Cleaning Polymer Surfaces with the PHI 06-C60 Sputter Ion Gun

Introduction

Polymer surfaces have been studied by XPS for over 30 years. During that time analysts have been limited in their ability to probe below surface contamination or into organic thin films because removing material with sputter ion guns caused significant chemical damage to organic and polymer based materials. The new PHI 06-C60 C_{60} sputter ion gun has been shown to provide the ability to remove surface contaminants from polymer surfaces and to depth profile organic thin films while causing minimal damage to the remaining surface.[1] This new capability has the potential to open many new application areas for XPS. To demonstrate this capability data was collected from a commercial polymer (PET) container using Ar and C_{60} ions to remove a surface contamination layer.

Experimental

A commercial PET beverage container with a printed product labeling wrapper was used for this study. The wrapper was removed and the exposed PET surface was analyzed to identify the composition and thickness of a possible contaminant left on the PET, using a PHI XPS instrument equipped with a monochromatic Al x-ray source. One section of this material was sputter cleaned using a 500 V Ar ion beam at a 45˚ incidence angle relative to the plane of the sample surface. A second section of the same material was sputter cleaned using a 10 kV C_{60} ion beam at 20˚ incidence angle relative to the plane of the sample surface.

Results

Figure 2 shows survey spectra collected after sputtering the PET container multiple times with a 10 kV C_{60} ion beam. Figure 3 contains similar data collected after sputtering the PET container with a 500 V Ar ion beam. Both data sets show the presence of a contamination layer that contains Si. Using PHI *MultiPak* to extract quantitative elemental information from the survey spectra, compositional sputter depth profiles were created for both samples and are shown in figures 4 and 5. The depth profile data shows the contamination layer to be approximately 1 nm thick. High energy resolution Si 2p spectra indicate that the silicon has a binding energy typical for that of a silicone.

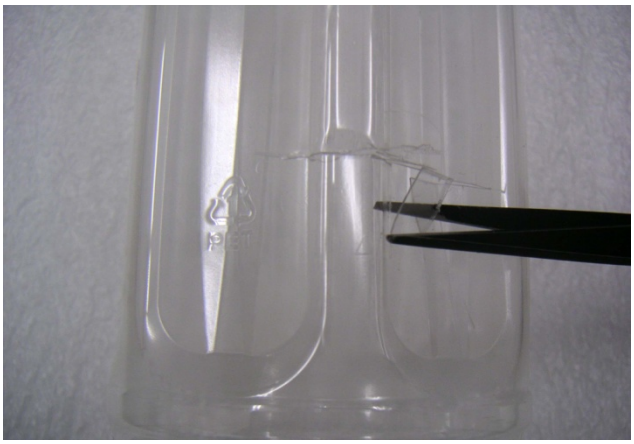

Figure 1. Photograph of the commercial PET container that was examined for the presence of surface contaminants.

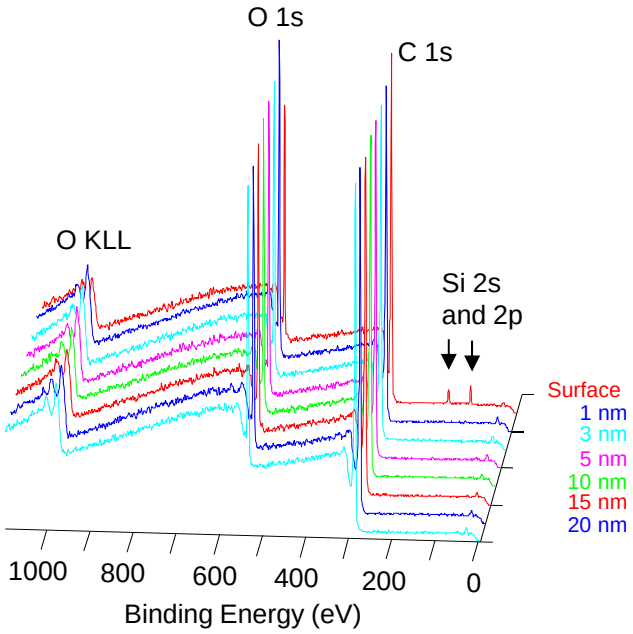

Figure 2. Spectra from the PET container obtained after sputtering the surface with a 10 kV C_{60} ion beam.

