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Threshold Levels for Wettability in Nano- and Micro-meter Periodic Structures*

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***Abstract*— The purposes of this study are to clarify the relationship between surface wettability and the pitch and size of periodic structures on the surface and to determine the thresholds at which the wettability switches from being hydrophobic to hydrophilic. To this various nano- and micro-meter scale periodic structures were fabricated. By applying a fine periodic structure to the surface, the wettability can be controlled between + 50° (hydrophobic) and -55° (hydrophilic). The pitch of the periodic structure at which the wettability switches from hydrophilic to hydrophobic was found to between 500 and 1,000 nm. Additionally, the height of the periodic structure at which the wettability switches from hydrophobic to hydrophilic was found to between 300 and 700 nm.**

I. Introduction

Immunosensor devices are commonly fabricated in glass, silicon, and polymers. In these immunosensors, the micro-scale environment affects the non-specific binding of proteins to the surface of microchannels. This is especially important in immunoassays where key reagents such as antibodies and enzyme labels can become adsorbed on hydrophobic surfaces, seriously degrading the assay performance. To address this, different strategies have been applied to block or modify the surfaces of microchannels, the most common of which to pre-coat the surface with a blocking agent such as bovine serum albumin (BSA). While sufficient for some applications, the surface modification is not permanent, and the resulting surface is somewhat heterogeneous [1].

Wettability is an important aspect of materials and is governed by both the surface chemical composition and the geometric structure of the surface [2]. A closely related phenomenon in nature is the lotus-effect, which refers to surfaces that are difficult to wet. When the water contact angle exceeds 150°, it is referred to as a super-hydrophobic surface [3]. The main characteristics of super-hydrophobic surfaces are their roughness on the micrometer scale and the presence of a periodic structure [4]-[5].

The principal relationship between surface roughness and wettability was worked out by Cassie and Baxter [6], as well as Wenzel [7]-[8]. Since then many researchers have contributed to a better understanding of the behavior. However, the thresholds, in terms of the periodicity and size of features on the surface, at which a surface switches from being hydrophobic to hydrophilic have not yet been clarified.

The authors have designed and fabricated a number of nano- and micro-meter scale periodic structures, with the aim of clarifying these wettability thresholds. The effect of the scale of these structures on the contact angle was examined experimentally.

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II. Theoretical Formulae for Water Repellency

A. Young- Dupre equation

If a water droplet is placed on a solid surface in air, the solid – air and water – air interfaces come together with a static contact angle θ. The value of θ can be determined by considering the conditions for which the total energy of the system is minimized, and is given by Young's equation as follows:

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta \quad (1)$$

where γ_{SL}, γ_{SV}, and γ_{LV} are the surface tensions of the solid – water, solid – air, and water – air interfaces, respectively (γ_{LV} = 72.8 × 10^{-3} mN/m; water).
Using the free energy of adhesion work W_A (mN/m), the Dupre equation is shown to be as follows:

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \quad (2)$$

A combination of equations (1) and (2) yields the Young-Dupre equation,

$$W_A = \gamma_{LV}(1 + \cos\theta) \quad (3)$$

Good has described the free energy of adhesion work W_A to be given by the geometric average of the cohesive energy of each interface as follows [9]:

$$W_A = W_{SL} = 2\sqrt{\gamma_{SV} \cdot \gamma_{LV}} \quad (4)$$

Finally, the contact angle, θ, is expressed by the Young-Dupre equation.

$$\cos\theta = 2\,\Phi\,\sqrt{\frac{\gamma_{SV}}{\gamma_{LV}}} - 1 \quad (5)$$

where, Φ : correction factor (= 1 for water).

B. Wenzel equation

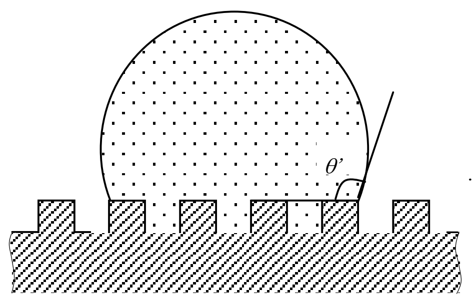
Young-Dupre equation given above can be applied to a smooth surface. However, the wettability changes if the solid has a rough surface. When the pores in the surface become filled with water, as depicted in Figure 1A, Wenzel showed that the following equation could be used for the relationship between the roughness of the solid, r, the contact angle of the smooth surface, θ, and the contact angle with rough surface, θ' [10]:

$$\cos\theta' = r\,(\gamma_{SV} - \gamma_{SL})/\,\gamma_{LV} = r \cdot \cos\theta \qquad (6)$$

where, r : the surface ratio, which is given by the total surface area including the sides and bottoms divided by the total surface area of the convex part, i.e. $r > 1$.

