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Metal-assisted SIMS and cluster ion bombardment for ion yield enhancement

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ABSTRACT

In addition to structural information, a 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 paper focuses on the investigation of the effects of two of these methods, metal-assisted SIMS and polyatomic primary ion bombardment. For this purpose, thicker layers of polystyrene (PS), 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}^+) primary ions. 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.

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1. Introduction

Two successful methods for the enhancement of the secondary ion yield are the use of polyatomic primary ion bombardment, showing an increase of three to four orders of magnitude [5] and metal-assisted SIMS (MetA-SIMS), which may lead to an enhancement of more than 2 orders of magnitude when using monoatomic primary ions (Ga^+ , In^+ , Au^+) [1–4]. 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+} primary ion bombardment [6]. However, if a thin gold layer is deposited on a polymer sample, a slight yield decrease is observed using C_{60}^+ primary ions [7]. In order to evaluate whether these differences are due to the varied primary ion species or to the sample system, identical pristine and gold-coated polystyrene (PS) samples were analyzed with monoatomic (Ar^+ , Ga^+ , Xe^+ , Bi^+) and polyatomic (SF_5^+ , Bi_3^+ , C_{60}^+) primary ion species.

2. Experimental

Thick polystyrene layers were prepared onto cleaned silicon substrates by plasma polymerization of styrene monomers (99.5%; Acros organic, Belgium) using inductively coupled plasma at the rf of 13.56 MHz in an in-house-built vacuum chamber. The plasma parameters were set to 30 W, 1 hPa and 3 min.

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. The sample set consisted 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 between metal atoms, gold is not uniformly distributed on the sample surface [8]. The size of the gold islets was determined by transmission electron microscopy (Philips Tecnai 10, 80 kV). For this purpose, polymerized polystyrene was grown on a carbon-coated copper grid and coated with gold (20 nmol/cm^2), which produced mostly gold islets (Fig. 1) with less than 10 nm in diameter and some bigger islets.

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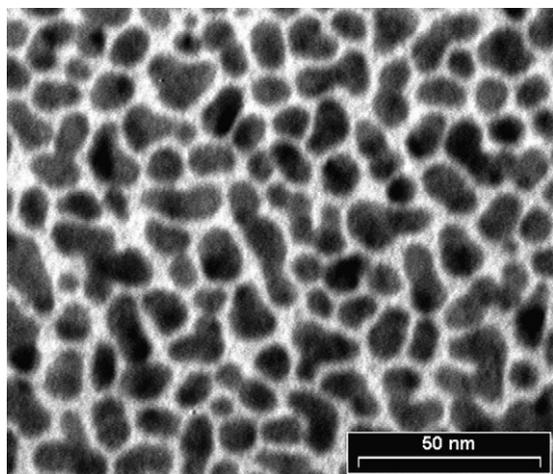


Fig. 1. TEM image of a polystyrene sample covered with 20 nmol/cm² (2 nm equivalent layer thickness) gold (dark islets).

They were separated by uncovered areas with a width of some nanometers.

SIMS experiments were performed using three time-of-flight secondary ion mass spectrometry (TOF-SIMS) instruments: (1) a TOF-SIMS instrument equipped with a 25 kV liquid metal ion gun (Bi_n⁺, Ga⁺, IONTOF GmbH) and an in-house-built 10 kV electron ionization gun (Ar⁺, Xe⁺, SF₅⁺); (2) a TOF-SIMS IV (IONTOF GmbH) equipped with a 25 kV Ga⁺ and a 9 kV SF₅⁺ primary ion (PI) source; (3) 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 C₆₀⁺ 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⁺, SF₅⁺ and 12 keV for Ga⁺, Bi⁺, Bi₃⁺ and C₆₀⁺. Additionally, Ga⁺, Bi⁺, and Bi₃⁺ were used with 25 keV. A maximal fluence of 10¹² ions/cm² (monoatomic PI) and 10¹¹ ions/cm² (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: (a) 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 [9]; (b) to monitor the aging effect, repeat measurements using Ar⁺ bombardment were carried out, finding a secondary ion yield change of less than 20%; (c) 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 primary ions) was calculated. In most cases, the relative standard deviation was less than 10%, in a few cases up to 20%.

3. Results

For spincoated 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 C₇H₇⁺,

but C₈H₉⁺. Metal-cationized fragments and molecules were reported to have higher yields than the related fragment or molecule ions [4,10]. But on the PS samples, gold-cationized fragment ions had significantly smaller yields than the shown characteristic fragments.

For all characteristic fragment ions emitted from the PS sample bombarded with monoatomic primary ions, a gold deposition of 0.2 and 2.0 nm equivalent thickness generally leads to an enhancement of the secondary ion yield (Fig. 2a). This enhancement is nearly the same for Xe⁺ and Bi⁺, more pronounced for Ar⁺ and with up to one order of magnitude highest for Ga⁺ ion bombardment. With one exception, increasing the mass of the primary ions leads to an increased yield from pristine as well as from gold-coated samples.

