Recent Advances in SIMS
Room Great Lakes B - Session RA+BS+FM+SS-TuM2

Beams, Theory Optimization and Methods

Moderator: Gregory Fisher, Physical Electronics USA

10:00am **RA+BS+FM+SS-TuM2-1 Chemical Structure of Organic Molecules Sputtered with Cluster Ions***, **Jiro Matsuo**,* Kyoto University, Japan **INVITED**

Much attention is now devoted to the study of gas cluster ion beams (GCIB), not only for fundamental research, but also for practical applications, such as organic depth profiling and 3-dimensional molecular analysis in XPS or SIMS. Extremely high energy density and multiple collisions are responsible for “cluster effects”, which play an important role during their sputtering process of organic molecules. It has been demonstrated that large cluster ion beams have a great potential to sputter organic molecules without any residual damage on the surface, because cluster ion beams are equivalently low energy ion beams. It has also been reported that cluster ions can enhance the yields of secondary ions, and this provides a unique opportunity for SIMS with organic materials. However, there is no report on molecular structure of sputtered species from organic materials. We have concerned that organic molecules sputtered with large cluster ions are destroy, or not. Secondary molecular ion yields are usually very low(<1E-4), and most of sputtered species are neutral, which is hardly measured. Therefore, SIMS spectra never tell us molecular structure of sputtered species. Capturing of neutral species and electrospray ionization mass spectrometry (ESI-MS) technique were utilized to explore molecular structure of sputtered neutral species.Fundamental phenomena of cluster ion collision with organic molecules will be discussed in conjunction with possible applications.

10:40am **RA+BS+FM+SS-TuM2-5 Cluster-Induced Desorption/Ionization of Polystyrene – Detailed Information on Material Properties Based on a Soft Desorption Process***, P. Schneider, F. Verloh,* Justus Liebig University Giessen, Germany*; **Michael Dürr,*** Justuts Liebig University Giessen, Germany

Polymer materials are of growing importance for a variety of applications in the field of optical electronics, including organic light emitting diodes and solar cells. As the detailed molecular properties of the polymer molecules determine the electrical and optical properties of these devices, sample characterization is a crucial step for both research and production purposes, thus making a powerful analytical tool mandatory. Secondary-ion mass spectrometry (SIMS) is a widespread method for the characterization of solid samples of polymers and organic materials in general, however, it typically comes with significant fragmentation induced by the primary ions [1]. While this can be of advantage, e.g., for identification of larger molecules or for depth profiling of polymer samples, characterization of sample properties like the mass distribution of the smaller molecules requires a non-destructive approach.

Desorption/Ionization induced by Neutral SO_2 Clusters (DINeC) is such a soft desorption method [2,3]. In this contribution, we investigate in detail cluster-induced desorption of non-polar polystyrene oligomers. Clear peak progressions corresponding to intact polystyrene molecules are observed in the mass spectra and no fragmentation was detected; efficient desorption was deduced from quartz crystal microbalance measurements. Molecular dynamics simulations further show that desorption proceeds via dissolvation in the polar cluster fragments even in the case of the non-polar polystyrene molecules. Experimentally, a reduced desorption efficiency for samples composed of molecules with higher chain length is observed. This is in contrast to the results of the molecular dynamics simulations, which indicate that, in a simple model, the desorption efficiency is largely independent of the chain length of the molecules. Backed by additional experiments with samples containing different distributions of chain length, the reduced desorption efficiency for longer molecules is attributed to an increasing entanglement of the polystyrene molecules with increasing chain length [4].

References:

[1] P. Schneider, et al., Anal. Chem. 92, 15604 (2020).
[2] C. R. Gebhardt, et al., Angew. Chem., Int. Ed. 48, 4162 (2009).
[3] A. Portz, et al., Biointerphases 15, 021001 (2020).
[4] P. Schneider, et al., J. Am. Soc. Mass Spectrom. 33, 832 (2022).

11:00am **RA+BS+FM+SS-TuM2-7 Ibeam: Large Argon Cluster Ion Beams as a Versatile Vacuum-Based Tool for the Fabrication of Protein Thin Films***, **Vincent Delmez**, B. Tomasetti, C. Poleunis,* Université Catholique de Louvain, Belgium*; C. Lauzin, C. Dupont-Gillain,* université Catholique de Louvain, Belgium*; A. Delcorte,* Université Catholique de Louvain, Belgium

The controlled immobilization of proteins at interfaces is a powerful tool for the synthesis and preparation of biofunctional materials. To this purpose, vacuum-based approaches such as soft-landing offer a valuable alternative to the traditional adsorption-based methods performed in solution and expand the scope of possible applications. By diverting a ToF-SIMS from its analytical function, we developed an alternative soft-landing technique, relying on the soft sputtering of biomolecules by large cluster ion beams (Fig. 1). Practically, a pool of proteins (the target) is bombarded by large Ar clusters, and the ejecta is collected on a solid surface (the collector). All ejected particles are collected regardless of their charge state, hence improving the deposition rate with respect to existing soft-landing methods. Small peptides, angiotensin and bradykinin, were used to optimize the transfer. ToF-SIMS analysis revealed the presence of intact protein molecules on the collector, and showed that lowering the energy per atom in the cluster projectiles promotes the deposition of intact molecules versus fragmented ones. ToF-SIMS was also used to *in-situ*measure the deposited protein thickness, as a procedure based on the attenuation of the substrate signal intensity was developed for thickness determination. The latter was used to demonstrate that our deposition method allows a precise control on the transferred quantity, from (sub)mono- to multilayers, with theoretically no thickness limitation. The deposition rate as well as the homogeneity of the deposited films could be largely improved by varying the clusters’ impinging angle with respect to the target surface, from 15° to 45°. We then used this cluster-assisted deposition method, coined iBeam, to investigate the transfer of larger enzymes. Lysozyme was used as a model. SDS-PAGE electrophoresis confirmed the presence of intact lysozyme on the collector, while positive enzymatic activity assay demonstrated the preservation of the three-dimensional structure of the transferred proteins. Our current experiments indicate that even larger proteins, e.g. trypsin, 24kDa, can be successfully transferred (Fig. 2). iBeam deposition can be achieved on any vacuum compatible collector material, and offers possibilities to build complex multilayers that are out of reach of existing protein immobilization techniques.

