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Kinetic energy distributions of molecular and cluster ions sputtered from self-assembled monolayers of octanethiol on gold

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Abstract

Self-assembled monolayers (SAMs) of alkanethiols are an ideal model system to study the mechanisms that lead to emission of organic species under keV ion bombardment. In this contribution, we focus on the emission processes of gold-molecule cluster ions, which are not fully understood yet. To gain insights into these processes, monolayers of octanethiol $\text{CH}_3(\text{CH}_2)_7\text{SH}$ adsorbed on gold are investigated using time-of-flight secondary ion mass spectrometry (ToF-SIMS). First, the static SIMS conditions are verified using the degradation of the SAM signals as a function of ion fluence. Second, the kinetic energy distributions (KEDs) of fragment, parent and cluster ions ejected upon 15 keV Ga^+ ion bombardment are measured. The peak maxima, FWHMs and high energy tails of the distributions are analyzed for Au-thiolate clusters, as well as thiol fragments. After calibration of the energy spectra using monoatomic ions, we find that the KEDs of all the clusters containing the thiolate molecule peak at about 1.2 eV. Besides, the distributions of the gold-molecule cluster ions including $\text{Au}(\text{M}-\text{H})_2^-$, the most intense cluster peak in the spectrum, are significantly narrower than that of the hydrocarbon fragments. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Understanding molecular desorption mechanisms from organic surfaces under energetic ion bombardment is of great interest for the development of surface analysis techniques like SIMS, FABMS or PDMS. To improve our knowledge of these complex phenomena, we investigate self-assembled monolayers (SAMs) of alkanethiols on gold [1]. These materials have been well characterized by several methods due to their potential

application in a wide area ranging from medicine to microelectronics [2]. Their ease of preparation, well-ordered structure and high stability, make them ideal model systems for fundamental aspect investigations.

Using different approaches, various mechanisms have been suggested to explain the sputtering of SAMs. For instance, on the grounds of laser postionisation experiments, a two-step mechanism comprising a gentle cleavage by chemical reaction followed by a thermal evaporation, has been proposed to explain the ejection of low energy neutral molecules from SAMs of phenylethanethiols on gold [3]. On the other hand, in recent molecular dynamic simulations, momentum transfer and collision cascades have been considered to model

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the sputtering from SAMs of n-alkanethiols on Au(111) [4]. The complete picture might result from the coexistence of both mechanisms.

Although several groups have investigated thiol overlayers by SIMS, there is still a lack of data on the emission of secondary ions and specifically clusters from such surfaces [5–7]. In the present contribution, SAMs of octanethiols $\text{CH}_3(\text{CH}_2)_7\text{SH}$ adsorbed on gold are studied using time-of-flight secondary ion mass spectrometry (ToF-SIMS) with a 15 keV Ga^+ primary ion beam. We focus on the emission processes of the molecular and gold-molecule cluster ions observed in the SIMS spectra because their formation mechanisms have not been completely described yet. For this purpose we measure the kinetic energy distributions (KEDs) of the relevant clusters. Our aim is to understand how different molecules gather to form a special Au-molecule cluster ion. In these preliminary results, it is found that the KEDs of the cluster ions and gold anions, peak at about 1.2 and 2 eV, respectively. Moreover, the KEDs of the gold-molecule clusters are significantly narrower than those of the hydrocarbon fragments. Our experimental results are interpreted in the light of recent molecular dynamics simulations of sputtering involving alkanethiol overlayers [4] and gold surfaces [8].

2. Material and methods

2.1. Sample preparation

The SAMs were prepared on gold films evaporated onto silicon substrates. The metalization was carried out in an Edwards evaporator. The Si wafers, cleaned with isopropanol, were first primed with a 5 nm adhesive layer of titanium (0.1 nm/s at $\sim 10^{-6}$ mbar), a 100 nm Au layer was then deposited in the same conditions. The Au/Ti/Si surfaces were immediately immersed in 1 mM fresh solution prepared with n-octanethiol (>98 %, Aldrich) diluted in absolute ethanol. After immersion during ~ 20 h, the samples were thoroughly rinsed in absolute ethanol, dried with a stream of N_2 gas and directly transferred into the vacuum system for SIMS analysis.