It can be seen that for low-mass primary ions (Ar⁺, Ga⁺), yield enhancement due to gold deposition is more probable and more pronounced than for higher mass primary ions (Xe⁺, Bi⁺), which show nearly the same enhancement. With higher mass primary ions, the yield obtained on the pristine samples is often even higher than the yield obtained with Ga⁺ on samples with the 2 nm gold layer.

Fig. 2b shows secondary ion yields of characteristic fragment ions emitted from the different PS samples under polyatomic ion bombardment. In contrast to the results shown in Fig. 2a, polyatomic ion bombardment leads to a decrease of the secondary

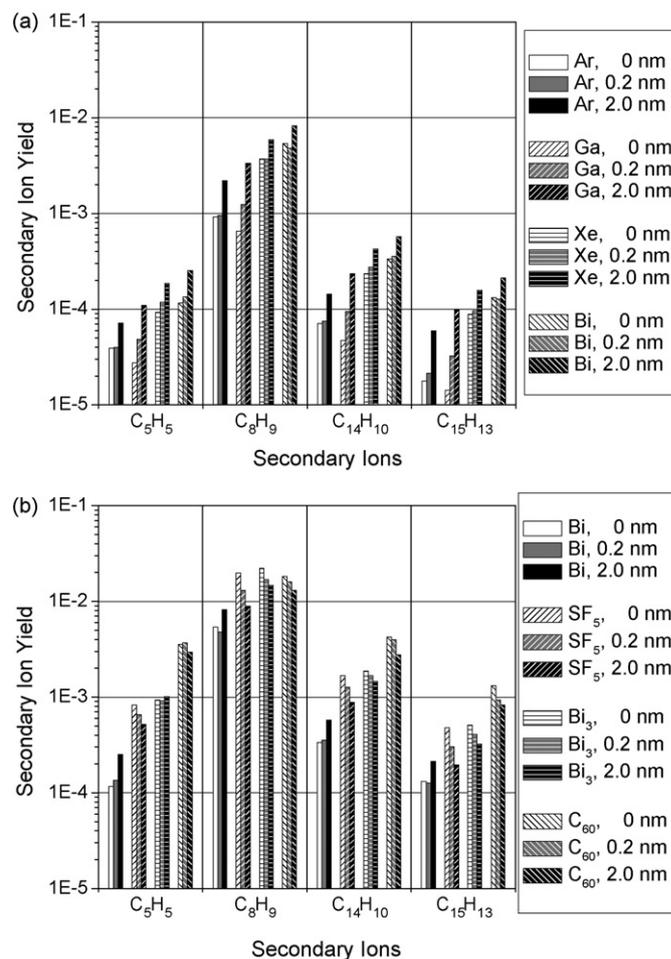


Fig. 2. Secondary ion yields of polystyrene characteristic fragment ions obtained from pristine and gold-covered surfaces using (a) different monoatomic primary ion species and (b) using different polyatomic primary ion species. To simplify the comparison with monoatomic ion bombardment, Bi⁺ data are added in the bottom figure.

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).

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. Similar results were also obtained for polymer dye mixtures [11].

Additionally, the effect of the primary ion energy was analyzed by changing the energy from 12 keV to 25 keV for Ga^+ , Bi^+ , and Bi_3^+ . For monoatomic Ga^+ and Bi^+ , the energy increase for all samples resulted in only slight yield changes. While yield decreased for some of the characteristic fragment ions (generally up to 20% and at most 60%), it increased for other fragment ions (generally up to 20% and at most 60%). Thereby, the samples with 2.0 nm gold deposition usually showed an increase, while the other samples usually showed a decrease. For polyatomic Bi_3^+ ion bombardment, only an increase in secondary ion yield was observed, ranging up to a factor of 2. This increase was independent from the amount of deposited gold.

4. Discussion

Although gold coverage reduces the area emitting organic fragment ions, in some cases an increase in secondary ion yield is observed. 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 process. Different primary ion parameters are known to affect energy depth distribution. At a given kinetic energy, the stopping power increases with increasing monoatomic primary ion mass, leading to an increased near-surface energy deposition. In the case of polyatomic primary ions, 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 primary ions, it will help to deposit more energy from the impinging mono- or polyatomic primary ions 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 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 primary ions than for polyatomic ones, especially monoatomic primary ions may penetrate the gold islets and may be deflected into surface-near trajectories due to the increased scattering of primary ions 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 primary ions, which cannot initially transfer a large

portion of their kinetic energy into the pristine organic sample surface. However, polyatomic primary ions 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 primary ions, 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 primary ions 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.

5. Conclusion

The effects of gold deposition and polyatomic primary ion bombardment, both separately and in combination, on secondary ion yield enhancement were investigated using thick-layer polystyrene samples. It can be concluded that secondary ion yields are significantly increased when using polyatomic primary ion species instead of monoatomic ions. The highest yields were obtained from pristine samples using polyatomic ion bombardment. Secondary 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. Nevertheless, further investigation on other sample systems is needed, because opposite behavior for Bi_3^{2+} ion bombardment on gold-coated biological samples [6] was shown.

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