Tuesday Afternoon, October 20, 2015

Applied Surface Science
Room: 212D - Session AS+BI-TuA

Challenges in the Characterization of Polymer/Organic/ Biological Systems

Moderator: Bonnie Tyler, National Physical Laboratory (NPL), Jeffrey Fenton, Medtronic plc

2:20pm **AS+BI-TuA1 ASSD 30th Anniversary Lecture: 30 Years (ToF-)SIMS of Organic Materials: from Monolayer to 3D Microarea Analysis**, ***Birgit Hagenhoff***, Tascon GmbH, Germany **INVITED**

The presentation will follow the development track and the learning curve of (ToF)-SIMS for the characterization of organic materials.

Starting in the early 70s of the last century, when Alfred Benninghoven, based on research results for Ag catalyst samples, started into what would later become the wide-spread field of Static SIMS, the talk will cover the following areas

· Static SIMS: early beginnings

· Static SIMS: the importance of noble metal substrates

· Static SIMS: from quadrupoles to Time-of-Flight Analyzers

· Charge compensation: the gateway to bulk analysis

· Organic Imaging: limits of lateral resolution

· Cluster ion guns: getting sub-µm using Au and Bi LMIGs

· The road to organic depth profiling: SF_5^+ and C_{60}^+ sputtering

· Organic depth profiling: the use of Ar cluster ion sputtering

· 3D Microarea Analysis: Status-quo and challenges for the future

3:00pm **AS+BI-TuA3 Characterization of the Buried Interface between a Bacterial-Biofilm Resistant Coating and a Silicon Catheter by using Gas Cluster ToF-SIMS and Raman Microscopy**, ***Bonnie Tyler***, National Physical Laboratory (NPL), UK, *A.L. Hook, M.R. Alexander*, University of Nottingham, UK, *A. Giovannozzi*, INRIM, *A. Pelster, H.F. Arlinghaus*, University of Muenster, Germany

Thin film coatings are widely used in medical devices in order to improve the biological response to the device without compromising its mechanical performance. These coatings are frequently organic in nature and are applied to a wide range of substrate materials. The challenge of ensuring a stable linkage between the coating and the underlying substrate is common to all of these systems. Defects at the interface between the coating and the substrate can result in failure of the medical device with potentially serious consequences. The study of buried interfaces in organic systems, like those common in medical devices, has in the past been a nearly intractable problem because sputter depth profiling with monatomic ions destroys the relevant chemical information. Recent advances in Gas Cluster Ion Beam technology have opened up exciting possibilities to better understand these buried interfaces. In this work, we have studied adhesion between an bacterial-biofilm resistant polymer coating and an oxygen plasma-treated polymer surface using Argon Cluster 3D-imaging Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Raman Microscopy. Analysis has been performed in both dry and hydrated state. The analysis provided several analytical challenges. Because the overlayer was not of uniform thickness, a depth scale correction was needed to reduce misleading artefacts at the interface. Analysis of the hydrated catheters required cryogenic analysis conditions. From the ToF-SIMS data we have been able to observe the presence of particles, cracks and water, and to monitor hydrophobic recovery at the interface between the coating and the catheter. Raman analysis has provided complementary information on the Van-Der-Waal interactions at the interface. The results have been compared to mechanical adhesion tests and help to provide a better understanding of the processes that influence adhesion between the coating and the catheter.

3:20pm **AS+BI-TuA4 How to Measure Reaction Rates on Surfaces?: Ambient Mass Spectrometry and XPS to Study the Rate of Organic Reactions on Functionalized Surfaces.**, *R. Sen, J. Escorihuela*, ***Han Zuilhof***, Wageningen University, Netherlands

Ultrathin coatings like self-assembled monolayers and polymer brushes have been used for a wide variety of studies and applications. Reactions within such monolayers or brushes are often difficult to follow, and their rates are typically not measurable: apart from a handful of cases in which electrochemical methods have been used, no rigorously measured kinetics on reactions within e.g. self-assembled monolayers are available. The current presentation will outline a generic approach, combining ambient mass spectrometry and XPS, to fill this gap, and provide a truly generic method to measure the rate of intramonolayer or intrapolymer organic reactions. Examples will include a variety of so-called click reactions, as these display a very high potential in materials science.

