Research Article

Investigation of methods to enhance the secondary ion yields in TOF-SIMS of organic samples

A. Heile,[a] D. Lipinsky,[a] N. Wehbe,[b] A. Delcorte,[b] P. Bertrand,[b] A. Felten,[c] L. Houssiau,[c] J.-J. Pireaux,[c] R. De Mondt,[d] P. Van Royen,[d] L. Van Vaeck[d] and H. F. Arlinghaus[a]*

In addition to structural information, detailed knowledge of the local chemical environment proves to be of ever greater importance, for example for the development of new types of materials as well as for specific modifications of surfaces and interfaces in multiple fields of materials science, or various biomedical and chemical applications. But the ongoing miniaturization, and therefore, reduction of the amount of material available for analysis constitute a challenge to the detection limits of analytical methods.

In the case of time-of-flight secondary ion mass spectrometry (TOF-SIMS), several methods of secondary ion yield enhancement have been proposed. This article focuses on the investigation of the effects of two of these methods, metal-assisted SIMS and polyatomic primary ion (PI) bombardment. For this purpose, thicker layers of organic molecules (polymers and dyes), both pristine, and metallized with different amounts of gold, were analyzed using monoatomic (Ar^+, Ga^+, Xe^+, Bi^+) and polyatomic (SF_5^+, Bi_3^+, C_{60}^+) PIs. It was found that polyatomic ions generally induce a significant increase of the secondary ion yield. On the other hand, with gold deposition, a yield enhancement can only be detected for monoatomic ion bombardment. Copyright © 2008 John Wiley & Sons, Ltd.

Introduction

Two successful methods for the enhancement of the secondary ion yield are metal-assisted secondary ion mass spectrometry (MetA-SIMS), which may lead to an enhancement of more than two orders of magnitude when using monoatomic primary ions (PIs) (Ga^+,[1,2] In^+,[3] Au^+[4]), and the use of polyatomic PI bombardment, showing an increase of three to four orders of magnitude.[5] Some attempts to combine these techniques show ambiguous results. It was shown that depositing a thin layer of gold on biological tissue leads to a yield enhancement of less than one order of magnitude using Bi_3^{2+} PI bombardment.[6] However, if a thin gold layer is deposited on a polymer sample, a slight yield decrease is observed using C_{60}^+ PIs.[7] To evaluate whether these differences are due to the varied PI species or the sample system, identical pristine and gold-coated samples were analyzed with monoatomic (Ar^+, Ga^+, Xe^+, Bi^+) and polyatomic (SF_5^+, Bi_3^+, C_{60}^+) PI species.

Experimental

Two sets of samples were prepared. One consisted of a set of polystyrene (PS) samples, prepared as thick-layer plasma-polymerized PS films using styrene as monomer (99.5%; Acros organic, Belgium). The layers were prepared onto cleaned silicon substrates using inductively coupled plasma at the rf of 13.56 MHz in an inhouse-built vacuum chamber. The plasma parameters were set to 30 W, 1 hPa, and 3 min.

The second set of samples was prepared as thick layers of a polymer dye mixture, dissolved in a mixture of tetrahydrofuran (Acros, Belgium), 2-butanone (VWR, Belgium) and 1-methoxy-2-propanol (Dow, USA) to ensure optimal coating properties. This solution contained 0.1% of an IR dye with a mass of 583 u (CAS No. 134127-48-3),[8] 0.8% of a blue dye with a mass of 469 u (CAS No. 2580-56-5),[8] and 14% novolak binder (Alnovol SPN452, Clariant, Germany). This mixture was spin-coated onto test-grade silicon wafers, which were cleaned for 5 min by ultrasonification in methanol (Acros Organics, Belgium) and dried in a stream of hot air. Spin coating was performed using an aliquot of 7.5 µl of the respective solutions at 2000 rpm for 60 s (acceleration from 0 to 2000 rpm in 25.5 s; deceleration in 10 s from 2000 to 0 rpm) on a Cookson Electronics Specialty Coating Systems G3-8 (PI-KEM Ltd.,

