



Interest of silver and gold metallization for molecular SIMS and SIMS imaging

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Abstract

The metallization procedure, recently proposed for signal improvement in organic secondary ion mass spectrometry (metal assisted-SIMS or MetA-SIMS), has been quantitatively evaluated for Irganox 1010 and polystyrene fragment and quasimolecular ions. In addition to gold, we investigate the effect of silver evaporation as a sample treatment prior to static SIMS analysis. Ion yields and yield enhancement factors are compared for Ag and Au-metallized molecular films, pristine coatings on silicon and sub-monolayers of the same molecules adsorbed on silver and gold. The results are sample-dependent but, as an example, the yield enhancement calculated for metallized polymer additive (Irganox 1010) films with respect to untreated coatings is larger than two orders of magnitude for the quasimolecular ion and a factor between 1 and 10 for characteristic fragments. The interest of the method for imaging SIMS applications is illustrated by the study of a non-uniform coating of polystyrene oligomers on a 100 μm polypropylene film.

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1. Introduction

Recently, gold metallization has been introduced as a novel sample preparation procedure for signal improvement in organic secondary ion mass spectrometry (SIMS) [1]. It was shown that not only the quasi-molecular ion intensities, but also the yields of positive and negative fragment ions, were significantly improved by the metallization procedure. Therefore, we proposed, in agreement with other users, to name the method “metal assisted-SIMS” or “MetA-SIMS”, in analogy with other terms used in the MS

community (matrix assisted laser desorption ionization, matrix enhanced-SIMS).

With respect to the traditional cationization method, consisting in the deposition of dilute analyte solutions on clean metal surfaces [2–4], sample metallization [5,6] has the distinct advantage that it can be applied to any type of material, irrespective of their nature and thickness. In particular, real-world, bulk organic samples prove to be excellent candidates for metallization.

In this article, we first quantify the secondary ion yield improvement for kDa molecules (Irganox 1010, low molecular weight polystyrene) under silver and gold metallization. In addition, it is also shown that metallization is beneficial for SIMS imaging of organic surfaces.

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2. Materials and methods

2.1. Samples

Irganox 1010 (CIBA; MW = 1176 Da; solution in cyclohexane) and low molecular weight polystyrene (PS) (scientific polymer products; $M_n = 2180$ Da; solution in toluene) have been used as model kilodalton molecules to study the yield enhancement provided by the metallization procedure. The solutions (1–10 mg/ml) were cast as films by depositing a droplet of the solution on a mirror-polished silicon substrate of about 1 cm^2 . The solvent was then allowed to freely evaporate. For comparison, molecular submonolayers on silver and gold substrates have been obtained by casting very dilute solutions (0.1 mg/ml) of the same molecules on silver foils and gold-metallized silicon wafers. The metal evaporation was carried out in an Edwards evaporator at an operating pressure of $\sim 10^{-6}$ mbar and a deposition rate of 0.1 nm/s, measured using a quartz crystal monitor. The metallized substrates were prepared by first evaporating a 5 nm titanium adhesive layer and then a 100 nm gold layer on 1 cm^2 silicon wafers. Conversely, the organic samples, cast on clean silicon wafers, as well as the bulk polymers, were metallized afterwards by evaporating 20 nmol of silver (or gold) per cm^2 on their top surface. This amount was shown to maximize the secondary ion yield enhancement in the case of gold metallized polystyrene oligomer films [3]. Prior to organic sample deposition/metallization, all the silicon substrates were rinsed in isopropanol and hexane (p.a. grade; Vel).

2.2. Secondary ion mass spectrometry (SIMS)

The secondary ion mass analyses and images were acquired in a PHI-EVANS time-of-flight SIMS spectrometer (TRIFT 1) using a 15 keV Ga^+ beam (FEI 83-2 liquid metal ion source; ~ 550 pA dc current; 22 ns pulse width bunched down to ~ 1 ns; 5 kHz repetition rate for the mass range 0–5 kDa) [7]. The experimental setup has been described in detail elsewhere [8]. Except when images were recorded, the ToF-SIMS mass spectra were collected over a mass range $0 < m/z < 5000$ for 600 s and a $180 \mu\text{m} \times 180 \mu\text{m}$ sample area, corresponding to a fluence of 3.5×10^{11} ions/ cm^2 . ToF-SIMS images were

obtained by rastering the 15 keV Ga^+ beam for 1800 s over a surface area of either $120 \mu\text{m} \times 120 \mu\text{m}$ (metallized sample) or $180 \mu\text{m} \times 180 \mu\text{m}$ (pristine sample), i.e. with a primary ion fluence of 2.3×10^{12} ions/ cm^2 or 10^{12} ions/ cm^2 , respectively. To improve the measured intensities, the secondary ions were post-accelerated to 10 keV before striking the detector.

