PHYSICAL ELECTRONICS
A DIVISION OF ULVAC-PHI

3D Characterization of PS/P2VP Block Copolymer Films by TOF-SIMS with GCIB Sputtering

Overview: Polymers are relatively inexpensive and are easily modified to achieve tailored chemical and physical properties. The 3-dimensional structure of a polymer blend is a primary factor in determining its physical properties. Imaging time-of-flight secondary ion mass spectrometry (TOF-SIMS) provides a unique tool to visualize 2-dimensional molecular information. With the use of new ion beams, such as a beam of massive inert gas cluster ions (e.g. $Ar_{2,500}^+$), it is also possible to visualize 3-dimensional molecular information. The recent introduction of liquid metal ion beams has increased the sensitivity of TOF-SIMS toward structurally significant molecular ions for the purpose of high contrast chemical imaging at a spatial resolution of ≤ 300 nm. In this Note we use a PHI *nanoTOF* to demonstrate the capability to collect and visualize, in 3 dimensions, structurally significant molecular information of phase-segregated block copolymer films composed of polystyrene (PS) and poly(2-vinylpyridine) (P2VP). The *nanoTOF* is equipped with a Bi cluster liquid metal ion gun (LMIG) for chemical imaging and an inert gas cluster ion beam (GCIB) column for nondestructive molecular depth profiling.

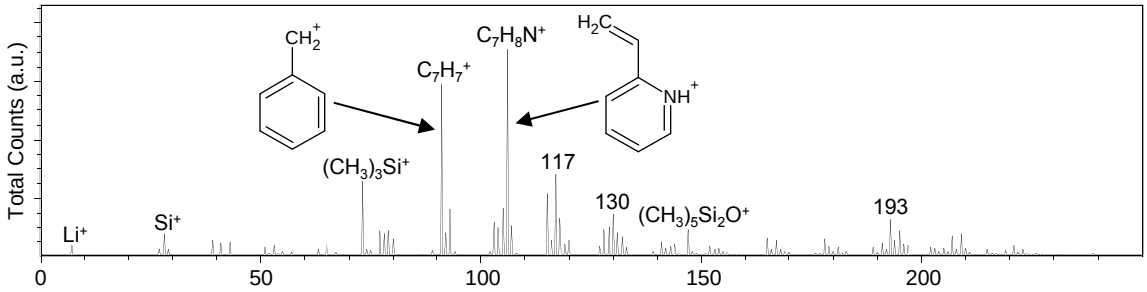

Figure 1. Positive ion polarity TOF-SIMS mass spectrum of the PS:P2VP block copolymer film. The structurally significant ions from PS ($C_7H_7^+$, 91 m/z) and from P2VP ($C_7H_8N^+$, 106 m/z) that are used for depth profile and 3D image analysis are indicated. Peaks arising from silicone contamination and the Si substrate are also indicated.

