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In situ observation of particle-induced desorption from a self-assembled monolayer by laser-ionization mass spectrometry

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We studied particle-stimulated desorption processes of highly ordered, self-assembled monolayers of biphenyl-based thiols covalently bound to Au/mica substrates with laser postionization in combination with mass spectrometry. Direct evidence was obtained that large molecular fragments are removed from these monolayers during impact of electrons with a kinetic energy of 1 keV. The damage that accumulates in the self-assembled monolayer with increasing electron dose was measured using ion-beam, sputter-initiated laser probing. Our results show that electron-induced desorption competes with the gradual erosion of the monolayer by the formation of a carbonaceous residual layer on the substrate. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1555261]

Many emerging nanotechnological applications rely on the development of well-defined surfaces functionalized with (sub)monolayer coverages of complex organic molecules.[1] A particularly promising trend is the exploitation of self-assembled monolayers (SAMs) as ultrathin resists in combination with electron-beam lithography. It has been shown that this approach permits structures to be written with a lateral resolution below 10 nm.[2,3] The suitability of such a novel resist is determined, among other parameters, by the nature and the efficiency of the modification in the SAM during irradiation by energetic electrons. Up to now, most insight on these issues has been based on the interpretation of the compositional or structural changes in pristine systems *after* irradiation.[4–10]

We demonstrate how laser probing of desorbed species can be exploited to study *in situ* the processes that occur during the dynamic interaction of organic, self-assembled monolayers with swift, charged projectiles. The reported procedure may furthermore be used to assess the radiation-induced damage during characterization sessions by standard analytical techniques based on particle-initiated probing, such as Auger electron spectroscopy. The development of highly sensitive surface characterization techniques becomes more and more important as they must keep up with the constant reduction of the amount of material available for analysis.

We probed the electron- and Ar^+-ion-stimulated desorption of molecular fragments from self-assembled monolayers of 2-(4′-methyl-biphenyl-4yl)-ethanethiol [$CH_3-C_6H_4C_6H_4CH_2CH_2-SH$ (BP2)][11] covalently bound to Au/mica substrates. Highly oriented polycrystalline Au films with a thickness of 200 nm were grown by thermal evaporation on freshly air-cleaved mica.[12] SAMs of BP2molecules were prepared by immersion of these Au substrates in an ethanolic solution [approx. 1 mmol in pure ethanol (99%, BDH Laboratory Supplies)] for at least 24 h. Biphenyl-terminated thiols are known to form highly ordered structures on Au (111).[11,13] Before the experiment, the BP2/Au samples were thoroughly rinsed with clean ethanol and dried in a dry nitrogen flow.

The photoionization measurements were performed with a laser-ionization mass spectrometer. The experimental setup is described in detail elsewhere.[14] In short, the apparatus consists of an ultrahigh vacuum chamber (base pressure below 2×10^{-10} hPa), in which an ion gun and an electron gun were used to direct energetic projectiles at 45° incidence onto a centrally located sample. The plume of desorbed particles was intersected (parallel to the sample surface at a distance of 4 mm), by a focused laser beam from a pulsed Nd:YAG pumped optical parametric oscillator delivering 6 ns pulses. Desorbed organic fragments were ionized using 259-nm-radiation with a fluence of 7.3×10^{17} photons/cm^2. At this wavelength, a large photoion yield was observed, most probably due to resonance-enhanced, two-photon ionization, as reported for benzene.[15] The photoions are subsequently detected in a time-of-flight mass spectrometer (with a mass resolution $m/\Delta m$ of about 200 in linear and 800 in reflectron mode).

Different experiments were designed to assess information on the molecular fragments desorbing from the BP2/Au sample during irradiation with energetic particles, as well as on the damage that is accumulating on the surface during such a bombardment. To discriminate between projectile-induced fragments desorbed from the surface and photofragments created during the detection, mass spectra were recorded upon photoionization of the free molecules in three

