from the minimum of interfacial energy at the triple-phase contact line, which is located at the most protruded circular line along the rippled structure. Using a drop impingement test, the stabilization of a Cassie Baxter state on the rippled structure was also verified. The experimental observation of wetting transition from a Cassie-Baxter to a Wenzel state is well explained by a revamped capillary pressure model, which was customized for the rippled structure.
Superhydrophobic surfaces have received a great deal of attention in recent decades because of their self-cleaning and low-drag properties, which provide desirable working efficiencies in many industrial applications, including dirt-free coatings and microfluidics for biotechnology. Superhydrophobic surfaces exhibit exceptional repellency to water. The contact angle of a water droplet on such surfaces reaches as high as above 150 up to 180°, which is a result of not only a chemical property but also a physical property, i.e., surface roughness. There are two possible origins for the increment of the contact angle: (1) the liquid impregnates the solid texture (Wenzel state), or (2) it sits on the top of the solid surface and leaves air underneath the texture (Cassie-Baxter state). In many industrial applications including the aforementioned cases, enhancing the mobility of the liquid droplet on surfaces is of great interest. Hence, various surface morphologies have been carefully fabricated to repel as much water from the surface as possible, using various techniques including lithographic fabrication and sol-gel process. To achieve this goal, two prerequisites must be satisfied: (1) the liquid must be suspended by the surface morphology (Cassie-Baxter state) and (2) there must be low liquid-solid contact.

Previously, a hollow pillar, i.e., a straight nanoshell, was demonstrated to have greater superhydrophobicity than a non-hollow pillar, i.e., a cylindrical nanopost. This difference was attributed to the notable decrease of contact area between water and solid surface due to the inherent shell structure. A simple geometrical calculation showed that the water-contact area fraction per unit area of the hollow pillar was reduced to one order of magnitude smaller than that of the non-hollow pillar. There was, however, a substantial difference between the measured and predicted contact angle from the Cassie-Baxter equation. It was thought that this difference arose from the extended contact area as a result of sag in the liquid-air interface between adjacent pillars. Given this extension, it is expected that a more advanced structure, which can be evolved from the aforementioned straight nanoshell, can demonstrate greater superhydrophobicity, including the robust stability of the Cassie-Baxter state. Thus, a 3-dimensional (3-D) straight nanoshell with a wriggly sidewall morphology (simply named the rippled nanoshell) is proposed, and its superhydrophobic properties are investigated in this work. For simple analytical study, a perfectly well-ordered structure is preferred, thus top-down based fabrication (photo-lithography) and deep reactive ion etching (DRIE) were used to make the rippled nanoshell array.

Figure 1 outlines the procedure for fabricating the perfectly well-ordered nanoshell array. The rippled nanoshell structure was prepared as the experimental group, and a straight nanoshell structure was also fabricated as a control group. That is, the superhydrophobicity was evaluated through vertically standing nanoshell structures with and without a wriggly sidewall profile. The overall procedure in detail was as follows. The starting material was a bare single crystalline 8-inch Si wafer with a (100) orientation. A thermal oxide was grown on the bulk Si with a thickness of 200 nm, which served as the hard
mask (etching stopper). Thereafter, a conventional photo-lithography was performed to define the well-ordered nanoshell array. And the exposed oxide and Si were sequentially etched out by DRIE for the formation of deep trench holes. It should be noted that the rippled structure on the sidewall of the trench hole was realized by the iterative plasma etching, which is comprised of two steps: sidewall passivation by CF\textsubscript{4} based plasma and isotropic etching by SF\textsubscript{6} based plasma, i.e., Bosch process.\textsuperscript{8} In this work, 10 cycles of DRIE were carried out for 15 μm height of the nanoshell. As the remaining photoresist is insufficient to act as the etching stopper during DRIE, the abovementioned thermally grown oxide served as etching stopper to protect the underlying bulk silicon. Afterwards, a thin silicon nitride layer with a thickness of 50 nm was deposited by low-pressure chemical vapor deposition (LPCVD). Here, the deposited nitride thickness will determine the thickness of the nanoshell, and thus it should be carefully designed.\textsuperscript{5} The nitride layer (structural layer) on the top of the bulk silicon (sacrificial layer) should be selectively removed by a chemical-mechanical polishing (CMP). Thus the nitride remains vertically inside the trench hole as a form of a sidewall. During the CMP, the remaining hard mask oxide also serves as the etching stopper, which prevents the underlying sacrificial silicon surface from being damaged. Next, the residual oxide was completely eliminated by buffered oxide etchant solution. Afterwards, the abovementioned wafer was submerged into 30% potassium hydroxide (KOH) solution at a temperature of 80 °C in order to etching the sacrificial bulk silicon. Through this process, the structural rippled nitride sidewall is exposed to air. The KOH etching time will determine the total revealed height of the rippled nitride sidewall. Finally, a thin layer of silane-terminated perfluoropolyether (PFPE, Nicca Korea, Korea) was coated on the revealed nitride to modify the surface wettability from hydrophilic to hydrophobic.

