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Low Damage Etching of Polymer Materials for Depth Profile Analysis Using Large Ar Cluster Ion Beam

Satoshi Ninomiya,[1*] Kazuya Ichiki,[2] Hideaki Yamada,[2] Yoshihiko Nakata,[2]
Toshio Seki,[2,4] Takaaki Aoki,[3,4] Jiro Matsuo[1,4]
[1]*Quant. Sci. and Eng. Center, Facult. Eng., Kyoto Univ. Gokasho, Uji, Kyoto 611-0011, Japan*
[2]*Dept. Nuclear Eng., Facult. Eng., Kyoto Univ. Sakyo, Kyoto 606-8501, Japan*
[3]*Dept. Elect. Sci. Eng., Facult. Eng., Kyoto Univ. Nishikyo, Kyoto 615-8510, Japan*
[4]*CREST, Japan Science and Technology Agency (JST), Chiyoda, Tokyo 102-0075, Japan*
[*]ninomiya@nucleng.kyoto-u.ac.jp

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In this study, we demonstrate low damage etching of polymer materials for depth profile analysis by using large Ar cluster ion beams. Recently, we have proposed to use keV-energy large cluster ions as primary ions for secondary ion mass spectrometry (SIMS). The intensities of molecular ions from the polymer films were kept constant after etching with large Ar cluster ions, though the primary ion fluence exceeded the static limit. These results prove that large cluster ion beam irradiation rarely leads to damage accumulation on the surface of the polymers, and these characteristics as etching beam could be also suitable for other depth profiling techniques. In addition, the surface chemical states of the polymers were measured with X-ray photoelectron spectrometry (XPS). The chemical states of the polymethyl methacrylate (PMMA) sample etched with Ar atomic ion beams differed significantly from those of the untreated sample, whereas the chemical states were maintained even after etching with large Ar cluster ion beams.

1. Introduction

Analytical methods using quantum beams have been developed and used widely in industrial applications. Among them, SIMS and XPS have been widely used in the surface and interface analysis of various materials. Depth profiling with these analytical methods has been one of the most powerful and frequently applied techniques for semiconductors and metals [1,2]. In depth profiling analysis, the sample surface is generally etched with a beam of keV atomic ions, and a sputter crater is formed by the incident ion beam, which is rastered over an area larger than the beam diameter. In contrast, for organic materials, depth profiling techniques have been rarely used, because etching beams damage them and it is difficult to obtain the information of the chemical structures. In the case of SIMS depth profiling, molecular ion signals from organic materials decrease with increasing incident ion fluence [3,4]. An upper limit of incident ion fluence can be determined by the damage, and the fluence is estimated to be about 1×10^{12}–1×10^{13} ions/cm^2 per spectrum. This fluence is well known as the static limit [4–6]. Therefore, the low-damage and high-rate etching techniques are required in depth profiling analysis.

Gas cluster ion beam processing has been investigated in order to perform surface smoothing and fast etching for metals and semiconductors [7,8], but until now, there are very few studies on the irradiation effects of large cluster ions on organic materials. Recently, we have reported unique secondary ion emission from amino acid and peptide samples under the incidence of large Ar cluster ions [9,10]. In our previous reports, the relative yields of the small fragment ions decreased drastically with increasing incident cluster size, and fragment ions were rarely observed at incident energy per atom of a few eV, though molecular ions of the amino acid and peptide were observed. These results indicated that large cluster ion beams could be very suitable for SIMS analysis of organic materials.

In this study, we demonstrate applications of large Ar cluster ion beams to depth profiling of polymer materials. Furthermore, the surface chemical states of the polymer materials are investigated by using XPS method after etching with large Ar cluster ion beams.

