Ultra Water-Repellent Surface Resulting from Complicated Microstructure of SiO₂ nano particles

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Wettability is determined by surface free energy and surface geometric structure. Therefore, ultra water-repellent surfaces require a large roughness and a low surface energy. In this study, we controlled 3-dimensional surface microstructure of SiO₂ nano particles by electrostatic self-assembly process, which is one of the techniques for fabricating organic thin film. The film of poly (allylamine hydrochloride), poly (acrylic acid) and SiO₂ nano particles fabricated by the process, was very complicated in surface microstructure. After removing polymer from film, and the surface hydrophobic treatment by dimethyldichlorosilane, the hydrophobic SiO₂ nano particle film showing a contact angle of larger than 160° for water droplets was obtained. The value was very large compared with the water contact angle on silicon wafer treated by dimethyldichlorosilane. The difference was strongly dependent on the surface microstructure.
Key words: ultra water-repellent, surface microstructure, electrostatic self-assembly process, section analysis

1. INTRODUCTION

Wettability is an important property of solid surface. And water-repellent surface is needed with a view to protecting from a stain and so on. When the surface free energy is low, the water-repellency is enhanced. So, water-repellent surface is usually designed by such as fluorinated compounds, which have low surface free energy. However, a water contact angle on the lowest surface free energy material (6.7mN/m; closest packed -CF₃ groups) is about 120°[1]. For getting high water-repellent surface, surface roughness is required, because surface wettability is dominated by not only surface free energy but also surface structure.

The leaves of certain plants show water-repellency very much, in spite of not containing fluorinated compounds. For example, a taro's leaf shows ultra water-repellency, and its surface is very complicated in structure, revealed by microscopic observation. Therefore, we can get an ultra water-repellent surface that isn't dependent on fluorinated compounds, if the surface microstructure is well controlled. Non-fluorinated compounds are useful because they are environmentally sound. The processing methods of getting ultra water repellent surfaces have been studied. The methods combine surface micro indented structure and low-surface-energy materials [2-7].

The contact angle θ between a flat solid surface and a liquid droplet is given by Young's equation (eq 1) [8].

$$\cos\theta = (\gamma_S - \gamma_{SL})/\gamma_L \qquad (1)$$

where γ_S, γ_L and γ_L are the interfacial tensions of the solid-vapor, the liquid-vapor and the solid-liquid interfaces, respectively.

Wenzel suggested that the contact angle θ' of liquid droplets on the rough solid surface was written as eq 2 [9,10].

$$\cos\theta' = r(\gamma_S - \gamma_{SL})/\gamma_L \qquad (2)$$

where r is a Wenzel's roughness factor, which is defined as the ratio of the actual area of rough surface to the geometric projected area. Then, the relationship between θ and θ' is given by eq 3.

$$\cos\theta' = r\cos\theta \qquad (3)$$

Since r is larger than 1, the wetting gets better in hydrophilic surface ($\theta' < \theta$ for $\theta < 90°$) and worse in hydrophobic surface ($\theta' > \theta$ for $\theta > 90°$).

Cassie and Baxter indicated that the contact angle $\theta*$ on a solid/air composite surface was written as eq 4 [11].

$$\cos\theta* = -1 + \phi_S(\cos\theta + 1) \qquad (4)$$

where ϕ_S is the solid fraction of the surface.

From eq 3 and eq 4, ultra water-repellent surfaces require large surface area and low contact rate on liquid-solid interface.

In this study, we report the fabrication method of 3-dimensional surface microstructure of SiO₂ nano particles by electrostatic self-assembly process, which is one of the techniques for fabricating organic thin film [12]. Just by the alternate dipping of the charged substrate to polycation and polyanion solutions sequentially, multilayers of the organic thin films can be formed on the substrate with controlling at a molecular level. And the solution of nano particles can be used to fabricate electrostatic self-assembly films [13-15]. We pay attention to the surface structure of the films, and know that the surface is very complicated in structure.

2. EXPERIMENTAL

2.1 Materials

Poly(acrylic acid) (M_w=90,000) (PAA) was obtained from Polysciences as a 25% aqueous solution. Poly(allylamine hydrochloride) (M_w= 70,000) (PAH) was obtained from Aldrich Chemical. Polyelectrolyte dipping solutions of 10^{-2} M (based on the repeat unit molecular weight) were made from 18.2MΩ pure water.

