SIMS Solutions in Materials and Life Sciences
Room Great Lakes C - Session SS-ThM4

Polymers

Moderators: Satoshi Ninomiya, University of Yamanashi, **Michaeleen Pacholski**, Dow Chemical Company

10:20am **SS-ThM4-11 Advances in Polymer Science by ToF-SIMS Depth Profiling**, ***Tanguy Terlier***, *D. Lee,* Rice University*; C. Bottoms,* University of Tennessee Knoxville*; A. Masud, A. Karim,* University of Houston*; G. Stein,* University of Tennessee Knoxville*; R. Verduzco,* Rice University **INVITED**

Over the last two decades, we have seen remarkable advances in the development and understanding of organic materials using ToF-SIMS. The introduction of polyatomic ion beam technology such as the argon gas cluster ion beam has made it possible to access quasi-intact molecular information and offered a high sputter efficiency for etching the organic films. This evolution has benefited polymer science by providing a tool to examine spatial variations in the chemistry of multicomponent polymer films. Thus, various studies have shown that it is now possible to monitor a variety of processes such as diffusion in photoresists and surface segregation in polymer blends. A key challenge is using ToF-SIMS data to extract quantitative parameters, such as diffusion constants or surface excesses, and this has motivated us to study how to quantify the depth-dependent composition of the ToF-SIMS depth profiles.

While the sputter mechanisms have been carefully studied, the quantification of the ion distribution in depth profiles remains challenging due to the ionization process and the complexity of the fragmentation mechanism.

This work will focus on different approaches to converting the profiles into quantitative information. To illustrate the challenges and the potential outcomes of the quantitative depth profiles, we have limited our investigation to the migration process with two-compound systems.

We will begin by presenting an overview of the analytical challenges in ToF-SIMS depth profiling of polymer films. We will then detail our approach for quantifying the depth-dependent composition in a polymer film, which consists of three steps: identification of characteristic molecular ions from pure material films; use of miscible blends with known composition to examine the linearity of the molecular ion ratio and measure the sputter yield for each mixture; and conversion of the ion intensity distribution into the composition as a function of depth.

With this procedure, we can elucidate the segregation behavior of bottlebrush polymer blended with linear polymer by determining the relationship between surface excesses at interfaces and properties of polymer films. We have also used this method to measure molecular diffusivities through analysis of bilayer samples and compared these observations with molecular simulations. Finally, we determined how to quantify the dopant concentration throughout a polymer film, which has permitted us to characterize the in-depth distribution of an ionic liquid in self-assembled block copolymer films.

Thus, we will demonstrate the possibilities of quantifying different types of the migration process in polymer films by ToF-SIMS.

11:00am **SS-ThM4-15 Keynote Industrial Talk: Characterizing Bonding of Perfluoropolyether Lubricants to Magnetic Recording Disks by Tof-Sims***,* ***Alan Spool,*** Western Digital Corporation **INVITED**

The bonding of perfluoropolyether lubricants to magnetic recording disks is one of the keys to longevity of the head disk interfaces in these devices.Bonding is defined in the industry by the degree to which the lubricant after application can be removed from the surface with a solvent rinse.The exact nature of the bonds between the lubricant and the disk is not fully understood.It may be either a result of hydrogen bonding between the alcohol end-groups on the polymer lubricants and surface moieties, or covalent bonding may occur.

In this study, the increasing difficulty in removing lubricant from the disk surface by solvent extraction is shown to directly correlate with changes in the TOF-SIMS spectra through the study of Z-Tetraol, a perfluoropolyether lubricant used in the industry for many years which has four alcohol groups, two at each end of the chain. The hypothesis that a stronger attachment to the surface would reduce the intensities of fragments whose formation would require desorption of intact or nearly intact polymer chain end-groups from the surface was confirmed by experiments in which disks with lubricant bonded to different degrees were analyzed.In addition to the identification of peaks in the complex negative ion spectra, their assignments to likely structures, and the comparisons of their intensities, disappearance cross section measurements were performed.The significance of the results with respect to ion formation mechanisms are considered.

