

Metal-assisted SIMS for three-dimensional analysis using shave-off section processing

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Three-dimensional microanalysis of the microstructure of organic materials is important in the development and progress of analytical methods on the micro-to-nanometer scales. We have developed a novel three-dimensional microanalysis method using focused ion beams for section processing (shave-off scanning) and time-of-flight secondary ion mass spectrometry for mapping. Shave-off scanning can effectively create an arbitrary section on a sample set against composite materials with a wide variety of shapes; three-dimensional sample images are then obtained by alternately operating two focused ion beams. In this study, we adapted metal-assisted secondary ion mass spectrometry for three-dimensional microanalysis. We have devised a unique method whereby gold is deposited on a section to be analyzed after every shave-off sectioning by setting a gold plate at the back of the sample. Consequently, gold was observed to be deposited on the created cross-section concurrently with shave-off sectioning, resulting in a substantially enhanced secondary ion intensity. Copyright © 2014 John Wiley & Sons, Ltd.

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Introduction

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a method used to determine the two-dimensional spatial distribution of chemical compounds in many materials and is now widely applied for polymer surface characterization. The ToF-SIMS spectrum gives information not only on the elements but also on the ion fragments derived from the organic materials. We have developed a dual focused ion beam (FIB) ToF-SIMS technique for accurate three-dimensional analysis.^[1–3] In particular, we have developed a novel etching method, called 'shave-off sectioning' using a Ga⁺ FIB, which reduces beam-induced damage.^[4] Shave-off scanning can effectively create an arbitrary section on a sample positioned against a composite material with wide a variety of shapes allowing us to obtain a three-dimensional sample image by alternately operating two FIBs.

In a preceding study, a section of the polymer poly(4,4'-oxydiphenylene-pyromellitimide) fabricated by the shave-off method was analyzed by ToF-SIMS. Moreover, a flatter section could be obtained by increasing shave-off processing time, and a certain rate of polymer fragment peaks was detected.^[5] Furthermore, to realize the three-dimensional microanalysis and a chemical/structural analysis of organic materials, we used a laminated film as a sample and examined two-dimensional ToF-SIMS mapping over the cross-section created by the shave-off scanning technique. However, we did not obtain sufficient information from the created cross-section, as reflected in the ion image obtained.^[6] We therefore focused on metal-assisted SIMS (MetA-SIMS), which enables us to enhance the secondary ion yields of organic materials,^[7,8] an effect that can be attributed to the chemical interaction between the metal and sample. However, this method is difficult to be adapted to three-dimensional analysis because of the necessity for the deposition of metallic clusters on the sample surface for each analytical measurement.

Herein, we propose a unique method using MetA-SIMS toward the highly sensitive three-dimensional ToF-SIMS analysis of organic materials.

Experimental

Method

To execute the three-dimensional analysis of organic materials using MetA-SIMS, we devised a method in which gold is deposited on every shave-off section used for analysis by setting a gold (Au) plate at the back of the sample (Fig. 1).

In this study, a sample of poly(4,4'-oxydiphenylene-pyromellitimide) (PMDA-ODA) was prepared on a Au plate (about 1 × 1 cm²:0.2 mm t, distributed by Nilaco) and a portion of the edge was sputtered off by shave-off scanning. Au plate was sufficiently smooth and large compared with the viewing field. We examined this cross-section created by scanning by further analysis using ToF-SIMS. In addition to this, we also prepared the section whose upper section had been scanned additionally in order to deposit more Au on the created cross-section. Three types of samples, including a control, were measured. The control was shaved-off PMDA section without Au deposition.

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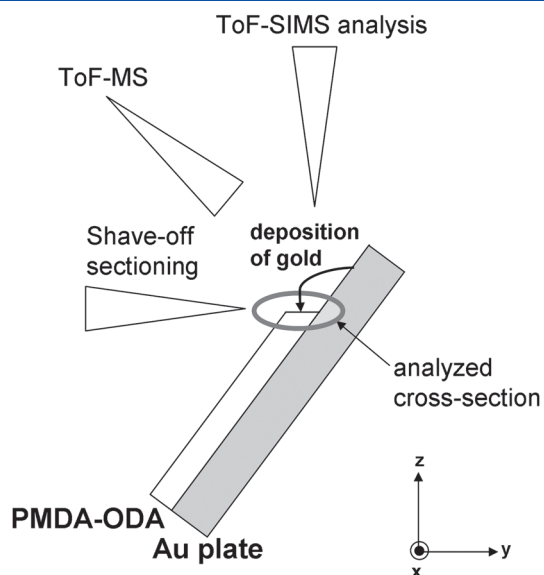


Figure 1. Schematic of three-dimensional microanalysis using metal-assisted secondary ion mass spectrometry and shave-off sectioning technique.

Shave-off cross-sectioning

Shave-off cross-sectioning was performed using an SMI3050SE apparatus (manufactured by SII Nanotechnology, now Hitachi High-Tech Science Corporation) at an accelerating voltage of 30 kV. The shave-off beam current was 10 nA, and the beam spot was 2 μm (empirical value by the apparatus).