According to this equation, the wettability of a rough surface is determined by the surface energy. This equation means that a rough surface becomes more hydrophobic ($\theta' > 90°$) if the contact angle with a smooth surface, θ, exceeds 90°, and becomes more hydrophilic ($\theta' < 90°$) if θ is less than 90°.

A



B

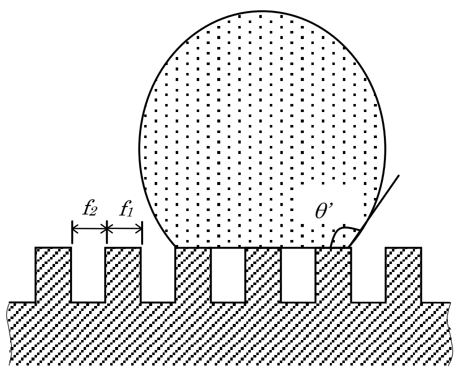


Figure 1. Rough surface (periodic structure) and the two states. A: Pores filled with water, the Wenzel state. B: The drop rests on a composite of solid and air, the Cassie state.

C. *Cassie-Baxter equation*

For a composite interface consisting of two materials with fractional areas of f_1 and f_2 (so that $f_1 + f_2 = 1$), the contact angle, θ', is given by the Cassie equation as follows:

$$\cos\theta' = f_1 \cos\theta_1 + f_2 \cos\theta_2 \qquad (7)$$

where, θ_1 and θ_2 are the contact angles with the two materials (°).

If the composite materials are a solid (f_1) and air (f_2), the contact angle, θ', is given by

$$\cos\theta' = f\cos\theta + (1-f)\,\cos 180°$$

$$= f\cos\theta + f - 1 \qquad (8)$$

In this condition, a water droplet rests on the composite of the solid and air (Figure 1B). The contact angle gradually approaches 180° by reducing the area of the solid whilst increasing the area of air.

III. Periodic Structures and Experimental Method

A. *Fabrication method of nano- and micro-meter periodic structures*

The development of micro-electromechanical systems (MEMS) has provided tools for highly precise, reproducible, and scalable methods to fabricate structures with micrometer sized dimensions [11]. This lithography-based approach can be used to produce periodic structures on silicon between the nano- and micro-meter scales.

To fabricate the periodic structures for this work, a 3 µm thick oxide layer was formed on a 500 µm thick silicon wafer. The wafer was then coated with photoresist using a spin coater. The photoresist was exposed to a pattern of intense light using a layout mask for each test-piece. The silicon was then wet etched to remove the unprotected oxide. The photoresist was removed from the substrate using resist stripper.

B. *Parameters of periodic structures*

Table 1 shows the specifications and measured results made on the 12 test-pieces with periodic structures, fabricated using MEMS processes. The tooth width, A, trench width, B, pitch, τ, and height, h, of the test-pieces are depicted in Figure 2.

TABLE I. The 12 different test-pieces to evaluate wettability from measurements of the contact angles.

Structure No.	Pitch τ (nm)		Height h (nm)		Aspect ratio (A/B)
	Designed	Measured	Designed	Measured	
1	1000	1056	700	703	1
2		1029			2
3	1000	1259	500	514	1
4		1148			2
5	1000	1192	300	349	1
6		1138			2
7	500	529	700	656	1
8		550			2
9	500	620	500	473	1
10		536			2
11	500	592	300	212	1
12		558			2

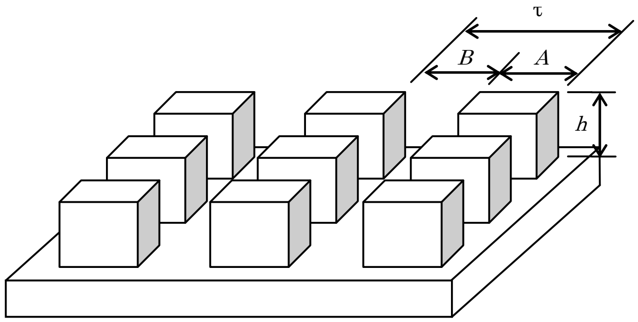


Figure 2. Parameter of the test-pieces with periodic structure fabricated on silicon by photolithography.

C. *Evaluation method of test-piece*

A scanning probe microscope (SPM; Nanonavi IIs/NanoCute, SII NanoTechnology Inc., Japan) was used to make observations of the scale of the test-pieces.

