

Depth Profiling of Polystyrene Using Charged Water Droplet Impact

Yuji Sakai,^{1,3*} Yoshitoki Iijima,² Riou Takaishi,¹ Daiki Asakawa¹ and Kenzo Hiraoka¹

¹Clean Energy Research Center, University of Yamanashi, Takeda 4-3-11, Kofu 400-8511, Japan

²Electron Optics Sales Division, JEOL Ltd.2-8-3 Akebono, Tachikawa, Tokyo 190-0012, Japan

³Japan Science and Technology Agency, Innovation Satellite Shizuoka, 3-5-1 Johoku, Nakaku, Hamamatsu,432-8561,Japan

*ysakai-as@yamanashi.ac.jp

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The molecular depth profiling of polymer by the electrospray droplet impact (EDI) have been performed. The multiply-charged water droplets with kinetic energy of $\sim 10^6$ eV were irradiated to a bulk and a spin coated polymer samples. The synthetic polymer as bulk polystyrene (PS) and spin coated PS on Si substrate were adopted as typical polymers. When a target is etched by EDI, the ablation of the target is suppressed to minimal, i.e. the shallow surface etching with non-recognizable damage on the surface is realized. It was found that X-ray photoelectron spectroscopy (XPS) spectra for PS were independent on the irradiation time by EDI. This indicates that EDI is a unique technique for the surface etching of the polymer materials without leaving any damage on the etched surface.

1. Introduction

The depth profiling analysis by Auger electron spectroscopy (AES), XPS and secondary ion mass spectrometry (SIMS) is one of the most useful technique for the observation of the cross sectional elemental distribution. The depth profiles are obtained by alternately recording the intensity of specific peaks and removing material from the sample surface by the ion beam etching. AES and XPS depth profiling are usually coupled with Ar ion beam etching in many instruments. The Ar ion beam etching induces the degradations and preferential sputtering for the samples. In SIMS depth profiling, it was found that the degradations of the polymers by the cluster ion etching are suppressed to some extent by using the low energy ions or the cluster ions. For reducing these degradations, the cluster ion projectiles are now being used i.e., cluster-SIMS [1][2][3]. XPS instruments coupled with the cluster ion beam source such as C₆₀ provide the lower sample degradations. The XPS depth profiling using C₆₀⁺ was found to reduce the polymer sample damage [4]. However, some carbon deposition and deoxygenation were observed on some of the polymer samples. Recently, a new ionization method, the electrospray droplet impact (EDI) ionization has been developed for matrix-free SIMS [5][6].

The projectiles used in EDI are extremely large water cluster ions with masses of about a few 10^6 u. The charged water droplets impact on a target, and

molecular-level etching is realized without damaging the sample underneath the surface. In the related work, the SiO₂ on Si, poly ethylene terephthalate (PET), and InP samples etched by EDI were examined by XPS in detail [7]. It was found that the etched surfaces by EDI were extremely smooth and no degradation and no preferential sputtering took place. In contrast, molecular depth profiling of polymer samples using other SIMS techniques generally induces the degradations of polymers induced by ion beam etching.

In this work, the polystyrene (PS) was selected as a model synthetic polymer for applying EDI to the molecular depth profiling. The PS sample is widely used in industry with the unique characteristics as thermal flexibility and durability. The depth profiling of PS treated by Ar and C₆₀ ion beams is a rather difficult task. It was reported that the surface composition of PS were changed after irradiation of Ar and C₆₀ ion beams [8]. In this work, EDI is applied to the depth profile analysis for spin coated PS. The surface chemical compositions of PS with the EDI etching were analyzed by XPS and EDI/SIMS. It was found that EDI is capable of shallow surface etching with little surface damage.

