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Original Paper

Secondary ion mass spectrometry using size-selected gas cluster ion beam

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We measured secondary ions emitted from PMMA (polymethyl methacrylate) by a size-selected Ar cluster-ion beam. Incident Ar cluster-ion beam with an acceleration energy of 5 keV and a mean size of about 700, 1000 and 1350 atoms/cluster were used. We found that the yield of the large fragment ions (*m/z*: ~800) emitted from PMMA solid film increased with increasing the size of incident Ar cluster-ions, while those were little observed for Ar monomer-ion bombardment. These results suggest that the decomposition of polymer film is successfully suppressed by decreasing the kinetic energy of constituent atoms of a cluster ion.

1. Introduction

Mass-analyses of organic- or bio-molecules on substrates have been carried out by employing various types of ionization techniques for secondly ion mass spectrometry (SIMS). Recently, cluster-ion beams have been recognized as a primary projectile for desorption of high mass secondary ions in SIMS experiments [1-9]. Experimentally, various degrees of enhancement of high mass secondary ions yields have been observed, depending on the type of projectile and target material. On the other hand, theoretical calculations are beginning to unravel some of the phenomena of cluster induced sample erosion [10, 11]. However, the reasons behind the unique properties of cluster-ion beams are still not well understood.

The gas-cluster-ion beam (GCIB) can induce simultaneous collisions of numerous atoms which have very low mean kinetic energy of several eV, because a mean kinetic energy of each constituent atom of a cluster is provided by dividing the acceleration energy of a gas-cluster-ion by the number of constituent atoms (cluster size). Such a characteristic property of the gas-cluster-ion impact causes unique effects on solid surfaces, which are never present in the irradiation of mono atomic ion. In our previous study [12], we have developed the apparatus for the bombardment of huge-sized GCIB and characterized their bombardments on the surfaces. We investigated the damage formation on a highly orientated pyrolytic graphite (HOPG) surface by varying acceleration energy and cluster size of Ar cluster-ions. Our result suggested that the kinetic energy per constituent atom of the cluster was the most important variable to the damage formation. Molecular dynamics (MD) studies also suggested that cluster size was one of the most important parameters in the such bombardment effects[13,14]. In order to elucidate such effects of incident gas-cluster-ions more precisely, we newly designed and developed the size-selected GCIB apparatus for SIMS[15], where the kinetic energy per constituent atom of the cluster can be controlled by selecting the cluster size and the acceleration voltage of the gas-cluster-ion.

In this study, we measured secondary ions emitted from the polymer film under the bombardment of a size-selected Ar cluster-ion beam by using the developed apparatus. We found that the yield of the large fragment ions (*m/z*: ~ 800) emitted from PMMA (polymethyl methacrylate) was enhanced by the bombardment of Ar cluster ions, as compared with that by Ar monomer ions bombardment. Furthermore, it was found that the yields of secondary ions from PMMA strongly depended on the size of incident cluster-ions as well as their mass.

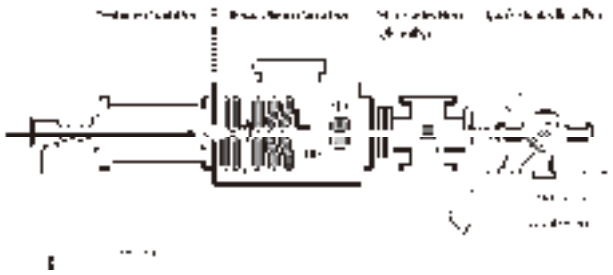

Figure 1 Schematic view of size-selected gas cluster ion beam line and analytical chamber. NZ: Nozzle, SK: Skimmer, IO: Ionization filed, FD: First ion deflector, MA: Magnet, SD: Second ion deflector, SA: Sample.

2. Experiment

Schematic view of size-selected gas cluster-ion beam apparatus for SIMS is shown in Figure 1. All experiments were performed in a high-vacuum chamber, which mainly consists of four parts: a source chamber, an ionization chamber, a cluster size-selection chamber and an analytical chamber[15]. The source chamber was equipped with a metal nozzle for a neutral-cluster beam formation. Ionization and cluster size-selection chamber housed the ionization and acceleration fields for a cluster-ion beam formation, and two pairs of ion-deflector for a cluster size-selection. The analytical chamber was equipped with a sample manipulator and a time-of-flight mass spectrometer for secondary ions.

The gas-cluster formation and ionization techniques have been described elsewhere [16,17]. Neutral Ar clusters were produced by a super sonic expansion of Ar gas from a conical-shaped metal nozzle with a 0.1 mm-diameter orifice at a high stagnation pressure of 1.13 MPa. Neutral Ar clusters were collimated by a skimmer with a 0.5 mm-diameter orifice and introduced into the ionization chamber where the neutral clusters were ionized by the electron impact. The ionized Ar clusters were extracted by the acceleration voltage of 5 keV toward the sample. Mono atomic and small cluster ions were removed by the magnet.

