Research Article

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Strongly reduced fragmentation and soft emission processes in sputtered ion formation from amino acid films under large Ar$_n^+$ ($n \leq 2200$) cluster ion bombardment

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The analysis of organic and biological substances by secondary-ion mass spectrometry (SIMS) has greatly benefited from the use of cluster ions as primary bombarding species. Thereby, depth profiling and three-dimensional (3D) imaging of such systems became feasible. Large Ar$_n^+$ cluster ions may constitute a further improvement in this direction. To explore this option, size-selected Ar$_n^+$ cluster ions with 300 $\leq n \leq 2200$ (bombarding energies 5.5 and 11 keV) were used to investigate the emission of positive secondary ions from four amino acid specimens (arginine, glycine, phenylalanine, and tyrosine) by time-of-flight SIMS. For all cluster sizes, the protonated molecule of the respective amino acid is observed in the mass spectra. With increasing cluster size the number of fragment ions decreases strongly in relation to the intact molecules, to the extent that the fraction of fragment ions amounts to less than 10% in some cases. Such ‘soft’ emission processes also lead the ejection of dimers and even multimers of the amino acid molecules. In the case of the phenylalanine, secondary ion species composed of up to at least seven phenylalanine moieties were observed. Tentatively, the ionization probability of the emitted molecules is envisaged to depend on the presence of free protons in the emission zone. Their number can be expected to decrease concurrently with the decreasing amount of fragmentation for large Ar$_n^+$ cluster ions (i.e. for low energies per cluster atom). Copyright © 2011 John Wiley & Sons, Ltd.

Secondary-ion mass spectrometry (SIMS) is a highly sensitive analytical technique for the characterization of the surface and near-surface region of solids.$^{[1,2]}$ Basically, SIMS utilizes energetic primary ions which interact with the analyte; the energy deposited thereby at the surface may lead to an ejection of atoms and molecules from this very surface, a process usually termed sputtering. For mass spectrometry, only the charged fraction of the sputtered flux can be used directly. In its beginnings, SIMS was extensively employed for the analysis of inorganic materials, and the detection of dopants in semiconductors figured prominently among those applications. It was quickly realized, however, that organic substances could also be subjected to SIMS characterization. In order to prevent the destruction of such fragile materials, the total primary ion fluence during an analysis has to be kept low, to the extent that each impinging ions ‘sees’ an undisturbed surface area. Hence, this approach was called static SIMS. Because time-of-flight (TOF) mass spectrometers are now used almost exclusively for this approach, TOF-SIMS is often used synonymously for low-fluence SIMS analyses.$^{[3]}$

The realization of this low-fluence regime would require high detection efficiencies. A way to achieve that objective at least partially came with the observation that by utilizing cluster ions as projectiles in lieu of atomic ions, ions representing intact molecules could be sputtered from organic samples even at fluences far above the static limit. Following first attempts,$^{[4–6]}$ this direction of organic surface mass spectrometry was vigorously explored by many researchers (for reviews, see$^{[7–10]}$). A very promising example was the development and use of C$_{60}^+$ cluster ion beams.$^{[11,12]}$

Several studies have examined the ion yields for a considerable variety of cluster species and target materials.$^{[8,10,13,14]}$ Very generally, with increasing cluster size the yields appear to increase (sometimes even quite dramatically) while the number of emitted fragment ions is reduced, to the extent that depth profiling of (thick) organic and biological layers and three-dimensional (3D) imaging becomes feasible.$^{[15–18]}$ Of course, the question may arise: If larger is better, how large is best? And: What kind of cluster ions larger than C$_{60}^+$ could be useful for SIMS? A possible answer could be the use of large gas-cluster ions such as Ar$_n^+$*. The application of Ar$_n^+$* cluster ions (with up to $n=10$ 000 or more) was pioneered by the Kyoto group of Yamada and Matsuo.$^{[19,20]}$ Initially, these beams were primarily employed in research devoted to surface modifications and sputtering.$^{[21,22]}$ But the advantages that those cluster ions may have for SIMS were immediately recognized$^{[23]}$ and several reports showing this have been published recently.$^{[24–27]}$ While a detailed comparison of Ar$_n^+$* cluster ions with the well-established C$_{60}^+$ ion beams

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was carried out recently, many aspects of the ion emission processes under Ar** cluster ion impact are largely unexplored.

