Coverage Estimation of Silane Functionalized Perfluoropolyether Layer by using Time of Flight Secondary Ion Mass Spectrometry, Atomic Force Microscopy and Ion Scattering Spectroscopy

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Ultra-thin Silane functionalized perfluoropolyether (SF-PFPE) layers, which have been widely used for antifouling and repelling coats, were investigated by time of flight secondary ion mass spectrometry (ToF-SIMS), atomic force microscopy (AFM), and ion scattering spectroscopy (ISS). Surface coverage of the layers coated on native oxide, thermal oxide, and silica substrates by an annealing method was estimated at less than unity by ToF-SIMS, which was supported by island-like layers observed in AFM images. Amount of unreacted SF-PFPE molecules in the layers, which will affect chemical stability of the layers, was also estimated by ToF-SIMS. A difference between surface coverage estimated by ToF-SIMS and ISS was discussed.

INTRODUCTION

Silane functionalized perfluoropolyether (SF-PFPE) polymers, a kind of silane coupling agent, have a couple of useful properties such as antifouling and repelling [1]. Thus the polymers have been widely applied to surface treatment of glasses, LCDs and touch-pannels. Antifouling and repelling properties and slipperiness of a SF-PFPE-coated surface are easily affected by surface coverage and morphology of the SF-PFPE layer. SF-PFPE polymers are coated by means of silane coupling reactions, which are started with hydrolyzation of alkoxysilane or chlorosilane groups of the polymer. The amount of unreacted residues of SF-PFPE molecules in the layer is also an important factor to be controlled because the residues can be hydrolyzed by moisture in the atmosphere and will affect the chemical stability of the layer. The unreacted residues should be reduced by promoting silane coupling reactions effectively.

In order to investigate such material properties, we should choose surface sensitive methods because a typical thickness of a SF-PFPE layer is less than several nanometers.

Time of flight secondary ion mass spectrometry (ToF-SIMS) is suitable for analyses of the SF-PFPE layers because the information depth, one nanometer, is smaller than a typical thickness of the layer. The method is quite useful to examine unreacted residues of SF-PFPE molecules because both molecular and elemental information can be obtained.

Ion scattering spectroscopy (ISS) is also known as an extreme surface sensitive method so that it has been applied mostly to clean surfaces prepared in an ultra high vacuum (UHV). Recently, quantification of surface density of fluorine atoms by an ISS method was reported for fluorinated thiol self assembled molecules coated on a gold substrate from ethanol solution [2]. Thus ISS is not a promising method only for investigation of clean surfaces in a UHV but also for estimation of surface coverage of a fluorocarbon layer coated under an atmosphere in a practical way.

In this work, we examined SF-PFPE layers coated by an annealing method on a few kinds of substrates, and estimated the surface coverage and the amount of unreacted residues of SF-PFPE molecules using ToF-SIMS and ISS. We also investigated morphology of the SF-PFPE layers by atomic force microscopy (AFM). The difference between the surface coverage estimated by ToF-SIMS and ISS are discussed.

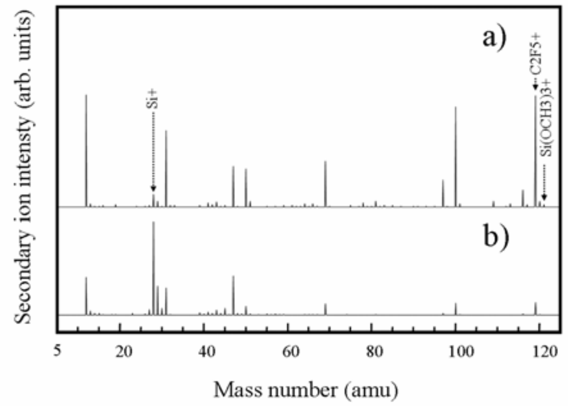

Fig. 1. ToF-SIMS spectra of SF-PFPE layers on silicon substrate annealed at 200 (a) and 350 (b) ^{o}C.

EXPERIMENTAL

We prepared four substrates: a native oxide layer, a thermal oxide layer (t= 100 nm), a silica layer (t= 120 nm), and a sputtered aluminum layer (t= 800 nm), on silicon wafers. SF-PFPE layers were coated on substrates by immersing in a commercial methoxysilane- functionalized PFPE solution, which was diluted to 1 vol% with 1-methoxyheptafluoropropanes (MHFP). Immediately, the substrates were annealed at temperatures below 400°C in dry nitrogen gas in order to fix the SF-PFPE molecules on the substrates. Then, the substrates were rinsed in a MHFP solution and dried in air.

ToF-SIMS measurements were performed using a TRIFT II mass spectrometer (ULVAC-PHI) by irradiating pulsed garrium ion beams to samples. The analysis area was 100 µm x 100 µm. Total garrium ion dose during a measurement was less than 2 x 10^{12} ions/cm^2.

