Incident Angle Dependence in Polymer TOF-SIMS Depth Profiling with C$_{60}$ Ion Beams

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Cluster ions such as C$_{60}^{+}$ are well used as the sputtering ions for polymer depth profiling. The molecules of analyte surfaces are occasionally damaged by the ion bombardment during sputtering, leading to a loss of the molecular information. In order to obtain a proper polymer depth profile, sputtering conditions shall be optimized, however, they have not been investigated sufficiently. This study, incident angle dependence was investigated at the angle from 48° to 76° with respect to the surface normal. Samples used were the bulk polycarbonate (PC), bulk polystyrene (PS), and Irganox1010/Irganox3114 organic multi layer film. Irganox3114 layers were deposited at the several depths in the Irganox1010 film as markers to evaluate the interface resolution. Characteristic TOF-SIMS spectra from PC and PS were retained even after sputtering hundreds of nanometers at 76°, although the loss of the molecular information due to carbon deposition and/or damage accumulation was observed at 48°. From the depth profile of Irganox1010/Irganox3114, significant improvement of interface resolution was obtained at 76° over that at 48°. This work indicates that glancing angle sputtering clearly becomes one of the approaches to optimize C$_{60}$ polymer depth profiling. [DOI: 10.1380/ejssnt.2009.878]

Keywords: TOF-SIMS; Polymer depth profiling; Incident angle dependence; C$_{60}$

I. INTRODUCTION

Time of flight secondary ion mass spectrometry (TOF-SIMS) has been widely used to characterize various kinds of materials, especially organic materials [1]. It gives us not only surface atomic/molecular species but also in-depth distribution information. It is, recently, becoming quite important to investigate the molecular information at the polymer-polymer or polymer-substrate interfaces, and also to examine the diffusion of additives, because these characteristics dominate the performance of products. In TOF-SIMS depth profiling, as in dynamic SIMS, cesium or oxygen ions are generally used as a sputtering ion. However, these ion sources frequently degrade the surface morphology and chemistry, especially for organic materials. It is reported that C$_{60}$ sputtering realizes extremely low damage for organic materials [2] and, using x-ray photoelectron spectroscopy (XPS), it shows better effectiveness with higher incident angle [3]. Cramer et al. [4] explicitly reported C$_{60}$ sputtering is not suitable for bulk or spin-coated polycarbonate (PC) and polystyrene (PS) materials. They recommended cesium sputtering for PC and oxygen sputtering for PS. In TOF-SIMS analysis, metal cluster ions such as Au$_{13}$ or Bi$_{3}$ are used to enhance secondary yields for detection of high mass ions compared to monoatomic ions like Ga, Au, or Bi. It should be noted that all these liquid metal primary ion sources increase fragmentation, and that a C$_{60}$ primary ion source is the best candidate for TOF-SIMS analysis because fragmentation of polymeric materials is restrained [5–7], as reviewed by Mahoney [8].

From much published information, and from our experience, we endeavor to perform depth profiling of PC and PS using C$_{60}$, and to make a comparison against a previous report [4]. We have studied the incident angle dependence of some polymeric materials among the parameters that should be optimized which include: (i) ion beam energy/current, (ii) incident angle, (iii) temperature, and (iv) beam properly, but little has been studied regarding the incident angle [9, 10]. It has also predicted

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FIG. 3: TOF-SIMS spectra from PC samples; (a) before sputtering, after sputtering of $8 \times 10^{14}$ ions/cm$^2$ (b) at 76° and (c) at 48°. The ordinate values are expanded to show the change of C$_{14}$H$_{11}$O$_2$ in the mass range of $m/z$ 200 to 250 is shown in (a'), (b') and (c').

by molecular dynamics (MD) simulations that damage accumulation is reduced when applying glancing angle irradiation of cluster ions [11, 12]. In this study, the bulk PC and PS samples are shown to be analyzed with little damage accumulation to a depth of several hundred nanometers, and Irganox1010/Irganox3114 organic multilayer film shows the very sharp interface widths using C$_{60}$ for both sputtering and TOF-SIMS analysis.

II. EXPERIMENTAL

Polymer depth profiles were obtained using TOF-SIMS instruments (TRIFT V nanoTOF, ULVAC-PHI Inc.) equipped with a C$_{60}$ ion gun. Depth profiles were collected by alternating SIMS acquisition and sputtering. C$_{60}^+$ ions with the energy of 20 keV were used for SIMS acquisition (pulsed mode; ~10 ns pulse, ~8 kHz) and sputtering (DC mode). Under these typical operating conditions, the current and diameter of C$_{60}$ beam were 400 pA and about 10 µm, respectively. The incident angle of C$_{60}$ beam was varied by sample tilting, and both sputtering and analysis were performed at the same tilt angle. The raster sizes of the C$_{60}$ beam for sputtering and SIMS acquisition were 400 µm × 400 µm and 40 µm × 40 µm, respectively. When the incident angle was 66° and 76° with the respect to the surface normal, raster sizes were expanded to 1.56 and 2.77 times due to the oblique irradiation. The SIMS acquisition was carried out at the center of the sputtered area.

The samples used were the bulk PC (CT301325, Goodfellow) and bulk PS (ST313120, Goodfellow), and Irganox1010/Irganox3114 organic multilayer film [13], where the last one was considered to be an example of a laminate structure. Irganox3114 layers were deposited at the depth of 50, 100, 200 and 300 nm depth in the Irganox1010 film as markers to evaluate the interface resolution.

TOF-SIMS depth profiles were obtained by acquiring negative secondary ions (SI) for PC and Irganox1010/Irganox3114 and by positive SIs for PS. The 10 eV electrons were irradiated for charge compensation during the TOF-SIMS measurements. Sputtered depths were measured with a mechanical stylus profiler (Dektak 6M, Veeco).