4:20pm **AS+BI-TuA7 Surface versus Bulk Chemistry of Reverse Osmosis Membranes**, ***Tamlin Matthews***, *R. Cieslinski, M. Paul, A. Roy*, The Dow Chemical Company

The polyamide layer of reverse osmosis (RO) thin-film composite membranes is ~100 nm thick. Separation of this thin layer from the supporting layers is a complex process and can only be done chemically, which results in a fragile polyamide layer and makes characterization challenging. X-ray photoelectron spectroscopy (XPS, near-surface) and Rutherford backscattering spectrometry (RBS, bulk) have been applied to characterize the polyamide layer, without the need to separate polyamide from the supporting layers. The combination of these methods allows the comparison of bulk vs. near-surface carboxylic acid content, which is a driver in RO performance. Additionally, elemental composition, thickness, and roughness of the RO membranes can be compared in systems with systematically changed monomers. This talk will focus on how the application of XPS and RBS can be used together for surface vs bulk chemical composition.

4:40pm **AS+BI-TuA8 Effect of Deep UV Irradiation on Polyester Family Polymers**, ***Lopamudra Das***, *M.J. Kelley*, College of William and Mary

In films and fibers, desired attributes of these polymers are often surface-mediated. Radical chemistry launched by deep UV offers attractive opportunities for surface modification, free of the environmental burdens of wet chemistry. We report the effect of 172 nm irradiation in the absence of oxygen on PET, PTT, PBT and PEN films, observed by FTIR, XPS and ToF-SIMS. Initial findings include carboxylic acid production and a loss of carbonyl carbon. To better understand surface reactivity, samples of each polymer were treated with silver trifluoroacetate or with heavy water.

5:00pm **AS+BI-TuA9 Going beyond State of the Art in SIMS Imaging in the Life-Sciences and for Organic Devices**, ***Ian Gilmore***, National Physical Laboratory, UK **INVITED**

In this celebratory 30th year of the Applied Surface Science Division, we can be sure that secondary ion mass spectrometry will feature strongly in the "Top-30" hit-parade. For example, SIMS, with its ability for high-sensitivity analysis has played an important role in the semiconductor industry measuring dopant profile concentrations. The rapid growth of the semiconductor industry is popularly summarised by Moore's law[1]; which shows that over the last five decades the number of transistors in a chip doubles every two years. Recently, Scannell et al[2] show that the reverse is the case for the pharmaceutical industry and the number of drugs per billion dollars of investment has dropped from around 50 to less than 1 over a similar timescale. They call this "Eroom's" law, Moore's law in reverse.

Analogously to the semiconductor industry, SIMS could now provide important benefits to the pharmaceutical industry. The challenge here is to measure where drugs go at the cellular level, even within specific organelles, to answer long-standing questions about whether drug concentrations are sufficiently high in the right places to have a therapeutic effect, or if the medicine is lodging within cellular components and causing toxicity. If anomalies were spotted earlier it might help to explain toxicities or lack of efficacy of a medicine and reduce costly late-stage failures. [3,4]

To meet this challenge, NPL in collaboration with GlaxoSmithKline, ION-TOF GmbH, Thermo Fisher Scientific and the University of Nottingham is building a revolutionary new instrument, the 3D nanoSIMS,[4] which incorporates the powerful Thermo Scientific™ Orbitrap™ mass analyzer for high-performance identification of drugs and metabolites. The stunning capability of SIMS to study drugs in tissue and cells will be highlighted and the characteristics of the new instrument will be outlined. The benefits of combining SIMS with the new generation of ambient mass spectrometry techniques and the rapidly rising challenge of Big Data will also be discussed.

References:

[1] Moore, Gordon E.. "Cramming more components onto integrated circuits" (PDF). Electronics Magazine. (1965)

[2] Scanwell, J.W., Blanckley, A., Boldon, H., Warrington B., Nat. Rev. Drug Discovery., 11, 191-99 (2012)

[3] C T Dollery, Clinical Pharmacology & Therapeutics, (2013); 93, 263–266.