The present work attempts to examine the effect of the cluster size on formation by studying the yields of molecular ion species under Ar** cluster ion irradiation for an extended range of sizes (n = 300–2200). A rather limited number of experiments with a similar objective have been carried out using Ar** cluster ions. Four amino acids (arginine, glycine, phenylalanine, and tyrosine) were chosen as targets, because of the biological relevance of these materials. Amino acids were studied in some very early static SIMS investigations in the 1970s by Benninghoven and co-workers. A recent TOF-SIMS analysis of amino acids identified the most prominent peaks observed in their mass spectra.

EXPERIMENTAL

The measurements of secondary ions were carried out using a gas cluster ion beam apparatus. The instrument consists of a source chamber, an ionization chamber and an analytical chamber, incorporating the target and a linear time-of-flight secondary-ion mass spectrometer. Neutral Ar clusters were formed by the supersonic expansion of a high-pressure gas (0.35 MPa) through a nozzle (0.1 mm diameter) and were then introduced into the ionizing chamber. The neutral Ar clusters were ionized by electrons from a hot filament (electron energy 300 eV). Ionized Ar** clusters (with n being the number of Ar atoms) were extracted towards the target by accelerating voltages of either 7.5 or 13 kV. Magnets installed between the ionizing and analytical chambers remove monomer and very small cluster ions present in the cluster ion beam. For these settings, the size distribution of the Ar** cluster had a maximum at n ~ 800 and decreased by about an order of magnitude for n = 300 and n = 2200.

The primary ion beam was pulsed at a frequency of 1 kHz with a deflector located at the end of the ionization chamber (pulse width = 5 µs). Initial mass filtering of the Ar** beam was carried out by using a secondary ion deflector, operated at the same time width, positioned further down the primary ion column where the ion pulse has broadened due to the spread in cluster size (and hence velocity). By varying the delay time between these two deflectors a rather narrow range of Ar cluster sizes could be selected to irradiate the sample. From this timing scheme, a mass resolution of the primary beam of M/ΔM ~ 10 was estimated.

The target was kept at a potential of 2 kV; therefore, the impact energy of the ions was either 5.5 or 11 keV. The DC ion current (integrated over all cluster sizes) was about 6 nA and the primary ion beam had an incident angle of 45° with respect to the surface normal. The total ion fluences was of the order of 2 × 10^11 ions/cm² for a typical SIMS data acquisition time of 30 s (i.e., for 30 000 cycles).

The sputtered secondary ions were extracted from the target and accelerated to a kinetic energy of 2 keV. The beam of secondary ions was also chopped with a width of 200 ns, with the secondary-ion chopper installed at the end of the flight path of the ions. This secondary-ion deflector is known as an interleaved comb ion (mass) deflection gate and it was developed for TOF mass spectrometry. This deflector consists of two electrically insulated sets of thin wires mounted parallel to each other; for chopping, a low-voltage pulse is applied between the wires. The secondary-ion chopping and detection periods were, respectively, used as the start and the stop signals for the TOF-SIMS measurement. By these means, the secondary ions produced by cluster ions of a specific size could selectively be measured by changing the time delay between the primary and the secondary ion beam chopping. The length of the flight tube was about 400 mm. In this study, Ar** cluster ions in the range n = 300–2200 were employed. The complete timing principle is illustrated in Ichiki et al.

The base and working pressures in the analytical chamber were 5 × 10⁻⁷ and 2 × 10⁻⁵ Pa, respectively.

The thin-film targets of four amino acids [arginine (C6H14N2O2, MW = 174.2 g/mol), glycine (C2H5NO2, MW = 75.1 g/mol), phenylalanine (C9H11NO2, MW = 165.2 g/mol), and tyrosine (C9H11NO3, MW = 181.2 g/mol)] were deposited on clean Si wafers by thermal evaporation. The thickness of the films was measured by spectroscopic ellipsometry and was about 200 nm for all materials.

RESULTS

The major goal of the present work was the investigation of the influence of the cluster size and the (total) cluster energy on the emission processes of sputtered ions from amino acids; ultimately, this information could be useful for SIMS analyses. Previous studies with Ar** clusters as well as those using smaller clusters demonstrated that with increasing cluster size n (i.e., increasing number of atoms in the cluster) the fraction of ions from the intact molecule emitted is increased and the number of fragment ions is reduced. For large clusters, however, the yield may decrease because of the very low energy per atom in the cluster. In a qualitative way this can be observed from mass spectra taken with clusters of different values of n. Figure 1 illustrates this for the phenylalanine film bombarded by 5.5 keV Ar** cluster with n = 300, 600, and 900. At n = 300 there are two prominent peaks seen in the spectrum, one at m/z 166 which is due to the protonated phenylalanine molecule [M+H]+ and one at m/z 120 which corresponds to [M+H−HCO2H]+. In addition, there are minor peaks at m/z <120 and a distinct peak at m/z 331 which is from the phenylalanine dimer, [M2+H]+. (The emission of dimers and multimers will be discussed in more detail below.)

