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# Stretching the limits of static SIMS with $C_{60}^{+}$

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## Abstract

Pristine and Au-covered molecular films have been analyzed by ToF-SIMS (TRIFT[TM]), using 15 keV Ga$^+$ (FEI) and 15 keV $C_{60}^{+}$ (Ionoptika) primary ion sources. The use of $C_{60}^{+}$ leads to an enormous yield enhancement for gold clusters, especially when the amount of gold is low (2 nmol/cm$^2$), i.e. a situation of relatively small nanoparticles well separated in space. It also allows us to extend significantly the traditional mass range of static SIMS. Under 15 keV $C_{60}^{+}$ ion bombardment, a series of clusters up to a mass of about 20,000 Da (Au$_{100}^-$: 19,700 Da) is detected. This large yield increase is attributed to the hydrocarbon matrix (low-atomic mass), because the yield increase observed for thick metallic films (Ag, Au) is much lower. The additional yield enhancement factors provided by the Au metallization procedure for organic ions (MetA-SIMS) have been measured under $C_{60}^{+}$ bombardment. They reach a factor of 2 for the molecular ion and almost an order of magnitude for Irganox fragments such as $C_4H_9^+$, $C_{15}H_{23}O^+$ and $C_{16}H_{23}O^-$.
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## 1. Introduction

Buckminsterfullerene ($C_{60}^{+}$) projectiles induce a drastic enhancement of the parent and fragment ion yields in static SIMS of organic materials [1]. Under 15 keV bombardment, the yields increase by two orders of magnitude in comparison with Ga$^+$ primary ions for various organic samples, including PS oligomer and Irganox 1010 spin-coated films as well as adsorbed protein layers [1,2]. In the case of PS films, positively charged oligomers are directly desorbed, without the need of a cationizing metal atom/ion. Recently, new outstanding properties of fullerenes have emerged, e.g. the measured damage cross sections are so low that depth profiling organic materials is possible, the topography induced upon erosion of metallic samples is very limited [3]. These 'magical' properties open the door to new applications such as large molecule imaging and 3D analysis of organic multilayers and biological tissues. All these effects are caused by the different physics at play with fullerene projectiles that began unraveling, with the help of careful experiments and molecular dynamics simulations [4]. It is quite clear now that buckyballs transfer their energy in the top surface layers, creating

an overheated nanovolume that relaxes via collective atomic and molecular motions. Despite these amazing yield improvements and the mesoscopic character of the interaction, which places $C_{60}^{+}$-SIMS somewhere between traditional SIMS and MALDI, there is no report showing a significant extension of the mass range under fullerene bombardment.

The directions of this study are two-fold. First, we show that $C_{60}^{+}$ is able to desorb and ionize metal clusters up to a mass of at least 20,000 Da, which constitutes an extension of the mass range of static SIMS by a factor of 2. Second, we investigate the organic ion yield enhancements provided by the combination of fullerene projectile bombardment and gold cluster evaporation on the surface of organic materials (MetA-SIMS) [5].

## 2. Materials and methods

### 2.1. Samples

Samples of polystyrene (PS, $M_w$ = 1780 Da; $M_n$ = 1630 Da) and a polymer additive (Irganox 1010, $M_w$ = 1176 Da) were dissolved to a concentration of 1 mg/mL. The dissolved molecules were cast on 1 cm$^2$ substrates by depositing a droplet of the solution on the supports and allowing the solvent to evaporate. Some of the organic samples cast on cleaned (2-propanol; hexane) silicon wafers were metallized afterward by

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evaporating gold at a fluence of 2 and 20 nmol/cm$^2$ (the equivalents of 2 and 20 Å gold layers) onto their top surface. The evaporation was carried out in an Edwards evaporator at an operating pressure of $10^{-6}$ mbar and a deposition rate of 0.1 nm/s [5].

## 2.2. Secondary ion mass spectrometry

The secondary ion mass analyses were performed in a PHI-EVANS time-of-flight SIMS (TRIFT 1) [6]. To improve the measured intensities, the secondary ions were postaccelerated by a high voltage (7 kV) in front of the detector. No charge compensation was needed. The 15 keV Ga$^+$ beam was obtained from a FEI 83-2 liquid metal ion source (1.2 nA dc current; 22 ns pulse width bunched down to 1 ns). The 15 keV C$_{60}^+$ measurements were conducted using a primary ion beam system (IOG-C60-20) from Ionoptika Ltd. (2–100 pA dc current with apertures of 300–1000 μm and a 50 V grid voltage) [1]. The contribution from C$_{60}^{2+}$ was eliminated by a double set of blanking plates. The primary ion current was measured in a small aperture of the sample holder, with and without a positive bias of 27 V (to cancel the effects of secondary electron emission).