Evaluation of Au deposition amount

Estimation of the amount of Au deposited after cross-sectioning were performed by X-ray photoelectron spectroscopy (XPS). XPS spectra were obtained using the PHI Quantera SXMTM instrument (ULVAC-PHI). The measurement data was relativized to eliminate the influences of measurement deviation. More specifically, relative values were obtained by comparison of Au and carbon 1 s peak intensities in the XPS spectra.

Measurements by time-of-flight secondary ion mass spectrometry

Time-of-flight secondary ion mass spectrometry cross-sectional measurements were performed to confirm whether the deposited Au would function in Meta-SIMS analyses. ToF-SIMS analysis was performed with a dual FIB ToF-SIMS instrument. Mass spectra were acquired using $^{69}\text{Ga}^+$ ion pulses at an impact energy of 20 keV, ion current of 1 nA in the dc mode, pulse width of 40 ns, and pulse frequency of 5 kHz. In this study, copper plates were placed on the both sides of the sample for the purpose of electric conduction, and then we analyzed the region with size of $320 \times 320 \mu\text{m}^2$ including the sample. Mass spectra were drawn by extracting the data from only the sample. The extracted area for additional scanning upper section was about $35 \times 116 \mu\text{m}^2$, and almost the same area for the rest of samples. Total ion doses in these measurements were below the static limit. Positive secondary ions were collected from the sample. The m/z scale was calibrated using H^+ and Na^+ ions.

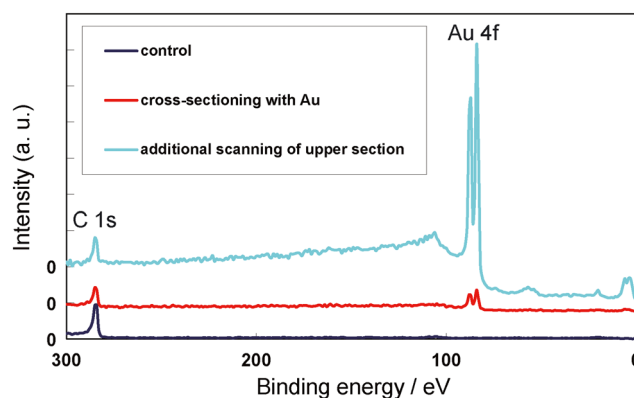


Figure 2. X-ray photoelectron spectroscopy spectra of cross-sections for each measurement (wide spectra).

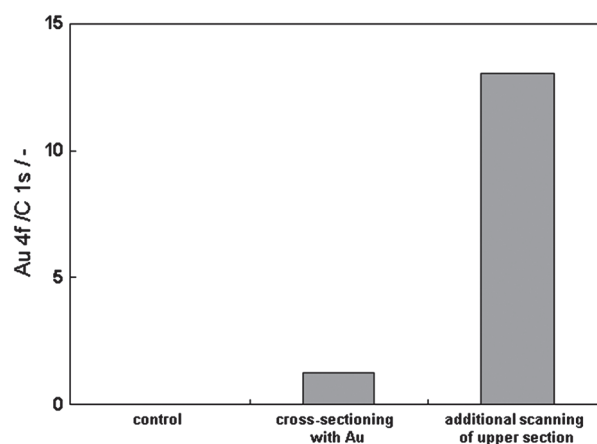


Figure 3. Comparison of Au deposition amounts for each cross-section.

Results and discussion

X-ray photoelectron spectroscopy spectra

Figure 2 shows the XPS spectra of cross-section under each condition: a control, the cross-section obtained by setting a gold plate at the back of the sample (cross-sectioning with Au plate), and additional scanning of the upper section after shave-off sectioning. These results verified the deposition of Au onto the sample cross-section from the back Au plate. Further scanning of the upper section showed an increase in the intensity of deposited Au by as much as ten times as compared with only cross-sectioning with the Au plate. Figure 3 shows a comparison of Au intensity after each measurement. The Au relative intensity was obtained by dividing the Au 4f peak area by the C 1 s peak area. Average film thickness was calculated from photoionization cross-section, density and XPS Au 4f and C 1 s intensity ratio, assuming the mean free paths for both photoelectrons were almost the same. Average film thickness of cross-sectioning with Au and additional scanning of upper section estimated to be 0.12 and 0.96 nm, respectively. As indicated in Fig. 2, C 1 s peak could be seen. It was indicated that real Au deposition was not homogeneous, but island growth. In addition, deposited Au is considered to make three-dimensional nanostructure according to the Volmer-Weber growth mechanism^[9] As stated previously, cross-sectioning

with the Au plate was performed, and gold was deposited onto the analyzed sections with every sectioning event. Furthermore, increased scanning of the upper section enabled an increase in Au deposition.

