Oil Repellent Evaluation Using Resonance Principle

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The contact angle is measured when evaluating oil repellency in water in the static wettability of a solid. Basically, it is common to observe the shape of a solid water droplet, oil or solid interface with a camera or a telescope and evaluate it from an image. The phenomenon of wetting is whether liquid is likely to adhere to the solid surface or not, and is discussed in terms of the contact angle. Although this method can evaluate the wettability of the surface at an instant, it is difficult to evaluate when maintaining the state of wettability or when changing the environment. Therefore, we considered a method that can evaluate the condition while observing the progress of the wettability on the surface. For surface wettability, we report a new oil repellent evaluation method using the resonance principle. In the near future, this new evaluation method can contribute to dynamic wetness that incorporates the elements of time.

Keywords: Oil repellent evaluation, Porous materials, QCM method, Resonance principle, Interface science, Antifouling technology

1. Introduction

In recent years, in addition to the characteristics possessed by the material itself, there is a demand for a material having a further function or having a plurality of functions. Specifically, the use of surface technology for environmental problems, energy, medical applications, etc. has increased expectations beyond various technological limits. Therefore, researches on surface functions for adding different functions to solid surfaces are actively conducted [1-6]. Although there are various functions in which the surface is involved, in particular, control of wettability to a liquid is used in daily life, industry, industry and the like. For example, cleaning of various substrates in the electronics industry is an important technology. In the transportation industry represented by automobiles and railways, rainwater improves visibility by means of water repelling technology of the windshield and body. In addition, in the automatic driving technology, there is a need for a technology that can accurately obtain information from sensors even if the environment changes due to mud or salt water. Thus, there are a wide variety of applied techniques that are affected by surface wetting.

Wetting properties of solid surfaces have long been dealt with in basic science such as surface physics, colloid interface science, and hydrodynamics [7-11]. The phenomenon of wetting is whether liquid is likely to adhere to the solid surface or not, and is discussed in terms of the contact angle. The wet state is formed on the line where solid, gas and liquid phases meet. (three phase line) When evaluating by contact angle, in order to consider droplets on a macroscopic scale, the situation is often different on a micro or nano scale.

We have developed oil repellent technology as a new metamaterial technology [12-15]. The nanoporous structure found in snail shells is oil repellent. By making full use of semiconductor technology, we have demonstrated oil repellent effect by imitating nano-sized structures. Next, as an applied technology to industry, a sheet having oil repellency was developed, and oil repellency
evaluation was performed by contact angle. However, although this method can evaluate the wettability of the surface at an instant, it is difficult to evaluate when maintaining the state of wettability or when changing the environment. There was no problem up to the evaluation of the oil repellent sheet, but when developing the oil repellent tube as a further development, it was necessary to make an evaluation with the passage of time taken into consideration.

From these backgrounds, this study proposes a new wetness evaluation method. The oil-repellent measurement which used the resonance principle which can evaluate a state is shown, observing progress of the wettability in the surface.

2. Evaluation method using resonance principle

When evaluating the dissolution of the resist, the QCM method (quartz crystal microbalance) [16-18] is used (Figs. 1 and 2). The QCM method allows you to measure the mass of the resist during development using the QCM substrate. If you know the resin density, you can convert the measured mass to a thickness. Thus, this method allows analysis of both the dissolution behavior of the resist and the swelling that occurs during development.

A new oil repellency evaluation can be performed by using this QCM method. By preparing nanostructures on a QCM substrate and measuring changes in resist thickness and frequency, the amount of oil adhering to the substrate can be determined. Therefore, it becomes possible to perform oil repellency evaluation of the nanostructure over time.

3. Experiment of oil repellent evaluation using QCM

First, a quartz mold is fabricated to fabricate nanostructures on a QCM substrate. The quartz mold was designed so that φ200 nm and φ100 nm pillars were arranged in a 10 mm square area in a square lattice shape with a pitch of 400 nm. After applying a resist to the quartz surface by spin coating, EB lithography is performed using a large area ultrafast electron beam lithography system (F7000S-KYT01) manufactured by Advantest. After development, the quartz was etched using a magnetic neutral wire discharge dry etching apparatus (NLD-570) manufactured by ULVAC (Fig. 3).

Next, using the produced quartz mold, hole patterns with a diameter of 200 nm and a diameter of 100 nm were formed on a QCM substrate in a square lattice shape with a pitch of 400 nm by a nanoinprint lithography [19] in a 10 mm square area (Fig. 4).