3. Results and discussion

3.1. Ion yield enhancement

Irganox 1010 and PS oligomers ($M_n = 2180$ Da), spin cast on a silicon substrate and covered with 20 nmoles/ cm^2 of either gold or silver, have been analyzed by ToF-SIMS. As an example, the mass spectrum of Au-cationized polystyrene has been presented in Ref. [1]. For both molecules and metals, the positive secondary ion mass spectra exhibit prominent peaks attributed to the metal-cationized molecules. In order to assess the intensity enhancement provided by the metallization procedure, the yields of fragment and quasi-molecular ions were calculated by ratioing the peak areas and the measured primary ion fluence. Table 1 lists them for one characteristic fragment of each molecule ($\text{C}_4\text{H}_9\text{O}^+$ for Irganox and C_7H_7^+ for polystyrene) and for their quasimolecular ions. The results are compared to pristine organic layers and to submonolayers cast on silver and gold. For positive fragment ions, the enhancement factor provided by the metallization with respect to pristine surfaces is between four and eight. In comparison, casting a submonolayer of the same substances on a metal support gives rise to a yield enhancement between 2 and 20, depending on the sample and metal.

The signal improvement is dramatic for intact molecules. In the case of Irganox, one can distinguish between the actual molecular ion (M^+) and the quasimolecular ion ($\text{M} + \text{Me}^+$). If the intensity of the quasimolecular ion, measured for the Au-metallized sample, is divided by the intensity of the molecular ion measured for the pristine sample, an enhancement factor equal to 661 is obtained (447 for the Ag-metallized sample). It should be noted that submonolayers deposited on silver exhibit an even larger enhancement while submonolayers on gold show less

Table 1

Emission yields of fragment and quasi-molecular ions sputtered from Irganox 1010 and polystyrene obtained from different sample preparation procedures

| | Irganox | | Polystyrene | |
|---------|--|---|--|---|
| | C ₄ H ₉ O ⁺ [10 ⁻²] | M ⁺ [10 ⁻⁴] ^a | C ₇ H ₇ ⁺ [10 ⁻²] | M ⁺ [10 ⁻⁴] ^a |
| Si/M | 1.7 | 0.015 ^b | 0.7 | 0.0 |
| Ag/M | 12 | 19 ^b /443 ^c | 11 | 57 ^c |
| Au/M | 4.0 | 0.2 ^b /1.8 ^c | 16 | 62 ^c |
| Si/M/Ag | 13 | 0.08 ^b /6.6 ^c | 2.9 | 5.3 ^c |
| Si/M/Au | 8.9 | 0.5 ^b /9.8 ^c | 6.0 | 14 ^c |

Substrate/M refers to sub-monolayer deposited on a substrate. Si/M/metal indicates deposition of a metal layer on top of the organic molecule.

^a Molecular or quasimolecular ion.

^b Positive molecular ion.

^c Metal-cationized molecule.

improvement than metallized layers for Irganox molecular cations.

For PS oligomers, the entire molecule is not observed *at all* on the pristine sample and therefore, yield enhancement factors cannot be calculated. In contrast, intense metal-cationized molecule distributions are observed in the mass spectra of metallized polystyrene and the yield of the cationized 16-mer of polystyrene measured for the Au-metallized sample (14×10^{-4}) is only four times lower than for sub-monolayers deposited on silver and gold substrates.

Even though the results depend on the molecule, metal and secondary ion in question, Table 1 shows that Meta-SIMS always provides a significant, sometimes dramatic, yield enhancement.

3.2. SIMS imaging

Compared to deposition of sub-monolayer on metal substrates, an important advantage of the method is that it can be applied to virtually any type of organic sample, including bulk molecular solids and polymers. For instance, real-world samples can be characterized with improved sensitivity, which appears particularly attractive for imaging SIMS applications. Even though the deposited metal is expected to form a pattern of clusters or islands on the surface [1,9], the characteristic size of these inhomogeneities is smaller than the lateral resolution achievable in molecular SIMS imaging and therefore does not compromise the features relevant for SIMS imaging.

