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# XPS Depth Profiling of Polystyrene with a $C_{60}$ Cluster Ion Source

**Overview:** Since its introduction in 2004[1] the $C_{60}$ cluster ion source has been widely used with both XPS and TOF-SIMS for the depth profiling of many organic materials[2]. Due to its high sputter rate for type II polymers[3], the removal rate can be greater than the damage depth of the incident $C_{60}$ ion resulting in a surface after $C_{60}$ ion bombardment which has an undamaged chemical and molecular composition. The high sputter rate has been attributed to the high rate of polymer chain scission associated with cluster beam bombardment of typical type II polymers[3]. With optimized ion gun parameters, the removal of all forms of ultra-thin organic contamination as well as type II polymer depth profiles up to several hundred nm's have been reported. The depth profiling of type I polymers has been much more problematic. Type I polymers typically undergo chain crosslinking under ion beam irradiation. Polystyrene, one of the most widely used consumer plastics, has an aromatic ring and a hydrocarbon backbone typical of type I polymers. This Note explores the use of Zalar Rotation™ (azimuthal rotation), a $LN_2$ cold stage, and a 20 keV $C_{60}$ cluster ion source to optimize the XPS depth profiling experimental parameters for characterizing 100 nm thin films of polystyrene.

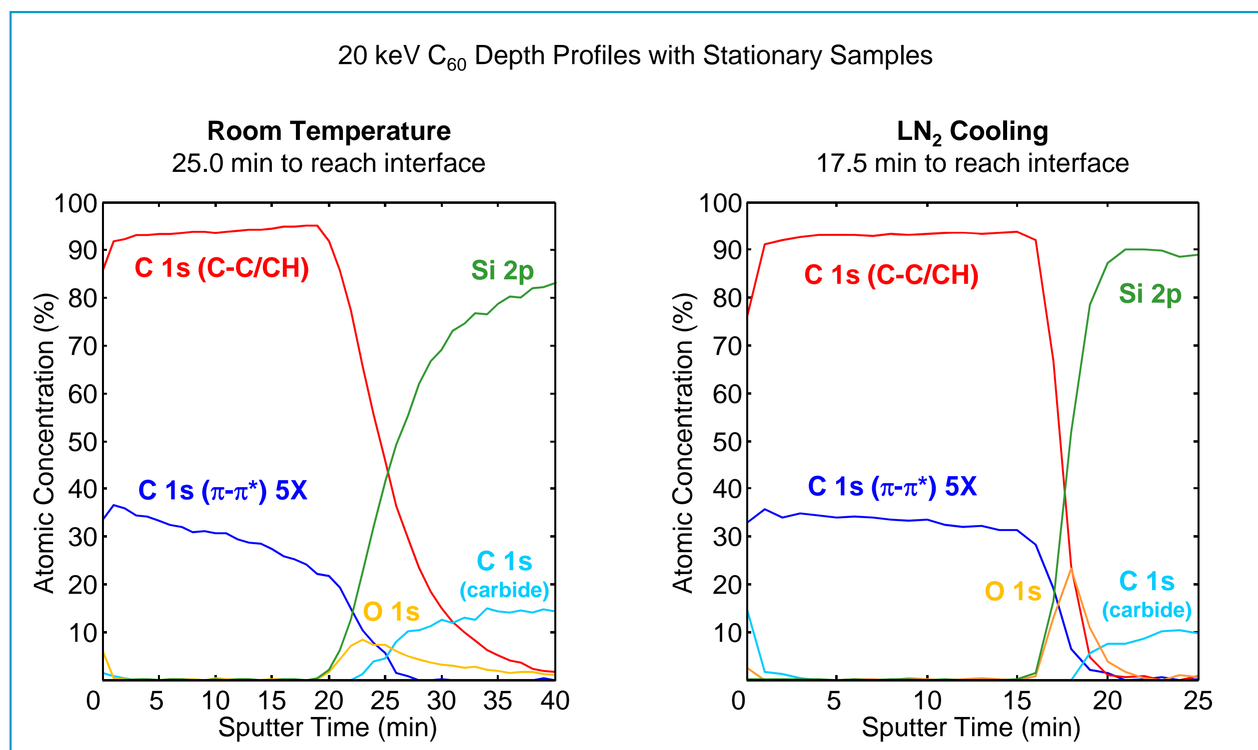


*Figure 1. Left panel shows the concentration depth profile of a stationary 100 nm thick sample of polystyrene at room temperature. The concentrations of the C-C and C-H C 1s peak as well as the C 1s ($\pi$-$\pi$*) peak (scale expansion of 5X) are shown. The presence of a native silicon oxide on the silicon wafer substrate is also noted. Implantation of carbon as silicon carbide in the silicon wafer is also noted. The right panel shows a similar depth profile where the sample was cooled with $LN_2$.*

