

Formation of SiO:CH Ultra Water Repellent Thin Films by Inductively Coupled RF PECVD

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Abstract : In this paper, the UWR thin films were prepared by RF PECVD. The relationships between the deposition conditions and the film properties such as morphological and chemical properties of the films were discussed. Moreover, from the analysis of plasma diagnostics using OES, formation mechanism of UWR thin films was discussed.

Key words : Ultra water repellent thin films, SiO:CH, OES, FT-IR, PECVD

1. Introduction

During the past decades, researchers have paid attention to the study of hydrophobic materials that can be found in nature [1-3]. The primary example studied showing this behavior is hydrophobic leaves. Many kinds of leaf surfaces of plants have been studied to investigate the effect of roughness and water repellency [4]. One of the most famous examples is lotus leaves. Lotus leaves have micro and nano-structures in the surface together with wax crystals, leading to ultra water- repellency. Water droplets on the lotus surface are almost spherical and roll off easily, which is usually referred to as the "lotus effect". Inspired by such as ultra water repellent (UWR) living organisms in nature, artificial UWR surfaces have attracted great interest in both fundamental research and industrial fields due to an expansion of requirements in the reduction of frictional drag on ship hulls, prevention of adhesion of raindrops or snowflakes onto windows and antennas, traffic indicators with self cleaning surface, metal refining, stain resistant

textiles, and cell motility [5-10].

On the basis of these aspects, various approaches have been proposed for the preparation of UWR surfaces via the construction of an appropriate surface geometry structure. In particular, Takai have succeeded in fabricating transparent and highly-durable UWR thin films at room temperature by microwave PECVD (MPECVD) using organosilicon molecules [11]. However, in the usage of microwave in the field, it has limitations due to a cost performance and its manageability. Therefore, it is necessary to change a plasma source from microwave to radio frequency, which can control easily.

In this paper, the UWR thin films were prepared by RF PECVD instead of MPECVD method. The relationships between the deposition conditions and the film properties such as morphological and chemical properties of the films were discussed. Moreover, from the analysis of plasma diagnostics using OES, formation mechanism of UWR thin films was discussed.

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2. Experimental procedure

This work was carried out with the RF PECVD system. The reactant used in this work was trimethylmethoxysilane [TMMOS; $(\text{CH}_3)_3\text{SiOCH}_3$]. The films were prepared under various RF power in the range of 50 ~ 200 W and the total pressure of Ar and TMMOS of 500 Pa. Deposition time was fixed at 3 minutes. After deposition, water-droplet contact angle of the films was measured by a static water contact angle meter (Kyowa Interface Science, CA-D and Kuluss, DSA10-Mk2). The surface morphology was observed by a field-emission scanning electron microscope (FESEM, JEOL, JSM-6330F). The chemical bonding states were characterized by a Fourier transform infrared spectrometer (FT-IR, Digilab, FTS-7000). Plasma diagnostics was performed by optical plasma emission spectroscopy (OES, Chromex, 500-IS).

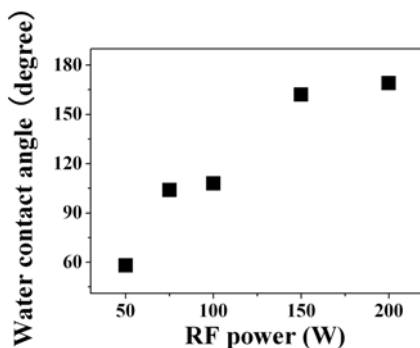


Figure 1: Effect of RF power on water contact angle of thin films.

3. Results and discussion

3.1 Deposition of UWR thin films

Figure 1 shows the relation between water-droplet contact angles of the films and RF power. The water-droplet contact angle of the deposited films increases with the RF power. In the deposition conditions at 150 and 200 W, the water-droplet contact angle exceeds 150° , called ultra-water repellency.

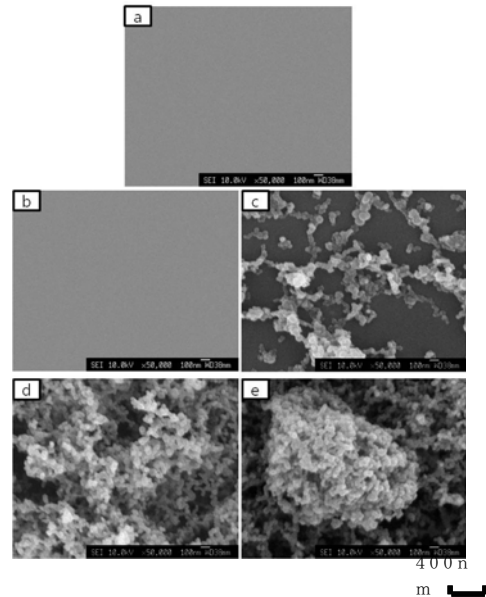


Figure 2: FESEM images of the films prepared at various RF powers ((a): 50W, (b): 75W, (c): 100W, (d): 150W and (e): 200W).