11:20am **RA+BS+FM+SS-TuM2-9 Optimisation of MeV TOF SIMS Technique for Hybrid Targets Imaging and Inorganic Material Depth Profiling***, M. Barac,* Ruder Boskovic Institute, Jozef Stefan International Postgraduate School (Slovenia), Croatia*; M. Brajkovic, **Zdravko Siketic**,* Ruder Boskovic Institute, Croatia*; J. Kovac,* Jozef Stefan Institute, Slovenia*; I. Bogdanovic Radovic,* Ruder Boskovic Institute, Croatia*; I. Srut Rakic,* Institute of Physics, Croatia*; J. Ekar,* Jozef Stefan Institute, Slovenia

MeV TOF SIMS is a variation of the standard technique TOF SIMS, in which primary ions with energies of ~MeV/amu accelerated by a particle accelerator are used for ion/molecule desorption. Since the electronic stopping in this energy range is much more pronounced than the nuclear stopping, the energy transfer to the target constituents is much "softer" (e.g. vibrational molecular modes are excited). In this way, a higher yield of molecular secondary ions and less fragmentation are achieved compared to monoatomic keV SIMS. MeV SIMS is mainly used for chemical imaging of organic molecules with masses up to 1000 Da, with applications in biomedical research, forensics, cultural heritage, etc.

This work explores the idea of using primary ions with energies in the range of 100 keV - 5 MeV for SIMS, where due to similar contributions of nuclear and electronic stopping power both, inorganic species, as well as larger biomolecules, can be desorbed simultaneously from the sample. Thus, LE (Low Energy) MeV SIMS is an option to analyse hybrid (organic/inorganic) samples. The dependence of the secondary ion yield on the primary ion energy of leucine and various inorganic targets was studied first. The ability to image hybrid organic/inorganic samples was demonstrated on target having a lateral distribution of Cr and leucine. It was demonstrated that the contrast between the organic and inorganic regions decreases almost completely as the energy of the primary ion beam energy was lowered from several MeV to a few hundred keV. In addition, LE MeV SIMS ability for depth profiling in a dual beam mode with Ar gun was also explored. LE MeV SIMS depth profiling of a Cr- ITO bilayer sample in a dual beam mode was investigated, and the obtained depth profile was compared with the profile obtained with a well-established keV SIMS with Bi_3^+ ion beam. The depth profiles showed solid chemical sensitivity to inorganic secondary ions and satisfactory depth resolution.

The systematic study of MeV TOF SIMS in the low energy range will open new possibilities for the fundamental understanding of the effects of primary ion stopping power on the detection of secondary ions of organic and inorganic species. LE MeV SIMS can also be considered as the method of choice for imaging and depth profiling of inorganic materials in the laboratories performing standard Ion Beam Analysis, but without commercially available SIMS instruments, providing additional information on the depth profile and chemical composition of the sample.

11:40am **RA+BS+FM+SS-TuM2-11 Reactive Molecular Dynamics Simulations of Lysozyme Desorption Under Ar Cluster Impact***, **Samuel Bertolini**, A. Delcorte,* Université Catholique de Louvain, Belgium

Using large gas cluster ion beams (Ar^{+}_{3000}), it is possible to successfully desorb and transfer intact nonvolatile (bio)molecules such as lysozyme (14kDa) onto a collector surface [1]. Nevertheless, from the cluster impact up to the complete desorption of the protein, the cluster supplies energy to the protein. The collision can potentially induce fragmentation and/or denaturation of the lysozyme. To shed light on the Ar cluster-induced desorption mechanism of lysozymes, molecular dynamics (MD) simulations were performed using reactive force fields (ReaxFF) [2]. The ReaxFF calculates the energy of the system associated with the bond order of each atom, permitting reaction on-the-fly. Compared to previous modelling of large molecule desorption by Ar clusters which involved simple hydrocarbon polymers [3], these new simulations offer a realistic view of the protein behavior, accounting for all the specific interactions which stabilize its three-dimensional structure (hydrogen bonds, disulfide bridges). Prior to the bombardment simulations, some of the necessary interactions were parametrized based on density functional theory (DFT) calculations, using a set of small molecules. Then, one or more lysozymes were adsorbed and relaxed at room temperature on a gold surface with a (543) orientation. The gold surface contains several step defects, allowing stronger and more realistic adsorption of a protein on the surface. The relaxed surfaces were finally bombarded by Ar clusters with a 45° incidence angle. The simulations investigate different cluster sizes (from 1000 to 5000 atoms) and energies per atom (from 0.5 to 5 eV), and how those parameters affect desorption as well as the concomitant chemical reactions and/or protein unfolding events. This allows us to better understand the final structure of the desorbed proteins as a function of the interaction parameters and, in turn, the results of the experiments.

[1] V. Delmez et al., A. Deposition of Intact and Active Proteins In Vacuo Using Large Argon Cluster Ion Beams, *J. Phys. Chem. Lett.***2021**, *12*, 952−957.

[2] Weiwei Zhang and Adri C. T. van Duin, Improvement of the ReaxFF Description for Functionalized Hydrocarbon/Water Weak Interactions in the Condensed Phase. J. Phys. Chem. B 2018, 122, 14, 4083–4092.

[3] A. Delcorte, A Microscopic View of Macromolecule Transfer in the Vacuum using Gas and Bismuth Clusters. *J. Phys. Chem. C*, **2022**, *126*, 7307–7318.

12:00pm **RA+BS+FM+SS-TuM2-13 Hybrid SIMS: New Adaptive Ion Injection System (AIIS) for Improved Repeatability of Quantitative Orbitrap™ SIMS Measurements***, **Sven Kayser**, J. Zakel, D. Rading, A. Pirkl, H. Arlinghaus,* IONTOF GmbH, Germany*; A. Franquet, V. Spampinato,* IMEC, Belgium

To boost the performances of the next generation transistors, new materials and device architectures have been investigated in the semiconductor industries[1]. In this context, strained-Ge and SiGe channel FET's have received high interest due to their excellent hole mobility[2] and recently obtained results have encouraged the semiconductor device industry to incorporate them in its latest FinFET technology[3,4]. As a consequence, characterization techniques have to provide chemical information and high sensitivity with a spatial resolution compatible with the device structure of down to 10 nm.

During the last years we demonstrated that the improved mass resolution of the Hybrid SIMS[5] instrument, which integrated the Orbitrap™ mass analyzer into a SIMS instrument, has been extremely beneficial for advanced semiconductor structure analysis. Especially the application of the so-called Self-Focusing SIMS (SF-SIMS)[6,7] approach opened up new possibilities for the analysis of next generation devices.

Despite the very encouraging first results it also become clear that, depending on the individual analytical conditions, the Orbitrap™ mass analyzer can suffer from oversteering and saturation effects. These effects limited the repeatability, absolute quantification and matching to other analytical techniques. To overcome this limitation, we developed a unique adaptive injection system for the Orbitrap™ mass analyzer. The new system automatically adapts the number of injections (i.e., Orbitrap™ sprctra per frame) or number of pixels within the field of view to avoid oversteering and saturation effects in real time.

