Polymer analysis by pulsed radiofrequency glow discharge mass spectrometry

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We have evaluated the analytical capabilities of radiofrequency glow discharge mass spectrometry for some polymers. A prototype instrument developed with Tofwerk AG and Horiba Jobin Yvon combines a pulsed RF glow discharge with a time-of-flight mass spectrometer.

Sputtering and subsequent plasma reactions produce a mass spectrum consisting of mostly small molecular fragments that can be used to identify polymers (‘fingerprint’ spectra). We have used both positive and negative ions to demonstrate depth profiling of spin coated PMMA/Si, PETi/Si, PMMA/PET and PS/PETi/Si thin films.

To understand the polymer mass spectra in more detail, we compared GD-ToF-MS results from PTFE with ToF-SIMS and found evidence of gas-phase reactions occurring in the plasma. We also compared mass spectra from different polymers with similar elemental compositions (PET, PBT and PMMA) and found the same molecular ions ($C_xH_yO_z^+$); only the relative abundance of the ions was different for different polymers. We also found $C_xH_y^+$ ions that could not be produced simply by sputtering as they are not present in the polymer structure.

Parametric studies (pressure, power and RF pulse length) showed that the mass spectra were very sensitive to changes in the discharge conditions. For all the polymers we studied (PET, PBT, PE, PTFE), lower pressure resulted in lower ion signals in general while gas phase reactions seemed to become less significant. The peak power affected the mass spectrum in a peculiar way. Some polymer related peaks had a maximum at 5 W, others had a maximum at 15 W while the third group did not show significant power dependence in the 5–70 W range. The effect of the pulse length was different on different polymers. The PE mass spectrum did not depend on pulse length, while all the ions from PET decreased by a factor of 10 and all the ions from PTFE dropped by a factor of 100 as the pulse length increased from 100 µs to 500 µs. These results suggest that the sputtered molecular material has a strong effect on the plasma and that the ion signals are not simply proportional to the amount of material sputtered.