The surface morphology of the films observed by FESEM is shown in Figures 2. Under 50 and 75 W of the RF power, the surface morphology of the films is quite flat without any texture nor nano-clusters. Under 100 ~ 200 W of the RF power, the nano-clusters which are in size of several tens of nm can be observed. From the spherical shape, these nano-clusters were supposed to be originated from a polymerization process in the gas phase and deposit on the substrate. The SEM images indicate that the morphology depends clearly on the RF power. Under the lower RF power (100 W), the surface morphology of the films is approximately flat with low density of the nano-clusters. Because of the smooth surface structure, the water droplet contact angle of the film deposited at 100 W does not exhibit the ultra water repellency. The films deposited at higher RF power, on the other hand, show micrometer scaled roughness. For example at 200 W of the RF power, micro-size particles pores which consist of

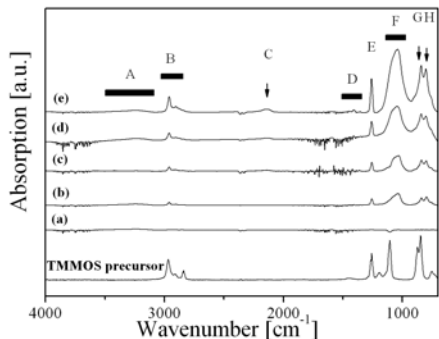


Figure 3: FT-IR absorption spectra for the TMMOS reactant and films ((a): 50W, (b): 75W, (c): 100W, (d): 150W and (e): 200W). The alphabet notations are defined in the text.

nano-clusters are observed. These films have particular nano-textures with nano-scale pores of a few hundreds nanometer in diameter among the cancellous web-like structure of the nano-cluster agglomerates or the micro-particles. The rough surfaces of the films result in the water contact angles greater than 150° . The geometrical effect for these film surfaces is ascribable not only to the expansion of the nominal surface area (Wenzel-style effect [12]), 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 [13]).

3.2 Chemical bonding states of UWR thin films

The FT-IR spectra of the films are shown in Figure 3. Each absorption band was identified as O-H stretching (A), C-H stretching (B), Si-H stretching (C), Si-CH₃ stretching (D), Si-CH₃ symmetric deformation (E), poly Si-X-Si asymmetric (F), Si-(CH₃)₃ rocking (G) and poly Si-O-Si deformation (H) [14-15]. In the FT-IR spectrum for the film deposited at 50 W, there is no absorption band related to Si, instead, only two absorption bands, A (O-H) and B (C-H), were observed. This result indicates that SiO:CH film deposition does not occur in this condition, but the

small amount of radicals impinge onto the substrate to modify the substrate surface. Then the surface is predominantly covered with -OH termination, which is known as hydrophilic functional group. Therefore, water-droplet contact angle of the surface at 50 W is markedly low comparing with the other samples. At the RF power of 75 ~ 200 W, SiO:CH deposition can be confirmed from the existence of the absorption band F in the FT-IR spectra, where no variation in the sorts of the detected band is observed. The absorption intensities of these absorption bands grow with an increase in the RF power except the band A (O-H), which shows maximum absorption intensity at the RF power of 100 W. The band B (C-H) becomes broader with an increase in the RF power. These results show that the film consists of Si-X-Si (X=O, CH_x) and/or -CH₂- networks with -OH, -CH₃ and -H terminations. The basic chemical bonding states of the terminations seem to be not far from that of the reactant molecule since the positions and the fundamental shapes of the absorption bands B, E and G are similar to the reactant except the broadening of these bands, which is due to the diverseness of the bonding states. Therefore, the films are supposed to be formed through plasma polymerization reaction of partly-dissociated reactant molecules and termination of the dangling bonds by the small fragments of the reactant molecules such as methyl radicals and hydrogen atoms.

The film surface is covered both with hydrophobic functional groups (-CH₃ and -H) and hydrophilic ones (-OH). Since the amount of the latter is much smaller than the former, the deposited film surfaces show strong hydrophobicity. The water contact angle of the -CH₃ terminated flat surface is reported as $\sim 110^\circ$ [16]. The film prepared in this study shows much higher value, greater than 150° . It is obvious that the ultra water repellency of the film surfaces is enhanced with the geometrical effect.