Ion yield enhancement

The acquired positive ion ToF-SIMS spectra are shown in Fig. 4(a)–(c), which depict control, cross-sectioning only with the Au plate, and additional scanning of the upper section, respectively. The expanded figures of each spectrum are depicted in the upper right of each spectrum. Except for the control measurement (Fig. 4(a)), the major signals in the m/z range up to 69 were attributed to the typical hydrocarbon ions from PMDA-ODA. Two strong peaks at $m/z=63$ and 65 were Cu^+ derived from copper plate for electric conduction. It is obvious that the secondary ion intensity of the cross-section with deposited metallic clusters was enhanced substantially compared with the untreated one. On

the other hand, although there was not small Au deposition amount, the secondary ion intensity of additional scanning measurements was as much as that of only sectioning with the Au plate, especially over $m/z=70$ indicating that cross-sectioning measurements with the Au plate reached a limit in the enhancement of secondary ion intensity. Moreover, the facts supported that Au deposition was island growth. Previous reports have described experimental results in which secondary ion intensity was increased after Au deposition up to a film thickness of 8 nm; when the deposited film thickness was increased over 8 nm, the intensity was constant or decreased.^[10] Therefore, in this study, the limiting value of Au concentration on the surface, which is comparable with a thickness of 8 nm, was achieved or exceeded during shave-off cross-sectioning. MetA-SIMS analysis could be put into practice simply by shave-off cross-sectioning with the Au plate. The method enables us to conduct MetA-SIMS very easily, because Au is deposited at the place where sectioning, at the time of sectioning.

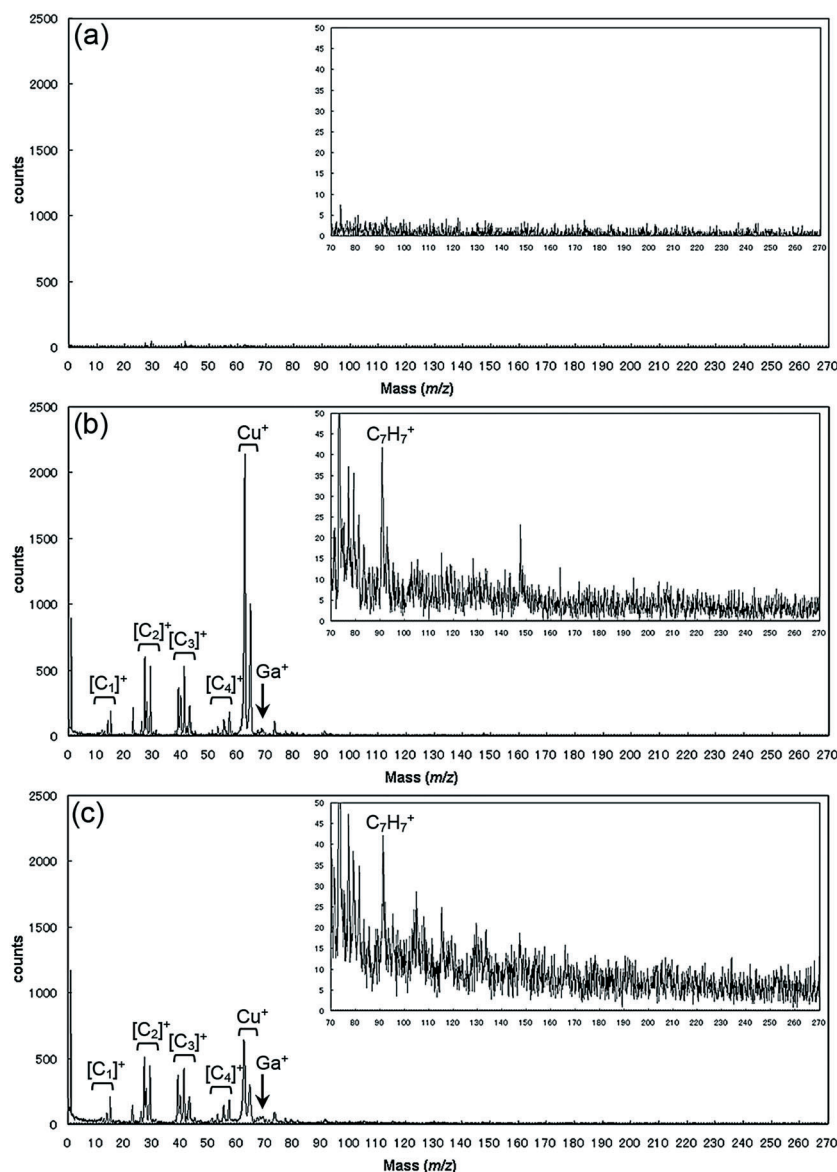


Figure 4. Positive ion Time-of-flight secondary ion mass spectrometry spectra: (a) control, (b) cross-sectioning with Au plate only, and (c) additional scanning of the upper section.

Conclusion

We have demonstrated a unique method applying both MetA-SIMS and shave-off sectioning (3D MetA-SIMS), for the highly sensitive three-dimensional microanalysis of a PMDA-ODA polymer, in which gold was deposited on the section to be analyzed after each shave-off sectioning by setting a gold plate at the back of the sample. Consequently, Au was deposited on the cross-section created by shave-off sectioning, resulting in a substantial enhancement in secondary ion intensity from the cross-section. These results suggest that this method combining MetA-SIMS, and shave-off sectioning is very effective for the three-dimensional microanalysis of organic materials.

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