

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 destroyed, 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*, Justus 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 dissolution 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 \sim 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.

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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. Zakeł*, *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 industries¹. In this context, strained-Ge and SiGe channel FET's have received high interest due to their excellent hole mobility² 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 SIMS⁵ 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 became 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™ sprcra 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).
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- [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/June (2016).

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