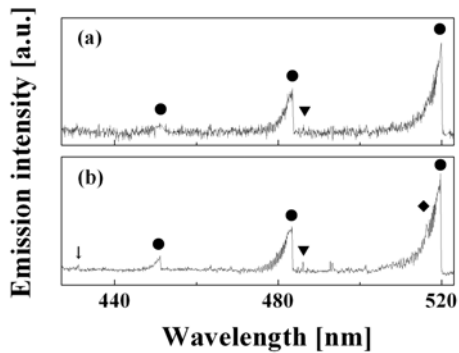


Figure 4: Optical emission spectra of inductively coupled plasma, during deposition of the UR and the UWR films at the RF power of (a) 100 W, (b) 150 W. A triangle(▼), circles(●), a diamond(◆) and an arrow(↓) indicate the lines from atomic H, CO Ångström emission bands, C2Swan system and CH band, respectively.

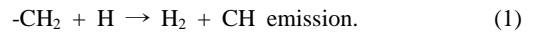
3.3 Plasma diagnostics in the formation of UWR thin films

Figures 4 show the optical emission spectra in visible range for the Ar-TMMOS plasma recorded during deposition of the WR (a) and the UWR (b) films. Emissions from Ar, H, CO and H₂ were detected mutually. At 150 W of RF power, however, emission bands from emissions CH (4300 Å system, A²Δ-X²Π) and C₂(swan system, A³Π_g-X³Π_u) were also detected at 431 and 516 nm, respectively. About the CO emission, the Ångström system band (B¹Σ⁺ A¹Π) were observed between

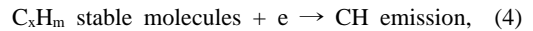
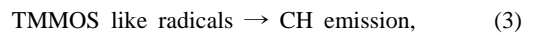
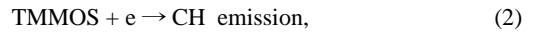
Table 1: Optical emission spectrum intensities of H_α and H_β at inductively coupled silane plasma with 420 Pa TMMOS and 80Pa Ar, during deposition of UWR thin films.

Deposition condition			H _α	H _β	H _β /H _α
Ar (Pa)	TMMOS (Pa)	RF Power (W)	Intensity (counts)	Intensity (counts)	
80	420	100	907	109	0.12
80	420	150	11377	665	0.06

480 and 560 nm wavelengths. In the range of 560 ~ 690 nm, overlapped lines from H₂ can be seen. One of the origins of the CH molecule is supposed to be the hydrogen abstraction reaction, which comes mainly from dissociation of the -CH₃ groups in the TMMOS.



Moreover, those can be emitted through



In the low power regime, Equation (2) should be predominant and hence all the emission intensities as well as the deposition rate are proportional to the RF power. In a RF power regime of 40 - 100 W the contribution of Equation (3) - (5) becomes appreciable, because the emission intensities increase with the RF power whereas the deposition rate is constant. Two methyl radicals (CH_x+CH_y) recombine into a hydrocarbon molecule(C₂H_{x+y}), which can be also striped by the hydrogen abstraction reaction resulting in the C₂ radical formation. That is, in the 500 Pa of relatively high pressure, similar plasma reactions happen in compared with those in low pressure. However, appearance of emissions of CH and C₂ radicals at the 500 Pa of pressure and 150 W of RF power, which is condition for the UWR films, provide a clue of the recombination reaction as well as the clustering phenomenon, i.e. the clusters can be formed only in the condition of severe recombination reaction.

Table 1 shows the optical emission intensities of H_α and H_β during the deposition of the water-repellent thin films. From the optical emission intensities of atomic H_α (656 nm) and H_β (486

nm), the OES intensity increased approximately 10,000 and 500 counts with RF power, respectively. However, a relative intensity of H_{β}/H_{α} decreased with the RF power. From the relation between the optical emission intensity and the electron temperature, it is well known that H_{β}/H_{α} can indicate the electron temperature in plasma [17-19]. These results suggest that higher RF power increases the electron density, which is mainly due to the further activation of dissociative ionization reaction in the plasma, while the increased electron density influences a decrease of the electron temperature. Since the RF plasma of the Ar-TMMOS mixture gas is used in this study, the above mentioned dissociation reactions (1) - (4) can be induced by the collision with metastable Ar* (11.55 or 11.72 eV), which has much higher energy than the bond dissociation energies of C-H (4.27 eV), H-H (4.52 eV) and C-O (3.64 eV) [20-21].

4. Summary

UWR thin films on Si (100) substrates were prepared by RF-PECVD. Contact angle of the deposited film was greater than 150°. This ultra water repellency was due to the combination effect of CH₃-terminated surfaces and the surface roughness which is self-assembled with nano-clusters and their agglomerates. From the result of the optical emission spectroscopy, existence of H, CO, CH, C₂, and H₂ were proved in organosilicon plasma for the fabrication of UWR thin films, which can describe the formation reaction of the ultra water repellent film in the plasma as polymerization of partly dissociated reactant molecules.

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