Irradiation Sensitivity of Self-Assembled Monolayers with an Introduced “Weak Link”

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The irradiation sensitivity of n-alkanethiolate SAMs can be enhanced by the incorporation of an irradiation-sensitive functional group as a predetermined breaking point into the alkyl chain. Following this general strategy, several different sulfur-containing functional entities with a variable position in the alkyl chain were tested. In some cases, the incorporation of these entities resulted in a noticeable enhancement of the irradiation-induced desorption (by about 30%), even though the chains were not exclusively cut at the position of the incorporated group, but the scission events related to the “weak links” were just added to those in the alkyl matrix. The position of the incorporated group on the alkyl chain was found to be most essential for its performance as a weak link; the enhancement of irradiation-induced desorption was observed only when the groups were placed close to the SAM—ambient interface.

1. Introduction

Self-assembled monolayers (SAMs) are chemisorbed monomolecular films, in which the adsorbate molecules self-organize in a specific way: they are aligned with a headgroup bonded to the substrate while the chainlike carboxylic tail is oriented upright with a high degree of intermolecular order.1,2 Among other SAMs, the rather less flexible organic tail of longish methyl-terminated molecules1 can be broken up by an irradiation treatment with electrons, ions, or X-rays.4–6 Their irradiation-induced dehydrogenation, desorption of molecular fragments, and loss of orientational order increase the wettability, reactivity, and permeability of AT films, which enables their application as a positive resist in micro- and nanolithography.6–9

Chemical structures of materials used to fabricate the SAMs are shown in Figure 1. The structures I–V are used below as the names of the corresponding films. I is taken as a reference system.

Recently, we have shown that the effectiveness of AT SAMs as a monomolecular lithographic resist can be noticeably enhanced by the insertion of functional entities, serving as a predetermined breaking point, into the molecular backbone.10 The aim of the present study is an extension of this approach by the investigation of the effect of the chemical identity and the position of the inserted functionality on the response of AT films toward electron irradiation. We have chosen sulfur-based moieties, as the S–C bond is known to be weaker (≈60 kcal mol$^{-1}$) than the C–C bond (≈88 kcal mol$^{-1}$), and investigated AT SAMs with sulfide, sulfone, and sulfonyl-phenoxy groups incorporated into the alkyl chain (see Figure 1). Even though the case of the sulfide functionality has been studied previously,10,11 we show the data for these films here as well to provide a direct comparison with the other systems.

2. Experimental Section

We investigated SAMs formed from n-octadecanethiol CH$_3$–(CH$_2$)$_{17}$–SH (I), 11-(n-hexylmercapto)undecanethiol CH$_3$–(CH$_2$)$_{10}$–S(CH$_2$)$_6$SH (II), 11-(n-hexylsulfonyl)undecanethiol CH$_3$–(CH$_2$)$_{10}$–SO$_2$(CH$_2$)$_6$SH (III), 6-(n-decyloxysulfanyl)hexylthiol CH$_3$–(CH$_2$)$_{6}$–SO$_2$(CH$_2$)$_6$SH (IV), and 5-(4-decylsulfonylphenoxy)pentanethiol CH$_3$–(CH$_2$)$_{9}$–SO$_2$C$_6$H$_4$O(CH$_2$)$_5$SH (V). The former system was taken as a reference, as it is a nonsubstituted n-alkanethiol with

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the equivalent chain length. It was purchased from Sigma-Aldrich; the synthesis of the other substances is described elsewhere.\textsuperscript{12,13} The substrates were (111) textured Au films, prepared by thermal evaporation of 200 nm of gold (99.99% purity) onto polished 3 in. single-crystal silicon (100) wafers (Silicon Sense) that had been precoated with a 5 nm titanium adhesion layer. The substrates were immersed for 24 h into a 1 mM solution of the substances in ethanol. After this period, they were rinsed in the solvent and dried in a stream of pure nitrogen gas. In the case of III–V, additional rinsing in chloroform followed by a final rinse step in ethanol was required to remove the remaining physisorbed molecules from the surface. All glassware was carefully cleaned in piranha solution, rinsed in Millipore water, and dried in air. The fabricated SAMs were stored in an Ar atmosphere.

