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# Molecular ion yield enhancement induced by gold deposition in static secondary ion mass spectrometry

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## ABSTRACT

Static ToF-SIMS was used to evaluate the effect of gold condensation as a sample treatment prior to analysis. The experiments were carried out with a model molecular layer (Triacontane  $M = 422.4$  Da), upon atomic ( $\text{In}^+$ ) and polyatomic ( $\text{Bi}_3^+$ ) projectile bombardment. The results indicate that the effect of molecular ion yield improvement using gold metallization exists only under atomic projectile impact. While the quasi-molecular ion ( $\text{M}+\text{Au}^+$ ) signal can become two orders of magnitude larger than that of the deprotonated molecular ion from the pristine sample under  $\text{In}^+$  bombardment, it barely reaches the initial intensity of ( $\text{M}-\text{H}^+$ ) when  $\text{Bi}_3^+$  projectiles are used. The differences observed for mono- and polyatomic primary ion bombardment might be explained by differences in near-surface energy deposition, which influences the sputtering and ionization processes.

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## 1. Introduction

Static secondary ion mass spectrometry (SIMS) is a powerful technique, widely used for many applications such as surface characterization and molecular imaging. One of the major remaining challenges in organic SIMS concerns the improvement of the molecular secondary ion yields. Several routes were proposed in order to achieve this goal. Among them, the use of cluster projectiles ( $\text{Au}_n^+$ ,  $\text{Bi}_n^+$ ,  $\text{C}_{60}^+$ ) constitutes a particularly efficient approach, leading to very large yield enhancements especially in the high mass region of the spectra [1,2]. In addition to the properties of the incident projectiles, the performance of SIMS analysis is largely dependent on the details of the sample preparation (matrix effect). Therefore, specific sample preparation protocols may constitute another solution to improve the yield. For instance, the evaporation of a small quantity of noble metal such as Au and Ag on top of the sample surface significantly enhances the SIMS signal as well as the lateral resolution of surface imaging by SIMS [3–5].

In this experimental study, a medium mass molecule (Triacontane  $m/z \sim 422.4$  Da) is used in order to assess the effect of the gold deposition on the molecular ion yields upon atomic ( $\text{In}^+$ ) and cluster ( $\text{Bi}_3^+$ ) projectile impact.

## 2. Experimental

### 2.1. Sample preparation for ToF-SIMS

The triacontane molecular sample ( $\text{C}_{30}\text{H}_{62}$ ) was first dissolved in benzene to a concentration of  $\sim 10$  mg/ml. This solution was subsequently spin-coated on a clean silicon wafer and the samples were metallized afterwards, by evaporating various quantities of gold on the surface. With this procedure, pristine molecular samples and samples metallized with increasing gold deposit (from 0 up to 15 nm equivalent thickness) were obtained. A third set of samples was prepared by evaporating gold directly onto the silicon substrate, without the molecule of interest. This procedure helped us to clearly discriminate the peaks induced by impurities from the peaks generated by the triacontane sample. Spin-coating was performed using a KARL SUSS spin-coater, by letting a droplet of the sample solution evaporate at 5000 rpm during 60 s. Gold deposition was carried out using a Cressington 208HR sputter coater system. The deposited metal amount was measured using a quartz crystal microbalance with a resolution of about 0.1 nm (equivalent thickness). Prior to organic sample spin-coating and/or gold metallization, the silicon substrates were rinsed in 2-propanol and hexane and dried in a stream of hot air.

### 2.2. Secondary ion mass spectrometry (SIMS)

The secondary ion mass analyses were performed using two different time-of-flight SIMS instruments. The first one was a PHI-EVANS time-of-flight SIMS (TRIFT 1) using a 12 keV  $\text{In}^+$  beam. The

