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Emission of neutral molecules from ion-bombarded thiol self-assembled monolayers

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Abstract

We have investigated ion-stimulated desorption of neutral molecules emitted from 8 keV Ar^+ ion-bombarded self-assembled monolayers (SAMs) of phenethyl mercaptan (PEM) $C_6H_5CH_2CH_2$–SH and 2-(4′-methyl-biphenyl-4yl)-ethanethiol (BP2) $CH_3C_6H_4C_6H_4CH_2CH_2$–SH deposited on Au(1 1 1) substrate. Neutral molecules were detected by laser postionization mass spectrometry. Only molecular fragments were detected from ion-bombarded systems. The mass spectra obtained for sputtered and gas phase fragments indicate that molecules recorded during ion bombardment were indeed emitted from the surface and were not the result of photofragmentation induced by the ionizing laser beam. From experimentally obtained time-of-flight (TOF) distributions, it was determined that the majority of desorbed neutral molecules leave the surface with very low translational energies. As the sample temperature is reduced, the distributions become broader and shift to longer flight times. The shift is more pronounced for molecules from BP2 and increases with the mass of the recorded molecular fragment. We postulate that the emission of molecules is initiated by processes which gently break molecular bonds (e.g., chemical reactions, secondary electrons). The formed fragments are loosely bound to the surface and can be removed by evaporation. At the investigated temperature range (170–350 K), the observed emission delay is attributed to the time required for the molecule to evaporate from the surface and is not influenced by the bond breaking rate. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Self-assembled monolayers (SAMs) of organic species chemisorbed to metal and semiconductors surface are currently of enormous interest for basic research, as well as for technological applications due to their conceptual simplicity, ease of preparation, and the unusually high structural integrity [1,2]. The adsorption of organothiols from solution onto gold substrates is a reliable method for the preparation of stable films and surface functionalization. The most widely studied SAMs

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consist of hydrocarbon chains with functional groups at either end [2]. The molecules within the SAM are covalently bound to a substrate, and the chain–chain interactions (e.g., Van der Waals forces or dipole–dipole interactions) drive the formation of highly ordered and densely packed monolayers of high stability due to the strong bonding of the molecules to the surface.

The intentional and controlled modification of SAMs by particle interactions opens new possibilities for lithographic patterning to produce nanostructures [3,4]. Presently, there is only a limited understanding of the fundamental processes initiated by the energetic ions that lead to the modification of the SAMs and to the ejection of neutral molecular species from the surface [5–14]. In the present work we proceed with the investigation of the sputtering process of a thiol SAM and consider sample temperature- and fragment mass-related effects on the emission characteristics. We employ laser postionization time-of-flight (TOF) spectrometry to study desorption of neutral molecules from SAMs of phenethyl mercaptan (PEM) $C_6H_5CH_2CH_2S$ (PEM) and 2-(4′-methyl-biphenyl-4yl)-ethanethiol (BP2) $CH_3C_6H_4C_6H_4CH_2CH_2$–SH (BP2) adsorbed on an Au(1 1 1) substrate. Both molecules form SAMs by covalently binding the sulfur atom to the gold. Although the phenyl and biphenyl-based thiol adsorption geometry is still under discussion [15,16], the main result from structural investigation is that both of them can form ordered and ultrathin (~1–3 nm) structures.

2. Experimental

The experimental setup used to measure the TOF distributions of sputtered neutral particles has been described in detail elsewhere [17]. Briefly, the measurements were performed in an ultrahigh vacuum chamber (1.5×10^{-10} Torr base pressure) equipped with low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) for surface characterization. An approximately 15 μA continuous Ar^+ ion beam was chopped into 450 ns wide pulses of 8 keV Ar^+ that bombarded the surface at 45°. The ejected neutral species were detected by postionization using 6 ns laser pulses at $\lambda = 259.03$ nm. The laser beam was focused to a ribbon shape parallel to the sample surface plane at a fixed distance of ca. 1 cm in front of the sample. Before each experiment this distance was determined with an accuracy of 0.01 cm using a telescope mounted on a micrometer.

The density TOF distributions of the neutral molecules were recorded by varying the delay between the Ar^+ ion pulse and the postionizing laser pulse. The photoionized particles were accelerated by 1400 V potential toward a position sensitive microchannel plate (MCP) detector. Only neutral molecules emitted within 20° of the normal to the surface were detected. While this mode of operation enables accurate angular and time base measurements, the gated detector provides a mass resolution of approximately 20 at m/z 100. Mass distributions were measured by scanning the detector gate at a fixed time delay between the impact of the ion pulse and the laser pulse. All measurements were done with a total dose below 10^{12} ions/cm^2.

