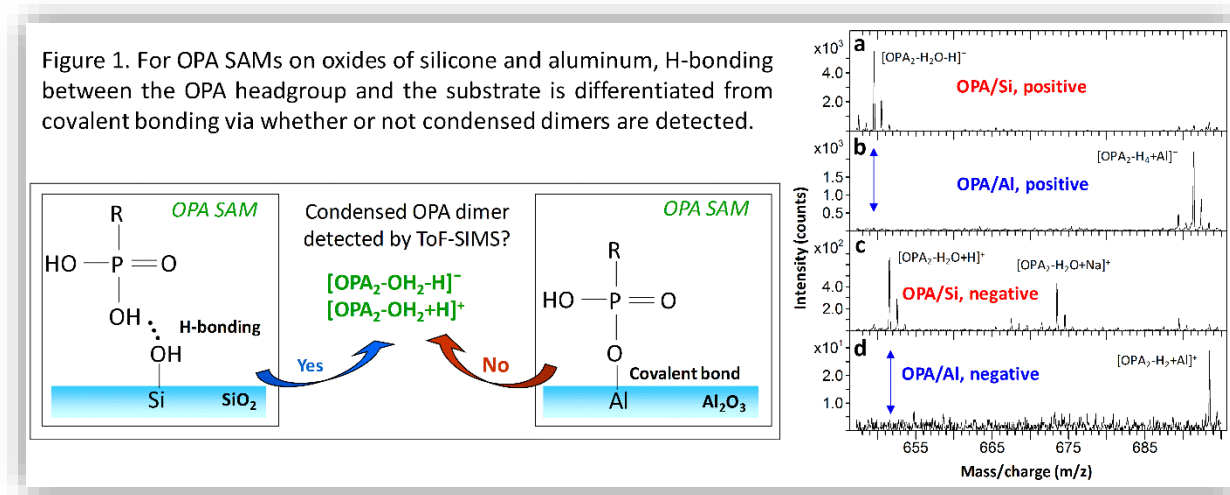# Applications of Time-of-Fight Secondary Ion Mass Spectrometry (ToF-SIMS) in Surface/Interface Chemistry and Materials Science

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ToF-SIMS is a powerful, surface-sensitive analytical technique that provides rich chemical information hidden in the (secondary) ions generated from the surface of the specimen bombarded by an energetic (primary) beam. Its imaging and depth profiling capabilities make ToF-SIMS a unique exploratory surface/interfacial analysis technique. The following examples illustrate the depth and breadth of the powerful ToF-SISM technique.

ToF-SIMS as an exploratory technique for surface/interfacial chemistry

The detection of condensed OPA dimers serves as an analytical criterion for ToF-SIMS to reveal the bonding mode of OPA molecules in their SAMs on different oxides. As shown in **Figure 1**, condensed octadecylphosphonic acid (OPA) dimers, i.e., two OPA molecules combined with the loss of a water molecule, were detected by ToF-SIMS on OPA self-assembled monolayers (SAMs) that are only weakly bonded on the native oxide layer of a silicon wafer ([Anal. Chem. 2010, 82, 3371-3376](#)). In contrast, these condensed dimers were absent on OPA SAMs formed on the oxide layer of an aluminum film, where the OPA molecules are chemically bonded on the substrate through P-O-Al linkage. These observations lead us to conclude that the OPA molecules in their SAMs have to be free from chemical bonding with the substrate in order for the primary ion beam to generate ion fragments of the condensed dimer.

Figure 1. For OPA SAMs on oxides of silicone and aluminum, H-bonding between the OPA headgroup and the substrate is differentiated from covalent bonding via whether or not condensed dimers are detected.