It is known that the nanostructures become oil repellent. The QCM substrate with nano-holes is placed in oil water and attached. Then, after taking out the QCM substrate, evaluation in a state where oil is peeled from the nanostructure is performed by putting it in water (Fig. 5).
4. Results and consideration of oil repellent evaluation by QCM method

The QCM substrate is oscillated at 5 [MHz] using a function generator. The QCM substrate with oiled nano-holes was placed in water. As shown in Fig. 6, it can be seen that oil is peeled from the nano-hole with time. After the QCM substrate was put in water, oil began to peel after 4 seconds and half was peeled after 79 seconds.

Next, data on elapsed time and frequency obtained from the QCM method is shown in Figs. 7-10. It can be seen that there is no change in the QCM itself, and no change in the resist sheet without a pattern. However, in the case of the 200 nm nanohole pattern, it is understood that the mass is increased at the center because the frequency is decreased. In addition, it was found that the frequency tended to increase after 130 seconds, and the data in Fig. 11 showed that the oil peeled off from the end and the oil collected at the center was gradually taken in water. The 100 nm nanohole pattern more notably embodies the 200 nm result.
5. Conclusion
The oil repellency evaluation was performed using the QCM method in consideration of the behavior when oil adheres and the time course. With the passage of time, the evaluation of the oil repellency state and the peeling state of the oil in the nanohole from the obtained frequency were found. It is a new evaluation method using the resonance principle to understand the wetting on solid surfaces.

References
1. A. Marmer, *Langmuir*, 22 (2006) 1400.
2. B. Bhushan, *Philos. Trans. R. Soc.*, 367 (2009) 1445.
3. B. Bhushan and E. K. Her, *Langmuir*, 26 (2010) 8207.
4. E. P. Ivanova, J. Hasan, H. K. Webb, V. K. Truong, G. S. Watoson, J. A. Watson, V. A. Baulin, S. Pogodin, J. Y. Wang, M. J. Tobin, C. Lobbe, and R. J. Crawford, *Small*, 16 (2012) 2489.
5. J. Knippers, K. G. Nickel, and T. Speck, “Biomimetic Research for Architecture and Building Construction” Springer International Pub. Co., Switzerland, (2016) 408.
6. A. G. Domel, M. Saadat, J. C. Weaver, H. H. Hariri, K. Bertolodi, and G. V. Lauder, *J. R. Soc. Interface*, 15 (2018) 1742.
7. C. G. L. Furmidge, *J. Colloid Sci.*, 17 (1962) 309.
8. S. Suzuki and T. Okazaki, *Bull. Chem. Soc. Jpn.*, 84 (1981) 330.
9. L. H. Tanner, *J. Phys. D. Appl. Phys.*, 90 (1989) 7577.
10. R.-D. Sun, T. Nishikawa, A. Nakajima, T. Watanabe, and K. Hashimoto, *Polym. Degrad. Stabil.*, 78 (2002) 479.
11. H. Noguchi, A. nakajima, T. Watanabe, and K. Hashimoto, *Water Sci. Technol.*, 46 (2002) 27.
12. T. Nishino, H. Tanigawa, and A. Sekiguchi, *J. Photopolym. Sci. Technol.*, 31 (2018) 129.
13. A. Sekiguchi, Y. Matsumoto, H. Minami, T. Nishino, H. Tanigawa, K. Tokumaru, and F. Tsumori, *J. Photopolym. Sci. Technol.*, 31 (2018) 121.
14. A. Sekiguchi, Y. Matsumoto, H. Minami, T. Nishino, H. Tanigawa, K. Tokumaru, and F. Tsumori, *Proc. SPIE*, 10728 (2018) 107280L.
15. T. Nishino, H. Tanigawa, and A. Sekiguchi, *Proc. SPIE*, 10728 (2018) 1072804.
16. A. Sekiguchi, M. Isono, Y. Kono, and Y. Sensu, *J. Photopolym. Sci. Technol.*, 17 (2004) 107.
17. S.-W. Lee, W. D. Hinsberg, and K. K. Kanazawa, *Anal. Chem.*, 74 (2002) 125.
18. K. K. Kanazawa, *Analyt.*, 130 (2005) 1459.
19. S. Y. Chou, P. R. Kreauss, and P. J. Renstom, *Appl. Phys. Lett.*, 67 (1996) 3114.