Low Damage Etching and SIMS Depth Profiling with Large Ar Cluster Ions

Satoshi Ninomiya[1], Kazuya Ichiki[2], Hideaki Yamada[2], Yoshihiko Nakata[2],
Yoshiro Honda[2], Toshio Seki[2,4], Takaaki Aoki[3,4], Jiro Matsuo[1,4]

[1] Quantum Science and Engineering Center, Kyoto University, Gokasho, Uji, Kyoto, 611-0011, Japan
Fax: 81-774-38-3978, e-mail: ninomiya@nucleng.kyoto-u.ac.jp
[2] Department of Nuclear Engineering, Kyoto University, Sakyo, Kyoto, 606-8501, Japan
[3] Department of Electronic Science and Engineering, Kyoto University, Nishikyo, Kyoto, 615-8510, Japan
[4] CREST, Japan Science and Technology Agency (JST), Chiyoda, Tokyo, 102-0075, Japan

We investigated the etching and secondary ion yields of an arginine target bombarded with large Ar cluster ions at incident energies up to 18 keV. The mean size of Ar cluster ions was about 1000 atoms per ion, and the collision energy per incident atom was between a few and a few tens of eV. The sputtering yields of arginine increased linearly with an increase in ion energy, and the yield at 13 keV was of the order of 100 molecules per incident ion. The intensities of the secondary ions kept constant even after etching the arginine film target with large Ar cluster ions. These results indicate that large Ar cluster ions can be used as powerful tools for depth profiling with secondary ion mass spectrometry.
Key words: Ar cluster ion, biomolecule, secondary ion, TOF

1. INTRODUCTION

Depth profiling with secondary ion mass spectrometry (SIMS) has been rarely used for biomolecular materials, because incident atomic ion beams with energy in the keV range produce weak signals for large molecules and, in most cases, damage them. In recent studies it has been expected that cluster ion beams may solve these problems. For example, it is confirmed that cluster ions such as C_{60}^+, Au_3^+ and Bi_3^+ produce enhanced sputtering and secondary ion yields compared to atomic ions [1−3]. However, biomolecular samples are also damaged by these cluster ion beams, and SIMS depth profiling for biomolecular samples has not been fully achieved yet.

In our previous study, secondary ions were measured for an arginine target under the incidence of large Ar cluster ions and the effects of incident energy and cluster size on secondary ion yields were investigated [4]. When large Ar cluster ions such as 10 keV Ar_{1500} (6.7 eV/atom) bombarded an arginine target, molecular ions of arginine were detected with little fragment ions. It can therefore be assumed that large cluster ions can etch biomolecular samples without serious damage. In the present study we measured secondary ion yields before and after etching biomolecular samples with large Ar cluster ions and investigated the validity of Ar cluster ions for SIMS depth profiling.

2. EXPERIMENTAL

We measured sputtering yields and secondary ion spectra of organic compounds under large Ar cluster ion bombardment. Large Ar cluster ions were produced by gas cluster ion beam (GCIB) apparatus; the details of the GCIB techniques and equipment have been described elsewhere [5,6]. The biomolecular sample was an amino acid of arginine (Arg, $C_6H_{14}N_4O_2$, 174.21 u). Thin film targets of arginine were prepared on clean Si wafers by the spin-coating technique. We measured the film thickness with a profile laser microscope (KEYENCE, VK8500) and a contact surface profiler (ULVAC,

Dektak3). The thickness of the arginine film was about 100-200 nm.

Measurements of the sputtering yields and secondary ion mass spectra were performed with the small GCIB apparatus and it is comprised of a source chamber, an ionization chamber and an analytical chamber, and each chamber is pumped with a turbo molecular pump, as shown in Fig. 1. Neutral Ar clusters are formed by supersonic expansion of high-pressure gas (7×10^5 Pa) through a nozzle and then pass through the ionization chamber. Electrons ejected from a hot filament are accelerated toward the neutral Ar clusters and ionize them. The ionized Ar clusters are extracted towards the analytical chamber with accelerating voltages of 3–18 kV. Magnets installed between the ionizing and analytical chambers remove small cluster and monomer ions included in the cluster ion beams. On the other hand, it is also possible that only Ar monomer ions are incident on the target, when atoms in an argon atmosphere are ionized by electron impacts and accelerated towards the target. When Ar monomer ions were incident, the nozzle to produce neutral clusters and the magnets to remove monomer and small cluster ions were not used.