## 3. Results

### 3.1. Yield enhancement of organic ions with C$_{60}^+$

As a preliminary test, the secondary ion (SI) yields obtained under bombardment of pristine Irganox 1010 and PS oligomer thin films with 15 keV Ga$^+$ and C$_{60}^+$ were investigated. The yield enhancement factors (C$_{60}^+$-SI yield/Ga$^+$-SI yield) are summarized in Table 1. They attain two orders of magnitude for large fragments and parent ions, as reported by Weibel et al. [1]. The enhancement factors for the molecular ions of PS are not well defined because these molecular ions are not observed under 15 keV Ga$^+$ bombardment. Complementary experiments performed with smaller PS oligomers ($M_w$ = 590 Da; $M_n$ = 550 Da) indicate a yield enhancement factor that is actually larger than $10^4$ for molecular ions [2].

### 3.2. Effects of C$_{60}^+$ on the desorption of gold clusters

The evaporation of gold on the organic film results in the formation of a mixed surface layer containing organic molecules and metal clusters. For this study, two different

regimes of metallization were considered. In the first case, 2 nmol/cm$^2$ (2 Å layer equivalent) were evaporated on the organic films. For organic samples such as polystyrene, this quantity of metal induces a surface structure where 1–3 nm gold clusters are well separated on the surface [7,8]. In the second case, 20 nmol/cm$^2$ were evaporated (20 Å layer equivalent). This gold quantity corresponds to a regime in which large clusters with a characteristic length of 10–20 nm start coalescing into islands, with channels of bare organic material between them [8]. This is the situation that was found to be the most advantageous for organic ion yield enhancement upon 15 keV Ga$^+$ ion bombardment [5].

As was the case for organic ions (Table 1), the emission of gold cluster ions from an ''organic matrix'' is greatly enhanced by the use of C$_{60}^+$ projectiles. The most striking effect is observed for a coverage of 2 Å of gold. The enhancement factor is three orders of magnitude or larger for Au$_n^{+/-}$ clusters ($4.9 \times 10^3$ for Au$_3^-$ – see Fig. 1; $8.9 \times 10^3$ for Au$_3^+$ – not shown). In comparison, the yield increase is more moderate for atomic Au ions ($1.5 \times 10^2$ for Au$^-$; $1.6 \times 10^2$ for Au$^+$) in the same conditions of gold coverage. For a 20 Å equivalent gold overlayer, the *relative* yield increase of gold cluster, when going from Ga$^+$ to C$_{60}^+$ projectiles, is slightly lower but the *total yield* of small Au$_{2-5}^{+/-}$ clusters sputtered by C$_{60}^+$ is the largest ($2.2 \times 10^{-2}$ for Au$_3^-$ – see Fig. 1; $2.8 \times 10^{-3}$ for Au$_3^+$ – not shown). One noticeable effect is the intensity decay as a function of the cluster size. In the considered range of clusters, this intensity decrease is very limited for the 2 Å gold overlayer, but it is exponential for the 20 Å overlayer. In all cases, the decay is slightly more pronounced under fullerene bombardment. A tentative explanation is proposed in the discussion.

Upon C$_{60}^+$ bombardment, the extent of the useful mass distribution of adsorbed Au$_n^{+/-}$ clusters is also exceptional. The negative mass spectrum of a film of Irganox covered with 2 nmol/cm$^2$ of gold is shown in Fig. 2 (primary ion fluence: $8.4 \times 10^6$ ions). Even though the signal/noise ratio decreases
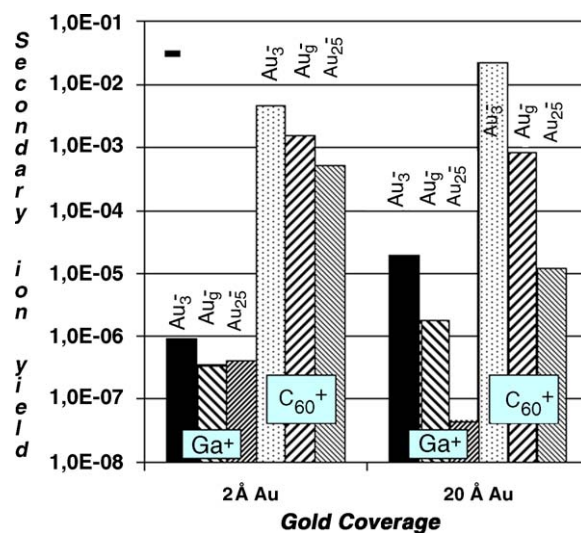
Table 1
Yield enhancement factors ($Y_{C_{60}^+}/Y_{Ga^+}$) of a series of secondary ions sputtered from pristine films of Irganox 1010 and polystyrene oligomers ($M_w$ = 1780 Da; $M_n$ = 1630 Da) cast on silicon