In this presentation we will explain the working principle, apply new adaptive ion injection system to different sample systems and report the advances for the measurement repeatability, the quantification and the matching to other analytical techniques.

References:

[1] S. Datta, *Electrochem*. Soc. Interface **22** 41 (2013).
[2] J. Mitard et al., *Jap. J. Appl. Phys.***50** 04DC17-1 (2011).
[3] M.J.H. van Dal et al., *IEEE International Electron Devices Meeting (IEDM)* 23.5.1- 23.5.4 (2012).
[4] R. Pillarisetty, *Nature***479** 324 (2011).
[5] MK Passarelli, A Pirkl, et al., *Nature Methods*, **14**, 1175–1183 (2017)
[6]A. Franquet et al., *Applied Surface Science***365**, 143-152 (2016).
[7]A. Franquet et al., *J. Vac. Sci. Technol.* B **34**(3), May/Jun (2016).

Recent Advances in SIMS
Room Great Lakes Promenade & A1 - Session RA6-TuP
Recent Advances in SIMS Poster Session

RA6-TuP-1 Experimental and Theoretical Analysis of Tricyclic Antidepressants Using 213 Nm Picosecond Laser Desorption Postionization Mass Spectrometry*, T. Zagorac,* University of Illinois Chicago*; H. López Pena,* Virginia Commonwealth University*; J. Gross,* University of Illinois Chicago*; K. Moore Tibbetts,* Virginia Commonwealth University*; **Luke Hanley**,* University of Illinois Chicago

Imipramine class tricyclic antidepressants have low ionization efficiencies that render them difficult to detect using secondary ion mass spectrometry [1]. Imipramine ionization efficiency was previously studied with 800 nm, ~75 fs laser desorption photoionization mass spectrometry (fs-LDPI-MS) [2] and a significant precursor (M^+) ion was detected. Here we examine the use of 213 nm, ~30 ps-LDPI-MS for detection of imipramine, desipramine, amitriptyline and clomipramine via 7.9 eV single photon ionization. Precursor and fragment ion signal for all four compounds are compared to electron impact mass spectral libraries and ps-LDPI-MS displayed higher M^+ signal than electron impact for all four compounds. Furthermore, detection of imipramine by ps-LDPI-MS shows slightly less fragmentation than did fs-LDPI-MS [2]. A power study on the effect of desorption laser irradiance on the survival yield of the precursor ion shows that the desorption laser irradiances in the ps-LDPI-MS are significantly lower and M^+ survival yields are slightly higher than those for fs-LDPI-MS. Ionization energies of imipramine, desipramine, amitriptyline, clomipramine, and several of their major fragments are predicted using density functional theory calculations and used to explain the observed ps-LDPI-MS data. Low mass amine containing fragments are calculated to have low ionization energies, so their experimental observation might arise at least in part from dissociation during laser desorption. Results are discussed in terms of the application of 7.9 eV single photon ionization to laser secondary neutral mass spectrometry of drug compounds.

1) Vorng, J.-L.; Kotowska, A. M.; Passarelli, M. K.; West, A.; Marshall, P. S.; Havelund, R.; Seah, M. P.; Dollery, C. T.; Rakowska, P. D.; Gilmore, I. S., *Anal. Chem.* **2016,***88*, 11028.

2) Pieterse, C. L.; Rungger, I.; Gilmore, I. S.; Wickramasinghe, R. C.; Hanley, L., *J. Phys. Chem. Lett.* **2020,***11*, 8616.

RA6-TuP-3 Analysis of Organic Principal Component Distribution Using Orbitrap/TOF Hybrid SIMS*, Y. Jeong, J. Lee, H. Moon, J. Sung,* Korea Basic Science Institute, Republic of Korea*; . Suh,* Pusan National University, Republic of Korea*; **Jong Sung Jin**,* Korea Basic Science Institute, Republic of Korea

An analysis method was presented to confirm the distribution of small molecules according to the depth in the organic multilayer thin film using the newly developed Orbitrap/TOF Hybrid SIMS. With the conventional TOF-SIMS analysis method, ions such as CN^-, which correspond to the nitrogen component present in the molecule, were observed. This method has a limitation in obtaining only the information of the molecule to be analyzed accurately. Using Orbitrap/TOF Hybrid SIMS, we developed an analysis method that can obtain information on only the relevant molecules whose distribution is to be reported. In particular, by identifying each characteristic peak from the results of MVSA statistical processing, it was possible to infer different mechanisms of behavioral change depending on the molecular structure.

RA6-TuP-7 Epi SiGe Application using METRION® in-line SIMS System*, **Lawrence Rooney**, S. Okada,* Nova

The epitaxial process is a well-established deposition technique in semiconductor fabrication because it enables the ability to achieve much higher doping concentrations than can be obtained via ion implantation. As we move toward <5nm technology, a key process for enabling gate-all-around FET (GAAFET) is the stacked multi-lattice of Silicon (Si) and Silicon-germanium (SiGe) epi process for constructing the nanosheets.

Germanium (Ge) content in SiGe correlates to channel stress, and the germanium fraction (Ge%) has been increasing steadily as we move towards smaller technology nodes. When stress is high, epi layers can suffer from multiple problems such as defect formation, facet formation, non-uniform strain, etc. The challenge is greater when moving from planar to 3D structures, where uniformity of strain and control of defect density are important. Often, multiple epi layers of SiGe with varying thicknesses, Ge%, and Boron doping are deposited to optimize the device structure and process integration.

Enabling process control on the layer thickness, Ge%, and Boron doping concentration in these complicated SiGeB epi stacks is critical in high-volume manufacturing (HVM), and there is no single in-line metrology that is able to do the measurement.

This paper describes how in-line Secondary Ion Mass Spectrometry (SIMS) could be a solution to this problem by providing material composition profiles as a function of depth – resulting in thickness, Ge% and Boron concentration data from each nanosheet.

RA6-TuP-9 Detection of Contaminants in Positive and Negative Ion Mode Using in-Line SIMS with an Oxygen Primary Ion Beam*, **Julia Hoffman**, S. Okada,* Nova

Utilizing Secondary Ion Mass Spectrometry (SIMS) for in-line metrology is a newly emerging method of process control that requires contamination-free measurements, enabling SIMS on product wafers. SIMS measurements of negative ions are usually associated with a Cesium primary ion beam. Unfortunately, when Cesium is present in Silicon, it forms trap states in the Si band gap, which can cause serious leakage issues for Si-base transistors. Therefore, Cesium is considered a very damaging contaminant in semiconductor devices.

To enable contaminant-free inline SIMS a choice of Oxygen ion source is a preferable choice since it is generally benign and not considered a contaminant. This kind of source is typically used for positive secondary ion measurements. By switching the secondary spectrometer polarity between positive and negative ion modes, an Oxygen primary ion source can be used successfully to measure both positive and negative

species.

