

Molecular secondary ion formation under cluster bombardment: A fundamental review

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Abstract

A brief review is given regarding the application of cluster ion beams as desorption probes in molecular SIMS. The general observation is that the efficiency of secondary ion formation, particularly that of complex molecular species, is significantly enhanced if polyatomic projectiles are employed instead of atomic species. Apart from the sensitivity increase, cluster bombardment also appears to allow for molecular depth profiling studies without the accompanying damage accumulation normally associated with atomic projectiles. A few fundamental aspects are addressed in an attempt to highlight the physics behind these observations. It appears that much of the benefit associated with cluster bombardment is connected to the fact that these projectiles give access to very high sputter yields which are not accessible with atomic primary ions.

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1. Introduction

One of the most exciting recent developments in molecular secondary ion mass spectrometry concerns the use of polyatomic species or “clusters” as projectiles to desorb the analyte molecules from the investigated surface [1]. Already about 20 years ago, it had been realized that projectile species containing more than one atom may lead to a drastic increase of yields, i.e., average numbers of particles desorbed per projectile impact, and may therefore greatly enhance the sensitivity of the technique. Although being explored from a fundamental perspective in several groups, however, this fact has for a long time been widely neglected in the analytical SIMS community. In retrospective, this was probably due to the apparent difficulty to generate cluster ion beams of sufficient intensity to be utilized for practical surface analysis. Quite recently, the situation has changed dramatically. The advent of commercially available, compact cluster ion sources which are compatible with existing SIMS instrumentation has sparked renewed interest in the use of polyatomic projectiles in SIMS. In fact, the field is currently undergoing an extremely rapid transition, and one may expect polyatomic species to become the dominant projectiles used in

routine (molecular) SIMS in the near future [1]. The present paper is intended to provide a brief assessment of the role polyatomic projectiles play with respect to molecular secondary ion formation, including the present state and the historical development leading to it. Due to the stringent space limitation, the paper will concentrate on the compilation of a few essential experimental facts, restricting the analysis to the keV impact energy range where the interaction between projectiles and solid is dominated by nuclear stopping. Theoretical models of the particle emission process under conditions as generated by cluster impact have been extensively reviewed [2] and will therefore only be touched briefly. Other important aspects of cluster-surface interaction like surface smoothing, cluster beam deposition, etc. will not be covered here.

2. The past

The observation of “cluster effects” in ion bombardment-induced desorption of surface species dates back to the 1970s, when Andersen and Bay [3] observed a large increase of the (total) sputter yield bombarding elementary surfaces with diatomic instead of atomic projectiles. The enhancement was found to be nonlinear in the sense that the yield observed under impact of a polyatomic projectile containing n atoms is larger than that produced by its n constituents impinging indepen-

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dently with the same velocity, the magnitude of the corresponding nonlinear enhancement factor $k_n = Y_n/(nY_1)$ being of the order of 2 (for $n = 2$). Extending this work to triatomic projectiles ($n = 3$), Thompson and coworkers [4,5] later observed nonlinear enhancement factors ranging up to 10 for Sb_3^+ ions bombarding metallic surfaces. At the same time, Wittmaack [6] first reported a corresponding nonlinear enhancement of secondary ion yields when bombarding a silicon surface with rare gas dimer ions. A few years later, Appelhans and Delmore [7] first investigated the application of cluster bombardment in organic surface analysis. They demonstrated that the molecular ion yields observed from various pharmaceutical overlayers on metal substrates are enhanced by factors of 10–25 if neutral or negatively charged SF_6 projectiles are used instead of isoenergetic Cs^+ ions of almost equal mass. In the same work, they investigated the accumulation of chemical damage induced by the different projectiles and demonstrated that the yield increase was much more pronounced than that of the disappearance cross-section – defined by the exponential decay of the molecular ion signal observed with increasing primary ion fluence [8] – leading to a net gain of sensitivity to retrieve molecular information with the polyatomic projectile.