The control group (with a straight nanoshell array) was also prepared, but without using the Bosch process. Except for the process related to the rippled sidewall morphology, all other processes and dimensions were the same as the experimental group. The two sets of superhydrophobic devices (control vs. experimental group) were prepared as shown in Fig. 2. In particular, the wriggly sidewall was carefully fabricated so as to trim the reentrant corner as much as possible.

In order to evaluate the water repellency of the fabricated surfaces, the contact angle and the sliding angle of a water droplet were rigorously characterized using a contact angle meter (DM 701, Kyowa Interface Science Co. Ltd., Japan). 5 μL of de-ionized water was dropped onto the prepared superhydrophobic samples from a needle of a microsyringe, while the volume was precisely controlled by a dispenser system. A side view of the water droplet was then taken exactly one second later, to avoid any problem with regard to motion of the droplet, and a static contact angle of the sessile droplet was measured from the photographic image using image analysis software (FAMAS, Kyowa Interface Science Co. Ltd., Japan). Then, the sliding angle was measured by tilting the stage; a series of pictures of the sessile droplet was taken for every one-degree tilt
of the stage, which was automatically controlled by the instrument. The sliding angle was then defined as the inclination angle at which the test droplet began to slide for a certain amount of pixels from its initial position. An advancing and a receding angle were also measured at that time, corresponding to the maximum and minimum contact angle, respectively. Results for all tests were obtained from ten repeated measurements.

Figure 3a represents the measured sliding angle on three kinds of prepared surfaces: a flat (without nanoshell) surface, the straight nanoshell array with a spacing of 7 µm, and the rippled nanoshell array with a spacing of 7 µm. The results show that the sliding angle decreases in the order of the flat surface (30°) >> the straight nanoshell array (6°) > the rippled nanoshell array (4°). The significant decrease in the sliding angle of the two nanoshell arrays compared to the flat surface can be explained by the conspicuous increase in hydrophobicity, which was confirmed by measuring the contact angle.

To interpret the additional decrease in the sliding angle of the rippled nanoshell array, an advancing (θ_{adv}) and a receding contact angle (θ_{rec}) were carefully measured, respectively. Even though the contact angle hysteresis (i.e., θ_{adv} − θ_{rec}) was comparable between the two nanoshell arrays, the receding angle (152.5°) of the rippled nanoshell array was larger than that of the straight nanoshell array (149°). Since the receding angle is inversely related to the sliding angle⁹, the rippled nanoshell array exhibited a lower sliding angle (4°) compared to the straight nanoshell array (6°). This difference was statistically significant from 10 repeated measurements (Figure 3b). The sliding angle of the rippled nanoshell array was further decreased by increasing the spacing among the adjacent nanoshells. The sliding angle was decreased down to 1° when the spacing (L_{spac} in figure 2) was increased to 20 µm. Under such condition, it becomes very difficult for the water droplet to attach and hold onto the rippled nanoshell array. Thus the rippled nanoshell array is more suitable than the straight nanoshell array as a superhydrophobic surface.