* Correspondence to: H. F. Arlinghaus, Physikalisches Institut, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 10, D-48149 Münster, Germany. E-mail: arlinghaus@uni-muenster.de

a Physikalisches Institut, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 10, D-48149 Münster, Germany

b PCPM, Université catholique de Louvain, Croix du Sud 1, B-1348 Louvain-la-Neuve, Belgium

c LISE Laboratory, University of Namur, Rue de Bruxelles 61, B-5000 Namur, Belgium

d Department Chemistry (CDE), University of Antwerp, Universiteitsplein1, B-2610 Wilrijk, Belgium

UK). After spin coating, the samples were dried on an electrical heating plate for 30 s at 50 °C.

Metallization of the samples was carried out by thermal evaporation from gold wire under high vacuum (about 10^{-6} hPa). A quartz balance was used to measure the deposited amount of metal. Both sets of samples (PS samples, polymer dye samples) consist of pristine samples and of samples with two defined gold layer thicknesses. Assuming the same sticking coefficient for the monitor and the organic sample, the layers correspond to 0.2 nm and 2.0 nm equivalent thickness. This is an indicator for the amount of the deposited gold (2 nmol/cm^2, 20 nmol/cm^2) and does not reveal the real thickness of the layer. Due to differences in the adhesion between metal and organic molecules and cohesion of metal atoms, gold is not uniformly distributed on the sample surface.[9] The size of the gold islets was determined by transmission electron microscopy (Philips Tecnai 10, 80 kV). For this purpose, polymerized PS was grown onto a carbon-coated copper grid and coated with gold (20 nmol/cm^2) which produced, as published before,[7] mostly gold islets with less than 10 nm in diameter and some bigger islets which were separated by uncovered areas with a width of some nanometers.

SIMS experiments were performed using three time-of-flight (TOF) SIMS instruments: (i) a TOF-SIMS instrument equipped with a 25 kV liquid metal ion gun (Bi$_n^+$, Ga$^+$, IONTOF GmbH) and an inhouse-built 10 kV electron ionization gun (Ar$^+$, Xe$^+$, SF$_5^+$); (ii) an IONTOF TOF-SIMS IV equipped with a 25 kV Ga$^+$ and a 9 kV SF$_5^+$ PI source; (iii) a PHI EVANS TOF-SIMS (TRIFT 1) using a 15 kV liquid metal ion source (Ga$^+$, FEI 83-2, FEI, USA) and a 15 kV C$_{60}^+$ PI beam (IOG-C60-20, Ionoptika Ltd., UK).

The angle of incidence of all PI sources was 45°. Unless stated otherwise, impact energy of the PI was 10 keV for Ar$^+$, Xe$^+$, SF$_5^+$ and 12 keV for Ga$^+$, Bi$^+$, Bi$_3^+$ and C$_{60}^+$. Additionally, Ga$^+$, Bi$^+$, Bi$_3^+$ were used with 25 keV. A maximal fluence of 10^{12} ions/cm^2 (monoatomic PI) and 10^{11} ions/cm^2 (polyatomic PI), respectively, leads to a loss of signal intensity of less than 10%. Charge compensation with low-energy electrons (about 20 eV) was used when necessary.

To ensure comparability of absolute secondary ion yields obtained with different TOF-SIMS instruments several steps were taken: (i) samples were prepared a month before they were sent to the different laboratories and measured within a 2-week range. This way, differences within the sets of samples can be minimized. These might be caused by alteration of the surface, which could occur especially in the first weeks after preparation[10]; (ii) to monitor aging effects, repeat measurements using Ar$^+$ bombardment were carried out, finding a secondary ion yield change of less than 20%; (iii) for internal cross calibration, every laboratory used gallium ion bombardment. Because the Ga data obtained by the different laboratories were quite similar, it was not necessary to normalize the data.

With each ion gun setting, three spectra were acquired from each sample and the mean of the secondary ion yields (signal intensity divided by number of used PIs) was calculated. In most cases, the relative standard deviation was less then 10%, and in a few cases up to 40%.