To exemplify the applicability of the method for SIMS imaging, a non-uniform surface of alternating

polystyrene and polypropylene (PP) areas has been designed and characterized with and without metallization pretreatment. A 100 μm -thick, biaxially stretched PP film was chosen as a substrate for an inhomogeneous coating of PS oligomers. In practice, the pattern was created by the non-uniform drying of a droplet of dilute PS oligomer solution, which was directly cast on the PP film. The positive secondary ion mass spectrum of a 120 $\mu\text{m} \times 120 \mu\text{m}$ area of the sample, obtained for a primary ion fluence of 2.3×10^{12} ions/cm², is shown in Fig. 1. At first sight, the fingerprint region of the mass spectrum ($0 < m/z < 200$) appears very similar to the PP spectra reported in the literature [10,11]. One important difference is that the absolute intensities are more than two orders of magnitude larger than those reported earlier (in particular, the same polypropylene and ToF-SIMS setup were used as in Ref. [11]). Two other differences related to the specific sample structure should be noticed. First, there are some intense unsaturated ion peaks in the spectrum, for instance C₇H₇⁺ ($m/z = 91$), indicating the presence of PS on the surface. Second, as a result of the metallization procedure, there is a pronounced gold peak at $m/z = 197$. The overall intensity enhancement is probably due to two different factors: (i) the suppression of sample charging owing to the conducting paths created at the surface by the gold pattern; (ii) the specific desorption/ionization enhancement provided by the metallization, as also observed for very thin samples (Table 1).

In contrast with pristine PP or PS samples, the high mass range of the mass spectrum of our

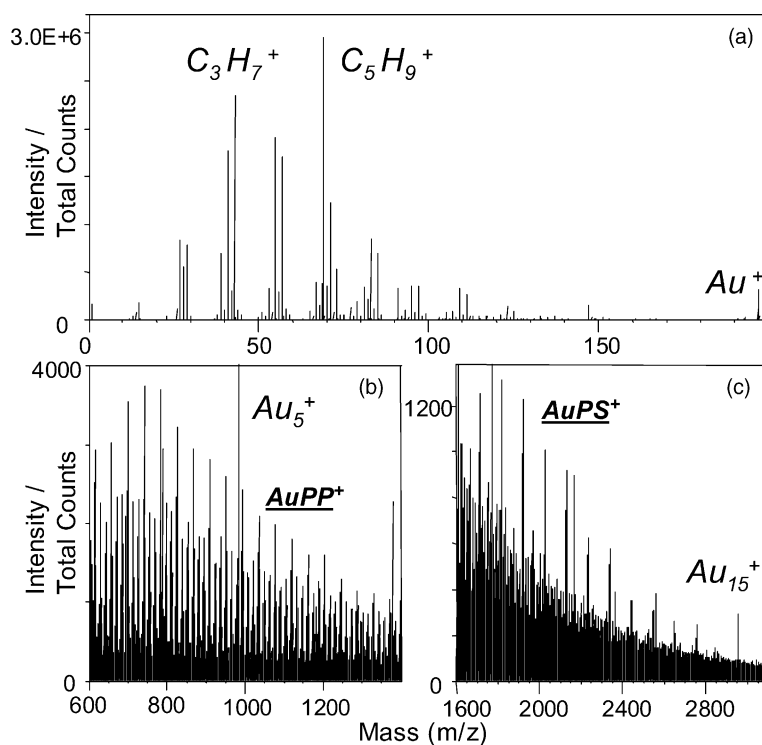


Fig. 1. Frame (a) positive ion mass spectrum (2.3×10^{12} ions/cm²) of a non-uniform overlayer of polystyrene oligomers on a 100 μ m-thick polypropylene film, after evaporation of 20 nmol/cm² of gold. Frame (b) distribution of Au-cationized PP chain segments. Frame (c) distribution of Au-cationized PS oligomers.

“micropatterned” sample is also very rich (Fig. 1b and c). Beside Au_n^+ cluster ion peaks, large Au-cationized PP chain segments form a distinct distribution in the range 500–1500 Da, with a maximum at 750–800 Da (Fig. 1b). In addition, Au-cationized PS oligomers constitute another distribution extending between 1500 and 2500 Da, with a maximum at 1800 Da. All these peaks are obviously induced by the presence of gold on the surface.

Fig. 2 shows four fragment ion images measured for the Au-metallized surface (Fig. 2a and b, spectrum of Fig. 1) and for an equivalent but non-metallized sample (Fig. 2c and d). Fig. 2a and c correspond to the most characteristic ion of PP ($C_5H_9^+$; $m/z = 69$), while Fig. 2b and d correspond to the most intense peak of the PS spectrum ($C_7H_7^+$; $m/z = 91$). The two images acquired from the metallized sample show an excellent signal/noise ratio and are perfect complements, indicating that this area of the PP sample is covered with 20 μ m-wide stripes of PS oligomers.

