

Accurate and reproducible in-depth observation of organic–inorganic hybrid materials using FIB-TOF-SIMS

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(Received 14 November 2017; accepted 12 January 2018; published 30 January 2018)

In order to overcome the limitations of sputter depth profiling, the authors have introduced focused ion beam-time-of-flight secondary ion mass spectrometry (FIB-TOF-SIMS). In this article, the authors summarize our investigation into the capability of Ar-gas cluster ion beam (GCIB) to remove FIB-induced molecular damage. The analysis of organic–inorganic hybrid mixture samples is applied and discussed. The authors demonstrate a method whereby the accurate and reproducible chemical depth distributions of atomic and molecular moieties in hybrid materials are successfully acquired. Our results reveal the approach of using Ar-GCIB for molecular recovery of FIB straggle to be highly reproducible and amenable to three-dimensional materials characterization. *Published by the AVS.* <https://doi.org/10.1116/1.5013670>

I. INTRODUCTION

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is the most powerful of the surface analysis techniques in providing high detection sensitivity for both elemental and molecular species at high spatial resolution. For these reasons, TOF-SIMS has been used in fields such as metals, semiconductors, advanced electronic devices, polymers, pharmaceuticals, and biomaterials. In TOF-SIMS, chemical information comes from within 1 to 2 nm of the surface. Therefore, in order to obtain the information underneath the surface, removing the surface layer(s) is necessary. Since the structures and compositions of the devices and materials are usually complex, the importance of three-dimensional chemical analysis has been increasing. The sputter depth profiling method has been commonly used to examine elemental and molecular depth distributions beyond the surface. This method can conveniently provide the depth profiles as well as three-dimensional images from a specified region. In general, sputtering ions such as cesium and oxygen ions are utilized for inorganic materials while cluster ions such as C_{60}^+ and Ar_n^+ are utilized for organic materials. However, when the sample is composed of an organic–inorganic hybrid mixture or even a pure material with layers of differing composition, sputter depth profiling will cause difficulty in obtaining the accurate depth distributions of the various components due to the differential sputtering. As a consequence, the results of depth profiles and/or three-dimensional chemical images become complicated and difficult to understand.¹ In order to overcome the limitation of sputter depth profiling, we have proposed and reported a novel approach to directly observe the sample cross-section fabricated by focused ion beam (FIB) with TOF-SIMS used for atomic and molecular imaging.²

FIB is one of the sample processing techniques that has been widely used for failure analysis of semiconductor

devices having complex and fine structures. Since the probe size of FIB is a few nanometers, sample fabrication at any particular region can be carried out easily. After the development of the lift-out method, FIB has been mainly used as sample preparation for scanning electron microscope and transmission electron microscope observations.³ In FIB processing, a high energy ion beam is used for milling and sectioning and the damage to the sample is found to be remarkable. For example, in single crystal samples, it is well known that the sample surface fabricated by FIB turns amorphous.⁴ Therefore, usually after FIB processing, low energy Ar ions are used to remove the damaged layer.⁵ However, for organic materials, this method gives no benefit because the monoatomic ions also destroy the molecular structures.⁶ In this study, as an alternative to low energy Ar ions, we have attempted to remove the FIB-induced damaged layer using an Ar-gas cluster ion beam (Ar-GCIB). In this paper, we aimed to obtain the accurate chemical depth distributions of complicated organic–inorganic hybrid materials. Hence, the investigations of FIB-induced damage layer on polymer surface are carried out, and the cross-section observations of organic–inorganic hybrid materials are demonstrated.

II. EXPERIMENT

A. Samples

In this experiment, we used (1) a commercially available polycarbonate (PC) film (Goodfellow Cambridge, Ltd.), (2) a PC film covered with ~ 100 nm-thick platinum layer, and (3) bulk PC with glass fibers having a diameter of dozens of microns, also covered with ~ 100 nm-thick platinum layer.