Prior to evaluating the wettability, the test-pieces were ultrasonically cleaned in alcohol, and dried for 20 minutes at 20°C in a thermostatically controlled chamber. A microscope (× 100, VH-E500, Keyence Co., Japan) and image-analysis software (Image J, Open source) were used to measure the contact angles. The amount of water dropped onto the surface was set to 1 µl.

IV. Results and Discussion

A. *Shape of periodic structure*

Periodic structure was observed in three-dimensional directions (Figure 3, showing test-piece No.5). The measured values of the width and height were almost the same as the designed values, the differences were 1 - 20% in maximum (Figure 4, showing test-piece No.5).

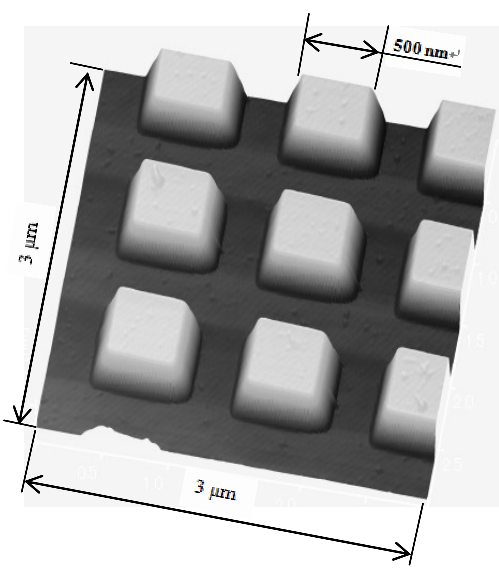


Figure 3. SPM image of the scales of the test-piece No.5.

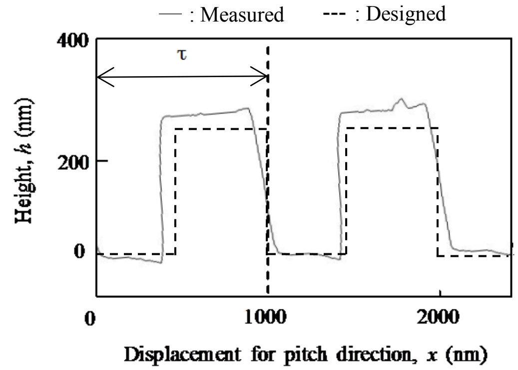


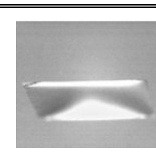
Figure 4. Measured results of the surface of the test-piece No.5 using the SPM.

B. *Evaluation of wettability*

The contact angles of the periodic structure on each test-piece were compared to that of a flat surface as the base-line. Not only hydrophilic but also hydrophobic tendencies were observed for the test-pieces. Test-piece No.6, which hasτ = 1,000 nm, height *h* = 300 nm, and aspect ratio A/B = 2 (Table 2) gave the maximum increase in contact angle, from 55° to 105.1°. The maximum decrease in contact angle, from 55° to 5°or less, was found for test-piece No.8, which has pitch τ = 500 nm, height *h* = 700 nm, and aspect ratio A/B = 2. Thus, with the application of a fine periodic structure to the surface, the wettability of a surface can be controlled over a large covering contact angles from + 50° (hydrophobic) to -55° (hydrophilic). That is, although the same material is used, the wettability of the surface can be controlled with a more than 100° range for the contact angle.

In addition, the pitch of the periodic structure at which the wettability switches from hydrophilic to hydrophobic was found to between 500 (hydrophilic) and 1,000 (hydrophobic) nm. Additionally, the height of the periodic structure at which the wettability switches from hydrophobic to hydrophilic was found to between 300 (hydrophobic) and 700 (hydrophilic) nm. Significant relationship was not found between the wettability and the aspect ratio, A/B.

TABLE II. Top data of the contact angles for both hydrophobicity and hydrophilicity in the 12 different test-pieces.

Hydrophobic	Flat surface	Hydrophilic
		
105.1° (+50.1°) No.6	55°	5° or less (-50°) No.8

C. *Comparison of theoretical and measured values*

Figure 5A shows the calculated results using the Wenzel equation (Eq.(6)) and Figure 5B shows the calculations using the Cassie-Baxter equation (Eq.(8)). Measured results from the test-pieces (No.1 – 12) are included in the plots. Although the absolute values of the theoretical and experimental results were not in agreement well, the tendencies were similar.