Results

For spin-coated PS, characteristic fragment ions are well known.[1] Plasma-polymerized PS shows the same characteristic fragment ions, but different relative intensities. For example, the most abundant fragment ion from plasma-polymerized PS is not C$_7$H$_7^+$, but C$_8$H$_9^+$. Characteristic for the polymer dye mixture are the molecular ions of the dyes (C$_{33}$H$_{32}$N$_3^+$, 470 u; C$_{40}$H$_{40}$N$_2$Cl$^+$, 583 u) and two fragment ions (C$_8$H$_9$O$^+$, 121 u; C$_9$H$_{11}$O$^+$, 135 u) from the novolak binder, originating from the monomer structure. Since a clear peak was not always detectable for C$_{40}$H$_{40}$N$_2$Cl$^+$, secondary ion yields below 10^{-6} may be affected by background noise. Therefore, these yields may be overestimated. Metal-cationized fragments and molecules were reported to have higher yields than the related fragment or molecule ions.[4,11] But on the PS samples, gold-cationized fragment ions had significantly smaller yields than the shown characteristic fragments. On the polymer dye mixture, no characteristic cationized fragment or molecule ions were found.

Monoatomic primary ion bombardment

For all characteristic fragment ions emitted from the PS sample bombarded with monoatomic PIs, a gold deposition of 0.2 and 2.0 nm equivalent thickness generally leads to an enhancement of the secondary ion yield. This enhancement is nearly the same for Xe$^+$ and Bi$^+$, more pronounced for Ar$^+$, and with up to an order of magnitude highest for Ga$^+$ ion bombardment (Fig. 1). With one exception, increasing the mass of the PIs leads to an increased yield from pristine as well as gold-coated samples.

Characteristic signals from the polymer dye mixture exhibit a somewhat different behavior compared to PS (Fig. 2). For nearly every PI species used, a 0.2 nm coverage of gold leads to a decrease in the yield of characteristic ions. Increasing the coverage of gold to 2 nm leads to an enhancement, so that in some cases the yield exceeds that obtained from pristine samples.

For both sample sets it can be seen that for low-mass PIs (Ar$^+$, Ga$^+$), yield enhancement due to gold deposition is more probable and more pronounced than for higher-mass PIs (Xe$^+$, Bi$^+$), which show nearly the same enhancement. With higher-mass PIs, the yield obtained on the pristine samples is often even higher than the yield obtained with Ga$^+$ on samples with a 2 nm gold layer.

Polyatomic primary ion bombardment

Figure 3 shows secondary ion yields of characteristic fragment ions emitted from the different PS samples under polyatomic ion bombardment. To simplify comparison with monoatomic ion bombardment, Bi$^+$ data are added. In contrast to Bi$^+$ results, polyatomic ion bombardment leads to a decrease of the secondary ion yield with increasing gold deposition. This decrease is more pronounced for SF$_5^+$ ion bombardment. Also notable is the fact that compared to Bi$_3^+$ or SF$_5^+$, C$_{60}^+$ shows quite different relative peak intensities (ratio of the yields of different secondary ions obtained from the same sample).

For the polymer dye mixture, the secondary ions show the same behavior; however, the yield decrease due to gold deposition is more pronounced (Fig. 4). Nevertheless, for both sets of samples, all characteristic secondary ion yields obtained with polyatomic ion bombardment on pristine samples were higher than the yields obtained with monoatomic ion bombardment, regardless of whether the samples were pristine or gold-covered.