Three types of SiO₂ particle (Si-7, Si-12 and Si-30) were obtained from Japan aerosil. Average diameter values of Si-7, Si-12 and Si-30 were 7nm, 12nm and 30nm, respectively. 0.05wt% SiO₂ particle mixed into PAH solution, and pH adjusted to 6.5 by the adding of NaOH. The ζ potential of SiO₂ nano particles in PAH solution was measured with ZEECOM (Microtech).

Silane coupling agent, dimethyldichlorosilane (DMDS)(Shin-Etsu Chemical) was used for surface hydrophobic treatment. Organic solvent, hexane (Junsei Chemical) was dried carefully with a molecular sieve 3A 1/16 (Junsei) before use.

Substrate was silicon wafer, which had 3000Å silicon oxide layer. The surface was etched by KOH solution and was cleaned by UV-O₃ treatment, then silicon oxide was charged negatively in aqueous solution.
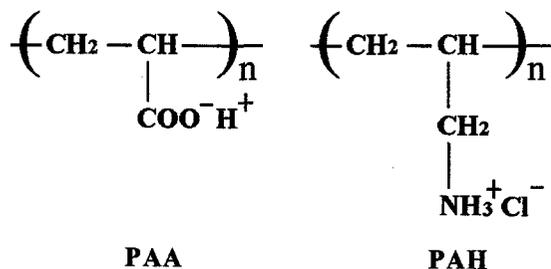

PAA   **PAH**

Figure 1. Chemical formula of PAA and PAH.

2.2 Preparation of electrostatic self-assembly films

In the first stage, a precursor film was deposited on the substrate. The substrate was dipped into PAH solution (10^{-2} unit M, pH6.5) for 5 minutes, and rinsed by pure water for 1 minute, three times. Next dipped into PAA solution (10^{-2} unit M) for 5 minutes, and rinsed, three times. Repeated three cycles, the precursor film, (PAH/PAA)₃, was obtained.

Next, electrostatic self-assembly film was grown by repeating the following steps: (1) dipped into PAH and SiO₂ particles mixture solution for 10 minutes; (2) rinsed by pure water for 1 minute, three times; (3) dipped into PAA solution for 10 minutes; (4) rinsed by pure water for 1 minute, three times. After one cycle (this 4 steps), 1bilayer of the electrostatic self-assembly film was deposited on substrate. By repeating the cycle, the electrostatic self-assembly films of 5 bilayers, 10 bilayers and 20 bilayers were obtained. After deposition, the films ware dried at 70°C for 1 hour

in vacuum.

The surface structure of the electrostatic self-assembly films was observed with a field emission scanning electron microscope. The observation revealed that the electrostatic self-assembly film didn't deposit as layer-by-layer but "island growth" in the early stage of adsorption (before about 10 bilayers). After about 10 bilayers deposition on substrate, the film grew all over the surface.

2.3 Preparation of water-repellent surface

The electrostatic self-assembly films were treated at high-temperature 650°C for 1 hour to remove polyelectrolytes (PAH and PAA). After the high-temperature treatment, SiO₂ nano particle films were obtained. The removal process was needed because the binding power between silane coupling agent and polyelectrolyte wasn't strong very much. By elementary analysis of the film's surfaces before and after high-temperature treatment measured with an X-ray photoelectron spectroscopy, it was confirmed that polyelectrolytes were removed from the film by the high-temperature treatment.

DMDS made the SiO₂ nano particle films hydrophobic. Under dry nitrogen atmosphere, 1ml of DMDS was dissolved into 250ml of hexane. The SiO₂ nano particle films were dipped into the silane coupling solution at room temperature for 15 hours. After dipping, the films were rinsed with hexane, and dried at 90°C for 1 hour. Finally, the films were rinsed with 18.2MΩ pure water to remove the residual chlorine, and dried at 90°C for 1 hour. For comparison, silicon wafer was also treated with DMDS by the same procedure, and then flat hydrophobic plate was obtained.

2.4 Surface observation

Surface microstructures of hydrophobic films were observed with an atomic force microscope (nanoscope IIIa, Digital Instruments) (AFM). Silicon cantilever was used for the tapping mode of the AFM.

