Fundamentals
Room Great Lakes Promenade & A1 - Session FM-TuP
Fundamentals Poster Session

FM-TuP-1 To Fix or Not Fix Biofilms to Study Microbial Soil Aggregation, *Y. Zhang,* Huazhong Agricultural University, China*; J. Son,* Pacific Northwest National Laboratory*;* ***Xiao-Ying Yu,*** Oak Ridge National Laboratory

Bacterial biofilms are a main player in organic processing and soil aggregation. Characterization and understanding of the biofilm interactions with soil components is important to improve our knowledge in the biosphere and rhizosphere. We present two approaches to prepare biofilms suitable for high resolution mass spectral imaging using time-of-flight secondary ion mass spectrometry (ToF-SIMS). *Shewanella* MR-1 was used as the model bacteria biofilm due to their known traits in soil chemistry and microbiology. A mixture of silica, alumina, and iron oxide was used as the model soil system.

First, we took a static approach. The bacteria were inoculated in a multi-well cell culture dish at their log phase. Then soil components were added to the culturing well. The mixture of the bacteria biofilms and soil components were scratched off carefully using a pipette tip and deposited onto the clean silicon (Si) wafers before ToF-SIMS analysis. In the second approach, we used a microfluidic cell to culture biofilms. We made a modification to include a clean Si wafer as the main substrate for biofilm attachment in the microfluidic chamber. The soil component was mixed with the growth media at a ratio of 1:1 by volume as nutrients to support the biofilms' growth. A series of samples were collected to capture the temporal progression of the biofilms and the soil components in a course of several days, respectively, based on the growth curve of the strain. An IONTOF GmbH TOF-SIMS V spectrometer was used.

SIMS spectra were used to compare the effectiveness of the static and flow-cell culture methods. Characteristic fatty acids peaks such as myristic acid (m/z^- 227, $C_{14}H_{27}O_2^-$), palmitic acid (m/z^- 227, $C_{14}H_{27}O_2^-$), and arachidic acid (m/z^- 227, $C_{14}H_{27}O_2^-$) as well as an interesting biomarker riboflavin peak (m/z− 241, $C_{12}H_9N_4O_2^-$) are observed in the dynamic setup results. In contrast, the static setup does not seem to provide as much information, indicating that it is not optimal to prepare biofilm samples containing minerals for ToF-SIMS. Our results demonstrate that sample preparation is critical to study biofilms. Microfluidics is more flexible in microbial culture and media tuning; both are important in simulating a variety of conditions to understand microbes and soil interactions at the microscale. Also, characteristic signals of biofilms are not buried under the mineral components in the dynamic setup, which is imperative in understanding the role of biofilms in soil aggregation that occurs at the microbe-mineral interface.

FM-TuP-3 Matrix Enhancement in Time-of-Flight Secondary Ion Mass Spectrometry, *T. Adolphs, Y. Pohkrel, R. Peterson, H. Arlinghaus,* ***Bonnie J Tyler,*** University of Münster, Germany

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is one of the most important techniques for chemical imaging of nanomaterials and biological samples with high lateral resolution.However, low ionization efficiency limits detection of many molecules at low concentrations or in very small volumes.One promising approach to increasing the sensitivity of the technique is by addition of a matrix that promotes ionization and desorption of important analyte molecules.This approach is known as Matrix-Enhanced Secondary-Ion Mass Spectrometry (ME-SIMS).We have investigated the effect of matrix acidity on molecular ion formation in three different biomolecules.A series of cinnamic-acid based matrices that vary in acidity was employed to systematically investigate the influence of matrix acidity on analyte ion formation.The positive ion signal for all three biomolecules showed a strong increase for more acidic matrices.The most acidic matrix was then vapor-deposited onto mouse brain sections. This led to significant enhancement of lipid signals from the brain.This work confirms that proton donation plays an important role in the formation of molecular ions in ToF-SIMS.

FM-TuP-5 Oxygen Detection Limit with Magnetic Sector Dynamic SIMS, ***Alexandre Merkulov,*** IMEC, Belgium

Information on hydrogen, carbon and oxygen impurities (atmospheric gas species) introduced during processing and/or ageing is of major importance for a better understanding of semiconductor device lifetime and failure modes.Dynamic SIMS is often used in evaluating the concentration of impurities in solids because of its high sensitivity and depth profiling capabilities with good depth resolution and high throughput. Continuous ion beam sputtering with high density primary beam providing high sensitivity and reduced background contribution from residual gases within the analytical chamber. The magnetic sector SIMS tools are supplied with UHV analysis chamber with optimized vacuum conditions, minimizing the background level created by residual gases sticking to the sample surface.

