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Applied Surface Science 141 (1999) 339–344

applied surface science

Desorption of neutral molecules from self-assembled monolayers subjected to keV ion bombardment

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Received 29 May 1998; accepted 31 July 1998

Abstract

Laser postionization in combination with mass spectrometry was used to detect neutral molecules desorbed from self-assembled monolayers of phenethyl mercaptan and benzyl mercaptan on gold upon 8 keV Ar^+ bombardment. From experimentally obtained time distributions, it was determined that the majority of the desorbed neutral molecules leave the surface with low translational energies of about 0.03 eV. As the substrate temperature is reduced, the distributions become broader and shift to longer flight times. In combination with mass distributions, these results indicate that the thermal desorption process is initiated by chemical reactions in the organic layer, creating fragments of the original molecule weakly bound to the surface, prior to release. © 1999 Elsevier Science B.V. All rights reserved.

PACS: 82.80 Ms; 79.20 Rf; 68.18

Keywords: Laser postionization; Ion beam induced desorption; Self-assembled monolayers

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1. Introduction

Self-assembled monolayers (SAMs) are a novel class of materials with promising applications in different technological fields such as nanofabrication, chemical and biological sensing as well as tribology [1–4]. SAMs are ordered molecular assemblies formed by the adsorption of an active surfactant on a solid surface. The most widely studied SAMs consist of short hydrocarbon chains with functional groups at either end [5]. The molecules 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. SAMs are formed spontaneously on a variety of surfaces by exposing the substrate to the molecules in the gas phase or by immersing the substrate in a solution containing the molecules [2]. Apart from ease and speed of fabrication, SAMs exhibit a high stability due to the strong bonding of the molecules to the surface. Furthermore, SAMs can be custom-designed for the desired application by using the most suitable functional group.

The fabrication of SAMs and the characterization of their structural, chemical and physical properties is of great current interest [5]. Infrared spectroscopy

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PII: S0169-4332(98)00521-2

[6], scanning probe microscopies [7,8] and ellipsometry [9] are often applied to characterize the organic surfaces in a non-destructive way. Because of their unmatched sensitivity, however, invasive techniques based on energetic probes such as fast particles and photons play a central role in the surface-analysis of molecular systems [10,11]. The interaction between the energetic probes and the surface not only leads to the desorption of molecules from the surface, but also may result in radiation-induced damage of the SAM [12]. Although this might be considered as an undesirable side effect for an analytical technique, the intentional and controlled modification of SAMs by particle interactions opens new possibilities for lithographic patterning to produce nanostructures [13–15]. Presently, there is only a limited understanding on the fundamental processes initiated by the energetic probes that lead to the modification of the SAM and to the ejection of molecular species from the surface.

In this work, we employ laser postionization to study the desorption of neutral molecules from SAMs of phenethyl mercaptan $C_6H_5CH_2CH_2SH$ (PEM) and benzyl mercaptan $C_6H_5CH_2SH$ (BM) on gold surfaces. Both molecules form SAM's by covalently binding the sulfur atom to the gold. The SAMs are bombarded with short pulses of Ar^+ ions with an energy of 8 keV. The desorbed neutral molecules were postionized during a short laser pulse after they travel a fixed distance from the sample surface and are subsequently detected by mass spectrometry. By varying the delay between the impact of the primary ions and the laser pulse, time distributions are obtained. Our results indicate that the collision-induced molecular desorption from these SAM's is a two-step process. In the first step, the impact of the projectiles initiates chemical reactions that gently fragment the surface-bound molecule. Subsequently, these fragments remain physisorbed on the substrate until they evaporate.

2. Experimental

Self-assembled monolayers were spontaneously formed by immersing gold-coated substrates in solutions containing 30 mM phenethyl mercaptan or benzyl mercaptan in ethanol for several days. The samples were rinsed with ethanol and kept in vacuum (10^{-8} Torr) overnight before introduction into the UHV analysis chamber (with a base pressure 2×10^{-10} Torr) to remove excessive unbound molecules from the surface. The sample stage has both cooling and heating facilities to vary the temperature of the substrate between 150 and 360 K. The desorption process was initiated by bombarding the samples with 450 ns pulses of 8 keV Ar^+ ions, at 45° incidence, focused to a 3 mm diameter spot on the sample. Secondary ions were electrostatically rejected. The desorbed neutral molecules were detected by multiphoton ionization using the frequency-doubled output of a dye laser (Spectra Physics PDL-3 in combination with wavelength extender WEX-1) at 259.04 nm or the frequency quadrupled output of the Spectra Physics GCR-5 Nd:YAG pump laser at 266 nm. Laser photoionization at 266 nm is a non-resonant process requiring at least two photons for most fragments. Tuning the laser to 259.01 nm, which drives a ground-state originating transition for benzene, was found to enhance greatly the ionization efficiency. At both wavelengths, energies of about 3 mJ were used in laser pulses of 6 ns. 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 of the molecules in the laser ionization volume was recorded as a function of time by systematically varying the time delay between the primary ion and laser pulses [16]. This time delay corresponds to the flight time of the neutral molecule from the sample surface to the laser plane plus any measurable delay time to ejection from the surface. After photoionization the molecules were mass selectively detected by time-of-flight mass spectrometry using a gated, position sensitive microchannel plate detector. 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. The desorbed neutral molecules were collected within an angular range of $\pm 20°$ around the normal to the surface, where the signal was found to be maximal.