B. Measurement conditions

A conventional TOF-SIMS instrument (PHI *nanoTOF* II, ULVAC-PHI, Inc.) was used. In addition to the bismuth cluster ion column for TOF-SIMS acquisition, the instrument was

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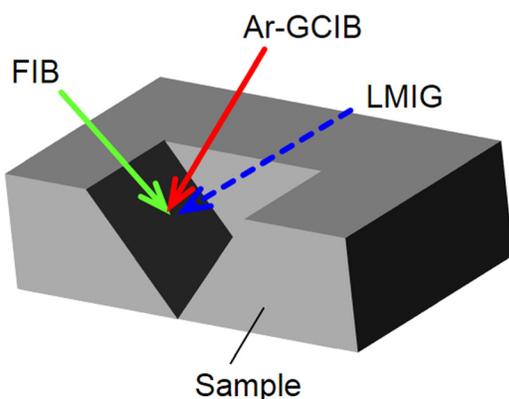


FIG. 1. (Color online) Configuration of LMIG, FIB gun and Ar gas cluster ion gun.

equipped with a FIB column and an Ar-gas cluster ion column. The following procedure was introduced to observe the cross-section of organic–inorganic hybrid materials: (1) fabricate slanted sidewalls by FIB milling, (2) polish the FIB-cut surfaces by Ar-GCIB, and (3) observe the cross-section surface using a mass pure Bi_3^{++} analysis beam. Figure 1 shows the configuration of each ion column and the ion beam conditions are summarized in Table I. The incident angle of the FIB is 48° , the magnification of depth direction will be ~ 1.5 times larger than the actual depth. A defocused beam of 10 eV electrons was used during TOF-SIMS measurement and sputtering for charge neutralization. All TOF-SIMS acquisitions were completed within the static limit, and it was confirmed that there was no significant changes of secondary ion intensities during the measurements. For measuring the crater depth, a stylus depth profiler (Dektak 6 M, Veeco) was used.

III. RESULTS AND DISCUSSION

A. Limitation of sputter depth profiling method

Figure 2 shows the result of sputter depth profiling of PC and glass fiber hybrid mixture. TOF-SIMS acquisition was performed by 60 keV Bi_3^{++} , and 20 keV Ar_{2500}^+ was used for sputtering; the raster sizes were $150 \times 150 \mu\text{m}$ and $500 \times 500 \mu\text{m}$, respectively. The intensity of $\text{C}_9\text{H}_{11}\text{O}^+$, which is one of the characteristic PC peaks in positive SIMS, showed a decrease with sputtering time. The reduction of $\text{C}_9\text{H}_{11}\text{O}^+$ intensity is due to the differential sputtering between the polymer matrix and the glass fibers. The sputtering rate on PC is much higher than that on glass,⁷ therefore, PC is continuously removed from the surface and the glass remains with an increasing fraction as the sputtering

TABLE I. Typical measurement conditions of each ion beam.

	Analysis	Milling	Polishing
Ion species	Bi_3^{++}	Ga^+	Ar_{2500}^+
Energy (keV)	60	30	20
Ion current (nA)	7.8	7.3	10
Raster size (μm)	100	150	500
Incident angle (deg)	40	48	40

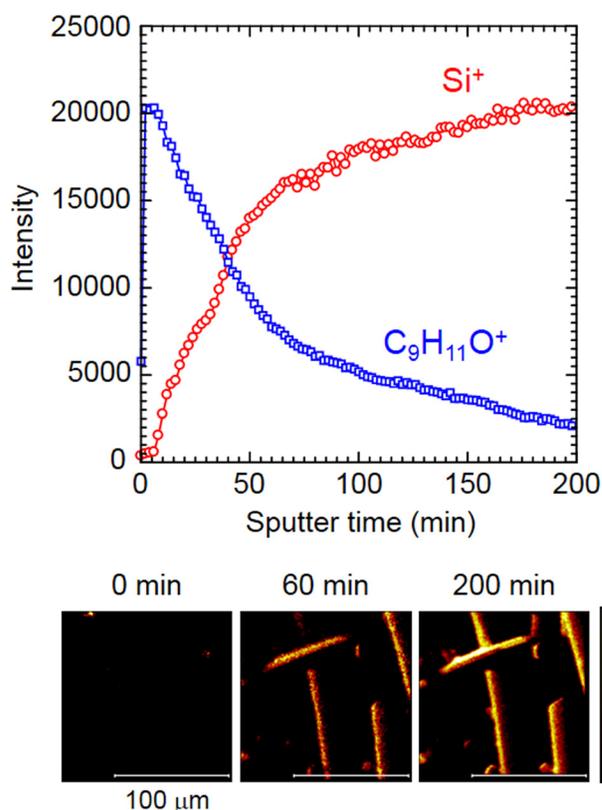


FIG. 2. (Color online) Depth profiles of Si^+ and $\text{C}_9\text{H}_{11}\text{O}^+$ from a PC and glass fiber mixture sample obtained using a conventional sputter depth profile method. The change of the Si^+ images at three points during the depth profile analysis is also shown.