Energy dependence

Additionally, the effect of PI energy was analyzed by changing it from 12 keV to 25 keV for Ga$^+$, Bi$^+$ and Bi$_3^+$. For monoatomic
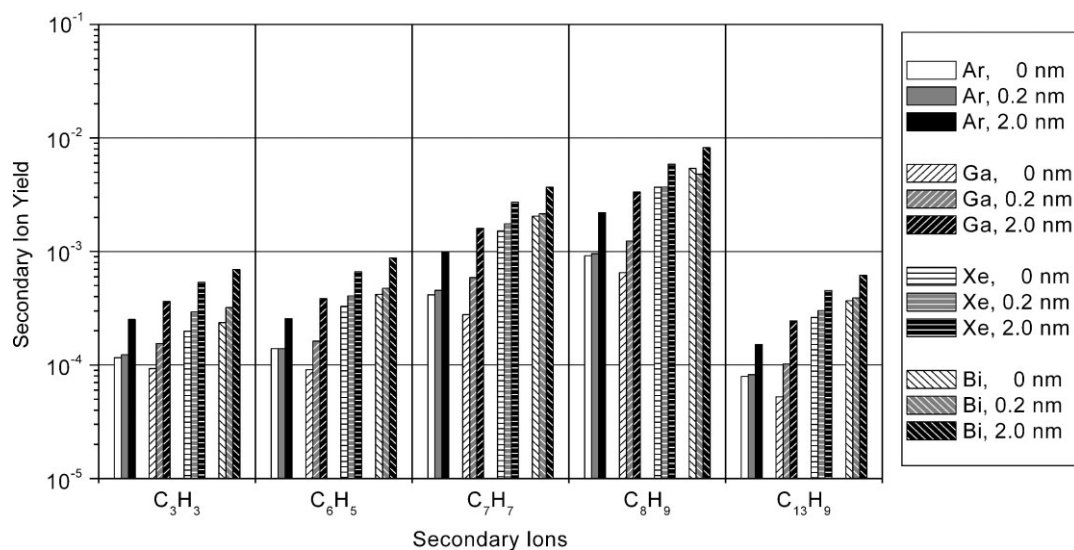
Figure 1. Secondary ion yields of polystyrene characteristic fragment ions obtained from pristine and gold-covered surfaces using different monoatomic primary ion species.
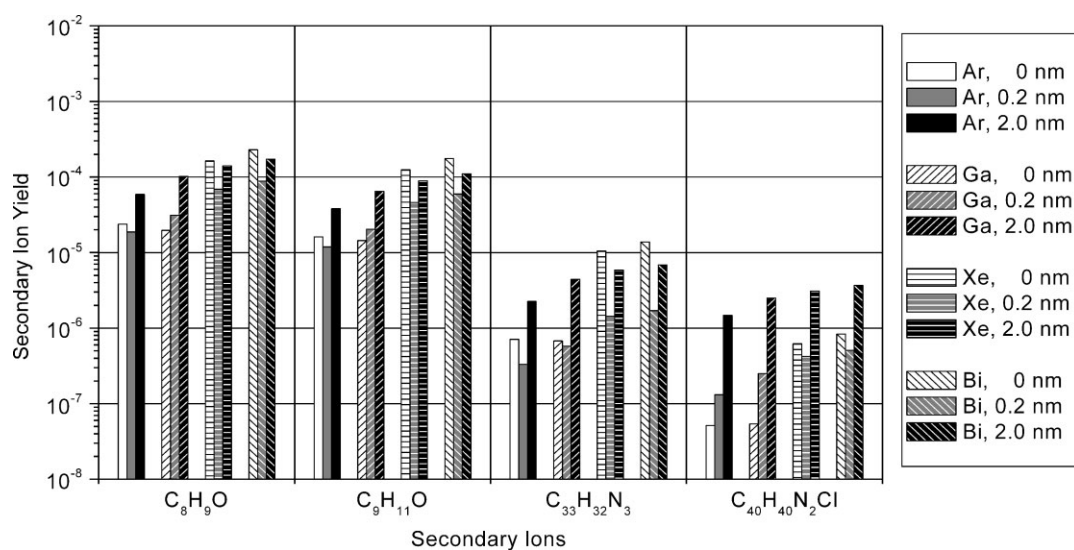

Figure 2. Secondary ion yields of characteristic ions of polymer fragments ($C_8H_9O^+$, $C_9H_{11}O^+$) and dye molecules ($C_{33}H_{32}N_3^+$, $C_{40}H_{40}N_2Cl^+$) obtained from pristine and gold-coated thick-layer polymer dye samples using different monoatomic primary ion species.