The electron irradiation was carried out in ultrahigh vacuum (UHV) by a flood gun at a kinetic energy of 10 eV, a current density of 2.5 mA cm\textsuperscript{-2}, and an irradiation dose up to 8 mC cm\textsuperscript{-2}. The pristine and irradiated samples were characterized in situ by X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. In addition, ex situ characterization by contact angle measurements and infrared reflection–absorption spectroscopy (IRRAS) has been performed. The NEXAFS measurements were performed at the carbon K-edge with linearly polarized synchrotron light (a polarization factor of \approx 92\%). The incident angle of the light was varied from 90° (E-vector in the surface plane) to 20° (E-vector near the surface normal) in steps of 10°–20° to monitor the orientational order within the films. This approach is based on the so-called linear dichroism in X-ray absorption, that is, the dependence of the cross section of the resonant photoexcitation process on the orientation of the electric field vector of the linearly polarized light with respect to the molecular orbital of interest.\textsuperscript{15} The spectra were acquired in the partial electron yield mode with a retarding voltage of \approx 150 V. The energy resolution was \approx 0.65 eV. The energy scale was referenced to a characteristic \pi + resonance of a highly oriented pyrolytic graphite (HOPG) sample at 285.38 eV.\textsuperscript{16} The IRRAS spectra were taken with a BIO-RAD FTIR absorption spectrometer in reflection mode in dry air. A perdeuterated dodecanethiolate SAM on gold was used as a reference.

### 3. Results and Discussion

#### 3.1. Pristine Films

The first step of this study was the characterization of the pristine SAMs to gain information on the influence of the incorporated groups on structure and packing density in the films. The corresponding C 1s, S 2p, and O 1s XPS spectra are shown in Figures 2a, b, and 3a, respectively. The spectra are characteristic for intact and well-ordered SAMs. The C 1s spectra for all SAMs but V exhibit only one emission line, which can be related to the alkyl backbone. The exact BE positions of the emission for the films I, II, III, and IV are slightly different within an energy range of 284.8–284.9 eV, manifesting an influence of the incorporated functionalities on the chemical identity and structure of the films. In the case of V, the main C 1s emission is shifted to lower BEs (284.5 eV) as compared to that of the pure aliphatic films due to the contribution of the phenyl ring.\textsuperscript{17} There is also a weak high BE shoulder at 286.3 eV attributed to the carbon atoms adjacent to the ether entity. For all films with the incorporated functionality, the full widths at half-maximum (fwhm's) of the C 1s emission are noticeably larger than that for I, which suggests a smaller degree of orientational order or and a larger chemical inhomogeneity. The total intensity of the C 1s signal for I is by \approx 10–15% larger than those for the films with incorporated sulfur-derived groups, which implies a smaller packing density in the latter systems. This conclusion was additionally supported by the quantitative analysis of the Au 4f spectra (not shown), which was performed to estimate the thickness of the films (see below).

In the S 2p spectra in Figure 2b, a doublet related to the thiylate headgroup is observed for all SAMs at \approx 162.0 eV (all energies are given for S 2p\textsubscript{3/2}).\textsuperscript{17,18} The sulfur-based functionalities in the molecular backbone cause the appearance of a second S 2p doublet at higher BEs. In the case of the sulfone and sulfanyl-phenoxy entities, it is situated at 167.7 and 167.4 eV, respectively, while for the sulfide functionality (II) it is perceptible at 163.3 eV. In the case of IV, this peak is situated at 531.4 eV and accompanied by a high BE component at 532.5 eV attributed to the ether entity.