continues. The variation of Si^+ signal in the images during the depth profiling is also shown in Fig. 2. The results indicate that the region occupied by glass fiber was expanding as Ar_{2500}^+ sputtering continued. In this case, not only the depth profiles but also the three-dimensional images cannot describe the accurate depth distributions. This exemplifies the limitation of the sputter depth profiling.

B. Investigation of FIB-induced damage on polymer surface

Before processing the FIB cross-section, we evaluated the FIB-induced damage on the PC surface. A bulk PC surface was irradiated with 30 keV Ga^+ ions. In this evaluation, the incident angle of Ga^+ ions was 40° . The dose of Ga^+ ions was calculated as 4.0×10^{15} ions/ cm^2 from the beam current (7.3 nA), raster size ($150 \times 150 \mu\text{m}$), and the irradiation time (20 s). Figure 3(a) shows the negative ion spectrum of the PC surface. The characteristic PC peaks such as $\text{C}_{14}\text{H}_{11}\text{O}_2^-$, $\text{C}_9\text{H}_9\text{O}^-$, $\text{C}_6\text{H}_5\text{O}^-$, etc., were observed clearly. After Ga^+ ion irradiation, the PC peaks disappeared, and C_n^- peaks became most significant [Fig. 3(b)]. The change of the spectrum suggested that the destruction of PC molecular structure and carbonization (i.e., polymer reduction) had occurred on the surface due to the Ga^+ ion irradiation. Then, 20 keV Ar_{2500}^+ ions were irradiated onto the damaged surface with raster size of $500 \mu\text{m}^2$. As shown in Fig. 3(c), all the characteristic PC peaks up to high m/z region were recovered by

