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Ion-induced erosion of organic self-assembled monolayers

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Abstract

Laser post-ionization mass spectrometry combined with Scanning Tunneling Microscopy (STM) has been used to investigate processes of ion-stimulated erosion of self-assembled monolayers (SAM) of phenethyl mercaptan $C_6H_5CH_2CH_2S$ (PEM) deposited on gold. Results indicate that only PEM fragments are emitted from the surface. Most of the PEM fragments (predominantly $C_6H_5CH_2CH_3$ with $m/z = 106$) are emitted with thermal kinetic energies. STM images collected on 8 keV H_2^+-irradiated surfaces with a system tuned to probe electronic states of sulfur atoms show no additional damage induced by irradiation. This indicates that sulfur atoms are not removed from the surface during hydrogen bombardment. It is proposed that the emission of SAM molecules is initiated by chemical reactions which gently break C–S bonds. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

A unique property of ion beams to desorb non-fragmented molecules has been utilized in chemical characterization of organic surfaces [1–3]. Within this wide range of applications there is a need for better fundamental understanding of the processes taking place during ion-beam induced desorption of organic molecules. Molecules forming so-called Self-Assembled Monolayers (SAM's) are especially interesting. SAM's are ordered molecular assemblies spontaneously formed by the adsorption of an active surfactant on a solid surface. They have numerous promising applications in different technological fields such as nanofabrication, chemical and biological sensing as well as tribology [4]. The most widely studied SAM's consist of short hydrocarbon chains with functional groups at either end [5]. 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, as shown schematically in Fig. 1.

The intentional and controlled modification of SAM's by particle interactions opens new possibilities for lithographic patterning to produce nanostructures. Presently there is only a limited

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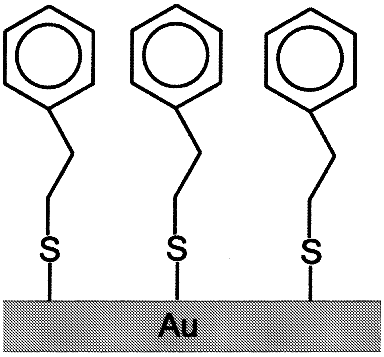

Fig. 1. A schematic representation of PEM monolayer.

understanding of the fundamental processes initiated by the energetic ions that lead to the modification of the SAM and to the ejection of molecular species from the surface. In this communication we present time-of-flight (TOF) and kinetic energy distributions of neutral molecules sputtered by 8 keV Ar^+ and H_2^+ from phenethyl mercaptan $C_6H_5CH_2CH_2S$ (PEM) adsorbed on Au{1 1 1} substrate. The damage induced to the gold substrate and PEM monolayer by these projectiles after low dose bombardment is also measured with a Scanning Tunneling Microscope (STM).

2. Experimental

The experimental setup used to measure the TOF distributions of sputtered neutral particles has been described in detail elsewhere [6]. Briefly, the measurements were performed in an ultra high vacuum chamber (1.5×10^{-10} Torr base pressure) equipped with low energy electron diffraction (LEED) and Auger Electron spectroscopy (AES) for surface characterization. A desorption event was initiated by 450 ns 8 keV Ar^+ and H_2^+ ion pulses. The ejected neutral species were detected by post-ionization using 6 ns laser pulses at $\lambda = 259.04$ 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. The ionized particles were accelerated toward a position-sensitive microchannel plate (MCP) detector. The density time-of-flight distributions of the neutral molecules were recorded by varying the delay between the ion pulse and the laser pulse. The angle of incidence of the primary ion beam was 45° and the desorbed neutral molecules were detected normal to the surface within an angular range of +20°.

STM images were acquired with Park Scientific Instrument microscope Autoprobe VP2 model. The scanning system of this instrument consists of a piezoelectric tube, which enables for 10 μm maximum scanning range. For the coarse tip positioning an "inertial drive translation stage" mechanism is used. Vibration isolation of the microscope platform is accomplished by spring suspension systems and eddy current damping. Autoprobe VP2 can work as an STM, AFM and NCAFM (non-contact AFM) microscope and can be operated both in air and under UHV conditions.

Phenethyl mercaptan monolayers were prepared by immersing a vapor-deposited gold substrate in 30 mM ethanol solution of these molecules. The gold substrate was kept in solution for five days prior to use and was rinsed with ethanol before introduction into the analysis chamber to remove excess unbound molecules from the surface.