2. Experimental

SIMS measurement was carried out using the small type of gas cluster ion beam apparatus; the details of the gas cluster ion beam technique and equipment were described elsewhere [7,11]. The schematic experimental setup for SIMS instrument is presented in Fig. 1. The instrument consists of a source chamber, an ionization chamber and an

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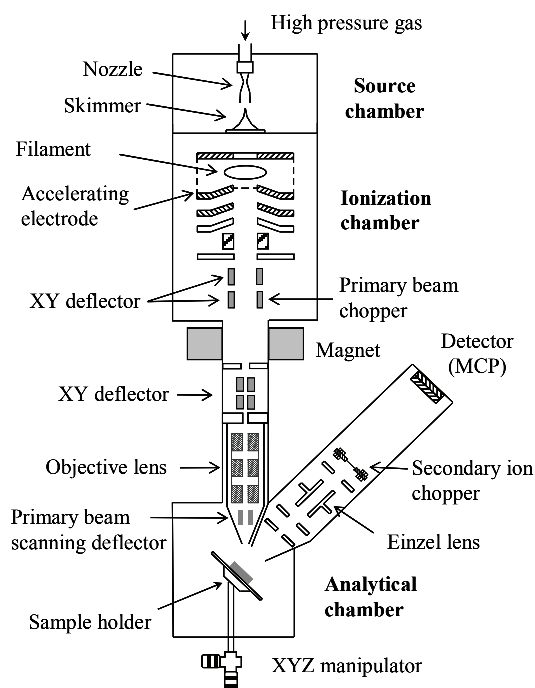

Fig. 1 Experimental setup for SIMS with large Ar cluster ions.

analytical chamber. A linear type of flight tube is connected to the analytical chamber. The incident energy of Ar cluster beam was 5.5 keV. The current and diameter of the Ar cluster ion beams were about 10 nA and 0.2 mm, respectively. The mean cluster size used in the SIMS study was 700 atoms per cluster. The primary ion beam was incident on a solid target at an angle of 45° with respect to the surface normal. Secondary ions were extracted with kinetic energy of 2 keV and detected with a microchannel plate (MCP) set on the axis of the surface normal. Secondary ion spectra were obtained with a time-of-flight (TOF) technique combined with the double deflection method [10]. The times of the secondary-ion chopping and detection were respectively used as the start and stop signals for the TOF measurement. The pulse repetition rate of the primary and secondary ion chopping was 1000 Hz and TOF measurements were taken for 10 s. In depth profiling measurements, a continuous Ar cluster ion beam was raster-scanned over an area of typically 3 mm × 5 mm by the scanning deflector installed just in front of the sample holder (Fig. 1), whereas in SIMS analysis, a pulsed Ar cluster beam was raster-scanned over an area of typically 0.6 mm × 1.0 mm to avoid the edge effect. The base and working pressure in the analytical chamber were 1 × 10^{-6} and 1 × 10^{-4} Pa, respectively.

XPS analysis of polymer materials was carried out with Quantum-2000 instrument (ULVAC-PHI, Japan) using Al-Kα radiation with a beam diameter of 20 μm. The narrow scan spectra of C1s and O1s peaks were obtained before and after etching with 20 keV Ar monomer and cluster ion beams. Ion beam etching was performed in the commercial type of gas cluster ion beam irradiation apparatus [7]. The mean cluster size used in the etching process was 2000 atoms/cluster. It is also possible that Ar monomer ions are incident in the same apparatus. The incident ion fluence was 5×10^{15} ions/cm^2 for both Ar monomer and cluster etchings. The primary ion beam was incident on the target at an angle of 0° with respect to the surface normal. The base and working pressure in the irradiation chamber were 3 × 10^{-5} and 7 × 10^{-3} Pa, respectively.

PMMA bulk material for XPS measurements was obtained from Misumi Co. (Tokyo, Japan) and cut into 10 mm × 10 mm pieces. PMMA powder (molecular weight = 700000 ~ 750000 u, repeat unit mass = 100 u) was obtained from Nacalai Tesque (Kyoto, Japan). The PMMA powder was dissolved in toluene as 2 wt% solutions. The thin film samples of PMMA were prepared by spin-casting on indium tin oxide (ITO) covered glass substrates (PMMA/ITO/Glass, 10 mm × 10 mm), and the spinning speed was 3000 rpm. Spin times were between 30 and 60 s.