High density Cs primary ion beam is often used because of high electronegativity of most of light element species, so, the Cs surface retention increases the negative secondary ions yield. Reducing the sputtering energy leads to increased Cs surface retention, thus, the ion yield. At the same time, it might reduce the surface scattering of oxygen containing molecular species scattering from the vacuum atmosphere (gettering effect). The sputtering events density on the surface (last event of the sputtering cascade) is also a parameter to take into account for equilibrium surface concentration estimation of vacuum species elements. However, this sputtering density variation depends on primary beam density and, as a parameter of solid-ion interaction, on the sputtering yield. The angle of incidence and sputtering energy are the parameters influencing the sputter yield. The effect of sputtering energy on the light element detection limits is an aspect of current study.

The idea of varying the sputter rate during the SIMS analysis is well developed approach allowing to estimate the background from the vacuum atmosphere or surrounding environment. Extrapolating the sputter rate to the infinite value, when vacuum contamination from the chamber is negligible small compared to oxygen containing into the sample being analyzed, the detection limit can be reduced drastically. In case the signal become independent on sputter rate, the background is determined by the vacuum contamination nearby the analysis area. Moreover, the vacuum atmosphere quality and geometrical layout of analytical area influencing the gaseous species background in secondary ions spectra are the very important parameters to be investigated. The statistical analysis of big data pool on Oxygen (Hydrogen) detection limits, observed with various impact energy and very different sputter rates will be presented.

FM-TuP-7 Depth Profiling Study in TAPC Monolayer Using Laser Desorption Ionization and Home-Built Ar-GCIB, ***Ji Young Baek,*** Korea Basic Science Institute, Republic of Korea*; C. Choi,* Korea Basic Science Institute , Republic of Korea*; M. Choi,* Korea Basic Science Institute, Republic of Korea

Depth profiling ToF-SIMS analysis has widely been performed to obtain the information of multi-layered organic samples. The depth profiling of the organic sample has generally been analyzed by using a gas cluster ion beam (GCIB) as a sputter gun and a liquid metal ion beam (LMIB) as an analysis gun. However, this kind of ordinary ToF-SIMS analysis shows lots of unnecessary signals are observed in the low mass region due to the high energy of the analysis ion beam and a result of the secondary ionization process. In practice, this makes it difficult to interpret a mass spectrum and a depth profile. In order to solve the difficulties of interpretation even in the organic light-emitting diode (OLED) analysis, we used a nano second UV laser (λ = 355 nm) as an analysis mode. Because most of OLED materials contain a chromophore which absorb UV light, so it can be easily ablated and ionized by laser pulse.

Here, we performed the depth profiling analysis of 50 nm TAPC monolayer sample using laser desorption ionization (LDI) and home-built Ar-GCIB. By controlling parameters of LDI, we found an optimal analysis condition that analyzed OLED sample with less damage and by taking a GCIB as a sputter, we tried to reach below ~ 1 nm resolution as an optimal sputtering of OLED materials. The depth profile was plotted as the integral value of the parent ion peak as a function of the number of scan. The depth resolution of TAPC monolayer was about 1.78 nm per point. The depth profiling of an OLED material could be successfully and more easily analyzed using GCIB-LDI ToFMS system. The capability of this type of depth profiling analysis will be demonstrated for real organic devices in the near future.

FM-TuP-9 Novel Approaches for Measuring Cork Material: Measurements and Applications, ***Natalie Sievers,*** PNNL

The unique properties of cork materials including porosity, elasticity, friability, and complex/heterogeneous composition present interesting challenges for SIMS measurements. Several studies have been dedicated to imaging internal structures and characterizing coatings and adhesives used in bottling processes where cork is utilized. These previous studies establish that there is a need for characterizing these materials. Unlike previously utilized methods, dynamic SIMS allows better depth resolution and detection limits while maintaining a relatively small spot size. This would be advantageous when trying to quantify trace amounts of elements

or understanding uniformity with depth. However, there has not been a detailed study using dynamic SIMS to determine optimal analytical conditions for characterizing such an unconventional material.