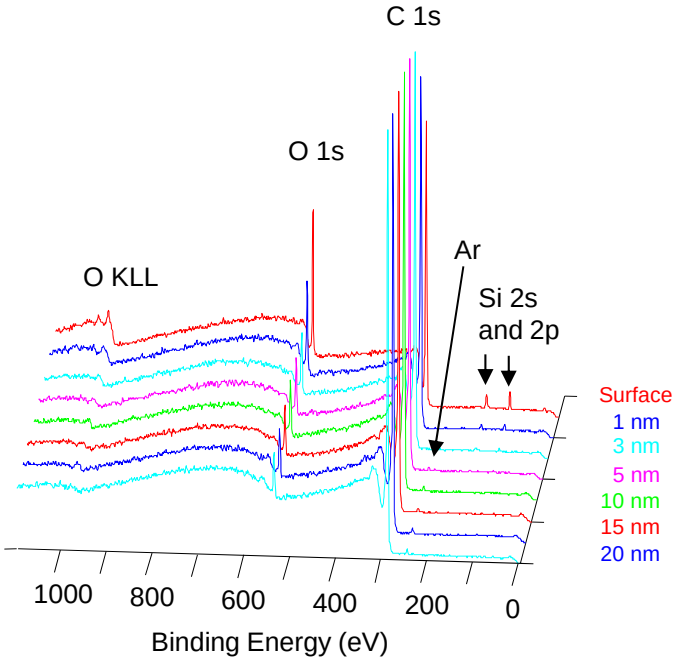

Figure 3. Spectra from the PET container obtained after sputtering the surface with a 500 V Ar ion beam.

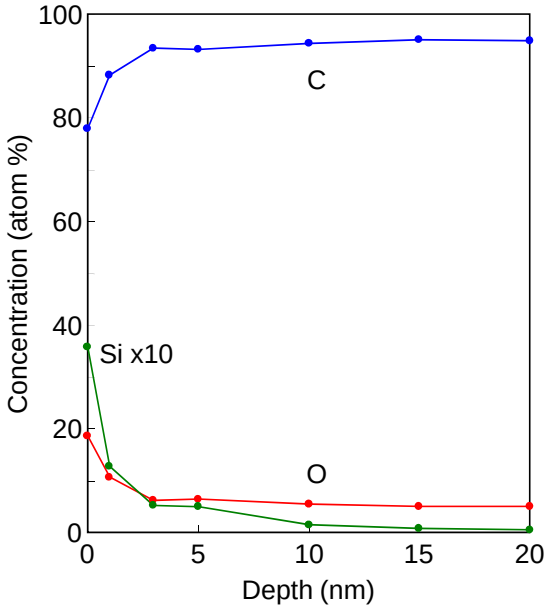

Figure 5. Sputter depth profile of contaminated PET container obtained using 500 V Ar ion beam

Both C_{60} and Ar sputtering removed the silicone contamination layer. However, the quantitative sputter depth profile plots in Figures 4 and 5 show the preferential removal of O from the PET surface with Ar sputtering and little or no loss of O when using the C_{60} ion beam for sputtering. The sputter etch rates were based on an SiO_2 film sputtered under the same conditions.

High energy resolution C and O spectra obtained as a function of sputtering depth using a 10 kV C_{60} ion beam are shown in Figure 6. The C 1s and O 1s spectral shapes remain nearly constant as a function of sputter depth while etching with the C_{60} ion beam. The ratio of the two O 1s peaks is 1 to 1, as expected for PET, with the exception of the surface spectrum where O from the silicone enhances the intensity of the lower binding energy peak. The C 1s spectra maintain the characteristic shape of PET down to the final depth of 20 nm.