III. RESULTS AND DISCUSSION

Figure 1 shows the C$_{60}^+$ dose dependence of the peak intensity of C$_{14}$H$_{11}$O$_2$ ($m/z$ 211) which is one of the characteristic molecular fragment ions of PC. After C$_{60}$ sputtering to a primary ion dose density (PIDD) of $5 \times 10^{15}$ ions/cm$^2$ at 76, 66 and 48° angle of incidence, the peak intensities decreased to about 1/4, 1/270 and 1/2,300 from the initial intensity. These results denote that the glancing angle sputtering minimizes the reduction of the peak intensity. The crater depths after depth profiling at 76, 66 and 48° reached 610, 260 and 150 nm, respectively. Relationship between crater depth and C$_{60}^+$ ion dose is shown in Fig. 2. A linear relationship between ion dose and crater depth is clearly shown up to 500 nm at the angle of incidence of 76°, though the sputtered depth is saturated at less than 150 nm at 48°. It is thought that the sputtering rate and carbon deposition rate is balanced above the ion dose of $0.5 \times 10^{15}$ ions/cm$^2$. Figure 3 shows the mass spectrum before sputtering (a) and after sputtering to $8 \times 10^{14}$ ions/cm$^2$ at (b) 76° and (c) 48°. The spectrum taken at 76° in Fig. 3(b) was not changed from the initial one in Fig. 3(a), while the spectrum was completely changed at 48° as shown in Fig. 3(c). In Fig. 3(c), it is noted that the peaks featuring PC such like C$_{2}$OH

http://www.ssj.org/ejssnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejssnt/)
(m/z 41), C₆H₅O⁻ (m/z 93) and C¹₄H₁₁O₂⁻ (m/z 211), drastically decrease from the initial state, while C₇⁻ and (C₉⁺H₃⁻) peaks are becoming dominant. In Figs. 3(a'), 3(b') and 3(c'), the ordinate values are expanded to show the change of C¹₄H₁₁O₂⁻ in the mass range of m/z 200 to 250.

Figure 4 shows the results of the depth profiling of PS at (a) 76° and (b) 48°. The mass peak intensities of C₃H₇⁺ (m/z 91), C₆H₅⁺ (m/z 105) and C₈H₁⁺ (m/z 115) are almost constant during sputtering at 76°, but they rapidly decay at 48°, meaning that the reduction of the PS peak intensities is suppressed by glancing angle sputtering. Crater depth after sputtering to 3.2×10¹⁴ ions/cm² at 76° was 170 nm, while the crater depth after sputtering to 1.0×10¹⁵ ions/cm² at 48° was only 80 nm despite a three-fold increase in ion dose, although it is not shown in this paper.

The constant sputtering rate in the range of more than 200 nm at 76° is also observed for the PS sample as shown in Fig. 5. Figure 6 shows the mass spectra before (a) and after sputtering to 2×10¹⁴ ions/cm² at (b) 76° and (c) 48°. There is almost no change between the spectrum of the initial surface and that of the area sputtered at 76°. However, C₇⁺ and (C₉⁺H₃⁺) peaks are dominant in the spectrum of the area sputtered at 48°, similar to what was observed for PC. The C₇ and (C₉⁺H₃) peaks shown in Fig. 3(c) and Fig. 6(c) suggest that either carbon deposition or reduction of the polymer chemistry to carbon occurs at low incidence angle sputtering. Kozole et al. [14] reported the increase in the amount of the deposited carbon by C₆₀ sputtering on silicon surfaces between 75° and 40°. Cheng et al. [9] developed a simple model describing the molecular ion intensities under cluster ion bombardment accompanied by molecular sputtering yield, the damage cross-section, and altered layer thickness. From their model, molecular ion intensities between initial and steady state is expressed by the following formula,

\[
\frac{S_{SS}}{S_0} = \frac{Y}{Y + n\sigma_D},
\]

where \(S_0\) and \(S_{SS}\) are molecular ion intensities at the initial and the steady states, respectively, and \(n, \sigma_D,\) and \(Y\) are the density of molecules in the sample, the altered layer thickness, the damage cross-section, and the sputtering yield, respectively. In order to retain \(S_{SS}\) as
same as $S_0$, the altered layer thickness $d$ should be small and/or the sputter yield $Y$ should be sufficiently larger than $n \sigma D$. Present results suggest that carbon deposition exceeds the sputtering yield at 48°, resulting in the loss of the molecular information.

Figures 7 shows the depth profiles of C$_{33}$H$_{46}$N$_3$O$_5^-$ (m/z 564) ions from Irganox3114 and the full width at half maximum (FWHM) at the respective layer in Fig. 8. Significant reduction of the C$_{33}$H$_{46}$N$_3$O$_5^-$ peak intensity was observed at 48° incidence angle for the deeper layers, and the FWHM measurement of the delta layer width show a dramatic improvement at 76° incidence angle. It is thought that both the effects of a higher sputtering yield and a reduction in the altered layer thickness are the result of proper C$_{60}$ depth profiling conditions (i.e. high sputter angle incidence).

IV. CONCLUSION

In order to optimize the sputtering conditions of polymeric materials, the incident angle dependence ranging from 48° to 76° with respect to the surface normal was investigated. The samples that were studied included two bulk polymers, PC and PS, and a polymer laminate (Irganox multilayer). The results reveal that (i) the retention of molecular information is improved as a function of sputter depth and (ii) the interface resolution is improved as a function of sputter depth when sputtering at high incidence (glancing) angles. Glancing angle sputtering is shown to be a valuable approach for depth profiling and 3D imaging of organic materials with C$_{60}$ bombardment.

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