Supporting Information for "High Resolution Multi-Modal Chemical Imaging Platform for Organics and Inorganics"

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Spatial resolution of the HIM-SIMS using the BAM-L200 sample

In Fig. 1a, we show a chemical image of the BAM-L200 reference sample material to evaluate spatial resolution of the HIM-SIMS. In the chemical image, the peaks of each period grating were analyzed through the Gaussian peak fitting using Origin Pro Version 8.0, as shown in Fig. S1.



Figure S1. Gaussian peak fitting results for chemical imaging signals of the BAM-L200 reference sample to estimate spatial resolution of the HIM-SIMS for period grating of (a) 76.5 nm, (b) 57 nm, (c) 42 nm, (d) 31 nm, (e) 23 nm, (f) 17.5 nm and (g) the stripe width of 3.5 nm.

Results of the electrode depth profiling (chemical and topography images)

Figure S2 shows the depth profiling result of Fig. 1b in a linear scale of y-axis. Figure S3 shows chemical and surface topography images measured for depth profiling of a gold electrode with a titanium adhesion layer on a SiO₂/Si substrate. Three detectors were used to collect the chemical images of m/z~28 for silicon (Fig. S3(a)), 48 for titanium (Fig. S3(b)) and 197 for gold (Fig. S3(c)). Silicon and titanium have the overlapped signals from hydrocarbon contamination, and thus, weak signals at the top surface of the

electrode were measured. By increasing the number of scans, the signals of $m/z \sim 28$ and 48 decreased since the hydrocarbon contaminants were removed by neon ion milling. At the same time, the gold signal at $m/z \sim 197$ decreased and at the 5th scan, the titanium signal appeared locally due to the spatial variation of a sputtering rate of gold, as seen in the topography images in Fig. S3(d). The root-mean-square (rms) roughness of the sputtered area increases upon the consecutive sputtering as shown in Fig. S4(a). An initial rms roughness of the gold electrode was measured 0.6 ± 0.07 nm, but after the 1st scan, the surface roughness increases to 2.1±0.2 nm with the sputtered depth of 11.8±1.7 nm. Continuing sputtering of the electrode resulted in the increase of the surface roughness to 7.8±1.3 nm (64±5.0 nm) at the 5th scan. Since the sputtering yield of gold is larger than titanium, more gold was sputtered out rather than titanium which finally reduced the surface roughness and the overall sputtering rate (slope of the plot in Fig. S4(b)) after the 5th scan. After the 9th scan, the silicon signals started to be measured at the depth of 82±5.0 nm with the surface roughness of 5.5±1.6 nm. After the most of gold was removed, the sputtering rate remained constant and the surface roughness again increased upon sputtering since the sputtering yields of silicon oxide and titanium are similar and thus, the neon beam conditions (dwell time and pixel spacing) dominates the surface roughness. At the 12th scan, both of titanium and silicon signals were significantly enhanced which resulted from the matrix effect by the pronounced amounts of oxygen from the SiO₂ substrate. After the oxide layer was removed, the signal intensities dropped which can be seen in the chemical images at the 16th scan, but still we can measure the distribution of titanium and silicon at the depth of 107.6±5.6 nm after the 21st scan.



Figure S2. Depth profiling of the gold electrode with a titanium adhesion layer on the SiO_2/Si substrate with a linear scale of y-axis.



Figure S3. Change of the chemical images of (a) Si⁺ ($m/z\sim28$), (b) Ti⁺ ($m/z\sim48$) and Au⁺ ($m/z\sim197$) with (d) the corresponding topography images measured using the AFM by increasing the number of scans equivalent to the increase of total exposure time (52.4 s/scan). While that of gold chemical images was fixed as 0~1250 cps, the color bar scale (unit of counts per second) for silicon and titanium was varied to observe the change of chemical images more clearly: 0~1250 cps from the 1st scan to the 7th scan, 0~2500 cps for the 9th scan and the 21st scan, 0~10000 cps for the 12th scan and 0~7500 cps for the 16th scan. The color bar scale for topography images is from 0 to 20 nm. The scale bar of all the images is 1 µm.



Figure S4. (a) Change of surface roughness (rms values) along the depths, and (b) the change of the depth depending on the number of scans corresponding to the total exposure time (ion doses).

Chemical imaging of metal-epoxy interfaces

In chemical analysis of metal surfaces, wrong chemical information can be given due to a surface contamination such as sodium, potassium and omnipresent organic molecules. It is clearly verified through chemical imaging of metal surfaces using the HIM-SIMS, which allows *in-situ* material processing in order to provide accurate chemical information.



Figure S5. Mass spectrum of an epoxy sample showing the representative peaks of an epoxy sample under $m/z\sim100$ in a positive ion mode.