A cluster size-selection was performed by employing the two pair of ion-deflectors, on the basis of TOF technique. First, the primary cluster-ion beam was chopped by the first ion-deflector with a pulsed (15 μs) high voltage of 1.0 kV at a repetition rate of 100 Hz. During the flight between the first and the second ion-deflector, the pulse width of the cluster beam spread because of the size difference among the cluster ions. Accordingly, the specific size of cluster ions was obtained by passing the pulsed cluster ion beam through the second ion-deflector at a properly delayed time after the chopping by the first ion-deflector. The second ion-deflector was placed at 351 mm downstream from the first ion-deflector and operated with a pulsed (10 μs) high voltage of 1.0 kV.

The size-selected cluster-ion beam was collimated to be 5mm in diameter and incident on the sample at an angle of 45° with respect to the surface normal. The thin PMMA film target was prepared on a clean Si substrate by spin-coating technique. The thickness of the PMMA film was ~500 nm.

The secondary ion mass spectrometry for cluster-ion beam incidents was performed using liner TOF-tube (443mm). In our experiment, the pulse width of an incident beam after size-selection still spread to ~10 μs, which was not enough to be used as a trigger of TOF measurements. Instead, we used a device [18] for gating the secondary ion beam in a short pulse. The gate-device consists of two electrically insulated sets of thin wires mounted parallel to each other and perpendicular to the target surface normal. The wire diameter is 0.05 mm and the distance between wires is 1.0 mm. Secondary ions were extracted into the parallel electrode by the extraction voltage of -0.5 kV. The distance between the extractor and the sample was 30 mm. The secondary ions unaffectedly pass through the gate when the wire sets are held at the same potential (gate open). On the other hand, when the wire sets are held at opposite potentials of equal magnitude, the secondary ions are deflected (gate closed). The secondary ions passed thorough the gate were detected by a micro channel plate (MCP) and the ion signals were accumulated by the multichannel scaler (FAST ComTec P7888-1). The logic-pulse signal (pulse width: 1μs) to produce the high voltage pulses applied to the gate device was used as a start signal for the TOF measurement. In these conditions, the mass resolution ($m/\Delta m$) was estimated to be ~ 20 at m/z = 800. In our experimental setup, the feature of the TOF spectra of the

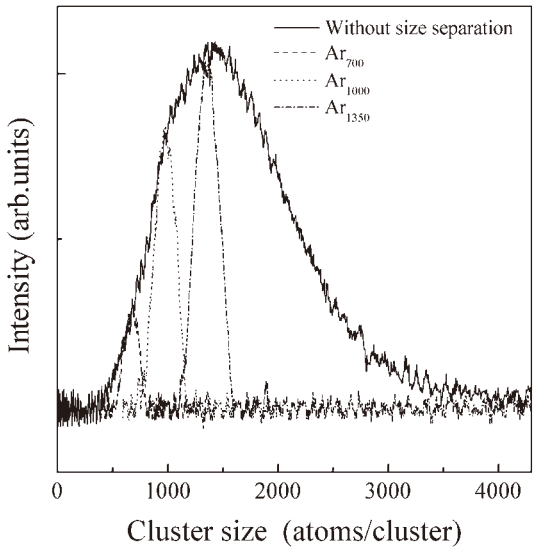

Figure 2 Cluster size distributions of Ar-GCIB with and without size separation.

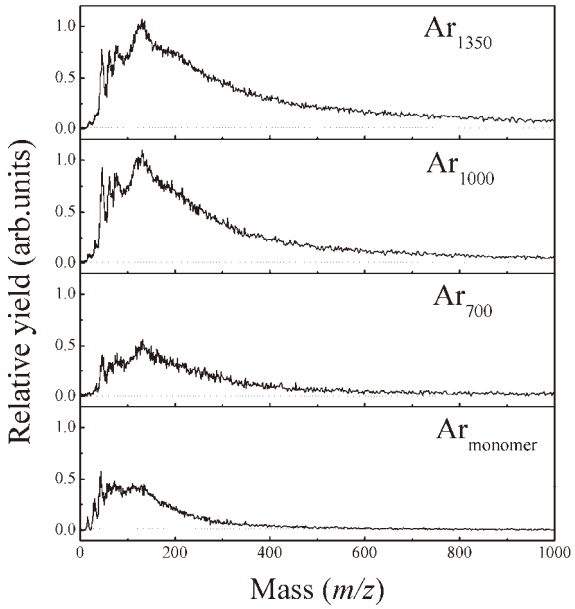

Figure 3 Mass spectra of PMMA for Ar_{700}, Ar_{1000}, Ar_{1350} cluster-ions incident and $Ar_{monomer}$ ion incident.

secondary ions, namely, the relative strength of the various kinds of ions significantly depends on the timing when the gate device is opened. This is because the position of the gate device is 183 mm apart from the sample and so the flight time required between them is different by the mass of the secondary ions. For examples, secondary ions of m/z = 100 and 1000 need 6.8 and 21.7 μs, respectively to arrive at the gate device after desorption from the sample. In order to solve such the problem, we repeatedly measured the TOF spectra of secondary ions by varying the opening time at the gate device and summed up them. The relative yield of the secondary ions was calculated by dividing the summed spectra by the current of incident cluster ions.