#### 3.2. Irradiated Films

In Figure 4, the normalized carbon K-edge NEXAFS spectra for an X-ray incidence angle of 55° of all SAMs with the sulfur-based groups are shown, along with the difference between the spectra acquired at normal and grazing (20°) X-ray incidence (at the bottom). The spectra reveal characteristic absorption resonances of an intact

![Figure 2](image_url)

**Figure 2.** C 1s (a) and S 2p (b and c) XPS spectra of pristine (a,b) and irradiated (c) I–V. The irradiation dose was 8 mC cm\textsuperscript{-2}. Individual spectral components are indicated (see the text for details).
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and 301 eV, respectively. The respective C–C and C–C’ resonances at 293.3 and 301 eV, respectively. The respective σ* orbitals are presumably directed along the molecular backbone, whereas the transition dipole moment of the R* resonance is perpendicular to the molecular axis.21,22 The oscillator strength of the latter resonance is proportional to the length of the intact, all-trans conformed alkyl chain,22 so that the sharper R* resonances for III and IV indicate a higher degree of conformational order in these films as compared to II or V. For I, the R* resonance is even more intense than those for III and IV, which is quite understandable because the alkyl chain of I is not separated into two parts by the sulfone functionality. In the case of V, there is an additional absorption resonance at 285.4 eV, which is related to the ππ* orbitals of the phenyl entity.

Figure 3. O 1s XPS spectra of pristine (a) and irradiated (bc) III, IV, and V. The irradiation dose was 1 mC cm−2 (b) and 8 mC cm−2 (c). Individual spectral components are indicated (see the text for details).

Figure 4. Carbon K-edge NEXAFS spectra of pristine (bottom but one spectra) and irradiated II–V acquired at an X-ray incidence angle of 55°. Bottom curves: the difference between the spectra of the pristine films acquired at normal and grazing (20°) X-ray incidence. The dashed lines correspond to zero. Aliphatic chain, including a sharp R* resonance at 287.7 eV15,19 and the σ* C–C and σ* C–C’ resonances at 293.3 and 301 eV, respectively. The respective σ* orbitals are presumably directed along the molecular backbone, whereas the transition dipole moment of the R* resonance is perpendicular to the molecular axis.21,22 The oscillator strength of the latter resonance is proportional to the length of the intact, all-trans conformed alkyl chain,22 so that the sharper R* resonances for III and IV indicate a higher degree of conformational order in these films as compared to II or V. For I, the R* resonance is even more intense than those for III and IV, which is quite understandable because the alkyl chain of I is not separated into two parts by the sulfone functionality. In the case of V, there is an additional absorption resonance at 285.4 eV, which is related to the ππ* orbitals of the phenyl entity.

The difference spectra in Figure 4 show that the intensity of the NEXAFS resonances varies with the incidence angle of X-rays, which implies an alignment of the molecular chains in the investigated films, just in the same way as in conventional n-alkanethiolate SAMs.21,22 Both the aliphatic chains in II–V and the phenyl entity in V have an upright orientation, as for example suggested by an increase in the intensity of the R* (II–V) and π* (V) resonances on going from grazing to normal incidence geometry. A quantitative analysis of the NEXAFS data within the so-called difference spectra approach resulted in average tilt angles of the aliphatic chains in II, III, IV, and V of 39°, 42°, 38°, and 39°, respectively. These values were derived by a comparison to the respective difference spectra for the nonsubstituted dodecanethiolate SAMs on Au, which have a tilt angle of 33° taken as a reference.21,22 Note that this value is slightly higher than the respective angle derived from more precise X-ray-diffraction studies3,23 as NEXAFS spectroscopy gives an average value of the tilt angle over the X-ray spot region, including both ordered and disordered areas, whereas X-ray diffraction probes only the ordered (crystalline) regions.3

The derived values of the average tilt angles agree rather well with the thickness of the investigated films, which was estimated on the basis of the Au 4f XPS spectra, assuming an exponential attenuation of the Au 4f signal by the covering organic layer. The films II, III, and IV were found to be about 20 ± 0.3 Å thick, whereas the thickness of V was estimated to be 22 ± 0.3 Å.