2. Experimental

SIMS depth profiling was performed by using an orthogonal time-of-flight mass spectrometer (Accu-TOF-MASS, JEOL, Japan) equipped with an

EDI gun. The EDI projectiles were formed by electro spraying 0.01M trifluoroacetic acid (TFA) aqueous solution at atmospheric pressure. The charged droplets were sampled through an orifice with 400 μ m diameter into the vacuum chamber, and transported into a quadrupole ion guide. The m/z of the primary droplet projectiles are estimated from the RF voltage applied to the ion guide to be in the range of $1 \times 10^4 - 5 \times 10^4$. The charged water droplets after exiting the ion guide were accelerated by 10kV, focused by the Einzel lens and impacted on the target. The typical cluster may be represented as $[(H_2O)_{90000} + 100H]^{100+}$. The secondary ions formed by EDI are transported into a second quadrupole ion guide and mass-analyzed by an orthogonal TOF-MS. The polymer sample placed on stainless-steel substrate was analyzed with no charge compensation. The charging of the polymer film during the EDI etching was confirmed to be totally negligible.

XPS depth profiling was performed by the crater edge profiling method obtained by XPS line scan analysis across the "crater edge" formed by the EDI etching [9]. After EDI etching, the sample was exposed in an ambient air and transported to the XPS instrument. The surface chemical composition was analyzed by XPS (JPS-9200, JEOL, Japan) with a base pressure of about 7×10^{-8} Pa using a monochromatic AlK α source (1486.6eV) with 0.65 eV energy resolution for Ag3d $_{5/2}$ at a constant pass energy of 10eV. An electron flood gun was used to neutralize the sample charged by photoelectron emission. For comparative study for EDI and Ar ion etching, the depth profile by Ar ion etching was made using an Ar ion gun installed in the XPS apparatus.

The bulk PS was a sheet with 0.05 mm thickness supplied by Goodfellow (England). The spin coated PS was prepared on Si(100) substrate using about 0.06% solution of the bulk PS dissolved in toluene. The film was made by using a spin coater with 5000 rpm for 180 s and annealed at 90°C for 5min. The thickness of the PS film was measured by a spectroscopic ellipsometer (SE800: SENTECH Instruments, Germany). The film thickness of spin coated PS on Si(100) was adjusted to be 10 nm.

3. Results and Discussion

3-1. SIMS depth profiling

Figure 1 shows EDI/SIMS depth profiling of spin coated PS. Characteristic secondary ions of PS ($C_8H_7^+$: m/z 103 a.u.) and Si substrate ($(SiO_2)(CF_3COOH)H^+$: m/z 175 a.u.) are measured as a function of EDI irradiation time. A peak of m/z 103 a.u. was a few counts at just starting the etching, but strongly detected after several second etching. Maybe, the top surface of spin coated PS were some contamination. The interface between PS and Si appeared about 3min

after the EDI irradiation. Accordingly, the etching rate of PS for EDI is estimated to be 3.3 nm/min.

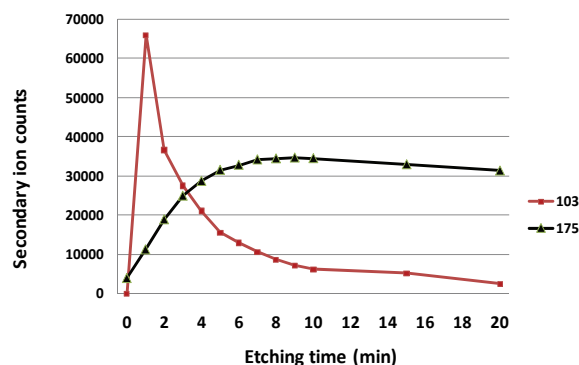


Fig. 1 SIMS Depth profiles of spin coated PS by EDI etching.