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**Depth Profile Measurements:** Spin cast 100 nm thin films of polystyrene were prepared on silicon wafer with a native silicon oxide on the surface. The samples were analyzed in a PHI *VersaProbe* II equipped with a scanning x-ray monochromator and a computer controlled 5-axis cold stage to facilitate stationary and Zalar Rotation depth profiling at both room temperature and with $LN_2$ cooling. The 20 keV $C_{60}$ cluster ion source provided an incident beam 70º from sample normal for all depth profiles. The rastered 10 nA ion beam current produced a sputter rate of 1.2 nm/min with a standard $SiO_2$ thin film calibration sample.

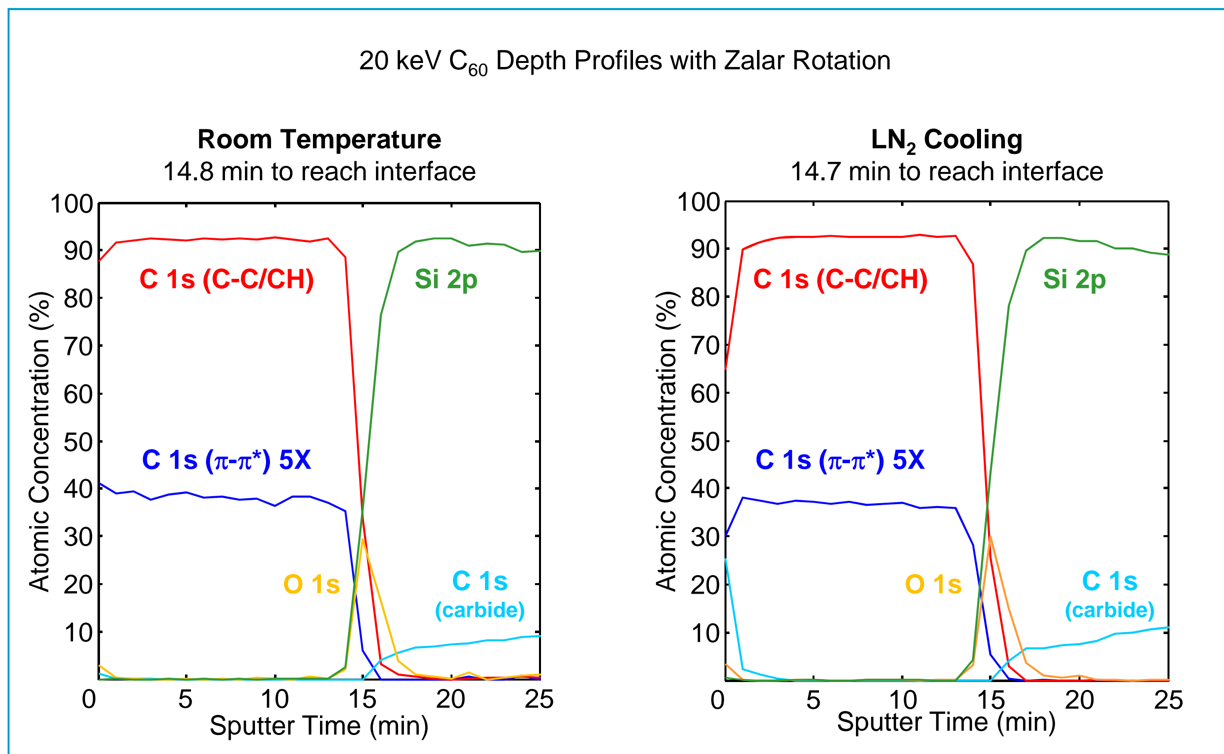


*Figure 2. Left panel shows the concentration depth profile with Zalar Rotation of a 100 nm thick sample of polystyrene at room temperature. The right panel shows a similar depth profile with Zalar Rotation and the sample cooled with $LN_2$.*