In sputtering yield measurements, the arginine samples were irradiated with non size-selected Ar cluster ion beams, the average size of the beams was about 1000 atoms/cluster, and the beams were incident on the sample in the analytical chamber at an angle of 45° with respect to the surface normal. The incident ion beams were raster-scanned over an area of typically 1×1.5 mm^2. The sputtering yields were calculated from the ion beam current, irradiation time, raster scanned area and etching depth of the arginine sample. The etching depth was measured with the contact surface profiler.

The SIMS equipment is connected to the small GCIB apparatus and it is comprised of a flight tube, as shown in Fig. 1. The maximum current density of both the Ar
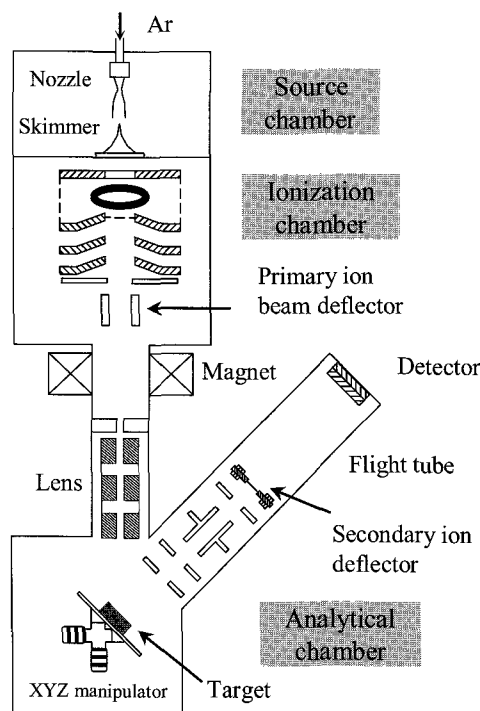
Fig. 1. Experimental setup for sputtering yield and SIMS measurements with Ar cluster ion beam.

Fig. 2. Sputtering yields of arginine bombarded with Ar cluster ions.

cluster and monomer beam was 10 μA/cm². The base and working pressures in the analytical chamber were 2×10^{-6} and 5×10^{-5} Pa, respectively.

The linear time of flight (TOF) technique was used to obtain secondary ion spectra. The process that we used to accurately measure the effect of the size of the large incident cluster ion on secondary ion spectra is described below. First, the primary ion beam was chopped to a width of 5 μs by applying a high-voltage pulse (above 500 V) between the parallel electrodes (primary ion beam deflector, 20 mm effective deflector length). Before the pulsed ion beam impacts on the target, the pulse width spreads beyond 50 μs because of the size difference of incident cluster ions. In other words, small clusters reach the target earlier than large clusters. Therefore, the effect of cluster size on secondary ion emission can be measured by installing an additional secondary-ion deflector between the target and the secondary-ion detector, which is controlled to pass the secondary ions only for a certain time interval, depending on the flight time of the primary cluster ions. The secondary-ion deflector consists of two electrically insulated sets of fine wires mounted parallel to each other. This electrode is called 'the interleaved comb ion (mass) deflection gate', and has been proved to be valuable tool for TOF mass spectrometry by Weinkauf *et al.* [7] and Vlasak *et al.* [8]. For the interleaved comb deflector, secondary ions pass it in ten nano seconds because of the short deflector length. In this study, the interleaved comb ion deflector was equipped with wires of 0.35 mm diameter spaced at a distance of 0.85 mm, which allows chopping secondary ions to a width of 200 ns every 1 ms by applying a relatively low-voltage pulse (below 300 V) between the wires. We can selectively
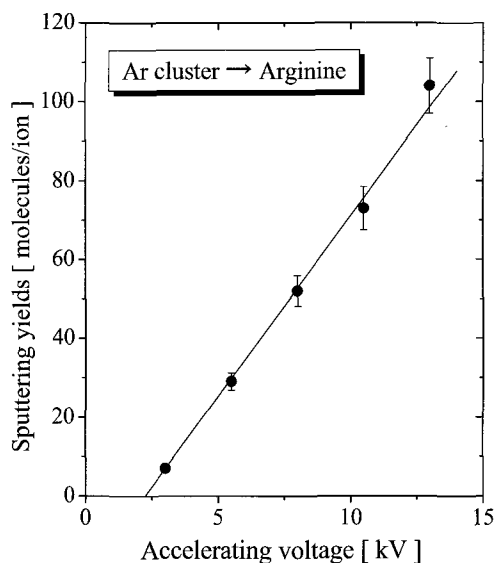
measure secondary ions produced by cluster ions of different sizes by changing the time interval between chopping of the primary and secondary ions. The timing of the secondary-ion chopping and detection was respectively used as the start and stop signal for the TOF measurement. The pulse repetition rate of the primary and secondary ion chopping was 1000 Hz and TOF measurements were taken for 20–200 s. Secondary ions were extracted towards the detector with an accelerating voltage of 2 kV and were detected with a microchannel plate (MCP) set on the axis of the surface normal.