Generally, the measured ion intensities vary with cluster size. This finding is illustrated in Fig. 2 for the arginine sample, but was observed for all amino acid films. (Figs. 1 and 2 plot the measured intensities which have not been corrected for the variation of the flux of cluster ions with size.) The figure shows that with increasing cluster size the intensities of the [M+H]+ ion and the fragment ions decrease. To some extent this is due to the decrease in the cluster abundance distribution, i.e., the number of cluster ions per pulse (about a factor of ten between n ~ 800 and n ~ 2200). On the other hand, with increasing n, the energy per atom in the cluster decreases (i.e., the energy is shared among an increasing number of atoms). Although this may favor soft ejection processes (see below), the energy per atom is being reduced to the point that sputtering is
of the [M+H]+ ion signal. (For arginine the most abundant signals of the fragment ions fall off more strongly than that of the [M+H]+ ion signal. For arginine the most abundant fragment ion is found at m/z 70, [C₄H₈N]+.) The mass spectra for the other amino acid films exhibit similar trends in terms of decreasing fragmentation for larger cluster ions.

In order to outline this dependence of fragmentation on cluster size in more quantitative terms, Fig. 3 depicts for all amino acid samples and the two bombarding energies the intensity ratios of the most prominent fragment ions to the ion from the protonated molecule as a function of cluster size n. The data show that this ratio generally decreases quite pronouncedly with increasing size, in particular for the 5.5 keV irradiations. For these, the fragment-to-[M+H]+ ion intensity ratio approaches 0.1, with the exception of the glycine sample (for this specimen, the intensities under 5.5 keV bombardment were fairly low and could be determined only for n ≤1000). The reduction in fragmentation with increasing size is seen to be less pronounced for 11 keV impact; and for both energies it appears to level off beyond a specific value of n. These findings corroborate the suggestion that, for a given total energy, larger clusters lead to a ‘softer’ emission event, inducing less fragmentation and an enhanced emission of intact [M+H]+ ions.

The presence of such soft ejection processes can be inferred also from the increasing emission of dimers and even larger multimers. (While dimers could be identified as being [M₂+H]⁺, the identity of larger molecular moieties could not be determined due to a lack of mass resolution.) With the exception of the arginine sample, the emission of dimers and trimers was observed for all specimens. Their intensities usually increase relative to those of the monomer species with increasing cluster size. Figure 4 depicts the dimer-to-monomer intensity ratios for the bombardment of phenylalanine. For the largest cluster used for the two energies that ratio is ~1 for 11 keV, while it is much higher (~6) for 5.5 keV.

The emission of even larger molecular cluster is illustrated in Fig. 5. The mass spectrum shows the detection of phenylalanine multimers ions Mₚ⁺ with up to at least p =7 phenylalanine entities (and possibly more). The emission of such large molecular species from the surface by sputtering requires clearly a highly correlated transfer of energy to the nascent molecule, with just enough energy to cause a lift-off, but not more in order to prevent break-up. The concerted motion of a large number of cluster atoms (1200 in the case of Fig. 5) upon impact apparently favors these conditions.

**DISCUSSION**

Whereas the data of the preceding section have clearly demonstrated that the cluster size has a decisive influence on the ion intensities and the intensity ratios, a parameter probably quite relevant in terms of understanding the emission (and ionization) mechanisms would be the energy per cluster atom, E/n, where the bombarding energy E was 5.5 and 11 keV in this work. Obviously, this quantity relates to the cluster’s impact velocity. More importantly perhaps, E/n constitutes the average energy that each of the cluster atoms carries upon the break-up of cluster in the interaction with the surface. However, it should be noted that in large clusters such as the ones studied here the motion of individual cluster atoms may be still severely restricted due to their mutual interactions.
even at the point when most of the (weak) bonds within the cluster have been severed. Hence, initially the cluster can be expected to interact with the solid as an entity and only at a later stage the single atoms may start their independent collision processes.

Sputtering and ion yields under cluster-ion bombardment are frequently discussed in terms of so-called non-linear effects. This refers to the observation that the yield under irradiation with a cluster composed of \( n \) atoms is often higher than \( n \) times the yield of a single atom when evaluated at the

**Figure 3.** Intensity ratios of the most abundant fragment ion to the protonated molecule as a function of the cluster size \( n \) for the different amino acid samples at bombarding energies of 5.5 and 11 keV.