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dc current was  $\sim 600$  pA. To maximize the measured intensities, the secondary ions were post-accelerated by a high voltage (7 kV) in front of the detector. The ToF-SIMS mass spectra were obtained by collecting the secondary ion signal in the mass range  $0 < m/z < 5000$  for the 180 s-bombardment of a  $120 \mu\text{m} \times 120 \mu\text{m}$  sample area. This choice of parameters corresponds to a projectile fluence of  $2.4 \times 10^{11}$  ions/cm<sup>2</sup>, ensuring static bombardment conditions. The second instrument was a TOF-SIMS IV (IONTOF GmbH) equivalent equipped with a liquid metal ion gun ( $\text{Bi}_n^+$ ). The energy of the  $\text{Bi}_3^+$  cluster projectiles was also 12 keV. The fluence in this case did not exceed  $1.7 \times 10^{11}$  ions/cm<sup>2</sup>. For the experiments using these different projectiles we ensured that the primary ion dose calculated are almost the same so that the curves showing the secondary ion yields in Figs. 2 and 3 below are directly comparable. Three mass spectra were recorded for each sample with each ion gun setup and the averages of the secondary ion yields (signal intensity divided by number of used primary ions) were calculated.

Metallized samples are expected to evolve with time. Therefore the time between sample preparation and measurements was kept close to 2 h in all cases.

### 3. Results and discussion

#### 3.1. $\text{In}^+$ ToF-SIMS analysis

The three positive secondary ion mass spectra of Fig. 1 represent the experimental results obtained when the pristine sample and two Au-metallized samples (2 nm 12 nm) were bombarded by  $\text{In}^+$ . These mass spectra show that, upon Au metallization, the intensity of the molecular ion peaks  $\text{M}^+$  and  $(\text{M}-\text{H})^+$  increase strongly in comparison with the pristine samples. Moreover the evaporation of Au on top of these samples allows us to detect the Au-cationized quasi-molecular ions  $(\text{M} + \text{Au}-x\text{H})^+$ , with an intensity increasing with the thickness of the metal layer. Fig. 2 represents the calculated yields for the molecular ions (a) and the Au-cationized ions (b). All the considered secondary ion yields increase with the thickness of the gold layer up to  $\sim 6$  nm of gold, beyond which they remain constant ( $\sim 3 \times 10^{-4}$ ) in the investigated metallization range. The yield enhancement factor can be

large between the metallized sample and the pristine sample. For example, the emission yield for the deprotonated molecular ions  $(\text{M}-\text{H})^+$  is multiplied by a factor of  $\sim 22$  after evaporation of 6 nm of Au.

Gold-cationized molecules  $(\text{M}+\text{Au})^+$ , also very specific for diagnostic, even display larger yields ( $10^{-3}$ ). The enhancement factor of these ions reaches the value of 1300 compared to the lowest amount of Au evaporated (0.5 nm). The dynamics of the yield increase up to large metal coverages suggests molecular diffusion during or after sample metallization [6].

The scanning electron microscopy images recorded for gold indicate that during the early stage of growth, the Au particles initially form droplet-like islands which grow and coalesce into larger islands as the Au coverage increases. The size of the Au island is about 15–20 nm for 2 nm evaporated Au. For higher Au dose ( $>4$  nm) the clusters partially coalesce to produce elongated structure which grow and connect to form a continuous network across the surface ( $\geq 12$  nm) [7]. The persistence of the molecular signal up to very large gold coverages (15 nm) is probably due to molecular diffusion already during metallization.

#### 3.2. $\text{Bi}_3^+$ ToF-SIMS analysis

Cluster projectiles usually lead to a pronounced increase of the molecular secondary ion intensities with respect to atomic projectiles. Using  $\text{Bi}_3^+$  primary ions in combination with gold metallization, our goal was to check whether the yield enhancements induced by metallization upon atomic ion bombardment also extended to cluster primary ions. Fig. 3 illustrates the evolution of the molecular and the quasi-molecular ion yields of triacontane as a function as the deposited gold thickness. First, the molecular ion yields, obtained with polyatomic bismuth projectiles on pristine samples, are two orders of magnitude higher than the yields obtained with atomic indium primary ions. In addition, the evolution of the signals upon metallization reveals a completely different behavior under  $\text{Bi}_3^+$  bombardment. In that case, the deprotonated ion signal decreases dramatically with the presence of gold. A qualitatively similar yield decrease has been already shown when using a  $\text{C}_{60}^+$  projectile to analyze Au-coated

