

Infrared Spectroscopic study on interaction between plasma and solid surface

プラズマ-表面相互作用の赤外分光計測

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We investigate interaction between self-assembled monolayer (SAM), deposited with octadecyltrichlorosilane, and plasma generated in 30% hydrogen peroxide water (H_2O_2), with in-situ and real-time infrared absorption spectroscopy in multiple internal reflection geometry (MIR-IRAS). The IR data indicate that plasma generated OH, and that the amount of CH_2 and CH_3 are decreased with plasma exposure. It is suggested that SAM is etched by generated OH.

1. Introduction

Plasma bio- and medical application has been attractive in these days [1]. A lot of efforts have been made to develop the applications. Many reports have showed a lot of methods for bio- and medical applications thus far. Unsolved problems have remained. One of them is mechanism of the interaction between bio materials and plasmas. Biomaterials are hard to be treated, because the bio molecules, such as proteins, carbohydrate and so on, have heavy weights and complicated molecular structures. Model materials of bio materials are preferred. Parts of model molecules should have a molecular structures, similar to bio-molecules.

We choose self-assembled monolayer (SAM). A SAM consists of chemically definite monomers, which has definite chemical structures. The monomers are organic materials with various functional groups, such as amine group (NH_2), methyl group (CH_3), thiol group (SH). These functional groups are important to bio-molecules, especially proteins, amino acids containing NH and SH.

Bio-materials are compatible to water, because living cells are surrounded with water. Then, it is important to investigate interactions between bio-model molecules and plasma in water. We have paid attention to plasma generated in liquid. We have generated plasma in ethanol using barrier discharge to deposit amorphous carbon films [2].

We used infrared absorption spectroscopy in multiple internal reflection geometry (MIR-IRAS), to investigate the interaction. This is because we can monitor the chemical states of the SAM during plasma even in liquid as well as in vacuum, with this method. We have made the MIR-IRAS monitoring system for liquid process [3]. Both of the chemical changes in liquid and chemical states

of deposits can be measured with this in-situ and real-time infrared spectroscopy. SAM is suitable to this method, because particular SAM can be deposited on Si prism surface, if source monomer contains siloxane bonds in it.

In this study we investigate interaction between SAM and plasma with MIR-IRAS. We choose the CH_3 terminated SAM, which is suitable to basic study because the SAM contains only CH_2 and CH_3 . We can easily distinguish the reactions.

2. Experiments

A Fourier transform infrared (FTIR) spectrometer (JASCO: FT-6100, Tokyo, Japan) employing a mercury cadmium telluride (MCT) detector was used in this study for MIR-IRAS monitoring. The total IR light path was purged with H_2O -free and CO_2 -free air, generated by the FTIR purge generator (Parker Hannifin, Haverhill, MA, USA). The plasma was generated by applying 10kHz high voltage power supply to the core line in the glass tube, compared with grounded meshed metal surrounded over the glass tube. Detailed schematics were described in the previous paper [3].

The MIR prism was prepared from n-type P-doped, double-side polished Si(100) wafers with a resistivity of approximately $10 \Omega \text{ cm}$. The dimensions were $10 \times 40 \times 0.5 \text{ mm}^3$, with 45° bevels on each short edge. Each Si prism was cleaned using conventional RCA cleaning, and the prism surface was covered with chemical oxides produced in a boiled H_2SO_4/H_2O_2 solution. IRAS spectra were acquired using the spectrum of the chemical-oxide-covered surface as the reference spectrum. After the prism surface was cleaned again, 2.5 mM octadecyltrichlorosilane (OTS: Tokyo Chemical Industry, Tokyo, Japan) solution in

toluene was dropped on the surface at RT to form SAM. The SAM is denoted as OTS-SAM in this paper. We generated plasma in 30% hydrogen peroxide water (H_2O_2), because plasma is easily generated in H_2O_2 , compared with in water.

3. Result and discussion

We measured IR absorption spectra of OTS-SAM during plasma in H_2O_2 , as shown in Fig. 1. The vertical axis indicates the difference absorbance from the prism before plasma exposure. Upward peaks indicate increasing portions on the prism and the downward peaks indicate decreasing portions. We observed that the downward peak at approximately 3200 cm^{-1} , which is attributed to hydrogen bonding OH [4], indicating that the OH of water. The decrease means that the water goes apart from the MIR prism. The reason would be due to bubble generation. We also observed the upward peak at 3600 cm^{-1} , which is attributed to isolated OH [4]. It indicates that OH generated in plasma. The generated OH was adsorbed on the prism. OH was also observed with optical emission spectroscopy (OES). This means that OH generation can be detected with MIR-IRAS. The downward peaks are observed at 2850 and 2915 cm^{-1} , attributed to CH_2 components [4] of the OTS-SAM. A downward peak is also observed at 2956 cm^{-1} , attributed to CH_3 components [4] of the OTS-SAM. These indicate that the CH_2 and CH_3 in OTS-SAM were etched by plasma. The main species would be OH, generated in the plasma, because OH is strong oxidant.

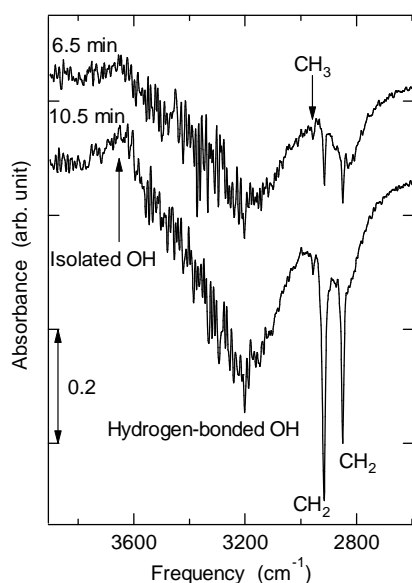


Fig. 1 Infrared absorption spectra of OTS-SAM exposed to plasma generated in 30% hydrogen peroxide water (H_2O_2) at different exposure time.

Comparing the increasing rate of CH_2 peaks with that of CH_3 peak, that of CH_2 is higher than that of CH_3 . It indicates that the CH_2 is not etched in the initial stage of plasma exposure, CH_3 is etched in the initial stage of plasma exposure. Although we consider various reasons, one of most plausible reason is attributed to arrangement of the OTS-SAM. OTS-SAM is terminated with CH_3 and contains 17 species of CH_2 and bonded with a Si prism using Si-O bonds. It means that CH_3 is located at the surface of the OTS-SAM, and that the CH_3 is in contact with H_2O_2 , a frontier of the influence of the plasma. Then, the etching is preceded from the surface into bulk region of the OTS-SAM.

This study indicates MIR-IRAS is a suitable in-situ and real-time measurement for reactions in liquid. In the near future, we will investigate interactions between plasma in liquid and SAM with various functional group, to elucidate the interaction between plasma and bio-materials.

4. Summary

Self-assembled monolayer (SAM) was assumed as a model material of bio-materials in this study. To understand the interaction between bio-molecules and plasma, an interaction between OTS-SAM and plasma in 30% hydrogen peroxide water (H_2O_2) was investigated with in-situ and real-time MIR-IRAS. The IR data indicate that plasma generated OH, and that the amount of CH_2 components and that of CH_3 are decreased with plasma exposure. It would indicate that the OTS-SAM is etched by OH generated in plasma.

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