Irganox 1010

| C$_2$H$_3^+$ | C$_4$H$_9^+$ | C$_{14}$H$_{19}$O$^+$ | C$_{15}$H$_{23}$O$^+$ | (M-C$_{17}$H$_{25}$O$_3$)$^+$ | (M + Na)$^+$ | Total |
|---|---|---|---|---|---|---|
| 42 | 35 | 33 | 43 | 122 | 90 | 49 |

Polystyrene

| C$_3$H$_3^+$ | | C$_7$H$_7^+$ | C$_{15}$H$_{13}^+$ | M$^+$ | | Total |
|---|---|---|---|---|---|---|
| 75 | | 139 | 162 | >$10^2$ | | 118 |



Fig. 1. Secondary ion yields of negative gold clusters (Au$_3^-$, Au$_9^-$ and Au$_{25}^-$) sputtered from two gold-metallized Irganox 1010 films (2 and 20 nmol Au/cm$^2$).
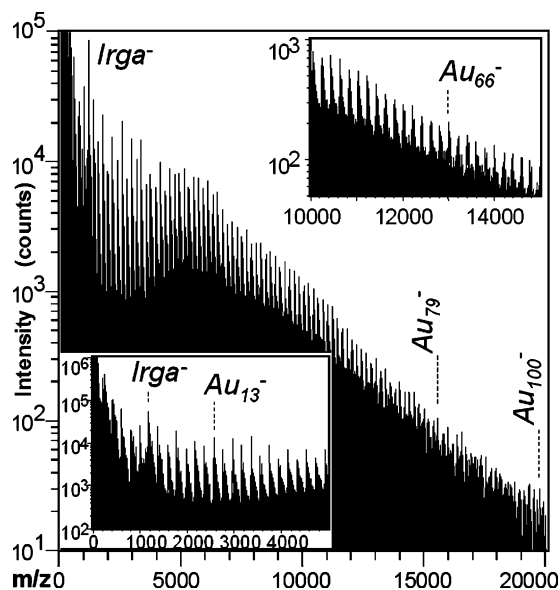
Fig. 2. Negative secondary ion mass spectrum of a gold-metallized Irganox 1010 film (2 nmol Au/cm$^2$) induced by $C_{60}^+$ primary ions (primary ion fluence: $8.4 \times 10^6$ ions).
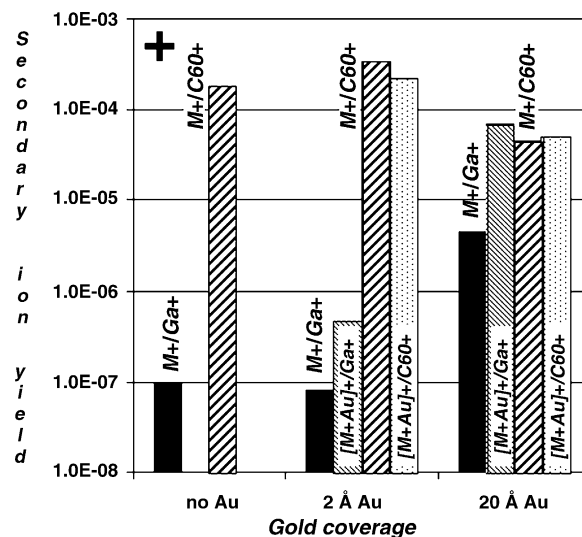


Fig. 3. Secondary ion yields of positive molecular ions, $M^+$ and quasimolecular ions $(M + Au)^+$, sputtered from a pristine and two gold-metallized Irganox 1010 films (2 and 20 nmol Au/cm$^2$).

significantly with mass, cluster peaks are detected up to about 20 kDa (see $Au_{100}^-$ at $m/z = 19{,}700$). Details of the mass spectrum in the insets emphasize the clarity and regularity of the distribution even beyond 10 kDa. Such a mass spectrum could not be obtained under $Ga^+$ bombardment. Instead, with increasing ion fluence, the signal/noise ratio worsens at high mass, probably because large ion fluences induce irreversible damage in the sample surface. It is also important to note that the detection efficiency decreases significantly with mass in our system, even below 10 kDa and with a postacceleration voltage of 7 keV. For large clusters as those observed under $C_{60}^+$ bombardment, it certainly becomes the limiting factor in our measurements.

