Simulation of Secondary Ion Position on the Detector for Three-dimensional Shave-off Method

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The concept of three-dimensional (3D) shave-off secondary ion mass spectrometry (SIMS) is that enables to obtain the depth information of the sample simultaneously with the mass information using the vertical axis of a two-dimensional position-sensitive detector in the mass analyzer. In this study, we simulated the trajectory of secondary ions sputtered from a virtual sample in the 3D shave-off SIMS system and investigated the magnification ratio of the ions. The simulation results showed that we could distinguish the depth position of the secondary ions sputtered from a sample by the detected position in our concept of 3D shave-off SIMS.

Keywords Shave-off; Secondary ion mass spectrometry; Monte Carlo simulation; Secondary ion trajectory

I. INTRODUCTION

Secondary ion mass spectrometry (SIMS) is a useful surface analysis technique having high sensitivity as well as a high spatial resolution. The shave-off method had been proposed to analyze quantitatively uneven samples with a multichannel parallel detection system in the SIMS [1]. The shave-off depth profiling has enabled to analyze the various materials and devices [2–4] and was developed to obtain two-dimensional data with high resolution [5]. Recently, our group designed a new concept of three-dimensional (3D) shave-off SIMS introducing the magnification lens system. Unlike conventional 3D SIMS obtained by combining two-dimensional data and images along surface erosion, the 3D shave-off system could obtain the depth and mass information of the sample simultaneously with surface erosion. Therefore, this system enables to reduce the time of analysis as well as overcome a drawback in topographical information of SIMS imaging. It will be useful to analyze 3D internal structure and element distribution of a complex structure such as Li transition metal oxide. In general, Characterization of the elemental distribution, chemical composition, and structure in Li-ion battery cathode materials consisting of several micro-sized spherical particles is very important in relation to battery performance and degradation. Mapping of the materials has been required a variety of techniques such as energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), focused ion beam and scanning electron microscopy (FIB-SEM), time-of-flight secondary ion mass spectrometry (ToF-SIMS), etc. due to their respective drawbacks. However, the new 3D shave-off SIMS system would be able to quickly analyze the distribution of particles as well as the 3D structure of electrodes independently.

Through the previous studies, the introduced magnification lens system had verified that the secondary ions were enlarged only in the depth direction (Z axis) and converged on the Mattuach-Herzog type mass analyzer in the SIMS [6]. As the simulation results, the secondary ions sputtered from a micrometer-sized sample were magnified to a millimeter size at the detector and had 1.4 μm of the Z-axial resolution [7].

In this study, we had conducted to simulate the trajectory of the secondary ions in the 3D shave-off SIMS system...
using several simulations before fabricating a prototype of the system. The simulation observed the trajectories of the secondary ions from the sputtering process to convergence to the mass detector. The secondary ions were assumed to be sputtered from a virtual sample composed of two elements by the focused ion beam. The simulation was performed using the SDTrimSP code (Static and Dynamic Trim for Sequential and Parallel computer, version 5.07) [8] and the SIMION program (version 8.1) [9]. One of the binary collision approximation codes, SDTrimSP, was used to estimate the sputtering yield and calculate values about the ion bombardment by the focused ion beam. The SIMION program was used to simulate the trajectory of ions in the 3D shave-off SIMS system.

II. SIMULATION MODEL

A. Sample

The simulation was conducted with a virtual sample composed of two elements. One of the elements was silicon (Si), and the other was germanium (Ge). Figure 1(a) illustrates a schematic diagram of the simulation sample. The sample was a combination of 27 voxels; 22 voxels of Si and 5 voxels of Ge. Each voxel was 2 μm wide in all lateral dimensions. To investigate the detected position of secondary ions according to their sputtering position, 9 points (from P1 to P9) were designated to the sputtering position on the sample, as shown in Figure 1(b). Each point was determined by the type of the elements and the depth of the sample.

B. Procedure of the simulation

Three information (parameters) of the sputtered particles, sputtered position from the sample, initial energy, and emission angles were required to simulate the trajectories of the secondary ions in the 3D shave-off SIMS. Figure 2 depicts the three steps of this simulation for the required parameters.