**Figure 4.** Intensity ratios of the dimer to monomer molecules sputtered from phenylalanine as a function of the cluster size \( n \). Parameter is the impact energy of the \( \text{Ar}_n^+ \) cluster ions.

**Figure 5.** Mass spectra from the phenylalanine sample under 11 keV \( \text{Ar}_{1200}^+ \) cluster ion irradiation showing the emission of phenylalanine multimers \( M_p \) containing up to \( p = 7 \) phenylalanine molecules.
same impact velocity. The occurrence of such a non-linear effect could therefore be inferred from plotting the yields of different clusters and/or energies as a function of $E/n$.

Figure 6 shows the normalized intensities of the [M+H]$^+$ ions sputtered from the amino acid specimens as a function of $E/n$ for both impact energies. It can be seen that the intensities are relatively constant for $E/n > 10$ eV, but decrease very strongly below $E/n < 10$ eV. In the latter range, the decrease is rather similar for the different samples; the lowest signal levels that could be detected ($\sim 10^{-3}$ of the maximum intensity) were obtained at values as low as $E/n \sim 3$ eV and $E/n \sim 4.5$ eV for bombarding energies of 5.5 and 11 keV, respectively. Clearly, these average impact energies for Ar atoms in such large clusters are much lower than the energy that an individual Ar atom would need to have in order to effect sputtering. This observation strongly supports the conclusion that sputtering by large clusters (i.e., at low energies per cluster atom) leads to a distinct reduction of fragment ions in the emitted flux of [M+H]$^+$ ions and is highly beneficial for SIMS analyses. On the other hand, this favorable feature could come at the cost of lower ion intensities and might, therefore, not be fully exploitable.

Only a few previous experiments have also examined the behavior of molecular secondary-ion yields in this regime of (very) low impact energies per cluster atom. In agreement with the present data, those results indicate that the ion intensities decrease rapidly for $E/n < 10$ eV/atom. Specifically, Moritani et al. have demonstrated that the ion-yield dependence on $E/n$ for fragment ions emitted from polystyrene could be classified into three distinct types which are attributable to the different dissociation energy of the specific bonding site of the molecule. For $E/n < 3$ eV/atom a very strong decrease in intensity was observed for fragment ions. In a recent report, Rabbani et al. carried out a detailed comparison of C$_6$H$_6$ and Ar$_{n+}$ cluster ion beams for TOF-SIMS application. Pertinent to the present discussion are the findings that (i) at a given beam energy the sputter rate of organic samples is approximately constant as a function of cluster size; (ii) at a fixed beam energy there is a roughly linear reduction in ionization efficiency with increasing Ar cluster size; and (iii) the mechanisms of ion formation appear to be influenced by the energy and nuclearity of the primary ions.

Molecular-dynamics (MD) computer simulations have determined the dependence of the (ion) yields on cluster size; this approach provides results on the total yields, whereas experimental studies include, in addition, effects due to the ionization of the emitted species. Unfortunately, most of that work was done for other bombarding clusters and/or targets, and higher energies. Hence, these results may provide only some guidelines as to which mechanisms might be responsible for the intensity variations seen in Fig. 6. MD simulations of the sputtering of organic overlayers on Ag with a large, slow projectile (Ar$_{2053}$) show a very distinct decrease of the total yield for $E/n < 2.5$ eV. Below 1 eV per atom no material is removed; above this value and up to 5 eV per atom only intact molecules are found to be ejected. Very recent MD simulations studied the sputtering of a polyethylene oligomer target by cluster species that cover a wide range in mass, from $\sim 320$ u up to $\sim 23000$ u. Using cluster impact energies between 2 and 15 keV, a considerable spectrum of sputtering conditions was investigated. Generally, that work shows two distinct regimes: beyond 1 eV/nucleon (in Delcorote et al., the energy is given in eV per nucleon as the projectiles are composed of different atoms, i.e., 40 eV/atom in the case of Ar), the sputtering yield depends only on the total projectile energy and not on the projectile nuclearity; below 1 eV/nucleon, yields are influenced by both the energy and the nuclearity. In the latter range...
which is the one relevant for this experiment, there is minimal (or no) fragmentation and the mass of emitted molecules approaches the total ejected mass. Furthermore, the slope in plots of yield vs. $E/n$ changes at that boundary. However, the lowest value of $E/n \sim 0.2$ eV/nucleon given in Delcorte et al.\textsuperscript{[51]} corresponding to $E/n \sim 8$ eV/atom, is clearly above the lowest energies in the present situation.