There is also a series of ~ 10 μ m-wide PS spots (circles) under the main PS feature. Although less intense, images can also be recorded using the quasi-molecular ion distributions of PP and PS (spectra of Fig. 1b and c). They will be discussed in detail in a more complete paper on the subject [12]. In comparison, the images acquired from a larger area of the pristine sample are weak and suffer from significant sample charging. The scale indicates an average intensity that is more than one order of magnitude lower for these images. The dark and bright regions, similar in both images, do not reflect sample features but electric charging, even though an electron floodgun was used in this case. The actual sample feature, a stripe of polystyrene extending from the bottom left to the top right corner, noticeable on the $C_7H_7^+$ image (Fig. 2d), is almost invisible in the PP fragment image (Fig. 2c). Comparing the images presented in Fig. 2 provides a clear illustration of the beneficial effect of the metallization procedure for organic SIMS imaging.

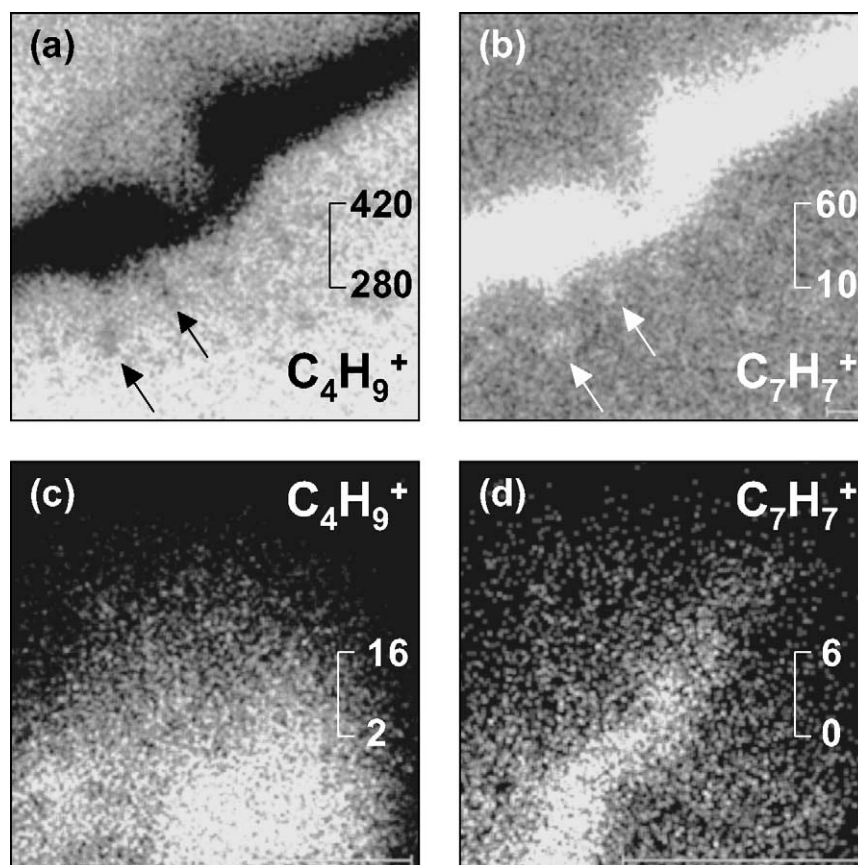


Fig. 2. Secondary ion images from an overlayer of polystyrene oligomers on a polypropylene film. Frames (a and b) images of the $C_4H_9^+$ and $C_7H_7^+$ ions sputtered from the Au-metallized sample ($120\ \mu\text{m} \times 120\ \mu\text{m}$). Frames (c and d) images of the $C_4H_9^+$ and $C_7H_7^+$ ions sputtered from the pristine sample ($180\ \mu\text{m} \times 180\ \mu\text{m}$).

4. Conclusion

Covering organic surfaces with minute amounts of silver or gold induces a significant sensitivity improvement for static SIMS analyses. For Irganox 1010 and polystyrene, the positive fragment ion yields are, on average, enhanced by less than one order of magnitude, but the molecular ion yields increase by more than two orders of magnitude, owing to an efficient cationization of the molecules by the metal.

Such yield enhancements are promising for imaging SIMS applications where sensitivity usually constitutes a serious issue. Our example shows that sample charging is suppressed and much better quality images are obtained when a bulk, insulating polymer surface is coated with gold prior to analysis. This technique

should be very useful for imaging non-uniform organic samples such as polymer blends [13], polymer surface covered with additives [14] or even cells and drug/biomolecule arrays [15]. It should lead to an even greater improvement when used in combination with polyatomic primary ion beams [16].

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