

# Abstract

A method for the direct detection of the molecular ions of a very small amount of poly(dimethylsiloxane)(PDMS) on a solid surface was investigated. It was found that a TOF-SIMS analysis of silver-deposited surfaces (silver deposition/TOF-SIMS) is useful for this purpose. Molecular ions include information about structure (end groups, functional groups, etc.) and molecular weight, which are needed to evaluate organic substances. Using this method, silvercationized quasi-molecular ions of PDMS were clearly detected on solid surfaces, and their

structure and molecular weight were evaluated. In addition, their images obtained from the ions showed no interference from the deposited silver. Application of this method to the analysis of a paint defect allowed determination of the cause of the defect. Silver-cationized ions were detected on solid surfaces not only from PDMS, but also from other organic materials, including certain types of lubricant additives and fluorine oils. Therefore, it was confirmed that this method is useful for the analysis of ultrathin substances on actual industrial materials.

Keywords TOF-SIMS, Silver deposition, Silver cationization, Molecular weight evaluation, Poly(dimethylsiloxane)

固体表面に極微量付着したシリコーンオイル (PDMS)の分子量と分子構造を直接評価するため, 分子構造や分子量分布の情報を含む分子イオン を検出する方法を検討し,試料表面に銀を蒸着 してTOF-SIMSで分析する銀蒸着/TOF-SIMS法が 有効であることを見出した。この方法により, 固体表面に付着したPDMSから銀によってカチオ ン化された擬似分子イオンを検出することが可

## 要

旨

能となり、構造と分子量分布の評価および蒸着し た銀に影響されない面分布の評価も可能となっ た。この方法を塗装のはじき解析に適用したとこ ろ、はじき原因となったPDMSが判別でき、原因 が解明できた。この方法は、PDMSだけでなくオ イル添加剤、フッ素オイルなど幅広く応用可能で あることも確認し、固体表面上の極微量有機物の 分析に有効であることを示した。

キーワード

飛行時間型二次イオン質量分析(TOF-SIMS),銀蒸着,銀カチオン化,分子量評価,ポリジメチルシロキサン

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## 1. Introduction

Poly(dimethylsiloxane) (PDMS) often causes defects in bonding and painting due to surface contamination of industrial materials. Analytical methods capable of detecting PDMS are required in order to determine the causes of these problems. For this purpose, time-of-flight secondary ion mass spectrometry (TOF-SIMS) is one of the most powerful techniques, owing to its surface sensitivity and selectivity, and thus has been widely used.<sup>1)</sup> Unfortunately, while conventional TOF-SIMS analysis is capable of detecting the PDMS causing these defects, it remains incapable of providing a more specific determination of the causes of these problems. This is due to the fact that although TOF-SIMS can easily detect fragment ions of PDMS, it cannot detect the molecular ions, which are required to determine the structures and the molecular weights of contaminants. It is well known that silver-cationized quasi-molecular ions can be detected from substances deposited on a silver substrate with the assistance of silver cationization and the molecular weight distribution can be evaluated.<sup>2, 3)</sup> However, it is difficult to apply this technique to the analysis of ultrathin substances and substances on uneven substrates because of the need to transfer the substances to a silver substrate. It is also difficult to observe the ion images generated.

In an attempt to directly detect silver-cationized ions on polymer surfaces, a method using a TEM grid to apply silver patterning to a sample surface was proposed.<sup>4, 5)</sup> However, because no silver was present on the marking areas of the TEM grid and a thick silver layer (about 150 nm) covered the substances in other areas, material in certain areas was undetectable and no ion images of the material could be observed.

Recently, A. Delcorte et al. proposed a method capable of detecting gold-cationized ions of high mass area on the surfaces of high-molecular weight polymers such as polyethylene and polypropylene via gold metallization of the surfaces.<sup>6)</sup>

The authors have attempted to directly detect silver-cationized ions having a formula identical to that of molecular ions of PDMS on a solid surface by using silver metallization, which can be expected to have the greatest cationization effect.<sup>7)</sup> It was found that TOF-SIMS analysis of silver-deposited sample surfaces (silver deposition/TOF-SIMS) was useful for this purpose. This paper describes the utility of this method and its applications.

## 2. Experimental

#### 2.1 Sample preparation

Silicone oil was dissolved in toluene at concentrations ranging from 0.02 to 0.3 mg/ml. One  $\mu$ l of the solutions was deposited on a silicon substrate of approximately 25 mm<sup>2</sup> and the solvent was allowed to evaporate.