3. Results and discussions

Figure 2 shows the cluster-size distribution of the Ar cluster-ion with and without size separation. The cluster size before size separation distributes very widely from ~400 to ~4000 atoms/cluster. We obtained the narrower size distributions with their peak size of 700, 1000 and 1350 atoms/cluster after size separation by adjusting the delay time between the two ion-deflectors to 60, 72 and 83 μs, respectively. The size resolution ($m/\Delta m$) at the full width at half maximum (FWHM) of the peak and the ion current density of the size-selected cluster-ion beam were ≥ 5 and ≥ 10 nA/cm^2, respectively.

Figure 3 shows the secondary-ion mass spectra of PMMA on the Si substrate for Ar_{700}, Ar_{1000}, Ar_{1350} ion and $Ar_{monomer}$ beam incidents with a kinetic energy of 5 keV. The yield of secondary ion at m/z = 125 for Ar_{1350} cluster-ion incident was normalized to 1.0. When Ar cluster ions were incident to the sample, we observed a broad peak at m/z = 125. Furthermore, signals even at m/z > 200 were also observed although individual peaks were not observed in this region because of the limited mass resolution. It was obvious that the secondary ion yield increased with increasing the size of incident cluster. On the other hand, there were weaker signals at m/z > 200 when $Ar_{monomer}$ was incident to the sample as compared with the results for cluster ion incidents. A monomer units of PMMA is methyl methacrylate (MMA), of which mass is m/z = 100. So, it can be considered that the ions at m/z > 200 remain still in polymerized species.

Figure 4 shows the incident cluster size dependences of secondary ion yields at m/z = 100, 125, 300, 500 and 800, respectively. The secondary ion yields at m/z = 100 and 125 increased with increasing the incident cluster size from Ar_{700} to Ar_{1000} although the secondary ion yields did not go up by the incident of Ar_{1350}. On the other hand, the secondary ion yields at m/z = 500 and 800 were monotonically increased with increasing the incident cluster size. These results show that the dependency of the secondary ion yields on the cluster size is different by the mass of the secondary ion.

Such the incident cluster size effect can be discussed from the view point of the kinetic energy per constituent atom of the cluster ion. The cluster size and the acceleration energy (5 keV) used in present experiment correspond to 3-8 eV/atom, as shown in Figure 4. These values are close to the dissociation energies of chemical bonds forming the polymer. The changes in the kinetic

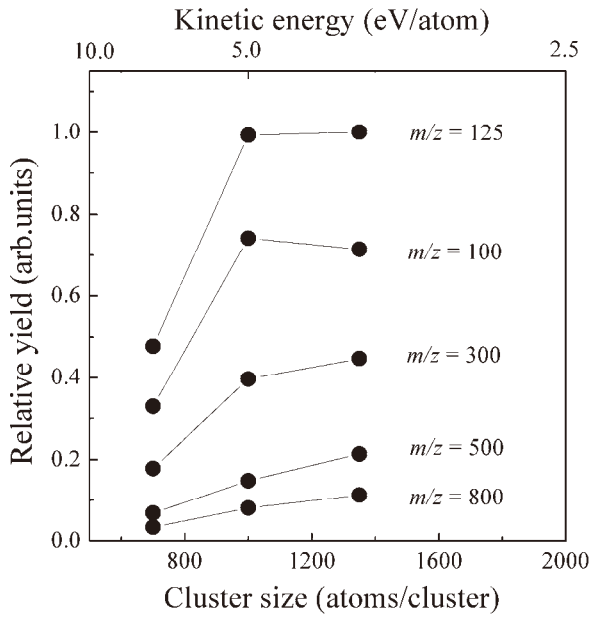

Figure 4 Incident cluster size dependences of secondary ion yields emitted from the PMMA solid film, of which mass were m/z = 100, 125, 300, 500 and 800, respectively.

energy per atom may induce the difference in the behavior of the dissociation of the polymer. In conclusion, size-selected gas cluster ion beam should be used as a primary beam for low-damage molecular SIMS.

4. Summary

The usefulness of a size-selected Ar cluster-ion beam for SIMS was investigated. The secondary ion yields from PMMA sample was drastically enhanced by the bombardment of the Ar cluster ions with the mean size of 700, 1000, and 1350, as compared with the case by Ar monomer ion bombardment. Furthermore, the dependency of the secondary ion yield on the cluster size is different by masses of the secondary ions. The yield of the secondary ions having large masses (m/z > 500) was simply increased with the increase of the cluster size. The present results on the cluster-size effect could elucidate a way where a kinetic energy per constituent atom is dissipated to dissociate polymer molecules in a solid.

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