While an Oxygen primary ion source may not provide the same sensitivity to negative secondary ions as a Cesium primary ion beam, the ability to directly measure a range of species without the risk of contamination creates a wide field for in-line SIMS applications.

In this paper, the use of an Oxygen primary ion source for positive and negative secondary ion detection is being investigated on an in-line SIMS tool. We evaluate sensitivity levels of detecting contaminants like O, F^-, Cl^- in positive and negative ion mode with an Oxygen primary beam, as well as the use of proxy species or alternate isotopes for improved results.

Recent Advances in SIMS
Room Great Lakes C - Session RA-WeM2

Cluster and Novel Ion Sources

Moderators: Arnaud Delcorte, Université Catholique de Louvain, **Christine Mahoney**, Corning Research and Development Corporation

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

[1] J.S. Fletcher, J.C. Vickerman, N. Winograd, Label free biochemical 2D and 3D imaging using secondary ion mass spectrometry, Curr. Opin. Chem. Biol. 15.5 (2011) 733–740.

[2] I. Yamada, J. Matsuo, Z. Insepov, D. Takeuchi, M. Akizuki, and N. Toyod, J. Vac. Sci. Technol. A, 14(3), 1996, 781

[3]S.J. Lee, C.M. Choi, B.K. Min, J.Y. Baek, J.Y. Eo, M.C. Choi, Development of an argon gas cluster ion beam for ToF-SIMS analysis, Bull. Korean Chem. Soc. 40.9 (2019) 877–881.

[4] Sang Ju Lee, Aram Hong, Jinwan Cho, Chang Min Choi, Ji Young Baek, Jae Yeong Eo, Byeong Jun Cha, Woo Jun Byeon, Jin Young We, Sangwon Hyun, Minwoo Jeon, Choelho Jeon, Dong Jin Ku, Myoung Choul Choi*, Applied Surface Science, 572, 2022, 151467

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

[1] S. Ninomiya, Y. Sakai, R. Watanabe, M. Sogou, T. Miyayama, D. Sakai, K. Watanabe, L.C. Chen, K. Hiraoka, *Rapid Commun. Mass Spectrom*. **30**, 2279 (2016).

[2] S. Ninomiya, L.C. Chen, K. Hiraoka, *J. Vac. Sci. Technol. B***36**, 03F134 (2018).

[3] S. Ninomiya, Y. Sakai, L.C. Chen, K. Hiraoka, *Mass Spectrometry***7**, A0069 (2018).

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.

SIMS Solutions in Materials and Life Sciences
Room Great Lakes C - Session SS+RA-WeM4

High Resolution and MS/MS Methods I

Moderators: Gregory Fisher, Physical Electronics USA, **Andrew Giordani**, Procter & Gamble Company

10:20am **SS+RA-WeM4-11 A Novel Method for Measuring Young's Modulus Using Water Cluster SIMS*, Naoko Sano*, *A. Bellew,* Ionoptika Ltd., UK

Many techniques are available to measure mechanical properties such as material hardness, for example, nanoindentation. However, certain materials or structures provide challenges to measuring the actual hardness, such as when an underlying material is much softer than the one above, *e.g.*, an ice cube sitting on water.

Water Cluster SIMS is a powerful technique for analysing organic and biological samples. The enhanced sensitivity provided by the water cluster beam enables ultra-clear 2D and 3D analysis of high-mass compounds. In this work, we will explore a novel use of Water Cluster SIMS – for measuring the modulus of elasticity by the dissociation of water cluster ions.

It has been observed in SIMS spectra that water cluster ions colliding with a surface dissociate into smaller ions with the formula $[(H_2O)_n\text{+H}]^+$, where $2 \leq n \leq 100$. Additionally, the dissociation rate appears to depend on the surface's physical properties and the energy of the ion beam.

Initial results have demonstrated a relationship between Young's modulus and the observed ion intensity. The ability to measure the mechanical properties of a surface in situ whilst performing SIMS measurements would be especially beneficial for thin multilayer films and those materials where other measurements have failed.

10:40am **SS+RA-WeM4-13 Toward the Analysis of Hydrated Biological Specimens Using Atom Probe Tomography*, Daniel Perea,*** Pacific Northwest National Laboratory **INVITED**

Within the field of materials science, the adage that *structure determines properties* is foundational to the field, while a similar adage underpins the field of structural biology where *form follows function*. This concept is beautifully exemplified by proteins, where function from providing structural support, motility, transport, and enzymatic activity, is as varied as their unique amino acid sequence and resultant complex physical 3-D structure. Currently, the application of individual or combinations of established analytical techniques such as cryo electron microscopy, nuclear magnetic resonance spectroscopy, mass spectrometry, and X-ray crystallography are commonly used determine protein structure from ensembles of isolated proteins or protein crystals. However, the need to make measurements from ensembles of isolated proteins or crystals means that information is lost, for example, ionic gradients with respect to the native aqueous environment. Here I will explore the question*, can the analytical technique Atom Probe Tomography (APT), which produces 3D atom-by-atom composition point cloud maps, be applied to map macromolecular structure and ionic gradients of hydrated biological materials*? Recent work by our group has established the ability of APT to map gradients over nanoscale distances within an embedded protein specimen. More recently, established approaches for the preparation, handling, and transfer of cryogenically frozen hydrated specimens provides a route for the site-specific targeting of hydrated biological samples for cryo-APT analysis, including regions containing proteins cryogenically embedded in water ice. In this talk, I will discuss recent progress toward this end, which importantly includes the development of machine learning models aimed at mapping macromolecular structure from the 3-D point cloud composition maps.

11:20am **SS+RA-WeM4-17 Identification of Organic Molecules Produced from a Surface using Laser and QIT-ToF-SIMS*, Chang Min Choi,*** *J. Baek, J. Eo, M. Choi,* Korea Basic Science Institute, Republic of Korea

Over the past few decades, time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been continuously developed and used as a powerful instrument for a surface analysis[1]. Since the gas cluster ion beam (GCIB) developed, ToF-SIMS has helped us to detect a bigger organic ion from biological samples including tissues, cells, and so on[2-3]. Even though it has great advantages using GCIB for observing a secondary molecular ion, simple ToF mass spectra often have a difficulty assigning a peak which might exist candidates having a similar mass. Recently, some ToF-SIMS developers have been trying to add tandem mass spectrometric function for the accurate molecular identification[4].