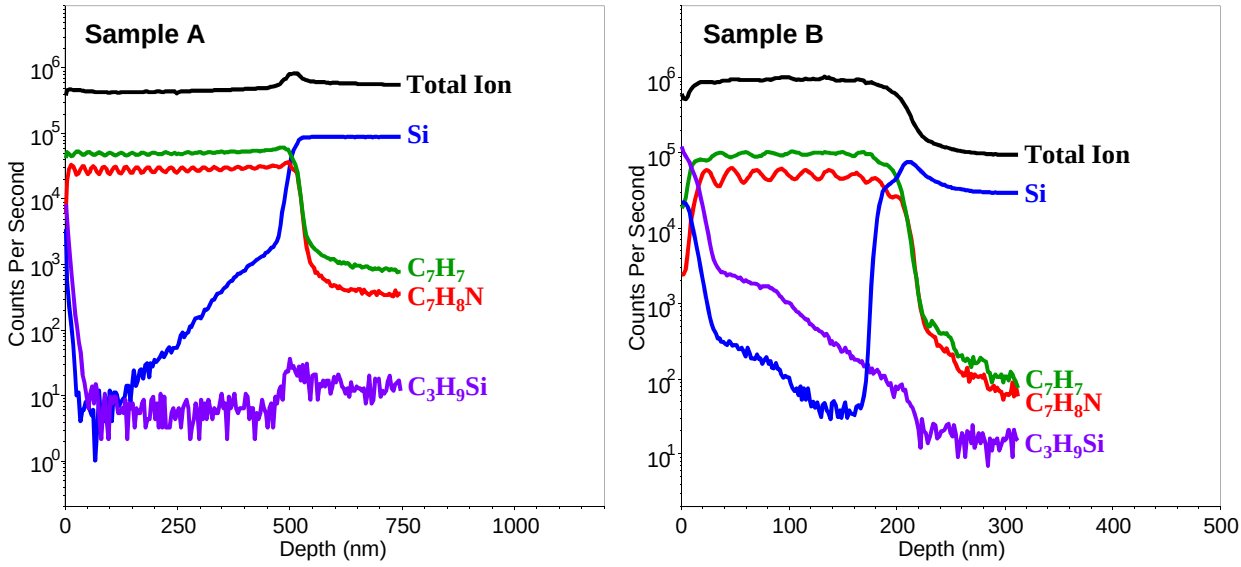

Figure 2. Positive ion polarity depth profiles of PS:P2VP block copolymer films. (Sample A) The film is approximately 500 nm thick and is comprised of 40 inhomogeneous layers of PS and P2VP. The copolymer film is more disordered near the Si interface. Very little silicone contamination is observed, and is present predominantly at the surface. (Sample B) The copolymer film is approximately 220 nm thick and is comprised of 18 inhomogeneous layers of PS and P2VP. The film is more ordered in comparison to Sample A, but there is a higher level of silicone contamination as revealed by the $C_3H_9Si^+$ (73 m/z) profile.

Experimental: The block copolymer films were analyzed in the as-received state. All TOF-SIMS measurements were made on a PHI TRIFT V *nanoTOF* equipped with a Bi cluster LMIG and a GCIB column. A 60 keV Bi_3^{++} primary ion beam, operating at a DC current of 10 nA (Sample A) or 3.2 nA (Sample B), was used to acquire chemical images in the positive secondary ion polarity. The analysis beam was digitally rastered at 256 pixels x 256 pixels over a 200 µm x 200 µm field-of-view. The primary ion dose was maintained well within the static limit, $9.8x10^6$ Bi_3^{++}/cm^2 (Sample A) or $6.5x10^{10}$ Bi_3^{++}/cm^2 (Sample B), for each analysis cycle. Depth profiling was accomplished using a beam of 5 keV $Ar_{2,500}^+$ delivered from the GCIB column at a DC current of 5 nA, and digitally rastered over a 400 µm x 400 µm area, at a dose of $1.4x10^{14}$ $Ar_{2,500}^+/cm^2$ per sputter cycle. Charge compensation was easily achieved with ≤ 15 eV e^- and ≤ 10 eV Ar^+ delivered by the PHI-patented dual-beam charge neutralization system. A raw data stream file was collected to allow full post-acquisition evaluation (i.e. retrospective analysis) as well as 3D imaging and 3D iso-surface modeling.