2.5 Wettability measurement

Contact angles of water droplets on the hydrophobic film's surfaces were measured with an optical contact angle meter (CA-DT, Kyowa Interface Science). Water droplets were placed on the films by a tip of microsyringe. The diameter of the droplets was about 1mm. Before the measurement, the film was vibrated gently by tapping the stand to obtain the static contact angle (equilibrium contact angle).

3. RESULTS AND DISCUSSION

3.1 Dispersion of SiO₂ nano particles in PAH

The relationship among pH of mixture solution (PAH and Si-30), ζ potential of SiO₂ particles, and stability of dispersion was shown in table I. PH of the solution was adjusted by the adding of NaOH or HCl. The result indicated that the ζ potential and dispersion of SiO₂ nano particles were affected by pH of the mixture solution. In this paper, we adopted pH 6.5 of the mixture solution.

Table I. Relationship among pH of PAH and SiO_2 particles (Si-30) mixture solution, ζ potential of SiO_2 particles and stability of SiO_2 nano particles dispersion.

pH of the solution	ζ potential /mV	Stability of dispersion *
2.5	- **	- **
3.5	37.9	Δ
3.7 ***	41.4	O
4.5	40.8	O
5.5	37.0	O
6.5	36.8	O
7.5	34.4	O
8.5	27.7	O
9.5	21.8	Δ

* Stability of dispersion: O; good (pH 3.7 ~ pH 8.5), Δ; not good (pH 3.5 and pH 9.5.)
** SiO_2 particle didn't dispersed in the solution of pH 2.5.
*** No adding of NaOH or HCl.

We also could get the electrostatic self-assembly films by using the mixture solution of pH 3.7, pH 4.5, pH 5.5, pH 7.5 and pH 8.5. Surface microstructure, film thickness and wettability of the electrostatic self-assembly film made of PAH and PAA was affected by pH of the solutions [16].

And we also obtained similar results of ζ potential measurement of Si-7 and Si-12.

3.2 Result of water contact angle measurement and surface observation

Figure 2 was a photograph of water droplets placed on hydrophobic SiO_2 nano particle films of 20bilayers (SiO_2; Si-12), and the contact angle was 166° for water droplet.
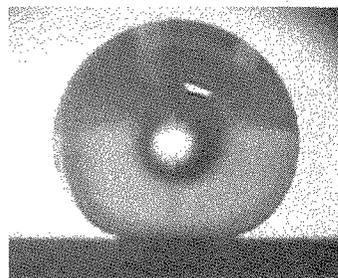
Figure 3 was AFM image of hydrophobic SiO_2 nano particle films of 5 bilayers, 10 bilayers and 20 bilayers (SiO_2; Si-30). The observation revealed that SiO_2 nano particle film was more complicated as the number of bilayers was larger. The result of water contact angle measurement and surface roughness (Rms) calculated from the AFM images was shown in table II. Surface roughness (Rms) was the standard deviation of the height values within the given area and was calculated as

$$Rms = \sqrt{\sum (Zi - Zave)^2 / N} \qquad (5)$$

where $Zave$ was the average of the height values within the AFM image, Zi was the height value, and N was the number of points within the AFM image.

3.3 Relationship between surface microstructure and wettability

The relationship between surface roughness (Rms) and water contact angle of prepared films was shown in figure 4. In the result, it couldn't be asserted that even a water contact angle was large as surface roughness was large. In this study, we paid attention to the section analysis obtained from AFM image. Figure 5 was the result of section analysis of Si-30 film of 5 bilayers and Si-12 film of 10 bilayers that had near surface roughness. From figure 5(b), it was shown that the surface formed uneven structure that had two types of periodic formation, one was about 500~1000nm, and the other was about 100nm. Therefore, it was supposed that the structure produced low contact rate between water and surface on liquid-solid interface, consequently showed ultra water-repellency.


