Mass Separation of Water Cluster Ion Beam Using Two Rotating Electric Fields and Sputtering of a Polymer Thin Film

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Selection of the cluster size of an ion beam is a key factor for controlling sputtering speeds or the damaged layer of polymer materials. We developed a two rotating electric fields (REFs) type of mass spectrum (MS) filter or analyzer using a novel principle. The REF-MS can continuously separate typical sizes of cluster ions by optimizing the frequencies of the REFs. In this study, we developed an electrospray ionization (ESI) gun column to optimize the cluster sizes of a water ion beam by REF-MS.

Annular ring patterns of size-selected clusters were observed using optimized focusing frequencies on typical water molecule clusters. The patterns were compared with the results of the finite difference simulation method. We sputtered a spin-coated polymer film using a size-filtered water cluster ion beam. A sputtering crater was observed on the polystyrene film sputtered by the size-optimized water cluster ion beam. Here, we discuss the cluster size dependence of sputtering speeds for an ion beam for typical numbers of water clusters.

Keywords REF-MS; ESI; Water cluster ion beam

I. INTRODUCTION

We developed a two rotating electric fields (REFs) type of mass spectrum (MS) filter or analyzer using a novel principle. For the first trial, the two REFs were used as a mass filter or a cluster size filter for liquid metal ion sources (LMISs). The REF-MS separated isotopes of $^{69}$Ga$^+$ and $^{71}$Ga$^+$ ions and monomer and cluster ions using an AuGe LMIS [1–3]. The detailed principles of the REF-MS have been described in our previous papers [4, 5]. In this study, we developed an electrospray ionization (ESI) gun column as a cluster ion beam emitter for REF-MS applications. The advantages of the REF-MS as a cluster ion beam size separator are listed below.

1. The cluster ion beam can maintain continuous and direct conditions during the REF-MS sequence.
2. The cluster ion beam can also maintain its convergence to the axis of the inside optics of the REF-MS.
3. Cluster sizes can be filtered by optimizing the frequency of the REFs.
4. Transmission efficiency is 100% for the optimized cluster ions.
5. The optics can be designed compactly within 20 mm inner diameter by 200–300 mm long.

In this study, we examined the ability to separate different sizes of water cluster ions using the REF-MS.

Generally, it is important to investigate soft sputtering and ion processing techniques to evaluate the depth direction and interface of soft materials (e.g., organic electroluminescence, organic solar cells, and organic semiconductors). In previous studies, C$_{60}^+$ and Ar$_{2000}^+$ gas cluster ion beams (GCIBs) were compared with respect to the sputtering yields of different polymer materials [6]. They showed that Ar-GCIB is a better tool in terms of the efficiency of sputtering yields and less damaged layers in organic materials. Ar-GCIB is now widely used as a surface...
cleaning tool and primary ion beam for secondary ion mass spectrometry (SIMS) [7]. We have also separated Ar-GCIB using a REF-MS, and the distributions of cluster intensity are in agreement with the functionally fixed time of flight (TOF) MS spectrogram [8]. In this study, we investigated the sputtering of an organic thin film using a mass-separated water cluster ion beam for soft sputtering effects. We discuss the behavior of the interaction between the cluster size and sputtered polymer surfaces.

II. EXPERIMENTAL

A. ESI phenomenon

Electrospray is a phenomenon caused by an electric field. When a strong electric field is applied to a capillary tip to which a sample liquid is supplied, the surface electric field density \( p \) at that point increases proportionally. However, when \( p \) exceeds a critical value, the sample liquid at the tip of the capillary forms a Taylor cone, and ESI occurs [9]. This is because the liquid becomes unstable because of Coulomb repulsion between the excess charges in the same region [10].

ESI methods have generally been applied under atmospheric pressure for the detection of the mass charge ratio \((m/Z)\) using a TOF filter. It is possible that the liquid becomes frozen at the tip of the capillary because of evaporative cooling, and the supply of liquid stops. ESI is possible even under vacuum by using a volatile liquid with a low freezing point, such as methanol [11]. It has been reported that the space charge field effect becomes negligible for charged droplets that are accelerated by a high electric field when the beam is focused in a vacuum chamber [12–15]. In this experiment, the vacuum-ESI method was introduced to separate water molecule clusters using REF-MS.