Both SAMs of $C_6H_5CH_2CH_2SH$ (Aldrich, 99%) and HS–CH_2–CH_2–C_6H_4–C_6H_4–CH_3 (synthesized at the Institut für Angewandte Physikalische Chemie, Universität Heidelberg, see [18] for details) were prepared by immersing of the polycrystalline gold substrate in a 1 mM solution of the given thiol in ethanol for 24 h. After the incubation time samples were washed with pure ethanol, subsequently dried in a nitrogen stream, and immediately placed in the vacuum chamber.

3. Results and discussion

The mass distributions of photoionized neutral molecules sputtered by 8 keV Ar^+ ions from PEM and BP2 surface are shown in Fig. 1. The solid line indicates mass spectra of ion-bombarded SAMs, while the broken line depicts photoionized gas phase molecules. The spectrum of PEM exhibits prominent peaks around $m/z = 106$, 92 and 78. The spectrum of BP2 is more diversified and shows peaks around $m/z = 196$, 182, 168, 118, 92. The peaks at $m/z = 106$ for PEM and 196 for BP2 can be assigned to the $C_6H_5CH_2CH_3$ and $CH_3CH_2C_6H_4C_6H_4CH_3$, respectively. No peaks are

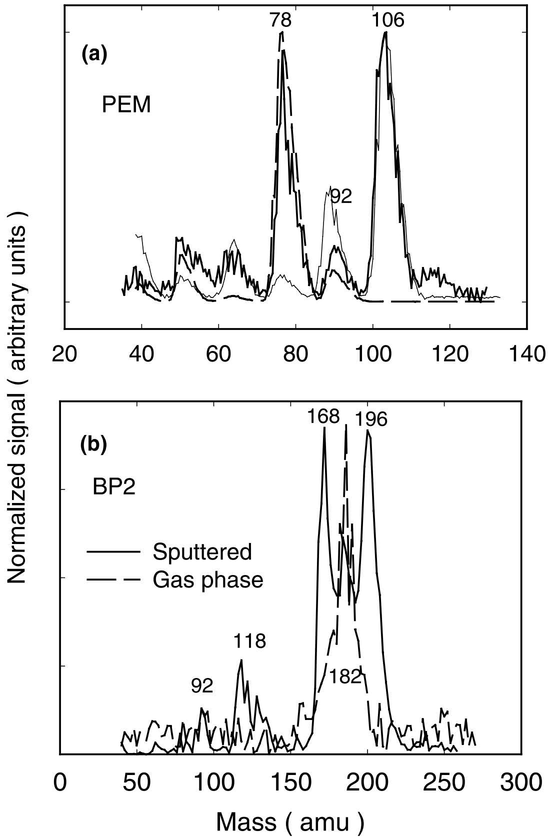

Fig. 1. Mass distribution of neutral molecules emitted from 8 keV Ar^+ ion-bombarded (a) phenethyl mercaptan (PEM) and (b) 2-(4′-methyl-biphenyl-4yl)-ethanethiol (BP2) self-assembled monolayers. The solid line depicts the data obtained during ion bombardment, while the broken line indicates the distributions of photoionized gas phase molecules. The spectra were collected at room temperature and are peak normalized.

discernable at m/z 138 (PEM) and 228 (BP2), indicating that PEM and BP2 molecules fragment before photoionization or in the laser beam. The peaks at $m/z = 106$ for PEM and at m/z 196, 168, 118 and 92 for BP2 are not present in photoionized gas phase mass distributions, which proves that these particles are not formed by the laser but are emitted from the surface. It should also be mentioned at this point that other fragments are emitted from the surface. A mass distribution of positive and negative ions ejected from ion-bombarded PEM or BP2 exhibits a plethora of peaks not present in Fig. 1 because only neutral fragments containing a benzene ring can be ionized by our laser.