#### 2.2 Silver deposition

Two methods of silver deposition, the diode sputtering method and the vacuum evaporation coating method, were evaluated. The former method was performed using an Eico Engineering IB-3 ion sputter device. The target current was 3 mA and the argon pressure was 10 Pa. The distance between the silver target and sample was approximately 60 mm and various silver coating times ranging from 0.5 to 3 min were used. The latter method was performed using a JEOL JEE-5B vacuum evaporation coating device. The pressure used was  $4 \times 10^{-3}$  Pa. The calculated amount of silver on the substrate ranged from approximately 27 to 210 nmol/cm<sup>2</sup> (corresponding to thicknesses of 3-20 nm).

#### 2.3 Measurement

The TOF-SIMS measurements were performed using a Physical Electronics TFS-2100 (TRIFT II) instrument. Mass spectra were acquired using bunched <sup>69</sup>Ga<sup>+</sup> ion pulses with an impact energy of 15 keV. The total ion doses in these measurements were approximately  $5 \times 10^{11}$  ions/cm<sup>2</sup> under a static limit.

#### 3. Results and discussion

#### 3.1 Silver deposition conditions

With the silver deposition/TOF-SIMS method, there is concern that the sample may sustain damage due to the direct deposition of silver on the sample surface. If damage occurs on the sample surface, it can be expected that either no silver-cationized ions will be detected or that the molecular weight distribution of the silver-cationized ions will differ from that of the sample deposited on the silver



substrate. This section describes the silver deposition conditions that did not cause damage to the sample surfaces.

# 3.1.1 Diode sputtering method

This method is more convenient than the vacuum evaporation coating method because it does not require as high of a vacuum. The deposition time required is about 5 minutes, about one tenth that of the vacuum evaporation coating method.

With deposition at room temperature (about  $20^{\circ}$ C), neither silver-cationized ions nor fragment ions were detected. Optical microscope observation of the silver-deposited sample surfaces revealed that the surfaces were covered with a thin film, which was identified as SiO<sub>2</sub> by reflection infrared spectroscopy (IR). It was judged that the SiO<sub>2</sub> film was generated by the thermal oxidation of PDMS; in other words, the sample surfaces were damaged by the silver deposition under the conditions used. Therefore, an attempt was made to cool the samples so as to prevent the occurrence of damage on the surface due to thermal oxidation during silver deposition.

Samples deposited on the silicon substrates were cooled during silver deposition by placing them on an aluminum block that had been cooled to about  $-20^{\circ}$ C. The spectrum obtained is shown in **Fig. 1** (b). Silver-cationized ions were detected on the sample and the molecular weight distribution was similar to that of the sample on the silver substrate (Fig. 1 (d)). This result indicates that thermal damage to the sample surfaces can essentially be prevented by cooling the sample to around  $-20^{\circ}$ C during deposition.

#### 3.1.2 Vacuum evaporation coating method

It can be expected that sample surfaces will sustain less damage with the use of this method than that with the diode sputtering method because of the low kinetic energy applied, which is about 1/100 that of the diode sputtering method. The PDMS spectrum obtained using this method is shown in Fig. 1 (c). Silver-cationized ions were clearly detected on samples with silver deposited at room temperature (about 20°C) and the molecular weight distribution was similar to that of the sample on the silver substrate (Fig. 1 (d)). The correspondence between these spectra indicates that the damage sustained by the sample surfaces with this method was negligible. From this perspective, the vacuum evaporation coating method possesses an advantage over the diode sputtering method. Accordingly, the vacuum evaporation coating method was used for subsequent experiments.

## 3.2 Effects on ion images

The images of  $Ag^+$  and silver-cationized ions obtained from the sample deposited with approximately 50 nmol/cm<sup>2</sup> of silver are shown in **Fig. 2**. The image of the silver-cationized ions showed no interference from the deposited silver. The reason why there are hardly any silver or silvercationized ions visible in the bottom portion of these images is attributable to the fact that the PDMS was of greater than monolayer thickness in the center of the droplet and thus the deposited silver sank completely into the PDMS.

An AFM (atomic force microscope) image of a silicone wafer with a deposited silver surface is



#### Fig. 1 TOF-SIMS spectra of PDMS.

(a): sample on a silicon substrate; (b): silver deposited sample using the diode sputtering method; (c): silver deposited sample using the vacuum evaporation coating method;
(d): sample on a silver substrate.

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shown in **Fig. 3**. The deposited silver had the appearance of an isolated clump of about several dozen nanometers, a size sufficiently smaller than the lateral resolution of TOF-SIMS (about 0.2  $\mu$ m). Therefore, it was judged that the images of the silver-cationized ions received no interference from the deposited silver.

# **3.3** Molecular weight evaluation and silicone structure

The spectra from two types of PDMS deposited with approximately 50 nmol/cm<sup>2</sup> of silver are shown in Fig. 4. The number average molecular weights of these two types of PDMS are approximately 3,800 and 28,000. Use of the silver deposition/TOF-SIMS method allowed the detection of two types of silver-cationized ions: silver-cationized linear fragments and silver-cationized cyclic fragments. Silver-cationized linear fragments have a formula identical to that of the molecular ion and silver-cationized cyclic fragments represent a series corresponding to an integral number of repeat units.<sup>8)</sup> Thus, the functional groups can be determined from the intervals of these fragments, which corresponded to the repeat units, and the end groups can be determined based on the silvercationized linear fragments, which had an integral number of repeat units plus two end groups.