B. Design of an ESI gun column

An ESI gun column was specifically developed for the REF-MS chamber [16, 17]. A solution of water, ethanol (80:20), and trifluoroacetic acid (TFA: 0.01 M) was pressurized by nitrogen gas (0.2–0.45 MPa) and carried to a silica capillary through a PEEK tube. The silica capillary tip (10 ± 1 μm) was installed on the beam line of the vacuum ESI gun column. The extractor surrounded the silica capillary tip on the surface. The ESI gun column was differentially pumped using a turbo molecular pump (TMP: TMU210, PFEIFFER, 210 L s\(^{-1}\)) and a leak valve. The water cluster ion beam generated in the ESI gun column was converged by a condenser lens and formed a cross-over on the movable aperture. The high-density ion beam focused on a spot using an objective lens without working REF-MS. Upon operating REF-MS, the ion beam spot drew annular patterns according to the charge mass ratios on the fluorescent screen.

Figure 1: Schematic design of the ESI column and REF-MS filter optics. A solution of water, ethanol (80:20), and 0.01 M TFA was pressurized by nitrogen gas (0.2–0.45 MPa) and carried to a silica capillary through a PEEK tube. The silica capillary tip (10 ± 1 μm) was installed on the beam line of the vacuum ESI gun column. The extractor surrounded the silica capillary tip on the surface. The ESI gun column was differentially pumped by TMP (210 L s\(^{-1}\)) and a leak valve. The water cluster ion beam generated in the ESI gun column was converged by a condenser lens and formed a cross-over on the movable aperture. The high-density ion beam focused on a spot using an objective lens without working REF-MS. Upon operating REF-MS, the ion beam spot drew annular patterns according to the charge mass ratios on the fluorescent screen.
and REF-MS filter optics. We applied ion optical geometries from the focused ion beam (FIB) gun column. The extractor (4 mmϕ) is surrounded a silica capillary tip on the surface. The voltages on the silica capillary tip and extractor could be independently controlled from 0 kV to 10 kV. When the differential voltage of the silica capillary tip exceeded 2.3 kV, ESI occurred, and the vacuum increased from $5.5 \times 10^{-4}$ Pa to $1.2 \times 10^{-3}$ Pa. We typically supply 10 kV for ESI beam acceleration. The acceleration voltage was optimized for the AC voltage (210 V) of the two REFs. The water cluster ion beam generated in the ESI gun column was converged using a condenser lens and formed a cross-over on a movable aperture. The high-density ion beam focused on a spot using an objective lens without REF-MS. Upon operating the REF-MS, the ion beam spot drew annular patterns according to their own charge mass ratios.

C. Test samples for sputtering

To estimate the sputtering effect of the water cluster ion beam, we prepared a spin-coated polymer film on a Si substrate. The sputtering test sample polymers included polystyrene (PS) 2400 [NMIJ CRM 5001-a, a molecular weight (Mw) of 2413 ± 20] and poly-methyl-methacrylate (PMMA) (Cat# 037A, Mw of 35,000). First, each polymer was completely dissolved in methylbenzene (FUJIFILM Wako Chemical). Second, each solvent was dropped on a Si wafer ($2 \times 2$ cm$^2$), and finally, a thin polymer film was covered (50−200 nm thickness) using a spin coater that maintained a rotating speed of 3000 rpm (ACT-220A II, ACTIVE).

The water cluster ion beam generated in the ESI gun column was mass separated by the REF-MS, and it projected two-dimensional annular ring patterns on a fluorescent screen (F2222, Hamamatsu Photonics). The annular ring patterns were optimized by the extractor, condenser lens, and objective lens. Each annular ring can be identified by its own water cluster size using theoretical calculations (SIMION™, Scientific Instrument Services). To estimate the sputtering effect, the fluorescent screen was replaced by spin-coated polymers on a Si substrate by maintaining the ion beam conditions. The depth and morphology of the sputter crater on the polymers were observed using a laser microscope (VK-X, KEYENCE). To detect the intensity of the ESI, a Faraday cup was originally installed by switching the fluorescent screen.