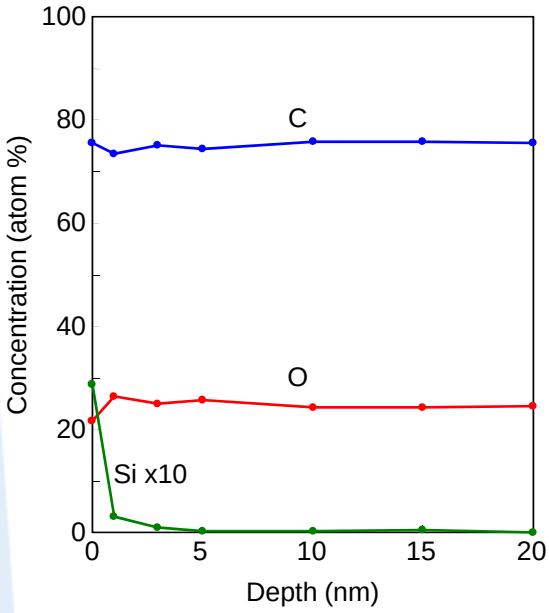

Figure 4. Sputter depth profile of contaminated PET container obtained using 10 kV C_{60} ion beam

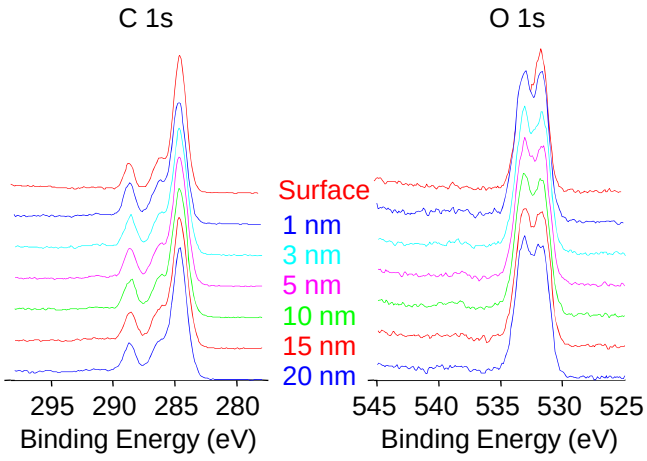

Figure 6. High resolution C 1s (left) and O 1s (right) spectra of the PET container obtained as a function of sputtering depth with a 10 kV C_{60} ion beam

High energy resolution C and O spectra obtained as a function of sputtering depth using a 500 V Ar ion beam are shown in Figure 7. The O 1s spectra initially show the loss of the lower binding energy peak associated with the silicone contamination. However, as sputtering continues the O 1s spectra show a loss of total O as a function of depth. In a similar manner the C 1s spectra show a loss of O containing C species. Together the O and C spectra show the chemical damage that occurs when sputtering the PET container with an Ar ion beam.

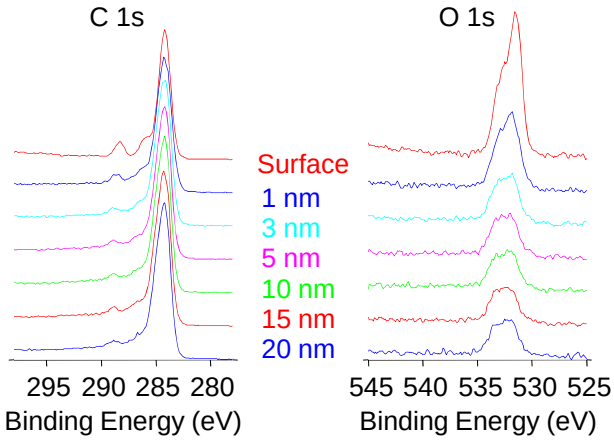

Figure 7. High resolution C 1s (left) and O 1s (right) spectra of the PET container obtained as a function of sputtering depth with a 500 V Ar ion beam

High energy resolution C and O spectra were obtained after sputtering to a depth of 50 nm with a 10 kV C_{60} ion beam on the PET container. Curve-fits of the C 1s and O 1s spectra are shown in Figures 8 and 9 respectively. The strong π–π* shake-up satellites observed in the C 1s data indicate a very low level of chemical damage occurred with the C_{60} sputter cleaning.