### 3.3. Cumulated effects of $C_{60}^+$ and a gold coverage on the desorption of organic ions

Here, we focus on the secondary yields of molecular, quasimolecular and fragment ions obtained upon the combined effects of gold coverage and buckminsterfullerene ion bombardment. Fig. 3 shows the evolution for positive ions. For $Ga^+$ bombardment, similar behaviors as those described in Ref. [9] are observed. Maximum enhancement factors of 45 and 678 are observed for the molecular ion $M^+$ and the quasimolecular ion $(M + Au)^+$ of Irganox, respectively, with 20 Å of gold. The situation is very different under fullerene ion bombardment. In that case, the gold deposition procedure provides a minor improvement (a factor of 1.9 for $M^+$ with 2 Å of gold). Note that the molecular ion yield enhancement factor obtained with $C_{60}^+$ for pristine Irganox ($1.8 \times 10^3$) still overcomes the improvement provided by Au metallization, even when $(M + Au)^+$ is considered ($\sim 0.7 \times 10^3$). One also observes a gradual increase of the negative ion yields under 15 keV $Ga^+$ bombardment, up to a factor of 11 for $M^-$ and 444

for $C_{16}H_{23}O^-$, with 20 Å of gold (not shown). When $C_{60}^+$ projectiles are used, the negative molecular ion yield increases by a factor of 2.6 with 2 Å of gold and then decreases below its initial value when 20 Å of gold are evaporated. The $C_{16}H_{23}O^-$ fragment ion yield increases by a somewhat larger factor (8 with 2 Å of gold). In summary, for the considered molecule, the yield enhancement provided by the Au metallization procedure is low when $C_{60}^+$ is used as a projectile, e.g. a factor of 2 for the molecular ion. Nevertheless, for characteristic Irganox fragments such as $C_4H_9^+$, $C_{15}H_{23}O^+$ and $C_{16}H_{23}O^-$, it reaches almost one order of magnitude. The fact that $(M + Au)^+$ is not more intense than $M^+$ under $C_{60}^+$ beam bombardment highlights the exceptional ionization efficiency of buckminsterfullerene projectiles.

### 4. Discussion and conclusion

In our measurements with mixed metal-organic samples, the average yield increase is even larger for gold clusters than for organic ions (Irganox 1010 and polystyrene). The yield improvement is significantly beyond three orders of magnitude for $Au_{3-25}^{+/-}$ clusters, which is also largely more than the measured values for thick metal films. For silver surfaces, enhancement factors of 3.7, 12.5 and 25 have been measured by Sun et al. for $Ag^+$, $Ag_2^+$ and $Ag_3^+$, respectively [10]. Therefore, we attribute the observed results to the specific structure of the sample, where gold clusters or islands are dispersed in an organic matrix. Another clue is provided by the decay of the intensity with increasing cluster size. The rapid decay (exponential/power law) observed in the high gold coverage regime (20 nmol/cm$^2$) evokes the results obtained for bulk metallic crystals [11]. On the other hand, the behavior observed in the low gold coverage regime (2 nmol/cm$^2$) is more specific (Fig. 1): large clusters are extracted relatively easily from the matrix, as witnessed by the measured ion yields. Considering the expected morphology of the sample, i.e. relatively small

clusters well separated on the organic surface, it is plausible that the projectile may ''kick off'' intact nanoparticles or break them apart in the surface. In this context, the relatively lower cluster yield enhancement (or faster yield decay, see $Au_9^{+/-}$ and $Au_{25}^{+/-}$) observed with $C_{60}^+$ when going from 2 Å coverage to 20 Å coverage probably mirrors the comparatively lower efficiency of fullerenes at sputtering clusters from a heavy metal matrix.

The positive effect of metallization on the secondary ion yields of organic ions is exceptional upon $Ga^+$ bombardment, but rather limited with $C_{60}^+$ projectiles (less than one order of magnitude). In addition, the largest yields correspond to a different value of the gold coverage for $Ga^+$ and $C_{60}^+$ (2 nmol/$cm^2$ with $C_{60}^+$ and 20 nmol/$cm^2$ with $Ga^+$). It is known that Irganox 1010 may diffuse and partly cover the gold clusters/ islands [9]. Therefore, Irganox molecules adsorbed on metal islands should lead to an enhanced signal under $Ga^+$ bombardment [5], but not under $C_{60}^+$ bombardment, because – again – heavy metal substrates do not produce large yield enhancements with fullerene projectiles [4]. These considerations might explain the decrease (respectively, increase) of the organic ion yields with increasing gold coverage under fullerene (respectively, gallium) bombardment. To address this point more completely, one should test the effects of the metallization procedure for other types of organic samples, including high molecular weight polymers that cannot diffuse over the gold nanoparticles [5].

In summary, we observe that the large yield enhancement generally measured for $C_{60}^+$ bombardment of purely organic materials also extends to metal nanoparticles embedded in an organic matrix. Fullerene projectiles lead to a significant expansion of the accessible mass range for such samples. The yield enhancement factors are strongly dependent on the gold coverage, i.e. on the microstructure of the surface layer, which is interpreted as a consequence of the greater efficiency of $C_{60}^+$ to desorb organic materials than metallic layers. The metallization procedure, proposed for organic ion yield enhancement under monatomic projectile bombardment (MetA-SIMS) [5,9], appears comparatively less efficient with fullerene projectiles.

## Acknowledgements

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