We also wanted to resolve the aforementioned problem and developed a quadrupole ion trap time-of-flight secondary ion mass spectrometer (QIT-ToF-SIMS). Secondary molecular ions are generated from a sample surface with 20 keV toluene ion projectile produced by a UV pulse[5]. The generated secondary ions from a surface are transferred to a QIT though an extraction electrode and a set of electrostatic lens. After ion accumulation in QIT, the stored waveform inverse Fourier transform (SWIFT) pulse are applied to the QIT for the selection of an interested molecular ion. A nano second (ns) laser pulse is irradiated onto the selected secondary ion in the QIT for the photo-induced dissociation (PID). The PID-resulting ions are detected by reflectron ToF-MS. The electronic absorption probability is obtained by recording photodepletion of the secondary molecular ion as a function of the laser wavelength.

In this work, different molecular ions with similar mass are separated by photodepletion spectra. This would help us not only eliminate candidates with a confusion come from a similar mass but also research photophysical and photochemical properties of secondary molecular ions sputtered from surface. Furthermore, we anticipate PID study for a secondary ion open a chance to see a surface in a new perspective.

References

[1] N. Winograd, *Anal. Chem.***2015**, *87*, 328-333.

[2] A. S. Mohammadi, N. T. n. Phan, J. S. Flecher, A. G. Ewing, *Anal. Bioanal. Chem.***2016**, *408*, 6857-6868.

[3] H. Tian, L. J. Sparvero, A. A. Amoscato, A. Bloom, H. Bayır, V. E. Kagan, N. Winograd, *Anal. Chem.***2017**, *89*, 4611-4619.

[4] M. K. Passarelli, A. Pirkl, R. Moellers, D. Grinfeld, F. Kollmer, R. Havelund, C. F. Newman, P. S. Marshall, H. Arlinghaus, M. R. Alexander, A. West, S. Horning, E. Niehuis, A. Makarov, C. T. Dollery, I. S. Gilmore, *Nat. Methods***2017**, *14*, 1175-1183.

[5] C. M. Choi, S. J. Lee, J. Y. Baek, J. J. Kim, M. C. Choi, *Appl. Surf. Sci.***2018**, *458*, 805-809.

11:40am **SS+RA-WeM4-19 Cryo-ToF-SIMS and OrbiSIMS investigations of Sr^{2+} Diffusion in Bone Marrow*, Christine Kern*,** *A. Pauli, R. Jamous, T. El Khassawna, M. Rohnke,* Justus Liebig University Giessen, Germany

Osteoporosis, a systemic bone disease, is characterized by increased fracture risk and delayed, incomplete fracture healing. To improve fracture healing, next generation biomaterials are functionalized with drug release systems. Here, we are interested in the local release of healing-promoting agents, such as Sr^{2+} ions. In previous work, we studied Sr^{2+} release from functionalised bone cements and its dispersion in the mineralised areas of rat bone by time-of-flight secondary ion mass spectrometry (ToF-SIMS).[1, 2] In this work, we investigate Sr^{2+} transport within the more complex, highly viscous bone marrow. As analytical tools for tracking and spatially resolving the Sr^{2+} diffusion within bone marrow we apply 2D and 3D ToF-SIMS and orbitrap secondary ion mass spectrometry (OrbiSIMS). In a first approach, a ToF-SIMS depth profiling protocol under cryogenic conditions was specifically developed for determination of diffusion coefficients in bovine bone marrow. The validity of our experimental approach is shown within a time-dependent experimental series. Average diffusion coefficients of Sr^{2+} in different bovine bone marrow areas were obtained [fast diffusion: $D_{\text{bovine,FD}}=(2.09\pm2.39)\cdot10^{-9}\ \text{cm}^2\text{s}^{-1}$); slow diffusion: $D_{\text{bovine,SD}}=(1.52\pm1.80)\cdot10^{-10}\ \text{cm}^2\text{s}^{-1}$; total area: $D_{\text{bovine,TA}}= (1.94\pm2.40)\cdot10^{-9}\ \text{cm}^2\text{s}^{-1}$]. In a subsequent proof-of-concept study, the developed protocol was successfully applied to the determination of Sr^{2+} diffusion in bone marrow of osteoporotic rats [$D_{\text{rat,FD}}=(7.64\pm1.70)\cdot10^{-10}\ \text{cm}^2\text{s}^{-1}$); $D_{\text{rat,SD}}=(5.47\pm1.17)\cdot10^{-10}\ \text{cm}^2\text{s}^{-1}$); $D_{\text{rat,TA}}= (7.50\pm1.62)\cdot10^{-10}\ \text{cm}^2\text{s}^{-1}$]. For both bovine and rat bone marrow, high-resolution 2D and 3D mass spectrometric imaging analysis as well as OrbiSIMS spectral analysis revealed a correlation of slower Sr^{2+} diffusion in bone marrow areas with high intensity of lipid/fatty acid signals and fast Sr^{2+} diffusion in areas with less intensity of lipid signals. The mass spectrometric results are correlated with histological stainings. Overall, our results provide important insights about Sr^{2+} diffusion in bone marrow and show that both cryo-ToF-SIMS and cryo-OrbiSIMS are useful tools for the investigation of rapid diffusion in water-containing highly viscous media.

[1] M. Rohnke, et al., Strontium release from Sr2+-loaded bone cements and dispersion in healthy and osteoporotic rat bone, J. Controlled Release 262 (2017) 159

[2] C. Kern, et al., Investigation of strontium transport and strontium

quantification in cortical rat bone by time-of-flight secondary ion mass spectrometry, J. R. Soc. Interface 16 (2019) 20180638

12:00pm **SS+RA-WeM4-21 Diagenetic Degradation of Organic Molecules in Fossils Characterized by ToF-SIMS***, **Peter Sjövall,*** RISE Research Institutes of Sweden*; M. Jarenmark, J. Lindgren,* Lund University, Sweden

Fossils constitute the only source of information that we have of the evolution of life on Earth prior to the emergence of humans. This knowledge is constantly increasing as new fossils are discovered and studied by an increasing number of advanced analytical techniques [1]. For example, organic residues in >50 million-year-old fossils have been found to contain molecular species that can be attributed to endogenous biomolecules of the once living animal, including the pigments eumelanin and heme, whereas claims of preserved proteins are more controversial. An important advantage of ToF-SIMS over conventional mass-spectrometric techniques is the possibility to associate molecular information directly with specific microstructures on a fossil surface, thereby providing additional confidence in the biomolecular assignments. However, the complexity of organic residues often limits the amount of molecular information that can be obtained from ToF-SIMS analysis, and diagenetic degradation adds additional uncertainties to the biomolecular identification. In this work, we subjected eumelanin and two abundant structural proteins, collagen and elastin, to extended treatments at high temperatures and pressures to simulate diagenetic maturation. The samples were analysed by ToF-SIMS and complementary techniques to monitor induced molecular transformations, and the results were then compared against data acquired from a selection of exceptionally preserved fossils. For eumelanin, the resilient properties of this macromolecule were demonstrated by only minor changes to the spectra even after harsh experimental maturation, as expected from the well-documented preservation of this pigment in the fossil record [2]. In contrast, the results for the proteins showed considerable spectral changes upon high T/P treatment, including decreasing signal intensities of typical amino-acid-specific ions and increasing intensities of ions consistent with N-containing heterocyclic compounds, in agreement with recent suggestions [3] that “N-heterocycles” represent degraded proteinaceous matter in fossils. Our results indicate that biomolecules undergo transformations during diagenesis that lead to the formation of more stable molecular structures, which in the studied fossil may or may not preserve information about their original identity.