III. RESULTS AND DISCUSSION

A. Comparison between annular ring patterns and simulation results

Figure 2 shows the two-dimensional annular patterns of the mass-separated water cluster ion beams that were obtained on the fluorescent screen with the optimized frequencies for focusing typical clusters ($f = 788, 997$, and 1298 kHz). Each pattern was selected from the typical frequencies by focusing on a center spot and composed of different sizes and intensities of annular ring patterns. The difference was due to the $m/Z$ trajectories of the water clusters. If it can be assumed that these patterns originated from singly charged water ion clusters ($[(H_2O)_nH]^+$, $n$: numbers of water molecules in the clusters), the annular patterns can be compared with the results of the theoretical calculations. The ion trajectories were simulated by potential arrays of REFs using the finite difference method (SIMION™). The simulation results and numbers of water are listed in Figure 3, and the number of clusters on each color band is shown in Table 1. There are analogies between the annular patterns and the simulation results for the same frequencies.

Because the single REF-MS only separates species of different $m/Z$, it is not possible to distinguish between singly-charged clusters and multiply-charged clusters with correspondingly higher masses. In principle, REF-MS can solve this problem via MS/MS separation in a second mass filter [1, 3]. The disagreement between the annular patterns and simulation results can be affected by the presence of multi-charged water cluster ions. However, clear-lined annular patterns cannot be explained by complex multi-charged clusters and it seems reasonable to believe that clusters with these low $m/Z$ values are singly charged. In particular, the REF-MS acts as a low mass filter for high frequencies, and some wide ranges of heavier clusters draw bright bands near central spots that are minimally affected by the REFs. Singly
charged clusters are stable for small numbers of molecules \((n \leq 100)\), and multi-charged clusters mainly appear in larger clusters [13]. Additionally, the annular patterns disappeared at frequencies for the large cluster numbers in the case of REF-MS.

B. Sputtering of the spin-coated polymer film by size cluster

We sputtered a spin-coated PS film using a size-filtered water cluster ion beam \([(H_2O)_nH]^+\) for 16 h at \(f = 1298\) kHz. A sputtering crater was observed on the PS film sputtered with the size-filtered water cluster ion beam (Figure 4). The diameter of the crater was approximately 100 μm, and a 20–30 μm fringed deep ring was formed. The deep ring structure was formed by small spiral scanning using the REFs. The typical frequencies are usually optimized and finally determined on the image of the fluorescent screen.

To estimate the sputtering effect, we irradiated the spin-coated PMMA film using three different clusters of water molecules \((n = 70, 44, \text{and } 26)\) for 4 h. The results are shown in Table 2. The optimized frequency for each number was also determined by the center spot on the fluorescent screen. The Faraday cup (2 mmΦ) was fixed to the center spot to measure the cluster ion beam current (R8240, ADVANCE). We compared the sputtering speed according to the depth and depth/current dimension. The results indicated that the cluster size dependence of the sputtering speed did not considerably change for a small water cluster ion beam. This agrees with other studies on cluster size dependency of sputtering yields [6, 18, 19].

IV. CONCLUSIONS

We developed an ESI gun column for optimizing cluster...
sizes of a water ion beam using REF-MS. By using this new system, annular ring patterns of size-selected clusters were observed at optimized frequencies. The annular ring patterns almost agreed with the simulation results of singly charged water clusters. We sputtered a spin-coated PS and PMMA film using a size-filtered water cluster ion beam. A sputtering crater was observed on the PS film that was sputtered. A deep ring fringed structure was created by small spiral scanning by the REFs. Additionally, the cluster size dependence of the sputtering speed on the PMMA thin film was not considerably changed for a small water cluster ion beam.

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Table 2: Comparison of the sputtering speed according to depth and depth/current dimension for differently sized water clusters.

| Sample | Frequency $^a$ (kHz) | Cluster size $^b$ (numbers) | Current $^c$ (pA) | Sputtered depth $^d$ (nm) | Depth/Current $^e$ (nm pA$^{-1}$) |
|--------|----------------------|----------------------------|------------------|--------------------------|----------------------------------|
| a      | 788                  | 70                         | 1.86             | 56                       | 30.1                             |
| b      | 997                  | 44                         | 2.45             | 61                       | 24.9                             |
| c      | 1294                 | 26                         | 1.39             | 39                       | 28.1                             |

$^a$ Frequencies: optimized from the fine lines on the center spot on the fluorescent screen.
$^b$ Cluster size: Number of water molecules in [(H$_2$O)$_n$H]$^+$.  
$^c$ Current: Primary ion beam current focused on the spot and induced into the Faraday cup
$^d$ Sputtered depth: The depth of the crater on the PMMA thin film as estimated by the laser microscope
$^e$ Depth/Current: The sputtering efficiency estimated by the ratio between the sputtered depth and current

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