Data-driven ToF-SIMS analysis approach

The rich chemical information provided by ToF-SIMS ion mass spectra lies in the form of fragment ions, which often amount to hundreds, leading to the possibility of identifying chemicals and exploring surface chemistry. Facing such a daunting number of ions (i.e., variables) detected in ToF-SIMS, dimensionality reduction techniques such as principal component analysis (PCA), a multivariate data analysis method, have proven useful in revealing similarities or differences of ions in terms of the variability of their intensities and can be used to differentiate a polymer with different molecular weights or different polymers. The original variables (i.e., ions in the ToF-SIMS case) are transformed to a much smaller

number of new orthogonal variables (PCs), which are linear combinations of the original variables. he PCs are transformed from the original data under the condition that the first PC accounts for as much of the variance in the original data as possible, with the following PCs picking up the remaining maximum variances subsequently. PCA allows one to compare numerous observations (data) over multiple variables in a biplot, which is constructed by a plot of the scores of the observations on two PCs (often the first two PCs) overlapped with a plot of loadings of the variables on the same two PCs. A biplot visualizes the similarities and differences among the multivariate observations, their relationships with the variables and the correlations between the variables.

Shown in **Figure 2** (Surf. Interface Anal. 2017, 49, 1431-1441) is a covariance biplot for the scores of the observations as points and loadings of the variables as arrowed lines, both on PC1 and PC2, for polyethylene (PE), polypropylene (PP), polyisoprene (PIP) and polystyrene (PS). The score of an observation on a PC is the sum of the individual ion intensity of each variable multiplied by the loading of the corresponding variable on the PC. In other words, it is the projection of all the C_nH^- intensities of an observation on a PC, or how an observation is expressed as a single point on the PC axis. A score plot is used to determine similarities or differences among observations. The score plot in **Figure 2** shows that the four polymers are separated into four groups.

An arrowed line of a variable may be called a "*variable vector*", serving to point the direction of the variable in the PCs coordinates. The smaller an angle between two variable vectors of two C_nH^-, the more similarly the two variables behave
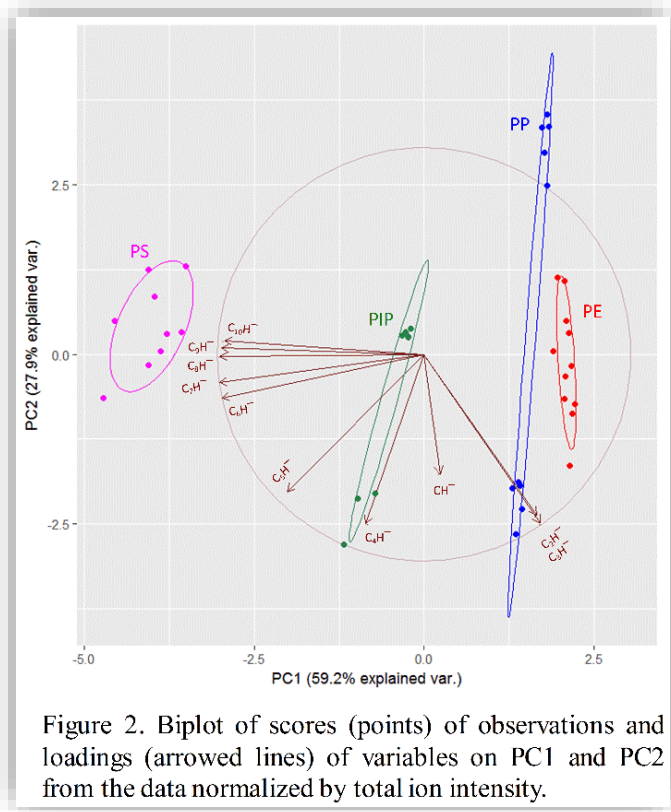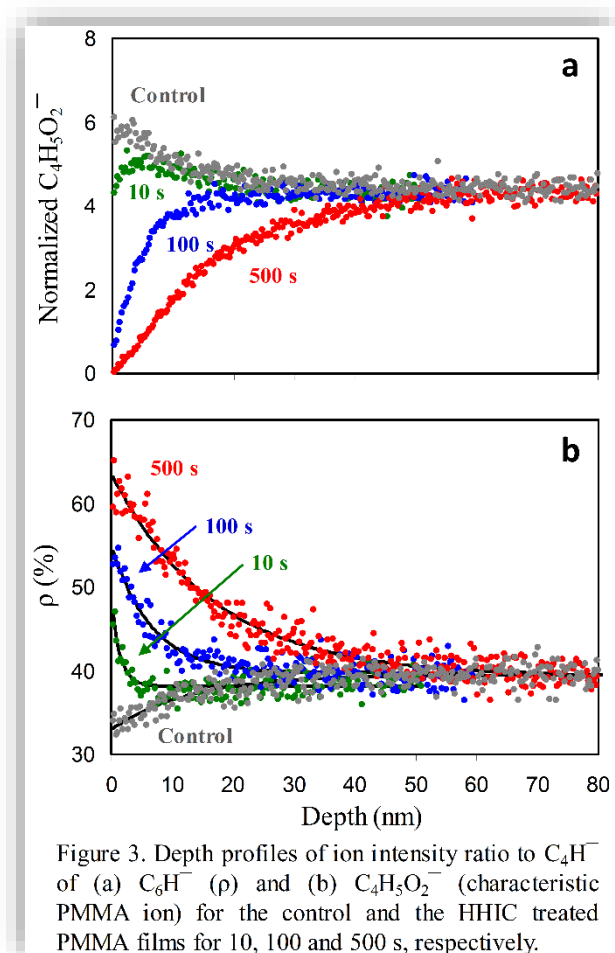