The TOF distributions (density) of laser postionized neutral molecular fragments of PEM at m/z 106 and of BP2 at m/z 196, 168 and 118 after 8 keV Ar^+ ion bombardment are shown in Fig. 2. The spectra are peak normalized. Open markers indicate the room temperature Maxwell–Boltzmann time (density) distributions. It is evident that the majority of fragments desorb with low (thermal) energies. Desorption with thermal energy is surprising since PEM and BP2 molecules form a strong bond (2–3 eV) with the gold substrate

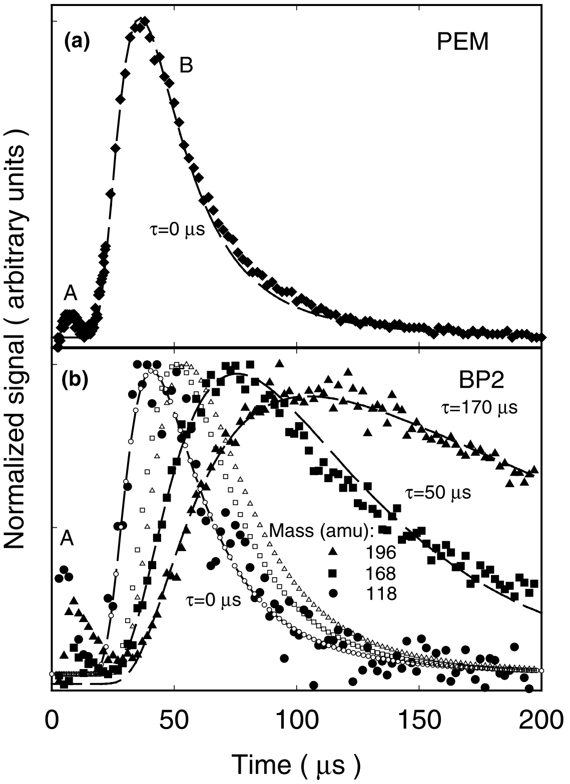

Fig. 2. Time (density) distributions of molecular fragments emitted from 8 keV Ar^+ ion-bombarded phenethyl mercaptan (PEM) and 2-(4′-methyl-biphenyl-4yl)-ethanethiol (BP2). Solid markers indicate experimental data for (a) m/z 106 PEM fragment (◆); (b) m/z 196 (▲), 168 (■) and 118 (●) BP2 molecular fragments. The spectra were collected at room temperature (295 K). Open markers indicate room temperature Maxwell–Boltzmann density distributions, while broken lines indicate the best fit of formula (2) to the experimental data. Parameter τ describes the mean desorption delay.

(S–Au bond) and the binding energy between S and C atoms is also strong [19]. Only a minor fraction of emitted molecules has higher kinetic energies (peak A). These molecules are sputtered with kinetic energies of the order of 1 eV. Peak A was not present when light projectiles (H_2^+) were used to stimulate desorption, whereas desorption of low energy fragments (peak B) was still very abundant [5]. This observation indicates that high energy molecules are emitted as a result of a direct momentum transfer from the incident ion to the gold substrate and finally to the organic layer [5].

Direct bond scission by the primary particle impact followed by unzipping of the chain to generate molecular fragments was invoked to explain ion formation from bombarded polymer surfaces. Recently, Chenakin adopted this picture and assumed that high-rate scission and ion-induced fragmentation of standing hydrocarbon chains is a predominant process of sputtering self-assembled hexadecanethiol monolayers on Ag(1 1 1) [9,13,14]. Our results clearly indicate that direct bond scission is not the main mechanism behind the release of neutral molecular fragments from PEM/Au and BP2/Au. The high energies involved in a direct ballistic interaction would certainly cause the molecules to be promptly ejected with high kinetic energies. However, experimentally determined translational energies of the majority of the desorbed fragments are found to be about two orders of magnitude smaller than the Au–S or S–C binding energies.

A possible scenario leading to a low energy emission of PEM and BP2 fragments may involve chemical reaction stimulated by the primary ions. Computer simulations show that many of the surface molecules near the primary ion impact zone are severely damaged and yield reactive species such as $H^\bullet$, as well as other ionic and neutral molecular fragments [20–23]. These unstable species can react with intact molecules and sever the chemical bonds. Bond scission by chemical reactions is more gentle than direct bond scission by ion impact and is more likely to form products which may be trapped at the surface and finally evaporate with low kinetic energies. A possible reaction that leads to formation of fragments 106 and 196 may be the following:

$$\mathrm{RS\text{–}Au_{(surface)}} + \mathrm{H}^\bullet \rightarrow \mathrm{RH} + \mathrm{S\text{–}Au_{(surface)}}, \qquad (1)$$

where R stands for $C_6H_5CH_2CH_2$ and $CH_3C_6H_4C_6H_4CH_2CH_2$ in case of PEM and BP2, respectively. Direct scission of the sulfur–carbon bond is endothermic by approximately 2–3 eV [19], while cleavage by reaction (1) is estimated to be exothermic by 1.7 eV [5]. Since reactive fragments formed during ion impact can penetrate far away from the ion impact point, the area from where the molecules can desorb is larger than the surface area influenced by the collision cascade that develops in the substrate. This property could account for a high damage cross section measured for 800 eV He^+ bombarded hexadecanethiol by Chenakin et al. [9,13,14].