3. Results and discussion

To establish the mechanisms of molecular desorption from self-assembled monolayers, we provide mass distributions and time distributions of neutral organic fragments at different surface temperatures. This strategy allows us to differentiate between ballistic events, which are not temperature dependent, and other desorption mechanisms which may involve activated processes. This approach is used here to examine two model systems: PEM/Au and BM/Au. The samples were analyzed at different temperatures between 183 and 355 K.

In Fig. 1 the time distribution of the *m/z* 106 fragment desorbed from PEM/Au after bombardment with 8 keV Ar^+ projectiles at room temperature is shown. The maximum density of desorbed molecules (peak B) passes through the laser plane approximately 40 μs after the impact of the primary ions. Moreover, a small peak (peak A) is present at low flight times. When the surface temperature is decreased, there is a dramatic influence on the shape of the time distributions and an overall reduction of the signal intensity. The time distributions are observed to broaden and to shift toward longer times, as shown in Fig. 2. Here, the time distributions measured at 240 and 300 K are shown for the *m/z* 106 fragment ejected from PEM/Au (Fig. 2a) and for the *m/z* 92 fragment ejected from BM/Au (Fig. 2b), respectively. In Fig. 3, mass spectra are shown in order to compare the photoion signals from PEM/Au and BM/Au at 300 K (Fig. 3a,b) and 240 K (PEM/Au: Fig. 3c and BM/Au: Fig. 3d). Mass spectra for both SAMs show prominent peaks at *m/z* 78. This is not surprising since resonant ionization of benzene (78 Da) in the ground state at 259.04 nm enhances the sensitivity for this molecular fragment. At 300 K the mass spectra from desorbed PEM/Au show a prominent peak at *m/z* 106, while

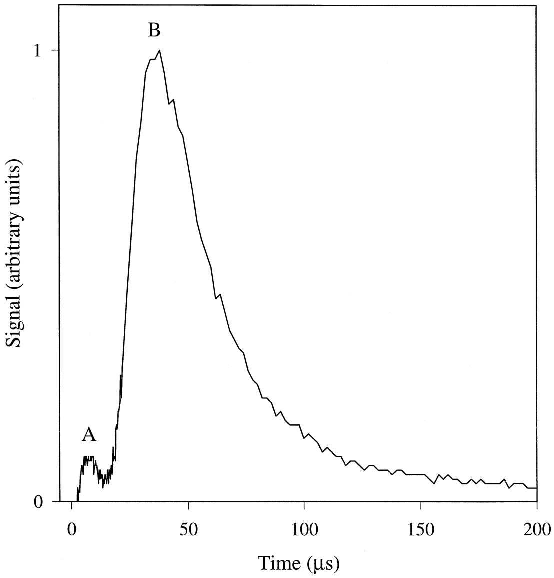

Fig. 1. Time (density) distribution for desorbed neutral molecules (with *m/z* 106) upon bombardment of a PEM/Au SAM with 8 keV Ar^+ ions at room temperature. The distribution shows that a small fraction of the molecules is emitted almost immediately after the ion impact (peak A), but the majority is released more slowly (peak B).