[4] The 3D nanoSIMS project, http://www.npl.co.uk/news/3d-nanosims-label-free-molecular-imaging [2013 [http://www.npl.co.uk/news/3d-nanosims-label-free-molecular-imaging%20%5b2013]]

5:40pm **AS+BI-TuA11 Can *In Situ* Liquid SIMS Provide Enough Signals for Biology and Environmental Research?**, ***Zihua Zhu***, *Y. Zhou, X. Hua, J. Yu, J.E. Evans, D. Lao, X.-Y. Yu*, Pacific Northwest National Laboratory

In situ liquid SIMS is an R&D 100 award winner that was developed in PNNL since 2010. System for analysis at the liquid vacuum interface (SALVI) coupled with liquid SIMS has proven to be a promising new tool to provide molecular information at solid/liquid interfaces.[1,2] However, our initial data showed that signals of secondary positive ions were too low to be usable in some cases.[2,3] In addition, it was difficult to obtain strong negative molecular ion signals with m/z > 100.[2] These two drawbacks make SIMS community wonder the potential applications of this new analytical approach. In this presentation, we report that strong positive and negative molecular signals are achievable after we optimize the SIMS experimental conditions. Our results show that both beam current and primary ion species (e.g., Bi^+, Bi_3^+, Bi_3^{2+}) play important roles in achieving optimal molecular signals at the liquid interface. Data sets from three model systems, including an ionic liquid, water, and several liposome solutions, will be presented. In addition, beam damage at the liquid surface will also be discussed.

[1] B. Liu, X. Y. Yu, Z. Zhu, X. Hua, L. Yang, Z. Wang, *Lab Chip*, **2014**, *14*, 855.

[2] X. Hua, X. Y. Yu, Z. Wang, L. Yang, B. Liu, Z. Zhu, A. E. Tucker, W. B. Chrisler, E. A. Hill, S. Thevuthasan, Y. Lin, S. Liu, and M. J. Marshall, *Analyst*, **2014**, *139*, 1609.

[3] L. Yang, Z. Zhu, X. Y. Yu, S. Thevuthasan, J. P. Cowin, *Anal. Methods*,**2013**, *5*, 2515.

6:00pm **AS+BI-TuA12 Fundamental Metrology for Tissue Imaging by SIMS - A Study of Cholesterol and Determination of the Argon Cluster Sputtering Yield**, *P.D. Rakowska, M.P. Seah,* ***Rasmus Havelund***, *I.S. Gilmore*, National Physical Laboratory, UK

Secondary Ion Mass Spectrometry (SIMS) has become an invaluable tool to study organic and biological samples. An important biological application is in the analysis of mammalian cellular membranes. Considerable contribution to the field comes with the use of large cluster ion beams, and in recent years the application of argon gas cluster ion beam has emerged as the prevailing method.

Cholesterol, as a key component of nearly all mammalian cell membranes, is of particular interest. It alters the physical properties of the membranes, interacts with neighbouring lipids and proteins and is involved in numerous biomolecular processes. Being able to detect, identify and characterise the distribution of cholesterol in biological samples has vast implications in medical sciences. To do this, we need to underpin the basic metrology involved. It is important to evaluate cholesterol sputtering yields for argon cluster sputtering over a range of energy and cluster sizes so that a general description of the molecule behaviour may be established.

In this study, we compared the use of $C_{60}^{+(+)}$ and Ar_n^+ as sputtering ions for depth profiling of cholesterol thin films. Films of different thicknesses were prepared by thermal evaporation and the sputtering yields of cholesterol were measured from depth profiles made using 2.5 to 20 keV Ar_{1000}^+ and Ar_{5000}^+ and 10 and 20 keV $C_{60}^{+(+)}$ sputtering beams. We show that, at room temperature, the $C_{60}^{+(+)}$ ions caused significant damage but gave a well-behaved depth profile whereas Ar_n^+ gas clusters left the material undamaged but the very clean layer readily restructured making the profiles much more complex. This restructuring does not occur at room temperature normally but results from the actions of the beams in the sputtering process for profiling in SIMS. The sputtering yields from these restructured films are up to twice that for material not so restructured. Good profiles may be made by reducing the sample temperature. This is likely to be necessary for many lower molecular weight materials (below 1000 Da) to avoid the movement of molecules. The yields for both $C_{60}^{+(+)}$ and Ar_n^+ fit the universal yield equation [1]. Our results show that considerable differences can occur between the measurements performed with the two ion clusters, affected, in addition, by factors such as sample temperature or exposure to light. These will be discussed.

[1] M.P. Seah, J. Phys. Chem. C, 2013, 117 (24), pp 12622–12632

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