3. RESULTS AND DISCUSSION

Figure 2 shows the sputtering yields of arginine as a function of accelerating voltage of incident Ar cluster ions. The sputtering yields of arginine molecules increased linearly with an increase in acceleration voltage, and the yield from arginine at 13 kV was of the order of 100 molecules (2600 atoms) per incident ion. This sputtering yield is extremely high compared to metals bombarded by atomic ions [9].

Figure 3 shows m/z spectra of positively charged secondary ions for the arginine target bombarded with Ar monomer (Ar^+) and Ar cluster (Ar_{300} and Ar_{1500}) ions. The secondary ion intensities are normalized by those of the molecular arginine ions. Many fragment ions such as CH_2N^+ (m/z 28), CH_4N^+ (m/z 30), $CH_3N_2^+$ (m/z 43), $CH_5N_3^+$ (m/z 59) and $C_4H_8N^+$ (m/z 70) were detected with high intensity under the incidence of 8 keV Ar atomic ions, and the yield of protonated arginine molecular ion ($Arg+H^+$, m/z 175) was extremely low compared to those of typical fragment ions (Fig. 3 (a)). The absolute yield of $Arg+H^+$ was about 1×10^{-5} per incident ion in our experimental setup. The high yields of characteristic fragment ions and the low yields of protonated molecular ions are in good agreement with the conventional SIMS studies for amino acids [10,11].

With the incidence of large Ar cluster ions, the appearance of the spectra changed dramatically. The spectra of Fig. 3 (a), (b) and (c) were obtained under the
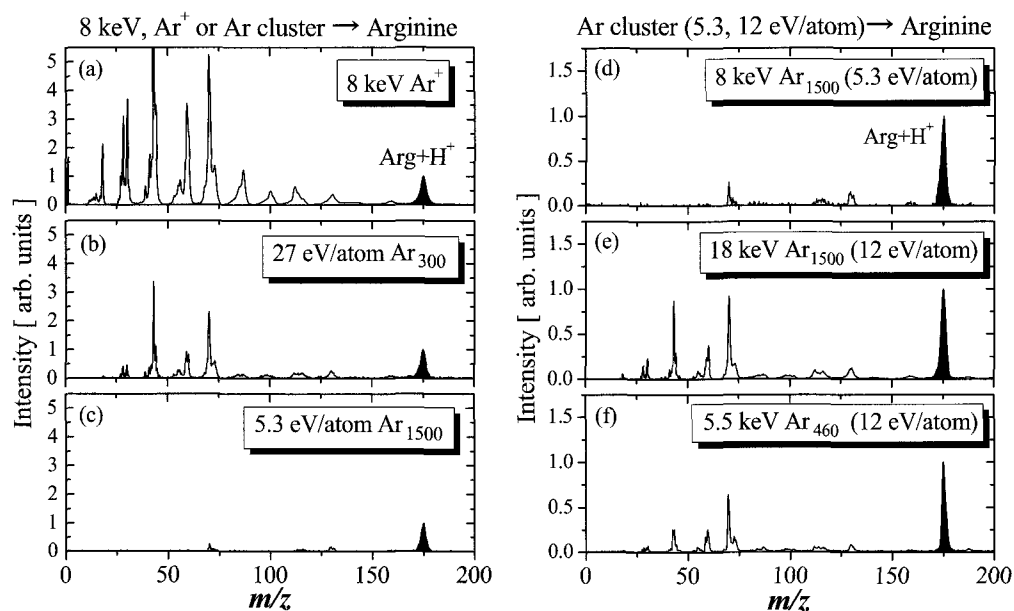
Fig. 3. Mass spectra of positively charged secondary ions for the arginine target bombarded at the conditions indicated on each spectrum: (a) Ar^+, 8 keV, (b) Ar_{300} cluster, 8 keV, (c) Ar_{1500} cluster, 8 keV, (d) Ar_{1500} cluster, 8 keV, (e) Ar_{1500} cluster, 18 keV and (f) Ar_{460} cluster, 5.5 keV. (Note that the conditions for (c) and (d) are the same.)