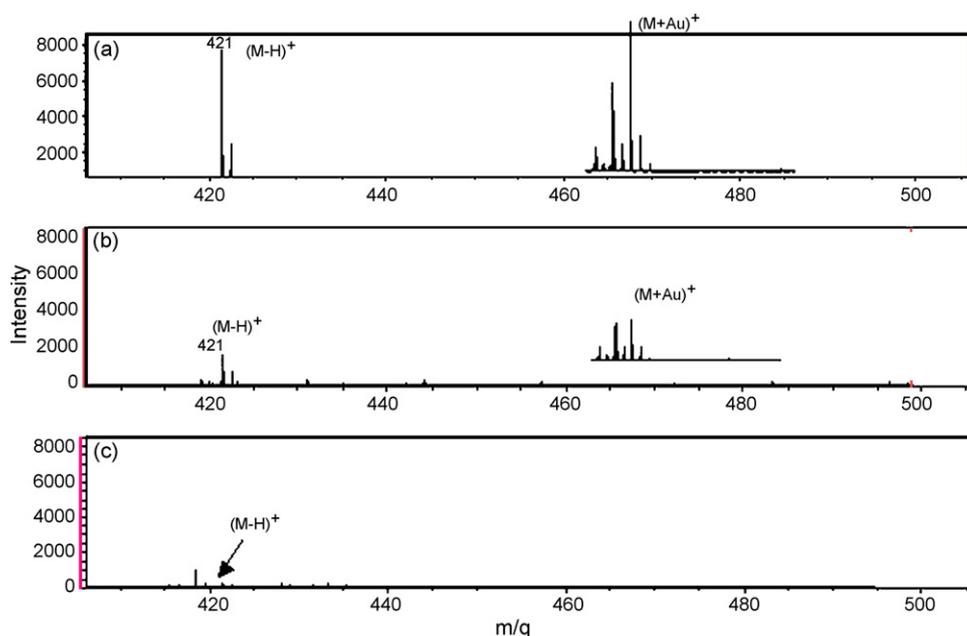
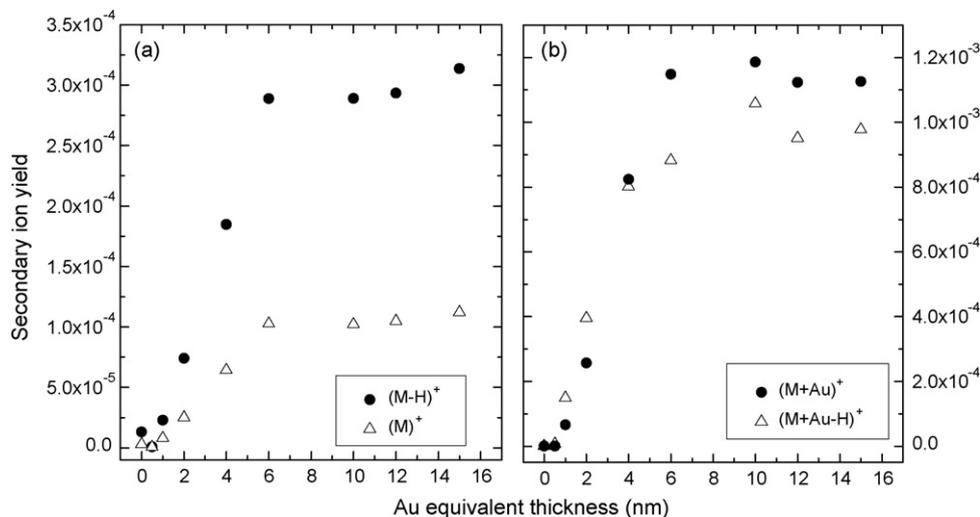
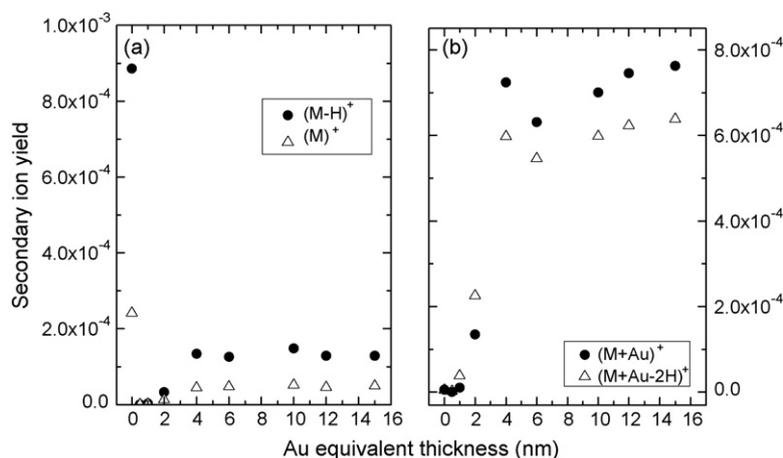