From a detailed inspection of these simulation results one may conclude that for sputtered molecules the dependence of the molecular yield on $E/n$ is much less pronounced than is found in this work for ionized cluster (cf. Fig. 6). Hence, this difference would be strong evidence that the ion-intensity decrease toward low $E/n$ is (largely) due to an ionization effect.

While the specific mechanisms of ion formation in sputtered molecular species are not known, the presence of H atoms appears to be of importance because the detected positively charged molecules generally have a proton attached to them. This is also the case for the molecules sputtered from the various amino acids in this study, see Fig. 1. Hence, protons generated in the bombarding event may constitute a source for the formation of such protonated molecules. It was proposed that cluster ion projectiles are prodigious producers of protons in the impact region of the ions and that this environment could enhance the secondary-ion yield by proton cationization.\textsuperscript{[53–57]} Recent MD simulations have actually shown that, for 5–20 keV $C_{60}$ bombardment of octane and octatetraene crystals, the number of H atoms generated in a sputtering event can be substantial.\textsuperscript{[58]} For example, about 200 free H atoms are created in a 10 keV impact event and there is a roughly linear relation between that number and the energy. These free H atoms are found to be located both in the plume of the sputtered material and in the crater region. On the other hand, the number of reacted molecules at 10 keV is about 80 and 150 for the octane and octatetraene targets, respectively, again varying approximately linearly with energy. Two findings from the simulations appear to be relevant for this work: (i) In each impact event, a large number of free H atoms is generated; if these were ionized, they would, in principle, be available for the formation of protonated molecules. (ii) Both the number of H atoms and that of reacted molecules (which eventually may end up as sputtered fragment ions) decrease linearly with decreasing impact energy. Hence, for very low energies there would be neither H atoms for protonation reactions (resulting in low yields of sputtered molecular ions) nor fragment ions in the emitted flux. That corresponds exactly to what is observed in the present experiments.

From these considerations one may argue that the presence (or absence) of H atoms in the collision region constitutes a decisive factor for the formation of molecular secondary ions of the kind [M+H]$^+$ which are typical for many organic substances. As the simulations indicate a direct scaling of the numbers of reacted molecules and free H atoms, experimentally the measured fragment ion yields (being correlated with the reacted ones) may represent the availability of H species in the emission event and, therefore, the ionization efficiency via proton attachment. In other words, low fragment yields would correspond to low yields of protonated molecules.

Apart from the availability of protons, the ion yields of protonated molecules are expected to depend on the respective gas-phase basicity (GB)\textsuperscript{[59]} of that species. Generally, a high value of GB could result in higher yields and a scaling with the magnitude of GB for different molecules may occur. For amino acids, gas-phase basicities have been compiled,\textsuperscript{[60]} for the four amino acids studied in this work (arginine, glycine, phenylalanine, and tyrosine) the values of GB are 991.6, 848.1, 887.4, and 891.6 kJ/mol, respectively, and those of glycine and arginine bracket the GBs of 20 amino acids.\textsuperscript{[61]} The comparable values of the GBs agree with the rather similar ion intensities observed for the four amino acids investigated. Generally, the chemical environment in which the molecule of interest is analyzed can have a profound effect on the detection of that molecule.\textsuperscript{[61]} Through analyzing mixtures of compounds of known gas-phase basicity, the importance of this property on the emission of secondary ions from a surface was investigated.\textsuperscript{[62]} The outcome of these experiments demonstrated that strong suppression of the [M+H]$^+$ ion signal of one molecule in a mixture can occur due to the presence of the other, with the gas-phase basicity of the compounds being a good indicator of the secondary ions detected.

CONCLUSIONS

The sputtered flux from various amino acid specimens under bombardment by large Ar cluster ions was investigated by TOF-SIMS. The emission of the protonated molecules and of fragment ions exhibits a pronounced dependence on the cluster size. With increasing size the ion intensities generally decrease whereas the ratio of intact molecules to fragment ions increases strongly. This distinct reduction in decomposition processes is envisaged also to cause a decrease in the number of free H-atoms available for the protonation of sputtered molecules; this expectation is corroborated by the dramatic attenuation of the yield of emitted protonated molecules for large clusters. This finding indicates the occurrence of a rather pronounced variation of the ionization probability of the sputtered molecules.

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REFERENCES

Sputtered ions from amino acids under Ar\textsubscript{n} cluster ion bombardment


