Characteristics of Ultra Water-repellent Films Prepared by Capacitively-coupled Plasma CVD with Fluorocarbon-free Reactant

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Abstract: Ultra water-repellent films were prepared by the capacitively-coupled plasma CVD method with fluorocarbon-free reactant. By controlling the deposition time, we achieved various surface morphologies. The relationships among the static water contact angle, the morphological properties, and the growth process of the films were discussed.

Keywords: Ultra Water Repellency, Capacitively Coupled Plasma CVD, Surface Morphology

1. INTRODUCTION

Ultra water-repellent films, with a water contact angle greater than 150°, are attractive materials in many industrial fields such as prevention of adhesion of raindrops or snowflakes, traffic indicators with self-cleaning surface, enhancement of flow conductance in tubes and pipes, reduction of frictional drag on ship hulls, metal refining, corrosion protection for metals, stain-resistant textiles and cell mobility [1-4].

There are two factors to increase water-repellent property. One is the chemical factor that is related to the surface energy, and the other is the geometric factor which is involved in the true surface area resulting in an increase in nominal surface energy. In particular, geometric factor is more important than chemical one to show ultra water repellency. Practically, smooth -CF₃ terminated surfaces show the water contact angle of ~120° [5]. Therefore, in order to realize the ultra water repellency, geometric factor is necessary.

We have succeeded in fabricating ultra water-repellent films with rough surface structure at room temperature by using a remote-type microwave plasma CVD (MPECVD) method with reactant molecules with C-H functional groups instead of C-F groups which have quite high global warming coefficients [1,2]. However, it is difficult to deposit the films on large area by the remote-type MPECVD method. In order to apply the films to many industrial products, it is necessary to deposit them on large area. The capacitively-coupled plasma enhanced CVD (CCP-CVD) has been known as an easy method to generate large-size uniform plasma.

In this paper, we report on fabrication of ultra water-repellent films by the CCP-CVD method instead of the remote-type MPECVD. By controlling the deposition time, we achieved various surface morphologies. The relationships among the static water contact angle, the morphological properties, and the growth process of the films were discussed.

2. EXPERIMENTAL

Figure 1 shows the conventional CCP-CVD system used in this study. The chamber was connected to vacuum system and two gas supply lines for Ar and a reactant organosilicon. The electrode interval was kept at 30 mm. A 13.56 MHz generator supplied radio-frequency (rf) power. The reactant organosilicon was trimethylmethoxysilane (TMMOS; (CH₃)₃SiOCH₃). Substrates were p-type Si(100) plates cutted from a 5" wafer into the size of 25 mm×25 mm. The substrate was located at the anode plate. Firstly Ar gas was introduced into the chamber until the pressure of 15 Pa and then adjusted to the pressure of 30 Pa by controlling vacuuming rate. Secondly, the reactant TMMOS gas was introduced until the total pressure of Ar and TMMOS reached at 80 Pa. The rf power was fixed at 300 W. The films were prepared under various deposition time in the range of 3 to 90 s. Static water contact angle of deposited film surfaces was measured with a contact angle meter (Kuluss, DSA10-Mk2). Surface morphologies of the films were observed with a field emission scanning electron microscope (FESEM; JEOL, JSM-6330F). Chemical bonding states of the films were analyzed by a Fourier-transform infrared spectrometer (FT-IR; Digilab, FTS-7000). 3D roughness data of the films were measured by a laser scanning microscope (KEYENCE, VK8710). The roughness factor is defined as the ratio of the real surface area to the projected area.

Fig. 1 Schematic diagram of the CCP-CVD system
3. RESULTS AND DISCUSSION

Fig. 2 shows static water contact angle \( \theta \) of the films prepared at various deposition time. At the deposition time shorter than 10 s, the films show a constant \( \theta \) value around 80°. In contrast, in the deposition time region longer than 30 s, \( \theta \) increases with deposition time and reaches >150° at the deposition time of 60 s. At the deposition time of 90 s, \( \theta \) value shows 159°.

The surface morphologies of the films observed by FESEM are shown in Fig. 3 and Fig. 4. At 3 s of deposition time (Fig. 3(a), Fig. 4(a)), a few nano-clusters can be observed, but the surface morphology of the film is quite flat without any texture. At more than 10 s of deposition time (Fig. 4(b) ~ (e)), we can observe the nano-clusters which are in size of several tens of nm. These clusters probably originate from a plasma polymerization process.