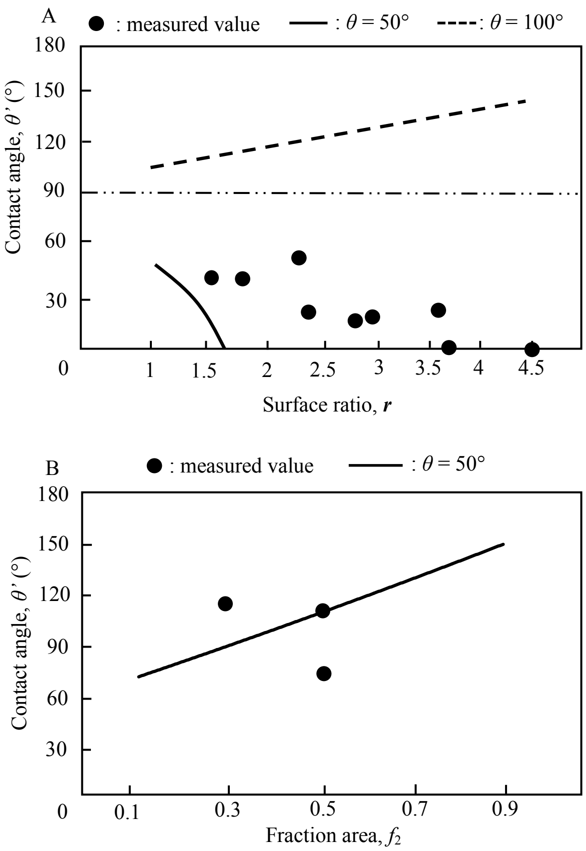


Figure 5. Comparison of contact angles between the theoretical and the experimental results. A Wenzel equation. B: Cassie-Baxter equation.

V. CONCLUSION

The threshold for the wettability of periodic structures between the nano- and micro-meter scales was evaluated both theoretically and experimentally. Our results indicated the following:

i) The threshold for the pitch for wettability was found to be between τ = 500 (hydrophilic) and 1,000 nm (hydrophobic).

ii) The threshold for the height for wettability was found to be between h = 300 (hydrophobic) and 700 nm (hydrophilic).

Further studies are needed to establish the conditions for super-hydrophobicity and super- hydrophilicity using both the chemical composition of the surface and nano- and micro-scale periodic structures.

REFERENCES

[1] A. Bange, H. B. Halsall, W. R..Heineman, "Microfluidic immunosensor systems," *Biosens Bioelectron.* vol.20, no.12, pp.2488–2503, Dec. 2005.

[2] D. L. Schmidt, C. E. Coburn, B. M. DeKoven, G. E. Potter, G. F. Meyers, D. A. Fischer, "Water-based non-stick hydrophobic coatings," Nature, vol. 368, pp. 39–41, 1994.

[3] K. Koch, W. Barthlott, "Superhydrophobic and superhydrophilic plant surfaces: an inspiration for biomimetic materials," *Philos. Transact. A Math. Phys. Eng. Sci*. vol.367, no.1893, pp.1487–1509, Apr. 2009.

[4] R. Fürstner, W. Barthlott, C. Neinhuis, P. Walzel, "Wetting and self-cleaning properties of artificial superhydrophobic surfaces," *Langmuir*, vol.21, no.3, pp.956–961, Apr. 2005.

[5] Z. Guo, F. Zhou, J. Hao, W. Liu, "Stable Biomimetic Super-Hydrophobic Engineering Materials," *J. Am. Chem. Soc.*, vol.127, no.45, pp.15670–15671, Oct. 2005.

[6] A. B. D. Cassie, S. Baxter, "Wettability of porus surface," Trans. Faraday Soc., vol. 40 pp.546–551, 1944.

[7] R. N. Wenzel, "Surface Roughness and Contact Angle," *J. Phys. Chem.*, vol.53, no.9, pp.1466–1467, 1949.

[8] R. N. Wenzel, "Resistance of solid surfaces to wetting by water," Ind. Eng. Chem., vol.28, no.8, pp.988–994, 1936.

[9] R. J. Good, "Contact Angle, Wettability, and Adhesion," R. F. Gould Ed. Washington, D. C.: American Chemical Society, 1964, pp.74-87.

[10] P-G. de Gennes, F. Brochard-Wyart, D. Quere, "Capillarity and Wetting Phenomena," A. Reisinger Trans. New York: Springer Science+Business Media Inc., 2004, pp.217–226.

[11] M. J. Madou, Fundamentals of Microfabrication, p. 760-769, CRC, Boca Raton, FL (1997).