Titanium-epoxy interface

Figure S6(a) shows the removal of surface contamination by *in-situ* milling for 40 min to enhance the intensity of titanium peaks. Mass spectra were collected over the area of a titanium side, not including epoxy. After milling, the isotope ratios were improved closer to those of naturally occurring titanium. The removal of surface contamination in order to have accurate chemical information is visually demonstrated in chemical imaging of a titanium-epoxy interface with Ti⁺ (m/z~48) mapping. Chemical imaging was conducted consecutively, which also removes surface contaminations, and thus, the titanium signal becomes more prominent showing a very sharp interface, as depicted in Figure S6(b). The chemical imaging was done on the 5 µm × 5 µm area (1024 × 1024 pixels) with 25 keV Ne⁺ beam and a current of 50 pA. The last image in Figure S6(b) was obtained after a total milling for 22 min.



Figure S6 (a) Improved mass spectrum of a titanium after milling for 40 min and (b) chemical images (⁴⁸Ti⁺ mapping) of a titanium-epoxy interface upon consecutive imaging, inducing *in-situ* milling of surface contaminations, which made the interface far more apparent.

Copper-epoxy interface

Figure S7 shows chemical images of a copper-epoxy interface along with a HIM SE surface topography image. Sodium (m/z~23) and copper (m/z~63) were mapped over the interface surface. Sodium (surface contamination) distribution in Figure S7(b) was clearly identified and proven to be non-uniform over the studied surface, which could not be observed through SE signals (Figure S7(a)) due to the very thin nature of the sodium contamination. At the same time, a clear copper-epoxy interface image was obtained through a copper mapping, as shown in Figure S7(c). The chemical imaging was conducted over the 15 μ m × 15 μ m area (1024 × 1024 pixels) using a 25 keV Ne⁺ beam and a current of 3.5 pA. Figure S7(d) shows mass spectra of copper surface before and after removal of the surface contaminations. Isotopes of the copper (m/z~63 and 65) can be clearly observed in the spectra, which ratio was reduced from 2.51 to 2.27 after removing surface contaminations (milling for 40 min). This highlights the capability of the HIM-SIMS platform to provide an accurate chemical information by *in-situ* milling of surface contamination.



Figure S7 (a) SE topography image of a copper-epoxy interface showing no trace of surface contamination which was, however, revealed through the HIM-SIMS with (b) chemical mapping of sodium ($m/z\sim23$) providing its detailed spatial distribution, (c) chemical mapping of copper ($m/z\sim63$) showing a clear interface with epoxy, and (d) mass spectra of a copper surface before and after milling for 40 min.

Iron-epoxy interface

An iron-epoxy interface was analyzed first by collecting mass spectra before and after *in-situ* milling within areas of 7 μ m × 7 μ m and 1 μ m × 1 μ m, respectively, as shown in Fig. S8(a). The scanning area was zoomed into a smaller window to speed up milling of contamination. Four stable isotopes of iron can be clearly identified at *m/z*~54, 56 (primary), 57 and 58. Isotope ratios are summarized in the tables inserted in Fig. S8(a). Significant reduction of the intensity of the surface contaminations was achieved after milling for 35 min, which also significantly improved isotope ratios. An abnormally high isotope ratio of ⁵⁷Fe against 2.12% of a naturally occurring ⁵⁷Fe is due to the presence of epoxy in the analysis area (an overlapping peak of C₄H₉⁺). Figures S8(b) and S8(c) show chemical images of sodium (*m/z*~23) and iron (*m/z*~56) with SE topography image before and after milling for 15 min. Sodium distribution can be identified through chemical imaging, although, it cannot be imaged in the SE topography image. High intensity of iron can be due to iron particles and rough surfaces which can be seen in the SE image. After milling, sodium was totally removed, and the iron surface was flattened, showing an apparent interface with epoxy.



Figure S8. (a) Mass spectra of an iron-epoxy interface showing significant contamination before milling, which leads to relatively weak intensities of iron peaks with wrong isotope ratios. After milling for 35 min, iron peaks become more prominent due to the removal of surface contaminations, providing more accurate isotope ratios. Surface topography images and chemical mapping of sodium and iron (b) before and (c) after milling.

Mass resolution of the HIM-SIMS over various elements and molecular fragments

Using the spectra obtained in this study, we estimated mass resolutions $(m/\Delta m)$ depending on elements and molecular fragments as plotted in Figure S9. It shows the trend that the mass resolution for elements is almost 200 more or less, regardless of mass, except for iron $(m/\Delta m \sim 330)$. Mass resolution of hydrocarbon molecular fragments from the epoxy sample increases with mass, showing higher mass resolution than a similar mass of elemental ions. It may be due to a larger size of molecular fragments which results in their more directional flow induced by a magnetic field. Elemental ions are more prone to the Brownian motion dominance which can lead to scattering of ions and broaden a peak. The highest resolution in this study was 420 for an organosiloxane peak ($m/z\sim147$).



Figure S9. Mass spectral resolution of the HIM-SIMS for the peaks of various elemental ions and molecular fragment ions.

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