Figure 2. Biplot of scores (points) of observations and loadings (arrowed lines) of variables on PC1 and PC2 from the data normalized by total ion intensity.

in terms of their variability in their ion intensities. In other words, two variables are positively or negatively correlated if the angle between their variable vectors is close to 0 or 180º, respectively. On the other hand, an angle close to 90º indicates that the two variables are not correlated at all. The loading plot in **Figure 2** shows clearly the similarities among C_6H^- to $C_{10}H^-$ for their significant contributions to PC1. By contrast, the variable vectors of C_2H^- and C_3H^- point to (approximately) the opposite direction and with increased loadings on PC2. This indicates that the intensities of the two groups of ions vary in opposite directions, that is, when the ion intensities of one group measured on a polymer sample increase, those of the other group decrease.

Assisted by the PCA results, we confirmed that lower and higher "carbon density" polymers favor the formation of smaller (e.g., C_2H^- and C_3H^-) and larger (i.e., C_6H^- to $C_{10}H^-$) C_nH^-, respectively. Moreover, we found that the variability of the C_4H^- intensity against different polymers is relatively small in comparison with other C_nH^- intensities. The PCA results shown in **Figure 2** verified our argument that with increased "carbon density", ion intensities of larger C_nH^- increase while those of smaller C_nH^- decrease. Therefore, it is the "carbon density" of polymers dictate the variability of C_nH^- intensities, which is captured by PC1.

A ToF-SIMS approach to quantifying and depth profiling cross-linking degrees of thin polymers