Up to the mid-1980s, the choice of polyatomic projectiles was essentially dictated by the ability to produce the respective ion beams using conventional gas ion sources. As a consequence, only a few different clusters had been employed in the nuclear stopping regime relevant in cluster SIMS. The first systematic study of the dependence of cluster effects on the nuclearity, i.e., the number of constituent atoms, of the projectile was published by Blain et al. [9,10], who used $(\text{CsI})_n\text{Cs}^+$ ions generated by sputtering of a CsI target to bombard various sample surfaces. The essential results of this study were that (1) the secondary ion yield increases proportional to the square of the projectile impact velocity, (2) the observed yield increases nonlinearly with increasing projectile nuclearity and (3) the yield increase is more pronounced for molecular species than for atomic ions. The first result was later confirmed in a number of follow-up studies employing different projectiles and must therefore be regarded as a general feature of cluster SIMS. The second point mentioned above can be quantified by an analysis of the nonlinear enhancement factor as defined above. For the molecular ion yield of phenylalanine, for instance, the respective data are listed in Table 1.

Monitoring the Au^- ion yield off a pure gold surface, on the other hand, leads to a significantly smaller enhancement, demonstrating the third point mentioned above. As a general

trend, it was found that the nonlinear enhancement effect is largest between mono- and diatomic projectiles and decreases with increasing projectile nuclearity. Later work performed by the same group [13,14] indicated that the yield enhancement becomes linear for projectiles containing more than approximately seven atoms. Even under these conditions, however, one should note that the yields strongly increase with increasing projectile nuclearity.

The spectrum of available projectile species was broadened in 1991 by Benguerba et al. [11], who used a liquid metal ion source to produce Au_n^+ projectile clusters of widely varying nuclearity n . Using bombarding energies between 5 and 30 keV, they measured $(M - \text{H})^-$ molecular ion yield enhancement factors on phenylalanine which are also listed in Table 1, corroborating the earlier results obtained with different projectiles. At the same time, however, they report an increased fragmentation with increasing projectile nuclearity (see also [15] and references therein). The range of investigated primary ion species was expanded even further by the same group introducing C_{60}^+ as a projectile for cluster SIMS [16], leading, for instance, to an about 20-fold enhanced molecular ion yield on phenylalanine as compared to isoenergetic Cs^+ ions.

A particularly interesting approach to the use of polyatomic projectiles in SIMS was published by Mahoney et al. [17], who used massive clusters containing up to 10^6 glycerol molecules to bombard organic analytes embedded in a glycerol matrix. Although nothing is said about the absolute ion yield enhancement, they observe a much cleaner spectrum dominated by the molecular $(M - \text{H})^-$ ion peak in comparison with keV Cs^+ ion bombardment which produced a heavily fragmentation dominated spectrum. Note that although the total energy of the massive cluster projectile is as large as about 8 MeV, this corresponds to an impact energy of only several eV per glycerol molecule impinging independently with the same velocity. Since this energy does not suffice to generate any sputtering, the mere observation of a SIMS spectrum under cluster bombardment manifests an infinite nonlinear yield enhancement. The original work was later extended [18–21], demonstrating the possibility to detect molecular ions of biomolecules ranging up to 12,000 Da from surfaces with and without glycerol matrices. A similar approach was pursued by the Uppsala group [22], who developed the use of massive biomolecules (“macromolecules”) as projectiles in SIMS.

One particular aspect of this work concerns the chemical damage if the static limit is abandoned. As demonstrated by Cornett et al. [20], the molecular ion signal reaches a stable steady state value, from which it does not decrease any more even if large primary ion fluences are applied. Moreover, it was shown that the mass spectrum acquired under these conditions is still dominated by the molecular ion peak, demonstrating for the first time that the ion beam induced accumulation of chemical damage, inevitably leading to a complete destruction of the molecular information in experiments using atomic primary ions, may in principle be prevented using cluster projectiles. This important observation opens the door to molecular depth profiling applications of cluster SIMS which will be discussed in more detail below.