In addition to the sliding angle characteristics, the contact angle of the rippled nanoshell array was found to be larger than that of the straight nanoshell array. For instance, the straight nanoshell array with a spacing of 7 µm exhibited a contact angle of 159 ± 2° and the rippled nanoshell array showed a contact angle of 161 ± 2°. As shown in figure 3c, the contact angle of the rippled nanoshell array was further increased up to 166° when the spacing was increased to 20 µm.

It should, however, be noted that the measured contact angles on the straight and the rippled nanoshell array were both smaller than the theoretically predicted contact angle (approximately 170°) from the well-known Cassie-Baxter model⁶, which assumed that a droplet had only a partial contact with the top side of the solid surface. In other words, an additional liquid-solid contact area on the side of the nanoshell structure should be considered to analyze the decrease in the contact
angle. The contact angle of a water droplet, in fact, is decreased as a water-solid interfacial area is increased. Hence, given the larger contact angle of the rippled nanoshell array as compared to the straight nanoshell array, there is likely a considerable difference in the extended water-solid interfacial area on the sidewall of the structure, between the two comparative nanoshell arrays.

That difference can be attributed to an inherent feature of the rippled sidewall, which is that the total interfacial energy of a water droplet in contact with the rippled structure displays a minimum when the triple-phase contact line (i.e., solid-liquid-vapor) is located at the most protruded circular line along the rippled structure.\textsuperscript{10} The triple-phase contact line on the rippled nanoshell array is pinned at the first circular line from the top side of the structure, so that the extended water-solid interfacial area of the side of the structure is smaller than that of the straight nanoshell array. And it should be noted that the multi-convex shape of the rippled nanoshell structure can help to pin the triple-phase contact line over and over, and thus leading to stable Cassie-Baxter state. Since the local energy minimum attributed to the rippled structure can be overcome under forced impalement of a liquid, such multiple structure is desirable. The pinning of the triple-phase contact line near the reentrant structure has been similarly described with different structures in other publications.\textsuperscript{4, 7, 11-13}

The decrease in the water-solid interfacial area of the rippled sidewall was confirmed with the aid of a droplet impinging test in a roundabout way. For the impinging test, a water droplet of 15 µL was released from a height of 10 mm above the nanoshell array. The release height was chosen so that a water droplet bounced from the surface. The dynamic behavior of the droplet was \textit{in-situ} recorded via high-speed camera (IDP-Express R2000, Photonics, USA) to count the number of bounces until the droplet adhered to the surface (Figure 4a). The results were obtained from five repeated measurements. During the rebound, the water droplet completely recovered its initial size, indicating that the droplet was in the stable Cassie-Baxter state.\textsuperscript{14-17} For fair comparison, the same measurement was also conducted on the straight nanoshell array.

Figure 4b shows the number of rebounds of the droplet onto the rippled nanoshell array with a spacing of 7 µm, and on the straight nanoshell array with a spacing of 7 µm. A droplet impacting on the rippled nanoshell array rebounded more times than one impacting on the straight nanoshell array, supporting the conclusion that the droplet on the rippled nanoshell array exhibited a smaller water-solid contact area. The number of rebounds increased with the array spacing due to the resulting decrease in the effective contact area between a droplet and the surface. But, a water droplet was stuck on the surface under the condition of the 20 µm spacing, even though the contact angle was maximized at the 20 µm spacing.
The capillary pressure for the rippled nanoshell array was evaluated to interpret the sticking failure when the spacing was 20 µm. Dash and co-workers derived an equation of capillary pressure for a surface composed of a hollow pillar as follows:18

\[
P_{C, \text{straight}} = -4 \gamma_{LA} \cos \theta_{y} \frac{\phi}{t(1 - \phi)}
\]

where \( \gamma_{LA} \) is the surface tension of the liquid (that is, 0.072 N/m for water), \( \theta_{y} \) is the Young’s contact angle (determined on a flat surface of the same material, i.e., PFPE-coated silicon nitride), \( \phi \) is the area fraction of solid in contact with the liquid, and \( t \) is the thickness of the hollow pillar. The capillary pressure for the straight nanoshell array can be evaluated from this equation. For the rippled nanoshell array, the pinning of the triple-phase contact line should be considered. Thus the revamped capillary pressure model is derived as follows:

