Cross-Section Analysis of a Laminated Film by Dual FIB ToF-SIMS

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Three-dimensional microanalysis for a minute structure that consists of organic compounds and polymers is important to make progress and to practically use the method to analyze a micro-nanometer order area. We developed a novel three-dimensional microanalysis method by means of focused ion beams (FIB) for section processing (shave-off scanning) and ToF-SIMS for mapping method. In this study, in order to obtain three-dimensional sample image, we used a laminated film as a sample and examined two-dimensional ToF-SIMS mapping over the cross-section created by shave-off scanning. We could obtain ion map and ToF-Mass spectra of polymer samples. This result suggested that shave-off section processing can suppress the damage by primary ions.

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I. INTRODUCTION

Various composite materials such as high-performance resin and liquid crystal have been manufactured according to making progress on organic syntheses. And these materials are put into practice and have been in wide application to many products. For the characterization, molecular structure information and microanalysis for a minute structure are required. Especially three-dimensional microanalysis for minute structure that consists of organic compounds and polymer is difficult. But it is expected to be a more important field in the future. For microanalysis method, Auger electron spectroscopy (AES), electron-probe microanalysis (EPMA), etc. are used practically. But these methods can get only information that appears atomic composition and distribution on the sample surface. So it is difficult to analyze inside a sample and of a chemical structure such as molecular sequence and functional group that is important as organic information [1–3].

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) can determine the two-dimensional spatial distribution of chemical compounds in many materials and is now widely used for polymer surface characterization. ToF-SIMS gives not only the atomic information but also the fragment ions of the organic structure. We have developed Dual FIB ToF-SIMS for accurate three-dimensional analysis [4, 5]. For getting informative fragment ions, FIB dose is limited in order not to destroy surface structure completely by FIB (static limit). Shave-off scanning can create an arbitrary section on a sample effectively against composites with wide variety of shape. We can obtain three-dimensional sample image by operating two FIB alternately. In the preceding study, section of polymer (polystyrene) fabricated by shave-off processing was analyzed by ToF-SIMS. And by increasing shave-off processing time, flatter section was made up and a certain rate of polymer fragment peaks were detected [6].

In this study, for the purpose of realization of three-dimensional microanalysis and a chemical and structural analysis of the organic materials, we used a laminated film as a sample and examined two-dimensional ToF-SIMS mapping over the cross-section created by shave-off scanning.

II. EXPERIMENTAL

There were three experimental steps, that is, shave-off section processing by shave-off FIB in the first, and the processed section analysis by pulse FIB in the second. Then lastly we produced two-dimensional maps.

A. Sample preparation

In this study, we used biaxially-stretched nylon film (ONy) and biaxially-stretched polypropylene film (OPP) as a sample because we took food packaging films into account. Such laminated films are used for food packaging in many cases. The thicknesses were 15 μm and 20 μm, respectively. We laminated two films with glue. Adhesive material was alpha-cyanoacrylate. The laminated film one day after gluing was used for ToF-SIMS measurement.

B. ToF-SIMS analysis

ToF-SIMS analysis was performed using a Dual FIB ToF-SIMS instrument, the instrument has been also de-
This instrument has two Ga ion guns and ToF-Mass spectrometer. One ion gun (Ionoptika, IOG25) carries out section processing by shave-off scanning, and the other gun (Eiko Engineering, FI-1000) analyzes the section with ToF-SIMS. The scheme of Dual FIB ToF-SIMS analysis is depicted in Fig. 1.

Accelerating voltage of both shave-off scanning and ToF-SIMS analysis was 20 kV. Shave-off beam current was 9 nA. FIB dose area for shave-off scanning was 180 μm × 72 μm. In particular, the processing region of sample was about 90 μm × 72 μm. Positive secondary ions were collected from the sample. Typical primary beam current in ToF-SIMS analysis was 3 pA in the dc mode. Width of beam pulse was 40 ns. Pulse frequency was 5 kHz. And ToF-SIMS analyzing time was 540 s. At this condition, FIB dose density of $2.0 \times 10^{13}$ ions/cm$^2$ was applied to the samples. The m/z-scale was calibrated using the H$^+$ and Ga$^+$ ions.