Table 1
Nonlinear enhancement factor k_n observed for $(M - \text{H})^-$ molecular ion yield of phenylalanine upon transition from monoatomic to polyatomic projectile ions containing n atoms

Projectiles	k_2	k_3	k_4	k_5
$(\text{CsI})_n\text{Cs}^+$	–	7	–	12
Au_n^+	4	5	6	9

For definition of k_n see text (data reproduced from Refs. [9,11,12]).

In 1994, Szymczak and Wittmaack [23] investigated the role of the charge state of both projectiles and detected secondary ions with respect to the cluster-induced ion yield enhancement of organic molecules on a silicon surface. They found that the yield enhancement is

- the more pronounced the larger the mass of the emitted secondary ions;
- only very weakly dependent on the charge state of the projectile;
- significantly larger for negative than for positive secondary ions.

The first observation is in accordance with earlier studies, again corroborating the fact that particularly the yields of complex molecular species are enhanced under cluster bombardment. The third observation was tentatively attributed to an enhanced negative ion formation mechanism involving attachment of co-emitted electrons.

The role of complexity of the desorbed molecular species was addressed 1996 by Baudin et al. [24], who investigated the yield enhancement of secondary cluster ions sputtered from inorganic and organic targets as a function of the emitted cluster size. A series of similar studies was later performed by Belykh et al. [25–31] for metallic targets. It was again found that the yield enhancement induced by polyatomic projectiles strongly increases with increasing size of the emitted cluster, the magnitude of the nonlinear enhancement factor ranging from values around n (the projectile nuclearity) for sputtered atomic species to several orders of magnitude for emitted clusters containing about 10 atoms. These findings were complemented by measurements of the kinetic emission energy distribution of the ejected particles, which was found to undergo a drastic change, indicating a different desorption mechanism under cluster bombardment. Since these investigations were restricted to secondary ions, however, it was not clear whether the observed cluster effects originated from variations of the desorption yields or the ionization probability of the desorbed species. That question was later addressed by Heinrich and coworkers [32–34], who performed similar experiments on sputtered neutral metal clusters under polyatomic projectile bombardment, demonstrating that the observed yield enhancement is primarily due to an enhanced desorption mechanism.

A systematic study of organic molecular ion formation under cluster impact was published in 1998 by Koetter and Benninghoven [35], who bombarded various polymer surfaces with SF_5^+ projectiles and measured both yields and disappearance cross-sections of the observed secondary ion signals. Similar studies were also performed for Langmuir–Blodgett layers on metal substrates [36–39] as well as polymer additives [36,40] using, in addition, a number of different C_nH_m^+ and C_nF_m^+ projectile ions up to $n = 10$ and $m = 8$. These studies revealed that upon switching from rare gas ions to isoenergetic cluster projectile ions the molecular (fragment) ion yields Y increase far more than the disappearance cross-section σ , indicating that the yield enhancement significantly outweighs

the increase in chemical damage accumulation associated with the cluster projectile. In order to quantify these results, they introduced the ion formation efficiency $E = Y/\sigma$, which was found to increase by factors ranging from 6 to 60, the effect being much more pronounced for multilayer systems than for organic monolayers on metal substrates [36,37,39]. At the time, the enhancement appeared to saturate for projectiles containing more than six atoms, but later studies involving C_{60}^+ projectiles [41] disproved that notion (see below).

A breakthrough in molecular SIMS was reached when Gillen and coworkers [42,43] demonstrated the possibility to perform sputter depth profile analysis of organic overlayers while maintaining the molecular information. Using C_n^- projectile ions, they observed a stable molecular ion signal throughout the sputter removal of the entire film. Similar observations were made later using SF_5^+ [44–53], Au_n^+ and C_{60}^+ projectiles [54–58], indicating that the cluster projectile must have the unique ability to remove chemical damage at comparable rate as produced. For biomolecules embedded in an ice matrix, it was demonstrated that chemical damage accumulated during atomic projectile bombardment can even be removed again using cluster projectiles [57].