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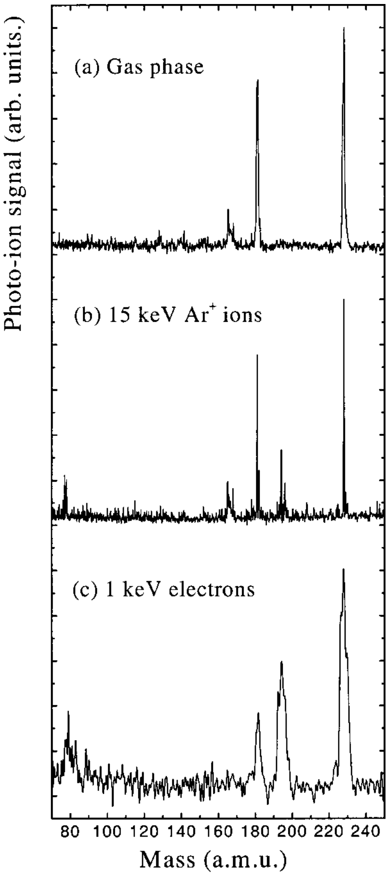

FIG. 1. Mass spectra of neutral molecules obtained upon photoionization of (a) BP2 molecules in vapor phase above the Au substrate, (b) molecules desorbed from BP2/Au during bombardment by 15-keV Ar^+ ions, and (c) molecules desorbed from BP2/Au during irradiation by 1-keV electrons.

different configurations: (a) BP2 molecules in the gas phase and molecules desorbed from BP2/Au SAMs upon (b) 15-keV Ar^+-ion and (c) 1-keV electron bombardment of the system. The results are summarized in Fig. 1.

In the first configuration, a BP2/Au sample was inserted in the apparatus without undergoing the thorough rinsing-and-drying procedure described earlier. The Au surface is then covered both by chemisorbed molecules forming the SAM and by molecules loosely entangled in the monolayer. These physisorbed molecules are in a dynamic equilibrium with molecules in the gas phase above the substrate. The vapor pressure of this ensemble was found to be high enough to laser-probe the molecules without the need of an energetic projectile to initialize the desorption. The resulting fragmentation pattern [Fig. 1(a)] shows groups of mass peaks around m/z values of 165, 181, and 228, the last one corresponding to the mass of the complete BP2 molecule. The other fragments result from breaking C–C bonds in the alkane chain. Their abundance was found to be strongly dependent on the photon fluence, and they are thus considered as the products of the photofragmentation of the complete molecule.

Next, BP2 SAMs were prepared on Au substrates, and care was taken to remove all physisorbed remnants before the data acquisition. Within the instrumental detection limit, no gas-phase species could be detected. The monolayer was then subjected to a pulsed (duration of 500 ns) 15-keV Ar^+-ion bombardment. The recorded mass spectrum is shown in Fig. 1(b) (total ion dose 5×10^{10} ions/cm^2). In addition to the mass peaks already observed in the physisorption experiment, molecular fragments with m/z values around 78 and 194 are also apparent. This observation confirmed that these fragments are not created during photofragmentation. Previous studies showed that the emission of molecules upon ion impact is predominantly initiated by processes involving chemical reactions or interactions with secondary electrons that gently cleave the adsorbate–surface bond or a bond within the molecule.[16–19] The resulting fragments are subsequently loosely bound (physisorbed) to the surface until they eventually evaporate in thermal equilibrium with the surface.

In the third configuration, BP2/Au systems—care being taken to remove all physisorbed species—were bombarded with 1-keV electron beam (electron density 4×10^{12} electrons/cm^2 s) with a total electron dose delivered during the entire experiment time of $35\,\mu$C/cm^2 (2.2×10^{14} electrons/cm^2). Figure 1(c) shows *direct* evidence that medium-energy electrons are capable of initiating the desorption of large neutral molecules from the organic overlayer, including both the intact molecule forming the SAM and the desulferized fragment. Up to now, only *indirect* evidence for electron-stimulated desorption of thiolated species on Au has been reported.[6–8] Moreover, it was recently concluded that cleavage of thiolate–substrate bonds by low-energy electrons interacting with biphenyl SAMs is *not* accompanied by the removal of complete molecules.[9] The photoion signals obtained following electron-stimulated desorption [Fig. 1(c)] are considerably smaller than those acquired during the ion-induced desorption experiments, which we primarily attribute to the lower projectile flux in the former case. To improve the signal-to-noise ratio, the mass spectrometer was therefore operated in its linear mode, resulting in a reduced mass resolution.

The electron-induced damage in the SAM was monitored *in situ* as a function of the accumulated dose. Therefore, a pristine SAM made of BP2 molecules was characterized and uniformly exposed to a 150-eV beam during four consecutive sessions, until the SAM received a total dose of $1000\,\mu$C/cm^2 (6.2×10^{15} electrons/cm^2). In between two sessions, the damage in the BP2/Au system was investigated by ion-initiated laser probing. The ion dose per data point was kept as low as 2 nC/cm^2 (1.3×10^{10} ions/cm^2) in order to keep ion-induced damage low enough. Ion- and electron-induced damage were considered to be uncorrelated, and the data are corrected for ion-initiated degradation, which was found to be of the order of a few percent.