2.2. Kinetic energy distribution measurements

The experimental setup and the KED measurement procedure have been already described in detail elsewhere [9,10]. Briefly, the KEDs were obtained in a PHI-EVANS ToF microscope microprobe using a (5 kHz) pulsed $^{69}\text{Ga}^+$ beam (15 keV; 600 pA DC current; 2 ns pulse width) [11]. The primary ion beam was focused (0.2 μm) and rastered onto a (130 \times 130 μm^2) area. The secondary ions, accelerated by a (3000 \pm Δ) V potential applied on the sample, were energy analyzed by means of a slit (1.5 eV passband) placed at the cross over preceding the second hemispherical electrostatic analyzer. Prior to detection, a post acceleration voltage (7 kV) was applied to improve the detection efficiency. The different energy windows of the KED were selected by varying the sample voltage, a $\Delta = 1$ V increase corresponding to a 1 eV decrease in the KED. By this way, about 20 mass spectra were recorded in the mass range 0–2000 amu during 300 s acquisition time (1.6×10^{12} ions/ cm^2 per spectrum). During these experiments, two sets of measurements were carried out on different areas in order to obtain more statistics. Finally the zero of the energy scale was estimated by fitting KEDs of atomic ions using the Sigmund–Thompson function [12]. It is worthwhile to mention that we have obtained similar results by using another procedure found in literature [13]. In this procedure, zero emission energy corresponds to the position at which the intensity of the low energy side of the KED, reaches 50% of the peak intensity.

3. Results

3.1. Mass spectra

Mass spectra have been measured for both ion polarities. We focus only on the negative spectra, because they contain more information corresponding to molecular and gold-molecule cluster ions. The low mass region, up to 100 amu, exhibits essentially small fragments, the predominant ones being CH^- ($m/z = 13$), C_2H^- ($m/z = 25$), S^- ($m/z = 32$), and SH^- ($m/z = 33$) (Fig. 1). These