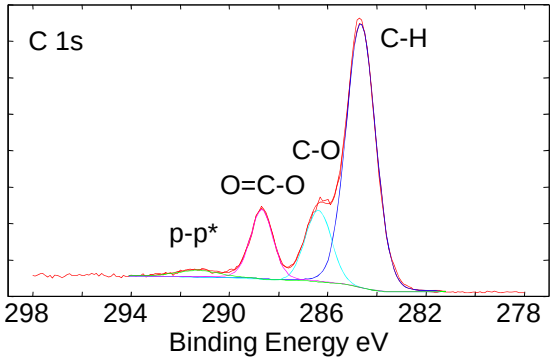

Figure 8. High energy resolution C 1s spectrum obtained after a 50 nm C_{60} sputter etch

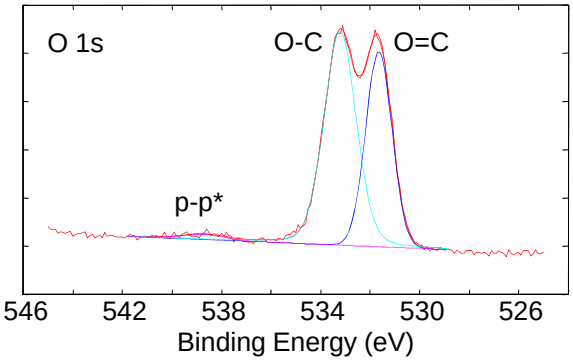

Figure 9. High energy resolution O 1s spectrum obtained after a 50 nm C_{60} sputter etch

X-ray monochromator excited valence band spectra can also provide a powerful tool to understand chemical changes in polymers. Figure 10 shows the valence band spectra from the PET container sputtered to the depths of 2 nm and 50 nm with a 10kV C_{60} ion beam and a reference spectrum acquired from pure PET. [2] A detailed comparison of these spectra indicate that the 10 kV C_{60} ion beam leaves the surface with very little observed chemical damage. A small difference at approximately 7 eV binding energy may be due to a small loss of hydrogen caused by the C_{60} sputtering.

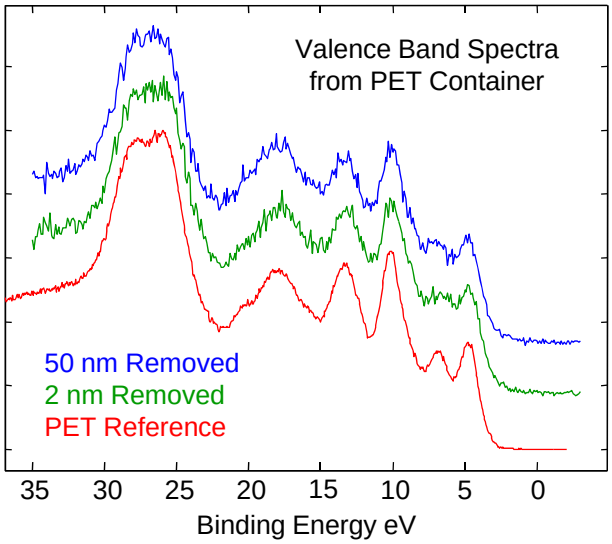

Figure 10. High energy resolution valence band spectra obtained after 2 nm and 50 nm C_{60} sputter etchings compared to a PET reference spectrum

Conclusions

A surface contamination layer on a PET container was removed with a C_{60} ion beam, which caused minimal chemical damage to the remaining polymer surface. Depth profiling the PET container to a depth of 50 nm with a C_{60} ion beam produced data that showed nearly constant chemical composition. In contrast a low energy Ar ion beam used to obtain the same measurements produced data that showed evidence of significant chemical damage that increased with sputtering depth.

References:

[1] PHI Technical Bulletin: Organic Depth Profiling with the PHI 06-C60 Sputter Ion Gun
[2] The XPS of polymers Database, Surface Spectra, Ed. By G. Beamson and D. Briggs

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