Zharnikov and co-workers have recently reported that low energy electrons (10 eV) can efficiently damage and chemically modify SAM layers of dodecanethiolate, octadecanethiolate and eicosanethiolate [24]. They observed that excitation of antibonding molecular orbitals and ionization of particular molecular groups mediated by these electrons results in a cleavage of individual molecular bonds. Ion bombardment is associated with emission of low energy secondary electrons. Therefore, such a process could also contribute to molecular desorption. We observe that after irradiation with a total dose of approximately 10^{13} ions/cm^2 the signal of desorbed neutral molecular fragments decreases to ca. 20% of its original value. A comparable decrease in the average layer thickness occurred in experiments of Zharnikov et al. at an irradiation dose of 3000 μC/cm^2. Assumption that a bond breaking by secondary electrons was a sole process leading to molecular desorption would require, therefore, a secondary electron yield of several thousands. Such a value is rather improbable, but a contribution from this mechanism cannot be ignored.

Only the spectra of the fragments with m/z 118, 106, and 92 (not shown) can be satisfactorily described with a room-temperature Maxwell–Boltzmann distribution. The spectra of other fragments are delayed and poorly described by this function. The shape of the spectra also depends on the surface temperature, as shown in Fig. 3. As the temperature decreases the time distributions are

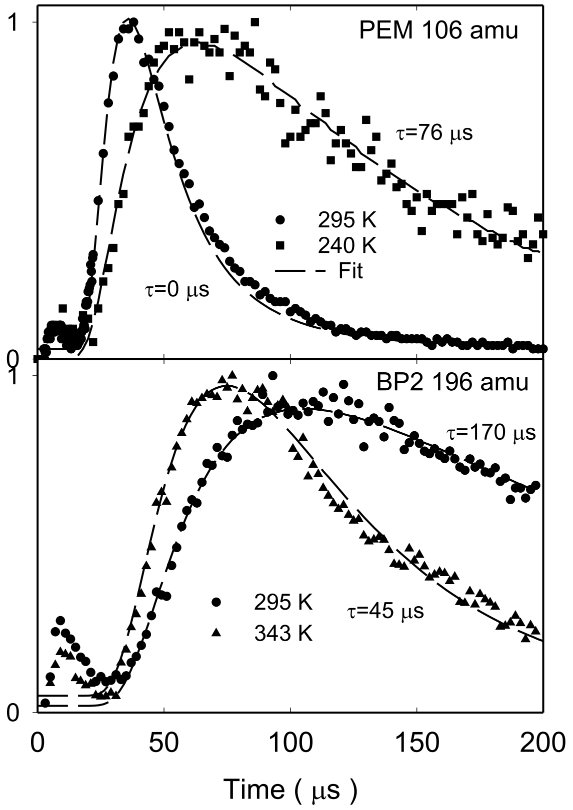

Fig. 3. Time (density) distributions of m/z 106 and 196 molecular fragments emitted from 8 keV Ar^+ ion-bombarded phenethyl mercaptan (PEM) and 2-(4′-methyl-biphenyl-4yl)-ethanethiol (BP2) at various sample temperatures. Broken line indicates the best fit of formula (2) to the experimental data. Parameter τ describes the mean desorption delay.

observed to broaden and to shift toward longer times. Similar effects have been observed in our previous study for ion-bombarded phenethyl and benzyl mercaptans [11]. The desorption delay can be taken into account by convoluting the Maxwell–Boltzmann time density distribution with a first-order rate equation (exponential decay):

$$I(t) = C\int_0^t \left[\left(t-t'\right)^{-4}\exp\left(-md^2/2kT\left(t-t'\right)^2\right)\right] \times \exp(-t'/\tau)\,\mathrm{d}t'. \tag{2}$$

In this equation, $I(t)$ represents the photoion signal as a function of t, the time between the impact of the primary ion (at $t = 0$) and the arrival of the molecules at the laser plane. The mass of the molecule is given by m, d is the distance between the sample surface and the laser plane, k is the Boltzmann constant and T is the “translational temperature” of the desorbed molecular ensemble. The mean delay to desorption is given by τ. The model described by Eq. (2) was fit to the experimental data for both PEM/Au and BP2/Au with C, T and τ as adjustable parameters. These fits, shown as dashed lines in Figs. 2 and 3, are in good agreement with the experimental data.