The beginning of the millenium was characterized by the appearance of new instrumentation designed for the use of cluster SIMS as a routine analysis technique. For once, an ion source developed to generate projectiles like Ar_{2000} was adapted for use in SIMS analysis [59,60]. The advantage of such massive gas projectiles is that also reactive clusters like $(\text{O}_2)_n$ can easily be generated in order to exploit the oxygen matrix effect for sensitivity enhancement. Second, commercial sources producing Au_n^+ [61], Bi_n^+ [62] and C_{60}^+ [63–65] cluster ions have been developed which deliver sufficient cluster ion current for routine analysis and allow focusing to spot sizes of micron (C_{60}^+) or even sub-micron (Au_n^+ , Bi_n^+) diameter for imaging analysis. The availability of these sources, which are readily incorporated into existing SIMS instrumentation, has sparked the field of cluster SIMS. When comparing Au_3^+ to Ga^+ projectiles, molecular secondary ion yield enhancements by more than two orders of magnitude have been reported [61], leading to a substantial increase of the ion formation efficiency. Similar effects were found for Bi_m^+ projectiles [62]. Even larger yield enhancements are observed for C_{60}^+ projectiles [1,54,55,57,63–71], ranging from typically two orders of magnitude up to an exceptional case of a 20,000-fold increase [72].

In a most recent development, Tempez et al. [73] have investigated the use of massive gold clusters containing about 400 atoms, which can also be generated in a liquid metal ion source. In combination with a new development in TOF SIMS instrumentation featuring orthogonal extraction of the secondary ions, they find a molecular ion yield enhancement on Gramicidin by factors of 70, 1000 and 20,000 when compared to Au_5 , Au and Ga projectiles, respectively. Moreover, no indication of damage accumulation is found with increasing primary ion fluence, whereas the usual exponential decay is observed for Au_5 . The implications of these observations are currently being explored.

3. The present state

As of today, a suite of primary ion species has been established for use in routine cluster SIMS analysis (see Table 2). From a practical standpoint, it has been established that all polyatomic projectiles lead to a significant increase in molecular ion yields when compared to atomic projectiles of comparable mass and energy. The magnitude of that enhancement depends on the particular projectile–sample combination, being generally less pronounced for monolayer overlayers on metallic substrates than for thick organic layers [36,37,39,74] or (sub)monolayers on such substrates [41]. Probably the most comprehensive comparison of different cluster projectiles was published by Kersting et al. [41], who investigated sub-monolayers of a polymer additive deposited on an organic matrix. From these data, one can extract “typical” factors illustrating the order of magnitude of the yield enhancement effect as displayed in Table 2.

The yield enhancement is generally more pronounced for complex molecular ions than for smaller fragments. As an example, Fig. 1 depicts a static SIMS analysis of histamine molecules embedded in an ice matrix using Ga^+ and C_{60}^+ projectiles. It is seen that (i) the signal of larger $(\text{H}_2\text{O})_6\text{H}^+$ matrix cluster ions is much more enhanced than that of $(\text{H}_2\text{O})\text{H}^+$ and (ii) the molecular ion signal clearly exhibits a larger enhancement than all histamine-related fragments. In the context of organic SIMS, molecular ion yields generally appear to be much more enhanced than, for instance, the total sputter yield of the sample (by a factor of ~ 30 in the example of Fig. 1). These findings clearly point at a more efficient desorption mechanism of molecular species under cluster bombardment. In many cases, the use of cluster projectiles leads to a “cleaner” molecular spectrum indicating less fragmentation (see Fig. 1). However, it should be noted that also the opposite has been reported (see, for instance, Ref. [15] and references therein), making the picture not entirely clear in this respect.

The yield enhancement is not counterbalanced by a similar increase in chemical damage. In fact, disappearance cross-sections measured under cluster impact appear to be roughly comparable to those determined for atomic projectiles (cf. Table 2). As a consequence, the yield enhancement leads to a corresponding increase in ion formation efficiency, i.e., the

Table 2

Relative values of secondary ion yield Y , disappearance cross-section σ and ion formation efficiency E for different projectile ions as evaluated for the quasi-molecular ion $(M - \text{H})^+$ of Irganox 1010

	Y_r	σ_r	E_r
Ga^+ (10 keV)	1	1	1
Cs^+ (10 keV)	12.5	1.4	8.7
SF_5^+ (10 keV)	137.5	2.3	60.0
Au^+ , Bi^+ (12 keV)	27.5	1.3	21.4
Au_2^+ , Bi_2^+ (12 keV)	268.8	4.0	67.1
Au_3^+ , Bi_3^+ (12 keV)	1225.0	4.8	257.1
C_{60}^+ (10 keV)	2000.0	0.9	2142.3

In order to illuminate the relative role of different projectiles, the measured quantities were normalized to those determined under Ga^+ bombardment (data reproduced from Ref. [41] with permission of the authors and Elsevier).