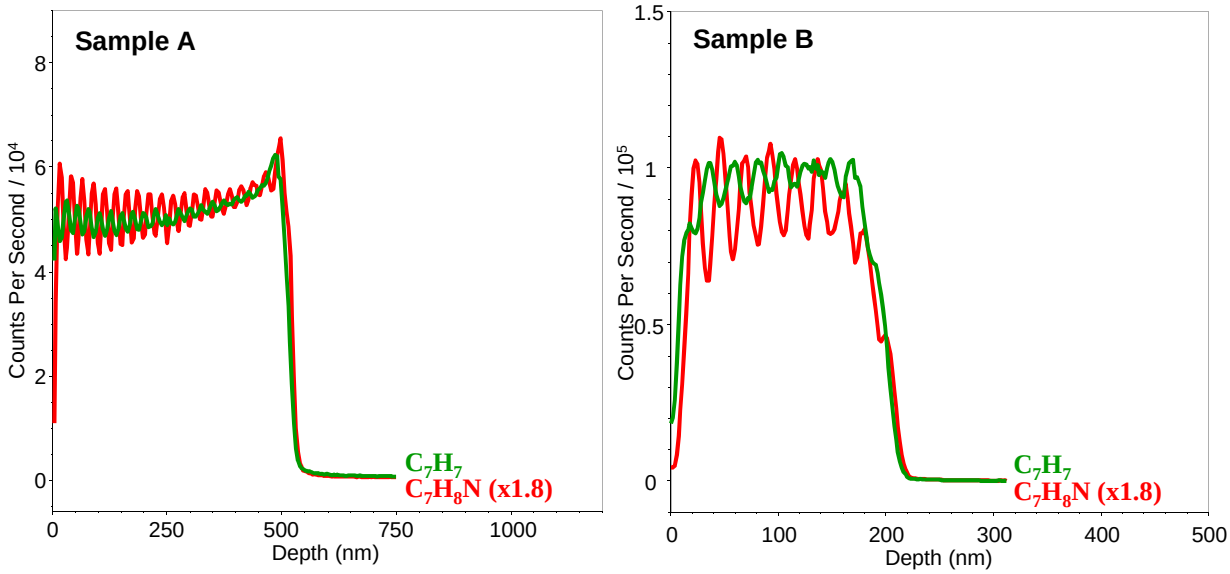

Figure 3. Positive ion polarity depth profiles of the PS:P2VP block copolymer films. (Sample A) The depth profiles of PS and P2VP are shown on a linear scale to reveal the 40 layers (20 bi-layers). The phase segregation appears to produce greater layer separation near the surface. (Sample B) The depth profiles of PS and P2VP are shown on a linear scale to reveal the 18 layers (9 bi-layers). The phase segregation in each bi-layer appears more complete, and more uniform as a function of depth.

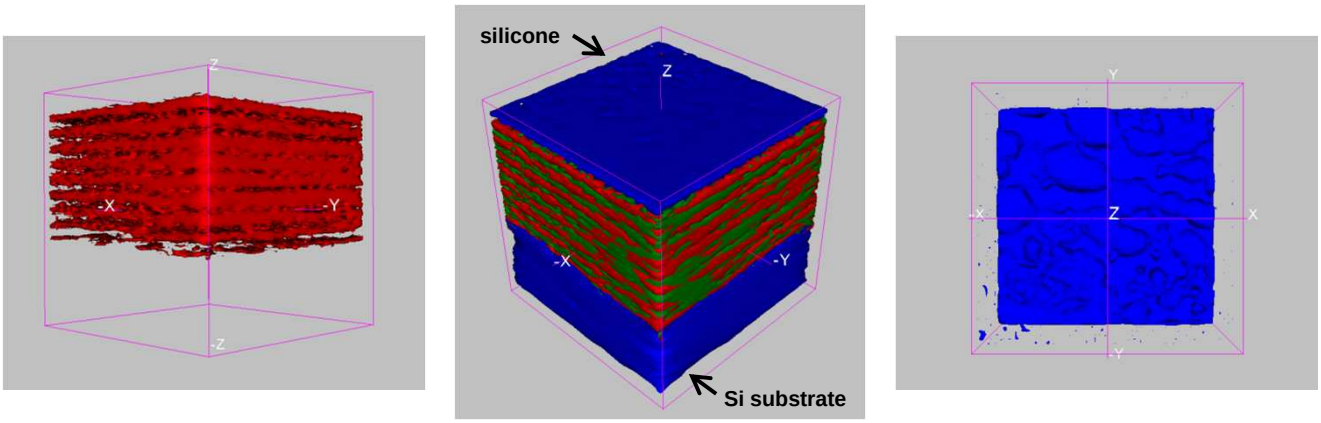

Figure 4. 3D TOF-SIMS chemical iso-surface images from the positive secondary ion polarity of the PS:P2VP block copolymer film of Sample B. In each 3D image, the lateral (surface) field-of-view is 200 µm x 200 µm. (LEFT) A side view of the 3D iso-surface model of $C_7H_8N^+$ revealing the 9 layers of P2VP in the 220 nm thick copolymer film. (CENTER) A 3D iso-surface overlay of $C_7H_8N^+$ (P2VP, red), $C_7H_7^+$ (PS, green) and Si^+ (blue) showing the silicone at the surface, the 18 alternating layers of PS and P2VP in the 220 nm thick copolymer film, and the Si substrate. (RIGHT) A top-down view of the 3D iso-surface model of Si^+ illustrating the inhomogeneity at the copolymer/substrate interface.