**Figure 2.** Water droplet on hydrophobic SiO_2 nano particle film (SiO_2; Si-12, 20 bilayers).
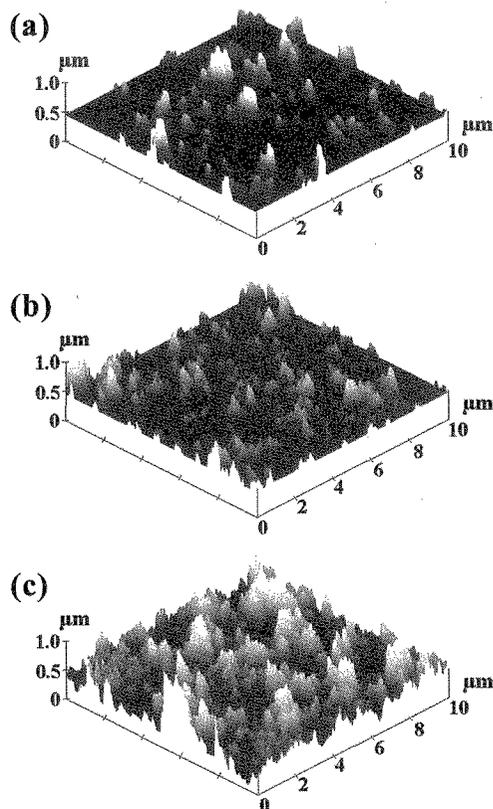
Figure 3. AFM image of hydrophobic SiO_2 nano particle films (a) 5 bilayers, (b) 10 bilayers, (c) 20 bilayers (SiO_2; Si-30).

Table II. Results of water contact angle (C.A.) measurement and surface roughness (Rms) calculated from AFM images of prepared films.

Samples	C.A.	Rms /nm
Si-7		
5 bilayers	119°	59.4
10 bilayers	147°	68.9
20 bilayers	165°	158.0
Si-12		
5 bilayers	128°	71.6
10 bilayers	162°	83.6
20 bilayers	166°	102.4
Si-30		
5 bilayers	107°	82.2
10 bilayers	126°	76.7
15 bilayers	163°	146.7
Silicon wafer	101°	3.8
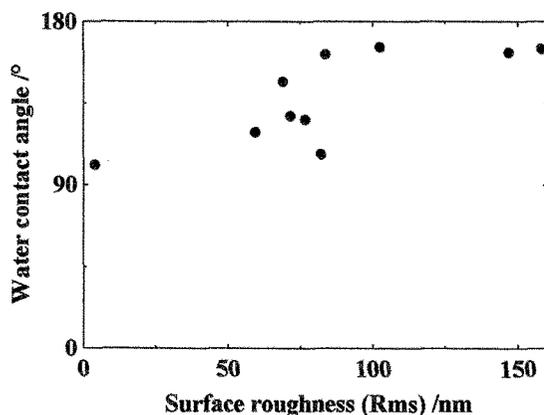
Figure 4. Relationship between surface roughness (Rms) and water contact angle of prepared films.

(a)

(b)

Horizontal /μm
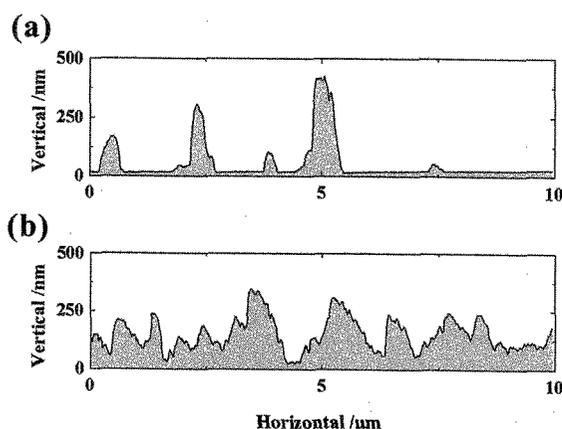
Figure 5. Section analysis of prepared films,
(a) Si-30, 5 bilayers(Rms=82.2nm,C.A.=107°),
(b) Si-12, 10 bilayers(Rms=83.6nm,C.A.= 162°).

Namely, it was understood that surface roughness (Rms) wasn't necessarily dominant factor of water repellency. Therefore, it was important for discussing relationship between water-repellency and surface microstructure to estimate contact rate between water and surface on liquid-solid interface by section analysis.

4. CONCLUSIONS

We showed the fabrication method of SiO₂ nano particle film by using electrostatic self-assembly process. The film's surface was very complicated in structure, and after surface hydrophobic treatment by DMDS, the SiO₂ nano particle film showed ultra water-repellency. The ultra water-repellency resulted from low contact rate between water and surface on liquid-solid interface. We made it clear that ultra water-repellent surface was realized without using fluorinated compounds.

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