Recent Advances in SIMS
Room Great Lakes C - Session RA-WeM2
Cluster and Novel Ion Sources

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8:40am **RA-WeM2-1 Study of Mixed-gas Cluster Ion Beam for TOF SIMS***, Myoung Choul Choi,* Korea Basic Science Institute, Republic of Korea

Time-of-Flight Secondary ion mass spectrometry (ToF-SIMS) offers new possibilities for surface analysis of various organic samples such as materials science, material defect analysis, semiconductor analysis, and biological analysis. Advances in ToF-SIMS are based on developing novel first-order cluster ion beams for molecular analysis. Au3+ and Bi3+ cluster ions increased the secondary ion yield of high-mass molecular samples by 100-1000 fold compared with conventional atomic ion beams [1]. In particular, Ar cluster ion beams are being studied for both sputtering and analysis.[2] Despite several advantages of Ar gas clusters, the secondary ion yield of molecules sputtered by GCIB decreases with increasing cluster size. In addition, although there is a problem in that spatial resolution is low due to a relatively large beam size compared to a liquid metal ion beam, improvement of the gas cluster ion beam to minimize sample damage in the primary ion beam analysis has been continuously required. Recently, although the Ar mixed gas and CO2 have improved, the change in the characteristics of the cluster ion beam concerning the Ar and CO2 mixing ratio has not been studied in detail. If the gas cluster ion beam can be controlled by the ratio of the gas mixture, more effective cluster ion beam improvement will be possible.

Over the past few years, the Korea Basic Science Institute (KBSI) has been developing cluster ion guns and ToF-SIMS for three-dimensional (3D) mass imaging analysis of organic materials and bio samples [3].

In this study, the characteristic change of the cluster ion beam according to the ratio of Ar and CO2 mixed gas was measured.[4] Also, to improve the ToF-SIMS analysis, we propose the Ar and CO2 mixed gas ratio of the GCIB source. This mixed gas method can improve the efficiency of secondary ions and increase spatial and depth resolution compared to pure Ar gas.

Reference

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9:00am **RA-WeM2-3 Properties of Vacuum Electrospray Droplet Ion Beams Produced by Capillaries with Different Inner Diameters***, Satoshi Ninomiya, S. Tsuneki,* University of Yamanashi, Japan*; L. Chen,* University of Yamanashi, Malaysia*; K. Hiraoka,* University of Yamanashi, Japan

We have been studying a vacuum electrospray droplet ion (V-EDI) beam gun as a new massive cluster ion beam for secondary ion mass spectrometry (SIMS). In the previous studies, the V-EDI gun was installed in a time-of-flight SIMS (TOF-SIMS) system, and the secondary ion spectra produced by the V-EDI beams were measured for several biomolecular samples[1-3]. The fragment ion generation was strongly suppressed and the protonated intact molecules were observed with high intensities. However, the basic characteristics of the V-EDI beams are not enough revealed. In this study, the properties of V-EDI beams produced by capillaries with different inner diameters will be investigated.

The moderately focused (~0.5 mm) V-EDI beams which were generated by vacuum electrospray of a 0.01 M trifluoroacetic acid aqueous ethanol solution (water/ethanol=4:1) were raster-scanned over an area of typically 4.5x4.0 mm^2 at a scan speed of 0.1 Hz for short (300~1000 s) or long (2000~50000 s) time. For sputtering yield evaluation, primary 8 kV V-EDI beams produced from capillaries with different inner diameters (5, 10 and 15 µm) were irradiated uniformly on polymer or plasticizer film (~100 nm) samples prepared by spin-coating. The irradiated samples were analyzed with atomic force microscopy (AFM) and spectroscopic ellipsometry. The microscopic images of the films irradiated for short periods were observed with AFM, and the sputtering volumes per primary ion were calculated from the diameter and depth of the impact crater. The thicknesses of the films irradiated for long periods were observed with spectroscopic ellipsometry, and the sputtering volumes per primary ion were calculated from the difference in film thickness between irradiated area and non-irradiated area.

The sputtering volume per primary ion depended strongly on the inner diameter of each capillary. The sputtering volumes of the V-EDI beam generated by the capillary with an inner diameter of 5 µm were smaller than those by other capillaries (i.d. 10 and 15 µm). The differences in sputtering volume are assumed to be originated from the droplet ion size included in the V-EDI beams obtained from capillaries with different inner diameters.

References

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9:20am **RA-WeM2-5 Effects of Reactive Gas Cluster Ion Beams on Yields and Matrix Effects in SIMS***, Matija Lagator, I. Berrueta Razo ,* The University of Manchester, UK*; N. Lockyer,* University of Manchester, UK

Two of the greatest challenges in SIMS research are low ionization yields and matrix effects. Polyatomic water beams demonstrate that primary ion beam chemistry can increase yields while reducing matrix effects. We report a study demonstrating that carrier gas chemistry alters the SIMS characteristics of water cluster beam. The study aims to test if carbon dioxide reacts with water clusters thus increasing the likelihood of clusters acting as proton donors.

By applying water clusters with a reactive (CO_2 containing) carrier gas to drug standards we were able to measure the effect on the secondary ion yield. We show that compared to an inert (Ar) carrier gas, the yield observed with reactive water clusters is up to 50 times higher (Figure 1). This implies a change in primary cluster composition as a result of using a reactive carrier gas.

Matrix affects arise from the often unpredictable interaction of surface species which results in an ionization suppression/enhancement effect. Complex sample environments present a greater obstacle due to a myriad of potential chemical interactions. We show that by applying the newly developed chemically reactive water cluster beam, it is possible to reduce the matrix effects achieving a higher level of quantification over a range of drug concentrations (Fig. 2).

Together these observations indicate a novel methodology promoting the application of SIMS in a more sensitive and more quantitative manner to complex samples.

9:40am **RA-WeM2-7 Development of a High Throughput Microscope-Mode Secondary Ion Imaging Mass Spectrometer***, Maria Elena Castellani, N. Smith, Y. Jia, M. Burt,* Oxford University, UK*; J. Bunch,* National Physical Laboratory, U.K.*; Z. Takats,* Imperial College London, UK*; M. Brouard,* Oxford University, UK*; F. Green,* Rosalind Franklin Institute, UK

Secondary ion mass spectrometry (SIMS) is a surface analysis mass spectrometric technique that analyses solid samples by collecting the secondary ions produced by impact between the sample and a primary ion beam. When using stigmatic optics and a position-sensitive detector, microscope mode SIMS imaging can acquire spatially resolved images with high speed and throughput.

We hereby describe the conceptualisation, development and testing of a high-throughput microscope-mode SIMS imaging instrument that combines a highly defocussed microprobe mode SIMS C_{60} primary ion beam with novel extraction optics, pulsed extraction of the secondary ions, and a multichannel-plate/phosphor screen assembly. Exploiting a Pixel Imaging Mass Spectrometry (PImMS) camera, we recorded the spatially resolved mass spectrum images in seconds.

Mass and spatial resolution were tested through metal grid samples, comparing the findings with previous ones obtained with another microscope-mode imaging mass spectrometer. Hence, microscope-mode

SIMS imaging appears as a promising technique for the rapid simultaneous analysis of multiple composite samples.

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