The emission delay can be explained by the plausible assumption that the time of formation of the molecular fragments, plus the time they remain physisorbed at the surface after the chemical bond with the surface is broken, cannot be neglected. The time delay between the impact of the primary ion beam and the firing of the laser, used as the time in the abscissa of Figs. 2 and 3, is thus composed of two parts. The first delay is the time between the impact of the primary ion and the actual desorption of the molecular fragment from the surface. The second contribution to the total time is the actual flight time the molecule needs to reach the laser plane having a specific translational energy.

A comparison of TOF distributions of m/z 106 and 196 fragments can be used to determine which step in the desorption process is temperature constrained. These two fragments are formed by scission of exactly the same bond (C–S bond) in PEM and BP2 molecules. Therefore, one would expect a comparable emission delay for both these fragments if only the bond breaking rate was a determining factor. Contrary to this supposition, it is evident from Fig. 2 that emission of m/z 106 fragment is not delayed, while a delay of 170 μs is required to reproduce properly the time distribution of m/z 196 fragment. Furthermore, our data show that the delay depends on the mass of ejected fragment. Low mass fragments are emitted promptly and the heavier the fragment, the larger is observed delay. This trend correlates with a decrease of the vapor pressure (evaporation efficiency) of organic molecules similar to the fragments measured in our experiment for larger molecules [25], which would indicate that evaporation rate controls the desorption. A trapping of cut off fragments within the SAM layer can also contribute to the delay. Such trapping can conceivably occur through a bonding of these fragments to the irradiation-induced carbon radicals in the SAM matrix or through the Van der Waals interactions of these fragments with the adjacent hydrocarbon chains. The interaction will be larger for larger (heavier) molecules which may account for the observed increase of the emission delay with the mass of ejected fragment. All above factors allow us to conclude that in the temperature range investigated in this work, the bond scission is a prompt process while the delay is controlled by the desorption rate of physisorbed molecule.

4. Summary

We have investigated ion-stimulated desorption of neutral molecular fragments from 8 keV Ar^+ ion-bombarded SAMs of PEM and BP2. The desorbed neutral molecules were postionized during a short laser pulse after they travel a fixed distance from the sample surface and were detected by mass spectrometry. Our results indicate that most of the neutral molecules are emitted with low (thermal) energies. Low energy molecular desorption of a majority of emitted neutral molecules is a two-step process. In the first step, the impact of the projectiles initiates processes (e.g., chemical reactions, secondary electrons) that gently fragment the surface-bound molecule. Created fragments remain physisorbed on the substrate until they evaporate. The emission of neutral fragments can be delayed. The delay depends on the surface temperature, and on the mass of emitted fragment. It is postulated that bond scission is a prompt process while the delay is controlled by the desorption/evaporation rate. Only a limited number of molecules are emitted with hyperthermal kinetic energies. These molecules are ejected by direct collisions with projectiles and with ejecting substrate particles.

The processes described in this work are not limited to sputtering of SAMs. They should be present in any experiment with the desorption of organic molecules. However, only in thin, tightly bound systems these processes will be favored compared to other ejection mechanisms. In very thin layers like SAMs the excess energy released in exothermic reaction as well as the energy deposited by the primary projectile can be efficiently dissipated in the metal substrate. In thick organic samples the heat transfer is very poor. As a result, the excess heat will accumulate and lead to thermal-like emission with effective temperature much higher than the temperature of the bulk sample [22,26,27]. In such systems heat generated by the primary projectile, as well as the processes induced by the development of the molecular collision cascade, can obscure the phenomena initiated by chemical reactions and secondary electrons. On the other hand in thin, loosely bound systems, most of the particles will be emitted by collisions of adsorbed molecules with ejecting substrate atoms. As indicated by computer simulations [22,23], such a process leads to emission of molecules with average energy of a few eV. Again, this process is very efficient for weakly bound molecules and obscures the phenomena initiated by gentle bond scission mechanisms taking place in SAMs. The formation of reactive fragments and emission of secondary electrons can be initiated by light projectiles. Efficient sputtering of PEM and hexadecanethiol layers has been observed previously with H_2^+ and He^+ projectiles [5,9,13,14]. Therefore, we expect that this mechanism should contribute to erosion of SAM layers during electron and photon bombardment. Unfortunately, no kinetic energy spectra of desorbed molecules have been measured so far for electron and photon projectiles.

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