The conclusions that the investigated SAMs are of high quality and good orientational order were additionally supported by the inspection of the respective IRRAS data presented in Figure 5. Especially in the case of III and IV, the position of the characteristic asymmetric vibration for the methylene entities was found to be around 2920 cm−1, which is characteristic for a nearly crystalline arrangement of the aliphatic backbones in the all-trans conformation. Also, the measurements of advancing contact angle of H2O (~110°) indicated a quite high degree of orientational order at the SAM–ambient interface of all investigated films.

3.2. Effect of Electron Irradiation. The irradiation of II, III, IV, and V by electrons leads to a similar

Irradiation Sensitivity of SAMs

Figure 6. Effective thickness reduction of the investigated films in the course of irradiation. The values were estimated based on the attenuation of the Au 4f XPS signal.

The desorption of sulfone species and the sulfone-to-sulfidet transformation affect the O 1s XPS spectra (Figure 3) as well. The intensity of the sulfone-related O 1s component at 532.2 eV decreases significantly in the course of irradiation. If corrected for the remaining film thickness, this decrease agrees with the reduction of the S 2p sulfone component. For V, the intensity of the O 1s ether component at ca. 532.5 eV increases in the course of irradiation. This rise is explained by a reduced attenuation of the O 1s signal by the thinner organic overlayer (due to the irradiation-induced desorption). Thus one can conclude that the ether group is quite stable against the electron irradiation, which is also supported by the analysis of IRRAS spectra of V (Figure 5), where the Ph–O stretching mode was observed at 1261 cm⁻¹.

The decomposition of the layer was accompanied by the destruction of the intra- and intermolecular order, as was already mentioned above. This was manifested by the decrease of the R* resonance intensity (see Figure 4) and the reduction of the linear dichroism of the NEXAFS spectra. Already after irradiation with a dose of 1 mC cm⁻², no linear dichroism was observed for most of the resonances. The only exception was the π* resonance of the phenyl entity in V, which still exhibited a linear dichroism after a dose of 8 mC cm⁻². This behavior is in accordance with the well-known radiation resistance of aromatic films. The loss of intramolecular order in the aliphatic segments is also exhibited by the IRRAS spectra in Figure 5, where the corresponding CH₂ stretching modes became less distinct after irradiation. Also, the asymmetric stretching mode of CH₃ shifted to higher wavenumbers, which is known to be indicative for a reduced degree of crystallinity. In addition, the H–O contact angles clearly decreased after irradiation, manifesting an enhanced roughness and chemical inhomogeneity of the film surface.

3.3. Influence of the Position of the Weak Link.
The AT SAMs with sulfide, sulfone, and sulfonyl-phenoxy groups incorporated into alkyl chain showed similar degradation under electron irradiation as n-alkanethiolate films, including the loss of the orientational and conformational order, partial dehydrogenation with C=C double bond formation, desorption of film fragments, reduction of pristine thiolate species, and the appearance of new sulfur species. At the same time, the extent of the irradiation-induced desorption was found to be significantly enhanced by the introduction of sulfur-derived functionalities, as long as they were placed nearby the SAM—ambient interface. For II and III, the model of a weak link as a predetermined breaking point obviously worked, even though the chains were not cut exclusively at the position of the S or SO₂ group. Instead, the more likely scission events at the “weak links” were just added to those in the alkyl matrix. In the case of deeper lying sulfur-derived functionalities such as in IV and V, the thickness reduction was not stronger than for the n-alkanethiolate SAMs, which suggests that the position of the incorporated group is very essential for its performance as a predetermined breaking point. Tentatively, there are two reasons for this effect. First, a dipole–dipole coupling of the electronically excited dissociative state with its image at the metal surface can result in a quenching of the excited state. The probability for this process decreases with increasing separation from the metal surface. The difference in electron flux by going from the ambient to film interface is presumably significant.24,27 Second, even if quenching of the excited state does not occur and the bond is broken, the cutoff molecular fragment can be trapped in the chemically active hydrocarbon matrix, with the probability for this process increasing with increasing separation from the film—ambient interface.24 The difference in electron flux by going from the film—ambient to film—substrate interface is presumably of main importance as the inelastic mean free path of 10 eV electrons (about 20 Å) is comparable with the film thickness. In addition, inelastic electrons from the substrate will also contribute to the dissociation reaction.

