Monday Afternoon, October 25, 1999

Applied Surface Science Division
Room 610 - Session AS1-MoA

Molecular Mass Spectrometry including Interpretation
Moderator: S.J. Pachuta, 3M

2:40pm AS1-MoA3 Interpretation of Static SIMS Spectra, *D. Briggs,* Siacon Consultants Ltd., U.K. **INVITED**
Static SIMS has rapidly developed into a powerful tool for the molecular characterisation of surfaces, with modern time-of-flight (ToF) instruments capable of providing both high mass resolution (m/Δm >7000)and high spatial resolution (~ 0.1 micron). Although most of the emphasis to date has been in the application to organic/polymeric systems the technique has equal potential for the surface characterisation of inorganic materials. However, the information content of ToFSIMS spectra is enormous and the interpretation of 'unknown' spectra consequently poses a serious challenge. There is a widespread feeling that the full exploitation of the technique is limited by interpretation problems, particularly with the pressure to deskill/automate all analytical operations. Compared with other forms of mass spectrometry and especially EI-MS, SIMS presents extra problems for spectral interpretation: the physical basis of the ion formation process is very poorly understood, the spectra are influenced by the primary ion used and by the matrix from which the ions originate and there are no established 'rules' for fragmentation. The development of searchable databases of standard spectra has been a key feature of other molecular spectroscopies and this approach clearly represents a way forward for SIMS. Aspects of the development of the only stand-alone database[1] will be discussed in the light of these issues. [Footnote Text] [Footnote 1]The Static SIMS Library, SurfaceSpectra Ltd, Manchester, UK

3:20pm AS1-MoA5 Characterization of Polymer Additives by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), *R. Kersting,* TASCON GmbH, Germany*; R. Verlaek,* DSM Research, The Netherlands*; B. Hagenhoff,* TASCON GmbH, Germany*; A.P. Pijpers,* DSM Research, The Netherlands*; B.C. Schwede,* ION-TOF GmbH, Germany
Polymers used for industrial purposes generally contain various additives to improve the product performance. Substance classes include anti-oxidants, plasticizers and flame retardants. Typical concentrations are in the order of some 100 to 1000 ppm. Although much is known about the bulk composition of the additive containing polymer not many information on the surface composition of real industry polymers is available. Generally, Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is an ideally suited analytical technique to characterize the surface composition because it offers detailed molecular information with high sensitivity. On the other hand the surface concentration in real world systems can be very small, even below the detection limit of normal TOF-SIMS analysis. Therefore most TOF-SIMS studies of polymer additives have concentrated on pure materials or highly concentrated model systems. Recently, we have started a systematic study on the secondary ion emission behaviour of polymer additives using model systems containing the additives in their normally applied concentrations and embedding them into their normal host polymer. The study aims at the automated identification of additives in real world samples from their TOF-SIMS spectra. Special emphasis is therefore laid on the emission pattern for use in a spectra library and the determination of detection limits. Different primary ion bombardment conditions (monoatomic primary ions: Ar^+, Ga^+; polyatomic primary ions: SF_5^+) were used to study the influence of primary ion mass and polyatomicity on the secondary ion emission. We will present our first results obtained on antioxidants. Whereas most substances can be analyzed to satisfaction using primary ions like Ar^+ or Ga^+, it turned out that in some cases polyatomic primary ions (SF_5^+) had to be used in order to reach acceptable detection limits.

3:40pm AS1-MoA6 Secondary Ion Emission from LB-Layers Under Molecular Primary Ion Bombardment, *D. Stapel, M. Thiemann,* Universität Münster, Germany*; B. Hagenhoff,* TASCON GmbH, Germany*; A. Benninghoven,* Universität Münster, Germany
Secondary ion yields $Y(X_i^q)$ increase considerably when changing from atomic to molecular primary ions, whereas the simultaneous increase in the corresponding damage cross section $\sigma(X_i^q)$ is much smaller. This holds in particular for thick molecular samples like LB multilayers or polymers. For LB multilayers we found yield increases up to a factor of 1000, when changing from Ar^+ to SF_5^+ bombardment. This phenomenon is important for practical analytical applications of TOF-SIMS, because yields, damage cross sections, and the resulting ion formation efficiencies E=Y/σ determine the achievable sensitivity as well as the achievable lateral resolution. The secondary ion emission of well defined model LB systems were investigated for a more detailed understanding of the complex sputtering and ion formation processes especially under different molecular primary ion bombardment. We investigated three series of LB layers (n=1, 3, 5, 7 ; n : number of monolayers) under 1 - 10 keV O^+, Ne^+, Ar^+, Xe^+, O_2^+, CO_2^+, SF_5^+, $C_7H_7^+$, $C_{10}H_8^+$, $C_6F_6^+$ and $C_{10}F_8^+$ bombardment. $Y(X_i^q)$ as well as $\sigma(X_i^q)$ were determined. Our experimental results demonstrate a more pronounced yield and efficiency enhancement for multilayers (n>1). The increase in Y, σ and E features a saturation behaviour for molecular primary ion species containing more than 6 atoms. We could not find an influence of the chemical composition of the primary ion (SF_5^+/$C_7H_7^+$ e.g.) on this enhancement under static SIMS conditions. We compared the secondary ion and secondary neutral emission depths under atomic and molecular primary ion bombardment, and determined the influence of primary ion energy on secondary ion emission.