Fig. 1. Positive ToF-SIMS spectra of triacontane spin-coated on Si wafers: (a) 12 nm Au metallized sample, (b) 2 nm Au metallized sample and (c) pristine sample. PI fluence:  $2.4 \times 10^{11}$  ions/cm<sup>2</sup>  $\text{In}^+$ .



**Fig. 2.** Evolution of the molecular ion yields of triacontane upon  $\text{In}^+$  bombardment, as a function of the equivalent deposited gold thickness (a) molecular ions and (b) Au-cationized molecular ions.



**Fig. 3.** Evolution of the molecular ion yields of triacontane upon  $\text{Bi}_3^+$  bombardment, as a function of the equivalent deposited gold thickness (a) molecular ions and (b) Au-cationized molecular ions.

polymer samples [6]. In parallel, the Au-cationized molecular signal rises to a maximum yield that is similar to that of the deprotonated molecule in the pristine sample but lower than in the case of indium. Our interpretation is that, while molecules that are near, or adsorbed on, the metal see their sputtering yield and ionization probability enhanced upon atomic ion bombardment, the reverse effect occurs with bismuth clusters.

The differences observed for the two projectiles may be related to the mechanisms by which the secondary ions are emitted. With the same total energy of 12 keV,  $\text{Bi}_3^+$  clusters penetrate less into the bombarded organic surface than  $\text{In}^+$ , because of their lower energy per atom. Consequently  $\text{Bi}_3^+$  deposit their energy more efficiently in the upper layers of the solid. For this reason, the molecular sputtering yields are significantly larger with  $\text{Bi}_3^+$  in the case of pristine organic films. After gold evaporation the deposited metal forms clusters, allowing a molecular diffusion towards the surface through the metal layer. In the case of low mass monoatomic primary ions ( $\text{In}^+$ ), the secondary ion yield increases with the gold deposition, because the gold islets, with a large stopping power, help confine the  $\text{In}^+$  ion energy in the top surface layer. The adsorbed molecules are therefore more efficiently sputtered. Under Bismuth cluster bombardment, the energy density depos-

ited in the solid surface is much higher so that a spike is created and a crater is formed in the metal. Recent simulations show that, in the case of polystyrene monolayers on silver, the resulting yields are lower for polyatomic projectiles than for monoatomic projectiles [8]. This reduction is partly due to the small amount of organic material actually present on the surface. In addition, the same simulations show that the impact of polyatomic projectiles might lead to more fragmentation of the ejected species due to their higher internal energies. This effect contributes to further reduce the enhancement factor of the detected species.

#### 4. Conclusion

The effect of gold covering organic surfaces on the molecular secondary ion yields measured upon ion bombardment was investigated using atomic and polyatomic projectiles. These experiments confirm that the molecular ion yield enhancement due to gold deposition can only be detected for monoatomic ion bombardment, whereas for polyatomic ion bombardment, a decrease in yield is observed. Our current investigations aim to extend this study by testing the effect of another noble metal (Ag) and of several other projectiles ( $\text{Ga}^+$ ,  $\text{C}_{60}^+$ ).

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