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Prolific cluster emission in sputtering of phenylalanine by argon-cluster ion bombardment

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ABSTRACT

Large Ar_n^+ cluster ions (with $n \sim 1500$ Ar atoms per cluster) with a bombarding energy of 10 keV were used to investigate the sputter-induced emission of positive secondary ions from a phenylalanine specimen by orthogonal time-of-flight SIMS. An abundant flux of phenylalanine cluster ions $(M_n+H)^+$ with $n \leq 12$ was observed. The yield of dimers relative to monomers is found to amount to 50 − 60% whereas that of trimers and tetramers is roughly 10%. Tentatively, this prolific formation of these cluster species can then be ascribed to the concerted action of the large number of Ar atoms within their impact zone at the surface: these low-energy Ar species (with an average energy of only few eV) may effect the soft cleavage of the phenylalanine bonds in the solid and lead, eventually, to the intact emission of these phenylalanine moieties.

1. Introduction

In secondary-ion mass spectrometry (SIMS) [1,2], the use of cluster ions as projectiles in lieu of atomic ions has become widespread in recent years (for reviews, see [3–6]). This development was primarily caused by the observation that intact molecular ions could be sputtered from organic and biological samples even at fluences far above the static limit, i.e. beyond the *low-fluence* regime for which each impinging ions impacts onto an undisturbed surface area [7]. In particular, the application of Ar_n^+ cluster ions (with up to $n = 10{,}000$ or more) has increased dramatically and several reports on their use in SIMS have been published in the past decade [8–23]. Some of these studies have demonstrated that argon cluster bombardment of organic solids may lead to a *soft* emission process so that large intact molecules or even molecular clusters can be desorbed (sputtered) from the surface while the fraction of fragmenting species would be small. Quite generally, under cluster bombardment the yields of sputtered ions appear to increase (sometimes pronouncedly) with increasing cluster size, whereas the number of emitted fragment molecules is reduced, to the extent that depth profiling of (thick) organic and biological layers and 3D imaging became feasible (for reviews, see [24–27]).

While the emission of (large) intact organic or biological molecular ions thus was substantially advanced, the possible ejection of cluster species, i.e. moieties composed of a certain number of the molecules present at the surface has not been studied in detail [28,29]. This is somewhat surprising as the sputtering of clusters from elemental and inorganic specimens has been widely investigated [30,31]. In the present work, Ar_n^+ cluster ions were used to study the emission of intact clusters from an amino acid, phenylalanine. This target was chosen because we had noted some cluster emission already in a previous study [21], but a more specific investigation was limited then by the mass resolution and sensitivity of the set-up used. Depending on their abundance, such cluster of molecular species could play an important role in the analysis of the target and, therefore, may warrant a closer examination. In addition, such an investigation may shed light on the emission process proper which is still not well understood.

2. Experimental

The experiments were carried out in a new SIMS instrument built in the group of Matsuo at Kyoto University [32] which consists of a gas cluster ion source and primary beam line and an orthogonal time-of-flight mass spectrometer (TOF-MS) for the detection of sputtered secondary ions. In the ion source, neutral Ar

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clusters are formed by the supersonic expansion of a high-pressure gas (0.35 MPa) through a nozzle (0.1 mm diameter) and are then introduced into the ionizing chamber. The neutral Ar clusters are ionized by electrons from a hot filament (electron energy 300 eV). Similar to a previous gas-cluster ion beam apparatus [33–35], ionized Ar_n^+ clusters (with n being the number of Ar atoms) are extracted toward the target by accelerating voltages of up to 15 kV. For these settings, the source produces an asymmetric size distribution of Ar_n^+ cluster ions which ranges from $n \sim 500$ to $n \sim 4000$ and exhibits a full-width at half maximum of ~1500; this distribution has a mean value of $n \sim 1500$. In the following we therefore refer to this beam as Ar_{1500}^+ ions, but no further size selection was carried out in the present study, contrary to our recent work [21,23]. Magnets installed between the ionizing and analytical chambers remove monomers and very small cluster present in the cluster ion beam.

The measurements were done using an ion impact energy of 10 keV. The cluster beam hits the target at an incidence angle of 45° and the ion current was 40 pA; it was scanned across an area of 500 μm × 500 μm. Mass spectra were acquired for 10 s which results in a total ion fluence of 1×10^{12} Ar_n^+ ions/cm^2.

The detection of ions sputtered from the sample was performed in an orthogonal time-of-flight mass spectrometer (TOF-MS) which is part of a commercial system (JMS-T100LC AccuTOF manufactured by JEOL Ltd.). It employs an rf-only quadrupole ion guide for the transport of secondary ions to the entrance of the TOF proper and enables the efficient transmission of ions in a wide m/z range by focusing them to the optical axis [36]. The mass analyzer is an orthogonal acceleration TOF-MS [37,38], incorporating a 2-stage acceleration and a single-stage reflectron. Ions that have passed through the MS are recorded by means of a microchannel plate detector.

A mass calibration was performed before each analytical run employing a specimen of 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC) which exhibits a number of quite distinct mass peaks (at m/z 184.1, 790.6, and 1580.2). In this way, a mass accuracy of ~10^{-4} was achieved in the mass spectra. The mass resolution obtained under these conditions was $M/\Delta M_{FWHM} \sim 5000$ [39].