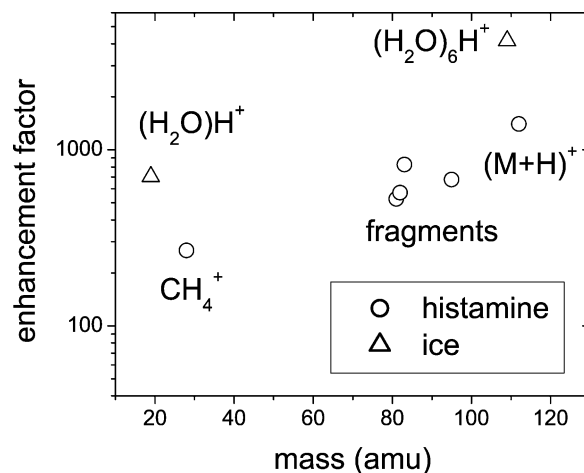


Fig. 1. Enhancement factor between static secondary ion yields produced by 20-keV C_{60}^+ and 15-keV Ga^+ projectile ions impinging onto a frozen water ice sample doped with histamine.

molecular detection sensitivity per unit of chemical damage, with typical gain factors listed also in Table 2. It is particularly this observation which makes cluster projectiles ideally suited for high resolution molecular imaging analysis [62].

At least in some cases, cluster projectiles are able to retrieve molecular information outside the static limit, opening the door to molecular sputter depth profiling applications. An example is reproduced in Fig. 2, which shows a C_{60}^+ -induced depth profile across a 200-nm trehalose layer doped with a small peptide on a silicon substrate [58]. The molecular ion signal is found to drop exponentially into a steady state value persisting across the entire layer, until the substrate interface of typically 10 nm width [43–45,47–49,53,75] is reached. At small primary ion fluences, fluctuations are observed which are different for secondary ions derived from the analyte (here: peptide) and the matrix (here: trehalose) and have been tentatively attributed to a chemical variation of the ionization probability [58]. The

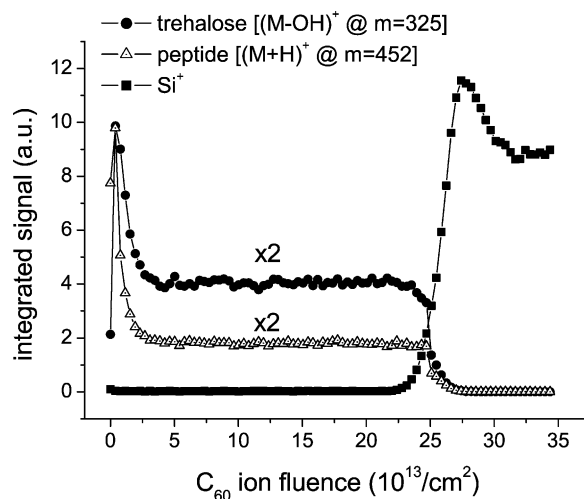


Fig. 2. Molecular depth profile of a 200-nm trehalose film doped with a small peptide (GGYR) spin cast onto Si. Both the sputter erosion as well as the (static) data acquisition were performed using 20-keV C_{60}^+ projectiles (data taken from Ref. [58]).

measured erosion rate can be converted into a very large total sputter yield of several hundred molecular equivalents of trehalose ($\sim 70,000$ amu) per projectile impact. Similar yields (~ 2700 H_2O molecule equivalents or $\sim 49,000$ amu per impact) have been observed for amorphous water ice bombarded with the same projectiles and energy [54].