[1] Lindgren et al., Soft-tissue evidence for homeothermy and crypsis in a Jurassic ichthyosaur, Nature 564, 359-365 (2018)

[2] Jarenmark et al., Chemical Evaluation of eumelanin maturation by ToF-SIMS and alkaline peroxide oxidation HPLC analysis, Int. J. Mol. Sci., 22, 161 (2021)

[3] Wiemann et al., Nat. Commun. 9:4741 (2018)

Recent Advances in SIMS
Room Great Lakes B - Session RA-ThM3

HR Imaging and Spectrometry

Moderators: Laura Creon, CAMECA, **Albert Fahey**, Corning Incorporated

10:20am **RA-ThM3-11 Highest Resolution Sims Imaging Performed on Focused Ion Beam - Based Platforms***, **Jean-Nicolas Audinot**, O. De Castro, P. Philipp, A. Biesemeier, H. Hoang, T. Wirtz,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

FIB–SEM platforms are equipped with a Focused Ion Beam (FIB) column and a focussed electron beam column. This combination is used for a vast number of applications, including nano-patterning applications, sample preparation, imaging in various electron microscopy (EM) modes (SE, BSE, EBSD, STEM) and chemical analysis (WDS/ EDX). However, electron beam probes for EDX analysis have a large interaction volume in the sample, and EDX does not allow detection of light elements (H, Li, ...) and trace elements (<1% in at.). Ion sources have seen significant improvements in source brightness in recent years, resulting in better spatial resolution and current densities. The gas field ion source (GFIS) emitting He^+ or Ne^+ ions has a brightness of 10^9 $Acm^{-2}sr^{-1}$ and thus enables a spatial resolution of 0.3 nm or 2 nm for He^+ or Ne^+ beams, respectively[1]. Likewise, a low temperature ion source (LoTIS) working with Cs ions and reaching a brightness of 10^7 $Acm^{-2}sr^{-1}$ can produce nm-sized probe sizes while maintaining high ion currents, which is of great interest not only for their ability to mill a variety of structures, but also to provide structural and morphologic information with (sub)nm resolution[2,3].

Therefore, the prospect of connecting SIMS spectrometers to FIB-SEM platforms to combine high spatial resolution imaging with high sensitivity analytical data has emerged. To maximize the extraction and detection of secondary ions (SI), LIST developed a compact SIMS system based on a double focussing magnetic sector spectrometer that is optimized for state-of-the-art FIB platforms [2,4]. The design of the SIMS system first optimizes the SI collection by placing a small retractable extraction box as close as possible to the surface of the sample. The extracted SI are then post-accelerated and focussed into the mass spectrometer. After mass filtering, SI are detected using either a multi-collector system that allows simultaneous counting of several isotopes or using a newly developed continuous focal plane detector, which allows detection of the full mass spectrum of each sputtered voxel.

Here, we will review the performance of the FIB-SEM-SIMS platforms developed at LIST by showing applications, focusing on specific methodologies, correlative microscopy, and high-resolution 3D chemical imaging. Thus, we will show that the SIMS data correlated with other data obtained on the FIB-SEM platforms, such as SE images, can provide solutions for current and future analytical challenges.

[1] T. Wirtz et al., Annu. Rev. Anal. Chem. 12, 2019

[2] B. Knuffman, A. V. Steele, and J. J. McClelland, J. Appl. Phys. 114, 2013

[3] J. N. Audinot et al., Reports Prog. Phys. 84, 2021

10:40am **RA-ThM3-13 Integrated Spatial Multiomics using Successive $(H_2O)_n$-GCIB-SIMS and C_{60}-SIMS Imaging to Delineate Tissue Heterogeneity at Single-cell Resolution***, **Hua Tian**,* Pennsylvania State University

Tissue is highly organized with diverse cells that interact and communicate. Together with numerous biomolecules (e.g. metabolites and lipids) of cellular processes, the multilevel heterogeneities drive the biological function and disease-associated discoordination[1-2]. This spatial complexity is often ignored by traditional tissue assay. Mass spectrometry imaging holds the potential to visualize the heterogeneous cell organization and biomolecules in their context. However, it is challenging to achieve high spatial resolution and high chemical sensitivity toward different biomolecules. Moreover, the correlation of spatial omics in a single sample is impossible due to the difficulty of preserving the fast-changing metabolites.

To overcome these analytical hurdles, innovative technology and methodology are developed for omics imaging in single cells. On the same frozen-hydrated tissue, successive $(H_2O)_{n\ (n>28k)}$-GCIB-SIMS and C_{60}-SIMS imaging are employed to profile untargeted metabolites/lipids and targeted proteins by lanthanides antibodies (~ 40 in one acquisition) at 1 µm resolution. The novel ion source, $(H_2O)_{n(n>28k)}$-GCIB enhances chemical sensitivity, improves beam focus, reduces matrix effect, and extends detection ranges up to *m/z* 6000 [3-12]. Coupled with cryogenic analysis, the tissue is analyzed at near nature state, retaining the spatiotemporal distribution of metabolites and lipids. The AI-aided computational processing is used to register the omics in different cell types for further discriminant analysis.

With the new development, a number of tissues are imaged. On breast cancer tissue, the high population of macrophages (CD68) and less infiltration of immune cells (CD45, CD4) are observed, as well as the variation of the metabolic state in different cells. Several phosphatidylinositol species are concentrated in the epithelial tumor cells (pan-cytokeratin), along with desaturated lipids and GSH, indicating the mechanism of immune resistance and antioxidation for tumor survival [27]. Eight ganglioside GM3s correlate with the Ki-67 expressing cells, likely the markers of neoplastic transformation of breast tissue[37]. On liver tissue, distinct lipid clusters colocalize with periportal and pericentral proteins, and metabolic and lipidomic signature varies in distinct liver cells (*e.g.,* sinusoidal, Kupffer, hepatocytes, Ito stellate, immune cells). Similar to protein markers, further clustering analysis shows that metabolites and lipids classify the cell types for the first time. The multimodal SIMS imaging opens broad applications for exploring various biological phenomena of cellular/biomolecular interactions in health/disease.