An electron spectrometer system equipped with an ion gun (ESCALAB 250, Thermo) was used for ISS measurements. Helium ions of 896 eV were irradiated to the surface. The scattering angle was set at 130°. The analysis area was about 1 mm diameter. No further cleaning of sample surfaces prior to ToF-SIMS and ISS measurements was executed after the preparation processes.

Tapping AFM measurements were performed using a Nanoscope III system (DI).

Thermogravimetric analysis (TGA) was carried out using a Q-500 system (TA Instruments) in order to examine the thermal stability of SF-PFPE molecules.

Infrared spectroscopy (IR) was executed using an FTS7000 system (Digilab) to estimate amount of water involved in the thermal oxide and silica layers of substrates.

RESULTS AND DISCUSSION

ToF-SIMS spectra of SF-PFPE layers on native oxide substrates are shown in Fig. 1. In the spectra, $^{31}CF^+$, $^{47}CFO^+$, $^{50}CF_2^+$, $^{69}CF_3^+$, $^{97}C_2F_3O^+$, $^{100}C_2F_4^+$, and $^{119}C_2F_5^+$ fragment ions are strongly detected. These fragment ions are derived from PFPE parts of the SF-PFPE molecules. $^{121}Si(OCH_3)_3^+$ fragment ions observed in (a) are derived from methoxysilane groups of the unreacted molecules. The intensities of fragment ions derived from the PFPE parts (31, 47, 50, 69, 97, 100 and 119 amu) are decreased by annealing at 350°C although fragment ion intensities of $^{28}Si^+$ and $^{45}SiOH^+$ are increased. The Si^+ and $^{45}SiOH^+$ fragment ions can be derived from the native oxide surface exposed partially as well as from methoxysilane groups or the hydrolyzed ones of the SF-PFPE molecules.

Surface coverage of the SF-PFPE layers coated on the native oxide, thermal oxide and silica substrates can be estimated by the intensity ratio of $C_2F_5^+$ and Si^+ fragment ions characteristic of the layer and the substrates, respectively. $C_2F_5^+/Si^+$ intensity ratio is given by the following equation:

$$C_2F_5^+/Si^+ = C_2F_5^+/(Si^{+(l)} + Si^{+(s)}) \qquad (1).$$

Superscripts (l) and (s) correspond to Si^+ ions emitted from the layer and exposed substrate, respectively. The influence from the layer cannot be omitted because methoxysilane groups or the hydrolyzed ones are involved in the layer. So, if the substrate is completely covered with the layer, $C_2F_5^+/Si^+$ should equal to $C_2F_5^+/Si^{+(l)}$. We tried to estimate the $C_2F_5^+/Si^{+(l)}$ value by measuring ToF-SIMS spectra of the layer on an aluminum substrate (not shown here). Since silicon atoms hardly exist on the substrate, only $Si^{+(l)}$ ions can be detected for the layer on the aluminum substrate. $C_2F_5^+/Si^{+(l)}$ ratio for the layer on the aluminum substrate was estimated at 44 ± 1. $C_2F_5^+/Si^{+(l)}$ ratios for the layers on the native oxide, thermal oxide and silica substrates are supposed to be

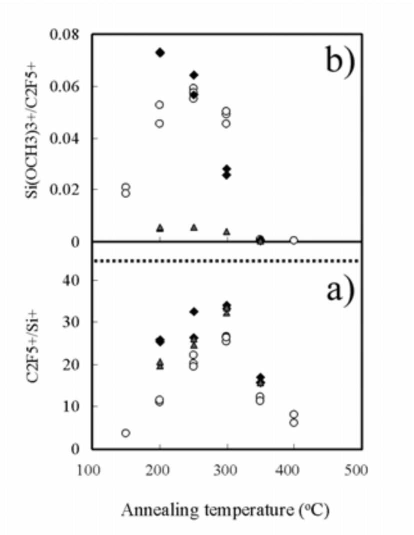

Figure 2. Relationships between $C_2F_5^+/Si^+$ (a) and $Si(OCH_3)_3^+/ C_2F_5^+$ (b) intensity ratios, and annealing temperature for SF-PFPE layers. Dotted line in (a) shows the intensity ratio for the layer coated on an aluminum substrate. Circle, rhombus, and triangles correspond to native oxide, thermal oxide, and silica substrates, respectively.

the same value although the ratios can be affected by the substrates or environment of the SF-PFPE layers.

