Organic Secondary Ion Mass Spectrometry: Signal Enhancement by Water Vapor Injection

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The enhancement of the static secondary ion mass spectrometry (SIMS) signals resulting from the injection, closely to the sample surface, of H_2O vapor at relatively high-pressure, was investigated for a set of organic materials. While the ion signals are generally improved with increasing H_2O pressure upon 12 keV Ga^+ bombardment, a specific enhancement of the protonated ion intensity is clearly demonstrated in each case. For instance, the presence of H_2O vapor induces an enhancement by one order of magnitude of the $[M + H]^+$ static SIMS intensity for the antioxidant Irgafos 168 and a ~1.5-fold increase for polymers such as poly(vinyl pyrrolidone). (J Am Soc Mass Spectrom 2010, 21, 2005–2010) © 2010 American Society for Mass Spectrometry

In the last two decades, static SIMS has become one of the most useful techniques for organic, polymeric, and biochemical materials characterization [1–5]. In conjunction with instrumental developments, specific sample preparation procedures have been proposed to improve the molecular signal intensities for organic materials. The utilization of matrices, such as those used in matrix-assisted laser desorption ionization (MALDI), was found to improve sensitivity very significantly by increasing the intensity of the protonated molecular ions [6, 7]. Another protocol, using metal condensation over the organic surface, was called metal assisted-SIMS (MetA-SIMS). It was found to enhance the yields of characteristic ions by one or two orders of magnitude depending on the sample, and even more in some instances [8–10]. With the advent of polyatomic projectiles, such as $SF_5{}^+$, $C_{60}{}^+$, $Bi_n{}^+$, and $Au_n{}^+$, huge molecular ion yield enhancements have been measured (up to 1000-fold increases in signal compared with Ga^+ atomic projectiles), leading to a revolution of the field of organic SIMS characterization [11–15]. With the additional molecular depth profiling capabilities of $SF_5{}^+$ and $C_{60}{}^+$ cluster beams, one can now hope to relate the performance characteristics of organic devices to their surface molecular composition in a much more quantitative way. Nevertheless, in spite of these multiple improvements, useful molecular signals remain low for the next generation of organic SIMS applications, involving nanometer-scale 3D molecular characterization of surfaces. Indeed, if some current cluster beams can be focused to a diameter of 100 nm or less, the corresponding reduction of the interrogated volume raises again the level of sensitivity needed for analysis. Therefore, what the field needs today is a method that can be associated to cluster beam bombardment to provide an additional level of molecular signal enhancement.

Since the emergence of SIMS, it has been shown that the ionization probability depends highly on the chemical environment [16]. This effect is routinely used in SIMS depth profiling by applying oxygen sputtering to increase positive ion yields and cesium sputtering to increase negative ion yields [17, 18]. In those cases, the secondary ion yields strongly increase with the concentration of the reactive species. Ions can also be formed by the recombination of a sputtered neutral atom M or cluster with an emitted Cs^+ ion giving a MCs^+ secondary ion, an effect that is used for quantitative depth profiling [19]. It has also been recognized in inorganic SIMS that the secondary ion yield is high for elements that form a strong ionic bond with oxygen [20], fluorine [21], or chlorine [22]. Following this idea, different gas flooding techniques have been proposed. For instance, Gao et al. [22] and Sielanko et al. [23] found significant secondary ion yield enhancements for many elements, using CCl_4 gas flooding combined with oxygen ion bombardment and CF_2Cl_2 gas flooding under cesium ion bombardment, respectively. In addition, it is known from the focused ion beam (FIB) milling of organic materials that H_2O injection at high-pressure increases the sputter rates by a factor of 10 and more [24]. Even the sputtering of diamond is enhanced by H_2O injection. Finally, the water ice present upon sample freezing of biological materials for SIMS analysis is also believed to be an efficient source of protons for cationization [25–27]. Therefore, flooding the analyzed surface with H_2O gas appears to be a promising approach to enhance the molecular ion yields in organic SIMS.

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In this article, we report on H_2O vapor flooding experiments that lead to a significant enhancement of the positive SIMS intensities of a set of organic materials. This new protocol, tested with a 12 keV Ga^+ primary beam, is easily transferable to other bombardment conditions. The role of the H_2O pressure in the specific intensity enhancement of protonated ions emitted from a polymer antioxidant and from high-molecular-weight polymers was examined in detail.