3. Results and discussion

The mass distribution of photoionized neutral molecules sputtered by 8 keV Ar^+ from PEM surface is shown in Fig. 2. The spectrum exhibits a prominent peak at $m/z = 106$ which is due to the PEM fragment $C_6H_5CH_2CH_3$. No molecular ion is observed. The peak at $m/z = 106$ is also visible in the spectrum of a laser-ionized gas-phase of ethyl benzene ($C_6H_5CH_2CH_3$) molecules, which shows that these molecules can be directly photoionized. The peak at $m/z = 106$ is not present in photoionized gas-phase PEM mass distribution, which indicates that particles composing this peak are not created from fragmentation of larger molecules in the laser field. All these observations prove that molecular fragment at $m/z = 106$ visible in the spectrum of sputtered PEM is emitted from the surface.

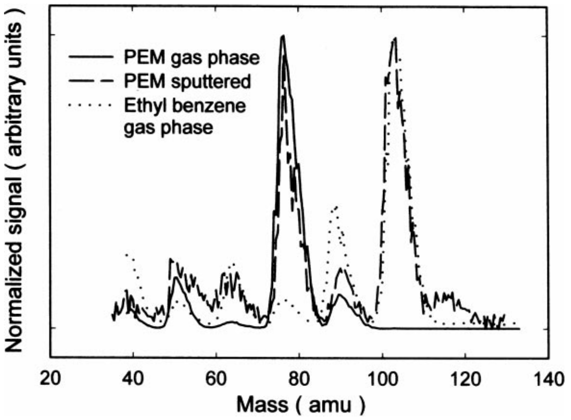

Fig. 2. Mass spectra of particles photoionized with 259.04 nm photons from sputtered, gas-phase PEM and gas-phase ethyl benzene $C_6H_5CH_2CH_3$.

The time-of-flight distributions (density) and kinetic energy distribution of laser post-ionized neutral molecular fragment of PEM at *m/z* 106, after 8 keV projectile bombardment are shown in Fig. 3(a) and (b), respectively. The spectra are peak normalized. It is evident that fragments desorb predominantly from PEM/Au with thermal energies. This is surprising since PEM molecules form a strong bond (2–3 eV) with the gold substrate (S–Au bond) and the binding energy between S and C atoms is also strong [5]. Only a minor fraction of emitted molecules has higher kinetic energies. A careful analysis using different projectiles showed that these molecules are sputtered with kinetic energies of the order of 1 eV by a direct momentum transfer from the incident ion to the gold substrate and finally to the organic layer [7].

We have postulated that low energy emission of PEM fragments can be explained by chemical reactions stimulated by the primary ions [7]. Direct bond scission by projectile impact can be excluded since it would cause the molecules to eject with high kinetic energy. 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. 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. Direct scission of the sulfur–gold bond is endothermic by approximately 2–3 eV, while cleavage by reaction with a hydrogen radical is estimated to be exothermic by 1.7 eV [7]. If evaporation is involved, the process should be temperature dependent. Indeed, such dependence has

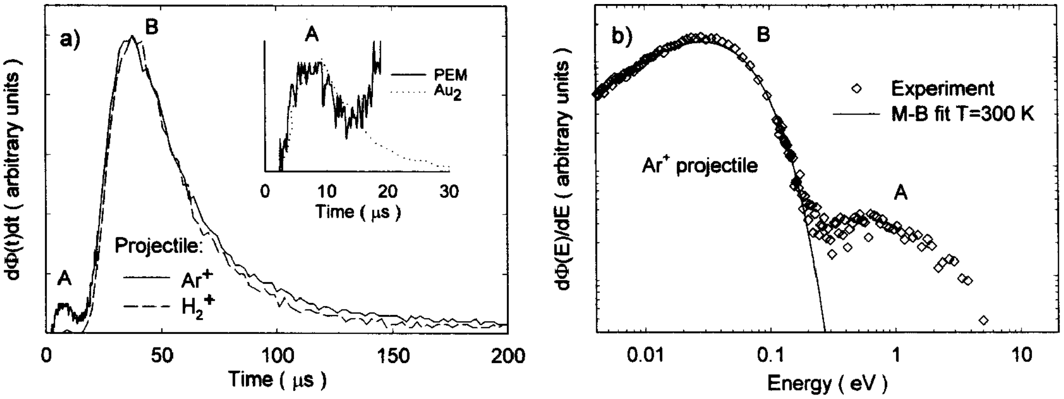

Fig. 3. (a) Time-of-flight (density) and (b) kinetic energy distributions of the molecular fragment ($m/z = 106$) emitted from room temperature PEM monolayer bombarded with 8 keV projectiles. The high and low translational energy components are labeled A and B, respectively. The dotted line in the inset of (a) represents the spectrum of Au dimers sputtered from the Au substrate. The solid line in (b) indicates a fit of the Maxwell–Boltzmann distribution with $T = 300$ K.