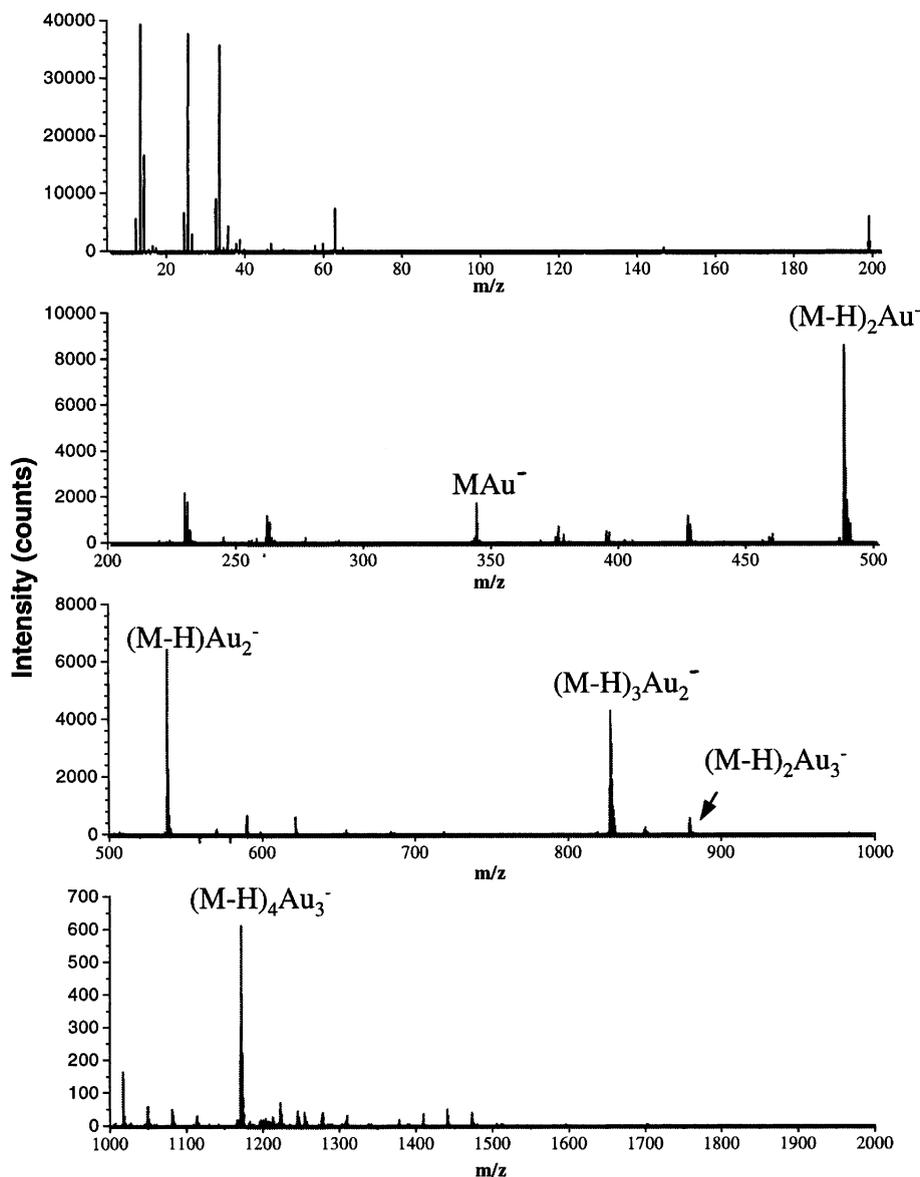


Fig. 1. Negative ToF-SIMS spectrum of an octanethiol SAM on gold under 15 keV Ga^+ bombardment.

peaks are weakly present in the negative spectra of pristine gold surfaces but after the self assembly process, their intensity is strongly enhanced by the organosulfur chains of the SAM.

At higher mass, peaks corresponding to the substrate signal Au^- , gold and sulfur containing cluster ions Au_x^- and Au_xS^- , as well as the quasi-

molecular ion $(\text{M}-\text{H})^-$ (M being the whole adsorbed molecule) are observed. We also detect gold-molecule cluster ions in various combinations. These species are MAu^- clusters ($m/z = 343$), dialkanethiolate ions $(\text{M}-\text{H})_2\text{Au}^-$ at $m/z = 487$ (the most intense cluster peak) and other Au-thiolate cluster ions: $(\text{M}-\text{H})\text{Au}_2^-$ ($m/z = 539$),

(M–H)₃Au₂[−] ($m/z = 829$), (M–H)₂Au₃[−] ($m/z = 881$) up to the tetramers (M–H)₄Au₃[−] ($m/z = 1171$). Sulfonate species were observed in another study [14], indicating air oxidation of the SAMs [15], but not in our case, where all the samples have been freshly prepared (Fig. 1).

3.2. Degradation of the self-assembled monolayers

Despite several precautions taken to remain within static conditions, degradation of the aimed sample area is significant during KED measurements, because of the repeated bombardment sequences. Therefore, the SAM signals must be corrected for this degradation effect. For this purpose, we measured the evolution of the secondary ion yields during approximately 12 bombardment sequences on the same area. The curves giving the yield versus acquisition time were adequately fitted by exponential decay functions. The corrected energy distributions were then obtained by dividing the measured intensities by these exponential functions. In the course of this procedure, the disappearance cross-sections σ have been calculated for all the secondary ions, assuming uniform ion fluence. σ values for the most characteristic ions are given in Table 1. It is seen that

Table 1

Disappearance cross-section σ for some of the characteristic secondary ions sputtered from SAMs of octanethiols on gold under 15 keV Ga⁺ bombardment

Mass	SI, $I_p = 0.166$ pA, $A = 1.69$ cm ²	σ (10^{-16} cm ²)
13	CH [−]	235
145	(M–H) [−]	426
197	Au [−]	191
343	MAu [−]	632
487	(M–H) ₂ Au [−]	941
539	(M–H)Au ₂ [−]	426
829	(M–H) ₃ Au ₂ [−]	941
1171	(M–H) ₄ Au ₃ [−]	985

the σ values of most of the Au-thiolate cluster ions are higher than that of (M–H)[−], Au[−] and CH[−] ions. Besides, the highest σ value is similar for the (M–H)₂Au[−], (M–H)₃Au₂[−], and (M–H)₄Au₃[−] ions. The fact that Au-thiolate cluster ions undergo more damage than the parent molecular ion has also been observed by Rading et al. for large alkanethiols [7].