Samples of phenylalanine ($C_9H_{11}NO_2$, molecular weight 165.19 g/mol) were prepared in two different ways. In the first approach, an aqueous solution with a concentration of 7 g/L was prepared. From this solution, drops of 50 μL were applied onto the surfaces of 1 cm × 1 cm pieces of Si wafers. Upon drying, this procedure resulted in surface areas of ~5 mm diameter covered with phenylalanine. In the second method, thin films (thickness ~175 nm) of phenylalanine were prepared by thermal evaporation onto Si wafers. In both cases, the Si substrates were thoroughly cleaned before deposition. For each measurement several mass spectra were recorded across the surface areas to check for the homogeneity and reproducibility of the deposits.

3. Results and discussion

The goal of the present work was the investigation of the cluster emission pattern from phenylalanine under cluster-ion bombardment. Fig. 1 displays a mass spectrum obtained from the phenylalanine sample under 10 keV Ar_{1500}^+ cluster bombardment (mass spectra up to m/z ~2000 can be recorded in the present experimental set-up). The spectrum shows the presence of the protonated molecular ion $(M+H)^+$ of phenylalanine (m/z 166.1). The peaks at lower masses can be assigned to the immonium species of phenylalanine (m/z 120.1) and to fragments (m/z 93.1 and 103.1). For higher masses, a distinct pattern of mass peaks is observed that are due to the emission of protonated phenylalanine cluster ions

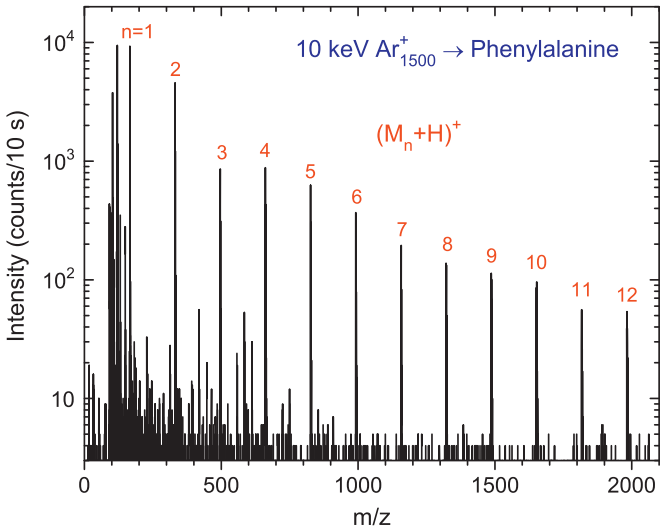

Fig. 1. Mass spectrum from phenylalanine sample (prepared from solution) under 10 keV Ar_n^+ cluster ion bombardment. The protonated molecular ion $(M+H)^+$ and phenylalanine cluster species $(M_n+H)^+$ ($1 \le n \le 12$) are labeled.

$(M_n+H)^+$ with $n \le 12$. (Fig. 1 indicates that even larger clusters might exist but the limit of the mass range accessible prevents their detection.) Apart from these cluster ions, the mass spectrum exhibits very few other species; this observation indicates that there is little fragmentation and, hence, that the phenylalanine cluster constitute very stable species once they have been formed in the sputtering event.

In order to ascertain the precise identity of those cluster ions, extended mass spectra were recorded in the pertinent mass ranges. Fig. 2 (upper panel) shows the measured isotopic distribution of the $(M_{12}+H)^+$ cluster ion of phenylalanine ($C_{108}H_{132}N_{12}O_{24}+H$). The individual isotopomers (starting with m/z 1981.7) can clearly be resolved. The isotopic abundance distribution of the $(M_{12}+H)^+$ ion agrees very well with theoretical predictions (lower panel).

In fact, for the six of the isotopomers that can be detected unambiguously the relative abundances deviate by less than 20%. The larger deviation seen for the heaviest isotopomer is probably due to the low ion signal and possible uncertainties associated with the background subtraction. The data in Fig. 2 and similar ones for the other cluster confirm that indeed $(M_n+H)^+$ ions are emitted during sputtering.

The mass spectra of phenylalanine exhibit a characteristic pattern of phenylalanine cluster emission as shown in Fig. 1. It appears to be largely independent of the sample preparation method (evaporation vs applying a drop from a solution, cf. Section 2). This finding is illustrated in Fig. 3: the yields (corrected for the isotopic abundances) of cluster ion species $(M_n+H)^+$ normalized to the respective signals of the protonated molecular ion $(M+H)^+$ of phenylalanine are plotted vs the cluster size n for these two approaches.

The results obtained indicate that for phenylalanine a rather distinct emission pattern of cluster emission is observed (cf. Figs. 1 and 3). The data also show that the phenylalanine cluster formation process is largely independent of the preparation procedure. Surprisingly, the relative yield of dimers is very high (0.5–0.6) while the yield of trimers and tetramers still amounts to some 10%. If the flux of the detected ion species were representative of the total emitted flux, this result would imply that a substantial fraction of phenylalanine molecules is sputtered as clusters. (Unfortunately, essentially nothing is known as to the ionization probability of those cluster species.) This somewhat unexpected observation is possibly related to the rather high sputtering yield of phenylalanine under Ar cluster bombardment: ~90 (200) phenylalanine