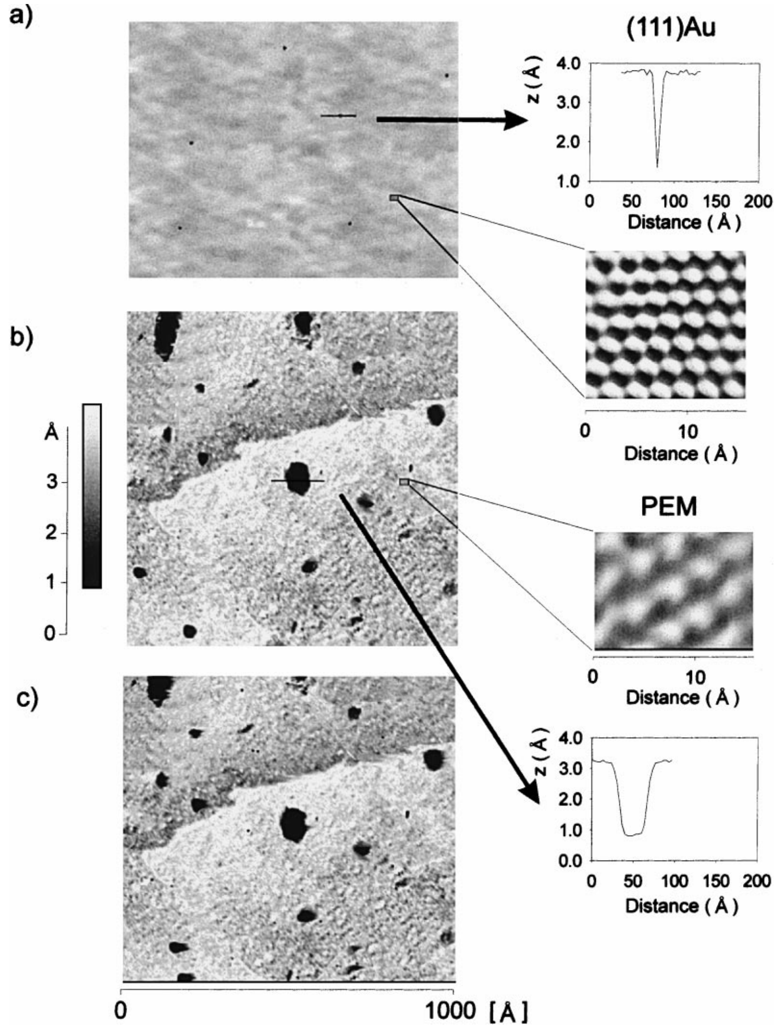

Fig. 4. 1000 Å×1000 Å STM pictures of (a) clean Au{1 1 1} substrate bombarded with 8 keV H_2^+ ions; PEM monolayer (b) prior and (c) after irradiation with 8 keV H_2^+ projectiles. The total dose of bombarding ions was 1×10^{13} ions/cm^2. On the right side of main images 10 Å×10 Å frames of Au{1 1 1} and PEM monolayers are shown with the surface profiles measured along the drawn line. The image (a) was obtained in constant-current mode, tunneling current $I_T = 0.5$ nA, bias voltage $V_B = 68$ mV, while images (b) and (c) were recorded in a constant-current mode, tunneling current $I_T = 4$ nA, bias voltage $V_B =$ mV.

been observed recently and described by a convolution of the Maxwell–Boltzmann distribution with a first-order rate equation to account for the delay in the overall desorption [8]. A possible reaction may be the following:

$$C_6H_5CH_2CH_2S\text{–}Au_{(surface)} + H^{\bullet} \rightarrow C_6H_5CH_2CH_3 + S\text{–}Au_{(surface)} \qquad (1)$$