Figures 2 a) and b) show the EDI mass spectra for spin coated PS 1 min and 5 min after the start of EDI etching. All the major ions observed can be attributed to protonated clusters of trifluoroacetic acid molecules $(CF_3COOH)_nH^+$ (e.g., m/z 115 with $n=1$) and their water clusters. The ions originating from PS are detected, namely, at m/z 91, 103, 178, and 205. The ions originated from Si substrate are assigned as $(SiO_2)_n(CF_3COOH)H^+$, namely, at m/z 175 and 235 and $(SiO_2)_n(H_2O)(CF_3COOH)H^+$ at m/z 193 and 253. The depth profiles for another characteristic fragments for PS at m/z 91, 178, 205 a.u. were almost similar to Fig. 1. The EDI mass spectra showed that PS was etched with the appearance of the characteristic fragments for PS during EDI etching. That is, no damage accumulation on the surface of PS etched by EDI is recognized.

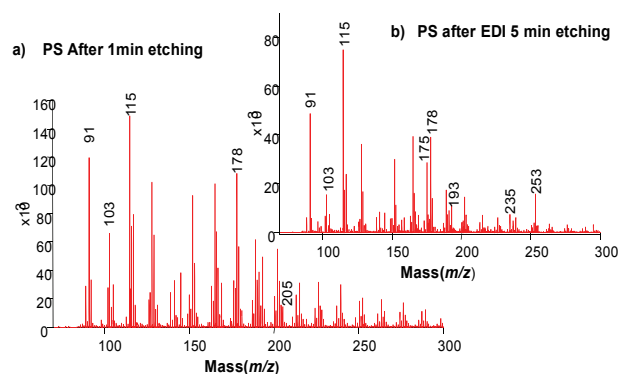


Fig. 2 EDI mass spectra of spin coated PS, 1min and 5 min after the start of EDI etching.

3-2. XPS depth profiling

An etched surface of the bulk PS by EDI was analyzed by XPS [10]. Figure 3 shows the C1s spectra of the bulk PS etched by EDI for 0, 30, 90 and 120 min. The characteristic peaks of PS are C1s and shake-up peaks originated from $\pi-\pi^*$ transitions in the aromatic ring of PS. No change of the XPS spectra for 120 min droplets irradiation is indicative of damage-less or even damage-free EDI etching.

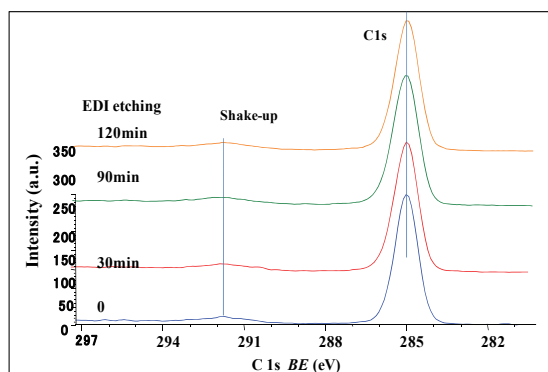


Fig. 3 XPS spectra of C1s and shake-up peaks, for bulk PS, measured as a function of EDI etching time.

Figure 4 shows the change of full width at half maximum (FWHM) of C1s and area intensity of shake-up peaks as a function of EDI irradiation time. The widths and peak positions of C1s peaks for the bulk PS were kept almost constant for 120min EDI irradiation. The aromatic rings of PS suffer from no recognizable damage by EDI etching. These results suggest that the peak intensity and chemical bonding states of PS do not change by EDI etching.

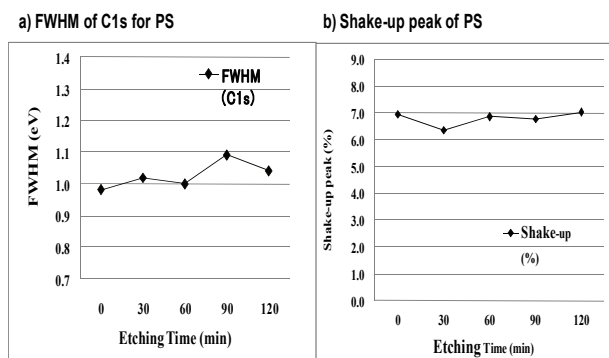


Fig. 4 Depth profiles of (a) FWHM of C1s peak, for bulk PS, as a function of EDI etching time, and (b) area intensity of shake-up peak as a function of EDI etching time.