Experimental

Samples

Various organic molecules, including antioxidant *Tris* (2,4-di-*tert*-butylphenyl) phosphite (Irgafos 168) and four polymers (poly(vinyl pyrrolidone), PVP; poly(4-vinyl pyridine), P4VP; poly(methyl methacrylate), PMMA; and polystyrene, PS) were dissolved to a concentration of 10 mg/mL in the appropriate solvent (Table 1) and spin-cast (10,000 rpm^{-1}; 4000 rpm; 60 s) on a clean 1 cm × 1 cm silicon wafer. Thickness measurements of the organic films were made using a spectroscopic ellipsometer UVISEL M200, HORIBA Jobin-Yvon (Longjumeau Cedex, France). Resulting organic film thicknesses are shown in Table 1.

TOF-SIMS Instrument

The secondary ion mass analyses were performed in a Phi-EVANS (Chanhassen, MN, USA) time-of-flight SIMS (TRIFT 1) using a 15 keV Ga^+ beam (~1 nA DC current; 22 ns pulse width bunched down to 1 ns; 5 kHz repetition rate) with the sample voltage at 3 kV [28]. To improve the measured intensities, the secondary ions were post-accelerated by a high voltage (7 kV) in front of the microchannel plate detector. TOF-SIMS spectra in the mass range $0 < m/z < 1000$ were obtained by collecting the secondary ion signals from 180 s acquisitions on a 120 × 120 μm^2 sample area. The total ion fluence accumulated during an acquisition cycle was 8.1×10^{11} ions/cm^2, which ensured the static bombardment conditions. For reproducibility the SIMS measurements were made on three different samples (three measurements on each).

Gas Injection System

A modification was made in the sample chamber to introduce water vapor closely to the sample surface using a gas injection system, illustrated schematically in Figure 1. The gas injection system and the differential pumping are adapted to reach sufficiently high pressures at the sample surface while the pressure of the chamber remains low. The H_2O vapor was fed to the sample surface through a 0.5-mm-diameter injector needle positioned to within 1 mm of the sample. To prevent the close proximity of the nozzle to the surface from adversely affecting the secondary ion extraction field and degrading the collection efficiency, the nozzle was electrically grounded. The gas flow from the reservoir was controlled using a needle valve and the gas pressure at the entrance of the injector needle was monitored using a variable leak Granville-Phillips valve (Boulder, CO, USA). The pressure measured at the entrance of the injector was about 1×10^{-3} Torr. The real partial pressure at the sample surface during the water vapor flooding might be different from the measured pressure in the chamber, because of the gauge location in the instrument. But at the equilibrium, the measured chamber pressures should be proportional to the pressures at the sample surface, with the ratio remaining constant during the pressure variation. The pressure at the sample should be close to the measured entrance pressure, while the pressure of the chamber remains below $\approx 5 \times 10^{-5}$ Torr.

Results and Discussion

The goal of this article is to assess the interest of the injection of high-pressure water vapor in the selvedge region of organic samples for SIMS analysis. The choice of the used set samples is motivated by the wish to test the ability of the proposed water vapor protocol to enhance SIMS intensities for both low and high molecular weight organic materials. The discussion is divided in two sections. The first section investigates the case of the quasi-molecular ions of a low molecular weight polymer additive. The second section addresses the effect of the H_2O gas on the enhancement of the fingerprint ions of high molecular weight polymers. It should be mentioned here that for clean aluminum and silicon substrates, we did not measure any effect of the H_2O pressure on the characteristic secondary ion yields.

Polymer Additive

The polymer additive analyzed in the context of this study is the antioxidant Irgafos 168. The absolute intensity of the

Table 1. Description of the samples

Molecule	Acronym	M_w (Da)	Source	Solvent	Thickness (nm)
Irgafos 168 *Tris* (2,4-di-*tert*-butylphenyl) phosphite	Irgafos 168	647	Ciba Specialty Chemicals Inc.	Toluene	103.5 ± 2.4
poly(vinyl pyrrolidone)	PVP	29000	Sigma-Aldrich	Ethanol	106.7 ± 4.3
poly(4-vinyl pyridine)	P4VP	60000	Sigma-Aldrich	Ethanol	105.8 ± 1.8
poly(methyl methacrylate)	PMMA	30000	Sigma-Aldrich	Acetone	88.7 ± 1.2
Polystyrene	PS	30000	Sigma-Aldrich	Toluene	92.4 ± 1.6