11:00am **RA-ThM3-15 Preliminary Development of Microscope Mode Secondary Ion Mass Spectrometry Imaging***, **Felicia Green**,* Rosalind Franklin Institute, UK*; M. Castellani, A. Eyres, Y. Jia, M. Brouard,* Oxford University, UK*; J. Bunch, Z. Takats,* Rosalind Franklin Institute, UK*; S. Thompson, P. Blenkinsopp,* Ionoptika Ltd, UK

We want to achieve parallel detection of hundreds of thousands of chemical species, to enable rapid localisation of molecular interactions in tissues. Microscope-mode imaging mass spectrometry has the potential to provide rapid imaging of the many chemical constituents present at a surface in a variety of applications; it decouples acquisition time from spatial resolution and is a promising route to attaining MS images in seconds rather than days. This project aims to construct a unique stigmatic imaging secondary ion mass spectrometry (SIMS) instrument, which allows the rapid molecular mapping of biological tissues at unprecedented speed, with good mass range and mass resolution.

Here we describe the development and initial results from a secondary ion mass spectrometer coupled with microscope mode detection. Stigmatic ion microscope imaging enables us to decouple the primary ion beam focus from spatial resolution and is a promising route to attaining higher throughput for mass spectrometry imaging (MSI). Using a commercial C_{60}^+ primary ion beam source, we are able to defocus the probe beam to give uniform intensity across a 1 mm area. This allows simultaneous desorption of ions across a large field of view and with the potential to get an MSI of a 1mm area in a matter of seconds. Moreover, we can distinguish features with better than 20 µm spatial resolution. Then coupling the probe to a position sensitive detector, we are able to show the detection of a range of positive and negative secondary ions from both metals and dyes. Each of the spectra took less than a minute to acquire and although the present mass resolution is sufficient, we can see the scope for significant improvements with planned upgrades in the instrumentation. Simulations show that we have the potential of achieving >10,000 mass resolution over a 400 m/z range, and up to 2 µm spatial resolution simultaneously. As we move to complex biological samples this will become increasingly important, but will not incur any loss in speed. These initial experiments suggest a very promising set up to achieve rapid secondary ion mass spectrometry imaging with data comparable to microprobe mode SIMS.

11:20am **RA-ThM3-17 Implementation of an OTOF-SIMS on a FIB/SEM UHV Workstation for Correlative Imaging at High Spatial Resolution and High Mass Resolution***, **Jean Almoric Almoric**,* Orsay Physics, France*; T. Genieys,* CIMAP, France*; A. Houel,* Orsay Physics, France

Due to technology advances in most of the science field (microelectronics, metallurgy, life science), the need of highly resolved analysis technics is rising. In this context, the instruments used to analyze materials at nanoscale are driven by a constant optimization of their spatial resolution. The latest generation of Focused Ion Beam (FIB) using Ga^+ ion source and developed by Orsay Physics can go down to an imaging resolution of 2.5 nm [1]. Integrated into a workstation and coupled with an electron microscope (SEM), this equipment allows nano-patterning [2], implantation [3], preparation of TEM coverslips, cross sectioning and 3D tomography. In addition to conventional detectors (SE, BSE…), advanced analytical tools can be added to the workstation such as an orthogonal time-of-flight secondary ion mass spectroscopy (OTOF-SIMS).

In this work, we studied the possibilities offered by a correlative approach, combining several analysis and imaging tools (O-TOF SIMS, SEM, FIB and GIS) in a single versatile and customizable UHV platform called "NanoSpace". Chemical mapping combining a high spatial resolution (<30nm) and a high mass resolution (FWHM 4500 on ^{28}Si) was reached by pulsing the secondary ion beam instead of the primary one. The injection of reactive precursors near the surface using a gas injection system was done to increase the secondary ionization and allowed to achieve high useful yields despite the use of a primary Ga^+ ion source. This great improvement of the transmission and mass resolution was able thanks to the redesign and the optimization of the secondary ions extraction column from an O-TOF spectrometer. Correlative analysis and innovative approach had been applied to the study of different materials, in particular a nickel-based superalloys. These materials contain precipitates of a few tens of nanometers which have been chemically characterized by a semi-quantification protocol, which is not possible by SEM-EDX [4].

[1] S. Guillous et al; A new setup for localized implantation and live-characterization of keV energy multiply charged ions at the nanoscale; Review of Scientific Instruments 87, 113901 (**2016**)

[2] A. Benkouider et al; Ultimate nanopatterning of Si substrate using filtered LMAIS-focused ion beam; Thin Solid Films (**2013**)

[3] M. Lesik et al; Magnetic measurements on micrometer-sized samples under high pressure using designed NV centers; Science 366, 1359-1362 (**2019**)

[4] J. Almoric et al; Implementation of Nanoscale Secondary-Ion Mass Spectrometry Analyses: Application to Ni-Based Superalloys, Physica Status Solidi (a), 2100414 (**2022**)

11:40am **RA-ThM3-19 Polyamide Chemical Bonding with Titanium and Aluminum Probed with ToF-SIMS and XPS***, P. Hirchenhahn,* ***Laurent Houssiau,*** University of Namur, Belgium

Structures joining metals and polymers are increasingly demanded as they combine the high mechanical resistance of the metal with the functionality and low weight of the polymer. Laser welding turns out to be a fast and efficient method to bind directly metals to polymers with no need for adhesives or mechanical fastening, but the root cause for adhesion is still poorly understood. In this contribution, we show how titanium alloys and polyamide-6.6 (PA or Nylon™) can be easily joined by shining a laser on the metal side. The very nature of the chemical bond was then probed with ToF-SIMS and XPS [1]. The first batch of samples was made of raw materials directly welded to each other, then disassembled. The fracture was both cohesive and adhesive, so that surface analysis could be directly performed on the adhesive fracture sites. Signals from the polymer and the metals were recorded simultaneously on the Ti side, proving that a very thin layer of PA was still present after fracture. Hybrid ions containing Ti and PA elements (C,H,N,O) were observed and only two of them exhibited a sharp increase in the welded area, i.e. $CHNOTi^+$ and $CHNOTi^-$, clearly pointing at the formation of C-O-Ti bonds at the interface. The second batch of samples were made by spincoating thin PA layers on Ti plates, followed by laser welding and subsequent dissolution of the polymer with trifluoroethanol. Interestingly, a very thin polymeric film remained on the Ti substrate after dissolution on the welded area but also on the non-welded area, allowing an assessment of the heat effect on binding. A PCA analysis was ran to identify which ions intensities were most changing in the weld. Ions from the substrate decreased while ions from the polymer increased in the weld, hinting at a thicker polymer residual layer. Moreover, most hybrid ions decreased in the weld, with the exception of ions containing C,H,N,O and Ti (e.g. $CHNOTi^-$ or $CHNO_2Ti^-$), confirming the formation of C-O-Ti bonds assisted by laser heat. A mechanism is proposed, with amide groups reacting with Ti hydroxide groups to create covalent C-O-Ti bonds along with imine formation in the polymer chain. This is also supported by a weak contribution of imine groups in XPS high resolution N1s spectrum. The results will be briefly compared with a previous work [2] carried out on Al laser welded to PA, which led to a similar conclusion: the formation of C-O-Al bonds upon heating with the laser beam.