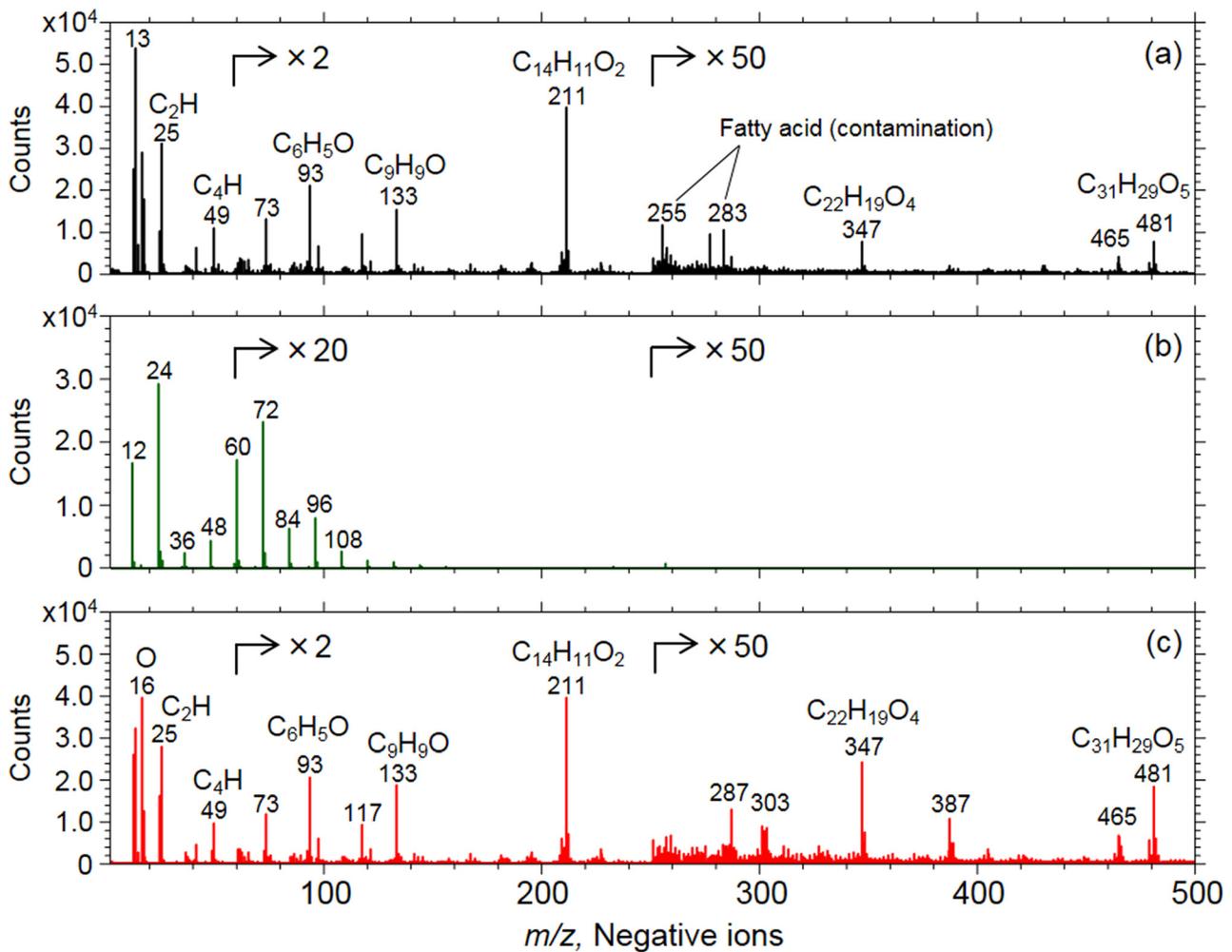


Fig. 3. (Color online) Negative ion spectra of the PC surface (a) as-received, (b) after Ga^+ ion irradiation, and (c) after removing the FIB-induced damage layer by Ar-GCIB sputtering.

Ar-GCIB irradiation. In this study, we defined the recovery time as the time where $\text{C}_{14}\text{H}_{11}\text{O}_2^-$ intensity reached its original intensity. Figure 4 shows the recovery time with respect to the Ga^+ ion dose. The required recovery time increased with the increase of Ga^+ ion dose; however, it reached saturation at $\sim 10^{16}$ ions/cm². This result suggests that the FIB-

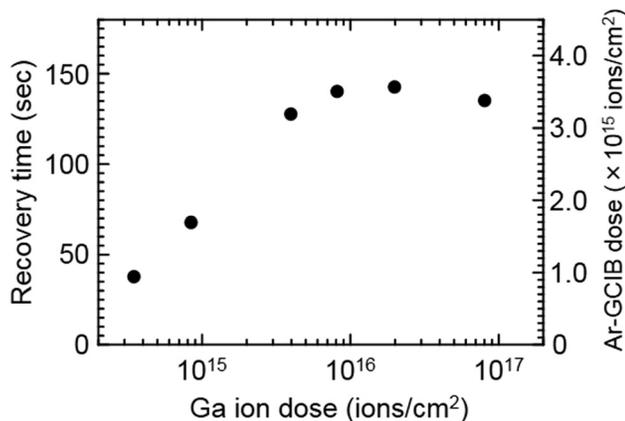


Fig. 4. Recovery time of the characteristic $\text{C}_{14}\text{H}_{11}\text{O}_2^-$ peak with respect to the Ga^+ ion dose by Ar-GCIB sputtering. The scale at the right of the plot shows the corresponding Ar_{2500}^+ ion dose.

induced damaged layer can be removed even after a long period of FIB irradiation.

Next, we also evaluated the thickness of FIB-induced damaged layer into the PC surface. In order to determine the thickness of the damaged layer, the crater depth before and after removing the damaged layer by Ar-GCIB sputtering was measured. After the Ga^+ ion irradiation for 500 s on the PC surface with the raster size of $150\ \mu\text{m}$ square ($=1.0 \times 10^{17}$ ions/cm²), the crater depth was 120 nm (Fig. 5, dotted line). Subsequently, Ar-GCIB irradiation within a $500\ \mu\text{m}$ square area was performed on the same position. While monitoring the $\text{C}_{14}\text{H}_{11}\text{O}_2^-$ intensity in the FIB-induced area, the Ar-GCIB irradiation was stopped when the intensity recovered back to the original value, and the crater depth was measured again. The crater depth from the top surface was 170 nm (Fig. 5, solid line), thus the thickness of the damaged layer was calculated to be 50 nm ($=170-120$). On the other hand, the crater depth at the region without Ga^+ ion irradiation was 510 nm. The sputtering rate of the damaged area was approximately ten times lower than that of the undamaged area. The drastic decrease of the sputtering rate at the damaged area was due to the carbonization by Ga^+ ion irradiation. The penetration depth of 30 keV Ga^+