4. A few fundamental aspects

4.1. Why are desorption yields enhanced under cluster bombardment?

The crucial parameter governing the physics of particle emission induced by the projectile impact is the energy density introduced into the sub-surface region. Qualitatively, it is clear that a polyatomic projectile must deposit more of its energy closer to the surface, since the constituent atoms impinge with reduced velocity and therefore penetrate less deep than a single atomic projectile with the same kinetic energy. If the deposited energy density becomes comparable to the binding energy within the solid, the nature of the impact induced event changes from a linear collision cascade to a dense collisional spike. This change can be monitored by looking at the emission velocity distribution of the sputtered or desorbed species, which changes drastically from that predicted by linear cascade theory to one predicted by a phase explosion of a supercritically heated subsurface volume [76]. This picture is also corroborated by visualizations of recent molecular dynamics computer simulations of cluster bombardment [77–79]. An interesting characteristic of the emission mechanism is that the velocity distributions of atomic and molecular species leaving the surface tend to become similar [76,80], indicating that desorbed molecules may be entrained into a relatively slowly moving gas flow instead of being knocked off the surface by single collisions. This picture suggests that the energy density must not significantly exceed the internal binding energy of a desorbed molecule, since otherwise unimolecular fragmentation reactions will counteract the enhanced desorption efficiency [81]. For the specific case of sputtered metal clusters, this effect was shown experimentally by Heinrich and coworkers [32,33] and predicted theoretically by Colla and Urbassek [82].

4.2. Do cluster projectiles help to ionize desorbed species?

In trying to unravel the fundamental processes leading to enhanced molecular ion yields under cluster bombardment, an important question is whether the observed effects are caused by an enhanced *desorption* mechanism or by an enhanced *ionization* of the desorbed species (or both). For metal clusters sputtered from metallic targets, this question has been settled by comparative measurements of neutral and ionized species leaving the surface [32,33,83,84]. The result of these studies is that the ionization probability of both atomic and molecular (cluster) species sputtered from such surfaces is not enhanced under polyatomic projectile impact. One notable exception is observed for SF_m^+ projectiles, which incorporate fluorine into

the surface and therefore lead to a drastically enhanced positive ionization probability of all emitted species by means of a well-known chemical matrix effect [85,86].

Corresponding systematic studies on molecular species desorbed from organic surfaces are still lacking. In principle, it seems feasible that projectile impact-induced chemical reactions may modify chemical ionization paths like protonation, deprotonation, etc. Two different categories of such modifications can be discerned. First, proton transfer reactions may occur in the same collisional spike also inducing the desorption process, leading to chemical ionization within one single impact event. These effects would be visible in a static SIMS experiment using different projectile species. Second, bombardment-induced chemical modification may accumulate with increasing projectile fluence. While this chemical damage efficiently wipes out the molecular information for atomic projectiles, it might in cluster SIMS act as a source of ionizing agents such as liberated protons. The effect may be illustrated on a depth profile across a 20 nm amorphous ice layer deposited onto a silver surface [87] depicted in Fig. 3. Secondary ion signals of protonated and non-protonated H_2O molecules show a distinctly different behavior as a function of projectile fluence, indicating a strong variation of the proton availability for chemical ionization. The m/z 19/18 signal ratio indicates an increasing protonation efficiency with increasing projectile fluence, until a steady state is reached. In fact, MD simulations reveal that protons may be liberated and trapped in the bulk of an ice target bombarded with energetic ions [88]. Both the static and the dynamic value of the 19/18 ratio depend on the projectile, indicating different levels of chemical ionization enhancement under bombardment with different projectiles like Au_n^+ and C_{60}^+ [87,89]. In this context, it should be noted that similar variations of the 19/18 ratio are also observed in depth profiles like that shown in Fig. 2, suggesting that the initial fluctuation of the molecular signal may be attributable to a chemically modified ionization process. If metallic projectiles are used for sputter removal, a metallization of the (sub)surface region is built up which may in principle also lead to a modified ionization efficiency of