[1] P. Hirchenhahn, A. Al Sayyad, J. Bardon, P. Plapper, L. Houssiau; *Talanta***2022**, 123539

[2] P. Hirchenhahn, A. Al Sayyad, J. Bardon, P. Plapper, L. Houssiau; *ACS Omega***2021**, 6, 33482-33497

Author Index

Bold page numbers indicate presenter

— A —
Almoric, J.: RA-ThM3-17, **7**
Arlinghaus, H.: RA+BS+FM+SS-TuM2-13, 2
Audinot, J.: RA-ThM3-11, **7**
— B —
Baek, J.: SS+RA-WeM4-17, 5
Barac, M.: RA+BS+FM+SS-TuM2-9, 1
Bellew, A.: SS+RA-WeM4-11, 5
Berrueta Razo , I.: RA-WeM2-5, 4
Bertolini, S.: RA+BS+FM+SS-TuM2-11, **2**
Biesemeier, A.: RA-ThM3-11, 7
Blenkinsopp, P.: RA-ThM3-15, 7
Bogdanovic Radovic, I.: RA+BS+FM+SS-TuM2-9, 1
Brajkovic, M.: RA+BS+FM+SS-TuM2-9, 1
Brouard, M.: RA-ThM3-15, 7; RA-WeM2-7, 4
Bunch, J.: RA-ThM3-15, 7; RA-WeM2-7, 4
Burt, M.: RA-WeM2-7, 4
— C —
Castellani, M.: RA-ThM3-15, 7
Castellani, M.: RA-WeM2-7, **4**
Chen, L.: RA-WeM2-3, 4
Choi, C.: SS+RA-WeM4-17, **5**
Choi, M.: RA-WeM2-1, **4**; SS+RA-WeM4-17, 5
— D —
De Castro, O.: RA-ThM3-11, 7
Delcorte, A.: RA+BS+FM+SS-TuM2-11, 2; RA+BS+FM+SS-TuM2-7, 1
Delmez, V.: RA+BS+FM+SS-TuM2-7, **1**
Dupont-Gillain, C.: RA+BS+FM+SS-TuM2-7, 1
Dürr, M.: RA+BS+FM+SS-TuM2-5, **1**
— E —
Ekar, J.: RA+BS+FM+SS-TuM2-9, 1
El Khassawna, T.: SS+RA-WeM4-19, 5
Eo, J.: SS+RA-WeM4-17, 5
Eyres, A.: RA-ThM3-15, 7
— F —
Franquet, A.: RA+BS+FM+SS-TuM2-13, 2
— G —
Genieys, T.: RA-ThM3-17, 7
Green, F.: RA-ThM3-15, **7**; RA-WeM2-7, 4
Gross, J.: RA6-TuP-1, 3
— H —
Hanley, L.: RA6-TuP-1, **3**
Hiraoka, K.: RA-WeM2-3, 4
Hirchenhahn, P.: RA-ThM3-19, 8
Hoang, H.: RA-ThM3-11, 7
Hoffman, J.: RA6-TuP-9, **3**
Houel, A.: RA-ThM3-17, 7
Houssiau, L.: RA-ThM3-19, **8**
— J —
Jamous, R.: SS+RA-WeM4-19, 5
Jarenmark, M.: SS+RA-WeM4-21, 6
Jeong, Y.: RA6-TuP-3, 3
Jia, Y.: RA-ThM3-15, 7
Jia, Y.: RA-WeM2-7, 4
Jin, J.: RA6-TuP-3, **3**
— K —
Kayser, S.: RA+BS+FM+SS-TuM2-13, **2**
Kern, C.: SS+RA-WeM4-19, **5**
Kovac, J.: RA+BS+FM+SS-TuM2-9, 1
— L —
Lagator, M.: RA-WeM2-5, **4**
Lauzin, C.: RA+BS+FM+SS-TuM2-7, 1
Lee, J.: RA6-TuP-3, 3
Lindgren, J.: SS+RA-WeM4-21, 6
Lockyer, N.: RA-WeM2-5, 4
López Pena, H.: RA6-TuP-1, 3
— M —
Matsuo, J.: RA+BS+FM+SS-TuM2-1, **1**
Moon, H.: RA6-TuP-3, 3
Moore Tibbetts, K.: RA6-TuP-1, 3
— N —
Ninomiya, S.: RA-WeM2-3, **4**
— O —
Okada, S.: RA6-TuP-7, 3; RA6-TuP-9, 3
— P —
Pauli, A.: SS+RA-WeM4-19, 5
Perea, D.: SS+RA-WeM4-13, **5**
Philipp, P.: RA-ThM3-11, 7
Pirkl, A.: RA+BS+FM+SS-TuM2-13, 2
Poleunis, C.: RA+BS+FM+SS-TuM2-7, 1
— R —
Rading, D.: RA+BS+FM+SS-TuM2-13, 2
Rohnke, M.: SS+RA-WeM4-19, 5
Rooney, L.: RA6-TuP-7, **3**
— S —
Sano, N.: SS+RA-WeM4-11, **5**
Schneider, P.: RA+BS+FM+SS-TuM2-5, 1
Siketic, Z.: RA+BS+FM+SS-TuM2-9, **1**
Sjövall, P.: SS+RA-WeM4-21, **6**
Smith, N.: RA-WeM2-7, 4
Spampinato, V.: RA+BS+FM+SS-TuM2-13, 2
Srut Rakic, I.: RA+BS+FM+SS-TuM2-9, 1
Suh, .: RA6-TuP-3, 3
Sung, J.: RA6-TuP-3, 3
— T —
Takats, Z.: RA-ThM3-15, 7; RA-WeM2-7, 4
Thompson, S.: RA-ThM3-15, 7
Tian, H.: RA-ThM3-13, **7**
Tomasetti, B.: RA+BS+FM+SS-TuM2-7, 1
Tsuneki, S.: RA-WeM2-3, 4
— V —
Verloh, F.: RA+BS+FM+SS-TuM2-5, 1
— W —
Wirtz, T.: RA-ThM3-11, 7
— Z —
Zagorac, T.: RA6-TuP-1, 3
Zakel, J.: RA+BS+FM+SS-TuM2-13, 2