An approach based on ToF-SIMS was developed to determine the degree of cross-linking on the surface and its variations in a nanometer-scale depth of organic materials. ToF-SIMS is extremely surface sensitive and capable of depth profiling with the use of a sputter ion beam to remove controllable amounts of substance. Poly(methyl methacrylate) (PMMA) films spin-coated on a Si substrate were cross-linked using a recently developed, surface sensitive, hyperthermal hydrogen projectile bombardment technique. The ion intensity ratio between two ubiquitous hydrocarbon species C_6H^- and C_4H^- detected in ToF-SIMS, denoted as ρ, was used to assess the degree of cross-linking of the PMMA films. The cross-linking depth of the PMMA films was revealed by depth profiling ρ into the polymer films using a C_{60}^+ sputter beam. The control PMMA film spin-coated on a Si substrate was characterized by $\rho=32\%$ on its surface when using a 25 keV Bi_3^+ primary ion beam. This parameter on the PMMA films subjected to HHIC treatment for 10, 100 and 500 s increased to 45%, 56% and 65%, respectively. The depth profiles of ρ obtained using a 10 keV C_{60}^+ ion beam resembled an exponential decay, from which the cross-linking depth was estimated to be 3, 15 and 39 nm, respectively, for the three cross-linked PMMA films. As shown in **Figure 3a** the characteristic PMMA ion $C_4H_5O_2^-$ shows the variation of cross-linking degree of PMMA ([Rapid Commun. Mass Spectrom. 2018, 31, 381-388](#)). **Figure 3b** shows that the ion intensity ratio ρ between C_6H^- to C_4H^- detected in ToF-SIMS provides a unique and simple means to assess the degree of cross-linking of the surface of PMMA films cross-linked by the surface sensitive hyperthermal hydrogen projectile bombardment technique. The ToF-SIMS approach is capable of depth profiling ultra thin organic films nanometer resolutions.

Figure 3. Depth profiles of ion intensity ratio to C_4H^- of (a) C_6H^- (ρ) and (b) $C_4H_5O_2^-$ (characteristic PMMA ion) for the control and the HHIC treated PMMA films for 10, 100 and 500 s, respectively.

ToF-SIMS 3D imaging

As an antibiotic that prevents and treats infections caused by Gram-positive bacteria such as *Staphylococcus aureus*, vancomycin incorporated in a biodegradable polymer poly(lactide-*co*-glycolide) provides an effective way to construct controlled-release drug delivery systems. Developments associated with this promising system have been largely limited to the areas of drug delivery kinetics and biodegradability. In order to provide surface analytical approaches to this important system, the applicability of TioF-SISM in three-dimensional molecular imaging for a model system consisting of alternating layers of PLGA and vancomycin is demonstrated.