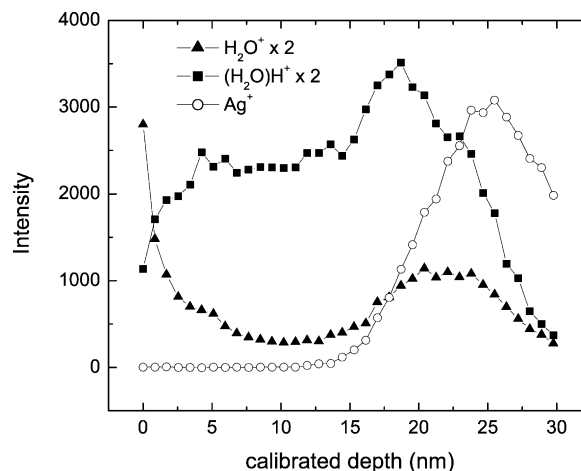


Fig. 3. Depth profile of a 20 nm ice film deposited onto a silver surface obtained with 20-keV C_{60}^+ projectiles [87].

organic molecules [90]. Clearly, more work is needed to clarify these points.

4.3. Why does molecular depth profiling seem to work with cluster projectiles?

In order to address that question, the erosion dynamics of the sample surface must be considered. Following an idea originally proposed by Gillen et al. [91], a simple model can be invoked which is based on the assumption of an altered layer of thickness d being modified by the ion bombardment. Three fluxes are considered which modify the concentration of analyte molecules in this layer, namely (1) the flux of molecules disappearing from the altered layer due to desorption from the surface, (2) the number of molecules disappearing from the altered layer due to chemical damage and (3) a supply flux of fresh molecules from the bulk due to erosion of the surface. Details of the model will be published elsewhere [92]. A steady state molecular signal is reached when disappearance and supply fluxes balance. While the disappearance flux is governed by the damage cross-section (which cannot be changed) and/or the desorption rate, the supply flux depends on the erosion rate and, hence, on the total sputter yield. Analysis shows that a sizeable steady state signal is only possible if the sputter yield exceeds relatively large values. For the specific case depicted in Fig. 2, for instance, one can calculate a limiting value of about 400 trehalose molecule equivalents which must be removed per projectile impact in order to ensure a steady state molecular ion signal at about half the initial value. Sputter yields of that magnitude are impossible to achieve with atomic primary ions, therefore precluding meaningful molecular depth profile analysis using such projectiles. They are, however, feasible under bombardment with cluster projectiles, as has been recently shown for a number of cases [54–58,68,93,94]. On the basis of these considerations, the above question can be answered in the sense that cluster projectiles apparently offer the unique ability to remove chemical damage as fast as it is created, uncovering fresh, undamaged analyte species in each individual impact event.

4.4. Differences between clusters

Among the suite of projectiles which are currently available for use in routine SIMS analysis, a number of differences are found which may render particular clusters more suitable for a specific analytical task than others. If the primary concern of the analysis is ultimate detection sensitivity for molecular species, one would probably choose the projectile delivering the largest ion formation efficiency. The data available so far suggest that this would point to the projectile containing as many constituents as possible, with the mass of the constituents being as closely as possible matched to that of the substrate atoms [95,98].

If, on the other hand, molecular imaging analysis is required with the highest possible lateral resolution, other points must also be considered. As pointed out recently [62], the useful lateral resolution in molecular imaging applications is not only

Table 3

Comparison of different projectiles with respect to typical values of total sputtering yield, disappearance cross-section σ , mean range and erosion depth for different projectiles impinging onto a generic organic or ice surface with kinetic impact energies of the order of 10 keV

	Yield	σ (cm ²)	Range (nm)	Erosion depth (nm)
Au ⁺	20	3×10^{-13}	23	0.02
SF ₅ ⁺	100	5×10^{-13}	9.8	0.06
Au ₃ ⁺	1000	1×10^{-12}	19	0.3
C ₆₀ ⁺	2000	2×10^{-13}	2.6	3.3
Au ₄₀₀ ⁴⁺	20000	2×10^{-13}	6.6	3.4

For origin of data see text.

determined by the primary ion beam diameter, but is also limited by the ion formation efficiency via the requirement that at least one ion must be detected in a pixel. As a consequence, achievable spot size and efficiency must be matched for highest possible resolution molecular imaging. At present, this requirement seems to be best fulfilled for the liquid metal ion sources producing Au_m⁺ or Bi_m⁺ projectiles [62]. Upcoming new developments in C₆₀⁺ ion source technology, however, indicate that this situation may change in the near future [96].