![Fig. 2 Static water contact angle of the films prepared at various deposition time.](image)

![Fig. 3 FESEM images at low magnification of the films prepared by the CCP-CVD method at various deposition time ((a) 3 s (b) 10 s (c) 30 s (d) 60 s (e) 90 s).](image)

![Fig. 4 FESEM images at high magnification of the films prepared by the CCP-CVD method at various deposition time ((a) 3 s (b) 10 s (c) 30 s (d) 60 s (e) 90 s).](image)
in the gas phase and deposit on the substrate. At early stage of the film deposition (3 s, 10 s, 30 s), the surface morphology of the films is approximately flat with low density of the nano-clusters (Fig. 3(a) ~ (c)). From the facts that the bare Si surface and the film deposited for 3 s show the water contact angles of <10° and >80°, respectively, there is a smooth hydrophobic film grown on the Si substrate even though no texture is observed in SEM. That is to say, the growth of the hydrophobic film and the deposition of the nano-clusters occur concurrently. Because the smooth structure is dominant, the films deposited for a short term do not exhibit the ultra water repellency. The films deposited for longer time (60 s, 90 s), on the other hand, have rough surfaces with high density of the nano-clusters (Fig. 3(d), (e)). In particular, the film deposited for 90 s has a cancellous web-like structure, which seems to arise from the agglomeration of the nano-clusters (Fig. 4(e)). Although the agglomeration of the nano-clusters is observed at 10 s, the size and density of the agglomerates become larger and higher with deposition time. Because of the rough surface structures, the films deposited for long term exhibit the ultra water repellency. The relation between the water repellency and the surface roughness will be discussed later.

The FT-IR spectra of the films are shown in Fig. 5. Each absorption band was identified as O-H stretching (A), C-H stretching (B), Si-H stretching (C), Si-CH₃ (D), Si-CH₃ symmetric deformation (E), Si-O-C or Si-X-Si where X=O, CH₃ (F), Si-O stretching (G), Si-C rocking (H) and poly Si-O-Si, Si-CH₃-Si (I) [8,9]. In the FT-IR spectra of the films prepared at various deposition times, there are no variations in the sorts of the detected band. The band F (Si-O-C or Si-X-Si where X=O, CH₃) of the film deposited for 60 second is relatively large and sharp compared with the films deposited for 30 and 90 second. The absorption intensity of the band D (Si-CH₃) grows with an increase of the deposition time. The bands A (O-H) and B (C-H) become broader with an increase of the deposition time. However, there is not significant difference in the framework structure of the films. Therefore, we can say that these films consist of Si-X-Si (X=O, CH₃) and/or -CH₂-networks with -OH, -CH₃ and -H terminations. The film surfaces are covered with the hydrophobic functional groups (-CH₃ and -H) together with the hydrophilic ones (-OH). Since the amount of the latter is much smaller than the former, the film surfaces show hydrophobicity. The water contact angle of the -CH₃-terminated flat surface is reported as ~110° [10]. The film surfaces prepared in this study shows much higher value, greater than 150°. Therefore it is obvious that the ultra water repellency of the film surfaces is enhanced by the geometric factor.

Fig. 6 shows relations between static water contact angle and roughness factor of the films prepared at various deposition time. To describe the wet property on rough surfaces, Wenzel defined roughness factor as the ratio of the real surface area to the projected area [6]. In the wet property at rough surface, Contribution of solid surface energy increases. That is to say, water-repellent surface becomes more repellent and water-attracting surface becomes more attracting. The Wenzel-style effect is available in the case of small surface roughness. In the case of large surface roughness, on the other hand, Cassie-style effect is available, where air gets into a solid liquid interface [7]. Then, water contact angle dramatically improves since water contact angle between air and water is 180°. Compared with roughness factor of 2.8 and 6.5 at Fig. 6, static water contact angle value reaches saturation region. Therefore we cannot apply Wenzel-style effect to roughness factor of 2.8 and 6.5 in Fig. 6 at least. That is, a mode shifts from Wenzel-style effect to Cassie-style effect around two latter half of roughness factor.

The geometrical effect for these film surfaces is ascribable not only to the expansion of the nominal surface area (Wenzel-style effect [6]), but also to the air trapping between the water-droplet and agglomerated textures on the film surfaces which minimizes the contact area (Cassie-style effect [7]).

4. CONCLUSIONS
We succeeded in preparation of ultra water-repellent films by CCP-CVD method with TMMOS that is fluoro-carbon-free reactant. The TMMOS reactant molecules were partly-dissociated and then polymerized in the plasma. The methyl fragments terminating the polymer networks have a role to show hydrophobicity. The film had high surface roughness, which significantly enhanced water repellency.
REFERENCES