same total incident energy condition (8 keV). That is, as the size of the incident Ar cluster ion increases, its incident energy per atom decreases. The same incident energy per atom condition corresponds to the same incident velocity condition. The intensities of fragment ions decreased with increasing incident cluster size and decreasing incident velocity (i.e. energy per atom) (Fig. 3 (b) and (c)) compared to the intensities of $Arg+H^+$ ions (Fig. 3 (a)). As shown in Fig. 3 (c), characteristic fragment ions were rarely detected, though $Arg+H^+$ ions were undoubtedly observed. The absolute yield of $Arg+H^+$ at 8 keV Ar_{1500} incidence was about $1×10^{-3}$ per incident ion, and the value was extremely high compared to 8 keV Ar monomer ion incidence. However, since both size and velocity of incident ions were different for Fig. 3 (b) and (c), it is not clear which of the two parameters contributes to the decrease of fragment ion yield ratios. On the other hand, Fig. 3 (d) and (e) show the spectra of secondary ions for arginine under the same incident cluster size (Ar_{1500}) conditions. In this case, increasing the incident velocity increased the fragment ion yield ratios, at constant cluster size. Furthermore, Fig. 3 (e) and (f) show the spectra for arginine under the same incident energy per atom (12 eV/atom) conditions. In this case, fragment ion yields at 5.5 keV Ar_{460} incidence were still high, though the total incident energy decreased. These results appear to be the strongest proof that the decrease of fragment ion yield ratios is determined by incident velocity and not by size and total incident energy. From these results presented in this section, it is assumed that slow and large cluster ions can effectively etch and ionize biomolecular samples with little damage.

Next, we measured the secondary ion yields for the arginine films after etching with large Ar cluster ions.

Figure 4 shows the effect of incident ion fluence on the molecular ion yields for the arginine film bombarded with 15 keV Ar cluster ions. The molecular ion yields were normalized by the yield at the fluence of $5×10^{13}$ ions/cm². The mean size of Ar cluster ion beams for etching was about 1000 atoms/cluster, i.e. the mean energy per atom was 15 eV/atom. Regarding this measurement we wish to note that incident ion beam scanning for exclusion of edge effects was not carried out. The incident energy per atom of 15 keV Ar_{1000} cluster ions is 15 eV/atom, and fragment ions are also produced at this condition. In fact, the yield of $Arg+H^+$

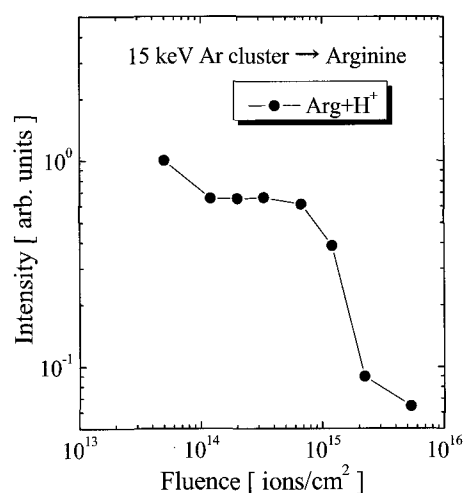
Fig. 4. The effect of incident ion fluence of $Arg+H^+$ ions from arginine bombarded with 15 keV Ar cluster ions.

