Plasma Chemical Formation of Water-Repellent Organic Thin Film on Potential-Controlled Electroconductive Substrate

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1. Introduction

Water repellency has been required in various fields, and so extensive studies on the preparation of water-repellent surface have been carried out so far.[1-3] Recently, super water repellent surface has become a major interest, whose contact angle against waterdrop exceeds 150 degrees. From that point of view, we have reported the preparation of super water-repellent non-woven fabrics by an inductively coupled radio-frequency (RF) plasma of fluorohydrocarbon (FHC).[4] We, also, have proposed a unique dynamic plasma CVD method to prepare super water-repellent organic thin films with chemical and morphological gradient toward the depth on a non-metallic substrate such as quartz and plastic materials.[5] We have, however, experienced that it is rather difficult to prepare the similar super water-repellent thin film by an inductively coupled plasma CVD just on a metallic or electroconductive substrate such as silicon substrate. The difficulty may arise from the eddy current generated at the substrate surface by the influence of an inductively coupled high frequency exposure. If the speculation is actually to the point, the water repellency of the plasma film formed on the electroconductive substrate will be improved by applying the positive voltage directly to the substrate to reduce the magnitude of the interfering eddy current. On the contrary, applying the

negative voltage to the substrate will reduce the water repellency because of the negative charge to enhance the eddy current. In this study, from that point of view, the relationship between the water repellency of thin films resulted from the inductively coupled plasma CVD of vinylidene fluoride (VDF, $\text{CH}_2=\text{CF}_2$) on silicon substrates and the electric potential applied to them was examined to obtain some mechanistic hints for application.

2. Method

The plasma apparatus was shown in Fig. 1, which was consisted of a 13.56-MHz RF generator, an RF power meter, a tuner, a copper coil tubing, and a 4.5-cm outer diam. and 50-cm length Pyrex reactor tube equipped with vacuum gauges, gas pressure control valves, and mass flow controllers via taper joints. Square silicon substrates (10-mm side length and 0.5-mm thickness) were used as electroconductive samples. They were placed at two positions of 2 and 3 in the reactor tube in Fig. 1, i.e. 2-cm and 5-cm downstream positions from the downstream end of the copper coil tubing, respectively, after they were preliminary rinsed with ammonia-buffered hydrofluoric acid solution (containing 22% ammonium bifluoride) and pure water to remove the surface oxide layer and dried successively, and assembled as shown in Fig. 2. Then, the reactor tube was evacuated below 0.1 Pa

Fig. 1 Plasma apparatus used.

Fig. 2 Assembly of a silicon substrate sample.

and gaseous VDF was introduced into the reactor tube through an upstream gas inlet. Then, inductively coupled plasma was generated under 1-100 Pa VDF vapor pressure. CVD reactions were carried out under a constant VDF gas flow and pressure. A typical plasma condition was P , 40 W; r_{VDF} , 20 cm³min⁻¹; and p_{VDF} , 130 Pa. Substrates were kept at room temperature during plasma CVD. The water repellency of thin films were evaluated by measuring the contact angle of 1.6-mm diam. drops of water with a contact anglemeter (Kyowa Kaimenkagaku Co. Ltd., type FACE CA-D).

3. Results and Discussion

The contact angle of a waterdrop (θ) against the thin film prepared by the inductively coupled VDF plasma CVD on an electrically isolated silicon substrate fixed at the position 2 in the reactor was ca. 95 degrees. The water-repellent film preparation on silicon was carried out under the following plasma conditions: P , 40 W; r_{VDF} , 20 cm³min⁻¹; and p_{VDF} , 130 Pa, which were empirically appropriate to prepare the super water-repellent film ($\theta > 165$ degrees) on quartz and even other non-metallic substrates.[4,5] We consider that the remarkable deterioration of water repellency on silicon may be caused by the eddy current generated at the substrate surface. When the positive direct current voltage was applied to the

Fig. 3. Relationship between the electric potential applied to silicon substrates and the contact angle of waterdrops against thin films derived from the inductively coupled VDF plasma on the substrates fixed at the position 2 in the reactor: P , 40 W; r_{VDF} , 20 cm³min⁻¹; and p_{VDF} , 130 Pa.

silicon substrate in order to reduce the magnitude of the eddy current, θ was increased and the water repellency was improved. When, on the contrary, the negative direct current voltage was applied to it to promote the eddy current, θ was decreased and the water repellency still more deteriorated. All of the experimental data of θ to the electric potential (E) applied to silicon substrates were plotted in Fig. 3. The plot clearly shows the positive correlation between E and θ within the experimental limits of -500 V to +500 V just as we have expected. These data suggest that a wide variety of water-repellent thin films can be prepared systematically on silicon substrates and even on other electroconductive substrates using the inductively coupled FHC plasma just by changing the electric voltage applied to the substrate. Further study is now in progress.

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