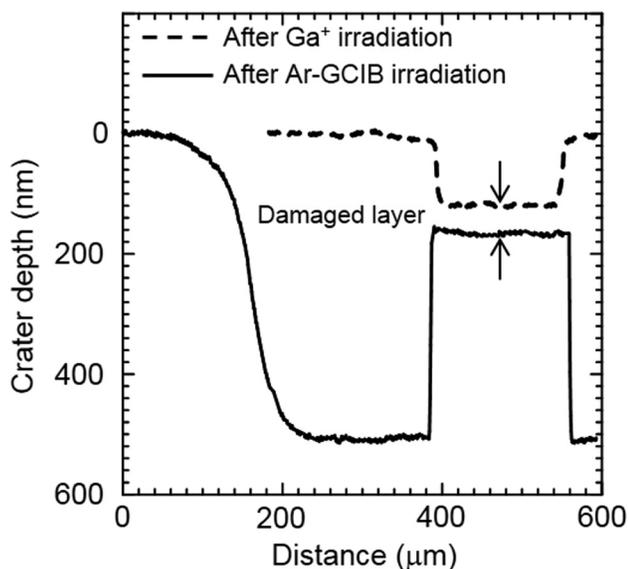


Fig. 5. Crater profiles after Ga^+ ion irradiation (dashed line) and after removing the damaged layer by Ar-GCIB sputtering (solid line). Thickness of the damaged layer was measured to be ~ 50 nm.

ions into the solid was estimated using TRIM code.⁸ We assumed that the target material was carbon in the simulation. The simulation results indicated that the maximum penetration depth of 30 keV Ga^+ ions was 44 nm.⁹ The experimental and calculated results reveal the same damaged layer thickness when considering a real polymer is used for the experiment but carbon was used for the calculated results. In actual applications of FIB-TOF-SIMS, the

damaged layer should be thinner than 50 nm because the FIB-exposed surface is formed on the slanted cross-section, i.e., at a more grazing angle.

C. Cross-section observation of Pt (100 nm)/PC

Based on the above investigations, we applied a new method to the analysis of organic-inorganic hybrid materials. A PC film covered with 100 nm-thick platinum was milled by FIB for 2 h to expose a surface for analysis. The scanning ion microscope (SIM) image and negative ion spectrum from FIB-cut surface are shown in Figs. 6(a) and 6(b), respectively. The carbonization and Ga residues were observed in the spectrum. We used 20 keV Ar_{2500}^+ ions for removing the damaged layer, and continued the irradiation until the $\text{C}_{14}\text{H}_{11}\text{O}_2^-$ intensity reached the steady state value. After Ar-GCIB irradiation for 240 s, the FIB-induced damage and Ga residues were removed, and the characteristic PC peaks had been restored [Fig. 6(c)]. These results reveal that it is possible to recover the molecular information even though the FIB fabrication was done for a long period of time with a high irradiation dose.

D. Cross-section observation of Pt (100 nm)/PC-glass hybrid mixture

We applied the aforementioned approach to the analysis of a PC/glass fiber hybrid mixture covered with 100 nm-thick platinum layer. FIB milling was carried out and Fig. 7(a) shows the TOF-SIMS images of the FIB-cut surface. The ellipse shape structure in the Si^- image reveals the cross-section of glass fibers, but no PC signals were