For applications in molecular depth profiling, it is important that chemical damage induced by the projectile impact is efficiently removed. Therefore, high sputter yields are ultimately needed. Table 3 lists tentative “typical” values of total sputter yields expected for bombardment of a generic organic bulk material with different projectiles at an impact energy of the order of 10 keV. The relative scaling between Au⁺, Au₃⁺, SF₅⁺ and C₆₀⁺ was taken from secondary ion yield data of Irganox 1010 overlayers on polymer substrates [41], the scaling between Au⁺ and Au₄₀₀⁴⁺ was taken from similar data on Gramicidin overlayers on a metal substrate [73]. The absolute calibration in terms of total yields was performed using sputter yield data measured on ice samples with Au_m⁺ [87] and C₆₀⁺ [54] projectiles. In order to assess the damage accumulation during sputter erosion, we estimate the depth of the volume removed after a single projectile impact using the sputter yield, a sample density representative of ice (0.9 g/cm³) and the disappearance cross-section data taken from Ref. [41]. In doing so, we tentatively assume the lateral dimension of the removed volume to be of the same order as the measured disappearance cross-section. The resulting erosion depth is listed in Table 3.

These values must now be compared to the damage depth, i.e., the depth to which the bombarded solid is affected by the projectile impact. The latter is estimated by calculating the mean range of the individual projectile constituents using the SRIM2003 computer code [97]. If the erosion depth exceeds the damage depth, the damage created by one projectile impact is efficiently removed during the same event, exposing fresh undamaged molecules for further analysis in subsequent projectile impacts. Only in this case, it should be possible to accumulate large ion fluences beyond the static limit for sputter depth profiling without destroying the molecular information. Among the projectiles listed in Table 3, only C₆₀⁺ appears to

fulfill that requirement, rendering these projectiles particularly suited for molecular depth profiling applications. Au_n^+ (and the physically equivalent Bi_n^+) come close and should apparently work the better the larger the projectile nuclearity n . SF_5^+ as well as atomic projectiles must on the basis of these considerations clearly be ruled out as general tools for molecular depth profiling applications. Nevertheless, a number of studies indicate SF_5^+ to be applicable for such an analysis in some cases [45,46–53,99]. Clearly, the picture drawn in Table 3 is not complete and much more work is needed to clarify these points.

To conclude this section, it should be mentioned that the optimum performance with respect to a specific analytical task may require the combination of several projectiles. As an example, it appears feasible to combine the superior damage balance of C_{60}^+ for sputter erosion of organic samples with the high lateral resolution provided by Au_n^+ or Bi_n^+ for static image acquisition in order to accomplish high resolution molecular 3D analysis of organic films. Details of such protocols are currently being explored.

5. Conclusions

Looking at the rapid development the field undergoes at the present time, it becomes apparent that the molecular SIMS community has probably for long been “shooting with the wrong bullets” [100]. The transition from atomic to cluster projectiles provides a boost in analytical sensitivity to retrieve molecular information on the chemical state of the surface by orders of magnitude. Although the fundamental understanding of the observed cluster effects is certainly far from being complete, details are emerging quickly. It is apparent that cluster projectiles generate significantly different emission physics than atomic projectiles, leading to an enhanced desorption of particularly molecular species. The apparent ability to overcome the static limit offered by such projectiles constitutes a breakthrough with respect to many future applications of molecular SIMS. The possibility to accumulate significant primary ion fluences without destroying the surface chemistry opens the door towards molecular depth profiling analysis, which may bear great implications with respect to applications of SIMS in the analysis of many organic and biological samples.

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