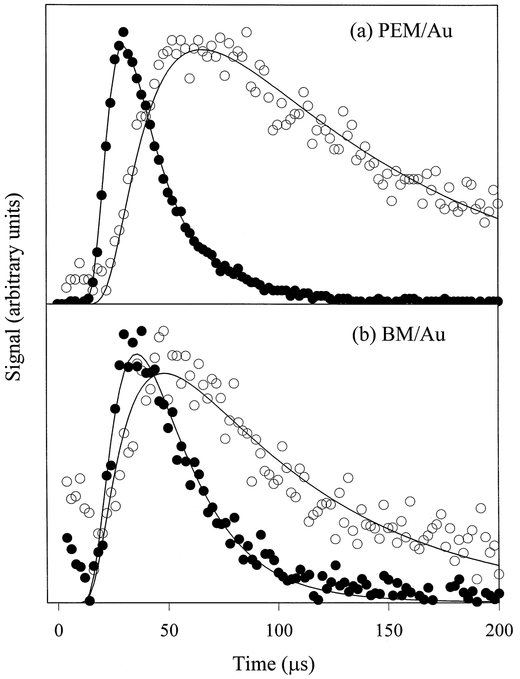

Fig. 2. Time (density) distributions obtained from (a) *m/z* 106 desorbed from PEM/Au and (b) *m/z* 92 desorbed from BM/Au. In both panels, the filled and open symbols represent data obtained at room temperature and 240 K, respectively. The solid curves indicate the best fit using a Maxwell–Boltzmann density distribution convoluted with a first-order rate equation.

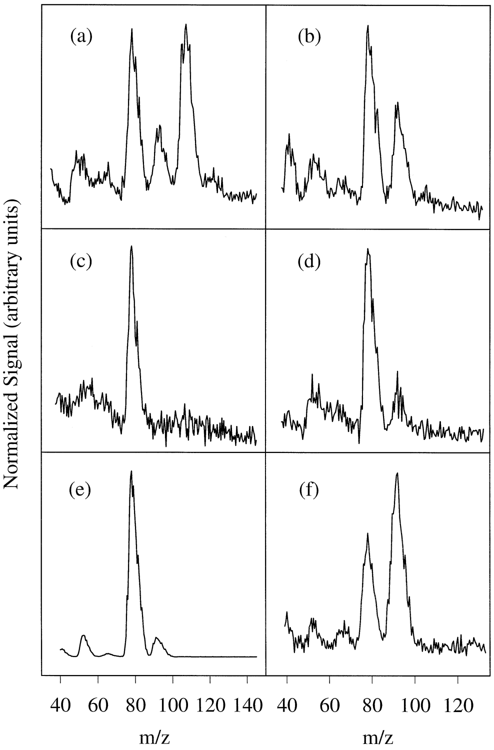

Fig. 3. Mass spectra for particles photoionized using a focused laser beam at 259.04 nm. The upper two rows represent spectra taken after ion beam induced desorption at room temperature ((a) from PEM/Au and (b) from BM/Au) and 240 K ((c) from PEM/Au and (d) from BM/Au). The last row shows room temperature gas phase spectra for PEM (e) and BM (f) taken under the same experimental conditions.

bombardment of BM/Au yields an intense peak at m/z 92. The overall signal is reduced at lower temperatures, but the photoion signal at m/z 106 and 92 decreases rapidly until it is virtually indistinguishable from the background below 200 K.

Consider first the molecular species that arrive at the laser plane with flight times on the order of 10 μs. A careful analysis using different projectiles showed that these molecules are sputtered with kinetic energies of the order of 1 eV by momentum transfer from the incident ion to the gold substrate and finally to the organic layer [17].

The vast majority of the fragments released from PEM/Au or BM/Au arrives at the ionization volume after a much longer time. The desorption process requires the molecules to break a S–C or a Au–S bond, both of which are of the order of 2–3 eV in strength [4]. 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 [18]. 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 (111) [19]. Our results clearly indicate that direct bond scission is not the main mechanism behind the release of neutral molecular fragments from PEM/Au and BM/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.

We propose that the overall desorption process is a two-step process. In a first step, the primary particle's energy released into the solid and the molecular overlayer is used to initiate a chemical reaction. This reaction results in a gentle cleavage of the bond between the S and the C atom, leaving the fragmented SAM physisorbed to the surface. Then, in a second step, the physisorbed fragment evaporates. The overall process can be described by first-order kinetics with a temperature-dependent rate [17].

A possible process is the breaking of the S–C bond by reaction with a hydrogen species

$$\mathrm{RS} - \mathrm{Au}_{(s)} + \mathrm{H} \rightarrow \mathrm{RH} + \mathrm{S} - \mathrm{Au}_{(s)} \qquad (1)$$

where R stands for $C_6H_5CH_2CH_2$ and $C_6H_5CH_2$ in case of PEM and BM, respectively. From molecular dynamics simulations, it is known that these hydrogen species are formed near the impact zone directly after the primary ion hits the surface [20]. At least some of these highly reactive species will interact with nearby intact molecules and initiate the bond scission. Evidence for the occurrence of reaction (1) comes from a comparison of the mass spectra from ion bombarded SAMs (Fig. 3, upper panels) and mass spectra obtained by photoionizing gaseous PEM and BM (Fig. 3, lower panels). No peaks are discernable at m/z 138 (PEM) or m/z 124 (BM), indicating that PEM or BM molecules fragment before photoionization can take place. In the spectrum obtained from ion beam desorbed PEM/Au, a peak at m/z 106 is clearly present, while this peak is absent in the gas phase spectrum. This proves that $C_6H_5CH_2CH_3$ (ethylbenzene with m/z 106) is emitted from the surfaces. In both BM spectra the same molecular fragments are present. However, the relative intensity of the m/z 92 fragment is significantly lower in the spectrum obtained from ion beam desorbed BM/Au. This is a strong indication that this peak principally originates from $C_6H_5CH_3$ (toluene with m/z 92), formed during the desorption process.