3.3. Kinetic energy distributions

The KEDs of selected secondary species are displayed in Fig. 2. Two main characteristics can

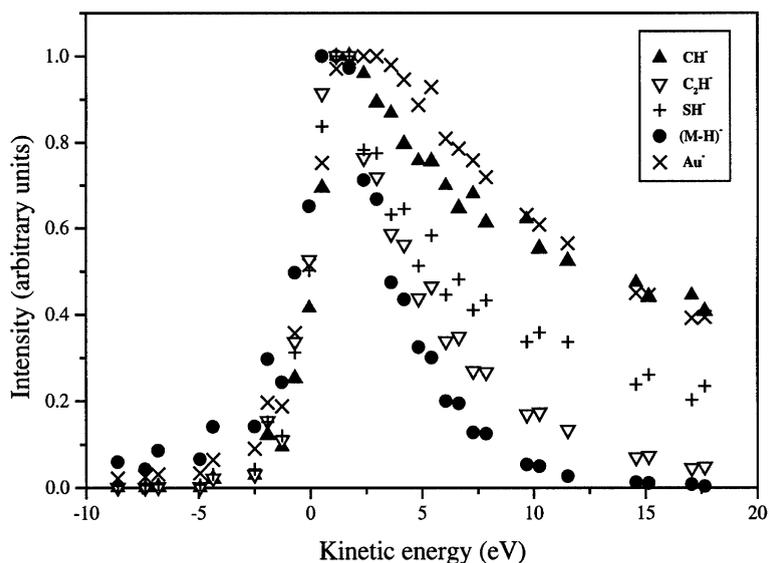


Fig. 2. KEDs of secondary species sputtered from SAMs of octanethiol on gold under 15 keV Ga⁺ bombardment.

be pointed out from this comparison. First, the distributions of all the particles, except for Au^- , peak at the same energy, around 1.2 eV. The second feature of interest is that the curve shape in the high energy region varies according to the size of the ejected particles. For instance, the high energy tail of the KED of intact molecular ion $(\text{M-H})^-$, is steeper than those of the CH^- , C_2H^- and SH^- fragment ions and of the Au^- atomic ion. Accordingly, the FWHM decreases from 13 eV for Au^- to 4 eV for $(\text{M-H})^-$. The distribution of the molecular ion does not extend beyond 15 eV. For comparison, the order of magnitude of the observed kinetic energies is close to the desorption energy of about 1.3 eV for $(\text{M-H})^-$ ion measured by Rading et al. for octanethiols on gold [7].

The KEDs of the most intense Au-thiolate cluster ions are compared in Fig. 3. It is seen that the distributions of $(\text{M-H})_2\text{Au}^-$, $(\text{M-H})_3\text{Au}_2^-$ and $(\text{M-H})_4\text{Au}_3^-$ ions almost merge together and are narrower than that of the MAu^- and $(\text{M-H})\text{Au}_2^-$ ions. In other words, Au-molecule cluster ions containing only one molecule eject or survive with a higher average energy. In particular, $(\text{M-H})\text{Au}_2^-$ clusters have on average, more kinetic energy than any other cluster.

4. Discussion

At first sight, the energy distributions of fragment ions in Fig. 2 show that their emission mechanism is collisional. In comparison, Wino-grad's group results concerning neutral molecular desorption under 8 keV Ar^+ bombardment of SAMs on Au [3] show a dominant contribution peaking at low energy, 0.03 eV, which reminds a thermal emission process. Nevertheless, they also detect a minor ballistic contribution at 1 eV, which is comparable to our observation. Like this minor contribution, our results are consistent with more classical collision cascade scenarios as those observed in MD simulations of alkanethiol layer sputtering under Ar (700 eV) bombardment [4]. On the one hand, the potentials and the interaction times used in MD simulations cannot describe bond breaking by chemical reactions leading to thermal emission process as proposed by Riederer et al. [3]. On the other hand, such a low energy ejection is unlikely for ions because of the high neutralization probability and the strong image force interaction.

In addition, the decrease of the KED widths with increasing fragment size, from monoatomic to