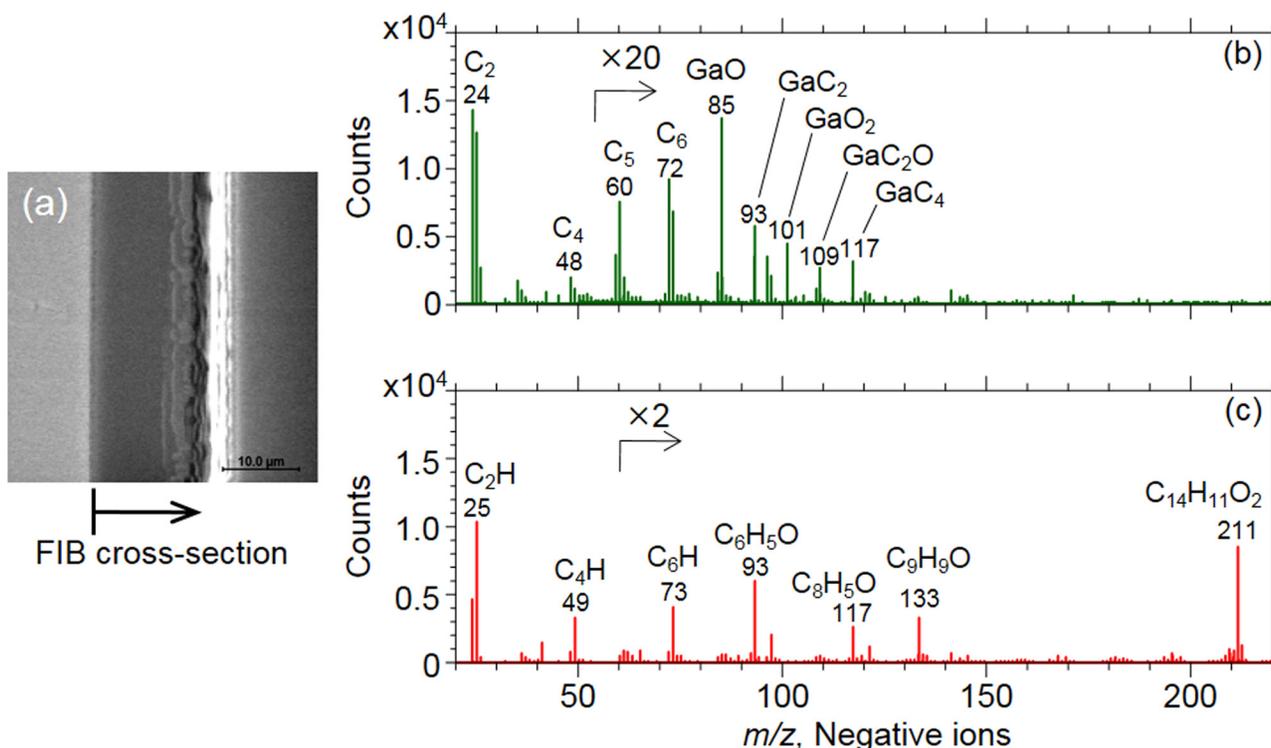


Fig. 6. (Color online) (a) SIM image of the platinum-coated polycarbonate after FIB fabrication. TOF-SIMS spectra from FIB-cut surface (a) after FIB milling and (b) after Ar-GCIB polishing.