The multilayer PLGA/vancomycin/PLGA spin-coated on a Si substrate (**Figure 4a**) was depth profiled using a 10 keV C_{60}^+ sputter ion beam ([Biointerphases 2018, 13, 03B401](#)). It has been verified that there are numerous ion species that are suitable for depth profiling the layered structure. For clarity purposes, presented in **Figure 4g** depth profiles of CN^-, Cl^- and $C_7H_4O_2Cl^-$ for vancomycin and $C_2H_3O_3^-$ and $C_3H_3O_3^-$ for PLGA. Shown in **Figure 4b** is overlapped images of Cl^- (red) and $C_3H_3O_3^-$ (green) depicting the cross section of the layered structure. **Figures 4c-4f** show ion images of Cl^- and $C_3H_3O_3^-$ of the planes at four different depth indicated by the arrowed lines between them and **Figure 4b**. Therefore, ToF-SIMS is a powerful technique to identify molecules (and elements) and their 3D locations with a lateral resolution of ~1 μm and a depth resolution of 1 nm.
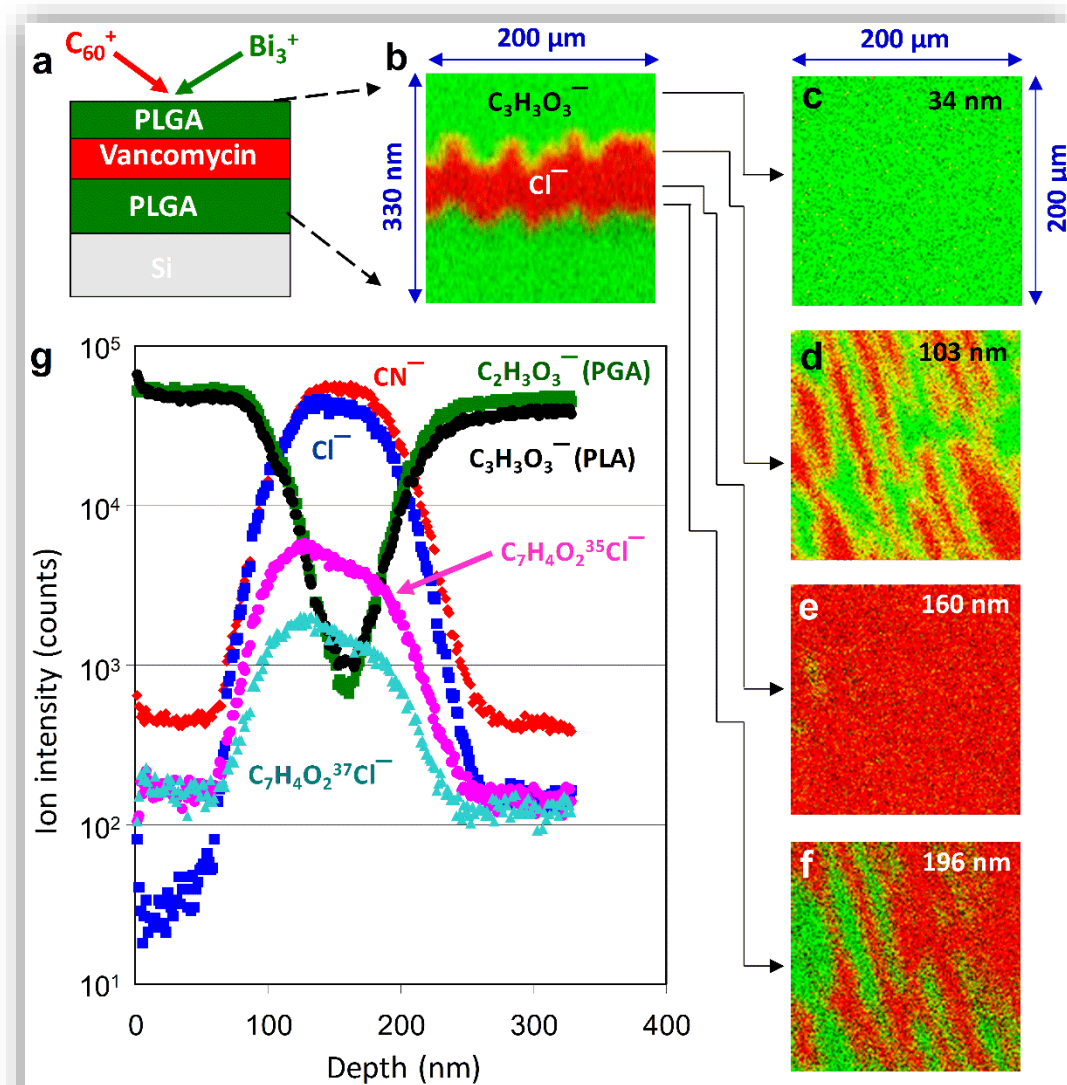

Figure 4. The PLGA/vancomycin/PLGA layers prepared on a Si wafer (a) and a cross section (b) of the layers expressed by intensities of $C_3H_3O_3^-$ (green in color) and Cl^- (red) for PLGA and vancomycin, respectively. As shown in b, the probed depth is 330 nm over a rastered area of 200 μm × 200 μm. The overlapped images of $C_3H_3O_3^-$ and Cl^- (c-f) show distributions of PLGA and vancomycin at depths of 34, 103, 160 and 196, respectively. The depth profiles (g) of ions CN^-, Cl^-, $C_7H_4O_2{}^{35}Cl^-$ and $C_7H_4O_2{}^{37}Cl^-$ represent vancomycin layer, while those of $C_2H_3O_3^-$ and $C_3H_3O_3^-$ the PLGA layers.