3.4. Stability of the Thiolate Anchor. Another interesting phenomenon is the enhanced stability of the thiolate headgroups in the AT SAMs with sulfide, sulfone, and sulfonyl-phenoxy functionalities incorporated into the alkyl chain. The dependence of the remaining amount of the thiolate species in these systems on electron dose is presented in Figure 8, along with the analogous curve for the thiolate headgroups in the AT SAMs with sulfide, sulfone, and sulfonyl-phenoxy functionalities, as long as they were placed nearby the SAM—ambient interface. For II and III, the model of a weak link as a predetermined breaking point obviously worked, even though the chains were not cut exclusively at the position of the S or SO₂ group. Instead, the more likely scission events at the “weak links” were just added to those in the alkyl matrix. In the case of deeper lying sulfur-derived functionalities such as in IV and V, the thickness reduction was not stronger than for the n-alkanethiolate SAMs, which suggests that the position of the incorporated group is very essential for its performance as a predetermined breaking point. Tentatively, there are two reasons for this effect. First, a dipole–dipole coupling of the electronically excited dissociative state with its image at the metal surface can result in a quenching of the excited state. The probability for this process decreases with increasing separation from the metal surface. The difference in electron flux by going from the ambient to film interface is presumably significant.24,27 Second, even if quenching of the excited state does not occur and the bond is broken, the cutoff molecular fragment can be trapped in the chemically active hydrocarbon matrix, with the probability for this process increasing with increasing separation from the film—ambient interface.24 The difference in electron flux by going from the film—ambient to film—substrate interface is presumably of main importance as the inelastic mean free path of 10 eV electrons (about 20 Å) is comparable with the film thickness. In addition, inelastic electrons from the substrate will also contribute to the dissociation reaction.

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Figure 7. The dependence of the intensity of the individual components in the S 2p XPS spectra of II, III, IV, and V on the irradiation dose. The intensities have been obtained from a self-consistent analysis of the entire data set for a given system.

Figure 8. The dependence of the amount of the thiolate species in the investigated films on the electron dose. The irradiation-induced thickness reduction was taken into account.


4. Conclusion

The insertion of a functional entity into the alkyl chain of alkanethiolate SAMs affects the sensitivity of these systems toward ionizing radiation. In particular, the irradiation-induced thickness reduction could be significantly enhanced (by about 30%) by the incorporation of the sulfur-derived functionalities as a predetermined breaking point, even though the chains were not exclusively cut at the position of the incorporated group, but the scission events related to the weak links were just added to those in the alkyl matrix. Among the investigated sulfide, sulfone, and sulfonyl-phenoxy groups, the identity of the chosen functionality was found not to be decisive for this effect. At the same time, the position of the incorporated group along the alkyl chain was very essential for its performance as a predetermined breaking point. The enhancement of irradiation-induced desorption was observed only when the groups were placed close to the SAM–ambient interface. Otherwise, the effect of the weak link was neutralized by an enhanced quenching of the excited states via the dipole–dipole interaction with the substrate and a trapping of molecular fragments in the highly reactive (under electron irradiation) hydrocarbon layer.

Apart from the enhanced irradiation-induced desorption, which affected the “outer” part of the films, the extent of damage at the thiolate–substrate interface was significantly reduced by the introduction of the sulfur-derived functionality into the alkyl spacer. This stabilizing effect on the “deeper” part of the film varied with the chemical identity of the incorporated functionality and was most pronounced for the sulfone and sulfonyl-phenoxy functionalities. It was tentatively explained by an enhanced coupling of the SAM constituents and an additional cross-linking mediated by the irradiation-modified functionalities.

The results clearly show that the response of monomolecular films toward electron irradiation is a complex process, which, however, can be tailored to a definite extent by a versatile architecture of the film constituents.

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