The spin coated PS with thickness of 10nm on the Si(100) substrate was analyzed by XPS as shown in Table 1. The FWHM for C1s peak of spin coated PS is found to be smaller than that of the bulk PS. This suggests the spin coating makes it possible for the polymer molecules to align more regularly to form crystalline structure.

Table 1 The XPS experimental data for C1s and shake-up peak of bulk and spin coated PS.

	C1s			shake-up ($\pi-\pi^*$)		
	B.E.(eV)	FWHM(eV)	Ratio(%)	B.E.(eV)	FWHM(eV)	Ratio(%)
Bulk PS	285.0	0.94	92.1	291.7	1.32	7.9
Spin coated PS	285.0	0.82	94.1	291.4	2.39	5.9

Figure 5(a), (b) show the XPS depth profiles of the spin coated PS on Si(100) etched by Ar ion (a) and EDI (b) etching, respectively. The depth profile in Fig. 5(a) was measured using 500eV Ar ion projectiles. The etching rate of Ar was about 20nm/min for standard SiO₂. The depth profile in Fig. 5(b) was measured by XPS multi-point measurement across the crater edge of the spin coated PS after 180 min EDI etching. XPS multi-point spectra were measured in the range from the non-etched region to the bottom of the crater where almost all PS has been etched off. The analyzing spot for XPS analysis is 0.5 mm in diameter.

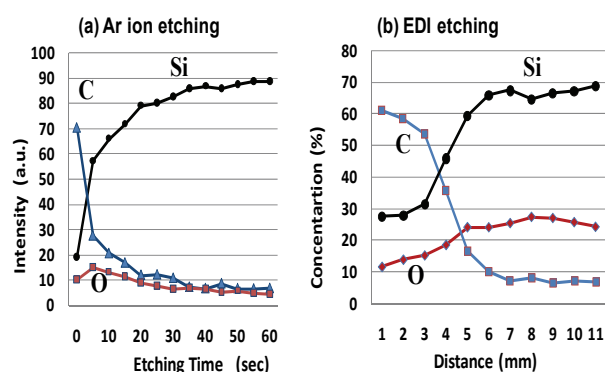


Fig. 5 XPS Depth profiles of spin coated PS: (a) depth profiling by Ar ion etching and (b) crater edge profiling after EDI etching.

In Fig. 5(b), the width of the crater edge is about 4mm in this experiment, distance from 2 to 6 mm. At the crater bottom, the Si substrate was appeared after EDI etching, and the oxygen profile shows high oxygen content in the region of the exposed Si

substrate. We supposed that the high oxygen content originated from the adsorbed water during the sample transfer in the ambient air. The ~10% of initial O1s concentration in Fig.5 b) may be originated from SiO₂ on Si substrate under the PS film. The O1s intensity increased at the bottom of the crater may be mainly originated from the moisture trapped in the sample when it was exposed in the ambient air.

Figures 6(a) and (b) show the C1s spectra of spin coated PS before and after the etching by Ar ion and EDI, respectively. In Fig.6 (a) for Ar ion etching, the C1s peak of PS shows the graphitic carbon of the sample (i.e., peak broadening and peak shift to the lower binding energy), and the formation of C-O and C=O bond groups. Fig. 6 (b) for EDI etching shows that the binding energies of C1s peak and shake-up peak keep their original values, i.e., no graphitization and benzene ring rupture take place. These results are almost same to data of the bulk PS [10].