4:00pm AS1-MoA7 Enriched Spectral-information from TOF-SIMS Spectra of Self Assembled Monolayers: More Than Just Molecular Ions, *D.J. Graham, B.D. Ratner,* University of Washington
Engineered biomaterials that accurately trigger complex biological processes such as healing require complex surface modifications. This increase in complexity must be met by equally capable surface analysis tools such as TOF-SIMS. To extract information from complex organic surfaces, one should consider the spectrum as a whole, instead of selecting only a few key peaks. This study demonstrates that the information content of a TOF-SIMS spectrum does not reside solely in the molecular and cluster ions, but that each region of the spectrum contains enough information to clearly distinguish the samples. For this study dodecanethiol self-assembled monolayers (SAMs) were prepared from 0.01mMol solutions in ethanol for different times (2sec,1min,5min,15 min,30 min,1hr,24hr,6d). Principal component analysis (PCA) models from the TOF-SIMS negative and positive spectra were constructed using the entire data set and from partial data sets from mass ranges m/z=0-100,100-200,200-300,400-500,500-1000. Scores plots from the PCA models show that data from each set were able to distinguish the samples. Regions containing the molecular ions showed enhanced ability to distinguish the samples. In the overall model it was seen that there is a relative increase in the intensity of low mass hydrocarbon fragments (C to C3) with increasing time. Similar trends were seen in the positive spectra where a relative increase of C to C4 hydrocarbon fragments was seen with increasing time. This increase was accompanied by a decrease in the intensity of C5 and above hydrocarbon fragments. This data suggests that as the SAM surface becomes more ordered and crystalline, the emission of longer fragments from the thiol chains is reduced relative to the emission of short fragments. As there is also an enhancement of the emission of the thiol head group ion, it is believed that these short fragments arise by the clipping of the tops of the assembled layer by the primary ion or energetic secondary ions.

4:20pm AS1-MoA8 Static SIMS with Polyatomic Primary Ions, *A. Benninghoven, D. Stapel, O. Brox, B. Burkhardt, H.F. Arlinghaus, C. Crone, M. Thiemann,* Universität Münster, Germany
Polyatomic primary ion bombardment results in an increase in secondary ion yields Y and damage cross sections σ in such a way that the ion formation efficiency E = Y/σ increases. Investigated samples include metal and semiconductor surfaces (Ag, Si, GaAs) in different oxidation states, bulk and spin coated polymers with additives (PET, PC, PI, PP, PTFE, PMMA, PEG), SA- and LB - mono and - multilayers (thioles, arachidic acid on Au, PMA on Ag), hydrocarbon contamination layers on Si and GaAs, monolayers of biomolecules on Ag and other substrates, and biopolymers, technical polymers and pharmaceuticals isolated in an organic matrix. They have been bombarded by a variety of primary ions in the keV range O, Ne, Ar, Xe, O_2, CO_2, SF_5, C_7H_7, $C_{10}H_8$, C_6F_6 and $C_{10}F_8$. For atomic primary ions we found an increase in secondary ion yields with increasing mass of the primary ion, but only relatively small increases in efficiency. Compared with atomic ion bombardment, molecular primary ion bombardment always results in a yield and efficiency enhancements. No significant influence of the chemical

composition of the primary ions on secondary ion yields has been observed, as long as static SIMS conditions were met. Yield and efficiency enhancements show saturation behaviour for primary ions composed of more than 6 (heavy) atoms. We found a strong dependence of the enhancement effects on the considered secondary ion species and a smaller averaged secondary ion emission depth for molecular primary ion bombardment. We will summarize our experimental results and will discuss them in the frame of a simple model. Whereas yield and damage cross section enhancements can be explained - at least partially - by an increase in sputter yields, the observed increase in ion formation efficiencies for molecular primary ions indicates a more efficient ionization process for polyatomic primary ion impact.