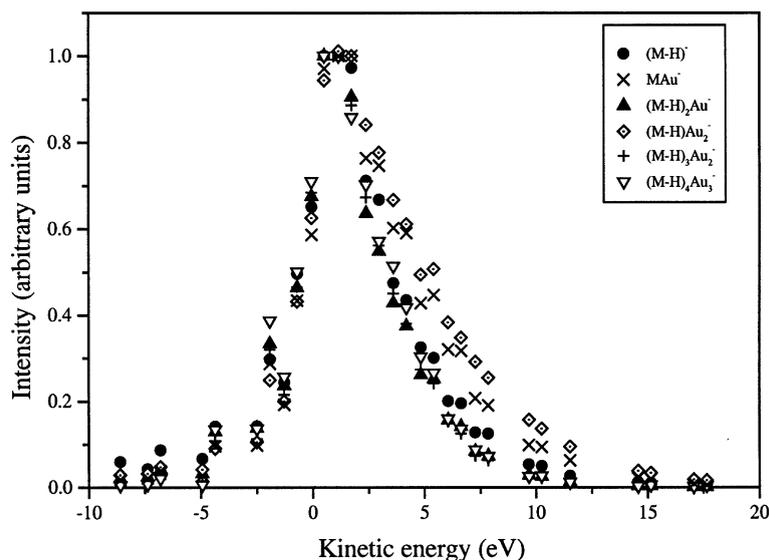


Fig. 3. KEDs of the most intense Au-thiolate cluster ions sputtered from SAMs of octanethiol on gold under 15 keV Ga^+ bombardment.

polyatomic species, is similar to the size effect identified for short molecules [16] and polymer surfaces [17]. This size effect has been explained by the higher overall energy directly needed to produce strongly fragmented species, reflected in the KEDs, and by the internal energy dependent fragmentation of excited species after their emission [18].

Interpreting the KED of cluster ions is more challenging. Again, the peak energy value and the high energy tails obtained in this work provide support to collisionally-induced emission mechanisms. In general, the tails of the distributions remind those measured for cationized polystyrene oligomers, which have been well explained by recent MD simulations [18]. The pronounced intensity ($\sim 30\%$ of the peak integral) observed for negative apparent energies also indicates that the unimolecular dissociation of larger aggregates in the acceleration section of the spectrometer constitutes a significant formation channel for gold-molecule clusters [19]. At this stage however, we do not have sufficient data to interpret the exact shape of the distributions and the fine structure among the KEDs reported in Fig. 3 for different types of clusters.

Complementary theoretical results help us to envision the emission process of metal-thiol clusters. Indeed, in parallel with experiments, Monte Carlo simulations have been performed using the SRIM version [20] of the TRIM code [21]. In these calculations, we use the same bombardment conditions as the experiment and the sample is an equivalent layer (10 Å) of polyethylene on a gold surface (500 Å). As expected, the results show that the major part of the projectile energy is dissipated in the gold substrate and that the collision cascades develop essentially in this region. Knowing that in our experimental conditions, the energy deposition in the metal is not strongly influenced by the organic layer, we believe that processes as those proposed by Colla et al. in studying the emission of clusters from Au surfaces might help explaining our experimental observations [8]. In this hypothesis, the clusters are emitted via a collective motion from a protruding gold region located around the projectile impact point. Qualitatively close mechanisms have been shown to induce the emission of polystyrene oligomers adsorbed on silver surfaces

[18]. Assuming that the same kind of processes also occur with thiol-covered gold surfaces, it is reasonable to believe that the upward concerted motion generated in the gold substrate pushes entire molecules and molecule-metal clusters together towards the vacuum. Conversely, it is unlikely that clusters as big as $(M-H)_4Au_3^-$ could be formed simply via recombination of smaller species emitted in separate local events. To verify this hypothesis, we plan to perform MD simulations of thiol overlayer sputtering under 15 keV particle bombardment, reproducing the exact conditions of our measurements. The comparison of the KEDs and the microscopic insights of the simulations should provide us with a more complete understanding of the underlying physics. Even though ionisation is not considered in the MD model, previous studies show that the simulations are able to describe the properties of secondary ions when they are emitted via collisional processes [18].

5. Conclusion

Our ToF-SIMS instrument has been used to measure the KEDs of gold-molecule cluster ions ejected from SAMs of octanethiol on gold under 15 keV Ga^+ bombardment. It is found that all the gold-molecule cluster ions eject with energies of about 1.2 eV, indicating that collisional effects are responsible of their emission. Metastable decay of excited aggregates in the acceleration section of the spectrometer also appear to be an important formation channel for gold-molecule clusters. On the grounds of TRIM calculations and published MD results, we suggest that Au-thiolate cluster ions might be formed via collective motion induced within a perturbed region of the gold surface after collision cascades. MD calculations conducted with 15 keV projectiles and with the use of a long-range term in the hydrocarbon potential are desirable to corroborate the experimental energy distributions and to improve the interpretation of our results.

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