Relationships between $C_2F_5^+/Si^+$ intensity ratio and annealing temperature of the SF-PFPE layers are shown in Fig.2 (a). Surface coverage of the layers on the native oxide, thermal oxide and silica substrates is supposed to be less than unity because all the $C_2F_5^+/Si^+$ ratios are lower than the ratio of the layer on aluminum substrate, 44 ± 1 (dotted line in Fig.2). $C_2F_5^+/Si^+$ ratio of the native oxide substrates increases with annealing at less than 300°C although further annealing decreases it. The $C_2F_5^+/Si^+$ relationships of the thermal oxide and silica substrates are similar to that of silicon substrates although the relationship curves of the thermal oxide and silica substrates are shifted higher than that of the silicon substrates. The higher $C_2F_5^+/Si^+$ ratios for the thermal oxide and silica substrates can be derived from decrease of Si^+ ion yields of the substrate rather than from increase of surface coverage of the layer.

$Si(OCH_3)_3^+/C_2F_5^+$ ratio can be used to estimate the amount of the unreacted residue in the layer in order to know the promotion degree of silane coupling reactions, the coating reactions. By monitoring $Si(OCH_3)_3^+/C_2F_5^+$ ratio as well as the $C_2F_5^+/Si^+$ ratio, not only surface coverage but also quality of the SF-PFPE layer can be known. Relationships between $Si(OCH_3)_3^+/C_2F_5^+$ ratio and annealing temperature are also shown in Fig. 2 (b).

Two relationships in Fig. 2 (a) and (b) show that three stages of the layer formation exist for the native oxide substrate. The first stage is found at less than 250°C, where both the $C_2F_5^+/Si^+$ and $Si(OCH_3)_3^+/C_2F_5^+$ ratios increases with annealing. The augment in both the ratios indicates that unreacted SF-PFPE molecules are involved in the layer as it is grown on the substrate by annealing. The second stage is found at annealing temperature from 250 to 300°C, where $Si(OCH_3)_3^+/C_2F_5^+$ ratio is turned to decrease by annealing although $C_2F_5^+/Si^+$ ratio still increases. The decrease of $Si(OCH_3)_3^+/C_2F_5^+$ ratio contrary to the increase of the $C_2F_5^+/Si^+$ ratio shows that the coating reactions, silane coupling reactions, are promoted effectively by annealing. The third stage corresponds to the layer formation by further annealing, where $C_2F_5^+/Si^+$ ratio is turned to decrease and $Si(OCH_3)_3^+/C_2F_5^+$ ratio becomes negligibly small. The reduction of the ratios at the third stage can be reflected from a thermal destruction of the SF-PFPE molecules because a decrease in weight was observed at more than 300°C in the TGA results (not shown here).

The relationship between $Si(OCH_3)_3^+/C_2F_5^+$ ratio and annealing temperature of the thermal oxide substrate is similar to that of the silicon substrates. $Si(OCH_3)_3^+/C_2F_5^+$ ratio of the silica substrate is quite lower than that of the other substrates. An infrared inspection revealed that the silica layer contains observable amount of water (not shown here). The lower $Si(OCH_3)_3^+/C_2F_5^+$ ratio is supposed that the unreacted residues were hydrolyzed effectively by the water.

AFM images of the silicon substrates coated with the layers annealed at 150 (a), 200 (b) and 350 (c) °C are displayed in Fig. 3. Islands formed with a lot of protrusions, each of which is as small as a few nanometers, are observed at the surface annealed at 150°C. The size of each island is a few hundred nanometers and the height is about 1.7 nm. The islands are connected each other and grown by annealing at 200°C (b). The islands can be attributed to the SF-PFPE