4:40pm **AS1-MoA9 Quantitative ToF-SIMS and XPS Studies of Surface Structures in Alkyl Side-Chain Polyetherurethanes**, *S.C. Porter, D.G. Castner, B.D. Ratner,* University of Washington
Surface enrichment of polyether soft segment (SS) is typical in segmented polyetherurethanes (PEUs). The incorporation of surface active side-chains (SC) into the relatively polar hard segment (HS) block of the polymer significantly alters the surface structure. PEUs having various lengths and densities of alkyl SCs were synthesized. XPS analysis showed that PEUs with long SCs had high surface concentrations of hydrocarbon (HC) chains. Similarly, HS blocks were drawn toward, and concentrated just below, the HC rich surface. Positive ToF-SIMS spectra of these polymers contained fragments unique to both the HS and SS of the PEUs. Numerous HC fragments from the set, ($^+C_xH_{2x+1}$ and $^+C_xH_{2x-1}$; $x <= 7$), could be indirectly associated with the length and/or density of alkyl SCs. Negative spectra contained fragments unique to individual SC species and HS fragments analogous to those found in the positive spectra. Ion ratios were used to determine the HS/SS (pos. spectra) and SC/HS (neg. spectra) surface concentration ratios. The HS/SS and SC/HS ratios increased with both side-chain length and density. Comparison of log(HS/SS) to actual concentration ratios obtained from XPS data, yielded linear correlations. The correlations improved as the sampling depth of the XPS experiments approached that of SIMS. The presence of isomeric HS fragment pairs in both positive and negative SIMS spectra provided an intrinsic reference for direct comparisons of the intensity of the positive HC fragments with a negative SC fragment. An analytical relation based on theoretical ion intensities was established for a series of PEUs having the same SC. Ion ratios from the positive spectra and a ratio from the negative spectra were shown to be directly proportional. The proportionality constant was solely a function of the ionization probabilities for the various ions utilized. HC fragments which did not contain contributions from either the HS or SS showed good correlations with the SC fragment intensity.

5:00pm **AS1-MoA10 Molecular Secondary Neutral Emission from Molecular Overlayers under SF_5^+-Bombardment**, *A. Schnieders, M. Schröder, D. Stapel, H.F. Arlinghaus, A. Benninghoven,* Universität Münster, Germany
It is well known that TOF-SIMS and in favourable cases laser postionization of sputtered neutrals (Laser-SNMS) are powerful tools for the analysis of organic surface species. Many efforts have been made to enhance the sensitivity and the efficiency of these techniques. Especially the use of polyatomic primary ions for the analysis of molecular overlayers results in an enhanced secondary ion emission compared to the use of atomic primary ions. We have investigated the influence of polyatomic primary ions on the secondary neutral emission with the intention to improve our understanding of the processes of molecular sputtering and ion formation. We used a reflectron-type time-of-flight mass spectrometer equipped with an electron impact gas ion source for sputtering. As primary ion species we chose Ar^+, Xe^+, and SF_5^+. For postionization of sputtered neutral molecular species a subpicosecond excimer laser system operating at 248 nm was available. As model systems we used molecular layers of adenine and alanine prepared on liquid nitrogen cooled substrates (Si, Au, ...). They were produced by evaporation of the molecules from a Knudsen cell under UHV condition. During overlayer formation the flux of sputtered secondary neutrals and secondary ions was continuously monitored under static sputtering conditions. We determined the influence of the substrate and of the layer thickness on the secondary ion and neutral yields under bombardment with the different primary ions. We found that neutral as well as ion yields from a submonolayer coverage are higher than for a multilayer. The yield enhancement depends on the sputtering conditions. We also determined kinetic energy distributions and disappearance cross sections as a function of layer thickness. A detailed discussion with special emphasis on the

sputter process - including results on the internal excitation of sputtered molecules - will be presented.

Author Index

Bold page numbers indicate presenter

— A —

Arlinghaus, H.F.: AS1-MoA10, 2; AS1-MoA8, 1

— B —

Benninghoven, A.: AS1-MoA10, 2; AS1-MoA6, 1; AS1-MoA8, **1**

Briggs, D.: AS1-MoA3, **1**

Brox, O.: AS1-MoA8, 1

Burkhardt, B.: AS1-MoA8, 1

— C —

Castner, D.G.: AS1-MoA9, 2

Crone, C.: AS1-MoA8, 1

— G —

Graham, D.J.: AS1-MoA7, 1

— H —

Hagenhoff, B.: AS1-MoA5, 1; AS1-MoA6, 1

— K —

Kersting, R.: AS1-MoA5, **1**

— P —

Pijpers, A.P.: AS1-MoA5, 1

Porter, S.C.: AS1-MoA9, **2**

— R —

Ratner, B.D.: AS1-MoA7, **1**; AS1-MoA9, 2

— S —

Schnieders, A.: AS1-MoA10, **2**

Schröder, M.: AS1-MoA10, 2

Schwede, B.C.: AS1-MoA5, 1

Stapel, D.: AS1-MoA10, 2; AS1-MoA6, **1**; AS1-MoA8, 1

— T —

Thiemann, M.: AS1-MoA6, 1; AS1-MoA8, 1

— V —

Verlaek, R.: AS1-MoA5, 1