11:40am **SS-ThM4-19 Depth Profiling in Thick Polymer Films with Ar and O_2 Gas Cluster Ion Beam Sources***,* ***Christine Mahoney,*** *K. Adib, R. Yongsunthon,* Corning Research and Development Corporation*; B. Burger,* Corning Varioptic, France

Gas cluster ion beam sources (GCIB) are a very important tools at Corning and have many uses ranging from sputter cleaning of glass surfaces to depth profiling of organic coatings.Recently, we have been utilizing both Ar GCIB and O_2 GCIB sources to probe the chemistries of both glass and polymer substrates.Here we describe our most recent work in depth-profiling of thick (>500 nm) polymeric films under different ion beam conditions.Two important polymer systems were interrogated:1) parylene C films (~4 µm), and 2) plasma polymerized hexa(methyldisiloxane) (HMDSO), a silicone-based film with an irregular structure (~500 nm).Both films represent classes of materials that can be used for making hydrophobic conformal coatings.The literature regarding the surfaces and in-depth analysis of these materials is sparse.The overall effect of ion beam impact energy (5 keV, 10 keV and 20 keV), as well as the chemistry of the ion beam (O_2 vs Ar GCIB) on the resulting depth profiles were investigated.Furthermore, the chemistry and morphology of the sputtered crater bottoms were characterized in detail with a combination of X-Ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM).The results highlight the importance of beam chemistry in polymeric depth profiling with GCIB.

12:00pm **SS-ThM4-21 Gas Cluster Ion Scattering: A Local Probe of the Ferroelectric to Paraelectric Transition in P(VDF-ran-TrFE) Copolymers***, M. Chundak, C. Poleunis, A. Jonas,* ***Arnaud Delcorte,*** Université Catholique de Louvain, Belgium

Secondary ion mass spectrometry (SIMS) is widely recognized for its detailed information on the chemical and molecular composition of surfaces and coatings, with submicron lateral resolution and nanoscale depth resolution. The technique reached a new pinnacle with the use of large gas cluster ion beams (GCIB), such as $Ar_{500\text{-}5000}^+$, which induce softer desorption from organic and biological samples, with important applications in bio-imaging, damageless depth-profiling and even protein soft-landing [1]. Ar-GCIB can also provide local information about the physical properties of polymer surfaces, in a variant of the technique coined gas cluster ion scattering spectrometry or GCISS. Indeed, the distribution of backscattered Ar_n^+ ($n \leq 7$) clusters observed in the positive SIMS spectra proved to depend on the surface structural and mechanical properties. For instance, GCISS was used to locally determine the glass transition temperature of (ultra)thin films of thermoplastics, thermosets and even plasma-deposited coatings [2], where classical techniques are inadequate.

For this contribution, GCISS was applied to polyvinylidene fluoride-trifluoroethylene P(VDF-*ran*-TrFE) ferroelectric copolymers with a range of compositions (Fig. 1). The Ar_n^+ ion intensities were measured upon 10 keV Ar_{3000}^+ bombardment of the films and the intensity ratios $Ar_2^+/(Ar_2^++Ar_3^+)$ and $Ar_2^+/(Ar_2^++Ar_4^+)$), representing the dissociation rate of the Ar cluster projectiles, are shown to depend on the structural changes of the polymer surfaces. These intensity ratios provide direct access to the surface transition temperature T_T (related to the bulk glass transition T_g of the material), but are also sensitive to more subtle changes such as the ferroelectric to paraelectric transition of P(VDF-*ran*-TrFE) occurring at the Curie temperature (T_c) [3]. Comparison with our DSC measurements and with mechanical measurements from the literature show that the surface Curie transition remains close to the bulk value in these copolymers. This study confirms that GCISS constitutes a versatile approach for the local measurement of physical transitions occurring in polymer thin films.

[1] A. Delcorte et al., *Large cluster ions: Soft local probes and tools for organic and bio surfaces*, Phys. Chem. Chem. Phys., 2020, 22, 17427-17447.

[2] N. Vinx et al., *Investigating the relationship between the mechanical properties of plasma polymer-like thin films and their glass transition temperature*, Soft Matter, 2021,17, 10032-10041.

[3] M. Chundak et al., *Probing the Surface Curie Temperature of Ferroelectric P(VDF-ran-TrFE) Copolymers by Argon Gas Cluster Ion Scattering*, J. Phys. Chem. C 2022, 126, 1125−1131.

Author Index

Bold page numbers indicate presenter