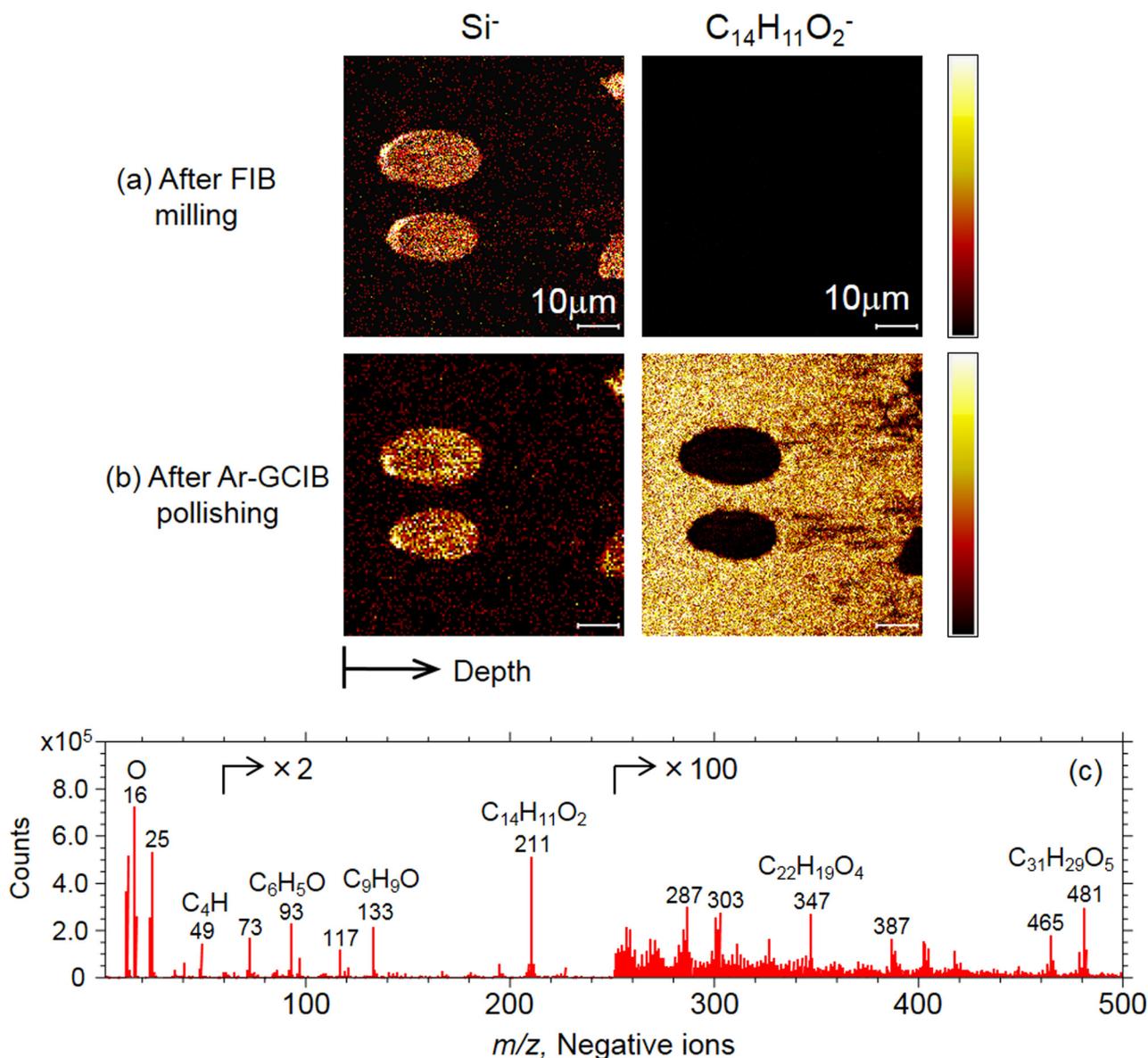


Fig. 7. (Color online) TOF-SIMS images of the glass fiber-filled and platinum-coated polycarbonate (a) after FIB milling and (b) after Ar-GCIB polishing. (c) Negative ion spectrum extracted from the PC region (i.e., excluding the glass fibers) after both FIB milling and Ar-GCIB polishing.

observed on the surface. After polishing the FIB-cut surface using Ar-GCIB, the PC peaks reemerged [Fig. 7(b)]. Figure 7(c) shows the extracted TOF-SIMS spectrum from PC region. All the characteristic PC peaks were recovered including those in the high m/z region. For comparison with and without glass fiber loading, see Figs. 3(c) and 7(c). By applying this approach, it was possible to obtain the detailed and accurate depth distributions of both elemental and molecular ions.

Conventionally, in TOF-SIMS, we had given up the possibility to collect any molecular information at-depth when the surface was covered by a metal layer or if the sample was composed of an organic-inorganic hybrid mixture. However, the combination of FIB and Ar-GCIB delivers a novel and reproducible method to obtain the accurate depth distributions of both elemental and molecular species.

IV. SUMMARY AND CONCLUSIONS

We have drastically improved the capability for and reproducibility of obtaining accurate chemical and depth distributions within complex organic-inorganic hybrid materials using FIB-TOF-SIMS. To achieve this, we first investigated the FIB-induced damage on PC surface, and then found the appropriate conditions to remove the FIB-induced damaged layer with Ar-GCIB. We applied the investigation results to the analysis of organic-inorganic hybrid materials. As a result, the accurate chemical depth distributions of hybrid materials were successfully obtained. Based on this approach, the limitation of sputter depth profiling for 2D and 3D imaging of complicated organic-inorganic mixed structure is resolved.

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