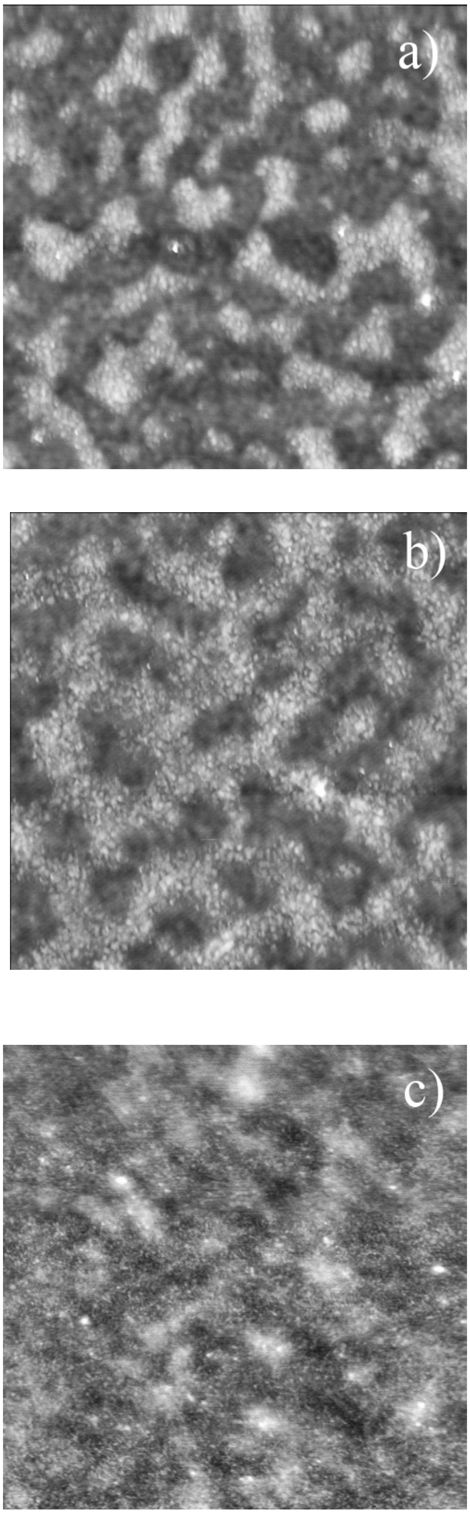

Fig. 3. AFM images of SF-PFPE layers on native oxide substrates. The annealing temperatures are 150 (a), 200 (b) and 350 (c) °C. The size of all the image is 1 μm x 1 μm.

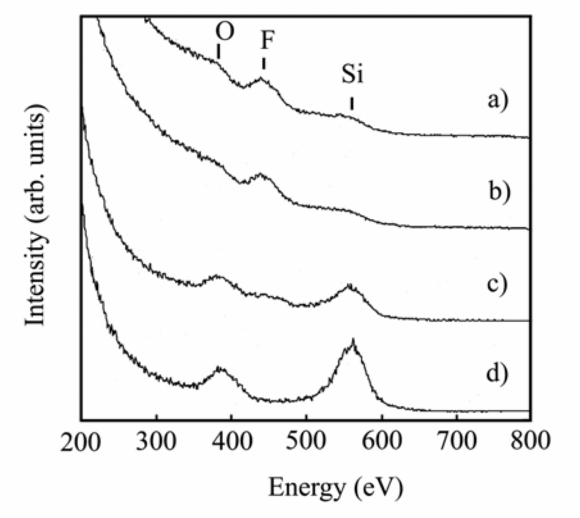

Fig. 4. ISS spectra of native oxide substrates coated with SF-PFPE layer annealed at 350 (a), 300 (b), 200 (c) °C, and of a bare silicon wafer (d).

layers since the growth of the islands corresponds to the increase of surface coverage upon annealing at less than 300°C. However, the islands become unclear and the small protrusions become dispersed on the surface annealed at 350°C (c), and at the temperature the thermal destruction of the SF-PFPE molecules can occur. Average height of the protrusions decreases to less than 1 nm. The similar change in surface morphology of silica substrates coated with the layer upon annealing was observed (not shown here).

ISS spectra of the silicon substrates coated with the layer annealed at 350 (a), 300 (b), and 200 (c) °C are shown in Fig. 4. The spectrum of the bare silicon substrate (d) is also displayed in the figure. Si and O peaks of the bare silicon substrate are found at 560 and 390 eV and no carbon peak is observed. A fluorine peak of the layer annealed at 200°C appears at about 440 eV, and the intensity increases at 300°C. The increase of the fluorine peak intensity can correspond to that of surface coverage of the SF-PFPE layer as indicated by the relationship of $C_2F_5^+/Si^+$ ratio shown in Fig. 2. However, the ISS spectrum is not changed by further annealing although the $C_2F_5^+/Si^+$ ratio is decreased. The discrepancy can be explained as following.

As observed by AFM measurements, the thickness of the island-like SF-PFPE layer, annealed at 150°C, that decreases from 1.7 to less than 1 nm by annealing at 350°C. The thinning of the layer can reduce the amount of fragment ions of the SF-PFPE molecules although the amount of backscattered ions from the surface of the layer is not affected. So, the difference between surface coverage estimated by ISS and ToF-SIMS can be attributed to the difference in the information depth. The nominal decrease of the surface coverage can be found only by ToF-SIMS because the information depth is about ten times larger than that of ISS.

SUMMARY

Ultra-thin antifouling/repelling layer formed by an annealing method was investigated. Not only the surface coverage, but also amount of unreacted molecules in the layer was estimated by ToF-SIMS. Surface coverage of the layers was estimated at less than 1 by ToF-SIMS, which was supported by island-like layers observed in AFM images. Discrepancy between surface coverage estimated by ToF-SIMS and that estimated by ISS can be caused by the difference in information depth.

REFERENCES

[1] For example, United State Patent, No. 6,183,874.

[2] H. H. Brongerma, A. Gildenpfennig, A. W. D. van der Gon, R. D. Van de Grampel, W. P. A. Jansen, A. Knoester, J. Laven, M. M. Viitanen, Nucl. Instr. and Meth. in Phys. Res. B **190**, 11 (2002).