It is evident that the surface of PS does not suffer from any chemical modification by EDI etching. We conjecture that the kinetic energy of impinging water droplet at the moment of impact on the target by EDI is efficiently converted to the internal energies of water droplets and also to the surface layers of PS in the selvedge of the colliding interface. The rest of the kinetic energy of the droplet may be well dissipated as shock waves propagating through the target and the water droplet. This explains that EDI is capable of damage-less surface etching for PS.

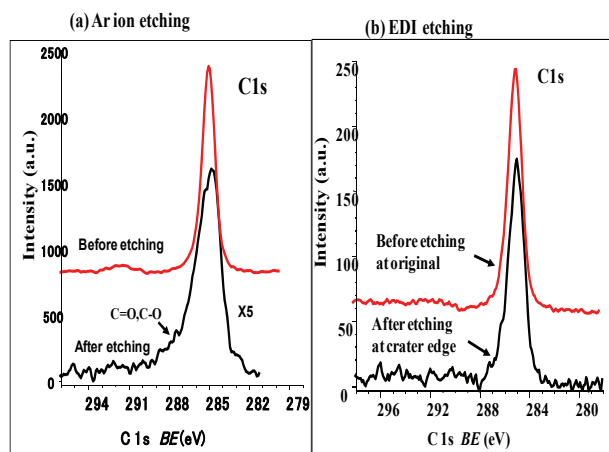


Fig. 6 XPS spectra of C1s for spin coated PS measured at (a) the interface for Ar ion etching and at (b) crater edge for EDI etching.

4. Conclusion

EDI mass spectra do give the information on the composition of the polymer samples. No charge compensation is necessary for the EDI operation. For PS, the abundant positive secondary ions originating from the polymer were observed. From EDI/SIMS depth profiling, the etching rate for PS of 3.3 nm/min is deduced. By observation of the characteristic mass spectra for PS, that is, no damage accumulation on the surface of PS etched by EDI is recognized.

XPS depth profiling for the spin coated PS were examined by Ar ion and EDI etching. It was found that PS samples etched by EDI do not suffer from any recognizable chemical modification and graphitization. In this work, it is confirmed that EDI has the extremely soft etching ability for organic materials. The unique nature of EDI may be originated from the occurrence of the in-phase collision between the water droplet and the solid sample, where a greater part of the colliding kinetic energy is dissipated as the shock wave propagating through the colliding systems.

5. Acknowledgements

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6. References

- [1] N.Davies, D.E.Weibel, P.Blenkinsopp, N.Lockyer, R.Hill and J.C.Vickerman, *Appl. Sur. Sci.* **203-204**, 223 (2003).
- [2] N. Toyoda, J. Matsuo, and I. Yamada, *Nucl. Instr. Meth. Phys. Res. B* **216**, 379 (2004).
- [3] D.E.Weibel, N.Lockyer and J.C.Vickerman, *Appl. Surf. Sci.* **231-232**, 146 (2004).
- [4] N.Sanada, A.Yamamoto, R.Oiwa and N.Ohashi, *Surf. Interf. Anal.* **36**, 280 (2004).
- [5] K.Hiraoka, D.Asakawa, S.Fujimaki, A.Takamizawa, K.Mori, *Eur.Phys. J.D*, **38**, 225 (2006).
- [6] K.Hiraoka, K.Mori, D.Asakawa, *J.Mass Spectrom.*, **41**, 894 (2006).
- [7] Y.Sakai, Y.Iijima, R.Takaishi, D. Asakawa and K. Hiraoka, *J. Surf. Anal.* **14**, 466 (2008).
- [8] N. Nieuwjaer, C. Poleunis, A.Delcorte, and P. Bertrand, *Surf. Interface. Anal.* **41**, 6(2009).
- [9] D.Briggs and J.Grant(Eds), *Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy* (2004) IM Publication and Surface Spectra Limited.
- [10] Y.Sakai, Y.Iijima, R.Takaishi, D. Asakawa and K. Hiraoka, (to be published in JVST).