Ga^+ and Bi^+, the energy increase resulted in only slight yield changes for all samples. While yield decreased for some of the characteristic fragment and molecular ions (generally up to 20%, and at most 60%), yield increased for other fragment or molecular ions (generally up to 20%, and at most 60%). Usually, the samples with 2.0 nm gold deposition showed an increase, while the other samples showed a decrease. For polyatomic Bi_3^+ ion bombardment, an increase in secondary ion yield was observed, ranging up to a factor of two for fragment ions and up to a factor of three for molecular ions. This increase was independent from the amount of gold deposited.

Discussion

Although gold coverage reduces the area emitting organic fragment and molecule ions, in some cases an increase in

secondary ion yield is observed. The differences observed for mono- and polyatomic PI bombardment might be explained by differences in near-surface energy deposition, which influences the sputtering and ionization process. Different PI parameters are known to affect energy depth distribution. At a given kinetic energy, the stopping power increases with increasing monoatomic PI mass, leading to an increased near-surface energy deposition. In the case of polyatomic PIs, their kinetic energy is divided up among the constituents. Therefore, the constituents are stopped faster and even more energy is deposited in the regions near the sample surface. Deposition of gold may even increase this effect. Since gold has a higher stopping power as compared to organic material, and since it can also increase the scattering of PIs, it will help to deposit more energy from the impinging mono- or polyatomic PIs nearer to the surface. This may lead to enhanced desorption of organic material via several direct or indirect means: assuming molecules of the sample material have moved onto the
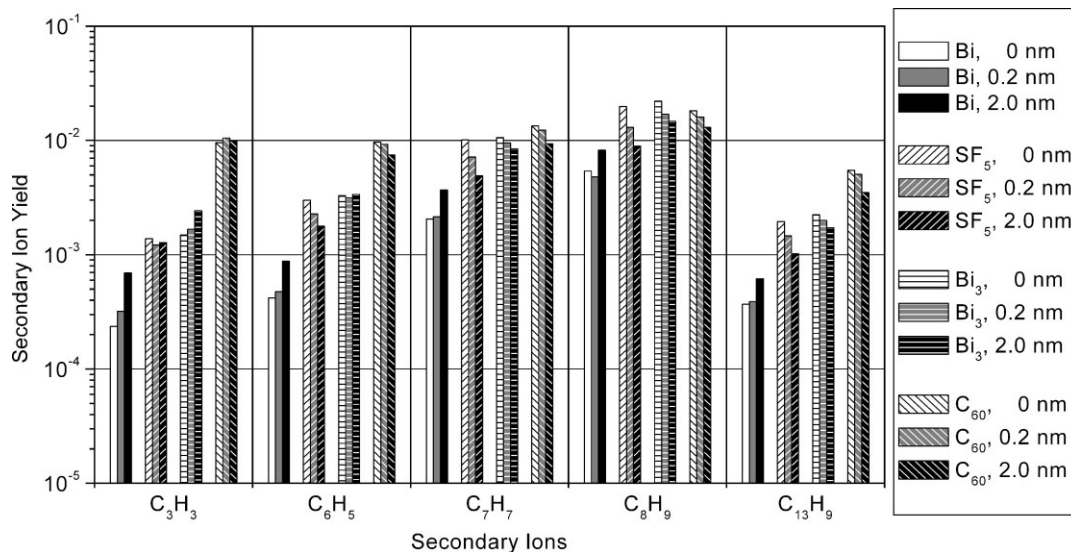
Figure 3. Secondary ion yields of polystyrene characteristic fragment ions obtained from pristine and gold-covered surfaces using different primary ion species.
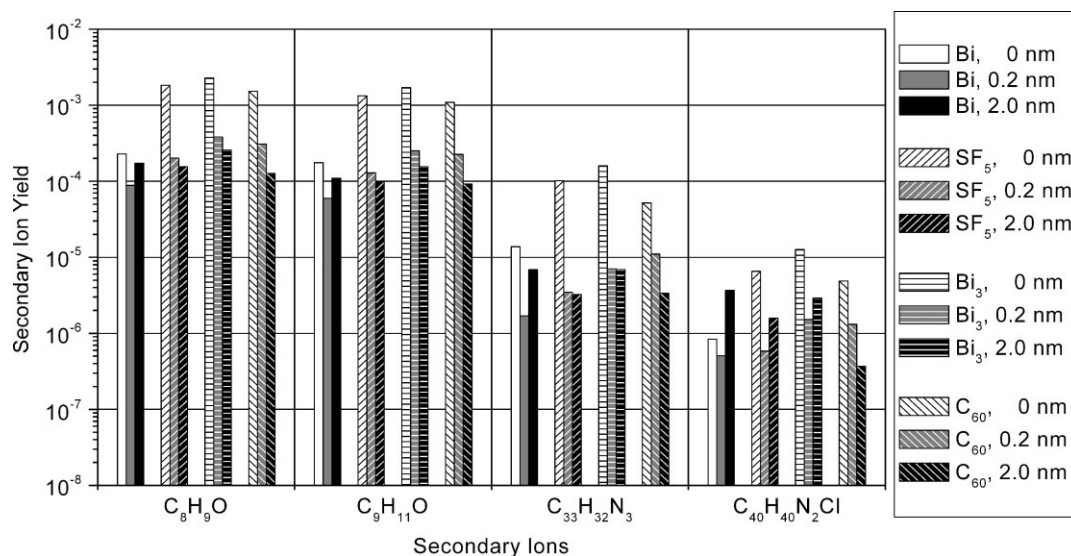