This concept was further tested by measuring the damage induced in the substrate and PEM layer by primary ions. PEM molecules, as almost all SAM's, form an insulating layer. In our previous study of the morphology of docosanethiol ($HS\text{–}(CH_2)_{21}CH_3$ (DCT) and dodecanethiol ($HS\text{–}(CH_2)_{11}CH_3$) (DDT) deposited on gold, we showed that at these conditions STM images are obtained by measuring the tunneling current between the tip and the sulfur atom bound to the surface [9]. The following observation can additionally support this finding. In the present study we have used the same setting for the nanoprobe as in Ref. [9] ($I_T = 4$ nA, bias voltage $V_B = 100$ mV). We have obtained images of PEM molecules showing $(\sqrt{3} \times \sqrt{3})$R 30° reconstruction, although the ordering was much worse compared to DCT or DDT samples. Since the tail groups of these two groups of molecules are quite different, one would expect to use different tunneling states if the process was to occur through the terminal group of the molecule. The possibility to monitor the sulfur arrangement gives us the unique opportunity to verify reaction (1) directly. If this reaction is valid, one can expect that the desorption of low energy molecular fragments should not influence images recorded from the PEM monolayer. The only modification can be caused by ballistic atom removal. To eliminate this factor we have used H_2^+ ions to initiate desorption. As it is visible in Fig. 2, no ballistic component is present for this projectile while the low-energy emission is significant. In these studies a total dose of approximately 1×10^{13} ions/cm^2 was used, which roughly corresponds to 0.02 monolayer removal if a sputtering yield of 1 is assumed. In fact, much lower ballistic sputtering yield can be expected for 8 keV H_2^+ projectiles. Several randomly selected areas of H_2^+-irradiated samples were probed. The measurements performed on a clean gold surface show that within an area of 1000 Å×1000 Å only a few pits with a minimum diameter of approximately 15 Å are formed (see Fig. 4(a)). The depth of these pits is ~2.5 Å, which corresponds to the substrate layer separation in Au{1 1 1}. This indicates that low dose sputtering only removes first layer atoms. This conclusion agrees with similar measurements reported by Lang et al. [10] as well as with computer simulations [11]. The measurements performed on a PEM surface prior to ion bombardment are presented in Fig. 4(b). The image shows depressions with a depth similar to that observed on a bombarded clean surface. However, their diameter is much larger. Such features have been reported in the literature for other SAM's [12–15]. It is believed that they are caused by defects formed in the gold substrate immersed in solution during monolayer formation [14,15].

The image obtained on H_2^+-irradiated PEM surface from the same area as presented in Fig. 4(b) is shown in Fig. 4(c). The damage pattern looks similar to the one recorded on fresh PEM surface. There are few additional pits but comparison with Fig. 4(a) indicates that they can be attributed to ballistic sputtering. It should be mentioned that although 1000 Å×1000 Å images are shown here, the comparison between fresh and ion-bombarded PEM surfaces was done by looking at subsections of these images in which atomic resolution could be achieved. No new structures that would account for a large emission of low energy fragments were found. This observation supports the scenario in which desorption of low energy PEM fragments occur due to chemical scission of C–S bond by the chemical reaction given by formula (1).

4. Conclusions

Laser post-ionization technique as well as STM have been used to investigate processes that occur during 8 keV Ar^+ and H_2^+ bombardment of self-assembled monolayers of phenethyl mercaptan $C_6H_5CH_2CH_2S$ (PEM). Emission is dominated by molecular fragments $C_6H_5CH_2CH_3$ at $m/z = 106$. We show that these fragments are emitted from the surface and are not the result of photofragmentation of PEM molecules. While a minor collision-induced ejection is observed only with the heavier primary ion, most molecular fragments of PEM at $m/z = 106$ desorb with thermal kinetic energies for both Ar^+ and H^+ ion particles. The STM probe tuned to monitor sulfur atoms at the surface does not show any modification of the arrangement of these atoms after H_2^+ bombardment, which stimulates a significant emission of molecular fragments. We postulate that emission of these molecules is caused by a chemical reaction, which gently breaks C–S bond, and then allows $C_6H_5CH_2CH_3$ fragments to evaporate. This reaction is stimulated by reactive species like $H^\bullet$ formed after damage of intact PEM molecule in the primary ion impact zone.

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