In the case of low-molecular weight PDMS, the relative intensity of the silver-cationized linear fragments  $(\bullet)$  was high, whereas in the



Ag<sup>+</sup>

silver-cationized ions

**Fig. 2** Secondary ion images of  $Ag^+$  and silvercationized ions obtained from PDMS.  $200\mu m^2$  field of view. case of high-molecular weight PDMS, the relative intensity of the silver-cationized cyclic fragments ( $\Delta$ ) was high. X. Dong et al. studied the fragmentation of various types of PDMS deposited on silver substrates and demonstrated that the relative intensity of the silver-cationized cyclic fragments increased as the molecular weight increased.<sup>8)</sup> With our method, it was found that the molecular weight could be evaluated by comparing the relative



**Fig. 3** AFM image of a silicon wafer surface (left) and the silver surface deposited on the silicon wafer using the vacuum evaporation coating method (right).



Fig. 4 Silver deposition/TOF-SIMS spectra (upper) of PDMS. The number in parentheses is the number average molecular weight. ●: silver-cationized linear fragment; Δ : silver-cationized cyclic fragment. The structures of linear fragment (lower left) and cyclic fragment (lower right).

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intensities of these fragments as well as the conventional method of using silver substrate. We conclude that it is possible to evaluate the molecular weight and structure of ultrathin silicone oil on material surfaces using the silver deposition/TOF-SIMS method.

#### 4. Applications

#### 4.1 Analysis of paint defects

We applied the silver deposition/TOF-SIMS method to determine the cause of a paint defect. Silver-cationized ions of PDMS were detected on the paint defect surface and the structure and the relative molecular weight of the causative PDMS were evaluated. This PDMS was found to correspond to one of the silicone oils used in the painting process, and so the cause of the problem





**Fig. 5** Secondary ion images of silver-cationized linear fragment ( $\bullet$ ) and silver-cationized cyclic fragment ( $\Delta$ ) obtained from vinyl-terminated PDMS (upper). 200 $\mu$ m<sup>2</sup> field of view. Silver deposition/TOF-SIMS spectra extracted from selected area (a) and (b) indicated in the image (lower).

was determined.

#### 4. 2 Segregation of PDMS on silicon substrate

Vinyl-terminated PDMS deposited onto a silicon substrate was analyzed using the silver deposition/TOF-SIMS method. Figure 5 shows the ion images obtained of the linear and cyclic fragments. The mass spectra extracted from the selected area are indicated in the image. It was found that the ratio of silver-cationized linear fragments to silver-cationized cyclic fragments varied with the measured area, and that the cyclic fragments were concentrated outside of the circle and the linear fragments were distributed toward the center of the circle. It was judged that, in this sample, the silver-cationized cyclic fragments came from higher-molecular weight PDMS and the silvercationized linear fragments came from lowermolecular weight PDMS. Therefore, the ion images indicate that PDMS with different molecular weights was segregated when the solvent evaporated from the silicon substrate.

# 4.3 Analysis of other organic materials

The silver deposition/TOF-SIMS method was applied to detection of other organic materials, including a lubricant additive (a succinimide-type dispersant) and fluorine oil. Silver-cationized quasimolecular ions from these substances were detected on solid surfaces (**Fig. 6**) and their structures were



**Fig. 6** Silver deposition/TOF-SIMS spectra (a) lubricant additive (succinimide-type dispersant) (b) fluorine oil (demunum S-20).

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determined. In the analysis of the lubricant additive, silver-cationized quasi-molecular ions of oil, which was the solvent for the additive, were detected as well. Consequently, it was determined that the silver-cationized ions were detected not only from PDMS, but also from other organic materials, such as certain types of lubricant additives, fluorine oils, etc. on solid surfaces. Therefore, the silver deposition/TOF-SIMS method was proven to be useful for the evaluation of ultrathin substances on solid surfaces.

## 5. Conclusions

The silver deposition/TOF-SIMS method was investigated for use in the direct detection of silvercationized ions having a formula identical to that of molecular ions of PDMS on solid surfaces and was found to be useful for this purpose. Based on the silver-cationized ions detected by this method, it was possible to determine the structure of the PDMS and to evaluate its molecular weight. Application of this method to the analysis of a paint defect allowed determination of the cause of the defect. Silvercationized ions were detected on solid surfaces not only from PDMS, but also from other organic materials, including certain types of lubricant additives and fluorine oils. Therefore, it was confirmed that this method is useful for the analysis of ultrathin substances on actual industrial materials.

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