### C. Two-dimensional ion mapping

Position of the laminated film sample was found by Secondary Electron Image (SEI). In this study, we analyze the region with size of 240 μm × 240 μm in the sample. In the first place, the edge of the sample was sputtered off. And then we examined the cross-section created by shave-off scanning and tried to obtain two-dimensional ToF-SIMS maps.

### III. RESULTS AND DISCUSSION

Figure 2 shows SE images (SEIs) and ion maps. Image (a) is the sample before shave-off scanning, which was observed from shave-off FIB. (b) is after shave-off scanning. The white enclosed area shown in (a) is sputtered area. Image (c) is also SEI, but it was observed from ToF-SIMS FIB (not pulsed). Cross-section on the sample was the top of edge (dark area). The created section shown in (c) was analyzed by ToF-SIMS. The acquired positive ion ToF-SIMS spectrum is shown in Fig. 3. In the m/z range up to 240, the major signals are due to the typical hydrocarbon ions from three kinds of polymer composing of the laminated film. The ions from OPP are at m/z 27, 29, 39, 41, 43, 55, 57, 69, 71, etc. and from ONy at m/z 30, 31, 41, 45, 55, 56, 69, 98, 100, 114, etc. In addition, (d) and (e) shown in Fig. 2 were two-dimensional ion maps. (d) is the total ion map, (e) is ion map of m/z 69. A large part of the signal at m/z 69 was from gallium ions of FIB. The signals around m/z 150 are thought to
be organic solvent of phthalate compounds contained in alpha-cyanoacrylate, or unrelated contamination of plastic plasticizer. These compounds are said to have very high sensitivity against SIMS analysis.

Total ion intensity is very low in the whole area of the cross-section. One possibility is to cause damage to the cross-section by shave-off processing. Table I shows the ion counts of each polymer at $m/z$ 69 and 71. Ion counts of “total” were detected from 240 $\mu$m $\times$ 240 $\mu$m area, and each polymer from 18 $\mu$m $\times$ 18 $\mu$m area. Shave-off FIB consists of the mixture of $^{69}$Ga and $^{71}$Ga, and pulse FIB consists of only $^{69}$Ga. Considering the abundance ratio of $^{69}$Ga and $^{71}$Ga, the $m/z$ 71 signals are very low as shown in Table I. And the processed section was dark in (e), the $m/z$ 69 ions were not obtained much from this area. Thus, the map suggests that shave-off section processing can suppress the damage by primary ions. Conversely, in Table I $m/z$ 71 signals at the total ion are much lower than $m/z$ 69 signals. The $m/z$ 69 signals were not only from gallium but also from OPP and ONy. In addition to this, implantation of primary ions is thought to be occurred. Thus, $m/z$ 69 signals were so strong.

Although the damage of the cross-section was suggested to be suppressed, ion counts from the cross-section were insufficient to produce the ion map. There is another possibility that OPP and ONy are originally polymer materials with low-sensitivity, or the second possibility is the effect of an insulating film (i.e. charge-up) on the total ion intensity and $m/z$ 69 signal intensity. Therefore discussion of cross-section by shave-off processing for more precise analysis is required.

As shown in Fig. 2(c), there is a line in the middle at the cross-section. This line is an alpha-cyanoacrylate layer. Lower-left side of this line is OPP, and the upper-right side of this line is ONy. Figure 4 shows the spectra
collected from two square areas shown Fig. 2(c) which corresponds to OPP and ONy cross-sections, respectively. Each square part covers 18 μm × 18 μm. The differences between OPP and ONy spectra can be found at the peaks from m/z 50 to m/z 60. While the ONy peaks were so weak, the stronger OPP peaks could be observed.

As a result, clear ion maps with characteristic signals of the materials were not observed from the cross-section. This indicates the necessity of increase of the sensitivity, particularly from the cross-section. Another possibility to improvement the maps may be introduction of multivariate analysis of mass spectra for more effective usage of the spectral information.

IV. CONCLUSION

We used a laminated film as a sample and examined two-dimensional ToF-SIMS mapping over the cross-section created by shave-off scanning. We could observe cross-section of the sample and ToF-Mass spectra and two-dimensional ion maps were obtained precisely. And in ion map, it is suggested that shave-off section processing can suppress the damage by primary ions. Because OPP and ONy peaks can be observed, ion maps of polymer sample will be obtained over the cross-section created by shave-off scanning.

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