3. Results and discussion

Fig. 2 (a) shows the TOF-SIMS spectrum of positively charged secondary ions produced from the PMMA/ITO/Glass target bombarded with 5.5 keV Ar_{700} ions before etching. Characteristic fragment ions such as *m/z* 69 ($C_4H_5O^+$) and *m/z* 115 ($C_6H_{11}O_2^+$) and protonated molecular ions of the repeat unit $C_5H_9O_2^+$ (*m/z* 101) were detected for PMMA. These species were good agreement with those from conventional TOF-SIMS measurements [3,4]. On the other hand, surface contaminants (*m/z* 73) such as polydimethylsiloxane (PDMS) were also detected. Fig. 2 (b) shows the secondary ion spectrum after etching with 5.5 keV Ar cluster ions at the fluence of 1.1 × 10^{14} ions/cm^2. In this study, incident Ar cluster ions were not size-selected before irradiating the sample during the etching process, and the sample was exposed to irradiation by Ar cluster ions of various sizes. During SIMS analysis, the secondary ion chopper was used and only the secondary ions produced from Ar_{700} ions impacts were detected. The ratio of the intensity of the *m/z* 69 peak to that of the static SIMS condition decreased to 50 % at most. Fig. 2 (c) shows the secondary ion spectrum after etching with 5.5 keV

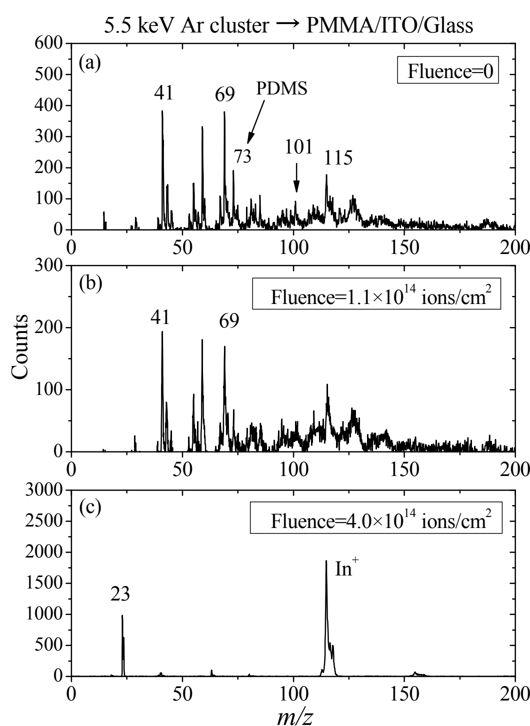

Fig. 2 Positive secondary ion spectra for the PMMA/ITO/Glass target (a) before and after etching with 5.5 keV Ar cluster ions at the fluences of (b) 1.1 × 10^{14} and (c) 4.0 × 10^{14} ions/cm^2.

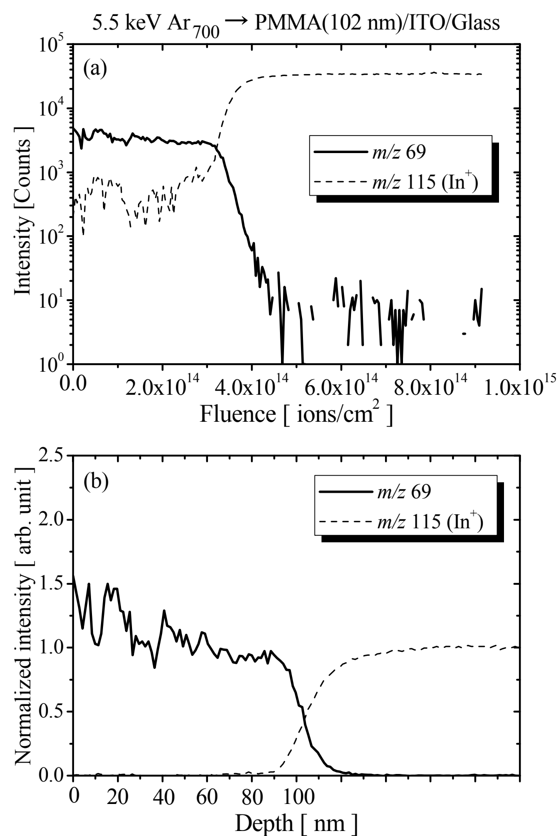

Fig. 3 (a) Variation of the intensities of the *m/z* 69 and 115 peaks for the PMMA/ITO sample with incident ion fluence. (b) Depth profiles of the *m/z* 69 and 115 peaks.