Figure 4. Secondary ion yields of characteristic ions of polymer fragments ($C_8H_9O^+$, $C_9H_{11}O^+$) and dye molecules ($C_{33}H_{32}N_3^+$, $C_{40}H_{40}N_2Cl^+$) obtained from pristine and gold-coated thick-layer polymer dye samples using different primary ion species.

gold islets, they can be sputtered more efficiently. A more indirect way would be the dissipation of energy deposited in the gold islets into the surrounding uncovered areas via displaced gold atoms. Furthermore, since the energy per constituent is much higher for monoatomic PIs than for polyatomic ones, especially monoatomic PIs may penetrate the gold islets and may be deflected into near-surface trajectories due to the increased scattering of PIs in gold. The effects observed are stronger for samples with 2 nm gold deposition than for samples with smaller amounts of gold (0.2 nm gold deposition). Combining all these assumptions, the increase of the secondary ion yield due to gold deposition should be highest for low-mass monoatomic PIs, which cannot initially transfer a large portion of their kinetic energy into the pristine organic sample surface. However, polyatomic PIs do transfer much of their kinetic energy into the organic surface. The deposited gold may still increase the near-surface energy deposition; however, the

resulting yield enhancement is so small that it cannot compensate for the yield decrease due to the reduction of uncovered organic sample area. These assumptions are supported by the observed energy dependency. In the case of monoatomic PIs, an increase in kinetic energy leads to an increase of secondary ion yield only if a 2 nm gold layer is present, preventing deep implantation. Since in the investigated energy range polyatomic PIs still deposit most of their energy in the upper organic layers, the observed increase of the secondary ion yield is independent from the deposition of gold.

Summary and Conclusion

The effects of gold deposition and polyatomic primary ion (PI) bombardment, both separately and in combination, on secondary ion yield enhancement were investigated using thick-layer polymer samples. In summary, for the samples investigated,

an enhancement of the secondary ion yield due to gold deposition could only be detected for monoatomic ion bombardment, whereas polyatomic ion bombardment of gold-coated polymer samples resulted in a decrease in yield. However, the secondary polymer fragment ion yield was, in general, still higher in both Au-coated and non-Au-coated polymer samples when using polyatomic PI species as opposed to monoatomic PIs. In general, the highest yields were obtained from pristine samples using polyatomic ion bombardment. For the different polyatomic PI species it can be observed that ions with a lower number of constituents (SF_5^+ and Bi_3^+) show more similar relative peak intensities compared to C_{60}^+. Yields for all polyatomic PIs used are in the same order of magnitude. However, opposite behavior was shown for Bi_3^{2+} ion bombardment on gold-coated biological samples,[6] illustrating the need for further investigation using different sample systems.

Acknowledgements

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