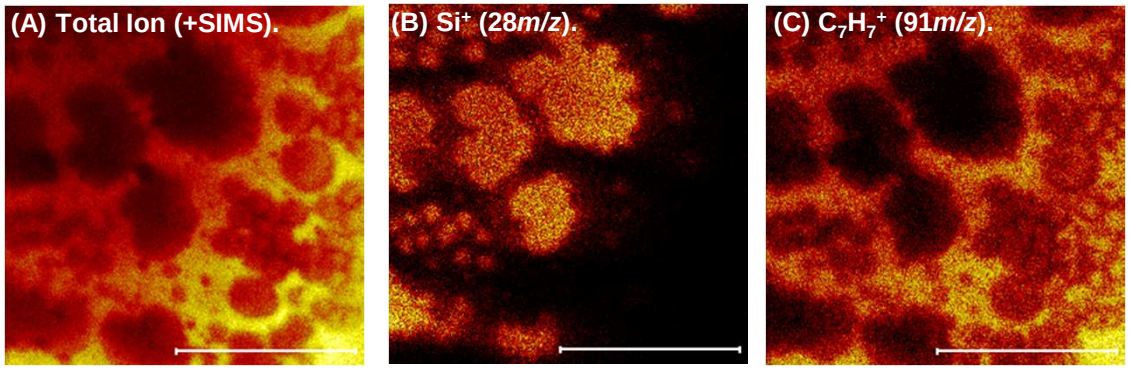

Figure 5. Positive ion polarity TOF-SIMS chemical images of the block copolymer thin film Sample B following collection of the depth profile and 3D image data. Each image is a 200 µm x 200 µm field-of-view (the marker is 100 µm). The Si^+ and $C_7H_7^+$ images in panels (B) and (C), respectively, reveal a high degree of inhomogeneity at the copolymer/substrate interface.

Results: The structurally significant molecular ions of PS and P2VP used for depth profiling and 3D imaging are identified in Figure 1. The secondary ions that are characteristic of the substrate and the silicone contamination are also identified. The depth profiles of Samples A and B are given in Figure 2. The depth profiles of Sample A, as well as the PS and P2VP signals plotted on a linear scale in Figure 3, reveal 20 phase-segregated bi-layers of the block copolymer. The profiles of Sample A indicate a surface layer of silicone contamination but, more importantly, indicates a high degree of disorder in the 200 – 250 nm of the copolymer film above the substrate. The disorder is recognized by the increasing slope of the Si^+ profile (Figure 2A) and the decreasing magnitude of the $C_7H_7^+$ and $C_7H_8N^+$ oscillations (Figure 3A). Similarly, the depth profiles of Sample B reveal that the block copolymer has phase-segregated to 9 bi-layers. A higher degree of phase segregation is indicated by the large signal variation between the layers as shown on the linear scale plot in Figure 3B. The depth profiles of Sample B also indicate a greater quantity of silicone contamination which has migrated throughout the film. However, the Si^+ profile of Sample B indicates less disorder near the copolymer/substrate interface as indicated by the sharp rise in the Si^+ signal at the interface.

A set of 3D images given in Figure 4 exposes the general structure of the block copolymer film of Sample B. Namely, as represented by the 3D iso-surface model of $C_7H_7^+$, the block copolymer is not segregated into chemically homogeneous layers. Upon close inspection of the 3D image data one may deduce that the PS and P2VP layers are comprised of micelle structures and are not phase pure. A 3D iso-surface overlay further illustrates the impure phases of the block copolymer film, and also shows the silicone surface contamination layer as well as the Si substrate. A top-down view of the Si substrate 3D iso-surface model reveals some chemical inhomogeneity at the copolymer/substrate interface that appears in the iso-surface model as topographic features. The chemical inhomogeneity at the copolymer/substrate interface is further illustrated in Figure 5 where the displayed images were acquired within the depth profile crater following the depth profile/3D image data acquisition. The images produced from the Si^+ and the $C_7H_7^+$ signals are complimentary and reveal the micelle structure within the phase-segregated domains of the copolymer.

Conclusion: 3D TOF-SIMS chemical imaging was demonstrated with the PHI TRIFT V *nanoTOF* using a Bi cluster LMIG and an $Ar_{2,500}^+$ GCIB to observe the structure of a spontaneously phase-segregated PS:P2VP block copolymer. The high sensitivity of *nanoTOF*'s TRIFT analyzer, combined with new ion beam technologies for nondestructive molecular depth profiling, enables 3D visualization of molecular structures.

Acknowledgements and References:
We gratefully acknowledge Dr. Thomas Mates from UC – Santa Barbara for providing the samples.

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