The decrease of the normalized photoion signal from the complete molecule (m/z 228) and the desulferized fragment (m/z 194) as function of the accumulated dose is shown in Fig. 2. For both fragments, the photoion signal decreases monotonically as function of the dose. We define the critical dose d_c as the accumulated electron dose corresponding to the midpoint value of the difference between the photoion signal obtained from the SAM prior to irradiation and after being exposed to a large electron dose (indicated by the dotted lines in Fig. 2). From our experiments, this critical dose is estimated to be close to $300\,\mu$C/cm^2 (1.9×10^{15} electrons/cm^2). Such a high value for d_c is associated with a regime in which a substantial amount of C–H

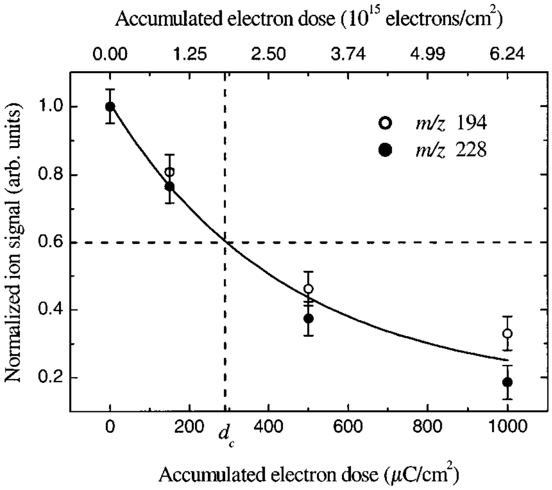

FIG. 2. Photoion signals from the thiolate (m/z 228) and the desulfurized molecular fragment (m/z 194) as a function of the accumulated electron dose during the uniform irradiation of BP2/Au with 150-eV electrons. The signals were obtained by photoionizing particles released from the surface by a short ion pulse.

bonds is already cleaved, resulting in a highly hydrogen-deficient film.[4,5] With increasing dose, the further erosion of the monolayer is usually attributed to the cross-linking of the damaged chains, leading to the formation of a carbonaceous layer on the substrate,[4,5] eventually associated with the removal of carbon-containing material.[6–8]

Our results show that at least a fraction of intact molecules and their large fragments leave the substrate (directly or indirectly) upon interaction with the energetic electrons, and thus at least a second electron-induced process is in competition with a gradual decomposition of the molecules forming the molecular overlayer. Although the disappearance of the photoion signal can be reasonably well described by a simple exponential decay (included in Fig. 2 to guide the eye), a more specific kinetic rate law is needed to model two (or more) processes.

Since biphenyl-based SAMs exposed to electrons show an increased wet-etching resistance (presumably because of the electron-induced cross-linking between neighboring phenyl groups) the possibilities to use such molecules as ultrathin, negative-contrast pattern resists for electron lithography purposes are under exploration.[2,3] Desorption of (parts of) the molecules may well contribute to limit the ultimate resolution of the patterns that can be achieved with such resists. Further work is needed to assess the contributing parameters and their importance in regulating erosion-inducing processes in such systems. Due to its inherent sensitivity and selectivity, laser-ionization mass spectrometry might be a viable, if not the only, candidate to perform such experiments.

In conclusion, we demonstrated the applicability of laser-ionization mass spectrometry to study the dynamic interaction of 15-keV Ar^+ ions and 1-keV electrons with a SAM made of 2-(4′-methyl-biphenyl-4yl)-ethanethiol (BP2) molecules covalently bound to Au/mica substrates. We present *direct* evidence that energetic electrons can induce the desorption of large, fragile, molecular fragments. The damage induced during electron irradiation of a BP2/Au SAM was evaluated *in situ* as function of the accumulated dose. These results indicate that electron-induced desorption is in competition with the formation of a carbon-rich residual film on the surface, which is commonly accepted to be the prime erosion process of a SAM. Biphenyl-based SAMs are proposed as promising candidates for ultrathin, negative resists. The desorption of a substantial fraction of the monolayer during electron irradiation might contribute to limit the resolution that can be ultimately obtained for substrate patterning by e-beam writing.

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