**Results:** The table below summarizes the four different conditions used for the depth profiling. The concentration of the C 1s ($\pi$-$\pi$*) peak is a measure of the intact aromatic ring in the polystyrene during the depth profile. The interface width provides an indication of the roughening of the crater bottom during the profile. The sputter time to the interface is an indication of the average sputter rate for the polystyrene film with the experimental conditions used.

| Experimental Conditions | ($\pi$-$\pi$*) Relative Reduction | Interface Width | Sputter Time to Interface |
|---|---|---|---|
| Stationary Room Temperature | 39 % | 21.6 nm | 25.0 min. |
| Stationary $LN_2$ Cooling | 10% | 10.9 nm | 17.5 min. |
| Zalar Rotation Room Temperature | 6% | 6.0 nm | 14.8 min. |
| Zalar Rotation $LN_2$ Cooling | 4% | 5.8 nm | 14.7 min. |

The broad interface width and the long sputter time to the interface for the stationary sample at room temperature compared to the other conditions suggests that a slower sputter rate is also associated with roughening at the bottom of the sputter crater. Previous XPS and TOF-SIMS depth profiles of poly(ethylene terephthalate), a type II polymer, with $C_{60}$ have suggested that the slow sputter rate and the broad interface may be associated with carbon (perhaps as crosslinking) buildup as a function of sputter time. Carbon buildup could also help explain the high 39% relative reduction in the C 1s ($\pi$-$\pi^*$) peak intensity. Cooling with $LN_2$ has been suggested as a way of decreasing free radical induced crosslinking. The 2x decrease in the reduction of the C 1s ($\pi$-$\pi^*$) peak intensity as well as the 4x reduction in the measured interface width and the faster sputter rate obtained by cooling a stationary sample with $LN_2$ suggests much less buildup of the slower sputtering carbon material.

The greatest improvement is observed with Zalar Rotation. There is a 3.5x decrease in the reduction of the C 1s ($\pi$-$\pi^*$) peak intensity as well as a 6.5x reduction in the measured interface width and the faster sputter rate obtained by rotating the sample at room temperature. The reduction of crater roughening with Zalar Rotation has been demonstrated for over 20 years for inorganic samples. This data shows a dramatic improvement for organic depth profiling, even with type I polymers. An additional small improvement in the reduction in the C 1s ($\pi$-$\pi^*$) peak intensity as well as a reduction in the measured interface width and even faster sputter rate is observed by combining Zalar Rotation with $LN_2$ sample cooling.

It is interesting to note that cooling the sample as well as Zalar Rotation has almost no effect on the implantation of carbon from the $C_{60}$ ion beam into the silicon wafer and the formation of silicon carbide. A minor artifact of $LN_2$ sample cooling is a very thin layer of oxygen (probably $H_2O$) which is observed in the first cycle of the two profiles acquired with $LN_2$ cooling, although no temperature induced oxygen deposition was observed after the start of the depth profiles. It is also noteworthy that the 20 keV $C_{60}$ cluster ion source has a sputter rate of approximately 25 $nm^3$/ion for this most challenging type I polymer.

**Conclusion:** $C_{60}$ cluster ion depth profiling has been shown to provide excellent XPS chemical state information with minimal damage on a 100 nm thick type I polymer sample (polystyrene) when combined with Zalar (azimuthal) Rotation. $LN_2$ cooling of the sample for either stationary (significant improvement) or Zalar rotation depth profiling (minor improvement) also improves the chemical state integrity of the polystyrene depth profile. The PHI *VersaProbe* II can be equipped with a unique optional computer controlled stage that facilitates Zalar Rotation at either room temperature or with $LN_2$ cooling.

**References:**

1. N. Sanada, A. Yamamoto, R. Oiwa and Y. Ohashi, *Surf. Interface Anal.,* **36** 280 (2004).
2. T. Nabuta and T. Ogawa, *J. Mater. Sci.* **44**, 1800 (2009).
3. C. Mahoney, *Mass Spectrometry Reviews***,** DOI 10.1002/mas

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