\[
P_{C, \text{ripple}} = -4 \gamma_{LA} \cos(\theta_{y} + \theta_{z}) \frac{\phi}{t(1 - \phi)}
\]

where \( \theta_{z} \) is defined as the local reentrant angle (\( \theta_{z} = 11^\circ \)) as depicted in Figure 2. Although the capillary pressure for the rippled nanoshell array with the spacing of 20 µm (1.83 kPa) was estimated to have increased by 106 %, as compared with that for the straight nanoshell array with a spacing of 20 µm (0.89 kPa), it was not sufficient to endure the impacting pressure (1.86 kPa). In addition to explaining the sticking failure of the water droplet, the experimental observation of the drop rebounding is also well explained by the revamped capillary pressure model. For the nanoshell array surfaces having 7 or 10 µm of spacing, which the rebound of the impinging droplet was observed on, each of the capillary pressures is evaluated to be larger than the impacting pressure.

Although the capillary pressure larger than the drop impacting pressure is prerequisite of a superhydrophobic surface for the existence of Cassie-Baxter state, the larger capillary pressure does not imply the better superhydrophobic properties. Actually, lowering \( \phi \) improves the superhydrophobicity, while it decreases the capillary pressure. Therefore, the optimal nanoshell surface for the drop impinging test, i.e., the rippled nanoshell array with 10 µm of spacing, did not correspond to the most superhydrophobic sample, i.e., the rippled nanoshell array with 20 µm of spacing.

In summary, the change in nanoshell morphology from a straight to a rippled structure effectively enhances superhydrophobicity. The enhancement effect was attributed to the stabilized energy at the triple-phase contact-line and was confirmed by the droplet impinging test. The experimental observation of the wetting transition from the Cassie-Baxter to the Wenzel state was well explained by the revamped capillary pressure model. It is believed that the proposed rippled nanoshell array would be suitable for a superhydrophobic surface application like microfluidics, and provide added stability.
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**Figure Captions**

**Figure 1.** (Color online) A schematic illustration of the fabrication process: 1) thermal oxidation of a single crystalline silicon wafer with a (100) orientation, 2) patterning an array of holes on a thermal oxide film by conventional photolithography, 3) reactive ion etching of the bulk silicon substrate in two distinct ways—either normal one-step etching for the straight nanoshell, or time-multiplexed etching known as Bosch process for the rippled nanoshell, 4) deposition of a silicon nitride film, 5) selective removal of top side of the silicon nitride film by chemical mechanical polishing (CMP), 6) removal of the remaining oxide and subsequent recessing of the bulk silicon.

**Figure 2.** (Color online) (a) A series of FE-SEM images obtained for the fabricated arrays: (first row) the straight nanoshell array, (second row) and the rippled nanoshell array. The scale bars of images are 20, 10, and 2 μm from left to right, respectively. The spacing ($L_{spac}$) is defined in the image. (b) Cross-sectional SEM images of the rippled nanoshell. The local reentrant angle ($\theta_s$) is defined in the image.

**Figure 3.** (Color online) (a) Effect of surface topography on the hydrophobic behavior: Advancing (▲), receding (▼), and sliding contact angles of a water droplet for the samples—a flat surface, and two nanoshell surfaces having either a straight or rippled structure. (b) Sliding angle distribution of the two comparative nanoshell arrays. (c) Contact angles and sliding angles of a water droplet on the two kinds of nanoshell array plotted with respect to the distance between the nanoshells.

**Figure 4.** (Color online) (a) Bouncing droplets: a series of snapshots of a water droplet with R = 1.3 mm hitting the nanoshell array surface with an impact velocity within a range from 0.3 to 0.5 m/s. The interval between snapshots was 6.67 ms. The hydrodynamic pressure acting on the surface was estimated to 1.86 kPa.\textsuperscript{16, 18, 19} The water droplet was completely retained its initial size during the rebound, indicating that the surface is superhydrophobic. (b) The number of bounces is plotted for each sample. The lengths in the figure indicate the nanoshell distance.
REFERENCES