Firstly, the erosion process of the sample by the focused ion beam (current: 260 pA, diameter: 147 nm) with the shave-off method (the X-axis interval length: 10 nm, the Y-axis interval length: 1.68 nm) was calculated by the erosion equation [10, 11]. The sputtering yield as a function of the ion incidence angle for the 30 keV Ga ion irradiation of Ge and Si has followed the data measured by the SDTrimSP shown in Figure 3. The angle of incidence was measured at each designated sputtering position (P1−P9), and then the values were used as the input parameters to the next step. In the second step, the initial energy and emission angle of the sputtered particles were obtained by the SDTrimSP code. The sputtered particles generated by the 30 keV Ga+ ions of 107 irradiation on the sample.

Subsequently, the obtained information for sputtering particles with energy of less than 10 eV was provided as input values to the SIMION program for calculation of the ion trajectories. On average that the particles having an energy under 10 eV accounted for 48% of total sputtering particles.

The design and setting of the 3D shave-off SIMS system in the SIMION program are shown in Figure 4. The workbench of the 3D shave-off SIMS system was described in more detail on previous studies [6, 7].
III. RESULTS

In 3D shave-off SIMS, the depth information of the secondary ions would be obtained as a vertical axis position of the microchannel plate (MCP) detector in the mass spectrometry. Figure 5 presents the cross-sectional shape of the sample (upper) and the position of sputtered secondary ions on the detector (lower) after (a) once, (b) 8 times, (c) 14 times, and (d) 20 times of line scanning (a step of the Y-axis scanning). The sample was totally removed by the beam after 3571 of line scanning. After 20 times of line scanning, the cross-sectional shape of the sample and the angle of incidence were similar regardless of the element. It is due to having a similar sputtering yield of the Ge and Si when the angle of incidence is over 80°, as shown in Figure 3. The shave-off method always has a high angle of incidence over 80° as a result of using only the side of the beam to shave the edge of the sample [12–15]. Therefore, the sample shows a difference in the erosion depth between Ge and Si at the start of the scan, however, when the steady-state of the shave-off scanning with a high angle of incidence of the over 80°, the difference of them would decrease, and then eventually it would show the same erosion depth.

The dotted lines in the scatterplot of Figure 5 show the intensity of the secondary ions within the detected range. The secondary ions appeared in the inverse direction of the sample at the detector. The sputtered ions from the upper side of the sample (P1, P2, P3, and P4) were detected at the bottom of the detector (negative values of \(Z_{\text{detector}}\)), and the ions sputtered from the bottom of the sample (P5, P6, P7, P8, and P9) appeared at the upper part of the detector (positive values of \(Z_{\text{detector}}\)). This inverse direction was caused by the electric field effects inside of the 3D shave-off SIMS system.

![Figure 4: Workbench of the 3D shave-off SIMS system in the SIMION program.](image)

![Figure 5: Position on the detector of secondary ions sputtered from each point (P1–P9) of the sample after (a) once, (b) 8 times, (c) 14 times, and (d) 20 times of the line scanning (a step of Y-axis scanning).](image)
Figure 6 presents the Z-axis positions of secondary ions of Ge (a) and Si (b) on the detector according to the depth of the sputtering position after 20-line scanning. The secondary ions of Ge were sputtered from the positions of P1, P3, P7, and P8, which were positioned at 0, 2, 4, and 6 μm from the top of the sample, respectively. The Si ions were sputtered from the positions of P2, P4, P5 (P6), and P9, which were positioned at 0, 2, 4, and 6 μm from the sample surface, respectively. Table 1 summarizes the Z-axis position of the P1–P9 distributions of Figure 6. When the sputtering position of the secondary ions was lowered by 2 μm from the top of the sample, the peak position of the distribution was increased by about 0.4 mm for Ge and 0.2 mm for Si. Blue dash lines in Figure 6 show least-squares fitting of each distribution peak. From this result, we could know the magnification ratio of each element in 3D shave-off SIMS.

In addition, the two elements (Ge, Si) had a difference in the length of the dispersion on the detector. The average lengths of the distribution of the secondary ions were about 1 mm for Ge ions and 0.7 mm for Si ions. It is due to the difference in the mass-to-charge ratio, and Ge has a larger magnification with a longer flight path than Si.