In order to understand how these, and similar materials, behave under various conditions, a methodical investigation was conducted in which several conditions are used in order to understand how cork material performs during dynamic SIMS acquisitions. Initial work shows that the types and sizes of cork materials used in wine production is highly variable and that careful consideration must be taken during sample prep. The results of this work will (1) demonstrate the ability to prepare and measure the various types of complex composite materials, (2) outline optimal analytical conditions, and (3) determine detection limits for an array of isotopes.

FM-TuP-11 AFM Observation of Topography Development on Si Surface During O_2^+ Ion Beam Sputtering as a Function of Ion Energy, Angle of Incidence and Dose, ***Masayuki Hatada***, *T. Miyamoto,* Toray Research Center, Inc., Japan

Surface rippling on Si by oblique incident O_2^+ ion beam is a well-known phenomenon [1,2] but there has been no satisfactory theory of its mechanism. Recent progress in the experiment and the theory of rippling on Si surface by oblique incident Ar^+ [3] could be helpful for understanding the rippling mechanism caused by O_2^+ if we had a kind of phase diagram of surface topography as a function of ion energy, angle of incidence and dose. We observed Si(100) surface topography by atomic force microscopy (AFM) over a range of these O_2^+ ion parameters, typically down to the depth of secondary ion intensity change completion.

References:

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FM-TuP-13 Why Do I Always Fall to Pieces? Understanding Beam-Based Lipid Bond Breakage Through Molecular Dynamics and Density Functional Theory Calculations, ***Michael Taylor***, The Pacific Northwest National Laboratory*; W. Kew, A. Anderson, M. Engelhard, C. Anderton,* The Pacific Northwest National Laboratory

INTRO: In-source fragmentation (ISF) is a significant problem in beam-based ionization. High degrees of ISF produces complex spectra, rich with fragment species that may be misinterpreted as intact molecules. The orientation of a surface interacting molecule is a substantial driver behind the degree of ISF. For example, in secondary ion mass spectrometry (SIMS), portions of a molecule will experience differential degrees of ion beam dosage, altering fragmentation patterns. Molecular dynamics (MD) when used in combination with density functional theory calculations (DFT) can identify the orientation and specific intramolecular bonds that are weakened in a molecule. The relative intensity of fragment can be then compared against bond energies to validate molecular orientations. For the first time, we have combined empirical data (SIMS/laser-desorption ionization; LDI) with quantum mechanical modelling data (MD/DFT) of palmitoylsphingomyelin (SM34:1) to explore how lipid orientation relates to ISF between the two methods.

METHODS: MD simulations were performed to model the interaction of SM 34:1 on gold. SM 34:1 was then drop cast at a monolayer concentration matching the maximum packing density (MD). SIMS (IONTOF V) and LDI (Bruker 15-T FTICR-MS) measurements were taken from the sample spot. Correlations between the relative intensities of fragment species and calculated bond dissociation energies for the two major lipid orientations were then compared.

RESULTS: MD simulations on gold revealed a preference for surface adsorption of the phosphocholine (PC) headgroup of SM 34:1. This was consistent with the theory of a strong charge-based surface interaction of the polar headgroup. Increasing the number of molecules modelled revealed changes in lipid orientation. A higher surface density resulted more molecules interacting via the terminal trimethylamine headgroup compared to whole headgroup. Additionally, simulations demonstrated a maximum packing density of 1.2 molecules/nm^2. MD of a single molecule revealed two major conformation, full and partial adsorption of the PC headgroup. DFT calculations revealed the electronic structure of both conformations. Corresponding beam analysis by SIMS identified abundant high m/z fragments [M - CH_3, M - N-$(CH_3)_3$, M – $C_2H_4N(CH_3)_3$] in combination with low m/z fragments, whereas LDI analysis produced cation adducts (M + Na, M + K), in combination with the fragmented PC headgroup ($C_5H_{15}PNO_4^+$) as major species. Comparison of bond dissociation energies of the PC headgroup fragments in SIMS (m/z 184, m/z 104, m/z 86, m/z 58) found a strong correlation between the summed bond and adsorption energies (R^2 = 0.94).

Author Index

Bold page numbers indicate presenter