Although the average translational energy of the emitted molecules can be considered as being thermal, the time distributions shown in Fig. 2 are poorly described by classical Maxwell–Boltzmann time density distributions [17]. This can be explained by the plausible assumption that the time of formation of the molecular fragments, e.g. by the scission reaction (1), 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. 1 and 2, 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 with a specific translational energy needs to reach the laser plane. This desorption delay can be taken into account by convoluting the Maxwell–Boltzmann time density distribution with a first-order exponential decay:

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

In this equation, $I(t)$ represents the photoion signal as 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, and t' is the desorption delay. 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 fitted to the experimental data for both PEM/Au and BM/Au at various temperatures with C, T and τ as adjustable parameters. These fits, shown as solid lines in Fig. 2, are in excellent agreement with the experimental data. The strong temperature dependence observed in the time distributions is reflected in the values for the mean desorption delay fit parameter τ, as shown in Table 1. For both SAMs, the desorption delay of the molecular fragments upon ion bombardment tends to be longer at lower temperature, implying that the overall rate of desorption slows down at lower temperatures.

Which step in the desorption process is temperature constrained, is presently unclear. Although the incident ion strikes the target with a high energy, most of this will be readily absorbed into the gold substrate and used to develop a collision cascade, leading to the ejection of gold atoms and clusters. Since most of the energy of the primary ions is dissipated into the substrate, it cannot be used to initiate the scission of the bound molecules. This would imply that even a moderate variation of the substrate temperature could have a substantial influence on the kinetics governing the bond cleavage. Alternatively, it could be argued that the physisorbed molecules are thermally equilibrated to the surface. Desorption would then proceed at a temperature dependent rate. This thermal equilibrium should be reflected in the translational temperature T resulting in lower values at lower temperatures. However, this trend is not reflected in the fitted values for T

Table 1
Averaged values for the temperature (T_{fit}) and the mean desorption delay (τ_{fit}) obtained from Eq. (2) at different surface temperatures (T_{exp})

T_{exp} (K)	T_{fit} (K)		τ_{fit} (μs)	
	PEM/Au	BM/Au	PEM/Au	BM/Au
240 (10)	311 (11)	588 (10)	76 (16)	52 (25)
300 (10)	310 (17)	581 (47)	0.4 (2)	25 (10)
340 (10)	365 (16)	596 (50)	0.7 (4)	25 (4)

Estimated uncertainties are given between parentheses.

(Table 1), which tend to be roughly constant over the temperature range studied here. This could possibly be explained by the heating of the local environment when the molecule gets formed by an overall exothermic reaction like Eq. (1). Part of that energy might be stored into vibrational modes of the molecule, but part could also be used to increase the translational energy of the departing molecule.

4. Conclusions

Laser postionization in combination with mass spectrometry was used to measure the time distributions of neutral molecules desorbed from self-assembled monolayers of phenethyl mercaptan (PEM/Au) and benzyl mercaptan (BM/Au) on gold upon 8 keV Ar^+ bombardment. Our experimental results indicate that although a small fraction of the molecules is sputtered ballistically with high kinetic energies, the majority is thermally released from the surface. We propose to view this slow desorption as a two-step process. In a first step, highly reactive hydrogen species originating from the severely damaged impact site of the primary ion, initiate chemical reactions that result in the gentle cleavage of a chemical bond. Experimental evidence was found for the abundant release of ethylbenzene from PEM/Au and toluene from BM/Au. This is a strong indication that primarily C–S bonds are broken. In a second step the molecular fragments remain weakly bound to the surface until they are released with thermal translational energies. The temperature-dependent time distributions were found to be adequately described by a convolution of the Maxwell–Boltzmann distribution with a first-order rate equation to account for the delay in the overall desorption.

Acknowledgements

The financial support of the National Science Foundation, the National Institutes of Health, the Office of Naval Research, and the Polish Committee for Scientific Research Fund No. PB 1128/T08/96/11 and Maria Sklodowska-Curie Fund MEN/NSF-96-304 is gratefully acknowledged. E.V. is partially supported by the Fulbright-Hayes Association and a NATO Research Fellowship.

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