slightly decreased with increasing fluence ($<1\times14$ ions/cm^2), this trend shows that the arginine molecules were damaged a little. As the fluence increased, the yields of Arg+H$^+$ ions kept constant until the incident fluence reached 7×10^{14} ions/cm^2, as shown in Fig. 4. These results show that the Ar cluster ion beams can etch the arginine film without damage accumulation. In this case, SIMS depth profiling can be achieved, because molecular ion yields keep constant. On the other hand, signals of the molecular ions soon disappeared with increasing fluence, when keV atomic ions were incident on organic materials [12,13]. From the abovementioned results, it can be concluded that large cluster ion beams may become a powerful tool for SIMS depth profiling for organic materials.

4. SUMMARY

Sputtering and secondary ion yields for arginine were measured under the incidence of large Ar cluster ions at incident energies between 3 and 18 keV. Sputtering yields of arginine increased linearly with incident ion energy, and the yield at 13 keV was of the order of 100 molecules per incident ion. Yields of Arg+H$^+$ ions almost kept constant before and after etching with large Ar cluster ions. Large cluster ions should be highly effective in low damage etching and SIMS depth profiling for biomolecular samples.

ACKNOWLEDGEMENTS

REFERENCES

[1] D. Weibel, S. Wong, N. Lockyer, P. Blenkinsopp, R. Hill and J.C. Vickerman, *Anal. Chem.* **75**, 1754–1764 (2003).

[2] D. Touboul, F. Halgand, A. Brunelle, R. Kersting, E. Tallarek, B. Hagenhoff, and O. Laprévote, *Anal. Chem.* **76**, 1550–1559 (2004).

[3] D. Touboul, F. Kollmer, E. Niehuis, A. Brunelle and O. Laprévote, *J. Am. Soc. Mass Spectrom.* **16**, 1608–1618 (2005).

[4] S. Ninomiya, Y. Nakata, K. Ichiki, T. Seki, T. Aoki and J. Matsuo, *Nucl. Instr. and Meth. B* **256**, 493–496 (2007).

[5] I. Yamada, J. Matsuo, N. Toyoda, A. Kirkpatrick, *Mater. Sci. Eng. R* **34**, 231–295 (2001).

[6] T. Seki, J. Matsuo, G.H. Takaoka and I. Yamada, *Nucl. Instr. Meth. B* **206**, 902–906 (2003).

[7] R. Weinkauf, K. Walter, C. Weickhardt, U. Boesl and E.W. Schlag, *Z. Naturforschung A* **44**, 1219–1225 (1989).

[8] P.R. Vlasak, D.J. Beussman, M.R. Davenport and C.G. Enke, *Rev. Sci. Instrum.* **67**, 68–72 (1996).

[9] H.H. Andersen and H.L. Bay, "Sputtering by Particle Bombardment I" R. Behrisch, Ed., Springer-Verlag, Berlin Heidelberg New York, 145–218 (1981).

[10] A. Benninghoven, D. Jaspers and W. Sichtermann, *Appl. Phys.* **11**, 35–39 (1976).

[11] A. Benninghoven and W.K. Sichtermann, *Anal. Chem.* **50**, 1180–1184 (1978).

[12] S. Ninomiya, K. Ichiki, Y. Nakata, Y. Honda, T. Seki, T. Aoki and J. Matsuo, Extended Abstracts of 8th Workshop on Cluster Ion Beam Technology, 41–46 (2007).

[13] D. Briggs, "Practical Surface Science" Second Edition Volume 2 Ion and Neutral Spectroscopy, D. Briggs and M.P. Seah, Ed., John Wiley & Sons, England, 367–423 (1992).