IV. CONCLUSIONS

The concept of 3D shave-off SIMS has been developed to obtain the sample depth information with the secondary ion mass spectra. Prior to installation of the system, the trajectories of the secondary ions from sputtering to detecting were simulated using some simulation programs. The simulation conducted with a virtual sample composed of Ge and Si. The secondary ions of Ge and Si sputtered with a difference in depth of the sample of about 1 μm showed 0.2 mm (magnification: 200 times) and 0.1 mm (100 times) of the difference on the detector. The depth position of the secondary ions sputtered from the sample was distinguished on the mass detector by the peak of the secondary ion intensity distribution. In this study, we confirmed that the 3D shave-off SIMS system could obtain the depth position of the sample. Although the distribution of the secondary ions was still broad and there were overlap parts, it will be expected to improve by several methods such as optimizing the lens systems, introducing an energy filter and an alignment system. When the problems would be the complement, 3D shave-off SIMS is expected as a new method of SIMS to provide the 3D compositional data with a high axial resolution of the sample and a reduction of shape effects.

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| Point | Element | Max. | Min. | Length | Peak of distribution |
|-------|---------|------|------|--------|----------------------|
| P1    | Ge      | 0.03 | −1.24| 1.27   | −0.6                 |
| P2    | Si      | −0.02| −0.75| 0.73   | −0.3                 |
| P3    | Ge      | 0.38 | −0.69| 1.07   | −0.2                 |
| P4    | Si      | 0.19 | −0.5 | 0.69   | −0.1                 |
| P5    | Si      | 0.34 | −0.21| 0.55   | 0.1                  |
| P6    | Si      | 0.34 | −0.21| 0.55   | 0.1                  |
| P7    | Ge      | 0.72 | −0.32| 1.04   | 0.2                  |
| P8    | Ge      | 1.04 | 0     | 1.04   | 0.6                  |
| P9    | Si      | 0.82 | 0.04 | 0.78   | 0.4                  |
References

[1] H. Satoh, M. Owari, and Y. Nihei, J. Vac. Sci. Technol. B 6, 915 (1988).
[2] M. Nojima, B. Tomiyasu, Y. Kanda, M. Owari, and Y. Nihei, Appl. Surf. Sci. 203, 194 (2003).
[3] M. Fujii, Y. Ishizaki, M. Nojima, M. Owari, and Y. Nihei, Nucl. Instrum. Methods Phys. Res. B 267, 660 (2009).
[4] T. Sakamoto, K. Shibata, K. Takanashi, M. Owari, and Y. Nihei, e-J. Surf. Sci. Nanotechnol. 2, 45 (2004).
[5] D. Shirakura, B. Tomiyasu, and M. Owari, e-J. Surf. Sci. Nanotechnol. 14, 179 (2016).
[6] Y. Takagi, S.-H. Kang, K. Matsumura, T. Azuma, B. Tomiyasu, and M. Owari, e-J. Surf. Sci. Nanotechnol. 16, 324 (2018).
[7] K. Matsumura, S.-H. Kang, B. Tomiyasu, and M. Owari, J. Surf. Anal. 25, 172 (2019).
[8] A. Mutzke, R. Schneider, W. Eckstein, and R. Dohmen, SDTrimsP Version 5.00, IPP-Report 12/8 (Max-Planck-Institut für Plasmaphysik, Garching, 2011).
[9] https://simion.com
[10] D. Santamore, K. Edinger, J. Orloff, and J. Melngailis, J. Vac. Sci. Technol. B 15, 2346 (1997).
[11] T. Ishitani, K. Umemura, T. Ohnishi, T. Yaguchi, and T. Kamin, J. Electron Microsc. 53, 443 (2004).
[12] S.-H. Kang, K. Matsumura, T. Azuma, B. Tomiyasu, and M. Owari, J. Surf. Anal. 25, 165 (2019).
[13] S.-H. Kang, Y. Kim, B. Tomiyasu, and M. Owari, e-J. Surf. Sci. Nanotechnol. 16, 214 (2018).
[14] S.-H. Kang, M. Furushima, H. Asakura, A. Habib, Y. Kim, B. Tomiyasu, and M. Owari, J. Surf. Anal. 24, 164 (2017).
[15] S.-H. Kang, A study on the focused ion beam sputtering for the development of 3D shave-off SIMS, Ph.D. Thesis, The University of Tokyo, 2019.

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