Ar cluster ions at the fluence of 4.0 × 10^{14} ions/cm^2. In this case, In^+ ions from ITO were detected with extremely high intensity, and secondary ions from PMMA were rarely observed.

Figure 3 (a) presented the intensities of the peaks of *m/z* 69 and *m/z* 115 as a function of incident Ar cluster ion fluence. The intensities of the *m/z* 69 peak remained constant until the fluence reached a value of 3.0 × 10^{14} ions/cm^2. This result indicated that the PMMA sample was less damaged by large Ar cluster ion irradiation than by general etching beams such as keV-energy Ar atomic ions. On the other hand, the intensities of the peak around *m/z* 115 remained almost constant with increasing fluence, and increased suddenly when the *m/z* 69 intensities began to decrease. Therefore, the main component of the peak was assumed to be the fragment ions from PMMA at relatively low fluence, or In^+ ions from the ITO substrates at high fluence. At least two orders of magnitude of dynamic range were achieved in this experiment, and this dynamic range was considered sufficient for SIMS depth profiling of organic materials.

To convert the fluence to depth, a linear relation between fluence and etching depth must be confirmed. The linear dependence between etching depth and incident Ar cluster ion fluence was obtained for a thick leucine film (3.5 µm) in the previous report [12]. Therefore, the fluence of incident Ar cluster ions can be converted directly to a depth scale. To convert the fluence to depth, the fluence at half intensity of the steady state corresponded to the thickness of the film. The depth profiles of the *m/z* 69 and 115 peaks are illustrated in Fig. 3 (b). The intensities of the secondary ions were normalized by the averages at the steady state of the profiles, and were plotted on a linear scale. The thickness of the PMMA film was estimated from the depth of the etching crater, and was determined by averaging at least five data points obtained from the contact surface profiler (Veeco, Dektak3). The thickness of the PMMA film was 102 nm. In general, the depth resolution for SIMS depth profiling corresponds to the distance over which a change in signal from 84% to 16% is measured. From the 84–16% interface width, the depth resolution was estimated to be below 20 nm.

The surface chemical analysis of PMMA bulk samples was carried out by XPS. Narrow scan spectra of C1s and O1s regions were obtained before and after etching with 20 keV Ar monomer (Ar^+) and cluster ion beams at the fluence of 5 ×

10^{15} ions/cm^2. The etching depth was measured with the contact surface profiler, and it was about 1.9 µm for 20 keV Ar cluster incidence. The C1s envelop was deconvoluted into three components, and the binding energy scale was calibrated to 284.8 eV for the main C1s peak. The intensity of third peak at 289 eV after etching with Ar monomer ions decreased significantly compared to the non-irradiated sample, and it corresponds to the O-C=O group. On the other hand, the third peak intensity of the sample after etching with Ar cluster ions decreased slightly, and the decreasing ratio was extremely low. That is, it was found that oxygen atoms were not preferentially sputtered during Ar cluster ion beam etching. These results indicated that large cluster ion beams could etch organic materials with extremely low damage, though sputtering yields with Ar cluster ions were excellently high. Therefore, it could be concluded that large cluster ion beams could become a powerful tool for depth profiling techniques for organic materials.

4. Summary

Secondary ions were measured for PMMA/ITO/Glass targets before and after etching with 5.5 keV Ar cluster ion beams, and the variation of the secondary ion intensities with incident ion fluence was investigated. The intensities of the *m/z* 69 peak from PMMA remained constant with increasing incident ion fluence, until the interface was reached. The surface chemical states of the PMMA bulk samples were also measured with XPS before and after etching with 20 keV Ar monomer and cluster ions at the fluence of 5×10^{15} ions/cm^2. It was found that oxygen atoms were not preferentially sputtered during Ar cluster ion etching. The main conclusion of this study was that by using large Ar cluster ion beams, low damage etching of the PMMA samples was achieved. This study has proved that large Ar cluster ion beams have great potential for depth profiling analysis of organic materials, and further development of this technique could contribute to various fields in life sciences, such as biochemistry, pharmacy and medical science.

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